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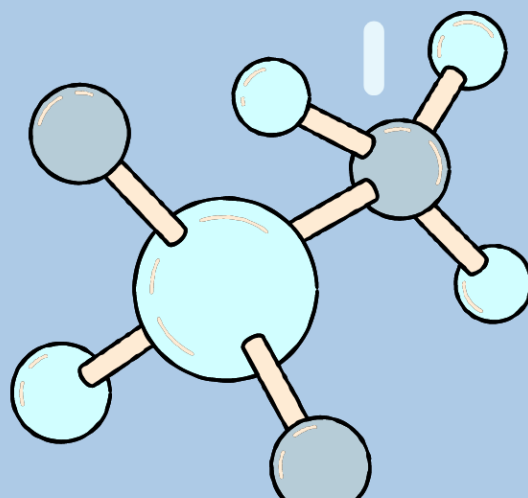
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Two Aspects of Electron Correlation: Multireference Diagnostics and London Dispersion Interactions

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Two Aspects of Electron Correlation: Multireference Diagnostics and London Dispersion Interactions

by

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Eskerrik asko denoi! Gracias a todos! Gràcies a tots! 谢谢你们!

丑奴儿·书博山道中壁

[宋] 辛弃疾

少年不识愁滋味，爱上层楼。爱上层楼，为赋新词强说愁。
而今识尽愁滋味，欲说还休。欲说还休，却道天凉好个秋。

Chou Nu Er · Muro Medio de la Carretera de Montaña Shubo

[Dinastía Song] Xin Qiji

Cuando somos jóvenes, no conocemos el sabor de la inquietud, disfrutamos subir a lo alto y mirar lejos. Disfrutamos subir a lo alto y mirar lejos, y nos esforzamos en expresar inquietud para escribir un nuevo verso libre de preocupaciones.

Ahora, habiendo probado el sabor de la inquietud, queremos expresarlo pero no podemos. Queremos expresarlo pero no podemos, ¡pero decimos, qué fresco es este día de otoño!

It is fantastic to find accurate, simplified, and meaningful rules from vast amounts of information in nature. This thesis was inspired by the equation of numbers presented below:

$$(-80538738812075974)^3 + 80435758145817515^3 + 12602123297335631^3 = 42,$$

where 42 was the last number below 100 that has been solved for the Diophantine equation (found by Andrew Booker from the University of Bristol and Andrew Sutherland from MIT, 2019, source see <https://www.bristol.ac.uk/news/2019/september/sum-of-three-cubes-.html>).

ABSTRACT

Electron correlation arises from the instantaneous interactions among electrons in atoms or molecules. Its ubiquitous nature beyond any one-electron system and its essential role in characterizing electronic structure render it of utmost importance in quantum chemistry and physics. In the context of correlated wavefunction methods, this thesis explains two aspects of electron correlation: the development and statistical analysis of various correlation measures including Multireference (MR) diagnostics, and the study of London dispersion interactions from the pair density perspective.

In the aspect of correlation measures and MR diagnostics, we first introduce some novel natural orbital-based correlation indices in terms of various ansatzes, which are universally applicable across all electronic structure methods. We present analytical connections between two natural orbital-based correlation indices, $\overline{I}_{\text{ND}}$ and $I_{\text{ND}}^{\text{max}}$, and two established electron correlation metrics: the leading term of a configuration interaction expansion, c_0 and the D_2 diagnostic. MR diagnostics are helpful in assessing the reliability of a calculation of single-reference methods. Although various MR diagnostics exist, many of them have been designed for specific methods. We explore relationships among various MR diagnostics and reduce them based on similarities. Thereby, a representative correlation measure is suggested with appropriate cutoff values for serving as effective MR diagnostics. Furthermore, extensive datasets are used for a thorough analysis of the agreement extent between each two MR diagnostics.

In the field of London dispersion interactions, we first establish a theoretical connection between the long-range dynamic correlation energy retrieved by electron-electron interaction energy and the dispersion energy based on the virial theorem. Then, we provide numerous numerical assessments over a collection of diatomic molecules at large separation and confirm that this relationship remains valid across various wavefunction methods. Among the pair density approaches, on one hand, we demonstrate the significance of using only few terms within the long-range components of correlated pair density to retrieve dispersion energies in diatomic molecules. On the other hand, we also use the long-range component of the correlated pair density partition $\Delta\rho_2^{\text{c}\Pi}$ to capture dispersion interactions. The numerical results for diatomic molecules align with the former approach which uses approximate pair density relying on few terms. Nonetheless, the pair density partition approach exhibits more robustness and can be extended to larger polyatomic molecules.

In addition, we introduce a novel concept of *dispersion hole* for identifying

and calculating dispersion interactions, and it reveals a connection between the pair density and dispersion energy. In the end, we present a minimal dispersion model based on the molecular hydrogen which helps interpret previous numerical results. We explore the universal $1/R^3$ decay in the long-range component of the Coulomb hole partition h_{cII} at large interatomic distances, denoted as R . Moreover, we demonstrate that this decay is a necessary but not sufficient condition when connecting to the dispersion energy. These findings can help gain some new insights into London dispersion from the pair density perspective.

RESUMEN

La correlación electrónica surge de las interacciones instantáneas entre electrones en átomos o moléculas. Su naturaleza ubicua más allá de cualquier sistema de un solo electrón y su papel esencial en la caracterización de la estructura electrónica la hacen de suma importancia en la química y la física cuánticas. En el contexto de los métodos de la función de onda correlacionada, esta tesis explica dos aspectos de la correlación electrónica: el desarrollo y análisis estadístico de varias medidas de correlación, incluyendo los diagnósticos de Multireferencia (MR), y el estudio de las interacciones de dispersión de London desde la perspectiva de la densidad de pares.

En el aspecto de las medidas de correlación y los diagnósticos MR, primero introducimos algunos índices de correlación basados en orbitales naturales, que son universalmente aplicables a través de todos los métodos de estructura electrónica. Presentamos conexiones analíticas entre dos índices de correlación basados en orbitales naturales, $\overline{I}_{\text{ND}}$ y $I_{\text{ND}}^{\text{max}}$, y dos métricas de correlación de electrones establecidas: el coeficiente dominante de una expansión de interacción de configuraciones, c_0 , y el diagnóstico D_2 . Los diagnósticos MR son útiles para evaluar la fiabilidad de un cálculo de métodos de referencia única. Aunque existen varios diagnósticos MR, muchos de ellos se han diseñado para métodos específicos. Exploramos las relaciones entre varios diagnósticos MR y los reducimos en función de las similitudes. De este modo, se sugiere una medida de correlación representativa con valores de corte apropiados para servir como diagnósticos MR eficaces. Además, se utilizan amplios conjuntos de datos para realizar un análisis exhaustivo del grado de concordancia entre cada uno de los dos diagnósticos MR.

En el campo de las interacciones de dispersión de London, primero establecemos una conexión teórica entre la energía de correlación dinámica de largo alcance obtenida mediante la energía de interacción electrón-electrón y la energía de dispersión basada en el teorema virial. A continuación, proporcionamos numerosas evaluaciones numéricas sobre una colección de moléculas diatómicas a gran separación y confirmamos que esta relación sigue siendo válida a través de varios métodos de función de onda. Entre los enfoques de densidad de pares, por un lado, demostramos la importancia de utilizar sólo unos pocos términos dentro de los componentes de largo alcance de la densidad de pares correlacionados para recuperar las energías de dispersión en moléculas diatómicas. Por otro lado, también utilizamos el componente de largo alcance de la partición de la densidad de pares correlacionados $\Delta\rho_2^{c_{\text{II}}}$ para capturar las interacciones de dispersión. Los resultados numéricos para moléculas diatómicas se alinean con el primer enfoque,

que utiliza la densidad de pares aproximada basándose en pocos términos. Sin embargo, el enfoque de partición de la densidad de pares es más robusto y puede extenderse a moléculas poliatómicas de mayor tamaño.

Además, introducimos un concepto novedoso de agujero de dispersión para identificar y calcular las interacciones de dispersión, y revela una conexión entre la densidad de pares y la energía de dispersión. Por último, presentamos un modelo de dispersión mínima basado en el hidrógeno molecular que ayuda a interpretar los resultados numéricos anteriores. Exploramos el decaimiento universal de $1/R^3$ en el componente de largo alcance de la partición de agujeros de Coulomb $h_{c\Pi}$ a grandes distancias interatómicas, denotado como R . Además, demostramos que este decaimiento es una condición necesaria pero no suficiente cuando se conecta con la energía de dispersión. Estos hallazgos pueden ayudar a obtener algunas nuevas ideas sobre la dispersión de London desde la perspectiva de la densidad de pares.

电子相关性产生于原子或分子中电子间的瞬时相互作用。它在任何单电子系统中都无处不在，而且在表征电子结构方面起着至关重要的作用，因此在量子化学和物理学中具有极其重要的意义。在相关波函数方法的背景下，本论文从两个方面解释了电子相关性：包括多参考诊断在内的各种相关性测量方法的开发和统计分析，以及从电子对密度的角度对伦敦色散相互作用的研究。

在相关测量和多参量诊断方面，我们首先介绍了一些新颖的基于自然轨道的相关指数，这些指数以各种解析方式表示，普遍适用于所有电子结构方法。我们提出了两个基于轨道的自然相关指数： $\overline{I}_{\text{ND}}$ 和 $I_{\text{ND}}^{\text{max}}$ 与两个已建立的电子相关度量之间的分析联系：配置相互作用展开的前导项和 D_2 诊断。多参考系诊断有助于评估单一参考方法计算的可靠性。虽然存在各种多参考系诊断方法，但其中许多都是针对特定方法设计的。我们探讨了各种多参考系诊断之间的关系，并根据相似性对其进行了缩减。因此，我们提出了一种具有代表性的相关测量方法，并给出了适当的临界值，以作为有效的多参考系诊断方法。此外，我们还利用大量数据集对每两种多参考系诊断之间的一致程度进行了全面分析。

在伦敦色散相互作用领域，我们首先根据维里定理，在通过电子-电子相互作用能量获得的长程动态相关能与色散能之间建立了理论联系。然后，我们对一系列大分离度的双原子分子进行了大量的数值评估，并证实这种关系在各种波函数方法中仍然有效。在电子对密度方法中，一方面，我们证明了仅使用相关电子对密度长程分量中的少数项来检索双原子分子色散能的重要性。另一方面，我们还利用相关电子对密度分区的长程分量 $\Delta\rho_2^{\text{CT}}$ 来捕捉弥散相互作用。双原子分子的数值结果与前一种方法一致，前一种方法使用依赖于少数项的近似电子对密度。尽管如此，电子对密度分割方法表现出更强的应用性，并可扩展到更大的多原子分子。

此外，我们还引入了一个新概念“色散孔”来识别和计算色散相互作用，它揭示了电子对密度和色散能之间的联系。最后，我们提出了一个基于分子氢的最小色散模型，它有助于解释之前的数值结果。我们探索了库仑空穴分区 h_{CT} 的长程分量在大原子间距（表示为 R ）下的普遍 $1/R^3$ 衰减。此外，我们证明了这种衰减是连接色散能的必要条件，但不是充分条件。这些发现有助于从原子电子对密度的角度对伦敦色散获得一些新的认识。

LIST OF ABBREVIATIONS

Acronym	Description
SR	Single-Reference
MR	MultiReference
PES	Potential Energy Surface
MO	Molecular Orbitals
AO	Atomic Orbitals
MO-LCAO	Molecular Orbital from Linear Combination of Atomic Orbitals
DET	Slater Determinant
WFN	Wavefunction
STO	Slater-Type Orbitals
GTO	Gaussian-Type Orbitals
FCI	Full Configuration Interaction
HF	Hartree-Fock
post-HF	post-Hartree-Fock
SCF	Self-Consistent-Field
RHF	Restricted Hartree-Fock
CI	Configuration Interaction
CISD	Configuration Interaction with Single and Double Excitations
MBPT	Many-Body Perturbation Theory
MPPT	Møller–Plesset Perturbation Theory
MP_n	<i>n</i> -th Order Møller–Plesset Perturbation Theory
MP1	First-Order Møller–Plesset Perturbation Theory
MP2	Second-Order Møller–Plesset Perturbation Theory
CC	Coupled Cluster
MCSCF	Multi-Configurational Self-Consistent Field
MRCI	Multi-Reference Configuration Interaction
CCSD	Coupled Cluster Single and Double Excitations
CCSD(T)	Coupled Cluster Singles and Doubles with Perturbative Triples
CSFs	Configuration State Functions
CIPSI	Configuration Interaction using a Perturbative Selection made Iteratively
SCI	Selected Configuration Interactions

CASSCF	Complete-Active-Space Self-Consistent Field
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
RASSCF	Restricted Active Space Self-Consistent Field
UHF	Unrestricted Hartree-Fock
MRCC	Multi-Reference Coupled-Cluster
CASPT2	Complete-Active-Space Second-Order Perturbation Theory
NEVPT2	<i>N</i> -Electron Valence State Perturbation Theory
DMs	Density Matrices
<i>n</i>-RDMs	<i>n</i> -Order Reduced Density Matrices
1-RDM	First-Order Reduced Density Matrix
2-RDM	Second-Order Reduced Density Matrix
NO	Natural Orbitals
RDMFT	Reduced Density Matrix Functional Theory
SD	Single-Determinant
DMRG	Density Matrix Renormalization Group
DFT	Density Functional Theory
DFAs	Density Functional Approximations
EEN	External Electron Number
NON	The Largest Occupation Number in Unoccupied Natural Orbitals
MRI	Multi-Reference Index
TAE	Total Atomization Energy
vdW	van der Waals
PT	Perturbation Theory
PT2	Second-Order Perturbation Theory
WFT	Wavefunction Theory
SAPT	Symmetry-Adapted Perturbation Theory
XDM	Exchange-hole Dipole Moment
MBD	Many-Body Dispersion
EDA	Energy Decomposition Analysis
QTAIM	Quantum Theory of Atoms in Molecules
CP	Critical Points
IQA	Interacting Quantum Atoms
NCI	Non-Covalent Interaction Index
DORI	Density Overlap Regions Indicator
MS	Model System
MAPE	Mean Absolute Percentage Error
sr	short range
lr	long range

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INTRODUCTION

In quantum chemistry, the accurate prediction of molecular energies and properties relies on sophisticated computational methods. Most practical methods have been developed to treat approximately electron correlation, which plays a crucial role in determining the electronic structure [4–7]. Particularly, an inadequate description of electron correlation can lead to incorrect predictions of various electronic structure properties: molecular geometries, binding energies, reaction energies and enthalpies, spectroscopic properties, etc. Electron correlation emerges from the instantaneous interactions between electrons and is inherent in systems with more than one electron. However, fully capturing electron correlation in many-body systems using current computational methods is challenging and often impractical [8–10]. To tackle this problem, the idea of separating electron correlation into dynamic correlation and nondynamic (static) correlation has been proposed and explored in various perspectives [11–13]. This separation scheme provides a valuable framework for understanding and approximating the electron correlation in quantum chemistry method development and applications.

Dynamic correlation is a ubiquitous phenomenon that arises from the instantaneous electron-electron repulsion and is associated with the motion of electrons in response to each other. For instance, London dispersion interactions are a particular type of dynamic correlation. In contrast, nondynamic (also referred to as “static”, “strong”) correlation is system-dependent and emerges due to the existence of multiple electronic configurations that make significant contributions

to the overall wavefunction. To address the challenges posed by treating electron correlation, various quantum chemistry computational methods have been developed over the past century. These methods can be broadly classified into two main categories based on their ability to capture dynamic or nondynamic correlation: Single-Reference (SR) and Multireference (MR) methods.

Single-Reference (SR) methods are designed to primarily capture dynamic correlation, as they assume that the electronic wavefunction can be well approximated by a single-determinant reference. These methods, such as Configuration Interaction (CI), Many-Body Perturbation Theory (MBPT), Coupled Cluster (CC), and Density Functional Theory (DFT), are computationally efficient and widely used in the study of atomic and molecular systems. However, SR methods are limited in their capacity to accurately calculate systems with significant nondynamic correlation. To tackle such cases, MR methods have been developed by using multiple determinants as reference. The MR methods, such as Complete-Active-Space Self-Consistent Field (CASSCF), Multi-Configurational Configuration Interaction (MRCI) and Density Matrix Renormalization Group (DMRG), are particularly useful for studying systems with MR characters (e.g., bond-breaking, open-shell systems, excited states, transition metal complexes). Nonetheless, the MR methods are typically more computationally demanding and complex compared to the SR methods. Particularly, these MR methods require a higher level of understanding and expertise from users, as they can not be treated as “black-box” approaches. Furthermore, it is important to note that methods attempting to simultaneously address both dynamic and nondynamic correlation, such as Full Configuration Interaction (FCI), Complete-Active-Space Second-Order Perturbation Theory (CASPT2), *N*-electron Valence State Perturbation Theory (NEVPT2), among others, are often challenging and not applicable to large systems due to computational limitations.

The choice between SR and MR methods depends on the presence of a predominant correlation in the system of interest. In general, SR methods are inadequate for treating the systems exhibiting significant MR character (or called strong-correlated systems), while MR methods can perform better on these systems. To aid researchers in assessing the appropriateness of an SR method for their calculations, MR diagnostics serve as helpful tools. In [Fig. 1.1](#), we present a simple algorithm of how the MR diagnostics work on the electronic structure calculations. Once completing a calculation using SR methods, MR diagnostics are applied to assess the adequacy of the calculation. If the assessment indicates that the molecular system exhibits only SR character, the SR calculation is considerably

Electronic Structure Calculations

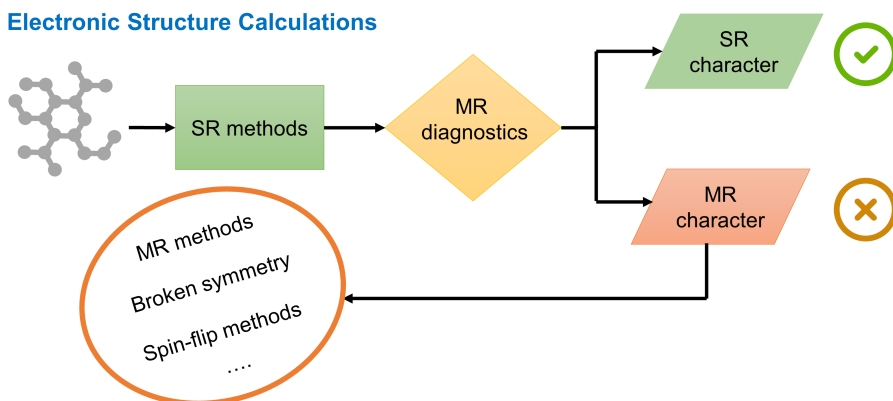


FIGURE 1.1: MR diagnostics aid to identify the appropriateness of SR methods for calculating a molecular system under consideration.

reliable. However, if it detects MR character of the molecular systems, it becomes necessary to consider alternative approaches for recalculating these molecules, including MR methods, broken symmetry solutions [14], spin-flip methods [15–17], etc. Additionally, MR diagnostics can be determined from the output of SR calculations or predicted empirically using machine learning techniques based on the input molecular structure data [18–22]. In this thesis, the first main topic revolves around MR diagnostics. We primarily focus on MR diagnostics derived from the output of SR calculations, and machine learning predictions will not be discussed.

Over the past decades, a variety of MR diagnostics have been proposed to identify the MR character. For wavefunction methods, these diagnostics can be broadly divided into two main families: wavefunction-based diagnostics and energy-based diagnostics. Wavefunction-based diagnostics can be further categorized into three primary subgroups. The first subgroup is c_0 -based diagnostics (e.g., c_0 , c_0^2 [23, 24]), which are applicable to methods such as CI, CASSCF, and others. The second subgroup includes amplitude-based diagnostics (e.g., T_1 [25], D_1 [1, 26], D_2 diagnostics [1]), specifically designed for methods like MBPT, CC methods. Lastly, the third subgroup consists of natural orbital-based indices (e.g., I_{ND} [13], S_{corr} [27, 28], M_{diag} [29]), which can be applied to almost all types of correlated wavefunction methods. On the other hand, energy-based diagnostics, such as %TAE[(T)] [30, 31] and % E_{corr} [(T)] [18] rely on the calculations of CC methods. By analyzing the total atomization energy or correlated energy contributions, they



FIGURE 1.2: Gecko and fine structure on its feet. Left image credit: blickwinkel/Alamy Stock Photo [37]; Middle image credit: Kellar Autumn 2006 [38]; Right image credit: authors of [39].

provide useful information on the presence and extent of the MR character in molecular systems.

In recent years, Martin *et al.* [31–35], Sprague *et al.* [36], Kulik *et al.* [18–22] and others have investigated a range of MR diagnostics. They attempted to assess the correlation (or similarity) between these MR diagnostics, categorize them into groups, or combine them for optimal predictions. Their work has inspired us to undertake this new development and analysis of these MR diagnostics. Current MR diagnostics in quantum chemistry face several challenges: (i) many diagnostics are specific to certain computational methods, limiting their applicability; (ii) existing diagnostics often lack consensus due to the use of different criteria and methodologies [18, 35, 36]; (iii) interpreting the results of these diagnostics can be complex, as they often provide numerical values without clear physical interpretations; (iv) wavefunction-based diagnostics are not correlated with energy-based diagnostics [18, 35]; (v) certain diagnostics require significant computational resources, making them impractical for large systems. Hence, the study of MR diagnostics in this thesis aims to tackle these challenges by developing more general, interpretable, and computationally efficient MR diagnostic tools.

The second major focus of this thesis is on dispersion interactions, which belong to van der Waals (vdW) interactions. The vdW interactions (or vdW forces) play a vital role in various phenomena observed in nature [40–46]. One fascinating example is found in the remarkable adhesive abilities of geckos, which allow them to effortlessly climb vertical surfaces and even walk on ceilings. The secret behind their incredible grip lies in the vdW forces that arise between the microscopic structures on their feet (see Fig. 1.2) and the surfaces they traverse [39]. The

vdW forces are distance-dependent interactions between atoms or molecules that are much weaker than chemical bonds (e.g., ionic, covalent bonds). However, geckos are able to climb due to the cumulative effect of these forces acting on the numerous microscopic structures on their feet. Beyond the example of geckos, vdW forces are also responsible for the aggregation of dust particles in the atmosphere and contribute to the formation of clouds and precipitation. These cohesive forces allow water molecules to stick together, forming droplets and exhibiting capillary action, where liquid can rise in narrow tubes against gravity, etc.

In 1873, Johannes Diderik van der Waals first introduced these forces in his PhD thesis “on the continuity of the gaseous and liquid state” at Leiden University [47]. Over several decades, through theoretical interpretations and experimental observations, vdW forces have been analyzed and classified based on the interactions of different types of electrical dipoles of molecules. These include permanent dipole-permanent dipole interactions (also known as the Keesom force) that involve attractive or repulsive electrostatic interactions [48–50], permanent dipole-induced dipole interactions (also known as the Debye force) that are associated with attractive induction interactions [51, 52], and induced dipole-induced dipole interactions¹ (known as the London dispersion force) that are attractive interactions [53].

The electrostatic and polarization forces can be easily interpreted using classical theory, where the charge distribution in atoms or molecules is represented in terms of multipoles and polarizability. However, the contribution of London dispersion interactions to interatomic and intermolecular interactions was understood only after the development of quantum mechanics [53]. In 1930, Fritz London derived the first approximation formalism to calculate the dispersion energy between two interacting atoms using quantum-mechanical perturbation theory [53]. Despite its rough approximation, the pioneering work of London provided a fundamental understanding of dispersion interactions in the framework of quantum mechanics.

London dispersion interactions arise from instantaneous correlations in the electron motions between two atoms or molecule groups. These emergent electromagnetic forces, which influence all matter containing electrons, are primarily attractive in nature [42]. From the perspective of electron correlation, they are categorized as part of dynamic correlation which occurs at long range with respect to the interelectronic distance. In particular, when the electrons on each atom or

¹In this thesis, we adopt the terminology “induced dipole-induced dipole interactions” as used in the textbook by Atkins and de Paula [46].

molecule create transient multipoles, these interactions arise between transient multipoles induced in the electron distributions. Although London dispersion interactions are characterized by weak attractive forces, they are ubiquitous in nature and play a substantial role in various fields of physics and chemistry. For instance, they are involved in the condensation of atoms and molecules, friction and adhesion phenomena [54], the selectivity of synthetic catalysts, the strength of receptor-drug interactions, the fidelity of base pairing in DNA [55], etc. Therefore, it is essential to accurately describe London dispersion in quantum chemistry to predict these properties and interactions.

In the context of electronic structure methods, the highest level with respect to accuracy, such as the FCI and Quantum Monte Carlo (QMC) [56, 57], or approximate high-level wavefunction methods including dynamic correlation: CCSD(T), CCSD, CISD, and MP2, can inherently account for dispersion to some extent. Nonetheless, they are limited by the high computational cost. On the other hand, in the framework of DFT, many widely used functionals (e.g., PBE [58], B3LYP [59, 60]) are known for their failures in describing the long-range dispersion interactions [61–65]. Although one of the most efficient and accurate methods, D3/D4, [66, 67] has been widely recognized by the DFT community recent years, they are *ad hoc* corrections that rely on optimized parameterization and precomputed polarizabilities. In addition, various other practical methods have been developed to address this issue during the past two decades [68–85]. Yet, it still remains a challenge to develop an accurate, efficient, general, and first-principle-motivated method to treat dispersion interactions in the context of DFT [86]. We refer to further details in [Chapter 3](#).

Within the quantum-mechanical framework, the majority of well-known approximate methods for handling dispersion necessitate two well-defined fragments (e.g., atoms, localized orbitals, or infinitesimal electron density regions) [87]. These fragments must be sufficiently separated by a distance denoted as R , ensuring they are beyond the range of density or orbital overlap. In such cases, second-order perturbation theory (PT2) describes the dispersion energy with a leading term of $1/R^6$. Following this line of development, one has the option to employ the Unsöld approximation, which suggests using the average energies to approximate the excitation energies in the sum-over-states expression which results from the PT2 treatment. Another common choice is the Casimir-Polder formula which introduces the so-called dynamic polarizabilities at imaginary frequencies. Nonetheless, the accuracy of the formal approach is usually constrained, and the computation or approximation of dynamic polarizabilities is challenging. More-

over, the polarizabilities of isolated atoms can significantly change in different molecules, materials, or solvent environments. [40]

Instead of relying on second-order perturbation theory treatment or polarizabilities, Baerends *et al.* [88–90] have revealed that the long-range components of pair density constructed from a limited set of two-electron AO quartets (e.g., $s_A p_A s_B p_B$) can effectively capture dispersion interactions in H_2 and He_2 systems. These two-electron AO quartet terms, as proposed by the authors, correspond to induced dipole-induced dipole interactions and account for London dispersion. In addition, recent work by our group has shown a connection between the long-range dynamic correlation component from the pair density partition (often referred to as the cumulant part of pair density) and London dispersion [3]. The long-range behavior of the dynamic correlation component from the correlated pair density has been demonstrated as a universal decay with the interatomic distance $1/R^3$ [3, 91]. Given this background, this thesis focuses on exploring further the role of the pair density in accounting for dispersion, particularly connecting to the long-range correlation nature of London dispersion. This work aims to provide a conceptual and applicable framework for modeling London dispersion interactions from the perspective of the pair density.

The chapters in the result sections of this thesis are outlined as follows:

Chapter 4 and Chapter 5 present the results related to the topic of electron correlation measures. Chapter 4 explores various correlation measures employed across a range of correlated wavefunction methods. This chapter begins by introducing normalization techniques for existing correlation metrics to ensure that they are size-intensive. For the purpose of comparison and analysis, some new natural orbital-based correlation metrics (referred to as indices) will be introduced to quantify dynamic and nondynamic electron correlation. Furthermore, we establish analytical connections between certain correlation metrics, which are subsequently verified through statistical assessments across various datasets. Chapter 5 extends our analysis, employing large datasets to explore the linear relationships among various correlation metrics. This chapter aims to reduce the number of effective MR diagnostics through (i) the linear relationships among these correlation metrics; (ii) their incapacity of detecting significant MR character when the system size increases. Through specific MR case studies, we demonstrate the limitations that render certain correlation metrics unreliable as MR diagnostics. After eliminating redundancies in the collection of numerous MR diagnostics, the focus then shifts to establishing cutoffs for a selection of few maximum-based correlation metrics. In the end, we introduce a robust representa-

tive maximum-based correlation index, namely $I_{\text{ND}}^{\text{max}}$, demonstrating its potential for wide applications across electronic structure calculations.

Chapter 6 to Chapter 8 focus on the results related to the topic of London dispersion. Our primary focus lies in understanding dispersion from the perspective of pair density partitions [3, 92] or long-range relevant components [42, 88–90]. In Chapter 6, we will examine two dispersion models applied to various diatomic systems. These models rely on approximate pair density constructed through the long-range relevant components, employing two distinct approaches: (i) considering induced dipole-induced dipole terms only [42, 88–90], which is referred to as Baerends’ model; (ii) adding few more induced multipole-induced multipole (higher multipole) terms, which is referred to as extended Baerends’ model. Each of these approximate pair densities yields an electron-electron interaction energy term, V_{ee} , associated with long-range dynamic correlation. The chapter will first establish a theoretical relationship between this long-range dynamic correlation described by the V_{ee} term and the total dispersion energy based on the virial theorem. Then, this relationship will be numerically examined through Baerends’ model and its extended counterpart.

Chapter 7 provides a comprehensive analysis of dispersion energy contributions from various energy decomposition terms in H_2 (singlet and triplet) and He_2 at large interatomic distances. The focus lies on the V_{ee} terms and their corresponding Coulomb hole partitions, particularly the long-range components responsible for dispersion. These findings extend to various diatomic and polyatomic molecules. We will numerically demonstrate how to use the long-range pair density partition to retrieve the dispersion energy captured by a correlated wavefunction with a given basis set. Moreover, the novel concept of *dispersion hole* will be introduced, along with relevant asymptotic conditions. This concept aids in calculating and identifying dispersion interactions during the separation of dimers.

Chapter 8 shows a minimal dispersion model based on the singlet H_2 molecule at large interatomic separations. While this strongly simplified model does not aim to pursue precise dispersion energy, it provides a qualitative description of dispersion beyond second-order perturbation theory. This model establishes connections between dispersion energy and the long-range component of the Coulomb hole partition, along with some asymptotic conditions. As the British statistician George Box famously said, “All models are wrong, but some are useful.” This dispersion toy model is derived from first principles, without the use of any empirical parameters. Moreover, it can accurately capture the dispersion

described by the FCI wavefunction of H_2 even with a very poor basis set. It serves to interpret relevant findings from numerical results in previous chapters, and brings new insights for the future development of more advanced dispersion models.

OBJECTIVES

Within the context of separating electron correlation into its dynamic and nondynamic components, this thesis endeavors to contribute novel insights into electron correlation from two distinct perspectives: MR diagnostics and London dispersion interactions. On one hand, we aim to advance the development and analysis of MR diagnostics that are helpful in detecting the presence of nondynamic correlation within molecular systems. On the other hand, we aim to understand London dispersion interactions through their character as long-range dynamic correlation that can be described by the pair density.

Concerning MR diagnostics (also referred to as a specific type of correlation measure), although numerous MR diagnostics are available in the literature, many of them are restricted in their applicability to specific methods. Collecting numerous diagnostics for the determination of the MR character of a molecular system is often impractical. Moreover, the criteria of many MR diagnostics can conflict with each other. Consequently, our first target is to determine the connections or similarities among various electron correlation measures. To achieve this, we aim to first develop analytical interpretations and then validate them by using statistical assessments across both small and big datasets. Secondly, our objective is to design a robust MR diagnostic using electron correlation indices with appropriate cutoffs that can be broadly applicable to all types of electronic structure methods. Thirdly, our goal is to rigorously evaluate the extent of concordance between these cutoffs and existing MR diagnostics across diverse datasets,

thereby reducing the number of MR diagnostics from a practical point of view.

Within the context of London dispersion interactions, by bypassing the traditional perturbative treatment within the framework of quantum mechanics, our primary goal is to gain insight into London dispersion interactions through a correlated pair density perspective, with a particular emphasis on the long-range component. The secondary goal is to establish a theoretical relationship between the long-range dynamic correlation described by the electron-electron interaction term and the total dispersion energy. Then, we also aim to explore the connection between the earlier established $1/R^3$ signature of London dispersion from the pair density perspective, and the $1/R^6$ asymptotic behavior of the dispersion energy [3, 91]. Through an analytical description of London dispersion interactions from the first principles based on simple H_2 models, we also aim to reveal the role of the pair density long-range partitions c_{II} [3] or long-range components (referred to as Baerends' model) [88–90] in the London dispersion interactions. The long-term objective is to develop advanced methods for describing London dispersion interactions that are accurate, cost-efficient, widely applicable, and grounded in the first principles.

THEORY AND METHODOLOGY

This chapter outlines the theoretical background and methodology of quantum chemistry for this thesis. We begin by introducing the Schrödinger equation, the Born–Oppenheimer approximation, the many-electron wavefunction, the variational principle, and a series of well-known Single-Reference (SR) and Multireference (MR) wavefunction ansatzes used in quantum chemistry to solve the electronic structure many-body problem. Then, we overview the partition of the pair densities and its correspondence with dynamic and nondynamic correlation. Finally, we introduce the two main topics of this thesis: the MR diagnostics and London dispersion interactions.

3.1 Wavefunction Methods in Quantum Chemistry

3.1.1 Schrödinger Equation

In quantum mechanics, the Schrödinger equation is one of the most fundamental formulations for studying quantum mechanical systems [93]. It describes explicitly the equation of motion of many-body systems (i.e., N electrons, N_{nuc} nuclei) of any states in a non-relativistic time-dependent form,

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle, \quad (3.1)$$

where i is the imaginary unit ($i^2 = -1$), $\hbar$ is Planck’s constant divided by 2π , and the function $|\Psi\rangle = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_{N_{\text{nuc}}}; t)$ is the many-body wavefunc-

tion depending on the electron coordinates, $\mathbf{x}$, the nuclear coordinates, $\mathbf{X}$, and the time variable t . Note that the electron and nuclear coordinate variables in the many-body wavefunction include the three-dimensional spatial coordinates and the spin coordinates. In this thesis, we only focus on systems at stationary states (all observables are independent of time). $\hat{H}$ denotes the time-independent Hamiltonian operator which only depends on the spatial coordinates of electrons and nuclei rather than their spin coordinates. The time-independent Schrödinger equation, Eq. (3.2), describes the wavefunction $|\Psi\rangle$ as an eigenfunction of the Hamiltonian operator with eigenvalue E , the total energy of the system.

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \quad (3.2)$$

The time-independent Hamiltonian operator of an N -particle system is defined as a sum of the kinetic energy and potential energy of electrons and nuclei operators,

$$\hat{H} = \hat{T} + \hat{V}, \quad (3.3)$$

where the kinetic energy operator $\hat{T}$ has an electronic and a nuclear term:

$$\begin{aligned} \hat{T} &= \hat{T}_e + \hat{T}_n \\ &= -\sum_i^N \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 - \sum_A^{N_{\text{nuc}}} \frac{\hbar^2}{2M_A} \nabla_{\mathbf{R}_A}^2. \end{aligned} \quad (3.4)$$

We note that m_e denotes the mass of the electron, and M_A represents the nuclear mass of atom A (with charge Z_A). The potential energy operator $\hat{V}$ generally includes three terms: the electron-nuclear attraction operator $\hat{V}_{\text{en}}$, the electron-electron interaction operator $\hat{V}_{\text{ee}}$ and the nuclear-nuclear Coulomb repulsion operator $\hat{V}_{\text{nn}}$,

$$\begin{aligned} \hat{V} &= \hat{V}_{\text{en}} + \hat{V}_{\text{ee}} + \hat{V}_{\text{nn}} \\ &= -\sum_i^N \sum_A^{N_{\text{nuc}}} \frac{Z_A e^2}{4\pi\epsilon_0 ||\mathbf{r}_i - \mathbf{R}_A||} + \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0 ||\mathbf{r}_i - \mathbf{r}_j||} + \sum_{A<B}^{N_{\text{nuc}}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 ||\mathbf{R}_A - \mathbf{R}_B||}. \end{aligned} \quad (3.5)$$

Quantum chemistry is a subject that applies the theory of quantum mechanics to problems in chemistry. The methods developed in quantum chemistry to directly solve the Schrödinger equation without relying on empirical data are also called *ab initio* approaches or from the first principles. However, the Schrödinger equation is too complex to be solved analytically for most physical systems, and the exact, closed-form solution of Eq. (3.2) has been only achieved for very few systems (e.g., the particle in a box, the harmonic oscillator, the hydrogen atom). Hence, for

many-body systems that contain more than one electron, employing approximate methods is indispensable.

One of the fundamental approximations extensively used in quantum chemistry is the Born–Oppenheimer approximation [94], which enables the separation of electron and nuclear motions based on the significant difference in mass between the nuclei and electrons (i.e., $M_A \gg m_i$ in Eq. (3.4)). Using the Born–Oppenheimer approximation, one can treat the coordinates of the nuclei as fixed compared to electrons, then the many-body wavefunction $|\Psi\rangle$ of an N -particle system can be expressed as a product of an electronic wavefunction $|\psi_{\text{el}}\rangle$ and a nuclear wavefunction $|\psi_{\text{nuc}}\rangle$,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, \mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_{N_{\text{nuc}}}) = \psi_{\text{el}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_{N_{\text{nuc}}}) \cdot \psi_{\text{nuc}}(\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_{N_{\text{nuc}}}), \quad (3.6)$$

where the electronic coordinate variables $\{\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N\}$ are parameterized in terms of the nuclear coordinate variables $\{\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_{N_{\text{nuc}}}\}$.

Analogously, the Hamiltonian operator $\hat{H}$ can be decomposed into separate electronic and nuclear components: $\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{nuc}}$. The electronic Hamiltonian (in atomic units)¹ is defined as

$$\begin{aligned} \hat{H}_{\text{el}} &= \hat{T}_{\text{e}} + \hat{V}_{\text{ee}} + \hat{V}_{\text{en}} \\ &= -\sum_i^N \frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \sum_i^N \sum_A^{N_{\text{nuc}}} \frac{Z_A}{\|\mathbf{r}_i - \mathbf{R}_A\|} + \sum_{i < j}^N \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|}. \end{aligned} \quad (3.7)$$

In addition, it is important to note that the nuclear repulsion energy operator, $\hat{V}_{\text{nn}}$, is determined by a set of fixed nuclear coordinates and charges, and the wavefunction is invariant to the addition of the $\hat{V}_{\text{nn}}$ operator in the electronic Hamiltonian. As a result, the electronic Hamiltonian $\hat{H}_{\text{el}}$ combined with the constant term $\hat{V}_{\text{nn}}$ leads to the formulation of the electronic Schrödinger equation,

$$(\hat{H}_{\text{el}} + \hat{V}_{\text{nn}})|\Psi_{\text{el}}\rangle = E_{\text{el}}|\Psi_{\text{el}}\rangle. \quad (3.8)$$

In this eigenvalue equation, Eq. (3.8), the eigenvector (wavefunction), $|\Psi_{\text{el}}\rangle$, is an antisymmetric function with respect to the electron coordinate exchange. The eigenvalue, E_{el} , denotes the electronic energy. The Born–Oppenheimer approximation yields the electronic Schrödinger equation, and gives rise to a significant concept known as the Potential Energy Surface (PES). The PES is constructed by plotting the values of electronic energy E_{el} as a function of all nuclear coordinates. It provides crucial insights into the energy landscape of a system, the

¹In atomic units, $\hbar = m_i = e = 4\pi\epsilon_0 = 1$. Atomic units (a.u.) are used in this thesis.

stability, equilibrium geometries, reaction pathways, energy barriers of molecules, etc. From now on, we will drop the subscript “el” from the Hamiltonian, the wavefunction, and the energy terms. This thesis will only focus on the non-relativistic, time-independent electronic Schrödinger equation for molecular systems.

3.1.2 Wavefunction Representation in Molecular Systems

According to the Schrödinger equation, the quantum states of a system can be described by their corresponding wavefunctions, and the state with the lowest energy is the electronic ground state of the system. In this thesis, we only focus on the ground-state energy. To determine the ground-state energy of molecular systems, one needs to solve the Schrödinger equation. The methodologies employed to find the wavefunction satisfying the Schrödinger equation are referred to as wavefunction methods. The wavefunction, $|\Psi\rangle$, can be represented by a vector or a linear combination of many basis vectors in the Hilbert space, then solving the partial differential equation (e.g., Schrödinger equation) is transformed into solving algebraic equations, which makes massive calculations feasible and efficient on computers.

When dealing with isolated atoms or molecules, the concept of “orbitals” is preferred to be the basis vectors of the wavefunction. Specifically, an orbital can be considered as the wavefunction of a single electron. In molecular electronic structure, the notion of Molecular Orbitals (MO) [95–98] is commonly used to describe electrons in molecules. The MO, denoted as ϕ , can be constructed from a linear combination of Atomic Orbitals (AO), χ , this treatment is known as the Molecular Orbital from Linear Combination of Atomic Orbitals (MO-LCAO) [99, 100],

$$\phi_i(x_A, y_A, z_A) = \sum_{\mu}^{N_{AO}} C_{\mu i} \chi_{\mu}(x_A, y_A, z_A), \quad (3.9)$$

where $C_{\mu i}$ denotes the MO coefficients, N_{AO} is the number of AO, (x_A, y_A, z_A) represents the three-dimensional electron spatial coordinates (x, y, z) with respect to a fixed nuclear center with spatial coordinates (A_x, A_y, A_z) .

$$r_A = \sqrt{x_A^2 + y_A^2 + z_A^2}, \quad (3.10a)$$

$$(x_A = x - A_x, \quad y_A = y - A_y, \quad z_A = z - A_z). \quad (3.10b)$$

In electronic structure theory, the set of AO can be Slater-type orbitals (STO) [101], Gaussian-type orbitals (GTO) [102], numerical atomic orbitals [103], etc. In 1930, Slater [101] used a nodeless exponential-type function to represent the essential component of an AO of the hydrogen atom. This exponential-type function is called

Slater-type orbitals [104]. A common expression for STO can be written in terms of spherical coordinate variables as

$$S_{\alpha,A,n,l,m}(r_A,\theta,\phi) = \mathcal{N}_{\text{sto}} r_A^{n-1} e^{-\zeta r_A} Y_{lm}(\theta,\phi), \quad (3.11)$$

where $\mathcal{N}_{\text{sto}}$ denotes the normalization factor, and ζ is a variational parameter (obtained from minimizing the total electronic energy of the atom) associated with the nuclear charge Z and the orbital quantum number n (integer value, $n \geq 1$). r_A denotes the radial distance between a fixed nuclear center with spatial coordinates (A_x, A_y, A_z) and an electron with spatial coordinates (x_1, y_1, z_1) in Eq. (3.10), and θ denotes polar angle, ϕ denotes azimuthal angle. The last term $Y_{lm}(\theta, \phi)$, represents spherical harmonic functions.

The electronic wavefunction must fulfill certain properties in order to properly describe an N -electron system. It must be continuous, single-valued, and square-integrable. Additionally, it must satisfy nuclear–electron and electron–electron cusp conditions (Kato’s cusp condition) [105]. A physically realistic wavefunction should also decay exponentially at large distances from the nuclei. The STO are ideal basis functions due to their ability to form the electronic wavefunction of an N -electron system that satisfies almost all the conditions. Moreover, it has been demonstrated that using only a small number of STO is sufficient to obtain highly accurate binding energies of many atoms and ions [106]. However, the main drawback of STO is the poor performance in evaluating molecular integrals and related derivatives, thus STO are not preferred by most modern quantum chemistry calculations.

In 1950, Boys proposed to use Gaussian-type orbitals [102] as an alternative option to replace the STO. The general formulation of atom-centered GTO written in Cartesian coordinates reads as

$$G_{\alpha,A,l_x,l_y,l_z}(x_A,y_A,z_A) = \mathcal{N}_{\text{gto}} x_A^{l_x} y_A^{l_y} z_A^{l_z} e^{-\alpha r_A^2}, \quad (3.12)$$

where $\mathcal{N}_{\text{gto}}$ denotes the normalization factor, α is the Gaussian orbital exponent, the sum of l_x, l_y and l_z determines the type of atomic orbital (i.e., s, p, d orbital). Although a single GTO can not directly satisfy Kato’s cusp conditions near the nuclei or exhibit true exponential decay at large distances, a common strategy is to use a linear combination of multiple GTO to fit an STO in order to achieve a certain accuracy. Nonetheless, with the main advantage of employing efficient algorithms for evaluating molecular integrals [107], the GTO have been the most widely applied basis functions in modern *ab initio* calculations.

In general, an electronic wavefunction of a molecular system can be represented in terms of many one-electron wavefunctions (i.e., molecular orbitals),

and the one-electron wavefunctions can be obtained by linear combinations of atomic orbitals (i.e., MO-LOAO), which form the basis set. In other words, this orbital picture transforms the N -electron problem into a set of one-electron functions spanned by an atomic basis, allowing *ab initio* methods to systematically approximate the wavefunction of molecular systems.

Furthermore, since electrons are fermions with a spin of $1/2$, it is essential to include spin information for a complete description of electrons. Thus, a molecular orbital consisting of a spatial orbital and a spin function is commonly known as a spin-orbital. In 1928, Hartree [108] introduced a wavefunction in the form of a simple product of spin orbitals for each electron,

$$\Psi^{\text{HP}}(1, 2, \dots, N) = \phi_1(1)\phi_2(2)\cdots\phi_N(N). \quad (3.13)$$

For convenience, we will henceforth use the notation, $1 \equiv \{\mathbf{r}_1, \sigma_1\}$, to represent the electron spatial $\{\mathbf{r}_1\}$ and spin $\{\sigma_1\}$ coordinates. Eq. (3.13) is referred to as the Hartree Product N -electron wavefunction in terms of N spin orbitals. In this ansatz, electrons are treated independently, thus the eigenvalue of Ψ^{HP} is simply the sum of the one-electron energies.

The N -electron wavefunction must be antisymmetric and satisfy the Pauli exclusion principle [109], which states that any two electrons in the system cannot have the same quantum numbers. As a consequence, the wavefunction should change the sign with respect to the interchange of both the spatial and spin coordinates of any two electrons,

$$\Psi(1, \dots, i, \dots, j, \dots, N) = -\Psi(1, \dots, j, \dots, i, \dots, N). \quad (3.14)$$

The Hartree Product is not an antisymmetric wavefunction, whereas a Slater determinant can easily enforce the antisymmetry in the wavefunction [110]. For an N -electron and N -spin-orbital system, the Slater determinant is given by

$$\Phi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \phi_3(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \phi_3(2) & \dots & \phi_N(2) \\ \vdots & \vdots & \vdots & & \vdots \\ \phi_1(N) & \phi_2(N) & \phi_3(N) & \dots & \phi_N(N) \end{vmatrix}, \quad (3.15)$$

where the normalization factor $1/\sqrt{N!}$ ensures the proper normalization of the wavefunction as long as $\{\phi_i(i)\}$ are also normalized, where i denotes the i -th spin orbital. Eq. (3.15) indicates that the wavefunction consists of N orthonormal spin orbitals $\{\phi_i(i)\}$, where each orbital can be occupied by an electron without specifying which electron occupies which orbital, this treatment ensures electrons

be indistinguishable. The N -electron wavefunction can be constructed using either a single Slater determinant or a linear combination of multiple determinants,

$$|\Psi\rangle = \sum_i^{N_{\text{det}}} c_i |\Phi_i\rangle, \quad (3.16)$$

where c_i denotes the coefficients of determinant $|\Phi_i\rangle$. These coefficients determine the contribution of each determinant to the overall wavefunction. The exact wavefunction of any N -electron system can be represented by a linear combination of all possible Slater determinants formed from a complete set of spin orbitals. The method solves the electronic Schrödinger equation by considering all possible electronic configurations within a given basis set is known as Full Configuration Interaction (FCI). In electronic structure calculations, the FCI method provides the exact (non-relativistic, Born–Oppenheimer approximate) wavefunction and energy for a given basis set. However, it is also the most computationally intensive method and is only feasible for very small systems.

3.1.3 The Variational Principle

The variational principle is very useful in quantum mechanics and mathematical optimization, and it forms the basis for many computational methods in quantum chemistry and physics. The variational principle states that any approximate well-behaved wavefunction yields energy above or equal to the exact ground-state energy, and this equality occurs if and only if the approximate wavefunction is equal to the exact ground-state wavefunction.

According to the variational principle, the energy is determined through the evaluation of the expectation value of the Hamiltonian operator with respect to a trial wavefunction, which is then divided by its norm [11],

$$E[\tilde{\Psi}(1, \dots, N)] = \frac{\langle \tilde{\Psi}(1, \dots, N) | \hat{H} | \tilde{\Psi}(1, \dots, N) \rangle}{\langle \tilde{\Psi}(1, \dots, N) | \tilde{\Psi}(1, \dots, N) \rangle} \geq E_0, \quad (3.17)$$

where E_0 is the ground-state energy of the system (the lowest eigenvalue of $\hat{H}$). If the trial wavefunction is not the true ground-state wavefunction, the computed energy will always be higher than E_0 .

Assuming the trial wavefunction is composed of a linear combination of a complete set of orthonormal wave functions, ψ_i , in the Hilbert space,

$$|\tilde{\Psi}(1, \dots, N)\rangle = \sum_i c_i |\psi_i(1, \dots, N)\rangle, \quad (3.18)$$

where c_i are the expansion parameters. To evaluate the energy, it is necessary to ensure that the trial wavefunction is normalized, all ψ_i are eigenfunctions of $\hat{H}$,

and each ψ_i is square integrable. Once these conditions are met, the energy can be expressed as

$$\begin{aligned}
 E[\tilde{\Psi}(1, \dots, N)] &= \frac{\int \dots \int \tilde{\Psi}^*(1, \dots, N) \hat{H} \tilde{\Psi}(1, \dots, N) d1 \dots dN}{\int \dots \int |\tilde{\Psi}|^2 d1 \dots dN} \\
 &= \frac{\int \dots \int \sum_i c_i \psi_i(1, \dots, N) \hat{H} \sum_j c_j \psi_j(1, \dots, N) d1 \dots dN}{\int \dots \int \sum_i c_i \psi_i(1, \dots, N) \sum_j c_j \psi_j(1, \dots, N) d1 \dots dN} \\
 &= \frac{\sum_{ij} c_i c_j \int \dots \int \psi_i(1, \dots, N) \hat{H} \psi_j(1, \dots, N) d1 \dots dN}{\sum_{ij} c_i c_j \int \dots \int \psi_i(1, \dots, N) \psi_j(1, \dots, N) d1 \dots dN} \quad (3.19) \\
 &= \frac{\sum_{ij} c_i c_j E_j \delta_{ij}}{\sum_{ij} c_i c_j \delta_{ij}} \\
 &= \frac{\sum_i c_i^2 E_i}{\sum_i c_i^2},
 \end{aligned}$$

where the Kronecker delta function δ_{ij} ensures the orthonormality of ψ_i ,

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{otherwise.} \end{cases} \quad (3.20)$$

Now the constraint of the normalization is imposed over these expansion parameters, $\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1$, i.e., $\sum_i c_i^2 = 1$. Thus, the difference between the energy from any approximate wavefunction $E[\tilde{\Psi}]$ and the ground-state energy E_0 is

$$E[\tilde{\Psi}] - E_0 = \sum_i c_i^2 (E_i - E_0) \geq 0. \quad (3.21)$$

As all the expansion parameters are real numbers, i.e., $c_i^2 \geq 0$, and $E_i - E_0$ must be greater than or equal to zero because E_0 is the lowest energy possible. Eq. (3.21) implies that any approximate wavefunction will generate an energy $E[\tilde{\Psi}]$ above or equal to the exact ground-state energy E_0 . To find the exact ground-state energy through the variational principle, a necessary condition is to minimize the energy $E[\tilde{\Psi}]$ with respect to all the c_i parameters in the wavefunction [111].

The variational principle provides a path for solving the Schrödinger equation and determining the ground-state energy. The methods that apply the variational principle to optimize the variational parameters are known as variational methods (e.g., FCI is a typical variational method).

3.1.4 Single-Reference Methods

In *ab initio* calculations, the Hartree-Fock (HF) theory holds an important position. The HF method assumes that the wavefunction can be represented by a single Slater determinant, rendering it an SR method. While it yields exact electronic energy values for one-electron systems, its accuracy diminishes for systems with multiple electrons. For such cases, the HF approximation treats each electron as if it interacts solely with the mean-field created by all other electrons, making it a mean-field method. Although the HF method often provides poor electronic structure calculations, it can serve as the starting point (or called “reference”) for more advanced post-HF methods that are also commonly classified as the SR methods.

The HF method is a variational method that minimizes the total energy of a single (Slater) determinant wavefunction. The following details of the HF adhere primarily to the lecture of Sherrill [112]. The minimization procedure uses the Lagrange’s method with the constraint that the spin orbitals are orthonormal, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$, where i and j denote spin-orbital indices. The Lagrangian,

$$\mathcal{L}[\{\phi_i\}] = E_{\text{HF}}[\{\phi_i\}] - \sum_{ij} \epsilon_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}), \quad (3.22)$$

contains undetermined Lagrange multipliers, ϵ_{ij} , and a set of orbitals $\{\phi_i\}$. By solving the first variation $\partial \mathcal{L} = 0$, one arrives at the Hartree-Fock equations of an N -electron system, the Fock eigenvalue equation, given by

$$\hat{F}_i(1) \phi_i(1) = \epsilon_i \phi_i(1), \quad (3.23)$$

where the eigenvectors $\phi_i(1)$ are spin orbitals, the eigenvalues ϵ_i are orbital energies, and $\hat{F}_i$ denotes the one-electron Fock operator over spin-orbital i ,

$$\hat{F}_i(1) = \hat{H}_{\text{core}}(1) + \sum_{j \neq i}^N (\hat{J}_j(1) - \hat{K}_j(1)). \quad (3.24)$$

$\hat{F}_i(1)$ is defined as a sum of the one-electron core Hamiltonian operator $\hat{H}_{\text{core}}$, the Coulomb operator $\hat{J}_j$, and the exchange operator $\hat{K}_j$ [112]. These operators are given by

$$\begin{aligned} \hat{H}_{\text{core}}(\mathbf{r}_1) &= -\frac{1}{2} \nabla_{\mathbf{r}_1}^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{r}_A|} \\ \hat{J}_j(1) \phi_i(1) &= \left(\int \phi_j^*(2) \frac{1}{r_{12}} \phi_j(2) d2 \right) \phi_i(1) \\ \hat{K}_j(1) \phi_i(1) &= \left(\int \phi_j^*(2) \frac{1}{r_{12}} \phi_i(2) d2 \right) \phi_j(1), \end{aligned} \quad (3.25)$$

where r_{12} represents the Euclidean distance between electrons 1 and 2,² and it is also referred as the interelectronic distance in this thesis. The one-electron core Hamiltonian, $\hat{H}_{\text{core}}$, is a sum of the kinetic energy and electron-nuclear attraction energy operators. We use spatial coordinates $\mathbf{r}_1$ in $\hat{H}_{\text{core}}$ for convenience since the operator itself is assumed spin-independent. The electron-electron repulsion operator is approximated by one-electron Coulomb and exchange operators. The Coulomb operator $\hat{J}_j$ is a local term associated with the electron–electron repulsion energy of the two electrons in the j -th spin-orbital. The exchange operator $\hat{K}_j$ is a non-local term associated with the electron exchange energy of the two electrons in the i -th and j -th spin-orbitals [113]. The Hartree-Fock equations define molecular orbitals (i.e., the HF orbitals). The HF orbitals, also known as canonical HF orbitals, are obtained through the diagonalization of the matrix representation of the Fock operator.

The Hartree-Fock calculations were originally done numerically by solving the HF differential equations. Nevertheless, due to the limited computational power and its poor scalability with system size, the application of numerical HF solutions was limited only to small molecular systems [114–119].

In 1951, Roothaan [100] and Hall [120] independently proposed an alternative solution to the Hartree-Fock equations. They introduced the MO-LCAO approach with non-orthogonal AO in a basis function space, enabling the transformation of differential equations into algebraic equations. This approach provides an efficient and practical solution for HF calculations. Following their approach, we introduce a set of known basis functions χ_μ , then the unknown molecular orbital ϕ_i can be expanded as a linear combination of atomic orbital basis functions with a set of expansion coefficients $C_{\mu i}$,

$$\phi_i(1) = \sum_{\mu=1}^{\mathcal{K}} C_{\mu i} \chi_\mu(1), \quad (3.26)$$

where $\mathcal{K}$ represents the total number of basis functions χ_μ . Then the Roothaan-Hall equation can be obtained as

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}, \quad (3.27)$$

where the overlap matrix $S_{\mu\nu}$ and Fock matrix $F_{\mu\nu}$ are

$$\begin{aligned} S_{\mu\nu} &= \int \chi_\mu^*(1) \chi_\nu(1) \, d1 \\ F_{\mu\nu} &= \int \chi_\mu^*(1) \hat{F}_i(1) \chi_\nu(1) \, d1, \end{aligned} \quad (3.28)$$

²Euclidean distance in real space, $r_{12} \equiv \|\mathbf{r}_1 - \mathbf{r}_2\| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$.

or compactly shown in a matrix form

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \quad (3.29)$$

where $\mathbf{C}$ represents the square matrix of the expansion coefficients C_{vi} , and ϵ denotes a diagonal matrix of the orbital energies ϵ_i , which are the eigenvalues of the Fock matrix $\mathbf{F}$. As the Fock matrix $\mathbf{F}$ depends on $\mathbf{C}$, solving the Eq. (3.29) must be done iteratively. The solution requires beginning with some initial guess orbitals, then forming and diagonalizing the Fock matrix $\mathbf{F}$ iteratively. Hence, this procedure is called the Self-Consistent-Field (SCF) method.

The SCF procedure determines the HF orbitals ϕ_i , and then the total electronic energy is calculated as the expectation value of the single-determinant HF wavefunction that is constructed by considering only occupied orbitals. In a closed-shell system with N electrons, where each orbital is doubly occupied, it is often assumed that the spatial part of the orbitals is identical for electrons with opposite spins, these orbitals are known as restricted spin orbitals. This assumption simplifies calculations and is commonly used in the Restricted Hartree-Fock (RHF) method, where the wavefunction is constructed using a single-determinant with restricted spin-orbitals. The expression for the electronic energy of RHF is given by,

$$\begin{aligned} E_{\text{RHF}} &= \langle \Psi_{\text{RHF}} | \hat{H} | \Psi_{\text{RHF}} \rangle \\ &= 2 \sum_i^{N/2} h_{ii} + \sum_{i,j}^{N/2} (2J_{ij} - K_{ij}), \end{aligned} \quad (3.30)$$

where the one-electron energy (kinetic energy + electron-nuclear attraction energy) in terms of orbitals, h_{ii} , is expectation value of the core hamiltonian,

$$h_{ii} = \langle i | \hat{H}_{\text{core}} | i \rangle = \int \phi_i^*(1) \hat{H}_{\text{core}}(1) \phi_i(1) d1, \quad (3.31)$$

and the two-electron (electron-electron interaction) energy in terms of orbitals is approximated by a sum of the two-electron repulsion integrals: Coulomb integral J_{ij} and the exchange integral K_{ij} ,

$$\begin{aligned} J_{ij} &= \langle ii | jj \rangle = \iint \phi_i^*(1) \phi_i(1) \frac{1}{r_{12}} \phi_j^*(2) \phi_j(2) d1 d2 \\ K_{ij} &= \langle ij | ji \rangle = \iint \phi_i^*(1) \phi_j(1) \frac{1}{r_{12}} \phi_j^*(2) \phi_i(2) d1 d2. \end{aligned} \quad (3.32)$$

As a pioneer Single-Reference method, the HF approximation allows to obtain around 99% of overall energy for most systems, but many important chemical phenomena can not be precisely described without the remaining 1% energy,

which is defined as correlation energy. According to the definition of Löwdin [121], the correlation energy is the difference between the exact energy and the HF energy³ in a complete basis (Hartree-Fock limit),

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}^{\infty}. \quad (3.33)$$

However, calculating the exact energy is usually infeasible. Thus, in practice, it is more convenient to follow the approach of Pines [122], Eq. (3.34). Namely, the total energy is computed by using a given method X (beyond the HF method) with an appropriate basis set. Then, the correlation energy recovered by this method is given by

$$E_{\text{corr}}^X = E_X - E_{\text{HF}}. \quad (3.34)$$

Let us remind two main reasons for the failures of the HF theory. Firstly, the HF wavefunction is constructed by only one single-determinant, and usually with an incomplete basis. Secondly, the HF approximation neglects the electron correlation, it assumes that each electron interacts with the average charge distribution of all other electrons rather than instantaneous electron-electron interaction. In general, for any system with more than one electron, the HF wavefunction will never achieve the exact energy even using a complete basis.

Next, we will introduce some post-HF (or referred to as “correlated”) wavefunction methods that account for electron correlation. To begin with, the general form of the FCI wavefunction can be expanded as a linear combination of all possible Slater determinants,

$$|\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots, \quad (3.35)$$

where c_i denotes coefficients of determinants, with the constraint of normalization of the wavefunction, and $\sum_i c_i^2 = 1$. The Latin letters i, j, k, l denote the occupied HF orbitals, and a, b, c, d label the unoccupied (virtual) HF orbitals. These determinants form the basis of configurations (e.g., ground-state reference Φ_0 , single excitation Φ_S , double excitation Φ_D). To incorporate electron correlation energy by including excitations from the HF occupied to virtual orbitals, several practical methods are commonly employed, such as variational methods, perturbational methods, and coupled-cluster methods.

³In this thesis, HF usually refers to the RHF for closed-shell systems or Restricted Open-shell Hartree-Fock (ROHF) for open-shell systems.

1) Variational methods

The Configuration Interaction (CI) method is one of the most commonly used variational methods. The basic idea is to minimize the energy variationally using a trial wavefunction formed by a linear combination of Slater determinants. Technically, this procedure is equivalent to diagonalize the Hamiltonian in a basis of N -electron Slater determinants. In practice, we use the notation of $H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle$, where the Slater determinants Φ_i are orthogonal, and the CI secular equation can be written in matrix form as

$$\mathbf{H}\mathbf{c} = \mathbf{E}\mathbf{c}, \quad (3.36)$$

where $\mathbf{c}$ represents the c_i coefficient vector (i.e., CI vector), $\mathbf{H}$ denotes the CI matrix and $\mathbf{E}$ denotes the CI energy vector. To calculate the CI energy, one needs to diagonalize the $\mathbf{H}$ matrix, the CI energy is obtained as the lowest eigenvalue of the $\mathbf{H}$ matrix, and the corresponding eigenvector gives the c_i coefficients associated with their Slater determinants [Eq. \(3.35\)](#).

The structure of the CI matrix is shown in [Fig. 3.1](#). This matrix is Hermitian and we only show the upper triangle part. The CI matrix is sparse, the elements between the ground-state (HF reference) and singly excited configurations are zero due to Brillouin’s theorem, and the coupling matrix elements between ground-state and triple excitation determinants are zero by applying the Condon–Slater rules. In fact, all matrix elements of the Hamiltonian between Slater determinants that differ by more than two spin orbitals vanish. In addition, it usually requires orbitals obtained from the HF method, as well as the one and two-electron integrals⁴ (in Mulliken notation),

$$\begin{aligned} (p|\hat{h}|q) &= \int \phi_p^*(\mathbf{r}_1) \hat{H}_{\text{core}}(\mathbf{r}_1) \phi_q(\mathbf{r}_1) d\mathbf{r}_1 \\ (pq|rs) &= \int \int \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \frac{1}{r_{12}} \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (3.37)$$

where p, q, r, s denote general MO indices. The computation cost for generating two-electron integrals over AO is up to M^4 , where M is the number of basis functions, and the step of transforming the integrals from the AO to the MO basis makes it increase to M^5 . Hence, the computation cost of CI methods primarily arises from the generation and storage of two-electron integrals.

⁴Notice that in [Eq. \(3.37\)](#), we use spatial coordinates in the integrals. The Hamiltonian operator is usually spin-independent (except studying systems involving heavy elements, strong spin-orbit coupling, etc.), it is often more convenient to factor out the spin dependence.

$$\begin{pmatrix} \Phi_0 \\ \Phi_S \\ \Phi_D \\ \Phi_T \\ \vdots \end{pmatrix} \begin{pmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & 0 & \langle \Phi_0 | \hat{H} | \Phi_D \rangle & 0 & \dots \\ & \langle \Phi_S | \hat{H} | \Phi_S \rangle & \langle \Phi_S | \hat{H} | \Phi_D \rangle & \langle \Phi_S | \hat{H} | \Phi_T \rangle & \dots \\ & & \langle \Phi_D | \hat{H} | \Phi_D \rangle & \langle \Phi_D | \hat{H} | \Phi_T \rangle & \dots \\ & & & \langle \Phi_T | \hat{H} | \Phi_T \rangle & \dots \\ & & & & \vdots \end{pmatrix}$$

FIGURE 3.1: Structure of the CI Matrix

Unfortunately, the number of Slater determinants grows exponentially with system size, resulting in the enormous cost of calculations. For instance, given a $2M$ spin orbitals ($2M = M_\alpha + M_\beta$) in an N -electron system ($N = N_\alpha + N_\beta$), one can construct $\binom{M_\alpha}{N_\alpha} \binom{M_\beta}{N_\beta}$ different spin-preserved Slater determinants. As a consequence, the CI matrix element increases as well exponentially resulting in a huge matrix even for small molecules. Therefore, the FCI solution that includes all possible configurations is definitely impractical. The CI approximations that truncate expansion at a certain excitation level are more commonly employed. In particular, the approximate CI method that includes only single and double excitations (CISD) has been commonly applied.

The Single-Reference based CI hierarchy begin with the HF reference, and the Single-Reference CISD wavefunction is constructed from the HF wavefunction by adding new determinants of single and double excitations that promote electrons from the occupied to unoccupied (virtual) HF orbitals. The total energy of CISD is the sum of the HF reference energy and the CISD correlation energy,

$$\begin{aligned} E_{\text{CISD}} &= \langle \Phi_{\text{HF}} | \hat{H} | \Phi_{\text{HF}} \rangle + 2 \langle \Phi_{\text{HF}} | \hat{H} | \Phi_D \rangle + \langle \Phi_S | \hat{H} | \Phi_S \rangle + \\ &\quad 2 \langle \Phi_S | \hat{H} | \Phi_D \rangle + \langle \Phi_D | \hat{H} | \Phi_D \rangle \\ &= E_{\text{HF}} + E_{\text{corr}}^{\text{CISD}}. \end{aligned} \tag{3.38}$$

For a system containing only two electrons (e.g., H_2 , He), CISD is identical to FCI. However, for a system with three or four electrons, single and double excitations of CI wavefunction are not enough anymore to construct the exact wavefunction, it requires up to triples or quadruples. Consequently, for a system beyond two electrons, the correlation energy captured by CISD does not scale correctly with the size of the system, and the total energy of a combined system is not equal to the sum of the energies of the individual systems due to the neglect of higher-order excitations beyond singles and doubles. Hence, the CISD method becomes neither size extensive nor size consistent.

A method is size extensive if the energy of a system computed with this method scales linearly with the size of the system [123]. For example, the energy of a non-interacting n -atom system A is equivalent to the atom A energy multiplied by n , that is $E(n \cdot A) = n \cdot E(A)$. The size-consistency indicates that the energy of a combined dimer system AB is identical to the sum of energies of two independent monomers A and B [124], namely, $E(AB) = E(A) + E(B)$. In general, the HF and FCI methods are size extensive and size consistent,⁵ while CI methods truncated to any excitation level are neither size extensive nor consistent anymore [113, 125]. Here we note that the size-extensive and size-consistent properties are not only used for the energy and can be also applied to other quantities (e.g., MR diagnostics).

Size consistency is very important for studying chemical reactivities, dissociation energies, etc. The lack of size extensivity lowers the capacity of CISD for recovering correlation energy as the system size extends, thus limiting its application. We note that the size-consistency error can be partially corrected by approximating the quadruple excitations which are usually more significant after the double excitations, and these corrections can enhance the accuracy of CISD [126, 127]. However, handling large molecules with CISD is still challenging and impractical due to its computational cost, which scales as M^6 with the number of basis functions, M .

2) Perturbational methods

Perturbation theory assumes that if an actual problem only presents a slight difference from a known problem, this known problem usually can be taken as the reference to solve the unknown one. In quantum mechanics, Many-Body Perturbation Theory (MBPT) is known as a mathematical method that applies perturbation theory to solve the Schrödinger equation.

The basic idea of MBPT is to assume that the Hamiltonian of the system consists of two parts: the unperturbed part $\hat{H}^{(0)}$ and the perturbed part $\lambda\hat{H}'$ (which should be small),

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda\hat{H}', \quad (3.39)$$

where λ is a perturbation parameter ($0 \leq \lambda \leq 1$). If $\lambda = 0$, then $\hat{H}(\lambda = 0) = \hat{H}^{(0)}$ gives the unperturbed Hamiltonian, corresponding to the zeroth-order eigenfunction and eigenvalue which have a known solution,

$$\hat{H}^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)}. \quad (3.40)$$

⁵Some people might consider that the Restricted Hartree-Fock (RHF) method is not size consistent due to the lack of separability in the wavefunction (e.g., H_2 molecule dissociation at a large distance).

The ground-state wavefunction and energy can be expanded as a Taylor series in powers of the perturbation parameter λ ,

$$\begin{aligned}\Psi &= \lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots + \lambda^n \Psi^{(n)} \\ E &= \lambda^0 E^{(0)} + \lambda^1 E^{(1)} + \lambda^2 E^{(2)} + \dots + \lambda^n E^{(n)},\end{aligned}\tag{3.41}$$

where the $\Psi^{(1)}, \Psi^{(2)}, \dots$ and $E^{(1)}, E^{(2)}, \dots$ are first- and second-order, ... corrections to the wavefunction and the energy, respectively. Here we set the λ parameter to 1, then the n -th order energy or wavefunction is obtained by summing over all terms up to n -th order. Finally, the Schrödinger equation can be written in terms of perturbative corrections and solved for each order correction.

$$\begin{aligned}(\hat{H}^{(0)} + \hat{H}')(\Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots + \Psi^{(n)}) \\ = (E^{(0)} + E^{(1)} + E^{(2)} + \dots + E^{(n)})(\Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots + \Psi^{(n)}).\end{aligned}\tag{3.42}$$

In 1934, Møller and Plesset [128] first proposed a perturbative method for treating atoms and molecules by taking Hartree–Fock solution as the zeroth-order approximation. Later this approximation approach has been developed as Møller–Plesset Perturbation Theory (MPPT) [124, 129, 130]. In contrast to the CI methods, the MPPT hierarchy (or MPn methods up to the n -th order correction) is size consistent because the selection of interaction terms by the perturbation formalism produces size-consistency. Unlike CI variational methods, the MPn methods are not variational, and adding higher orders of the perturbation expansion can not guarantee achieving higher accuracy. In MPn methods, the most common way is to truncate up to the second-order, which is known as MP2 method.

The starting point of MPn method is to take the sum of one-electron Fock operator as the zeroth-order Hamiltonian, $\sum_i \hat{F}_i(1)$, and the zeroth-order wavefunction being the solution of this zeroth-order Hamiltonian. Then, the MP0 energy equals the sum of HF orbital energies.

$$E^{(0)} = \langle \Psi^{(0)} | \hat{H}^{(0)} | \Psi^{(0)} \rangle = \sum_i^N \epsilon_i.\tag{3.43}$$

Note that this simple sum of one-electron Fock operators leads to double counting of the electron-electron repulsion (Coulomb and exchange energies). In the first-order Correction of MPPT (MP1), the Hamiltonian correction, $\hat{H}^{(1)}$, eliminates the double-counted Coulomb and exchange operators in Eq. (3.44), resulting in the HF energy in Eq. (3.45) [131]. In other words, this correction reflects the difference between the true electron-electron interactions and the mean-field approximation.

$$\hat{H}^{(1)} = \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \sum_j^N (\hat{J}_j(i) - \hat{K}_j(i)),\tag{3.44}$$

Hence, the HF energy is equivalent to the zeroth-order plus first-order MPPT energy corrections,

$$\begin{aligned}
 E_{\text{MP1}} &= E^{(0)} + E^{(1)} \\
 &= \langle \Psi^{(0)} | \hat{H}^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \hat{H}^{(1)} | \Psi^{(0)} \rangle \\
 &= \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle \\
 &= E_{\text{HF}}.
 \end{aligned} \tag{3.45}$$

Since the zeroth-order and first-order correction ends up with the HF solution, then adding the second-order correction is necessary to account for the correlation energy. The second-order correction takes into account the double-excited configurations and their interactions with the ground-state configuration, after applying Condon–Slater rules. The second-order correction can be obtained as

$$E^{(2)} = \sum_i^{\text{occ}} \sum_{i < j}^{\text{occ}} \sum_a^{\text{vir}} \sum_{a < b}^{\text{vir}} \frac{[(ij|ab) - (ia|jb)]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \tag{3.46}$$

where ϵ_i denotes the energy of the i -th HF orbital. For the summation, “occ” represents the number of occupied orbitals, and “vir” denotes the number of virtual (unoccupied) orbitals. $E^{(2)}$ only depends on the orbital energies and two-electron integrals over MO basis. The total electronic energy of MP2 is calculated by summing the $E^{(0)}$, $E^{(1)}$ and $E^{(2)}$ terms. Hence, the correlation energy from MP2 calculation is, $E_{\text{MP2}}^{\text{corr}} = E^{(2)}$. In general, MP2 calculations can recover around 80 – 90% of the correlation energy. Moreover, MP2 is a relatively efficient method compared to other post-HF methods; it does not require an extra iterating process after the SCF calculation. The main computation cost (or bottle neck) of MP2 is due to the transformation of two-electron integrals from AO to MO, thus MP2 cost is roughly scaled as $\mathcal{O}(M^5)$, where M is the number of basis functions.

3) Coupled-cluster methods

The cluster expansion technique was initially developed by nuclear physicists in the 1950s [132, 133], but actual applications of coupled-cluster (CC) theory on quantum chemistry began after 1966. Čížek [134] extended the method for calculating electron correlation in atoms and molecules. The CC methods are one of the most successful *ab initio* methods in electronic structure calculations. In CC theory, the exact wavefunction, $|\Psi\rangle$, is expressed by using an exponential ansatz,

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}} |\Phi_0\rangle, \tag{3.47}$$

where $|\Phi_0\rangle$ is the reference wavefunction, and $\hat{T}$ denotes the cluster operator. Note that the reference wavefunction can be the Hartree-Fock wavefunction

(single-determinant), a Multi-Configurational Self-Consistent Field (MCSCF) wavefunction, a Multireference Configuration Interaction (MRCI) wavefunction, etc. Here we only present the case in which the Hartree-Fock wavefunction is used as a reference. The exponential ansatz can be expanded in Taylor series,

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!}, \quad (3.48)$$

where the cluster operator $\hat{T}$ is defined as a sum of N excitation terms (where N denotes the total number of electrons): all single excitations ($N = 1$), all double excitations ($N = 2$), all triple excitations ($N = 3$), etc.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N. \quad (3.49)$$

Applying the full cluster operator expansion terms to the reference (e.g., Hartree-Fock) wavefunction, Φ_0 , we can obtain all possible Slater determinants, so the full CC wavefunction is equivalent to the FCI wavefunction. Each cluster operator expansion term $\hat{T}_N$ or their product terms can generate configurations associated with cluster amplitudes (e.g., t_i^a, t_{ij}^{ab}),

$$\begin{aligned} \hat{T}_1|\Phi_0\rangle &= \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a |\Phi_i^a\rangle \\ \hat{T}_2|\Phi_0\rangle &= \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{vir}} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \\ \hat{T}_2^2|\Phi_0\rangle &= \sum_{\substack{i<j \\ k<l}}^{\text{occ}} \sum_{\substack{a<b \\ c<d}}^{\text{vir}} t_{ij}^{ab} t_{kl}^{cd} |\Phi_{ijkl}^{abcd}\rangle, \end{aligned} \quad (3.50)$$

The full CC expansion is impractical, thus requiring the adoption of a truncated cluster expansion. Due to the high complexity and computation cost, the cluster operator is usually truncated up to single and double excitations, which is known as CCSD method [135]. CCSD is widely used as a correlation method. Adding a correction of perturbative triples (also includes a singles/triples coupling term) produces the CCSD(T) [136], which is nowadays considered as the gold-standard method in the quantum chemistry community.

Unlike the CI methods, the CC methods are size extensive due to the exponential ansatz form of the wavefunction. The CC methods are size consistent because the CC wavefunction expansion contains both connected ($\hat{T}_N$) and disconnected ($\hat{T}_N^2$) terms, and the disconnected terms that contribute to higher excitation levels ensure the size-consistency. $\hat{T}_N$ corresponds to true N -electrons interacting simultaneously, while a disconnected term (e.g., $\hat{T}_N^2$) is associated with correlations

between N non-interacting electron pairs. More concretely, comparing the cluster expansion with the FCI wavefunction expansion in Eq. (3.35), we can draw a map between the cluster operators (and their products) and the CI coefficient c_i at each excitation level [125, 137].

$$\begin{aligned}
 c_0 &\leftrightarrow 1 \\
 c_S &\leftrightarrow \hat{T}_1 \\
 c_D &\leftrightarrow (\hat{T}_2 + \frac{1}{2}\hat{T}_1^2) \\
 c_T &\leftrightarrow (\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3) \\
 c_Q &\leftrightarrow (\hat{T}_4 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4) \\
 &\dots
 \end{aligned} \tag{3.51}$$

However, the CC methods are usually not solved variationally, because the extremely high complexity of variational CC wavefunction expansion leads to a very expensive treatment of nonlinear equations [138]. As a Single-Reference method, the coupled cluster single and double excitations (CCSD) energy is formulated by projecting CC Schrödinger equation onto the Single-Reference (Hartree-Fock) wavefunction,

$$E_{\text{CCSD}} = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{CCSD}} \rangle, \tag{3.52}$$

where the CCSD wavefunction is given by

$$\begin{aligned}
 |\Psi_{\text{CCSD}}\rangle &= e^{\hat{T}_1 + \hat{T}_2} |\Psi_{\text{HF}}\rangle \\
 &= \underbrace{(1)}_0 + \underbrace{\hat{T}_1}_S + \underbrace{\hat{T}_2 + \frac{1}{2}\hat{T}_1^2}_D + \underbrace{\hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 + \dots}_T |\Psi_{\text{HF}}\rangle.
 \end{aligned} \tag{3.53}$$

Now let us use a projection manifold, $\langle \Psi_\mu | = \langle \Psi_{\text{HF}} | \hat{t}_\mu^\dagger$, which involves all determinants of single and double excitations [139]. The projected CCSD equations is given by

$$\begin{aligned}
 \langle \Psi_{\text{HF}} | e^{-(\hat{T}_1 + \hat{T}_2)} \hat{H} e^{(\hat{T}_1 + \hat{T}_2)} | \Psi_{\text{HF}} \rangle &= E_{\text{CCSD}} \\
 \langle \Psi_\mu | e^{-(\hat{T}_1 + \hat{T}_2)} \hat{H} e^{(\hat{T}_1 + \hat{T}_2)} | \Psi_{\text{HF}} \rangle &= 0.
 \end{aligned} \tag{3.54}$$

By solving the above Eq. (3.54), we obtain the energy of CCSD, as well as the amplitudes. However, these nonlinear equations must be solved iteratively, so the CCSD requires an additional iterative process after the convergence of SCF. Furthermore, only the amplitudes of singles t_i^a and doubles t_{ij}^{ab} contribute directly

to the CCSD energy and the two-particle operator Hamiltonian. For closed-shell systems, the CCSD energy can be written as

$$E_{\text{CCSD}} = E_{\text{HF}} + \sum_{aibj} (t_{ij}^{ab} + t_i^a t_j^b) L_{iajb}, \quad (3.55)$$

where the term L_{iajb} can be calculated in terms of g_{iajb} which are the two-electron integrals in general MO basis,

$$L_{iajb} = 2g_{iajb} - g_{ibja}. \quad (3.56)$$

In general, CCSD generates energy with higher accuracy than CISD and MP2. In particular, it can recover around 98% of correlation energy in most weakly-correlated systems (e.g., nitrogen molecule at equilibrium, the ground state of methane), while it usually fails at calculating some strongly-correlated systems (e.g., nitrogen molecule separated at a large distance, the ground state of ozone molecule). The computational cost of CCSD is roughly scaled as $\mathcal{O}(M^6)$, while using some techniques (same for CISD), it can be reduced to $\mathcal{O}(M_{\text{occ}}^2 M_{\text{vir}}^4)$, where M_{occ} stands for the number of occupied orbitals and M_{vir} denotes the number of virtual orbitals.

3.1.5 Multireference Methods

The SR wavefunctions are insufficient to describe strongly correlated systems, such as nitrogen molecule dissociation, the ground state of the ozone molecule, transition metal complexes, and among others. The wavefunctions of these strongly correlated systems are predominantly influenced by multiple electronic configurations. To accurately describe such systems, MR wavefunction methods are commonly employed. MR wavefunction methods utilize a reference wavefunction that is a superposition of multiple Slater determinants, instead of a single-determinant (Hartree-Fock) wavefunction⁶.

The most common MR wavefunction method is Multi-Configuration Self-Consistent Field (MCSCF). In MCSCF theory, the multi-configurational (MC) wavefunction, $|\Psi_{\text{MC}}\rangle$, can be constructed as a linear combination of selected Slater determinants (or Configuration State Functions, CSFs),

$$|\Psi_{\text{MC}}\rangle = \sum_i^{\mathcal{M}} c_i |\Phi_i\rangle, \quad (3.57)$$

where $\mathcal{M}$ is the number of selected Slater determinants or CSFs. The MCSCF is a variational method. If the wavefunction $|\Psi_{\text{MC}}\rangle$ is constructed from all possible Slater determinants or CSFs, then the MCSCF gets equivalent to the FCI solution. Unlike Single-Reference CI methods, the orbitals within the selected configurations and the CI coefficients are both optimized in MCSCF procedure [140, 141]. Specifically, the MCSCF energy is computed by minimizing the expectation value in terms of orbitals, $\{\phi_i\}$, and CI coefficients, $\{c_i\}$, under some constraints (e.g., $\sum c_i = 1$ and $\langle \phi_i | \phi_j \rangle = \delta_{ij}$),

$$E_{\text{MCSCF}} = \min_{\{\phi_i\}} \min_{\{c_i\}} \frac{\langle \Psi_{\text{MC}} | \hat{H} | \Psi_{\text{MC}} \rangle}{\langle \Psi_{\text{MC}} | \Psi_{\text{MC}} \rangle}. \quad (3.58)$$

However, one of the technical difficulties of MCSCF methods is to effectively select appropriate configurations for constructing the MC wavefunction. A straightforward approach is applying some techniques to select significant configurations generated in the FCI space, such as Knowles (*a priori* selected) FCI algorithm [142], Configuration Interaction with Perturbative Selection through Iterations (CIPSI) [143] and other attainable selected CI algorithms [144–148]. These methods can achieve FCI accuracy by directly selecting FCI determinants, and they

⁶Some authors might consider that the HF wavefunction contains more than one Slater determinant in some open-shell cases (e.g., some He excited states), while it involves a single Slater determinant for closed-shell systems [113].

are often regarded as quasi-exact solutions rather than MCSCF methods. Unfortunately, the extremely high computational demand limits the applications of these methods.

More practically, one of the most widely applied MCSCF methods is the Complete-Active-Space Self-Consistent Field (CASSCF) method [149–152], in which selecting configurations is done indirectly by dividing the orbitals into active and inactive spaces. The active orbitals are chosen by users, and they are usually some frontier orbitals near the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). The inactive orbitals are always either doubly occupied (with 2 electrons) or empty (with 0 electrons). Here we use the common notation CASSCF(n, m) which means that n electrons and m active orbitals in CAS space are used to form all possible configurations in this reduced FCI wavefunction expansion. Then, the MCSCF optimization procedure is done with this CASSCF wavefunction. However, the CASSCF wavefunction, which is constructed through the FCI expansion within the CAS space, becomes excessively large and impractical when the CAS space expands significantly. On the other hand, another variant of CASSCF is the Restricted Active Space Self-Consistent Field (RASSCF) method [153]. In RASSCF, the active orbitals are split into three subspaces, RAS1, RAS2 and RAS3, the configurations are selected by following some additional rules, such as the configurations in RAS2 space can only be formed by exciting maximum 2 electrons from RAS1 to maximum 2 holes in RAS3 space. Despite the difficulty in optimizing RASSCF wavefunctions, they can usually handle larger active spaces than CASSCF thanks to these additional restriction rules. Nonetheless, CASSCF and RASSCF calculations are not black-box methods and require more technical expertise and insight than SR methods (e.g., HF, CISD, MP2, CCSD). Particularly, one needs to pay careful attention on selecting the active orbitals within active space in a CASSCF or RASSCF calculation. Moreover, as the computational cost scales exponentially, only limited active orbitals can be chosen.

It is worth noting that some helpful techniques for the selection of active orbitals in CAS space have been suggested. Pulay *et al.* [154] proposed some criteria based on the natural orbital occupation n_i of Unrestricted Hartree-Fock (UHF) calculations [155]. For example, the double-occupied UHF natural orbitals in the range of $0.02 < n_i < 1.98$ can be generally taken included in the CAS space. Another efficient approach is to select active orbitals based on sorted n_i from an MP2 calculation [156]. Recently, Reiher *et al.* [157–159] developed an [autoCAS](#) program [160] by using orbital entanglement measures to systematically select

active statically corrected orbitals for CASSCF calculations. Particularly, the orbital entanglement indices show noticeable potential to reduce the complexity of MCSCF methods.

Furthermore, Multireference Configuration Interaction (MRCI) methods have been developed over several decades [161–167]. These variational methods include many configurations in the MRCI wavefunction to achieve lower energy and high accuracy. However, truncated MRCI methods lack size extensivity and size consistency, making them impractical for large systems or systems with numerous active orbitals and excitations. Furthermore, alternative MR wavefunction methods have been implemented over the past decades, such as Multireference Coupled-Cluster (MRCC) [168–171], as well as perturbation theory-based methods like Complete-Active-Space second-order Perturbation Theory (CASPT2) [172, 173] and *N*-electron Valence State Perturbation Theory (NEVPT2) [174]. Nevertheless, these MR methods are computationally demanding and are impractical for large systems.

3.2 Pair Density and its Partitions

3.2.1 Reduced Quantities

The concept of Density Matrices (DMs) was first introduced by Landau [175], von Neumann [176], and others in later of the 1920s, it was initially developed to handle mixtures of pure states or describe the properties of ensemble quantum systems [177–179]. In a quantum system, the wavefunction describes only a pure state, while the DMs describe a statistical ensemble of pure states (i.e., mixed states). Furthermore, Born’s probability density interpretation of the wavefunction [180] established the connection between the wavefunction and the DMs. The N -order DMs which describe the probability distribution of finding a particle in a specific quantum state, can be obtained from N -electron wavefunction,

$$\rho_N(1, 2, \dots, N; 1', 2', \dots, N') = \Psi^*(1, 2, \dots, N) \Psi(1', 2', \dots, N'). \quad (3.59)$$

When considering the correlation between particles, the concept of n -Order Reduced Density Matrices (n -RDMs) becomes helpful, providing information about the correlation of motion between n particles in a system. The n -RDMs of an N -electron system can be directly derived from the N -order DMs [121, 179, 181],

$$\rho_n(1, \dots, n; 1', \dots, n') = \binom{N}{n} n! \int \dots \int \rho_N(1, \dots, N; 1', \dots, n', n+1, \dots, N) \quad (3.60)$$

$$d(n+1) \dots dN,$$

where the normalization follows McWeeny’s convention [182].

In quantum chemistry or physics, among the n -RDMs, the first-order RDM (1-RDM) and the second-order RDM (2-RDM) are the most used [179, 181]. They are the only ones required for calculating electronic energies, and they offer advantages such as containing fewer variables than the wavefunction of an N -electron system. Moreover, certain quantities derived from the 1-RDM and 2-RDM play significant roles in various molecular analyses. For instance, the 1-RDM provides Natural Orbitals (NO) and occupation numbers, while the 2-RDM yields the pair density [121, 179, 181]. Additionally, the 2-RDM explicitly determines the total angular spin momentum [183].

The 2-RDM, noted as $\rho_2(1, 2; 1', 2')$, describes exactly a two-electron quantum system in mixed states. The 2-RDM can be obtained from a wavefunction,

$$\rho_2(1, 2; 1', 2') = N(N-1) \int \dots \int \Psi^*(1, 2, 3 \dots N) \Psi(1', 2', 3 \dots N) d3 \dots dN, \quad (3.61)$$

where N is the total number of electrons. The diagonal components of the 2-RDM ($1=1'$ and $2=2'$) give the electron pair density $\rho_2(1, 2)$, which is related to the

probability of finding two electrons at positions 1 and 2, regardless of the position of the other $N - 2$ electrons,

$$\begin{aligned}\rho_2(1,2) &= N(N-1) \int \cdots \int \Psi^*(1,2,3\dots N) \Psi(1,2,3\dots N) d3\dots dN \\ &= \rho_2(1,2;1',2')|_{1'=1,2'=2}.\end{aligned}\tag{3.62}$$

The normalization factor $N(N-1)$ ensures the integration of $\rho_2(1,2)$ to give the number of (unsorted) electron pairs. The pair density contains explicit information on the relative motion of electron pairs.

Since electronic Hamiltonian is written as a sum of one-electron and two-electron operators, and the two-electron operator which accounts for electron-electron repulsion is expressed through the Coulomb operator $1/r_{12}$, the 2-RDM is the lowest-rank n -RDM that is required to calculate the total electronic energy. Unfortunately, because of the N -representability problem, there is no guarantee that minimizing the energy with respect to the 2-RDM will result in a variational solution. Until very recently, Mazziotti *et al.* [184] found a solution for N -representability conditions concerning the ground-state 2-RDM. Their approach generates a complete hierarchy of 2-RDM constraints without explicit dependencies on higher-rank n -RDMs or the wavefunction.

With respect to the 1-RDM, noted as $\rho_1(1;1')$, the necessary and sufficient N -representability conditions are known and easily imposed [185]. The 1-RDM based approximation methods, which calculate energy only as a functional of 1-RDM, have been developed and known as the Reduced Density Matrix Functional Theory (RDMFT) [186–193]. The 1-RDM is written as

$$\rho_1(1;1') = N \int \cdots \int \Psi^*(1,2,3\dots N) \Psi(1',2,3\dots N) d2\dots dN,\tag{3.63}$$

where the normalization factor corresponds to the number of electrons. The 1-RDM can be yielded straightforwardly from 2-RDM by reduction of one coordinate,

$$\rho_1(1;1') = \frac{1}{N-1} \int \rho_2(1,2;1',2')|_{2'=2} d2.\tag{3.64}$$

The 1-RDM is a Hermitian matrix, and it can be diagonalized with a unitary matrix. The eigenvalues are called the natural orbital occupation numbers n_i and the eigenvectors are natural orbitals ϕ_i^{NO} . The N -representability of the 1-RDM requires that the eigenvalues n_i (spin-summed, i.e., $n_i = \sum_{\sigma} n_i^{\sigma}$) must be between 0 and 2, and their sum should be the number of electrons N [121, 185, 194].

The one-electron density, $\rho_1(1)$, used in the popular Density Functional Theory (DFT) [195] is equivalent to the diagonal components of the 1-RDM, denoted

as $\rho_1(1) \equiv \rho_1(1;1)$. Thus, $\rho_1(1)$ can be expressed in terms of spin-natural orbital occupation numbers n_i^σ and spin-natural orbitals $\phi_{i,\sigma}^{\text{NO}}(1)$,

$$\rho_1(1) = \sum_{\sigma,i} n_i^\sigma |\phi_{i,\sigma}^{\text{NO}}(1)|^2. \quad (3.65)$$

Moreover, $\rho_1(1)$ can also be yielded by the pair density by integrating out one coordinate,

$$\rho_1(1) = \frac{1}{N-1} \int \rho_2(1,2) d2. \quad (3.66)$$

The development of Density Functional Approximations (DFAs) aims to seek a universal energy density functional. In the framework of DFT, Hohenberg-Kohn theorems [196] state that the whole information of a quantum system is contained in the ground-state one-electron density. Thus, this statement must also hold for any other higher-order n -RDMs.

The one-electron energies (i.e., kinetic energy and electron-nuclear attraction energy) can be explicitly determined by the 1-RDM. To calculate the two-electron energy (i.e., electron-electron repulsion energy), the full 2-RDM is not required. Instead, the diagonal part of 2-RDM (i.e., the pair density) is sufficient to calculate the electron-electron repulsion energy. Thence, the total electronic energy (i.e., its expectation value) can be evaluated as an explicit functional of the 2-RDM [197],

$$E[\rho_2(1,2;1',2')] = T[\rho_1(1;1')] + V_{\text{en}}[\rho_1(1)] + V_{\text{ee}}[\rho_2(1,2)] \quad (3.67)$$

and the kinetic energy term T , electron-nuclear attraction energy term V_{en} , and electron-electron repulsion energy term V_{ee} , after summing over the electron spin are given by:

$$T[\rho_1(\mathbf{r}_1; \mathbf{r}'_1)] = -\frac{1}{2} \int \nabla_{\mathbf{r}'_1}^2 \rho_1(\mathbf{r}_1; \mathbf{r}'_1) |_{\mathbf{r}'_1=\mathbf{r}_1} d\mathbf{r}_1, \quad (3.68)$$

$$V_{\text{en}}[\rho_1(\mathbf{r}_1)] = - \sum_A^{N_{\text{nuc}}} \int \frac{Z_A \rho_1(\mathbf{r}_1)}{||\mathbf{r}_1 - \mathbf{R}_A||} d\mathbf{r}_1, \quad (3.69)$$

$$V_{\text{ee}}[\rho_2(\mathbf{r}_1, \mathbf{r}_2)] = \frac{1}{2} \iint \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (3.70)$$

where the interelectronic distance, $r_{12} = ||\mathbf{r}_1 - \mathbf{r}_2||$, was defined previously in Eq. (3.25).

For a Single-Determinant (SD) wavefunction, the 2-RDM can be written in terms of the 1-RDM [121],

$$\begin{aligned} \rho_2^{\text{SD}}(1,2;1',2') &= \begin{vmatrix} \rho_1^{\text{SD}}(1;1') & \rho_1^{\text{SD}}(1;2') \\ \rho_1^{\text{SD}}(2;1') & \rho_1^{\text{SD}}(2;2') \end{vmatrix} \\ &= \rho_1^{\text{SD}}(1;1')\rho_1^{\text{SD}}(2;2') - \rho_1^{\text{SD}}(1;2')\rho_1^{\text{SD}}(2;1'). \end{aligned} \quad (3.71)$$

A general approximation of the 2-RDM for non-SD wavefunctions is given by [198, 199]

$$\rho_2^{\text{SD}}(1, 2; 1', 2') = \rho_1(1; 1')\rho_1(2; 2') - \rho_1(1; 2')\rho_1(2; 1'). \quad (3.72)$$

The cumulant part of 2-RDM [200–205], which measures the correlations between pairs of electrons in a quantum system, can be deduced from the actual 2-RDM,

$$\rho_2^{\text{cumul}}(1, 2; 1', 2') = \rho_2(1, 2; 1', 2') - \rho_2^{\text{SD}}(1, 2; 1', 2'). \quad (3.73)$$

Likewise, the SD pair density and cumulant part of the actual pair density can be written as [3],

$$\rho_2^{\text{SD}}(1, 2) \equiv \rho_2^{\text{SD}}(\rho_1, 1, 2) = \rho_1(1)\rho_1(2) - \rho_1(1; 2)\rho_1(2; 1) \quad (3.74)$$

$$\rho_2^{\text{cumul}}(1, 2) \equiv \rho_2^{\text{cumul}}(\rho_1, 1, 2) = \rho_2(1, 2) - \rho_2^{\text{SD}}(1, 2). \quad (3.75)$$

The V_{ee} energy term calculated from $\rho_2^{\text{SD}}(1, 2)$, denoted as $V_{\text{ee}}^{\text{SD}}$, can be expressed as the sum of HF Coulomb and exchange energy functionals:

$$\begin{aligned} V_{\text{ee}}^{\text{SD}}[\rho_2^{\text{SD}}(1, 2)] &= \frac{1}{2} \iint \frac{\rho_2^{\text{SD}}(1, 2)}{r_{12}} d1 d2 \\ &= \underbrace{\frac{1}{2} \iint \frac{\rho_1(1)\rho_1(2)}{r_{12}} d1 d2}_{J[\rho_1(1)]} + \underbrace{\frac{1}{2} \iint \frac{-\rho_1(1; 2)\rho_1(2; 1)}{r_{12}} d1 d2}_{K[\rho_1(1; 1')]} \end{aligned} \quad (3.76)$$

Hence, the V_{ee} energy term of actual pair density can be calculated as a sum of $V_{\text{ee}}^{\text{SD}}[\rho_2^{\text{SD}}(1, 2)]$ and $C[\rho_2^{\text{cumul}}(1, 2)]$,

$$\begin{aligned} V_{\text{ee}}[\rho_2(1, 2)] &= V_{\text{ee}}^{\text{SD}}[\rho_2^{\text{SD}}(1, 2)] + C[\rho_2^{\text{cumul}}(1, 2)] \\ &= J[\rho_1(1)] + K[\rho_1(1; 1')] + C[\rho_2^{\text{cumul}}(1, 2)]. \end{aligned} \quad (3.77)$$

3.2.2 Pair Density in the AO Basis

The pair density can also be represented in the AO basis, as shown in Eq. (3.78). We note that this representation will be frequently used in our work of using approximate pair density to evaluate V_{ee} , particularly in the study of London dispersion interactions (we refer to Chapter 6 to Chapter 8).

$$\rho_2(1, 2) = \sum_{\mu\nu\sigma\lambda} {}^2D_{\mu\nu\sigma\lambda} \chi_{\mu}^*(1) \chi_{\nu}(1) \chi_{\sigma}^*(2) \chi_{\lambda}(2), \quad (3.78)$$

where ${}^2D_{\mu\nu\sigma\lambda}$ denotes the matrix representation of the 2-RDM in the AO basis. Each element is associated with a two-electron AO term, $\chi_{\mu}^*(1) \chi_{\nu}(1) \chi_{\sigma}^*(2) \chi_{\lambda}(2)$. The indices μ , ν , σ , and λ correspond to the AO indices. Since we employ real

orbitals, then the superscript “*” will be dropped out from now on. Then, the electron-electron interaction energy V_{ee} can be evaluated by

$$\begin{aligned} V_{ee} &= \frac{1}{2} \int \int \frac{\rho_2(1,2)}{r_{12}} d1 d2 \\ &= \frac{1}{2} \sum_{\mu\nu\sigma\lambda} {}^2D_{\mu\nu\sigma\lambda} \int \int \frac{\chi_\mu(1)\chi_\nu(1)\chi_\sigma(2)\chi_\lambda(2)}{r_{12}} d1 d2. \end{aligned} \quad (3.79)$$

Following Eq. (3.78) and Eq. (3.79), the actual correlated pair density and electron-electron interaction energy can be described as a sum of all the contributions from two-electron AO quartets. Moreover, once using the 2-RDM of Hartree-Fock (HF) in Eq. (3.78) and Eq. (3.79), we recover the HF results. The contribution of V_{ee} to the correlation energy, denoted as, V_{ee}^{corr} , (see Eq. (3.89) defined in Section 3.2.4), can be analyzed term by term based on the two-electron AO quartets, $\chi_\mu(1)\chi_\nu(1)\chi_\sigma(2)\chi_\lambda(2)$.

$$\begin{aligned} V_{ee}^{\text{corr}} &= \frac{1}{2} \int \int \frac{[\rho_2(1,2) - \rho_2^{\text{HF}}(1,2)]}{r_{12}} d1 d2 \\ &= \frac{1}{2} \sum_{\mu\nu\sigma\lambda} ({}^2D_{\mu\nu\sigma\lambda} - {}^2D_{\mu\nu\sigma\lambda}^{\text{HF}}) \int \int \frac{\chi_\mu(1)\chi_\nu(1)\chi_\sigma(2)\chi_\lambda(2)}{r_{12}} d1 d2. \end{aligned} \quad (3.80)$$

Likewise, the first-order reduced density matrix can be expressed in the AO basis,

$$\rho_1(1;1') = \sum_{\mu\nu} {}^1D_{\mu\nu} \chi_\mu(1)\chi_\nu(1'), \quad (3.81)$$

where ${}^1D_{\mu\nu}$ denotes the matrix representation of the 1-RDM in the AO basis, and it is associated with each one-electron AO term, $\chi_\mu(1)\chi_\nu(1')$. Thus, the SD approximate pair density can be written as

$$\begin{aligned} \rho_2^{\text{SD}}(1,2) &= \rho_1(1)\rho_1(2) - \rho_1(1;2)\rho_1(2;1) \\ &= \sum_{\mu\nu\sigma\lambda} ({}^1D_{\mu\nu} {}^1D_{\sigma\lambda} - {}^1D_{\mu\lambda} {}^1D_{\sigma\nu}) \chi_\mu(1)\chi_\nu(1)\chi_\sigma(2)\chi_\lambda(2), \end{aligned} \quad (3.82)$$

where ${}^1D_{\mu\nu}$ corresponds to the matrix form of the 1-RDM in the AO basis. Thus the corresponding SD electron-electron interaction energy, V_{ee}^{SD} , can be written as

$$\begin{aligned} V_{ee}^{\text{SD}} &= \frac{1}{2} \int \int \frac{\rho_2^{\text{SD}}(1,2)}{r_{12}} d1 d2 \\ &= \frac{1}{2} \sum_{\mu\nu\sigma\lambda} ({}^1D_{\mu\nu} {}^1D_{\sigma\lambda} - {}^1D_{\mu\lambda} {}^1D_{\sigma\nu}) \int \int \frac{\chi_\mu(1)\chi_\nu(1)\chi_\sigma(2)\chi_\lambda(2)}{r_{12}} d1 d2. \end{aligned} \quad (3.83)$$

3.2.3 Intracule Density

The notion of intracule was introduced by Debye [206] in 1915 and first applied in quantum chemistry calculations by Coulson and Neilson in 1961 when they studied the electron correlation in the ground state of the helium atom [207]. The (three-dimensional position) intracule density, which characterizes the interaction between electron pairs [208], is given by

$$I(\mathbf{s}) = \int \int \rho_2(1,2) \delta(s - r_{12}) d1 d2, \quad (3.84)$$

where $\mathbf{s}$ denotes the interelectronic separation vector between the two electrons in real space, and its module is noted as, $s \equiv ||\mathbf{s}||$. The Dirac delta, δ , ensures the integration to be done only at $s = r_{12}$. As the electron spin coordinate variables have been integrated out, the intracule density is solely dependent on the interelectronic distance between two electrons. The intracule density is interpreted as the probability density of finding two electrons separated by a distance vector, $\mathbf{s}$.

The intracule approach provides a convenient way to visualize and analyze the electron-pair distribution. Moreover, the evaluation of V_{ee} in Eq. (3.70) can be performed analytically or numerically using the pair-density intracule [209–213],

$$V_{ee} = \frac{1}{2} \int \frac{I(\mathbf{s})}{s} d\mathbf{s}, \quad (3.85)$$

where $I(\mathbf{s})$ only depends on the variable $\mathbf{s}$. In practice, to calculate the intracule density, we need to substitute the two-electron three-dimensional spatial coordinate vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ of pair density $\rho_2(1,2)$ by extracule and intracule vectors, $\mathbf{R}_{12}$ and $\mathbf{r}_{12}$:

$$\mathbf{R}_{12} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \quad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2. \quad (3.86)$$

Then the pair density $\rho_2(1,2)$ turns into $\rho_2(\mathbf{R}_{12}, \mathbf{r}_{12})$, the three-dimensional intracule density can be obtained by integrating out the extracule vector $\mathbf{R}_{12}$

$$I(\mathbf{s}) = \int \int \rho_2(\mathbf{R}_{12}, \mathbf{r}_{12}) \delta(s - r_{12}) d\mathbf{R}_{12} d\mathbf{r}_{12}. \quad (3.87)$$

Subsequently, $I(\mathbf{s})$ can be transformed to the radial intracule density $I(s)$ which solely depends on the radial component of the intracule and reduces the dimensionality of variables. The three-dimensional intracule density can be expressed in terms of spherical coordinates $(r_{12}, \theta_{12}, \phi_{12})$ and multiplied by the Jacobian term $r_{12}^2 \sin \theta_{12}$, then the radial intracule density can be generated by integrating out the angular part: θ_{12} and ϕ_{12} ,

$$I(s) = \int \int \int I(r_{12}, \theta_{12}, \phi_{12}) r_{12}^2 \sin \theta_{12} \delta(s - r_{12}) d\theta_{12} d\phi_{12} dr_{12}. \quad (3.88)$$

The radial intracule density is a spherically averaged quantity and is more convenient for visualizing and analyzing the electron-pair distribution [214–218]. This thesis adopts the radial intracule density in the context of range separation, encompassing short-range ($s \rightarrow 0$) and long-range ($s \rightarrow R$) regions, where R represents the separation distance between two atoms or two molecular fragments.

3.2.4 Correlation Energy and the Coulomb Hole

Ziesche *et al.* [219] stated “the correlation energy of a state is an energetic measure of the strength of correlation present in that state”. To investigate the strength of correlation in terms of a certain reduced quantity (i.e., 1-RDM, electron density, pair density), we split the electron correlation energy, E_{corr}^X , as shown in Eq. (3.34), into three components: the contributions of the kinetic energy, the electron-nuclear attraction energy, and the electron-electron interaction energy,

$$\begin{aligned} E_{\text{corr}}^X &= E_X - E_{\text{HF}} \\ &= \underbrace{(T^X - T^{\text{HF}})}_{T^{\text{corr}}} + \underbrace{(V_{\text{en}}^X - V_{\text{en}}^{\text{HF}})}_{V_{\text{en}}^{\text{corr}}} + \underbrace{(V_{\text{ee}}^X - V_{\text{ee}}^{\text{HF}})}_{V_{\text{ee}}^{\text{corr}}}. \end{aligned} \quad (3.89)$$

In the context of method X being FCI, the variational principle ensures that the FCI energy will always be equal to or below the HF energy. As a result, the correlation energy must be negative (except for one-electron systems). Recently, Burke *et al.* [220] explored the conjecture that the HF kinetic energy would never exceed the exact kinetic energy (i.e., $T^{\text{corr}} \leq 0$), which was validated on some atoms, ions, or molecules at equilibrium. Nevertheless, there has not been yet rigorous proof for this conjecture. In practice, this conjecture is considered valid in most molecular systems. Furthermore, for a given molecular system, the V_{en} term is only determined by the one-electron density in Eq. (3.69), thus the magnitude of $|V_{\text{en}}^{\text{corr}}|$ depends on the density difference between method X and HF. In principle, a density more accurate than HF one can give a better estimation of $V_{\text{en}}^{\text{corr}}$. Since the electron-electron interaction energy is an explicit functional of the pair density (see Eq. (3.70)), an improvement of pair density beyond the HF level is expected to yield more accurate $V_{\text{ee}}^{\text{corr}}$. In this thesis, we are more interested in the $V_{\text{ee}}^{\text{corr}}$ term among these three correlation energy components, as it is directly linked to pair density.

As the HF energy is taken as reference to evaluate the correlation energy in Eq. (3.34), the HF method is usually considered as an uncorrelated method. Nonetheless, the electron motions described by the HF wavefunction are not completely independent, differing from the Hartree product wavefunction in

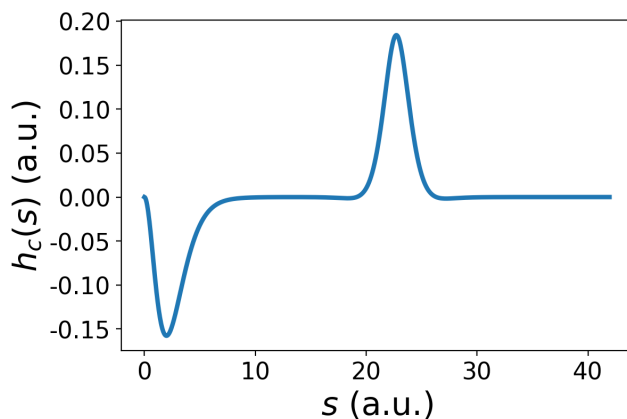


FIGURE 3.2: Coulomb hole represented by radial intracule density, obtained from H_2 molecule with internuclear separation of 12 Å, calculated at the FCI/aug-cc-pVTZ level.

Eq. (3.13), which treats electrons independently. The spin-separated HF pair density is given by

$$\begin{aligned}\rho_2^{\text{HF},\alpha\alpha}(1,2) &= \rho_1^{\text{HF},\alpha}(1)\rho_1^{\text{HF},\alpha}(2) - |\rho_1^{\text{HF},\alpha}(1;2)|^2 \\ \rho_2^{\text{HF},\alpha\beta}(1,2) &= \rho_1^{\text{HF},\alpha}(1)\rho_1^{\text{HF},\beta}(2).\end{aligned}\tag{3.90}$$

For two electrons with the same spin (referred to as “parallel spin” in some handbooks), the probability of these electrons being very close to each other should be very small [5]. In a particular case, the fact that the probability of finding both electron 1 and electron 2 at position 1 equals zero, $\rho_2^{\text{HF},\alpha\alpha}(1,1) = 0$, is indeed a direct consequence of the Pauli principle. Thus, the motion of electrons with the same spin is correlated in HF, this correlation is called the Fermi correlation. This type of correlation arises from the correct description of antisymmetry of the wavefunction of fermions. Therefore, the Fermi correlation is a direct consequence of the Pauli principle from the quantum nature of molecules [221]. Nonetheless, the two electrons with opposite spin, $\rho_2^{\text{HF},\alpha\beta}(1,2)$ only depends on the individual one-electron densities $\rho_1^{\text{HF},\alpha}(1)$ and $\rho_1^{\text{HF},\beta}(2)$. Hence, the two electrons with opposite spin are uncorrelated in HF,⁷ and the opposite spin correlation is also called Coulomb correlation.

In 1961, Coulson and Neilson [207] introduced the Coulomb hole as a measure of the Coulomb correlation in terms of the radial intracule density deviation from different ground-state wavefunctions of Helium. As defined by Coulson and

⁷In probability, $P(A \cap B) = P(A)P(B)$, indicates A and B are independent events.

Neilson, the Coulomb hole can be determined by taking the difference between the radial intracule densities from the exact and an uncorrelated reference (e.g., HF).⁸ More practically, the Coulomb hole can be evaluated as the radial intracule density difference between any actual correlation method X and HF [3],

$$h_c(s) \equiv \Delta I_c(s) = I^X(s) - I^{\text{HF}}(s). \quad (3.91)$$

where the difference between radial intracule densities, $\Delta I_c(s)$, can be transformed from the difference between pair densities, $\Delta \rho_2^c(1,2)$, by using Eq. (3.87) and Eq. (3.88),

$$\Delta \rho_2^c(1,2) = \rho_2^X(1,2) - \rho_2^{\text{HF}}(1,2), \quad (3.92)$$

Fig. 3.2 shows the Coulomb hole of the H_2 molecule dissociation at an inter-atomic distance of $R = 12 \text{ \AA}$, where R represents the separation distance between the two hydrogen atoms. The Coulomb hole exhibits two distinct peaks: one at short-range ($s \rightarrow 0$) and the other at long-range ($s \rightarrow R$), clearly separated from each other in this case. Coulson and Nielson [207] pointed out that electron correlation results in a reduced probability of finding the electrons in close proximity and an increased likelihood of the electrons being separated by larger distances. Consequently, the Coulomb hole exhibits negative values at short range, where electrons approach each other, and positive values at long range, where electrons are distant from each other. Notwithstanding, a counterintuitive secondary hole has been revealed in the ground state of the helium atom and helium-like ions, in which the hole shows small negative values at large separations of the two electrons. [222] Although the positive and negative areas of the Coulomb hole cancel each other out (i.e., a net integration of $h_c(s)$ over s equalling zero), integrating $h_c(s)/s$ over s yields $V_{\text{ee}}^{\text{corr}}$ as defined in Eq. (3.89).

3.2.5 Coulomb Hole Partitions

In recent years, our group [3, 13, 92] introduced a natural separation scheme for the Coulomb hole by utilizing the SD approximate pair density, defined in Eq. (3.74) [121]. This approach allows the division of the Coulomb hole into two distinct components: $h_{c_I}(s)$ and $h_{c_{II}}(s)$,

$$h_c(s) = h_{c_I}(s) + h_{c_{II}}(s) = I(\Delta \rho_2^{c_I}, s) + I(\Delta \rho_2^{c_{II}}, s), \quad (3.93)$$

where $I(\Delta \rho_2^{c_I}, s)$ and $I(\Delta \rho_2^{c_{II}}, s)$ represent that the intracule I is a function of $\Delta \rho_2^{c_I}$ and $\Delta \rho_2^{c_{II}}$, and in terms of the radial intracule variable s . By using Eq. (3.87) and

⁸Note that another well-known definition of the Coulomb hole not used in this thesis was proposed by McWeeny, and it is defined as the opposite-spin component of the exchange-correlation hole [182].

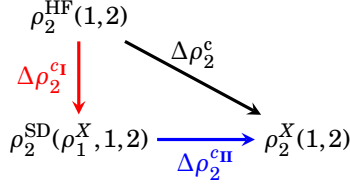


FIGURE 3.3: Decomposition of actual pair density [3].

Eq. (3.88), the above Eq. (3.93) of Coulomb hole partitions can be derived from the pair density partitions: $\Delta\rho_2^{c_I}$ and $\Delta\rho_2^{c_{II}}$,

$$\Delta\rho_2^c = \underbrace{\rho_2^{\text{SD}}(\rho_1^X, 1, 2) - \rho_2^{\text{HF}}(1, 2)}_{\Delta\rho_2^{c_I}} + \underbrace{\rho_2^X(1, 2) - \rho_2^{\text{SD}}(\rho_1^X, 1, 2)}_{\Delta\rho_2^{c_{II}}}, \quad (3.94)$$

where $\rho_2^{\text{SD}}(\rho_1^X, 1, 2)$ denotes the SD approximate pair density which is a function of the 1-RDM from method X , denoted as ρ_1^X . We note that $\Delta\rho_2^{c_{II}} \equiv \rho_2^{\text{cumul}}$ in Eq. (3.75).

Fig. 3.3 shows the scheme that decomposes the correlation part of the actual pair density, $\Delta\rho_2^c$, into $\Delta\rho_2^{c_I}$ (in path c_I) and $\Delta\rho_2^{c_{II}}$ (in path c_{II}), by using an SD approximate pair density. In recent years, the SD approximate pair density has been proven not to include dynamic correlation [3, 91, 193]. Thus, path c_I is designed to retrieve the difference between the SD approximate pair density $\rho_2^{\text{SD}}(\rho_1, 1, 2)$ and HF pair density $\rho_2^{\text{HF}}(\rho_1^{\text{HF}}, 1, 2)$ giving $\Delta\rho_2^{c_I}$. Path c_{II} is devised to evaluate the difference between the actual pair density $\rho_2(\rho_1, 1, 2)$ and the SD approximate pair density $\rho_2^{\text{SD}}(\rho_1, 1, 2)$ producing $\Delta\rho_2^{c_{II}}$. Note that $\Delta\rho_2^{c_{II}}$ coincides with the cumulant part of the pair density [200, 202]. It has been demonstrated [3, 92] that the pair density partitions $\Delta\rho_2^{c_I}$ and $\Delta\rho_2^{c_{II}}$ can be used to identify systems with dominant nondynamic or dynamic correlation.

With respect to energy, inspired by the correlation energy decomposition scheme proposed by Ludeña *et al.* [223, 224], Cioslowski [225], and previous work of our group [3, 92], the term $V_{\text{ee}}^{\text{corr}}$ can be decomposed into two parts: $\Delta V_{\text{ee}}^{c_I}$ and $\Delta V_{\text{ee}}^{c_{II}}$. Following the pair density partition in Fig. 3.3 and radial intracule transformation in Eq. (3.87) and Eq. (3.88), $\Delta V_{\text{ee}}^{c_I}$ can be calculated through $I(\Delta\rho_2^{c_I}, s)$ and $\Delta V_{\text{ee}}^{c_{II}}$ through $I(\Delta\rho_2^{c_{II}}, s)$,

$$V_{\text{ee}}^{\text{corr}} = \Delta V_{\text{ee}}^{c_I} + \Delta V_{\text{ee}}^{c_{II}} = \frac{1}{2} \int \frac{I(\Delta\rho_2^{c_I}, s)}{s} ds + \frac{1}{2} \int \frac{I(\Delta\rho_2^{c_{II}}, s)}{s} ds, \quad (3.95)$$

where $V_{\text{ee}}^{\text{corr}}$ denotes the correlation energy contributed by the electron-electron interaction, as defined in Eq. (3.89).

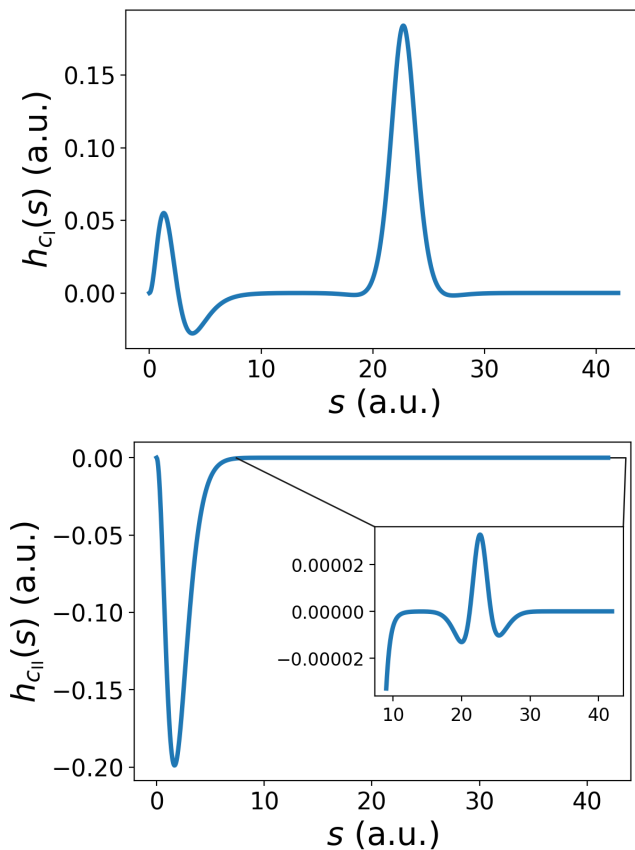


FIGURE 3.4: Coulomb hole partitions, obtained from the H_2 molecule separated at 12 Å, calculated at the FCI/aug-cc-pVTZ level.

Fig. 3.4 illustrates the partitions of the Coulomb hole (see Fig. 3.2) for the H_2 dissociation. The Coulomb hole is divided into two components: h_{cI} , which primarily contributes to the long-range electron correlation, and h_{cII} , which is mainly responsible for the short-range electron correlation. Furthermore, the inset figure exhibits the tiny long-range component of h_{cII} , which is useful for identifying London dispersion interactions [3, 91, 92], see follow-up Section 3.3 and Section 3.5.5.

3.3 Dynamic and Nondynamic Correlations

In the modern electronic structure theory, electron correlation as one of the fundamental concepts was first introduced by Wigner and Seitz [5] in 1934, when they studied the formation of metallic sodium. Nevertheless, until today, seeking an appropriate and efficient treatment of electron correlation remains a major challenge [3, 9, 13, 14, 92, 226–230]. Each approximation method is specifically designed to capture and recover the electron correlation energy to some extent, thus it is customary to categorize electron correlation in order to facilitate the development of new methods. Nowadays some distinct notions such as dynamic [231] or nondynamic (static) [232], Fermi or Coulomb [5, 121, 207], short-range or long-range [3, 92, 233, 234], left or right [235], radial or angular [236] correlation are routinely used by theoretical and computational chemists. Among these notions, probably the most widely discussed ones are the dynamic and nondynamic (static) correlation [3, 9, 11, 13, 14, 92, 223–225, 229–232, 237].

Dynamic correlation is associated with the instantaneous correlations between the motions of electrons. In other words, electrons avoid seeing each other due to the Coulomb repulsion. This type of correlation is universal and it can be well described by many SR correlated methods (e.g., MP2, CCSD, DFT). Nondynamic (static) correlation comes from near-degeneracies among orbitals (configurations), it is system-dependent and it becomes important for systems in which different orbitals have similar energies. Nondynamic correlation usually requires to be treated by MR methods (e.g., CASSCF, DMRG).

Another distinction between dynamic and nondynamic correlation is obtained through the CI coefficients of the FCI wavefunction expansion Eq. (3.35) in a molecular system. If the magnitude of CI coefficient of the HF reference, c_0 , is much larger than all other CI coefficients, $|c_i| \ll |c_0|$ (where $i \neq 0$), then the HF method is regarded as a suitable starting point for addressing systems dominated by dynamic correlation (e.g. H_2 at equilibrium distance, He atom, He-like atoms⁹). Otherwise, if one or more c_i are not small compared to c_0 , the nondynamic correlation becomes substantial. This often happens due to a small HOMO-LUMO energy gap, i.e., a near-degeneracy of HF occupied and virtual orbitals (e.g., stretched H_2 , Be atom, transition metals).

Hollett and Gill [14] identified two types of nondynamic correlations: type A and type B. The type A nondynamic correlation can be recovered from a broken symmetry solution (i.e., using the UHF as reference [155, 239, 240]), and it

⁹Or called isoelectronic series of He [238], such as He, Li^+ , Be^{2+} , B^{3+} , C^{4+} , N^{5+} .

happens when the orbitals have absolute near-degeneracy. For instance, in the H_2 molecule dissociation, the energy gap between HOMO and LUMO orbitals decreases, eventually vanishing at the dissociation limit. In UHF calculations, the loss of spin symmetry occurs when the single bond is stretched beyond a certain point known as the Coulson-Fisher (CF) point [241]. As the dissociation of H_2 goes beyond the CF point, the energy difference between RHF and UHF calculations becomes significant. On the other hand, the type B nondynamic correlation arises from relative near-degeneracy and can not be captured by a broken symmetry solution. Let us take the example of Be-like ions (e.g., Li^- , Be, B^+ , C^{2+} , N^{3+}). Although the increase of atomic charge, Z , results in a large HOMO-LUMO energy gap between $2s$ and $2p$ orbitals in absolute terms, it turns smaller relative to the actual orbital energies, so the system incurs relative near-degeneracy.

The dynamic correlation results in small changes in the electron density with respect to the HF reference. These small changes can be associated with local density changes that lead to significant effects on the energy. By contrast, the nondynamic correlation can provoke large changes in the electron density compared to the density from the SR wavefunction reference, and it is regarded as a global change in the electron density distribution [13, 223–225].

From the perspective of interelectronic separation, Handy and Cohen [11] explained that dynamic correlation can be connected to short-range interactions and nondynamic correlation to long-range ones. Nevertheless, this simple connection is incomplete. Some previous studies of our group [3, 92] have revealed that in the Coulomb hole partitions Eq. (3.93), h_{c_I} reflects the nondynamic correlation that predominates at long range, while $h_{c_{II}}$ reflects the dynamic correlation mainly at short range, but also at long range (London dispersion) [53]. Furthermore, in a particular case, we take an example of H_2 molecule dissociation (see Fig. 3.2 and Fig. 3.4), the long-range part (with positive intracule values) of the Coulomb hole is almost determined by h_{c_I} , while the short-range part (with negative intracule values) of the Coulomb hole is mainly determined by $h_{c_{II}}$. When the Coulomb operator $1/r_{12}$ is employed, the term $h_{c_{II}}$ becomes more significant at short range, as expected. The type of correlation that arises from the presence of isolated electrons at each atom in a molecule at the dissociation limit, should be classified as nondynamic correlation. Moreover, this nondynamic correlation is predominant at short range (e.g., it can be captured by short-range part of $h_{c_{II}}$ in the context of H_2 molecule dissociation).

3.4 Correlation Measures and Multireference Diagnostics

As we have presented previously, the correlation energy, the pair density, or Coulomb hole partitions can serve as correlation measures, despite that they measure the electron correlation from different perspectives. In this thesis, we focus on correlation measures that are represented by real numerical values, typically obtained through wavefunction, energy-based mathematical metrics. These metrics may not be normalized and can be sensitive to the system’s size. Although finding a universal and efficient correlation metric remains a challenge [10], various inherently statistical measures of electron correlation, such as leading coefficients of wavefunction $\{c_i\}$, CC or MPPT amplitudes $\{t_i^a, t_{ij}^{ab}\}$, and natural orbital occupations $\{n_i\}$, have been employed in the literature. In practice, most correlation measures (or referred metrics) target the quantification of nondynamic correlation [1, 10, 14, 18, 25, 31, 32, 154, 242–244], and few of them are for measuring dynamic correlation [11, 13, 23, 230, 245]. On the other hand, multireference (MR) diagnostics can be considered as a specific type of correlation measures. They should be able to identify the presence of significant nondynamic correlation in molecular systems that conventional SR methods cannot adequately describe. For this purpose, they should provide a clear binary classification of systems as either having MR or non-MR character. Moreover, they must be size-intensive, ensuring that these criteria remain unaffected by scaling the system size. In the context of size dependency, we highlight that they should have the capability to detect an MR system, even when this significant MR character is confined to a small portion of the system.

Over the past several decades, various MR diagnostics have been proposed. For correlated wavefunction methods, MR diagnostics can be mainly classified into two big families: wavefunction-based diagnostics and energy-based diagnostics [32]. On one hand, from the view of the output of correlated wavefunction methods, the wavefunction-based diagnostics can be divided into three primary subgroups: c_0 -based diagnostics (for CISD, CASSCF, etc.), amplitude-based diagnostics (for MP2, CCSD, etc.), and natural orbital-based diagnostics (for almost all types of correlated wavefunction methods). On the other hand, we can classify these MR diagnostics as average measures (e.g., T_1), variance measures (e.g., $\bar{V}$), maximum measures (e.g., D_1 , D_2 , c_0^2 , n_H , n_L), among others.

In terms of statistical metrics, the average measure provides an overall evaluation of MR character represented by these numbers, while the variance measure quantifies the extent to which the numbers deviate from their average value. Additionally, the maximum (or minimum) measure identifies the largest (or smallest)

element in this set, indicating the strongest manifestation of MR character. Both average measures and variance measures are sensitive to the size of the system. Particularly, if the MR character is concentrated in only a small fragment of a large molecule, the maximum measures may outperform the average or variance measure. However, maximum measures can be sensitive to outliers in the dataset. Especially, when the SR wavefunction fails, arbitrary outliers might be produced. For instance, in the dissociation of H_2 treated with MP2, some values in $\{n_i\}$ could be abnormal and unphysical, misleading the maximum measure.

Furthermore, there are numerous other diagnostics not covered in this thesis. Some examples are the Differential Density Matrix Overlap (DDMO) proposed by Cioslowski [246] for measuring static electron correlation: orbital entanglement measures developed by Reiher *et al.* [247] to assess static correlation in DMRG, and the large eigenvalue of the cumulant part of 2-RDM introduced by Raeber and Mazziotti [248] as a global indicator of off-diagonal long-range order. Additionally, there are diagnostics specific to hybrid functionals, such as the B_1 diagnostic for the B1LYP functional by Truhlar *et al.* [249] and the A_λ diagnostic by Martin *et al.* [32] which are based on the sensitivity of detecting systems with MR character to the amount of HF exchange is included in the hybrid Density Functional Approximations (DFAs). Grimme *et al.* [250] have suggested a local real-space measure of static correlation using fractional orbital occupations within finite-temperature DFT [251]. In this thesis, the focus is primarily on commonly used MR diagnostics in wavefunction methods.

3.4.1 c_0 -based MR Diagnostics

In the previous Section 3.3, we have discussed one of the distinctions between dynamic and nondynamic correlation by comparing the reference (or dominant) configuration coefficient c_0 value with other c_i values in the CI wavefunction expansion. Specifically, MR character is associated with the presence of significant magnitudes of c_i for configurations other than the reference configuration (the HF one). Hence, the c_0 value can be intuitively regarded as an MR diagnostic for CI methods such as CISD, CASSCF, etc. Indeed, c_0 -based MR diagnostics have been recognized by the quantum chemistry community for several decades [13, 18, 19, 23–25, 32, 33, 126, 252–254], and some thresholds such as $|c_0| \leq 0.95$, $1 - c_0^2 \geq 0.1$ have been employed to detect the MR character of molecular systems within CI methods [18, 19, 25, 32, 33, 253, 254].

Nevertheless, it has been widely discussed in the literature [3, 13, 18, 19, 23–25, 246, 252–255] that c_0^2 is not a reliable diagnostic for quantifying the magnitude

of electron correlation due to its strong dependence on the chosen reference. The coefficients c_i for orthonormal configurations correspond to the overlap between the overall wavefunction and the i -th configuration [10]. However, the overlap from truncated CI is not a size-extensive quantity, so only systems with the same number of electrons can be compared when using c_0 -based diagnostics [246]. Moreover, as the c_0 -based diagnostics for Single-Reference CI methods (e.g., CISD) is obtained using canonical HF orbitals, it has been criticized by Lee *et al.* [25] that c_0 is strongly biased toward the HF reference. Furthermore, the weight c_0^2 of the leading configuration in a CASSCF wavefunction has been used to diagnose the MR character in molecules or transition metals [23, 24, 32, 33, 253, 254]. However, c_0^2 value of CASSCF wavefunction might be sensitive to the construction of the active space. Hence, it turns out to be impractical for large active spaces [18, 254].

3.4.2 Amplitude-based MR Diagnostics

Amplitude-based MR diagnostics have been extensively utilized over the past three decades, despite their limitation of being applicable only to MP n or CC methods. These diagnostics involve energy calculations that incorporate single or double excitation amplitudes, such as t_i^a and t_{ij}^{ab} , respectively. As an early proposition, the largest amplitudes of t_i^a and t_{ij}^{ab} were suggested in the initial implementation of CCSD algorithm in the ACES program of Bartlett *et al.* [256] in 1982. The purpose was to warn users about the potential presence of MR character in certain SR calculations. Nevertheless, the largest amplitudes, which are sensitive to the choice of orbitals, tend to be less reliable as MR indicators and can become ambiguous [257].

Thereafter, Lee and Taylor [25] proposed the T_1 diagnostic for CCSD, which was shown to be superior to the c_0 diagnostic from CISD. T_1 diagnostic is defined as the Euclidean norm (also called “Frobenius norm” for matrices¹⁰ [258]) of the single-substitution amplitudes $\mathbf{t}_1$ divided by the square root of the number of correlated electrons, N_{corr} ,

$$T_1 = \frac{\|\mathbf{t}_1\|}{\sqrt{N_{\text{corr}}}}, \quad (3.96)$$

where the $\mathbf{t}_1$ amplitudes are also noted as t_i^a . The t_i^a amplitudes in Single-Reference CC wavefunctions govern orbital relaxation [252, 259, 260], and they indicate the suitability of the HF determinant as the zeroth-order wavefunction

¹⁰The Euclidean norm or Frobenius norm for a matrix is given by, $\|\mathbf{A}\| \equiv \|\mathbf{A}\|_F = \sqrt{\sum_{i,j} |a_{ij}|^2}$.

[261]. Therefore, the T_1 diagnostic as an average quantity of the t_i^a amplitudes was designed to evaluate the appropriateness of the HF reference. For CCSD, the criterion of $T_1 > 0.02$ has been proposed for indicating MR character of small molecules from the main element group of the periodic table [25]. Later, other criteria like $T_1 > 0.05$ for transition metals [253] and for actinide compounds [262, 263] have been also suggested. Nonetheless, the T_1 diagnostic has been pointed out as being sensitive to orbital rotation. As an example, a Brueckner rotation gives rise to vanishing single-excitation amplitudes [264], thus it will give a zero value of T_1 diagnostic. Some years later, Lee *et al.* [265] also extended the Euclidean norm approach in Eq. (3.96) to the MP2 method by using single-substitution amplitudes [266] from the MP2 wavefunction to define $\mathcal{T}_2$ diagnostic. However, it was pointed out by Nielsen and Janssen [244] that $\mathcal{T}_2$ diagnostic was not truly size-intensive, and its dependence on the size of systems leads to unexpected results when comparing systems of different size.

In contrast to using these average quantities as MR diagnostics, Nielsen and Janssen [1, 244] defined the D_1 and D_2 diagnostics as the maximum value of the 2-norm¹¹ of the two matrices obtained from t_i^a and t_{ij}^{ab} , respectively.

$$D_1 = \max\{\|\mathbf{T}^o\|_2, \|\mathbf{T}^v\|_2\}, \quad (3.97)$$

where $\mathbf{T}^o = [t_i^a]_{(o,v)}$, $\mathbf{T}^v = [t_i^a]_{(v,o)}$, the superscript $o(v)$ denotes the number of active occupied (virtual) orbitals, and the subscript (o,v) or (v,o) indicates the reshaped dimension of the t_i^a amplitude matrices.

$$D_2 = \max\{\|\mathbf{T}^o\|_2, \|\mathbf{T}^v\|_2\}, \quad (3.98)$$

where $\mathbf{T}^o = [t_{ij}^{ab}]_{(ov^2,o)}$, $\mathbf{T}^v = [t_{ij}^{ab}]_{(o^2v,v)}$, the subscript (ov^2,o) or (o^2v,v) indicates the reshaped dimension of the t_{ij}^{ab} amplitude matrices.

The D_1 and D_2 diagnostics can also be used in both CC and MP n methods. Lee *et al.* [265, 266] used the approach in Eq. (3.99) to generate the single-substitution amplitude $t_{ia}^{(2)}$ in MP2 wavefunction,

$$t_{ia}^{(2)} \equiv t_i^a = \frac{\sum_{cdk} (ac|kd) t_{ik}^{cd(1)} - \sum_{clk} (ck|il) t_{lk}^{ac(1)}}{\epsilon_i - \epsilon_a}, \quad (3.99)$$

where ϵ denotes the HF canonical orbital energy, the two-electron integrals are in spin-orbitals (in Mulliken notation). Since only the first-order approximation to

¹¹The 2-norm of the matrix, $\|\mathbf{A}\|_2 = \sqrt{\lambda_{\max}(\mathbf{A}^T \mathbf{A})}$, is defined as the square root of the largest eigenvalue of the matrix product $\mathbf{A}^T \mathbf{A}$, where $\mathbf{A}^T$ denotes the transpose of $\mathbf{A}$.

the double-substitution amplitudes is readily available, the double-substitution amplitudes can be obtained from the MP1 wavefunction. Namely, the $t_{ij}^{ab(1)}$ amplitudes [139, 265] can be calculated by

$$t_{ij}^{ab(1)} = \frac{(ia|jb) - (ja|ib)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (3.100)$$

Note that the t_{ij}^{ab} amplitudes used in the $D_2(\text{MP2})$ diagnostic of Janssen and Nielsen [1] were defined differently based on spatial-orbitals as

$$t_{ij}^{ab} = \frac{(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (3.101)$$

The D_1 and D_2 diagnostics are size-intensive and they are invariant to orbital rotations. Janssen and Nielsen [1, 244] suggested using both diagnostics together to assess the quality of MP2 and CCSD methods. Thresholds for D_1 and D_2 were provided for small closed-shell molecules (shown in Tab. 3.1). For instance, $D_1(\text{MP2}) \geq 0.04$, $D_1(\text{CCSD}) \geq 0.05$, $D_2(\text{MP2}) > 0.17$, and $D_2(\text{CCSD}) > 0.18$ indicate the inadequacy of MP2 and CCSD methods, respectively. Conversely, values below the diagnostic thresholds, such as $D_1(\text{MP2}) \leq 0.015$, $D_1(\text{CCSD}) \leq 0.02$, $D_2(\text{MP2}) \leq 0.15$, and $D_2(\text{CCSD}) \leq 0.15$, indicate reliable SR calculations. It is important to note that caution should be exercised within the regions between the adequacy and inadequacy criteria. These criteria for D_1 and D_2 can effectively detect the MR character of molecules under consideration.

TABLE 3.1: Criteria of D_1 and D_2 diagnostics proposed by Janssen and Nielsen [1, 244] for closed-shell molecules.

Quality of Method	$D_1(\text{MP2})$	$D_1(\text{CCSD})$	$D_2(\text{MP2})$	$D_2(\text{CCSD})$
Adequate	≤ 0.015	≤ 0.02	≤ 0.15	≤ 0.15
Inadequate	≥ 0.04	≥ 0.05	> 0.17	> 0.18

The limitations or shortcomings of T_1 and D_1 are summarized as follows:

- The T_1 diagnostic is an averaged quantity that fails to indicate the non-homogeneity of single-substitution amplitudes or possible singular double-substitution amplitudes. To overcome this limitation, Jiang *et al.* [253] suggested using maximal t_i^a and t_{ij}^{ab} amplitudes in conjunction with the T_1 diagnostic to identify MR character in molecules. Furthermore, Lee *et al.* [267] extended the T_1 diagnostic to open-shell CC theory, similar to its original definition for closed-shell CCSD.

- For open-shell systems, the above criteria for T_1 and D_1 become invalid, as these criteria were established based on closed-shell systems. Janssen *et al.* [268] proposed a different D_1 for Restricted Open-shell CCSD (ROCCSD) ($D_1 > 0.025$), indicating inadequate CCSD. However, Lee [26] criticized this ill-defined D_1 and introduced a revised version for open-shell molecules. Lee also emphasized that a large deviation between the ratio T_1/D_1 and $1/\sqrt{2}$ signifies a greater non-homogeneity of the electronic structure, but the ratio itself does not measure the inadequacy of the CCSD method. In addition, an open-shell D_2 diagnostic has not been defined in the literature.
- Both T_1 and D_1 diagnostics depend on the t_i^a amplitudes, which measure orbital relaxation. However, the presence of a Bruckner orbital can lead to zero values for both diagnostics. Bartlett *et al.* [269] noted that while T_1 (or D_1) diagnostics primarily measure orbital relaxation in the reference determinant, they do not capture multireference and nondynamic correlation. Additionally, large single-substitution amplitudes do not always imply MR character, as demonstrated in studies of transition metal compounds. [270, 271]
- Transition metal compounds require new thresholds for the T_1 and D_1 diagnostics to detect MR character. For example, $T_1 > 0.05$ and $D_1 > 0.15$ indicate MR character for 3d transition metals [253], while $T_1 > 0.045$ and $D_1 > 0.12$ are proposed for 4d transition metals [254].
- In a recent study of Stair and Evangelista [272], when they examined hydrogen model systems of different dimensionalities and found that in CCSD wavefunctions, they revealed that D_1 diagnostic primarily measures the importance of orbital rotations rather than direct electron correlation, while D_2 diagnostic is more closely connected to correlation effects.

3.4.3 Natural Orbital-based Correlation Indices

In Section 3.1.5, we have introduced the criterion of the UHF natural orbital occupations proposed by Pulay *et al.* [154, 242, 243] to help construct the active space of CASSCF wavefunctions. Later, Gordon *et al.* [273] demonstrated that the existence of non-physical (e.g., negative) natural orbital occupation values indicates MR character in the correlated SR wavefunction. We note that negative values of natural orbital occupation arise from the relaxed 1-RDM obtained through energy derivatives. Since natural orbital occupation numbers are available in

many quantum chemistry programs and can be readily obtained by diagonalizing the 1-RDM, natural orbital-based MR diagnostics show great potential as general MR diagnostics. In this section, we will present some correlation measures based on natural orbital occupation numbers, and most of them are used for quantifying nondynamic correlation.

1) Correlation entropy S_{corr}

In 1927, Von Neumann [176] introduced the concept “entropy” from thermodynamics to quantum mechanics. This concept is also widely recognized as “information entropy” or “Shannon entropy”, named after Shannon, who first applied it in the field of information theory [274]. Later, Jaynes [275, 276] utilized the information entropy in terms of the eigenvalues of the density matrix (i.e., natural orbital occupations). Collins [277] attempted to link the information entropy to correlation energy with a proportional relation under certain constraints. Unfortunately, this proportional relation is not practical to determine in a general sense. Furthermore, Ziesche [27, 28] proposed the information entropy as a measure of electron correlation strength, so it is nowadays also called “correlation entropy”. The common formula of correlation entropy, S_{corr} , is given in terms of natural orbital occupation numbers obtained from correlated wavefunctions. In this work, we take the form of S_{corr} given by Ziesche [27, 28] which is normalized by the number of electrons N ,

$$S_{\text{corr}} = -\frac{1}{N} \sum_{\sigma,i} n_i^{\sigma} \ln(n_i^{\sigma}), \quad (3.102)$$

where n_i^{σ} is the occupation number of the spin-natural orbital i with spin σ . Ziesche *et al.* [219, 278, 279] also showed that correlation entropy can be used to detect strong correlation in small molecular systems (e.g., stretched H_2 , harmonium atom [231], two-site Hubbard model [280, 281], etc.). Furthermore, Legeza and Sólyom [282] used the Von Neumann entropy to characterize the quantum (strong) correlation within the context of DMRG. Reiher *et al.* [247, 283] employed the entropy ansatz for single (and two) orbital-based entanglements, which help assess and classify quantitatively the electron correlation effects among molecular orbitals. In recent years, Martin *et al.* [32–35, 284] have done some comparisons between correlation entropy and other MR diagnostics, pointing out that the correlation entropy¹² is primarily linked to the type A static correlation [33, 34].

¹²In the work of Martin *et al.* [33, 34], the good connection is found between **unnormalized** correlation entropy (without being normalized by the number of electrons) and type A static correlation.

2) Indices n_H , n_L , and M_{diag}

Truhlar *et al.* [29] defined the M_{diag} diagnostic using natural orbital occupations from the dominant configuration in the context of CASSCF,

$$M_{\text{diag}} = \frac{1}{2} \left(2 - n_{\text{MCDONO}} + n_{\text{MCUNO}} + \sum_{j=1}^{n_{\text{SOMO}}} |n_j - 1| \right), \quad (3.103)$$

where n_{MCDONO} denotes doubly occupied natural orbital with the smallest occupation, and n_{MCUNO} stands for unoccupied natural orbital with the largest occupation. n_j represents the natural orbital occupation of j -th molecular orbital, and n_{SOMO} denotes the number of singly occupied molecular orbitals. We note that all these natural orbital occupations used above are from the dominant configuration of the ground state. As $0 \leq n_j \leq 2$, the upper bound of M_{diag} is $(2 + n_{\text{SOMO}})/2$, one must have $0 \leq M_{\text{diag}} \leq 1$ for closed-shell systems. While for the open-shell systems, the upper bound on M_{diag} depends on n_{SOMO} . Based on the calculations of DBH24 (the database of 24 barrier heights), they showed that the MR character of the molecules in this dataset varies from small ($M_{\text{diag}} < 0.05$) to modest ($0.05 \leq M_{\text{diag}} \leq 0.1$), and rises up significantly ($M_{\text{diag}} > 0.1$) [29]. This thesis centers on analyzing closed-shell systems, then M_{diag} can be simplified as,

$$M_{\text{diag}} = (2 - n_H + n_L)/2 \quad (3.104)$$

where n_H denotes the smallest occupation number among the first $N/2$ natural orbitals and n_L denotes the largest occupation number among the rest of natural orbitals [35], and they usually refer to the spin-natural orbital occupation of HOMO and LUMO orbitals for closed-shell systems¹³. Moreover, n_H, n_L have been also used to detect MR characters in some studies [18, 19, 29, 32, 33, 35].

3) Indices based on ansatz of $n_i^\sigma(1 - n_i^\sigma)$

In 1955, Löwdin [121] gave perhaps the earliest prototype of this type of indices in a quantity, ϑ_{nat} , which can be used to estimate how far the actual wavefunction is from the HF Single-Determinant approximation ($\vartheta_{\text{nat}}^{\text{HF}} = 0$). The quantity ϑ_{nat} is given by

$$\vartheta_{\text{nat}} = \frac{1}{N} \text{Tr}(\gamma - \gamma^2), \quad (3.105)$$

¹³The orbitals of HOMO and LUMO are determined based on the sorting of molecular orbital energies, whereas n_H and n_L are derived from the sorting of natural orbital occupation numbers. The occupation number n_H are usually the smallest in the HF occupied orbitals, and n_L are the largest in the HF unoccupied (virtual) orbitals for closed-shell systems.

where γ represents the 1-RDM, the trace of $(\gamma - \gamma^2)$ is normalized by the total number of electrons N . Some years later, Vedene H. Smith, Jr. [285] recalculated Löwdin's ϑ_{nat} in his index as a measure of "almost idempotency" of the 1-RDM, which was called "IAI" by Cioslowski [246, 286],

$$\vartheta_{\text{nat}} \equiv \text{IAI} = \sum_{\sigma,i} n_i^\sigma (1 - n_i^\sigma) = N - \sum_{\sigma,i} (n_i^\sigma)^2. \quad (3.106)$$

The IAI was proposed as a measure of electron correlation for approximate 1-RDMs. Notice that $\text{IAI} \geq 0$, and the equality occurs when n_i^σ are obtained from an uncorrelated wavefunction. For correlated wavefunction methods, IAI always gives a positive value with the upper bound of the number of electrons, N . Furthermore, Cioslowski also commented that IAI is a rough measure of the number of broken bonds in some small diatomic molecules [286].

Takatsuka *et al.* [287] incorporated the term IAI in their density function expression, which was employed to indicate the spatial distribution of unpaired electrons in ground-state molecules. Later on, this term and its deviations appeared again in other developments or applications for various purposes, for assessing the diradical character [287], for the application in the localization of the natural orbitals [286], for detecting the radical character of a molecule [288], or for characterizing unpaired electrons in molecules [287–291]. Furthermore, we note that Ziesche also extended the formulation of Löwdin Eq. (3.105) to k -order non-idempotency per particle to measure the electron correlation strength [28],

$$\vartheta_{\text{nat}}^k = \frac{1}{N} \text{Tr}(\gamma - \gamma^k) = 1 - \frac{1}{N} \sum_{\sigma,i} (n_i^\sigma)^k. \quad (3.107)$$

In recent years, our group [13, 230] proposed dynamic and nondynamic correlation indices I_{D} and I_{ND} , in terms of spin-natural orbital occupations. The principal idea is to decompose electron correlation into dynamic and nondynamic components by utilizing the cumulant of 2-RDM. Following this decomposition scheme, the simplified electron correlation indices in terms of n_i^σ for dynamic and nondynamic indices can be derived from a two-electron model [13]. The global I_{D} and I_{ND} indices are then obtained by summing the individual contributions from each orbital,

$$I_{\text{D}} = \frac{1}{4} \sum_{\sigma,i} [n_i^\sigma (1 - n_i^\sigma)]^{\frac{1}{2}} - \frac{1}{2} \sum_{\sigma,i} n_i^\sigma (1 - n_i^\sigma) \quad (3.108)$$

$$I_{\text{ND}} = \frac{1}{2} \sum_{\sigma,i} n_i^\sigma (1 - n_i^\sigma) \quad (3.109)$$

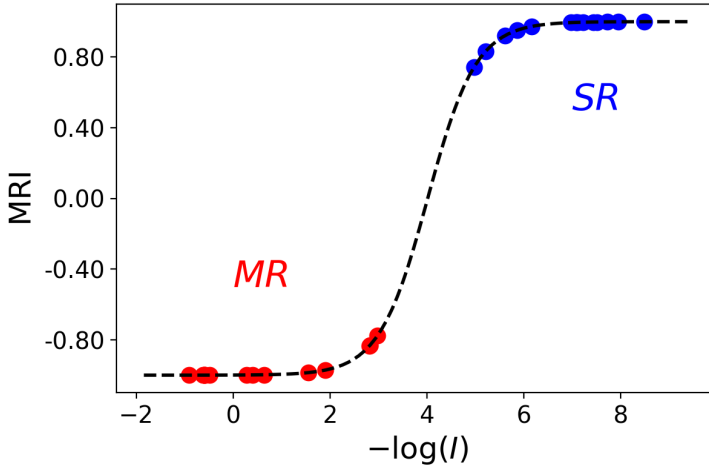


FIGURE 3.5: Plot of MRI versus $-\log(I)$ values for the test set of 15 MR and 15 SR systems [257].

$$I_{\text{tot}} = I_{\text{D}} + I_{\text{ND}} = \frac{1}{4} \sum_{\sigma,i} [n_i^{\sigma} (1 - n_i^{\sigma})]^{\frac{1}{2}}. \quad (3.110)$$

Notice that I_{ND} coincides with the form of IAI of Vedene H. Smith, Jr [285]. These correlation indices serve as a measure of the deviation from the idempotency of the 1-RDM. In a recent study, Martin *et al.* [34] reported that I_{ND} and unnormalized S_{corr} show a good linear correlation (i.e., their Pearson correlation coefficient $R = 0.994$ for the W4-17 dataset [292]). They discussed that I_{D} and I_{ND} are size-extensive, as their values for a dimer at $R \rightarrow \infty$ are exactly the sum of the respective monomer values. However, I_{D} and I_{ND} are not size-intensive, and their values scale with system size. Martin *et al.* [34] used the ratio r_{ND} as an intensive quantity,

$$r_{\text{ND}} = \frac{I_{\text{ND}}}{I_{\text{tot}}} = \frac{I_{\text{ND}}}{I_{\text{D}} + I_{\text{ND}}}. \quad (3.111)$$

However, this r_{ND} did not show good correlation (except with S_{corr}) or agreement with other existing MR diagnostics [18, 34]. Therefore, further analysis is needed to explore the potential of r_{ND} as an indicator for detecting MR character.

4) Other natural orbital-based indices

In a very recent paper, Bartlett *et al.* [257] proposed a similar quantity to I_{ND} , which was called the variance $\bar{V}$, and it is expressed in terms of spin-natural

orbital occupation numbers,

$$\bar{V} = \frac{1}{N} \sum_{\sigma,i}^{\text{occ}} n_i^{\sigma} (1 - n_i^{\sigma}) \approx \frac{1}{N} \sum_{\sigma,i}^{\text{vir}} n_i^{\sigma} (1 - n_i^{\sigma}). \quad (3.112)$$

where the $1/N$ normalization ensures $\bar{V}$ to be size-intensive. They further proposed that $\bar{V}$ can be computed using n_i^{σ} values derived from either occupied or unoccupied (virtual) natural orbitals. Both approaches yield identical variance values. In the same paper, they also proposed some other natural orbital-based indices: (i) the external electron number (EEN), namely, the summation of natural orbital occupations in virtual orbitals; (ii) the EEN index normalized by $1/N$ was defined as XEN; and (iii) the largest occupation number in unoccupied natural orbitals (NON). Furthermore, they also developed some other empirical natural orbital-based indices fitted with several parameters, such as $-\log(I)$ and the so-called “Multireference Index” (MRI) which were designed by fitting several parameters with the objective to separate 15 typical SR and 15 MR character systems (see Fig. 3.5),

$$F(n_i^{\sigma}) = e^{-\lambda(0.5-n_i^{\sigma})^q}, \quad (3.113)$$

$$\log(I) = \log\left(\sum_{\sigma,i} F(n_i^{\sigma})\right), \quad (3.114)$$

$$\text{MRI} = -\tanh(C + \log(I)), \quad (3.115)$$

where the logarithm base is 10, and the fitting parameters, $\lambda = 1500$, $q = 6$, and $C = 4.016$ are taken from reference [257].

3.4.4 Energy-based MR Diagnostics

To identify MR character using energy-based diagnostics, firstly we need to know how to retrieve nondynamic correlation energy from the total correlation energy. Handy *et al.* [11] suggested that the dynamic and nondynamic correlation energy can be separated by using the energy of a full-valence CASSCF calculation,

$$\begin{aligned} E_{\text{corr}} &= E_{\text{FCI}} - E_{\text{HF}} \\ &= \underbrace{E_{\text{FCI}} - E_{\text{CASSCF}}}_{\text{dynamic}} + \underbrace{E_{\text{CASSCF}} - E_{\text{HF}}}_{\text{nondynamic}}. \end{aligned} \quad (3.116)$$

Furthermore, Cioslowski [225] put forward a decomposition scheme of correlation energy (shown in Eq. (3.117)), by calculating an intermediate energy term ($E_{\text{FCI}}[\rho^{\text{HF}}]$) which is obtained by using the exact (FCI) energy functional with the

HF density,

$$E_{\text{corr}} = \underbrace{E_{\text{FCI}}[\rho] - E_{\text{FCI}}[\rho^{\text{HF}}]}_{\text{nondynamic}} + \underbrace{E_{\text{FCI}}[\rho^{\text{HF}}] - E_{\text{HF}}[\rho^{\text{HF}}]}_{\text{dynamic}}. \quad (3.117)$$

We note that the HF density, ρ^{HF} , should be reproducible by the FCI wavefunction through a density-constrained approach. According to Cioslowski [225], the term $E_{\text{FCI}}[\rho^{\text{HF}}]$ provides little flexibility to the wavefunction for density variations close to ρ^{HF} . It only captures dynamic correlation, which is associated with changes in wavefunction while ρ^{HF} is fixed. Thus, the difference between $E_{\text{FCI}}[\rho^{\text{FCI}}]$ and $E_{\text{FCI}}[\rho^{\text{HF}}]$ gives rise to nondynamic correlation. Unfortunately, acquiring the exact energy functional $E_{\text{FCI}}[\rho^{\text{HF}}]$ is impractical, which limits the applicability of this scheme despite its conceptual significance.

Later, Ludeña *et al.* [223, 224] proposed an alternative scheme (shown in Eq. (3.118)) in which the intermediate energy term ($E_{\text{HF}}[\rho^{\text{FCI}}]$) is calculated by using the HF energy functional with the FCI density reproduced by an SD wavefunction. Since the energy functional $E_{\text{HF}}[\rho^{\text{FCI}}]$ uses the FCI density, it shows significant variation compared to the uncorrelated reference (e.g., ρ^{HF}), thus $E_{\text{HF}}[\rho^{\text{FCI}}]$ is expected to account for nondynamic correlation.

$$E_{\text{corr}} = \underbrace{E_{\text{FCI}}[\rho^{\text{FCI}}] - E_{\text{HF}}[\rho^{\text{FCI}}]}_{\text{dynamic}} + \underbrace{E_{\text{HF}}[\rho^{\text{FCI}}] - E_{\text{HF}}[\rho^{\text{HF}}]}_{\text{nondynamic}}. \quad (3.118)$$

However, $E_{\text{HF}}[\rho^{\text{FCI}}]$ is more challenging to interpret, as $E_{\text{HF}}[\rho^{\text{FCI}}] - E_{\text{HF}}[\rho^{\text{HF}}] > 0$ in contrast to $E_{\text{corr}} < 0$. The positive portion of E_{corr} gives rise to difficulties in attributing a clear physical meaning. On the other hand, $E_{\text{HF}}[\rho^{\text{FCI}}]$ leads to a feasible functional, $\rho_2^{\text{HF}}[\rho_1^{\text{FCI}}]$, known as ρ_2^{SD} in Eq. (3.74). This scheme directly inspired our approach to decomposing the Coulomb hole (see Fig. 3.3). While the above decomposition schemes of correlation energy are conceptually valuable, they are impractical to serve as MR diagnostics due to their highly demanding computational costs.

Alternatively, Martin *et al.* [30, 31] proposed the %TAE[(T)] diagnostic as one of the by-products of the W4 theory,

$$\% \text{TAE}[(\text{T})] = \frac{\text{TAE}[\text{CCSD}(\text{T})] - \text{TAE}[\text{CCSD}]}{\text{TAE}[\text{CCSD}(\text{T})]} \cdot 100, \quad (3.119)$$

where the Total Atomization Energy (TAE) of a given molecule is

$$\text{TAE} = \left(\sum_i^{N_{\text{atoms}}} E_i \right) - E_{\text{total}}. \quad (3.120)$$

In experimental thermodynamics and computational chemistry, absolute energies are generally not favored compared to relative energy quantities [9]. In this sense, the accuracy of TAE has been shown to be more significant than the one of absolute energies, particularly in the early development of the W4 theory [30]. Furthermore, %TAE[(T)] metric serves as a measure of the significance of the perturbative triple contribution in CCSD(T). %TAE[(T)] has been shown a reliable energy-based diagnostic for assessing the relevance of nondynamic correlation effects [30, 31, 292, 293], and %TAE[(T)] has been widely employed in various studies to identify cases with MR character [18, 19, 31–34, 292, 293].

According to the results of the W4-11 dataset, Martin *et al.* [31] suggested that a %TAE[(T)] $\leq 2\%$ implies no significant MR character in the system under consideration, $2\% \leq \text{\%TAE}[(\text{T})] \leq 5\%$ indicates mild MR character, $5\% \leq \text{\%TAE}[(\text{T})] \leq 10\%$ indicates moderate MR character, and %TAE[(T)] $\geq 10\%$ reveals severe MR character in the system.

Based on the analysis of AD-3165 dataset containing calculations for 3165 molecular structures, Kulik *et al.* [18] introduced an additional energy-based MR diagnostic, % $E_{\text{corr}}[(\text{T})]$,

$$\text{\%}E_{\text{corr}}[(\text{T})] = \frac{E[\text{CCSD}] - E[\text{HF}]}{E[\text{CCSD}(\text{T})] - E[\text{HF}]} \cdot 100, \quad (3.121)$$

and they suggested that % $E_{\text{corr}}[(\text{T})] < 95\%$ indicates MR character.

3.5 Dispersion Interactions

Dispersion interactions can be classified as the attractive part of the van der Waals (vdW)-type interaction potential between atoms and molecules that are not directly bonded to each other. As early as in 1927, Wang [294] applied quantum mechanical methods to study the interaction between two hydrogen atoms at a large separation. He captured the long-range attraction energy, which exhibited $1/R^6$ asymptotic behavior. In 1930, London [53, 295] generalized the result to any two atoms or molecules by using approximate second-order perturbation treatment, and interpreted it as an induced dipole-induced dipole interaction effect. In the literature, the long-range dispersion interactions are commonly known as “London dispersion”. A general formulation of the potential energy of London dispersion is given by

$$E_{\text{disp}}(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} + \dots, \quad (3.122)$$

where C_6 , C_8 , and C_{10} stand for dispersion coefficients with positive values, while the negative signs indicate attractive dispersion interactions. The variable R denotes the interatomic (or inter-monomer) distance. Specifically, C_6 arises from induced dipole-induced dipole contribution, C_8 from induced dipole-induced quadrupole contribution, and C_{10} from induced quadrupole-induced quadrupole contribution to the dispersion interaction. Hence, the London dispersion energy of two well-separated atoms exhibits a $1/R^6$ predominant asymptotic behavior [296]. Furthermore, London dispersion is a type of long-range dynamic correlation, and it arises from the fluctuations of electron density which can create instantaneous dipoles (or quadrupoles, octopole, etc.). These instantaneous dipoles (or quadrupoles, etc.) can interact with other instantaneous dipoles (or quadrupoles, etc.), and lead to the London dispersion.

London dispersion is ubiquitous in all substances (e.g., they exist between any two atoms, in molecules, solids, proteins, DNA). Although it is considered a very weak intermolecular interaction, it is often non-negligible, because it scales with the system size so that massive, larger, or heavier atoms and molecules manifest larger dispersion interactions. For example, the dispersion interactions from two fragments or molecules containing 100 “HCNO” atoms can result in around -60 kcal/mol energy [297, 298]. London dispersion is important for binding interaction energies, providing a driving force for molecular aggregation that is crucial in thermodynamic stability, chemical selectivity, molecular recognition, protein folding, enzyme catalysis, etc. [42, 299]

3.5.1 Interpretation of Dispersion Interactions in Quantum Mechanics

In this section, we will review the interpretation of the origin of the van der Waals (London dispersion) interactions in the framework of quantum mechanics. Considering the fact that the dispersion energy is too small compared to the total electronic energy, Perturbation Theory (PT) is naturally a preferred option for treating dispersion, as London did [53, 295, 300]. The following review of the PT treatment for London dispersion primarily follows Stone [40, 44]. Given two interacting molecules A and B that are separated far enough, the overlap between their wavefunctions can be neglected. Hence, the unperturbed wavefunction of the system AB can be treated as a simple product function¹⁴ of the wavefunctions of molecules A and B

$$\Psi_{AB}^{mn} = \Psi_A^m \Psi_B^n = |mn\rangle, \quad (3.123)$$

where m and n denote the quantum states of molecules A and B, respectively. For the ground state of the two molecules, we have $m = n = 0$. For convenience, we will henceforth employ the notation of $|mn\rangle$ to represent the wavefunction of the AB interacting system. Then the unperturbed Hamiltonian is given by

$$H^{(0)} = H_A + H_B, \quad (3.124)$$

and the perturbed Hamiltonian contains the electrostatic interactions between electrons of molecule A and those of molecule B,

$$H^{(1)} = \sum_i^A \sum_j^B \frac{1}{r_{ij}}. \quad (3.125)$$

The total ground-state energy of the system can be written as a sum of the unperturbed energy and all the perturbed energies,

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots, \quad (3.126)$$

and the zeroth-order ground-state energy of the system AB is simply the sum of the ground-state energies of the isolated molecules A and B,

$$E^{(0)} = E_A^0 + E_B^0. \quad (3.127)$$

The first-order energy is just the expectation value of $H^{(1)}$ for the ground-state wavefunction $|00\rangle$, which corresponds to the classical electrostatic interaction

¹⁴Note that this wavefunction is not antisymmetric, but the correction for antisymmetry does not affect the total energy since the two molecules are far enough.

energy between the charge distributions of the two molecules,

$$E^{(1)} = \langle 00 | H^{(1)} | 00 \rangle. \quad (3.128)$$

While the second-order energy incorporates three parts: the induction energy of molecule A, the induction energy of molecule B, and the dispersion energy between molecules A and B,

$$E^{(2)} = E_{\text{ind}}^A + E_{\text{ind}}^B + E_{\text{disp}}^{\text{AB}}, \quad (3.129)$$

where

$$E_{\text{ind}}^A = - \sum_{m \neq 0} \frac{\langle 00 | H^{(1)} | m0 \rangle \langle m0 | H^{(1)} | 00 \rangle}{E_A^m - E_A^0} \quad (3.130)$$

$$E_{\text{ind}}^B = - \sum_{n \neq 0} \frac{\langle 00 | H^{(1)} | 0n \rangle \langle 0n | H^{(1)} | 00 \rangle}{E_B^n - E_B^0} \quad (3.131)$$

$$E_{\text{disp}}^{\text{AB}} = - \sum_{m \neq 0} \sum_{n \neq 0} \frac{\langle 00 | H^{(1)} | mn \rangle \langle mn | H^{(1)} | 00 \rangle}{E_A^m + E_B^n - E_A^0 - E_B^0}. \quad (3.132)$$

Using the multipole expansion, the perturbed Hamiltonian operator $H^{(1)}$ can be expanded as

$$H^{(1)} = T q^A q^B + T_\alpha (q^A \hat{\mu}_\alpha^B - \hat{\mu}_\alpha^A q^B) - T_{\alpha\beta} \hat{\mu}_\alpha^A \hat{\mu}_\beta^B + \dots, \quad (3.133)$$

where q^A represents the charge of atom A, and $\hat{\mu}^A$ denotes the dipole moment of atom A. Terms like T , T_α , and $T_{\alpha\beta}$ stand for the form of multipole interaction tensors, and the subscripts α and β represent x , y or z Cartesian components, following the usual Cartesian-tensor convention. In general, the multipole interaction tensors, $T_{\alpha\beta\dots\omega}$, are defined by

$$T_{\alpha\beta\dots\omega} = \nabla_\alpha \nabla_\beta \dots \nabla_\omega \frac{1}{R}, \quad (3.134)$$

where R denotes the module of the separation vector $\mathbf{R}$ between the two molecules A and B. Then,

$$\begin{aligned} T &= \frac{1}{R}, \\ T_\alpha &= \nabla_\alpha \frac{1}{R} = -\frac{R_\alpha}{R^3}, \\ T_{\alpha\beta} &= \nabla_\alpha \nabla_\beta \frac{1}{R} = \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{R^5}, \\ &\dots \end{aligned} \quad (3.135)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta.

For two neutral molecules, the charges $q^A = q^B = 0$, then the leading term becomes the dipole-dipole interaction.¹⁵ If we consider only the dipole-dipole interaction, then the dispersion energy in Eq. (3.132) can be rewritten as

$$\begin{aligned} E_{\text{disp}}^{\text{AB}} &= - \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A 0_B | T_{\alpha\beta} \hat{\mu}_\alpha^A \hat{\mu}_\beta^B | m_A n_B \rangle \langle m_A n_B | T_{\gamma\delta} \hat{\mu}_\gamma^A \hat{\mu}_\delta^B | 0_A 0_B \rangle}{E_A^m + E_B^n - E_A^0 - E_B^0} \\ &= -T_{\alpha\beta} T_{\gamma\delta} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle \langle 0_B | \hat{\mu}_\beta^B | n_B \rangle \langle n_B | \hat{\mu}_\delta^B | 0_B \rangle}{E_A^m + E_B^n - E_A^0 - E_B^0}. \end{aligned} \quad (3.136)$$

There are two commonly used approaches to handle this sum-over-states expression in Eq. (3.136). One approach is to use the Unsöld approximation [301] to replace the sum-over-states energies with averaged energies, as London [53] did. Firstly, we rearrange the expression above as

$$\begin{aligned} E_{\text{disp}}^{\text{AB}} &= -T_{\alpha\beta} T_{\gamma\delta} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{(E_A^m - E_A^0)(E_B^n - E_B^0)}{E_A^m - E_A^0 + E_B^n - E_B^0} \\ &\quad \times \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A \rangle \langle m_A | \hat{\mu}_\gamma^A | 0_A \rangle}{(E_A^m - E_A^0)} \frac{\langle 0_B | \hat{\mu}_\beta^B | n_B \rangle \langle n_B | \hat{\mu}_\delta^B | 0_B \rangle}{(E_B^n - E_B^0)}. \end{aligned} \quad (3.137)$$

Using the Unsöld (or closure) approximation [301], we replace the individual excitation energies with average energies, then the sum-over-states expression in Eq. (3.136) can be rewritten in terms of the average energies (U_A, U_B), the polarizabilities ($\alpha_A^{\alpha\gamma}, \alpha_B^{\beta\delta}$), and the second-order electrostatic (Cartesian) tensors ($T_{\alpha\beta}, T_{\gamma\delta}$). The dispersion energy can be obtained as

$$E_{\text{disp}}^{\text{AB}} \approx - \frac{U_A U_B}{4(U_A + U_B)} \alpha_A^{\alpha\gamma} \alpha_B^{\beta\delta} T_{\alpha\beta} T_{\gamma\delta}. \quad (3.138)$$

For more details of the derivations, we refer the reader to [40, 44, 302–304].

For atoms, $\alpha_A^{\alpha\gamma} = \bar{\alpha}_A \delta_{\alpha\gamma}$ and $\alpha_B^{\beta\delta} = \bar{\alpha}_B \delta_{\beta\delta}$, where $\bar{\alpha}_A$ and $\bar{\alpha}_B$ represent static polarizability of atom A and B, and they are experimentally accessible. Then we can reduce the products of $\alpha_A^{\alpha\gamma} \alpha_B^{\beta\delta}$ and of $T_{\alpha\beta} T_{\gamma\delta}$ to

$$\alpha_A^{\alpha\gamma} \alpha_B^{\beta\delta} T_{\alpha\beta} T_{\gamma\delta} = \frac{6\bar{\alpha}_A \bar{\alpha}_B}{R^6}. \quad (3.139)$$

Thus, the dispersion energy between two atoms can be approximated as

$$E_{\text{disp}}^{\text{AB}} \approx - \frac{3}{2} \frac{U_A U_B}{U_A + U_B} \frac{\bar{\alpha}_A \bar{\alpha}_B}{R^6}. \quad (3.140)$$

¹⁵The dispersion energy expression for charged molecules does not include the charge variable q .

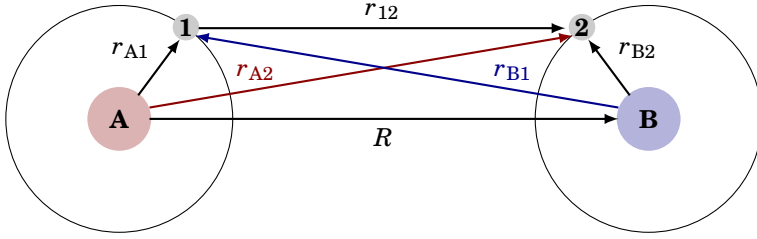


FIGURE 3.6: Position scalar variables of the H_2 molecule consisting of two well-separated hydrogen atoms with two electrons at each $1s$ atomic orbital. Assuming that the positions of two nuclei are fixed on the z -axis.

In Eq. (3.141), London used the first ionization energies (I_A and I_B) to approximate the average energies (U_A and U_B), and it is known as the London model [53, 295, 300]. The leading term coefficient of $E_{\text{disp}}^{\text{AB}}$ is evaluated by

$$C_6^{\text{AB}} \approx -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \bar{\alpha}_A \bar{\alpha}_B. \quad (3.141)$$

The early London model is instructive and helps understand dispersion through quantum mechanics, despite providing quite rough evaluations to dispersion energy [72].

Another approach was introduced by Casimir and Polder [305] when they applied quantum electrodynamics to study the effect of retardation on the dispersion interaction. They proposed the concept of polarizability at imaginary frequency (also known as “dynamic polarizability”) to represent the sum-over-states energy terms. For spherical atoms, this treatment helps derive a rigorous Casimir-Polder formula for dispersion energy,

$$E_{\text{disp}}^{\text{AB}} = -\frac{3}{\pi R^6} \int_0^\infty \bar{\alpha}_A(i\omega) \bar{\alpha}_B(i\omega) d\omega, \quad (3.142)$$

where $\bar{\alpha}_A(i\omega)$ and $\bar{\alpha}_B(i\omega)$ are dynamic polarizabilities of atom A and B, respectively. When $\omega = 0$, we get the static polarizabilities. However, the dynamic polarizabilities are unfortunately difficult to calculate accurately, being impractical, especially when dealing with large molecular systems.

Now let us take a basic example of H_2 molecule for illustrating the PT treatment of London dispersion. Consider the two well-separated hydrogen atoms shown in Fig. 3.6, with the internuclear distance, R , which is large enough so that the exchange effects can be neglected. We assume that the two atoms are in their ground state before considering their interactions. Then, the unperturbed (zeroth-order) wavefunction for this H_2 system is a simple product of two $1s$ orbitals over

each atom,

$$|\Psi^{(0)}\rangle = |0_A 0_B\rangle = |s_A(1)s_B(2)\rangle. \quad (3.143)$$

The small perturbation through the first-order Hamiltonian that describes the interaction between the two atoms, can be expanded in Taylor series in terms of $1/R$ and the leading term gives $1/R^3$ dependency,

$$\begin{aligned} \hat{H}^{(1)} &= -\frac{1}{r_{A2}} - \frac{1}{r_{B1}} + \frac{1}{R} + \frac{1}{r_{12}} \\ &= \frac{1}{R^3}(x_{A1}x_{B2} + y_{A1}y_{B2} - 2z_{A1}z_{B2}) + \dots, \end{aligned} \quad (3.144)$$

where x_{A1}, y_{A1}, z_{A1} and x_{B2}, y_{B2}, z_{B2} denote Cartesian coordinates of electron 1 and 2 relative to its nucleus, respectively. In the following, we consider only the leading term of $\hat{H}^{(1)}$ which corresponds to the interaction of the dipole moments of the two atoms, and higher-order multipole expansion will be neglected. The zeroth-order energy is a simple sum of the energies of two independent hydrogen atoms, while the first-order PT correction energy is zero due to the spherical symmetry of each atom (the relevant integrals vanished). Thus, the leading term of the second-order PT correction energy can be formulated as

$$\begin{aligned} E^{(2)} &= -\frac{1}{R^6} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{|\langle 0_A 0_B | (x_{A1}x_{B2} + y_{A1}y_{B2} - 2z_{A1}z_{B2}) | m_A n_B \rangle|^2}{\epsilon_A^m + \epsilon_B^n - 2\epsilon_0} \\ &= -\frac{C_6}{R^6}, \end{aligned} \quad (3.145)$$

where ϵ_A^m and ϵ_B^n represent energies of hydrogen atom A at m state and atom B at n state, respectively. And ϵ_0 denotes the ground-state energy of the hydrogen atom. Since $m_A \neq 0$ and $n_B \neq 0$, we have $\epsilon_A^m > \epsilon_0$ and $\epsilon_B^n > \epsilon_0$. Therefore, we can see that the second-order correction energy is negative, behaving as an attractive potential energy proportional to $1/R^6$.

By using the Unsöld approximation, and replacing ϵ_A^m and ϵ_B^n by zero (because their magnitudes are relatively very small compared to $|\epsilon_0|$), one can rearrange the expression of C_6 as

$$C_6 = -\frac{1}{2\epsilon_0} \langle 0_A 0_B | (x_{A1}x_{B2} + y_{A1}y_{B2} - 2z_{A1}z_{B2})^2 | 0_A 0_B \rangle. \quad (3.146)$$

Because 0_A and 0_B are basically $1s$ orbitals of atoms A and B with spherical symmetry, the expectation value of cross terms (e.g., $x_{A1}y_{A1}$, $x_{A1}z_{A1}$, etc.) get vanished. Then Eq. (3.146) can be simplified by using the expectation value of

the position variables of electrons 1 or 2, and we have $\langle r_1^2 \rangle = \langle r_2^2 \rangle = 3a_0^2$, where a_0 denotes Bohr radius.¹⁶ We note that the hydrogen atom energy term is $\epsilon_0 = -0.5a_0$. Finally, we obtain $C_6 = 6a_0^5$ which is only valid if $R \gg a_0$, the lower and upper bounds being $6 \leq C_6 \leq 8$ [306, 307].

The $1/R^6$ asymptotic behavior has always been considered a typical signature of London dispersion energy. From the H_2 molecule, we know that the $1/R^6$ dependence arises from the leading term of $\hat{H}^{(1)}$ expansion, namely, the dipole-dipole interaction operator. However, the accuracy of C_6 is sensitive to the choice of wavefunction. London and Eisenschitz (1930) [295] initially obtained a value of $C_6 = 6.47$ using a straightforward second-order PT treatment and the Unsöld approximation. Subsequently, Slater and Kirkwood (1931) [308] improved upon this value by incorporating a variational function in the perturbed wavefunction, yielding $C_6 = 6.49$. In a later study, Pauling and Beach (1935) [309] utilized a variety of variation functions, including 26 terms for the dipole-dipole interaction, leading to an improved value of $C_6 = 6.49903$. Thereby numerous results of the improved C_6 for H_2 molecule have been successively reported over several decades [310–318]. Among all these studies, perhaps the most precise one is $C_6 = 6.499026705405839313128194604$ from Masili and Gentil (2008) [316]. In recent years, Cancès *et al.* [317] revisited the approach of Slater and Kirkwood (1931) and slightly modified their approach for numerically achieving a high accuracy $C_6 = 6.499026705403\dots$. Recently, Gori-Gorgi *et al.* [318] introduced a variation wavefunction method without density distortion which is also capable of retrieving highly precise $C_6 = 6.4990267054058393\dots$. More recently, Cioslowski *et al.* [319] developed a particular RDMFT functional to compute the long-range interaction energy of two hydrogen atoms, resulting in $C_6 = 6.49902670540583931312819460413\dots$ with at least 30 correct digits.

Although the PT has demonstrated its usefulness in understanding London dispersion within the framework of quantum mechanics and yielding accurate results for small systems, it faces several disadvantages when applied to modeling dispersion interactions. Firstly, defining well-separated atoms or fragments is not a straightforward task in general. Moreover, the zeroth-order wavefunction and Hamiltonian of the two monomers must be well defined, and the interaction energy between the atoms or fragments should be significantly smaller than the individual energies to treat it as a small perturbation. Furthermore, higher-order PT becomes computationally expensive, making it impractical for higher-order multipole expansions, large molecules, or systems in excited states.

¹⁶In atomic units, the Bohr radius, $a_0 = 1 \text{ a.u.} = 1 \text{ Bohr}$.

3.5.2 Methods for Computing Dispersion Interaction Energies

The current *ab initio* methods available which can compute or include dispersion interaction energies in quantum chemistry are roughly categorized here into three families (see Tab. 3.2): wavefunction theory (WFT), density functional approximations (DFAs), and many other methods which can be used specifically for calculating dispersion energies.

TABLE 3.2: Quantum chemistry methods that recover dispersion energies

Category	Methods
WFT	FCI, CCSD, CCSD(T), MP2, CASPT2, etc.
DFAs	D3/D4, Tkatchenko-Scheffler, MBD, XDM, non-local or parameterized functionals, etc.
Others	TD-DFT, SAPT, variational approach of Gori-Giorgi, etc.

Correlated WFT methods that are capable of handling dynamic correlation, such as FCI, CCSD, CCSD(T), MP2, CASPT2, NEVPT2, etc., can naturally incorporate the dispersion interaction energies in the total electronic energy, at least to some extent, as they are integrated as part of dynamic correlation. Notwithstanding, the high-level WFT methods that can capture more accurate dispersion energies are computationally demanding and impractical for large systems, and the choice of basis set can also significantly affect the quantitative description of dispersion interactions in the wavefunction and energy.

As an alternative branch for solving the Schrödinger equation, the DFAs have become more and more favored in recent years. However, many widely used functionals (e.g., PBE [58], B3LYP [59, 60]) are known for their failures in describing the long-range dispersion interactions [61–65]. Various practical methods have been developed to address this deficiency during the past two decades, such as D3/D4 methods [66, 67], Tkatchenko-Scheffler method [68], Many-Body Dispersion (MBD) model [69, 70], Exchange-hole Dipole Moment model (XDM) [71–79], non-local functionals (e.g., vdW-DF1 [80], vdW-DF2 [81], vdW-DF3 [82], VV09 [83], VV10 [84]), parameterized functionals (e.g., M06 [85]), and among others. However, it still remains a challenge to develop an accurate, efficient, general, and first-principle-motivated method to treat dispersion interactions in the context of DFT. Since this thesis does not involve DFAs, we will not discuss

further dispersion treated with DFAs, and we refer the reader to [65, 69, 82, 87, 250, 297, 320–322].

There are many other methods designed for calculating dispersion energies. The dynamic polarizabilities evaluated by TD-DFT can also be used in the Casimir and Polder formula (in Eq. (3.142)) for calculating dispersion energies [323, 324]. Note that the semi-classical D3/D4 dispersion correction methods precomputed dynamic polarizabilities through TD-DFT.

The symmetry-adapted perturbation theory (SAPT) [325, 326] offers a breakdown of non-covalent interaction energies between atoms or molecules, enabling the decomposition of the interaction energy into physically interpretable partitions (e.g., electrostatic, exchange, induction, and dispersion terms). Nonetheless, in SAPT methods, the dispersion energy terms lead to the computational bottleneck, [327] and alternative approaches will be shown in Section 3.5.3, and higher-order SAPT methods are computationally demanding and thus less practical. For further details of the SAPT methods, we refer [325, 326].

Recently, Gori-Giorgi *et al.* [318, 328, 329] put forward a variational wavefunction approach targeting dispersion energies of a dimer by using its monomer pair densities. Even though this approach violates the Hellmann-Feynman theorem [330, 331], it is capable of achieving high accuracy dispersion energies for small neutral systems without using polarizabilities or virtual orbitals.

In the framework of Reduced Density Matrix Functional Theory (RDMFT), very few approximation methods were proposed to capture dispersion interactions. Specifically, Pernal [332] developed the long-range density matrix exchange-correlation functional, Piris *et al.* [333, 334] suggested using only Coulomb (J) and exchange (K) functionals to describe correctly the long-range asymptotic behavior of dispersion for helium dimer, while Cioslowski and Pernal [335] pointed out that the primitive natural spin-orbital functionals are incapable of recovering the dispersion component of the interaction energy due to the lack of terms quadratic in two-electron integrals. Cioslowski *et al.* [336] and Baerends *et al.* [89, 90] argued that a full description of the dispersion interaction requires the presence of both JK and non- JK terms. As mentioned previously, very recently, Cioslowski *et al.* [319] developed a particular RDMFT functional for calculating long-range interactions based on the molecular hydrogen. This approach achieved high accuracy in computing the dispersion energy coefficient C_6 for H_2 .

3.5.3 Methods for Identifying Dispersion Interactions

We have reviewed many methods that are capable of capturing dispersion energies, yet there are not many approaches designed for identifying dispersion interactions. In this thesis, we classify these methods into two groups: energy decomposition methods and visualization tools [337].

1) Energy decomposition methods

Among the energy decomposition analysis (EDA) [338, 339] schemes, the SAPT methods are the most commonly used for quantitatively characterizing dispersion energies. While the SAPT methods have the ability to explicitly separate the dispersion energies from the total interaction energy between atoms or fragments, they are usually computationally expensive to apply to large intramolecular cases and rely on the choice of reference wavefunctions. Martínez *et al.* [340] recently implemented a variant of the functional group SAPT partition (F-SAPT) algorithm to efficiently deal with large-scale systems (up to 3000 atoms and 25,000 basis functions). Nevertheless, in order to balance the capability and efficiency of the F-SAPT method, the dispersion and exchange-dispersion energy terms obtained from *ab initio* methods are substituted by Grimme’s D3 dispersion correction [66] added on top of DFAs. We note that Grimme’s D3/D4 method also enables the separate quantification of dispersion energies, so they can be used to identify dispersion energies in this context.

Very recently, Pernal *et al.* [341–343] extended SAPT to MCSCF wavefunction methods for treating systems with MR character, they also developed an approach to quantify the amount of tiny fraction of dispersion interaction recovered by the MCSCF calculations to avoid double counting of dispersion in the total interaction energy. However, using the MCSCF wavefunction with SAPT methods is definitely a complex and costly option, and the results are dependent on the active space of the wavefunction. On the other hand, SAPT and traditional EDA approaches face challenges in accounting for the effects of short-range regimes on very weak interactions [344].

Before proceeding further with other methods for identifying dispersion interactions, it is worthwhile presenting here the quantum theory of atoms in molecules (QTAIM) theoretical framework developed by Bader *et al.* [345, 346]. The QTAIM theory is based on the topological analysis of the electron density and it can provide a real-space atomic partition of energies or properties of molecules. The topological information of the electron density can be analyzed conveniently through the “critical points” (CP) which are the points in Cartesian space where

the first derivative of the density vanishes,

$$\nabla \rho(\mathbf{r}_c) = \mathbf{0}, \quad (3.147)$$

where $\mathbf{r}_c$ denotes the coordinate points in the Cartesian space.

For identifying these CP, such as local maxima, local minima, or saddle points, one needs to examine the second derivatives of $\rho(\mathbf{r})$, which are commonly arranged in the so-called ‘‘Hessian matrix’’:

$$\mathbf{H}(\mathbf{r}_c) = \nabla^T \nabla \rho(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_c} = \begin{bmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x^2} & \frac{\partial^2 \rho(\mathbf{r})}{\partial x \partial y} & \frac{\partial^2 \rho(\mathbf{r})}{\partial x \partial z} \\ \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial x} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y^2} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial z} \\ \frac{\partial^2 \rho(\mathbf{r})}{\partial z \partial x} & \frac{\partial^2 \rho(\mathbf{r})}{\partial z \partial y} & \frac{\partial^2 \rho(\mathbf{r})}{\partial z^2} \end{bmatrix}_{\mathbf{r}=\mathbf{r}_c}. \quad (3.148)$$

Since the Hessian matrix $\mathbf{H}(\mathbf{r}_c)$ is a real and symmetric matrix, it can be diagonalized by a unitary transformation, $\mathbf{U}$,

$$\mathbf{U}^T \mathbf{H}(\mathbf{r}_c) \mathbf{U} = \begin{bmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x_1^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial y_1^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial z_1^2} \end{bmatrix}_{\mathbf{r}_1=\mathbf{r}_c} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}, \quad (3.149)$$

where the three eigenvalues ($\lambda_1, \lambda_2, \lambda_3$) of the Hessian matrix provide the curvatures of $\rho(\mathbf{r}_c)$. With the non-zero eigenvalues, there are four types of stable CP that can be classified by the signs of curvatures: nuclear critical point, bond critical point, ring critical point, and cage critical point. [347].

The Interacting Quantum Atoms (IQA) [348, 349] approach following the QTAIM scheme provides the partition of a molecule into topological atoms in real space, and it is a useful tool for studying the electronic structure and chemical bonding. Compared to the SAPT methods, the IQA approach can explicitly identify short and long-range regime contributions in the energy partitions. Following the IQA approach, one can partition the total electronic energy in Eq. (3.8) into intra and interatomic energies through the use of 1-RDM and 2-RDM [344],

$$E = \underbrace{\sum_A T_A + \sum_A V_{en}^{AA} + \sum_A V_{ee}^{AA}}_{E_{intra}^A} + \underbrace{\sum_{A \neq B} V_{en}^{AB} + \frac{1}{2} \sum_{A \neq B} V_{ee}^{AB} + \frac{1}{2} \sum_{A \neq B} V_{nn}^{AB}}_{\frac{1}{2} E_{inter}^{AB}}, \quad (3.150)$$

and the pair density can be partitioned as

$$\begin{aligned}\rho_2(1,2) &= \rho_2^{\text{SD}}(1,2) + \rho_2^{\text{cumul}}(1,2) \\ &= \rho_2^{\text{Coul}}(1,2) + \rho_2^{\text{exch}}(1,2) + \rho_2^{\text{cumul}}(1,2).\end{aligned}\quad (3.151)$$

where the $\rho_2^{\text{SD}}(1,2)$ was defined previously in Eq. (3.74) and $\rho_2^{\text{cumul}}(1,2)$ in Eq. (3.75).

Thus, the interatomic energy partitions of V_{ee} (shown in Eq. (3.77)), denoted as $V_{\text{ee}}^{\text{AB}}$, can be evaluated in terms of Coulomb, $\rho_2^{\text{Coul}}(1,2)$, exchange, $\rho_2^{\text{exch}}(1,2)$, and cumulant, $\rho_2^{\text{cumul}}(1,2)$, energy terms, by integrating over the non-overlapping atomic domains A and B,

$$\begin{aligned}V_{\text{ee}}^{\text{AB}} &= \frac{1}{2} \int_{\text{A}} \int_{\text{B}} \frac{\rho_2(1,2)}{r_{12}} d1 d2 \\ &= \frac{1}{2} \int_{\text{A}} \int_{\text{B}} \frac{\rho_2^{\text{Coul}}(1,2)}{r_{12}} d1 d2 + \frac{1}{2} \int_{\text{A}} \int_{\text{B}} \frac{\rho_2^{\text{exch}}(1,2)}{r_{12}} d1 d2 + \frac{1}{2} \int_{\text{A}} \int_{\text{B}} \frac{\rho_2^{\text{cumul}}(1,2)}{r_{12}} d1 d2 \\ &= J_{\text{AB}}[\rho_1(1)] + K_{\text{AB}}[\rho_1(1;1')] + C_{\text{AB}}[\rho_2^{\text{cumul}}(1,2)].\end{aligned}\quad (3.152)$$

TABLE 3.3: Chemical interpretation of IQA pair density partitions [350].

$\rho_2(1,2)$ terms	characters
$\rho_2^{\text{Coul}}(1,2)$	electrostatic, charge transfer, ionicity, polarity
$\rho_2^{\text{exch}}(1,2)$	bonding, covalency, bond order, (hyper) conjugation
$\rho_2^{\text{cumul}}(1,2)$	van der Waals (vdW)

Recently, Popelier *et al.* [350] classified the pair density partitions in IQA between atoms A and B, as summarized in Tab. 3.3. The authors pointed out that the classical Coulomb energy term, $J_{\text{AB}}[\rho_1(1)]$, in Eq. (3.152) relates to charge transfer, the degree of ionicity, and bond polarity; the exchange energy term, $K_{\text{AB}}[\rho_1(1;1')]$, connects to the bond order [351] and degree of covalency; while the cumulant energy term, $C_{\text{AB}}[\rho_2(1,2)]$, is associated with the long-range dispersion interactions. They also showed a noticeable linear connection between the QTAIM delocalization index and bond correlation energies from MP4 based on some small systems. Another recent study by Martín Pendás *et al.* [352] demonstrated that the IQA/MP2 correlation energy partitions can help analyze the deformation of dispersive and charge-induced small vdW clusters.

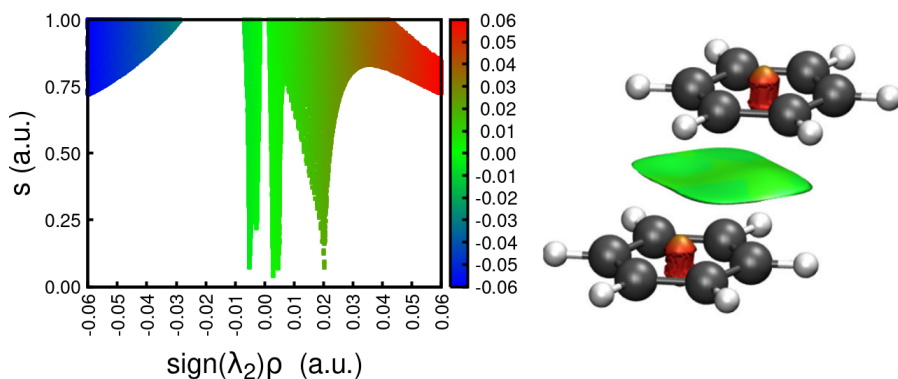


FIGURE 3.7: NCI plot and the reduced density gradient isosurface of the benzene dimer [2].

2) Visualization tools

Regarding visualization tools (or descriptors), one of the most prevalent methods for visualizing dispersion interactions in molecular systems is the non-covalent interaction index (NCI) [353], which is based on the topological analysis of electron density $\rho(r)$. The NCI identifies non-covalent interactions from the electron density and its derivative. The primary variable of NCI, the reduced density gradient, $s(\mathbf{r})$, is defined as

$$s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2(3\pi^2)^{1/3}\rho(\mathbf{r})^{4/3}}. \quad (3.153)$$

Fig. 3.7 shows an NCI plot [354] that has been widely adopted in recent years. The $s(\mathbf{r})$ as a function of $\text{sign}(\lambda_2)\rho(\mathbf{r})$ facilitates the straightforward visualization of the non-covalent interactions in molecules, where the term “ $\text{sign}(\lambda_2)$ ” represents the sign of the second largest eigenvalue (λ_2) of the Hessian matrix of the electron density. The blue color marks strong attractive interactions ($\lambda_2 < 0$), green color corresponds to weak dispersion interactions ($\lambda_2 \approx 0$) and red color is responsible for strong repulsive interactions ($\lambda_2 > 0$). The NCI is a powerful tool, and it is efficient and applicable to large systems (e.g., enzymes, DNA). Yet it is still a challenge to determine an explicit relationship between the NCI and the dispersion interaction energy, despite that very recently Boto *et al.* [354] reported a noticeable *ad hoc* linear relationship between $\rho(\mathbf{r})^{2.5}$ integral and the dispersion energy.

In the literature, there are some other visualization tools for analyzing the non-covalent interactions: the Density Overlap Regions Indicator (DORI) proposed by

Silva and Corminboeuf [355], which is similar to the NCI as a density-dependent bonding descriptor for identifying bonding and non-bonding regions; the London Dispersion Potential (LDP) maps defined by Pollice and Chen [356] through the modification of London formula with the homoatomic dispersion coefficients obtained from the D4 method of Grimme [67]; the Dispersion Interaction Density (DID) suggested by Wuttke and Mata [357] based on the spin-component scaled [358] local MP2 wavefunction, etc. Very recently, Pastorczak *et al.* [337] introduced a local indicator for visualizing and analyzing the dispersion interactions in Multireference situations (e.g., when the covalent bonds are particularly stretched or compressed).

3.5.4 Induced Dipole-Induced Dipole Two-Electron Terms

In addition to the prominent EDA or IQA schemes, we present some less-known specific energy or pair density terms to calculate and identify dispersion interactions. Firstly, considering only s and p atomic orbitals of singlet (or triplet) H_2 molecule, or Helium dimer, Baerends *et al.* [88–90] proposed few covalent atomic (primitive) orbital product terms (i.e., $s_A(1)p_A(1)s_B(2)p_B(2)$ two-electron AO terms) from the FCI wavefunction to represent vdW interactions. Analyzing these dispersion terms of the pair density, they interpreted that when electron 1 is near nuclei A, the conditional density gives an induced dipole contribution to electron 2 around nuclei B, which is in accordance with London’s description of the dispersion interactions as an induced dipole-induced dipole effect. For these induced dipole-induced dipole two-electron integral terms, Ángyán *et al.* [42] gave further description based on a Helium dimer example. They pointed out that this $1/R^3$ asymptotic behavior of the two-electron integrals, $(s_A(1)p_A(1)s_B(2)p_B(2))$, is responsible for dipole-dipole interaction,

$$(1s_A 2p_{zA} | 1s_B 2p_{zB}) = -\frac{2\mu_z^A \mu_z^B}{R^3} + \mathcal{O}(R^{-5}). \quad (3.154)$$

The transition dipole moment μ_z^A is given by

$$\mu_z^A = (1s_A | e(z_1 - A_z) | 2p_{zA}), \quad (3.155)$$

where z_1 and A_z denote the positions of electron 1 and atom A on the z -axis, respectively. Note that the $2p_{zA}$ atomic orbital substituted by $2p_{xA}$ or $2p_{yA}$ orbitals in Eq. (3.154) and Eq. (3.155) shows an analogous behavior. For further discussions, we refer to Chapter 6.

London dispersion originates from “purely” electron correlation effect, and can not be captured by the Hartree-Fock method [42, 359], as it corresponds to a

portion of correlation between distant electron pairs. Pulay [360] suggested that *in the vdW limit interpair correlation can be probably described by using only three correlation functions, corresponding to the three components of the instantaneous dipole moment*.

Recently, Head-Gordon *et al.* [361–363] proposed a compressed representation of the long-range part of electron correlation which is associated with dispersion interactions. By performing CCSD calculations with localized orbitals, they isolated the energy components associated with purely dipolar terms, which represent dispersion energies and show an asymptotic decay of $1/R^6$.

3.5.5 Asymptotic Conditions

Consider two interacting atoms or molecular fragments are separated at large distance R , the dipole-dipole interactions can be expanded as

$$\hat{V}_{dd} = \frac{\mathbf{d}_A \cdot \mathbf{d}_B}{R^3} - \frac{3(\mathbf{d}_A \cdot \mathbf{R})(\mathbf{d}_B \cdot \mathbf{R})}{R^5}, \quad (3.156)$$

where $\mathbf{d}_A$ and $\mathbf{d}_B$ represent the expectation value of the dipole moment of A and B, respectively. $\mathbf{R}$ corresponds to the vector connecting A and B two charge points, and $R = \|\mathbf{R}\|$ [43]. For the H_2 molecule, as shown in Eq. (3.144), the $1/R^3$ leading term of $\hat{H}^{(1)}$ expansion corresponds to the interactions of the dipole moments of the two Hydrogen atoms. Hence, apart from the typical $1/R^6$ asymptotic behavior of dispersion interaction energy, the $1/R^3$ asymptotic decay of dipole-dipole interactions is also well-known as it exists for any two interacting systems.

Recently, our group reexamined the perturbation theory with the Unsöld approximation for treating the dispersion interactions in a large-separated H_2 model, and revealed that the leading term in the distance-based expansion of the first-order correction of the pair density intracule shows a universal $1/R^3$ decay [91]. Furthermore, they also demonstrated that the intracule of the Coulomb hole partition in Eq. (3.93) at $r_{12} = R$, namely, $h_{cII}(R)$ shows $1/R^3$ predominant asymptotic behavior (see Fig. 3.8), this asymptotics of the long-range correlation component connects to the $1/R^6$ dependence of dispersion energy [3, 91].

Apart from this intracule $h_{cII}(R) \propto 1/R^3$ signature, Mazziotti *et al.* [364] proposed another signature of vdW interactions by using the squared Frobenius norm of the cumulant part of the 2-RDM which contains the connected part of the pair density and other information. They demonstrated that the squared Frobenius norm of the cumulant (i.e., the trace of the squared cumulant) shows $1/R^6$ asymptotic behavior. The squared Frobenius norm of the cumulant is size

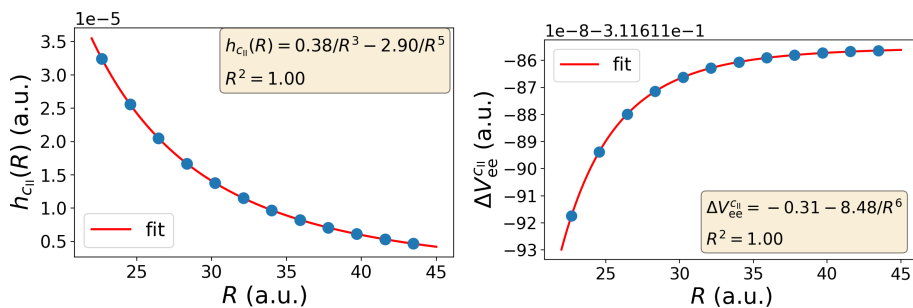


FIGURE 3.8: The intracule of the Coulomb hole partition in Eq. (3.93) at $r_{12} = R$, $h_{c_{II}}(R)$ and its corresponding energy term $\Delta V_{c_{II}}^{ee}$ against R from H_2 molecule at large separation, calculated at the FCI/aug-cc-pVDZ level.

extensive and it can be used to detect and quantify the vdW interactions between two atoms or molecular moieties.

More recently, Wang *et al.* [365, 366] have reported a linear correlation between the correlation entropy S_{corr} and the cumulant electron-electron interaction energy obtained from CI (or MCSCF) type wavefunctions. This finding suggests the potential for developing RDMFT functional approximations based on correlation entropy. However, it should be noted that this empirical relationship has only been validated for a limited range of molecular systems, such as H_2 and H_2O , when varying the geometry of the same molecule, and its underlying physical interpretation is still lacking. Further analysis is required to explore its generality to other molecular systems.

CORRELATION MEASURES

4.1 Introduction

The concept of natural orbitals (NO) and their occupation numbers originated from the 1-RDM of an FCI wavefunction or the best approximate CI wavefunction for a given basis set, which inherently contains essential electron correlation information [121]. In practice, most post-HF (or called “correlated”) wavefunction methods recover a significant portion of the total electron correlation (around 80 – 90%) [137]. The spin-natural orbital occupation numbers $\{n_i^\sigma\}$ obtained from the post-HF wavefunction can help measure the electron correlation retrieved by this method. In the uncorrelated case that employs a Single-Determinant (SD) wavefunction (e.g., $\{n_i^\sigma\}$ obtained from the HF wavefunction), $\{n_i^\sigma = 0\}$ corresponds to virtual orbitals, while $\{n_i^\sigma = 1\}$ is associated with occupied orbitals. Thus, by direct comparison to the reference of the uncorrelated wavefunction, the fractional numbers $\{0 < n_i^\sigma < 1\}$ obtained from a correlated wavefunction reflect the virtual orbitals in a single reference determinant that exhibit significant interaction with the electrons in the occupied orbitals of the reference determinant [179, 257].

The NO occupation numbers in general serve as a valuable tool for analyzing the electronic state and offer insights into the significance of individual orbitals for the description of electron correlation [139]. Natural orbitals and their occupation numbers are available for most modern electronic structure methods. In this work, our hypothesis is that these occupation numbers contain sufficient information

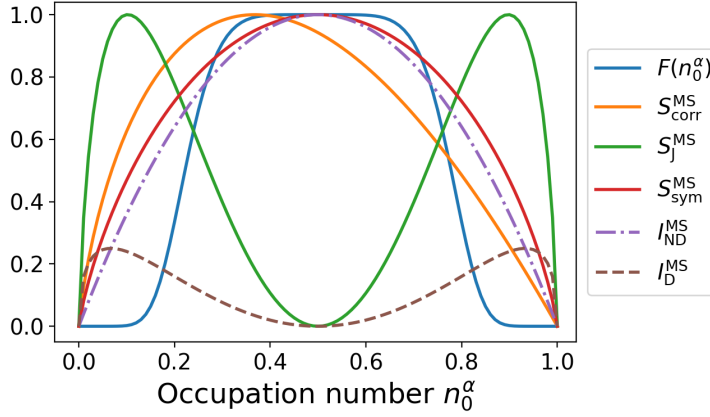


FIGURE 4.1: Plot of natural orbital occupation-based functions for a simple closed-shell model system (MS) consisting of two electrons and two orbitals. The maximum values of $S_{\text{corr}}^{\text{MS}}$, S_J^{MS} , $S_{\text{sym}}^{\text{MS}}$ and $I_{\text{ND}}^{\text{MS}}$ are all scaled to 1.0, respectively. I_D^{MS} and $I_{\text{ND}}^{\text{MS}}$ share the same scale factor.

to explain the electron correlation captured by the actual wavefunction method, although there are various ways to extract this information.

We adopt a statistical perspective to extract valuable information about electron correlation from $\{n_i^\sigma\}$. We begin by considering a simple closed-shell singlet model system (MS) consisting of two electrons and two orbitals [13]. The corresponding spin-natural orbital occupation numbers are denoted as $\{n_0^\alpha, n_0^\beta, n_1^\alpha, n_1^\beta\}$. Moreover, using the relationships $n_0^\alpha = n_0^\beta$ and $n_1^\alpha = n_1^\beta = 1 - n_0^\alpha$ for the closed-shell MS, we can reduce the occupation numbers to a single variable n_0^α . Subsequently, several ansatzes can be commonly applied over the MS:

- Dynamic and nondynamic correlation indices: $I_D^{\text{MS}} = [n_0^\alpha(1 - n_0^\alpha)]^{1/2} - 2n_0^\alpha(1 - n_0^\alpha)$ associated with Eq. (3.108), $I_{\text{ND}}^{\text{MS}} = n_0^\alpha(1 - n_0^\alpha)$ linked to Eq. (3.109) [13].
- Entropy-based quantities: $S_{\text{corr}}^{\text{MS}} = n_0^\alpha \ln(n_0^\alpha)$ employed in Eq. (3.102) or its variant $(1 - n_0^\alpha) \ln(1 - n_0^\alpha)$, along with their combinations such as $S_{\text{sym}}^{\text{MS}} = n_0^\alpha \ln(n_0^\alpha) + (1 - n_0^\alpha) \ln(1 - n_0^\alpha)$ and $S_J^{\text{MS}} = 4n_0^\alpha(1 - n_0^\alpha) \ln[4n_0^\alpha(1 - n_0^\alpha)]$.
- The “Cumulative Distribution Function” of Bartlett *et al.* [257], in Eq. (3.113), is denoted as $F(n_0^\alpha)$ for the MS.

For the closed-shell MS [13], the occupation number n_0^α around 0.5 typically indicates the presence of significant nondynamic correlation, while values close to 0 or 1 suggest a predominant dynamic correlation in the system. This inference is illustrated in Fig. 4.1, where the plots of various ansatzes against $\{n_0^\alpha\}$

demonstrate their ability to characterize different types of electron correlation. Specifically, $F(n_0^\alpha)$, $S_{\text{corr}}^{\text{MS}}$, $S_{\text{sym}}^{\text{MS}}$, and $I_{\text{ND}}^{\text{MS}}$ can serve as indicators of nondynamic correlation, while S_{J}^{MS} and I_{D}^{MS} are associated with dynamic correlation. Furthermore, although there are numerous mathematical functions that can be used for this purpose, it is not our purpose to investigate additional ansatzes in terms of $\{n_i^\sigma\}$ here, as they usually give similar insights into measuring electron correlation for the MS.

In this chapter, we aim to search for the connections between correlation metrics, particularly those categorized into different groups. We explore different statistical approaches to generate scalar values from spin-natural orbital occupation numbers $\{n_i^\sigma\}$. The natural choice is averaging, which yields quantities such as $\overline{I_{\text{D}}}$ (see Eq. (4.1)), $\overline{I_{\text{ND}}}$ (see Eq. (4.2)), S_{corr} (see Eq. (3.102)), S_{J} (see Eq. (4.5)), S_{sym} (see Eq. (4.4)), etc. The averaging approach means that we report the quantities per electron. Nonetheless, we also consider other options, including the variance (e.g., $\bar{V}$), maximum values similar to D_1 and D_2 (e.g., n_H , $I_{\text{ND}}^{\text{max}}$), or minimum values (e.g., $1 - c_0^2$, n_L). These statistical methods assist in the application of these ansatzes, enabling comparisons with the uncorrelated scenario (involving terms like n_i^σ , $1 - n_i^\sigma$, or both) to quantify electron correlation. Moreover, we compare these approaches to other existing correlation metrics/indices, such as c_0 -based diagnostics (e.g., $1 - c_0^2$), amplitude-based diagnostics (e.g., T_1 , D_1 , and D_2). In this work, we aim to develop more general correlation metrics using natural orbital occupation numbers. In addition, our goal is to apply these correlation metrics to various molecular systems in order to explore the connections among these correlation metrics.

4.2 Methodology

As defined by the International Union of Pure and Applied Chemistry (IUPAC), an extensive quantity is characterized by its magnitude being additive across subsystems (e.g., mass, volume, Gibbs energy). In contrast, an intensive quantity indicates that its magnitude is independent of the system’s extent (e.g., density, temperature, chemical potential) [367]. In this context, the terminology “intensive property” is identical to a size-intensive property. Here, “size” refers to its dependence on the number of electrons of a system, denoted as N . If a quantity denoted as Q is N -size-extensive, then it satisfies that $Q(n \cdot U) = n \cdot Q(U)$, where n represents the number of system units and U denotes one system unit. Consequently, normalizing the quantity $\overline{Q} = Q/N$ to transform it into a size-intensive quantity, becomes straightforward as the system is replicated with the addition of N electrons each time. The size-intensive property is important for MR diagnostic, applying a cutoff of an MR diagnostic is meaningful only if the diagnostic itself is size intensive. Otherwise, if the diagnostic values vary with the size of the system, it is not appropriate to use cutoffs to determine the MR character across different systems.

In this work, we suggest several approaches to transform certain size-extensive natural orbital-based indices into size-intensive ones. Martin *et al.* [34] pointed out that I_D and I_{ND} indices are size extensive but not size intensive. Particularly, the values of the original I_D in Eq. (3.108) and I_{ND} in Eq. (3.109) show linear growth as the molecular units are replicated. As illustrated in Fig. 4.2, the values of both I_D and I_{ND} of hydrogen chain and polyacetylene (PA) chain molecules scale linearly with the total number of electrons N , thus it reflects N -fold increases. In addition, the formulations of I_D and I_{ND} both require summation across all natural orbital contributions. These indices should always depend on the basis set size despite that this dependency is relatively mild.

Hence, to address this size-intensive property concern, one can normalize I_D and I_{ND} using the number of electrons. We suggest employing a normalization factor calculated as half of the total number of electrons, denoted as $N/2$. This normalization (i.e., original I_D and I_{ND} divided by $N/2$) confines the range of $\overline{I_{ND}}$ to $[0, 1]$, while $\overline{I_D}$ still extends to $[0, \infty)$. Then it yields two averaged quantities: $\overline{I_D}$ and $\overline{I_{ND}}$,

$$\overline{I_D} \equiv \frac{2I_D}{N} = \frac{1}{N} \left(\frac{1}{2} \sum_{\sigma,i} [n_i^\sigma (1 - n_i^\sigma)]^{\frac{1}{2}} - \sum_{\sigma,i} n_i^\sigma (1 - n_i^\sigma) \right), \quad (4.1)$$

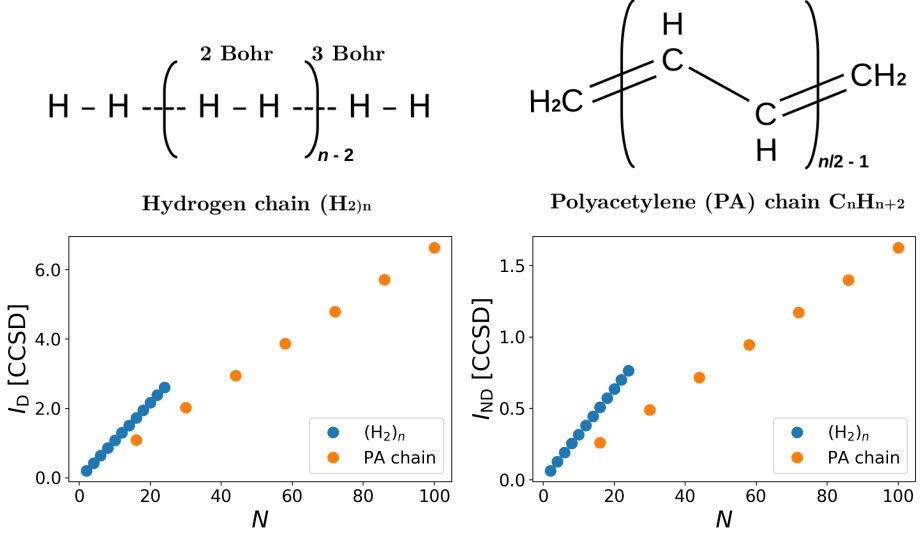


FIGURE 4.2: Top: Hydrogen chain and polyacetylene (PA) chain structures; Bottom: original I_D (left) and I_{ND} (right) for CCSD against total number of electrons N .

$$\overline{I_{ND}} \equiv \frac{2I_{ND}}{N} = \frac{1}{N} \sum_{\sigma,i} n_i^\sigma (1 - n_i^\sigma), \quad (4.2)$$

where n_i^σ is the occupation of the spin-natural orbital i with spin σ . We note that the difference between actual $\overline{I_{ND}}$ and $\bar{V}$ index of Bartlett *et al.* [257] is that $\overline{I_{ND}}$ is calculated by summing over all the natural orbital contributions, while $\bar{V}$ is obtained by either using occupied or virtual orbitals. $\overline{I_{ND}}$ computed from occupied and virtual orbitals are approximately equal for closed-shell molecules in CCSD calculations [257]. Thereby, we should have the following relation $\overline{I_{ND}} \approx 2\bar{V}$ for closed-shell molecules.

On the other hand, instead of considering the contribution from all the natural orbitals to calculate I_{ND} , alternatively, one can also employ the maximum value of $n_i^\sigma (1 - n_i^\sigma)$ as a new MR index, $I_{ND}^{\max}$, which indicates the nondynamic correlation of a system reflected by the orbital which is maximally correlated,

$$I_{ND}^{\max} = \max_{\sigma,i} \{n_i^\sigma (1 - n_i^\sigma)\}. \quad (4.3)$$

The quantity $I_{ND}^{\max}$ is size intensive, as it is obtained from a single spin-natural orbital occupation number ($0 \leq n_i^\sigma \leq 1$). The lower bound of $I_{ND}^{\max}$ is zero when n_i^σ is either 0 or 1, while the upper bound is 0.25, observed at $n_i^\sigma = 0.5$, which

corresponds to the maximum nondynamic correlation. Generally, a higher value of $I_{\text{ND}}^{\text{max}}$ indicates a stronger manifestation of MR character, and $I_{\text{ND}}^{\text{max}}$ can showcase the maximum effect of a particular orbital that impacts significantly the MR character.

In addition to the asymmetric correlation entropy S_{corr} , which was introduced previously, we also consider a symmetric entropy proposed by Shannon [274] in 1948 as part of his information theory. We adopt this formulation written in terms of $\{n_i^\sigma\}$, and normalize it by the total number of electrons N in the molecular system being studied.

$$S_{\text{sym}} = -\frac{1}{2N} \sum_{\sigma,i} [n_i^\sigma \ln(n_i^\sigma) + (1 - n_i^\sigma) \ln(1 - n_i^\sigma)]. \quad (4.4)$$

In Fig. 4.1, the distribution of scaled symmetric Shannon entropy is observed to closely resemble the distribution of I_{ND} for a closed-shell two-electron and two-orbital model system. Hence, they are expected to show noticeable similarities.

In a manner analogous to I_{D} , which serves as an indicator for dynamic correlation, we introduce an additional indicator, S_{J} , using the ansatz S_{J}^{MS} . In fact, this newly proposed indicator is based on Jaynes entropy which is a well-known concept from statistical mechanics and information theory [275, 276]. The Jaynes entropy (also known as “maximum entropy”) is commonly applied to find a probability distribution maximizing the entropy under given constraints. The prevalent formula is represented as $S_{\text{Jaynes}} = -\sum_i p_i \ln p_i$, where p_i stands for the probability distribution. In the context of NO occupation numbers, the behavior of n_i^σ tending toward 0 or 1 is revealed in relation to dynamic correlation, while approaching 0.5 is indicative of nondynamic correlation, and this can serve as a well-established constraint. Then we utilize the probability term “ $p_i = 4n_i^\sigma(1 - n_i^\sigma)$ ” in the Jaynes entropy formulation, where the factor of “4” guarantees that the maximum value of p_i is one. Upon summing over all spin-natural orbital contributions and being normalized by the total number of electrons N , this yields a new natural orbital-based correlation index,

$$S_{\text{J}} = -\frac{4}{N} \sum_{\sigma,i} n_i^\sigma(1 - n_i^\sigma) \ln[4n_i^\sigma(1 - n_i^\sigma)]. \quad (4.5)$$

Moreover, S_{J} is expected to indicate dynamic correlation when considering its resemblance in curve shape to I_{D} as a function of n_i^σ for the two-electron and two-orbital closed-shell model system (see scaled I_{D}^{MS} and S_{J}^{MS} curves in Fig. 4.1).

In addition, Cioslowski [246] mentioned that c_0 is not a size-extensive quantity and that only systems with the same number of electrons can be compared.

Hence, we normalize $1 - c_0^2$ diagnostic (especially for CISD) by the total number of electrons, yielding $(1 - c_0^2)/N$, which is expected to be size intensive. Alternatively, our group had recently suggested another normalization approach for $1 - c_0^2$ based on the problem of an infinite number of non-interacting atoms.¹

$$1 - c_0^2 \rightarrow 1 - c_0^{2/N}, \quad (4.6)$$

where c_0 is the reference configuration coefficient in CISD/CASSCF methods. We note that the absolute value of c_0 is required in [Eq. \(4.6\)](#). Within the normalization factor, N denotes the total number of electrons of the molecule being considered.

¹For a CI wave function expansion in systems dominated by dynamic correlation, the reference (HF) coefficient $c_0 \approx 1$. The rigorous condition for the normalization of the reference CI coefficient should be satisfied is that $|c_0|^{1/N} \approx 1$ for dynamic correlation predominant systems. Particularly, for non-interacting systems predominated by dynamic correlation (e.g., an infinite number of non-interacting helium atoms), this normalization approach in [Eq. \(4.6\)](#) prevents the $c_0^{2/N}$ term from vanishing [[3](#), [13](#), [255](#)].

4.3 Computational Details

All CISD, CCSD, and CCSD(T) calculations and geometry optimization processes were carried out by using an open-source quantum chemistry program, Psi4 [368–370], and all MP2 calculations were carried out with another open-source quantum chemistry package, PySCF [371, 372]. The molecular geometries and basis sets are listed as follows:

- 16 molecular systems with a total of 18 electrons [373], Ar, C₂H₆, CH₃F, CH₃NH₂, F₂, H₂O₂, H₂S, HCl, HOF, HOOH, Methanol, N₂H₄, NH₂F, PH₃, NH₂OH, SiH₄. The geometries were optimized at the MP2/6-31G* level [374–376], and the calculations of CISD/6-311G [377] were performed through Psi4. In addition, the Selected Configuration Interaction (SCI) method [378, 379] with 6-311G basis set was also employed using PySCF, and the SCI techniques can achieve nearly FCI solution for these small molecules.
- 7 small diatomic molecules at the equilibrium distance (R_e) and stretched geometry ($1.5R_e$) that have been studied by Handy *et al.* [11] and in the original I_D and I_{ND} article [13]. cc-pVTZ basis set [380] was employed.
- 34 small molecules of Nielsen and Janssen [1] from which they defined the D_1 and D_2 diagnostics for MP2 and CCSD, the geometries of these molecules were optimized by MP2 or CCSD with cc-pVTZ basis set [380]. This set is also referred to as the NJ34 dataset.

All the calculations of closed-shell molecules were done using restricted Hartree Fock (RHF) reference, with the frozen core option in post-HF methods (except for the 18-electron systems), and the energy convergence threshold was set to 10^{-8} a.u. In addition, we utilized our in-house Python3 program for the computation of all the natural orbital-based indices, as well as the D_1 and D_2 diagnostics of MP2. The program makes use of several libraries, including Numpy [381], Scipy [382], Pandas [383, 384], and Matplotlib [385]. Moreover, the Matplotlib library was employed for generating all the graphs in this chapter.

Since some approximate wave function methods like MP2, CISD, and CCSD methods do not satisfy the Hellmann-Feynman theorem [330, 331], their density matrices can be constructed in two manners: the unrelaxed density refers to the density obtained from the expectation value, while the relaxed density takes into account orbital relaxation and results from the energy derivative [139, 386]. Although the NO occupation numbers can be obtained from either unrelaxed or relaxed density matrices for these post-HF methods mentioned above, it should

be noted that the relaxed density is not always N -representable. This means that the occupation numbers of the natural orbitals can sometimes exceed one or even become negative [273, 387], which can lead to inappropriate evaluations of certain natural orbital-based MR indices that involve operations such as square roots or logarithms, for example, I_D^{MS} and $S_{\text{corr}}^{\text{MS}}$. To avoid these unphysical occupation numbers, we primarily used the unrelaxed density in most of the calculations presented in current chapter.

For the calculations involving unrelaxed densities, we utilized the PySCF package to compute the unrelaxed MP2 density matrices, neglecting SCF orbital relaxation. Additionally, the unrelaxed CISD or CCSD densities were evaluated using the Psi4 software. On the other hand, for the purpose of investigating some specific instances across the NJ34 dataset, we also evaluated the relaxed densities involving MP2 and CCSD calculations using Gaussian16 [388].

In the end, a complete set of correlation measures considered in this study is presented in Tab. 4.1. According to their statistical properties, these diagnostics are classified into five distinct groups: maximum (including minimum), average, ratio, and among other metrics.

TABLE 4.1: List of electron correlation measures used in the study.

Category	Correlation Metrics
Maximum	D_1 [244] and D_2 [1], n_H and n_L [32] $I_{\text{ND}}^{\text{max}}$ [389], NON [257], M_{diag} [29], $1 - c_0^2$ [253]
Average	T_1 [25], $\overline{I_D}$ and $\overline{I_{\text{ND}}}$ [13, 389], XEN [257] S_{corr} [27, 28], S_{sym} and S_J [390]
Ratio	r_{ND} [13, 34]
Other metrics	I_D and I_{ND} [13], MRI and $-\log(I)$ [257] $1 - c_0^{N/2}$ [3], $(1 - c_0^2)/N$ [389]

4.4 Results and Discussion

4.4.1 A Priori Analysis of Correlation Metrics

In this section, we present a priori analyses to explore the connections between various correlation metrics, with the goal of gaining initial insights into their relationships. Above all, among the correlation metrics based on CCSD, previous studies by Lee and Jiang *et al.* [26, 253] have reported a linear relationship between T_1 and D_1 . In the view of statistics, the average and maximum quantities can be correlated when they capture related aspects of the behavior of a system. For instance, in the context of correlation metrics, T_1 represents an average measure of the electron correlation contributed by the single-substitution amplitudes, while D_1 measure relies on the largest singular value of two square matrices constructed by the single-substitution amplitudes. The correlation between these two quantities indicates that the overall contribution and the maximum contribution from the single-substitution amplitudes are connected. Similarly, Martin *et al.* [33, 34] have observed correlations between the original I_{ND} and S_{corr} (without normalization), despite that they are not size-intensive quantities.

Among the average quantities, we expect a correlation, for instance, between $\overline{I_{\text{ND}}}$ and S_{corr} , S_{sym} , and XEN. The normalization approach used for $\overline{I_{\text{ND}}}$ and S_{corr} , which involves dividing by the total number of electrons N , does not affect their linear correlation. Thus, $\overline{I_{\text{ND}}}$ and S_{corr} should be still correlated. Furthermore, the linear correlation between $\overline{I_{\text{ND}}}$ and S_{sym} can be anticipated due to their similar curves against n_i^σ , as demonstrated in Fig. 4.1 for the closed-shell two-electron and two-orbital model system. Additionally, both XEN and $\overline{I_{\text{ND}}}$ can be expressed in terms of contributions from occupied and virtual orbitals,²

$$\text{XEN} = \frac{1}{N} \sum_{\sigma,i}^{\text{vir}} n_i^\sigma = 1 - \frac{1}{N} \sum_{\sigma,i}^{\text{occ}} n_i^\sigma, \quad (4.7)$$

$$\overline{I_{\text{ND}}} = \frac{1}{N} \sum_{\sigma,i}^{\text{occ}} n_i^\sigma (1 - n_i^\sigma) + \frac{1}{N} \sum_{\sigma,i}^{\text{vir}} n_i^\sigma (1 - n_i^\sigma). \quad (4.8)$$

and, as other authors have found, [257] we have heuristically identified that the contributions to $\overline{I_{\text{ND}}}$ from occupied and virtual natural orbitals are approximately equivalent (see Fig. A4 in Appendix A.3). Thus

$$\frac{1}{N} \sum_{\sigma,i}^{\text{occ}} n_i^\sigma (1 - n_i^\sigma) \approx \frac{1}{N} \sum_{\sigma,i}^{\text{vir}} n_i^\sigma (1 - n_i^\sigma). \quad (4.9)$$

²This thesis only focuses on closed-shell systems, the term “occupied (occ)” corresponds to the N highest occupied spin-natural orbitals with respect to the occupation numbers, and “virtual (vir)” corresponds to the rest spin-natural orbitals.

Hence, $\overline{I_{\text{ND}}}$ can be approximately written as

$$\begin{aligned}\overline{I_{\text{ND}}} &\approx \frac{2}{N} \sum_{\sigma,i}^{\text{vir}} n_i^\sigma (1 - n_i^\sigma) \\ &\approx 2\text{XEN} - \frac{2}{N} \sum_{\sigma,i}^{\text{vir}} |n_i^\sigma|^2 \\ &\approx 2\text{XEN},\end{aligned}\tag{4.10}$$

where the term $\frac{2}{N} \sum_{\sigma,i}^{\text{vir}} |n_i^\sigma|^2$ is usually significantly smaller than 2XEN . Particularly, it is commonly observed in the SR regime where n_i^σ approaches 0 or 1. Thus, $\overline{I_{\text{ND}}}$ is considered to be identical to 2XEN .

With respect to the maximum quantities, we anticipate a linear correlation between $I_{\text{ND}}^{\text{max}}$ and n_H , n_L , and NON . For closed-shell molecules computed using correlated wavefunction methods with an RHF reference, n_H and n_L are identified as the lowest and highest eigenvalues among the first $N/2$ and the remaining spin-natural orbitals (sorted in descending order), respectively.

$$n_H = 2 \min_{i \leq N/2} \{n_i^\sigma\},\tag{4.11}$$

$$n_L = 2 \max_{i > N/2} \{n_i^\sigma\},\tag{4.12}$$

then $I_{\text{ND}}^{\text{max}}$ is evidently contributed by either n_H or n_L ,

$$I_{\text{ND}}^{\text{max}} = \max \left\{ \frac{n_H}{2} \left(1 - \frac{n_H}{2}\right), \frac{n_L}{2} \left(1 - \frac{n_L}{2}\right) \right\}.\tag{4.13}$$

In the following, we will provide analytical descriptions of the observed linear correlations among these average quantities and maximum quantities, including $(1 - c_0^2)/N$ and $\overline{I_{\text{ND}}}$, as well as $1 - c_0^{2/N}$ and $\overline{I_{\text{ND}}}$ obtained from CISD calculations; $I_{\text{ND}}^{\text{max}}$ and D_2 obtained from MP2 and CCSD calculations.

(1) Connections between $(1 - c_0^2)/N$, $1 - c_0^{2/N}$, and $\overline{I_{\text{ND}}}$

We present an analytical explanation for the connection between $(1 - c_0^2)/N$, $1 - c_0^{2/N}$, and $\overline{I_{\text{ND}}}$ for CI methods. To begin with, the CI wavefunction of an N -electron system is given by

$$\Psi(1, \dots, N) = \sum_i c_i \Phi_i(1, \dots, N),\tag{4.14}$$

where c_i are the expansion coefficients c_0 being the one associated with the Hartree-Fock (HF) Slater determinant and assumed to be the dominant one. The Slater determinant $\Phi_i(1, 2, 3, \dots, N)$ are constructed from HF orbitals.

The trace of the CI density matrix in the MO basis, denoted as $\text{Tr}({}^1\mathbf{D})$, the sum of CI coefficient square multiplied by N , and the sum of NO occupation numbers are identical to N ,

$$\begin{aligned}
 \text{Tr}({}^1\mathbf{D}) &= N \int \cdots \int |\Psi(1, \dots, N)|^2 d1 \dots dN \\
 &= N \sum_i c_i^2 \\
 &= \sum_i n_i \\
 &= N.
 \end{aligned} \tag{4.15}$$

Moreover, $\text{Tr}({}^1\mathbf{D})$ can be computed by summing the contributions from both occupied and virtual orbitals,

$$\text{Tr}({}^1\mathbf{D}) = \text{Tr}({}^1\mathbf{D}^{\text{occ}}) + \text{Tr}({}^1\mathbf{D}^{\text{vir}}), \tag{4.16}$$

and in terms of matrix element form, and it can be evaluated using diagonal elements ${}^1D_{ii}$ and ${}^1D_{aa}$.

For the wavefunction of CISD, which only involves the ground state, single, and double excitations, the sum of CI coefficients read as

$$\begin{aligned}
 \sum_i c_i^2 &= c_0^2 + c_S^2 + c_D^2 \\
 &= c_0^2 + \sum_{ia} |c_i^a|^2 + \sum_{ijab} |c_{ij}^{ab}|^2 \\
 &= 1,
 \end{aligned} \tag{4.17}$$

where c_0^2 contributes to N occupied (spin) orbitals, $c_S^2 \equiv |c_i^a|^2$ contributes to $N - 1$ occupied orbitals (all except i) and one virtual orbital (a), $c_D^2 \equiv |c_{ij}^{ab}|^2$ contributes to $N - 2$ occupied orbitals (all except i, j) and two virtual orbitals (a, b).

Hence, $\text{Tr}({}^1\mathbf{D}^{\text{occ}})$ and $\text{Tr}({}^1\mathbf{D}^{\text{vir}})$ in [Eq. \(4.16\)](#) can be rewritten as

$$\text{Tr}({}^1\mathbf{D}^{\text{occ}}) = N c_0^2 + (N - 1) c_S^2 + (N - 2) c_D^2, \tag{4.18}$$

$$\begin{aligned}
 \text{Tr}({}^1\mathbf{D}^{\text{vir}}) &= N - \text{Tr}({}^1\mathbf{D}^{\text{occ}}) \\
 &= c_S^2 + 2c_D^2 \\
 &= 2(1 - c_0^2) - c_S^2,
 \end{aligned} \tag{4.19}$$

The NO occupation numbers $\{n_i\}$ are determined through the diagonalization of ${}^1\mathbf{D}$. It is assumed that the diagonal elements of ${}^1\mathbf{D}$ play a more significant role in generating n_i than the off-diagonal elements, and the impact of transforming

from MO to NO basis is neglected. If the term c_S^2 in both $\text{Tr}({}^1\mathbf{D}^{\text{occ}})$ and $\text{Tr}({}^1\mathbf{D}^{\text{vir}})$, as shown in Eq. (4.19), is sufficiently small to be disregarded, then

$$\text{Tr}({}^1\mathbf{D}^{\text{occ}}) \approx \sum_i^{\text{occ}} n_i \equiv \sum_{\sigma,i}^{\text{occ}} n_i^\sigma, \quad (4.20)$$

$$\text{Tr}({}^1\mathbf{D}^{\text{vir}}) \approx \sum_i^{\text{vir}} n_i \equiv \sum_{\sigma,i}^{\text{vir}} n_i^\sigma. \quad (4.21)$$

The derivation of the above approximations is supplied in Appendix A.1. By combining Eq. (4.19) and Eq. (4.21), one obtains

$$\sum_i^{\text{vir}} n_i \approx 2(1 - c_0)^2. \quad (4.22)$$

Then, by using the approximate relationship in Eq. (4.10), one attains

$$\overline{I_{\text{ND}}} \approx 2\text{XEN} \approx \frac{4(1 - c_0)^2}{N}. \quad (4.23)$$

Additionally, we have the option to expand the normalized indicator $1 - c_0^{2/N}$, in Eq. (4.6), through the Taylor series around the point where $1 - c_0^2 \rightarrow 0$,

$$1 - c_0^{2/N} = \frac{(1 - c_0^2)}{N} + \frac{(N - 1)(1 - c_0^2)^2}{2N^2} + \mathcal{O}((1 - c_0^2)^3). \quad (4.24)$$

Assuming that $1 - c_0^2 \approx 0$, the leading term of Eq. (4.24) is significantly larger than the second leading term. The leading term is identified as $(1 - c_0^2)/N$. It implies that the two normalization approaches (i.e., $(1 - c_0^2)/N$ and $1 - c_0^{2/N}$) yield almost identical results when $1 - c_0^2 \approx 0$. Consequently, our analytical interpretation based on non-strongly-correlated systems, suggests that c_0 -based correlation metrics are linked to $\overline{I_{\text{ND}}}$. And with appropriate normalization, it can serve as a reliable correlation measure. However, the use of $\overline{I_{\text{ND}}}$ is recommended over c_0 as it is not limited to CI methods involving CI expansions.

(2) Connection Between $I_{\text{ND}}^{\text{max}}$ and D_2 Diagnostic

For a closed-shell molecule, the unrelaxed electron density from MP2 in terms of HF canonical orbitals [391], denoted as ${}^1\mathbf{D}$ (or in matrix element form as ${}^1D_{pq}^{\text{MP2}}$), can be written as

$${}^1D_{pq}^{\text{MP2}} = {}^1D_{pq}^{\text{RHF}} + {}^1D_{pq}^{\text{corr}}, \quad (4.25)$$

$${}^1D_{ij}^{\text{RHF}} = 2\delta_{ij}, \quad (4.26)$$

$${}^1D_{ij}^{\text{corr}} = - \sum_{abk} t_{jk}^{ab} (4t_{ik}^{ab} - 2t_{ik}^{ba}), \quad (4.27)$$

$${}^1D_{ab}^{\text{corr}} = \sum_{ijc} t_{ij}^{bc} (4t_{ij}^{ac} - 2t_{ij}^{ca}), \quad (4.28)$$

$${}^1D_{ia}^{\text{corr}} = {}^1D_{ai}^{\text{corr}} = 0, \quad (4.29)$$

where the subscripts p, q denote arbitrary molecular orbital indices, i, j are the occupied ones at the HF level and a, b are virtual ones. The double-substitution amplitudes, shown in Eq. (3.101), are represented only in terms of $(ia|jb)$ integrals and corresponding orbital energies. The NO occupation numbers $\{n_i\}$ are routinely derived by diagonalizing the entire ${}^1\mathbf{D}$. However, in the case of MP2 using HF canonical orbitals, the single-substitution amplitudes vanish, $t_i^a = 0$, thus the elements in the occupied-virtual (ov) or virtual-occupied (vo) blocks of the unrelaxed ${}^1\mathbf{D}$ are zero. Consequently, the NO occupation numbers, $\{n_i\}$, from MP2 calculations can be determined by separately diagonalizing the occupied-occupied (oo) and virtual-virtual (vv) blocks within the unrelaxed ${}^1\mathbf{D}$ (see Appendix A.1).

For convenience, we use ${}^1\mathbf{D}_o$ to represent the combined matrix of D_{ij}^{corr} and ${}^1D_{ij}^{\text{RHF}}$, and ${}^1\mathbf{D}_v$ to represent the matrix D_{ab}^{corr} . Then, the minimum occupation number of occupied orbitals (n_H) and the maximum occupation number of virtual orbitals (n_L) can be evaluated by

$$n_H = \lambda_{\min}({}^1\mathbf{D}_o), \quad (4.30)$$

$$n_L = \lambda_{\max}({}^1\mathbf{D}_v), \quad (4.31)$$

where $\lambda_{\min}$ denotes the smallest eigenvalue of the matrix ${}^1\mathbf{D}_o$, and $\lambda_{\max}$ denotes the largest eigenvalue of the matrix ${}^1\mathbf{D}_v$.

On the other hand, the D_2 diagnostic, defined in Eq. (3.98), can be rewritten as [392, 393]

$$\begin{aligned} D_2 &= \max\{D_2^o, D_2^v\} \\ &= \max\left\{\sqrt{\lambda_{\max}(\mathbf{M}^T\mathbf{M})}, \sqrt{\lambda_{\max}(\mathbf{N}^T\mathbf{N})}\right\}, \end{aligned} \quad (4.32)$$

where the matrix $\mathbf{M}$ and $\mathbf{N}$ are represented by

$$\mathbf{M} = \sum_{abk} t_{ik}^{ab} t_{jk}^{ab}, \quad (4.33)$$

$$\mathbf{N} = \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc}. \quad (4.34)$$

We note that D_2^o in Eq. (4.32) stands for 2-norm of $\mathbf{T}^o$, and D_2^v for 2-norm of $\mathbf{T}^v$ in Eq. (3.98) presented in Chapter 3. The double-substitution amplitudes t_{ij}^{ab} , shown in Eq. (3.101), are formed using only $(ia|jb)/(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$ terms as Nielsen and Janssen did [1].

As Beran and Head-Gordon mentioned in a previous study [394], the 1-RDM can be approximately generated by t_{ij}^{ab} amplitudes that are transformed from $ov \times ov$ matrix to $o \times ov^2$ or $v \times o^2v$ matrices, as was used in the design of D_2 diagnostic. The occupation numbers $\{n_i\}$ obtained through this approach might be easier to interpret despite the deficiencies for describing pair- or higher-order correlations. In order to examine the theoretical reason behind the connection between D_2 and $I_{\text{ND}}^{\text{max}}$, we approximate the unrelaxed ${}^1\mathbf{D}$ by eliminating all the $t_{jk}^{ab} t_{ik}^{ba}$ and $t_{ij}^{bc} t_{ij}^{ca}$ terms,

$$\widetilde{{}^1\mathbf{D}}_{ij}^{\text{corr}} = -4 \sum_{abk} t_{ik}^{ab} t_{jk}^{ab}, \quad (4.35)$$

$$\widetilde{{}^1\mathbf{D}}_{ab}^{\text{corr}} = 4 \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc}. \quad (4.36)$$

Similarly, we use $\widetilde{{}^1\mathbf{D}}_o$ to denote the combined matrix of $\widetilde{\mathbf{D}}_{ij}^{\text{corr}}$ and ${}^1\mathbf{D}_{ij}^{\text{RHF}}$, and $\widetilde{{}^1\mathbf{D}}_v$ to represent the matrix $\widetilde{\mathbf{D}}_{ab}^{\text{corr}}$. Then the approximate $\tilde{n}_H$ and $\tilde{n}_L$ can be expressed in terms of D_2^o and D_2^v , respectively.

$$\tilde{n}_H = \lambda_{\min}(\widetilde{{}^1\mathbf{D}}_o) = 2 - 4(D_2^o)^2, \quad (4.37)$$

$$\tilde{n}_L = \lambda_{\max}(\widetilde{{}^1\mathbf{D}}_v) = 4(D_2^v)^2. \quad (4.38)$$

Thus following the definition of $I_{\text{ND}}^{\text{max}}$ in Eq. (4.13), one can reach an approximate $\widetilde{I}_{\text{ND}}^{\text{max}}$ which is directly connected to D_2 ,

$$\lim_{D_2 \rightarrow 0} I_{\text{ND}}^{\text{max}} = \widetilde{I}_{\text{ND}}^{\text{max}} = D_2^2(2 - 4D_2^2). \quad (4.39)$$

We note that $\widetilde{I}_{\text{ND}}^{\text{max}} \rightarrow I_{\text{ND}}^{\text{max}}$ for an unrelaxed MP2 electron density including corrections up to second-order in which we have neglected some small terms. In practice, the latter terms contribute to the electron density and thus affect the value of natural occupation numbers.

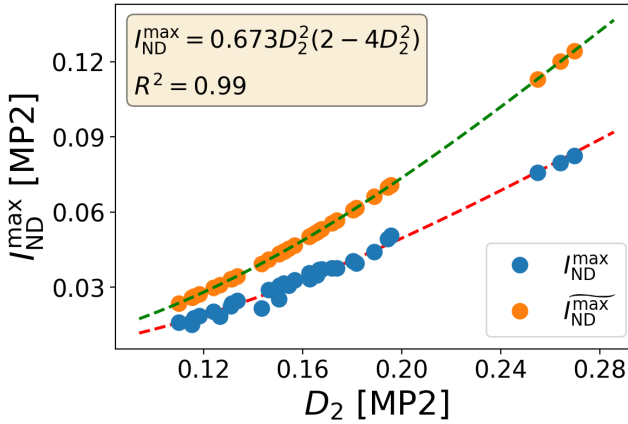


FIGURE 4.3: D_2 diagnostic against $I_{\text{ND}}^{\text{max}}$ and $\widetilde{I}_{\text{ND}}^{\text{max}}$ for the NJ34 dataset [1] calculated at the MP2/cc-pVTZ level of theory.

Based on the NJ34 dataset of Nielsen and Janssen [1] calculated at the MP2 level, we examine the relationships between approximate $\widetilde{I}_{\text{ND}}^{\text{max}}$ and $I_{\text{ND}}^{\text{max}}$, as shown in Tab. A1 and plotted in Fig. 4.3. The plots of $\widetilde{n}_H$ and n_H , $\widetilde{n}_L$ and n_L are shown in Fig. A1 in Appendix A.3, and we can see that $\widetilde{n}_H \leq n_H$, $\widetilde{n}_L \geq n_L$, $\widetilde{I}_{\text{ND}}^{\text{max}} \geq I_{\text{ND}}^{\text{max}}$ (more details see Appendix A.2). Furthermore, it has been observed that the impact of terms like $t_{jk}^{ab}t_{ik}^{ba}$ and $t_{ij}^{bc}t_{ij}^{ca}$ on generating of NO occupation numbers is relatively small in the SR regime, while it turns to be more significant in the MR regime. As illustrated in Fig. 4.3, we examined the approximate connection described in Eq. (4.39), and found a proportionally fitted connection between $I_{\text{ND}}^{\text{max}}$ and D_2 , which tends to evolve into a more linear relationship.

In addition, for the NJ34 dataset, we also investigated the natural orbital-based indices obtained from the relaxed density matrix. In general, the values of $I_{\text{ND}}^{\text{max}}$ obtained from relaxed density (computed at the MP2 or CCSD level) are almost all identical to the ones from unrelaxed density as shown in Fig. A2 (in Appendix A.3), except two significant outliers (i.e., O_3 and CN^+) from the MP2 results. Both molecules are considered to be in strong MR character regime. Tab. A4 (in Appendix A.3) shows the natural orbital occupation number and $I_{\text{ND}}^{\text{max}}$ of these two molecules calculated at the MP2 level. The n_L which contributes to $I_{\text{ND}}^{\text{max}}$ for O_3 molecule from relaxed density is remarkably less than the one from unrelaxed density, while the n_H which contributes to $I_{\text{ND}}^{\text{max}}$ for CN^+ molecule from relaxed density is obviously greater than the one from unrelaxed density. Thus, $I_{\text{ND}}^{\text{max}}$ calculated from unrelaxed and relaxed densities are usually the same except for some particular MR cases. If the primary concern is the connection

between $I_{\text{ND}}^{\text{max}}$ and D_2 in [Eq. \(4.39\)](#), it is necessary to take into account the situation where a significant distinction arises between unrelaxed and relaxed densities, particularly in certain nondynamic correlation regimes. However, if the focus is only on using the cutoffs of $I_{\text{ND}}^{\text{max}}$ as MR diagnostic (will be addressed in [Chapter 5](#)), then calculating $I_{\text{ND}}^{\text{max}}$ with a relaxed density is suitable as well.

4.4.2 Statistical Assessment of Correlation Metrics

(1) Analysis of a Collection of 18-Electron Systems

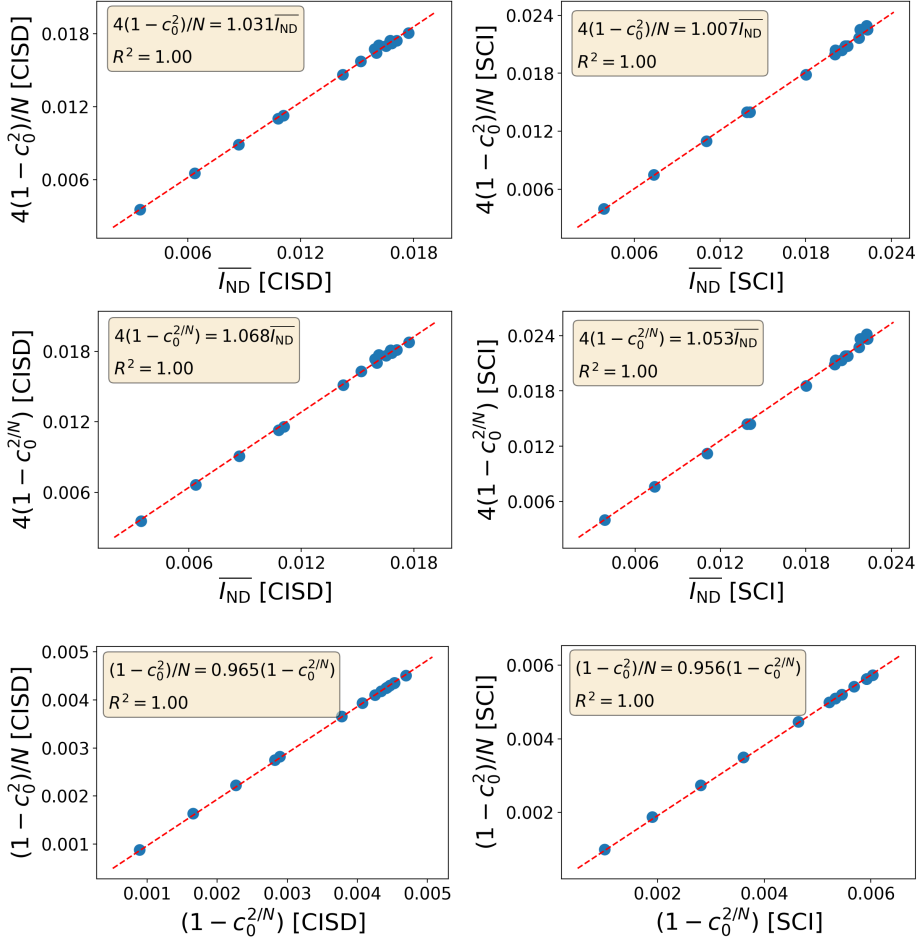


FIGURE 4.4: Linear relationships between $\overline{I_{ND}}$ and $4(1 - c_0^2)/N$ as well as $4(1 - c_0^{2/N})$ from CISC and Selected Configuration Interaction (SCI) calculations.

The N -dependence impact on the linear relationship (i.e., $4(1 - c_0^2)/N$, $4(1 - c_0^{2/N})$, and $\overline{I_{ND}}$ for CI methods) will be examined by a collection of 18-electron systems. The idea is inspired by the work of Gill *et al.* [373], where they quantified the MR character using the D_1 diagnostic from CCSD/6-311G calculations for each of these 18-electron systems. They also showed a linear relationship between

the correlation energy error predicted by the intracule functional model and the D_1 diagnostic. Furthermore, Cioslowski [246] pointed out that c_0 is not a size-extensive quantity and that only the systems with the same number of electrons can be compared. Hence, by considering these molecules with 18 electrons, we ensure a consistent comparison of systems with the same number of electrons. This comparison addresses the issue of N -dependence, which could probably affect the linear relationships in our a priori analysis.

Fig. 4.4 shows evident linear relationships between $\overline{I_{ND}}$ and $4(1 - c_0^2)/N$ as well as $4(1 - c_0^{2/N})$ from CISD and Selected Configuration Interaction (SCI) calculations. When fitting $\overline{I_{ND}}$ against $4(1 - c_0^2)/N$, both CISD and SCI data yielded similar slopes of approximately 1.0. This result is consistent with the approximate relationship established in Eq. (4.23). Moreover, it reveals that the result from the SCI solution, which incorporates higher-order excitations than singles and doubles, aligns more closely with the approximate relationship outlined in Eq. (4.23) for these 18-electron systems.

However, we also note a more noticeable difference in the linear fitting functions between the $4(1 - c_0^{2/N})$ term and $\overline{I_{ND}}$ for CISD and SCI calculations. This notable discrepancy in the linear fitting between $4(1 - c_0^{2/N})$ and $\overline{I_{ND}}$ for CISD and SCI data can be attributed to the larger values of $4(1 - c_0^{2/N})$ and is related to the higher-order expansion of $4(1 - c_0^{2/N})$. Therefore, the concern regarding the affect of N -dependence on the linear relationships for CI methods (i.e., between $4(1 - c_0^2)/N$, $4(1 - c_0^{2/N})$, and $\overline{I_{ND}}$) can be eliminated.

(2) Diatomic Molecule Dissociation

To assess these correlation metrics, we first review 7 small diatomic molecules at the equilibrium distance (R_e) and stretched geometry ($1.5R_e$) that have been studied by Handy *et al.* [11] and in the original I_D and I_{ND} article [13]. We carried out CISD and CCSD calculations with the cc-pVTZ basis set.

Tab. 4.2 shows the correlation metrics from CISD/cc-pVTZ. The behaviors of all the correlation metrics exhibit a consistent manner as the nondynamic correlation increases along the stretching of molecules, except the Be_2 which contains strong nondynamic correlation nature even at the ground-state equilibrium distance. As a result, all the correlation metrics of Be_2 exhibit larger values than other molecules. If we examine these molecules at R_e , it is observed that only Be_2 significantly surpasses the threshold of $1 - c_0^2 \leq 0.1$. In contrast, the remaining molecules are categorized as SR based on the values of $1 - c_0^2$, even though Li_2 and N_2 are in close proximity to the cutoff.

TABLE 4.2: CISD/cc-pVTZ, correlation metric values for a series of small diatomic molecules at each ground-state equilibrium R_e and stretched geometry $1.5R_e$ (optimized by CISD/cc-pVTZ) [11, 13].

Mol.	R_e					$1.5R_e$				
	$ c_0 $	$1 - c_0^2$	$1 - c_0^{2N}$	$\overline{I_D}$	$\overline{I_{ND}}$	$I_{ND}^{\max}$	$ c_0 $	$1 - c_0^2$	$1 - c_0^{2N}$	$\overline{I_{ND}}$
Be ₂	0.920	0.154	0.021	0.079	0.071	0.087	0.926	0.143	0.019	0.075
CO	0.956	0.086	0.006	0.083	0.023	0.021	0.920	0.154	0.012	0.089
F ₂	0.957	0.083	0.005	0.079	0.018	0.030	0.917	0.159	0.010	0.078
HF	0.978	0.044	0.004	0.075	0.017	0.014	0.968	0.063	0.006	0.078
Li ₂	0.952	0.094	0.016	0.048	0.058	0.085	0.927	0.141	0.025	0.043
LiH	0.985	0.030	0.008	0.051	0.029	0.029	0.972	0.056	0.014	0.052
N ₂	0.953	0.091	0.007	0.084	0.025	0.025	0.917	0.159	0.012	0.090

TABLE 4.3: CCSD/cc-pVTZ, correlation metric values for a series of small diatomic molecules at each ground-state equilibrium R_e and stretched geometry $1.5R_e$ (optimized by CCSD/cc-pVTZ) [11, 13].

Mol.	R_e					$1.5R_e$				
	T_1	D_1	D_2	$\overline{I_D}$	$\overline{I_{ND}}$	$I_{ND}^{\max}$	T_1	D_1	D_2	$\overline{I_{ND}}$
Be ₂	0.019	0.028	0.321	0.144	0.086	0.085	0.020	0.029	0.318	0.142
CO	0.018	0.039	0.162	0.128	0.030	0.027	0.103	0.214	0.228	0.136
F ₂	0.010	0.027	0.212	0.110	0.024	0.044	0.024	0.082	0.514	0.104
HF	0.007	0.012	0.118	0.114	0.019	0.016	0.016	0.041	0.199	0.120
Li ₂	0.017	0.024	0.321	0.104	0.058	0.085	0.039	0.055	0.398	0.094
LiH	0.010	0.015	0.174	0.118	0.029	0.029	0.037	0.053	0.232	0.122
N ₂	0.013	0.026	0.172	0.130	0.032	0.033	0.032	0.064	0.319	0.138

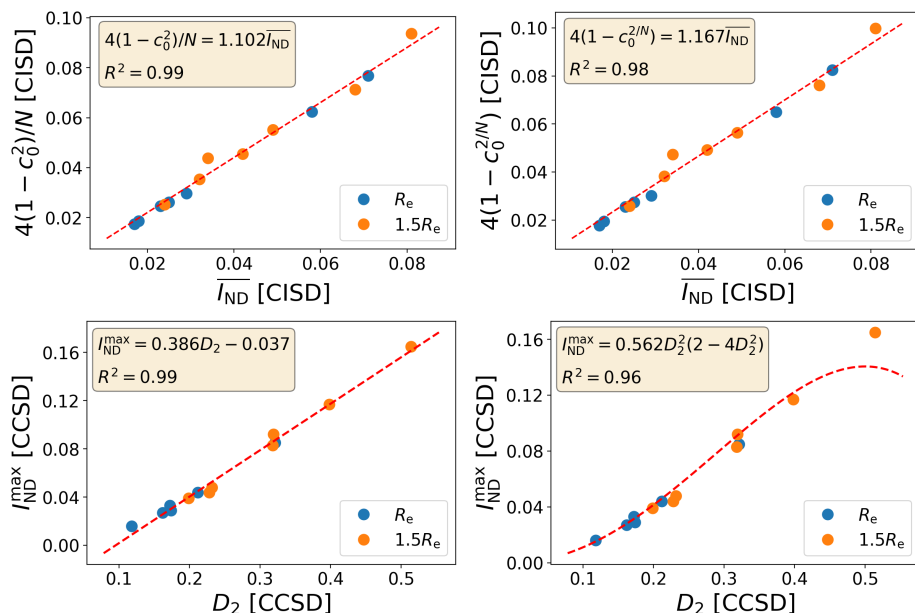


FIGURE 4.5: Relationships between correlation metrics of a series of ground-state small diatomic molecules at the equilibrium distance, R_e , and $1.5R_e$. Top: linear fitting of $\overline{I_{ND}}$ against $4(1 - c_0^2)/N$ (left) and $4(1 - c_0^{2/N})$ (right) calculated at the CISD/cc-pVTZ level. Bottom: linear fitting (left) and quartic fitting (right) of D_2 against $I_{ND}^{\max}$ calculated at the CCSD/cc-pVTZ level.

The correlation metrics obtained from CCSD/cc-pVTZ calculations are shown in [Tab. 4.3](#). With the exception of Be_2 , all the correlation metrics exhibit an increase as the molecules are stretched. At the equilibrium (R_e), the T_1 and D_1 do not meet their MR cutoffs for any molecule, while D_2 indicates MR character for Be_2 , F_2 , and Li_2 . Notably, both $\overline{I_{ND}}$ and $I_{ND}^{\max}$ show large values for Be_2 and Li_2 even at R_e , and $I_{ND}^{\max}$ is relatively large for F_2 . These observations align with the results of CISD, suggesting that these natural orbital-based indices tend to exhibit more agreement with D_2 .

In [Fig. 4.5](#), we display the notable correlation between these correlation metrics: two normalized diagnostics, $4(1 - c_0^2)/N$ and $4(1 - c_0^{2/N})$, along with $\overline{I_{ND}}$ obtained from the CISD calculations; and the D_2 diagnostic in relation to $I_{ND}^{\max}$ calculated at the CCSD level. On one hand, similar to the observations in the analysis of 18-electron systems, the linear relationship between $4(1 - c_0^2)/N$, $4(1 - c_0^{2/N})$, and $\overline{I_{ND}}$ still aligns with our previous a priori analysis and the assessment over

the collection of 18-electron systems. For CISD, both normalization approaches are equivalent in terms of ensuring that $1 - c_0^2$ remains size-intensive. On the other hand, the relationship between D_2 and $I_{\text{ND}}^{\text{max}}$, as established in Eq. (4.39), is not limited to MP2 and can also be extended to CCSD. By utilizing a single proportional parameter to simply scale the relationship in Eq. (4.39), we obtained a notable fitting for the data range ($D_2 \leq 0.4$), as shown in the bottom right plot in Fig. 4.5. Both $I_{\text{ND}}^{\text{max}}$ and D_2 are determined based on maximal values, and when the double-substitution amplitudes play a predominant role in generating the density matrix, their correlation aligns with expectations. This correlation can be represented by either a linear fit ($R^2 = 0.99$) or a proportional quartic function by scaling Eq. (4.39). Although the squared regression coefficient for the quartic fit is marginally lower than the linear one, it can be significantly improved when excluding data points where $D_2 > 0.5$. The quartic fit is particularly advantageous as D_2 approaches zero, as supported by our analytical explanation, and it remains valid within the range of $D_2 \leq 0.4$, while it fails obviously when D_2 approaches 0.5. Further discussion on this matter will be presented in Chapter 5.

The values of $\overline{I_{\text{D}}}$ presented in Tab. 4.2 and Tab. 4.3 exhibit insignificant changes along the stretched geometry. This result aligns with the findings of dynamic correlation energies reported by Handy *et al.* [11]. Moreover, most of the $\overline{I_{\text{D}}}$ values from CISD are close to their corresponding values from CCSD.

(3) Review the 34 Molecules of Nielsen and Janssen

In this study, our objective is to further explore the relationships among various correlation metrics calculated at the MP2 and CCSD levels of theory. This study includes examining relationships within the same categories as well as across different categories, such as amplitude-based and natural orbital-based indices, as well as average-based and maximum-based diagnostics. In this work, we revisit the 34 molecules originally studied by Nielsen and Janssen [1], in which they defined the D_1 and D_2 diagnostics for MP2 and CCSD. This dataset is also referred to as the NJ34 dataset within this study.

Firstly, within the category of amplitude-based diagnostics, there are no apparent linear correlations between single and double-substituted amplitude-based diagnostics. However, we note that T_1 and D_1 derived from CCSD exhibit a relatively consistent trend. Fig. 4.6 reveals that the D_2 diagnostic, $I_{\text{ND}}^{\text{max}}$, n_H , NON, even with $-\log(I)$ retain excellent linear correlations in both MP2 and CCSD calculations. Note that the value of NON (largest occupation number in unoccupied natural orbitals) is equivalent to $n_L/2$ for these closed-shell molecules, so the n_L index is omitted here. $I_{\text{ND}}^{\text{max}}$ arises from either n_H or n_L , thus it contains the information from n_H or n_L . Furthermore, it can be applied to a much broader range of electronic structure methods than D_2 , and it has an easier interpretation than empirical fitted indices like $-\log(I)$ and MRI. Therefore, the $I_{\text{ND}}^{\text{max}}$ index is promising to substitute n_H , n_L , NON, $-\log(I)$, MRI and D_2 , as they are linearly correlated and provide the same information. In addition, detailed data tables of these correlation metrics obtained from MP2 and CCSD calculations are provided in Appendix A.3 (see Tab. A2 and Tab. A3).

TABLE 4.4: Relationships between D_2 and $I_{\text{ND}}^{\text{max}}$ from the NJ34 dataset [1]

Method	Relationship	Fitting Function	Regression R^2
MP2	Linear	$I_{\text{ND}}^{\text{max}} = 0.422D_2 - 0.034$	0.986
	Quartic	$I_{\text{ND}}^{\text{max}} = 0.673D_2^2(2 - 4D_2^2)$	0.990
CCSD	Linear	$I_{\text{ND}}^{\text{max}} = 0.349D_2 - 0.028$	0.990
	Quartic	$I_{\text{ND}}^{\text{max}} = 0.543D_2^2(2 - 4D_2^2)$	0.988

The fittings of the relationship between D_2 and $I_{\text{ND}}^{\text{max}}$ are analogous to the results presented in the diatomic dissociation case, as shown in Fig. 4.5. For the

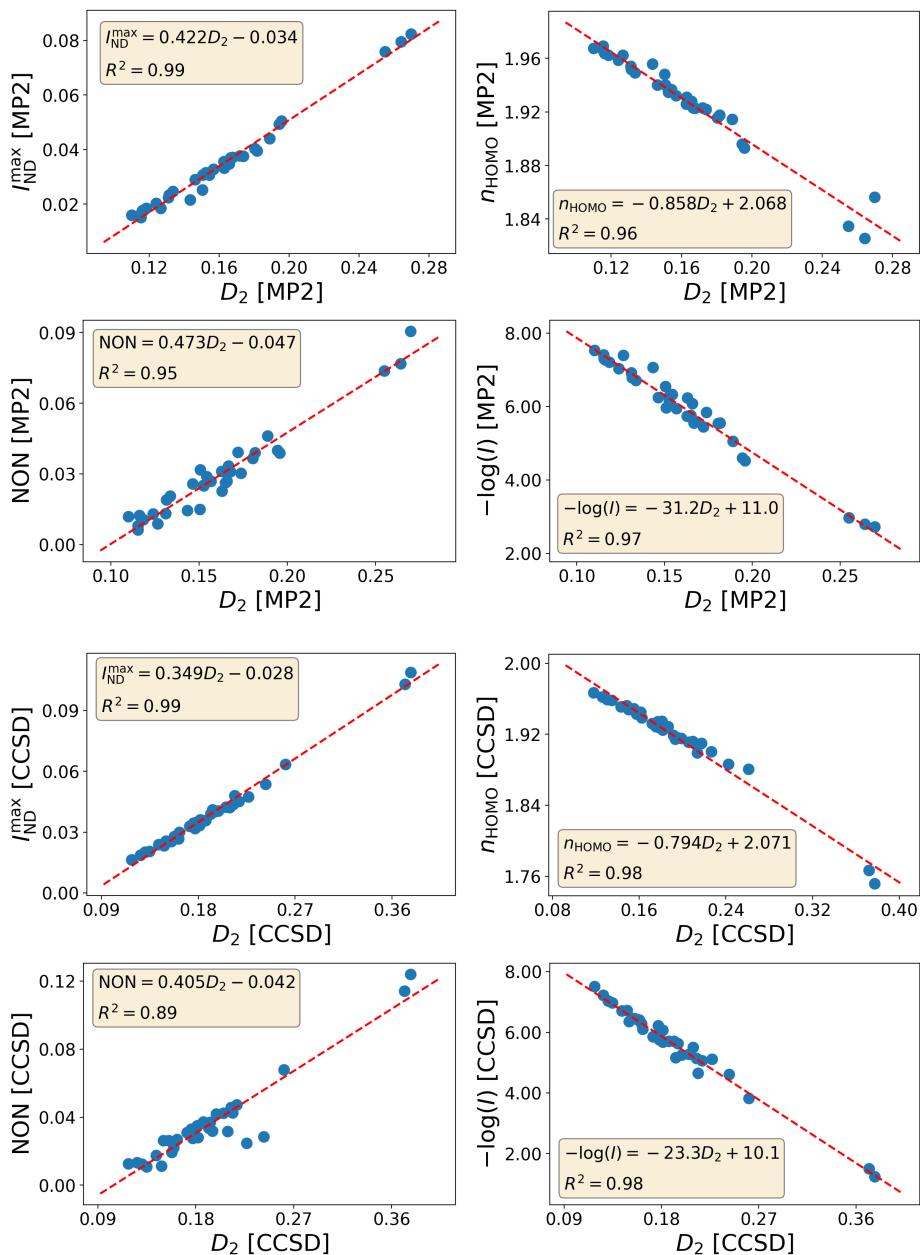


FIGURE 4.6: Linear relationships between D_2 diagnostic and other correlation metrics from MP2/cc-pVTZ and CCSD/cc-pVTZ calculations of the NJ34 dataset from Ref. [1].

NJ34 dataset, [Tab. 4.4](#), the relationship between D_2 and $I_{\text{ND}}^{\text{max}}$, as established in [Eq. \(4.39\)](#), is not limited to MP2 and can also be extended to CCSD. As we have discussed previously in the case of diatomic molecule dissociation, both the linear and quartic fittings (i.e, utilizing a single proportional parameter to scale the relationship in [Eq. \(4.39\)](#)), exhibited excellent performance (with squared regression $R^2 \approx 1.00$). Further discussion regarding these fittings, which can be used to determine cutoff values for $I_{\text{ND}}^{\text{max}}$ as effective MR diagnostic, will be elaborated on in [Chapter 5](#).

Next, Let us examine the linear correlation between $\overline{I_{\text{ND}}}$ and other correlation metrics obtained from MP2 and CCSD results, as shown in [Fig. 4.7](#). We observe that $\overline{I_{\text{ND}}}$ exhibits a significant linear correlation with S_{corr} , S_{sym} and XEN, with regression coefficients ($R^2 > 0.9$) for both MP2 and CCSD. The linear correlation between $\overline{I_{\text{ND}}}$ and S_{sym} is as expected, as the two indices exhibit similar curves against n_i^σ (as shown in [Fig. 4.1](#)) for the closed-shell two-electron and two-orbital model system. Moreover, the linear correlation between $\overline{I_{\text{ND}}}$ and correlation entropy S_{corr} suggests that the choice of an asymmetric distribution function (with the maximum point not occurring at $n_i^\sigma = 0.5$) does not significantly impact the behavior of average-based correlation metrics. Exceptionally, the MR indicator S_J , designed specifically for measuring dynamic correlation, does not show a significant correlation with $\overline{I_{\text{ND}}}$. In [Chapter 5](#), we will systematically study relationships among these correlation metrics using larger datasets, and explore the utility of these metrics as MR diagnostic tools.

In addition, through our analysis of the NJ34 dataset, we have verified that the contributions to $\overline{I_{\text{ND}}}$ from occupied natural orbitals and virtual orbitals are approximately equivalent, as mentioned by Bartlett *et al.* [\[257\]](#) in their study. This observation supports the formulation of $\overline{I_{\text{ND}}}$ in [Eq. \(4.10\)](#), where the latter term $\frac{2}{N} \sum_{\sigma,i}^{\text{vir}} |n_i^\sigma|^2$ is significantly smaller compared to 2XEN, especially when n_i approaches 0 or 1. This explains the linear relationship observed between XEN and $\overline{I_{\text{ND}}}$ in [Fig. 4.7](#), where $\overline{I_{\text{ND}}}$ can be approximately calculated by 2XEN. Nevertheless, the molecules CN^+ and C_2 exhibit the largest $\overline{I_{\text{ND}}}$ values, which lead to the slope of the fitting function with XEN greater than 0.5. These two molecules are characterized as MR by all the presented correlation metrics (more details on the cutoffs of $\overline{I_{\text{ND}}}$ and $I_{\text{ND}}^{\text{max}}$ for MR character will be provided in [Chapter 5](#)).

[Fig. 4.8](#) illustrates the linear relationships among T_1 , D_1 , and the size-extensive version of I_{ND} . Given that both T_1 and D_1 are derived from single-substitution amplitudes, the current analysis reveals a linear correlation between them, consistent with prior studies by other authors [\[35, 253\]](#). Furthermore,

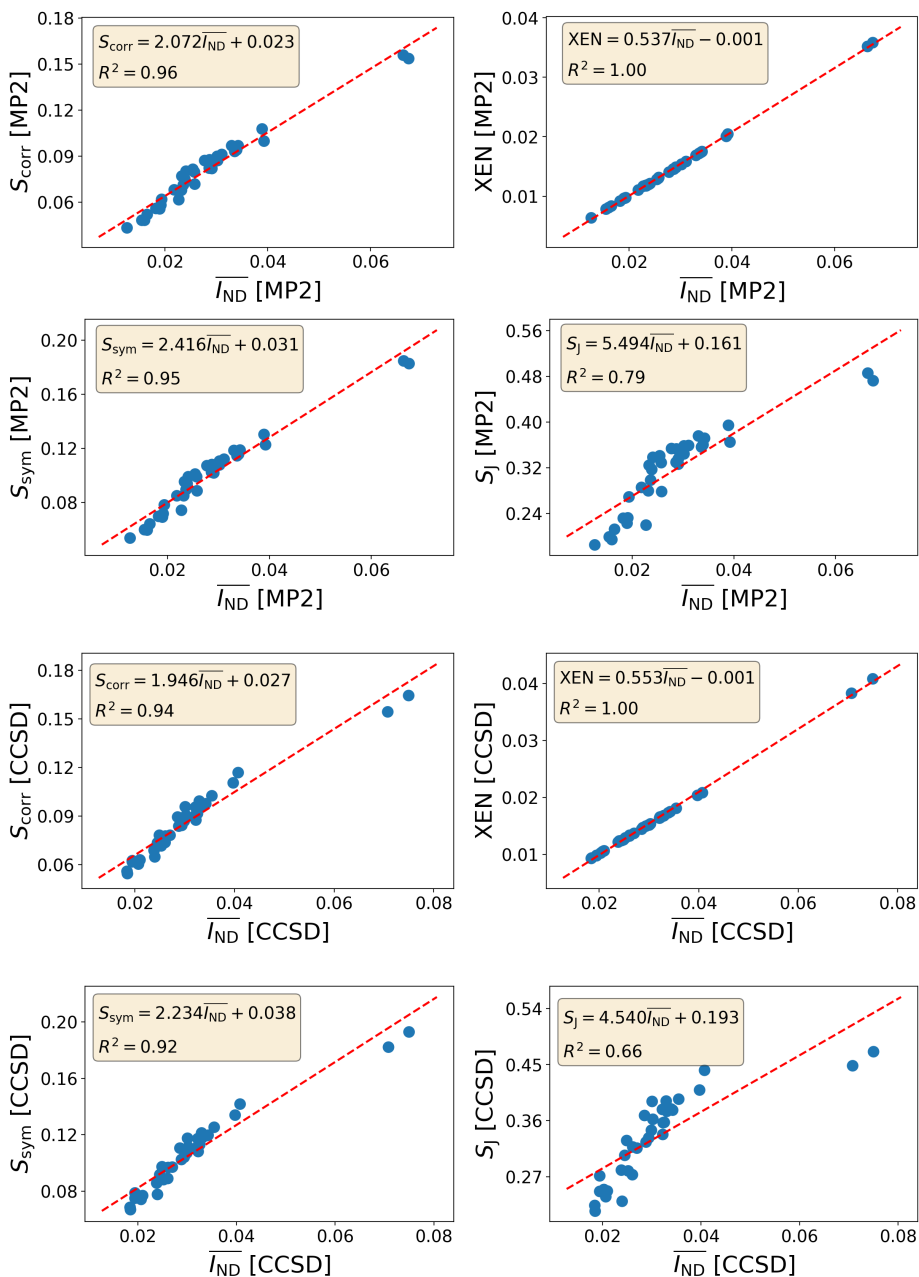


FIGURE 4.7: Linear relationships between $\overline{I}_{\text{ND}}$ and other natural orbital-based indices from MP2/cc-pVTZ and CCSD/cc-pVTZ calculations of the NJ34 dataset from Ref. [1].

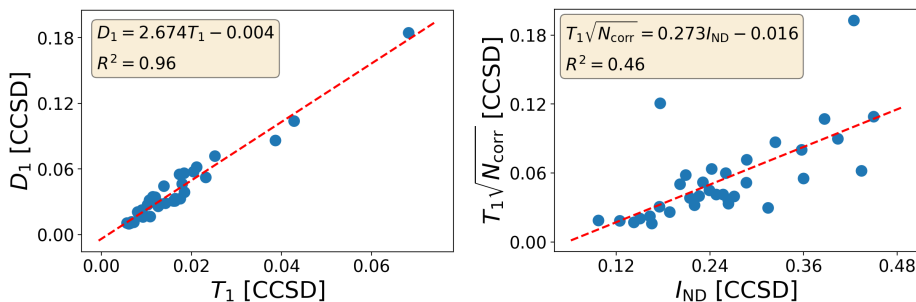


FIGURE 4.8: Linear relationships among T_1 , D_1 and I_{ND} from CCSD/cc-pVTZ calculations of the NJ34 dataset from Ref. [1].

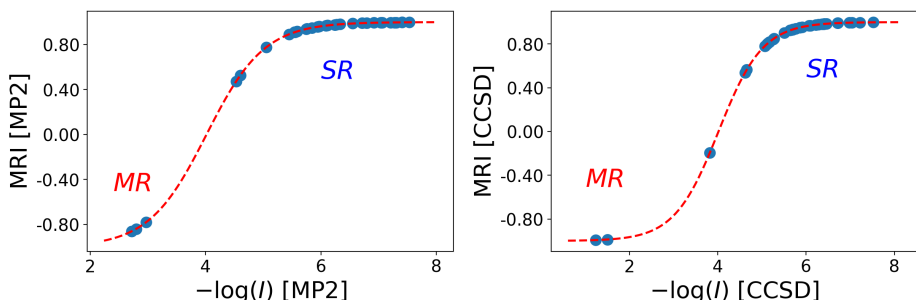


FIGURE 4.9: $-\log(I)$ versus MRI [257] from MP2/cc-pVTZ and CCSD/cc-pVTZ calculations of the NJ34 dataset in Ref. [1].

$T_1\sqrt{N_{\text{corr}}}$ and the size-extensive version of I_{ND} in Eq. (3.109) exhibit a moderate level of correlation, where N_{corr} stands for the number of correlated electrons. This implies a correlation between the size-intensive version of $\overline{I_{\text{ND}}}$ in Eq. (4.2) and T_1 , if they are normalized in the same way.

As illustrated in Fig. 4.9, the $-\log(I)$ and MRI from MP2 or CCSD typically categorize the majority of molecules into SR group, with only a few exceptions that exhibit strong MR character (i.e., CN^+ and C_2). The $-\log(I)$ and MRI were devised by Bartlett *et al.* [257] through fitting parameters to separate 15 SR and 15 MR character molecules. Although adjusting the fitting parameters might improve these indices in different situations, it is not our purpose here.

Through the statistical assessments of the linear relationships among various correlation metrics, despite working with relatively small datasets, we have been able to reduce these metrics based on their similarities. Within the category of maximum quantities, it is evident that $I_{\text{ND}}^{\text{max}}$, n_H , n_L , $-\log(I)$, MRI, and D_2 are

highly correlated. On the other hand, within the category of average quantities, $\overline{I_{\text{ND}}} \equiv 2\text{XEN}$ has been verified across different sets. Consequently, the natural orbital-based indices like S_{corr} , S_{sym} , and those introduced by Bartlett *et al.* [257], such as, NON, $-\log(I)$, MRI, and XEN, will be excluded from our subsequent analysis in [Chapter 5](#).

CORRELATION INDICES AS MR DIAGNOSTIC TOOLS

5.1 Introduction

MR diagnostics can be considered a specific type of correlation measure (or referred to as “metrics”) that are designed to identify MR character within systems. In literature, numerous correlation metrics have been introduced (we refer to [Section 3.4](#) in [Chapter 3](#)), and some of them have been proposed with specific cutoff values to serve as MR diagnostics, such as T_1 [25], D_1 [244], D_2 [1], M_{diag} [29], $\%TAE[(T)]$ [31], $\%E_{\text{corr}}[(T)]$ [18], and among others. Nonetheless, the application of MR diagnostics faces challenges with conflicting results, where different diagnostics may provide inconsistent indications of MR character [18, 19, 32, 253, 395, 396]. Previous studies have suggested diagnostic pairs that complement each other for optimal results [1, 26], while combining multiple diagnostics has been shown worse outcomes according to some authors [36]. Although energy-based diagnostics (e.g., $\%TAE[(T)]$, $\%E_{\text{corr}}[(T)]$) have been advocated by some authors, they require computationally expensive calculations, such as CCSD(T) [18, 19, 32–35] or FCI [11, 223–225]. Therefore, with the existence of numerous MR diagnostics, the need arises to reduce redundancy and effectively utilize MR diagnostics. Motivated by this, we aim to (i) identify the minimal set of representative MR diagnostics while avoiding redundancies; (ii) exclude MR diagnostics that are dependent on the system size. In this context, we refer not only to size-intensive diagnostics but also emphasize that even small portions of the system exhibiting

significant MR character should remain detectable by MR diagnostics regardless of increasing the system size; and (iii) develop robust MR diagnostics based on the correlation indices that can be applied across all electronic structure methods.

This chapter focuses on analyzing a collection of various correlation metrics, including (natural orbital-based) correlation indices (e.g., $\overline{I_{\text{ND}}}$, $I_{\text{ND}}^{\text{max}}$, n_H , n_L) and MR diagnostics (e.g., T_1 , D_1 , D_2 , $\%TAE[(T)]$, $\%E_{\text{corr}}[(T)]$). Our primary goal is to examine the linear relationships among these correlation metrics, as measured by the squared Pearson’s correlation coefficient (R^2). Through this analysis, we categorize and classify the correlation metrics based on their linear relationships, ultimately consolidating them into a single representative in each category. Subsequently, we provide some specific MR case studies by incrementally increasing the system size to evaluate the performance of these correlation metrics as MR diagnostics. In these typical MR system series, we consider that the MR character should be always identifiable regardless of the system size. Therefore, any correlation metrics identified as dependent on system size, and failing to indicate MR character in larger systems, will be discarded from the following analysis.

Our secondary objective is to establish MR cutoffs for (natural orbital-based) correlation indices through their linear relationships with other MR diagnostics that already have cutoff values. Then we will also assess the agreement among MR diagnostics based on these cutoff values. By addressing these objectives, we aim to provide a comprehensive guide for utilizing natural orbital-based correlation indices as effective MR diagnostic tools.

5.2 Computational Details

All CCSD and CCSD(T) calculations were performed by using an open-source quantum chemistry program, Psi4 [368–370]. We assessed the correlation indices and MR diagnostics derived from CCSD or CCSD(T) using a recently created cc-327 dataset, which consists of a total of 327 diverse molecular structures. The molecular geometries and basis sets are listed by several subgroups as follows:

- Strong correlated systems:
 - Hydrogen chains (H_{2n}) with varying chain lengths, where $n = 1, 2, \dots, 12$. The inter- H_2 unit distance was set to 3 Bohr, and the intra-unit distance was set to 2 Bohr. These calculations were performed using the aug-cc-pVDZ basis set. [397, 398]
 - Polyacetylene (PA) chains ($C_n H_{n+2}$) with varying chain lengths, where n took on values of 2, 4, 6, 8, and 10. The bond distances were adapted

as follows: intra-unit $r_{\text{CC}} = 1.34 \text{ \AA}$, $r_{\text{CH}} = 1.09 \text{ \AA}$, and $\theta_{\text{CCH}} = 121.5^\circ$, inter-unit $r_{\text{CC}} = 1.45 \text{ \AA}$. The calculations were performed using the Sadlej-pVTZ basis set. [399]

- Twisted ethylene (C_2H_4) structures, [400] the twisted angles ranging from 0 to 85° with an increment step of 5° . The aug-cc-pVTZ basis set [397, 398] was employed, and the geometries were adopted Ref. [400].
- Stretched p-quinodimethane (PQM) structures, [400] the geometries were optimized at the B3LYP level. The both-end C-C bond lengths were systematically stretched from 1.35 to $1.9 \text{ \AA}$ with a step of $0.05 \text{ \AA}$. These calculations utilized Pople’s 6-31G* basis set, which includes a diffuse function p with an exponent of 0.0523 . [400–403]
- Three diatomic molecular dissociations [3] with the aug-cc-pVDZ basis set: [397, 398] He_2 ($R = 3.0, 3.7, 4.4, 5.0 \text{ \AA}$), HeNe ($R = 3.1, 3.5, 4.5, 7.0 \text{ \AA}$), and HeAr ($R = 5.0, 4.3, 5.5, 8.0 \text{ \AA}$).
- The isoelectronic series of He [3] ($\text{He}, \text{Li}^+, \text{Be}^{2+}, \text{B}^{3+}, \text{C}^{4+}, \text{N}^{5+}$) using optimized even-tempered basis sets [404, 405] from Ref. [3] using the procedure outlined in Ref. [238].
- Polyhedra of He [3] consisting of 2, 3, 4, 5, and 6 helium atoms, positioned at a distance of $10 \text{ \AA}$ from the geometric center of the polyhedra, using the 6-31G basis set. [377]
- Bartlett’s 14 SR (excluding O_2 triplet) and 15 MR molecules [257]² with the cc-pVTZ basis set. [380, 398, 406]
- The W4-17 dataset, which includes 160 closed-shell molecules, [35, 292] with the cc-pVTZ basis set. [380]
- The S66 non-covalent interaction dataset [407] with the aug-cc-pVDZ basis set. [397, 398]

All MP2 calculations were carried out with another open-source quantum chemistry package, PySCF [371, 372], including in total 5090 closed-shell molecular structures from the GMTKN55 dataset [408] and the AD-3165 dataset [18]. In GMTKN55, we collected the values of D_2 for the 1925 closed-shell molecules among the total 2462 molecular structures, the rest are large molecules and have

²Due to a CCSD convergence problem with Psi4, we slightly modified the geometry of some molecules, and we computed N_2 at $R = 3.8 \text{ \AA}$, HF at $R = 3 \text{ \AA}$, C_2H_4 at 89°).

been discarded due to large computational cost requirements or because they were open-shell cases (the full table of excluded molecular structures is available in Ref. [389]). Henceforth, this dataset collection is referred as the GMTKN55-1925 dataset. The calculations for all molecules were carried out at the MP2 level with the def2-qzvp basis set. In the case of the WATER27 subset, it was increased with diffuse functions s and p for the oxygen atoms. In addition, in subsets G21EA, AHB21, and IL16, the diffuse functions s and p were added for all non-hydrogen atoms, and the diffuse functions s were added to the hydrogen atom. The core-electron of heavy elements in some systems of HEAVY28 (Pb, Sb, Te, Bi, I), HEAVYSB11 (Pb, Sn) and HAL59 (I) were replaced by the def2-ECP effective core potentials [408].

Using the AD-3165 dataset which was initially presented in a recent work of Kulik and coworkers [18], we repeated calculations over the entire AD-3165 dataset using MP2 with the cc-pVTZ basis set and obtained D_2 , $I_{\text{ND}}^{\text{max}}$, n_H , n_L , M_{diag} , etc. The results were merged with the ones of the GMTKN55-1925 dataset and are referred to as the mp-5090 dataset.

All the calculations of closed-shell molecules were done using a restricted Hartree-Fock (RHF) reference, with the frozen core option in post-HF methods, and the energy convergence threshold being set to 10^{-8} a.u. We utilized our in-house Python3 program for the computation of all the natural orbital-based indices, as well as the D_2 diagnostic of MP2. The program relies on several libraries, including Numpy [381], Scipy [382], Pandas [383, 384], and Matplotlib [385]. Additionally, the Matplotlib library was employed for generating all the graphs.

In this chapter, we always used the unrelaxed density to generate natural orbital occupation numbers in most of the calculations. The PySCF package was used to compute the unrelaxed MP2 density matrices, and the unrelaxed CCSD densities were evaluated using the Psi4 software.

Additionally, we also employed one size-intensive energy-based correlation metric based on the CCSD correlation energy and its spin-separated components: the percentage of opposite spin correlation contribution, $\%E_{\text{corr}}^{\alpha\beta}$,

$$\%E_{\text{corr}}^{\alpha\beta} = \frac{E_{\text{corr}}^{\text{CCSD}}(\alpha\beta)}{E_{\text{corr}}^{\text{CCSD}}} \times 100 = \frac{E_{\text{corr}}^{\text{CCSD}}(\alpha\beta)}{E_{\text{corr}}^{\text{CCSD}}(\alpha\beta) + E_{\text{corr}}^{\text{CCSD}}(\alpha\alpha)} \times 100. \quad (5.1)$$

The opposite spin correlation is more closely associated with short-range (dynamic) correlation rather than long-range (nondynamic) correlation [409]. According to the Pauli principle, the probability of finding two same-spin electrons at the same

spatial position must be zero, while it is generally nonzero for electrons with opposite spins. Thus, $\%E_{\text{corr}}^{\alpha\beta}$ is expected to measure dynamic correlation.

The comprehensive collection of correlation metrics examined in this chapter can be found in [Tab. 5.1](#). Compared to the list presented in [Tab. 4.1](#) from [Chapter 4](#), we have discarded certain similar correlation metrics. Since our focus in this chapter is on the correlation metrics applicable to the MP2, CCSD, and CCSD(T) levels of theory, c_0 -based diagnostics will not be considered here.

TABLE 5.1: List of electron correlation measures employed in the study.

Category	Correlation Metrics
Maximum	D_1 [244] and D_2 [1], n_H and n_L [32]
	$I_{\text{ND}}^{\text{max}}$ [389], M_{diag} [29]
Average	T_1 [25], S_J [390], $\overline{I_D}$ and $\overline{I_{\text{ND}}}$ [13, 389]
Ratio	$\%TAE[(T)]$ [30], $\%E_{\text{corr}}[(T)]$ [18]
	$\%E_{\text{corr}}^{\alpha\beta}$ [390], r_{ND} [34]

5.3 Results and Discussion

5.3.1 Exploring Linear Relationships Among Correlation Metrics

In this section, we collect various MR diagnostics from the cc-327 dataset. Our initial focus centers on exploring linear relationships among these diagnostics, which can be assessed through the squared Pearson’s correlation coefficient (R^2), see [Tab. A7](#) in Appendix A.4. Additionally, as demonstrated in the statistical assessment in [Chapter 4](#), the connection between D_2 and $I_{\text{ND}}^{\text{max}}$ is significant when $D_2 \leq 0.4$ or smaller, while the connection is poorer in severe MR regime (from $D_2 > 0.4$). Consequently, in order to avoid the affect of the data from severe MR character, we have performed further analyses to examine linear relationships when $D_2 \leq 0.4$ (refer to in [Tab. A8](#) in Appendix A.4) and when $D_2 \leq 0.3$ (refer to [Tab. 5.2](#)). Particularly, we note that by applying the criterion $D_2 \leq 0.4$ to the cc-327 dataset, we obtain a dataset consisting of 311 molecular structures, referred to as the cc-311 dataset. Similarly, utilizing the criterion $D_2 \leq 0.3$ yields a dataset of 299 molecular structures, denoted as the cc-299 dataset.

Firstly, we have categorized these MR diagnostics into distinct groups based on their linear relationships:

- Average quantities: S_J , $\overline{I_D}$, $\overline{I_{\text{ND}}}$
- Maximum quantities: $I_{\text{ND}}^{\text{max}}$, n_H , n_L , M_{diag} , D_2
- Single-excitations: T_1 , D_1
- Ratio: $\%E_{\text{corr}}^{\alpha\beta}$, r_{ND} , $\%TAE(T)$, $\%E_{\text{corr}}[(T)]$.

In the category of average quantities, it is unsurprising that both S_J and $\overline{I_D}$ exhibit consistently high correlation, as they both reflect dynamic correlation. The correlation between $\overline{I_{\text{ND}}}$ and S_J can be explained by our analysis of their mathematical ansatz, where we observe a heuristic linear relationship between these two metrics when the majority of n_i^σ values are close to 0 or 1. This behavior is evident in the singlet two-electron two-orbital model system (MS) as presented in [Chapter 4](#): when $n_i^\sigma \leq 0.1$ or $n_i^\sigma \geq 0.9$, both S_J^{MS} and $I_{\text{ND}}^{\text{MS}}$ show synchronous variations (i.e., they either increase or decrease together). However, in the range of $0.1 < n_i^\sigma < 0.9$, they exhibit inverse variations. In other words, $\overline{I_{\text{ND}}}$ and S_J are correlated for systems in the SR or mild MR regime (see [Tab. 5.2](#)), whereas this correlation is lost for systems in severe MR regime (see [Tab. A7](#)). In addition, we note that S_J and $\overline{I_D}$ are not correlated with any other MR diagnostics apart from $\overline{I_{\text{ND}}}$ (see [Tab. 5.2](#)), as expected.

TABLE 5.2: Squared Pearson’s correlation coefficients (R^2) for CCSD over 299 molecular structures ($D_2 \leq 0.3$).

R^2 matrix	S_J	$\overline{I_D}$	r_{ND}	$\overline{I_{ND}}$	$I_{ND}^{\max}$	n_H	n_L	M_{diag}	D_2	D_1	T_1	$\%E_{\text{corr}}^{\alpha\beta}$	$\%TAE(T)$	$\%E_{\text{corr}}[(T)]$
S_J	1.00	0.88	0.28	0.95	0.17	0.17	0.14	0.17	0.24	0.00	0.03	0.03	0.13	0.00
$\overline{I_D}$	0.88	1.00	0.06	0.74	0.06	0.06	0.05	0.05	0.09	0.00	0.00	0.07	0.16	0.01
r_{ND}	0.28	0.06	1.00	0.41	0.58	0.57	0.46	0.53	0.67	0.15	0.35	0.07	0.02	0.24
$\overline{I_{ND}}$	0.95	0.74	0.41	1.00	0.26	0.26	0.23	0.25	0.33	0.01	0.06	0.04	0.08	0.00
$I_{ND}^{\max}$	0.17	0.06	0.58	0.26	1.00	0.99	0.86	0.97	0.97	0.28	0.34	0.12	0.01	0.45
n_H	0.17	0.06	0.57	0.26	0.99	1.00	0.83	0.96	0.96	0.25	0.30	0.11	0.00	0.43
n_L	0.14	0.05	0.46	0.23	0.86	0.83	1.00	0.96	0.82	0.43	0.45	0.14	0.03	0.46
M_{diag}	0.17	0.05	0.53	0.25	0.97	0.96	0.96	1.00	0.93	0.35	0.39	0.13	0.01	0.47
D_2	0.24	0.09	0.67	0.33	0.97	0.96	0.82	0.93	1.00	0.29	0.39	0.11	0.01	0.42
D_1	0.00	0.00	0.15	0.01	0.28	0.25	0.43	0.35	0.29	1.00	0.75	0.33	0.07	0.42
T_1	0.03	0.00	0.35	0.06	0.34	0.30	0.45	0.39	0.39	0.75	1.00	0.27	0.18	0.48
$\%E_{\text{corr}}^{\alpha\beta}$	0.03	0.07	0.07	0.04	0.12	0.11	0.14	0.13	0.11	0.33	0.27	1.00	0.17	0.60
$\%TAE(T)$	0.13	0.16	0.02	0.08	0.01	0.00	0.03	0.01	0.01	0.07	0.18	1.00	1.00	0.19
$\%E_{\text{corr}}[(T)]$	0.00	0.01	0.24	0.00	0.45	0.43	0.46	0.47	0.42	0.42	0.48	0.60	0.19	1.00

Values with $R^2 \geq 0.7$ are indicated in bold text and displayed in blue.

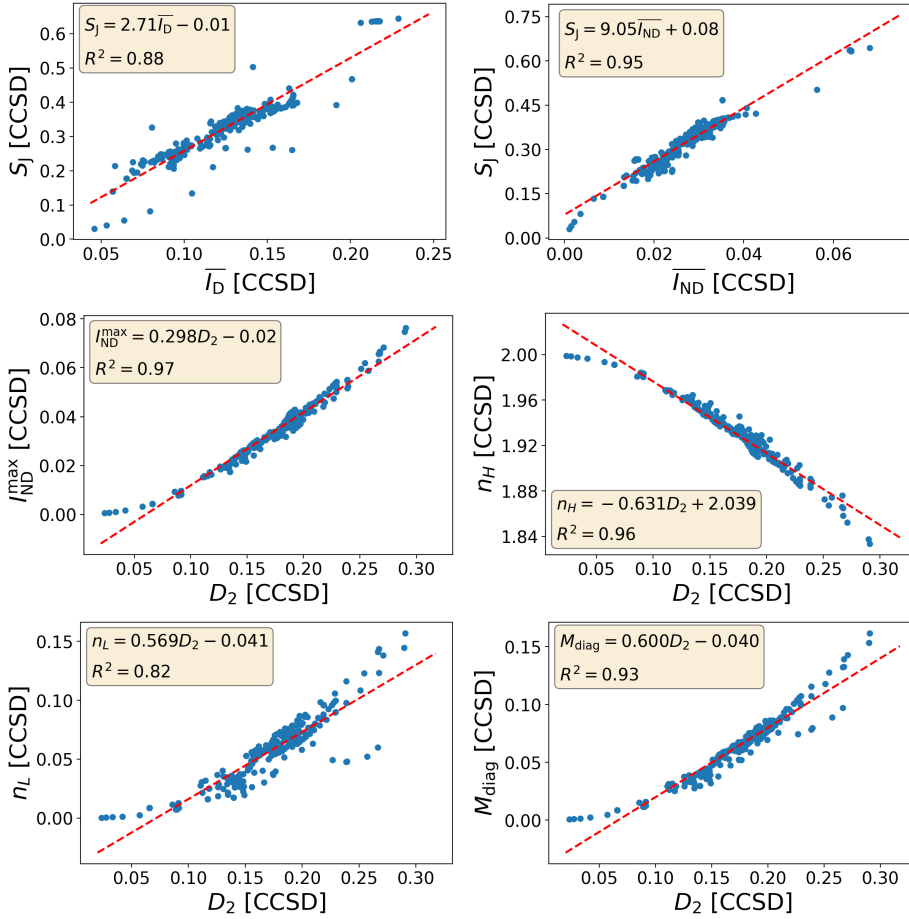


FIGURE 5.1: Linear relationships between pairs of MR diagnostics from CCSD over the cc-299 dataset ($D_2 \leq 0.3$).

Among the maximum quantities, we have previously demonstrated the relationships between D_2 and $I_{ND}^{\max}$, n_H , and n_L in the preceding chapter. Additionally, M_{diag} is linked to n_H and n_L by its definition in Eq. (3.104) for the closed-shell systems. Given the high correlation observed among these maximum quantities, it becomes apparent that one of them can serve as a representative metric for the others.

In the category of single-excitation metrics, there exists a correlation between T_1 and D_1 , as previously noted by other authors [18, 35, 253]. Despite the distinction in their statistical properties, with T_1 derived from average metrics and D_1 from maximum metrics, they show a correlation, especially in systems in the

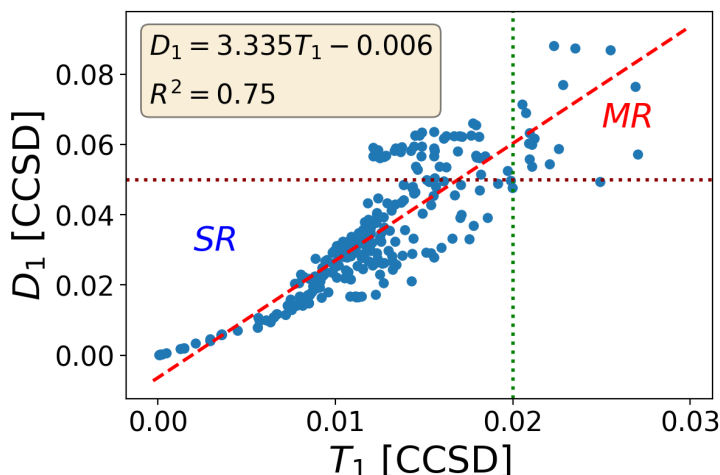


FIGURE 5.2: Linear relationships between T_1 and D_1 diagnostics from CCSD over the cc-299 dataset ($D_2 \leq 0.3$).

SR regime (both T_1 and D_1 are much smaller than their cutoffs). However, this correlation weakens as systems transition into the MR regime (one of the values of T_1 and D_1 is larger than their cutoffs).

As shown in Fig. 5.2, the relationships between the cutoff values of the maximum metric $D_1 \leq 0.05$ and the average metric $T_1 \leq 0.02$ are apparent. Notably, the majority of data points fall within the region where both metrics indicate SR character. Furthermore, almost no molecule tested in the cc-299 ($D_2 \leq 0.3$) dataset would be classified as MR according to T_1 but as SR to D_1 . This observation suggests that the cutoff for the maximum metric is more restrictive than the average metric. In other words, one can employ the cutoff of the maximum metric as a sole MR diagnostic, rendering the cutoff for the average metric unnecessary.

Within the category of ratio quantities, they are poorly correlated with each other or with any other metrics. In general, energy-based diagnostics show low correlations among themselves or with other wavefunction-based correlation indices, as previously noted by other authors [18, 35].

5.3.2 Assessing Correlation Metrics for Detecting MR Character

From our standpoint, MR diagnostics introduce an additional criterion for correlation measures: the ability to capture the most strongly correlated aspects within the system. This principle remains valid regardless of the system's size, even if only a small portion of it requires a necessary MR description, it validates the classification of the molecule as MR. In this context, it is only logical to employ correlation measures built upon the concept of maximal distance between wavefunctions. To support this argument, we design the following $\text{H}_2(\text{He})_{2n}$, $\text{O}_2(\text{Ne})_n$, and $\text{O}_2(\text{N}_2)_n$ molecular systems, and we aim to assess various electron correlation metrics as candidates for MR diagnostics.

(1) $\text{H}_2(\text{He})_{2n}$ molecular systems

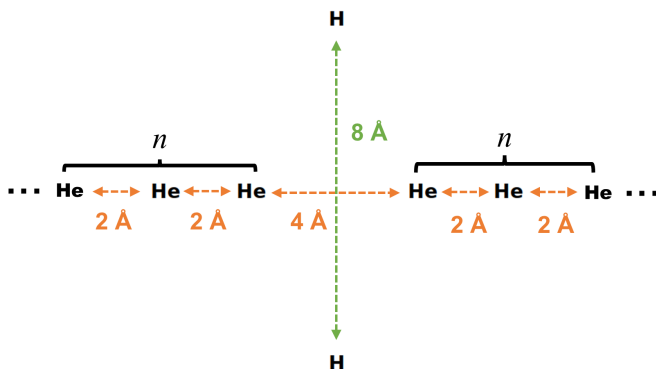


FIGURE 5.3: $\text{H}_2(\text{He})_{2n}$ molecular systems ($n = 1, 2, 3, 4, \dots$).

The $\text{H}_2(\text{He})_{2n}$ molecular systems ($n = 1, 2, 3, 4, \dots$) are all open-shell singlets with D_{2h} symmetry. As shown in Fig. 5.3, these systems have a consistent fixed geometry where all constituent atoms lie within a single plane. In this structure, a constant separation of $8 \text{ \AA}$ is maintained between the two hydrogen atoms (H-H). Positioned equidistantly between these hydrogen atoms, a linear arrangement of helium atoms (He) extends perpendicular to the H-H axis. Along this axis defined by the helium chain, every two adjacent helium atoms at each side of the H-H line are separated by $2 \text{ \AA}$. The larger systems are constructed by the addition of He_2 units to the smaller ones.

This system provides typical evidence that the maximum quantities remain constant regardless of the system's size expansion, as long as it does not introduce an additional portion exhibiting MR character. As shown in Tab. 5.3, these

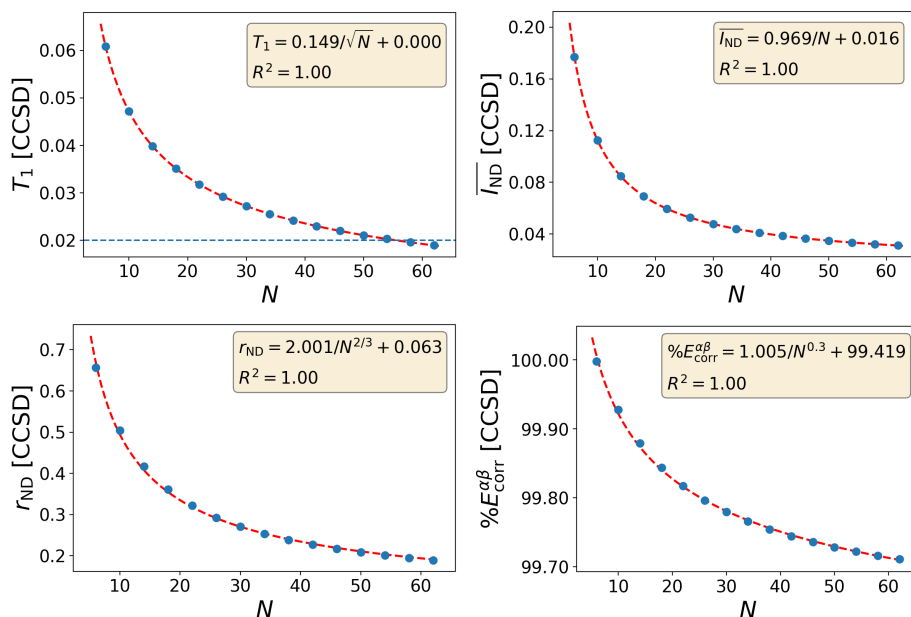


FIGURE 5.4: Average quantities or ratios as correlation metrics against the total number of electrons N for the $\text{H}_2(\text{He})_{2n}$ molecular systems, calculated at the CCSD/cc-pVDZ level of theory. As there are no core electrons frozen for the hydrogen and helium atoms, all electrons are correlated. The dashed line represents the cutoff for MR diagnostic.

maximum quantities consistently signify the presence of MR character within this system, even if it exists only within a small part of the overall structure. On the other hand, when considering average quantities or ratio-based correlation metrics, they show a clear dependence on the system size, as depicted in Fig. 5.4.

TABLE 5.3: Maximum quantities as correlation metrics for the $\text{H}_2(\text{He})_{2n}$ molecular systems, calculated at the CCSD/cc-pVDZ level of theory.

Mol.	n	D_1	D_2	n_H	n_L	$I_{\text{ND}}^{\text{max}}$
H_2He_2	1	0.1491	1.0222	1.0000	1.0000	0.25
H_2He_{10}	5	0.1489	1.0222	1.0000	1.0000	0.25
H_2He_{20}	10	0.1489	1.0222	1.0000	1.0000	0.25
H_2He_{30}	15	0.1489	1.0221	1.0000	1.0000	0.25

All of these metrics show the dependence of the system's size. For instance, the

T_1 diagnostic shows an inverse relationship with $\sqrt{N}$, where N denotes the total number of electrons. This relationship can be interpreted through its definition, which is expressed as $T_1 = \|t_1\|/\sqrt{N_{\text{corr}}}$. Here, the total number of correlated electrons, N_{corr} , equals N for hydrogen and helium atoms. The Euclidean norm of t_1 amplitudes remains constant at 0.149 and is independent of the system size. Consequently, as the system is extended by adding additional helium atoms, the values of T_1 steadily decrease and fall below its designated cutoff when $n = 14$. As the system size approaches infinity, T_1 will ultimately vanish.

As the system size increases, other average quantities and ratio quantities decay towards their respective limits, as illustrated in Fig. 5.4. They can be effectively fitted with an appropriate power of N , and exhibit an asymptotic decay trend as the system size increases. In particular, the limit of $\overline{I_{\text{ND}}}$ converges to the value of $\overline{I_{\text{ND}}}$ for a single helium atom. This convergence occurs because the original version of I_{ND} is size-extensive, and the average metric $\overline{I_{\text{ND}}}$ approaches that of a single helium atom as the system size approaches infinity. Since the CCSD and CCSD(T) energies are very close when treating the $\text{H}_2(\text{He})_{2n}$ molecular systems, the related (T) energy-based MR diagnostics like $\% \text{TAE}[(\text{T})]$ and $\% E_{\text{corr}}[(\text{T})]$ are not considered in the current analysis. Nonetheless, the subsequent examples of $\text{O}_2(\text{Ne})_n$ and $\text{O}_2(\text{N}_2)_n$ molecular systems are specifically for assessing these (T) energy-based MR diagnostics.

(2) $\text{O}_2(\text{Ne})_n$ molecular systems

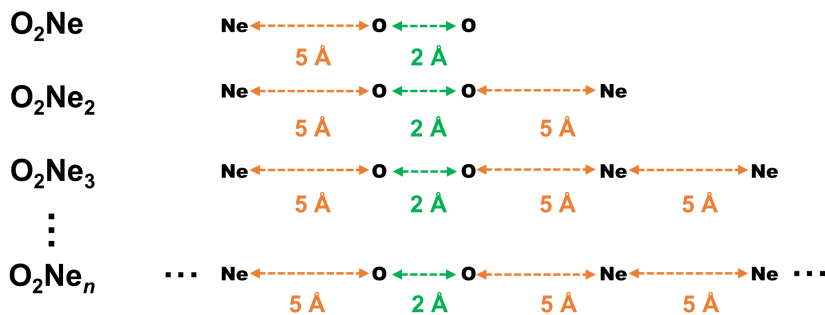


FIGURE 5.5: $\text{O}_2(\text{Ne})_n$ molecular systems ($n = 1, 2, 3, 4, \dots$).

The $\text{O}_2(\text{Ne})_n$ molecular systems ($n = 1, 2, 3, 4, \dots$) which are all open-shell singlets, are illustrated in Fig. 5.5. These systems consist of linear chain structures in which two oxygen atoms are separated by 2 Å. Neon atoms are alternately added

to each side of the oxygen atoms. The distances between neighboring neon atoms are consistently maintained at 5 Å, and the separation between two adjacent neon atoms remains at 5 Å as well.

TABLE 5.4: Maximum quantities as correlation metrics for the $\text{O}_2(\text{Ne})_n$ molecular systems, calculated at the CCSD/cc-pVDZ level of theory.

Mol.	n	D_1	D_2	n_H	n_L	$I_{\text{ND}}^{\text{max}}$
O_2Ne	1	0.0939	0.5683	1.3973	0.5985	0.2105
O_2Ne_2	2	0.0939	0.5683	1.3973	0.5985	0.2105
O_2Ne_3	3	0.0939	0.5683	1.3973	0.5985	0.2105
O_2Ne_4	4	0.0939	0.5683	1.3973	0.5985	0.2105
O_2Ne_5	5	0.0939	0.5683	1.3973	0.5985	0.2105
O_2Ne_6	6	0.0939	0.5683	1.3973	0.5985	0.2105

Similarly, for the initial system O_2Ne , all the MR diagnostics consistently indicate MR character. Moreover, with an increase in the system size, all the maximum-based MR diagnostics shown in Tab. 5.4 remain constant. We note that D_1 and D_2 greatly exceed their cutoff values.

In contrast, as shown in Fig. 5.6, all the average quantities or ratio metrics exhibit clear size-dependency (except $\% \text{TAE}[(\text{T})]$, which remains relatively constant around 36.62). Significantly, both T_1 and $\% E_{\text{corr}}[(\text{T})]$ fall below their cutoffs as the system size increases. Finally, as the system size approaches infinity, $\overline{I_{\text{ND}}}$ approaches 0.013, which corresponds to the value of $\overline{I_{\text{ND}}}$ for a single Ne atom.

According to the analysis of the current MR molecular systems, it becomes evident that all the average or ratio-based correlation measures (except $\% \text{TAE}[(\text{T})]$) are dependent on the system size. We note that $\% \text{TAE}[(\text{T})]$ should be also size-dependent, while it is not evident in the current MR case due to the zero contributions from individual neon atoms to $\% \text{TAE}[(\text{T})]$. In the subsequent MR case, we will illustrate how $\% \text{TAE}[(\text{T})]$ is sensitive to the variations in the system size. Hence, applying a cutoff for these average or ratio-based correlation metrics is not suitable as they are size-dependent, and they are inappropriate to be used as MR diagnostics. In contrast, the maximum-based correlation measures remain consistent regardless of system size. Moreover, n_H or n_L approaching 1.0 indicates a highly-correlated regime. With appropriate cutoffs, they are recommended for use as MR diagnostics.

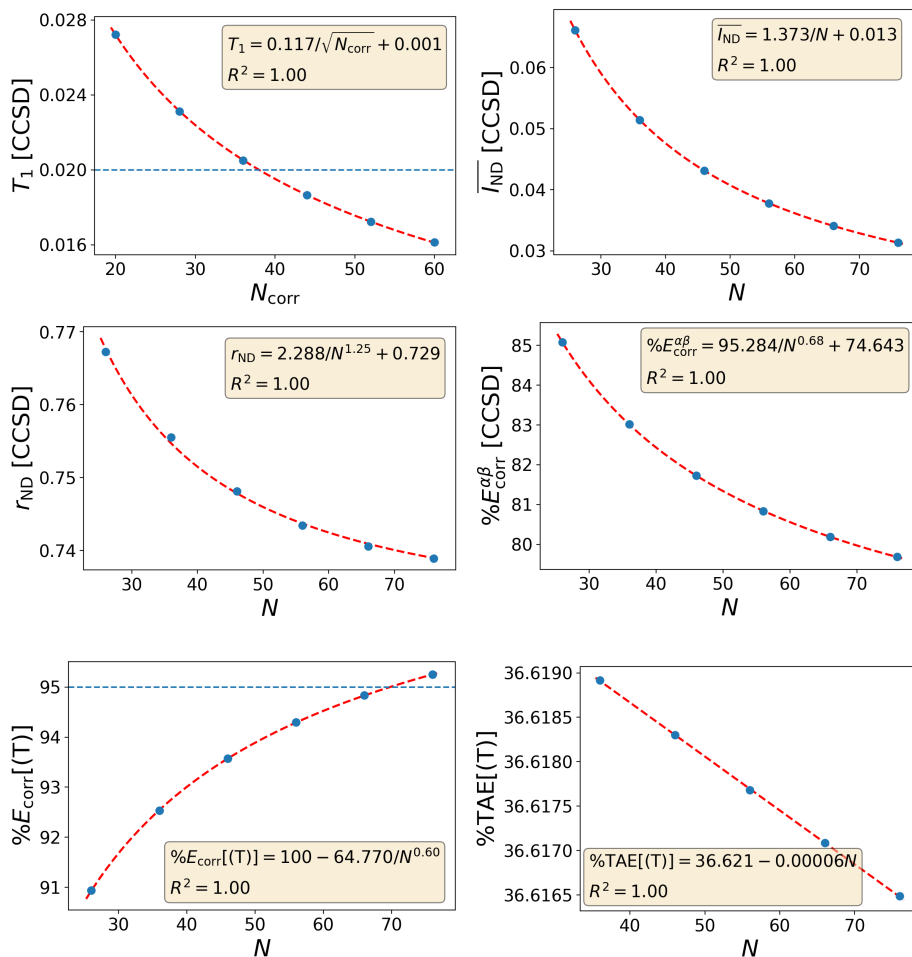


FIGURE 5.6: Average quantities or ratios as correlation metrics against the total number of electrons N for the $O_2(Ne)_n$ molecular systems, calculated at the CCSD/cc-pVDZ level of theory. The dashed line represents the cutoffs for MR diagnostics.

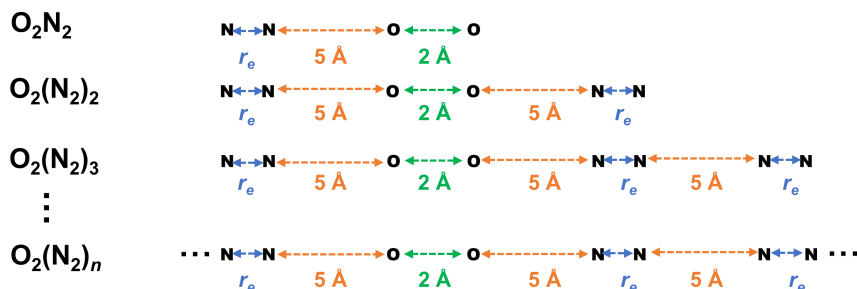
(3) $\text{O}_2(\text{N}_2)_n$ molecular systems

FIGURE 5.7: $\text{O}_2(\text{N}_2)_n$ molecular systems ($n = 1, 2, 3, 4, \dots$). The N_2 molecular units are at $r_e = 1.097 \text{ \AA}$.

Similar to the $\text{O}_2(\text{Ne})_n$ systems that we have presented previously, the $\text{O}_2(\text{N}_2)_n$ molecular systems ($n = 1, 2, 3, 4, \dots$) are designed by replacing the neon atoms of $\text{O}_2(\text{Ne})_n$ by N_2 molecular units which are at their equilibrium distance. As illustrated in Fig. 5.7, these systems consist of linear chain structures in which two oxygen atoms are separated by $2 \text{ \AA}$, and the N_2 molecular units are alternately added to each side of the oxygen atoms. The distances between neighboring N_2 units are consistently maintained at $5 \text{ \AA}$, and the separation between two adjacent N_2 units remains at $5 \text{ \AA}$ as well.

TABLE 5.5: Maximum quantities as correlation metrics for the $\text{O}_2(\text{N}_2)_n$ molecular systems, calculated at the CCSD/cc-pVDZ level of theory.

Mol.	n	D_1	D_2	n_H	n_L	$I_{\text{ND}}^{\text{max}}$
O_2N_2	1	0.0939	0.5682	1.3975	0.5983	0.2105
$\text{O}_2(\text{N}_2)_2$	2	0.0939	0.5681	1.3977	0.5981	0.2105
$\text{O}_2(\text{N}_2)_3$	3	0.0939	0.5681	1.3977	0.5981	0.2105
$\text{O}_2(\text{N}_2)_4$	4	0.0939	0.5681	1.3977	0.5981	0.2105
$\text{O}_2(\text{N}_2)_5$	5	0.0939	0.5681	1.3977	0.5981	0.2105
$\text{O}_2(\text{N}_2)_6$	6	0.0939	0.5681	1.3977	0.5981	0.2105

Tab. 5.5 shows the maximum-based correlation metrics. As expected, they are insensitive to the variation in the system size, and their values are consistent with the ones of $\text{O}_2(\text{Ne})_n$ that have been shown in Tab. 5.4. Therefore, they can reflect the maximum MR character in the system regardless of the system size.

Fig. 5.8 illustrates that the average-based and ratio-based MR diagnostics are size-sensitive, consistent with the results from $\text{H}_2(\text{He})_{2n}$ and $\text{O}_2(\text{Ne})_n$ systems. Especially, it demonstrates a clear decrease in $\% \text{TAE}[(\text{T})]$ when increasing system size of $\text{O}_2(\text{N}_2)_n$. This results in the cutoffs for $\% \text{TAE}[(\text{T})]$ invalid, as $\% \text{TAE}[(\text{T})]$ decreases from approximately 10% to 2%. The extrapolation indicates a further reduction to a very low value of 0.815, ultimately rendering it unsuitable as an MR diagnostic.

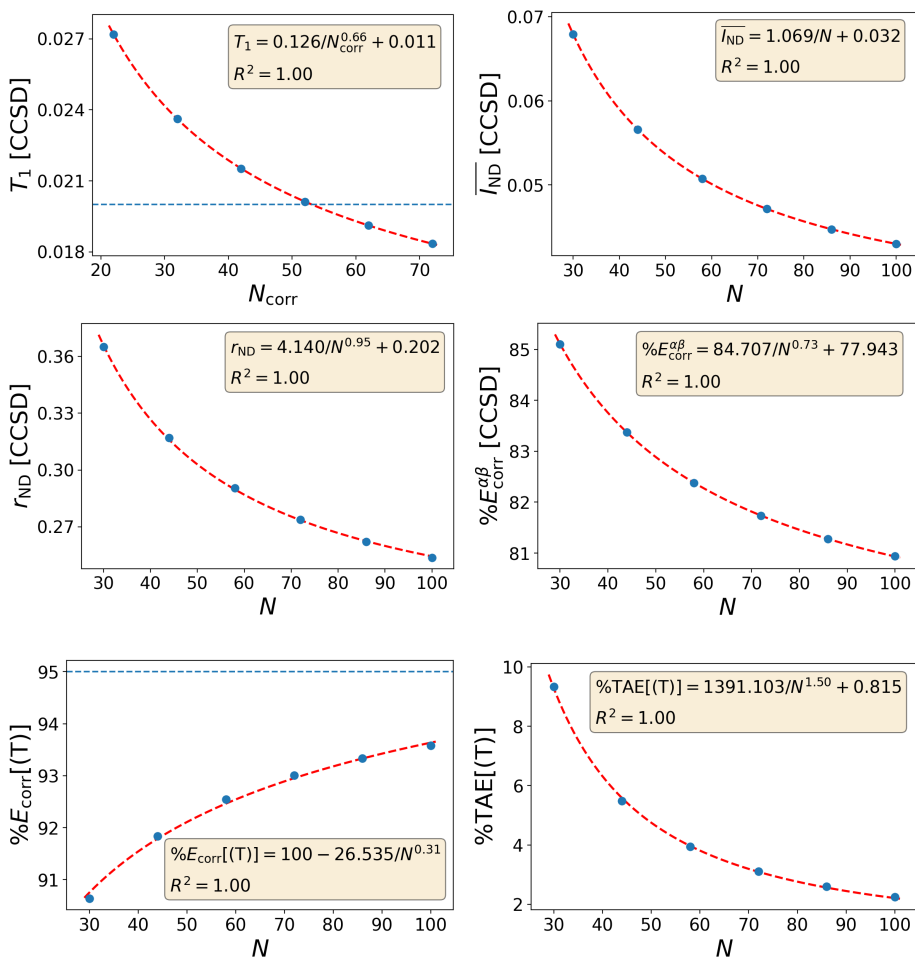


FIGURE 5.8: Average quantities or ratios as correlation metrics against the total number of electrons N for the $\text{O}_2(\text{N}_2)_n$ molecular systems, calculated at the CCSD/cc-pVDZ level of theory. The dashed line represents the cutoffs for MR diagnostics.

5.3.3 Cutoffs for $I_{\text{ND}}^{\text{max}}$ as an MR Diagnostic Tool

In the previous section, several correlation metrics, including $\overline{I_{\text{ND}}}$, r_{ND} , T_1 , $\%E_{\text{corr}}^{\alpha\beta}$, $\%E_{\text{corr}}[(T)]$ and $\%TAE[(T)]$ have been demonstrated to inappropriately serve as MR diagnostics, due to their susceptibility to system size variations and their inability to detect significant MR character in large systems. In addition, D_1 is not recommended to be MR diagnostic because of its susceptibility to orbital rotation. As previously discussed, a Bruckner rotation would yield zero values for single-substitution amplitudes (we refer to [Chapter 3](#)). Hence, we only consider these maximum quantities, including $I_{\text{ND}}^{\text{max}}$, n_H , n_L , M_{diag} , and D_2 that remain insensitive to system size as our chosen MR diagnostics.

Firstly, following the connection between $I_{\text{ND}}^{\text{max}}$ and D_2 that have been established previously in [Eq. \(4.39\)](#) in [Chapter 4](#), we employ one single fitting parameter, denoted as κ , to scale the relationship between D_2 and $I_{\text{ND}}^{\text{max}}$. The fitting function is given by

$$I_{\text{ND}}^{\text{max}} = \kappa[D_2^2(2 - 4D_2^2)]. \quad (5.2)$$

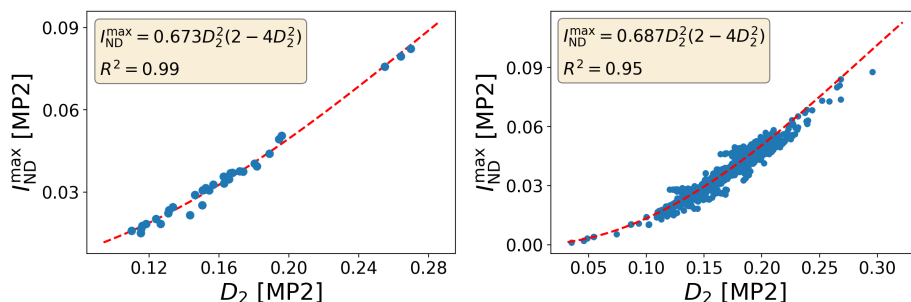
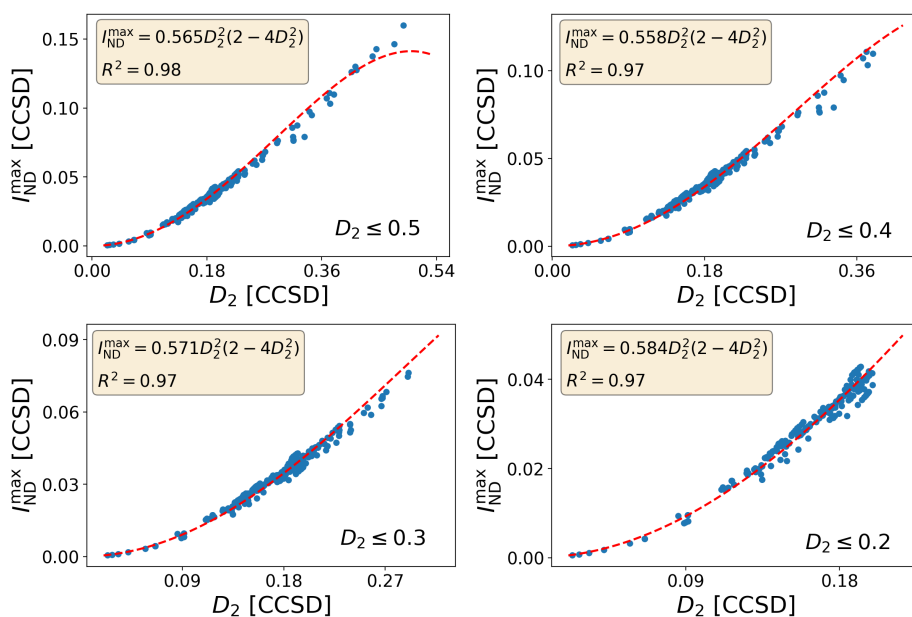


FIGURE 5.9: Fitting of D_2 against $I_{\text{ND}}^{\text{max}}$ for NJ34 set (left) and mp-5090 set (right), calculated at the MP2 level.

Analyzing the fittings of D_2 against $I_{\text{ND}}^{\text{max}}$ performed across the test datasets derived from MP2 calculations, as illustrated in [Fig. 5.9](#), we find an equivalence with the established D_2 cutoff values for MP2 ($D_2 > 0.15 - 0.17$) as suggested by Nielsen and Janssen [[1](#)]. Remarkably, the $I_{\text{ND}}^{\text{max}}$ cutoffs, obtained from the fitting functions, show minimal variation when utilizing either a modest MP2 test set (NJ34 set) or an extensive one (mp-5090). Furthermore, as shown in [Tab. 5.6](#), the agreement between the two diagnostic methods (quantified as the percentage of molecules classified consistently as MR or SR) exceeds 94%. This

TABLE 5.6: Equivalence between D_2 and $I_{\text{ND}}^{\text{max}}$ cutoffs for MR diagnostics based on the NJ34 and the mp-5090 datasets, calculated at the MP2 level

Set	Size	κ	Regression R^2	D_2	$I_{\text{ND}}^{\text{max}}$	Agreement(%)
NJ34	34	0.673	0.99	0.15	0.029	94
				0.17	0.037	97
mp-5090	5090	0.687	0.95	0.15	0.030	98
				0.17	0.037	96


FIGURE 5.10: Fitting of D_2 vs. $I_{\text{ND}}^{\text{max}}$ in the cc-327 dataset under varying D_2 criteria, calculated at the CCSD level.

observation validates the substitution of $D_2 > 0.15 - 0.17$ with $I_{\text{ND}}^{\text{max}} > 0.03 - 0.037$ for calculations at the MP2 level.

When performing fittings of D_2 against $I_{\text{ND}}^{\text{max}}$ using the CCSD datasets, selecting an appropriate fitting range within the CCSD dataset becomes crucial. This choice of fitting range relies on the fact that the maximum point of the fitting curve in Eq. (5.2) occurs at $D_2 = 0.5$. Ideally, the fitting is reliable only within the range of $0 \leq D_2 \leq 0.5$, with better accuracy achieved as the values approach

zero. Conversely, as values approach 0.5, deviations become more significant, and when D_2 exceeds 0.5, the fitting loses validity. In contrast to the MP2 datasets, where all D_2 values are less than or equal to 0.3, the CCSD datasets involve strong-correlated systems where $D_2 > 0.4$, and this can already significantly affect the fittings using Eq. (5.2) (see Fig. 5.10).

The purpose of the fittings is to ensure accuracy in the vicinity of these D_2 cutoffs (i.e., $D_2 > 0.15 - 0.18$ for CCSD). As a result, we performed tests with four different fitting ranges within the cc-327 dataset obtained from CCSD calculations, namely $D_2 \leq 0.5$, $D_2 \leq 0.4$, $D_2 \leq 0.3$, and $D_2 \leq 0.2$. The results of these four fittings, corresponding to the four different ranges in the cc-327 dataset, are presented in Fig. 5.10. While the fitting parameter κ varies slightly for different fitting ranges, these fitting curves closely align around the D_2 cutoff values, with squared regression coefficients (R^2) consistently exceeding 0.97. The established cutoff values of $I_{\text{ND}}^{\text{max}}$ derived from these fittings, based on the respective dataset ranges, are summarized in Tab. 5.7. Especially, these cutoff values show seldom variation relative to the choice of fitting range or dataset, with all agreements between the cutoffs of $I_{\text{ND}}^{\text{max}}$ and their corresponding D_2 cutoffs surpassing 95%. Consequently, we recommend the use of $I_{\text{ND}}^{\text{max}} > 0.024 - 0.034$ which is equivalent to $D_2 > 0.15 - 0.18$ as the MR diagnostic for CCSD calculations. We adopt the original cutoffs for D_2 as suggested by the authors [1]: $D_2 < 0.15$ indicates the SR regime, $D_2 > 0.18$ signifies inadequacy of the CCSD method, corresponding to the MR regime, and D_2 values between 0.15 and 0.18 suggest being cautionary on the current CCSD calculation.

TABLE 5.7: Equivalence between D_2 and $I_{\text{ND}}^{\text{max}}$ cutoffs for MR diagnostics based on the cc-327 dataset, calculated at the CCSD level

Data Range	Size	κ	Regression R^2	D_2	$I_{\text{ND}}^{\text{max}}$	Agreement(%)
$D_2 \leq 0.5$	318	0.565	0.98	0.15	0.024	96
				0.18	0.034	97
$D_2 \leq 0.4$	311	0.558	0.97	0.15	0.024	95
				0.18	0.034	97
$D_2 \leq 0.3$	299	0.571	0.97	0.15	0.025	96
				0.18	0.035	98
$D_2 \leq 0.2$	254	0.584	0.97	0.15	0.025	95
				0.18	0.035	98

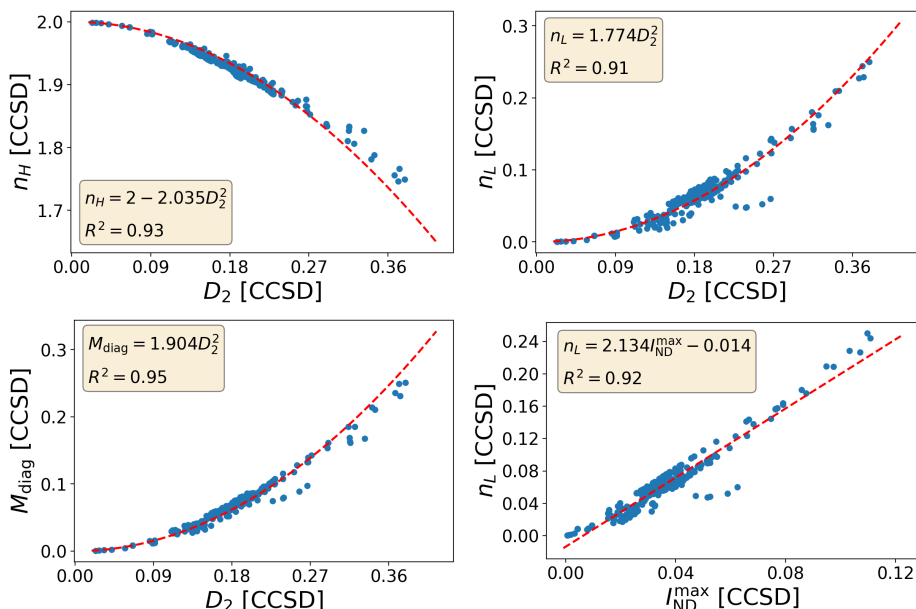


FIGURE 5.11: Relationships between pairs of MR diagnostics from CCSD over the cc-327 dataset ($D_2 \leq 0.4$), including 311 molecular structures.

TABLE 5.8: Equivalence of cutoffs of MR diagnostics and classification of MR(%) over the cc-327 dataset by each MR diagnostic from CCSD calculations.

Cutoffs	D_2	$I_{\text{ND}}^{\text{max}}$	n_H	n_L	M_{diag}
Level 1	0.15 [1]	0.024	1.950	0.040	0.04
MR(%)	76	80	79	74	81
Level 2	0.18 [1]	0.034	1.930	0.058	0.06
MR(%)	54	56	55	60	61
Level 3	-	0.048	1.900 [154]	0.0674 [257]	0.1 [29]
MR(%)	-	16	16	40	13
Level 4	-	0.06	-	0.116 [257]	-
MR(%)	-	11	-	11	-

* Note that $n_L = 2\text{NON}$ [257] for closed-shell molecules.

Furthermore, we also consider the suggested cutoff of $n_L \equiv 2\text{NON} = 0.116$ by Bartlett *et al.* [257], and we establish a trial cutoff of $I_{\text{ND}}^{\text{max}} = 0.06$ based on $n_i^\sigma = 0.058$, determined by the linearly fitted relationship, $n_L = 2.134I_{\text{ND}}^{\text{max}} - 0.014$. These

cutoff values for D_2 , $I_{\text{ND}}^{\text{max}}$, n_H , n_L , and M_{diag} are summarized in [Tab. 5.8](#). It is noteworthy that the cutoffs at Level 1 and Level 2, which correspond to the cutoffs of D_2 , tend to be relatively smaller, while the cutoffs at Level 3 are associated with $n_i = 1.9$ (except for n_L), and the highest cutoffs at Level 4 correspond to $n_L = 0.116$. The suggested cutoffs from these four levels are categorized based on their sensitivity in detecting MR character. Level 1 cutoffs are the most restrictive, and they classify over 70% the molecular structures as MR character in the cc-327 dataset. Level 2 cutoffs which are based on $D_2 = 0.18$, are often accepted in the literature [[18](#), [32](#), [34–36](#)], and they identify over 50% molecular structures with MR character. Level 3 cutoffs are less stringent, but they are worth being examined. On the other hand, level 4 cutoffs are the least restrictive, and using level 3 or level 4 to detect MR character does not significantly affect the MR(%) classified by $I_{\text{ND}}^{\text{max}}$. Hence, a higher cutoff than level 3 is not recommended.

EXTENDED BAERENDS' DISPERSION MODEL

6.1 Introduction

According to Gritsenko and Baerends [88], an FCI calculation for H_2 molecule (triplet) with a basis set that involves only $s + p$ orbitals can yield up to 51% of the binding energy compared to the benchmark data of Kolos and Wolniewicz [410]. Moreover, they have shown that by employing $s + p + d$ basis functions, the FCI method is capable of retrieving 91% of the reference energy, and the inclusion of f functions improved the accuracy to 98%. Moreover, they suggested that induced dipole-induced dipole two-electron terms from the FCI pair density account for London dispersion [88–90]. Gritsenko and Baerends [88] fitted the total energy difference between FCI and CAS(2,2) to determine $C_6 = 6.276$ and $C_8 = 161.994$ for the singlet H_2 molecule, using the aug-cc-pV6Z basis set, the interatomic separation distances R being set from 11.0 to 13.0 a.u. [90] In addition, as we have introduced in Chapter 3, they put forward that induced dipole-induced dipole two-electron AO quartets (i.e., $s_A(1)p_A(1)s_B(2)p_B(2)$ and $s_A(2)p_A(2)s_B(1)p_B(1)$) from the FCI pair density can account for London dispersion [88–90].

Ángyán *et al.* [42] also referred that the use of a basis set that incorporates higher angular momentum functions leads to higher instantaneous multipole moments. In particular, they pointed out that using these basis sets (e.g. including d - and f -type GTO) gives rise to non-vanishing transition quadrupole and octopole moments, which in turn contribute to dispersion energy terms such as $-C_8/R^8$

and $-C_{10}/R^{10}$, where R represents the interfragment distance. Therefore, using $s + p$ orbitals can only produce C_6 , while incorporating $s + p + d$ orbitals gives C_6 and C_8 , and employing $s + p + d + f$ orbitals we can include up to C_{10} . Furthermore, by performing CISD calculations on He_2 with the aug-cc-pV6Z basis set, they determined the dispersion coefficients $C_6 = 1.33475$, $C_8 = 12.4082$, and $C_{10} = 125.313$ through fitting the energy difference $E_{\text{corr}}(R) - E_{\text{corr}}(\infty)$ for R values ranging from 8 to 16 a.u.

In the context of RDMFT, they proposed an approximate RDMFT functional [88] to recover vdW binding energy of H_2 (triplet) molecule. This RDMFT functional incorporates the electron-electron interaction energy term derived from an approximate pair density. The approximate pair density was formed by using a finite set of combinations of natural orbital products, reflecting the interactions between a pair of instantaneous atomic multipoles resulting from intra-atomic $s \rightarrow p$, $s \rightarrow d$, or $s \rightarrow f$ excitations. In practice, the approximate pair density (referred as vdW pair density by Baerends *et al.* [88–90]) can be represented in terms of induced dipole-induced dipole two-electron AO quartets. This particular RDMFT functional (using eight natural orbitals) was shown to successfully recover 50% of the benchmark vdW binding energy of H_2 provided by Kolos and Wolniewicz [410].

With respect to the induced dipole-induced dipole terms, Ángyán *et al.* [42] presented a simplified model system: He_2 at large internuclear distances R , using a basis set consisting of two s orbitals and one p orbital on each helium atom. By employing this model, they derived an analytical correlation energy expression for CI with double excitations only (CID) and MP2, written in terms of these induced dipole-induced dipole two-electron integrals in AO basis. They demonstrated qualitatively a $1/R^6$ decay of the correlation energy resulting from London dispersion.

Baerends *et al.* [88–90] and Ángyán *et al.* [42] used induced dipole-induced dipole terms in their simplified model systems of H_2 and He_2 . Nevertheless, it remains unclear how much dispersion energy can be retrieved by the electron-electron interaction energy, V_{ee} , directly derived from these terms. Moreover, it is unknown how much C_6 can be retrieved using this model for larger systems beyond H_2 and He_2 . Additionally, when d orbitals are present, it becomes necessary to consider induced multipole-induced multipole terms corresponding to higher multipole effects. To the best of our knowledge, there are currently no studies that have revealed induced multipole-induced multipole two-electron terms from the perspective of pair density to retrieve dispersion energy beyond H_2 and He_2

molecules.

In this chapter, we will explore two dispersion models for various systems, using approximate pair densities: (i) constructed solely from induced dipole-induced dipole terms, referred to as Baerends' model, and (ii) incorporating extended induced multipole-induced multipole (higher multipole) terms, referred to as the extended Baerends' model. A detailed list of the terms employed in both models is provided in [Tab. 6.1](#). Using these two models, we will assess the contribution of the V_{ee} term to the total dispersion energy and gain insights into the role of the long-range pair density components in dispersion interactions. Following [Eq. \(3.78\)](#) and [Eq. \(3.79\)](#) presented previously in [Chapter 3](#), the V_{ee} term can be straightforwardly derived from approximate pair densities constructed using (i) Baerends' model ($\rho_2^{dd}(1,2)$, V_{ee}^{dd}), and (ii) extended Baerends' model ($\rho_2^{ext}(1,2)$, V_{ee}^{ext}). Employing various correlated wavefunction (post-HF) methods and basis sets, we will retrieve C_6 of a collection of diatomic systems.

TABLE 6.1: Baerends' model versus extended Baerends' model.

Terms	Baerends' model	Extended Baerends' model
$\rho_2(1,2)$	$\rho_2^{dd}(1,2)$	$\rho_2^{ext}(1,2)$
All two-electron	$s_A(1)p_A(1)s_B(2)p_B(2)$	$s_A(1)p_A(1)s_B(2)p_B(2)$
AO terms	$s_A(2)p_A(2)s_B(1)p_B(1)$	$s_A(2)p_A(2)s_B(1)p_B(1)$
		$p_A(1)d_A(1)s_B(2)p_B(2)$
		$p_A(2)d_A(2)s_B(1)p_B(1)$
		$s_A(1)p_A(1)p_B(2)d_B(2)$
		$s_A(2)p_A(2)p_B(1)d_B(1)$
		$p_A(1)d_A(1)p_B(2)d_B(2)$
		$p_A(2)d_A(2)p_B(1)d_B(1)$
V_{ee}	V_{ee}^{dd}	V_{ee}^{ext}
C_6	$C_6^{V_{ee}^{dd}}$	$C_6^{V_{ee}^{ext}}$

- Each p orbital incorporates 3 functions: p_x , p_y and p_z , each d orbital includes 5 spherical functions: d_{z^2} , $d_{x^2-y^2}$, d_{xy} , d_{yz} , d_{xz} .

6.2 Methodology

We extract the dispersion energy from the calculations of correlated wavefunction methods following two approaches: (i) by computing the correlation energy difference between a dimer and its individual monomers, and (ii) through the V_{ee} term which is derived from the correlated pair density. The latter approach is linked to the Baerends' and extended Baerends' models, while the former approach can serve as a reference which allows us to compare their performance.

On one hand, to retrieve the total dispersion energy from the total energy calculated by correlated wavefunction methods, we first follow the early work of Baerends *et al.* [90] or Ángyán *et al.* [42], and fit the correlation energy difference between a dimer AB and its two monomers A and B at large separations. The total dispersion energy can be obtained from

$$\begin{aligned} E_{\text{disp}}^{\text{AB}} &\equiv \Delta E_{\text{AB}} = (E_{\text{AB}}^X - E_{\text{AB},\infty}^X) - (E_{\text{AB}}^{\text{ref}} - E_{\text{AB},\infty}^{\text{ref}}) \\ &= (E_{\text{AB}}^X - E_{\text{A}}^X - E_{\text{B}}^X) - (E_{\text{AB}}^{\text{ref}} - E_{\text{A}}^{\text{ref}} - E_{\text{B}}^{\text{ref}}). \end{aligned} \quad (6.1)$$

The correlation energy is determined by the difference between total energy computed by a post-HF method X and by a reference method. For instance, in the case of a singlet H_2 molecule, we can employ FCI as the method X , and the CAS(2,2) can be chosen as a reference. When the H_2 molecule is infinitely separated, it results in two individual hydrogen atoms. In each hydrogen atom, there is only one electron, and there is no need to consider electron correlation. Hence, we can simply take $E_{\text{H}_2,\infty}^{\text{FCI}} = E_{\text{H}_2,\infty}^{\text{HF}} = 2E_{\text{H}}^{\text{HF}}$, then $\Delta E_{\text{H}_2} = E_{\text{H}_2}^{\text{FCI}} - E_{\text{H}_2}^{\text{CAS}(2,2)}$ for the singlet H_2 molecule. When dealing with noble gases, we can employ the HF energy as the reference for each system. Since this approach requires FCI or near FCI solutions and an appropriate reference method (e.g., HF, UHF, CASSCF), it becomes impractical for large systems.

On the other hand, we will calculate the dispersion energy through the V_{ee}^{dd} and V_{ee}^{ext} terms, as they have been shown a $1/R^6$ asymptotic behavior. Let us first provide a theoretical connection between V_{ee}^{dd} and V_{ee}^{ext} terms and the total $E_{\text{disp}}^{\text{AB}}$ through the virial theorem. The electronic virial theorem reads,

$$2T = -V - \sum_{\alpha} q_{\alpha} \frac{\partial E}{\partial q_{\alpha}}, \quad (6.2)$$

where q_{α} denotes nuclear Cartesian coordinates. Since the total electronic energy $E = V + T$, then

$$E = \frac{1}{2}V - \frac{1}{2}\sum_{\alpha} q_{\alpha} \frac{\partial E}{\partial q_{\alpha}}. \quad (6.3)$$

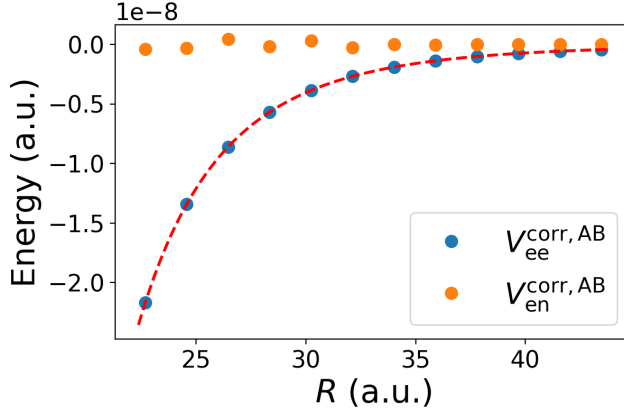


FIGURE 6.1: $V_{ee}^{\text{corr,AB}}$ and $V_{en}^{\text{corr,AB}}$ against the interatomic distances R in large-separated He_2 , calculated at the FCI/aug-cc-pVDZ level of theory, with energy terms extracted through IQA.

The virial theorem requires a wavefunction that satisfies the electronic Schrödinger equation, and the true wavefunctions of FCI and HF (i.e., Completed Basis Set limit) can satisfy it [113]. Then we have

$$\begin{aligned} E_{\text{corr}} &= \frac{1}{2}V^{\text{corr}} - \frac{1}{2}\sum_{\alpha} q_{\alpha} \frac{\partial E_{\text{corr}}}{\partial q_{\alpha}} \\ &= \frac{1}{2}V_{ee}^{\text{corr}} + \frac{1}{2}V_{en}^{\text{corr}} - \frac{1}{2}\sum_{\alpha} q_{\alpha} \frac{\partial E_{\text{corr}}}{\partial q_{\alpha}}, \end{aligned} \quad (6.4)$$

The correlation energy of the dimer system can be decomposed into the intra-monomer and inter-monomer contributions,

$$E_{\text{corr}} = E_{\text{corr}}^{\text{A}} + E_{\text{corr}}^{\text{B}} + E_{\text{corr}}^{\text{AB}}. \quad (6.5)$$

Following the virial theorem, the simplified relationship of $2T = -V$ is validated when $\partial E / \partial q_{\alpha} = 0$. For instance, at equilibrium or for diatomic molecules at dissociation. Let us assume a diatomic molecule AB at dissociation limit (i.e., $R \rightarrow \infty$), once completely separating the diatomic (dimer) and atomic (monomer) contributions, we have

$$E_{\text{corr}}^{\text{AB}} = \frac{1}{2}V_{ee}^{\text{corr,AB}} + \frac{1}{2}V_{en}^{\text{corr,AB}}. \quad (6.6)$$

The $V_{en}^{\text{corr,AB}}$ term decays more rapidly when R approaches infinity than $V_{ee}^{\text{corr,AB}}$, and a numerical evidence of He_2 at large separations is shown in Fig. 6.1. Consider

the separation of dynamic and nondynamic partitions within $V_{ee}^{\text{corr,AB}}$ term, then we have

$$V_{ee}^{\text{corr,AB}} = V_{ee}^{\text{ndy,corr,AB}} + V_{ee}^{\text{dy,corr,AB}}. \quad (6.7)$$

At the dissociation limit ($R \rightarrow \infty$), the intermonomer correlation energy can be split into nondynamic and dynamic correlation components at long-range inter-electronic regions, which corresponds to the long-range $V_{ee}^{\text{ndy,corr,lr}}$ and $V_{ee}^{\text{dy,corr,lr}}$,

$$\begin{aligned} E_{\text{corr}}^{\text{AB}} &= E_{\text{ndy,corr}}^{\text{AB}} + E_{\text{dy,corr}}^{\text{AB}} \\ &= \frac{1}{2} V_{ee}^{\text{ndy,corr,AB}} + \frac{1}{2} V_{ee}^{\text{dy,corr,AB}}. \end{aligned} \quad (6.8)$$

Since the nondynamic correlation partition terms $E_{\text{ndy,corr}}^{\text{AB}}$ or $V_{ee}^{\text{ndy,corr,AB}}$ do not account for dispersion, then the dispersion energy $E_{\text{disp}}^{\text{AB}}$ is retrieved by $E_{\text{dy,corr}}^{\text{AB}}$,

$$E_{\text{disp}}^{\text{AB}} = E_{\text{dy,corr}}^{\text{AB}} = \frac{1}{2} V_{ee}^{\text{dy,corr,AB}} \equiv \frac{1}{2} V_{ee}^{\text{dy,corr,lr}}, \quad (6.9)$$

where $V_{ee}^{\text{dy,corr,lr}}$ denotes the long-range dynamic correlation described by V_{ee} . At large R , we have $V_{ee}^{\text{dy,corr,lr}} \equiv V_{ee}^{\text{dy,corr,AB}}$.

Since V_{ee}^{dd} or V_{ee}^{ext} both result from long-range components of pair density related to dispersion, our hypothesis is that when using only $s + p$ basis functions, $V_{ee}^{dd} = V_{ee}^{\text{ext}} = 2E_{\text{disp}}^{\text{AB}}$, and when using $s + p + d$ basis functions, we have $V_{ee}^{\text{ext}} = 2E_{\text{disp}}^{\text{AB}}$. These relationships will be numerically examined in the next sections of this chapter.

6.3 Computational Details

We performed calculations at the MP2, CISD, CCSD, CCSD(T) levels for each molecule in a broad range of separations, using the PySCF package [371, 372]. Our in-house Python program, which relies on the Numpy [381], Scipy [382], and Pandas [383, 384] libraries, was employed for the evaluations of V_{ee}^{dd} and V_{ee}^{ext} . The SAPT calculations were performed using Psi4 [368, 369]. A convergence energy threshold was set at 10^{-12} (a.u.) for all the calculations. The basis sets employed were aug-cc-pVXZ (X=D,T,Q,5,6) [397, 398, 411]. Tab. 6.1 shows the extended induced multipole-induced multipole two-electron AO quartets. The two-electron integrals based on these terms were selected for calculating V_{ee}^{ext} . The dispersion energy coefficient C_6 terms (i.e., $C_6^{V_{ee}^{dd}}$ and $C_6^{V_{ee}^{\text{ext}}}$) were obtained by fitting the corresponding energy values in the large range of interatomic distances R (from 22.68 to 43.47 a.u.), using a nonlinear least squares technique

implemented in the Scipy [412] package. The values of V_{ee}^{dd} were fitted to the polynomial regression function, $-C_6^{V_{ee}^{dd}}/R^6$, whereas V_{ee}^{ext} values were fitted to $-C_6^{V_{ee}^{ext}}/R^6 - C_8^{V_{ee}^{ext}}/R^8$. In this chapter, we only focus on the C_6 terms, as it is the leading term of dispersion energy.

All the IQA calculations were done in collaboration with Prof. Ángel Martín Pendás, using a modified version of their Promolden program [344, 413], which provides energy partition results with exceptional precision.

6.4 Results and Discussion

TABLE 6.2: C_6 terms of H_2 and He_2 obtained from FCI.

Molecules	Basis	Config.	C_6	$C_6^{V_{ee}^{dd}}/2$	$C_6^{V_{ee}^{ext}}/2$	Lit.
H_2	AVTZ	$4s3p2d$	6.51	6.51	6.51	6.50
He_2	AVTZ	$4s3p2d$	1.47	1.47	1.47	1.46

- The basis set AVTZ denotes aug-cc-pVTZ.
- Lit. stands for literature, and the C_6 values from the literature were all sourced from [414].

Tab. 6.2 shows the C_6 terms of the singlet molecules of H_2 and He_2 calculated at the FCI level of theory with the aug-cc-pVTZ basis set ($4s3p2d$). The values of $C_6^{V_{ee}^{dd}}/2$ and $C_6^{V_{ee}^{ext}}/2$ for both H_2 and He_2 were found to be equivalent to the C_6 values obtained from the correlation energy in Eq. (6.1). Moreover, these values closely matched the values of C_6 reported in the literature [414]. Hence, for calculating C_6 of the H_2 and He_2 molecules, the extended Baerends' model, which includes induced multipole-induced multipole terms, did not result in any improvements from V_{ee}^{ext} when compared to V_{ee}^{dd} .

However, the $C_6^{V_{ee}^{dd}}/2$ values (in Tab. 6.4) for larger diatomic molecules beyond H_2 , He_2 , and Be_2 are far deviated from the C_6 values calculated from the correlation energy (in Tab. 6.3). In particular, the deviation error of Baerends' model compared to the reference values (in Tab. 6.3) is relatively high for larger noble gas dimers. On the other hand, as expected, the $C_6^{V_{ee}^{ext}}/2$ values shown in Tab. 6.5 have been significantly improved and were valid for all these correlated wavefunction methods. Noticeably, when increasing the basis set size in the HeNe case, the $C_6^{V_{ee}^{ext}}/2$ value retrieved from CCSD(T) approached the C_6 value in literature. Since the wavefunction methods rely on the choice of basis sets, our objective is not to achieve high agreement with the C_6 values from the literature for all the

TABLE 6.3: C_6 of diatomic molecules obtained from various methods.

Molecules	Basis	MP2	CISD	CCSD	CCSD(T)	Lit.
HeNe	AVDZ	2.12	2.18	2.27	2.49	3.03
HeNe	AVTZ	2.36	2.41	2.59	2.87	3.03
HeNe	AVQZ	2.41	2.44	2.66	2.97	3.03
HeNe	AV5Z	2.42	2.44	2.67	2.98	3.03
HeAr	AVDZ	8.78	7.76	8.44	9.09	9.55
HeKr	AVDZ	12.30	10.76	11.71	12.55	13.42
NeAr	AVDZ	15.86	12.43	13.92	15.27	19.5
Ne ₂	AVDZ	4.12	3.78	4.28	4.48	6.38
Ar ₂	AVDZ	69.52	44.93	52.70	58.14	64.3

• The basis set AVXZ denotes aug-cc-pVXZ (X=D,T,Q,5).

• Lit. stands for literature, and the C_6 values from the literature were all sourced from [414].

TABLE 6.4: $C_6^{V_{ee}^{dd}}/2$ of diatomic molecules obtained from various methods.

Molecules	Basis	MP2	CISD	CCSD	CCSD(T)	Lit.
HeNe	AVDZ	0.48	0.61	0.66	0.73	3.03
HeNe	AVTZ	0.49	0.58	0.64	0.72	3.03
HeNe	AVQZ	0.49	0.57	0.64	0.72	3.03
HeNe	AV5Z	0.49	0.56	0.63	0.71	3.03
HeAr	AVDZ	1.34	1.57	1.72	1.93	9.55
HeKr	AVDZ	1.93	2.19	2.40	2.68	13.42
NeAr	AVDZ	0.58	0.70	0.83	0.99	19.5
Ne ₂	AVDZ	0.21	0.27	0.32	0.37	6.38
Ar ₂	AVDZ	1.70	1.89	2.33	2.81	64.3
Be ₂	AVDZ	253.77	160.72	136.98	165.88	214

• The basis set AVXZ denotes aug-cc-pVXZ (X=D,T,Q,5).

• Lit. stands for literature, and the C_6 values from the literature were all sourced from [414].

TABLE 6.5: $C_6^{V_{ee}^{ext}}/2$ of diatomic molecules obtained from various methods.

Molecules	Basis	MP2	CISD	CCSD	CCSD(T)	Lit.
HeNe	AVDZ	2.12	2.17	2.31	2.49	3.03
HeNe	AVTZ	2.36	2.37	2.60	2.87	3.03
HeNe	AVQZ	2.42	2.40	2.66	2.96	3.03
HeNe	AV5Z	2.42	2.39	2.67	2.97	3.03
HeAr	AVDZ	8.74	7.68	8.45	9.10	9.55
HeKr	AVDZ	12.28	10.64	11.72	12.56	13.42
NeAr	AVDZ	15.86	12.22	13.92	15.27	19.5
Ne ₂	AVDZ	4.15	3.72	4.15	4.50	6.38
Ar ₂	AVDZ	69.54	44.02	52.72	58.16	64.3
Be ₂	AVDZ	252.79	159.48	135.52	192.05	214

- The basis set AVXZ denotes aug-cc-pVXZ (X=D,T,Q,5).
- Lit. stands for literature, and the C_6 values from the literature were all sourced from [414].

molecules we tested. Instead, a more reasonable comparison can be done between the C_6 values retrieved by fitting ΔE_{AB} in Eq. (6.1) and the ones obtained through Baerends’ model or the extended Baerends’ model, which are all evaluated using the same wavefunction method with a given basis set.

To assess the improvement in the results of C_6 obtained from the extended Baerends’ model ($C_6^{V_{ee}^{ext}}/2$), as shown in Tab. 6.5, compared to the ones from Baerends’ model ($C_6^{V_{ee}^{dd}}/2$) in Tab. 6.4, we use the C_6 values derived from the correlation energy in Tab. 6.3 as reference. Then we evaluate the Mean Absolute Percentage Error (MAPE) of $C_6^{V_{ee}^{dd}}/2$ and $C_6^{V_{ee}^{ext}}/2$ across various post-HF methods, as illustrated in Fig. 6.2. The MAPE values for $C_6^{V_{ee}^{dd}}/2$ exceed 80% for all these correlated wavefunction methods, while they drop significantly, falling below 1.54%, when considering the V_{ee}^{ext} model. Consequently, the extended V_{ee}^{ext} model can effectively retrieve dispersion energy from correlated wavefunction methods.

Through numerical assessment of the two pair density models to isolate dispersion from post-HF calculations on various diatomic systems, we first verified the theoretical connection between E_{disp}^{AB} and $V_{ee}^{dy,corr,lr}/2$. In practice, this relationship extends beyond true FCI, CASSCF, and HF methods to include non-variational methods such as MP2, CCSD, CCSD(T), and the variational method CISD which is not size-consistent. We note that the current numerical results do not really satisfy the virial theorem, especially when concerning the virial ratio derived

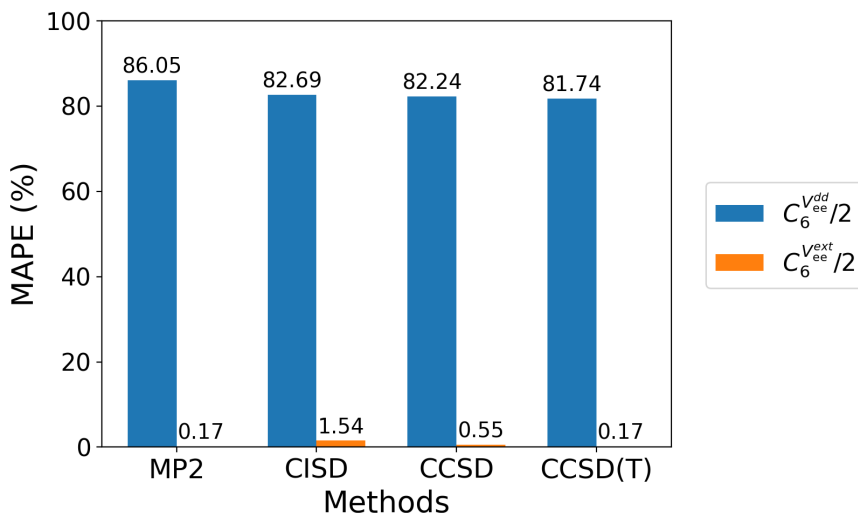


FIGURE 6.2: Mean Absolute Percentage Error (MAPE) comparison of C_6 retrieved from Baerends' model ($C_6^{V_{ee}^{dd}}/2$) and extended Baerends' model ($C_6^{V_{ee}^{ext}}/2$) over various post-HF methods. For each post-HF method, the reference C_6 values were taken from Tab. 6.3, and the data of Be_2 was not included because an appropriate dispersionless reference method was not found for Be_2 .

from correlation energy components (i.e., $V_{\text{corr}}/T_{\text{corr}} = -2$, also known as the correlated virial ratio [415]). However, compared to the correlated virial ratio, this relationship, $E_{\text{disp}}^{\text{AB}} = V_{\text{ee}}^{\text{dy,corr,lr}}/2$, demonstrates a lower sensitivity to the infinite separation of diatomic molecules and the incompleteness of basis set limits.

For the simple H_2 and He_2 molecules, we demonstrated the relationship $C_6^{V_{ee}^{dd}} = 2C_6$, which holds true for both Baerends' and extended Baerends's models. However, as we extended our analysis to larger systems, we found that including the extended induced multipole-induced multipole terms ($V_{\text{ee}}^{\text{ext}}$) becomes necessary to properly account for dispersion interactions. Remarkably, the extended Baerends' model shows a promising path for calculating C_6 of the diatomic systems. This model only relies on very few quartet term-based long-range components of the pair density, and it does not require a dispersionless reference method (e.g., HF, CASSCF) to isolate the long-range dynamic correlation. Our results highlight the significance of incorporating higher multipole terms when dealing with larger systems (in the presence of d orbitals). Notwithstanding, when it comes to polyatomic molecules, retrieving dispersion energy through $V_{\text{ee}}^{\text{ext}}/2$ remains a challenge. We consider one possible reason is that the approximate 2-RDM (in

the AO basis) of the extended Baerends' model also involves many other created instantaneous dipoles among atoms within the monomers, making it challenging to isolate their individual contributions to dispersion interactions between the two separated monomers. Therefore, further analysis might be required to address this issue.

DISPERSION IN PAIR DENSITY TERMS

7.1 Introduction

Hydrogen or helium dimers are frequently employed as primary examples in the study of London dispersion interactions. For the ground-state hydrogen or helium atoms, the overall shape of the charge distribution is spherical due to the spherical symmetry of the 1s atomic orbitals involved. However, due to the uncertainty principle [416], the charge distributions cannot remain stationary. The random fluctuation of these charge distributions generates instantaneous multipoles, giving rise to rapidly fluctuating fields and leading to London dispersion [41]. The helium dimer (He_2) is often mentioned in lectures or textbooks as a typical vdW system. However, its complexity arises from the coexistence of dispersion and intra-atomic electron correlation within each helium monomer. Hence, in the absence of intra-atomic electron correlation, the lowest triplet state of the H_2 molecule (two electrons with spin-up or spin-down) at large interatomic separations serves as the simplest comprehensible example of a vdW bonded system [297].

Baerends *et al.* [88–90] as well as Ángyán *et al.* [42] independently utilized induced dipole-induced dipole terms in their simplified model systems for H_2 or He_2 . As shown in the previous Chapter 6, these terms form the basis for constructing Baerends’ model, and this model has been demonstrated to be highly accurate for recovering C_6 of H_2 and He_2 systems by using the relationship $V_{ee}^{\text{dy,corr,AB}} = 2E_{\text{disp}}^{\text{AB}}$. For treating larger molecules that include d orbitals, we have

shown the necessity of using the extended Baerends' model by adding more terms. Yet, the contribution of dispersion energies from the electron-electron interaction energy partition terms (e.g., V_{ee}^{corr} , $\Delta V_{ee}^{c_I}$, $\Delta V_{ee}^{c_{II}}$), and the role of pair density partition c_{II} [3] in calculating the total dispersion energy have not been thoroughly explored.

In this chapter, we will first examine dispersion interactions in these three molecular systems: H_2 (singlet and triplet) [88, 90, 359, 417, 418], and He_2 at large interatomic separation distances. By employing FCI calculations, we extract the dispersion energy of these systems and analyze the dispersion terms in terms of total energy and pair density partitions. Firstly, we aim to understand the contribution of decomposed energy terms (e.g., T , V_{en} , V_{ee} , $\Delta V_{ee}^{c_I}$, $\Delta V_{ee}^{c_{II}}$, V_{ee}^{dd}) to dispersion energy, with a comprehensive analysis of H_2 and He_2 cases. Secondly, our objective is to use $\Delta V_{ee}^{c_{II},lr}$ to recover dispersion energy, and extend its applicability to various wavefunction methods over some larger dimer systems.

With respect to the pair density and Coulomb hole partitions, our main goal is to understand the relationship between the total dispersion energy and the Coulomb hole partition c_{II} , denoted as $h_{c_{II}}(s)$, [3, 92], particularly in the context of long-range regime. For this purpose, we introduce a new concept *dispersion hole*, which accounts for dispersion interactions in terms of interelectronic distance, and it can be applied to calculate and identify dispersion. Furthermore, our secondary goal is to understand the connection between $1/R^3$ asymptotic behavior of $h_{disp}(R)$ [3, 91] and the $1/R^6$ dependence of dispersion energy.

7.2 Computational Details

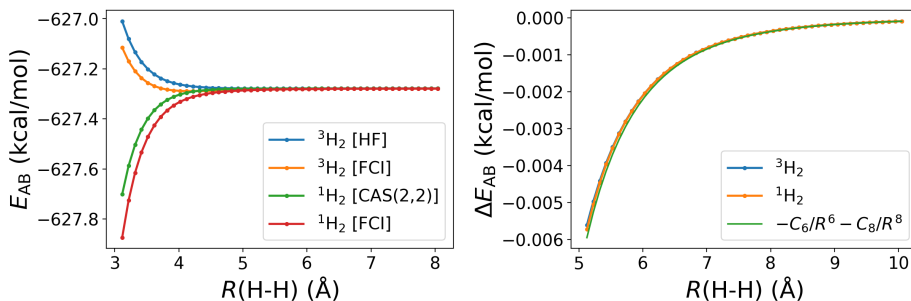


FIGURE 7.1: Potential energy surface E_{AB} and ΔE_{AB} for H_2 molecule (singlet $^1H_2$ and triplet $^3H_2$), calculated with aug-cc-pVTZ basis set. The reference dispersion curve $C_6 = 6.4990267054$ and $C_8 = 124.39908358$ are taken from Ref. [313].

To investigate the role of dispersion energy terms and partitions, as well as the basis set dependency on the dispersion energy coefficients (C_6 and C_8)¹, our assessments included both H_2 (singlet and triplet) and He_2 dissociation cases. For the dissociation of H_2 (singlet and triplet) over a large range of interatomic distances (R ranging from 22.68 to 43.47 a.u.), we employed truncated basis sets consisting of $s + p$, $s + p + d$, and $s + p + d + f$ orbitals in the aug-cc-pVXZ (X=D, T, Q, 5, 6) basis set. For the dissociation of He_2 , we employed the same range of interatomic distances (R) and utilized the aug-cc-pVXZ basis sets with X=D, T, and Q [397, 398, 411].

In the case of H_2 , we used FCI as the method X , and we adopted the CAS(2,2) as a reference for singlet and HF as a reference for triplet (see Fig. 7.1). When the H_2 molecule (both singlet and triplet) is infinitely separated, it results in two individual hydrogen atoms. In each hydrogen atom, there is only one electron and no electron correlation is needed to consider. Hence, we can simply take $E_{H_2,\infty}^{FCI} = E_{H_2,\infty}^{HF} = 2E_H^{HF}$, then $\Delta E_{H_2} = E_{H_2}^{FCI} - E_{H_2}^{ref}$.

All the HF, CASSCF, and FCI calculations were performed using the PySCF package [371, 372]. To evaluate the radial intracule, we used the open-source RH02_OPS program [419], which is based on the algorithm developed by Cioslowski and Liu [420]. In addition, to calculate various energy terms and partitions, we utilized an in-house program implemented in Python3, which uses Numpy [381], Scipy [382], and Pandas [383, 384] libraries. This program facilitated the calculations of kinetic energy (T), electron-nuclear attraction energy (V_{en}), electron-electron interaction energy (V_{ee}), Coulomb energy (J), exchange energy (K), as well as the V_{ee}^{corr} partitions: ΔV_{ee}^{cI} and ΔV_{ee}^{cII} , [3] along with the range-separated components: short-range terms $\Delta V_{ee}^{cI,sr}$ and $\Delta V_{ee}^{cII,sr}$, as well as the long-range terms $\Delta V_{ee}^{cI,lr}$ and $\Delta V_{ee}^{cII,lr}$. In practice, the range separation was achieved by selecting two-electron integrals in terms of AOs. Specifically, we considered only the terms such as $\chi_A(1)\chi_A(1')\chi_B(2)\chi_B(2')$ and $\chi_A(2)\chi_A(2')\chi_B(1)\chi_B(1')$, which contribute to the long-range interactions. We calculated first ΔV_{ee}^{cI} and ΔV_{ee}^{cII} coming from these terms. Then, the short-range interaction energies can be obtained by simply subtracting the long-range contributions.

For determining C_6 coefficients, we employed a non-linear least squares fitting technique from the Scipy package [412]. The fitting process involved obtaining the corresponding energy values at a large range of R and fitting them by polynomial regression functions (e.g., $-C_6/R^6$, or $-C_6/R^6 - C_8/R^8$). In particular, for basis sets that consist only of s type functions, like STO-3G, no dispersion energies can be

¹In this thesis, C_{10} will not be considered due to the issue of basis sets.

obtained. However, when p functions were included, it accounted for the induced dipole-induced dipole contribution to dispersion (C_6). Additionally, the inclusion of orbitals beyond p introduced the induced dipole-induced quadrupole term (C_8) and so on. Hence, for basis sets containing s and p functions, the fitting function became $-C_6/R^6$, while for basis sets with orbitals beyond p , the fitting function was modified to $-C_6/R^6 - C_8/R^8$.

In addition to the H_2 and He_2 systems, other dimer molecules used in this study were sourced from a recent study by Mazziotti *et al.* [364]. We performed computations (e.g., MP2, CISD, CCSD, CCSD(T)) for each dimer molecule in a broad range of separations, using the PySCF package [371, 372]. An in-house Python program, which relies on the Numpy [381], Scipy [382], and Pandas [383, 384] libraries, was employed for the evaluations of $\Delta V_{ee}^{c_{II}}$ and $\Delta V_{ee}^{c_{II},lr}$. A convergence threshold of energy was set at 10^{-12} a.u. for all the calculations. The basis sets employed were aug-cc-pVXZ (X=D,T,Q,5) [397, 398, 411]. The C_6 coefficient terms were obtained by fitting the corresponding energy values in the large R range of 22.68 to 43.47 a.u. using a non-linear least squares technique implemented in the Scipy [412] package. For all the molecules in this study using basis sets that include d orbitals or orbitals beyond d , the polynomial regression fitting function employed for the analysis is $-C_6/R^6 - C_8/R^8$. In this chapter, we only focus on the C_6 values, while the fitted C_8 values will not be discussed.

7.3 Results and Discussion

7.3.1 Dispersion in H_2 Molecule

Tab. 7.1 shows that the fitting of the total energy difference between the FCI and reference method tends to yield correct dispersion energy coefficients, compared with the literature $C_6 = 6.4990267054$ and $C_8 = 124.39908358$ of Thakkar [313]. Considering that C_6 and C_8 are determined by fitting ΔE_{AB} (Eq. (6.1)) as a function of R , the nonlinear least squares regression approach does not allow for achieving high precision of C_6 and C_8 . In addition, since the truncated basis sets achieved different degrees of convergence within the given separation distance range, a straightforward extrapolation of C_6 against the basis set is not possible. Even though it might be possible to improve the precision of determining C_6 by increasing the separation distance R for each basis set, this is not our current purpose. Our goal is to analyze the contribution of the electronic energy components to dispersion (e.g., T , V_{en} , and V_{ee}) and the long-range pair density partition c_{II} .

The total energy can be split into kinetic energy T , electron-nuclear attraction

TABLE 7.1: Dispersion coefficients C_6 and C_8 of H_2 (singlet and triplet). They were determined by fitting ΔE_{AB} in Eq. (6.1) over a fitting range of 22.68 to 43.47 a.u. The ΔE_{AB} term was obtained from the total energy difference between FCI and a reference method, CAS(2,2) for the singlet and HF for the triplet H_2 molecule.

Basis set	Singlet		Triplet	
	C_6	C_8	C_6	C_8
aug-cc-pVDZ (3s2p)	6.334		6.334	
aug-cc-pVTZ (4s3p)	6.506		6.506	
aug-cc-pVQZ (5s4p)	6.498		6.498	
aug-cc-pV5Z (6s5p)	6.480		6.480	
aug-cc-pV6Z (7s6p)	6.479		6.479	
aug-cc-pVTZ (4s3p2d)	6.505	74.229	6.505	74.227
aug-cc-pVQZ (5s4p3d)	6.497	96.471	6.497	96.470
aug-cc-pV5Z (6s5p4d)	6.478	109.856	6.478	109.855
aug-cc-pV6Z (7s6p5d)	6.477	119.711	6.477	119.723
aug-cc-pVQZ (5s4p3d2f)	6.496	97.882	6.496	97.881
aug-cc-pV5Z (6s5p4d3f)	6.475	112.430	6.475	112.433
aug-cc-pV6Z (7s6p5d4f)	6.474	122.911	6.474	122.911

energy V_{en} , electron-electron interaction energy V_{ee} and nuclear-nuclear repulsion energy V_{nn} . Considering that the classical Coulomb formalism of nuclear-nuclear repulsion energy V_{nn} does not account for the dispersion energy, our attention is solely directed towards the remaining three components: T , V_{en} , and V_{ee} . Hence, ΔE_{AB} is decomposed into contributions from T , V_{en} , and V_{ee} terms. The dispersion energy retrieved by each term still follows Eq. (6.1) and results in ΔT , ΔV_{en} , and ΔV_{ee} terms. The corresponding C_6 and C_8 terms of H_2 molecule (singlet and triplet) are exhibited in Tab. 7.2, Tab. 7.3 and Tab. 7.4, respectively. On one hand, it is observed that C_6 terms retrieved from both singlet and triplet states of the H_2 molecule are nearly identical, while they are slightly affected by the basis set truncation levels. In the following work, our main focus will be on C_6 terms, as C_8 terms are more susceptible to numerical errors. On the other hand, despite the fact that the one-electron energy terms ΔT and ΔV_{en} provide a more substantial contribution compared to the two-electron energy term ΔV_{ee} , they can partially cancel out each other due to having opposite signs, resulting in half the magnitude of the two-electron energy term ΔV_{ee} .

TABLE 7.2: Dispersion coefficients $C_6^{\Delta T}$ and $C_8^{\Delta T}$ of H_2 (singlet and triplet). They were determined by fitting ΔT over a fitting range of 22.68 to 43.47 a.u. The ΔT term was obtained from the T energy term difference between FCI and a reference method, CAS(2,2) for the singlet and HF for the triplet H_2 molecule.

Basis set	Singlet		Triplet	
	$C_6^{\Delta T}$	$C_8^{\Delta T}$	$C_6^{\Delta T}$	$C_8^{\Delta T}$
aug-cc-pVDZ (3s2p)	29.153		29.079	
aug-cc-pVTZ (4s3p)	31.806		31.796	
aug-cc-pVQZ (5s4p)	32.296		31.845	
aug-cc-pV5Z (6s5p)	32.813		31.807	
aug-cc-pV6Z (7s6p)	32.403		31.701	
aug-cc-pVTZ (4s3p2d)	30.763	831.552	31.077	448.696
aug-cc-pVQZ (5s4p3d)	30.119	1655.565	31.719	588.590
aug-cc-pV5Z (6s5p4d)	32.570	533.438	31.672	726.432
aug-cc-pV6Z (7s6p5d)	31.235	1333.760	31.553	844.214
aug-cc-pVQZ (5s4p3d2f)	32.151	604.777	31.716	593.504
aug-cc-pV5Z (6s5p4d3f)	31.545	1027.243	31.667	736.494
aug-cc-pV6Z (7s6p5d4f)	30.281	1739.949	31.537	862.228

An interesting observation in the case of the H_2 molecule (both singlet and triplet) is that $C_6^{\Delta V_{ee}}$ is approximately equal to $2C_6$. Taking into account the relationship $C_6^{V_{ee}^{dy,corr,lr}} = 2C_6$ established in [Chapter 6](#), the contribution of V_{ee} term to dispersion should only occur at the long-range interelectronic regime for the H_2 molecule. At very large separations of the H_2 molecule, we assume that the two-electron interactions consist of classical Coulomb repulsion and quantum dispersion interactions, resulting in $V_{ee}^{FCI} = V_{ee}^{disp} + 1/R$. As shown in [Tab. A9](#), $C_6^{\Delta V_{ee}}$ is also found to be identical to $C_6^{\Delta V_{ee}^*}$ which were obtained by simply fitting the energy difference: $V_{ee}^{FCI} - 1/R$. The V_{ee} term, $1/R$, for H_2 molecule will be discussed later in [Eq. \(7.5\)](#).

The V_{ee} term (shown in [Eq. \(3.77\)](#)) can be decomposed into Coulomb energy term, J , exchange energy term, K , and the cumulant energy term, C . Particularly, $C = 0$ for the HF method. [Tab. A10](#) and [Tab. A11](#) show the J and K contributions to the dispersion coefficient. The determination of $C_6^{\Delta J}$ for H_2 molecule (singlet) involved fitting the energy difference between J^{FCI} and $J^{CAS(2,2)}$, while $C_6^{\Delta J}$ and $C_6^{\Delta K}$ for H_2 molecule (triplet) were obtained by fitting the energy differences

TABLE 7.3: Dispersion coefficients $C_6^{\Delta V_{\text{en}}}$ and $C_8^{\Delta V_{\text{en}}}$ of H_2 (singlet and triplet). They were determined by fitting ΔV_{en} over a fitting range of 22.68 to 43.47 a.u. The ΔV_{en} term was obtained from the V_{en} energy term difference between FCI and a reference method, CAS(2,2) for the singlet and HF for the triplet H_2 molecule.

Basis set	Singlet		Triplet	
	$C_6^{\Delta V_{\text{en}}}$	$C_8^{\Delta V_{\text{en}}}$	$C_6^{\Delta V_{\text{en}}}$	$C_8^{\Delta V_{\text{en}}}$
aug-cc-pVDZ (3s2p)	-35.455		-35.389	
aug-cc-pVTZ (4s3p)	-38.273		-38.270	
aug-cc-pVQZ (5s4p)	-38.752		-38.310	
aug-cc-pV5Z (6s5p)	-39.247		-38.252	
aug-cc-pV6Z (7s6p)	-38.840		-38.146	
aug-cc-pVTZ (4s3p2d)	-37.286	-868.725	-37.607	-482.942
aug-cc-pVQZ (5s4p3d)	-36.636	-1707.214	-38.245	-637.316
aug-cc-pV5Z (6s5p4d)	-39.071	-594.372	-38.182	-783.713
aug-cc-pV6Z (7s6p5d)	-37.738	-1400.389	-38.064	-907.498
aug-cc-pVQZ (5s4p3d2f)	-38.664	-659.917	-38.241	-643.284
aug-cc-pV5Z (6s5p4d3f)	-38.045	-1089.624	-38.175	-795.655
aug-cc-pV6Z (7s6p5d4f)	-36.783	-1809.064	-38.046	-927.794

between J^{FCI} and J^{HF} , or between K^{FCI} and K^{HF} . In the case of H_2 molecule (singlet), the exchange term of V_{ee} is absent, resulting in $K = 0$. Conversely, in the H_2 molecule (triplet), $C_6^{\Delta J}$ and $C_6^{\Delta K}$ exhibit opposite signs and can partially cancel each other.

Next, we will explore the role of pair density partition in understanding the origin of dispersion arising from long-range Coulomb interactions. On one hand, following the pair density partition approach in Fig. 3.3 and using correlated pair density from method X (e.g., $X = \text{FCI}$ in the case of H_2 molecule), then $V_{\text{ee}}^{\text{corr}}$ can be partitioned into

$$V_{\text{ee}}^{\text{corr}} = V_{\text{ee}}^X - V_{\text{ee}}^{\text{HF}} = \Delta V_{\text{ee}}^{c_I} + \Delta V_{\text{ee}}^{c_{II}}, \quad (7.1)$$

$$\Delta V_{\text{ee}}^{c_I} = V_{\text{ee}}^{\text{SD}} - V_{\text{ee}}^{\text{HF}} = (J^X - J^{\text{HF}}) + (K^X - K^{\text{HF}}), \quad (7.2)$$

$$\Delta V_{\text{ee}}^{c_{II}} = V_{\text{ee}}^X - V_{\text{ee}}^{\text{SD}} = V_{\text{ee}}^X - J^X - K^X = C^X. \quad (7.3)$$

On the other hand, to identify the contribution of dispersion interactions from $\Delta V_{\text{ee}}^{c_I}$ and $\Delta V_{\text{ee}}^{c_{II}}$, a range separation treatment is required to isolate the long-range components that account for dispersion interactions. Then, only the long-range

TABLE 7.4: Dispersion coefficients $C_6^{\Delta V_{ee}}$ and $C_8^{\Delta V_{ee}}$ of H_2 (singlet and triplet). They were determined by fitting ΔV_{ee} over a fitting range of 22.68 to 43.47 a.u. The ΔV_{ee} term was obtained from the V_{ee} energy term difference between FCI and a reference method, CAS(2,2) for the singlet and HF for the triplet H_2 molecule.

Basis set	Singlet		Triplet	
	$C_6^{\Delta V_{ee}}$	$C_8^{\Delta V_{ee}}$	$C_6^{\Delta V_{ee}}$	$C_8^{\Delta V_{ee}}$
aug-cc-pVDZ (3s2p)	12.636		12.643	
aug-cc-pVTZ (4s3p)	12.973		12.981	
aug-cc-pVQZ (5s4p)	12.954		12.963	
aug-cc-pV5Z (6s5p)	12.914		12.925	
aug-cc-pV6Z (7s6p)	12.915		12.924	
aug-cc-pVTZ (4s3p2d)	13.028	111.403	13.035	108.471
aug-cc-pVQZ (5s4p3d)	13.014	148.122	13.022	145.196
aug-cc-pV5Z (6s5p4d)	12.978	170.790	12.987	167.135
aug-cc-pV6Z (7s6p5d)	12.979	186.339	12.988	183.007
aug-cc-pVQZ (5s4p3d2f)	13.008	153.020	13.020	147.662
aug-cc-pV5Z (6s5p4d3f)	12.976	174.811	12.984	171.593
aug-cc-pV6Z (7s6p5d4f)	12.975	192.026	12.983	188.477

dynamic correlation components can be connected to the relationship in [Eq. \(6.9\)](#) that has been established in [Chapter 6](#). Specifically, the connection lies between ΔV_{ee}^{cII} and E_{disp} .

In the case of the singlet H_2 molecule at large separation distance, we observe that the exact long-range electron-electron interaction energy includes a $1/R$ term and the dispersion term (shown in [Tab. A9](#) in Appendix A.5). Let us consider a simplified H_2 (singlet) model [\[3\]](#) to clarify the origin of the long-range $1/R$ energy term. In this model, a minimal basis set is used, where each atom is assigned one 1s GTO. We should emphasize that this model does not account for dispersion, as instantaneous dipole moments cannot be generated solely using spherically symmetric s-type basis functions even though it is calculated at the FCI level. Thus, it is also referred to as the minimal H_2 model in this study. At the dissociation limit (i.e., the interatomic distance $R \rightarrow \infty$), we can neglect the overlap between the two atomic orbitals. The FCI coefficients of the ground state and first double excitation state configurations both converge ($c_0 = -c_1 = 1/\sqrt{2}$). Therefore, as R goes to infinity, the exact spinless pair density is given by (see

support information in Ref. [3])

$$\begin{aligned}\rho_2^{\text{FCI}}(\mathbf{r}_1, \mathbf{r}_2)|_{R \rightarrow \infty} &= 2|\Psi_{\text{FCI}}(\mathbf{r}_1, \mathbf{r}_2)|^2|_{R \rightarrow \infty} \\ &= (|\chi_A(\mathbf{r}_1)|^2|\chi_B(\mathbf{r}_2)|^2 + |\chi_B(\mathbf{r}_1)|^2|\chi_A(\mathbf{r}_2)|^2).\end{aligned}\quad (7.4)$$

We note that the FCI pair density at the dissociation limit is exclusively contributed by the covalent two-electron AO quartets, indicating its long-range characteristics in relation to interelectronic distance. Then, the closed form of $V_{\text{ee}}^{\text{FCI}}|_{R \rightarrow \infty}$ can be determined as

$$\begin{aligned}V_{\text{ee}}^{\text{FCI}}|_{R \rightarrow \infty} &= \frac{1}{2} \int \int \frac{\rho_2^{\text{FCI}}(\mathbf{r}_1, \mathbf{r}_2)|_{R \rightarrow \infty}}{||\mathbf{r}_1 - \mathbf{r}_2||} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{N_s^4}{2} \int \int \frac{e^{-2\alpha(||\mathbf{r}_1 - \mathbf{r}_A||^2 + ||\mathbf{r}_2 - \mathbf{r}_B||^2)} + e^{-2\alpha(||\mathbf{r}_1 - \mathbf{r}_B||^2 + ||\mathbf{r}_2 - \mathbf{r}_A||^2)}}{||\mathbf{r}_1 - \mathbf{r}_2||} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{R},\end{aligned}\quad (7.5)$$

where $N_s = (2\alpha/\pi)^{3/4}$ denotes the normalization factor and α denotes the exponent of the 1s GTO basis function, respectively. The interatomic distance $R = ||r_A - r_B||$. The unit of energies is always in Hartree.

The spinless Single-Determinant (SD) approximate pair density (for $R \rightarrow \infty$) is written as (see support information in Ref. [3])

$$\begin{aligned}\rho_2^{\text{SD}}(\mathbf{r}_1, \mathbf{r}_2)|_{R \rightarrow \infty} &= 2|\Psi_{\text{SD}}(\mathbf{r}_1, \mathbf{r}_2)|^2|_{R \rightarrow \infty} \\ &= (|\chi_A(\mathbf{r}_1)|^2|\chi_B(\mathbf{r}_2)|^2 + |\chi_B(\mathbf{r}_1)|^2|\chi_A(\mathbf{r}_2)|^2) \\ &\quad + \frac{1}{2}(|\chi_A(\mathbf{r}_1)|^2|\chi_A(\mathbf{r}_2)|^2 + |\chi_B(\mathbf{r}_1)|^2|\chi_B(\mathbf{r}_2)|^2).\end{aligned}\quad (7.6)$$

In contrast to the FCI pair density, it includes contributions not only from covalent two-electron terms (long-range) but also from ionic two-electron terms (short-range). Then, the closed form of $V_{\text{ee}}^{\text{SD}}|_{R \rightarrow \infty}$ can be derived by

$$\begin{aligned}V_{\text{ee}}^{\text{SD}}|_{R \rightarrow \infty} &= \frac{1}{2} \int \int \frac{\rho_2^{\text{SD}}(\mathbf{r}_1, \mathbf{r}_2)|_{R \rightarrow \infty}}{||\mathbf{r}_1 - \mathbf{r}_2||} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{N_s^4}{2} \int \int \frac{e^{-2\alpha(||\mathbf{r}_1 - \mathbf{r}_A||^2 + ||\mathbf{r}_2 - \mathbf{r}_B||^2)} + e^{-2\alpha(||\mathbf{r}_1 - \mathbf{r}_B||^2 + ||\mathbf{r}_2 - \mathbf{r}_A||^2)}}{||\mathbf{r}_1 - \mathbf{r}_2||} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad + \frac{N_s^4}{4} \int \int \frac{e^{-2\alpha(||\mathbf{r}_1 - \mathbf{r}_A||^2 + ||\mathbf{r}_2 - \mathbf{r}_A||^2)} + e^{-2\alpha(||\mathbf{r}_1 - \mathbf{r}_B||^2 + ||\mathbf{r}_2 - \mathbf{r}_B||^2)}}{||\mathbf{r}_1 - \mathbf{r}_2||} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sqrt{\frac{\alpha}{\pi}} + \frac{1}{R}.\end{aligned}\quad (7.7)$$

The spinless Hartree-Fock pair density (for $R \rightarrow \infty$) reads (see support information in Ref. [3])

$$\begin{aligned}\rho_2^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)|_{R \rightarrow \infty} &= 2|\Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)|^2|_{R \rightarrow \infty} \\ &= \frac{1}{2}(|\chi_A(\mathbf{r}_1)|^2|\chi_B(\mathbf{r}_2)|^2 + |\chi_B(\mathbf{r}_1)|^2|\chi_A(\mathbf{r}_2)|^2) \\ &\quad + \frac{1}{2}(|\chi_A(\mathbf{r}_1)|^2|\chi_A(\mathbf{r}_2)|^2 + |\chi_B(\mathbf{r}_1)|^2|\chi_B(\mathbf{r}_2)|^2).\end{aligned}\quad (7.8)$$

Similar to the SD pair density, it also involves a mixture of contributions from covalent two-electron terms (long-range) and ionic two-electron terms (short-range). Then, the closed form of $V_{\text{ee}}^{\text{HF}}|_{R \rightarrow \infty}$ can be obtained as

$$\begin{aligned}V_{\text{ee}}^{\text{HF}}|_{R \rightarrow \infty} &= \frac{1}{2} \iint \frac{\rho_2^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)|_{R \rightarrow \infty}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{N_s^4}{4} \iint \frac{e^{-2\alpha(|\mathbf{r}_1 - \mathbf{r}_A|^2 + |\mathbf{r}_2 - \mathbf{r}_B|^2)} + e^{-2\alpha(|\mathbf{r}_1 - \mathbf{r}_B|^2 + |\mathbf{r}_2 - \mathbf{r}_A|^2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad + \frac{N_s^4}{4} \iint \frac{e^{-2\alpha(|\mathbf{r}_1 - \mathbf{r}_A|^2 + |\mathbf{r}_2 - \mathbf{r}_A|^2)} + e^{-2\alpha(|\mathbf{r}_1 - \mathbf{r}_B|^2 + |\mathbf{r}_2 - \mathbf{r}_B|^2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sqrt{\frac{\alpha}{\pi} + \frac{1}{2R}}.\end{aligned}\quad (7.9)$$

Therefore, the two partitions of $V_{\text{ee}}^{\text{corr}}$ in this H_2 model, using a minimal basis set composed solely of s -type GTOs, at $R \rightarrow \infty$ are obtained as

$$\Delta V_{\text{ee}}^{\text{cI}}|_{R \rightarrow \infty} = \frac{1}{2R}, \quad (7.10)$$

$$\Delta V_{\text{ee}}^{\text{cII}}|_{R \rightarrow \infty} = -\sqrt{\frac{\alpha}{\pi}}. \quad (7.11)$$

Fig. 7.2 illustrates the radial intracule density of the minimal (singlet) H_2 model at a separation of $R = 9.45$ a.u. The intracule curve of FCI only shows one peak at the long-range region ($s \rightarrow R$), while the intracule curves of HF and SD show two peaks, one at the short-range region ($s \rightarrow 0$) and the other at the long-range region ($s \rightarrow R$). One can observe that the SD intracule curve coincides with the HF curve in the short-range region and overlaps the FCI curve in the long-range region. In the short-range regime, the electron-electron interaction energy evaluated by using HF or SD radial intracule density remains a constant of $\sqrt{\alpha/\pi}$. This is due to the presence of the ionic two-electron terms, which arise from the use of Hartree-Fock Coulomb $\hat{J}$ and exchange $\hat{K}$ operators and compensate

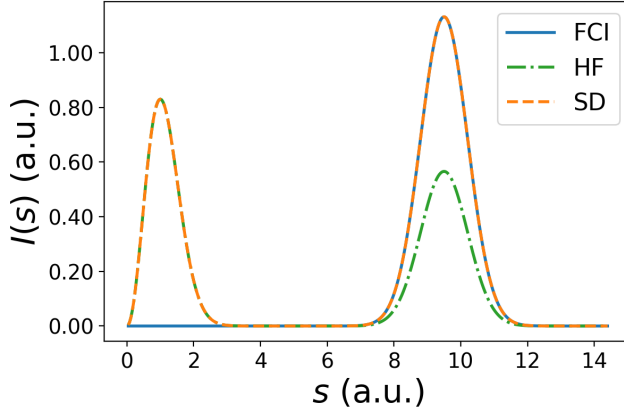


FIGURE 7.2: Radial intracule density of the minimal (singlet) H_2 model with a minimal basis set (1s GTO for each atom) at a separation distance $R = 9.45$ a.u. See support information in Ref. [3].

with the cumulant term in the FCI. In the long-range regime, the $1/R$ term in V_{ee} arises from the covalent two-electron terms. This term can be interpreted as the classical Coulomb repulsion within the H_2 model. The current H_2 model which utilizes a minimal basis set, is absent of a $1/R^6$ asymptotic behavior in all these V_{ee} terms, thus this model can not account for dispersion interactions. However, the inclusion of p functions in the basis set enables the creation of induced dipole-induced dipole terms, which are associated with dispersion interactions. In the next chapter, we will introduce a minimal dispersion model that extends beyond the H_2 minimal model and provide a more comprehensive insight into dispersion.

In Tab. 7.6 and Tab. 7.7, we examined $C_6^{\Delta V_{ee}^{cI}}$ and $C_6^{\Delta V_{ee}^{cII}}$ and its range separation components in singlet and triplet cases, respectively. For the purpose of this comparison, the results of $C_6^{\Delta J}$ and $C_6^{\Delta K}$ (see Tab. A10 and Tab. A11 in Appendix A.5) have been summarized in Tab. 7.6 and Tab. 7.7 for the case of singlet and triplet, respectively. The sum of $C_6^{\Delta J}$ and $C_6^{\Delta K}$ closely matches that of $C_6^{\Delta V_{ee}^{cI}}$, as well as $C_6^{\Delta V_{ee}^{cI,SR}}$, indicating that they all originate from the short-range effect. It is notable that the short-range terms, $C_6^{\Delta V_{ee}^{cI,SR}}$ and $C_6^{\Delta V_{ee}^{cII,SR}}$ can cancel each other out in both singlet and triplet cases, as they arise from the SD approximation at short-range and do not contribute to dispersion. Furthermore, we performed individual examinations of the term V_{ee}^{SD} from the SD approximation, which was evaluated with various truncated basis sets, including s , p , d , and f orbitals. It has been demonstrated that V_{ee}^{SD} exhibits a long-range behavior characterized solely by a $1/R$ term. This observation is consistent with the analytical derivations

obtained from the minimal H_2 model with $1s$ GTO basis set in Eq. (7.7). Consequently, it can be concluded that the SD approximation, even when supplemented with p orbitals, does not incorporate any dispersion energy contributions with a $1/R^6$ asymptotic behavior at long range. Firstly, we conclude that the dispersion energy arises from the cumulant part of pair density, as observed previously in [3, 91, 365]. Secondly, we have numerically demonstrated that the relationship $C_6^{\Delta V_{ee}^{c_{II},lr}} = 2C_6$ is validated in both singlet and triplet H_2 cases, implying that the long-range cumulant part of pair density accounts for the dispersion interactions.

TABLE 7.5: C_6 terms from pair density partitions for H_2 (singlet and triplet).

Range	h_{c_I}	$h_{c_{II}}$
short-range ($s \rightarrow 0$)	$(C_6^{\Delta J} + C_6^{\Delta K})$	$-(C_6^{\Delta J} + C_6^{\Delta K})$
long-range ($s \rightarrow R$)		$C_6^{\Delta V_{ee}}$

Tab. 7.5 summarizes the C_6 components obtained from pair density partitions with range separation in our current work, based on H_2 (singlet and triplet) cases at large separation distances. Notably, the contribution of $C_6^{\Delta V_{ee}}$ from V_{ee} can be obtained from the long-range part $h_{c_{II}}$ in both H_2 (singlet and triplet) cases, while the short-range part of $h_{c_{II}}$ results in a term like $-(C_6^{\Delta J} + C_6^{\Delta K})$, which can be canceled out by $C_6^{\Delta J} + C_6^{\Delta K}$ from the short-range part of h_{c_I} . The reasons behind these non-dispersion (short-range) C_6 components will be further discussed in Chapter 8, based on the minimal dispersion model. Additionally, it is worth noting that the relationship $C_6^{\Delta V_{ee}} = C_6^{\Delta V_{ee}^{c_{II},lr}} = 2C_6$ holds true for both singlet and triplet H_2 at the large separations.

TABLE 7.6: $C_6^{\Delta V_{ee}^{CI}}$ and $C_6^{\Delta V_{ee}^{CI}}$ of H₂ molecule **singlet**.

H ₂ (singlet) Basis set	$C_6^{\Delta J}$	$C_6^{\Delta K}$	$C_6^{\Delta V_{ee}^{CI}}$		$C_6^{\Delta V_{ee}^{CI}}$		$C_6^{\Delta V_{ee}}$
			total	sr	lr	total	sr
aug-cc-pVDZ (3s2p)	4.148	0	4.225	4.225	0	8.443	-4.225
aug-cc-pVTZ (4s3p)	5.236	0	5.407	5.407	0	7.606	-5.407
aug-cc-pVQZ (5s4p)	5.356	0	5.553	5.553	0	7.443	-5.553
aug-cc-pV5Z (6s5p)	5.449	0	5.539	5.539	0	7.420	-5.539
aug-cc-pV6Z (7s6p)	5.388	0	5.501	5.501	0	7.457	-5.501
aug-cc-pVTZ (4s3p2d)	5.208	0	5.218	5.218	0	7.792	-5.218
aug-cc-pVQZ (5s4p3d)	5.274	0	5.408	5.408	0	7.586	-5.408
aug-cc-pV5Z (6s5p4d)	5.447	0	5.357	5.357	0	7.599	-5.357
aug-cc-pV6Z (7s6p5d)	5.303	0	5.336	5.336	0	7.618	-5.336
aug-cc-pVQZ (5s4p3d2f)	5.394	0	5.347	5.347	0	7.644	-5.347
aug-cc-pV5Z (6s5p4d3f)	5.359	0	5.350	5.350	0	7.601	-5.350
aug-cc-pV6Z (7s6p5d4f)	5.227	0	5.288	5.288	0	7.661	-5.288

• Note that $C_6^{\Delta J}$ were retrieved by fitting $J[\text{FCI}] - J[\text{CAS}(2,2)]$ against R , and $C_6^{\Delta K} = 0$.

• In the range-separated components of ΔV_{ee}^{CI} and ΔV_{ee}^{CI} , short-range is noted as sr, long-range is noted as lr, and the total is a sum of sr and lr components.

• The fitting range is 22.68 to 43.47 a.u.

TABLE 7.7: $C_6^{\Delta V_{ee}^{CI}}$ and $C_6^{\Delta V_{ee}^{CI}}$ of H_2 molecule **triplet**.

H ₂ (triplet) Basis set	$C_6^{\Delta J}$	$C_6^{\Delta K}$	$C_6^{\Delta V_{ee}^{CI}}$			$C_6^{\Delta V_{ee}^{CI}}$			$C_6^{\Delta V_{ee}}$
			total	sr	lr	total	sr	lr	
aug-cc-pVDZ (3s2p)	13.034	-17.779	-4.721	-4.721	0	17.389	4.721	12.668	12.643
aug-cc-pVTZ (4s3p)	15.487	-20.441	-4.922	-4.922	0	17.935	4.922	13.012	12.981
aug-cc-pVQZ (5s4p)	15.580	-20.540	-4.926	-4.926	0	17.922	4.926	12.996	12.963
aug-cc-pV5Z (6s5p)	15.602	-20.549	-4.913	-4.913	0	17.871	4.913	12.959	12.925
aug-cc-pV6Z (7s6p)	15.557	-20.505	-4.914	-4.914	0	17.871	4.914	12.957	12.924
aug-cc-pVTZ (4s3p2d)	15.284	-20.183	-4.923	-4.923	0	17.935	4.923	13.012	13.035
aug-cc-pVQZ (5s4p3d)	15.592	-20.490	-4.927	-4.927	0	17.922	4.927	12.995	13.022
aug-cc-pV5Z (6s5p4d)	15.615	-20.495	-4.914	-4.914	0	17.873	4.914	12.959	12.987
aug-cc-pV6Z (7s6p5d)	15.568	-20.447	-4.916	-4.916	0	17.874	4.916	12.958	12.988
aug-cc-pVQZ (5s4p3d2f)	15.591	-20.488	-4.927	-4.927	0	17.920	4.927	12.993	13.020
aug-cc-pV5Z (6s5p4d3f)	15.613	-20.492	-4.914	-4.914	0	17.868	4.914	12.954	12.984
aug-cc-pV6Z (7s6p5d4f)	15.561	-20.438	-4.915	-4.915	0	17.868	4.915	12.952	12.983

• Note that $C_6^{\Delta J}$ were determined by fitting $J[\text{FCI}] - J[\text{HF}]$, while $C_6^{\Delta K}$ were by fitting $K[\text{FCI}] - K[\text{HF}]$.

• In the range-separated components of ΔV_{ee}^{CI} and ΔV_{ee}^{CI} , short-range is noted as sr, long-range is noted as lr, and the total is a sum of sr and lr components.

• The fitting range is 22.68 to 43.47 a.u.

7.3.2 Dispersion in He₂ Molecule

The Helium dimer (i.e., He₂ molecule) is a well-known vdW system. Since the dispersion interactions dominate the electron correlation between the two monomers separated at large R , taking the HF as a dispersion-free reference method in Eq. (6.1) is sufficient for our purpose of capturing the dispersion interactions. Considering the dispersion in He₂ at large separations, we evaluated ΔE_{AB} in eq. (6.1) using the target (e.g., FCI, CCSD(T), CCSD, CISD, MP2) and the reference (HF) methods.

Tab. 7.8 summarizes C_6 and its components of He₂ calculated using various methods with the aug-cc-pVDZ basis set that only includes s and p functions. The values of C_6 retrieved using FCI and CCSD(T) are 1.47 and 1.45, respectively, both of which exhibit high accuracy compared to the literature value of $C_6 = 1.46$ [44]. On one hand, similar to the case of H₂ molecule, the C_6 partition terms, $C_6^{\Delta T}$ and $C_6^{\Delta V_{ee}}$, exhibit opposite signs with $C_6^{\Delta V_{en}}$, and they can largely cancel out despite their great magnitudes. On the other hand, unlike the H₂ case which does not have the intra-monomer electron correlation, for He₂ the relationship $C_6^{\Delta V_{ee}} \approx C_6^{\Delta V_{ee}^{c_{II},lr}}$ does not hold true, as the C_6 terms retrieved from $\Delta V_{ee}^{c_{II},sr}$ and $\Delta V_{ee}^{c_{I},sr}$ values have the same signs and can not cancel out (except for MP2). Thus, the short-range partition of ΔV_{ee} exhibits a $1/R^6$ asymptotic behavior, which cannot be neglected, while it can not account for dispersion (for further analysis results of the short-range partition of ΔV_{ee} , we refer to Appendix A.5).

Although there is no obvious relationship found between $C_6^{\Delta V_{ee}}$ and the total C_6 , the relationship $C_6^{\Delta V_{ee}^{c_{II},lr}} = 2E_{disp}$ still holds true. As we have shown in Chapter 6, the total dispersion of He₂ can be retrieved by using the pair density of Baerends' model which is simply based on the induced-dipole induced dipole terms, thus we summarize the relationships, $2C_6 = C_6^{\Delta V_{ee}^{c_{II},lr}} = C_6^{\Delta V_{ee}^{lr}} = C_6^{V_{ee}^{dd}}$. In practice, the ΔV_{ee}^{lr} term requires the use of a suitable reference method to eliminate nondynamic correlation. The V_{ee}^{dd} term is limited by the two-electron AO quartets incorporated in the approximate pair density. Therefore, the $\Delta V_{ee}^{c_{II},lr}$ term offers greater potential for modeling dispersion based on this relationship.

Tab. 7.9 demonstrates further that the relationship, $C_6^{\Delta V_{ee}^{c_{II},lr}} = 2C_6$, always holds true when comparing the results from the same wavefunction method using different basis sets. When using FCI with a larger basis set, $C_6^{\Delta V_{ee}^{c_{II},lr}}/2$ equals the value of 1.46 from literature [44]. Nonetheless, this relationship remains robust across various approximate wavefunction methods (e.g., MP2, CISD, CCSD, CCSD(T)), even though they retrieve C_6 values to different extents. Additionally,

TABLE 7.8: Dispersion coefficient C_6 and its decomposed terms of He_2 molecule calculated by various wavefunction methods with the aug-cc-pVDZ basis set. The reference values of C_6 were retrieved by fitting ΔE_{AB} in Eq. (6.1), over the fitting range of 22.68 to 43.47 a.u.

C_6 terms	FCI	CCSD(T)	CCSD	CISD	MP2
C_6	1.47	1.45	1.37	1.37	1.13
$C_6^{\Delta T}$	6.67	6.98	7.15	7.39	0.42
$C_6^{\Delta V_{\text{en}}}$	-10.21	-10.47	-10.38	-10.66	-1.49
$C_6^{\Delta V_{\text{ee}}}$	5.01	4.94	4.60	4.64	2.20
$C_6^{\Delta J}$	4.30	4.38	4.27	4.35	0.62
$C_6^{\Delta K}$	-2.80	-2.80	-2.66	-2.70	-0.67
$C_6^{\Delta V_{\text{ee}}^{c\text{I}}}$	1.50	1.58	1.61	1.65	-0.06
$C_6^{\Delta V_{\text{ee}}^{c\text{I},\text{sr}}}$	1.50	1.58	1.62	1.65	-0.06
$C_6^{\Delta V_{\text{ee}}^{c\text{I},\text{lr}}}$	0.00	0.00	0.00	0.00	0.00
$C_6^{\Delta V_{\text{ee}}^{c\text{II}}}$	3.51	3.36	2.99	2.99	2.26
$C_6^{\Delta V_{\text{ee}}^{c\text{II},\text{sr}}}$	0.57	0.46	0.25	0.26	0.00
$C_6^{\Delta V_{\text{ee}}^{c\text{II},\text{lr}}}$	2.95	2.90	2.73	2.74	2.26
$C_6^{V_{\text{ee}}^{dd}}$	2.95	2.89	2.73	2.73	2.26

this relationship exhibits insensitivity to the choice of basis sets.

In order to understand why the use of induced-dipole induced dipole terms or $C_6^{\Delta V_{\text{ee}}^{c\text{II},\text{lr}}}$ can not align with the whole $C_6^{\Delta V_{\text{ee}}}$ contribution in He_2 case, we analyzed the $C_6^{\Delta V_{\text{ee}}}$ terms ($C_6^{\Delta V_{\text{ee}}^i}$) of He_2 at large R (i.e., from 22.68 to 43.47 a.u.) calculated at the FCI level,

$$C_6^{\Delta V_{\text{ee}}} = \sum_i C_6^{\Delta V_{\text{ee}}^i}, \quad (7.12)$$

and each individual fragment $C_6^{\Delta V_{\text{ee}}^i}$ can be obtained by fitting the corresponding energy term ΔV_{ee}^i as a function of R .

$$\begin{aligned}
 \Delta V_{\text{ee}}^i &= (V_{\text{ee}}^{\text{FCI},i} - V_{\text{ee}}^{\text{FCI},i,\infty}) - (V_{\text{ee}}^{\text{HF},i} - V_{\text{ee}}^{\text{HF},i,\infty}) \\
 &= \underbrace{V_{\text{ee}}^{\text{FCI},i} - V_{\text{ee}}^{\text{HF},i}}_{\text{dimer}} - 2 \underbrace{(V_{\text{ee}}^{\text{FCI},i} - V_{\text{ee}}^{\text{HF},i})}_{\text{monomers}},
 \end{aligned} \quad (7.13)$$

TABLE 7.9: $C_6^{\Delta V_{ee}^{c\Pi,lr}}/2$ and C_6 of He_2 molecule obtained from various wavefunction methods with the aug-cc-pVXZ (X=D,T,Q) basis set. The reference values of C_6 were retrieved by fitting ΔE_{AB} in Eq. (6.1), over the fitting range of 22.68 to 43.47 a.u.

Basis	Term	FCI	CCSD(T)	CCSD	CISD	MP2
aug-cc-pVDZ	$C_6^{\Delta V_{ee}^{c\Pi,lr}}/2$	1.47	1.45	1.38	1.37	1.13
(3s2p)	C_6	1.47	1.45	1.38	1.37	1.13
aug-cc-pVTZ	$C_6^{\Delta V_{ee}^{c\Pi,lr}}/2$	1.47	1.44	1.34	1.34	1.12
(4s3p2d)	C_6	1.47	1.44	1.34	1.34	1.12
aug-cc-pVQZ	$C_6^{\Delta V_{ee}^{c\Pi,lr}}/2$	1.46	1.43	1.33	1.33	1.12
(5s4p3d2f)	C_6	1.46	1.43	1.33	1.33	1.12

TABLE 7.10: Dispersion coefficient $C_6^{\Delta V_{ee}}$ and its range-separated terms of He_2 molecule calculated by various wavefunction methods with the aug-cc-pVDZ basis set.

C_6 terms	FCI	CCSD(T)	CCSD	CISD	MP2
$C_6^{\Delta V_{ee}}$	5.01	4.94	4.60	4.64	2.20
$C_6^{\Delta V_{ee}^{sr}}$	2.06	2.04	1.87	1.91	-0.06
$C_6^{\Delta V_{ee}^{lr}}$	2.95	2.89	2.73	2.73	2.26

where the term represents the contribution from some two-electron integral terms in the AO basis. The V_{ee} term is evaluated through Eq. (3.79) as presented in Chapter 3. Then, we calculated the individual contributions of ΔV_{ee}^i term by term (i.e., based on the angular momentum of the GTOs involved in the two-electron terms entering the V_{ee} expression), and specifically determined the terms that exhibit a $1/R^6$ dependence.

Tab. 7.11 shows all the $1/R^6$ dependent terms of ΔV_{ee}^i and their corresponding $C_6^{\Delta V_{ee}^i}$ values for the He_2 molecule, calculated using the FCI method with the aug-cc-pVDZ basis set. Remarkably, the $C_6^{\Delta V_{ee}^i}$ contributions from on-site “ssss” terms are found to be substantial, while the contributions from on-site “sppp” terms and the on-site “spsp” terms proposed by Baerends *et al.* [90] are relatively smaller. Notwithstanding, all these on-site “ssss”, “sppp”, and “spsp” terms collected in

TABLE 7.11: Non-zero terms of V_{ee} contributing to $C_6^{\Delta V_{ee}}$ of He_2 molecule calculated at the FCI/aug-cc-pVDZ level of theory. These terms are labeled with two-electron AO quartets in Mulliken notation, i.e., $\chi_\mu(1)\chi_\nu(1')\chi_\sigma(2)\chi_\lambda(2')$.

Notations	two-electron AO quartets	$C_6^{\Delta V_{ee}^i}$
on-site	$s_A(1)s_A(1')s_A(2)s_A(2')$	1.61
<i>ssss</i> terms	$s_B(1)s_B(1')s_B(2)s_B(2')$	1.61
on-site	$s_A(1)s_A(1')p_A(2)p_A(2')$	-0.39
<i>sspp</i> terms	$s_B(1)s_B(1')p_B(2)p_B(2')$	-0.39
Baerends' on-site terms	$s_A(1)p_A(1')s_A(2)p_A(2')$	-0.16
<i>spsp</i> terms	$s_B(1)p_B(1')s_B(2)p_B(2')$	-0.16
Baerends' dispersion terms	$s_A(1)p_A(1')s_B(2)p_B(2')$	1.47
<i>spsp</i> terms	$s_A(2)p_A(2')s_B(1)p_B(1')$	1.47

- Apart from some numerical errors, $\sum C_6^{\Delta V_{ee}^i} = 5.06$, is consistent with $C_6^{\Delta V_{ee}} = 5.01$ in [Tab. 7.8](#).

[Tab. 7.8](#) are ionic terms, and they correspond to the short-range correlations. Consequently, only the Baerends' dispersion terms, also known as induced dipole-induced dipole terms, namely, $s_A(1)p_A(1')s_B(2)p_B(2')$ and $s_A(2)p_A(2')s_B(1)p_B(1')$, which are long-range covalent terms, are responsible for dispersion. In addition, we note that the aug-cc-pVDZ basis set only includes $3s2p$, and the extended Baerends' model is not needed for this analysis.

7.3.3 Dispersion in Diatomic and Polyatomic Molecules

Now we will verify whether the previously established relationship of $C_6 = C_6^{\Delta V_{ee}^{c_{II},lr}}/2$ holds true for other systems beyond H_2 and He_2 . To accomplish this, we extend our numerical analysis to various dimer molecules which were sourced from Ref. [364]. Due to the computational limitations of performing FCI calculations for these systems, we employ SR wavefunction methods such as MP2, CISD, CCSD, or CCSD(T) for the assessment. Specifically, we examine whether $\Delta V_{ee}^{c_{II},lr}$ exhibits a leading term decay of $1/R^6$ at large interatomic or intermolecular separations when evaluated using these SR wavefunction methods, and we quantitatively assess the extent to which dispersion energy coefficient C_6 can be retrieved by $\Delta V_{ee}^{c_{II},lr}$ obtained from these SR wavefunction methods. Moreover, we examine whether the V_{ee}^{ext} term results from the extended Baerends' model (in Chapter 6) remains consistent with $\Delta V_{ee}^{c_{II},lr}$.

Tab. 7.12 shows the data of $C_6^{\Delta V_{ee}^{c_{II},lr}}/2$ for comparison with the literature values of C_6 . Firstly, it is worth noting that the leading term of the energy values of $\Delta V_{ee}^{c_{II},lr}$ for all the molecules consistently follows a $1/R^6$ dependence, indicating the character of dispersion interactions identified in the energy of $\Delta V_{ee}^{c_{II},lr}$. Secondly, in terms of quantifying the dispersion energies captured by $\Delta V_{ee}^{c_{II},lr}$, our results reveal that for the HeNe molecule employing the aug-cc-pVXZ (X=D,T,Q,5) basis sets, the values of $C_6^{\Delta V_{ee}^{c_{II},lr}}/2$ obtained from CCSD(T) approach the C_6 value of 3.03 from literature as the basis set size increases. Furthermore, with the aug-cc-pVDZ basis set, the values of $C_6^{\Delta V_{ee}^{c_{II},lr}}/2$ retrieved from these post-HF methods generally underestimate the actual C_6 , except for MP2 which sometimes overestimates C_6 for certain molecules such as Ar_2 , Be_2 , $ArSO_2$, $(CH_4)_2$, and $(SO_2)_2$. This comparison with C_6 from literature is inappropriate, as $C_6^{\Delta V_{ee}^{c_{II},lr}}/2$ is definitely method-dependent and basis-set-dependent, thus a more reasonable comparison should be with C_6 from ΔE_{AB} shown in Tab. 6.3 or C_6 retrieved by Baerends' model or extended Baerends' model in Chapter 6.

As we have demonstrated in Chapter 6, Baerends' model using an approximate pair density constructed from the induced dipole-induced dipole terms for these molecules can not yield accurate values for $C_6^{V_{ee}^{dd}}$ for large molecules (e.g., larger noble gas systems beyond He_2). This discrepancy becomes more significant as the size of the system increases. To address this limitation, we incorporate extended terms derived from d orbitals to get the extended Baerends' model. For noble gas diatomic molecules, the $C_6^{V_{ee}^{ext}}/2$ term exhibit close agreement with those of $C_6^{\Delta V_{ee}^{c_{II},lr}}$. Fig. 7.3 shows the Mean Absolute Percentage Error (MAPE) comparison between

TABLE 7.12: $C_6^{\Delta V_{ee}^{c\Pi,lr}}/2$ of various dimer molecule separation obtained from different wavefunction methods.

Molecules	Basis	MP2	CISD	CCSD	CCSD(T)	Lit.
HeNe	AVDZ	2.12	2.17	2.31	2.49	3.03
HeNe	AVTZ	2.36	2.37	2.60	2.87	3.03
HeNe	AVQZ	2.42	2.40	2.66	2.97	3.03
HeNe	AV5Z	2.42	2.39	2.67	2.98	3.03
HeAr	AVDZ	8.74	7.68	8.45	9.10	9.55
HeKr	AVDZ	12.28	10.64	11.72	12.56	13.42
NeAr	AVDZ	15.86	12.22	13.92	15.27	19.5
Ne ₂	AVDZ	4.15	3.72	4.15	4.50	6.38
Ar ₂	AVDZ	69.54	44.01	52.71	58.15	64.3
Be ₂	AVDZ	252.06	162.95	139.24	195.62	214
ArCO ₂	AVDZ	97.76	55.43	74.33	85.29	114.5
ArSO ₂	AVDZ	144.54	74.23	102.62		128.7
(NH ₃) ₂	AVDZ	83.94	51.57	64.83	79.47	89
(CH ₄) ₂	AVDZ	143.84	91.69	115.04	135.78	130
(CO ₂) ₂	AVDZ	150.43	77.35	114.48		159
(SO ₂) ₂	AVDZ	428.55	249.57	159.08		294

- The basis set AVXZ denotes aug-cc-pVXZ (X=D,T,Q,5).
- Lit. denotes the C_6 value from the literature. The reference C_6 value of dimer (NH₃)₂ was taken from [421], the reference C_6 of ArSO₂ was calculated by SAPT2+, while the reference C_6 for other molecules were taken from [414].
- Apart from those diatomic molecules, all the geometries of other polyatomic molecules were taken from [364].

$C_6^{\Delta V_{ee}^{c\Pi,lr}}$ and $C_6^{V_{ee}^{ext}}/2$ with the same reference C_6 from Tab. 6.3 in Chapter 6. The highest MAPE is 1.54% for $C_6^{V_{ee}^{ext}}/2$ and 1.45% for $C_6^{\Delta V_{ee}^{c\Pi,lr}}$ when using CISD, while for the rest post-HF methods the MAPE values are all below 0.5%, and both $C_6^{\Delta V_{ee}^{c\Pi,lr}}$ and $C_6^{V_{ee}^{ext}}/2$ approaches highly aligned with each other for these noble gas systems.

Nevertheless, it is necessary to emphasize that extended Baerends' model is applicable only to diatomic molecules so far. The extended Baerends' model is still challenging to handle polyatomic molecule dimers such as ArCO₂, (NH₃)₂, (CH₄)₂, and others. As we have discussed in Chapter 6, the approximate 2-RDM of the extended Baerends' model involves other created instantaneous dipoles within

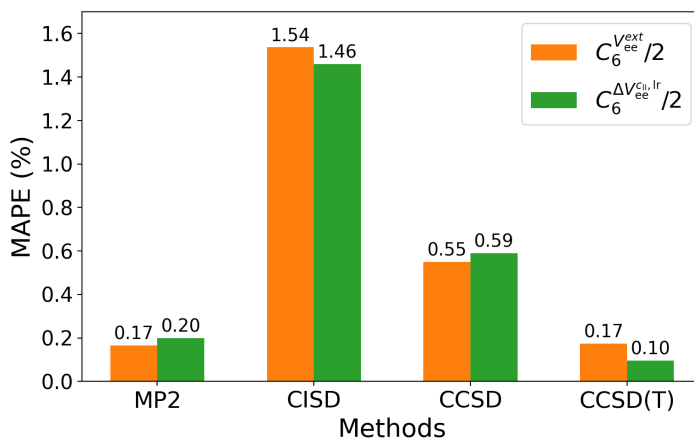


FIGURE 7.3: Mean Absolute Percentage Error (MAPE) comparison of C_6 retrieved from the long-range pair density partition c_{II} approach ($C_6^{\Delta V_{ee}^{c_{II},lr}}/2$) and the extended Baerends’ model ($C_6^{V_{ee}^{ext}}/2$) over various post-HF methods. For each *ab initio* method, the reference C_6 values were taken from [Tab. 6.3](#), and only diatomic molecules are included except Be_2 , because an appropriate reference method was not found to retrieve the dispersion energy of Be_2 from the correlation energy calculated by these post-HF methods.

the monomers, and the two-electron AO quartets are not directly connected to the induced dipole-induced dipole interactions from the two separated monomers. As a result, extended Baerends’ model captures not only dispersion in the polyatomic molecule dimers but also short-range correlations.

Based on various numerical assessments, we have demonstrated the potential of the relationship $C_6^{\Delta V_{ee}^{c_{II},lr}} = 2C_6$ for calculating dispersion solely through $\Delta V_{ee}^{c_{II},lr}$. This approach offers several advantages: (i) does not require a dispersionless reference method (unlike the approach in [Eq. \(6.1\)](#)), nor the calculation of monomers; (ii) it avoids using PT2 treatment or polarizabilities; (iii) it only requires approximating the pair density which must include the long-range dynamic correlation, and (iv) it implies a direct connection between the long-range part of the pair density partition c_{II} and the dispersion energy.

7.3.4 Dispersion Hole and Asymptotic Conditions

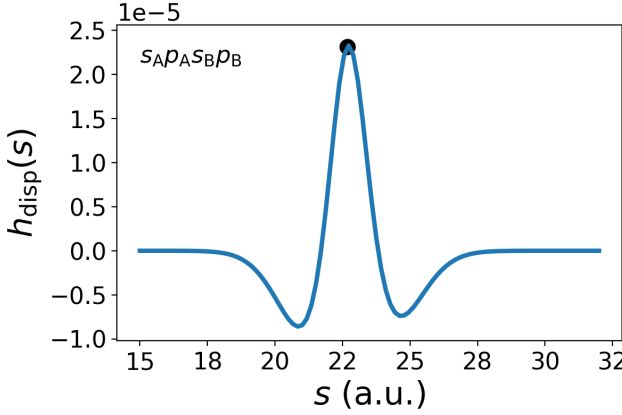


FIGURE 7.4: Dispersion hole $h_{\text{disp}}(s)$ represented by the radial intracule density, $I_{dd}(s)$, which is derived from induced-dipole induced dipole terms $s_A(1)p_A(1)s_B(2)p_B(2)$ and $s_A(2)p_A(2)s_B(1)p_B(1)$ of He_2 molecule separated by $R = 22.68$ a.u. And calculated at the FCI/aug-cc-pVDZ ($3s + 2p$) level of theory. The top black point represents the value of $h_{\text{disp}}(R)$.

In the previous sections, we have demonstrated the relationship between total dispersion energy and the dispersion energy retrieved from the $\Delta V_{\text{ee}}^{c_{\text{II}},\text{lr}}$ term,

$$E_{\text{disp}}^{\text{AB}} = \frac{\Delta V_{\text{ee}}^{c_{\text{II}},\text{AB}}}{2} \equiv \frac{\Delta V_{\text{ee}}^{c_{\text{II}},\text{lr}}}{2}, \quad (7.14)$$

and,

$$\begin{aligned} \Delta V_{\text{ee}}^{c_{\text{II}},\text{AB}} &= \frac{1}{2} \int_{\text{A}} \int_{\text{B}} \frac{\rho_2^{c_{\text{II}}}(1,2)}{r_{12}} d1 d2 \\ &= \frac{1}{2} \int_{\text{LR}} \frac{h_{c_{\text{II}}}(s)}{s} ds. \end{aligned} \quad (7.15)$$

Hence, the long-range part of pair density partition $\rho_2^{c_{\text{II}}}(1,2)$ can be directly connected to dispersion energy. For the convenience of visualization, we will employ its radial intracule, $h_{c_{\text{II}}}(s)$, in the following context.

To explore further this connection between the long-range component of $h_{c_{\text{II}}}(s)$ and dispersion energy, we introduce a novel concept: the *dispersion hole*, which can represent the long-range part of $h_{c_{\text{II}}}(s)$. To illustrate the curve of the dispersion hole, we use an example of a He_2 molecule with a large interatomic separation, calculated at the FCI/aug-cc-pVDZ level of theory. At large separation distances,

the radial intracule density $I_{dd}(s)$ which is derived from the induced-dipole induced dipole terms (i.e., using Baerends' model), is identical to the long-range part of $h_{cII}(s)$ in the case of He_2 . Fig. 7.4 shows the curve of radial intracule density $I_{dd}(s)$ against the interelectronic distance s , and it can be used to represent the dispersion hole in this He_2 case. However, it is worth noting that the dispersion hole can not be always represented by the radial intracule density from Baerends' model, because as we have demonstrated in Chapter 6 Baerends' model became invalid when including d orbitals for treating large molecules. In addition, since $I_{dd}(s)$ can be decomposed into contributions from $s_A p_{xA} s_B p_{xB}$, $s_A p_{yA} s_B p_{yB}$, and $s_A p_{zA} s_B p_{zB}$ terms, corresponding to x, y , and z components of dispersion hole, respectively. This decomposition can help the following analysis of the dispersion hole of He_2 .

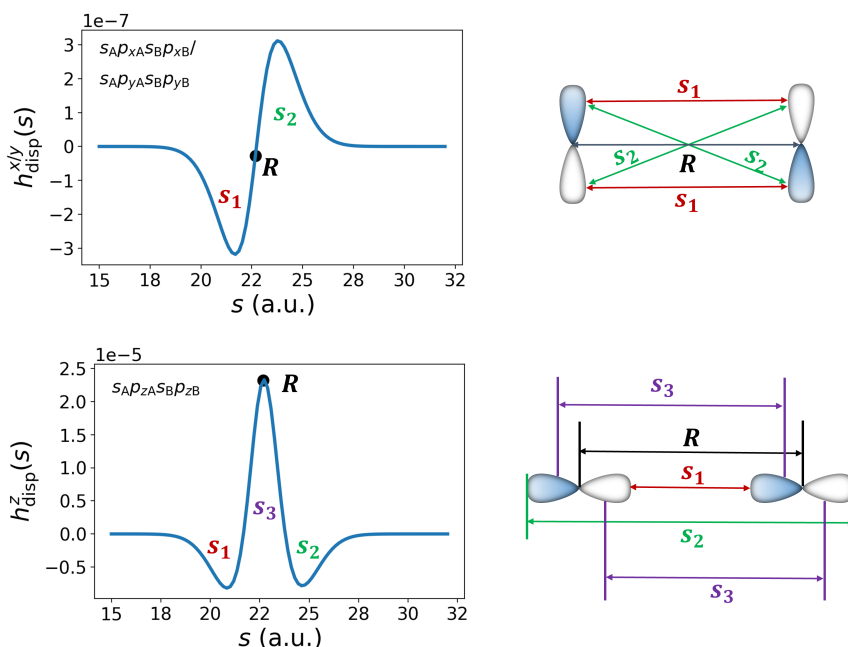


FIGURE 7.5: The x/y , and z components of dispersion hole $h_{\text{disp}}(s)$ of He_2 molecule separated by $R = 22.68$ a.u. And calculated at the FCI/aug-cc-pVDZ ($3s + 2p$) level of theory. The top left: $s_A p_{xA} s_B p_{xB} / s_A p_{yA} s_B p_{yB}$ contributions to $h_{\text{disp}}(s)$; The top right: p_x/p_y orbital illustration of the left and right side regions surrounding R . The bottom left: $s_A p_{zA} s_B p_{zB}$ contribution to $h_{\text{disp}}(s)$. The bottom right: p_z orbital illustration of the left and right side regions surrounding R . The black points denote the intracule value at $s = R$.

As shown in Fig. 7.5, As the two atoms are aligned along the z -axis, the z component of $h_{\text{disp}}(s)$ dominates the dispersion hole, with two orders of magnitude larger than the ones of x/y component of $h_{\text{disp}}(s)$. We note that the individual x/y components of the dispersion hole curves exhibit antisymmetry with respect to the point of $s = R$, while the individual z component shows full symmetry around $s = R$. However, the overall dispersion hole by combining the x, y, z components, in Fig. 7.4, shows slight asymmetry, with the left side curve slightly lower than the right side.

Due to the symmetry, the x and y components are equivalent, and both of them arise from the contributions of π or π^* molecular orbitals. Since the induced dipole-induced dipole terms are made by a product of four AOs, and the s -type AOs are spherically symmetric, then the positive and negative domains in the dispersion hole can be easily connected to the orientation of two interacting p -type AOs, as illustrated in the top right of Fig. 7.5. The regime $s_1 \leq R$ corresponds to an interaction between two p_x/p_y with opposite phases from two separated atoms, resulting in negative quantities. In contrast, the regime $s_2 \geq R$ corresponds to an interaction between two p_x/p_y with the same phase, yielding positive quantities. Analogously, this interpretation can be applied to the z component of the dispersion hole, as illustrated in the bottom right of Fig. 7.5. In particular, the region very close to R is labeled as s_3 . It accounts for the same phase of two p_z that generates positive quantities. Moreover, the peak occurring at R corresponds to the maximum induced dipole-induced dipole interactions contributed by the z component of the dispersion hole.

The dispersion hole, $h_{\text{disp}}(s)$, vanishes upon integration over the interelectronic distance, s .

$$\int h_{\text{disp}}(s) ds = 0. \quad (7.16)$$

The dispersion hole can be used to calculate dispersion energy,

$$E_{\text{disp}} = \frac{\Delta V_{\text{ee}}^{c_{\Pi}, \text{AB}}}{2} = \frac{1}{4} \int_{\text{LR}} \frac{h_{c_{\Pi}}(s)}{s} ds = \frac{1}{4} \int \frac{h_{\text{disp}}(s)}{s} ds, \quad (7.17)$$

where the factor of “2” in relationship $C_6^{\Delta V_{\text{ee}}^{c_{\Pi}, \text{lr}}} = 2C_6$ is incorporated. Consequently, the relationship shown in Eq. (7.17) provides a new path to model London dispersion only through a dispersion hole. Further discussion on the dispersion hole and its closed form from a minimal dispersion model will be in Chapter 8.

In addition, it has been previously demonstrated by our group, that the long-range peak of Coulomb hole partition at $s = R$, denoted as $h_{c_{\Pi}}(R)$, shows a leading term of $1/R^3$ [3, 91]. Hence, at $s = R$, the plot of the near peak point of $h_{\text{disp}}(R)$

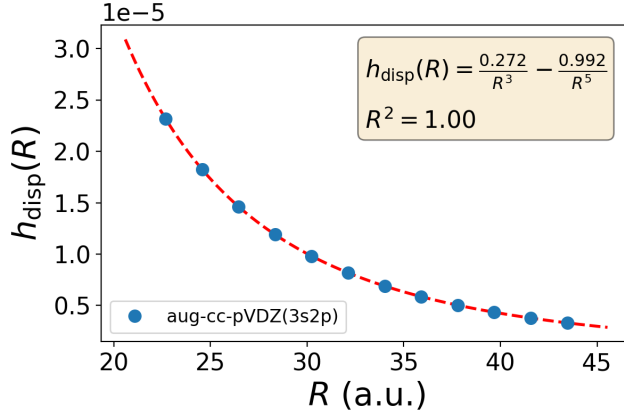


FIGURE 7.6: Dispersion hole of the largely-separated He_2 molecule calculated at the FCI/aug-cc-pVDZ ($3s + 2p$) level of theory. The black point represents the value of $h_{\text{disp}}(R)$.

in Fig. 7.4 against interatomic distance R should exhibit an asymptotic behavior of $1/R^3$. When expanding $h_{\text{disp}}(R)$ in terms of $1/R^n$, the fitting coefficients are denoted as D_3 , D_5 , etc.² Then, the expression of $h_{\text{disp}}(R)$ is given by

$$h_{\text{disp}}(R) = \frac{D_3}{R^3} + \frac{D_5}{R^5} + \dots \quad (7.18)$$

Fig. 7.6 shows the fitting of $h_{\text{disp}}(s)$, the leading term is explicitly $1/R^3$, and the corresponding fitting coefficient D_3 and D_5 are given by 0.272 and -0.992, respectively. This asymptotic condition can be applied to identify dispersion. Further investigation on the connection between D_3 , D_5 , and C_6 will be addressed in the following chapter.

In the case of He_2 calculated at the FCI/aug-cc-pVDZ ($3s2p$) level of theory, the dispersion hole can be simply represented by the radial intracule density of Baerends' model. Consequently, we will perform further analysis of the individual contributions from the x/y terms and the z terms to the $C_6^{V_{ee}^{dd}}$ terms, D_3 , and D_5 terms, respectively.

On one hand, from the view of dispersion energy C_6 terms, the x/y terms collectively contribute 1/3 to the total $C_6^{V_{ee}^{dd}}$, whereas the z terms contribute 2/3 to $C_6^{V_{ee}^{dd}}$. On the other hand, from the view of the approximate pair density constructed using induced-dipole induced dipole terms, the corresponding radial intracule

²We note that D_4/R^4 term is not considered. An analytical demonstration will be provided in the following chapter.

TABLE 7.13: Dispersion coefficient terms of He₂ molecule (FCI/aug-cc-pVDZ).

Terms	x/y terms		z terms		
	$C_6^{V_{ee}^{dd},(x/y)}$	$D_5(x/y)$	$C_6^{V_{ee}^{dd},(z)}$	$D_3(z)$	$D_5(z)$
Ratio	16.667%	16.659%	66.667%	100%	66.681%
Value	0.492	-0.165	1.966	0.272	-0.662

- x/y terms: $s_A(1)p_{xA}(1)s_B(2)p_{xB}(2), s_A(2)p_{xA}(2)s_B(1)p_{xB}(1)/$
 $s_A(1)p_{yA}(1)s_B(2)p_{yB}(2), s_A(2)p_{yA}(2)s_B(1)p_{yB}(1)$
- z terms: $s_A(1)p_{zA}(1)s_B(2)p_{zB}(2), s_A(2)p_{zA}(2)s_B(1)p_{zB}(1)$

density, $I_{dd}(s)$, shown in Fig. 7.4, is equivalent to $h_{c\Pi}(s)$. Notably, at a specific long-range point ($s = R$), we observe that the intracule $h_{c\Pi}(R)$ demonstrates a decay behavior of $1/R^3$. However, while the x/y terms contribution to $h_{c\Pi}(R)$ show an asymptotic behavior of $1/R^5$, the z terms exhibit a dependence on both $1/R^3$ and $1/R^5$. Therefore, the z terms contribute to the entire D_3 and contribute to nearly 2/3 of the D_5 . In other words, the $1/R^3$ leading term decay behavior serves as a necessary condition in the asymptotic behavior of $h_{c\Pi}(R)$, it alone is insufficient to fully identify the whole dispersion energy contribution from V_{ee}^{dd} or $\Delta V_{ee}^{c\Pi,lr}$. In addition, similar results have been obtained for the H₂ molecule, with the leading term coefficient D_3 observed to be insensitive to truncated basis sets. Further details for the results of the H₂ molecule are available in Appendix A.5.

MINIMAL DISPERSION MODEL BASED ON H_2

8.1 Introduction

In the previous chapter, we have shown that the H_2 (FCI) model with a minimal basis set (i.e., only using s -type functions) fails to describe the dispersion energies with the expected $1/R^6$ asymptotic behavior. As a result, it becomes necessary to augment the minimal basis set with p -type polarization functions in order to provide a minimal description of dispersion in H_2 [360, 422–424]. In this chapter, we present a minimal dispersion model based on the singlet H_2 molecule in its ground state, employing uncontracted $s + p$ Gaussian-type orbitals (GTO). Our primary focus is on the electron-electron interaction energy, V_{ee} , which can be obtained from the pair density. It is worth noting that V_{ee} is the only approximate energy component within the approximate functionals of RDMFT. Conversely, in the DFAs, both the kinetic energy term and the V_{ee} term require approximation. Hence, a well-suited approximation targeting on the V_{ee} term, particularly one that accounts for dispersion, can be helpful in the development of new functionals within the context of RDMFT or DFT.

In this chapter, our objective is to construct a minimal dispersion model of H_2 that will aid in analyzing the contribution of the induced dipole-induced dipole terms and the $\Delta V_{ee}^{c_{II},lr}$ term to the total dispersion energy, as well as to explore the connection between the $1/R^3$ asymptotic behavior of $h_{c_{II}}(R)$, and the corresponding contribution to the dispersion energy.

The overall procedure of the workflow for deriving the expression of V_{ee} can be summarized as follows. Starting with the $s + p$ Atomic Orbitals (**AOs**) basis functions, we employ the Linear Combination of Atomic Orbitals (LCAO) approach to construct Molecular Orbitals (**MOs**). Next, we generate all possible Slater Determinants (**DETs**) based on these MO and construct the FCI wavefunction (**WFN**) for the two-electron molecular system. By squaring the **WFN**, we obtain the **pair density**. The **intracule** transformation is then adopted to analytically evaluate all the two-electron integrals, and the resulting semi-analytical expression for V_{ee} will be given in terms of the CI coefficients, geometry (i.e., the interatomic distance, R), and basis set variables (i.e., exponents).

$$\chi(r) \rightarrow \phi(r) \rightarrow \Phi(1, 2) \rightarrow \Psi(1, 2) \rightarrow \rho_2(1, 2) \rightarrow I(s) \rightarrow V_{ee}$$

$$\mathbf{AO} \rightarrow \mathbf{MO} \rightarrow \mathbf{DET} \rightarrow \mathbf{WFN} \rightarrow \mathbf{pair\ density} \rightarrow \mathbf{intracule} \rightarrow V_{ee}$$

Subsequently, we derive various semi-analytical terms based on the intracule density or V_{ee} for further analysis, such as $h_{c\Pi}(s)$, V_{ee}^{corr} , $\Delta V_{ee}^{c\Pi,lr}$, and V_{ee}^{dd} .

8.2 Methodology

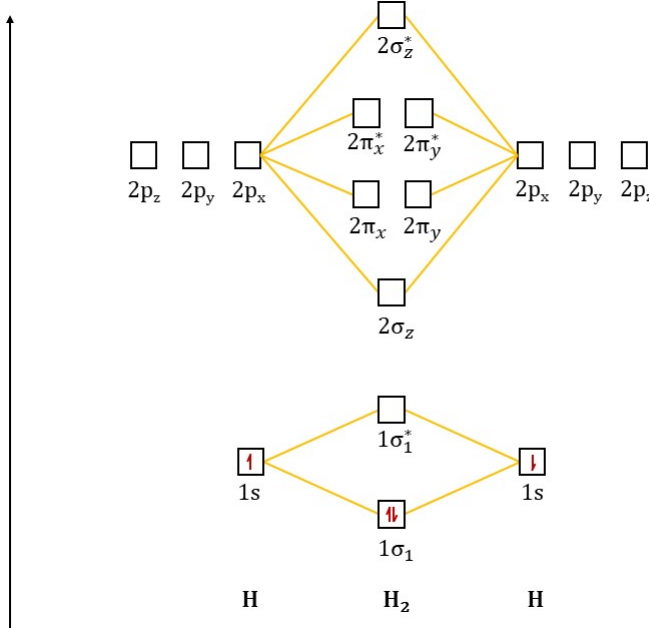
8.2.1 Wavefunction

This semi-analytical model for the singlet H₂ is based on two hydrogen atom centers, A and B, separated by a large distance R , with the interatomic axis aligned along the z -axis [3, 91]. The normalized Cartesian AO basis functions of atom A at (x_A, y_A, z_A) with one electron at (x, y, z) are depicted as:

$$\begin{aligned} s_A(x, y, z) &= \mathcal{N}_s e^{-\alpha_s[(x-x_A)^2+(y-y_A)^2+(z-z_A)^2]} \\ p_{xA}(x, y, z) &= \mathcal{N}_p (x-x_A) e^{-\alpha_p[(x-x_A)^2+(y-y_A)^2+(z-z_A)^2]} \\ p_{yA}(x, y, z) &= \mathcal{N}_p (y-y_A) e^{-\alpha_p[(x-x_A)^2+(y-y_A)^2+(z-z_A)^2]} \\ p_{zA}(x, y, z) &= \mathcal{N}_p (z-z_A) e^{-\alpha_p[(x-x_A)^2+(y-y_A)^2+(z-z_A)^2]}, \end{aligned} \tag{8.1}$$

where $\mathcal{N}_s$ and $\mathcal{N}_p$ represent the normalization factors of the basis functions, while α_s and α_p denote the exponents of the corresponding Gaussian functions. The same basis function forms are utilized for atom B.

The MO diagram of this H₂ model is illustrated in Fig. 8.1, we have utilized LCAO approach to combine 8 AOs and generate 8 MOs, the one with the lowest energy is the occupied orbital σ_1 that is used to form the ground-state configuration. Due to the symmetry, s and p_z orbitals are overlapped when forming the MO in this H₂ molecule which is aligned along the z -axis. As a result, all the

**FIGURE 8.1:** MO diagram of H_2 ($s + p$) model.

bonding orbitals σ and anti-bonding orbitals σ^* should be formed by mixing s and p_z orbitals. Nevertheless, we have the option to simplify the MOs, specifically the σ and σ^* orbitals, by forcing s and p_z orbitals not to be mixed. This simplification, however, does not compromise the primary objective for modeling the dispersion of the singlet H_2 at large interatomic distances when comparing the semi-analytical and numerical outcomes.

TABLE 8.1: Slater Determinants (DET) that conform the FCI expansion.

DET	$\sigma_1\sigma_1$	$\sigma_1^*\sigma_1^*$	$\sigma_z^*\sigma_z^*$	$\sigma_z\sigma_z$	$\pi_x\pi_x$	$\pi_x^*\pi_x^*$	$\pi_y\pi_y$	$\pi_y^*\pi_y^*$
CI coeff.	c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7

We construct 8 DETs by utilizing the 8 MOs. [Tab. 8.1](#) shows the 8 DETs, which include one ground-state and 7 double excitations. Let us take an example of Slater Determinants (DET) for the ground-state $\sigma_1\sigma_1$ which is the Hartree-Fock (HF) wavefunction,

$$\begin{aligned}
 \Phi_{\text{HF}}(1,2) &= \mathcal{N}_\Phi [\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)] (\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)) \\
 &= \mathcal{N}_\Phi [s_A(\mathbf{r}_1) + s_B(\mathbf{r}_1)] [s_A(\mathbf{r}_2) + s_B(\mathbf{r}_2)] (\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)), \quad (8.2)
 \end{aligned}$$

where $\mathcal{N}_\Phi$ represents the normalization factor of $\Phi_{\text{HF}}(1,2)$. The notation, $1 \equiv \{\mathbf{r}_1, \sigma_1\}$, represents the spatial and spin coordinates. The AO basis is orthonormal within each atom. The spin functions α or β ensure the antisymmetry in the HF wavefunction.

The FCI wavefunction for the singlet H₂ model system can be expressed as:

$$\Psi(1,2) = c_0 \Phi_{\text{HF}}(1,2) + \sum_{i=1}^7 c_i \Phi_i(1,2), \quad (8.3)$$

where the CI coefficient, c_i (see [Tab. 8.1](#)), fulfills the sum rule,

$$\sum_{i=0}^7 c_i^2 = 1. \quad (8.4)$$

In the FCI wavefunction of this H₂ model in [Eq. \(8.3\)](#), the CI coefficient of the Hartree-Fock determinant (c_0) is typically close to 1 at short interatomic distances ($R \rightarrow R_e$, where R_e denotes the equilibrium distance) and converges to $1/\sqrt{2}$ at the dissociation limit ($R \rightarrow \infty$) [[425](#)].

For the FCI wavefunction of the two-electron system in [Eq. \(8.3\)](#), the pair density can be obtained simply by taking the square of the wavefunction:

$$\rho_2(1,2) = 2|\Psi(1,2)|^2, \quad (8.5)$$

where the normalization follows McWeeny's convention [[182](#)]. The $\rho_2(1,2)$ and V_{ee} terms (e.g., $V_{\text{ee}}^{\text{corr}}$, $\Delta V_{\text{ee}}^{c\Pi}$) were evaluated using the matrix representation of 2-RDM in the AO basis, and the required two-electron integrals were evaluated through the integration of intracule. For more details, we refer the readers to go from [Eq. \(3.78\)](#) to [Eq. \(3.85\)](#) in [Chapter 3](#).

The 1-RDM and 2-RDM in the MO basis can be obtained by using the CI coefficients, and then they must be transformed from MO to AO basis. Considering our simplified models where s and p_z atomic orbitals do not mix, then the MO coefficients are simplified to $\pm \frac{1}{\sqrt{2}}$ for AOs that contribute to bonding or antibonding interactions. Hence, the final expressions of the contribution of V_{ee} to the correlation energy ($V_{\text{ee}}^{\text{corr}}$), or its partitions $\Delta V_{\text{ee}}^{c1}$ and $\Delta V_{\text{ee}}^{c\Pi}$ involve 11 variables: the interatomic distance (R), basis function exponents (α_s, α_p), and eight CI coefficients ($c_0, c_1, \dots, c_7$), which are derived from the FCI wavefunction of the H₂ model (with uncontracted $s + p$ basis functions).

In this work, the idea is to first collect all the $1/R^6$ asymptotic energy components within $V_{\text{ee}}^{\text{corr}}$, as well as within its partition $\Delta V_{\text{ee}}^{c\Pi}$, based on the two-electron AO quartets, at large separation distances R . Then these quartets will be employed to establish approximate pair density models to recover the dispersion of this simplified H₂ model system.

8.2.2 SP11dd and SP11cII Models

Now let us introduce two types of semi-analytical pair density models: SP11dd and SP11cII, which are designed for retrieving dispersion energy from $V_{\text{ee}}^{\text{corr}}$ and $\Delta V_{\text{ee}}^{\text{cII}}$, respectively. Both of these models will be expressed in a semi-analytical manner, and involve 11 variables for calculating energies, including R , α_s , α_p , and c_i (where $i = 0, 1, \dots, 7$). As the CI coefficients are obtained from numerical FCI calculations, these models are not truly analytical.

SP11dd model is implemented by incorporating the induced-dipole induced dipole terms shown in [Tab. 8.2](#), from the FCI pair density. In this simplified H_2 model system, the SP11dd model is identical to Baerends’s model [\[88–90\]](#) described previously in [Chapter 6](#).

TABLE 8.2: Induced dipole-induced dipole terms.

Terms	$s_A p_{xA}$	$s_A p_{yA}$	$s_A p_{zA}$
$s_B p_{xB}$	$s_A p_{xA} s_B p_{xB}$		
$s_B p_{yB}$		$s_A p_{yA} s_B p_{yB}$	
$s_B p_{zB}$			$s_A p_{zA} s_B p_{zB}$

• Each two-electron AO term of the pair density includes $\chi_A(1)\chi_A(1)\chi_B(2)\chi_B(2)$ and $\chi_A(2)\chi_A(2)\chi_B(1)\chi_B(1)$.

In this model, ${}^2D_{s_A p_A s_B p_B}$ in [Eq. \(3.79\)](#) can be determined by the corresponding CI coefficient products. Then the $\rho_2^{dd}(1, 2)$ term retrieved by the SP11dd model can be explicitly expressed in individual x, y, z terms:

$$\rho_2^{dd}(1, 2) = \rho_2^{dd,x}(1, 2) + \rho_2^{dd,y}(1, 2) + \rho_2^{dd,z}(1, 2), \quad (8.6)$$

and

$$\begin{aligned} \rho_2^{dd,x}(1, 2) &= -\mathcal{N}_x(c_0 - c_1)(c_4 - c_5)s_A(1)p_{xA}(1)s_B(2)p_{xB}(2), \\ \rho_2^{dd,y}(1, 2) &= -\mathcal{N}_y(c_0 - c_1)(c_6 - c_7)s_A(1)p_{yA}(1)s_B(2)p_{yB}(2), \\ \rho_2^{dd,z}(1, 2) &= -\mathcal{N}_z(c_0 - c_1)(c_2 - c_3)s_A(1)p_{zA}(1)s_B(2)p_{zB}(2), \end{aligned} \quad (8.7)$$

where $\mathcal{N}_x$, $\mathcal{N}_y$, and $\mathcal{N}_z$ represent the normalization factor for each term.¹ The corresponding radial intracule density I_{dd}^x , I_{dd}^y , and I_{dd}^z can be derived using [Eq. \(3.87\)](#) and [Eq. \(3.88\)](#) in [Chapter 3](#). The total radial intracule density $I_{dd} =$

¹We note that the normalization factor includes all the essential normalizations for AOs, MOs, DETs, and WFN.

$I_{dd}^x + I_{dd}^y + I_{dd}^z$. Consequently, the associated V_{ee}^{dd} terms retrieved by the SP11dd model can be determined from

$$\begin{aligned} V_{ee}^{dd,x} &= \frac{1}{2} \int \frac{I_{dd}^x(s)}{s} ds, \\ V_{ee}^{dd,y} &= \frac{1}{2} \int \frac{I_{dd}^y(s)}{s} ds, \\ V_{ee}^{dd,z} &= \frac{1}{2} \int \frac{I_{dd}^z(s)}{s} ds, \end{aligned} \quad (8.8)$$

thus,

$$V_{ee}^{dd} = V_{ee}^{dd,x} + V_{ee}^{dd,y} + V_{ee}^{dd,z}. \quad (8.9)$$

We note that due to the symmetry of two-electron integrals for the H₂ model system, the closed-form of two-electron integrals evaluated from $s_A(1)p_A(1)s_B(2)p_B(2)$ and $s_A(2)p_A(2)s_B(1)p_B(1)$ terms are equivalent. In addition, as the two hydrogen atoms are aligned along z -axis, the closed-form of two-electron integrals from $s_A(1)p_{xA}(1)s_B(2)p_{xB}(2)$ and $s_A(1)p_{yA}(1)s_B(2)p_{yB}(2)$ are also identical. Hence, the expression of V_{ee}^{dd} derived from the SP11dd model can be reduced only in terms of $s_A(1)p_{xA}(1)s_B(2)p_{xB}(2)$ and $s_A(1)p_{zA}(1)s_B(2)p_{zB}(2)$.

SP11cII model is formed by merging the induced dipole-induced dipole terms shown in [Tab. 8.2](#) from the FCI pair density, and the ionic terms collected in [Tab. 8.3](#) from the SD approximate pair density, and all of these terms show $1/R^6$ asymptotic behavior when contributing to energy.

The SP11cII model is constructed by approximating the pair density partition, $\Delta\rho_2^{c\Pi}(1,2)$, using very few terms shown in [Tab. 8.2](#) and [Tab. 8.3](#). This model is helpful for analyzing the short- and long-range part of the Coulomb hole partition, $h_{c\Pi}(s)$, as introduced previously in [Eq. \(3.93\)](#) in [Chapter 3](#).

The SP11cII model is designed for accurately recovering the entire $\Delta V_{ee}^{c\Pi}$ at large R , and it can be expressed as a sum of short-range and long-range components,

$$\Delta V_{ee}^{c\Pi} = \Delta V_{ee}^{c\Pi,sr} + \Delta V_{ee}^{c\Pi,lr} = \Delta V_{ee}^{c\Pi,sr} + V_{ee}^{dd}. \quad (8.10)$$

In the previous chapter (refer to [Chapter 7](#)), we demonstrated that $\Delta V_{ee}^{c\Pi}$ includes additional energy terms with a $1/R^6$ dependence at short-range, distinct from the long-range component, $\Delta V_{ee}^{c\Pi,lr}$. As we have revealed in [Chapter 7](#), the long-range component $\Delta V_{ee}^{c\Pi,lr}$ is equivalent to V_{ee}^{dd} in the cases of H₂ molecule (both singlet and triplet states) with an $s + p$ basis.

By performing a thorough term-wise analysis, we have systematically identified all the energy terms within $\Delta V_{\text{ee}}^{\text{cII}}$ that exhibit a $1/R^6$ asymptotic behavior at large R . Through this term-wise analysis approach applied to $\Delta V_{\text{ee}}^{\text{cII}}$, we have pinpointed not only the induced dipole-induced dipole (covalent) terms (as shown in [Tab. 8.2](#)), but also certain ionic energy terms that show a $1/R^6$ asymptotic behavior (as listed in [Tab. 8.3](#)). Specifically, the induced dipole-induced dipole terms exclusively arise from the FCI pair density, whereas the ionic terms originate from the SD approximate pair density. Moreover, the ionic terms distinctly exhibit short-range characteristics as we have demonstrated in the minimal H_2 model (in [Chapter 7](#)).

TABLE 8.3: Ionic terms contributing to $\Delta V_{\text{ee}}^{\text{cII}}$ which arise from the SD approximate pair density.

Terms	$s_{\text{A}}^2(2)$	$s_{\text{A}}(2)p_{\text{A}}(2)$	$p_{\text{A}}^2(2)$
$s_{\text{A}}^2(1)$	$s_{\text{A}}^2(1)s_{\text{A}}^2(2)$	$s_{\text{A}}^2(1)s_{\text{A}}(2)p_{\text{A}}(2)$	$s_{\text{A}}^2(1)p_{\text{A}}^2(2)$
$s_{\text{A}}(1)p_{\text{A}}(1)$	$s_{\text{A}}(1)p_{\text{A}}(1)s_{\text{A}}^2(2)$	$s_{\text{A}}(1)p_{\text{A}}(1)s_{\text{A}}(2)p_{\text{A}}(2)$	$s_{\text{A}}(1)p_{\text{A}}(1)p_{\text{A}}^2(2)$
$p_{\text{A}}^2(1)$	$p_{\text{A}}^2(1)s_{\text{A}}^2(2)$	$p_{\text{A}}^2(1)s_{\text{A}}(2)p_{\text{A}}(2)$	$p_{\text{A}}^2(1)p_{\text{A}}^2(2)$
• Each p orbital should be considered: p_x, p_y and p_z. For instance, $s_{\text{A}}^2(1)p_{\text{A}}^2(2)$ represents $s_{\text{A}}^2(1)p_{x\text{A}}^2(2)$, $s_{\text{A}}^2(1)p_{y\text{A}}^2(2)$, and $s_{\text{A}}^2(1)p_{z\text{A}}^2(2)$. • As treating the H_2 molecule, the ionic terms for atom B are identical to those for atom A.			

In particular, among these ionic terms, $s_{\text{A}}^2(1)s_{\text{A}}^2(2)$ and $s_{\text{B}}^2(1)s_{\text{B}}^2(2)$ provide the largest contributions to $\Delta V_{\text{ee}}^{\text{cII}}$. These terms appear in the SD approximate pair density, as demonstrated in the dispersionless simplified H_2 model with minimal basis set (i.e., using only 1s GTOs) shown in [Chapter 7](#). In addition, ionic terms such as $s_{\text{A}}(1)p_{\text{A}}(1)s_{\text{A}}(2)p_{\text{A}}(2)$ and $s_{\text{B}}(1)p_{\text{B}}(1)s_{\text{B}}(2)p_{\text{B}}(2)$ were referred to as “on-site correlation terms” by Baerends *et al.* [90] and are connected with local correlation within the atoms, while their contributions become negligible at large R as we have shown in the He_2 case in [Chapter 7](#).

8.3 Computational Details

All the semi-analytical expressions were derived using the Mathematica program [426]. The CI coefficients were obtained from a numerical FCI calculations of the H_2 molecule with some given input parameters of R , α_s and α_p , using the PySCF package [371, 372] and a modified version of Knowles and Handy’s program [238, 427]. The 1-RDM and 2-RDM were generated using the in-house DMN code

[428, 429]. The range of separation distances R was set from 7.56 to 18.90 a.u. For comparison, the corresponding numerical results of intracule and $\Delta V_{ee}^{c\Pi}$ were computed using the DMN code [428, 429] together with the open-source RH02_OPS program [419] based on the algorithm of Cioslowski and Liu [420].

8.4 Results and Discussion

In this section, we will present the results obtained from the semi-analytical models SP11dd and SP11cII. Firstly, we will identify the short- and long-range correlations from the radial intracule density and V_{ee} components obtained from both models. Next, we will present a simplified version of the SP11dd model under the specific condition of $\alpha_s = \alpha_p$. Then the asymptotic behavior of $h_{c\Pi}(R)$ from the SP11cII model will be investigated. Subsequently, the kinetic energy and electron-nuclear attraction energy contributions to dispersion energy will be taken into account to establish a complete minimal dispersion model of H₂. Finally, we will provide the expression of the dispersion hole that provides the dispersion energy from $\Delta V_{ee}^{c\Pi,lr}$ based on the minimal dispersion models of H₂.

In addition, we emphasize that all the models presented in this chapter are highly qualitative dispersion models. Due to the poor basis set employed, they provide unsurprisingly very low accuracy in calculating C_6 values, deviating significantly from the literature value of $C_6 = 6.499026705 \cdots$ for H₂ [316]. Nonetheless, these models can recover a correct portion of dispersion from the FCI wavefunction. They are helpful for understanding the connections between the dispersion hole and dispersion energy, as well as the relationship, $\Delta V_{ee}^{c\Pi,lr} = 2E_{\text{disp}}$, that was established in Chapter 6.

8.4.1 Short- and Long-range Correlation in SP11cII Model

At large separation distances (i.e., R is scanned from 7.56 to 18.90 a.u.), the numerical results of $\Delta V_{ee}^{c\Pi}$ evaluated by the SP11cII model can be fitted by

$$\Delta V_{ee}^{c\Pi} = A - \frac{C_6^{\Delta V_{ee}^{c\Pi}}}{R^6}, \quad (8.11)$$

where A represents a constant term that is independent of R , and it is not zero in this case. The positive value of $C_6^{\Delta V_{ee}^{c\Pi}}$ arises from the fitting coefficient over R^6 .

Fig. 8.2 shows a numerical example of V_{ee}^{dd} calculated with the model SP11dd, and $\Delta V_{ee}^{c\Pi}$ by the model SP11cII, under the specific setting condition of $\alpha_s = \alpha_p = 1.0$ for the basis function exponents. As we see, although both models yield

energies that decay as $1/R^6$, there is a small but significant gap of approximately 8% between the corresponding fitting coefficients (i.e., $C_6^{V_{ee}^{dd}} = 0.2448$ and $C_6^{\Delta V_{ee}^{cII}} = 0.2673$). As a result, we cannot assume that the SP11dd and SP11cII models are approximately identical. Since the additional $1/R^6$ terms (see [Tab. 8.3](#)) of SP11cII model can not be neglected, we need to verify whether they contribute to the long-range correlation.

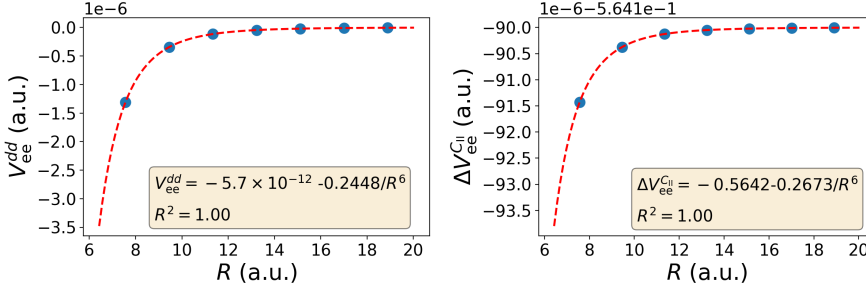


FIGURE 8.2: Model SP11dd vs. SP11cII.

Now we analyze the ionic terms of ΔV_{ee}^{cII} contribution to the short-range correlation through the radial intracule density and ΔV_{ee}^{cII} energy components. On one hand, we compare the radial intracule densities derived from both SP11dd and SP11cII models. [Fig. 8.3](#) shows a plot of intracule at $R = 9.45$ a.u. As expected, at the short-range regime (s_1), the magnitude of the radial intracule density from the SP11cII model (i.e., $h_{cII}(s)$) is more significant, while it is zero from the SP11dd model. At the long-range regime (s_2), which corresponds to a large interelectronic distance s approaches the interatomic distance R and each electron is associated with one atom, both intracule curves become indistinguishable (as shown in the inset plot of [Fig. 8.3](#)). Thus, by excluding the short-range correlation from the SP11cII model, both models exhibit immediate agreement. The intracule analysis reveals that the long-range part of the SP11cII model is identical to the SP11dd model, while the additional ionic terms in the SP11cII model only contribute to the short-range correlation.

On the other hand, the fitting function in [Eq. \(8.11\)](#) can also be decomposed into short- and long-range contributions. As the long-range contribution only results from covalent (i.e., the induced dipole-induced dipole) terms, the short-range correlation must come from the ionic terms, then [Eq. \(8.11\)](#) can be split into

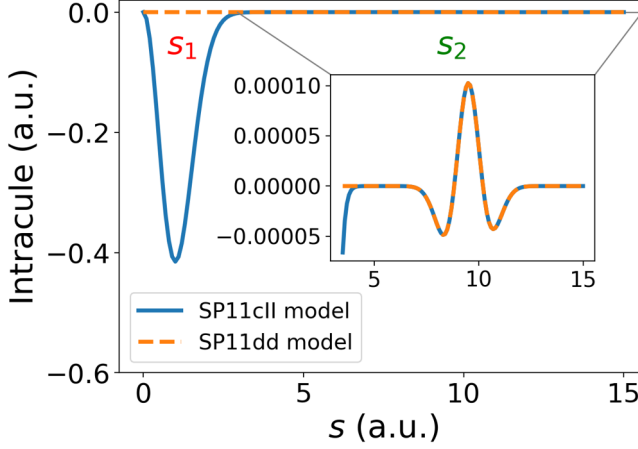


FIGURE 8.3: Comparison between the radial intracule densities I_{dd} from SP11dd and h_{cII} SP11cII models against the interelectronic distance s , the short-range regime represented by s_1 and long-range regime by s_2 . The calculations were performed on H₂ at an interatomic separation of 9.45 a.u., with uncontracted $s + p$ GTO basis set (using the exponents, $\alpha_s = \alpha_p = 1.0$) and the FCI level of theory. The inset figure shows that the radial intracule densities from these two models are identical at the long-range regime.

$$\begin{aligned}
 \text{short-range: } \Delta V_{ee}^{cII, sr} &= A - \frac{C_6^{\Delta V_{ee}^{cII, sr}}}{R^6}, \\
 \text{long-range: } \Delta V_{ee}^{cII, lr} &= -\frac{C_6^{\Delta V_{ee}^{cII, lr}}}{R^6}.
 \end{aligned} \tag{8.12}$$

The $C_6^{\Delta V_{ee}^{cII}}$ term in Eq. (8.11) is decomposed into two components: $C_6^{\Delta V_{ee}^{cII, sr}}$ and $C_6^{\Delta V_{ee}^{cII, lr}}$. Then, we perform a numerical analysis (see Tab. 8.4), and find that the short-range (ionic terms) contribute to both A and $C_6^{\Delta V_{ee}^{cII, sr}}$, while the long-range (covalent terms) give rise to $C_6^{\Delta V_{ee}^{cII, lr}}$.

Tab. 8.4 presents the numerical assessment on the $1/R^6$ dependent terms in the SP11dd and SP11cII models. The energy term ΔV_{ee}^{cII} is obtained by taking the difference between V_{ee}^{FCI} and V_{ee}^{SD} . The ionic term contribution to $\Delta V_{ee}^{cII, sr}$ is solely from V_{ee}^{SD} , and they arise from the SD approximate pair density rather than the FCI one. Hence, these ionic terms presented in V_{ee}^{SD} should not contribute to the true dispersion energy. Considering the (long-range) covalent terms are not incorporated in the SD approximate pair density, the SD approximate pair density is dispersionless, and it can effectively eliminate many other terms from

TABLE 8.4: Analysis of SP11dd and SP11cII models, using $\alpha_s = \alpha_p = 1.0$. The $C_6^{\Delta V_{ee}^{c\Pi}}$ term in Eq. (8.11), and its range-separated components: $C_6^{\Delta V_{ee}^{c\Pi, sr}}$ and $C_6^{\Delta V_{ee}^{c\Pi, lr}}$ in Eq. (8.12), which are represented by “sr” and “lr”, respectively.

Methods	Terms	$C_6^{\Delta V_{ee}^{c\Pi}}$ in Eq. (8.11)	
		sr	lr
FCI	covalent	0	0.2448
	ionic	0	0
SD	covalent	0	0
	ionic	-0.0225	0
SP11dd model	covalent	0	0.2448
SP11cII model	covalent+ionic	0.0225	0.2448

the FCI pair density that are unrelated to dispersion. Additional detailed data using different values of exponents can be found in Tab. A15 in Appendix A.6.

8.4.2 Simplified Model of SP11dd

Since we have demonstrated that the SP11dd model and the long-range part of the SP11cII model are identical for this H_2 model system, now we only focus on analyzing the SP11dd model which involves the induced-dipole induced dipole terms that account for London dispersion. However, the semi-analytical expression of this model still remains fairly complex. In order to gain more insights from this dispersion model, we present here a simplified semi-analytical expression of the SP11dd model in a particular scenario of basis function exponents, where $\alpha_s = \alpha_p = \alpha$, ($\alpha > 0$). Then, the intracule density of the SP11dd model can be simplified as

$$\begin{aligned}
 I_{dd}(s) = & \frac{e^{-\alpha(s+R)^2} s (-2\alpha R(s+R) + e^{4\alpha R s} (2\alpha R(R-s) + 1) - 1) F_{xy}}{4\sqrt{\pi}\alpha R^3} \\
 & - \frac{e^{-\alpha(s-R)^2} s (\alpha R (2\alpha R(s-R)^2 + R - 2s) + 1) F_z}{2\sqrt{\pi}\alpha R^3} \\
 & + \frac{e^{-\alpha(s+R)^2} s (\alpha R (2\alpha R(s+R)^2 + R + 2s) + 1) F_z}{2\sqrt{\pi}\alpha R^3},
 \end{aligned} \tag{8.13}$$

where s denotes the interelectronic distance, R is the interatomic distance, and F_{xy}, F_z are coefficient products composed of CI coefficients. F_{xy} is associated with $s_A p_{xA} s_B p_{xB}$ and $s_A p_{yA} s_B p_{yB}$, while F_z is associated with $s_A p_{zA} s_B p_{zB}$ (see Tab. 8.2)

$$\begin{aligned} F_{xy} &= (c_0 - c_1)(c_4 - c_5 + c_6 - c_7), \\ F_z &= (c_0 - c_1)(c_2 - c_3). \end{aligned} \quad (8.14)$$

We note here that both F_{xy} and F_z exhibit a $1/R^3$ dependence when plotted against R , and the fitting coefficients of $1/R^3$ for both F_{xy} and F_z are approximately equal in magnitude but with opposite signs. Specifically, F_{xy} can be written as $-F_0/R^3$ (where $F_0 > 0$), while F_z can be expressed as F_0/R^3 . We note that the coefficient products of these dispersion terms show $1/R^3$ dependent behavior, and the corresponding two-electron integrals (i.e., from induced-dipole induced dipole terms) are $1/R^3$ dependent as well, thus finally they contribute to dispersion energy ($1/R^6$) when they are combined together.

As R increases large, we can obtain the limit of the intracule $I_{dd}(s=R)$ as R approaches infinity. The expression of $I_{dd}(R)$ can be expanded in terms of $1/R$ as

$$I_{dd}(R) = L_0 + \frac{L_1}{R} + \frac{L_2}{R^2} + \frac{L_3}{R^3} + \dots \quad (8.15)$$

At $R \rightarrow \infty$, the lower order L_n/R^n dependent limits $L_0 = L_1 = L_2 = 0$, thus the leading term of $I_{dd}(R)$ is determined as

$$I_{dd}(R)|_{R \rightarrow \infty} = \frac{F_0}{2R^3} \sqrt{\frac{\alpha}{\pi}}, \quad (8.16)$$

where the F_0 comes from fitting $1/R^3$ term coefficient of F_{xy} and F_z . On the other hand, the V_{ee} expression of the SP11dd model is

$$\begin{aligned} V_{ee}^{dd} &= \frac{\left(\operatorname{erf}(\sqrt{\alpha}R) - 2\sqrt{\frac{\alpha}{\pi}} R e^{-\alpha R^2} \right) F_{xy}}{4\alpha R^3} \\ &\quad + \frac{\left(\operatorname{erfc}(\sqrt{\alpha}R) + 2\sqrt{\frac{\alpha}{\pi}} R e^{-\alpha R^2} (\alpha R^2 + 1) - 1 \right) F_z}{2\alpha R^3}, \end{aligned} \quad (8.17)$$

and by approximating the fitted factors F_{xy} and F_z to $-F_0/R^3$, ($F_0 > 0$) and F_0/R^3 respectively, we can also determine the leading term of V_{ee}^{dd} when R approaches infinity,

$$V_{ee}^{dd}|_{R \rightarrow \infty} = -\frac{3F_0}{4\alpha R^6}. \quad (8.18)$$

Therefore, it is apparent that there is a connection between the intracule $I_{dd}(R)$ in Eq. (8.16) and the dispersion energy of V_{ee}^{dd} in Eq. (8.18). Both of them depend on the fitting parameter F_0 and the GTO basis set exponent α .

Furthermore, in the general case where $\alpha_s \neq \alpha_p$, we can also achieve a closed-form expression for the intracule $I_{dd}(s=R)$. While this expression is more complex than the previous one, the fitting curves of F_{xy} and F_z still exhibit the relationship $F_{xy} = -F_0/R^3$ and $F_z = F_0/R^3$. Therefore, the leading term of the intracule $I_{dd}(R)$ can be determined as

$$I_{dd}(R)|_{R \rightarrow \infty} = \frac{4F_0}{R^3} \sqrt{\frac{2\alpha_s^3 \alpha_p^5}{\pi(\alpha_s + \alpha_p)^7}}. \quad (8.19)$$

If we let $\alpha_s = \alpha_p = \alpha$, we can retrieve [Eq. \(8.16\)](#).

The leading term of V_{ee}^{dd} is determined as

$$V_{ee}^{dd}|_{R \rightarrow \infty} = -\frac{24F_0}{R^6} \frac{\sqrt{\alpha_s^3 \alpha_p^5}}{(\alpha_s + \alpha_p)^5}, \quad (8.20)$$

and by making $\alpha_s = \alpha_p = \alpha$, it will return [Eq. \(8.18\)](#).

By combining [Eq. \(8.19\)](#) and [Eq. \(8.20\)](#) together, through F_0 , we obtain an analytical connection between the $1/R^3$ leading term of intracule I_{dd} and the $1/R^6$ leading term of dispersion energy contributed by V_{ee}^{dd} ,

$$V_{ee}^{dd}|_{R \rightarrow \infty} = -\frac{3\sqrt{2\pi}}{(\alpha_s + \alpha_p)^{3/2}} \frac{I_{dd}(R)|_{R \rightarrow \infty}}{R^3}, \quad (8.21)$$

and

$$C_6^{V_{ee}^{dd}}|_{R \rightarrow \infty} = \frac{3\sqrt{2\pi}}{(\alpha_s + \alpha_p)^{3/2}} D_3|_{R \rightarrow \infty}. \quad (8.22)$$

where the D_3 is the leading term coefficient of I_{dd} . As an easy check, if we set $\alpha_s = \alpha_p = 1.0$, and using the $D_3 = 0.092$ by fitting I_{dd} against R , then we obtain $C_6^{V_{ee}^{dd}} = 0.245$. Thus, the direct link shown in [Eq. \(8.21\)](#) is derived straightforwardly from the semi-analytical expression, which has been verified in the H_2 model using only $s + p$ basis functions. Although establishing a straightforward connection between $I_{dd}(R)$ and V_{ee}^{dd} is challenging due to basis set dependency in the current development, we highlight that the tight connection between D_3 and C_6 allow us to gain information of dispersion energy from a fixed D_3 .

8.4.3 Asymptotic Condition of $h_{c_{II}}(R)$

Since the SP11dd model and the long-range part of SP11cII model are equivalent, then we can use the intracule closed-form of SP11dd model to investigate the asymptotic behavior of $h_{c_{II}}(R)$. Based on the partial contributions of xy and z

terms (see Eq. (8.14)), the closed-form of $I_{dd}(R)$ in Eq. (8.19) can be split into

$$I_{dd}^{xy}(R)|_{R \rightarrow \infty} = -\frac{4F_0}{R^5} \sqrt{\frac{2\alpha_s^3 \alpha_p^5}{\pi(\alpha_s + \alpha_p)^9}}, \quad (8.23)$$

$$I_{dd}^z(R)|_{R \rightarrow \infty} = \frac{4F_0}{R^3} \sqrt{\frac{2\alpha_s^3 \alpha_p^5}{\pi(\alpha_s + \alpha_p)^7}} - \frac{8F_0}{R^5} \sqrt{\frac{2\alpha_s^3 \alpha_p^5}{\pi(\alpha_s + \alpha_p)^9}}, \quad (8.24)$$

then the corresponding dispersion energy term V_{ee}^{dd} can also be decomposed into two terms:

$$V_{ee}^{dd,xy}|_{R \rightarrow \infty} = -\frac{8F_0}{R^6} \frac{\sqrt{\alpha_s^3 \alpha_p^5}}{(\alpha_s + \alpha_p)^5}, \quad (8.25)$$

$$V_{ee}^{dd,z}|_{R \rightarrow \infty} = -\frac{16F_0}{R^6} \frac{\sqrt{\alpha_s^3 \alpha_p^5}}{(\alpha_s + \alpha_p)^5}. \quad (8.26)$$

We demonstrate that the contribution of the z term intracule, $I_{dd}^z(R)$, which decays as $1/R^3$ and $1/R^5$, accounts for 2/3 of the dispersion energy V_{ee}^{dd} . On the other hand, the xy term intracule $I_{dd}^{xy}(R)$ exhibits only a $1/R^5$ asymptotic behavior, and contributes to 1/3 of V_{ee}^{dd} . This result is consistent with the previous numerical analysis of the dispersion hole x/y and z components from Baerends' model, which was applied to the singlet H₂ molecule across different truncated basis sets, as discussed in Chapter 7. Hence, the $1/R^3$ leading term of $I_{dd}(R)$ or $h_{c\Pi}(R)$ is a necessary condition but not a sufficient condition for identifying the $1/R^6$ dependent dispersion energies from or V_{ee}^{dd} or $\Delta V_{ee}^{c\Pi,lr}$.

8.4.4 Inclusion of Kinetic Energy and Electron-Nuclear Attraction Energy Contribution to Dispersion

Up to this point, we only focus on the V_{ee} part contribution to dispersion energy without taking into account the contributions of the kinetic energy T and the electron-nuclear attraction energy V_{en} . In this section, we aim to investigate the roles of T and V_{en} in determining the total dispersion energy and provide a minimal dispersion model that allows us to describe these contributions. In the previous chapter, by using numerical results, we have demonstrated that for the dissociation of the singlet H₂, the difference between the kinetic energies $T^{\text{FCI}} - T^{\text{CAS}(2,2)}$ and the electron-nucleus attraction energies $V_{en}^{\text{FCI}} - V_{en}^{\text{CAS}(2,2)}$ contributes to the coefficients C_6^T and $C_6^{V_{en}}$, respectively. We also found that $T^{\text{CAS}(2,2)}$ and $V_{en}^{\text{CAS}(2,2)}$ do not contain the $1/R^6$ terms, implying that the dispersion energy $1/R^6$ terms only arise from the FCI. In this work, we perform a term-wise analysis of

T in terms of $\rho_1(1;1')$ and V_{en} in terms of $\rho_1(1)$, we refer to [Eq. \(3.68\)](#), [Eq. \(3.69\)](#) in [Chapter 3](#), then all the $1/R^6$ asymptotic energy terms which are based on one-electron AO terms used in $\rho_1(1;1')$ are determined.

By considering all these $1/R^6$ asymptotic energy terms (shown in [Tab. A16](#)), we can model dispersion energy terms from T and V_{en} , respectively. Combining these with the V_{ee} contribution, the complete minimal dispersion model for H_2 can be established. Nevertheless, we also aim to extend this semi-analytical model in order to compare it with the more realistic numerical FCI calculations, where the s and p_z orbitals are mixed to form σ and σ^* bonds due to symmetry, and in total 12 DET should be included in the realistic FCI wavefunction. To reconcile these differences between the non-mixed s and p_z based model and the mixed s and p_z based realistic FCI calculation, also to accommodate the 12 CI coefficients within the simplified H_2 model, where the wavefunction in [Eq. \(8.3\)](#) relies on 8 CI coefficients, we must ensure the normalization of the wavefunction with these CI coefficients used in the semi-analytical model. Hence, we impose a renormalization factor, $\mathcal{N}_c$, to renormalize the wavefunction,

$$\mathcal{N}_c = \sum_{i=0}^7 c_i^2. \quad (8.27)$$

Considering these one-electron AO terms contributing to dispersion collected in [Tab. A16](#), an approximate $\rho_1(1,1')$ and $\rho_1(1)$ can be constructed based on the FCI wavefunction in [Eq. \(8.3\)](#) of this simplified H_2 model system. Then, using [Eq. \(3.68\)](#) and [Eq. \(3.69\)](#) in [Chapter 3](#), the contributions of kinetic energy and electron-nucleus attractive energy to the dispersion energy can be retrieved by

$$T^{\text{disp}} = \frac{3\alpha_s[\frac{1}{2}(c_0 - c_1)^2 - \mathcal{N}_c] + \frac{5}{2}\alpha_p[(c_2 - c_3)^2 + (c_4 - c_5)^2 + (c_6 - c_7)^2]}{\mathcal{N}_c}, \quad (8.28)$$

$$V_{\text{en}}^{\text{disp}} = \frac{-4\sqrt{\frac{2\alpha_s}{\pi}}[\frac{1}{2}(c_0 - c_1)^2 - \mathcal{N}_c] - \frac{4}{3}\sqrt{\frac{2\alpha_p}{\pi}}[(c_2 - c_3)^2 + (c_4 - c_5)^2 + (c_6 - c_7)^2]}{\mathcal{N}_c}, \quad (8.29)$$

We note that the renormalization factor $\mathcal{N}_c$ in the numerator, combined with the term $(c_0 - c_1)^2/2$, can effectively cancel out the convergence behavior of c_0 and c_1 (i.e., c_0 converges to approximately $1/\sqrt{2}$ and c_1 approaches around $-1/\sqrt{2}$).

The $V_{\text{ee}}^{\text{disp}}$ part is derived from model SP11dd in [Eq. \(8.8\)](#) and [Eq. \(8.9\)](#), and it

reads,

$$V_{\text{ee}}^{\text{disp}} = \frac{8\sqrt{\alpha_s^3 \alpha_p^5}}{(\alpha_s + \alpha_p)^5 \mathcal{N}_c R^3} [2(c_0 - c_1)(c_2 - c_3) - (c_0 - c_1)(c_4 - c_5) - (c_0 - c_1)(c_6 - c_7)], \quad (8.30)$$

and we note here that the normalization factors $\mathcal{N}_x$, $\mathcal{N}_y$, and $\mathcal{N}_z$ used in Eq. (8.7) are combined within the closed-forms of the two-electron integrals.

8.4.5 A Full Semi-Analytical Minimal Dispersion Model of H₂

In the last section, we have introduced a minimal dispersion model based on the singlet H₂ that involves 11 variables (i.e., R , α_s , α_p , c_i where $i = 0, 1, \dots, 7$). Although we have obtained the closed form of some parts, the model still requires the CI coefficients that are generated from a numerical FCI calculation. Since the FCI is a variational method, the minimization procedure requires solving the partial differential equations, $\partial E / \partial c_i = 0$, over all the c_i coefficients, and allows us to calculate the total energy. Nonetheless, it is practically very difficult to handle everything analytically even for the H₂ model using uncontracted $s + p$ (GTO) basis functions.

Let us now consider some outputs from the numerical FCI calculations to simplify the model. In the case of the singlet H₂ molecule at large R , we can split the FCI total energy, E , into two parts: $E_{\text{CAS}(2,2)}$ and E_{disp} . As the CAS(2,2) energy² converges more rapidly than the FCI one, the corresponding $c_0 = -c_1 = \frac{1}{\sqrt{2}}$ in CAS(2,2) while it still remains a dispersive $1/R^6$ tail in the FCI case. Hence, at large R , the $E_{\text{CAS}(2,2)}$ term can be assumed as a constant that is independent of R , whereas E_{disp} is the only term that varies along the stretching of R . Hence, at a sufficiently large R , we can assume that $E - E_{\text{disp}}$ is constant. Then employing the variational principle to minimize the total energy of FCI becomes equivalent to minimizing E_{disp} ,

$$\min\{E\} \equiv \min\{E_{\text{disp}}\}. \quad (8.31)$$

The total dispersion energy of the minimal dispersion model is yielded by summing

²The CAS(2,2) method used here is equivalent to the H₂ model with minimal basis set (i.e., one 1s-orbital) shown in support information of Ref. [3]

over its three components in Eq. (8.28), Eq. (8.29) and Eq. (8.30),

$$\begin{aligned}
E_{\text{disp}} = & 3\alpha_s \left[\frac{1}{2}(c_0 - c_1)^2 - 1 \right] + \frac{5}{2}\alpha_p [(c_2 - c_3)^2 + (c_4 - c_5)^2 + (c_6 - c_7)^2] \\
& - 4\sqrt{\frac{2\alpha_s}{\pi}} \left[\frac{1}{2}(c_0 - c_1)^2 - 1 \right] - \frac{4}{3}\sqrt{\frac{2\alpha_p}{\pi}} [(c_2 - c_3)^2 + (c_4 - c_5)^2 + (c_6 - c_7)^2] \\
& + \frac{8\sqrt{\alpha_s^3 \alpha_p^5}}{(\alpha_s + \alpha_p)^5 R^3} [2(c_0 - c_1)(c_2 - c_3) - (c_0 - c_1)(c_4 - c_5) - (c_0 - c_1)(c_6 - c_7)].
\end{aligned} \tag{8.32}$$

We imposed a constraint to the renormalization factor $\mathcal{N}_c = 1$, thus solving the energy minimization problem with the constraint $\mathcal{N}_c = \sum_{i=0}^7 c_i^2 = 1$ requires a Lagrange multiplier λ , the Lagrangian can be then expressed as follows

$$\mathcal{L}(\{c_i\}, \lambda) = E_{\text{disp}}(\{c_i\}) + \lambda \left(\sum_{i=0}^7 c_i^2 - 1 \right). \tag{8.33}$$

Up to this point, although this Lagrangian is still hard to solve analytically, we can employ some numerical results as initial assumptions for simplifying the analytical solution. For instance, at large R , we notice that $c_0 = -c_1$, $c_2 = -c_3 = -2c_4 = 2c_5 = -2c_6 = 2c_7$ from numerical analysis in FCI calculations. This leads to an important simplification of the analytical solution for reducing the CI coefficient variables to only c_0 and c_2 . Solving the following partial differential equations yields explicitly analytical expressions of c_0 and c_2 only in terms of α_s , α_p and R .

$$\begin{aligned}
\frac{\partial \mathcal{L}(c_i, \lambda)}{\partial c_i} &= 0, \\
\frac{\partial \mathcal{L}(c_i, \lambda)}{\partial \lambda} &= 0.
\end{aligned} \tag{8.34}$$

The minimal dispersion model can be written as,

$$E_{\text{disp}} = T^{\text{disp}} + V_{\text{en}}^{\text{disp}} + V_{\text{ee}}^{\text{disp}}. \tag{8.35}$$

By adopting the analytical solutions of CI coefficients, we can obtain the simplified closed-form under the condition of $(-12\sqrt{2\alpha_s/\pi} + 9\alpha_s + 8\sqrt{2\alpha_p/\pi} - 15\alpha_p) < 0$, which is satisfied for the range of $\alpha_s > 0.007$ or $\alpha_p > 0.17$,

$$T^{\text{disp}} + V_{\text{en}}^{\text{disp}} = -\frac{1152\alpha_s^3\alpha_p^5}{(\alpha_s + \alpha_p)^{10}(-12\sqrt{2\alpha_s/\pi} + 9\alpha_s + 8\sqrt{2\alpha_p/\pi} - 15\alpha_p)R^6}, \tag{8.36}$$

$$V_{\text{ee}}^{\text{disp}} = \frac{2304\alpha_s^3\alpha_p^5}{(\alpha_s + \alpha_p)^{10}(-12\sqrt{2\alpha_s/\pi} + 9\alpha_s + 8\sqrt{2\alpha_p/\pi} - 15\alpha_p)R^6}, \tag{8.37}$$

thus we have

$$V_{ee}^{\text{disp}} = 2E_{\text{disp}}. \quad (8.38)$$

We note that this derivation result aligns with the previously established relationship in [Eq. \(6.9\)](#) in [Chapter 6](#).

The analytical results have been verified through numerical data obtained from FCI calculations via PySCF. [Tab. A15](#) in [Appendix A.6](#) shows the dispersion coefficient C_6 and its partition terms calculated from the minimal dispersion model, which is based on the singlet H₂ for various basis set exponents α_s and α_p ranging from 0.6 to 1.2, with a scanning range R set from 7.56 to 18.90 a.u. To examine $C_6^{\Delta E_{AB}}$ and $C_6^{\Delta V_{ee}}$, we calculated and fitted the energy difference between numerical calculations from FCI and CAS(2,2) against R , denoted by $\Delta E_{AB} = E_{AB}^{\text{FCI}} - E_{AB}^{\text{CAS(2,2)}}$, and $\Delta V_{ee} = V_{ee}^{\text{FCI}} - V_{ee}^{\text{CAS(2,2)}}$, respectively. These results are compared to the $\Delta V_{ee}^{c_{II}, \text{lr}}$ predicted by this semi-analytical model and are equivalent to $2C_6^{\Delta E_{AB}}$. Furthermore, we also verified that the numerically obtained V_{ee}^{dd} is identical to the one calculated by the full semi-analytical model in [Eq. \(8.37\)](#). Despite the accuracy of calculating dispersion, this simplified minimal dispersion model provides a simple closed-form and demonstrate the identical relationships between the terms: $C_6^{\Delta V_{ee}^{c_{II}, \text{lr}}}$, $C_6^{V_{ee}^{dd}}$, $C_6^{V_{ee}}$ and $2C_6^{\Delta E_{AB}}$.

8.4.6 Expression of the Dispersion Hole

The radial intracule density of SP11dd model ($I_{dd}(s)$) or the long-range part of SP11cII model vanish upon integrating over the scalar interelectronic distance s

$$\int I_{dd}(s) ds = \int_{\text{LR}} h_{c_{II}}(s) ds = 0. \quad (8.39)$$

In this minimal dispersion model of H₂, both $I_{dd}(s)$ and long-range part of $h_{c_{II}}(s)$ can be used to represent the dispersion hole, as we introduced in [Chapter 7](#).

$$\int h_{\text{disp}}(s) ds = 0, \quad (8.40)$$

In the model SP11dd, if we split the dispersion hole expression into contributions from the xy terms and the z term, then the closed-form of $h_{\text{disp}}(s)$ can be expressed as follows

$$h_{\text{disp}}(s) = h_{\text{disp}}^{xy}(s) + h_{\text{disp}}^z(s), \quad (8.41)$$

where

$$\begin{aligned}
 h_{\text{disp}}^{xy}(s) &= \frac{F_{xy}}{R^3(\alpha_s + \alpha_p)^{9/2}} \sqrt{\frac{2}{\pi}} \alpha_s^{3/2} \alpha_p^{5/2} \left(-4e^{-\frac{1}{2}(R-s)^2(\alpha_s + \alpha_p)}(-1 + R(s-R)(\alpha_s + \alpha_p)) \right. \\
 &\quad \left. - 4e^{-\frac{1}{2}(R+s)^2(\alpha_s + \alpha_p)}(1 + R(s+R)(\alpha_s + \alpha_p)) \right), \\
 h_{\text{disp}}^z(s) &= \frac{F_z}{R^3(\alpha_s + \alpha_p)^{9/2}} \sqrt{\frac{2}{\pi}} \alpha_s^{3/2} \alpha_p^{5/2} \left(-2e^{-\frac{1}{2}(R-s)^2(\alpha_s + \alpha_p)}(2 - 2Rs(\alpha_s + \alpha_p) \right. \\
 &\quad + R^4(\alpha_s + \alpha_p)^2 - 2R^3s(\alpha_s + \alpha_p)^2 + R^2(\alpha_s^2s^2 + 2\alpha_s\alpha_ps^2 + \alpha_s + \alpha_p^2s^2 + \alpha_p)) \\
 &\quad + 2e^{-\frac{1}{2}(R+s)^2(\alpha_s + \alpha_p)}(2 + 2Rs(\alpha_s + \alpha_p) + R^4(\alpha_s + \alpha_p)^2 + 2R^3s(\alpha_s + \alpha_p)^2 \\
 &\quad + R^2(\alpha_s^2s^2 + 2\alpha_s\alpha_ps^2 + \alpha_s + \alpha_p^2s^2 + \alpha_p)) \\
 &\quad - e^{-\frac{1}{2}(R-s)^2(\alpha_s + \alpha_p)}(4 + Rs(\alpha_s + \alpha_p)(-4 - 4R^2(\alpha_s + \alpha_p) + Rs(\alpha_s + \alpha_p)) \\
 &\quad + R^2(\alpha_s + \alpha_p)(2 + (2R^2 + s^2)(\alpha_s + \alpha_p)) \\
 &\quad + e^{-\frac{1}{2}(R+s)^2(\alpha_s + \alpha_p)}(4 + Rs(\alpha_s + \alpha_p)(4 + 4R^2(\alpha_s + \alpha_p) + Rs(\alpha_s + \alpha_p)) \\
 &\quad \left. + R^2(\alpha_s + \alpha_p)(2 + (2R^2 + s^2)(\alpha_s + \alpha_p)) \right), \tag{8.42}
 \end{aligned}$$

$$F_{xy} = F_x + F_y. \tag{8.43}$$

According to the numerical results of CI coefficients and the fittings of CI coefficient products shown in Eq. (8.14), we can make an approximation of $F_{xy} \approx -F_0/R^3$, ($F_0 > 0$) and $F_z \approx F_0/R^3$, and F_0 can be determined by using the analytical solutions of CI coefficients (as presented in Section 8.4.5),

$$F_0 = -\frac{96\sqrt{\alpha_s^3\alpha_p^5}}{(\alpha_s + \alpha_p)^5(-12\sqrt{2\alpha_s/\pi} + 9\alpha_s + 8\sqrt{2\alpha_p/\pi} - 15\alpha_p)}. \tag{8.44}$$

Fig. 8.4 shows the dispersion hole curves contributed by xy terms and z term, as well as the total one. As the diatomic molecule is aligned along the z -axis, the magnitudes of $h_{\text{disp}}^z(s)$ are roughly 100 times larger than the $h_{\text{disp}}^{xy}(s)$. In addition, we also examined that the analytical integration of Eq. (8.40) above resulted in zero for all three curves.

On the other hand, the dispersion hole expression above can be rearranged as

$$h_{\text{disp}}(s) = \frac{N_0 F_0}{R^6}(U^+ + U^-), \tag{8.45}$$

for convenience, the relevant terms are rewritten as

$$N_0 = \sqrt{\frac{2\alpha_s^3\alpha_p^5}{\pi(\alpha_s + \alpha_p)^9}}, \tag{8.46}$$

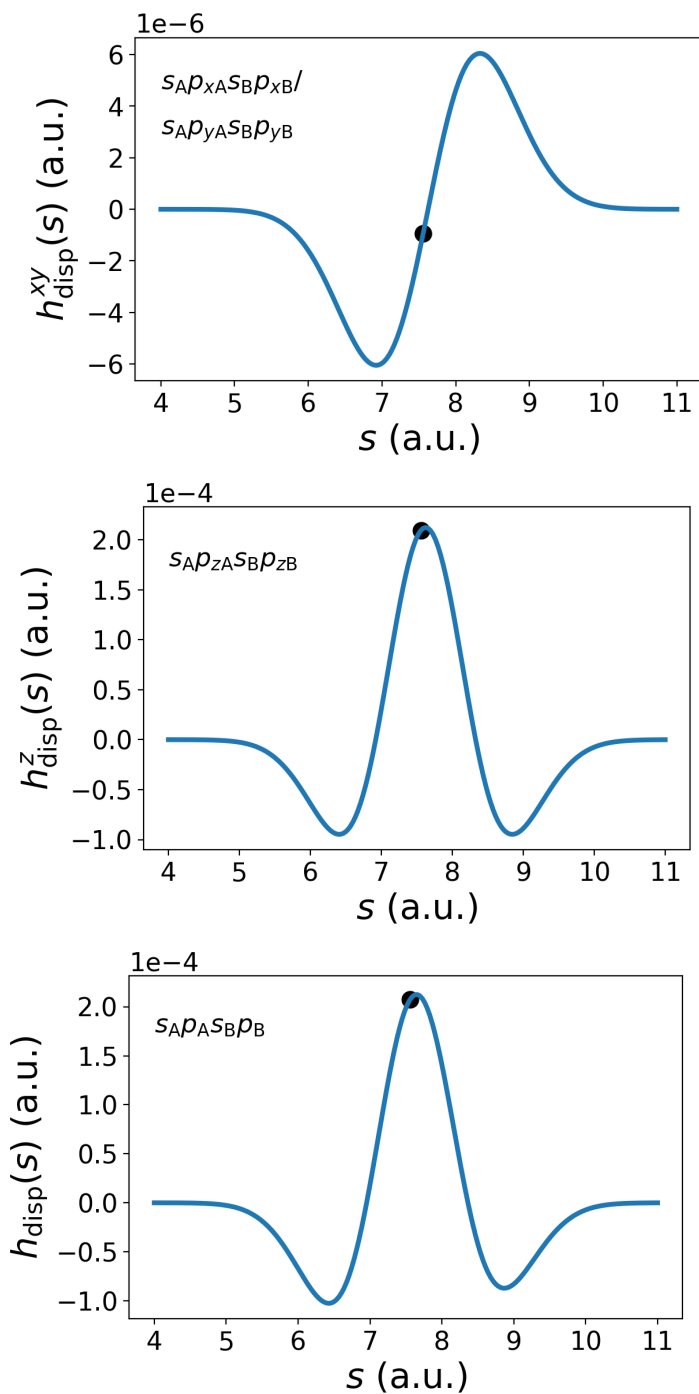


FIGURE 8.4: Dispersion hole of H₂ minimal dispersion model in Eq. (8.41) and Eq. (8.42) with uncontracted $s + p$ Gaussian-type basis functions (exponents $\alpha_s = \alpha_p = 1.0$). The interatomic distance $R = 7.56$ a.u. and the parameter F_0 in Eq. (8.44) equals 0.3264.

$$U^+ = e^{-\frac{\alpha_0}{2}(R+s)^2} (4\alpha_0^2 s R^4 + 8\alpha_0^2 s^2 R^3 + 4\alpha_0(2s + \alpha_0 s^3)R^2 + 12\alpha_0 s^2 R + 12s), \quad (8.47)$$

$$U^- = e^{-\frac{\alpha_0}{2}(R-s)^2} (-4\alpha_0^2 s R^4 + 8\alpha_0^2 s^2 R^3 - 4\alpha_0(2s + \alpha_0 s^3)R^2 + 12\alpha_0 s^2 R - 12s), \quad (8.48)$$

$$\alpha_0 = \alpha_s + \alpha_p. \quad (8.49)$$

In Eq. (8.45), the curves of U^+ and U^- against s are symmetric, and the integration of $h_{\text{disp}}(s)$ can be written as

$$\int h_{\text{disp}}(s) ds = \frac{N_0 F_0}{R^6} \left(\int U^+ ds + \int U^- ds \right), \quad (8.50)$$

where

$$\int U^+ ds = \frac{4e^{-\frac{1}{2}\alpha_0 R^2} (\alpha_0 R^2 + 3)}{\alpha_0}, \quad (8.51)$$

$$\int U^- ds = -\frac{4e^{-\frac{1}{2}\alpha_0 R^2} (\alpha_0 R^2 + 3)}{\alpha_0}. \quad (8.52)$$

Hence, the analytical integration of $h_{\text{disp}}(s)$ fully vanishes,

$$\int h_{\text{disp}}(s) ds = 0. \quad (8.53)$$

Notice that the term U^+ decay to zero in the range of $s \in [0, \infty)$, thus we can use only U^- term to substitute $U^+ + U^-$ terms in the expression of $h_{\text{disp}}(s)$. It could be helpful for modeling dispersion hole for future study.

CONCLUSIONS

Electron correlation plays a crucial role in quantum chemistry and physics. It has been regarded as nature’s “chemical glue”, facilitating the cohesion of atoms, making them form molecules and solids, thereby maintaining the cohesion of the real world [9, 10, 430]. The performance of quantum chemistry methods strongly relies on the approximations of electron correlation. Two primary aspects of electron correlation were addressed in this thesis: the development and statistical analysis of MR diagnostics (Chapter 4 and Chapter 5) and the study of London dispersion interactions through the correlated pair density perspective (Chapter 6 to Chapter 8).

In Chapter 4, we introduced normalization approaches for various correlation metrics to ensure their size-intensivity and also proposed several new indices to be electron correlation measures. Subsequently, we established analytical connections between certain correlation metrics across different categories (i.e., $\overline{I_{\text{ND}}}$ and $1 - c_0^2$ with appropriate normalizations, and $I_{\text{ND}}^{\text{max}}$ and D_2). These findings have been validated numerically through statistical assessments of various small datasets. Moreover, we applied the linear relationships determined through the statistical assessments to reduce the number of distinct correlation measures.

Chapter 5 focused on the application of correlation metrics as MR diagnostic tools. We first analyzed the linear relationships among MR diagnostics using large datasets. Through the linear relationships, we categorized those correlation metrics that provide similar information, proposing a single representative one to

substitute others. Then, we analyzed various correlation metrics across several typical MR systems while incrementally increasing the system size. We excluded a few correlation metrics from being considered MR diagnostics, as they failed to detect MR character in large systems. Afterwards, we suggested cutoffs for the remaining correlation metrics, based on their fitted relationships and known cutoffs of other MR diagnostics. In the end, only a small number of MR diagnostics can be used, and these maximum metrics, such as D_2 and $I_{\text{ND}}^{\text{max}}$, provide the same information. Consequently, we propose the use of $I_{\text{ND}}^{\text{max}}$ as a representative MR diagnostic tool with appropriate cutoffs, highlighting its potential for application across all types of electronic structure methods.

In [Chapter 6](#), we first derived a theoretical connection between dispersion energy and the long-range dynamic correlation described by the V_{ee} term, grounded in the virial theorem. To assess this theoretical connection, we examined two pair density-based dispersion models, namely Baerends’ model and the extended Baerends’ model. Then, we applied these two models to a group of diatomic molecule dissociation cases evaluated through various correlated wavefunction methods. Comparing the dispersion energy evaluated through these two models and retrieved from correlation energy using a dispersionless reference method, we confirm the validity of this theoretical connection, which remains robust regardless of the electronic structure methods and basis sets employed. In addition, the extended Baerends’s model has significantly improved the accuracy for retrieving dispersion energies of larger diatomic molecules beyond H_2 and He_2 , especially in the necessary presence of d orbitals within the basis set for the large systems.

[Chapter 7](#) provided an exhaustive numerical analysis of the contributions of various electronic energy components to dispersion in H_2 (singlet and triplet) and He_2 at large interatomic distances. We analyzed the dispersion energy contributed by the correlation energy components, particularly the ΔV_{ee} terms. Then, we assessed various molecular systems through the $\Delta V_{\text{ee}}^{\text{c}_{\text{II}},\text{lr}}$ term, which is derived from the long-range part of correlated pair density partition $\Delta \rho_2^{\text{c}_{\text{II}}}$. The application of the $\Delta \rho_2^{\text{c}_{\text{II}}}$ approach has been demonstrated to successfully retrieve dispersion energy captured by wavefunction method calculations with a given basis set. At the end, we introduced the concept of a *dispersion hole*. In general, it can be represented by the long-range part of the Coulomb hole partition, $h_{\text{c}_{\text{II}}}$, which has been shown connected to dispersion. The dispersion hole can be applied to aid in calculating and identifying dispersion interactions.

In [Chapter 8](#), a minimal dispersion model was presented for the molecular H_2 singlet at large interatomic separations. While this simplified model did not

aim for precise dispersion energy, it provided qualitative insights beyond second-order perturbation theory. Moreover, it helps understand the connection between dispersion energy and the long-range component of the Coulomb hole partition, offering new insights for the development of future advanced dispersion models.

Overall, we explored electron correlation in quantum chemistry from two perspectives: developing and assessing MR diagnostics based on correlation measures, and studying London dispersion interactions captured by SR wavefunction methods. Our work led to the introduction of new MR diagnostic approaches, allowing for a deeper understanding of nondynamic correlation effects. On one hand, we identified the significance of including extended induced multipole-induced multipole terms to accurately evaluate dispersion energies in larger diatomic molecules. On the other hand, we also revealed that the long-range part of the pair density partition $\Delta\rho_2^{cII}$ (also referred to as the long-range part of the cumulant of the pair density) is enough to determine the C_6 coefficient of dispersion interactions. These findings provide valuable insights into the development of electronic structure methods that include London dispersion interactions.

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A.1 Diagonalizing Density Matrix

Consider a compacted matrix that represents the occupied-occupied (*oo*), occupied-virtual (*ov*), virtual-occupied (*vo*), and virtual-virtual (*vv*) blocks in the one-electron density matrix, denoted as ${}^1\mathbf{D}$,

$${}^1\mathbf{D} = \begin{bmatrix} {}^1\mathbf{D}_{oo} & {}^1\mathbf{D}_{ov} \\ {}^1\mathbf{D}_{vo} & {}^1\mathbf{D}_{vv} \end{bmatrix} = \begin{bmatrix} {}^1\mathbf{D}_{ii} & {}^1\mathbf{D}_{ia} \\ {}^1\mathbf{D}_{ai} & {}^1\mathbf{D}_{aa} \end{bmatrix}, \quad (\text{A1})$$

we diagonalize it using a unitary matrix $\mathbf{U}$, and yields

$$\mathbf{U}({}^1\mathbf{D})\mathbf{U}^{-1} = \begin{bmatrix} \frac{1}{2}(\mathbf{X} + \mathbf{Y}) & 0 \\ 0 & \frac{1}{2}(\mathbf{X} - \mathbf{Y}) \end{bmatrix}, \quad (\text{A2})$$

where

$$\begin{aligned} \mathbf{X} &= {}^1\mathbf{D}_{ii} + {}^1\mathbf{D}_{aa}, \\ \mathbf{Y} &= \sqrt{({}^1\mathbf{D}_{ii} - {}^1\mathbf{D}_{aa})^2 + 4({}^1\mathbf{D}_{ia})({}^1\mathbf{D}_{ai})}. \end{aligned} \quad (\text{A3})$$

As ${}^1\mathbf{D}$ is a Hermitian matrix with real numbers, we have ${}^1\mathbf{D}_{ia} = {}^1\mathbf{D}_{ai}$. If the off-diagonal block elements (i.e., ${}^1\mathbf{D}_{ia}$) approach zero, then we can perform a Taylor series expansion of the term $\mathbf{Y}$ around the point where ${}^1\mathbf{D}_{ia}^2 \approx 0$,

$$\mathbf{Y} = \sqrt{({}^1\mathbf{D}_{ii} - {}^1\mathbf{D}_{aa})^2} + \frac{2({}^1\mathbf{D}_{ia})^2}{\sqrt{({}^1\mathbf{D}_{ii} - {}^1\mathbf{D}_{aa})^2}} + \mathcal{O}(({}^1\mathbf{D}_{ia}^2)^2). \quad (\text{A4})$$

If we take the leading term of $\mathbf{Y}$, the summations of eigenvalues over *oo* and *vv* blocks are approximated as

$$\begin{aligned} \sum_{\sigma,i}^{\text{occ}} n_i^\sigma &\approx \text{Tr}({}^1\mathbf{D}_{ii}), \\ \sum_{\sigma,i}^{\text{vir}} n_i^\sigma &\approx \text{Tr}({}^1\mathbf{D}_{aa}). \end{aligned} \quad (\text{A5})$$

A.2 Upper Bound of $I_{\text{ND}}^{\text{max}}$ for MP2

Given two positive semidefinite matrices, $\mathbf{A}$ and $\bar{\mathbf{A}}$, both being symmetric matrices of the same dimension and containing real numbers, then all their eigenvalues are non-negative. According to Courant-Fischer min-max theorem [431], the maximum eigenvalue of their matrix sum satisfies the upper bound inequality,

$$\lambda_{\text{max}}(\mathbf{A} + \bar{\mathbf{A}}) \leq \lambda_{\text{max}}(\mathbf{A}) + \lambda_{\text{max}}(\bar{\mathbf{A}}). \quad (\text{A6})$$

Consider the construction of occupied-occupied (oo) block of the unrelaxed density matrix of MP2, as shown in Eq. (4.27), the two matrices $\mathbf{A}$ and $\bar{\mathbf{A}}$ can be established by

$$\mathbf{A} = \sum_{abk} t_{jk}^{ab} t_{ik}^{ab}, \quad (\text{A7})$$

$$\bar{\mathbf{A}} = \sum_{abk} t_{jk}^{ab} t_{ik}^{ba}, \quad (\text{A8})$$

then

$$\begin{aligned} \tilde{n}_H &= 2 - 4\lambda_{\text{max}}(\mathbf{A}) \\ &\leq 2 - [\lambda_{\text{max}}(4\mathbf{A}) + \lambda_{\text{max}}(-2\bar{\mathbf{A}})] \\ &\leq 2 - \lambda_{\text{max}}(4\mathbf{A} - 2\bar{\mathbf{A}}) \\ &= n_H. \end{aligned} \quad (\text{A9})$$

Analogously, for the virtual-virtual (vv) block in Eq. (4.28),

$$\mathbf{B} = \sum_{ijc} t_{ij}^{bc} t_{ij}^{ac}, \quad (\text{A10})$$

$$\bar{\mathbf{B}} = \sum_{ijc} t_{ij}^{bc} t_{ij}^{ca}, \quad (\text{A11})$$

then

$$\begin{aligned} \tilde{n}_L &= 4\lambda_{\text{max}}(\mathbf{B}) \\ &\geq \lambda_{\text{max}}(4\mathbf{B}) + \lambda_{\text{max}}(-2\bar{\mathbf{B}}) \\ &\geq \lambda_{\text{max}}(4\mathbf{B} - 2\bar{\mathbf{B}}) \\ &= n_L. \end{aligned} \quad (\text{A12})$$

To demonstrate $\widetilde{I_{\text{ND}}^{\text{max}}}$ to be the upper bound of $I_{\text{ND}}^{\text{max}}$, let us first consider the difference between $I_{\text{ND}}^{\text{max}}$ and the approximate one $\widetilde{I_{\text{ND}}^{\text{max}}}$,

$$\Delta = I_{\text{ND}}^{\text{max}} - \widetilde{I_{\text{ND}}^{\text{max}}}. \quad (\text{A13})$$

As established in Eq. (4.13), $I_{\text{ND}}^{\text{max}}$ is determined either by n_H or n_L , allowing us to examine these two cases separately. If n_H contributes to $I_{\text{ND}}^{\text{max}}$ and $\tilde{n}_H$ to $\widetilde{I_{\text{ND}}^{\text{max}}}$, then

$$\begin{aligned}\Delta &= \frac{n_H}{2} \left(1 - \frac{n_H}{2}\right) - \frac{\tilde{n}_H}{2} \left(1 - \frac{\tilde{n}_H}{2}\right) \\ &= \left(\frac{n_H}{2} - \frac{\tilde{n}_H}{2}\right) \left(1 - \frac{n_H}{2} - \frac{\tilde{n}_H}{2}\right)\end{aligned}\tag{A14}$$

Since we focus on closed-shell singlet molecules calculated at the MP2 level, both n_H and $\tilde{n}_H$ are assumed to be not less than 1, and $n_H \geq \tilde{n}_H$ have been demonstrated in Eq. (A9), thus $\Delta \leq 0$.

Similarly, if n_L contributes to $I_{\text{ND}}^{\text{max}}$ and $\tilde{n}_L$ to $\widetilde{I_{\text{ND}}^{\text{max}}}$, then it is easy to achieve again $\Delta \leq 0$. Hence, $\widetilde{I_{\text{ND}}^{\text{max}}}$ serves as the upper bound of $I_{\text{ND}}^{\text{max}}$ for MP2.

A.3 Supplementary Results: Chapter 4

TABLE A1: MP2/cc-pVTZ, comparison between n_i -based indices and approximate $\tilde{n}_i$ -based indices for 34 molecules, geometries are optimized by MP2/cc-pVTZ [1].

Mol.	n_H	$\tilde{n}_H$	n_L	$\tilde{n}_L$	$I_{\text{ND}}^{\text{max}}$	$\widetilde{I_{\text{ND}}^{\text{max}}}$
HF	1.968	1.952	0.024	0.036	0.016	0.024
H ₂ O	1.964	1.946	0.025	0.038	0.018	0.026
NH ₃	1.962	1.944	0.021	0.033	0.019	0.027
CH ₄	1.966	1.947	0.016	0.026	0.017	0.026
HCl	1.959	1.939	0.026	0.041	0.020	0.030
SiH ₄	1.969	1.947	0.012	0.023	0.015	0.026
CO ₂	1.940	1.916	0.064	0.091	0.031	0.043
CIOH	1.949	1.929	0.041	0.064	0.025	0.034
H ₂ S	1.954	1.931	0.027	0.043	0.022	0.033
BeO	1.932	1.902	0.054	0.078	0.033	0.047
CO	1.940	1.914	0.052	0.077	0.029	0.041
HNC	1.936	1.907	0.050	0.076	0.031	0.044
N ₂	1.923	1.889	0.067	0.100	0.037	0.053
Cl ₂	1.935	1.907	0.050	0.080	0.032	0.044
CH ₂ O	1.952	1.931	0.038	0.059	0.024	0.033
HCN	1.923	1.888	0.062	0.093	0.037	0.053
FOH	1.937	1.905	0.058	0.093	0.031	0.045
Cl ₂ O	1.926	1.894	0.062	0.097	0.036	0.050
C ₂ H ₂	1.926	1.891	0.053	0.079	0.036	0.052
FNO	1.923	1.886	0.079	0.118	0.038	0.056
CH ₂ NH	1.928	1.890	0.054	0.087	0.035	0.052
C ₃	1.893	1.847	0.078	0.116	0.051	0.071
C ₂ H ₄	1.931	1.894	0.046	0.075	0.033	0.050
ClNO	1.915	1.869	0.092	0.143	0.044	0.066
H ₂ N ₂	1.922	1.879	0.061	0.099	0.038	0.057
CH ₂	1.962	1.936	0.018	0.029	0.018	0.031
F ₂	1.918	1.868	0.078	0.131	0.040	0.062
P ₂	1.896	1.849	0.080	0.121	0.049	0.070
HNO	1.916	1.870	0.073	0.118	0.040	0.061
BF	1.956	1.918	0.029	0.046	0.022	0.039
BCl	1.948	1.910	0.030	0.047	0.025	0.043
O ₃	1.856	1.768	0.181	0.291	0.082	0.124
CN ⁺	1.835	1.740	0.148	0.232	0.076	0.113
C ₂	1.826	1.721	0.154	0.247	0.080	0.120

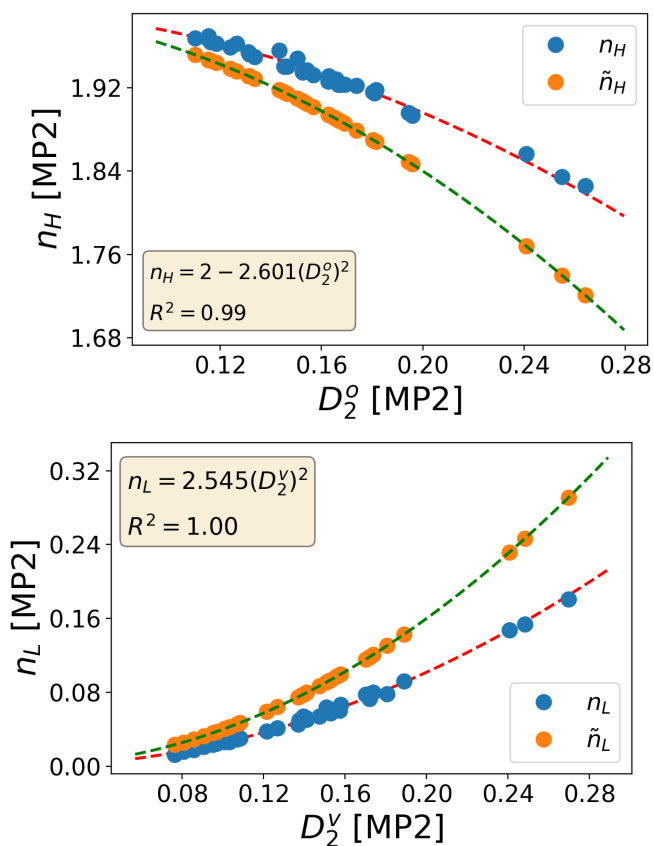


FIGURE A1: Plots between D_2 diagnostic and approximate natural orbital-based indices from MP2/cc-pVTZ for 34 molecules [1].

TABLE A2: MP2/cc-pVTZ, various MR diagnostics for the 34 molecules from [1], geometries are optimized at the MP2/cc-pVTZ level.

Mol.	D_1	D_2	$\overline{I}_{\text{ND}}$	$I_{\text{ND}}^{\text{max}}$	r_{ND}	n_H	NON
HF	0.010	0.110	0.019	0.016	0.145	1.968	0.012
H ₂ O	0.009	0.116	0.024	0.018	0.152	1.964	0.012
NH ₃	0.009	0.118	0.025	0.018	0.147	1.962	0.011
CH ₄	0.009	0.115	0.024	0.017	0.133	1.966	0.008
HCl	0.008	0.124	0.015	0.020	0.167	1.959	0.013
SiH ₄	0.009	0.115	0.013	0.015	0.123	1.969	0.006
CO ₂	0.043	0.151	0.029	0.031	0.188	1.940	0.032
CLOH	0.018	0.134	0.018	0.025	0.169	1.949	0.021
H ₂ S	0.011	0.131	0.017	0.022	0.162	1.954	0.013
BeO	0.053	0.157	0.034	0.033	0.209	1.932	0.027
CO	0.036	0.146	0.029	0.029	0.188	1.940	0.026
HNC	0.029	0.153	0.031	0.031	0.185	1.936	0.025
N ₂	0.026	0.167	0.034	0.037	0.208	1.923	0.033
Cl ₂	0.015	0.152	0.016	0.032	0.184	1.935	0.025
CH ₂ O	0.038	0.131	0.026	0.023	0.160	1.952	0.019
HCN	0.027	0.168	0.034	0.037	0.198	1.923	0.031
FOH	0.017	0.154	0.024	0.031	0.166	1.937	0.029
Cl ₂ O	0.028	0.163	0.019	0.036	0.190	1.926	0.031
C ₂ H ₂	0.024	0.165	0.033	0.036	0.184	1.926	0.026
FNO	0.052	0.172	0.029	0.038	0.195	1.923	0.039
CH ₂ NH	0.026	0.166	0.029	0.035	0.166	1.928	0.027
C ₃	0.050	0.196	0.039	0.051	0.216	1.893	0.039
C ₂ H ₄	0.024	0.163	0.028	0.033	0.155	1.931	0.023
ClNO	0.052	0.189	0.026	0.044	0.207	1.915	0.046
H ₂ N ₂	0.027	0.174	0.030	0.038	0.179	1.922	0.030
CH ₂	0.009	0.127	0.023	0.018	0.137	1.962	0.009
F ₂	0.023	0.182	0.023	0.039	0.175	1.918	0.039
P ₂	0.028	0.194	0.023	0.049	0.237	1.896	0.040
HNO	0.042	0.180	0.030	0.040	0.188	1.916	0.037
BF	0.026	0.143	0.022	0.022	0.157	1.956	0.015
BCl	0.021	0.150	0.019	0.025	0.180	1.948	0.015
O ₃	0.058	0.270	0.039	0.082	0.238	1.856	0.091
CN ⁺	0.101	0.255	0.067	0.076	0.322	1.835	0.074
C ₂	0.051	0.264	0.066	0.080	0.308	1.826	0.077

TABLE A3: CCSD/cc-pVTZ, various MR diagnostics for the 34 molecules from [1], geometries are optimized at the CCSD/cc-pVTZ level.

Mol.	T_1	D_1	D_2	$\overline{I}_{\text{ND}}$	$I_{\text{ND}}^{\text{max}}$	r_{ND}	n_H
HF	0.007	0.012	0.118	0.019	0.016	0.145	1.967
H ₂ O	0.007	0.011	0.126	0.025	0.019	0.156	1.962
NH ₃	0.006	0.010	0.131	0.029	0.020	0.158	1.959
CH ₄	0.007	0.012	0.135	0.030	0.021	0.154	1.958
HCl	0.006	0.011	0.143	0.018	0.024	0.183	1.951
SiH ₄	0.011	0.017	0.148	0.019	0.023	0.163	1.952
CO ₂	0.018	0.046	0.150	0.026	0.026	0.176	1.948
ClOH	0.009	0.022	0.155	0.020	0.025	0.179	1.949
H ₂ S	0.009	0.016	0.158	0.021	0.028	0.187	1.943
BeO	0.043	0.104	0.160	0.029	0.028	0.195	1.943
CO	0.018	0.039	0.162	0.030	0.027	0.189	1.945
HNC	0.016	0.033	0.163	0.033	0.030	0.191	1.938
N ₂	0.013	0.026	0.172	0.032	0.033	0.199	1.932
Cl ₂	0.008	0.021	0.176	0.018	0.034	0.198	1.929
CH ₂ O	0.018	0.056	0.177	0.030	0.032	0.178	1.934
HCN	0.014	0.029	0.178	0.034	0.035	0.197	1.928
FOH	0.009	0.021	0.181	0.024	0.033	0.170	1.935
Cl ₂ O	0.014	0.044	0.181	0.021	0.034	0.197	1.930
C ₂ H ₂	0.013	0.028	0.182	0.035	0.036	0.193	1.925
FNO	0.020	0.058	0.187	0.027	0.036	0.184	1.929
CH ₂ NH	0.012	0.034	0.192	0.032	0.039	0.178	1.919
C ₃	0.023	0.052	0.193	0.040	0.041	0.216	1.914
C ₂ H ₄	0.011	0.032	0.195	0.033	0.040	0.174	1.916
CINO	0.021	0.062	0.199	0.025	0.041	0.202	1.915
H ₂ N ₂	0.011	0.035	0.206	0.034	0.042	0.193	1.911
CH ₂	0.009	0.019	0.209	0.041	0.042	0.200	1.912
F ₂	0.010	0.027	0.212	0.024	0.044	0.179	1.909
P ₂	0.017	0.033	0.214	0.024	0.048	0.242	1.899
HNO	0.017	0.055	0.218	0.033	0.045	0.197	1.910
BF	0.016	0.031	0.227	0.029	0.047	0.191	1.900
BCl	0.016	0.031	0.242	0.026	0.054	0.219	1.886
O ₃	0.025	0.072	0.261	0.032	0.063	0.208	1.881
CN ⁺	0.068	0.185	0.372	0.071	0.103	0.346	1.767
C ₂	0.039	0.086	0.377	0.075	0.109	0.346	1.752

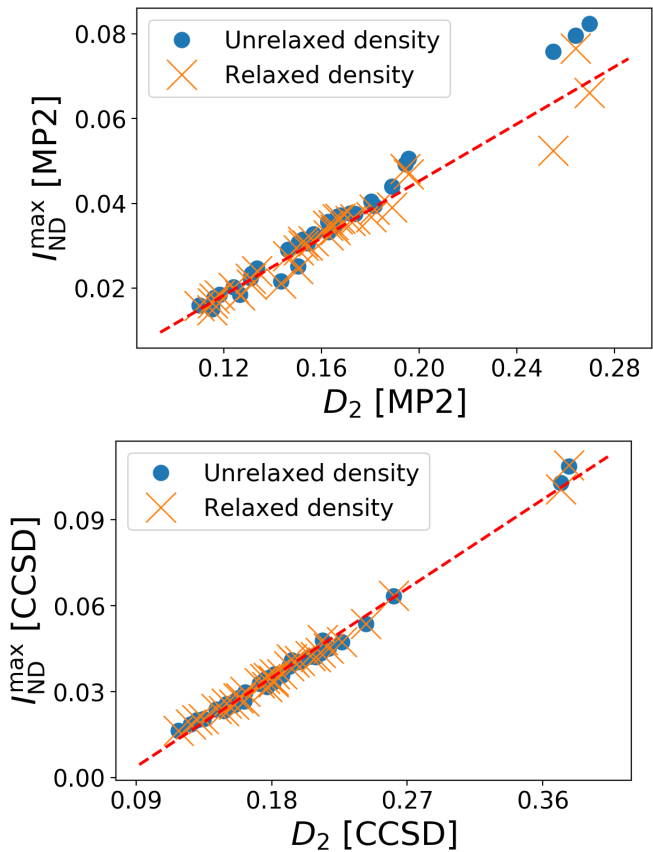


FIGURE A2: Plots between MR diagnostic pairs from MP2/cc-pVTZ and CCSD/cc-pVTZ of 34 molecules, geometries are optimized by MP2/cc-pVTZ and CCSD/cc-pVTZ, respectively [1]. The two outliers (from MP2) in strong nondynamic correlation regime are O_3 and CN^+ .

TABLE A4: MP2/cc-pVTZ, $I_{ND}^{\max}$ from unrelaxed and relaxed density of O_3 , CN^+ and C_2 molecules in strong nondynamic correlation regime. The occupation numbers in bold are the ones correspond to $I_{ND}^{\max}$.

Mol.	Unrelaxed density			Relaxed density		
	n_H	n_L	$I_{ND}^{\max}$	n_H	n_L	$I_{ND}^{\max}$
O_3	1.85633	0.18113	0.08236	1.85922	0.14222	0.06605
CN^+	1.83469	0.14761	0.07582	1.88889	0.10109	0.05247
C_2	1.82570	0.15375	0.07956	1.83295	0.13399	0.07655

A.4 Supplementary Results: Chapter 5

TABLE A5: Summary of linear fittings

Method	Dataset	Fitting Function	Regression R^2
SCI	18e-mols	$4(1 - c_0^2)/N = 1.007\overline{I_{\text{ND}}}$	0.998
SCI	18e-mols	$4(1 - c_0^{2/N}) = 1.053\overline{I_{\text{ND}}}$	1.000
SCI	18e-mols	$(1 - c_0^2)/N = 0.956(1 - c_0^{2/N})$	0.999
CISD	18e-mols	$4(1 - c_0^2)/N = 1.031\overline{I_{\text{ND}}}$	0.998
CISD	18e-mols	$4(1 - c_0^{2/N}) = 1.068\overline{I_{\text{ND}}}$	0.998
CISD	18e-mols	$(1 - c_0^2)/N = 0.965(1 - c_0^{2/N})$	1.000
CISD	Handy-7mols	$4(1 - c_0^2)/N = 1.102\overline{I_{\text{ND}}}$	0.987
CISD	Handy-7mols	$4(1 - c_0^{2/N}) = 1.167\overline{I_{\text{ND}}}$	0.984
CISD	Handy-7mols	$(1 - c_0^2)/N = 0.943(1 - c_0^{2/N})$	0.998
CCSD	Handy-7mols	$I_{\text{ND}}^{\text{max}} = 0.386D_2 - 0.037$	0.991
CCSD	NJ34	$I_{\text{ND}}^{\text{max}} = 0.349D_2 - 0.028$	0.990
CCSD	cc-311	$I_{\text{ND}}^{\text{max}} = 0.367D_2 - 0.030$	0.987
MP2	NJ34	$I_{\text{ND}}^{\text{max}} = 0.422D_2 - 0.034$	0.986
MP2	mp-5090	$I_{\text{ND}}^{\text{max}} = 0.373D_2 - 0.026$	0.953

TABLE A6: Summary of quartic fittings

Method	Dataset	Fitting Function	Regression R^2
CCSD	Handy-7mols	$I_{\text{ND}}^{\text{max}} = 0.562D_2^2(2 - 4D_2^2)$	0.959
CCSD	NJ34	$I_{\text{ND}}^{\text{max}} = 0.543D_2^2(2 - 4D_2^2)$	0.988
CCSD	cc-311	$I_{\text{ND}}^{\text{max}} = 0.558D_2^2(2 - 4D_2^2)$	0.973
MP2	NJ34	$I_{\text{ND}}^{\text{max}} = 0.673D_2^2(2 - 4D_2^2)$	0.990
MP2	mp-5090	$I_{\text{ND}}^{\text{max}} = 0.687D_2^2(2 - 4D_2^2)$	0.953
MP2	mp-5090	$I_{\text{ND}}^{\text{max}} = -6.203D_2^4 + 1.516D_2^2 - 0.001$	0.958

TABLE A7: Squared Pearson’s correlation coefficients (R^2) for CCSD over 327 molecular structures.

R^2 matrix	S_J	$\overline{I_D}$	r_{ND}	$\overline{I_{ND}}$	$I_{ND}^{\max}$	n_H	n_L	M_{diag}	D_2	D_1	T_1	$\%E_{\text{corr}}^{\alpha\beta}$	$\%TAE(T)$	$\%E_{\text{corr}}[(T)]$
S_J	1.00	0.86	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
$\overline{I_D}$	0.86	1.00	0.02	0.00	0.01	0.03	0.03	0.03	0.01	0.01	0.03	0.02	0.01	0.00
r_{ND}	0.00	0.02	1.00	0.75	0.71	0.79	0.79	0.79	0.69	0.35	0.62	0.00	0.08	0.11
$\overline{I_{ND}}$	0.01	0.00	0.75	1.00	0.45	0.57	0.57	0.57	0.45	0.18	0.43	0.03	0.04	0.03
$I_{ND}^{\max}$	0.00	0.01	0.71	0.45	1.00	0.93	0.94	0.94	0.88	0.51	0.53	0.01	0.09	0.29
n_H	0.00	0.03	0.79	0.57	0.93	1.00	0.99	1.00	0.86	0.45	0.56	0.00	0.12	0.22
n_L	0.00	0.03	0.79	0.57	0.94	0.99	1.00	1.00	0.88	0.46	0.56	0.00	0.12	0.24
M_{diag}	0.00	0.03	0.79	0.57	0.94	1.00	1.00	1.00	0.87	0.46	0.56	0.00	0.12	0.23
D_2	0.00	0.01	0.69	0.45	0.88	0.86	0.88	0.87	1.00	0.43	0.49	0.08	0.03	0.51
D_1	0.00	0.01	0.35	0.18	0.51	0.45	0.46	0.46	0.43	1.00	0.81	0.04	0.09	0.22
T_1	0.00	0.03	0.62	0.43	0.53	0.56	0.56	0.56	0.49	0.81	1.00	0.00	0.09	0.14
$\%E_{\text{corr}}^{\alpha\beta}$	0.01	0.02	0.00	0.03	0.01	0.00	0.00	0.00	0.08	0.04	0.00	1.00	0.06	0.52
$\%TAE(T)$	0.01	0.01	0.08	0.04	0.09	0.12	0.12	0.12	0.03	0.09	0.09	0.06	1.00	0.00
$\%E_{\text{corr}}[(T)]$	0.00	0.00	0.11	0.03	0.29	0.22	0.24	0.23	0.51	0.22	0.14	0.52	0.00	1.00

Values with $R^2 \geq 0.7$ are indicated in bold text and displayed in blue.

TABLE A8: Squared Pearson's correlation coefficients (R^2) for CCSD over 311 molecular structures ($D_2 \leq 0.4$).

R^2 matrix	S_J	$\overline{I_D}$	r_{ND}	$\overline{I_{ND}}$	$I_{ND}^{\max}$	n_H	n_L	M_{diag}	D_2	D_1	T_1	$\%E_{\text{corr}}^{a\beta}$	$\%TAE(T)$	$\%E_{\text{corr}}[(T)]$
S_J	1.00	0.86	0.28	0.87	0.16	0.15	0.13	0.15	0.22	0.02	0.04	0.03	0.09	0.01
$\overline{I_D}$	0.86	1.00	0.05	0.62	0.04	0.04	0.03	0.04	0.07	0.00	0.00	0.07	0.12	0.00
r_{ND}	0.28	0.05	1.00	0.52	0.64	0.63	0.56	0.61	0.72	0.32	0.44	0.04	0.00	0.40
$\overline{I_{ND}}$	0.87	0.62	0.52	1.00	0.35	0.35	0.33	0.35	0.42	0.11	0.19	0.04	0.06	0.08
$I_{ND}^{\max}$	0.16	0.04	0.64	0.35	1.00	0.99	0.92	0.98	0.97	0.37	0.37	0.06	0.00	0.53
n_H	0.15	0.04	0.63	0.35	0.99	1.00	0.92	0.98	0.96	0.36	0.36	0.05	0.00	0.50
n_L	0.13	0.03	0.56	0.33	0.92	0.92	1.00	0.98	0.88	0.45	0.42	0.06	0.00	0.52
M_{diag}	0.15	0.04	0.61	0.35	0.98	0.98	0.98	1.00	0.94	0.41	0.40	0.05	0.00	0.53
D_2	0.22	0.07	0.72	0.42	0.97	0.96	0.88	0.94	1.00	0.39	0.41	0.06	0.00	0.52
D_1	0.02	0.00	0.32	0.11	0.37	0.36	0.45	0.41	0.39	1.00	0.88	0.12	0.02	0.53
T_1	0.04	0.00	0.44	0.19	0.37	0.36	0.42	0.40	0.41	0.88	1.00	0.06	0.03	0.52
$\%E_{\text{corr}}^{a\beta}$	0.03	0.07	0.04	0.04	0.06	0.05	0.06	0.05	0.06	0.12	0.06	1.00	0.13	0.42
$\%TAE(T)$	0.09	0.12	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.13	1.00	0.10
$\%E_{\text{corr}}[(T)]$	0.01	0.00	0.40	0.08	0.53	0.50	0.52	0.53	0.52	0.53	0.52	0.42	0.10	1.00

Values with $R^2 \geq 0.7$ are indicated in bold text and displayed in blue.

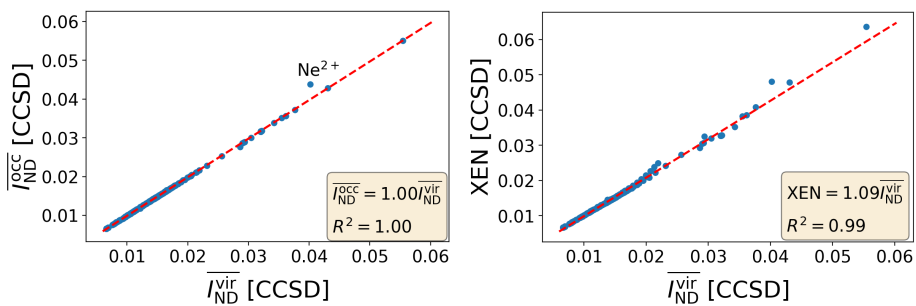


FIGURE A3: Linear relationship between $\overline{I_{\text{ND}}^{\text{vir}}}$ and $\overline{I_{\text{ND}}^{\text{occ}}}$, $\overline{I_{\text{ND}}^{\text{vir}}}$ and XEN, from cc-311 dataset calculated at CCSD level.

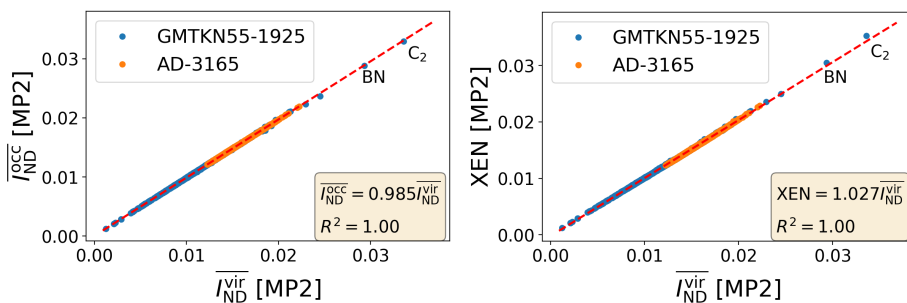


FIGURE A4: Linear relationship between $\overline{I_{\text{ND}}^{\text{vir}}}$ and $\overline{I_{\text{ND}}^{\text{occ}}}$, $\overline{I_{\text{ND}}^{\text{vir}}}$ and XEN, from mp-5090 dataset calculated at MP2 level.

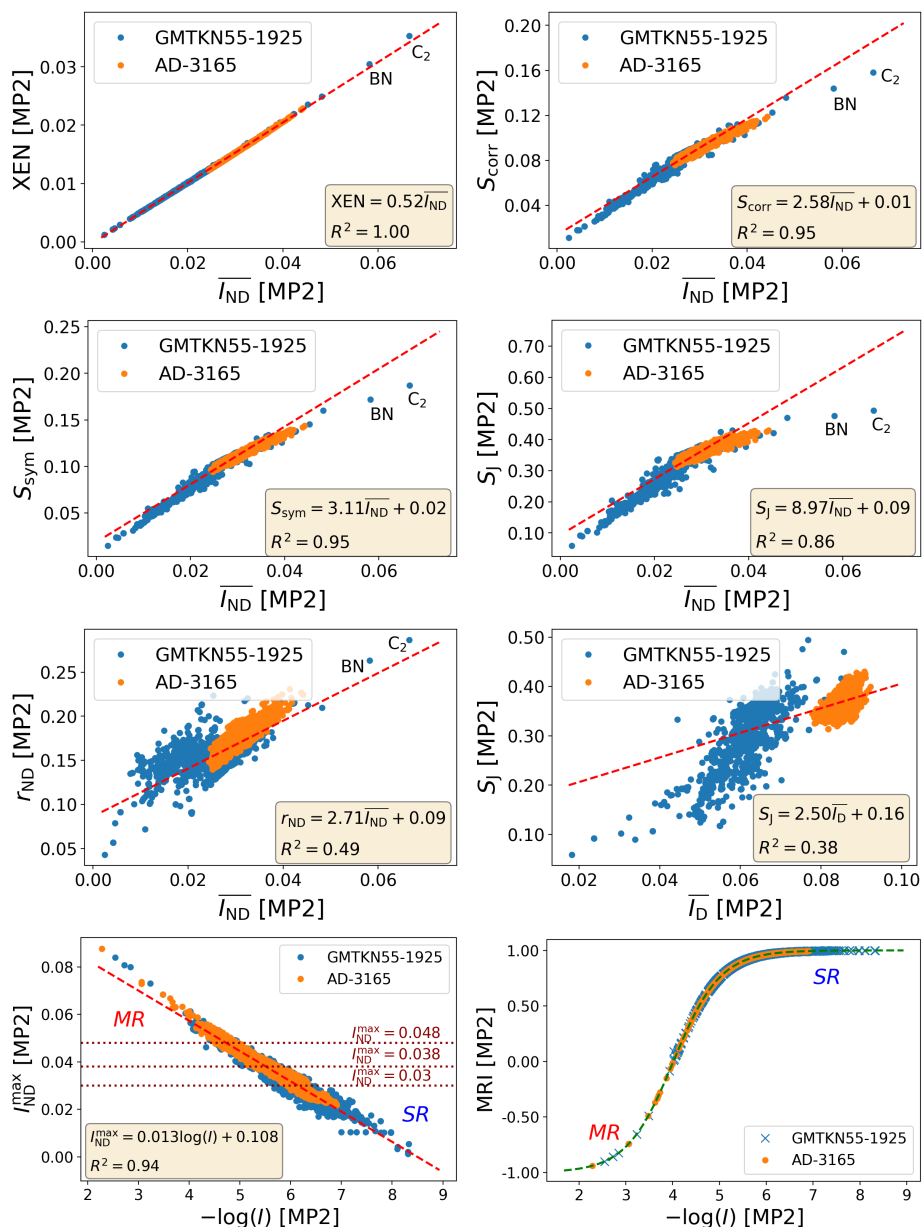


FIGURE A5: Plots between pairs of MR diagnostics from MP2 over the mp-5090 dataset.

A.5 Supplementary Results: Chapter 7

TABLE A9: Dispersion coefficients $C_6^{V_{ee}^*}$ and $C_8^{V_{ee}^*}$ of H_2 (singlet and triplet). They are obtained by fitting the energy difference $V_{ee}^{FCI} - 1/R$ over a fitting range of 22.68 to 43.47 a.u.

Basis set	Singlet		Triplet	
	$C_6^{V_{ee}^*}$	$C_8^{V_{ee}^*}$	$C_6^{V_{ee}^*}$	$C_8^{V_{ee}^*}$
aug-cc-pVDZ (3s2p)	12.636		12.644	
aug-cc-pVTZ (4s3p)	12.971		12.982	
aug-cc-pVQZ (5s4p)	12.952		12.964	
aug-cc-pV5Z (6s5p)	12.913		12.926	
aug-cc-pV6Z (7s6p)	12.911		12.923	
aug-cc-pVTZ (4s3p2d)	13.019	115.387	13.029	112.378
aug-cc-pVQZ (5s4p3d)	13.006	151.211	13.018	148.033
aug-cc-pV5Z (6s5p4d)	12.974	171.162	12.986	167.877
aug-cc-pV6Z (7s6p5d)	12.977	185.237	12.990	181.804
aug-cc-pVQZ (5s4p3d2f)	13.001	155.572	13.016	150.500
aug-cc-pV5Z (6s5p4d3f)	12.971	175.536	12.982	172.335
aug-cc-pV6Z (7s6p5d4f)	12.973	191.131	12.985	187.275

TABLE A10: Dispersion coefficients $C_6^{\Delta J}$ and $C_8^{\Delta J}$ of H_2 (singlet and triplet). They were determined by fitting ΔJ over a fitting range of 22.68 to 43.47 a.u. The ΔJ term was obtained from ΔJ energy term difference between FCI and CAS(2,2) for the singlet and HF for the triplet H_2 molecule.

Basis set	Singlet		Triplet	
	$C_6^{\Delta J}$	$C_8^{\Delta J}$	$C_6^{\Delta J}$	$C_8^{\Delta J}$
aug-cc-pVDZ (3s2p)	4.148		13.034	
aug-cc-pVTZ (4s3p)	5.236		15.487	
aug-cc-pVQZ (5s4p)	5.356		15.580	
aug-cc-pV5Z (6s5p)	5.449		15.602	
aug-cc-pV6Z (7s6p)	5.388		15.557	
aug-cc-pVTZ (4s3p2d)	5.208	73.825	15.284	166.959
aug-cc-pVQZ (5s4p3d)	5.274	140.660	15.592	232.321
aug-cc-pV5Z (6s5p4d)	5.447	89.640	15.615	295.460
aug-cc-pV6Z (7s6p5d)	5.303	182.002	15.568	349.644
aug-cc-pVQZ (5s4p3d2f)	5.394	80.405	15.591	234.329
aug-cc-pV5Z (6s5p4d3f)	5.359	135.074	15.613	299.596
aug-cc-pV6Z (7s6p5d4f)	5.227	219.557	15.561	357.601

TABLE A11: Dispersion coefficients $C_6^{\Delta K}$ and $C_8^{\Delta K}$ of H_2 molecule (triplet). They were determined by fitting ΔK over a fitting range of 22.68 to 43.47 a.u. The ΔK term was obtained from the K energy term difference between FCI and HF.

Basis set	Triplet	
	$C_6^{\Delta K}$	$C_8^{\Delta K}$
aug-cc-pVDZ (3s2p)	-17.779	
aug-cc-pVTZ (4s3p)	-20.441	
aug-cc-pVQZ (5s4p)	-20.540	
aug-cc-pV5Z (6s5p)	-20.549	
aug-cc-pV6Z (7s6p)	-20.505	
aug-cc-pVTZ (4s3p2d)	-20.183	-244.270
aug-cc-pVQZ (5s4p3d)	-20.490	-331.565
aug-cc-pV5Z (6s5p4d)	-20.495	-408.634
aug-cc-pV6Z (7s6p5d)	-20.447	-473.745
aug-cc-pVQZ (5s4p3d2f)	-20.488	-334.396
aug-cc-pV5Z (6s5p4d3f)	-20.492	-414.419
aug-cc-pV6Z (7s6p5d4f)	-20.438	-483.820

Tab. A12 presents the coefficients D_3 and D_5 retrieved from the $h_{c_{\text{II}}}(R)$ data fitting in the H_2 molecule for both the singlet and triplet cases. The results align with those obtained in the H_2 case. The coefficients D_3 , which correspond to the dispersion energy coefficient C_6 , are found to be identical in both singlet and triplet cases and are highly insensitive to the basis set size. Although the D_5 coefficients switch sign from negative to positive upon including d or f basis functions, we should be aware that higher-order terms, such as D_7 or D_9 , are likely to exist when d or f orbitals are introduced. This could explain the significant change in D_5 values with the increase of basis sets, and the increase in numerical error associated with higher-order terms in the data fitting should also be taken into account. Nevertheless, they tend to be converging.

TABLE A12: The coefficient D_3 and D_5 of H_2 (singlet and triplet).

Basis set	Singlet		Triplet	
	D_3	D_5	D_3	D_5
aug-cc-pVDZ (3s2p)	0.384	-2.904	0.384	-2.849
aug-cc-pVTZ (4s3p)	0.379	-2.862	0.379	-2.908
aug-cc-pVQZ (5s4p)	0.378	-2.911	0.378	-2.902
aug-cc-pV5Z (6s5p)	0.378	-2.796	0.378	-2.836
aug-cc-pV6Z (7s6p)	0.379	-3.079	0.378	-2.916
aug-cc-pVTZ (4s3p2d)	0.378	1.908	0.379	1.791
aug-cc-pVQZ (5s4p3d)	0.378	2.395	0.378	2.434
aug-cc-pV5Z (6s5p4d)	0.378	2.778	0.378	2.704
aug-cc-pV6Z (7s6p5d)	0.378	2.985	0.378	2.733
aug-cc-pVQZ (5s4p3d2f)	0.378	2.402	0.378	2.477
aug-cc-pV5Z (6s5p4d3f)	0.378	2.671	0.378	2.635
aug-cc-pV6Z (7s6p5d4f)	0.378	2.593	0.378	2.635

The results in Tab. A13 show that in the H_2 molecule singlet case, using the aug-cc-pVXZ (X=D,T,Q,5,6) truncated basis set (utilizing $s + p$ orbitals only). We first calculated the electron-electron interaction energy fragment, V_{ee}^{dd} . Then we retrieved the corresponding dispersion coefficient, $C_6^{V_{ee}^{dd}}$, by fitting the V_{ee}^{dd} energies against R . These calculations employed the induced-dipole induced-dipole two-electron AO quartets proposed by Baerends *et al.* [88–90]. Comparing these results to $C_6^{\Delta V_{ee}}$ of H_2 molecule singlet case in Tab. 7.4, it was found that the induced-dipole induced dipole terms are sufficient to accurately reproduce

TABLE A13: Dispersion coefficient $C_6^{V_{ee}^{dd}}$ and its partitions of H_2 singlet.

Basis set	x/y term		z term		Total
	$C_6^{V_{ee}^{dd},(x/y)}$	ratio	$C_6^{V_{ee}^{dd},(z)}$	ratio	
aug-cc-pVDZ (3s2p)	2.111	16.667%	8.445	66.667%	12.668
aug-cc-pVTZ (4s3p)	2.169	16.667%	8.675	66.667%	13.013
aug-cc-pVQZ (5s4p)	2.166	16.667%	8.664	66.667%	12.996
aug-cc-pV5Z (6s5p)	2.160	16.667%	8.639	66.667%	12.959
aug-cc-pV6Z (7s6p)	2.160	16.667%	8.638	66.667%	12.958

- x/y terms: $s_A(1)p_{xA}(1)s_B(2)p_{xB}(2), s_A(2)p_{xA}(2)s_B(1)p_{xB}(1)/$
 $s_A(1)p_{yA}(1)s_B(2)p_{yB}(2), s_A(2)p_{yA}(2)s_B(1)p_{yB}(1)$
- z terms: $s_A(1)p_{zA}(1)s_B(2)p_{zB}(2), s_A(2)p_{zA}(2)s_B(1)p_{zB}(1)$

$C_6^{\Delta V_{ee}}$. As the two atoms are aligned along the z -axis, the two-electron AO quartets such as $s_A p_{xA} s_B p_{xB}$ and $s_A p_{yA} s_B p_{yB}$ in the xy plane contribute in total around 1/3 of $C_6^{\Delta V_{ee}}$, while $s_A p_{zA} s_B p_{zB}$ term contributes around 2/3 of $C_6^{\Delta V_{ee}}$, and this contribution ratio is independent of the basis set size.

TABLE A14: The coefficient D_3 and D_5 terms and their contribution ratios of H_2 singlet.

Basis set	x/y term		z term		Total	
	$D_5(x/y)$	$D_3(z)$	$D_5(z)$	D_3	D_5	
aug-cc-pVDZ (3s2p)	16.623%	100%	66.754%	0.384	-2.988	
aug-cc-pVTZ (4s3p)	16.641%	100%	66.718%	0.379	-2.992	
aug-cc-pVQZ (5s4p)	16.644%	100%	66.712%	0.378	-2.984	
aug-cc-pV5Z (6s5p)	16.645%	100%	66.710%	0.378	-2.978	
aug-cc-pV6Z (7s6p)	16.643%	100%	66.713%	0.378	-2.980	

- x/y terms: $s_A(1)p_{xA}(1)s_B(2)p_{xB}(2), s_A(2)p_{xA}(2)s_B(1)p_{xB}(1)/$
 $s_A(1)p_{yA}(1)s_B(2)p_{yB}(2), s_A(2)p_{yA}(2)s_B(1)p_{yB}(1)$
- z terms: $s_A(1)p_{zA}(1)s_B(2)p_{zB}(2), s_A(2)p_{zA}(2)s_B(1)p_{zB}(1)$

In terms of radial intracule density, [Tab. A14](#) presents the coefficients D_3 and D_5 fitted by radial intracule density that is constructed only by the induced-dipole induced dipole terms, against R , which show good agreement with the D_3 and D_5 values obtained from $h_{cII}(R)$ of H_2 molecule singlet in [Tab. A12](#). In other words, when considering long-range distances at the point where $s = R$,

the radial intracule density resulting from the induced-dipole induced dipole terms is equivalent to $h_{c\Pi}(R)$. It also reveals that only the $s_A p_{zA} s_B p_{zB}$ term-based intracule fragments are responsible for D_3/R^3 , while both $s_A p_{xA} s_B p_{xB}$ and $s_A p_{yA} s_B p_{yB}$ term-based intracule density fragments can only be fitted to D_5/R^5 . Therefore, based on our analysis, we can conclude that the leading term D_3/R^3 asymptotic behavior of intracule $h_{c\Pi}(R)$ is a necessary condition, but it is not sufficient to fully account for the dispersion energy contribution from V_{ee} .

Fig. A6 illustrates the radial intracule density derived by the induced-dipole induced dipole terms, $I_{dd}(s)$. At large separation distance (e.g., $R = 22.68$ a.u.), the radial intracule density $I_{dd}(s)$ and long-range part of $h_{c\Pi}(s)$ are identical in H_2 case. Despite their small magnitudes, these intracule quantities are found to be insensitive to the size of the truncated basis sets.

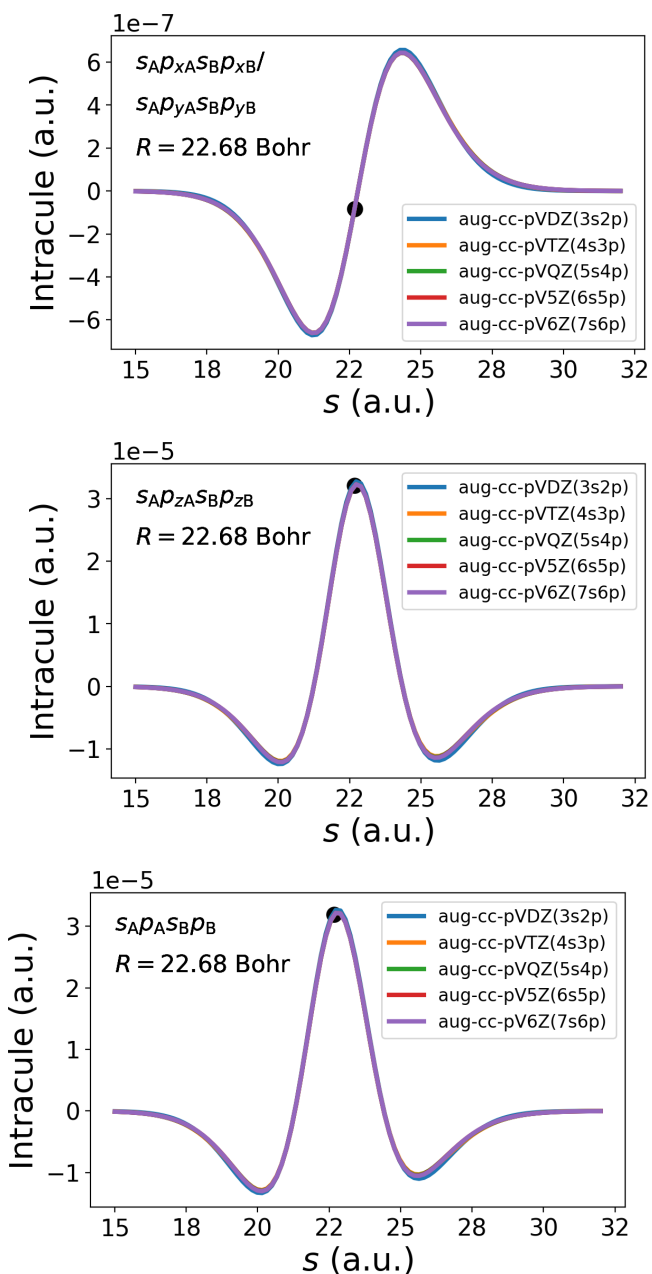


FIGURE A6: Radial intracule density, derived from induced-dipole induced dipole terms $s_A(1)p_A(1)s_B(2)p_B(2)$ and $s_A(2)p_A(2)s_B(1)p_B(1)$ of H_2 molecule singlet with FCI/aug-cc-pVXZ (X=D,T,Q,5,6) basis set (truncated s+ p functions). The black points denote the intracule value at $s = R$. The bottom plot is a combination of the top two plots.

A.6 Supplementary Results: Chapter 8

TABLE A15: The dispersion coefficient C_6 and its partitions from the minimal dispersion model based on the singlet H_2 .

Exponent		$2C_6^{\Delta E_{H_2}}$	$C_6^{\Delta V_{ee}}$	$C_6^{\Delta V_{ee}^{c\Pi, sr}}$	$C_6^{\Delta V_{ee}^{c\Pi, lr}}$	$C_6^{V_{ee}^{dd}}$	
α_s	α_p					numeric	analytic
0.6	0.6	1.0292	1.0226	0.1111	1.0291	1.0292	1.0293
0.6	0.7	0.8454	0.8415	0.0882	0.8454	0.8454	0.8455
0.6	0.8	0.6786	0.6763	0.0678	0.6786	0.6786	0.6787
0.6	0.9	0.5386	0.5372	0.0514	0.5386	0.5386	0.5386
0.6	1.0	0.4257	0.4247	0.0387	0.4256	0.4257	0.4257
0.6	1.1	0.3363	0.3357	0.0292	0.3363	0.3363	0.3363
0.6	1.2	0.2663	0.2659	0.0221	0.2663	0.2663	0.2663
0.7	0.6	0.7729	0.7677	0.0816	0.7729	0.7729	0.7730
0.7	0.7	0.6683	0.6651	0.0689	0.6683	0.6683	0.6684
0.7	0.8	0.5612	0.5592	0.0558	0.5612	0.5612	0.5612
0.7	0.9	0.4636	0.4623	0.0442	0.4636	0.4636	0.4636
0.7	1.0	0.3796	0.3787	0.0346	0.3796	0.3796	0.3796
0.7	1.1	0.3095	0.3090	0.0270	0.3095	0.3095	0.3095
0.7	1.2	0.2522	0.2518	0.0211	0.2522	0.2522	0.2522
0.8	0.6	0.5851	0.5808	0.0604	0.5850	0.5851	0.5852
0.8	0.7	0.5270	0.5243	0.0537	0.5270	0.5270	0.5271
0.8	0.8	0.4593	0.4575	0.0454	0.4592	0.4593	0.4593
0.8	0.9	0.3923	0.3911	0.0374	0.3922	0.3923	0.3923
0.8	1.0	0.3310	0.3303	0.0303	0.3310	0.3310	0.3310
0.8	1.1	0.2774	0.2769	0.0244	0.2774	0.2774	0.2774
0.8	1.2	0.2317	0.2313	0.0195	0.2317	0.2317	0.2317
0.9	0.6	0.4494	0.4459	0.0453	0.4494	0.4494	0.4495
0.9	0.7	0.4179	0.4156	0.0421	0.4179	0.4179	0.4180
0.9	0.8	0.3753	0.3738	0.0370	0.3753	0.3753	0.3753
0.9	0.9	0.3296	0.3286	0.0314	0.3296	0.3296	0.3296
0.9	1.0	0.2854	0.2847	0.0262	0.2853	0.2854	0.2854
0.9	1.1	0.2448	0.2444	0.0216	0.2448	0.2448	0.2449
0.9	1.2	0.2090	0.2086	0.0177	0.2090	0.2090	0.2090

Continue on the next page

TABLE A15: (Continued)

Exponent		$2C_6^{\Delta E_{H_2}}$	$C_6^{\Delta V_{ee}}$	$C_6^{\Delta V_{ee}^{c\Pi, sr}}$	$C_6^{\Delta V_{ee}^{c\Pi, lr}}$	$C_6^{V_{ee}^{dd}}$	
α_s	α_p					numeric	analytic
1.0	0.6	0.3518	0.3489	0.0347	0.3518	0.3518	0.3519
1.0	0.7	0.3349	0.3330	0.0335	0.3349	0.3349	0.3350
1.0	0.8	0.3080	0.3067	0.0303	0.3080	0.3080	0.3080
1.0	0.9	0.2767	0.2758	0.0264	0.2767	0.2767	0.2767
1.0	1.0	0.2448	0.2442	0.0225	0.2448	0.2448	0.2448
1.0	1.1	0.2143	0.2139	0.0190	0.2143	0.2143	0.2143
1.0	1.2	0.1864	0.1861	0.0159	0.1864	0.1864	0.1864
1.1	0.6	0.2817	0.2792	0.0271	0.2817	0.2817	0.2818
1.1	0.7	0.2723	0.2705	0.0270	0.2722	0.2723	0.2723
1.1	0.8	0.2548	0.2536	0.0250	0.2548	0.2548	0.2548
1.1	0.9	0.2331	0.2323	0.0223	0.2331	0.2331	0.2331
1.1	1.0	0.2099	0.2093	0.0194	0.2099	0.2099	0.2099
1.1	1.1	0.1869	0.1865	0.0167	0.1869	0.1869	0.1869
1.1	1.2	0.1652	0.1649	0.0142	0.1652	0.1652	0.1652
1.2	0.6	0.2315	0.2313	0.0217	0.2315	0.2315	0.2316
1.2	0.7	0.2251	0.2235	0.0221	0.2251	0.2251	0.2251
1.2	0.8	0.2131	0.2120	0.0209	0.2130	0.2131	0.2131
1.2	0.9	0.1976	0.1969	0.0190	0.1976	0.1976	0.1976
1.2	1.0	0.1805	0.1800	0.0168	0.1805	0.1805	0.1805
1.2	1.1	0.1630	0.1627	0.0146	0.1630	0.1630	0.1630
1.2	1.2	0.1461	0.1458	0.0127	0.1461	0.1461	0.1461

- $C_6^{\Delta E_{H_2}}$ is obtained by fitting the energy difference: $\Delta E_{H_2} = E_{H_2}^{FCI} - E_{H_2}^{CAS(2,2)}$, while $C_6^{\Delta V_{ee}}$ is by fitting $\Delta V_{ee} = V_{ee}^{FCI} - V_{ee}^{CAS(2,2)}$.
- The highlighted row in bold (basis function exponents $\alpha_s = \alpha_p = 1.0$) is the numerical example that we frequently refer to in this thesis.
- V_{ee}^{dd} represents the contributions of induced-dipole induced dipole terms [88–90] to V_{ee} , “numeric” results are evaluated numerically by selecting the induced-dipole induced dipole two-electron integrals (i.e., $s_A(1)p_A(1')s_B(2)p_B(2')$) within PySCF package, while “analytic” means to be calculated straightforwardly through Eq. (8.37).

TABLE A16: One and two-electron AO terms used in the minimal dispersion model of H_2 .

Terms	$s_A(1)s_B(2')$	$s_B(1)s_A(2')$	$p_A(1)p_B(2')$	$p_B(1)p_A(2')$
$s_A(1')s_B(2)$	$s_A(1)s_A(1') \int s_B^2(2)d2$		$s_A(1')p_A(1)s_B(2)p_B(2')$	
$s_B(1')s_A(2)$		$s_B(1)s_B(1') \int s_A^2(2)d2$		$s_A(2)p_A(2')s_B(1')p_B(1)$
$p_A(1')p_B(2)$	$s_A(1)p_A(1')s_B(2')p_B(2)$		$p_A(1)p_A(1') \int p_B^2(2)d2$	
$p_B(1')p_A(2)$		$s_A(2')p_A(2)s_B(1)p_B(1')$		$p_B(1)p_B(1') \int p_A^2(2)d2$

- The diagonal terms form the basis of 1-RDM targeting dispersion, and they contribute to $\mathcal{T}^{\text{disp}}$ and $V_{\text{en}}^{\text{disp}}$ terms in Eq. (8.28) and Eq. (8.29), respectively. Since the AOs are normalized, the term $\int \chi^2(2)d2 = 1$. The off-diagonal terms form the 2-RDM targeting dispersion, and they contribute to $V_{\text{ee}}^{\text{disp}}$ term in Eq. (8.30).
- Each p orbital should be considered: p_x , p_y , and p_z . For instance, the term, $p_B(1)p_B(1') \int p_A^2(2)d2 = p_B(1)p_B(1')$ represents $p_{xB}(1)p_{xB}(1')$, $p_{yB}(1)p_{yB}(1')$, and $p_{zB}(1)p_{zB}(1')$, etc.

