Assessment of a new approach for the two-electron cumulant in natural-orbital-functional theory

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(Received 22 August 2005; accepted 13 October 2005; published online 2 December 2005)

The Piris natural orbital functional (PNOF) based on a new approach for the two-electron cumulant has been used to predict adiabatic ionization potentials, equilibrium bond distances, and harmonic vibrational frequencies of 18 diatomic molecules. Vertical ionization potentials have been calculated for the same set of diatomic molecules and another set of 20 polyatomic molecules using energy-difference methods as well as the extended Koopman theorem. The PNOF properties compare favorably with the coupled-cluster-doubles results. The calculated PNOF values are in good agreement with the corresponding experimental data, considering the basis sets used (6-31G**). © 2005 American Institute of Physics. [DOI: 10.1063/1.2135289]

I. INTRODUCTION

In recent years a growing interest in methods based on natural-orbital-functional theory (NOFT) has been taken in quantum chemistry.1–39 In this formalism, the energy functional of the one-particle reduced-density matrix (1-RDM) is expressed in terms of the natural orbitals and their occupation numbers. A great advantage is that the kinetic energy is explicitly defined, and the NOFT therefore does not have to invoke the concept of a fictitious noninteracting particle system. Moreover, NOFT incorporates fractional occupation numbers in a natural way, which may provide a correct description of both dynamical and nondynamical correlations.

Actually, only the cumulant40 of the two-particle reduced-density matrix (2-RDM) needs to be reconstructed. An explicit form for this cumulant in terms of two symmetric matrices, Δ and Λ, has been recently proposed by Piris.41 The suggested form of these matrices (as functions of the natural occupation numbers) produces a natural orbital functional (NOF) that is reduced to the exact expression for the total energy in two-electron systems.15,42 One can generalize it to the N-electron system, except for the off-diagonal elements of Δ. Alternatively, the mean-value theorem and the partial-sum rule for matrix Δ provide a prescription for deriving a practical NOF.41

Considering real orbitals, the Piris natural orbital functional (PNOF) depends only on the Coulomb and exchange integrals and thus can be referred to as the so-called JK-only approximation.30 It has been shown that several proposed JK-only functionals cannot be derived from the N-representable ansatz for the 2-RDM.29 Kollmar has recently derived a JK-only 1-RDM functional starting from the pair-excitation multiconfiguration self-consistent-field (PEMCSCF) method and using necessary N-representability conditions for the 2-RDM.43 This functional gives a small fraction of the total correlation energy for the water molecule at the equilibrium distance, indicating that the accuracy of the JK-only functional form may be limited. We must note that despite being of the JK-only type, the PNOF can be derived in principle from an N-representable ansatz for the 2-RDM, and it recovers a reasonable fraction of the total correlation energy at the equilibrium geometries.41 In addition, the PNOF can be improved by providing a better approximation for the mean value Ji of the Coulomb interactions.

The prediction of molecular properties has been a frequent area of application in quantum chemistry.44–52 The objective of these studies is to systematically test the performance of correlated methods. The aim of this paper is to assess the capabilities of the PNOF for calculating molecular properties, namely, equilibrium bond distance, harmonic vibrational frequency, and ionization potential (IP).

Computationally speaking, NOFT in its current form is very demanding. Therefore, we have chosen a medium-size basis set (6-31G**) for the calculations, and we have compared our results with those obtained using the standard coupled-cluster-doubles (CCD) method. The performance of the PNOF has been established by carrying out a statistical analysis of the root-mean-square (rms) absolute differences with respect to experiment.

II. THEORY

We briefly describe here the theoretical framework of our approach. A more detailed description of the applied NOF can be found in Ref. 41.

The electronic energy E for N-electron systems is an exactly and explicitly known functional of the 1- and 2-RDMs, labeled hereafter as Γ and D, respectively,

$$E = \sum_{ij} h_{ij} \Gamma_{ji} + \sum_{ijkl} (ijkl) D_{ijkl}. \quad (1)$$

The spin orbitals \(\{\chi_i(x)\}\) constitute a complete orthonormal set of single-particle functions. \(h_{ij}\) denote the one-
electron matrix elements of the core Hamiltonian, and \((ij|kl)\) are the two-electron matrix elements of the Coulomb interaction.

The 1-RDM can be diagonalized by a unitary transformation of the spin orbitals, with the eigenvectors being the natural spin orbitals and the eigenvalues \(\{n_i\}\) representing the occupation numbers of the latter,

\[
\Gamma_{ji} = n_i \delta_{ji}. \tag{2}
\]

In the following, all representations used are assumed to refer to this basis.

We consider a spin-independent Hamiltonian, so only density-matrix blocks that conserve the number of each spin type are nonvanishing. Specifically, in the case of spin-compensated systems, the 1-RDM has spin blocks \(\Gamma^a=\Gamma^b\), whereas the 2-RDM has three nonzero blocks: \(D^{aa}, D^{ab}, \) and \(D^{bb}\). For singlet states, the first and the last blocks of the 2-RDM are also equal (\(D^{aa}=D^{bb}\)).

Let us consider the well-known cumulative expansion \(A^0\) of the nonzero blocks of the 2-RDM. Namely,

\[
D^{aa}_{kl,ij} = \frac{1}{2} (\Gamma^a_{ki} \Gamma^a_{lj} - \Gamma^a_{kj} \Gamma^a_{li}) + \lambda^{aa}_{kl,ij},
\]

\[
= \frac{n_j n_i}{2} (\delta_{ki} \delta_{lj} - \delta_{kj} \delta_{li}) + \lambda^{aa}_{kl,ij}, \tag{3}
\]

\[
D^{ab}_{kl,ij} = \frac{1}{2} (\Gamma^a_{ki} \Gamma^b_{lj} + \Gamma^b_{kj} \Gamma^a_{li}) + \frac{1}{2} (n_j n_i \delta_{ki} \delta_{lj} + \lambda^{ab}_{kl,ij}). \tag{4}
\]

It can be easily shown from the contraction relations for the 2-RDM blocks that spin components of the cumulant matrix fulfill the following sum rules:

\[
\sum_k \lambda^{aa}_{ik,ik} = n_i (n_i - 1) \delta_{ji}, \tag{5}
\]

\[
\sum_k \lambda^{ab}_{ik,jk} = 0. \tag{6}
\]

The matrix \(\lambda^{ab}\) must be antisymmetric; therefore we consider the following parallel-spin component:

\[
\lambda^{ab}_{kl,ij} = - \frac{\Delta_{ji}}{2} \delta_{ki} \delta_{lj} + \frac{\Delta_{lj}}{2} \delta_{kj} \delta_{li}, \tag{7}
\]

where \(\Delta\) is a symmetric matrix. The sum rule (5) and the approximate ansatz (7) imply the constraint

\[
\sum_j \Delta_{ji} = n_j (1 - n_j). \tag{8}
\]

The prime indicates that the \(i=j\) term is omitted. For \(\lambda^{ab}\), we can achieve a suitable approximation if we replace the second term in Eq. (7) with the dependence obtained in the improved Bardeen-Cooper-Schrieffer (IBCS) method, namely,

\[
\lambda^{ab}_{kl,ij} = - \frac{\Delta_{ji}}{2} \delta_{ki} \delta_{lj} + \frac{\Pi_{ij}}{2} \delta_{kj} \delta_{li}, \tag{9}
\]

where we have introduced a new symmetric matrix \(\Pi\). For convenient purposes as we see below, we define the matrix \(\Pi\) in terms of a new symmetric matrix \(\Lambda\):

\[
\Pi_{ij} = n_i n_j - \Delta_{ij} - \Lambda_{ij}. \tag{10}
\]

Combining Eqs. (6), (8), (9), and (10) results in

\[
2 \Delta_{ij} + \Lambda_{ii} = 2 n_i^2 - n_i. \tag{11}
\]

Using Eqs. (2), (3), (4), (7), (9), and (10), the energy [Eq. (1)] reads as

\[
E = 2 \sum_i n_i h_i + \sum_{ij} (n_j n_i - \Delta_{ij})(2 J_{ij} - K_{ij})
+ \sum_{ij} (n_j n_i - \Delta_{ij} - \Lambda_{ij}) L_{ij}, \tag{12}
\]

with the electronic repulsion integrals \(J_{ij} = (ij|ij)\), \(K_{ij} = (ij|jj)\), and \(L_{ij} = (ii|jj)\). Note that if \(\Delta_{ij} = 0\) and \(\Lambda_{ij} = n_j n_i\) (so \(\Pi_{ij} = 0\)), then the reconstruction proposed here yields the Hartree-Fock (HF) case as expected. Taking into account that \(L_{ij} = K_{ij}\) for real orbitals, expression (12) can be rewritten as

\[
E = 2 \sum_i n_i h_i + 2 \sum_{ij} (n_j n_i - \Delta_{ij}) J_{ij} - \sum_{ij} \Lambda_{ij} K_{ij}. \tag{13}
\]

From the requirement that for any two-electron system expression (13) should yield the exact energy functional of Ref. 15, one easily deduces that \(\Delta_{ij} = n_j n_i\) and

\[
\Lambda_{ij} = \text{sign}(\Lambda_{ij}) \sqrt{n_j n_i}, \tag{14}
\]

\[
\begin{align*}
\text{sign}(\Lambda_{ij}) &= \begin{cases} 
-1 & \text{if } i = 1, \ j = 1 \\
+1 & \text{if } i = 1, \ j \geq 2; \ i \geq 2, \ j = 1 \\
-1 & \text{if } i \geq 2, \ j = 2
\end{cases} \\
&= \begin{cases} 
+1 & \text{if } i \leq n_i, \ j \leq n_j \\
0 & \text{if } i > n_i, \ j > n_j \text{ or } i > n_j, \ j \leq n_i \\
-1 & \text{if } i > n_j, \ j > n_j
\end{cases}
\end{align*} \tag{15}
\]

for \(N=2\).

The functional form (14) of matrix \(\Lambda\) can be readily generalized to

\[
\Lambda_{ii} = - n_i, \tag{15}
\]

\[
\Lambda_{ij} = \text{sign}(\Lambda_{ij}) \sqrt{n_j n_i} \text{ if } i \neq j, \tag{16}
\]

where

\[
\text{sign}(\Lambda_{ij}) = \begin{cases} 
+1 & \text{if } i \leq n_i, \ j \leq n_j \\
0 & \text{if } i > n_i, \ j > n_j \text{ or } i > n_j, \ j \leq n_i \\
-1 & \text{if } i > n_j, \ j > n_j
\end{cases} \tag{17}
\]

Here, the number of HF closed shells is denoted as \(n_{co}\). Inserting Eq. (15) into the equality (11) affords

\[
\Delta_{ij} = n_i^2. \tag{18}
\]

By taking into account Eqs. (18) and (15), the energy functional (13) can be expressed as

\[
E = \sum_i n_i (2 h_i + K_{ii}) + 2 \sum_{ij} \left( n_j n_i - \Delta_{ij} \right) J_{ij} - \sum_{ij} \Lambda_{ij} K_{ij}. \tag{19}
\]

Unfortunately, \(\Delta_{ij} = n_j n_i\), taken from the \(N=2\) case, violates the sum rule (8) in the general case of \(N>2\). This means that the functional form of nondiagonal elements of \(\Delta\) is unknown for \(N\)-electron systems as yet. Nevertheless,
some constraints can be achieved for these quantities using known necessary conditions of 2-RDM $N$ representability.

The so-called $D$, $G$ and $Q$ conditions state that the two-electron density matrix $D$, the electron-hole density matrix $G$, and the two-hole density matrix $Q$ must be positive semidefinite. The analytic determined eigenvalues provided rigorous bounds on the magnitudes $\{\Delta_{ji}\}$ to guarantee that our reconstructed functional satisfies these positivity conditions. For more details, the reader can find this derivation in Ref. 41.

It is not evident how to approach $\Delta_{ji}$ for $j \neq i$, in terms of the occupation numbers. Due to this fact, the energy term in Eq. (19) which involves $\Delta_{ji}$ is rewritten as

$$
\sum_{ij} \Delta_{ji} J_{ij} = \sum_i J_i^0 \sum_j \Delta_{ji} = \sum_i J_i^0 n_i (1 - n_i),
$$

(20)

where $J_i^0$ denotes the mean value of the Coulomb interactions $J_{ij}$ for a given orbital $i$ taking over all orbitals $j \neq i$. Here, the sum rule for off-diagonal elements of matrix $\Delta$ [Eq. (8)] was used. Inserting this expression into Eq. (19), one obtains

$$
E = \sum_i (2n_i h_{ii} + n_i^2 K_{ii}) + \sum_{ij} (2n_j n_i J_{ij} - \Lambda_{ji} K_{ij}) + \sum_j n_j (1 - n_j) (K_{ij} - 2J_i^0).
$$

(21)

A further simplification is accomplished by setting $J_i^0 = K_{ii}/2$, which produces

$$
E = \sum_i (2n_i h_{ii} + n_i^2 K_{ii}) + \sum_{ij} (2n_j n_i J_{ij}) - \text{sign}(\Lambda_{ji})\sqrt{n_j n_i K_{ij}} - \sum_{ij} \sqrt{(1 - n_j)(1 - n_i) K_{ij}}.
$$

(22)

The last term in Eq. (22) was introduced in Ref. 41 to ensure that occupation numbers of lowest occupied levels only are close to unity. This implies that

$$
\Lambda_{ji} = \sqrt{n_j n_i} + \sqrt{(1 - n_j)(1 - n_i)} \quad \text{if} \quad i \leq n_{\text{co}}, \quad j \leq n_{\text{co}}, \quad i \neq j.
$$

(23)

Applying the well-known procedure of taking molecular orbitals as linear combination of atomic orbitals (MO-LCAO), Eq. (22) becomes a functional of the natural orbital coefficients $\{C_i\}$ and the occupation numbers $\{n_j\}. One has to minimize the energy both with respect to $\{C_i\}$ and $\{n_j\}$, subject to the following constraints:

1. the $N$-representability condition of the 1-RDM $(0 \leq n_i \leq 1)$,
2. the constant number of particles $2\sum_i n_i = N$, and
3. the orthonormality condition $C^\dagger S C = 1$ ($S$ is the overlap matrix).

III. RESULTS AND DISCUSSION

A. Vertical ionization potentials

The simplest treatment for determining vertical IPs is based on Koopman’s theorem, which states that the IP is given by the HF orbital energy with the opposite sign $(-\lambda_i)$, calculated in the neutral system.53 This approach ignores the relaxation of the molecular orbitals after the ionization. In order to take the orbital relaxation into account, the IP is approximated by the energy difference for positive ions $(M^+)$ and neutral molecules $(M^0)$: $E_{\text{SCF}}(M^+) - E_{\text{SCF}}(M^0)$, $(\Delta \text{SCF})$. Nevertheless, both approaches disregard the change in correlation energy associated with the ionization. This missing correlation effect can be considered by calculating the NOF total energies for ions and neutral molecules.36 Then, the vertical IP is here obtained by the energy difference: $E_{\text{PNOF}}(M^+) - E_{\text{PNOF}}(M^0)$, $(\Delta \text{PNOF})$, at the near-experimental geometries of $M^0$ given in Ref. 55.

The energy of the $N$–1 electron system can be reasonably well approximated by an orbital ionization. We assume that the annihilation of one electron occurs at the highest occupied molecular orbital (HOMO) of the HF approximation. According to this hypothesis, the other electrons are populating all available states with $2n_i$, except the HOMO which is populated with $n_{\text{HOMO}}=1$. With this assumption, the ground state of the ion is a $\tilde{S}_0$ eigenstate. The value of the energy can be obtained straightforward from Eq. (22):

$$
E = \sum_i (2n_i h_{ii} + n_i^2 K_{ii}) + \sum_{ij} (2n_j n_i J_{ij}) - \sum_{ij} \text{sign}(\Lambda_{ji})\sqrt{n_j n_i K_{ij}}
$$

$$
+ \left( h_{kk} + \sum_i (2J_i - K_{ij}) n_i \right)_{k=\text{HOMO}}.
$$

(24)

where $cl$ denotes the number of closed shells.

Alternatively, one can avoid energy-difference calculations determining the vertical IPs by use of the extended Koopman theorem (EKT) proposed by Morrell et al.56 and by Smith and Day.57 We must note that in exact NOFT, all the natural orbital eigenvalues are the same,7 and are equal to minus the vertical IP.56,58,59 However, we have here an approximate NOFT, so the energy functional still depends on the 2-RDM, and the optimum orbitals actually satisfy the Löwdin equation.60 The kernel of this equation can be transformed into a Hermitian kernel with a nondegenerate spectrum of eigenvalues $\nu$. The diagonalization of the matrix $\nu$ with the elements

$$
\nu_{ji} = \frac{\lambda_{ji}}{\sqrt{n_j n_i}},
$$

(25)

yields ionization potentials as eigenvalues.39 In Eq. (25), $\lambda_{ji}$ are the Lagrange multipliers concerning the orthonormality constraints on the natural orbitals.

Table I lists the obtained vertical IPs by $\Delta$CCD, $\Delta$PNOF, and PNOF-EKT, together with Koopman’s IPs, $\Delta$SCF, and
The total energies of neutral molecules and ions were calculated using the contracted Gaussian basis set 6-31G**. The CCD method as implemented in GAUSSIAN 94 suite of programs, with the keyword 5D, was used in order to calculate vertical ionization potentials obtained from the extended Koopman theorem. Experimental vertical ionization potentials from Ref. 55. Experimental adiabatic ionization potentials from Ref. 55. Experimental vertical ionization potential for CH$_4$ from Ref. 63. Experimental vertical ionization potential for CS from Ref. 64. Experimental vertical ionization potential for HCl from Ref. 67. Experimental vertical ionization potential for SiO from Ref. 68. Root-mean-square absolute error of the methods.

A survey of this table reveals that Koopman’s IPs tend to be larger than the ΔSCF values, and the prevailing trend is that the values increase, moving from ΔSCF to ΔCCD, then from ΔCCD to PNOF-EKT, and then from PNOF-EKT to ΔPNOF. For BeO, HBO, LiH, and MgS molecules the ΔPNOF values are smaller than the ΔCCD results, whereas in case of CS, FH, H$_2$O, HNC, and LiH the ΔPNOF IPs are smaller than the PNOF-EKT values.

Table I shows also that our ΔPNOF calculated values are

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Koopmans$^a$</th>
<th>ΔSCF$^b$</th>
<th>ΔCCD$^c$</th>
<th>ΔPNOF$^d$</th>
<th>PNOF-EKT$^e$</th>
<th>Expt.$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlH</td>
<td>7.782</td>
<td>6.144</td>
<td>8.010</td>
<td>10.072</td>
<td>8.821</td>
<td>7.649</td>
</tr>
<tr>
<td>BF</td>
<td>10.676</td>
<td>9.781</td>
<td>10.727</td>
<td>11.541</td>
<td>10.696</td>
<td>11.120$^g$</td>
</tr>
<tr>
<td>BeO</td>
<td>10.337</td>
<td>7.784</td>
<td>8.543</td>
<td>9.733</td>
<td>9.733</td>
<td>9.733$^g$</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>11.867</td>
<td>9.590</td>
<td>10.655</td>
<td>12.504</td>
<td>11.536</td>
<td>11.490$^i$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>13.532</td>
<td>10.968</td>
<td>12.068</td>
<td>12.917</td>
<td>13.085</td>
<td>12.620</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>13.068</td>
<td>11.634</td>
<td>11.325</td>
<td>13.358</td>
<td>12.522</td>
<td>11.700</td>
</tr>
<tr>
<td>LiH</td>
<td>8.164</td>
<td>7.037</td>
<td>7.760</td>
<td>7.567</td>
<td>8.000</td>
<td>7.900$^f$</td>
</tr>
<tr>
<td>MgO</td>
<td>8.449</td>
<td>5.618</td>
<td>8.013</td>
<td>8.904</td>
<td>7.489</td>
<td>8.760$^f$</td>
</tr>
<tr>
<td>MgS</td>
<td>8.049</td>
<td>7.963</td>
<td>8.872</td>
<td>8.497</td>
<td>7.953</td>
<td>7.953$^f$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>16.632</td>
<td>15.946</td>
<td>15.419</td>
<td>17.902</td>
<td>16.738</td>
<td>15.581</td>
</tr>
<tr>
<td>NaOH</td>
<td>8.591</td>
<td>5.822</td>
<td>7.096</td>
<td>7.841</td>
<td>7.841</td>
<td>7.841$^f$</td>
</tr>
<tr>
<td>P$_2$</td>
<td>10.141</td>
<td>10.442</td>
<td>10.411</td>
<td>11.258</td>
<td>10.390</td>
<td>10.620</td>
</tr>
<tr>
<td>PN</td>
<td>11.988</td>
<td>10.942</td>
<td>12.105</td>
<td>12.918</td>
<td>12.267</td>
<td>11.880$^f$</td>
</tr>
<tr>
<td>RMS$^n$</td>
<td>6.9%</td>
<td>12.0%</td>
<td>3.8%</td>
<td>11.0%</td>
<td>5.4%</td>
<td>5.4%$^n$</td>
</tr>
</tbody>
</table>

$^a$–$^n$ Refer to footnotes.
TABLE II. Bond length ($r_e$) of the selected molecules in a.u.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF</th>
<th>CCD</th>
<th>PNOF</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF</td>
<td>1.650</td>
<td>1.667</td>
<td>1.674</td>
<td>1.654</td>
</tr>
<tr>
<td>AlH</td>
<td>1.651</td>
<td>1.649</td>
<td>1.661</td>
<td>1.648</td>
</tr>
<tr>
<td>BeO</td>
<td>1.296</td>
<td>1.331</td>
<td>1.315</td>
<td>1.331</td>
</tr>
<tr>
<td>BeS</td>
<td>1.733</td>
<td>1.744</td>
<td>1.746</td>
<td>1.742</td>
</tr>
<tr>
<td>BF</td>
<td>1.261</td>
<td>1.283</td>
<td>1.276</td>
<td>1.263</td>
</tr>
<tr>
<td>BH</td>
<td>1.227</td>
<td>1.232</td>
<td>1.233</td>
<td>1.232</td>
</tr>
<tr>
<td>CO</td>
<td>1.114</td>
<td>1.139</td>
<td>1.132</td>
<td>1.128</td>
</tr>
<tr>
<td>CS</td>
<td>1.519</td>
<td>1.536</td>
<td>1.542</td>
<td>1.535</td>
</tr>
<tr>
<td>FH</td>
<td>0.900</td>
<td>0.920</td>
<td>0.917</td>
<td>0.917</td>
</tr>
<tr>
<td>HCl</td>
<td>1.265</td>
<td>1.271</td>
<td>1.273</td>
<td>1.275</td>
</tr>
<tr>
<td>LiH</td>
<td>1.630</td>
<td>1.627</td>
<td>1.626</td>
<td>1.596</td>
</tr>
<tr>
<td>MgO</td>
<td>1.738</td>
<td>1.781</td>
<td>1.786</td>
<td>1.749</td>
</tr>
<tr>
<td>MgS</td>
<td>2.150</td>
<td>2.170</td>
<td>2.178</td>
<td>2.143</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.078</td>
<td>1.112</td>
<td>1.099</td>
<td>1.098</td>
</tr>
<tr>
<td>P$_2$</td>
<td>1.859</td>
<td>1.905</td>
<td>1.893</td>
<td>1.893</td>
</tr>
<tr>
<td>PN</td>
<td>1.455</td>
<td>1.499</td>
<td>1.487</td>
<td>1.491</td>
</tr>
<tr>
<td>SiO</td>
<td>1.488</td>
<td>1.520</td>
<td>1.520</td>
<td>1.510</td>
</tr>
<tr>
<td>RMS$^c$</td>
<td>1.41%</td>
<td>0.96%</td>
<td>0.98%</td>
<td>...</td>
</tr>
<tr>
<td>F$_2$</td>
<td>1.347</td>
<td>1.420</td>
<td>1.487</td>
<td>1.412</td>
</tr>
<tr>
<td>RMS$^d$</td>
<td>1.7%</td>
<td>0.9%</td>
<td>1.5%</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$Hartree-Fock equilibrium geometries.
$^b$CCD equilibrium geometries.
$^c$Natural-orbital-functional equilibrium geometries computed in this work.
$^d$Experimental equilibrium geometries from Ref. 55.
$^e$Root-mean-square absolute error of the methods.

A systematic increase of the bond lengths, the harmonic vibrational frequencies

TABLE III. Vibrational frequencies ($\omega_r$) of the selected molecules in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF</th>
<th>CCD</th>
<th>PNOF</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF</td>
<td>859</td>
<td>842</td>
<td>833</td>
<td>802</td>
</tr>
<tr>
<td>AlH</td>
<td>1763</td>
<td>1730</td>
<td>1711</td>
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<td>13.2%</td>
<td>4.2%</td>
<td>6.1%</td>
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$^a$Hartree-Fock vibrational frequencies.
$^b$CCD vibrational frequencies.
$^c$Natural-orbital-functional vibrational frequencies computed in this work.
$^d$Experimental vibrational frequencies from Refs. 55.
$^e$Root-mean-square absolute error of the methods.

The correlated bond lengths are mostly longer than the experimental values. Exceptions to this statement are AlH, LiH, and MgS due probably to the deficiencies in the 6-31G$^*$ basis set.

The CCD, PNOF, and PNOF-EKT methods show rms absolute errors from the experimental values for AlH, LiH, and MgS due probably to the deficiencies in the 6-31G$^*$ basis set.

It has long been recognized that the HF method gives reduced bond lengths. We find that the HF bond lengths are shorter than the experimental ones for AlF, BeO, BeS, BF, BH, CO, CS, F$_2$, FH, HCl, MgO, N$_2$, P$_2$, PN, and SiO molecules. Conversely, the HF method overestimates the experimental values for AlH, LiH, and MgS due to the deficiencies in the 6-31G$^*$ basis set.

Generally, the inclusion of electron correlation leads to an increase of the bond lengths. The exceptions are AlH, for which the CCD bond length is decreased, and LiH, for which the CCD and PNOF bond lengths are smaller than the HF distances.

The correlated bond lengths are mostly longer than the experimental values. Exceptions to this statement are the bond distance predicted by CCD for HCl and the bond distances calculated by PNOF for BeO, HCl, and PN molecules. The rms absolute errors compared with experiments are 1.5% and 0.9% for PNOF and CCD methods, respectively. In case of the F$_2$ molecule, we must note that the PNOF bond length is too long. Excluding this molecule, the PNOF method shows a rms absolute error from the experiment of 0.98% closer to the CCD rms absolute error of...
are reproduced expected trends of this property with respect to experiment. The selected set of molecules are presented in Table III. The F2 vibrational frequency is too low. Because longer bonds tend to diminish the force constants, values show rms absolute errors with respect to the experimental frequencies is similar to CCD. The PNOF and CCD frequency results are systematically larger, and the correlated vibrational frequencies move closer to experimental data. By both methods, the PNOF-EKT vertical IPs are in better agreement with the corresponding experimental data and are closer to CCD results. The PNOF and CCD methods show rms absolute errors compared with experiments of 9.7% and 3.7%, respectively.

If we compare the results obtained by ΔPNOF for vertical and adiabatic IPs (see Tables I and IV), we can observe that the vertical IP values are about 2.0% higher than the adiabatic IPs, and that is precisely what we expect. In cases of CO and SiO molecules, the adiabatic IPs are higher than the vertical IPs. Note that the vertical IPs from Table I were calculated at the experimental geometries. We have calculated the vertical IPs at the PNOF-optimized geometry for these molecules. We have found then that the vertical IPs (17.506 and 13.406 eV for CO and SiO, respectively) are higher than the adiabatic IPs, accordingly with the expected trend.

IV. CONCLUSIONS

The recent obtained PNOF (Ref. 41) was used to determine vertical ionization potentials for a set of 38 selected molecules at the experimental geometries. For the subset of 18 diatomic molecules, we have also presented the adiabatic ionization potentials, the equilibrium bond distances, and the harmonic vibrational frequencies. To our knowledge, this is the first report of adiabatic ionization potentials via NOFT.

The functional yields molecular properties as well as those obtained by the standard ab initio technique, namely, CCD. Comparison with experimental results showed the PNOF geometries and frequencies to be generally no better than or inferior to those predicted by the CCD method within the 6-31G** basis set. The ΔPNOF values of ionization potentials tend to be slightly higher than the experimental results. This expected trend is caused by the underestimation of the correlation energy for ions, according to our working hypothesis for the ion ground state ($\theta_{\text{HOMO}}=1$). On the other hand, the PNOF-EKT vertical IPs are in better agreement with the corresponding experimental data and are closer to CCD results.

In general, we observed that the overall trends with the introduction of the electronic correlation by PNOF are satisfactory. The reliability of the PNOF in the prediction of the studied properties has been illustrated. The knowledge of the energy derivatives and energy Hessian will provide in the future very useful information to determine efficiently the most stable conformation of polyatomic molecules.

ACKNOWLEDGMENTS

The authors are very grateful for the generous financial support of the Alexander von Humboldt (AvH) Foundation and the German Academic Exchange Service (DAAD).

Two-electron cumulant