

## Validity of the Extended Koopmans' Theorem

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**Abstract:** The generalized Koopmans' theorem (EKT) yields an estimate of ionization potentials (IPs) of an  $N$ -electron system. This estimate ( $\text{IP}^{\text{EKT}}$ ) is obtained as an eigenvalue of a generalized eigenvalue problem. Katriel and Davidson provided a proof [Katriel, J.; Davidson, E. R. *Proc. Natl. Acad. Sci. U.S.A.*, **1980**, 77, 1403.] that the EKT predicts the exact lowest IP for ground states of Coulomb systems. However, subsequently, several articles have been published challenging the exactness of the EKT and providing disproofs. This apparent contradiction is resolved by demonstrating that the lowest eigenvalue of the generalized Koopmans' procedure does, in general, not exist. This explains why contradictory results are obtained about the lowest  $\text{IP}^{\text{EKT}}$  since its existence has implicitly been assumed. Nonetheless, it will also be shown here that the generalized Koopmans' approach gives IPs that are arbitrarily close to the exact lowest ionization energy. The eigenvalues obtained according to the EKT have an accumulation point given by the exact lowest IP.

### 1. Introduction

Koopmans' theorem<sup>1</sup> is widely used to estimate ionization energies on the basis of Hartree–Fock calculations. In view of the usefulness of this theorem, considerable efforts have been made to generalize Koopmans' theorem by broadening its Hartree–Fock framework. An extended Koopmans' theorem (EKT), based on correlated wave functions, has been developed by Day, Smith, and Garrod<sup>2,3</sup> and Morrell, Parr, and Levy.<sup>4</sup> The EKT is presently employed on a regular basis as witnessed by several recent publications including.<sup>5–8</sup> The EKT makes use of an extended Fock operator  $F(1,1')$  constructed from the one- and two-particle density matrix of a correlated wave function.  $i$  (e.g., 1 or  $1'$ ) stands for the spatial and spin coordinates ( $\mathbf{r}_i, \sigma_i$ ) indexed with  $i$ . An approximation ( $\text{IP}^{\text{EKT}}$ ) to the lowest ionization potential (IP) of the  $N$ -particle ground state ( $\psi$ ) is then obtained as the lowest eigenvalue of the generalized eigenvalue problem<sup>2,4</sup> (implicitly assuming that the lowest eigenvalue does exist)

$$\int d1' F(1,1') \varphi(1') = \text{IP}^{\text{EKT}} \int d1' \gamma(1,1') \varphi(1'), \quad (1)$$

where

$$F(1,1') = h(1)\gamma(1,1') + \int d2 \frac{\Gamma(1,2;1',2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (2)$$

$h(1) = -1/2\Delta_{r_1} + v(1)$  is the one-particle Hamiltonian.  $v$  denotes a local external potential.  $\gamma(1,1')$  and  $\Gamma(1,2;1',2')$  are given by

$$\gamma(1,1') = \langle \psi | \hat{\Psi}^\dagger(1') \hat{\Psi}(1) | \psi \rangle \quad (3)$$

and

$$\Gamma(1,2;1',2') = \langle \psi | \hat{\Psi}^\dagger(1') \hat{\Psi}^\dagger(2') \hat{\Psi}(2) \hat{\Psi}(1) | \psi \rangle \quad (4)$$

respectively.  $\hat{\Psi}(1)$  stands for a field operator,<sup>9</sup> which annihilates an electron in the state corresponding to the argument of the operator. The fact that only the one- and two-particle density matrices are needed to construct  $F(1,1')$  has contributed to the popularity of the extended Koopmans' procedure because these quantities are available in many quantum chemistry program codes.

Morrell, Parr, and Levy<sup>4</sup> have shown that the “lowest” eigenvalue (implicitly assuming it exists) of the generalized eigenvalue problem eq 1 is given by the asymptotic, exponential decay length of the electron density, that is,  $\lim_{r \rightarrow \infty} \rho(r) \propto \exp(-2(\text{IP}^{\text{EKT}})^{1/2} r)$ . They also conjectured that the decay length of the density is equal to the exact lowest

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ionization energy. This conjecture was supported by Ahlrichs,<sup>10</sup> Levy and Parr,<sup>11</sup> and Katriel and Davidson.<sup>12</sup> The question whether the lowest ionization energy obtained from the EK procedure is exact has been discussed extensively in the literature. Up to, now no completely satisfying answer has been found. Katriel and Davidson<sup>12</sup> argued that  $\text{IP}^{\text{EKT}}$  is equal to the exact ionization energy. Their argument is based on the asymptotic behavior of the wave function as one electron wanders away from the finite system. Doubts about the exactness of the EK procedure have been raised by Smith and Öhrn.<sup>13</sup> Pickup<sup>14</sup> and Pickup and Snijders<sup>15</sup> analyzed the EK procedure using the perturbation expansion of the ionization energy. They showed that in general certain second-order contributions of the expansion of the exact IP are missing in the perturbation expansion of  $\text{IP}^{\text{EKT}}$ . Andersen and Simons arrived at the same conclusion.<sup>16</sup> Olsen and Sundholm<sup>17</sup> presented a numerical investigation of the perturbation expansion and concluded that the missing terms in the EKT perturbation expansion are zero and that the  $\text{IP}^{\text{EKT}}$  is exact. More recently, a sufficient condition for the validity of the EKT has been derived<sup>18</sup> that is difficult to verify in practical calculations, however. Despite these attempts to resolve the paradox concerning the exactness of  $\text{IP}^{\text{EKT}}$ , a satisfying solution has not been found in the sense that the shortcomings of either the proof, the disproof, or of both have not been discovered.

Numerical studies have been undertaken<sup>19–28</sup> to obtain a better understanding of the accuracy of the EK procedure. Without going into details, we state the main results of these investigations. Comparison of the lowest ionization energy, as obtained from Full-CI calculations,<sup>22,24–28</sup> with  $\text{IP}^{\text{EKT}}$  obtained employing the Full-CI density matrices shows that there is strong numerical evidence that these two quantities converge toward the same number upon increasing the size of the one-particle basis set. We want to stress that it is of course not possible to resolve the paradox, apparent in the formal investigations of the EKT, via numerical calculations. However, the accuracy of the numerical results underlines the usefulness of the EK procedure.

In the present work, we will show that a careful interpretation of the results of Katriel and Davidson and the findings of Pickup and Snijders,<sup>14,15</sup> and Andersen and Simons<sup>16</sup> removes the incompatibilities. We argue that the question whether the lowest eigenvalue of the EK procedure gives the exact lowest IP or not is not the right question to ask since the lowest eigenvalue of the EKT eigenvalue problem does, in general, not exist. However, all proofs and disproofs given previously implicitly assume that a lowest eigenvalue does exist.

To close the introduction we provide an outline of the article. In section 2, the working equations of the EKT for the lowest IP are derived. In section 3, the argument by Katriel and Davidson is examined, it is shown that their findings do not support the conclusion that  $\text{IP}^{\text{EKT}}$  is exact. The asymptotic behavior of the wave function is then used in section 4 to show that no eigenvalue of the EK procedure can yield the exact lowest IP. In the last section (section 5), we show that it is however possible to find eigenvalues of eq 1, which are arbitrarily close (but not equal) to the exact,

lowest ionization energy, that is, the eigenvalues of the EKT eigenvalue problem have an accumulation point at the exact, lowest IP.

## 2. Working Equations of the Extended Koopmans' Theorem

Following,<sup>2,3</sup> we summarize the extended Koopmans' procedure as far as it is relevant for the present work. We start from the ansatz

$$|\psi^{N-1}\rangle = \mathcal{N}^{-1/2} \int d1 \varphi(1) \hat{\Psi}(1) |\psi\rangle \quad (5)$$

for the  $(N - 1)$ -particle wave function.  $\mathcal{N}$  denotes an appropriate normalization constant. The linear combination of  $\hat{\Psi}(1)$  operators in eq 5 annihilates an electron in the orbital  $\varphi(1)$  in  $|\psi\rangle$ . The amplitude  $\varphi(1)$  constitutes the actual variational parameter in eq 5. Using this trial function in the Raleigh–Ritz quotient and varying the energy with respect to the amplitude  $\varphi(1)$  leads to an eigenvalue equation for  $\varphi(1)$

$$\int d1' \{ \langle \psi | \hat{\Psi}^\dagger(1) \hat{H} \hat{\Psi}(1') | \psi \rangle - E^{(N-1)} \langle \psi | \hat{\Psi}^\dagger(1) \hat{\Psi}(1') | \psi \rangle \} \varphi(1') = 0 \quad (6)$$

where we assume, as throughout the paper, that all wave functions and orbitals are real. Since we are interested in the difference between the energy  $E^{N-1}$  of the approximate  $(N - 1)$ -particle wave function and the energy  $E$  of the  $N$ -particle system, we add  $0 = d1' \{ -\langle \psi | \hat{\Psi}^\dagger(1) \hat{\Psi}(1') \hat{H} | \psi \rangle + E \langle \psi | \hat{\Psi}^\dagger(1) \hat{\Psi}(1') | \psi \rangle \} \varphi(1')$  to eq 6. Furthermore, we make use of the definition of the one-particle density matrix,  $\gamma(1, 1') = \langle \psi | \hat{\Psi}^\dagger(1) \hat{\Psi}(1') | \psi \rangle$ , to obtain

$$\begin{aligned} \int d1' \{ \langle \psi | \hat{\Psi}^\dagger(1) \hat{H} \hat{\Psi}(1') | \psi \rangle - \langle \psi | \hat{\Psi}^\dagger(1) \hat{\Psi}(1') \hat{H} | \psi \rangle + \\ (E - E^{(N-1)}) \langle \psi | \hat{\Psi}^\dagger(1) \hat{\Psi}(1') | \psi \rangle \} \varphi(1') = 0 \Leftrightarrow \\ \int d1' \{ -\langle \psi | \hat{\Psi}^\dagger(1) [\hat{\Psi}(1'), \hat{H}] | \psi \rangle - \text{IP}^{\text{EKT}} \gamma(1, 1') \} \varphi(1') = 0 \end{aligned} \quad (7)$$

The eigenvalues of this generalized eigenvalue problem are obviously bound from below by the exact, lowest ionization energy of the  $N$ -particle system. We define the extended Fock operator  $F(1, 1')$  by

$$F(1, 1') = -\langle \psi | \hat{\Psi}^\dagger(1) [\hat{\Psi}(1'), \hat{H}] | \psi \rangle \quad (8)$$

and recast eq 7 to yield extended Hartree–Fock equation

$$\int d1' F(1, 1') \varphi(1') = \text{IP}^{\text{EKT}} \int d1' \gamma(1, 1') \varphi(1') \quad (9)$$

Analogous to Hartree–Fock orbitals, the eigenfunctions  $\varphi_i$  of this generalized eigenvalue problem do not only have a well defined energy but also a well defined occupation number since the  $\varphi_i$  are orthogonal in the metric given by the one-particle density matrix

$$\int d1 d1' \varphi_i(1) \gamma(1, 1') \varphi_j(1') = 0 \text{ for } i \neq j \quad (10)$$

The eigenvalues of the metric  $\gamma(1, 1')$  vary in the interval  $[0, 1]$ . Note that orbitals with a vanishing norm in the metric

$\gamma(1,1')$  do not represent eigenfunctions of the EKT eigenvalue problem. We do not expect to find the smallest, nonzero eigenvalue of  $\gamma(1,1')$  in a Coulomb system, and we will also show that it is not possible to find a  $\varphi_i$  with the lowest energy eigenvalue (i.e., lowest  $\text{IP}^{\text{EKT}}$ ).

An explicit expression for  $F(1,1')$  is obtained by evaluating the commutator in eq 7. This leads to the representation of  $F(1,1')$  given in the introduction. Replacing the exact one-particle density matrix and two-particle density matrix of the  $N$ -particle system in eq 9 by the corresponding quantities in the Hartree–Fock approximation leads back to the well-known Hartree–Fock equations.

### 3. Revisiting the Proof of the Exactness of $\text{IP}^{\text{EKT}}$

The proof of the exactness of the EK procedure<sup>12</sup> is based on the behavior<sup>12,29,30</sup> of the ground-state wave function of a Coulomb system as the  $N$ th electron wanders away from the others ( $r_N \gg r_1, \dots, r_{N-1}$ , where  $r_i = |\mathbf{r}_i|$ ). The earlier literature<sup>12,29</sup> does not completely describe the asymptotic behavior in the case where the  $(N-1)$ -electron system is degenerate (for a detailed discussion see ref 30). However, the basic idea presented here does not depend on whether the  $(N-1)$ -particle ground-state is degenerate or not, and for the sake of simplicity we focus on the case where the  $(N-1)$ -particle state is nondegenerate and where the results of Katriel and Davidson<sup>12</sup> and others<sup>29</sup> concerning the asymptotic behavior of the ground-state wave function are complete. To summarize these results, we focus on the coordinate of the  $N$ th electron and take the limit  $r_N \rightarrow \infty$ . The  $N$ -particle wave function as a function of the coordinates of the remaining  $(N-1)$ -electrons collapses toward the energetically lowest accessible<sup>29</sup>  $(N-1)$ -particle state  $\psi^{N-1}(1, \dots, N-1)$ . Accessible  $(N-1)$ -particle states are states which can be reached from the  $N$ -particle state by removing one electron, without violating symmetry restrictions.<sup>29</sup> The detailed derivation shows that<sup>12,29,30</sup>

$$\lim_{r_N \rightarrow \infty} \psi(1, \dots, N) = N^{-1/2} \rho^{1/2}(N) \psi^{N-1}(1, \dots, N-1) \quad (11)$$

$\rho(N)$  denotes the spin density. The wave function of the  $(N-1)$ -particle system is entirely contained in the wave function of the  $N$ -particle system in the sense of the limiting procedure of eq 11. In general, however, we do not expect that the  $N$ -electron system collapses toward the exact  $(N-1)$ -particle system for any *finite distance* between the  $N$ th electron and the  $(N-1)$ -particle system.

To make the relation of eq 11 to the ansatz eq 5 for the  $(N-1)$ -particle wave function more explicit we note that eq 11 is equivalent to

$$\lim_{r_N \rightarrow \infty} \hat{\Psi}(N)|\psi\rangle = \rho^{1/2}(N)|\psi^{N-1}\rangle \Rightarrow |\psi^{N-1}\rangle = \lim_{r_N \rightarrow \infty} \rho^{-1/2}(N) \hat{\Psi}(N)|\psi\rangle \quad (12)$$

In their argument in favor of the exactness of the EKT, Katriel and Davidson discussed a slightly different representation of eq 12, which we now introduce. To express eq 12 in terms of the natural spin orbitals (NSO's)  $n_i(l)$  of  $\psi$ ,

we expand  $\hat{\Psi}(N)$  in terms of the NSO's (including the NSO's with zero occupation number)

$$\begin{aligned} \hat{\Psi}(N) &= \sum_I n_i(N) \int dN' n_i(N') \hat{\Psi}(N') \\ &= \sum_i n_i(N) \hat{a}_{n_i} \end{aligned} \quad (13)$$

so that

$$|\psi^{N-1}\rangle = \lim_{r_N \rightarrow \infty} \rho^{-1/2}(N) \sum_i n_i(N) \hat{a}_{n_i} |\psi\rangle \quad (14)$$

$\hat{a}_{n_i}$  denotes the destruction operator corresponding to the orbital  $n_i$ . Equation 14 appears to indicate<sup>12</sup> that the lowest ionization energy, obtained according to the EK procedure, is exact since the  $(N-1)$ -particle wave function can be obtained from  $\psi$  by annihilation of an electron. This would imply that there exists an orbital, say  $\varphi(N)$ , such that

$$\begin{aligned} \int dN \varphi(N) \hat{\Psi}(N) |\psi\rangle &= \hat{a}_\varphi |\psi\rangle \\ &\propto |\psi^{N-1}\rangle \end{aligned} \quad (15)$$

However, all eq 14 (or equivalently eq 12) is saying is that there exists a *sequence* of orbitals

$$\varphi_{r_N}(\mathbf{r}) \sigma_N = \rho^{-1/2}(\mathbf{r}_N) \sqrt{\delta(\mathbf{r} - \mathbf{r}_N)} \sigma_N \quad (16)$$

such that we obtain the lowest accessible  $(N-1)$ -electron state if  $\varphi_{r_N}(\mathbf{r}) \sigma_N$  is annihilated in  $\psi$  and if we take the limit  $r_N \rightarrow \infty$ . This does not mean that taking the limit  $r_N \rightarrow \infty$ , before annihilating the orbital  $\varphi_{r_N}(\mathbf{r}) \sigma_N$ , defines an orbital  $\varphi$  with the property  $\hat{a}_\varphi |\psi\rangle \propto |\psi^{N-1}\rangle$ . Taking  $r_N \rightarrow \infty$  before applying  $\hat{a}_{\varphi_{r_N} \sigma_N}$  to  $\psi$  would (according to eq 12) mean that we destroy a particle at infinite separation from the finite system and multiply the result by  $\infty = \lim_{r_N \rightarrow \infty} \rho^{-1/2}(\mathbf{r}_N)$ , an operation which is meaningless.

### 4. Disproof of the Exactness of $\text{IP}^{\text{EKT}}$

In the preceding section we have shown that the argument given by Katriel and Davidson does not imply that the lowest ionization energy can be obtained as the lowest eigenvalue of the EK procedure. Now we provide a proof that no eigenvalue of the generalized EKT eigenvalue equation (eq 9) can be equal to the lowest IP of the  $N$ -particle system. This result is intuitively clear since the eigenfunction of the extended Fock operator will be nonzero for finite distances to the  $(N-1)$ -particle system so that the  $(N-1)$ -particle system gets polarized by the  $N$ th-electron and this in turn raises the energy compared to the exact  $(N-1)$ -particle ground state.

The asymptotic collapse of the wave function of a finite system (i.e.,  $\lim_{r_N \rightarrow \infty} \psi(1, \dots, N) = N^{-1/2} \rho^{1/2}(N) \psi^{N-1}(1, \dots, N-1)$ ) leads to conditions on the two-particle density matrix of a finite system. We get for instance

$$\begin{aligned}
& \lim_{r_1 \rightarrow \infty} \Gamma(1, 2; 1, 2') \\
&= N(N-1) \lim_{r_1 \rightarrow \infty} \int d3, \dots, dN \psi(1, 2', 3, \dots, N) \psi(1, 2, 3, \dots, N) \\
&= \rho(1)(N-1) \int d3, \dots, dN \psi^{N-1}(2', 3, \dots, N) \psi^{N-1}(2, 3, \dots, N) \\
&= \rho(1) \gamma^{N-1}(2, 2') \quad (17)
\end{aligned}$$

Now we assume that the EK procedure predicts the exact, lowest ionization energy, that is, that there exist a  $\varphi$  such that

$$|\psi^{N-1}\rangle = \gamma_{\varphi\varphi}^{-1/2} a_{\varphi} |\psi\rangle \quad (18)$$

The normalization factor  $\gamma_{\varphi\varphi}$  is given by  $\gamma_{\varphi\varphi} = \langle \psi | a_{\varphi}^{\dagger} a_{\varphi} | \psi \rangle$ . We use eq 18 to evaluate a certain two-particle density matrix element, namely

$$\begin{aligned}
\int d2 d2' \varphi(2) \varphi(2') \Gamma(1, 2; 1, 2') &= \langle \psi | a_{\varphi}^{\dagger} \hat{\Psi}^{\dagger}(1) \hat{\Psi}(1) a_{\varphi} | \psi \rangle \\
&= \gamma_{\varphi, \varphi} \rho^{N-1}(1) \quad (19)
\end{aligned}$$

In the limit  $r_1 \rightarrow \infty$ , eq 19 is incompatible with eq 17 because the density matrix element falls off like  $\rho^{N-1}(1)$  instead of showing the correct  $\rho(1)$  behavior. The exponential decay of the electron density of a system is given by  $\exp(-2(2I)^{1/2}r)$ , and since in all examples of interacting Coulomb systems known to us  $I^N < I^{N-1}$ , we see that  $\rho^{N-1}$  becomes exponentially small compared to  $\rho$  as  $r_1 \rightarrow \infty$ . These considerations show that the asymptotic behavior of the wave function as  $r_N \rightarrow \infty$  leads to the conclusion that the EK procedure does not have an eigenvalue which is equal to the exact ionization energy.

## 5. Discussion and Conclusion

We have shown that no eigenvalue of the extended Hartree–Fock equation (eq 1) yields the exact, lowest IP. On the other hand, it can readily be verified that the EK procedure has the potential to give an arbitrarily good approximation to the lowest IP. It is always possible to find an orbital  $\phi$ , with the corresponding energy  $\epsilon = \langle \psi | a_{\phi}^{\dagger} a_{\phi} | \psi \rangle^{-1} \cdot \int d1 d1' \phi(1) F(1, 1') \phi(1')$ , satisfying the inequality

$$\epsilon < \frac{\langle \psi | \hat{\Psi}^{\dagger}(1) (H - E) \hat{\Psi}(1) | \psi \rangle}{\langle \psi | \hat{\Psi}^{\dagger}(1) \hat{\Psi}(1) | \psi \rangle} \quad (20)$$

for any given  $\mathbf{r}_1$ . For the spatial part of  $\phi$ , we could for instance choose  $\phi(\mathbf{r}) = \sqrt{[\delta(\mathbf{r} - \mathbf{R})]}$ , with  $|\mathbf{R}| \gg r_1$ . This shows that the lowest IP can be approximated by the EK procedure with any desired accuracy, since  $\hat{\Psi}(1)|\psi\rangle$  asymptotically collapses toward  $|\psi^{N-1}\rangle$  as  $r_1$  increases.

Our discussion implies that the eigenfunctions of the extended Hartree–Fock equation, which are close in energy to the lowest ionization energy, have a rather counterintuitive character; they minimize the interaction with the  $(N-1)$ -particle system, and not much can be learned from them about the  $N$ -particle system. This has important implications for the choice of basis sets for the EK approach. It is necessary to add basis functions which make it possible for an electron to travel far away from

the remaining electrons. On the other hand, the corresponding eigenfunctions will have a very small occupation number so that the generalized eigenvalue problem eq 1 might become ill-conditioned.<sup>27</sup>

Our findings are compatible with the perturbation theoretical disproofs of the exactness of the EK procedure.<sup>14–16</sup> In these disproofs, EKT eigenvalues are shown to be different from the exact, lowest ionization energy. However, it is not shown that it is impossible to find EK eigenvalues which are arbitrarily close to the exact, lowest ionization energy.

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## References

- (1) Koopmans, T. A. *Physica* **1934**, *1*, 104.
- (2) Day, O. W.; Smith, D. W.; Garrod, C. *Int. J. Quantum Chem. Symp.* **1974**, *8*, 501.
- (3) Smith, D. W.; Day, O. W. *J. Chem. Phys.* **1975**, *62*, 113.
- (4) Morrell, M. M.; Parr, R. G.; Levy, M. *J. Chem. Phys.* **1975**, *62*, 549.
- (5) Piris, M.; Matxain, J. M.; Ugalde, J. M. *J. Chem. Phys.* **2008**, *129*, 014108.
- (6) Vetere, V.; Monari, A.; Bendazzoli, G. L.; Evangelisti, S.; Paulus, B. *J. Chem. Phys.* **2008**, *128*, 024701.
- (7) Angelotti, W. F. D.; Streit, L.; Fonseca, A. L. D.; Custodio, R. *Int. J. Quantum Chem.* **2008**, *108*, 2459.
- (8) Ayers, P. W.; Melin, J. *Theor. Chem. Acc.* **2007**, *117*, 371.
- (9) Fetter, A. L.; Walecka, J. D. *Quantum Theory of Many-Particle Systems*; McGraw-Hill: New York, 1971, pp 12–21.
- (10) Ahlrichs, R. *J. Chem. Phys.* **1976**, *64*, 2706.
- (11) Levy, M.; Parr, R. G. *J. Chem. Phys.* **1976**, *64*, 2707.
- (12) Katriel, J.; Davidson, E. R. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 4403.
- (13) Smith, H. V.; Öhrn, Y. On a formula for electron binding energies In *Reduced Density Operators with Applications to Physical and Chemical Systems II*; Erdahl, R. M., Ed.; Queens' University: Kingston, Ontario, 1974, p 193.
- (14) Pickup, B. T. *Chem. Phys. Lett.* **1975**, *33*, 422.
- (15) Pickup, B. T.; Snijders, J. G. *Chem. Phys. Lett.* **1988**, *153*, 69.
- (16) Andersen, E.; Simons, J. *J. Chem. Phys.* **1977**, *66*, 1067.
- (17) Olsen, J.; Sundholm, D. *Chem. Phys. Lett.* **1998**, *288*, 282.
- (18) Pernal, K.; Cioslowski, J. *J. Chem. Phys.* **2001**, *114*, 4359.
- (19) Day, O. W.; Smith, D. W.; Morrison, R. C. *J. Chem. Phys.* **1975**, *62*, 115.

- (20) Ellenbogen, J. C.; Day, O. W.; Smith, D. W.; Morrison, R. C. *J. Chem. Phys.* **1977**, *66*, 4795.
- (21) Morrison, R. C. *Chem. Phys. Lett.* **1979**, *62*, 131.
- (22) Morrison, R. C. *J. Chem. Phys.* **1992**, *96*, 3718.
- (23) Morrison, R. C.; Liu, G. *Int. J. Quantum Chem.* **1992**, *13*, 1004.
- (24) Sundholm, D.; Olsen, J. *J. Chem. Phys.* **1993**, *98*, 3999.
- (25) Morrison, R. C. *J. Chem. Phys.* **1993**, *99*, 6221.
- (26) Sundholm, D.; Olsen, J. *J. Chem. Phys.* **1993**, *99*, 6222.
- (27) Morrison, R. C.; Dixon, C. M.; Mizell, J. R. *Int. J. Quantum Chem. Symp.* **1994**, *28*, 309.
- (28) Morrison, R. C. *Int. J. Quantum Chem.* **1994**, *49*, 649.
- (29) Levy, M.; Perdew, J. P.; Sahni, V. *Phys. Rev. A* **1984**, *30*, 2745.
- (30) Ernzerhof, M.; Burke, K.; Perdew, J. P. *J. Chem. Phys.* **1996**, *105*, 2798.

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