The extended Koopmans' theorem for orbital-optimized methods: Accurate computation of ionization potentials

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The extended Koopmans' theorem (EKT) provides a straightforward way to compute ionization potentials (IPs) from any level of theory, in principle. However, for non-variational methods, such as Møller–Plesset perturbation and coupled-cluster theories, the EKT computations can only be performed as by-products of analytic gradients as the relaxed generalized Fock matrix (GFM) and one- and two-particle density matrices (OPDM and TPDM, respectively) are required [J. Cioslowski, P. Piskorz, and G. Liu, J. Chem. Phys. **107**, 6804 (1997)]. However, for the orbital-optimized methods both the GFM and OPDM are readily available and symmetric, as opposed to the standard post Hartree–Fock (HF) methods. Further, the orbital optimized methods solve the N-representability problem, which may arise when the relaxed particle density matrices are employed for the standard methods, by disregarding the orbital Z-vector contributions for the OPDM. Moreover, for challenging chemical systems, where spin or spatial symmetry-breaking problems are observed, the abnormal orbital response contributions arising from the numerical instabilities in the HF molecular orbital Hessian can be avoided by the orbital-optimization. Hence, it appears that the orbital-optimized methods are the most natural choice for the study of the EKT. In this research, the EKT for the orbital-optimized methods, such as orbital-optimized second- and third-order Møller–Plesset perturbation [U. Bozkaya, J. Chem. Phys. **135**, 224103 (2011)] and coupled-electron pair theories [OCEPA(0)] [U. Bozkaya and C. D. Sherrill, J. Chem. Phys. **139**, 054104 (2013)], are presented. The presented methods are applied to IPs of the second- and third-row atoms, and closed- and open-shell molecules. Performances of the orbital-optimized methods are compared with those of the counterpart standard methods. Especially, results of the OCEPA(0) method (with the aug-cc-pVTZ basis set) for the lowest IPs of the considered atoms and closed-shell molecules are substantially accurate, the corresponding mean absolute errors are 0.11 and 0.15 eV, respectively. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4825041]

I. INTRODUCTION

Modern quantum chemistry offers several methods for the computation of ionization potentials (IPs), such as the electron propagator theory (EPT),[1–5] equation of motion (EOM) methods,[6–11] and the extended Koopmans' theorem (EKT).[12–14] Among these methods, the EKT provides a straightforward way to compute IPs from any level of theory.[15–24] Especially, the energy-derivative approach of Cioslowski, Piskorz, and Liu[21] extended the scope of the EKT to all wave function based methods. In that approach one can perform an EKT computation as a by-product of analytic gradients. Hence, in principle the EKT formalism can be applied to any method for which analytic gradients are available.

The exactness of the EKT was subject of a debate in the past.[25–34] In 1993, Sundholm and Olsen[30] examined the exactness of the EKT computing IPs of Be (^1S) with the EKT based on the multiconfiguration Hartree–Fock (MCHF) method, and comparing it with the configuration interaction (CI) calculations on Be$^+$ (^2S). They showed that the difference between the lowest IPs obtained from two methods approaches to zero as the size of the basis set increases. Hence, Sundholm and

Olsen[30] concluded that the EKT is exact for the lowest IP. In a 1998 study, Olsen and Sundholm[31] further examined the exactness of the EKT by a perturbation theory analysis. They obtained IPs as energy differences and employing the EKT approach. Analysis of the perturbative expansions showed that the EKT is exact for each perturbation order. Olsen and Sundholm[31] also noted that the missing second-order terms for many-electron systems identified by Pickup and Snijders[28] simply vanish in the complete basis set limit. In 2009, Vanfleteren et al.[33] discussed the exactness of the results from the EKT by analyzing the wave function asymptotics and they concluded that one obtains the exact IP when an electron is removed from an orbital, "removal orbital," which is concentrated in the asymptotic region. In another 2009 study, Ernzerhof[34] discussed that the lowest eigenvalue of the EKT procedure in general does not exist. However, IPs obtained from the EKT are arbitrarily close to the exact lowest ionization energy.

There has been continuing interest for the orbital-optimized Møller–Plesset perturbation theory (MP) and coupled-cluster (CC) methods.[35–59] Previous studies demonstrated that the orbital-optimized methods are very beneficial for the molecular systems with problematic electronic structures such as molecules suffering from

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symmetry breaking instabilities, free radicals, transition states, transition-metal complexes, and molecules at stretched geometries.[35–42, 45, 53, 56, 57]

As discussed previously, the energy-derivative approach of Cioslowski *et al.*[21] extended the applicability of the EKT to non-variational methods, such as MP and CC theories. However, there are several disadvantages of this approach. In that approach one uses the relaxed particle density-matrices (PDMs) and the relaxed generalized Fock matrix (GFM). Hence, the orbital relaxation contributions are included in these matrices by solving the orbital Z-vector[60] equation. However, it is well-documented that for challenging chemical systems where spatial or spin symmetry-breaking instabilities are observed, the orbital response equations may be ill-conditioned; this is the reason why unphysical vibrational frequencies are observed for such systems with Hartree–Fock (HF) orbitals.[35, 36, 39, 40, 61–64] Further, Kurlancheek and Head-Gordon[54] demonstrated that the orbital response equations generally have a singularity problem at the unrestriction point where spin-restricted orbitals become unstable to unrestriction. These singularities lead to the extremely large or small eigenvalues of the one-particle density matrix (OPDM). These unphysical eigenvalues may lead to abnormal molecular properties such as vibrational frequencies. Kurlancheek and Head-Gordon[54] also noted that although the energy appears well behaved, the N-representability condition may be violated in such cases. However, the orbital optimized methods solve this N-representability problem by disregarding the orbital Z-vector contributions for the OPDM. In addition to the N-representability problem, unphysical response contributions may also break the symmetry of the relaxed OPDM and GFM. Moreover, even in the case of closed-shell molecules the N-representability condition may be frequently violated[21] due to the orbital response contributions even though the orbital Z-vector equations are well-conditioned. Cioslowski *et al.*[21] suggested a procedure to overcome the N-representability problem by simply disregarding the natural orbitals with negative or zero eigenvalues. However, this procedure does not, in general, guarantee that the response contributions will not destroy the quality of the GFM and will not lead abnormal IPs in the case of symmetry-breaking problems.

In symmetry-breaking problems, one may consider to use the unrelaxed GFM and the unrelaxed OPDM in order to avoid abnormal Z-vector contributions. The unrelaxed OPDM can be defined as symmetric for any wave function,[35] hence, one can solve the positive-definiteness problem for the OPDM by this way. However, the unrelaxed GFM is not symmetric for the MP and CC methods; hence, one may get unreal eigenvalues. Even if all eigenvalues of the unrelaxed GFM are real, the computed IPs will not match with the experimental ones in such cases. On the other hand, the orbital-optimized methods solve all these mentioned problems. For the orbital-optimized methods both the GFM and OPDM are already available and symmetric, and the stationary properties of their wave functions prevent unphysical response contributions. Hence, one may consider orbital-optimized methods as the most suitable and robust methods for the study of the EKT approach.

In this research, the EKT for the orbital-optimized methods, such as orbital-optimized second- and third-order Møller–Plesset perturbation theories (OMP2[35, 39] and OMP3,[36, 41] as well as OMP2.5[42]) and the orbital-optimized coupled-electron pair theory [OCEPA(0)],[40] are presented. The EKT approaches for the orbital-optimized methods are applied to IPs of the second- and third-row atoms, and closed- and open-shell molecules. Performances of the orbital-optimized methods are compared with those of the counterpart standard methods, such as MP2, MP2.5,[65–67] MP3, and CEPA(0). For the standard methods, the energy-derivative approach of Cioslowski *et al.*[21] is employed. The presented equations have been implemented in a new computer code and added to the PSI4 package.[68]

II. THEORETICAL APPROACH

A. Orbital-optimized methods

In this section we present an overview of the orbital-optimized MP and CC methods, such as OMP2, OMP2.5, OMP3, and OCEPA(0). For a more detailed discussion of these methods one can refer to our previous studies.[35–42] For the parametrization of the wave functions, we will follow our previous studies.[35–41] The orbital variations may be carried out with an exponential unitary operator,[69–72]

$$\tilde{\hat{p}}^{\dagger} = e^{\hat{K}} \hat{p}^{\dagger} e^{-\hat{K}}, \tag{1}$$

$$\tilde{\hat{p}} = e^{\hat{K}} \hat{p} e^{-\hat{K}}, \tag{2}$$

$$|\tilde{p}\rangle = e^{\hat{K}} |p\rangle, \tag{3}$$

where $\hat{p}^{\dagger}$ and $\hat{q}$ are creation and annihilation operators, and $\hat{K}$ is the orbital rotation operator:

$$\hat{K} = \sum_{p,q} K_{pq} \hat{p}^{\dagger} \hat{q} = \sum_{p>q} \kappa_{pq} (\hat{p}^{\dagger} \hat{q} - \hat{q}^{\dagger} \hat{p}), \tag{4}$$

$$\mathbf{K} = Skew(\boldsymbol{\kappa}), \tag{5}$$

where κ_{pq} are the orbital rotation parameters. The effect of the orbital rotations on the molecular orbital (MO) coefficients can be written as

$$\mathbf{C}(\boldsymbol{\kappa}) = \mathbf{C^{(0)}} e^{\mathbf{K}}, \tag{6}$$

where $\mathbf{C^{(0)}}$ is the initial MO coefficient matrix and $\mathbf{C}(\boldsymbol{\kappa})$ is the new MO coefficient matrix as a function of $\boldsymbol{\kappa}$. Now, let us define a variational energy functional (Lagrangian) as a function of $\boldsymbol{\kappa}$ for each considered method:

OMP2:[35, 39]

$$\widetilde{E}(\boldsymbol{\kappa}) = \langle 0|\hat{H}^{\kappa}|0\rangle \; + \; \langle 0|\big(\hat{W}_N^{\kappa}\hat{T}_2^{(1)}\big)_c|0\rangle$$

$$+ \; \langle 0|\big\{\hat{\Lambda}_2^{(1)}\big(\hat{f}_N^{\kappa}\hat{T}_2^{(1)} \; + \; \hat{W}_N^{\kappa}\big)_c\big\}_c|0\rangle, \tag{7}$$

OMP3:[36, 38, 41]

$$\widetilde{E}(\boldsymbol{\kappa}) = \langle 0|\hat{H}^{\kappa}|0\rangle$$

$$+ \; \langle 0|\big(\hat{W}_N^{\kappa}\hat{T}_2^{(1)}\big)_c|0\rangle \; + \; \langle 0|\big(\hat{W}_N^{\kappa}\hat{T}_2^{(2)}\big)_c|0\rangle$$

$$+ \; \langle 0|\{\hat{\Lambda}_2^{(1)}\big(\hat{f}_N^{\kappa}\hat{T}_2^{(1)} \; + \; \hat{W}_N^{\kappa}\big)_c\}_c|0\rangle$$

$$+ \; \langle 0|\{\hat{\Lambda}_2^{(1)}\big(\hat{f}_N^{\kappa}\hat{T}_2^{(2)} \; + \; \hat{W}_N^{\kappa}\hat{T}_2^{(1)}\big)_c\}_c|0\rangle$$

$$+ \; \langle 0|\{\hat{\Lambda}_2^{(2)}\big(\hat{f}_N^{\kappa}\hat{T}_2^{(1)} \; + \; \hat{W}_N^{\kappa}\big)_c\}_c|0\rangle, \tag{8}$$

OMP2.5:[42]

$$
\begin{aligned}
\widetilde{E}(\kappa) &= \langle 0|\hat{H}|0\rangle \\
&+ \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(1)})_c|0\rangle + \frac{1}{2}\langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(2)})_c|0\rangle \\
&+ \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}_c|0\rangle \\
&+ \frac{1}{2}\langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(2)} + \hat{W}_N^\kappa \hat{T}_2^{(1)})_c\}_c|0\rangle \\
&+ \frac{1}{2}\langle 0|\{\hat{\Lambda}_2^{(2)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}_c|0\rangle,
\end{aligned}
\tag{9}
$$

OCEPA(0):[40]

$$
\begin{aligned}
\widetilde{E}(\kappa) &= \langle 0|\hat{H}^\kappa|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2)_c|0\rangle \\
&+ \langle 0|\{\hat{\Lambda}_2(\hat{W}_N^\kappa + \hat{H}_N^\kappa \hat{T}_2)_c\}_c|0\rangle,
\end{aligned}
\tag{10}
$$

where $|0\rangle$ is the reference determinant (Fermi-vacuum), $\hat{T}_2$ and $\hat{\Lambda}_2$ are the usual cluster double excitation and de-excitation operators, subscript c means only connected diagrams are included, and $\hat{H}^\kappa$, $\hat{f}_N^\kappa$, $\hat{W}_N^\kappa$, and $\hat{H}_N^\kappa$ are defined as

$$
\hat{H}^\kappa = e^{-\hat{K}}\hat{H}e^{\hat{K}},
\tag{11}
$$

$$
\hat{f}_N^\kappa = e^{-\hat{K}}\hat{f}_N^d e^{\hat{K}},
\tag{12}
$$

$$
\hat{W}_N^\kappa = e^{-\hat{K}}\hat{W}_N e^{\hat{K}},
\tag{13}
$$

$$
\hat{H}_N^\kappa = e^{-\hat{K}}\hat{H}_N e^{\hat{K}},
\tag{14}
$$

where $\hat{H}$ is the Hamiltonian operator, $\hat{H}_N$ is the normal ordered Hamiltonian operator, and $\hat{f}_N$ and $\hat{W}_N$ are one- and two-electron components of the normal ordered Hamiltonian operator.[6,73,74]

The first and second derivatives of the energy with respect to the parameter κ at $\kappa = 0$ can be written as

$$
w_{pq} = \left.\frac{\partial \widetilde{E}}{\partial \kappa_{pq}}\right|_{\kappa=0},
\tag{15}
$$

$$
A_{pq,rs} = \left.\frac{\partial^2 \widetilde{E}}{\partial \kappa_{pq}\partial \kappa_{rs}}\right|_{\kappa=0}.
\tag{16}
$$

Then the energy can be expanded up to second-order as follows:

$$
\widetilde{E}^{(2)}(\kappa) = \widetilde{E}^{(0)} + \kappa^\dagger w + \frac{1}{2}\kappa^\dagger A\kappa,
\tag{17}
$$

where **w** is the MO gradient vector, κ is the MO rotation vector, and **A** is the MO Hessian matrix. Hence, minimizing the energy with respect to κ yields

$$
\kappa = -\mathbf{A}^{-1}\mathbf{w}.
\tag{18}
$$

This final equation is nothing but the usual Newton–Raphson step. Hence, the orbitals are rotated until the convergence.

B. The extended Koopmans' theorem

In some of *ab initio* methods, such as Hartree–Fock, multi-configuration self-consistent field (MCSCF), and configuration interaction, the energy of a molecular system is obtained as an expectation value of the Hamiltonian operator. For such methods, the derivation of the EKT and working equations were reported in previous studies.[12–18] On the other hand, for the other class of *ab initio* methods, such as MP and CC methods, the energy of the molecular system is computed as an projection rather than as an expectation value. Although Cioslowski *et al.*[21] reported EKT methods based on MP and CC theories, such as MP2, MP3, and QCISD, in their formalism they employed an expectation value for the ionized state despite the fact that the energy of the neutral state is computed as a projection. Hence, we would like to revise the derivation of EKT for projective approaches, such as MP and CC theories, which is more general than the expectation value approach.

Let us assume that the following eigenvalue equation is satisfied for the neutral state

$$
\hat{H}|\Psi^N\rangle = E^N|\Psi^N\rangle,
\tag{19}
$$

where E^N and $|\Psi^N\rangle$ are the energy and the wave function of the neutral state. Then, we may obtain the energy of the neutral state from the following projection as

$$
E^N = \langle\Phi^N|\hat{H}|\Psi^N\rangle,
\tag{20}
$$

where $|\Phi^N\rangle$ is the reference wave function of the N-electron system. It is convenient to choose a $|\Psi^N\rangle$ wave function which satisfies the following intermediate normalization condition as

$$
\langle\Phi^N|\Psi^N\rangle = 1.
\tag{21}
$$

For example, if we choose $|\Phi^N\rangle = |0^N\rangle$ (where $|0^N\rangle$ is the HF wave function for the N-electron system) and $|\Psi^N\rangle = e^{\hat{T}}|0^N\rangle$ (where $e^{\hat{T}}$ is the usual cluster excitation operator), then Eq. (20) will give the CC energy.

Now, let us turn our attention to the ionized state and express the energy of the $(N-1)$-electron system as follows:

$$
E^{N-1} = \langle\Phi^{N-1}|\hat{H}|\Psi^{N-1}\rangle,
\tag{22}
$$

where E^{N-1} and $|\Psi^{N-1}\rangle$ are the energy and the wave function of the ionized state, and $|\Phi^{N-1}\rangle$ is the reference wave function. We may express $|\Phi^{N-1}\rangle$ and $|\Psi^{N-1}\rangle$ in terms of those for the N-electron system:

$$
|\Psi^{N-1}\rangle = \hat{A}|\Psi^N\rangle,
\tag{23}
$$

$$
\langle\Phi^{N-1}| = \langle\Phi^N|\hat{A}^\dagger.
\tag{24}
$$

The operators $\hat{A}^\dagger$ and $\hat{A}$ are defined as follows:

$$
\hat{A}^\dagger = \sum_p c_p^* \hat{p}^\dagger,
\tag{25}
$$

$$
\hat{A} = \sum_p c_p \hat{p},
\tag{26}
$$

where $\{c_p\}$ are the expansion coefficients, and $\hat{p}^\dagger$ and $\hat{p}$ are the creation and annihilation operators, respectively. Let us further assume that $|\Psi^{N-1}\rangle$ also satisfies the intermediate normalization condition

$$\langle \Phi^{N-1}|\Psi^{N-1}\rangle = \langle \Phi^N|\hat{A}^\dagger \hat{A}|\Psi^N\rangle = 1. \qquad (27)$$

Now, we can construct a Lagrangian, which consists of the energy difference between the $(N-1)$- and N-electron systems, subject to Eq. (27):

$$\mathcal{L} = E^{N-1} - E^N + e(\langle \Phi^N|\hat{A}^\dagger \hat{A}|\Psi^N\rangle - 1), \qquad (28)$$

where e is the Lagrangian multiplier. Now we can express Eq. (28) as

$$\mathcal{L} = \langle \Phi^N|\hat{A}^\dagger \hat{H} \hat{A}|\Psi^N\rangle - \langle \Phi^N|\hat{H}|\Psi^N\rangle$$
$$+ e(\langle \Phi^N|\hat{A}^\dagger \hat{A}|\Psi^N\rangle - 1). \qquad (29)$$

Since $|\Psi^N\rangle$ is an eigenfunction of $\hat{H}$ the second term of Eq. (29) can be written as

$$\langle \Phi^N|\hat{H}|\Psi^N\rangle = \langle \Phi^N|\hat{A}^\dagger \hat{A}\hat{H}|\Psi^N\rangle. \qquad (30)$$

Then, we can re-write Eq. (29) as follows:

$$\mathcal{L} = \langle \Phi^N|\hat{A}^\dagger[\hat{H}, \hat{A}]|\Psi^N\rangle + e(\langle \Phi^N|\hat{A}^\dagger \hat{A}|\Psi^N\rangle - 1). \qquad (31)$$

Now, minimizing the Lagrangian with respect to $\hat{A}^\dagger$ we obtain

$$\langle \Phi^N|\hat{p}^\dagger[\hat{H}, \hat{A}]|\Psi^N\rangle + e\langle \Phi^N|\hat{p}^\dagger \hat{A}|\Psi^N\rangle = 0. \qquad (32)$$

More explicitly, we can write

$$\sum_q c_q(\langle \Phi^N|\hat{p}^\dagger[\hat{H}, \hat{q}]|\Psi^N\rangle + e\langle \Phi^N|\hat{p}^\dagger \hat{q}|\Psi^N\rangle) = 0. \qquad (33)$$

The second term of Eq. (33) is the one-particle density-matrix of the N-electron system

$$\gamma_{pq} = \langle \Phi^N|\hat{p}^\dagger \hat{q}|\Psi^N\rangle, \qquad (34)$$

and the first term of Eq. (33) gives the generalized-Fock matrix, which is also known as the orbital Lagrangian:

$$F_{pq} = -\langle \Phi^N|\hat{p}^\dagger[\hat{H}, \hat{q}]|\Psi^N\rangle. \qquad (35)$$

The GFM can be expressed as follows:[35,36,39,40]

$$F_{pq} = \sum_r h_{pr}\gamma_{rq} + 2\sum_{r,s,t}\langle rs||tp\rangle\Gamma_{rstq}, \qquad (36)$$

where h_{pr} is the one-electron Hamiltonian matrix element, $\langle pr||st\rangle$ is the antisymmetrized two-electron integral, and Γ_{rstq} is the two-particle density-matrix (TPDM), which is defined as

$$\Gamma_{pqrs} = \frac{1}{4}\langle \Phi^N|\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}|\Psi^N\rangle. \qquad (37)$$

Hence, we can cast Eq. (33) into the following form:

$$\sum_q (F_{pq} - e\gamma_{pq})c_q = 0. \qquad (38)$$

Equivalently, we can re-write Eq. (38) as follows:

$$\mathbf{Fc} = e\gamma \mathbf{c}, \qquad (39)$$

$$\mathbf{FC} = \gamma \mathbf{Ce}, \qquad (40)$$

where C is the matrix of eigenvectors and $\mathbf{e}$ is the diagonal matrix of eigenvalues (energies).

It is also noteworthy to express that Eq. (40) is quite similar to self-consistent field (SCF) eigenvalue equation ($\mathbf{fC} = \mathbf{SCe}$). In the SCF case, the occupied block of the GFM reduces to the occupied block of the Fock matrix, and the occupied block of the OPDM reduces to the occupied block of the overlap matrix. Hence, only IPs corresponding to occupied orbitals have physical meanings even though we diagonalize the entire GFM.

Now, we can apply the same technique as one did for the SCF case and define the following intermediates:

$$\mathbf{F}' = \gamma^{-1/2}\mathbf{F}\gamma^{-1/2}, \qquad (41)$$

$$\mathbf{C} = \gamma^{-1/2}\mathbf{C}'. \qquad (42)$$

Then, we can write our final equation as

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{e}. \qquad (43)$$

For orbital-optimized methods, the GFM and OPDM are already available and symmetric, and the OPDM is always positive-definite. Hence, the above procedure for the diagonalization of the GFM is numerically well-conditioned. However, for the standard methods, such as MP2, MP3, and CEPA(0), the GFM is not symmetric. Cioslowski *et al.*[21] suggest to use the relaxed GFM, which includes orbital response contributions and it is symmetric, as well as relaxed PDMs instead of the unrelaxed ones. Hence, this approach solves the symmetry problem of the GFM. However, the positive-definiteness of the relaxed OPDM is not guaranteed, hence the N-representability condition may be violated.[21,54] Although, it is possible to eliminate eigenvectors of the OPDM corresponding to negative eigenvalues employing some numerical tricks,[21] it does not change the fact of having a qualitatively wrong OPDM. Additionally, this procedure does not, in general, guarantee that the response contributions will not destroy the quality of the GFM and will not lead unphysical IPs for challenging chemical systems. Considering all these concerns about the EKT based on the standard MP and CC theories, one may consider the orbital-optimized methods as the most suitable and robust methods for the study of the EKT.

Now, let us evaluate the pole strength for the EKT. The Feynman–Dyson amplitude[75] can be written as

$$g_r = \langle \Psi^{N-1}|\hat{r}|\Psi^N\rangle, \qquad (44)$$

where g_r is the Feynman–Dyson amplitude. We can express Eq. (44) more explicitly as follows:

$$g_r = \sum_s c_s^* \gamma_{sr}. \qquad (45)$$

Now, we can define the pole strength P as

$$P = \sum_r |g_r|^2. \qquad (46)$$

Then, inserting Eq. (45) into Eq. (46) we obtain

$$P = \mathbf{c}^\dagger \gamma\gamma \mathbf{c}. \qquad (47)$$

III. RESULTS AND DISCUSSION

Results from the EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) approaches were obtained for the second- and third-row atoms, closed- and open-shell molecules for comparison with those from the HF (Koopmans' theorem, KT), EKT-MP2, EKT-MP2.5, EKT-MP3, and EKT-CEPA(0) methods. The experimental geometries were used for all considered closed-shell molecules and some of the open-shell molecules, for which the experimental geometries are available.[21,76,77] Geometries of open-shell structures, for which the experimental geometries are not available, were taken from our previous studies,[78–82] which were obtained at the B3LYP/6-311G(d,p) level,[83–87] as well as from the computational chemistry comparison and benchmark database (CCCBDB).[88] For the EKT computations, Dunning's augmented correlation-consistent polarized valence triple-ζ and correlation-consistent polarized valence triple-ζ (aug-cc-pVTZ and cc-pVTZ) basis sets[89,90] were employed without the frozen core approximation. All computations were performed with our programs in the PSI4 package.[68]

A. Atoms

In order to assess the performance of the EKT for the orbital-optimized methods we start with the second- and third-row atoms. For the considered atoms, IPs (in eV) from the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with the aug-cc-pVTZ basis set are reported in Table I, while mean absolute errors (MAEs) are presented graphically in Figure 1. Similarly, those from the cc-pVTZ basis sets are reported in the supporting information.[91] The MAE values with the aug-cc-pVTZ basis set are 0.51 (KT), 0.37 (EKT-MP2), 0.21 (EKT-MP2.5), 0.17 (EKT-MP3), 0.14 [EKT-CEPA(0)], 0.44 (EKT-OMP2), 0.26 (EKT-OMP2.5), 0.17 (EKT-OMP3), and 0.11 [EKT-

OCEPA(0)] eV. Hence, all considered EKT approaches significantly improve upon the KT (by 0.07–0.40 eV). Especially, the performance of the EKT-OCEPA(0) approach is noteworthy, there is almost a 5-fold reduction in MAE compared to KT. The orbital optimization increases the MAE of MP2 and MP2.5 (by 0.07 and 0.05 eV), while slightly decreases the MAE of EKT-CEPA(0) (by 0.03 eV).

In previous studies[31,33,34] it was discussed that it is very important to employ diffuse basis sets in the EKT computations as in case of anions.[92,93] However, tight diffuse functions (such as DZP++[94–96]) may destroy the quality of the computed electron affinities (EAs), as it was observed for anions, but some basis sets (such as TZVP and TZVPP[97,98]) may provide better EAs even though they do not contain diffuse functions *per se*.[93,99] In such cases, for a particular basis set some functions with small exponents may act as moderate level diffuse functions.[93,99] Hence, in order to evaluate the effect of diffuse functions on the computed IPs, we also perform the same computations with the cc-pVTZ basis set.[91] The MAE values obtained with the cc-pVTZ basis set (Table S1 of the supplementary material[91]) are 0.51 (KT), 0.44 (EKT-MP2), 0.23 (EKT-MP2.5), 0.14 (EKT-MP3), 0.12 [EKT-CEPA(0)], 0.40 (EKT-OMP2), 0.25 (EKT-OMP2.5), 0.25 (EKT-OMP3), and 0.36 [EKT-OCEPA(0)] eV. Hence, for the EKT-CEPA(0), EKT-OMP2, and EKT-OMP2.5 methods the cc-pVTZ basis set slightly decreases MAEs (by 0.01–0.04 eV), while for the EKT-MP2, EKT-MP2.5, EKT-OMP3, and EKT-OCEPA(0) approaches it increases the MAE values (by 0.01–0.25 eV). Especially, for the EKT-OMP3 and EKT-OCEPA(0) methods the MAE values are substantially reduced (by 32%–69%) when the aug-cc-pVTZ basis set is employed.

B. Closed-shell molecules

As the second step of our investigation, we apply the EKT approaches to closed-shell molecules. For the considered diatomic and linear molecules, IPs (in eV) from the HF (KT),

TABLE I. The lowest ionization potentials (in eV) for the 2nd and 3rd row atoms at the aug-cc-pVTZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) levels.

Atom	Ionization	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	Exp[a]
Li	$^2S \to {}^1S$	5.34	5.35	5.35	5.35	5.35	5.33	5.36	5.35	5.35	5.39
Be	$^1S \to {}^2S$	8.42	8.70	8.84	8.99	9.79	8.66	8.78	8.91	9.53	9.32
B	$^2P \to {}^1S$	8.67	8.22	8.21	8.20	8.18	8.19	8.20	8.20	8.19	8.30
C	$^3P \to {}^2P$	11.94	11.22	11.24	11.26	11.27	11.14	11.17	11.20	11.21	11.26
N	$^4S \to {}^3P$	15.53	14.46	14.55	14.63	14.66	14.32	14.44	14.54	14.57	14.53
O	$^3P \to {}^4S$	14.20	13.07	13.31	13.54	13.60	12.90	13.19	13.46	13.51	13.62
F	$^2P \to {}^3P$	18.51	16.70	17.19	17.64	17.60	16.42	17.01	17.56	17.49	17.42
Ne	$^1S \to {}^2P$	23.16	20.52	21.45	22.17	21.94	20.32	21.24	22.10	21.79	21.56
Na	$^2S \to {}^1S$	4.96	4.99	5.00	5.00	5.00	4.99	4.98	4.97	4.97	5.14
Mg	$^1S \to {}^2S$	6.89	7.24	7.36	7.48	7.86	7.18	7.28	7.38	7.46	7.65
Al	$^2P \to {}^1S$	5.93	5.72	5.75	5.79	5.91	5.74	5.78	5.83	5.95	5.98
Si	$^3P \to {}^2P$	8.20	7.93	7.97	8.02	8.11	7.93	7.98	8.03	8.12	8.05
P	$^4S \to {}^3P$	10.67	10.32	10.37	10.43	10.49	10.31	10.37	10.43	10.50	10.49
S	$^3P \to {}^4S$	10.32	9.76	9.88	10.00	10.12	9.76	9.90	10.04	10.15	10.36
Cl	$^2P \to {}^3P$	13.09	12.41	12.57	12.74	12.83	12.36	12.55	12.73	12.82	12.97
Ar	$^1S \to {}^2P$	16.09	15.27	15.47	15.68	15.71	15.19	15.43	15.66	15.70	15.76

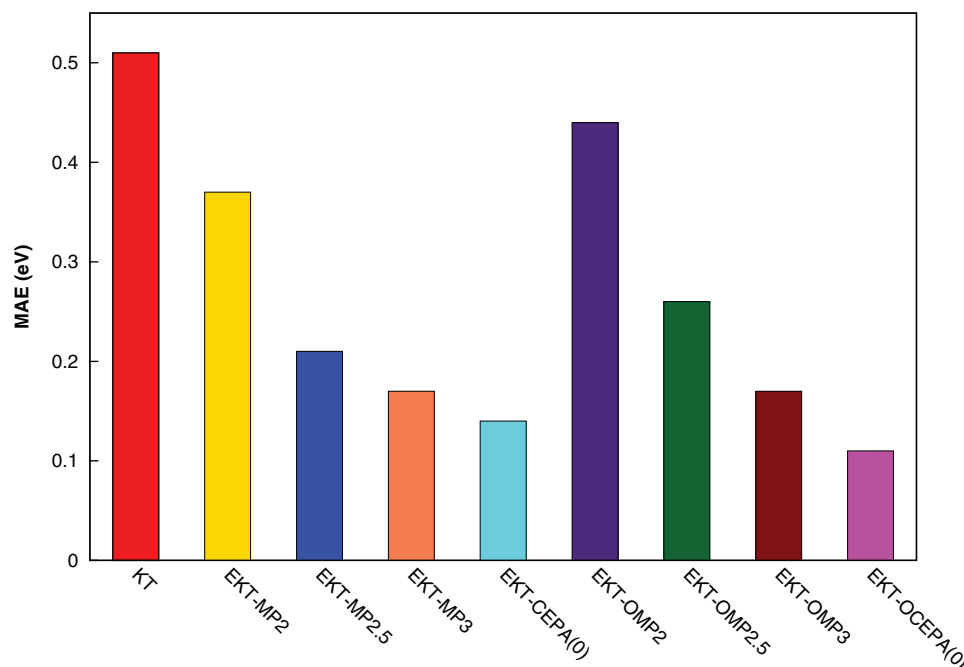[a]Data from Flores-Moreno *et al.*[100]

FIG. 1. Mean absolute errors in the lowest ionization potentials of 2nd and 3rd row atoms for the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (the aug-cc-pVTZ basis set was employed).

EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with the aug-cc-pVTZ basis set are reported in Table II, while those for the nonlinear molecules are provided in Table III. The corresponding MAEs are presented graphically in Figures 2 and 3. It is well-known that the lowest IPs obtained from the EKT approaches match better with experiments than the second, third, and other IPs.[29–34] In other words, the EKT approach is more successful for the electron removal procedure from the highest occupied molecular orbital (HOMO) than those for inner valence orbitals. Hence, it is appropriate to evaluate the lowest IPs and the others separately. The MAE values for the lowest IPs (Figure 2) are 0.71 (KT), 0.68 (EKT-MP2), 0.22 (EKT-MP2.5), 0.34 (EKT-MP3), 0.25 [EKT-CEPA(0)], 0.90 (EKT-OMP2), 0.30 (EKT-OMP2.5), 0.31 (EKT-OMP3), and 0.15 [EKT-OCEPA(0)] eV. The EKT-OCEPA(0) approach again provides quite accurate lowest IPs, improving upon KT and EKT-CEPA(0) by 0.56 and 0.10 eV, respectively, which means there are almost 5- and 2-fold reductions in MAEs compared to KT and EKT-CEPA(0). All considered EKT methods, especially those of $O(N^6)$ methods (where N is the number of basis functions), perform substantially better than KT (by 0.37–0.56 eV), while $O(N^5)$ methods (EKT-MP2 and EKT-OMP2) fail to enhance the KT approach, but EKT-OMP2 surprisingly yields even a larger MAE (by 0.19 eV) than KT. The orbital optimization increases the MAEs of MP2 and MP2.5 (by 0.22 and 0.08 eV), while decreases the MAE of EKT-MP3 and EKT-CEPA(0) (by 0.03 and 0.10 eV).

The MAE values obtained with the cc-pVTZ basis set (Tables S2 and S3 of the supplementary material[91]) are 0.67 (KT), 0.67 (EKT-MP2), 0.21 (EKT-MP2.5), 0.30 (EKT-MP3), 0.28 [EKT-CEPA(0)], 0.75 (EKT-OMP2), 0.23 (EKT-OMP2.5), 0.50 (EKT-OMP3), and 0.42 [EKT-OCEPA(0)]

eV. Hence, for the KT, EKT-MP2, EKT-MP3, EKT-OMP2, and EKT-OMP2.5 methods the cc-pVTZ basis set decreases MAEs (by 0.01–0.25 eV), while for the EKT-OCEPA(0), EKT-OMP3, and EKT-OCEPA(0) approaches it increases the MAE values (by 0.03–0.23 eV). Especially, for the EKT-OMP3 and EKT-OCEPA(0) methods the MAE values are substantially reduced (by 38%–64%) when the aug-cc-pVTZ basis set is employed, while for EKT-OMP2 the MAE value is significantly raised (by 20 %).

When we consider all IPs the MAE values become (Figure 3) 1.70 (KT), 0.53 (EKT-MP2), 0.49 (EKT-MP2.5), 0.94 (EKT-MP3), 0.74 [EKT-CEPA(0)], 0.97 (EKT-OMP2), 0.32 (EKT-OMP2.5), 0.85 (EKT-OMP3), and 0.49 [EKT-OCEPA(0)] eV. Hence, for the KT, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP3, and EKT-OCEPA(0) methods the MAE values significantly increase (by 0.07–0.99 eV). Especially, the KT approach dramatically fails (by 1.70 eV) for the IPs corresponding to inner valence orbitals, whereas the MAEs of EKT-MP2.5, EKT-MP3, EKT-CEPA(0), and EKT-OCEPA(0) increase roughly by a factor of 3. However, the MAE of EKT-OMP2.5 increases by only 0.02 eV, and that of EKT-MP2 decreases by 0.15 eV, surprisingly. The orbital optimization decreases the MAEs of all $O(N^6)$ methods, by 0.09–0.25 eV, indicating that the orbital relaxation effects are very important for inner valence orbitals. Further, for all $O(N^6)$ methods the aug-cc-pVTZ basis set provides considerably lower MAEs (by 0.01–0.41 eV) than cc-pVTZ. Hence, it appears that diffuse functions are more important for the description of inner valence orbitals.

C. Open-shell molecules

As the final step of our investigation we apply the EKT approaches to open-shell molecules. Previous

TABLE II. Vertical ionization potentials (in eV) for the diatomic and linear closed-shell molecules at the aug-cc-pVTZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) levels.

Molecule	MO	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	Exp[a]
N_2	σ_g	17.27	15.04	15.69	16.35	15.88	14.33	15.34	16.26	15.77	15.60
	π_u	16.72	16.70	16.90	17.07	17.20	16.73	16.87	17.02	17.07	16.68
	σ_u	21.22	18.48	19.26	20.08	19.53	17.51	18.77	19.96	19.14	18.78
HF	π	17.70	15.40	16.16	16.96	16.74	14.86	15.92	16.88	16.50	16.19
	σ	20.92	19.31	19.96	20.62	20.38	18.99	19.83	20.51	20.29	19.90
CO	σ	15.10	13.61	13.97	14.34	14.22	13.20	13.76	14.26	14.10	14.01
	π	17.43	16.36	16.85	17.32	17.06	16.43	16.91	17.36	17.14	16.85
	σ	21.90	19.30	20.20	21.18	20.56	18.42	19.86	21.12	20.35	19.78
C_2H_2	π_u	11.19	10.83	11.18	11.52	11.63	10.86	11.18	11.48	11.50	11.49
	σ_g	18.56	16.70	17.18	17.67	17.54	16.18	16.88	17.63	17.37	16.70
	σ_u	20.91	18.82	19.31	19.80	19.60	18.15	18.91	19.67	19.33	18.70
HCN	π	13.50	13.17	13.52	13.84	13.92	13.20	13.51	13.81	13.80	13.61
	σ	15.85	13.31	14.13	15.00	14.57	12.29	13.61	15.07	14.31	14.01
	$\sigma*$	22.16	20.22	20.69	21.17	20.92	19.61	20.36	21.08	20.68	19.86
HCCF	π	11.38	10.75	11.14	11.52	11.57	10.73	11.14	11.51	11.44	11.50
	π	20.69	17.80	18.65	19.52	19.18	16.67	18.00	19.36	18.63	18.00
	σ	19.78	17.86	18.34	18.83	18.68	17.23	17.99	18.72	18.48	18.00
	σ	23.44	20.82	21.65	22.48	22.05	19.87	21.15	22.40	21.71	21.20
	σ	28.63	26.69	27.03	27.29	27.13	26.38	26.81	27.03	26.77	24.30
NNO	π	13.38	11.91	12.60	13.36	12.99	11.79	12.65	13.34	12.95	12.89
	σ	19.02	16.01	16.98	18.02	17.38	14.43	16.38	17.97	16.89	16.38
	π	20.77	18.40	19.20	20.08	19.41	17.08	18.66	19.92	18.86	18.23
	σ	22.70	19.56	20.79	22.13	21.23	18.04	20.36	22.07	20.77	20.11
NCCN	π_g	13.58	12.83	13.29	13.75	13.74	12.87	13.33	13.73	13.68	13.51
	σ_g	16.99	14.09	14.97	15.92	15.44	12.77	14.34	15.81	14.92	14.49
	σ_u	17.42	14.44	15.36	16.34	15.83	13.14	14.73	16.13	15.32	14.86
	π_u	16.35	15.16	15.62	16.12	15.85	14.96	15.58	16.12	15.79	15.60
	σ_g	26.63	24.03	24.83	25.84	25.22	22.94	24.46	25.72	24.92	22.80
CO_2	π_g	14.83	12.99	13.64	14.29	13.97	12.66	13.52	14.31	13.89	13.79
	π_u	19.46	17.30	18.00	18.71	18.25	16.44	17.62	18.65	18.02	17.60
	σ_u	20.24	17.50	18.44	19.43	18.94	16.37	17.98	19.42	18.56	18.08
	σ_g	21.81	18.87	19.87	20.93	20.38	17.56	19.34	20.91	19.94	19.40
OCS	π	11.48	10.66	10.98	11.30	11.23	10.61	11.00	11.34	11.23	11.24
	$\pi*$	17.93	15.53	16.25	16.93	16.40	14.60	15.79	16.82	16.12	15.53
	σ	17.34	15.62	16.09	16.53	16.35	14.93	15.86	16.49	16.26	16.04
	$\sigma*$	21.18	18.01	19.07	20.14	19.52	16.60	18.37	20.11	18.92	17.96
FCN	π	13.65	12.91	13.34	13.75	13.72	12.89	13.34	13.74	13.64	13.65
	σ	16.35	13.83	14.63	15.47	15.06	12.91	14.22	15.41	14.84	14.56
	π	22.20	19.33	20.17	21.03	20.63	18.12	19.54	20.89	20.12	19.30
	σ	25.30	22.70	23.53	24.37	23.87	21.59	23.00	24.31	23.55	22.60
HCl	π	12.99	12.26	12.48	12.69	12.75	12.19	12.44	12.69	12.74	12.77
	σ	17.03	16.28	16.49	16.71	16.75	16.21	16.46	16.70	16.72	16.60
	σ	30.41	28.74	27.86	28.16	27.52	28.23	28.05	27.78	27.50	25.80
F_2	π_g	18.16	15.15	15.78	16.88	16.52	14.02	15.42	16.77	16.18	15.87
	π_u	22.10	18.63	19.34	20.56	20.11	17.14	18.77	20.36	19.52	18.80
	σ_g	20.49	21.27	20.94	21.48	21.85	20.44	20.93	21.38	21.68	21.10
CS	σ	12.82	10.87	11.42	12.00	11.73	10.03	11.06	11.96	11.54	11.34
	π	12.61	12.80	12.83	12.92	13.03	12.78	12.83	12.88	12.90	12.90
	σ	18.85	17.18	17.56	17.96	17.25	16.79	17.41	17.91	17.08	18.03
P_2	π_u	10.12	9.93	10.36	10.55	10.70	10.24	10.36	10.48	10.58	10.65
	σ_g	11.12	10.11	10.46	10.87	10.79	9.91	10.43	10.92	10.81	10.84

[a] Data from Chong *et al.*[76] and Cioslowski *et al.*[21]

TABLE III. Vertical ionization potentials (in eV) for the nonlinear closed-shell molecules at the aug-cc-pVTZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) levels.

Molecule	MO	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	Exp[a]
H_2O	b_1	13.89	11.95	12.60	13.27	13.06	11.51	12.40	13.23	12.95	12.78
	a_1	15.92	14.14	14.81	15.48	15.27	13.71	14.62	15.48	15.16	14.83
	b_2	19.54	18.34	18.88	19.44	19.29	18.12	18.81	19.47	19.21	18.72
CH_4	t_2	14.85	13.95	14.20	14.46	14.52	13.82	14.14	14.44	14.46	14.4
	a_1	25.70	23.88	24.04	24.16	24.19	23.43	23.60	23.71	23.82	23.0
NH_3	a_1	11.69	10.27	10.74	11.21	11.13	9.85	10.50	11.06	11.06	10.8
	e	17.10	15.99	16.41	16.85	16.81	15.80	16.34	16.90	16.73	16.8
H_2CO	b_2	12.23	10.15	10.90	11.68	11.41	9.40	10.60	11.52	11.22	10.9
	b_1	14.25	13.58	14.03	14.46	14.33	13.59	14.07	14.51	14.42	14.5
	a_1	17.38	15.17	15.98	16.81	16.48	14.42	15.66	16.61	16.28	16.1
	b_2	19.41	17.64	18.06	18.48	18.32	17.06	17.70	18.22	17.96	17.0
	a_1	23.97	21.93	22.32	22.69	22.48	21.30	21.88	22.41	22.03	21.4
CH_3CN	e	12.55	11.87	12.22	12.56	12.58	11.90	12.23	12.55	12.50	12.46
	a_1	15.13	12.59	13.36	14.17	13.80	11.66	12.90	14.05	13.52	13.17
	e	17.10	15.84	16.18	16.53	16.46	15.51	16.03	16.49	16.36	15.7
	a_1	18.93	16.95	17.51	18.09	17.86	16.29	17.21	18.01	17.65	17.4
	a_1	28.27	26.03	26.45	26.83	26.66	25.47	26.13	26.68	26.40	24.9
CHF_3	a_1	16.02	14.22	14.76	15.29	15.13	13.72	14.50	15.22	14.95	14.8
	a_2	17.94	16.29	15.90	16.78	16.48	14.40	15.56	16.66	16.20	15.5
	e	18.41	15.80	16.56	17.36	17.06	15.03	16.15	17.24	16.75	16.2
	e	19.49	16.86	17.63	18.39	18.09	16.00	17.14	18.24	17.74	17.2
	e	22.63	20.36	21.11	21.72	21.41	19.65	20.67	21.62	21.20	20.7
	a_1	23.08	21.09	21.45	22.07	21.84	20.15	21.05	21.92	21.54	20.7
	a_1	27.00	24.63	25.20	25.82	25.57	23.94	24.83	25.65	25.32	24.4
C_2H_6	e_g	13.27	12.28	12.55	12.83	12.87	12.14	12.48	12.82	12.80	12
	a_{1g}	13.76	12.43	12.84	13.27	13.25	12.14	12.69	13.25	13.16	12.7
	e_u	16.22	15.04	15.32	15.61	15.63	14.81	15.19	15.55	15.53	15.0
	a_{2u}	22.89	21.16	21.38	21.58	21.60	20.81	21.11	21.37	21.41	20.4
	a_{1g}	27.63	25.77	25.96	26.08	26.10	25.11	25.45	25.72	25.72	23.9
C_2H_4	b_{3u}	10.23	9.44	10.35	10.73	10.98	9.92	10.29	10.64	10.81	10.68
	b_{3g}	13.84	12.64	12.95	13.26	13.29	12.41	12.82	13.22	13.23	12.8
	a_g	15.93	14.37	14.75	15.15	15.11	13.97	14.50	15.04	14.96	14.8
	b_{2u}	17.50	15.95	16.27	16.58	16.57	15.54	15.99	16.43	16.32	16.0
	b_{1u}	21.55	19.65	19.94	20.18	20.17	19.04	19.45	19.82	19.62	19.1
	a_g	28.09	26.26	26.56	26.80	26.65	25.36	25.86	26.23	26.18	23.6
H_2CS	b_2	9.59	8.83	9.06	9.36	9.45	8.73	9.04	9.34	9.41	9.38
	b_1	11.39	11.42	11.66	11.90	12.10	11.36	11.60	11.84	12.01	11.76
	a_1	14.74	13.52	13.84	14.17	14.14	13.28	13.73	14.15	14.09	13.85
	b_2	17.56	15.67	16.09	16.52	16.38	14.92	15.65	16.34	15.68	15.2
	a_1	22.14	20.04	20.36	20.65	20.40	19.32	19.84	20.30	19.73	19.9
NSF	a'	12.70	10.71	11.39	12.12	11.84	10.53	11.47	12.29	11.88	11.82
	a'	15.05	12.84	13.59	14.37	14.01	11.85	13.31	14.45	13.79	13.5
	a''	14.02	12.85	13.90	14.28	14.27	13.01	13.83	14.25	14.16	13.87
	a'	18.22	15.32	16.32	17.31	16.76	13.89	15.89	17.39	16.37	15.62
	a''	19.11	17.04	17.26	18.25	17.76	15.30	16.78	18.23	17.24	16.47
	a'	19.29	16.94	17.58	18.45	17.92	15.66	17.13	18.46	17.45	17.2
$CH_2 = CF_2$	b_1	10.78	9.97	10.40	10.86	10.93	9.88	10.38	10.85	10.88	10.70
	b_2	16.37	14.69	15.20	15.60	15.55	13.97	14.91	15.54	15.42	14.9
	a_1	17.39	15.31	15.90	15.60	16.31	14.54	15.50	16.34	16.00	15.8
	b_2	18.17	15.62	16.28	16.96	16.68	15.01	15.84	16.88	16.36	16.1
	a_2	18.78	15.97	16.76	17.64	17.38	14.96	16.16	17.31	16.72	16.1
	a_1	20.46	18.08	18.67	19.28	19.10	17.28	18.18	19.10	18.67	18.2
	b_1	20.76	18.09	18.86	19.62	19.36	17.10	18.23	19.34	18.65	18.2
	b_2	21.85	19.52	20.37	20.90	20.76	18.73	19.76	20.76	20.27	19.7
	a_1	24.13	21.58	22.27	22.96	22.65	20.72	21.78	22.78	22.22	21.5
cis-CHF=CHF	b_1	10.68	9.78	10.24	10.74	10.83	9.68	10.22	10.72	10.77	10.62
	a_1	15.80	13.69	14.32	14.88	14.72	12.91	13.88	14.76	14.41	14.0

TABLE III. (*Continued.*)

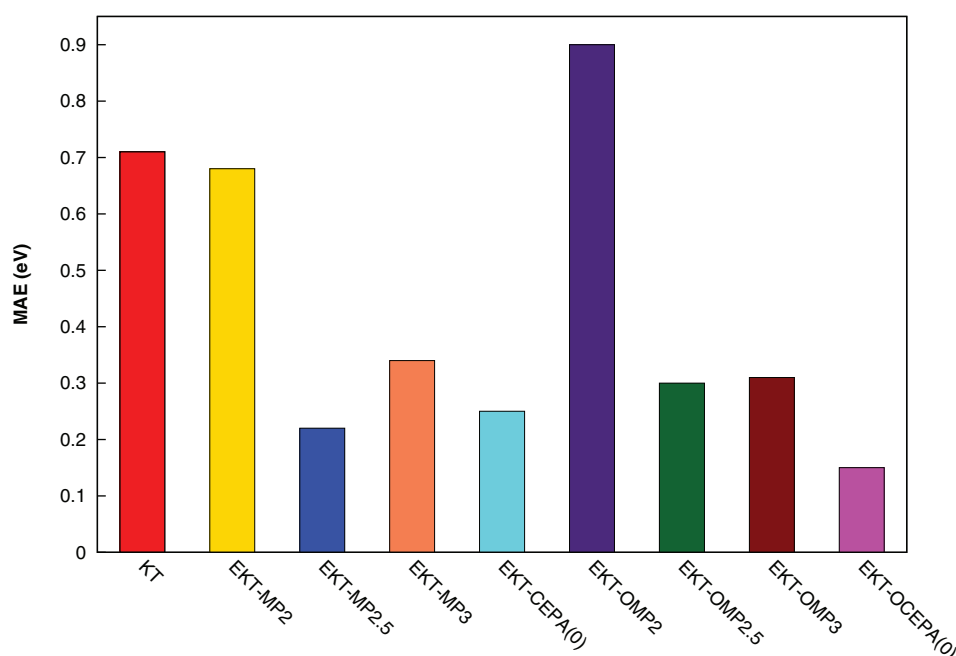| Molecule	MO	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	Exp[a]
	b_2	16.78	14.53	15.22	15.86	15.65	13.70	14.81	15.74	15.37	14.9
	a_2	18.78	15.93	16.77	17.60	17.26	14.99	16.22	17.43	16.77	16.2
	b_2	19.07	16.67	17.33	18.03	17.77	15.98	16.92	17.91	17.43	17.1
	b_1	19.52	16.99	17.72	18.46	18.21	15.99	17.11	18.22	17.66	17.1
	a_1	20.58	18.48	19.19	19.75	19.46	17.61	18.66	19.66	19.20	18.8
	a_1	21.24	18.94	19.51	20.10	19.92	18.14	19.02	19.91	19.50	18.8
	b_2	23.42	21.07	21.65	22.23	21.97	20.25	21.16	22.05	21.60	20.9

[a]Data from Chong *et al.*[76] and Cioslowski *et al.*[21]

FIG. 2. Mean absolute errors in the lowest vertical ionization potentials of the closed-shell molecules for the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (the aug-cc-pVTZ basis set was employed).
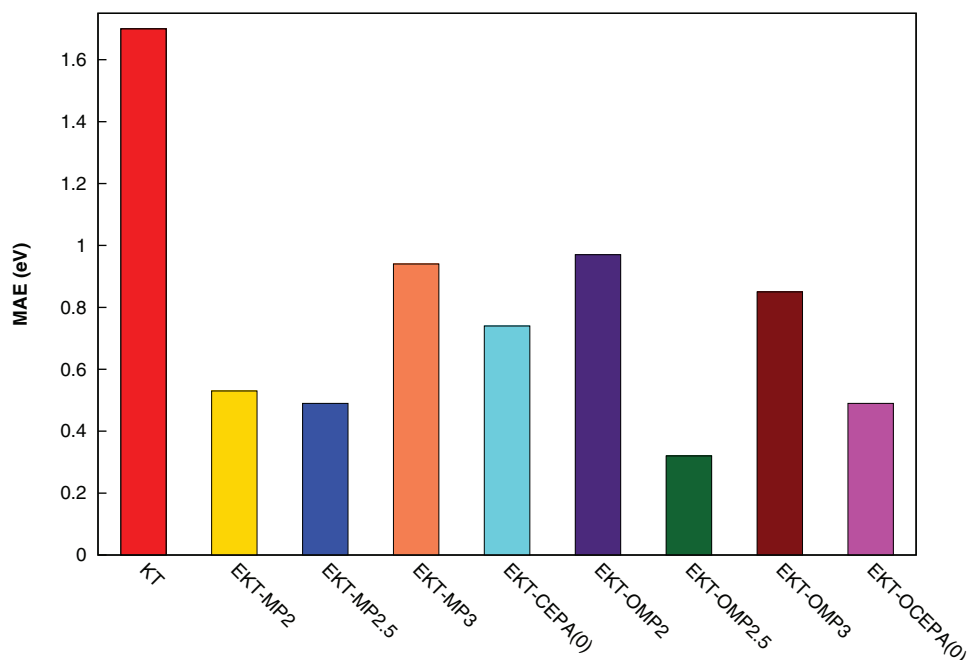

FIG. 3. Mean absolute errors in the various vertical ionization potentials of the closed-shell molecules for the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (the aug-cc-pVTZ basis set was employed).

TABLE IV. The lowest vertical ionization potentials (in eV) for open-shell molecules at the aug-cc-pVTZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) levels.

Molecule	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	Exp[a]
· CH_3	10.46	9.45	9.62	9.78	9.86	9.29	9.52	9.73	9.81	9.84
· CH_2CH_3	9.52	8.32	8.53	8.75	8.80	8.05	8.34	8.65	8.67	8.38
· $CH(CH_3)_2$	8.83	7.48	7.74	8.01	8.04	7.04	7.45	7.87	7.83	7.55
· $CH=CH_2$	10.78	9.57	9.84	10.06	10.09	9.00	9.41	9.78	9.64	8.95
· CH_2-$CH=CH_2$	9.25	7.73	7.98	8.24	8.28	7.36	7.76	8.16	8.28	8.07
· CH_2Cl	10.56	9.19	9.51	9.77	9.78	8.76	9.19	9.59	9.54	9.32
· CH_2CN	11.55	9.52	9.93	10.36	10.12	9.44	9.96	10.47	10.37	10.30
· CHO	11.12	9.16	9.66	7.41	9.96	8.50	9.32	9.97	9.64	9.80
· NH-NH_2	9.90	8.01	8.44	8.88	8.79	7.05	7.93	8.58	8.30	7.90
NH_2	12.61	11.42	11.78	12.14	12.18	11.17	11.65	12.11	12.10	11.40
OH	13.98	12.42	12.86	13.29	13.27	12.10	12.69	13.22	13.18	13.02
NO	11.65	9.31	9.93	10.54	10.27	8.38	9.35	10.25	9.78	9.25
NO_2	13.57	10.64	11.55	12.50	11.99	9.27	10.95	12.33	11.48	9.80
NF	14.79	12.74	13.05	13.45	13.35	11.80	12.57	13.15	12.91	12.63
NH	13.83	12.96	13.21	13.46	13.59	12.86	13.17	13.46	13.58	13.49

[a]Data from Dewar *et al.*[101] and the National Institute of Standards and Technology (NIST).[77]

studies[35, 36, 38–41, 45, 53] demonstrated that the orbital-optimized methods perform substantially better than the standard methods for open-shell molecules suffering from spin or spatial symmetry breaking problems. Hence, such systems are interesting for comparing performances of the orbital-optimized methods with the standard ones. For the considered molecules, IPs (in eV) from the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with the aug-cc-pVTZ basis set are reported in Table IV, while the MAE values are presented graphically in Figure 4. The MAE values are 1.51 (KT), 0.35 (EKT-MP2), 0.43 (EKT-MP2.5), 0.79 (EKT-MP3), 0.60 [EKT-CEPA(0)], 0.65 (EKT-OMP2), 0.29 (EKT-OMP2.5), 0.53 (EKT-OMP3), and 0.39 [EKT-

OCEPA(0)] eV. Especially, the performance of the EKT-OMP2.5 method is remarkable, there is a more than 5-fold reduction in MAE compared to KT. Further, the orbital-optimized methods significantly (by 0.14–0.21 eV) improve upon their canonical counterparts, except for the MP2/OMP2 case. Failures of the standard methods are attributed to spin-contamination in the reference unrestricted HF (UHF) wave functions.

The MAE values obtained with the cc-pVTZ basis set (Table S4 of the supplementary material[91]) are 1.46 (KT), 0.38 (EKT-MP2), 0.41 (EKT-MP2.5), 0.61 (EKT-MP3), 0.57 [EKT-CEPA(0)], 0.54 (EKT-OMP2), 0.28 (EKT-OMP2.5), 0.53 (EKT-OMP3), and 0.46 [EKT-OCEPA(0)] eV. Hence, for all methods, except for EKT-MP2 and EKT-OCEPA(0),
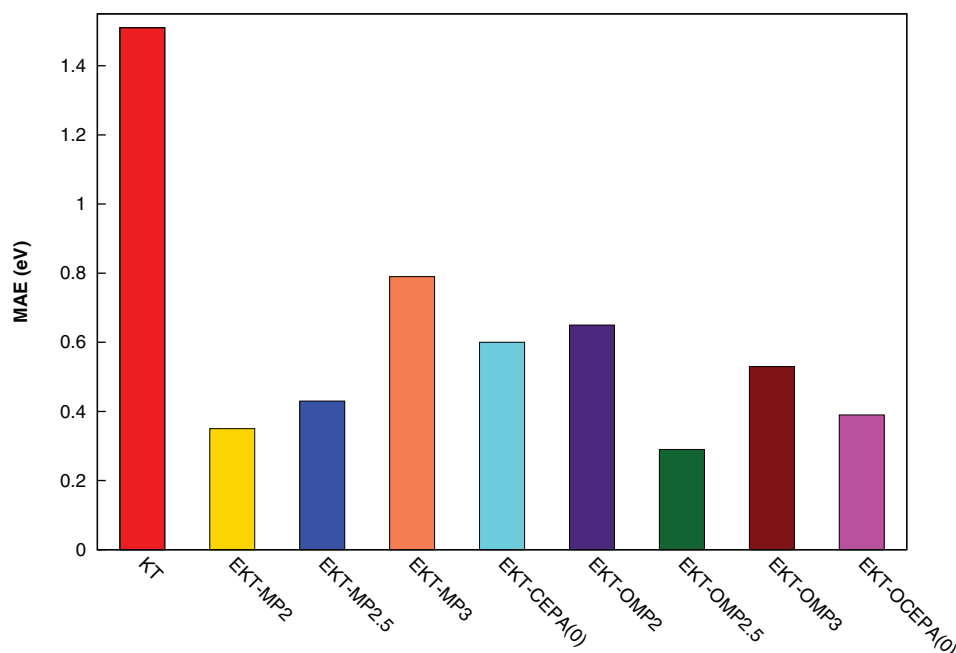

FIG. 4. Mean absolute errors in the lowest vertical ionization potentials of the open-shell molecules for the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2, EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (the aug-cc-pVTZ basis set was employed).

the cc-pVTZ basis set provides lower MAEs than aug-cc-pVTZ by 0.01–0.18 eV. On the other hand, for the EKT-MP2 and EKT-OCEPA(0) approaches the MAE values of the cc-pVTZ basis set are higher (by 0.03–0.07 eV) than those of aug-cc-pVTZ. Thus, for most of the considered methods diffuse functions do not help to enhance the computed IPs, but worsen them. However, it appears that there is a harmony between the EKT-OCEPA(0) method and the aug-cc-pVTZ basis set.

IV. CONCLUSIONS

The extended Koopmans' theorem for the orbital-optimized methods, such as orbital-optimized MP2 and MP3 (OMP2[35,39] and OMP3,[36,41] as well as OMP2.5[42]) and the orbital-optimized CEPA(0) [OCEPA(0)],[40] have been presented. The presented methods have been applied to ionization potentials of the second- and third-row atoms, and closed- and open-shell molecules. Performances of the orbital-optimized methods have been compared with those of the counterpart standard methods, such as MP2, MP2.5, MP3, and CEPA(0).

For the orbital-optimized methods both the generalized-Fock matrix and the one-particle density matrix are readily available and symmetric, as opposed to the standard electron correlation methods where the Hartree–Fock orbitals are employed. Further, the orbital optimized methods solve the N-representability problem, which may arise when the relaxed particle density matrices are employed for the standard methods,[21] by disregarding the orbital Z-vector contributions for the OPDM. Moreover, for challenging chemical systems, where spin or spatial symmetry-breaking problems are observed, the unphysical orbital response contributions arising from the numerical instabilities in the HF electronic Hessian can be avoided by the orbital-optimization. Hence, it appears that the orbital-optimized methods are the most natural choice for the study of the EKT.

For the second- and third-row atoms, the performance of the EKT-OCEPA(0) method is remarkable, it yields the lowest mean absolute error of 0.11 eV. There is almost a 5-fold reduction in MAE compared to the Koopmans' theorem. Errors of the EKT-MP2.5 (MAE = 0.21 eV) , EKT-MP3 (0.17 eV), EKT-CEPA(0) (0.14 eV), and EKT-OMP3 (0.17 eV) methods are also tolerable. For closed-shell molecules, the EKT-OCEPA(0) method again ensures quite reliable lowest IPs (MAE = 0.15 eV), improving upon KT by 0.56 eV. Similarly, the EKT approaches based on the other $O(N^6)$ methods (where N is the number of basis functions), provide significantly better IPs than KT (by 0.37–0.56 eV), while $O(N^5)$ methods (EKT-MP2 and EKT-OMP2) fail to improve upon KT, indicating that one needs to consider second-order effects in amplitude equations for accurate IPs. Further, for inner valence orbitals, the KT approach dramatically fails (by 1.70 eV) for the corresponding IPs, while errors of the EKT approaches are several times lower than that of KT. However, the performance of the EKT is not as accurate as that for the lowest IPs. It is well-known that descriptions of inner valence orbitals are more difficult than those of frontier orbitals. Further, for the inner valence orbitals, the orbital-optimized

methods significantly improve upon (by 0.09–0.25 eV) the standard methods, indicating that the orbital relaxation effects are more important for core orbitals than those for frontier orbitals.

For open-shell molecules, the performance of the EKT-OMP2.5 method (MAE = 0.29 eV) is noteworthy, there is a more than 5-fold reduction in MAE compared to KT. Further, the orbital-optimized methods substantially enhance (by 0.14–0.21 eV) their standard counterparts, except for the MP2/OMP2 case. Failures of the canonical methods are attributed to spin-contamination in the reference UHF wave functions.

In order to investigate the effects of diffuse functions on the computed IPs, all computations have also been performed with the cc-pVTZ basis set in addition to aug-cc-pVTZ. Our results demonstrate that tight diffuse basis sets, such as aug-cc-pVTZ, may not be the most suitable choice for the EKT computations, instead the common basis sets without "official diffuse functions" may provide better results. Further, the effect of basis function diffuseness depends on the theoretical methods, and the employed theory and the basis set should be evaluated together rather than considering separately. For the lowest IPs, the tight diffuse basis set, aug-cc-pVTZ, is helpful for EKT-OMP3 and EKT-OCEPA(0), but performances of the other methods are generally better with cc-pVTZ. However, for inner valence orbitals, the aug-cc-pVTZ provides better IPs than cc-pVTZ for the most of the considered methods.

Overall, the EKT approach based on the orbital-optimized methods provides a straightforward, as well as an accurate way to compute IPs. Especially, the lowest IPs of atoms and closed-shell molecules can be computed very accurately.

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