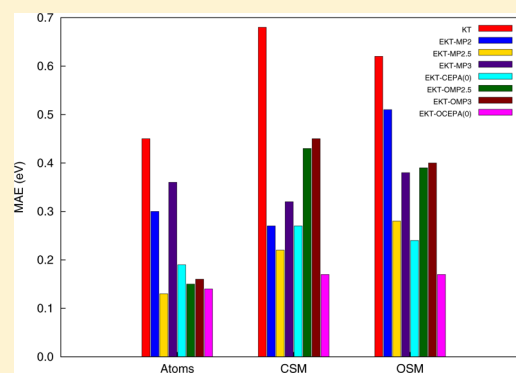


Accurate Electron Affinities from the Extended Koopmans' Theorem Based on Orbital-Optimized Methods

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ABSTRACT: The extended Koopmans' theorem (EKT) provides a systematic way to compute electron affinities (EAs) from any level of theory. Although, it is widely applied to ionization potentials, the EKT approach has not been extensively applied to computations of electron affinities. We present the first benchmarking study to investigate the performances of the EKT methods for predictions of EAs. We assess the performances of the EKT approaches based on orbital-optimized methods [Bozkaya, U. *J. Chem. Phys.* 2013, 139, 154105], such as the orbital-optimized third-order Møller–Plesset perturbation theory and the orbital-optimized coupled-electron pair theory [OCEPA(0)], and their standard counterparts for EAs of the selected atoms, closed- and open-shell molecules. Especially, results of the OCEPA(0) method (with the aug-cc-pVQZ basis set) for EAs of the considered atoms and molecules are very promising, the corresponding mean absolute errors are 0.14 and 0.17 eV, respectively.



1. INTRODUCTION

Accurate computations of ionization potentials (IPs) and electron affinities (EAs) are among the most challenging problems in modern quantum chemistry. Contemporary methods for the computation of IPs and EAs are the electron propagator theory (EPT),^{1–5} equation of motion (EOM) methods,^{6–14} and the extended Koopmans' theorem (EKT).^{15–17} Among these methods, the EKT approach offers a systematic way to compute IPs (and EAs) from any level of theory.^{18–28} Especially, with the prescription of Cioslowski et al.,²⁵ it is possible to combine the EKT approach with all wave function based methods. In their approach, one can carry out an EKT computation as a by product of analytic gradients. Thus, the EKT formalism can be employed to any method for which analytic gradients are available. Further, it is remarkable to note that the EKT was shown to be exact for the lowest IPs.^{29–38}

Over the past few decades, there has been continuing interest for the orbital-optimized many-body perturbation theory (MBPT) and coupled-cluster (CC) methods.^{39–58} Previous studies demonstrated that the orbital-optimized Møller–Plesset perturbation (MP) theory and CC methods are very helpful for molecular systems with challenging electronic structures, such as symmetry-breaking problems,^{39,40,43–45,48} transition states, free radicals,^{42,47,49} bond-breaking problems,^{41,60,59} and open-shell noncovalent interactions.⁴⁶

In our recent study, we implemented¹⁸ the EKT approach for orbital-optimized methods.^{39–47} As discussed previously,¹⁸ orbital-optimized methods are well-designed for the EKT computations since particle density-matrices (PDMs) and the generalized Fock matrix (GFM) are readily available and symmetric. Further, the N-representability condition is guaranteed for the one-particle density-matrix (OPDM) and

abnormal response contributions, which may arise in case of spin or space symmetry-breaking problems, to OPDM and GFM were avoided due to stationary properties of orbital-optimized methods.

Despite its success in prediction of ionization potentials, the EKT approach has not been extensively applied to computations of electron affinities. In this study, we assess the performance of the EKT approach based on orbital-optimized methods,¹⁸ such as the orbital-optimized third-order Møller–Plesset perturbation theory (OMP3^{40,45} as well as OMP2.5⁶¹) and the orbital-optimized coupled-electron pair theory [OCEPA(0)],⁴⁴ and their standard counterparts for electron affinities of the selected atoms, closed- and open-shell molecules. Performances of the various post-Hartree–Fock (HF) methods are assessed comparing their results with the experimental EA values.

2. THEORETICAL APPROACH

2.1. Orbital-Optimized Methods. Here, we present a summary of the orbital-optimized MP and CC methods, such as OMP3, OMP2.5, and OCEPA(0). For a more detailed discussion of these methods, one can refer to our previous studies.^{39–45,61} The orbital variations may be performed employing an exponential unitary operator^{62–65}

$$\tilde{p}^\dagger = e^{\hat{K}} p^\dagger e^{-\hat{K}} \quad (1)$$

$$\tilde{p} = e^{\hat{K}} p e^{-\hat{K}} \quad (2)$$

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$$|\tilde{p}\rangle = e^{\hat{K}}|p\rangle \quad (3)$$

where \hat{p}^\dagger and \hat{q} are creation and annihilation operators, $e^{\hat{K}}$ is the orbital rotation operator, \tilde{p}^\dagger , \tilde{p} , and $|\tilde{p}\rangle$ are transformed creation, annihilation operators and a transformed spin-orbital, respectively. The operator \hat{K} can be written as

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

$$\mathbf{K} = \text{skew}(\kappa) \quad (5)$$

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

$$\mathbf{C}(\kappa) = \mathbf{C}^{(0)} e^{\mathbf{K}} \quad (6)$$

where $\mathbf{C}^{(0)}$ and $\mathbf{C}(\kappa)$ are the initial and transformed MO coefficient matrices, respectively. Now, let us define a variational energy functional (Lagrangian) as a function of κ for each considered method

OMP3:^{40,42,45}

$$\begin{aligned} \tilde{E}(\kappa) = & \langle 0|\hat{H}^\kappa|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(1)})_c|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(2)})_c|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(2)} + \hat{W}_N^\kappa \hat{T}_2^{(1)})_c\}|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(2)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}|0\rangle \end{aligned} \quad (7)$$

OMP2.5:⁶¹

$$\begin{aligned} \tilde{E}(\kappa) = & \langle 0|\hat{H}|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(1)})_c|0\rangle + \frac{1}{2} \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(2)})_c|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}|0\rangle \\ & + \frac{1}{2} \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(2)} + \hat{W}_N^\kappa \hat{T}_2^{(1)})_c\}|0\rangle \\ & + \frac{1}{2} \langle 0|\{\hat{\Lambda}_2^{(2)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}|0\rangle \end{aligned} \quad (8)$$

OCEPA(0):⁴⁴

$$\begin{aligned} \tilde{E}(\kappa) = & \langle 0|\hat{H}^\kappa|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2)_c|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2(\hat{W}_N^\kappa + \hat{H}_N^\kappa \hat{T}_2)_c\}|0\rangle \end{aligned} \quad (9)$$

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}^κ , \hat{f}_N^κ , \hat{W}_N^κ , and \hat{H}_N^κ are defined as

$$\hat{H}^\kappa = e^{-\hat{K}} \hat{H} e^{\hat{K}} \quad (10)$$

$$\hat{f}_N^\kappa = e^{-\hat{K}} \hat{f}_N^d e^{\hat{K}} \quad (11)$$

$$\hat{W}_N^\kappa = e^{-\hat{K}} \hat{W}_N e^{\hat{K}} \quad (12)$$

$$\hat{H}_N^\kappa = e^{-\hat{K}} \hat{H}_N e^{\hat{K}} \quad (13)$$

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-particle components of the normal ordered Hamiltonian operator.^{6,66,67} It should be noted that Lagrangians of eqs 7–9 will be

stationary with respect to amplitudes and orbital-rotation parameters upon convergence.

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

$$w_{pq} = \left. \frac{\partial \tilde{E}}{\partial \kappa_{pq}} \right|_{\kappa=0} \quad (14)$$

$$A_{pq,rs} = \left. \frac{\partial^2 \tilde{E}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_{\kappa=0} \quad (15)$$

Then the Lagrangian may be expanded up to second-order as follows:

$$\tilde{E}^{(2)}(\kappa) = \tilde{E}^{(0)} + \kappa^\dagger \mathbf{w} + \frac{1}{2} \kappa^\dagger \mathbf{A} \kappa \quad (16)$$

where \mathbf{w} is the MO gradient vector, κ is the MO rotation vector, and \mathbf{A} is the MO Hessian matrix. Hence, minimizing the Lagrangian with respect to κ , we obtain

$$\kappa = -\mathbf{A}^{-1} \mathbf{w} \quad (17)$$

This final equation is just the usual Newton–Raphson step. Thus, MOs are rotated until the convergence achieved.

2.2. Extended Koopmans' Theorem (EKT). In this section, we present an overview of the EKT approach for MP and CC methods, for which energy computed as projections rather than as expectation values. For a more detailed discussion one can refer to previous studies.^{18–28} Let us assume that the energy of the neutral state can be computed as

$$E^N = \langle \Phi^N | \hat{H} | \Psi^N \rangle \quad (18)$$

where E^N and $|\Psi^N\rangle$ are the energy and the wave function of the neutral state, respectively, and $|\Phi^N\rangle$ 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

$$\langle \Phi^N | \Psi^N \rangle = 1 \quad (19)$$

For example, for the CC methods $|\Phi^N\rangle$ is the HF wave function for the N -electron system and $|\Psi^N\rangle = e^{\hat{T}} |\Phi^N\rangle$ (where $e^{\hat{T}}$ is the usual cluster excitation operator).

Similarly, we can express the energy of the $(N-1)$ -electron system as follows

$$E^{N-1} = \langle \Phi^{N-1} | \hat{H} | \Psi^{N-1} \rangle \quad (20)$$

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. Wave functions of the $(N-1)$ -electron system ($|\Phi^{N-1}\rangle$ and $|\Psi^{N-1}\rangle$) can be written in terms of those for the N -electron system

$$|\Psi^{N-1}\rangle = \hat{O} |\Psi^N\rangle \quad (21)$$

$$\langle \Phi^{N-1} | = \langle \Phi^N | \hat{O}^\dagger \quad (22)$$

the operators \hat{O}^\dagger and \hat{O} are defined as follows

$$\hat{O}^\dagger = \sum_p c_p^* \hat{p}^\dagger \quad (23)$$

$$\hat{O} = \sum_p c_p \hat{p} \quad (24)$$

Table 1. Electron Affinities (in eV) and Maximum Absolute Deviations ($|\Delta|_{\max}$) for the Considered Atoms at the aug-cc-pVQZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) Levels

atom	neutral \rightarrow anion	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	exp ^a
Li	$2S \rightarrow 1S$	0.39	0.21	0.28	0.35	0.81	0.35	0.39	0.60	0.62
B	$2P \rightarrow 3P$	0.77	0.30	0.32	0.32	0.26	0.20	0.23	0.22	0.28
C	$3P \rightarrow 4S$	2.12	1.19	1.53	1.59	1.57	1.16	1.35	1.40	1.26
O	$3P \rightarrow 2P$	2.18	0.82	1.43	2.01	1.90	1.23	1.93	1.75	1.46
F	$2P \rightarrow 1S$	4.92	2.85	3.43	6.17	4.09	3.41	3.79	3.92	3.40
Na	$2S \rightarrow 1S$	0.36	0.11	0.41	0.36	0.62	0.35	0.39	0.50	0.55
Al	$2P \rightarrow 3P$	0.61	0.36	0.38	0.39	0.43	0.36	0.38	0.45	0.43
Si	$3P \rightarrow 4S$	1.69	1.31	1.36	1.40	1.46	1.32	1.37	1.47	1.39
P	$4S \rightarrow 3P$	0.68	0.29	0.43	0.58	0.72	0.45	0.59	0.71	0.75
S	$3P \rightarrow 2P$	2.33	1.65	1.86	2.08	2.16	1.79	2.07	2.14	2.08
Cl	$2P \rightarrow 1S$	4.09	3.20	3.50	3.81	3.80	3.40	3.79	3.76	3.61
Ge	$3P \rightarrow 4S$	1.63	1.29	1.34	1.39	1.43	1.32	1.37	1.44	1.23
Se	$3P \rightarrow 2P$	2.20	1.68	1.86	2.05	2.12	1.83	2.06	2.11	2.02
Br	$2P \rightarrow 1S$	3.79	3.14	3.37	3.61	3.62	3.31	3.60	3.60	3.36
$ \Delta _{\max}$		1.52	0.65	0.34	2.77	0.69	0.29	0.47	0.52	

^aData from Rienstra-Kiracofe et al.⁸²

where $\{c_p\}$ are the expansion coefficients. The $|\Psi^{N-1}\rangle$ wave function can be chosen to satisfy the following intermediate normalization condition

$$\langle \Phi^{N-1} | \Psi^{N-1} \rangle = \langle \Phi^N | \hat{O}^\dagger \hat{O} | \Psi^N \rangle = 1 \quad (25)$$

Then, minimizing the energy difference between the ionized and neutral states with respect to expansion coefficients of eq 24, subject to the constraint given by eq 25, we obtain

$$\mathbf{FC} = \gamma \mathbf{Ce} \quad (26)$$

where \mathbf{C} is the matrix of eigen vectors, and \mathbf{e} is the diagonal matrix of eigen values (ionization energies), \mathbf{F} is the GFM, and γ is the OPDM, which are defined as

$$\gamma_{pq} = \langle \Phi^N | \hat{p}^\dagger \hat{q} | \Psi^N \rangle \quad (27)$$

$$F_{pq} = -\langle \Phi^N | \hat{p}^\dagger [\hat{H}, \hat{q}] | \Psi^N \rangle \quad (28)$$

3. RESULTS AND DISCUSSION

Results from the EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) approaches were obtained for the selected 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. In our previous study,¹⁸ it was demonstrated that the EKT approach based on the orbital-optimized second-order Møller–Plesset perturbation theory^{39,43} (EKT-OMP2) fails to improve upon MP2 for the prediction of IPs, but it worsen the computed values. Therefore, the EKT-OMP2 method was not considered in this study.

Electron affinity computations were performed as the lowest IP of anions at the optimized geometry of neutrals (vertical electron affinities, VEA). The experimental geometries were used for considered closed- and open-shell molecules, for which the experimental geometries are available.⁶⁸ For the molecules where the experimental geometries are not available, optimized geometries were taken from our previous studies,^{69–73} which were obtained at the B3LYP/6-311G(d,p) level,^{74–78} as well as from the computational chemistry comparison and benchmark database (CCCBDB).⁷⁹ For the EKT computations, Dunning's

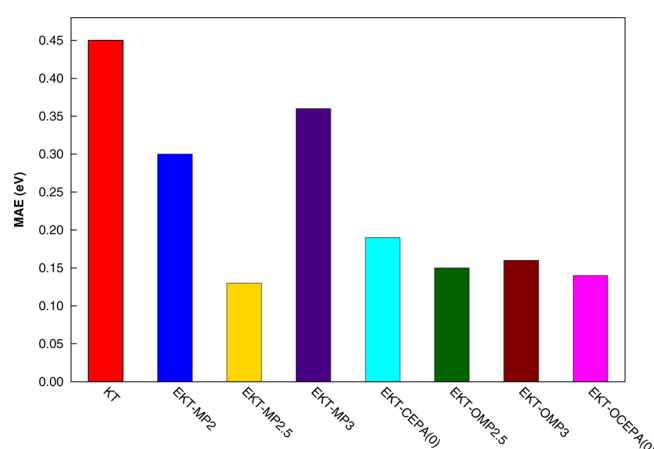


Figure 1. MAEs (in eV) in electron affinities of considered atoms for HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (aug-cc-pVQZ basis set was employed).

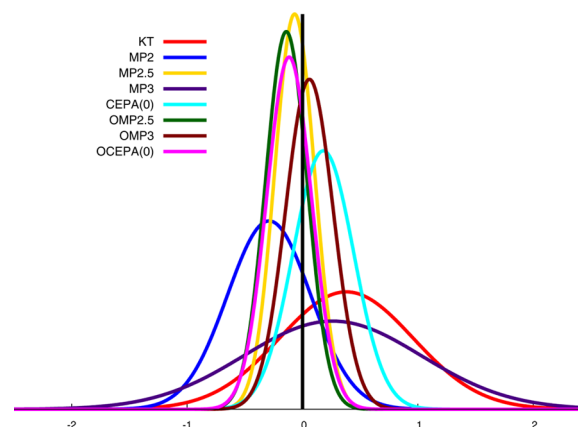


Figure 2. Normal (Gaussian) distribution of errors (in eV) in electron affinities of considered atoms for HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (aug-cc-pVQZ basis set was employed).

Table 2. Vertical Electron Affinities (in eV) and Maximum Absolute Deviations ($|\Delta|_{\max}$) for the Considered Closed-Shell Molecules at the aug-cc-pVQZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) Levels

molecule	neutral \rightarrow anion	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	exp ^a
LiH	$^1\Sigma^+ \rightarrow ^2\Sigma^+$	0.28	0.29	0.29	0.30	0.31	−0.01	0.50	0.24	0.34
BH ₃	$^1A'_1 \rightarrow ^2A'_1$	−0.54	−0.24	−0.23	−0.23	−0.22	−0.16	−0.23	−0.08	0.04
C ₂	$^1\Sigma_g^+ \rightarrow ^2\Sigma_g^+$	3.56	2.86	3.26	3.63	3.63	3.25	3.60	3.28	3.27
C ₂ H ₂ ^b	$^1A_1 \rightarrow ^2B_2$	1.59	0.57	0.70	0.88	0.84	−0.33	1.05	0.47	0.49
SiH ₂	$^1A_1 \rightarrow ^2B_1$	1.26	0.87	0.93	0.98	1.01	0.91	0.99	1.06	1.12
HNO	$^1A' \rightarrow ^2A''$	1.47	0.45	0.62	0.94	0.76	−0.29	0.37	0.12	0.34
HCF	$^1A' \rightarrow ^2A''$	1.33	0.43	0.49	0.63	0.60	0.06	0.40	0.30	0.54
C ₃	$^1\Sigma_g^+ \rightarrow ^2\Pi_g$	3.21	1.70	1.99	2.34	2.25	1.75	1.50	2.14	2.00
O ₃	$^1A_1 \rightarrow ^2B_1$	3.50	2.22	2.78	3.37	3.12	1.71	3.17	2.21	2.10
CF ₂	$^1A_1 \rightarrow ^2B_1$	0.88	0.14	0.20	0.27	0.25	−0.60	−0.23	−0.29	0.18
SiO ₂	$^1\Sigma_g^+ \rightarrow ^2A_1$	1.47	1.12	1.34	1.60	1.54	1.34	1.62	1.55	2.10
P ₂	$^1\Sigma_g^+ \rightarrow ^2\Pi_u$	0.99	0.33	0.44	0.61	0.58	0.19	0.57	0.50	0.59
SO ₂	$^1A_1 \rightarrow ^2B_1$	2.00	0.77	1.02	1.30	1.19	0.53	1.22	0.91	1.11
SiF ₂	$^1A_1 \rightarrow ^2B_1$	0.35	−0.35	−0.23	−0.11	−0.09	−0.05	0.05	0.06	0.10
$ \Delta _{\max}$		1.40	0.98	0.76	1.27	1.02	0.82	1.07	0.55	

^aData from Rienstra-Kiracofe et al.⁸² ^bVinylidene.

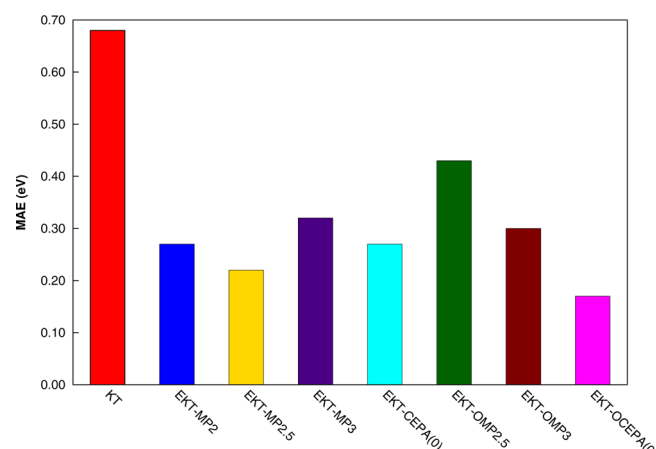


Figure 3. MAEs (in eV) in electron affinities of considered closed-shell molecules for HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (aug-cc-pVQZ basis set was employed).

augmented correlation-consistent polarized valence quadruple- ζ (aug-cc-pVQZ) basis set^{80,81} was employed, as it is well-known that diffuse functions are necessary for anions.^{82,83} For open-shell molecules, the unrestricted orbitals were employed, and no mixing of α and β spin orbitals was allowed. All electrons were correlated for post-Hartree–Fock methods. Throughout this research, all computations were performed with our codes in the psi4 package.⁸⁴

3.1. Atoms. To assess the performances of the EKT methods, we start with atoms. For the considered atoms, EAs (in eV) from the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with the aug-cc-pVQZ basis set are reported in Table 1. Mean absolute errors (MAEs) are presented graphically in Figure 1, while normal (Gaussian) distribution of errors are depicted in Figure 2.

The MAE values with the aug-cc-pVQZ basis set are 0.45 (KT), 0.30 (EKT-MP2), 0.13 (EKT-MP2.5), 0.36 (EKT-MP3), 0.19 [EKT-CEPA(0)], 0.15 (EKT-OMP2.5), 0.16 (EKT-OMP3), and 0.14 [EKT-OCEPA(0)] eV. Hence, all considered

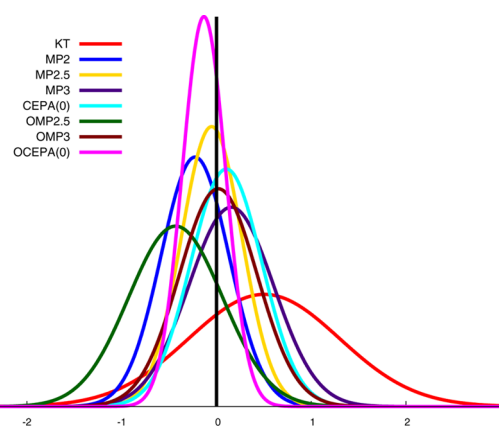


Figure 4. Normal (Gaussian) distribution of errors (in eV) in electron affinities of considered closed-shell molecules for HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (aug-cc-pVQZ basis set was employed).

EKT approaches significantly improve upon KT (by 0.09–0.32 eV). Performances of all orbital-optimized methods and EKT-MP2.5 are remarkable, there are 3-fold reductions in the MAE compared to KT. The orbital optimization greatly improves the performance of MP3 (almost a 2-fold reduction in MAE), while it enhances the result of CEPA(0) by 0.05 eV, and slightly deteriorates the performance of MP2.5, by 0.02 eV.

Next, we consider the standard deviations (σ) of the errors to assess the performances of the EKT approaches. The σ values are 0.58 (KT), 0.36 (EKT-MP2), 0.17 (EKT-MP2.5), 0.77 (EKT-MP3), 0.26 [EKT-CEPA(0)], 0.18 (EKT-OMP2.5), 0.21 (EKT-OMP3), and 0.19 [EKT-OCEPA(0)] eV. Especially, results of EKT-MP2.5, EKT-OMP2.5, and EKT-OCEPA(0) are significantly accurate, there are 3-fold reductions in standard deviations compared to KT. Further, it is surprising that the σ value of EKT-MP3 (0.77 eV) is even larger than that of KT (0.58 eV). The reason for that high σ value of EKT-MP3 is the EA of the F atom. The EKT-MP3 prediction for the EA of the F atom is 6.17 eV, which is quite larger than the experimental value of 3.40 eV.⁸² The corresponding pole strength for EKT-

Table 3. Vertical Electron Affinities (in eV) and Maximum Absolute Deviations ($|\Delta|_{\max}$) for the Considered Open-Shell Molecules at the aug-cc-pVQZ HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) Levels

molecule	neutral \rightarrow anion	KT	EKT-MP2	EKT-MP2.5	EKT-MP3	EKT-CEPA(0)	EKT-OMP2.5	EKT-OMP3	EKT-OCEPA(0)	exp ^a
BeH	$^2\Sigma^+ \rightarrow ^1\Sigma^+$	0.51	0.26	0.29	0.33	0.45	0.28	0.33	0.19	0.70
CH	$^2\Pi \rightarrow ^3\Sigma^-$	2.11	1.18	1.33	1.48	1.48	1.07	1.33	1.31	1.24
NH	$^3\Sigma^- \rightarrow ^2\Pi$	3.02	0.68	0.82	1.01	0.85	0.05	0.75	0.36	0.37
CH ₃	$^2A_2'' \rightarrow ^1A_1'$	0.10	−0.51	−0.26	0.00	−0.14	−0.34	−0.04	−0.15	0.08
NH ₂	$^2B_1 \rightarrow ^1A_1$	1.34	0.51	0.78	1.28	0.96	0.50	1.28	0.86	0.77
OH	$^2\Pi \rightarrow ^1\Sigma^+$	2.97	1.34	2.02	3.21	2.34	1.73	3.51	2.19	1.83
C ₂ H	$^2\Sigma^+ \rightarrow ^1\Sigma^+$	3.57	2.73	3.17	3.68	3.48	2.54	3.72	3.21	2.97
CN	$^2\Sigma^+ \rightarrow ^1\Sigma^+$	5.24	3.60	4.02	4.48	4.30	3.59	4.44	4.08	3.86
BO	$^2\Sigma^+ \rightarrow ^1\Sigma^-$	2.86	2.21	2.37	2.53	2.57	2.25	2.16	2.52	2.51
NCH ₂	$^2B_1 \rightarrow ^1A_1$	1.32	0.34	0.54	1.10	0.72	0.80	1.11	0.51	0.51
SiH	$^2\Pi \rightarrow ^3\Sigma^-$	1.53	1.15	1.18	1.23	1.26	1.13	1.20	1.27	1.28
NO	$^2\Pi \rightarrow ^3\Sigma^-$	1.17	0.25	0.35	0.72	0.42	−0.66	0.03	−0.23	0.03
SiH ₃	$^2A_1 \rightarrow ^1A_1$	0.82	0.55	0.68	0.85	0.90	0.66	0.85	0.88	1.41
CH ₃ O	$^2A' \rightarrow ^1A_1$	2.81	1.18	1.74	2.60	2.07	1.93	2.78	1.87	1.57
O ₂	$^3\Sigma_g^- \rightarrow ^2\Pi_g$	0.99	0.62	0.87	0.22	0.26	−0.42	0.43	0.10	0.45
PH	$^3\Sigma^- \rightarrow ^2\Pi$	0.91	0.58	0.78	0.99	1.10	0.74	0.90	0.97	1.03
HO ₂	$^2A'' \rightarrow ^1A'$	1.95	0.65	0.95	1.54	1.21	0.38	2.04	0.91	1.08
PH ₂	$^2B_1 \rightarrow ^1A_1$	1.23	0.82	1.00	1.20	1.24	0.99	1.20	1.25	1.27
SH	$^2\Pi \rightarrow ^1\Sigma^+$	2.58	1.88	2.13	2.38	2.42	2.07	2.40	2.41	2.32
FO	$^2\Pi \rightarrow ^1\Sigma^+$	3.31	1.56	2.03	2.73	2.37	1.55	2.50	2.10	2.27
C ₃ H ₃ ^b	$^2B_1 \rightarrow ^1A'$	0.80	0.15	0.46	0.78	0.65	0.40	1.03	0.66	0.92
CH ₃ C ₂	$^2A' \rightarrow ^1A_1$	3.06	2.31	2.73	3.19	3.10	2.46	3.16	2.93	2.72
C ₂ O	$^3\Sigma^- \rightarrow ^2\Pi$	2.12	1.54	1.96	2.48	2.36	1.85	2.30	2.25	2.29
HCNN	$^2A'' \rightarrow ^1A'$	1.76	0.88	1.31	1.88	1.69	1.41	1.90	1.73	1.69
NCO	$^2\Pi \rightarrow ^1\Sigma^+$	3.99	2.78	3.31	3.82	3.61	3.24	3.75	3.58	3.61
N ₃	$^2\Pi_g \rightarrow ^1\Sigma_g^+$	2.87	1.86	2.43	2.98	2.67	2.46	2.99	2.71	2.76
CH ₂ CHO ^c	$^2A'' \rightarrow ^1A'$	1.83	1.12	1.47	1.86	1.69	1.42	1.92	1.70	1.82
AlO	$^2\Sigma^+ \rightarrow ^1\Sigma^+$	2.70	2.18	2.53	2.92	2.85	2.43	2.97	2.77	2.60
BO ₂	$^2\Pi_g \rightarrow ^1\Sigma_g^+$	5.66	3.85	4.54	5.33	4.90	4.34	5.53	4.76	4.32
NO ₂	$^2A_1 \rightarrow ^1A_1$	2.58	1.14	1.54	2.01	1.85	1.06	2.28	1.60	2.27
SiF	$^2\Pi \rightarrow ^3\Sigma^-$	1.11	0.66	0.72	0.79	0.81	0.67	0.76	0.82	0.81
PO	$^2\Pi \rightarrow ^1\Sigma^+$	0.46	−0.06	0.08	0.31	0.24	0.00	0.30	1.07	1.09
SO	$^3\Sigma^- \rightarrow ^2\Pi$	1.34	0.51	0.81	1.14	1.08	0.64	1.15	1.03	1.13
ClO	$^2\Pi \rightarrow ^1\Sigma^+$	3.18	1.67	2.19	2.94	2.54	1.92	2.82	2.37	2.28
SF	$^2\Pi \rightarrow ^1\Sigma^+$	2.53	1.73	1.98	2.25	2.28	1.88	2.24	2.23	2.29
Al ₂	$^3\Pi_u \rightarrow ^4\Pi_u$	1.40	1.21	1.29	1.38	1.47	1.33	1.41	1.47	1.46
Si ₂	$^3\Sigma_g^- \rightarrow ^2\Sigma_g^+$	1.70	1.81	1.97	2.07	2.28	1.87	2.05	2.20	2.20
AlO ₂	$^2\Pi_g \rightarrow ^1\Sigma_g^+$	0.20	3.46	4.45	5.62	4.82	4.26	5.76	4.65	4.23
PO ₂	$^2A_1 \rightarrow ^1A_1$	3.51	2.52	2.92	3.34	3.24	2.80	3.70	3.17	3.42
S ₂	$^3\Sigma_g^- \rightarrow ^2\Pi_g$	1.71	1.08	1.20	1.54	1.55	1.46	1.56	1.54	1.67
$ \Delta _{\max}$		4.03	1.15	1.02	1.39	0.85	1.21	1.68	0.67	

^aData from Rienstra-Kiracofe et al.⁸² ^bPropargyl radical. ^cVinyloxy radical.

MP3 is 0.61, which indicates a problem for the computed value. In general, the pole strength of a certain IP (and EA) should be greater than or equal to 0.80.^{3,85} However, optimized orbitals helps to overcome this failure of EKT-MP3, and EKT-OMP3 yields the EA of 3.79 eV for the F atom, which is much closer to the experimental value of 3.40 eV, the corresponding pole strength value is 0.83.

3.2. Closed-Shell Molecules. As the second step of our investigation, we apply the EKT approaches to closed-shell molecules. For the considered closed-shell molecules, EAs (in eV) from the KT, EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with the aug-cc-pVQZ basis set are reported in Table

2. The MAE values are presented graphically in Figure 3, while normal (Gaussian) distribution of errors are depicted in Figure 4.

The MAE values are 0.68 (KT), 0.27 (EKT-MP2), 0.22 (EKT-MP2.5), 0.32 (EKT-MP3), 0.27 [EKT-CEPA(0)], 0.43 (EKT-OMP2.5), 0.30 (EKT-OMP3), and 0.17 [EKT-OCEPA(0)] eV. Hence, all EKT approaches significantly improve upon KT (by 0.25–0.51 eV). Especially, the performance of the EKT-OCEPA(0) method is noteworthy, there is a 4-fold reduction in the MAE compared to KT. Further, while the orbital optimization helps to enhance the EKT-CEPA(0) method, situations are vice versa in cases of EKT-MP2.5 and EKT-MP3.

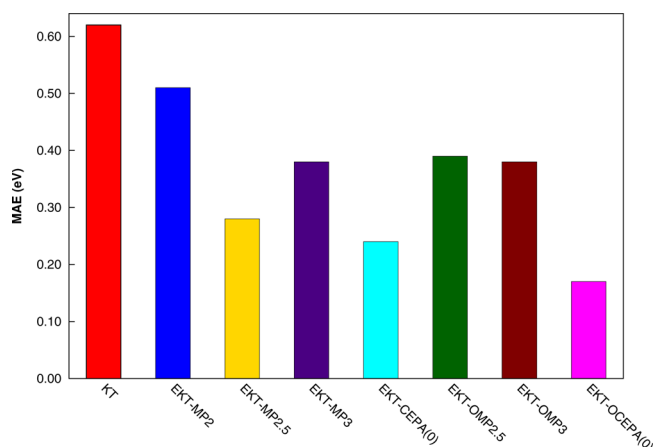


Figure 5. Mean absolute errors (in eV) in electron affinities of considered open-shell molecules for the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (aug-cc-pVQZ basis set was employed).

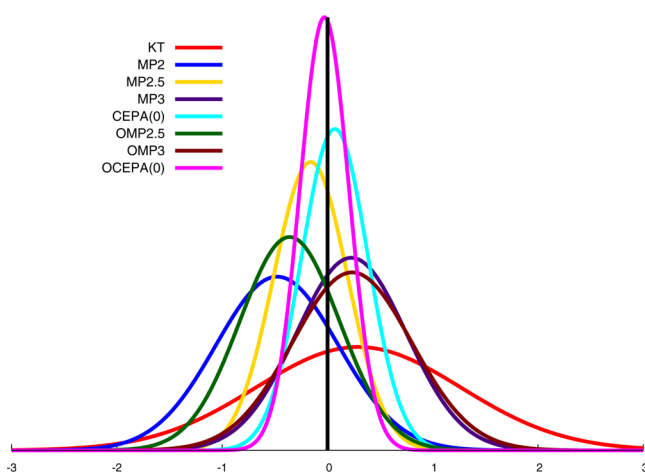


Figure 6. Normal (Gaussian) distribution of errors (in eV) in electron affinities of considered open-shell molecules for the HF (KT), EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with respect to experiment (aug-cc-pVQZ basis set was employed).

Now, we consider the σ values in order to assess the performances of the considered methods. The σ values are 0.80 (KT), 0.36 (EKT-MP2), 0.32 (EKT-MP2.5), 0.45 (EKT-MP3), 0.38 [EKT-CEPA(0)], 0.49 (EKT-OMP2.5), 0.41 (EKT-OMP3), and 0.23 [EKT-OCEPA(0)] eV. Results of EKT-OCEPA(0) are again significantly accurate, there is more than a 3-fold reduction in the standard deviations compared to KT.

3.3. Open-Shell Molecules. As the final step of our assessment, we consider open-shell molecules. Previous studies showed that performances of orbital-optimized methods are significantly better than those of standard methods, where HF orbitals are employed, for open-shell molecular systems suffering from spin or spatial symmetry breaking problems.^{39,40,42–46,48,49} For the considered molecules, EAs (in eV) from the KT, EKT-MP2, EKT-MP2.5, EKT-MP3, EKT-CEPA(0), EKT-OMP2.5, EKT-OMP3, and EKT-OCEPA(0) methods with the aug-cc-pVQZ basis set are reported in Table 3. The MAE values are presented graphically in Figure 5, while normal (Gaussian) distribution of errors are depicted in Figure

6. The MAE values are 0.62 (KT), 0.51 (EKT-MP2), 0.28 (EKT-MP2.5), 0.38 (EKT-MP3), 0.24 [EKT-CEPA(0)], 0.39 (EKT-OMP2.5), 0.38 (EKT-OMP3), and 0.17 [EKT-OCEPA(0)] eV. Thus, all EKT approaches again remarkably improve upon KT (by 0.11–0.45 eV). Especially, the performance of the EKT-OCEPA(0) method is noteworthy, there is a more than 3-fold reduction in the MAE compared to KT. Further, the σ values are 0.98 (KT), 0.58 (EKT-MP2), 0.35 (EKT-MP2.5), 0.52 (EKT-MP3), 0.31 [EKT-CEPA(0)], 0.47 (EKT-OMP2.5), 0.57 (EKT-OMP3), and 0.23 [EKT-OCEPA(0)] eV. Results of EKT-OCEPA(0) are again quite accurate, there is more than 4-fold reduction in the standard deviations compared to KT.

4. CONCLUSIONS

In this study, a detailed assessment of the extended Koopmans' theorem (EKT) for electron affinities (EAs) has been presented. In context of the EKT approach, the orbital-optimized third-order Møller–Plesset perturbation theory (OMP3^{40,45} as well as OMP2.5⁶¹) and the orbital-optimized coupled-electron pair theory [OCEPA(0)],⁴⁴ and their standard counterparts have been considered. Results of the considered EKT methods are obtained for the selected atoms, closed- and open-shell molecules for comparison with those of the experimental values.

For the considered atoms, the performances of the EKT-MP2.5, EKT-OCEPA(0), EKT-OMP2.5, and EKT-OMP3 methods are remarkable; the corresponding mean absolute errors (MAE) are 0.13–0.16 eV and standard deviations of errors (σ) are 0.17–0.21 eV. There are roughly 3-fold reductions in the MAE and σ compared to the Koopmans' theorem (KT). For closed-shell molecules, the EKT-OCEPA(0) method again provides quite reliable EAs (MAE = 0.17 eV and σ = 0.23 eV), there is again a 3–4-fold reduction in errors compared to KT. Similarly, the EKT approaches based on the other methods ensure significantly better EAs than KT (by 0.25–0.48 eV). For open-shell molecules, all considered EKT approaches provide significantly better EAs than KT (by 0.11–0.45 eV in the MAE and by 0.40–0.75 eV in the σ). Especially, the performance of the EKT-OCEPA(0) method (MAE = 0.17 and σ = 0.23 eV) is noteworthy, there are more than 3- and 4-fold reductions in the MAE and σ , respectively, compared to KT.

Moreover, the OCEPA(0) method significantly reduces the MAE values compared to CEPA(0) (by 26–37%), indicating that the orbital relaxation effects are important in the case of CEPA(0). However, this result is not valid for the MP3 and MP2.5 cases. Especially, for MP2.5, the orbital optimization procedure deteriorates the quality of the computed EAs. In our recent study,¹⁸ we observed that for the MP2.5 method, the optimized orbitals are quite helpful for the electron removal procedures from the inner valence orbitals; however, for the lowest IPs, the performance of OMP2.5 is worse than that of MP2.5. Hence, we may here observe a similar situation for the lowest EAs for the MP2.5 case.

Overall, the EKT approach provide a systematic and an accurate way to compute EAs. Especially, the EKT-OCEPA(0)/aug-cc-pVQZ level of theory provides very accurate EAs for a broad range of chemical systems.

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Notes

The authors declare no competing financial interest.

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