Ionization potentials and electron affinities from the extended Koopmans' theorem applied to energy-derivative density matrices: The EKTMPn and EKTQCISD methods

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Ionization potentials and electron affinities from the extended Koopmans' theorem applied to energy-derivative density matrices: The EKTMPn and EKTQCISD methods

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The extended Koopmans' theorem (EKT) is combined with the energy-derivative formalism for the one- and two-particle reduced density matrices. Such a combination produces a versatile methodology for calculations of ionization potentials and electron affinities that, being applicable to any level of electron correlation treatment, is more general than the equation-of-motion (EOM) formalism. General expressions for the Feynman–Dyson amplitude, the pole strength, and the one-particle reduced density matrix of the hole state are derived. Like the electron propagator theory (EPT), the present approach provides a one-electron description of the electron attachment–detachment processes that is advantageous from the interpretive point of view. Numerical tests show that EKT calculations are capable of affording ionization potentials with accuracy comparable to that of the EPT methods but at a substantially lower computational cost. © *1997 American Institute of Physics.* [S0021-9606(97)03041-9]

I. INTRODUCTION

Contemporary quantum chemistry offers several approaches to the calculation of ionization potentials (IPs) and electron affinities (EAs). In principle, IPs and EAs can be computed at any level of theory as the ground- and excited-state energies of the ions M^+ and M^- relative to the ground-state energy of the respective parent system M. In practice, however, some or all of the excited states of M^+ and M^- may not be amenable to electronic structure calculations. For example, since it is often difficult to converge the Hartree–Fock (HF) equations to excited states that belong to the same irreducible representation as the ground state, methods such as ΔSCF, ΔMP2, etc. can produce only one or a few IPs and EAs for a given system.

This problem is completely circumvented in the electron propagator theory (EPT) in which IPs and EAs are obtained directly as eigenvalues of (approximate) propagator matrices.[1,2] Being energy dependent, these matrices have to be recomputed several times for each IP or EA until self consistency is achieved. Although such a formalism offers the advantage of providing an intuitively clear one-electron description of ionization and electron attachment processes, the iterative nature of EPT calculations makes them computationally expensive. In general, there is no direct one-to-one correspondence between the approximate EPT methods and the levels of theory applicable to the ground state of the parent system.

The equation-of-motion (EOM) method constitutes a useful alternative to the energy-difference calculations of IPs and EAs within the coupled-cluster theory and related approaches such as QCI.[3] This method is capable of affording very accurate IPs and EAs, but has not been generalized to other levels of theory.

The formalism of the extended Koopmans' theorem (EKT)[4,5] possesses distinct advantages over the aforedescribed approaches. Not only does it describe the electron detachment–attachment in terms of one-electron quantities, but it also provides a means of producing entire manifolds of IPs and EAs in a single-step process that, as shown below, requires only by-products of energy-gradient calculations as input. Consequently, unlike their EPT and EOM counterparts, EKT-based calculations can be carried out in conjunction with any level of theory at negligible computational cost.

In the past, a more widespread use of EKT in electronic structure calculations has been hindered by a prolonged dispute concerning its exactness[6] and the lack of efficient implementations at levels of theory other than CI[6,7] or MCSCF.[8] The former issue has now been resolved with theoretical research and extensive numerical tests that appear to indicate that EKT is exact for the first IP and capable of yielding highly accurate higher IPs. The latter issue is addressed in this paper.

II. THE EXTENDED KOOPMANS' THEOREM

Let Ψ^N be the ground-state eigenfunction of the second-quantized Hamiltonian $\hat{H}$ that describes the N-electron system under consideration. Let $\{\phi_p\}$ be a complete set of the HF spin–orbitals corresponding to $\hat{H}$ and $\{\hat{a}_p\}$ be the set of annihilation operators associated with $\{\phi_p\}$. The normalized $(N-1)$-electron wave function Ψ^{N-1} of the ionized system (''the hole state'') is written as

$$\Psi^{N-1} = \left(\sum_{pq} C_p^* C_q \langle \Psi^N | \hat{a}_p^+ \hat{a}_q | \Psi^N \rangle \right)^{-1/2}$$

$$\times \left(\sum_p C_p \hat{a}_p \right) \Psi^N, \tag{1}$$

where the coefficients $\mathbf{C}$ minimize the expression[4–8]

$$e(\mathbf{C}) = \langle \Psi^{N-1} | \hat{H} | \Psi^{N-1} \rangle - \langle \Psi^N | \hat{H} | \Psi^N \rangle$$

$$= \left(\sum_{pq} C_p^* C_q \langle \Psi^N | \hat{a}_p^+ [\hat{H}, \hat{a}_q] | \Psi^N \rangle \right) \Bigg/$$

$$\left(\sum_{pq} C_p^* C_q \langle \Psi^N | \hat{a}_p^+ \hat{a}_q | \Psi^N \rangle \right). \tag{2}$$

Minimization of $e(\mathbf{C})$ gives rise to the secular equation[4–8]

$$\mathbf{F}\mathbf{C} + e_1 \mathbf{\Gamma}\mathbf{C} = 0, \tag{3}$$

where $\mathbf{\Gamma}$ is the one-particle reduced density matrix (the 1-matrix)

$$\Gamma_{pq} \equiv \langle \Psi^N | \hat{a}_p^+ \hat{a}_q | \Psi^N \rangle, \tag{4}$$

that corresponds to Ψ^N and $\mathbf{F}$ is given by

$$F_{pq} \equiv -\langle \Psi^N | \hat{a}_p^+ [\hat{H}, \hat{a}_q] | \Psi^N \rangle$$

$$= \sum_r h_{pr} \Gamma_{qr} + 2 \sum_{rst} \gamma_{qrst} \langle pr \| st \rangle. \tag{5}$$

In Eq. (5), $\mathbf{h}$ is the core Hamiltonian, $\{\langle pr \| st \rangle\}$ is the set of antisymmetrized two-electron integrals produced from $\{\phi_p\}$, and γ is the symmetrical component of the two-particle reduced density matrix (the 2-matrix), defined as

$$(1/2)\langle \Psi^N | \hat{a}_q^+ \hat{a}_r^+ \hat{a}_t \hat{a}_s | \Psi^N \rangle \equiv \gamma_{qrst} - \gamma_{qrts}. \tag{6}$$

The matrix $\mathbf{F}$ is known as the generalized Fock matrix[9] or the Lagrangian.[10]

Under the assumption of the set $\{\hat{a}_p \Psi^N\}$ of $(N-1)$-electron wave functions being complete [Eq. (1) providing an exact representation of Ψ^{N-1}], solution of Eq. (3) yields e_1 as the exact lowest IP pertaining to the electron detachment that produces Ψ^{N-1} from Ψ^N.[4–8] Approximations to higher IPs are obtained as the other solutions $\{e_i\}$ of Eq. (3).

Although this fact has not been previously given much attention in the chemical literature, EKT can also be used to compute electronic properties other than energy. For example, the 1-matrix $\mathbf{\Gamma}^{N-1}$ that corresponds to Ψ^{N-1}, from which all the one-electron properties of M^+ can be calculated, is readily obtained from the wave function of Eq. (1),

$$\Gamma_{pq}^{N-1} \equiv \langle \Psi^{N-1} | \hat{a}_p^+ \hat{a}_q | \Psi^{N-1} \rangle$$

$$= 2[\mathrm{Tr}(\mathbf{C}^+ \mathbf{\Gamma} \mathbf{C})]^{-1} \sum_{rs} C_r^* C_s (\gamma_{rpsq} - \gamma_{rpqs}). \tag{7}$$

The Feynman–Dyson amplitude[2] (also known as the Dyson spin–orbital[11]) is defined as

$$\psi \equiv N^{1/2} \langle \Psi^{N-1} | \Psi^N \rangle. \tag{8}$$

where the integration runs over the coordinates of $N-1$ electrons. Combining Eqs. (1) and (8) yields

$$\psi = [\mathrm{Tr}(\mathbf{C}^+ \mathbf{\Gamma} \mathbf{C})]^{-1/2} \sum_p (\mathbf{C}^+ \mathbf{\Gamma})_p \phi_p. \tag{9}$$

The self-overlap of ψ, which is known as the pole strength,[1,2] equals simply

$$P \equiv \langle \psi | \psi \rangle = \mathrm{Tr}(\mathbf{C}^+ \mathbf{\Gamma} \mathbf{\Gamma}^+ \mathbf{C}) / \mathrm{Tr}(\mathbf{C}^+ \mathbf{\Gamma} \mathbf{C}). \tag{10}$$

It should also be noted that analogous considerations for the electron attachment processes lead to the conclusion that solutions $\{\tilde{e}_i\}$ of the equation

$$\widetilde{\mathbf{F}}\widetilde{\mathbf{C}} + \tilde{e}_i (\mathbf{1} - \mathbf{\Gamma})\widetilde{\mathbf{C}} = \mathbf{0} \tag{11}$$

where

$$\widetilde{F}_{pq} = h_{pq} + 2 \sum_{rs} \Gamma_{rs} \langle ps \| qr \rangle - F_{pq}, \tag{12}$$

and $\mathbf{1}$ is a unit matrix, furnish approximate EAs.[4] At present, nothing is known about the accuracy of these approximations.

III. THE ENERGY-DERIVATIVE DENSITY MATRICES

In practical calculations, only approximations to $\mathbf{\Gamma}$ and γ are available and the set $\{\phi_p\}$ is finite. Fortunately, approximate $\mathbf{\Gamma}$ and γ can be obtained even within electron-correlation formalisms such as MP2 or CCSD that do not produce Ψ^N at all. In fact, expressions for the energy-derivative $\mathbf{\Gamma}$ and γ, which are widely used in contemporary calculations of energy gradients and other first-order response properties,[3,12] can be derived within any method in which the electron correlation energy E_c is defined in terms of the Hartree–Fock spinorbital energies $\{\epsilon_p\}$ and the integrals $\{\langle pq \| rs \rangle\}$

$$E_c = E_c[\{\epsilon_p\}, \{\langle pq \| rs \rangle\}]. \tag{13}$$

For the sake of simplicity, here and in the following it is assumed that the spin-orbitals are real. The labels $p, q, \ldots$ pertain to any HF spin-orbitals; $i, j, \ldots$ pertain to the occupied HF spin-orbitals; and $a, b, \ldots$ pertain to the virtual HF spin-orbitals.

Consider a real, one-electron perturbation $\chi \mathbf{Q}$. The first-order derivative of E_c with respect to χ equals

$$E_c^\chi \equiv (\partial E_c / \partial \chi)_{|\chi=0}$$

$$= \sum_p A_p \epsilon_p^\chi + \sum_{pqrs} B_{pqrs} (\langle p^\chi q \| rs \rangle + \langle pq^\chi \| rs \rangle$$

$$+ \langle pq \| r^\chi s \rangle + \langle pq \| rs^\chi \rangle), \tag{14}$$

where

$$A_p \equiv \partial E_c / \partial \epsilon_p \quad \text{and} \quad B_{pqrs} \equiv \partial E_c / \partial \langle pq \| rs \rangle. \tag{15}$$

Thanks to the antisymmetry of both the tensor $\mathbf{B}$ and the double-bar integrals, Eq. (14) can be simplified to

$$E_c^\chi = \sum_p A_p \epsilon_p^\chi + 2\sum_{pqrs} B_{pqrs}(\langle p^\chi q\|rs\rangle + \langle pq\|r^\chi s\rangle). \tag{16}$$

Since

$$|p^\chi\rangle = \sum_q U_{qp}^\chi |q\rangle, \tag{17}$$

where the matrix $\mathbf{U}^\chi$ has the property[12]

$$U_{qp}^\chi = -U_{pq}^\chi, \tag{18}$$

Eq. (16) can be rewritten as

$$E_c^\chi = \sum_p A_p \epsilon_p^\chi + 2\sum_{pw}(D_{pw}-D_{wp})U_{wp}^\chi, \tag{19}$$

with

$$D_{pw} \equiv \sum_{qrs} B_{pqrs}\langle wq\|rs\rangle. \tag{20}$$

The derivatives ϵ^χ and $\mathbf{U}^\chi$ are related to $\mathbf{Q}$ through the coupled perturbed Hartree–Fock (CPHF) equations.[13] In particular[12]

$$U_{ai}^\chi = \sum_{bj}(\mathbf{R}^{-1})_{ai,bj}Q_{bj}(\epsilon_j-\epsilon_b)^{-1} \tag{21}$$

where

$$R_{ai,bj} = \delta_{ai,bj} + [\langle ab\|ij\rangle + \langle aj\|ib\rangle](\epsilon_a-\epsilon_i)^{-1}, \tag{22}$$

for the virtual–occupied block of $\mathbf{U}^\chi$, whereas

$$U_{ki}^\chi = -(1-\delta_{ki})(\epsilon_k-\epsilon_i)^{-1}$$
$$\times\left[Q_{ki} + \sum_{gm} U_{gm}^\chi(\langle km\|ig\rangle + \langle kg\|im\rangle)\right] \tag{23}$$

and

$$U_{fa}^\chi = -(1-\delta_{fa})(\epsilon_f-\epsilon_a)^{-1}$$
$$\times\left[Q_{fa} + \sum_{gm} U_{gm}^\chi(\langle fm\|ag\rangle + \langle fg\|am\rangle)\right], \tag{24}$$

for the occupied–occupied and virtual–virtual blocks, respectively. The orbital energy derivatives equal[12]

$$\epsilon_p^\chi = Q_{pp} + 2\sum_{gm} U_{gm}^\chi\langle pm\|pg\rangle. \tag{25}$$

The energy-derivative $\mathbf{\Gamma}$ is a sum of the Hartree–Fock and electron-correlation contributions

$$\Gamma_{pq} = \nu_p\delta_{pq} + \Delta_{pq}, \tag{26}$$

the latter being given by [compare Eq. (19)]

$$\Delta_{rs} \equiv \partial E_c^\chi/\partial Q_{rs}$$
$$= \sum_p A_p(\partial\epsilon_p^\chi/\partial Q_{rs}^\chi)$$
$$+ 2\sum_{pw}(D_{pw}-D_{wp})(\partial U_{wp}^\chi/\partial Q_{rs}^\chi). \tag{27}$$

In Eq. (26), ν_p is the occupancy of ϕ_p (equal to either 0 or 1). Combining Eqs. (25) and (27), one obtains

$$\Delta_{rs} = A_r\delta_{rs} + 2\sum_{pgm} A_p(\partial U_{gm}^\chi/\partial Q_{rs}^\chi)\langle pm\|pg\rangle$$
$$+ 2\sum_{pw}(D_{pw}-D_{wp})(\partial U_{wp}^\chi/\partial Q_{rs}^\chi). \tag{28}$$

Consequently, [see Eqs. (21)–(24) and (28), note the factors of 1/2 where appropriate]

$$\Delta_{bj} = \Delta_{jb} = (\epsilon_j-\epsilon_b)^{-1}\sum_{ai}(\mathbf{R}^{-1})_{ai,bj}Z_{ai} \tag{29}$$

where

$$Z_{ai} = 2(D_{ia}-D_{ai}) + \sum_p A_p\langle pi\|pa\rangle + 2\sum_{kl}(1-\delta_{kl})$$
$$\times(\epsilon_l-e_k)^{-1}(D_{lk}-D_{kl})\langle ki\|la\rangle + 2\sum_{gf}(1-\delta_{fg})$$
$$\times(\epsilon_g-\epsilon_f)^{-1}(D_{gf}-D_{fg})\langle fi\|ga\rangle, \tag{30}$$

for the virtual–occupied block of $\mathbf{\Gamma}$. Similarly, one arrives at

$$\Delta_{ki} = A_k\delta_{ki} + 2(1-\delta_{ki})(\epsilon_i-\epsilon_k)^{-1}(D_{ik}-D_{ki}) \tag{31}$$

and

$$\Delta_{fa} = A_f\delta_{fa} + 2(1-\delta_{fa})(\epsilon_a-\epsilon_f)^{-1}(D_{af}-D_{fa}), \tag{32}$$

for the occupied–occupied and virtual–virtual blocks, respectively. One should note that the electron-conservation sum rule

$$\sum_i \Delta_{ii} + \sum_a \Delta_{aa} = 0, \tag{33}$$

implies that

$$\sum_p A_p = 0. \tag{34}$$

An analogous derivation that invokes real two-electron perturbations leads in a straightforward manner to the expression for the energy-derivative $\boldsymbol{\gamma}$, which reads

$$\gamma_{pqrs} = (1/2)\delta_{pr}\delta_{qs}\nu_p\nu_q + (1/2)(\delta_{pr}\nu_p\Delta_{qs} + \delta_{qs}\nu_q\Delta_{pr})$$
$$+ B_{pqrs}. \tag{35}$$

The sum rule [compare Eqs. (4) and (6)]

$$\Gamma_{pr} = 2(N-1)^{-1}\sum_q(\gamma_{pqrq}-\gamma_{pqqr}), \tag{36}$$

is not satisfied unless [compare Eqs. (31) and (32), note the antisymmetry of $\mathbf{B}$]

$$\sum_q B_{pqrq} = (1/4)(\nu_p+\nu_r-1)\Delta_{pr} \tag{37}$$

or

$$\sum_q B_{aqiq} = \sum_q B_{iqaq} = 0, \tag{38a}$$

$$\sum_q B_{aqbq} = -(1/4)A_a\delta_{ab} - (1/2)(1-\delta_{ab})$$

$$\times (\epsilon_b - \epsilon_a)^{-1}(D_{ba} - D_{ab}), \tag{38b}$$

$$\sum_q B_{iqjq} = (1/4)A_i\delta_{ij} + (1/2)(1-\delta_{ij})$$

$$\times (\epsilon_j - \epsilon_i)^{-1}(D_{ji} - D_{ij}). \tag{38c}$$

One should note that the conditions (38) are violated by methods such as MP2 and CCSD. Consequently, the energy-derivative 2-matrices produced by those methods do not sum up to the number of electron pairs $(1/2)N(N-1)$.

IV. THE GENERALIZED FOCK MATRIX (THE LAGRANGIAN) AND ITS DIAGONALIZATION

With the $\mathbf{\Gamma}$ and $\mathbf{\gamma}$ furnished by above formalism, the generalized Fock matrix (the Lagrangian) $\mathbf{F}$ can be constructed for any approximate electron-correlation method for which the energy gradients are available. Combining Eqs. (5), (26), and (35) yields

$$F_{pq} = \sum_r h_{pr}\Gamma_{qr} + 2\sum_{trs} \gamma_{qrst}\langle pr\|st\rangle$$

$$= \sum_r h_{pr}(\nu_q\delta_{qr} + \Delta_{qr}) + \sum_{rst} (\delta_{qs}\delta_{rt}\nu_q\nu_r$$

$$+ \delta_{qs}\nu_q\Delta_{rt} + \delta_{rt}\nu_r\Delta_{qs})\langle pr\|st\rangle$$

$$+ 2\sum_{rst} B_{qrst}\langle pr\|st\rangle$$

$$= \nu_q h_{pq} + \sum_r h_{pr}\Delta_{qr} + \nu_q\sum_r \nu_r\langle pr\|qr\rangle$$

$$+ \nu_q\sum_{rt} \Delta_{rt}\langle pr\|qt\rangle + \sum_{rs} \nu_r\Delta_{qs}\langle pr\|sr\rangle + 2D_{qp}$$

$$= \nu_q\left(h_{pq} + \sum_r \nu_r\langle pr\|qr\rangle\right)$$

$$+ \sum_s \Delta_{qs}\left(h_{ps} + \sum_r \nu_r\langle pr\|sr\rangle\right)$$

$$+ \nu_q\sum_{rt} \Delta_{rt}\langle pr\|qt\rangle + 2D_{qp}. \tag{39}$$

The substitution

$$\epsilon_p\delta_{pq} = h_{pq} + \sum_r \nu_r\langle pr\|qr\rangle, \tag{40}$$

produces the final expression for $\mathbf{F}$ that reads

$$F_{pq} = \nu_q\epsilon_p\delta_{pq} + \epsilon_p\Delta_{qp} + \nu_q\sum_{rt} \Delta_{rt}\langle pr\|qt\rangle + 2D_{qp}. \tag{41}$$

Thus, in practical implementations of the EKT formalism, $\mathbf{F}$ can be assembled from the 1-matrix $\mathbf{\Gamma}$, the set $\{\langle pq\|rs\rangle\}$ of antisymmetrized two-electron integrals, and the intermediate matrix $\mathbf{D}$ that is itself employed in the construction of $\mathbf{\Gamma}$. Entering the expression for the first derivative of the electronic energy with respect to nuclear displacements,[3,12] F is a by-product of energy-gradient calculations that can be readily reutilized in conjunction with the EKT formalism. If desired, the matrix $\widetilde{\mathbf{F}}$ [Eq. (12)] can be computed from $\mathbf{F}$ in a single step.

Unlike that derived from truncated CI wave functions,[4,5] the Lagrangian defined in Eq. (41) is always Hermitian (see the Appendix). On the other hand, positive-definiteness of the energy-derivative approximations to $\mathbf{\Gamma}$ [Eqs. (26) and (29)–(32)] cannot be guaranteed and is commonly violated in actual calculations. For this reason, it is impractical to solve Eq. (3) by transforming it to the equivalent eigenproblem

$$\mathbf{fc} + e_1\mathbf{c} = 0 \tag{42}$$

where

$$\mathbf{f} \equiv \mathbf{\Gamma}^{-1/2}\mathbf{F}\mathbf{\Gamma}^{-1/2} \quad \text{and} \quad \mathbf{c} \equiv \mathbf{\Gamma}^{1/2}\mathbf{C}, \tag{43}$$

as advocated in some publications on EKT.[5,8] Instead, it is computationally expedient to transform both $\mathbf{\Gamma}$ and $\mathbf{F}$ to the basis of natural spin–orbitals (in which $\mathbf{\Gamma}$ is diagonal), discard the rows and columns that correspond to negative occupation numbers, and then diagonalize the truncated $\mathbf{f}$ to obtain approximate e_1 and the other members of the set $\{e_i\}$. These approximations are then used as a starting points for final calculations in which $\{e_i\}$ are computed as the roots of the polynomial

$$W(x) \equiv \det(\mathbf{F} - x\mathbf{\Gamma}). \tag{44}$$

Once $\{e_i\}$ are available, the corresponding vectors $\mathbf{C}$ can be easily evaluated.

As one can easily conclude from the arguments presented in Sec. II of this paper, IPs produced by the EKT formalism are variational with respect to the one-electron basis of spin–orbitals, i.e., are bound to decrease with increasing quality of basis sets from which these spin–orbitals are constructed. By the same token, IPs computed from Lagrangians and 1-matrices derived from CI and MC SCF wave functions constitute upper bounds to their exact counterparts. Obviously, this property is not shared by IPs calculated from the energy-derivative quantities.

V. NUMERICAL TESTING

The aforedescribed EKT formalism has been implemented in the GAUSSIAN 94[14] suite of programs. Ionization potentials of a large number of molecules have been computed from Lagrangians and 1-matrices obtained within the MP2, MP3, MP4SDQ, and QCISD approximate electron correlation treatments. Selected results of these EKTMP2, EKTMP3, EKTMP4SDQ, and EKTQCISD calculations are presented together with their EPT2 and EPT3 counterparts in Tables I–III.

Inspection of IPs of several small molecules reveals that, despite its considerably lower computational cost, the EK-

TABLE I. Ionization potentials of selected small molecules.[a]

Mol.	Hole state	Ionization potential [eV]							
		KT	EPT2	EPT3	EKTMP2	EKTMP3	EKTMP4SDQ	EKTQCISD	Exp.[b]
CH_4	t_2	14.85	14.11	14.42	13.92	14.45	14.55	14.56	14.4
			(0.920)	(0.929)	(0.928)	(0.928)	(0.930)	(0.931)	
	a_1	25.70	23.43	23.59	23.88	24.25	24.37	24.26	23.0
			(0.879)	(0.868)	(0.914)	(0.905)	(0.902)	(0.893)	
NH_3	a_1	11.60	10.17	11.01	10.10	11.06	11.01	11.02	10.8
			(0.900)	(0.931)	(0.918)	(0.930)	(0.928)	(0.926)	
	e	16.97	15.99	16.67	15.87	16.68	16.65	16.67	16.8
			(0.913)	(0.938)	(0.924)	(0.934)	(0.931)	(0.931)	
H_2O	b_1	13.73	11.51	13.08	11.70	13.02	12.78	12.84	12.78
			(0.894)	(0.942)	(0.918)	(0.939)	(0.930)	(0.930)	
	a_1	15.72	13.82	15.29	13.93	15.20	14.91	14.99	14.83
			(0.900)	(0.944)	(0.918)	(0.939)	(0.928)	(0.928)	
	b_2	19.31	18.18	19.24	18.18	19.15	18.97	19.04	18.72
			(0.915)	(0.948)	(0.924)	(0.942)	(0.932)	(0.935)	
HF	π	17.50	14.71	16.83	15.10	16.60	16.21	16.31	16.19
			(0.902)	(0.951)	(0.922)	(0.946)	(0.933)	(0.934)	
	σ	20.69	18.95	20.49	19.11	20.27	19.96	20.06	19.9
			(0.917)	(0.952)	(0.927)	(0.947)	(0.934)	(0.936)	
N_2	σ_g	17.21	15.06	15.94	14.90	16.30	15.91	16.02	15.60
			(0.885)	(0.932)	(0.922)	(0.937)	(0.927)	(0.928)	
	π_u	16.66	17.17	16.64	16.88	17.16	17.23	17.20	16.68
			(0.917)	(0.929)	(0.926)	(0.933)	(0.934)	(0.932)	
	σ_u	21.15	18.15	19.74	18.47	20.13	19.51	19.67	18.78
			(0.850)	(0.915)	(0.909)	(0.927)	(0.910)	(0.911)	
CO	σ	15.06	14.04	13.96	13.55	14.33	14.13	14.22	14.01
			(0.914)	(0.921)	(0.933)	(0.928)	(0.922)	(0.921)	
	π	17.39	16.48	17.44	16.61	17.41	17.45	17.45	16.85
			(0.887)	(0.926)	(0.905)	(0.929)	(0.923)	(0.923)	
	σ	21.87	18.46	21.63	19.36	21.26	20.30	20.63	19.78
			(0.849)	(0.951)	(0.903)	(0.937)	(0.902)	(0.911)	
C_2H_2	π_u	11.15	11.33	11.27	10.95	11.53	11.63	11.58	11.49
			(0.907)	(0.922)	(0.909)	(0.920)	(0.930)	(0.925)	
	σ_g	18.51	16.75	17.46	16.71	17.63	17.43	17.43	16.7
			(0.878)	(0.916)	(0.925)	(0.926)	(0.913)	(0.905)	
	σ_u	20.87	18.67	19.20	18.79	19.79	19.42	19.40	18.7
			(0.855)	(0.893)	(0.913)	(0.914)	(0.895)	(0.877)	
H_2CO	b_2	12.16	9.75	11.68	10.09	11.56	10.70	10.90	10.9
			(0.874)	(0.939)	(0.914)	(0.936)	(0.888)	(0.879)	
	b_1	14.17	13.75	14.39	13.69	14.40	14.52	14.54	14.5
			(0.886)	(0.911)	(0.892)	(0.912)	(0.907)	(0.906)	
	b_1	17.30	14.76	16.80	15.15	16.73	16.04	16.23	16.1
			(0.864)	(0.936)	(0.904)	(0.931)	(0.901)	(0.904)	
	b_2	19.34	17.16	18.28	17.52	18.44	18.06	18.19	17.0
			(0.855)	(0.907)	(0.924)	(0.929)	(0.902)	(0.899)	
	b_1	23.90	21.49	22.29	21.86	22.73	22.48	22.53	21.4
			(0.865)	(0.893)	(0.924)	(0.926)	(0.915)	(0.913)	

[a]All ionization potentials calculated with the cc-pVTZ basis set at the following experimental geometries: CH_4: $R_{CH} = 1.085$ Å; NH_3: $R_{NH} = 1.012$ Å, $\alpha_{HNH} = 106.67°$; H_2O: $R_{OH} = 0.957$ Å, $\alpha_{HOH} = 104.52°$; HF: $R_{HF} = 0.917$ Å; N_2: $R_{NN} = 1.098$ Å; CO: $R_{CO} = 1.128$ Å; C_2H_2: $R_{CC} = 1.203$ Å, $R_{CH} = 1.061$ Å; H_2CO: $R_{CO} = 1.230$ Å, $R_{CH} = 1.060$ Å, $\alpha_{HCO} = 117.1°$ (Ref. 15). Pole strengths are given in parentheses.
[b]Reference 8.

TMP2 approach rivals the EPT2 method in accuracy. In particular, out of the 23 EKTMP2/cc-pVTZ IPs listed in Table I, 12 are more accurate than their EPT2/cc-pVTZ counterparts, 10 are less accurate, and one is approximately the same. In all instances, improvements over the predictions based upon the Koopmans' theorem (KT), including the restoration of the proper energy ordering in the case of the N_2 molecule, are observed. As far as the lowest IPs are concerned, the EPT3 and EKTMP3 methods are also comparable in accu-

racy, but the performance of the latter formalism is mixed for the higher IPs. The same is true about the EKTQCISD/cc-pVTZ-level of theory, at which the experimental values of the lowest IPs are reproduced within less than 0.25 eV (with the exception of N_2 for which the discrepancy amounts to 0.42 eV), whereas the errors for the higher IPs vary widely from less than 0.35 eV for NH_3, H_2O, N_2 (the lower IP), HF and H_2CO (the lower IPs) to ~1 eV for CH_4, N_2 (the higher IP), CO, C_2H_2, and H_2CO (the higher IPs).

TABLE II. Ionization potentials of the benzene molecule.[a]

Hole state	Ionization potential [eV]							
	KT	EPT2	EPT3	EKTMP2	EKTMP3	EKTMP4SDQ	EKTQCISD	Exp.[b]
e_{1g}	8.95	8.66 (0.889)	8.86 (0.908)	9.10 (0.925)	9.72 (0.937)	9.55 (0.934)	9.58 (0.930)	9.25
e_{2g}	13.27	11.30 (0.876)	12.23 (0.919)	11.64 (0.923)	12.71 (0.935)	12.55 (0.927)	12.58 (0.926)	11.53
a_{2u}	13.43	11.64 (0.834)	12.27 (0.831)	12.40 (0.917)	13.46 (0.940)	13.42 (0.942)	13.45 (0.940)	12.38
e_{1u}	15.80	13.55 (0.861)	14.55 (0.904)	14.08 (0.919)	15.10 (0.932)	15.00 (0.926)	15.03 (0.926)	13.98
b_{2u}	16.59	13.64 (0.834)	15.14 (0.902)	14.99 (0.917)	16.42 (0.945)	16.24 (0.942)	16.24 (0.942)	14.86
b_{1u}	17.38	15.14 (0.856)	15.67 (0.885)	15.67 (0.921)	16.50 (0.929)	16.46 (0.924)	16.47 (0.922)	15.46
a_{1g}	19.08	16.45 (0.834)	17.56 (0.876)	17.34 (0.915)	18.35 (0.934)	18.35 (0.934)	18.38 (0.934)	16.84

[a]All ionization potentials calculated with the 6-31G** basis set at the experimental geometry (R_{CC}= 1.397 Å, R_{CH}= 1.084 Å) (Ref. 15). Pole strengths are given in parentheses.
[b]Reference 16.

The data obtained from calculations on aromatic hydrocarbons are even more encouraging. In the case of benzene (Table II), the EKTMP2/6-31G** IPs are more accurate than the results of both the OVGF/cc-pVDZ and P3/cc-pVDZ calculations reported by Ortiz.[22] It should be noted, however, that favorable cancellation of errors is partially responsible for the close agreement between the EKTMP2/6-31G** and experimental IPs, as indicated by the worsening of accuracy

TABLE III. Ionization potentials of selected polycyclic aromatic hydrocarbons.[a]

Molecule	Hole state	Ionization potential [eV]		
		KT	EKTMP2	Exp.
benzene	e_{1g}	8.96	9.11 (0.925)	9.25[b] 9.24[c,d]
	e_{2g}	13.28	11.65 (0.923)	11.53[b]
	a_{2u}	13.46	12.42 (0.917)	12.38[b] 12.25[c,d]
	e_{1u}	15.82	14.10 (0.919)	13.98[b]
	b_{2u}	16.61	15.01 (0.917)	14.86[b]
	b_{1u}	17.39	15.68 (0.921)	15.46[b]
	a_{1g}	19.11	17.38 (0.915)	16.84[b]
naphthalene	a_u	7.66	8.02 (0.923)	8.15[c,d,e] 8.14[f]
	b_{1u}	8.51	8.84 (0.920)	8.87[c] 8.88[d]
	b_{2g}	10.33	10.02 (0.919)	10.08[c] 10.10[d]
	b_{3g}	12.01	11.12 (0.924)	10.83[c]
anthracene	b_{2g}	6.81	7.34 (0.919)	7.41[c] 7.40[d]
	b_{3g}	8.27	8.72 (0.917)	8.54[c] 8.52[d]
	a_u	9.27	9.24 (0.922)	9.19[c] 9.16[d]
	b_{2g}	10.90	10.31 (0.913)	10.18[c] 10.13[d]
	b_{1u}	11.06	10.56 (0.918)	10.28[c] 10.21[d]
phenanthrene	b_1	7.52	7.91 (0.921)	7.86[c]
	a_2	7.86	8.26 (0.919)	8.15[c]
	a_2	9.38	9.36 (0.917)	9.28[c]
	b_1	10.25	10.04 (0.918)	9.89[c]
	b_1	11.53	10.93 (0.920)	10.59[c]
pyrene	b_{3g}	6.87	7.40 (0.917)	7.41[g]
	b_{2g}	7.95	8.45 (0.916)	8.26[g]
	b_{1u}	9.25	9.12 (0.918)	9.00[g]
	a_u	9.77	9.61 (0.914)	9.29[g]
	b_{1u}	10.84	10.41 (0.918)	9.96[g]

[a]All ionization potentials calculated with the 6-31G** basis set at the MP2/6-31G** optimized geometries. Pole strengths are given in parentheses.
[b]Reference 16.
[c]Reference 17.
[d]Reference 18.
[e]Reference 19.
[f]Reference 20.
[g]Reference 21.

upon improvement of the electron correlation treatment (see the EKTMP3, EKTMP4SDQ, and EKTQCISD entries in Table II). In light of the variational properties of the EKT formalism discussed in the previous section of this paper, the use of better basis sets is bound to alleviate this problem.

The excellent accuracy of the EKTMP2/6-31G** predictions for IPs of benzene carries over to polycyclic benzenoid hydrocarbons. IPs computed as by-products of MP2/6-31G** geometry optimizations of naphthalene, anthracene, phenanthrene, and pyrene, which are compiled in Table III, reproduce the respective experimental values within 0.2 eV in most cases. Comparison of this data with the previously published results of the OVGF/cc-pVDZ and P3/cc-pVDZ calculations on naphthalene and anthracene[23] reveals that accuracy of the EKTMP2 method matches that of much more expensive approaches.

VI. DISCUSSION AND CONCLUSIONS

The combination of the extended Koopmans' theorem and the energy-derivative formalism for density matrices produces a versatile methodology for calculation of ionization potentials and electron affinities. Such a methodology possesses some resemblance to the EOM formalism but, being applicable to any level of electron correlation treatment, is more general. Like the electron propagator theory, the present approach provides a one-electron description of the electron attachment–detachment processes that is advantageous from the interpretive point of view. However, EKT calculations produce IPs of comparable accuracy at a substantially lower computational cost.

With the MP2 approach fast becoming the method of choice for calculations of geometries and energetics of medium- and large-size organic molecules, the EKTMP2 formalism is certain to replace the Koopmans' theorem as the ''black box'' estimator of ionization potentials. The use of higher levels of theory, such as EKTMP4 or EKTCCSD(T), will make it possible to compute the lowest IPs with very high accuracy. Because of the minimal computational effort involved, now it makes sense to couple every geometry optimization with the evaluation of IPs.

In principle, as demonstrated in Secs. II and IV of this paper, an analogous methodology can be applied to the computation of electron affinities. Research in this direction is currently in progress.

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APPENDIX

Although the r.h.s. of Eq. (41) is not manifestly symmetrical with respect to the permutation of the indices p and q, it is straightforward to prove that $\mathbf{F}^T = \mathbf{F}$ (or in the general case of complex spin–orbitals that $\mathbf{F}$ is Hermitian). To do that, consider

$$F_{pq} - F_{qp} = \Delta_{qp}(\epsilon_p - \epsilon_q) + (\nu_q - \nu_p)\sum_{rt} \Delta_{rt}\langle pr\|qt\rangle$$
$$+ 2(D_{qp} - D_{pq}). \tag{A1}$$

Substituting Eq. (31) into the above expression, one obtains for the occupied–occupied block

$$F_{ik} - F_{ki} = \Delta_{ki}(\epsilon_i - \epsilon_k) + 2(D_{ki} - D_{ik})$$
$$= [A_k \delta_{ki} + 2(1 - \delta_{ki})(\epsilon_i - \epsilon_k)^{-1}(D_{ik} - D_{ki})]$$
$$\times (\epsilon_i - \epsilon_k) + 2(D_{ki} - D_{ik}) = 0. \tag{A2}$$

Similarly, for the virtual–virtual block [compare Eq. (32)]

$$F_{af} - F_{fa} = \Delta_{fa}(\epsilon_a - \epsilon_f) + 2(D_{fa} - D_{af})$$
$$= [A_f \delta_{fa} + 2(1 - \delta_{fa})(\epsilon_a - \epsilon_f)^{-1}(D_{af} - D_{fa})]$$
$$\times (\epsilon_a - \epsilon_f) + 2(D_{fa} - D_{af}) = 0. \tag{A3}$$

Finally, combining Eqs. (22), (29)–(32), and (41), one obtains for the virtual–occupied block

$$F_{jb} - F_{bj} = \Delta_{bj}(\epsilon_j - \epsilon_b) + (\nu_b - \nu_j)\sum_{rt} \Delta_{rt}\langle jr\|bt\rangle$$
$$+ 2(D_{bj} - D_{jb})$$
$$= \sum_{ai} (\mathbf{R}^{-1})_{ai,bj}Z_{ai} - \sum_{ki} \Delta_{ki}\langle jk\|bi\rangle$$
$$- \sum_{fa} \Delta_{fa}\langle jf\|ba\rangle - \sum_{b'j'}\Delta_{b'j'}(\langle jb'\|bj'\rangle$$
$$+ \langle jj'\|bb'\rangle) + 2(D_{bj} - D_{jb})$$
$$= \sum_{ai} (\mathbf{R}^{-1})_{ai,bj}Z_{ai} - \sum_{ki} [A_k \delta_{ki}$$
$$+ 2(1 - \delta_{ki})(\epsilon_i - \epsilon_k)^{-1}(D_{ik} - D_{ki})]\langle jk\|bi\rangle$$
$$- \sum_{fa} [A_f \delta_{fa} + 2(1 - \delta_{fa})(\epsilon_a - \epsilon_f)^{-1}$$
$$\times (D_{af} - D_{fa})]\langle jf\|ba\rangle - \sum_{ai}\sum_{b'j'} (\epsilon_{j'} - \epsilon_{b'})^{-1}$$
$$\times (\mathbf{R}^{-1})_{ai,b'j'}(\langle jb'\|bj'\rangle$$
$$+ \langle jj'\|bb'\rangle)Z_{ai} + 2(D_{bj} - D_{jb})$$
$$= \sum_{ai} (\mathbf{R}^{-1})_{ai,bj}Z_{ai} + \sum_{ai}\sum_{b'j'} (R_{b'j',bj} - \delta_{b'j',bj})$$
$$\times (\mathbf{R}^{-1})_{ai,b'j'}Z_{ai} - 2\sum_{ki} (1 - \delta_{ki})(\epsilon_i - \epsilon_k)^{-1}$$
$$\times (D_{ik} - D_{ki})\langle jk\|bi\rangle - 2\sum_{fa} (1 - \delta_{fa})$$

$$\times (\epsilon_a - \epsilon_f)^{-1}(D_{af} - D_{fa})\langle jf \| ba \rangle$$

$$+ 2(D_{bj} - D_{jb}) - \sum_p A_p \langle jp \| bp \rangle$$

$$= \sum_{ai} \sum_{b'j'} R_{b'j',bj}(\mathbf{R}^{-1})_{ai,b'j'} Z_{ai} - Z_{bj} = 0, \quad (A4)$$

which completes the proof.

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