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Assessment of transition operator reference states in electron propagator calculations

Roberto Flores-Moreno,[a] V. G. Zakrzewski,[b] and J. V. Ortiz[c]

Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849-5312, USA

The transition operator method combined with second-order, self-energy corrections to the electron propagator (TOEP2) may be used to calculate valence and core-electron binding energies. This method is tested on a set of molecules to assess its predictive quality. For valence ionization energies, well known methods that include third-order terms achieve somewhat higher accuracy, but only with much higher demands for memory and arithmetic operations. Therefore, we propose the use of the TOEP2 method for the calculation of valence electron binding energies in large molecules where third-order methods are infeasible. For core-electron binding energies, TOEP2 results exhibit superior accuracy and efficiency and are relatively insensitive to the fractional occupation numbers that are assigned to the transition orbital. © *2007 American Institute of Physics.*
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I. INTRODUCTION

Koopmans's theorem (KT) is useful when calculating ionization potentials and electron affinities.[1] However, unbalanced error cancellations may occur in this approximation. On one side, it neglects electron correlation and, on the other, final-state orbital relaxation effects are ignored. For valence ionization energies, these corrections usually are opposite in sign, but in many cases the cancellation of errors is poor. Relaxation effects may be included by using the ΔE_{SCF} method,[2] in which Hartree-Fock calculations are performed on initial and ionized states. However, this approach and its correlated generalizations that involve subtraction of two large total energies have computational and conceptual disadvantages. Electron propagator theory[3–5] provides a direct alternative for the calculation of ionization energies and electron affinities.

Perturbative electron propagator methods that are based on Hartree-Fock reference states generate corrections to KT that take correlation and relaxation effects into account.[6] From an analysis of the second-order approximation to the electron propagator, Pickup and Goscinski[6] concluded that "upon ionization of an electron in spin-orbital k, the ionization energy described in the lowest order by ϵ_k is corrected by reorganization effects of the remaining spin orbitals." They also concluded that the second-order electron propagator includes "changes in pair correlation energies due to reorganization." Thus, approximate electron propagators include correlation and relaxation corrections.

Systematic improvements in electron propagator approximations produce improved results for ionization potentials. However, these improvements may require lengthy calculations or large quantities of memory.[7] For example, the diagonal, third-order approximation [and therefore the outer valence Green function (OVGF) methods[4] as well] requires a step with ov^4 arithmetic scaling (where o and v are, respectively, the number of occupied and virtual spin orbitals) and its self-energy formulae depend on the full set of transformed two-electron repulsion integrals.[7] Even the diagonal, partial third-order method (P3) for ionization energies has an o^2v^3 step and calls for transformed integrals with one occupied and three virtual indices in its rate-limiting contraction.[8] A method of comparable accuracy with less than fifth-power arithmetic dependence on molecular size and without the need for a full transformation of electron repulsion integrals to the Hartree-Fock orbital basis would widen the scope of applications in a significant manner.

A direct method which offers a simple way to recover most of the relaxation effects is also highly desirable. Such a method exists and is known as the transition operator method (TOM). The TOM is an uncorrelated, self-consistent field (SCF) procedure and is a special case of the grand-canonical Hartree-Fock method.[9] Correlated electron propagator corrections to the TOM have been considered previously.[10–13] In this work, we reexamine this idea for the second-order approximation to the electron propagator and compare the results with higher-order approximations that are widely used. It is shown that the TOM combined with the second-order electron propagator produces results that compete well with more computationally demanding approximations such as OVGF and P3. Thus, reliable treatment of much larger molecular systems may be realized using this approach.

In Sec. II, the theory of the TOM is described. Formulae, in a suitable form for programming, are also given. Section III presents some results of our implementation and compares them with normal electron propagator calculations. In Sec. IV, we conclude.

[a] Electronic mail: rflores@auburn.edu
[b] Electronic mail: vgz@auburn.edu
[c] Electronic mail: ortiz@auburn.edu

II. THEORY

The TOM was introduced first by Slater in Xα calculations.[14,15] Janak proved that this method can also be used more generally in density functional theory.[16,17] According to Janak's theorem,[18]

$$E_{N-1} - E_N = \int_0^1 \epsilon_i(n)\,dn, \tag{1}$$

where E_N and E_{N-1} are the energies of the N and $N-1$ electron systems and the integration variable n is the occupation number of the spin orbital that pertains to a given ionization energy or electron affinity. The simplest numerical approximation for this integral is a one-point quadrature,

$$\int_0^1 \epsilon_i(n)\,dn \approx \epsilon_i(1/2)(1-0) = \epsilon_i(1/2). \tag{2}$$

Obviously, this is not the most accurate numerical integration and one might consider using more points. For example, the unrestricted generalized transition state method proposed by Williams *et al.*[19] and extensively applied by Chong[20,21] involves a two point quadrature. A single-point quadrature has the benefit of yielding the ionization energy as a result of a single calculation. Furthermore, one gets a single reference system for further improvements such as those described below.

From a practical point of view, the TOM is realized by removing a fraction of an electron (in most cases $1/2$) from a given spin orbital. The resulting SCF produces molecular orbitals that resemble those of the initial (N electron) and final ($N-1$ electron) systems. When doing electron propagator calculations with TOM spin orbitals, fractional occupation numbers occur in the reference system. This choice results in modifications of the usual two-particle-one-hole ($2ph$) and two-hole-one-particle ($2hp$) contributions to the self-energy and addition of new terms that reflect the half-hole-half-particle description of the transition spin orbital. Derivations of electron propagator approximations have been expressed in terms of grand-canonical reference ensembles, of which the TOM is a special case.[10,12,13,22,23] (One, therefore, is calculating electron binding energies of a grand-canonical ensemble.) In the usual diagonal, second-order approximation to the electron propagator, the following equation has to be solved:

$$\omega_k = \epsilon_k + \sum_{q,s<t} \frac{|\langle kq \| st \rangle|^2 N_{qst}}{\omega_k + \epsilon_q - \epsilon_s - \epsilon_t}, \tag{3}$$

with

$$N_{qst} = n_q(1 - n_s - n_t) + n_s n_t, \tag{4}$$

where ϵ_q and n_q are, respectively, the energy and occupation number for spin orbital q. ω_k is the negative of the ionization energy for the case in which an electron is extracted from spin orbital k. Electron repulsion integrals are expressed in terms of Dirac notation where $\langle kq \| st \rangle = \langle kq | st \rangle - \langle kq | ts \rangle$. The indices q, s, and t label general spin orbitals. Indices i, j, and k are used for occupied spin orbitals; a and b are used for virtual spin orbitals. (Note that the transition orbital is grouped with the occupied orbitals, but it has a fractional occupation number.) Equation (3) is generally expressed in terms of the $2ph$ and $2hp$ contributions. For the case of integer occupation numbers (when the TOM is not used), the working formula is as follows:

$$\omega_k = \epsilon_k + \sum_{a,i<j} \frac{|\langle ka \| ij \rangle|^2}{\omega_k + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_{i,a<b} \frac{|\langle ki \| ab \rangle|^2}{\omega_k + \epsilon_i - \epsilon_a - \epsilon_b}. \tag{5}$$

The sums in Eq. (5) correspond to the $2hp$ and $2ph$ contributions. The N_{qst} constants of Eq. (3) are equal to unity for these contributions and to zero for any other. However, when the TOM is employed, the transition spin orbital has an occupation of $1/2$ and, therefore, the normalization constants for the $2ph$ and $2hp$ terms are not always equal to 1. Furthermore, contributions reflecting the partially occupied nature of the transition orbital occur such that

$$\omega_k = \epsilon_k + \sum_{a,i<j} \frac{|\langle ka \| ij \rangle|^2 n_i n_j}{\omega_k + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_{i,a<b} \frac{|\langle ki \| ab \rangle|^2}{\omega_k + \epsilon_i - \epsilon_a - \epsilon_b}$$
$$+ \sum_{a,i} \frac{|\langle ki \| ka \rangle|^2 (1 - n_k)}{\omega_k + \epsilon_i - \epsilon_k - \epsilon_a}. \tag{6}$$

The latter formula is valid for any choice of n_k between zero and unity, provided that k is the only fractionally occupied spin orbital. Note that a factor of n_i in the second term is not needed, for the term where $i=k$ vanishes. Pickup and Goscinski's classification of relaxation, polarization, and correlation terms remains intact,[6] except that relaxation contributions for an ionization energy in the first sum (where i or $j=k$) and for an electron affinity in the last sum of Eq. (6) are weighted by factors of n_k and $(1-n_k)$, respectively. With an initial guess of $\omega_k \approx \epsilon_k$, the first iteration of Eq. (6) yields

$$\omega_k = \epsilon_k + \sum_{a,i<j}^{i,j \neq k} \frac{|\langle ka \| ij \rangle|^2}{\epsilon_k + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_{i,a<b} \frac{|\langle ki \| ab \rangle|^2}{\epsilon_k + \epsilon_i - \epsilon_a - \epsilon_b}$$
$$+ (1 - 2n_k) \sum_{a,i} \frac{|\langle ki \| ka \rangle|^2}{\epsilon_i - \epsilon_a}. \tag{7}$$

As identified by Pickup and Goscinski, the last summation in Eq. (7) is a relaxation term. Note that it vanishes for $n_k = 1/2$. For $n_k \neq 1/2$, this term will tend to correct the inadequate treatment of relaxation in the reference TOM and will enhance (*vide infra*) the stability of the solution of Eq.

TABLE I. Ne ionization energies (eV).

Method	$1s$	$2s$	$2p$
KT	891.79	52.53	23.14
ΔE_{SCF}	868.35	49.20	19.70
TOM	868.16	49.10	19.54
Eq. (5)	866.22	46.98	19.96
Eq. (6)	868.93	48.34	20.97
Ref. 13	868.91	48.37	20.91
Expt.[a]	870.2	48.26	21.56

[a]See Ref. 26.

TABLE II. Ionization energies of atoms (eV).

Atom	Ionization	KT	EP2	EP3	OVGF	P3	TOEP2	Expt.[a]
Li	$^2S \rightarrow {}^1S$	5.34	5.35	5.35	5.35	5.35	5.35	5.39
Be	$^1S \rightarrow {}^2S$	8.42	8.89	9.03	9.23	8.84	8.89	9.32
B	$^2P \rightarrow {}^1S$	8.65	8.40	8.31	8.50	8.22	8.36	8.30
C	$^3P \rightarrow {}^2P$	11.91	11.30	11.25	11.35	11.10	11.25	11.26
N	$^4S \rightarrow {}^3P$	15.48	14.44	14.53	14.58	14.31	14.48	14.53
O	$^3P \rightarrow {}^4S$	14.15	12.93	13.42	13.39	13.07	13.04	13.62
F	$^2P \rightarrow {}^3P$	18.40	16.37	17.49	17.14	16.92	16.85	17.42
Ne	$^1S \rightarrow {}^2P$	23.00	20.12	22.07	21.44	21.21	21.03	21.56
Na	$^2S \rightarrow {}^1S$	4.96	4.98	5.00	5.00	4.98	4.98	5.14
Mg	$^1S \rightarrow {}^2S$	6.89	7.34	7.44	7.55	7.30	7.34	7.65
Al	$^2P \rightarrow {}^1S$	5.93	5.91	5.92	5.93	5.81	5.90	5.98
Si	$^3P \rightarrow {}^2P$	8.18	8.10	8.11	8.11	7.98	8.08	8.05
P	$^4S \rightarrow {}^3P$	10.65	10.49	10.48	10.48	10.35	10.49	10.49
S	$^3P \rightarrow {}^4S$	11.00	10.83	10.93	10.95	10.77	10.03	10.36
Cl	$^2P \rightarrow {}^3P$	13.05	12.58	12.74	12.74	12.58	12.70	12.97
Ar	$^1S \rightarrow {}^2P$	16.06	15.39	15.63	15.60	15.49	15.61	15.76
Average $|\Delta|$		0.50	0.36	0.16	0.15	0.28	0.23	

[a]See Ref. 35.

(6) with respect to the choice of fractional occupation number.

Only a partial integral transformation from the atomic basis is needed. Because all necessary integrals contain the index k, the transformation has a fourth-power scaling. Arithmetic operations in the evaluation of correlation corrections to the TOM orbital energy scale cubically. Therefore, the rate-limiting step has quartic scaling. The largest block of electron repulsion integrals, needed in the second term of Eq.

(6), requires memory that scales as ov^2. These arithmetic and memory advantages are procured at the price of repeating TOM calculations for each electron binding energy of interest.

In general, ionization energies are positive, i.e., the system is more stable with the electron included. Thus, removal of an electron fraction from a molecular spin-orbital makes the system less stable. In most cases, a higher orbital energy in the TOM calculation results. Although the optimal mo-

TABLE III. Valence ionization energies (eV).

Molecule	Orbital	KT	EP2	EP3	OVGF	P3	TOEP2	Expt.[a]
B_2H_6	$1b_{3g}$	12.85	12.21	12.30	12.36	12.14	12.30	11.9
CH_4	$1t_2$	14.80	14.07	14.37	14.32	14.22	14.34	14.40
C_2H_4	$1b_{3u}$	10.24	10.33	10.52	10.48	10.55	10.65	10.51
	$1b_{3g}$	13.77	12.75	13.17	13.06	12.98	13.00	12.85
	$3a_g$	15.94	14.48	14.98	14.77	14.89	14.94	14.66
	$1b_{2u}$	17.48	15.89	16.41	16.17	16.11	16.25	15.87
	$2b_{1u}$	21.52	19.34	19.79	19.61	19.44	19.69	19.23
HCN	1π	13.49	13.68	13.58	13.61	13.96	14.00	13.61
HNC	1π	14.13	13.74	14.11	14.02	14.11	14.11	12.55
NH_3	$3a_1$	11.60	10.17	11.01	10.74	10.73	10.65	10.8
N_2	$1\pi_u$	16.47	17.05	16.45	16.63	17.18	17.38	16.98
	$3\sigma_g$	17.17	15.02	15.92	15.35	15.93	15.47	15.60
	$2\sigma_u$	21.30	18.20	19.89	19.08	19.30	18.59	18.78
CO	5σ	15.09	14.06	13.98	13.85	14.27	14.13	14.01
	1π	17.28	16.37	17.36	17.07	17.04	16.88	16.91
H_2CO	$2b_2$	11.99	9.94	11.53	11.04	10.90	10.38	10.9
H_2O	$1b_1$	13.73	11.50	13.08	12.61	12.49	12.29	12.78
	$1a_1$	15.76	13.86	15.34	14.91	14.77	14.56	14.74
	$1b_2$	19.21	18.08	19.14	18.87	18.74	18.68	18.51
HF	1π	17.50	14.70	16.83	16.02	15.94	15.66	16.19
	3σ	20.68	18.94	20.48	19.84	19.84	19.64	20.00
F_2	$1\pi_g$	18.05	14.20	16.52	15.58	15.62	14.89	15.83
	$3\sigma_g$	20.46	20.46	21.15	21.00	21.04	21.06	21.1
	$1\pi_u$	22.05	17.35	20.12	19.01	18.89	18.10	18.8
Average $|\Delta|$		1.17	0.62	0.49	0.25	0.25	0.36	

[a]See Refs. 8 and 36 for geometry details and experimental values.
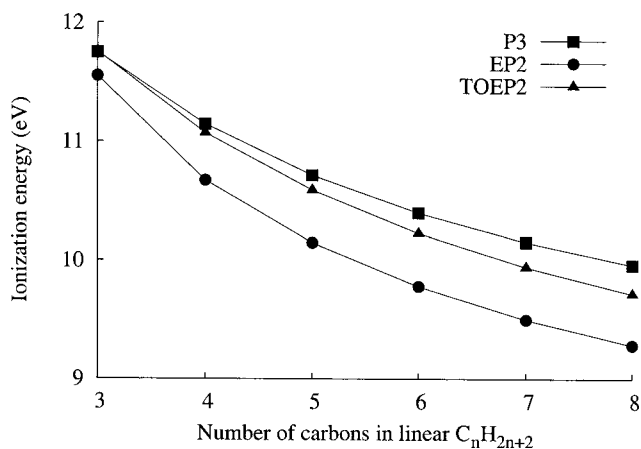
FIG. 1. Improvement of TOEP2 over EP2 for ionization energies of alkane chains.

FIG. 3. CEBEs for orbital 1s of N.

lecular orbitals of the system with all the electrons and the system with a fraction of an electron removed are very similar, they differ in spatial distribution and energy. In many cases, energy reordering will occur when the TOM is applied. In order to achieve correct TOM calculations, special care should be exercised to verify that the electron fraction is removed from the same orbital in every SCF iteration. However, the number label (energy position) of the transition orbital may change during the iterations. Correct assignments of occupation numbers to spin orbitals may be achieved in most cases by employing overlap criteria. If, for two consecutive iterations of the SCF, the molecular orbital coefficients are $\mathbf{C}^I$ and $\mathbf{C}^{I+1}$, the overlap between the molecular orbitals of the successive iterations is given by

$$\mathbf{M} = (\mathbf{C}^I)^\dagger \mathbf{S} \mathbf{C}^{I+1}, \tag{8}$$

where $\mathbf{S}$ is the atomic orbital overlap matrix. The matrix $\mathbf{M}$ differs from the identity matrix $\mathbf{I}$ in two respects: orbital ordering and small variations in element values. Denoting by $\mathbf{M}'$ the result of ordering $\mathbf{M}$ to obtain the maximum coincidence with the identity matrix, the difference

$$\Delta = \mathbf{M}' - \mathbf{I} \approx 0 \tag{9}$$

will be a matrix with only small values. The closer the SCF is to convergence, the smaller are the elements of this matrix. This principle is employed in assigning occupation numbers to orbitals after each SCF iteration.
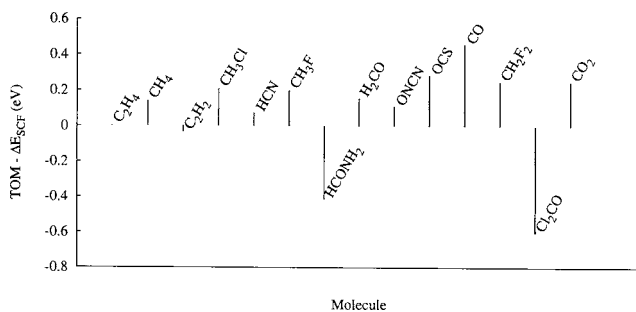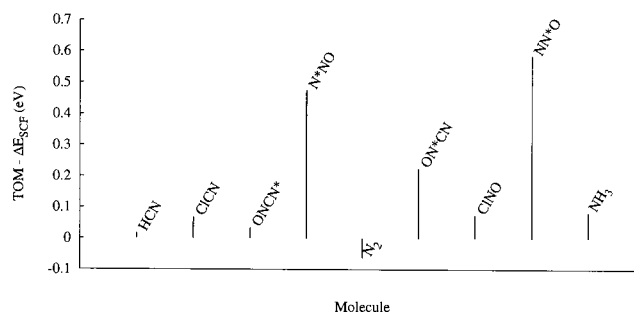
III. RESULTS AND DISCUSSION

All the calculations presented in this work were done with a new implementation of the TOM method and a modified version of the quasiparticle (diagonal self-energy) electron propagator programs in GAUSSIAN 03.[24] In all calculations presented below, the cc-pVTZ basis set[25] was used unless otherwise specified. All core orbitals were included in the electron propagator calculations.

In previous applications of the TOM with the electron propagator,[10,13] the ionization energies of the neon atom were reported. Here, we revisit this system with the same basis set used previously[13,26] as a validation of the new implementation (see Table I). The results of the TOM combined with the second-order electron propagator (TOEP2) improve over the normal electron propagator calculation by as much as 1 eV. Comparison of the first two rows of Table I shows that the relaxation energy amounts to more than 20 eV for the 1s case. This correction is much larger than its correlation counterpart. The ordinary second-order approximation to the electron propagator accounts for most of the relaxation. However, the TOM result is more accurate than the correlated value obtained with ordinary second order and is a reasonable zeroth-order choice for subsequent propagator improvements.

Only a few systems have been treated with the TOEP2 method.[10,13] A larger number of calculations are needed for a better estimation of quality. Due to its low arithmetic scaling properties, TOEP2 can be very useful in the treatment of large molecular systems. Furthermore, it is important to consider whether it is preferable to use approximations with third-order terms or instead to include relaxation with the TOM reference state. Because the answer to this question could depend on the nature of the ionization process, we focus first on valence ionizations. In Table II, the results for
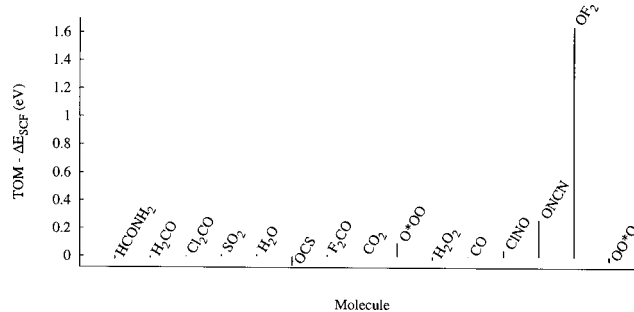

FIG. 2. CEBEs for orbital 1s of C.

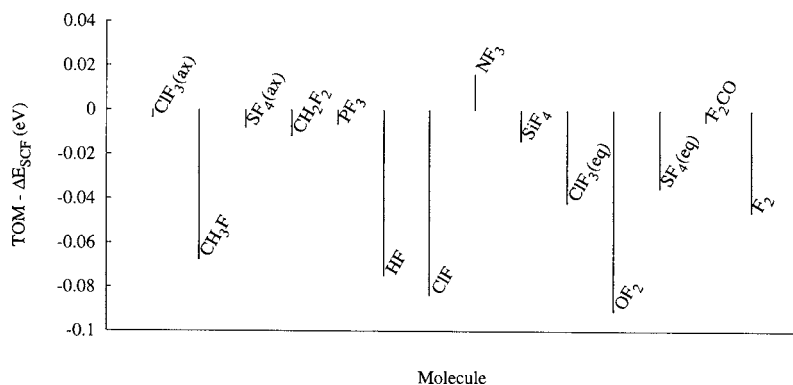
FIG. 4. CEBEs for orbital 1s of O.

FIG. 5. CEBEs for orbital $1s$ of F.

atomic first ionization energies are listed. The TOEP2 method is compared to widely used approximations of the electron propagator including second-order (EP2), third-order (EP3), P3, and OVGF methods. It appears that, for these systems, P3 does not offer a clear advantage over EP2. However, if only closed-shell systems are considered, it does. (Open shell P3 calculations are discussed in Ref. 27.) For the $2s$ and $3s$ shells, the use of TOEP2 does not offer any improvement over EP2. The advantage of the TOM reference is more important in noble-gas atoms. The accuracy of the TOEP2 method is much better than that of EP2 and even better than that of P3.

Calculation of atomic ionization potentials allows us to test the performance of TOEP2 on various elements. On the other hand, atoms are special cases, for they are small in spatial extent and have a central force potential. Tests on small molecular systems have greater relevance to potential applications on large systems. Table III shows the results for valence ionization energies of a set of closed-shell molecules. TOEP2 has a smaller average error than EP2 and EP3. However, for valence ionization energies of closed-shell molecules, P3 and OVGF are superior to TOEP2.

Although TOEP2 is outperformed by the P3 and OVGF methods, its accuracy is much better than that of EP2. In many applications to large molecules, a mean absolute deviation of 0.36 eV might be useful for making assignments of spectra, especially if the experimental error bars are of a comparable magnitude, and the TOEP2 may constitute a good compromise between accuracy and efficiency. For example, in Fig. 1 we compare the calculated ionization energies of alkane chains obtained with the P3 and second-order approximations. The accuracy of TOEP2 is very close to that of P3. The relaxation correction to the second-order approximation is as much as 0.4 eV for pentane and larger alkanes. Unlike EP2, TOEP2 can be used as a reliable method for the calculation of electron binding energies in large molecules. P3 and OVGF methods are more accurate but have a fifth-power arithmetic scaling. Therefore, among the diagonal approximations to the electron propagator, TOEP2 offers an attractive compromise between accuracy and computational cost in the treatment of large systems.

To evaluate the performance of TOEP2 on core-electron binding energies (CEBEs), we calculate the $1s$ ionization energies on a test set of molecules with C, N, O, and F nuclei.[20] Experimental geometries[28,29] are used and comparisons are made to experimental CEBEs.[30] The CEBEs under consider-

ation are of the order of hundreds of eVs. Relaxation energies are more than 10 eV. Therefore, if one could recover 90% of the relaxation energy, the remaining error would still be about 1 eV. (In many experiments, the error bars are approximately this large.) Thus, correct treatment of relaxation becomes crucial in the calculation of CEBEs. In the application of TOM, care should be taken to recover the relaxation energy in an accurate way. In most cases, an occupation number of $1/2$ for the transition orbital will suffice. However, there are cases where considerable errors are introduced by this choice. For example, Fig. 2 shows discrepancies between TOM and ΔE_{SCF} results for C $1s$ ionization energies exceeding 0.3 eV in several cases. Figures 3–5 show the corresponding data for the $1s$ orbitals of N, O, and F, respectively. For the O $1s$ ionization energy in OF_2, TOM and ΔE_{SCF} differ by 1.6 eV. In general, TOM results are sensitive to transition-orbital occupation numbers.

Fortunately, as can be deduced from Eq. (7), the results of the TOEP2 method are not as sensitive to the choice of the fractional occupation number. For example, the optimum occupation number for the case of the $1s$ orbital of OF_2 is about
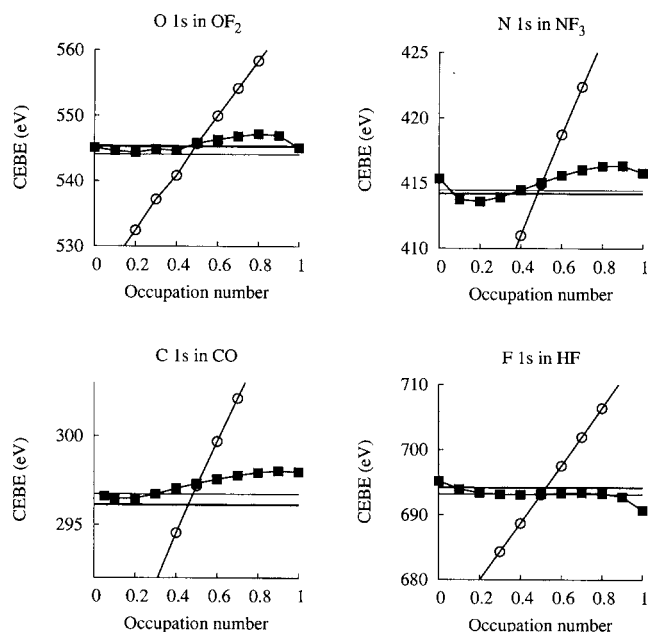

FIG. 6. Variation of CEBEs with respect to the occupation number of the transition orbital. Empty circles ($\bigcirc$) correspond to TOM results. Filled squares ($\blacksquare$) are used for TOEP2 results. The thin line is the ΔE_{SCF} value and the thick line is the experimental reference.

TABLE IV. C 1s electron binding energies (eV).

Molecule	KT	EP2	EP3	OVGF	P3	TOEP2	Expt.[a]
C_2H_4	305.64	291.81	294.08	293.42	292.74	292.19	290.79
CH_4	304.92	291.59	293.44	292.94	292.35	291.15	290.86
C_2H_2	305.90	291.99	294.81	293.91	293.32	292.14	291.17
CH_3Cl	307.21	293.48	295.49	295.01	294.38	292.94	292.4
HCN	307.23	294.35	296.01	295.48	294.90	293.32	293.5
CH_3F	307.70	294.82	295.95	295.65	295.20	294.12	293.65
$HCONH_2$	308.91	296.14	296.96	296.74	296.65	294.99	294.45
H_2CO	308.54	295.97	296.79	296.57	296.35	295.31	294.47
ONCN	308.71	295.27	297.20	296.71	297.68	294.32	294.52
OCS	311.20	297.68	298.34	298.16	298.46	297.40	295.2
CO	309.11	297.97	298.03	298.02	298.24	297.33	296.13
CH_2F_2	310.26	297.84	298.15	298.16	293.93	297.05	296.40
Cl_2CO	312.20	298.26	300.06	299.84	300.46	297.36	296.75
CO_2	311.79	299.91	299.59	299.67	300.23	299.76	297.66
Average $|\Delta|$	14.38	1.37	2.64	2.38	2.28	0.87	

[a]See Ref. 30.

TABLE V. N 1s electron binding energies (eV).

Molecule	KT	EP2	EP3	OVGF	P3	TOEP2	Expt.[a]
HCN	424.44	406.22	413.13	410.49	409.77	406.52	406.36
ClCN	424.63	406.04	412.87	412.75	409.67	406.76	406.45
ONCN*[b]	425.51	406.99	414.12	411.45	410.68	406.98	407.26
N*NO[b]	427.12	408.95	414.66	412.44	412.56	409.10	408.66
N_2	426.59	409.64	414.52	412.83	412.35	409.63	409.83
ON*CN[b]	429.76	412.18	415.80	415.74	417.89	411.19	411.05
ClNO	431.40	413.68	416.60	415.58	416.93	412.67	411.48
NN*O[b]	431.12	413.32	417.50	416.01	416.40	414.33	412.57
NF_3	432.76	415.81	416.93	416.83	416.79	415.05	414.2
Average $|\Delta|$	18.39	0.78	5.36	4.03	3.91	0.59	

[a]See Ref. 30.
[b]The asterisk follows the atom in which the 1s orbitals is found.

TABLE VI. O 1s electron binding energies (eV).

Molecule	KT	EP2	EP3	OVGF	P3	TOEP2	Expt.[a]
$HCONH_2$	558.45	535.69	548.39	543.28	541.67	536.83	537.74
H_2CO	559.86	537.40	549.29	544.61	543.06	538.50	539.48
Cl_2CO	5661.11	538.24	550.74	545.74	544.14	539.12	539.72
SO_2	561.12	537.74	552.60	545.86	544.79	540.54	539.84
H_2O	559.33	537.88	546.77	543.68	542.54	539.48	539.86
OCS	562.14	593.00	552.95	546.92	545.64	540.04	540.3
F_2CO	561.06	538.9	549.60	545.60	544.25	540.25	540.77
CO_2	561.89	539.44	551.59	546.66	545.50	541.40	541.19
O*OO[b]	563.43	540.27	554.68	547.78	547.35	541.81	541.5
H_2O_2	561.32	539.44	548.27	545.12	543.97	540.92	541.8
CO	562.35	541.17	553.06	547.79	546.15	541.86	542.39
ClNO	564.78	542.06	554.83	549.53	548.13	542.45	542.65
ONCN	563.66	541.36	551.38	547.40	546.51	541.73	543.43
OF_2	566.60	545.10	551.54	549.26	548.88	545.83	545.33
OO*O[b]	569.21	546.19	555.16	551.46	552.16	546.22	546.2
Average $|\Delta|$	20.94	1.55	9.92	5.23	4.17	0.58	

[a]See Ref. 30.
[b]The asterisk follows the atom in which the 1s orbitals is found.

TABLE VII. F 1s electron binding energies (eV).

Molecule	KT	EP2	EP3	OVGF	P3	TOEP2	Expt.[a]
ClF$_3$(ax)[b]	715.72	689.24	706.19	699.08	697.49	692.51	692.22
CH$_3$F	714.87	689.71	702.86	698.16	696.33	691.68	692.66
SF$_4$(ax)[b]	715.88	689.87	705.11	699.14	697.55	693.04	692.88
CH$_2$F$_2$	715.88	690.82	703.64	699.10	697.36	693.20	694.15
PF$_3$	716.73	691.32	705.15	700.01	698.43	694.20	694.18
HF	715.30	690.74	702.94	698.64	697.16	693.20	694.18
ClF	717.12	691.34	705.86	700.25	698.55	693.06	694.44
NF$_3$	718.04	692.82	705.22	700.81	699.19	695.54	694.45
SiF$_4$	716.70	691.62	704.84	700.03	698.52	694.55	694.70
ClF$_3$(eq)[b]	718.99	693.41	706.21	701.47	700.18	694.80	694.76
OF$_2$	718.35	693.05	705.40	700.92	699.28	696.15	695.07
SF$_4$(eq)[b]	718.61	693.17	706.23	701.45	700.06	695.01	695.26
F$_2$CO	718.08	693.03	705.49	701.06	699.61	695.91	695.43
F$_2$	719.21	694.27	705.49	701.41	700.18	695.41	696.69
Average |Δ|	22.78	2.58	10.72	5.78	4.24	0.59	

[a]See Ref. 30.
[b]For the case of axial (ax) and equatorial (eq) fluorine atoms, each is evaluated separately.

0.459 instead of 0.5. Whereas the difference in the corresponding TOM results for the CEBE is about 1.6 eV, the variation in the TOEP2 result is less than 0.2 eV. Figure 6 shows the variation of CEBEs calculated with TOM and with TOEP2 with respect to the occupation number of the transition orbital. The TOEP2 results are remarkably stable with respect to this parameter.

Tables IV–VII show the calculated values for C, N, O, and F 1s CEBEs. Comparison is made to KT values and to diagonal self-energy approximations of the electron propagator. Koopmans results are in error by as much as 14–23 eV. Second-order electron propagator calculations correct about 90% of the deviation, producing an average absolute deviation of 0.78–2.58 eV. When relaxation effects are included with TOEP2, the average absolute deviation goes down to 0.58–0.87 eV. This range is modified to 0.51–0.91 eV when relativistic corrections are applied using the same values as in Ref. 20. When scaled basis sets (as suggested by Chong and Hu[21]) were tested with adjustments for varying occupation numbers,[31] the results for carbon and nitrogen improved, but those for oxygen and fluorine are deteriorated. EP3, P3, and OVGF are not good choices for the calculation of

CEBEs. Whereas they are considerably less efficient than EP2 and TOEP2, their results for CEBEs are clearly worse. It is likely that relaxation effects for 1s ionization energies are sufficiently strong to compromise the stability of perturbative methods which depart from ordinary, Hartree-Fock orbital energies. TOEP2 is a convenient alternative for the calculation of CEBEs.

We conclude with comparisons to full configuration interaction (FCI) results[32–34] on the electron detachment energies of F$^-$, N$_2$, CO, and the two lowest states of CH$_2$. The data of Table VIII indicate that the P3 method performs better than second order, third order, OVGF, and TOEP2. However, the latter method's average absolute error is approximately equal to that of OVGF and is less than those of second- and third-order calculations. These results suggest that TOEP2 is an attractive compromise of accuracy and efficiency for calculations of valence electron binding energies.

IV. CONCLUSIONS

The transition operator method has been used to generate zeroth-order orbital energies which account for relaxation ef-

TABLE VIII. Comparison of electron propagator results with full-CI calculations of valence ionization energies (eV).

Molecule	Orbital	EP2	EP3	OVGF	P3	TOEP2	FCI
F$^-$	$3t_{1u}$	0.86	6.34	4.74	3.63	2.15	3.03[a]
N$_2$	$3\sigma_g$	14.69	15.76	15.31	15.60	15.12	15.87[b]
	$1\pi_u$	16.82	16.41	16.52	16.94	17.13	17.01[b]
	$2\sigma_u$	17.94	19.79	18.98	19.05	18.32	19.12[b]
CO	5σ	13.82	13.77	13.66	14.02	13.87	14.37[b]
	1π	16.06	17.38	16.84	16.72	16.60	16.89[b]
CH$_2$($^1A_1$)	$3a_1$	9.80	9.94	9.94	9.90	9.72	10.26[c]
CH$_2$($^3B_1$)	$1b_1$	10.34	10.29	10.41	10.04	9.84	10.16[c]
Average |Δ|		0.84	0.78	0.53	0.25	0.52	

[a]Using "DZP+Diffuse" basis set (Ref. 32).
[b]Using "DZP+Diffuse" (Ref. 33).
[c]Using "DZP" basis set (Ref. 34).

fects in electron propagator calculations of ionization energies. It has been demonstrated by calculations on a set of typical closed-shell molecules that the second-order approximation for the electron propagator using such a reference state produces valence ionization energies of a quality that is comparable to that of approximations with third-order terms. Therefore, we propose the use of this approach for the calculation of electron binding energies of large molecular systems.

Numerical tests show that calculated core-electron binding energies are sensitive to the fractional occupation numbers of the transition orbitals at the SCF level, but not in the second-order approximation to electron propagator. Thus, half-occupied spin orbitals are used.

The failure of methods with third-order terms in the treatment of core-electron binding energies has been numerically demonstrated. Average errors were reduced to less than 1 eV when using the transition operator method with second-order self-energy corrections. The latter method is an excellent compromise between accuracy and efficiency, for improvement of these results would require inclusion of fourth- and higher-order terms.

The combination of the TOM and diagonal second-order self-energy corrections significantly extends the range of applicability of electron propagator calculations. Its implementation requires only minor modifications of the standard diagonal second-order approximation to the electron propagator.

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