An Efficient, Renormalized Self-Energy for Calculating the Electron Binding Energies of Closed-Shell Molecules and Anions

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ABSTRACT: The energy-dependent, nonlocal correlation potential known as the self-energy that appears in the Dyson equation has a pole and residue structure that enables renormalizations of its low-order, perturbative contributions to be estimated. The partial third-order (P3) approximation has been extensively applied to the ionization energies of closed-shell, organic molecules and is the most successful example of a low-order, self-energy method. A renormalization based on the P3 self-energy estimates higher-order contributions by scaling low-order terms that chiefly describe final-state relaxation. The resulting P3+ self-energy retains the accuracy and efficiency of the P3 approximation, but also improves the latter method's performance with respect to the calculation of anion electron detachment energies without the introduction of adjustable parameters. An application to an anion that previously has yielded only to more intricate treatments of electron correlation demonstrates the power of this simple, new approximation.

Key words: electron propagator; self-energy; anions; P3+; approximation

Introduction

Quantum chemists have always returned to one-electron equations to inform their qualitative reasoning about electronic structure and to provide efficient strategies for computation [1]. In recent years, the one-electron equations provided by Kohn–Sham theory have formed the framework for the optimization of model chemistries [2]. The frontier of this field features increasingly complex exchange-correlation potentials that are functionals of the orbitals of a reference determinant. With the introduction of adjustable parameters, considerable scope for the extrapolation and interpolation of chemical data lies at the disposal of the computational chemist.

An alternative one-electron formalism provided by electron propagator theory [3] is based on a systematically improvable approach to correlation potentials. Here, the complexity of the nonlocal, energy-dependent correlation operator known as the self-energy grows quickly with respect to order in the fluctuation potential. Whereas only two self-energy diagrams occur in second order, there are 18 in third order. The exaggeration of the correlation effects that is typical of second-order calculations of electron binding energies usually is overcompensated in third-order results.

A recent trend in perturbative total energy calculations of low order is to introduce parameters that improve predictive capabilities for certain properties in a class of molecules [4]. Thus the strengths of ab initio, many-body theory such as retention of size-extensivity and proper description of dispersion effects are appropriated by the empirical focus of parameterized methods. Such a strategy also enables the computational practitioner to make useful extrapolations in a set of chemically similar molecules on the basis of methods that have been calibrated astutely.

A similar approach has been taken with electron propagator calculations. Components of the second-order self-energy with the same or mixed spin indices have been scaled with independent factors to produce a method with enhanced predictive capabilities for the valence ionization energies of closed-shell molecules [5]. In contrast, other workers have employed unaltered, self-energy formulas with semiempirical Hamiltonians [6].

Here an attempt is made to improve the predictive capabilities of a simple self-energy approximation that has proven its utility in the assignment of photoelectron spectra of organic molecules. This method, known as the partial third-order (P3) approximation, has clear advantages over many ab initio, correlated methods in the number of arithmetic operations it requires and in the dimensions of the computational intermediates it generates [7]. With polarized, triple-ζ basis sets, it consistently provides predictions of ionization energies that lie within approximately 0.2 eV of experimental peaks. Spectral assignments for polyheterocyclic aromatic compounds, nucleic acids, nucleotides, amino acids, porphyrins, and other organic molecules have been efficiently realized with P3 calculations. Unfortunately, applications to systems with stronger electron correlation in initial or final states have yielded less accurate results. Assignments of the photoelectron spectra of anions often require accuracy of 0.1–0.2 eV, for experimental samples often consist of more than one isomer. Clusters in which anions are coordinated to metals in positive oxidation states present similar challenges. Therefore, the need for a method with computational requirements that are similar to those of the P3 approximation but with enhanced predictive capabilities is apparent. The new approximation that emerges from this attempt, P3+, is derived below. An application to the photoelectron spectrum of a metal oxide anion that has attracted considerable interest among experimentalists illustrates the predictive and interpretive capabilities of the P3+ self-energy.

Theory

THE PARTIAL THIRD-ORDER SELF-ENERGY

From the Dyson equation for the electron propagator, the following one-electron equations may be deduced:

$$[F + \Sigma(E)]\phi^{\text{Dyson}} = E\phi^{\text{Dyson}}, \tag{1}$$

where F is the Fock operator that depends on the one-electron density matrix of the reference state and $\Sigma(E)$ is the self-energy operator. Electron binding energies correspond to those values of E which satisfy the Dyson equation and the associated eigenfunctions are known as Dyson orbitals. For an electron detachment energy from an N-electron reference state that is associated with a final state s, the Dyson orbital reads

$$\phi_s^{\text{Dyson}}(x_1) = N^{1/2} \int \Psi_N(x_1, x_2, x_3, \ldots, x_N) \Psi^*_{s,N-1}(x_2, x_3, x_4, \ldots, x_N)dx_2dx_3dx_4 \ldots dx_N, \tag{2}$$

where x_t is the space–spin coordinate for electron t. For electron affinities, where an electron is added to the reference state, the Dyson orbital is given by

$$\phi_s^{\text{Dyson}}(x_1) = (N + 1)^{1/2} \int \Psi_{s,N+1}(x_1, x_2, x_3, \ldots, x_{N+1}) \Psi^*_N(x_2, x_3, x_4, \ldots, x_{N+1})dx_2dx_3dx_4 \ldots dx_{N+1}. \tag{3}$$

For valence ionization energies of closed-shell molecules, the off-diagonal matrix elements of the self-energy operator in the canonical Hartree–Fock basis may be neglected and the Dyson equation is reduced to a simple form:

$$\epsilon_r + \Sigma_{rr}(E) = E, \tag{4}$$

where ϵ_r is a Hartree–Fock orbital energy. In the diagonal approximation of the self-energy matrix, the Dyson orbital equals the square root of the pole strength times a canonical Hartree–Fock orbital. After iterating with respect to E to find a pole, the pole strength, P_r is given by

$$P_r = \left[1 - \frac{d\Sigma_{rr}(E)}{dE}\right]^{-1}. \tag{5}$$

For real spin–orbitals, the diagonal, P3 self-energy matrix elements for electron detachment energies read

$$\Sigma_{pp}^{\mathrm{P3}} = \frac{1}{2}\sum_{iab}\frac{\langle pi\|ab\rangle\langle ab\|pi\rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b} + \frac{1}{2}\sum_{aij}\frac{\langle pa\|ij\rangle[\langle ij\|pa\rangle + W_{paij} + U_{paij}(E)]}{E + \epsilon_a - \epsilon_i - \epsilon_j}, \tag{6}$$

where

$$W_{paij} = \frac{1}{2}\sum_{bc}\frac{\langle pa\|bc\rangle\langle ij\|bc\rangle}{\epsilon_i + \epsilon_j - \epsilon_b - \epsilon_c} + (1 - P_{ij})\sum_{bk}\frac{\langle pk\|bi\rangle\langle jk\|ba\rangle}{\epsilon_j - \epsilon_k - \epsilon_a - \epsilon_b} \tag{7}$$

and

$$U_{paij}(E) = -\frac{1}{2}\sum_{kl}\frac{\langle pa\|kl\rangle\langle kl\|ij\rangle}{E + \epsilon_a - \epsilon_k - \epsilon_l} - (1 - P_{ij})\sum_{bk}\frac{\langle pb\|jk\rangle\langle ak\|bi\rangle}{E + \epsilon_b - \epsilon_j - \epsilon_k}, \tag{8}$$

where occupied and virtual spin–orbitals are designated, respectively, by $i, j, k, \ldots$ and $a, b, c, \ldots$ indices [8]. This approximation retains all second-order terms and has some two-hole, one-particle terms in third order. For electron affinities, the roles of occupied and virtual indices are reversed. The rate-limiting contraction pertains to the first term in the W intermediate, which scales as o^2v^3, where o and v are the numbers of occupied and virtual orbitals, respectively. Because p is an occupied index for electron detachment energies, the largest required subset of transformed two-electron integrals is the $\langle pa\|bd\rangle$ set; a complete integral transformation is not needed. These computational requirements are similar to those imposed by second-order perturbation theory for ground states. Practical calculations, especially those where symmetry-adapted algorithms may be employed, are likely to be bound by the integral transformation step instead of the contractions required for evaluation of self-energy matrix elements.

SELF-ENERGY RENORMALIZATIONS

It is possible to express the exact form of the self-energy matrix in the following form:

$$\Sigma_{pq}(E) = \sum_{I}^{nh(n-1)p}\frac{V_I Z_I}{E - f_I - X_I} + \sum_{A}^{np(n-1)h}\frac{V_A Z_A}{E - f_A - X_A}. \tag{9}$$

I and A are indices of secondary operators, such as those of the two-hole, one-particle (2hp) or two-particle, one-hole (2ph) types. The terms of lowest order in the residues are given by

$$V_{aij} = \langle pa\|ij\rangle\langle ij\|qa\rangle, \tag{10}$$

and

$$V_{iab} = \langle pi\|ab\rangle\langle ab\|qi\rangle. \tag{11}$$

Zeroth-order poles occur at values of E where the following terms vanish:

$$f_{aij} = E + \epsilon_a - \epsilon_i - \epsilon_j, \tag{12}$$

$$f_{iab} = E + \epsilon_i - \epsilon_a - \epsilon_b. \tag{13}$$

By setting all Z factors to unity and neglecting the X terms, the second-order self-energy matrix element, $\Sigma_{pq}^{(2)}(E)$, is recovered.

If one lets

$$Z_I = 1 - Y_I \tag{14}$$

and expands the denominators of the exact form in powers of $(E - f_I - X_I)^{-1}$, then

$$\sum_I \frac{V_I Z_I}{E - f_I - X_I} = \sum_I \frac{V_I}{E - f_I}\left[1 + \frac{X_I}{E - f_I} + \dots\right] - \sum_I \frac{V_I Y_I}{E - f_I}\left[1 + \frac{X_I}{E - f_I} + \dots\right]. \quad (15)$$

The assumption that the X factors are small is implicit here. An approximate form with a scaled interaction may be written as

$$\sum_I \frac{V_I Z_I}{E - f_I - X_I} \approx [1 - Y(E)] \sum_I \frac{V_I}{E - f_I} \times \left[1 + \frac{X_I}{E - f_I} + \dots\right], \quad (16)$$

where $Y(E)$ is assumed to vary slowly with E. Comparisons between terms in the last equation with those that have an equal number of $(E - f_I - X_I)^{-1}$ denominators in the P3 approximation suggest that a reasonable approximation is

$$Y(E) = \frac{-\frac{1}{2}\Sigma_{aij}\langle pa\|ij\rangle W_{paij}(E + \epsilon_a - \epsilon_i - \epsilon_j)^{-1}}{\Sigma^{(2)}_{pp}(E)}. \quad (17)$$

One may estimate higher-order effects with

$$\sum_I \frac{V_I Z_I}{E - f_I - X_I} \approx [1 + Y(E)]^{-1} \sum_I \frac{V_I}{E - f_I} \times \left[1 + \frac{X_I}{E - f_I} + \dots\right]. \quad (18)$$

Therefore, a renormalized extension of the P3 self-energy, with the designation P3+, may be expressed as

$$\Sigma^{\mathrm{P3+}}_{pp} = \frac{1}{2}\sum_{iab}\frac{\langle pi\|ab\rangle\langle ab\|pi\rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b} + [1 + Y(E)]^{-1}\frac{1}{2}\sum_{aij}\frac{\langle pa\|ij\rangle[\langle ij\|pa\rangle + W_{paij} + U_{paij}(E)]}{E + \epsilon_a - \epsilon_i - \epsilon_j}. \quad (19)$$

Evaluation of P3+ matrix elements requires practically no additional computational work with respect to P3 calculations. Similar arguments were employed in the derivation of the B version of the outer-valence Green's function procedure [9], but no numerical parameters are introduced presently to influence the selection of one renormalization procedure versus another [10].

TABLE I

Mean absolute deviations, eV.

Initial states	Basis	P3	P3+ [11]
Molecules	cc-pvtz	0.20	0.19
Molecules	cc-pvqz	0.28	0.19
Anions	aug-cc-pvtz	0.25	0.11
Anions	aug-cc-pvqz	0.29	0.13

Tests were performed on the 31 valence, vertical ionization energies below 20 eV of 11 typical, closed-shell molecules (N_2, CO, F_2, HF, H_2O, NH_3, CH_4, C_2H_4, C_2H_2, HCN, and H_2CO) and on the lowest vertical electron detachment energies of 10 closed-shell anions (F^-, OH^-, NH_2^-, Cl^-, SH^-, PH_2^-, CN^-, BO^-, AlO^-, and AlS^-) [11]. Whereas the mean absolute deviations for molecules shown in Table I are approximately the same for P3 and P3+, for anions there is a clear advantage for the latter method. The stability of the results with respect to basis set improvement also is better for P3+. No numerical parameters are introduced in the performance of P3+ calculations.

The first term in the P3+ self-energy expression may be considered to describe the elimination of certain reference-state, pair energies in the final state with $N - 1$ electron. These effects are treated only through second-order in the fluctuation potential. This approximation is likely to restrict the applicability of the P3+ method to nonmetallic systems. The most important effects that are described by the remaining terms involve final-state orbital relaxation. Introduction of the $[1 + Y(E)]^{-1}$ factor prevents the overestimation of these effects that occurs when unscreened interactions are employed.

$Al_3O_3^-$ Photoelectron Spectra

The following application of the P3+ method illustrates its ability to treat correlation effects in anions and molecules where a subtle competition between covalent and ionic interactions requires quantitatively accurate predictions to support qualitative interpretations of chemical bonding. The photoelectron spectrum of $Al_3O_3^-$ features an elec-

TABLE II
$Al_3O_3^-$ vertical electron detachment energies, eV.

Anion	Final state	BD-T1	P3	P3+ [17]	Expt. [12]
Book	$^2B_2$	3.07	2.85	2.84	2.96
	$^2A_1$	3.73	3.49	3.48	3.7
Kite	$^2A_1$	2.36	2.02	2.01	2.25
	$^2B_2$	5.37	5.73	5.30	5.2

tron binding energy at 2.25 eV whose peak intensity varies markedly with laser fluence and the degree of O_2 seeding in the He carrier gas that transports the mass-selected anion to the site of photodetachment [12]. In addition, more intense peaks have been reported in several papers and the unusual phenomenon of anion photoisomerization has been confirmed [12–14]. Optimizations of a large number of ground-state structures yielded two isomers with nearly identical total energies [15]. These minima, designated the book and kite, may be expected to have vertical electron detachment energies that correspond to the peaks of the experimental spectrum.

To obtain a consistent interpretation of the experiments, it was necessary in previous studies [15] to employ an advanced electron propagator technique (BD-T1 [1]) based on a Brueckner doubles, coupled-cluster reference state and a full, renormalized treatment of the 2ph plus 2hp operator manifold. The BD-T1 results of Table II were obtained with the 6-311+G(2*df*) basis set. Close agreement with experimental peaks is obtained for the first two vertical electron detachment energies of both isomers, which are simultaneously present in the experimental samples. Whereas the P3 approximation works well for the book isomer, it fails badly for the kite structure. (These calculations employed the same basis set and were performed with a modified version of Gaussian 03 [16].) In contrast, the P3+ approximation gives an accurate account of the photoelectron spectra of both anions [17]. The reference state calculation that precedes the BD-T1 calculation limits the application of this method to relatively small systems. In addition, the pole search procedure that is entailed by the renormalized treatment of the full manifold of 2hp and 2ph operators requires many interations with o^2v^3 arithmetic scaling factors. The P3+ method produces results of similar accuracy with considerably smaller computational effort.

In the book isomer, the two lowest electron detachment energies correspond to metal-centered Dyson orbitals, in accord with the Aufbau rules [18] that usually govern the electronic structure of aluminum oxide clusters. According to these guidelines for counting electrons, each O center is considered to be a dianion. Therefore, each $Al_3O_3^-$ cluster is regarded as having four metal-centered, valence electrons that are assigned to two Dyson orbitals which connect the closed-shell, anionic reference state to the ground and first excited states of the neutral doublet clusters. At the Koopmans level, a similar prediction is made for the kite isomer. However, these uncorrelated predictions are qualitatively incorrect for the kite isomer, for the order of the first four final states is erroneous. Correlated methods are necessary to assign an oxygen-centered Dyson orbital to the second electron detachment energy of the kite anion. Whereas the first electron detachment energy corresponds to a Dyson orbital that is localized chiefly on an Al atom with two oxide neighbors, the Dyson orbital that pertains to the second electron detachment energy exhibits a σ antibonding interaction between the same two oxides.

Conclusions

The P3 approximation has enjoyed considerable success in the assignment and interpretation of the photoelectron spectra of organic molecules, especially heterocyclic compounds. A rich variety of applications to molecules with biochemical importance has been enabled by the computational efficiency and conceptual clarity of this method. However, the poorer performance of the P3 self-energy in predicting electron detachment energies of anions has compelled the use of more exact methods with higher computational requirements in studies of metal oxide anions. The simple renormalization procedure that distinguishes the P3+ method from its immediate predecessor avoids exaggeration of final-state relaxation effects with virtually no additional computational labor.

The success of the P3+ method in assigning and interpreting the photoelectron spectrum of $Al_3O_3^-$ is related to its ability to predict the electron detachment energy of OH^- to within 0.1 eV of experiment with a polarized, triple-ζ basis that is augmented with diffuse functions. Similar success in describing anions with F and N atoms bodes well for applications to other clusters with metals in high oxidation states. The conceptual simplicity of the P3+ self-energy and its lack of adjusted parameters are encouraging portents. Applications of this promising computational and interpretive tool to larger metal oxide clusters that pertain to the stoichiometric and catalytic chemistry of nanoparticles and active surfaces are now in progress.

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