Three Approximations to the Nonlocal and Energy-Dependent Correlation Potential in Electron Propagator Theory

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ABSTRACT: The historical dilemma that pits accuracy against interpretability in molecular electronic structure calculations may be resolved with electron propagator theory. In the interpretation of electron binding energies, electron propagator theory provides a systematically improvable description of electron correlation while retaining one-electron concepts, such as Dyson orbitals, of wide-ranging interpretive facility. The nonlocal, energy-dependent correlation potential, known as the self-energy, which occurs in the one-electron equations of electron propagator theory may be approximated in practical calculations. The partial third-order approximation has been employed in many calculations on large molecules. Applications to fragments of nucleic acids show how qualitative, orbital-based insights emerge from calculations that suffice to quantitatively assign photoelectron spectra. A quasiparticle virtual orbital method for improving the efficiency of this method shows considerable promise. Simple perturbative approaches may be combined with renormalizations that incorporate final-state orbital relaxation effects with the use of reference ensembles that correspond to Slater's transition state method. Such approximations produce useful predictions for core as well as valence electron binding energies. Another approximation that is based on highly correlated reference states and a renormalized treatment of the self-energy shows considerable flexibility in the accurate prediction of electron binding energies. This method suffices to make definitive assignments of photoelectron spectra of double Rydberg anions, species whose ground state electronic structure requires assignment of electrons to nonvalence orbitals.   © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 110: 706–715, 2010

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Introduction

Quantum chemistry is chiefly about two things. Its first agenda issues from the concepts of quantum mechanics and advances in the technology of computation. This foundation enables quantum chemists to calculate a variety of properties with an ever-expanding scope of molecular size and with increasing accuracy. The accompanying goal of methodological development is to produce techniques that allow the deduction of observable quantities from quantum mechanical principles and numerical approximations of demonstrated and, in the best case, controllable quality. Such capabilities are of greatest use when competing experimental techniques are expensive, hazardous, or technically difficult. They also can propitiate dialog with experimentalists who require information that is complementary to their measurements and that enables analysis of their data. In the advancement of this deductive agenda, quantum chemistry takes its place in the toolbox of a relatively new profession: computational chemist.

For historical reasons, quantum chemistry has another agenda, that of qualitative interpretation. The advent of valence theory predates that of quantum mechanics and this conceptual inheritance is intimately interwoven into the fabric of chemical pedagogy. In the early stages of a typical education in chemistry, students are exposed to electron pair concepts which originated in the first decades of the twentieth century, to classical notions of repulsions between pairs, to hybridization and resonance theories that are loosely based on quantum mechanical concepts, and to molecular orbitals for diatomic molecules. Perhaps the greatest pedagogical benefit of such an approach to teaching chemistry is the mnemonic advantage it provides to the student who is expected to infer an impressive variety of structural, thermodynamic, and kinetic information from a few principles of bonding. That these teaching devices inculcate expectations which are usually correct is a tribute to the success of the pioneers of valence theory. Contemporary quantum chemists therefore are interested in conceptual connections between their best computational tools and the traditions of valence theory. Establishing such links offers the prospect of generalizing and deepening the qualitative foundations of routine chemical reasoning.

In recent decades, both agendas have advanced with the aid of molecular orbital theory. The prominence of molecular orbital concepts in formulating experimental and computational problems has two principal sources. First, the applicability of computational techniques that are based on molecular orbital concepts has grown remarkably. Increased computational power and improved self-consistent field algorithms are the chief causes of this trend. Second, molecular orbital theory has an accompanying set of interpretational tools (such as analyses of Dirac density matrices, atomic partitioning schemes and one-electron, model Hamiltonians) for the extraction of qualitative conclusions from voluminous data. As a result, a wide variety of chemical phenomena have been explained in molecular orbital terms.

Quantum chemists are aware of the limitations of this approach, for systematic, nonempirical treatments of electron correlation are often needed to provide quantitatively reliable predictions of observables. Configuration interaction, many-body perturbation theory, and its coupled-cluster generalizations are among the ab initio approaches that are applied to the correlation problem [1]. Unfortunately, the interpretational tools that accompany these devices are not as developed or transparent as their uncorrelated counterparts. To the user of correlated methods, there appears to be a dilemma that pits accuracy against interpretability in molecular electronic structure theory.

Electron Propagator Concepts

Electron propagator theory [2] offers a way to bypass this dilemma. This approach to ab initio calculations offers a systematic treatment of electron correlation that may be improved to an exact limit. However, the one-electron concepts of electron propagator theory generate a set of interpretive tools that enable facile extraction of qualitative conclusions from complex calculations. In principle, it is possible to perform exact calculations on electron binding energies, associated transition probabilities, total energies, and one-electron properties with the retention of an orbital interpretation of all results.

In electron propagator theory, the Dyson equation provides the foundation of practical calculations and subsequent, qualitative interpretation. All of the solutions of the Dyson equation may be cast in the following form,

$$[F + \mathbf{\Sigma}(\varepsilon_p)]\phi_p^{\text{Dyson}} = \varepsilon_p\phi_p^{\text{Dyson}},$$

where

- F is the Fock operator with kinetic energy, nuclear attraction, Coulomb and exchange components that depends on a reference, one-electron density matrix,
- $\Sigma(E)$ is the nonlocal, energy-dependent, self-energy operator wherein orbital relaxation and correlation effects reside,
- ε_p is an electron binding (attachment or detachment) energy that is obtained self-consistently with respect to the energy argument of the self-energy operator and
- ϕ_p^{Dyson} is the Dyson orbital that corresponds to the transition energy ε_p.

Using closed forms for the self-energy operator, it is possible to generate systematic improvements to the self-energy operator up to an exact limit wherein exact electron binding energies and Dyson orbitals are obtained. For an electron detachment (from an N-electron reference state to a final state labeled by p with $N - 1$ electrons), the relationship between the corresponding Dyson orbital and many-electron state functions (Ψ) is given by

$$\phi_p^{\text{Dyson}}(x_1) = N^{-1/2} \int \Psi_N(x_1, x_2, x_3, \ldots, x_N)$$

$$\times \, \Psi^*_{p, N-1}(x_2, x_3, x_4, \ldots, x_N) dx_2 dx_3 dx_4 \ldots dx_N,$$

where x_q is the space-spin coordinate for electron q. The Dyson orbital therefore may be conceived as an overlap function between states with differing numbers of electrons. By using the frozen orbital approximations of Koopmans's theorem for the initial (N electron) and final ($N - 1$ electron) states, one may obtain canonical Hartree–Fock orbitals as approximations to Dyson orbitals. Insertion of full configuration interaction wavefunctions in the same integral above would yield exact Dyson orbitals. However, a more direct route to Dyson orbitals which reflects the effects of final-state, orbital relaxation and electron correlation is afforded by the Dyson equation. For electron attachment energies, the corresponding Dyson orbitals are given by

$$\phi_p^{\text{Dyson}}(x_1) = (N + 1)^{-1/2} \int \Psi_{p, N+1}(x_1, x_2, x_3, \ldots, x_{N+1})$$

$$\times \, \Psi^*_N(x_2, x_3, x_4, \ldots, x_{N+1}) dx_2 dx_3 dx_4 \ldots dx_{N+1},$$

where the final state labeled by p has $N + 1$ electrons. In general, the Dyson orbitals are not normalized to unity. Instead, their norms are known as pole strengths and they may vary between zero and unity. Photoionization intensities [3], several kinds of electron scattering cross sections, and other transition probabilities are proportional to pole strengths. In an exact electron propagator, the sum of the electron detachment pole strengths equals N, the number of electrons in the reference state. The number of these transitions greatly exceeds N, for correlation (shake-up) states are much more numerous than the number of electrons in the molecule in question. Correlation states also may occur for electron attachment energies.

Self-Energy Approximations

Approximate methods that fall short of the exact limit are defined by the form of the self-energy operator. Three classes of approximations may be identified.

- Perturbative, quasi-particle methods are based on low-order corrections to the diagonal elements of the self-energy matrix in the canonical Hartree–Fock basis and neglect of nondiagonal elements. (The latter assumption is often called the quasi-particle approximation.) Iterations with respect to E are performed on a simplified (quasi-particle) equation for electron binding energies:

$$E = \varepsilon_p^{\text{HF}} + \Sigma_{pp}(E).$$

The first term is the usual result from Koopmans's theorem.

- Renormalized, quasiparticle approximations employ an equation of the same form, but the reference orbital energy includes certain kinds of corrections in all orders of perturbation theory. Care must be taken to exclude these corrections from the self-energy term.
- Renormalized, nondiagonal methods consider the full set of self-energy matrix elements and include certain classes of self-energy terms in all orders of perturbation theory. Electron binding energies, ε_p, and Dyson orbitals, ϕ_p^{Dyson}, are obtained from equations of the following form,

$$[\mathbf{F} + \mathbf{\Sigma}(\varepsilon_p)]\mathbf{C}_p = \mathbf{C}_p \varepsilon_p,$$

where $\mathbf{F}$ and $\mathbf{\Sigma}$ are matrices whose rank equals the size of an orthonormal orbital basis, $\{\chi\}$. The eigen-vector (which is determined in the previous equation only up to a constant) yields the Dyson orbital according to

$$\phi_p^{\mathrm{Dyson}} = \mathbf{\Sigma}_r \chi_r C_{rp}$$

such that its norm equals the pole strength, P_p, where

$$P_p = \mathbf{C}_p^{\dagger}\mathbf{C}_p.$$

Perturbative Quasiparticle Approximations

The diagonal approximation to the self-energy matrix in the canonical Hartree–Fock basis implies a simplified form of the Dyson orbital

$$\phi_q^{\mathrm{Dyson}} = P_q^{0.5}\phi_q^{\mathrm{HF}}$$

where the pole strength, P_q, may be calculated using

$$P_q = [1 - d\mathbf{\Sigma}_{qq}(E)/dE]^{-1}.$$

When these pole strengths do not exceed $\sim$0.85, this class of approximations is not likely to produce credible results, for the assumptions on which per-turbative arguments are based become invalid. However, for those cases where the Koopmans de-scription of final states is qualitatively meaningful, diagonal, quasi-particle calculations provide an ef-ficient and accurate means of assigning transitions.

The partial third-order approximation [4] (P3) to the self-energy has proven to be useful in the study of large, closed-shell, organic molecules. In tests with triple ζ plus polarization basis sets, it typically yields average errors of $\sim$0.2 eV in the calculation of ionization energies below 20 eV. In practical calculations, the arithmetic bottleneck occurs not in the evaluation of self-energy matrix elements, but in the preceding partial transformation of electron repulsion integrals to the Hartree–Fock basis. For one, noniterative contraction, the set of transformed integrals with one occupied and three virtual indi-ces is needed; storage of these integrals on disk may be avoided with a semi-direct algorithm. If an MP2 calculation [1] is feasible, it is likely that P3 calcu-lations may be executed without difficulty.

Other perturbative, quasi-particle approximations also have proven to be widely applicable. The outer valence Green's function [2(b), 5] (OVGF) approxima-tion involves the evaluation of all third-order terms in the self-energy and a scheme to choose the best of three estimates for higher-order corrections. This method is somewhat harder to execute than P3, for in the calculation of ionization energies it requires trans-formed integrals with four virtual indices. The result-ing arithmetic bottleneck occurs in the evaluation of a certain self-energy term that scales as ov^4, where o and v are the numbers of occupied and virtual va-lence orbitals, respectively. This step must be re-peated with every energy iteration of the Dyson equa-tion. As with the P3 method, storage of the integrals with four virtual indices may be avoided through a semi-direct algorithm.

Application: Photoelectron Spectra of Nucleotides

Gas-phase, anion photoelectron spectra of the four nucleotides of DNA [6] (consisting of a phos-phate anion, a sugar molecule and a purine or pyrimidine base) exhibited broad peaks corre-sponding to electron detachment energies above $\sim$6 eV. An anomalously low peak near 5 eV occurred in the photoelectron spectrum of the guanosine anion. Because guanine has a lower ionization energy than thymine, cytosine, or adenine, this low-energy peak was assigned to a base-centered, π orbital. How-ever, isolated phosphate anions have lower electron detachment energies than sugar or base molecules. Conformational effects therefore could be responsi-ble for a change in the order of final states with holes in distinct regions of a nucleotide.

The assignment of peaks to orbitals with phos-phate, base, or some other kind of localization may be facilitated by performing P3 calculations [7]. Many conformations of these anionic species were considered; results for the most stable structures are considered here. From Table I and Figure 1, it is clear that the Dyson orbitals for the first few elec-tron detachment energies are confined to phosphate or base regions of adenosine. Comparison of the calculated results reveals that the ordering of final states changes when relaxation and correlation ef-fects are considered. Such corrections are larger when an electron is detached from the anionic phosphate group than when it is removed from a base π orbital. The lowest peak corresponds to a near degeneracy of two uncharged states that cor-

respond to phosphate-centered and base-centered Dyson orbitals. For the guanosine case, there are fewer discrepancies between the P3 and Koopmans orderings of the final states, although the quantitative effects of relaxation and correlation remain large for the final states with phosphate-centered holes. The lowest electron detachment energy clearly corresponds to a Dyson orbital that closely resembles it counterpart for free guanine. Studies of other conformations of nucleotides disclose that the order of final states may depend on conformational changes. From these calculations, one may conclude that the phosphate anion's Coulomb field has a large, destabilizing effect on the π orbitals of bases and that the polarizability of the latter molecules stabilizes the phosphate orbitals. These two trends combine to produce near degeneracies of neutral states with phosphate and base holes and indicate the need for correlated calculations.

Quasiparticle Virtual Orbitals

The sharp power dependence of arithmetic bottlenecks on the number of virtual orbitals motivates a search for a more compact set of unoccupied, Hartree–Fock orbitals that retains the full effects of relaxation and correlation. In many previous works, virtual canonical orbitals with energies above a certain threshold were discarded in the evaluation of self-energy matrix elements. By comparing results with a series of thresholds, estimates
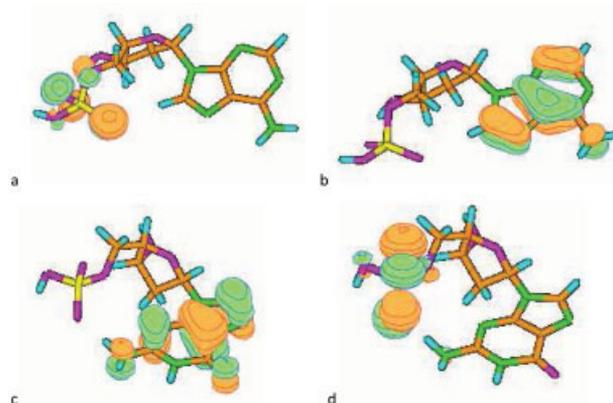

FIGURE 1. (a) Phosphate-centered Dyson orbital for the lowest vertical electron detachment energy of adenosine; (b) Base-centered Dyson orbital for the second lowest vertical electron detachment energy of adenosine; (c) Base-centered Dyson orbital for the lowest vertical electron detachment energy of guanosine; (d) Phosphate-centered Dyson orbital for the second lowest vertical electron detachment energy of guanosine. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of infeasible calculations with the full set of virtual orbitals could be made.

An alternative procedure for generating a smaller set of virtual, canonical Hartree–Fock orbitals is based on the electron density difference matrix, **D**, that corresponds to an easily executed, second-order quasiparticle calculation [8]. By diagonalizing the virtual–virtual block of this matrix and discarding the eigenfunctions with the lowest absolute values, one obtains a reduced set of virtual orbitals. After determining the Fock matrix elements in this reduced space, another diagonalization produces a set of quasiparticle virtual orbitals (QVOs) that are canonical and therefore suitable for insertion in the usual formulae for self-energy matrix elements. In preliminary tests with a variety of quasiparticle approximations, QVOs which are half as numerous as the original set of Hartree–Fock virtual orbitals introduce errors of only a few hundredths of an eV. This technique shows considerable promise in extending the ambit of electron propagator methodology to larger molecules.

TABLE I
Nucleotide vertical electron detachment energies (eV).

Anion	Dyson orbital	Koopmans	P3 [7]	Experiment [6]
Adenosine	Phosphate	7.84	6.07	6.05
	Adenine π	6.16	6.15	
	Phosphate	8.21	6.39	~6.4
	Phosphate	8.38	6.62	~6.7
	Phosphate	8.43	6.76	
	Adenine π	7.75	6.89	~6.9
Guanosine	Guanine π	5.25	5.01	5.05
	Phosphate	7.94	6.18	~6.1
	Phosphate	8.31	6.54	~6.4
	Phosphate	8.54	6.75	~6.8
	Guanine n	8.65	6.84	~6.9
	Guanine π	8.12	6.96	~7.0

Renormalized Quasiparticle Approximations

There are many cases where a self-consistent field (SCF) procedure may yield a good approxima-

tion to a Dyson orbital, but higher-order corrections to the diagonal elements of the self-energy matrix remain important. In the OVGF method [2(b), 5], ratios that involve second-order and third-order self-energy diagrams are employed to estimate corrections in fourth and higher orders. Another approach focuses not on higher-order corrections to the self-energy term in the quasi-particle equation, but on obtaining a reference orbital energy that incorporates high-order relaxation effects. Slater's transition state approach provides such an orbital energy through an SCF procedure where Fock matrix elements read

$$F_{pq} = h_{pq} + \Sigma_r \langle pr\|qr\rangle n_r$$

and where n_r is a spin-orbital occupation number [9]. Whereas these occupation numbers have values of unity or zero in the usual case, Slater's transition operator method (TOM) introduces a single spin-orbital with an occupation number of ½ the corresponding energy is considered to be an approximate electron binding energy that incorporates the effects of orbital relaxation between states where a similar spin-orbital has occupation numbers of unity or zero. Janak's theorem [10] provides an alternative perspective on this approach by relating SCF orbital energies to partial derivatives of total energies with respect to occupation numbers:

$$\varepsilon_r^{SCF} = \delta E^{SCF}/\delta n_r.$$

Thus, in a single-point quadrature, the TOM spin-orbital energy provides an estimate of a ΔSCF result.

Fractional occupation numbers may be accommodated in electron propagator theory through the introduction of grand-canonical ensemble averages in the evaluation of self-energy matrix elements [11]. For example, second-order matrix elements read

$$\Sigma_{pq}^{(2)}(E) = 1/2\Sigma_{ija} n_i n_j (1 - n_a)\langle pa\|ij\rangle\langle ij\|qa\rangle$$
$$\times (E + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} + 1/2\Sigma_{abi}(1 - n_a)(1 - n_b)n_i$$
$$\langle pi\|ab\rangle\langle ab\|qi\rangle(E + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1},$$

where the usual summations over occupied (i,j) and virtual (a,b) spin-orbitals are recovered when the occupation numbers are either unity or zero. Because only diagonal $(p = q)$ elements are needed in quasi-particle calculations, all electron repulsion in-

tegrals for a given final state have the p index in common. Therefore, in preparation for iterations on the quasi-particle equation for a given final state, a partial integral transformation may be performed that has a fourth-power instead of a fifth-power dependence on the number of basis functions. The resulting arithmetic bottleneck should be similar to that of a conventional SCF iteration.

The choice of an occupation number of ½ for the transition spin-orbital does not necessarily provide an orbital energy that is in close agreement with a ΔSCF calculation. However, an analysis of the terms in the second-order self-energy provides an alternative justification for this custom. When the transition orbital energy, ε_k^{TOM}, is used as an initial guess in the quasiparticle equation, the following expression for the energy is usually close to convergence:

$$E \approx \varepsilon_k^{TOM} + \Sigma_{kk}^{(2)}(\varepsilon_k^{TOM}).$$

For the case where only one spin-orbital (k) has an occupation number that is not equal to unity or zero, the self-energy term may be separated into three contributions where

$$\Sigma_{kk}^{(2)}(\varepsilon_k^{TOM}) = 1/2\Sigma_a\Sigma_{ij}^{\neq k}|\langle ka\|ij\rangle|^2(\varepsilon_k^{TOM} + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1}$$
$$+ 1/2\Sigma_i\Sigma_{ab}^{\neq k}|\langle ki\|ab\rangle|^2(\varepsilon_k^{TOM} + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1}$$
$$+ (1 - 2n_k)\Sigma_a\Sigma_i|\langle ki\|ka\rangle|^2(\varepsilon_i - \varepsilon_a)^{-1},$$

where $n_i = n_j = 1$ and $n_a = n_b = 0$. The first and second terms correspond to correlation effects, the third term, which describes orbital relaxation, vanishes when $n_k = ½$ [12]. For other choices of n_k, these terms reappear and tend to cancel the corresponding variations in ε_k^{TOM}. Therefore, second-order quasiparticle results are more stable with respect to n_k than uncorrected ε_k^{TOM} values [13].

Application: Valence and Core Ionization Energies

Numerical tests of this transition operator plus second-order electron propagator method (TOEP2) have been performed on a variety of closed-shell molecules and compared to results with other methods [13]. For valence ionization energies of closed-shell molecules, the first row of data in Table II indicates that the TOEP2 method produces mean absolute errors that are less than those of Koop-

TABLE II _____
Average absolute errors of calculated ionization energies (eV) [8].

	Koopmans	Second order	Third order	P3	OVGF	TOEP2
Valence	1.17	0.62	0.49	0.25	0.25	0.36
C 1s Core	14.4	1.4	2.6	2.3	2.4	0.9
N 1s Core	18.4	0.8	5.4	3.9	4.0	0.6
O 1s Core	20.9	1.6	9.9	4.2	5.2	0.6
F 1s Core	22.8	2.6	10.7	4.2	5.8	0.6

mans's theorem and low-order quasi-particle methods. Methods that have been extensively applied to such transition energies, such as P3 and OVGF, are better by ~0.1 eV. Whereas third-order, P3 and OVGF methods have fifth-power arithmetic bottlenecks, the TOEP2 approximation has only a fourth-power dependence on the size of the basis set. Only the Koopmans and second-order methods are more efficient. (In the latter case, this advantage originates from the use of a common set of spin-orbitals for all final states.) The TOEP2 method is an attractive alternative when tackling large molecules where the highest accuracy is not necessary to interpret experiments.

The advantages of the TOEP2 method are greater for core electron binding energies. Table II also provides a summary of tests performed on 1s ionization energies of closed-shell molecules [13]. In such cases, the effects of orbital relaxation are large. Only the TOEP2 method generates mean absolute errors below 1 eV. The third-order, P3 and OVGF methods have inferior predictive ability.

Renormalized Nondiagonal Approximations

Methods of higher accuracy and flexibility may require perturbative corrections in all orders. For such cases, the superoperator form of the self-energy provides a basis for systematic improvements [2(e)]. First, the space of field operator products that change the number of electrons by one is introduced. Second, a metric is defined in this space according to

$$(X|Y) = \langle 0|[X^\dagger, Y]_+|0\rangle,$$

where X and Y are members of the field operator product space and $|0\rangle$ is a reference state. The field operator space is orthonormalized with this metric

and subsequently partitioned into a primary space with simple annihilation operators (**a**) and a secondary space (**f**) consisting of products of m creation operators and m+1 annihilation operators such that m is an integer greater than or equal to one. Finally, Hamiltonian ($\hat{H}$) and identity ($\hat{I}$) superoperators are introduced such that $\hat{H}X = [X,H]$ (where H is the second-quantized Hamiltonian) and $\hat{I}X = X$. In this notation, the elements of the self-energy matrix read

$$\mathbf{\Sigma}_{pq}(E) = (a_p|\hat{H}\mathbf{f})(\mathbf{f}|(E\hat{I} - \hat{H})\mathbf{f})^{-1}(\mathbf{f}|\hat{H}a_q),$$

where f is a vector of triple (**f**$_3$), quintuple (**f**$_5$), and higher (**f**$_7$, **f**$_9$, **f**$_{11}$,…) field operator products that reduce the number of electrons by one. (Sometimes terms which arise from correlated corrections to the one-electron density matrix in the evaluation of the Fock operator in the quasi-particle equation are called constant, or energy-independent, contributions to the self-energy.) In the limit of a complete set of operators in **f**, the electron binding energies calculated with the self-energy become exact. Should this limit be reached with the employment of an exact reference state, $|0\rangle$, the Dyson orbitals also become exact. These limits are analogous to the exhaustion of the configuration space in variational calculations of state functions.

Many renormalized self-energies may be constructed with Hartree–Fock reference states by introducing an approximate **f** space. For example, the two-particle-hole Tamm-Dancoff approximation [2(b)] is obtained by making the following choices: $|0\rangle \approx$ Hartree–Fock> and $\mathbf{f} \approx \mathbf{f}_3$. To obtain all third-order terms in the self-energy, perturbative corrections to Hartree–Fock reference states are needed. (These corrections will also appear in the density matrices that are used to calculate Fock matrix elements and give rise to the so-called constant diagrams.) An example of this approach is the

TABLE III
BD-T1 vertical electron detachment energies (eV).

Structure	BD-T1 [15]	Experiment [14]
$H^-(NH_3)$	1.07	1.11 ± 0.02
Tetrahedral NH_4^-	0.48	0.47 ± 0.02

widely used third-order algebraic diagrammatic construction or ADC [3] method [2(b)].

A related strategy employs the Bruecker-doubles coupled cluster wavefunction (BD) in constructing a reference space and also introduces the triple field operator ($\mathbf{f} \approx \mathbf{f}_3$) truncation of the operator space [2(c)]. The approximate Brueckner orbitals of the BD approximation are used to construct all matrix elements of the Fock and self-energy operators. This method, known as BD-T1, exhibits considerable versatility in the calculation of electron binding energies. It generates mean absolute deviations of ~0.15 eV for ionization energies of closed-shell molecules, ~0.05 eV for closed-shell anions, and ~0.2% for 1s core electron binding energies.

Application: Double Rydberg Anions

The first photoelectron spectrum of an anion-molecule complex pertained to mass-selected species with the formula NH_4^- [14]. The principal peak was assigned to electron detachment from a hydride ion coordinated to an ammonia molecule. The displacement between a satellite peak and the principal peak approximately equaled a symmetric stretch excitation energy on the ammonia molecule. The spectrum of ND_4^- showed the expected shift in the satellite peak. However, a low-intensity peak also appeared at a markedly lower electron binding energy. Assignment of this feature to a vibrationally excited initial state of the $H^-(NH_3)$ anion-molecule complex was ruled out by the invariance of its position with respect to deuteration. Instead, the existence of a tetrahedral isomer was proposed in which two diffuse electrons were attached to an ammonium cation, thus forming a double Rydberg anion.

Geometry optimizations with correlated total energies encounter an anion-molecule minimum with C_s symmetry [15]. Attempts to find minima with trigonal bipyramidal or square pyramidal geometries are unsuccessful. In fact, optimizations that depart from initial structures of these types converge to a tetrahedral minimum.

Calculations at the BD-T1 level with exhaustive sets of diffuse basis functions lead to the results of Table III [15(c)]. For both isomers, decisive agreement with experiment obtains. The Dyson orbital for the anion-molecule complex in Figure 2 has high amplitudes near the hydride anion's nucleus with only minor delocalization onto a nearby ammonia N—H bond. For the tetrahedral case, the largest amplitudes in Figure 3 occur outside the hydrogen nuclei. A nodal surface occurs near the same nuclei. A second, radial node occurs within the nitrogen-centered lobe. In the united atom limit, this orbital resembles a Na^-, 3s function with two radial nodes. Thus the experimentalists' appellation of double Rydberg anion is qualitatively justified. In NH_4^-, two diffuse electrons are subject to the nonspherical potential of an ammonium cation.

Similar calculations [15(c)] have enabled assignment of the photoelectron spectrum of $N_2H_7^-$ [14(c)], where the most abundant species, $H^-(NH_3)_2$, accounts for the most intense peaks. Unlike the NH_4^- spectrum, this case produces two low-energy peaks instead of one. Geometry optimizations produce, in addition to a $H^-(NH_3)_2$ structure with C_2 symmetry, two minima. The first of these may be represented as an anion-molecule complex consisting of tetrahedral NH_4^- and a nearby ammonia molecule. The second has a hydrogen-bridged structure that is similar to that of $N_2H_7^+$, where an ammonium cation donates a proton to the lone pair of an ammonia molecule. Once again, BD-T1 calculations with large, diffuse basis sets provide a decisive assignment, with the predictions lying within or barely outside the experimental errors limits. The Dyson orbital for electron detachment from the anion-molecule double Rydberg anion closely resembles that of free, tetrahedral NH_4^-. For the remaining double Rydberg anion, the largest amplitudes are found outside the three hydrogens of the tetrahedral fragment which are not engaged in a hydrogen bond with the lone pair of the ammonia molecule fragment.

Double Rydberg anions with stable geometries and positive electron detachment energies have been predicted for a pyramidal, C_{3v} form for OH_3^- as well [16]. Three oxygen-containing analogues of the $N_2H_7^-$ structures have been found for $O_2H_5^-$: $H^-(OH_2)_2$, $OH_3^-(OH_2)$, and a hydrogen-bridged species [16(b)]. Substitution of a methyl group for a hydrogen leads to stable double Rydberg anions with the formulas $NH_3CH_3^-$ and $OH_2CH_3^-$ [17].

Amino and hydroxyl groups may be substituted for hydrogens in the stable $NH_3NH_2^-$ and NH_3OH^- double Rydberg anions [17]. A tetrahedral form of PH_4^- also has been predicted [15(b)].

Double Rydberg anions represent a generalization of the electron pair concept of classical valence theory. Here, in addition to the familiar bond pairs and lone pairs that were posited by Lewis and Langmuir at the beginning of the twentieth century, another kind of pattern emerges in which stable molecular cations may bind two additional electrons to form a ground-state anion. The least bound electrons of the double Rydberg anions correspond to Dyson orbitals with extra-valence character.

Conclusions

Three kinds of self-energy approximations display the versatility of electron propagator theory in interpreting photoelectron spectra. Perturbative, quasi-particle methods are efficient and accurate tools for the study of large molecules. Application of the P3 approximation to the photoelectron spectra of nucleotides enabled the assignment of peaks to phosphate-centered and base-centered Dyson orbitals. With the advent of the quasi-particle virtual orbital technique, applications of even greater scope may be anticipated. The transition operator method provides reference orbital energies that include relaxation effects and subsequent self-energy corrections may be used to generate useful esti-
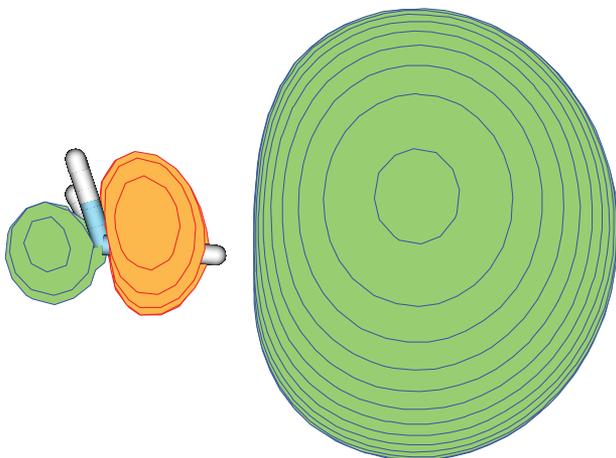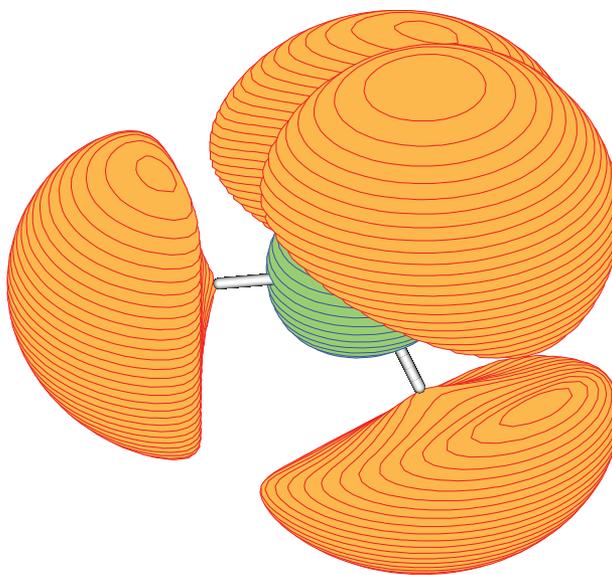

FIGURE 3. Dyson orbital for vertical electron detachment energy of tetrahedral NH_4^-. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mates of valence and core ionization energies. Renormalized methods are needed for higher accuracy and have been applied to the definitive assignment of anion photoelectron spectra which reflect the presence of double Rydberg anions.

In all of these calculations, one-electron equations with a nonlocal, energy-dependent potential have been solved. Final-state, orbital relaxation effects and the effects of differential correlation between states may be systematically treated and improved. For each electron binding energy that is calculated in this way, the corresponding Dyson orbital is generated. Interpretations based on orbital concepts follow from this approach to electronic structure. To quantitatively accurate calculations, qualitative, pictorial interpretations may be rigorously associated.

FIGURE 2. Dyson orbital for vertical electron detachment energy of $H^-(NH_3)$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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