Toward an Exact One–Electron Picture of Chemical Bonding

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This article is dedicated to the author's graduate advisor, Professor Yngve Öhrn.

Contents

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1 Conceptual Goals for One–Electron Theories

One–electron pictures of molecular electronic structure continue to inform interpretations of structure and spectra. These models are the successors of qualitative valence theories that attempt to impose patterns on chemical data and to stimulate experimental tests of predictions. Therefore, in formulating a one–electron theory of chemical bonding, it is desirable to retain the following conceptual advantages.

One–electron Energies Orbital energies should be equal to ionization energies and electron affinities (electron binding energies). They should be the eigenvalues of a one–electron operator with an effective, many–electron potential. All ionization energies should be predicted, without artificial distinctions between core versus valence or principal versus shakeup descriptions of final states. Bound and unbound electron–attached states should correspond to negative and positive orbital energies, respectively.

One–electron States For each electron binding energy, there should be a corresponding orbital that is an eigenfunction of the same effective, one–electron operator. Orbitals should display phase relationships that permit interpretations in terms of kinetic energy and interference effects. Transition probabilities corresponding to the electron binding energies should be related to the same orbitals. Effects of electron detachment or attachment on nuclear positions should depend on forces associated with the orbitals.

Density Matrices One–electron density matrices of initial and final states should be related to the orbitals used to interpret electron binding energies. Their eigenvalues should lie between zero and unity and their traces should equal the number of electrons in each state. One–electron properties should be size–extensive.

Total Energies Total energies should be related to orbitals and their energies. They should be size–extensive as well.

Numerical Representation The theory should be systematically improvable with respect to basis sets or integration schemes.

Independence There should be no parameters which have been adjusted to reproduce certain data from experiment or from unrelated sources.

Potential Energy Surfaces All potential energy surfaces generated with this theory should be smooth. No discontinuities due to symmetry reduction should occur.

Electron Correlation The theory should have a limiting case of exact total energies, electron binding energies and corresponding transition probabilities.

Hartree–Fock (HF), molecular orbital theory satisfies most of the criteria, but qualitative failures and quantitative discrepancies with experiment often render it useless. Methods that systematically account for electron correlation, employed in pursuit of more accurate predictions, often lack a consistent, interpretive apparatus. Among these methods, electron propagator theory [1] is distinguished by its retention of many conceptual advantages that facilitate interpretation of molecular structure and spectra [2, 3, 4, 5, 6, 7, 8, 9].

2 Electron Propagator Poles and Residues

The physical meaning of the electron propagator rests chiefly in its poles (energies where singularities lie) and residues (coefficients of the terms responsible for the singularities) [1]. In its spectral form, the r, s element of the electron propagator matrix is

$$G_{rs}(E) = \lim_{\eta \to 0} \{ \sum_n \frac{\langle N|a_r^\dagger|N-1,n\rangle\langle N-1,n|a_s|N\rangle}{E + E_n(N-1) - E_0(N) - i\eta} + \sum_m \frac{\langle N|a_s|N+1,m\rangle\langle N+1,m|a_r^\dagger|N\rangle}{E - E_m(N+1) + E_0(N) + i\eta} \}. \quad (1)$$

The propagator matrix is energy–dependent; poles occur when E equals an ionization energy, $E_0(N) - E_n(N-1)$, or an electron affinity, $E_0(N) - E_m(N+1)$. Dyson orbitals (DOs) for ionization energies are defined by

$$\phi_n^{Dyson,IE}(x_1) = \int \Psi_N(x_1, x_2, x_3, \ldots, x_N)\Psi_{N-1,n}^*(x_2, x_3, x_4, \ldots, x_N) \, dx_2 dx_3 dx_4 \cdots dx_N, \quad (2)$$

and are related to propagator residues (also known as Feynman–Dyson amplitudes) by

$$\phi_n^{Dyson,IE}(x) = \sum_r \phi_r(x)\langle N-1,n|a_r|N\rangle. \quad (3)$$

For electron affinities, the corresponding relationships are

$$\phi_n^{Dyson,EA}(x_1) = \int \Psi_N^*(x_2, x_3, x_4, \ldots, x_{N+1})\Psi_{N+1,n}(x_1, x_2, x_3, \ldots, x_{N+1}) \, dx_2 dx_3 dx_4 \cdots dx_{N+1} \quad (4)$$

and

$$\phi_n^{Dyson,EA}(x) = \sum_r \phi_r(x)\langle N+1,n|a_r^\dagger|N\rangle. \quad (5)$$

Many kinds of transition probabilities depend on DOs. Photoionization cross sections, σ^{PI}, are proportional to the absolute squares of matrix elements between DOs and continuum orbitals, or

$$\sigma^{PI} = \kappa^{PI} |\langle \phi^{Dyson} | \hat{T} \phi^{Continuum} \rangle|^2, \tag{6}$$

where κ^{PI} is a constant and $\hat{T}$ is a transition operator describing the interaction between electrons and the radiation field [10]. DOs also are useful in computing cross sections for various electron scattering processes [11, 12].

For the final state, n, the pole strength, P_n, is defined by

$$P_n = \int |\phi_n^{Dyson}(x)|^2 dx. \tag{7}$$

Normalized DOs therefore read

$$\psi_n^{Dyson}(x) = P_n^{-\frac{1}{2}} \phi_n^{Dyson}(x). \tag{8}$$

In the uncorrelated limit, where the many–electron Fock operator replaces the full electronic Hamiltonian, familiar objects of HF theory are recovered as special cases. $|N\rangle$ becomes a HF, determinantal wavefunction for N electrons and $|N \pm 1\rangle$ states become the frozen–orbital wavefunctions that are invoked in Koopmans's theorem. Poles equal canonical orbital energies and DOs are identical to canonical orbitals.

It is possible to use full or limited configuration interaction wavefunctions to construct poles and residues of the electron propagator. However, in practical propagator calculations, generation of this intermediate information is avoided in favor of direct evaluation of electron binding energies and DOs.

3 Operator Space Diagonalization

Through introduction of superoperators and a corresponding metric [13], the propagator may be represented more compactly [2, 6]. Superoperators act on field operator products, X, where the number of annihilators exceeds the number of creators by one. The identity superoperator, $\hat{I}$, and the Hamiltonian superoperator, $\hat{H}$, are defined by

$$\hat{I}X = X \tag{9}$$

and

$$\hat{H}X = [X, H]_-, \tag{10}$$

respectively. The superoperator metric, defined by

$$(\mu|\nu) = \langle N|[\mu^\dagger, \nu]_+|N\rangle, \tag{11}$$

depends on the choice of the N-electron reference state, $|N\rangle$. Consideration of ionization energy and electron affinity poles in a single propagator leads to the anticommutator, $\mu^\dagger\nu + \nu\mu^\dagger$, contained in the metric definition. (Had this discussion considered either the first or second summations in equation 1, the anticommutator would have been abandoned in favor of $\mu^\dagger\nu$ or $\nu\mu^\dagger$, respectively.) With this notation, one may write

$$G_{rs}(E) = (a_r|(E\hat{I} - \hat{H})^{-1}a_s). \tag{12}$$

Thus the matrix elements of the electron propagator are related to field operator products arising from the superoperator resolvent, $(E\hat{I} - \hat{H})^{-1}$, that are evaluated with respect to $|N\rangle$. In this sense, electron binding energies and DOs are properties of the reference state.

In matrix notation, equation 12 is rewritten as

$$\mathbf{G}(E) = (\mathbf{a}|(E\hat{I} - \hat{H})^{-1}\mathbf{a}), \tag{13}$$

where the rank of the propagator matrix equals the number of spin-orbitals. After inner projection,

$$\mathbf{G}(E) = (\mathbf{a}|\mathbf{u})(\mathbf{u}|(E\hat{I} - \hat{H})\mathbf{u})^{-1}(\mathbf{u}|\mathbf{a}), \tag{14}$$

where $\mathbf{u}$ is the vector of all X field operator products. An inverse matrix instead of an inverse superoperator is considered henceforth.

If $\mathbf{u}$ is partitioned into the primary space, $\mathbf{a}$, and an orthogonal space of product operators, $\mathbf{f}$, the partitioned form of the propagator matrix reduces to

$$\mathbf{G}(E) = \begin{bmatrix} \mathbf{1} & \mathbf{0} \end{bmatrix} \begin{bmatrix} E\mathbf{1} - (\mathbf{a}|\hat{H}\mathbf{a}) & -(\mathbf{a}|\hat{H}\mathbf{f}) \\ -(\mathbf{f}|\hat{H}\mathbf{a}) & E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f}) \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \tag{15}$$

Poles of the propagator therefore occur at values of E that are equal to eigenvalues, ω, of the superoperator Hamiltonian matrix:

$$\omega_n \begin{bmatrix} \mathbf{U_{a,n}} \\ \mathbf{U_{f,n}} \end{bmatrix} = \begin{bmatrix} (\mathbf{a}|\hat{H}\mathbf{a}) & (\mathbf{a}|\hat{H}\mathbf{f}) \\ (\mathbf{f}|\hat{H}\mathbf{a}) & (\mathbf{f}|\hat{H}\mathbf{f}) \end{bmatrix} \begin{bmatrix} \mathbf{U_{a,n}} \\ \mathbf{U_{f,n}} \end{bmatrix} \tag{16}$$

or

$$\mathbf{U}\omega = \hat{\mathbf{H}}\mathbf{U}. \tag{17}$$

In the new basis of operators,

$$\mathbf{G}(E) = \begin{bmatrix} \mathbf{1} & \mathbf{0} \end{bmatrix} [\mathbf{U}(E\mathbf{1} - \omega)^{-1}\mathbf{U}^\dagger] \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \tag{18}$$

The DO corresponding to the pole, ω_n, is

$$\phi_n^{Dyson} = \sum_r \phi_r U_{r,n}^* \tag{19}$$

and the pole strength reads

$$P_n = \sum_r |U_{r,n}|^2. \tag{20}$$

Note that contributions from the secondary sector of the eigenvectors, $\mathbf{U_f}$, do not appear in the residues, for the summation index, r, pertains to spin–orbitals only.

Because this route to poles and residues requires only solutions of equation 17, the usual matrix diagonalization techniques characteristic of CI calculations may be applied [14, 15]. The chief conceptual difference between diagonalization of $\hat{\mathbf{H}}$ and diagonalization of the Hamiltonian matrix in Hilbert space is that operators, not many–electron configurations, form the basis. In addition, solutions correspond not to state energies, but to electron binding energies. For each of these energy differences, there corresponds an operator expressed as a linear combination of X components.

Simultaneous treatment of the ionization energy and electron affinity components of the electron propagator allows operator mixings that are not present in Hilbert space methods for energy differences. For ionization energies, operators corresponding to virtual (particle or p) orbitals, shakeon (two particle, one hole or 2p–h) and other (3p–2h, 4p–3h, 5p–4h, et cetera) processes may contribute to the eigenvector, $\mathbf{U}$, in addition to the usual CI–like operators for occupied (hole or h) orbitals, shakeup (two hole, one particle or 2h–p) and other (3h–2p, 4h–3p, 5h–4p, et cetera) processes that generate (N–1)–electron states in Hilbert space when operating on a reference configuration. Electron affinity operators also have h, p, 2h–p, 2p–h and higher–operator–product constituents.

4 Solving One–Electron Equations

Partitioning the operator manifold can lead to efficient strategies for finding poles and residues that are based on solutions of one–electron equations with energy–dependent effective operators [16]. In equation 15, only the upper left block of the inverse matrix is relevant. After a few elementary matrix manipulations, a convenient form of the inverse–propagator matrix emerges, where

$$\mathbf{G}^{-1}(E) = E\mathbf{1} - (\mathbf{a}|\hat{H}\mathbf{a}) - (\mathbf{a}|\hat{H}\mathbf{f})\left[E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f})\right]^{-1}(\mathbf{f}|\hat{H}\mathbf{a}). \tag{21}$$

Because

$$(a_r|\hat{H}a_s) = h_{rs} + \sum_{tu}(rs||tu)\rho_{tu}, \tag{22}$$

where ρ is the one–electron density matrix, the primary operator space block of $\hat{\mathbf{H}}$ may be considered to be a generalized Fock matrix, $\mathbf{F}$. It is possible to

separate the correlated and uncorrelated contributions to the $(\mathbf{a}|\hat{H}\mathbf{a})$ block. In the canonical MO basis,

$$(a_r|\hat{H}a_s) = \epsilon_r\delta_{rs} + \sum_{tu}(rs||tu)\rho^c_{tu} = F_{rs}, \tag{23}$$

where the correlation contribution to the one–electron density matrix is ρ^c and

$$\rho = \rho^{HF} + \rho^c. \tag{24}$$

Elements of the zeroth–order, inverse–propagator matrix are

$$\mathbf{G}_0^{-1}(E)_{rs} = (E - \epsilon_r)\delta_{rs}. \tag{25}$$

(The poles correspond to Koopmans's theorem.) The inverse–propagator matrix and its zeroth–order counterpart therefore are related through

$$\mathbf{G}^{-1}(E) = \mathbf{G}_0^{-1}(E) - \mathbf{\Sigma}(\infty) - \mathbf{\Sigma}'(E) \tag{26}$$

where

$$\mathbf{\Sigma}(\infty)_{rs} = (a_r|\hat{H}a_s)_{correlation} = \sum_{tu}(rs||tu)\rho^c_{tu} \tag{27}$$

and

$$\mathbf{\Sigma}'(E) = (\mathbf{a}|\hat{H}\mathbf{f})\left[E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f})\right]^{-1}(\mathbf{f}|\hat{H}\mathbf{a}). \tag{28}$$

Corrections to the zeroth–order, inverse propagator in equation 26 are gathered together in a term known as the self–energy matrix, $\mathbf{\Sigma}(E)$. The Dyson equation may be written as

$$\mathbf{G}^{-1}(E) = \mathbf{G}_0^{-1}(E) - \mathbf{\Sigma}(E). \tag{29}$$

In the self–energy matrix, there are energy–independent terms and energy–dependent terms:

$$\mathbf{\Sigma}(E) = \mathbf{\Sigma}(\infty) + \mathbf{\Sigma}'(E). \tag{30}$$

In the limit of $|E| \to \infty$, $\mathbf{\Sigma}(E)$ approaches its energy–independent component, $\mathbf{\Sigma}(\infty)$.

When $|det\mathbf{G}(E)| \to \infty$, E is a pole. It is equivalent to require $\mathbf{G}^{-1}(E)$ to have a vanishing eigenvalue at the pole energy, where

$$\mathbf{G}^{-1}(E)\mathbf{C}(E) = 0\mathbf{C}(E). \tag{31}$$

This condition implies that

$$[\epsilon + \mathbf{\Sigma}(E)]\,\mathbf{C}(E) = E\mathbf{C}(E). \tag{32}$$

The latter expression may be rewritten as

$$[\mathbf{F} + \mathbf{\Sigma}'(E)]\,\mathbf{C}(E) = E\mathbf{C}(E). \tag{33}$$

Here, an effective one–electron operator matrix has Fock and energy–dependent, self–energy terms. From this matrix expression, one may abstract one–electron equations in terms of the generalized Fock and energy–dependent, self–energy operators:

$$[F + \Sigma'(E)]\,\phi^{Dyson} \equiv \Gamma(E)\phi^{Dyson} = E\phi^{Dyson}. \tag{34}$$

When E is an eigenvalue of $\Gamma(E)$, E is a pole. The corresponding operator, $\Gamma(E)$, is nonlocal and energy-dependent. In its exact limit, it incorporates all relaxation and differential correlation corrections to canonical orbital energies.

A normalized DO is determined by an eigenvector of $\Gamma(E_{pole})$ according to

$$\psi^{Dyson}(x) = \sum_r \phi_r(x) C_r(E_{pole}), \tag{35}$$

and satisfies

$$\langle \psi^{Dyson} | \psi^{Dyson} \rangle = 1 \tag{36}$$

provided $\mathbf{C}^\dagger\mathbf{C} = 1$. The normalization factor, $\sqrt{P}$, occurring in

$$\phi^{Dyson}(x) = \sqrt{P}\psi^{Dyson} \tag{37}$$

is related to the pole strength, P, such that

$$P = \left[1 - \mathbf{C}^\dagger(E_{pole}) \frac{d\mathbf{\Sigma}(E)}{dE} \mid_{E=E_{pole}} \mathbf{C}(E_{pole})\right]^{-1}. \tag{38}$$

When $\mathbf{\Sigma}(E)$ is neglected, P equals unity for each Koopmans final state.

Results on valence ionization energies of closed–shell molecules generally indicate that off–diagonal elements of the self–energy matrix in the canonical basis are small and have a negligible effect on poles and DOs. Diagonal self–energy approximations explicitly neglect these matrix elements and, as a consequence of equation 35, constrain the DOs to be equal to canonical orbitals. The associated pole search becomes especially easy, for the zeros of the diagonal elements of the Dyson equation can be found by solving

$$E = \epsilon_p + \Sigma_{pp}(E). \tag{39}$$

The usual initial guess, $\epsilon_p + \Sigma_{pp}(\epsilon_p)$, usually leads to convergence in three iterations. Relationships between diagonal self–energy approximations, the transition operator method, the ΔSCF approximation and perturbative treatments of electron binding energies have been analyzed in detail [17, 18].

5 Approximations

5.1 Perturbative $\Sigma(E)$ for Large Molecules

The usual choice of superoperator metric starts from a HF wavefunction plus perturbative corrections [4, 5]:

$$(Y|Z) = (HF|(1 + T^\dagger)[Y^\dagger, Z]_+(1 + T)|HF) \tag{40}$$

where

$$T = T_2^{(1)} + T_1^{(2)} + T_2^{(2)} + T_3^{(2)} + T_4^{(2)} + \cdots. \tag{41}$$

The level of excitation in $T_e^{(f)}$ is indicated by the subscript, e, and the order is defined by the superscript, f. For example, second–order, triple excitations are represented by $T_3^{(2)}$. Coupled–cluster parametrizations of this metric [19] suggest an alternative form:

$$(Y|Z) = \langle HF|e^{-T}[Y^\dagger, Z]_+ e^T|HF\rangle. \tag{42}$$

This choice produces asymmetric superoperator matrices. A simplified final form for the self–energy matrix that does not require optimization of cluster amplitudes is sought for large molecules; the approximation

$$e^T \approx 1 + T_2^{(1)} \tag{43}$$

therefore is made.

With this choice, several third–order terms that appeared with the usual metric are eliminated. The new self–energy matrix in third order is asymmetric and is expressed by

$$\begin{aligned}\boldsymbol{\Sigma}(E) = (\mathbf{a}|\hat{H}\mathbf{f}_3)^{(1)}\{E\mathbf{1} - (\mathbf{f}_3|\hat{H}\mathbf{f}_3)^{(0)}\}^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})^{(1)} \\ +(\mathbf{a}|\hat{H}\mathbf{f}_3)^{(1)}\{E\mathbf{1} - (\mathbf{f}_3|\hat{H}\mathbf{f}_3)^{(0)}\}^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})^{(2)} \\ +(\mathbf{a}|\hat{H}\mathbf{f}_3)^{(1)}\{E\mathbf{1} - (\mathbf{f}_3|\hat{H}\mathbf{f}_3)^{(0)}\}^{-1}(\mathbf{f}_3|\hat{V}\mathbf{f}_3)^{(1)}\{E\mathbf{1} - (\mathbf{f}_3|\hat{H}\mathbf{f}_3)^{(0)}\}^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})^{(1)},\end{aligned} \tag{44}$$

where $\mathbf{f}_3$ is a vector whose elements are 2h–p or 2p–h operators. Note that energy–independent terms in the third–order, self–energy matrix are not retained.

Two observations suggest additional economies. First, numerical results for ionization energies show that third–order, 2p–h terms in equation 44 are small relative to their 2h–p counterparts. Terms arising from these operators are important in second order, however. Second, evaluation of the third–order, 2p–h terms requires integrals with four virtual indices. Because of the large number of these integrals that typically is generated, their storage is often avoided through semidirect algorithms [20]. Contractions involving integrals with four virtual indices remain the bottleneck in third–order calculations.

Neglect of third–order, 2p–h terms produces this self–energy matrix:

$$\begin{aligned}\Sigma(E)_{pq} = \frac{1}{2}\sum_{iab}\frac{\langle pi||ab\rangle\langle ab||qi\rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b} \\ +\frac{1}{2}\sum_{aij}\frac{\langle pa||ij\rangle W_{qaij}}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \frac{1}{2}\sum_{aij}\frac{U_{paij}(E)\langle ij||qa\rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j}\end{aligned} \tag{45}$$

where i, j, k are occupied indices, a, b, c are virtual indices, p, q are general indices,

$$W_{qaij} = \langle qa||ij\rangle + \frac{1}{2}\sum_{bc}\frac{\langle qa||bc\rangle\langle bc||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_b - \epsilon_c} + (1 - P_{ij})\sum_{bk}\frac{\langle qk||bi\rangle\langle ba||jk\rangle}{\epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b} \quad (46)$$

and

$$U_{paij}(E) = -\frac{1}{2}\sum_{kl}\frac{\langle pa||kl\rangle\langle kl||ij\rangle}{E + \epsilon_a - \epsilon_k - \epsilon_l} - (1 - P_{ij})\sum_{bk}\frac{\langle pb||jk\rangle\langle ak||bi\rangle}{E + \epsilon_b - \epsilon_j - \epsilon_k}. \quad (47)$$

This partial third–order expression has been designated by the abbreviation P3 [21].

Comparison of the self–energy matrix elements of equation 45 with older, related methods [7, 15] reveals the advantages of the P3 approximation. Among the intermediates required in third order is

$$V_{piab}(E) = \frac{1}{2}\sum_{cd}\frac{\langle pi||cd\rangle\langle cd||ab\rangle}{E + \epsilon_i - \epsilon_c - \epsilon_d} + (1 - P_{ab})\sum_{jc}\frac{\langle pj||bc\rangle\langle ic||ja\rangle}{E + \epsilon_j - \epsilon_b - \epsilon_c}. \quad (48)$$

The first summation requires electron repulsion integrals with four virtual indices. Efficient algorithms that avoid the storage of these integrals have been discussed in detail [20]. For every orbital index, p, this OV^4 contraction must be repeated for each energy considered in the pole search; it is usually the computational bottleneck.

In the diagonal, P3 approximation, nondiagonal elements of the self–energy matrix are neglected. The first contraction in equation 46 is the most demanding, for it has an arithmetic scaling factor of O^2V^3. This step also requires electron repulsion integrals with one occupied and three virtual indices. The W intermediate is energy–independent and must be evaluated once only for each ionization energy of interest.

The diagonal, P3 self–energy was compared with older propagator methods for 19 ionization energies of six closed–shell molecules with the correlation–consistent, triple ζ basis [21]. The average absolute errors in eV were: 1.34 for Koopmans's theorem, 0.25 for 3+ (a method similar to ADC(3) [7]), 0.25 for OVGF–B (a method based on a scaled, third–order self–energy [7]) and 0.19 for P3. The P3 procedure exhibits accuracy at least as good as that of other methods, superior arithmetic scaling and no need for electron repulsion integrals with four virtual indices.

5.2 Renormalized Methods

According to equation 15, eigenvalues of the superoperator Hamiltonian matrix, $\hat{\mathbf{H}}$, are poles (electron binding energies) of the electron propagator. Several renormalized methods can be defined in terms of approximate $\hat{\mathbf{H}}$ matrices. The

latter are defined by the operator manifold and the reference state employed in the superoperator metric. Renormalized spin–orbitals may be generated according to the so–called Brueckner doubles (BD) recipe [22]. Here, a coupled–cluster singles and doubles wavefunction is reduced to the form

$$|BD\rangle = e^{T_2}|Brueckner\rangle \tag{49}$$

by rotation of the orbitals in the reference determinant, $|Brueckner\rangle$. A convenient reference metric is given by

$$(Y|Z) = \langle Brueckner| \left[Y^\dagger, Z\right]_+ e^{T_2}|Brueckner\rangle. \tag{50}$$

To take advantage of procedures used for configuration interaction calculations, eigenvalues of the symmetrized matrices, $\frac{1}{2}\{\hat{\mathbf{H}} + \hat{\mathbf{H}}^\dagger\}$, are computed.

This choice requires only one major modification in programs written for canonical, HF orbitals. In the Brueckner orbital basis, elements of the $\hat{\mathbf{H}}_{h,p}$ and $\hat{\mathbf{H}}_{p,h}$ blocks of the superoperator Hamiltonian matrix no longer vanish. Double replacement amplitudes from T_2 replace their first–order counterparts that are used in the P3 method. Orbitals that diagonalize the $\hat{\mathbf{H}}_{h,h}$ and $\hat{\mathbf{H}}_{p,p}$ blocks may be chosen without altering the BD ansatz. Electron repulsion integrals and diagonal elements of the generalized Fock matrix in the approximate Brueckner orbital basis therefore replace integrals and orbital energies in the canonical, HF basis. The $\hat{\mathbf{H}}$ matrix employed in calculations described below has the form

$$\hat{\mathbf{H}} = \begin{bmatrix} \hat{\mathbf{H}}_{h,h} & \hat{\mathbf{H}}_{h,p} & \hat{\mathbf{H}}_{h,2hp} & \hat{\mathbf{H}}_{h,2ph} \\ \hat{\mathbf{H}}_{p,h} & \hat{\mathbf{H}}_{p,p} & \hat{\mathbf{H}}_{p,2hp} & \hat{\mathbf{H}}_{p,2ph} \\ \hat{\mathbf{H}}_{2hp,h} & \hat{\mathbf{H}}_{2hp,p} & \hat{\mathbf{H}}_{2hp,2hp} & \hat{\mathbf{H}}_{2hp,2ph} \\ \hat{\mathbf{H}}_{2ph,h} & \hat{\mathbf{H}}_{2ph,p} & \hat{\mathbf{H}}_{2ph,2hp} & \hat{\mathbf{H}}_{2ph,2ph} \end{bmatrix}. \tag{51}$$

An additional approximation is introduced here: elements of the $\hat{\mathbf{H}}_{2hp,2ph}$ block are neglected. Since this block vanishes identically when HF reference states are used, the present approximation may be regarded as an improvement to the so–called 2p–h TDA [7, 23, 24] method with orbital and reference–state renormalizations [25, 26, 27].

6 Applications

6.1 Benzopyrene

Benzo[a]pyrene, a molecule with five, fused, hexagonal rings, is among the most carcinogenic of the polycyclic aromatic hydrocarbons (PAHs). Such biological activity may be related to the electronic structure of benzo[a]pyrene and its metabolites. Ionization energies of these molecules therefore have been investigated with photoelectron spectroscopy [28].

The diagonal, P3 self-energy is ideal for interpreting these experiments [29]. All occupied MOs except for 1s-like core orbitals were included in electron propagator calculations performed with the 6-311G(d,p) basis [30]. Pole strengths (P), listed immediately beneath P3 ionization energies in Table I, indicate that the Koopmans description of each final state is qualitatively valid, for shakeup character is minor. A symmetry-adapted, semidirect algorithm was employed [20]. Programs are incorporated in a modified version of GAUSSIAN-94 [31]. Because of limitations on memory and disk storage, virtual orbitals were dropped in the P3 calculations. A total of 310 occupied and virtual valence orbitals was retained; only virtual orbitals with energies above 2.71 atomic units were dropped.

Table I: Benzo[a]pyrene Ionization Energies (eV)

Orbital	KT	P3 P	Expt. [32]	Orbital Type
10a″	6.90	7.02	7.12	π
		0.87		
9a″	7.94	7.93	8.05	π
		0.86		
8a″	9.04	8.67	8.79	π
		0.85		
7a″	9.43	8.95	8.97	π
		0.86		
6a″	10.18	9.49	9.51	π
		0.84		
5a″	10.77	9.89	9.95	π
		0.83		
56a′	12.51	10.84		σ
		0.88		

In the photoelectron spectrum [32, 33], the sharp peak at 7.12 eV is followed by four regularly spaced peaks of lesser intensity up to 7.7 eV. This vibrational structure is due to the delocalized nature of the corresponding DO. There are no especially large amplitudes in the so-called bay region. A similar pattern of results obtains for the second cationic state. In the spectrum, a sharp peak at 8.00 eV exhibits a subsidiary peak at 8.2 eV that is succeeded by less distinct shoulders up to 8.4 eV. These features also are due to vibrational excitation in the second electronic state. Larger discrepancies between uncorrelated and correlated results occur for the third final state. P3 calculations with the full complement of virtual orbitals will approach 8.7 eV, in excellent agreement with experiment. Correlation effects are quantitatively important for the fourth and fifth final states as well. In the experimental report, the highest energy feature that was assigned occurred at 9.95 eV. No attempt was made therein to assign

higher energy features to specific electronic states. Around 10.5 eV, the lowest discernible features appear. A clearly separable local maximum occurs around 10.9 eV. This feature is part of a broad system with many maxima up to 12.0 eV. This system, in turn, is followed by several, broad, jagged features up to 16 eV. According to the P3 results, the first final state with a σ hole occurs between 10.9–11.0 eV. (This estimate is based on the observation that inclusion of more virtual orbitals increases the predicted ionization energies.) The extensive nuclear rearrangements induced by removal of a σ electron may account for the structure seen on the low energy side of the 10.9–11.0 eV estimate.

6.2 1,10 Phenanthroline

Diaza derivatives of PAHs possess unique chelating properties, display extensive biological activity and are widely used in analytical chemistry, pharmacology and molecular biology [34]. These molecules have been thoroughly scrutinized for antitumor activity, carcinogenicity and mutagenicity. The ability of some phenanthrolines to inhibit electron transfer in biological systems has attracted attention. Derivatives of phenanthrolines have been studied for their potential anti–viral (including anti–HIV) properties.

Ionization energies from molecules with adjacent nitrogen lone pairs usually are assigned with the aid of a simple, two–level splitting model. Here, two lone–pair hybrids produce two combinations, the out–of–phase σN_- and the in–phase σN_+. Relative positions are determined by "through–space" or "through–bond" interactions. Photoelectron spectra of molecules with two aza centers usually are assumed to have two bands corresponding to ionizations from nitrogen lone–pair orbitals. Unfortunately, this concept may lead to erroneous assignments, especially when bands overlap. In azabenzenes, numerous final state misorderings from Koopmans's theorem have been revealed [35].

Because the two nitrogen atoms in 1,10 phenanthroline are separated by less than 3 Å, electron correlation has important consequences for the order of final states. The first ionization energy relates to a π MO with a distribution pattern similar to that of the parent hydrocarbon, phenanthrene. The P3 result shown in Table II is very close to the experimental value [34]. The second ionization band with the experimental maximum at ~8.8 eV represents the overlapping of two cationic states, π_2 $^2A_2$ and the out–of–phase, nitrogen lone–pair hybrid combination, $^2B_2$. A strong resemblance obtains between the former's MO and its π_2 counterpart in phenanthrene. The MO $19b_2$, corresponding to the third ionization, while having some C–C bonding character, consists chiefly of non–bonding, lone–pair hybrids. In this case, the MO with an antibonding combination of lone–pair hybrids lies above its bonding counterpart. P3 ionization energies obtained for these states are 8.67 and 8.87 eV, respectively. In the spectrum, there is a large peak at 8.8 eV with a shoulder at 8.6–8.7 eV. Both features are explained by these calculations. The fourth ionization occurs from an MO dominated by an in–phase combination of lone–pair hybrids,

$21a_1$. P3 results are in excellent agreement with experiment. An assignment made on the basis of INDO calculations is incorrect [36]. The peak at ~8.4 eV was assigned to an out–of–phase combination of nitrogen lone–pair hybrids; the in–phase combination was assigned to a feature at 11.76 eV. Our calculations predict the energy splitting of the two lone–pair levels to be only 0.4–0.5 eV and place these levels much closer to the first two π levels. Correlation corrections to Koopmans's theorem must be included in calculations that are performed to interpret this spectrum. The next three ionizations pertain to π cationic states and the calculated energies are in good agreement with the experimental values.

Table II: 1,10–Phenanthroline Ionization Energies (eV)

State	KT	P3	Expt. [36]	Orbital
$^2B_1$	8.29	8.39	8.35	π_1
$^2A_2$	8.62	8.67	8.82	π_2
$^2B_2$	10.82	8.87		σN_-
$^2A_1$	11.28	9.33	9.39	σN_+
$^2A_2$	10.62	10.17	10.11	π_3
$^2B_1$	10.86	10.37	10.47	π_4
$^2B_1$	12.49	11.47	11.16	π_5

6.3 Anions

Anion photoelectron spectroscopy [37, 38] and photodetachment techniques [39] provide accurate information on electron detachment energies of negative ions. Ten closed–shell anions considered here exhibit sharp peaks, indicative of minor or vanishing final–state nuclear rearrangements, in their photoelectron spectra. Comparisons between theory and experiment are straightforward, for differences between vertical and adiabatic electron detachment energies (VEDEs and AEDEs, respectively) are small.

These data are ideal tests for renormalized *ab initio* methods. Perturbative propagator methods have yielded poor agreement with experiment for F^- and OH^- [40]. For example, OVGF predictions for F^- and OH^- with a polarized, triple ζ basis augmented with diffuse functions are 5.00 and 2.86 eV, respectively.

Table III displays VEDEs obtained with the Brueckner–reference methods discussed in Section 5.2 and augmented, correlation–consistent, triple–ζ basis sets [41]. AEDEs include zero–point energy differences and relaxation energies pertaining to geometrical relaxation on the neutral's potential energy surface. The average absolute error with respect to experiment is 0.05 eV [26].

Table III: Electron Detachment Energies (eV)

Anion	Final State	VEDE	AEDE	Expt. [26]
F^-	^2P	3.54		3.40
OH^-	$^2\Pi$	1.85	1.85	1.83
NH_2^-	$^2B_1$	0.68	0.70	0.77 ± 0.005
Cl^-	^2P	3.61		3.61
SH^-	$^2\Pi$	2.29	2.30	2.32 ± 0.01
PH_2^-	$^2B_1$	1.20	1.22	1.27 ± 0.01
BO^-	$^2\Sigma^+$	2.57	2.54	2.51 ± 0.01
CN^-	$^2\Sigma^+$	3.83	3.83	3.86
AlO^-	$^2\Sigma^+$	2.72	2.69	2.60 ± 0.03
AlS^-	$^2\Sigma^+$	2.74	2.68	2.60 ± 0.03

For F^-, still the most difficult case, the pole strength is 0.90. The 2p orbital in the reference determinant dominates the normalized DO with a coefficient of 0.9997. In the **U** vector of equation 17, the $a^\dagger_{3p\beta}a_{2p\alpha}a_{2p\beta}$ contribution ≈ 0.1.

For OH^-, the pole strength is 0.89 and the 1π coefficient in the normalized DO is 0.9994. A 2h–p operator, $a^\dagger_{2\pi\beta}a_{1\pi\alpha}a_{1\pi\beta}$, also has a **U** element that is approximately 0.1.

Similar results follow for the remaining anions with eight valence electrons. Pole strengths are between 0.88 and 0.90 for NH_2^-, SH^- and PH_2^-. A somewhat larger value, 0.95, obtains for Cl^-. For NH_2^- and PH_2^-, there are 2h–p **U** elements for both final states with absolute values between 0.1 and 0.2. The operators in question have the form $a^\dagger_{tb_1\beta}a_{nb_1\alpha}a_{nb_1\beta}$ or $a^\dagger_{tb_1\beta}a_{nb_1\alpha}a_{ma_1\beta}$, where n and m are labels for occupied orbitals and t is an unoccupied orbital label.

For diatomics with ten valence electrons, pole strengths lie between 0.86 and 0.89. DOs are dominated by a single occupied orbital in all cases. In the normalized DO for the $^2\Sigma^+$ state of AlO, there are other contributions with coefficients near 0.02. For the $^2\Sigma^+$ states of BO and AlO, certain $a^\dagger_{t\sigma\beta}a_{n\sigma\alpha}a_{n\sigma\beta}$ operators have **U** elements that are approximately 0.1. Recent experimental work has produced a revised figure, 2.508 ± 0.008 eV, for the electron affinity of BO [42] and the entry in Table III is in excellent agreement. Similar agreement occurs for the electron affinities of CN, AlO and AlS.

6.4 Ozone

Applications of electron propagator methods with a single–determinant reference state seldom have been attempted for biradicals such as ozone, for operator space partitionings and perturbative corrections therein assume the dominance of a lone configuration in the reference state. Assignments of the three lowest cationic states were inferred from asymmetry parameters measured with Ne I, He I and He II radiation sources [43].

Correlated variational calculations with small basis sets provided qualitative descriptions of the cationic states in terms of symmetry–adapted or localized orbitals. Hay, Dunning and Goddard's GVB–CI description of ground state O_3 consists of a $6a_1^2 4b_2^2 1b_1^2 1a_2^2$ reference and a $1a_2^2 \rightarrow 2b_1^2$ double excitation [44]. Here, a singlet–coupled, biradical pair of electrons is placed on two p_π orbitals centered on terminal oxygens. Application of $4b_2$, $6a_1$ or $1a_2$ annihilation operators to this state produces a valence–bond description of the cations where holes occur in terminal–atom π or lone–pair σ orbitals. Kosugi, Kuroda and Iwata emphasized the importance of 2h–p configurations in describing the $^2A_1$ and $^2B_2$ states [45]. Malmquist, Ågren and Roos observed the importance of single and double replacements from $1b_1$ to $2b_1$ for the $^2A_2$ state [46].

OVGF calculations reversed the order of the $^2A_2$ and $^2B_2$ states [47]. Fock–space, multi–reference, coupled–cluster calculations with a 5s4p2d basis obtained excellent agreement with experiment [48]. Recent multiconfigurational, spin–tensor, electron propagator calculations were based on an active orbital space defined by the irreducible representations of the three highest occupied and three lowest unoccupied HF orbitals [49]. Six electrons are assigned to an active space consisting of $6a_1$, $4b_2$, $1a_2$, $2b_1$, $7a_1$ and $5b_2$ orbitals. (Symmetry adaptation of 2p atomic orbitals produces a space that also contains $5a_1$, $1b_1$ and $3b_2$ constituents.) The results are relatively insensitive to basis improvements and are in excellent agreement with experiment.

The Brueckner–reference method discussed in Section 5.2 and the cc–pvqz basis set without g functions were applied to the vertical ionization energies of ozone [27]. Errors in the results of Table IV lie between 0.07 and 0.17 eV; pole strengths (P) displayed beside the ionization energies are approximately equal to 0.9. Examination of cluster amplitudes and elements of U vectors for each ionization energy reveals the reasons for the success of the present calculations. The cluster operator amplitude for the double excitation to $2b_1^2$ from $1a_2^2$ is approximately 0.19. For each final state, the most important operator pertains to an occupied spin–orbital in the reference determinant, but there are significant coefficients for 2h–p operators. For the $^2A_2$ case, a balanced description of ground state correlation requires inclusion of a 2p–h operator as well. The $2b_1$ orbital's creation or annihilation operator is present in each of the 2h–p and 2p–h operators listed in Table IV. Pole strengths are approximately equal to the square of the principal h operator coefficient and contributions by other h operators are relatively small.

Table IV: Ozone Ionization Energies (eV) and Operators

n	ν	ν Type	$\lvert U_{\nu,n}\rvert$	P	Pole	Expt. [43]
$^2A_1$	$(6a_1\alpha)$	h	0.93	0.88	12.66	12.73
	$(2b_1\beta)^\dagger(4b_2\alpha)(1a_2\beta)$	2h–p	0.14			
$^2B_2$	$(4b_2\alpha)$	h	0.93	0.88	12.83	13.00
	$(2b_1\beta)^\dagger(6a_1\alpha)(1a_2\beta)$	2h–p	0.14			
$^2A_2$	$(1a_2\alpha)$	h	0.93	0.87	13.65	13.54
	$(2b_1\beta)^\dagger(1b_1\alpha)(1a_2\beta)$	2h–p	0.14			
	$(1a_2\beta)^\dagger(2b_1\alpha)(2b_1\beta)$	2p–h	0.18			

7 Conclusions

Electron propagator theory generates a one–electron picture of electronic structure that includes electron correlation. One–electron energies may be obtained reliably for closed–shell molecules with the P3 method and more complex correlation effects can be treated with renormalized reference states and orbitals. To each electron binding energy, there corresponds a Dyson orbital that is a correlated generalization of a canonical molecular orbital. Electron propagator theory enables interpretation of precise *ab initio* calculations in terms of one–electron concepts.

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Students who join the Öhrn research group soon discover that graduate school, in Yngve's view, is a license to learn. The scientific individuality of each of Yngve's present and former students has been built on this foundation of freedom and on the patient friendship of an exemplary advisor.

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