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Electron Propagator Theory and Application

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ABSTRACT

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1. Introduction

Propagators gained early prominence in formal many-body theory of fermion systems (see *e.g.* [1] and references therein). Concerns about the elimination of unlinked terms in perturbation expansions and the associated correct scaling with system size naturally led to the propagator concept. Treatment of double-time Green's functions [2] or, equivalently, propagators established that they provide a useful link between quantum mechanical treatments of pure state systems at the absolute zero and that of ensembles at finite temperature. Condensed matter theory employed the propagator concept to great advantage (see *e.g.* the review by Hedin and Lundqvist [3]) and propagator theory for finite systems [4, 5, 6] led to new ideas for the treatment of molecular systems. A detailed treatment by Linderberg and Öhrn [7] of a variety of spectroscopies for molecular systems further developed and applied propagators. This paper focuses on the electron propagator theory and its application to molecular systems.

The electron propagator is naturally described in Fock space in terms of field operators. Depending on only two electron position and spin coordinates and a time or energy parameter it is in many ways the optimal theoretical quantity with a dynamical equation from which it can be determined in various approximations. It contains a wealth of information. Not only vertical electron binding energies (ionization potentials and electron affinities) [8, 9] [10], but also electron scattering amplitudes [11], photoionization intensities [9, 12], total energies [13, 14], one-electron reduced density matrices [7, 15] and therefore permitting the calculation of one-electron properties [16]. Derivatives of molecular electron binding energies with respect to nuclear displacements [17, 18] have also been determined within the electron propagator theory. Basically all properties of a molecule are contained in the propagator. Thus electronic and rovibrational spectra [10] and the particulars of chemical bonding can be treated in terms of the electron propagator [19, 20].

Given a set of orthonormal spin orbitals $\{\phi_p(\xi)\}$ and the associated set of electron field operators $\{a_p, a_p^\dagger\}$ satisfying the anticommutation relations (at equal times)

$$[a_p, a_q]_+ = [a_p^\dagger, a_q^\dagger]_+ = [a_p, a_q^\dagger]_+ - \delta_{pq} = 0 \tag{1}$$

the electron propagator matrix is defined with elements

$$\begin{aligned} \langle\langle a_p(t); a_q(t') \rangle\rangle = &-i\theta(t-t')\langle 0|a_p(t)a_q^\dagger(t')|0\rangle \\ &+ i\theta(t'-t)\langle 0|a_q^\dagger(t')a_p(t)|0\rangle. \end{aligned} \tag{2}$$

Here

$$\theta(t) = \int_{-\infty}^{t} \delta(\tau)\mathrm{d}\tau \tag{3}$$

is the Heaviside step function expressed in terms of the Dirac delta function, and $|0\rangle$ is the N-electron ground state. Atomic units are used throughout so for instance $\hbar = 1$ and the Heisenberg equation of motion for the field operators is

$$i\frac{\mathrm{d}}{\mathrm{d}t}a_p(t) = [a_p(t), H]_-, \tag{4}$$

A-1

where the commutator on the right contains the many-electron Hamiltonian expressed in the basis electron field operators

$$H = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r. \tag{5}$$

The one-electron integrals involving the electron kinetic energy and the electron-nuclear attraction terms are

$$h_{pq} = \int \phi_p^*(\xi)(-\frac{1}{2}\vec{\nabla}^2 - \sum_{\kappa=1}^{N_n} \frac{Z_\kappa}{|\vec{r} - \vec{R}_\kappa|})\phi_q(\xi)\mathrm{d}\xi \tag{6}$$

and the antisymmetric two-electron integrals are $\langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle$ with

$$\langle pq|rs\rangle = \int \mathrm{d}\xi_1 \int \mathrm{d}\xi_2 \phi_p^*(\xi_1)\phi_q^*(\xi_2)\frac{1}{|\vec{r}_1 - \vec{r}_2|}\phi_r(\xi_1)\phi_s(\xi_2). \tag{7}$$

The electron propagator is most commonly studied via its Fourier transform

$$\langle\langle a_p; a_q^\dagger\rangle\rangle_E = \int_{-\infty}^{\infty} \langle\langle a_p(t); a_q^\dagger(t')\rangle\rangle \exp[-iE(t-t')]\mathrm{d}(t-t'), \tag{8}$$

which has the spectral representation [21, 7]

$$\begin{aligned}\langle\langle a_p; a_q^\dagger\rangle\rangle_E = \lim_{\eta\to+0} \sum_m \Big[&\frac{\langle 0|a_p|m\rangle\langle m|a_q^\dagger|0\rangle}{E + E_0(N) - E_m(N+1) + i\eta} \\ &+ \frac{\langle 0|a_q^\dagger|m\rangle\langle m|a_p|0\rangle}{E - E_0(N) + E_m(N-1) - i\eta}\Big].\end{aligned} \tag{9}$$

showing the typical pole structure, when the energies are discrete as they always are in a finite basis set. The energy eigenstates are used in this formal expression, *i.e.*

$$\begin{aligned} H|0\rangle &= E_0(N)|0\rangle, \\ H|m\rangle &= E_m(N \pm 1)|m\rangle \end{aligned} \tag{10}$$

and only the N+1 and N-1 electron states are involved as intermediates in the spectral representation.

It is obvious from the spectral representation that the electron propagator has a special significance for photoelectron spectroscopy and other processes where electron binding energies are measured. The numerator contains the so called Feynman-Dyson amplitudes

$$\begin{aligned} f_p(m) &= \langle 0|a_p|m\rangle, \\ g_p(m) &= \langle m|a_p|0\rangle, \end{aligned} \tag{11}$$

which are obtained as residues at the particular poles of interest. These amplitudes are important in the theoretical determination of transition probabilities for electron attachment or detachment processes. For instance, the intensity of a particular structure corresponding to the final positive

ion state m in a photoelectron spectrum of a neutral species is proportional to the pole strength [8, 9] $\Gamma_m = \sum_p |g_p(m)|^2$.

The propagator in equation (9) satisfies the equation of motion

$$\begin{aligned} E\langle\langle a_p; a_q^\dagger\rangle\rangle_E &= \langle 0|[a_p, a_q^\dagger]_+|0\rangle + \langle\langle [a_p, H]_-; a_q^\dagger\rangle\rangle_E \\ &= \langle 0|[a_p, a_q^\dagger]_+|0\rangle + \langle\langle a_p; [H, a_q^\dagger]_-\rangle\rangle_E \end{aligned} \tag{12}$$

which can be readily shown by using the identity

$$E(E-x)^{-1} = 1 + x(E-x)^{-1} \tag{13}$$

with $x = E_m(N+1) - E_0(N)$ or $x = E_0(N) - E_m(N-1)$ in the spectral representation and utilizing the properties (10) of the energy eigenstates. The two equivalent forms of the equation of motion (12) are useful in manipulating the chain of equations that obviously results when the corresponding equation of motion is written for the propagator on the right, which involves the commutator with the Hamiltonian, yielding an even more involved propagator on the right with, say, a double commutator $[[a_p, H]_-, H]_-$, and so on. Approximate treatments of the propagator equations include the termination of this chain of equations at some suitable level or assumptions that permit the summation of the expansions. This so called decoupling problem was addressed in its generality by Linderberg and Öhrn [6] by linearizing the equation of motion. There has also appeared discussions of truncation schemes expressed in terms of diagrammatic expansions by Cederbaum and Domcke [10], the moment conserving decoupling using Padé approximants as well as various renormalization schemes discussed by Öhrn and Born [22], and decoupling procedures expressed in terms of superoperators [23].

Although equivalent to other procedures the superoperator formulation provides a particularly attractive shorthand notation. It proceeds by introducing a linear space L of fermion-like field operators

$$L = \{a_p^\dagger, a_p^\dagger a_q^\dagger a_r (p<q), a_p^\dagger a_q^\dagger a_r^\dagger a_s a_t (p<q<r; t<s), \cdots\}, \tag{14}$$

which supports a scalar product

$$(X|Y) = \langle 0|[X^\dagger, Y]_+|0\rangle, \quad X, Y \in L. \tag{15}$$

The superoperator identity $\hat{I}$ and superoperator Hamiltonian $\hat{H}$ are defined on L such that

$$\begin{aligned} \hat{I}X &= X \\ \hat{H}X &= [H, X]_-. \end{aligned} \tag{16}$$

Iterating the second form of the equation (12) yields

$$\begin{aligned} \langle\langle a_p; a_q^\dagger\rangle\rangle_E &= \frac{(a_p^\dagger|a_q^\dagger)}{E} + \frac{(a_p^\dagger|\hat{H}a_q^\dagger)}{E^2} + \frac{(a_p^\dagger|\hat{H}^2 a_q^\dagger)}{E^3} + \cdots \\ &= (a_p^\dagger|(E\hat{I} - \hat{H})^{-1} a_q^\dagger), \end{aligned} \tag{17}$$

i.e. a matrix element of the superoperator resolvent. The full matrix can be expressed as

$$\mathbf{G}(E) = (\mathbf{a}^\dagger|(E\hat{I} - \hat{H})^{-1}\mathbf{a}^\dagger) \tag{18}$$

with the field operators arranged in a suitable row array on the right and column array on the left.

Using an inner projection [24] manifold $\mathbf{h} \in L$ the superoperator inverse can be transformed to a matrix inverse

$$\mathbf{G}(E) = (\mathbf{a}^\dagger|\mathbf{h})(\mathbf{h}|(E\hat{I} - \hat{H})\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}^\dagger). \tag{19}$$

This expression is the starting point for the approximate treatments of the electron propagator.

2. Approximations to the Electron Propagator

Partitioning of inner projection manifold

The simplest decoupling of equation (12) is to consider the so called moment expansion in equation (17) and make the assumption that higher moments are powers of the first moment

$$\mathbf{F} = (\mathbf{a}^\dagger|\hat{H}\mathbf{a}^\dagger). \tag{20}$$

This is often referred to as the geometric approximation. Denoting $(\mathbf{a}^\dagger|\mathbf{a}^\dagger) = \mathbf{S}$ the moment expansion (17) becomes

$$\begin{aligned} \mathbf{G}(E) &\approx E^{-1}\mathbf{S}[1 + E^{-1}\mathbf{S}^{-1}\mathbf{F} + E^{-2}\mathbf{S}^{-1}\mathbf{F}\mathbf{S}^{-1}\mathbf{F} + \cdots] \\ &= \mathbf{S}(E\mathbf{S} - \mathbf{F})^{-1}\mathbf{S} = (\mathbf{a}^\dagger|(E\hat{I} - \hat{H})\mathbf{a}^\dagger)^{-1} = \mathbf{G}_0(E) \end{aligned} \tag{21}$$

The anticommutation relations (1) yielding

$$S_{pq} = (a_p^\dagger|a_q^\dagger) = \langle 0|[a_p, a_q^\dagger]_+|0\rangle = \delta_{pq}, \tag{22}$$

and

$$\begin{aligned} F_{pq} &= (a_p^\dagger|\hat{H}a_q^\dagger) = \langle 0|[a_p, [H, a_q^\dagger]_-]_+|0\rangle \\ &= h_{pq} + \sum_{r,s}\langle pr||qs\rangle\langle 0|a_r^\dagger a_s|0\rangle \end{aligned} \tag{23}$$

have been employed, where in the last expression F_{pq} is a matrix element of the Fock operator in the spin orbital basis. The single-particle reduced density matrix has the elements

$$\gamma_{sr} = \langle 0|a_r^\dagger a_s|0\rangle \tag{24}$$

and can be diagonalized simultaneously with $\mathbf{F}$ to give occupation numbers $\langle n_r\rangle$, *i.e.* $\gamma_{sr} = \langle n_r\rangle\delta_{sr}$ and $\mathbf{x}^\dagger\mathbf{F}\mathbf{x} = \epsilon$ for some suitable unitary transformation $\mathbf{x}$. Comparing equation (21) with the formal spectral representation (9) it is possible to write

$$G_{0pq}(E) = \lim_{\eta\to+0}\sum_r x_{pr}\left[\frac{\langle n_r\rangle}{E - \epsilon_r - i\eta} + \frac{1 - \langle n_r\rangle}{E - \epsilon_r + i\eta}\right]x_{qr}^*. \tag{25}$$

For the case that the occupation numbers are 0 or 1 the reference state $|0\rangle$ must be a single determinant in terms of the self-consistent field (SCF) spin orbitals

$$\chi_r = \sum_p \phi_p x_{pr} \tag{26}$$

or equivalently expressed in terms of the field operators and the vacuum state as

$$|0\rangle = \prod_{i=1}^{N} a_i^\dagger |vac\rangle \equiv \prod_i i^\dagger |vac\rangle. \tag{27}$$

In the following the electron field operators $\{a_r \equiv r\}$ refer to the SCF spin orbitals $\{\chi_r\}$. It then follows through (25) that at this level of approximation, the occupied spin orbital energies must be identified with ionization potentials and the unoccupied ones with electron affinities as is done through Koopmans theorem.

This is considered the lowest level of approximation and used as a starting point for all higher level treatments of the electron propagator. The SCF spin orbitals and then also the corresponding electron field operators naturally separate into an occupied set labeled by *i,j,k* ... and an unoccupied set labeled by *a,b,c,* .... The labels *p,q,r,* ... refer to either set.

The inner projection manifold h used in the expression (19) need only contain fermionlike operators [25] *i.e.*

$$\begin{aligned} \{\mathbf{h}\} &= \{\mathbf{h}_1\} \cup \{\mathbf{h}_3\} \cup \{\mathbf{h}_5\} \cup \cdots \\ &= \{a^\dagger, i^\dagger\} \cup \{a^\dagger b^\dagger i, i^\dagger j^\dagger a\} \cup \{a^\dagger b^\dagger c^\dagger ij, i^\dagger j^\dagger k^\dagger ab\} \cup \cdots \end{aligned} \tag{28}$$

and truncations of this manifold corresponds to various approximation schemes. It is convenient to use an orthonormal set of inner projection basis elements [25] so that $(\mathbf{h}_i|\mathbf{h}_i) = 1$, and $(\mathbf{h}_i|\mathbf{h}_j) = 0$ for $i \neq j$.

A first step in seeking adequate approximation schemes for the electron propagator is a partitioning of the inner projection manifold. When the aim is to obtain a theoretical photoelectron spectrum it is convenient to choose the partitioning

$$\begin{aligned} \mathbf{h} &= \{\mathbf{h}_1, \mathbf{f}\} \\ \mathbf{f} &= \{\mathbf{h}_3\} \cup \{\mathbf{h}_5\} \cup \cdots \end{aligned} \tag{29}$$

such that equation (19) becomes

$$\mathbf{G}(E) = [\mathbf{1} \quad \mathbf{0}] \begin{bmatrix} E\mathbf{1} - (\mathbf{a}^\dagger|\hat{H}\mathbf{a}^\dagger) & -(\mathbf{a}^\dagger|\hat{H}\mathbf{f}) \\ -(\mathbf{f}|\hat{H}\mathbf{a}^\dagger) & E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f}) \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \tag{30}$$

The partitioned form of the inverse matrix yields

$$\begin{aligned} \mathbf{G}^{-1}(E) &= E\mathbf{1} - (\mathbf{a}^\dagger|\hat{H}\mathbf{a}^\dagger) - (\mathbf{a}^\dagger|\hat{H}\mathbf{f})[E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f})]^{-1}(\mathbf{f}|\hat{H}\mathbf{a}^\dagger) \\ &= \mathbf{G}_0^{-1}(E) - \Sigma(E), \end{aligned} \tag{31}$$

where the unperturbed propagator and the self-energy term have been defined to show the relation to the so called Dyson-like equation for the propagator [1]. An untruncated manifold f means no approximation only a reformulation of the propagator equations. In order to arrive at a definite approximation and provide algorithms for the calculation of the matrix elements defining the propagator, a reference state and a truncation of the inner projection field operator manifold must be chosen.

Choice of reference state

The Hartree-Fock or SCF single determinantal state $|0\rangle = |HF\rangle$ provides the natural starting point for the choice of reference state at various levels of approximation. Although the electron propagator theory can be fully developed within a perturbation theory framework with only the SCF single determinantal reference state and choice of inner projection manifold [22] it is desirable to keep a balance between the level of description of the reference state $|0\rangle$ and that of the inner projection manifold f. Such a balance kept through various orders of perturbation theory guarantees hermiticity of the superoperator Hamiltonian matrix and the elimination of spurious terms [25]. Starting from a partitioning of the Hamiltonian and thus also of the superoperator Hamiltonian

$$\begin{aligned} H &= H_0 + \delta H \\ H_0 &= \sum_p \epsilon_p p^\dagger p \\ \delta H &= \sum_{p,q,r,s} \langle pq||rs\rangle \left[\frac{1}{4} p^\dagger q^\dagger s r - \delta_{qs}\langle n_s\rangle p^\dagger r\right] \end{aligned} \tag{32}$$

the reference state can be expressed in terms of Rayleigh-Schrödinger perturbation theory (RSPT) [26, 27], or coupled-cluster (CC) theory. Also multiconfigurational SCF (MCSCF) theory has been implemented [28] for the electron propagator reference state. This treatise employs reference states based on RSPT and CC theory.

The hermiticity problem consists of the equation

$$(X|\hat{H}Y) = (Y|\hat{H}X)^* \tag{33}$$

not being satisfied for an approximate reference state or more generally for a density operator

$$\rho = \rho_0 + \delta\rho + \delta^2\rho + \cdots + \delta^n\rho \tag{34}$$

correct through order n in perturbation theory. The average defining the propagator matrices is then a trace, *i.e.*

$$\langle\cdots\rangle \equiv \mathrm{Tr}\{\rho\cdots\}. \tag{35}$$

Since

$$\begin{aligned} \langle[X^\dagger,[H,Y]_-]_+\rangle - \langle[Y^\dagger,[H,X]_-]_+\rangle^* &= \langle[H,[X^\dagger,Y]_+]_-\rangle \\ &= \mathrm{Tr}\{\rho[H,[X^\dagger,Y]_+]_-\} = \mathrm{Tr}\{[\rho,H]_-[X^\dagger,Y]_+]_-\} \end{aligned} \tag{36}$$

and since

$$[\rho_0, H_0]_- = 0 \tag{37}$$

and

$$[\delta^k\rho, H_0]_- + [\delta^{k-1}\rho, \delta H]_- = 0 \tag{38}$$

are assumed to hold for $k = 1, 2, \ldots, n$, the error term is of order n+1, *i.e.*

$$(X|\hat{H}Y) - (Y|\hat{H}X)^* = \mathrm{Tr}\{[\delta^n\rho, \delta H]_-[X^\dagger, Y]_+\}. \tag{39}$$

The Rayleigh-Schrödinger perturbation expansion for the reference state,

$$|0\rangle_{RSPT} = (1 + K_1 + K_2 + K_3 + \cdots)|HF\rangle, \tag{40}$$

is defined by

$$K_1 = \sum_i \sum_a k_i^a a^\dagger i \,, \tag{41}$$

$$K_2 = \sum_{i>j} \sum_{a>b} k_{ij}^{ab} a^\dagger i b^\dagger j \,, \tag{42}$$

and

$$K_3 = \sum_{i>j>k} \sum_{a>b>c} k_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k \,, \tag{43}$$

with , in particular

$$k_{ij}^{ab} = \frac{\langle ij||ab\rangle}{D_{ij}^{ab}} \,, \tag{44}$$

and

$$k_i^a = \frac{1}{2}\left[\sum_{jbc} \frac{\langle bc||aj\rangle}{D_i^a} k_{ij}^{bc} - \sum_{jkb} \frac{\langle ib||jk\rangle}{D_i^a} k_{jk}^{ab}\right]. \tag{45}$$

The denominators are defined as

$$D_i^a = \epsilon_i - \epsilon_a \,, \tag{46}$$

and

$$D_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \,. \tag{47}$$

The concept of order in the perturbation expansion of the electron propagator ultimately means order in terms of the electron-electron interaction or equivalently two-electron integrals. The inclusion of electron correlation through first order in the reference state is achieved with the double excitation terms K_2 whereas also the K_1 terms are needed for second-order corrections.

Coupled-cluster renormalization of the reference state

The coupled-cluster (CC) expression [29] for the reference state

$$|0\rangle_{CC} = e^T |HF\rangle \,, \tag{48}$$

is defined by

$$T = T_1 + T_2 + T_3 + \ldots + T_N \,, \tag{49}$$

with N being the number of electrons of the system, and

$$T_1 = \sum_i \sum_a t_i^a a^\dagger i \,, \tag{50}$$

$$T_2 = \sum_{i>j} \sum_{a>b} t_{ij}^{ab} a^\dagger i b^\dagger j \,, \tag{51}$$

$$T_3 = \sum_{i>j>k} \sum_{a>b>c} t_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k \,, \tag{52}$$

and so on.

The T amplitudes contain infinite order contributions to each excitation level from the HF state. Thus, replacing the RSPT K amplitudes with the CC T amplitudes may be considered a renormalization procedure since certain classes of perturbation terms or diagrams are summed to infinite order [30, 31]. This idea has already been employed in work on the polarization propagator [32, 33].

Details of the coupled-cluster approach

Expansion of the exponential in the CC method gives,

$$\begin{aligned} |0\rangle_{CC} &= [1 + T_1 + (T_2 + \frac{1}{2}T_1^2) + \ldots]|HF\rangle \\ &= [1 + \sum_i \sum_a t_i^a a^\dagger i + \sum_{i>j} \sum_{a>b} t_{ij}^{ab} a^\dagger b^\dagger i j \\ &+ \frac{1}{2}(\sum_i \sum_a t_i^a a^\dagger i)(\sum_j \sum_b t_j^b b^\dagger j) + \ldots]|HF\rangle \,, \end{aligned} \tag{53}$$

where the last term can be rewritten as

$$\begin{aligned} \frac{1}{2}(\sum_i \sum_a t_i^a a^\dagger i)(\sum_j \sum_b t_j^b b^\dagger j) &= \sum_{i>j} [(\sum_a t_i^a a^\dagger i)(\sum_b t_j^b b^\dagger j)] \\ &= \sum_{i>j} \sum_{a>b} [(t_i^a t_j^b a^\dagger i b^\dagger j) + (t_i^b t_j^a b^\dagger i a^\dagger j)] \,, \end{aligned} \tag{54}$$

and since for the orthonormal basis of SCF spin orbitals,

$$b^\dagger i a^\dagger j = -a^\dagger i b^\dagger j \,, \tag{55}$$

the CC reference state becomes,

$$\begin{aligned} |0\rangle_{CC} &= [1 + T_1 + (T_2 + \frac{1}{2}T_1^2) + \ldots]|HF\rangle \\ &= [1 + \sum_i \sum_a t_i^a a^\dagger i + \sum_{i>j} \sum_{a>b} \tau_{ij}^{ab} a^\dagger i b^\dagger j + \ldots]|HF\rangle \,, \end{aligned} \tag{56}$$

where,

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \,. \tag{57}$$

Restricting the coupled-cluster expansion to single and double (CCSD) excitations, *i.e.*

$$|0\rangle_{CC} \approx |0\rangle_{CCSD} = e^{(T_1+T_2)}|HF\rangle \,, \tag{58}$$

the equations for the T amplitudes become [34],

T_1 equation:

$$D_i^a t_i^a = \sum_b t_i^b F_{ab} - \sum_j t_j^a F_{ji} + \sum_{jb} t_{ij}^{ab} F_{jb} + \\ - \sum_{jb} t_j^b \langle ja||ib\rangle - \frac{1}{2}\sum_{ibc} t_{ij}^{bc}\langle ja||bc\rangle - \frac{1}{2}\sum_{jkb} t_{jk}^{ab}\langle kj||bi\rangle \,, \tag{59}$$

T_2 equation:

$$D_{ij}^{ab} t_{ij}^{ab} = \langle ij||ab\rangle + P(ab)\sum_c t_{ij}^{ac}\left(F_{bc} - \frac{1}{2}\sum_k t_k^b F_{kc}\right) + \\ - P(ij)\sum_k t_{ik}^{ab}\left(F_{kj} + \frac{1}{2}\sum_c t_j^c F_{kc}\right) + \frac{1}{2}\sum_{kl}\tau_{kl}^{ab} W_{klij} + \\ + \frac{1}{2}\sum_{cd}\tau_{ij}^{cd} W_{abcd} + P(ij)P(ab)\sum_{kc}\left(t_{ik}^{ac} W_{kbcj} - t_i^c t_k^a \langle kb||cj\rangle\right) + \\ + P(ij)\sum_c t_i^c \langle ab||cj\rangle - P(ab)\sum_k t_k^a \langle kb||ij\rangle \,, \tag{60}$$

where,

$$F_{ab} = \sum_{kc} t_k^c \langle ka||cb\rangle - \frac{1}{2}\sum_{klc}\tilde{\tau}_{kl}^{ac}\langle kl||bc\rangle \,, \tag{61}$$

$$F_{ji} = \sum_{ak} t_k^a \langle jk||ia\rangle + \frac{1}{2}\sum_{kab}\tilde{\tau}_{ik}^{ab}\langle jk||ab\rangle \,, \tag{62}$$

$$F_{jb} = \sum_{ia} t_i^a \langle ij||ba\rangle \,, \tag{63}$$

$$W_{klij} = \langle kl||ij\rangle + P(ij)\sum_a t_j^a \langle kl||ia\rangle + \frac{1}{4}\sum_{ab}\tau_{ij}^{ab}\langle kl||ab\rangle \,, \tag{64}$$

$$W_{abcd} = \langle ab||cd\rangle - P(ab)\sum_i t_i^b \langle ai||cd\rangle + \frac{1}{4}\sum_{ij}\tau_{ij}^{ab}\langle ij||cd\rangle \,, \tag{65}$$

and,

$$W_{kbcj} = \langle kb||cj\rangle + \sum_a t_j^a \langle kb||ca\rangle - \sum_i t_i^b \langle ki||cj\rangle + \\ - \sum_{ia}\left(\frac{1}{2}t_{ji}^{ab} + t_j^a t_i^b\right)\langle ki||ca\rangle \,. \tag{66}$$

The effective two-particle excitation operators τ and $\tilde{\tau}$ are

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \,, \tag{67}$$

and,

$$\tilde{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2}\left(t_i^a t_j^b - t_i^b t_j^a\right) \,, \tag{68}$$

respectively. In the above equations, $P(ij)$ and $P(ab)$ denote the permutational interchange operations.

The k coefficients in the RSPT expansion can be obtained from the couple-cluster *ansatz* through iteration of the T equations. For instance, the first iteration of the T_2 equation gives K_2, that is,

$$k_{ij}^{ab} = t_{ij}^{ab}(1) = \frac{\langle ij||ab\rangle}{D_{ij}^{ab}}\,, \tag{69}$$

which, when applied in the T_1 equation yields

$$k_i^a = t_i^a(1) = \frac{1}{2}\left[\sum_{jbc}\frac{\langle aj||bc\rangle}{D_i^a}t_{ij}^{bc}(1) - \sum_{jkb}\frac{\langle jk||ib\rangle}{D_i^a}t_{jk}^{ab}(1)\right]. \tag{70}$$

Consequently, it is possible to write reference states for the electron propagator approach as expansion coefficients of the perturbation theory or as converged T amplitudes from the solution of the couple-cluster equations.

Also, in comparing the RSPT and CC wave functions, it is clear that

$$\begin{array}{ccc}
|0\rangle_{RSPT} = (1 + K_1 + K_2 + \ldots)|HF\rangle & & \\
\Updownarrow & & \\
|0\rangle_{CCSD} = (1 + T_1 + (T_2 + T_1^2/2) + \ldots)|HF\rangle & & \\
\Downarrow & & \\
CC - EP & \leftrightarrow & RSPT - EP \\
\Uparrow & & \\
t_i^a & \leftrightarrow & k_i^a \\
\tau_{ij}^{ab} & \leftrightarrow & k_{ij}^{ab}\,.
\end{array} \tag{71}$$

From the definition of the spectral representation (9) it follows that the elements of the electron propagator matrix $\mathbf{G}(E)$ become infinite when E equals an electron binding energy. Then, the elements of the inverse $\mathbf{G}^{-1}(E)$ vanish at such an energy. This result can be used to device iterative methods to find the electron propagator poles and residues at a given level of perturbation expansion.

Order analysis

Truncation of the inner projection operator manifold f and the use of RSPT for the reference state based on the so called Møller-Plesset partitioning of the Hamiltonian as expressed in equation (32) facilitates an order analysis of the electron propagator. In particular, the self-energy (see [26]) and consequently properties as *e.g.* electron binding energies and the one-electron reduced density matrix can be calculated to a given desired order of electron correlation or electron interaction. Starting from the inverse propagator matrix as given in equation (31) and using a shorthand notation the following expression is obtained

$$\mathbf{G}^{-1}(E) = \mathbf{R}_{aa}(E) - \mathbf{R}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{R}_{fa}, \tag{72}$$

where

$$\begin{aligned} \mathbf{R}_{aa}(E) &= (\mathbf{a}^\dagger|(E\hat{I}-\hat{H})\mathbf{a}^\dagger) = E\mathbf{1}-\mathbf{H}_{aa} \\ \mathbf{R}_{af} &= (\mathbf{a}^\dagger|(E\hat{I}-\hat{H})\mathbf{f}) = -\mathbf{H}_{af} \\ \mathbf{R}_{fa} &= (\mathbf{f}|(E\hat{I}-\hat{H})\mathbf{a}^\dagger) = -\mathbf{H}_{fa} = -\mathbf{H}_{af}^\dagger \\ \mathbf{R}_{ff}(E) &= (\mathbf{f}|(E\hat{I}-\hat{H})\mathbf{f}) = E\mathbf{1}-\mathbf{H}_{ff} \end{aligned} \tag{73}$$

The RSPT expression for the reference state then permits the expansion

$$\mathbf{R}_{af} = -\sum_{i=1}^{n}\mathbf{H}_{af}^{(i)} \tag{74}$$

where the fact that $\mathbf{H}_{af}^{(0)} = 0$ has been used. Together with corresponding expansions for the other matrices this gives an expression for the inverse electron propagator matrix through order n as

$$\mathbf{G}_n^{-1}(E) = \mathbf{R}_{aa}^{(0)} + \sum_{i=1}^{n}\mathbf{R}_{aa}^{(i)} - \left[\left(\sum_{i=1}^{n_1}\mathbf{H}_{af}^{(i)}\right)\left(\sum_{i=0}^{n_2}\mathbf{R}_{ff}^{(i)}\right)^{-1}\left(\sum_{i=1}^{n_1}\mathbf{H}_{af}^{\dagger(i)}\right)\right]^{(n)}. \tag{75}$$

The first-order propagator vanishes and the lowest order expressions are obtained by calculating the various matrices to specific orders and by choosing the operator manifold f as follows

$$\begin{aligned} &\mathrm{n}=2 \Rightarrow \mathrm{n}_1=1,\mathrm{n}_2=0;\mathbf{f}=\mathbf{h}_3, \\ &\mathrm{n}=3 \Rightarrow \mathrm{n}_1=2,\mathrm{n}_2=1;\mathbf{f}=\mathbf{h}_3, \\ &\mathrm{n}=4 \Rightarrow \mathrm{n}_1=3,\mathrm{n}_2=2;\mathbf{f}=\mathbf{h}_3\cup\mathbf{h}_5, \end{aligned} \tag{76}$$

which will be further elaborated in the following sections.

Obviously the inversion of the very large matrix $\mathbf{R}_{ff}(E)$ is one of the difficult problems that has to be addressed. An inversion could be performed by employing a reduced linear equation (RLE) scheme [35] but rapidly becomes impractical with increasing basis sets. A number of approximate treatments have been proposed [8, 36, 37] with varying success. The order concept can be preserved with the identity

$$\begin{aligned} \mathbf{R}_{ff}^{-1}(E) &\equiv (\mathbf{R}_{ff}^{(0)} + \sum_{i=1}^{n}\mathbf{R}_{ff}^{(i)})^{-1} \\ &\equiv (\mathbf{R}_{ff}^{(0)})^{-1} - (\mathbf{R}_{ff}^{(0)})^{-1}(\sum_{i=1}^{n}\mathbf{R}_{ff}^{(i)})(\mathbf{R}_{ff}^{(0)} + \sum_{i=1}^{n}\mathbf{R}_{ff}^{(i)})^{-1} \end{aligned} \tag{77}$$

which can be iterated and truncated [38, 39, 8].

Method of solution

The general expression for the element

$$G_{pq}(E) = (a_p|(E\hat{I}-\hat{H})^{-1}a_q)\,. \tag{78}$$

of the electron propagator matrix $\mathbf{G}(E)$ is symmetry blocked, where each block is formed by the spin orbital indices p and q belonging to the same irreducible representation of the orbitals.

In addition, the electron propagator matrix $\mathbf{G}(E)$ is spin blocked. Therefore, it is sufficient to solve separately the electron propagator equations for each symmetry and spin block pq.

For a given block and energy E it is possible to construct the matrix,

$$\begin{aligned}\mathbf{W}(E) &= E\mathbf{1} - \mathbf{G}^{-1}(E) = E\mathbf{1} - (\mathbf{R}_{aa}(E) - \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{af}^{\dagger}) \\ &= E\mathbf{1} - ((\mathbf{a}^{\dagger}|(E\hat{1} - \hat{H})|\mathbf{a}^{\dagger}) - \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{af}^{\dagger}) \\ &= E\mathbf{1} - ((E\mathbf{1} - \mathbf{H}_{aa} - \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{af}^{\dagger}) \\ &= \mathbf{H}_{aa} + \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{af}^{\dagger},\end{aligned} \tag{79}$$

which allows the expression

$$(\mathbf{1}E - \mathbf{W}(E))\mathbf{G}(E) = \mathbf{1}. \tag{80}$$

This shows that the diagonalization

$$\begin{aligned}\mathbf{U}^{\dagger}\mathbf{W}(E)\mathbf{U} = \mathbf{\Lambda}(E) &= \begin{bmatrix} \lambda_1(E) & \cdots & 0 \\ & \ddots & \\ \vdots & \lambda_p(E) & \vdots \\ & & \ddots \\ 0 & \cdots & \lambda_n(E) \end{bmatrix} \\ &= \mathbf{U}^{\dagger}(\mathbf{H}_{aa} + \mathbf{R}_{ab}^{\dagger}\mathbf{R}_{bb}^{-1}(E)\mathbf{R}_{ab})\mathbf{U}\,,\end{aligned} \tag{81}$$

is important, with n being the dimension of the symmetry pq block, and the eigenvalue corresponding to the spin orbital of interest (p) should be the p-th pole (E_p) of the electron propagator matrix. This eigenvalue can be used as the next guess for an iterative search of the p-th pole or used to obtain a guess for a Newton-Raphson procedure. Since the derivatives of $\mathbf{W}(E)$ with respect to E can be evaluated analytically, a Newton-Raphson procedure can be efficiently employed to calculate the next guess for E, so that usually, after 3 or 4 iterations the difference between the input E and the eigenvalue is less than 10^{-5} Hartree.

Layzer [40] treated such (in general nonhermitian) eigenvalue problems. When

$$\mathbf{U}_r(E) = \{U_{pr}\}, \;\; p = 1, 2, \cdots, n \tag{82}$$

is the eigenvector of $\mathbf{W}(E)$ corresponding to the eigenvalue $\lambda_r(E)$ and $\mathbf{U}_r^*(E)$ is the eigenvector of $\mathbf{W}^{\dagger}$ corresponding to eigenvalue $\lambda_r^*(E)$ the expansion

$$G_{pq}(E) = \sum_r \frac{U_{pr}(E)U_{qr}^*(E)}{E - \lambda_r(E)} \tag{83}$$

follows. The types of possible solutions have been discussed by Csanak *et al* [11] and details have been explored by Purvis and Öhrn [8]. The pole of interest E_r is found when

$$E_r = \lambda_r(E_r) \tag{84}$$

and within a finite basis the E_r are real and discrete. Elementary residue calculus gives

$$\lim_{E \to E_R} = [(E - E_r)G_{pq}(E)] = \Gamma_r U_{pr}(E_r)U^*_{qr}(E_r), \tag{85}$$

where

$$\Gamma_r = \left[1 - \frac{d\lambda_r(E)}{dE}\right]_{E=E_r} \tag{86}$$

is the pole strength introduced earlier. The resulting expression

$$G_{pq}(E) = \sum_r \frac{\Gamma_r U_{pr}(E_r)U_{qr}(E_r)}{E - E_r} \tag{87}$$

can then be compared to the spectral representation (9) to find

$$\begin{aligned} \langle 0|a_p|r\rangle &= \Gamma_r^{1/2} U_{pr}(E_r(N+1) - E_0(N)) \\ \langle r|a_p|0\rangle &= \Gamma_r^{1/2} U_{pr}(E_0(N) - E_r(N-1)). \end{aligned} \tag{88}$$

The Feynman-Dyson amplitudes directly associated with the various electron binding energies are then

$$\chi^{FDA}(\xi) = \sum_p \chi_p(\xi) U_{pr}(E_r)\Gamma_r^{1/2} \tag{89}$$

in terms of the canonical molecular SCF spin orbitals.

The relationship of these amplitudes to the electron propagator

$$\begin{aligned} G(\xi, \xi'; E) &= \langle\langle \psi(\xi); \psi^\dagger(\xi') \rangle\rangle_E \\ &= \lim_{\eta \to +0} \sum_r \left[\frac{f_r(\xi) f_r^*(\xi')}{E + E_0(N) - E_r(N+1) + i\eta} + \frac{g_r(\xi) g_r(\xi')}{E - E_0(N) + E_r(N-1) - i\eta} \right] \end{aligned} \tag{90}$$

defined in position and spin coordinate space becomes obvious from the expansion

$$\psi(\xi, t) = \sum_p \chi_p(\xi) a_p(t) \tag{91}$$

of the fundamental electron field operators $\psi(\xi, t)$ and their adjoints in the basis. The Feynman-Dyson amplitudes then are of two kinds associated with electron attachment processes and with electron detachment processes, respectively (compare equation (11)

$$\begin{aligned} f_r(\xi) &= \sum_p \chi_p(\xi) \langle 0|a_p|r\rangle = \sum_p \chi_p(\xi) U_{pr} \Gamma_r^{1/2} \\ g_r(\xi) &= \sum_p \chi_p(\xi) \langle r|a_p|0\rangle = \sum_p \chi_p(\xi) U_{pr} \Gamma_r^{1/2}. \end{aligned} \tag{92}$$

Solution scheme

1. choose r
2. get block pq
3. get guess for E_r
4. construct $\mathbf{W}(E) = \mathbf{H}_{aa} + \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E_r)\mathbf{H}_{af}^{\dagger}$
5. diagonalize $\mathbf{UW}(E_r) = \lambda(E_r)\mathbf{1}$
6. get the eigenvalue λ_r associated with r
7. set $E_{new}^{(i)} = \lambda_r$
8. get new guess (Newton-Raphson):

$$E_{i+1} \simeq E_i - \mathbf{G}^{-1}(E_i)/\left(\frac{\partial \mathbf{G}^{-1}(E)}{\partial E}\right)_{E=E_i} \tag{93}$$

9. $|E_i - E_{i-1}| < 10^{-5}$?
   a. ? yes $\Rightarrow$ $Pole = E_i$
   b. ? no $\Rightarrow$ go to step 3

Order analysis of the propagator matrices

Second-order electron propagator

In the following the subscript 1 refers to the $\mathrm{h}_1 = \mathrm{a}^{\dagger}$ part of the field operator manifold and the subscript 3 to the h_3 part and so on. Through second order the inverse of the electron propagator matrix then becomes

$$\mathbf{G}_{(2)}^{-1}(E) = \mathbf{R}_{11}^{(0)} - \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(1)})^{\dagger}, \tag{94}$$

where

$$\begin{aligned}
(\mathbf{R}_{11}^{(0)}(E))_{pq} &= (E - \epsilon_p)\delta_{pq} \\
(\mathbf{H}_{13}^{(1)})_{p,abi} &= \langle pi||ab\rangle \\
(\mathbf{H}_{13}^{(1)})_{p,ija} &= \langle pa||ij\rangle \\
(\mathbf{R}_{33}^{(0)}(E))_{abi,cdj} &= (E + \epsilon_i - \epsilon_a - \epsilon_b)\delta_{ac}\delta_{bd}\delta_{ij} \\
(\mathbf{R}_{33}^{(0)}(E))_{ija,klb} &= (E + \epsilon_a - \epsilon_i - \epsilon_j)\delta_{ik}\delta_{jl}\delta_{ab}.
\end{aligned} \tag{95}$$

The second-order self-energy matrix then has the elements

$$(\Sigma^{(2)}(E))_{pq} = \frac{1}{2}\sum_{i,a,b}\frac{\langle pi||ab\rangle\langle ab||qi\rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b} + \frac{1}{2}\sum_{i,j,a}\frac{\langle pa||ij\rangle\langle ij||qa\rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j}, \tag{96}$$

where the factor of 1/2 comes from the relaxation of the ordered indices.

Third-order electron propagator

A similar treatment through third order yields [38, 41, 26]

$$\begin{aligned} \mathbf{G}_{(3)}^{-1}(E) &= \mathbf{G}_{(2)}^{-1}(E) \\ &+ \mathbf{H}_{11}^{(3)} - \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(1)})^{\dagger} \\ &- \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(2)})^{\dagger} - \mathbf{H}_{13}^{(2)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(1)})^{\dagger}, \end{aligned} \tag{97}$$

where

$$(\mathbf{H}_{11}^{(3)})_{pq} = \sum_{a,b}\langle pa||bq\rangle\kappa_{ab} - \sum_{i,j}\langle pi||qj\rangle\kappa_{ij} + \sum_{i,a}(1+P(ia))\langle pi||qa\rangle k_i^a, \tag{98}$$

with

$$\begin{aligned} \kappa_{ab} &= \sum_c \sum_{i>j} k_{ij}^{ac} k_{ij}^{bc}, \\ \kappa_{ij} &= \sum_l \sum_{a>b} k_{il}^{ab} k_{jl}^{ab} \end{aligned} \tag{99}$$

and where $P(ia)$ is the permutational interchange operation. The second-order matrices are

$$\begin{aligned} (\mathbf{H}_{13}^{(2)})_{abi,p} &= \sum_{m>n}\langle ip||mn\rangle k_{mn}^{ab} + (1-P(ab))\sum_{m,c}\langle pc||ma\rangle k_{im}^{bc} \\ (\mathbf{H}_{13}^{(2)})_{ija,p} &= \sum_{b>c}\langle ap||bc\rangle k_{ij}^{bc} + (1-P(ij))\sum_{m,c}\langle pm||ci\rangle k_{jm}^{ac} \end{aligned} \tag{100}$$

and the first-order diagonal terms are

$$\begin{aligned} (\mathbf{H}_{33}^{(1)})_{abi,cdj} &= \delta_{ij}\langle ab||cd\rangle - \delta_{ac}\langle bj||di\rangle + \delta_{ad}\langle bj||ci\rangle + \delta_{bc}\langle aj||di\rangle - \delta_{bd}\langle aj||ci\rangle \\ (\mathbf{H}_{33}^{(1)})_{ija,klb} &= \delta_{ab}\langle ij||kl\rangle + \delta_{ik}\langle jb||la\rangle - \delta_{il}\langle jb||ka\rangle - \delta_{jk}\langle ib||la\rangle + \delta_{jl}\langle ib||ka\rangle, \end{aligned} \tag{101}$$

Fourth order and partial fourth order electron propagator

Without including the operator manifold $\mathbf{h}_5$ the full fourth-fourth order propagator matrix can be expressed as

$$\begin{aligned} \mathbf{G}_{(4)}^{-1}(E) = \mathbf{G}_{(3)}^{-1}(E) &+ \mathbf{H}_{11}^{(4)} - \mathbf{H}_{13}^{(2)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(2)\dagger} \\ &- \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(3)\dagger} - \mathbf{H}_{13}^{(3)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(1)\dagger} \\ &- \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(2)\dagger} \\ &- \mathbf{H}_{13}^{(2)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(1)\dagger} - \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(2)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(1)\dagger} \\ &- \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{13}^{(1)\dagger}. \end{aligned} \tag{102}$$

It is generally more important to include the contributions from the $\mathbf{h}_5$ manifold before increasing the order of the expansion [36] and one therefore finds it justifiable to study the electron propagator through what has been coined the "partial fourth-order" [19, 37], where only the terms formed from the matrices already obtained in third order are retained.

Density matrices and many-electron wavefunction

The first-order reduced density matrix or the one-matrix can be calculated from (90) as

$$\gamma(\xi|\xi') = \langle 0|\psi^\dagger(\xi')\psi(\xi)|0\rangle = -i \lim_{t'\to t+0} \langle\langle \psi(\xi,t); \psi^\dagger(\xi',t')\rangle\rangle$$
$$= (2\pi i)^{-1} \int_C \langle\langle \psi(\xi); \psi^\dagger(\xi')\rangle\rangle_E \mathrm{d}E, \tag{103}$$

where the contour C consists of the real axis and a semicircle in the upper half of the complex E-plane (see [7]). Residue calculus yields

$$\gamma(\xi|\xi') = \sum_r g_r(\xi) g_r^*(\xi'), \tag{104}$$

which can be compared to the equivalent definition

$$\gamma(\xi|\xi') = N \int \Phi_0(\xi,\xi_1,\xi_2,\ldots\xi_{N-1})\Phi_0^*(\xi',\xi_1,\xi_2\ldots\xi_{N-1})\mathrm{d}\xi_1\mathrm{d}\xi_2\ldots\mathrm{d}\xi_{N-1} \tag{105}$$

in terms of the ground state N-electron wavefunction Φ_0. Introducing the complete set of $(N-1)$-electron states Φ_r, satisfying

$$\sum_r \Phi_r(X)\Phi_r^*(X') = \delta(X-X') \tag{106}$$

with the compound coordinate $X = (\xi_1,\xi_2,\ldots\xi_{N-1})$. Then

$$\gamma(\xi|\xi') = N \sum_r \int \Phi_0(\xi,X)\Phi_r^*(X)\Phi_0^*(\xi',X')\Phi_r(X')\mathrm{d}X\mathrm{d}X' \tag{107}$$

and we can identify the Feynman-Dyson amplitudes with the so-called overlap amplitudes

$$g_r(\xi) = N^{1/2} \int \Phi_0(\xi,X)\Phi_r^*(X)\mathrm{d}X. \tag{108}$$

Obviously, if both wavefunctions in (108) are single determinants differing in one spin orbital, that spin orbital will correspond to the Feynman-Dyson amplitude, while for correlated wavefunctions the amplitudes are more general. In addition to being important for describing intensities in photoelectron spectra Feynman-Dyson amplitudes are also relevant for (e, 2e) experiments (see *e.g.* [42]).

Photoionization intensities

The electron propagator can be used to calculate total energies, excitation energies, and one-electron properties in general. However, it is perhaps most useful in the study of photoelectron spectroscopy. In addition to the electron binding energies it can also be used to obtain estimates of photoelectron intensities.

The differential photoionization cross section, *i.e.* the probability that the systems absorbs one photon causing a transition from the ground state with wavefunction $|0\rangle = \Phi_0$ to an excited

state $|r\rangle$ consisting of a bound ion state with wavefunction $|N-1,r\rangle = \Phi_r$ and an electron escaping into the solid angle $d\Omega$ with wave vector $\vec{k}_f$ is

$$\frac{d\sigma_r}{d\Omega} = \frac{k_f}{2\pi c|A_0|^2\omega}|\langle r|\sum_{j=1}^{N}\vec{A}(\vec{r}_j)\cdot\vec{\nabla}_j|0\rangle|^2. \tag{109}$$

The vector potential of the monochromatic radiation field is $\vec{A}(\vec{r}) = A_0\vec{n}e^{i\vec{k}\cdot\vec{r}}$ with polarization vector $\vec{n}$ and frequency ω. The approximate form of final (antisymmetric) state wavefunction

$$|r\rangle = O_{AS}N^{1/2}v(\vec{k}_f,\xi_N)\Phi_r(\xi_1,\xi_2,\ldots\xi_{N-1}) \equiv O_{AS}N^{1/2}v(\vec{k}_f,\xi_N)\Phi_r(X), \tag{110}$$

contains a photoelectron amplitude v, which should be a Feynman-Dyson continuum amplitude, but for a molecular system one usually has to settle for an assumed form. The antisymmetric projector is

$$O_{AS} = N^{-1}[1 - \sum_{k=1}^{N-1}P_{kN}] \tag{111}$$

with the simple interchange permutations P_{kN} of electron labels. This form of final wavefunction permits us to write

$$\begin{aligned}\langle r|\sum_{j=1}^{N}\vec{A}(\vec{r}_j)\cdot\vec{\nabla}_j|0\rangle = &\int v^*(\vec{k}_f,\xi)\vec{A}\cdot\vec{\nabla}g_r(\xi)d\xi \\ &+ \int v^*(\vec{k}_f,\xi)p_r(\xi)d\xi,\end{aligned} \tag{112}$$

with

$$p_r(\xi) = (N-1)N^{1/2}\int\Phi_r^*(X)\vec{A}(\vec{r}_1)\cdot\vec{\nabla}_1\Phi_0(X,\xi)dX. \tag{113}$$

The second term vanishes if $v(\vec{k}_f,\xi)$ is strongly orthogonal to Φ_0 , which can be accomplished by making $v(\vec{k}_f,\xi)$ orthogonal to the bound state basis. But even when strong orthogonality does not exist the second *term* is small for photoelectron energies far from threshold.

Retaining only the first term on the right of equation (112) and averaging over all incident photon directions relative the fixed molecular frame and over the polarization directions assuming a random orientation of the molecules as in a gaseous sample and for unpolarized light, equation (109) becomes

$$\frac{d\sigma_r}{d\Omega} = \frac{k_f}{3\pi c\omega}|\int v^*(\vec{k}_f,\vec{r})\vec{\nabla}g_r(\vec{r})d\vec{r}|^2. \tag{114}$$

To obtain this result also the dipole approximation was invoked, *i.e.* $e^{i\vec{k}\cdot\vec{r}} \approx 1$ and multiplication by a factor 2 done to account for the two possible spin states of the ejected electron. The choice of a plane wave, an orthogonalized plane wave, or a Coulomb wave for $v(\vec{k}_f,\xi)$ has been tried with varying success depending on the system and the photon energy [12, 43]. The

orthogonalized plane wave choice seems to work reasonably well for the detachment of an electron from a negative ion leaving a neutral species. A plane wave is convenient, but not particularly good under any conditions. It results in [22]

$$\frac{d\sigma_r}{d\Omega} = \frac{k_f}{3\pi\alpha\omega}|\vec{P}_r|^2$$
$$\vec{P}_r = -i\vec{k}_f(2\pi)^{-3/2}\sum_{p,q} c_{pr}e^{-i\vec{k}_f\cdot\vec{R}_q}\int e^{-i\vec{k}_f\cdot\vec{r}}\phi_p(\vec{r})d\vec{r}, \tag{115}$$

where the Feynman-Dyson amplitude has been expressed as a linear combination of atomic orbitals (GTO's) $\{\phi_p\}$

$$g_r(\vec{r}) = \sum_{p,q}\phi_p(\vec{r}-\vec{R}_q)c_{pr}. \tag{116}$$

The total cross section is given by integrating over all photoelectron directions

$$\sigma_r = \frac{k_f}{3\pi\alpha\omega}\int|\vec{P}_r|^2 d\Omega. \tag{117}$$

Sometimes the ratios of pole strengths are used to predict relative intensities of structures in a photoelectron spectrum and that can work for peaks of not too disparate photoelectron energy.

The Vectorized Electron Propagator (VEP) program

Approximations to various orders in perturbation theory of the electron propagator have been implemented in the Vectorized Electron Propagator (VEP) program. Poles and associated pole strengths are computed. This code is designed to be efficient by minimizing the number of floating point operations and by exploiting vector and parallel features of modern hardware. This is accomplished by avoiding redundant calculations through the definition of appropriate intermediates and by using symmetry wherever suitable.

The VEP code exploits the spin and point group symmetry to block the matrices from which the propagator matrix is built. Direct product decomposition (DPD) is used with a scheme that avoids redundant symmetry checks before each contraction. This procedure makes the code adapted to take advantage of parallel architectures.

Another feature of the VEP program is possibility of renormalized treatment of the reference state of the propagator via the use of CC amplitudes as well as the standard MBPT amplitudes. This is accomplished by interfacing the VEP code with the ACESII program system.

The DPD scheme

Efficient evaluation of matrix products necessary for the electron propagator calculations can be exemplified by a contraction

$$Q = T \times W. \tag{118}$$

The indices of the matrices can be divided into two categories , on the one hand the "target indices" $t_1, t_2, \cdots$, which label the matrix Q and the "common" indices $c_1, c_2, \cdots$ over which the

contraction is performed. The target indices may further be divided into those which Q shares with T and those which it shares with W, such that

$$Q_{t_1(T),t_2(T),\cdots,t_1(W),t_2(W)\cdots} = \sum_{c_1,c_2,\cdots} T_{t(T),c} W_{c,t(W)} \tag{119}$$

Each element of Q, T, and W vanishes unless the direct product of the irreducible representations of all indices labeling the quantity in question contains the totally symmetric representation. For abelian (sub)groups this requires only the following conditions to be fulfilled:

$$\begin{aligned} \Gamma(t_1(T)) \otimes \Gamma(t_2(T)) \otimes \cdots &= \Gamma(t_1(W)) \otimes \Gamma(t_2(W)) \otimes \cdots \\ \Gamma(t_1(T)) \otimes \Gamma(t_2(T)) \otimes \cdots &= \Gamma(c_1) \otimes \Gamma(c_2) \otimes \cdots \\ \Gamma(c_1) \otimes \Gamma(c_2) \otimes \cdots &= \Gamma(t_1(W)) \otimes \Gamma(t_2(W)) \otimes \cdots \end{aligned} \tag{120}$$

The details of the computational strategy as to storage of the data structures, the manipulation in core memory, the functionality of various subroutines, etc. are reported in a separate publication [44].

3. Results

The photoelectron spectroscopy (PES) offers techniques to study the electronic structure of atoms and molecules including transient and unstable species. This makes it a powerful tool to study reaction mechanisms in gas phase and on surfaces. PES has been used, for instance, to elucidate the electronic structure of donor-acceptor (DA) complexes.

As an illustration the electron propagator program VEP is used to calculate the main peaks of borane (BH_3) with donors such as H_2O and CO. These simple applications are limited to a second-order treatment of the electron propagator (EP2).

Monomeric borane has a very short life time, but is a strong Lewis acid and may be stabilized by forming complexes with Lewis bases [45]. BH_3 resembles a transition metal atom in a low oxidation state, in the sense that it can form complexes with, say, carbon monoxide and phosphorous trifluoride having negligible basicity. It has been suggested that the complexes of BH_3 with CO or PF_3 are formed via a π-type delocalization of the BH_3 e-orbitals into unoccupied CO and PF_3 orbitals. The study of systems such as $BH_3 \bullet CO$ and $BH_3 \bullet H_2O$ may provide experience as to the reliability and suitability of the electron propagator as a tool for analyzing PES experiments on heterogeneous catalysis, for instance, CO chemisorption and reactions (methanol synthesis) on low oxidation state d^{10} transition metal oxide surfaces, such as ZnO($10\bar{1}0$) and also CuCl(111) [46].

Molecular Geometries

The electron propagator program is implemented in the ACES II program system [47]. All calculation presented were performed on an IBM RS/6000-580. The basis sets are correlated consistent pVDZ [48], which consist of (9s4p1d/[3s2p1d] for first row elements and (4s1p)/[2s1p] for hydrogen. All structures are optimized at the RHF/MBPT[2] level of theory. The results are listed in Table 1.

Table 1 Optimized geometries at the MBPT[2] level with pVDZ bases. The notation H_s means that the proton lies in the symmetry plane of the C_s point group.

Complex	Point Group	Geometrical Parameter	MBPT[2]/pVDZ	Experimental
$H_3B{\cdot}CO$	C_{3v}	BC	1.565 Å	1.540 Å
		CO	1.144 Å	1.131 Å
		BH	1.217 Å	1.194 Å
		CBH	103.8°	104.2°
$H_3B{\cdot}OC$	C_{3v}	BO	2.585 Å	
		CO	1.147 Å	
		BH	1.203 Å	
		OBH	90.9°	
$H_3B{\cdot}OH_2$	C_s	BO	1.730 Å	
		OH	0.963 Å	
		BH&BH_s	1.214	
		OBH	100.6°	
		OBH_s	103.7°	
H_3B	D_{3h}	BH	1.203 Å	
CO	$C_{\infty v}$	CO	1.147 Å	1.128 Å
H_2O	C_{2v}	OH	0.964 Å	0.958 Å
		HOH	102.0°	104.5°

Symmetry

The effects of molecular symmetry on the performance of the code is illustrated by calculating the PES of BH_3 at the EP2 level in the pVTZ basis, i.e. (10s5p2d1f)/[4s3p2d1f]//(5s2p1d)/[3s2p1d] in the maximal Abelian subgroup C_{2v} and in C_1. The theoretical factors of reduction (in computing time or total number of floating point operations) due to symmetry (FRS) have been defined [34] and is found in many cases for total energy calculations using the CCSD (coupled-cluster singles and doubles) level of theory to be close to the symmetry group order square. As displayed in Table 2 the present calculation does not quite reach that efficiency improvement with the symmetry treatment, but still a respectable reduction in computing time is achieved.

Table 2 An FRS is a "factor of reduction due to symmetry" of cpu time used. The VEP code in the ACES II program system achieves for this case a factor of more than 10 speed up in the execution of the code.

Molecule	Size of basis	Point Group	Achieved FRS
BH_3	72	C_1	1.0
		C_{2v}	10.3

Donor-Acceptor PES

The photoelectron spectrum with a UV source (UPS) of $H_3B{\cdot}OH_2$ calculated at the SCF (Koopmans' theorem) and the EP2 levels are compared to experimental results [49] in Table 3.

Table 3 Electron propagator poles at the SCF level (Koopmans) and at the EP2 level are compared with experiment for the $H_3B{\cdot}OH_2$ complex.

Assignment	Koopmans (eV)	EP2 (eV) (Pole Strength)	Experiement UPS (eV)
π(B-H) 7a′	11.3	10.5 (0.93)	9.7
π(B-H) 7a″	11.8	11.1 (0.94)	10.6
σ(B-O) 6a′	15.6	13.5 (0.91)	11.8
n(O) 5a′	16.4	14.2 (0.90)	13.2
n(O) + σ(B-O) 4a′	20.7	18.6 (0.89)	14.4

Due to the hydrolysis of diborane the experimental investigation of the $H_3B{\cdot}OH_2$ complex is difficult [45] and introduces some uncertainty about whether the observed features in the HeI spectrum really is due to $H_3B{\cdot}OH_2$ or something else. The agreement between the calculated (EP2) peaks and the UPS spectrum is as expected except for the observed feature at 14.4 eV. This is not consistent with the theoretical result, but before suggesting that this feature might not be due to $H_3B{\cdot}OH_2$ the electron propagator calculations have to be carried to the third or partial fourth order and also a larger basis used.

Comparison of the Koopmans' theorem and the EP2 results with experiment for the $H_3B{\cdot}CO$ complex is presented in Table 4.

Table 4 Electron propagator poles at the SCF (Koopmans) level and at the EP2 level compared with experiment for the $H_3B{\cdot}CO$ complex.

Assignment	Koopmans' (eV)	EP2 (eV) (Pole Strenth)	Experiment UPS (eV)
2e (B-H)	12.8	11.9 (0.92)	11.9
$6a_1$ (B-C)	15.1	13.9 (0.91)	14.1
1e (C-O)	18.6	17.1 (0.87)	17.0
$5a_1$ (CO)	21.6	18.1 (0.85)	18.5*

* Adiabatic ionization energy

Similar calculations are carried out for the $H_3B{\cdot}OC$ complex and are reported in Table 5.

Table 5 Comparison of the electron propagator poles at the SCF (Koopmans) level and at the EP2 level with the same UPS spectrum as in Table 4.

Assignment	Koopmans (eV)	EP2 (eV) (Pole strength)	Experiment UPS (eV)
2e (B-H)	13.2	12.6 (0.94)	11.9
$6a_1$ (B-C)	15.3	14.0 (0.92)	14.1
1e (C-O)	17.5	16.3 (0.89)	17.0
$5a_1$ (B-H)	18.7	17.5 (0.92)	
			18.5*
$4a_1$ (C-O)	22.5	19.0 (0.86)	

*Adiabatic ionization energy

There is definitely a better agreement between the calculated and the observed PES for $H_3B{\cdot}CO$ than for $H_3B{\cdot}OC$ indicating the discriminatory power of the electron propagator theory even at this primitive level.

In conclusion one can again reaffirm what already has been established by many workers in the field, namely that the propagator theory is an appropriate and practical approach to the interpretation and prediction of spectra. The results presented here also show that in order to contain truly quantitative agreement with experiment it is necessary to consider electron propagator theory at the third and partial fourth order and to also be able to accommodate larger basis sets.

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Tables

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