

# A complete treatment of the electron propagator through third order\*

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Using the superoperator formalism we demonstrate how the electron propagator can be obtained consistent through third order in the electronic interaction and we establish the connection to the corresponding diagrammatic perturbation expansion of the self-energy. We further indicate some deficiencies in the third order theory of Simons and Smith for calculating ionization potentials and electron affinities.

## I. INTRODUCTION

The electron propagator<sup>1</sup> or the one electron Green's function has been used for some time in the study of electron spectroscopy.<sup>2-9</sup> The advantages of using the electron propagator arise because the transition energies and the transition strengths are obtained directly as poles and residues of the propagator, respectively. Several alternative procedures for decoupling the equation of motion for the electron propagator have been developed.<sup>2-5</sup> In this work we use the superoperator formalism of Goscinski and Lukman<sup>10</sup> as the framework for our development of an electron propagator which is consistent through third order. In an alternative derivation using the equation of motion formalism of Rowe,<sup>11</sup> Simons and Smith<sup>7</sup> attempted to obtain an equation of motion which was consistent through third order. Purvis and Öhrn<sup>12</sup> pointed out some deficiencies in the theory of Simons and Smith<sup>7</sup>; these deficiencies are again demonstrated in this paper. We show further how the electron propagator can be obtained consistent through third order. The consistency is made more transparent by demonstrating that all second and third order self-energy diagrams<sup>5</sup> are included in our formalism.

In Sec. II we derive the expression for the desired electron propagator and we demonstrate the relationship to the third order diagrams of Cederbaum.<sup>5</sup> In Sec. III we present our concluding remarks.

## II. THEORY

The equation of motion for the spectral electron propagator<sup>1</sup> can be written within the superoperator formalism as<sup>9,10</sup>

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

where  $\hat{I}$  and  $\hat{H}$  are the superoperator identity and Hamiltonian, respectively, and the  $\mathbf{a}$  are a set of annihilation operators  $\mathbf{a} = \{a_i\}$ , which are arranged in a super row vector. The superoperator scalar product is defined in the conventional fashion.<sup>9</sup> The superoperator resolvent  $(E\hat{I} - \hat{H})^{-1}$  can be approximated via the inner projection technique<sup>13</sup> and the equation of motion then takes the form

$$\mathbf{G}(E) = (\mathbf{a} | \mathbf{h} | \mathbf{h} | E\hat{I} - \hat{H} | \mathbf{h})^{-1} (\mathbf{h} | \mathbf{a}) , \quad (2)$$

where  $\mathbf{h}$  is a projection manifold which, if chosen to be complete and orthonormal, makes Eqs. (1) and (2) iden-

tical. The operator space

$$\{\mathbf{h}_1, \mathbf{h}_3, \mathbf{h}_5, \dots\} = \{a_i, a_i^* a_k a_l, a_i^* a_j^* a_k a_l a_r, \dots\} \\ k > l, i > j, k > l > r, \dots \quad (3)$$

spans the manifold  $\mathbf{h}$ . We now discuss appropriate selections of  $\mathbf{h}$  which, in conjunction with our choice of the reference state, ensure that the electron propagator is calculated correctly through third order in the electronic interaction.

It is well known that the projection manifold  $\mathbf{h}_1, \mathbf{h}_3$  in connection with the Hartree-Fock (HF) ground state is able to give the electron propagator correct through second order in the electronic interactions.<sup>3</sup> We demonstrate how, using a correlated ground state and the same projection manifold, we are able to get the electron propagator correct through third order in the electronic interaction.

The effect of including  $\mathbf{h}_5$  in the projection manifold, where the HF ground state is used as reference state, has been discussed by Tyner *et al.*,<sup>14</sup> and from their analysis it is clear that  $\mathbf{h}_5$  introduces terms which are at least fourth order in the electronic interaction, independent of the choice of reference state. We therefore concentrate on using  $\mathbf{h}_1, \mathbf{h}_3$  as our projection manifold in our search for a theory which is consistent through third order.

As the reference state in our analysis we use a correlated wavefunction given by

$$|0\rangle = N^{-1/2} \left\{ 1 + \sum_{\beta\delta} (K_{\beta\delta}^p a_\beta^* a_\delta) + \sum_{\substack{m>n \\ \alpha>\beta}} (K_{\alpha\beta}^{mn} a_m^* a_n^* a_\alpha a_\beta) \right. \\ \left. + \sum_{\substack{m>n>p \\ \alpha>\beta>\delta}} (K_{\alpha\beta\delta}^{mnp} a_m^* a_n^* a_p^* a_\alpha a_\beta a_\delta) + \dots \right\} |HF\rangle , \quad (4)$$

where the  $a^*$  are a set of HF creation operators and where indices  $m, n, p, q(\alpha, \beta, \delta, \gamma)$  refer to unoccupied (occupied) spin orbitals in the HF ground state and  $i, j, k, l, r$  are unspecified spin orbitals. We take the correlation coefficients from Rayleigh-Schrödinger perturbation theory

$$K_{\alpha\beta}^p = \sum_{\substack{m>n \\ \alpha>\beta}} \{ \langle p\alpha || mn \rangle \delta_{\delta\beta} - \langle p\beta || mn \rangle \delta_{\alpha\delta} + \langle \beta\alpha || \delta m \rangle \delta_{np} - \langle \beta\alpha || \delta n \rangle \delta_{pm} \} \frac{\langle mn || \alpha\beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\alpha + \epsilon_\beta - \epsilon_n - \epsilon_m)}$$

+higher order terms in the electronic interaction =  $K_{\alpha\beta}^p(2, 3, \dots)$ , (5)

$$K_{\alpha\beta}^{mn} = \frac{\langle mn || \alpha\beta \rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n} + \text{higher order terms in the electronic interaction}$$

$$= K_{\alpha\beta}^{mn}(1, 2, \dots), \quad (6)$$

$$K_{\alpha\beta\delta}^{mnp} = K_{\alpha\beta\delta}^{mnp}(2, 3, \dots), \quad (7)$$

where the first number in the bracket indicates the lowest order in the electronic interaction. The  $\epsilon_i$  indicate HF orbital energies and the two electron integral  $\langle mn || \alpha\beta \rangle$  refers to the charge densities  $m\alpha$  and  $n\beta$ , and

$$\langle mn || \alpha\beta \rangle = \langle mn | \alpha\beta \rangle - \langle mn | \beta\alpha \rangle. \quad (8)$$

In our analysis we consider the projection manifold  $\{h_1, h_3\}$ , where the  $h_3$  space for convenience has been redefined as

$$h_3 = \{ a_i^* a_k a_l + (a_i^* a_l) a_k - \langle a_i^* a_k \rangle a_l \}. \quad (9)$$

The choice of the subspace  $h_3$  ensures that this space is orthogonal to  $h_1$ :

$$(h_1 | h_3) = 0, \quad (10)$$

even for a correlated reference state. We also have the following orthogonality relations:

$$(h_1 | h_1) = 1, (h_3 | h_3) = \mathbf{S}(0, 2, 3, \dots). \quad (11)$$

Using Eqs. (10) and (11), Eq. (2) can be partitioned<sup>13</sup> into the form

$$\mathbf{G}^{-1}(E) = (h_1 | E\hat{I} - \hat{H} | h_1) - (h_1 | \hat{H} | h_3)(h_3 | \hat{E}I - \hat{H} | h_3)^{-1}(h_3 | \hat{H} | h_1) = \mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C}, \quad (12)$$

where the matrices  $\mathbf{A}$ ,  $\mathbf{B}$ ,  $\mathbf{C}$ , and  $\mathbf{D}$  are defined as

$$\begin{aligned} \mathbf{A} &= (h_1 | E\hat{I} - \hat{H} | h_1), \\ \mathbf{B} &= (h_1 | \hat{H} | h_3), \\ \mathbf{D} &= (h_3 | E\hat{I} - \hat{H} | h_3), \\ \mathbf{C} &= (h_3 | \hat{H} | h_1). \end{aligned} \quad (13)$$

We will now make an order by order analysis of Eq. (12) in which we retain only those terms which are zeroth, first, second, or third order in the electronic interaction. Since the  $\mathbf{B}$  and  $\mathbf{C}$  matrices are at least of first order, we need to consider only that part of the  $\mathbf{D}$  matrix which is zeroth and first order. This constrains the indices in the projection manifold  $h_3$  to be of the form  $a_m^* a_\alpha a_\beta$ ,  $\alpha > \beta$ , or  $a_\alpha^* a_m a_n$ ,  $m > n$ , since operators such as  $a_m^* a_n a_\alpha$  lead to matrix elements in the  $\mathbf{D}$  matrix which are at least of second order. The resulting subspace  $h_3$  is thus identical to that used in calculating the electron propagator correct through second order.<sup>9</sup> To calculate the electron propagator through third order in the electron repulsions, we thus need to obtain the  $\mathbf{B}$  and  $\mathbf{C}$  matrices through second order, the  $\mathbf{D}$  matrix through first order, and the  $\mathbf{A}$  matrix through third order.

Previous attempts to obtain the electron propagator

correct through third order<sup>7</sup> have used as reference state

$$|0\rangle = N_0^{-1/2} \left( 1 + \sum_{\substack{m>n \\ \alpha>\beta}} K_{\alpha\beta}^{mn} a_m^* a_n^* a_\alpha a_\beta \right) |HF\rangle, \quad (14)$$

where the  $K_{\alpha\beta}^{mn}$  are determined from first order Rayleigh-Schrödinger perturbation theory. In calculating the  $\mathbf{B}$ ,  $\mathbf{C}$ , and  $\mathbf{D}$  matrix elements correct through second and first order, respectively, no changes are obtained from considering the higher correlated ground state in Eq. (4). The matrix elements of  $\mathbf{B}$ ,  $\mathbf{C}$ , and  $\mathbf{D}$  can be found in Refs. 7 and 12. Notice that, to second order in electron interactions,  $\mathbf{C}^+ = \mathbf{B}$ . In the  $\mathbf{A}$  matrix we need to include all terms up to third order. The  $\mathbf{A}$  matrix elements obtained by using Eq. (14) as a reference state need to be modified by third order terms which result from interaction between the singly excited states and the HF ground state. The triply excited states which also result from a second order Rayleigh-Schrödinger perturbation calculation do not introduce third order terms. We thus have to add to the  $\mathbf{A}$  matrix elements given in Ref. 7 the terms  $\delta A_{ij}$ :

$$\delta A_{ij} = \sum_{p\delta} \frac{\langle jp || i\delta \rangle \langle \delta\beta || mn \rangle \langle mn || p\beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\delta + \epsilon_\beta - \epsilon_m - \epsilon_n)} \quad (A3)$$

$$+ \sum_{p\delta} \frac{\langle j\delta || ip \rangle \langle p\beta || mn \rangle \langle mn || \delta\beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\delta + \epsilon_\beta - \epsilon_m - \epsilon_n)} \quad (A4)$$

$$+ \sum_{p\delta} \frac{\langle jp || i\delta \rangle \langle \delta n || \beta\alpha \rangle \langle \alpha\beta || pn \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_n)}. \quad (A5)$$

$$+ \sum_{p\delta} \frac{\langle j\delta || ip \rangle \langle \beta\alpha || \delta n \rangle \langle pn || \alpha\beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_n)}. \quad (A6)$$

We thereby have calculated the electron propagator consistently through third order.

A comparison with a diagrammatic perturbation expansion of the self-energy makes it further transparent that we have really included all terms through third order in our analysis of the electron propagator. In Fig. 1 we have displayed the terms A3-A6 as diagrams using the rules of Brandow<sup>15</sup> which combine the Goldstone diagrams with the antisymmetrized vertices of Hugenholtz. The diagrams labeled A3-A6 are identical to the third order diagrams given by Cederbaum<sup>5</sup> in which dots refer to antisymmetrized vertices. The diagrams A3-A6 were shown by Purvis and Öhrn<sup>12</sup> to be the only missing third order diagrams<sup>5</sup> which evolve from a theory where the reference state is given by Eq. (14). The analysis of Purvis and Öhrn<sup>12</sup> considered  $(h_3 | E\hat{I} - \hat{H} | h_3)$  as two matrices;  $\mathbf{u}$  which contains  $E$  and orbital energies (zeroth order terms) and  $\mathbf{M}$  which contains the two electron integrals (first order terms). Making use of the identity  $(\mathbf{u} + \mathbf{M})^{-1} = \mathbf{u}^{-1} - \mathbf{u}^{-1}\mathbf{M}(\mathbf{u} + \mathbf{M})^{-1}$  to expand the in-

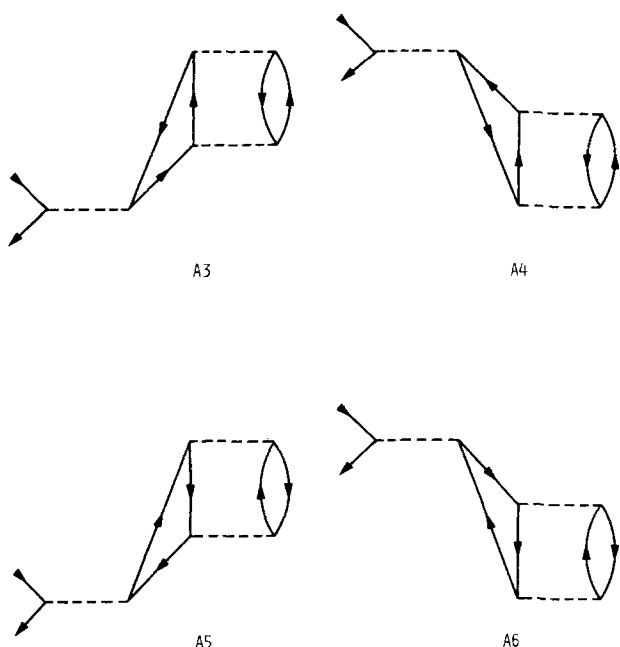


FIG. 1. The third order diagrams representing the terms A3–A6 defined in the text.

verse, Purvis and Öhrn<sup>12</sup> identified the diagrams C1–C6 and D1–D6 of Cederbaum<sup>5</sup> to originate from the  $\mathbf{BD}^{-1}\mathbf{C}^+$  term, while the diagrams A1–A2 were found to arise from the  $\mathbf{A}$  matrix previously given in Ref. 7. We thus have accounted for all third order diagrams which arise from an expansion of the self-energy.<sup>5</sup> The electron propagator calculation thus needs to use the correlated ground state given in Eq. (4) as a reference state and the subspace  $\{h_1, h_3\}$  given by Eq. (9) as the projection manifold to be correct through third order.

The omission of terms corresponding to diagrams A3–A6 in the earlier work of Simons *et al.*<sup>16</sup> probably did not cause significant ( $\pm 0.1$  eV) errors. Cederbaum<sup>5</sup> has found, from numerical experience on  $\text{N}_2$  and other molecules, that the contribution to valence-shell ionization energies made by diagrams A3–A6 are very small, the sum being  $\sim 0.03$  eV. Thus, Cederbaum's numerical results provide evidence that the exclusion of diagrams A3–A6 may not have caused significant errors in Simons' early calculations.

### III. DISCUSSION

We have shown how the electron propagator can be obtained correctly through third order. Our development stresses the fact that a complete treatment of the inverse of the  $\mathbf{D}$  matrix is needed to guarantee that all desired terms are included. Computational applications have so far only been carried out using a diagonal approximation to the  $\mathbf{D}$  matrix.<sup>16</sup> This situation is unsatisfactory and should be improved. A unitary transformation which brings the  $\mathbf{D}$  matrix closer to diagonal form is related to the theory of linear response<sup>4</sup> as dis-

cussed by Jørgensen and Purvis.<sup>17</sup> Using this kind of procedure we would expect to get an approximation to the propagator which would be nearly complete through third order. The energy shifted denominators which result from evaluating the  $\mathbf{D}$  matrix correspond to the result of summing certain classes of diagrams to infinite order,<sup>5</sup> which implies that the electron propagator treatment has the computational advantage of expressing these summations in closed form. In a diagrammatic summation of self-energy diagrams one has to explicitly account for each energy shifted denominator through each order.<sup>5</sup> We finally note that the side shifted diagrams given in Fig. 1 do not appear in the third order theory of Simons and Smith<sup>7</sup> for calculating ionization potentials and electron affinities. These diagrams result from using a more highly correlated wavefunction than the one considered by Simons and Smith<sup>7</sup> as the reference state.

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