

# The electron propagator and superoperator resolvent

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In this paper we demonstrate how the definition of the one-particle Green's function, or electron propagator, can be extended to include averages over nonexact reference states without affecting the exact nature of the poles of this function. We also make connections between this Green's function and an average value of the superoperator resolvent.

It is the purpose of this paper to present a few clarifying remarks concerning the definition and pole structure of the one-electron Green's function or electron propagator<sup>1</sup> and to show its relationship to the resolvent of the superoperator Hamiltonian within the scalar product introduced by Goscinski and Lukman.<sup>2</sup> The most common definition<sup>1</sup> of the representation of the double-time electron propagator within the (complete) set of Fermion creation  $\{C_i^+\}$  and annihilation  $\{C_j\}$  operators is

$$G_{ij}(t, t') = (1/i) \langle TC_i^+(t) C_j(t') \rangle, \quad (1)$$

where  $T$  denotes the time-ordered product, the operators are in the Heisenberg representation, and the symbol  $\langle \rangle$  represents an average value either over a pure state or an ensemble,<sup>3</sup>  $\langle \rangle = \sum_K P_K \langle K | \cdot | K \rangle$ . If one assumes that the states  $\{|K\rangle\}$  defining the average value

are exact eigenstates of the (time independent) Hamiltonian  $H$ , then it is easy to show<sup>1</sup> that  $\mathbf{G}(t, t')$  depends only on the time difference  $(t - t')$ . However, if the states in the average value are taken to be merely a convenient set of reference states (e.g., a Hartree-Fock single determinant or an ensemble of such Slater determinants), then  $\mathbf{G}(t, t')$  depends on both  $t$  and  $t'$ . Because we are interested in defining an electron propagator with a minimum of restrictive conditions, we propose that Eq. (1) be replaced by the new definition

$$G_{ij}(t) \equiv (1/i) \langle TC_i^+(t) C_j(o) \rangle. \quad (2)$$

To examine the formal properties of this  $\mathbf{G}(t)$ , we expand the states  $\{|K\rangle\}$  which appear in the average value in terms of the exact eigenstates  $\{|\psi_\mu\rangle\}$  of  $H$  ( $|K\rangle = \sum_\mu a_{K\mu} |\psi_\mu\rangle$ ) to obtain ( $N$  indicates the number electrons)

$$G_{ij}(t) = \frac{1}{i} \sum_K \sum_{\mu, \nu, \gamma} P_K a_{K\mu}^* a_{K\nu} \{ \theta(t) \langle \psi_\mu^N | C_i^+ | \psi_\nu^{N-1} \rangle \langle \psi_\nu^{N-1} | C_j | \psi_\mu^N \rangle \exp[i(E_\mu^N - E_\nu^{N-1})t] - \theta(-t) \langle \psi_\mu^N | C_j | \psi_\nu^{N+1} \rangle \langle \psi_\nu^{N+1} | C_i^+ | \psi_\mu^N \rangle \times \exp[i(E_\nu^{N+1} - E_\mu^N)t] \}, \quad (3)$$

from which we immediately see that the Fourier transform  $\mathbf{G}(E)$  of  $\mathbf{G}(t)$  has simple poles at the, in principle, exact energy differences  $E = E_\nu^{N-1} - E_\mu^N$  and  $E = E_\mu^N - E_\nu^{N+1}$ , i.e., at the ionization potentials and electron affinities of the system. The residues of  $\mathbf{G}(E)$  are seen from Eq. (3) to be related to the transition elements  $\langle \psi_\nu^{N-1} | C_j | \psi_\mu^N \rangle$ ,  $\langle \psi_\nu^{N+1} | C_i^+ | \psi_\mu^N \rangle$ , and the matrix  $\sum_K P_K a_{K\mu}^* \times a_{K\nu}$ .<sup>4</sup> The most important point made possible by this analysis is that the definition given in Eq. (2) allows an electron propagator to be defined with respect to an average  $\langle \rangle$  over nonexact reference states while still preserving the exact nature of its poles (electron affinities and ionization potentials). Of course, one is still faced with the problem of how to best go about computing the elements of  $\mathbf{G}$ ; Eq. (3) is of no help since it contains all of the exact eigenstates of  $H$ .

To make progress toward the practical calculation of  $\mathbf{G}$ , let us look more carefully at the Fourier transform of Eq. (2):

$$G_{ij}(E) = \langle [(E\hat{1} - \hat{H})^{-1} C_i^+ C_j] + \langle C_j [(E\hat{1} - \hat{H})^{-1} C_i^+] \rangle, \quad (4)$$

which contains the superoperators  $\hat{1}$  and  $\hat{H}$  introduced by Goscinski and Lukman<sup>2</sup> ( $\hat{1}C_i^+ \equiv C_i^+$ ,  $\hat{H}C_i^+ \equiv [C_i^+, H]$ ). To obtain Eq. (4) we made use of the identity

$$\exp(iHt)A \exp(-iHt) = [\exp(-i\hat{H}t)A], \quad (5)$$

which can easily be verified by expanding the exponentials and using the above definition of  $\hat{H}$ . Thus the Fourier transform operation has led to an expression for  $\mathbf{G}(E)$  which contains the superoperator resolvent  $(E\hat{1} - \hat{H})^{-1}$ .<sup>1</sup> Finally, by employing the scalar product introduced in Ref. 2 [ $(A|B) \equiv \langle A^* B + BA^* \rangle$ ,  $(A|\hat{H}|B) \equiv \langle A^* (\hat{H}B) + (\hat{H}B)A^* \rangle$ ],  $\mathbf{G}(E)$  can be written as

$$G_{ij}(E) = (C_j^+ | (E\hat{1} - \hat{H})^{-1} | C_i^+). \quad (6)$$

From the discussion presented earlier, we know that, if  $\mathbf{G}(E)$  could be computed without further approximation, its poles would correspond to exact electron affinities and ionization potentials even though the average  $\langle \rangle$  is not over exact eigenstates.

For the moment, let us assume that we have constructed a set of orthonormal operators  $\{q_k^*\}$ , which we collect into a column vector  $\mathbf{q}^*$ , which are complete in the sense that a resolution of the identity superoperator can be written as

$$\hat{1} = |\mathbf{q}^*\rangle \langle \mathbf{q}^*| = \sum_K |q_k^*\rangle \langle q_k^*|, \quad (7)$$

where the average  $\langle \rangle$  used in defining this set is identical to that used in defining  $\mathbf{G}$ . The reader is referred to Appendix A for a discussion of how such a complete set is constructed in practice. Let us further assume that the set of operators  $\{q_k^*\}$  is constructed by taking

the set of simple creation operators  $\{C_i^+\}$  followed by the remainder of the complete set (which will contain operators of the form  $C_i^+C_j^+C_K$ ,  $C_i^+C_j^+C_K^+C_lC_m$ , etc.) referred to as  $\{h_k^+\}$ ,

$$q^+ = [C^+, h^+]. \quad (8)$$

This assumption is neither an approximation nor an inconvenient restriction.

The set of operators  $q^+$  introduced above can be used to obtain a computationally tractable form for the desired propagator  $G(E)$  by first using the fact that  $G$  is simply a subblock of the larger matrix  $\mathcal{G}(E)$  defined by

$$\mathcal{G}_{k,i}(E) \equiv (q_k^+ | (E\hat{1} - \hat{H})^{-1} | q_i^+). \quad (9)$$

Using Eq. (7) and the fact that the  $q^+$  are orthonormal we can also write

$$\delta_{k,i} = \sum_m (q_k^+ | (E\hat{1} - \hat{H}) | q_m^+) (q_m^+ | (E\hat{1} - \hat{H})^{-1} | q_i^+), \quad (10)$$

which states that  $\mathcal{G}$  is the inverse of the matrix  $(q^+ | E\hat{1} - \hat{H} | q^+)$ . By decomposing  $q^+$  as  $[C^+, h^+]$  we partition the matrix  $\mathcal{G}^{-1}$  into four blocks,

$$\mathcal{G}^{-1} = \begin{pmatrix} (C^+ | E\hat{1} - \hat{H} | C^+) & (C^+ | E\hat{1} - \hat{H} | h^+) \\ (h^+ | E\hat{1} - \hat{H} | C^+) & (h^+ | E\hat{1} - \hat{H} | h^+) \end{pmatrix}. \quad (11)$$

The desired  $G$  is then obtained by solving for the inverse of the matrix shown in Eq. (11) in terms of its four blocks, the result being

$$G(E) = [(C^+ | E\hat{1} - \hat{H} | C^+) - (C^+ | E\hat{1} - \hat{H} | h^+) [(h^+ | E\hat{1} - \hat{H} | h^+)^{-1} \\ \times (h^+ | E\hat{1} - \hat{H} | C^+)^{-1}]. \quad (12)$$

Equation (12) is identical in form to the result obtained by Pickup and Goscinski,<sup>5</sup> the fundamental difference being that the average value used in Eq. (2), and thus in Eq. (12), is not assumed to be a trace over exact eigenstates of  $H$ . In principle, if the set of operators  $[C^+, h^+]$  is complete, then Eq. (12) is correct for any average  $\langle \rangle$  and the poles of the resulting  $G(E)$  are exact ionization potentials and electron affinities. This conclusion is very similar to that reached by Löwdin in his elegant study of resolvents, reduced resolvents, and the partitioning technique.<sup>6,7</sup> In these works, Löwdin showed, for example, that the function  $W(E) \equiv \langle \phi | (E - H)^{-1} | \phi \rangle$  has poles whenever  $E$  is equal to one of the exact eigenenergies of  $H$ , provided that the (arbitrary, normalized) reference function  $|\phi\rangle$  is not orthogonal to the corresponding eigenfunction of  $H$ . Just as it is the occurrence of the exact operator  $(E - H)^{-1}$  which makes the poles of  $W(E)$  exact, it is the presence of the exact superoperator  $(E\hat{1} - \hat{H})^{-1}$  in Eq. (9) which

make the poles of  $\mathcal{G}(E)$  exact, even if the reference states used in  $\langle \rangle$  are not.

Various approximations to the electron propagator as expressed in Eq. (12) have been developed by several authors.<sup>5,8-14</sup> Each approximation involves choosing a convenient set of reference states  $\{|K\rangle\}$  and weights  $P_K$  to define the average  $\langle \rangle$  as well as choosing a set of operators  $\{h^+\}$ . In a previous publication, Jørgensen and the author<sup>8</sup> demonstrated how one could obtain elements of the  $G^{-1}(E)$  matrix correct through third order in electron interactions by choosing  $\{h^+\}$  to include only operators of the form  $C_i^+C_jC_k^+$  and choosing a single reference state  $|\phi\rangle$  equal to the second-order Rayleigh-Schrödinger ground state wave function. According to the analysis presented here, there are other choices of the average  $\langle \rangle$  and other choices of  $h^+$  which could also yield  $G^{-1}$  through third order. It is not the purpose of the present paper to discuss such uses of Eq. (12), therefore we shall not dwell further on these points now. Our purpose has been to demonstrate how, by defining the electron propagator as in Eq. (2), one can derive, for an arbitrary average value  $\langle \rangle$ , the fundamental equation [Eq. (12)] which has been used by many investigators as a starting point for the development of computationally tractable approximations. It is our hope that, by making a clear analogy with Löwdin's work on resolvents in which the reference function  $|\phi\rangle$  need not be an exact eigenstate, we have extended the present understanding of Green's functions and superoperator resolvents.

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## APPENDIX A

Our goal is to establish and clarify the completeness relation given in Eq. (7) which has been used in the developments presented in this paper. We assume that we have found a set of operators  $\{O_\lambda^+\}$  which, when operating on some reference state,<sup>15</sup> generate a complete orthonormal set of functions  $\{O_\lambda^+|\phi\rangle\}$  for the system of interest. We further assume that these operators obey the consistency equation  $O_\lambda|\phi\rangle = 0$ .

The completeness relation indicated in Eq. (7) must be proven within the framework of the scalar product given below:

$$(A|B) \equiv \langle \phi | A^+B + BA^+ | \phi \rangle \quad (A1)$$

which can, using the assumed completeness relation, be written as

$$(A|B) = \sum_\lambda \{ \langle \phi | A^+O_\lambda^+ | \phi \rangle \langle \phi | O_\lambda B | \phi \rangle + \langle \phi | BO_\lambda^+ | \phi \rangle \langle \phi | O_\lambda A^+ | \phi \rangle \} \quad (A2)$$

$$= \sum_\lambda \{ \langle \phi | A^+O_\lambda^+ + O_\lambda^+A^+ | \phi \rangle \langle \phi | O_\lambda B + BO_\lambda | \phi \rangle + \langle \phi | A^+O_\lambda + O_\lambda A^+ | \phi \rangle \langle \phi | O_\lambda^+B + BO_\lambda^+ | \phi \rangle \}, \quad (A3)$$

which is equivalent to

$$(A|B) = \sum_{\lambda} \{(A|O_{\lambda}^*)(O_{\lambda}^*|B) + (A|O_{\lambda})(O_{\lambda}|B)\}. \quad (\text{A4})$$

Thus the desired superoperator completeness relation is

$$\hat{1} = \sum_{\lambda} \{|O_{\lambda}^*\rangle\langle O_{\lambda}^*| + |O_{\lambda}\rangle\langle O_{\lambda}|\}. \quad (\text{A5})$$

If, for example, the reference state  $|\phi\rangle$  is chosen to be the  $N$  electron ground state Hartree-Fock Slater determinant in which spin orbitals  $\{\phi_{\alpha}, \alpha = 1, \dots, N\}$  are occupied and spin orbitals  $\{\phi_{\beta}, \beta = N+1, \dots\}$  are unoccupied, then the set  $\{O_{\lambda}^*\}$  consists of  $\{C_{\beta}^{\dagger}, C_{\alpha}, C_{\beta}^{\dagger}C_{\alpha}C_{\alpha}^{\dagger}, C_{\beta}^{\dagger}C_{\beta}C_{\alpha}, \dots\}$  and  $\{O_{\lambda}\}$  is  $\{C_{\beta}, C_{\alpha}^{\dagger}, C_{\alpha}C_{\alpha}^{\dagger}C_{\beta}, C_{\alpha}^{\dagger}C_{\beta}C_{\beta}^{\dagger}, \dots\}$ . Moreover, in this special case, the general completeness relation given in Eq. (A5), when operating on the functions  $|q_k^*\rangle$ , which were shown in the text to involve creation of an electron, reduces to

$$\hat{1} = \sum_k |q_k^*\rangle\langle q_k^*|, \quad (\text{A6})$$

because the terms  $(O_{\lambda}^*|q^*) = 0$  when  $O_{\lambda}^* = C_{\alpha}, C_{\beta}C_{\beta}^{\dagger}C_{\alpha}$ , etc., and  $(O_{\lambda}|q^*) = 0$  when  $O_{\lambda} = C_{\beta}, C_{\alpha}C_{\alpha}^{\dagger}C_{\beta}$ , etc. Thus, the only terms which remain when Eq. (A5) operates on a function which involves electron creation are those components of  $O_{\lambda}^*$  and  $O_{\lambda}$  which also involve addition of an electron, e.g.,  $C_{\beta}^{\dagger}, C_{\beta}^{\dagger}C_{\alpha}C_{\alpha}^{\dagger}, \dots; C_{\alpha}^{\dagger}, C_{\alpha}^{\dagger}C_{\beta}C_{\beta}^{\dagger}, \dots$ , these operators are simply the set of operators  $q^*$ . Therefore, the completeness relation required in the text is given by Eq. (A6). The analogous resolution of the identity for operators which conserve the number of electrons is demonstrated below in Appendix B.

## APPENDIX B

Although the scalar product defined above is somewhat unusual, it is still possible to provide a convenient resolution of the identity for number-conserving operators within this definition. If the above reference function  $|\phi\rangle$  is taken to be the Hartree-Fock Slater determinant composed of the  $N$  spin orbitals  $\{\phi_{\alpha}, \alpha = 1, 2, \dots, N\}$  having the lowest orbital energies, we can construct a complete set of antisymmetric  $N$ -electron functions by forming all Slater determinants in which one, two, three, ... up to  $N$  of the spin orbitals in  $|\phi\rangle$  have been replaced by "excited orbitals"  $\{\phi_{\beta}\}$ . These singly, doubly, etc. excited determinants will be represented in terms of the orbital creation and annihilation operators<sup>2</sup> as  $C_{\beta}^{\dagger}C_{\alpha}|\phi\rangle, C_{\beta}^{\dagger}C_{\alpha}^{\dagger}C_{\beta}C_{\alpha}|\phi\rangle, C_{\beta}^{\dagger}C_{\alpha}^{\dagger}C_{\gamma}^{\dagger}C_{\beta}C_{\alpha}|\phi\rangle, \dots$ , which can be represented collectively as  $\{O_{\lambda}^*|\phi\rangle\}$ . Notice that the adjoint  $O_{\lambda}$  of each of the above excitation operators obeys  $O_{\lambda}|\phi\rangle = 0$ , e.g.,  $C_{\alpha}^{\dagger}C_{\beta}|\phi\rangle = 0$ .

Within the normal scalar product involving simple integrals between Slater determinants, the completeness relation is  $1 = |\phi\rangle\langle\phi| + \sum_{\lambda} O_{\lambda}^*|\phi\rangle\langle\phi|O_{\lambda}$ . By inserting this well-known result into the superoperator scalar product, we can write<sup>2</sup>  $(A|B) \equiv \langle\phi|A^*B - BA^*|\phi\rangle$  as

$$\sum_{\lambda} \{\langle\phi|A^*O_{\lambda}^*|\phi\rangle\langle\phi|O_{\lambda}B|\phi\rangle - \langle\phi|BO_{\lambda}^*|\phi\rangle\langle\phi|O_{\lambda}A^*|\phi\rangle\} \\ + \langle\phi|A^*|\phi\rangle\langle\phi|B|\phi\rangle - \langle\phi|B|\phi\rangle\langle\phi|A^*|\phi\rangle,$$

or by using the fact that  $O_{\lambda}|\phi\rangle = 0$ , as

$$\sum_{\lambda} \{\langle\phi|A^*O_{\lambda}^* - O_{\lambda}^*A^*|\phi\rangle\langle\phi|O_{\lambda}B - BO_{\lambda}|\phi\rangle \\ - \langle\phi|A^*O_{\lambda} - O_{\lambda}A^*|\phi\rangle\langle\phi|O_{\lambda}^*B - BO_{\lambda}^*|\phi\rangle\}.$$

Notice that each term in this result is itself a superoperator scalar product, so we can finally write

$$(A|B) = \sum_{\lambda} \{(A|O_{\lambda}^*)(O_{\lambda}^*|B) - (A|O_{\lambda})(O_{\lambda}|B)\}, \quad (\text{B1})$$

and thus the desired resolution of the identity is

$$1 = \sum_{\lambda} \{|O_{\lambda}^*\rangle\langle O_{\lambda}^*| - |O_{\lambda}\rangle\langle O_{\lambda}|\}. \quad (\text{B2})$$

It is important to understand that the Hartree-Fock reference state  $|\phi\rangle$  can be employed here because it generates a complete set of determinants through the action of the set of basic excitation operators  $\{O_{\lambda}^*\}$ ; it is not necessary that  $|\phi\rangle$  be the exact  $N$ -electron ground state. So, if one is interested in evaluating operator matrix elements of the form  $\langle\phi|A^*B - BA^*|\phi\rangle$ , where  $|\phi\rangle$  is the Hartree-Fock determinant, then the resolution of the identity given in Eq. (2) will prove to be useful.

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<sup>1</sup>For a good survey of Green's function theory, see J. Lindenberg and Y. Ohrn, *Propagators in Quantum Chemistry* (Academic, London, 1973).

<sup>2</sup>O. Goscinski and B. Lukman, *Chem. Phys. Lett.* **7**, 573 (1970).

<sup>3</sup>For normalization  $\sum_K P_K = 1$ .

<sup>4</sup>Clearly, if the states  $\{|K\rangle\}$  used in the average  $\langle\rangle$  are orthogonal to a given exact eigenstate, e.g., by symmetry, then no information concerning ionization energies of this state can be obtained from **G**.

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<sup>15</sup>If we plan to use a single state for the calculation of the average value  $\langle\rangle$ , the analysis of this Appendix is complete. However, for cases which involve a trace over several states (say,  $|k\rangle, k=1, 2, \dots, M$ ), the developments of this Appendix must be generalized by requiring that  $\{O_{\lambda}^*|k\rangle, k=1, 2, \dots, M\}$  form a complete set and that  $O_{\lambda}|k\rangle = 0$ , for all  $\lambda$  and for all  $k$ .