Perturbative solution of equations of motion for excitation and ionization processes

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The equations of motion (EOM) which correspond to electronic excitation or ionization events are analyzed within the framework of perturbation theory. The choice of the Hartree–Fock Hamiltonian as the zeroth order Hamiltonian permits the perturbation equations to be solved in a convenient closed form. A comparison of the results for excitation processes with those given by the random phase approximation (RPA) is made. The role of two particle–two hole excitation operators, which are absent in the RPA, is discussed. Finally, connections are made between the Green's function approach to calculating ionization energies and the perturbation theory treatment of the EOM corresponding to ionization processes.

I. INTRODUCTION

For some time now, equations-of-motion[1] (EOM) and Green's function[2] (GF) methods have been successfully employed to compute energy differences (electronic excitation[3-8] or ionization[9-15]) and transition probabilities for atomic and molecular systems. These approaches have an advantage in that they permit the direct calculation of the desired energy difference; separate calculations on the parent and daughter species are not required.

In both the EOM and GF formalisms, one must eventually choose a set of basis operators in terms of which the electronic excitation or ionization process is to be described. For example, in the random phase approximation[16] (RPA) or time-dependent Hartree–Fock approximation[7,17] (TDHF), one expresses the electronic excitation operator as a combination of particle–hole $\{C_m^+ C_\alpha\}$ and hole–particle operators $\{C_\alpha^+ C_m\}$, where the $C_i^+ (C_i)$ are Fermion creation (destruction) operators, and indices α, β, etc. (m, n, etc.), refer to occupied (unoccupied) Hartree–Fock spin orbitals. In this paper, our attention is directed toward developing a systematic scheme for choosing the set of basis excitation or ionization operators. This scheme is based upon an order-by-order perturbation theory solution of the EOM in which the zeroth order Hamiltonian is taken to be the Hartree–Fock Hamiltonian. By treating the problem in a perturbative manner, we are able to identify those operators that must be included in any EOM or GF theory to guarantee that the excitation or ionization energy is obtained correctly through a given order.

In Sec. II we develop the general perturbation theory framework within which the electronic excitation and ionization problems are to be analyzed. In Sec. III we show that the operator space which is used in the RPA treatment of electronic excitation processes is not sufficient to guarantee that the excitation operator (excitation energy) is correct through first order (second order). Section IV contains our treatment of the EOM for ionization events as well as a comparison with the results of second-order Green's function calculations. In Sec. V we present our concluding remarks.

II. PERTURBATION THEORY FOR THE EOM

The EOM governing the excitation operator O_λ^+ and the excitation energy E_λ is written as[1]

$$\hat{H} O_\lambda^+ \equiv [H, O_\lambda^+] = E_\lambda O_\lambda^+, \tag{1}$$

where H is the electronic Hamiltonian of the system. By decomposing O_λ^+, E_λ, and the Hamiltonian H into zeroth, first, etc. order terms

$$H = H_0 + V, \tag{2a}$$

$$O_\lambda^+ = O_{\lambda 0}^+ + O_{\lambda 1}^+ + O_{\lambda 2}^+ + \cdots, \tag{2b}$$

$$E_\lambda = E_{\lambda 0} + E_{\lambda 1} + E_{\lambda 2} + \cdots, \tag{2c}$$

one obtains from Eq. (1) a series of operator equations, the first three of which are shown below:

$$\hat{H}_0 O_{\lambda 0}^+ = E_{\lambda 0} O_{\lambda 0}^+, \tag{3a}$$

$$\hat{H}_0 O_{\lambda 1}^+ + \hat{V} O_{\lambda 0}^+ = E_{\lambda 0} O_{\lambda 1}^+ + E_{\lambda 1} O_{\lambda 0}^+, \tag{3b}$$

$$\hat{H}_0 O_{\lambda 2}^+ + \hat{V} O_{\lambda 1}^+ = E_{\lambda 0} O_{\lambda 2}^+ + E_{\lambda 1} O_{\lambda 1}^+ + E_{\lambda 2} O_{\lambda 0}^+. \tag{3c}$$

Let us, for the moment, assume that the exact zeroth-order excitation operators $\{O_{\lambda 0}^+\}$ have been determined. Later, the precise forms of the $O_{\lambda 0}^+$ for both electronic excitation and ionization processes will be explicitly displayed. For now, we need only assume that the complete set of $O_{\lambda 0}^+$ and $E_{\lambda 0}$ have been found. To solve Eq. (3b) for the first-order excitation operator $O_{\lambda 1}^+$ and energy $E_{\lambda 1}$, we first take the commutator of Eq. (3b) with the adjoint excitation operator $O_{\lambda' 0}$, after which we form the expectation value of the result with respect to the reference state $|g\rangle$. The requirements imposed upon $|g\rangle$ by the form of $O_{\lambda 0}^+$ and by the assumption that the $\{O_{\lambda 0}^+ |g\rangle\}$ form a complete set of excited (or ionic) states are discussed in Appendix A. For now if suffices to say that $|g\rangle$ does not have to be the exact ground state of the system of interest. In fact, for the specific choice of H_0 made in the next section, i.e., the Hartree–Fock Hamiltonian, $|g\rangle$ can, without loss of generality, be chosen to be the Hartree–Fock ground state $|0\rangle$.

The result of carrying out the above steps can be expressed as follows:

$$(O_{\lambda' 0}^+ | \hat{H}_0 | O_{\lambda 1}^+) + (O_{\lambda' 0}^+ | \hat{V} | O_{\lambda 0}^+) = E_{\lambda 0}(O_{\lambda' 0}^+ | O_{\lambda 1}^+) + E_{\lambda 1}(O_{\lambda' 0}^+ | O_{\lambda 0}^+), \tag{4}$$

where we have introduced the shorthand notation[18]

$$(A | \hat{V} | B) \equiv \langle g | A^+ [V, B] \pm [V, B] A^+ | g \rangle, \tag{5}$$

in which the $+ (-)$ sign is used if A and B are Fermion (Boson) type operators.[2] The assumption that the excitation operators can be chosen to obey the normalization

condition $(O_\lambda^+ | O_\lambda^+) = 1$, through each order in the perturbation allows one to conclude that

$$(O_{\lambda 0}^+ | O_{\lambda 0}^+) = 1 \tag{6}$$

and

$$(O_{\lambda 0}^+ | O_{\lambda 1}^+) = 0 . \tag{7}$$

With Eqs. (6)–(7), the result shown in Eq. (4) reduces to two equations which yield $E_{\lambda 1}$ and $O_{\lambda 1}^+$:

$$(O_{\lambda 0}^+ | \hat{V} | O_{\lambda 0}^+) = E_{\lambda 1} \quad (\text{for } \lambda' = \lambda) \tag{8}$$

and

$$(O_{\lambda' 0}^+ | O_{\lambda 1}^+) = (O_{\lambda' 0}^+ | \hat{V} | O_{\lambda 0}^+) [E_{\lambda 0} - E_{\lambda' 0}]^{-1} \tag{9}$$

for $\lambda' \neq \lambda$. In writing Eq. (9) we have assumed that the states λ and λ' are not degenerate in zeroth order. To simplify the mathematical development of this paper, this assumption will be maintained; the treatment of degenerate cases would involve the application of the degenerate perturbation theory formalism in a straightforward fashion. In zeroth order, it is quite likely that the excitation or ionization operators $\{O_{\lambda 0}^+\}$ would contain degeneracies. However, by forming linear combinations of these degenerate operators, we obtain a set of operators which possess the correct symmetry (spin and space) to map the parent's ground state $|g\rangle$ into an excited or ionic state which is also of pure symmetry. In what follows, we assume that we have already formed this symmetry-adapted set of zeroth-order operators which block diagonalize our perturbation equations. Thus, in writing Eq. (9), we need only assume that no two zeroth-order operators which are of the same symmetry are degenerate.

Although it appears that Eq. (9) gives the exact first-order excitation operator $O_{\lambda 1}^+$ in terms of the zeroth-order operators $O_{\lambda' 0}^+$, care must be taken in interpreting Eq. (9). It is certainly true that the number $(O_{\lambda' 0}^+ | O_{\lambda 1}^+)$ gives the expansion coefficient of $O_{\lambda 1}^+$ in terms of $O_{\lambda' 0}^+$; however, knowledge of such expansion coefficients is not sufficient to determine $O_{\lambda 1}^+$ unless the zeroth-order operators form a complete set of excitation operators. It is shown in Appendix A that the $O_{\lambda' 0}^+$ form a complete set if this set of zeroth-order operators includes both the full set of excitation operators $O_{\lambda 0}^+$ for which $O_{\lambda 0} | g\rangle = 0$ and the full set of de-excitation operators $O_{\mu 0}^+$, which are merely the adjoints of the excitation operators $(O_{\mu 0}^+ = O_{\lambda 0}, O_{\mu 0} = O_{\lambda 0}^+)$, for which $\langle g | O_{\mu 0}^+ = 0$. Collecting the $O_{\lambda 0}^+$ and $O_{\mu 0}^+$ into vectors, the completeness relation derived in Appendix A within the scalar product defined in Eq. (5) and used in Eq. (9) is given by

$$1 = |O_{\lambda 0}^+, O_{\mu 0}^+) \Delta^{-1} \begin{pmatrix} O_{\lambda 0}^+ \\ O_{\mu 0}^+ \end{pmatrix}, \tag{10}$$

or

$$1 = |O_{\lambda 0}^+, O_{\lambda 0}) \Delta^{-1} \begin{pmatrix} O_{\lambda 0}^+ \\ O_{\lambda 0} \end{pmatrix} \tag{11}$$

where the matrix Δ is expressed as

$$\Delta = \begin{pmatrix} (O_{\lambda 0}^+ | O_{\lambda 0}^+) & (O_{\lambda 0}^+ | O_{\lambda 0}) \\ (O_{\lambda 0} | O_{\lambda 0}^+) & (O_{\lambda 0} | O_{\lambda 0}) \end{pmatrix}. \tag{12}$$

Thus, in Eq. (9) one needs to compute both the matrix elements $(O_{\lambda' 0}^+ | O_{\lambda 1}^+)$ and $(O_{\mu' 0}^+ | O_{\lambda 1}^+) \equiv (O_{\lambda' 0} | O_{\lambda 1}^+)$. The first-order excitation operator is then given in terms of the zeroth-order operators by

$$|O_{\lambda 1}^+) = |O_{\lambda' 0}^+, O_{\lambda' 0}) \Delta^{-1} \begin{pmatrix} (O_{\lambda' 0}^+ | O_{\lambda 1}^+) \\ (O_{\lambda' 0} | O_{\lambda 1}^+) \end{pmatrix}. \tag{13}$$

This is the general result for $O_{\lambda 1}^+$; later in this paper we discuss Eq. (13) in a more specific manner for operators O_λ^+ which correspond either to electronic excitation or ionization processes. Before these subjects are treated, however, it should be mentioned that, in addition to the above expressions for $E_{\lambda 1}$ and $O_{\lambda 1}^+$, one can obtain the following equations for the second- and third-order excitation energies:

$$E_{\lambda 2} = (O_{\lambda 0}^+ | \hat{V} | O_{\lambda 1}^+), \tag{14}$$

and

$$E_{\lambda 3} = (O_{\lambda 0}^+ | \hat{V} - E_{\lambda 1} | O_{\lambda 2}^+), \tag{15}$$

where

$$|O_{\lambda 2}^+) = |O_{\lambda' 0}^+, O_{\lambda' 0}) \Delta^{-1} \begin{pmatrix} (O_{\lambda' 0}^+ | O_{\lambda 2}^+) \\ (O_{\lambda' 0} | O_{\lambda 2}^+) \end{pmatrix}, \tag{16}$$

and

$$(O_{\lambda' 0}^+ | O_{\lambda 2}^+) = (O_{\lambda' 0}^+ | \hat{V} - E_{\lambda 1} | O_{\lambda 1}^+) [E_{\lambda 0} - E_{\lambda' 0}]^{-1}. \tag{17}$$

Equations (14) and (15) are analogous to the usual second- and third-order energy expressions of Rayleigh–Schrödinger perturbation theory.[19]

In summary, we have shown how the EOM given in Eq. (1) can be solved in a perturbative fashion. Closed expressions for $E_{\lambda 1}$, $E_{\lambda 2}$, $E_{\lambda 3}$, and $O_{\lambda 1}^+$ have been given. It now remains for us to evaluate the matrix elements appearing in these expressions for specific choices of H_0, $|g\rangle$, and the $\{O_{\lambda 0}^+\}$. This is carried out in the following two sections.

III. ELECTRONIC EXCITATION PROCESSES

If the zeroth-order Hamiltonian is chosen to be the Hartree–Fock Hamiltonian

$$H_0 = \sum_i \epsilon_i C_i^+ C_i, \tag{18}$$

the exact zeroth-order excitation operators which conserve the number of electrons (generate excited states rather than ionic states) are given by[20]

$$O_{\lambda 0}^+; O_{\lambda 0} = C_m^+ C_\alpha, \ C_m^+ C_n^+ C_\beta C_\alpha, \ \cdots ; \quad C_\alpha^+ C_m, \ C_\alpha^+ C_\beta^+ C_n C_m,$$

$$(\alpha < \beta, \ m < n \cdots) \tag{19}$$

and the reference state $|g\rangle$ which is consistent (i.e., for which $O_{\lambda 0} | g\rangle = \langle g | O_{\lambda 0}^+ = 0$) with these operators is the Hartree–Fock ground state $|0\rangle$. Operators of the form $C_\alpha^+ C_\beta$ or $C_m^+ C_n$ are excluded from our set of zeroth-order excitation operators because they do not generate excited Slater determinants when operating (either to

the right or to the left) on $|0\rangle$. As was mentioned in Sec. II, the zeroth-order operators must be chosen to process the correct space and spin symmetry. Thus, for example, if we are interested in studying singlet → singlet transitions from a closed-shell parent, the operator $C_m^+ C_\alpha$ becomes (more explicitly) $(1/\sqrt{2})[C_{m\uparrow}^+ C_{\alpha\uparrow} + C_{m\downarrow}^+ C_{\alpha\downarrow}]$, where the up and down arrows label the z component of the excited electron's spin. Spatial symmetry considerations must also be added to this singlet operator. Because the inclusion of spin and spatial symmetry adds significantly to the complication of the equations obtained here, and because our major concern is to demonstrate how the perturbation equations can be used to generate order-by-order approximations to excitation or ionization energies, we shall employ the non-

symmetry adapted spin orbital operators $C_m^+ C_\alpha$ in our discussion. Of course, in actual calculations, proper account of spin and space symmetry must be taken.

For the set of excitation operators given in Eq. (19), the Δ matrix reduces to

$$\Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{20}$$

which allows us to write $E_{\lambda 1}$ and $O_{\lambda 1}^+$, for a state whose zeroth-order excitation operator is $C_m^+ C_\alpha$, as

$$E_{\lambda 1} = (C_m^+ C_\alpha | \hat{V} | C_m^+ C_\alpha) = \langle m\alpha | \tilde{\alpha} m \rangle \tag{21}$$

and

$$O_{\lambda 1}^+ = \sum_{\lambda'} \{ O_{\lambda' 0}^+ (O_{\lambda' 0}^+ | O_{\lambda 1}^+) - O_{\lambda' 0}^+ (O_{\lambda' 0}^+ | O_{\lambda 1}^+) \}$$

$$= \sum_{n, \beta}' [\langle m\beta | \alpha\tilde{n} \rangle (\epsilon_m - \epsilon_\alpha - \epsilon_n + \epsilon_\beta)^{-1} C_n^+ C_\beta + \langle mn | \alpha\tilde{\beta} \rangle (\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)^{-1} C_\beta^+ C_n]$$

$$+ \sum_{\substack{p<n \\ \gamma<\beta}} [\delta_{\gamma\alpha} \langle pn | m\tilde{\beta} \rangle - \delta_{\beta\alpha} \langle pn | m\tilde{\gamma} \rangle + \delta_{nm} \langle \alpha p | \gamma\tilde{\beta} \rangle - \delta_{pm} \langle \alpha n | \gamma\tilde{\beta} \rangle](\epsilon_m - \epsilon_\alpha - \epsilon_p - \epsilon_n + \epsilon_\gamma + \epsilon_\beta)^{-1} C_n^+ C_p^+ C_\gamma C_\beta. \tag{22}$$

The second-order energy $E_{\lambda 2}$ is seen from Eqs. (9), (13), and (14) to be obtainable from Eq. (22) by removing the creation and annihilation operators and squaring the two-electron integrals in the numerators.[21] It can be shown that the particle–hole $\{C_m^+ C_\alpha\}$ and hole–particle $\{C_\alpha^+ C_m\}$ components of $O_{\lambda 1}^+$ given in Eq. (22) are identical to those which would be obtained by a first-order perturbation theory solution of the random-phase approximation (RPA) equations which is briefly discussed in Appendix B. The two particle–two hole (2p–2h) $\{C_m^+ C_n^+ C_\beta C_\alpha\}$ components of $O_{\lambda 1}^+$ must be included to obtain O_λ^+ correctly through first order. In higher RPA treatments, such 2p–2h terms are included.[7] The primary role of the 2p–2h terms in $O_{\lambda 1}^+$ is to provide an accurate description of the electron correlation in the excited state which through zeroth order is given by $C_m^+ C_\alpha |0\rangle$. For example, the first 2p–2h terms in Eq. (22) generate, when operating on $|0\rangle$, the following configurations $\langle pn | \bar{m}\beta \rangle C_n^+ C_p^+ C_\alpha C_\beta |0\rangle$, each of which is identical to $\langle pn | \bar{m}\beta \rangle C_n^+ C_p^+ C_m C_\beta (C_m^+ C_\alpha |0\rangle)$. Expressed in this form, it is clear that such configurations are doubly excited relative to the zeroth-order excited states $C_m^+ C_\alpha |0\rangle$, which allows one to conclude that they involve the correlation of the excited orbital (m) with all of the occupied orbitals (β) except the orbital $\alpha(\beta \neq \alpha)$ from which the electron has been excited. The other 2p–2h terms in Eq. (22) can be given analogous physical interpretations.

In carrying out an actual calculation, one must first evaluate the orbital energies and two-electron integrals which appear in Eqs. (21) and (22). For the specific excited state which is described in zeroth order by the energy difference $\epsilon_m - \epsilon_\alpha$, one obtains the first-order correction to the excitation energy from Eq. (21). The

second-order correction is computed by forming the sums in Eq. (22), e.g.,

$$\sum_{n, \beta} |\langle m\beta | \tilde{\alpha} n \rangle|^2 (\epsilon_m - \epsilon_\alpha - \epsilon_n + \epsilon_\beta)^{-1} + \sum_{n, \beta} |\langle mn | \tilde{\alpha}\beta \rangle|^2$$
$$\times (\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)^{-1} + \text{the } (2p-2h) \text{ terms}.$$

In this manner, one is able to calculate, in terms of the orbital energies and two-electron integrals, the first- and second-order corrections to the specific zeroth-order excitation energy of interest. The state is labeled by the single electron promotion $\phi_\alpha \to \phi_m$. To study excited states whose zeroth-order energy differences correspond to two-electron excitations $(\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)$, one must derive expressions analogous to Eqs. (21) and (22) in which the zeroth-order excitation operator for the state of interest is $C_m^+ C_n^+ C_\beta C_\alpha$. We are presently involved in carrying out such a derivation of the first- and second-order corrections to the excitation energies of these doubly excited states.

The principal conclusion of the above analysis is that the first-order correction to an excitation operator which in zeroth-order equals $C_m^+ C_\alpha$ contains particle–hole, hole–particle, and certain two particle–two hole components. Thus, the common RPA procedure does not describe O_λ^+ correctly through first order; it is lacking the 2p–2h contributions. If one carries out a perturbative analysis of O_λ^+, one can, by including p–h, h–p, and 2p–2h contributions, compute O_λ^+ through first order. Perturbation corrections to states which are described in zeroth order by $C_\alpha^+ C_m$ or $C_n^+ C_\beta C_\alpha$ could also be treated using the above analysis. In the h–p case $(C_\alpha^+ C_m)$ one finds that the excitation energy is, order by order, equal to minus the excitation energy corresponding to the zeroth-order operator $C_m^+ C_\alpha$. By assuming that $O_{\lambda 0}^+$ is a 2p–2h operator

$(C_m^+ C_n^+ C_\beta C_\alpha)$, one is able to develop corrections to zeroth-order states which are dominated by doubly excited configurations. Such doubly excited states are currently receiving a great deal of attention from both experimental and theoretical researchers.[22] We plan to use the present analysis to investigate the excitation energies associated with such states. We are also pursuing a study of the third-order excitation energies of states which, in zeroth-order, are described by the single-excitation operators $C_m^+ C_\alpha$.

IV. IONIZATION PROCESSES

Again choosing the Hartree–Fock Hamiltonian as H_0, one can proceed as in Sec. III to find the set of exact zeroth-order excitation operators. In the present case, however, one restricts the class of operators to those which either remove or add an electron, i. e., ionization operators. The desired set of operators is

$$\{O_{\lambda 0}^+; O_{\lambda 0}\} = \{C_m^+, C_\alpha, C_m^+ C_\alpha C_n^+, C_\beta C_m^+ C_\alpha, \cdots ; C_m, C_\alpha^+,$$
$$C_n C_\alpha^+ C_m, C_\alpha^+ C_m C_\beta^+, \cdots\} \quad (\alpha < \beta, \ m < n, \text{ etc.}),$$
(23)

which obey the required $O_{\lambda 0} |g\rangle = 0 = \langle g| O_{\lambda 0}^+$, if $|g\rangle$ is taken to be the Hartree–Fock ground state $|0\rangle$.

For the above set of operators, the Δ matrix appearing in Eq. (13) reduces to the unit matrix, and the resulting first-order energy and excitation operator corresponding to a zeroth-order operator $O_{i0}^+ = C_i^+$ is given by

$$E_{i1} = (C_i^+ | \hat{V} | C_i^+) = 0, \tag{24}$$

and

$$O_{i1}^+ = \sum_\lambda \{O_{\lambda 0}^+ (O_{\lambda 0}^+ | O_{i1}^+) + O_{\lambda 0}(O_{\lambda 0} | O_{i1}^+)\}$$

$$= \sum_{\substack{m<n \\ \alpha}} \{\langle i\alpha | \widetilde{mn}\rangle [\epsilon_i + \epsilon_\alpha - \epsilon_m - \epsilon_n]^{-1} C_m^+ C_\alpha C_n^+\}$$

$$+ \sum_{\substack{\alpha<\beta \\ m}} \{\langle im | \widetilde{\beta\alpha}\rangle [\epsilon_i + \epsilon_m - \epsilon_\alpha - \epsilon_\beta]^{-1} C_\alpha^+ C_m C_\beta^+\}. \tag{25}$$

The second-order ionization energy E_{i2} is obtained from Eq. (25) by removing the creation and annihilation operators and squaring the two-electron integrals. As for the electronic excitation operators discussed in Sec. III, the third-order ionization energy can be computed by using Eqs. (15)–(17).

To carry out a calculation of the ionization potential or electron affinity of a molecule which is described in Koopmans' theorem by ϵ_i, one must first evaluate the orbital energies and two-electron integrals appearing in Eq. (25). The second-order correction to the Koopmans' theorem energy difference can then be computed from Eq. (25) as

$$\sum_{\substack{m<n \\ \alpha}} |\langle i\alpha | \widetilde{mn}\rangle|^2 (\epsilon_i + \epsilon_\alpha - \epsilon_m - \epsilon_n)^{-1}$$

$$+ \sum_{\substack{\alpha<\beta \\ m}} |\langle im | \widetilde{\alpha\beta}\rangle|^2 (\epsilon_i + \epsilon_m - \epsilon_\alpha - \epsilon_\beta)^{-1}.$$

Ionic states which are described in zeroth order by energy differences of the form $\epsilon_m + \epsilon_n - \epsilon_\alpha$ or $\epsilon_\alpha + \epsilon_\beta - \epsilon_m$ are usually referred to as shake-up states because they can be thought of as corresponding to the removal or addition of an electron followed by the excitation of another electron. To handle such states within the perturbative formalism presented here, one must derive an expression analogous to Eq. (25) for the second-order correction to the ionization energy of the specific shake-up state of interest. We are currently carrying out such a derivation.

It is interesting to notice that the second-order ionization energy obtained above is identical to that which results from a second-order Green's function ($\mathbf{G}(E)$) calculation in which the pole of $\mathbf{G}(E)$ is approximated by $\epsilon_i + \Sigma_{ii}(\epsilon_i)$, where $\Sigma(E)$ is the self-energy appearing in the Dyson equation[23] for $\mathbf{G}(E)$,

$$\mathbf{G} = \mathbf{G}^0 + \mathbf{G}^0 \Sigma \mathbf{G} . \tag{26}$$

Thus, unlike the electronic excitation case, the space of operators needed to compute $O_{\lambda 1}^+$ is identical to the space used in the conventional second-order Green's function studies. A comparison of the third-order energy obtained in this fashion to that which is obtained in a diagrammatic Green's function analysis[11] is now being carried out in our research group. The results of this study will appear in a future publication.

This completes our analysis of those ionization operators which, in zeroth order, are described by C_i^+. An analogous derivation can be carried through for the zeroth-order operators $C_n^+ C_\alpha C_m^+$ which correspond to shake-up states of the ion.

V. CONCLUSION

In this paper we have presented a perturbation theory analysis of the EOM in which the excitation or ionization energy (and operator) are obtained in order-by-order expansions. By choosing the Hartree–Fock ground state $|0\rangle$ as our reference function and the Hartree–Fock Hamiltonian as our zeroth-order Hamiltonian, we were able to obtain exact expressions for $E_{\lambda 1}$, $E_{\lambda 2}$, $E_{\lambda 3}$, and $O_{\lambda 1}^+$ in terms of a set of zeroth-order energies $\{E_{\lambda 0}\}$ and operators $\{O_{\lambda 0}^+, O_{\lambda 0}\}$. Closed formulas for these quantities were given for electronic excitations whose zeroth-order operators are $C_m^+ C_\alpha$ as well as for ionizations whose zeroth-order operators are C_i^+.

In our analysis of electronic excitation processes, we were able to show that certain two particle–two hole operators $\{C_m^+ C_n^+ C_\beta C_\alpha\}$ are present in the correct first-order excitation operator. The fact that these terms are not included in the conventional random-phase approximations implies that the RPA is not capable of yielding excitation energies (excitation operators) which are correct through second (first) order.

In analyzing those ionization states which are described in zeroth order by C_i^+, we found that the correct first-order ionization operator contains only those terms which are present in the second-order Dyson equation of Green's function theory. We can, therefore, conclude that a solution of the Dyson equation is capable

of yielding ionization energies which are correct through second order.

Although the results of this paper do not necessarily provide more economical or more highly accuracte methods for studying excitation and ionization processes, they do allow us to generate, in a systematic and reasonable fashion, that set of operators which *must* be included in any theory (EOM, GF, etc.) in order to guarantee that O_λ^+ or E_λ is computed correctly through some chosen order. This primary result will hopefully be a valuable tool for use in developing new approaches to investigate electronic or ionization spectroscopy.

ACKNOWLEDGMENTS

APPENDIX A

Our goal is to establish and clarify the completeness relation given in Eq. (11) which has been extensively used in the developments presented in Sec. II. We assume that we have found a set of (number conserving or ionizing) operators $\{O_{\lambda 0}^+\}$ which, when operating on some reference state $|g\rangle$, generate (with $|g\rangle$)[24] a complete set of functions $\{O_{\lambda 0}^+|g\rangle$ for the system of interest. We further assume that these operators obey the consistency equation $O_{\lambda 0}|g\rangle = 0$.

The completeness relation indicated in Eq. (11) must be proven within the framework of the scalar product

given below:

$$(A|B) \equiv \langle g|A^+B \pm BA^+|g\rangle . \tag{A1}$$

If Eq. (11) does express a resolution of the identity operator, we can rewrite $(A|B)$ as

$$(A|B) = [(A|O_{\lambda 0}^+), (A|O_{\lambda 0})]\Delta^{-1}\begin{bmatrix}(O_{\lambda 0}^+|B)\\(O_{\lambda 0}|B)\end{bmatrix} . \tag{A2}$$

If the set of operators $O_{\lambda 0}^+$, $O_{\lambda 0}$ are chosen as indicated in Secs. III and IV, the basis operators can easily be shown to obey the following orthonormality conditions:

$$(O_{\lambda 0}^+|O_{\lambda 0}^+) = 1 , \tag{A3}$$

$$(O_{\lambda 0}^+|O_{\lambda 0}) = (O_{\lambda 0}|O_{\lambda 0}^+) = 0, \tag{A4}$$

$$(O_{\lambda 0}|O_{\lambda 0}) = \pm 1 ; \tag{A5}$$

then the Δ matrix reduces to

$$\Delta = \begin{pmatrix}1 & 0\\0 & \pm 1\end{pmatrix} , \tag{A6}$$

and Eq. (A1) can be rewritten as

$$(A|B) = \sum_\lambda \{(A|O_{\lambda 0}^+)(O_{\lambda 0}^+|B) \pm (A|O_{\lambda 0})(O_{\lambda 0}|B)\}. \tag{A7}$$

Writing out explicitly the four scalar products which appear on the right hand side of Eq. (A7) and using the consistency conditions $(O_{\lambda 0}|g\rangle = 0)$, we obtain

$$(A|B) = \sum_\lambda \{\langle g|A^+O_{\lambda 0}^+ \pm O_{\lambda 0}^+A^+|g\rangle \langle g|O_{\lambda 0}B \pm BO_{\lambda 0}|g\rangle \pm \langle g|A^+O_{\lambda 0} \pm O_{\lambda 0}A^+|g\rangle \langle g|O_{\lambda 0}^+B \pm BO_{\lambda 0}^+|g\rangle\}$$

$$= \sum_\lambda \{\langle g|A^+O_{\lambda 0}^+|g\rangle \langle g|O_{\lambda 0}B|g\rangle \pm \langle g|BO_{\lambda 0}^+|g\rangle \langle g|O_{\lambda 0}A|g\rangle\}. \tag{A8}$$

Since the set of functions $\{O_{\lambda 0}^+|g\rangle\}$ forms a complete set of excited electronic or ionic states, e.g., in the electronic excitation case they generate the set of singly, doubly, triply, etc. excited Slater determinants which are known to be complete if the spin orbital basis used in their construction is complete, we can use the completeness relation within the common (wavefunction) scalar product

$$1 = \sum_\lambda O_{\lambda 0}^+|g\rangle \langle g|O_{\lambda 0} \quad \text{for ionic states} \tag{A9}$$

or

$$1 = \sum_\lambda O_{\lambda 0}^+|g\rangle \langle g|O_{\lambda 0} + |g\rangle \langle g| \quad \text{for excited states} \tag{A9'}$$

to express Eq. (A8) as

$$(A|B) = \langle g|A^+B|g\rangle \pm \langle g|BA^+|g\rangle . \tag{A10}$$

The term $[\langle g|A^+|g\rangle \langle g|B|g\rangle - \langle g|B|g\rangle \langle g|A^+|g\rangle]$, which arises in the electronic excitation case, vanishes identically. Thus, we are left with

$$(A|B) = \langle g|A^+B \pm BA^+|g\rangle,$$

which demonstrates that the completeness relation

given in Eq. (11) is indeed consistent with our definition of the scalar product.

APPENDIX B

In the random phase approximation (RPA), as discussed by Rowe,[1] or in the equivalent TDHF which has been previously reviewed by Jørgensen,[7] the approximate electronic excitation operator

$$O_\lambda^+ = \sum_{m,\alpha}\{Y_{m\alpha}(\lambda)C_m^+C_\alpha - Z_{m\alpha}(\lambda)C_\alpha^+C_m\} \tag{B1}$$

is substituted into the basic equations of motion

$$\langle g|O_{\lambda'}[H, O_\lambda^+] - [H, O_\lambda^+]O_{\lambda'}|g\rangle$$
$$= \delta_{\lambda\lambda'}\Delta E_\lambda \langle g|O_{\lambda'}O_\lambda^+ - O_\lambda^+O_{\lambda'}|g\rangle$$

or

$$(O_{\lambda'}^+|H|O_\lambda^+) = \delta_{\lambda\lambda'}\Delta E_\lambda(O_{\lambda'}^+|O_\lambda^+) \tag{B2}$$

to yield the following working equations:

$$\begin{pmatrix}A & B\\-B^\dagger & -A^*\end{pmatrix}\begin{pmatrix}Y(\lambda)\\Z(\lambda)\end{pmatrix} = \Delta E_\lambda \begin{pmatrix}Y(\lambda)\\Z(\lambda)\end{pmatrix} . \tag{B3}$$

The **A** and **B** matrices are defined by

$$A_{m\epsilon,n\theta} = \langle g | [C_\epsilon^+ C_m, [H, C_n^+ C_\theta]] | g \rangle = (C_m^+ C_\epsilon | \hat{H} | C_n^+ C_\theta) \quad (B4)$$

and

$$B_{m\epsilon,n\theta} = \langle g | [C_\epsilon^+ C_m, [H, C_\theta^+ C_n]] | g \rangle = (C_m^+ C_\epsilon | \hat{H} | C_\theta^+ C_n), \quad (B5)$$

which, if evaluated using the Hartree–Fock ground state $|0\rangle$ for $|g\rangle$, reduce to

$$A_{m\epsilon,n\theta} = \delta_{mn}\delta_{\epsilon\theta}(\epsilon_m - \epsilon_\theta) + \langle m\theta | \epsilon\tilde{n} \rangle \quad (B6)$$

and

$$B_{m\epsilon,n\theta} = \langle mn | \tilde{\epsilon}\theta \rangle . \quad (B7)$$

If Eq. (B3) is solved by the partitioning technique[25] in which the $\{Z_{n\beta}\}$ and $\{Y_{m'\alpha'}\}$ are eliminated in favor of the single expansion coefficient $Y_{m\alpha}$, one obtains (through second order)

$$\Delta E_\lambda = A_{m\alpha,m\alpha} + \sum_{\substack{n,\beta \\ (\neq m,\alpha)}} [A_{m\alpha,n\beta}^2 (\Delta E_\lambda - \epsilon_n + \epsilon_\beta)^{-1}$$
$$+ B_{m\alpha,n\beta}^2 (\Delta E_\lambda + \epsilon_n - \epsilon_\beta)^{-1}]. \quad (B8)$$

Making use of Eqs. (B6) and (B7) and approximating ΔE_λ by $\epsilon_m - \epsilon_\alpha$ on the right hand side of Eq. (B8), one obtains

$$\Delta E_\lambda = \epsilon_m - \epsilon_\alpha + \langle m\alpha | \tilde{\alpha}m + \sum_{\substack{n,\beta \\ (\neq m,\alpha)}} | \langle m\beta | \tilde{\alpha}n \rangle |^2$$

$$(\epsilon_m - \epsilon_\alpha + \epsilon_\beta - \epsilon_n)^{-1} + | \langle mn | \tilde{\alpha}\beta \rangle |^2 (\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)^{-1}].$$
$$(B9)$$

This is precisely the same as $E_{\lambda 1}$ [see Eq. (21)] plus the p–h and h–p contributions to $E_{\lambda 2}$ which were discussed following Eq. (22) of the text.

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†On leave from Dept. of Chem., Aarhus University, Aarhus, Denmark.
[1]See, for example, D. J. Rowe, Rev. Mod. Phys. 40, 153 (1968); D. J. Rowe, *Nuclear Collective Motion: Models and Theory* (Methuen, London, 1970). The eigenoperators and eigenvalues of the super operator Hamiltonian are easy to understand. The eigenoperator O_λ^+ can be expanded in a complete set of (e.g., for ionization potentials) basis operators $|k^{N-1}\rangle\langle 1^N|$

$$O_\lambda^+ = \sum_{N=0} \sum_{k,1} C_{k,1}^{(N)} |k^{N-1}\rangle \langle 1^N| ,$$

where the functions $|k^{N-1}\rangle$ and $|1^N\rangle$ are exact $N-1$ and N electron eigenstates. The Eq. (1) can then be written as

$$[H, O_\lambda^+] = E_\lambda O_\lambda^+$$

or

$$\sum_{N=0} \sum_{k,1} C_{k,1}^{(N)} \{E_k^{N-1} - E_1^N - E_\lambda\} |k^{N-1}\rangle\langle 1^N| = 0 .$$

Because the $|k^{N-1}\rangle\langle 1^N|$ are complete and linearly independent, we can conclude that either $C_{k,1}^{(N)} = 0$ or $E_\lambda = E_k^{N-1} - E_1^N$; that is, the O_λ^+ are given by

$$O_\lambda^+ = |k^{N-1}\rangle\langle 1^N|$$

and

$$E_\lambda = E_k^{N-1} - E_1^N .$$

This establishes that the exact eigenoperators are indeed operators which map from an exact N-electron eigenstate to an exact $N-1$ electron eigenstate and that the eigenenergies are indeed exact ionization potentials. Analogous proofs can be carried through for the electron affinity and excitation energy situations. Because $O_\lambda^+ = |k^{N-1}\rangle\langle 1^N|$, it is clear that the exact excitation or ionization operators generate states which have the proper spin and spatial symmetry for the system under study.
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