PHYSICAL REVIEW A VOLUME 16, NUMBER 3 SEPTEMBER 1977

Excitation operators and the extended random-phase approximation. I. Theory[*]

A. C. Lasaga[†] and M. Karplus
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 9 March 1977)

An analysis of extended random-phase approximations is made with emphasis on the justification of the simplifying assumptions used in applications. It is demonstrated that in a complete operator space, the equations of motion in expectation value form, supplemented by the ground-state annihilation condition, yield the exact result for excitation operators and are equivalent to the operator equation of motion. Certain operators that are normally neglected have to be included to obtain the exact solution; some of these additional operators are shown to be important while others are expected to have small effects. The random-phase approximation and its self-consistent variants are analyzed, and a number of improvements that can be introduced without increasing the difficulty of the calculations are suggested.

I. INTRODUCTION

Equation-of-motion methods, often referred to as the random-phase approximation (RPA) or the time-dependent Hartree-Fock theory, have been applied to a variety of atomic and molecular systems in recent years.[1-17] An essential element in these applications has been the use of equations of motion that involve excitation-operator expectation values, rather than the operators themselves. The results obtained are thus dependent on the form of the wave function used for obtaining the expectation values. In the normal random-phase approximation (NRPA), Hartree-Fock wave functions are employed. Stimulated by Rowe's very clear description of these methods, a number of workers have developed formulations that go beyond the normal RPA. Shibuya and co-workers,[18,19] in particular, have been instrumental in introducing new approximations and determining their effects on the excitation energies and other properties of molecules. The extension developed by them, called the self-consistent RPA (SC-RPA), corresponds to replacement of the Hartree-Fock ground-state wave function by one that takes explicit account of correlation corrections. The calculations of Shibuya *et al.* using only one-particle-hole terms in the excitation operator suggest that introduction of a self-consistent ground-state leads to satisfactory values of excitation energies and oscillator strengths. A difficulty in evaluating their conclusions is that it is not always clear whether the apparent improvements over the normal RPA are due to the fact that the method is better or to an accidental cancellation of errors (e.g., resulting from limitations in the basis set). This question is made particularly cogent by an analysis of the two-electron case,[20] in which it has been demonstrated that the explicit inclusion of ground-state correlation by the self-consistency requirement yields excitation energies ($\omega_n = E_n - E_0$) that satisfy the inequalities $\omega_n^{\text{SC-RPA}} \geq \omega_n^{\text{TDA}} \geq \omega_n^{\text{NRPA}}$, where TDA stands for the Tamm-Dancoff approximation. Since TDA singlet excitations have been found to be too large in most applications, the SC-RPA does not lead to improved results; for triplets, the NRPA values are generally too low, so the SC-RPA can be better. Further, it was suggested that for reliable excitation energy calculations with the SC-RPA a better representation of the excited states had to be introduced to achieve a balance between the ground- and excited-state correlation corrections. Shibuya, Rose, and McKoy[19] have recently taken an important step in this direction by introducing two-particle-hole terms into the excitation operator. Because of the complications of the resulting equation of motion, they introduced certain simplifying approximations, as well. From their applications and those made by others, it appears that this augmented RPA leads to considerably improved results.

In this paper, we attempt to clarify the basis of the equation-of-motion method by considering the structure of the exact excitation operator (Sec. II). To illustrate the analysis, we determine the form of the excitation operator for the two-electron case. In Sec. III, we review and evaluate certain extensions of the RPA, following the hierarchy of Rowe[21] and of McKoy and Shibuya.[18,19] The analysis suggests alternative approximations which lead to slightly more complicated formulas, but give more consistent results. In paper II, we will illustrate the methodology by discussing the π-electron spectrum of ethylene and test the various approximations by calculations on the π-electron spectrum of polyenes represented by a Hamiltonian of the Pariser-Parr-Pople (PPP) type.

II. THEORY OF THE EXCITATION OPERATOR: APPLICATION TO THE TWO-ELECTRON PROBLEM

The equation of motion for a system with Hamiltonian H and a harmonic spectrum of frequency

ω can be written

$$[H, O^\dagger] = \omega O^\dagger , \tag{1}$$

where $O^\dagger$ is the appropriate excitation operator. Rowe has suggested that Eq. (1) can be replaced, for the restricted excitation space of interest in atomic and molecular problems, by equations of motion involving expectation values of the form

$$\langle 0 | [R, H, O_\lambda^\dagger] | 0 \rangle = \omega_\lambda \langle 0 | [R, O_\lambda^\dagger] | 0 \rangle , \quad \omega_\lambda \equiv E_\lambda - E_0 \tag{2}$$

where $O_\lambda^\dagger$ is the excitation operator to the specific state $|\lambda\rangle$ with energy E_λ, $|0\rangle$ is the ground-state wave function with energy E_0, R is an arbitrary operator in the operator space (which includes O_λ) and $[R, H, O_\lambda^\dagger]$ is the symmetrized double commutator

$$[R, H, O_\lambda^\dagger] = \tfrac{1}{2}([R,[H,O_\lambda^\dagger]] + [[R,H], O_\lambda^\dagger]). \tag{3}$$

The operators $O_\lambda^\dagger$ which are the solutions to Eq. (2) should have the properties

$$O_\lambda^\dagger |0\rangle = |\lambda\rangle , \quad O_\lambda |0\rangle = 0 , \tag{4}$$

that is, $O_\lambda^\dagger$ creates the excited state $|\lambda\rangle$ when it operates on $|0\rangle$ and its adjoint O_λ gives zero when it operates on $|0\rangle$.

The usual procedure of determining $O_\lambda^\dagger$ begins with an assumed form for both $O_\lambda^\dagger$ and $|0\rangle$ that involves unknown coefficients. In the initial calculation $|0\rangle$ is approximated by the Hartree-Fock solution. An attempt is then made to solve Eq. (2) subject to the condition that the second of Eqs. (4) is satisfied; that is, the annihilation condition is introduced as a means of finding the ground-state wave function in a self-consistent fashion. An apparent advantage of this approach, versus that of direct solution of Eq. (1), is that the elementary excitations that have to be included in $O_\lambda^\dagger$ are limited to those that yield nonzero contributions when acting on $|0\rangle$. Thus, for a given "size" of calculation a better approximation to the specific form of $O_\lambda^\dagger$ required for excitation to the state λ can be obtained. Also, as stressed by Rowe and others, the double commutator appearing in Eq. (2) should be relatively insensitive to errors in the approximate ground state; in a later paper, we give a simple example that illustrates this conjecture.

There are two basic questions that have to be considered in employing Rowe's formulation of the equations of motion. The first concerns the nature of the operators that have to be included in $O_\lambda^\dagger$ so that, given the exact ground-state function, the solution of Eq. (2) yields the exact excitation operator $O_\lambda^\dagger$. Secondly, since Eqs. (2) and (4) make use of the ground-state wave function $|0\rangle$, as well as of the excitation operator $O_\lambda^\dagger$, and neither is known initially, it is necessary to determine whether the iterative procedure that starts with an approximate expression for $|0\rangle$ converges to the exact excitation operator and to the exact ground state.

The approximation to the exact $O_\lambda^\dagger$ is expected to improve as the number of elementary excitations (one particle-hole, two particle-hole, etc.) included in $O_\lambda^\dagger$ is increased. However, as already pointed out by Rowe, the exact solution to Eqs. (2) and (4) is not unique. For each $O_\lambda^\dagger$, there are an infinite number of solutions of the form

$$O_\lambda^\dagger = |\lambda\rangle\langle 0| + \sum_{i,j\neq 0} C_{ij} |E_i\rangle\langle E_j| \tag{5}$$

for any coefficients C_{ij}, where $\{|E_i\rangle\}$ is the set of exact excited states of the Hamiltonian H. If we require that $O_\lambda^\dagger$ satisfy the operator eigenvalue equation of motion [Eq. (1)], we have the solution $O_\lambda^\dagger = |\lambda\rangle\langle 0|$. For a given ω_λ, this solution is unique if there does not exist a pair of states, $|E_1\rangle$ and $|E_2\rangle$, such that

$$\omega_\lambda = E_\lambda - E_0 = E_1 - E_2 . \tag{6}$$

For the later case, $O_\lambda^\dagger$ could be any linear combination of $|\lambda\rangle\langle 0|$ and $|E_1\rangle\langle E_2|$. Barring accidental degeneracies (as in a really harmonic spectrum) and the trivial case $\omega_\lambda = 0$ (for which all $|\lambda\rangle\langle\lambda|$ are solutions), there will be no states satisfying Eq. (6). If such a degeneracy does exist (and we give a simple example in the PPP model for ethylene in paper II), the domain of $O_\lambda^\dagger$ can be restricted so as to select the desired solution, $|\lambda\rangle\langle 0|$.

We have written the unique solution to Eq. (1) in Dirac notation as $|\lambda\rangle\langle 0|$. In the usual procedure, one constructs $O_\lambda^\dagger$ employing an operator space that is made up of second-quantized products of creation and annihilation operators. The first question raised above concerns the nature of the products that have to be included to obtain an exact solution for $O_\lambda^\dagger$. Since the molecular Hamiltonian,

$$H = \sum_i \epsilon_i a_i^\dagger a_i + \frac{1}{2} \sum_{ijkl} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - \sum_{jk\gamma} (V_{\gamma j \gamma k} - V_{\gamma j k \gamma}) a_j^\dagger a_k \tag{7}$$

[in standard notation, where i, j, k, l can be holes or particles; Greek letters refer to holes only; and $V_{ijkl} \equiv \langle i(1) j(2) | 1/r_{12} | k(1) l(2) \rangle$] conserves the particle number, the operator space can be correspondingly restricted. For an N-electron system this implies that any operator product which annihilates or creates more than N electrons in a row is equivalent to the null operator. Thus, if we assume "normal ordering" of the operators in the basis of the operator space, we need only consider a finite number of different types of particle and hole operators. For an N-electron system, the complete operator space can be constructed from the basis

$$\{c_{i_2}^\dagger c_{i_1}, c_{i_4}^\dagger c_{i_3}^\dagger c_{i_2} c_{i_1}, \ldots, c_{i_{2N}}^\dagger c_{i_{2N-1}}^\dagger \ldots, c_{i_N} \ldots, c_{i_1}\}$$

where i_m can be a particle or a hole. This set guarantees that if an operator R is in the complete space, the commutator $[H,R]$ also belongs to the space. Thus, the space is closed with respect to commutation with H, and we can expand $O_\lambda^\dagger$ in terms of this set of elements. Consequently, Eq. (1) can be treated as an eigenvalue equation (not necessarily Hermitian) with the unique solution $|\lambda\rangle\langle 0|$ that is guaranteed by the above discussion.

Although the set of operator types is finite, it is important to realize that, in contrast to previous applications, the operator space cannot be restricted to those of the particle-hole form (one p-h, two p-h, etc.). Operators of the particle-particle or hole-hole type, which conserve particle number (such operators will be called "density-shift" operators) are essential for an exact solution to the operator equation.

Given the exact operator equation, Eq. (1), and the nature of its solutions, we are in a position to analyze the properties of Rowe's equation of motion. In particular, we wish to examine the operator $O_\lambda^\dagger$ which satisfies Eq. (2) subject to $O_\lambda|0\rangle = 0$ [Eq. (4)], and to determine if it is guaranteed that $O_\lambda^\dagger|0\rangle = |\lambda\rangle$ with both $|0\rangle$ and $|\lambda\rangle$ exact eigenstates when the complete operator space is used. We expand the excitation operator $O_\lambda^\dagger$ (dropping the subscript λ for simplicity) as

$$O^\dagger = \sum_{n,m} C_{nm} |n\rangle\langle m| \tag{8a}$$

and the trial ground-state wave function $|0\rangle$ as

$$|0\rangle = \sum_j A_j |j\rangle, \tag{8b}$$

where $|n\rangle$, $|m\rangle$, and $|j\rangle$ are exact eigenstates of H. Substitution from Eq. (8) into Eq. (2) yields the relation

$$\sum_{n,l} \left(\sum_j [(2E_n - E_j - E_l - 2\omega) C_{nj} A_j A_l^* - E_j C_{jl} A_j^* A_n] \langle l|R|n\rangle \right) = 0 \tag{9}$$

while the consistency condition [Eq. (4)] requires that for each m,

$$\sum_j C_{jm}^* A_j = 0. \tag{10}$$

If the operator space is complete, as described above, we can construct operators R that are the exact solutions of the operator equation $[H,R] = \omega' R$ for all possible ω'; that is, we can find operators of the form $R = |t\rangle\langle n|$ for all exact $|t\rangle$ and $|n\rangle$ in the operator space. If R is a sum of all such operators, we have $\langle l|R|n\rangle \neq 0$ for every n and l, so that each of the coefficients in Eq. (9) must vanish individually. Thus,

$$\sum_j [(2E_n - E_j - E_l - 2\omega) C_{nj} A_j A_l^* - E_j C_{jl} A_j^* A_n] = 0, \quad (\text{all } n, l). \tag{11}$$

If it were established that $|0\rangle$ is the exact ground-state wave function (i.e., only A_0 nonzero), Eq. (11) would reduce to

$$C_{nl} \text{ arbitrary } (n, l \neq 0), \quad C_{0l} = 0 \ (\text{all } l) \tag{12a}$$

and

$$(2E_n - 2E_0 - 2\omega) C_{n0} = 0 \ (\text{all } n). \tag{12b}$$

For each n there exists the nontrivial solution $C_{n0} = 1$, $\omega = E_n - E_0$. Thus, Eq. (11) shows that the exact spectrum is obtained from Eq. (2) if the exact ground state $|0\rangle$ is used and $O_\lambda^\dagger$ is expanded in the complete operator space.

The above result leaves unresolved the question of the existence of mixed-state solutions, $|\bar{0}\rangle$, as in Eq. (8b), which exactly satisfy Eqs. (2) and (4) even in the limit of the complete operator space. To examine this possibility, we first show that there is at most one mixed state, $|\bar{0}\rangle$, with N nonzero coefficients A_i, which satisfies Eq. (11) with nonzero coefficients C_{nm} (A_n and A_m nonzero). If $|\bar{0}\rangle$ is a mixture of N exact states, the independent variables to be determined from Eqs. (2) and (4) are the N^2 different coefficients C_{nm} (A_n and A_m nonzero), N different nonzero A_i, and one ω. These variables must satisfy N^2 equations for the C_{nm} coefficients given by Eq. (11), N equations from Eq. (10), and two normalization conditions (one for $|\bar{0}\rangle$ and one for $O_\lambda^\dagger|\bar{0}\rangle$). There is one dependent equation in the N^2 set, since it is possible to derive the relation

$$\sum_k \sum_j [(2E_k - E_j - E_k - 2\omega) C_{kj} A_j A_k^* - E_j C_{jk} A_j^* A_k] = 0 \tag{13}$$

from the n consistency equations [Eq. (10)]. Thus, the number of independent equations is $N^2 + N + 2 - 1 = N^2 + N + 1$, which is exactly equal to the number of independent variables. This demonstrates that there is at most one ω and one $|\bar{0}\rangle$ that can satisfy Eq. (2) if $|\bar{0}\rangle$ is a mixed state with N nonzero A_i's. It should be noted that if for some reason *all* the C_{nm} are zero ($A_n, A_m \neq 0$), the above considerations no longer hold (e.g., in the case $N = 1$, $C_{00} = 0$); we consider this special case below in deriving Eq. (15). To show that $|\bar{0}\rangle$ cannot correspond to a real nonzero value of ω, we proceed as follows. The lowest N value of interest is $N=2$, so we write

$$|\bar{0}\rangle = A_i|i\rangle + A_j|j\rangle, \tag{14}$$

where $|i\rangle$ and $|j\rangle$ stand for any two exact states with $E_i \neq E_j$ and $\omega_{ij} = E_j - E_i \neq 0$; if $E_i = E_j$, $|i\rangle$ and $|j\rangle$ are degenerate so that the linear combination in Eq. (14) is an eigenfunction of H and $N=1$. Applying Eqs. (10) and (11) to $N=2$, we find that a solution for ω exists if and only if (see Appendix)

$$\omega_{ij} = 0 \text{ and } \omega = 0. \tag{15}$$

Since ω_{ij} is nonzero by assumption, we have a contradiction and the theorem is true for $N=2$. If we have an exact solution that is a linear combination of three exact states (e.g., $|\bar{0}\rangle = A_i|i\rangle + A_j|j\rangle + A_k|k\rangle$), we can derive a solution for $N=2$ by projecting out $|i\rangle$ from the domain of the operators $R, H, O^\dagger$; e.g., for

$$H' = \sum_{l \neq i} E_l |l\rangle\langle l|,$$

the state

$$|\bar{0}\rangle' = A_j|j\rangle + A_k|k\rangle$$

is an exact solution of Eq. (2) expressed in terms of the projected operators. Since the proof for $N=2$ is general and does not depend on the specific nature of R, H, and $O^\dagger$ (i.e., R', H', and $O^{\dagger\prime}$ can be used instead of R, H, and $O^\dagger$), it is clear that $|\bar{0}\rangle'$ cannot be an exact solution. Thus, we are led to a contradiction, which makes the theorem applicable to $N=3$. This iteration procedure can be generalized to a mixed solution for N states; that is, the impossibility of a mixed state for $N=2$ eliminates all others.

The above argument demonstrates that for a complete operator space, the equations of motion of of Rowe [Eq. (2)] combined with the consistency criterion [Eq. (4)] yield the exact eigenstates of the molecular Hamiltonian H. The completeness of the space is essential since it was necessary to require that it contain all operators, $R = |l\rangle\langle n|$, where $|l\rangle$ and $|n\rangle$ are exact eigenstates of H. The operator space shown to be required for the construction of the exact $O_\lambda^\dagger$ is such an operator space, though it is expected that satisfactory approximations can be obtained within a more limited subspace.

Two-electron problem

To illustrate the general ideas developed above and make clear the need to consider the complete operator space, we consider the two-electron problem. In this case, the excitation operator $O^\dagger$ reduces to the expression

$$O^\dagger = \sum_{m,n} C_{mn} a_m^\dagger a_n + \sum_{\substack{r>m \\ s>n}} D_{mn,rs} a_m^\dagger a_r^\dagger a_n a_s, \tag{16}$$

where the sums go over all particles and holes. Thus, in addition to one- and two-particle-hole operators, there are the terms involving hole-hole and particle-particle operators (density-shift operators). To obtain the exact formula for this case and to avoid the need to resort to an iterative procedure, we use the operator equation [Eq. (1)] instead of the expectation-value equation [Eq. (2) with Eq. (4)]. When the Hamiltonian equation (7) and Eq. (16) are introduced into Eq. (1), we obtain for the two-electron problem the following system of equations for the coefficients C_{mn} and $D_{mn,rs}$ and the eigenvalue ω:

$$\omega C_{mn} = (\epsilon_m - \epsilon_n) C_{mn} - \sum_{k\gamma} (V_{\gamma m\gamma k} - V_{\gamma mk\gamma}) C_{kn} + \sum_{k\gamma} (V_{\gamma k\gamma n} - V_{\gamma kn\gamma}) C_{mk} \tag{17}$$

and

$$\begin{aligned}
\omega D_{mn,rs} = {} & (\epsilon_r + \epsilon_m - \epsilon_s - \epsilon_n) D_{mn,rs} + \sum_i [(V_{irns} - V_{irsn}) C_{mi} + (V_{imsn} - V_{imns}) C_{ri}] \\
& + \sum_i [(V_{rmni} - V_{mrni}) C_{is} + (V_{mrsi} - V_{rmsi}) C_{in}] - \sum_{\gamma\kappa} [(V_{\gamma m\gamma k} - V_{\gamma mk\gamma}) D_{kn,rs} + (V_{\gamma r\gamma k} - V_{\gamma rk\gamma}) D_{mn,ks}] \\
& + \sum_{\gamma j}^{\kappa} [(V_{\gamma j\gamma n} - V_{\gamma jn\gamma}) D_{mj,rs} + (V_{\gamma j\gamma s} - V_{\gamma js\gamma}) D_{mn,rj}] + \frac{1}{2} \sum_{il} (V_{imil} D_{ln,rs} + V_{iril} D_{mn,ls}) \\
& - \frac{1}{2} \sum_{ij} (V_{ijis} D_{mn,rj} + V_{ijin} D_{mj,rs}) - \frac{1}{2} \sum_{ik} (V_{imks} D_{kn,ri} + V_{irks} D_{mn,ki}) - \frac{1}{2} \sum_{ik} (V_{imkn} D_{ki,rs} + V_{irkn} D_{mi,ks}) \\
& - \frac{1}{2} \sum_{il} (V_{imil} D_{ln,rs} + V_{iril} D_{mn,ls}) + \frac{1}{2} \sum_{lk} (V_{rmkl} D_{ln,ks} + V_{mrkl} D_{kn,ls}) + \frac{1}{2} \sum_{ki} (V_{imks} D_{kn,ri} + V_{irks} D_{mn,ki}) \\
& + \frac{1}{2} \sum_{ki} (V_{imkn} D_{ki,rs} + V_{irkn} D_{mi,ks}) + \frac{1}{2} \sum_{ij} (V_{ijis} D_{mn,rj} + V_{ijin} D_{mj,rs}) + \frac{1}{2} \sum_{ij} (V_{ijns} D_{mj,ri} + V_{ijsn} D_{mi,rj}).
\end{aligned} \tag{18}$$

In a many-particle system, we would have additional terms in $O^{\dagger}$, but Eqs. (17) and (18) would remain the same; however, there would be C and D terms in the higher-order equations.

In all past applications of the equation-of-motion method for two-electron or more complicated systems, the expressions for $O^{\dagger}$ corresponding to Eq. (16) and the equations corresponding to Eqs. (17) and (18) [but obtained from Eqs. (2) and (4)] have been drastically simplified. Most calculations have used only the first term of Eq. (16) and restricted it to particle-hole contributions. Recently, a few calculations have been done including both terms of Eq. (16), but again limiting the operators to those of the particle-hole type ($1p$-h, $2p$-h). Particle-particle or hole-hole type contributions have never been considered, nor have the higher operator products (e.g., $3p$-h) that contribute for systems composed of more than two electrons.

Other than for model systems of the two-electron type (e.g., PPP ethylene, which is treated in a later paper), the most detailed analysis for the two-electron case has been given by Ostlund and Karplus.[20] They considered $1\,p$-h contributions to $O^{\dagger}$ and showed that these are sufficient to obtain the exact ground-state wave function in the approximation that the correlation correction arises only from double excitations. Also, they found that in this approximation all the excitation energies are equal to those from the Tamm-Dankoff approximation shifted by a constant term equal to the ground-state correlation energy. They further suggested that to obtain improved excitation energies, an extended form of RPA including additional terms in the excitation operator would have to be introduced. All possible terms appear in the complete excitation operator given in Eq. (16). In what follows, we estimate the magnitude of the most important of these, other than the $2p$-$2h$ operator which has already been included in some recent studies.[19]

Even though Eqs. (17) and (18) form an eigenvalue equation, we treat it in a perturbation sense and use our knowledge of the approximate ω to estimate the coefficients. To make explicit the notation for the two-electron case, we label the two hole states as α and β. We assume, as is known for other calculations, that the $1p$-$1h$ coefficients $C_{i\gamma}$ ($\gamma=\alpha,\beta$) are large and that the $C_{\gamma i}$ ($\gamma=\alpha,\beta$) are small. The size of the "density shift" $1p$-$1p$ terms, C_{ij}, which are assumed to be small relative to the $C_{i\gamma}$, can then be estimated from Eq. (17) as

$$C_{ij}\cong\frac{1}{\omega-(\epsilon_i-\epsilon_j)}[(V_{\beta\alpha\beta j}-V_{\beta\alpha j\beta})C_{i\alpha}+(V_{\alpha\beta\alpha j}-V_{\alpha\beta j\alpha})C_{i\beta}]. \tag{19}$$

Since $\epsilon_i-\epsilon_j$ is usually smaller than $\epsilon_i-\epsilon_\gamma$, the denominator in Eq. (19) is larger than that for the $1p$-$1h$ $C_{i\gamma}$ coefficients. Furthermore, Eq. (19) is seen to depend on the size of the $3h$-$1p$ matrix elements of the type $V_{\beta\alpha\beta j}$. For ethylene in the PPP model, these matrix elements are zero. In the general case, they are expected to be fairly small. We show in what follows, that these coefficients are linked to the size of the single-excitation coefficients in the exact ground state $|0\rangle$; their contribution is thus zero if $|0\rangle$ is approximated by the Hartree-Fock ground state. A corresponding analysis is applicable to the $1h$-$1h$ coefficients, $C_{\alpha\beta}$.

Another operator of interest corresponds to the terms $D_{ij,\alpha s}$. It involves a product of a density-shift operator $a_i^{\dagger}a_j$ with a $1p$-$1h$ operator $a_\alpha^{\dagger}a_s$, where i, j, and s are particles and α is a hole. The value of the $D_{ij,\alpha s}$ can be estimated from Eq. (18); it is

$$D_{ij,\alpha s}\cong\frac{1}{\omega+(\epsilon_j+\epsilon_s-\epsilon_\alpha-\epsilon_i)}\times[(V_{\alpha\alpha js}-V_{\alpha\alpha sj})C_{i\alpha}+(V_{\beta\alpha js}-V_{\beta\alpha sj})C_{i\beta}]. \tag{20}$$

It is seen that the $D_{ij,\alpha s}$ is proportional to the $2p$-$2h$ matrix elements of the type $V_{\beta\alpha js}$. This means that they are related to the ground-state correlation correction and, particularly, to the double-excitation coefficients in $|0\rangle$. Consequently, this type of term is expected to be more important than the $1p$-$1p$ density-shift terms in Eq. (19). In a higher-order theory, operators of the type $D_{ij,\alpha s}$ should be included, therefore, while the operators of the type C_{ij} can probably be neglected.

We can obtain further insight into the nature of the corrections to the standard theory by analyzing the form of the exact operator $O^{\dagger}$ in the two-electron case. The exact wave functions for the ground and excited state can be written

$$\begin{aligned}|0\rangle&=N_0\Big(1+\sum_{m\gamma}C^{(0)}_{m\gamma}D^{\dagger}_{m\gamma}+\sum_{\substack{mn\\ \gamma\delta}}C^{(0)}_{m\gamma,n\delta}D^{\dagger}_{m\gamma}D^{\dagger}_{n\delta}\Big)|\mathrm{HF}\rangle,\\ |E\rangle&=\Big(C^{(e)}_{\mathrm{HF}}+\sum_{m\gamma}C^{(e)}_{m\gamma}D^{\dagger}_{m\gamma}+\sum_{\substack{mn\\ \gamma\delta}}C^{(e)}_{m\gamma,n\delta}D^{\dagger}_{m\gamma}D^{\dagger}_{n\delta}\Big)|\mathrm{HF}\rangle,\end{aligned} \tag{21}$$

where $D^{\dagger}_{m\gamma}=a^{\dagger}_m a_\gamma$ and γ,δ take on the hole state values α and β, N_0 is the ground-state normalization coefficient, and the $C^{(0)}, C^{(e)}$ are the coefficients of the various contributions to the ground and excited state, respectively. Writing the exact excitation operators as $O^{\dagger}=|E\rangle\langle 0|$, we have

$$O^\dagger = N_0\Big(C^{(e)}_{\mathrm{HF}} + \sum_{m\gamma} C^{(e)}_{m\gamma} D^\dagger_{m\gamma} + \sum_{\substack{mn\\ \gamma\delta}} C^{(e)}_{m\gamma,n\delta} D^\dagger_{m\gamma} D^\dagger_{n\delta}\Big)\,|\mathrm{HF}\rangle\langle\mathrm{HF}|$$

$$\times\Big(1 + \sum_{m\gamma} C^{(0)*}_{m\gamma} D_{m\gamma} + \sum_{\substack{mn\\ \gamma\delta}} C^{(0)*}_{m\gamma,n\delta} D_{m\gamma} D_{n\delta}\Big). \qquad (22)$$

To proceed further we need to write $|\mathrm{HF}\rangle\langle\mathrm{HF}|$ in second-quantized form. The general expression can be obtained from

$$|\mathrm{HF}\rangle = \prod_\gamma c^\dagger_\gamma |\ \rangle, \qquad (23)$$

where the product is over all holes γ and $|\ \rangle$ is the vacuum state. For the present purpose we can restrict the Hilbert space to include only two-electron functions. This makes it possible to omit the vacuum projector and write

$$|\mathrm{HF}\rangle\langle\mathrm{HF}| = \prod_\gamma c^\dagger_\gamma \prod_\delta c_\delta = c^\dagger_\alpha c^\dagger_\beta c_\beta c_\alpha . \qquad (24)$$

If we insert this operator into Eq. (22) and commute all the hole operators to the right, we obtain after some algebra

$$O^\dagger = N_0\Big(C^{(e)}_{\mathrm{HF}} + \sum_{m\gamma} C^{(e)}_{m\gamma} D^\dagger_{m\gamma} + \sum_{\substack{mn\\ \gamma\delta}} C^{(e)}_{m\gamma,n\delta} D^\dagger_{m\gamma} D^\dagger_{n\delta}\Big)$$

$$\times\Big(\hat N_\alpha \hat N_\beta - \sum_m C^{(0)*}_{m\beta} D_{m\alpha} D^\dagger_{\beta\alpha} - \sum_m C^{(0)*}_{m\alpha} D_{m\beta} D^\dagger_{\alpha\beta} + \sum_m C^{(0)*}_{m\alpha} D_{m\alpha} \hat N_\beta + \sum_m C^{(0)*}_{m\beta} D_{m\beta} \hat N_\alpha + 2\sum_{mn} C^{(0)*}_{m\beta,n\alpha} D_{m\beta} D_{n\alpha}\Big), \qquad (25)$$

where α and β are again used as the specific hole indices of the two-electron case and $\hat N_\alpha = D^\dagger_{\alpha\alpha}$, $\hat N_\beta = D^\dagger_{\beta\beta}$, are the number operators. In deriving Eq. (25), we define any operator that yields zero when acting on any two-electron function of the restricted Hilbert space as equal to the zero operator. In general, if an operator yields zero when acting on all the elements of the restricted Hilbert space, we set it equal to the zero operator. If the difference of two operators yields zero, the two operators are equivalent. This relationship between operators imposed by the restriction of the Hilbert space is of some importance. We call this result "restriction equivalence" and will have occasion to use it in a subsequent paper.

For example, to derive Eq. (25) operators of the type $D_{m\alpha} D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta}$ which were obtained when $|\mathrm{HF}\rangle\langle\mathrm{HF}|$ in Eq. (22) was commuted through to the front of the expression, were set equal to zero, since they yield zero when operating on *any* two-electron wave function (i.e., $D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta}$ yield nonzero functions only when acting on $|\mathrm{HF}\rangle$, but then $D_{m\alpha}|\mathrm{HF}\rangle = 0$). The other operator types set equal to zero are $D_{m\alpha} D_{n\beta} D^\dagger_{\alpha\beta}$, $D_{m\alpha} D_{n\alpha} D^\dagger_{\beta\alpha}$, $D_{m\alpha} D_{n\beta} D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta}$, $D_{m\alpha} D_{n\beta} D^\dagger_{\alpha\alpha}$, and $D_{m\alpha} D_{n\alpha} D^\dagger_{\beta\beta}$.

To simplify Eq. (25), we let $C^{(0)}_{m\gamma} = 0$; that is, we omit the single excitations in $|0\rangle$. Under this assumption, $O^\dagger$ becomes

$$O^\dagger = N_0\Big(C^{(e)}_{\mathrm{HF}} D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta} + \sum_{m\gamma} C^{(e)}_{m\gamma} D^\dagger_{m\gamma} + \sum_{\substack{mn\\ \gamma\delta}} C^{(e)}_{m\gamma,n\delta} D^\dagger_{m\gamma} D^\dagger_{n\delta} + 2C^{(e)}_{\mathrm{HF}} \sum_{mn} C^{(0)}_{m\beta,n\alpha} D_{n\alpha} D_{m\beta} + 2\sum_{mn} C^{(e)}_{m\alpha} C^{(0)}_{m\beta,n\alpha} D_{n\beta}$$

$$+ 2\sum_{mn} C^{(e)}_{n\alpha} C^{(0)}_{m\beta,n\alpha} D_{m\beta} + 2\sum_{mn} C^{(e)}_{m\beta} C^{(0)}_{m\alpha,n\beta} D_{n\alpha} + 2\sum_{mn} C^{(e)}_{n\alpha} C^{(0)}_{m\alpha,n\beta} D_{m\alpha} + 2\sum_{m'\neq m,n} C^{(e)}_{m'\alpha} C^{(0)}_{m\beta,n\alpha} D^\dagger_{m'm} D_{n\beta}$$

$$+ 2\sum_{m'\neq m,n} C^{(e)}_{m'\beta} C^{(0)}_{m\beta,n\alpha} D^\dagger_{m'm} D_{n\alpha} + 2\sum_{\substack{m'n'\\ mn}} C^{(e)}_{m'\alpha,n'\beta} C^{(0)}_{m\beta,n\alpha} D^\dagger_{m'm} D^\dagger_{n'n}\Big), \qquad (26)$$

where γ, δ equal α, β in the summations.

To obtain Eq. (26) the operators $D^\dagger_{m\alpha} D^\dagger_{n\beta} D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta}$ and $D^\dagger_{m\alpha} D^\dagger_{n\beta}$ were set equal, since they act identically in the restricted space of two-electron functions (i.e., they both give nonzero only when acting on $|\mathrm{HF}\rangle$ and then they both yield $|{}^{mn}_{\alpha\beta}\rangle$. Another use of restriction equivalence was made in simplifying $D^\dagger_{m\alpha} D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta}$ to $D^\dagger_{m\alpha}$. Although these two operators are not identical when the full two-electron space is considered (e.g., $D^\dagger_{m\alpha} D^\dagger_{\alpha\alpha} D^\dagger_{\beta\beta} |{}^{n}_{\beta}\rangle = 0$ but $D^\dagger_{m\alpha} |{}^{n}_{\beta}\rangle = |{}^{mn}_{\alpha\beta}\rangle \neq 0$), they are equivalent if we further omit singly excited configurations from the space, as we have done in $|0\rangle$. Finally, operators like $D^\dagger_{m'\alpha} D^\dagger_{n'\beta} D_{n\alpha} D_{m\beta}$ or $D^\dagger_{m'\alpha} D_{n\alpha} D_{m\beta}$ can be simplified to $D^\dagger_{m'm} D^\dagger_{n'n}$ and $D^\dagger_{m'm} D_{n\beta}$, respectively, by use of restriction equivalence.

The absence of the density-shift operator $D^\dagger_{mn}$ by itself in Eq. (26) shows its dependence on $C^{(0)}_{m\gamma}$. If single excitations had been included, a set of terms of the form

$$-N_0 C^{(e)}_{n\beta} C^{(0)*}_{m\beta} (\hat N_\beta - 1) \hat N_\alpha D^\dagger_{nm}$$

or

$$-N_0 C^{(e)}_{n\alpha} C^{(0)*}_{m\beta} D^\dagger_{nm} D^\dagger_{\beta\alpha}$$

would result. The first of these two terms is basically a $D^\dagger_{nm}$ density-shift term, with the added constraint that there be an electron in state α and none in state β. Of course, this constraint would yield zero if only double excitations were included in $|0\rangle$. Terms like $D^{\dagger}_{m'm}D_{n\beta}$, that do contribute when $C^{(0)}_{m\gamma}$ is zero, are proportional to $C^{(e)}_{m'\alpha}C^{(0)}_{m\beta,n\alpha}$ and are thus non-negligible, since both $C^{(e)}_{m'\alpha}$ and $C^{(0)}_{m\beta,n\alpha}$ are expected to be significant. In fact, the magnitude of these density-shift terms is proportional to the product of the doubly excited coefficients, $C^{(0)}_{m\alpha,n\beta}$, of the exact ground state [e.g., the $V_{\beta\alpha js}/\Delta\epsilon$ in Eq. (20)] and the single-excitation coefficients, $C^{(e)}_{m'\alpha}$ of the excited state [e.g., the $C_{i\alpha}$ in Eq. (20)], verifying the conclusion obtained earlier. Moreover, Eq. (26) suggests that if the particular excited state has a strong double-excitation character (e.g., the ${}^1A_g^-$ state in linear polyenes; see paper II), density-shift terms of the type $D^{\dagger}_{m'm}D^{\dagger}_{n'n}$ should also be included. If we compare the coefficient of $D^{\dagger}_{m'm}D_{n\beta}$ with that of $D_{n\beta}$ in Eq. (26), we see that the usual inclusion of terms like $D_{n\beta}$ in $O^{\dagger}$ require a fuller treatment of the $D^{\dagger}_{m'm}D_{n\beta}$ terms. Correspondingly, inclusion of $D_{m\alpha}D_{n\beta}$ type terms in $O^{\dagger}$ requires consideration of terms like $D^{\dagger}_{m'm}D_{n'n}$. Otherwise, good numerical results may reflect either the minor role of the $D_{n\alpha}$ or $D_{m\alpha}D_{n\beta}$ terms or, in cases with a large correlation corrections, a fortuitous cancellation of the effect of the density-shift terms.

III. GENERAL RPA EQUATIONS

Having demonstrated that Rowe's formulation of the equation of motion [Eq. (2)] yields the correct result if a sufficiently general excitation operator is used, we consider certain approximations that have been introduced in applying Eq. (2) to molecular systems. The formulation and development given here follows the work of Rowe,[21] of Shibuya and McKoy,[18] and of Shibuya, Rose, and McKoy.[19]

The simplest physical basis for the excitation operator consists of the particle-hole operators $(c^{\dagger}_i c_{\alpha}, c^{\dagger}_{\alpha} c_i)$, where we use the standard labeling of particle creation and annihilation operators, $c^{\dagger}_i$ and c_i, by Roman subscripts and of hole creation and annihilation operators, c_{α} and $c^{\dagger}_{\alpha}$, by Greek subscripts. Particles and holes are defined as the unoccupied and occupied Hartree-Fock orbitals, respectively. Since $c^{\dagger}_i c_{\alpha}|\mathrm{HF}\rangle$ is not an eigenstate of S^2, it is often convenient to use a spin-adapted basis. We denote the spin-adapted particle-hole operators with total spin S and S_z quantum number M by $\{C^{\dagger}_{i\alpha}(SM), C_{i\alpha}(SM)\}$[18,22] where, for example,

$$C^{\dagger}_{i\alpha}(00) \equiv (1/\sqrt{2})(c^{\dagger}_{i\uparrow}c_{\alpha\uparrow} + c^{\dagger}_{i\downarrow}c_{\alpha\downarrow})$$

($\uparrow$ or $\downarrow$ refer to the two spin states and the letters stand for the spatial orbitals only; the notation is that of Shibuya and McKoy.[18])

If we expand the excitation operator, $O^{\dagger}_{\lambda}(SM)$, in this basis set, we have

$$O^{\dagger}_{\lambda}(SM) = \sum_{m\gamma} [Y_{m\gamma}(\lambda S)C^{\dagger}_{m\gamma}(SM) - Z_{m\gamma}(\lambda S)C_{m\gamma}(\bar{S}\bar{M})], \tag{27}$$

where λ labels the excited state, and

$$C_{m\gamma}(\bar{S}\bar{M}) \equiv (-1)^{S+M}C_{m\gamma}(S, -M).$$

Inserting Eq. (27) into Eq. (2) and letting $R = C^{\dagger}_{m\gamma}(SM)$ and $C_{m\gamma}(SM)$, we obtain the general RPA equation for $\underline{Y}$, $\underline{Z}$ and ω; that is,

$$\begin{pmatrix} \underline{A}(S) & \underline{B}(S) \\ -\underline{B}(S)^* & -\underline{A}(S)^* \end{pmatrix} \begin{pmatrix} \underline{Y}(\lambda S) \\ \underline{Z}(\lambda S) \end{pmatrix} = \omega(\lambda S) \begin{pmatrix} \underline{D} & 0 \\ 0 & \underline{D} \end{pmatrix} \begin{pmatrix} \underline{Y}(\lambda S) \\ \underline{Z}(\lambda S) \end{pmatrix}, \tag{28}$$

where

$$\begin{aligned} A_{m\gamma,n\delta}(S) &= \langle 0|[C_{m\gamma}(SM), H, C^{\dagger}_{n\delta}(SM)]|0\rangle, \\ B_{m\gamma,n\delta}(S) &= -\langle 0|[C_{m\gamma}(SM), H, C_{n\delta}(\bar{S}\bar{M})]|0\rangle, \\ D_{m\gamma,n\delta} &= \langle 0|[C_{m\gamma}(SM), C^{\dagger}_{n\delta}(SM)]|0\rangle. \end{aligned} \tag{29}$$

Since Eqs. (28) and (29) are based on matrix elements of the exact, but unknown, ground state $|0\rangle$, it is necessary to approximate $|0\rangle$. This raises the problem of doing so consistently in the RPA theoretical framework. In most applications to closed-shell systems, the ground state $|0\rangle$ has been assumed to be the Hartree-Fock ground state or an approximation of the pair-correlation type has been used. In the latter,

$$|0\rangle \cong N_0 e^{U}|\mathrm{HF}\rangle, \tag{30}$$

$$U \equiv \sum_{\substack{mn \\ \gamma\delta}} K_{m\gamma,n\delta}c^{\dagger}_{m\uparrow}c^{\dagger}_{n\downarrow}c_{\delta\downarrow}c_{\gamma\uparrow} + \tfrac{1}{2}L_{m\gamma,n\delta}(c^{\dagger}_{m\uparrow}c^{\dagger}_{n\uparrow}c_{\delta\uparrow}c_{\gamma\uparrow} + c^{\dagger}_{m\downarrow}c^{\dagger}_{n\downarrow}c_{\delta\downarrow}c_{\gamma\downarrow}), \tag{31}$$

where the coefficients $\underline{K}$ and $\underline{L}$ are defined by Shibuya and McKoy[18] and N_0 is a normalization constant. Usually the exponential is expanded and only the first-order term in U is included. It is assumed that the higher-order terms, as well as single and triple excitations, are negligible for the ground state of closed-shell systems.

A. NRPA equations

If we set $U = 0$ in Eq. (30), $|0\rangle = |\mathrm{HF}\rangle$. When this approximation to $|0\rangle$ is inserted into Eq. (28) and (29), we obtain the normal RPA equation (NRPA) which has the same form as Eq. (29) except that the $\underline{D}$ matrix reduces to the unit matrix.

Previous investigators have analyzed some of the properties of the NRPA.[23,24] Thouless[25] has shown that the $|\mathrm{HF}\rangle$ state is stable to variations in the wave function if and only if the Hermitian matrix

$$\begin{pmatrix} \underline{A} & \underline{B} \\ \underline{B}^* & \underline{A}^* \end{pmatrix} \tag{32}$$

is positive definite, where A and B are the NRPA matrices. It can also be shown[23] that the stability of the $|\mathrm{HF}\rangle$ state is sufficient to guarantee that the eigenvalues of the NRPA are real. Since this is not a necessary condition, it is possible to have only real NRPA eigenvalues even when the stability condition is not satisfied.

One of the symmetry properties of the RPA equations is that if $(\underline{Y},\underline{Z})$ is an eigenvector with frequency ω, $(\underline{Z},\underline{Y})$ is the eigenvector with frequency $-\omega$. Thus, the frequency eigenvalues come in ± pairs, except for a possible zero eigenvalue.[23] The eigenvector orthogonality condition[23] is such that if $(\underline{Y}_\lambda,\underline{Z}_\lambda)$ and $(\underline{Y}_{\lambda'},\underline{Z}_{\lambda'})$ are two eigenvectors,

$$\underline{Y}_\lambda^\dagger \underline{Y}_{\lambda'} - \underline{Z}_\lambda^\dagger \underline{Z}_{\lambda'} = \delta_{\lambda\lambda'}; \tag{33}$$

in particular, this implies

$$\underline{Y}_\lambda^\dagger \underline{Z}_{\lambda'} - \underline{Z}_\lambda^\dagger \underline{Y}_{\lambda'} = 0. \tag{34}$$

The NRPA excitation frequencies are always lower than the single configuration-interaction (CI) excitation frequencies. For the lowest NRPA eigenvalue, E_1^{RPA}, this can be shown from a theorem by Thouless.[23] He derived the relation (valid if there are no zero eigenvalues),

$$(\underline{Y}^\dagger,\underline{Z}^\dagger)\begin{pmatrix} \underline{A} & \underline{B} \\ \underline{B}^* & \underline{A}^* \end{pmatrix}\begin{pmatrix} \underline{Y} \\ \underline{Z} \end{pmatrix}\left[\left|(\underline{Y}^\dagger,\underline{Z}^\dagger)\begin{pmatrix} \underline{Y} \\ -\underline{Z} \end{pmatrix}\right|\right]^{-1} \geq |E_1^{\mathrm{RPA}}| \tag{35}$$

which holds for any vector $(\underline{Y},\underline{Z})$; the proof of Eq. (35) is based on the completeness of the set of eigenvectors of the NRPA, expanding $(\underline{Y},\underline{Z})$ in terms of this complete set and using Eq. (32) and the orthogonality condition [Eq. (34)]. Since the matrix $\underline{A}$ in the NRPA is the single CI matrix, we can let $(\underline{Y},\underline{Z}) = (\underline{X}_1, 0)$ where $\underline{X}_1$ is the lowest eigenvector of the single CI matrix with eigenvalue E_1^{CI}. Thus, the left-hand side is exactly E_1^{CI}, and we have

$$E_1^{\mathrm{CI}} \geq |E_1^{\mathrm{RPA}}|. \tag{36}$$

It can be shown that a corresponding relation is true for all the frequencies of the single CI and NRPA equations. For the second eigenvalue, for example, we expand the first two eigenvectors of the single CI matrix, $\underline{X}_1$ and $\underline{X}_2$, in terms of the complete basis of NRPA eigenvectors:

$$\begin{pmatrix} \underline{X}_i \\ 0 \end{pmatrix} = \sum_{n=1}^{N}\left[\alpha_{ni}\begin{pmatrix} \underline{Y}_n \\ \underline{Z}_n \end{pmatrix} + \beta_{ni}\begin{pmatrix} \underline{Z}_n \\ \underline{Y}_n \end{pmatrix}\right], \tag{37}$$

where $i = 1$ or 2 and N is the number of NRPA eigenvectors with positive eigenvalues; the N eigenvectors with eigenvalues $-\omega$ are included in the second set of terms. Multiplying Eq. (37) by $(\underline{Y}_n^\dagger, -\underline{Z}_n^\dagger)$ and $(\underline{Z}_n^\dagger, \underline{Y}_n^\dagger)$ and using Eqs. (33) and (34), we obtain

$$\alpha_{ni} = \underline{Y}_n^\dagger \underline{X}_i, \quad \beta_{ni} = -\underline{Z}_n^\dagger \underline{X}_i, \quad i = 1, 2. \tag{38}$$

We define the vector $\underline{X} = (a\underline{X}_1 + b\underline{X}_2, 0)$, such that $a^2 + b^2 = 1$ and $a\alpha_{11} + b\alpha_{12} = 0$; i.e., $\underline{X}$ is normalized and orthogonal to the first (lowest) NRPA eigenvector with positive eigenvalue. We have

$$\underline{X}^\dagger \begin{pmatrix} \underline{A} & \underline{B} \\ \underline{B}^* & \underline{A}^* \end{pmatrix} \underline{X} = \bar{E} = (a\underline{X}_1 + b\underline{X}_2)^\dagger \underline{A}(a\underline{X}_1 + b\underline{X}_2) \leq E_2^{\mathrm{CI}}, \tag{39}$$

since $\underline{A}$ is the single CI matrix and $\underline{X}_1, \underline{X}_2$ are its eigenvectors. Expanding the left-hand side of Eq. (39), using Eqs. (32)–(34) and (37), we obtain

$$\begin{aligned} \bar{E} &= \sum_{n=1}^{N} (|a\alpha_{n1} + b\alpha_{n2}|^2 + |a\beta_{n1} + b\beta_{n2}|^2)|E_n^{\mathrm{RPA}}| \\ &\geq \sum_{n=2}^{N} |a\alpha_{n1} + b\alpha_{n2}|^2 |E_m^{\mathrm{RPA}}| \\ &\geq |E_2^{\mathrm{RPA}}| \sum_{n=2}^{N} |a\alpha_{n1} + b\alpha_{n2}|^2. \end{aligned} \tag{40}$$

Since $\underline{X}$ is normalized, we have

$$\underline{X}^\dagger \underline{X} = 1 = \sum_n (|a\alpha_{n1} + b\alpha_{n2}|^2 - |a\beta_{n1} + b\beta_{n2}|^2).$$

Thus,

$$\sum_{n=2}^{N} |a\alpha_{n1} + b\alpha_{n2}|^2 \geq 1, \tag{41}$$

where the $n = 1$ term drops out due to the orthogonality relation on $\underline{X}$. Equations (39), (40), and (41) together yield

$$E_2^{\mathrm{CI}} \geq \bar{E} \geq |E_2^{\mathrm{RPA}}|. \tag{42}$$

A corresponding development for the higher eigenvalues shows that

$$E_n^{\mathrm{CI}} \geq |E_n^{\mathrm{RPA}}|. \tag{43}$$

A useful relationship between the CI and RPA eigenvalues can be obtained by expanding the NRPA eigenvectors in a perturbation series. We take as the zeroth-order states, $(\underline{X}_n, 0)$ and $(0, \underline{X}_n)$, which are the exact eigenvectors of the matrix

$$\begin{pmatrix} \underline{A} & 0 \\ 0 & -\underline{A} \end{pmatrix} \tag{44}$$

with zeroth-order energies equal to $\pm E_n^{\mathrm{CI}}$. From first-order perturbation theory, the eigenvectors of the NRPA matrix, $(\underline{Y}_n, \underline{Z}_n)$, are given by

$$\underline{Y}_n^{(1)} = \underline{X}_n,$$

$$Z_n^{(1)} = -\sum_m \frac{(\underline{X}_m^\dagger | \underline{B} | \underline{X}_n)}{E_n^{\mathrm{CI}} + E_m^{\mathrm{CI}}} X_m \tag{45}$$

and the energy to second-order is

$$E_n^{\mathrm{RPA}(2)} = E_n^{\mathrm{CI}} - \sum_m \frac{(\underline{X}_m^\dagger | \underline{B} | \underline{X}_n)^2}{E_n^{\mathrm{CI}} + E_m^{\mathrm{CI}}} \tag{46}$$

since there is no first-order contribution. Equation (46) shows that $E_n^{\mathrm{CI}} \geq E_n^{\mathrm{RPA}}$ to second order, in agreement with the more general result [Eq. (43)]. An immediate consequence is that

$$\sum_n (E_n^{\mathrm{CI}} - E_n^{\mathrm{RPA}}) = \sum_{m,n} \frac{(\underline{X}_m^\dagger | \underline{B} | \underline{X}_n)^2}{E_n^{\mathrm{CI}} + E_m^{\mathrm{CI}}} . \tag{47}$$

In Sec. III B, we shall see that the right-hand side of Eq. (47) is an approximation to the correlation correction arising from including double excitations in the ground state.

B. SC-RPA equations

As demonstrated in Sec. II, it is possible to obtain the exact ground state $|0\rangle$ and the exact excitation energies ω, if Eqs. (2) and (4) are solved self-consistently. If one approximates the ground state by the expression $|0\rangle = N_0(|\mathrm{HF}\rangle + U|\mathrm{HF}\rangle)$, the problem is reduced to solving iteratively for U, as given by Eq. (31). This is the basis for the SC-RPA method or higher RPA.[18] The matrix elements of Eq. (28), which are given below [see Eq. (64)], depend on the $\underline{K}$ and $\underline{L}$ coefficients in Eq. (31) or equivalently on the coefficients $C_{m\gamma,n\delta}(S)$ which are defined by

$$C_{m\gamma,n\delta}(S) \equiv K_{m\gamma,n\delta} + (-1)^{(S)}(L_{m\gamma,n\delta} - L_{m\delta,n\gamma}). \tag{48}$$

In the formulation of Ref. 18 and in this subsection, only terms linear in the coefficients C are included in evaluating the matrix elements; the initials LSC-RPA will be used for this approximation. Substituting with Eqs. (27), (30), and (48) into Eq. (4), we obtain the self-consistency condition

$$\sum_{n\gamma} Y_{n\delta}^*(\lambda S) C_{n\delta,m\gamma}(S) = Z_{m\gamma}(\lambda S) \tag{49}$$

or, in matrix form for each λ,

$$\underline{CY}_\lambda = \underline{Z}_\lambda. \tag{50}$$

For a given $(\underline{Y}_\lambda, \underline{Z}_\lambda)$ vector determined by solving Eq. (28), Eq. (50) can be used to find new coefficients $\underline{C}$. These new $\underline{C}$'s yield new matrices in Eq. (28), which in turn serve to determine new $(\underline{Y}_\lambda, \underline{Z}_\lambda)$ eigenvectors until self-consistency is achieved.

As pointed out by Shibuya and McKoy,[18] the coefficients $\underline{C}$ have a necessary symmetry, due to the symmetry of the $\underline{K}$ and $\underline{L}$ in Eq. (48), namely

$$C_{m\gamma,n\delta}(S) = C_{n\delta,m\gamma}(S). \tag{51}$$

(We will now consider real $\underline{C}$'s for simplicity.) Equation (50) does not show this symmetry explicitly. Since $\underline{C}$ is obtained by iteration with Eqs. (2) and (49), it is necessary to demonstrate that the required symmetry follows from these equations. The main results we need are the orthogonality relations given in Eqs. (48). Writing Eqs. (33) and (34) in terms of the matrices $\underline{Y}$ and $\underline{Z}$ consisting of the vectors $\underline{Y}_\lambda, \underline{Z}_\lambda$ arranged in columns and subtracting the two resulting equations, we obtain

$$(\underline{Y} - \underline{Z})^{-1} = (\underline{Y} + \underline{Z})^\dagger. \tag{52}$$

Since in most molecular problems the $\underline{Z}$ coefficients represent a small correction due to the ground state correlation, $||\underline{Z}||/||\underline{Y} - \underline{Z}|| \ll 1$ and we can use Eqs. (50) and (52) to rewrite $\underline{C}$ as

$$\underline{C} = \sum_{n=1}^{\infty} (-1)^{n+1} [\underline{Z}(\underline{Y} + \underline{Z})^\dagger]^n. \tag{53}$$

The symmetry of $\underline{C}$ can, therefore, be determined from the symmetry of $\underline{Z}(\underline{Y} + \underline{Z})^\dagger$. Since $\underline{ZZ}^\dagger$ is always symmetric, we must show only that $\underline{ZY}^\dagger$ is symmetric. We know that $\underline{Y}^\dagger \underline{Z}$ is symmetric from Eq. (34). The difference between Eq. (52) and its transpose yields

$$2(\underline{YZ}^\dagger - \underline{ZY}^\dagger) = 0; \tag{54}$$

i.e., $\underline{ZY}^\dagger$ is symmetric.

A similar development can be used to show the symmetry of $\underline{C}$ for the case when

$$||\underline{Z}|| > ||\underline{Y} - \underline{Z}||.$$

It is clear from the above that the proof of the symmetry of $\underline{C}$ depends on the orthogonality of the RPA eigenvectors. This will be relevant in the consideration of improvements to the SC-RPA (see Sec. III C).

Since the leading term in Eq. (53) for $\underline{C}$ is $\underline{ZY}^\dagger$, $\underline{Y}$ is by comparison with Eq. (49) an approximately orthogonal matrix. If we insert the approximate values of $\underline{Y}$ and Z obtained from the NRPA by perturbation theory [Eq. (45)], we obtain

$$C_{ij} = (\underline{ZY}^\dagger)_{ij} = -\sum_{k,m} \frac{(\underline{X}_m^\dagger | \underline{B} | \underline{X}_k)}{E_k^{\mathrm{CI}} + E_m^{\mathrm{CI}}} X_{im} X_{jk}, \tag{55}$$

where X_{im} refers to the ith element in the mth eigenvector of the single CI calculation. Equation (55) is the first term of an expansion for C_{ij} found by Sanderson[26] in his development of the quasiboson approximation. In Eq. (55) the X_{im} refers to either the singlet or triplet single CI eigenvector and $\underline{B}$ the appropriate NRPA matrix $\underline{B}(S)$.[18] Thus, C_{ij} may be obtained from either spin calculation; however, in what follows we will use the *singlet* results in order to compare with E_{corr}.

Equation (55) can also be obtained by a first-order perturbation calculation for the ground-state correlation coefficients C_{ij} defined by

$$|0\rangle = N_0\Big(|\mathrm{HF}\rangle + \frac{1}{2}\sum_{ij} C_{ij} D_i^\dagger D_j^\dagger |\mathrm{HF}\rangle\Big) \tag{56}$$

where we treat the single CI (singlet) eigenvectors as the zeroth-order states.[26] (Note, here, $D_i^\dagger$ and $D_j^\dagger$ stand for the creation operators of the ith and jth *particle-hole* pairs.) If we now calculate the correlation energy E_{corr} to second order from Eq. (56), we obtain

$$\begin{aligned} E_{\mathrm{corr}} &\equiv \langle 0|H|0\rangle - \langle \mathrm{HF}|H|\mathrm{HF}\rangle, \qquad (57)\\ &\cong \sum_{ij} C_{ij} B_{ij}. \end{aligned}$$

B_{ij} stands for the matrix elements of the *singlet B* matrix in the NRPA, where i and j are the ith and jth singly excited configurations. Introduction of Eq. (55) for the C_{ij} coefficients (singlet case) into Eq. (57) yields

$$E_{\mathrm{corr}} \cong -\sum_{mn} \frac{(\underline{X}_m^\dagger|\underline{B}(0)|\underline{X}_n)^2}{E_n^{\mathrm{CI}} + E_m^{\mathrm{CI}}}. \tag{58}$$

Comparing with Eqs. (46) and (47), we see that

$$\begin{aligned} -E_{\mathrm{corr}} &\cong \sum_n [E_n^{\mathrm{CI}}(0) - E_n^{\mathrm{NRPA}}(0)]\\ &= \sum_n [\omega_{\mathrm{CI}}^n(0) - \omega_{\mathrm{NRPA}}^n(0)] = -E_{\mathrm{corr}}^{\mathrm{NRPA}}, \qquad (59) \end{aligned}$$

where the sum is over the singlet eigenvalues, justifying the statement made earlier. Equation (59) has been derived in a somewhat different way from time-dependent Hartree-Fock theory.[24] In time-dependent Hartree-Fock theory one obtains

$$-E_{\mathrm{corr}} \approx \frac{1}{4}\sum_n (\omega_{\mathrm{CI}}^n - \omega_{\mathrm{NRPA}}^n) \tag{60}$$

when one sums over both singlet and triply degenerate triplet eigenvalues; this is the origin of the factor of $\frac{1}{4}$. It is evident that in general, Eqs. (59) and (60) yield different results.

Recently, Huo[27] indicated that the NRPA frequency was lower than the single CI frequency by some fraction of the correlation energy of the ground state. The present analysis allows a simple derivation of this result. From Eq. (53),

$$C_{ij} = \sum_m Z_{im} Y_{jm},$$

where Z_{im} and Y_{jm} are the ith and jth vector components of the NRPA eigenvector $(\underline{Y}_m, \underline{Z}_m)$. If we now truncate each summation so that $C_{ij}^{\mathrm{app}}(n) \approx Z_{in} Y_{jn}$ for a fixed n and use Eq. (45), we have that

$$C_{ij}^{\mathrm{app}}(n) = -\sum_m \frac{(\underline{X}_m^\dagger|\underline{B}|\underline{X}_n)}{E_n^{\mathrm{CI}} + E_m^{\mathrm{CI}}} X_{im} X_{jn}. \tag{61}$$

When Eq. (61) is inserted into the expression for the correlation energy, Eq. (58)

$$E_{\mathrm{corr}}^{\mathrm{app}}(n) = \sum_{ij} C_{ij}^{\mathrm{app}} B_{ij} = -\sum_m \frac{(\underline{X}_m^\dagger|\underline{B}|\underline{X}_n)^2}{E_n^{\mathrm{CI}} + E_m^{\mathrm{CI}}}. \tag{62}$$

Comparing Eqs. (62) and (46), we see that indeed $E_n^{\mathrm{CI}}(0) - E_n^{\mathrm{NRPA}}(0)$ equals the fraction of the correlation energy that results from the truncated part of the C_{ij} coefficients. We will show in paper II how we can use this simple relation to interpret the difference between each single CI and NRPA frequency.

C. Renormalization

In applying the SC-RPA equation to two-electron systems, the exact expressions for the matrices $\underline{A}$, $\underline{B}$, and $\underline{D}$ given in Eq. (15) have been used by several workers.[20,28] However, for most calculations of systems with more than two electrons (an exception is an unpublished study[29] of CO), the matrices have been approximated by including only the terms linear in the correlation coefficients $C_{m\gamma,n\delta}(S)$.[18] It has been shown by Rowe[21] that the terms of order C^2, which give the first correction to N_0, can be included without altering the simple NRPA form of the basic equations. This approach, called the renormalized SC-RPA (RSC-RPA) leads to matrix elements of the form

$$\begin{aligned} A_{m\gamma,n\delta}(S) &= N_0^2[A_{m\gamma,n\delta}^u(S) - \tfrac{1}{2}\delta_{\gamma\delta}(\epsilon_m + \epsilon_n - 2\epsilon_\gamma)p_{mn}^{(2)}\\ &\qquad + \tfrac{1}{2}\delta_{mn}(2\epsilon_m - \epsilon_\gamma - \epsilon_\delta)p_{\gamma\delta}^{(2)}],\\ B_{m\gamma,n\delta}(S) &= N_0^2 B_{m\gamma,n\delta}^u, \qquad (63)\\ D_{m\gamma,n\delta} &= N_0^2(\delta_{mn}\delta_{\gamma\delta} + \delta_{mn}p_{\gamma\delta}^{(2)} - \delta_{\gamma\delta}p_{mn}^{(2)}), \end{aligned}$$

where $A_{m\gamma,n\delta}^u(S)$ and $B_{m\gamma,n\delta}^u(S)$ are the "unrenormalized" matrix elements, i.e., the terms from Eq. (29) linear in C,

$$\begin{aligned} A_{m\gamma,n\delta}^u(S) &= A_{m\gamma,n\delta}^{\mathrm{NRPA}}(S) - \delta_{\gamma\delta}\sum_{q\mu\nu}\tfrac{1}{2}[V_{mq\mu\nu}C_{n\mu,q\nu}^*(0)\\ &\qquad + V_{\mu\nu nq}C_{m\mu,q\nu}(0)]\\ &\qquad - \delta_{mn}\sum_{pq\nu}\tfrac{1}{2}[V_{pq\gamma\nu}C_{p\delta,q\nu}(0) + V_{\delta\nu pq}C_{p\gamma,q\nu}(0)], \end{aligned} \tag{64}$$

$$\begin{aligned} B_{m\gamma,n\delta}^u(S) &= B_{m\gamma,n\delta}^{\mathrm{NRPA}}(S) - (-1)^S\sum_{p\mu}[V_{m\mu\delta p}C_{p\mu,n\gamma}(0)\\ &\qquad + V_{n\mu\gamma p}C_{p\mu,m\delta}(0)]\\ &\qquad - \sum_{p\mu}[V_{m\mu p\delta}C_{p\gamma,n\mu}(S) + V_{n\mu p\gamma}C_{m\mu,p\delta}(S)]\\ &\qquad + \sum_{pq}V_{mnpq}C_{p\gamma,q\delta}(S) + \sum_{\mu\nu}V_{\mu\nu\gamma\delta}C_{m\mu,n\nu}(S), \end{aligned}$$

and

$$p^{(2)}_{mn}=\tfrac{1}{2}\sum_{p\mu\nu}\sum_{S}C'_{p\mu,m\nu}(S)C_{p\mu,n\nu}(S),$$

$$p^{(2)}_{\gamma\delta}=\delta_{\gamma\delta}\sum_{m}p^{(2)}_{mm}-\tfrac{1}{2}\sum_{\substack{p\,q\\ \mu}}\sum_{S}C'_{p\mu,q\gamma}(S)C_{p\mu,q\delta}(S), \tag{65}$$

$$N_0^2=1-\sum_{m}p^{(2)}_{mm},$$

where $C'_{m\gamma,n\delta}=K_{m\gamma,n\delta}+\frac{1}{2}(-1)^S(K_{m\gamma,n\delta}-K_{m\delta,n\gamma})$ and is thus related to the C in Eq. (48) by

$$\begin{aligned}C'_{m\gamma,n\delta}(0)&=\tfrac{3}{4}C_{m\gamma,n\delta}(0)+\tfrac{1}{4}C_{m\gamma,n\delta}(1),\\ C'_{m\gamma,n\delta}(1)&=\tfrac{3}{4}C_{m\gamma,n\delta}(1)+\tfrac{1}{4}C_{m\gamma,n\delta}(0).\end{aligned} \tag{66}$$

(Note that we assume all quantities are real for simplicity.) Generally, one further approximates $D_{m\gamma,n\delta}$ by its diagonal elements[19]

$$D_{m\gamma,n\delta}=N_0^2\delta_{mn}\delta_{\gamma\delta}(1+p^{(2)}_{\gamma\delta}-p^{(2)}_{mn}). \tag{67}$$

It is then possible to recover the form of the NRPA matrix equations [see Eq. (28) and (28′) of Ref. 19]. As in the regular SC-RPA equations, the eigenvectors, $\underline{\bar{Y}}_\lambda$ and $\underline{\bar{Z}}_\lambda$, satisfy

$$\underline{\bar{Y}}^\dagger_\lambda\underline{\bar{Y}}_{\lambda'}-\underline{\bar{Z}}^\dagger_\lambda\underline{\bar{Z}}_{\lambda'}=\delta_{\lambda\lambda'}, \tag{68}$$

where

$$\bar{Y}_{m\gamma}=f_{m\gamma}Y_{m\gamma},\quad \bar{Z}_{m\gamma}=f_{m\gamma}Z_{m\gamma},$$

$$f_{m\gamma}\equiv(1+p^{(2)}_{\gamma\gamma}-p^{(2)}_{mm})^{1/2}.$$

At this point it is well to consider the differences between the present approach and that of Shibuya, Rose, and McKoy.[19] First, they include the normalization factor N_0^2, which is common to all matrix elements, approximately in their equations; that is, they multiply the matrix elements above [Eq. (63)] by $N_0^2=1-\sum_m p^{(2)}_{mm}$, keeping only terms up to order C^2 or VC in the results, where V represents the potential terms. The unrenormalized $\underline{A}^u$ diagonal matrix elements contain terms involving the SCF-orbital energies ϵ_i; hence, we keep terms of the type ϵC^2 when multiplying $\underline{A}$ by N_0^2. On the other hand, all the unrenormalized $\underline{B}$ matrix elements are of the V or VC type, and so multiplication by N_0^2 leaves these matrix elements unchanged to order VC or C^2. Thus, the effect of multiplying the $\underline{A}$ matrix elements by N_0^2 in this approximate manner is not the same as that of multiplying the $\underline{B}$ matrix elements by N_0^2. Shibuya *et al.* include the multiplication of N_0^2 in this uneven fashion in their matrix elements, while in the present approach, the N_0^2 factor is kept in all terms and so cancels from both sides of Eq. (28) to begin with. Calculations comparing the two approaches will be given in paper II.

A deeper problem with the renormalized equations is that it is not possible to do an exact self-consistent cycle. The reason for this is that, as shown in Eq. (68), $\underline{\bar{X}}$ and $\underline{\bar{Y}}$, not $\underline{X}$ and $\underline{Y}$, are now the eigenvectors which are orthonormalized with respect to the RPA metric. However, the inclusion of C^2 terms in the matrix elements and the self-consistency criterion [Eq. (4)] still leads to the result that $\underline{C}=\underline{Z}\underline{Y}^{-1}$ (the next order correction to the consistent $\underline{C}$ matrix would arise from $3p$-$3h$ terms in $O^\dagger$). As shown in Sec. III B, $\underline{C}$ is symmetric if the matrices $\underline{Y}$ and $\underline{Z}$ satisfy Eqs. (51) and (52), which in this case they do not. Hence, if we obtain $\underline{\bar{Y}}$ and $\underline{\bar{Z}}$ from renormalized equations and use them to determine $\underline{Y}$ and $\underline{Z}$, the new C matrix (obtained from $\underline{C}=\underline{Z}\underline{Y}^{-1}$) is not necessarily symmetric, and therefore unphysical. This is indeed what is found in the applications of paper II.

The detailed analysis of the general RPA equations in the earlier section (Sec. II) shows that the self-consistency condition can be applied correctly in higher order; i.e., we approach the exact ground state, $|0\rangle$, as we expand the operator space and thus must obtain the correct (and therefore symmetric) matrix elements C_{ij}. For example, the results for H_2 obtained by Ostlund and Karplus[20] used renormalized matrix elements [although they never actually used Eq. (49)] to show that a symmetric $\underline{C}$ matrix satisfied the RSC-RPA equations if no single excitations were present in $|0\rangle$. What this makes clear is that it is not correct, in general, to include only the $1p$-$1h$ operators in $O^\dagger_\lambda$ and carry the matrix elements to order C^2 self-consistency. In fact, the consistent treatment of the C^2 terms may be done only after $2p$-$2h$, as well as some density-shift terms are added to $O^\dagger$, as in the two-electron case. (The next section, which adds $2p$-$2h$ operators approximately, does not by itself overcome the consistency problem.) The applications given in paper II are derived by diagonalizing the renormalized SC-RPA matrices obtained by using the self-consistent coefficients from unrenormalized singlet and triplet calculations to evaluate the $p^{(2)}_{mn}$ and $p^{(2)}_{\gamma\delta}$ matrices. This should be reasonable as the matrix elements are not very sensitive to the exact values of the C coefficients.

D. $2p$-$2h$ operators

As was suggested earlier[20] and is clear from the considerations in Sec. II, valid results for excited states require that operators other than $1p$-$1h$ operators be included in $O^\dagger$. The extension of the SC-RPA to include $2p$-$2h$ operators can be handled in several ways.[19, 30-33] One of the methods is to relate the SC-RPA matrices to the standard perturbation treatments of the polarization or particle-hole propagator.[30-33] In this section we consider the treatment of the $2p$-$2h$ operators given in the current equation-of-motion papers.[19]

The excitation operator $O_\lambda^\dagger$ including $2p$-$2h$ operators can be written

$$O_\lambda^\dagger = \sum_{m\gamma} Y_{m\gamma}(\lambda S) C_{m\gamma}^\dagger(SM) - Z_{m\gamma}(\lambda S) C_{m\gamma}(\overline{S}\overline{M})$$
$$+ \sum_{m\gamma n\delta} [Y_{m\gamma,n\delta}^{(2)}(\lambda S)\Gamma_{m\gamma,n\delta}^\dagger(SM)$$
$$- Z_{m\gamma,n\delta}^{(2)}(\lambda S)\Gamma_{m\gamma,n\delta}(\overline{S}\overline{M})], \tag{69}$$

where the $2p$-$2h$ operators, $\Gamma_{m\gamma,n\delta}^\dagger(SM)$, are defined in Shibuya *et al.*[19] Introduction of this form for $O_\lambda^\dagger$ into Eq. (2) yields the extended RPA equation [Eqs. (33a) and (33b) of Ref. 19]. By a standard partitioning, the coefficients $\underline{Y}^{(2)}$ and $\underline{Z}^{(2)}$ are related to $\underline{Y}$ and $\underline{Z}$ in terms of an ω-dependent matrix. The resulting expression for $\underline{Y}$ and $\underline{Z}$ is

$$\begin{pmatrix} \underline{\overline{A}}_1 & \underline{\overline{B}} \\ -\underline{\overline{B}}^* & -\underline{\overline{A}}_2^* \end{pmatrix} \begin{pmatrix} \underline{Y} \\ \underline{Z} \end{pmatrix} = \omega \begin{pmatrix} \underline{D} & 0 \\ 0 & \underline{D}^* \end{pmatrix} \begin{pmatrix} \underline{Y} \\ \underline{Z} \end{pmatrix}, \tag{70}$$

where $\underline{\overline{A}}_1 = \underline{A} - \underline{\Delta}_a$, $\underline{\overline{B}} = \underline{B} - \underline{\Delta}_b$, and $\underline{\overline{A}}_2 = \underline{A} - \underline{\Delta}_d$ and

$$\begin{pmatrix} \underline{\Delta}_a & \underline{\Delta}_b \\ -\underline{\Delta}_b^* & -\underline{\Delta}_d^* \end{pmatrix} \equiv \begin{pmatrix} \underline{A}^{(1,2)} & \underline{B}^{(1,2)} \\ -\underline{B}^{(1,2)*} & -\underline{A}^{(1,2)*} \end{pmatrix} \begin{pmatrix} \underline{A}^{(2,2)} - \omega\underline{D}^{(2,2)} & \underline{B}^{(2,2)} \\ -\underline{B}^{(2,2)*} & -\underline{A}^{(2,2)*} - \omega\underline{D}^{(2,2)*} \end{pmatrix}^{-1} \begin{pmatrix} \underline{A}^{(1,2)\dagger} & \underline{B}^{(1,2)\dagger} \\ -\underline{\tilde{B}}^{(1,2)} & -\underline{\tilde{A}}^{(1,2)} \end{pmatrix} . \tag{71}$$

Given the excitation operator [Eq. (69)], these equations are exact. However, a direct iterative solution would be very difficult. Shibuya *et al.*[19] have suggested that, since the $2p$-$2h$ contributions and the correlation correction to the ground state are expected to be small, it is valid to approximate the $2p$-$2h$ matrix elements by replacing $|0\rangle$ with $|\mathrm{HF}\rangle$ in the required expectation values. This makes $B^{(1,2)}$, $\underline{B}^{(2,2)}$, and therefore $\underline{\Delta}_b$ equal to 0, so that $\underline{\overline{B}} = \underline{B}$. With this approximation,

$$\underline{\Delta}_a = \underline{A}^{(1,2)}(\underline{A}^{(2,2)} - \omega\underline{D}^{(2,2)})^{-1}\underline{A}^{(1,2)\dagger}$$

and

$$\underline{\Delta}_d = \underline{A}^{(1,2)}(\underline{A}^{(2,2)} + \omega\underline{D}^{(2,2)})^{-1}\underline{A}^{(1,2)\dagger}.$$

To further simplify $\underline{\overline{A}}$, they assumed that $\underline{A}^{(2,2)}$ can be approximated by ignoring the interaction terms (i.e., terms in V) so that $A_{m'\gamma',n'\delta';m\gamma,n\delta}^{(2,2)} = (\epsilon_m + \epsilon_n - \epsilon_\gamma - \epsilon_\delta)\delta_{m'n',mn}\delta_{\gamma'\delta',\gamma\delta}$. Furthermore, $\underline{D}^{(2,2)}$ is equal to the identity matrix $\underline{I}$ if $|0\rangle = |\mathrm{HF}\rangle$. Finally, the eigenvalue of Eq. (70) is obtained from Eq. (28) by means of perturbation theory, with ω in $\underline{\Delta}_a$ and $\underline{\Delta}_d$ set equal to the $1p$-$1h$ SC-RPA excitation energy, $\omega^{1p\text{-}1h}$.

Although the approximations of Shibuya, Rose, and McKoy have the important attribute that they lead to a tractable set of equations, it has not been demonstrated that they are always justified for molecular problems. In what follows we consider certain improvements in the treatment of the $2p$-$2h$ terms that do not lead to more complicated equations. The first of these is concerned with the treatment of ω in $\underline{\Delta}_a$ and $\underline{\Delta}_d$. Instead of using the $1p$-$1h$ value of ω in these terms, we can perform an iteration on ω. Starting with the $1p$-$1h$ excitation energy, we calculate by perturbation theory the corrected ω ($\omega = \omega^{1p\text{-}1h} - \Delta\omega$) and use the corrected ω to recalculate the $\underline{\Delta}_a$ and $\underline{\Delta}_d$ matrices. The results lead to a new correction $\Delta\omega$ and the process is repeated until convergence is achieved.

The requirement of ω iteration, then, is that we find a "fixed point" excitation energy; that is, an excitation energy $\overline{\omega}$ which leads to a self-consistent correction $\Delta\omega$, so that $\overline{\omega} = \omega^{1p\text{-}1h} - \Delta\omega$. Since it is possible to find more than one fixed point ω from a given $\omega^{1p\text{-}1h}$, we obtain a multivalued function in going from $\omega^{1p\text{-}1h}$ to the $\overline{\omega}$'s. This multivaluedness reflects the proper behavior of the CI solutions as we add more configurations; i.e., there are clearly more full CI states than single CI states so the mapping from one to the other is necessarily multivalued. This property of the "fixed point" results is a fundamental difference between the present $2p$-$2h$ treatment and that of Shibuya *et al.*[19] (see paper II).

The second revision is concerned with the treatment of $A^{(2,2)}$, in which the interaction terms (V terms) were neglected by McKoy. It is necessary to introduce these terms approximately while still preserving the simplicity of the approach; that is, avoiding the need to diagonalize matrices involving more than $1p$-$1h$ excitations. A scheme to deal with $\underline{A}^{(2,2)}$ and still leave $\underline{\Delta}_a$ and $\underline{\Delta}_d$ as simple perturbations, is to decompose $\underline{A}^{(2,2)}$ as a sum of its diagonal and off-diagonal parts, i.e., $\underline{A}^{(2,2)} = \underline{A}_{\mathrm{diag}}^{(2,2)} + \Delta\underline{A}^{(2,2)}$. We use the full diagonal elements of $\underline{A}^{(2,2)}$ in $\underline{A}_{\mathrm{diag}}^{(2,2)}$, and thus include V terms in addition to the ϵ terms (see above). $\Delta\underline{A}^{(2,2)}$ is composed of the smaller off-diagonal elements of the $A^{(2,2)}$ matrix. If $||\Delta\underline{A}^{(2,2)}/(\underline{A}_{\mathrm{diag}}^{(2,2)} - \omega\underline{I})|| < 1$, we can also include $\Delta\underline{A}^{(2,2)}$ in a simple form by using the truncated series,

$$(\underline{A}^{(2,2)} - \omega\underline{I})^{-1} \cong (\underline{A}_{\mathrm{diag}}^{(2,2)} - \omega\underline{I})^{-1} - (\underline{A}_{\mathrm{diag}}^{(2,2)} - \omega\underline{I})^{-1}\Delta\underline{A}^{(2,2)}(\underline{A}_{\mathrm{diag}}^{(2,2)} - \omega\underline{I})^{-1}, \tag{72}$$

with Eq. (72), we obtain

$$\begin{aligned}\Delta_a = {} & A^{(1,2)}(A^{(2,2)}_{\mathrm{diag}} - \omega I)^{-1}A^{(1,2)\dagger} \\ & - A^{(1,2)}(A^{(2,2)}_{\mathrm{diag}} - \omega I)^{-1}\Delta A^{(2,2)} \\ & \times (A^{(2,2)} - \omega I)^{-1}A^{(1,2)\dagger} . \end{aligned} \qquad (73)$$

A corresponding expression is obtained for $\underline{\Delta}_d$, namely, Eq. (73) where each $-\omega \underline{I}$ is replaced by $+\omega \underline{I}$ while $\underline{\Delta}_b = 0$. Both $\underline{\Delta}_a$ and $\underline{\Delta}_d$ can be evaluated with little extra work since they require only matrix multiplications over all the $2p$-$2h$ terms. These approximations are expected to be an improvement over the previous expressions; quantitative evaluations of the importance of the corrections are given in the paper II.

To examine the consistency of including the interaction terms in $\underline{A}^{(2,2)}_{\mathrm{diag}}$, we use the two-electron system for which the wave function $|0\rangle$ is assumed to have the simple form[20]

$$|0\rangle = N_0\left(|\mathrm{HF}\rangle + \frac{1}{4}\sum_{\substack{m\gamma \\ n\delta}} C_{m\gamma,n\delta}\left|{}^{n\delta}_{m\gamma}\right\rangle\right),$$

where $|{}^{n\delta}_{m\gamma}\rangle$ is a doubly excited spin-adapted Slater determinant.

If we let $\underline{C} = 0$ (i.e., approximate $|0\rangle$ by $|\mathrm{HF}\rangle$), the matrix elements simplify to

$$A^{(1,2)}_{r'\alpha';r\alpha,s\beta} = \langle r'\alpha' | H | {}^{r\alpha}_{s\beta}\rangle ,$$

$$\underline{B}^{(1,2)} = 0, \quad \underline{B}^{(2,2)} = 0,$$

$$A^{(2,2)}_{r'\alpha's'\beta';r\alpha,s\beta} = \langle {}^{r'\alpha'}_{s'\beta'} | H - E_{\mathrm{HF}} | {}^{r\alpha}_{s\beta}\rangle \underline{D}^{(2,2)} = \underline{I} .$$

If we approximate $A^{(2,2)}$ by its diagonal elements, Eq. (71) yields

$$\begin{aligned}(\Delta_a)_{m\gamma,n\delta} & = \sum_{\substack{r\alpha \\ s\beta}} \frac{A^{(1,2)}_{m\gamma;r\alpha,s\beta}A^{(1,2)\dagger}_{n\delta;r\alpha,s\beta}}{A^{(2,2)}_{r\alpha,s\beta;r\alpha,s\beta} - \omega} , \\ & = \sum_{\substack{r\alpha \\ s\beta}} \frac{\langle m\gamma | H | {}^{r\alpha}_{s\beta}\rangle \langle {}^{r\alpha}_{s\beta} | H | n\delta\rangle}{\langle {}^{r\alpha}_{s\beta} | H | {}^{r\alpha}_{s\beta}\rangle - E_{\mathrm{HF}} - \omega} . \end{aligned} \qquad (74)$$

The first-order perturbation theory expression for $\Delta\omega$, using only $\underline{\Delta}_a$ (since $\underline{\Delta}_b = 0$ and $\underline{\Delta}_d$ is very small) becomes $\Delta\omega = \underline{Y}^\dagger \underline{\Delta}_a \underline{Y}$ where $\underline{Y}$ is the $1p$-$1h$ coefficient of $O^\dagger_\lambda$ [see Eqs. (70) and (71)]. Consequently, we can write

$$\Delta\omega = \sum_{\substack{m\gamma \\ n\delta}} \sum_{\substack{r\alpha \\ s\beta}} Y_{m\gamma} Y_{n\delta} \frac{\langle m\gamma | H | {}^{r\alpha}_{s\beta}\rangle \langle {}^{r\alpha}_{s\beta} | H | n\delta\rangle}{\langle {}^{r\alpha}_{s\beta} | H | {}^{r\alpha}_{s\beta}\rangle - E_{\mathrm{HF}} - \omega}$$

or

$$\Delta\omega = \sum_{\substack{r\alpha \\ s\beta}} \frac{\langle \lambda | H | {}^{r\alpha}_{s\beta}\rangle \langle {}^{r\alpha}_{s\beta} | H | \lambda\rangle}{\langle {}^{r\alpha}_{s\beta} | H | {}^{r\alpha}_{s\beta}\rangle - E_\lambda} , \qquad (75)$$

where $|\lambda\rangle = \sum_{m\gamma} Y_{m\gamma} | m\gamma\rangle$ is the λth excited state in the $1p$-$1h$ representation and $E_\lambda = E_{\mathrm{HF}} + \omega$.

Equation (75) shows that in this scheme $\Delta\omega$ is the result of a second-order perturbation calculation, where we treat $|\mathrm{HF}\rangle$, the $1p$-$1h$ excited states $|\lambda\rangle$, and the doubly excited states $|{}^{r\alpha}_{s\beta}\rangle$ as the unperturbed eigenstates. It is clear that this conclusion follows only if we evaluate the diagonals of $\underline{A}^{(2,2)}$, $\langle {}^{r\alpha}_{s\beta} | H | {}^{r\alpha}_{s\beta}\rangle$, with the interaction terms. As pointed out earlier, this contrasts with the scheme of Shibuya *et al.*[19], where they only include the ϵ-dependent terms in $\underline{A}^{(2,2)}$.

Furthermore, since the SC-RPA uses a correlated ground state to compute $\omega^{1p\text{-}1h}$, the expression $E_\lambda = E_{\mathrm{HF}} + \omega^{1p\text{-}1h}$ used in Eq. (75) is not quite correct if we are to obtain $\Delta\omega$ in a consistent second-order scheme. The reason for this is that $\omega^{1p\text{-}1h}$ already includes the ground-state correlation and yet the proper quantity to use from the perturbation interpretation of Eq. (75) is $\omega^{\text{single CI}}$. However, instead of trying to eliminate the ground-state correlation energy from $\omega^{1p\text{-}1h}$, we can also include the $|\lambda\rangle$-state correlation energy in ω. This results in a more balanced ω, which is closer to $\omega^{\text{single CI}}$, while preserving the electron correlation in the RPA scheme. The correction to ω is precisely what the ω iteration accomplishes.

IV. CONCLUSIONS

The extended RPA offers a new and promising way of treating the electron correlation problem in the excitation spectra of atoms and molecules, as well as of calculating their dynamic properties such as the oscillator strengths for the electronic transitions. Since most approximate treatments have been based on the double commutators formulation introduced by Rowe, we have analyzed this approach and demonstrated that it converges to the exact result in the limit of a complete operator space. We then derived the exact two-electron excitation operator and used it to determine the contributions made by the possible operator types. Particular emphasis was given to the operators excluded in most applications of the RPA, namely, the "density- shift" operators. We showed that certain "density-shift" operators can be as important as some of the operators normally included in extended treatments.

The variational principle derived by Thouless for the NRPA matrix is extended to prove that the nth NRPA excitation energy is less than the nth single CI excitation energy. A perturbation treatment is introduced for a comparison of the NRPA and single CI excitation energies and to show that their differences are related to the ground-state correlation energy.

The self-consistent RPA (SC-RPA) is analyzed. It is shown that the ground-state coefficients possess an intrinsic symmetry, which should be maintained by the SC-RPA calculations. The orthogonality conditions on the eigenvectors of the linearized SC-RPA equations and the consistency requirement on the ground-state coefficients are found to be sufficient to ensure this symmetry. However, certain approximate extended treatments, including the renormalized SC-RPA of Shibuya and McKoy do not lead to symmetric coefficients. If carried out exactly to all orders, however, the SC-RPA leads to the exact ground state and thus to symmetric coefficients.

We have proposed an extended RPA, which is a modification of the renormalized RPA and corrects certain deficiencies in the latter without complicating the required calculations. The inclusion of interaction terms in the diagonal matrix elements of the $\underline{A}^{(2,2)}$ matrix was shown to be consistent with the level of approximation in the theory. The introduction of an iteration in ω is expected to improve the accuracy of the results. Furthermore, the ω iteration alters the theory in an important way, since it leads to the proper multivalued behavior of the excited-state spectrum.

APPENDIX

We prove the following theorem relating to Eqs. (14) and (15) in the text:

Theorem. If an exact solution in the complete operator space to Rowe's equations of motions [Eqs. (2) and (4)] gives the "ground state"

$$|\bar{0}\rangle = A_i|i\rangle + A_j|j\rangle, \tag{A1}$$

where $|i\rangle$ and $|j\rangle$ are two exact eigenstates of the molecular Hamiltonian with eigenvalues E_i and E_j, then $\omega_{ij} = E_j - E_i = 0$.

Proof. If $|\bar{0}\rangle$ is given by Eq. (A1), Eq. (10) in the text becomes (after taking the complex conjugate)

$$\begin{aligned} C_{ii}A_i^* + C_{ji}A_j^* &= 0, \\ C_{ij}A_i^* + C_{jj}A_j^* &= 0, \end{aligned} \tag{A2}$$

and Eq. (11) reduces to

$$-2\omega|A_i|^2C_{ii} - (\omega_{ij} + 2\omega)A_jA_i^*C_{ij} - E_i|A_i|^2C_{ii} - E_jA_j^*A_iC_{ji} = 0, \quad \text{for } n=i,\ l=i; \tag{A3}$$

$$-(\omega_{ij} + 2\omega)A_iA_j^*C_{ii} - 2(\omega_{ij} + \omega)|A_j|^2C_{ij} - E_i|A_i|^2C_{ij} - E_jA_iA_j^*C_{jj} = 0, \quad \text{for } n=i,\ l=j; \tag{A4}$$

$$2(\omega_{ij} - \omega)|A_i|^2C_{ji} + (\omega_{ij} - 2\omega)A_jA_i^*C_{jj} - E_iA_i^*A_jC_{ii} - E_j|A_j|^2C_{ji} = 0, \quad \text{for } n=j,\ l=i; \tag{A5}$$

$$(\omega_{ij} - 2\omega)A_iA_j^*C_{ji} - 2\omega|A_j|^2C_{jj} - E_iA_i^*A_jC_{ij} - E_j|A_j|^2C_{jj} = 0, \quad \text{for } n=j,\ l=j. \tag{A6}$$

If we use Eq. (A2) to eliminate C_{ji} and C_{jj} from Eqs. (A3)–(A6), we obtain

$$(\omega_{ij} - 2\omega)|A_i|^2C_{ii} - (\omega_{ij} + 2\omega)A_i^*A_jC_{ij} = 0, \tag{A3$'$}$$

$$-(\omega_{ij} + 2\omega)A_iA_jC_{ii} + [\omega_{ij}|A_i|^2(A_j/A_j^*) - (2\omega_{ij} + 2\omega)A_j^2]C_{ij} = 0, \tag{A4$'$}$$

$$[\omega_{ij}A_i^*A_j - 2(\omega_{ij} - \omega)|A_i|^2(A_i/A_j)^*]C_{ii} - (\omega_{ij} - 2\omega)A_i^{*2}(A_j/A_j^*)C_{ij} = 0, \tag{A5$'$}$$

$$-(\omega_{ij} - 2\omega)|A_i|^2C_{ii} + (\omega_{ij} + 2\omega)A_jA_i^*C_{ij} = 0. \tag{A6$'$}$$

Note that (A3′) and (A6′) are the same equation, in agreement with the counting principle given in the text. Using Eqs. (A3′) and (A4′) we obtain the relationship

$$|A_i/A_j|^2 = (3\omega_{ij} - 2\omega)/(\omega_{ij} + 2\omega) \tag{A7}$$

as long as $\omega \neq -\frac{1}{2}\omega_{ij}$ and $C_{ii} \neq 0$. From Eqs. (A3′) and (A5′), if $\omega \neq -\frac{1}{2}\omega_{ij}$ and $C_{ii} \neq 0$, we can derive

$$|A_i/A_j|^2 = (\omega_{ij} + 2\omega)/(3\omega_{ij} - 2\omega). \tag{A8}$$

(If $3\omega_{ij} - 2\omega = 0$, then the equations yield $\omega_{ij} = 0$.) Finally, using Eq. (A8) in (A7) we arrive at

$$-8\omega_{ij} = 0.$$

Thus, the theorem is proved as long as $C_{ii} \neq 0$ and $\omega \neq -\frac{1}{2}\omega_{ij}$. If $C_{ii} = 0$ and $\omega \neq -\frac{1}{2}\omega_{ij}$, $C_{ij} = 0$ from Eq. (A3′). Then Eq. (A2) implies that $C_{ji} = C_{jj} = 0$ also. If $C_{ii} = 0$ and $\omega = -\frac{1}{2}\omega_{ij}$, then Eq. (A5′) demands that either $C_{ij} = 0$ or $\omega_{ij} = 0$ (or both). Hence, in this case C_{ij}, C_{ji}, and C_{jj} are zero if $\omega_{ij} \neq 0$. Finally, if $C_{ii} \neq 0$ and $\omega = -\frac{1}{2}\omega_{ij}$, Eq. (A3′) implies that $\omega_{ij} = 2\omega$ and hence that $\omega_{ij} = 0$.

We have shown, so far, that either the theorem is true ($\omega_{ij} = 0$) or all $C_{ii}, C_{ij}, C_{ji}, C_{jj}$ are zero. To complete the proof, we take up the case that the latter is true. If the C_{ii}, C_{ij}, C_{ji}, and C_{jj} coefficients are zero, for $O^\dagger|\bar{0}\rangle \neq 0$, there must be at least one nonzero C_{ni} or C_{nj} coefficient, where $n \neq i,j$. Equations (11) in the text for $n \neq i,j$ and $l = i$ become

$$2(E_n - E_i - \omega)|A_i|^2C_{ni} + (2E_n - E_j - E_i - 2\omega)A_jA_i^*C_{nj} = 0, \tag{A9}$$

and for $n \neq i,j$ and $l = j$,

$$2(E_n - E_j - \omega)|A_j|^2C_{nj} + (2E_n - E_j - E_i - 2\omega)A_iA_j^*C_{ni} = 0. \tag{A10}$$

If both C_{ni} and C_{nj} are nonzero, then equating the ratio $(A_i/A_j)(C_{ni}/C_{nj})$ from both Eqs. (A9) and (A10), we have

$$\frac{2\omega - 2E_n + E_j + E_i}{2E_n - 2\omega - 2E_i} = \frac{2\omega - 2E_n + 2E_j}{2E_n - 2\omega - E_j - E_i}$$

or $(E_i+E_j)^2=4E_iE_j$; i.e., $\omega_{ij}=0$. If $C_{ni}=0$, Eqs. (A9) and (A10) imply that $2E_n-E_j-2\omega=0$ and $2(E_n-E_j-\omega)=0$; i.e., $\omega_{ij}=0$. The same follows if $C_{nj}=0$. This concludes all the possibilities and the theorem is proven. Thus, $\omega_{ij}=0$ is either a contradiction, if $|i\rangle$ and $|j\rangle$ are nondegenerate eigenstates, or if they are degenerate, $|\bar{0}\rangle$ is already an exact eigenstate of H.

---

*Supported in part by a grant from the National Science Foundation (CHE 7617569).

†Supported in part by the Parker Foundation.

[1] T. H. Dunning and V. McKoy, J. Chem. Phys. 47, 1735 (1967).

[2] T. Shibuya and V. McKoy, J. Chem. Phys. 54, 1738 (1971).

[3] B. Lukman and A. Azman, Mol. Phys. 16, 201 (1969).

[4] J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys. 58, 74 (1973).

[5] W. Coughran, J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys. 58, 2699 (1973).

[6] P. H. S. Martin, D. Yeager, and V. McKoy, Chem. Phys. Lett. 25, 182 (1974).

[7] J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys. 60, 2700 (1974).

[8] D. Yeager and V. McKoy, J. Chem. Phys. 60, 2714 (1974).

[9] D. Yeager and V. McKoy, J. Chem. Phys. 61, 755 (1974).

[10] C. W. McCurdy and V. McKoy, J. Chem. Phys. 61, 2820 (1974).

[11] P. H. S. Martin, T. N. Rescigno, and V. McKoy, Chem. Phys. Lett. 29, 496 (1974),

[12] G. R. Williams, Chem. Phys. Lett. 30, 495 (1975).

[13] R. F. Stewart, D. K. Watson, and A. Dalgarno, J. Chem. Phys. 63, 3222 (1975).

[14] M. W. Ribarsky, Phys. Rev. A 12, 1739 (1975).

[15] D. G. Truhlar, Int. J. Quantum Chem. Symp. VII, 807 (1973).

[16] G. R. J. Williams and D. Poppinger, Mol. Phys. 30, 1005 (1975).

[17] O. Matsuoka and H. Ito, Theoret. Chim. Acta. 39, 111 (1975).

[18] T. Shibuya and V. McKoy, Phys. Rev. A 2, 2208 (1970).

[19] T. Shibuya, J. Rose, and V. McKoy, J. Chem. Phys. 58, 500 (1973).

[20] N. Ostlund and M. Karplus, Chem. Phys. Lett. 11, 450 (1971).

[21] D. J. Rowe, Rev. Mod. Phys. 40, 153 (1968).

[22] T. Terasaka and T. Matsushita, Chem. Phys. Lett. 4, 384 (1969).

[23] D. J. Thouless, Nucl. Phys. 22, 78 (1961).

[24] A. D. McLachlan and M. A. Ball, Rev. Mod. Phys. 34, 844 (1964).

[25] D. J. Thouless, Nucl. Phys. 21, 225 (1960).

[26] E. A. Sanderson, Phys. Lett. 19, 141 (1965).

[27] W. M. Huo, J. Chem. Phys. 62, 2072 (1975).

[28] T. Shibuya and V. McKoy, J. Chem. Phys. 53, 3308 (1970).

[29] N. Ostlund and M. Karplus (unpublished).

[30] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, New York, 1973).

[31] P. Jorgensen, J. Oddershede, and M. Ratner, Chem. Phys. Lett. 32, 111 (1975).

[32] F. S. M. Tsui and K. F. Freed, Chem. Phys. Lett. 32, 245 (1975).

[33] K. D. Jordan, Chem. Phys. Lett. 36, 264 (1975).