An equations of motion approach for open shell systems*

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(Received 8 January 1975)

A straightforward scheme is developed for extending the equations of motion formalism to systems with simple open shell ground states. Equations for open shell random phase approximation (RPA) are given for the cases of one electron outside of a closed shell in a nondegenerate molecular orbital and for the triplet ground state with two electrons outside of a closed shell in degenerate molecular orbitals. Applications to other open shells and extension of the open shell EOM to higher orders are both straightforward. Results for the open shell RPA for lithium atom and oxygen molecule are given.

I. INTRODUCTION

In several recent papers,[1,2] we have described the equations of motion method as a conceptually and computationally simple method for obtaining properties of direct physical interest to spectroscopists, e.g., transition energies and moments. We have applied the equations of motion method at various levels of approximation to several atoms and small molecules including H_2, N_2, CO, H_2O, CO_2, H_2CO, and C_6H_6.[3]

For closed shell systems, the simple approximations, i.e., the Tamm–Dancoff approximation (TDA) and the random phase approximation (RPA), generally give oscillator strengths in good agreement with experiment. To obtain good agreement with experimental excitation energies and to eliminate instabilities in the triplet manifold a higher order scheme is required.[1,2] We have used the resulting transition densities and discrete oscillator strength distributions in these approximations to calculate frequency-dependent polarizabilities and photoionization cross sections from both ground[4] and metastable states.[5] The TDA and RPA results have also been used to calculate transition moments between excited states in He[5] and N_2.[6] In electron–molecule scattering we have calculated Born inelastic cross sections[7] and discussed how these RPA results can be used to construct an optical potential.[8]

There are many systems of chemical interest with open shell ground states, e.g., Li, O_2, and many molecular ions. The purpose of this paper is to extend the equations of motion methods to atoms and molecules with simple open shell ground states in a clear straightforward manner. Although we limit the scope of this paper to the open shell random phase approximation, it is easy to extend the method to higher orders. This is the first step in a more general equations of motion theory.

In Sec. II, we review the equations of motion method and explain the modifications necessary for open shells. In particular, in Sec. III the cases of one electron outside a closed shell in a nondegenerate orbital and two electrons outside a closed shell in two degenerate molecular orbitals are examined and the formulas derived for the open shell random phase approximation (OSRPA).

We report results for lithium atom and oxygen molecule in Sec. IV. For lithium, since most low-lying transitions are $2s \rightarrow np$ there is little change due to correlation effects between the TDA and the RPA. For the Schumann–Runge transition in oxygen ($X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$) we calculate an oscillator strength in good agreement with experiment. However, several excitation energies are not consistent, indicating that a higher order scheme is necessary to accurately predict spectra. For several uses, e.g., discretization of the continuum, when one requires a distribution of f values, the RPA results may be adequate. For both Li and O_2 no matrix larger than 50×50 was diagonalized.

II. THEORY

A. General theory

Consider the excitation operator $O_\lambda^\dagger$ which when operating on the exact ground state $|0\rangle$ generates an excited state $|\lambda\rangle$, i.e.,

$$O_\lambda^\dagger|0\rangle = |\lambda\rangle . \tag{1}$$

Operating with the Hermitian conjugate operator O_λ on the ground state gives

$$O_\lambda|0\rangle = 0 . \tag{2}$$

We can solve for $O_\lambda^\dagger$ and the corresponding excitation energy, $\omega_\lambda = E_\lambda - E_0$, from the equations of motion[9]

$$\langle 0|[\delta O_\lambda, H, O_\lambda^\dagger]|0\rangle = \omega_\lambda \langle 0|[\delta O_\lambda, O_\lambda^\dagger]|0\rangle , \tag{3}$$

where δO_λ is a variation of the operator O_λ, H is the Hamiltonian, and the symmetric double commutator is defined

$$2[A, B, C] = [[A, B], C] + [A, [B, C]] . \tag{4}$$

We can obtain the matrix element $\langle\lambda|W|0\rangle$ of the operator W from

$$\langle\lambda|W|0\rangle = \langle 0|[O_\lambda, W]|0\rangle . \tag{5}$$

Equation (3) is exact. For many electron atoms and molecules Eq. (3) cannot be solved exactly. There are two approximations which can be made. The excitation operator may be expanded as sums of one-body operators, two-body operators, etc. We can approximate $O_\lambda^\dagger$ by truncating this sum. For example, in closed-shell systems we can restrict $O_\lambda^\dagger$ to be a sum over one-body operators

$$O_\lambda^\dagger = \sum_{m'\gamma'} (Y_{m'\gamma'} c_{m'}^\dagger c_{\gamma'} - Z_{m'\gamma'} c_{\gamma'}^\dagger c_{m'}) . \tag{6}$$

If $O_\lambda^\dagger$ is expanded a sum of elementary excitation operators $C_i^\dagger$, which we will call p-h excitation operators, and the corresponding Hermitian conjugates

$$O_\lambda^\dagger = \sum_i (Y_i C_i^\dagger - Z_i C_i) \tag{7}$$

the following matrix equation results from Eq. (3):

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} Y(\lambda) \\ Z(\lambda) \end{pmatrix} = \hbar\omega_\lambda \begin{pmatrix} \mathbf{U} & \mathbf{V} \\ -\mathbf{V}^* & -\mathbf{U}^* \end{pmatrix} \begin{pmatrix} Y(\lambda) \\ Z(\lambda) \end{pmatrix}, \tag{8}$$

where

$$\begin{aligned} A_{ij} &= \langle 0|[C_i, H, C_j^\dagger]|0\rangle, \\ B_{ij} &= -\langle 0|[C_i, H, C_j]|0\rangle, \\ U_{ij} &= \langle 0|[C_i, C_j^\dagger]|0\rangle, \\ V_{ij} &= -\langle 0|[C_i, C_j]|0\rangle. \end{aligned} \tag{9}$$

Matrices **A** and **U** are Hermitian, **B** is symmetric, and **V** is antisymmetric.

A second approximation is to use a nonexact ground state, e.g., the Hartree–Fock ground state or some single correlated state. The use of the double commutator on the left and the commutator on the right of Eq. (3) reduces the particle–hole rank of the expression, making it less sensitive to the choice of the approximate ground state. Hence, in many cases, a low level choice of ground state, e.g., the restricted Hartree–Fock (RHF) in Eqs. (8) and (9) may suffice.

B. The closed shell

In the RPA $O_\lambda^\dagger$ is restricted to the simple sum in Eq. (6) and the ground state is chosen to be the Hartree–Fock ground state. In the TDA the Z amplitudes are assumed to be identically zero, i.e., correlation is completely neglected. The TDA and RPA matrix elements of Eq. (9) are given elsewhere.[10]

In general, many TDA and RPA oscillator strengths agree well with experiment while energies do not as well. Additionally, in the triplet manifold low-lying states often have imaginary eigenvalues which represent instabilities in the RPA. An advantage of the RPA solution is that by including the Z amplitudes in Eq. (8), we implicitly assume a correlated ground state, even though the Hartree–Fock ground state is used throughout and no correlation coefficients are explicitly calculated. The RPA oscillator strengths also satisfy the Thomas–Reiche–Kuhn summation rule.

To obtain more reliable excitation energies and to eliminate triplet instabilities, we extend the approximations used in Eq. (3) to higher orders by explicitly including correlation in the ground state[1] and by including double excitation operators in $O_\lambda^\dagger$ in a perturbative scheme.[2] The method is called the equations of motion method including double excitation mixing [EOM $(1p-1h)+(2p-2h)$]. We have achieved excellent experimental agreement for both energies and oscillator strengths for several atoms and molecules.[3]

C. Open shell systems

An advantage of deriving the RPA from the equations of motion (3) is that the extension of the method to open shell ground states at all levels of approximation is straightforward. The form of the Eq. (8) for open shell cases remains the same, however, no general expression for the submatrices **A** and **B** can be given.

For the OSTDA and OSRPA we approximate $|0\rangle$ by the restricted Hartree–Fock ground state. The orthonormal sets of molecular orbitals are obtained from the OCBSE open shell Hartree–Fock method of Hunt, Dunning, and Goddard.[11] This method does not explicitly make use of the off-diagonal Lagrange multipliers to maintain orbital orthogonality. The converged SCF orbitals satisfy[11]

$$\langle i|H_k - H_i Q_{ik}|k\rangle, \quad k=1, M;\ i>k, \tag{10}$$

where there are P molecular orbitals, M occupied, and $Q_{ik}=0$ if $i>M$, $Q_{ik}=1$ if $i\leq M$. H_k is the usual Hartree–Fock one-electron operator for orbital ϕ_k, i.e., $H_k = fF_k$ where f is the fractional occupation number. If i and k are in the same shell $Q_{ik}=0$.

The Hamiltonian can be written

$$\mathcal{H} = \sum_{i'j'} h_{i'j'} c_{i'}^\dagger c_{j'} + \frac{1}{2} \sum_{i'j'k'l'} V_{i'j'k'l'} c_{j'}^\dagger c_{i'}^\dagger c_{k'} c_{l'} \tag{11}$$

$$= \sum_{ij} h_{ij}(c_{i\alpha}^\dagger c_{j\alpha} + c_{i\beta}^\dagger c_{j\beta}) - \frac{1}{2} \sum_{ij} \sum_k V_{ikkj}(c_{i\alpha}^\dagger c_{j\alpha} + c_{i\beta}^\dagger c_{j\beta}) + \frac{1}{2} \sum_{ijkl} V_{ijkl}(c_{i\alpha}^\dagger c_{k\alpha} + c_{i\beta}^\dagger c_{k\beta})(c_{j\alpha}^\dagger c_{l\alpha} + c_{j\beta}^\dagger c_{l\beta}), \tag{12}$$

where primed indices denote spin orbitals and unprimed indices orbitals. The sums are over all orbitals. In general we will use lower case Greek letters for pure hole orbitals; m, n, p, ... for pure particle (virtual) orbitals; Ω_1 and Ω_2 for the open shell orbitals; and i, j, k, l for any of the three types. Figure 1 illustrates this nomenclature. V_{ijkl} is defined

$$V_{ijkl} = \int \phi_i^*(1)\phi_j^*(2)(r_{12})^{-1}\phi_k(1)\phi_l(2)d\tau. \tag{13}$$

Throughout this paper real orbitals will be assumed.

Equation (10) can be used to rewrite Eq. (12) in terms of on-diagonal Lagrange multipliers which are associated with the orbital energies. The exact form of the Hamiltonian will thus depend on the open shell case.

We can use Eq. (12) and an appropriate set of p-h excitation operators in Eq. (9). If $|0\rangle$ is approximated by the restricted Hartree–Fock wavefunction with spin S, M_S, the result is the open shell RPA. Equation (8) reduces to the standard closed shell RPA form.

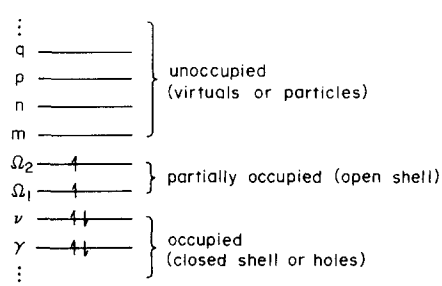

FIG. 1. Labeling of the particle–hole basis for an open shell.

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix}\begin{pmatrix} Y \\ Z \end{pmatrix} = \hbar\omega_\lambda \begin{pmatrix} Y \\ Z \end{pmatrix}. \tag{14}$$

For closed shell systems $O_\lambda^\dagger$ contains only one-body operators in the TDA and RPA. We write $O_\lambda^\dagger$ as in Eq. (7)

$$O_\lambda^\dagger = \sum_i (Y_i C_i^\dagger - Z_i C_i) \tag{15}$$

and consider that $C_i^\dagger$ operating on the open shell restricted Hartree–Fock ground state generates a configuration which is an eigenfunction of $\hat{S}^2$ and $\hat{M}_S$. For open shell ground states unless certain two-body p-h operators are included in Eq. (14) we cannot account for all linearly independent configurations which are eigenfunctions of $\hat{S}^2$ and $\hat{M}_S$ for a given orbital occupancy. These two-body p-h excitation operators allow for spin-flipping of the open shell electron in addition to a simple excitation, e.g., they include p-h operators such as $c_{m\alpha}^\dagger c_{\nu\alpha} c_{\Omega\beta}^\dagger c_{\Omega\alpha}$.

A simple example will clarify this. Lithium has a $|1s\alpha 1s\beta 2s\alpha\rangle$ ground state. This state is an eigenfunction of $\hat{S}^2$ and $\hat{M}_S$ with spin $\frac{1}{2}$ and spin projection $\frac{1}{2}$. If the p-h operator $C_i^\dagger$ operating on $|1s\alpha 1s\beta 2s\alpha\rangle$ excites an electron from a $1s$ orbital to a $3s$ orbital keeping $M_S = \frac{1}{2}$, there are three possibilities

$$|1s\alpha\, 2s\alpha\, 3s\beta\rangle,\ |1s\beta 2s\alpha\, 3s\alpha\rangle,\ |1s\alpha\, 2s\beta\, 3s\alpha\rangle. \tag{16}$$

Linear combinations of these kets must be taken to form configurations which are eigenfunctions of $\hat{S}^2$ with eigenvalue $\frac{3}{4}$. There are two independent combinations which have spin $\frac{1}{2}$. The third ket in Eq. (16) involves a change of spin of the $2s$ electron from α to β. Its p-h excitation operator is $C^\dagger = -c_{3s\alpha}^\dagger c_{1s\beta} c_{2s\beta}^\dagger c_{2s\alpha}$, a two-body operator. That is

$$-c_{3s\alpha}^\dagger c_{1s\beta} c_{2s\beta}^\dagger c_{2s\alpha} |1s\alpha\, 1s\beta 2s\alpha\rangle \rightarrow |1s\alpha\, 2s\beta\, 3s\alpha\rangle. \tag{17}$$

All $C_i^\dagger$'s are chosen to generate orthonormal states which are eigenfunctions of $\hat{S}^2$ and $\hat{M}_S$ when operating on the restricted HF ground state.

A further consideration in choosing the p-h operators is that they be tensor operators of a given rank k in spin space and that the Hermitian conjugate operator C_i be a tensor of the same rank and have the same transformation properties within a phase under rotation of the spin space. Although the p-h excitation operators chosen in this manner are not the simplest possible, they assure a unique definition of the B matrices of the equations of motion. We can form excited states with pure spin S' by operating with tensor operators $T_q^{(k)\dagger}$

$$|\Gamma S' M_S'\rangle = \sum_{q, M_S} T_q^{(k)\dagger} |SM_S\rangle \langle kSqM_S | kSS'M_S'\rangle, \tag{18}$$

where Γ differentiates states of the same spin. A similar equation exists for $T_q^{(k)}$. If k is zero, the dipole allowed states, then there is only one term on the right hand side of Eq. (18) and the Clebsch–Gordon coefficient is unity. For example, to generate the excited singlet manifold of O_2 starting from the ground state triplet with $M_S = 0$, we can choose a set of p-h excitation operators of rank 1 component 0 which generate pure states with $S' = 0$, $M_S' = 0$ when operating on the restricted Hartree–Fock ground state. The Hermitian conjugate operator C_i operating on the correlated state by Eq. (18) may not generate pure states. Similarly $C_i^\dagger$ operating on the correlated state may not generate pure states. We expect therefore the excited state manifold which has a different spin from the ground state to have slight errors in higher order schemes due to contamination of other spin states.

We now derive explicitly the open shell random phase approximation for two simple cases. These cases are those of a single electron outside a closed shell in a nondegenerate molecular orbital and of two electrons outside a closed shell in two degenerate molecular orbitals in a triplet state. These cases are among the most common open shell ground states, e.g., for the first case lithium atom and many molecular ions and for the triplet case O_2. With very slight modifications the triplet case can be applied to the lowest triplet state of closed shell atoms and molecules. Extensions to other open shells are obvious.

We have derived all formulas for these open shell systems via a computer program. Starting from the input p-h operators and Hamiltonian and by Wick's theorem[9] this program generates a set of formulas on magnetic tape which are in turn read into a standard randon phase approximation program. Hence, even though programming considerations for each open shell case may appear lengthy, in reality the entire procedure is automated.

In summary our OSRPA procedure is:

1. Perform an open shell SCF OCBSE[11] calculation to obtain an orthonormal basis.

2. Rewrite $\mathcal{H}$ in terms of OCBSE orbital energies, choosing the particle states to be eigenfunctions of the last open shell Fock operator.

3. Use the restricted Hartree–Fock ground state $|HF\rangle$ as an approximation to $|0\rangle$ in Eq. (8).

4. Choose excitation operators $O_\lambda^\dagger$ such that the p-h excitation operators $\{C_i^\dagger\}$ operating on $|HF\rangle$ generate configurations which are eigenfunctions of $\hat{S}^2$ and $\hat{M}_S$. Furthermore all $C_i^\dagger$ are one-body operators except for those which change the spin of the open shell electron or which move an electron between degenerate open shell molecular orbitals. The latter $C_i^\dagger$ will be two-body operators.

5. The $C_i^\dagger$ are chosen so that $C_i^\dagger$ and C_i are tensor operators of the same rank and hence the Hermitian conjugate pairs transform in the same manner under rotation of the spin space.

Extending this method to higher orders is straightforward. The ground state $|0\rangle$ can be replaced by a simple correlated ground state instead of the restricted Hartree–Fock ground state. Correlation coefficients can be obtained from perturbation theory or possibly an iterative scheme.[1] This is the higher open shell random phase approximation (HOSRPA). Double excitations can be accounted for in a manner similar to closed shell methods.[2] Again by including spin flipping in the open shell molecular orbitals we may have to include certain classes of three-body and even four-body operators to properly account for the number of independent configura-

tions of a given spin for an orbital occupancy.

Other open shell random phase approximations have been proposed for atoms and molecules.[12,13] Our method is a simple and clear way to extend the RPA to open shell systems. We differ from Armstrong[12] in that we have included certain two-body tensors in our excitation operators, we use a specific restricted Hartree–Fock particle–hole basis, we have generalized to molecules, and we always require

$$O_\lambda|0\rangle = 0\,. \tag{19}$$

We differ from Jørgensen[13] by choosing an approximation to $|0\rangle$ that is an eigenfunction of $\hat{S}^2$, $\hat{M}_S$, and $\hat{N}$, where $\hat{N}$ is the number operator. Furthermore our $C_i^\dagger$ operators include certain two-body operators and when operating on the ground state produce kets which are always eigenfunctions of $\hat{S}^2$, $\hat{M}_S$, and $\hat{N}$. We believe that our method offers the most straightforward extensions to higher orders.

D. Transition moments

For closed shell molecules, we can expand Eq. (5) in terms of the Y and Z amplitudes of Eq. (8) to yield

$$\langle 0|D|n\rangle = \mathrm{D_{on}} = \sqrt{2}\left[\sum_{m\gamma}(Y^*_{m\gamma}+Z^*_{m\gamma})\mathrm{d}_{m\gamma}\right], \tag{20}$$

where D is the transition moment and $d_{m\gamma}$ is $\langle m|\mathbf{r}|\gamma\rangle$. For open shell cases Eq. (20) is no longer correct but must be modified to

$$\mathrm{D} = \sum_i R_i(Y_i+Z_i)\mathrm{d}_i\,, \tag{21}$$

where the sum is over all possible particle–hole pairs including those pairs with spin flip in the open shell and electron rearrangement among degenerate open shell orbitals. R_i is a number which may be zero. For example, for a simple doublet ground state as in Li, R_i may be 1.0, −1.0, $-\sqrt{2}$, or 0 depending on the kind of excitation.

III. OPEN SHELL OPERATORS AND MATRIX ELEMENTS

A. Doublet

The ground state is $|$(closed shell)$\,\Omega\alpha\rangle$. We limit the equations to the case where Ω is nondegenerate, although the degenerate case is no more difficult. For this system the Hamiltonian is

$$\mathcal{H} = \sum_i \epsilon_i(c^\dagger_{i\alpha}c_{i\alpha}+c^\dagger_{i\beta}c_{i\beta}) + \sum_{ij}\Bigg(\sum_\nu (V_{i\nu\nu j}-2V_{i\nu j\nu}) + b(\tfrac{1}{2}V_{i\Omega\Omega j}-V_{i\Omega j\Omega}) - \frac{1}{2}\sum_k V_{ikkj}\Bigg)(c^\dagger_{i\alpha}c_{j\alpha}+c^\dagger_{i\beta}c_{j\beta}) + \frac{1}{2}\sum_{ijkl}V_{ijkl}(c^\dagger_{i\alpha}c_{k\alpha}+c^\dagger_{i\beta}c_{k\beta})(c^\dagger_{j\alpha}c_{l\alpha}+c^\dagger_{j\beta}c_{l\beta})\,, \tag{22}$$

where

$b=1$ when i and j are in the closed shell or when i or j is a virtual and the other is in the closed shell,

$b=2$ when i or j is open and the other is closed,

$b=0$ all other cases.

$$\epsilon_\gamma = h_{\gamma\gamma}+\sum_\nu(2J_{\gamma\nu}-K_{\gamma\nu})+\tfrac{1}{2}(2J_{\Omega\gamma}-K_{\Omega\gamma})\,, \tag{23}$$

$$\epsilon_\Omega = h_{\Omega\Omega}+\sum_\nu(2J_{\Omega\nu}-K_{\Omega\nu})\,, \tag{24}$$

$$\epsilon_m = h_{mm}+\sum_\nu(2J_{m\nu}-K_{m\nu})\,, \tag{25}$$

The possible excitations are shown in Fig. 2. The operators are given in Table I, the A matrix elements in Table II, and the B matrix elements in Table III. R values from Eq. (21) are in Table IV for the doublet (dipole allowed) manifold.

TABLE I. Spherical tensor p–h operators for the doublet $|$(closed shell)$\Omega\alpha\rangle$ ground state.

Doublet excited state ($S=\frac{1}{2}$, $M_S=\frac{1}{2}$)

$C^\dagger_{\Omega\nu}(00) = -c^\dagger_{\Omega\alpha}c_{\nu\alpha}-c^\dagger_{\Omega\beta}c_{\nu\beta}$

$C^\dagger_{m\Omega}(00) = c^\dagger_{m\alpha}c_{\Omega\alpha}+c^\dagger_{m\beta}c_{\Omega\beta}$

${}_1C^\dagger_{m\nu}(00) = 1/\sqrt{2}\,(c^\dagger_{m\beta}c_{\nu\beta}+c^\dagger_{m\alpha}c_{\nu\alpha}$

${}_2C^\dagger_{m\nu}(00) = \sqrt{2/3}\,(-c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega\beta}c_{\Omega\alpha}-c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega\alpha}c_{\Omega\beta}+\tfrac{1}{2}c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega\beta}c_{\Omega\beta}+\tfrac{1}{2}c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega\beta}c_{\Omega\alpha}-\tfrac{1}{2}c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega\alpha}c_{\Omega\alpha}-\tfrac{1}{2}c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega\beta}c_{\Omega\beta})$

Quartet excited state ($S=\frac{3}{2}$, $M_S=\frac{1}{2}$)

$C^\dagger_{m\nu}(10) = 1/\sqrt{3}\,(c^\dagger_{m\alpha}c_{\nu\alpha}-c^\dagger_{m\beta}c_{\nu\beta}-c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega\beta}c_{\Omega\alpha})$

TABLE II. A matrix formulas for the doublet $|$(closed shell)$\,\Omega\alpha\rangle$ ground state.

Doublet matrices

1. $A_{(\Omega\text{-}H1),(\Omega\text{-}H2)} = \delta_{H1H2}(\epsilon_\Omega-\epsilon_{H1}+V_{\Omega\Omega\Omega\Omega})-V_{H1\Omega H2\Omega}+\frac{1}{2}V_{H1H2\Omega\Omega}$
2. $A_{(P1\text{-}\Omega),(\Omega\text{-}H2)} = -V_{H2P1\Omega\Omega}$
3. $A_{(P1\text{-}\Omega),(P2\text{-}\Omega)} = \delta_{P1P2}(\epsilon_{P1}-\epsilon_\Omega)$
4. $A_{1(P1\text{-}H1),(\Omega\text{-}H2)} = 1/\sqrt{2}\,(-\delta_{H1H2}V_{P1\Omega\Omega\Omega}-2V_{H1H2P1\Omega}+V_{H1P1H2\Omega})$
5. $A_{1(P1\text{-}H1),(P2\text{-}\Omega)} = 1/\sqrt{2}\,(\delta_{P1P2}V_{H1\Omega\Omega\Omega}+2V_{H1P2P1\Omega}-V_{H1P1\Omega P2})$
6. $A_{1(P1\text{-}H1),1(P2\text{-}H2)} = \delta_{H1H2}\delta_{P1P2}(\epsilon_{P1}-\epsilon_{H1})+\delta_{H1H2}\times(V_{P1\Omega P2\Omega}-\frac{1}{2}V_{P1P2\Omega\Omega})+2V_{H1H2P1P2}-V_{H1P1H2P2}$
7. $A_{2(P1\text{-}H1),(\Omega\text{-}H2)} = \sqrt{3/2}\,(V_{H1P1H2\Omega}-\delta_{H1H2}V_{P1\Omega\Omega\Omega})$
8. $A_{2(P1\text{-}H1),(P2\text{-}\Omega)} = \sqrt{3/2}(V_{H1P1\Omega P2}-V_{H1\Omega\Omega\Omega}\delta_{P1P2})$
9. $A_{2(P1\text{-}H1),1(P2\text{-}H2)} = \sqrt{3}/2(\delta_{H1H2}V_{P1P2\Omega\Omega}-\delta_{P1P2}V_{H1H2\Omega\Omega})$
10. $A_{2(P1\text{-}H1),2(P2\text{-}H2)} = \delta_{H1H2}\delta_{P1P2}(\epsilon_{P1}-\epsilon_{H1})+\delta_{H1H2}\times(V_{P1\Omega P2\Omega}+\frac{1}{2}V_{P1P2\Omega\Omega})+\delta_{P1P2}V_{H1H2\Omega\Omega}-V_{H1P1H2P2}$

Quartet matrices

1. $A_{(P1\text{-}H1),(P2\text{-}H2)} = \delta_{P1P2}\delta_{H1H2}(\epsilon_{P1}-\epsilon_{H1})+\delta_{H1H2}(V_{P1\Omega P2\Omega}-V_{P1P2\Omega\Omega})-\frac{1}{2}\delta_{P1P2}V_{H1H2\Omega\Omega}-V_{H1P1H2P2}$

B. Open shell triplet

The ground state is $|$(closed shell)$\,\Omega_1\alpha\Omega_2\alpha\rangle$, where Ω_1 and Ω_2 may be degenerate. For this case the Hamilto-

TABLE III. B matrix formulas for the doublet $|$(closed shell)$\Omega\alpha\rangle$ ground state.

Doublet matrices

1. $B_{(\Omega\text{-}H1),(\Omega\text{-}H2)} = 0$
2. $B_{(P1\text{-}\Omega),(\Omega\text{-}H2)} = -\frac{3}{2} V_{H2P1\Omega\Omega}$
3. $B_{(P1\text{-}\Omega),(P1\text{-}\Omega)} = 0$
4. $B_{1(P1\text{-}H1),(\Omega\text{-}H2)} = \sqrt{2}\,(-V_{H1H2P1\Omega} + \frac{1}{2} V_{H1H2\Omega P1})$
5. $B_{1(P1\text{-}H1),(P2\text{-}\Omega)} = \sqrt{2}\,(V_{H1P2P1\Omega} - \frac{1}{2} V_{H1P1P2\Omega})$
6. $B_{1(P1\text{-}H1),1(P2\text{-}H2)} = 2V_{H1H2P1P2} - V_{H1H2P2P1}$
7. $B_{2(P1\text{-}H1),(\Omega\text{-}H2)} = \frac{1}{2}\sqrt{3/2}\, V_{H1H2\Omega P1}$
8. $B_{2(P1\text{-}H1),(P2\text{-}\Omega)} = \frac{1}{2}\sqrt{3/2}\, V_{H1P1P2\Omega}$
9. $B_{2(P1\text{-}H1),1(P2\text{-}H2)} = 0$
10. $B_{2(P1\text{-}H1),2(P2\text{-}H2)} = -V_{H1H2P2P1}$

Quartet matrices

1. $B_{(P1\text{-}H1),(P2\text{-}H2)} = -\sqrt{2/3}\, V_{H1H2P2P1}$

nian is

$$\mathcal{H} = \sum_i \epsilon_i (c_{i\alpha}^\dagger c_{i\alpha} + c_{i\beta}^\dagger c_{i\beta}) + \sum_{ij}\Big(\sum_\nu (\tfrac{1}{2} V_{i\nu\nu j} - 2V_{i\nu j\nu}) + \sum_\Omega [(b - \tfrac{1}{2}) V_{i\Omega\Omega j} - V_{i\Omega j\Omega}] - \sum_p \tfrac{1}{2} V_{ippj}\Big)(c_{i\alpha}^\dagger c_{j\alpha} + c_{i\beta}^\dagger c_{j\beta})$$
$$+ \frac{1}{2}\sum_{ijkl} V_{ijkl}(c_{i\alpha}^\dagger c_{k\alpha} + c_{i\beta}^\dagger c_{k\beta})(c_{j\alpha}^\dagger c_{l\alpha} + c_{j\beta}^\dagger c_{l\beta}), \qquad (26)$$

where

$b = 1$ when i and j are each either open shell or virtual,

$b = 0$ when i or j is open and the other is closed,

$b = \frac{1}{2}$ all other cases.

$$\epsilon_\gamma = h_{\gamma\gamma} + \sum_\nu (2J_{\gamma\nu} - K_{\gamma\nu}) + \frac{1}{2}\sum_\Omega (2J_{\Omega\gamma} - K_{\Omega\gamma}), \qquad (27)$$

$$\epsilon_\Omega = h_{\Omega\Omega} + \sum_\nu (2J_{\nu\Omega} - K_{\nu\Omega}) + \sum_\Omega (J_{\Omega\Omega} - K_{\Omega\Omega}), \qquad (28)$$

$$\epsilon_m = h_{mm} + \sum_\nu (2J_{\nu m} - K_{\nu m}) + \sum_\Omega (J_{\Omega m} - K_{\Omega m}). \qquad (29)$$

The various possible excitations are shown in Fig. 3. Ω_1 and Ω_2 are not degenerate except in g, since the same kinds of excitations are present for the lowest triplet excited state of a closed shell molecule. Type g excitations are not included if Ω_1 and Ω_2 are not degenerate. For excitations of type e there are three triplets and two singlets, only one of the triplets is generated by a one-body operator. Type f excitations are for the different

TABLE IV. R values for the doublet $|$(closed shell)$\Omega\alpha\rangle$ ground state.

$R_{(\Omega\text{-}H1)} = 1.0$

$R_{(P1\text{-}\Omega)} = -1.0$

$R_{1(P1\text{-}H1)} = -\sqrt{2}$

$R_{2(P1\text{-}H1)} = 0$

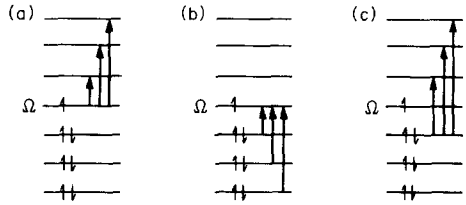

FIG. 2. Possible excitations for the simple doublet. The figure on the right includes the possibility of spin flipping of the electron in the $\Omega\alpha$ spin orbital.

possible states for the ground state orbital occupancy if Ω_1 and Ω_2 are degenerate, e.g., the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states in O_2.

The p-h operators and R values are given in Tables V and VI. The p-h excitation operators for the singlet manifold are appropriate for the $M_S = 0$ ground state while for the triplet (dipole allowed) manifold p-h excitation operators are for the $M_S = 1$ ground state. These formulas do not apply if Ω_1 and Ω_2 are nondegenerate or if there is one or more additional orbitals degenerate with Ω_1 and Ω_2, e.g., carbon atom. However, these cases involve only minor modifications and are no more difficult. The formula list for the A and B matrices is lengthy and is not included. The formulas are available upon request from the authors.

IV. APPLICATIONS

A. Lithium

Lithium atom provides the simplest case for the doublet open shell formulation of Sec. III. The basis set used consists of 10s and 8p contracted Gaussian functions. The results for this calculation along with experimental and Hartree–Fock results are given in Table VII.

Since the low-lying transitions in Li principally are $2s \rightarrow ns$, np there is little change in the correlation energy upon excitation. Hence, the TDA and RPA results are almost identical to three figure accuracy. This agrees with the Hartree–Fock calculations of Goddard[14] where no correlation effects are included. The TDA and RPA energies and oscillator strengths agree well with experiment.

The Thomas–Reiche–Kuhn sum rule, i.e.,

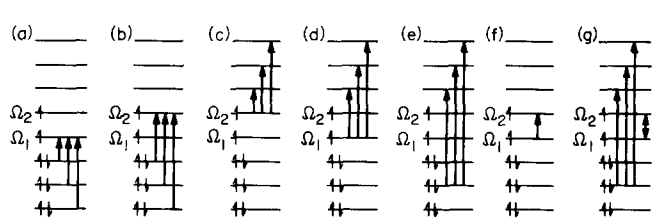

FIG. 3. Possible excitations of the triplet $|$(closed shell) $\Omega_1\alpha\Omega_2\alpha\rangle$ ground state. e includes possible spin flipping in the open shell. f includes different open shell states for the same orbital occupancy if Ω_1 and Ω_2 are degenerate. g is included only for degenerate Ω_1 and Ω_2.

TABLE V. Spherical tensor p-h operators for the triplet $|$(closed shell)$\Omega_1\Omega_2\rangle$ ground state. Ω_1 and Ω_2 are degenerate.

Triplet excited states, $|$(closed shell)$\Omega_1\alpha\Omega_2\alpha\rangle$ ground state

a. $C^\dagger_{\Omega_1\nu}(00) = -c^\dagger_{\Omega_1\alpha}c_{\nu\alpha} - c^\dagger_{\Omega_1\beta}c_{\nu\beta}$

b. $C^\dagger_{\Omega_2\nu}(00) = c^\dagger_{\Omega_2\alpha}c_{\nu\alpha} + c^\dagger_{\Omega_2\beta}c_{\nu\beta}$

c. $C^\dagger_{m\Omega_2}(00) = c^\dagger_{m\alpha}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\Omega_2\beta}$

d. $C^\dagger_{m\Omega_1}(00) = -c^\dagger_{m\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\beta}c_{\Omega_1\beta}$

e. ${}_1C^\dagger_{m\nu}(00) = 1/\sqrt{2}(c^\dagger_{m\alpha}c_{\nu\alpha} + c^\dagger_{m\beta}c_{\nu\beta})$

f. ${}_2C^\dagger_{m\nu}(00) = \frac{1}{2}((c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\beta} + c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\alpha}$
$+ c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\beta}) + \frac{1}{2}(-c^\dagger_{m\alpha}c_{\nu\alpha}c_{\Omega_2\beta}c_{\Omega_2\beta}$
$- c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\alpha} + c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta})$
$+ \frac{1}{2}(-c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta}))$

${}_3C^\dagger_{m\nu}(00) = 1/\sqrt{2}((c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\beta}$
$- c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\alpha} - c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\beta})$
$+ \frac{1}{2}(-c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta} - c^\dagger_{m\pi}c_{\nu\beta}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\alpha}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta})$
$- \frac{1}{2}(-c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta}))$

g. ${}_4C^\dagger_{m\nu}(00) = 1/\sqrt{2}(C^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\beta}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta} + c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_1\alpha}$
$+ c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\beta} + c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta})$

${}_5C^\dagger_{m\nu}(00) = 1/\sqrt{2}(c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\beta}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta} - c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_1\alpha}$
$- c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta})$

Singlet excited states, $|$(closed shell)$\frac{\Omega_1\alpha\Omega_2\beta + \Omega_1\beta\Omega_2\alpha}{\sqrt{2}}\rangle$ ground state

a. $C^\dagger_{\Omega_1\nu}(10) = c^\dagger_{\Omega_1\alpha}c_{\nu\alpha} - c^\dagger_{\Omega_1\beta}c_{\nu\beta}$

b. $C^\dagger_{\Omega_2\nu}(10) = -c^\dagger_{\Omega_2\alpha}c_{\nu\alpha} + c^\dagger_{\Omega_2\beta}c_{\nu\beta}$

c. $C^\dagger_{m\Omega_2}(10) = c^\dagger_{m\beta}c_{\Omega_2\beta} - c^\dagger_{m\alpha}c_{\Omega_2\alpha}$

d. $C^\dagger_{m\Omega_1}(10) = c^\dagger_{m\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\beta}c_{\Omega_1\beta}$

e. ${}_2C^\dagger_{m\nu}(10) = 1/\sqrt{6}(c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha} - c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\alpha}$
$+ c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\beta} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha}$
$- c^\dagger_{m\alpha}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\alpha} + c^\dagger_{m\beta}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\beta})$

${}_3C^\dagger_{m\nu}(10) = 1/2\sqrt{2}\ (c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\alpha}$
$+ c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta})$

f. ${}_1C^\dagger_{\Omega_2\Omega_1}(10) = \frac{1}{2}(c^\dagger_{\Omega_1\beta}c_{\Omega_2\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\beta} - c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta}$
$+ c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha} - c^\dagger_{\Omega_1\alpha}c_{\Omega_2\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\alpha}$
$- c^\dagger_{\Omega_2\beta}c_{\Omega_1\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\beta} + c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta}$
$- c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\alpha} + c^\dagger_{\Omega_2\alpha}c_{\Omega_1\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\alpha})$

${}_2C^\dagger_{\Omega_2\Omega_1}(10) = \frac{1}{2}(c^\dagger_{\Omega_1\beta}c_{\Omega_2\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\beta} - c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\beta}$
$+ c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_1\alpha} - c^\dagger_{\Omega_1\alpha}c_{\Omega_2\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_1\alpha}$

TABLE V (*Continued*)

Singlet excited states, $|$(closed shell)$\frac{\Omega_1\alpha\Omega_2\beta + \Omega_1\beta\Omega_2\alpha}{\sqrt{2}}\rangle$ ground state

$+ c^\dagger_{\Omega_2\beta}c_{\Omega_1\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\beta} - c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\beta}$
$+ c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_2\alpha} - c^\dagger_{\Omega_2\alpha}c_{\Omega_1\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_2\alpha})$

g. ${}_4C^\dagger_{m\nu}(10) = 1/2\sqrt{2}\ (c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha} + c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta}$
$- c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha})$

${}_5C^\dagger_{m\nu}(10) = 1/2\sqrt{2}\ (c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha}$
$+ c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\beta}c_{\Omega_2\beta} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_1\alpha}c_{\Omega_2\alpha} - c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta}$
$+ c^\dagger_{m\beta}c_{\nu\beta}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha} - c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\beta}c_{\Omega_1\beta} + c^\dagger_{m\alpha}c_{\nu\alpha}c^\dagger_{\Omega_2\alpha}c_{\Omega_1\alpha})$

$$S(0) = \sum_\lambda f_{0\lambda} \tag{30}$$

in the TDA and RPA are 3.03 and 2.83, respectively. The exact value is of course 3. The frequency independent polarizability $S(-2) = \Sigma(f_{o\eta}/\omega^2_{o\eta})$ is $169a_0^3$ and $170a_0^3$ in the TDA and RPA, respectively, compared to the variational estimate of Stacey and Dalgarno[15] of $163.1a_0^3$.

The results for Li are in good agreement with experiment primarily because the low-lying lithium atom transitions involve predominantly $2s \rightarrow ns$, np transitions. The orbital energy of the $1s$ electrons is -2.478 a.u. and the $2s$ electron -0.196 a.u. For cases where there are several valence electrons in addition to the open shell electron, e.g., H_2CO^+, the TDA and RPA results will differ and agreement with experiment will not in general be as good. As in the closed shell cases,[3] higher order schemes should give close experimental agreement.

We have also done an additional calculation where only one-body p-h operators are included in the excitation operator, i.e., formulas (7)–(10) in Tables II and III are set equal to zero. The resulting TDA and RPA results are identical to those of Table VII. This is because the two-body p-h excitation operators describe excitations from the closed $(1s)^2$ shell and hence are relatively unimportant.

B. O_2

The ground state Hartree–Fock orbital occupancy of O_2 is

TABLE VI. R values for the triplet $|$(closed shell)$\Omega_1\alpha\Omega_2\alpha\rangle$ ground state.

$R_{(H1\text{-}\Omega1)} = -1.0$
$R_{(H1\text{-}\Omega2)} = 1.0$
$R_{(P1\text{-}\Omega2)} = 1.0$
$R_{(P1\text{-}\Omega1)} = -1.0$
$R_{1(P1\text{-}H1)} = \sqrt{2}$
$R_{2(P1\text{-}H1)} = 0.0$
$R_{3(P1\text{-}H1)} = 0.0$
$R_{4(P1\text{-}H1)} = 0.0$
$R_{5(P1\text{-}H1)} = 0.0$

TABLE VII. OSTDA and OSRPA results for Li. Basis set is [10s 8p].

State		Exp[a] ΔE (eV)	Exp[b] f	HF[c] ΔE (eV)	TDA ΔE (eV)	TDA f	RPA ΔE (eV)	RPA f
$2\,^2P$	$1s^2 2p$	1.85	0.753	1.84	1.83	0.758	1.83	0.758
$3\,^2S$	$1s^2 3s$	3.37	···	3.33	3.33	···	3.33	···
$3\,^2P$	$1s^2 3p$	3.84	0.006	3.80	3.80	0.004	3.80	0.004
$4\,^2S$	$1s^2 4s$	4.34	···	···	4.30	···	4.30	···
$4\,^2P$	$1s^2 4p$	4.52	0.005	···	4.50	0.003	4.50	0.004

[a] *Atomic Energy Levels*, compiled by C. E. Moore, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D.C., 1947).
[b] Compiled by T. C. Caves and A. Dalgarno, J. Quant. Spectrosc. Radiat. Transfer 12, 1539 (1972).
[c] Reference 14.

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_{ux})^2(1\pi_{uy})^2 1\pi_{gx} 1\pi_{gy}$$

leading to $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$ states. $^3\Sigma_g^-$ is the ground state.

The basis set is the $\langle 4s\,3p\rangle$ set of contracted Gaussians of Dunning.[16] All calculations were done at the ground state experimental geometry of 1.207 Å. The TDA and RPA results for low-lying transitions are given in Table III. Columns 7 and 8 are RPA results where no two-body terms were included. No matrix larger than 50×50 was diagonalized.

Even though there are large discrepancies between these results and the results of large CI calculations and experiment, there are several interesting features. Most striking is the excellent agreement of the transition moment of the Schumann–Runge transition $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$ regardless of approximation. Experiment gives 0.193.[17] For the other allowed transition, $X^3\Sigma_g^- \rightarrow {}^3\Pi_u$, the calculated transition moment is very small and the excitation energy is 10.58 eV. Experimentally this transition may have been observed at 9.97 or 10.29 eV.[18] The potential curve may be theoretically dissociative.[19]

Both the triplet and singlet manifolds can give instabilities (imaginary solutions). We show in the appendix that since Brillouin's theorem is not satisfied for restricted Hartree–Fock ground states, instabilities do not necessarily imply that there is another approximation to the ground state, perhaps of broken symmetry, which lies below the approximate ground state used here. In fact, instabilities imply nothing about the ground state and may occur for an excited state of any spin multiplicity.

For most of the other transitions both the TDA and RPA results are low, e.g., $C^3\Delta_u$, $A^3\Sigma_u^+$, $c^1\Sigma_u^-$. This indicates that we are describing the excited state much better than the ground state. This could be easily corrected by extending the RPA to higher orders. In the HRPA[1] the ground state correlation coefficients are calculated explicitly. Inclusion of double excitation type operators in the closed shell EOM then gives excitation energies in general excellent experimental agreement.[2,3]

A simpler procedure that will improve excitation energies is a multiconfigurational random phase approximation approach.[20] In this procedure after a RHF calculation is done on the ground state, a limited number of correlation coefficients are calculated explicitly by a small configuration interaction calculation. Excitations can be from or to the correlated orbitals in addition to ordinary excitations from the strictly closed shell configuration.[21] For example in ethylene we could assume the ground state to be approximately

$$|0\rangle \simeq K_0 |\mathrm{HF}\rangle + K_1 \left| \begin{matrix} \pi^* & \bar{\pi}^* \\ \pi & \bar{\pi} \end{matrix} \right\rangle . \tag{31}$$

K_0 and K_1 are determined from a 2×2 CI calculation. In addition to excitations from the HF ground state there can be excitations from the π^* orbitals and to the π orbitals. The MCRPA can also be used for extending excited state potential curves to large internuclear distances.

The MCRPA or HRPA approach is necessary in O_2

TABLE VIII. Low lying transitions in O_2.

State	Principal transition	TDA ΔE (eV)	TDA f	RPA ΔE (eV)	RPA f	RPA (one-body) ΔE(eV)	RPA (one-body) f	ΔE (eV) CI	ΔE (eV) Exp[d]
$C^3\Delta_u$	$1\pi_u \rightarrow 1\pi_g$	3.91		a		a		6.41[b]	6.1
$A^3\Sigma_u^+$	$1\pi_u \rightarrow 1\pi_g$	4.05		a		a		6.54[b]	6.1
$^3\Pi_g$	$3\sigma_g \rightarrow 1\pi_g$	6.42		5.74		6.37			8.20[c]
$B^3\Sigma_u^-$	$1\pi_u \rightarrow 1\pi_g$	7.67	0.207	5.81	0.196	6.26	0.201	9.51[b]	8.3
$^3\Pi_u$	$1\pi_g \rightarrow 3\sigma_u$	10.80	0.0003	10.58	0.001	10.92	0.0006	11.34[c]	9.97 or 10.29
$a^1\Delta_g$		0.72		0.59					0.98
$b^1\Sigma_g^+$		2.15		2.09					1.63
$c^1\Sigma_u^-$	$1\pi_u \rightarrow 1\pi_g$	3.64		a		a		6.19[b]	6.1
$1\Pi_g$	$3\sigma_g \rightarrow 1\pi_g$	8.19		7.74		8.40		9.65[c]	
$^1\Delta_u$	$1\pi_u \rightarrow 1\pi_g$	10.11		9.71		12.81		14.53[b]	
$^1\Pi_u$	$1\pi_g \rightarrow 3\sigma_u$	12.74		12.57		12.93		16.36[c]	

[a] RPA instability.
[b] Reference 22.
[c] H. Schaefer and F. Harris, J. Chem. Phys. 48, 4946 (1968).
[d] Reference 18.

for this basis set. This can be seen by examining the A and B matrices for ${}^3\Sigma_u^-$ states. The smallest on-diagonal elements for the A matrix is 0.310 a.u. for $\pi_u \rightarrow \pi_g$ transitions. The largest elements in the B matrix are off diagonal and are 0.165 and 0.172. They correspond to deexcitations from the $(1\pi_u)^2(1\pi_g)^4$ and $(1\pi_u)^3(1\pi_g)^3(3\sigma_g \rightarrow 3\sigma_u)$ components of the ground state respectively. We have found for closed shell RPA calculations that when B matrix elements are of similar magnitude as the on-diagonal A matrix elements the RPA approximation begins to break down. Morokuma and Konishi[22] in large scale CI calculations report a contribution to the $X^3\Sigma_g^-$ ground state of 1.5% for configuration $(1\pi_u)^2(1\pi_g)^4$ and 2.0% for $(1\pi_u)^3(1\pi_g)^3(3\sigma_g \rightarrow 3\sigma_u)$ states.

The discrepancies between the RPA including only one-body p-H operators (columns 7 and 8) and the RPA with open shell spin flip operators (columns 5 and 6) indicate that especially for excitation energies certain classes of two-body operators are important and should be included

$S(0)$ for the TDA is 7.19 and 5.79 for the RPA. $\alpha_\perp$, the perpendicular component of the frequency independent polarizability, is $2.78a_0^3$ in the TDA and $2.71a_0^3$ in the RPA. $\alpha_\parallel$, the parallel component, is $18.6a_0^3$ in the TDA and $21.5a_0^3$ in the RPA. Langhoff[23] gives the perpendicular component as $8.17a_0^3$ and the parallel component as $15.5a_0^3$.

V. CONCLUSIONS

We have derived an open shell random phase approximation starting from a restricted Hartree–Fock ground state. Using an equations of motion approach, we choose p-h excitation operators which are one-body and certain types of two-body spherical tensors which when operating on the ground state generate configurations which are eigenfunctions of $\hat{S}^2$ and $\hat{M}_S$. We have developed an automated procedure to calculate A and B matrix element formulas of the equations of motion which are needed in the OSTDA and OSRPA solutions for several different open shells with little more work than for closed shells. The matrices separated by spin and spatial symmetry are usually no more than 50×50.

We report results for two calculations using two different open shell ground states. As expected Li results agree quite well with experiment. O_2 results do not except for oscillator strengths. These results are due to correlation effects manifested in the B matrix elements that are large with respect to on-diagonal A matrix elements.

Even though for a case as complicated as O_2 the OSRPA fails to give a good description of the low-lying excitation spectra, we believe that for certain purposes useful information can be obtained from a limited calculation. For example, in those applications where one needs all the excitation energies and transition densities as a discrete approximation to the complete spectrum the RPA results are usually sufficient. These applications include the frequency-dependent polarizabilities and their related applications to photoionization and photodetachment cross sections and approximate optical potentials for electron–molecule scattering. It is clear from a comparison of the closed and open-shell RPA formulations that the open-shell optical potential is not a simple extension of the closed shell case. The resulting RPA vectors can also be used to calculate transition moments between excited states.[5] We can use the formalism to directly calculate excitation energies starting from the lowest triplet excited state of a closed shell system.

Furthermore, using the equations of motion, Eq. (3), it is straightforward although somewhat tedious to extend the method to higher orders. These ideas are being actively investigated in this laboratory. We can expect good agreement with experiment as with closed shell EOM calculations.

ACKNOWLEDGMENT

The authors would like to thank Poul Jørgensen for many stimulating discussions on the random phase approximation.

APPENDIX

Analogously to Thouless[24] we examine instabilities in the open shell RPA when $|0\rangle$ is approximated by the restricted Hartree–Fock ground state.

Let $|T\rangle$ be a state generated by the anti-Hermitian operator e^T,

$$|T\rangle = e^{\hat{T}}|\rangle \tag{A1}$$

where $\hat{T}$ is single-particle–hole form with the additional two-body operators which can flip the open shell spin and excite. It can easily be shown[25] that

$$\langle T|\hat{H}|T\rangle = \langle|H|\rangle + \langle|[H, T]|\rangle + \tfrac{1}{2}\langle|[T^\dagger, H, T]|\rangle + \cdots . \tag{A2}$$

For closed shell systems, the Hartree–Fock variational condition is that the energy be stationary with respect to all single excitations, that is

$$\langle|[H, T]|\rangle = 0 . \tag{A3}$$

Equation (A3) is known commonly as Brillouin's theorem.

If Eq. (A3) holds, then for the Hartree–Fock solution to be a true minimum

$$\langle|[T^\dagger, H, T]|\rangle \geq 0 . \tag{A4}$$

This implies that the RPA matrix is positive definite, i.e., has only positive or zero eigenvalues and that the RPA energy ω_λ can never be complex. Of course, for finite basis set expansions for closed shell Hartree–Fock ground states we can obtain imaginary solutions of the RPA matrix equations for triplet excited states. This means that a state with lower energy which is not necessarily an eigenfunction of $\hat{S}^2$ can be found.[26]

For a restricted HF open shell ground state in general, only a limited form of Brillouin's theorem is satisfied,[27] that is

$$\langle|[H, T]|\rangle \neq 0 \tag{A5}$$

even if T is restricted to purely one body operators. Hence, the RPA matrix is not necessarily positive definite. Thus, instabilities in the RPA solutions do not indicate that a lower ground state can be found. We expect for open shell RPA calculations when a restricted

HF ground state is used as an approximation to $|0\rangle$ fundamental instabilities in any spin manifold which cannot be eliminated by increasing the size of the basis set but may be only by going to higher order approximations.

*Supported by a grant from the National Science Foundation.
†Contribution No. 5034.

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