APPLICATIONS OF THE EQUATIONS OF MOTION METHOD

Thesis by

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ABSTRACT

Part I

In Part I several applications of the equations of motion method for closed shell around states are discussed. The equations of motion method is used to study the excitation energies and intensities of formaldehyde, water, and CH^+. A formalism is developed for studying intraexcited state transition densities, and applications are made to He and N_2. This section is composed of three published manuscripts and two manuscripts submitted for publication.

In H_2CO the calculated excitation energies and oscillator strengths agree well with experiment and suggest explanations for some unusual features recently observed in the optical absorption and electron scattering spectrum in the vacuum ultraviolet.

To explain the inelastic feature at 4.5 eV in the spectrum of water and to study its spectrum in some detail, several calculations on the excited states of water using the equations of motion method are made. We conclude that the calculated vertical excitation energy of 6.9 eV for the $^3B_1$ state corresponds to the strong feature at 7.2 eV observed in low-energy electron scattering spectrum. The 4.5 eV inelastic process almost certainly does not correspond to a vertical excitation of water at the ground state geometry. The other excitation energies and oscillator strengths agree well with experiment.

The equations of motion method is used to study the $X'\Sigma^+$-$A'\Pi$ system in CH^+. In a computationally simple scheme, these calculations, which were done in modest sized basis sets, provide transition moments and oscillator strengths that agree with the best CI calculations to date.

An approximation for transition moments between excited states consistent with the approximations and assumptions normally used to obtain transition moments between the ground and excited states in the random phase approximation and its higher order approximations is derived. The result is applied to the calculation of the photoionization cross sections of the 2^3S and 2'S metastable states of helium by a numerical analytical continuation of the frequency dependent polarizability. The procedure completely avoids the need for continuum basis functions. The cross sections agree well with the results of other calculations. We also predict an accurate two-photon decay rate for the 2'S metastable state of helium. The entire procedure is immediately applicable to several problems involving photoionization of metastable states of molecules.

We report the transition moments between the excited states of molecular nitrogen including their dependence on internuclear distance. These moments are calculated non-empirically using a many-body approach --the equations of motion method. These results suggest that it may be simpler to calculate these transition moments and their variation with internuclear distance rather than to attempt to extract this information from available experimental intensity data.

Part II

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. Application 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.

Part III

A simple method for directly calculating ionization potentials and electron affinities is discussed. Formulas are given through third order in interaction matrix elements and described in detail. Results are presented for the ionization potentials of He, N_2, and OH^- using several different approximations.

Appendix

A computer program General Mating XVI written in Fortran IV, which has the ability to derive formulas for second quantized excitation operators and Hamiltonians or various one-body and two-body operators using correlated or uncorrelated Hartree-Fock ground states, is described and listed. The program uses Wick's theorem to expand strings of electron creation and desctruction operators.

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Science

Man, introverted man, having crossed
In passage and but a little with the nature of things this
latter century
Has begot giants; but being taken up
Like a maniac with self-love and inward conflicts cannot
manage his hybrids.
Being used to deal with edgeless dreams,
Now he's bred knives on nature turns them also inward:
they have thirsty points though.
His mind forbodes his own destruction;
Actaeon who saw the goddess naked among leaves and his
hounds tore him.
A little knowledge, a pebble from the shingle,
A drop from the oceans: who would have dreamed this infinitely
little too much?

... Robinson Jeffers

Part I

Application of the Equations of Motion Method for Excitation Energies to Molecules with Closed Shell Ground States

(A)

Equations of Motion Method: Excitation Energies and Intensities in Formaldehyde

I. INTRODUCTION

In recent papers[1, 2] we have discussed the equations of motion method as an approach for direct calculation of the properties of physical interest in spectroscopy, e.g., transition frequencies, intensities and scattering cross sections. By using a theory specifically designed for studying these relative properties one can avoid many of the difficulties involved in obtaining accurate values for absolute quantities such as the total energies. We have derived several approximations to the solution of the equations of motion for the operator O_λ^+ which generates the state $|\lambda\rangle$ from the ground state $|0\rangle$. In the equations of motion method the approximation which includes single particle-hole (1p-1h) and two particle-two hole (2p-2h) components[3] in O_λ^+, referred to as the (1p-1h) + (2p-2h) approximation, gives results for transition frequencies and intensities in N_2, CO, C_2H_4,[2] C_6H_6,[4] and CO_2[5] in good agreement with experiment.

In this paper we present results on the excited states of formaldehyde. These results include transition energies and oscillator strengths for transitions below 2000 Å which allow us to explain some unusual features recently observed in the optical absorption[6] and electron scattering spectrum.[7] These studies were stimulated by the recent discovery of formaldehyde in interstellar dust clouds[8] and provided accurate absorption coefficients between 2400 and 912 Å. The absorption coefficients in the vacuum ultraviolet are large and hence absorption of photons in this spectral region is important in determining the fate of formaldehyde in the interstellar radiation field. Some of the unusual features in the spectrum that our results can explain include the prediction of a ${}^1B_1(\sigma\rightarrow\pi^*)$ state at 9.2 eV with a very low oscillator strength and equal oscillator strengths for the transitions to the ${}^1B_2$ $(2b_23pa_1)$ and ${}^1B_2(2b_24pa_1)$ states. The calculated f-value for each transition is 0.04 compared with the observed value of 0.03. This distribution of intensities is unusual for a Rydberg series. Another interesting feature of the spectrum is the apparent absence of any band which could be related to the $\pi\rightarrow\pi^*$ valence transition. Our results show a transition to a ${}^1A_1(\pi, \pi^*)$ state at 10.10 eV with primarily intra-valence character but with a f-value of only 0.10. From the characteristics of this state there is clearly an interaction between the neighboring ${}^1A_1(2b_2npb_2)$ states and the π^* valence state as discussed by Mentall et al.[6]

In the next section we give a very brief outline of our method. Section III discusses the results of our calculations with different basis sets designed to study specific features in the observed spectrum. Section IV gives a summary of our conclusions.

II. THEORY

We have discussed the equations of motion method in recent papers[1, 3] and we will give only a very brief summary of the theory in this section. It can be shown that the operator O_λ^+ which generates an excited state $|\lambda\rangle$ from the ground state, i.e., $|\lambda\rangle = O_\lambda^+|0\rangle$, is exactly a solution of the equation of motion[9]

$$\langle 0|[\delta O_\lambda, H, O_\lambda^+]|0\rangle = \omega_\lambda \langle 0|[\delta O_\lambda, O_\lambda^+]|0\rangle \qquad (1)$$

where δO_λ^+ is a variation of the amplitudes specifying O_λ^+ and ω_λ the excitation frequency. The double commutator is defined as

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

We have derived various approximations to the solution of Eq. (1).[1, 3] If O_λ^+ is restricted to single particle-hole (1p-1h) form Eq. (1) becomes

$$\begin{bmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B}^* & -\underset{\sim}{A}^* \end{bmatrix} \begin{bmatrix} \underset{\sim}{Y}(\lambda) \\ \underset{\sim}{Z}(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} \underset{\sim}{D} & O \\ O & \underset{\sim}{D} \end{bmatrix} \begin{bmatrix} \underset{\sim}{Y}(\lambda) \\ \underset{\sim}{Z}(\lambda) \end{bmatrix} \tag{3}$$

where the elements of $\underset{\sim}{A}$, $\underset{\sim}{B}$, and $\underset{\sim}{D}$ are defined in Ref. (1). We have also shown that the theory including 2p-2h amplitudes in $O_\lambda{}^+$ is equivalent to a renormalized 1p-1h theory. We have derived an approximate perturbative scheme for solving these equations including 1p-1h and 2p-2h amplitudes. Unless we state otherwise the results of the equations of motion method will always refer to this approximation, i.e., 1p-1h + 2p-2h approximation.

III. RESULTS

The first step in an equations of motion calculation is to carry out a self-consistent field calculation on the ground state of the molecule. These SCF orbitals form the particle-hole basis. The ground state electron configuration of formaldehyde is

$$1a_1{}^2 2a_1{}^2 3a_1{}^2 4a_1{}^2 1b_2{}^2 5a_1{}^2 1b_1{}^2 2b_2{}^2 . \tag{4}$$

These calculations were done at the currently accepted ground state experimental geometry.[10] In these calculations we used a [3s2p/1s] valence basis of contracted Gaussian functions[2] to which we added diffuse Gaussian basis functions on the atomic centers and at the center of charge. We have found that such a basis can adequately describe the intravalence transitions and also transitions to the first members of the Rydberg series. The basis must also contain these Rydberg components so as to study the valence-Rydberg mixing probably responsible for some features in the formaldehyde spectrum. Since the equations of motion method involves commutators that lead to operators of low rank, we can expect a basis with a small number of valence components to be adequate for carrying out calculations on most excited states including intravalence transitions. The diffuse components of our basis includes an s function with an exponent of 0.05 on each atomic center, a p function with an exponent of 0.05 on the carbon and oxygen centers, an s function and a set of p functions with an exponent of 0.016 at the center of charge and also a p_x and p_y function with an exponent of 0.005 at the center of charge. In these calculations we truncated the particle basis slightly so as to use available computer programs. The resulting matrices were no larger than of order 30 x 30.

Table I shows the excitation energies fortwelve transitions in formaldehyde along with the oscillator strengths for the seven dipole-allowed transitions. The calculated results listed in the third column agree well with the observed values in the fourth column. The experimental values for transitions to the $^1A_2(n\rightarrow\pi^*)$ and $^3A_2(n\rightarrow\pi^*)$ states are the estimated vertical excitation energies.[11] The $^1A_1\rightarrow{}^3A_1(\pi\rightarrow\pi^*)$ has not been observed experimentally but could probably be seen quite easily in low-energy high-angle electron scattering off formaldehyde.

The calculated excitation energy of 9.2 eV for the $^1A_1 \rightarrow {}^1B_1(\sigma \rightarrow \pi^*)$ transition is close to the value of 9 eV inferred from the observed spectrum by Mentall et al.[6] The oscillator strength of this transition is only 0.002 in agreement with the assignment of weak absorption features between 1340 and 1430 Å (8.7 - 9.4 eV) to the $^1B_1(\sigma \rightarrow \pi^*)$ state. This is the only intravalence transition assigned in the observed spectrum below 2000 Å.

The $^1A_1(\pi \rightarrow \pi^*)$ state is one of the puzzling aspects in the interpretation of the spectrum of formaldehyde. No feature was observed in either the absorption[6] or electron scattering[7] spectrum which could be related to the $\pi \rightarrow \pi^*$ excitation. We predict an excitation energy of 10.1 eV and an f-value of 0.1 for this transition. This state is a valence-like state with some admixture of Rydberg character through its interaction with nearby Rydberg states.[6] For example the change in the average value of $\sum_i (x_i^2 + y_i^2)$ for the transition is about 15 $(\text{a.u.})^2$ which is larger than typical values for pure intravalence transitions, i.e., 2-3 $(\text{a.u.})^2$ but much smaller than the values of 20-50 $(\text{a.u.})^2$ which characterize the first members of Rydberg series. The f-value of 0.1 for this transition is clearly brought about by the mixing of the intravalence $(\pi \rightarrow \pi^*)$ state and the $^1A_1$ Rydberg states with the configurations $(2b_2nb_2)$ and $(1b_1nb_1)$ in the present calculation. This basis does not allow for the mixing of $^1A_1(2b_2ndb_2)$ states since it does not contain ndb_2 functions. From the model calculations of Mentall et al.,[6] we can expect strong mixing between the $\pi \rightarrow \pi^*$ state and the $^1A_1(2b_2ndb_2)$ states. In the valence [3s2p/1s] basis[2] the $^1A(\pi \rightarrow \pi^*)$ state has a large f-value of about 0.4 which decreases due to Rydberg-valence mixing. If the final f-value for this transition does remain close to 0.1 we will not expect to see a strong feature in the absorption since this intensity will be spread over the entire band which can easily be 1 eV wide. Our results show a $^1A_1$ state near the $2b_2$ ionization potential which has a large f-value of 0.2 . This may be an important feature in the spectrum but our present results are insufficient to identify it reliably. We are now carrying out more extensive calculations including the $^1A_1(2b_2\ ndb_2)$ states in order to understand the intensity distribution in the 8-12 eV region. This includes a study of the generalized oscillator strength as a function of the square of the momentum transfer. The presence and position of minima in these oscillator strengths as a function of q^2 should clarify many of these questions.

The other results in Table I are all for Rydberg transitions of the type $2b_2 \rightarrow ns$ and $2b_2 \rightarrow np$. The excitation energies agree well with experiment and the f-values explain some interesting features in the spectrum. The $^1B_2(2b_2\ 3pa_1)$ and $^1B_2(2b_2\ 4pa_1)$ states have observed f-values of 0.032. This is an unusual distribution of intensities for two successive members of a Rydberg series. The calculated f-value of 0.04 for both transitions reproduces the observed distribution of intensity. These f-values are also far greater than the values given by the single-configuration approximation.[6] The observed term value of 2.9 eV for the $^1A_1(n \rightarrow 3pb_2)$ state is larger than the corresponding term value in typical np series, e.g., around 2.4 eV. This is again probably due to the perturbation of this state by the $^1A_1(\pi \rightarrow \pi^*)$ state. The calculated f-value of 0.05 for the $^1A_1(n \rightarrow 3pb_2)$ state is larger than the observed value of 0.017 but here we can expect some redistribution of f-values when $^1A_1(2b_2\ ndb_2)$ states are included. This mixing of the $^1A_1(2b_2ndb_2)$ states can also put the $^1A_1(2b_23pb_2)$ state below the $^1B_2(2b_2\ 3pa_1)$. No experimental f-value was reported for the $^1A_1(2b_24pb_2)$ state but a visual estimate of the absorption coefficients shows that the transition to this state is much less intense than the $^1A_1 \rightarrow {}^1B_2(2b_2\ 4pa_1)$ transition. The calculated f-values agree with this trend. We have also calculated the excitation frequencies to the triplet Rydberg states but these results are not listed in Table I since they are usually within 0.3 eV of the corresponding singlet excitation energies.

We also obtain excitation energies and intensities of transitions to Rydberg states leading to the second ionization potential. These include the $^1B_1(\pi \rightarrow 3s)$ and $^1B_1(\pi \rightarrow 3pa_1)$ states at 11.2 and 12.2 eV's with f-values of 0.06 and 0.02 respectively.

In the fifth column of Table I we list the excitation energies for many of these transitions obtained by the configuration interaction (CI) method. Many of these are results from extensive CI studies involving matrices ranging in order from 150 x 150[12] to 450 x 450.[13] The results agree well with the observed values and with those obtained from the equations of motion method. It is not our purpose to compare the conceptual or computational differences between these two methods. Excitation frequencies and intensities are just two quantities among others which the EOM method is designed to obtain. Other properties include cross sections for processes such as photoionization and electron molecule scattering.[5]

An interpretation of the formaldehyde spectrum in the vacuum ultraviolet requires an understanding of the $^1A(\pi\rightarrow\pi^*)$ state and its perturbation by the adjacent Rydberg states. For this reason we have carried out some additional calculations on this state and others with a different atomic basis. Configuration interaction calculations had previously placed the $^1A(\pi\rightarrow\pi^*)$ state at around 11.4 eV[12, 14] with an f-value of 0.4.[12] However, Whitten[13] recently obtained a vertical excitation energy of 9.90 eV in a very extensive CI calculation involving 468 configurations. This lowering relative to his previous result[14] is partly due to the inclusion of d-type polarization functions in the basis and, more importantly, to an effective inclusion of sigma-pi correlation. To study the behavior of this state in a more flexible valence atomic basis we have done two additional calculations. In the first calculation we used a larger valence [4s3p/2s] basis of contracted Gaussian functions[15] and for the second calculation this basis was augmented by xz, yz, and z^2 d-type polarization functions and diffuse s and p_x functions on the carbon and oxygen centers. The basis of the second calculation has both a larger valence component and the flexibility to reflect valence-Rydberg mixing. We obtained excitation energies of 9.90 and 9.66 eV from the first and second calculation respectively. The f-values are both close to 0.10. These results again indicate the presence of an intravalence $^1A_1(\pi\rightarrow\pi^*)$ state around 9.9 eV.

IV. CONCLUSIONS

We have used the equations of motion method to study the excitation energies and intensities of formaldehyde in the vacuum ultraviolet. This region of the formaldehyde spectrum has only recently been studied experimentally and shows some unusual features.[6] The calculated transition energies and intensities agree well with the observed values and suggest explanations for some of the unusual behavior in the spectrum. In agreement with experiment we see that intensities in the $^1A_1(2b_2npb_2)$ series are normal but very unusual in the $^1B_2(2b_2npa_1)$ series. Another interesting conclusion is the location of a $^1A_1(\pi\rightarrow\pi^*)$ state at around 9.9 eV but with the low f-value of 0.1. This state is being perturbed by valence-Rydberg mixing. The generalized oscillator strength as a function of q^2 will be useful in studying these perturbations quantitatively.

Table I. Excitation Energies and Intensities in Formaldehyde.[a]

State	Main Transition	ΔE[b] (EOM)	ΔE (Obs.)	ΔE (CI)	f (EOM)	f (Obs.)[h]
$^3A_2$	$n \to \pi^*$	3.46	3.54[c]	3.41[e]		
$^1A_2$	$n \to \pi^*$	4.04	3.84[c]	3.81		
$^3A_1$	$\pi \to \pi^*$	5.29	----	5.56		
$^1A_1$	$\pi \to \pi^*$	10.10	----	9.90[f]	0.10	
$^1B_1$	$\sigma \to \pi^*$	9.19	9.0[d]	9.03	0.002	
$^1B_2$	$n \to 3s$	7.28	7.08	7.38	0.02	0.028
$^1B_2$	$n \to 3pa_1$	8.12	8.14	8.39	0.04	0.032
$^1A_1$	$n \to 3pb_2$	8.15	7.97	8.11	0.05	0.017
$^1A_2$	$n \to 3pb_1$	8.35	----	7.99[g]		
$^1A_1$	$n \to 4pb_2$	9.40	9.58		0.004	-----[i]
$^1A_2$	$n \to 4pb_1$	9.47	----			
$^1B_2$	$n \to 4pa_1$	9.55	9.63		0.04	0.032

[a] Vertical excitation energies.

[b] Results from the EOM method in the (1p-1h) + (2p-2h) approximation. All energies in eV's.

[c] Low energy electron impact results of A. Chutjian, Jet Propulsion Laboratory (Pasadena) (to be published).

[d] The next six experimental values are from Ref. 6.

[e] CI calculations of Ref. 13.

[f] Reference 14.

[g] Reference 15.

[h] Reference 7.

[i] Observed to be much weaker than the transition to the $^1B_2(2b_2 4pa_1)$.

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(B)

Assignments in the Electronic Spectrum of Water

I. INTRODUCTION

Despite the importance of the water molecule there is considerable question as to the location, intensities, and nature of transitions to its lower excited electronic states. A recent study by Claydon, Segal, and Taylor[1] which combined available experimental evidence with the suggestions of semiempirical calculations provided a consistent interpretation of the facts known at the time. Even more recently, however, Knoop, Brongersma, and Oosterhoff[2] and Trajmar et al.[3] have reported electron impact spectra of H_2O which raise a serious question as to the nature of the inelastic process observed by many workers at 4.5 eV in H_2O. Despite the fact that the calculation of the excitation energy to the lowest triplet state of a molecule should be straightforward, the calculations reported in the literature[1] all find the $^3B_1$ state to be the lowest excited state of H_2O and to have a vertical excitation energy above 6 eV. Moreover there are no reliable or extensive calculations of the oscillator strengths for the several dipole-allowed transitions below 10 eV. These quantities are needed in the analysis of the relative intensities of several transitions observed in the electron impact spectrum of water.[4]

In view of this discrepancy and the questions raised by recent electron impact spectra of H_2O,[2,3] and in order to provide reliable estimates of the oscillator strengths of several transitions we have carried out an extensive calculation of the excited state manifold of H_2O at the vertical geometry using the equations-of-motion method.[5] One of our conclusions from this study is that the vertical excitation energy to the

$^3B_1$ state is in the vicinity of 6.9 eV and almost certainly corresponds to the strong feature at 7.2 eV observed by Knoop et al.[2] in their low-energy electron scattering spectrum. The triplet character of the feature at 7.2 eV is also supported by the electron impact spectra of Trajmar et al.[3, 6] The 4.5 eV inelastic process almost certainly does not correspond to a vertical excitation of H_2O in the ground state geometry. The experimental evidence regarding the existence of an inelastic feature at 4.5 eV seems unambiguous[6] and to put this problem into the perspective we shall begin by considering the experimental evidence regarding the 4.5 eV and 7.2 - 7.5 eV regions. We shall then describe our calculations of the excitation energies and f-values of several transitions by the equations-of-motion method. The results, including the f-values agree well with available data.

II. EXPERIMENTAL EVIDENCE FOR STATES AT 4.5 eV AND 7.2 - 7.5 eV

Until the recent low-energy electron impact spectra were reported[2, 3, 6] there had been a real question as to the nature and existence of the inelastic feature at 4.5 eV in the spectrum of water. The feature is extremely weak and had never been observed in the gas phase optical spectrum. However, Larzal et al.[7] observed weak absorption at 4.5 eV using a 80 cm path length of liquid water. This process presumably corresponds to the structure at 4.0 ± 0.1 eV reported by Hunter, Lewis, and Hamill[8] in their low-energy electron reflection spectra of a thin film of ice at 77°K. These authors[7, 8] attribute their observation to absorption to the $^3B_1$ state of water, presumably in the Franck-Condon region. No structure was observed at lower energy.[7, 8] This absorption observed in condensed phases could conceivably be due to a number of causes other than excitation to an excited state of H_2O. In particular, dimer absorption or absorption due to OH radicals formed through radiation damage are possible, although the dissociation energy for the process $H_2O \rightarrow H(^2S) + OH(X\,^2\Pi)$ is 5.11 eV.

Hamill and coworkers[9, 10] have, however, provided additional, but indirect and inconclusive evidence for the existence of a state around 4.5 eV. By electron impact on alcohols a water fragment can be formed in an excited state. For example, for ethanol

$$e^- + C_2H_5OH \rightarrow C_2H_4^+ + H_2O + 2e^-$$

The ionization efficiency curve for $C_2H_4^+$ from ethanol exhibited several "breaks" which occur at the same energy intervals as those for $C_2H_4^+$ from ethane and ethylene, but 4.3 eV above the onset for this process there was an additional break in the efficiency curve. At the onset of the process H_2O in its ground state was formed, but at 4.3 eV above onset excited state water can also be formed so that an upward break in the efficiency curve is produced by an additional channel for $C_2H_4^+$ generation. Lewis and Hamill[11] have also reported that this process occurs for the cyclic alcohols c-C_5H_9OH and c-$C_6H_{11}OH$ to produce water and $C_5H_8^+$ and $C_6H_{10}^+$,respectively. By methods similar to those used for ethanol, Lewis and Hamill[11] found and extra "break" in the efficiency curves at 4.3 eV and 4.5 eV for c-C_5H_9OH and c-$C_6H_{11}OH$, respectively.

These experiments offer supplementary evidence for a value of the lowest singlet-triplet excitation energy of about 4.5 eV. It is important to realize that in the case of H_2O being formed as a neutral fragment of the electron impact on alcohols, the value measured might represent a minimum (or non-vertical) transition energy rather than a transition determined by Franck-Condon factors.

More definitive data for the existence of the inelastic feature at 4.5 eV are provided by low-energy electron impact spectra since the cross section for excitation of triplet states is considerably enhanced under these conditions. These cross sections also have a distintive angular distribution. The 4.5 eV feature is weak in these spectra. Schulz[12] observed an energy loss process with an onset of about 3.4 eV with the trapped electron method. A threshold electron impact spectrum using SF_6 as a scavenger[13] was similar to Schulz's spectrum except that the low energy electron loss feature was observed to have an onset at 4.4 eV. Raff[14] observed the feature on electron impact with 30 eV electrons while Lassettre _et al._[15] did not observe this feature in the electron impact spectrum at low scattering angles and impact energies above 100 eV. However Lassettre _et al._[16] did observe very weak scattering with an onset of about 4.4 eV in another spectra at low scattering angles and impact energies between 30 and 60 eV.[16] From their trapped electron spectrum of water Azria and Fiquet-Fayard[17] concluded that the 4.5 eV energy loss feature is due to contamination, but the preponderance of evidence is clearly against this conclusion. From a study of the pressure and primary beam dependence of the trapped electron current Knopp has shown that it is very unlikely that the 4.5 eV feature could be due to excitation of OH radicals or molecular complexes of water.[18]

More detailed and convincing data are provided by the work of Trajmar and coworkers.[3,6] They have shown that the differential cross section of electrons inelastically scattered with an energy loss of 4.5 eV is consistent with a singlet-triplet transition. Their studies also rule out any contribution to this feature from water dimers or hot bands. In more recent spectra at very low impact energies Trajmar[6] has also observed the 4.5 eV feature with a very enhanced cross section and also a transition at 7.2 eV with the characteristics of a singlet-triplet transition. Finally, Knoop et al.[2] recently reported a low-energy electron impact spectrum taken by the double retarding potential difference method. They observe the 4.5 eV inelastic feature and, more interestingly, also found a strong transition peaked at 7.2 eV which is distinct from the 7.5 eV ($^1B_1$) feature and which they assign as due to the $^3B_1$ or $^3A_2$ state. They did not find a peak at 7.5 eV for the cross sections for singlets are low in their method.

This is the current experimental situation on the transitions in H_2O at 4.5 eV and also 7.2 eV and 7.5 eV. We now discuss our calculations on the spectra of the water molecule from which we will assign the transition at 7.2 eV as the vertical excitation to the $^3B_1$ state. Our results also show that there is no vertical excitation energy at the ground state geometry in this molecule around 4.5 eV.

III. THEORY

We have used the equations-of-motion method to calculate the excitation energies and oscillator strengths for several transitions in the water molecule. The equations-of-motion method is an approach for the direct calculation of the properties of physical interest in spectroscopy, e. g., excitation energies and intensities. By using a theory specifically designed for studying these relative properties one can avoid many of the difficulties involved in obtaining highly accurate values for absolute quantities such as the total energies. We have discussed this method in recent papers[5, 19] and here we will give only a very brief summary of the theory. It can be shown that the operator O_λ^+ which generates an excited state $|\lambda\rangle$ from the ground state, i.e., $|\lambda\rangle = O_\lambda^+ |0\rangle$, is exactly a solution of the equation of motion[20]

$$\langle 0 | [\delta O_\lambda, H, O_\lambda^+] | 0 \rangle = \omega_\lambda \langle 0 | [\delta O_\lambda, O_\lambda^+] | 0 \rangle \tag{1}$$

where δO_λ^+ is a variation of the amplitudes specifying O_λ^+ and ω_λ the excitation frequency. The double commutator is defined as

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

We have derived various approximations to the solution of Eq. (1).[5, 19] If O_λ^+ is restricted to single particle-hole (1p-1h) form Eq. (1) becomes

$$\begin{bmatrix} \underset{\sim}{A} & \underset{\wedge}{B} \\ -\underset{\wedge}{B}^* & -\underset{\wedge}{A}^* \end{bmatrix} \begin{bmatrix} \underset{\wedge}{Y}(\lambda) \\ \underset{\wedge}{Z}(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} \underset{\wedge}{D} & O \\ O & \underset{\wedge}{D} \end{bmatrix} \begin{bmatrix} \underset{\wedge}{Y}(\lambda) \\ \underset{\wedge}{Z}(\lambda) \end{bmatrix} \tag{3}$$

where the elements of $\underset{\frown}{A}$, $\underset{\frown}{B}$, and $\underset{\frown}{D}$ are defined in Ref. 5 and $Y(\lambda)$ and $\underset{\frown}{Z}(\lambda)$ are the amplitudes of O_λ^+. We have also derived perturbation-like schemes for solving Eq. (1) including both 1p-1h and 2p-2h operators.[19] At this level of approximation we have obtained accurate excitation energies and oscillator strengths for transitions in N_2,[21] CO,[21] C_2H_4,[21] H_2CO,[22] CO_2,[23] and C_6H_6.[24] We now discuss the application of this method to the spectrum of the water molecule.

IV. RESULTS

The electron configuration of the ground state of water is

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$$

In an equations-of-motion calculation one first carries out a self-consistent field calculation on the ground state of the molecule to generate a particle-hole basis. We have used the currently accepted ground state experimental geometry[25] and carried out calculations[26] using different basis sets to study the effect of the composition of the orbital basis on the excitation energies and f-values. We will refer primarily to the results obtained in the largest basis but will also discuss the results in other basis sets whenever the differences in the results illustrate some important feature. For this largest basis we used a [3s2p/1s] valence basis contracted from a (7s3p/3s) Gaussian basis[27] to which we added a diffuse s function with an orbital exponent of 0.038 on each hydrogen and two s functions with exponents of 0.089 and 0.022 and two sets of p functions also with exponents of 0.089 and 0.022 on the oxygen center. Polarization functions have been shown to be important in ground state SCF calculations on water[28] and hence we added to our basis a contracted set of d-polarization functions on oxygen with exponents of 1.322 and 0.3916 and coefficients 0.3579 and 0.7596, respectively, and a set of p-polarization functions, on hydrogen with an exponent of 1.16. Another calculation was done with this same basis but from which the polarization functions were deleted. The differences in the results of the two calculations are not very significant but may amount to 0.3 to 0.5 eV in the excitation energies to some states. In the calculations, all molecular orbital levels except the highest particle state and the lowest hole state are included.[29]

Table I shows the excitation energies for ten transitions in water along with the oscillator strengths for the four dipole-allowed transitions. These are results of the calculation using the 1p-1h plus 2p-2h (1p-1h + 2p-2h) approximation[19] to the solution of the equation of motion, Eq. (1) and the basis set containing the polarization functions. The lowest calculated vertical excitation energy is about 6.9 eV and is to the $^3B_1$ ($1b_1 \rightarrow 3s$) state. The corresponding singlet transition energy is 7.2 eV and hence the B_1 singlet-triplet splitting is 0.3 eV. Hence we can now assign the peak observed by Knopp[2] at 7.2 eV as the $^3B_1$ state, 0.2 eV below the observed transition to the $^1B_1$ state.[3] Clearly the inelastic feature at 4.5 eV is not a vertical transition to the $^3B_1$ state. From the accuracy of the results on several other molecules we are confident that the predicted value of 6.9 eV for the vertical excitation energy to the $^3B_1$ state would be within 5-10% of the true value. If one assumes that the transition is highly non-vertical the $^3B_1$ potential energy curve would have to drop by over 2 eV relative to the vertical value. Bader and Gangi[30] calculated the energy difference between linear H_2O and H_2O in the ground state geometry to be 0.13 eV for the lowest triplet surface. Linear H_2O is only a saddle point on this surface. The calculated f-value of 0.05 for the transition to the $\tilde{A}\ ^1B_1$ state agrees well with the experimental value of 0.04.

We assign the peak observed at 9.1 eV by Knopp et al.[2] as a transition to the $^1A_2$ ($1b_1 \rightarrow 3py$) state with a calculated excitation energy of 9.02 eV. The $\tilde{B}\ ^1A_1$ ($3a_1 \rightarrow 3s$) excitation energy of 9.54 eV agrees well with the observed value of 9.67. The triplet state observed by Trajmar[3] at 9.81 eV is probably a transition to one of three triplet states, i.e., the $^3A_1$ ($3a_1 \rightarrow 3s$) at 9.34 eV, $^3A_1$ ($1b_1 \rightarrow 3px$) at 9.39 eV, or the $^3B_1$ ($1b_1 \rightarrow 3pz$) at 9.47 eV. From the good agreement between the calculated and observed excitation energies for the $^1A_1$ ($3a_1 \rightarrow 3s$) state, the assignment may be narrowed down to the $^3A_1$ ($1b_1 \rightarrow 3px$) or $^3B_1$ ($1b_1 \rightarrow 3pz$) states. The $\tilde{B}\ ^1A_1$ excitation energy of 9.54 eV agrees well with the observed value of 9.67 eV while the excitation energies to the $\tilde{C}\ ^1B_1$ ($1b_1 \rightarrow 3pz$) and $\tilde{D}\ ^1A_1$ ($1b_1 \rightarrow 3px$) states are both about 5% below the observed values. The predicted f-value of 0.06 for the transition to the $\tilde{B}\ ^1A_1$ state, observed as a broad continuum, is close to the experimental value of 0.05. There are no experimental f-values available for transitions to the $\tilde{D}\ ^1A_1$ and $\tilde{C}\ ^1B_1$ states, but Lassettre[4] estimated the ratio of f-values for these two transitions to be about 1.3 from high energy electron impact studies. Our calculated f-values give a ratio of about 3.

As expected, the excitation energies obtained from the calculations without the polarization functions are very close to those in Table I for transitions to states which are primarily excitations out of the $1b_1$ orbital. This is because the $1b_1$ orbital is almost the oxygen 2px orbital which is relatively nonbonding. However the excitation energies to states which arise primarily from an excitation out of the $3a_1$ bonding orbital are all about 0.3 - 0.4 eV lower than those of Table I.

CONCLUSIONS

The available experimental evidence for the existence of an inelastic feature at 4.5 eV in the spectrum of water is very convincing. To explain the nature of this process and to study the spectrum of water in some detail we have carried out several calculations on the excited states of water at the vertical geometry using the equations-of-motion method.[5] We conclude that our calculated vertical excitation energy of 6.9 eV for the $^3B_1$ state corresponds to the strong feature at 7.2 eV observed by Knoop *et al.*[2] in their low-energy electron scattering spectrum. The 4.5 eV inelastic process almost certainly does not correspond to a vertical excitation of water at the ground state geometry. The other excitation energies and oscillator strengths agree well with experiment. We can assign the state observed at 9.1 eV[2] as a $^1A_2(1b_1 \rightarrow 3py)$ and the triplet state at 9.81 eV as probably a $^3A_1$ or $^3B_1$ and not a $^3A_2$ excitation.

Table I. Vertical Excitation Energies and Oscillator Strengths in Water[a]

State	Main Transition	ΔE[b] (EOM)	ΔE (Obs.)	ΔE[c] (CI)	f[b] (EOM)	f (Obs.)
$^3B_1$	$1b_1 \rightarrow 3s$	6.89	7.2[d]	7.3		
$\tilde{A}\ ^1B_1$	$1b_1 \rightarrow 3s$	7.22	7.4[e]	7.6	0.05	0.04[g]
$^3A_2$	$1b_1 \rightarrow 3py$	8.97		9.3		
$^1A_2$	$1b_1 \rightarrow 3py$	9.02	9.1[d]	9.5		
$^3A_1$	$3a_1 \rightarrow 3s$	9.34		9.4		
$^3A_1$	$1b_1 \rightarrow 3px$	9.39				
$^3B_1$	$1b_1 \rightarrow 3pz$	9.47				
$\tilde{C}\ ^1B_1$	$1b_1 \rightarrow 3pz$	9.48	10.0[f]		0.006	---[h]
$\tilde{B}\ ^1A_1$	$3a_1 \rightarrow 3s$	9.54	9.67	9.8	0.06	0.05[g]
$\tilde{D}\ ^1A_1$	$1b_1 \rightarrow 3px$	9.61	10.17		0.02	----[h]

[a] All energies in eV's.

[b] Results from the EOM method in the 1p-1h + 2p-2h approximation. See Ref. 19.

[c] N. W. Winter, private communcation.

[d] Reference 2.

[e] Reference 3.

[f] The next three experimental energies are from Ref. 4.

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[h] The observed ratio of f-values for the $\tilde{D}\ ^1A_1$ and $\tilde{C}\ ^1B_1$ states is about 1.2. See Ref. 4.

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(C)

Oscillator Stregths for the $X^1\Sigma^+ - A^1\Pi$ System in CH^+ from the Equations of Motion Method

1. INTRODUCTION

With the recent expansion of the field of astrochemistry and studies of the formation and evolution of interstellar clouds, the need has arisen for accurate and reliable molecular data[1] on species not previously investigated in any detail either experimentally or theoretically. A thorough discussion of current astrophysical and astrochemical problems related to molecule formation in interstellar space can be found in Ref. 2.

A typical example of a situation where the lack of reliable molecular data has seriously affected the development of models for the formation of interstellar molecules is that of the relative abundances of CH and CH^+ and their formation through radiative association processes from atoms and ions.[3] In particular, the rate of association of C and H^+ to form CH^+ depends on the oscillator strength of the $X^1\Sigma^+ - A^1\Pi$ transition in CH^+.[3-5] CH^+ is charged and a highly reactive species, which makes spectroscopic studies in the laboratory difficult. Under these circumstances, detailed theoretical calculations become appealing. One of the early theories[6] of the formation of CH^+ was initially discarded because the assumed f-values lead to low rates of radiative association. However, the work of Solomon and Klemperer[3] revived the interest in this radiative association mechanism by reevaluating the rates by using better f-values.

In addition to these direct processes Julienne and Krauss[4] have discussed an alternative mechanism, namely, indirect radiative association (inverse predissociation) leading to the formation of other species as well, such as NO, CH, CO, C_2, etc. In these studies a reliable source of intensities is necessary if we are to reduce the uncertainties in models of the interstellar medium.

For these reasons, considerable effort has been put into the *ab initio* quantum mechanical calculation of the potential energy curves[7] and oscillator strengths[8] of CH^+. Similar work has been done on CH[9].

In this paper we present the oscillator strength of the $X^1\Sigma^+ - A^1\Pi$ transition of CH^+ as computed by the Equations of Motion Method.[10] Our result is in good agreement with the extensive CI calculations of Green *et al.*,[7] and Yoshimine *et al.*[8] The results presented are important because they constitute an independent confirmation of the results of Green *et al.*, and Yoshimine *et.al.*, using a different approach. Moreover, computationally the method is simple and relatively inexpensive. This is an important feature since the rapidly expanding fields of astrophysics and astrochemistry of the interstellar medium require reliable estimates of molecular parameters such as excitation energies and transition moments at various geometries. Since it is not always possible to study the systems of interest experimentally, we must resort to theoretical calculations that, while still reliable, do not represent a major computational effort.

2. THEORY AND RESULTS

The Equations of Motion (EOM) Method for calculating excitation energies and transition moments has been thoroughly described elsewhere[10] and here we only outline some of the central ideas.

In this approach we define an excitation operator such that

$$O_\lambda^+ |O\rangle = |\lambda\rangle \tag{1}$$

where $|\lambda\rangle$ is some excited state and $|0\rangle$ is the ground state. It then can be shown that O_λ^+ satisfies an equation of motion[11] given by

$$\langle O|[\delta O_\lambda, H, O_\lambda^+]|O\rangle = \omega_\lambda \langle O|[\delta O_\lambda, O_\lambda^+]|O\rangle \tag{2}$$

where the double commutator is defined by

$$2[A,B,C] = [[A,B],C] + [A,[B,C]] \tag{3}$$

ω_λ is the excitation frequency and δO_λ^+ represents a variation of the amplitudes specifying O_λ^+. If O_λ^+ is assumed to be composed of single particle-hole pairs (1p-1h) the equations of motion become

$$\begin{bmatrix} \underset{\wedge}{A} & \underset{\wedge}{B} \\ -\underset{\wedge}{B}^* & -\underset{\wedge}{A}^* \end{bmatrix} \begin{bmatrix} \underset{\wedge}{Y}(\lambda) \\ \underset{\wedge}{Z}(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} \underset{\wedge}{D} & O \\ O & \underset{\wedge}{D} \end{bmatrix} \begin{bmatrix} \underset{\wedge}{Y}(\lambda) \\ \underset{\wedge}{Z}(\lambda) \end{bmatrix} \tag{4}$$

The elements of the matrices $\underset{\wedge}{A}$, $\underset{\wedge}{B}$, and $\underset{\wedge}{D}$, are given in Ref. 10. $\underset{\wedge}{Y}$ and $\underset{\wedge}{Z}$ are the amplitudes we wish to calculate. Higher order approximations (inclusion of 2p-2h components) to the exact Eq. 2 can also be easily constructed. In the above approach we obtain spectroscopic quantities of interest, e.g. transition intensities directly, and avoid the calculation of highly accurate and elaborate total wavefunctions and absolute energies for the different electronic states separately.

In this paper we report calculations on CH^+ using two different gaussian basis sets: a [3S2P/2S] contracted from a (9S5P/4S)[12a] primitive basis and a more recent version of the [3S2P/2S] contraction[12b] to which we added polarization functions. The final basis was then [3S2P1D/2S1P].

In Table I we summarize the results we obtain with the two bases and compare them with the best CI calculations to date.[7, 8] We have performed the calculation only at one internuclear distance, namely 1.12 Å, which is the ground state equilibrium geometry. The first column in the table, labeled RPA (Random Phase Approximation) is derived from lowest order single particle-hole pair (1p-1h) solutions to the equations of motion. (See Ref. 10). The column labeled EOM, contains results that were not fully iterated.[10] Continuing the iterations may have improved the excitation energy somewhat within the rather small basis set being used. The basis was chosen to provide good results for the $X\,^1\Sigma^+$ - $A\,^1\Pi$ transition moment, since this is the one transition that bears the most astrophysical interest.

The values we have computed are compared with those obtained by interpolating from the data in references 7 and 8. Overall agreement is good. We want to point out that the size of the problem (computational effort) is determined by the number of 1p-1h excitations included in Eq. 4. In our larger basis ([3S2P1D/2S1P]) this amounts only to 12, which means that at most only 12 × 12 matrices must be diagonalized for states of Π symmetry. Another feature of EOM calculations that makes them particularly practical is that an SCF run is needed only once and on the ground state exclusively. From a single calculation we obtain most of the low-lying states (all of the symmetries allowed by the basis set being used). As in any basis set expansion technique the quality of the final results depends on the nature and the size of the basis used. However, we have found in general that valence basis sets of relatively poor quality still give very good transition moments and excitation energies to states with small diffuse components.

In conclusion, the EOM scheme can provide reliable molecular spectral data such as excitation energies and oscillator strengths in a computationally simple fashion. Applications to other molecules of interest in astrophysics are underway.

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Table 1.

Vertical Excitation Energy and Oscillator Strength for the $X^1\Sigma^+$-$A^1\Pi$ Transition in CH^+

Property	[3S2P/2S] RPA	[3S2P1D/2S1P] EOM	CI of Refs. 7, 8
Excitation Energy(eV)	2.37	2.50	3.32[a]
Transition Moment(au)	0.34	0.31	0.30[a]
Oscillator Strength	0.014	0.011	0.0147[a]

[a] Values interpolated from the data in references 7 and 8.

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(D)

Some Applications of Excited State--Excited State Transition Densities

I. INTRODUCTION

In the equations of motion method or any of its approximations, e.g. the random phase approximation or time-dependent Hartree-Fock, the quantities calculated directly are the transition densities between the ground and excited states.[1] Relative quantities between the ground and excited states such as transition moments can then be readily obtained from these transition densities and the necessary matrix elements between basis states. For several applications excited state-excited state transition densities are needed. These include the study of transition intensities between excited states of molecules of interest in the development of gas phase lasers, e.g. the $C^3\Pi_u \rightarrow B^3\Pi_g$ lasing transition in N_2 and in atmospheric emissions where transitions between excited states play an important role. Other properties such as two-photon decay of metastable states and the polarizabilities of excited states require infinite summations over excited state-excited state transition moments and frequencies.

The purpose of this paper is to show how excited state-excited state transition moments can be calculated directly from the set of ground state-excited state transition densities obtained from a single equations of motion calculation. First we derive the simple relationship expressing the excited state-excited state transition moment directly in terms of the ground state-excited state transition densities. Then we discuss two interesting applications of this result. The first application is to the calculation of the photoionization cross sections of the $2\,^3S$ and $2\,^1S$ metastable states of helium. In this calculation of photoionization cross sections we completely avoid the need for constructing continuum solutions of the wave equation normally needed to describe the final-state continuum wave functions. The central idea is to use the excited state-excited state transition moments to obtain a discrete representation of the frequency-dependent polarizability at complex values of the energy. Numerical analytic continuation can then be used to obtain the photoionization cross sections. We have previously applied this procedure to obtain photoionization cross sections for He and H_2 ground states in good agreement with experiment.[2, 3] As a second application we use these excited state moments to predict the two-photon decay rate of the $2\,^1S$ metastable state of helium. Both the calculated photoionization cross sections of the $2\,^1S$ and $2\,^3S$ states of helium and the two-photon decay rate of the $2\,^1S$ state agree well with the results of other calculations and available experimental data.

II. THEORY

In the study of dynamical properties of atoms and molecules the quantities of direct physical interest are relative quantities between two states, e.g. excitation frequencies, $\omega_{0\lambda}$, and transition matrix elements, $< 0 | M | \lambda >$, between states $|0>$ and $|\lambda>$. For example in the frequency-dependent polarizability $\alpha(\omega)$

$$\alpha(\omega) = \underset{\lambda_i \neq 0}{S} \frac{2\,\omega_{0\lambda_i} |< 0 | \vec{D} | \lambda_i >|^2}{\omega_{0\lambda_i}^2 - \omega^2} \tag{1}$$

one is concerned with a set of frequencies $\{\omega_{0\lambda}\}$ and the off-diagonal matrix elements of the dipole operator, $\vec{D}$. The summation in Eq. (1) implies an integration over the continuum. The evaluation of one-particle transition matrix elements simply requires a knowledge of the one-particle transition density, $\rho_{0\lambda}(\vec{r}', \vec{r})$

$$\rho_{0\lambda}(\vec{r}', \vec{r}) = < 0 | \rho(\vec{r}', \vec{r}) | \lambda > \tag{2}$$

where $\rho(\vec{r}', \vec{r})$ is the one-particle density operator

$$\rho(\vec{r}', \vec{r}) = \hat{\psi}^\dagger(\vec{r}')\,\hat{\psi}(\vec{r}) \tag{3}$$

in second quantized form with $\hat{\psi}^\dagger(\vec{r})$ and $\hat{\psi}(\vec{r})$ the field operators, e.g.

$$\hat{\psi}^\dagger(r) = \sum_k \varphi_k^*(r)\, a_k^\dagger \tag{4}$$

where $\varphi_k(r)$ and $a_k^\dagger$ are single-particle states and creation operators respectively. The transition matrix element of a one-particle operator M can then be written

$$<0\,|\,M\,|\,\lambda> \; = \iint d\vec{r}\, d\vec{r}\,'\; \delta(\vec{r}-\vec{r}\,')\; M(\vec{r})\rho_{0\lambda}(\vec{r}\,', \vec{r}) \qquad (5)$$

where the integration over the δ function is performed after $M(r)$ is applied. Since the one-particle transition density is sufficient to evaluate the physically significant matrix elements, one should design a theory that concentrates directly on this quantity. In the equations of motion method as well as in several other many-body methods, e.g. in the theory of Green's function, we calculate the transition density directly.

In the equations of motion method one calculates the elements of the ground state-excited state transition densities by solving the equation of motion of the excitation operator $O_\lambda^\dagger$ defined such that $O_\lambda^\dagger\,|\,0> \; = \;|\,\lambda>$. It can be shown that if the operator $O_\lambda^\dagger$ is restricted to single particle-hole form, i.e.

$$O_\lambda^\dagger \;=\; \sum_{m\gamma} Y_{m\gamma}(\lambda)\, a_m^\dagger\, a_\gamma \;-\; Z_{m\gamma}(\lambda)\, a_\gamma^\dagger\, a_m \qquad (6)$$

the amplitudes $Y_{m\gamma}(\lambda)$ and $Z_{m\gamma}(\lambda)$ satisfy the equation[4]

$$\begin{pmatrix} \underset{\frown}{A} & \underset{\frown}{B} \\ -\underset{\frown}{B}^* & -\underset{\frown}{A}^* \end{pmatrix} \begin{pmatrix} \underset{\frown}{Y}(\lambda) \\ \underset{\frown}{Z}(\lambda) \end{pmatrix} = \omega_{0\lambda} \begin{pmatrix} \underset{\frown}{D} & 0 \\ 0 & \underset{\frown}{D} \end{pmatrix} \begin{pmatrix} \underset{\frown}{Y}(\lambda) \\ \underset{\frown}{Z}(\lambda) \end{pmatrix} \qquad (7)$$

The matrices $\underset{\frown}{A}$, $\underset{\frown}{B}$, and $\underset{\frown}{D}$ are ground state expectation values of second quantized operators[1] and $\omega_{0\lambda}$ the excitation energy. The amplitudes $Y_{m\gamma}$ and $Z_{m\gamma}$ are elements of the transition density which, to a good approximation, can be written as

$$\rho_{0\lambda}(\vec{r}',\vec{r}) = \langle 0 \,|\, [\rho, O_\lambda^\dagger] \,|\, 0 \rangle \approx \sum_{m\gamma} Y_{m\gamma}\, \phi_m^*(\vec{r}')\, \phi_\gamma(\vec{r}) + Z_{m\gamma}\, \phi_\gamma^*(\vec{r}')\, \phi_m(\vec{r}) \tag{8}$$

where φ_m and ϕ_γ are particle and hole states respectively. The equations of motion, Eq. (7), can be solved straightforwardly in various approximations for ground to excited state transition energies and densities. Applications to several molecules, e. g. H_2, N_2, CO, H_2O, CO_2, H_2CO, and C_6H_6,[5] show that the method yields accurate dipole transition moments.

For several applications it would be convenient to derive excited state-excited state transition moments directly from the set of ground state-excited state transition densities $\{\rho_{0\lambda}\}$ obtained from the solution of Eq. (7). Consider the matrix element of the one-body operator between states $|\lambda_i\rangle$ and $|\lambda_j\rangle$. From the properties of the operators $O_{\lambda_i}^\dagger$ and $O_{\lambda_j}^\dagger$ we can write

$$\langle \lambda_i \,|\, M \,|\, \lambda_j \rangle = \langle 0 \,|\, O_{\lambda_i}\, M\, O_{\lambda_j}^\dagger \,|\, 0 \rangle \tag{9}$$

We now exploit the formal properties of the excitation operators to rewrite Eq. (9) as the expectation value of commutators of the operators O_{λ_i}, M and $O_{\lambda_j}^\dagger$

$$\langle \lambda_i \,|\, M \,|\, \lambda_j \rangle = \langle 0 \,|\, [O_{\lambda_i}, M, O_{\lambda_j}^\dagger] \,|\, 0 \rangle + \tfrac{1}{2} \langle 0 \,|\, [O_{\lambda_i}, O_{\lambda_j}^\dagger]\, T \,|\, 0 \rangle + \tfrac{1}{2} \langle 0 \,|\, T\, [O_{\lambda_i}, O_{\lambda_j}^\dagger] \,|\, 0 \rangle \tag{10}$$

where the double commutator is defined as

$$2\,[O_{\lambda_i},\ M,\ O^{\dagger}_{\lambda_j}] = [[O_{\lambda_i}, M], O^{\dagger}_{\lambda_j}] + [O_{\lambda_i}, [M, O^{\dagger}_{\lambda_j}]] \qquad (11)$$

The advantage in going from the expectation value of the direct product of operators O_{λ_i}, M, $O^{\dagger}_{\lambda_j}$ of Eq. (9) to the expectation value of the double commutator of these operators, Eq. (11), is due to the observation that the double commutator is a simpler operator, i. e. of lower particle-hole rank, than the straightforward product.[6] The expectation value of the double commutator can then be expected to be less sensitive to the details of the ground state wavefunction.[4]

The right-hand side of Eq. (10) is now evaluated in three different approximations. First in the random phase approximation (RPA) the second and third terms of Eq. (10) vanish since $[O_{\lambda_i}, O^{\dagger}_{\lambda_j}] = \delta_{\lambda_i\lambda_j}$, $|\lambda_i> \neq |\lambda_j>$, and the expectation value of the double commutator is evaluated over the Hartree-Fock ground state. In the RPA we obtain

$$<\lambda_i|M|\lambda_j> \approx \sum_{n\nu}\sum_{m\gamma} [Y^{*}_{n\nu}(\lambda_i)\, Y_{m\gamma}(\lambda_j) + Z^{*}_{n\nu}(\lambda_i)\, Z_{m\gamma}(\lambda_j)]$$

$$[T_{nm}\,\delta_{\nu\gamma} - T_{\gamma\nu}\,\delta_{nm}] \qquad (12)$$

In Eq. (12) m and n denote particle states and γ and ν hole states. The amplitudes $\{Z_{n\nu}\}$ implicitly account for electron correlation in the ground state. The $\{Y_{n\nu}\}$ amplitudes are the dominant effect in Eq. (12) since they represent the main correlation effects in the excited state. If we completely neglect electron correlation in the ground state, i.e. set $|0\rangle = |HF\rangle$ and $\{Z_{n\nu}\} = 0$, we obtain

$$\langle \lambda_i | M | \lambda_j \rangle \approx \sum_{n\nu} \sum_{m\gamma} Y^*_{n\nu}(\lambda_i)\, Y_{m\gamma}(\lambda_j)\, [T_{nm}\, \delta_{\nu\gamma} - T_{\gamma\nu}\, \delta_{nm}] \quad (13)$$

This corresponds to assuming that the excited state is composed of single excited states relative to the HF ground state, i.e. single excitation configuration interaction or the Tamm-Dancoff approximation (TDA). Equation (13) should normally be a good approximation to the transition matrix element.

The third approximation to $\langle \lambda_i | M | \lambda_j \rangle$ can be obtained by solving Eq. (7) for the $\{Y_{n\nu}\}$ and $\{Z_{n\nu}\}$ amplitudes in a higher order scheme. This higher random phase approximation is discussed in ref. 1 and is often needed in discussing excitations to low-lying triplet electronic states where the RPA may show instabilities. In this approximation (HRPA) we have

$$\langle \lambda_i | M | \lambda_j \rangle \approx \sum_{n\nu} \sum_{m\gamma} [Y^*_{n\nu}(\lambda_i)\, Y_{m\gamma}(\lambda_j) + Z^*_{n\nu}(\lambda_i)\, Z_{m\gamma}(\lambda_j)]$$

$$[T_{\gamma\nu}\, \rho_{nm} + T_{nm}\, \rho_{\nu\gamma} - \tfrac{1}{2}\, \delta_{\nu\gamma} (\sum_p T_{mp}\, \rho_{pn} + T_{np}\, \rho_{pm})$$

$$- \tfrac{1}{2}\, \delta_{nm} \sum_\delta (T_{\nu\delta}\, \rho_{\delta\gamma} + T_{\gamma\delta}\, \rho_{\delta\nu})] \quad (14)$$

where ρ is the ground state density matrix, γ, δ and ν hole states and m, n, and p particle states. In the HRPA the second and third terms of Eq. (10) do not exactly vanish but can be expected to be small and are neglected in deriving Eq. (14). We recall that these terms do vanish in the RPA since $[O_{\lambda_i}, O^\dagger_{\lambda_j}] = \delta_{\lambda_i \lambda_j}$. There are examples where it is important to use Eq. (14) instead of Eq. (12) or Eq. (13), e.g. in certain transitions in N_2. These results will be discussed in a separate paper.[7]

In the next section we discuss the applications of these transition moments to the calculation of photoionization cross sections of the $2\,^1S$ and $2\,^3S$ metastable states of helium and of the two-photon decay rate of the $2\,^1S$ state of helium.

III. APPLICATIONS

A. Photoionization cross sections of metastable states

Photoionization of excited state species plays an important role in several physical systems. For example, photoionization of rare gas excimers is an important reaction that may limit the laser gain of these systems. In previous calculations of photoionization cross sections of metastable states,[8, 9] as well as for ground states, accurate atomic or molecular continuum eigenfunctions are needed to describe the final states of the systems.[10] We have recently shown how one can completely avoid the need for continuum eigenfunctions in the calculation of atomic and molecular photoionization cross sections.[11, 12] These calculated photoionization cross sections for He[11] and H_2[12] in their ground states agree well with other calculations and experiment. The central idea is to obtain a discrete representation of the frequency-dependent polarizability which, although not directly useful at physical energies in the continuum, often provides an adequate representation of the polarizability for complex values of the energy. Numerical analytic continuation can then be used to return to the real energy axis where the physical information is desired. This L^2 method for calculating photoionization cross sections was suggested by Broad and Reinhardt[13] who applied it to atomic hydrogen.

To apply this method to the calculation of photoionization cross sections of excited states we start from the frequency-dependent polarizability of the excited state. For the state $|\lambda_i>$ we have

$$\alpha_{\lambda_i}(z) = \sum_{\lambda_i \neq \lambda_j} \frac{f_{\lambda_i\lambda_j}}{\omega^2_{\lambda_i\lambda_j} - z^2} + \int_{\epsilon_I}^{\infty} \frac{g_{\lambda_i}(\epsilon)\, d\epsilon}{\epsilon^2 - z^2} \tag{15}$$

where z is complex and $\omega_{\lambda_i\lambda_j}$, $f_{\lambda_i\lambda_j}$, and $g_{\lambda_i}(\epsilon)$ are the transition frequencies and the bound and continuum oscillator strengths respectively and ϵ_I is the first ionization threshold of the system. In the neighborhood of $z = \omega + i\eta$ with $\eta \to 0$

$$\alpha_{\lambda_i}(\omega) = \sum_{\lambda_i \neq \lambda_j} \frac{f_{\lambda_i\lambda_j}}{\omega^2_{\lambda_i\lambda_j} - \omega^2} + P\int_{\epsilon_I}^{\infty} \frac{g_{\lambda_i}(\epsilon)\, d\epsilon}{\epsilon^2 - \omega^2} + i\pi\, \frac{g_{\lambda_i}(\omega)}{2\omega} \tag{16}$$

This gives the relation between the photoionization cross sections of state $|\lambda_i>$, σ_{λ_i}, and the imaginary part of its polarizability

$$\sigma_{\lambda_i}(\omega) = \lim_{\eta \to 0} \frac{4\pi\omega}{c}\, \mathrm{Im}\,[\alpha_{\lambda_i}(\omega + i\eta)] \tag{17}$$

$\alpha(z)$ of Eq. (15) is first approximated by a finite sum over approximate oscillator strengths $\tilde{f}_{\lambda_i\lambda_j}$ and frequencies $\tilde{\omega}_{\lambda_i\lambda_j}$

$$\tilde{\alpha}_{\lambda_i}(z) = \sum_{\lambda_i \neq \lambda_j} \frac{\tilde{f}_{\lambda_i\lambda_j}}{\tilde{\omega}^2_{\lambda_i\lambda_j} - z^2} \tag{18}$$

To continue $\alpha_{\lambda_i}(z)$ analytically on to the real axis, we construct a low-order rational-fraction representation of $\alpha_{\lambda_i}(z)$ by fitting it to the approximate $\tilde{\alpha}_{\lambda_i}(z)$ of Eq. (18) at a number of points in the complex plane.[14] With this smooth representation of $\tilde{\alpha}_{\lambda_i}(z)$ we can now calculate $\alpha_{\lambda_i}(z)$, and hence $\sigma_{\lambda_i}(z)$, at real energies where the original discrete approximation, Eq. (18) is unphysical.

The finite set of oscillator strengths, $\tilde{f}_{\lambda_i\lambda_j}$, and transition frequencies, $\tilde{\omega}_{\lambda_i\lambda_j}$, needed to obtain $\tilde{\alpha}_{\lambda_i\lambda_j}$, Eq. (18), is generated by solving the equations of motion, Eq. (7), for the transition frequencies, $\omega_{0\lambda}$. The resulting transition amplitudes, $Y_{n\nu}$ and $Z_{n\nu}$, give, through Eqs. (12), (13), or (14), the excited state-excited state transition moments, $\tilde{M}_{\lambda_i\lambda_j}$, which, along with $\tilde{\omega}_{\lambda_i\lambda_j}$, define $\tilde{f}_{\lambda_i\lambda_j}$

$$\tilde{f}_{\lambda_i\lambda_j} = \tfrac{2}{3}\,\tilde{\omega}_{\lambda_i\lambda_j}\; \left|\langle \lambda_i \,|\, \vec{D} \,|\, \lambda_j \rangle\right|^2 \qquad (19)$$

$\vec{D}$ is the dipole moment operator and the transition moment $M_{\lambda_i\lambda_j}$ is evaluated in the three approximations discussed above, i.e. Eqs. (12), (13), and (14). In the calculation of the photoionization cross sections of the $2\,^1S$ and $2\,^3S$ metastable states of helium we use a finite set of eight discrete oscillator strengths, i.e. $f_{\lambda_i\lambda_j}$ $(2\,^{1,3}S \rightarrow n\,^{1,3}P)$ $n = 2, 3, \ldots 9$ in Eq. (18). Table I lists these oscillator strengths in the RPA which are used in the calculation of the photoionization cross sections. We do not list the oscillator strengths in the other approximations for all eight transitions since all the approximations can be expected to give similar results where excited state correlation effects are not critical, e.g. in the $1s\,2s\,(2\,^1S) \rightarrow 1s\,2p\,(2\,^1P)$ transition the main effect is included in the TDA. In Table II we do however show the first three oscillator strengths and compare them with the results of other calculations.

Figures 1 and 2 show the calculated photoionization cross sections for the $2\,^1S$ and $2\,^3S$ metastable states of helium. These cross sections are for the continuous background photoionization below the n = 2 threshold. The fitting points for determining the rational-fraction representation of $\tilde{\alpha}_{\lambda_i}(z)$ were chosen with a real part between each pair of $\omega^2_{\lambda_i\lambda_j}$ values of Table I and the imaginary parts were varied over a region of the complex plane. For the different choices of the fitting points the calculated cross sections agree within 2-8% of one another. In Figs. 1 and 2 we also plot the cross sections obtained by Norcross[8] and Jacobs[9] who used Hartree-Fock and correlated initial state wavefunctions respectively and close-coupling final state wavefunctions. The agreement between these results and the present calculation is good. Within the experimental uncertainty of ∓ 14% the various calculations agree well with the measured values.[15] The accuracy of our calculated cross sections could be improved by using a discrete set of $f_{\lambda_i\lambda_j}$'s and $\omega_{\lambda_i\lambda_j}$'s specifically designed to give photoionization cross sections of these metastable states. The f-values used in this calculation were obtained from a calculation originally designed to give ground-excited state energies and transition moments.

Finally it should be emphasized that since this method completely avoids the use of continuum eigenfunctions, the techniques used here can be easily extended to molecules.[16] Some immediate applications would be the study of photoionization of excited states of rare-gas dimers and other molecular gas lasers. For example photoionization of the $A\,^1\Sigma_u^+$ state is critical in determining the possible gain of the proposed He_2 ultra-violet laser. These calculations can also provide estimates of the stimulated emission cross section, another important parameter in these laser systems.

B. Two-photon decay of the $2\,^1S$ metastable state

As a second application and more in the purpose of a check on the discrete oscillator strength distribution of Table I, we now calculate the probability of two-photon decay of helium in the $2\,^1S$ level, i.e.

$$\mathrm{He}\,(2\,^1S) \rightarrow \mathrm{He}\,(1\,^1S) + \hbar\omega_1 + \hbar\omega_2 \qquad (20)$$

Accurate estimates, including those of a coupled Hartree-Fock calculation[17] and variational procedures,[18] have been obtained for this decay rate and hence this application can serve as a useful calibration of our discrete f-distribution.

Since the theory of two quantum processes has been discussed elsewhere[17, 18] our discussion of the basic equations will be brief. The probability of two-photon transitions can be formally expressed as an infinite summation over intermediate states. If $\hbar\omega_{0f}$ is the energy of the two-photon He $(2\,^1S) \rightarrow$ He $(1\,^1S)$ transition of Eq. (20) the probability $A(y)\,dy$ that a photon will be emitted in the frequency range $\omega_{0f}\,dy$ is given by

$$A(y) = 5.299 \times 10^3 \omega_{0f}^5 y^3 (1 - y)^3 \left| M(y) \right|^2 \qquad (21)$$

where $y = \omega_1/\omega_{0f}$ and $M(y)$ is the two-photon transition matrix element

$$M(y) = \sum_{\lambda} <2^1S \mid D_Z \mid \lambda^1P><\lambda^1P \mid D_Z \mid 1^1S>$$

$$\left\{ \frac{\omega_{0f}}{\omega_{0\lambda} + y\,\omega_{0f}} + \frac{\omega_{0f}}{\omega_{0\lambda} + (1 - y)\,\omega_{0f}} \right\} \qquad (22)$$

where D_Z is the z component of the dipole moment operator. The summation in Eq. (22) requires the transition moments between the ground and intermediate states, $< \lambda^1P \mid D \mid 1^1S >$, and between the metastable and intermediate states $<2^1S \mid D \mid \lambda^1P>$. The ground-excited state transition moments are directly available from the solution of Eq. (7) in any approximation, e.g. the RPA or time dependent Hartree-Fock approximation and the excited state-metastable state transition moments can be derived in any of the approximations discussed in Eqs. (12), (13), or (14). Direct substitution of these moments and the corresponding energy differences yield estimates of the probability distribution $A(y)$. The Einstein A coefficient for two-photon emission is just the integral

$$A = \tfrac{1}{2} \int_0^1 A(y)\, dy \qquad (23)$$

In Table III we list the values of $A(y)$ obtained using the RPA transition moments and frequencies throughout Eq. (22). It is important to note that for excited state-excited state transition moments we define the RPA as our approximation of Eq. (12) to the exact expression, Eq. (10). The agreement with the coupled Hartree-Fock calculations[17] and variational calculations[18] is good but the results are generally about 10% too high. This is partly due to the strong ω_{of} frequency dependence of A (y) rather than the sum over intermediate states in M (y). For example, if we use the experimental ω_{of} in Eq. (21), the calculated A (y) falls within 2-3% of the accurate results of reference 18. These results are also listed in Table III. The Einstein A coefficient derived from our A (y) of the second column of Table I is 55.6 sec^{-1} compared with 51.3 sec^{-1} of reference 18. With the A (y) derived from the experimental ω_{of}, i.e. the third column of Table III, we obtain an A coefficient of 49.7 sec^{-1}.

IV. CONCLUSIONS

We have derived an approximation for transition moments between excited states consistent with the approximations and assumptions normally used to obtain transition moments between the ground and excited states in the random phase approximation. The basic procedure is to exploit the formal properties of the excitation operators $O^{\dagger}_{\lambda_i}$, defined on the ground state, i.e. $O^{\dagger}_{\lambda_i} | 0 >$, to rewrite the transition moment $< \lambda_i | M | \lambda_j >$ as an expectation value of double commutators, Eq. (10), over the ground state wavefunction. The resulting expression can then be written in terms of the ground-excited transition amplitudes. Eq. (12) can be viewed as an RPA definition of transition moments between excited states.[6] Although for some applications the lower order TDA or single excitation CI may suffice, there are cases where a higher order solution is necessary to calculate excited state-excited state transition moments.[7]

The results for the photoionization cross sections of the $2\,^1S$ and $2\,^3S$ metastable states of helium demonstrate some of the useful applications of these discrete oscillator strength distributions for excited state-excited state transitions. Most importantly, these results indicate that it is also not necessary to employ continuum basis functions in the calculation of photoionization cross sections of metastable states. This can be very significant for molecular photoionization where it is very difficult to obtain adequate continuum eigenfunctions. Some immediate applications could be to the photoionization of rare gas excimers involved in proposed gas lasers, e. g. the He_2 UV laser. From the calculated two-photon emission cross sections of the $2\,^1S$ state helium, the procedure could also be an easy and direct approach to two-photon emission cross sections in molecular systems.

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TABLE I. RPA Transition Moments and Oscillator Strengths for the $2\,^1S \rightarrow \lambda\,^1P$ and $2\,^3S \rightarrow \lambda\,^3P$ Transitions Used to Evaluate $\tilde{\alpha}_{\lambda_i}(z)$, Eq. (18)[a]

$2\,^1S \rightarrow$	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$6\,^1P$	$7\,^1P$	$8\,^1P$	$9\,^1P$
$\lvert M \rvert^b$	3.021	0.9047	0.5945	0.6430	0.4793	0.1646	0.0296	0.0036
f^b	0.3917	0.1442	0.0815	0.1334	0.1428	0.0480	0.0060	0.0003
$2\,^3S \rightarrow$	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$	$6\,^3P$	$7\,^3P$	$8\,^3P$	$9\,^3P$
$\lvert M \rvert$	2.330	0.3884	0.2971	0.4208	0.4971	0.3310	0.0922	0.0098
f	0.6094	0.0407	0.0289	0.0723	0.1634	0.1806	0.0552	0.0025

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[a] $f_{\lambda_i\lambda_j} = 2\,\omega_{\lambda_i\lambda_j} \lvert M \rvert^2$ for S → P transitions.

[b] in atomic units.

TABLE II. Transition Moments and Oscillator Strengths for the $2\,^1S \rightarrow \lambda\,^1P$ and $2\,^3S \rightarrow \lambda\,^3P$ Transitions in Different Approximations

$2\,^1S$ →		$2\,^1P$	$3\,^1P$	$4\,^1P$
TDA[a]	$\lvert M \rvert$	3.035	0.9255	0.6053
	f	0.3824	0.1494	0.0839
RPA[a]	$\lvert M \rvert$	3.021	0.9047	0.5945
	f	0.3917	0.1442	0.0815
HRPA[a]	$\lvert M \rvert$	3.012	0.9285	0.5985
	f	0.3766	0.1526	0.0831
Weiss[b]	$\lvert M \rvert$	2.916	0.9020	0.4699
	f	0.3764	0.1478	0.0508
Schiff[c]	$\lvert M \rvert$	2.916	0.9129	
	f	0.3764	0.1514	

Table II (continued)

$2\,^3S$ →		$2\,^3P$	$3\,^3P$	$4\,^3P$
TDA	$\lvert M \rvert$	2.364	0.4283	0.3194
	f	0.5857	0.0480	0.0325
RPA	$\lvert M \rvert$	2.330	0.3884	0.2971
	f	0.6094	0.0407	0.0289
HRPA	$\lvert M \rvert$	2.341	0.4319	0.3168
	f	0.5819	0.0497	0.0326
Weiss	$\lvert M \rvert$	2.531	0.5230	0.2896
	f	0.5391	0.0641	0.0240
Schiff	$\lvert M \rvert$	2.5314	0.5247	
	f	0.5391	0.0645	

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[a] See text.

[b] A. W. Weiss, J. Res. Natl. Bur. Std. (U.S.) 71A, 163 (1967).

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TABLE III. Relative Probabilities for Two-Photon Emission of the 2^1S Level of Helium

y^a	$A(y)^b$	$A(y)^c$	$A(y)^d$
0.00	0.0	0.0	0.0
0.05	28.1	24.7	25.2
0.10	65.5	58.2	59.9
0.15	94	83.8	86.4
0.20	115	103	106
0.25	130	116	120
0.30	141	126	130
0.35	149	133	137
0.40	154	138	142
0.45	157	141	145
0.50	158	141	145

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[a] $y=\omega_1/\omega_{0f}$ where ω_1 is the frequency of one of the two photons.

[b] Using the definition of the RPA for excited state-excited state transition moments of Eq. (12). A(y) is in units of $\sec^{-1}$.

[c] Eqs. (21) and (22) of text with the initial-final state experimental energy differences.

[d] Reference 18.

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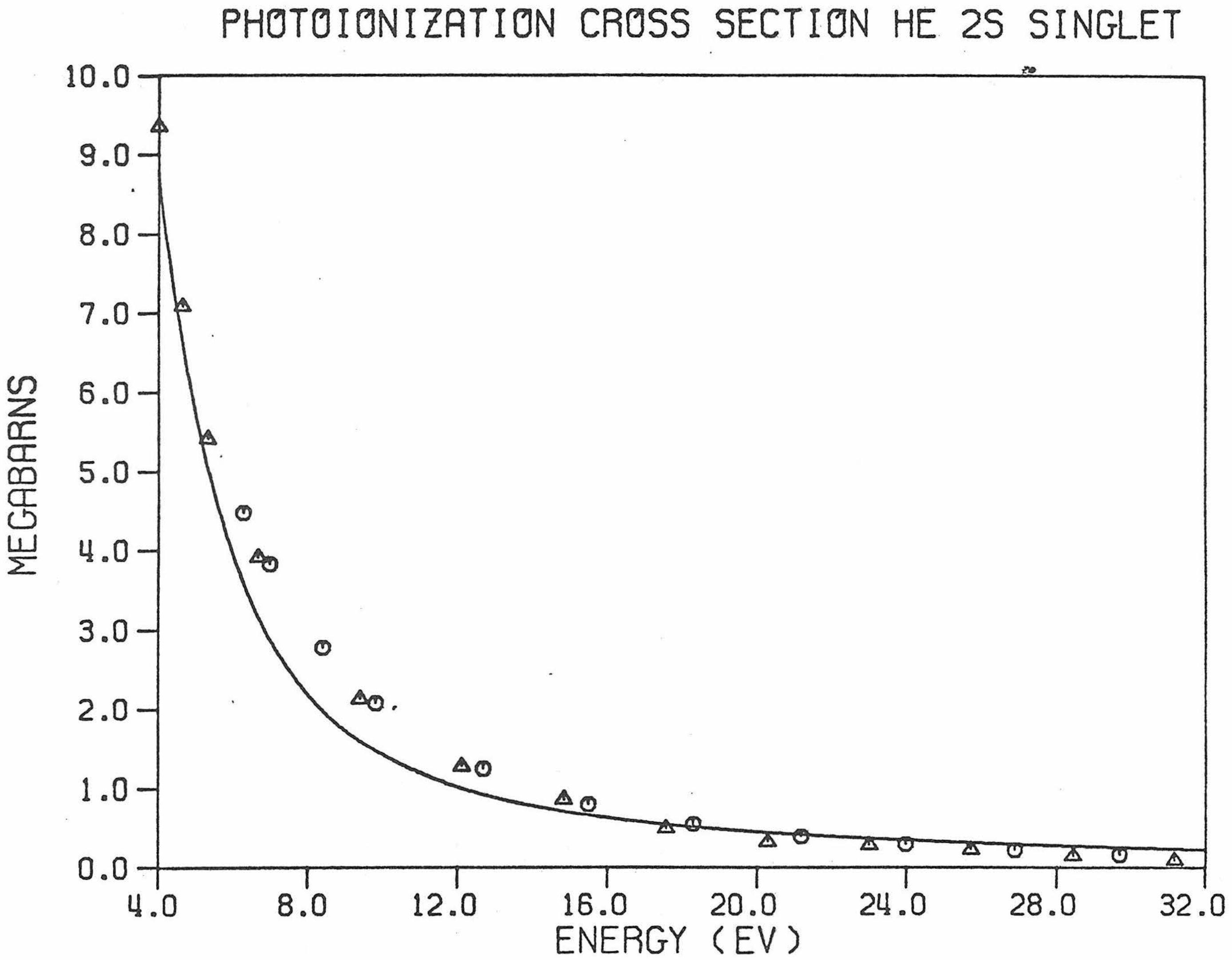
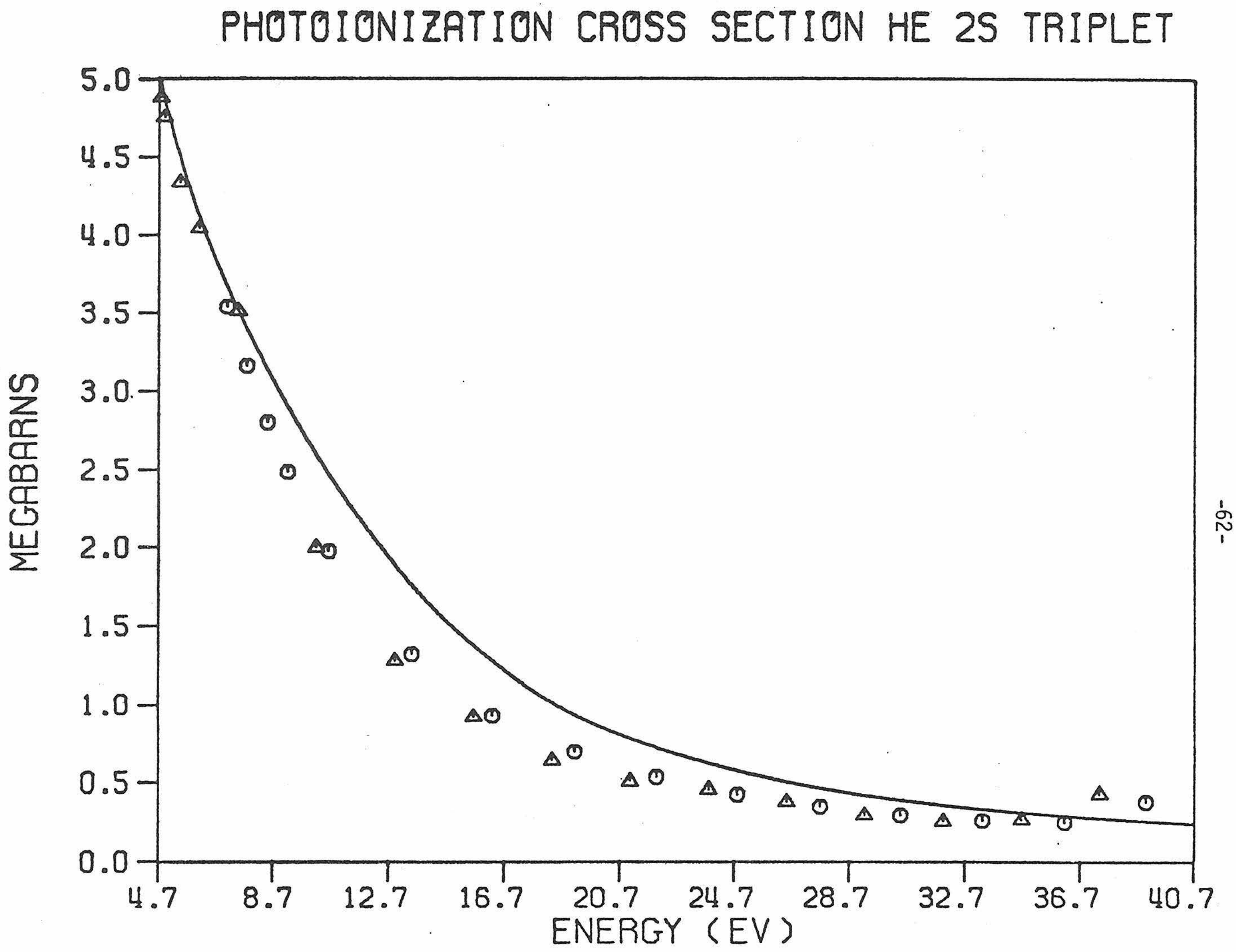
Figure Captions

Fig. 1. Photoionization cross sections of the $2\,^1S$ state of helium in megabarns. The curve shows the present cross sections obtained by numerical analytic continuation. The triangles and octagons are the calculated results of Norcross (ref. 8) and Jacobs (ref. 9) respectively.

Fig. 2. Photoionization cross sections of the $2\,^3S$ state of helium in megabarns. The curve shows the present cross sections obtained by numerical analytic continuation. The triangles and octagons are the calculated results of Norcross (ref. 8) and Jacobs (ref. 9) respectively.


PHOTOIONIZATION CROSS SECTION HE 2S SINGLET
MEGABARNS
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
ENERGY (EV)


PHOTOIONIZATION CROSS SECTION HE 2S TRIPLET
MEGABARNS
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4.7
8.7
12.7
16.7
20.7
24.7
28.7
32.7
36.7
40.7
ENERGY (EV)

(E)

Transition Moments between Excited Electronic States of N_2

Introduction

Emission intensities between the various excited states of molecular nitrogen are important in the analysis of radiative processes in the atmosphere. For example the first positive band of N_2 ($B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$) gives one of the major contributions to the radiation from hot air in the visible and near infrared at temperatures up to 10^4 K and is a strong emitter in auroral displays. Transitions between the $W\,^3\Delta_u$ and $B\,^3\Pi_g$ states can also be expected to play an important role in the aurora and in atmospheric radiative transfer [*Covey et al.*, *1973*]. Excited state-excited state electronic transition moments and their dependence on internuclear distance are obviously needed to explain and predict these band intensities. These transition moments must also be known in order to include cascade contributions to the vibrational population of states of N_2 in normal auroras, e.g. the $B\,^3\Pi_g \rightleftharpoons W\,^3\Delta_u$ and $B\,^3\Pi_g \rightleftharpoons A\,^3\Sigma_u^+$ cascade processes [*Cartwright et al.*, *1971*]. Transition moments between excited states can also be important in the modelling of gas phase lasers, e.g. the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ lasing transition in N_2.

In this paper we report transition moments and their dependence on internuclear distance for a large number of transitions between excited states of N_2. These include the following band systems: $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ (first positive system), $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ (second positive system), $B'\,^3\Sigma_u^- \rightarrow B\,^3\Pi_g$ (infrared afterglow system), $B\,^3\Pi_g \rightarrow W\,^3\Delta_u$, $a\,^1\Pi_g \rightarrow w\,^1\Delta_u$, $a\,^1\Pi_g \rightarrow a'\,^1\Sigma_u^-$, and $a\,^1\Pi_g \rightarrow b\,^1\Pi_u$. We also report moments for transitions between the $a\,^1\Pi_g$ state and the more complex

$^1\Sigma_u^+$ states. These transition moments are calculated non-empirically using the equations of motion method [Shibuya and McKoy, 1970] which is a many-body approach to the direct calculation of the quantities of physical interest in spectroscopy, i. e. excitation energies and transition moments. We report results at several levels of approximation to the equations of motion, and from the results of several applications to other molecules we expect these transition moments in N_2 to be quantitatively reliable.

In this paper we do not emphasize the quantum mechanical details of the many-body theory or computational aspects of our solutions. Such details can be found elsewhere [Yeager et al., 1975]. The point we do want to stress is that transition moments between ground and excited states or between excited states themselves can be calculated quite accurately through the theoretical models and computational procedures which have been developed in the field of molecular quantum mechanics. This is particularly so for the diatomic molecules of interest in atmospheric processes.

In the next section we give a very brief outline of the theoretical approach we use to calculate these excited state-excited transition moments in N_2. We then present the results for many band systems for six internuclear distances between $R = 0.90$ Å and $R = 1.40$ Å. The actual values are given in Tables I and II and the results for some transitions are plotted. The moments are also fitted to simple polynomials of the form $a + bR$ and $a + bR + cR^2$. In these forms the results can be easily used in the analysis of experimental data.

Theory

We have recently proposed the equations of motion method as an approach for the direct calculation of the relative quantities, e.g. transition energies and moments between the ground and excited states of a molecule, of interest in spectroscopy [Shibuya and McKoy, 1970]. The method is based on the solution of the equation of motion satisfied by the excitation operator, $O_\lambda^\dagger$, defined such that $O_\lambda^\dagger |0> = |\lambda>$ where $|0>$ and $|\lambda>$ are the ground and excited state of the system respectively [Rowe, 1968]. Excitation energies, $\omega_{0\lambda}$, and transition densities, $\rho_{0\lambda}$, for the transition $|0> \rightarrow |\lambda>$ are obtained from the solution of the equation of motion. The transition density provides the information needed to calculate the transition moment $< 0|\vec{M}|\lambda >$ where $\vec{M}$ is the electric dipole moment operator. A series of approximate solutions to these equations of motion have been derived [Shibuya et al., 1973] and applied to various molecules [H_2CO: Yeager and McKoy, 1974; H_2O: Yeager et al., 1974; CO_2: McCurdy and McKoy, 1974; N_2, CO, C_2H_4: Rose et al., 1973]. The important implication of these results for the present purpose is that the method yields accurate dipole transition moments.

Recently we have also derived expressions for the transition moment between excited states consistent with the approximations and assumptions normally used to obtain transition moments between the ground and excited states in the equations of motion method [Yeager et al., 1975]. The basic procedure is to exploit the formal properties of the excitation operators $O_\lambda^\dagger$, defined on the ground state, λ_i, to rewrite the transition moment, $< \lambda_i | M | \lambda_j >$, between excited states in a specific and useful form. We have used the resulting expressions to evaluate the transition moments between the $2\,^1S$ ($2\,^3S$) metastable state of helium and the $n\,^1P$ ($n\,^3P$) states. In this paper we will use these several approximations in the equation of motion method to the excited state-excited state transition moments between the low-lying excited states of N_2. These three approximations -- the Tamm-Dancoff approximation (TDA), the random phase approximation (RPA), and higher random phase approximation (HRPA) -- have been discussed in detail previously [Yeager et al., 1975].

Results

The ground state electron configuration of N_2 is $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g)^2$. The principal electron configuration of the $A\,^3\Sigma_u^+$, $b'\,^1\Sigma_u^+$, $B'\,^3\Sigma_u^-$, $a'\,^1\Sigma_u^-$, $W\,^3\Delta_u$, and $w\,^1\Delta_u$ states is $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^3 (3\sigma_g)^2 (1\pi_g)$ and that of the $B\,^3\Pi_g$ and $a\,^1\Pi_g$ state is $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g) (1\pi_g)$. In a previous paper [Coughran et al., 1973] we reported the excitation energies and dipole transition moments from the ground state to these excited states at several internuclear distances. The basis set used in these calculations and other details are given in that paper. The basis set consists of a valence [4s 3p] basis contracted from a (9s 5p) set of primitive Gaussian functions. In addition two diffuse $d\pi$ and $p\sigma$ Gaussian functions are included at the center of the molecule. We use the transition densities and other results of these calculations to calculate the transition moments between the excited states of N_2.

Tables I and II give these transition moments for the triplet-triplet and singlet-singlet transitions respectively. In Table III we also list the coefficients of the polynomials of the form $M(R) = a + bR$ and $M(R) = a + bR + cR^2$ obtained by a least-squares fit of the data of Tables I and II. These results should be immediately useful to those who try to extract the dependence of the electronic transition moment on the r-centroid from experimental intensity data. In such analyses, e.g. [Cunio and Jansson, 1968] and [Jeunehomme, 1966], the transition moment is expanded in polynomials of the r-centroid whereas our expansion of the electronic transition moment is in terms of the internuclear distance. These expansions are not identical but some approximate comparisons can be made.

From Tables I and III we see that the transition moments for the B $^3\Pi_g$ - W $^3\Delta_u$ and B $^3\Pi_g$ - A $^3\Sigma_u^+$ transitions are almost equal and both show considerable R-dependence. In their model calculations Cartwright [Cartwright et al., 1971] assumed a value for the B → W transition moment equal to 1.7 and 0.85 of the B → A transition moment at R = 1.3 Å. These choices were made to see the effect of this transition moment on the predictions of their models. We see that the assumption of $M(B \rightarrow W) = 0.85\ M(B \rightarrow A)$ is in fact close to our predictions.

We also comment on the transitions involving the $^1\Sigma_u^+$ states. Avoided crossings among these states make these states interesting. The c′ state is primarily a $3\sigma_g \rightarrow 3\sigma_u$ excitation, the b′ state $\pi_u \rightarrow \pi_g$, and the e′ state $3\sigma_g \rightarrow 4p\sigma$. These are deperturbed states [Dressler, 1969; Coughran et al., 1973] which correspond to hypothetical electronic states of the same symmetry which are allowed to cross. For the $^1\Sigma_u^+$ states we have simply used the lowest two Σ_u^+ states in our calculations. Neither the b′ nor the e′ states are always in the two lowest states and the relative ordering may differ somewhat depending on the approximation used.

Figures 1 to 6 show the transition moments of several transitions in various approximations. In general the HRPA results should be regarded as the most reliable.

Conclusions

We have used a recently proposed many-body theory -- the equations of motion method -- to calculate the transition moments between excited states of molecular nitrogen. From the results of previous applications of this method we expect the predicted transition moments to be accurate. These transition moments and their dependence on internuclear distance can be immediately useful in the analysis of experimental intensity data. With the present theoretical methods and computational procedures of quantum chemistry we conclude that it is probably simpler to calculate the variation of transition moments with internuclear distance in diatomic molecules than to attempt to obtain this dependence from a detailed analysis of experimental intensity data.

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TABLE I. Transition Moments Between Excited Triplet States[a]

R (au)	R (Å)	TDA	RPA	HRPA	TDA	RPA	HRPA
		$B\,^3\Pi_g - W\,^3\Delta_u$			$B\,^3\Pi_g - A\,^3\Sigma_u^+$		
1.701	0.90	0.308	0.318	0.311	0.329	0.350	0.362
1.890	1.00	0.295	0.312	0.300	0.301	0.338	0.318
2.068	1.094[b]	0.277	-[c]	0.284	0.280	-[c]	0.296
2.268	1.20	0.250	-	0.260	0.254	-	0.273
2.457	1.30	0.222	-	0.233	0.227	-	0.248
2.645	1.40	0.191	-	0.203	0.197	-	0.217
		$B\,^3\Pi_g - B'\,^3\Sigma_u^-$			$B\,^3\Pi_g - C\,^3\Pi_u$		
	0.90	0.308	0.306	0.308	1.53	1.55	1.55
	1.00	0.294	0.293	0.295	1.58	1.59	1.60
	1.094	0.274	-[c]	0.277	1.59	-[c]	1.62
	1.20	0.246	-	0.252	1.59	-	1.62
	1.30	0.215	-	0.224	1.57	-	1.61
	1.40	0.180	-	0.195	1.54	-	1.58

[a] Absolute value of the transition moment in atomic units. 1 au = 2.542 D. See text for discussion of the headings TDA, RPA, and HRPA.

[b] Experimental internuclear distance of the ground state.

[c] - in this column indicates an instability in this approximation.

TABLE II. Transition Moments Between Excited Singlet States of N_2[a]

R (au)	R (Å)	TDA	RPA	HRPA	TDA	RPA	HRPA
		$a\,^1\Pi_g$ - $w\,^1\Delta_u$			$a\,^1\Pi_g$ - $c'\,^1\Sigma_u^+$		
1.701	0.90	0.269	0.269	0.266	0.729	0.701	0.951
1.890	1.00	0.263	0.263	0.263	0.430	0.404	0.555
2.068	1.094[b]	0.245	0.246	0.248	0.295[c]	0.195[c]	0.385[c]
2.268	1.20	0.218	0.220	0.224	0.251	0.252	0.334
2.457	1.30	0.188	0.194	0.196	0.179	0.166	0.269
2.645	1.40	0.155	0.176	0.167	-[d]	-[d]	0.233
		$a\,^1\Pi_g$ - $b'\,^1\Sigma_u^+$			$a\,^1\Pi_g$ - $e'\,^1\Sigma_u^+$		
	0.90	-[d]	-	-	0.162	0.153	0.182
	1.00	-	0.043	-	0.044	-[d]	0.138
	1.094	0.107[c]	0.247[c]	0.093[c]	-[d]	-	-[d]
	1.20	0.051	0.066	0.027	-	-	-
	1.30	0.017	0.064	0.094	-	-	-
	1.40	0.0002	0.038	0.086	-	-	-
		$a\,^1\Pi_g$ - $a'\,^1\Sigma_u^-$			$a\,^1\Pi_g$ - $b\,^1\Pi_u$		
	0.90	0.307	0.311	0.312	1.45	1.47	1.42
	1.00	0.282	0.291	0.288	1.53	1.54	1.54
	1.094	0.256	0.271	0.263	1.54	1.56	1.57
	1.20	0.224	0.253	0.232	1.53	1.55	1.56
	1.30	0.191	0.264	0.200	1.51	1.54	1.54
	1.40	0.158	-[e]	0.165	1.47	1.52	1.50

[a] Absolute value of the transition moment in atomic units (au). 1 au = 2.542 D. See text for discussion of the headings TDA, RPA, and HRPA.

[b] Experimental equilibrium internuclear distance of the ground state.

[c] The b′ $^1\Sigma_u^+$ and c′ $^1\Sigma_u^+$ states are close to each other at this geometry and there is significant mixing of the particle-hole amplitudes (one-electron excitations) usually associated with each state.

[d] In this column - means that at this geometry this $^1\Sigma_u^+$ state is not one of the two lowest $^1\Sigma_u^+$ states in this approximation.

[e] Unstable in this approximation.

TABLE III. Coefficients of the Least Squares Fit Polynomial to the HRPA Data of Tables I and II

Transition	$M(R)$[a] $= a + bR$			$M(R) = a + bR + cR^2$			
	a	b	RMS[b]	a	b	c	RMS[b]
$a\,^1\Pi_g - w\,^1\Delta_u$ [c]	0.5128	-0.1295	0.0039	0.0380	0.2932	-0.0929	0.0017
$a\,^1\Pi_g - c'\,^1\Sigma_u^+$	0.9456	-0.2714	0.0057	7.271	-5.707	1.157	0.0453
$a\,^1\Pi_g - a'\,^1\Sigma_u^-$	0.5813	-0.1558	0.0035	0.3987	0.0161	-0.0395	0.0001
$a\,^1\Pi_g - b\,^1\Pi_u$	-	-	-	-0.9557	2.266	-0.5068	0.0152
$B\,^3\Pi_g - W\,^3\Delta_u$	0.5497	-0.1296	0.0036	0.1988	0.1835	-0.0689	0.0005
$B\,^3\Pi_g - A\,^3\Sigma_u^+$	0.5663	-0.1307	0.0023	0.7506	-0.2875	0.0330	0.0046
$B\,^3\Pi_g - B'\,^3\Sigma_u^-$	0.5529	-0.1344	0.0028	0.2528	0.1327	-0.0586	0.0010
$B\,^3\Pi_g - C\,^3\Pi_u$	-	-	-	0.2798	1.206	-0.2706	0.0028

[a] In atomic units.

[b] Root Mean Square error.

[c] The transition moment at R = 0.90 Å was excluded from the $M(R) = a + bR$ fit for the $a\,^1\Pi_g$ - $w\,^1\Delta_u$, $B\,^3\Pi_g$ - $W\,^3\Delta_u$, $B\,^3\Pi_g$ - $A\,^3\Sigma_u^+$, and $B\,^3\Pi_g$ - $B'\,^3\Sigma_u^-$ transitions. The transition moments at R = 0.90 Å and R = 1.00 Å were excluded from the linear fit for the $a\,^1\Pi_g$ - $c'\,^1\Sigma_u^+$ transition.

Figure Captions

Fig. 1. Transition moment for the $a\,^1\Pi_g - w\,^1\Delta_u$ transition in the three different approximations. ——— HRPA, – – – RPA, ——— – TDA. See Shibuya et al. [1970] and text for an explanation of these approximations.

Fig. 2. Transition moment for the $a\,^1\Pi_g - c'\,^1\Sigma_u^+$ transition in the three different approximations. ——— HRPA, – – – RPA, ——— – TDA. See Shibuya et al. [1970] and text for an explanation of these approximations.

Fig. 3. Transition moment for the $a\,^1\Pi_g - b'\,^1\Sigma_u^+$ transition in the three different approximations. ——— HRPA, – – – RPA, ——— – TDA. See Shibuya et al. [1970] and text for an explanation of these approximations.

Fig. 4. Transition moment for the $B\,^3\Pi_g - A\,^3\Sigma_u^+$ transition in the three different approximations. ——— HRPA, – – – RPA, ——— – TDA. See Shibuya et al. [1970] and text for an explanation of these approximations.

Fig. 5. HRPA transition moments for the $a\,^1\Pi_g - a'\,^1\Sigma_u^-$ transition (left) and the $a\,^1\Pi_g - b\,^1\Pi_u$ transition (right).

Fig. 6. HRPA transition moments for the $B\,^3\Pi_g - W\,^3\Delta_u$ transition (upper left), $B\,^3\Pi_g - B'\,^3\Sigma_u^-$ transition (upper right), and the $B\,^3\Pi_g - C\,^3\Pi_u$ transition (lower left).

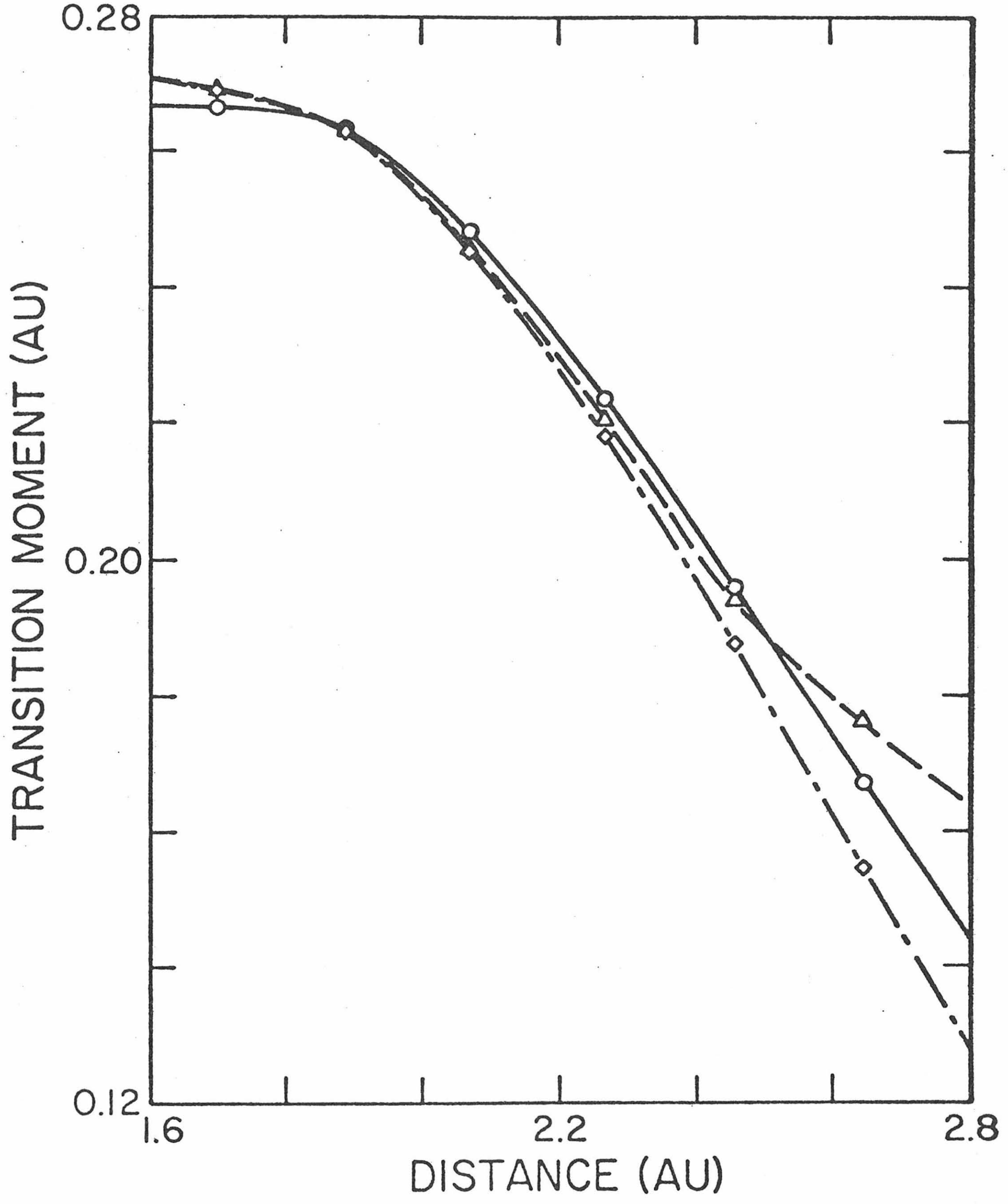

Fig. 1

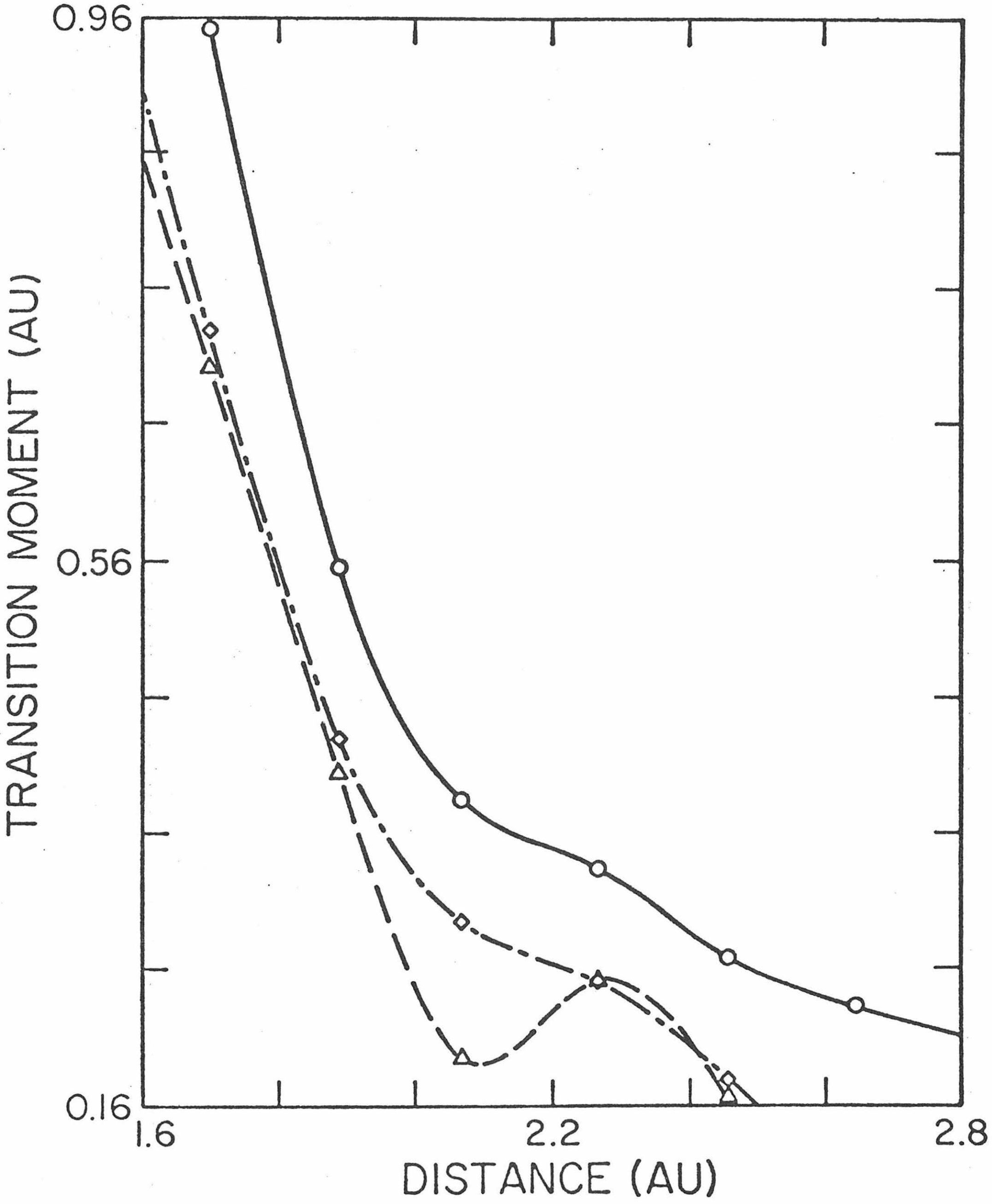

Fig. 2

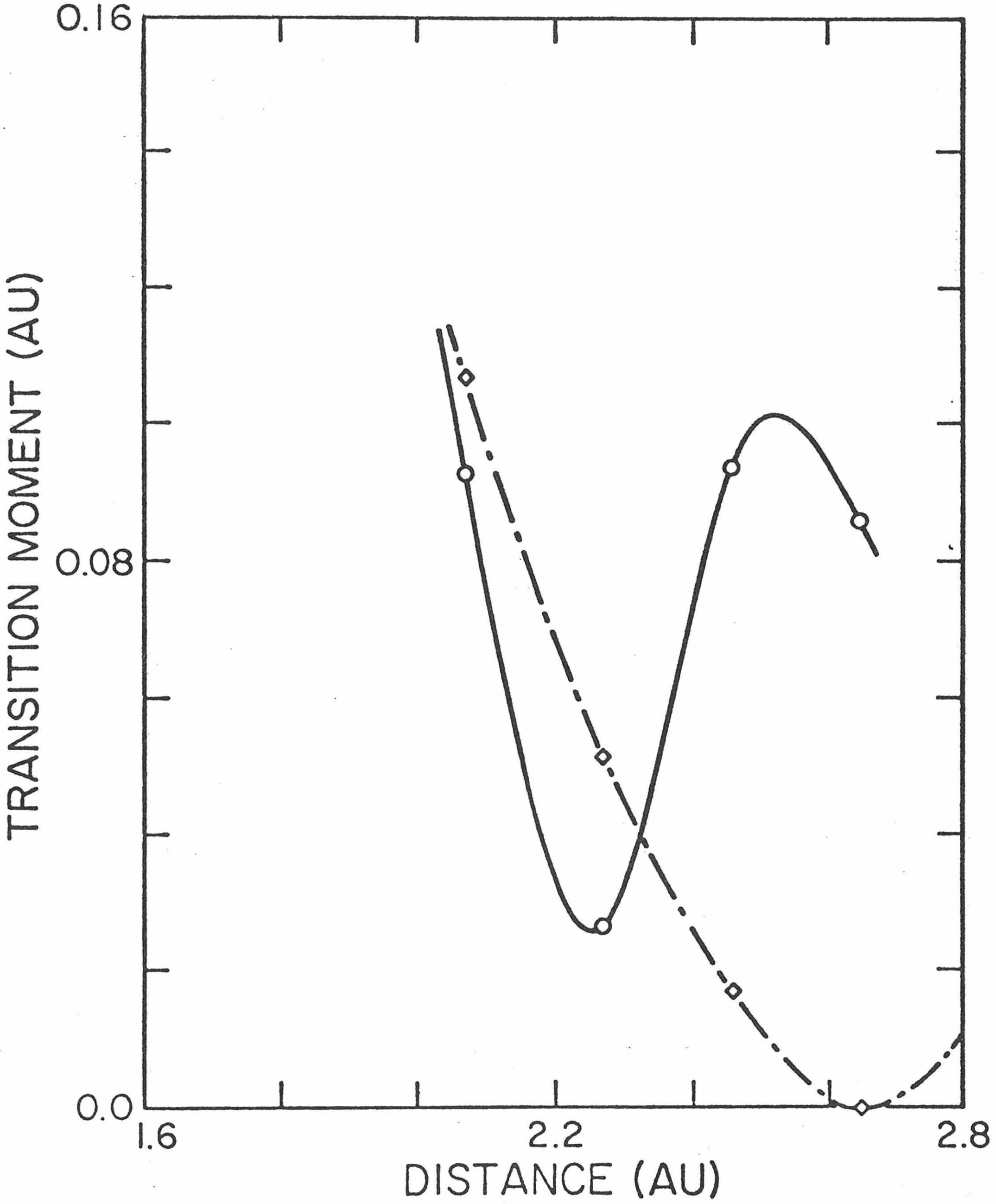

Fig. 3

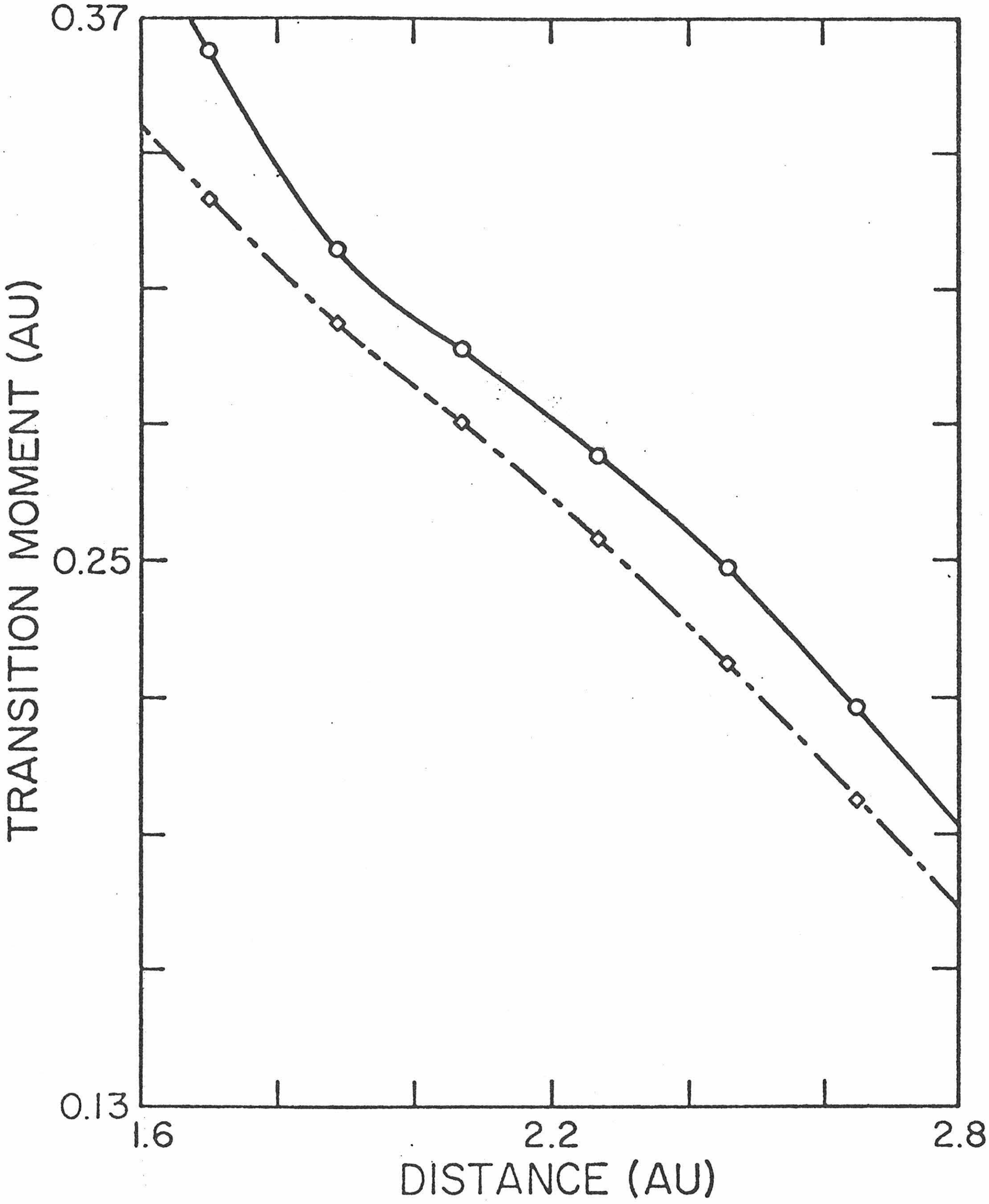

Fig. 4

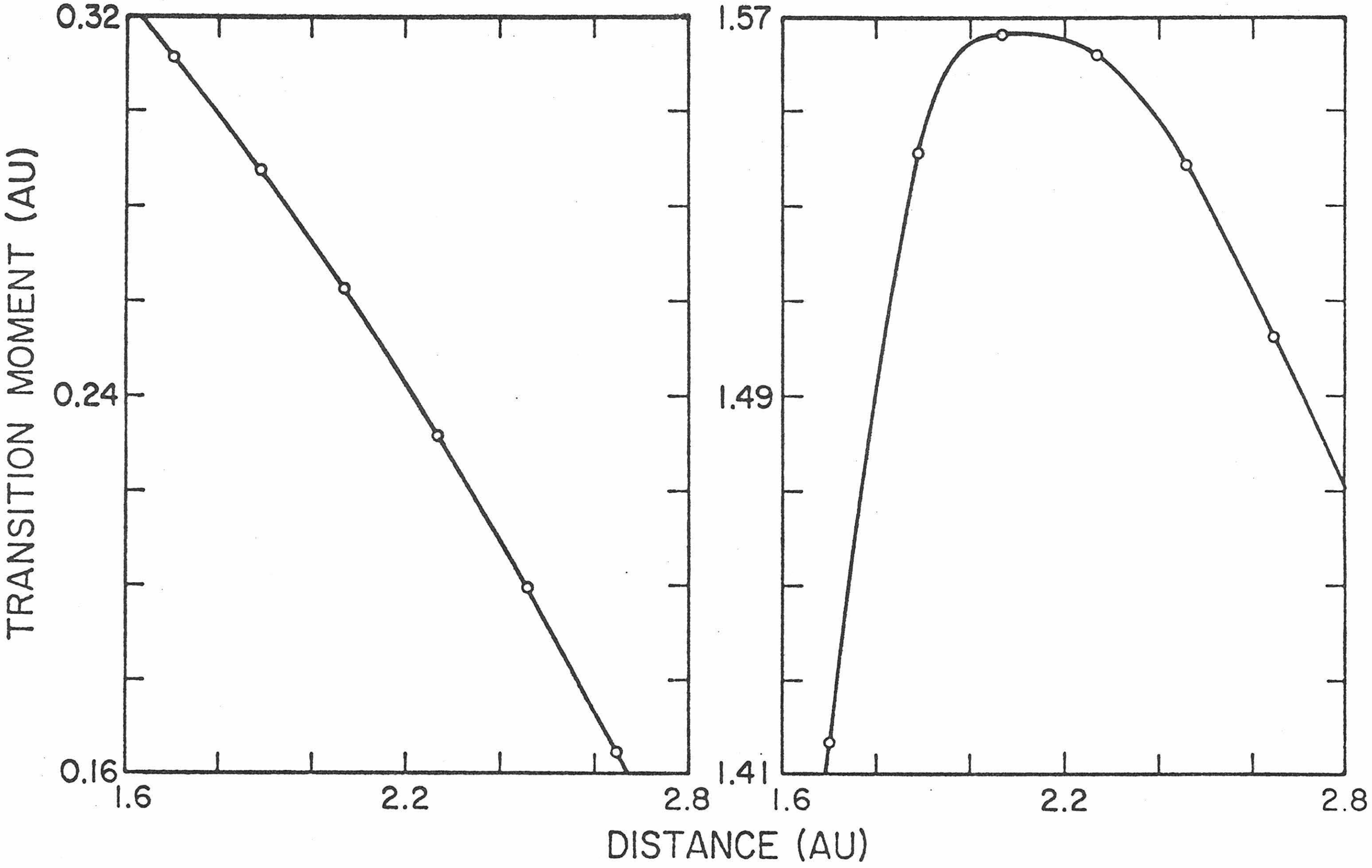
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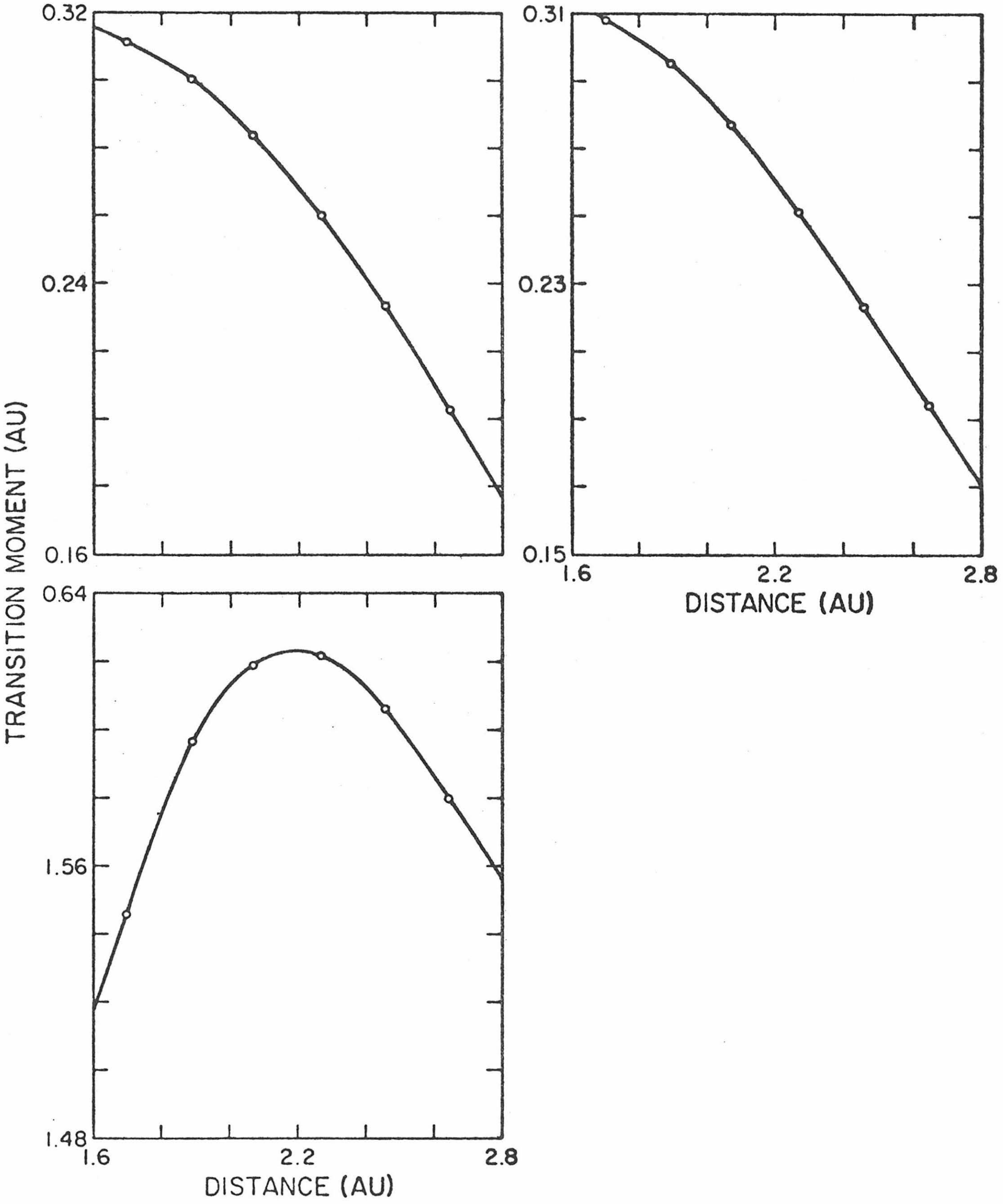
Fig. 5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TRANSITION MOMENT (AU)
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DISTANCE (AU)

Fig. 6

Part II

An Equations of Motion Approach for Open Shell Systems

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 method 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 Section II, we review the equations of motion method and explain the modifications necessary for open shells. In particular, in section 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 section IV. For lithium, since most low-lying transitions are 2s → 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 $|0>$ generates an excited state $|\lambda>$, i.e.

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

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

$$O_\lambda |0> = 0 \tag{2}$$

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

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

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 $<\lambda|W|0>$ of the operator W from

$$<\lambda|W|0> = <0|[O_\lambda, W]|0> \tag{5}$$

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)

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

where

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

Matrices $\underset{\frown}{A}$ and $\underset{\frown}{U}$ are Hermitian, $\underset{\frown}{B}$ is symmetric, and $\underset{\frown}{V}$ is antisymmetric.

A second approximation is to use a nonexact ground state, e.g. the Hartree-Fock ground state or some simple 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 $\underset{\sim}{A}$ and $\underset{\sim}{B}$ can be given.

For the OSTDA and OSRPA we approximate $|0>$ 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]

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

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

$$\mathcal{H} = \sum_{i'j'} h_{i'j'} , \; c^{\dagger}_{i'} \, c_{j'} + \tfrac{1}{2} \sum_{i'j'k'l'} V_{i'j'k'l'} \; c^{\dagger}_{j'} \, c^{\dagger}_{i'} \, c_{k'} \, c_{l'} \tag{11}$$

$$= \sum_{ij} h_{ij} \, (c^{\dagger}_{i\alpha} \, c_{j\alpha} + c^{\dagger}_{i\beta} \, c_{j\beta}) - \tfrac{1}{2} \sum_{ij} \sum_{k} V_{ikkj} \, (c^{\dagger}_{i\alpha} \, c_{j\alpha} + c^{\dagger}_{i\beta} \, c_{j\beta})$$

$$+ \tfrac{1}{2} \sum_{ijkl} V_{ijkl} \, (c^{\dagger}_{i\alpha} \, c_{k\alpha} + c^{\dagger}_{i\beta} \, c_{k\beta}) \, (c^{\dagger}_{j\alpha} \, c_{l\alpha} + c^{\dagger}_{j\beta} \, c_{l\beta}) \tag{12}$$

where primed indices denote spin orbitals and unprimed indices oribtals. 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

$$V_{ijkl} = \int \varphi_i^*(1)\, \varphi_j^*(2)\, \frac{1}{r_{12}}\, \varphi_k(1)\, \varphi_l(2)\, d\tau \tag{13}$$

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 $|0>$ 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.

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

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 $c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{\mu\beta}\, c_{\mu\alpha}$.

A simple example will clarify this. Lithium has a $|1s\alpha\ 1s\beta\ 2s\alpha >$ 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 $C^{\dagger}_i$ operating on $|1s\alpha\ 1s\beta\ 2s\alpha >$ excites an electron from a 1s orbital to a 3s orbital keeping $M_S = \frac{1}{2}$, there are three possibilities

$$|1s\alpha\ 2s\alpha\ 3s\beta >, \quad |1s\beta\ 2s\alpha\ 3s\alpha >, \quad |1s\alpha\ 2s\beta\ 3s\alpha > \tag{16}$$

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 $C^{\dagger} = -c^{\dagger}_{3s\alpha}\, c_{1s\beta}\, c^{\dagger}_{2s\beta}\, c_{2s\alpha}$, a two-body operator. That is

$$-c^{\dagger}_{3s\alpha}\, c_{1s\beta}\, c^{\dagger}_{2s\beta}\, c_{2s\alpha}\, |1s\alpha\ 1s\beta\ 2s\alpha > \rightarrow |1s\alpha\ 2s\beta\ 3s\alpha > \tag{17}$$

All $C^{\dagger}_i$'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 $T_q^{(k)\dagger}$

$$|\Gamma S' M_S' > = \sum_{q, M_S} T_q^{(k)\dagger} \, | S M_S > < k S q M_S | k S S' M_S' > \tag{18}$$

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 in higher order schemes which has a different spin from the ground state to have slight errors 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 random 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 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 $|\mathrm{HF}>$ as an approximation to $|0>$ in Eq. (8).

4. Choose excitation operators $O_\lambda^\dagger$ such that the p-h excitation operators $\{C_i^\dagger\}$ operating on $|\mathrm{HF}>$ 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 $|0>$ 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 shall 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 configurations 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

$$O_\lambda \,|\, 0 > \;=\; 0 \tag{19}$$

We differ from Jørgensen[13] by choosing an approximation to $|\,0>$ 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

$$< 0 \,|\, D \,|\, n > \;=\; \vec{D}_{on} = \sqrt{2}\left[\sum_{m\gamma} (Y^*_{m\gamma} + Z^*_{m\gamma})\, \vec{d}_{m\gamma}\right. \tag{20}$$

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

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

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 $|(\text{closed shell})\,\Omega\alpha>$. 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

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

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 Figure 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.

B. Open shell triplet

The ground state is $|(\text{closed shell})\, \Omega_1 \alpha \Omega_2 \alpha >$ where Ω_1 and Ω_2 may be degenerate. For this case the Hamiltonian is

$$\mathcal{H} = \sum_{i} \epsilon_i \left(c^{\dagger}_{i\alpha} c_{i\alpha} + c^{\dagger}_{i\beta} c_{i\beta} \right) + \sum_{ij} \Big(\sum_{\nu} \left(\tfrac{1}{2} V_{i\nu\nu j} - 2 V_{i\nu j\nu} \right) +$$

$$\sum_{\Omega} \left((b - \tfrac{1}{2}) V_{i\Omega\Omega j} - V_{i\Omega j\Omega} \right) - \sum_{p} \tfrac{1}{2} V_{ippj} \Big) \left(c^{\dagger}_{i\alpha} c_{j\alpha} + c^{\dagger}_{i\beta} c_{j\beta} \right)$$

$$+ \tfrac{1}{2} \sum_{ijkl} V_{ijkl} \left(c^{\dagger}_{i\alpha} c_{k\alpha} + c^{\dagger}_{i\beta} c_{k\beta} \right) \left(c^{\dagger}_{j\alpha} c_{l\alpha} + c^{\dagger}_{j\beta} c_{l\beta} \right) \qquad (26)$$

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.

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

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

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

The various possible excitations are shown in Figure 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 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 $\underset{\frown}{A}$ and $\underset{\frown}{B}$ 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 part 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 → 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.

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

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

The results for Li are in good agreement with experiment primarily because the low-lying lithium atom transitions involve predominantly 2s → ns, np transitions. The orbital energy of the 1s electrons is -2.478 au and the 2s electron -0.196 au. 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 through 10 in Tables II and III are set equal to zero The resulting TDA and RPA results are identical to those of Table IX. 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

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

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 $< 4s\ 3p >$ 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 eV 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

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

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 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 au 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 f 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 2.78 a_0^3 in the TDA and 2.71 a_0^3 in the RPA. $\alpha_{||}$, the parallel component, is 18.6 a_0^3 in the TDA and 21.5 a_0^3 in the RPA. Langhoff[23] gives the perpendicular component as 8.17 a_0^3 and the parallel component as 15.5 a_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 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.

Table I. Spherical Tensor p-h Operators for the Doublet $|(\text{closed shell})\,\Omega\alpha>$ Ground State

Doublet Excited State ($S = \frac{1}{2}$, $M_S = \frac{1}{2}$)

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

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

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

$$\begin{aligned}{}_2C^{\dagger}_{m\nu}(00) = \sqrt{2/3}\,(&-c^{\dagger}_{m\alpha}\,c_{\nu\beta}\,c^{\dagger}_{\Omega\beta}\,c_{\Omega\alpha} - c^{\dagger}_{m\beta}\,c_{\nu\alpha}\,c^{\dagger}_{\Omega\alpha}\,c_{\Omega\beta}\\ &+ \tfrac{1}{2}\ {}^{\dagger}_{m\alpha}\,c_{\nu\alpha}\,c^{\dagger}_{\Omega\beta}\,c_{\Omega\beta} + \tfrac{1}{2}\,c^{\dagger}_{m\beta}\,c_{\nu\beta}\,c^{\dagger}_{\Omega\alpha}\,c_{\Omega\alpha}\\ &- \tfrac{1}{2}\,c^{\dagger}_{m\alpha}\,c_{\nu\alpha}\,c^{\dagger}_{\Omega\alpha}\,c_{\Omega\alpha} - \tfrac{1}{2}\,c^{\dagger}_{m\beta}\,c_{\nu\beta}\,c^{\dagger}_{\Omega\beta}\,c_{\Omega\beta})\end{aligned}$$

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 $|(\text{closed shell})\, \Omega\alpha >$ Ground State

Doublet Matrices

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

2. $A_{(P1-\Omega),(\Omega-H2)} = -\, V_{H2P1\Omega\Omega}$

3. $A_{(P1-\Omega),(P2-\Omega)} = \delta_{P1P2}\,(\epsilon_{P1} - \epsilon_{\Omega})$

4. $A_{1(P1-H1),(\Omega-H2)} = 1/\sqrt{2}\,(-\,\delta_{H1H2}\, V_{P1\Omega\Omega\Omega} - 2\, V_{H1H2P1\Omega}$
   $+ V_{H1P1H2\Omega})$

5. $A_{1(P1-H1),(P2-\Omega)} = 1/\sqrt{2}\,(\delta_{P1P2}\, V_{H1\Omega\Omega\Omega} + 2\, V_{H1P2P1\Omega}$
   $-\, V_{H1P1\Omega P2})$

6. $A_{1(P1-H1),1(P2-H2)} = \delta_{H1H2}\,\delta_{P1P2}\,(\epsilon_{P1} - \epsilon_{H1}) + \delta_{H1H2}$
   $(V_{P1\Omega P2\Omega} - \frac{1}{2}\, V_{P1P2\Omega\Omega}) + 2\, V_{H1H2P1P2} - V_{H1P1H2P2}$

7. $A_{2(P1-H1),(\Omega-H2)} = \sqrt{3/2}\,(V_{H1P1H2\Omega} - \delta_{H1H2}\, V_{P1\Omega\Omega\Omega})$

8. $A_{2(P1-H1),(P2-\Omega)} = \sqrt{3/2}\,(V_{H1P1\Omega P2} - V_{H1\Omega\Omega\Omega}\,\delta_{P1P2})$

9. $A_{2(P1-H1),1(P2-H2)} = \sqrt{3}/2\,(\delta_{H1H2}\, V_{P1P2\Omega\Omega} - \delta_{P1P2}\, V_{H1H2\Omega\Omega})$

Table II (continued)

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

Quartet Matrices

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

Table III. B Matrix Formulas for the Doublet $|(\text{closed shell})\,\Omega\alpha>$ Ground State

Doublet Matrices

1. $B_{(\Omega-H1),(\Omega-H2)} = 0$

2. $B_{(P1-\Omega),(\Omega-H2)} = -\frac{3}{2} V_{H2P1\Omega\Omega}$

3. $B_{(P1-\Omega),(P1-\Omega)} = 0$

4. $B_{1(P1-H1),(\Omega-H2)} = \sqrt{2}\,(-V_{H1H2P1\Omega} + \frac{1}{2} V_{H1H2\Omega P1})$

5. $B_{1(P1-H1),(P2-\Omega)} = \sqrt{2}\,(V_{H1P2P1\Omega} - \frac{1}{2} V_{H1P1P2\Omega})$

6. $B_{1(P1-H1),1(P2-H2)} = 2\,V_{H1H2P1P2} - V_{H1H2P2P1}$

7. $B_{2(P1-H1),(\Omega-H2)} = \frac{1}{2}\sqrt{3/2}\;V_{H1H2\Omega P1}$

8. $B_{2(P1-H1),(P2-\Omega)} = \frac{1}{2}\sqrt{3/2}\;V_{H1P1P2\Omega}$

9. $B_{2(P1-H1),1(P2-H2)} = 0$

10. $B_{2(P1-H1),2(P2-H2)} = -\,V_{H1H2P2P1}$

Quartet Matrices

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

Table IV. R Values for the Doublet

$|(\text{closed shell})\,\Omega\alpha>$ Ground State

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

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

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

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

Table V. Spherical Tensor p-h Operators for the Triplet $|(\text{closed shell})\, \Omega_1\, \Omega_2 >$ Ground State. Ω_1 and Ω_2 are degenerate.

Triplet Excited States, $|(\text{closed shell})\, \Omega_1 \alpha \Omega_2 \alpha >$ 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. ${}_1C^{\dagger}_{m\nu}(00) = 1/\sqrt{2}\, (c^{\dagger}_{m\alpha}\, c_{\nu\alpha} + c^{\dagger}_{m\beta}\, c_{\nu\beta})$

$$
\begin{aligned}
{}_2C^{\dagger}_{m\nu}(00) = \tfrac{1}{2}\, ((& c^{\dagger}_{m\alpha}\, c_{\nu\beta}\, c^{\dagger}_{\Omega_2 \beta}\, c_{\Omega_2 \alpha} + c^{\dagger}_{m\beta}\, c_{\nu\alpha}\, c^{\dagger}_{\Omega_2 \alpha}\, c_{\Omega_2 \beta} \\
& + c^{\dagger}_{m\alpha}\, c_{\nu\beta}\, c^{\dagger}_{\Omega_1 \beta}\, c_{\Omega_1 \alpha} + c^{\dagger}_{m\beta}\, c_{\nu\alpha}\, c^{\dagger}_{\Omega_1 \alpha}\, c_{\Omega_1 \beta}) \\
& + \tfrac{1}{2}\, (-c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c_{\Omega_2 \beta}\, c_{\Omega_2 \beta} - c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{\Omega_2 \alpha}\, c_{\Omega_2 \alpha} \\
& + c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{\Omega_2 \alpha}\, c_{\Omega_2 \alpha} + c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{\Omega_2 \beta}\, c_{\Omega_2 \beta}) \\
& + \tfrac{1}{2}\, (-c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{\Omega_1 \beta}\, c_{\Omega_1 \beta} - c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{\Omega_1 \alpha}\, c_{\Omega_1 \alpha} \\
& + c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{\Omega_1 \alpha}\, c_{\Omega_1 \alpha} + c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{\Omega_1 \beta}\, c_{\Omega_1 \beta}))
\end{aligned}
$$

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

$$- c^\dagger_{m\alpha}\, c_{\nu\beta}\, c^\dagger_{\Omega_1\beta}\, c_{\Omega_1\alpha} - c^\dagger_{m\beta}\, c_{\nu\alpha}\, c^\dagger_{\Omega_1\alpha}\, c_{\Omega_1\beta})$$

$$+ \tfrac{1}{2}\ (-c^\dagger_{m\alpha}\, c_{\nu\alpha}\, c^\dagger_{\Omega_2\beta}\, c_{\Omega_2\beta} - c^\dagger_{m\beta}\, c_{\nu\beta}\, c^\dagger_{\Omega_2\alpha}\, c_{\Omega_2\alpha}$$

$$+ c^\dagger_{m\alpha}\, c_{\nu\alpha}\, c^\dagger_{\Omega_2\alpha}\, c_{\Omega_2\alpha} + c^\dagger_{m\beta}\, c_{\nu\beta}\, c^\dagger_{\Omega_2\beta}\, c_{\Omega_2\beta})$$

$$- \tfrac{1}{2}\ (-c^\dagger_{m\alpha}\, c_{\nu\alpha}\, c^\dagger_{\Omega_1\beta}\, c_{\Omega_1\beta} - c^\dagger_{m\beta}\, c_{\nu\beta}\, c^\dagger_{\Omega_1\alpha}\, c_{\Omega_1\alpha}$$

$$+ c^\dagger_{m\alpha}\, c_{\nu\alpha}\, c^\dagger_{\Omega_1\alpha}\, c_{\Omega_1\alpha} + c^\dagger_{m\beta}\, c_{\nu\beta}\, c^\dagger_{\Omega_1\beta}\, c_{\Omega_1\beta}))$$

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, $\left|(\text{closed shell})\, \frac{s\iota_1\alpha\, s\iota_2\beta + s\iota_1\beta\, s\iota_2\alpha}{\sqrt{2}}\right>$ Ground State

a. $C^{\dagger}_{s\iota_1\nu}(10) = c^{\dagger}_{s\iota_1\alpha}\, c_{\nu\alpha} - c^{\dagger}_{s\iota_1\beta}\, c_{\nu\beta}$

b. $C^{\dagger}_{s\iota_2\nu}(10) = -c^{\dagger}_{s\iota_2\alpha}\, c_{\nu\alpha} + c^{\dagger}_{s\iota_2\beta}\, c_{\nu\beta}$

c. $C^{\dagger}_{m s\iota_2}(10) = c^{\dagger}_{m\beta}\, c_{s\iota_2\beta} - c^{\dagger}_{m\alpha}\, c_{s\iota_2\alpha}$

d. $C^{\dagger}_{m s\iota_1}(10) = c^{\dagger}_{m\alpha}\, c_{s\iota_1\alpha} - c^{\dagger}_{m\beta}\, c_{s\iota_1\beta}$

e. $${}_2C^{\dagger}_{m\nu}(10) = 1/\sqrt{6}\, (c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_2\beta}\, c_{s\iota_2\beta} - c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_2\alpha}\, c_{s\iota_2\alpha}$$

$$- c^{\dagger}_{m\alpha}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_2\beta}\, c_{s\iota_2\alpha} + c^{\dagger}_{m\beta}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_2\alpha}\, c_{s\iota_2\beta}$$

$$+ c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_1\beta} - c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_1\alpha}\, c_{s\iota_1\alpha}$$

$$- c^{\dagger}_{m\alpha}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_1\alpha} + c^{\dagger}_{m\beta}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_1\alpha}\, c_{s\iota_1\beta})$$

$${}_3C^{\dagger}_{m\nu}(10) = 1/2\sqrt{2}\, (c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_1\alpha}\, c_{s\iota_1\alpha} - c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_1\beta}$$

$$+ c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_1\alpha}\, c_{s\iota_1\alpha} - c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_1\beta}$$

$$- c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_2\alpha}\, c_{s\iota_2\alpha} + c^{\dagger}_{m\beta}\, c_{\nu\beta}\, c^{\dagger}_{s\iota_2\beta}\, c_{s\iota_2\beta}$$

$$- c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_2\alpha}\, c_{s\iota_2\alpha} + c^{\dagger}_{m\alpha}\, c_{\nu\alpha}\, c^{\dagger}_{s\iota_2\beta}\, c_{s\iota_2\beta})$$

f. $${}_1C^{\dagger}_{s\iota_2 s\iota_1}(10) = \tfrac{1}{2}\, (c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_2\alpha}\, c^{\dagger}_{s\iota_1\alpha}\, c_{s\iota_1\beta} - c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_2\beta}\, c^{\dagger}_{s\iota_1\beta}\, c_{s\iota_1\beta}$$

$$+ c^{\dagger}_{\Omega_1\alpha} c_{\Omega_2\alpha} c^{\dagger}_{\Omega_1\alpha} c_{\Omega_1\alpha} - c^{\dagger}_{\Omega_1\alpha} c_{\Omega_2\beta} c^{\dagger}_{\Omega_1\beta} c_{\Omega_1\alpha}$$

$$- c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\alpha} c^{\dagger}_{\Omega_2\alpha} c_{\Omega_2\beta} + c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\beta} c^{\dagger}_{\Omega_2\beta} c_{\Omega_2\beta}$$

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

$${}_2C^{\dagger}_{\Omega_2\Omega_1}(10) = \tfrac{1}{2} (c^{\dagger}_{\Omega_1\beta} c_{\Omega_2\alpha} c^{\dagger}_{\Omega_1\alpha} c_{\Omega_1\beta} - c^{\dagger}_{\Omega_1\beta} c_{\Omega_2\beta} c^{\dagger}_{\Omega_1\beta} c_{\Omega_1\beta}$$

$$+ c^{\dagger}_{\Omega_1\alpha} c_{\Omega_2\alpha} c^{\dagger}_{\Omega_1\alpha} c_{\Omega_1\alpha} - c^{\dagger}_{\Omega_1\alpha} c_{\Omega_2\beta} c^{\dagger}_{\Omega_1\beta} c_{\Omega_1\alpha}$$

$$+ c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\alpha} c^{\dagger}_{\Omega_2\alpha} c_{\Omega_2\beta} - c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\beta} c^{\dagger}_{\Omega_2\beta} c_{\Omega_2\beta}$$

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

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

$$+ c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_1\beta} c_{\Omega_2\beta} - c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_1\alpha} c_{\Omega_2\alpha}$$

$$+ c^{\dagger}_{m\beta} c_{\nu\beta} c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\beta} - c^{\dagger}_{m\beta} c_{\nu\beta} c^{\dagger}_{\Omega_2\alpha} c_{\Omega_1\alpha}$$

$$+ c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\beta} - c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_2\alpha} c_{\Omega_1\alpha})$$

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

$$+ c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_1\beta} c_{\Omega_2\beta} - c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_1\alpha} c_{\Omega_2\alpha}$$

$$- c^{\dagger}_{m\beta} c_{\nu\beta} c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\beta} + c^{\dagger}_{m\beta} c_{\nu\beta} c^{\dagger}_{\Omega_2\alpha} c_{\Omega_1\alpha}$$

$$- c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_2\beta} c_{\Omega_1\beta} + c^{\dagger}_{m\alpha} c_{\nu\alpha} c^{\dagger}_{\Omega_2\alpha} c_{\Omega_1\alpha})$$

Table VI. R Values for the Triplet
$|(\text{closed shell})\ \Omega_1\alpha\Omega_2\alpha >$ Ground State

$R_{(H1-\Omega 1)} = -1.0$

$R_{(H1-\Omega 2)} = 1.0$

$R_{(P1-\Omega 2)} = 1.0$

$R_{(P1-\Omega 1)} = -1.0$

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

$R_{2(P1-H1)} = 0.0$

$R_{3(P1-H1)} = 0.0$

$R_{4(P1-H1)} = 0.0$

$R_{5(P1-H1)} = 0.0$

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

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[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] Ref. 14.

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	CI	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]	

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[a] RPA instability.

[b] Ref. 22.

[c] H. Schaefer and F. Harris, J. Chem. Phys. 48, 4946 (1968).

[d] Ref. 18.

APPENDIX

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

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

$$| T > = e^{\hat{T}} | > \tag{32}$$

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

$$< T|\hat{H}|T > = < |H| > + < | [H, T] | > + \tfrac{1}{2} < | [T^\dagger, H, T] | > + \ldots \tag{33}$$

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

$$< | [H, T] | > = 0 \tag{34}$$

Equation (34) is known commonly as Brillouin's theorem.

If Eq.(34) holds, then for the Hartree-Fock solution to be a true minimum

$$< | [T^\dagger, H, T] | > \geq 0 \tag{35}$$

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 a function 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

$$< | [H, T] | > \neq 0 \tag{36}$$

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 $|0>$ 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.

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Figure Captions

Fig. 1. Labeling of the particle-hole basis for an open shell.

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.

Fig. 3. Possible excitations of the triplet $|$(closed shell) $\Omega_1\alpha\Omega_2\alpha >$ 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.

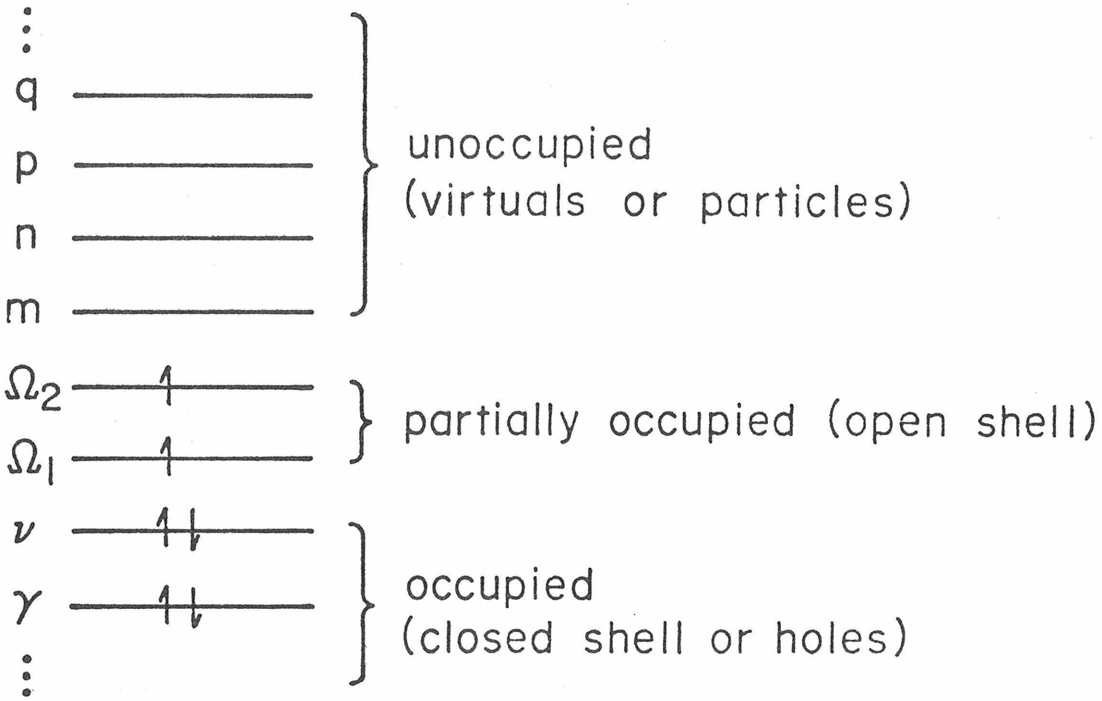
q
p
n
m
Ω_2
Ω_1
ν
γ
unoccupied
(virtuals or particles)
partially occupied (open shell)
occupied
(closed shell or holes)

Fig. 1

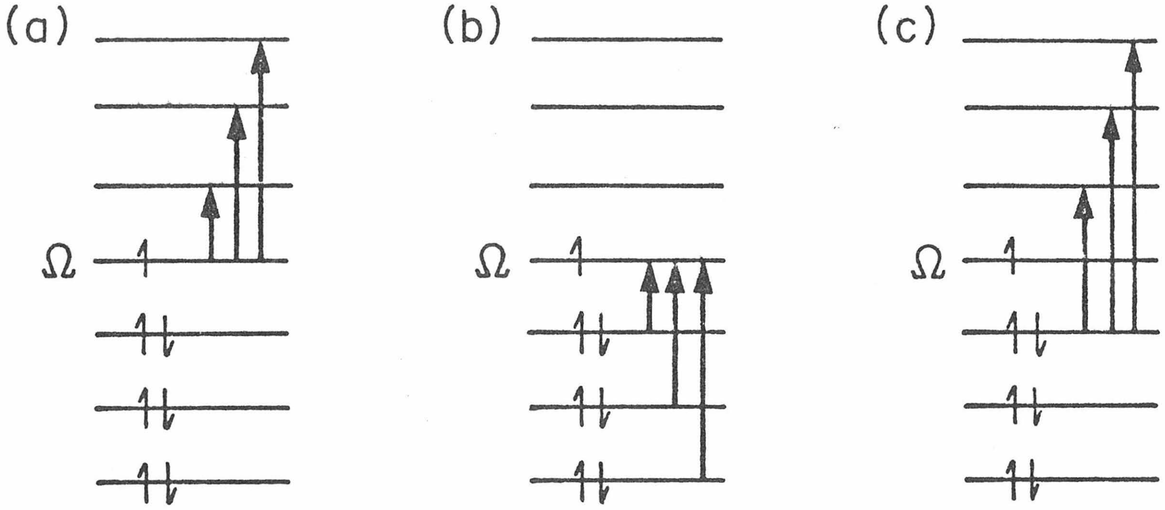

Fig. 2

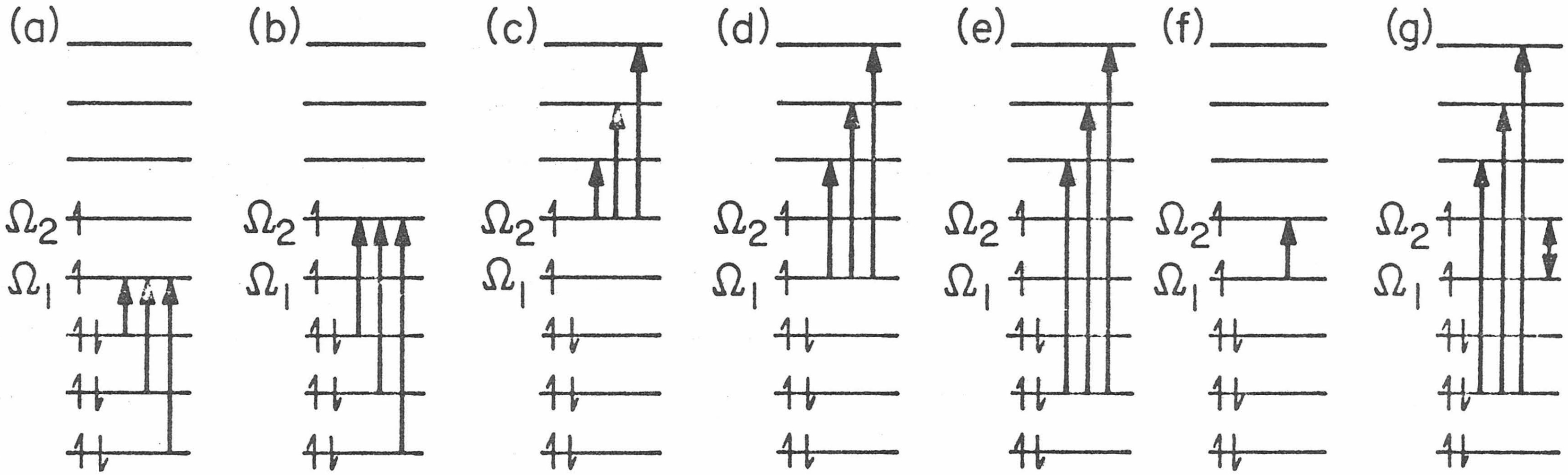

Fig. 3

Appendix B. $\mathcal{A}$ and $\mathcal{B}$ Matrix Formulas for Triplet Excited States, $|$(closed shell) $\Omega_1\alpha\Omega_2\alpha >$ Ground State. Ω_1 and Ω_2 are degenerate. Zero formulas are not listed.

A Matrix Formulas

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

2. $A_{(\Omega 2-H1),(\Omega 1-H2)} = V_{H1\Omega 1H2\Omega 2} - V_{H1H2\Omega 2\Omega 1} +$
$\delta_{H1H2}(-V_{\Omega 1\Omega 1\Omega 1\Omega 2} - V_{\Omega 1\Omega 2\Omega 2\Omega 2})$

3. $A_{(\Omega 2-H1),(\Omega 2-H2)} = \delta_{H1H2}(\epsilon_{\Omega 2} - \epsilon_{H1} + V_{\Omega 2\Omega 2\Omega 2\Omega 2} +$
$V_{\Omega 1\Omega 1\Omega 2\Omega 2}) - V_{H1\Omega 2H2\Omega 2} - \frac{1}{2} V_{H1H2\Omega 1\Omega 1} + \frac{1}{2} V_{H1H2\Omega 2\Omega 2}$

4. $A_{(P1-\Omega 2),(\Omega 1-H2)} = - V_{H2P1\Omega 1\Omega 2}$

5. $A_{(P1-\Omega 2),(\Omega 2-H2)} = V_{H2P1\Omega 2\Omega 2}$

6. $A_{(P1-\Omega 2),(P2-\Omega 2)} = \delta_{P1P2}(\epsilon_{P1} - \epsilon_{\Omega 2}) + V_{P1P2\Omega 2\Omega 2}$
$- V_{P1\Omega 2P2\Omega 2}$

7. $A_{(P1-\Omega 1),(\Omega 1-H2)} = V_{H2P1\Omega 1\Omega 1}$

8. $A_{(P1-\Omega 1),(\Omega 2-H2)} = - V_{H2P1\Omega 2\Omega 1}$

9. $A_{(P1-\Omega 1),(P2-\Omega 2)} = V_{P1\Omega 1P2\Omega 2} - V_{P1P2\Omega 1\Omega 2}$

10. $A_{(P1-\Omega 1),(P2-\Omega 1)} = \delta_{P1P2}(\epsilon_{P1} - \epsilon_{\Omega 1}) + V_{P1P2\Omega 1\Omega 1} -$

$V_{P1\Omega 1P2\Omega 1}$

11. $A_{1(P1-H1),(\Omega 1-H2)} = -\frac{1}{\sqrt{2}}\,\delta_{H1H2}(V_{P1\Omega 1\Omega 1\Omega 1} +$

$V_{P1\Omega 1\Omega 2\Omega 2}) + \sqrt{2}\,(-V_{H1H2P1\Omega 1} + \frac{1}{2}V_{H1P1H2\Omega 1})$

12. $A_{1(P1-H1),(\Omega 2-H2)} = \frac{1}{\sqrt{2}}\,\delta_{H1H2}(V_{P1\Omega 1\Omega 1\Omega 2} + V_{P1\Omega 2\Omega 2\Omega 2})$

$+ \sqrt{2}\,(V_{H1H2P1\Omega 2} - \frac{1}{2}V_{H1P1H2\Omega 2})$

13. $A_{1(P1-H1),(P2-\Omega 2)} = \frac{1}{\sqrt{2}}\,\delta_{P1P2}(V_{H1\Omega 1\Omega 1\Omega 2} + V_{P1\Omega 2\Omega 2\Omega 2})$

$+ \sqrt{2}\,(V_{H1P2P1\Omega 2} - \frac{1}{2}V_{H1P1\Omega 2P2})$

14. $A_{1(P1-H1),(P2-\Omega 1)} = -\frac{1}{\sqrt{2}}\,\delta_{P1P2}(V_{H1\Omega 1\Omega 1\Omega 1} + V_{H1\Omega 1\Omega 2\Omega 2})$

$- \sqrt{2}\,(V_{H1P2P1\Omega 1} + \frac{1}{2}V_{H1P1\Omega 1P2})$

15. $A_{1(P1-H1),1(P1-H1)} = \delta_{H1H2}\,\delta_{P1P2}(\epsilon_{P1} - \epsilon_{H1}) +$

$\frac{1}{2}\delta_{H1H2}(V_{P1P2\Omega 1\Omega 1} + V_{P1P2\Omega 2\Omega 2}) + 2V_{H1H2P1P2} -$

$V_{H1P1H2P2}$

16. $A_{2(P1-H1),(\Omega 1-H2)} = -V_{H1P1H2\Omega 1} + \delta_{H1H2}(V_{P1\Omega 1\Omega 2\Omega 2}$

$+ V_{P1\Omega 1\Omega 1\Omega 1})$

17. $A_{2(P1-H1),(\Omega 2-H2)} = V_{H1P1H2\Omega 2} - \delta_{H1H2}(V_{P1\Omega 2\Omega 2\Omega 2} +$

$V_{P1\Omega 1\Omega 1\Omega 2})$

18. $A_{2(P1-H1),(P2-\Omega 2)} = - V_{H1P1\Omega 2P2} + \delta_{P1P2} (V_{H1\Omega 2\Omega 2\Omega 2} +$
$V_{H1\Omega 1\Omega 1\Omega 2})$

19. $A_{2(P1-H1),(P2-\Omega 1)} = V_{H1P1\Omega 1P2} - \delta_{P1P2} (V_{H1\Omega 1\Omega 2\Omega 2} +$
$V_{H1\Omega 1\Omega 1\Omega 1})$

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

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

22. $A_{3(P1-H1),(\Omega 1-H2)} = \frac{1}{\sqrt{2}} V_{H1P1H2\Omega 1} + \frac{1}{\sqrt{2}} \delta_{H1H2} (V_{P1\Omega 1\Omega 2\Omega 2}$
$- V_{P1\Omega 1\Omega 1\Omega 1})$

23. $A_{3(P1-H1),(\Omega 2-H2)} = \frac{1}{\sqrt{2}} V_{H1P1H2\Omega 2} + \frac{1}{\sqrt{2}} \delta_{H1H2} (V_{P1\Omega 1\Omega 1\Omega 2}$
$- V_{P1\Omega 2\Omega 2\Omega 2})$

24. $A_{3(P1-H1),(P2-\Omega 2)} = - \frac{1}{\sqrt{2}} V_{H1P1\Omega 2P2} + \frac{1}{\sqrt{2}} \delta_{P1P2} (V_{H1\Omega 2\Omega 2\Omega 2}$
$- V_{H1\Omega 1\Omega 1\Omega 2})$

25. $A_{3(P1-H1),(P2-\Omega 1)} = - \frac{1}{\sqrt{2}} V_{H1P1\Omega 1P2} + \frac{1}{\sqrt{2}} \delta_{P1P2} (V_{H1\Omega 1\Omega 1\Omega 1}$
$- V_{H1\Omega 1\Omega 2\Omega 2})$

26. $A_{3(P1-H1),1(P2-H2)} = \frac{1}{2}\delta_{P1P2}(V_{H1H2\Omega2\Omega2} - V_{H1H2\Omega1\Omega1}) +$

$\frac{1}{2}\delta_{H1H2}(V_{P1P2\Omega1\Omega1} - V_{P1P2\Omega2\Omega2})$

27. $A_{3(P1-H1),2(P2-H2)} = \frac{1}{\sqrt{2}}\delta_{P1P2}(V_{H1H2\Omega2\Omega2} - V_{H1H2\Omega1\Omega1})$

$+ \frac{1}{\sqrt{2}}\delta_{H1H2}(V_{P1P2\Omega2\Omega2} - V_{P1P2\Omega1\Omega1})$

28. $A_{3(P1-H1),3(P2-H2)} = \delta_{H1H2}\delta_{P1P2}(\epsilon_{P1} - \epsilon_{H1} +$

$2V_{\Omega1\Omega1\Omega2\Omega2}) + \delta_{H1H2}\frac{1}{2}(V_{P1P2\Omega2\Omega2} + V_{P1P2\Omega1\Omega1}) -$

$V_{H1P1H2P2}$

29. $A_{4(P1-H1),(\Omega1-H2)} = -\frac{1}{\sqrt{2}}V_{H1P1H2\Omega2} + \frac{1}{\sqrt{2}}\delta_{H1H2}(V_{P1\Omega1\Omega2\Omega1}$

$+ V_{P1\Omega1\Omega1\Omega2})$

30. $A_{4(P1-H1),(\Omega2-H2)} = \frac{1}{\sqrt{2}}V_{H1P1H2\Omega1} - \frac{1}{\sqrt{2}}\delta_{H1H2}(V_{P1\Omega1\Omega2\Omega2}$

$+ V_{P1\Omega2\Omega1\Omega2})$

31. $A_{4(P1-H1),(P2-\Omega2)} = -\frac{1}{\sqrt{2}}V_{H1P1\Omega1P2} + \delta_{P1P2}\frac{1}{\sqrt{2}}(V_{H1\Omega2\Omega1\Omega2}$

$+ V_{H1\Omega1\Omega2\Omega2})$

32. $A_{4(P1-H1),(P2-\Omega1)} = \frac{1}{\sqrt{2}}V_{H1P1\Omega2P2} - \delta_{P1P2}\frac{1}{\sqrt{2}}(V_{H1\Omega1\Omega1\Omega2}$

$+ V_{H1\Omega1\Omega2\Omega1})$

33. $A_{4(P1-H1),1(P2-H2)} = \frac{1}{2}\delta_{P1P2}(V_{H1H2\Omega1\Omega2} + V_{H1H2\Omega2\Omega1}) -$

$\frac{1}{2}\delta_{H1H2}(V_{P1P2\Omega1\Omega2} + V_{P1P2\Omega2\Omega1})$

34. $A_{4(P1-H1),\,2(P2-H2)} = \delta_{P1P2} \frac{1}{\sqrt{2}} (V_{H1H2\Omega 1\Omega 2} + V_{H1H2\Omega 2\Omega 1})$
$+ \delta_{H1H2} \frac{1}{\sqrt{2}} (V_{P1P2\Omega 2\Omega 1} + V_{P1P2\Omega 1\Omega 2})$

35. $A_{4(P1-H1),\,3(P2-H2)} = \delta_{P1P2} \frac{1}{2} (V_{H1H2\Omega 1\Omega 2} - V_{H1H2\Omega 2\Omega 1})$
$+ \delta_{H1H2} \frac{1}{2} (-V_{P1P2\Omega 2\Omega 1} + V_{P1P2\Omega 1\Omega 2}) +$
$\delta_{P1P2} \delta_{H1H2} (V_{\Omega 1\Omega 1\Omega 1\Omega 2} - V_{\Omega 1\Omega 2\Omega 2\Omega 2})$

36. $A_{4(P1-H1),\,4(P2-H2)} = \delta_{H1H2} \delta_{P1P2} (\epsilon_{P1} - \epsilon_{H1} - V_{\Omega 1\Omega 2\Omega 1\Omega 2}$
$+ \frac{1}{2} V_{\Omega 2\Omega 2\Omega 2\Omega 2} + \frac{1}{2} V_{\Omega 1\Omega 1\Omega 1\Omega 1}) + \frac{1}{2} \delta_{H1H2} (V_{P1P2\Omega 2\Omega 2}$
$+ V_{P1P2\Omega 1\Omega 1}) - V_{H1P1H2P2}$

37. $A_{5(P1-H1),\,(\Omega 1-H2)} = -\frac{1}{\sqrt{2}} V_{H1P1H2\Omega 2} +$
$\delta_{H1H2} \frac{1}{\sqrt{2}} (V_{P1\Omega 1\Omega 2\Omega 1} - V_{P1\Omega 1\Omega 1\Omega 2})$

38. $A_{5(P1-H1),\,(\Omega 2-H2)} = -\frac{1}{\sqrt{2}} V_{H1P1H2\Omega 1} +$
$\delta_{H1H2} \frac{1}{\sqrt{2}} (-V_{P1\Omega 1\Omega 2\Omega 2} + V_{P1\Omega 2\Omega 1\Omega 2})$

39. $A_{5(P1-H1),\,(P2-\Omega 2)} = -\frac{1}{\sqrt{2}} V_{H1P1\Omega 1P2} +$
$\delta_{P1P2} \frac{1}{\sqrt{2}} (V_{H1H2\Omega 1\Omega 2} - V_{H1\Omega 1\Omega 2\Omega 2})$

40. $A_{5(P1-H1),\,(P2-\Omega 1)} = -\frac{1}{\sqrt{2}} V_{H1P1\Omega 2P2} +$
$\delta_{P1P2} \frac{1}{\sqrt{2}} (V_{H1\Omega 1\Omega 2\Omega 1} - V_{H1\Omega 1\Omega 1\Omega 2})$

41. $A_{5(P1-H1),\,1(P2-H2)} = \frac{1}{2} \delta_{P1P2} (V_{H1H2\Omega 1\Omega 2} - V_{H1H2\Omega 2\Omega 1})$
$+ \frac{1}{2} \delta_{H1H2} (V_{P1P2\Omega 1\Omega 2} - V_{P1P2\Omega 2\Omega 1})$

42. $A_{5(P1-H1),\,2(P2-H2)} = \frac{1}{\sqrt{2}}\,\delta_{P1P2}\,(V_{H1H2\Omega1\Omega2} - V_{H1H2\Omega2\Omega1})$

$+ \frac{1}{\sqrt{2}}\,\delta_{H1H2}\,(V_{P1P2\Omega2\Omega1} - V_{P1P2\Omega1\Omega2})$

43. $A_{5(P1-H1),\,3(P2-H2)} = \delta_{P1P2}\,\delta_{H1H2}\,(V_{\Omega1\Omega1\Omega1\Omega2} + V_{\Omega1\Omega2\Omega2\Omega2})$

$+ \delta_{H1H2}\,(2\,V_{P1\Omega1P2\Omega2} - \frac{1}{2}\,V_{P1P2\Omega1\Omega2} - \frac{1}{2}\,V_{P1P2\Omega2\Omega1})$

$+ \delta_{P1P2}\,(-2\,V_{H1\Omega1H2\Omega2} + \frac{1}{2}\,V_{H1H2\Omega1\Omega2} + \frac{1}{2}\,V_{H1H2\Omega2\Omega1})$

44. $A_{5(P1-H1),\,4(P2-H2)} = \frac{1}{2}\,\delta_{H1H2}\,\delta_{P1P2}\,(V_{\Omega1\Omega1\Omega1\Omega1} -$

$V_{\Omega2\Omega2\Omega2\Omega2}) + \delta_{H1H2}\,(V_{P1\Omega1P2\Omega1} - V_{P1\Omega2P2\Omega2} +$

$\frac{1}{2}\,V_{P1P2\Omega2\Omega2} - \frac{1}{2}\,V_{P1P2\Omega1\Omega1}) + \delta_{P1P2}\,(V_{H1\Omega2H2\Omega2} -$

$V_{H1\Omega1H2\Omega1} - \frac{1}{2}\,V_{H1H2\Omega2\Omega2} + \frac{1}{2}\,V_{H1H2\Omega1\Omega1})$

45. $A_{5(P1-H1),\,5(P2-H2)} = \delta_{H1H2}\,\delta_{P1P2}\,(\epsilon_{P1} - \epsilon_{H1} - V_{\Omega1\Omega2\Omega1\Omega2}$

$+ 2\,V_{\Omega1\Omega1\Omega2\Omega2} + \frac{1}{2}\,V_{\Omega2\Omega2\Omega2\Omega2} + \frac{1}{2}\,V_{\Omega1\Omega1\Omega1\Omega1} +$

$\delta_{H1H2}\,\frac{1}{2}(V_{P1P2\Omega1\Omega1} + V_{P1P2\Omega2\Omega2}) - V_{H1P1H2P2}$

B Matrix Formulas

2. $B_{(\Omega 2-H1),(\Omega 1-H2)} = V_{H1H2\Omega 1\Omega 2} - V_{H1H2\Omega 2\Omega 1}$

4. $B_{(P1-\Omega 2),(\Omega 1-H2)} = -V_{H2P1\Omega 1\Omega 2}$

5. $B_{(P1-\Omega 2),(\Omega 2-H2)} = \frac{3}{2} V_{H2P1\Omega 2\Omega 2} + \frac{1}{2} V_{H2P1\Omega 1\Omega 1}$

7. $B_{(P1-\Omega 1),(\Omega 1-H2)} = \frac{3}{2} V_{H2P1\Omega 1\Omega 1} + \frac{1}{2} V_{H2P1\Omega 2\Omega 2}$

8. $B_{(P1-\Omega 1),(\Omega 2-H2)} = -V_{H2P1\Omega 2\Omega 1}$

9. $B_{(P1-\Omega 1),(P2-\Omega 2)} = V_{P1P2\Omega 2\Omega 1} - V_{P1P2\Omega 1\Omega 2}$

11. $B_{1(P1-H1),(\Omega 1-H2)} = -\sqrt{2}\,(V_{H1H2P1\Omega 1} - \frac{1}{2} V_{H1H2\Omega 1P1})$

12. $B_{1(P1-H1),(\Omega 2-H2)} = \sqrt{2}\,(V_{H1H2P1\Omega 2} - \frac{1}{2} V_{H1H2\Omega 2P1})$

13. $B_{1(P1-H1),(P2-\Omega 2)} = \sqrt{2}\,(V_{H1P2P1\Omega 2} - \frac{1}{2} V_{H1P1P2\Omega 2})$

14. $B_{1(P1-H1),(P2-\Omega 1)} = -\sqrt{2}\,(V_{H1P2P1\Omega 1} - \frac{1}{2} V_{H1P1P2\Omega 1})$

15. $B_{1(P1-H1),1(P2-H2)} = 2\,V_{H1H2P1P2} - V_{H1H2P2P1}$

16. $B_{2(P1-H1),(\Omega 1-H2)} = -\frac{5}{8} V_{H1H2\Omega 1P1}$

17. $B_{2(P1-H1),(\Omega 2-H2)} = \frac{5}{8} V_{H1H2\Omega 2P1}$

18. $B_{2(P1-H1),(P2-\Omega 2)} = -\frac{5}{8} V_{H1P1P2\Omega 2}$

19. $B_{2(P1-H1),(P2-\Omega 1)} = \frac{5}{8} V_{H1P1P2\Omega 1}$

21. $B_{2(P1-H1),2(P2-H2)} = - V_{H1H2P2P1}$

22. $B_{3(P1-H1),(\Omega 1-H2)} = \frac{1}{4\sqrt{2}} V_{H1H2\Omega 1P1}$

23. $B_{3(P1-H1),(\Omega 2-H2)} = \frac{1}{4\sqrt{2}} V_{H1H2\Omega 2P1}$

24. $B_{3(P1-H1),(P2-\Omega 2)} = - \frac{1}{4\sqrt{2}} V_{H1P1P2\Omega 2}$

25. $B_{3(P1-H1),(P2-\Omega 1)} = - \frac{1}{4\sqrt{2}} V_{H1P1P2\Omega 1}$

28. $B_{3(P1-H1),3(P2-H2)} = - V_{H1H2P2P1}$

29. $B_{4(P1-H1),(\Omega 1-H2)} = - \frac{3}{4\sqrt{2}} V_{H1H2\Omega 2P1}$

30. $B_{4(P1-H1),(\Omega 2-H2)} = \frac{3}{4\sqrt{2}} V_{H1H2\Omega 1P1}$

31. $B_{4(P1-H1),(P2-\Omega 2)} = - \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 1}$

32. $B_{4(P1-H1),(P2-\Omega 1)} = \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 2}$

36. $B_{4(P1-H1),4(P2-H2)} = - V_{H1H2P2P1}$

37. $B_{5(P1-H1),(\Omega 1-H2)} = \frac{3}{4\sqrt{2}} V_{H1H2\Omega 2P1}$

38. $B_{5(P1-H1),(\Omega 2-H2)} = \frac{3}{4\sqrt{2}} V_{H1H2\Omega 1P1}$

39. $B_{5(P1-H1),(P2-\Omega 2)} = \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 1}$

40. $B_{5(P1-H1),(P2-\Omega 1)} = \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 2}$

45. $B_{5(P1-H1),5(P2-H2)} = V_{H1H2P2P1}$

Appendix C. $\mathcal{A}$ and $\mathcal{B}$ Matrix Formulas for Singlet Excited States, $|(\text{closed shell})\, \Omega_1\alpha\Omega_2\beta + \Omega_1\beta\Omega_2\alpha > /\sqrt{2}$ Ground State. Ω1 and Ω2 are degenerate. Zero formulas are not listed.

A Matrix Formulas

1. $A_{(\Omega 1-H1),(\Omega 1-H2)} = \delta_{H1H2}(\epsilon_{\Omega 1} - \epsilon_{H1} + V_{\Omega 1\Omega 1\Omega 1\Omega 1} + V_{\Omega 1\Omega 1\Omega 2\Omega 2}) + \frac{3}{2} V_{H1H2\Omega 2\Omega 2} + \frac{1}{2} V_{H1H2\Omega 1\Omega 1} - V_{H1\Omega 1H2\Omega 1}$

2. $A_{(\Omega 2-H1),(\Omega 1-H2)} = V_{H1\Omega 1H2\Omega 2} + V_{H1H2\Omega 2\Omega 1} - \delta_{H1H2}(V_{\Omega 1\Omega 1\Omega 1\Omega 2} + V_{\Omega 1\Omega 2\Omega 2\Omega 2})$

3. $A_{(\Omega 2-H1),(\Omega 2-H2)} = \delta_{H1H2}(\epsilon_{\Omega 2} - \epsilon_{H1} + V_{\Omega 2\Omega 2\Omega 2\Omega 2} + V_{\Omega 1\Omega 1\Omega 2\Omega 2}) - V_{H1\Omega 2H2\Omega 2} + \frac{3}{2} V_{H1H2\Omega 1\Omega 1} + \frac{1}{2} V_{H1H2\Omega 2\Omega 2}$

4. $A_{(P1-\Omega 2),(\Omega 1-H2)} = 2\, V_{H2P1\Omega 2\Omega 1} - V_{H2P1\Omega 1\Omega 2}$

5. $A_{(P1-\Omega 2),(\Omega 2-H2)} = -\, V_{H2P1\Omega 2\Omega 2}$

6. $A_{(P1-\Omega 2),(P2-\Omega 2)} = \delta_{P1P2}(\epsilon_{P1} - \epsilon_{\Omega 2}) + 2\, V_{P1P2\Omega 1\Omega 1} + V_{P1P2\Omega 2\Omega 2} - V_{P1\Omega 2P2\Omega 2}$

7. $A_{(P1-\Omega 1),(\Omega 1-H2)} = -\, V_{H2P1\Omega 1\Omega 1}$

8. $A_{(P1-\Omega 1),(\Omega 2-H2)} = 2\, V_{H2P1\Omega 1\Omega 2} - V_{H2P1\Omega 2\Omega 1}$

9. $A_{(P1-\Omega 1),(P2-\Omega 2)} = V_{P1P2\Omega 1\Omega 2} + V_{P1\Omega 1P2\Omega 2}$

10. $A_{(P1-\Omega 1),(P2-\Omega 1)} = \delta_{P1P2}(\epsilon_{P1} - \epsilon_{\Omega 1}) + 2\,V_{P1P2\Omega 2\Omega 2} +$

$V_{P1P2\Omega 1\Omega 1} - V_{P1\Omega 1P2\Omega 1}$

11. $A_{2(P1-H1),(\Omega 1-H2)} = \sqrt{\tfrac{3}{2}}\,(-V_{H1P1H2\Omega 1} + \delta_{H1H2}\,(V_{P1\Omega 1\Omega 1\Omega 1} +$

$V_{P1\Omega 1\Omega 2\Omega 2}))$

12. $A_{2(P1-H1),(\Omega 2-H2)} = \sqrt{\tfrac{3}{2}}\,(V_{H1P1H2\Omega 2} - \delta_{H1H2}\,(V_{P1\Omega 1\Omega 1\Omega 2} +$

$V_{P1\Omega 2\Omega 2\Omega 2}))$

13. $A_{2(P1-H1),(P2-\Omega 2)} = \sqrt{\tfrac{3}{2}}\;V_{H1P1\Omega 2P2} - \delta_{P1P2}\,(V_{H1\Omega 2\Omega 2\Omega 2} +$

$V_{H1\Omega 1\Omega 1\Omega 2})$

14. $A_{2(P1-H1),(P2-\Omega 1)} = \sqrt{\tfrac{3}{2}}\;(-V_{H1P1\Omega 1P2} + \delta_{P1P2}\,(V_{H1\Omega 1\Omega 1\Omega 1} +$

$V_{H1\Omega 1\Omega 2\Omega 2}))$

15. $A_{2(P1-H1),2(P2-H2)} = \delta_{P1P2}\,\delta_{H1H2}\,(\epsilon_{P1} - \epsilon_{H1}) +$

$\delta_{H1H2}\;\tfrac{3}{2}\;(V_{P1P2\Omega 1\Omega 1} + V_{P1P2\Omega 2\Omega 2}) + \delta_{P1P2}\,(V_{H1H2\Omega 1\Omega 1}$

$+ V_{H1H2\Omega 2\Omega 2}) - V_{H1P1H2P2}$

16. $A_{3(P1-H1),(\Omega 1-H2)} = \sqrt{2}\;(-V_{H1H2P1\Omega 1} + \tfrac{1}{2}\;V_{H1P1H2\Omega 1} +$

$\tfrac{1}{2}\;\delta_{H1H2}\,(V_{P1\Omega 1\Omega 2\Omega 2} - V_{P1\Omega 1\Omega 1\Omega 1}))$

17. $A_{3(P1-H1),(\Omega 2-H2)} = \sqrt{2}\;(-V_{H1H2P1\Omega 2} + \tfrac{1}{2}\;V_{H1P1H2\Omega 2} +$

$$\delta_{H1H2}\ \tfrac{1}{2}\ (V_{P1\Omega1\Omega1\Omega2} - V_{P1\Omega2\Omega2\Omega2}))$$

18. $A_{3(P1-H1),(P2-\Omega2)} = \sqrt{2}\ (V_{H1P2P1\Omega2} - \tfrac{1}{2}\ V_{H1P1\Omega2P2}) +$

$$\delta_{P1P2}\ \tfrac{1}{2}\ (V_{H1\Omega2\Omega2\Omega2} - V_{H1\Omega1\Omega1\Omega2}))$$

19. $A_{3(P1-H1),(P2-\Omega1)} = \sqrt{2}\ (V_{H1P2P1\Omega1} - \tfrac{1}{2}\ V_{H1P1\Omega1P2} +$

$$\delta_{P1P2}\ \tfrac{1}{2}\ (V_{H1\Omega1\Omega1\Omega1} - V_{H1\Omega1\Omega2\Omega2}))$$

20. $A_{3(P1-H1),2(P2-H2)}\ \ \frac{\sqrt{3}}{2}\ (\delta_{P1P2}\ (V_{H1H2\Omega1\Omega1} - V_{H1H2\Omega2\Omega2})$

$$+\ \delta_{H1H2}\ (V_{P1P2\Omega2\Omega2} - V_{P1P2\Omega1\Omega1}))$$

21. $A_{3(P1-H1),3(P2-H2)} = \delta_{P1P2}\ \delta_{H1H2}\ (\epsilon_{P1} - \epsilon_{H1} + 2\ V_{\Omega1\Omega1\Omega2\Omega2})$

$$+\ \delta_{H1H2}\ \tfrac{1}{2}\ (V_{P1P2\Omega1\Omega1} + V_{P1P2\Omega2\Omega2}) + 2\ V_{H1H2P1P2}$$

$$-\ V_{H1P1H2P2}$$

22. $A_{4(P1-H1),(\Omega1-H2)} = \sqrt{2}\ (V_{H1H2P1\Omega2} - \tfrac{1}{2}\ V_{H1P1H2\Omega2} +$

$$\tfrac{1}{2}\ \delta_{H1H2}\ (V_{P1\Omega1\Omega2\Omega1} + V_{P1\Omega1\Omega1\Omega2}))$$

23. $A_{4(P1-H1),(\Omega2-H2)} = \sqrt{2}\ (-V_{H1H2P1\Omega1} + \tfrac{1}{2}\ V_{H1P1H2\Omega1} -$

$$\tfrac{1}{2}\ \delta_{H1H2}\ (V_{P1\Omega1\Omega2\Omega2} + V_{P1\Omega2\Omega1\Omega2}))$$

24. $A_{4(P1-H1),(P2-\Omega2)} = \sqrt{2}\ (V_{H1P2P1\Omega1} - \tfrac{1}{2}\ V_{H1P1\Omega1P2} +$

$$\tfrac{1}{2}\ \delta_{P1P2}\ (V_{H1\Omega2\Omega1\Omega2} + V_{H1\Omega1\Omega2\Omega2}))$$

25. $A_{4(P1-H1),(P2-\Omega1)} = \sqrt{2}\ (-V_{H1P2P1\Omega2} + \tfrac{1}{2}\ V_{H1P1\Omega2P2} -$

$\frac{1}{2}\,\delta_{P1P2}\,(V_{H1\Omega1\Omega1\Omega2} + V_{H1\Omega1\Omega2\Omega1}))$

26. $A_{4(P1-H1),\,2(P2-H2)} = \frac{\sqrt{3}}{2}\,(-\delta_{P1P2}\,(V_{H1H2\Omega1\Omega2} + V_{H1H2\Omega2\Omega1})$

$+\ \delta_{H1H2}\,(V_{P1P2\Omega2\Omega1} + V_{P1P2\Omega1\Omega2}))$

27. $A_{4(P1-H1),\,3(P2-H2)} = \delta_{P1P2}\,\delta_{H1H2}\,(V_{\Omega1\Omega1\Omega1\Omega2} - V_{\Omega1\Omega2\Omega2\Omega2})$

$+\ \delta_{H1H2}\,\frac{1}{2}\,(V_{P1P2\Omega1\Omega2} - V_{P1P2\Omega2\Omega1}) + \frac{1}{2}\,\delta_{P1P2}\,(V_{H1H2\Omega1\Omega2}$

$-\ V_{H1H2\Omega2\Omega1}))$

28. $A_{4(P1-H1),\,4(P2-H2)} = \delta_{P1P2}\,\delta_{H1H2}\,(\epsilon_{P1} - \epsilon_{H1} - V_{\Omega1\Omega2\Omega1\Omega2}$

$+\ \frac{1}{2}\,V_{\Omega2\Omega2\Omega2\Omega2} + \frac{1}{2}\,V_{\Omega1\Omega1\Omega1\Omega1}) + \delta_{H1H2}\ \frac{1}{2}\,(V_{P1P2\Omega2\Omega2} +$

$V_{P1P2\Omega1\Omega1}) + 2\,V_{H1H2P1P2} - V_{H1P1H2P2}$

29. $A_{5(P1-H1),\,(\Omega1-H2)} = \sqrt{2}\ (V_{H1H2P1\Omega2} - \frac{1}{2}\,V_{H1P1H2\Omega2} +$

$\delta_{H1H2}\ \frac{1}{2}\,(V_{P1\Omega1\Omega2\Omega1} - V_{P1\Omega1\Omega1\Omega2}))$

30. $A_{5(P1-H1),\,(\Omega2-H2)} = \sqrt{2}\ (V_{H1H2P1\Omega1} - \frac{1}{2}\,V_{H1P1H2\Omega1} +$

$\delta_{H1H2}\ \frac{1}{2}\,(V_{P1\Omega2\Omega1\Omega2} - V_{P1\Omega1\Omega2\Omega2}))$

31. $A_{5(P1-H1),\,(P2-\Omega2)} = \sqrt{2}\ (V_{H1P2P1\Omega1} - \frac{1}{2}\,V_{H1P1\Omega1P2} +$

$\frac{1}{2}\,\delta_{P1P2}\,(V_{H1\Omega2\Omega1\Omega2} - V_{H1\Omega1\Omega2\Omega2}))$

32. $A_{5(P1-H1),\,(P2-\Omega1)} = \sqrt{2}\ (V_{H1P2P1\Omega2} - \frac{1}{2}\,V_{H1P1\Omega2P2} +$

$\frac{1}{2}\,\delta_{P1P2}\,(V_{H1\Omega1\Omega2\Omega1} - V_{H1\Omega1\Omega1\Omega2}))$

33. $A_{5(P1-H1),2(P2-H2)} = \frac{\sqrt{3}}{2} (\delta_{P1P2} (V_{H1H2\Omega2\Omega1} - V_{H1H2\Omega1\Omega2})$
$+ \delta_{H1H2} (V_{P1P2\Omega2\Omega1} - V_{P1P2\Omega1\Omega2}))$

34. $A_{5(P1-H1),3(P2-H2)} = \delta_{H1H2}\, \delta_{P1P2} (V_{\Omega1\Omega1\Omega1\Omega2} + V_{\Omega1\Omega2\Omega2\Omega2})$
$+ \delta_{H1H2} (2\, V_{P1\Omega1P2\Omega2} - \frac{1}{2} V_{P1P2\Omega2\Omega1} - \frac{1}{2} V_{P1P2\Omega1\Omega2}) +$
$\delta_{P1P2} (-2\, V_{H1\Omega1H2\Omega2} + \frac{1}{2} V_{H1H2\Omega1\Omega2} + \frac{1}{2} V_{H1H2\Omega1\Omega2})$

35. $A_{5(P1-H1),4(P2-H2)} = \frac{1}{2} \delta_{P1P2}\, \delta_{H1H2} (V_{\Omega1\Omega1\Omega1\Omega1} - V_{\Omega2\Omega2\Omega2\Omega2})$
$+ \delta_{H1H2} (V_{P1\Omega1P2\Omega1} + \frac{1}{2} V_{P1P2\Omega2\Omega2} - \frac{1}{2} V_{P1P2\Omega1\Omega1} -$
$V_{P1\Omega2P2\Omega2}) + \delta_{P1P2} (-V_{H1\Omega1H2\Omega1} - V_{H1\Omega1H2\Omega2} -$
$\frac{1}{2} V_{H1H2\Omega2\Omega2} + \frac{1}{2} V_{H1H2\Omega1\Omega1})$

36. $A_{5(P1-H1),5(P2-H2)} = \delta_{P1P2}\, \delta_{H1H2} (\epsilon_{P1} - \epsilon_{H1} + 2\, V_{\Omega1\Omega1\Omega2\Omega2}$
$- V_{\Omega1\Omega2\Omega1\Omega2} + \frac{1}{2} V_{\Omega2\Omega2\Omega2\Omega2} + \frac{1}{2} V_{\Omega1\Omega1\Omega1\Omega1} +$
$\delta_{H1H2}\ \frac{1}{2} (V_{P1P2\Omega2\Omega2} + V_{P1P2\Omega1\Omega1}) + 2\, V_{H1H2P1P2} -$
$V_{H1P1H2P2}$

37. $A_{1(\Omega2-\Omega1),(\Omega1-H2)} = -2\, V_{H2\Omega1\Omega1\Omega2} - V_{H2\Omega2\Omega2\Omega2} + V_{H2\Omega1\Omega2\Omega1}$

38. $A_{1(\Omega2-\Omega1),(\Omega2-H2)} = -2\, V_{H2\Omega1\Omega2\Omega2} - V_{H2\Omega1\Omega1\Omega1} + V_{H2\Omega2\Omega1\Omega2}$

39. $A_{1(\Omega2-\Omega1),(P2-\Omega2)} = V_{P1\Omega1\Omega1\Omega1} + 2\, V_{P2\Omega1\Omega2\Omega2} - V_{P2\Omega2\Omega1\Omega2}$

40. $A_{1(\Omega2-\Omega1),(P2-\Omega1)} = 2\, V_{P2\Omega1\Omega1\Omega2} - V_{P2\Omega1\Omega2\Omega1} + V_{P2\Omega2\Omega2\Omega2}$

41. $A_{1(\Omega 2-\Omega 1), 2(P2-H2)} = \frac{5}{2}\sqrt{\frac{1}{6}}\,(V_{H2P2\Omega 2\Omega 1} - V_{H2P2\Omega 1\Omega 2})$

42. $A_{1(\Omega 2-\Omega 1), 3(P2-H2)} = 2\sqrt{2}\; V_{H2\Omega 1P2\Omega 2} - \frac{1}{\sqrt{2}}\, V_{H2P2\Omega 2\Omega 1} - \frac{1}{\sqrt{2}}\, V_{H2P2\Omega 1\Omega 2}$

43. $A_{1(\Omega 2-\Omega 1), 4(P2-H2)} = \sqrt{2}\; V_{H2\Omega 1P2\Omega 1} - \sqrt{2}\; V_{H2\Omega 2P2\Omega 2} - \frac{1}{\sqrt{2}}\, V_{H2P2\Omega 1\Omega 1} + \frac{1}{\sqrt{2}}\, V_{H2P2\Omega 2\Omega 2}$

45. $A_{1(\Omega 2-\Omega 1), 1(\Omega 2-\Omega 1)} = 2\, V_{\Omega 1\Omega 1\Omega 2\Omega 2} - V_{\Omega 1\Omega 2\Omega 1\Omega 2} + \frac{1}{2}\, V_{\Omega 2\Omega 2\Omega 2\Omega 2} + \frac{1}{2}\, V_{\Omega 1\Omega 1\Omega 1\Omega 1}$

46. $A_{2(\Omega 2-\Omega 1), (\Omega 1-H2)} = V_{H2\Omega 1\Omega 2\Omega 1} - V_{H2\Omega 2\Omega 2\Omega 2}$

47. $A_{2(\Omega 2-\Omega 1), (\Omega 2-H2)} = V_{H2\Omega 1\Omega 1\Omega 1} - V_{H2\Omega 2\Omega 1\Omega 2}$

48. $A_{2(\Omega 2-\Omega 1), (P2-\Omega 2)} = V_{P2\Omega 1\Omega 1\Omega 1} - V_{P2\Omega 2\Omega 1\Omega 2}$

49. $A_{2(\Omega 2-\Omega 1), (P2-\Omega 1)} = V_{P2\Omega 1\Omega 2\Omega 1} - V_{P2\Omega 2\Omega 2\Omega 2}$

50. $A_{2(\Omega 2-\Omega 1), 2(P2-H2)} = \frac{5}{2}\sqrt{\frac{1}{6}}\,(V_{H2P2\Omega 2\Omega 1} + V_{H2P2\Omega 1\Omega 2})$

51. $A_{2(\Omega 2-\Omega 1), 3(P2-H2)} = \sqrt{\frac{1}{2}}\,(V_{H2P2\Omega 1\Omega 2} - V_{H2P2\Omega 2\Omega 1})$

53. $A_{2(\Omega 2-\Omega 1), 5(P2-H2)} = \sqrt{2}\; V_{H2\Omega 1P2\Omega 1} - \sqrt{2}\; V_{H2\Omega 2P2\Omega 2} - \frac{1}{\sqrt{2}}\, V_{H2P2\Omega 1\Omega 1} + \frac{1}{\sqrt{2}}\, V_{H2P2\Omega 2\Omega 2}$

54. $A_{2(\mathscr{k}2-\mathscr{k}1),1(\mathscr{k}2-\mathscr{k}1)} = \frac{1}{2} V_{\mathscr{k}1\mathscr{k}1\mathscr{k}1\mathscr{k}1} - \frac{1}{2} V_{\mathscr{k}2\mathscr{k}2\mathscr{k}2\mathscr{k}2}$

55. $A_{2(\mathscr{k}2-\mathscr{k}1),2(\mathscr{k}2-\mathscr{k}1)} = - V_{\mathscr{k}1\mathscr{k}2\mathscr{k}1\mathscr{k}2} + \frac{1}{2} V_{\mathscr{k}1\mathscr{k}1\mathscr{k}1\mathscr{k}1} +$

$\frac{1}{2} V_{\mathscr{k}2\mathscr{k}2\mathscr{k}2\mathscr{k}2}$

B Matrix Formulas

2. $B_{(C\ell 2-H1),(C\ell 1-H2)} = V_{H1H2C\ell 2C\ell 1} - V_{H1H2C\ell 1C\ell 2}$

4. $B_{(P1-C\ell 2),(C\ell 1-H2)} = -V_{H2P1C\ell 1C\ell 2}$

5. $B_{(P1-C\ell 2),(C\ell 2-H2)} = -\frac{1}{2} V_{H2P1C\ell 2C\ell 2} - \frac{3}{2} V_{H2P1C\ell 1C\ell 1}$

7. $B_{(P1-C\ell 1),(C\ell 1-H2)} = -\frac{3}{2} V_{H2P1C\ell 2C\ell 2} - \frac{1}{2} V_{H2P1C\ell 1C\ell 1}$

8. $B_{(P1-C\ell 1),(C\ell 2-H2)} = -V_{H2P1C\ell 2C\ell 1}$

9. $B_{(P1-C\ell 1),(P2-C\ell 2)} = V_{P1P2C\ell 1C\ell 2} - V_{P1P2C\ell 2C\ell 1}$

11. $B_{2(P1-H1),(C\ell 1-H2)} = -\frac{1}{2\sqrt{6}} V_{H1H2P1C\ell 1}$

12. $B_{2(P1-H1),(C\ell 2-H2)} = \frac{1}{2\sqrt{6}} V_{H1H2P1C\ell 2}$

13. $B_{2(P1-H1),(P2-C\ell 2)} = \frac{1}{\sqrt{6}} V_{H1P1P2C\ell 2} - \frac{1}{2\sqrt{2}} V_{H1P2P1C\ell 2}$

14. $B_{2(P1-H1),(P2-C\ell 1)} = \frac{1}{2\sqrt{6}} V_{H1P2P1C\ell 1} - \frac{1}{\sqrt{6}} V_{H1P1P2C\ell 1}$

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

16. $B_{3(P1-H1),(C\ell 1-H2)} = -\frac{3}{2\sqrt{2}} V_{H1H2P1C\ell 1} + \frac{3}{4\sqrt{2}} V_{H1H2C\ell 1P1}$

17. $B_{3(P1-H1),(C\ell 2-H2)} = -\frac{3}{2\sqrt{2}} V_{H1H2P1C\ell 2} + \frac{3}{4\sqrt{2}} V_{H1H2C\ell 2P1}$

18. $B_{3(P1-H1),(P2-\Omega 2)} = \frac{3}{2\sqrt{2}} V_{H1P2P1\Omega 2} - \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 2}$

19. $B_{3(P1-H1),(P2-\Omega 1)} = \frac{3}{2\sqrt{2}} V_{H1P2P1\Omega 1} - \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 1}$

21. $B_{3(P1-H1),3(P1-H1)} = 2\, V_{H1H2P1P2} - V_{H1H2P2P1}$

22. $B_{4(P1-H1),(\Omega 1-H2)} = \frac{3}{2\sqrt{2}} V_{H1H2P1\Omega 2} - \frac{3}{4\sqrt{2}} V_{H1H2\Omega 2P1}$

23. $B_{4(P1-H1),(\Omega 2-H2)} = -\frac{3}{2\sqrt{2}} V_{H1H2P1\Omega 1} + \frac{3}{4\sqrt{2}} V_{H1H2\Omega 1P1}$

24. $B_{4(P1-H1),(P2-\Omega 2)} = \frac{3}{2\sqrt{2}} V_{H1P2P1\Omega 1} - \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 1}$

25. $B_{4(P1-H1),(P2-\Omega 1)} = -\frac{3}{2\sqrt{2}} V_{H1P2P1\Omega 2} + \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 2}$

28. $B_{4(P1-H1),4(P2-H2)} = 2\, V_{H1H2P1P2} - V_{H1H2P2P1}$

29. $B_{5(P1-H1),(\Omega 1-H2)} = -\frac{3}{2\sqrt{2}} V_{H1H2P1\Omega 2} + \frac{3}{4\sqrt{2}} V_{H1H2\Omega 2P1}$

30. $B_{5(P1-H1),(\Omega 2-H2)} = -\frac{3}{2\sqrt{2}} V_{H1H2P1\Omega 1} + \frac{3}{4\sqrt{2}} V_{H1H2\Omega 1P1}$

31. $B_{5(P1-H1),(P2-\Omega 2)} = -\frac{3}{2\sqrt{2}} V_{H1P2P1\Omega 1} + \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 1}$

32. $B_{5(P1-H1),(P2-\Omega 1)} = -\frac{3}{2\sqrt{2}} V_{H1P2P1\Omega 2} + \frac{3}{4\sqrt{2}} V_{H1P1P2\Omega 2}$

36. $B_{5(P1-H1),5(P2-H2)} = -2\, V_{H1H2P1P2} + V_{H1H2P2P1}$

41. $B_{1(\Omega 2-\Omega 1),2(P2-H2)} = -\frac{1}{\sqrt{6}} V_{H2P2\Omega 1\Omega 2} + \frac{1}{\sqrt{6}} V_{H2P2\Omega 2\Omega 1}$

50. $B_{2(\Omega 2-\Omega 1),2(P2-H2)} = -\frac{1}{\sqrt{6}} V_{H2P2\Omega 1\Omega 2} - \frac{1}{\sqrt{6}} V_{H2P2\Omega 2\Omega 1}$

Part III

A Simple Method for the Direct Calculation of Ionization Potentials and Electron Affinities

I. INTRODUCTION

The determination of electron affinities and ionization potentials is an important problem of both theoretical and experimental interest. The locations and strengths of transitions are important in atmospheric, biological, and interstellar processes. For example, in ESCA[1] and in photodetachment[2] and photoelectron[3] spectroscopy, ionization potentials and electron affinities are directly measured.

Theoretically, Koopmann's theorem[4] has been the mainstay of many low level calculations. From Koopmann's theorem we can say that ionization potentials and electron affinities can in certain cases be predicted by the canonical Hartree-Fock orbital energies. This result depends on correlation energy changes and relaxation effects upon electron removal or addition being approximately equal but opposite in sign and hence canceling. Although these effects are expected to be opposite in sign there is no theoretical reason for the correlation energy changes and relaxation to be equal in magnitude. For example, in H_2CO using a [4s 3p/2s] contracted Gaussian basis set we obtain an orbital energy of -14.64 eV for an electron in the $1b_1$ orbital, while the experimental IP is 14.47 eV. However, the lowest ionization potential is by Koopmann's theorem 12.09 eV compared to 10.88 eV experimentally. An additional problem arises for electron affinities where basis sets in an SCF calculation must be large enough to allow for the SCF virtuals to converge to the more spatially diffuse negative ion orbitals.

To remedy the sporadic agreement of Koopmann's theorem with experiment, large scale configuration interaction calculations can be performed on both the molecular and ionic states.[5] The resulting energies are ionization potentials and electron affinities. These are in excellent agreement with experiment but can involve tedious basis set optimization and large amounts of computer time and core. Furthermore, in accurate configuration interaction calculations and in related calculations using Rayleigh-Schroedinger perturbation theory[6] ionization potentials and electron affinities are the result of a subtraction of two large numbers to obtain a much smaller number.

The equations of motion (EOM) method for atoms and molecules[7] can directly calculate excitation energies accurately without determining either total energies or wavefunctions explicitly. The resulting energies and amplitudes can be used to easily determine many properties of experimental and theoretical interest, e.g. oscillator strengths, transition moments between excited states,[8, 9] two photon decay probabilities,[8] Born inelastic scattering cross sections,[10] photoionization cross sections,[8, 11] and optical potentials.[12]

In view of the relative ease of calculation and the excellent experimental agreement of the EOM, we proposed in 1972[13] a similar way to calculate ionization potentials, electron affinities, and the positions of simple electron-molecule resonances. It is the purpose of this paper to more fully expand and examine the equations and to discuss some calculations for the ionization potentials of He, N_2, and OH^-. Independently, Simons and Smith[14] proposed a similar method. These methods are related to the Green's function method of Cederbäum et al.[15] and the propagator method of Purvis and Öhrn.[16]

In section II the theory for the equations of motion method for ionization potentials and electron affinities will be developed and expanded from reference 13. We will briefly discuss the relationship of this method to the method of Simons[14] and to Green's function and propagator methods. Results for He, N_2, and OH^- are discussed in section III.

II. THEORY

Consider an operator $O_\lambda^\dagger$ which when operating on the exact initial state $|0>$ with N electrons generates a state with one less or one more electron, i.e.

$$O_\lambda^\dagger\, |0, N> = |\lambda, N \pm 1> \tag{1}$$

where $|\lambda>$ is a state which is an eigenfunction of the number operator with eigenvalue one greater or one less than $|0>$. This is similar to the equations of motion operator $O_\lambda^{\dagger\,EX}$ for excited states,[7] except that $O_\lambda^{\dagger\,EX}$ is an operator which generates excited states of a system with the same number of particles as the ground state.

$O_\lambda^\dagger$ for ionization potentials and electron affinities can be written as a sum of operator strings with an odd number of electron creation and destruction operators, i.e. the net effect of $O_\lambda^\dagger$ must be the addition or removal of an electron. Rowe's equation of motion[17] can be used to determine the energy change associated with the operator $O_\lambda^\dagger$. Since $O_\lambda^\dagger$ has an odd number of creation and destruction operators the appropriate equation is Rowe's equation of motion for Fermi-like transfer operators,[17] i.e.

$$<0|\, \{\delta O_\lambda, \mathcal{H}, O_\lambda^\dagger\}\, |0> = \omega_\lambda <0|\, \{\delta O_\lambda, O_\lambda^\dagger\}\, |0> \tag{2}$$

where

$$\{A, B, C\} = \tfrac{1}{2}\{\, [A, B], C\} + \tfrac{1}{2}\{A, [B, C]\} \tag{3}$$

$$= ABC - CBA + \tfrac{1}{2}\, CAB - \tfrac{1}{2}\, ACB + \tfrac{1}{2}\, BCA - \tfrac{1}{2}\, BAC \tag{4}$$

ω_λ is the negative of the electron affinity or the ionization potential

$$\omega_\lambda = E_\lambda - E_0 \tag{5}$$

Equation (2) is exact. However it cannot be solved exactly for most systems of chemical interest. There are two approximations which we can use to solve Eq. (2). $O_\lambda^\dagger$ can be written as an infinite sum of odd numbers of creation and destruction operators. This sum may be truncated. For example, for electron affinities $O_\lambda^\dagger$ may be truncated after simple electron addition,

$$O_\lambda^\dagger = \sum_{i'} Y_{i'} c_{i'}^\dagger \tag{6}$$

where the sum is over all spin orbitals.

A second approximation is made in the choice for $|0>$, e.g. we can choose the ground state to be the Hartree-Fock ground state. The use of the symmetric double anticommutator in Eq. (2) assures that the equations will be of low particle-hole rank. That is, by writing Eq. (2) with as many commutators or anticommutators as we can, the resulting ionization potentials and electron affinities, ω_λ will be relatively insensitive to the approximation used for the ground state.

So far all the equations have been completely general and apply to both electron affinities and ionization potentials. For the remainder of this section only ionization potentials will be considered. The theory for electron affinities is analogous. In fact, exactly the same equations result so that one calculation may yield both ionization potentials and electron affinities.

Furthermore, we restrict either $|0>$ or $|\lambda>$ to be well described by a closed shell. This restriction is not severe since for many cases either the initial or final system is closed shell, e.g. to calculate the electron affinity of OH we can calculate the ionization potential of the closed shell OH^-.

The Hamiltonian is

$$\hat{\mathcal{H}} = \sum_i \epsilon_i (c^\dagger_{i\alpha} c_{i\alpha} + c^\dagger_{i\beta} c_{i\beta}) + \sum_{ij} (\sum_\nu (V_{i\nu\nu j} - 2 V_{i\nu j\nu}) - \tfrac{1}{2} \sum_p V_{ippj}) (c^\dagger_{i\alpha} c_{j\alpha} + c^\dagger_{i\beta} c_{j\beta}) + \tfrac{1}{2} \sum_{ijkl} V_{ijkl} (c^\dagger_{i\alpha} c_{k\alpha} + c^\dagger_{i\beta} c_{k\beta}) (c^\dagger_{j\alpha} c_{l\alpha} + c^\dagger_{j\beta} c_{l\beta}) \qquad (7)$$

where Greek letters are holes or orbitals occupied in a Hartree Fock ground state calculation; m, n, p, ... are particles or virtual orbitals; and i, j, k, l are either holes or particles. V_{ijkl} is defined

$$V_{ijkl} = \int \varphi_i^*(1)\, \varphi_j^*(2)\, \frac{1}{r_{12}}\, \phi_k(1)\, \varphi_l(2)\, d\tau_{12} \qquad (8)$$

To determine a reasonable form for $O^\dagger_\lambda$ consider the initial state $|0>$ to be the Hartree-Fock ground state and all possible double excitations, i.e.

$$|0> \approx N_0 (|HF> + |\chi> \qquad (9)$$

where N_0 is a normalization constant and $|\chi>$ is a correlation function.

$$| \chi > = \sum_{\substack{m \leq n \\ \gamma \leq \nu}} C^{mn}_{\gamma\nu} \left| {}^{mn}_{\gamma\nu} \right> \tag{10}$$

Equation (10) can be rewritten[7]

$$| 0 > \approx N_0 \Big(|HF> + \tfrac{1}{4} \sum_{mn\gamma\nu} \big[C_{m\gamma, n\delta}(0) \big(\tfrac{1}{2} c^{\dagger}_{m\alpha} c_{\gamma\alpha} c^{\dagger}_{n\alpha} c_{\delta\alpha} + c^{\dagger}_{m\alpha} c_{\gamma\alpha} c^{\dagger}_{n\beta} c_{\delta\beta} + c^{\dagger}_{m\beta} c_{\gamma\beta} c^{\dagger}_{n\alpha} c_{\delta\alpha} + \tfrac{1}{2} c^{\dagger}_{m\beta} c_{\gamma\beta} c^{\dagger}_{n\beta} c_{\delta\beta} \big) +$$

$$C_{m\gamma, n\delta}(1) \big(-\tfrac{1}{2} c^{\dagger}_{m\alpha} c_{\gamma\alpha} c^{\dagger}_{n\alpha} c_{\delta\alpha} + c^{\dagger}_{m\alpha} c_{\gamma\alpha} c^{\dagger}_{n\beta} c_{\delta\beta} +$$

$$c^{\dagger}_{m\beta} c_{\gamma\beta} c^{\dagger}_{n\alpha} c_{\delta\alpha} - \tfrac{1}{2} c^{\dagger}_{m\beta} c_{\gamma\beta} c^{\dagger}_{n\beta} c_{\delta\beta} \big) \big] \tag{11}$$

All correlation coefficients are assumed to be small.

The important effects for ionization potentials are:

1. Removal of an electron from a hole.
2. Removal of an electron from a particle level.
3. Removal of an electron from a hole and excitation of one of the remaining hole electrons.
4. Removal of an electron from a particle level and deexcitation of the remaining particle electron.

2-4 are higher order processes for ionization potentials. 2 and 4 do not exist unless the initial state is correlated.

Hence we can write

$$O^{\dagger}_{\lambda} = \sum_i Y_i (-c^{\dagger}_{i\beta}) + \sum_{\substack{r \\ m\gamma\nu \\ \nu \geq \gamma}} Y^{(2)}_{(m\gamma\nu)_r} \Gamma^{\dagger}_{(m\gamma\nu)_r} - \sum_{\substack{r \\ pm\gamma \\ p \geq m}} Z^{(2)}_{(pm\gamma)_r} \textcircled{H}_{(pm\gamma)_r} \tag{12}$$

In Eq. (12) the operators are spin-adapted so the subscript r refers to the various possible spin couplings, e.g. there are two ways to couple three electrons in three different orbitals to form doublet states with $M_S = \frac{1}{2}$. $\Gamma^\dagger$ is an operator which has the effect of removing an electron from a hole and exciting a different hole electron. Ⓗ is an operator which removes an electron from a particle level and deexcites the remaining electron in a particle state. The $\Gamma^\dagger$ and Ⓗ operators are given in Table I.

If Eq. (12) is used in Eq. (2) we obtain the following matrix equations.

$$\underset{\frown}{\mathcal{A}}\, Y + \left(\underset{\frown}{\mathcal{A}}^{(1,2)} \;\; \underset{\frown}{\mathcal{B}}^{(1,2)}\right) \begin{pmatrix} Y^{(2)} \\ Z^{(2)} \end{pmatrix} = \omega_\lambda \left(\underset{\frown}{\mathcal{D}}\, Y + \left(\underset{\frown}{\mathcal{D}}^{(1,2)} \underset{\frown}{\mathcal{F}}^{(1,2)}\right) \begin{pmatrix} Y^{(2)} \\ Z^{(2)} \end{pmatrix} \right) \tag{13}$$

$$\left(\underset{\frown}{\mathcal{A}}^{(1,2)} \; \underset{\frown}{\mathcal{B}}^{(1,2)}\right)^\dagger Y + \begin{pmatrix} \underset{\frown}{\mathcal{A}}^{(2,2)} & \underset{\frown}{\mathcal{C}}^{(2,2)} \\ \underset{\frown}{\mathcal{C}}^{(2,2)^\dagger} & -\; \underset{\frown}{\mathcal{B}}^{(2,2)} \end{pmatrix} \begin{pmatrix} Y^{(2)} \\ Z^{(2)} \end{pmatrix}$$

$$= \omega_\lambda \left[\left(\underset{\frown}{\mathcal{D}}^{(1,2)^\dagger} \;\; \underset{\frown}{\mathcal{F}}^{(1,2)^\dagger}\right) Y + \begin{pmatrix} \underset{\frown}{\mathcal{D}}^{(2,2)} & \underset{\frown}{\mathcal{G}}^{(2,2)} \\ \underset{\frown}{\mathcal{G}}^{(2,2)^\dagger} & \underset{\frown}{\mathcal{F}}^{(2,2)} \end{pmatrix} \begin{pmatrix} Y^{(2)} \\ Z^{(2)} \end{pmatrix} \right] \tag{14}$$

where

$$\mathcal{A}_{ij} = \langle 0 | \{c^\dagger_{i\beta}, \mathcal{H}, c_{j\beta}\} | 0 \rangle$$

$$\mathcal{D}_{ij} = \langle 0 | \{c^\dagger_{i\beta}, c_{j\beta}\} | 0 \rangle \equiv \delta_{ij}$$

$$\mathcal{A}^{(1,2)}_{ij(m\gamma\nu)_r} = - \langle 0 | \{c^\dagger_{i\beta}, \mathcal{H}, \Gamma_{(m\gamma\nu)_r}\} | 0 \rangle$$

$$\mathcal{B}^{(1,2)}_{i;(pm\gamma)_r} = <0|\{c^{\dagger}_{i\beta}, \mathcal{H}, \textcircled{H}_{(pm\gamma)_r}\}|0>$$

$$\mathcal{D}^{(1,2)}_{i;(m\gamma\nu)_r} = -<0|\{c^{\dagger}_{i\beta}, \Gamma^{\dagger}_{(m\gamma\nu)_r}\}|0>$$

$$\mathcal{F}^{(1,2)}_{i;(pm\gamma)_r} = <0|\{c^{\dagger}_{i\beta}, \textcircled{H}_{(pm\gamma)_r}\}|0>$$

$$\mathcal{A}^{(2,2)}_{\underline{(m\gamma\nu)}_{\underline{r}},(m\gamma\nu)_r} = <0|\{\Gamma_{\underline{(m\gamma\nu)}_{\underline{r}}}, \mathcal{H}, \Gamma^{\dagger}_{(m\gamma\nu)_r}\}|0>$$

$$\mathcal{C}^{(2,2)}_{\underline{(m\gamma\nu)}_{\underline{r}},(pm\gamma)_r} = -<0|\{\Gamma_{\underline{(m\gamma\nu)}_{\underline{r}}}, \mathcal{H}, \textcircled{H}_{(pm\gamma)_r}\}|0>$$

$$\mathcal{D}^{(2,2)}_{\underline{(m\gamma\nu)}_{\underline{r}},(m\gamma\nu)_r} = <0|\{\Gamma_{\underline{(m\gamma\nu)}_{\underline{r}}}, \Gamma^{\dagger}_{(m\gamma\nu)_r}\}|0>$$

$$\mathcal{G}^{(2,2)}_{\underline{(m\gamma\nu)}_{\underline{r}},(pm\gamma)_r} = <0|\{\Gamma_{\underline{(m\gamma\nu)}_{\underline{r}}}, \textcircled{H}_{(pm\gamma)_r}\}|0>$$

$$\mathcal{B}^{(2,2)}_{\underline{(pm\gamma)}_{\underline{r}},(pm\gamma)_r} = -<0|\{\textcircled{H}^{\dagger}_{\underline{(pm\gamma)}_{\underline{r}}}, \mathcal{H}, \textcircled{H}_{(pm\gamma)_r}\}|0>$$

$$\mathcal{F}^{(2,2)}_{\underline{(pm\gamma)}_{\underline{r}},(pm\gamma)_r} = <0|\{\textcircled{H}^{\dagger}_{\underline{(pm\gamma)}_{\underline{r}}}, \textcircled{H}_{(pm\gamma)_r}\}|0> \qquad (15)$$

The most important process for ionization potentials is single electron removal. All the matrices which involve an operator that is simply electron removal are in Eq. (13). Equation (14) is coupled to Eq. (13) through the ionization potential ω_λ and the vectors $Y^{(2)}$ and $Z^{(2)}$. Equation (14) can be solved for $\begin{pmatrix} Y^{(2)} \\ Z^{(2)} \end{pmatrix}$, i.e.

$$\begin{pmatrix} Y^{(2)} \\ Z^{(2)} \end{pmatrix} = - \begin{pmatrix} \underset{\frown}{\mathcal{A}}(2,2) - \omega_\lambda \underset{\frown}{\mathcal{D}}(2,2) & \underset{\frown}{\mathcal{C}}(2,2) - \omega_\lambda \underset{\frown}{\mathcal{G}}(2,2) \\ \underset{\frown}{\mathcal{C}}(2,2)^\dagger - \omega_\lambda \underset{\frown}{\mathcal{G}}(2,2)^\dagger & -\underset{\frown}{\mathcal{B}}(2,2) - \omega_\lambda \underset{\frown}{\mathcal{L}}(2,2) \end{pmatrix}^{-1}$$

$$\times \left(\underset{\frown}{\mathcal{A}}(1,2) - \omega_\lambda \underset{\frown}{\mathcal{D}}(1,2) \quad \underset{\frown}{\mathcal{B}}(1,2) - \omega_\lambda \underset{\frown}{\mathcal{L}}(1,2) \right)^\dagger Y \tag{16}$$

$$= - \underset{\frown}{A}^{-1} \underset{\frown}{R}^\dagger Y \tag{17}$$

Combining (17) with (13)

$$\underset{\frown}{\mathcal{A}} Y - \underset{\frown}{R} \underset{\frown}{A}^{-1} \underset{\frown}{R}^\dagger Y = \omega_\lambda Y \tag{18}$$

$$(\underset{\frown}{\mathcal{A}} - \Delta \underset{\frown}{\mathcal{A}}) Y = \omega_\lambda Y \tag{19}$$

Equation (19) must be solved iteratively for ω_λ since $\Delta \underset{\frown}{\mathcal{A}}$ depends on ω_λ through Eq. (16). For example, the first guess for ω_λ can be Koopmann's theorem value. It is used in constructing $\Delta \underset{\frown}{\mathcal{A}}$. A new ω_λ is chosen from the eigenvalues of (19) which is the closest to $\omega_\lambda^{\text{Koop.}}$ and this is used to form the new $\Delta \underset{\frown}{\mathcal{A}}$. This process continues until two successive iterations do not differ by more than a predetermined amount, e.g. 10^{-5} Hartrees. The procedure usually converges within ten iterations.

The formulas of Eq. (14) in terms of orbital energies and interaction matrix elements are derived using a formula generating program.[17] The ground state is assumed to be as in Eq. (11). If the correlation coefficient $C_{m\gamma, n\delta}$ is obtained from Rayleigh-Schroedinger perturbation theory, it is proportional to electron interaction matrix elements. All formulas used in Eq.

(19) are derived so that Eq. (19) is third order in the electron interaction matrix elements, i.e. $\underset{\wedge}{\mathcal{A}}$ formulas are generated to order ϵC^3 and VC^2, $\underset{\wedge}{R}$ formulas to order ϵC^2 and VC, and $\underset{\wedge}{A}$ formulas to order ϵC and V. This truncation by orders is reasonable since the terms most important for the ionization potentials are contained in $\underset{\wedge}{\mathcal{A}}$.

$$\mathcal{A}_{ij} = -\epsilon_i \delta_{ij} - \sum_{\nu\gamma} \rho^{(2)}_{\nu\gamma} (2V_{i\nu j\gamma} - V_{i\nu\gamma j}) - \sum_{pq} \rho_{pq} (2V_{ipjq} - V_{ipqj}) \qquad (20)$$

where

$$\begin{aligned} \rho^{(2)}_{\nu\gamma} &= -\tfrac{1}{2} \sum_{pq\mu} \sum_{S} C'_{p\mu,\,q\nu}(S)\, C_{p\mu,\,q\gamma}(S) \\ \rho_{pq} &= \tfrac{1}{2} \sum_{m\mu\nu} \sum_{S} C'_{m\mu,\,q\nu}(S)\, C_{m\mu,\,p\nu}(S) \end{aligned} \qquad (21)$$

and

$$\begin{aligned} C'_{p\nu,\,q\gamma}(0) &= \tfrac{3}{4} C_{p\nu,\,q\gamma}(0) + \tfrac{1}{4} C_{p\nu,\,q\gamma}(1) \\ C'_{p\nu,\,q\gamma}(1) &= \tfrac{1}{4} C_{p\nu,\,q\gamma}(0) + \tfrac{3}{4} C_{p\nu,\,q\gamma}(1) \end{aligned} \qquad (22)$$

Note that through second order in interaction matrix elements $\mathcal{A}_{ij}$ is purely on-diagonal and is given by Koopmann's theorem.

Matrices $\underset{\wedge}{\mathcal{D}}(1,2)$, $\underset{\wedge}{\mathcal{L}}(1,2)$, $\underset{\wedge}{\mathcal{C}}(2,2)$, and $\underset{\wedge}{\mathcal{E}}(2,2)$ are zero. Matrices $\underset{\wedge}{\mathcal{D}}$, $\underset{\wedge}{\mathcal{D}}(2,2)$, and $\underset{\wedge}{\mathcal{L}}(2,2)$ are unit matrices. The formulas for matrices $\underset{\wedge}{\mathcal{A}}(1,2)$, $\underset{\wedge}{\mathcal{B}}(1,2)$, $\underset{\wedge}{\mathcal{A}}(2,2)$, and $\underset{\wedge}{\mathcal{B}}(2,2)$ are given in Tables II and III.

The $Y^{(2)}$ amplitudes correspond to electron removal and excitation of another hole electron. This is a core relaxation process.

The $Z^{(2)}$ amplitudes are electron removal from a particle level and deexcitation of the remaining particle electron. Thus, the $Z^{(2)}$ amplitudes are a correlation effect. We expect the inclusion of $Y^{(2)}$ amplitudes to lower the calculated ionization potential and the $Z^{(2)}$ amplitudes to raise it.

In actual calculations, the matrix sizes are reduced by choosing $O_\lambda^\dagger$ operators which generate states of a specific spatial symmetry. However the A matrix is still very large, e.g. for a calculation of the $OH^- \; X\,{}^1\Sigma^+ \rightarrow {}^2\Pi_g$ state using a $< 4s\ 3p\ 2d_\pi / 2s\ 1p > + R\,s_0 + R\,p_0 + R\,s_H$ basis set the A matrix is 1050 × 1050. There are several approximations which can be made to reduce the size of the calculation.

The simplest approximation is to ignore the $\Delta\underset{\wedge}{\mathcal{A}}$ correction in Eq. (19) to $\underset{\wedge}{\mathcal{A}}$. If simultaneously terms second order in the correlation coefficients are set equal to zero in $\underset{\wedge}{\mathcal{A}}$ we have Koopmann's theorem. Neither approximations works very well as will be shown in section III.

A second approximation is to calculate all terms in Eq. (19) only to second order, i.e. $\underset{\wedge}{\mathcal{A}}$ terms to order ϵC^2 and VC, $\underset{\wedge}{R}$ terms to order ϵV and V, and $\underset{\wedge}{\mathsf{A}}$ terms to order ϵ. Also off diagonal $\underset{\wedge}{\mathsf{A}}$ terms are assumed equal to zero. This approximation is identical to the second order Green's function techniques of Cederbäum <u>et al.</u>[15] or the Born collision approximation of Purvis and Öhrn.[16] Although for a few molecular cases this method works well, e.g. H_2CO,[18] usually it does not.[15]

A slightly different approximation is to assume $\underset{\wedge}{A}$ diagonal terms are calculated to order ϵ C and V. Off diagonal $\underset{\wedge}{A}$ terms are zero. These are the shifted Born collision results of Purvis and Öhrn.[16] Again results are inconsistent.

Selective inversion of blocks of the $\underset{\wedge}{A}$ matrix where all formulas are calculated to second order is another possibility. This corresponds to the spin symmetry diagonalized shifted Born collision approximation[16] and symmetry diagonalized shifted Born collision approximation.[16] Ionization potentials in these approximations do not agree well with experiment.

A more reliable approximation is to retain all terms in Eq. (18) to third order, except that $\underset{\wedge}{A}$ is assumed to be diagonal. Simons[19] reports agreement to ± 0.15 eV with experiment for diatomic molecules using Slater basis sets. However, Simons[19] does not spin-symmetry adapt $O_\lambda^\dagger$. Hence spurious quartet components exist in $\underset{\wedge}{A}^{-1}$. We have also found that using the spin symmetry adapted operators which eliminate the spurious quartet components of Table I and Gaussian basis sets, agreement with experiment is good but not in general within ± 0.15 eV.

There are two further approximations which should result in good experimental agreement consistently. Selective inversion of $\underset{\wedge}{A}$ while maintaining all formulas to the order given in Tables II and III seems to be very promising. The assumption that off-diagonal $\underset{\wedge}{A}$ elements are small and hence can be zeroed may not be a valid assumption. The selection of the sections of the $\underset{\wedge}{A}^{-1}$ matrix to invert can be based on the magnitude of the corresponding on-diagonal $\underset{\wedge}{A}$ terms, e.g. if the on-diagonal $\underset{\wedge}{A}$ element differs by less than a certain value from the Koopmann's theorem ionization potential, then that element's indices are included in a list which is used to form the sub $\underset{\wedge}{A}$ matrix for inversion. Another choice is based on the kinds of holes and particles that compose the three indices of an $\underset{\wedge}{A}$ row or column, e.g. if we are interested in ionization from the b_1 orbital of H_2CO then all indices in $\underset{\wedge}{A}$ which contain the b_1 orbital are included in the list for sub $\underset{\wedge}{A}$ matrix inversion.

A second approximation is to use improved virtual orbitals (IVO)[20] for the parts of $\underset{\wedge}{A}$ that are assumed to be diagonal. The IVO or frozen core orbitals are the virtual orbitals that are obtained if the occupied orbitals are "frozen" and the virtuals are orbitals appropriate for an electron in a field of N-1 electrons. For ordinary virtual orbitals an electron is moving in the field of N other electrons. IVO orbitals are obviously much more appropriate for the process of electron removal with electron excitation. We expect off-diagonal $\underset{\wedge}{A}$ elements to be smaller than when regular virtual orbitals are used. Hence, the inverted matrix will be closer to diagonal form. The formulas given in Tables II and III will be slightly different if IVO orbitals are used.

In summary and as a practical description of an actual calculation, the considerations for doing an ionization potential or electron affinity calculation of this kind are given.

1. The system must be well described by an HF closed shell

in either its initial or final state.

2. The basis set used must be flexible enough to describe both the initial and final states well. For calculations between a negative ion and a molecule or atom this may require the addition of several diffuse functions to ordinary valence basis sets.

3. The correlation coefficients are determined by either Rayleigh-Schroedinger perturbation theory or self-consistently from an equations-of-motion for excited state calculation.[7]

4. Equation (19) is solved iteratively by one of the better approximations described in this section.

III. APPLICATIONS

A. He

The basis set used for the SCF calculation on the ground state of He is composed of 10 s and 5 p Cartesian Gaussian functions. The basis is taken from Huzinaga[21] with the p exponents approximating a Slater function scaled so that the expectation value of r is the same as calculated by Pekeris.[22] The correlation coefficients are calculated by Rayleigh-Schroedinger perturbation theory.

Results are given in Table IV. Obviously both the core relaxation $\underset{\wedge}{\mathcal{A}}^{(1,2)}$ terms and the correlation $\underset{\wedge}{\mathcal{B}}^{(1,2)}$ terms must be included in any ionization potential calculation for He where $\Delta\underset{\wedge}{\mathcal{A}}$ in Eq. (19) is not assumed to be zero. For example, row 3 without $\underset{\wedge}{\mathcal{B}}^{(1,2)}$ terms gives an ionization potential of 23.57 eV. The inclusion of $\underset{\wedge}{\mathcal{B}}^{(1,2)}$ in row 4 gives an ionization potential of 24.42 eV, in good agreement with the experimental result 24.58 eV.

Doll and Reinhardt[23] use a large basis set of Slater's including d functions. Their result is a calculation to second order. If we assume that the third order terms in $\underset{\wedge}{\mathcal{A}}$ are a purely additive effect and do not couple with any $\Delta\underset{\wedge}{\mathcal{A}}$ effects, from row 4 we obtain an ionization potential to second order of 24.33 eV. The shifted denominator result of row 6 is 24.55 eV.

The second order results are in better agreement with experiment than are the third order results of rows 7 and 8. However, none of the results when both $\underset{\wedge}{\mathcal{A}}^{(1,2)}$ and $\underset{\wedge}{\mathcal{B}}^{(1,2)}$ matrices are included differ from experiment by more than 0.27 eV. Even the

Koopmann's theorem result is only 0.40 eV from experiment. As shown by Cederbäum et al.[15, 18] second order results can give good experimental agreement for some molecules but for many molecules higher order results are required.

B. N_2

The ground state configuration of N_2 is

$$(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(1\pi_u)^4\,(3\sigma_g)^2.$$

We have performed a ground state SCF calculation on N_2 at ground state equilibrium geometry, 2.068 au. The basis set is $<3s\ 2p>$ contracted Gaussian set optimized for neutral N with the contraction coefficients obtained from Dunning.[24] We give the results in Table V.

Koopmann's theorem ionization potentials are in error by as much as 2.2 eV ($B^2\Sigma_u^+$). In addition the Koopmann's theorem result differentiates only slightly between the $X^1\Sigma_g^+ \rightarrow X^2\Sigma_g^+$ and $X^1\Sigma_g^+ \rightarrow A^2\Pi_u$ ionization potentials, 16.99 eV and 17.04 eV. Experimentally the difference is 1.38 eV. The Koopmann's theorem ordering of the ionization potentials is correct.

Second order calculations involve calculating $\underset{\wedge}{\mathcal{A}}$ to order ϵC^2 and VC, $\underset{\wedge}{\mathcal{A}}^{(1,2)}$ and $\underset{\wedge}{\mathcal{B}}^{(1,2)}$ to order ϵC and V, and assuming $\underset{\wedge}{A}$ is diagonal and to order ϵ. Second order results do not improve experimental agreement in N_2 and predict the ion states in the wrong order.

Third order calculations with the $\underset{\wedge}{A}^{-1}$ denominators expanded as $\frac{1}{1+\chi} \approx 1 - \chi$ and only third order terms are retained improve the results considerably. However, the calculated ionization potential calculations to the $X\,^2\Sigma_g^+$ and $B\,^2\Sigma_u^+$ states are too low by 0.88 eV and 0.78 eV respectively. The calculated $A\,^2\Pi_u$ ionization potential is 0.18 eV too high.

If interaction matrix elements are kept in the $\underset{\frown}{A}^{-1}$ denominators the $X\,^1\Sigma_g^+ \rightarrow X\,^2\Sigma_g^+$ ionization potential improves to 14.92 eV. This compares with Simons'[26] result of 15.69 eV. Simons uses a double zeta Slater basis set augmented with $3d\pi$ functions. We calculate using this approximation except with the operators being spin symmetry adapted in a $< 3s\ 2p\ 1d_\pi >$ Gaussian basis set an ionization potential of 15.13 eV. Further improvements in the basis set should result in better experimental agreement. We feel, however, that using Gaussian basis functions we cannot consistently achieve Simons' experimental agreement in this approximation.

Furthermore, by not using operators which generate pure doublets when operating on the ground state, spurious quartet contributions are introduced in $\underset{\frown}{A}^{-1}$ in Simons' scheme. This may compensate somewhat for the assumption that $\underset{\frown}{A}$ is diagonal.

C. OH^-

The ground state configuration of OH^- is

$$(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4\,.$$

The basis set we used is the $< 4s\ 3p/2s >$ Gaussian basis set of

Dunning[27] augmented by dπ polarization functions on O and p polarization functions on H.[28] A diffuse s function with exponent 0.09 and a diffuse set of p functions with exponent 0.07 on oxygen and a diffuse s function with exponent 0.05 are included to better describe the negative ion ground state. We calculate the ionization potential of OH^- at 1.781 au the ground state equilibrium geometry of both OH and OH^-. Thus we calculate the vertical detachment energy of OH^-, $X^+\Sigma^+ \rightarrow 2\Pi$. Results are given in Table VI.

The Koopmann's theorem result is over 1 eV higher than the experimental energy. Second order effects overcompensate reducing the detachment energy to a small negative number. The third order result with V in the denominator in $\underset{\frown}{A}$ is in excellent experimental agreement.

IV. CONCLUSION

We have developed an equations of motion approach for ionization potentials and electron affinities.[13] We propose several approximations to obtain ionization potentials, including a method similar to the one used by Simons.[14] However, we spin-symmetry adapt all operators, thus assuring that there is no introduction of spurious quartet components. It is obvious that the equations must be solved to at least third order in the interaction.

Using large, standard Gaussian basis sets obtained from the literature which are optimized for SCF calculations on the neutral ground state, we do not obtain consistently ionization potentials which agree with experiment as well as Simons. We conclude that either using Gaussian basis sets extensive optimization including the addition of polarization and possibly diffuse functions must be done or that Simons use of non-spin adapted symmetry operators introduces compensating errors which correct for the approximations made inverting the large matrix $\underset{\frown}{A}$.

We propose two further approximations, i.e. the selective inversion of sections of $\underset{\frown}{A}$ in third order and the use of improved virtual orbitals for parts of $\underset{\frown}{A}$ which are assumed diagonal. We feel that these approximations may lead to consistent experimental agreement for relatively small unoptimized Gaussian basis sets without extending the equations to higher orders.

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Table I. $\Gamma^\dagger$ and $\textcircled{H}$ operators ($\nu > \gamma$, p > m)

$$\Gamma^\dagger_{m\gamma\gamma} = - c_{\gamma\beta}\, c^\dagger_{m\alpha}\, c_{\gamma\alpha}$$

$$\Gamma^\dagger_{(m\nu\gamma)_1} = - 1/\sqrt{2}\, (c_{\nu\alpha}\, c^\dagger_{m\alpha}\, c_{\gamma\beta} - c_{\nu\beta}\, c^\dagger_{m\alpha}\, c_{\gamma\alpha})$$

$$\Gamma^\dagger_{(m\nu\gamma)_2} = \sqrt{2/3}\, (c_{\nu\beta}\, c^\dagger_{m\beta}\, c_{\gamma\beta} + \tfrac{1}{2}\, c_{\nu\alpha}\, c^\dagger_{m\alpha}\, c_{\gamma\beta} + \tfrac{1}{2}\, c_{\nu\beta}\, c^\dagger_{m\alpha}\, c_{\gamma\alpha})$$

$$\textcircled{H}_{mm\gamma} = - c_{m\beta}\, c^\dagger_{\gamma\alpha}\, c_{m\alpha}$$

$$\textcircled{H}_{(pm\gamma)_1} = - 1/\sqrt{2}\, (c_{p\beta}\, c^\dagger_{\nu\alpha}\, c_{m\alpha} - c_{p\alpha}\, c^\dagger_{\nu\alpha}\, c_{m\beta})$$

$$\textcircled{H}_{(pm\gamma)_2} = - \sqrt{2/3}\, (c_{m\beta}\, c^\dagger_{\nu\beta}\, c_{p\beta} + \tfrac{1}{2}\, c_{m\alpha}\, c^\dagger_{\nu\alpha}\, c_{p\beta} + \tfrac{1}{2}\, c_{m\beta}\, c^\dagger_{\nu\alpha}\, c_{p\alpha})$$

Table II. $\underset{\frown}{\mathcal{A}}^{(1,2)}$ and $\underset{\frown}{\mathcal{B}}^{(1,2)}$ formulas. H = hole, P = particle.
H4 > H3 and P4 > P3.

$$\mathcal{A}^{(1,2)}_{i,\ P3H3H3} = -V_{i\ H3H3P3} + \sum_{\substack{H5,\,H6,\\ P5,\,P6}} [-V_{i\ H6H3P6}\ C\,(0)_{P3H3,\ P6H6}$$

$$-V_{i\ P3P6P5}\ C\,(0)_{P5H3,\ P6H3} + V_{i\ H3P6H6}\ (C\,(0)_{P3H3,\ P6H6} +$$

$$C\,(0)_{P3H6,\ P6H3}) + \tfrac{1}{2}\,\delta_{i\ H3}\ (V_{H6P5P6P3}\ C\,(0)_{P5H3,\ P6H6}$$

$$-V_{i\ H6H5P6}\ C\,(0)_{P3H5,\ P6H6})]$$

$$\mathcal{A}^{(1,2)}_{i,\ (P3H4H3)_1} = 1/\sqrt{2}\,\{V_{i\ H4H3P3} + V_{i\ H3H4P3}$$

$$+\sum_{\substack{H5,\,H6\\ P5,\,P6}} [V_{i\ H6H3P6}\ C\,(0)_{P3H4,\ P6H6} + V_{i\ H6H4P6}\ C\,(0)_{P3H3,\ P6H6}$$

$$+V_{i\ P3P5P6}\ (C\,(0)_{P5H3,\ P6H4} + C\,(0)_{P5H4,\ P6H3})$$

$$-V_{i\ H3P6H6}\ (C\,(0)_{P3H4,\ P6H6} + C\,(0)_{P3H6,\ P6H4})$$

$$-V_{i\ H4P6H6}\ (C\,(0)_{P3H3,\ P6H6} + C\,(0)_{P3H6,\ P6H3})$$

$$-\tfrac{1}{2}\,\delta_{i\ H3}\ (V_{H6P5P6P3}\ C\,(0)_{P5H4,\ P6H6} - V_{H5H6H4P6}\ C\,(0)_{P3H5,\ P6H6})$$

$$-\tfrac{1}{2}\,\delta_{i\ H4}\ (V_{H6P5P6P3}\ C\,(0)_{P5H3,\ P6H6} - V_{H5,\ H6H3P6}\ C\,(0)_{P3H5,\ P6H6})]\}$$

Table II (continued)

$$\mathcal{A}^{(1,2)}_{i,\,(P3H4H3)_2} = \sqrt{3/2}\,\{(V_{i\,H3H4P3} - V_{i\,H4H3P3})$$

$$+ \sum_{\substack{H5,\,H6\\ P5,\,P6}} [- V_{i\,H6H3P6}\, C^{(0)}_{P3H4,\,P6H6} + V_{i\,H6H4P6}\, C^{(0)}_{P3H3,\,P6H6}$$

$$+ \tfrac{1}{3} V_{i\,P5P6P3}\, (C^{(0)}_{P5H3,\,P6H4} - C^{(0)}_{P5H4,\,P6H3})$$

$$- \tfrac{1}{3} V_{i\,H6P6H4}\, (C^{(0)}_{P3H3,\,P6H6} - C^{(0)}_{P3H6,\,P6H3})$$

$$+ \tfrac{1}{3} V_{i\,H6P6H3}\, (C^{(0)}_{P3H4,\,P6H6} - C^{(0)}_{P3H6,\,P6H4})$$

$$+ \tfrac{1}{2} \delta_{i\,H3}\, (V_{H6P5P6P3}\, C^{(0)}_{P5H4,\,P6H6} - V_{H5H6H4P6}\, C^{(0)}_{P3H5,\,P6H6})$$

$$+ \tfrac{1}{2} \delta_{i\,H4}\, (V_{H5H6H3P6}\, (C^{(0)}_{P3H5,\,P6H6} - V_{H6P5P6P3}\, C^{(0)}_{P5H3,\,P6H6})]\}$$

$$\mathcal{B}^{(1,2)}_{i,\,P3P3H3} = V_{i\,H3P3P3} + \sum_{\substack{H5,\,H6\\ P5,\,P6}} [$$

$$+ V_{i\,H6P3P6}\, C^{(0)}_{P3H3,\,P6H6}$$

$$- V_{i\,P6H6P3}\, (C^{(0)}_{P3H3,\,P6H6} + C^{(0)}_{P3H6,\,P6H3})$$

$$+ V_{i\,H5H6H3}\, C^{(0)}_{P3H5,\,P3H6}$$

Table II (continued)

$$- \tfrac{1}{2}\, \delta_{i\,P3}\; V_{H5H6H3P6}\; C(0)_{P3H5,\, P6H6}$$

$$+ \tfrac{1}{2}\, \delta_{i\,P3}\; V_{H6P1P6P5}\; C(0)_{P5H3,\, P6H6} \quad]$$

$${}^{(1,2)}_{i,\,(P4P3H3)_1} \quad = \quad 1/\sqrt{2}\, \{ V_{i\,H3P4P3} + V_{i\,H3P3P4}$$

$$+ \sum_{\substack{H5,\,H6\\ P5,\,P6}} [V_{H6iP6P4}\; C(0)_{P3H3,\, P6H6} + V_{H6iP6P3}\; C(0)_{P4H3,\, P6H6}$$

$$- V_{H6P6iP3}\; (C(0)_{P4H3,\, P6H6} + C(0)_{P4H6,\, P6H3})$$

$$- V_{H6P6iP4}\; (C(0)_{P3H3,\, P6H6} + C(0)_{P3H6,\, P6H3})$$

$$+ V_{H5H6H3i}\; (C(0)_{P3H5,\, P4H6} + C(0)_{P3H6,\, P4H5})$$

$$- \tfrac{1}{2}\, \delta_{i\,P3}\; (V_{H5H6H3P6}\; C(0)_{P4H5,\, P6H6} - V_{H6P5P6P4}\; C(0)_{P5H3,\, P6H6})$$

$$- \tfrac{1}{2}\, \delta_{i\,P4}\; (V_{H5H6H3P6}\; C(0)_{P3H5,\, P6H6} - V_{H6P5P6P3}\; C(0)_{P5H3,\, P6H6})] \}$$

$${}^{(1,2)}_{i,\,(P4P3H3)_2} \quad = \quad \sqrt{3/2}\, \{ V_{i\,H3P3P4} - V_{i\,H3P4P3}$$

$$+ \sum_{\substack{H5,\,H6\\ P5,\,P6}} [- V_{H6iP6P4}\; C(0)_{P3H3,\, P6H6} + V_{H6iP6P3}\; C(0)_{P4H3,\, P6H6}$$

Table II (Continued)

$$-\frac{1}{3} V_{H6P6iP3} (C(0)_{P4H3, P6H6} - C(0)_{P4H6, P6H3})$$

$$+\frac{1}{3} V_{H6P6iP4} (C(0)_{P3H3, P6H6} - C(0)_{P3H6, P6H3})$$

$$+\frac{1}{3} V_{H5H6iH3} (C(0)_{P3H5, P4H6} - C(0)_{P3H6, P4H5})$$

$$-\frac{1}{2} \delta_{iP3} (V_{H5H6H3P6} C(0)_{P4H5, P6H6} - V_{H6P5P6P4} C(0)_{P5H3, P6H6}$$

$$+\frac{1}{2} \delta_{iP4} (V_{H5H6H3P6} C(0)_{P3H5, P6H6} - V_{H6P5P6P3} C(0)_{P5H3, P6H6})]\}$$

Table III. $\underset{\wedge}{\mathcal{A}}^{(2,2)}$ and $\underset{\wedge}{\mathcal{B}}^{(2,2)}$ formulas. H = hole, P = particle. H2 > H1, H4 > H3, P2 > P1, and P4 > P3.

$$\mathcal{A}^{(2,2)}_{(\mathrm{P1H1H1}),(\mathrm{P3H3H3})} = \delta_{\mathrm{H1H3}}\,\delta_{\mathrm{P1P3}}\,(\epsilon_{\mathrm{P1}} - 2\epsilon_{\mathrm{H1}}) +$$

$$\delta_{\mathrm{P1P3}}\,V_{\mathrm{H1H1H3H3}} + \delta_{\mathrm{H1H3}}\,(V_{\mathrm{H1H1P1P3}} - 2\,V_{\mathrm{H1P1H1P3}})$$

$$\mathcal{A}^{(2,2)}_{(\mathrm{P1H2H1})_1,(\mathrm{P3H3H3})} = \delta_{\mathrm{H1H3}}\,\frac{1}{\sqrt{2}}\,(2\,V_{\mathrm{H1P1H2P3}} - V_{\mathrm{H1H2P3P1}})$$

$$- \delta_{\mathrm{P1P3}}\,\sqrt{2}\,V_{\mathrm{H1H2H3H3}} + \frac{1}{\sqrt{2}}\,\delta_{\mathrm{H2H3}}\,(2\,V_{\mathrm{H1P1H2P3}} -$$

$$V_{\mathrm{H1H2P1P3}})$$

$$\mathcal{A}^{(2,2)}_{(\mathrm{P1H2H1})_1,(\mathrm{P3H4H3})_1} = \delta_{\mathrm{H1H3}}\,\delta_{\mathrm{H2H4}}\,\delta_{\mathrm{P1P3}}\,(\epsilon_{\mathrm{P1}} - \epsilon_{\mathrm{H1}} - \epsilon_{\mathrm{H2}}) +$$

$$\delta_{\mathrm{H1H3}}\,(-V_{\mathrm{H2P1H4P3}} + \tfrac{1}{2}\,V_{\mathrm{H2H4P1P3}}) + \delta_{\mathrm{H1H4}}\,(-V_{\mathrm{H2P1H3P3}} +$$

$$\tfrac{1}{2}\,V_{\mathrm{H2H3P1P3}}) + \delta_{\mathrm{P1P3}}\,(V_{\mathrm{H1H2H3H4}} + V_{\mathrm{H1H2H4H3}})$$

$$\mathcal{A}^{(2,2)}_{(\mathrm{P1H2H1})_2,(\mathrm{P3H3H3})} = \delta_{\mathrm{H1H3}}\,\sqrt{\tfrac{3}{2}}\,V_{\mathrm{H1H2P3P1}} -$$

$$\sqrt{\tfrac{3}{2}}\,\delta_{\mathrm{H2H3}}\,V_{\mathrm{H1H2P1P3}}$$

$$\mathcal{A}^{(2,2)}_{(\mathrm{P1H2H1})_2,(\mathrm{P3H4H3})_1} = -\,\delta_{\mathrm{H1H3}}\,\frac{\sqrt{3}}{2}\,V_{\mathrm{H2H4P1P3}} -$$

$$\delta_{\mathrm{H1H4}}\,\frac{\sqrt{3}}{2}\,V_{\mathrm{H2H3P1P3}} + \delta_{\mathrm{H2H3}}\,\frac{\sqrt{3}}{2}\,V_{\mathrm{H1H4P1P3}}$$

$$+ \delta_{\mathrm{H2H4}}\,\frac{\sqrt{3}}{2}\,V_{\mathrm{H1H3P1P3}}$$

$$\mathcal{A}^{(2,2)}_{(\mathrm{P1H2H1})_2,(\mathrm{P3H4H3})_2} = \delta_{\mathrm{H1H3}}\,\delta_{\mathrm{H2H4}}\,\delta_{\mathrm{P1P3}}\,(\epsilon_{\mathrm{P1}} - \epsilon_{\mathrm{H1}} - \epsilon_{\mathrm{H2}})$$

Table III (continued)

$$+ \delta_{H1H3} (-V_{H2P1H4P3} + \frac{3}{2} V_{H2H4P1P3}) +$$

$$\delta_{H1H4} (V_{H2P1H3P3} - \frac{3}{2} V_{H2H3P1P3}) + \delta_{H2H3} (V_{H1P1H4P3}$$

$$- \frac{3}{2} V_{H1H4P1P3}) + \delta_{H2H4} (-V_{H1P1H3P3} + \frac{3}{2} V_{H1H3P1P3})$$

$$+ \delta_{P1P3} (V_{H1H2H3H4} - V_{H1H2H4H3})$$

$$-\mathcal{B}^{(2,2)}_{(P1P1H1),(P3P3H3)} = \delta_{H1H3} \delta_{P1P3} (\epsilon_{H1} - 2\epsilon_{P1}) -$$

$$\delta_{H1H3} V_{P1P1P3P3} + \delta_{P1P3} (2 V_{H1P1H3P1} - V_{H1H3P1P1})$$

$$-\mathcal{B}^{(2,2)}_{(P2P1H1)_1,(P3P3H3)} = \delta_{H1H3} (-\sqrt{2}) V_{P1P2P3P3} +$$

$$\delta_{P1P3} \frac{1}{\sqrt{2}} (2 V_{H1P1H3P2} - V_{H1H3P2P1}) +$$

$$\delta_{P2P3} \frac{1}{\sqrt{2}} (2 V_{H1P1H3P2} - V_{H1H3P1P2})$$

$$-\mathcal{B}^{(2,2)}_{(P2P1H1)_1,(P4P3H3)_1} = \delta_{H1H3} \delta_{P1P3} \delta_{P2P4} (\epsilon_{H1} - \epsilon_{P1} - \epsilon_{P2})$$

$$- \delta_{H1H3} (V_{P1P2P3P4} + V_{P1P2P4P3}) + \delta_{P1P3} (V_{H1P2H3P4}$$

$$- \tfrac{1}{2} V_{H1H3P2P4}) + \delta_{P1P4} (V_{H1P2H3P3} - \tfrac{1}{2} V_{H1H3P2P3})$$

$$+ \delta_{P2P3} (V_{H1P1H3P4} - \tfrac{1}{2} V_{H1H3P1P4}) + \delta_{P2P4} (V_{H1P1H3P3}$$

$$- \tfrac{1}{2} V_{H1H3P1P3})$$

Table III (continued)

$$-\mathcal{B}^{(2,2)}_{(P2P1H1)_2,(P3P3H3)} - \sqrt{\tfrac{3}{2}}\,\delta_{P1P3}\,V_{H1H3P2P1} + \sqrt{\tfrac{3}{2}}\,\delta_{P2P3}\,V_{H1H3P1P2}$$

$$-\mathcal{B}^{(2,2)}_{(P2P1H1)_2,(P4P3H3)_1} = -\delta_{P1P3}\,\frac{\sqrt{3}}{2}\,V_{H1H3P2P4} - \delta_{P1P4}\,\frac{\sqrt{3}}{2}\,V_{H1H3P2P3} + \frac{\sqrt{3}}{2}\,\delta_{P2P3}\,V_{H1H3P1P4} + \frac{\sqrt{3}}{2}\,\delta_{P2P4}\,V_{H1H3P1P3}$$

$$-\mathcal{B}^{(2,2)}_{(P2P1H1)_2,(P4P3H3)_2} = \delta_{H1H3}\,\delta_{P1P3}\,\delta_{P2P4}\,(\epsilon_{H1} - \epsilon_{P1} - \epsilon_{P2}) + \delta_{H1H3}\,(V_{P1P2P4P3} - V_{P1P2P3P4}) + \delta_{P1P3}\,(V_{H1P2H3P4} - \frac{3}{2}\,V_{H1H3P2P4}) + \delta_{P1P4}\,(-V_{H1P2H3P3} + \frac{3}{2}\,V_{H1H3P2P3}) + \delta_{P2P3}\,(-V_{H1P1H3P4} + \frac{3}{2}\,V_{H1H3P1P4}) + \delta_{P2P4}\,(V_{H1P1H3P3} - \frac{3}{2}\,V_{H1H3P1P3})$$

Table IV. He ionization potential in different approximations. The basis set is (10s 5p).

Order of the Terms in Eq. (19)					
$\mathcal{U}$	$\mathcal{U}^{(1,2)}$	$\mathcal{Q}^{(1,2)}$	Diagonal?	$\overset{A}{\wedge}$ Order	Ionization potential (eV)
$\epsilon C, V$[a]	0	0	--	0	24.98
$\epsilon C^2, VC^2$	0	0	--	0	24.89
$\epsilon C^3, VC^2$	$\epsilon C, V$	0	yes	ϵ	23.57
$\epsilon C^3, VC^2$	$\epsilon C, V$	$\epsilon C, V$	yes	ϵ	24.42
$\epsilon C^3, VC^2$	$\epsilon C, V$	0	yes	$\epsilon C, V$	23.68
$\epsilon C^3, VC^2$	$\epsilon C, V$	$\epsilon C, V$	yes	$\epsilon C, V$	24.64
$\epsilon C^3, VC^2$	$\epsilon C^2, VC$	$\epsilon C^2, VC$	yes	$\epsilon C, V$	24.85
$\epsilon C^3, VC^2$	$\epsilon C^2, VC$	$\epsilon C^2, VC$	yes	$\epsilon C, V$[b]	24.84
Doll and Reinhardt[c]					24.65
Experiment[d]					24.58

---

[a] Koopmann's theorem.

[b] We have used $\frac{1}{1+\chi} \approx 1 - \chi$ and have retained only third order terms in Δ .

[c] Reference 23.

[d] C. Moore, Natl. Bur. Std. (US) Cir. 467, Vol. 1 (1949).

Table V. N_2 Ionization Potentials

Approximation $X^1\Sigma_g^+ \rightarrow$	Ionization Potential (eV) $X^2\Sigma_g^+$	$B^2\Sigma_u^+$	$A^2\Pi_u$
Koopmann's Theorem	16.99	21.01	17.04
Second order[a]	14.17	17.21	17.42
Third order with V in denominator[a]	14.92	--	--
Third order[a]	14.72	18.00	17.16
Cederbäum second order[b]	14.68	17.35	16.95
Propagator[c]	14.91	17.55	17.23
Simons[d]	15.69	18.63	17.03
Experiment[e]	15.60	18.78	16.98

---

[a] See discussion in text.

[b] Reference 25.

[c] Reference 16.

[d] Reference 26.

[e] Reference 3.

Table VI. Vertical Detachment Energies of OH^-

Approximation	ΔE (eV)
Koopmann's theorem	2.929
Second order	-0.184
Third order, V in the denominator	2.061
Simons	1.74[a]
Experiment	1.825[b]

---

[a] W. D. Smith, T. Chen, and J. Simons, "Theoretical Studies of Molecular Ions. Vertical Detachment Energy of OH^-," (to be published.

[b] H. Hotop, T. A. Patterson, and W. C. Lineberger, J. Chem. Phys. 60, 1806 (1974).

APPENDIX

General Mating XVI: A Program to Calculate Formulas from Second Quantized Operators

APPENDIX

General Mating XVI: A computer program to derive formulas from second quantized excitation operators

A. Introduction

The program called general mating XVI will derive formulas through second order in the correlation coefficients, i.e. ϵC^2, TC^2, and VC, from input second quantized excitation operators using Wick's theorem. The program reads in and stores sets of second quantized operators: correlation functions, p-h excitation operator one, and p-h excitation operator two.

It accepts creation or destruction operators in literal or integer form, converts them to three new sets of integers, one for the printing of input (PROP), one for actual operator input and Wick's theorem manipulation (OP), and one for final data treatment and printout (PAOP). After evaluation the formulas are printed out or optionally written on computer tape in coded form.

Wick's theorem for our purposes here is[1]

$$
\begin{aligned}
\langle HF|ABCD\ldots|HF\rangle &= a_1\langle HF|AB|HF\rangle\langle HF|CD|HF\rangle\ldots \\
&+a_2\langle HF|AC|HF\rangle\langle HF|BD|HF\rangle\ldots+a_3\langle HF|AD|HF\rangle\langle HF|BC|HF\rangle\ldots \\
&+\ldots \qquad (1)
\end{aligned}
$$

where ABCD... are creation and destruction operators, $|HF\rangle$ is a single determinant Hartree-Fock ground state, and a_n is a real phase factor. $<HF|AB|HF>$ is called a contraction. a_n is determined by the number of permutations required to rearrange ABCD . . . so that contracted pairs are adjacent, e.g. a_2 in (1) is -1 and a_3 is $+1$ provided there is no further rearrangement of creation and destruction operators after the first tour.

Program limitations are as follows.

(a) Possible ground states include the closed shell, $|(\text{closed shell})\,\Omega\alpha>$, $|(\text{closed shell})\,\Omega_1\alpha\Omega_2\alpha>$, and $k_1\,|(\text{closed shell})\,\Omega_1\alpha\Omega_1\beta>$ $+\,k_2\,|(\text{closed shell})\,\Omega_2\alpha\Omega_2\beta>$ where Ω, Ω_1, and Ω_2 are open shell molecular orbitals.

(b) The ground state may be adjusted to another spin projection or spin including multideterminants by the use of a program option which can change the spin component and occupation number of the open shell orbitals.

(c) The open shell molecular orbitals must be obtained from the OCBSE method of Hunt, Dunning, and Goddard[2] with the virtual (particle) orbitals eigenfunctions of the last open shell Fock operator.

(d) Possible operators are

1. $\hat{\mathcal{H}}$ where

$$\mathcal{H}_c = \sum_{ij} \left[\epsilon_i \delta_{ij} - \tfrac{1}{2} \sum_p V_{ippj} + \sum_\nu \left(\tfrac{1}{2} V_{i\nu\nu j} - 2\,V_{i\nu j\nu}\right) \right] (c^+_{i\alpha} c_{j\alpha} + c^+_{i\beta} c_{j\beta}) + \tfrac{1}{2} \sum_{ijkl} V_{ijkl} \,(c^+_{i\alpha} c_{k\alpha} c^+_{j\alpha} c_{l\alpha} + c^+_{i\alpha} c_{k\alpha} c^+_{j\beta} c_{l\beta} + c^+_{i\beta} c_{k\beta} c^+_{j\alpha} c_{l\alpha} + c^+_{i\beta} c_{k\beta} c^+_{j\beta} c_{l\beta}) \qquad (2)$$

$$\epsilon_i = h_{ii} + \sum_{\nu} (2 J_{i\nu} - K_{i\nu}) \tag{3}$$

$$\begin{aligned}\mathcal{H}_d = \sum_{ij} [\epsilon_i \delta_{ij} &+ \sum_{\nu} (V_{i\nu\nu j} - 2 V_{i\nu j\nu}) + b\,(\tfrac{1}{2} V_{i\Omega\Omega j} - V_{i\Omega j\Omega}) \\ &- \tfrac{1}{2} \sum_{k} V_{ikkj})\,(c^{+}_{i\alpha} c_{j\alpha} + c^{+}_{i\beta} c_{j\beta}) + \\ &\tfrac{1}{2} \sum_{ijkl} V_{ijkl}\,(c^{+}_{i\alpha} c_{k\alpha} + c^{+}_{i\beta} c_{k\beta})\,(c^{+}_{j\alpha} c_{l\alpha} + c^{+}_{j\beta} c_{l\beta})\end{aligned} \tag{4}$$

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

$$\epsilon_{\gamma} = h_{\gamma\gamma} + \sum_{\nu} (2 J_{\gamma\nu} - K_{\gamma\nu}) + \tfrac{1}{2} (2 J_{\Omega\gamma} - K_{\Omega\gamma}) \tag{5}$$

$$\epsilon_{\Omega} = h_{\Omega\Omega} + \sum_{\nu} (2 J_{\Omega\nu} - K_{\Omega\nu}) \tag{6}$$

$$\epsilon_m = h_{mm} + \sum_{\nu} (2 J_{m\nu} - K_{m\nu}) \tag{7}$$

$$\begin{aligned}\mathcal{H}_t = \sum_{ij} [\epsilon_i \delta_{ij} &+ \sum_{\nu} (V_{i\nu\nu j} - 2 V_{i\nu j\nu}) + \sum_{\Omega} (b\, V_{i\Omega\Omega j} - V_{i\Omega j\Omega}) \\ &- \tfrac{1}{2} \sum_{k} V_{ikkj}]\,(c^{+}_{i\alpha} c_{j\alpha} + c^{+}_{i\beta} c_{j\beta}) \\ &+ \tfrac{1}{2} \sum_{ijkl} V_{ijkl}\,(c^{+}_{i\alpha} c_{k\alpha} + c^{+}_{i\beta} c_{k\beta})\,(c^{+}_{j\alpha} c_{l\alpha} + c^{+}_{j\beta} c_{l\beta})\end{aligned} \tag{8}$$

where b = 1 when i and j are each either open shell or virtual molecular orbitals.

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

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

$$\epsilon_{\gamma} = h_{\gamma\gamma} + \sum_{\nu} (2J_{\gamma\nu} - K_{\gamma\nu}) + \tfrac{1}{2} \sum_{\Omega} (2J_{\Omega\gamma} - K_{\Omega\gamma}) \qquad (9)$$

$$\epsilon_{\Omega} = h_{\Omega\Omega} + \sum_{\nu} (2J_{\nu\Omega} - K_{\nu\Omega}) + \sum_{\underline{\Omega}} (J_{\underline{\Omega}\Omega} - K_{\underline{\Omega}\Omega}) \qquad (10)$$

$$\epsilon_{m} = h_{mm} + \sum_{\nu} (2J_{\nu m} - K_{\nu m}) + \sum_{\Omega} (J_{\Omega m} - K_{\Omega m}) \qquad (11)$$

As usual lower case Greek letters are closed shell holes; Ω, $\underline{\Omega}$, Ω_1, and Ω_2 are open shell orbitals; m, n, p. . . . are particles; and i, j, k, l are any orbital.

$$V_{ijkl} = \int \varphi_i^*(1)\, \varphi_j^*(2)\, \frac{1}{r_{12}}\, \varphi_k(1)\, \varphi_l(2)\, d\tau_1\, d\tau_2 \qquad (12)$$

2. $$\hat{T} = \sum_{ij} T_{ij} (c^+_{i\alpha} c_{j\alpha} + c^+_{i\beta} c_{j\beta}) \qquad (13)$$

3. $$\hat{\epsilon} = \sum_{ij} \epsilon_i \delta_{ij} (c^+_{i\alpha} c_{j\alpha} + c^+_{i\beta} c_{j\beta}) \qquad (14)$$

4. $$\hat{V} = \sum_{ijkl} V_{ijkl} (c^+_{j\alpha} c^+_{i\alpha} c_{k\alpha} c_{l\alpha} + c^+_{j\alpha} c^+_{i\beta} c_{k\beta} c_{l\alpha} + c^+_{j\beta} c^+_{i\alpha} c_{k\alpha} c_{l\beta} + c^+_{j\beta} c^+_{i\beta} c_{k\beta} c_{l\beta}) \qquad (15)$$

5. Unit operator

6. $$C^+_{\lambda} \qquad (16)$$

where C^+_{λ} is a p-h excitation operator composed of several $\mathcal{C}^+_R$'s that may have up to eight creation and destruction operators a row (a string), i. e.

$$C_{\lambda}^{+} = \sum_{R} A_R \mathcal{C}_R^{+} \qquad (17)$$

where A_R is a real number and $\mathcal{C}_R^{+}$ is a string of creation and destruction operators. $\mathcal{C}_R^{+}$ can have at most two creation and destruction operators operating on the hole orbitals and two operating on the particle space. There is no limitation in $\mathcal{C}_R^{+}$ on the number of open shell creation and destruction operators (up to eight).

One operator out of 1-5 above can be chosen and up to two kinds of p-h excitation operators.

B. A brief description of each subroutine

1. MAIN. Main contains the storage array BIGOT for variable dimensioning. In this subroutine the title for the run is read in and program options and limits are read in or set by default. Subroutines READIN and DOIT are called. The last card in the data deck is read and specifies whether the current data are to be analyzed and if more data follows.

2. BLOCK DATA. Block data defines the ON and NO matrices, where NO contains the literal values corresponding to PROP integers and ON contains the literal values corresponding to PAOP integers.

3. READIN. In READIN the operators are read in and stored. First any changes in the M_S value of the ground state or MCRPA[3], then the ket correlation function, the first p-h excitation operator, and finally the last p-h excitation operator.

4. DOIT. In DOIT each formula for input p-h excitation

operators is expanded for calculation. That is, each p-h operator is expanded in terms of $\mathcal{C}_R$'s (see equation (17)). Correlation functions and any change in M_S value of the ground state are expanded in terms of creation and destruction operators. Subroutines SETUP, EFORM and PUNWRT are called.

5. SETUP. SETUP expands any commutors, locates the positions of i, j, k, and l, and processes matrices to pass to WICKET.

6. WICKET. WICKET expands matrices M and MM passed to it from SETUP by Wick's theorem. TV is called.

7. TV. Subroutine TV processes data from WICKET in terms of p-h operators, operators (1-5) above, or correlation functions. TFORM or VFORM may be called. SYM may also be called.

8. TFORM. Subroutine TFORM stores resulting one-body formulas in submatrices according to the Kronecker delta functions which are in the formula. TFORM may call SYM and PUNWRT.

9. VFORM. Subroutine VFORM stores resulting two-body formulas in submatrices according to the Kronecker delta functions which are in the formula. VFORM may call PUNWRT.

10. EFORM. EFORM expands one-body formulas in terms of orbital energies and two-body interaction matrix elements. VFORM is called.

11. SYM. Subroutine SYM takes care of any symmetry in the correlation function.

12. PUNWRT. Subroutine PUNWRT writes out the matrices ETIMS, EN, EC, and ED from subroutines TFORM and EFORM and

matrices VTIMS, V, C, and VD from subroutine VFORM. These are the resulting formulas if PUNWRT is called from the appropriate place in subroutine DOIT. The formulas may be written out on both printed output and tape.

References

1. D. J. Rowe, Nuclear Collective Motion, Models and Theory, (Methuen and Co. Ltd., London, 1970).
2. W. J. Hunt, T. H. Dunning, and W. A. Goddard, Chem. Phys. Lett. **3**, 606 (1969); W. A. Goddard, T. H. Dunning, and W. J. Hunt, Chem. Phys. Lett. **4**, 231 (1969); W. J. Hunt, W. A. Goddard, and T. H. Dunning, Chem. Phys. Lett. **6**, 147 (1970).
3. D. L. Yeager, Ph.D. Thesis, California Institute of Technology, 1975.

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C GENERAL MATING XVI
C PROGRAM TO CALCULATE TDA, RPA, HRPA, AND EOM FORMULAS.
C CURRENT LIMITATIONS ARE THROUGH SECOND ORDER IN V FOR SINGLE EXCITA-
C TION MATRIX ELEMENTS AND VC FOR DOUBLE EXCITATION (NO EC**2).
C EVENTUALLY THIS PROGRAM WILL BE ABLE TO DO SECOND ORDER IN C FOR BOTH
C SINGLES AND DOUBLES.
C OPTIONS WHICH CANNOT BE CURRENTLY USED ARE:XH XPAND NOC WHEN IDX.NE.0
C CONTAINS THE OPTION TO GHANGE TO AN ARBITRARY MS OS GS.
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 NAMGS,PREFAC,THEEND,COMP(5)
      INTEGER*2 OPORD(4),HTE(3)
      COMMON/CASCA/IDX
      COMMON/BANQUO/CHMS
      COMMON/LIMITS/STAG,STOG,STAM,STOM,STAI,STOI,STAJ,STOJ,STAK,STOK,ST
     ?AL,STOL,ILIMT,LCLR,UCLR,MINICC,MAXICC
      COMMON/ALBANY/CO1,CO3,CO4,O1,O3,O4
      COMMON/DUKE/IPRINT
      COMMON/RICH/NEQ
      COMMON/HOST/CORY
      COMMON/SPEED/GS
      COMMON/LEAR/PMFAC,CTAPE,ENGL, GSEND,ISHOW,              JTAPE
      COMMON/FRANCE/ISTAT,JSTAT,ISTOP,JSTOP,ILF,IRF
      COMMON/ANTONY/ETH
      COMMON/BRUTJS/Q(4,6),NAC(6),DAC(6),AQ,IOT
      COMMON /TOM/ NOSP
      DIMENSION QQ(4,6),DDAC(6),DDDAC(6)
C BIGOT MUST BE DIMENSIONED CORY*252+(NTY(1)+NTY(2))*121+28
      DIMENSION MARK(26),BIGOT(8000)
      DIMENSION NAMGS(6),TITLE(20),G(3),LIMM(6),NTY(2),LIMG(4)
      DATA LIMM/1,1,1,2,6,6/
      DATA LIMG/0,2,2,6/
      DATA COMP/8HTHE END ,8HREPEAT  ,8HOLD CORR,8HDUMP    ,8HLIMITS  /
      DATA NAMGS/'CLOSED S','HELL    ','OPEN SHE','LL A    ','OPEN SHE',
     X'LL AA   '/
      DATA G/2,3,4/
      DATA OPORD/'  ',' A',' C',' B'/
      DATA QQ/2,4,3,1,4,2,3,1,2,3,4,1,3,2,4,1,3,4,2,1,4,3,2,1/
      DATA DDAC/1,-2,-2,-2,1,-2/
      DATA DDDAC/1,-2,-2,2,-1,2/
      DATA HTE/'E ','T ','H '/
      THEEND=COMP(1)
      CCORY=0
    1 READ(5,2000)TITLE
      CO1=1
      CO3=1
      CO4=1
      STAG=1
      STOG=6
      STAM=1
      STOM=6
      STAI=1
      STOI=0
      STAJ=1
      STOJ=0
      STAK=1
      STOK=0
      STAL=1
      STOL=0
      LCLR=1
      UCLR=3
      IOT=0
      IRF=0
```

```
      ILF=0
      READ(5,2010)GS,NDCY,PMFAC,IPRINT,JTAPE,CTAPE,ISHOW,CORY,ILIMT,ETH,
     ?ENGL,IBIT,IDX,CHMS,NEQ,NOSP
      IF(IDX.NE.0)UCLR=2
C NDCY=0 NO A,B,AND C
C NDCY=1 READ IN A,B,AND C POSITIONS
C NDCY=2 AC-CA
C NDCY=3 AB-BA
C NDCY=4 SYMMETRIC DOUBLE COMMUTATOR
C NDCY=5 SYMMETRIC DOUBLE ANTICOMMUTATOR
C ETH=-1 NO OPERATOR
C ETH=0 E
C ETH=1 T
C ETH=2 H
C GS=1 OR 0 CLOSED SHELL
C GS=2 OPEN SHELL RESTRICTED HF A GS
C GS=3 OPEN SHELL RESTRICTED HF AA GS
C IDX.GT.0  DOUBLE EXCITATION MATRIX ELEMENTS.INEQUALITY RESTRICTION.
C IDX.LT.0  DOUBLE EXCITATION MATRIX ELEMENTS.NO INEQUALITY RESTRICTION.
C CHMS.NE.0 READ IN CHANGE IN GROUND STATE
C CHMS.LT.0  CORRELATED GS
C CHMS.EQ.-10 CORRELATED GS WITH INDIVIDUAL FUNCTIONS PRINTED OUT.
C NEQ.NE.0 CALCULATE ON DIAGONAL FORMULAS ONLY
C NOSP.NE.0 CHANGE COEFFICIENT OF ONE BODY-V(I,NU,J,NU) TERM
      IF(NDCY.EQ.0)STOM=1
      IF(ETH.LT.2)STOG=2
      IF(NDCY.LT.2)GO TO 14
      IF(3-NDCY)4,7,11
    4 DO 6 J=1,6
      NAC(J)=1
      DAC(J)=DDAC(J)
      IF(NDCY.EQ.5)DAC(J)=DDDAC(J)
      DO 5 I=1,4
    5 Q(I,J)=QQ(I,J)
    6 CONTINUE
      AQ=3
      STOM=6
      IOT=1
      IRF=1
      ILF=1
      GO TO 14
    7 NAC(1)=1
      NAC(2)=-1
      DAC(1)=1
      DAC(2)=1
      Q(1,1)=2
      Q(2,1)=4
      Q(3,1)=1
      Q(1,2)=4
      Q(2,2)=2
      Q(3,2)=1
      AQ=2
      STOM=2
      IOT=1
      ILF=1
      GO TO 14
   11 NAC(1)=1
      DAC(1)=1
      NAC(2)=-1
      DAC(2)=1
      Q(1,1)=2
      Q(2,1)=3
```

```
      Q(3,1)=1
      Q(1,2)=3
      Q(2,2)=2
      Q(3,2)=1
      AQ=2
      STOM=2
      ILF=1
      IRF=1
   14 IF(CTAPE.EQ.0)CTAPE=JTAPE
      CORE=CORY
      IF(CORY.LT.0)CORE=0
      IF(CORY.LT.0)CORY=CCORY
      CCORY=CORY
      CO1=1
      CO3=1
      CO4=1
      IF(CORY.EQ.0)GO TO 15
      CO1=CORY
      CO3=2*CORY+1
      CO4=8*CORY
   15 MARK(1)=1
      MARK(2)=CORY*8+MARK(1)+1
      MARK(3)=CORY*16+MARK(2)+1
      MARK(4)=CORY*2+MARK(3)+2
      MARK(5)=CORY*8+MARK(4)+1
      MARK(6)=CORY*5+MARK(5)+1
      MARK(7)=CORY*64+MARK(6)+1
      MARK(8)=CORY*64+MARK(7)+1
      MARK(9)=CORY*64+MARK(8)+1
      MARK(10)=MARK(9)+16*CORY+1
      MARK(11)=MARK(10)+CORY+1
      MARK(12)=MARK(11)+CORY+1
      MARK(13)=MARK(12)+CORY+1
      MARK(14)=MARK(13)+CORY+1
      MARK(15)=MARK(14)+CORY+1
      MARK(16)=MARK(15)+CORY+1
      MARK(17)=MARK(16)+CORY+1
   20 WRITE(6,2020)TITLE
      IF(IPRINT.NE.6.AND.IPRINT.NE.0)WRITE(IPRINT,2020)TITLE
      IF(JTAPE.GT.2)WRITE(JTAPE)TITLE
      IF(JTAPE.NE.CTAPE.AND.CTAPE.GT.2)WRITE(CTAPE)TITLE
      IF(GS.EQ.0)GS=1
      GSEND=G(GS)
      WRITE(6,2030)NAMGS((GS-1)*2+1),NAMGS((GS-1)*2+2)
      IF(CHMS.LT.0)GSEND=4
      IF(CHMS.LT.0)WRITE(6,2210)
      IF(PMFAC.EQ.0)PMFAC=1
      IF(ISHOW.NE.0)WRITE(6,2040)
      IF(ISHOW.EQ.0.AND.JTAPE.GT.20)WRITE(6,2050)JTAPE
      IF(ISHOW.EQ.0.AND.CORY.NE.0.AND.CTAPE.GT.2)WRITE(6,2060)CORY,CTAPE
      IF(ISHOW.EQ.0.AND.CORY.NE.0.AND.CTAPE.LE.2)WRITE(6,2065)CORY
      IF(CORY.NE.0.AND.CORE.EQ.0)WRITE(6,2070)
      IF(IDX.GT.0)WRITE(6,2190)
      IF(IDX.LT.0)WRITE(6,2195)
      IF(NOSP.NE.0)WRITE(6,2200)NOSP
      PREFAC=PMFAC
      IF(ILIMT.EQ.0.AND.THEEND.NE.COMP(5))GO TO 30
      READ(5,2010)STAG,STOG,STAM,STOM,STAI,STOI,STAJ,STOJ,STAK,STOK,STAL
     ?,STOL,LCLR,UCLR,MINICC,MAXICC
      IF(STAG.EQ.0)STAG=1
      IF(STOG.EQ.0)STOG=LIMG(ETH+2)
      IF(STAM.EQ.0)STAM=1
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      IF(STOM.EQ.0)STOM=LIMM(NDCY+1)
      IF(STAI.EQ.0)STAI=1
      IF(STAJ.EQ.0)STAJ=1
      IF(STAK.EQ.0)STAK=1
      IF(STAL.EQ.0)STAL=1
      IF(LCLR.EQ.0)LCLR=1
      IF(UCLR.EQ.0.AND.IDX.NE.0)UCLR=2
      IF(UCLR.EQ.0)UCLR=3
   30 IF(STOI.EQ.0)STOI=GSEND
      IF(STOJ.EQ.0)STOJ=GSEND
      IF(STOK.EQ.0)STOK=GSEND
      IF(STOL.EQ.0)STOL=GSEND
      IF(NDCY.NE.1)GO TO 38
      ICT=0
      IRF=0
      ILF=0
      READ(5,2110)Q
      DO 35 J=1,6
      STOM=J-1
      DO 31 I=1,4
      QA=I-1
      IF(Q(I,J).EQ.0)Q(I,J)=1
      IF(Q(I,J).EQ.1)GO TO 32
   31 CONTINUE
   32 CONTINUE
      IF(J.NE.1)GO TO 34
      AQ=QA
      DO 33 I=1,QA
      IF(Q(I,J).EQ.2)ILF=1
      IF(Q(I,J).EQ.3)IRF=1
      IF(Q(I,J).EQ.4)IOT=1
   33 CONTINUE
   34 CONTINUE
      IF(AQ.NE.QA)GO TO 36
   35 STOM=STOM+1
   36 READ(5,2010)NAC
      READ(5,2010)DAC
      IF(IOT.EQ.0)WRITE(6,2120)
      IF(ETH.GE.0)WRITE(6,2125)HTE(ETH+1)
      DO 37 I=1,STOM
   37 WRITE(6,2130)NAC(I),DAC(I),(OPORD(Q(J,I)),J=1,AQ)
   38 CONTINUE
      IF(IOT.EQ.0)ETH=-1
      IF(IOT.EQ.0)STOG=0
      IF(NDCY.EQ.0)WRITE(6,2140)
      IF(NDCY.EQ.2)WRITE(6,2150)
      IF(NDCY.EQ.3)WRITE(6,2160)HTE(ETH+1)
      IF(NDCY.EQ.4)WRITE(6,2170)HTE(ETH+1)
      IF(NDCY.EQ.5)WRITE(6,2180)HTE(ETH+1)
      WRITE(6,2025)PREFAC
      IF(THEEND.EQ.COMP(5).OR.ILIMT.NE.0)  WRITE(6,2100)STAG,STOG,STAM,S
     ?TOM,STAI,STOI,STAJ,STOJ,STAK,STOK,STAL,STOL,LCLR,UCLR ,MINICC,MAXI
     ?CC
      IF(IPRINT.NE.0       .AND.IPRINT.NE.6)WRITE(6,2100)STAG,STOG,STAM,S
     ?TOM,STAI,STOI,STAJ,STOJ,STAK,STOK,STAL,STOL,LCLR,UCLR ,MINICC,MAXI
     ?CC
      IF(THEEND.EQ.COMP(5))GO TO 39
      IF(IBIT.EQ.0)READ(5,2010)NTY(1),NTY(2)
      IILF=ILF
      ISTAT=1
      ISTOP=NTY(1)
      JSTAT=ISTOP+1
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```
      JSTOP=ISTOP+NTY(2)
      IF(NTY(2).EQ.0)JSTOP=ISTOP+NTY(1)
      01=NTY(1)+NTY(2)
      IF(ILF.NE.0.AND.IRF.NE.0.AND.NTY(2).EQ.0)01=2*NTY(1)
      IF(IBIT.NE.0)ILF=0
      03=01+1
      04=4*01
      MARK(18)=MARK(17)+01*2+1
      MARK(19)=MARK(18)+04*2+1
      MARK(20)=MARK(19)+04+1
      MARK(21)=MARK(20)+01+2
      MARK(22)=MARK(21)+01*5+1
      MARK(23)=MARK(22)+04*8+1
      MARK(24)=MARK(23)+04*8+1
      MARK(25)=MARK(24)+04*8+1
      MARK(26)=MARK(25)+04+1
      CALL READIN(CORE,BIGOT(MARK(1)),BIGOT(MARK(2)),BIGOT(MARK(3)),BIGO
     ?T(MARK(4)),BIGOT(MARK(5)),BIGOT(MARK(6)),BIGOT(MARK(7)),BIGOT(MARK
     ?(8)),BIGOT(MARK(9)),BIGOT(MARK(10)),BIGOT(MARK(11)),BIGOT(MARK(12)
     ?),BIGOT(MARK(13)),BIGOT(MARK(14)),BIGOT(MARK(15)),BIGOT(MARK(16)),
     ?BIGOT(MARK(17)),BIGOT(MARK(18)),BIGOT(MARK(19)),BIGOT(MARK(20)),
     ?BIGOT(MARK(21)),BIGOT(MARK(22)),BIGOT(MARK(23)),BIGOT(MARK(24)),
     ?BIGOT(MARK(25)),BIGOT(MARK(26)))
      ILF=IILF
      IF(NTY(2).EQ.0)JSTOP=ISTOP
   39 READ(5,2080)THEEND
      DO 40 I=1,5
      IF(THEEND.EQ.COMP(I))GO TO 45
   40 CONTINUE
      GO TO 50
   45 CONTINUE
C CONT=0 TAPE CONTAINS ONLY ZERO ORDER
C CONT=1 TAPE CONTAINS ONLY ZERO AND FIRST
C CONT=2 TAPE CONTAINS ONLY ZERO AND SECOND
C CONT=3 TAPE CONTAINS ONLY ZERO THRU SECOND
C CONT=-CONT.EXCLUDE ZERO ORDER
      IF(LCLR.NE.3.AND.UCLR.EQ.2) CONT=1
      IF(LCLR.EQ.3.AND.UCLR.EQ.3) CONT=2
      IF(LCLR.NE.3.AND.UCLR.EQ.3) CONT=3
      IF(CORY.EQ.0) CONT=0
      DONT=-CONT
      IF(CTAPE.EQ.JTAPE)CONT=0
      IF(JTAPE.GT.2)WRITE(JTAPE)GS,NDCY,ETH,ILF,IRF,IOT,NTY(1),NTY(2),CO
     ?RY,CONT,IDX
      IF(CTAPE.NE.JTAPE.AND.CTAPE.GT.2)WRITE(CTAPE)GS,NDCY,ETH,ILF,IRF,I
     ?OT,NTY(1),NTY(2),CORY,DONT,IDX
      IF(CTAPE.GT.2.AND.CORY.NE.0)WRITE(CTAPE)(BIGOT(MARK(15)+KQ-1) ,
     ?BIGOT(MARK(16)+KQ-1),KQ=1,CORY)
      CALL DOIT(BIGOT(MARK(1)),BIGOT(MARK(2)),BIGOT(MARK(3)),BIGOT(MARK(
     ?4)),BIGOT(MARK(5)),BIGOT(MARK(6)),BIGOT(MARK(7)),BIGOT(MARK(8)),BI
     ?GOT(MARK(9)), BIGOT(MARK(10)),BIGOT(MARK(11)),BIGOT(MARK(12)),BIGO
     ?T(MARK(13)),BIGOT(MARK(14)),BIGOT(MARK(15)),BIGOT(MARK(16)),BIGOT(
     ?MARK(17)),BIGOT(MARK(18)),BIGOT(MARK(19)),BIGOT(MARK(20)),
     ?BIGOT(MARK(21)),BIGOT(MARK(22)),BIGOT(MARK(23)),BIGOT(MARK(24)),
     ?BIGOT(MARK(25)),BIGOT(MARK(26)))
      IF(JTAPE.GT.2)END FILE JTAPE
      IF(CTAPE.NE.JTAPE.AND.CTAPE.GT.2)END FILE CTAPE
      IF(THEEND.EQ.COMP(1))STOP
      IF(THEEND.EQ.COMP(2))GO TO 1
      IF(THEEND.EQ.COMP(4))CALL UABEND(99)
      CORE=0
      IF(THEEND.EQ.COMP(3).OR.THEEND.EQ.COMP(5))GO TO 20
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   50 WRITE(6,2090)THEEND
      STOP 1
 2000 FORMAT(20A4)
 2010 FORMAT(16(2X,I3))
 2020 FCRMAT(1H1,20A4)
 2025 FORMAT(1H0,' THE PREFACTOR IS ',F12.8)
 2030 FORMAT(///,1H0,' THE GROUND STATE IS ',3A8)
 2040 FORMAT(1H0,' THIS IS A NONCALCULATING RUN')
 2050 FORMAT(1H0,' THE FORMULAS ARE OUTPUT ON UNIT ',I2)
 2060 FORMAT(1H0,' THERE ARE ',I3,' CORRELATION FUNCTIONS WITH FORMULAS
     XWRITTEN ON UNIT' ,16(1X,I2))
 2065 FORMAT(1H0,' THERE ARE ',I3,' CORRELATION FUNCTIONS.')
 2070 FCRMAT(1H0,' THE CORRELATION FUNCTIONS ARE THE SAME AS THE PREVIOU
     ?S CALCULATION.')
 2080 FORMAT(A8)
 2090 FCRMAT(1H0,' THEEND IS ',A8 ,'.THIS IS NOT VALID.')
 2100 FORMAT(1H0,' STAG=',I2,' STOG=',I2,' STAM=',I2,' STOM=',I2,' STAI=
     ?',I2,' STOI=',I2,' STAJ=',I2,' STOJ=',I2,' STAK=',I2,' STOK=',I2,'
     ? STAL=',I2,' STOL=',I2,' LCLR=',I2,' UCLR=',I2,/40X,' MINICC=',I2,
     ?' MAXICC=',I2)
 2110 FOFMAT(6(4(1X,I1),2X))
 2120 FORMAT(1H0,' MATRIX ELEMENTS ARE EVALUATED FOR THE FOLLOWING ORDER
     ?ING.A=FIRST OPERATOR.',                          'C=SECOND OPERATOR.
     ?'/)
 2125 FORMAT(1H0,' MATRIX ELEMENTS ARE EVALUATED FOR THE FOLLOWING ORDER
     ?ING.A=FIRST OPERATOR.B=',A2,                     '.C=SECOND OPERATOR.
     ?'/)
 2130 FORMAT(1H ,20X,I3,' /',I3,6X,3(A2,2X))
 2140 FORMAT(1H0,' NO A,B,AND C')
 2150 FORMAT(1H0,'  A C-C A')
 2160 FORMAT(1H0,' COMMUTATOR B=',A2)
 2170 FORMAT(1H0,' SYMMETRIC DOUBLE COMMUTATOR B=',A2)
 2180 FORMAT(1H0,' SYMMETRIC DOUBLE ANTICOMMUTATOR B=',A2)
 2190 FORMAT(1H0,' DOUBLE EXCITATION MATRIX ELEMENTS.INEQUALITY RESTRICT
     ?ION.')
 2195 FORMAT(1H0,' DOUBLE EXCITATION MATRIX ELEMENTS.NO INEQUALITY RESTR
     ?ICTION.')
 2200 FORMAT(1H0,' NOSP=',I2)
 2210 FORMAT(1H0,' CORRELATED GROUND STATE.K1(O1AO1B)+K2(O2AO2B).')
      END
      BLOCK DATA
      IMPLICIT INTEGER(A-H,O-Z)
      COMMCN/PRINCE/ON(23)
      COMMON/SILVIA/NO(200)
      DIMENSION A(25)
      EQUIVALENCE (A(1),NO(176))
      DATA ON/' H1 ',' H2 ',' H5 ',' H6 ',' H7 ',' H8 ',' MU ',' NU ','
     ?P1 ',' P2 ',' P5 ',' P6 ',' P7 ',' P8 ','  M ','  N ',' O1 ',' O2
     ?',' H3 ',' H4 ',' P3 ',' P4 ','    '/
      DATA A/'O2B-','O2A-','O1B-','O1A-','P4B-','P4A-','P3B-','P3A-'
     ?,'H4B-','H4A-','H3B-','H3A-','    ','H3A+','H3B+','H4A+','H4B+'
     ?,'P3A+','P3B+','P4A+','P4B+','O1A+','O1B+','O2A+','O2B+'/
      DATA NO/'O2B-','O2A-','O1B-','O1A-','P2B-','P2A-','P1B-','P1A-','H
     X2B-','H2A-','H1B-','H1A-','    ','H1A+','H1B+','H2A+','H2B+','P1A+
     X','P1B+','P2A+','P2B+','O1A+','O1B+','O2A+','O2B+','O2B-','O2A-','
     XO1B-','O1A-','P6B-','P6A-','P5B-','P5A-','H6B-','H6A-','H5B-','H5A
     X-','    ','H5A+','H5B+','H6A+','H6B+','P5A+','P5B+','P6A+','P6B+',
     X'O1A+','O1B+','O2A+','O2B+','O2B-','O2A-','O1B-','O1A-','P8B-','P8
     XA-','P7B-','P7A-','H8B-','H8A-','H7B-','H7A-','    ','H7A+','H7B+'
     X,'H8A+','H8B+','P7A+','P7B+','P8A+','P8B+','O1A+','O1B+','O2A+','O
     X2B+','O2B-','O2A-','O1B-','O1A-','    ','    ',' MB-',' MA-','
     X','    ','MUB-','MUA-','    ','MUA+','MUB+','    ','    ',' MA+',
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     X' MB+','    ','    ','O1A+','O1B+','O2A+','O2B+','O2B-','O2A-','O1
     XB-','C1A-','    ','    ',' NB-',' NA-','    ','    ','NUB-','NUA-'
     X,'    ','NUA+','NUB+','    ','    ',' NA+',' NB+','    ','    ','O
     X1A+','O1B+','O2A+','O2B+','O2B-','O2A-','O1B-','O1A-','    ','
     X',' PB-',' PA-','    ','    ','PIB-','PIA-','    ','PIA+','PIB+','
     X    ','    ',' PA+',' PB+',
     X'    ','    ','O1A+','O1B+','O2A+','O2B+','O2B-','O2A-','O1B-','O1
     XA-','    ','    ',' QB-',' QA-','    ','    ','XIB-','XIA-','    '
     X,'XIA+','XIB+','    ','    ',' QA+',' QB+','    ','    ','O1A+','O
     X1B+','O2A+','O2B+'/
      END
      SUBROUTINE READIN(CORE,PREC,CFAC,JSC,NCOP,TITLEC,COP,PAC,PRC,CAR,T
     ?OC,CHS,CPS,HHPP,INOC,PSUM,HSUM,PRE,FAC,NOP,JST,TITLE1,OP,PAOP,PROP
     ?,LR,BUGGY)
C SUBROUTINE TO READ IN AND STORE THE CORRELATION FUNCTION AND OPERATORS
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 PREC,CFAC,PRE,FAC,MSPRE,HFAC
      COMMON/CASCA/IDX
      COMMON/MACB/MSPRE,HFAC(2),CHOP(2,4),DHOP(2,4),MMSS(2),PACHP(2,4),
     ?PADHP(2,4),PRCHP(2,4),PRDHP(2,4),LMS,BMS,BBMS,NMS
      COMMON/BANQUO/CHMS
      COMMON/PRINCE/ON(23)
      COMMON/SILVIA/NO(200)
      COMMON/ALBANY/CO1,CO3,CO4,O1,O3,O4
      COMMON/LEAR/PMFAC,CTAPE,ENGL, GSEND,ISHOW,              JTAPE
      COMMON/FRANCE/ISTAT,JSTAT,ISTOP,JSTOP,ILF,IRF
      DIMENSION          CFAC(CO4),JSC(CO3),NCOP(CO4),TITLEC(CO1,5),COP
     ?(CO4,8),PAC(CO4,8),PRC(CO4,8),            TOC(CO1),CHS(CO1),CPS(CO1
     ?),PREC(CO1,4),CAR(CO1,4,4),HHPP(CO1),INOC(CO1),PSUM(CO1),HSUM(CO1)
      DIMENSION PRE(O1),FAC(O4),NOP(O4),JST(O3),TITLE1(O1,5),OP(O4,8),PA
     ?OP(O4,8),PROP(O4,8),LR(O4),BUGGY(O1)
      DIMENSION RLCH(25)
      DIMENSION        LRCH(25),PA(12,3),C(4),CEN2(8),ENG1(6)
      DATA ENG1/'H1  ','H2  ','P1  ','P2  ','O1  ','O2  '/
      DATA PA/3,3,4,4,11,11,12,12,17,17,18,18,1,1,2,2,9,9,10,10,17,17,18
     ?,18,2,2,20,20,10,10,22,22,17,17,18,18/
      DATA RLCH/0,0,0,0,1,1,1,1,-1,-1,-1,-1,0,1,1,1,1,-1,-1,-1,-1,0,0,0,
     ?0/
      DATA LRCH/1,-1,1,-1,1,1,1,1,-1,-1,-1,-1,0,1,1,1,1,-1,-1,-1,-1,1,-1
     X,1,-1/
   10 JSC(1)=1
      CT=0
      MSPRE=1.D0
      HFAC(1)=1.D0
      MMSS(1)=0
      NMS=0
      IF(CHMS.EQ.0)GO TO 13
C READ IN NEW GROUND STATE
      READ(5,2010)MSPRE
      IF(MSPRE.EQ.0.D0)MSPRE=1.D0
      WRITE(6,2150)MSPRE
      READ(5,2020)NMS
      IF(NMS.EQ.0)GO TO 13
      DO 1290 I=1,NMS
      DO 1210 J=1,4
      CHOP(I,J)=0
 1210 DHOP(I,J)=0
      IF(ENGL.EQ.0)READ(5,2010)HFAC(I),(CHOP(I,J),J=1,4)
      IF(ENGL.EQ.0)GO TO 1230
      READ(5,2015)HFAC(I),(CEN2(K),K=1,4)
      DO 1220 K=1,4
      DO 1215 L=1,25
```

```
 1215 IF(CEN2(K).EQ.NO(L).AND.L.NE.13)CHOP(I,K)=L-13
 1220 CONTINUE
 1230 IF(HFAC(I).EQ.0.DO)HFAC(I)=1.DO
      BUM=0
      DC 1240 J=1,4
 1240 IF(CHOP(I,J).NE.0)BUM=BUM+1
      MMSS(I)=BUM
      DO 1250 J=1,BUM
      DOPE=CHOP(I,J)
      DHOP(I,J)=-CHOP(I,BUM+1-J)
      PACHP(I,J)=PA(IABS(DOPE),1)
      PRCHP(I,J)=DOPE+13
      DOPE=DHOP(I,J)
      PADHP(I,J)=PA(IABS(DOPE),1)
 1250 PRDHP(I,J)=DOPE+13
      WRITE(6,2060)HFAC(I),(NO(PRCHP(I,J)),J=1,BUM)
 1290 CONTINUE
   13 CONTINUE
      IF(CCPE.EQ.0)GO TO 310
C READ IN CORRELATION
      DO 200 I=1,CORE
      READ(5,2000)(TITLEC(I,J),J=1,5),TOC(I),CHS(I),CPS(I),HHPP(I),INOC(
     ?I),PSUM(I),HSUM(I)
      IF(I.NE.1.AND.TOC(I).EQ.0)TOC(I)=TOC(I-1)+1
      IF(I.EQ.1.AND.TOC(1).EQ.0)TOC(1)=1
      NOC=INOC(I)
      DO 30 L=1,NOC
      IF(ENGL.EQ.0)READ(5,2010)PREC(I,L),C
      IF(ENGL.NE.0)READ(5,2015)PREC(I,L),(CEN2(K),K=1,4)
      DO 20 K=1,4
      IF(ENGL.EQ.0)GO TO 17
      DO 14 J=1,6
      IF(CEN2(K).EQ.ENG1(J))C(K)=2*J-1
   14 IF(CEN2(K).EQ.NO(38))C(K)=0
   17 CONTINUE
      IF(C(K).NE.0)CAR(I,K,L)=PA(IABS(C(K)),1)
      IF(C(K).EQ.0)CAR(I,K,L)=23
   20 CONTINUE
   30 IF(PREC(I,L).EQ.0.DO)PREC(I,L)=1.DO
      READ(5,2020)NUM
      JSC(I+1)=JSC(I)+NUM
      JSTA=JSC(I)
      JSTO=JSC(I+1)-1
      IF(JSTO.GT.C04)STOP 2
      DO 150 J=JSTA,JSTO
      IF(JSTO.LT.JSTA)GO TO 140
      IF(ENGL.EQ.0)READ(5,2010)CFAC(J),(COP(J,K),K=1,8)
      IF(ENGL.EQ.0)GO TO 80
      READ(5,2015)CFAC(J),(CEN2(K),K=1,8)
      DO 60 K=1,8
      COP(J,K)=0
      DO 50 L=26,50
   50 IF(CEN2(K).EQ.NO(L).AND.L.NE.38)COP(J,K)=L-38
   60 CONTINUE
   80 IF(CFAC(J).EQ.0.0)CFAC(J)=1.DO
      BUM=0
      DO 100 K=1,8
      PRC(J,K)=38
  100 IF(COP(J,K).NE.0)BUM=BUM+1
      NCCP(J)=BUM
      DO 120 K=1,BUM
      DOPE=COP(J,K)
```

```
      PAC(J,K)=PA(IABS(DOPE),1)
  120 PRC(J,K)=DOPE+63
  140 CONTINUE
  150 CONTINUE
  200 CONTINUE
      WRITE(6,2030)
      CORED=JSC(CORE+1)-1
C CALCULATE LEFT CORRELATION
      DO 300 I=1,CORE
      NOC=INOC(I)
      IF(TOC(I).NE.CT)WRITE(6,2070)TOC(I)
      CT=TOC(I)
      WRITE(6,2040)I,(TITLEC(I,J),J=1,5),(ON(CAR(I,J,1)),J=1,4),PREC(I,1
     ?)
      IF(NOC.LE.1)GO TO 205
      DO 202 L=2,NOC
  202 WRITE(6,2045)(ON(CAR(I,J,L)),J=1,4),PREC(I,L)
  205 WRITE(6,2050)
      II=CORE+I
      JSC(II+1)=CORED+JSC(I+1)
      JSTA=JSC(II)
      JSTO=JSC(II+1)-1
      IF(JSTO.GT.C04)STOP 2
      DO 280 JJ=JSTA,JSTO
      IF(JSTO.LT.JSTA)GO TO 270
      J=JJ-CORED
      DO 210 JJJ=1,8
  210 PRC(JJ,JJJ)=38
      CFAC(JJ)=CFAC(J)
      BUM=NCOP(J)
      NCOP(JJ)=BUM
      DO 220 K=1,BUM
      DOPE=COP(J,K)
      KK=BUM+1-K
      COP(JJ,KK)=-DOPE
      DOPED=COP(JJ,KK)
      IF(DOPE.EQ.3.OR.DOPE.EQ.4.OR.DOPE.EQ.7.OR.DOPE.EQ.8) COP(J,K)=DOPE
     X-2
      IF(DOPE.EQ.-3.OR.DOPE.EQ.-4.OR.DOPE.EQ.-7.OR.DOPE.EQ.-8)COP(J,K)=D
     XOPE+2
      PAC(JJ,KK)=PA(IABS(DOPED),1)
      PRC(JJ,KK)=COP(JJ,KK)+38
      IF(DOPED.EQ.3.OR.DOPED.EQ.4.OR.DOPED.EQ.7.OR.DOPED.EQ.8)COP(JJ,KK)
     X=DOPED-2
  220 IF(DOPED.EQ.-3.OR.DOPED.EQ.-4.OR.DOPED.EQ.-7.OR.DOPED.EQ.-8)COP(JJ
     X,KK)=DOPED+2
      WRITE(6,2060)CFAC(J),(NO(PRC(JJ,KK)),KK=1, 8 ),(NO(PRC(J,K)),K=1,
     X 8)
      DO 230 K=1,BUM
  230 PRC(J,K)=PRC(J,K)-25
  270 CONTINUE
  280 CONTINUE
      IF(CHS(I).NE.0)WRITE(6,2080)CHS(I)
      IF(CPS(I).NE.0)WRITE(6,2090)CPS(I)
      IF(HHPP(I).NE.0)WRITE(6,2100)HHPP(I)
      IF(PSUM(I).GT.0)WRITE(6,2110)
      IF(PSUM(I).LT.0)WRITE(6,2120)
      IF(HSUM(I).GT.0)WRITE(6,2130)
      IF(HSUM(I).LT.0)WRITE(6,2140)
  300 CONTINUE
  310 ISTA=ISTAT
      ISTO=ISTOP
```

```
      JST(1)=1
      IF(ILF.EQ.0.AND.IRF.EQ.0)RETURN
      IJKSTA=2
      IJKSTO=3
      IF(ILF.EQ.0)IJKSTA=3
      IF(IRF.EQ.0)IJKSTO=2
      IF(ILF.EQ.0)ISTA=JSTAT
      IF(ILF.EQ.0)ISTO=JSTOP
      DO 600 IJK=IJKSTA,IJKSTO
      DO 500 I=ISTA,ISTO
      READ(5,2000)(TITLE1(I,J),J=1,5),BUGGY(I)
      READ(5,2010)PRE(I)
      IF(PRE(I).EQ.0.0)PRE(I)=1.D0
      READ(5,2020)NUM
      JST(I+1)=NUM+JST(I)
      JSTA=JST(I)
      JSTO=JST(I+1)-1
      IF(JSTO.GT.04 )STOP 3
      DO 400 J=JSTA,JSTO
      IF(ENGL.EQ.0)READ(5,2010)FAC(J),(OP(J,K),K=1,8)
      IF(ENGL.EQ.0)GO TO 340
      READ(5,2015)FAC(J),(CEN2(K),K=1,8)
      DO 330 K=1,8
      OP(J,K)=0
      DO 320 L=1,25
  320 IF(CEN2(K).EQ.NO(L).AND.L.NE.13)OP(J,K)=L-13
  330 CONTINUE
  340 IF(FAC(J).EQ.0.0)FAC(J)=1.D0
      BUM=0
      LR(J)=0
      DO 350 K=1,8
  350 IF(OP(J,K).NE.0)BUM=BUM+1
      NOP(J)=BUM
      DO 380 K=1,BUM
      LRLR=0
      DOPE=OP(J,K)
      PAOP(J,K)=PA(IABS(DOPE),IJK)
      PROP(J,K)=DOPE+13
      IF(IDX.EQ.0)GO TO 353
      IF(IJK.EQ.3.AND.PAOP(J,K).EQ.2)PAOP(J,K)=19
      IF(IJK.EQ.3.AND.PAOP(J,K).EQ.10)PAOP(J,K)=21
      IF(IJK.EQ.3)PROP(J,K)=DOPE+188
  353 CONTINUE
      IF(IJK.EQ.2)GO TO 355
      PR=PROP(J,K)
      IF(PR.EQ.7.OR.PR.EQ.8.OR.PR.EQ.11.OR.PR.EQ.12)PROP(J,K)=PR-2
      IF(PR.EQ.14.OR.PR.EQ.15.OR.PR.EQ.18.OR.PR.EQ.19)PROP(J,K)=PR+2
  355 IF(DOPE.EQ.3.OR.DOPE.EQ.4.OR.DOPE.EQ.7.OR.DOPE.EQ.8)OP(J,K)=DOPE-2
      IF(DOPE.EQ.-3.OR.DOPE.EQ.-4.OR.DOPE.EQ.-7.OR.DOPE.EQ.-8)OP(J,K)=OP
     X(J,K)+2
      IF(LR(J).EQ.2)GO TO 370
      LRLR=LRCH(DOPE+13)
      IF(CHMS.NE.0)LRLR=RLCH(DOPE+13)
  360 IF(LR(J).EQ.0)LR(J)=LRLR
      IF(LR(J).NE.LRLR.AND.LRLR.NE.0)LR(J)=2
  370 CONTINUE
  380 CONTINUE
  400 CONTINUE
  500 CONTINUE
      ISTA=JSTAT
  600 ISTO=JSTOP
      RETURN
```

```
 2000 FORMAT(5A4,7(3X,I2))
 2010 FORMAT(F16.8,4X,8(2X,I3))
 2015 FORMAT(F16.8,4X,8(A4,1X))
 2020 FORMAT(16(3X,I2))
 2030 FORMAT(//////,1H0,30X,' THE CORRELATION FUNCTION (SUM OVER H5,H6,H
     ?7,H8,P5,P6,P7,AND P8)'//)
 2040 FORMAT(1H0,I3,1X,5A4,1X,'(',A4,3(',',A4),')',' TIMES ',F12.8)
 2045 FORMAT(1H ,25X,'(',A4,3(',',A4),')',' TIMES ',F12.8)
 2050 FORMAT(1H0,20X,' LEFT FUNCTION',43X,'RIGHT FUNCTION'/)
 2060 FORMAT(1H ,F12.8,15X,8(A4,1X),16X,8(A4,1X))
 2070 FORMAT(1H0,' CORRELATION FUNCTIONS OF TYPE ',I2)
 2080 FORMAT(1H ,30X,' ON EXCHANGE OF INDICES ONE AND TWO THE SYMMETRY I
     ?S ',I2)
 2090 FORMAT(1H ,30X,' ON EXCHANGE OF INDICES THREE AND FOUR THE SYMMETR
     ?Y IS ',I2)
 2100 FORMAT(1H ,30X,' ON EXCHANGE OF INDICIES ONE AND TWO WITH THREE AN
     ?D FOUR THE SYMMETRY IS ',I2)
 2110 FORMAT(1H ,30X,'P4.GT.P3')
 2120 FORMAT(1H ,30X,'P4.GE.P3')
 2130 FORMAT(1H ,30X,'H4.GT.H3')
 2140 FORMAT(1H ,30X,'H4.GE.H3')
 2150 FORMAT(1H0,' CHANGE MS OPERATORS FOLLOW.THE PREFACTOR IS ',F12.8)
      END
      SUBROUTINE DOIT(PREC,CFAC,JSC,NCOP,TITLEC,COP,PAC,PRC,CAR,TOC,CHS,
     ?CPS,HHPP,INOC,PSUM,HSUM,PRE,FAC,NOP,JST,TITLE1,OP,PAOP,PROP,LR,
     ?BUGGY)
C SUBROUTINE TO CYCLE OVER OPERATORS AND CORRELATION FUNCTIONS.
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 PRE,PREFAC,FAC,CFAC,PREC,PREF,P1REF,P2REF,P3REF,P4REF,P5REF
     ?,MSPRE,HFAC
      REAL TTIME
      COMMON/BANQUO/CHMS
      COMMON/ANTONY/ETH
      COMMON/LIMITS/STAG,STOG,STAM,STOM,STAI,STOI,STAJ,STOJ,STAK,STOK,ST
     ?AL,STOL,ILIMT,LCLR,UCLR,MINICC,MAXICC
      COMMON/RICH/NEQ
      COMMON/MACB/MSPRE,HFAC(2),CHOP(2,4),DHOP(2,4),MMSS(2),PACHP(2,4),
     ?PADHP(2,4),PRCHP(2,4),PRDHP(2,4),LMS,BMS,BBMS,NMS
      COMMON/LEAR/PMFAC,CTAPE,ENGL, GSEND,ISHOW,            JTAPE
      COMMON/ALBANY/C01,C03,C04,01,03,04
      COMMON/FRANCE/ISTAT,JSTAT,ISTOP,JSTOP,ILF,IRF
      COMMON/EDMUND/PREF,NMOST,IC,CLR,RLT(5),LRIJK(256),D(44),SN(5)
      COMMON/PUCK/PC,PCC
      COMMON/CURRAN/S(5,8),SS(5,8),SSS(5,8),SLOP(256,4),ROP(256,4)
      COMMON/REGAN/IT,TAPE,CT,ICC,CTT,MSTO,ICHG
      COMMON/DUKE/IPRINT
      COMMON/HOST/CORY
      COMMON/GOBBO/NTU(5),MTU(5)
      COMMON/TUBAL/NEN(5),NEMM(5)
      COMMON/PORTIA/P1REF(8),CC(8),CF(8,4),XP,XH,XHP,NOC,ISY,XXP,XXH,XXH
     ?P,NNOC,MMNN,BB(4)
      COMMON/CASCA/IDX
      COMMON/HAMLET/M(44),MM(44),N(44)
      COMMON/PRINCE/ON(23)
      COMMON/SILVIA/NO(200)
      COMMON/JULIET/HCK,HHCK,PCK,PPCK
      DIMENSION           CFAC(C04),JSC(C03),NCOP(C04),TITLEC(C01,5),COP
     ?(C04,8),PAC(C04,8),PRC(C04,8),              TOC(C01),CHS(C01),CPS(C01
     ?),PREC(C01,4),CAR(C01,4,4),HHPP(C01),INOC(C01),PSUM(C01),HSUM(C01)
      DIMENSION PRE(01),FAC(04),NOP(04),JST(03),TITLE1(01,5),OP(04,8),PA
     ?OP(04,8),PROP(04,8),LR(04),BUGGY(01)
      DIMENSION ITEST(7,12),KIND(4,6),IJOP(4,5),PA(4,2),LRL(4,4),TITB(8)
```

```
   DATA TITB/'    ','    ','    ','    ','    ','    ','    ','    '/
   DATA KIND/3,4,5,5,1,2,5,5,1,1,2,2,1,3,2,4,3,1,4,2,3,3,4,4/
   DATA IJOP/1,5,9,11,-1,-5,-9,-11,2,6,10,12,-2,-6,-10,-12,0,0,0,0/
   DATA PA/7,15,17,18,8,16,17,18/
   DATA LRL/0,-1,0,0,0,1,0,0,0,-1,-1,-1,0,1,1,1/
   IDSTA=1
   BIMS=1
   EIMS=NMS
   BJMS=1
   EJMS=NMS
   SMN=0
   IF(CHMS.EQ.-10)SMN=NMS
   IF(JTAPE.EQ.0)IDSTA=2
   IF(LCLR.EQ.3)IDSTA=CORY+IDSTA
   DORY=2*CORY+1
   IF(UCLR.NE.3)DORY=CORY+1
   XYZ=C
   SSTOG=STOG
10 DO 1000 ICY=ISTAT,ISTOP
   BUG=0
   PREFAC=PMFAC
   JSTA=JSTAT
   JSTO=JSTOP
   IF(JSTO.LT.JSTAT)JSTO=ICY+ISTOP
   IF(NEQ.NE.0)JSTA=ICY+ISTOP
   IF(NEQ.NE.0)JSTO=ICY+ISTOP
   IF(IRF.EQ.0)JSTO=0
   KSTA=1
   KSTO=0
   IF(ISTOP.EQ.0)GO TO 20
   KSTA=JST(ICY)
   KSTO=JST(ICY+1)-1
   BUG=BUGGY(ICY)
   PREFAC=PRE(ICY)*PMFAC
20 DO 960 JCY=JSTA,JSTO
   BEFORE=RTIME(DDDD)
   OTIME=BEFORE
   XYZ=XYZ+1
   IF(JTAPE.GT.2)WRITE(JTAPE)(TITLE1(ICY,K),K=1,5),(TITLE1(JCY,K),K=1
  ?,5),(TITB(K),K=1,8)
   IF(CTAPE.NE.JTAPE.AND.CTAPE.GT.2)WRITE(CTAPE)(TITLE1(ICY,K),K=1,5)
  ?,(TITLE1(JCY,J),J=1,5),(TITB(J),J=1,8)
   LSTA=1
   LSTO=0
   IF(JSTO.EQ.0)GO TO 40
   LSTA=JST(JCY)
   LSTO=JST(JCY+1)-1
   BUG=BUGGY(JCY)
   PREFAC=PRE(JCY)*PMFAC
30 CONTINUE
   IF(ISTOP.EQ.0.OR.JSTO.EQ.0)GO TO 40
   BUG=BUGGY(ICY)*BUGGY(JCY)
   PREFAC=PRE(ICY)*PRE(JCY)*PMFAC
40 CONTINUE
   WRITE(6,2000)XYZ
   IF(IPRINT.NE.6.AND.IPRINT.GT.0)WRITE(IPRINT,2000)XYZ
   IF(ISTOP.EQ.0)GO TO 55
   IF(                 JSTO.NE.0)WRITE(6,2010)(TITLE1(ICY,K),K=1,5),(TI
  ?TLE1(JCY,K),K=1,5)
   IF(JSTO.EQ.0)WRITE(6,2010)(TITLE1(ICY,K),K=1,5)
   WRITE(6,2030)
   WRITE(6,2025)PRE(ICY)
```

```
      DO 50 KCY=KSTA,KSTO
      BUM=NOP(KCY)
      WRITE(6,2040)FAC(KCY),(NO(PROP(KCY,K)),K=1,BUM)
   50 CONTINUE
   55 CONTINUE
      IF(JSTO.EQ.0)GO TO 73
      IF(ISTOP.EQ.0)WRITE(6,2010)(TITLE1(JCY,K),K=1,5)
      WRITE(6,2050)
      WRITE(6,2025)PRE(JCY)
      DO 70 LCY=LSTA,LSTO
      BUM=NOP(LCY)
      WRITE(6,2040)FAC(LCY),(NO(PROP(LCY,K)),K=1,BUM)
   70 CONTINUE
      DO 955 CRIME=1,SMN
      DO 950 KRIME=1,SMN
   73 DO 940 ID=IDSTA,DORY
      IC=ID-ID/(CORY+2)*CORY-1
      IF(ID.EQ.(CORY+1).AND.LCLR.EQ.3)IC=0
      IF(IC.NE.0.AND.MINICC.LT.0.AND.IC.LT.IABS(MINICC))GO TO 935
      IF(LCLR.GT.3.OR.UCLR.GT.3)IC=0
      IF((LCLR.GT.3.OR.UCLR.GT.3).AND.ID.GT.IDSTA)GO TO 935
      RLCL=LCLR
      RLCU=UCLR
      IF(UCLR.EQ.3)RLCU=2
      IF(ID.GT.CORY+1)RLCL=3
      IF(IC.GT.CORY+1)RLCU=3
      IF(IC.EQ.0)RLCL=1
      IF(IC.EQ.0)RLCU=0
      XP=0
      XH=0
      XHP=0
      NOC=0
      DO 75 I=1,4
      DO 74 II=1,4
   74 CF(I,II)=0
   75 CONTINUE
      TAPE=JTAPE
      IF(IC.NE.0)TAPE=CTAPE
      IF(TAPE.LT.0)GO TO 935
      CT=0
      BEG=1
      BEND=1
      P1REF(1)=1.D0
      IF(IC.EQ.0)GO TO 100
      CT=TOC(IC)
      WRITE(6,2065)IC,CT
      IF(IPRINT.NE.6.AND.IPRINT.GT.0)WRITE(IPRINT,2065)IC,CT
  100 CONTINUE
      CCORY=0
      IF(ID.GT.CORY+1)CCORY=IC
      IF(ID.GT.CORY+1.AND.MAXICC.NE.0)CCORY=IABS(MAXICC)
      IF(MAXICC.EQ.-99)CCORY=IC
      YROCC=1
      IF(ID.GT.CORY+1.AND.MINICC.NE.0)YROCC=IABS(MINICC)
      BBEG=1
      BBEND=1
      DO 930 ICC=YROCC,CCORY
      P1REF(5)=1.D0
      XXP=0
      XXH=0
      XXHP=0
      CTT=0
```

```
      NNCC=0
      DO 107 I=1,4
      DO 106 J=4,8
  106 CF(J,I)=0
      NEMM(I)=1
      MTU(I)=1
      NEN(I)=0
  107 NTU(I)=0
      NEN(5)=0
      NEMM(5)=1
      MTU(5)=1
      NTU(5)=0
      IF(ID.LE.CORY+1)GO TO 108
      CTT=TOC(ICC)
      IF(SSTOG.GT.1)STOG=2
      WRITE(6,2067)ICC,CTT
      IF(IPRINT.NE.6.AND.IPRINT.GT.0)WRITE(IPRINT,2067)ICC,CTT
  108 IQ=0
      IF(IPRINT.GT.0)WRITE(IPRINT,2060)
      IF(IPRINT.GT.0)WRITE(IPRINT,2020)
      DO 920 IMS=BIMS,EIMS
      DO 1080 K=1,12
 1080 ITEST(1,K)=0
      BMS=MMSS(IMS)
      IF(BMS.EQ.0)GO TO 1085
      DO 1083 K=1,BMS
      DOPE=DHOP(IMS,K)
      M(K)=DOPE
      SCOPE=IABS(DOPE)
      ITEST(1,SCOPE)=ITEST(1,SCOPE)+DOPE
      MM(K)=M(K)
      N(K)=PADHP(IMS,K)
 1083 O(K)=PRDHP(IMS,K)
 1085 DO 910 JMS=BJMS,EJMS
      IF(CHMS.EQ.-10)WRITE(6,2150)BIMS,BJMS
      P2REF=PREFAC*MSPRE*MSPRE*HFAC(IMS)*HFAC(JMS)
      BBMS=MMSS(JMS)
      LMS=JMS
      DO 1086 K=1,12
 1086 ITEST(2,K)=ITEST(1,K)
      IF(BBMS.EQ.0)GO TO 1090
      DO 1087 K=1,BBMS
      DOPE=CHOP(JMS,K)
      SCOPE=IABS(DOPE)
 1087 ITEST(2,SCOPE)=ITEST(2,SCOPE)+DOPE
 1090 CONTINUE
      DO 900 CLR=RLCL,RLCU
      MSTO=4
      IF(IC.EQ.0)MSTO=0
      IF(CLR.EQ.3)MSTO=8
      ICHG=1
      IF(CLR.EQ.3.AND.IC.EQ.ICC)ICHG=2
      DC=IABS(2-CLR)*CORY
      JLM=1
      IF(CLR.EQ.3.AND.IC.NE.ICC)JLM=2
      IF(CLR.EQ.3.AND.MAXICC.LT.0)JLM=1
      DO 890 MMNN=1,JLM
      ZIC=0
      ZICC=0
      IF(IC.EQ.0)GO TO 113
      BDC=(2-MMNN)*DC+IC
      BBDC=(MMNN-1)*DC+ICC
```

```
    BEG=JSC((2-MMNN)*BDC+(MMNN-1)*BBDC)
    BEND=JSC((2-MMNN)*BDC+(MMNN-1)*BBDC+1)-1
    ZIC=(2-MMNN)*IC+(MMNN-1)*ICC
    XP=CPS(ZIC)
    XH=CHS(ZIC)
    XHP=HHPP(ZIC)
    NOC=INOC(ZIC)
    DO 110 LII=1,NOC
    DO 109 ILL=1,4
109 CF(ILL,LII)=CAR(ZIC,ILL,LII)
110 P1REF(LII)=PREC(ZIC,LII)
    IF(CCORY.EQ.0)GO TO 113
    BBEG=JSC((MMNN-1)*BDC+(2-MMNN)*BBDC)
    BBEND=JSC((MMNN-1)*BDC+(2-MMNN)*BBDC+1)-1
    ZICC=(MMNN-1)*IC+(2-MMNN)*ICC
    XXP=CPS(ZICC)
    XXH=CHS(ZICC)
    XXHP=HHPP(ZICC)
    NNOC=INOC(ZICC)
    DO 112 LII=1,NNOC
    DO 111 ILL=1,4
    LLI=ILL+4
    CF(LLI,LII)=CAR(ZICC,ILL,LII)
    FC=CF(LLI,LII)
111 IF(FC.NE.17.AND.FC.NE.18)CF(LLI,LII)=FC+2
    LIY=LII+4
112 P1REF(LIY)=PREC(ZICC ,LII)
113 PC=ZIC
    PCC=ZICC
    IF(CLR.EQ.2)PC=0
    IF(CLR.EQ.2)PCC=ZIC
    HCK=C
    IF(PC.NE.0)HCK=HSUM(PC)
    PCK=0
    IF(PC.NE.0)PCK=PSUM(PC)
    HHCK=0
    IF(PPC.NE.0)HHCK=HSUM(PPC)
    PPCK=0
    IF(PPC.NE.0)PPCK=PSUM(PPC)
    STOG=SSTOG
    IF(CLR.EQ.3.AND.STOG.GT.1)STOG=2
    DO 880 BE=BEG,BEND
    IF(BEND.LT.BEG)GO TO 870
    DO 114 K=1,12
114 ITEST(3,K)=ITEST(2,K)
    SN(1)=0
    RLT(1)=0
    IF(IC.EQ.0)GO TO 130
    P2REF=PREFAC*CFAC(BE)*MSPRE*MSPRE*HFAC(IMS)*HFAC(JMS)
    BUM=NCOP(BE)
    IF(CLR.EQ.2)GO TO 118
    DO 115 K=1,BUM
    L=K+BMS
    M(L)=COP(BE,K)
    MM(L)=M(L)
    N(L)=PAC(BE,K)
115 O(K)=PRC(BE,K)
118 DO 120 K=1,BUM
    DOPE=COP(BE,K)
    SCOPE=IABS(DOPE)
    ITEST(3,SCOPE)=ITEST(3,SCOPE)+DOPE
    S(1,K)=DOPE
```

```
    SS(1,K)=PAC(BE,K)
120 SSS(1,K)=PRC(BE,K)
    SN(1)=BUM
130 SN(5)=0
    RLT(5)=0
    DO 840 BBE=BBEG,BBEND
    IF(BBEND.LT.BBEG)GO TO 830
    DO 135 K=1,12
135 ITEST(4,K)=ITEST(3,K)
    IF(CLR.NE.3)GO TO 150
    BUM=NCOP(BBE)
    P2REF=PREFAC*CFAC(BE)*CFAC(BBE)*MSPRE*MSPRE*HFAC(IMS)*HFAC(JMS)
    DO 140 K=1,BUM
    DOPE=COP(BBE,K)
    SCOPE=IABS(DOPE)
    ITEST(4,SCOPE)=ITEST(4,SCOPE)+DOPE
    S(5,K)=DOPE
    SS(5,K)=PAC(BBE,K)
    IF(SS(5,K).NE.17.AND.SS(5,K).NE.18)SS(5,K)=SS(5,K)+2
140 SSS(5,K)=PRC(BBE,K)+25
    SN(5)=BUM
150 DO 800 KCY=KSTA,KSTO
    DO 160 K=1,12
160 ITEST(5,K)=ITEST(4,K)
    P3REF=P2REF
    SN(2)=0
    IF(KSTO.EQ.0)GO TO 180
    P3REF=P2REF*FAC(KCY)
    BUM=NOP(KCY)
    DO 170 K=1,BUM
    DOPE=OP(KCY,K)
    SCOPE=IABS(DOPE)
    ITEST(5,SCOPE)=ITEST(5,SCOPE)+DOPE
    S(2,K)=DOPE
    SS(2,K)=PAOP(KCY,K)
170 SSS(2,K)=PROP(KCY,K)
    SN(2)=BUM
    RLT(2)=LR(KCY)
180 DO 700 LCY=LSTA,LSTO
    DO 190 K=1,12
190 ITEST(6,K)=ITEST(5,K)
    P4REF=P3REF
    SN(3)=0
    IF(LSTO.EQ.0)GO TO 255
    P4REF=P3REF*FAC(LCY)
    BUM=NOP(LCY)
    DO 250 K=1,BUM
    DOPE=OP(LCY,K)
    SCOPE=IABS(DOPE)
    ITEST(6,SCOPE)=ITEST(6,SCOPE)+DOPE
    S(3,K)=DOPE
    SS(3,K)=PAOP(LCY,K)
250 SSS(3,K)=PROP(LCY,K)
    SN(3)=BUM
    RLT(3)=LR(LCY)
255 DO 400 GPS=STAG,STOG
    P5REF=P4REF
    IF(GPS.EQ.5.AND.ILIMT.EQ.0)GO TO 390
    IF(GPS.GT.2)P5REF=P4REF/2
    IF(GPS.EQ.4.AND.ILIMT.EQ.0)P5REF=P4REF
    NMOST=0
    KLEND=STOK
```

```
      IF(GPS.LE.2)KLEND=1
      LKEND=STOL
      IF(GPS.LE.2)LKEND=1
      SN(4)=0
      PREF=P5REF
      IF(STOG.NE.0)GO TO 258
      DO 257 K=1,12
      IF(ITEST(6,K).NE.0)GO TO 390
  257 CONTINUE
      GO TO 381
  258 CONTINUE
      DO 260 K=1,12
  260 ITEST(7,K)=ITEST(6,K)
      ISER=KIND(1,GPS)
      JSER=KIND(2,GPS)
      KSER=KIND(3,GPS)
      LSER=KIND(4,GPS)
      DO 380 I=STAI,STOI
      IDOPE=IJOP(I,ISER)
      ISCOPE=MAX0(IABS(IDOPE),1)
      ITEST(7,ISCOPE)=ITEST(7,ISCOPE)+IDOPE
      IROPE=PA(I,1)
      DO 360 J=STAJ,STOJ
      JDOPE=IJOP(J,JSER)
      JROPE=PA(J,2)
      JSCOPE=MAX0(IABS(JDOPE),1)
      ITEST(7,JSCOPE)=ITEST(7,JSCOPE)+JDOPE
      DO 340 K=STAK,KLEND
      KDOPE=IJOP(K,KSER)
      KROPE=PA(K,1)
      KSCOPE=MAX0(IABS(KDOPE),1)
      ITEST(7,KSCOPE)=ITEST(7,KSCOPE)+KDOPE
  270 DO 320 L=STAL,LKEND
      LDOPE=IJOP(L,LSER)
      LROPE=PA(L,2)
      LSCOPE=MAX0(IABS(LDOPE),1)
      ITEST(7,LSCOPE)=ITEST(7,LSCOPE)+LDOPE
      DO 300 KLKK=1,12
      IF(ITEST(7,KLKK).NE.0)GO TO 310
  300 CONTINUE
      PREF=P5REF
      NMOST=NMOST+1
      SLOP(NMOST,1)=IDOPE
      SLOP(NMOST,2)=JDOPE
      SLOP(NMOST,3)=KDOPE
      IF(GPS.GT.2)SLOP(NMOST,2)=KDOPE
      IF(GPS.GT.2)SLOP(NMOST,3)=JDOPE
      SLOP(NMOST,4)=LDOPE
      ROP(NMOST,1)=IROPE
      ROP(NMOST,2)=JROPE
      ROP(NMOST,3)=KROPE
      IF(GPS.GT.2)ROP(NMOST,2)=KROPE
      IF(GPS.GT.2)ROP(NMOST,3)=JROPE
      ROP(NMOST,4)=LROPE
      LRIJK(NMOST)=0
      IF(I.LE.2.OR.CHMS.EQ.0)LRIJK(NMOST)=LRL(I,ISER)
      RR=0
      IF(GPS.LT.3.AND.(J.LE.2.OR.CHMS.EQ.0))RR=LRL(J,JSER)
      IF(GPS.GT.2.AND.(L.LE.2.OR.CHMS.EQ.0))RR=LRL(L,LSER)
      IF(LRIJK(NMOST).EQ.0)LRIJK(NMOST)=RR
      IF(RR.EQ.1.AND.LRIJK(NMOST).EQ.-1)LRIJK(NMOST)=2
  310 CONTINUE
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```
 320 ITEST(7,LSCOPE)=ITEST(7,LSCOPE)-LDOPE
 340 ITEST(7,KSCOPE)=ITEST(7,KSCOPE)-KDOPE
 360 ITEST(7,JSCOPE)=ITEST(7,JSCOPE)-JDOPE
 380 ITEST(7,ISCOPE)=ITEST(7,ISCOPE)-IDOPE
     IF(NMOST.EQ.0)GO TO 390
 381 CONTINUE
     IF(IPRINT.LE.0)GO TO 385
     QI=1
     IF(GPS.GT.2)QI=2
     IF(QI.EQ.1.AND.QI.NE.IQ)WRITE(IPRINT,2120)
     IF(QI.EQ.2.AND.QI.NE.IQ)WRITE(IPRINT,2130)
     IQ=QI
 385 CALL SETUP
     IF(BUG.EQ.0.OR.IPRINT.LE.0)GO TO 390
     JPR=IPRINT
     CALL PUNWRT(JPR,1,5,0)
     IF(IT.EQ.0)WRITE(IPRINT,2110)
 390 CONTINUE
 400 CONTINUE
 700 CONTINUE
 800 CONTINUE
 830 CONTINUE
 840 CONTINUE
 870 CONTINUE
 880 CONTINUE
 890 CONTINUE
 900 CONTINUE
 910 CONTINUE
 920 CONTINUE
     WRITE(6,2100)
     IF(IC.NE.0.AND.CCORY.NE.0)WRITE(6,2140)IC,ICC
     IWTP=0
     IF(TAPE.GT.2)IWTP=3
     IF(ETH.EQ.0.OR.ETH.EQ.2)CALL EFORM
     CALL PUNWRT(6,1,5,IWTP)
     IF(IT.EQ.0)WRITE(6,2110)
     NEWMID=RTIME(DDDD)
     TTIME=(OTIME-NEWMID)/1000.0
     OTIME=NEWMID
     IF(ID.LE.CORY+1)WRITE(6,2080)TTIME,IC
     IF(ID.GT.CORY+1)WRITE(6,2085)TTIME,IC,ICC
 930 CONTINUE
 935 CONTINUE
 940 CONTINUE
 950 CONTINUE
 955 CONTINUE
     AFTER=RTIME(DDDD)
     TTIME=(BEFORE-AFTER)/1000.0
     WRITE(6,2090)TTIME
 960 CONTINUE
1000 CONTINUE
     RETURN
2000 FORMAT(////,1H0,I3,2X,'**********',28X,'**********',28X,'*********
    ?*',28X,'**********')
2010 FORMAT(1H0,5A4,5X,5A4)
2020 FORMAT(1H ,'IC',2X,'ICC',5X,'     PLMN     ',20X,'OPERATORS')
2025 FORMAT(1H ,15X,F12.8,' TIMES'/)
2030 FORMAT(1H0,' THE FIRST OPERATOR '/)
2040 FORMAT(1H ,20X,F12.8,4X,8(A4,1X))
2050 FORMAT(1H0,' THE SECOND OPERATOR '/)
2060 FORMAT(1H0,' EVALUATION FOR THE FOLLOWING OPERATORS (SUM OVER HOLE
    ?S MU,NU,PI,XI AND PARTICLES M,N,P,Q)')
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2065 FORMAT(1H0,'CORRELATION COEFFICIENT ',I2,' TYPE ',I2)
2067 FORMAT(1H0,10X,'CORRELATION COEFFICIENT ',I2,' TYPE ',I2)
2070 FORMAT(1H0,I3,1X,5A4,1X,'(',A4,3(',',A4),')',' TIMES ',F12.8,' TIM
    ?ES')
2080 FORMAT(1H ,' IT TAKES ',F5.2,' SECONDS FOR CORRELATION FUNCTION ',
    ?I3)
2085 FORMAT(1H ,' IT TAKES ',F5.2,' SECONDS FOR CORRELATION FUNCTIONS '
    ?,I3,' AND ',I3)
2090 FORMAT(1H ,' THE FORMULA TAKES',F6.2,' SECONDS TO GENERATE.')
2100 FORMAT(1H0,' THE FORMULA FOLLOWS.SUM OVER HOLES MU AND NU AND PART
    ?ICLES M AND N.')
2110 FORMAT(1H0,50X,'*****NULL FORMULA*****'/)
2120 FORMAT(1H ,24X,'ONE BODY')
2130 FORMAT(1H ,24X,'TWO BODY')
2140 FORMAT(1H ,10X,'THE CORRELATION FUNCTIONS ARE IN ORDER ',I2,3X,I2)
2150 FORMAT(1H0,' K(',I2,')      K(',I2,').')
     END
     SUBROUTINE SETUP
C SUBROUTINE TO EXPAND THE COMMUTATORS.
     IMPLICIT INTEGER(A-H,O-Z)
     REAL*8 PLMN,PREF,MSPRE,HFAC
     COMMON/LIMITS/STAG,STOG,STAM,STOM,STAI,STOI,STAJ,STOJ,STAK,STOK,ST
    ?AL,STOL,ILIMT,LCLR,UCLR,MINICC,MAXICC
     COMMON/MACB/MSPRE,HFAC(2),CHOP(2,4),DHOP(2,4),MMSS(2),PACHP(2,4),
    ?PADHP(2,4),PRCHP(2,4),PRDHP(2,4),LMS,BMS,BBMS,NMS
     COMMON/PUCK/PC,PCC
     COMMON/BRUTUS/Q(4,6),NAC(6),DAC(6),AQ,IOT
     COMMON/LEAR/PMFAC,CTAPE,ENGL, GSEND,ISHOW,            JTAPE
     COMMON/SILVIA/NO(200)
     COMMON/BANQUO/CHMS
     COMMON/HAMLET/M(44),MM(44),N(44)
     COMMON/EDMUND/PREF,NMOST,IC,CLR,RLT(5),LRIJK(256),O(44),SN(5)
     COMMON/CURRAN/S(5,8),SS(5,8),SSS(5,8),SLOP(256,4),ROP(256,4)
     COMMON/DUKE/IPRINT
     COMMON/LAUNCE/SUM,P(4)
     COMMON/PRIEST/PLMN
     DIMENSION CUM(5)
  10 BEND=AQ+1
     IF(IC.EQ.0.OR.CLR.EQ.1)BEND=AQ
     MBEG=1
     MENDIT=6
     IF(IC.EQ.0.AND.STAM.LT.0)MBEG=-STAM
     IF(IC.EQ.0.AND.STOM.LT.0)MENDIT=-STOM
     IF(STAM.GT.0)MBEG=STAM
     IF(STOM.GT.0)MENDIT=STOM
     CUM(1)=BMS
     IF(CLR.NE.2)CUM(1)=SN(1)+BMS
     SN(4)=2
     IF(SLOP( 1,3).NE.0)SN(4)=4
     IF(ICT.EQ.0)SN(4)=0
     P(1)=0
     P(2)=0
     P(3)=0
     P(4)=0
     STO=SN(4)
     FUN=SN(1) +SN(2)+SN(3)+SN(5)+SN(4)+BMS+1
     SUM=FUN-1+BBMS
     DO 1000 IK=1,NMOST
     IF(STO.EQ.0)GO TO 30
     DO 20 K=1,STO
     S(4,K)=SLOP(IK,K)
     SS(4,K)=ROP(IK,K)
```

```
   20 SSS(4,K)=75+(25*K)-12+S(4,K)
      RLT(4)=LRIJK(IK)
   30 DO 800 MCY=MBEG,MENDIT
      PLMN=PREF*NAC(MCY)/DAC(MCY)
      IF(DABS(PLMN).LT.1.D-5)GO TO 790
      IT=RLT(Q(1,MCY))
      ITT=RLT(Q(BEND,MCY))
      IF((CLR.EQ.1.OR.IC.EQ.0).AND.ITT.GE.1)GO TO 790
      IF((IC.EQ.0.OR.CLR.EQ.2).AND.(IT.EQ.-1.OR.IT.EQ.2))GO TO 790
   50 DO 600 BE=1,BEND
      F=Q(BE,MCY)
      IF(CLR.EQ.3.AND.F.EQ.1)F=5
      BS=CUM(BE)+1
      CUM(BE+1)=BS+SN(F)-1
      NUM=CUM(BE+1)
      DO 300 B=BS,NUM
      ABC=B-BS+1
      M(B)=S(F,ABC)
      MM(B)=M(B)
      N(B)=SS(F,ABC)
  300 O(B)=SSS(F,ABC)
      IF(F.NE.4)GO TO 590
      P(3)=0
      P(4)=0
      DO 400 B=BS,NUM
      BB=B-BS+1
  400 P(BB)=B
      IF(SLOP(IK,3).EQ.0)GO TO 590
      B=P(2)
      P(2)=P(3)
      P(3)=B
  590 CONTINUE
  600 CONTINUE
      IF(BBMS.EQ.0)GO TO 710
      DO 700 K=FUN,SUM
      L=K+1-FUN
      M(K)=CHOP(LMS,L)
      MM(K)=M(L)
      N(K)=PACHP(LMS,L)
  700 O(K)=PRCHP(LMS,L)
  710 CONTINUE
      IF(IPRINT.GT.0)WRITE(IPRINT,2000)PC,PCC,PLMN,(NO(O(B)),B=1,SUM)
      IF(ISHOW.EQ.0)CALL WICKET
  790 CONTINUE
  800 CONTINUE
 1000 CONTINUE
      RETURN
 2000 FORMAT(1H ,I2,2X,I3,5X,F12.8,3X,20(1X,A4))
      END
      SUBROUTINE WICKET
C SUBROUTINE TO DO WICK'S THEOREM
      IMPLICIT INTEGER(A-H,O-Z)
      COMMON/BANQUO/CHMS
      COMMON/LAUNCE/SUM,P(4)
      COMMON/HAMLET/M(44),MM(44),N(44)
      COMMON/JULIA/ESIGN,NUM,MEN(22),WOMEN(22),MATE(4)
      DIMENSION MPO(22),WPO(22),STAR(22),XSIGN(22),BLISS(22),BLESS(22,22
     2)
   10 NUM=SUM/2
      MATE(1)=0
      MATE(2)=0
      MATE(3)=0
```

```
      MATE(4)=0
      IMBEG=1
      MNU=0
      WNU=0
C LOCATE POSITIONS OF MEN AND WOMEN
      DO 50 I=1,SUM
      MW=M(I)
      IF(MW.EQ.1.OR.MW.EQ.2.OR.MW.EQ.-5.OR.MW.EQ.-6)GO TO 30
      IF(CHMS.GE.0.AND.(MW.EQ.9.OR.MW.EQ.-10.OR.MW.EQ.11.OR.MW.EQ.-12))
     ?GO TO 30
      IF(CHMS.LT.0.AND.(MW.EQ.9.OR.MW.EQ.10.OR.MW.EQ.-11.OR.MW.EQ.-12))
     ?GO TO 30
      WNU=WNU+1
      WPO(WNU)=I
      GO TO 40
   30 MNU=MNU+1
      MPO(MNU)=I
   40 CONTINUE
   50 CONTINUE
      DO 80 I=1,NUM
      HERR=MPO(I)
      MEN(I)=N(HERR)
      MAN=M(HERR)
      MUM=0
      DO 60 J=1,NUM
      DAMEN=WPO(J)
      WOMAN=M(DAMEN)
      CHILD=MAN+WOMAN
      IF(CHILD.NE.0.OR.DAMEN.LT.HERR)GO TO 55
      MUM=MUM+1
      BLESS(MUM,I)=DAMEN
   55 CONTINUE
   60 CONTINUE
      IF(MUM.EQ.0)RETURN
      STAR(I)=0
   80 BLISS(I)=MUM
  100 DO 300 IM=IMBEG,NUM
      MI=IM
      MINE=NUM+1-IM
      WSTR=STAR(MINE)+1
      MUM=BLISS(MINE)
      DO 120 IW=WSTR,MUM
      STAR(MINE)=IW
      DAMEN=BLESS(IW,MINE)
      WOMAN=MM(DAMEN)
      IF(WOMAN.NE.0)GO TO 150
  120 CONTINUE
      GO TO 500
  150 HERR=MPO(MINE)
      MM(HERR)=0
      MM(DAMEN)=0
      WOMEN(MINE)=N(DAMEN)
      DO 200 J=1,4
      IF(P(J).EQ.HERR)MATE(J)=WOMEN(MINE)
  200 IF(P(J).EQ.DAMEN)MATE(J)=MEN(MINE)
      STA=HERR+1
      STO=DAMEN-1
      SGN=0
      DO 250 J=STA,STO
  250 IF(MM(J).NE.0)SGN=SGN+1
      XSIGN(MINE)=SGN
  300 IF(MINE.NE.NUM)XSIGN(MINE)=XSIGN(MINE+1)+SGN
```

```
      ESIGN=XSIGN(1)
      ESIGN=(-1)**ESIGN
  400 CALL TV
      MM(HERR)=M(HERR)
  450 MM(DAMEN)=M(DAMEN)
  500 IMBEG=MI-1
      IF(IMBEG.EQ.0)RETURN
      STAR(MINE)=0
      MINE=NUM+1-IMBEG
      MI=MI-1
      WI=STAR(MINE)
      HERR=MPO(MINE)
      DAMEN=BLESS(WI,MINE)
      MUM=BLISS(MINE)
      MM(HERR)=M(HERR)
      MM(DAMEN)=M(DAMEN)
      IF(WI.EQ.MUM)GO TO 500
      GO TO 100
      END
      SUBROUTINE TV
C SUBROUTINE TO SET UP AND CALL TFORM AND VFORM
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 RD,FACT,PLMN,P1REF,PREF
      COMMON/CASCA/IDX
      COMMON/EDMUND/PREF,NMOST,IC,CLR,RLT(5),LRIJK(256),O(36),SN(5)
      COMMON/JULIA/ESIGN,NUM,MEN(22),WOMEN(22),MATE(4)
      COMMON/PORTIA/P1REF(8),CC(8),CF(8,4),XP,XH,XHP,NOC,ISY,XXP,XXH,XXH
     ?P,NNOC,MMNN,BB(4)
      COMMON/PRIEST/PLMN
      COMMON/ANTONY/ETH
      DIMENSION CN(8),IJ(4),TYP(4)
      DATA TYP/1,2,9,10/
   10 GPS=2
      IF(MATE(3).EQ.0)GPS=1
      IF(IABS(ETH).EQ.1)GPS=0
      SPG=GPS*2
      IF(ETH.EQ.1)SPG=2
      TL=0
      TU=0
      UTLU=1
      RD=ESIGN*PLMN
      IF(IDX.EQ.0)GO TO  80
      DO 20 DD=1,4
   20 BB(DD)=0
      DO 30 DD=1,NUM
      MAN=MAX0(MEN(DD),WOMEN(DD))
      WOMAN=MIN0(MEN(DD),WOMEN(DD))
      IF(WOMAN.GT.2)GO TO 25
      IF(             (MAN.EQ.19.OR.MAN.EQ.20).AND.BB(WOMAN).NE.0.AND.
     ?BB(WOMAN).NE.MAN)RETURN
      IF(             (MAN.EQ.19.OR.MAN.EQ.20))BB(WOMAN)=MAN
   25 NAMOW=WOMAN-6
      IF(WOMAN.NE.9.AND.WOMAN.NE.10)GO TO 30
      IF(                              (MAN.EQ.21.OR.MAN.EQ.22).AND.BB
     ?(NAMOW).NE.MAN.AND.BB(NAMOW).NE.0)RETURN
      IF(                              (MAN.EQ.21.OR.MAN.EQ.22))BB(NAM
     ?OW)=MAN
   30 CONTINUE
      IF(BB(3).EQ.22.AND.BB(4).EQ.21.AND.IDX.GT.0)RETURN
      IF(BB(1).EQ.20.AND.BB(2).EQ.19.AND.IDX.GT.0)RETURN
      IF(BB(1).EQ.BB(2).AND.BB(1).NE.0)RETURN
      IF(BB(3).EQ.BB(4).AND.BB(3).NE.0)RETURN
```

```
      UPH=1
      DO 50 DD=1,4
   50 IF(BB(DD).NE.0)UPH=UPH+1
      GC TO 100
   80 DO 90 DD=1,NUM
      MAN=MAXO(MEN(DD),WOMEN(DD))
      WOMAN=MINO(MEN(DD),WOMEN(DD))
      IF(WCMAN.EQ.1.AND.MAN.EQ.2)TL=2
   90 IF(MAN.EQ.10.AND.WCMAN.EQ.9)TU=1
      UPH=UTLU+TL+TU
  100 CCNTINUE
      IF(SPG.EQ.0)GO TO 140
      MAYL=MINO(MATE(1),MATE(2),MATE(3),MATE(4))
      MAYU=MAXO(MATE(1),MATE(2),MATE(3),MATE(4))
      IF(MAYL.EQ.7.AND.MAYU.EQ.8.OR.MAYL.EQ.15.AND.MAYU.EQ.16)GO TO 120
      DO 110 IJK=1,SPG
  110 IF(MATE(IJK).EQ.8.OR.MATE(IJK).EQ.16)MATE(IJK)=MATE(IJK)-1
      GO TO 140
  120 IF(MATE(2).EQ.7.OR.MATE(2).EQ.15)MATE(2)=MATE(2)+1
      IF(MATE(1).EQ.8.OR.MATE(1).EQ.16)MATE(1)=MATE(1)-1
  140 DO 300 NNN=1,NOC
      DC 290 NNNN=1,NNOC
      DC 150 KJI=5,8
      IJK=KJI-4
      IJ(IJK)=MATE(IJK)
      CC(IJK)=CF(IJK,NNN)
      CN(IJK)=CC(IJK)
      CC(KJI)=CF(KJI,NNNN)
      CN(KJI)=CC(KJI)
  145 CCNTINUE
  150 CCNTINUE
      FACT=RD*P1REF(NNN)*P1REF(NNNN+4)
      ISY=1
      IF(IC.EQ.0)GO TO 190
      ISY=0
      IF(ETH.EQ.1)ISY=-3
      IF(ETH.EQ.-1)ISY=-5
      IF(XH.EQ.0.AND.XP.EQ.0.AND.XHP.EQ.0.AND.NOC.EQ.0.AND.XXH.EQ.0.AND.
     ?XXP.EQ.0.AND.XXHP.EQ.0.AND.NNOC.EQ.0.AND.MMNN.NE.2)ISY=1
      DO 180 DD=1,NUM
      MAN=MAXO(MEN(DD),WOMEN(DD))
      WOMAN=MINO(MEN(DD),WOMEN(DD))
      MMAN=MAN
      WWCM=WOMAN
      IF((MMAN.EQ.19.OR.MMAN.EQ.20).AND.(WWOM.GT.2.AND.WWOM.LT.9))MAN=WW
     ?OM
      IF((MMAN.EQ.19.OR.MMAN.EQ.20).AND.(WWOM.GT.2.AND.WWOM.LT.9))WOMAN=
     ?MMAN
      IF((MMAN.EQ.21.OR.MMAN.EQ.22).AND.(WWOM.GT.10.AND.WWOM.LT.19))MAN=
     ?WWCM
      IF((MMAN.EQ.21.OR.MMAN.EQ.22).AND.(WWOM.GT.10.AND.WWOM.LT.19))WOMA
     ?N=MMAN
      IF(MAN.EQ.7.OR.MAN.EQ.8.OR.MAN.GE.15.AND.MAN.LE.18)GO TO 170
      IF(MAN.GT.4.AND.MAN.LT.7.AND.WOMAN.GT.2.AND.WOMAN.LT.5.OR.MAN.GT.1
     ?2.AND.MAN.LT.15.AND.WOMAN.GT.10.AND.WOMAN.LT.13)GO TU 165
      DC 160 EE=1,8
      IF(MAN.EQ.CN(EE)      )CC(EE)=WOMAN
  160 IF(WCMAN.EQ.CN(EE)      )CC(EE)=MAN
      GO TC 170
  165 DO 168 EE=1,4
      DO 167 EEE=5,8
  167 IF(MAN.EQ.CN(EEE).AND.WOMAN.EQ.CN(EE))CC(EEE)=WOMAN
```

```
  168 CONTINUE
  170 CONTINUE
  180 CONTINUE
  190 CONTINUE
      IF(SPG.EQ.0.OR.IDX.EQ.0)GO TO 240
      DO 230 EE=1,SPG
      DO 220 EEE=1,4
      IF(CC(EE).EQ.BB(EEE))CC(EE)=TYP(EEE)
  220 IF(IJ(EE).EQ.BB(EEE))IJ(EE)=TYP(EEE)
  230 CONTINUE
  240 CONTINUE
      IF(ISY.LE.0)CALL SYM(IJ,FACT)
      IF(ISY.EQ.0)ISY=-1
  250 I=IJ(1)
      J=IJ(2)
      K=IJ(3)
      L=IJ(4)
      IF(GPS.LE.1)CALL TFORM(I,J,FACT,UPH)
      IF(GPS.EQ.2)CALL VFORM(I,J,K,L,FACT,UPH)
  260 CONTINUE
  290 CONTINUE
  300 CONTINUE
      RETURN
      END
      SUBROUTINE TFORM(F,FF,T,X)
C SUBROUTINE TO FORM THE ENERGY MATRIX
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 T,ETIMS,TT,P1REF
      COMMON/PORTIA/P1REF(8),CC(8),CF(8,4),XP,XH,XHP,NOC,ISY,XXP,XXH,XXH
     ?P,NNCC,MMNN,BB(4)
      COMMON/CLOWN/ETIMS(5,200),EN(5,200,2),EC(5,200,8),ED(5,200,4)
      COMMON/TUBAL/NEN(5),NEMM(5)
      COMMON/REGAN/IT,TAPE,CT,ICC,CTT,MSTO,ICHG
      DIMENSION                P(4),IJ(4)
      TT=T
      IJ(1)=F
      IJ(2)=FF
      IJ(3)=0
      IJ(4)=0
      ISY=-2
      IF(IJ(2).NE.0)ISY=-4
      IF(IJ(1).EQ.0)ISY=-6
    1 NUT=NEN(X)
      TUN=NEMM(X)
      DO 19 CHG=1,ICHG
C INTERCHANGE CC
      IF(CHG.EQ.2)CALL SYM(IJ,TT)
      SF=MIN0(IJ(1),IJ(2))
      FS=MAX0(IJ(1),IJ(2))
      S=SF
      SS=FS
      IF(SF.EQ.0)S=FS
      IF(SF.EQ.0)SS=SF
      IF(S.EQ.18.AND.SS.EQ.0)S=17
      IF(NUT.EQ.0)GO TO 20
   12 DO 18 A=1,NUT
      B=A
      IF(TUN.LE.NUT.OR.CHG.EQ.2)GO TO 13
      IF(DABS(ETIMS(X,B)).LT.1.D-5   )ETIMS(X,B)=0.D0
      IF(ETIMS(X,B).EQ.0.D0)TUN=A
   13 CONTINUE
      DO 14 MUST=1,MSTO
```

```
      IF(EC(X, B ,MUST).NE.CC(MUST))GO TO 17
   14 CONTINUE
      DO 15 MUST=1,4
      IF(ED(X,B,MUST).NE.BB(MUST))GO TO 17
   15 CONTINUE
      IF(S.EQ.EN(X,B,1).AND.SS.EQ.EN(X,B,2))GO TO 30
   17 CONTINUE
   18 CONTINUE
   19 CONTINUE
   20 IF(TUN.GT.NUT)NUT=TUN
      IF(NUT.GT.200)GO TO 40
      EN(X,TUN,1)=S
      EN(X,TUN,2)=SS
      ETIMS(X,TUN)=TT
      NEN(X)=NUT
      NEMM(X)=NUT+1
      DO 21 MUST=1,4
   21 ED(X,TUN,MUST)=BB(MUST)
      DO 23 MUST=1,8
   23 EC(X,TUN,MUST)=CC(MUST)
      RETURN
   30 ETIMS(X,B)=ETIMS(X,B)+TT
      IF(B.EQ.NUT.AND.ETIMS(X,B).EQ.0.D0)NUT=NUT-1
      IF(B.EQ.TUN.OR.TUN.GT.NUT)TUN=NUT+1
      NEMM(X)=TUN
      NEN(X)=NUT
      RETURN
   40 WRITE(6,2000)
      CALL PUNWRT(6,X,X,1)
      NUTTY=0
      NEN(X)=0
      NEMM(X)=1
      GO TO 1
 2000 FORMAT(1H0,' ***EN AND ETIMS MATRICES ARE NOT LARGE ENOUGH***'//)
      END
      SUBROUTINE VFORM(Q,R,S,T,M,PH)
C SUBROUTINE TO CONSTRUCT THE TWO-BODY TERMS
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 M,VTIMS,MM,P1REF
      COMMON/REGAN/IT,TAPE,CT,ICC,CTT,MSTO,ICHG
      COMMON/PORTIA/P1REF(8),CC(8),CF(8,4),XP,XH,XHP,NOC,ISY,XXP,XXH,XXH
     ?P,NNOC,MMNN,BB(4)
      COMMON/GOBBO/NTU(5),MTU(5)
      COMMON/OSRIC/VTIMS(5,300),V(5,300,4),C(5,300,4),VD(5,300,4)
    1 MM=M
      II=MINO(Q,S)
      KK=MAXO(Q,S)
      JJ=MINO(R,T)
      LL=MAXO(R,T)
      IF(JJ-II)10,20,30
   10 NI=II
      II=JJ
      JJ=NI
      NK=KK
      KK=LL
      LL=NK
      GO TO 30
   20 IF((LL-KK).GE.0)GO TO 30
      NK=KK
      KK=LL
      LL=NK
   30 CONTINUE
```

```
  32 MEW=NTU(PH)
     WEM=MTU(PH)
     IF(MEW.EQ.0)GO TO 50
     DO 40 A=1,MEW
     B=A
     IF(WEM.LE.MEW)GO TO 33
     IF(DABS(VTIMS(PH,A)).LT.0.00001)VTIMS(PH,A)=0.D0
     IF(VTIMS(PH,A).EQ.0.D0)WEM=B
  33 CONTINUE
     DO 34 MUST=1,MSTO
     IF(C(PH,A,MUST).NE.CC(MUST))GO TO 38
  34 CONTINUE
     DO 36 MUST=1,4
     IF(VD(PH,A,MUST).NE.BB(MUST))GO TO 38
  36 CONTINUE
     IF(II.EQ.V(PH,A,1).AND.JJ.EQ.V(PH,A,2).AND.KK.EQ.V(PH,A,3).AND.LL
    ?.EQ.V(PH,A,4))GO TO 60
  38 CONTINUE
  40 CONTINUE
  50 IF(WEM.GT.MEW)MEW=WEM
     IF(MEW.GT.300)GO TO 80
     V(PH,WEM,1)=II
     V(PH,WEM,2)=JJ
     V(PH,WEM,3)=KK
     V(PH,WEM,4)=LL
     VTIMS(PH,WEM)=MM
     NTU(PH)=MEW
     MTU(PH)=MEW+1
     DO 53 MUST=1,4
     VD(PH,WEM,MUST)=BB(MUST)
  53 C(PH,WEM,MUST)=CC(MUST)
     RETURN
  60 VTIMS(PH,B)=VTIMS(PH,B)+MM
     IF(B.EQ.NUT.AND.VTIMS(PH,B).EQ.0.D0)MEW=MEW-1
     IF(B.EQ.WEM.OR.WEM.GT.MEW)WEM=MEW+1
     MTU(PH)=WEM
     NTU(PH)=MEW
     RETURN
  80 WRITE(6,2000)
     CALL PUNWRT(6,PH,PH,2)
     NTU(PH)=0
     MTU(PH)=1
     GO TO 32
2000 FORMAT(1H0,' ***V AND VTIMS MATRICES ARE NOT LARGE ENOUGH***'//)
     END
     SUBROUTINE EFORM
     IMPLICIT INTEGER(A-H,O-Z)
     REAL*8 Z,SACT,P1REF,PREF,ETIMS
     COMMON/PORTIA/P1REF(8),CC(8),CF(8,4),XP,XH,XHP,NOC,ISY,XXP,XXH,XXH
    ?P,NNOC,MMNN,BB(4)
     COMMON/EDMUND/PREF,NMOST,IC,CLR,RLT(5),LRIJK(256),O(36),SN(5)
     COMMON/BANQUO/CHMS
     COMMON/SPEED/GS
     COMMON/ANTONY/ETH
     COMMON/CLOWN/ETIMS(5,200),EN(5,200,2),EC(5,200,8),ED(5,200,4)
     COMMON/TUBAL/NEN(5),NEMM(5)
     COMMON/CASCA/IDX
     COMMON/TOM/NOSP
     DIMENSION XTRX(4,2),IJ(4)
     DATA IJ/0,0,0,0/
     DATA XTRX/3,4,0,0,2,0,4,0/
  10 DO 500 PPH=1,5
```

```
      PH=6-PPH
      NUT=NEN(PH)
      NEMM(PH)=1
      NEN(PH)=0
      IF(NUT.EQ.0)GO TO 490
      DO 400 J=1,NUT
      IF(ETIMS(PH,J).EQ.0.D0)GO TO 390
      Z=ETIMS(PH,J)
      ETIMS(PH,J)=0.D0
      X=EN(PH,J,1)
      Y=EN(PH,J,2)
      DO 11 K=1,4
   11 BB(K)=ED(PH,J,K)
      DO 12 K=1,8
   12 CC(K)=EC(PH,J,K)
      IF(ETH.EQ.0.OR.CLR.EQ.3)GO TO 50
   15 U=7
      V=15
      IF(X.EQ.7.OR.Y.EQ.7)U=8
      IF(X.EQ.15.OR.Y.EQ.15)V=16
      SACT=Z/2
      CALL VFORM(X,U,U,Y,SACT,PH)
      IF(CHMS.LT.0)CALL VFORM(X,17,17,Y,SACT,PH)
      SACT=-Z/2
      CALL VFORM(X,V,V,Y,SACT,PH)
      IF(CHMS.LT.0)CALL VFORM(X,18,18,Y,SACT,PH)
      SACT=(-Z)*2
      IF(NOSP.NE.0)SACT=(-Z)*NOSP
      CALL VFORM(X,U,Y,U,SACT,PH)
      IF(CHMS.LT.0)CALL VFORM(X,17,Y,17,SACT,PH)
      IF(GS.EQ.1)GO TO 50
      IF(GS.EQ.3)GO TO 20
      SACT=-Z/2
      IF((X.GE.9.AND.X.LT.19.OR.X.EQ.21.OR.X.EQ.22).AND.(Y.GE.9.AND.Y.LT
     ?.19.OR.Y.EQ.21.OR.Y.EQ.22))CALL VFORM(X,17,17,Y,SACT,PH)
      SACT=Z/2
      IF((X.LT.9.OR.X.EQ.19.OR.X.EQ.20).AND.Y.EQ.17.OR.X.EQ.17.AND.(Y.LT
     ?.9.OR.Y.EQ.19.OR.Y.EQ.20))CALL VFORM(X,17,17,Y,SACT,PH)
      SACT=-Z
      IF((X.LT.9.OR.X.EQ.19.OR.X.EQ.20).AND.Y.EQ.17.OR.X.EQ.17.AND.(Y.LT
     ?.9.OR.Y.EQ.19.OR.Y.EQ.20))SACT=SACT*2
      IF((X.LT.9.OR.X.EQ.19.OR.X.EQ.20).OR.(Y.LT.9.OR.Y.EQ.19.OR.Y.EQ.20
     ?))CALL VFORM(X,17,Y,17,SACT,PH)
      GO TO 50
   20 SACT=0.D0
      IF((X.GE.9.AND.X.LT.19.OR.X.EQ.21.OR.X.EQ.22).AND.(Y.GE.9.AND.Y.LT
     ?.19.OR.Y.EQ.21.OR.Y.EQ.22))SACT=Z/2
      IF((X.LT.9.OR.X.EQ.19.OR.X.EQ.20).AND.(Y.EQ.17.OR.Y.EQ.18))SACT=-Z
     ?/2
      IF((Y.LT.9.OR.Y.EQ.19.OR.Y.EQ.20).AND.(X.EQ.17.OR.X.EQ.18))SACT=-Z
     ?/2
      IF(SACT.NE.0.D0)CALL VFORM(X,17,17,Y,SACT,PH)
      IF(SACT.NE.0.D0)CALL VFORM(X,18,18,Y,SACT,PH)
      SACT=-Z
      CALL VFORM(X,17,Y,17,SACT,PH)
      CALL VFORM(X,18,Y,18,SACT,PH)
   50 MPH=PH
      XYX=0
      XX=MIN0(X,Y)
      YY=MAX0(X,Y)
      IF(XX.LT.9.AND.((YY.GT.8.AND.YY.LT.19).OR.YY.GT.20))GO TO 390
      IF((XX.GT.8.AND.XX.LT.17).AND.(YY.GT.16.AND.YY.LT.21))GO TO 390
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      IF((XX.EQ.19.OR.XX.EQ.20).AND.(YY.EQ.21.OR.YY.EQ.22))GO TO 390
      SACT=Z
      XXX=XX
      YYY=YY
      IF((XX.GT.10.AND.XX.LT.19).AND.(YY.EQ.21.OR.YY.EQ.22))XX=YYY
      IF((XX.GT.10.AND.XX.LT.19).AND.(YY.EQ.21.OR.YY.EQ.22))YY=XXX
      IF((XX.GT.2.AND.XX.LT.9).AND.(YY.EQ.19.OR.YY.EQ.20))XX=YYY
      IF((XX.GT.2.AND.XX.LT.9).AND.(YY.EQ.19.OR.YY.EQ.20))YY=XXX
      IF(XX.EQ.1.AND.YY.EQ.2)XYX=1
      IF(XX.EQ.9.AND.YY.EQ.10)XYX=2
      IF(XYX.NE.0.AND.IDX.EQ.0)MPH=XTRX(PH,XYX)
      IF(X.EQ.Y)XYX=3
      IF(XYX.NE.0.OR.CC(1).EQ.0)GO TO 65
      XYX=4
      DO 60 K=1,8
   60 IF(YY.EQ.CC(K))CC(K)=XX
      IJ(1)=XX
      IF(ISY.LE.0.AND.XYX.NE.0)CALL SYM(IJ,SACT)
      XX=IJ(1)
   65 CONTINUE
      IF(IDX .NE.0)GO TO 70
      IF(XYX.NE.0)CALL TFORM(XX,0,SACT,MPH)
      GO TO 390
   70 CONTINUE
      IF(XX.GT.2)GO TO 73
      IF(XX.EQ.1.AND.YY.EQ.2)GO TO 390
      IF(XX.EQ.19.AND.YY.EQ.20)GO TO 390
      IF((YY.EQ.19.OR.YY.EQ.20).AND.BB(XX).NE.YY.AND.BB(XX).NE.0)GO TO 3
     ?90
      IF(YY.EQ.19.OR.YY.EQ.20)BB(XX)=YY
   73 NAMOW=XX-6
      IF(XX.EQ.9.AND.YY.EQ.10)GO TO 390
      IF(XX.EQ.21.AND.YY.EQ.22)GO TO 390
      IF(XX.NE.9.AND.XX.NE.10)GO TO 78
      IF((YY.EQ.21.OR.YY.EQ.22).AND.BB(NAMOW).NE.YY.AND.BB(NAMOW).NE.0)G
     ?O TO 390
      IF(YY.EQ.21.OR.YY.EQ.22)BB(NAMOW)=YY
   78 CONTINUE
      IF(BB(1).EQ.20.AND.BB(2).EQ.19.AND.IDX.GT.0)GO TO 390
      IF(BB(1).EQ.BB(2).AND.BB(1).NE.0)GO TO 390
      IF(BB(3).EQ.22.AND.BB(4).EQ.21.AND.IDX.GT.0)GO TO 390
      IF(BB(3).EQ.BB(4).AND.BB(3).NE.0)GO TO 390
   80 MPH=1
      DO 90 DD=1,4
   90 IF(BB(DD).NE.0)MPH=MPH+1
  100             CALL TFORM(XX,0,SACT,MPH)
  390 CONTINUE
  400 CONTINUE
  490 CONTINUE
  500 CONTINUE
      RETURN
      END
      SUBROUTINE SYM(IJ,M)
C SUBROUTINE TO MODIFY THE FORMULAS FOR CORRELATION COEFFICIENT SYMMETRY
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 M,P1REF
      COMMON/PORTIA/P1REF(8),CC(8),CF(8,4),XP,XH,XHP,NOC,ISY,XXP,XXH,XXH
     ?P,NNOC,MMNN,BBB(4)
      DIMENSION IJ(4),MA(8),CN(8),CCH(8),HCC(8),PS(4)
      DIMENSION P(4),ABC(4),CBA(4)
      DATA ABC/1,5,3,7/
      DATA CBA/2,6,4,8/
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      DATA CCH/4,3,12,11,6,5,14,13/
      DATA HCC/3,4,11,12,5,6,13,14/
      DATA MA/3,4,1,2,7,8,5,6/
      IF(ISY.EQ.-1)GO TO 200
      IF(NOC.EQ.0.AND.NNOC.EQ.0.OR.ISY.EQ.-2)GO TO 95
      IF(ISY.EQ.-4.OR.ISY.EQ.-6)GO TO 95
C RENAMING CC DUE TO NOC
      DO 10 A=1,4
      PS(A)=0
      IF(IJ(A).EQ.0)GO TO 9
      DO 5 B=1,8
    5 IF(IJ(A).EQ.CC(B))PS(A)=B
    9 CONTINUE
   10 P(A)=0
      DO 30 A=5,8
      DO 20 B=1,4
   20 IF(CC(A).EQ.HCC(B))P(B)=A
   30 CONTINUE
      DO 40 A=1,8
   40 CN(A)=CC(A)
      DO 50 A=1,4
      IF(CC(A).EQ.CCH(A).AND.P(A).NE.0)CC(P(A)   )=HCC(A)
      IF(CC(A).EQ.CCH(A))CC(A)=HCC(A)
      B=A+4
   50 IF(CC(B).EQ.CCH(B))CC(B)=HCC(B)
      DO 90 A=1,4
   90 IF(PS(A).NE.0)IJ(A)=CC(PS(A))
   95 CONTINUE
      IF(MMNN.EQ.2.AND.(ISY.EQ.0.OR.ISY.EQ.-3.OR.ISY.EQ.-5))GO TO 100
      IF(ISY.EQ.-2.OR.ISY.EQ.-4.OR.ISY.EQ.-6)GO TO 100
      GO TO 200
  100 CONTINUE
      DO 103 A=1,4
      PS(A)=0
      IF(IJ(A).EQ.0)GO TO 102
      DO 101 B=1,4
      BB=B+4
      IF(IJ(A).EQ.CC(B))PS(A)=BB
  101 IF(IJ(A).EQ.CC(BB))PS(A)=B
  102 CONTINUE
  103 P(A)=0
      DO 108 A=5,8
      DO 106 B=1,4
  106 IF(CC(A).EQ.HCC(B))P(B)=A-4
  108 CONTINUE
      DO 110 A=1,8
  110 CN(A)=CC(A)
      DO 120 A=1,4
      B=A+4
      CC(A)=CN(B)
  120 CC(B)=CN(A)
      DO 150 A=1,4
      B=A+4
      IF(P(A).NE.0)CC(P(A))=HCC(P(A))
      IF(P(A).NE.0)CC(B)=HCC(P(A))
      IF(CC(A).EQ.HCC(B))CC(A)=HCC(A)
  150 IF(CC(B).EQ.HCC(A).AND.P(A).EQ.0)CC(B)=HCC(B)
      DO 160 A=1,4
  160 IF(PS(A).NE.0)IJ(A)=CC(PS(A))
C HOLE AND PARTICLE SYMMETRY
  200 CONTINUE
      IF(XH.EQ.0.AND.XXH.EQ.0.AND.XP.EQ.0.AND.XXP.EQ.0)GO TO 510
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      DO 500 AB=1,4
      IF(AB.EQ.1)HXP=XH
      IF(AB.EQ.2)HXP=XXH
      IF(AB.EQ.3)HXP=XP
      IF(AB.EQ.4)HXP=XXP
      IF(HXP.EQ.0)GO TO 490
      DO 210 A=1,4
      B=A+4
      CN(B)=CC(B)
      PS(A)=0
  210 CN(A)=CC(A)
      A1=ABC(AB)
      A2=CBA(AB)
      IF(ISY.GT.-1.OR.ISY.LT.-4)GO TO 240
      IF(IJ(1).EQ.A2.OR.IJ(2).EQ.A2)GO TO 490
      IF(IJ(1).EQ.A1.OR.IJ(2).EQ.A1)GO TO 300
  240 CCNTINUE
      IF(CN(A2).EQ.HCC(A2))GO TO 400
      IF(CN(A1).EQ.HCC(A1))GO TO 300
      CC(A1)=MIN0(CN(A1),CN(A2))
      CC(A2)=MAX0(CN(A1),CN(A2))
      IF(CC(A1).NE.CN(A1))M=M*HXP
      GO TC 490
  300 CC(A1)=CN(A2)
      IF(CC(A1).EQ.HCC(A2))CC(A1)=HCC(A1)
      CC(A2)=HCC(A2)
      IF(AB.EQ.2.OR.AB.EQ.4)GO TO 340
      P(A1)=0
      P(A2)=0
      DO 310 A=5,8
      IF(CN(A).EQ.HCC(A2))P(A2)=A
  310 IF(CN(A).EQ.HCC(A1))P(A1)=A
      IF(P(A1).NE.0)CC(P(A1))=CC(A2)
      IF(P(A2).NE.0)CC(P(A2))=CC(A1)
  340 DO 350 A=1,4
      IF(IJ(A).EQ.CN(A1))PS(A)=A2
  350 IF(IJ(A).EQ.CN(A2))PS(A)=A1
      DO 360 A=1,4
  360 IF(PS(A).NE.0)IJ(A)=CC(PS(A))
      M=M*HXP
      GO TO 490
  400 CONTINUE
      IF(CN(A1).NE.HCC(A1).OR.IJ(3).EQ.0)GO TO 490
      DC 410 A=1,4
      IF(IJ(A).EQ.HCC(A1))Z=A
  410 IF(IJ(A).EQ.HCC(A2))ZZ=A
      MP=MA(Z)
      MPP=MA(ZZ)
      IF(Z.EQ.MPP)GO TO 490
      N=MIN0(IJ(MP),IJ(MPP))
      IF(N.EQ.IJ(MP))GO TO 490
      IJ(MPP)=IJ(MP)
      IJ(MP)=N
      M=M*XHP
  490 CONTINUE
  500 CCNTINUE
  510 CONTINUE
      IF(XHP.EQ.0.AND.XXHP.EQ.0)RETURN
C HOLE-HCLE PARTICLE-PARTICLE SYMMETRY
      Q=2
      IF(XHP.EQ.0)GO TO 690
      ASTA=1
```

```
      ASTO=4
      A1=1
      A2=2
      A3=3
      A4=4
      PHX=XHP
  530 DO 550 A=1,8
  550 CN(A)=CC(A)
      IF(ISY.GT.-1.OR.ISY.LT.-4)GO TO 553
      IF(IJ(1).EQ.HCC(A4).OR.IJ(2).EQ.HCC(A4))GO TO 690
      IF(IJ(1).EQ.HCC(A3).OR.IJ(2).EQ.HCC(A3))GO TO 554
      IF(IJ(1).EQ.HCC(A2).OR.IJ(2).EQ.HCC(A2))GO TO 690
      IF(IJ(1).EQ.HCC(A1).OR.IJ(2).EQ.HCC(A1))GO TO 554
  553 ZZ=MAX0(CN(A3),CN(A4))
      Z=MIN0(CN(A3),CN(A4))
      IF(ZZ.NE.9.AND.ZZ.NE.10.AND.ZZ.NE.21.AND.ZZ.NE.22.OR.Z.NE.9.AND.Z.
     ?NE.10.AND.Z.NE.21.AND.Z.NE.22)GO TO 5540
      IF(Z.NE.ZZ.OR.CN(1).NE.3. OR.CN(2).NE.4)GO TO 5537
      P1=0
      P2=0
      DO 5535 A=1,4
      IF(IJ(A).EQ.3)P1=MA(A)
 5535 IF(IJ(A).EQ.4)P2=MA(A)
      IF(P2.LT.P1)GO TO 554
 5537 CONTINUE
      IF(ZZ.EQ.CN(A4))GO TO 690
      GO TO 554
 5540 CONTINUE
      HH=MAX0(CN(A1),CN(A2))
      H=MIN0(CN(A1),CN(A2))
      IF(HH.NE.1.AND.HH.NE.2.AND.HH.NE.19.AND.HH.NE.20. OR.H.NE.1.AND.H.
     ?NE.2.AND.H.NE.19.AND.H.NE.20)GO TO 5545
      IF(H.NE.HH.OR.CN(3).NE.11. OR.CN(4).NE.12)GO TO 5544
      P3=0
      P4=0
      DO 5532 A=1,4
      IF(IJ(A).EQ.11)P3=MA(A)
 5532 IF(IJ(A).EQ.12)P4=MA(A)
      IF(P4.LT.P3)GO TO 554
 5544 CONTINUE
      IF(HH.EQ.CN(A2))GO TO 690
      GO TO 554
 5545 CONTINUE
      IF(ZZ.EQ.21.OR.ZZ.EQ.22)ZZ=MIN0(CN(A3),CN(A4))
      IF(ZZ.EQ.21.OR.ZZ.EQ.22)Z=MAX0(CN(A3),CN(A4))
      IF(HH.EQ.19.OR.HH.EQ.20)HH=MIN0(CN(A1),CN(A2))
      IF(HH.EQ.19.OR.HH.EQ.20)H=MAX0(CN(A1),CN(A2))
      IF(ZZ.EQ.CN(A4).AND.Z.NE.HCC(A3))GO TO 690
      IF(ZZ.EQ.HCC(A4).AND.Z.EQ.HCC(A3).AND.HH.EQ.CN(A2))GO TO 690
  554 CC(A1)=CN(A2)
      IF(CC(A1).EQ.HCC(A2))CC(A1)=HCC(A1)
      CC(A2)=CN(A1)
      IF(CC(A2).EQ.HCC(A1))CC(A2)=HCC(A2)
      CC(A3)=CN(A4)
      IF(CC(A3).EQ.HCC(A4))CC(A3)=HCC(A3)
      CC(A4)=CN(A3)
      IF(CC(A4).EQ.HCC(A3))CC(A4)=HCC(A4)
      DO 560 A=1,4
      PS(A)=0
      IF(IJ(A).EQ.0)GO TO 557
      DO 555 B=ASTA,ASTO
  555 IF(IJ(A).EQ.CN(B))PS(A)=MA(1+ASTO+(2-Q)*4-B)
```

```
  557 CONTINUE
  560 P(A)=0
      IF(Q.EQ.1)GO TO 590
      DO 568 A=5,8
      DO 564 B=1,4
  564 IF(CN(A).EQ.HCC(B))P(B)=A
  568 CONTINUE
      DO 570 A=1,4
  570 IF(P(A).NE.0)CC(P(A)   )=CCH(A)
  590 M=M*PHX
      DO 620 A=1,4
  620 IF(PS(A).NE.0)IJ(A)=CC(PS(A))
  630 CONTINUE
  690 Q=Q-1
      ASTA=5
      ASTO=8
      A1=5
      A2=6
      A3=7
      A4=8
      PHX=XXHP*Q
      IF(PHX.NE.0)GO TO 530
      RETURN
      END
      SUBROUTINE PUNWRT(W,IS,WIS,ONTO)
C SUBROUTINE TO PRINT AND WRITE THE FORMULAS ON TAPE.
      IMPLICIT INTEGER(A-H,O-Z)
      REAL*8 DEL(2,4),ETIMS,VTIMS,PREF,PRM,NUM,EHOLD(200),VHOLD(300)
      REAL ENG(22)
      COMMON/PRINCE/ON(23)
      COMMON/REGAN/IT,TAPE,CT,ICC,CTT,MSTO,ICHG
      COMMON/CASCA/IDX
      COMMON/GOBBO/NTU(5),MTU(5)
      COMMON/TUBAL/NEN(5),NEMM(5)
      COMMON/JULIET/HCK,HHCK,PCK,PPCK
      COMMON/EDMUND/PREF,NMOST,IC,CLR,RLT(5),LRIJK(256),O(36),SN(5)
      COMMON/OSRIC/VTIMS(5,300),V(5,300,4),C(5,300,4),VD(5,300,4)
      COMMON/CLOWN/ETIMS(5,200),EN(5,200,2),EC(5,200,8),ED(5,200,4)
      DIMENSION DUMMY(12),IDTYP(5),PRTY(2,4),TYP(4),BB(4)
      DATA DUMMY/0,0,0,0,0,0,0,0,0,0,0,0/
      DATA DEL/'        ','        ','D(P1-P2)','        ','D(H1-H2)','
     ?        ','D(P1-P2)','D(H1-H2)'/
      DATA ENG/' H1-',' H2-','    ','    ','    ','    ','    ','    ',
     ?' P1-',' P2-','    ','    ','    ','    ','    ','    ','    ','
     ? ','H3  ','H4  ','P3  ','P4  '/
      DATA IDTYP/1,8,18,8,1/
      DATA TYP/1,2,9,10/
   10 IT=0
      DUMMY(1)=IC
      DUMMY(2)=CT
      DUMMY(3)=ICC
      IF(CLR.NE.3)DUMMY(3)=0
      DUMMY(4)=CTT
      IDSTC=0
      DUM=0
      NUM=0.D0
      DO 500 I=IS,WIS
      IF(I.EQ.5.AND.IDX.EQ.0)GO TO 490
      KK=0
      KKK=0
      KSTA=1
      KKSTA=1
```

```
   NUN=NEN(I)
   IF(CNTO.EQ.2)NUN=0
   G=0
   IF(NUN.EQ.0)GO TO 30
   DO 20 K=   1,NUN
   IF(DABS(ETIMS(I,K)).LT.1.D-5 )ETIMS(I,K)=0.DO
   IF(ETIMS(I,K).EQ.0.DO)GO TO 19
   IF(IDX.EQ.0)GO TO 15
   EC1=EC(I,K,1)
   EC2=EC(I,K,2)
   IF(HCK.NE.0.AND.(EC1.EQ.2.AND.EC2.EQ.1.OR.EC1.EQ.20.AND.EC2.EQ.19)
  ?)GO TO 18
   IF(HCK.LT.0.AND.EC1.NE.0.AND.EC1.NE.23.AND.EC1.EQ.EC2)GO TO 18
   EC1=EC(I,K,3)
   EC2=EC(I,K,4)
   IF(PCK.NE.0.AND.(EC1.EQ.10.AND.EC2.EQ.9.OR.EC1.EQ.22.AND.EC2.EQ.21
  ?))GO TO 18
   IF(PCK.LT.0.AND.EC1.NE.0.AND.EC1.NE.23.AND.EC1.EQ.EC2)GO TO 18
15 CONTINUE
   IF(HHCK.EQ.0.AND.PPCK.EQ.0)GO TO 19
   EC1=EC(I,K,5)
   EC2=EC(I,K,2)
   IF(HHCK.EQ.0)GO TO 16
   IF(EC1.EQ.4.AND.EC1.EQ.3.AND.HCK.NE.0)GO TO 18
   IF(IDX.NE.0.AND.(EC1.EQ.2.AND.EC2.EQ.1.OR.EC1.EQ.20.AND.EC2.EQ.19)
  ?)GO TO 18
   IF(IDX.NE.0.AND.HHCK.LT.0.AND.EC1.NE.0.AND.EC1.NE.23.AND.EC1.EQ.EC
  ?2)GO TO 18
16 CONTINUE
   IF(PPCK.EQ.0)GO TO 19
   EC1=EC(I,K,7)
   EC2=EC(I,K,8)
   IF(PCK.NE.0.AND.EC1.EQ.12.AND.EC2.EQ.11)GO TO 18
   IF(IDX.NE.0.AND.(EC1.EQ.10.AND.EC2.EQ.9.OR.EC1.EQ.22.AND.EC2.EQ.21
  ?))GO TO 18
   IF(IDX.NE.0.AND.PPCK.LT.0.AND.EC1.NE.0.AND.EC1.NE.23.AND.EC1.EQ.EC
  ?2)GO TO 18
   GO TO 19
18 ETIMS(I,K)=0.DO
19 CONTINUE
   EHOLD(K)=ETIMS(I,K)
20 IF(ETIMS(I,K).NE.0.0)G=1
   IF(G.EQ.0)NUN=G
30 CONTINUE
   MEW=NTU(I)
   IF(ONTO.EQ.1)MEW=0
   G=0
   IF(MEW.EQ.0)GO TO 50
   DO 40 K=1,MEW
   IF(DABS(VTIMS(I,K)).LT.1.D-5 )VTIMS(I,K)=0.DO
   IF(IDX.EQ.0.OR.VTIMS(I,K).EQ.0)GO TO 39
   EC1=C(I,K,1)
   EC2=C(I,K,2)
   IF(HCK.NE.0.AND.(EC1.EQ.2.AND.EC2.EQ.1.OR.EC1.EQ.20.AND.EC2.EQ.19)
  ?)GO TO 38
   IF(HCK.LT.0.AND.EC1.NE.0.AND.EC1.NE.23.AND.EC1.EQ.EC2)GO TO 38
   EC1=C(I,K,3)
   EC2=C(I,K,4)
   IF(PCK.NE.0.AND.(EC1.EQ.10.AND.EC2.EQ.9.OR.EC1.EQ.22.AND.EC2.EQ.21
  ?))GO TO 38
   IF(PCK.LT.0.AND.EC1.NE.0.AND.EC1.NE.23.AND.EC1.EQ.EC2)GO TO 38
   GO TO 39
```

```
   38 VTIMS(I,K)=0.D0
   39 VHOLD(K)=VTIMS(I,K)
   40 IF(DABS(VTIMS(I,K)).NE.0.0)G=1
      IF(G.EQ.0)MEW=G
   50 CONTINUE
      IF(NUN.EQ.0.AND.MEW.EQ.0)GO TO 490
      IF(IDX.NE.0)IDSTO=IDTYP(I)
      IF(IDX.EQ.0)WRITE(W,2000)(DEL(J,I),J=1,2)
      DO 450 ID=1,IDSTO
      IF(IDX.EQ.0)GO TO 51
      IF(KSTA.GT.NUN)KK=0
      IF(KSTA.EQ.0.OR.NUN.EQ.0.OR.KSTA.GT.NUN)GO TO 100
      DO 5000 K=KSTA,NUN
      KK=K
      IF(ETIMS(I,K).NE.0.D0)GO TO 5010
 5000 CONTINUE
      KK=0
 5010 CONTINUE
      KSTA=KK
      IF(KK.EQ.0)GO TO 100
      JJ=0
      DO 5030 K=1,4
      BB(K)=ED(I,KK,K)
      IF(BB(K).EQ.0)GO TO 5020
      JJ=JJ+1
      PRTY(1,JJ)=TYP(K)
      PRTY(2,JJ)=BB(K)
 5020 CONTINUE
 5030 CONTINUE
      IF(JJ.NE.0)WRITE(W,2100)(ENG(PRTY(1,J)),ENG(PRTY(2,J)),J=1,JJ)
   51 FLAG=-(I*2-1)
      IT=IT+1
      IF(CNTO.GT.2)WRITE(TAPE)FLAG,NUM,(DUMMY(K),K=1,12)
      IF(CNTO.GT.2.AND.IDX.NE.0)WRITE(TAPE)(PRTY(1,J),PRTY(2,J),J=1,JJ)
      DO 70 K=KSTA,NUN
      PRM=ETIMS(I,K)
      IF(PRM.EQ.0.D0)GO TO 60
      IF(IDX.EQ.0)GO TO 5120
      DO 5110 L=1,4
      IF(BB(L).NE.ED(I,K,L))GO TO 60
 5110 CONTINUE
 5120 SIN=EN(I,K,1)
      SSIN=EN(I,K,2)
      FTH=2
      IF(SIN.EQ.0)FTH=0
      IF(SIN.NE.0.AND.SSIN.NE.0)FTH=1
      IF(FTH-1)52,54,56
   52 IF(IC.EQ.0)WRITE(W,2060)PRM
      IF(IC.NE.0.AND.CLR.NE.3)WRITE(W,2070)PRM,(ON(EC(I,K,L)),L=1,4)
      IF(CLR.EQ.3)WRITE(W,2075)PRM,(ON(EC(I,K,L)),L=1,8)
      GO TO 58
   54 IF(IC.EQ.0)WRITE(W,2080)PRM,ON(SIN),ON(SSIN)
      IF(IC.NE.0.AND.CLR.NE.3)WRITE(W,2090)PRM,ON(SIN),ON(SSIN),(ON(EC(I
     ?,K,L)),L=1,4)
      IF(CLR.EQ.3)WRITE(W,2095)PRM,ON(SIN),ON(SSIN),(ON(EC(I,K,L)),L=1,8
     ?)
      GO TO 58
   56 IF(IC.EQ.0)WRITE(W,2010)PRM,ON(SIN)
      IF(IC.NE.0.AND.CLR.NE.3)WRITE(W,2020)PRM,ON(SIN),(ON(EC(I,K,L)),L=
     ?1,4)
      IF(CLR.EQ.3)WRITE(W,2025)PRM,ON(SIN),(ON(EC(I,K,L)),L=1,8)
   58 CONTINUE
```

```
      IF(ONTO.GT.2)WRITE(TAPE)DUM,PRM,SIN,SSIN,DUM,DUM,(EC(I,K,L),L=1,8)
      ETIMS(I,K)=0.D0
   60 CONTINUE
   70 CONTINUE
      KSTA=KK+1
  100 CONTINUE
      IF(MEW.EQ.0)GO TO 400
      IT=IT+1
      FLAG=-(I*2)
      IF(ONTO.GT.2)WRITE(TAPE)FLAG,NUM,(DUMMY(K),K=1,12)
      IF(KK.NE.0.OR.IDX.EQ.0)GO TO 220
      IF(KKSTA.GT.MEW)GO TO 455
      DO 150 K=KKSTA,MEW
      KKK=K
      IF(VTIMS(I,K).NE.0.D0)GO TO 160
  150 CONTINUE
      GO TO 455
  160 CONTINUE
      KKSTA=KKK
      JJ=0
      DO 180 K=1,4
      BB(K)=VD(I,KKK,K)
      IF(BB(K).EQ.0)GO TO 170
      JJ=JJ+1
      PRTY(1,JJ)=TYP(K)
      PRTY(2,JJ)=BB(K)
  170 CONTINUE
  180 CONTINUE
      IF(JJ.NE.0)WRITE(W,2100)(ENG(PRTY(1,J)),ENG(PRTY(2,J)),J=1,JJ)
      IF(ONTO.GT.2.AND.IDX.NE.0)WRITE(TAPE)(PRTY(1,J),PRTY(2,J),J=1,JJ)
  220 DO 270 K=KKSTA,MEW
      PRM=VTIMS(I,K)
      IF(PRM.EQ.0.D0)GO TO 260
      IF(IDX.EQ.0)GO TO 250
      DO 230 L=1,4
      IF(BB(L).NE.VD(I,K,L))GO TO 260
  230 CONTINUE
  250 CONTINUE
      IF(IC.EQ.0)WRITE(W,2030)PRM,(ON(V(I,K,L)),L=1,4)
      IF(IC.NE.0)WRITE(W,2040)PRM,(ON(V(I,K,L)),L=1,4),(ON(C(I,K,L)),L=1
     ?,4)
      IF(ONTO.GT.2)WRITE(TAPE)DUM,PRM,(V(I,K,L),L=1,4),(C(I,K,L),L=1,4)
     ?,DUM,DUM,DUM,DUM
      VTIMS(I,K)=0.D0
  260 CONTINUE
  270 CONTINUE
      IF(KKK.NE.0)KKSTA=KKK+1
  400 CONTINUE
  450 CONTINUE
  455 CONTINUE
      IF(NUN.EQ.0)GO TO 470
      DO 460 K=1,NUN
  460 ETIMS(I,K)=EHOLD(K)
  470 CONTINUE
      IF(MEW.EQ.0)GO TO 490
      DO 480 K=1,MEW
  480 VTIMS(I,K)=VHOLD(K)
  490 CONTINUE
  500 CONTINUE
      FLAG= -9-1/2**IT
      IF(ONTO.GT.2)WRITE(TAPE)FLAG,NUM,(DUMMY(K),K=1,12)
      WRITE(W,2000)
```

```
      RETURN
 2000 FORMAT(1H0,2A8)
 2010 FORMAT(1H ,20X,F12.8,3X,'E(',A4,')')
 2020 FORMAT(1H ,20X,F12.8,3X,'E(',A4,')',3X,'C(',A4,3(',',A4),')')
 2025 FORMAT(1H ,20X,F12.8,3X,'E(',A4,')',2(3X,'C(',A4,3(',',A4),')'))
 2030 FORMAT(1H ,40X,F12.8,3X,'V(',A4,3(',',A4),')')
 2040 FORMAT(1H ,40X,F12.8,3X,'V(',A4,3(',',A4),')' ,3X,'C(',A4,3(',',A4
     ?),')')
 2060 FORMAT(1H ,10X,F12.8)
 2070 FORMAT(1H ,10X,F12.8,3X,'C(',A4,3(',',A4),')')
 2075 FORMAT(1H ,10X,F12.8,3X,'C(',A4,3(',',A4),')',3X,'C(',A4,3(',',A4)
     ?,')')
 2080 FORMAT(1H ,30X,F12.8,3X,'T(',A4,',',A4,')')
 2090 FORMAT(1H ,30X,F12.8,3X,'T(',A4,',',A4,')',3X,'C(',A4,3(',',A4),')
     ?')
 2095 FORMAT(1H ,30X,F12.8,3X,'T(',A4,',',A4,')',3X,'C(',A4,3(',',A4),')
     ?',3X,'C(',A4,3(',',A4),')')
 2100 FORMAT(1H0,4(A4,A4))
      END
```

PROPOSITIONS

PROPOSITION I

Abstract

Rowe's first open shell equations of motion method is applied to atoms and molecules with a few large ground state correlation coefficients. Explicitly including these correlation coefficients incorporates some effects that are present in the equations of motion method including double excitation mixing, EOM((1p-1h) + (2p-2h)). In the multiconfiguration random phase approximation (MCRPA) excitation energies and transition moments are expected to be better than ordinary RPA calculations. The triplet instability problem for low-lying states should be less important. In addition, multiconfiguration equations of motion methods can be used for cases where ordinary EOM methods break down, e.g., H_2 at large internuclear distances.

Proposition I. The Multiconfiguration Random Phase Approximation (MCRPA).

The equations of motion method[1,2] has been successfully applied to the calculation of the excitation energies and transition moments for atoms and molecules which can be well described by a restricted Hartree-Fock SCF ground state.[3] The equations of motion method is a conceptually and computationally simple method which is used to calculate directly quantities of physical interest. The resulting amplitudes and energies can be used to calculate transition moments between excited states,[4,5] two-photon emission probabilities,[4] photoionization cross sections from both ground[6] and metastable states,[4] Born inelastic electron-molecule scattering cross sections,[7] and optical potentials for electron molecule scattering.[8]

Even though computational costs for an equations of motion calculation are usually not large for diatomic or small polyatomic molecules, for larger molecules and more flexible basis sets the computer costs become significant for higher order calculations, e.g., the equations of motion method including double excitation mixing (EOM (1p-1h) + (2p-2h))[2]. Lower order calculations, the Random Phase Approximation (RPA), while cheaper, can result in inconsistent experimental agreement for transition energies. In addition, RPA calculations can yield imaginary excitation energies or instabilities which imply for closed shell ground states that a state of energy lower than the calculated HF ground state, possibly of broken symmetry, exists.[9]

For many atoms and molecules the ground state is not well described by a simple single determinant SCF calculation, but have two or more configurations which are important, e.g., the doubly excited $\pi \rightarrow \pi^*$ configuration in ethylene.[10] Many molecules cannot be described by an HF SCF calculation on dissociation but require a mixing of several configurations, e.g., H_2 .

Recently Rowe[11] proposed an open shell method for nuclei which can be applied in a straightforward manner to atoms and molecules. This method involves a small configuration interaction calculation to determine configuration coefficients and occupation numbers for the ground state. The limited CI ground state is used in an equations of motion calculation. Thus there may be both excitations to and excitations from certain hole and particle orbitals.

With a multiconfiguration ground state one can achieve better agreements for both transition energies and moments at a low level approximation, i.e., the multiconfiguration random phase approximation (MCRPA), with the diagonalization of relatively small matrices. Thus computer times may be significantly reduced. Moreover, the instability problem should not be as severe and low lying triplet state excitation energies should be easily determined for HF closed shell ground states without going to higher orders. Systems which require a multiconfigurational approach like H_2 on dissociation which cannot be calculated using more traditional EOM methods can be handled simply in the multiconfiguration equations of motion (MCEOM). Thus the MCEOM is a powerful extension of current molecular equations of motion procedures.

I propose developing Rowe's first open shell procedure for atoms and molecules. In the remainder of this proposition the equations will be examined and discussed. All formulas can be easily derived by use of formula generating programs.[10] For simplicity the discussion will be restricted to atoms and molecules which in a Hartree-Fock molecular orbital scheme have a closed shell ground state and have only two important ground state configurations, the Hartree-Fock state and a doubly excited configuration. Extensions to different multiconfigurational ground states including configurations from a CI calculation on an open shell HF ground state are straightforward. Also, only the multiconfiguration TDA and RPA are discussed in detail. Multiconfiguration higher RPA and multiconfiguration EOM ((1p-1h) + (2p-2h)) are obvious extensions. The resultant equations can be used in several calculations including ethylene at ground state experimental geometry and N_2 at large internuclear distances.

Consider an atom or molecule with a ground state which is well described as

$$|0> \simeq N_0(K_1|(\text{closed shell})\eta\alpha\eta\beta> + K_2|(\text{closed shell})p\alpha p\beta>) \qquad \text{(I-1)}$$

where

$$N_0 = \frac{1}{\sqrt{K_1^2 + K_2^2}} \qquad \text{(I-2)}$$

and K_1 and K_2 are correlation coefficients. A Hartree-Fock SCF calculation is performed on the first configuration on the right hand side of (1) and 2x2 configuration interaction calculation is done to obtain K_1 and K_2. Throughout this proposition lower case Greek letters are orbitals occupied in the single determinant SCF calculation; m,n,p,q,···

are virtual or unoccupied orbitals in the SCF calculation; and i,j,k,ℓ are either occupied or unoccupied orbitals. In this case the secular matrix to be diagonalized is[12]

$$\begin{pmatrix} -\Delta E & K_{p\eta} \\ K_{p\eta} & 2\varepsilon_p - 2\varepsilon_\eta + J_{\eta\eta} + J_{pp} + 2K_{p\eta} - 4J_{p\eta} - \Delta E \end{pmatrix} \qquad \text{(I-3)}$$

where all the orbital energies, and coulomb and exchange integrals are obtained from the SCF calculation. ΔE is the correlation energy. An example of this is ethylene. Dunning[10] using a minimum basis set of Slater functions calculates K_1 to be 0.968805 and K_2 to be -0.247825 where K_1 is the coefficient of the HF ground state and K_2 is the coefficient of the configuration where the π orbital is replaced by the π^* orbital.

An operator $O_\lambda^\dagger$ when acting on the ground state $|0>$ generates an excited state $|\lambda>$. The conjugate operator O_λ acting on $|0>$ gives 0 . From these two conditions Rowe[3] has shown that

$$<0| [\delta O_\lambda, H, O_\lambda^\dagger]|0> = \omega_\lambda <0|[\delta O_\lambda, O_\lambda^\dagger]|0> \qquad \text{(I-4)}$$

where the symmetric double commutator is defined

$$2[A,B,C] = [[A,B],C] + [A,[B,C]] \qquad \text{(I-5)}$$

Equation (I-4) is exact. There are two approximations that can be made to solve (I-4).

The ground state $|0>$ is replaced by some approximate state. The use of the symmetric double commutator on the left of Eq. (I-4) and the commutator on the right assure that the resulting equations will be of lower particle-hole rank than if fewer commutators had been used. Thus the resulting energies will be relatively insensitive to the choice of ground state. In the cases of MCTDA and MCRPA, ground state (I-1) is chosen.

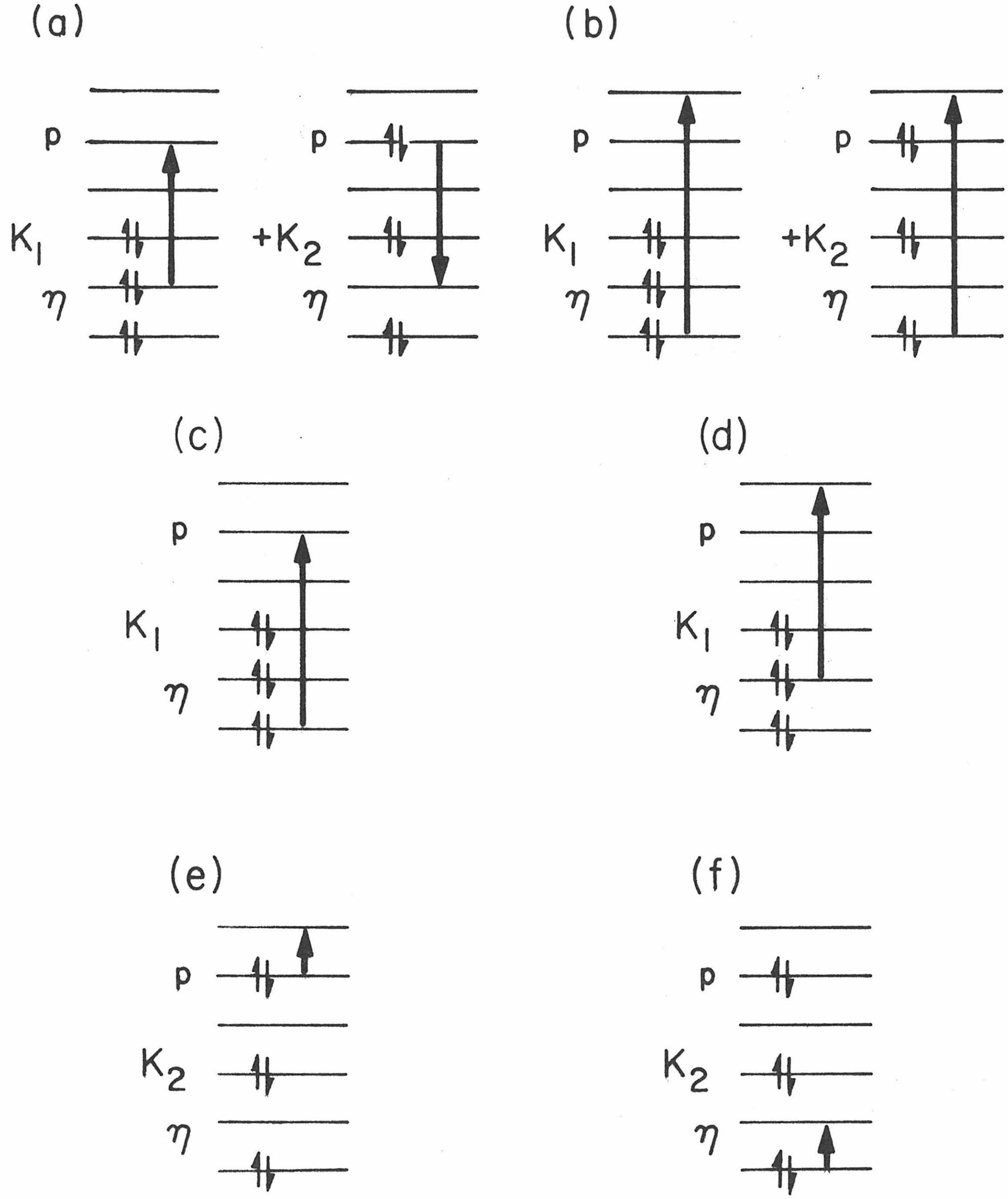
The second approximation is the form of $O_\lambda^\dagger$. As for ordinary closed shell ground state TDA and RPA, $O_\lambda^\dagger$ is constructed of linear combinations of one-body p-h excitation operators. However, because the ground state is (I-1) certain orbitals have both excitations from them and excitations to them. Figure 1 illustrates this. $O_\lambda^\dagger$ for singlet states is written

$$
\begin{aligned}
O_\lambda^\dagger(00) = {} & \frac{1}{\langle 0|[C_{p\eta}(00),C_{p\eta}^\dagger(00)]|0\rangle^{1/2}} \left(Y_{p\eta}C_{p\eta}(00) - Z_{p\eta}C_{p\eta}(\overline{00})\right) \\
& + \sum_{\substack{n\neq p \\ \gamma\neq\eta}} \frac{1}{\langle 0|[C_{n\gamma}(00),C_{n\gamma}^\dagger(00)]|0\rangle^{1/2}} \left(Y_{n\gamma}C_{n\gamma}(00) - Z_{n\gamma}C_{n\gamma}(\overline{00})\right) \\
& + \sum_{\gamma\neq\eta} \frac{1}{\langle 0|[C_{p\gamma}(00),C_{p\gamma}^\dagger(00)]|0\rangle^{1/2}} \left(Y_{p\gamma}C_{p\gamma}(00) - Z_{p\gamma}C_{p\gamma}(\overline{00})\right) \\
& + \sum_{n\neq p} \frac{1}{\langle 0|[C_{n\eta}(00),C_{n\eta}^\dagger(00)]|0\rangle^{1/2}} \left(Y_{n\eta}C_{n\eta}(00) - Z_{n\eta}C_{n\eta}(\overline{00})\right) \\
& + \sum_{n\neq p} \frac{1}{\langle 0|[C_{np}(00),C_{np}^\dagger(00)]|0\rangle^{1/2}} \left(Y_{np}C_{np}^\dagger(00) - Z_{np}C_{np}(\overline{00})\right) \\
& \sum_{\gamma\neq\eta} \frac{1}{\langle 0|[C_{\eta\gamma}(00),C_{\eta\gamma}^\dagger(00)]|0\rangle^{1/2}} \left(Y_{\eta\gamma}C_{\eta\gamma}^\dagger(00) - Z_{\eta\gamma}C_{\eta\gamma}(\overline{00})\right)
\end{aligned}
\tag{I-6}
$$

where $C_{ij}^\dagger(00)$ is a one-body tensor operator.

Figure 1.

Possible single excitations for $N_o(K_1|(\text{closed shell})\eta\alpha\eta\beta> + K_2|(\text{closed shell})p\alpha p\beta>)$ ground state.


(a)
p
K$_1$
η
p
+K$_2$
η
(b)
p
K$_1$
η
p
+K$_2$
η
(c)
p
K$_1$
η
(d)
p
K$_1$
η
(e)
p
K$_2$
η
(f)
p
K$_2$
η

$$C^{\dagger}_{ij}(00) = \frac{1}{\sqrt{2}} (c_{i\alpha} c_{j\alpha} + c_{i\beta}\, c_{j\beta}) \qquad \text{(I-7)}$$

$$C_{ij}(\overline{00}) = C_{ij}(00) \qquad \text{(I-8)}$$

Evaluating the commutators in (I-6) using

$$\begin{aligned} n_1 &= K_1^2 \\ n_2 &= K_2^2 \end{aligned} \qquad \text{(I-9)}$$

$$\begin{aligned} O^{\dagger}_{\lambda}(00) = {} & \left(Y_{p\eta} \frac{1}{(n_1 - n_2)^{1/2}} C^{\dagger}_{p\eta}(00) - Z_{p\eta} \frac{1}{(n_1 - n_2)^{1/2}} C_{p\eta}(\overline{00})\right) \\ & + \sum_{\substack{n \neq p \\ \gamma \neq \eta}} \left(Y_{n\gamma} C_{n\gamma}(00) - Z_{n\gamma} C_{n\gamma}(\overline{00})\right) \\ & + \sum_{\gamma \neq \eta} \left(Y_{p\gamma} \frac{1}{(1 - n_1)^{1/2}} C_{p\gamma}(00) - Z_{p\gamma} \frac{1}{(1 - n_1)^{1/2}} C_{p\gamma}(\overline{00})\right) \\ & + \sum_{n \neq p} \left(Y_{n\eta} \frac{1}{n_1^{1/2}} C^{\dagger}_{n\eta}(00) - Z_{n\eta} \frac{1}{n_1^{1/2}} C_{n\eta}(\overline{00})\right) \\ & + \sum_{n \neq p} \left(Y_{np} \frac{1}{n_2^{1/2}} C^{\dagger}_{np}(00) - Z_{np} \frac{1}{n_2^{1/2}} C_{np}(\overline{00})\right) \\ & + \sum_{\gamma \neq \eta} \left(Y_{\eta\gamma} \frac{1}{(1 - n_2)^{1/2}} C_{\eta\gamma}(00) - Z_{\eta\gamma} \frac{1}{(1 - n_2)^{1/2}} C_{\eta\gamma}(00)\right) \end{aligned} \qquad \text{(I-10)}$$

A similar equation exists for the triplet manifold.

Use of (I-6) or (I-10) in (I-4) gives matrix equations in RPA or time dependent Hartree-Fock form

$$\begin{pmatrix} \underset{\sim}{A} & \underset{\sim}{B} \\ -\underset{\sim}{B} & -\underset{\sim}{A} \end{pmatrix} \begin{pmatrix} Y \\ Z \end{pmatrix} = \omega_{\lambda} \begin{pmatrix} Y \\ Z \end{pmatrix} \qquad \text{(I-11)}$$

where $\underset{\sim}{A}$ is Hermitian and $\underset{\sim}{B}$ is symmetric.

$$A_{ij,k\ell} = \langle 0|\left[\frac{C_{ij}(00)}{\langle 0|[C_{ij}(00),C^{\dagger}_{ij}(00)]|0\rangle^{1/2}}\ ,\ H\ ,\ \frac{C^{\dagger}_{k\ell}(00)}{\langle 0|[C_{k\ell}(00),C^{\dagger}_{k\ell}(00)]|0\rangle^{1/2}}\right]|0\rangle \tag{I-12}$$

$$B_{ij,k\ell} = -\langle 0|\left[\frac{C_{ij}(00)}{\langle 0|[C_{ij}(00),C^{\dagger}_{ij}(00)]|0\rangle^{1/2}}\ ,\ H\ ,\ \frac{C_{k\ell}(\overline{00})}{\langle 0|[C_{k\ell}(00),C^{\dagger}_{k\ell}(00)]|0\rangle^{1/2}}\right]|0\rangle \tag{I-13}$$

(I-6), (I-10), and (I-12) differ from ordinary closed shell ground state RPA operators and equations by the presence of terms such as $\frac{1}{\langle 0|[C_{ij}(00),C^{\dagger}_{ij}(00)]|0\rangle^{1/2}}$ and $\frac{1}{(n_1 - n_2)^{1/2}}$. By choosing $0^{\dagger}_{\lambda}$ as in Eq. (I-6), Eq. (I-11) results. Thus only slight modifications need to be made in standard RPA programs. Without the inclusion of the denominators in (I-6) a matrix equation of a more complicated form than (I-11) is obtained and hence more difficult methods are required to obtain energies and amplitudes.

$\underset{\sim}{A}$ and $\underset{\sim}{B}$ for the MCRPA cannot be written in one form in terms of orbital energies and interaction matrix elements. In (I-12) and (I-13) the formula depends on the indices i,j,k,ℓ . The formulas can easily be derived by means of formula writing programs.[14]

Consider now the ordinary closed shell Tamm Dancoff Approximation for the same system. $|0\rangle$ is replaced by the Hartree-Fock ground state $|HF\rangle$ and $O_{\lambda}^{\dagger TDA}$ is

$$O_{\lambda}^{\dagger TDA}(00) = \sum_{n\gamma} Y_{n\gamma} C_{n\gamma}(00) \tag{I-14}$$

In the MCTDA all Z amplitudes except Z_p in (I-10) are zero. From examining Fig. 1 in the MCTDA and hence MCRPA, we are explicitly including excitations from a correlated state and certain double excitations from the HF single determinant state. In the ordinary TDA all excitations in Fig. (1) from the K_1 configuration are allowed. The K_2 configuration in (a) corresponds to a deexcitation from a correlated ground state, and in (b), (e), and (f) to excitation from a correlated ground state. In (b) the K_2 configuration is a triple excitation from the Hartree-Fock ground state and in (e) and (f) a double excitation. Performing an MCTDA or MCRPA calculation corresponds to explicitly calculating and including the K_2 correlation coefficient. (a) and (b) include certain higher random phase approximation effects.[1] (e) and (f) explicitly account for certain ordinary double excitation mixing. Hence, performing an MCRPA calculation includes some of the effects of the EOM((1p-1h) + (2p-2h)). However, computationally MCRPA calculations are much smaller and less time consuming.

EOM((1p-1h) + (2p-2h)) results are usually in excellent agreement with experiment.[3] By including certain of the more important ordinary higher RPA and double excitation mixing effects in the MCRPA the triplet instability problem should be reduced and good agreement with experiment should result at a low level of approximation.

Transition moments may be obtained from

$$W_{o\lambda} = \langle 0|[O_\lambda,\hat{W}]|0\rangle \tag{I-15}$$

where $\hat{W}$ is defined

$$\begin{aligned} \hat{W} &= \sum_{ij} \sqrt{2}\, T_{ij} C_{ij}(00) \\ T_{ij} &= \langle i|T|j\rangle \end{aligned} \tag{I-16}$$

Replacing O_λ by the Hermitian conjugate of (I-10) yields

$$\begin{aligned} W_{o\lambda} = {} & \sqrt{2}\,\{(n_1 - n_2)^{1/2}\,(Y_{p\eta} + Z_{p\eta})W_{p\eta} \\ & + \sum_{\substack{n\neq p \\ \gamma\neq\eta}} (Y_{n\gamma} + Z_{n\gamma})W_{n\gamma} \\ & + \sum_{\gamma\neq\eta} (1-n_1)^{1/2}\,(Y_{p\gamma} + Z_{p\gamma})W_{p\gamma} \\ & + \sum_{n\neq p} n_1^{1/2}\,(Y_{n\eta} + Z_{n\eta})W_{n\eta} + \sum_{n\neq p} n_2^{1/2}\,(Y_{np} + Z_{np})W_{np} \\ & + \sum_{\gamma\neq\eta} (1-n_2)^{1/2}\,(Y_{\eta\gamma} + Z_{\eta\gamma})W_{\eta\gamma} \end{aligned} \tag{I-17}$$

For problems in which traditional EOM methods break down because all correlation coefficients are not small, MCEOM methods can be used, e.g., the potential curves of excited states of many molecules at large internuclear distances. Schemes in higher order than the MCRPA can be employed if necessary. In the MCHRPA all correlation coefficients except for K_1 and K_2 in Eq. (I-1) are determined by Rayleigh Schrodinger perturbation theory or iteratively and hence are assumed small. For the MCEOM ((1p-1h) + (2p-2h)) in addition to the MCHRPA correlation coefficients double excitation corrections to $O_{\lambda}^{\dagger}$ are included in a perturbative-like scheme.[2] In this case double excitation operators may include excitations both to and from orbitals η and p .

In this proposition multiconfiguration equation of motion methods have been developed to the extent that only small modifications to existing formula writing and EOM programs are required. The MCRPA matrix equations, (I-11), are of the same form as RPA equations. The MCRPA incorporates certain ordinary HRPA and double excitation effects in a straightforward manner. At this low level approximation oscillator strengths and transition energies should be obtained in good experimental agreement at computer costs considerably less than higher order EOM schemes. Furthermore, instability problems should be reduced. Higher order multiconfiguration methods can be easily developed and may be useful for molecules at large internuclear distances. The MCEOM energies and vectors can be used as a discrete representation of the continuum and in other ways similar to EOM energies and amplitudes.

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PROPOSITION II

An Examination of Oscillation Strengths in the Equations of Motion Method

Abstract

The length, velocity, and mixed forms of the oscillator strength in molecules are equal in the Random Phase Approximation (RPA). The three forms are shown to be equal through first order in the Higher Random Phase Approximation (HRPA or EOM (1p-1h)), and through second order the differences are expected to be small. It is proposed to make a numerical study of the three forms in the HRPA and to investigate the oscillator strength in the Equations-of-Motion including Double Excitation Mixing.

The strength of an electronic transition in atoms and molecules is proportional to the oscillator strength f of that transition. For fairly strong transitions f is approximately one. Recently the Random Phase Approximation has been utilized to calculate matrix elements for use in determining photoionization cross sections in atoms[1] and molecules.[2] Thus it is important to be able to accurately and easily calculate dipole moment matrix elements.

Chandraskhar[3] in 1945 explained that the use of the variational principle to determine wave functions resulted with "...a good approximation to the wave function only in that it yields a good approximation to the wave function in a region giving the main contribution to the energy integral, whereas other regions are important in the transition integral."[4] That is, in the dipole length formulation

$$f_{o\lambda}^{(r)} = \frac{2}{3}\,\omega_{\lambda o}\,|\langle 0|\hat{\vec{r}}|\lambda\rangle|^2 \tag{II-1}$$

where $f_{o\lambda}^{(r)}$ is the oscillator strength for the transition $0 \rightarrow \lambda$, and $\hat{\vec{r}}$ is the total electronic position operator, large radial distances are emphasized, while in the other formulations

$$f_{o\lambda}^{(m)} = \frac{2}{3}\,(|\langle 0|\hat{\vec{m}}|\lambda\rangle|^2 / \omega_{\lambda o}) \tag{II-2}$$

where $\hat{\vec{m}}$ is the total electronic momentum operator and

$$f_{o\lambda}^{(mr)} = \frac{2}{3}\,(-\,\frac{i}{2})[\langle 0|\hat{\vec{r}}|\lambda\rangle \cdot \langle\lambda|\hat{\vec{m}}|0\rangle - \langle 0|\hat{\vec{m}}|\lambda\rangle \cdot \langle\lambda|\hat{\vec{r}}|0\rangle] \tag{II-3}$$

different regions of space are stressed. In fact, Hansen[5] has shown that an expression similar to (II-3) yields consistent results when comparisons are made between Hartree-Fock and "correlated" wave functions. That is, although for an exact wave function identities exist between (II-1), (II-2), and (II-3), for the Hartree-Fock wave function no equalities exist. In practice, use of a finite basis set expansion to approximate the Hartree-Fock ground and excited states can only make matters worse.

Independently, Harris[6] and Amus'ya et al.[2] showed that while the Hartree-Fock wave functions can never yield consistent oscillator strengths and hence photoionization cross section among expressions (II-1) - (II-3), the Random Phase Approximation will. Perhaps somewhat exuberantly the author of a text on photoionization processes states that the "...degree of agreement between the three forms (of oscillator strengths) is often taken as a measure of the exactness of the wave function employed."[6] It is the purpose of this proposition to investigate the various forms of the Equations-of-Motion (EOM) to higher order than the RPA (the HRPA), to show that the three forms (II-1) - (II-3) are equivalent through first order terms, to propose that a numerical study be made of the three forms in HRPA, and to propose a similar investigation including double excitations in the EOM.

Consider the Random Phase Approximation (RPA) and the Higher Random Phase Approximation (HRPA). In the latter form of the Equations-of-Motion the operator 0_λ^+ remains the same as in the RPA, namely,

$$0_\lambda^+(SM) = \sum_{m\gamma} [Y_{m\gamma}(\lambda S) C_{m\gamma}^+(SM) - Z_{m\gamma}(\lambda S)\, C_{m\gamma}(\overline{SM})] \qquad \text{(II-4)}$$

where for convenience spatial symmetry is ignored. However, when matrix elements are evaluated the Hartree-Fock ground state $|HF>$ is replaced by a better approximation to the ground state

$$|0> = N_0[|HF> + |\chi>] \quad ; \qquad \langle\chi|HF> = 0 \tag{II-5}$$

where χ is the correlation wave function for the ground state.[7] In either approximation, the transition amplitude is given by

$$<0|\hat{T}|\lambda> = <0|[\hat{T},0_\lambda^+]|0> \tag{II-6}$$

where T is any one-electron operator. Substituting (II-4) into (II-6) yields

$$<0|\hat{T}|\lambda> = \sqrt{2} \sum_{\substack{ij\\m\gamma}} T_{ij} <0|[C_{ij}^+(00),\ Y_{m\gamma}(\lambda S)C_{m\gamma}^+(SM) - Z_{m\gamma}(\lambda S)C_{m\gamma}(\overline{SM})]|0> \tag{II-7}$$

$$= \sqrt{2} \sum_{\substack{m\gamma\\\nu}} (T_{\nu m}Y_{m\gamma}(\lambda 0) + T_{m\nu}\ Z_{m\gamma}(\lambda 0))\ \rho_{\gamma\nu} - \sqrt{2} \sum_{\substack{m\gamma\\n}} (T_{\gamma n}Y_{m\gamma}(\lambda 0) + T_{n\gamma}\ Z_{m\gamma}(\lambda 0))\ \rho_{mn} \tag{II-8}$$

where

$$\rho_{ij} = \sqrt{2} <0|C_{ij}^+(00)|0> \tag{II-9}$$

and

$$T_{ij} = <i|\hat{T}|j> \tag{II-10}$$

the one-body operator closed with two states which span the space of interest (usually the Hartree-Fock single-particle states). Notice that the order of writing subscripts is important on the T's since all one-body operators will not be real.

Now if the total electronic momentum operator $\hat{\vec{m}}$ is substituted for $\hat{T}$,

$$\langle 0|\vec{m}|\lambda\rangle = \sqrt{2}\sum_{\substack{m\gamma\\ \nu}} \vec{m}_{\gamma m}(Y_{m\gamma}(\lambda 0) - Z_{m\gamma}(\lambda 0))\ \rho_{\gamma\nu}$$
$$- \sqrt{2}\sum_{\substack{m\gamma\\ n}} \vec{m}_{\gamma n}(Y_{m\gamma}(\lambda 0) - Z_{m\gamma}(\lambda 0))\ \rho_{mn} \tag{II-11}$$

where the following property of the $\hat{\vec{m}}$ operator has been used

$$\vec{m}_{\gamma m} = -\vec{m}_{m\gamma} \tag{II-12}$$

Harris[5] derives the following relationship

$$\vec{m}_{\nu p} = (\omega_{p\nu}/i)\vec{r}_{\nu p} + (1/i)\sum_{\gamma q} \vec{r}_{\gamma q}(V_{q\gamma p\nu} - V_{q\gamma\nu p}) \tag{II-13}$$

Note that $\vec{r}_{\nu p} = \vec{r}_{p\nu}$. In the Random Phase Approximation, $\rho_{\gamma\nu} = \delta_{\nu\gamma}$, $\rho_{mn} = 0$, and from

$$\sum_{n\delta(\Gamma)} [\mathcal{A}_{m\gamma,n\delta}(S)\ Y_{n\delta}(\lambda S) + \mathcal{B}_{m\gamma,n\delta}(S)\ Z_{n\delta}(\lambda S)]$$
$$= \omega(\lambda\Gamma S)\sum_{n\delta(\Gamma)} \mathcal{D}_{m\gamma,n\delta}\ Y_{n\delta}(\lambda S)$$

$$\sum_{n\delta(\Gamma)} [\mathcal{A}^{*}_{m\gamma,n\delta}(S)Z_{n\delta}(\lambda S) + \mathcal{B}^{*}_{m\gamma,n\delta}(S)Y_{n\delta}(\lambda S)$$
$$= -\omega(\lambda\Gamma S)\sum_{n\delta(\Gamma)} \mathcal{D}^{*}_{m\gamma,n\delta}Z_{n\delta}(\lambda S) \tag{II-14}$$

we obtain

$$\omega_\lambda Y_{m\gamma} = \omega_{m\gamma} Y_{m\gamma} + \sum_{n\delta} [(2V_{m\delta\gamma n} - V_{m\delta n\gamma}) Y_{n\delta} + (2V_{mn\gamma\delta} - V_{mn\delta\gamma}) Z_{n\delta}] \tag{II-15}$$

$$-\omega_\lambda Z_m = \omega_{m\gamma} Z_{m\gamma} + \sum_{n\delta} [(2V_{m\delta\gamma n} - V_{m\delta n\gamma}) Z_{n\delta} - (2V_{mn\gamma\delta} - V_{mn\delta\gamma}) Y_{n\delta}] \tag{II-16}$$

Substitution of (II-13), (II-14), and (II-15) into equation (II-11) results with

$$<0|\hat{\vec{m}}|\lambda> = \frac{\omega_\lambda}{i} <0|\hat{\vec{r}}|\lambda> \tag{II-17}$$

making the three forms of the oscillator strength be equal. This is simply the result derived by Harris.

Now equation (II-11) will be extended to the HRPA. From the HRPA equations[8]

$$\begin{aligned}\omega_{m\gamma} Y_{m\gamma} = {} & \omega_\lambda Y_{m\gamma} + \omega_\lambda \sum_{n\delta} \delta_{mn} \rho^{(2)}_{\gamma\delta} Y_{n\delta} - \omega_\lambda \sum_{n\delta} \rho^{(2)}_{mn} \delta_{\gamma\delta} Y_{n\delta} \\ & - \sum_{n\delta} (2V_{m\delta\gamma n} - V_{m\delta n\gamma}) Y_{n\delta} - \sum_{n\delta} (2V_{mn\gamma\delta} - V_{mn\delta\gamma}) Z_{n\delta} \\ & + \frac{1}{2} \sum_{n} \omega_{m\gamma} \rho^{(2)}_{mn} Y_{n\gamma} + \frac{1}{2} \sum_{n} \omega_{n\gamma} \rho^{(2)}_{mn} Y_{n\gamma} - \frac{1}{2} \sum_{\delta} \omega_{m\gamma} Y_{m\delta} \rho_{\gamma\delta} \\ & - \frac{1}{2} \sum_{\delta} \rho^{(2)}_{\gamma\delta} \omega_{m\delta} Y_{m\delta} - \sum_{n\delta} \delta_{\gamma\delta} \mathcal{J}_{mn} Y_{n\delta} + \sum_{n\delta} J_{mn} \mathcal{J}_{\gamma\delta} Y_{n\delta} \\ & - \sum_{n\delta} S_{m\gamma;n\delta} Z_{n\delta} - \sum_{n\delta} X_{m\gamma,n\delta} Z_{n\delta}\end{aligned} \tag{II-18}$$

$$-\omega_{m\gamma} Z_{m\gamma} = \sum_{n\delta} (2V_{m\delta\gamma n} - V_{m\delta n\gamma}) Z_{n\delta} + \sum_{n\delta} (2V_{mn\gamma\delta} - V_{mn\delta\gamma})$$

$$+ \omega_{\lambda} Z_{m\gamma} + \omega_{\lambda} \sum_{n\delta} \delta_{mn} \rho^{(2)}_{\gamma\delta} Z_{n\delta} - \omega_{\lambda} \sum_{n\delta} \delta_{\gamma\delta} \rho^{(2)}_{mn} Z_{n\delta}$$

$$+ \sum_{n\delta} \delta_{\gamma\delta} [\mathcal{J}_{mn} - \frac{1}{2} \omega_{m\gamma} \rho^{(2)}_{mn} - \frac{1}{2} \omega_{n\gamma} \rho^{(2)}_{mn}] Z_{n\delta}$$

$$- \sum_{n\delta} \delta_{mn} [\mathcal{J}_{\gamma\delta} - \frac{1}{2} \omega_{m\gamma} \rho^{(2)}_{\gamma\delta} - \frac{1}{2} \omega_{m\delta} \rho^{(2)}_{\gamma\delta}] Z_{n\delta}$$

$$+ \sum_{n\delta} S_{m\gamma,n\delta} Y_{n\delta} + \sum_{n\delta} X_{m\gamma,n\delta} Y_{n\delta} \qquad \text{(II-19)}$$

where

$$A_{m\gamma,n\delta} = A^{o}_{m\gamma,n\delta}(0) + \delta_{\gamma\delta}[\mathcal{J}_{mn} - \frac{1}{2} (\varepsilon_m + \varepsilon_n - 2\varepsilon_\gamma) \rho^{(2)}_{mn}]$$

$$- \delta_{mn}[\mathcal{J}_{\gamma\delta} - \frac{1}{2}(2\varepsilon_m - \varepsilon_\gamma - \varepsilon_\delta) \rho^{(2)}_{\gamma\delta}]$$

$$B_{m\gamma,n\delta} = B^{o}_{m\gamma,n\delta}(0) + S_{m\gamma,n\delta} + X_{m\gamma,n\delta}(0)$$

$A^{o}_{m\gamma,n\delta}(0)$ = matrix element of RPA above

$B^{o}_{m\gamma,n\delta}(0)$ = matrix element of RPA above

$$S_{m\gamma,n\delta} = - \sum_{p\mu} \{V_{m\mu\delta p} C_{p\mu,n\gamma}(0) + V_{n\mu\gamma p} C_{p\mu,m\gamma}(0)\}$$

$$\mathcal{J}_{mn} = - \frac{1}{2} \sum_{q\mu\nu} \{V_{mq\mu\nu} C^{*}_{n\mu,q\nu}(0) + V_{\mu\nu nq} C_{m\mu,q\nu}(0)\}$$

$$\mathcal{J}_{\gamma\delta} = \frac{1}{2} \sum_{pq\nu} \{V_{pq\gamma\nu} C^{*}_{p\delta,p\nu}(0) + V_{\delta\nu pq} C_{p\gamma,q\nu}(0)\} \qquad \text{(II-20)}$$

$$X_{m\gamma,n\delta}(0) = \sum_{\mu\nu} V_{\mu\nu\gamma\delta} C_{m\mu,n\nu}(0) + \sum_{pq} V_{mnpq} C_{p\gamma,q\delta}(0)$$

$$- \sum_{p\mu} \{V_{m\mu p\delta} C_{p\gamma,n\mu}(0) + V_{n\mu p\gamma} C_{p\delta,m\mu}(0)\}$$

Substitution of (II.18) and (II-19) into (II-11) and dropping all terms quadratic and higher in the correlation coefficients except terms of the type $\omega_{ij}C^2$ to yield a consistent order in perturbation theory results with

$$<0|\hat{\vec{m}}|\lambda> = \frac{\omega_\lambda}{i} <0|\hat{\vec{r}}|\lambda> + \text{O.T.} \tag{II-21}$$

where

$$\begin{aligned}
\text{O.T.} = \sqrt{2}\,(\tfrac{1}{i}) \sum_{m\gamma} \vec{r}_{m\gamma}[(\omega_\lambda \sum_{n\delta} \delta_{mn}\, \rho^{(2)}_{\gamma\delta}\, Y_{n\delta} \\
- \omega_\lambda \sum_{n\delta} \delta_{\gamma\delta}\, \rho^{(2)}_{mn}\, Y_{n\delta} + \tfrac{1}{2} \sum_{n\delta} \omega_{m\gamma}\, \rho^{(2)}_{mn}\, Y_{m\delta}\, \delta_{\gamma\delta} \\
+ \tfrac{1}{2} \sum_{n\delta} \omega_{m\delta}\, \rho^{(2)}_{mn}\, \delta_{\gamma\delta} Y_{n\delta} - \tfrac{1}{2} \sum_{n\delta} \delta_{mn}\omega_{m\gamma}\, Y_{n\delta}\, \rho^{(2)}_{\gamma\delta} \\
- \tfrac{1}{2} \sum_{n\delta} \omega_{m\delta}\, \rho^{(2)}_{\gamma\delta}\, Y_{n\delta}\, \delta_{mn} - \sum_{n\delta} \delta_{\gamma\delta}\, \mathcal{T}_{mn}\, Y_{n\delta} \\
+ \sum_{n\delta} \delta_{mn}\, \mathcal{T}_{\gamma\delta}\, Y_{n\delta} - \sum_{n\delta} S_{m\gamma,n\delta}\, Z_{n\delta} - \sum_{n\delta} X_{m\gamma,n\delta} Z_{n\delta} \\
+ \omega_\lambda \sum_{n\delta} \delta_{mn}\, \rho^{(2)}_{\gamma\delta}\, Z_{n\delta} - \omega_\lambda \sum_{n\delta} \delta_{\gamma\delta}\, \rho^{(2)}_{mn}\, Z_{n\delta} + \sum_{n\delta} \delta_{\gamma\delta}[T_{mn} \\
- \tfrac{1}{2}\, \omega_{m\delta}\, \rho^{(2)}_{mn} - \tfrac{1}{2}\, \omega_{n\gamma}\, \rho^{(2)}_{mn}]\, Z_{n\delta} - \sum_{n\delta} \delta_{mn}[T_{\gamma\delta} - \tfrac{1}{2}\, \omega_{m\gamma}\, \rho^{(2)}_{\gamma\delta} \\
- \tfrac{1}{2}\, \omega_{m\delta}\, \rho^{(2)}_{\gamma\delta}]\, Z_{n\delta} + \sum_{n\delta} S_{m\gamma,n\delta} Y_{n\delta} + \sum_{n\delta} X_{m\gamma,n\delta} Y_{n\delta}]
\end{aligned} \tag{II-22}$$

All of (II-22) are second order terms and hence are likely to be small.

Now if $\omega_\lambda Y_{n\delta}$ and $\omega_\lambda Z_{n\delta}$ are replaced by their values in (II-18) and (II-19) and higher order terms dropped, all expressions involving ω's in (II-22) cancel, provided

$$\sum_{m\gamma} \vec{r}_{m\gamma} \sum_{n\delta} \omega_{m\delta}\, \rho^{(2)}_{mn}\, \delta_{\gamma\delta}\, Y_{n\delta} \simeq \sum_{m\gamma} \vec{r}_{m\gamma} \sum_{n\delta} \omega_{n\delta}\, \delta_{\gamma\delta}\, \rho^{(2)}_{mn}\, Y_{n\delta} \qquad \text{(II-23)}$$

$$\sum_{m\gamma} \vec{r}_{m\gamma} \sum_{n\delta} \omega_{n\delta}\, \delta_{mn} \rho^{(2)}_{\gamma\delta}\, Y_{n\delta} \simeq \sum_{m\gamma} \vec{r}_{m\gamma} \sum_{n\delta} \omega_{m\gamma}\, \rho^{(2)}_{\gamma\delta}\, Y_{n\delta}\, \delta_{mn}$$

In addition, from calculations on N_2 and CO^9 the X terms are small and can be ignored. The terms remaining

$$\begin{aligned} \text{T.R.} = \sqrt{2}\,(\tfrac{1}{1})\, \Big\{ & \tfrac{1}{2} \sum_{\substack{q\mu\nu \\ mn\gamma}} \vec{r}_{m\gamma} (V_{mq\mu\nu} C^{*}_{n\mu,q\nu} + V_{\mu\nu nq} C_{m\mu,q\nu}) \\ & - \tfrac{1}{2} \sum_{\substack{pq\nu \\ m\gamma\delta}} \vec{r}_{m\gamma} (V_{pq\gamma\nu} C^{*}_{p\delta,q\nu} + V_{\delta\nu pq} C_{p\gamma,q\nu}) \\ & - \sum_{\substack{p\mu \\ n\delta, m\gamma}} \vec{r}_{m\gamma} (V_{m\mu\delta p} C_{p\mu,n\gamma} + V_{n\mu\gamma p} C_{p\mu,m\delta}) \Big\} (Y_{n\delta} - Z_{n\delta}) \end{aligned} \qquad \text{(II-24)}$$

do not in general cancel. However, the relatively good agreement between theoretical predictions based on the length formulation and experiment indicate that the effects are probably small. It would be interesting to evaluate the magnitude of these terms.

The methodology for including double excitation theory in order to compare forms (I-1) - (I-3) is exactly the same. It can easily be shown that the additional effects will be proportional to $Y^{(2)}$ $C^{mn}_{\gamma\delta}$ and thus very small.

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PROPOSITION III

Abstract

Partitioning techniques are discussed for bound state configuration interaction calculations. A simple partitioning technique is described which could provide a straightforward approach for calculating total energies. This method could also be used as a scheme to select important configurations for a more complete treatment.

Proposition III. Partitioning Techniques in Configuration Interaction Calculations

Partitioning techniques were first described by Löwdin and others in the late 1940's.[1] Since then there has been considerable interest in the method.[2,3] The basic idea is to divide a linear set of equations so that the subspace of interest is separate. Hence in a large eigenvalue problem we can concentrate on the part of the space of importance in a particular problem. Schemes have been developed for calculating the coupling correction of one part of the space to another without using large amounts of computer time or core.[3] Since in many cases of interest the coupling correction is small, perturbative schemes seem promising both as a quick, simple method for calculating eigenvalues and eigenvectors, and as a way to determine a reliable partition where the correction is treated only approximately.

In this proposition the partitioning technique is described. I propose developing a similar scheme for configuration interaction calculations and performing a series of calculations on simple systems such as He and H_2 to test its efficacy.

It may be possible to use this partitioning technique to test the importance of certain configurations in a calculation. A simple partitioned CI is initially calculated. Those configurations which contribute to the energies perturbatively by more than a certain amount are included in the main matrix in the final calculation. All remaining configurations are treated perturbatively.

In a configuration interaction calculation the following equations are solved for the energy E and the eigenvectors $\{C\}$:

$$\underset{\sim}{H}\,\underset{\sim}{C} = \underset{\sim}{E}\,\underset{\sim}{C} \tag{III-1}$$

$$H_{ij} = \langle i|H|j\rangle \tag{III-2}$$

$$= \int \Phi^{*}\, \hat{H}\Phi_{j}\, d\tau \tag{III-3}$$

$\hat{H}$ is the Hamiltonian and $\{\Phi\}$ is a complete orthonormal set which spans the vector space of interest. The wavefunction Ψ_{ℓ} is

$$\Psi_{\ell} = \sum_{k} C_{k\ell}\, \Phi_{k} \tag{III-4}$$

For many problems in atomic and molecular quantum mechanics the vector space is extremely large so that the space must be truncated, e.g., in a configuration interaction calculation where $\{\Phi\}$ is truncated to be a Hartree-Fock SCF wavefunction and all single and double excitations.

Suppose there are subsets $\{A\}$ and $\{B\}$ of $\{\Phi\}$ where $\{A\}$ is a part of the space of special interest or importance and $\{B\}$ is the remainder, e.g., in a CI ground state calculation on a system with a closed shell SCF ground state $\{A\}$ could include the SCF state and selected double excitations, and $\{B\}$ could be the remaining double and some quadruple excitations.

Equation (1) can be symbolically rewritten

$$\langle A|\hat{H}|A\rangle\ C_A + \langle A|\hat{H}|B\rangle\ C_B = E\ C_A \qquad \text{(III-5)}$$

$$\langle B|\hat{H}|A\rangle\ C_A + \langle B|\hat{H}|B\rangle\ C_B = E\ C_B \qquad \text{(III-6)}$$

Solving (6) for C_B we obtain

$$C_B = -\ \langle B|(\hat{H}-E)^{-1}|B\rangle\ \langle B|\hat{H}|A\rangle\ C_A \qquad \text{(III-7)}$$

Using Eq. (7) in Eq. (5) results with

$$\langle A|\hat{H}|A\rangle\ C_A - \langle A|\hat{H}|B\rangle\ \langle B|(H-E)^{-1}|B\rangle\ \langle B|\hat{H}|A\rangle\ C_A = E\ C_A \qquad \text{(III-8)}$$

or

$$(\underset{\sim}{H} + \underset{\sim\sim}{\Delta H})\ \underset{\sim}{C}_A = \underset{\sim}{E}_A\ \underset{\sim}{C}_A \qquad \text{(III-9)}$$

where

$$\Delta H_{ij} = -\sum_{k\ell} \langle i|\hat{H}|k\rangle\ \langle k|(\hat{H}-E_A)^{-1}|\ell\rangle\ \langle \ell|\hat{H}|j\rangle \qquad \text{(III-10)}$$

$|i\rangle$ and $|j\rangle$ are members of $\{A\}$ and $|k\rangle$ and $|\ell\rangle$ are members of $\{B\}$.

Equation (9) is a smaller eigenvalue problem than Eq. (1). However, $\underset{\sim\sim}{\Delta H}$ contains the inverse of a matrix of $\{B\}$. For large configuration interaction calculations this matrix inversion can involve large amounts of computer time and core. Furthermore $\underset{\sim\sim}{\Delta H}$ contains E so that usually an iterative scheme must be used to solve Eq. (9). An advantage of using (9) is that only the $\{A\}$ part of the space eigenvalues and eigenvectors is calculated. For many problems this subspace is the most important so that $\underset{\sim\sim}{\Delta H}$ may be calculated by an approximate scheme.

For simplicity consider the ground state of a system that can be well described by the Hartree-Fock SCF closed shell ground state. A finite basis set expansion yields a set of basis states. We can consider for example in {A} the Hartree-Fock single determinant state and selected double excitations. In {B} we include remaining double, quadruple, etc. excitations. Instead of Eq. (1),for simplicity we solve

$$(\underset{\sim}{H}-\underset{\sim}{E}_0)\underset{\sim}{C} = (\Delta \underset{\sim}{E})\ \underset{\sim}{C} \qquad \text{(III-11)}$$

where E_0 is the SCF energy, and

$$\Delta E = \underset{\sim}{E} - \underset{\sim}{E}_0 \qquad \text{(III-12)}$$

The equations for the matrices are given by the standard formulas.[5] Equation (10) becomes

$$\Delta(H-E_0)_{ij} = \sum_{k\ell} \langle i|(\hat{H}-E_0)|k\rangle \ \langle k|(\hat{H}-E_0-\Delta E_A)^{-1}|\ell\rangle \ \ \langle \ell|(\hat{H}-E_0)|j\rangle \qquad \text{(III-13)}$$

Since, for example, the number of quadruple excitations is large, the inverse of $\underset{\sim}{H} - \underset{\sim}{E}_0 - \underset{\sim\sim}{\Delta E}_A$ is large and may involve considerable computer time.

We write

$$\underset{\sim}{H} - \underset{\sim}{E}_0 - \underset{\sim\sim}{\Delta E}_A = \underset{\sim}{F}_1 - \underset{\sim}{G}_1 \qquad \text{(III-14)}$$

where $\underset{\sim}{F}_1$ is the on diagonal part of $\underset{\sim}{H} - \underset{\sim}{E}_0 - \underset{\sim\sim}{\Delta E}_A$, and $\underset{\sim}{G}_1$ is the off-diagonal matrix. Equation (14) can also be written

$$\underset{\sim}{H} - \underset{\sim}{E_o} - \Delta \underset{\sim}{E_A} = \underset{\sim}{F_2} - \underset{\sim}{G_2} \qquad \text{(III-15)}$$

where $\underset{\dagger}{F_2}$ is the on diagonal matrix of orbital energies and $\Delta \underset{\sim}{E_A}$, and $\underset{\sim}{G_2}$ is everything else. Equations (14) and (15) are combined

$$\underset{\sim}{H} - \underset{\sim}{E_o} - \Delta \underset{\sim}{E_A} = \underset{\sim}{F} - \underset{\sim}{G} \qquad \text{(III-16)}$$

where

$$\begin{pmatrix} \underset{\sim}{F} \\ \\ \underset{\sim}{G} \end{pmatrix} = \begin{pmatrix} \underset{\sim}{F_1} \\ \\ \underset{\sim}{G_1} \end{pmatrix} \text{ or } \begin{pmatrix} \underset{\sim}{F_2} \\ \\ \underset{\sim}{G_2} \end{pmatrix} \qquad \text{(III-17)}$$

$$(\underset{\sim}{F} - \underset{\sim}{G})^{-1} = \underset{\sim}{F}^{-1} + \underset{\sim}{F}^{-1} \underset{\sim\sim}{GF}^{-1} + \underset{\sim}{F}^{-1} \underset{\sim\sim}{GF}^{-1} \underset{\sim\sim}{GF}^{-1} + \cdots \qquad \text{(III-18)}$$

Since in both Eq. (14) and Eq. (15) F is diagonal, F^{-1} is diagonal. In the case of Eq. (15) for quadruples

$$\underset{\sim}{F_2}^{-1} = \left(\frac{1}{\varepsilon_m + \varepsilon_n + \varepsilon_p + \varepsilon_q - \varepsilon_\gamma - \varepsilon_\nu - \varepsilon_\eta - \varepsilon_\rho - \Delta E_A}\right) \delta_{k\ell} \qquad \text{(III-19)}$$

where k and ℓ are quadruple excitations out of the Hartree-Fock ground state,

$$\left| \begin{matrix} m\ n\ p\ q \\ \gamma\ \nu\ \eta\ \rho \end{matrix} \right. > \ ;$$

ε is the orbital energy, m,n,p,q are particles, and γ,ν,η,ρ are holes. For $\underset{\sim}{F_1}$ Eq. (19) is modified by interaction matrix elements in the denominator. Equations (18) and (19) are similar to equations of many-body perturbation theory[6] where the Green's function is expanded in terms of the free particle Green's function and the two-body interactions.

If Eq. (18) is truncated after the first term, Eq. (13) becomes for quadruple excitations

$$\Delta(H_{ij} - E_o\delta_{ij}) \simeq - \sum_k \frac{|<i|(\hat{H}-E_o)|k>|^2}{(\varepsilon_m + \varepsilon_n + \varepsilon_p + \varepsilon_q - \varepsilon_\gamma - \varepsilon_\nu - \varepsilon_\eta - \varepsilon_\rho - \Delta E_A + \mathcal{U}_{12})} \tag{III-17}$$

where $\mathcal{U}_{12}$ is zero if Eq. (15) is used and is interaction matrix elements if Eq. (14) is used. Similar equations are used for double excitation mixing corrections in the equations of motion method including double excitations[4,7] and equations of motion method for ionization potentials.[8]

If {A} contains N_1 configurations and {B} contains N_2 configurations, an unpartitioned CI calculation involves the diagonalization of an $(N_1 + N_2) \times (N_1 + N_2)$ matrix. Using this partitioning technique an $N_1 x N_1$ matrix is diagonalized. The total number of elements stored in the unpartitioned case is $(N_1 + N_2)(N_1 + N_2 + 1)/2$ and in the partitioned case $N_1(N_1+1)/2 + \frac{N_1N_2}{2} + N_2$. Thus there can be considerable savings in computer costs using this scheme.

Equation (17) is much less complicated than the actual inversion of $(\underset{\sim}{H} - \underset{\sim}{E}_o - \underset{\sim}{\Delta E}_A)$ in Eq. (13). However, the assumption that $(\underset{\sim}{H} - \underset{\sim}{E}_o - \underset{\sim\sim}{\Delta E}_A)$ is diagonal may not be a reasonable approximation. It would be interesting to test the validity of Eq. (17) for several small molecules for both approximations Eq. (14) and Eq. (15) using selected doubles and quadruples, and to compare the result with the unpartitioned CI containing the same configurations. If Eq. (17) or a similar partitioning scheme can be used there may be considerable savings in computer costs for configuration interaction calculations. Similar methods have been independently proposed by Segal.[9]

An additional advantage of the partitioning scheme, Eq. (17), is that the method can be used as a test to determine which configurations are the most important and must be included in {A} . Again, we will use the example of the ground state of a closed shell SCF system. Initially {B} contains selected doubles and quadruples, and {A} contains the ground state and certain doubles.

Equation (9) is

$$(\underset{\sim}{H} + \underset{\sim\sim}{H} - \underset{\sim}{E}_o)\ \underset{\sim}{C}_A \ = \ (\underset{\sim\sim}{\Delta E}_A)\ C_A \qquad \text{(III-18)}$$

From perturbation theory

$$\Delta E_A^{(1)} \ = \ \tilde{C}_A^{(0)}\ \underset{\sim\sim}{\Delta H}\ C_A^{(0)} \qquad \text{(III-19)}$$

where

$$(\underset{\sim}{H} - \underset{\sim}{E}_o)\ \underset{\sim}{C}_A^{(0)} = \underset{\sim\sim}{\Delta E}_A^{(0)}\ \underset{\sim}{C}_A^{(0)} \qquad \text{(III-20)}$$

Equation (20) is an eigenvalue problem which is solved exactly. The energy change $\Delta E_A^{(1)}$ is determined from Eq. (19) using the scheme in Eq. (16) where ΔE_A is approximated by $\Delta E_A^{(0)}$. Two new sets {A'} and {B'} are selected. The new {A'} contains {A} and all configurations for which $|\Delta E_A^{(1)}|$ for that configuration is larger than a certain value. {B'} contains all remaining configurations. A partitioned CI is calculated using new sets {A'} and {B'} . ΔE_A is determined iteratively.

The partitioning technique in configuration interaction is briefly examined and discussed. An approximation scheme is developed, and it is proposed to use the scheme for a series of cases to test its validity. As shown in Eq. (19), the technique can easily be used to select the configurations to be used for an unpartitioned configuration interaction calculation.

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PROPOSITION IV

MOLECULAR CONTRACTIONS OF GAUSSIAN BASIS SETS

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MOLECULAR CONTRACTIONS OF GAUSSIAN BASIS SETS

Abstract

Two-body three and four center integrals in molecules are more easily calculated using Gaussian functions than Slater functions. However, Gaussian basis sets do not describe the electron density as well as Slater functions. Consequently, larger basis sets of Gaussians are required for an equivalent description. To reduce the size of subsequent self-consistent field (SCF) or configuration interaction (CI) calculations, various contraction schemes have been developed. Usually these methods involve a contraction of the Gaussian primitives to approximate the atomic orbitals from an SCF calculation. Several new contraction schemes are discussed. These contractions involve a simple molecular SCF calculation. The contraction coefficients for atoms in a certain functional group are the coefficients which approximate the optimal orbitals for that group. It is anticipated that better energies and properties can be calculated using these sets; or, equivalently, smaller basis sets may be used in many calculations.

To obtain molecular orbitals in a self-consistent field (SCF) calculation for molecules, a finite basis set expansion is used,

$$\phi_i = \sum_{\eta} C_{\eta i} \chi_{\eta} \qquad \text{(IV-1)}$$

where ϕ_i is the molecular orbital, $\{\chi_\eta\}$ are the basis functions, and $\{C\}$ are the expansion coefficients. The best approximation to the Hartree-Fock molecular orbitals is obtained from[1]

$$F\phi_i = \varepsilon_i \phi_i \qquad \text{(IV-2)}$$

where F is the Fock Operator. Equation (IV-2) is solved iteratively since F contains integrals involving the orbitals.

A reasonable choice for the basis functions $\{\chi\}$ are Slater functions centered on the atoms of the form

$$\chi_\eta^s = N_\eta^s r^{n-1} \exp(-\rho_{s\eta} r) \qquad \text{(IV-3)}$$

n is the principal quantum number, N^s is a normalization constant, and ρ_s is an exponent which may depend on the atom and the problem to be solved.

Two-body three and four center integrals of the form

$$\int \chi_i^*(1)\, \chi_j^*(2)\, \frac{1}{r_{12}}\, \chi_k(1)\, \chi_\ell(2)\, d\tau_1 d\tau_2 \qquad \text{(IV-4)}$$

are evaluated in solving Eq. (IV-2). The calculation of these integrals for large basis sets can involve large amounts of computer time.[2] Boys[3] proposed using Gaussian functions

$$\chi_\eta^g = N_\eta^g\, r^{n-1} \exp(-\rho_{g\eta} r^2) \qquad \text{(IV-5)}$$

These functions simplify considerably the evaluation of two-body integrals. Since a Gaussian function lacks a cusp at $r = 0$, the electron density near a nucleus is not described as well as with a Slater. Hence Gaussian basis sets several times the size of Slater basis sets are often needed to attain the same energy.[4] Thus the computational advantages of Gaussians are diminished, although not eliminated.

A further problem is that the large basis sets result with the diagonalization of large SCF matrices. Dunning[5] has shown that certain groups of basis functions can be grouped (contracted) together with fixed coefficients to reduce the size of the matrices. For example, basis composed of 9s primitive Gaussian functions and 5p primitive Gaussian functions is reduced to 4s and 3p contracted Gaussian functions. These contraction coefficients are usually chosen to approximate an atomic SCF calculation using the primitive basis. The coefficient of each contracted Gaussian is variationally determined in a SCF calculation. Although the SCF energies of molecules using contracted functions are slightly higher for molecules than using equivalent sized Slater basis, a few of the primitive Gaussian functions in the valence space are allowed to vary freely so that the bonding region should be described fairly well.

Empirically many properties of larger molecules can be viewed as cumulative effect of many local contributions.[6] For example, $n \rightarrow \pi^*$ transitions are observed in homologous series of molecules containing carbonyl groups. Similar results are seen for dipole moments, reactivities, bond energies, and ionization potentials. A better primitive

Gaussian contraction would take into account the effects of bonding and possibly nearest neighbor interactions. Such optimal contractions for different functional groups and atoms are calculated for a representative small molecule, e.g., for carbonyl CO, H_2CO, or $(CH_3)_2CO$. The resultant contraction coefficients are obtained from the invariant atomic orbital method of Cusachs and Aldrich[7] or some other similar localization scheme.[8] The functional contraction coefficients are then used in other calculations for the group or atom, e.g., transition metal carbonyls. This method will result in better energies and charge densities. Smaller contracted basis sets may be used than when atom optimized contracted sets are used. Functional contraction coefficients may be obtained with little expense, using molecular wave functions described in the literature.

In the remainder of this paper, we will briefly describe the segmented contraction scheme of Dunning[5] and the general method of Raffenetti.[9] Then we will discuss how to obtain contraction coefficients from the invariant atomic orbital method of Cusachs and Aldrich.[7]

In a segmented contraction,[5] an SCF calculation is done for the ground state of the atom using the completely uncontracted Gaussian primitive basis. The exponents in Eq. (5) are obtained from an optimization scheme for the uncontracted basis set, e.g., see reference 4. The output vectors for a certain symmetry orbital are examined and a reasonable initial division of the primitive space into a fixed number of contracted functions is made. For example, a 9s primitive space may be divided into a (6s, 1s, 2s) contracted space. The coefficients of the primitives within each contracted function are fixed. They are usually obtained by simply selecting the coefficients from the atomic function and renormalizing. The partitioning of the primitive space is varied keeping the number of contracted functions fixed. No primitive is used in more than one function. The partition with the energy closest approaching the SCF energy of the uncontracted set is used for later molecular calculations. Dunning[5,10] has published a series of papers describing the method in detail and listing contraction coefficients.

Raffenetti's[9] general contraction scheme is physically more appealing. The restriction of not using a primitive in more than one contracted function is dropped. For first row atoms all primitives are used in a contraction for the 1s, 2s, and 2p functions with the fixed coefficients from an SCF atomic ground state calculation. In addition, other functions are included which are either the virtual orbitals from the atomic calculation or the most diffuse Gaussians of the set. Thus there is a rather good atomic description of the SCF 1s, 2s, and 2p functions. Dunning's segmented scheme required only minor modifications to the readily available POLYATOM series of programs. However, to use Raffenetti's method using POLYATOM is very expensive or requires a new integrals program.

Both the segmented and general contractions are optimized for the ground state SCF of an atom. The valence orbitals can change considerably upon bond formation.[11] Even core electron binding energies change as much as 10 eV depending on the molecular environment.[12]

Subtle changes in the electron charge density may be important for the calculation of one-body properties[7], and configuration interaction calculations where molecular orbitals based on atomic contractions are used may not as rapidly converge. Bearing these considerations in mind, a simple yet effective procedure is to optimize contractions for molecules and not atoms. It may be possible to choose an optimal set of contraction coefficients for a given atom in a molecule or for a given functional group. In the latter case we retain our intuitive ideas about molecules and the chemical bond.

The coefficients are found by the method of Cusachs and Aldrich[7] which they used to obtain invariant atomic orbitals by radial moment analysis of accurate molecular orbitals. This scheme differs from theirs in that we do not construct optimal atomic orbitals but instead use the coefficients directly for an optimal molecular contraction. For simplicity, we describe a segmented contraction scheme. Extensions to general schemes are obvious. Finally, a simple method is proposed which should yield good molecular contractions at minimal cost.

A simple prototype molecule or molecules is selected and a completely uncontracted LCAO SCF calculation is performed. The contraction scheme is chosen. It may be segmented, general, or some combination. The primitives of a contracted group are renormalized for each molecular orbital. These new coefficients are averaged over all molecular orbitals with the weighting function the old normalization integral. Thus optimal contraction coefficients for atoms in molecules are easily obtained.

For general or combined contractions molecular orbitals that are primarily inner shell are separated from the other orbitals. These are then used to construct optimal 1s contractions. The most diffuse primitive Gaussians are included in the contracted set and are allowed to vary freely.

We can use the contraction coefficients for atoms in a certain functional group in more complicated molecules. The molecular environment will thus be better described and we expect better theoretical one-body properties and energies as well as better CI convergence.

A simple, straightforward procedure for obtaining contraction coefficients is to expand the invariant atomic orbitals of Cusachs and Aldrich[7] in terms of Gaussians using

$$\rho_{gi} = (n_s \rho_s)^2 \alpha_i \qquad \text{(IV-6)}$$

where α_i are given by Huzinaga.[4] Analogously, a comparison could be made between calculated r^k moments and a Gaussian expansion to determine the contraction coefficients. Again valence space primitive Gaussians are included in the contracted space and allowed to vary freely.

Several basis set contraction schemes are proposed which would more optimally describe the molecular environment than currently used methods based on atomic SCF calculations. The resulting contraction coefficients can be used for functional groups or atoms in more complicated molecules.

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PROPOSITION V

SOME ASPECTS OF SHAKEUP STATES IN PHOTOELECTRON SPECTROSCOPY

PROPOSITION V

Abstract

A new method is proposed for predicting relative energies and intensities of shakeup satellite structure in photoelectron spectroscopy. Combinational states are shown to be weakly coupled to simple ionization. Hence, these states most likely are not observable. For closed shell ground state atoms and molecules simple shakeup states are actually twin peaks corresponding to the two possible ways to couple three unpaired electrons to doublet states. This satellite structure may be observable in C_2O_3. A calculation is proposed to clarify the spectra of CuO and Cu_2O.

In photoelectron spectroscopy a photon ionizes an atom or molecule.[1] The intensity of the scattered electrons is measured as a function of kinetic energy and possibly angle. In this proposition we will not be concerned with the latter. For valence electrons the photon source is often the vacuum UV or He(I) resonance line at 21.22 eV or the He(II) resonance line at 40.8 eV.[1] The aluminum $K\alpha$ line at 1487 eV and the magnesium $K\alpha$ line at 1254 eV are often used to study both core and valence electrons.[2]

If the photon has sufficiently high energy the molecule may simultaneously excite or ionize in addition to the initial ionization. This phenomenon is observed as low intensity peaks ("satellites") in the electron spectra at electron energies lower (or binding energies higher) than the main peaks. The excitation process to bound states accompanying ionization is called "shakeup", and excitation to a continuum state accompanying ionization is "shakeoff." Progress has been made correlating shakeup and shakeoff states to molecular structure.[2-4]

In this proposition a few aspects of shakeup states in photoelectron spectroscopy are examined. Most of the examples will be for photoelectron spectroscopy of the inner shell. The ejected electron will be assumed to be of high energy so that ejected electron-ion interactions can be safely ignored. Similar ideas are of course applicable to photoelectron spectroscopy of the valence shell.

We propose a new method for the calculation of positions and intensities of shakeup states and briefly discuss a similar method for

Auger spectroscopy. We then examine the predictions of shakeup energies by both relaxed ion virtual space methods and ordinary bound state excitation energies. The fact that closed shell photoelectron spectra should yield two doublet shakeup states at very close energies is pointed out. The possibility of observing combinational states is discussed. Finally we note the feasibility of doing large scale calculations on transition metal compounds to resolve such questions as the existence of shakeup states in d^{10} compounds like Cu_2O.

The theoretical method is simple and involves the diagonalization of relatively small matrices. We solve

$$\langle 0|\ \{\delta O_\lambda,\ H,\ O_\lambda^+\}|0\rangle = \omega_\lambda \langle 0|\{\delta O_\lambda,\ O_\lambda^+\}\ |0\rangle \qquad \text{(V-1)}$$

where ω_λ is the photoelectron binding energy and O_λ^+ is the ionization operator composed of a linear combination of electron removal operators, electron removal with simple excitation and deexcitation operators, and possibly electron removal with double excitation and deexcitation operators. We include in O_λ^+ only operators for which a given electron, ν , is removed, except for simple electron ejection where electrons in any orbital including virtuals may be removed. This effectively limits matrix size in diagonalization. There are many combinational operators (electron removal with double excitation) so that they are not included, included perturbatively, or selectively diagonalized in the main matrix. For simplicity they will not be considered here at present.

Equation (V-1) is evaluated over a restricted Hartree-Fock ground state and no correlation coefficients are explicitly evaluated

$$\begin{pmatrix} \underset{\sim}{\mathcal{A}} & \underset{\sim}{\mathcal{A}}^{(1,2)} & \underset{\sim}{\mathcal{B}}^{(1,2)} \\ \tilde{\underset{\sim}{\mathcal{A}}}^{(1,2)} & \underset{\sim}{\mathcal{A}}^{(2,2)} & 0 \\ \tilde{\mathcal{B}}^{(1,2)} & 0 & -\underset{\sim}{\mathcal{B}}^{(2,2)} \end{pmatrix} \begin{pmatrix} Y \\ Y^{(2)} \\ Z^{(2)} \end{pmatrix} =$$

$$\omega_\lambda \begin{pmatrix} Y \\ Y^{(2)} \\ Z^{(2)} \end{pmatrix} \qquad \text{(V-2)}$$

Matrix elements in Eq. (V-2) are given elsewhere.[6] Terms in $\underset{\sim}{\mathcal{A}}$ corresponding to electron removal from a particle level and $\underset{\sim}{\mathcal{B}}$ terms are due to electron correlation in the molecular ground state. Relaxation effects are in $\underset{\sim}{\mathcal{A}}$, $\underset{\sim}{\mathcal{A}}^{(1,2)}$, and $\underset{\sim}{\mathcal{A}}^{(2,2)}$

In actual calculations Eq. (V-2) is block diagonalized by symmetry and for small molecules in basis sets of double zeta quality, most symmetry matrices will be less than 50x50.

Intensities of shakeup peaks relative to the main peak in the dipole approximation are given by

$$\left| \frac{<\psi(N)\ |\vec{r}|\ \psi^{S}_{\lambda'}(N-1)\ u(\vec{r})>}{<\psi(N)|\vec{r}|\psi_{\lambda}(N-1)\ u(\vec{r})>} \right|^2 \qquad \text{(V-3)}$$

where $\psi(N)$ is the ground state, $\psi^{S}_{\lambda'}(N-1)$ is a shakeup state, $\psi_{\lambda}(N-1)$ is the ionic state corresponding to the main peak, and $u(\vec{r})$ is a free electron plane wave state. Equation (V-3) is rewritten

$$P_s \simeq |<HF|\ c_\nu\ O^{S^+}_{\lambda'}\ |HF>|^2 \qquad \text{(V-4)}$$

This is simply the probability that there is a λ' shakeup peak relative to the main photoelectron peak. This equation is identical to the probability of observing a peak in the sudden approximation.[5] We do not consider electron ionization occurring before excitation but regard the processes as simultaneous.

Since this proposition is not intended to be a detailed theoretical examination of Eqs. (V-1)-(V-4) but rather applications oriented, it is pointed out that similar methods can be used for Auger spectroscopy. Rowe's equations of motion for Bose-like transfer operators[7] are used instead of Eq. (V-1). O_λ^+ operators now contain principally linear combinations of two electron removal operators and two electron removal with excitation and deexcitation. Again, all ejected electrons are assumed to have high energy.

Two methods are in general use for the calculation of shakeup state positions and intensities. We feel that the method outlined above is probably a better approximation. Here the other two models are briefly described.

A much used approach is to calculate wave functions and shakeup state energies for the relaxed ion. That is, the Hartree-Fock orbitals are allowed to relax after electron removal. The shake-up state wave function is then obtained from this relaxed wave function by the single transition approximation in which an electron is promoted to a single virtual orbital[8] or by single excitation CI.[9] In the former the excitation energy is some average energy difference between the virtual electron energy which moves in a potential appropriate for the N electron system and the core electron which moves in the ionic N-1 potential. Even the single electron CI[9] ignores ground state electron correlation and coupling between simple ionization and shakeup.

Another commonly used estimation of shakeup peak positions is to simply use bound state excitation energies.[3,4] This approximation assumes the sudden approximation is completely valid and no relaxation occurs upon electron removal.

For closed shell molecules all shakeup peaks are actually twin peaks due to the two possible doublet spin couplings of three electrons in different MO's. Of course, intensities by Eq. (V-4) may differ considerably. Preliminary calculations on N_2 at equilibrium geometry indicates that the splitting is usually on the order of 0-3 eV with most between 1-2 eV. Thus some observed satellites in photoionization[2] and complexities[8] in the spectra may be partially due to the twin satellite structure. For example, in the ESCA spectrum of C_3O_2 gas[2] there is a sharp satellite peak 7.9 ± 0.2 eV below the main C 1s peak. Smaller less distinct peaks are observable around 10 eV and 14 eV. The structure around 10 eV may be the other doublet spin state associated with the peak at 7.9 eV. More detailed theoretical investigation is obviously required. The complex structure in $(C_6H_6)_aCr$ between 5.7 eV and 30 eV may be partially due to overlapping doublets associated with the same transitions.[3]

Another consideration is the possibility of combinational states,[3] i.e., ionization with double excitation. Although such states are not forbidden in photoelectron spectroscopy, an examination of the most important coupling matrix element between single excitation and combinational states in Eq. (V-2) shows that the coupling involves only two-body interactions of the type $V_{\gamma\underline{\gamma}p\underline{p}}$ where γ and $\underline{\gamma}$ are holes and p and $\underline{p}$ are particles. These matrix elements should not be very large. Hence, the probability that an ion will result in combinational state upon photoionization is small from Eq. (V-4). The assignment of the shakeup band around 7 eV from the main Cr 2p peaks in the X-ray photoelectron spectra of $Cr(CO)_6$ as possibly a combination band[3] is probably not correct.

Finally, we discuss the applicability of this method to transition metal compounds and complexes. For example, the positions and intensities of the shakeup states related to the Cu 2p main peak in CuO and Cu_2O can be predicted. Experimentally off the shelf CuO and Cu_2O exhibit satellite structure relative to the Cu 2p peak. This is surprising for Cu_2O which has a d^{10} metal ion since satellite structure is predicted as ligand→metal 3d. That is, octahedral Cu^{I} ion has a configuration $(t_{2g})^6(e_g)^4$ so that ignoring correlation effects, there is no empty 3d orbital for the L→M charge transfer. The observed satellites disappear after heating the sample in vacuum for 20 min at $200^{o}C$ [10] and are hence most likely due to adsorbed high binding energy oxygen[10] or to CuO contamination.[12]

Pignataro et al.[3,4] predict that with the removal of an electron from a localized orbital the shakeup process is enhanced when the ionized electron is from an atom which is an acceptor in a charge transfer process. Hence, the structure observed by Schön[11] starting around 5 eV higher binding energy than the O 1s peaks in Cu_2O is probably M→L charge transfer.

To theoretically examine the spectra of CuO or CuO_2 using Eq. (V-1) - (V-4) requires large amounts of computer time and core. However, with rapidly developing computer technology, transition metal SCF calculations are no longer prohibitive.[13] Furthermore, pseudopotential techniques[4] have been recently developed to accurately replace the transition metal Ar core. Of course, for the latter photoelectron spectra of the metal inner shell could no longer be predicted. The use of Eq. (V-1) to Eq. (V-4) for CuO and CuO_2 should further elucidate the spectra, particularly the presence of absence of cuprous ion satellites and M → L transitions near ligand main peaks.

In this proposition we have proposed a new method to theoretically predict relative energies and intensities of shakeup satellites and Auger spectra. We emphasize that shakeup states arising from closed shell ionization are really twin states which can be as much as 3 eV apart. Combinational state coupling with simple electron removal is shown to be small, and hence these states are probably in most cases unobservable. We observe that structure around 535 eV in Cu_2O may be M → L charge transfer satellites, and propose a calculation to further elucidate CuO and Cu_2O spectra.

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