Energy-Shift Theory of Low-Lying Excited Electronic States of Molecules*

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The present research is directed toward understanding the low-lying excited electronic states of atoms and molecules. Such excited states play essential roles in atmospheric photochemistry, charge transfer processes, and chemical reaction dynamics. The excitation energies and oscillator strengths between these states and the ground state are the principal concerns of this investigation. A new theory, referred to as the energy-shift theory, is put forth as a means of directly calculating molecular electronic excitation spectra. Within this theory, four computationally tractable approximations are developed, two of which allow the use of experimental data on higher states to aid the calculations. The method is shown to have some advantages over other direct calculation schemes currently being used in this and other laboratories, the primary advantage being the separation of low- and high-energy excitations which arises naturally in the energy-shift formalism. The relation of this approach to Green's function theory is discussed.

INTRODUCTION

The theoretical study of molecular electronic excitation energies and oscillator strengths is important both in interpreting experimentally observed spectra and in predicting the photochemical behavior of molecules which have not been thoroughly examined by experiment. Until quite recently, the prediction of excitation energies and oscillator strengths required the calculation of the wavefunctions and energies of the individual states of interest. The excitation energy is then obtained as the difference of the two calculated energies, and the oscillator strength[1] is computed from the matrix element of the electric dipole operator between the wavefunctions of the two states. A serious disadvantage of this approach is that it requires a separate variational (or perturbation) calculation for each electronic state of interest. Moreover, large cancellation errors are likely to be introduced when the excitation energy is calculated as a difference of two numbers which are often quite similar. Finally, if one is interested only in predicting the transition properties of the molecule, e.g., oscillator strengths, dipole moment differences, and excitation energies, then much of the information contained in the individual wavefunctions is of no interest and adds only to the expense and time involved in the computation.

In hopes of overcoming some of the difficulties mentioned above, several chemists and physicists have recently begun to use and extend theories which were used previously by nuclear[2-14] and many-body[15-18] physicists to calculate transition properties of other systems. Two notable examples are the many-body Green's function (GF) method which has been exploited cleverly by Linderberg and Öhrn,[19-21] Reinhardt and Doll,[22] and Schneider, Taylor, and Yaris,[23] and the Equations of Motion (EOM) approach used by McKoy[24-28] and others.[29-35] In both of the above theories, complete knowledge of the properties of the individual states, i.e., the wavefunctions, is sacrificed to make possible the direct calculation of the transition properties, thus minimizing both the problems of cancellation and the amount of calculated information which is

not of immediate interest. A major disadvantage of these methods has to do with the celebrated N-representability problem[36-37]: once approximations are introduced into the theory, how can one be certain that there exist properly antisymmetric wavefunctions (even if approximate) which correspond to the calculated transition properties?

In addition to the problem of N-representability, the physical content of the mathematical approximations used in the theories discussed above is somewhat vague. For example, the self-energy operator, which introduces the effects of electron correlation into the equation governing the one-particle GF, is usually expanded in a divergent perturbation series. The resulting expansion of the GF is also divergent, even in the Fredholm sense, and the attachment of physical meaning to the terms in this expansion is difficult, to say the least. In another formulation of the GF theory, one is faced with the problem of truncating or decoupling a hierarchy of equations analogous to the BBGKY equations[38] of statistical mechanics. This is usually done[19-21] by approximating various two-electron operators as sums of one-electron operators. The difficulties with this approach are twofold: there is no well-defined method for improving on the first approximation and there is no way to estimate the terms which have been neglected in the decoupling process. The principal disadvantage of the EOM approach is that it does not allow the incorporation of known facts concerning higher excited states into the calculation of low-lying excitations.

The theoretical research presented here overcomes one of the primary objections to both the GF and EOM theories. It provides the chemist with a *systematic* approach for calculating the excitation energies and oscillator strengths of low-lying excited states, in which experimental or theoretical knowledge of higher states can be employed to aid the calculation. A sequence of approximations can be defined in which the role of the higher excited states in determining the low-lying excitations is quite clear. The introduction of a projection operator onto the subspace of low-lying excited states allows the clear separation of high- and low-

energy excitations in the proposed formalism. A new energy-shift function, which contains the effects of the higher excited states on the states of interest, can be approximated by using experimentally measured spectra.

THE ENERGY-SHIFT THEORY

In statistical mechanics one is often interested in formulating the equations of motion of dynamical properties in such a manner that a clear separation of time scales is realized. For example, in hydrodynamic theories[39] the number, momentum, and energy densities vary on a (slow) macroscopic time scale. In developing reasonable approximate hydrodynamic equations, it is very advantageous if the exact equations governing the time and spatial behavior of the hydrodynamic variables display a clear separation of slow varying and rapidly varying terms. If this is the case, one can often introduce rather simple approximations to the rapidly varying terms without appreciably affecting the accuracy of the resulting solutions.

In connection with this time-scale separation problem, Mori[40] has derived exact equations for the equilibrium-averaged time correlation functions $\langle A_i(t) A_j^+ \rangle$ of any set of operators $\{A_i\}$. In these equations a separation of time scales appears naturally. Choosing the set of operators to be[41] $\{C_r^+ C_\alpha, C_\alpha^+ C_r\}$, and taking the zero-temperature limit, we can use Mori's results to obtain new equations of motion for the following matrix elements:

$$X_{ij,kl}(t) = \langle g \mid C_i^+(t) C_j(t) C_l^+ C_k \mid g \rangle, \quad (1)$$

where the index pairs i, j and k, l are either[42] α, r or r, α. Using the definition of the Heisenberg time-dependent operators, it is easily shown that the poles and residues of the one-sided Fourier transform of $X_{ij,kl}(t)$ are directly related to the excitation energies and oscillator strengths between the exact excited electronic states and the ground state $\mid g \rangle$.

The Mori equations[40] discussed above are written in matrix form below

$$\frac{d}{dt}\mathbf{X}(t) + \frac{i}{\hbar}\mathbf{X}(t)\mathbf{S}^{-1}\mathbf{\Omega} + \frac{i}{\hbar}\int_0^t d\tau \mathbf{X}(\tau)\mathbf{S}^{-1}\mathbf{M}(t-\tau) = 0, \quad (2)$$

with[43]

$$\Omega_{ij,kl} \equiv -\langle g \mid [H, C_i^+ C_j] C_l^+ C_k \mid g \rangle, \quad (3)$$

$$S_{ij,kl} \equiv \langle g \mid C_i^+ C_j C_l^+ C_k \mid g \rangle. \quad (4)$$

The matrix $\mathbf{M}(t)$ is defined in terms of the projector P onto the subspace of the operators $\{C_\alpha^+ C_r \text{ and } C_r^+ C_\alpha\}$

$$PB(t) \equiv \sum_{k,l} \sum_{m,n} \langle g \mid B(t) C_l^+ C_k \mid g \rangle S_{kl,mn}^{-1} C_m^+ C_n, \quad (5)$$

as follows:

$$M_{kl,mn}(t) = (i/\hbar) \langle g \mid$$
$$\times \{\exp[(i/\hbar)t(1-P)H^x](1-P)[H, C_k^+ C_l]\}$$
$$\times (1-P)[H, C_n^+ C_m] \mid g \rangle. \quad (6)$$

H^x is used to represent the commutator with the Hamiltonian

$$H^x B \equiv [H, B]. \quad (7)$$

Denoting $(1-P)[C_k^+ C_l, H]$ by f_{kl} allows us to write Eq. (6) more briefly as

$$M_{kl,mn}(t) = (i/\hbar) \langle g \mid$$
$$\times \{\exp[(i/\hbar)t(1-P)H^x]f_{kl}\} f_{nm} \mid g \rangle. \quad (6')$$

The content and properties of $\mathbf{M}(t)$ can be seen by inserting a complete set of eigenstates of H to the right of the braces in Eq. (6'). It has been assumed thus far that the low-lying excited states consist *mainly* of single excitations $(C_r^+ C_\alpha \mid g \rangle$ and $C_\alpha^+ C_r \mid g \rangle)$ of the ground state, whereas the higher excited states are composed mainly of double and higher excitations. Analyzing the result of inserting the complete set mentioned above, one can see that single, double, and higher excitations of $\mid g \rangle$ contribute only terms of high-frequency time dependence to $\mathbf{M}(t)$. In addition, these terms are of small magnitude unless $\mid g \rangle$ contains a great deal of configuration interaction (CI) involving single, triple, and higher excitations of the single-determinant approximation to $\mid g \rangle$. The only remaining function in the complete set, $\mid g \rangle$ itself, also contributes a term of high-frequency time dependence to $\mathbf{M}(t)$. The magnitude of this term is determined by the importance of doubly excited configurations in the CI expansion of $\mid g \rangle$.

From these observations, it follows that the one-sided Fourier transform of $\mathbf{M}(t)$

$$\mathbf{M}(E) = \int_0^\infty \exp\left(\frac{i}{\hbar}tE\right)\mathbf{M}(t)dt \quad (8)$$

possesses only high-energy poles corresponding to *approximate* higher excitation energies of the molecule. As will be seen shortly, this important property of the *energy-shift matrix* $\mathbf{M}(E)$ allows us to obtain reasonable approximate equations governing the low-frequency behavior of $\mathbf{X}(t)$. Because the poles of the one-sided Fourier transform of $\mathbf{X}(t)$ correspond to electronic excitation energies, this implies that Eq. (2), together with a reasonable approximation to $\mathbf{M}(t)$, can be used to probe low-lying excited states of molecules.

Taking the one-sided Fourier transform of Eq. (2) gives the fundamental equation of the energy-shift theory

$$\mathbf{X}(E)[E\mathbf{1} - \mathbf{S}^{-1}\mathbf{\Omega} - \mathbf{S}^{-1}\mathbf{M}(E)] = i\hbar\mathbf{S}, \quad (9)$$

where $\mathbf{1}$ is the unit matrix and $\mathbf{X}(E)$ is the transform of $\mathbf{X}(t)$. The energy-shift matrix $\mathbf{M}(E)$, which possesses only high-energy poles, is weakly dependent on E for values of E much less than the higher excitation energies. Because we are interested in only the low-energy poles of $\mathbf{X}(E)$, the E-dependence of $\mathbf{M}(E)$ can be treated in approximate fashion.

The lowest approximation which can be made is to neglect the $\mathbf{M}(E)$ matrix. The resulting $\mathbf{X}(E)$ is given in terms of the eigenvalues λ_i and eigenvectors[44] $\mathbf{U}_i, \mathbf{V}_i$

of the matrices $S^{-1}\Omega$ and $(S^{-1}\Omega)^+$

$$S^{-1}\Omega U_i = \lambda_i U_i, \qquad (10)$$

$$(S^{-1}\Omega)^+ V_i = \lambda_i V_i, \qquad (11)$$

as follows:

$$X(E) = i\hbar S \sum_j (E - \lambda_j)^{-1} U_j V_j^+. \qquad (12)$$

In this approximation, the excitation energies are equal to the λ_j, and the residues of $X(E)$, which determine the transition strengths, are equal to the elements of $SU_jV_j^+$. The physical content of Eq. (12) is most easily understood by examining the matrix $S^{-1}\Omega$, whose eigenvalues and eigenvectors determine $X(E)$. By rewriting Eq. (3) in the form

$$\Omega_{kl,mn} = \langle g \mid C_k^+ C_l (H - E_g) C_n^+ C_m \mid g \rangle, \qquad (13)$$

it is clear that the eigenvalues and eigenvectors of $S^{-1}\Omega$ are identical to the energies and expansion coefficients which would arise in a linear variational problem with Hamiltonian $(H - E_g)$ and *nonorthogonal* basis functions $C_n^+ C_m \mid g \rangle$. Thus, the excitation energies arrived at by neglecting the energy-shift matrix are the same as the energy differences obtained in a CI calculation using the $\{C_n^+ C_m \mid g \rangle$ and $\mid g \rangle\}$ as basis functions. The above remarks are only true if the function $\mid g \rangle$ is the exact ground state. In the research presented here, we have not yet discussed appropriate choices of $\mid g \rangle$. In the application of the energy-shift theory to atomic and molecular systems, one eventually is faced with the problem of calculating various ground-state expectation values, e.g., the first- and second-order density matrices of $\mid g \rangle$. For practical calculations, we have in mind two reasonable alternatives: if accurate configuration interaction approximations to $\mid g \rangle$ are available, they can be used in our theory; otherwise, one will probably have to use a single-determinant approximation for $\mid g \rangle$. The latter choice would, of course, greatly reduce the complexity of the computational problem. Clearly, a complete subhierarchy of energy-shift theories can be developed by making various approximations to $\mid g \rangle$. Because we do not wish to unnecessarily complicate matters in this introductory paper, we shall not discuss the choice of $\mid g \rangle$ any further.

To make progress beyond the results presented above, more reasonable approximations to the energy-shift matrix must be constructed. Some especially promising possibilities are now presented.

It follows from our earlier discussion of the E-dependence of $M(E)$ that the energy shift matrix can be written in the following form:

$$M(E) = \sum_n (E - E_n^0)^{-1} M_n, \qquad (14)$$

where the E_n^0 are approximate higher excitation energies of the molecule, and the M_n are expansion coefficients. We can make Eq. (14) practical by employing a truncated expansion in which we use experimentally determined excitation energies[45] and

theoretically calculated coefficients M_n. The method of computation is derived and outlined below.

Expanding Eq. (14) asymptotically in powers of E^{-1} gives

$$M(E) = E^{-1} \sum_n M_n + E^{-2} \sum_n E_n^0 M_n$$
$$+ E^{-3} \sum_n (E_n^0)^2 M_n + \cdots. \quad (15)$$

We can also use a theorem relating the expansion of $M(E)$ in powers of E^{-1} to the Taylor series expansion of $M(t)$ to write

$$M(E) = \sum_{l=0} E^{-(l+1)} A^{(l+1)}, \qquad (16)$$

where

$$A_{pq,rs}^{(l+1)} = (-1)^{l+1} \langle g \mid \{[(1-P)H^x]^{l+1} C_p^+ C_q\}$$
$$\times (1-P) H^x C_s^+ C_r \mid g \rangle. \quad (17)$$

For a given ground wavefunction, the matrices $A^{(l+1)}$ can be calculated, although for higher l values, the effort involved would probably be quite substantial. For this reason, we have in mind truncations of Eq. (14) involving only a few terms. By equating the coefficients of E^{-1} appearing in Eqs. (15) and (16), we obtain a set of algebraic equations relating the unknown expansion coefficients M_n to the theoretically calculated $A^{(l+1)}$ and the E_n^0 which are taken from experiment. For example, if the expansion in Eq. (14) is limited to two terms, Eqs. (15) and (16) imply

$$A^{(1)} = M_1 + M_2, \qquad (18a)$$

$$A^{(2)} = E_1^0 M_1 + E_2^0 M_2, \qquad (18b)$$

which can easily be solved to give

$$M_1 = (E_1^0 - E_2^0)^{-1} (A^{(2)} - E_2^0 A^{(1)}), \qquad (19a)$$

and

$$M_2 = (E_1^0 - E_2^0)^{-1} (E_1^0 A^{(1)} - A^{(2)}). \qquad (19b)$$

Once the M_n have been computed, Eq. (14) gives an expression for $M(E)$ which can be used in Eq. (9) to calculate $X(E)$. The inclusion of more and more terms in Eq. (14) thus provides a *systematic* series of approximation to $M(E)$. In this scheme, the poles of $X(E)$ are located by searching (with the aid of a computer) for values of E for which the elements of $[E\mathbf{1} - S^{-1}\Omega - S^{-1}M(E)]^{-1}$ diverge. To expedite the calculation, the eigenvalues of $S^{-1}\Omega$ can be used as initial guesses in the pole-searching process. The residue at the pole E_k, which determines the transition strength to excited state $\mid k \rangle$, is $i\hbar S[1 + S^{-1}\sum_n (E_k - E_n^0)^{-2} M_n]^{-1}$.

The amount of numerical work involved in the above searching procedure may become prohibitively large for large molecules such as those commonly studied by semiempirical molecular orbital methods. Therefore, it is important to consider a further approximation of the theory described above. As was implied earlier, the energy-shift matrix is strongly dependent on E only within neighborhoods of the poles E_n^0. Thus, in cal-

culating the low-energy poles of $\mathbf{X}(E)$ it is reasonable to neglect the E-dependence of Eq. (14) and write

$$\mathbf{M}(E) \cong -\sum_n \mathbf{M}_n/E_n^0 = \mathbf{M}(0). \qquad (20)$$

The resulting $\mathbf{X}(E)$ is a generalization of that given in Eqs. (10–12), in which the matrix $\mathbf{S}^{-1}\mathbf{\Omega}$ is replaced by $\mathbf{S}^{-1}\mathbf{\Omega} + \mathbf{S}^{-1}\mathbf{M}(0)$. Once the elements $\mathbf{M}_n$ and E_n^0 constituting $\mathbf{M}(0)$ are determined, the excitation energies and residues are easily obtained by solving two matrix eigenvalue problems analogous to Eqs. (10) and (11). This is clearly a major computational advantage over the preceding more general approximation.

In the event that the $\mathbf{A}^{(l+1)}$ beyond $\mathbf{A}^{(2)}$ are very difficult to compute, a geometric approximation of $\mathbf{M}(E)$, analogous to that used by Linderberg and Ratner[20] for Green's functions, may prove useful. This approximation is easily obtained by first rewriting Eq. (16) as

$$\mathbf{M}(E) = E^{-1}\mathbf{A}^{(1)}[1 + E^{-1}(\mathbf{A}^{(1)})^{-1}\mathbf{A}^{(2)}$$
$$+ E^{-2}(\mathbf{A}^{(1)})^{-1}\mathbf{A}^{(3)} + \cdots] \quad (21)$$

and then approximating the power series geometrically:

$$\mathbf{M}(E) \cong E^{-1}\mathbf{A}^{(1)}[1 - E^{-1}(\mathbf{A}^{(1)})^{-1}\mathbf{A}^{(2)}]^{-1}$$
$$= \mathbf{A}^{(1)}[E1 - (\mathbf{A}^{(1)})^{-1}\mathbf{A}^{(2)}]^{-1}. \qquad (22)$$

Equation (22) provides a simple parameterization of the energy shift involving only $\mathbf{A}^{(1)}$ and $\mathbf{A}^{(2)}$, which can be used in Eq. (9) to calculate $\mathbf{X}(E)$. This approximation is also useful when no information about higher excitation energies is available. In this theory, the poles of $\mathbf{X}(E)$ are determined by searching for values of E at which elements of $[E1 - \mathbf{S}^{-1}\mathbf{\Omega} - \mathbf{S}^{-1}\mathbf{M}(E)]^{-1}$ diverge. The residue of $\mathbf{X}(E)$ at the pole E_k is

$$i\hbar \mathbf{S}\{1 + \mathbf{S}^{-1}\mathbf{A}^{(1)}[E_k 1 - (\mathbf{A}^{(1)})^{-1}\mathbf{A}^{(2)}]^{-2}\}^{-1}.$$

Of course, if the pole-searching process proves to be too costly for a specific molecule, one can further approximate $\mathbf{M}(E)$ by $\mathbf{M}(0)$ and proceed as was described in the preceding paragraph.

This concludes our discussion of the approximations to the energy-shift matrix. Although we have already made considerable progress, future research efforts must be directed toward making the above approximations as computationally useful as possible.

RELATION OF ENERGY-SHIFT THEORY TO GREEN'S FUNCTIONS

The two-body, energy-dependent Green's function matrix is defined[19] in the following manner:

$$G_{ij,kl}(E) \equiv \frac{-i}{\hbar} \int_{-\infty}^{\infty} \exp\left(\frac{i}{\hbar} Et\right)$$
$$\times \langle g \mid T C_i^+(t) C_j(t) C_k^+ C_l \mid g \rangle dt, \quad (23)$$

where T is the Wick time ordering operator. By using the definition of T and the identity

$$\langle g \mid C_k^+ C_l C_i^+(t) C_j(t) \mid g \rangle$$
$$= \langle g \mid C_k^+(-t) C_l(-t) C_i^+ C_j \mid g \rangle, \quad (24)$$

one can show that the Green's function matrix is closely related to $\mathbf{X}(E)$:

$$i\hbar G_{ij,kl}(E) = X_{ij,lk}(E) + X_{kl,ji}(-E), \qquad (25)$$

where E is considered to be a complex variable

$$E = \mathrm{Re}E + i\delta, \qquad (26)$$

whose (positive) imaginary part is allowed to approach zero. $X_{ij,lk}(E)$ has poles along the lower side of the positive real E axis at values of the electronic excitation energies, and $X_{kl,ji}(-E)$ has corresponding poles along the upper side of the negative real E axis. Thus, it is clear from Eq. (25) that $G_{ij,kl}(E)$ possesses poles along both the positive and negative real axes. This result is, of course, well known in Green's function theory.

The principal differences between the Green's function approach and the energy-shift theory are contained in the equations of motion used to calculate the $\mathbf{G}(E)$ or $\mathbf{X}(E)$ matrices. In the Green's function formalism, the Heisenberg equation of motion

$$i\hbar d C_i^+(t) C_j(t)/dt = [C_i^+(t) C_j(t), H] \qquad (27)$$

is used to obtain the following starting equation:

$$E G_{ij,kl}(E) = \delta_{jk}\langle g \mid C_i^+ C_l \mid g \rangle - \delta_{il}\langle g \mid C_k^+ C_j \mid g \rangle$$
$$\times \frac{-i}{\hbar} \int_{-\infty}^{\infty} \exp\left(\frac{i}{\hbar} Et\right) \langle g \mid T[C_i^+(t) C_j(t), H]$$
$$\times C_k^+ C_l \mid g \rangle dt. \quad (28)$$

To arrive at a closed equation for $\mathbf{G}(E)$, one can (approximately) expand the commutator appearing in Eq. (28) in terms of single excitations:

$$[C_i^+(t) C_j(t), H] \cong \sum_{k,l} A_{ij,kl} C_k^+(t) C_l(t). \quad (29)$$

At least two reasonable possibilities exist for the choice of the expansion coefficients $A_{ij,kl}$. One can approximate the exact commutator $[C_i^+(t) C_j(t), H]$ by its projection onto the space of the operators $\{C_a^+(t) C_r(t)$ and $C_r^+(t) C_a(t)\}$, which results in

$$A_{ij,kl} = \sum_{m,n} \langle g \mid [C_i^+ C_j, H] C_n^+ C_m \mid g \rangle S_{mn,kl}^{-1}. \quad (30)$$

Another criterion for determining $A_{ij,kl}$ has been put forth by Linderberg and Öhrn.[19] They choose the expansion coefficients to minimize the sum of the norms of the two functions

$$[C_i^+ C_j, H] \mid g \rangle - \sum_{k,l} A_{ij,kl} C_k^+ C_l \mid g \rangle \qquad (31)$$

and

$$[C_i{}^+C_j, H]^+ \mid g \rangle - \sum_{k,l} A_{ij,kl}{}^* C_l{}^+C_k \mid g \rangle. \quad (32)$$

This procedure gives the following expression:

$$A_{ij,kl} = \langle g \mid [C_i{}^+C_j, H]C_l{}^+C_k + C_l{}^+C_k[C_i{}^+C_j, H] \mid g \rangle. \quad (33)$$

Because Eqs. (30) and (33) are not identical, we conclude that the Linderberg–Öhrn truncation scheme neglects some components of $[C_i{}^+C_j, H]$ which lie in the space of single excitations. Of course, this does not imply that the truncation generated by Eq. (33) is inaccurate. In fact, this truncation has been successfully applied to a wide range of molecular problems.[19,21] It should also be mentioned that Linderberg and Öhrn have developed more sophisticated truncation schemes[19] involving higher-order Green's functions.

From the above discussion, it is clear that the approximation given in Eq. (29), when substituted into Eq. (28), leads to a closed equation for the elements of $\mathbf{G}(E)$, regardless of which expression for $A_{ij,kl}$ is used. The final equation governing $\mathbf{G}(E)$ is written below:

$$EG_{ij,kl}(E) = \delta_{jk}\langle g \mid C_i{}^+C_l \mid g \rangle - \delta_{il}\langle g \mid C_k{}^+C_j \mid g \rangle$$
$$+ \sum_{m,n} A_{ij,mn}G_{mn,kl}(E). \quad (34)$$

In comparing Eq. (34) to Eq. (9), one notices that Eq. (9) contains the additional E-dependent term $\mathbf{S}^{-1}\mathbf{M}(E)$. Because the energy-shift matrix reflects, through its high-energy poles, the presence of higher excited states, we feel that the absence of an E-dependent matrix in Eq. (34) is a disadvantage of the Green's function method.

The lowest approximation to the energy-shift theory, which is obtained by neglecting $\mathbf{M}(E)$ in Eq. (9), can be shown to be equivalent to Eq. (34) with the coefficients $A_{ij,kl}$ given by Eq. (30). Because the Linderberg–Öhrn truncation [Eq. (33)] differs from Eq. (30), we conclude that Eq. (33) neglects some of the terms contained in $\mathbf{S}^{-1}\mathbf{\Omega}$, while including, in an *energy-independent fashion*, some contributions to $\mathbf{S}^{-1}\mathbf{M}(E)$ from higher excited states. This observation points out another potential advantage of our energy-shift method: in our formalism, all effects of higher excited states are *isolated* in $\mathbf{M}(E)$. Because $\mathbf{M}(E)$ has only high-energy poles, it will, perhaps, permit rather simple approximations of its low-energy structure to be reasonably accurate. Moreover, Eqs. (14)–(17) provide a well-defined means of generating approximations to the energy-shift matrix.

Finally, there exists the possibility of employing experimental knowledge about higher excitation energies to aid the construction of the energy-shift matrix. This can be especially advantageous for molecules whose higher states have been thoroughly studied but whose low-lying states are in question.

TREATMENT OF DOUBLE EXCITATIONS IN LOW-LYING EXCITED STATES

For some molecular systems, our assumption that the space of low-lying excited states is spanned by single excitations $\{C_r{}^+C_\alpha \mid g\rangle$ and $C_\alpha{}^+C_r \mid g\rangle\}$ may not be valid. In this event, the energy-shift theory must be extended to properly include the presence of double excitations $\{C_r{}^+C_\alpha C_s{}^+C_\beta \mid g\rangle$ and $C_\alpha{}^+C_r C_\beta{}^+C_s \mid g\rangle\}$ in the excited states of interest. This extension of the above theory is accomplished by decomposing the energy-shift matrix in such a manner that the contributions of double excitations are isolated from the terms arising from triple and higher excitations. The technique for realizing this decomposition is now presented.

Because the electronic Hamiltonian H consists of one- and two-particle operators, the f_{kl}

$$f_{kl} \equiv (1-P)[C_k{}^+C_l, H] \quad (35)$$

contain only double excitations, the single excitations having been annihilated by the operator $(1-P)$. Therefore the operator $'P$, defined by

$$'PB \equiv \sum_{k,l} \sum_{m,n} \langle g \mid Bf_{kl}{}^+ \mid g \rangle 'S_{kl,mn}{}^{-1}f_{mn}, \quad (36)$$

with

$$'S_{kl,mn} \equiv \langle g \mid f_{kl}f_{mn}{}^+ \mid g \rangle, \quad (37)$$

is a projector onto a subspace of double excitations.

In his definitive works on statistical mechanical time correlation functions, Mori developed a formalism involving the projectors P and $'P$ which can be used to obtain a closed equation for the energy-shift matrix $\mathbf{M}(E)$. In this equation there exists a clear isolation of those contributions to $\mathbf{M}(E)$ which arise from operators lying within the double-excitation space spanned by the $\{f_{kl}\}$. The final matrix equation can be written in a form which is analogous to that of Eq. (9) as follows:

$$\mathbf{M}(E)[E\mathbf{1} - 'S^{-1}{}'\Omega - 'S^{-1}{}'\mathbf{M}(E)] = i\hbar'S, \quad (38)$$

where

$$'\Omega_{ij,kl} \equiv -\langle g \mid \{(1-P)[f_{ij}, H]\}f_{kl}{}^+ \mid g \rangle. \quad (39)$$

The matrix element $'M_{ij,kl}(E)$ is the one-sided Fourier transform of

$$'M_{ik,kl}(t) \equiv (i/\hbar)\langle g \mid$$
$$\times \{\exp[(it/\hbar)(1-P-'P)H^x](1-P-'P)[f_{ij}, H]\}$$
$$\times (1-P-'P)[f_{kl}{}^+, H] \mid g \rangle. \quad (40)$$

The presence of the projector $(1-P-'P)$ in Eq. (40) implies that neither the single excitations $\{C_r{}^+C_\alpha \mid g\rangle$, $C_\alpha{}^+C_r \mid g\rangle\}$ nor the double excitations $\{f_{kl} \mid g\rangle\}$ contribute to $'M(E)$. Moreover, it is clear from Eq. (39) and the above discussion both that the single excitations do not appear in $'\Omega$ and that all contributions of the $\{f_{kl}\}$ to $\mathbf{M}(E)$ are contained in $'\Omega$.

Because we are interested in probing low-lying excited states which are assumed to be spanned by the functions $\{C_\alpha{}^+C_r \mid g\rangle, C_r{}^+C_\alpha \mid g\rangle, f_{\alpha r} \mid g\rangle$ and $f_{r\alpha} \mid g\rangle\}$ we can hopefully obtain reasonable results for the energy-shift matrix by employing rather simple approximations for $'\mathsf{M}(E)$ in Eq. (38). The lowest approximation which can be made is to neglect $'\mathsf{M}(E)$. This leads to an expression analogous to Eq. (12), giving $\mathsf{M}(E)$ in terms of the eigenvalues $('\lambda_j)$ and eigenvectors $('\mathsf{U}_j, '\mathsf{V}_j)$ of $('\mathsf{S}^{-1}'\Omega)$, and $('\mathsf{S}^{-1}'\Omega)^+$:

$$\mathsf{M}(E) = i\hbar'\mathsf{S} \sum_j (E - '\lambda_j)^{-1}{}'\mathsf{U}_j{}'\mathsf{V}_j{}^+. \qquad (41)$$

This approximation for $\mathsf{M}(E)$, when substituted into Eq. (9), yields a theory for $\mathsf{X}(E)$ which incorporates the effects of double excitations $(f_{kl} \mid g\rangle)$ in the low-lying excited states of interest.

The computational difficulty of the above scheme for treating double excitations is determined by the amount of effort needed to generate elements of the $'\mathsf{S}$ and $'\Omega$ matrices.[46] Because this effort will probably be substantial for all but very simple molecular systems, we feel that more sophisticated approximations to $'\mathsf{M}(E)$ are impractical at present.

In principle, we can develop a well-defined series of approximations for $'\mathsf{M}(E)$ by proceeding in a fashion analogous to that employed earlier in deriving approximate expressions for the energy-shift matrix. However, due to the practical difficulties discussed above and the inherent complexity of $'M_{ij,kl}(t)$ as given in Eq. (40), we shall not treat this matter further. Rather, we plan to concentrate our efforts in the immediate future on making the energy-shift theory presented here as computationally useful as possible. This will, of course, involve a considerable amount of calculational research in which the approximations discussed in this paper are tested on molecular systems whose low-lying excited states are well understood. We believe that the theoretical framework described in this paper will enable us to make significant advances in both interpreting and predicting the electronic excitation energies and oscillator strengths of low-lying excited states of molecules.

1 The oscillator strength between excited state $\mid j\rangle$ and the ground state $\mid g\rangle$ is given by $f_j = 2/3\Delta E_j \mid \langle j \mid \mathbf{r} \mid g\rangle\mid^2$, where ΔE_j is the excitation energy to state $\mid j\rangle$ and all quantities are given in atomic units.

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41 The $C_i{}^+$ and C_j are fermion creation and annihilation operators, respectively. The indices α and β label single-particle functions (spin orbitals) which are occupied in the single- or few-determinant approximation to the ground state wavefunction. Similarly, the indices r and s label unoccupied spin orbitals. The true ground state wavefunction is designated as $\mid g\rangle$.

42 From now on, the index pairs $i, j; k, l;$ and m, n will be either of type α, r or r, α. Terms involving α, β or r, s will not occur.

43 The significance of the Ω matrix is easily understood for the following simple Hamiltonian $H = \Sigma_i E_i C_i{}^+ C_i$. In this case $\Omega_{ij,kl} = (E_j - E_i) \langle g \mid C_i{}^+ C_j C_l{}^+ C_k \mid g\rangle$. Thus, Ω contains some contributions to the excitation energies. The remaining contributions to the excitation energies are contained in the matrix $\mathsf{M}(t)$. The presence of $\mathsf{M}(t)$ in the equations of motion causes the predicted excitation energies to be shifted from the values calculated by neglecting $\mathsf{M}(t)$. This alteration of the energy spectrum is the origin of the name of the energy-shift theory. S is simply the overlap or metric matrix for the space of functions $\{C_i{}^+C_k \mid g\rangle\}$.

44 Because $\mathsf{S}^{-1}\Omega$ is not symmetric, we must introduce the eigenvectors of $\mathsf{S}^{-1}\Omega$ and its Hermitian conjugate $(\mathsf{S}^{-1}\Omega)^+$. The row vector $\mathsf{V}_i{}^+$ is formed by taking the Hermitian conjugate of the column vector V_i.

45 We have in mind molecules for which some of the higher excitation energies are known but for which uncertainty exists concerning the ordering of the lower states.

46 Notice that the dimensions of the matrices appearing in Eq. (38) are identical to those occurring in Eq. (9). Thus, the extension of the energy-shift theory to include the effects of double excitations does not alter the amount of effort needed to carry out the matrix algebra in a practical calculation.