Application of the RPA and Higher RPA to the V and T States of Ethylene

Tai-Ichi Shibuya and Vincent McKoy*

Arthur Amos Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91109

(Received 24 August 1970)

We have applied our proposed higher random-phase approximation (HRPA) to the T and V states of ethylene. In the HRPA, unlike the RPA, one solves for the excitation frequencies and the ground-state correlations self-consistently. We also develop a simplified scheme (SHRPA) for solving the equations of the HRPA, using only molecular integrals sufficient for the usual RPA calculations. The HRPA removes the triplet instability which often occurs in the RPA. The excitation energy for the $N{\to}T$ transition is now in good agreement with experiment. The $N{\to}V$ transition energy increases by 15% over its RPA value. The $N{\to}V$ oscillator strength changes only very slightly. These results are also useful in explaining the appearance and ordering of states obtained in recent direct open-shell SCF calculations.

I. INTRODUCTION

There are various nonempirical methods of calculating the excitation energies of transitions in atomic and molecular systems. The usual way is to solve the Schrödinger equation separately for the ground and excited states and then to calculate the properties of the transitions using the known eigensolutions. These eigenfunctions range in accuracy from the Hartree–Fock approximation to large configuration interaction expansions. If one is interested in relative quantities such as excitation energies and oscillator strengths such procedures are not optimal. The equations-of-motion method and its various approximations are one approach to calculating these relative quantities directly, treating the stationary-state wavefunctions as of secondary importance.[1] These methods retain the basic physical effects and at the same time reduce the computational effort. The random-phase approximation (RPA) is a low-order approximation to the equations of motion. The RPA has been used to predict excitation energies in atoms[2] and more recently to study the low-lying excited states of ethylene and formaldehyde.[3] The results for transitions to singlet excited states were encouraging, but the RPA worked poorly for triplet excited states.[3] With the very approximate SCF wavefunctions used, the excitation frequency to the triplet state turned out imaginary. With an improved SCF wavefunction the triplet state is stabilized, but the excitation energy is still far off from experiment. This is due in part to the fact that the RPA violates the exclusion principle to some degree.

This paper is concerned with the application of a higher-order approximation to the equations of motion. Starting from the equations-of-motion method[1] we have recently derived a higher-order RPA[4] in which we solve for the excitation frequencies and ground-state correlations in a self-consistent fashion. In the equation for the excitation frequency we obtain all matrix elements up to terms linear in the ground-state correlation coefficients and in turn retain only up to linear terms in the cluster expansion in the equation determining the ground state. The scheme reduces to the usual RPA

if these correlation coefficients are set to zero. Here we apply our higher RPA (HRPA) to the T and V ($\pi{\to}\pi^*$) states of ethylene. The triplet state (T) is now in good agreement with experiment, and the excitation frequency for the transition to the singlet state ($N{\to}V$) increases by 15% in going from the RPA to the HRPA. We also develop a simplified scheme (SHRPA) for solving the equations of the HRPA. The results of this scheme are very close to those of the complete solution, but yet it requires only those matrix elements already needed for the RPA. This is a very important simplication since the preparation of additional integrals, e.g., particle–particle interactions, would add considerably to the computational effort. Any of these schemes would still require less effort than a configuration interaction study.

We also discuss the results of some more extensive calculations on ethylene at the RPA level. The basis sets are extensive enough to yield Rydberg states in addition. These results are useful in explaining the appearance and ordering of states obtained in the direct open-shell SCF calculations.

II. THE HIGHER RPA[4]

We write the correlated ground-state wavefunction, $| 0 \rangle$, as

$$| 0 \rangle = N_0 e^U | \text{HF} \rangle; \qquad \langle 0 | 0 \rangle = 1;$$
$$e^U = 1 + U + \tfrac{1}{2}U^2 + \cdots, \qquad (1)$$

where $| \text{HF} \rangle$ is the Hartree–Fock (HF) ground-state wavefunction. The operator U generates the pair correlations (two particle-hole pairs) and can be written[4]

$$U = \sum_{mn\gamma\delta} \{ K_{m\gamma,n\delta} c_{m\alpha}{}^+ c_{n\beta}{}^+ c_{\delta\beta} c_{\gamma\alpha} + \tfrac{1}{2}(K_{m\gamma,n\delta} - K_{m\delta,n\gamma})$$
$$\times \tfrac{1}{2}(c_{m\alpha}{}^+ c_{n\alpha}{}^+ c_{\delta\alpha} c_{\gamma\alpha} + c_{m\beta}{}^+ c_{n\beta}{}^+ c_{\delta\beta} c_{\gamma\beta}) \}, \quad (2)$$

where $c_{i\alpha}{}^+$ creates an electron in orbital state i and spin state α and $c_{i\alpha}$ does the reverse. The operators $c_{i\alpha}{}^+$ and $c_{i\alpha}$ satisfy the usual anticommutation relations. The letters m, n, p, q denote particle states and the Greek letters γ, δ, μ, ν hole states. Letters i, j, k, l denote either

particle or hole states. Thus

$$c_{m\alpha} \mid HF \rangle = c_{\gamma\alpha}^+ \mid HF \rangle = 0. \qquad (3)$$

The correlation coefficients K form a symmetrical matrix, i.e.,

$$K_{m\gamma,n\delta} = K_{n\delta,m\gamma}. \qquad (4)$$

We denote the excited states of the system by $\mid \lambda\Gamma SM \rangle$, where S and M are the spin symmetries, Γ the spatial symmetry (the irreducible representation of the molecular symmetry group), and λ the different states with the same symmetry ΓSM. We write

$$\mid \lambda\Gamma SM \rangle = O^+(\lambda\Gamma SM) \mid 0 \rangle;$$

$$\langle \lambda'\Gamma'S'M' \mid \lambda\Gamma SM \rangle = \delta_{\lambda'\lambda}\delta_{\Gamma'\Gamma}\delta_{S'S}\delta_{M'M}. \qquad (5)$$

We have the equation of motion

$$[H, O^+(\lambda\Gamma SM)] \mid 0 \rangle = \omega(\lambda\Gamma S) O^+(\lambda\Gamma SM) \mid 0 \rangle \qquad (6a)$$

and

$$O(\lambda\Gamma SM) \mid 0 \rangle = 0, \qquad (6b)$$

where H is the Hamiltonian and $\omega(\lambda\Gamma S)$ the excitation energy for the transition $\mid 0 \rangle \rightarrow \mid \lambda\Gamma SM \rangle$. We expand

$$O^+(\lambda\Gamma SM) \cong \sum_{m\gamma(\Gamma)} \{ Y_{m\gamma}(\lambda S) C_{m\gamma}^+(SM)$$
$$- (-)^{S+M} Z_{m\gamma}(\lambda S) C_{m\gamma}(S-M) \} \qquad (7a)$$

with

$$\sum_{m\gamma(\Gamma)} \{ Y_{m\gamma}^*(\lambda'S') Y_{m\gamma}(\lambda S) - Z_{m\gamma}^*(\lambda'S') Z_{m\gamma}(\lambda S) \}$$
$$= \delta_{\lambda'\lambda}\delta_{S'S}, \qquad (7b)$$

where $C_{m\gamma}^+(SM)$ is a symmetry-adapted particle-hole creation operator defined as

$$C_{m\gamma}^+(1, M) = -c_{m\alpha}^+ c_{\gamma\beta} \qquad (M=1)$$
$$= (1/\sqrt{2})(c_{m\alpha}^+ c_{\gamma\alpha} - c_{m\beta}^+ c_{\gamma\beta}) \qquad (M=0)$$
$$= c_{m\beta}^+ c_{\gamma\alpha} \qquad (M=-1)$$
$$C_{m\gamma}^+(0, 0) = (1/\sqrt{2})(c_{m\alpha}^+ c_{\gamma\alpha} + c_{m\beta}^+ c_{\gamma\beta}), \qquad (8)$$

and $C_{m\gamma}(SM)$ is the adjoint operator. Specifically all the irreducible representations of the symmetry group of ethylene (D_{2h}) are one dimensional. The summations in Eqs. (7) extend over only those pairs $m\gamma$ which belong to the given irreducible representation Γ.

From the equation of motion and the variational method[1] we have shown that the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ satisfy the equation[5]

$$\begin{bmatrix} A^{(\Gamma)}(S) & B^{(\Gamma)}(S) \\ -B^{(\Gamma)*}(S) & -A^{(\Gamma)*}(S) \end{bmatrix} \begin{bmatrix} Y^{(\Gamma)}(\lambda S) \\ Z^{(\Gamma)}(\lambda S) \end{bmatrix}$$
$$= \omega(\lambda\Gamma S) \begin{bmatrix} Y^{(\Gamma)}(\lambda S) \\ Z^{(\Gamma)}(\lambda S) \end{bmatrix}, \qquad (9a)$$

where

$$A^{(\Gamma)}(S) = A^{0(\Gamma)}(S) + A^{(1)(\Gamma)}(S),$$
$$B^{(\Gamma)}(S) = B^{0(\Gamma)}(S) + B^{(1)(\Gamma)}(S). \qquad (9b)$$

Equations (9a) with matrix elements given by Eq. (9b) are the equations of the higher RPA. The matrix elements of A^0 and B^0 are those of the usual RPA, i.e.,

$$A_{m\gamma,n\delta}^0(S) = \delta_{mn}\delta_{\gamma\delta}(\epsilon_m - \epsilon_\gamma) + [1 + (-1)^S]V_{m\delta\gamma n} - V_{m\delta n\gamma},$$
$$B_{m\gamma,n\delta}^0(S) = V_{mn\gamma\delta} + (-)^S(V_{mn\gamma\delta} - V_{mn\delta\gamma}\phi_i), \qquad (10)$$

where ϵ_i are the Hartree–Fock orbital eigenvalues and V_{ijkl} defined by

$$V_{ijkl} = \langle \phi_i(1)\phi_j(2), (1/r_{12})\phi_k(1)\phi_l(2) \rangle. \qquad (11)$$

The matrix elements of $A^{(1)}$ and $B^{(1)}$ are linear in the correlation coefficients and are given by[6]

$$A_{m\gamma,n\delta}^{(1)} = \delta_{\gamma\delta}T_{mn} - \delta_{mn}T_{\gamma\delta};$$
$$B_{m\gamma,n\delta}^{(1)}(S) = (-)^S S_{m\gamma,n\delta} + X_{m\gamma,n\delta}(S);$$
$$S_{m\gamma,n\delta} = -\sum_{p\mu} \{ V_{m\mu\delta p}C_{p\mu,n\gamma}(0) + V_{n\mu\gamma p}C_{p\mu,m\delta}(0) \};$$
$$T_{mn} = -\frac{1}{2}\sum_{q\mu\nu} \{ V_{mq\mu\nu}C_{n\mu,q\nu}^*(0) + V_{\mu\nu nq}C_{m\mu,q\nu}(0) \};$$
$$T_{\gamma\delta} = \frac{1}{2}\sum_{pq\nu} \{ V_{pq\gamma\nu}C_{p\delta,q\nu}^*(0) + V_{\delta\nu pq}C_{p\gamma,q\nu}(0) \}.$$

(If orbitals are real, then

$$T_{mn} = \frac{1}{2}\sum_{\mu} S_{m\mu,n\mu}; \qquad T_{\gamma\delta} = -\frac{1}{2}\sum_{p} S_{p\gamma,p\delta};$$
$$X_{m\gamma,n\delta}(S) = \sum_{\mu\nu} V_{\mu\nu\gamma\delta}C_{m\mu,n\nu}(S) + \sum_{pq} V_{mnpq}C_{p\gamma,q\delta}(S)$$
$$- \sum_{p\mu} \{ V_{m\mu p\delta}C_{p\gamma,n\mu}(S) + V_{n\mu p\gamma}C_{p\delta,m\mu}(S) \}. \qquad (12)$$

In Eq. (12) we have used the correlation coefficients

$$C_{m\gamma,n\delta}(S) = K_{m\gamma,n\delta} + (-)^S(K_{m\gamma,n\delta} - K_{m\delta,n\gamma}). \qquad (13)$$

The elements $C_{m\gamma,n\delta}$ form a symmetrical matrix since K is a symmetrical matrix:

$$C_{m\gamma,n\delta}(S) = C_{n\delta,m\gamma}(S). \qquad (14a)$$

Moreover, if $\gamma = \delta$ or $m = n$, the second term on the right-hand side of Eq. (13) vanishes and the C's are equal to the K's, i.e., for $\gamma = \delta$

$$C_{m\gamma,n\gamma}(0) = C_{m\gamma,n\gamma}(1) = K_{m\gamma,n\gamma} \qquad (14b)$$

with a similar equation for $m = n$.

Equation (9a) reduces to the usual RPA if the correlation coefficients are set to zero in Eq. (9b). It further reduces to the Tamm–Dancoff approximation (TDA) if the amplitudes Z are also set to zero. To solve Eqs. (9) in the HRPA we need the coefficients $\{C_{m\gamma,n\delta}\}$. From Eq. (6b) we have, for $m\gamma \in \Gamma$,

$$Z_{m\gamma}^*(\lambda S) = \sum_{n\delta(\Gamma)} C_{m\gamma,n\delta}(S) Y_{n\delta}^*(\lambda S);$$
$$C_{m\gamma,n\delta}(S) = 0, \qquad n\delta \notin \Gamma, \qquad (15)$$

which contains the vectors **Y** and **Z**. We consequently solve Eqs. (9) and (15) iteratively. Crude estimates of the $\{C_{m\gamma,n\delta}\}$ can be obtained from Eqs. (15) by using the results of the TDA or the usual RPA if stable. We discuss these procedures in Sec. III. With these initial estimates of the correlation coefficients the matrix elements of A and B, Eq. (9b), can be evaluated and the HRPA equations solved. With these estimates of **Y** and **Z** we solve Eq. (15) for new C's. Repeating the procedure we obtain self-consistent solutions for ω, **C**, **Y**, and **Z**. Initial estimates of the C's can also be obtained from Rayleigh–Schrödinger perturbation theory. [See Eq. (35b).]

Besides the excitation energy we also need the transition moment. For electric-dipole allowed transitions we have

$$\mathbf{D} = -\langle E \mid \mathbf{r} \mid 0 \rangle, \quad (16)$$

where **r** is the position vector and $\mid E \rangle$ the excited-state wavefunction. For singlet excited states we have

$$\mathbf{D}(\lambda\Gamma) = -\langle 0 \mid [O(\lambda\Gamma 00), \mathbf{r}] \mid 0 \rangle. \quad (17)$$

With the matrix elements of **r** and the density matrix elements defined as

$$\mathbf{d}_{ij}{}^0 = \langle \phi_i \mid \mathbf{r} \mid \phi_j \rangle; \quad (18)$$

$$\rho_{ij} = \langle 0 \mid c_{i\alpha}{}^+ c_{j\alpha} \mid 0 \rangle, \quad (19)$$

we obtain

$$\mathbf{D}(\lambda\Gamma) = -\sqrt{2} \sum_{m\gamma(\Gamma)} [Y_{m\gamma}{}^*(\lambda 0) + Z_{m\gamma}{}^*(\lambda 0)] \mathbf{d}_{m\gamma}, \quad (20)$$

where

$$\mathbf{d}_{m\gamma} = \sum_{\delta} \mathbf{d}_{m\delta}{}^0 \rho_{\gamma\delta} - \sum_{n} \mathbf{d}_{n\gamma}{}^0 \rho_{nm}. \quad (21)$$

We have shown that[4]

$$\rho_{\gamma\delta} = \delta_{\gamma\delta} + \rho_{\gamma\delta}{}^{(2)} + \rho_{\gamma\delta}{}^{(4)} + \cdots;$$

$$\rho_{nm} = \rho_{nm}{}^{(2)} + \rho_{mm}{}^{(4)} + \cdots, \quad (22)$$

where $\rho_{ij}{}^{(r)}$ is of order C^r. Thus to order C^3 we have

$$\rho_{\gamma\delta} = \delta_{\gamma\delta} + \rho_{\gamma\delta}{}^{(2)}, \qquad \rho_{nm} = \rho_{nm}{}^{(2)}. \quad (23)$$

From Eqs. (21) and (23) we have

$$\mathbf{d}_{m\gamma} = \mathbf{d}_{m\gamma}{}^0 - \left(\sum_n \mathbf{d}_{n\gamma}{}^0 \rho_{nm}{}^{(2)} - \sum_\delta \mathbf{d}_{m\delta}{}^0 \rho_{\gamma\delta}{}^{(2)} \right) \quad (24)$$

with $\rho^{(2)}$ given by[4]

$$\rho_{\gamma\delta}{}^{(2)} = -\tfrac{1}{2} \sum_{pq\mu} \sum_{S} C_{p\mu,q\gamma}{}'(S) C_{p\mu,q\delta}{}^*(S),$$

$$\rho_{nm}{}^{(2)} = \tfrac{1}{2} \sum_{p\mu\nu} \sum_{S} C_{p\mu,m\nu}{}'(S) C_{p\mu,n\nu}{}^*(S), \quad (25)$$

where

$$C_{m\gamma,n\delta}{}'(S) = K_{m\gamma,n\delta} + (-)^S \tfrac{1}{2} (K_{m\gamma,n\delta} - K_{m\delta,n\gamma}). \quad (26)$$

In the RPA the transition moment is given by Eq. (20) with $\mathbf{d}_{m\gamma}{}^0$ and the **Y** and **Z** of the usual RPA. The oscillator strength $f(\lambda\Gamma)$ is

$$f(\lambda\Gamma) = \tfrac{2}{3}\omega(\lambda\Gamma 0) \mid D(\lambda\Gamma) \mid^2. \quad (27)$$

In general the RPA and HRPA can be expected to give very good estimates of the oscillator strength. This is not only true for photon absorption. For example Schneider has recently calculated the generalized oscillator strength as a function of momentum transfer for the inelastic scattering of high-energy electrons off of helium.[7] His RPA results with a modest basis are in excellent agreement with those derived using very extensive wavefunctions for the ground and excited states to evaluate the matrix elements.[8]

III. SOLUTION OF EQ. (15)

With the amplitudes **Y** and **Z**, Eq. (15) can be solved for the correlation coefficients C's by da Providência's method.[9] We can also use Sanderson's method[10] to solve Eq. (15) for the C's. This is an iterative method which starts from the TDA solutions and is then convenient when the usual RPA is unstable, e.g., for transitions to some triplet states. The TDA equation is written as

$$\mathbf{A}^{0(\Gamma)}\mathbf{Y}^{(\Gamma)}(\lambda S) = w(\lambda\Gamma S)\mathbf{Y}^{(\Gamma)}(\lambda S), \quad (28)$$

where the elements of $\mathbf{A}^0$ are given in Eq. (10). The coefficients C's are obtained by iterative solution of the equation[10]

$$C_{m\gamma,n\delta}{}^{(\Gamma)}(S) = \sum_{\kappa,q} Y_{m\gamma}{}^{(\Gamma)}(\kappa S) \bar{C}_{\kappa,\lambda}{}^{(\Gamma)}(S) Y_{n\delta}{}^{(\Gamma)*}(\lambda S), \quad (29a)$$

where

$$\bar{C}_{\kappa,\lambda}{}^{(\Gamma)}(S)$$

$$= -\frac{\bar{B}_{\kappa\lambda}{}^{(\Gamma)}(S) + \sum_{\kappa'\lambda'} \bar{C}_{\kappa\kappa'}{}^{(\Gamma)}(S) \bar{B}_{\kappa'\lambda'}{}^{(\Gamma)*}(S) \bar{C}_{\lambda'\lambda}{}^{(\Gamma)}(S)}{w(\kappa\Gamma S) + w(\lambda\Gamma S)}, \quad (29b)$$

$$\bar{B}_{\kappa\lambda}{}^{(\Gamma)}(S) \equiv \sum_{m\gamma,n\delta} Y_{m\gamma}{}^{(\Gamma)*}(\kappa S) B_{m\gamma,n\delta}{}^{(\Gamma)}(S) Y_{n\delta}{}^{(\Gamma)}(\lambda S). \quad (29c)$$

We will use these equations only to obtain the initial estimate of the C's to start the iterative solution of the equations of the HRPA. Hence we use the zero order of Eq. (29b), i.e.,

$$\bar{C}_{\kappa\lambda}{}^{(\Gamma)}(S) \cong -\bar{B}_{\kappa\lambda}{}^{(\Gamma)}(S) / [w(\kappa\Gamma S) + w(\lambda\Gamma S)]. \quad (29d)$$

In the iterative solution of the HRPA scheme we use da Providencia's method[9] to solve Eq. (15), i.e.,

$$C_{m\gamma,n\delta}{}^{(\Gamma)}(S) = C_{m\gamma,n\delta}{}^{0(\Gamma)}(S)$$

$$- \sum_{q\nu(\Gamma)} C_{m\gamma,q\nu}{}^{(\Gamma)}(S) Q_{q\nu,n\delta}{}^{(\Gamma)}(S), \quad (30a)$$

where

$$C_{m\gamma,n\delta}{}^{0(\Gamma)}(S) \equiv \sum_{\lambda} Y_{m\gamma}{}^{(\Gamma)}(\lambda S) Z_{n\delta}{}^{(\Gamma)*}(\lambda S),$$

$$Q_{m\gamma,n\delta}{}^{(\Gamma)}(S) \equiv \sum_{\lambda} Z_{m\gamma}{}^{(\Gamma)}(\lambda S) Z_{n\delta}{}^{(\Gamma)*}(\lambda S). \quad (30b)$$

Very accurate solutions are actually obtained by simply substituting the C^0 of Eq. (30b) into the second term of the right-hand side of Eq. (30a). When calculations were carried out through five iterations for those $C_{m\gamma,n\delta}$ with particle-hole pairs $m\gamma$ and $n\delta$ both belonging to the B_{3u} irreducible representation,[11] the differences between the first and fifth iterated values of C's were less than 10^{-6}. In fact, we have found that C^0 are already quite good approximation, and errors are only less than 10^{-4}.

IV. A SIMPLIFIED HRPA

The purpose of the present application of the HRPA is not only to test the scheme but also to develop some simplifying and practical approximations. The simplified scheme (SHRPA) should (i) be a closed self-consistent scheme within each class of transitions and (ii) require no more molecular integrals (interaction matrix elements) than the usual RPA.

The condition (i) is easily achieved by retaining in the self-consistent scheme only those correlation coefficients made up of particle-hole pairs of the same symmetry as the excited state under study. The other classes of coefficients are simply set to zero in the scheme. In an earlier calculation on ethylene[3] we saw that the usual RPA became unstable for the transition to the $^3B_{3u}$ state, while for transitions to other states even the TDA works well. This implies that some correlation coefficients associated with $^3B_{3u}$ elementary excitations are so large that they affect significantly the transition frequency to the lowest state of this symmetry. On the other hand, this also implies that transitions to other classes of states depend only slightly on these same ground-state correlation coefficients in spite of their magnitude. This observation supports the separability of the HRPA for each class of transition, i.e., each irreducible representation of the molecular symmetry group.

The second condition (ii) is accomplished by omitting the correction term X in $B^{(1)}$ of Eq. (12). The general justification of this approximation is not easy. In the usual RPA, particle–particle and hole–hole interactions, V_{mnpq} and $V_{\mu\nu\gamma\delta}$, respectively, do not make a contribution to any matrix elements. In general, the last term tends to cancel the first two, making $X_{m\gamma n\delta}(S)$, Eq. (12), small. In Sec. VI we will see that a direct numerical check shows this to be a very good approximation.

Equations (14a) and (14b) are two symmetry requirements which the coefficients $C_{m\gamma n\delta}$ should satisfy. The requirement, Eq. (14a), is always satisfied. However, Eq. (14b) is not necessarily satisfied. This is essentially due to the fact that the RPA theories more or less all violate the exclusion principle to some extent. In the HRPA the extent of this violation is reduced. We have studied this feature analytically in the simple model system of two π electrons in the double bond of ethylene.[12] This involves only a single correlation coefficient κ and the term X becomes exactly zero. We

expand κ in a power series of the parameter $g(<1)$ which measures the strength of the interaction between the electrons. The difference in κ for the $S=0$ and $S=1$ solutions is of order g^4 in the HRPA but of order g^2 in the RPA. The leading term in this expansion is of order g. In the present study of excitations in the ethylene molecule we have many more coefficients $C_{m\gamma,n\delta}(S)$. The largest are those with $m=n$ or $\gamma=\delta$, and these should exactly satisfy Eq. (14b). But, for example, the estimates of $C_{\pi^*\pi,\pi^*\pi}(S)$ for $S=0$ and 1 are -0.09 and -0.45, respectively, when obtained directly from the TDA solutions by Sanderson's method, and -0.10 and -0.34, respectively, when obtained directly from the RPA solutions. After iterative refinement in the HRPA scheme these discrepancies become much smaller and for instance the values of $C_{\pi^*\pi,\pi^*\pi}(S)$ for $S=0$ and 1 become -0.166 and -0.147, respectively.

Thus, in the iterative solution of these equations, we will take the average

$$K_{m\gamma,n\delta}=\tfrac{1}{2}[C_{m\gamma,n\delta}(0)+C_{m\gamma,n\delta}(1)], \qquad (31)$$

and substitute these K's for both $C(0)$'s and $C(1)$'s, i.e.,

$$C_{m\gamma,n\delta}(0)=C_{m\gamma,n\delta}(1)=K_{m\gamma,n\delta} \qquad (32)$$

for all $m\gamma$ and $n\delta$. From Eq. (13) this implies

$$K_{m\gamma,n\delta}\cong K_{m\delta,n\gamma}. \qquad (33)$$

This means that if the particle-hole pairs $m\gamma$ and $n\delta$ belong to a given symmetry, then $K_{m\delta,n\gamma}$ is also included even though particle-hole pairs $m\delta$ and $n\gamma$ may not be of the right symmetry for the state under study. Inclusion of these extra coefficients $K_{m\delta n\gamma}$ partly violates requirement (1) of the SHRPA and would cause an overcounting when we extend our calculation to include excited states of other symmetries. Thus, we will exclude these extra $K_{m\delta,n\gamma}$ from our simplified scheme. We have checked this numerically and shown that the inclusion of these terms causes very small changes.

First-order perturbation theory gives

$$K_{m\gamma,n\delta}\cong -V_{mn\gamma\delta}/(\epsilon_m+\epsilon_n-\epsilon_\gamma-\epsilon_\delta), \qquad (34)$$

and hence

$$K_{m\gamma,n\delta}-K_{m\delta,n\gamma}\cong -(V_{mn\gamma\delta}-V_{mm\delta\gamma})/(\epsilon_m+\epsilon_n-\epsilon_\gamma-\epsilon_\delta). \qquad (35a)$$

The right-hand side of Eq. (35a) certainly vanishes when $m=n$ or $\delta=\gamma$. For $m\neq n$ and $\delta\neq\gamma$ it does not necessarily vanish, although the absolute value of Eq. (35a) is undoubtedly smaller than that of Eq. (34). Hence the $K_{m\gamma,n\delta}$ with $m\neq n$ and $\gamma\neq\delta$ should be unimportant compared to those elements with $m=n$ or $\gamma=\delta$. This supports the approximation made in Eq. (32). The substitution of Eq. (34) into Eq. (13) gives

$$C_{m\gamma,n\delta}(S)\cong -B^0_{m\gamma,n\delta}(S)/(\epsilon_m+\epsilon_n-\epsilon_\gamma-\epsilon_\delta), \quad (35b)$$

which satisfy the symmetry requirement Eq. (14b).

In summary, the proposed simplified scheme for solving the equations of the HRPA is as follows: For particle-hole pairs $m\gamma$ and $n\delta$ belonging to a class of states Γ we write (assuming all orbitals to be real)

$$A_{m\gamma,n\delta}^{(1)} = \delta_{\gamma\delta}T_{mn} - \delta_{mn}T_{\gamma\delta};$$

$$B_{m\gamma,n\delta}^{(1)}(S) = (-1)^{S}S_{m\gamma,n\delta},$$

where

$$S_{m\gamma,n\delta} = -\sum_{p\mu(\Gamma)}(V_{m\mu\delta p}K_{p\mu,n\gamma} + V_{n\mu\gamma p}K_{p\mu,m\delta});$$

$$T_{mn} = \tfrac{1}{2}\sum_{\substack{\mu \\ [m\mu(\Gamma),n\mu(\Gamma)]}}S_{m\mu,n\mu}; \qquad T_{\gamma\delta} = -\tfrac{1}{2}\sum_{\substack{p \\ [p\gamma(\Gamma),p\delta(\Gamma)]}}S_{p\gamma,p\delta},$$

$$(36)$$

where

$$\sum_{\substack{p \\ [p\gamma(\Gamma)]}}$$

indicates that the summation includes only those particle-hole pairs which belong to the Γ representation. With these $\mathbf{A}^{(1)}$ and $\mathbf{B}^{(1)}$ Eqs. (9) are solved for $S=0$ and 1. We then use the solutions $\mathbf{Y}$ and $\mathbf{Z}$ to solve Eq. (15) for the correlation coefficients for $S=0$ and 1 separately. The new set of $K_{m\gamma,n\delta}$ is obtained from Eq. (31).

In the SHRPA we have

$$\rho_{\gamma\delta}^{(2)} = -\sum_{p\mu(\Gamma)}\sum_{\substack{q \\ [q\gamma(\Gamma),q\delta(\Gamma)]}}K_{p\mu,q\gamma}K_{p\mu,q\delta},$$

$$\rho_{nm}^{(2)} = \sum_{p\mu(\Gamma)}\sum_{\substack{\nu \\ [m\nu(\Gamma),n\nu(\Gamma)]}}K_{p\mu,m\nu}K_{p\mu,n\nu}. \qquad (37)$$

V. THE GROUND-STATE CORRELATION ENERGY

The ground-state correlation energy is defined as

$$E_{\text{corr}} = \langle 0 \mid H \mid 0\rangle - E_{\text{HF}}, \qquad (38)$$

where

$$E_{\text{HF}} \equiv \langle \text{HF} \mid H \mid \text{HF}\rangle = 2\sum_{\gamma}\epsilon_{\gamma} - \sum_{\gamma\delta}(2J_{\gamma\delta} - K_{\gamma\delta}) \qquad (39)$$

for the closed-shell system. $J_{\gamma\delta}$ and $K_{\gamma\delta}$ are the usual Coulomb and exchange integrals. From Eqs. (1) and (2) for $\mid 0\rangle$ and Eq. (38), we have

$$E_{\text{corr}} = E^{(1)} + E^{(2)} + E^{(3)} + \cdots, \qquad (40)$$

where $E^{(r)}$ is of order C^{r} (or K^{r}). The first few terms are

$$E^{(1)} = 2\langle \text{HF} \mid HU \mid \text{HF}\rangle;$$

$$E^{(2)} = \langle \text{HF} \mid U^{+}HU \mid \text{HF}\rangle - E_{\text{HF}}\langle \text{HF} \mid U^{+}U \mid \text{HF}\rangle;$$

$$E^{(3)} = \langle \text{HF} \mid U^{+}HUU \mid \text{HF}\rangle - E^{(1)}\langle \text{HF} \mid U^{+}U \mid \text{HF}\rangle;$$

$$E^{(4)} = \tfrac{1}{4}\{\langle \text{HF} \mid U^{+}U^{+}HUU \mid \text{HF}\rangle$$

$$- E_{\text{HF}}\langle \text{HF} \mid U^{+}U^{+}UU \mid \text{HF}\rangle\}$$

$$- E^{(2)}\langle \text{HF} \mid U^{+}U \mid \text{HF}\rangle, \qquad (41)$$

where we have expanded N_0^2 [Eq. (1)] as follows:

$$N_0^{-2} \equiv \langle \text{HF} \mid e^{U^{+}}e^{U} \mid \text{HF}\rangle$$

$$= 1 + \langle \text{HF} \mid U^{+}U \mid \text{HF}\rangle$$

$$+ \tfrac{1}{4}\langle \text{HF} \mid U^{+}U^{+}UU \mid \text{HF}\rangle + \cdots. \qquad (42)$$

We have

$$\langle \text{HF} \mid U^{+}U \mid \text{HF}\rangle \cong -\sum_{\gamma}\rho_{\gamma\gamma}^{(2)} = \sum_{m}\rho_{mm}^{(2)}. \qquad (43)$$

In the usual perturbation theory, $E^{(1)}$ is the second-order energy

$$E^{(1)} = 2\sum_{mn\gamma\delta}V_{mn\gamma\delta}C_{m\gamma,n\delta}(0)$$

$$= 2\sum_{\gamma}T_{\gamma\gamma} = -2\sum_{m}T_{mm}. \qquad (44)$$

The calculations discussed in Sec. VI are restricted to particle-hole pairs of the same symmetry as the V and T states ($^{1}B_{3u}$ and $^{3}B_{3u}$). We will therefore not try to estimate the total correlation energy but only that part coming from excitations of this symmetry.

VI. APPLICATION OF THE HRPA

To test our proposed scheme we have carried out calculations on the T and V states of ethylene. These are the triplet and singlet states arising primarily from the $\pi \rightarrow \pi^{*}$ transition. We choose this example so we can compare the results with those of more extensive calculations we have done using the RPA. In Sec. VII we will discuss the results of RPA calculations using basis sets large enough to give Rydberg states in addition to the V state. Those calculations were done in order to explain the ordering of the states obtained in a direct SCF calculation relative to the experimentally observed ones.

With the molecule in the xy plane the T and V states are $^{3}B_{3u}$ and $^{1}B_{3u}$, respectively. We must first carry out the SCF calculation for the planar ground state of ethylene. With its 16 electrons we obtain eight occupied orbitals and a set of virtual orbitals. These are the hole and particle levels, respectively. Clearly the quality of the hole states and the number of particle states depend on the size of the basis set. In the previous calculation on ethylene we used the minimal basis set of Slater atomic orbitals.[3] This is a very limited basis, and for the present calculations we use the SCF orbitals of a more extensive calculation with a contracted set of Gaussian orbitals. The Appendix gives the pertinent results of this calculation including the hole and particle levels.[13] The basis is a contracted $[3s2p/1s]$ Gaussian set, which is derived from an initial set of nine s-like and five p-like Gaussians on each of two carbon atoms and four s-like Gaussians on each of four hydrogens. This set is then contracted down to three s-like and two p-like (for each of three components) orbitals on each carbon and one s-like function on each hydrogen. The HF energy of this basis is -77.9832 a.u.

We have eight occupied orbitals and 14 particle levels. Of the particle states we only include the first 12 since the last two levels have very little effect on the excitation energies of interest. For similar reasons the two lowest hole levels are neglected. The elementary excitations are either from the π-bonding to a π-antibonding ($\pi \rightarrow \pi^*$) orbital or from a σ-bonding to σ-antibonding ($\sigma \rightarrow \sigma^*$) orbital. With five σ and one π level and two π^* and 10 σ^* levels we have 14 particle-hole pairs of B_{3u} symmetry. Of these two are $\pi \rightarrow \pi^*$ excitations and 12 $\sigma \rightarrow \sigma^*$ excitations. The coupling together of the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ excitations is an electron correlation effect. For convenience we number the levels 1–20 and label the excitations numerically. Levels 3–7 are σ holes, 8 the π-hole levels, 9 and 15 π^*-particle levels and the other all σ-particle levels. In Tables AI–AIII of the Appendix we list the quantities, including the molecular integrals, required for the present calculations.

The results of the TDA, RPA, and the simplified HRPA are shown in Table I. The excitation energies for the $N \rightarrow V$, T transitions are denoted by $\omega(V)$ and $\omega(T)$, and D and f are the transition moment (absolute value) and oscillator strength, respectively, for the $N \rightarrow V$ transition. The numbers in parentheses are the values for D and f without the corrections quadratic in the correlation coefficients [Eq. (24)]. In the calculation SHRPA(X) the correction term $X_{m\gamma,n\delta}(S)$ is included in the matrix element $B_{m\gamma,n\delta}{}^{(1)}$. The agreement between this result and the SHRPA calculation, which does not include the term $X_{m\gamma,n\delta}(S)$, justifies our proposal to omit this term in setting up the $B^{(1)}$ matrix. In the SHRPA(A) calculations we specifically include the coefficients $K_{m\delta,n\gamma}$ discussed in Sec. IV. The close agreement between the SHRPA and SHRPA(A) results supports dropping these extra elements.

In the TDA result the excitation energy is measured relative to the HF ground-state energy. This is just a configuration interaction using singly excited configurations of the type $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$. The TDA excitation energy and oscillator strength are 8.43 eV and 0.71 a.u., respectively, for the $N \rightarrow V$ transition. With a minimal basis of Slater orbitals we obtained a TDA excitation energy of 10.17 eV, and we will see in Sec. VII that the most extensive calculation with a large Gaussian basis gives 7.82 eV. The RPA predicts an excitation energy of 7.94 eV and an oscillator strength of 0.52. We notice, however, that in going to the SHRPA this value increases by 15% to 9.39 eV. This is probably due to the fact that the RPA overestimates the correlation energy in the excited state and illustrates the importance of the correlation effects introduced in going from the RPA to the HRPA. It would obviously be interesting to compare this value with the excitation energy that would be obtained by doing a full CI on the ground and excited states. This would be an extensive calculation even with this basis set and, in fact, this is one of the difficulties the equations-of-motion method tries to circumvent. However, Whitten[14] has carried out such a

CI calculation on the $N \rightarrow V$ transition using a set of basis functions which should be similar in accuracy to ours. He obtains an excitation energy of 9.2 eV. The calculations with the HRPA are much simpler than those of a CI calculation, while the above results show that it is probably quite accurate.

There is a significant change in the excitation energy for the $N \rightarrow T$ transition in going from the RPA to the HRPA. The RPA excitation energy for this transition is 1.5 eV, in very poor agreement with the experimental value of 4.6 eV. The removal of this deficiency of the RPA in treating this low-lying triplet state was one of the goals of this proposed higher random-phase approximation. The failure of the RPA is due to the fact that the RPA violated the exclusion principle to some degree. The HRPA does much better in this respect and predicts an excitation energy of 4.95 eV in good agreement with the observed value of 4.6 eV. In a previous application[3] of the RPA to this state using a minimal basis set of Slater orbitals the excitation frequency came out imaginary.

The magnitude of the transition moment decreases in going from the TDA to the RPA to the SHRPA and the corrections quadratic in the correlation coefficients [Eq. (24)] further decrease the transition moment. There is only a small change in the oscillator strength in going from the RPA to the HRPA, i.e., 0.52–0.46. In general, we expect the RPA to give a good estimate of the oscillator strength even in calculations with rather small basis sets. For example, the RPA with the minimal basis set of Slater orbitals already gave an oscillator strength of 0.51. We have also studied this feature analytically in the model system of two π electrons in ethylene.[12] We expand the oscillator strength in a power series of the parameter $g(<1)$ which measures the strength of the interaction between the electrons. This shows that the leading term in the error for the oscillator strength in the HRPA is of order g^3 while that in the RPA is of order g^2. The leading term in this expansion is a constant. This analysis clearly shows why the change in the oscillator strength is small in going from the RPA to the HRPA. The following argument illustrates the same behavior for the transition moment. The experimental oscillator strength is about 0.34. If we use the experimental excitation energy of 7.6 eV, Eq. (27) gives a value of 1.35 for the transition moment D, in good agreement with the calculated value of 1.42 in Table I, and in Sec. VII we will show that more extensive calculations give a transition moment even closer to the derived value of 1.35.

Table II gives the amplitudes $Y_{m\gamma}$ and $Z_{m\gamma}$ for the $N \rightarrow V$ and $N \rightarrow T$ transitions in the various approximations. The first column is the numerical designation for the particle-hole pair. Levels 9 and 15 are π^* particle levels and level 8 is the π orbital. Levels 3–7 are σ hole levels. Hence (9, 8) stands for a $\pi \rightarrow \pi^*$ component and (12, 7) for a $\sigma \rightarrow \sigma^*$. The σ and σ^* levels are crudely either bonding or antibonding with respect to the C–C

TABLE I. The T and V states of ethylene: excitation energies, transition moments, and oscillator strengths in the various approximations.

	TDA	RPA	SHRPA	SHRPA(X)[c]	SHRPA(A)[d]	Exp.[e]
$\omega(V)$[a]	8.43	7.94	9.39	9.38	9.44	7.6
$\omega(T)$[a]	3.40	1.50	4.95	4.92	4.95	4.6
$D(V)$[b]	1.85	1.63	1.42 (1.55)[f]	1.44 (1.56)	(1.55)	
$f(V)$[b]	0.71	0.52	0.46 (0.55)	0.48 (0.56)	(0.56)	~0.34

[a] In eV's.
[b] In a.u.'s.
[c] This calculation includes the correction terms $X_{m\gamma,n\delta}(S)$ in $B^{(1)}$, Eq. (12).

[d] This calculation does not include the correction terms $X_{m\gamma,n\delta}$ in $B^{(1)}$, Eq. (12), but does include the additional coefficients $K_{m\delta,m\gamma}$, Eq. (33).
[e] See Ref. 3.
[f] The values in parentheses are those evaluated with $\mathbf{d}_{ij}{}^0$ only [Eq. (24)].

or C–H bond. Note the significant changes in the $Z_{m\gamma}$ amplitudes for the $N \rightarrow T$ transition in going from the RPA to the HRPA. This is particularly true for the $\pi \rightarrow \pi^*$ components $(9, 8)$ and $(15, 8)$ which change from -0.7140 and 0.2688 in the RPA to -0.1566 and 0.0663, respectively, in the SHRPA.

In Table III we show some of the correlation coefficients $C_{m\gamma,n\delta}(S)$ derived only from B_{3u} particle-hole pairs. For convenience we list only those coefficients greater in magnitude than 0.025 for either $S = 0$ or 1. We see that the coefficients with $m = n$ or $\gamma = \delta$ for $S = 0$ and 1 are very close to each other. Note that the matrix of these coefficients is symmetrical, i.e., $C_{m\gamma,n\delta}(S) = C_{n\delta,m\gamma}(S)$ and that the correlation coefficient $K_{m\gamma,n\delta}$ is given by the average of $C_{m\gamma,n\delta}(S)$ for $S = 0$ and 1 [Eq. (31)].

With these correlation coefficients we can evaluate the density matrix elements $\rho_{ij}{}^{(2)}$ according to Eq. (37) (Table IV). These values only include the contribution from B_{3u} particle-hole pairs, and hence the sum of the diagonal elements should be regarded as the B_{3u} part of $\langle \mathrm{HF} \mid U^+U \mid \mathrm{HF} \rangle$ [Eq. (43)]. These estimates of $\rho_{ij}{}^{(2)}$ were used to calculate the corrections to the transition moment [Eq. (24)]. The correlation coefficients can also be used to obtain an estimate of part of the total correlation energy of the ground state. The same limitation is true, and hence we only obtain that part of the correlation energy due to two particle-hole pairs both of B_{3u} symmetry. From Eq. (44) we obtain

$$E_{\mathrm{corr}}(B_{3u}) = -4.8 \text{ eV}. \tag{45}$$

Finally we list the matrix elements $S_{m\gamma,n\delta}$ and T_{ij}, Eq. (36), in Tables V and VI. Again these elements only contain the contribution from B_{3u} excitations. The first-order correction $B_{m\gamma,n\delta}{}^{(1)}(S)$ of the **B** matrix is just $(-1)^S S_{m\gamma,n\delta}$. The elements $A_{m\gamma,n\delta}{}^{(1)}$ are evaluated using the T_{ij} elements and are shown in Table VII.

VII. FURTHER RESULTS WITH THE TDA AND RPA

In Sec. VI we presented the results of calculations on the T and V states of ethylene using a moderately

accurate basis set to describe the hole and particle states. This basis is a convenient one with which to carry out the caluclations and compare the results in all three approximations, i.e., TDA, RPA, and HRPA. This $[3s2p/1s]$ basis set is derived by contracting a primitive set of nine s-like and five p-like Gaussians on the carbons and four s-like Gaussians on the hydrogens down to three s-like and two p-like orbitals on the carbons and one s-like function on the hydrogens.[13] The accuracy of these calculations will increase as the basis set becomes less contracted. This is obviously due to the added flexibility introduced by having more linear coefficients determined by the SCF process, but it also depends on how the primitive basis is contracted. As the basis set becomes less contracted the description of the occupied orbitals improves and we have a larger number of particle states. We have carried out a series of calculations on the $^1B_{3u}(V)$ and $^3B_{3u}(T)$ states of ethylene in which we successively use the occupied (hole) and unoccupied (particle) orbitals of Hartree–Fock calculations of increasing accuracy.[15] From these results we can see what happens to the excitation energies in the TDA and RPA as the number of particle states increases, i.e., more particle-hole pairs.

We first give the results in which the basis set has primarily valence-like atomic orbital character. With this basis we can expect to adequately describe both the ground and valence-shell excited states.[16] In a transition to a valence excited state an electron is transferred from a molecular orbital, which is taken as a linear combination of appropriate atomic orbitals, to a molecular orbital composed of atomic orbitals with the same principal quantum number, but with different phases. The $\pi \rightarrow \pi^*$ transition in ethylene, with its large transition moment $D \approx 1.35$, is presumably of this type. With such a basis we clearly cannot describe Rydberg states. This distinction between valence and Rydberg excited states will become important in a later section.

In Table VIII we list the excitation energies and oscillator strenths in the TDA and RPA of a series of calculations using a basis set with only valence atomic orbital character but with increasing flexibility.[13,15]

TABLE II. The amplitudes $Y_{m\gamma}$ and $Z_{m\gamma}$ for the V and T states.

(m, γ)	$N \rightarrow V$			$N \rightarrow T$		
	TDA	RPA	SHRPA	TDA	RPA	SHRPA
	$Y_{m\gamma}$			$Y_{m\gamma}$		
(9, 8)	0.9763	0.9915	1.0017	0.9721	1.2048	0.9879
(15, 8)	−0.0414	−0.0720	−0.0498	−0.2242	−0.3541	−0.2165
(12, 7)	0.1008	0.0751	0.0755	−0.0129	−0.0339	−0.0249
(17, 7)	−0.0370	−0.0320	−0.0326	−0.0143	−0.0446	−0.0301
(10, 6)	0.0179	0.0164	0.0148	−0.0064	−0.0015	−0.0027
(18, 6)	−0.0330	−0.0261	−0.0245	0.0103	0.0337	0.0216
(19, 6)	0.1365	0.1108	0.0987	−0.0237	−0.0477	−0.0317
(14, 5)	0.0808	0.0607	0.0587	−0.0116	−0.0315	−0.0215
(20, 5)	0.0158	0.0109	0.0094	−0.0119	−0.0302	−0.0200
(16, 4)	0.0525	0.0395	0.0377	−0.0301	−0.0733	−0.0472
(11, 4)	−0.0036	−0.0023	−0.0027	0.0012	0.0102	0.0039
(10, 3)	−0.0463	−0.0351	−0.0333	0.0182	0.0413	0.0255
(18, 3)	−0.0086	−0.0036	−0.0026	0.0292	0.0547	0.0379
(19, 3)	−0.0433	−0.0327	−0.0268	0.0352	0.0643	0.0429
	$Z_{m\gamma}$			$Z_{m\gamma}$		
(9, 8)		−0.0832	−0.1467		−0.7140	−0.1566
(15, 8)		0.0225	0.0524		0.2688	0.0663
(12, 7)		0.0285	0.0233		0.0276	0.0122
(17, 7)		−0.0197	−0.0181		0.0403	0.0202
(10, 6)		0.0106	0.0094		−0.0015	−0.0018
(18, 6)		−0.0092	−0.0066		−0.0323	−0.0172
(19, 6)		0.0683	0.0560		0.0386	0.0154
(14, 5)		0.0273	0.0224		0.0273	0.0127
(20, 5)		0.0075	0.0060		0.0270	0.0135
(16, 4)		0.0174	0.0140		0.0676	0.0344
(11, 4)		0.0062	0.0063		−0.0132	−0.0082
(10, 3)		−0.0172	−0.0143		−0.0368	−0.0167
(18, 3)		−0.0083	−0.0077		−0.0462	−0.0218
(19, 3)		−0.0297	−0.0247		−0.0537	−0.0237

TABLE III. Correlation coefficients $C_{m\gamma, n\delta}(S)$ derived from B_{3u} particle-hole pairs.

(m, γ)	(n, δ)	$C_{m\gamma, n\delta}(S)$ [a]		(m, γ)	(n, δ)	$C_{m\gamma, n\delta}(S)$	
		$S = 0$	$S = 1$			$S = 0$	$S = 1$
9, 8	9, 8	−0.1657	−0.1466	14, 5	9, 8	0.0294	0.0088
15, 8	9, 8	0.0655	0.0578	14, 5	15, 8	−0.0293	−0.0068
15, 8	15, 8	−0.0440	−0.0412	14, 5	12, 7	−0.0066	−0.0310
12, 7	9, 8	0.0298	0.0083	14, 5	19, 6	−0.0284	−0.0052
12, 7	15, 8	−0.0283	−0.0071	20, 5	17, 7	−0.0128	−0.0279
17, 7	17, 7	−0.0341	−0.0385	16, 4	9, 8	0.0213	0.0286
18, 6	17, 7	0.0043	0.0292	16, 4	17, 7	−0.0114	−0.0270
19, 6	9, 8	0.0685	0.0107	16, 4	18, 6	0.0161	0.0283
19, 6	15, 8	−0.0471	−0.0092	16, 4	16, 4	−0.0285	−0.0302
19, 6	12, 7	−0.0253	−0.0068	19, 3	9, 8	−0.0312	−0.0195
19, 6	19, 6	−0.0409	−0.0408	19, 3	15, 8	0.0261	0.0128

[a] This list includes those coefficients larger in magnitude than 0.025 for either $S = 0$ or 1. Also note $C_{m\gamma, n\delta}(S) = C_{n\delta, m\gamma}(S)$.

TABLE IV. The density matrix elements[a] $\rho_{ij}{}^{(2)}$ (B_{3u} contribution).

Hole states		Particle states	
(γ, δ)[b]	$1+\rho_{\gamma\delta}{}^{(2)}$	(m, n)[b]	$\rho_{mn}{}^{(2)}$
3, 3	0.9952	9, 9	0.03250
4, 4	0.9960	10, 10	0.00181
5, 5	0.9960	11, 11	0.00012
6, 3	0.9980	12, 12	0.00243
6, 6	0.9920	14, 14	0.00242
7, 7	0.9947	15, 9	−0.01559
8, 8	0.9591	15, 15	0.00835
		16, 11	−0.00048
		16, 16	0.00392
		17, 12	0.00163
		17, 17	0.00284
		18, 10	0.00162
		18, 18	0.00274
		19, 10	0.00137
		19, 18	−0.00088
		19, 19	0.00821
		20, 14	0.00168
		20, 20	0.00158

[a] $\rho_{ij}{}^{(2)} = \rho_{ji}{}^{(2)}$; also $-\Sigma_\gamma \rho_{\gamma\gamma}{}^{(2)} = \Sigma_m \rho_{mm}{}^{(2)} = 0.067$.
[b] All other elements are zero.

The first column of Table VIII specifies how the original $(9s5p/4s)$ Gaussian basis[17] is contracted down to generate the basis for each calculation. For example, in the calculation with the contracted basis $[4s2p/2s]$ there are four s-like and two p-like functions on the carbons and two s-like functions on the hydrogens. This

TABLE V. Matrix elements[a] $S_{m\gamma, n\delta}$.

(m, γ)	(n, δ)[b]	$S_{m\gamma, n\delta}$[c]	(m, γ)	(n, γ)[b]	$S_{m\gamma, n\delta}$[c]
9, 8	9, 8	0.0523	10, 3	10, 6	0.0013
15, 8	9, 8	−0.0345	10, 3	18, 6	0.0013
15, 8	15, 8	0.0240	10, 3	19, 6	0.0006
12, 7	12, 7	0.0077	10, 3	10, 3	0.0052
17, 7	12, 7	0.0044	18, 3	10, 6	0.0042
17, 7	17, 7	0.0086	18, 3	18, 6	0.0045
10, 6	10, 6	0.0013	18, 3	19, 6	0.0050
18, 6	10, 6	0.0019	18, 3	10, 3	0.0038
18, 6	18, 6	0.0061	18, 3	18, 3	0.0036
19, 6	10, 6	−0.0015	19, 3	10, 6	−0.0110
19, 6	18, 6	−0.0082	19, 3	18, 6	−0.0077
19, 6	19, 6	0.0254	19, 3	19, 6	−0.0166
14, 5	14, 5	0.0088	19, 3	10, 3	0.0075
20, 5	14, 5	0.0067	19, 3	18, 3	0.0050
20, 5	20, 5	0.0071	19, 3	19, 3	0.0121
16, 4	16, 4	0.0142			
11, 4	16, 4	−0.0016			
11, 4	11, 4	0.0004			

[a] Contributions only from B_{3u} particle-hole pairs. $B_{m\gamma, n\delta}{}^{(1)}(S) = (-1)^S S_{m\gamma, n\delta}$.
[b] All other elements are zero.
[c] $S_{m\gamma, n\delta} = S_{n\delta, m\gamma}$.

calculation uses 17 of the 20 virtual orbitals as particle states and has 17 particle-hole pairs of which two are of the $\pi \to \pi^*$ type. The number of particle-hole pairs increases as we go from the $[3s1p/1s]$ to $[4s3p/2s]$. We will not discuss the quantitative details of these calculations since the results show an obvious trend. The excitation energy in the TDA goes from 9.90 eV in the $[3s1p/1s]$ basis to 8.15 eV in the $[4s3p/2s]$, while the oscillator strength, f, changes from 0.63 to 0.62. Recall that in the TDA we are just taking the excited state wavefunction as a linear combination of the appropriate single excitations out of the HF ground state. As the number of particle states increases the description of the π^* orbital improves and we also include more $\sigma-\pi$

TABLE VI. Matrix elements T_{ij} [Eq. (36)][a].

Hole states		Particle states	
(γ, δ)[b]	$T_{\gamma\delta}$[c]	(m, n)[b]	T_{mn}
3, 3	−0.0105	9, 9	0.0261
4, 4	−0.0073	10, 10	0.0032
5, 5	−0.0079	11, 11	0.0002
6, 3	0.0154	12, 12	0.0039
6, 6	−0.0164	14, 14	0.0044
7, 7	−0.0081	15, 9	−0.0173
8, 8	−0.0381	15, 15	0.0120
		16, 11	−0.0008
		16, 16	0.0071
		17, 12	0.0022
		17, 17	0.0043
		18, 10	0.0029
		18, 18	0.0049
		19, 10	0.0030
		19, 18	−0.0016
		19, 19	0.0187
		20, 14	0.0034
		20, 20	0.0035

[a] Contributions only from B_{3u} particle-hole pairs.
[b] All other elements are zero.
[c] $\Sigma_m T_{mm} = -\Sigma_\gamma T_{\gamma\gamma} = 0.0884$ a.u. $= 2.41$ eV.

correlation. We will see that the inclusion of $\sigma-\pi$ correlation has a very important effect on the description of this state. This will become obvious when we discuss the results of open-shell SCF calculations on the V state.

The most extensive calculation in the RPA, Table VIII, gives an excitation energy of 7.68 eV for the $N \to V$ transition. The oscillator strength is 0.46. We expect this excitation energy to increase by some amount when we include the corrections of the higher RPA. Note that the oscillator strenth only changes slightly as the basis set increases. This is the expected behavior of the oscillator strength in the RPA. For the $N \to T$ transition we obtain an excitation energy of about 3.4 eV in the TDA. We only list the RPA excitation energy in the $[3s2p/1s]$ basis. The excitation

energies, with the other basis sets will also agree poorly with the experimental value of 4.6 eV. We have discussed the reason for this failure and one has to use the HRPA to study these states.

Recently Dunning et al.[18] reported very extensive nonempirical open-shell SCF calculations on the (π, π^*) states of ethylene using the $[4s2p/2s]$ valence basis of Gaussian functions augmented in the π and π^* molecular orbitals (MO) by three successively diffuse $2p\pi$-like Gaussian-type functions (GTF). We now add a number prefix to π and π^* since in the extended basis SCF calculations there is more than one of each type. For example the $(1\pi, 1\pi^*)$ state has an electron in the lowest π and π^* level. With the molecule in the xy plane they report the values of 42.08 and 2.74 a.u. for the matrix element $\langle 1\pi^* \mid z^2 \mid 1\pi^* \rangle$ in the $^1(1\pi, 1\pi^*)$ and $^3(1\pi, 1\pi^*)$ states, respectively, with vertical excitation

TABLE VII. First-order corrections $A_{m\gamma,n\delta}^{(1)}$ [Eq. (36)].[a]

(m, γ)	(n, δ)[b]	$A_{m\gamma,n\delta}^{(1)}$	(m, γ)	(n, δ)[b]	$A_{m\gamma,n\delta}^{(1)}$
9, 8	9, 8	0.0643	20, 5	20, 5	0.0114
15, 8	9, 8	−0.0172	16, 4	16, 4	0.0144
15, 8	15, 8	0.0501	11, 4	16, 4	−0.0008
12, 7	12, 7	0.0120	11, 4	11, 4	0.0075
17, 7	12, 7	0.0022	10, 3	10, 6	−0.0054
17, 7	17, 7	0.0124	10, 3	10, 3	0.0137
10, 6	10, 6	0.0196	18, 3	18. 6	−0.0054
18, 6	10, 6	0.0029	18, 3	10, 3	0.0029
18, 6	18, 6	0.0212	18, 3	18, 3	0.0153
19, 6	10, 6	0.0030	19, 3	19, 6	−0.0054
19, 6	18, 6	−0.0016	19, 3	10, 3	0.0030
19, 6	19, 6	0.0351	19, 3	18, 3	−0.0016
14, 5	14, 5	0.0123	19, 3	19, 3	0.0292
20, 5	14, 5	0.0034			

[a] Only contributions from B_{3u} excitations included.
[b] All other elements are zero.

energies of 7.41 and 3.33 eV. The π^* orbital in the $^1(1\pi, 1\pi^*)$ state is diffuse and very different from the π^* orbital in the $^3(1\pi, 1\pi^*)$ state. Hence the $^3(1\pi, 1\pi^*)$ state is valence-like while the $^1(1\pi, 1\pi^*)$ state is Rydberg-like. Recently we have shown that the lowest $^1(\pi, \pi^*)$ state obtained by direct SCF calculation in the ground-state geometry of ethylene is actually a member of a Rydberg series and should not be identified with the spectroscopically observed V state.[19] One of the arguments supporting this interpretation is based on the results of TDA and RPA calculations on the T and V states but with the same basis as used in the direct open-shell SCF calculations.[18] This is the $[4s2p/2s]$ valence basis plus three diffuse $2p_z$ GTF's. We designate this basis $[4s2p/2s]+R(3p_z)$. We will now see that the first $^1B_{3u}$ state in the TDA and RPA is a valence-like state with a very different orbital character from any $(\pi, \lambda\pi^*)$ state of the SCF calculations. This valence-like state is then followed by Rydberg states. We now discuss these results and their implications.

TABLE VIII. The $^1B_{3u}$ and $^3B_{3u}(\pi \rightarrow \pi^*)$ states of ethylene: excitation energies and oscillator strengths in the TDA and RPA.

Basis set[a]		TDA	RPA
$N \rightarrow V\,(^1B_{3u})$			
$[3s1p/1s]$	ω	9.90	9.21
	f	0.63	0.43
$[3s2p/1s]$	ω	8.43	7.93
	f	0.71	0.52
$[4s2p/2s]$	ω	8.19	7.71
	f	0.65	0.48
$[4s3p/2s]$	ω	8.15	7.68
	f	0.62	0.46
$N \rightarrow T\,(^3B_{3u})$[b]			
$[3s1p/1s]$	ω	3.50	
$[3s2p/1s]$	ω	3.40	1.50
$[4s2p/2s]$	ω	3.36	
$[4s3p/2s]$	ω	3.35	

[a] See text for explanation of this notation. This is a valence basis set. All energies in eV's.
[b] The RPA results for the $N \rightarrow T$ transition can be expected to agree poorly with experiment. See text and Table I.

Table IX lists some results of these calculations. These calculations were carried out by Dunning and are discussed in Ref. 13. We see that addition of the diffuse $2p_z$ basis functions has not caused any drastic changes in the V or T states. The TDA excitation energy of the $N \rightarrow V$ transition goes from 8.19 eV in a valence basis to 7.82 eV in the augmented basis and the oscillator strength is likewise reduced from 0.65 to 0.54. The most

TABLE IX. The T and V states of ethylene in a basis containing valence and Rydberg atomic orbital character.

Basis set[a]		TDA	RPA
$N \rightarrow V\,(^1B_{3u})$			
$[4s2p/2s]+R(3pz)$	ω	7.82	7.46
	f	0.54	0.44
	$\langle 1\pi^* \mid z^2 \mid 1\pi^* \rangle$[c]	10.69[d]	7.47[d]
$[4s2p/2s]$[b]	ω	8.19	7.71
	f	0.65	0.48
	$\langle 1\pi^* \mid z^2 \mid 1\pi^* \rangle$	4.20	
$N \rightarrow T\,(^3B_{3u})$			
$[4s2p/2s]+R(3pz)$	ω	3.37	
	$\langle 1\pi^* \mid z^2 \mid 1\pi^* \rangle$	2.78	
$[4s2p/2s]$	ω	3.36	
	$\langle 1\pi^* \mid z^2 \mid 1\pi^* \rangle$	2.66	

[a] See text for explanation of notation in this column.
[b] This is a valence-like basis.
[c] The molecule is in the xy plane. This is a measure of the spatial extent of the π^* orbital.
[d] From a natural orbital analysis.

interesting change is in the spatial extent of the π^* orbital. The π^* density becomes more diffuse changing the matrix element, $\langle \pi^* \mid z^2 \mid \pi^* \rangle$, from 4.20 a.u. in a valence basis set to 10.69 a.u. in the basis set with diffuse functions. Note, however, that this same matrix element for the π^* orbital of the triplet (T) state is only 2.66 a.u. and is unaffected by the addition of the diffuse basis functions. This difference in the tail region of the π^* MO between the triplet and singlet excited states can obviously have an important effect on the interaction between molecules in a molecular crystal, e.g., the exciton splitting. The RPA results show the same trend as those of the TDA with ω decreasing from 7.71 to 7.46 eV and f from 0.48 to 0.44 a.u. By comparison with results using the $[3s2p/1s]$ we can expect the ω of the RPA to increase in the HRPA and the transition moment to decrease.

These results above can now be compared with the predictions of the open-shell SCF calculations on the lowest $^1B_{3u}$ and $^3B_{3u}$ states of configuration (π, π^*). The excitation energy of this $^1B_{3u}$ state is 7.41 eV and the π^* MO is very diffuse, e.g., $\langle 1\pi^* \mid z^2 \mid 1\pi^* \rangle \approx 42$ a.u., while for the $^3B_{3u}$ state they are 3.33 eV and ≈ 2.75 a.u., respectively.[18,19] Clearly the $^3B_{3u}$ state of the SCF scheme can be identified with the T state of the TDA results (Table IX). But the first $^1B_{3u}$ state of the SCF calculations, or any other of these SCF states (all of which are successively more diffuse) cannot be identified with the lowest state of this symmetry in the TDA or RPA. The valence-like V state of the TDA is unrelated to any of the bound states of the SCF states, all of which are Rydberg-like. What has probably happened is that the V state in Hartree–Fock theory would be beyond the HF ionization potential (9.03 eV) and is so heavily contaminated with spuriously calculated lower-energy Rydberg components (because of orthogonality) that it shows very little resemblance to the spectroscopic V state.[19] The oscillator strength of the first (π, π^*) $^1B_{3u}$ SCF state is 0.15.[18] Electron correlation, in particular between the π electrons in the ground state, should reduce this. Neglecting changes in the Σ core between the ground and excited $^1(1\pi, 1\pi^*)$ SCF states, the oscillator strength is about 0.075.[19,20] In the calculation with the extended basis $[4s2p/2s] + R(3pz)$ both the TDA and RPA show two states, in addition to the V state, below the ionization potential. In the RPA these states lie at 8.89 and 9.44 eV with oscillator strengths of 0.02 and 0.006, respectively. They are clearly Rydberg states. Comparison of the f value of 0.02 of the second state in RPA and the f value of about 0.08 (neglecting core changes) for the lowest SCF (π, π^*) state suggests that they could be identified with the same spectroscopic state.

VIII. DISCUSSION

We have applied our recently proposed higher-random-phase approximation (HRPA)[4] to the $T(^3B_{3u})$

and $V(^1B_{3u})$ states of ethylene. The HRPA is a higher-order approximation to the solution of the equations of motion[1] in which we solve for the excitation frequencies of the excited states and the correlated ground state in a self-consistent fashion. In comparison, in the RPA one uses Hartree–Fock ground state in evaluating the matrix elements which appear in the equations for the excitation. Consequently ground-state correlation coefficients do not appear in these equations although the effects of these correlation on the properties of the excitation are included to some degree. In the HRPA we obtain both the excitation frequencies and the ground-state correlation coefficients self-consistently. We have also proposed a simplified scheme (SHRPA) for solving the HRPA equations, which is not only a good approximation to the HRPA but also does not require any more molecular integrals than the usual RPA does. This is a significant advantage of the SHRPA since the preparation of the molecular integrals (interaction matrix elements) is one of the most laborious parts of the entire calculation. The number of two-electron molecular integrals required by the RPA or SHRPA is much less than that required in a CI scheme.

The SHRPA removes many of the deficiences of the RPA. For example, in an extensive RPA calculation we preduct an excitation energy of 1.5 eV for the $N \rightarrow T$ in ethylene, in poor agreement with the experimental value of 4.6 eV. With the SHRPA we obtain 4.95 eV. For the $N \rightarrow V(^1A_{1g} \rightarrow {}^1B_{3u})$ transition the excitation energy increases from 7.93 eV in the RPA to 9.39 eV in the HRPA, clearly showing that the effects linear in the correlation coefficients which are included in the HRPA are also important for this transition. The change in the oscillator strength $(N \rightarrow V)$ is comparatively small going from 0.52 in the RPA to 0.46 in the HRPA, in good agreement with the estimated experimental value of 0.34. Although we do not have the CI value in this basis for the $N \rightarrow V$ excitation energy, we estimate that it should be close to the HRPA value of 9.4 eV. CI calculations by Whitten[14] in a basis which should be similar in accuracy to ours do in fact give an excitation energy of 9.2 eV. The increase in excitation energy in going from the RPA to HRPA is due to the fact that the RPA overestimates the correlation effects in the excited states.

In this example we have considered only transitions to states belonging to B_{3u} symmetry. We chose this class of transitions because it contains the T and V states (B_{3u}) which are the lowest excited states, and thus the major part of the ground-state correlation is associated with particle-hole pairs of this symmetry. With the correlation coefficients of this class one can now calculate all the matrix elements of **A** and **B** to first order in the correlation coefficients, e.g., $A_{m\gamma,n\delta}{}^0 + A_{m\gamma,n\delta}{}^{(1)}$ for any pairs of $m\gamma$, $n\delta$ and use these to calculate the next important class of excitation. The equations of the SHRPA can then be solved as we have done for the B_{3u} class. With the correlation coefficients

for this class of transition we can go back to the B_{3u} class and recalculate the **A** and **B** matrices. We expect, however, that the changes in the excitation energies for the B_{3u} transitions will be small. We have seen[21] that for the excited states of ethylene other than B_{3u} the TDA and RPA give almost the same excitation frequencies. This suggests that the HRPA corrections will be small for these transitions unlike for the B_{3u} transitions, and that for an excited state of symmetry Γ only those correlation coefficients associated with particle-hole pairs of this same symmetry will be important.

The RPA and HRPA are methods specifically designed for calculating relative quantities such as excitation energies and oscillator strengths directly and hence treating stationary-state wavefunctions as of secondary importance. For example, in our applications to ethylene the lowest $^1B_{3u}$ state in extensive TDA and RPA calculations is definitely valence-like in character and is to be identified with the spectroscopically observed V state (e.g., a calculated and observed oscillator strength of 0.46 and about 0.34, respectively). In contrast, direct open-shell calculations on $^1B_{3u}$ (π, π^*) states give a very diffuse or Rydberg-like state.[18,19] The results obtained by these direct methods, and discussed in this paper, can explain the appearance and ordering of the states coming out of the open-shell SCF calculations. No valence-like state shows up in the SCF calculations, and this probably indicates that the V state in HF theory would be beyond the HF ionization potential (9.03 eV) and is so heavily contaminated with spuriously calculated Rydberg components through orthogonality requirements so as to show little resemblance to the spectroscopic V state.[19]

ACKNOWLEDGMENTS

APPENDIX

The molecular orbitals used in the present calculations are the SCF–MO's obtained using a contracted $[3s2p/1s]$ Gaussian basis. We have discussed this basis in Sec. VI and Table AI gives the symmetries and orbital energies of the 20 MO's. The first eight orbitals are occupied, and we only use 12 of the 14 available virtual (particle) states. The hole-state (occupied) and particle-state (unoccupied) orbitals couple to form B_{3u} pairs as follows:

(8, 9)	(5, 14)	(2, 11)
(8, 15)	(5, 20)	(2, 16)
(7, 12)	(4, 16)	(1, 10)
(7, 17)	(4, 11)	(1, 18)
(6, 10)	(3, 10)	(1, 19)
(6, 18)	(3, 18)	
(6, 19)	(3, 19)	

We do not use the last five particle-hole pairs since the particle-hole energy separations are too large for them to have any effect on the properties of the transition.

The dipole transition moment $\mathbf{d}_{m\gamma}^0$ between hole (γ)- and particle (m)-states are listed in Table AII. Tables

TABLE AI. SCF molecular orbitals.[a]

MO	Symmetry[b]	ϵ_γ (in a.u.)	MO	Symmetry[b]	ϵ_m (in a.u.)
1	$1a_g$	-11.27103	9	$1b_{2g}$	0.13553
2	$1b_{3u}$	-11.26951	10	$3b_{3u}$	0.37535
3	$2a_g$	-1.03127	11	$4a_g$	0.40961
4	$2b_{3u}$	-0.80252	12	$2b_{2u}$	0.42796
5	$1b_{2u}$	-0.66670	13	$2b_{1u}$	0.48520
6	$3a_g$	-0.59478	14	$2b_{1g}$	0.48626
7	$1b_{1g}$	-0.52593	15	$2b_{2g}$	0.60297
8	$1b_{1u}$	-0.38651	16	$5a_g$	0.64019
			17	$3b_{2u}$	0.66080
			18	$4b_{3u}$	0.73049
			19	$5b_{3u}$	0.89088
			20	$3b_{1g}$	1.22853

[a] At the equilibrium configuration of the ground state.
[b] The molecule in the xy plane with the x axis along the C–C bond. With the molecule in the yz plane with z along the C–C bond (IUPAP convention) we would have these changes: $a_g \rightarrow a_g$; $b_{1g} \rightarrow b_{2g}$; $b_{2g} \rightarrow b_{3g}$; $b_{1u} \rightarrow b_{2u}$; $b_{2u} \rightarrow b_{3u}$; $b_{3u} \rightarrow b_{1u}$.

TABLE AII. Dipole transition moments, $\mathbf{d}_{m\gamma}^0$, between hole and particle states.[a]

(m, γ)	$d_{m\gamma}^0$ [b]	(m, γ)	$d_{m\gamma}^0$
(9, 8)	1.43780	(14, 5)	0.25223
(15, 8)	-0.08267	(20, 5)	0.21226
(12, 7)	0.22814	(16, 4)	0.10758
(17, 7)	0.97950	(11, 4)	-0.47525
(10, 6)	-0.74517	(10, 3)	-0.29936
(18, 6)	-0.02068	(18, 3)	0.04991
(19, 6)	-0.76362	(19, 3)	0.29997

[a] Component along the C–C bond; in a.u.
[b] At the equilibrium configuration of the ground state.

TABLE AIII. Molecular integrals.[a]

A. $V_{m\gamma n\delta}$

(n,δ) → / (m,γ) ↓	(9,8) / (20,5)	(15,8) / (16,4)	(12,7) / (11,4)	(17,7) / (10,3)	(10,6) / (18,3)	(18,6) / (19,3)	(19,6)	(14,5)
(9,8)	0.368835							
(15,8)	−0.109157	0.376618						
(12,7)	−0.001517[b]	0.006130	0.311799					
(17,7)	−0.002858	0.003464	0.035784	0.370723				
(10,6)	−0.004031	−0.001816	−0.014355	−0.006318	0.303011			
(18,6)	0.003430	−0.000601	−0.009144	−0.044328	0.042106	0.367249		
(19,6)	−0.010509	0.013883	0.004395	−0.008057	0.036143	−0.020792	0.522166	
(14,5)	−0.001591	0.008693	0.081413	0.034187	−0.016911	−0.007247	0.007213	0.312239
(20,5)	−0.007942	0.004887	0.032637	0.120944	−0.000279	−0.039397	−0.003196	0.070503
	0.378578							
(16,4)	−0.017649	0.017412	0.032932	0.060711	−0.045147	−0.123920	0.033436	0.020367
	0.050143	0.390663						
(11,4)	−0.000065	−0.004226	0.011257	−0.012492	0.053383	−0.010773	−0.018547	−0.007412
	0.001302	−0.009353	0.280078					
(10,3)	0.003773	−0.036745	−0.018978	−0.009828	−0.004986	−0.007247	−0.031685	−0.035941
	−0.012143	−0.040134	0.039184	0.293723				
(18,3)	0.029478	−0.015680	−0.010452	−0.039164	−0.007247	0.006751	−0.006714	−0.014028
	−0.051503	−0.103665	−0.008235	0.042988	0.349596			
(19,3)	0.034201	−0.029214	−0.007153	−0.018829	−0.031685	−0.006714	−0.123585	−0.017117
	−0.036368	0.023061	−0.021701	0.054402	−0.007954	0.550046		

B. $V_{mn\gamma\delta}$

(n,δ) → / (m,γ) ↓	(9,8) / (20,5)	(15,8) / (16,4)	(12,7) / (11,4)	(17,7) / (10,3)	(10,6) / (18,3)	(18,6) / (19,3)	(19,6)	(14,5)
(9,8)	0.097324							
(15,8)	−0.062185	0.063572						
(12,7)	−0.025423[c]	0.029072	0.025946					
(17,7)	0.012647	0.004910	0.008953	0.054571				
(10,6)	−0.003095	−0.006372	−0.007830	−0.007418	0.014440			
(18,6)	0.015779	−0.014961	−0.011605	−0.023312	0.007529	0.031231		
(19,6)	−0.071321	0.061300	0.034535	−0.006467	−0.001866	−0.020407	0.099155	
(14,5)	−0.030254	0.033482	0.028699	0.008857	−0.008450	−0.010627	0.039743	0.032715
(20,5)	−0.017609	0.022886	0.018245	0.039606	−0.004653	−0.022738	0.021179	0.020189
	0.039893							
(16,4)	−0.036440	0.035536	0.023903	0.026610	−0.013328	−0.039267	0.040604	0.024229
	0.031748	0.056028						
(11,4)	0.002098	−0.006367	−0.004743	−0.003866	0.008354	0.000260	−0.003348	−0.006469
	−0.003513	−0.003919	0.007308					
(10,3)	0.024962	−0.030050	−0.019274	−0.007667	0.007447	0.007452	−0.032338	−0.022488
	−0.015448	−0.018856	0.006576	0.018924				
(18,3)	0.021331	−0.018486	−0.010774	−0.016771	0.003616	0.020030	−0.017891	−0.010561
	−0.018550	−0.028165	0.000132	0.008467	0.016134			
(19,3)	0.046792	−0.044580	−0.022618	−0.012621	−0.006595	0.902407	−0.058324	−0.028083
	−0.027012	−0.013770	0.002658	0.024985	0.009965	0.064175		

TABLE AIII (Continued)

(n,δ)	(9, 8)	(15, 8)	(12, 7)	(17, 7)	(10, 6)	(18, 6)	(19, 6)	(14, 5)
(m,γ)	(20, 5)	(16, 4)	(11, 4)	(10, 3)	(18, 3)	(19, 3)		

C. $V_{mn\delta\gamma}$

	(9, 8)	(15, 8)	(12, 7)	(17, 7)	(10, 6)	(18, 6)	(19, 6)	(14, 5)
(9, 8)	0.097324							
(15, 8)	−0.062185	0.063572						
(12, 7)	−0.001077[d]	0.004320	0.025946					
(17, 7)	−0.005228	0.003566	0.008953	0.054571				
(10, 6)	−0.000717	−0.001515	−0.002960	0.001932	0.014440			
(18, 6)	0.007924	−0.001562	−0.006685	−0.039528	0.007529	0.031231		
(19, 6)	−0.002941	0.003198	0.007263	0.007706	−0.001866	−0.020407	0.099155	
(14, 5)	−0.002568	0.004721	0.038724	0.024794	−0.003997	−0.004151	0.005232	0.032715
(20, 5)	−0.006340	0.004582	0.023153	0.049616	0.001405	−0.024068	0.004112	0.020189
	0.039893							
(16, 4)	−0.021865	0.014947	0.006922	0.032858	−0.023097	−0.042207	0.013445	0.007050
	0.024981	0.056028						
(11, 4)	0.007867	−0.003221	−0.001968	0.00831	0.022355	0.008878	0.006335	−0.002824
	0.001061	−0.003919	0.007308					
(10, 3)	0.007838	−0.012132	−0.010582	−0.008845	0.007447	0.003616	−0.006595	−0.010844
	−0.007778	−0.016588	−0.001013	0.018924				
(18, 3)	0.017584	−0.011995	−0.004532	−0.011486	0.007452	0.020030	0.002407	−0.001696
	−0.012290	−0.029401	−0.005869	0.008467	0.016134			
(19, 3)	0.019201	−0.017417	−0.007667	−0.016866	−0.032338	−0.017891	−0.058324	−0.009515
	−0.012684	0.004560	−0.001869	0.024985	0.009965	0.064175		

[a] $V_{mγnδ} = \langle m(1)\gamma(2), r_{12}^{-1}n(1)\delta(2) \rangle$.

[b] For example, this is the integral $\langle 12(1)\ 7(2), r_{12}^{-1}\ 9(1)\ 8(2) \rangle$; all integrals are in a.u. and for the ground-state geometry.

[c] For example, this is the integral $\langle 12(1)\ 9(2), r_{12}^{-1}\ 7(1)\ 8(2) \rangle$; all integrals are in a.u. and for the ground-state geometry.

[d] For example, this is the integral $\langle 12(1)\ 9(2), r_{12}^{-1}\ 8(1)\ 7(2) \rangle$; all integrals are in a.u. and for the ground-state geometry.

AIII.A–AIII.C list the various two-electron interaction integrals needed to carry out the RPA and SHRPA calculations for B_{3u} transitions.

* Alfred P. Sloan Foundation Fellow.
† Contribution No. 4122.
[1] D. J. Rowe, Rev. Mod. Phys. 40, 153 (1968).
[2] P. L. Altick and A. E. Glassgold, Phys. Rev. 133, A632 (1964).
[3] T. H. Dunning and V. McKoy, J. Chem. Phys. 47, 1735 (1967); 48, 5263 (1968).
[4] T. Shibuya and V. McKoy, "Higher Random-Phase Approximation as an Approximation to the Equations of Motion," Phys. Rev. A (to be published).
[5] Only the results are given here. See Ref. 4 for the detailed discussions.
[6] Note that in these equations T_{ij} does not denote the matrix element of a single-particle operator.
[7] B. Schneider, "Inelastic Scattering of High Energy Electrons from Atoms: The Helium Atom," Phys. Rev. A (Preprint) (to be published). The calculations are done within the Born approximation.
[8] Y. K. Kim and M. Inokuti, Phys. Rev. 175, 176 (1968).
[9] J. da Providência, Phys. Letters 21, 668 (1966).
[10] E. A. Sanderson, Phys. Letters 19, 141 (1965).
[11] We use the coordinate system of Ref. 3. This would be B_{1u} in the notation recommended by IUPAP.
[12] T. Shibuya and V. McCoy, J. Chem. Phys. 53, 3308 (1970).
[13] For details see T. H. Dunning, Ph.D. dissertation, California Institute of Technology, Pasadena, Calif. (1970).
[14] J. Whitten (private communication).
[15] These calculations were done by T. H. Dunning, Jr., see Ref. 13 for some details.
[16] A. J. Merer and R. S. Mulliken, Chem. Rev. 69, 639 (1969).
[17] For a discussion of this basis see N. W. Winter, T. H. Dunning, Jr., and J. H. Letcher, J. Chem. Phys. 49, 1871 (1968).
[18] T. H. Dunning, W. J. Hunt, and W. A. Goddard, Chem. Phys. Letters 4, 147 (1969).
[19] H. Basch and V. McKoy, J. Chem. Phys. 53, 1628 (1970).
[20] This is actually the root mean square product value of the length and velocity operators.
[21] See, for instance, Table VIII in the first paper of Ref. 3.