3466 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (12), 3466—3471 (1976) [Vol. 49, No. 12

The Approximate Self-Consistent Renormalized RPA: The Electronic Excited States of DNA Bases in the CNDO/S Method

Hirotoshi ITO and Yasumasa J. I'HAYA

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182

(Received August 12, 1976)

Comments are given upon the *approximate* self-consistent renormalized RPA(SCrRPA) presented in our previous papar which assumes the correlated ground state wavefunction to be the linear combination of the Hartree-Fock ground state and doubly excited states, in the CI language. The rationalization of the approximate SCrRPA is made from the results computed by the *complete* SCrRPA, whose recipe is simply made. Finally, a numerical comparison of the several RPA methods is made as to the electronic spectra of four DNA bases by using the CNDO/S method.

In the pi-electron semiempirical theories like the Pariser-Parr-Pople model[1)] and the valence electron theories such as the CNDO/S[2,3)] and the INDO/S[4)] methods, the configuration interaction (CI) method has been conventionally used to determine the excitation energies of molecules. On the other side, the random-phase approximation (RPA) has conceptually advantages over the CI method. The latter, when only all the singly excited configurations are included, is actually the same as the Tamm-Dancoff approximation (TDA) which is the lowest order approximation of the equations-of-motion method. For instance, in the CI language, the RPA can include certain *doubly* excited configurations (Z-terms; vide post), in addition to all the *singly* excited configurations (Y-terms). However, the standard RPA often gives the inconsistent solution such as the triplet instability on account of Eq. 3b (vide post). In this respect, the normal RPA (nRPA) is not necessarily superior to the TDA.

This deficiency of the nRPA can be overcome not only by the modification of the HF bases but also by introducing the correlated ground state, instead of the HF ground state, as a reference state.[5)] The latter RPA is referred to as a higher RPA. On the basis of the correlated ground state assumed, several modifications to the nRPA have been proposed. The higher RPA derived by Shibuya and McKoy[6)] and the self-consistent RPA presented by Ostlund and Karplus[7)] are in these streams. The self-consistent polarization propagator approximation (SPPA)[8)] is a similar approach. Previously, we also have applied the renormalized higher RPA(rRPA) in Rowe-Simons' formalism[9,10)] to the various conjugated molecules.[5)]

The rRPA method is based upon the assumption of the correlated ground state which involves the corrections of electron correlation introduced for the Hartree-Fock ground state. Previously, we calculated the non-integral occupation number, *i.e.*, the charge densities from the coefficients of the correlated ground state wavefunction (HF+doubly excited CI's) determined by admixing the Hartree-Fock ground state with various doubly excited configurations using the perturbation theory. In the present paper, we compute the correlated charge densities from the RPA ground state determined by Sanderson and da Providência's recipe.[11,12)] As will be mentioned below, the correlated ground state is determined by the self-consistent solution of the rRPA equation (SCrRPA) in an iterative way.

In this case, a trial well correlated ground state may yield approximately a self-consistent solution at several rounds of iterative calculations. In fact, it is demonstrated that the correlated ground state wavefunction in our previous works[5,14)] gives an approximate solution of the SCrRPA. The central concern of the present paper is therefore focussed upon the rationalization of the *approximate* SCrRPA in our previous treatment rather than the *complete* SCrRPA. The detailed report of the latter will be presented elsewhere.[13)] In the following, we outline the rRPA method, then give some comments upon these two assumptions of the correlated ground state, and finally present some numerical results for DNA bases.

Renormalized Higher RPA

The rRPA equation which was originally given by Rowe[9)] and later reformulated by Simons[10)] explicitly for the singlet and triplet states is written down for the real basis in the following matrix form

$$\begin{pmatrix} \tilde{A}(S) & \tilde{B}(S) \\ -\tilde{B}^*(S) & -\tilde{A}^*(S) \end{pmatrix} \begin{pmatrix} \tilde{Y}(\lambda S) \\ \tilde{Z}(\lambda S) \end{pmatrix} = \omega_\lambda \begin{pmatrix} \tilde{Y}(\lambda S) \\ \tilde{Z}(\lambda S) \end{pmatrix} \tag{1}$$

with

$$\begin{aligned} \tilde{A}_{\mathrm{ph,vf}}(S) &= \delta_{\mathrm{pv}}\delta_{\mathrm{hf}}(E_{\mathrm{p}}-E_{\mathrm{h}}) \\ &\quad + (2)^{-1}(\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}(\rho_{\mathrm{f}}-\rho_{\mathrm{v}})^{1/2} \\ &\quad \times (<\mathrm{pf}|\mathrm{hv}> + (-)^S<\mathrm{pf}|\mathrm{hv}> - <\mathrm{pf}|\mathrm{vh}>) \\ \tilde{B}_{\mathrm{ph,vf}}(S) &= (2)^{-1}(\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}(\rho_{\mathrm{f}}-\rho_{\mathrm{v}})^{1/2} \\ &\quad \times (<\mathrm{pv}|\mathrm{hf}> + (-)^S<\mathrm{pv}|\mathrm{hf}> - \langle\mathrm{pv}|\mathrm{fh}>) \\ <ij|kl> &= \langle i(1)j(2)|1/r_{12}|k(1)l(2)> \\ \tilde{Y}_{\mathrm{ph}}(\lambda S) &= (2)^{-1/2}(\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}Y_{\mathrm{ph}}(\lambda S) \\ \tilde{Z}_{\mathrm{ph}}(\lambda S) &= (2)^{-1/2}(\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}Z_{\mathrm{ph}}(\lambda S) \end{aligned}$$

from which the TDA and the nRPA are derived as special case. E_i is an orbital energy for the ith Hartree-Fock molecular orbital (MO) ϕ_i. Subscripts ph and vf are used to label the *p*article-*h*ole pair and the *v*acant-*f*illed molecular orbital pair states, respectively. $Y_{\mathrm{ph}}(\lambda S)$ and $Z_{\mathrm{ph}}(\lambda S)$ without tildes are the unrenormalized amplitudes for the singly excited creation operator $0^+_{\lambda\mathrm{SM}}$

$$0^+_{\lambda\mathrm{SM}} = \sum_{\mathrm{ph}} (Y_{\mathrm{ph}}(\lambda S)C^+_{\mathrm{ph}}(SM) - Z_{\mathrm{ph}}(\lambda S)C_{\mathrm{ph}}(\overline{SM})) \tag{2}$$

which produces the λth excited state $|\lambda SM>$ when operating on the correlated ground state $|0>$:

$$0^{+}_{\lambda SM}|0> = |\lambda SM> \tag{3a}$$

$$0_{\lambda SM}|0> = 0 \quad (\text{all } \lambda SM) \tag{3b}$$

Here $C^{+}_{\mathrm{ph}}(\mathrm{SM})$ and $C_{\mathrm{ph}}(\overline{\mathrm{SM}})$ are the particle-hole pair creation and annihilation operators, respectively, in the same notation of Ref. 6, S and M being the total spin angular momentum and its z-projection, respectively. ρ_i represents the correlated charge density, *i.e.*, the non-integral occupation number of the ith orbital in the correlated ground state, defined by

$$\begin{aligned}\rho_i &= (2)^{1/2}<0|(2)^{-1/2}(a^{+}_{i\alpha}a_{i\alpha}+a^{+}_{i\alpha}a_{i\beta})|0> \\ &= (2)^{1/2}<0|C^{+}_{ii}(00)|0>\end{aligned} \tag{4}$$

where $a^{+}_{i\sigma}$ and $a_{i\sigma}$ are the Fermion creation and annihilation operators, respectively, for the ith spin-orbital $\phi_i\sigma_i$.

The correlated RPA ground state is usually assumed to be as follows

$$|0> = N_0 e^{U}|HF> \tag{5}$$

with

$$U = (1/2)\sum_{S=0,1}\sum_{i}\sum_{\mathrm{ph}\in\Gamma_i}\sum_{\mathrm{vf}\in\Gamma_i} C_{\mathrm{ph,vf}}(S)C^{+}_{\mathrm{ph}}(\overline{S0})C^{+}_{\mathrm{vf}}(S0) \tag{6a}$$

$$\Gamma_i \times \Gamma_i \in \Gamma_{\mathrm{HF}}. \tag{6b}$$

Here N_0 is the normalization constant

$$N_0^{-2} = 1 + <HF|U^{\dagger}U|HF> \tag{7}$$

and Γ denotes the irreducible representation of a certain set of excited states under consideration.

Equations 3a and 3b should be a simultaneous solution of Eq. 1, which is therefore iteratively solved in the self-consistent manner. Thus the coefficients $C_{\mathrm{ph,vf}}(S)$ can be given by a solution of Eq. 3b. However, it is known that we can safely bypass the problem of solving Eq. 3b by indirectly guessing a good starting ground state.[5,6,14,15] If we know the coefficients $C_{\mathrm{ph,vf}}(S)$ of such starting ground state, the charge densities can be calculated. Invoking the identity, Operator × e^U, one obtaines

$$\begin{aligned}\rho_{\mathrm{u}} &= (2)^{1/2} <0|C^{+}_{\mathrm{uu}}(00)|0> \\ &= (2)^{1/2}N_{\mathrm{o}}<0|e^{U}\{C^{+}_{\mathrm{uu}}(00) + [C^{+}_{\mathrm{uu}}(00),U] \\ &\qquad - (2!)^{-1}[U,[C^{+}_{\mathrm{uu}}(00),U]]+\cdots\}|HF> \\ &= (2)^{-1}\sum_{S}\sum_{\mathrm{h}}\sum_{\mathrm{vf}}|C_{\mathrm{uh,vf}}(S)|^2 \quad (\text{for all } \Gamma_i)\end{aligned} \tag{8}$$

where we use the normalization condition of Eq. 7 and assume the orthogonality condition:

$$\begin{aligned}&\ll C^{+}_{\mathrm{uo}}(S0)C^{+}_{\mathrm{eg}}(\overline{S0})|HF>|C^{+}_{\mathrm{ph}}(S0)C^{+}_{\mathrm{vf}}(\overline{S0})|HF\gg \\ &\qquad = <\Psi_{\mathrm{uo,eg}}(S)|\Psi_{\mathrm{ph,vf}}(S)> \\ &\qquad = \delta_{\mathrm{uo,ph}}\delta_{\mathrm{eg,vf}}\end{aligned} \tag{9}$$

We have used the notation uo and eg for the *u*noccupied-*o*ccupied and *e*xcited *g*round state molecular orbital pairs. In the braces of the second line of Eq. 8 the terms higher than the second term vanish, formally, under the assumption of Eq. 6.

$$\begin{aligned}\rho_{\mathrm{o}} &= 2^{1/2}<0|C^{+}_{\mathrm{oo}}(00)|0> \\ &= 2 - (1/2)\sum_{S}\sum_{\mathrm{p}}\sum_{\mathrm{vf}}|C_{\mathrm{po,vf}}(S)|^2 \quad (\text{for all } \Gamma_i)\end{aligned} \tag{10}$$

In the present paper, the starting charge densities ρ_i's are computed by using Eqs. 5, 8, and 10 together with the relationship such as suggested by Shibuya and McKoy:[15]

$$C^{\mathrm{trial}}_{\mathrm{ph,vf}}(S) \approx (E_{\mathrm{p}}+E_{\mathrm{v}}-E_{\mathrm{h}}-E_{\mathrm{f}})^{-1}B^{\mathrm{nRPA}}_{\mathrm{ph,vf}}(S) \tag{11}$$

As a matter of course, these coefficients are computed for all the particle-hole pair (ph, vf) configurations in the RPA equation. A trial correlated ground state may also be obtained either by solving the CI secular equation constructed by admixing the Hartree-Fock ground state with the doubly excited singlet configurational state, or by the corresponding perturbation treatment.[5,14] From the case when we use Eq. 11 to compute ρ_i, we should not conclude that in the CI method (*cf.* Eq. 16 below) the triplet correlation effect is formally unable to be taken into account because of the spin-orthogonality between the ground and triplet configurational state functions. As will be discussed in the next section, it should be considered that in the CI method the triplet correlation effect is implicitly included as an average of spin-flips through the $\boldsymbol{B}(S)$ matrix of the RPA equation.

If we follow Sanderson and da Providência,[11,12] we can determine a solution of Eq. 3b for the trial rRPA equation, whose matrix elements are computed by the coefficients $C_{\mathrm{ph,vf}}(S)$ assumed initially in accordance with Eq. 11. Then, we can newly determine the coefficients as

$$\boldsymbol{C}^{\mathrm{new}} = (\tilde{\boldsymbol{Y}}^{-1}\tilde{\boldsymbol{Z}})^{\mathrm{trial}} = (\tilde{\boldsymbol{Z}}\tilde{\boldsymbol{Y}}^{-1})^{\mathrm{trial}} \tag{12}$$

which gives the new correlated charge densities. Thus, the self-consistent solution of the rRPA equation, that is SCrRPA, may be obtained iteratively. The convergence criterion used is that $|\rho_i(\mathrm{new})-\rho_i(\mathrm{old})| \leqq 10^{-5}$ for all the MO's.

The oscillator strength $f_{\lambda 0}$ for the λth renormalized states is computed by

$$f_{\lambda 0} = (2/3)\omega_{\lambda}|\boldsymbol{D}_{\lambda 0}|^2 \quad (\omega_{\lambda}, \boldsymbol{D}_{\lambda 0} \text{ in a.u.}) \tag{13}$$

with

$$\boldsymbol{D}_{\lambda 0} = -\sum(\tilde{Y}^{*}_{\mathrm{ph}}(\lambda 0)+\tilde{Z}^{*}_{\mathrm{ph}}(\lambda 0))\tilde{\boldsymbol{d}}_{\mathrm{ph}} \tag{14}$$

and

$$\begin{aligned}\tilde{\boldsymbol{d}}_{\mathrm{ph}} &= (\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}\boldsymbol{d}_{\mathrm{ph}} \\ &= (\rho_{\mathrm{h}}-\rho_{\mathrm{p}})^{1/2}<\phi_{\mathrm{p}}(1)|\mathbf{r}(1)|\phi_{\mathrm{h}}(1)>\end{aligned} \tag{15}$$

Comments on the Approximately Self-Consistent Ground-State Correlation Amplitude: $C_{\mathrm{ph,vf}}(S)$

For the assumption of Eq. 5 together with those of Eq. 11 and/or Eq. 12, we can also assume the following familiar perturbation expansion, Eq. 16, in the CI method. By using the former assumption, we compute the starting correlated charge densities and perform the SCrRPA calculations in order to compare with our previous work based upon the latter assumption.

The criterion for determining the configurational functions to be chosen in Eq. 16 was set up within 10^{-3} in the absolute values of their coefficients. We broke off the CI calculation at the stage that the number of configurations amounted to fifty and computed the charge densities. We thus truncated the configurations adopted in the RPA equation. In this section, we shall clarify the similarity and the dissimilarity of these two methods for the RPA ground state, and further elucidate the meaning of the CI (TDA) method for the $B(S)$ matrix of the RPA equation.

In the CI language, the correlated ground state may be described by

$$\begin{aligned}|0> &= N_0\Big\{|HF> - \sum_{ij}\sum_{kl}\frac{<\Phi_{ij}^{kl}(00)|\mathscr{H}|HF>}{\Delta^1E_{ij}^{kl}}|\Phi_{ij}^{kl}(00)> \\ &+ \sum_{mn}\sum_{st}\sum_{ij}\sum_{kl}\frac{<\Phi_{mn}^{st}(00)|\mathscr{H}|\Phi_{ij}^{kl}(00)><\Phi_{ij}^{kl}(00)|\mathscr{H}|HF>}{\Delta^1E_{mn}^{st}\qquad\qquad\qquad\Delta^1E_{ij}^{kl}} \\ &\times|\Phi_{mn}^{st}(00)>+\cdots\Big\} \\ &= N_0(|HF>+\sum_{ij}\sum_{kl}C_{ij}^{kl}|\Phi_{ij}^{kl}(00)>+0(\text{2nd order}))\end{aligned} \tag{16}$$

with

$$\Delta^1E_{ij}^{kl} = <\Phi_{ij}^{kl}(00)|\mathscr{H}|\Phi_{ij}^{kl}(00)> - <HF|\mathscr{H}|HF>.$$

The HF ground-state and the five types of doubly excited configurational wavefunction $\Phi_{ij}^{kl}(SM)$ are given in terms of the following Slater determinants:[16)]

$$|HF> = |1\bar{1}2\bar{2}\ldots\mathrm{f}\bar{\mathrm{f}}\ldots\mathrm{k}\bar{\mathrm{k}}\ldots\mathrm{o}\bar{\mathrm{o}}\ldots\mathrm{g}\bar{\mathrm{g}}\ldots| \tag{17}$$

$$\begin{aligned}\Phi_{\mathrm{hh}}^{\mathrm{pp}}(00) &= a_{\mathrm{p}\alpha}^{+}a_{\mathrm{p}\beta}^{+}a_{\mathrm{h}\beta}a_{\mathrm{h}\alpha}|HF> = |\mathrm{f}\bar{\mathrm{f}}\mathrm{p}\bar{\mathrm{p}}| \\ &= C_{\mathrm{ph}}^{+}(00)C_{\mathrm{ph}}^{+}(00)|HF>\end{aligned} \tag{18}$$

$$\begin{aligned}\Phi_{\mathrm{hh}}^{\mathrm{pv}}(00) &= (2)^{-1/2}(a_{\mathrm{p}\alpha}^{+}a_{\mathrm{v}\beta}^{+}+a_{\mathrm{v}\alpha}^{+}a_{\mathrm{p}\beta}^{+})a_{\mathrm{h}\beta}a_{\mathrm{h}\alpha}|HF> \\ &= (2)^{-1/2}(|\mathrm{p}\bar{\mathrm{v}}|+|\mathrm{v}\bar{\mathrm{p}}|) \\ &= (2)^{1/2}C_{\mathrm{ph}}^{+}(00)C_{\mathrm{vh}}^{+}(00)|HF> \quad (\mathrm{p}\neq\mathrm{v})\end{aligned} \tag{19}$$

$$\begin{aligned}\Phi_{\mathrm{fh}}^{\mathrm{pp}}(00) &= (2)^{-1/2}a_{\mathrm{p}\alpha}^{+}a_{\mathrm{p}\beta}^{+}(a_{\mathrm{h}\beta}a_{\mathrm{f}\alpha}+a_{\mathrm{f}\beta}a_{\mathrm{h}\alpha})|HF> \\ &= (2)^{-1/2}(|\mathrm{f}\bar{\mathrm{h}}\mathrm{p}\bar{\mathrm{p}}|+|\mathrm{h}\bar{\mathrm{f}}\mathrm{p}\bar{\mathrm{p}}|) \\ &= (2)^{1/2}C_{\mathrm{pf}}^{+}(00)C_{\mathrm{ph}}^{+}(00)|HF> \quad (\mathrm{f}\neq\mathrm{h})\end{aligned} \tag{20}$$

$$\begin{aligned}\Phi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{I})(00) &= (2)^{-1}(a_{\mathrm{p}\alpha}^{+}a_{\mathrm{v}\beta}^{+}+a_{\mathrm{v}\alpha}^{+}a_{\mathrm{p}\beta}^{+})(a_{\mathrm{h}\beta}a_{\mathrm{f}\alpha}+a_{\mathrm{f}\beta}a_{\mathrm{h}\alpha})|HF> \\ &= (2)^{-1}(|\mathrm{f}\bar{\mathrm{h}}\mathrm{p}\bar{\mathrm{v}}|+|\bar{\mathrm{f}}\mathrm{h}\bar{\mathrm{p}}\mathrm{v}|-|\bar{\mathrm{h}}\mathrm{f}\mathrm{p}\bar{\mathrm{v}}|-|\mathrm{h}\bar{\mathrm{f}}\bar{\mathrm{p}}\mathrm{v}|) \\ &= (2)^{-1}(C_{\mathrm{pf}}^{+}(00)C_{\mathrm{vh}}^{+}(00) \\ &\quad +C_{\mathrm{ph}}^{+}(00)C_{\mathrm{vf}}^{+}(00))|HF> \quad (\mathrm{p}\neq\mathrm{v},\mathrm{f}\neq\mathrm{h})\end{aligned} \tag{21}$$

$$\begin{aligned}\Phi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{II})(00) &= (2\sqrt{3})^{-1}\{2(a_{\mathrm{p}\alpha}^{+}a_{\mathrm{v}\alpha}^{+}a_{\mathrm{h}\alpha}a_{\mathrm{f}\alpha}+a_{\mathrm{p}\beta}^{+}a_{\mathrm{v}\beta}^{+}a_{\mathrm{h}\beta}a_{\mathrm{f}\beta}) \\ &\quad +(a_{\mathrm{p}\alpha}^{+}a_{\mathrm{v}\beta}^{+}-a_{\mathrm{v}\alpha}^{+}a_{\mathrm{p}\beta}^{+})(a_{\mathrm{h}\beta}a_{\mathrm{f}\alpha}-a_{\mathrm{f}\beta}a_{\mathrm{h}\alpha})\}|HF> \\ &= (2\sqrt{3})^{-1}\{2(|\mathrm{f}\mathrm{h}\bar{\mathrm{p}}\bar{\mathrm{v}}|+|\bar{\mathrm{f}}\bar{\mathrm{h}}\mathrm{p}\mathrm{v}|) \\ &\quad -|\mathrm{f}\bar{\mathrm{h}}\mathrm{p}\bar{\mathrm{v}}|-|\bar{\mathrm{f}}\mathrm{h}\bar{\mathrm{p}}\mathrm{v}|-|\bar{\mathrm{f}}\mathrm{h}\mathrm{p}\bar{\mathrm{v}}|-|\mathrm{f}\bar{\mathrm{h}}\bar{\mathrm{p}}\mathrm{v}|\} \\ &= (3)^{-1/2}(C_{\mathrm{pf}}^{+}(00)C_{\mathrm{vh}}^{+}(00) \\ &\quad -C_{\mathrm{ph}}^{+}(00)C_{\mathrm{vf}}^{+}(00))|HF> \quad (\mathrm{p}\neq\mathrm{v},\mathrm{f}\neq\mathrm{h})\end{aligned} \tag{22}$$

Following Murrell and McEwen,[16)] the matrix element between Φ_{ij}^{kl} (00) and $|HF\rangle$ are easily written down in terms of the matrix elements of $B(S)$ in the RPA equation as

$$<\Phi_{\mathrm{hh}}^{\mathrm{pp}}(00)|\mathscr{H}|HF> = B_{\mathrm{ph,ph}}(0) = -B_{\mathrm{ph,ph}}(1) \tag{23}$$

$$\begin{aligned}<\Phi_{\mathrm{hh}}^{\mathrm{pv}}(00)|\mathscr{H}|HF> &= (2)^{1/2}B_{\mathrm{ph,vh}}(0) \\ &= -(2)^{1/2}B_{\mathrm{ph,vh}}(1)\end{aligned} \tag{24}$$

$$<\Phi_{\mathrm{fh}}^{\mathrm{pp}}(00)|\mathscr{H}|HF> = (2)^{1/2}B_{\mathrm{ph,pf}}(1) \tag{25}$$

$$\begin{aligned}<\Phi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{I})(00)|\mathscr{H}|HF> &= -<\mathrm{pv}|\mathrm{fh}> - <\mathrm{pv}|\mathrm{hf}> \\ &= (2)^{-1}(3B_{\mathrm{ph,vf}}(1) - B_{\mathrm{ph,vf}}(0))\end{aligned} \tag{26}$$

$$\begin{aligned}<\Phi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{II})(00)|\mathscr{H}|HF> &= (3)^{1/2}(<\mathrm{pv}|\mathrm{hf}>-<\mathrm{pv}|\mathrm{fh}>) \\ &= (\sqrt{3}/2)(B_{\mathrm{ph,vf}}(1)+B_{\mathrm{ph,vf}}(0))\end{aligned} \tag{27}$$

which indicate that the ground-state correlation amplitude in this scheme is also determined by the singlet and triplet $B(S)$ matrices just as in Eq. 11.

The derivation of Eqs. 26 and 27 is not straightforward. Nakayama and I'Haya[17)] adopted the four-electron spin-functions which are different from Eqs. 21 and 22:

$$\begin{aligned}\Psi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{I})(00) &= (2\sqrt{3})^{-1}\{2(|\mathrm{f}\bar{\mathrm{h}}\bar{\mathrm{p}}\mathrm{v}|+|\bar{\mathrm{f}}\mathrm{h}\mathrm{p}\bar{\mathrm{v}}|) \\ &\quad -|\mathrm{f}\bar{\mathrm{h}}\mathrm{p}\bar{\mathrm{v}}|-|\bar{\mathrm{f}}\mathrm{h}\bar{\mathrm{p}}\mathrm{v}|-|\bar{\mathrm{f}}\bar{\mathrm{h}}\mathrm{p}\mathrm{v}|-|\mathrm{f}\mathrm{h}\bar{\mathrm{p}}\bar{\mathrm{v}}|\}\end{aligned} \tag{28}$$

$$\Psi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{II})(00) = (2)^{-1}\{|\mathrm{f}\bar{\mathrm{h}}\mathrm{p}\bar{\mathrm{v}}|+|\bar{\mathrm{f}}\mathrm{h}\bar{\mathrm{p}}\mathrm{v}|-|\bar{\mathrm{f}}\bar{\mathrm{h}}\mathrm{p}\mathrm{v}|-|\mathrm{f}\mathrm{h}\bar{\mathrm{p}}\bar{\mathrm{v}}|\}, \tag{29}$$

and obtained the corresponding matrix elements

$$<\Psi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{I})(00)|\mathscr{H}|HF> = (3)^{1/2}B_{\mathrm{ph,vf}}(1) \tag{30}$$

$$<\Psi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{II})(00)|\mathscr{H}|HF> = -B_{\mathrm{ph,vf}}(0). \tag{31}$$

It has been pointed out by Anno and Teruya[18)] that a set of Eqs. 21 and 22 is transformed into that of Eqs. 28 and 29, and that any unitary transformation of a set of spin-functions given in Eqs. 21 and 22 may be adopted as the configurational basis functions. This implies that an arbitrary degree of freedom of spin-flips is endowed for the four-electron spin-functions. Such an inverse transformation gives

$$\begin{pmatrix}\Phi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{I}) \\ \Phi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{II})\end{pmatrix}=\begin{pmatrix}\cos 150° & \sin 150° \\ -\sin 150° & \cos 150°\end{pmatrix}\begin{pmatrix}\Psi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{I}) \\ \Psi_{\mathrm{fh}}^{\mathrm{pv}}(\mathrm{II})\end{pmatrix} \tag{32}$$

from which we can obtain Eqs. 26 and 27 by using Eqs. 30 and 31.

From Eq. 16, the correlated charge densities are written down as (i, j: holes and k, l: particles)

$$\rho_j = 2 - N_0^2\sum_{i}\sum_{kl}|C_{ij}^{kl}|^2(1+\delta_{ij}) \tag{33a}$$

$$\rho_{\mathrm{k}} = N_0^2\sum_{ij}\sum_{l}|C_{ij}^{kl}|^2(1+\delta_{lk}) \tag{34a}$$

which are easily derived in the following way by introducing the one-electron operator in the first quantization, for which we set $e_\nu=1$ after integration:

$$\begin{aligned}\rho_j &= <0|\sum_{\nu}e_\nu\delta_{\nu j}|0> \\ &= N_0^2(1+\sum_{ij'}\sum_{kl}|C_{ij'}^{kl}|^2+\cdots)<HF|\sum_{\nu}e_\nu\delta_{\nu j}|HF> \\ &\quad + N_0^2\sum_{ij'}\sum_{kl}|C_{ij'}^{kl}|^2[<\Phi_{ij'}^{kl}|\sum_{\nu}e_\nu\delta_{\nu j}|\Phi_{ij'}^{kl}> \\ &\qquad - <HF|\sum_{\nu}e_\nu\delta_{\nu j}|HF>]+\cdots \\ &= 2 + N_0^2\sum_{ij'}\sum_{kl}|C_{ij'}^{kl}|^2(e_k\delta_{kj}+e_l\delta_{lj} \\ &\qquad -e_i\delta_{ij}-e_{j'}\delta_{j'j})+\cdots\end{aligned} \tag{33b}$$

and similarly

$$\rho_k = <0|\sum_{\nu}e_\nu\delta_{\nu k}|0>, \tag{34b}$$

δ_{ij} being the Kronecker delta. Note that Eqs. 33a, b and 34a, b correspond to Eqs. 8 and 10 respectively.

TABLE 1. EXCITATION ENERGIES (ω, in eV), OSCILLATOR STRENGTHS (f), AND THE DIRECTIONS OF POLARIZATION(θ) FOR FOUR DNA BASES (ω, in eV)[a]

Molecule		SCrRPA			rRPA[b]			TDA[b]			nRPA[b]			Exptl[c]		
		ω	f	θ	ω	f	θ	ω	f	θ	ω	f	θ	ω	f	θ
Adenine	Singlet															
	$n\pi^*$	4.47	0.0004		4.42	0.0004		4.36	0.0004		4.36	0.0004		4.6	0.049	
	$\pi\pi^*$	4.68	0.096	8°	4.63	0.101	12°	4.58	0.100	2°	4.50	0.098	9°	4.758	0.249	−3°
	$n\pi^*$	4.79	0.001		4.75	0.001		4.70	0.001		4.70	0.001				
	$\pi\pi^*$	4.85	0.286	69°	4.80	0.279	70°	4.74	0.354	67°	4.67	0.284	69°	5.988	0.529	92°
	$n\pi^*$	5.08	0.013		5.02	0.014		4.96	0.013		4.96	0.013				
	$\pi\pi^*$	5.684	0.011	−13°	5.63	0.011	−10°	5.59	0.013	−31°	5.51	0.010	−8°			
	$n\pi^*$	5.683	0.001		5.66	0.0009		5.60	0.001		5.60	0.009				
	$\pi\pi^*$	6.40	0.580		6.36	0.580		6.43($n\pi^*$)	0.005		6.27	0.582				
	Triplet															
	$\pi\pi^*$	2.62			2.50			2.73			2.28			3.06[d]		
	$\pi\pi^*$	3.46			3.37			3.46			3.18					
Thymine	Singlet															
	$n\pi^*$	3.95	0.001		4.09	0.001		3.95	0.001		3.95	0.001				
	$n\pi^*$	4.84	0.000		4.88	0.000		4.84	0.000		4.84	0.000				
	$\pi\pi^*$	5.23	0.388	−4°	5.17	0.387	−4°	5.12	0.509	−4°	4.93	0.388	−4°	4.686	0.183	
	$\pi\pi^*$	6.41	0.154	96°	6.37	0.155	96°	6.26	0.176	96°	6.23	0.156	96°	6.046	0.314	
	$n\pi^*$	6.79	0.003		6.87	0.003		6.79	0.003		6.78	0.003				
	Triplet															
	$\pi\pi^*$	2.10			1.97			2.24			1.27			2.79[d]		
	$n\pi^*$	3.95			4.09			3.95			3.95					
Guanine	Singlet															
	$\pi\pi^*$	3.99	0.299	−68°	3.93	0.298	−68°	3.87	0.375	−68°	3.80	0.294	−68°			
	$n\pi^*$	4.13	0.003		4.10	0.003		4.02	0.002		4.02	0.003				
	$\pi\pi^*$	4.87	0.200	42°	4.83	0.197	42°	4.78	0.249	43°	4.67	0.198	42°	4.507	0.123	
	$n\pi^*$	4.94	0.004		4.88	0.004		4.84	0.004		4.84	0.004				
	$\pi\pi^*$	5.18	0.093	15°	5.14	0.093	15°	5.08	0.105	16°	4.99	0.096	14°	5.039	0.236	
	$n\pi^*$	5.20	0.013		5.17	0.013		5.09	0.013		5.09	0.013				
	$n\pi^*$	5.70	0.002		5.67	0.002		5.61	0.002		5.61	0.002				
	$\pi\pi^*$	6.53	0.114		6.50	0.116		6.40	0.128		6.37	0.106		6.324	0.564	
	Triplet															
	$\pi\pi^*$	2.22			2.13			2.27			1.88			3.05[d]		
	$\pi\pi^*$	2.77			2.70			2.77			2.43					
Cytosine	Singlet															
	$n\pi^*$	4.50	0.0001		4.46	0.0001		4.39	0.0001		4.38	0.0001				
	$\pi\pi^*$	4.61	0.158	45°	4.55	0.157	45°	4.52	0.196	46°	4.41	0.156	45°	4.64	0.116	9°
	$n\pi^*$	4.74	0.002		4.70	0.002		4.64	0.002		4.64	0.002				
	$\pi\pi^*$	6.02	0.173	−13°	5.99	0.169	−9°	5.93	0.130	−8°	5.89	0.161	−12°	6.308	0.698	10.5°
	$n\pi^*$	6.36	0.006		6.32	0.006		6.27	0.006		6.27	0.006				
	$\pi\pi^*$	6.45	0.712	137°	6.41	0.716	137°	6.48	1.013	138°	6.30	0.725	138°			104°
	$n\pi^*$	7.15	0.0001		7.12	0.0001		7.07	0.0001		7.07	0.0001				
	Triplet															
	$\pi\pi^*$	2.48			2.38			2.61			2.12			3.02[d]		
	$\pi\pi^*$	4.12			4.06			4.04			3.90					

a) 40 particle-hole pairs=5(unocc.)×8(occ.) are taken into account. For molecular geometries, see Ref. 21. $n\pi^*$ denotes the σ-π^* and π-σ^* transitions. As for definition of the transition moment directions, θ, see Ref. 22. b) Taken from our previous paper, Ref. 14, with some numerical revision. c) From Refs. 23 and 24. d) K. Imakubo, T. Higashimura, and T. Sidei, *J. Phys. Soc. Jpn.*, **22**, 339 (1967).

It is thus found that the use of Eq. 16 is one of ways to compute the approximately self-consistent charge density ρ_i and is quite similar to the use of Eq. 11. It is also clear that not only the singlet but also the triplet correlation effects are effectively included in Eq. 16 through the $B(S)$ matrix as in Eq. 11.

Numerical Results and Discussion

In the computation, we consider the 40 particle-hole pair configurations obtained by raising an electron from the *eight* highest occupied molecular orbitals to one of the *five* lowest vacant molecular orbitals. The computed results are listed in the first column of Table 1, and compared with the results of our previous work[14] and the experimental values. It is observed that the lowest triplet levels obtained by the SCrRPA are very much refined compared with those calculated with the rRPA. The computed oscillator strengths and the directions of polarizations are almost the same in these RPA's. Table 1 shows that the relationship ω(SCγ-RPA)$>\omega$(rRPA; Eq. 16)$>\omega$(TDA)$>\omega$(nRPA) holds for most cases. More detailedly, the following relationship holds for the four DNA bases:

$$\omega(\text{SCrRPA})>\omega(\text{rRPA; Eq. 16})>\omega(\text{rRPA; Eq. 11})>\omega(\text{TDA})>\omega(\text{nRPA}) \tag{35}$$

After all, the starting correlated RPA ground state obtained with Eq. 11 needs some more iteration steps to attain to a self-consistent renormalized solution, under the constraint of Eq. 12. It can be safely said that the correlated ground state (HF+doubly excited CI's) based upon Eq. 16 in the above treatment yields a satisfactorily approximate SCrRPA solution. The sequence of Eq. 35 indicates that the SCrRPA produces the upper bounds for the energy levels, while the nRPA yields the lower bounds.

The self-consistency was attained after nine iterations for adenine, guanine and cytosine, whereas thymine could not reach self-consistency even after thirteen iterations. We fixed the correlated charge densities as $\rho(\text{new}')=(1/2)\{\rho(\text{new})+\rho(\text{old})\}$ at every iteration step to get a quick convergence. In order to carry out the

Table 2. Pure $\pi\pi^*$ excitation energies (ω, in eV) and oscillator strengths (f) of four DNA bases, for which all the possible $\pi\pi^*$ configurations are taken from the CNDO/S basis MO's

Molecule	SCrRPA		rRPA		TDA		nRPA	
	ω	f	ω	f	ω	f	ω	f
Adenine	Singlet							
	4.71	0.10	4.62	0.10	4.55	0.10	4.46	0.10
	4.88	0.27	4.79	0.27	4.73	0.34	4.64	0.27
	5.71	0.01	5.61	0.01	5.57	0.01	5.48	0.01
	6.46	0.60	6.38	0.60	6.46	0.75	6.28	0.60
	Triplet							
	2.37		2.15		2.57		1.84	
	3.24		3.07		3.34		2.83	
Thymine	Singlet							
	5.36	0.41	5.29	0.41	5.20	0.54	5.02	0.41
	6.46	0.16	6.40	0.16	6.26	0.18	6.23	0.16
	7.40	0.12	7.35	0.12	7.24	0.16	7.18	0.10
	7.47	0.02	7.41	0.02	7.32	0.02	7.23	0.04
	Triplet							
	1.96		1.76		2.13		0.76	
	4.57		4.47		4.59		4.20	
Guanine	Singlet							
	4.04	0.30	3.94	0.30	3.87	0.38	3.78	0.30
	4.92	0.19	4.82	0.19	4.76	0.24	4.64	0.19
	5.20	0.08	5.11	0.08	5.05	0.09	4.95	0.08
	6.57	0.11	6.49	0.11	6.39	0.13	6.35	0.10
	Triplet							
	2.02		1.81		2.13		1.46	
	2.64		2.45		2.63		2.12	
Cytosine	Singlet							
	4.66	0.17	4.62	0.17	4.54	0.20	4.45	0.16
	6.06	0.15	6.03	0.15	5.94	0.11	5.90	0.13
	6.54	0.81	6.52	0.81	6.55	1.12	6.37	0.82
	7.48	0.11	7.46	0.11	7.40	0.11	7.36	0.11
	Triplet							
	2.38		2.30		2.55		1.94	
	4.02		3.97		3.95		3.74	

self-consistent calculation of thymine within the limited time (10 min), we therefore had to divide the 80×80 RPA matrix into the two matrices for the $(\pi\pi^* + \sigma\sigma^*)$ elements and the $(\sigma\pi^* + \pi\sigma^*)$ elements. As immediately understood from Eq. 6, such division of the matrix truncates, to some extent, the correlation effect arising from the other symmetry group, but this error seems to be not very large. Perhaps, some other suitable molecular geometries of thymine may give a self-consistent solution for the 40 particle-hole pairs after 9—10 iterations, without dividing the matrix. In fact, for the molecular geometry of thymine given in Ref. 20 we obtain the self-consistency after seven iterations. The results of the SCrRPA are as follows; 3.34 eV ($n\pi^*$, $f=0.018$), 4.36 ($n\pi^*$, $f=0.012$), 5.63 ($\pi\pi^*$, $f=0.019$, $\theta=-2°$), 6.97 ($\pi\pi^*$, $f=0.301$, $\theta=60°$), 7.02 ($n\pi^*$, $f=0.002$)eV for the singlets, and 2.08 ($n\pi^*$), 4.00 ($n\pi^*$)eV for the triplets. These results are somewhat different from those of Table 1.

We also carried out the SCrRPA calculation for all the possible pure $\pi\pi^*$ particle-hole pair configurations taken from the CNDO/S basis molecular orbitals, and found that Eq. 35 holds for the four bases of DNA as shown in Table 2. In particular, it should be noted that the pure $\pi\pi^*$ triplet levels are worse than those of Table 1 obtained from the RPA equations for the 40 particle-hole pair configurations involved the $\pi\pi^*$, $\sigma\sigma^*$, $\sigma\pi^*$, and $\pi\sigma^*$-transitions explicitly. Clearly, comparison of the results in Tables 1 and 2 suggests the great importance of the effect of σ-electron clouds to the refinement of the pure $\pi\pi^*$ triplet levels, which corresponds to the involvement of the dynamical screening by σ-electrons in π-electron transitions as mentioned by Shibuya, I'Haya, and McKoy.[19]

Finally, it should be mentioned that putting aside the problem how to include the electron correlation effect, re-parametrization of CNDO/S method is needed to refine the present results numerically. Especially, the lowest triplet levels of these DNA bases do not agree well with the experimental values. Such disagreement comes from the fact that the Nishimoto-Mataga approximation in the CNDO/S method reproduces the singlet levels well, but makes the triplet levels relatively low. Perhaps, the use of the INDO/S method[4,13] in the SCrRPA may be one of ways for taking steps.

References

1) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," Benjamin, New York, N. Y. (1963).
2) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).
3) R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972).
4) H. Ito and Y. J. I'Haya, *Bull. Chem. Soc. Jpn.*, **49**, 940 (1976).
5) O. Matsuoka and H. Ito, *Theor. Chim. Acta*, **39**, 111 (1975).
6) T. Shibuya and V. McKoy, *Phys. Rev.*, **A2**, 2208 (1970).
7) N. Ostlund and M. Karplus, *Chem. Phys. Lett.*, **11**, 450 (1971).
8) P. Jørgensen, J. Oddershede, and M. Ratner, *J. Chem. Phys.*, **61**, 710 (1974).
9) D. J. Rowe, *Rev. Mod. Phys.*, **40**, 153 (1968).
10) J. Simons, *J. Chem. Phys.*, **55**, 1218 (1971).
11) E. A. Sanderson, *Phys. Lett.*, **19**, 141 (1965).
12) J. da Providência, *Phys. Lett.*, **21**, 668 (1966).
13) H. Ito and Y. J. I'Haya, submitted for publication.
14) H. Ito and Y. J. I'Haya, *Chem. Phys. Lett.*, **38**, 271 (1976).
15) T. Shibuya and V. McKoy, *J. Chem. Phys.*, **54**, 1738 (1971).
16) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).
17) N. Nakayama and Y. J. I'Haya, *Rept. Univ. Electro-Commun.*, **22**, 73 (1971).
18) T. Anno and H. Teruya, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **8**, 131 (1972).
19) T. Shibuya, Y. J. I'Haya, and V. McKoy, *Int. J. Quantum Chem.*, **9**, 505 (1975).
20) R. Gerdil, *Acta Crystallogr.*, **14**, 333 (1961).
21) R. Rein, *Adv. Quantum Chem.*, **7**, 335 (1973).
22) H. DeVoe and I. Tinoco, *J. Mol. Biol.*, **4**, 518 (1962).
23) A. F. Fucaloro and L. S. Forster, *J. Am. Chem. Soc.*, **93**, 6433 (1971).
24) P. Voet, W. B. Greatzer, R. A. Cox, and P. Doty, *Biopolymers*, **1**, 193 (1963).