A Linear Response Polarizability Theory for an Extended Fano-DeVoe Model with Comments on the Joint Use of Both Short- and Long-Range Inter(sub)molecular Interaction Approximations

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An approach to extend the Fano-DeVoe model is presented for copolymer systems by making use of the Green's operator method within the dipole-dipole approximation. We derive a model Hamiltonian for a system by expanding its primitive Hamiltonian in terms of a bare complete basis set consisting of zero-order one-site and two-site excitation states in the first-order perturbation theory. A generalized extension of the Fano-DeVoe theory can be given by the polarizability tensor derived for this model Hamiltonian. As a more refined way, we derive another model Hamiltonian by expanding the primitive Hamiltonian of the system in terms of the corrected complete basis set consisting of the first-order excitation states. With such model Hamiltonians, we can fabricate polarizability theories on the same footing with the exciton wave function approaches based on the usual perturbation theory. Simplified schemes for the latter model Hamiltonians are applied to the copolymer system consisting of such chromophores that have permanent dipole moments in their ground states. Even if the constituent chromophores do not have permanent moments, extension of the Fano-DeVoe model is made by allowing for the total polymer ground state wave function corrected in terms of two-site excitation states. To circumvent the deficiency of the dipole approximation in the region of short separations of submolecules, we show a recipe as to how to make use of the monopole approximation together with the dipole approximation in conformity with the compromized idea of Moffitt.

When predicting the UV absorption as well as the CD and ORD spectra for free molecules[1] and molecular aggregates,[2] polarizability tensors afford their bandshape functions. In the previous paper,[2] we presented such a polarizability tensor theory for the real DNA molecules, which have the highly repeating sequences of base pairs. This formulation for copolymer systems is essentially the same as the decorrelation approximation[3] for homogeneous systems and the polarizability theory for homopolymer systems sketched by Herzenberg and Modinos[4] as a Fano-DeVoe model.[5-7] Also, DeVoe's coupled oscillator theory[8] which was semiclassically derived for copolymers and has been applied successfully to various biomolecules[9,10] falls under the cetegory of this model. We showed that the polarizability tensor equation[2] is of the same form as the matrix equation for the scalar polarizability in DeVoe's theory. However, if the kth submolecule for a copolymer (N-mer) has k_f oscillators, the size of the latter matrix equation is $(\sum_{k=1}^{N} k_f)\times(\sum_{k=1}^{N} k_f)$, whereas the size of our tensor matrix is always limited to be $3N\times 3N$. This means that for the large N-mer with large number of k_f transitions, the oscillator formalism comes to require extremely longer computing time than the tensor formalism needs. Furthermore, we can use in our formalism the Green's operator methos which offers a convenient tool capable of expanding the polarizability theory in different ways by use of model Hamiltonians designed on the same footing with the usual exciton wave function approaches.

Herzenberg and Modinos[4] first used the terminology of the Fano-DeVoe model for the polarizability theory of homopolymers. However, in this paper, both DeVoe's scalar polarizability theory[8] and our polarizability theory[2] for copolymers are referred to as the original Fano-DeVoe model. The theories on the optical properties of molecular aggregates have often been developed by the usual perturbation theory on the basis of the exciton-state wave function approaches, in which we can find analogous treatments useful for the present purpose. For instance, some of the wave function approaches[13,14,19] can refine the polymer-state wave functions by taking into account the static field effect of permanent moment $\boldsymbol{\mu}_{00}^{(\mathrm{site})}$ of a certain chromophore onto the rest of constituent chromophores for the polymer system. We hope to develop polarizability theories in parallel with the works made by such perturbational approaches; we extend our previous polarizability tensor theory for the UV absorption and CD spectra by designing a model Hamiltonian on the same footing with the exciton theory given in Tinoco's review[19] on optical activity. Also, it is another concern to consider how the interactions between transition and permanent dipole moments are involved in the present theory.

Most of polarizability theories were not able to involve the effect of permanent dipole moments of submolecules. However, by making use of the so-called transition matrix method[14,15] based on a Green's operator approach, Rebenold has presented the linear response theory which contains the static effect,[16,17] i.e., the static interaction terms of the inner excited f→g transitions of a certain submolecule with the ground states of the rest of submolecules such as $|fm>\{\sum_{g\neq f}\sum_{k\neq m}\boldsymbol{\mu}_{fg}^{(m)}\cdot \boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)}<gm|$. Having a glance at the original Fano-DeVoe model Hamiltonian,[2] one may perhaps be apt to judge it impossible to bring the static effect in the polarizability tensor theory in a usual way rather than in an artificial way. This is

because, in the expansion[20] of inter(sub)molecular interaction in terms of Legndre's polynomials, the terms including the point charge defined as the sum of net charges on nuclei vanish for neutral submolecules with permanent moments. However, we must note that even if there are no such point charges in permanent-polarized submolecules, each atom of these submolecules has nonzero net charge which exerts the static field effect to other submolecules. In this paper, we will derive such a model Hamiltonian that can involve the static effect in a natural fashion.

We build the polarizability theory within the dipole-dipole approximation. However, the dipole approximation is valid only for large separations between charge clouds, so that it is better to introduce the monopole-monopole approximation[18–20] at least for the nearest neighbors of monomer units and the dipole-dipole approximation for the remaining neighbors, following Moffitt.[18] In this joint use of the two approximations for the Fano-DeVoe type of polarizability tensor theory, it is impossible to use the monopole approximation without changing its present form,[2] as will be shown in the following section. In order to make use of the monopole approximation, it is of course necessary to obtain the transition and permanent monopole densities at each atom in the monomers. For the case where the sizes of chromophores in a copolymer are larger than or nearly equal to the separations of adjacent monomers, it is expected that the monopole approximation between the near neighbors becomes operative to remedy the dipole approximation. DNA and protein molecules are certainly the cases.[18,24–26]

In the next section, we first present a new scheme to extend the Fano-DeVoe model. Then, we simplify this scheme and apply it to the copolymer system of such constituent chromophores that have permanent dipole moments. Finally, we show a recipe as to how to make use of the short-range-oriented monopole approximation together with the long-range-oriented dipole approximation.

An Extended Fano-DeVoe Model Hamiltonian and the Polarizability

We will develop a polarizability tensor theory for describing the UV absorption and CD bandshapes of nucleic acids, in which the subunits of the purine and pryrimidine bases have the permanent dipole moments that are as large as the transition moments in magnitude.[24–25]

To begin with, let us assume that for the electronic Hamiltonian of the mth monomer H_m°, we know the eigenfunctions of the fth excitation states $\xi_f^{(m)}$ with the eigenvalues $E_f^{(m)}$ (f=0; ground state). Let V_{mn} be an interaction operator between the two submolecules located at sites m and n. The total Hamiltonian of the copolymer(N-mer) is then given by

$$H=\sum_{m=1}^{N} H_m^\circ+\sum_{n=1}^{N-1}\sum_{m>n}^{N} V_{mn}=H^\circ+V, \tag{1}$$

in which V_{mn} involves all the Coulomb interactions among electrons and nuclei of both submolecules separated by the distance R_{mn}. Neglecting higher-order terms in the expansion of V_{mn}, we approximate it for the two neutral submolecules by the dipole-dipole term:

$$V_{mn}=\boldsymbol{\mu}_m\cdot(R_{mn}^2\mathbf{1}-3\,\boldsymbol{R}_{mn}\boldsymbol{R}_{mn})R_{mn}^{-5}\cdot\boldsymbol{\mu}_n=\boldsymbol{\mu}_m\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_n, \tag{2}$$

where $\boldsymbol{U}_{mn}$ defines the unit dipole interaction tensor, and $\boldsymbol{\mu}_m$ is the electric dipole moment operator centered at site m:

$$\boldsymbol{\mu}=\sum_{\mathrm{A}}^{\mathrm{Nuc}} Z_{\mathrm{A}}\, e\, \boldsymbol{r}_{m\mathrm{A}}-\sum_{i}^{\mathrm{Elec}} e\, \boldsymbol{r}_{mi}. \tag{3}$$

Z_{A} is the effective nuclear charge on nucleus A. In relation with Eq. 2, we dropped lower-order interaction terms involving point charges which vanish for neutral submolecules. Here, we define the point charges of a certain submolecule by the quantity which is equal to the summation of net charges on atoms in the submolecule. However, even if the total point charges are zero, permanent-polarlized subunits have nonzero net charges on nuclei. Such submolecules can exert the electrostatic effect to the ground as well as excited states of other submolecules. In the following section, we wish to show that the static field effect can be brought in the usual polarizability theories by deriving a model Hamiltonian.

For the polymer ground state $|0\rangle$ of the assembly of hypothetically non-interacting chromophores, we may take the product of the ground state wavefunctions of N submolecules, $\xi_0^{(m)}$, such that

$$|0\rangle=|\prod_{m=1}^{N}\xi_0^{(m)}\rangle. \tag{4}$$

The composite excited state $|fm\rangle$ considering only the fth local excitation at site m, $\xi_f^{(m)}$, is then given by

$$|fm\rangle=|\xi_f^{(m)}\prod_{n\neq m}\xi_0^{(n)}\rangle, \tag{5}$$

which may be referred to as one-site excitation state. For simplicity, we shall ignore the additional effect due to the antisymmetrization of those composite states with respect to the exchange of all the electrons between any pair of (sub)molecules. Furthermore, we define a two-site excitation state such as

$$|smtn\rangle=|\xi_s^{(m)}\xi_t^{(n)}\prod_{k\neq m,n}\xi_0^{(k)}\rangle. \tag{6}$$

(A) Polarizability for the Bare Basis Set-Dependent Model Hamiltonian. Let us denote a set of these states defined above as $\{|\psi\rangle\}$, $|0\rangle$ being the polymer ground state. We confine ourselves to weak and intermediate coupling cases, where no reorganization of electrons may occur in the polymer system retaining the identity of submolecules. Even if there exist such interaction terms as $\langle\psi|V|0\rangle$ and $\langle 0|V|\psi\rangle$ that are large but not huge in magnitude, it is convenient not to take into account the direct mixing of $|0\rangle$ with the rest of $\{|\psi\rangle\}$ in the total wavefunctions of a polymer, $|\mathrm{polymer}(L)\rangle$, but to correct $|0\rangle$ by using the first-order perturbation theory.

We can expand the polymer-state wave function in term of $\{|\psi\rangle\}$ as follows:

$$|\mathrm{polymer}(L)\rangle=\sum_{\psi\neq0}^{\mathrm{All}}|\psi\rangle\langle\psi|\,\mathrm{polymer}(L)\rangle,\qquad L=1,2,3,\cdots \tag{7}$$

with the assumption

$$1=\sum_{\psi\neq0}^{\mathrm{All}}|\psi\rangle\langle\psi|, \tag{8}$$

where we exclude the ground state $|0\rangle$ for the reason mentioned above.

Now, we expand the primitive Hamiltonian H of Eq. 1 in terms of $\{|\psi\rangle\}$ and put a model Hamiltonian as

$$\begin{aligned}\bar{H}&=\sum_{\psi,\psi'\neq0}\sum|\psi\rangle\langle\psi|H|\psi'\rangle\langle\psi'|-\langle0|H|0\rangle\\&=\sum_{\psi,\psi'\neq0}\sum|\psi\rangle\{\langle\psi|H|\psi'\rangle-\delta_{\psi,\psi'}\langle0|H|0\rangle\}\langle\psi'|\\&=\sum_{\psi'\neq0}\varepsilon_{\psi,0}|\psi\rangle\langle\psi|+\{\overset{\mathrm{intrasite}}{\sum_{\psi\neq\psi'}\sum}|\psi\rangle\langle\psi|V|\psi'\rangle\langle\psi'|\\&\quad+\overset{\mathrm{intersite}}{\sum_{\psi'\neq\psi'}\sum}|\psi\rangle\langle\psi|V|\psi'\rangle\langle\psi'|\}\\&=\bar{H}_0+\bar{V}\end{aligned} \tag{9}$$

with

$$\varepsilon_{\psi,0}=\langle\psi|H|\psi\rangle-\langle0|H|0\rangle. \tag{10}$$

This model Hamiltonian formally gives the generalized extension of the Fano-DeVoe model. The $\varepsilon_{\psi,0}$ represents the modified excitation energy of a monomer embedded in the hypothetical polymer. By putting solely $|\psi\rangle=|fm\rangle$ in Eq. 9 and neglecting not only the level-shift in the $\varepsilon_{\psi,0}$ of the following Eq. 18 but also the mth intrasite $f\rightarrow$g transition terms such as

$$\begin{aligned}&\sum_f\sum_g\sum_m|fm\rangle\langle fm|V|gm\rangle\langle gm|=\\&\quad\sum_f\sum_g\sum_m\sum_k|fm\rangle\boldsymbol{\mu}_{fg}^{(m)}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)}\langle gm|,\quad(f,g\neq0)\end{aligned} \tag{11}$$

one can obtain the polarizability tensor for the original Fano-DeVoe model Hamiltonian which was first derived by the present authors.[2]

For a hypothetically non-interacting copolymer molecule, the crude Green's operator is defined as

$$\begin{aligned}G^\circ(E)&=(E-\bar{H}_0+i\eta)^{-1}\\&=(1/E)\{1+[(\bar{H}_0-i\eta)/E]+[(\bar{H}_0-i\eta)/E]^2+\cdots\}\\&=(1/E)\{\sum_{\psi\neq0}|\psi\rangle\langle\psi|+\sum_{\psi\neq0}[(\varepsilon_{\psi,0}-i\eta_\psi)/E]|\psi\rangle\langle\psi|\\&\quad+\sum_{\psi,\psi'\neq0}\sum[(\varepsilon_{\psi,0}-i\eta_\psi)/E][(\varepsilon_{\psi',0}-i\eta'_{\psi'})/E]\\&\quad\times|\psi\rangle\langle\psi|\psi'\rangle\langle\psi'|+\cdots\}\\&=\sum_{\psi\neq0}\frac{|\psi\rangle\langle\psi|}{E-\varepsilon_{\psi,0}+i\eta_\psi}.\end{aligned} \tag{12}$$

For a weak coupling case where $\{|\psi\rangle\}$ do not strongly mix with the ground state $|0\rangle$, we define the monomer polarizability tensor α(E) as

$$\alpha(E)=-\langle0|\boldsymbol{\mu}G^\circ(E)\boldsymbol{\mu}|0\rangle=\sum_{\psi\neq0}\frac{-\langle0|\boldsymbol{\mu}|\psi\rangle\langle\psi|\boldsymbol{\mu}|0\rangle}{E-\varepsilon_{\psi,0}+i\eta_\psi}, \tag{13}$$

with

$$\boldsymbol{\mu}=\sum_{m=1}^{N}\boldsymbol{\mu}_m. \tag{14}$$

For a complete basis set which spans the one- and two-site excitation states, we note that the diagonal Hamiltonian $\bar{H}_0$ and the interaction part $\bar{V}$ in Eq. 9 are written down as

$$\bar{H}_0=\sum_f\sum_m\varepsilon_{fm,0}|fm\rangle\langle fm|+\sum_s\sum_m\sum_t\sum_n\varepsilon_{smtn,0}|smtn\rangle\langle smtn|, \tag{15}$$

$$\begin{aligned}\bar{V}&=\sum_{m>m}\sum\ \sum_f\sum_g|fm\rangle\boldsymbol{\mu}_{f0}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{0g}^{(m)}\langle gn|\\&\quad+\sum_m\sum_f\sum_{g\,(g\neq f)}|fm\rangle\{\sum_{k\neq m}\boldsymbol{\mu}_{fg}^{(m)}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)}\}\langle gm|\\&\quad+\sum_{m>n}\sum\sum_s\sum_t\{\sum_f[|fm\rangle\boldsymbol{\mu}_{fs}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{0t}^{(n)}\langle smtn|\\&\quad+|fn\rangle\boldsymbol{\mu}_{0s}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{ft}^{(n)}\langle smtn|]\\&\quad+\sum_g[|smtn\rangle\boldsymbol{\mu}_{s0}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{tg}^{(n)}\langle gn|\\&\quad+|smtn\rangle\boldsymbol{\mu}_{sg}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{t0}^{(n)}\langle gm|]\}\\&\quad+\sum_{m>n}\sum\ \sum_f\sum_g\sum_s\sum_{t\,(f,g\neq s,t)}|fmgn\rangle\boldsymbol{\mu}_{fs}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{gt}^{(n)}\langle smtn|.\end{aligned} \tag{16}$$

Here, the first term is the original Fano-DeVoe type of operator. The terms after the first one in Eq. 16 show the interaction operators of the inner excited transition moments $\boldsymbol{\mu}_{fg}^{(\mathrm{site})}$ (involving 0→0), which are classfied into three types of electric moments such as $\boldsymbol{\mu}_{00}^{(\mathrm{site})}$, $\boldsymbol{\mu}_{0f}^{(\mathrm{site})}$, and $\boldsymbol{\mu}_{fg}^{(\mathrm{site})}$. In particular, the second term is a special version of the transition matrix theory[14,15] for the static field effect of permanent dipole moments $\boldsymbol{\mu}_{00}^{(\mathrm{site})}$ on all the transition moments $\boldsymbol{\mu}_{fg}^{(\mathrm{site})}$ for a specific site and similar effect for the rest of all the sites.

Thus, the matrix element of the monomer polarizability tensor with respect to sites m and n is given by

$$\begin{aligned}\alpha_{mn}(E)&=-\sum_f\sum_g\langle0|\boldsymbol{\mu}|fm\rangle\langle fm|G^\circ(E)|gn\rangle\langle gn|\boldsymbol{\mu}|0\rangle\\&\quad-\sum_s\sum_t\sum_f\sum_g\ \sum_k\sum_l\langle0|\boldsymbol{\mu}|smtk\rangle\\&\quad\times\langle smtk|G^\circ(E)|flgn\rangle\langle flgn|\boldsymbol{\mu}|0\rangle\\&=\sum_f\delta_{\mathrm{mn}}\frac{-\langle0|\boldsymbol{\mu}|fm\rangle\langle fm|\boldsymbol{\mu}|0\rangle}{E-\varepsilon_{fm,0}+i\eta_{fm}}\\&\quad+\sum_s\sum_t\frac{-\langle0|\boldsymbol{\mu}|smtn\rangle\langle smtn|\boldsymbol{\mu}|0\rangle}{E-\varepsilon_{smtn,0}+i(\eta_{sm}+\eta_{tn})},\end{aligned} \tag{17}$$

in which $\langle0|\boldsymbol{\mu}|fm\rangle$ is nothing but $\boldsymbol{\mu}_{0f}^{(m)}$ and where $\varepsilon_{fm,0}$ and $\varepsilon_{smtn,0}$ are calculated to be as follows:

$$\varepsilon_{fm,0}=E_{f0}^{(m)}+\sum_{k\neq m}\boldsymbol{\mu}_{ff}^{(m)}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)}-\sum_{k\neq m}\boldsymbol{\mu}_{00}^{(m)}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)}, \tag{18}$$

$$\varepsilon_{smtn,0}=E_{s0}^{(m)}+E_{t0}^{(n)}+\boldsymbol{\mu}_{ss}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{tt}^{(n)}-\boldsymbol{\mu}_{00}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{00}^{(n)}. \tag{19}$$

The $E_{f0}^{(m)}=(E_f^{(m)}-E_0^{(m)})$ is the excitation energy of the mth free monomer. The tensor $\alpha_{mn}(E)$ is diagonal, since the second term in Eq. 17 vanishes due to $\langle0|\boldsymbol{\mu}|smtn\rangle=0$. However, this electric moment comes to be nonvanishing if we replace the bare ground state $|0>$ with the more exact ground state $|\tilde{0}>$. Actually, we assume the corrected ground state as follows:

$$|\tilde{0}>=|0>-\sum_{k\neq m}\varepsilon_{\psi,0}^{-1}<\psi|V|0>|\psi>\equiv|0>-\sum_{\psi\neq m}C_{\psi,0}|\psi>, \tag{20}$$

where $C_{\psi,0}=C_{0,\psi}$. It should be noted that $|0>$ does not mix with one-site excitation states but mix only with two-site excitation states, unless submolecules have permanent dipole moments.

For the true Green's operator

$$\begin{aligned}G(E)&=(E-\bar{H}+i\eta)^{-1}\\&=G^{\circ}(E)+G^{\circ}(E)\bar{V}G^{\circ}(E)+G^{\circ}(E)\bar{V}G^{\circ}(E)\bar{V}G^{\circ}(E)+\cdots,\end{aligned} \tag{21}$$

we can derive the polymer polarizability tensor ${}^{p}\boldsymbol{\alpha}_{mn}(E)$ as follows:

$$\begin{aligned}{}^{p}\boldsymbol{\alpha}_{mn}(E)=&-\sum_{f,\,g\neq0}\sum<0|\boldsymbol{\mu}|fm><fm|G(E)|gn><gn|\boldsymbol{\mu}|0>\\&-\sum_{s,\,t,\,f,\,g\neq0}\sum\sum\sum\sum_{k}\sum_{l}<0|\boldsymbol{\mu}|smtk>\\&\times<smtk|G(E)|flgn><flgn|\boldsymbol{\mu}|0>.\end{aligned} \tag{22}$$

The second term of Eq. 22 vanishes due to $<0|\boldsymbol{\mu}|smtk>=0$ and $<flgn|\boldsymbol{\mu}|0>=0$. For the first term of Eq. 22, we only point out that in addition to the original Fano-DeVoe type of matrix elements, various types of matrix elements of one-site part of $G^{\circ}(E)$,

$$\Sigma_{f}\Sigma_{m}|fm><fm|G^{\circ}(E)|fm><fm|,$$

mixing with two-site part of $G^{\circ}(E)$,

$$\Sigma_{s}\Sigma_{m}\Sigma_{t}\Sigma_{n}|smtn><smtn|G^{\circ}(E)|smtn><smtn|,$$

are produced by matching of the bra- and ket-operators for the various types of combinations of the seven interaction operators of Eq. 16. Because of the complexity, we will mention about the matrix elements of Eq. 22 any more. However, it is here interesting to observe that the second term of Eq. 16 leads to the first-order polarizability tensor:

$$\begin{aligned}&-\sum_{f,\,g\neq0(g\neq f)}\sum<0|\boldsymbol{\mu}|fm><fm|G^{\circ}(E)\\&\qquad\times[\text{2nd term of }\bar{V}]G^{\circ}(E)|gm><gm|\boldsymbol{\mu}|0>\delta_{mn}\\&=\sum_{f,\,g\neq0(f\neq g)}\sum\frac{-\boldsymbol{\mu}_{0f}^{(m)}\{\sum_{k\neq m}\boldsymbol{\mu}_{fg}^{(m)}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)}\}\boldsymbol{\mu}_{g0}^{(m)}}{(E-\varepsilon_{fm,0}+i\eta_{fm})(E-\varepsilon_{gm,0}+i\eta_{gm})}\delta_{mn},\end{aligned} \tag{23}$$

which indicates that the static field effect involved is quite large, when $\varepsilon_{fm,0}$ and $\varepsilon_{gm,0}$ are nearly degenerate.

For the intermediate coupling case where there exists a strong mixing of $\{|fm>\}$ with $|0>$, we must evaluate the average value of the correlated ground state $|\tilde{0}>$ instead of the bare ground state $|0>$. Namely, we have a more refined polymer polarizability tensor:

$$\begin{aligned}{}^{rp}\boldsymbol{\alpha}(E)&=-<\tilde{0}|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|\tilde{0}>\\&={}^{p}\boldsymbol{\alpha}(E)+\sum_{\psi\neq0}<0|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|\psi>C_{\psi,0}\\&\quad+\sum_{\psi\neq0}C_{0,\psi}<\psi|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|0>\\&\quad-\sum_{\psi,\,\psi'\neq0}\sum C_{0,\psi}<\psi|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|\psi'>C_{\psi',0}.\end{aligned} \tag{24}$$

The treatment of Eq. 24 is thus quite analogous to that of the renormalized random-phase approximation for a free molecule. The theoretical procedure outlined above will be more generalized in (B) which contains the calculations of Eqs. 22 and 24.

(B) Polarizability for the Corrected Basis Set-Dependent Model Hamiltonian. Instead of the bare basis set $\{|\psi>\}$ of the excited states, let us make use of a basis set corrected by the first-order perturbation theory, that is,

$$\begin{aligned}|\tilde{\psi}>&=|\psi>+\varepsilon_{\psi,0}^{-1}<0|V|\psi>|0>+\sum_{\psi'\neq\psi}\varepsilon_{\psi,\psi'}^{-1}<\psi'|V|\psi>|\psi'>\\&\equiv|\psi>+C_{0,\psi}|0>+\sum_{\psi'\neq\psi}C_{\psi',\psi}|\psi'>\\&=|\psi>+C_{\psi,0}|0>+\sum_{\psi'\neq\psi}C_{\psi,\psi'}|\psi'>,\end{aligned} \tag{25}$$

where $\varepsilon_{\psi,\psi'}$ denotes an energy difference $<\psi|H|\psi>-<\psi'|H|\psi'>$. Again, we must note that the two-site excitation states for ψ always mix with the ground state, while the one-site excitation states can mix with the ground state only if the constituent chromophores have permanent dipole moments $\boldsymbol{\mu}_{00}^{(\mathrm{site})}$. Then, similar to Eq. 7, the wave function for the copolymer system is expanded in terms of the corrected basis set as[19]

$$|\mathrm{polymer}(L)>=\sum_{\psi\neq0}|\tilde{\psi}><\tilde{\psi}|\mathrm{polymer}(L)>,\quad L=1,2,3,\cdots \tag{26}$$

where we assume the completeness for the $\{|\tilde{\psi}>\}$.

The model Hamiltonian is now set to be

$$\begin{aligned}\tilde{H}&=\sum_{\psi,\psi'\neq0}\sum|\tilde{\psi}><\tilde{\psi}|H|\tilde{\psi}'><\tilde{\psi}'|-<\tilde{0}|H|\tilde{0}>\\&=\sum_{\psi\neq0}\tilde{\varepsilon}_{\psi,0}|\tilde{\psi}><\tilde{\psi}|+\sum_{\psi\neq\psi}\sum|\tilde{\psi}><\tilde{\psi}|V|\tilde{\psi}'><\tilde{\psi}'|\\&=\sum_{\psi\neq0}\tilde{\varepsilon}_{\psi,0}|\tilde{\psi}><\tilde{\psi}|+\{\overset{\text{intrasite}}{\sum_{\psi\neq\psi'}\sum}|\tilde{\psi}><\tilde{\psi}|V|\tilde{\psi}'><\tilde{\psi}'|\\&\quad+\overset{\text{intersite}}{\sum_{\psi\neq\psi'}\sum}|\tilde{\psi}><\tilde{\psi}|V|\tilde{\psi}'><\tilde{\psi}'|\}\\&=\tilde{H}_0+\tilde{V},\end{aligned} \tag{27}$$

with

$$\tilde{\varepsilon}_{\psi,0}=<\tilde{\psi}|H|\tilde{\psi}>-<\tilde{0}|H|\tilde{0}>. \tag{28}$$

Equation 27 gives the more generalized Fano-DeVoe model Hamiltonian than that defined by Eq. 9. The modified excitation energy $\tilde{\varepsilon}_{\psi,0}$ is formally corrected up to the order of V^2 by the usual perturbation theory. Also, we define the crude and true Green's operators for $\tilde{H}_0$ and $\tilde{H}$, respectively, as follows:

$$\tilde{G}^{\circ}(E)=(E-\tilde{H}_0+i\tilde{\eta})^{-1}=\sum_{\psi\neq0}\frac{|\tilde{\psi}><\tilde{\psi}|}{E-\tilde{\varepsilon}_{\psi,0}+i\tilde{\eta}_{\psi}}, \tag{29}$$

$$\tilde{G}(E)=(E-\tilde{H}+i\tilde{\eta})^{-1}=\tilde{G}^{\circ}(E)+\tilde{G}^{\circ}(E)\tilde{V}\tilde{G}(E), \tag{30}$$

which may be called a dressed or effective and/or renormalized Green's operator, if we follow the terminology of Mattuck.[23]

The monomer and polymer polarizability tensors for Eqs. 29 and 30 are defined by the average values over the bare ground state $|0>$ as follows:

$$\tilde{\boldsymbol{\alpha}}(E)=-<0|\boldsymbol{\mu}\tilde{G}^{\circ}(E)\boldsymbol{\mu}|0>=\sum_{\psi\neq0}\frac{-<0|\boldsymbol{\mu}|\tilde{\psi}><\tilde{\psi}|\boldsymbol{\mu}|0>}{E-\tilde{\varepsilon}_{\psi,0}+i\,\tilde{\eta}_{\psi}}, \tag{31}$$

$$\begin{aligned}{}^{p}\tilde{\boldsymbol{\alpha}}(E)&=-<0|\boldsymbol{\mu}\tilde{G}(E)\boldsymbol{\mu}|0>\\&=-<0|\boldsymbol{\mu}(\tilde{G}^{\circ}(E)+\tilde{G}^{\circ}(E)\tilde{V}\tilde{G}(E)+\cdots)\boldsymbol{\mu}|0>.\end{aligned} \tag{32}$$

Unfortunately, it becomes more complicated to calculate the matrix elements for the dressed ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$ than to do so for the bare ${}^{p}\boldsymbol{\alpha}(E)$, so that it may be hopeless to linearlize ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$ by intuitively finding and summing up kinds of modules comprising simple types of polarizabilities and unit interaction factors just like the derivation of the original Fano-DeVoe polarizability.[2]

The most generalized tensor ${}^{rp}\tilde{\boldsymbol{\alpha}}(E)$ for a copolymer is formally obtained by taking the average over the correlated ground state as follows:

$$\begin{aligned}{}^{rp}\tilde{\boldsymbol{\alpha}}(E)&=-<\tilde{0}|\boldsymbol{\mu}\tilde{G}(E)\boldsymbol{\mu}|\tilde{0}>\\&={}^{p}\tilde{\boldsymbol{\alpha}}(E)+\sum_{\psi\neq0}<0|\boldsymbol{\mu}\tilde{G}(E)\boldsymbol{\mu}|0>C_{\psi,0}\\&\quad+\sum_{\psi\neq0}C_{0,\psi}<\psi|\boldsymbol{\mu}\tilde{G}(E)\boldsymbol{\mu}|0>\\&\quad-\sum_{\psi,\psi'\neq0}\sum C_{0,\psi}<\psi|\boldsymbol{\mu}\tilde{G}(E)\boldsymbol{\mu}|\psi'>C_{\psi',0},\end{aligned} \tag{33}$$

which may be referred to as a self-consistent renormalized RPA, while Eq. 32 is called simply a renormalized RPA.

In what follows, we will mention the procedures described in (A) and (B) in more detail for comparatively simple cases.

(C) Polarizability for the Model Hamiltonian of the bare $\{|fm>\}$. The choice of the bare basis set consisting of one-site excitation states for the total Hamiltonian $\overline{H}(=\overline{H}_{\circ}+\overline{V})$ leads to the following operators

$$\overline{H}_0=\sum_{f}\sum_{m}\varepsilon_{fm,0}|fm><fm|, \tag{34}$$

$$\begin{aligned}\overline{V}&=\overset{\text{intersite}}{\sum_{f}\sum_{m}\sum_{g}\sum_{n}}|fm>\boldsymbol{\mu}^{(m)}_{f0}\cdot U_{mn}\cdot\boldsymbol{\mu}^{(n)}_{0g}<gn|\\&\quad+\overset{\text{intrasite}}{\sum_{f}\sum_{m}\sum_{g\neq f}}|fm><fm|V|gm><gm|\\&=\overline{V}_{FD}+\overline{V}_{S}\end{aligned} \tag{35}$$

where $\overline{V}_{FD}$ denotes the original Fano-DeVoe type of interaction operator. $\overline{V}_{S}$ given by $\sum_k\boldsymbol{\mu}^{(m)}_{fg}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}^{(k)}_{00}$ signifies the operator for the Bayley, Nielsen, Schellman type of static field effect[15] to the mth intrasite f→g transitions: i.e., the operator for the intrasite f→g excitation state of the mth subunit which interacts with the ground states of the rest of the kth permanent-polarized subunits. For the off-diagonal static interaction term $<fm|V|gm>$, $\varepsilon_{fm,0}$ contains the diagonal element $<fm|V|fm>$ which is given by the second term of Eq. 18. It may be convenient for the calculations of ${}^{p}\boldsymbol{\alpha}(E)$ to specify that for example the element $<fm|V|gn>$ represented by $\boldsymbol{\mu}^{(m)}_{0f}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}^{(n)}_{0g}$ implies such a scalar quantity that the operation of $\boldsymbol{\mu}\cdot\boldsymbol{U}\cdot\boldsymbol{\mu}$ has already been performed.

From the calculation of $-<0|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|0>$ with $G(E)=[E-(\overline{H}_{\circ}+\overline{V})+i\eta]^{-1}$, we can obtain ${}^{p}\boldsymbol{\alpha}_{mn}(E)$. However, inclusion of $\overline{V}_S$ brings about too much complexity, so that we shall collect only several important terms to be linearlized as shown in the following; for the convenience of this purpose, we put

$${}^{p}\overline{V}_{FD}(E)=\overline{V}_{FD}+\overline{V}_{FD}G^{\circ}(E)\overline{V}_{FD}+\overline{V}_{FD}G^{\circ}(E)\overline{V}_{FD}G^{\circ}(E)\overline{V}_{FD}+\cdots, \tag{36}$$

$${}^{p}\overline{V}_{S}(E)=\overline{V}_{S}+\overline{V}_{S}G^{\circ}(E)\overline{V}_{S}+\overline{V}_{S}G^{\circ}(E)\overline{V}_{S}G^{\circ}(E)\overline{V}_{S}+\cdots. \tag{37}$$

Thus, we have

$${}^{p}\boldsymbol{\alpha}_{mn}(E)=-\sum_{f,\,g\neq0}\sum<0|\boldsymbol{\mu}|fm><fm|G(E)|gn><gn|\boldsymbol{\mu}|0> \tag{38a}$$

$$\begin{aligned}&\simeq-\sum_{f,g\neq0}\sum\{\boldsymbol{\mu}^{(m)}_{0f}<fm|G^{\circ}(E)+G^{\circ}(E){}^{p}\overline{V}_{FD}(E)G^{\circ}(E)|gn>\boldsymbol{\mu}^{(n)}_{g0}\\&\quad+\boldsymbol{\mu}^{(m)}_{0f}<fm|G^{\circ}(E){}^{p}\overline{V}_{S}(E)G^{\circ}(E)|gn>\boldsymbol{\mu}^{(n)}_{g0}\\&\quad+\boldsymbol{\mu}^{(m)}_{0f}<fm|G^{\circ}(E){}^{p}\overline{V}_{S}(E)G^{\circ}(E){}^{p}\overline{V}_{FD}(E)G^{\circ}(E)|gn>\boldsymbol{\mu}^{(n)}_{g0}\\&\quad+\boldsymbol{\mu}^{(m)}_{0f}<fm|G^{\circ}(E){}^{p}\overline{V}_{FD}(E)G^{\circ}(E){}^{p}\overline{V}_{S}(E)G^{\circ}(E)|gn>\boldsymbol{\mu}^{(n)}_{g0}\\&\quad+\boldsymbol{\mu}^{(m)}_{0f}<fm|G^{\circ}(E){}^{p}\overline{V}_{FD}(E)G^{\circ}(E){}^{p}\overline{V}_{S}(E)G^{\circ}(E)\\&\qquad\qquad\times{}^{p}\overline{V}_{FD}(E)G^{\circ}(E)|gn>\boldsymbol{\mu}^{(n)}_{g0}\\&\quad+\boldsymbol{\mu}^{(m)}_{0f}<fm|G^{\circ}(E){}^{p}\overline{V}_{S}(E)G^{\circ}(E){}^{p}\overline{V}_{FD}(E)G^{\circ}(E)\\&\qquad\qquad\times{}^{p}\overline{V}_{S}(E)G^{\circ}(E)|gn>\boldsymbol{\mu}^{(n)}_{g0}\}\\&=\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}^{-1}_{mn}\cdot\boldsymbol{\alpha}_{nn}(E)-\sum_{f\neq g}\sum\boldsymbol{\mu}^{(m)}_{0f}K^{fg}_{mm}(E)\boldsymbol{\mu}^{(m)}_{g0}\delta_{mn}\\&\quad+\sum_{f}\sum_{\neq t}\sum_{k}\boldsymbol{\mu}^{(m)}_{0f}K^{ft}_{mm}(E)\boldsymbol{\mu}^{(m)}_{t0}\cdot\{\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}_{mk}\cdot\boldsymbol{U}_{kn}\cdot\boldsymbol{\alpha}_{nn}(E)\\&\quad+\sum_{k}\sum_{t}\sum_{\neq g}\boldsymbol{\alpha}_{mm}(E)\cdot\boldsymbol{U}_{mk}\cdot\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}^{-1}_{kn}\cdot\boldsymbol{\mu}^{(n)}_{0t}K^{tg}_{nn}(E)\boldsymbol{\mu}^{(n)}_{g0}\\&\quad-\sum_{k}\sum_{l}\sum_{j}\sum_{t}\sum_{\neq g}\boldsymbol{\alpha}_{mm}(E)\cdot\boldsymbol{U}_{mk}\cdot\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}^{-1}_{kl}\cdot\boldsymbol{\mu}^{(l)}_{0t}K^{tg}_{ll}(E)\boldsymbol{\mu}^{(l)}_{g0}\\&\qquad\qquad\times\{\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}_{lj}\,\boldsymbol{U}_{jn}\cdot\boldsymbol{\alpha}_{nn}(E)\\&\quad-\sum_{k}\sum_{f}\sum_{\neq t}\sum_{s}\sum_{\neq g}\boldsymbol{\mu}^{(m)}_{0f}K^{ft}_{mm}(E)\boldsymbol{\mu}^{(m)}_{t0}\cdot\{\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}_{mk}\cdot\boldsymbol{U}_{kn}\\&\qquad\qquad\times\boldsymbol{\mu}^{(n)}_{0s}K^{sg}_{nn}(E)\boldsymbol{\mu}^{(n)}_{g0},\ m,\ n=1,2,3,\cdots,\ N\end{aligned} \tag{38b}$$

with the relationships

$$\begin{aligned}\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}^{-1}_{mn}&=\delta_{mn}-\boldsymbol{\alpha}_{mm}(E)\cdot\boldsymbol{U}_{mn}\\&\quad+\sum_{k}\boldsymbol{\alpha}_{mm}(E)\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\alpha}_{kk}(E)\cdot\boldsymbol{U}_{kn}-\cdots,\end{aligned} \tag{39}$$

$$\begin{aligned}\{\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}_{mn}&=\delta_{mn}-\boldsymbol{U}_{mn}\cdot\boldsymbol{\alpha}_{nn}(E)\\&\quad+\sum_{k}\boldsymbol{U}_{mk}\cdot\boldsymbol{\alpha}_{kk}(E)\cdot\boldsymbol{U}_{kn}\cdot\boldsymbol{\alpha}_{nn}(E)-\cdots,\end{aligned} \tag{40}$$

where we put

$$K^{fg}_{mm}(E)=\left\{\frac{<fm|V|gm>}{E-\varepsilon_{fm,0}+i\,\eta_{fm}}+\sum_{t\neq f,g}\frac{<fm|V|tm><tm|V|gm>}{(E-\varepsilon_{fm,0}+i\,\eta_{fm})(E-\varepsilon_{tm,0}+i\,\eta_{tm})}+\cdots\right\}\Big/(E-\varepsilon_{gm,0}+i\,\eta_{gm}) \tag{41}$$

In Eq. 38b, the first term gives the pure Fano-DeVoe type of polarizability tensor components,[2] and the second term corresponds to the tensor components involving the static field effect appeared in the transition matrix theory.[15] The remaining four terms show only the simple geometric progressive parts of the tensor components produced from all the crossed terms of $\overline{V}_{FD}$ and $\overline{V}_S$. From the fact that by inspection of Eq. 38b the corrections to the ordinary Fano-DeVoe polarizability tensor are at least the first order in $\langle\psi|V|\psi'\rangle$ for the permanent-polarized system, it is indicated that Eq. 38b gives a significant extension of the Fano-DeVoe model, when the magnitudes of $\boldsymbol{\mu}_{fg}^{(\text{site})}$ and $\boldsymbol{\mu}_{00}^{(\text{site})}$ are large.

Furthermore, for the intermediate coupling case, a higher approximation than that of ${}^{p}\boldsymbol{\alpha}_{mn}(E)$ can be made as follows:

$$\begin{aligned}
{}^{rp}\boldsymbol{\alpha}_{mn}(E) = {}^{p}\boldsymbol{\alpha}_{mn}(E) &+ \sum_f \sum_g \langle 0|\boldsymbol{\mu}|fm\rangle\langle fm|G(E)\boldsymbol{\mu}|gn\rangle C_{gn,0} \\
&+ \sum_f \sum_s \sum_k \sum_t \langle 0|\boldsymbol{\mu}|fm\rangle\langle fm|G(E)\boldsymbol{\mu}|sktn\rangle C_{sktn,0} \\
&+ \sum_f \sum_g C_{0,fm}\langle fm|\boldsymbol{\mu}G(E)|gn\rangle\langle gn|\boldsymbol{\mu}|0\rangle \\
&+ \sum_s \sum_t \sum_k \sum_g C_{0,smtk}\langle smtk|\boldsymbol{\mu}G(E)|gn\rangle\langle gn|\boldsymbol{\mu}|0\rangle \\
&- \sum_f \sum_g C_{0,fm}\langle fm|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|gn\rangle C_{gn,0} \\
&- \sum_f \sum_s \sum_k \sum_t C_{0,fm}\langle fm|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|sktn\rangle C_{sktn,0} \\
&- \sum_s \sum_t \sum_j \sum_g C_{0,smtj}\langle smtj|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|gn\rangle C_{gn,0} \\
&- \sum_s \sum_t \sum_j \sum_f \sum_k \sum_g C_{0,smtj}\langle smtj|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|fkgn\rangle C_{fkgn,0},
\end{aligned} \tag{42}$$

which gives the renormalized RPA. The final result of Eq. 42 is not specified for saving space. Actually, the correction terms after the first term in Eq. 42 may be unnecessary to calculate, since the static interactions in Eq. 38b are sufficiently taken into account through $\overline{V}_S$ given by Eqs. 11 and 35. However, for the case where the permanent moments are all zero, the correction terms related with two-site excitations become operative, so that Eq. 42 becomes

$$\begin{aligned}
{}^{rp}\boldsymbol{\alpha}_{mn}(E) &= {}^{p}\boldsymbol{\alpha}_{mn}(E) \\
&+ \sum_s \sum_k \sum_t \{[\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}]^{-1}_{mk}\cdot\boldsymbol{\mu}_{0s}^{(k)} C_{sktn,0}\,\boldsymbol{\mu}_{0t}^{(n)}/(E-\varepsilon_{sk,0}+i\,\eta_{sk}) \\
&+ [\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}]^{-1}_{mn}\cdot\boldsymbol{\mu}_{0t}^{(n)} C_{sktn,0}\,\boldsymbol{\mu}_{0s}^{(k)}/(E-\varepsilon_{tn,0}+i\,\eta_{tn}) \\
&+ \boldsymbol{\mu}_{t0}^{(k)} C_{0,smtk}\,\boldsymbol{\mu}_{0s}^{(m)}/(E-\varepsilon_{sm,0}+i\,\eta_{sm})\cdot[\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)]^{-1}_{mn} \\
&+ \boldsymbol{\mu}_{s0}^{(m)} C_{0,smtk}\,\boldsymbol{\mu}_{0t}^{(k)}/(E-\varepsilon_{tk,0}+i\,\eta_{tk})\cdot[\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)]^{-1}_{kn}\} \\
&+ O(C_{0,smtj}\,C_{fktn,0}),
\end{aligned} \tag{43}$$

which means that in this case the correction of the polymer ground state produced only by the two-site excitations gives the extension of the pure Fano-DeVoe model.

Thus, we can obtain the UV absorption and the CD and ORD bandshape functions either from the calculations[1,2] of $3^{-1}\,Tr\ {}^{p}\boldsymbol{\alpha}_{mn}(E)$ and $12^{-1}\boldsymbol{R}_{mn}\cdot({}^{p}\boldsymbol{\alpha}_{mn}(E):\boldsymbol{\varepsilon})$ for Eq. 38b, or from the calculations of $3^{-1}\,Tr\ {}^{rp}\boldsymbol{\alpha}_{mn}(E)$ and $12^{-1}\boldsymbol{R}_{mn}\cdot({}^{rp}\boldsymbol{\alpha}_{mn}(E):\boldsymbol{\varepsilon})$ for Eq. 42 and/or Eq. 43.

(D) Polarizability for the model Hamiltonian of the Corrected $\{|\tilde{f}\tilde{m}\rangle\}$. The expansion of the primitive Hamiltonian of Eq. 1 in terms of the corrected basis set of the one-site excitation states $\{|\tilde{f}\tilde{m}\rangle\}$ leads to

$$\begin{aligned}
\tilde{H} &= \sum_f \sum_m \tilde{\varepsilon}_{fm,0}|\tilde{f}\tilde{m}\rangle\langle\tilde{f}\tilde{m}| \\
&+ \{\overset{\text{intrasite}}{\sum_{g\neq f} \sum \sum_m} |\tilde{f}\tilde{m}\rangle\langle\tilde{f}\tilde{m}|V|\tilde{g}\tilde{m}\rangle\langle\tilde{g}\tilde{m}| \\
&+ \overset{\text{intersite}}{\sum_f \sum_m \sum_g \sum_n} |\tilde{f}\tilde{m}\rangle\langle\tilde{f}\tilde{m}|V|\tilde{g}\tilde{n}\rangle\langle\tilde{g}\tilde{n}|\,\} \\
&= \tilde{H}_0+\tilde{V} = \tilde{H}_0+\{\tilde{V}_S+\tilde{V}_{FD}\},
\end{aligned} \tag{44}$$

with

$$|\tilde{f}\tilde{m}\rangle = |fm\rangle + C_{0,fm}|0\rangle, \tag{45a}$$

The corrected ground state is written down as

$$|\tilde{0}\rangle = |0\rangle - \sum_g \sum_n C_{gn,0}|gn\rangle - \sum_s \sum_m \sum_t \sum_n C_{smtn}|smtn\rangle. \tag{46a}$$

Since $|0\rangle$ of Eq. 4 can be defined in N different ways by $|0k\rangle$ for $k=1,2,\cdots,N$ and since we wish to represent explicitly the site-dependence of $C_{0,fm}$, $C_{gn,0}$, and $C_{smtn,0}$ so as to show to what extent the transition moments are intermolecularly mixed with which site of the permanent dipole moment in the $|0\rangle$, we write Eqs. 45a and 46a as in the following:

$$\begin{aligned}
|\tilde{f}\tilde{m}\rangle &= |fm\rangle + \sum_k \varepsilon_{fm,0}^{-1}\,\boldsymbol{\mu}_{00}^{(k)}\cdot\boldsymbol{U}_{km}\cdot\boldsymbol{\mu}_{0f}^{(m)}|0k\rangle \\
&= |fm\rangle + \sum_k C_{0,fm}^{(k)}|0k\rangle,
\end{aligned} \tag{45b}$$

$$\begin{aligned}
|\tilde{0}_j\rangle &= |0_j\rangle - \sum_g \sum_n C_{gn,0}^{(j)}|gn\rangle \\
&- \sum_s \sum_t \sum_n C_{sjtn,0}^{(jn)}|sjtn\rangle, \quad j=1,2,\cdots,N
\end{aligned} \tag{46b}$$

where the two-site excitation coefficients are expressed in terms of $\varepsilon_{sjtn,0}^{-1}\,\boldsymbol{\mu}_{s0}^{(j)}\cdot\boldsymbol{U}_{jn}\cdot\boldsymbol{\mu}_{0t}^{(n)}$. The fth excitation energy of the mth submolecule is obtained as

$$\begin{aligned}
\tilde{\varepsilon}_{fm,0} &= \langle\tilde{f}\tilde{m}|H|\tilde{f}\tilde{m}\rangle - \langle\tilde{0}|H|\tilde{0}\rangle \\
&\simeq \{1+\sum_k 2|C_{fm,0}^{(k)}|^2\}\,\varepsilon_{fm,0} + \sum_g \sum_n 2|C_{gn,0}^{(m)}|^2\,\varepsilon_{fn,0} \\
&+ \sum_s \sum_t \sum_n 2|C_{smtn,0}^{(mn)}|^2\,\varepsilon_{smtn,0}.
\end{aligned} \tag{47}$$

Similarly, the transfer integrals over modified interactions come to be of the forms

$$\begin{aligned}
\langle\tilde{f}\tilde{m}|V|\tilde{g}\tilde{m}\rangle &= \sum_k \boldsymbol{\mu}_{fg}^{(m)}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}_{00}^{(k)} + \sum_l \boldsymbol{\mu}_{f0}^{(m)}\cdot\boldsymbol{U}_{ml}\cdot\boldsymbol{\mu}_{00}^{(l)} C_{gm,0}^{(l)} \\
&+ \sum_k C_{0,fm}^{(k)}\,\boldsymbol{\mu}_{00}^{(k)}\cdot\boldsymbol{U}_{km}\cdot\boldsymbol{\mu}_{g0}^{(m)} + \sum_k \sum_l C_{0,fm}^{(k)}\,\boldsymbol{\mu}_{00}^{(k)}\cdot\boldsymbol{U}_{kl}\cdot\boldsymbol{\mu}_{00}^{(l)} C_{gm,0}^{(l)},
\end{aligned} \tag{48}$$

$$\begin{aligned}
\langle\tilde{f}\tilde{m}|V|\tilde{g}\tilde{n}\rangle &= \boldsymbol{\mu}_{f0}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{0g}^{(n)} + \sum_l \boldsymbol{\mu}_{f0}^{(m)}\cdot\boldsymbol{U}_{ml}\cdot\boldsymbol{\mu}_{00}^{(l)} C_{gn,0}^{(l)} \\
&+ \sum_k C_{0,fm}^{(k)}\,\boldsymbol{\mu}_{00}^{(k)}\cdot\boldsymbol{U}_{kn}\cdot\boldsymbol{\mu}_{g0}^{(n)} + \sum_k \sum_l C_{0,fm}^{(k)}\,\boldsymbol{\mu}_{00}^{(k)}\cdot\boldsymbol{U}_{kl}\cdot\boldsymbol{\mu}_{00}^{(l)} C_{gn,0}^{(l)}.
\end{aligned} \tag{49}$$

In (C), it has been shown that the intrasite interaction $\langle fm|V|gm\rangle$ as well as the renormalization such as $-\langle\tilde{0}|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|\tilde{0}\rangle$ can introduce the static effect in the polarizability theory, while Fano-DeVoe's intersite interaction term $<fm|V|gn>$ does not contain the static effect. However, in (D) we have noted that the Fano-DeVoe type of interaction term $<\tilde{f}\tilde{m}|V|\tilde{g}\tilde{n}>$ can involve the electrostatic modification against the bare interaction term $<fm|V|gm>$ by using the one-site excitation states mixed with the ground state.

For later convenience, let us define the f,g-matrix elements of the monomer polarizability tensor $\tilde{\boldsymbol{\alpha}}_{mn}(E)$ by

$$\tilde{\boldsymbol{\alpha}}_{fm,gm}(E)=-<0|\boldsymbol{\mu}|\tilde{f}\tilde{m}><\tilde{g}\tilde{n}|\boldsymbol{\mu}|0>/(E-\tilde{\varepsilon}_{gn,0}+i\,\tilde{\eta}_{gn}), \tag{50}$$

in relation with the diagonal elements

$$\begin{aligned}\tilde{\boldsymbol{\alpha}}_{mm}(E)&=-\sum_f\sum_g <0|\boldsymbol{\mu}|\tilde{f}\tilde{m}><\tilde{f}\tilde{m}|\tilde{G}^{\circ}(E)|\tilde{g}\tilde{n}><\tilde{g}\tilde{n}|\boldsymbol{\mu}|0>\\&=\sum_f\sum_g \tilde{\boldsymbol{\alpha}}_{fm,gn}(E)\delta_{mn}\delta_{fg},\end{aligned} \tag{51}$$

Calculation of the modified transition moment yields

$$<0|\boldsymbol{\mu}|\tilde{f}\tilde{m}>\equiv\tilde{\boldsymbol{\mu}}_{0f}^{(m)}=\boldsymbol{\mu}_{0f}^{(m)}+\sum_k C_{0,fm}^{(k)}\boldsymbol{\mu}_{00}^{(k)}. \tag{52}$$

Then, we introduce the following definitions for the components of $\tilde{\boldsymbol{\alpha}}_{mm}(E)$

$$\tilde{\boldsymbol{\alpha}}_{mm}^{oo}(E)=\sum_{f\neq 0}-\boldsymbol{\mu}_{0f}^{(m)}\boldsymbol{\mu}_{f0}^{(m)}/(E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}), \tag{53a}$$

$$\tilde{\boldsymbol{\alpha}}_{mm}^{lo}(E)=\sum_{f\neq 0}-\tilde{\boldsymbol{\mu}}_{0f}^{(m)}\boldsymbol{\mu}_{f0}^{(m)}/(E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}), \tag{53b}$$

$$\tilde{\boldsymbol{\alpha}}_{mm}^{ol}(E)=\sum_{f\neq 0}-\boldsymbol{\mu}_{0f}^{(m)}\tilde{\boldsymbol{\mu}}_{f0}^{(m)}/(E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}), \tag{53c}$$

While original Fano-DeVoe's polymer polarizability can be linearlized in terms of the monomer polarizability components, the polymer polarizability tensor ${}^{p}\tilde{\alpha}_{mn}(E)$ cannot be expressed simply in terms of the monomer polarizability tensors $\tilde{\alpha}_{mm}(E)$ and interaction tensors U. We therefore derive ${}^{p}\tilde{\alpha}_{mn}(E)$ in the following by use of the polarizability components $\tilde{\alpha}_{fm,gn}(E)$ newly defined by Eq. 50. The calculations are performed in the same way as Eq. 38a:

$$\begin{aligned}{}^{p}\tilde{\boldsymbol{\alpha}}_{mn}(E)&=-\sum_{f,\,g\neq 0}\sum <0|\boldsymbol{\mu}|\tilde{f}\tilde{m}><\tilde{f}\tilde{m}|\tilde{G}(E)|\tilde{g}\tilde{n}><\tilde{g}\tilde{n}|\boldsymbol{\mu}|0>\\
&\simeq-\sum_f\sum_g\tilde{\boldsymbol{\mu}}_{0f}^{(m)}<\tilde{f}\tilde{m}|\tilde{G}^{\circ}(E)+\tilde{G}^{\circ}(E)\tilde{V}_{FD}\tilde{G}^{\circ}(E)\\
&\qquad+\tilde{G}^{\circ}(E)\tilde{V}_{FD}\tilde{G}^{\circ}(E)\tilde{V}_{FD}\tilde{G}^{\circ}(E)+\cdots|\tilde{g}\tilde{n}>\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\\
&-\sum_f\sum_g\tilde{\boldsymbol{\mu}}_{0f}^{(m)}<\tilde{f}\tilde{m}|\tilde{G}^{\circ}(E)\tilde{V}_S\tilde{G}(E)\\
&\qquad+\tilde{G}^{\circ}(E)\tilde{V}_S\tilde{G}^{\circ}(E)\tilde{V}_S\tilde{G}^{\circ}(E)+\cdots|\tilde{g}\tilde{n}>\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\\
&-\sum_f\sum_g\{\tilde{\boldsymbol{\mu}}_{0f}^{(m)}<fm|\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_S(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_S(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)|gn>\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\\
&+\tilde{\boldsymbol{\mu}}_{0f}^{(m)}<fm|\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_{FD}(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_S(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)|gn>\tilde{\boldsymbol{\mu}}_{g0}^{(n)}+\\
&\tilde{\boldsymbol{\mu}}_{0f}^{(m)}<fm|\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_{FD}(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)\\
&\qquad\times\quad{}^{p}\tilde{V}_S(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_{FD}(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)|gn>\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\\
&+\tilde{\boldsymbol{\mu}}_{0f}^{(m)}<fm|\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_S(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_{FD}(E)\\
&\qquad\times\quad\tilde{G}^{\circ}_{\mathrm{FD}}(E)\,{}^{p}\tilde{V}_S(E)\tilde{G}^{\circ}_{\mathrm{FD}}(E)|gn>\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\},\end{aligned} \tag{54}$$

except for the third term in which we put merely the pure Fano-DeVoe part as $\tilde{G}^{\circ}_{FD}(E)=\sum_{\psi}(E-\tilde{\varepsilon}_{\psi,0}+i\tilde{\eta}_{\psi})^{-1}|\psi><\psi|$ in the $\tilde{G}^{\circ}(E)$. Also, we make use of the $<fm|$and$|gn>$ instead of the $<\tilde{f}\tilde{m}|$ and $|\tilde{g}\tilde{n}>$, and employ only the bare interaction operator $\overline{V}$ instead of the dressed interaction operator $\tilde{V}$. The reason for this last treatment is that the components of the third terms are clearly at least second order in the bare interaction $<\psi|V|\psi'>$ and therefore the corrections produced by such truncation of the third term become third order in $<\psi|V|\psi'>$.

The working formula for the polymer polarizability tensor is obtained from Eq. 54:

$$\begin{aligned}{}^{p}\tilde{\boldsymbol{\alpha}}_{mn}(E)&\simeq{}^{p}\tilde{\boldsymbol{\alpha}}_{mm}^{FD}(E)+{}^{p}\tilde{\boldsymbol{\alpha}}_{mm}^{S}(E)\delta_{mm}\\
&+\sum_{f\neq t}\sum_k\sum\tilde{\boldsymbol{\mu}}_{0f}^{(m)}\tilde{K}_{mm}^{ft}(E)\boldsymbol{\mu}_{t0}^{(m)}\cdot\{\mathbf{1}+\boldsymbol{U}\cdot\tilde{\boldsymbol{\alpha}}^{oo}(E)\}_{mk}^{-1}\cdot\boldsymbol{U}_{kn}\cdot\tilde{\boldsymbol{\alpha}}_{nn}^{ol}(E)\\
&+\sum_k\sum_{t\neq g}\sum\tilde{\boldsymbol{\alpha}}_{mm}^{lo}(E)\cdot\boldsymbol{U}_{mk}\cdot\{\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{oo}(E)\cdot\boldsymbol{U}\}_{kn}^{-1}\cdot\boldsymbol{\mu}_{0f}^{(n)}\tilde{K}_{nn}^{tg}(E)\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\\
&-\sum_k\sum_l\sum_j\sum_{t\neq g}\sum\tilde{\boldsymbol{\alpha}}_{mm}^{lo}(E)\cdot\boldsymbol{U}_{mk}\cdot\{\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{oo}(E)\cdot\boldsymbol{U}\}_{kl}^{-1}\cdot\boldsymbol{\mu}_{0f}^{(l)}\tilde{K}_{ll}^{tg}(E)\tilde{\boldsymbol{\mu}}_{g0}^{(l)}\\
&\times\{\mathbf{1}+\boldsymbol{U}\cdot\tilde{\boldsymbol{\alpha}}^{oo}(E)\}_{lj}^{-1}\cdot\boldsymbol{U}_{jn}\cdot\tilde{\boldsymbol{\alpha}}_{nn}^{ol}(E)-\sum_{f\neq t}\sum_k\sum\sum_{s\neq g}\sum\tilde{\boldsymbol{\mu}}_{0f}^{(m)}\tilde{K}_{mm}^{ft}(E)\boldsymbol{\mu}_{t0}^{(m)}\\
&\times\{\mathbf{1}+\boldsymbol{U}\cdot\tilde{\boldsymbol{\alpha}}^{oo}(E)\}_{mk}^{-1}\cdot\boldsymbol{U}_{kn}\cdot\boldsymbol{\mu}_{0s}^{(n)}\tilde{K}_{ll}^{sg}(E)\tilde{\boldsymbol{\mu}}_{g0}^{(n)}\quad m,n=1,2,3,\cdots,\mathrm{N}\end{aligned} \tag{55}$$

with

$$\begin{aligned}K_{mm}^{fg}(E)=\Bigg\{&\frac{<\tilde{f}\tilde{m}|V|\tilde{g}\tilde{m}>}{E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}_{fm}}+\sum_{t\neq f,g}\\
&\times\frac{<\tilde{f}\tilde{m}|V|\tilde{t}\tilde{m}><\tilde{t}\tilde{m}|V|\tilde{g}\tilde{m}>}{(E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}_{fm})(E-\tilde{\varepsilon}_{tm,0}+i\,\tilde{\eta}_{tm})}+\cdots\Bigg\}\Big/\\
&(E-\tilde{\varepsilon}_{gm,0}+i\,\tilde{\eta}_{gm})\end{aligned} \tag{56}$$

where $\{\mathbf{1}+\boldsymbol{U}\cdot\tilde{\boldsymbol{\alpha}}^{oo}(E)\}^{-1}_{kn}$ and $\{\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{oo}(E)\cdot\boldsymbol{U}\}^{-1}_{mk}$ have similar expressions as Eqs. 39 and 40. Equatition 55 is a renormalized RPA. The first and second terms are put into a single equation:

$$\begin{aligned}{}^{p}\tilde{\boldsymbol{\alpha}}_{mn}^{FD}(E)+{}^{p}\tilde{\boldsymbol{\alpha}}_{mn}^{S}(E)\delta_{mm}&=\sum_{f,\,g\neq 0}\sum\tilde{\boldsymbol{\alpha}}_{fm,gn}(E)\{\delta_{mn}\delta_{fg}\\
&+\frac{<\tilde{f}\tilde{m}|V|\tilde{f}\tilde{n}>}{E-\tilde{\varepsilon}_{fm,0}+i\tilde{\eta}_{fm}}+\sum_{s\neq f,g}\sum_k\frac{<\tilde{f}\tilde{m}|V|\tilde{s}\tilde{k}><\tilde{s}\tilde{k}|V|\tilde{g}\tilde{n}>}{(E-\tilde{\varepsilon}_{fm,0}+i\tilde{\eta}_{fm})(E-\tilde{\varepsilon}_{sk,0}+i\tilde{\eta}_{sk})}\\
&+\sum_k\sum_l\sum_{s\neq t,f,g,}\sum_{t\neq g,f,s}\\
&\frac{<\tilde{f}\tilde{m}|V|\tilde{s}\tilde{k}><\tilde{s}\tilde{k}|V|\tilde{t}\tilde{l}><\tilde{t}\tilde{l}|V|\tilde{g}\tilde{n}>}{(E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}_{fm})(E-\tilde{\varepsilon}_{sk,0}+i\,\tilde{\eta}_{sk})(E-\tilde{\varepsilon}_{tl,0}+i\,\tilde{\eta}_{tl})}\\
&\equiv\sum_{f,\,g\neq 0}\sum\tilde{\boldsymbol{\alpha}}_{fm,gn}(E)\,{}^{p}B_{mn}^{fg}(E),\end{aligned} \tag{57}$$

where we must note that the $n=m$ case corresponds to the Bayley, Nielsen, and Schellman type of polarizability tensor ${}^{p}\tilde{\boldsymbol{\alpha}}^{s}(E)$.

The scalar quantity ${}^{p}B_{mn}^{fg}(E)$ defines the coefficient for the $\tilde{\boldsymbol{\alpha}}_{fm,gn}(E)$. ${}^{p}B_{mn}^{fg}(E)$ involves the interaction elements $\{<\tilde{f}\tilde{m}|V|\tilde{g}\tilde{n}>\}$ up to infinite orders. It goes without saying that ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$ involves the usual Fano-DeVoe type of term $\{\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{oo}(E)\cdot\boldsymbol{U}\}^{-1}\cdot\tilde{\boldsymbol{\alpha}}^{oo}(E)$. If we resolve all the interaction matrices into the form $\boldsymbol{\mu}\cdot\boldsymbol{U}\cdot\boldsymbol{\mu}$, by use of which if we try to express ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$ in terms of the average of dyadic products $\boldsymbol{\mu}G^{\circ}(E)\boldsymbol{\mu}$ over the polymer ground state and unit dipole interaction tensors $\boldsymbol{U}$, we must face with a tremendous variety of complicated matrix elements of ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$, so that it becomes difficult to outline the total image of the theory. However, as shown in Eqs. 55 and 57, it is not difficult to compute ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$ up to higher orders of V without resolving matrix elements into small pieces such as $\boldsymbol{\mu}\cdot\boldsymbol{U}\cdot\boldsymbol{\mu}$. Namely, Eq. 55 gives a simple expression for ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$, in which Eq. 57 is represented in terms of scalar modules such as $<\tilde{f}\tilde{m}|V|\tilde{g}\tilde{n}>$. In addition to this merit, ${}^{p}B(E)$ defined by Eq. 57 can easily be linearlized in terms of simple matrix elements such as

$$B_{mn}^{fg}(E)=<\tilde{f}\tilde{m}|V|\tilde{g}\tilde{n}>/(E-\tilde{\varepsilon}_{fm,0}+i\,\tilde{\eta}_{fm}). \tag{58}$$

In the following, we show that ${}^{p}B(E)$ can formally be calculated up to infinite orders of V without resort to such reckless term-by-term calculations as that of Eq. 57.

In relation with Eq. 57, we can put

$$\begin{aligned}{}^{p}B_{mn}^{fg}(E)&=\delta_{mn}\delta_{fg}+B_{mn}^{fg}(E)+\sum_{s}\sum_{k}B_{mk}^{fs}(E)B_{kn}^{sg}(E)\\&\quad+\sum_{s}\sum_{k}\sum_{t}\sum_{l}B_{mk}^{fs}(E)B_{kl}^{st}(E)B_{ln}^{tg}(E)+\cdots\\&=\delta_{mn}\delta_{fg}+\sum_{s}\sum_{k}B_{mk}^{fs}(E)\{\delta_{kn}\delta_{sg}\\&\quad+\sum_{t}\sum_{l}B_{kl}^{st}(E){}^{p}B_{ln}^{tg}(E)\}\\&=\delta_{mn}\delta_{fg}+\sum_{s}\sum_{k}B_{mk}^{fs}(E){}^{p}B_{kn}^{sg}(E)=\{[1-B(E)]^{-1}\}_{mn}^{fg},\end{aligned} \tag{59a}$$

where $B(E)$ is a $(\sum_{m=1}^{N}f_m)\times(\sum_{k=1}^{N}S_k)$ matrix, f_m being the number of the fth oscillators of the mth site. In more detail, if we define the block matrices ${}^{p}B_{mn}(E)$ and $B_{mk}(E)$ with the elements ${}^{p}B_{mn}^{fg}(E)$ and $B_{mk}^{fs}(E)$. Equation 59a yields the relationship of an unknown matrix ${}^{p}B(E)$ with the known matrix $B(E)$ as follows:

$${}^{p}B(E)=1+B(E)\,{}^{p}B(E),\text{ i.e., }{}^{p}B(E)=\{1-B(E)\}^{-1}, \tag{59b}$$

which gives the involvement of infinite orders of the interaction $\tilde{V}$ in Eq. 57. Actually, it may be sufficient to carry out the calculations of several higher terms in the braces of Eq. 57 without use of Eqs. 59a and 59b.

If we follow the scheme of Eq. 42 which corresponds to the intermediate coupling case, we have

$$\begin{aligned}{}^{rp}\tilde{\boldsymbol{\alpha}}_{mn}(E)&={}^{p}\tilde{\boldsymbol{\alpha}}_{mn}(E)\\&\quad+\sum_{k}\sum_{f}\sum_{g}C_{0,fm}^{(k)}<fm|\boldsymbol{\mu}\tilde{G}^{\circ}(E)|\tilde{g}\tilde{n}><\tilde{g}\tilde{n}|\boldsymbol{\mu}|0>\\&\quad+\sum_{k}\sum_{f}\sum_{g}<0|\boldsymbol{\mu}|\tilde{f}\tilde{m}><\tilde{f}\tilde{m}|\tilde{G}^{\circ}(E)\boldsymbol{\mu}|gn>C_{gn,0}^{(k)}\\&\quad+\sum_{k}\sum_{s}\sum_{t}\sum_{g}C_{0,smtk}^{(m,k)}<smtk|\boldsymbol{\mu}\tilde{G}^{\circ}(E)|\tilde{g}\tilde{n}><\tilde{g}\tilde{n}|\boldsymbol{\mu}|0>\\&\quad+\sum_{k}\sum_{f}\sum_{s}\sum_{t}<0|\boldsymbol{\mu}|\tilde{f}\tilde{m}><\tilde{f}\tilde{m}|\tilde{G}^{\circ}(E)\boldsymbol{\mu}|sktn>C_{sktn,0}^{(k,n)}\\&\quad+O(|C_{mix}|^{2}),\end{aligned} \tag{60}$$

which is the self-consistent renormalized RPA. The transition moments necessary for the calculations of Eq. 60 are reduced to

$$<fm|\boldsymbol{\mu}|\tilde{g}\tilde{n}>=\boldsymbol{\mu}_{fg}^{(m)}\delta_{mn}+\sum_{k}C_{0,gn}^{(k)}\boldsymbol{\mu}_{f0}^{(m)}\delta_{mk}, \tag{61}$$

$$<\tilde{f}\tilde{m}|\boldsymbol{\mu}|gn>=\boldsymbol{\mu}_{fg}^{(m)}\delta_{mn}+\sum_{k}C_{0,gn}^{(k)}\boldsymbol{\mu}_{g0}^{(m)}\delta_{nk}, \tag{62}$$

$$<smtk|\boldsymbol{\mu}|\tilde{g}\tilde{n}>=\delta_{mn}\delta_{sg}\boldsymbol{\mu}_{t0}^{(k)}+\delta_{kn}\delta_{tg}\boldsymbol{\mu}_{s0}^{(m)}, \tag{63}$$

$$<\tilde{f}\tilde{m}|\boldsymbol{\mu}|sktn>=\delta_{mk}\delta_{sf}\boldsymbol{\mu}_{0t}^{(n)}+\delta_{mn}\delta_{ft}\boldsymbol{\mu}_{0s}^{(k)}, \tag{64}$$

As mentioned before regarding to Eq. 43, it may be not necessary to carry out the calculations of the correction terms for Eq. 60. However, for a polymer system of the constituent monomers having no permanent dipole moment, we need to calculate Eq. 60 as follows:

$$\begin{aligned}{}^{rp}\tilde{\boldsymbol{\alpha}}_{mn}(E)&=[\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{\circ\circ}(E)\cdot\boldsymbol{U}]_{mn}^{-1}\cdot\tilde{\boldsymbol{\alpha}}_{nn}^{\circ\circ}(E)\\&\quad+\sum_{s}\sum_{k}\sum_{t}\{[\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{\circ\circ}(E)\cdot\boldsymbol{U}]_{mk}^{-1}\cdot\boldsymbol{\mu}_{0s}^{(k)}C_{sktn,0}\boldsymbol{\mu}_{0t}^{(n)}/\\&\quad(E-\tilde{\varepsilon}_{sk,0}+\mathrm{i}\,\tilde{\eta}_{sk})\\&\quad+[\mathbf{1}+\tilde{\boldsymbol{\alpha}}^{\circ\circ}(E)\cdot\boldsymbol{U}]_{mn}^{-1}\cdot\boldsymbol{\mu}_{0t}^{(n)}C_{sktn,0}\boldsymbol{\mu}_{0s}^{(k)}/(E-\tilde{\varepsilon}_{tn,0}+i\,\tilde{\eta}_{tn})\\&\quad+\boldsymbol{\mu}_{t0}^{(k)}C_{0,smtk}\boldsymbol{\mu}_{0s}^{(m)}/(E-\tilde{\varepsilon}_{sm,0}+i\,\tilde{\eta}_{sm})\cdot[\mathbf{1}+\boldsymbol{U}\cdot\tilde{\boldsymbol{\alpha}}^{\circ\circ}(E)]_{mn}^{-1}\\&\quad+\boldsymbol{\mu}_{s0}^{(m)}C_{0,smtk}\boldsymbol{\mu}_{0t}^{(k)}/(E-\tilde{\varepsilon}_{tk,0}+i\,\tilde{\eta}_{tk})\cdot[\mathbf{1}+\boldsymbol{U}\cdot\tilde{\boldsymbol{\alpha}}^{\circ\circ}(E)]_{kn}^{-1}\}\\&\quad+O(C_{0,smtj}C_{fkgn,0}),\end{aligned} \tag{65}$$

which is the same as Eq. 43 except for the excitation energies replaced by Eq. 47, where the mixing coefficients of one-site excitation states vanish.

For the dressed polarizability tensors derived above, we can obtain the bandshape functions of the UV absorption, CD, and ORD spectra for the DNA molecules, either from the calculations[1,2] of $3^{-1}\,Tr\,{}^{p}\tilde{\boldsymbol{\alpha}}_{mn}(E)$ and $12^{-1}\boldsymbol{R}_{mn}\cdot({}^{p}\tilde{\boldsymbol{\alpha}}_{mn}(E):\boldsymbol{\varepsilon})$ by making use of Eq. 55, or from the calculations of $3^{-1}\,Tr\,{}^{rp}\tilde{\boldsymbol{\alpha}}_{mn}(E)$ and $12^{-1}\boldsymbol{R}_{mn}\cdot({}^{rp}\tilde{\boldsymbol{\alpha}}_{mn}(E):\boldsymbol{\varepsilon})$ by making use of Eq. 60 and/or Eq. 65.

Joint Use of Short-Range Monopole and Long-Range Dipole Approximations in All the Interaction Integrals $<\psi|V|\psi'>$

The use of the dipole approximation makes it easy to calculate the polarizability tensors, since the transition moments are easily obtainable from the experimental data. However, in order to circumvent the deficiency of the dipole approximation in short distances, it is recommendable to make use of the monopole approximation for the near or nearest neighbors, and to make use of the dipole approximation for the distant monomers, when the data for the monopole densities are easily available. Especially, in very long-chain polymers, such joint use of different approximations will clearly have a lot of practical merits. Consequently, let us show how to introduce the monopole approximation in the present polarizability theory. All the interaction integrals $<\psi|V|\psi'>$ as well as the mixing coefficients $C_{0,\psi}$ and $C_{\psi,0}$ are reduced to the forms such as $\boldsymbol{\mu}_{sf}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{gt}^{(n)}\equiv V_{mn}^{(sf,gt)}$.

The scalar potential $V_{mn}^{(sf,gt)}$ is expressed by

$$\begin{aligned}V_{mm}^{(sf,gt)}&=\boldsymbol{\mu}_{sf}^{(m)}\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\mu}_{gt}^{(n)}\\&=[\boldsymbol{\mu}_{sf}^{(mx)}\;\boldsymbol{\mu}_{sf}^{(my)}\;\boldsymbol{\mu}_{sf}^{(mz)}]\begin{bmatrix}U_{mn}^{(xx)}&U_{mn}^{(xy)}&U_{mn}^{(xz)}\\U_{mn}^{(yx)}&U_{mn}^{(yy)}&U_{mn}^{(yz)}\\U_{mn}^{(zx)}&U_{mn}^{(zy)}&U_{mn}^{(zz)}\end{bmatrix}\begin{bmatrix}\boldsymbol{\mu}_{gt}^{(nx)}\\\boldsymbol{\mu}_{gt}^{(ny)}\\\boldsymbol{\mu}_{gt}^{(nz)}\end{bmatrix}\\&\simeq\sum_{A}^{\text{atoms}}\sum_{B}q_{sf,A}^{(m)}q_{gt,B}^{(n)}/R_{mA,nB},\end{aligned} \tag{66}$$

where the final replacement from the dipole approximation is the so-called transition monopole approximation[9-14,21,22] with the monopole densities separated by the distance $R_{mA,nB}$. Particularly, $q^{(m)}_{0f,A}$ denotes the usual 0→f transition monopole density at atom A in the mth submolecule, and $q^{(m)}_{00,A}$ specifies the permanent monopole density. The knowledge of the transition and permanent monopole densities of a monomer may be obtained by some molecular orbital calculations[9] or by the semiempirical estimates.[10-14,21,22]

The ${}^{p}\boldsymbol{\alpha}(E)$ appeared in Eq. 38b takes the following various forms:

$$\begin{aligned}{}^{p}\boldsymbol{\alpha}(E)&=\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}^{-1}\cdot\boldsymbol{\alpha}(E)\\&=\{\boldsymbol{\alpha}^{-1}(E)+\boldsymbol{U}\}^{-1}\\&=\boldsymbol{\alpha}(E)\cdot\{\boldsymbol{\alpha}(E)+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}\cdot\boldsymbol{\alpha}(E)\end{aligned}\tag{67}$$

where the second line indicates the equivalence to DeVoe's coupled oscillator theory.[8] The third line is found to be convenient to introduce the transition and permanent monopole approximations for the near neighbor interactions.

It is also convenient for the monopole approximation to rewrite Eqs. 39 and 40 as follows:

$$\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}^{-1}=\boldsymbol{\alpha}(E)\cdot\{\boldsymbol{\alpha}(E)+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1},\tag{68}$$

$$\{\mathbf{1}+\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}=\{\boldsymbol{\alpha}(E)+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}^{-1}\cdot\boldsymbol{\alpha}(E).\tag{69}$$

In order to introduce the monopole approximation for the near neighbor submolecules, the matrix elements for $\boldsymbol{\alpha}(E)\cdot U\cdot\boldsymbol{\alpha}(E)$ are calculated as

$$\begin{aligned}&\boldsymbol{\alpha}_{mm}(E)\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\alpha}_{nn}(E)\\&=\sum_{f}\sum_{g}(E-\varepsilon_{fm,0}+i\,\eta_{fm})^{-1}(E-\varepsilon_{gn,0}+i\,\eta_{gm})^{-1}\,V^{(f0,0g)}_{mn}\,\boldsymbol{\mu}^{(m)}_{0f}\,\boldsymbol{\mu}^{(n)}_{g0},\end{aligned}\tag{70}$$

where the dyadic product $\boldsymbol{\mu}^{(m)}_{0f}\boldsymbol{\mu}^{(n)}_{g0}$ is expressed in terms of the multiplication of the column matrix $\boldsymbol{\mu}^{(m)}_{0f}$ by the row matrix $\boldsymbol{\mu}^{(n)}_{g0}$ and the Coulomb energy $V^{(f0,0g)}_{mn}$ is calculated by Eq. 66.

For non-near neighbors, we can also make use of the monopole approximation, but it is suffcient to make use of the dipole approximation. For the latter case, it may be convenient to calculate the corresponding matrix elements in a way different from Eq. 70 in algolithm as follows:

$$\begin{aligned}&\boldsymbol{\alpha}_{mm}(E)\cdot\boldsymbol{U}_{mn}\cdot\boldsymbol{\alpha}_{mn}(E)\\&\quad=\sum_{f}\sum_{g}(E-\varepsilon_{fm,0}+i\,\eta_{fm})^{-1}(E-\varepsilon_{gn,0}+i\,\eta_{gn})^{-1}\times\\&\quad\quad\{\boldsymbol{\mu}^{(m)}_{0f}\,\boldsymbol{\mu}^{(m)}_{f0}\}\cdot\boldsymbol{U}_{mn}\cdot\{\boldsymbol{\mu}^{(n)}_{0f}\,\boldsymbol{\mu}^{(n)}_{f0}\},\end{aligned}\tag{71}$$

where $\boldsymbol{\mu}^{(m)}_{0f}\boldsymbol{\mu}^{(m)}_{f0}$ is a 3×3 matrix.

It is practically important to note that the inverse of the matrix $\{\boldsymbol{\alpha}(E)+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\cdot\boldsymbol{\alpha}(E)\}$ concerned should be obtained in units of 10^{-24} cm^3 according to the numerical treatment of the previous paper,[2] whereas the inverse of $\{\mathbf{1}+\boldsymbol{\alpha}(E)\cdot\boldsymbol{U}\}$ can always be calculated to be at most in the vicinity of unity or with much smaller values in its matrix elements.

Summary and Discussion

We have presented a new approach capable of extending the Fano-DeVoe model. Such an approach is inherently based upon the dipole-dipole approximation, which has however a deficiency in the near neighbors of submolecules. In the previous section, we have shown how to bring in the monopole approximation by changing the present forms of polymer polarizability tensors derived. Thus, following Moffitt's idea, it becomes possible to use jointly the short-range-oriented monopole and long-range-oriented dipole approximations in the present theory.

We can first point out that this approach makes it possible to calculate the polarizability tensors by involving the static effect of permanent dipole moments for some DNA molecules and polypeptides,[13-15,17] whereas the ordinary Fano-DeVoe model cannot involve the static field effect in calculations. It should be noted that inclusion of the static effect in the theory is made in the three ways: (i) We can observe the static effect in the level-shift energy of the excitation energy $\varepsilon_{\psi,0}$ given by Eqs. 18 and 19; (ii) The static effect is clearly found to be involved, if we see that the second terms of Eqs. 16 and 35 are expressed by Eq. 11, which corresponds to the static field effect appeared in the transition matrix theory;[15] (iii) The static effect is taken into account by use of the exact basis set $\{|\tilde{\psi}>\}$ as well as by the renormalization of $-<\tilde{0}|\boldsymbol{\mu}G(E)\boldsymbol{\mu}|\tilde{0}>$ of Eqs. 24, 42, and 43 and/or $-<\tilde{0}|\boldsymbol{\mu}\tilde{G}(E)\boldsymbol{\mu}|\tilde{0}>$ of Eqs. 33, 60, and 65. If there is no static effect due to $\boldsymbol{\mu}^{(\mathrm{site})}_{00}=0$, Eq. 38b embodies the original Fano-DeVoe model. Even for this case, as shown in Eq. 43 and also Eq. 65, we can extend the pure Fano-DeVoe model by the renormalization of the polymer ground state through two-site excitation states.

In relation with (ii), we must note that Eq. 38a without truncation is identical to Rabenold's linear response theory.[16,17] His derivation is based upon the transition matrix theory[15] with the use of Green's operator method. Let us take a look at his formulation in terms of our notations. The polymer polarizability tensor is expressed by

$$\begin{aligned}{}^{p}\boldsymbol{\alpha}(E)&=-\sum_{\psi,\psi'\neq0}\sum<0|\boldsymbol{\mu}|\psi><\psi|(E-\bar{H}+i\,\eta)^{-1}|\psi'><\psi'|\boldsymbol{\mu}|0>\\&=-\sum_{f}\sum_{g}\sum_{m}\sum_{n}\boldsymbol{\mu}^{(m)}_{0f}\{\{[(E\mathbf{1}-\varepsilon+i\,\eta)\bar{\boldsymbol{V}}_{S}]-\bar{\boldsymbol{V}}_{FD}\}^{-1}\}^{fg}_{mn}\,\boldsymbol{\mu}^{(n)}_{g0},\end{aligned}\tag{72}$$

whose matrix elements are

$$\{\bar{\boldsymbol{V}}_{S}\}^{fg}_{mn}=\delta_{mn}<fm|V|gm>=\delta_{mn}\sum_{k\neq m(f\neq g)}\boldsymbol{\mu}^{(m)}_{fg}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}^{(k)}_{00},\tag{73}$$

$$\{\bar{\boldsymbol{V}}_{FD}\}^{fg}_{mn}=<fm|V|gm>=\boldsymbol{\mu}^{(m)}_{f0}\cdot\boldsymbol{U}_{mk}\cdot\boldsymbol{\mu}^{(n)}_{g0},\tag{74}$$

$$\{E\mathbf{1}-\varepsilon+i\,\eta\}^{fg}_{mn}=(E-\varepsilon_{fm,0}+i\,\eta_{fm})\delta_{mn}\delta_{fg}.\tag{75}$$

The $[(E\mathbf{1}-\varepsilon+i\eta)-\tilde{\boldsymbol{V}}_{s}]$ in Eq. 72 is an m,m-block diagonal matrix with the off-diagonal $f,g,$-elements, while the Fano-DeVoe type interaction $\overline{V}_{FD}$ is an m,n-block off-diagonal matrix. The f,f-diagonal elements $<fm|V|fm>$ of $\overline{V}_S$ for the static field effect are included in the excitation energy $\varepsilon_{fm,0}$. If we follow Rabenold, the equivalence of the two theories can be shown by diagonalizing each m,m-block diagonal matrix of Eq. 72 as follows:

$$\boldsymbol{X}^{+}[(E\mathbf{1}-\varepsilon+i\eta)-\overline{V}_S]\boldsymbol{X}=E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta}, \tag{76}$$

with the eigenvector:

$$\boldsymbol{X}=\mathrm{diag}\{\boldsymbol{X}_1, \boldsymbol{X}_2, \dots \quad, \boldsymbol{X}_N\}, \tag{77}$$

by use of which we newly define the dressed interaction matrix for the polymer system

$$\{{}^{px}\overline{V}_{FD}\}_{mn}=\sum_f\sum_j\sum_g\sum_k X^{+}_{m,fj}\{\overline{V}_{FD}\}^{fg}_{jk}X_{gk,n}. \tag{78}$$

In Eq. 72, we can express the secular matrix in terms of the block diagonal matrix of Eq. 77, X, as follows:

$$\begin{aligned}\boldsymbol{X}^{+}\{[(E\mathbf{1}-\varepsilon+i\eta)-\overline{V}_S]-\overline{V}_{FD}\}X&=(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})-\boldsymbol{X}^{+}\overline{V}_{FD}\boldsymbol{X}\\ &\equiv(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})-{}^{px}\overline{V}_{FD}\end{aligned} \tag{79}$$

where the first term is given by Eq. 76. Equation 79 gives rise to

$$\{[(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})-\overline{V}_S]-\overline{V}_{FD}\}^{-1}=\boldsymbol{X}\{(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})-{}^{px}\overline{V}_{FD}\}^{-1}\boldsymbol{X}^{+}. \tag{80}$$

Thus, if we make an allowance for

$$\begin{aligned}\{{}^{px}\overline{V}_{FD}\}^{fg}_{jk}&=\sum_m\sum_n X^{+}_{j,fm}<fm|V|gn>X_{gn,k}\\ &=<\bar{f}\bar{j}|V|\bar{g}\bar{k}>=\bar{\boldsymbol{\mu}}^{(j)}_{f0}\cdot\boldsymbol{U}_{jk}\cdot\bar{\boldsymbol{\mu}}^{(k)}_{0g},\end{aligned} \tag{81}$$

with the relationships

$$|\bar{g}\bar{k}>=\sum_n|gn>X_{gn,k}, \tag{82}$$

$$\begin{aligned}\{[(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})-{}^{px}\overline{V}_{FD}]^{-1}\}^{fg}_{jk}&=(E-\bar{\varepsilon}_{fj,0}+\mathrm{i}\,\bar{\eta}_{fj})^{-1}\delta_{jk}\delta_{fg}\\ &+(E-\bar{\varepsilon}_{fj,0}+i\bar{\eta}_{fj})^{-1}\{{}^{px}\overline{V}_{FD}\}^{fg}_{jk}(E-\bar{\varepsilon}_{gk,0}+i\bar{\eta}_{gk})^{-1}+\dots,\end{aligned} \tag{83}$$

we note that Eq. 72 can be reduced to

$$\begin{aligned}{}^{p}\boldsymbol{\alpha}(E)&=-\sum_f\sum_m\sum_g\sum_n\sum_j\sum_k\boldsymbol{\mu}^{(m)}_{0f}X_{fm,j}\{[(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})\\ &\qquad-{}^{px}\overline{V}_{FD}]^{-1}\}^{fg}_{jk}X^{+}_{k,gn}\boldsymbol{\mu}^{(n)}_{g0},\\ &=-\sum_f\sum_j\sum_g\sum_k\bar{\boldsymbol{\mu}}^{(j)}_{0f}\{[(E\mathbf{1}-\bar{\varepsilon}+i\bar{\eta})-{}^{px}\overline{V}_{FD}]^{-1}\}^{fg}_{jk}\bar{\boldsymbol{\mu}}^{(k)}_{g0}\\ &=-\sum_f\sum_k\{\mathbf{1}+\bar{\boldsymbol{\alpha}}(E)\cdot\boldsymbol{U}\}^{-1}_{jk}\cdot\bar{\boldsymbol{\alpha}}_{kk}(E),\end{aligned} \tag{84}$$

where we put

$$\bar{\boldsymbol{\mu}}^{(j)}_{0f}=\sum_m\boldsymbol{\mu}^{(m)}_{0f}X_{fm,j}, \tag{85}$$

$$\bar{\boldsymbol{\alpha}}_{kk}(E)=-\sum_f\bar{\boldsymbol{\mu}}^{(k)}_{0f}\bar{\boldsymbol{\mu}}^{(k)}_{g0}/(E-\bar{\varepsilon}_{fk,0}+i\bar{\eta}_{fk}). \tag{86}$$

Equation 86 defines the kth monomer polarizability tensor corrected by the permanent moments in the rest of monomers. Equation 84 is rather more beautifully linearlized than Eq. 38b. However, Eq. 84 together with Eq. 85 needs the process of the diagonalization for the $\{(E\mathbf{1}-\varepsilon+i\eta)-\overline{V}_s\}$ of each submolecule to obtain X, whereas Eq. 38b requires only to solve the inverse matrix.

In the opening section, we have insisted upon that the theories should be built up so as to be capable of comparing the works made by the ordinary perturbational wavefunction approaches.[19] By doing so, we might find their similarities and clarify the relationships of the present theory with the well-known literature. By applying the present theory to the calculations of quantities such as $<0|\boldsymbol{\mu}G(E)\cdot\boldsymbol{m}|0>$ and $<0|\boldsymbol{\mu}\tilde{G}(E)\cdot\boldsymbol{m}|0>$, $\boldsymbol{m}$ being the magnetic moment operator, we can construct a new polarizability theory capable of discussing the UV absorption, CD, and ORD spectra on the same footing with as that mentioned in Tinoco's review,[19] in which a corrected basis set $\{|\tilde{\psi}>\}$ was introduced. If we confine ourselves to lower-orders approximation in $\overline{V}$ and/or $\tilde{V}$, it will be not so difficult to directly apply the schemes of (A) and (B) for the CD and ORD bandshape calculations without resort to the simplifications of (C) and (D). Such a lower-orders truncation may bring about the theoretical similarity with the results for the ordinary perturbational approaches. However, it is extremely hard to calculate ${}^{p}\boldsymbol{\alpha}(E)$, ${}^{rp}\boldsymbol{\alpha}(E)$, ${}^{p}\tilde{\boldsymbol{\alpha}}(E)$, and ${}^{rp}\tilde{\boldsymbol{\alpha}}(E)$ up to higher orders as mentioned in (A) and (B), so that the simplification is introduced in (C) and (D). Even in the simplified schemes, if we wish to apply the working formula of Eq. 55 to large polymer systems, we must face with the difficulty of solving the inverse matrix extremely larger than the $3N$X$3N$ matrix of the working formula of Eq. 38b in (C). The deficiency of DeVoe's coupled oscillator theory also is this case. However, if we wish to allow for the static effect in terms of only the data of $\boldsymbol{\mu}^{(\mathrm{site})}_{00}$ and $\boldsymbol{\mu}^{(\mathrm{site})}_{0f}$ by dropping $\boldsymbol{\mu}^{(\mathrm{site})}_{fg}$ which is not easily available, Eq. 55 is clearly preferred to Eq. 38b. It is again to be pointed out that the renormalized RPA's given by Eqs. 43 and 65 are kind of extensions of the Fano-DeVoe model for the polymer of the constituent chromophores without permanent dipole moments. Applying the theory to the real DNA molecules, the bandshape calculations of UV absorption and CD spectra are now in progress involving the permanent dipole moments.[24–26]

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