Theor Chim Acta (1988) 73: 147-154

Theoretica Chimica Acta

On the Hartree-Fock approximation to the electronic structure of molecule in the intense radiation field and the strong vibronic coupling*

Yoshihiro Asai[1], Tokio Yamabe[1]†‡ and Kenichi Fukui[2]‡**

[1] Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan
[2] Kyoto Institute of Technology, Kyoto 606, Japan

(Received April 20, revised July 27/Accepted September 2, 1987)

The Hartree-Fock approximation has been generalized to incorporate the nonadiabatic effect of molecular vibration previously by Tachibana et al. Here, we will derive the Hartree-Fock equation which reflects also the non-linear effect of the infrared radiation field as well by using the Bloch-Nordsieck transformation which was discussed first by Nguyen-Dang and Bandrauk in the field of molecular physics. The Hartree-Fock equation reflects the non-adiabatic coupling between an electron and a molecular vibration and between the electron and a infrared radiation fields. The infrared radiation field also affects the dynamics of nuclear motion.

Key words: Hartree-Fock approximation — Bloch-Nordsieck transformation — Dressed molecular Hamiltonian — Vibronic coupling

1. Introduction

The dynamic electronic structure of the molecular system has been studied previously by Tachibana et al. [1]. The dynamic electronic structure studied does

---

* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

** *Present address*: Electrotechnical Laboratory, Umezono, Sakura-mura, Ibaraki 305, Japan

† *Also belongs to*: Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

‡ *Also belongs to*: Institute for Fundamental Chemistry, 15 Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606, Japan

not take into account the background radiation field. The background radiation field is important in a vibronic system such as the ionic crystal system [2]. The polaron, the exciton, and the phonon are important elementary excitations in condensed matter physics [3] and the coupling between the molecular vibration and the electronic motion are important in their structure. Also the background radiation field, whose effect cannot be neglected, is implicit in them. Consequently it is interesting to investigate the vibronic coupling mechanism of a molecular system where the radiation field is coupled with the particle motion. A theory which is applicable for all wavelengths about the vibronic system exposed to a radiation field is awaited but it seems difficult to obtain a lucid theoretical framework. Here, the dynamic electronic structure of the molecular system which is influenced by the molecular vibration and the effect of the infrared radiation field is investigated by generalizing the theoretical framework used previously [1]. The couplings among the electronic motion, the molecular vibration, and the intense radiation field can be studied by the coupled equations which will be derived here. These will be the fundamental equations for the nonlinear optical property of the molecular system.

2. Dressed molecular Hamiltonian

Recently, the dressed molecular Hamiltonian [4] which includes explicitly the radiative correction in the molecular system has been studied by revising the Bloch–Nordsieck transformation used in the study of the radiative correction of an electron in the early days of quantum electrodynamics [5]. Then it will be interesting to apply the method which is used in the previous paper [1] to the dressed molecular Hamiltonian. The effect of the radiative correction as well as the molecular vibration can be incorporated into the one electron orbital.

The total Hamiltonian of the molecular system exposed in the radiation field within the minimal coupling [4, 6] scheme is given as follows:

$$\begin{aligned} H_{\mathrm{TOT}} = {} & \sum_i (\tfrac{1}{2}m)\{\boldsymbol{p}_i + (e/c)\boldsymbol{A}(\boldsymbol{r}_i)\}^2 + \tfrac{1}{2}\sum_{i,j} (e^2/r_{ij}) - \sum_{\alpha,i} (Z_\alpha e^2/r_{i\alpha}) \\ & + \sum_\alpha (\tfrac{1}{2}M_\alpha)\{\boldsymbol{P}_\alpha - (Z_\alpha e/c)\boldsymbol{A}(\boldsymbol{R}_\alpha)\}^2 + \tfrac{1}{2}\sum_{\alpha,\beta} (Z_\alpha Z_\beta e^2/R_{\alpha\beta}) \\ & + \tfrac{1}{2}\int \{|\dot{\boldsymbol{A}}(\boldsymbol{x})|^2 + c^2|\nabla \times \boldsymbol{A}(\boldsymbol{x})|^2\}\, dx^3, \end{aligned} \tag{1}$$

where $\boldsymbol{p}_i$ and $\boldsymbol{r}$ are the momentum and the coordinate of the electron whose mass and charge are denoted by m and $-e$, and $\boldsymbol{P}_\alpha$ and $\boldsymbol{R}_\alpha$ are the momentum and the coordinate of the αth nucleus whose mass and charge are denoted by M_α and $Z_\alpha e$, respectively. The speed of the light is denoted by c. In terms of the dynamical variables of the quantized radiation field $P_{k,\lambda}$ and $Q_{k,\lambda}$, the Coulomb-gauge vector potential $\boldsymbol{A}(\boldsymbol{r}, \boldsymbol{t})$ can be expressed as follows:

$$\boldsymbol{A}(\boldsymbol{r}, \boldsymbol{t}) = 2c(\pi/V)^{1/2} \sum \varepsilon_{k,\lambda}[\sin(\boldsymbol{k}\cdot\boldsymbol{r})Q_{k,\lambda} + \omega_k^{-1}\cos(\boldsymbol{k}\cdot\boldsymbol{r})P_{k,\lambda}], \tag{2}$$

where $\varepsilon_{k,\lambda}$, V and ω_k denote one of the two independent polarization unit vectors for the transverse radiation with the wave vector $\boldsymbol{k}$, quantization volume of the free field radiation, and the frequency of the radiation mode $\mathbf{k}$ which is given by

$$\omega_k = c|\boldsymbol{k}|. \tag{3}$$

Then the total Hamiltonian H_{TOT} is expressed as follows:

$$H_{\mathrm{TOT}} = H_{\mathrm{mol}} + H_{\mathrm{rad}} + V_{\mathrm{int}}, \tag{4.1}$$

$$H_{\mathrm{mol}} = \sum_{\alpha} (\tfrac{1}{2}M_\alpha)\boldsymbol{P}_\alpha^2 + \tfrac{1}{2}\sum_{\alpha,\beta} (Z_\alpha Z_\beta e^2/R_{\alpha\beta}) + \sum_{i} (\tfrac{1}{2}m)\boldsymbol{p}_i^2 + \tfrac{1}{2}\sum_{i,j} (e^2/r_{ij}) - \sum_{\alpha,i} (Z_\alpha e^2/r_{i,\alpha}), \tag{4.2}$$

$$H_{\mathrm{rad}} = \tfrac{1}{2}\sum_{k,\lambda} \{P_{k,\lambda}^2 + \omega_k^2 Q_{k,\lambda}^2\}, \tag{4.3}$$

$$V_{\mathrm{int}} = (e/mc)\sum_{i} \boldsymbol{A}(\boldsymbol{r})\cdot\boldsymbol{p}_i - (e/c)\sum_{\alpha} (Z_\alpha/M_\alpha)\boldsymbol{A}(\boldsymbol{R}_\alpha)\cdot\boldsymbol{P}_\alpha + (e^2/2c^2)\left\{(1/m)\sum_{i} |\boldsymbol{A}(\boldsymbol{r}_i)|^2 + \sum_{\alpha} (Z_\alpha^2/M_\alpha)|\boldsymbol{A}(\boldsymbol{R}_\alpha)|^2\right\}. \tag{4.4}$$

If the radiation field considered is limited to the infrared radiation, $\boldsymbol{A}(\boldsymbol{r})$ can be approximated to be [4, 6]

$$\boldsymbol{A}(\boldsymbol{r}, \boldsymbol{t}) \sim 2c(\pi/V)^{1/2}\sum_{k,\lambda} \varepsilon_{k,\lambda}\omega_k^{-1}P_{k,\lambda}. \tag{5}$$

The interaction term between the radiation fields and the particles can be given as

$$V_{\mathrm{int}} = 2e(\pi/V)^{1/2}\left\{(1/m)\sum_{i} \boldsymbol{p}_i - \sum_{\alpha} (Z_\alpha/M_\alpha)\boldsymbol{P}_\alpha\right\}\cdot\sum \varepsilon_{k,\lambda}\omega_k^{-1}P_{k,\lambda} + 2e^2(\pi/V)\left\{(1/m) + \sum_{\alpha} (Z_\alpha/M_\alpha)\right\}\sum_{k,\lambda}\sum_{l,\eta} \varepsilon_{k,\lambda}\cdot\varepsilon_{l,\eta}(\omega_k\omega_l)^{-1}P_{k,\lambda}P_{l,\eta}, \tag{6}$$

where the second term of the right-hand side of the equation can be neglected [4], if the focus is put on the direct coupling of the particles and the radiation. Defining the unitary operator U:

$$U = \exp\left[-2i(e/\hbar)(\pi/V)^{1/2}\sum_{k,\lambda} \omega_k^{-1}\left\{\sum_{i} (1/m)\boldsymbol{p}_i - \sum_{\alpha} (Z_\alpha/M_\alpha)\boldsymbol{P}_\alpha\right\}\cdot\varepsilon_{k,\lambda}Q_{k,\lambda}\right], \tag{7}$$

the dynamical variables are transformed as follows [4]

$$\acute{P}_{k,\lambda} = UP_{k,\lambda}U^{\dagger} \sim P_{k,\lambda} + 2e(\pi/V)^{1/2}\omega_k^{-1}\left\{\sum_{i} (1/m)\boldsymbol{p}_i - \sum_{\alpha} (Z_\alpha/M_\alpha)\boldsymbol{P}_\alpha\right\}\cdot\varepsilon_{k,\lambda}, \tag{8.1}$$

$$\acute{Q}_{k,\lambda} = UQ_{k,\lambda}U^{\dagger} = Q_{k,\lambda}, \tag{8.2}$$

$$\acute{\boldsymbol{p}}_i = U\boldsymbol{p}_iU^{\dagger} = \boldsymbol{p}_i, \tag{8.3}$$

$$\acute{\boldsymbol{r}}_i = U\boldsymbol{r}_i U^\dagger \sim \boldsymbol{r}_i - 2(e/m)(\pi/V)^{1/2} \sum_{k,\lambda} \omega_k^{-1} Q_{k,\lambda} \varepsilon_{k,\lambda}, \tag{8.4}$$

$$\acute{\boldsymbol{P}}_\alpha = U\boldsymbol{P}_\alpha U^\dagger = \boldsymbol{P}_\alpha, \tag{8.5}$$

$$\acute{\boldsymbol{R}}_\alpha = U\boldsymbol{R}_\alpha U^\dagger \sim \boldsymbol{R}_\alpha + 2e(Z_\alpha/M_\alpha)(\pi/V)^{1/2} \sum_{k,\lambda} \omega_k^{-1} Q_{k,\lambda} \varepsilon_{k,\lambda}, \tag{8.6}$$

where the linear expansion of the exponential operator is used. Using the transformed dynamical variables, the Hamiltonian is rewritten

$$\begin{aligned} H_{\mathrm{rad}} + V_{\mathrm{int}} = {} & \tfrac{1}{2} \sum \{ \acute{P}_{k,\lambda}^2 + \omega_k^2 \acute{Q}_{k,\lambda}^2 \} \\ & - 2e^2(\pi/V) \sum_{k,\lambda} \omega_k^{-2} \left(\left\{ \sum_i (1/m) \acute{\boldsymbol{p}}_i - \sum_\alpha (Z_\alpha/M_\alpha) \acute{P}_\alpha \right\} \cdot \varepsilon_{k,\lambda} \right)^2, \end{aligned} \tag{9.1}$$

$$\begin{aligned} H_{\mathrm{mol}} = {} & \sum_\alpha (\tfrac{1}{2} M_\alpha) \acute{\boldsymbol{P}}_\alpha^2 + \tfrac{1}{2} \sum_{\alpha,\beta} \{ Z_\alpha Z_\beta e^2 / (\acute{R}_{\alpha\beta} - \lambda_{\alpha\beta}) \} \\ & + \sum_i (\tfrac{1}{2} m) \acute{\boldsymbol{p}}_i^2 + \tfrac{1}{2} \sum_{i,j} (e^2/\acute{r}_{ij}) - \sum_{\alpha,i} \{ Z_\alpha e^2 / (\acute{r}_{i\alpha} - \xi_\alpha) \}, \end{aligned} \tag{9.2}$$

where $\acute{R}_{\alpha\beta} - \lambda_{\alpha\beta}$ and $\acute{r}_{i\alpha} - \zeta_\alpha$ are concretely given as follows [4]

$$\acute{R}_{\alpha\beta} - \lambda_{\alpha\beta} = \left| \acute{\boldsymbol{R}}_\alpha - \acute{\boldsymbol{R}}_\beta - 2e(\pi/V)^{1/2} \{ (Z_\alpha/M_\alpha) - (Z_\beta/M_\beta) \} \sum_{k,\lambda} \omega_k^{-1} \acute{\boldsymbol{Q}}_{k,\lambda} \varepsilon_{k,\lambda} \right|, \tag{10.1}$$

$$\acute{r}_{i\alpha} - \xi_\alpha = \left| \acute{\boldsymbol{r}}_i - \acute{\boldsymbol{R}}_\alpha + 2e(\pi/V)^{1/2} \{ (1/m) + (Z_\alpha/M_\alpha) \} \sum_{k,\lambda} \omega_k^{-1} \acute{Q}_{k,\lambda} \varepsilon_{k,\lambda} \right|, \tag{10.2}$$

The Hamiltonian of the radiation field in terms of the transformed dynamical variables is obtained by substituting the transformed dynamical variables into the original dynamical variables. The Hamiltonian of the molecular system is obtained through the substitution of the transformed dynamical variables into the original dynamical variables and the following replacement of the transformed nuclear coordinate:

$$\acute{\boldsymbol{R}}_\alpha \rightarrow \acute{\boldsymbol{R}}_\alpha - \Delta \acute{\boldsymbol{R}}_\alpha (\{ \acute{Q}_{k,\lambda} \}), \tag{11.1}$$

$$\Delta \boldsymbol{R}_\alpha (\{ Q_{k,\lambda} \}) = 2e(\pi/V)^{1/2} \{ (1/m) + (Z_\alpha/M_\alpha) \} \sum_{k,\lambda} \omega_k^{-1} \acute{Q}_{k,\lambda} \varepsilon_{k,\lambda}. \tag{11.2}$$

This replacement has the effect of modifying the Hamiltonian of the molecular system through the nuclear–electron and nuclear–nuclear Coulomb potential. The dressed molecular Hamiltonian of the total system can be written as follows:

$$\begin{aligned} H_{\mathrm{TOT}} = {} & H_{\mathrm{rad}}(\{ \acute{P}_{k,\lambda}, \acute{Q}_{k,\lambda} \}) + H_{\mathrm{mol}} \left(\left\{ \acute{\boldsymbol{p}}_i, \acute{\boldsymbol{P}}_\alpha, \acute{\boldsymbol{r}}_i, \acute{\boldsymbol{R}}_\alpha - \theta \sigma_\alpha \sum_{k,\lambda\&} \omega_k^{-1} \acute{Q}_{k,\lambda} \varepsilon_{k,\lambda} \right\} \right) \\ & - \tfrac{1}{2} \theta^2 \sum_{k,\lambda} \omega_k^{-2} \left[\left\{ (1/m) \sum_i \acute{\boldsymbol{p}}_i - \sum_\alpha (Z_\alpha/M_\alpha) \acute{\boldsymbol{P}}_\alpha \right\} \cdot \varepsilon_{k,\lambda} \right], \end{aligned} \tag{12}$$

where the substitution and the replacement are denoted symbolically, and where θ and σ_α are given by

$$\theta = 2e(\pi/V)^{1/2}, \tag{13.1}$$

$$\sigma_\alpha = \{ (1/m) + (Z_\alpha/M_\alpha) \}. \tag{13.2}$$

The third term on the right-hand side of Eq. (15) is corrected by the mass renormalization [5, 6] correction and hence can be neglected. It is interesting to point out that the coupling between the radiation field and the molecule is incorporated in the parametric dependence of the molecular Hamiltonian on the coordinate variable of the photon field. Then the situation resembles the vibronic problem of the molecular system.

3. Hartree–Fock equation of molecule in the intense radiation field and strong vibronic coupling

Now with this dressed Hamiltonian [4], studied by Nguyen-Dang and Bandrauk, it is interesting to derive the electronic wavefunction which is suitable to describe the coupling between the radiation field and the particle motion of the molecule and the nonadiabatic coupling [1] between the nuclear motions and the electronic motions. Let the total wavefunction Ψ of the system be given by the following product:

$$\Psi = \Psi_e(\{\acute{\boldsymbol{r}}_i;\, \acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\})\Psi_n(\{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}) \times \Psi_p(\{\acute{Q}_{k,\lambda}\}), \tag{14}$$

where Ψ_e and Ψ_n are the electronic wavefunction and the nuclear wavefunction at the displaced nuclear configuration $\{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}$, respectively. The photon eigenstate is denoted by Ψ_p. The right-hand side of the semicolon in the brace denotes the parametric dependences of the wavefunction. If the single Slater determinantal electronic wavefunction constructed from the spin orbitals φ

$$\varphi_i = \psi_i(\acute{\boldsymbol{r}};\, \{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\})\theta, \tag{15}$$

where ψ_i denotes the space orbital and θ the spin function, is adopted as Ψ_e, the electron orbitals coupled with the nuclear motions and the radiation field are determined variationally, using the following energy functional:

$$E = \langle\Psi|H|\Psi\rangle - \sum_{ij} \varepsilon_{ij}\langle\Psi_p|\langle\Psi_n|\langle\psi_i|\psi_j\rangle - \delta_{ij}|\Psi_n\rangle|\Psi_p\rangle - \lambda(\langle\Psi_n|\Psi_n\rangle - 1)$$
$$- \eta(\langle\Psi_p|\Psi_p\rangle - 1). \tag{16}$$

The electron orbitals $\{\psi_j\}$ are expanded in the basis set orbitals $\{\chi_k\}$:

$$\psi_j(\acute{\boldsymbol{r}};\, \{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}) = \sum_r c_{rj}\chi_r(\acute{\boldsymbol{r}};\, \{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}), \tag{17}$$

where the basis set orbitals $\{\chi_r\}$ should satisfy the following orthonormalization condition:

$$\langle\Psi_p|\langle\Psi_n|\langle\chi_r|\chi_s\rangle|\Psi_n\rangle|\Psi_p\rangle = \delta_{rs}. \tag{18}$$

The basis set orbitals $\{\chi_r\}$ is naturally taken to be a set of adiabatic molecular orbitals including the virtual orbitals. The expansion in Eq. (17) enables us to reflect the effect which corresponds the "virtual transition" induced by the nonadiabatic effects of molecular vibrations and the intense radiation field on the molecular orbital manifold. The electronic off-diagonal terms of Eq. (28) in [4(a)], which represent the correlation effects induced by the nonadiabatic interaction and the effect of the radiation field are taken into account in the diagonal correction of the SCF equation through a mixing of a virtual orbitals as discussed below. The contribution of the nonadiabatic-interaction-induced radiative transitions between electronic states to the total energy will be concretely represented in a formula, if we use the particle-hole representation [1(c)]. If the variation of the $\{c_{ri}\}$ is performed, the Fock equation which determines the electron orbitals coupled with the nuclear motion and the radiation field can be written in atomic units as follows:

$$\underline{f}\underline{c}_{ri} = \varepsilon_i \underline{c}_{ri}, \tag{19.1}$$

$$f = \langle \Psi_p | \langle \Psi_n | \underline{F} + \underline{\Delta} | \Psi_n \rangle | \Psi_p \rangle, \tag{19.2}$$

$$\underline{\Delta} = \underline{\Delta}^{\mathrm{vib}} + \underline{\Delta}^{\mathrm{rad}}, \tag{19.3}$$

$$\begin{aligned} \Delta_{rs}^{\mathrm{vib}} = \sum_l \Big[& \tfrac{1}{2} \langle \partial\chi_r/\partial\acute{Q}_l | \partial\chi_s/\partial\acute{Q}_l \rangle + \tfrac{1}{2} \sum_j^{\mathrm{occ}} \sum_{tu} c_{tj}^* c_{uj} \{ \langle \partial\chi_r/\partial\acute{Q}_l | \chi_s \rangle \langle \chi_t | \partial\chi_u/\partial\acute{Q}_l \rangle \\ & + \langle \partial\chi_t/\partial\acute{Q}_l | \chi_u \rangle \langle \chi_r | \partial\chi_s/\partial\acute{Q}_l \rangle - \langle \partial\chi_r/\partial\acute{Q}_l | \chi_u \rangle \langle \chi_t | \partial\chi_s/\partial\acute{Q}_l \rangle \\ & - \langle \partial\chi_t/\partial\acute{Q}_l | \chi_s \rangle \langle \chi_r | \partial\chi_u/\partial\acute{Q}_l \rangle \} \Big], \end{aligned} \tag{19.4}$$

$$\begin{aligned} \Delta_{rs}^{\mathrm{rad}} = \tfrac{1}{2}\theta^2 \sum_{k,\lambda} \sum_{\alpha\beta} \sigma_\alpha \sigma_\beta \omega_k^{-2} \Big[& \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \chi_r | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \chi_s \rangle + \sum_j^{\mathrm{occ}} \sum_{tu} c_{tj}^* c_{uj} \\ & \times \{ \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \chi_r | \chi_s \rangle \langle \chi_t | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \chi_u \rangle \\ & + \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \chi_t | \chi_u \rangle \langle \chi_r | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \chi_s \rangle \\ & - \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \chi_r | \chi_u \rangle \langle \chi_t | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \chi_s \rangle \\ & - \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \chi_t | \chi_s \rangle \langle \chi_r | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \chi_u \rangle \} \Big], \end{aligned} \tag{19.5}$$

where the nuclear coordinates and the photon coordinate dependencies of the electronic wavefunctions are implicit in the right-hand side of the Eqs. (19.4) and (19.5), and where grad_α denotes $\partial/\partial\acute{R}_\alpha$. The mass-weighted coordinate of the lth ro-vibrational motion of nuclei is denoted by $\acute{Q}_l$. The usual Fock matrix at the nuclear configuration $\acute{R}_\alpha - \Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})$ is denoted by F in Eq. (19.2). The summation over l in Eq. (19.2) means that the summation is performed all over the modes of the ro-vibrational nuclear motions. The nuclear wavefunction $\Psi_n\{\acute{R}_\alpha - \Delta\acute{R}_\alpha(\{\acute{Q}_{k,\lambda}\})\}$ is determined by the following equation:

$$\begin{aligned} \langle \Psi_p | \Big[& -\tfrac{1}{2} \sum_l (\partial^2/\partial\acute{Q}_l^2) + \tfrac{1}{2} \sum_{\alpha\beta} \{ Z_\alpha Z_\beta / (\acute{R}_{\alpha\beta} - \lambda_{\alpha\beta}) \} + E^{\mathrm{el}}(\{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}) \\ & + \sum_l D_l(\{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}) + \sum_{k,\lambda} D_{k,\lambda}(\{\acute{\boldsymbol{R}}_\alpha - \Delta\acute{\boldsymbol{R}}_\alpha(\{\acute{Q}_{k,\lambda}\})\}) - E \Big] \Psi_n | \Psi_p \rangle = 0, \end{aligned} \tag{20}$$

where E^{el} is the electronic energy and where D_l and $D_{k,\lambda}$ are the nonadiabatic corrections between electronic motions and the lth ro-vibrational nuclear motions and between the electronic motions and the radiation field to the total adiabatic respectively:

$$D_l = \sum_{ij}^{\mathrm{occ}} \{\langle \partial\psi_j/\partial \acute{Q}_l | \partial\psi_j/\partial \acute{Q}_l \rangle - \langle \partial\psi_j/\partial \acute{Q}_l | \psi_i \rangle \langle \psi_i | \partial\psi_j/\partial \acute{Q}_l \rangle\}, \tag{21.1}$$

$$\begin{aligned} D_{k,\lambda} = \sum_{ij}^{\mathrm{occ}} \sum_{k,\lambda} \sum_{\alpha\beta} \theta^2 \sigma_\alpha \sigma_\beta \omega_k^{-2} \{ & \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \psi_j | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \psi_j \rangle \\ & - \langle \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\alpha\, \psi_j | \psi_i \rangle \langle \psi_i | \varepsilon_{k,\lambda} \cdot \mathrm{grad}_\beta\, \psi_j \rangle \}. \end{aligned} \tag{21.2}$$

Equations (19) and (20) determine the electronic motion and the nuclear motion of the molecule exposed in the infrared radiation field where the nonadiabatic coupling between the electronic motion and the nuclear motion cannot be neglected and they will be the fundamental equations for the quantum mechanical nonlinear optical property of the vibronic system. Any order quantum mechanical nonlinear optical property of a molecule can be evaluated by the electronic wavefunction obtained. A calculation of the nonlinear optical property is now replaced by an evaluation of a derivative of the electronic wavefunction with respect to the parameter $Q_{k,\lambda}$. This is analogous to the evaluation of the derivative with respect to the nuclear coordinate.

4. Conclusion

Hartree-Fock approximation is generalized to incorporate the effect of the vibronic coupling and the nonlinear effect of the intense infrared radiation field into one electron orbitals. On this foundation, the vibronic coupling and the nonlinear optical property of a molecule can be studied at the same time. The competition or the cooperation between the two effects is interesting. The nonadiabatic nuclear motion will induce the internal electromagnetic field or radiation field in the material. The nonlinear optical properties of the vibronic systems will hence be an interesting problem to be studied theoretically. The theory which is applicable for all wavelengths is awaited. The phase factor change accompanying the change of the nuclear coordinate parameter which has received attention in the gauge field theory is an interesting problem with this respect. The present theory would also be interesting in the microscopic theory of superconductivity where the non-BCS pairing mechanism has been discussed at great length. Especially, a reconsideration of the proposed mechanism of photoinduced superconductivity of Kumar and Sinha [7] will be interesting in the next step, where the incorporation of the translational symmetry is necessary. The Bogoljubov transformation may be of help to discuss the microscopic theory on the basis of the Hartree-Fock approximation. Therefore it would be interesting first to study the formal structure of the Hartree-Fock equation for molecules which reflects the vibronic coupling and the nonlinear effect of the electromagnetic field.

Acknowledgments. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan, for which the authors express their gratitude. One of the authors (Y.A.) would like to express great thankfulness to Prof. G. G. Hall for his critical readings of this manuscript.

References

1. (a) Tachibana A, Yamabe T, Hori K, Asai Y (1984) Chem Phys Lett 106:36; (b) Tachibana A, Hori K, Asai Y, Yamabe T (1984) J Chem Phys 80:6170; (c) Tachibana A, Hori K, Yamabe T (1984) Chem Phys Lett 112:279
2. Born M, Huang K (1954) Dynamical theory of crystal lattice. Clarendon Press, Oxford
3. Kittel, C (1963) Quantum theory of solids. Wiley, New York
4. (a) Nguyen-Dang TT, Bandrauk AD (1983) J Chem Phys 79:3256; (1984) 80:4926 (b) Bandrauk AD, Nguyen-Dang TT (1985) J Chem Phys 83:2840
5. (a) Schwinger J (ed) (1958) Selected papers on quantum electrodynamics. Dover, New York (b) Pauli W, Fierz M (1938) Nuovo Cimento 15:167 (c) Bloch F, Nordsieck A (1937) Phys Rev 52:54 (d) Welton TA (1948) Phys Rev 74:1157
6. (a) Loudon R (1973) The quantum theory of light. Clarendon Press, Oxford (b) Power EA (1964) Introductory quantum electrodynamics. Longmans, London
7. Kumar N, Sinha KP (1968) Phys Rev 174:482