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## A novel dynamic exciton expression based on the ab initio MO CI based quantum master equation approach

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### ABSTRACT

We propose a novel dynamic exciton expression based on the quantum master equation approach using the ab initio molecular orbital (MO) singly excited configuration interaction (CI) method developed in our previous paper [J. Chem. Phys. 120 (2004) 2359]. This expression is derived from the partition of polarization density in the configuration basis into the electron and hole contributions, and can describe both the coherent and incoherent dynamics of electron and hole density distributions, e.g., dynamic electric polarization, exciton recurrence and exciton migration.

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### 1. Introduction

Coherent dynamics of exciton (an electron-hole pair) in molecular aggregates and supermolecular systems is one of the recent hot topics as well as relaxation (dissipative) processes in view of a fundamental understanding of dynamical quantum features of many-electron systems and of potential applications in photonics and optoelectronics [1–29]. As typical examples, exciton migration [6–22], e.g., energy migration in dendrimers [6–9], and exciton recurrence motion [23–29], e.g., coherent energy transfer [23,24] and oscillatory fluorescence anisotropy of two chromophores [25–27], have been intensely investigated experimentally and theoretically. The former and latter behaviors correspond to the relaxation (incoherent) and coherent processes in the exciton manifold, respectively. On the theoretical side, there have been lots of treatments based on the molecular aggregate models, e.g., Frenkel exciton model [30], in which a pair of electron and hole moves under a constraint of taking the same position with each other, and the exchange between electrons (holes) at different positions is prohibited. In general, these treatments can well describe the exciton dynamics in molecular aggregates with weak interactions, e.g., van der Waals (dipole-dipole) interactions, whereas cannot describe that in aggregates with strong interactions, e.g., charge transfer interactions, and in supermolecular systems with extended electron delocalization.

In the previous paper [14], we propose a simulation scheme of exciton dynamics based on the quantum master equation (QME) approach using the ab initio molecular orbital (MO) configuration

interaction (CI) method, which can treat the exchange of electrons (holes) at different positions. In this scheme, hereafter referred to as MOQME, one-exciton states are calculated by the ab initio MO singly excited CI (SCI) method, and the effective coupling between exciton and phonon (nuclear vibrations), which is the origin of exciton relaxation [11–14], is considered in the Markov approximation [13,14]. The electron and hole densities are obtained, respectively, from the system density matrices in the SCI configuration basis  $\{|i(a \rightarrow r)\rangle\}$  ( $a$  and  $r$  indicate the occupied and virtual orbitals, respectively) multiplied by the corresponding occupied  $[\|\psi_a(\mathbf{r})\|^2]$  and virtual  $[\|\psi_r(\mathbf{r})\|^2]$  spatial orbital densities. This description is considered to be reasonable because the spatial integrations of electron and hole density distributions at arbitrary time  $t$  give electron and hole numbers  $n$  ( $0 \leq n \leq 1$ ) generated at  $t$ , respectively. Indeed, the relaxation dynamics, i.e., energy migration, in dendritic molecules is described well by this scheme and is analyzed using relaxation parameters determined by the spatial exciton distribution corresponding to each configuration [14]. On the other hand, this exciton expression cannot represent coherent phenomena, e.g., electric polarization and exciton recurrence, described by off-diagonal system density matrices because that is only composed of diagonal parts of system density matrices. In this Letter, we propose a novel dynamic exciton expression based on the SCI calculation scheme in order to remove the deficiency in the MOQME approach. Although there have been several static analysis methods for exciton coherency based on the transition density matrices [31,32], the present novel expression allows us to clarify the spatio-temporal contribution of exciton to both coherent and relaxation (incoherent) dynamics as well as to partition the contribution into that of a specific configuration  $i(a \rightarrow r)$ , which is useful for illuminating the primary exciton contribution to the dynamics.

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## 2. Methodology

### 2.1. Conventional exciton expression in the MOQME approach

Before introducing a novel exciton expression, a brief explanation of the MOQME approach is provided as well as a conventional exciton expression presented in the previous paper [14]. We employ the Hartree-Fock (HF) ground ( $|^1\Psi_1\rangle$ ) and singly excited Slater determinant ( $|^1\Psi_a^r\rangle$ ) as the exciton basis  $\{|i\rangle\}$  (referred to as one-exciton basis) involving the singlet ground (vacuum)  $|1\rangle(\equiv|^1\Psi_1\rangle)$  and one-exciton  $\{|i\rangle(\equiv|^1\Psi_a^r\rangle) (i = 2, 3, \dots, N)$  states. We employ letters  $a, b, \dots$  and  $r, s, \dots$  to represent the HF occupied and virtual orbitals, respectively. The  $\alpha$ th electronic state of the molecule,  $|\alpha\rangle(\equiv|^1\Psi_\alpha\rangle)$  (which composes SCI state basis), calculated by the SCI method can be expanded as

$$|\alpha\rangle = \sum_i^N |i\rangle \langle i|\alpha\rangle = \sum_i^N |i\rangle C_{i\alpha}, (\alpha = 1, \dots, M) \quad (1)$$

Here,  $M$  indicates the number of electronic states involving the ground and excited states used in the MOQME approach, and the expansion coefficients  $\{C_{i\alpha}\}$  (referred to as CI coefficients) are obtained by the ab initio SCI calculation using the Gaussian 03 program package [33]. The one-exciton is assumed to be created by irradiating a continuous wave (cw) laser field  $F^l \cos \omega t$ , where  $F^l$  is a laser amplitude in the  $l$ -direction, and we consider for convenience that the incident laser is a plane wave with a frequency  $\omega$ , a wave vector  $k$  traveling perpendicular to the molecular plane, and a polarization vector parallel to  $l$  axis. The exciton is assumed to interact with a nuclear vibration, i.e., phonon state, in a weak coupling manner, in which the coupling only gives a random oscillation of the diagonal part (exciton energy), which destroys the coherency between the exciton states. According to the standard method of relaxation theory [34], we take the trace over the phonon bath states, which is assumed to be in the thermal equilibrium state at temperature  $T$ , and thus derive the quantum master equation [in the atomic units ( $\hbar = e = m = 1$ )] for the reduced system density matrices  $\{\rho_{\alpha\beta}\}$  in the Born-Markov approximation [13,14]:

$$\dot{\rho}_{\alpha\alpha} = -\sum_{\beta} \Gamma_{\alpha\alpha;\beta\beta} \rho_{\beta\beta} - F^l \sum_{\beta} (\mu_{\alpha\beta}^l \rho_{\beta\alpha} - \rho_{\alpha\beta} \mu_{\beta\alpha}^l) \quad (2)$$

and

$$\dot{\rho}_{\alpha\beta} = -i(\omega_{\alpha} - \omega_{\beta}) \rho_{\alpha\beta} - \sum_{\gamma,\delta} \Gamma_{\alpha\beta;\gamma\delta} \rho_{\gamma\delta} - F^l \sum_{\gamma} (\mu_{\alpha\gamma}^l \rho_{\gamma\beta} - \rho_{\alpha\gamma} \mu_{\gamma\beta}^l), \quad (\alpha \neq \beta) \quad (3)$$

where  $\mu_{\alpha\beta}^l$  indicates the  $l$ th component of transition moment between excited states  $\alpha$  and  $\beta$ , and the first term on the right-hand side of Eq. (2) and the second term on the right-hand side of Eq. (3) represent relaxation terms characterized by the relaxation parameters [13,14]:

$$\begin{aligned} \Gamma_{\alpha\alpha;\beta\beta} &= 2\delta_{\alpha\beta} \sum_{\gamma} \sum_i^N |C_{i\alpha}|^2 |C_{i\gamma}|^2 \gamma_i (\omega_{\beta} - \omega_{\gamma}) \\ &\quad - 2 \sum_i^N |C_{i\alpha}|^2 |C_{i\beta}|^2 \gamma_i (\omega_{\beta} - \omega_{\alpha}), \end{aligned} \quad (4)$$

and

$$\begin{aligned} \Gamma_{\alpha\beta;\gamma\delta} &= \sum_{\lambda} \sum_i^N [\delta_{\beta\alpha} C_{i\alpha}^* |C_{i\lambda}|^2 C_{i\gamma} \gamma_i (\omega_{\gamma} - \omega_{\lambda}) \\ &\quad + \delta_{\alpha\gamma} C_{i\delta}^* |C_{i\lambda}|^2 C_{i\beta} \gamma_i (\omega_{\delta} - \omega_{\lambda})] - \sum_i^N [C_{i\alpha}^* C_{i\gamma} C_{i\delta}^* C_{i\beta} \{\gamma_i (\omega_{\gamma} - \omega_{\alpha}) \\ &\quad + \gamma_i (\omega_{\delta} - \omega_{\beta})\}]. \end{aligned} \quad (5)$$

The factor  $\gamma_i(\omega)$ , which involves the exciton-phonon coupling coefficient and satisfies the thermal equilibrium condition, is assumed to be given by [13,14,17]

$$\gamma_i(\omega) = \frac{2\gamma_{i0}}{1 + \exp(-\omega/k_B T)}, \quad (6)$$

where  $\gamma_{i0}$  is a high-temperature limit of  $\gamma_i(\omega)$ . The fact that the relaxation parameters [Eqs. (4) and (5)] depend on the products of CI coefficients as well as energy difference terms [Eq. (6)] turns out to cause the structure dependence of exciton relaxation dynamics, e.g., exciton migration in dendritic systems [13,14].

In the MOQME approach, we first have to numerically solve the quantum master equation, Eqs. (2) and (3), in the SCI state basis  $\{|\alpha\rangle\}(\equiv|^1\Psi_\alpha\rangle)$  because the relaxation parameters, Eqs. (4) and (5), are represented in the SCI state basis including the HF ground and singly excited states. Second, in order to relate the system density matrices to the electron and hole densities, we convert the system density matrices ( $\rho_{\alpha\alpha}$ ) in the SCI state basis to those ( $\rho_{ij}^{\text{ex}}$ ) in the one-exciton basis  $\{|i\rangle\}(\equiv|^1\Psi_a^r\rangle)$  as

$$\rho_{ij}^{\text{ex}}(t) = \sum_{\alpha,\beta} C_{i\alpha} C_{j\beta}^* \rho_{\alpha\beta}(t) \quad (7)$$

In the previous paper [14], we define the electron  $[\rho_{\text{elec}}(\mathbf{r}, t)]$  and hole  $[\rho_{\text{hole}}(\mathbf{r}, t)]$  densities by

$$\rho_{\text{elec}}(\mathbf{r}, t) = \sum_{i=2}^N \rho_{ii}^{\text{ex}}(t) |\psi_r(\mathbf{r})|^2, \text{ and } \rho_{\text{hole}}(\mathbf{r}, t) = \sum_{i=2}^N \rho_{ii}^{\text{ex}}(t) |\psi_a(\mathbf{r})|^2, \quad (8)$$

where  $\psi_r(\mathbf{r})$  and  $\psi_a(\mathbf{r})$  represent virtual and occupied orbitals for singly excited configuration  $i(a \rightarrow r)$ , respectively. The spatial integrations of these densities are shown to give the excited population,  $1 - \rho_{11}^{\text{ex}}(t)$ , corresponding to the created electron (hole) numbers, where  $\rho_{11}^{\text{ex}}(t)$  indicates the HF ground state population. It is noted that these expressions involve only diagonal density matrices,  $\rho_{ii}^{\text{ex}}(t)$ , and thus are not sufficient for describing the coherent dynamics originating in the off-diagonal density matrices,  $\rho_{ij}^{\text{ex}}(t)$ , though the conventional expressions are useful for the relaxation (incoherent) dynamics such as energy migration [14].

### 2.2. Novel exciton expression in the MOQME approach

In order to obtain a novel exciton expression, which can also describe coherent dynamics such as dynamic electric polarization and exciton recurrence, we consider the polarization density  $\rho_{\text{pol}}(\mathbf{r}, t)$ :

$$\begin{aligned} \rho_{\text{pol}}(\mathbf{r}, t) &\equiv \rho(\mathbf{r}, t) - d_{11}(\mathbf{r}) = \sum_{i=2}^N [d_{ii}(\mathbf{r}) - d_{11}(\mathbf{r})] \rho_{ii}^{\text{ex}}(t) \\ &\quad + 2 \sum_{i=2}^N d_{1i}(\mathbf{r}) \rho_{1i}^{\text{ex real}}(t) + 2 \sum_{i < j (i,j \neq 1)}^N d_{ij}(\mathbf{r}) \rho_{ij}^{\text{ex real}}(t), \end{aligned} \quad (9)$$

where  $\rho(\mathbf{r}, t)$  indicates the reduced one-electron density for position  $r$  at time  $t$ ,  $d_{ij}(\mathbf{r})$  indicate the reduced one-electron density matrices in the one-exciton basis  $\{|i\rangle\}$  including the HF ground state  $|1\rangle$ , and  $\{\rho_{ij}^{\text{ex real}}(t)\}$  represent the real parts of system density matrices in the one-exciton basis obtained from Eqs. (2), (3), and (7). Using  $\rho_{\text{pol}}(\mathbf{r}, t)$ , we obtain the  $l$ th component of polarization,  $P^l(t)$ , by

$$P^l(t) = \int \rho_{\text{pol}}(\mathbf{r}, t) (-r^l) d^3 \mathbf{r} \quad (10)$$

Eq. (9) can be expressed using the occupied  $\{[\psi_a(\mathbf{r}), \psi_b(\mathbf{r}), \dots]\}$  and virtual  $\{[\psi_r(\mathbf{r}), \psi_s(\mathbf{r}), \dots]\}$  MOs as

$$\begin{aligned}
\rho_{\text{pol}}(\mathbf{r}, t) = & \sum_{i(a \rightarrow r)=2}^N [|\psi_r(\mathbf{r})|^2 - |\psi_a(\mathbf{r})|^2] \rho_{ii}^{\text{ex}}(t) \\
& + 2 \sum_{i(a \rightarrow r)=2}^N \sqrt{2} \psi_a(\mathbf{r}) \psi_r(\mathbf{r}) \rho_{ii}^{\text{ex real}}(t) \\
& + 2 \sum_{i(a \rightarrow r) < j(a \rightarrow s) \ (ij \neq 1)}^N \psi_r(\mathbf{r}) \psi_s(\mathbf{r}) \rho_{ij}^{\text{ex real}}(t) \\
& - 2 \sum_{i(a \rightarrow r) < j(b \rightarrow r) \ (ij \neq 1)}^N \psi_a(\mathbf{r}) \psi_b(\mathbf{r}) \rho_{ij}^{\text{ex real}}(t). \quad (11)
\end{aligned}$$

We can appropriately define the relationship between  $\rho_{\text{pol}}(\mathbf{r}, t)$  and electron [ $\rho_{\text{elec}}(\mathbf{r}, t)$ ] and hole [ $\rho_{\text{hole}}(\mathbf{r}, t)$ ] densities as

$$\rho_{\text{pol}}(\mathbf{r}, t) \equiv \rho_{\text{elec}}(\mathbf{r}, t) - \rho_{\text{hole}}(\mathbf{r}, t) \quad (12)$$

which implies that the deviation of the electron distribution from the hole distribution gives the polarization density. From the comparison of Eqs. (11) and (12), we assume that the expression of Eq. (11) is partitioned into  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$  as

$$\begin{aligned}
\rho_{\text{elec}}(\mathbf{r}, t) = & \sum_{i(a \rightarrow r)=2}^N \left[ |\psi_r(\mathbf{r})|^2 \rho_{ii}^{\text{ex}}(t) + \sqrt{2} \psi_a(\mathbf{r}) \psi_r(\mathbf{r}) \rho_{ii}^{\text{ex real}}(t) \right. \\
& \left. + 2 \sum_{j(a \rightarrow s)(>i)}^N \psi_r(\mathbf{r}) \psi_s(\mathbf{r}) \rho_{ij}^{\text{ex real}}(t) \right], \quad (13)
\end{aligned}$$

and

$$\begin{aligned}
\rho_{\text{hole}}(\mathbf{r}, t) = & \sum_{i(a \rightarrow r)=2}^N \left[ |\psi_a(\mathbf{r})|^2 \rho_{ii}^{\text{ex}}(t) - \sqrt{2} \psi_a(\mathbf{r}) \psi_r(\mathbf{r}) \rho_{ii}^{\text{ex real}}(t) \right. \\
& \left. + 2 \sum_{j(b \rightarrow r)(>i)}^N \psi_a(\mathbf{r}) \psi_b(\mathbf{r}) \rho_{ij}^{\text{ex real}}(t) \right] \quad (14)
\end{aligned}$$

Here, the terms composed of only virtual (occupied) orbitals [see the first, the third and the fourth terms on the right-hand side of Eq. (11)] are partitioned into the contributions to electron (hole) densities, while the contribution of terms involving the products of virtual and occupied orbitals [the second term in Eq. (11)] is separated into electron and hole densities equally. Both the spatial integrations of  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$  are found to give the excited population,  $1 - \rho_{ii}^{\text{ex}}(t)$ , in the same manner as the conventional definition, Eq. (8), due to the orthogonality relation of MOs. It is shown that the conventional electron and hole densities [Eq. (8)] correspond to the first terms on the right-hand side of Eqs. (13) and (14), respectively, whereas the second and third terms of those equations represent the contributions of off-diagonal density matrices, i.e., polarization, between the ground (1) and one-exciton [ $i(a \rightarrow r)$ ] configurations, and those between one-exciton configurations,  $i(a \rightarrow r)$  and  $j(a \rightarrow s)$  for  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $b \rightarrow r$  for  $\rho_{\text{hole}}(\mathbf{r}, t)$ , respectively. These second and third terms, which do not exist in the conventional definition, Eq. (8), turn out to be the origin of the polarization of electron and hole densities. Although the electron and hole densities should take values between 0 and 1 by definition,  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$  [Eqs. (13) and (14)] have the possibility of taking negative values for some positions  $r$  at  $t$  because of the polarization terms involved. In such case, we regard the negative electron (hole) density as positive hole (electron) density. It is found from Eqs. (13) and (14) that the electron and hole densities are partitioned into the contribution of each one-exciton configuration  $i(a \rightarrow r)$ , the feature of which is useful for illuminating the primary contribution of one-exciton to the exciton dynamics. Eqs. (10), (12), (13), and (14) also provide the relationship between the polarization and the electron/hole density distributions, which helps us to clarify the exciton contribution to the (non)linear optical phenomena. For instance, the Fourier transformation of the

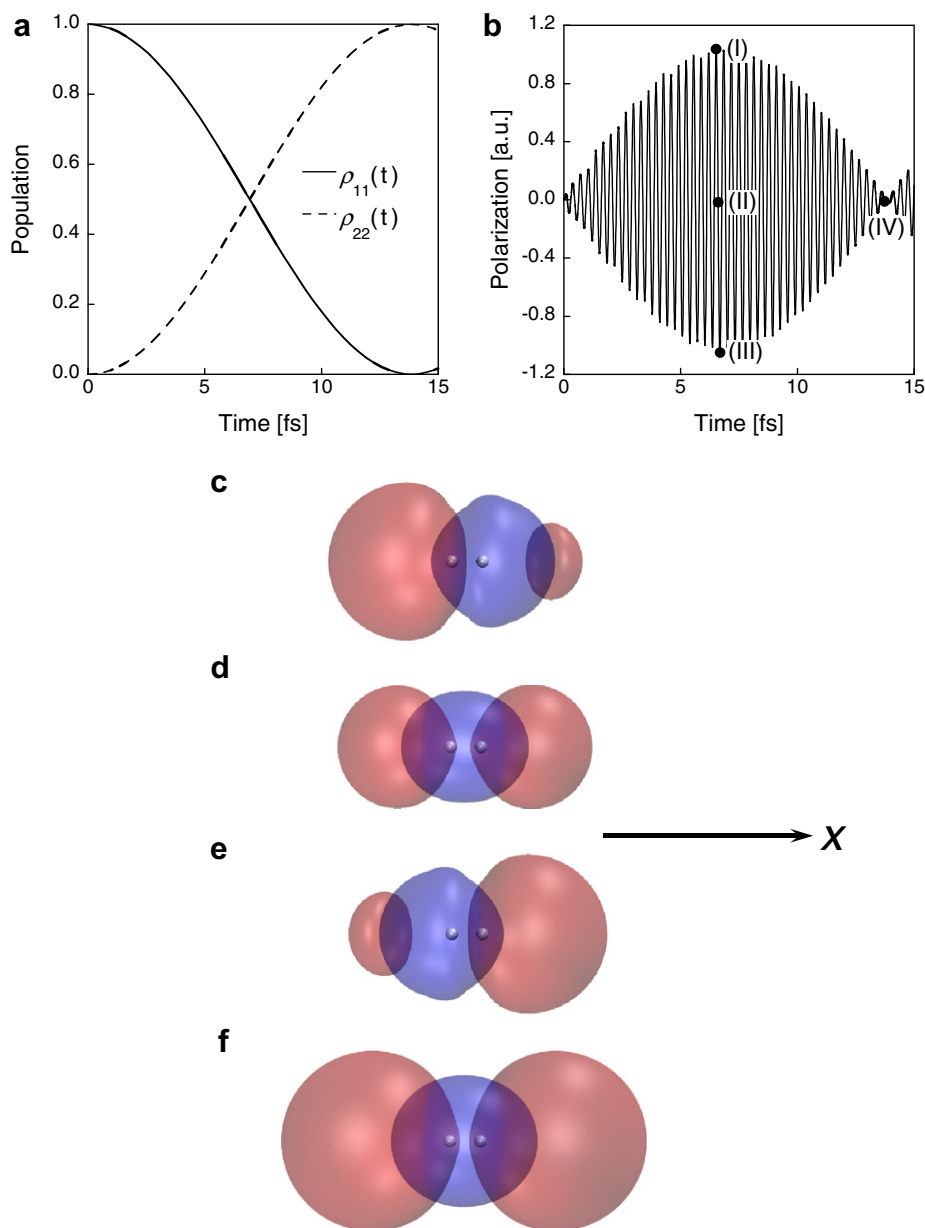
polarization density provides the dynamic (hyper)polarizability density [35,36] (by dividing by laser field amplitudes), which can elucidate the spatial contributions of electrons to the dynamic (hyper)polarizability.

### 3. Example: H<sub>2</sub> molecule in the presence of resonant electric field

In order to confirm the performance of our novel exciton expression, we examine the electron dynamics of H<sub>2</sub> molecule under a cw laser, which has a power of  $10^6$  MW/cm<sup>2</sup>, a polarization vector along the bond axis ( $x$  axis) and a frequency in resonance with the first dipole allowed excited state of H<sub>2</sub> molecule (with excitation energy  $E_2 = 103520$  cm<sup>-1</sup> and transition moment  $\mu_{21}^x = 2.612D$ ). The bond distance ( $r_{\text{H-H}} = 0.7389$  Å) is optimized by the full CI/(6)-31G(\*) +  $sp(\zeta_{s,p} = 0.0406)$  method, and the excited states are calculated by the SCI/(6)-31G(\*) +  $sp$  method including full singly excited configurations ( $N = 18$  including the HF ground configuration). We numerically solve Eqs. (2) and (3) using all singly excited states ( $M = 18$  including the HF ground state) without the relaxation terms since we just confirm the performance of the novel exciton expression [Eqs. (13) and (14)] in the present section. The time evolutions of the ground and excited state populations,  $\rho_{11}(t)$  and  $\rho_{22}(t)$ , in the SCI state basis and of polarization  $P^x(t)$  [ $2\rho_{12}^{\text{real}}(t)\mu_{21}^x$ ] are shown in Figs. 1a and b, respectively. As is well known,  $\rho_{11}(t)$  and  $\rho_{22}(t)$  exhibit Rabi oscillations, and the oscillatory amplitude of  $P^x(t)$  is shown to increase with the increase in time  $t$  and to be maximized for the superposition state of 50% ground and 50% first excited states. The electron [ $\rho_{\text{elec}}(\mathbf{r}, t)$ ] and hole [ $\rho_{\text{hole}}(\mathbf{r}, t)$ ] densities around the times giving positive and negative maximum amplitudes of  $P^x(t)$  [see (I) and (III) in Fig. 1b] are shown in Fig. 1c ( $t = 6.522$  fs) and 1e ( $t = 6.683$  fs), respectively, while the distributions at the middle time [ $t = 6.606$  fs, see (II) in Fig. 1b] are shown in Fig. 1d. As shown in Figs. 1c and e,  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$  distributions are asymmetric and the polarization direction of  $\rho_{\text{elec}}(\mathbf{r}, t)$  is opposite to that of  $\rho_{\text{hole}}(\mathbf{r}, t)$ , in contrast to the nearly symmetric distributions of those densities shown in Fig. 1d. In such superposition region, the spatially asymmetric left-right oscillations of  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$  around the center of H<sub>2</sub> molecule are observed, which lead to the dynamic polarization in the direction of bond axis. It turns out that the distribution of  $\rho_{\text{elec}}(\mathbf{r}, t)$ , increasing and decreasing alternately on both sides of the symmetry plane, is distinctly separated into left-right regions along the bond axis, which reflects the anti-bonding virtual, i.e., electron, orbital  $\psi_r(\mathbf{r})$  (LUMO) with a node plane (symmetry plane), whereas that of  $\rho_{\text{hole}}(\mathbf{r}, t)$  is distributed over both H atoms, which reflects the node-less (bonding) feature of occupied, i.e., hole, orbital  $\psi_a(\mathbf{r})$  (HOMO). As  $\rho_{22}(t)$  approaches 1, i.e.,  $\rho_{11}(t)$  approaches 0, the oscillatory amplitude of  $P^x(t)$  gradually disappears, and alternatively, the symmetric distributions of  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$  develop to reproduce the spatial features of the virtual and occupied orbitals, respectively [see Fig. 1f at  $t = 13.720$  fs, corresponding to (IV) in Fig. 1b]. From these results, the present novel exciton expression turns out to describe the coherent exciton dynamics such as dynamic polarization in addition to the variation in the spatial distributions of diagonal density matrices.

### 4. Summary

We have presented a novel expression of electron and hole densities, constituting one-exciton, based on the polarization density calculated by the ab initio MO SCI method. These electron and hole densities can describe the coherent exciton dynamics, e.g., dy-



**Fig. 1.** Time evolution of diagonal density matrices,  $\rho_{11}(t)$  and  $\rho_{22}(t)$ , in the SCI state basis (a) and polarization,  $P^x(t)$ , (b) in the presence of a cw laser field (with a power of  $10^6$  MW/cm<sup>2</sup> and a frequency  $\omega = 103520$  cm<sup>-1</sup>) with the polarization along the bond axis ( $x$ -axis) of H<sub>2</sub> molecule calculated by the SCI/(6)-31G(\*) +*sp* method. Electron (red iso-surface with +0.0008 a.u.) and hole (blue iso-surface with +0.0008 a.u.) density distributions,  $\rho_{\text{elec}}(\mathbf{r}, t)$  and  $\rho_{\text{hole}}(\mathbf{r}, t)$ , at  $t_I = 6.522$  fs (c),  $t_{II} = 6.606$  fs (d),  $t_{III} = 6.683$  fs (e) and  $t_{IV} = 13.720$  fs (f) are shown with a coordinate axis. The black circles (I), (II), (III) and (IV) shown in Fig. 1b represent  $P^x(t)$  at  $t_I$ ,  $t_{II}$ ,  $t_{III}$  and  $t_{IV}$ , respectively.

dynamic polarization and exciton recurrence, in addition to the dynamics of diagonal density matrices, e.g., Rabi oscillation and exciton migration. These expressions could contribute to the illumination of the mechanism of exciton dynamics through partitioning the total exciton contribution into that specified by each one-exciton basis, i.e., one-exciton configuration  $i(a \rightarrow r)$ . An extension of SCI scheme to multiply excited CI scheme to treat multi-exciton dynamics is also expected to be straightforward. Such extension is expected to elucidate electron correlation effects on the exciton dynamics and is necessary for the description of high-order nonlinear optical response properties, e.g., second hyperpolarizability. The advantage of this approach will be better demonstrated in case of decoherence processes, i.e., when both the exciton recurrence (coherent) and relaxation (incoherent) behaviors appear in supermolecules and aggregates with strong interactions. Such studies are in progress in our laboratory.

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