Third-order nonlinear optical responses of molecules in the intermediate and strong correlation regime: Variation of second hyperpolarizability in the bond dissociation

Masayoshi Nakano\textsuperscript{a,}\textsuperscript{*}, Satoru Yamada\textsuperscript{b} and Kizashi Yamaguchi\textsuperscript{b}

\textsuperscript{a}Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
\textsuperscript{b}Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Abstract. The variations in the longitudinal second hyperpolarizabilities ($\gamma$) in the bond-dissociation processes of molecules (H\textsubscript{2} and LiH) are investigated by the finite-field (FF) approach using several \textit{ab initio} molecular orbital (MO) methods, i.e., spin-restricted methods (RHF, RMP\textsubscript{n} ($n = 2, 4$), RHF coupled cluster (RCC)) and spin-unrestricted methods (UHF, UMP\textsubscript{n} ($n = 2, 4$), UHF coupled cluster (UCC)) as well as approximate spin-projected methods (APUHF and APUMP\textsubscript{n}). The variation of $\gamma$ in the bond dissociation process is expected to elucidate the feature of third-order nonlinear optical (NLO) properties of molecules, e.g., open-shell organic and transition metal compounds, which belong to the intermediate and strong correlation regime. The calculation methods except for CC exhibit a cusp in the variation of $\gamma$ at the triplet instability threshold, and remarkable electron-correlation dependency of the variation in $\gamma$ is observed in the intermediate and large bond-distance region, corresponding to intermediate and strong correlation regime, respectively. From the results of the most accurate methods (UCCSD(T) or RCCSD(T)) employed in this study, not only significant increase and decrease behavior of the magnitude of $\gamma$ value is observed in the intermediate dissociation region of these molecules but also even the change in the sign of $\gamma$ value appears in the dissociation process of LiH.

Keywords: Nonlinear optics, second hyperpolarizability, open-shell, electron-correlation, \textit{ab initio} MO methods

Mathematics Subject Classification: 6.5L12, 6.5L15

1. Introduction

Theoretical and experimental research of nonlinear optical (NLO) properties of molecular systems has been actively done over the past 20 years or more [1–7] because organic and organo-metallic conjugated compounds exhibit large nonlinear optical susceptibilities (hyperpolarizabilities at the microscopic level) with fast response times and the feasibility of controlling hyperpolarizabilities by the modification of molecular electronic structures. Most of molecules for NLO materials have been thermally stable

\textsuperscript{*}Corresponding author. E-mail: mnaka@cheng.es.osaka-u.ac.jp.
closed-shell neutral systems. In our previous studies [5,8–23], however, several charged and/or open-shell systems are expected to have remarkable enhancement or reduction of the magnitude of the second hyperpolarizabilities, \( \gamma \), and further drastic change of their signs by slightly modifying the structure and charged/spin states of such molecules. In particular, several compounds involving transition metals are predicted to have extraordinary large magnitude of \( \gamma \) and to show unique contributions of various orbital interactions concerning \( p \) and \( d \) electrons, the feature of which have not been observed in conventional hydrocarbon systems [5,11,20]. Recently, various molecular based nano-structures involving transition metals have been synthesized and have shown remarkably large hyperpolarizabilities [5,24].

Such charged and/or open-shell systems also tend to exhibit significant electron-correlation effects as compared to conventional closed-shell neutral systems [5,8–23] in addition to the large basis set dependency, which usually appears in the calculation of hyperpolarizability. This feature is considered to be a source of high sensitivity of hyperpolarizabilities with respect to slight changes of structures and charged and/or spin states of molecules. Therefore, the study on the NLO responses of molecules in the intermediate and strong correlation regime is now one of the current topics in chemical physics and is also important from the viewpoint of engineering science. In quantum chemistry, the electron-correlation dependences of physical and chemical properties such as response properties have been often investigated using the behavior of those properties in the bond-dissociation processes of relatively small-size molecules/atoms, which can be treated by the \textit{ab initio} molecular orbital (MO) methods involving various electron-correlation effects with extended basis sets. Actually, there are lots of sophisticated \textit{ab initio} MO studies on the hyperpolarizabilities of small-size molecules/atoms [25–32]. For example, the variations in polarizability (\( \alpha \)) and \( \gamma \) in the bond-dissociation process have been investigated and it has been found that they exhibit enormous enhancements of \( \alpha \) and \( \gamma \) in the intermediate dissociation region [33]. Inversely, the behaviors of such properties in the bond-dissociation process are useful for clarifying the features of various \textit{ab initio} electron-correlation approaches because such properties exhibit distinct electron-correlation dependence as compared with the total energy. In this study, therefore, we investigate the behavior of longitudinal static \( \gamma \) in the dissociation processes of relatively small-size systems, i.e., hydrogen molecule (\( \text{H}_2 \)) and lithium hydride (\( \text{LiH} \)) by the finite-field (FF) approach [24] using spin-restricted and spin-unrestricted Hartree-Fock (HF) and post-HF methods. In the former approach, RHF, restricted \( n \)th-order Møller-Plesset (RMP\( n \)), restricted coupled cluster (RCC) methods are employed, whereas the latter approach includes UHF, UMP\( n \), and UCC methods. We also examine the applicability of approximate spin-projected UHF and UMP\( n \) (APUHF and APUMP\( n \)) methods, which approximately but effectively remove spin contamination errors and have greatly succeeded in reproducing the shape of potential energy curves calculated by the large-scale CASSCF and CASPT2 levels [35]. In addition to the variation in \( \gamma \) values, the spatial contributions of electrons to \( \gamma \) are examined using the “second hyperpolarizability (\( \gamma \)) density” [10,36] in the bond-dissociation process. For the dissociation process of \( \text{H}_2 \) molecule, we further investigate “two-electron \( \gamma \) density” distributions of a one-dimensional model of \( \text{H}_2 \) calculated by the many-electron wavepacket (MEWP) approach [33, 37], which can provide numerically exact solutions of multi-electron systems. Since this density plot can provide a quasi-classical picture of hyperpolarization, i.e., the deviation of electron pair from its average distribution, we can analyze the real-space configuration of electron pair in the virtual excitation process describing \( \gamma \) in the bond-dissociation process. The results obtained in this study, though they are concerned with simple small-size molecules, are expected to be useful for considering the applicability of various \textit{ab initio} MO methods to the calculation of \( \gamma \) values for interesting intermediate- and strong-correlated molecular systems such as transition-metal and charged radical compounds.

This paper is organized as follows. In Section 2, we first explain our classification rule of \( \gamma \) as well as the condition providing static negative \( \gamma \), which is rare in general, and its model systems, most of
which belong to intermediate- and strong-correlation regime. The calculated models and calculation procedures are presented in Section 3 as well as a brief explanation of the FF-MEWP method. The hyperpolarizability density analysis and its extension to multi-electron case are explained in Section 4. The variations in $\gamma$ values and their density plots in the dissociation processes for $\text{H}_2$ and $\text{LiH}$ calculated by various ab initio MO methods are discussed in Section 5, including the classical picture of $\gamma$ for the dissociation process of a one-dimensional $\text{H}_2$ model calculated by the MEWP method. This is followed by a conclusion in Section 6.

2. Classification rule of second hyperpolarizability ($\gamma$)

In this section, we explain our classification rule, i.e., structure-property relation, of $\gamma$ based on the perturbation theory and a condition providing negative $\gamma$ in order to clarify the importance of the intermediate- and strong- electron-correlated molecules as candidates of novel third-order NLO systems.

The perturbative formula of $\gamma$ can be partitioned into three types of contributions (I, II and III) [5, 8]. For convenience, we here consider the partition in the static $\gamma$, which is considered to be a good approximation to the off-resonant $\gamma$. The analytical expression of $\gamma$ is given by

$$\gamma = \gamma^I + \gamma^{II} + \gamma^{III}$$  \hspace{1cm} (1)

where

$$\gamma^I = \sum_{n=1} \frac{(\mu_{n0})^2(\mu_{nm})^2}{E_{n0}^3},$$  \hspace{1cm} (2)

$$\gamma^{II} = -\sum_{n=1} \frac{(\mu_{n0})^4}{E_{n0}^3},$$  \hspace{1cm} (3)

and

$$\gamma^{III} = \sum_{m,n=1} \frac{(\mu_{m0})^2(\mu_{mn})^2}{E_{n0}^2E_{m0}}.$$  \hspace{1cm} (4)

Here, $\mu_{n0}$ is the transition moment between the ground and the $n$th excited states, $\mu_{nm}$ is the transition moment between the $n$th and the $m$th excited states, $\mu_{nn}$ is the difference of dipole moments between the ground and the $n$th excited states and $E_{n0}$ is the transition energy given by $(E_n - E_0)$. From these equations, apparently, the contributions of types I and III are positive in sign, whereas the contribution of type II is negative. For conventional molecular compounds with large positive $\gamma$, there are two characteristic cases: i) $|\gamma^I| > |\gamma^{III}|(\gamma > 0)$ and ii) $|\gamma^I| = 0, |\gamma^{II}| < |\gamma^{III}|(\gamma > 0)$. In the case i, the compounds have large asymmetric charge distributions which are responsible for large $\mu_{nn}$, whereas in the case ii, the compounds are centrosymmetric systems in which the contributions of type I disappear. The third case, i.e., iii) $|\gamma^I| = 0, |\gamma^{II}| > |\gamma^{III}|(\gamma < 0)$, is interesting because the systems with negative static $\gamma$ is rare in general and the sign of real part of third-order nonlinear optical susceptibility $\chi^{(3)}_{\text{real}}$ is important for the application in nonlinear optics [38]: positive and negative $\chi^{(3)}_{\text{real}}$ exhibit self-focusing and self-defocusing effects, respectively. Case iii systems are symmetric ($\mu_{nn} = 0$) and mostly exhibit strong virtual excitation between the ground and the first excited states ($|\mu_{n0}| > |\mu_{mn}|$). This indicates
that the symmetric systems with large ground-state polarizability ($\alpha_0$) tend to exhibit negative $\gamma$. Figure 1 shows resonance structures mainly contributing to the ground state of $\pi$-conjugated systems with large $\alpha_0$, i.e., (a) charged soliton-like oligomer [10,16,39], (b) nitronyl nitroxide radical [14,15,17], (c) anion radical state of pentalene [8,13] and (d) cation radical state of TTF ($\text{TTF}^+$) and (e) cation radical state of TTP ($\text{TTP}^+$) [18,19,22]. These indicate the resonances between polarized structures with mutually opposite directions, and can significantly contribute to the stability of ground-state electronic structures. The large contributions of these resonance structures also correspond to the fact that the magnitude of transition moment ($\mu_n^0$) between the ground and the first excited states are large. As seen from the previous results for these systems [8,10,13–19,22,39], a system with resonance structures contributing to the stability of the ground state and inducing the polarization in the mutually opposite direction tends to exhibit negative $\gamma$ and remarkable electronic structure dependences of the $\gamma$. The large contributions of the stable resonance structures with large dipole moments correspond to an enhancement of the magnitude of the transition moment ($\mu_n^0$) between the ground and the allowed first excited states. This contribution also leads to a reduction of the transition energy ($E_n^0$) between the ground and the allowed first excited states with large contributions from the resonance structures. As a result, a system with large contribution of symmetric resonance structures with invertible polarization, which is referred to as SRIP, satisfies our criteria for the system to have a negative $\gamma$ [5,13].

Since most of systems with large contributions of SRIP are found to be in charged radical and/or highly polarized neutral states, the electron-correlation effects on their $\gamma$ values are expected to be significant. Namely, the magnitude and sign of $\gamma$ for such systems are expected to be drastically changed by slight chemical and physical perturbations. This feature suggests a possibility that systems with large SRIP contributions are candidates for novel third-order NLO molecular systems, e.g., controllable NLO systems. In this study, therefore, we investigate the relation between $\gamma$ and the degree of correlations using the bond-dissociation (to neutral species) models, in which the diradical character [40–42] increases as the bond dissociation proceeds from the equilibrium bond-length region (stable bonding region) to strong correlation (magnetic or diradical) region through the intermediate correlation region.
3. Calculated models and calculation procedures

3.1. Calculated simple molecules and various ab initio MO methods

Figure 2 shows calculated models: (a) hydrogen molecule (H$_2$) and (b) lithium hydride (LiH). The longitudinal components of $\gamma$ ($\gamma_{zzzz}$) for these models are examined in their bond-dissociation processes in order to investigate the variation of $\gamma$ in the weak-, intermediate- and strong-correlation regime and to elucidate the characteristics of several computational methods. To this end, we employ the spin-restricted (RHF) and spin-unrestricted (UHF) type post-HF methods, i.e., R(U)MP$_n$ ($n = 2$–$4$), R(U)CCSD, R(U)CCSD(T). The RHF-based post-HF methods are known to break down in the dissociation (strong correlation) regime since the starting RHF solution is heavily triplet-unstable [44–46]. Higher excitation operators such as SD(T) are necessary for removing the deficient behavior for systems with electrons more than three in the case of RCC scheme [35]. On the other hand, the UHF-based methods provide smooth dissociation energy curves in the whole region. However, it is well-known that the UHF based methods including relatively low-order electron correlation effects such as UMP$_2$ suffer from spin contamination effects and give a small hump in the intermediate bond-dissociation region of the potential energy curve [35]. In order to remove such spin contamination, an approximate spin-projection (AP) scheme has been presented by Yamaguchi et al. [40,47]. In this scheme, the lowest spin (LS) UHF-based solutions are projected only by the corresponding highest spin (HS) solutions. The APUHF X energy is given by [35]

$$\text{LS} E_{\text{APUHF X}} = \text{LS} E_{\text{UHF X}} + f_{\text{SC}} [\text{LS} E_{\text{UHF X}} - \text{HS} E_{\text{UHF X}}],$$

(5)

where $Y E_{\text{UHF X}}$ denotes the total energy of the spin state $Y$ by UHF X: X denotes various post-HF methods, e.g., MP$_n$, CCSD and quadratic CI (QCI) SD methods. The factor $f_{\text{SC}}$ for a spin multiplet $(2s + 1)$ is the fraction of spin contamination given by

$$f_{\text{SC}} = \frac{\text{LS} \langle S^2 \rangle_{\text{UHF X}} - s(s + 1)}{\text{HS} \langle S^2 \rangle_{\text{UHF X}} - \text{LS} \langle S^2 \rangle_{\text{UHF X}}}.$$

(6)

The AP UHF X methods (X = MP$_n$, CC) have been successfully applied to calculations of potential energy surfaces [35] and effective exchange integrals in the Heisenberg models for open-shell clusters [41, 48–50]. In this study, $\langle S^2 \rangle$ value of the singlet and triplet UHF based correlated methods (X) beyond UMP2 is estimated by extrapolation on the basis of the UMP2 approximation:

$$W \langle S^2 \rangle = W \langle S^2 \rangle_{\text{(UMP2)}} + g \left[ W \langle S^2 \rangle_{\text{(UMP2)}} - W \langle S^2 \rangle_{\text{(UHF)}} \right],$$

(7)

where

$$g = \frac{W E_{\text{(UHF X)}} - W E_{\text{(UMP2)}}}{W E_{\text{(UMP2)}} - W E_{\text{(UHF)}}}.$$

(8)
It is well-known that the multi-reference (MR) post-HF method is inevitable for quantitative descriptions of unstable molecules in the intermediate correlation regime if the many-body perturbation (PTn) and coupled cluster expansions are truncated in the low orders [40,41,51]. The UNO CASSCF can provide a relevant non-dynamical correlation corrections arising from the triplet instability of the RHF solution [51]. Although the UNO CASSCF with large CAS space and/or the second-order perturbation (PT2) method [52,53] based on the UNO CASSCF give reliable potential curves in the whole region [35], the use of small CAS space, which is sufficient for reproducing reliable potential energy curves, is predicted to fail in giving converged values of $\gamma$ for systems in the intermediate correlation regime [54]. The UNO CASSCF based MRCCSD(T) calculations will be necessary for providing reliable and sufficiently converged values of $\gamma$ for such systems though such calculations would be hard to apply to larger systems.

### 3.2. Finite-field (FF) method

Various theoretical approaches for calculating $\gamma$ have been presented in the literature. The sum-over-state (SOS) approach [1–8,55] based on the time-dependent perturbation theory (TDPT) is useful for elucidating the contribution of transitions between electronic excited states to $\gamma$. However, the application of this approach at the ab initio MO level is limited to the relatively small-size molecules since this needs transition properties (transition moments and transition energies) over many excited states, which are hard to describe precisely at the ab initio MO level at the present time. Alternatively, the approaches using numerical or analytical derivatives of total energy with respect to the applied electric field are widely employed for calculating static $\gamma$. Particularly, the FF approach using the CHF method at the semiempirical [56] and ab initio [57] MO levels, various electron-correlated ab initio MO methods [25–32,58] and the DF methods [12,21,59,60] has been widely employed for calculating static (hyper)polarizabilities. We here briefly explain the FF approach to the calculation of static $\gamma$ for the following discussion. The total Hamiltonian in the presence of a uniform electric field $F$ is expressed as

$$H = H_0 + \sum_i F \cdot r_i - \sum_i Z_I F \cdot R_I,$$

where indices $i$ and $I$ signify electrons and nuclei, respectively. $Z_I$ is the atomic number of the $I$th nucleus and $H_0$ is the field-free Hamiltonian. The total energy $E$ can be obtained as the expectation values $\langle \Psi | H | \Psi \rangle$ for the wavefunctions $| \Psi \rangle$ in the presence of the electric field. Similarly, the dipole moment $\mu$ is expressed as

$$\mu = \langle \Psi | \sum_i Z_I R_I - \sum_i r_i | \Psi \rangle.$$

The differentiation of total energy $E$ with respect to $F$ gives

$$\frac{\partial E}{\partial F} = \left( \frac{\partial \Psi}{\partial F} \right) H | \Psi \rangle + \langle \Psi | \frac{\partial H}{\partial F} | \Psi \rangle + \langle \Psi | H \left( \frac{\partial \Psi}{\partial F} \right).$$

If $| \Psi \rangle$ is the true wavefunction, the first and third terms on the right-hand side of Eq. (11) is equal to zero by the Hellmann-Feynman theorem [61]. The variational methods such as CHF satisfy the theorem. If the Hellmann-Feynman theorem is satisfied, the dipole moment defined by Eq. (10) can be expressed as

$$\mu^i = -\frac{\partial E}{\partial F^i}.$$


The total energy and dipole moment can be expanded as the power series of the applied field:

\[
E = E_0 - \sum_i \mu^i_0 F^i - \frac{1}{2} \sum_{i,j} \alpha_{ij} F^i F^j - \frac{1}{3} \sum_{i,j,k} \beta_{ijk} F^i F^j F^k - \frac{1}{4} \sum_{i,j,k,l} \gamma_{ijkl} F^i F^j F^k F^l - \ldots \tag{13}
\]

and

\[
\mu^i = \mu^i_0 + \sum_j \alpha_{ij} F^j + \sum_{jk} \beta_{ijk} F^j F^k + \sum_{jkl} \gamma_{ijkl} F^j F^k F^l - \ldots \tag{14}
\]

where \( \mu^i_0 \) is the permanent dipole moment. The Hellmann-Feynman theorem asserts that Eqs (13) and (14) are compatible. In this study, we use the definition of hyperpolarizability based on Eq. (13). Since we focus on the longitudinal components of \( \gamma \) (\( \gamma_{zzzz} \)) for small molecules shown in Fig. 2, the \( \gamma_{zzzz} \) values are calculated by the numerical differentiation of the total energy \( E \) with respect to the applied electric field:

\[
\gamma_{iiii} = \left\{ E(3F^z) - 12E(2F^z) + 39E(F^z) - 56E(0) + 39E(-F^z) - 12E(-2F^z) \right\} / \{36(F^z)^4\},
\]

where \( E(F^z) \) represents the total energy in the presence of the electric field \( F \) applied in the \( i \) direction. This method is referred to as the FF method. The total energies are calculated by various \( ab \) \( initio \) MO methods explained above. In order to avoid numerical errors, we use several minimum field strengths (0.0002 a.u. - 0.01 a.u.). After numerical differentiations using these fields, we adopt a numerically stable \( \gamma \).

### 3.3. Finite-field many-electron wave-packet (FF-MEWP) method

We here explain the FF-MEWP method for \( \text{H}_2 \) molecule [33], in which the wave-packet dynamics is performed in the spatial coordinates for a two-electron system at a fixed spin state. A one-dimensional \( \text{H}_2 \) is examined here as shown in Fig. 3. In the Born-Oppenheimer approximation, the electronic Hamiltonian involving the interaction with static electric field \( E(F^z) \) is written (in atomic units) by

\[
H_e = -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} - \frac{1}{x_{1A}} - \frac{1}{x_{1B}} - \frac{1}{x_{2A}} - \frac{1}{x_{2B}} + \frac{1}{x_{12}} + Fx_1 + Fx_2,
\]

Fig. 3. One-dimensional \( \text{H}_2 \) composed of two nuclei (A and B) and two electrons (1 and 2).
where \( x_1 \) and \( x_2 \) denote the coordinates for electrons 1 and 2, respectively, and \( x_{ij} \) indicates the distance between particles \( i \) and \( j \). The solution to a time-dependent Schrödinger equation involving the electronic Hamiltonian,

\[
i \frac{\partial}{\partial t} \Phi(x_1, x_2, t) = H_e \Phi(x_1, x_2, t),
\]

is the electronic wavefunction,

\[
\Phi(x_1, x_2, t) = \psi(x_1, x_2, t) \varphi(\omega_1, \omega_2, t),
\]

where \( \psi(x_1, x_2, t) \) and \( \varphi(\omega_1, \omega_2, t) \) represent the spatial and spin wave-functions, respectively, in which \( \omega_1 \) and \( \omega_2 \) indicate each spin coordinate. The singlet state of the two-electron system is considered here since we focus on the ground-state (hyper)polarizability of the \( H_2 \). For the singlet-state two-electron system, the spatial wave-function, which must be symmetric with respect to the interchange of the spatial coordinates of two electrons, is generally represented as

\[
\psi_s(x_1, x_2, t) = \phi_1(x_1, t) \phi_2(x_2, t) + \phi_2(x_1, t) \phi_1(x_2, t),
\]

where \( \phi_i(x, t) \) is the \( i \)th single-particle wave-function. Therefore, the time-dependent Schrödinger equation to solve is

\[
i \frac{\partial}{\partial t} \psi_s(x_1, x_2, t) = H_e \psi_s(x_1, x_2, t).
\]

The singlet spatial wave-function \( \psi_s(x_1, x_2, t) \) is simply written as \( \psi(x_1, x_2, t) \) for convenience hereafter. In the FF-MEWP method, a Gaussian wave-packet is considered as the initial \( i \)th single-particle wavefunction expressed by

\[
\phi_i(x_j, t = 0) = C \exp \left( \frac{ip(x_j - x_{i0}) - |x_j - x_{i0}|^2}{2\sigma^2} \right).
\]

Here, \( P \), \( x_{i0} \), and \( \sigma \) indicate momentum, coordinate of the center and width of the \( i \)th initial wavepacket, respectively. The symbol \( C \) denotes a normalization constant. Using Eqs (19) and (21), an initial singlet wavefunction is constructed. This wavefunction is superposed by singlet eigenstates involving the ground and excited states of the Hamiltonian \( H_e \). Since our desired wavefunction is the ground state that is generated by the relaxation method as shown in Eq. (26) later, the form of Eq. (21) is not so important. But it is significant that the spatial part of the ground-state singlet wavefunction for two-electron system is symmetric with respect to the exchange of two-electron coordinates as shown in Eq. (19).

In this study, we discretize the wave-function in real space. Therefore, the Coulomb potential is approximated by the following softened Coulombic form [62] in order to eliminate the singularity at the origin.

\[
1 \approx \frac{1}{x_{ij}} \sqrt{a + x_{ij}^2}
\]

where \( a \) is a parameter. Javanainen et al. [62] gave \( a = 1 \) for calculations of above threshold ionization (ATI) spectra for one-dimensional \( H \) atom. This potential falls off like the Coulomb potential at large \( |x_{ij}| \), but takes an asymptotic form of the Coulomb potential at short \( |x_{ij}| \).
M. Nakano et al. / Third-order nonlinear optical responses of molecules
685

\[ \Psi(n_2, n_1) \]

\[
\begin{array}{cccc}
(N,1) & (N,2) & (N,3) & (N,N) \\
(3,1) & (3,2) & (3,3) & (3,N) \\
(2,1) & (2,2) & (2,3) & (2,N) \\
(1,1) & (1,2) & (1,3) & (1,N) \\
\end{array}
\]

\[ x_i \]

|  

Fig. 4. Descretized coordinate plane for the one-dimensional two-electron system. A finite one-dimensional space is divided into \( N \) fragments. The numbers \( n_1 \) and \( n_2 \) represent the grid numbers of electrons 1 and 2, respectively.

After discretizing in space as shown in Fig. 4, the kinetic part on the right-hand side of Eq. (20) is approximated as

\[
-\frac{\psi(n_2 + 1, n_1, t) - 2\psi(n_2, n_1, t) + \psi(n_2 - 1, n_1, t)}{2(\Delta x)^2} - \frac{\psi(n_2, n_1 + 1, t) - 2\psi(n_2, n_1, t) + \psi(n_2, n_1 - 1, t)}{2(\Delta x)^2}
\]

(23)

Here, \( \psi(n_2, n_1, t) \) represents the wavefunction at the site \((x_2, x_1, \text{in which } x_1 = (n_i - 1)\Delta x(n_i = 0, 1, \ldots, N + 1(i = 1, 2))\). Similarly the potential part using the softened Coulombic form Eq. (22) is written by

\[
\left[ -\frac{1}{\sqrt{|(n_1 - n_A)\Delta x|^2 + 1}} - \frac{1}{\sqrt{|(n_2 - n_A)\Delta x|^2 + 1}} - \frac{1}{\sqrt{|(n_1 - n_B)\Delta x|^2 + 1}} + \frac{1}{\sqrt{|(n_2 - n_B)\Delta x|^2 + 1}} + F(n_1 - 1)\Delta x + F(n_2 - 1)\Delta x \right] \psi(n_2, n_1, t),
\]

(24)

where nuclei \( A \) and \( B \) are located at the coordinates \((n_A - 1)\Delta x\) and \((n_B - 1)\Delta x\), respectively. In this work, we adopt the fixed boundary condition as

\[
\psi(n_2, n_1 = 0, t) = \psi(n_2 = 0, n_1, t) = \psi(n_2, n_1 = N + 1, t) = \psi(n_2 = N + 1, n_1, t) = 0
\]

(25)

The time propagation of \( \psi(x_1, x_2, t) \) is carried out by solving Eq. (20) in the sixth-order Runge-Kutta scheme. According to Kosloff et al. [63], the singlet ground-state wavefunction under static electric fields can be obtained by propagating initial wavepackets in imaginary time, i.e., by setting \( \tau = it \) in Eq. (20). After sufficient long time propagation, the wave-packets relax to the ground state since all
excited states involved in the initial wavepackets decay to zero. The singlet ground-state wavefunction is represented by

$$\psi_g(x_1, x_2) = \lim_{\tau \to \infty} \frac{\psi(x_1, x_2, \tau)}{\int \int |\psi(x_1, x_2, \tau)|^2 dx_1 dx_2}$$

(26)

where $$\psi(x_1, x_2, \tau) = \psi(x_1, x_2, t)|_{t=\tau}$$. The total energy under static electric field, $$E(F)$$, is obtained as

$$E(F) = E_e(F) + \frac{1}{\sqrt{|(n_A - n_B)\Delta x|^2 + a}} - F(n_A - 1)\Delta x - F(n_B - 1)\Delta x,$$

(27)

in which the first term $$E_e(F)$$ denotes the electronic energy under the static electric field, the second term represents the nuclear repulsion, and the remaining terms describe the interaction between nuclei and electric field. Using the energies under several external fields and Eq. (15), we calculate the longitudinal static $$\gamma$$ for one-dimensional H$_2$ model.

4. Hyperpolarizability density analysis

In this section, we explain the reduced one-electron and many-electron hyperpolarizability densities using an example of $$\gamma$$. The reduced one-electron hyperpolarizability density, which is simply referred to as “hyperpolarizability density”, can provide an intuitive picture of spatial contributions of electrons to hyperpolarizability, while the many-electron hyperpolarizability density is used for an extraction of quasi-classical picture, which is a “deviation of electrons from their equilibrium positions”, for hyperpolarization [33].

4.1. Reduced one-electron hyperpolarizability density

The reduced one-electron density under static electric field $$F$$ for the one-dimensional system is expanded as [10,64]

$$\rho(r, F) = \rho^{(0)}(r) + \sum_j \rho^{(1)}(r)F_j + \frac{1}{2!} \sum_{jk} \rho^{(2)}(r)F_j F_k + \frac{1}{3!} \sum_{jkl} \rho^{(3)}(r)F_j F_k F_l + \ldots$$

(28)

The induced dipole moment is expressed by

$$\mu^i = \mu_0^i + \sum_j \alpha_{ij} F_j + \sum_{jk} \beta_{ijk} F_j F_k + \sum_{jkl} \gamma_{ijkl} F_j F_k F_l - \ldots$$

(29)

where $$\mu_0^i$$ denotes the ground-state permanent dipole moment. From Eqs (28) and (29), the $$\gamma$$ is represented by [10,64]

$$\gamma_{ijkl} = -\frac{1}{3!} \int r^i \rho^{(3)}_{jkl}(r)d^3r,$$

(30)

where the $$\rho^{(3)}_{jkl}(r)$$, which is defined as the reduced one-electron $$\gamma$$ densities, respectively, is obtained by

$$\rho^{(3)}_{jkl}(r) = \frac{\partial^3 \rho}{\partial F_j \partial F_k \partial F_l} \bigg|_{F=0}.$$

(31)
This quantity is reduced one-electron second hyperpolarizability density, or simply referred to as $\gamma$ density. This is calculated at each spatial point in the discretized space by using the following numerical differentiation formulae:

$$
\rho_{ijkl}^{(3)}(r) = \{\rho(r, 2F^i) - \rho(r, -2F^i) \} / 2(F^i)^3,
$$

(32)

where $\rho_{ijkl}(r, F^i)$ represents the reduced one-electron density at a spatial point $r$ in the presence of the field $F^i$.

In order to explain a method for analysis employing the plots of reduced one-electron (hyper)polarizability density, we consider a pair of localized $\rho_{iii}^{(3)}(r)$ shown in Fig. 5 [10]. The positive sign of $\rho_{iii}^{(3)}(r)$ implies that the second derivative of the charge density increases with the increase in the field. As can be seen from Eq. (30), the arrow from positive to negative $\rho_{iii}^{(3)}(r)$ shows the sign of the contribution to $\gamma$ determined by the relative spatial configuration between the two $\rho_{iii}^{(3)}(r)$. Namely, the sign of the contribution to $\gamma$ becomes positive when the direction of the thick arrow coincides with the positive direction of the coordinate system. The contribution to $\gamma$ determined by the $\rho_{iii}^{(3)}(r)$ of the two points is more significant, when their distance is larger.

### 4.2. Many-electron (hyper)polarizability density

From the relation between many-electron and reduced one-electron densities, the reduced one-electron $n$th-order (hyper)polarizability density is related to the $M$-electron $n$th-order (hyper)polarizability density as

$$
\rho_{ijkl}^{(n)}(r) = M \int \rho_{ijkl}^{(n)}(r_1, r_2, \ldots, r_M) d^3r_2 \cdots d^3r_M.
$$

(33)

Therefore, $\gamma$ is also expressed by

$$
\gamma_{ijkl} = -\frac{1}{3!} \int \left( \sum_{m} r_m^i \right) \rho_{ijkl}^{(3)}(r_1, r_2, \ldots, r_M) d^3r_1 d^3r_2 \cdots d^3r_M,
$$

(34)

where $\rho_{ijkl}^{(3)}(r_1, r_2, \ldots, r_M)$ is defined respectively by

$$
\rho_{ijkl}^{(3)}(r_1, r_2, \ldots, r_M) = \left. \frac{\partial^3 \rho^{(3)}(r_1, r_2, \ldots, r_M, F)}{\partial F^j \partial F^k \partial F^l} \right|_{F=0}.
$$

(35)

Here, the $M$-electron density under the static electric field $F$ is obtained by

$$
\rho(r_1, r_2, \ldots, r_M, F) = \psi^\dagger(r_1, r_2, \ldots, r_M, F) \psi(r_1, r_2, \ldots, r_M, F),
$$

(36)

where $\psi(r_1, r_2, \ldots, r_M, F)$ denotes a spatial wave-function under the static electric field $F$. The $M$-electron hyperpolarizability density is calculated numerically as

$$
\rho_{ijkl}^{(3)}(r_1, \ldots, r_M) = \{(\rho(r_1, \ldots, r_M, 2F) - \rho(r_1, \ldots, r_M, -2F) - 2(\rho(r_1, \ldots, r_M, F) - \rho(r_1, \ldots, r_M, -F) ) / 2(F^3).
$$

(37)
Fig. 5. Schematic diagram of the second hyperpolarizability (γ) densities (ρ_{iii}^{(3)}(r)). The white and black circles denote, respectively, positive and negative ρ_{iii}^{(3)}(r)’s. The size of circle represents the magnitude of ρ_{iii}^{(3)}(r) and the arrow shows the sign of ρ_{iii}^{(3)}(r) determined by the relative spatial configuration between these two ρ_{iii}^{(3)}(r)’s.

We here explain a method for analysis based on the many-electron hyperpolarizability density. The procedure of evaluating spatial contributions from their densities is basically the same as that in the reduced one-electron hyperpolarizability density analysis mentioned above. The two-electron hyperpolarizability density for the one-dimensional two-electron system (in the direction x) is considered for simplicity and for the latter application (See Section 5). Similarly to the case for the reduced one-electron hyperpolarizability density analysis, we consider two pairs of positive and negative localized densities on the two electron coordinate plane. They are located symmetrically with respect to the diagonal line x_1 = x_2 since the two electrons cannot be distinguished. Here, let us draw arrows from positive to negative densities similarly to the thick arrow shown in Fig. 5. In this case, we can draw arrows from positive (white circle) to negative (black circle) densities in two manners as shown in Fig. 6(a). In the first manner, two vectors (s and s’) are symmetric with respect to a diagonal line x_1 = x_2, while for the second one, two vectors (t and t’) intersect each other across the diagonal line x_1 = x_2. Let’s focus on the contribution from vector s. We decompose the vector s into vector components s_1 and s_2, which are along the coordinates x_1 and x_2, respectively. The contribution from the vector s is obtained by adding the contributions from the vectors s_1 and s_2. The sign of the contribution becomes positive when the directions of s_1 and s_2 coincides with the positive direction of the coordinates x_1 and x_2, respectively. The magnitude of the contribution from the vector s_i (i = 1, 2) increases with the increasing distance |s_i| and with the increasing with magnitude of the two localized densities.

In quantum theory, the position of an electron cannot be determined, and an electron wavefunction is extended in space. In this meaning, a choice of the position of an electron in the two-dimensional plane corresponds to an extraction of a classical picture of the electron. According to this viewpoint, a choice of a vector drawn from the positive to the negative two-electron hyperpolarizability density corresponds to an extraction of the classical picture of polarization relating to the hyperpolarizability specified by the vector. In Fig. 6(b), four classical pictures of polarization corresponding to the vectors (s, s’, t and t’) are shown as classical displacements of two-electron configurations at the starting and terminal points of these vectors. These classical displacements are divided into two types of the classical ones. The first type of displacements obtained by the vectors s and s’ have no interchanges of electrons 1 and 2 in the polarization process, while another type of displacements obtained by the vectors t and t’ have an
interchange of them. In general, therefore, plural classical pictures can be extracted from the same pair of positive and negative hyperpolarizability densities. In this study, however, the differences in electrons’ number do not need to be considered since the hyperpolarizability relates to only the displacement of the middle point of coordinates of two electrons.

5. Variations in $\gamma$ values and their density plots in the dissociation processes of $H_2$ and LiH

In this section, we investigate the variation in longitudinal $\gamma$ for $H_2$ and LiH by the FF method using several \emph{ab initio} MO methods. The $\gamma$ of one-dimensional $H_2$ is also calculated by the FF-MEWP method. Since the basis set dependency of the $\gamma$ for small-size molecules is known to be remarkable, we employ the 6-31G** basis sets augmented by diffuse and polarization functions: 6-31G**+sp ($\zeta_{s,p}=0.0406$) for H atom and 6-31G**+pd for Li ($\zeta_{p,d}=0.0164$), which are found to provide semi-quantitative $\gamma$ values. These exponents are determined from the outermost two exponents of 6-31G** by the even-tempered method. The \emph{ab initio} and DF calculations in this paper are performed using Gaussian 98 program package [65].

5.1. $H_2$

In $H_2$ system, the single and double excitation CI (SDCI) method is the full CI (FCI) method since $H_2$ has only two electrons. As seen from the variation feature of longitudinal $\gamma$ for $H_2$ shown in Fig. 7, the $\gamma$
Fig. 7. Variation in $\gamma$ value of $\text{H}_2$ by (a) restricted (RHF, RMP2, RMP4, RCCSD), (b) unrestricted (UHF, UMP2, UMP4, UCCSD), (c) approximate projection (APUHF, APUMP2, APUMP4) and (d) density functional (UBHandHLYP, APUBHandHLYP) methods. The SDCI (full CI in this case) result is also shown for comparison.
significantly increases from the equilibrium bond distance \((R = 0.74\ \text{Å})\) to intermediate bond distance, takes a maximum value \((\approx 2600\ \text{a.u.})\), which is 34 times as large as that at the equilibrium bond distance, at \(R = 2.1\ \text{Å}\) and then decreases to the sum of \(\gamma\) for H atom in the infinite bond distance.

Figure 7(a) shows the results for \(\text{H}_2\) calculated by the spin-restricted HF based methods. The RHF \(\gamma\) value is shown to only increase remarkably as the bond distance increases. It is found that the electron correlation effects by the MP\(n\) \((n = 2, 4)\) methods do not correct this remarkable increase behavior but more enhance the increase behavior. Such incorrect behavior is predicted to originate in the triplet instability of the RHF solution in \(R \geq 1.2\ \text{Å}\) [35]. The RCCSD method is shown to rectify this incorrect behavior and to give a behavior which coincides with that by the SDCI method except for the case beyond \(R > 2.8\ \text{Å}\). We here briefly mention the relation between UHF and RHF solutions as well as spin projected UHF solution [35]. The RHF solution of \(\text{H}_2\) exhibits triplet instability and is reorganized into singlet UHF solution, where the split HOMOs for the up and down spins are given by

\[
\chi_{\text{HO}} = \cos(\omega/2)\sigma + \sin(\omega/2)\sigma^*; \quad (38)
\]

\[
\eta_{\text{HO}} = \cos(\omega/2)\sigma - \sin(\omega/2)\sigma^*; \quad (39)
\]

where \(\sigma\) and \(\sigma^*\) are the bonding and anti-bonding RHF \(\sigma\) orbitals of \(\text{H}_2\). The orbital overlap between these split MOs in the UHF solution \(\langle \chi_{\text{HO}} \eta_{\text{HO}} \rangle\) is given by \(\cos \omega\). The spin density on the hydrogen atom and total spin angular momentum \(\langle S^2 \rangle\) are not zero in the UHF solution. The UHF solution exhibits a smooth energy dissociation curve although it suffers from spin contamination. The spin-projected UHF (PUHF) solution eliminating the triplet component from UHF is expressed by the 2x2 UHF natural orbital (UNO)-CI form as [35]

\[
\Psi(\text{PUHF}) = |\{\chi_{\text{HO}}|\eta_{\text{HO}}\rangle + \eta_{\text{HO}}|\chi_{\text{HO}}\rangle\rangle = \cos^2 \omega |\sigma\sigma| - \sin^2 \omega |\sigma^*\sigma^*| . \quad (40)
\]

In the two-electron system, APUHF and PUHF are equivalent to each other. The reoptimization of \(\omega\) provides the UNO CASSCF solution. The \(\gamma\) values by the UHF based methods are shown in Fig. 7(b). The UHF \(\gamma\) value exhibits a cusp at \(R = 1.2\ \text{Å}\) (triplet instability threshold) and provides a maximum \(\gamma\) value \((\approx 1800\ \text{a.u.})\) at \(R = 1.7\ \text{Å}\), which is shorter than that \((R = 2.1\ \text{Å})\) by the SDCI method. It is shown that the UMP\(n\) \((n = 2, 4)\) correlations more enhance the \(\gamma\) values at the HF level, while cannot move the maximum point. The cusp at \(R = 1.2\ \text{Å}\) are not shown to be removed by including higher-order UMP-like electron correlations though the cusp becomes small at the UMP4 level. The UCCSD method is shown to correct such deficient behavior and to reproduce the behavior by the SDCI method.

In Fig. 7(c), we investigate the effects of spin-contamination correction on the variation in \(\gamma\). Although the APUHF exhibits a cusp at \(R = 1.2\ \text{Å}\) similarly to the UHF method, the \(\gamma\) value takes a maximum value at a similar bond distance to that by the SDCI method. In addition, the APUMP\(n\) \((n = 2, 4)\) is found to reduce the deviation from the SDCI result. This feature suggests that the spin-contamination correction can significantly improve the variation of \(\gamma\) in the bond dissociation, i.e., from weak to strong correlation via the intermediate correlation regime. However, the small cusp is found to still exist at \(R = 1.2\ \text{Å}\) in the case of \(\gamma\) calculated by the APUMP4 method. Since the APUHF \((=\text{PUHF} \text{ for a two-electron system})\) result can be equivalent with that by the 2x2 UNO CASSCF method by reoptimizing the \(\omega\) in Eq. (38), and the UNO CASSCF method is found to provide a smooth variation which is equivalent to that by the SDCI method at \(R = 1.2\ \text{Å}\), the FF-APUHF and FF-APUMP4 methods are not found to completely reproduce the correct non-dynamical correlation correction around the triplet instability threshold \((R = 1.2\ \text{Å})\), which is obtained by the reoptimization of \(\omega\) Eq. (40). In contrast, judging from results in the intermediate and strong correlation regime \((R > 1.2\ \text{Å})\), the FF-AP scheme is predicted.
to effectively include non-dynamical correlation not only on the ground state but also the excited states in that region, and further the FF-APUMP method is expected to describe the dynamical correlation both on the ground and excited states. Recently, the density functional (DF) method is known to well reproduce the energies, properties and structures for molecules calculated by the *ab initio* MO electron-correlation methods. To check the applicability of the DF method to the γ for molecules in the intermediate and strong correlation regime, we examine the γ of H₂ by the BHandHLYP method (Fig. 7d). Although a cusp at \( R = 1.2 \, \text{Å} \) also appears and the γ value by the BHandHLYP method is shown to be more significantly overestimated than that by the SDCI method, the bond distance, at which γ takes a maximum value, obtained by the SDCI method is reproduced by the BHandHLYP method. This suggests that the BHandHLYP result somewhat includes the non-dynamical effects on γ though the DF methods with the present exchange correlation functionals are known to have some deficiencies in reproducing reliable magnitudes of (hyper)polarizabilities [66].

Figure 8 shows γ density distributions of H₂ at (a) \( R = 1.2 \, \text{Å} \), (b) \( R = 1.6 \, \text{Å} \), (c) \( R = 2.1 \, \text{Å} \) and (d) \( R = 3.2 \, \text{Å} \) calculated by the QCISD method, which is known to well reproduce the CCSD results. The γ densities are plotted on a plane located 0.5 a.u. above the molecular (\( z - x \)) plane. At (a) \( R = 1.2 \, \text{Å} \), there are found to be two types of positive contributions, in which internal contributions are much larger than the outer ones. At (b) \( R = 1.6 \, \text{Å} \), only a large positive contribution to γ is observed. At (c) \( R = 2.1 \, \text{Å} \), where the γ value takes maximum, the positive contribution is further enhanced, while at (d) \( R = 3.2 \, \text{Å} \), which corresponds to strong correlation (magnetic) regime, the whole γ density distributions are reduced and the contributions tend to be partitioned to that for each H atom.

### 5.2. One-dimensional H₂ model calculated by the FF-MEWP method

In order to better elucidate the relation between spatial contribution of two electrons and γ for H₂, the FF-MEWP method is applied to a one-dimensional H₂ model (Fig. 3). Figure 9 shows the variations in the longitudinal γ in the dissociation process of the one-dimensional H₂ (Fig. 3). Similarly to the *ab initio* results on real H₂ shown in Fig. 7, the γ increases slowly at the bond distance less than 1.6 Å and takes a maximum at 2.1 Å and then decreases. For the validity of the MEWP results, we here consider the effects of the softened Coulombic potential Eq. (22) on the hyperpolarizabilities. The use of this potential has two types of influences on electronic structures. One is caused by the effects on the electron-nucleus interaction, and the other is done by the effects on the electron-electron interaction. Since electrons distributed far from nuclei are known to primarily contribute to the hyperpolarizability, the use of the softened Coulombic potential is predicted to have a primary influence on the hyperpolarizability by reducing the Coulomb repulsion for an electron pair with short interelectronic distance nearly equal to or less than spatial grid interval ∆x. As mentioned above, however, the hyperpolarizability is found to be essentially characterized by electron distributions from extended and diffuse spatial regions. Therefore, qualitative features of hyperpolarizability could be meaningfully discussed if we used a sufficiently small grid ∆x and a sufficiently large coordinate plane. Actually, from the comparison of Figs 7 and 9, the characteristics of γ in the one-dimensional model H₂ obtained here can reproduce those of the longitudinal γ for real H₂.

The maximum γ at \( R \cong 2.1 \, \text{Å} \) implies that both theoretical and experimental searches of species with chemical bonds in the intermediate correlation regime are important in relation to molecular design of nonlinear optical materials, e.g., π-conjugated compounds with labile chemical bonds [5].

The two-electron and reduced one-electron γ densities at 3.0 a.u. (\( \cong 1.6 \, \text{Å} \)), 4.0 a.u. (\( \cong 2.1 \, \text{Å} \)) and 6.0 a.u. (\( \cong 3.2 \, \text{Å} \)) are shown in Fig. 10. Since the feature of one-electron γ density at each bond distance by
Fig. 8. The $\gamma$ density plots of H$_2$ at (a) $R = 1.2$ Å, (b) $R = 1.6$ Å, (c) $R = 2.1$ Å and (d) $R = 3.2$ Å calculated by the UQCISD method. The $\gamma$ densities are plotted on a plane located 0.5 a.u. above the molecular ($z - x$) plane. The contours are drawn from $-10$ a.u. to 10 a.u. (contour step: 1 a.u.). The positions of H atoms are shown by the vertical dotted lines.

the MEWP method is shown to be in agreement with that by the UQCISD method (see Fig. 8) though the $\gamma$ density distribution with two types of positive contributions by the UQCISD method (Fig. 8(a) $R = 1.2$ Å) corresponds to that at $R = 3.0$ a.u. ($\approx 1.6$ Å) by the MEWP method as shown in Fig. 10. This difference in the bond distance seems to originate in the difference in the spatial dimension and the softened Coulomb potential (Eq. (22)) used in the MEWP method. The two-electron $\gamma$ density of one-dimensional H$_2$ model is useful for predicting the classical picture of hyperpolarization of real H$_2$. We can see four pairs of positive and negative densities constructed from internal and external two pairs which give negative and positive $\gamma$ values, respectively. This feature can be also understood by the negative contribution in the bond region and positive one in the outer region in the reduced one-electron $\gamma$ density plots. As seen from the explanation in Section 2, the difference between internal and external contributions in the two-electron $\gamma$ density is predicted to be ascribed to the two types of virtual excitation processes (types II and III) in the one-dimensional H$_2$. In the present case, the $\gamma$ is composed of types II
and III contributions. It is presumed for H₂ that the type II paths mainly include the ground and low-lying ionic excited states, while the type III paths include higher-lying ionic excited states. Therefore, the internal and external contributions seem to correspond to type II and III processes, respectively. With the increase of the bond distance, the internal two-electron \( \gamma \) densities are stretched and divided along the diagonal line \( x_2 = -x_1 + 20 \), while the external extremum region is not much divided even at the bond distance 4.0 a.u.

This change in the two-electron coordinate system corresponds to the fact that a classical picture of polarization in the internal region rapidly turn from the ionic to the radical structure at small bond distance less than 3.0 a.u., while that in the external region continues to hold a polarization in the ionic structure even at larger bond distance (\( \approx 4.0 \) a.u.). This tendency of external region seems to be realized by the virtual excitation paths (type III) including higher-lying excited states which are more spread in space than lower excited states primarily contributing to the internal region.

The slow development of \( \gamma \) at the bond distance less than 3.0 a.u. seems to be caused by a reduction of the type III (positive contribution) by the type II (negative contribution), which are predicted to has the maximum at small bond distance less than 3.0 a.u. since the excited states involved mainly in the virtual excitation paths for seem to be the same as those of type II for \( \tilde{\gamma} \).

5.3. LiH

As an example of heteropolar molecule, we consider the variation in \( \gamma \) of LiH in the bond dissociation. The variations in \( \gamma \) by the RCCSD(T) Fig. 11(a) and UCCSD(T) Fig. 11(b) methods, which are found to be in good agreement with that by the FCI (four electron excitation CI in this case), show more complicated increase and decrease behavior, which involves even the change in sign of \( \gamma \) in contrast to H₂. It is found that the positive \( \gamma \) value of LiH in the equilibrium bond distance increases gradually, takes a local maximum at \( R = 2.8 \) Å, and then decreases until \( R = 3.5 \) Å, where the \( \gamma \) takes the negative minimum value. Beyond \( R = 3.5 \) Å, the \( \gamma \) value is shown to increase again, to take a positive maximum at \( R = 4.4 \) Å and to decrease toward to the sum of \( \gamma \) for independent H and Li atoms.
Fig. 10. Two-electron \( \gamma \) densities, reduced one-electron \( \gamma \) densities and classical pictures of polarization primarily contributing to \( \gamma \) for the one-dimensional \( \text{H}_2 \) model at each bond distance: (a) 1.6 a.u., (b) 3.0 a.u., (c) 4.0 a.u. and (d) 6.0 a.u. Contour lines are drawn from \(-50\) to \(50\) a.u. (contour step: \(5\) a.u.). Classical pictures corresponding to internal and external two-electron \( \gamma \) densities are shown. In classical pictures, ticks and white circles indicate the positions of nuclei and electrons, respectively. Thick arrows represent the displacements of two-electron configurations.

The results by the RHF based methods are shown in Fig. 11(a). All these results show smooth variations in the whole region of bond distance, while the variation feature is in disagreement with that by the UCCSD(T) method Fig. 11(b). The RHF result shows a gradual increase of \( \gamma \) (with a local maximum at \( R = 3.6 \) Å) and the subsequent decrease. It is found that the RMP2 and RMP4 correlation corrections cannot rectify such incorrect variation but enhance the magnitude of variation in \( \gamma \). Such incorrect behavior is predicted to originate in the triplet instability of the RHF solution in the intermediate and strong correlation regime. Although the RCCSD(T) results is shown to be in good agreement with the UCCSD(T) one, a slight difference is detected beyond about \( R = 4.0 \) Å. This indicates that even the correlation correction at the RCCSD(T) level is hard to completely remove the effect of triplet instability of the RHF solution of LiH in the large bond distance region.

Figure 11(b) shows the results by the UHF based methods. All the UHF based results show a cusp
Fig. 11. Variation in $\gamma$ value of LiH by (a) restricted (RHF, RMP2, RMP4, RCCSD(T)), (b) unrestricted (UHF, UMP2, UMP4, UCCSD(T)) and (c) approximate projection (APUHF, APUMP2, APUMP4) methods. The UCCSD(T), which well reproduces the full CI results in this case, is also shown for comparison.

at $R = 2.1$ Å. This feature represents a deficiency in the response feature of the UHF wavefunction of LiH at the triplet instability threshold similarly to the $H_2$ case Fig. 7(b). Beyond this cusp point, the $\gamma$ value by the UHF method is shown to decrease, to take a negative local minimum, and then to increase. It is shown that the change in sign of $\gamma$ from negative to positive occurs at $R = 3.2$ Å and then the $\gamma$ value takes a positive maximum at about $R = 3.8$ Å. It is noted that the number (2) of local extrema of $\gamma$ by the UHF method is less than that Eq. (3) by the UCCSD(T) method. The UMP2 correlation correction shows the enhancement of the first (negative) and the second (positive) peaks of $\gamma$, which are significantly smaller than those by the UCCSD(T) method, respectively. Namely, we can say that these UHF and UMP2 results cannot reproduce the first positive peak and the positions of the remaining peaks (negative and positive peaks) by the UCCSD(T) method. Although the UMP4 correlation correction is
shown to give a positive value just after a cusp at \( R = 2.4 \) Å, the variation of \( \gamma \) seems not to be smooth around that region.

The effects of approximate spin-projection (AP) on the UHF and UMP\(n\) (\(n = 2, 4\)) are shown in Fig. 11(c). The APUHF and APUMP\(n\) method is shown to generate the first positive peaks though they are shown to overshoot that by the UCCSD(T) method. It is also found that these AP methods change the second (negative) and the third (positive) peak positions by the UHF and UMP\(n\) methods to more approach those by the UCCSD(T) method, respectively, though the relative relation among the magnitudes of these peaks by the AP methods is not found to well reproduce that by the UCCSD(T) method. In order to improve the qualitative features of the APUMP4 results, higher-order dynamical correlation corrections would be required.

We next investigate the variation in \( \gamma \) densities located at 0.5 a.u. above the molecular plane, by the UHF, UMP2 and UQCISD methods (Fig. 12). Since the UQCISD method is found to provide a similar behavior to that UCCSD(T) method in the present case, we use the \( \gamma \) density by the UQCISD method to analyze the spatial contributions of electrons to \( \gamma \) by the UCCSD(T) method. The variations in \( \gamma \) densities by the UHF and UMP2 methods are found to be similar to each other. At \( R = 2.6 \) Å Fig. 12(a), where the \( \gamma \) value by the UHF method takes a negative local minimum, the dominant spatial contributions by the UHF and UMP2 methods are found to be caused by the virtual charge transfer (CT) between the H-Li bond region (with negative \( \gamma \) density) and the external region of Li with positive \( \gamma \) density. As the bond distance increases up to \( R = 3.5 \) Å (see Fig. 12(a)–(e)), the positive \( \gamma \) density around H atom is shown to be increased in the UHF and UMP2 results. For the UHF and UMP2 results at \( R = 3.1 \) Å Fig. 12(c), the positive contributions between the H atom region (with positive \( \gamma \) density) and bond region (with negative \( \gamma \) density) are found to cancel out the negative contributions between the bond region and the external region (with positive \( \gamma \) density) of Li atom. For the UHF and UMP2 results at \( R = 3.5 \) Å Fig. 12(e), the magnitude of \( \gamma \) density in the external region of Li atom is shown to decrease, so that the contribution to total \( \gamma \) by the UHF and UMP2 methods is primarily caused by the positive contribution originating from the virtual CT between the H atom (with positive \( \gamma \) density) and bond region (with negative \( \gamma \) density). In the large bond distance region (\( R = 4.5 \) Å shown in Fig. 12(g)) for the UHF and UMP2 results, the magnitude of \( \gamma \) densities are found to be decreased in the whole region, the feature of which is the origin of the decrease in total \( \gamma \) in the bond dissociation limit by the UHF and UMP2 methods. The variation in \( \gamma \) density from \( R = 2.6 \) Å to 3.1 Å by the UQCISD method (Figs. 12(a)–(c)) are not observed in those by the UHF and UMP2 methods. The variation of \( \gamma \) in this region corresponds to the first (positive) peak of \( \gamma \) by the UCCSD(T) method shown in Fig. 11(b), and the primary positive contribution is found to come from the virtual CT between the bond region (with positive \( \gamma \) density) and the external region of Li atom (with negative \( \gamma \) density). For the UQCISD results from \( R = 2.8 \) Å to 3.1 Å, the increase in the magnitude of negative \( \gamma \) density in the H atom region, the increase in the positive \( \gamma \) density in the bond region and the decrease in the magnitude of negative \( \gamma \) density in the external region of Li atom are observed. This feature causes the cancellation between positive and negative contributions, providing the decrease in the magnitude of \( \gamma \) in that region. For the UQCISD result at \( R = 3.5 \) Å Fig. 12(e), there is shown to be a large negative contribution between the bond region and the external region of Li atom. It is noted that this distribution is similar to that at \( R = 2.6 \) Å by the UHF and UMP2 methods (see Fig. 12(a)). The feature of \( \gamma \) density distribution at \( R = 4.5 \) Å Fig. 12(g) by the UQCISD method is also shown to be similar to that at \( R = 3.5 \) Å by the UHF and UMP2 methods Fig. 12(e). These similarities indicate that the first (negative) and second (positive) peaks of \( \gamma \) values by the UHF and UMP\(n\) methods correspond to the second and the third peaks of \( \gamma \) values by the UCCSD(T) method. However, the decrease in the magnitude of \( \gamma \) density in the Li atom region at \( R = 4.5 \) Å Fig. 12(g) by
the UQCISD method is shown to be more remarkable than that at $R = 3.5$ Å by the UHF and UMP2 methods. This corresponds to the fact that the last positive peaks at $R = 3.5$ Å by the UHF and UMP2 methods are significantly smaller than that at $R = 4.5$ Å by the UQCISD method. As a result, the UHF and UMP2 methods are suggested to reproduce qualitative $\gamma$ density distributions (spatial contributions of electrons to $\gamma$) in the second and the third peaks of $\gamma$ by the UQCISD method in the relatively strong correlation regime though the peak position and relative magnitudes of peaks by the UHF and UMP2 methods are different from those by the UQCISD method. The AP method somewhat improves these two peak position and their peak values, though the improved values are not still far from the UQCISD values, and also generates the first peak, which cannot be generated by the UHF and UMP2 methods. This suggests that the AP method tend to improve the non-dynamical correlation effects involved in the UHF method on $\gamma$ LiH.

6. Summary

We investigated in this study the variation in longitudinal $\gamma$ in the bond-dissociation process of small-size molecule, i.e., H$_2$ and LiH, in order to elucidate the feature of $\gamma$ for systems in intermediate and strong correlation regime. From the results by high-order electron correlated ab initio MO methods, e.g., UCCSD(T), the magnitude of $\gamma$ value in equilibrium bond distance, i.e., weak correlation, regime tends to be remarkably enhanced in the intermediate and strong correlation regime with labile chemical bonds. For H$_2$ molecule, the $\gamma$ value exhibits only an increase-decrease behavior with a peak, while for LiH molecule three peaks with significant magnitude of $\gamma$ appear and even the change in the sign of $\gamma$ is observed in the intermediate and strong correlation regime. These features suggest that the molecular systems with chemical bonds in the intermediate and strong correlation regime are candidates for novel third-order NLO systems, in which the magnitudes of $\gamma$ values can be significantly enhanced and/or their signs are changed by slight chemical modifications, e.g., change in the metal spieces and ligands in transition-metal compounds.

We also examined the applicability of various ab initio MO methods to $\gamma$ for molecules in the intermediate and strong correlation regime. The RHF and RMP$n$ methods are found to fail in giving qualitative variation in $\gamma$ in the bond-dissociation region due to the triplet instability of the RHF solution in that region. Although the RCCSD(T) method can remarkably improve the variation in $\gamma$, the variation shape of $\gamma$ is shown to somewhat deviate from the FCI result of LiH in the strong correlation regime. In contrast, the unrestricted CC methods, e.g., UCCSD(T), are found to be used for at least semi-quantitative study on the $\gamma$ for small-size systems. In contrast, the UHF and UMP$n$ ($n = 2, 4$) methods are found to fail in reproducing qualitative shape of variation in $\gamma$ in the whole bond-dissociation region though the $\gamma$ density distribution in the strong correlation regime is similar to that by the UQCISD method. The approximate spin-projected MP$n$ (APUMP$n$) methods tend to somewhat improve the variation in $\gamma$ but the correction at the APUMP4 level is predicted to be still insufficient for getting the qualitative variation in $\gamma$ judging from LiH results. Also from our previous studies [54], the CASSCF and CASSCF PT2 methods without extended active space seem to fail in providing convergent $\gamma$ in the present case. Probably, the multi-reference CC (MRCC) with relatively small active space or CCSDT and CCSDTQ methods based on the UHF solution will be necessary for obtaining reliable results of $\gamma$ for systems in the whole region from weak to strong correlation. For larger systems, however, the MRCC method is hard to apply to attractive NLO systems with extended $\pi$ conjugation. Recently, the DF method based on the UHF natural orbital (UNO) CASSCF, which is referred to as the CASDFT, has been developed [67]. This method has the advantage of effectively involving non-dynamical and dynamical correlation effects
Fig. 12. The $\gamma$ density plots of LiH (see Fig. 2 for the coordinate) at (a) $R = 2.6$ Å, (b) $R = 2.8$ Å, (c) $R = 3.1$ Å, (d) $R = 3.3$ Å, (e) $R = 3.5$ Å, (f) $R = 4.0$ Å and (g) $R = 4.5$ Å calculated by the UHF, UMP2 and UQCISD method. The $\gamma$ densities are plotted on a plane located 0.5 a.u. above the molecular ($z - x$) plane. The contours are drawn from $-10000$ a.u. to $10000$ a.u. (contour step: 2000 a.u.). The positions of H (left-side) and Li (right-side) atoms are shown by the dotted lines.

using much smaller computational resources than the MRCC. The FF method using such CASDFT is expected to provide reliable $\gamma$ values for larger systems in the intermediate and strong correlation regime.
Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research (No. 14340184) from Japan Society for the Promotion of Science (JSPS).

References
