

## Simplified Sum-Over-States Calculations and Missing-Orbital Analysis on Molecular Hyperpolarizability

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To clarify the origin of molecular hyperpolarizability  $\beta$ , we have developed the simplified sum-over-states method in the framework of *ab-initio* SCF method for calculating  $\beta$ , and the missing-orbital analysis method for analyzing  $\beta$ . These methods have been applied to diagonal and off-diagonal components,  $\beta_{zzz}$  and  $\beta_{zxx}$ , respectively, of various organic molecules with  $C_{2v}$  symmetry, and elucidated that these components should be explained by different models. The methods are further applied to  $\beta$  components of Si clusters, yielding results which explain qualitatively experimental results on second-harmonic-generation from oxide/Si interface.

### 1. INTRODUCTION

Molecular orbital (MO) calculations have been a practical tool for evaluating molecular optical nonlinearities such as the first order molecular hyperpolarizability tensor  $\beta$  [1-8]. They are also important to clarify the origins of these properties, enabling us to find ways to control the molecular nonlinearity of materials as well as new materials. Meantime, organic molecules with large  $\beta$  have been actively studied by MO calculations [1-8] because the large first-order nonlinear optical response has been found in organic crystals. Two methods, coupled-perturbed Hartree-Fock (CPHF) [8] and sum-over-states (SOS) [2,3] methods, are currently used to evaluate (hyper)polarizabilities with using MOs. *Ab-initio* CPHF calculations give the best accuracy, but they are inherently unable to describe the nonlinearity in terms of electronic states or MOs because this method gives polarizabilities as analytical derivatives of self-consistent-field (SCF) energy with respect to an applied external field. In SOS calculations, on the other hand, polarizabilities are represented by states in the time-dependent perturbation theory. However, most of SOS calculations have been done with using semi-empirical MOs, and may be insufficient to assess the electronic structure of important states.

We have developed the simplified SOS method which evaluates the molecular hyperpolarizabilities within the framework of *ab-initio* SCF theory, and the missing-orbital analysis which estimates the contribution of each excited *configuration* to  $\beta$  after evaluating  $\beta$  by the simplified SOS calculation [5]. In the simplified SOS method, we use singly excited *configurations* as excited-state wavefunctions instead of those obtained by a CI calculation. The missing-

orbital analysis is analogous to the missing state analysis, which was first proposed by Dirk and Kuzyk [4], but employs excited *configurations* in replace of excited *states*. The analysis for the missing states is then reduced to that for the missing orbital pair related to the excited configuration. In this paper, we briefly introduce the ability of these methods by the results on the diagonal and off-diagonal components of  $\beta$ ,  $\beta_{zzz}$  and  $\beta_{zxx}$ , respectively, of various organic molecules with  $C_{2v}$  symmetry [5-7], and then show the results on  $\beta$  components of Si clusters [10].

### 2. METHODS

In the sum-over-states (SOS) method [1-3], the molecular (hyper)polarizabilities are calculated by the sum of transition dipole matrix elements between ground state and excited state and those between excited states. In the most of previous SOS calculations, the wavefunction of the ground state is deduced by a SCF calculation and those for excited states are obtained by a singly excited CI calculation. By such restriction to the excited-state wavefunction, the dipole matrix elements can be reduced to one-electron dipole integrals over the ground-state SCF MOs. However, even if the CI calculation is restricted to single excitation and even if MOs used are restricted to semi-empirical ones such as CNDO or PPP, the large number of excited states may be hardly obtained. We thus introduces the following approximations in our simplified SOS method within the framework *ab-initio* SCF method. The excited-state wavefunctions are approximated by only one singly excited (in the singlet coupling) configuration  $\Psi_n = |i \rightarrow a\rangle$ , i.e., a configuration produced by one electron excitation from an occupied MO 'i' to an unoccupied MO 'a'. To be consistent with this

assumption, excitation energies are replaced by orbital energy differences, and the sum over all excited states are replaced by sums over all occupied and unoccupied MOs, as detailed elsewhere [5].

Eventually, the diagonal and off-diagonal components of  $\beta$ ,  $\beta_{zzz}$  and  $\beta_{zxx}$ , respectively, for a closed shell system are given at zero frequency as,

$$\beta_{zzz} = \frac{-6e^3}{\hbar^2} \sum_{i,a} \frac{\langle i|z|a\rangle}{\omega_{ia}} \left[ \sum_b \frac{\langle a|z|b\rangle\langle b|z|i\rangle}{\omega_{ib}} - \sum_j \frac{\langle i|z|j\rangle\langle j|z|a\rangle}{\omega_{ja}} \right], \quad (1-1)$$

$$\beta_{zxx} = \frac{-e^3}{\hbar^2} \sum_{i,a} \left\{ \frac{\langle i|x|a\rangle}{\omega_{ia}} \left[ \sum_b \frac{\langle a|z|b\rangle\langle b|x|i\rangle + \langle a|x|b\rangle\langle b|z|i\rangle}{\omega_{ib}} - \sum_j \frac{\langle i|z|j\rangle\langle j|x|a\rangle + \langle i|x|j\rangle\langle j|z|a\rangle}{\omega_{ja}} \right] \right. \\ \left. + \frac{\langle i|z|a\rangle}{\omega_{ia}} \left[ \sum_b \frac{\langle a|x|b\rangle\langle b|x|i\rangle}{\omega_{ib}} - \sum_j \frac{\langle i|x|j\rangle\langle j|x|a\rangle}{\omega_{ja}} \right] \right\}, \quad (1-2)$$

where  $|i\rangle$  and  $|j\rangle$  are occupied MOs,  $|a\rangle$  and  $|b\rangle$  are virtual MOs, and  $\hbar\omega_{ia}$  is the orbital energy difference. Formula for these  $\beta$  components in the case of second-harmonic-generation (SHG), i.e., frequency-dependent  $\beta$  [5], and those for an open shell system [10] are given elsewhere. To evaluate  $\beta$  components, only light computation is required because only SCF MOs and orbital energies of the ground state are necessary for their calculations. Furthermore, the  $\beta$  values for some organic molecules obtained by this method agree well [5] with the most reliable CPHF results [8].

The missing-orbital analysis [5] evaluates the relative contribution parameter  $\sigma$  [4] of a certain excited configuration by excluding its corresponding MO(s) pairs from the calculation of  $\beta$  components. That is, the contribution from the configuration  $|i \rightarrow a\rangle$ , i.e.,  $\sigma_{ia}$ , is evaluated by

$$\sigma_{ia} = \frac{\beta(\text{tot}) - (\beta(i \cdot) + \beta(\cdot a) - \beta(ia))}{\beta(\text{tot})}, \quad (2)$$

where  $\beta(\text{tot})$  is the calculated  $\beta$  with the complete MO set;  $\beta(i \cdot)$  or  $\beta(\cdot a)$ , is that excluding either the occupied MO 'i' or the unoccupied MO 'a'; and  $\beta(ia)$  is the calculated  $\beta$  with neither MO 'i' nor 'a'. Here,  $\beta$  represents any component of the first-order hyperpolarizability. If  $\sigma < 0$ , the configuration contributes negatively, while if  $\sigma > 1$ , the configuration is responsible for the sign of the  $\beta$  component.

Molecular structures assumed, basis sets used, and details of computation are given in the original

papers [5-7,10]. Programs for the simplified SOS calculations and the missing-orbital analysis were installed in the direct SCF program AMOSS [11].

### 3. RESULTS AND DISCUSSIONS

#### 3-1 Organic molecules

In various organic molecules we considered with  $C_{2v}$  symmetry, evaluated values of  $\beta_{zzz}$  and  $\beta_{zxx}$  at zero frequency for three molecules are given in Table I. Also given are the respective molecular permanent dipole moments  $\mu$  and average polarizabilities  $\alpha_{ave}$ . Here, molecules are placed in the  $zx$ -plane, and the molecular  $z$ -axis, which is the direction of the molecular permanent dipole moment, coincides with the direction of the principal axis of symmetry. Historically, *p*-nitroaniline (PNA) type molecules, i.e., benzenes *para*-substituted by a donor-acceptor pair, have been studied extensively by both MO calculations and experiments because of their large  $\beta_{zzz}$  value [1,3,8]. The large magnitude of  $\beta_{zzz}$  has been successfully described by the conventional two-state model which assumes the ground state and the charge-transfer (CT) excited state [1,3]. The CT is a forward CT because the dipole moment increases by the excitation, e.g., the CT for PNA occurs in one direction along the  $z$ -axis from the amino to nitro group. This has been confirmed by the missing-orbital analysis of  $\beta_{zzz}$  for PNA where  $\beta_{zzz}$  is contributed by only one excited configuration, the HOMO-LUMO-like  $|b_2 \rightarrow b_2^*\rangle$  configuration [5]. Here, the notation  $|b_2 \rightarrow b_2^*\rangle$  indicates one electron in  $b_2$  MO is excited to  $b_2^*$

**Table1 Hyperpolarizabilities of varioud organic molecules**

	$\beta_{zzz}$ ( $10^{-31}$ esu)	$\beta_{zxx}$	$\mu$ (Debye)	$\alpha_{ave}$ ( $\text{\AA}^3$ )
PNA	39.2	-11.3	8.43	12.2
ANA	41.8	-34.2	9.08	25.3
DDB	-14.0	-11.3	8.43	12.2

MO, and  $b_2$  MO is attributed to the 'out-of-plane'  $\pi$  orbital in  $C_{2v}$  symmetry [5-8].

Using of more straight dipolar  $\pi$  system, i.e., amino-nitropolynes, we have examined the relation between the magnitude of  $\beta_{zzz}$  and  $\pi$  conjugation extension in the  $z$ -direction by changing the number of acetylene ( $-C\equiv C-$ ) units [7]. As increasing the number of acetylene units,  $\beta_{zzz}$  increases rapidly. Meanwhile, one additional acetylene unit gives an increment of one  $b_2$  MO on the  $z$ -axis, thus  $\beta_{zzz}$  increases with the number of  $b_2$  MOs *lined up in the  $z$ -direction* [7]. If  $b_2$  MOs *line up in the  $x$ -direction*, however, an increase in its number is inefficient to  $\beta_{zzz}$ . An example of such case is 9-amino-10-nitroanthracene (ANA) [6] which has  $\beta_{zzz}$  with a similar magnitude as that of PNA (see Table1). Clearly, ANA has a  $\pi$  conjugation more extended in the  $x$ -direction and a larger number of  $b_2$  MOs *lined up in the  $x$ -direction*, but it has a CT character similar to that of PNA [6].

Though  $\beta_{zzz}$  has long been studied, the off-diagonal component, e.g.  $\beta_{zxx}$ , has rarely been examined, because its magnitude for  $C_{2v}$  molecules has been predicted to be very small based on the two-state model [3]. However, we have found that  $\beta_{zxx}$  must be described by a multi-state model [6], even for molecules having  $\beta_{zzz}$  that conforms with the two-state model. In the multi-state model,  $\beta_{zxx}$  is described by the ground state and at least two configurations belonging to two different irreducible representations of the symmetry. For instance, the missing-orbital analysis of  $\beta_{zxx}$  for amino-nitropolynes has shown that  $\beta_{zxx}$  is chiefly contributed by  $|a_2 \rightarrow b_2^*\rangle$  type configurations and HOMO-

LUMO-like  $|b_2 \rightarrow b_2^*\rangle$  type ones. The latter ones are the dominant contributors to  $\beta_{zzz}$  for these molecules. In amino-nitro-polynes,  $\beta_{zxx}$  is unchanged despite of an increase of the number of acetylene units and is irrelevant to the number of  $b_2$  MOs *lined up in the  $z$ -direction*.  $\beta_{zxx}$  unchanged is ascribed to that it is governed by only one occupied  $a_2$  MO localized on the nitro group, and hence  $\beta_{zxx}$  is independent of  $\beta_{zzz}$ . Here, an  $a_2$  MO is again an 'out-of-plane'  $\pi$  like orbital that is anti-symmetric to the reflection in the  $zy$ -plane.

The magnitude of  $\beta_{zxx}$  remains small for simple dipolar systems such as amino-nitro-polynes and PNA. Nevertheless,  $\beta_{zxx}$  can be greatly enhanced when the  $\pi$  conjugation system is extended in the  $x$ -direction [6,7]. As shown in Table1, the magnitude of  $\beta_{zxx}$  for PNA is about 1/3 that of  $\beta_{zzz}$ , but ANA, which is obtained by replacing benzene in PNA with anthracene, has  $\beta_{zxx}$  about three times larger than PNA. Hence the magnitude of  $\beta_{zxx}$  in ANA is similar to that of  $\beta_{zzz}$  which remains mostly unchanged by the replacement. This enhancement of  $\beta_{zxx}$  is attributed to a larger  $x$ -extension of the  $\pi$  conjugation in ANA, which accompanies a simultaneous increase in the number of  $a_2$  MOs *lined up in the  $x$ -direction*. This is in contrast to the increase in  $\beta_{zzz}$  as the number of  $b_2$  MOs *lined up in the  $z$ -direction*. Other than the use of a bulky substrate, the  $\pi$  conjugation extension in the  $x$ -direction can be accomplished by multiple substitutions [6,7]. For instance, 1,3-diamino-4,6-dinitrobenzene (DDB), which has a  $\pi$  conjugation substituted by two pairs of donor-acceptors on both sides of the  $z$ -axis, has  $\beta_{zxx}$  about three times larger than PNA [6] (see Table 1). According to the

**Table2 Hyperpolarizabilities of Si clusters**

	$\beta_{XXX}$ (a.u.)	$\beta_{ZXX}$	$\mu$ (Debye)
Si4	-19.5	-26.9	0.17
Si4-H	-10.3	3.3	0.14
Si7	169.9	-314.6	-0.25
Si7-H	-8.0	-4.1	-0.22

results of the missing-orbital analysis, DDB is characterized by two weak *ortho*-CT [6] streams localized on both sides of the z-axis, produced by *ortho*-positioned donor-acceptor pairs. This may be related to an unexpectedly small magnitude of  $\beta_{ZZZ}$ , that arises from the lack of contribution from a forward CT.

### 3-2 Si clusters

Second-harmonic-generation (SHG) measurement has been received much attention as a tool for characterizing interface through a non-destructive procedure. For interface of SiO<sub>2</sub>/Si(111) which is important to metal-oxide-semiconductor device technology, an intensity of SH light has been measured before/after annealing under hydrogen ambient [9], yielding two components of nonlinear susceptibility  $\chi^{(2)}_{ZXX}$  and  $\chi^{(2)}_{XXX}$ , where the z-axis coincides with the interface normal direction. It is found that  $\chi^{(2)}_{ZXX}$  is strongly decreased by hydrogen annealing, while  $\chi^{(2)}_{XXX}$  shows a small change. This result has been attributed to the termination of interfacial dangling bond (which is normal to the interface) with hydrogen by annealing [9]. To confirm such attribution, the simplified SOS calculation and the missing-orbital analysis are applied to  $\chi^{(2)}_{ZXX}$  and  $\chi^{(2)}_{XXX}$  of Si(111) surface being modeled by Si clusters such as Si<sub>4</sub>, Si<sub>7</sub>, and larger clusters [10]. In Si<sub>4</sub> cluster a Si atom with a dangling bond has three nearest neighbors in the second layer, and in Si<sub>7</sub> cluster three Si atoms are further added in the third layer, where sp<sup>3</sup> hybridized bonds at each edge Si atom are saturated by hydrogen atoms. The dangling bond on the center Si atom is assumed to be either with and without hydrogen termination. The molecular axes are chosen to be consistent with the experiment.

Table2 shows evaluated values of  $\beta_{XXX}$  and  $\beta_{ZXX}$  for Si clusters, where the dangling bond is terminated for Si<sub>4</sub>-H and Si<sub>7</sub>-H while it is left for Si<sub>4</sub> and Si<sub>7</sub>. It is found [10] that the third layer atoms importantly contributes to enlarge both  $\beta_{XXX}$  and  $\beta_{ZXX}$  because these values for Si<sub>7</sub> cluster is larger than Si<sub>4</sub> cluster. While the values of  $\beta_{XXX}$  and  $\beta_{ZXX}$  for Si<sub>7</sub>-H are very small and in a similar magnitude to those of Si<sub>4</sub>-H, the hydrogen termination reduces the magnitude of  $\beta$  especially  $\beta_{ZXX}$ . The missing-orbital analysis on Si<sub>7</sub>, on the other hand, indicates that dominant contributions to  $\beta_{XXX}$  and especially  $\beta_{ZXX}$  are from configurations that induce CT from the third layer Si atoms to the open shell dangling orbital through sp<sup>3</sup> hybridized  $\sigma$  bond [10]. These results consistently explain the experimental fact that SHG from oxide/Si interface is much affected by the termination of dangling bond on Si atom at the interface.

### REFERENCES

1. J. Zyss and D. S. Chemla, in: Nonlinear optical properties of organic molecules and crystals, Vol. 1, eds. D. S. Chemla and J. Zyss (Academic Press, New York, 1987)
2. D. Pugh and J. O. Morley, in: Nonlinear optical properties of organic molecules and crystals, Vol. 1, eds. D. S. Chemla and J. Zyss (Academic Press, New York, 1987)
3. S. J. Lalama and A. F. Garito, *Phys. Rev. A* **20** (1979) 1179
4. C. W. Dirk and M. G. Kuzyk, *Phys. Rev. A* **39** (1989) 1219
5. M. Tomonari, N. Ookubo, T. Takada, M. W. Feyereisen and J. Almlöf, *Chem. Phys. Lett.* **203** (1993) 603
6. M. Tomonari, N. Ookubo and T. Takada, *Chem. Phys. Lett.* **215** (1993) 453; *THEOCHEM (J. Mol. Struct.)* **311** (1994) 221; *Chem. Phys. Lett.* **236** (1995) 475
7. M. Tomonari, N. Ookubo and T. Takada, submitted.
8. C. Daniel and M. Dupuis, *Chem. Phys. Lett.* **171** (1990) 209
9. F. Ito and H. Hirayama, *Phys. Rev. B* **50** (1994) 11208
10. M. Tomonari, N. Ookubo and T. Takada, in progress.
11. Developed by NEC quantum chemistry group.