Mean Square Deviations of Interatomic Distances in Liquid Carbon Tetrachloride

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In simulating the X-ray scattering intensity of liquid carbon tetrachloride, the structural diffusion model for the bcc local structure has been refined by formulating the mean square deviations of interatomic distances by dividing them into two parts, namely, translational and rotational contributions. By this treatment, the simulation has not been improved in comparison with the modified Prins relation, but the description of the motion of carbon tetrachloride molecules in the liquid becomes clear. The degree of depolarization of the ν_1 Raman line is well accounted for by the use of the translational mean square deviations determined.

The structure of liquids has long been the least understood among those of the three phases of matter, and it still is. Nevertheless, it is fair to say that many works, especially recent diffraction experiments[1–5] and computer simulations,[6,7] have made it clear to a great extent.

From the stand-point of diffraction studies, it is convenient to use a visualized structure model for a liquid and calculate the diffraction intensity for the structure model, which is to be tested against the experimental intensity. In order to calculate the diffraction intensity of the structure model, it is necessary to construct a local lattice structure around a molecule and to express the structural diffusion by the width of atomic pair distribution. This will increase with the increase of the interatomic separations. Even in a molecular liquid, the expression for the diffraction intensity becomes more tractable if it is based on the atomic pair distribution, than on the molecular pair correlation function which is usually expanded in terms of Wigner rotation matrices.[8]

The mean square deviation of the interatomic distances due to the width of the pair distribution is often called the mean square amplitude,[2] by analogy with atomic distances in a free molecule where the distribution is caused exclusively by vibrational motion. If the local lattice structure is determined and the mean square deviation is given to each atomic pair by the use of a reasonably small number of parameters, the structure of a liquid may be said to be elucidated.

In previous papers,[2,3] it has been shown that the experimental X-ray scattering intensity of liquid carbon tetrachloride[4] is simulated in good approximation by the bcc model for the local lattice structure. In this model a chlorine atom of one molecule lies in a hollow formed by three chlorine atoms of the adjacent molecule, and the threefold axes of these molecules are aligned (see Fig. 2). This packing is called head-tail head-tail packing. By the repetition of this head-tail head-tail packing with the eclipsed arrangement for the off-axis chlorine atoms a bcc lattice is obtained. Accordingly our model for the local structure of liquid carbon tetrachloride is called a bcc model. The head-tail head-tail packing is highly stabilized for molecules with an octopole moment.[9] Moreover, this packing is known to be the fundamental orientational correlation in the plastic phase (Ia) of carbon tetrachloride.[5] It is scarcely to be doubtful that the bcc structure is the best and physically reasonable model for the local lattice structure of liquid carbon tetrachloride.

However, our knowledge about the mean square deviation to express the structural diffusion has not been satisfactory.[2] Usually, the mean square deviation l_{pq}^2 is related to the distance between the p-th and q-th atoms, r_{pq}, by the Prins relation,[10]

$$l_{pq}^2 = Dr_{pq},$$

or a modified structural diffusion relation proposed by Baer,[11]

$$l_{pq}^2 = D(r_{pq}-r_0).$$

However, it has been found that these relationships are not adequate expressions to simulate the X-ray scattering intensity from a molecular liquid such as carbon tetrachloride.[2] In this case, the distribution of the orientational fluctuation of each molecule as well as the distribution of the distance between molecular centers must be taken into account. On the basis of this inference, we derive in the present work a more sophisticated formulation for the mean square deviations for liquid carbon tetrachloride.

Mean Square Deviations

The reduced scattering intensity per molecule of liquid carbon tetrachloride is given by[2]

$$\begin{aligned} i(s) = {} & [8f_{\mathrm{C}}f_{\mathrm{Cl}}j_0(sr_{\mathrm{C-Cl}}) \exp(-l_{\mathrm{C-Cl}}^2 s^2/2) \\ & + 12f_{\mathrm{Cl}}^2 j_0(sr_{\mathrm{Cl-Cl}}) \exp(-l_{\mathrm{Cl-Cl}}^2 s^2/2)] \\ & + \sum_{p\neq q} f_p f_q j_0(sr_{pq}) \exp(-l_{pq}^2 s^2/2) + I_{\mathrm{c}} \end{aligned} \tag{1}$$

where $j_0(x)$ is the 0-th order spherical Bessel function, *i.e.*, $\sin x/x$; f_p is the atomic scattering factor of the p-th atom, and s is the scattering parameter defined by $4\pi\sin\theta/\lambda$, λ: wavelength, 2θ: scattering angle. The first bracketed term expresses the intensity of the atomic interference in the representative or central molecule itself, and $r_{\mathrm{C-Cl}}$, $r_{\mathrm{Cl-Cl}}$, $l_{\mathrm{C-Cl}}$, and $l_{\mathrm{Cl-Cl}}$ are interatomic distances and respective root mean-square deviations of a molecule, for which the values obtained by gas electron diffraction[12] are used. l_{pq} is the root mean-square deviation for the distance r_{pq}, and I_{c} is the inten-

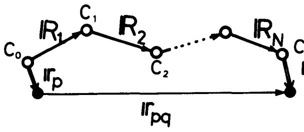

Fig. 1. The interatomic distance vector r_{pq}. The notation C_i shows the center of the i-th molecule; C_0 is the center of the representative or central molecule.

sity due to the interference of a central molecule and the continuum region. For the second term the summation for p is taken over atoms in the central molecule and for q over all atoms in the discrete structure region except for the central molecule.

We assume as a first approximation that the translational and rotational intermolecular motions are mutually independent. Then the mean square deviation l_{pq}^2 is divided into two parts, the translational contribution which reflects the distribution of the distance between molecular centers and the rotational contribution which is due to the orientational fluctuation, namely,

$$\begin{aligned} l_{pq}^2 &= \langle \Delta r_{pq}^2 \rangle \\ &= \langle \Delta r_{pq}^2 \rangle^{\mathrm{tr}} + \langle \Delta r_{pq}^2 \rangle^{\mathrm{rot}}, \end{aligned} \tag{2}$$

where Δr_{pq} is the displacement from the equilibrium distance r_{pq}. We neglect the intramolecular vibrational contribution to Δr_{pq}, which is smaller than those from the intermolecular translational and rotational motions.

Translational Contribution. Let $\boldsymbol{R}_i$ be the vector which links the centers of the (i-1)-th and i-th molecules that are the nearest neighbors to each other as is shown in Fig. 1. The vector $\boldsymbol{r}_p$ is the positional vector of the p-th atom from the center of the central molecule. The q-th atom belongs to the N-th molecule. The translational displacement $\Delta r_{pq}^{\mathrm{tr}}$ is given by

$$\Delta r_{pq}^{\mathrm{tr}} = \boldsymbol{\lambda}_{pq} \cdot (\Delta \boldsymbol{R}_1 + \Delta \boldsymbol{R}_2 + \cdots + \Delta \boldsymbol{R}_N) \tag{3}$$

where $\Delta \boldsymbol{R}_i$ is the displacement vector of $\boldsymbol{R}_i$ and $\boldsymbol{\lambda}_{pq}$ is the unit vector parallel to r_{pq}, namely

$$\boldsymbol{\lambda}_{pq} = (-\boldsymbol{r}_p + \boldsymbol{R}_{1N} + \boldsymbol{r}_q)/|-\boldsymbol{r}_p + \boldsymbol{R}_{1N} + \boldsymbol{r}_q|. \tag{4}$$

The vector $\boldsymbol{R}_{1N}$ is given by

$$\boldsymbol{R}_{1N} = \boldsymbol{R}_1 + \boldsymbol{R}_2 + \cdots + \boldsymbol{R}_N. \tag{5}$$

In general there are many choices for the path connecting the central molecule to the N-th molecule. In the present treatment the shortest possible path is chosen in considering that Eq. 6 below is exact only when the contributions from the translational motion perpendicular to $\boldsymbol{R}_i$ can be ignored, in other words, when all $\boldsymbol{R}_i$ are on a straight line (see Appendix).

Let the unit vector along the average direction of $\boldsymbol{R}_i$ be t_i. Then Eq. 3 becomes approximately

$$\Delta r_{pq}^{\mathrm{tr}} = \boldsymbol{\lambda}_{pq} \cdot (\Delta R_1 \boldsymbol{t}_1 + \Delta R_2 \boldsymbol{t}_2 + \cdots + \Delta R_N \boldsymbol{t}_N) \tag{6}$$

where ΔR_i is the component of $\Delta \boldsymbol{R}_i$ along the vector t_i. Now we make assumptions as follows;

$$\langle \Delta R_i^2 \rangle = A \quad \text{for all } i, \tag{7}$$

and

$$\langle \Delta R_i \Delta R_j \rangle = \begin{cases} a & \text{for neighboring } i \text{ and } j, \\ 0 & \text{otherwise.} \end{cases} \tag{8}$$

The assumptions mean that the mean square deviation of the intermolecular separation of the neighboring molecules is A, the magnitude of the effect of coupling of adjacent intermolecular distances is described by the parameter a, and that the direct interference to the mean square deviation from the non-neighboring intermolecular distances is neglected. We obtain the following relation by using the assumptions described above,

$$\langle \Delta r_{pq}^2 \rangle^{\mathrm{tr}} = [\sum_{i=1}^{N} (\boldsymbol{\lambda}_{pq} \cdot \boldsymbol{t}_i)^2] A + [2 \sum_{i,j}{}' (\boldsymbol{\lambda}_{pq} \cdot \boldsymbol{t}_i) \cdot (\boldsymbol{\lambda}_{pq} \cdot \boldsymbol{t}_j)] a \tag{9}$$

where $\sum_{i,j}{}'$ shows the summation for i and j only when the i-th and j-th intermolecular distances are in neighbors. The coefficients for A and a can be determined when the equilibrium position and orientation for each molecule are given by a visualized structure model of the liquid.

Rotational or Librational Motion in the Liquid. The rotational displacement $\Delta \boldsymbol{r}_p$ for the p-th atom in a molecule is approximately given by

$$\Delta \boldsymbol{r}_p = \boldsymbol{r}_p \times \Delta \boldsymbol{\Omega} \tag{10}$$

where $\Delta \boldsymbol{\Omega}$ is the rotational vector with the components $\Delta \Omega_x$, $\Delta \Omega_y$, and $\Delta \Omega_z$, which are the angles of rotation around the temporarily chosen space-fixed x, y, and z-axes, respectively. Equation 10 is exact to the first order of $\Delta \Omega$, that is, when the magnitude of $\Delta \boldsymbol{\Omega}$ is small. The displacement of the p-th and q-th atoms due to the rotational or librational motion becomes

$$\Delta r_{pq}^{\mathrm{rot}} = \boldsymbol{\lambda}_{pq} \cdot (\Delta \boldsymbol{r}_p - \Delta \boldsymbol{r}_q). \tag{11}$$

Now we also assume that for a molecule

$$\langle \Delta \Omega_s \Delta \Omega_t \rangle = W \delta_{st} \tag{12}$$

and for the neighboring i-th and j-th molecules

$$\langle \Delta \Omega_s^i \Delta \Omega_t^j \rangle = w \delta_{st}, \tag{13}$$

where

$$s \text{ or } t = x,\ y, \text{ or } z$$

and δ is Kronecker's delta. For non-neighboring molecules, w is assumed to be zero. When we use the components x_p, y_p, and z_p for the vector $\boldsymbol{r}_p$, we rewrite Eq. 10 as

$$\Delta \boldsymbol{r}_p = X_p \cdot \Delta \boldsymbol{\Omega} \tag{14}$$

where

$$X_p = \begin{pmatrix} 0 & -z_p & y_p \\ z_p & 0 & -x_p \\ -y_p & x_p & 0 \end{pmatrix}$$

TABLE 1. THE COEFFICIENTS OF A, a, W, AND w FOR THE BCC MODEL[a)]

	$r_{pq}/\text{Å}$	Trans 1	Trans 2	Rot 1	Rot 2	$l_{pq}^2/\text{Å}^2$
C_0–C_1	5.90	1.0	0.0	0.0	0.0	0.203
C_0–C_2	6.813	0.667	0.667	0.0	0.0	0.291
C_0–Cl_{11}	7.670	1.0	0.0	0.0	0.0	0.203
C_0–Cl_{12}	5.566	0.910	0.0	3.129	0.0	0.501
C_0–Cl_{21}	7.967	0.689	0.601	1.527	0.0	0.434
C_0–Cl_{22}	5.968	0.628	0.628	2.721	0.0	0.549
Cl_{01}–Cl_{11}	5.90	1.0	0.0	0.0	0.0	0.203
Cl_{01}–Cl_{12}	3.914	0.818	0.0	3.671	2.658	0.361
Cl_{01}–Cl_{21}	6.813	0.667	0.667	4.177	0.0	0.713
Cl_{01}–Cl_{22}	5.188	0.667	0.460	5.690	0.0	0.817

a) Trans 1 and Trans 2 are the coefficients of A and a, in Eq. 9, respectively. Similarly, Rot 1 and Rot 2 are the coefficients of W and w, in Eq. 19, respectively.

From Eq. 11, we obtain the following relation

$$\langle \Delta r_{pq}^2 \rangle^{\text{rot}} = \langle (\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_p)^2 \rangle + \langle (\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_q)^2 \rangle - 2\langle (\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_p)(\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_q) \rangle. \tag{15}$$

Here,

$$\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_p = \tilde{\boldsymbol{\lambda}}_{pq} \cdot X_p \cdot \Delta \boldsymbol{\Omega} \tag{16}$$

where $\tilde{\boldsymbol{\lambda}}_{pq}$ is the transposed vector of $\boldsymbol{\lambda}_{pq}$. Therefore, we have

$$\langle (\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_p)^2 \rangle = \langle \tilde{\boldsymbol{\lambda}}_{pq} X_p \Delta \boldsymbol{\Omega} \Delta \tilde{\boldsymbol{\Omega}} \tilde{X}_p \boldsymbol{\lambda}_{pq} \rangle = W \tilde{\boldsymbol{\lambda}}_{pq} X_p \tilde{X}_p \boldsymbol{\lambda}_{pq}. \tag{17}$$

In the same way, we obtain the following relation,

$$\langle (\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_p)(\boldsymbol{\lambda}_{pq} \cdot \Delta \boldsymbol{r}_q) \rangle = \langle \tilde{\boldsymbol{\lambda}}_{pq} X_p \Delta \boldsymbol{\Omega}^p \Delta \tilde{\boldsymbol{\Omega}}^q \tilde{X}_q \boldsymbol{\lambda}_{pq} \rangle = w \tilde{\boldsymbol{\lambda}}_{pq} X_p \tilde{X}_q \boldsymbol{\lambda}_{pq}. \tag{18}$$

By using Eqs. 17 and 18, Eq. 15 becomes

$$\langle \Delta r_{pq}^2 \rangle^{\text{rot}} = [\tilde{\boldsymbol{\lambda}}_{pq} (X_p \tilde{X}_p + X_q \tilde{X}_q) \boldsymbol{\lambda}_{pq}] W + [-2 \tilde{\boldsymbol{\lambda}}_{pq} X_p \tilde{X}_q \boldsymbol{\lambda}_{pq}] w. \tag{19}$$

According to the assumptions, the second term vanishes except for the case that the p-th and q-th atoms belong to the neighboring molecules, respectively.

Results and Discussion

In our previous papers,[2,3] it was shown that the bcc model for the local lattice structure of liquid carbon tetrachloride was the best model for simulating the experimental X-ray scattering intensity. So we use the bcc model for the calculation of the bracketed coefficients in Eqs. 9 and 19.

After the calculation of the coefficients for all pairs p and q, we can set up an equation for the weighted structure function $si(s)$ with the parameters A, a, W, and w for the bcc model, where $i(s)$ is the reduced intensity (Eq. 1). The values for the structure parameters of the bcc model are the same as the ones in the previous paper,[2] namely, the first nearest neighbor distance R is 5.9 Å, the molecules up to the fourth nearest neighbors are included in the discrete structure region, and the radius of this structure region is 12.41 Å with the intentional damping factor l_c of 1.76 Å. In Table 1, the values of the coefficients of A and a in Eq. 9, and W and w in Eq. 19 for main atomic pairs are shown. The numbering of atoms is shown in Fig. 2.

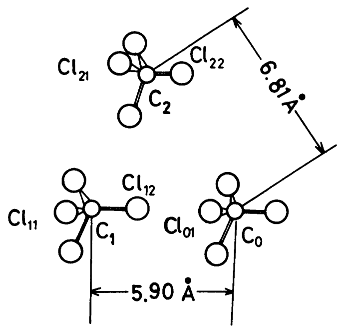

Fig. 2. The arrangement of the first and second nearest neighbor molecules in the bcc local lattice structure model for liquid carbon tetrachloride.

TABLE 2. THE REFINED PARAMETERS[a)]

$A/\text{Å}^2$	0.203 (0.041)	W/rad^2	0.101 (0.023)
$a/\text{Å}^2$	0.233 (0.122)	w/rad^2	−0.066 (0.023)

a) The values in the parentheses are standard deviations.

Carrying out a least-squares analysis by the use of our experimental $si(s)$ of the liquid carbon tetrachloride,[4] we determine the values of the fitting parameters A, a, W, and w. The s-region ranging from 1.5 to 6 Å^{-1} is used for the least-squares analysis. The result is shown in Table 2. The reliability factor defined by

$$R = \left[\sum |si(s)_{\text{exp}} - si(s)_{\text{calcd}}|^2 / \sum |si(s)_{\text{exp}}|^2 \right]^{1/2} \tag{20}$$

is 0.23. The calculated $si(s)_{\text{calcd}}$ curve using these refined parameters is shown by the solid curve in Fig. 3, with the experimental values denoted by circles.

As is shown in Fig. 3, the agreement between the experimental and calculated $si(s)$ curves has not been improved by the present treatment, in comparison with the case of using the modified Prins relation with two D constants as described in Ref. 2. By comparing the mean square amplitudes of the present treatment with respective ones obtained by the latter treatment,[2] it has proved that the values for chlorine–chlorine atomic pairs are very similar to each other, while the values

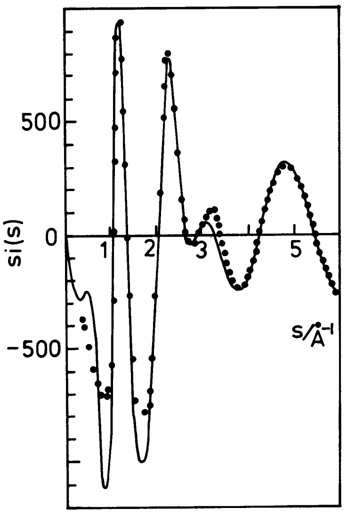

Fig. 3. The weighted structure functions $si(s)$ for liquid carbon tetrachloride. The solid curve is the calculated one and circles are experimental values.[4]

for carbon–carbon atomic pairs are significantly different. The smaller scattering power of carbon–carbon pairs makes no difference in the agreement of the $si(s)$ curves. From the point of view of only simulating the experimental $si(s)$ curve, the modified Prins relation with two D constants and the present treatment are in fair agreement. However, the physical meaning of the parameters is clear and the description of the motion of carbon tetrachloride molecules in the liquid becomes considerably clear by the present analysis.

From the value of A, 0.203 Å^2, the translational root mean-square deviation between the central and the first nearest-neighbor molecules (pair C_0–C_1) becomes 0.45 Å. The translational root mean-square deviation between the central molecule and the second nearest neighbors (pair C_0–C_2) becomes 0.54 Å. For the chlorine atoms in neighboring molecules (Cl_{01}–Cl_{11}), the value l_{pq} becomes 0.60 Å.

From the magnitude of W, 0.101 rad^2, we obtain

$$\sqrt{\langle\Delta\Omega^2\rangle} = \sqrt{\langle\Delta\Omega_x^2+\Delta\Omega_y^2+\Delta\Omega_z^2\rangle} = 0.551\ \text{rad} = 31.5^\circ \qquad (21)$$

This value shows that the root mean-square of the librational or the orientational fluctuation of a molecule is 31.5°. The error caused by using the approximated equation (Eq. 10) is estimated to be about 10% in the worst case for this considerably large amplitude of $\sqrt{<\Delta\Omega^2>}$.

The negative sign of w shows that the rotational motion is gear-like. When a molecule rotates, the nearest molecules rotate in the reverse direction, being dragged by the first molecule. Since the magnitude of $|w/W|$ is less than unity, the rotation of the first molecule is not conveyed to the nearest molecules in the perfectly coherent phase. This incoherence causes the disturbance in rotation of the molecules, *i.e.*, the rotational diffusion. However, the ratio of $|w/W|$ amounts to 0.66, which shows that by the direct effect of the rotation of a molecule the nearest neighboring molecules are dragged about 0.66× (the rotational amplitude of the molecule). It may be said that carbon tetrachloride molecules have a tendency to keep the most stabilized orientational correlation, namely, the head-tail head-tail packing in the liquid even if the molecules are vigorously moving.

Bartoli and Litovitz discussed the motion of carbon tetrachloride molecule in the liquid[13] from an analysis of the orientational broadening of Raman bands. However, it is difficult to relate the present results to their values, because both analyses are based on different theoretical points of view; in the present work a time-averaged quantity is looked for, while in the Raman studies time-correlation is the main concern.

Steinhauser and Neuman carried out molecular dynamics study for liquid carbon tetrachloride.[14] According to their result about the velocity autocorrelation function, the period of the vibratory motion of the reference particle in the cage of its neighbors was roughly 0.3 ps. If we assume that the molecules move translationally with a velocity determined by the thermal energy, half of the mean free path for the collision, which is the distance corresponding to a fourth of the period of the vibratory motion mentioned above, can be estimated as 0.10 Å, which agrees in order of magnitude with our value of 0.45 Å for the translational root mean-square deviation of the neighboring molecules. However, we are somewhat uncertain about the extent to which the correspodence between the two quantities can be physically meaningful.

Hyodo and Fujiyama ascribed the small but significant depolarization degree of the ν_1 Raman line of liquid carbon tetrachloride to the fluctuation of the local field which is felt by each molecule in the condensed phase, and formulated the expression for the degree of depolarization in terms of the mean square amplitudes of the distances between molecular centers.[15] Calculating the degree of depolarization by the use of their formula (Eq. 25 in Ref. 15) and the present translational amplitudes, we obtain the value of 0.0042. The magnitude is in good agreement with the experimental value of 0.0039.[16]

The present study suggests that by the detailed analysis of the mean square deviations of interatomic distances in liquids obtained by diffraction methods we can obtain information on the dynamics of liquids, which may be complementary to that obtained by spectroscopic techniques.

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Appendix

Expressions where Perpendicular Displacements are Included. Let s_i be the unit vector perpendicular to t_i and on the plane formed by $\boldsymbol{t}_i$ and $\boldsymbol{\lambda}_{pq}$, and ΔP_i the displacement along $\boldsymbol{s}_i$. The motion perpendicular to both $\boldsymbol{t}_i$ and $\boldsymbol{s}_i$ has no effect at all. Then we have in place of Eq. 6,

$$\Delta r_{pq}^{\mathrm{tr}} = \boldsymbol{\lambda}_{pq}\cdot(\Delta R_1\boldsymbol{t}_1+\Delta P_1\boldsymbol{s}_1+\Delta R_2\boldsymbol{t}_2+\Delta P_2\boldsymbol{s}_2+\cdots) \qquad (\mathrm{A.1})$$

The following assumptions are reasonably made in addition to Eqs. 7 and 8;

$$\begin{aligned} &\langle\Delta P_i^2\rangle = B \\ &\langle\Delta P_i\Delta P_j\rangle = 0 \qquad \text{for } i \neq j \\ &\langle\Delta P_i\Delta R_i\rangle = 0 \\ &\langle\Delta P_i\Delta R_j\rangle = \begin{cases} b & \text{for } j = i+1 \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \qquad (\mathrm{A.2})$$

Then we have

$$\begin{aligned} \langle\Delta r_{pq}^2\rangle^{\mathrm{tr}} = &\sum_{i=1}^{N}(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_i)^2A + \sum_{i=1}^{N}(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{s}_i)^2B \\ &+ 2\sum_{i,j}{}'(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_i)\cdot(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_j)a \\ &+ 2\sum_{i,j}{}'(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{s}_i)\cdot(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_j)b \end{aligned} \qquad (\mathrm{A.3})$$

corresponging to Eq. 9 in the text.

In comparing Eqs. 9 and A.3, we must regard the parameter A in the text as the effective value of

$$A + \frac{\sum(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{s}_i)^2}{\sum(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_i)^2}B \qquad (\mathrm{A.4})$$

and a as that of

$$a + \frac{\sum'(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{s}_i)\cdot(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_j)}{\sum'(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_i)\cdot(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_j)}b. \qquad (\mathrm{A.5})$$

In the case of the present study, the maximum value of $(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{s}_i)$ is about 1/2 and the minimum value of $(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{t}_i)$ is $\sqrt{3}/2$, and most of the $(\boldsymbol{\lambda}_{pq}\cdot\boldsymbol{s}_i)$ terms are nearly zero, so the coefficient of B in Eq. A.5 is much smaller than 1/3. In the same way, the coefficient of b is much smaller than $1/\sqrt{3}$. The averaged quantity B is probably of the same order of magnitude as A, but it is ignored because of the small coefficients that appear in the practical computation for the case of carbon tetrachloride. Little is known about a and b, which must be strongly dependent on the angle between $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$. At the present stage of investigations, we should be content with the fact that only the effective value of Eq. A.5 can be determined.

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