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## Path-integral effective-potential theory for EXAFS cumulants compared with the second-order perturbation

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The path-integral effective-potential (EP) method was applied to the calculations of EXAFS cumulants. The EXAFS cumulants up to the fourth order for diatomic Br<sub>2</sub> were evaluated and compared to the results by the first- and second-order perturbation theory and also the experiments. The second-order perturbation formulas for the even-order cumulants ( $C_2$  and  $C_4$ ) are newly presented. The advantages and disadvantages of the EP method are discussed.

**Keywords:** path integral; effective potential method; perturbation; cumulants.

### 1. Introduction

Recently great attention has been paid to the temperature dependence of EXAFS, which provides information on thermal vibrations including anharmonicity. The theory concerning the relationship between the EXAFS cumulants and vibrational potentials has been developed, which is based on the quantum-statistical perturbation theory (Rabus 1991; Frenkel & Rehr, 1993; Fujikawa & Miyayama, 1993; Yokoyama *et al.*, 1996a, 1996b). The perturbation method, however, includes several intrinsic difficulties for practical use: complicated formulation and computation of many-atom systems and less reliability in large anharmonic systems. For instance, the fourth-order cumulant by the first-order perturbation is negative in the case of a positive fourth-order force constant and needs the second-order perturbation to yield meaningful results.

Another quantum-statistical approach is to solve the Feynman's path integral. This method can handle greater anharmonicity. The path-integral effective-potential (EP) method has been developed by means of the variational concept (Cucoli *et al.*, 1995). Very recently, the EP theory was for the first time applied to EXAFS of two-body systems (Fujikawa *et al.*, 1997) and subsequently the results of multi-dimensional real systems such as solid fcc Kr and Ni were reported (Yokoyama, 1998), which are in excellent agreement with the experimental data.

In this proceeding, because of a limited length of the article, let us confine ourselves in a diatomic system of Br<sub>2</sub>. The EXAFS cumulants up to the fourth order are evaluated for diatomic Br<sub>2</sub> by means of the EP and the second-order perturbation (P2) theories. Analytical forms of the cumulants using the P2 theory are newly reported. The results are compared also with the experiments. Advantages and disadvantages of the EP method are discussed.

### 2. Experimental and Data Analysis

K-edge EXAFS spectra of gaseous Br<sub>2</sub> were taken by means of the conventional transmission mode at Beamline 10B in Photon Factory using a Si(311) channel-cut crystal as a monochromator.

Gaseous Br<sub>2</sub> with a saturated evaporation pressure at room temperature was stored in a quartz-and-Pyrex cell with thin quartz windows for the x-ray transmission. The measurement temperatures were 300–543 K.

The Br K-edge EXAFS oscillation function  $k^3\chi(k)$  of gaseous Br<sub>2</sub> was extracted according to a common procedure: pre and post-edge background subtraction and subsequent normalization. The obtained  $k^3\chi(k)$  function was once Fourier transformed, and after Fourier filtering of the intramolecular Br–Br shell of interest, the curve-fitting analysis was performed in  $k$  space using the fourth-order cumulant-expansion formula, although the fourth order contains large errors. Details of the analysis and the data quality can be seen in the previous works (Yokoyama *et al.*, 1996a; Yokoyama, 1998).

### 3. Theory

Let us first derive the second-order perturbation formulas of the EXAFS cumulants up to the fourth order ( $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$ ). The second-order perturbation is important for even-order cumulants since the first- and second-order perturbation provides the same order of magnitude. On the other hand, odd-order cumulants may be described within the first order.

The thermal average of some physical quantity  $\langle \hat{A} \rangle$  is expressed using a trace as

$$\langle \hat{A} \rangle = \frac{1}{Z} \text{Tr} \hat{A} e^{-\beta(\hat{H}_0 + \hat{H}')} \quad (1)$$

where  $Z = \text{Tr} e^{-\beta(\hat{H}_0 + \hat{H}')}$  is the partition function,  $\hat{H}_0$  and  $\hat{H}'$  the non-perturbed and perturbed Hamiltonian operators, respectively, and  $\beta = (k_B T)^{-1}$  ( $k_B$  the Boltzmann constant and  $T$  the temperature). In the second-order perturbation, the trace is given as the following integral form

$$\text{Tr} \hat{A} e^{-\beta(\hat{H}_0 + \hat{H}')} \cong \text{Tr} \hat{A} e^{-\beta\hat{H}_0} \left( 1 - \int_0^\beta \tilde{H}'(t_1) dt_1 + \int_0^\beta \int_0^{t_1} \tilde{H}'(t_1) \tilde{H}'(t_2) dt_2 dt_1 \right), \quad (2)$$

where  $\tilde{H}'(\beta) = e^{\beta\hat{H}_0} \hat{H}' e^{-\beta\hat{H}_0}$ . The partition function is obtained in a similar equation [ $\hat{A} = 1$  in Eq. (2)]. When the non-perturbed Hamiltonian is exactly solved, the second-order thermal average can analytically be evaluated.

A two-body system whose interatomic potential  $V(r)$  is written as a polynomial form of

$$V(r) = \frac{1}{2} \kappa_0 (r - r_0)^2 - \kappa_3 (r - r_0)^3 + \kappa_4 (r - r_0)^4 + \dots \quad (3)$$

( $\kappa_0$ ,  $\kappa_3$ ,  $\kappa_4$  are, respectively, the harmonic, third-order and fourth-order force constants) is investigated here. The third- and fourth-order potential terms are regarded as a perturbed Hamiltonian, while the harmonic term can be used as a non-perturbed Hamiltonian. Using the eigenvalues and eigenfunctions of the non-perturbed harmonic oscillator, the integral of Eq. (2) is analytically evaluated. The second-order partition function is consequently be obtained as

$$Z = Z^{(0)} + Z^{(1)} + Z^{(2)} + \dots \quad (4)$$

$$Z^{(0)} = \frac{1}{1-z}, \quad (5)$$

$$Z^{(1)} = \frac{\kappa_4 \sigma_0^4}{k_B T} \frac{3(1+z)^2}{(1-z)^3}, \quad (6)$$

$$Z^{(2)} = \frac{\kappa_3^2 \sigma_0^6}{(\hbar\omega)(k_B T)} \frac{11z^2 + 38z + 11}{(1-z)^3}, \quad (7)$$

where  $\omega = \sqrt{\kappa_0/\mu}$  ( $\mu$  the reduced mass),  $\sigma_0^2 = \hbar/(2\mu\omega)$  ( $\hbar$  the Planck constant divided by  $2\pi$ ), and  $z = e^{-\beta\hbar\omega}$ . The consequent formulas up to the fourth-order cumulant (the first order for  $C_1$  and  $C_3$ , and the second order for  $C_2$  and  $C_4$ ) are given as follows:

$$C_1 = \langle r - r_0 \rangle \cong C_1^{(1)} = \frac{6\kappa_3\sigma_0^4}{\hbar\omega} \frac{1+z}{1-z}, \quad (8)$$

$$C_2 = \langle (r - r_0 - C_1)^2 \rangle \cong C_2^{(0)} + C_2^{(1)} + C_2^{(2)}, \quad (9)$$

$$C_2^{(0)} = \sigma_0^2 \frac{1+z}{1-z}, \quad (10)$$

$$C_2^{(1)} = -\frac{\kappa_4\sigma_0^6}{\hbar\omega} \frac{12(1+z)^2}{(1-z)^2} - \frac{\kappa_4\sigma_0^6}{k_B T} \frac{24z(1+z)}{(1-z)^3}, \quad (11)$$

$$C_2^{(2)} = \frac{\kappa_3^2\sigma_0^8}{(\hbar\omega)^2} \frac{4(13z^2 + 58z + 13)}{(1-z)^2} + \frac{\kappa_3^2\sigma_0^8}{(\hbar\omega)(k_B T)} \frac{24z(1+z)}{(1-z)^3}, \quad (12)$$

$$C_3 = \langle (r - r_0 - C_1)^3 \rangle \cong C_3^{(1)} = \frac{\kappa_3\sigma_0^6}{\hbar\omega} \frac{4(z^2 + 10z + 1)}{(1-z)^2} \quad (13)$$

and

$$C_4 = \langle (r - r_0 - C_1)^4 \rangle \cong -3C_2^{(2)} \cong C_4^{(1)} + C_4^{(2)}, \quad (14)$$

$$C_4^{(1)} = -\frac{\kappa_4\sigma_0^8}{(\hbar\omega)^2} \frac{12(z^3 + 9z^2 + 9z + 1)}{(1-z)^3} - \frac{\kappa_4\sigma_0^8}{k_B T} \frac{144z^2}{(1-z)^4}, \quad (15)$$

$$C_4^{(2)} = \frac{\kappa_3^2\sigma_0^{10}}{(\hbar\omega)^2} \frac{12(5z^3 + 109z^2 + 109z + 5)}{(1-z)^3} + \frac{\kappa_3^2\sigma_0^{10}}{(\hbar\omega)(k_B T)} \frac{720z^2}{(1-z)^4}. \quad (16)$$

Note that the first-order perturbation terms of the even-order cumulants,  $C_2^{(1)}$  and  $C_4^{(2)}$  are negative, while  $C_2^{(2)}$  and  $C_4^{(1)}$  are positive.

The theory of the path-integral EP method was already established (Cuccolli *et al.*, 1995). In the Feynman's path-integral theory, the density matrix  $\rho(x)$  ( $x$  the real-space coordinate) in the one-dimensional system is given in a functional integral form of

$$\begin{aligned} \rho(x) &= \frac{1}{Z} \langle x | e^{-\beta\hat{H}} | x \rangle \\ &= \frac{1}{Z} \int_{(x,0) \Rightarrow (x,\hbar\beta)} \wp[x(u)] e^{-A[x(u)]/\hbar}, \end{aligned} \quad (17)$$

where  $A[x(u)]$  is the Euclidean action. The EP method assumes a trial Euclidean action  $A_0[x(u)]$ . In the present case, since we will treat thermal vibration, the harmonic action is a good candidate for the trial function:

$$A_0[x(u)] = \int_0^{\hbar\beta} du \left[ \frac{1}{2} \mu \dot{x}^2 + \frac{1}{2} \mu \omega^2(\bar{x}) x^2 + w(\bar{x}) \right], \quad (18)$$

where

$$\bar{x} = \frac{1}{\hbar\beta} \int_0^{\hbar\beta} du x(u) \quad (19)$$

is the average path, and  $\omega^2$  and  $w$  are the variational parameters.

An explicit form of the density matrix  $\rho(\bar{x})$  for a harmonic oscillator is known, and the trial density matrix  $\rho_0(\bar{x})$  for the present two-body (one-dimensional) case is consequently described in a integral form of

$$\rho_0(\bar{x}) \cong \sqrt{\frac{\mu}{2\pi\hbar^2\beta}} e^{-V_{eff}(\bar{x})} \frac{1}{\sqrt{2\pi\alpha(\bar{x})}} \int_{-\infty}^{\infty} dx e^{-\frac{(x-\bar{x})^2}{2\alpha(\bar{x})}} \quad (20)$$

where

$$\alpha(\bar{x}) = \frac{\hbar}{2\mu\omega(\bar{x})} \left( \coth f(\bar{x}) - \frac{1}{f(\bar{x})} \right), \quad f(\bar{x}) = \frac{\beta\hbar\omega(\bar{x})}{2} \quad (21)$$

and

$$V_{eff}(\bar{x}) = w(\bar{x}) + \frac{1}{\beta} \ln \frac{\sinh f(\bar{x})}{f(\bar{x})}. \quad (22)$$

Here,  $\alpha(\bar{x})$  is the pure quantum fluctuation (difference between the quantum-mechanical and classical Debye-Waller factors) and  $V_{eff}(\bar{x})$  is the *effective potential*. The variational parameters  $w(\bar{x})$  and  $\omega^2(\bar{x})$  are optimized using the Jensen-Feynman inequality as

$$w + \frac{1}{2}\omega^2\alpha = \frac{1}{\sqrt{2\pi\alpha}} \int_{-\infty}^{\infty} dx V(\bar{x} + x) e^{-\frac{(x-\bar{x})^2}{2\alpha}} \quad (23)$$

and

$$\omega^2 = \frac{1}{\mu\sqrt{2\pi\alpha}} \int_{-\infty}^{\infty} dx \frac{d^2V(\bar{x} + x)}{dx^2} e^{-\frac{(x-\bar{x})^2}{2\alpha}}. \quad (24)$$

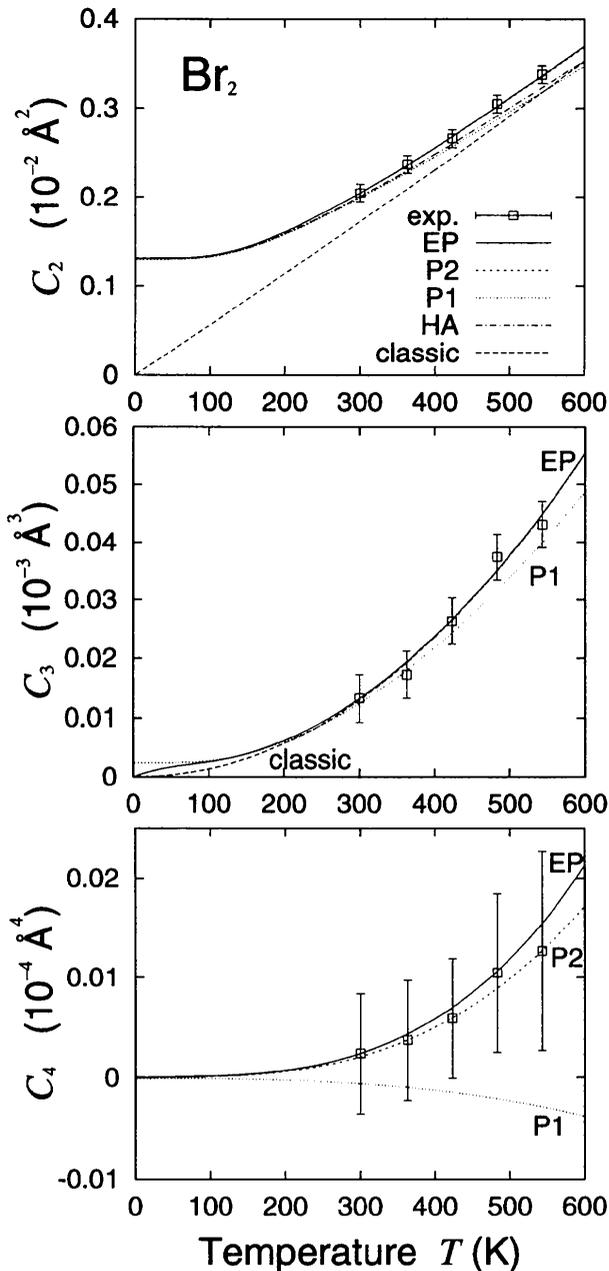
Using  $\rho_0(\bar{x})$  in Eq. (20), the EXAFS cumulants of any order can be calculated numerically.

#### 4. Results and Discussion

Employing the literature values of  $\kappa_0=2.459$  (mdyn/Å),  $\kappa_3=1.756$  (mdyn/Å<sup>2</sup>) and  $\kappa_4=1.058$  (mdyn/Å<sup>3</sup>) from the vibrational spectra for Br<sub>2</sub> (Huber & Herzberg, 1979), the EXAFS cumulants  $C_2$ ,  $C_3$  and  $C_4$  for the intramolecular Br-Br shell were calculated numerically. Figure 1 shows the EP results, together with the first- and second-order perturbation (P1 and P2, respectively); the harmonic results are also given as HA for  $C_2$  ones. The classical and experimental EXAFS data are also plotted.

In the  $C_2$  plot, the P1 results are slightly underestimated especially at high temperature compared to the EP ones because of a negative value for the first-order perturbed term, while the P2 ones agree very well with the EP ones. Although  $C_4$  is negative in the first-order perturbation, the second order (P2) approaches the EP results. There seems, however, still some underestimation for  $C_4$  in the P2 results compared to the EP ones and this indicates that higher-order perturbation would be required.

In the case of  $C_3$ , similar trends are observed. The P1 method estimates a little smaller value than the EP ones, again indicating a requirement of higher-order perturbation. The classical method shows essentially the same results as the EP one at  $T > 200$  K. As temperature goes down from  $\sim 200$  K, the classical value converges to zero monotonically as a function of  $T^2$  and gradually deviates from the two quantum-statistical methods. This is caused by the zero-point anharmonicity. At  $T < 100$  K, the EP value begins to deviate from the P1 result and converges to zero at  $T = 0$  K. In the present pair potential, there should be some finite (positive)  $C_3$  at  $T = 0$  K, implying that the P1 method predicts more appropriate  $C_3$  at a very low temperature region.



**Figure 1**

Temperature dependence of  $C_2$ ,  $C_3$  and  $C_4$  of  $\text{Br}_2$  evaluated by the EP (solid lines), the classical (classic; long-dashed lines), and the P1 (dotted lines for  $C_2$ ,  $C_3$  and  $C_4$ ) and P2 (short-dashed lines for  $C_2$  and  $C_4$ ) methods, together with the experimental data (diamonds with error bars). For  $C_2$ , the results of the harmonic approximation are also given (HA; dot-dashed line).

In order to discuss advantages and disadvantages of the EP method by comparing the perturbation theory, a previous work for many-atom systems by Yokoyama (1998) is also referred to here. In the case of solids, the perturbation calculation is extremely complicated even within the first order and the second-order perturbation would be almost inaccessible. In the perturbation calculations of solid Kr (Yokoyama *et al.*, 1997), a finite-size cluster was assumed to reduce the computational load, and thus only the EXAFS cumulants for the first-nearest neighbor Kr-Kr shell were phys-

ically meaningful. On the contrary, in the EP method the three-dimensional periodicity and higher-neighbor interactions are more easily included using the low-coupling approximation (Cuccoli *et al.*, 1995) and the results were found to agree excellently with the experimental data of solid Kr not only for the first-neighbor but for higher-neighbor shells. Moreover, many-body interactions can be treated in the EP method. To describe metallic bonds appropriately, the pair-potential approximation seems to be insufficient, and the potentials given by, for instance, the embedded-atom method (EAM) should be employed. In the previous study (Yokoyama, 1998), the EP calculation was successfully performed by combining the EAM potential of fcc Ni, and the results were found to be in excellent agreement with the experiments. Conclusively, in the EP calculations of solids, one can include many degrees of vibrational freedom, three-dimensional periodicity, higher-NN interactions, many-body interactions such as metallic bonds and larger anharmonicity in a straightforward manner, and reliable EXAFS cumulants can be obtained not only for the first-nearest shell but for higher-neighbor ones. In this point, one can recognize that the EP method is superior to the perturbation.

In the present calculations for a one-dimensional system of  $\text{Br}_2$ , some disadvantage of the EP method was seen in the estimation of  $C_3$  at low temperature. In Fig. 1(b), a strange decrease in  $C_3(\text{EP})$  was found at the temperature less than  $\sim 100$  K. This is because in the EP method the vibrational properties tend to be harmonic at the 0 K limit. This should also be true for  $C_4$ , although  $C_4$  is essentially zero and less important at low temperature. The perturbation theory can predict more accurate  $C_3$  at low temperature. The EP method is not reliable for strong quantum systems. At higher temperatures, however, the first- or second-order perturbation theory is insufficient to describe appropriate anharmonicity and higher-order expansion would be required. It can be concluded that the EP method is more practical and reliable for common systems with one degree of vibrational freedom as well as many degrees of freedoms.

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