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APPLICATION OF PATH-INTEGRAL FOR STUDYING EXAFS CUMULANTS

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Abstract. *In this work, the path-integral effective potential (PIEP) method has been applied to re-study the temperature dependence of extended X-ray absorption fine structure (EXAFS) cumulants of materials. Using the trial density matrix and effective potential expression, we derived the analytical expressions of the first three EXAFS cumulants in the first shell of materials. The cumulant relation is also calculated to determine the temperature range in which the PIEP method could be applied. Our results are compared with available experimental data as well as with those calculated by the first-order perturbation approach in anharmonic Einstein model and the reasonable agreements are achieved.*

Keywords: EXAFS cumulants, path-integral, effective potential.

I. INTRODUCTION

On the determination of the local structures of materials, the extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is one of powerful techniques. The EXAFS data can be theoretically analyzed by means of the cumulant expansion method [1]. There are several approaches used to study the temperature dependence of anharmonic EXAFS cumulants such as perturbation approach in Einstein model [2] and Debye model [3], and statistical moment method [4]. However, most of these methods still can not be valid at very high temperature due to the strong anharmonic contributions. Recently, the path-integral effective potential (PIEP) method has been efficiently used to theoretically study thermodynamic properties of materials [5–8]. This method has included the anharmonic contributions as well as the quantum effects.

In present paper, in order to expose the efficiency of PIEP on studying the thermodynamic properties of materials, we are going to re-investigate the EXAFS cumulants of diatomic Br₂ by PIEP in the wide range of temperature from 0 to 800 K. Our calculations for the first three EXAFS cumulants are going to be compared with the results of the first-order perturbation theory (PT) and experimental data when possible.

II. FORMALISM

In this section, we firstly briefly report the results of the PIEP method that have been established by Cuccoli [5], Yokoyama [6, 7] and Miyanaga *et. al.* [8]. In the quantum statistical physics, the average of a physical quantity $\langle A \rangle$ can be calculated by

$$\langle A \rangle = \frac{1}{Z} \int dx \rho(x) A(x) \quad (1)$$

where $\rho(x)$ is the density matrix and Z is the partition function.

In the PIEP theory, the trial Euclidean action $A_0[x(u)]$ is assumed as the harmonic action with the trial density matrix for two-body case has the form as

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

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, $\bar{x} = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} du x(u)$ is the average path; $\alpha(\bar{x})$, $A_0[x(u)]$ and $V_{eff}(\bar{x})$ are, respectively, the pure quantum fluctuation, trial Euclidean action and effective potential, which are correspondingly defined as follows

$$\alpha(\bar{x}) = \frac{\hbar}{2\mu\omega(\bar{x})} \left(\coth f(\bar{x}) - \frac{1}{f(\bar{x})} \right), \quad f(\bar{x}) = \frac{\beta\hbar\omega(\bar{x})}{2} \quad (3)$$

$$A_0[x(u)] = \int_0^{\beta\hbar} du \left[\frac{1}{2} \mu \dot{x}^2 + \frac{1}{2} \mu \omega^2(x) x^2 + w(\bar{x}) \right], \quad (4)$$

$$V_{eff}(\bar{x}) = w(\bar{x}) + \frac{1}{\beta} \ln \frac{\sinh f(\bar{x})}{f(\bar{x})} \quad (5)$$

The variational parameters $w(\bar{x})$ and $\omega^2(x)$ can be optimized by using the Jensen-Feynman inequality [6, 7] as

$$F \leq F_0 + \frac{1}{\beta\hbar} \langle A - A_0 \rangle_0, \quad (6)$$

where F and F_0 are the true and trial free energies of system.

The expressions of $w(\bar{x})$ and $\omega^2(x)$ have been reported in [8] as

$$\omega^2 = \omega_0^2 + 12 \frac{k_4}{\mu} \alpha - 6 \frac{k_3}{\mu} \bar{x} + 12 \frac{k_4}{\mu} \bar{x}^2 \quad (7)$$

$$w = \frac{k_0}{2} \bar{x}^2 - k_3 \bar{x}^3 + k_4 (\bar{x}^4 - 3\alpha^2) \quad (8)$$

here, k_0 , k_3 and k_4 are the harmonic, third-order and fourth-order force constants, respectively, which describe the interatomic potential $V(r)$ between two-body system as

$$V(r) \approx \frac{1}{2} k_0 (r - r_0)^2 - k_3 (r - r_0)^3 + k_4 (r - r_0)^4 \quad (9)$$

Thus, the first three EXAFS cumulants of materials within the effective-potential approximation now can be determined as follows

$$\begin{aligned}\sigma^{(1)} &= \langle r - r_0 \rangle \cong \frac{1}{Z_0} \int \bar{x} \rho_0(\bar{x}) d\bar{x} \\ \sigma^2 = \sigma^{(2)} &= \left\langle \left(r - r_0 - \sigma^{(1)} \right)^2 \right\rangle \cong \frac{1}{Z_0} \int \bar{x}^2 \rho_0(\bar{x}) d\bar{x} - \left[\sigma^{(1)} \right]^2 \\ \sigma^{(3)} &= \left\langle \left(r - r_0 - \sigma^{(1)} \right)^3 \right\rangle \cong \frac{1}{Z_0} \int \bar{x}^3 \rho_0(\bar{x}) d\bar{x} - 3\sigma^{(1)}\sigma^2 - \left[\sigma^{(1)} \right]^3\end{aligned}\quad (10)$$

where Z_0 is the trial partition function.

Using these above results, we can calculate the first three EXAFS cumulants of Br_2 numerically.

III. NUMERICAL CALCULATIONS AND DISCUSSIONS

In this section, the derived results are applied to numerically calculate the EXAFS cumulants of diatomic Br_2 . The force constants of Br_2 have been proposed as in [6, 9]: the harmonic force constant $k_0 = 2.459 \cdot 10^{-8} (\text{N}/\text{\AA})$, the third and fourth order force constants $k_3 = 1.756 \cdot 10^{-8} (\text{N}/\text{\AA}^2)$ and $k_4 = 1.058 \cdot 10^{-8} (\text{N}/\text{\AA}^3)$.

In the Figs. 1-3, we present the PIEP as well as first-order PT calculations for the first three EXAFS cumulants of diatomic Br_2 as the functions of temperature T . As it can be seen from the Figs. 2 & 3, the PIEP results are very good in agreement with the available experimental EXAFS data [10] and in Figs. 1 & 2, at low temperature $T \leq 300$ K the PIEP results are in consistent with those of PT calculations. At low temperature, these results contain the values $\sigma_0^{(1)} = 0.280 \cdot 10^{-2} (\text{\AA})$ and $\sigma_0^{(2)} = 0.131 \cdot 10^{-2} (\text{\AA}^2)$ which correspond to the zero-point vibrations of the first and second order EXAFS cumulants of diatomic Br_2 . It denotes that the quantum effects have been included in these evaluations. At temperature $T > 300$ K, the present PIEP determinations are greater than those of PT calculations. It is because of the increasing of anharmonicity when temperature increases. In the first order PT with Einstein model, it assumes that all atoms vibrate with the same frequency ω_E for all temperature range which corresponds to the neglecting of the anharmonicity at high temperature. Moreover, by fitting method, we confirm that the $\sigma^{(1)}$ and $\sigma^{(2)}$ in PT calculations are proportion to T at high temperature (about $T > 300$ K) while the results of PIEP are not really linear to T (seemly proportion to T^2). Our fitting parameters at $T > 400$ K of PIEP and PT approaches are shown in Table 1.

We show the third EXAFS cumulant of Br_2 in Fig. 3. At the temperature $T > 100$ K, the similar trends are still observed as in Figs. 1&2. However, there is a strange behavior of PIEP $\sigma^{(3)}$ at $T \downarrow 100$ K: It decreases little by little to zero at $T = 0$ K limit which means that in this case, the zero-point vibration (or quantum fluctuation) has been neglected. There are some reasons which can simply explain this difference: (1) the one-dimensional calculation for diatomic Br_2 ; (2) the vibrational properties tends to be harmonic at 0 K [7]. This result implies that, the PT method should be used instead of PIEP in evaluating EXAFS $\sigma^{(3)}$ of Br_2 at low temperature. In order to cross-check this conclusion, we make a calculation of the cumulant relation $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ which can be considered as the cumulant investigation standard for Br_2 in the temperature range 0 – 800 K. Results of PIEP as well as first-order PT approach are showed in the Fig. 4. The values

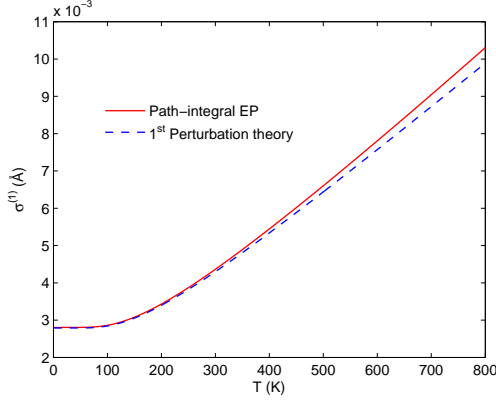


Fig. 1. Temperature-dependence of the first EXAFS cumulant of Br_2 .

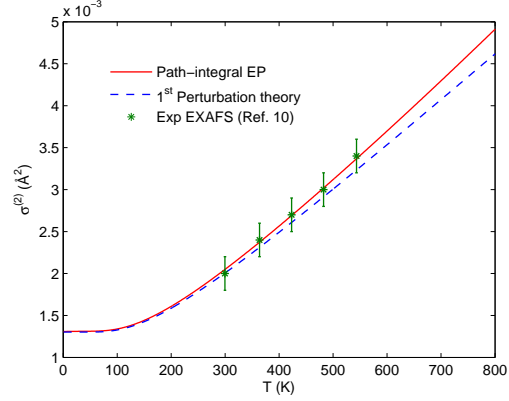


Fig. 2. Temperature-dependence of the second EXAFS cumulant of Br_2 .

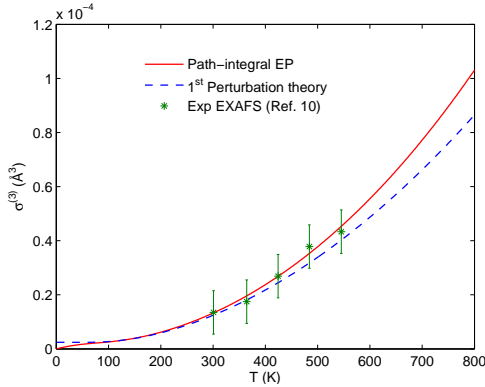


Fig. 3. Temperature-dependence of the third EXAFS cumulant of Br_2 .

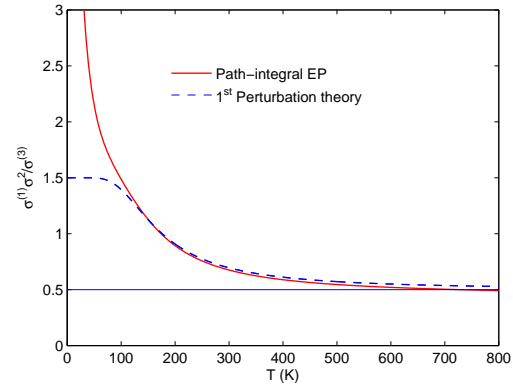


Fig. 4. Temperature-dependence of the cumulant relation $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ of Br_2 .

of cumulant relation of these two methods little by little reduce to the constant value of $1/2$ at temperature about 700 K. Furthermore, at temperature below 100 K, the cumulant relation in PIEP model reach very-high value which does not satisfy the condition obtained from experiment [11] before. This result denotes that PIEP method is not suitable for evaluating the third order EXAFS cumulant at low temperature. At temperature $T > 100$ K, the third EXAFS cumulant $\sigma^{(3)}$ calculated by PIEP as well as PT trends to proportion to the square of temperature T^2 . We display the fitting parameters of PIEP and PT results in Table 1.

IV. CONCLUSIONS

In this work, the PIEP approach has been applied to study the temperature dependence of EXAFS cumulants of diatomic materials. Using this trial density matrix expression, we have performed numerical calculations of first three EXAFS cumulants for diatomic Br_2 . Our results are in agreement with available experimental data as well as with those calculated by the first-order perturbation approach. This research has pointed out the potential of PIEP method on study

Table 1. Results of fitting PIEP and PT calculations (in temperature range $T > 400$ K) as functions $\sigma^{(n)} = a_0 + a_1T + a_2T^2$, $n = 1, 2, 3$.

	$\sigma^{(1)}(PT)$	$\sigma^{(2)}(PT)$	$\sigma^{(3)}(PT)$	$\sigma^{(1)}(PIEP)$	$\sigma^{(2)}(PIEP)$	$\sigma^{(3)}(PIEP)$
a_0	$7.41 \cdot 10^{-4}$	$3.46 \cdot 10^{-4}$	$4.61 \cdot 10^{-7}$	$1.11 \cdot 10^{-3}$	$5.28 \cdot 10^{-4}$	$7.91 \cdot 10^{-6}$
a_1	$1.14 \cdot 10^{-5}$	$5.33 \cdot 10^{-6}$	$-1.04 \cdot 10^{-9}$	$1.01 \cdot 10^{-5}$	$4.69 \cdot 10^{-6}$	$-3.90 \cdot 10^{-8}$
a_2	0	0	$1.36 \cdot 10^{-10}$	$1.70 \cdot 10^{-9}$	$9.87 \cdot 10^{-10}$	$1.97 \cdot 10^{-10}$

thermodynamic and mechanical properties of materials such as thermal expansion, bulk modulus, mean-square fluctuation...

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