

## Thermal effects on EXAFS: Ensemble averages and real-space approach

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Thermal effects on EXAFS are considered from a general perspective. The equivalence between canonical average and real space average is demonstrated without approximations in both classical and quantum regimes. The link between distribution of interatomic distances and the Hamiltonian of the system is clarified. The role of the one-dimensional effective potential is critically discussed.

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### I. INTRODUCTION

Since the 1970s, thermal effects on EXAFS have been described, in the single scattering case, by an average over a one-dimensional distribution  $\rho(r)$ :<sup>1</sup>

$$\int_0^\infty \rho(r) \frac{e^{-2r/\lambda(k)}}{r^2} e^{2ikr} dr. \quad (1)$$

This “real space” interpretation led to a relatively simple parametrization, which facilitated the analysis and contributed to a widespread use of EXAFS. The distribution  $\rho(r)$  has often been approximated by a Gaussian one, whose variance  $\sigma^2$  corresponds to the parallel mean square relative displacement<sup>2</sup>  $\langle \Delta u_{\parallel}^2 \rangle$ . Anharmonicity effects were again parametrized, for moderately disordered systems, within the framework of the cumulant method.<sup>3</sup> The actual sensitivity of EXAFS to an effective distribution  $P(r, \lambda)$  was then emphasized and the corrections due to the factors  $e^{-2r/\lambda(k)}$  and  $1/r^2$  were estimated.<sup>4</sup> More recently, the difference between EXAFS and crystallographic distance was recognized.<sup>5</sup> This discrepancy, of geometrical origin,<sup>6</sup> can be used to obtain the mean square relative displacement perpendicular to interatomic bonds<sup>7</sup>  $\langle \Delta u_{\perp}^2 \rangle$ . An up to date account on the physical interpretation of EXAFS cumulants can be found in Ref. 8.

A more general approach to thermal disorder in EXAFS can be based on ensemble averages. For example, Beni and Platzman<sup>2</sup> and later Poiarkova and Rehr<sup>9</sup> started from the relation

$$\langle e^{2ikr} \rangle = \frac{\text{Tr}(e^{-\beta H} e^{2ikr})}{\text{Tr}(e^{-\beta H})} = e^{2ikR_c} e^{-2k^2 \langle \Delta u_{\parallel}^2 \rangle}. \quad (2)$$

However, several assumptions are implicit in Eq. (2):

(i) only the main factor  $e^{2ikr}$  is considered, neglecting the influence of the terms  $e^{-2r/\lambda(k)}$  and  $1/r^2$ ;

(ii) the EXAFS distance  $\langle r \rangle = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$  is considered equivalent to the crystallographic distance  $R_c = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$ , neglecting the effect of perpendicular vibrations<sup>7,8</sup>  $\langle \Delta u_{\perp}^2 \rangle$  and possibly of higher order terms;

(iii) third and higher order cumulants are not included;

(iv) the Hamiltonian of the system is considered in harmonic approximation. Such approximations become evidently inappropriate when accurate experimental results are to be obtained<sup>8</sup> and the support of a safe underlying theory is required.

Third and fourth order cumulants have been calculated in the framework of an ensemble average<sup>10</sup> through a three-dimensional quantum perturbative approach, still maintaining however the approximations (i) and (ii).

The equivalence of the two approaches (real space and canonical average) is often considered as trivial but, to our knowledge, it has never been demonstrated on general grounds, including the low-temperature quantum regime. Fujikawa and Miyanaga<sup>10</sup> investigated the relation between real space and canonical approach, in harmonic approximation and considering only central force interactions. They concluded that the equivalence could not be guaranteed at low temperatures.

In this paper, we demonstrate the formal equivalence of the two approaches, real space and ensemble averages, and find the link between the distribution  $\rho(r)$  and the Hamiltonian  $H$  (or, classically, the potential energy  $V$ ) of the system, on the grounds of rather general formal arguments. We will start from the general expression<sup>3</sup>

$$\left\langle \frac{e^{-2r/\lambda(k)}}{r^2} e^{2ikr} \right\rangle, \quad (3)$$

still neglecting the weak dependence of the scattering factor on the instantaneous configuration  $r$  (Ref. 11). We will define this thermal average as a canonical average, restricting ourselves to the case of a single coordination shell, i.e., to a single scattering path.

The paper is organized as follows. In Sec. II the simple one-dimensional case of a two-atomic system will be considered both in classical and quantum regimes. In Sec. III the same procedure will be generalized to the three-dimensional case of a many-atomic system. The concept of effective potential will be critically discussed in Sec. IV. Section V will be dedicated to discussion and conclusions.

### II. ONE-DIMENSIONAL TWO-ATOMIC SYSTEM

As a one-dimensional system, we consider a two-atomic molecule, without rotational motion and vibrating only along the bond direction. The motion of the center of mass can be easily separated from the relative motion, both in the classical and quantum cases.<sup>12</sup> Since the pair potential energy  $V$  depends only on the relative distance  $r$ , the system is characterized by two conjugate variables: the position  $r$  and the

momentum  $p$ , which in the quantum case become the operators  $\hat{r}$  and  $\hat{p}$ .

### A. Classic treatment

For the sake of simplicity, we define the function

$$f(r) = \frac{e^{-2r/\lambda(k)} e^{2ikr}}{r^2}, \quad (4)$$

so that the calculations will be made for a generic  $f(r)$ .

The average over a canonical ensemble is defined by

$$\langle f(r) \rangle = \frac{1}{Z} \int f(r) e^{-\beta V(r)} dr, \quad (5)$$

where  $Z$  is the partition function

$$Z = \int e^{-\beta V(r)} dr$$

and  $V(r)$  is the potential energy of the system. Since the probability density of finding the system in the position  $r$  is given by

$$\rho(r) = Z^{-1} e^{-\beta V(r)}, \quad (6)$$

one obviously obtains

$$\langle f(r) \rangle = \int f(r) \rho(r) dr. \quad (7)$$

By means of Eqs. (3) and (4) one arrives at Eq. (1).

### B. Quantum treatment

The canonical average of  $f(\hat{r})$  is given by

$$\langle f(\hat{r}) \rangle = \frac{1}{Z} \text{Tr}[f(\hat{r}) e^{-\beta H(\hat{r}, \hat{p})}] \quad (8)$$

where  $Z$  is the partition function

$$Z = \text{Tr}(e^{-\beta H(\hat{r}, \hat{p})})$$

and  $H = \hat{p}^2 / (2\mu) + V(\hat{r})$  is the Hamiltonian operator.

Let us now consider atomic thermal vibrations of amplitude significantly smaller than the average interatomic distance  $\langle r \rangle$ . This seems not to be a restrictive hypothesis, since strongly anharmonic systems can be treated in classical approximation. Anyway, the domain of  $f(r)$  (or, equivalently, of its real and imaginary parts) can be considered safely distant from zero. Now,  $f(\hat{r})$  is a function of the operator  $\hat{r}$  and—in the appropriate domain discussed above—it can be formally defined as a power expansion of  $\hat{r}$  (Ref. 12):

$$f(\hat{r}) = \sum_j f_j \hat{r}^j. \quad (9)$$

This step is a fundamental one in the demonstration, since it expresses a complicated, oscillatory damped function  $f(\hat{r})$  [see Eq. (4)] in terms of simple powers of  $\hat{r}$ . Indicating the eigenstates and eigenvalues of the operator  $\hat{r}$  by  $|r\rangle$  and  $r$ , respectively, it follows from Eq. (9) that

$$f(\hat{r})|r\rangle = f(r)|r\rangle. \quad (10)$$

Making use of Eq. (10), we can now evaluate the trace of Eq. (8) in the coordinate representation:

$$\langle f(\hat{r}) \rangle = \frac{1}{Z} \int \langle r | e^{-\beta H(\hat{r}, \hat{p})} | r \rangle f(r) dr. \quad (11)$$

Since the probability density of obtaining the eigenvalue  $r$  of position is given by

$$\rho(r) = Z^{-1} \langle r | e^{-\beta H(\hat{r}, \hat{p})} | r \rangle, \quad (12)$$

one again obtains Eq. (7) and the thesis is proved.

## III. THREE-DIMENSIONAL MANY-ATOMIC SYSTEM

The three-dimensional system is characterized by  $N$  non-collinear atoms. The Hamiltonian is a function of  $6N$  variables, i.e., atomic positions  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$  and their conjugate momenta  $\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$ . In the quantum case, one deals with the position and momentum vectorial operators  $\hat{\mathbf{r}}_i, \hat{\mathbf{p}}_i$  ( $i = 1, 2, \dots, N$ ).

Without loss of generality, we label by 1 and 2 the absorber and back-scatterer atoms, respectively. EXAFS samples the modulus  $r$  of their instantaneous distance.

### A. Classic treatment

The canonical average is defined by

$$\langle f(r) \rangle = \frac{1}{Z} \int f(r) e^{-\beta V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N, \quad (13)$$

where  $Z$  is the partition function

$$Z = \int e^{-\beta V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

and  $V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is the potential energy of the system. A change of variables permits us to separate the motion of the center of mass from the relative motion of absorber and back-scatterer atoms:

$$\mathbf{r}_{CM} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}, \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1. \quad (14)$$

Since the Jacobian of the transformation (14) is unitary, we can rewrite Eq. (13) as

$$\langle f(r) \rangle = \frac{\int f(r) g(\mathbf{r}) d\mathbf{r}}{\int g(\mathbf{r}) d\mathbf{r}}, \quad (15)$$

where  $g(\mathbf{r})$  is the three-dimensional radial density function given by

$$g(\mathbf{r}) = \int e^{-\beta V(\mathbf{r}, \mathbf{r}_{CM}, \mathbf{r}_3, \dots, \mathbf{r}_N)} d\mathbf{r}_{CM} d\mathbf{r}_3 \cdots d\mathbf{r}_N \quad (16)$$

and normalized such that  $\int g(\mathbf{r}) d\mathbf{r} = N$ , where  $N$  is the coordination number of the shell. If  $g(\mathbf{r})$  is divided by the (con-

stant) numerical density of particles, one obtains the so-called “pair distribution function.”

The integral in Eq. (15) can be simplified by changing into spherical coordinates  $r, \theta, \phi$ . We can define the angular average of  $g(\mathbf{r})$  (Ref. 13) by

$$\frac{1}{4\pi} \int_{\Omega} g(\mathbf{r}) d\Omega = \langle g(\mathbf{r}) \rangle_{\Omega} = g(r), \quad (17)$$

where  $d\Omega = \sin \theta d\theta d\phi$ . In this way, Eq. (15) becomes:

$$\langle f(r) \rangle = \frac{\int g(r) f(r) r^2 dr}{\int g(r) r^2 dr}. \quad (18)$$

The one-dimensional, normalized distribution of instantaneous interatomic distances  $\rho(r)$  sampled by EXAFS can be properly defined as<sup>13</sup>

$$\rho(r) = (4\pi/N) r^2 \langle g(\mathbf{r}) \rangle_{\Omega}. \quad (19)$$

The substitution of this equation in Eq. (18) gives again Eq. (7) and the thesis is proved.

### B. Quantum treatment

The canonical average is defined by

$$\langle f(\hat{r}) \rangle = \frac{1}{Z} \text{Tr} [f(\hat{r}) e^{-\beta H(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \dots, \hat{\mathbf{r}}_N; \hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \dots, \hat{\mathbf{p}}_N)}], \quad (20)$$

where  $Z$  is the partition function

$$Z = \text{Tr} [e^{-\beta H(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \dots, \hat{\mathbf{r}}_N; \hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \dots, \hat{\mathbf{p}}_N)}]$$

and  $H = \sum_i \hat{\mathbf{p}}_i^2 / (2m_i) + V(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \dots, \hat{\mathbf{r}}_N)$  is the Hamiltonian operator. We can label by  $|\mathbf{r}_i\rangle$  and  $\mathbf{r}_i$  the eigenstates and eigenvalues of the operator  $\hat{\mathbf{r}}_i$ , respectively:

$$\hat{\mathbf{r}}_i |\mathbf{r}_i\rangle = \mathbf{r}_i |\mathbf{r}_i\rangle \quad \text{for } i = 1, 2, \dots, N.$$

Since the operators  $\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \dots, \hat{\mathbf{r}}_N$  represent a complete set of commuting observables (C.S.C.O.), the product of their eigenstates  $\{|\mathbf{r}_1\rangle |\mathbf{r}_2\rangle \cdots |\mathbf{r}_N\rangle\}$  forms a complete basis of the  $3N$ -dimensional Hilbert space. The classical change of variables, described by Eq. (14), becomes in the quantum case a change of operators and the new basis of the Hilbert space is given by the eigenvectors of the new C.S.C.O.  $\{|\mathbf{r}\rangle |\mathbf{r}_{CM}\rangle |\mathbf{r}_3\rangle \cdots |\mathbf{r}_N\rangle\}$ . This is the most suitable basis to evaluate the trace of Eq. (20):

$$\langle f(\hat{r}) \rangle = \frac{1}{Z} \int \langle \mathbf{r}, \mathbf{r}_{CM}, \mathbf{r}_3, \dots, \mathbf{r}_N | e^{-\beta H} f(\hat{r}) \times | \mathbf{r}, \mathbf{r}_{CM}, \mathbf{r}_3, \dots, \mathbf{r}_N \rangle d\mathbf{r} d\mathbf{r}_{CM} d\mathbf{r}_3 \cdots d\mathbf{r}_N. \quad (21)$$

The vectorial operator  $\hat{\mathbf{r}}$ , defined in terms of its scalar component operators as  $(\hat{x}, \hat{y}, \hat{z})$ , obeys the equation  $\hat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle$ . The scalar operator  $\hat{r}^2$  is defined by  $\hat{r}^2 = \hat{\mathbf{r}}\hat{\mathbf{r}} = \hat{x}^2 + \hat{y}^2 + \hat{z}^2$  and obeys the equation  $\hat{r}^2|\mathbf{r}\rangle = r^2|\mathbf{r}\rangle$ . The function  $f(r)$  in Eq. (4) can also be regarded as a function  $\tilde{f}(r^2)$ , where  $r = \sqrt{r^2}$ . Since the domain of  $f(r)$  is safely away from zero, remembering Eq. (9) we can write

$$f(\hat{r})|\mathbf{r}\rangle = \tilde{f}(\hat{r}^2)|\mathbf{r}\rangle = \tilde{f}(r^2)|\mathbf{r}\rangle = f(r)|\mathbf{r}\rangle. \quad (22)$$

In Eq. (21), the operator  $f(\hat{r})$  acts only on the ket  $|\mathbf{r}\rangle$  of the basis. So it is possible to use Eq. (22) and write the canonical average of  $f(\hat{r})$  as in Eq. (15), where now the three-dimensional radial density function is given by

$$g(\mathbf{r}) = \int \langle \mathbf{r}, \mathbf{r}_{CM}, \mathbf{r}_3, \dots, \mathbf{r}_N | e^{-\beta H(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \dots, \hat{\mathbf{r}}_N; \hat{\mathbf{p}}_1, \hat{\mathbf{p}}_2, \dots, \hat{\mathbf{p}}_N)} \times | \mathbf{r}, \mathbf{r}_{CM}, \mathbf{r}_3, \dots, \mathbf{r}_N \rangle d\mathbf{r}_{CM} d\mathbf{r}_3 \cdots d\mathbf{r}_N. \quad (23)$$

From now on the demonstration proceeds in the same way as in the three-dimensional classical case: one introduces the EXAFS one-dimensional distribution  $\rho(r)$  as in Eq. (19) in terms of the angular average  $\langle g(\mathbf{r}) \rangle_{\Omega}$ , which is in turn given by Eq. (17). In this way, one obtains again Eq. (7) and the thesis is proved.

### IV. EFFECTIVE POTENTIAL

The distribution of distances  $\rho(r)$  in many atomic systems has frequently been related to a one-dimensional effective potential  $V_{\text{eff}}(r)$ .<sup>3,14,15</sup> For analogy with the true one-dimensional system one classically defines  $V_{\text{eff}}(r)$ :

$$\rho(r) = Z^{-1} e^{-\beta V_{\text{eff}}(r)}. \quad (24)$$

This equation can obviously be inverted to obtain  $V_{\text{eff}}(r) = (-1/\beta) \ln \rho(r) + \text{const.}$

The quantum link between  $\rho(r)$  and  $V_{\text{eff}}(r)$  is given by

$$\rho(r) = Z^{-1} \langle r | e^{-\beta H_{\text{eff}}(\hat{r}, \hat{p})} | r \rangle, \quad (25)$$

where  $H_{\text{eff}}(\hat{r}, \hat{p}) = \hat{p}^2 / (2\mu) + V_{\text{eff}}(\hat{r})$  is an effective Hamiltonian. Contrary to Eq. (24), Eq. (25) cannot be inverted, so  $V_{\text{eff}}$  can be explicitly obtained from an EXAFS experiment only at sufficiently high temperatures, when one is safely in a classical regime.<sup>16</sup> Nor it is obvious that the minimum of the potential corresponds to the maximum of the distribution in quantum regime.

It is well established that  $V_{\text{eff}}(r)$  does not represent the true local interaction potential between absorber and back-scatterer atoms in the crystal. The introduction of an effective potential has then been justified on the grounds that its shape seems to be insensitive to thermal changes.<sup>8</sup> Anyway, the position of  $V_{\text{eff}}(r)$  shifts with temperature and its asymmetry cannot reproduce the crystallographic thermal expansion.<sup>8</sup>

It is important to point out now that the effective potential  $V_{\text{eff}}(r)$  is not involved in the calculations leading from the three-dimensional canonical average to the average over the distribution  $\rho(r)$  performed in Sec. III. Besides, the true canonical temperature dependence enters in  $\rho(r)$  through the radial density function  $g(\mathbf{r})$ , which is defined in quantum regime by Eq. (23).

It seems thus that the soundness of using the effective potential for many-atomic systems is based on phenomenological arguments, within the limits of experimental uncertainty, rather than on a rigorous demonstration.

## V. DISCUSSION AND CONCLUSIONS

The equivalence between canonical average and real space integral has been assumed valid by many authors and questioned by others.<sup>10</sup> The demonstration of the equivalence presented in this work has been performed relaxing several approximations previously used<sup>9</sup> when approaching to canonical thermal averages in EXAFS. In particular, no explicit form was assumed for the Hamiltonian  $H$  (and then this treatment intrinsically accounts for anharmonicity) or the interatomic distance  $r$ . Also, corrections due to the finite mean free path and spherical wave nature of the EXAFS photoelectron have been implicitly taken into account, since the calculations were carried out for a generic function  $f(r)$ .

The validity of the real space thermal average is not limited to the classical approximation, but holds in the general quantum case. The description of thermal effects in terms of a distribution of distances is the most widely used since the earliest works on EXAFS and the most useful for practical purposes. Indeed, the distribution  $\rho(r)$  represents the actual physical information embedded in EXAFS spectra and, if

parametrized in terms of its cumulants, it can be reconstructed through suitable data analysis. Recent experimental results have shown that it is possible to measure the quantum effects on the third cumulant at very low temperatures,<sup>7,8</sup> so that in principle the distribution  $\rho(r)$  can never be considered normal. While in the one-dimensional case the definition of the distribution  $\rho(r)$  and its link with the Hamiltonian of the system are quite immediate, the reduction of the three-dimensional reality of a many-atomic system to an one-dimensional distribution of distances requires a more careful treatment, through the introduction of a radial distribution function.

The present work, definitively assessing the equivalence between canonical average and real space approach, puts on firmer grounds the standard treatment of thermal disorder in EXAFS. Further efforts should be done to generalize the formal treatment to the case of multiple scattering paths, either relying on a distribution of instantaneous half path lengths<sup>11</sup> or on configurational averages over a distribution of generalized coordinates.<sup>17</sup>

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