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Nuclear Motion Effects on the Density Matrix of Crystals: An Ab initio Monte Carlo Harmonic Approach

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In the frame of the Born-Oppenheimer approximation, nuclear motions in crystals can be simulated rather accurately using a harmonic model. In turn, the electronic first-order density matrix (DM) can be expressed as the statistically weighted average over all its determinations each resulting from an instantaneous nuclear configuration. This model has been implemented in a computational scheme which adopts an ab initio one-electron (Hartree-Fock or Kohn-Sham) Hamiltonian in the Crystal program. After selecting a supercell of reasonable size and solving the corresponding vibrational problem in the harmonic approximation, a Metropolis algorithm is adopted for generating a sample of nuclear configurations which reflects their probability distribution at a given temperature. For each configuration in the sample the “instantaneous” DM is calculated, and its contribution to the observables of interest is extracted. Translational and point symmetry of the crystal as reflected in its average DM are fully exploited. The influence of zero-point and thermal motion of nuclei on such important first-order observables as X-ray structure factors and Compton profiles can thus be estimated.

I. INTRODUCTION

\[ V_{ij} = \left( \frac{\partial^2 E}{\partial x_i \partial x_j} \right) \]

\[ \pi = \frac{1}{N} \sum_{j=1}^{N} w_j \]

Detailed information about the electronic structure of crystalline compounds is provided by observables related to the one-electron density matrix (DM), such as the electron charge density (ECD) \([\rho(\mathbf{r})]\) and the electron momentum density (EMD) \([\pi(\mathbf{p})]\). The ECD is obtainable from diffraction experiments and is straightforwardly related to the topological features of the system in direct space, thus to position of nuclei and characteristics of bonds. The EMD can be reconstructed from directional Compton scattering experiments: the analysis of the distribution in momentum space of the slow valence electrons is known to provide valuable complementary insight into the chemical features of the system.

Quite recently, the entrance into a new age of molecular quantum chemistry has been declared: “In the fourth age we are able to incorporate into our quantum chemical treatment the motion of nuclei [...] and compute accurate, temperature-dependent, effective properties, thus closing the gap between measurements and electronic structure computations”. The approach presented here goes in that direction and allows for the description, even if approximate, of nuclear motion effects on the electronic density matrix and related properties of crystalline materials.

Rarely diffraction or Compton scattering experiments are carried out at sufficiently low temperature such that the effect of thermal nuclear motion can be completely neglected. Due to the fact that core and inner-valence electrons of atoms follow the movement of the respective nuclei, when ECD and related X-ray structure factors (XSF) are considered, it is mandatory to account for the effect of finite temperature, for instance by means of atomic harmonic Debye-Waller thermal factors. An enormous amount of literature has been devoted to the approximate evaluation of such effects in order to allow for a correct interpretation of the X-ray scattering data. In particular, attempts to go beyond the harmonic approximation and to properly describe thermal diffuse scattering have been presented extensively. The rigid-atom approximation, which involves an arbitrary partition into atomic subregions of the total ECD of the system, is, however, usually retained. The approach that we present in this paper allows to go beyond such a questionable, even if effective in most cases, approximation.

The situation is completely different as concerns the other fundamental DM-related property, EMD: in this case the usual approximation of completely neglecting nuclear motions can result in a reasonable estimate of the Compton profiles (CP) and the effect of finite temperature is seldom explicitly considered, although few ad hoc models have been reported. After recalling that the content of information of a rich set of directional CPs is the same as that of the EMD, the following question can be asked: why is the distribution of electron velocities so scarcely affected by the movement of the nuclei? The answer is physically intuitive. The velocity of core electrons is hardly affected by the movement of their respective nuclei; that of valence electrons is more sensitive to the instantaneous change of the distances between neighboring nuclei, but the effect is in a sense a second-order one. It is therefore to be expected that rather sophisticated computations are required in order to unambiguously recognize the response of CPs to nuclear motion.
We shall show in Section III that the present method actually can.

The information contained in the DM of a crystal, which is complementary to that concerning total energy and related quantities, is extremely helpful for assessing merits and limitations of computational schemes for crystals. We have recently shown that very accurate directional Compton profiles (CP), as can be measured from the inelastic scattering of high intensity synchrotron radiation by single-crystal samples, can reveal subtle aspects of the electronic structure of periodic systems. In the cases of Urea, Silicon and Quartz the theoretical CPs obtained using single-determinantal approximations to the ground-state wave function were found in fact to present definite discrepancies with respect to the experiment, which were partly removed when use was made of an ab initio technique based on a multi-determinantal description of the wave function. This interesting outcome has encouraged us to take a closer look to the possible reasons for the residual differences between theoretical and experimental CPs. In this paper we address one of the aspects which are usually disregarded when simulating EMDs that is, the effect of zero-point and thermal motion of nuclei on DM-derived quantities. The effect of temperature on both the ECD and the EMD is treated here on the same footing.

Before describing analytically in Section II the model adopted, let us anticipate its essentials.

The Born-Oppenheimer (BO) approximation will be systematically adopted, according to which the eigenfunctions $\Psi_M(R)$ and the associated eigenvalues $E_M$ which describe the nuclear motions result from the Schrödinger equation for the nuclei in the potential field $V(R)$; in turn, $V(R)$ is the ground-state energy of the many-electron system corresponding to nuclei fixed in configuration $R$. The Boltzmann probability distribution for the nuclei at a temperature $T$ can be expressed as follows:

$$P_T(R) = \frac{1}{Z(T)} \sum_M \exp(-E_M/k_B T) |\Psi_M(R)|^2 ;$$

$$Z(T) = \sum_M \exp(-E_M/k_B T) .$$

where $k_B$ is Boltzmann's constant and $Z(T)$ the nuclear partition function.

By invoking again the BO approximation, the statistically averaged DM will be given by:

$$\tau_T(r;r') = \int dR \ P_T(R) \ \gamma(r;r'|R) .$$

This expression looks formidable, in particular because the integrand is extended in principle to the nuclear coordinates of the whole crystal, and translational symmetry cannot be exploited, except for a trivial invariance of $P_T(R)$ with respect to a translation of all nuclear coordinates by the same lattice vector. We shall show below that the use of the harmonic approximation combined with a supercell (SC) model will make the evaluation of $\tau_T$ computationally feasible.

Practically, the approach to be described here has been implemented in the ab initio public program CRYSTAL which solves the “periodic” problem for a number of one-electron self-consistent-field Hamiltonians. Either the Hartree-Fock (HF) approximation, or one of a variety of Density-Functional-Theory (DFT) schemes in the Kohn-Sham formulation, or still hybrid-exchange techniques can be adopted. The extension of the present approach to post-HF techniques is discussed with reference to the public CRYSCOR program.

In this paper we present the formalism of a new ab initio Monte Carlo approach to the rigorous study of nuclear motion effects on a variety of DM-related properties of crystalline materials, both in position and momentum space. The influence of the main parameters of the method is investigated, with reference to the simple test case represented by the cubic crystal of silicon, in order to demonstrate its accuracy and consistency; preliminary results on both X-ray structure factors and CPs are presented.

The plan of this paper is as follows. Section II exposes the procedure adopted for evaluating the thermally averaged observables and it is divided into six subsections. Section II A presents and justifies the SC-harmonic model of nuclear motions which gives us an explicit expression of $P_T(R)$. Section II B describes the Metropolis algorithm here adopted for generating a set $\{R_J\}$ of nuclear configurations distributed according to $P_T$; the statistical significance of the sampling set and the choice of a suitable “Metropolis step” is discussed theoretically and numerically taking crystalline silicon as a test case. Section II C demonstrates how it is possible to exploit the full symmetry of the crystal which is preserved in the average observables, thus increasing by a large factor the significance of the sampling set. In Section II D the computational set-up adopted in CRYSTAL for solving the harmonic problem and collecting preliminary information is discussed in general terms. Section II E shows how the DM associated to each given nuclear configuration of the sampling set can be obtained from SC calculations performed with CRYSTAL. In Section II F, we consider the possibility of approximately correcting the statistical DM obtained from a Hartree-Fock (HF) calculation in order to include correlation effects by using the CRYSCOR program which implements Moller-Plesset perturbation theory truncated at order two (MP2) in a local fully periodic formulation. In Section III the above procedure is applied to crystalline silicon and some preliminary results are reported as concerns the computation of X-ray dynamical structure factors and thermal CPs. The intent is here to investigate the effect of the main parameters involved in the computed properties. Some general conclusions are drawn and an outline of prospective work is sketched in Section IV. Explicit formulae for the determination of the expansion coefficients of the DM observables and details about
their computational implementation are provided in the Appendices.

II. THEORETICAL DETERMINATION OF THE STATISTICAL DENSITY MATRIX

A. Supercell-harmonic description of nuclear motions

The quantum-mechanical description of the nuclear motions in the BO approximation is dictated by the shape of the potential energy surface $V(R)$. Let us fix for definiteness some notations. The configuration $R$ which describes the instantaneous position of all nuclei in the crystal can be specified by assigning to each of them the displacement with respect to their equilibrium position:

$$R = \{ \ldots , [(R_0)_a + g + d^a_i], \ldots \} .$$  (3)

The index $a (a = 1, \ldots , N)$ labels the general nucleus in the unit cell and $(R_0)_a$ is its equilibrium position in the reference zero cell; the lattice vector $g = \sum_{m=1}^3 b^m_a a_m$ identifies the general crystal cell where $a_m$ are the direct lattice vectors: in a cyclic crystal model the integers $b^m_a$ run from 0 to $L^m - 1$. When dealing with cubic crystals (as here for simplicity) all $L_n$'s are set to a common value $L$. $V(R)$ is a function of the displacements $d^a_i$ or, equivalently, of their cartesian coordinates $x^a_i$, the index $j$ running from 1 to $3N$. By expanding in a Taylor series $V(R)$ with respect to these coordinates about the equilibrium $R_0$ configuration, after setting $V(R_0) = 0$, and exploiting translational invariance, the usual expression is obtained:

$$V(R) = \frac{L^3}{2} \sum_{i,j} V^{ij}_g x^i_0 x^j_0 + O_3(\{x^g\}) .$$  (4)

The harmonic approximation which will be adopted here consists in neglecting all $O_3$ terms. This truncation to second-order terms implies that the potential energy only depends on the independent (non-coherent) motion of two atoms at a time; it however does not entail, as we shall see, that the same property holds true for the resulting probability distribution $P_T(R)$.

Before using the consequences of the harmonic approximation, it is expedient to justify briefly its use in the present context. Its enormous success is due not only to its simplicity but also to its predicting power. The evaluation of the second-order derivatives with respect to the displacement coordinates around the equilibrium configuration ($V^{ij}_g$) can nowadays be performed accurately and cheaply by standard periodic codes based on one-electron Hamiltonians. The solution of the corresponding Schrödinger equation is straightforward, as we shall recall in a moment. The accurate description of vibrational frequencies for most crystalline compounds when suitable Hamiltonians are adopted is a strong argument in its favor. Its main deficiencies in this respect are the need for anharmonic corrections when very light atoms are involved and for long-range terms to account for the longitudinal-optical/transverse-optical (LO/TO) splitting in ionic compounds. More generally relevant is the fact that in the harmonic approximation the equilibrium positions of atoms do not change with temperature (see below).

It is shown in standard textbooks that translational invariance permits us to factorize the harmonic Schrödinger equation for the nuclear motions into $L^3$ separate ones, each associated to a wavevector $k = \sum_{n=1}^3 (\kappa_n/L) b_n$ where $b_n$ are the reciprocal lattice vectors and the indices $\kappa_n$ run from 0 to $L^m - 1$. After defining for each $k$ the $3N \times 3N$ dynamical matrix $W^k$, with elements:

$$W^k_{ij} = \frac{1}{\sqrt{M_j M_i}} \sum_g \exp(i k \cdot g) V^{ij}_g$$

($M_i$ being the mass of the nucleus associated to the $i$-th coordinate), the solution is obtained through the diagonalization of $W^k$:

$$(U^k) V^k U^k = \Lambda^k$$  (5)

The elements of the diagonal $\Lambda^k$ matrix provide the vibrational frequencies $\nu^k = \sqrt{\kappa}$ (here and in the following atomic units are adopted), while the columns of the $U^k$ matrix give the corresponding normal coordinates:

$$q^k_i = \frac{1}{\sqrt{L^3}} \sum_{j=1}^{3N} \sqrt{M_j} U^k_{ij} \sum_g \exp(i k \cdot g) x^g_j .$$

The general eigenfunction and the corresponding eigenvalue are identified by the vector of non-negative integers $M = \{ m_1^k, \ldots , m_N^k \}$, which assigns the level of excitation of all vibrational modes (phonons): $\Psi_M(R) = \prod_{i,k} \mathbb{H}_{m_i^k} \left( \lambda_i^{k^\dagger} q^k_i \right)$ ;

$$E_M = \sum_{i,k} \epsilon_{m_i^k} = \left( m_i^k + \frac{1}{2} \right) \frac{\nu_i^k}{2 \pi} .$$  (7)

$\mathbb{H}_m(x)$ is proportional to the normalized associated Hermite function of order $m$; the correspondence $R \leftrightarrow \{x^g\} \leftrightarrow \{q^k\} \leftrightarrow \{\xi^k\} = \{ (\lambda_i^{k^\dagger} q^k_i) \}$ is implicit here and in the following. $\xi$ are the frequency-scaled coordinates; $\xi = 1$ corresponds to the classical elongation.

Substitution in equation (1) and exploitation of the simple dependence of $E_M$ on the excitation levels, results in the following compact expression of the probability distribution for the nuclei in the harmonic $\{ [h] \}$ approximation:

$$P_T^{(h)}(R) = \prod_{i,k} p_T(\xi_i^k) ;$$

$$p_T(\xi_i^k) = \left[ 1 - \exp \left( - \frac{\nu_i^k}{2 \pi k_B T} \right) \right] \times$$

$$\times \sum_{m_i^k} \exp \left( - \frac{m_i^k \nu_i^k}{2 \pi k_B T} \right) [\mathbb{H}_{m_i^k}(\xi_i^k)]^2 .$$  (8)
Note that the zero of energy has been set here at the fundamental harmonic level $E_0$. The product $\prod$ excludes the three zero-frequency modes which correspond to pure translations.

From $P_T^{(b)}$ the average value of the product of a given multiplet of displacement coordinates can be obtained after integration over all remaining coordinates. Trivially, $(\langle x_i^b \rangle_T^{(b)}) = 0$ for all coordinates: only the inclusion of anharmonic corrections can account for their temperature dependence, in particular for the change of volume with temperature. Of special interest is the $(3N) \times (3NL^3)$ rectangular matrix $X$ which gives the average value of pair-products (due to translational invariance, the first coordinate can be assigned to the zero cell):

$$X_i^k = \langle x_i^0 \cdot x_j^k \rangle_T^{(b)} .$$

Here $(\cdots)^{(b)}_T$ denotes the expectation with respect to the harmonic probability density of the displacements at temperature $T$. The $3 \times 3$ blocks along the diagonal of the square submatrix $\{X_i^0\}$ define the so-called atomic displacement parameters (ADP) which are used in the analysis of X-ray factors. The $X$ matrix can also be calculated analytically in the harmonic approximation.

B. Sampling the nuclear configurations

Having at hand the explicit though approximate expression (8) for the harmonic distribution of nuclear motions, we want to generate from there a set of coordinates $\{R_I\}$ $(I = 1, \ldots, T)$ such as to provide a non-biased estimate of the statistically averaged DM as defined in equation (2) whose accuracy will depend on the size $T$ of the sample:

$$\gamma_T^{(b)}(r; r') \approx \frac{1}{T} \sum_{I=1}^{T} \gamma(r; r'|R_I) .$$

A Metropolis algorithm will be adopted for this purpose which can be described as follows, $r$ representing each time a new random number from a uniform distribution in the interval $[0, 1]$.

1. Choose a temperature $T$ and select the size $T$ of the sample and a step $\tau$ of exploration of the normal coordinates. Set the current $I$ value to 1. Choose a starting configuration $R_I \equiv \{x_i^0\}_I$ (for instance, set initially to 1 all normal coordinates) and calculate the corresponding value $P_I = P_T^{(b)}(\{R_I\})$ from equation (8).

2. Generate a new trial configuration $R'_I$ by adding to each normal coordinate of the $I$-th step the quantity $(2r - 1)\tau$; calculate $P'_I = P_T^{(b)}(\{R'_I\})$.

3. If $P'_I / P_I < r$ , then “reject the step forward” and back-substitute the trial configuration with the current one ($R'_I = R_I$, $P'_I = P_I$).

4. Set I to I+1 and define: $R_I = R'_I$, $P_I = P'_I$. If $I < T$, then go to step 2 for a new trial; otherwise exit the procedure.

This kind of selection is simple and rapid. Before discussing the reliability and usefulness of the collected sample $\{R_I\}$, let us define an equivalent Weighted Coordinate Sample (WCS):

$$\{\{R_J, w_J\} \} = \{R_I\} .$$

Here the index $J = 1, \ldots, N$ labels each newly accepted configuration, while the weight $w_J$ is the number of times that configuration is repeated at steps 3-4 of the Metropolis procedure before accepting a new one. $N$ is thus the actual number of accepted configurations. Equation (10) can then be rewritten as follows:

$$\gamma_T^{(b)}(r; r') \approx \frac{1}{N} \sum_{J=1}^{N} w_J \gamma(r; r'|R_J) .$$

The average weight $\overline{\gamma} = T/N$ obviously increases with increasing $\tau$ (it is less likely with a large exploration step to move from a reasonable configuration to another of comparable probability). It has originally been suggested, for the maximum significance of a sample of size $T$, to select $\tau$ in such a way that $\overline{\gamma} \approx 2$, that is that half of the trials are accepted on average. However, a lot of work has been done to calibrate the optimal acceptance rate of such algorithm in its several formulations.

The remaining part of this section is devoted to the discussion of how to choose reasonable values for $N$ and $\tau$; as a test case, we consider the crystal of silicon. In order to decouple the nuclear motions of atoms formally assigned to different unit cells in the crystal, the use of a supercell (SC) is necessary, as far as systems with small unit cells are considered. In the case of crystalline silicon, for instance, a repetitive SC corresponding to $L = 2$ (with reference to the conventional cubic cell of this face-centered-cubic crystal), which contains 64 atoms, is essentially adequate. This corresponds to $3NL^3 - 3 = 189$ normal modes to be sampled.

In order to appreciate the significance of a given set of accepted weighted nuclear configurations (defined by $N$ and $\tau$), we can evaluate from it selected multiplet-products $\langle \Pi \rangle = \langle \langle x_i^1 x_j^2 \rangle \rangle$ of displacement coordinates and associate to them their corresponding standard deviations $\sigma_\Pi$ about their average $\langle \Pi \rangle$. For finite sampling size all $\sigma_\Pi$’s should be zero. To define standard deviations $\sigma_\Pi$, once fixed the values of $N$ and $\tau$, the Metropolis algorithm is repeated 1000 times so that, at the end, we are left with 1000 determinations of $\langle \Pi \rangle$ from which an average $\langle \Pi \rangle$ and a corresponding standard deviation
two pair-products of displacement coordinates for silicon as a function of temperature, in $10^{-4}$ Å²; a diagonal element ($\langle x^0_i x^0_i \rangle$, namely the anisotropic displacement parameter (ADP), and the most important out-of-diagonal element which refers to the simultaneous displacement of two nearest neighbor atoms in the Si-Si-Si plane ($\langle x^0_i x^0_j \rangle$). The standard deviations concern sets of weighted configurations of approximately the same size ($T \approx 3000$) but obtained with four different $\tau$ values, as indicated; the respective average weights $\bar{w}$ are reported. These results refer to the PBE functional with the 6-21G* basis set from Ref. 35 on a conventional SC with $L = 2$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$(\Pi)_{av}$ ($\langle x^0_i x^0_i \rangle$, $\langle x^0_i x^0_j \rangle$)</th>
<th>$\sigma_{\Pi}$ ($\langle x^0_i x^0_i \rangle$, $\langle x^0_i x^0_j \rangle$)</th>
<th>$\tau$</th>
<th>$w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.026 3.192</td>
<td>0.077 0.061 0.4 41.1</td>
<td>0.096 0.081 0.3 10.9</td>
<td>0.147 0.134 0.2 3.8</td>
</tr>
<tr>
<td>100</td>
<td>23.841 4.892</td>
<td>0.097 0.082 0.4 33.8</td>
<td>0.117 0.105 0.3 9.7</td>
<td>0.176 0.156 0.2 3.6</td>
</tr>
<tr>
<td>200</td>
<td>33.263 8.604</td>
<td>0.142 0.131 0.4 21.3</td>
<td>0.215 0.209 0.3 7.3</td>
<td>0.317 0.304 0.2 3.1</td>
</tr>
<tr>
<td>300</td>
<td>45.995 13.352</td>
<td>0.239 0.223 0.4 13.8</td>
<td>0.342 0.335 0.3 5.6</td>
<td>0.486 0.472 0.2 2.7</td>
</tr>
</tbody>
</table>

$\Pi$ are easily obtained. Tables I and II clearly show how such average values are stable.

Table I shows the dependence on temperature of two important pair-products $(\Pi)_{av}$ and of their standard deviations for $T \approx 3000$ and for four values of $\tau$: 0.1, 0.2, 0.3 and 0.4. The values there reported are obtained with the PBE generalized gradient functional$^{36}$ of the DFT and a 6-21G* basis set from Ref. 35, on a conventional SC with $L = 2$. The first pair-product in this table represents the atomic anisotropic displacement parameter (ADP) of crystalline silicon which is here obtained as a by-product of the scheme. The value at 300 K ($45.99 \times 10^{-4}$ Å²), for instance, can be compared to the corresponding analytical determination of it: 45.98 $\times 10^{-4}$ Å².$^{31}$ The following can be observed.

The average weight $w$ of each set of weighted configurations decreases with temperature, as expected, and it is about an order of magnitude larger with the larger $\tau$. A step $\tau \approx 0.1 - 0.2$ corresponds to the standard Metropolis choice, since the weight in that case is about 2 at all temperatures. The much better performance of the sets of weighted configurations obtained using $\tau = 0.4$ is evident from the fact that the corresponding $\sigma_{\Pi}$'s are smaller by about a factor 5 with respect to the case $\tau = 0.1$. It can incidentally be noted that those standard deviations increase with temperature, and that for given $T$, $\tau$ their value is practically the same for the two pair-products.

As it is known from standard statistical analysis, the standard deviations $\sigma_{\Pi}$'s are proportional to $1/\sqrt{N}$. The size of the sample required for a given accuracy can be estimated from that dependence and from the data of $\bar{w}$ reported in Table I. Let us recall that the size of the sample $T = N \times \bar{w}$ defines the number $N$ of self-consistent-field calculations to be performed on a supercell without any symmetry (apart from the translational one at the SC scale). In order to reduce the computational resources needed and to make this technique feasible at all, the lowest number of configurations compatible with a chosen accuracy has to be selected.

To drive such a choice, we report in Table II the standard deviations $\sigma_{\Pi}$’s related to the average $(\Pi)_{av} = (\langle x^0_i x^0_i \rangle, \langle x^0_i x^0_j \rangle)$ pair-product of displacement coordinates (i.e. to the ADP) at $T = 298.15$ K as a function of the adopted Metropolis step $\tau$ and number of accepted configurations $N$. Computational parameters are as in Table I. It is seen that the standard deviations are reduced both by increasing the number of accepted configurations $N$ and increasing the step $\tau$. Since the computational cost is proportional to $N$, it is expedient to exploit the dependence from $\tau$. From the table it can be inferred that, even with $500 \leq N \leq 1000$, good accuracies ($\approx 0.3\%$) could be reached by using high values for the step; for $\tau = 0.5$ the average
TABLE III: Average square of the frequency-scaled normal coordinates \( \langle \xi^2 \rangle (N, \tau, T) \) in a sample of \( N = 1000 \) configurations, as a function of the adopted step \( \tau \) at two temperatures: 0.001 K and 298.15 K.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \tau )</th>
<th>0.001</th>
<th>298.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.4988</td>
<td>0.8734</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.5012</td>
<td>0.8754</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.4989</td>
<td>0.8723</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.5019</td>
<td>0.8710</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.4993</td>
<td>0.8754</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.5031</td>
<td>0.8731</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.5087</td>
<td>0.8766</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.5163</td>
<td>0.8798</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.5274</td>
<td>0.8845</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.5315</td>
<td>0.8887</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>0.5362</td>
<td>0.8930</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>0.5389</td>
<td>0.8972</td>
<td></td>
</tr>
</tbody>
</table>

The weight \( \overline{\mathbf{w}} \) of each configuration in equation (12) turns out to be 42.2 that is very convenient in this case.

Unluckily, as mentioned before, step \( \tau \) can not be increased indefinitely without deteriorating the significance of the statistical sample. For instance, given a particular choice of temperature \( T \), number of accepted configurations \( N \) and step \( \tau \), let us define the quantity:

\[
\langle \xi^2 \rangle (N, \tau, T) = \frac{1}{N^3NL^3} \sum_{j=1}^{N} \sum_{\mathbf{ik}} |\xi_{i,j}^{k}|^2 \, . \tag{13}
\]

This is a measure of the average square of the frequency-scaled normal coordinates in the sample. When \( T = 0 \) K, all the \( 3NL^3 \) phonons in the crystal are found in their fundamental state and \( \langle \xi^2 \rangle (N, 0, 0K) \) should be theoretically equal to 1/2. In Table III, we report this quantity as a function of the adopted step \( \tau \), for a sample of \( N = 1000 \) configurations at two temperatures: 0.001 K and 298.15 K. The data for \( T = 0.001 \) K clearly show a diverging deviation from the expected value of 1/2 for \( \tau \geq 0.7 \). A similar divergence is observed also in the data at 298.15 K.

At the end, we have seen how, to obtain a reliable statistically averaged DM according to equation (12), the electronic problem for the supercell comprising \( NL^3 \) atoms should be solved about a thousand times (\( N \approx 10^3 \)). The additional difficulty must be considered that no symmetry is retained by the general \( R_f \) configuration except the translational one at the SC scale. Space group symmetry can however be exploited while performing the averaging procedure, as described in the next section.

C. Full exploitation of symmetry

The general symmetry operator \( \hat{S} \) of our cyclic crystal and its effect on any function of the space coordinates can be expressed as follows:

\[
\hat{S} \{V|g_s + t(V_s)\} \quad ;
\]

\[
\hat{S} \{f(..., r, ..., r', ...)\} = f(..., r_s, ..., r_s', ...) \quad ;
\]

\[
\mathbf{r}_s = (V_s)^{-1} \mathbf{r} - g_s - t(V_s) \quad . \tag{14}
\]

Here \( V \) is a \( 3 \times 3 \) matrix which effects a point symmetry operation on the \( \mathbf{r} \) coordinates; there are \( h \) different such matrices which form on the whole the point group of the crystal. \( g = \sum_{m=1}^{3} (l_m, \text{mod} L) \alpha_m \) is the general lattice vector of the cyclic crystal, while \( t(V) \) is a fractional translation which may be associated to a subgroup of \( V \) rotations (in symmorphic space groups, all \( t(V) \)'s are \( 0 \)). The order of the cyclic space group is then \( S = hL^3 \). Each sampled \( R_f \) is in fact representative of \( S \) equivalent configurations. When evaluating the thermal average \( \overline{\gamma} (Y) \) of a quantity of interest \( Y \), this property can be used to reduce the sample size from \( N \) (as it would be required if no account of symmetry were taken) to \( N/S \) for a given significance. Let us see now how this is possible with reference to the two most important DM-related quantities, namely the ECD, \( \rho (\mathbf{r}) \), and the EMD, \( \pi (\mathbf{p}) \) (see Introduction).

The scheme below summarizes the relation between these quantities and the DM in the coordinate and momentum representation, related to each other by a six-dimensional Fourier transformation (6D-FT):

\[
\gamma (\mathbf{r}_s, \mathbf{r'}_s) \xrightarrow{\text{6-D-FT}} \rho (\mathbf{r}) = \rho (\mathbf{r}_s)
\]

\[
\gamma (\mathbf{p}_v, \mathbf{p'}_v) \xrightarrow{\text{6-D-FT}} \pi (\mathbf{p}) = \pi (\mathbf{p}_v)
\]

\[
\gamma (-\mathbf{p}, -\mathbf{p'}) \xrightarrow{\text{6-D-FT}} \pi (\mathbf{p}) = \pi (-\mathbf{p}) \, . \tag{15}
\]

Here \( \xrightarrow{\text{D}} \) means taking the diagonal of a two-variable function, while \( \mathbf{p}_v = V^{-1} \mathbf{p} \). The relation in the last line is due to time reversal symmetry, and is valid even if the point group does not contain the inversion. Note the different symmetry features of ECD and EMD for the perfect crystal, which must be preserved when performing the thermal average.

A symmetry-adapted form of the thermally averaged ECD is simply obtained by its expansion in an orthonormal set of symmetrized plane waves (SPW) \{\( \Omega_i (\mathbf{r}) \)\}, associated to the different \( \text{stars} \) of \( \mathbf{K} \) vectors of the reciprocal lattice. Each star is characterized by a representative vector \( \mathbf{K}_s \), and by a subgroup of \( V \) rotations \((V_s \, , \, i = 1, h_s)\) which generate all members of the star \( \{\mathbf{K}_s \, , \, i = 1, h_s\} \) when applied to \( \mathbf{K}_s \). We then can write
(W is the volume of the primitive cell):

\[ \Psi_T(r) = \sum_s A_s \Phi_s(r) = \sum_s A_s \left\{ \sum_{i=1}^{N_e} \omega_s^i \exp(i \mathbf{K}_s \cdot r) \right\} ; \]

\[ \omega_s^i = \frac{1}{h_s \sqrt{W}} \exp \left[ -i \mathbf{K}_s \cdot \mathbf{t}(\mathbf{r}_i) \right] . \]  \hspace{1cm} (16)

Note that the \( A_s \) coefficients are precisely the structure factors related to the thermal ECD. While a large number of terms must be considered if we want to accurately reproduce all fine details of the ECD (in particular the distribution of core electrons), we are actually interested in the effect of nuclear motions on the low-index X-ray structure factors; so perhaps the first few hundred terms in the expansion are sufficient.

The statistically averaged EMD can be expressed in a symmetry-adapted form as follows:

\[ \Pi_T(p) = \sum_{j,\ell,s} C_{j,\ell,s} \Phi_{j,\ell,s}(p) , \]

\[ \Phi_{j,\ell,s}(p) = f_j(p) \Phi_{\ell,s}(\theta, \phi) . \]  \hspace{1cm} (17)

Here \( f_j(p) \) is a suitable set of radial functions, while \( \Phi_{\ell,s}(\theta, \phi) \) are symmetrized combinations of spherical harmonics (SSH) of angular quantum number \( \ell \). They can be obtained by first applying the totally symmetric projection operator of the point group \( \mathcal{F} = \sum_{\nu} \mathcal{V} \) to the general \( Y_{\ell m}(\theta, \phi) \), then normalizing the resulting functions and eliminating redundancies. Note that in the formation of the projector \( \mathcal{F} \) we must supplement the operators of the original point group with those resulting from their multiplication by the inversion, if the latter is not among them (see equation 15). For this same reason, only SSH of even \( \ell \) can contribute.

In the Appendix we shall provide explicit expressions for the evaluation of the expansion coefficients in equations (16) and (17) in the case where the instantaneous DM is the result of a calculation performed using a one-electron Hamiltonian and a basis set of Gaussian type orbitals (GTO).

D. The solution of the harmonic problem

All calculations to be analyzed in the following concern a periodic non-conducting system described by a nuclear configuration \( \mathcal{R} \):

\[ \hat{H}^X \psi^X_1(r) = \epsilon^X_1 \psi^X_1(r) . \]  \hspace{1cm} (18)

where \( X \) labels a one-electron Hamiltonian. From there, both the ground-state energy \( V^X[\mathcal{R}] \) and the DM are obtained:

\[ \gamma(\mathbf{r}; \mathbf{r}'|\mathcal{R}) = \sum_i \gamma^X_i(\mathbf{r}) [\psi^X_i(\mathbf{r}')]^* \]  \hspace{1cm} (19)

In these equations \( i \) is a composite label for the crystalline orbitals \( \psi^X_i \), which includes a wave-vector and a band index; \( \sum_i \) runs over all solutions belonging to the occupied manifold, that is to say \( N_d/2 \) lowest bands, \( N_d \) being the number of electrons in the unit cell. All such one-electron calculations are performed here by means of the CRYSTAL program, whose characteristics and capabilities are described elsewhere. It is just expedient to recall that the same basis set is adopted as in standard molecular codes that is, the crystalline orbitals are expressed as a linear combination of GTOs. By this conventional name we mean a “contraction” of \( M_\mu \) normalized Gaussian primitives of angular momentum components \( \ell, m \) centered in \( \mathbf{R}_A \):

\[ \chi_\mu(\mathbf{r}_A) = \sum_{j=1}^{M_\mu} d_{j\mu} G_{t\mu}^m(\alpha_j \mathbf{r}_A) ; \]

\[ G_{t\mu}^m(\alpha; \mathbf{r}) = N_{t\mu}^m(\alpha) X^\ell,m(r) \exp[-\alpha r^2] . \]  \hspace{1cm} (20)

Here \( \mathbf{r}_A = \mathbf{r} - \mathbf{R}_A, X^\ell,m \) are real solid harmonics and \( N_{t\mu}^m \) normalization coefficients; \( d_{j\mu} \) are known as “contraction coefficient”, \( \alpha_j^\mu \) as “exponent” of the general primitive which contributes to the \( \chi_\mu \) GTO. We shall adopt here the standard choice of taking as \( \mathbf{R}_A \) the nuclear coordinates, even if CRYSTAL allows the use of GTOs centered in “ghost atoms” at a general position.

The quality (and cost) of a CRYSTAL calculation depends basically on the choice of the effective Hamiltonian \( \hat{H}^X \) and on that of the GTO basis set. In order to analyze this issue, let us recall the information which is required by the present scheme.

The vibrational problem must first be solved as described in Section II A for obtaining the probability distribution for the nuclei, \( P_{\mathcal{R}}^{(0)}(\mathcal{R}) \). This kind of calculations concern the perfect system \( [\mathcal{R} = \mathcal{R}_0 = \{ \ldots, [\mathcal{R}_3]_g + \mathbf{g}, \ldots \} , \) see equation (3) \], so the power of the CRYSTAL code as regards the use of symmetry is fully exploited. The requirement is that the equilibrium configuration \( \mathcal{R}_0 \) and the Hessian matrix of the second derivatives of the energy about it, \( \{ \mathbf{V}^{(2)} \} \), be accurately described. As anticipated in Section II A the solution of the vibrational harmonic problem also permits us to select an appropriate SC size for the sampling of the displacement coordinates.

These preliminary calculations which concern the perfect system also allow us to collect some quantities to be used for performing the integrals in equations (A1) and (A5). If a post-HF correction has to be performed, CRYSTAL must provide the reference HF solution for CRYSCOR; this issue will be dealt with in Section II F.

E. One-electron supercell calculations

Totally different calculations are needed for obtaining the DM determinations \( \gamma(\mathbf{r}; \mathbf{r}'|\mathcal{R}_J) \) from which the statisti-
A basis set is different for each \( R \) over \( \text{GTOs} \) and to the relatively large size of the \( \text{SC} \), the sums \( r \) \( L \) in the last line runs over the \( \text{within the SC or in its neighborhood.} \) The primed sum \( \cdot \) \( \text{ment of the DM:} \) \( \rho \) \( \chi \) \( \text{EMD.} \) The Fourier transform of the \( \text{GTO} \) in any event, under the hypotheses adopted, the \( \text{SC} \) \( \text{recalled in the Introduction that going beyond a} \) \( \text{other words they are associated to the zero wavevector} \) \( \text{prime index} \( i \) fully identifies them.

From the representation of the crystalline orbitals in the \( \text{GTO basis set, and from equation (19), we then have:} \)

\[
\psi_i^J(r) = \sum_\mu a_{\mu,i}^J \sum_g \chi_\mu(r_A^J - Lg);
\]

\[
\gamma(r, r'|R_J) = \sum_{\mu,\nu} P_{\mu,\nu}^J \times \left( \sum_{g,g'} \chi_\mu(r_A^J - Lg) \chi_\nu(r_B^J - Lg') \right);
\]

\[
P_{\mu,\nu}^J = 2 \sum_i a_{\mu,i}^J a_{\nu,i}^J \tag{21}
\]

In the sums above, \( \mu (\nu) \) runs over the \( \text{GTOs centered in all the} \) \( L^3 \) \( \text{atoms} A (B) \) in the supercell. Note that the basis set is different for each \( R _J; \) in fact, even if all atoms equivalent to the reference one in the primitive cell (\( A \sim a \), see equation 3) share the same set of \( \text{GTOs as defined} \) in equation (20), their center \( (R_0)_a + g + d_0^g \) \( \text{depends on the specific configuration.} \) Due to the short range of the \( \text{GTOs and to the relatively large size of the SC, the sums over} \) \( g, g' \) \( \text{can be limited to the first star of lattice vectors about the origin, if we are interested in} r, r' \) \( \text{coordinates within the SC or in its neighborhood.} \) The primed sum \( \text{in the last line runs over the} N_{el} L^3/2 \) \( \text{occupied orbitals; their real character at} \) \( \Gamma \) \( \text{has been considered.} \)

The \( \text{ECD is immediately obtained as the diagonal element of the DM:} \) \( \rho(r|R_J) = \gamma(r, r'|R_J). \) \( \text{Consider now the EMD. The Fourier} \) \( \text{transform of the GTO} \) \( \chi_\mu(r_A^J) \) \( \text{can be written as} \) \( \chi_{\mu}^F(p) \) \( \text{exp} \{ \text{i} \mathbf{p} \cdot (r_A^J) \}, \) \( \text{where the factor} \) \( \chi_{\mu}^F(p) \) \( \text{is the Fourier transform of the} \mu-th \text{GTO centered in the origin, and is therefore independent of} J, \) \( \text{and the same for all} A \sim a. \) Using the definition (15) and equation (21), we then have:

\[
\pi(p|R_J) = \sum_{\mu,\nu} \left( \frac{\partial}{\partial \mathbf{p}} \chi_{\mu}^F(p) \right) \left[ \chi_{\nu}^F(p) \right]^* \tag{22}
\]

\[
\left( \frac{\partial}{\partial \mathbf{p}} \chi_{\mu}^F(p) \right) = \sum_{A=a, B=b} P_{\mu,\nu}^J \exp \{ \text{i} \mathbf{p} \cdot (r_A^J - r_B^J) \}
\]

**F. Post-Hartree-Fock correction to the DM**

We recalled in the Introduction that going beyond a mono-determinantal description of the DM seems critically important especially as concerns observables such as the CPs which are related to the distribution of electron velocities. A preliminary analysis is here performed about the possibility of including in a unified model the effects of nuclear motions accounted for with the harmonic scheme just presented, and those of electron correlation treated with a multi-determinantal post-HF \textit{ab initio} technique. Let us admit that the harmonic problem can be solved with an appropriate one-electron Hamiltonian at a reasonable level of accuracy (see Section II D); we then concentrate on the correlation correction to the DM. We shall consider for this purpose the prospective use of our periodic local MP2 code \\textsc{Cryscor}, which has been applied successfully to the simulation of the DM of crystalline systems.

The full exploitation of the crystalline symmetry, the clever use of the local-correlation Ansatz combined with powerful density fitting techniques for the evaluation of two-electron integrals, make the \\textsc{Cryscor} calculations relatively cheap; in particular, quasi-linear scaling of the computational cost with the “size” of the problem is achieved, to be compared to the \((N_{el})^3\) scaling of standard schemes based on the use of canonical orbitals. The main outcome of a \\textsc{Cryscor} calculation is the MP2 energy \( E^{(2)} \). Our main interest here, however, is in the correlated DM which is obtained from the excitation amplitudes owing to a Lagrangian technique that is, by evaluating the first-order orbital-unrelaxed response of the energy of the system to an arbitrary external one-electron perturbation.

In principle, such correction should be applied to each instantaneous DM \( \gamma^{\text{HF}}(r, r'|R_J) \) resulting from a Crystal SC calculation (see equation 21). We would so obtain for each configuration \( R_J \) a corrected \( P \) matrix in the corresponding basis set: \( P_{\mu,\nu}^{\text{HF}} \rightarrow P_{\mu,\nu}^{\text{MP2}} \). The expansion coefficients of the thermally averaged observables including the correlation correction could then be obtained by simply feeding such corrected \( P \) matrix in the expressions provided in Section II E.

While formally straightforward, this scheme is practically unfeasible at present because it would require a very large number of SC \\textsc{Cryscor} calculations. All the simplifications due to exploitation of point symmetry are there lost, and the cost would be prohibitively high.

A much simpler scheme can be tentatively explored. The MP2-DM is first evaluated for the equilibrium configuration \( R_0 \), which has the full symmetry of the perfect crystal:

\[
P_{\mu,\nu}^{\text{MP2}} = P_{\mu,\nu}^{\text{HF}} + P_{\mu,\nu}^{\text{corr}}.
\]

From \( P_{\mu,\nu}^{\text{corr}} \) the correlation corrections to the “static” HF observables (that is, by neglecting nuclear motion) can be obtained. These corrections are then simply summed to the thermally averaged ones computed using the HF Hamiltonian. This approximation is equivalent to summing the same corrective \( P_{\mu,\nu}^{\text{corr}} \) matrix to the general \( P_{\mu,\nu}^{\text{HF}} \) one, by formally identifying \( \chi_{\mu}(r_A^J - Lg) \) with...
\[ \chi_\mu(r_A - Lg): \]
\[ P_{\mu,\nu}^{J,MP2} \approx P_{\mu,\nu}^{J,HF} + P_{\mu,\nu}^{\rho,corr}. \quad (23) \]

The idea behind this simplified scheme is that, while the effects on the DM of the changes of internuclear distances (primarily, Pauli repulsion effects) due to nuclear motions are essentially taken into account at the one-electron level, those associated to the instantaneous Coulomb repulsion between electrons of different spin are less critically dependent on the nuclear coordinates. It can be observed that in the frame of this approximate scheme the basis set employed for the determination of \( P_{\mu,\nu}^{\rho,corr} \) and related observables could (and should) be much richer than that used in the SC HF calculations.

### III. PRELIMINARY RESULTS

In this section we present some preliminary results which are intended to investigate the effect on computed one-electron properties of the number \( \mathcal{N} \) of nuclear configurations (i.e., of single-point self consistent field calculations) (considering the cubic crystal of silicon and we compute X-ray structure factors \( F_{hkl} \) (the consolidated set of 19 reflections of Ref. 41) and a directional CP \( J_{\mu\nu}(p) \) (along the crystallographic direction \([hkl] \equiv [111]\)). It is shown below that the effect of temperature (298 K) is clearly revealed by this approach as a function of \( \mathcal{N} \). Computed X-ray structure factors are compared to their experimental determinations.

This scheme has been implemented in the “periodic \( \text{ab initio} \) CRYSTAL program that is here used.\textsuperscript{52,23} All quantities of interest in the program are expressed as linear combinations of Gaussian “primitive” functions centered in high-symmetry positions: these functions, atomic orbitals, AO, constitute the so-called basis set (BS). We start from a 6-21G* BS from Ref. 35 which was also used in a recent study of the ECD of crystalline silicon (BS1).\textsuperscript{1}

We further enrich this BS with three single-primitive polarization functions, one of \( d \) and two of \( f \) type with exponents of 0.3, 0.8, 0.2 a.u., respectively. In CRYSTAL, the truncation of infinite lattice sums is controlled by five thresholds, which are here set to 8,8,8,8,16. The Hamiltonian used for both the lattice dynamics and the calculation of the one-electron properties is the PBE functional of the DFT.\textsuperscript{36} A shrinking factor of 2 is adopted which corresponds to 8 k-points in the irreducible Brillouin zone.

In the case of crystalline silicon, a repetitive SC corresponding to \( L = 2 \) (a conventional cubic cell of this fcc crystal which contains 64 atoms) is essentially adequate. This corresponds to \( 3NL^3 - 3 = 189 \) modes to be sampled. A detailed discussion of the effect of the number of nuclear configurations \( \mathcal{N} \) and step \( \tau \) is addressed in Section II B. It is there demonstrated that values of \( \tau = 0.5 \) and 500 \( \leq \mathcal{N} \leq 1000 \) provide an accurate description of the nuclear motion effects on computed one-electron properties both in position and momentum spaces.

We first report results obtained for the dynamical structure factors of silicon at 298 K as computed with the Monte Carlo scheme illustrated above, with the PBE functional. The effect of the number \( \mathcal{N} \) of nuclear configurations in equation (12) is also reported. \( \mathcal{N} = 1 \) corresponds to the static case.

In Figure 1 we report the percentage differences \( R_{hkl}^{X} = (F_{hkl}^{X} - F_{hkl}^{exp})/F_{hkl}^{exp} \times 100 \) of dynamical structure factors of silicon at 298 K as computed with the PBE functional, up to \( \mathcal{N} = 1000 \). Given the computational parameters above, each of these calculations takes 2.5 hours, in average, running in parallel on 8 processors on a IBM-SP6 cluster at the CINECA supercomputing center. We have considered up to \( 10^8 \) nuclear configurations for a total CPU time of approximately \( 2 \times 10^4 \) hours.

FIG. 1: Percentage differences \( R_{hkl}^{X} = (F_{hkl}^{X} - F_{hkl}^{exp})/F_{hkl}^{exp} \times 100 \) of dynamical structure factors of silicon at 298 K as computed with the Monte Carlo scheme illustrated above, with the PBE functional. The effect of the number \( \mathcal{N} \) of nuclear configurations, used in equation (12) is also reported. \( \mathcal{N} = 1 \) corresponds to the static case. For \( \mathcal{N} = 1000, \) the agreement with the experiment can be described by an overall agreement factor of \( R = 1.83 \% \). Tacking into account the many approximations involved in such a scheme, an overall agreement lower than 2 % is to be considered a nice evidence of its effectiveness. Let us note that here the computed values overestimate the experiments (i.e. the dynamical correction is undershot). This might suggests that considering the intrinsic limitations of the adopted Hamiltonian
FIG. 2: Differences between the 298 K and 0 K directional CPs of silicon along the [111] direction. The CP at 298 K is computed from the average over \(N\) nuclear configurations \(J(p;N)\) while that at 0 K from a single nuclear configuration \(J(p;1)\).

that some of the thresholds involved in the Monte Carlo technique are still too poor as, for instance, the size of the adopted supercell or the number \(N\) of nuclear configurations adopted. As a consequence, a systematic way for further improving the description of thermal nuclear motion within such a scheme exists.

As regards CPs, a direct comparison with the experimental data is under analysis; in Figure 2 we report the differences between the directional CPs of silicon along the [111] crystallographic direction computed from the statistical average over \(N\) nuclear configurations \(J(p;N)\) at 298 K and that computed on a single (equilibrium, 0 K) nuclear configuration \(J(p;1)\). As discussed before for structure factors, also in this case the effect of \(N\) is quite evident and gives rise to a peculiar oscillating behavior of the CP.\(^{10,11}\) Again, the computed results are found to be almost converged for \(N \approx 500\). To be fair, even if unambiguously revealed, the effect of thermal nuclear motion on the total CPs of crystalline silicon is here found to be quite small (within 0.1 %) so that very accurate measurements are required for an experimental detection of it. The group of Y. Sakurai has been carrying out these experiments at two temperatures (10 and 300 K) at the synchrotron center of SPring-8 in Japan and the collected data will be analyzed in the next future.

To conclude, these preliminary results show that the approach illustrated in this paper is well-behaved as concerns its internal consistency and can definitely reveal the effect of thermal nuclear motion on computed one-electron properties of crystals in a fully ab initio fashion.

IV. CONCLUSIONS

A new approach for the ab initio study of thermal nuclear motion effects on a variety of one-electron properties of crystalline materials is presented which consists in the definition of a statistically averaged first-order density matrix via a Monte Carlo technique for the sampling of the harmonic lattice potential within Born-Oppenheimer approximation.

Both translational and point symmetries are fully exploited at each step of the procedure and a detailed discussion of this topic is reported.

This technique, which is rather general, allows for the rigorous study of the effect of temperature on the electron charge density, X-ray structure factors, Compton profiles and electron momentum density of a crystal. In particular, as concerns X-ray structure factors, it allows to go beyond the commonly adopted rigid-atom approximation which consists in arbitrarily partitioning the total electron charge density into subregions that can be associated to different atoms and in keeping such partition also when nuclear motions are taken into account (Debye-Waller factors are computed within such an assumption).

The preliminary results presented are intended to demonstrate that this approach can definitely reveal the effect of thermal nuclear motion on computed one-electron properties of crystals. This technique will be applied to the simulation of temperature effects on momentum-space directional Compton profiles of covalent crystalline silicon and ionic lithium fluoride for which accurate Compton scattering experiments have been carried out at 10 K and 300 K by our collaborators Y. Sakurai and M. Itou at the synchrotron center of SPring-8 in Japan and the collected data will be analyzed in the next future.

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APPENDIX A: EXPANSION COEFFICIENTS: THE FORMULAE

In this Appendix we provide explicit expressions for the determination of the expansion coefficients of \(\overline{\rho}_T(r)\) and \(\overline{\pi}_T(p)\) in terms of symmetrized functions, as defined in Section II.C. We shall assume that the instantaneous \(\text{DM}\gamma(r,r'|R_J)\) is available in a GTO representation as discussed in Sections II.E and II.F.

Due to the orthonormality of symmetrized plane-waves (SPW), the expansion coefficients of \(\overline{\rho}_T\) as resulting from
a weighted coordinate sample (WCS) $\{\mathcal{R}_j, w_j\}$ are simply given by [use is made of equations (16) and (21)]:

\[
A_s = \sum_j \frac{w_j}{N^2} \left\{ \sum_{\mu,\nu} P_{\mu j} \sum_{G \cdot g} \sum_{i=1}^{b_i} \int \right. \left. \chi_{\mu}(r'_A - L g) \chi_{\nu}(r'_B - L g') \exp \left[ i \mathbf{K}_i \cdot \mathbf{r} \right] \right\}
\]

(A1)

In Appendix C of reference 42 it is shown how to evaluate analytically the integral following the strategy proposed by McMurchie and Davidson\textsuperscript{43} that is, by using as an expansion set Hermitian Gaussian Type Functions (HGTFS):

\[
\Lambda[p, P; t, u, v] = \left( \frac{\partial}{\partial x} \right)^t \left( \frac{\partial}{\partial y} \right)^u \left( \frac{\partial}{\partial z} \right)^v \exp \left( -p |\mathbf{r}_P|^2 \right),
\]

(A2)

where $\mathbf{r}_P = \mathbf{r} - P \equiv (x - P_x, y - P_y, z - P_z)$. The product of two GTOs defined as in equation (20), with angular momentum quantum numbers $\ell$ and $\ell'$, respectively, can be expressed as a linear combination of HGTFS:

\[
\chi_{\mu}(r_A) \chi_{\nu}(r_{A'}) = \sum_{j',t,u,v} F[\mu; j'; j', t, u, v] Z_{Aj,A'j'} \Lambda[p_{jj'}; P_{jj'}; t, u, v], \quad \text{where:}
\]

(A3)

\[
p_{jj'} = \alpha_{\mu j}^* + \alpha_{\nu j'}^*; \quad P_{jj'} = \left( \frac{\alpha_{\mu j}^* \mathbf{A} + \alpha_{\nu j'}^* \mathbf{A'}}{p_{jj'}} \right), \quad Z_{Aj,A'j'} = \exp \left( -\alpha_{\mu j}^* \alpha_{\nu j'}^* |\mathbf{A} - \mathbf{A'}|^2 / p_{jj'} \right)
\]

(A4)

The indices $j, j'$ run over all primitives of the two GTOs, while $t, u, v$ are triplets of integers such that $t + u + v = \ell + \ell'$. The $F$ coefficients can be obtained owing to recursion relations as explained in reference 42; they are independent of $\mathcal{R}$ and can thus be calculated once and for all. The integral in equation (A1) thus reduces to a linear combination of Fourier transforms of HGTFS:

\[
\int \right. \left. \chi_{\mu}(r_A) \chi_{\nu}(r_{A'}) = \sum_{t, u, v} F[\mu; j'; j', t, u, v] Z_{Aj,A'j'} \Lambda[p_{jj'}; P_{jj'}; t, u, v] \exp \left( i \mathbf{K} \cdot \mathbf{r} \right) \exp \left( -p |\mathbf{r}_P|^2 \right)
\]

(A5)

While exploring the WCS, the quantity in curly brackets in equation (A1) is thus easily obtained for each $s$, and progressively summed up to finally provide the thermally averaged structure factors.

The extraction of the expansion coefficients of the EMD (equation 17) follows a different pattern. It is first necessary to specify the $\{\Phi_{j,\ell,s}(\mathbf{p})\}$ set. Our choice has been to construct it by starting from an auxiliary set $\mathcal{G}$ of “Gaussian primitives” defined as in equation (20) but in momentum space, and all centered in the origin: $\mathcal{G} \equiv \{G_{\ell}^m(\alpha; \mathbf{p})\}$; they are precisely the product of a radial function by a spherical harmonics. After applying to each of them the projector $\mathcal{F}$, eliminating redundancies and normalizing the result as specified in Section II C, we are left with $n$ symmetrized functions:

\[
\Phi_{j,\ell,s}(\mathbf{p}) = \sum_m a_{j,\ell,s,m} G_{\ell}^m(\alpha_{j\ell}; \mathbf{p}).
\]

(A6)

Because of the inversion symmetry, only even $\ell$’s are needed. We have verified that using a relatively restricted $\mathcal{G}$ set with suitably chosen “exponents” ($\alpha_{j\ell}$) allows a faithful reproduction of the momentum distribution of typical crystalline systems. This choice provides us with an analytic form of the thermally averaged EMD, very convenient for subsequent manipulations. On the other hand, it entails the non-orthonormality and, possibly, the linear dependency of the expansion set. A standard technique is adopted to get rid of this problem. After obtaining by a unitary transformation $(U^\dagger SU = \Sigma)$ eigenvalues and eigenvectors of the $n \times n$ overlap $S$ matrix (whose evaluation is straightforward), we can eliminate linear dependencies by excluding from $\Sigma$ rows and columns related to eigenvalues below a pre-fixed threshold $\Sigma \rightarrow \Sigma \longrightarrow \Sigma$, and from $U$ the corresponding columns $(U \longrightarrow U)$. The $n \times m$
matrix $A = \mathbf{U} \Sigma^{-1/2}$ allows us to define an orthonormal set of $m \leq n$ functions:

$$FV(p) = \sum_{j,s} A_{j,s,V} \Phi_{j,s}(p) .$$

Reference can be made formally to this $\{FV(p)\}$ set for obtaining a convenient expression for the expansion coefficients of the thermally averaged EMD:

$$\langle C_{V,\ell,s}^{(h)} \rangle_T = \sum_{j,s,V} A'_{j',\ell',s',V} A_{j,s,V} \int d\mathbf{p} \Phi_{j,s}(p) \pi(p|R_J) .$$

The integral in the last line has to be evaluated for each given nuclear configuration by using the correspond-


