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Position and momentum densities. Complementarity at work: refining a quantum model from different data sets

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Abstract

Although Bragg and Compton scattering are well-established techniques, only very few attempts to simultaneously combine information originating from these two experiments have been made so far. This remark also holds for Bragg neutron magnetic combined with X-ray scattering. We propose a quite general procedure to refine a quantum model from different data sets using basic Bayesian probability theory. As an illustration, a qualitative preliminary study to extract chemical information such as charge transfer in ionic-covalent compounds is reported.
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Keywords: C. Ab initio calculations; C. X-ray diffraction; D. Electronic structure

1. Introduction

One electron Reduced Density Matrices (1RDM) are widely accepted to play a central role in the description of electronic properties. Their diagonal elements are the well-known electron densities in the chosen representation space. Theoretical and experimental approaches are numerous but it turns out that there is no unique way to obtain both diagonal as well as non-diagonal elements of the 1RDM to a good degree of accuracy. After a brief reminder on the construction of density matrices and their relationships with X-ray scattering experiments (Sections 2 and 3), we will propose a possible strategy for refining a model of 1RDM (Section 4) from experimental data sets of multiple origins. Section 5 illustrates the joint refinement strategy for a simple model wavefunction in ionic solids.

2. Density matrices and X-ray scattering

The usefulness of density matrices is well established as a substitute to *N*-electron wavefunction when mere

one- or two-electron properties are examined [1–5]. As a brief reminder, we emphasize here the connections between density matrices and some X-ray scattering cross-sections [6].

For a system of *N* interacting electrons described by a unique wavefunction $\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)$, where $\vec{x}_j$ stands for both the spin and the position coordinates of the *j*th electron, i.e. $\vec{x}_j = (s_j, \vec{r}_j)$, the pure state *N*-electron density matrix is defined by the quantity:

$$\Gamma(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N; \vec{x'}_1, \vec{x'}_2, ..., \vec{x'}_N)$$
$$= \Psi^*(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)\Psi(\vec{x'}_1, \vec{x'}_2, ..., \vec{x'}_N) \quad (1)$$

At non-zero temperature, the electron gas can no longer be described by a unique wavefunction and a thermodynamic mixture of pure states is to be taken into account. If $\wp_i$ is the probability for the system to be found in the state $|\Psi_i\rangle$, the density matrix is then a weighted superposition of pure states density matrices:

$$\Gamma(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N; \vec{x'}_1, \vec{x'}_2, ..., \vec{x'}_N)$$
$$= \sum_i \wp_i \Psi_i^*(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)\Psi_i(\vec{x'}_1, \vec{x'}_2, ..., \vec{x'}_N) \quad (2)$$

Only the one- or two-electron, spinless reduced density matrices are needed in the calculation of expected values of

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[1] Partially supported by the Ministère Français des Affaires Étrangères.

one- or two-electron operators. They are respectively defined as:

$$\Gamma_1(\vec{r}_1; \vec{r}_1') = N \sum_i \wp_i \int [\Psi_i^*(\vec{x}_1, ..., \vec{x}_N) \Psi_i(\vec{x}_1', ..., \vec{x}_N)]_{s'=s}$$
$$\times ds_1 \, d^3x_2 \cdots d^3x_N \qquad (3)$$

$$\Gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1', \vec{r}_2') = \binom{N}{2} \sum_i \wp_i \int [\Psi_i^*(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)$$
$$\times \Psi_i(\vec{x}_1', \vec{x}_2', ..., \vec{x}_N')]_{s'=s}$$
$$\times ds_1 \, d^3s_2 \, d^3x_3 \cdots d^3x_N \qquad (4)$$

One- and two-electron reduced density matrices (hereafter referred to as 1RDM and 2RDM, respectively) can be calculated from quantum mechanics first principles. However, for extended systems such as solids, most of the theoretical approaches are either limited to the Hartree–Fock approximation, in which case the 1RDM is idempotent and its eigenvalues are 1 or 0, or make use of the Density Functional Theory and most of the effort then concentrates on the diagonal part of the 1RDM.

On the experimental side, there is no unique experimental setup to directly determine the total density matrices. Only partial information are accessible from each experiment and here is probably a test case for the complementarity of different experimental approaches. Limiting ourselves to the spinless 1RDM, and to the most popular X-ray scattering experiments, we can mention:

- the elastic X-ray scattering, where the dynamical structure factor reduces to

$$S_{el}(\vec{q}, \omega) = \left| \int \Gamma_1(\vec{r}; \vec{r}') e^{-i\vec{q}\cdot\vec{r}} \, d^3r \right|^2 \delta(\omega) \qquad (5)$$

where $\vec{q}$ is the scattering vector and $\hbar\omega$, the energy transfer.

- the inelastic X-ray scattering at the high momentum and energy transfer limit, the so-called 'Compton regime' in the 'Impulse Approximation' (IA) framework. If we define $p_z = (m\omega/q) - (\hbar q/2)$, with $\vec{u} = \vec{q}/q$, the dynamical structure factor writes:

$$S_{IA}(\vec{q}, \omega) = \frac{m}{\hbar q} J\vec{u}(p_z)$$

$$= \frac{m}{\hbar q} \int \left[\int \Gamma_1(\vec{r}; \vec{r} - \vec{t}) d^3r \right] e^{ip_z \vec{t}\cdot\vec{u}} \, d^3t \qquad (6)$$

The so-called 'Directional Compton Profile' (DCP), $J\vec{u}(p_z)$, therefore measures the Fourier transform of the auto-correlation function, i.e. the 'off-diagonal trace' of the 1RDM whereas the elastic scattering gives the Fourier transform of the diagonal elements of the 1RDM. Clearly, the two techniques are highly complementary and ought to be used in conjunction, possibly with other experimental methods.

3. Simple illustration of the complementarity

In order to emphasize the complementarity of the two approaches, we make use of an oversimplified model for a diatomic molecule. A unique orbital is considered as a combination of two functions respectively centered on each atom. Each atomic orbital is built from an s-type function with a flexible additional polarization p-type function

$$\Psi(\vec{r}) = \mathcal{N}[\Phi_a(\zeta_a \vec{r}) + \lambda\Phi_b(\zeta_b\vec{r})] \qquad (7)$$

and

$$\Phi_{a/b}(\vec{r}) = \phi_s(r) + \mu_{a/b}\phi_{p_z}(\vec{r}) \qquad (8)$$

Figs. 1–3 report different cases corresponding to bonding or anti-bonding coupling with different polarization states. The figures clearly show the complementarity between the charge density and the autocorrelation function in the investigation of the nature of the chemical bond. In particular, as it is now well established, the accurate knowledge of $\rho(\vec{r})$, via X-ray diffraction, is essential for a determination of the position of each atomic species, but also for a reliable analysis of the symmetry of the electron distribution around the nuclei. On the other hand, though it is seldom as dramatic as in this example, the autocorrelation function, $B(\vec{t}) = \int \Gamma_1(\vec{r}; \vec{r} - \vec{t}) d^3r$, turns out to be very sensitive to the polarization of the electron cloud as well as to the relative phases of the atomic orbitals participating in the most delocalized one-electron molecular wavefunction.

4. From single to joint refinement of the 1RDM

This part was largely inspired by the suggestions of Sivia [7].

Let us consider a physical model $\mathcal{M}$, which we postulate to have a great relevance to the system under study. We further assume that $\mathcal{M}$ depends on a set of free parameters $\{\alpha_n\}$. It is accepted that this model is formalized as a 1RDM in some analytical or numerical form.

Assuming the pertinence of the model, we are interested in finding the most probable values for the parameters, given a set of available experimental data, hereafter referred to as $\{D\}$. In other words, we wish to guess the $\{\alpha_n\}$ that maximize the conditional probability $\mathcal{P}(\{\alpha_n\}|\{D\}, \mathcal{I})$, where $\mathcal{I}$ stands for all the available information about the system apart from the set of measurements $\{D\}$. This information is usually at the origin of the inference of $\mathcal{M}$. Using Bayes theorem, assuming an unbiased model, independent data points each obeying a gaussian distribution law and postulating a flat distribution for $\mathcal{P}(\{\alpha_n\}|\mathcal{I})$ and $\mathcal{P}(\{D\}|\mathcal{I})$, it is then shown that:

$$\mathcal{P}(\{D\}|\{\alpha_n\}, \{\sigma\}, \mathcal{I}) = \left(\prod_j \frac{1}{\sqrt{2\pi\sigma_j^2}} \right) \exp\left[-\sum_i \frac{|D_i^m - D_i|^2}{\sigma_i^2} \right]$$

$$(9)$$