

8.7. Analysis of charge and spin densities

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8.7.1. Outline of this chapter

Knowledge of the electron distribution is crucial for our understanding of chemical and physical phenomena. It has been assumed in many calculations (*e.g.* Thomas, 1926; Fermi, 1928; and others), and formally proven for non-degenerate systems (Hohenberg & Kohn, 1964) that the electronic energy is a functional of the electron density. Thus, the experimental measurement of electron densities is important for our understanding of the properties of atoms, molecules and solids. One of the main methods to achieve this goal is the use of scattering techniques, including elastic X-ray scattering, Compton scattering of X-rays, magnetic scattering of neutrons and X-rays, and electron diffraction.

Meaningful information can only be obtained with data of the utmost accuracy, which excludes most routinely collected crystallographic data sets. The present chapter will review the basic concepts and expressions used in the interpretation of accurate data in terms of the charge and spin distributions of the electrons. The structure-factor formalism has been treated in Chapter 1.2 of Volume B (*ITB*, 1992).

8.7.2. Electron densities and the n -particle wavefunction

A wavefunction $\psi(1, 2, 3, \dots, n)$ for a system of n electrons is a function of the $3n$ space and n spin coordinates of the electrons. The wavefunction must be antisymmetric with respect to the interchange of any two electrons. The most general density function is the n -particle density matrix, of dimension $4n \times 4n$, defined as

$$\Gamma^n(1, 2, \dots, n; 1', 2', \dots, n') = \psi(1, 2, \dots, n)\psi^*(1', 2', \dots, n'). \quad (8.7.2.1)$$

In this expression, each index represents both the continuous space coordinates and the discontinuous spin coordinates of each of the n particles. Thus, the n -particle density matrix is a representation of the state in a $6n$ -dimensional coordinate space, and the n -dimensional (discontinuous) spin state.

The p th reduced density matrix can be derived from (8.7.2.1) by integration over the space and spin coordinates of $n-p$ particles,

$$\begin{aligned} \Gamma^p(1, 2, \dots, p; 1', 2', \dots, p') \\ = \binom{n}{p} \int \Gamma^n(1, 2, \dots, p, p+1, \dots, n; 1', 2', \dots, p', \\ p+1, \dots, n) d(p+1) \dots dn. \end{aligned} \quad (8.7.2.2)$$

According to a basic postulate of quantum mechanics, physical properties are represented by their expectation values $\langle F \rangle$ obtained from the corresponding operator equation,

$$\langle F \rangle = \langle \psi | \hat{F} | \psi \rangle / \langle \psi | \psi \rangle, \quad (8.7.2.3)$$

where \hat{F} is a (Hermitian) operator. As almost all operators of interest are one- or two-particle operators, the one- and two-particle matrices $\Gamma^1(1; 1')$ and $\Gamma^2(1, 2; 1', 2')$ are of prime interest. The charge density, or *one-electron density*, can be obtained from $\Gamma^1(1; 1')$ by setting $1' = 1$ and integrating over the spin coordinates, *i.e.*

$$\begin{aligned} \rho(\mathbf{r}) &= n \int \Gamma^1(1, 1) ds_1 \\ &= n \int \psi(1, 2, \dots, n)\psi^*(1, 2, \dots, n) ds_1 d2 \dots dn. \end{aligned} \quad (8.7.2.4)$$

An electron density $\rho(\mathbf{r})$ that can be represented by an antisymmetric N -electron wave function and is derivable from that wave function through (8.7.2.4) is called N -representable. As in any real system, the particles will undergo vibrations, so (8.7.2.4) must be modified to allow for the continuous change in the configuration of the nuclei. The commonly used Born–Oppenheimer approximation assumes that the electrons rearrange instantaneously in the field of the oscillating nuclei, which leads to the separation

$$\psi = \psi_e(\mathbf{r}, \mathbf{R}) \cdot \psi_N(\mathbf{R}), \quad (8.7.2.5)$$

where \mathbf{r} and \mathbf{R} represent the electronic and nuclear coordinates, respectively, and ψ_e is the electronic wavefunction, which is a function of both the electronic and nuclear coordinates. The time-averaged, one-electron density $\langle \rho(\mathbf{r}) \rangle$, which is accessible experimentally through the elastic X-ray scattering experiment, is obtained from the static density by integration over all nuclear configurations:

$$\langle \rho(\mathbf{r}) \rangle = \int \rho(\mathbf{r}, \mathbf{R}) P(\mathbf{R}) d\mathbf{R}, \quad (8.7.2.6)$$

where $P(\mathbf{R})$ is the normalized probability distribution function of the nuclear configuration \mathbf{R} . The total X-ray scattering can be derived from the two-particle matrix $\Gamma(1, 2, 1', 2')$ through use of the two-particle scattering operator. The total X-ray scattering includes the inelastic incoherent Compton scattering, which is related to the momentum density $\pi(\mathbf{p})$.

The wavefunction in momentum space, defined by the coordinates $\hat{\mathbf{J}} = \hat{\mathbf{p}}_j, s_j$ of the j th particle (here the caret indicates momentum-space coordinates), is given by the Dirac–Fourier transform of ψ ,

$$\begin{aligned} \hat{\psi}(\hat{1}, \hat{2}, \dots, \hat{n}) &= (2\pi\hbar)^{-3n/2} \int \psi(1, 2, \dots, n) \\ &\times \exp\left(-i/\hbar \sum_j \mathbf{p}_j \cdot \mathbf{r}_j\right) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n, \end{aligned} \quad (8.7.2.7)$$

leading, in analogy to (8.7.2.2), to the one-electron density matrix

$$\pi^1(\hat{1}, \hat{1}') = n \int \psi(\hat{1}, \hat{2}, \dots, \hat{n})\psi^*(\hat{1}', \hat{2}, \dots, \hat{n}) d\hat{2} \dots d\hat{n}, \quad (8.7.2.8)$$

and the momentum density

$$\pi(p) = \int \pi^1(\hat{1}, \hat{1}) ds_1. \quad (8.7.2.9)$$

The spin density distribution of the electrons, $s(\mathbf{r})$, can be obtained from $\Gamma^1(1, 1')$ by use of the operator for the z component of the spin angular momentum. If

$$\begin{aligned} s(\mathbf{r}, \mathbf{r}') &= (2M)^{-1} \int s_z(1)\Gamma(1, 1') ds_1, \\ s(\mathbf{r}) &= s(\mathbf{r}, \mathbf{r}), \end{aligned} \quad (8.7.2.10)$$

where M , the total magnetization, is the eigenvalue of the operator

$$S_z = \sum_i s_z(i).$$