

Density and density matrices

I. GENERAL DEFINITIONS

We consider an N -electron system, with even N , in a singlet ground state Ψ . Indicating with $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ the space and spin coordinates of the i -th electron, the one-body and two-body spin-integrated densities are defined as

$$n(\mathbf{r}_1) = N \sum_{\sigma_1} \int d\mathbf{x}_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2; \quad (1)$$

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1 \sigma_2} \int d\mathbf{x}_3 \cdots d\mathbf{x}_N |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2. \quad (2)$$

These are the most common normalizations; other choices are possible. The one-body density obviously obtains from the two-body one as

$$n(\mathbf{r}_1) = \frac{1}{N-1} \int d\mathbf{r}_2 n^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \quad (3)$$

It is customary to define the (dimensionless) pair-correlation function g by means of

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2) \quad (4)$$

The two-body density becomes uncorrelated whenever the two coordinates are very far apart:

$$n^{(2)}(\mathbf{r}, \mathbf{r}') \simeq n(\mathbf{r})n(\mathbf{r}') \quad \text{for } |\mathbf{r} - \mathbf{r}'| \rightarrow \infty. \quad (5)$$

That means that the pair-correlation function g goes to 1 for large interparticle distances. At small distances g is smaller than 1, due to both the Pauli principle and electron-electron repulsion.

It is also customary to define the "exchange-correlation hole" as

$$n_{\text{xc}}(\mathbf{r}, \mathbf{r}') = n^{(2)}(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') [g(\mathbf{r}, \mathbf{r}') - 1]. \quad (6)$$

This function integrates to $-N$, i.e. to -1 per electron, and measures the depletion in the probability of finding one electron in the neighborhood of a given one. The meaning of this is very transparent in the simple case of the uniform electron gas, where $n(\mathbf{r}) = n_0$ is constant and

$$n_{\text{xc}}(|\mathbf{r} - \mathbf{r}'|) = n_0^2 [g(|\mathbf{r} - \mathbf{r}'|) - 1]; \quad (7)$$

the spherical function $g(r) - 1$ integrates thus to -1 .

The spin-integrated one-body density matrix is

$$\rho(\mathbf{r}_1, \mathbf{r}'_1) = N \sum_{\sigma_1 \sigma'_1} \delta_{\sigma_1 \sigma'_1} \int d\mathbf{x}_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (8)$$

The one-body density is its diagonal in Schrödinger representation: $n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$. In any system $\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0$ whenever $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$. We state (with no justification here) that in condensed matter the decay is exponential in insulators and polynomial in metals.

II. SINGLE-DETERMINANT WAVEFUNCTIONS

We specialize the above general definitions to the case where the N -electron singlet wavefunction (N even) is a single determinant:

$$\Psi = \frac{1}{\sqrt{N!}} |\varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2 \cdots \varphi_{N/2} \bar{\varphi}_{N/2}|, \quad (9)$$

where φ_j and $\bar{\varphi}_j$ are spin-up and spin-down spinorbitals, sharing the same spatial orbital $\varphi_j(\mathbf{r})$. The N spinorbitals and the $N/2$ orbitals are orthonormal. Eq. (9) is appropriate for either the Hartree-Fock (HF) approximation, or the Kohn-Sham (KS) noninteracting Hamiltonian in the framework of DFT. In fact, the *exact* eigenfunctions of a system of noninteracting fermions can be written in single-determinant form.

The (spin-integrated) single-particle density matrix ρ is twice the projector over the occupied manifold:

$$\rho(\mathbf{r}, \mathbf{r}') = 2P(\mathbf{r}, \mathbf{r}') = 2 \sum_{j=1}^{N/2} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}'). \quad (10)$$

For the uncorrelated Ψ , Eq. (9), all ground-state properties can be explicitly cast in terms of the projector P .

The general expression for the two-body spin-integrated density, Eq. (2), becomes

$$n^{(2)}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') - 2|P(\mathbf{r}, \mathbf{r}')|^2. \quad (11)$$

The two-body density becomes uncorrelated whenever the two coordinates are very far apart, as it must be:

$$n^{(2)}(\mathbf{r}, \mathbf{r}') \simeq n(\mathbf{r})n(\mathbf{r}') \quad \text{for} \quad |\mathbf{r} - \mathbf{r}'| \rightarrow \infty. \quad (12)$$

A single-determinant is by definition an *uncorrelated* wavefunction. Nonetheless the Pauli principle implies that the pair-correlation function $g(\mathbf{r}, \mathbf{r}')$ is always smaller than 1, and significantly smaller than 1 at short interparticle distances $|\mathbf{r} - \mathbf{r}'|$. For instance Eq. (11) at $\mathbf{r} = \mathbf{r}'$ yields

$$n^{(2)}(\mathbf{r}, \mathbf{r}) = \frac{1}{2}n^2(\mathbf{r}) \quad (13)$$

and $g(\mathbf{r}, \mathbf{r}) = 1/2$. This feature would be present even for *noninteracting* electrons, and is often called “Fermi correlation”. The genuine correlation, due to electron-electron interactions, is often called “Coulomb correlation”.

In the single-determinant case With the given normalization in Eq. (2), the two-body density integrates to $N(N - 1)$ (over both coordinates), while the first term in Eq. (11) integrates to N^2 . The second term therein is minus twice the trace of P^2 ; we notice that $P^2 = P$, and that the trace of P is $N/2$. We thus recover the correct integrated value.

III. GAUGE ARBITRARINESS & LOCALIZATION

A transformation of the electromagnetic gauge changes the Hamiltonian, hence the wavefunctions and the density matrices, while all measurable quantities are gauge-invariant. Once the electromagnetic gauge fixed, the many-body wavefunction is arbitrary by a phase factor: even this is called gauge arbitrariness. For a single determinant wave function, a further gauge arbitrariness exists.

Any unitary transformation U of the occupied orbitals between themselves

$$\varphi_i \rightarrow \tilde{\varphi}_i(\mathbf{r}) = \sum_{j=1}^{N/2} U_{ij} \varphi_j(\mathbf{r}) \quad (14)$$

yields *the same* many-body wavefunction, Eq. (9), apart for a phase factor. This is usually called a “gauge transformation”. The physical properties of the electronic ground state are gauge-invariant. In particular the density matrix is (twice) the projector over the occupied manifold (of dimension $N/2$) in the Hilbert space, and does not depend on the choice of a particular (orthonormal) basis in that manifold.

In a molecule, the canonical RHF orbitals (and the KS orbitals) are typically delocalized over the whole molecule; in a crystalline solid they have the Bloch form, hence their modulus is cell-periodical. It may be useful to describe the same ground state as a Slater determinant

of *localized* orbitals by means of a gauge transformation. Notice that while the canonical orbitals are eigenfunctions of a mean-field Hamiltonian, the transformed orbitals are no longer such; they are only eigenstates of the density matrix.

The localization can be achieved by some arbitrary criterion, and the most popular choice is to impose minimum quadratic spread (in average) for the transformed orbitals, i.e

$$\min = \lambda^2 = \frac{2}{N} \sum_{i=1}^{N/2} (\langle \tilde{\varphi}_i | r^2 | \tilde{\varphi}_i \rangle - | \langle \tilde{\varphi}_i | \mathbf{r} | \tilde{\varphi}_i \rangle |^2) \quad (15)$$

The orbitals obtained in this way go under the name of “Boys orbitals” in quantum chemistry, and “maximally localized Wannier functions” (MLWFs) in condensed matter physics (for either crystalline or noncrystalline *insulating* materials). In a covalent material, and considering the valence electrons only, the localized orbitals are typically localized in the bond regions. For instance, in a methane (CH₄) tetrahedral molecules the four valence orbitals transform to four equivalent hybrids centered on the bonds. For details, figures, and more, see: N. Marzari et al., Rev. Mod. Phys. **84**, 1419 (2012).