

Density Matrices

Density-Functional Theory of Atoms and Molecules
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Chapter 2



Electron density

In an electronic system, the number of electrons per unit volume in a given state is the *electron density* for that state. This quantity will be of great importance in this book; we designate it by $\rho(\mathbf{r})$. Its formula in terms of Ψ is

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

This is a nonnegative simple function of three variables, x , y , and z , integrating to the total number of electrons,

$$\int \rho(\mathbf{r}) d\mathbf{r} = N$$



Dirac notation

In one-to-one correspondence with the space of all kets $|\Psi\rangle$, there is a dual space consisting of *bra vectors* $\langle\Psi|$. For an arbitrary bra $\langle\Phi|$ and ket $|\Psi\rangle$, the *inner product* $\langle\Phi|\Psi\rangle$ is defined by

$$\langle\Phi|\Psi\rangle = \sum_i \Phi_i^* \Psi_i$$

$$\langle\Phi|\Psi\rangle = \int \Phi^*(\mathbf{r})\Psi(\mathbf{r}) d\mathbf{r}$$

$$\langle\Phi|\Psi\rangle = \langle\Psi|\Phi\rangle^*$$

$$\langle\Psi|\Psi\rangle = 1$$



Dirac notation

Consider now a complete basis set $\{|f_i\rangle\}$ (for example, the eigenstates of some Hamiltonian), satisfying the orthonormality conditions

$$\langle f_i | f_j \rangle = \delta_{ij} \quad (2.1.5)$$

Then any ket $|\Psi\rangle$ can be expressed in terms of the ket basis set $|f_i\rangle$ by

$$|\Psi\rangle = \sum_i \Psi_i |f_i\rangle \quad (2.1.6)$$

Taking the inner product of $|\Psi\rangle$ with a bra $\langle f_j|$, we find the j th component of $|\Psi\rangle$ in the representation of the $|f_i\rangle$,

$$\Psi_j = \langle f_j | \Psi \rangle \quad (2.1.7)$$



Dirac notation

If the basis set is continuous, the orthonormality condition becomes

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$$

where $\delta(\mathbf{r} - \mathbf{r}')$ is the Dirac delta function, and for an arbitrary ket $|\Psi\rangle$,

$$|\Psi\rangle = \int \Psi(\mathbf{r}) |\mathbf{r}\rangle d\mathbf{r} \quad (2.1.9)$$

and

$$\Psi(\mathbf{r}) = \langle \mathbf{r} | \Psi \rangle \quad (2.1.10)$$

Here $\Psi(\mathbf{r})$ is precisely the ordinary wave function in coordinate space. If a basis set $|\mathbf{p}\rangle$ were used, one would instead get the momentum-space function. Bras may be expanded similarly.



An operator \hat{A} transforms a ket into another ket in the Hilbert space,

$$\hat{A} |\Psi\rangle = |\hat{A}\Psi\rangle = |\Psi'\rangle \quad (2.1.11)$$

The *adjoint* of \hat{A} , denoted by \hat{A}^\dagger , transforms the corresponding bra,

$$\langle\Psi| \hat{A}^\dagger = \langle\hat{A}\Psi| = \langle\Psi'| \quad (2.1.12)$$

An operator is *self-adjoint*, or *Hermitian*, if it equals its adjoint; operators corresponding to observables always have this property. For normalized ket and bra, (2.1.11) can be written

$$\hat{A} |\Psi\rangle = (|\Psi'\rangle \langle\Psi|) |\Psi\rangle \quad (2.1.13)$$

and (2.1.12) as

$$\langle\Psi| \hat{A}^\dagger = \langle\Psi| (|\Psi\rangle \langle\Psi'|) \quad (2.1.14)$$

When a bra $\langle |$ and a ket $| \rangle$ are juxtaposed, one has an inner product if $\langle |$ is before $| \rangle$, i.e. $\langle || \rangle = \langle | \rangle$; and an operator if $| \rangle$ is before $\langle |$.



Dirac notation

The projection property is manifest when \hat{P}_i acts on the ket $|\Psi\rangle$ of (2.1.6):

$$\begin{aligned}\hat{P}_i |\Psi\rangle &= |f_i\rangle \langle f_i | \Psi\rangle \\ &= \Psi_i |f_i\rangle\end{aligned}\tag{2.1.16}$$

Note that only the part of $|\Psi\rangle$ associated with $|f_i\rangle$ is left. Projection operators have the property

$$\hat{P}_x \cdot \hat{P}_x = \hat{P}_x\tag{2.1.17}$$

For this reason, they are said to be *idempotent*.

$$|\Psi\rangle = \sum_i \langle f_i | \Psi\rangle |f_i\rangle = \sum_i |f_i\rangle \langle f_i | \Psi\rangle$$

$$\sum_i |f_i\rangle \langle f_i| = \sum_i \hat{P}_i = \hat{I}$$



Dirac notation

Let the kets $|\alpha_i\rangle$ be the complete set of eigenkets of the linear operator \hat{A} , with eigenvalues a_i . Then

$$\begin{aligned}\hat{A} |\alpha_i\rangle &= a_i |\alpha_i\rangle, & \hat{A} |\alpha_i\rangle \langle \alpha_i| &= a_i |\alpha_i\rangle \langle \alpha_i| \\ \hat{A} &= \hat{A} \sum_i |\alpha_i\rangle \langle \alpha_i| = \sum_i a_i |\alpha_i\rangle \langle \alpha_i|\end{aligned}\tag{2.1.25}$$

Here again the sum becomes an integral in the continuous case.

If particle spin is included in the above, then the closure relation is

$$\int d\mathbf{x} |\mathbf{x}\rangle \langle \mathbf{x}| = \sum_s \int d\mathbf{r} |\mathbf{r}, s\rangle \langle \mathbf{r}, s| = \hat{I}\tag{2.1.26}$$

With this interpretation of integrals, all of the above equations may be regarded as including spin, with \mathbf{r} replaced by \mathbf{x} .



We now turn to a quantum system of many identical particles, for which the foregoing concepts and formulas go through when suitably generalized. However, a new feature appears—the antisymmetry (or symmetry) of fermion (or boson) wave functions with respect to exchange of indices (coordinates) of any two particles. The antisymmetric and symmetric states span subspaces of the N -particle Hilbert space, \mathcal{H}_N , the subspaces denoted by \mathcal{H}_N^A and \mathcal{H}_N^S . We focus on \mathcal{H}_N^A , since electrons are fermions. In \mathcal{H}_N , a normalized basis ket for N particles in suitably defined states $|\alpha_1\rangle, |\alpha_2\rangle, \dots, |\alpha_N\rangle$, respectively, is

$$|\alpha_1\alpha_2 \cdots \alpha_N\rangle = |\alpha_1\rangle |\alpha_2\rangle \cdots |\alpha_N\rangle \quad (2.1.27)$$

while for fermions, a typical normalized antisymmetric basis ket would be

$$|\alpha_1\alpha_2 \cdots \alpha_N\rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P |\alpha_1\alpha_1 \cdots \alpha_N\rangle \quad (2.1.28)$$



Dirac notation

where the P 's are operators permutating particle coordinates and $(-1)^P$ is the parity of the permutation P . The closure relation in \mathcal{H}_N is

$$\sum_{\alpha_1, \alpha_2, \dots, \alpha_N} |\alpha_1 \alpha_2 \cdots \alpha_N\rangle \langle \alpha_1 \alpha_2 \cdots \alpha_N| = \hat{I} \quad (2.1.29)$$

while that in \mathcal{H}_N^A is

$$\sum_{\alpha_1, \alpha_2, \dots, \alpha_N} \frac{1}{N!} |\alpha_1 \alpha_2 \cdots \alpha_N\rangle \langle \alpha_1 \alpha_2 \cdots \alpha_N| = \hat{I} \quad (2.1.30)$$

The summations in both formulas become integrals if the indices are continuous.



Dirac notation

$$\Psi(\mathbf{r}) = \langle \mathbf{r} | \Psi \rangle$$

Generalizing (2.1.10), the N -electron coordinate wave function is related to the abstract ket vector in \mathcal{H}_N^A by

$$\Psi_N(x_1 x_2 \cdots x_N) = (\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N | \Psi_N \rangle \quad (2.1.31)$$

In the case that $|\Psi_N\rangle$ takes the form (2.1.28), describing N independent electrons moving in N one-electron states, one can show from (2.1.31) that Ψ_N is a Slater determinant of the form of (1.3.1).

$$|\alpha_1 \alpha_2 \cdots \alpha_N \rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P |\alpha_1 \alpha_1 \cdots \alpha_N \rangle$$



Density operators

$$\Psi_N(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N)$$

$$\gamma_N(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_N, \mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) \equiv \Psi_N(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N)$$

Density operators: $|\Psi_N\rangle\langle\Psi_N| = \hat{\gamma}_N$

$$\begin{aligned}\langle\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_N|\hat{\gamma}_N|\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N\rangle &= (\mathbf{x}'_1\mathbf{x}'_2 \cdots |\Psi_N\rangle\langle\Psi_N|\mathbf{x}_1\mathbf{x}_2 \cdots) \\ &= \Psi_N(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N)\end{aligned}$$



Density operators

Note that $\hat{\gamma}_N$ is a projection operator. We then have for normalized Ψ_N ,

$$\text{tr}(\hat{\gamma}_N) = \int \Psi_N(\mathbf{x}^N) \Psi_N^*(\mathbf{x}^N) d\mathbf{x}^N = 1 \quad (2.2.5)$$

where the *trace* of the operator \hat{A} is defined as the sum of diagonal elements of the matrix representing \hat{A} ,

$$\langle \hat{A} \rangle = \text{tr}(\hat{\gamma}_N \hat{A}) = \text{tr}(\hat{A} \hat{\gamma}_N)$$



Density operators

An operator description of a quantum state becomes necessary when the state cannot be represented by a linear superposition of eigenstates of a particular Hamiltonian \hat{H}_N (“by a vector in the Hilbert space \mathcal{H}_N ”). This occurs when the system of interest is part of a larger closed system, as for example an individual electron in a many-electron system, or a macroscopic system in thermal equilibrium with other macroscopic systems. For such a system one does not have a complete Hamiltonian containing only its own degrees of freedom, thereby precluding the wave-function description. A state is said to be *pure* if it is described by a wave function, *mixed* if it cannot be described by a wave function.

A system in a mixed state can be characterized by a probability distribution over all the accessible pure states.



Density operators

$$\hat{\Gamma} = \sum_i p_i |\Psi_i\rangle \langle \Psi_i| \quad (2.2.7)$$

where p_i is the probability of the system being found in the state $|\Psi_i\rangle$, and the sum is over the complete set of all accessible pure states. With the $|\Psi_i\rangle$ orthonormal, the rules of probability require that p_i be real and that

$$p_i \geq 0, \quad \sum_i p_i = 1 \quad (2.2.8)$$

Note that if the interactions can induce change in particle number, the accessible states can involve different particle numbers.



Density operators

$$\begin{aligned}\text{Tr}(\hat{\Gamma}) &= \sum_i \sum_k p_i \langle f_k | \Psi_i \rangle \langle \Psi_i | f_k \rangle \\ &= \sum_i p_i \langle \Psi_i | \sum_k | f_k \rangle \langle f_k | \Psi_i \rangle \\ &= \sum_i p_i \langle \Psi_i | \Psi_i \rangle = \sum_i p_i = 1\end{aligned}$$

$$\begin{aligned}\langle f_k | \hat{\Gamma} | f_l \rangle &= \sum_i p_i \langle f_k | \Psi_i \rangle \langle \Psi_i | f_l \rangle \\ &= \sum_i p_i \{ \langle f_l | \Psi_i \rangle \langle \Psi_i | f_k \rangle \}^* \\ &= \langle f_l | \hat{\Gamma} | f_k \rangle^*\end{aligned}$$

It also is positive semidefinite:

$$\langle f_k | \hat{\Gamma} | f_k \rangle = \sum_i p_i |\langle f_k | \Psi_i \rangle|^2 \geq 0$$

The p_i are the eigenvalues of $\hat{\Gamma}$.



Density operators

The foregoing definitions and properties also hold for time-dependent pure-state density operators $\hat{\gamma}_N$ and ensemble density operators $\hat{\Gamma}$. From the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\Psi_N\rangle = \hat{H} |\Psi_N\rangle \quad (2.2.15)$$

we find

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\gamma}_N &= \left(\frac{\partial}{\partial t} |\Psi_N\rangle \right) \langle \Psi_N| + |\Psi_N\rangle \frac{\partial}{\partial t} \langle \Psi_N| \\ &= \frac{\hat{H}}{i\hbar} |\Psi_N\rangle \langle \Psi_N| - |\Psi_N\rangle \langle \Psi_N| \frac{\hat{H}}{i\hbar} \end{aligned}$$

so that

$$i\hbar \frac{\partial}{\partial t} \hat{\gamma}_N = [\hat{H}, \hat{\gamma}_N] \quad (2.2.16)$$



Density operators

$$i\hbar \frac{\partial}{\partial t} \hat{\Gamma} = [\hat{H}, \hat{\Gamma}]$$

$$[\hat{H}, \hat{\Gamma}] = 0 \quad \text{for a stationary state}$$

