

2

DENSITY MATRICES

2.1 Description of quantum states and the Dirac notation

In this chapter, the concepts and form of elementary quantum mechanics are generalized. This allows use of variables other than coordinates for the description of a state, permits ready discussion of physical states that cannot be described by wave functions, and prepares the way for formally considering the number of particles to be variable rather than constant. Taking advantage, as appropriate, of the identity of electrons and the fact that we are exclusively concerned with systems and equations that involve two-particle interactions at worst, several tools are developed for formal analysis: Dirac notation, density operators, and density matrices. We follow Dirac (1947) and Messiah (1961); see also Szabo and Ostlund (1982, especially pp. 9–12), and Weissbluth (1978).

We begin with the quantum state of a single-particle system. Such a state was described in Chapter 1 by a wave function $\Psi(\mathbf{r})$ in coordinate space (neglecting the spin for the moment). It can also be equivalently “represented” by a momentum-space wave function that is the Fourier transform of $\Psi(\mathbf{r})$. This, together with the quantum superposition principle, leads one to construct a more general and abstract form of quantum mechanics. Thus, one associates with each state a *ket vector* $|\Psi\rangle$ in the linear vector space \mathcal{H} , called the *Hilbert space* (Messiah 1961, pp. 164–166). The linearity of the Hilbert space implements the superposition principle: a linear combination of two vectors $C_1|\Psi_1\rangle + C_2|\Psi_2\rangle$ is also a ket vector in the same Hilbert space, associated with a realizable physical state.

Just as a vector in three-dimensional coordinate space can be defined by its three components in a particular coordinate system, the ket $|\Psi\rangle$ can be completely specified by its components in any particular *representation*. The difference is that the Hilbert space here has an infinite number of dimensions.

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

$$\langle\Phi|\Psi\rangle = \sum_i \Phi_i^* \Psi_i \quad (2.1.1)$$

This is for the case that both $\langle \Phi |$ and $|\Psi\rangle$ are represented in a discrete basis with components Φ_i^* and Ψ_i . If the representation is continuous, one has an integral rather than a sum, for example,

$$\langle \Phi | \Psi \rangle = \int \Phi^*(\mathbf{r})\Psi(\mathbf{r}) d\mathbf{r} \quad (2.1.2)$$

where the integral is equivalent to the sum of all component products with different values of \mathbf{r} . Thus, the inner product of a ket and a bra is a complex number and satisfies

$$\langle \Phi | \Psi \rangle = \langle \Psi | \Phi \rangle^* \quad (2.1.3)$$

If

$$\langle \Psi | \Psi \rangle = 1 \quad (2.1.4)$$

we call $|\Psi\rangle$ and $\langle \Psi |$ normalized. The bra $\langle \Psi |$ is said to be the *conjugate* of the ket $|\Psi\rangle$.

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 $|f_i\rangle$,

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

where (2.1.5) has been used. If the basis set is continuous, the orthonormality condition becomes

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') \quad (2.1.8)$$

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 $\langle |$.

A very important type of operator is the *projection operator* onto a normalized ket $|X\rangle$:

$$\hat{P}_x = |X\rangle \langle X| \quad (2.1.15)$$

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

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

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

$$\hat{P}_x \cdot \hat{P}_x = \hat{P}_x \quad (2.1.17)$$

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

By inserting (2.1.7) into (2.1.6), we get

$$\begin{aligned} |\Psi\rangle &= \sum_i \langle f_i | \Psi\rangle |f_i\rangle = \sum_i |f_i\rangle \langle f_i | \Psi\rangle \\ &= \left\{ \sum_i |f_i\rangle \langle f_i| \right\} |\Psi\rangle \end{aligned} \quad (2.1.18)$$

from which follows

$$\sum_i |f_i\rangle \langle f_i| = \sum_i \hat{P}_i = \hat{I} \quad (2.1.19)$$

where \hat{I} is the identity operator. This is the *closure relation*. The corresponding expression for a continuous basis set is

$$\int d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| = \int d\mathbf{r} \hat{P}_\mathbf{r} = \hat{I} \quad (2.1.20)$$

The closure relation greatly facilitates transformation between different representations, which makes the Dirac notation so useful. As an

example, we compute the inner product

$$\begin{aligned}\langle \Phi | \Psi \rangle &= \langle \Phi | \hat{I} | \Psi \rangle \\ &= \sum_i \langle \Phi | f_i \rangle \langle f_i | \Psi \rangle \\ &= \sum_i \Phi_i^* \Psi_i\end{aligned}\quad (2.1.21)$$

which is identically (2.1.1). Or, consider the effect of the operator \hat{A} in (2.1.11),

$$\langle f_i | \hat{A} | \Psi \rangle = \sum_j \langle f_i | \hat{A} | f_j \rangle \langle f_j | \Psi \rangle = \langle f_i | \Psi' \rangle \quad (2.1.22)$$

where the complex numbers $\langle f_i | \hat{A} | f_j \rangle$ constitute the matrix representation of \hat{A} in the basis set $|f_i\rangle$. [Such a matrix in full in fact defines the operator.] If we use a continuous basis set, (2.1.22) becomes

$$\langle \mathbf{r}' | \hat{A} | \Psi \rangle = \int d\mathbf{r} A(\mathbf{r}', \mathbf{r}) \Psi(\mathbf{r}) = \Psi'(\mathbf{r}') \quad (2.1.23)$$

where $A(\mathbf{r}', \mathbf{r}) = \langle \mathbf{r}' | \hat{A} | \mathbf{r} \rangle$. Equation (2.1.23) indicates that an operator can be *nonlocal*. An operator \hat{A} is *local* if

$$A(\mathbf{r}', \mathbf{r}) = A(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r}) \quad (2.1.24)$$

Often the potential part of a one-body Hamiltonian \hat{H} is local, in which case the Schrödinger equation (1.1.1) is just a differential equation. The Hartree-Fock exchange operator in (1.3.12) is nonlocal.

As another example of the use of (2.1.15), we may prove the formula for the decomposition of a Hermitian operator into its eigenfunctions. Let the kets $|\alpha_i\rangle$ be the complete set of eigenkets of the linear operator \hat{A} , with eigenvalues a_i . Then

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

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

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

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

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

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

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.

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

$$\Psi_N(x_1x_2 \cdots x_N) = (\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N | \Psi_N \rangle \quad (2.1.31)$$

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).

2.2 Density operators

We now consider an even more general description of a quantum state. By (1.1.10), the quantity

$$\Psi_N(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) \Psi_N^*(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) \quad (2.2.1)$$

is the probability distribution associated with a solution of the Schrödinger equation (1.1.1), with the Hamiltonian operator \hat{H}_N . The main result of the present chapter will be to establish the utility of quantities of the type

$$\gamma_N(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_N, \mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) \equiv \Psi_N(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_N) \Psi_N^*(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) \quad (2.2.2)$$

which is more general than (2.2.1) in that the variables in the first factor

are primed. The two sets of independent quantities $\mathbf{x}'_1\mathbf{x}'_2\cdots$ and $\mathbf{x}_1\mathbf{x}_2\cdots$ can be thought of as two sets of indices that give (2.2.2) a numerical value, in contrast with the single set $\mathbf{x}_1\mathbf{x}_2\cdots$ that suffices for (2.2.1). We therefore may think of (2.2.2) as an element of a matrix, which we shall call a *density matrix*. If we set $\mathbf{x}_i = \mathbf{x}'_i$ for all i , we get a diagonal element of this matrix, the original (2.2.1). Equivalently, (2.2.2) can be viewed as the coordinate representation of the *density operator*,

$$|\Psi_N\rangle\langle\Psi_N| = \hat{\gamma}_N \quad (2.2.3)$$

since

$$\begin{aligned} \langle\mathbf{x}'_1\mathbf{x}'_2\cdots\mathbf{x}'_N|\hat{\gamma}_N|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N\rangle &= \langle\mathbf{x}'_1\mathbf{x}'_2\cdots|\Psi_N\rangle\langle\Psi_N|\mathbf{x}_1\mathbf{x}_2\cdots\rangle \\ &= \Psi_N(\mathbf{x}'_1\mathbf{x}'_2\cdots\mathbf{x}'_N)\Psi_N^*(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N) \end{aligned} \quad (2.2.4)$$

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} , or the integral if the representation is continuous as in (2.2.5). One can also verify from (1.1.12) that

$$\langle\hat{A}\rangle = \text{tr}(\hat{\gamma}_N\hat{A}) = \text{tr}(\hat{A}\hat{\gamma}_N) \quad (2.2.6)$$

of which (1.1.12) is the coordinate representation.

In view of (2.2.6), the density operator $\hat{\gamma}_N$ of (2.2.3) carries the same information as the N -electron wave function $|\Psi_N\rangle$. $\hat{\gamma}_N$ is an operator in the same space as the vector $|\Psi_N\rangle$. Note that while $|\Psi\rangle$ is defined only up to an arbitrary phase factor, $\hat{\gamma}_N$ for a state is unique. $\hat{\gamma}_N$ also is Hermitian.

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. To accomplish this description, we generalize the density operator of (2.2.3) to the *ensemble*

density operator

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

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.

For a system in a pure state, one p_i is 1 and the rest are zero; $\hat{\Gamma}$ of (2.2.7) then reduces to $\hat{\gamma}_N$ of (2.2.3). By construction, $\hat{\Gamma}$ is normalized: In an arbitrary complete basis $|f_k\rangle$,

$$\begin{aligned} \text{Tr}(\hat{\Gamma}) &= \sum_i \sum_k p_i \langle f_k | \Psi_i \rangle \langle \Psi_i | f_k \rangle \\ &= \sum_i p_i \langle \Psi_i | \sum_k |f_k\rangle \langle f_k | \Psi_i \rangle \\ &= \sum_i p_i \langle \Psi_i | \Psi_i \rangle = \sum_i p_i = 1 \end{aligned} \quad (2.2.9)$$

[Here and later Tr means the trace in Fock space (see Appendix C), containing states with different numbers of particles, in contrast to the trace denoted by tr in (2.2.5), in N -particle Hilbert space.] $\hat{\Gamma}$ is Hermitian:

$$\begin{aligned} \langle f_k | \hat{\Gamma} | f_l \rangle &= \sum_i p_i \langle f_k | \Psi_i \rangle \langle \Psi_i | f_l \rangle \\ &= \sum_i p_i \{ \langle f_l | \Psi_i \rangle \langle \Psi_i | f_k \rangle \}^* \\ &= \langle f_l | \hat{\Gamma} | f_k \rangle^* \end{aligned} \quad (2.2.10)$$

It also is positive semidefinite:

$$\langle f_k | \hat{\Gamma} | f_k \rangle = \sum_i p_i |\langle f_k | \Psi_i \rangle|^2 \geq 0 \quad (2.2.11)$$

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

For a system to be in a pure state, it is necessary and sufficient for the density operator to be idempotent:

$$\hat{\gamma}_N \cdot \hat{\gamma}_N = |\Psi\rangle\langle\Psi| \langle\Psi| \langle\Psi\rangle = |\Psi\rangle\langle\Psi| = \hat{\gamma}_N \quad (2.2.12)$$

The ensemble density operator in general lacks this property:

$$\hat{\Gamma} \cdot \hat{\Gamma} = \sum_i p_i^2 |\Psi_i\rangle\langle\Psi_i| \neq \hat{\Gamma} \quad (2.2.13)$$

For a mixed state, the expectation value for the observable \hat{A} is given by a natural generalization of (2.2.6),

$$\langle A \rangle = \text{Tr}(\hat{\Gamma}\hat{A}) = \sum_i p_i \langle \Psi_i | \hat{A} | \Psi_i \rangle \quad (2.2.14)$$

Note that this is very different from what (1.1.12) gives when $|\Psi\rangle$ is a linear combination $\sum_i C_i |\Psi_i\rangle$, in which case cross terms $\langle \Psi_i | \hat{A} | \Psi_j \rangle$ enter.

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

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

where the brackets denote the commutator. More generally, the linearity of (2.2.7) leads to

$$i\hbar \frac{\partial}{\partial t} \hat{\Gamma} = [\hat{H}, \hat{\Gamma}] \quad (2.2.17)$$

This is clearly true if $\hat{\Gamma}$ of (2.2.7) only involves states with the same number of particles (canonical ensemble case). If, on the other hand, states with different numbers of particles are allowed, to interpret (2.2.17) one has to use the Hamiltonian in second-quantized form (see Appendix C), which is independent of the number of particles. The Hamiltonian in (2.2.17) is only for the subsystem of interest, neglecting all its interactions with the rest of the larger closed system.

For a stationary state, $\hat{\Gamma}$ is independent of time. Therefore, from (2.2.17)

$$[\hat{H}, \hat{\Gamma}] = 0 \quad \text{for a stationary state} \quad (2.2.18)$$

Accordingly, \hat{H} and $\hat{\Gamma}$ can share the same eigenvectors.

2.3 Reduced density matrices for fermion systems

The basic Hamiltonian operator of (1.1.2) is the sum of two symmetric "one-electron" operators and a symmetric "two-electron" operator. It

also does not depend on spin. Similarly, operators corresponding to other physical observables are of one-electron or two-electron type and often are spin free. Wave functions Ψ_N are antisymmetric. These facts mean that the expectation value formulas (1.1.12) or (2.2.6), and (2.2.14) can be systematically simplified by integrating the $\Psi_N \Psi_N^*$ product of (2.2.1), or its generalization (2.2.7), over $N-2$ of its variables. This gives rise to the concepts of *reduced density matrix* and *spinless density matrix*, which we now describe (Löwdin 1955a,b, McWeeny 1960, Davidson 1976).

One calls (2.2.1) the *Nth order density matrix* for a pure state of an N -electron system. One then defines the *reduced density matrix of order p* by the formula

$$\begin{aligned} \gamma_p(\mathbf{x}'_1 \mathbf{x}'_2 \cdots \mathbf{x}'_p, \mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_p) \\ = \binom{N}{p} \int \cdots \int \gamma_N(\mathbf{x}'_1 \mathbf{x}'_2 \cdots \mathbf{x}'_p \mathbf{x}_{p+1} \cdots \mathbf{x}_N, \mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_p \cdots \mathbf{x}_N) d\mathbf{x}_{p+1} \cdots d\mathbf{x}_N \end{aligned} \quad (2.3.1)$$

where $\binom{N}{p}$ is a binomial coefficient. In particular,

$$\begin{aligned} \gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2) \\ = \frac{N(N-1)}{2} \int \cdots \int \Psi(\mathbf{x}'_1 \mathbf{x}'_2 \mathbf{x}_3 \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3 \cdots \mathbf{x}_N) d\mathbf{x}_3 \cdots d\mathbf{x}_N \end{aligned} \quad (2.3.2)$$

and

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = N \int \cdots \int \Psi(\mathbf{x}'_1 \mathbf{x}_2 \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (2.3.3)$$

Note that the second-order density matrix γ_2 normalizes to the number of electron pairs,

$$\text{tr } \gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2) = \iint \gamma_2(\mathbf{x}_1 \mathbf{x}_2, \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = \frac{N(N-1)}{2} \quad (2.3.4)$$

while the first-order density matrix γ_1 normalizes to the number of electrons,

$$\text{tr } \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = \int \gamma_1(\mathbf{x}_1, \mathbf{x}_1) d\mathbf{x}_1 = N \quad (2.3.5)$$

Note also that γ_1 can be obtained from γ_2 by quadrature,

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = \frac{2}{N-1} \int \gamma_2(\mathbf{x}'_1 \mathbf{x}_2, \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_2 \quad (2.3.6)$$

Here the full four-variable $\gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2)$ is not necessary, only the three-variable $\gamma_2(\mathbf{x}'_1 \mathbf{x}_2, \mathbf{x}_1 \mathbf{x}_2)$.

The reduced density matrices γ_1 and γ_2 as just defined are coordinate-space representations of operators $\hat{\gamma}_1$ and $\hat{\gamma}_2$, acting, respectively, on the one- and two-particle Hilbert spaces. Like $\hat{\gamma}_N$, these operators are positive semidefinite,

$$\gamma_1(\mathbf{x}_1, \mathbf{x}_1) \geq 0 \quad (2.3.7)$$

$$\gamma_2(\mathbf{x}_1\mathbf{x}_2, \mathbf{x}_1\mathbf{x}_2) \geq 0 \quad (2.3.8)$$

and they are Hermitian,

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = \gamma_1^*(\mathbf{x}_1, \mathbf{x}'_1) \quad (2.3.9)$$

$$\gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_1\mathbf{x}_2) = \gamma_2^*(\mathbf{x}_1\mathbf{x}_2, \mathbf{x}'_1\mathbf{x}'_2) \quad (2.3.10)$$

Antisymmetry of γ_N also requires that any reduced density matrix change its sign on exchange of two primed or two unprimed particle indices; thus

$$\gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_1\mathbf{x}_2) = -\gamma_2(\mathbf{x}'_2\mathbf{x}'_1, \mathbf{x}_1\mathbf{x}_2) = -\gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_2\mathbf{x}_1) = \gamma_2(\mathbf{x}'_2\mathbf{x}'_1, \mathbf{x}_2\mathbf{x}_1) \quad (2.3.11)$$

The Hermitian reduced density operators $\hat{\gamma}_1$ and $\hat{\gamma}_2$ admit eigenfunctions and associated eigenvalues,

$$\int \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) \psi_i(\mathbf{x}_1) d\mathbf{x}_1 = n_i \psi_i(\mathbf{x}'_1) \quad (2.3.12)$$

and

$$\int \gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_1\mathbf{x}_2) \theta_i(\mathbf{x}_1\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = g_i \theta_i(\mathbf{x}'_1\mathbf{x}'_2) \quad (2.3.13)$$

For $\hat{\gamma}_1$, the eigenfunctions $\psi_i(\mathbf{x})$ are called *natural spin orbitals*, and the eigenvalues n_i the *occupation numbers*; these are very important concepts. From the rule for expressing an operator in terms of its eigenvectors, (2.1.25), we have

$$\hat{\gamma}_1 = \sum_i n_i |\psi_i\rangle \langle \psi_i| \quad (2.3.14)$$

or

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = \sum_i n_i \psi_i(\mathbf{x}'_1) \psi_i^*(\mathbf{x}_1) \quad (2.3.15)$$

Similarly,

$$\hat{\gamma}_2 = \sum_i g_i |\theta_i\rangle \langle \theta_i| \quad (2.3.16)$$

where the g_i again are occupation numbers; the $|\theta_i\rangle$ are two-particle functions called *natural geminals*, which in accord with (2.3.11) are defined to be antisymmetric. From (2.3.7) and (2.3.8) also follow

$$n_i \geq 0, \quad g_i \geq 0 \quad (2.3.17)$$

Differential equations for the natural orbitals ψ_i have been discussed briefly by Löwdin (1955a). Their long-range behavior is given by Morrell,

Parr, and Levy (1975):

$$\psi_i \sim \exp [-(2I_{\min})^{1/2}r] \quad (2.3.18)$$

where I_{\min} is the smallest ionization potential of the system.

Comparing (2.3.14) and (2.3.16) with (2.2.7) and recalling the probabilistic interpretation of (2.2.7), one sees that n_i is proportional to the probability of the one-electron state $|\psi_i\rangle$ being occupied; similarly g_i is proportional to the probability of the two-electron state $|\theta_i\rangle$ being occupied.

For a mixed state, a corresponding set of definitions of reduced density matrices and operators is appropriate, and the same properties all hold. For the case in which all participating states have the same particle number, N , we denote the $\hat{\Gamma}$ of (2.2.7) as the N th-order density operator $\hat{\Gamma}_N$. The p th-order mixed state density matrix is then

$$\begin{aligned} & \Gamma_p(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_p, \mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_p) \\ &= \binom{N}{p} \int \cdots \int \Gamma_N(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_p\mathbf{x}_{p+1} \cdots \mathbf{x}_N, \mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) d\mathbf{x}_{p+1} \cdots d\mathbf{x}_N \end{aligned} \quad (2.3.19)$$

corresponding to an operator $\hat{\Gamma}_p$. Similarly one has $\hat{\Gamma}_2$ and $\hat{\Gamma}_1$, the second of which will be of special importance for us. It corresponds to the matrix

$$\Gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = N \int \cdots \int \sum_i p_i \Psi_i(\mathbf{x}'_1\mathbf{x}_2 \cdots \mathbf{x}_N) \Psi_i^*(\mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (2.3.20)$$

where the Ψ_i are the various N -electron states entering the mixed state in question. Many of the formulas below hold for mixed states as well as pure states, but we will not specify this in every case.

Now consider the expectation value, for an antisymmetric N -body wave function Ψ , of a one-electron operator

$$\hat{O}_1 = \sum_{i=1}^N O_1(x_i, x'_i) \quad (2.3.21)$$

We have

$$\begin{aligned} \langle \hat{O}_1 \rangle &= \text{tr}(\hat{O}_1 \gamma_N) \\ &= \int O_1(\mathbf{x}_1\mathbf{x}'_1) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}'_1 \end{aligned} \quad (2.3.22)$$

If the one-electron operator is local in the sense of (2.1.24), as are most operators in molecular physics, we conventionally only write down the diagonal part; thus

$$\hat{O}_1 = \sum_{i=1}^N O_1(x_i) \quad (2.3.23)$$

and the corresponding expectation-value formula is

$$\langle \hat{O}_1 \rangle = \int [O_1(\mathbf{x}_1) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1)]_{\mathbf{x}'_1 = \mathbf{x}_1} d\mathbf{x}_1 \quad (2.3.24)$$

All two-electron operators that concern us are local, and so we may denote the operators by their diagonal part, neglecting the two delta functions. That is, we write

$$\hat{O}_2 = \sum_{i < j}^N O_2(x_i, x_j) \quad (2.3.25)$$

and obtain for the corresponding expectation value

$$\begin{aligned} \langle \hat{O}_2 \rangle &= \text{tr}(\hat{O}_2 \gamma_N) \\ &= \iint [O_2(\mathbf{x}_1, \mathbf{x}_2) \gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2)]_{\mathbf{x}'_1 = \mathbf{x}_1, \mathbf{x}'_2 = \mathbf{x}_2} d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (2.3.26)$$

For the expectation value of the Hamiltonian (1.1.2), combining all the parts, we obtain

$$\begin{aligned} E &= \text{tr}(\hat{H} \hat{\gamma}_N) = E[\gamma_1, \gamma_2] = E[\gamma_2] \\ &= \int [(-\frac{1}{2} \nabla_1^2 + v(\mathbf{r}_1)) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1)]_{\mathbf{x}'_1 = \mathbf{x}_1} d\mathbf{x}_1 + \iint \frac{1}{r_{12}} \gamma_2(\mathbf{x}_1 \mathbf{x}_2, \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (2.3.27)$$

It is because of (2.3.6) that in fact only the second-order density matrix is needed. In the next section, we will further simplify this equation by integrating over the spin variables.

One might hope to minimize (2.3.27) with respect to γ_2 , thus avoiding the problem of the $4N$ -dimensional Ψ . This hope has spawned a great deal of work (see for example Coleman 1963, 1981, Percus 1978, Erdahl and Smith 1987). There is a major obstacle to implementing this idea, however, realized from pretty much the beginning. Trial γ_2 must correspond to some antisymmetric Ψ , that is, for any guessed γ_2 there must be a Ψ from which it comes via (2.3.2). This is the *N-representability problem* for the second-order density matrix.

It is a very difficult task to obtain the necessary and sufficient conditions for a reduced matrix γ_2 to be derivable from an antisymmetric wave function (Coleman 1963, 1981). A more tractable problem is to solve the *ensemble N-representability* problem for Γ_2 ; that is, to find the necessary and sufficient conditions for a Γ_2 to be derivable from a mixed-state (ensemble) Γ_2 by (2.3.19). It is in fact completely legitimate to enlarge the class of trial density operators for an N -electron problem from a pure-state set to the set of positive unit-trace density operators

made up from N -electron states, because

$$E_0 = \text{tr}(\hat{H}\hat{\Gamma}_N^0) \leq \text{tr}(\hat{H}\hat{\Gamma}_N) \quad (2.3.28)$$

That is, minimization of $\text{tr}(\hat{H}\hat{\Gamma}_N)$ leads to the N -electron ground-state energy and the ground state $\hat{\gamma}_N$ if it is not degenerate, or an arbitrary linear combination $\hat{\Gamma}_N$ (convex sum) of all degenerate ground states if it is degenerate. Thus, the search in (2.3.27) may be made over ensemble N -representable Γ_2 .

It is advantageous for this problem that the set of positive unit operators $\hat{\Gamma}_N$ is *convex*, and so also the allowable $\hat{\Gamma}_2$. [A set C is convex if for any two elements Y_1 and Y_2 of C , $P_1Y_1 + P_2Y_2$ also belongs to C if $0 \leq P_1$, $0 \leq P_2$, and $P_1 + P_2 = 1$.] The situation for $\hat{\Gamma}_2$ has not yet been practically resolved, though there has been progress (Coleman 1981). But for $\hat{\Gamma}_1$ a complete solution has been found, as will be described in §2.6. Given a $\hat{\Gamma}_1$,

$$\hat{\Gamma}_1 = \sum_i n_i |\psi_i\rangle\langle\psi_i| \quad (2.3.29)$$

the necessary and sufficient conditions for it to be N -representable are that

$$0 \leq n_i \leq 1 \quad (2.3.30)$$

for all of the eigenvalues of $\hat{\Gamma}_1$ (Löwdin 1955a, Coleman 1963). This conforms nicely with the simple rule that an orbital cannot be occupied by more than one electron—the naive Pauli principle.

For states that are eigenstates of \hat{H} , the Schrödinger equation itself gives equations relating reduced density matrices of different orders (Nakatsuji 1976, Cohen and Frishberg 1976).

2.4 Spinless density matrices

Many operators of interest do not involve spin coordinates, for instance the Hamiltonian operators for atoms or molecules. This makes desirable further reduction of the density matrices of (2.3.2) and (2.3.3), by summation over the spin coordinates s_1 and s_2 (McWeeney 1960).

We define the first-order and second-order *spinless density matrices* by

$$\begin{aligned} \rho_1(\mathbf{r}'_1, \mathbf{r}_1) &= \int \gamma_1(\mathbf{r}'_1 s_1, \mathbf{r}_1 s_1) ds_1 \\ &= N \int \cdots \int \Psi(\mathbf{r}'_1 s_1 \mathbf{x}_2 \cdots \mathbf{x}_N) \Psi^*(\mathbf{r}_1 s_1 \mathbf{x}_2 \cdots \mathbf{x}_N) ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \end{aligned} \quad (2.4.1)$$

and

$$\begin{aligned}\rho_2(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) &= \iint \gamma_2(\mathbf{r}'_1s_1\mathbf{r}'_2s_2, \mathbf{r}_1s_1\mathbf{r}_2s_2) ds_1 ds_2 \\ &= \frac{N(N-1)}{2} \int \cdots \int \Psi(\mathbf{r}'_1s_1\mathbf{r}'_2s_2\mathbf{x}_3 \cdots \mathbf{x}_N) \\ &\quad \times \Psi^*(\mathbf{r}_1s_1\mathbf{r}_2s_2\mathbf{x}_3 \cdots \mathbf{x}_N) ds_1 ds_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N\end{aligned}\quad (2.4.2)$$

We also introduce a shorthand notation for the diagonal element of ρ_2 ,

$$\begin{aligned}\rho_2(\mathbf{r}_1, \mathbf{r}_2) &= \rho_2(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2) \\ &= \frac{N(N-1)}{2} \int \cdots \int |\Psi|^2 ds_1 ds_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N\end{aligned}\quad (2.4.3)$$

and note that the diagonal element of $\rho_1(\mathbf{r}'_1, \mathbf{r}_1)$ is just the electron density of (1.5.1),

$$\begin{aligned}\rho(\mathbf{r}_1) &= \rho_1(\mathbf{r}_1, \mathbf{r}_1) \\ &= N \int \cdots \int |\Psi|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N\end{aligned}\quad (2.4.4)$$

Furthermore,

$$\rho_1(\mathbf{r}'_1, \mathbf{r}_1) = \frac{2}{N-1} \int \rho_2(\mathbf{r}'_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2) d\mathbf{r}_2\quad (2.4.5)$$

which follows directly from (2.3.6). In particular,

$$\rho(\mathbf{r}_1) = \frac{2}{N-1} \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2\quad (2.4.6)$$

The expectation value formulas of (2.3.24) and (2.3.26) now read, for spin-free operators $\mathcal{O}_1(\mathbf{r}_1)$ and $\mathcal{O}_2(\mathbf{r}_1\mathbf{r}_2)$,

$$\langle \hat{\mathcal{O}}_1 \rangle = \int [\mathcal{O}_1(\mathbf{r}_1)\rho_1(\mathbf{r}'_1, \mathbf{r}_1)]_{\mathbf{r}'_1=\mathbf{r}_1} d\mathbf{r}_1\quad (2.4.7)$$

and

$$\langle \hat{\mathcal{O}}_2 \rangle = \iiint [\mathcal{O}_2(\mathbf{r}_1\mathbf{r}_2)\rho_2(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2)]_{\mathbf{r}'_1=\mathbf{r}_1, \mathbf{r}'_2=\mathbf{r}_2} d\mathbf{r}_1 d\mathbf{r}_2\quad (2.4.8)$$

The energy formula of (2.3.27) becomes

$$\begin{aligned}E &= E[\rho_1(\mathbf{r}'_1, \mathbf{r}_1), \rho_2(\mathbf{r}_1, \mathbf{r}_2)] = E[\rho_2(\mathbf{r}'_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2)] \\ &= \int [-\frac{1}{2}\nabla_{\mathbf{r}}^2\rho_1(\mathbf{r}', \mathbf{r})]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r} + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \\ &\quad + \iint \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2\end{aligned}\quad (2.4.9)$$

The three terms in this formula represent respectively the electronic kinetic energy, the nuclear–electron potential energy, and the electron–electron potential energy. Though of course we still have the difficulties mentioned at the end of the previous section, it is salutatory that (2.4.9) involves only one function of three coordinates, $\rho(\mathbf{r})$, and two functions of six coordinates, $\rho_1(\mathbf{r}', \mathbf{r})$ and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$.

It is helpful to consider in a little more detail the third term in (2.4.9), the electron–electron repulsion energy. If this were purely classical, it would just be the self-repulsion energy of a distribution $\rho(\mathbf{r})$, the quantity

$$J[\rho] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.4.10)$$

where the factor 1/2 enters to prevent double counting. This suggests that we write

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)] \quad (2.4.11)$$

where $h(\mathbf{r}_1, \mathbf{r}_2)$, defined by this formula, is the *pair correlation function*—a symmetric function that incorporates all nonclassical effects. The function $h(\mathbf{r}_1, \mathbf{r}_2)$ satisfies an important integral condition or “sum rule”. Inserting (2.4.11) in the right-hand side of (2.4.6), one finds

$$\frac{N-1}{2} \rho(\mathbf{r}_1) = \frac{1}{2} \rho(\mathbf{r}_1) \left[N + \int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \right]$$

Hence, we have

$$\int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (2.4.12)$$

which must hold for all \mathbf{r}_1 . We shall later make use of this condition, which encodes a great deal of information. Another way to write it, going back to Slater (for example, Slater 1951), is obtained if we define the *exchange-correlation hole* (sometimes called the exchange-correlation charge) of an electron at \mathbf{r}_1 by

$$\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) \quad (2.4.13)$$

From (2.4.12), this is a unit charge with sign opposite to that of the electron,

$$\int \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (2.4.14)$$

In terms of ρ_{xc} , the electron-repulsion term in (2.4.9) becomes

$$\begin{aligned} V_{ee} &= \iint \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= J[\rho] + \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (2.4.15)$$

Sometimes it is convenient to have the spinless density matrices of (2.4.1) and (2.4.2) resolved into components arising from different spins or products of spins (McWeeney 1960, McWeeney and Sutcliffe 1969). First consider $\rho_1(\mathbf{r}'_1, \mathbf{r}_1)$ of (2.4.1). For any values of \mathbf{r}'_1 and \mathbf{r}_1 , this is the sum over spin of the diagonal parts of γ_1 ; that is,

$$\begin{aligned} \rho_1(\mathbf{r}'_1, \mathbf{r}_1) &= \gamma_1(\mathbf{r}'_1\alpha, \mathbf{r}_1\alpha) + \gamma_1(\mathbf{r}'_1\beta, \mathbf{r}_1\beta) \\ &= \rho_1^{\alpha\alpha}(\mathbf{r}'_1, \mathbf{r}_1) + \rho_1^{\beta\beta}(\mathbf{r}'_1, \mathbf{r}_1) \end{aligned} \quad (2.4.16)$$

where the second equality just defines the notation. Also, as a byproduct, the electron density itself is a sum of two components,

$$\rho(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}); \quad \rho^\sigma(\mathbf{r}) = \rho_1^{\sigma\sigma}(\mathbf{r}, \mathbf{r}), \quad \sigma = \alpha, \beta \quad (2.4.17)$$

When ρ^α and ρ^β are not equal, there is spin polarization, and the *spin density*,

$$Q(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \quad (2.4.18)$$

is not zero. Similarly, we find for ρ_2

$$\begin{aligned} \rho_2(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) &= \rho_2^{\alpha\alpha, \alpha\alpha}(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) + \rho_2^{\beta\beta, \beta\beta}(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) \\ &\quad + \rho_2^{\alpha\beta, \alpha\beta}(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) + \rho_2^{\beta\alpha, \beta\alpha}(\mathbf{r}'_1\mathbf{r}'_2, \mathbf{r}_1\mathbf{r}_2) \end{aligned} \quad (2.4.19)$$

where notation analogous to that of (2.4.16) has been used.

Cusp conditions on ρ_1 and ρ_2 are given on pp. 42–44 and 103–104 of Davidson (1976).

2.5 Hartree–Fock theory in density-matrix form

The trial wave function for the Hartree–Fock method is the single determinant of spin orbitals, (1.3.1). We now rework the Hartree–Fock theory in density-matrix language (Blaziot and Ripka 1986, p. 177, Löwdin 1955a,b). The result will be a formulation in which the dependent variable is the first-order density matrix itself.

Density matrices assume very simple forms when they are derived from a single determinant. The first-order reduced density matrix, called the *Fock–Dirac density matrix*, is

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = \sum_{i=1}^N \psi_i(\mathbf{x}'_1) \psi_i^*(\mathbf{x}_1) \quad (2.5.1)$$

where the ψ_i are orthonormal spin orbitals. To prove this formula, expand the determinant (1.3.1) in the first row and use (2.3.3), noting that the integration over $\mathbf{x}_2, \dots, \mathbf{x}_N$ of a product of two $(N-1)$ -electron Slater determinants gives $(N-1)!$ if the orbitals are the same in both, and gives zero otherwise. The second-order reduced density matrix can be calculated in a similar way by expanding the determinant in the first two rows (Laplace expansion). The result is

$$\begin{aligned} \gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_1\mathbf{x}_2) &= \frac{1}{2} \begin{vmatrix} \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) & \gamma_1(\mathbf{x}'_2, \mathbf{x}_1) \\ \gamma_1(\mathbf{x}'_1, \mathbf{x}_2) & \gamma_1(\mathbf{x}'_2, \mathbf{x}_2) \end{vmatrix} \\ &= \frac{1}{2} [\gamma_1(\mathbf{x}'_1, \mathbf{x}_1)\gamma_1(\mathbf{x}'_2, \mathbf{x}_2) - \gamma_1(\mathbf{x}'_1, \mathbf{x}_2)\gamma_1(\mathbf{x}'_2, \mathbf{x}_1)] \end{aligned} \quad (2.5.2)$$

More generally, one finds (Löwdin 1954b)

$$\begin{aligned} &\gamma_p(\mathbf{x}'_1\mathbf{x}'_2 \cdots \mathbf{x}'_p, \mathbf{x}_1\mathbf{x}_2 \cdots \mathbf{x}_p) \\ &= \frac{1}{p!} \begin{vmatrix} \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) & \gamma_1(\mathbf{x}'_1, \mathbf{x}_2) & \cdots & \gamma_1(\mathbf{x}'_1, \mathbf{x}_p) \\ \gamma_1(\mathbf{x}'_2, \mathbf{x}_1) & \gamma_1(\mathbf{x}'_2, \mathbf{x}_2) & \cdots & \gamma_1(\mathbf{x}'_2, \mathbf{x}_p) \\ \vdots & \vdots & & \vdots \\ \gamma_1(\mathbf{x}'_p, \mathbf{x}_1) & \gamma_1(\mathbf{x}'_p, \mathbf{x}_2) & \cdots & \gamma_1(\mathbf{x}'_p, \mathbf{x}_p) \end{vmatrix} \end{aligned} \quad (2.5.3)$$

so that the density matrix of any order is calculable from first-order density matrices.

In operator form, (2.5.1) reads

$$\hat{\gamma}_1 = \sum_{i=1}^N |\psi_i\rangle\langle\psi_i| \quad (2.5.4)$$

and can be regarded as the projector onto the space spanned by the N occupied spin orbitals. Not only is this form for $\hat{\gamma}_1$ a consequence of the wave function being a single determinant, but, conversely, if $\hat{\gamma}_1$ is of this form, the wave function must be a single determinant. The proof has two parts. First, it follows from (2.5.4) that $\hat{\gamma}_1$ has N eigenvectors with eigenvalues all equal to 1, the "occupied orbitals," and an infinite number of other eigenvectors with eigenvalues zero [compare (2.3.29)]. Construct an N -electron Slater determinant D with N eigenfunctions of $\hat{\gamma}_1$ with all eigenvalues equal to 1. This is a determinant giving $\hat{\gamma}_1$. The occupied-orbital set is not unique, because the determinant is invariant up to a phase factor to a unitary transformation [see the discussion following (1.3.26)]. Second, we can show that there can be no other determinant giving $\hat{\gamma}_1$. To see this, expand the wave function in a complete set of determinants built from the whole set of natural orbitals of $\hat{\gamma}_1$, calculate $\hat{\gamma}_1$, and compare with (2.5.4). All coefficients will be zero except the one associated with the original determinant built from the N occupied orbitals. There is then a one-to-one mapping between a Slater determinant and a density matrix of the form (2.5.1).

Equivalently, one may say that a necessary and sufficient condition for the N -electron wave function to be a single determinant (unique up to a unitary transformation) is that $\hat{\gamma}_1$ be idempotent with trace N :

$$\hat{\gamma}_1 \hat{\gamma}_1 = \hat{\gamma}_1 \quad (2.5.5)$$

$$\text{Tr } \hat{\gamma}_1 = N \quad (2.5.6)$$

These formulas follow immediately from (2.5.4); the argument that they imply (2.5.4) is that (2.5.5) requires the eigenvalues of $\hat{\gamma}_1$ to be either 1 or 0 and there are N eigenvectors with eigenvalues all equal to 1 [from (2.5.6)]. In coordinate representation, (2.5.5) and (2.5.6) read

$$\int \gamma_1(\mathbf{x}'_1, \mathbf{x}''_1) \gamma_1(\mathbf{x}''_1, \mathbf{x}_1) d\mathbf{x}''_1 = \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) \quad (2.5.7)$$

and

$$\int \gamma_1(\mathbf{x}_1, \mathbf{x}_1) d\mathbf{x}_1 = N \quad (2.5.8)$$

Inserting (2.5.2) in (2.3.27), the Hartree–Fock energy becomes [compare (1.3.2)]

$$\begin{aligned} E_{\text{HF}}[\gamma_1] = & \int [(-\frac{1}{2}\nabla_1^2 + v(\mathbf{x}_1))\gamma_1(\mathbf{x}'_1, \mathbf{x}_1)]_{\mathbf{x}'_1=\mathbf{x}_1} d\mathbf{x}_1 \\ & + \frac{1}{2} \iint \frac{1}{r_{12}} [\gamma_1(\mathbf{x}_1, \mathbf{x}_1)\gamma_1(\mathbf{x}_2, \mathbf{x}_2) - \gamma_1(\mathbf{x}_1, \mathbf{x}_2)\gamma_1(\mathbf{x}_2, \mathbf{x}_1)] d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \quad (2.5.9)$$

In the Hartree–Fock method, one seeks to minimize this functional of γ_1 , over the set of all γ_1 of the form (2.5.1), or, equivalently, over all γ_1 satisfying (2.5.7) and (2.5.8).

This constrained minimization can be implemented by using Lagrange undetermined multipliers (see Appendix A). The condition (2.5.7) depends on \mathbf{x}'_1 and \mathbf{x}_1 , so that the multiplier associated with it must depend on \mathbf{x}'_1 and \mathbf{x}_1 ; call it $\alpha(\mathbf{x}_1, \mathbf{x}'_1)$. Let β be the multiplier for (2.5.8). The variational problem may then be written as

$$\begin{aligned} \delta \left\{ E_{\text{HF}}[\gamma_1] - \iint d\mathbf{x}'_1 d\mathbf{x}_1 \alpha(\mathbf{x}_1, \mathbf{x}'_1) \left[\int \gamma_1(\mathbf{x}'_1, \mathbf{x}''_1) \gamma_1(\mathbf{x}''_1, \mathbf{x}_1) d\mathbf{x}''_1 - \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) \right] \right. \\ \left. - \beta \left[\int \delta(\mathbf{x}'_1 - \mathbf{x}_1) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) d\mathbf{x}'_1 d\mathbf{x}_1 - N \right] \right\} = 0 \quad (2.5.10) \end{aligned}$$

Taking the functional derivatives (see Appendix A), one gets the

Euler–Lagrange equation for the problem:

$$F(\mathbf{x}_1, \mathbf{x}'_1) - \int d\mathbf{y}_1 \alpha(\mathbf{y}_1, \mathbf{x}'_1) \gamma_1(\mathbf{x}_1, \mathbf{y}_1) \\ - \int d\mathbf{z}_1 \alpha(\mathbf{x}_1, \mathbf{z}_1) \gamma_1(\mathbf{z}_1, \mathbf{x}'_1) + \alpha(\mathbf{x}_1, \mathbf{x}'_1) - \beta \delta(\mathbf{x}'_1 - \mathbf{x}_1) = 0 \quad (2.5.11)$$

where $F(\mathbf{x}_1, \mathbf{x}'_1)$ is the matrix for the Fock operator \hat{F} in the coordinate representation,

$$F(\mathbf{x}_1, \mathbf{x}'_1) = \frac{\delta E_{\text{HF}}[\gamma]}{\delta \gamma(\mathbf{x}'_1, \mathbf{x}_1)} \\ = (-\frac{1}{2}\nabla_1^2 + v(\mathbf{x}_1)) \delta(\mathbf{x}'_1 - \mathbf{x}_1) + \delta(\mathbf{x}'_1 - \mathbf{x}_1) \int \frac{1}{r_{12}} \gamma_1(\mathbf{x}_2, \mathbf{x}_2) d\mathbf{x}_2 \\ - \frac{1}{r_{11'}} \gamma_1(\mathbf{x}_1, \mathbf{x}'_1) \quad (2.5.12)$$

The equivalence of this definition of the Fock operator with the previous (1.3.9) becomes clear if we calculate

$$\langle \mathbf{x}'_1 | \hat{F} | \psi \rangle = \int d\mathbf{x}_1 \langle \mathbf{x}'_1 | \hat{F} | \mathbf{x}_1 \rangle \langle \mathbf{x}_1 | \psi \rangle \\ = [-\frac{1}{2}\nabla_1^2 + v(\mathbf{x}'_1) + \hat{j}(\mathbf{x}'_1) - \hat{k}(\mathbf{x}'_1)] \psi(\mathbf{x}'_1) \quad (2.5.13)$$

where \hat{j} and \hat{k} are as defined in (1.3.11) and (1.3.12). Note the simple form of the last, the nonlocal exchange, term in (2.5.12).

Equation (2.5.11) can be regarded as the coordinate representation of an operator equation in one-particle space:

$$\hat{F} - \hat{\gamma}_1 \hat{\alpha} - \hat{\alpha} \hat{\gamma}_1 + \hat{\alpha} - \beta \hat{I} = 0 \quad (2.5.14)$$

where \hat{I} is the identity operator. Multiplying this equation on the right by $\hat{\gamma}_1$, and then on the left, and subtracting the results, we obtain

$$\hat{F} \hat{\gamma}_1 - \hat{\gamma}_1 \hat{F} = 0 \quad (2.5.15)$$

Thus the operators \hat{F} and $\hat{\gamma}_1$ commute and have common eigenfunctions. These common eigenfunctions are the Hartree–Fock orbitals of (1.3.31). The $\hat{\gamma}_1$ that is a solution of (2.5.15) can be constructed from these orbitals via (2.5.4). This γ_1 , denoted by γ_1^{HF} , thus minimizes the Hartree–Fock energy functional $E_{\text{HF}}[\gamma_1]$ of (2.5.9); that is,

$$E_{\text{HF}}[\gamma_1^{\text{HF}}] \leq E_{\text{HF}}[\gamma_1] \quad (2.5.16)$$

for any idempotent γ_1 of trace N . It is obvious that $E_{\text{HF}}[\gamma_1^{\text{HF}}]$ is above the true ground-state energy E (by the correlation energy), since $E_{\text{HF}}[\gamma_1^{\text{HF}}]$ is

the minimum over only the class of all determinantal wave functions. Lieb (1981) in fact proved a more general result than (2.5.16): γ_1 on the right-hand side of (2.5.16) can be replaced by any N -representable Γ_1 (satisfying (2.3.30)). In summary,

$$E_0 \leq E_{\text{HF}}[\gamma_1^{\text{HF}}] \leq E_{\text{HF}}[\Gamma_1] \quad (2.5.17)$$

Finally, we can express the Hartree–Fock energy functional in terms of the spinless first-order density matrix $\rho_1(\mathbf{r}'_1, \mathbf{r}_1)$ of the previous section, and exhibit the pair-correlation function and exchange-correlation hole for Hartree–Fock theory. From (2.5.2), we have, for the components of the diagonal part of ρ_2 ,

$$\begin{aligned} \rho_2^{\alpha\alpha, \alpha\alpha}(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2) &= \frac{1}{2}[\rho^\alpha(\mathbf{r}_1)\rho^\alpha(\mathbf{r}_2) - \rho_1^\alpha(\mathbf{r}_1, \mathbf{r}_2)\rho_1^\alpha(\mathbf{r}_2, \mathbf{r}_1)] \\ \rho_2^{\alpha\beta, \alpha\beta}(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2) &= \frac{1}{2}\rho^\alpha(\mathbf{r}_1)\rho^\beta(\mathbf{r}_2) \end{aligned} \quad (2.5.18)$$

where the notation of the last section has been used. Two other similar components can be written down if we exchange α and β spin labels in the above formulas. [Since the function $\rho_2^{\sigma_1\sigma_2, \sigma_1\sigma_2}(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2)$ is proportional to the probability of finding an electron at \mathbf{r}_1 with spin σ_1 and another electron at \mathbf{r}_2 with spin σ_2 , note from (2.5.18) that the determinantal wave function only describes the correlation of like-spin electrons—the “exchange effect” in Hartree–Fock theory.] The spinless second-order density matrix, by (2.4.19) and (2.5.18), becomes

$$\begin{aligned} \rho_2(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2) &= \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \\ &\quad - \frac{1}{2}[\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)\rho_1^{\beta\beta}(\mathbf{r}_2, \mathbf{r}_1)] \end{aligned} \quad (2.5.19)$$

Inserting (2.5.19) into (2.4.9), one gets the total energy formula

$$\begin{aligned} E_{\text{HF}}[\rho_1] &= \int [(-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1))\rho_1(\mathbf{r}'_1, \mathbf{r}_1)]_{\mathbf{r}'_1=\mathbf{r}_1} d\mathbf{r}_1 \\ &\quad + \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{2} \iint \frac{1}{r_{12}} [\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)\rho_1^{\alpha\alpha}(\mathbf{r}_2, \mathbf{r}_1) \\ &\quad + \rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2 \\ &= T[\rho_1] + V_{ne}[\rho] + J[\rho] - K[\rho_1] \end{aligned} \quad (2.5.20)$$

where

$$T[\rho_1] = \int [-\frac{1}{2}\nabla_1^2\rho_1(\mathbf{r}'_1, \mathbf{r}_1)]_{\mathbf{r}'_1=\mathbf{r}_1} d\mathbf{r}_1 \quad (2.5.21)$$

$$V_{ne}[\rho] = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \quad (2.5.22)$$

$$J[\rho] = \frac{1}{2} \iint \frac{1}{r_{12}} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.5.23)$$

and

$$K[\rho_1] = \frac{1}{2} \iint \frac{1}{r_{12}} [\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) \rho_1^{\alpha\alpha}(\mathbf{r}_2, \mathbf{r}_1) + \rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) \rho_1^{\beta\beta}(\mathbf{r}_2, \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.5.24)$$

For the closed-shell case of an even number of electrons pairwise occupying $N/2$ spatial orbitals,

$$\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1, \mathbf{r}_2) \quad [\text{closed shell}] \quad (2.5.25)$$

and (2.5.24) becomes

$$K[\rho_1] = \frac{1}{4} \iint \frac{1}{r_{12}} \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \quad [\text{closed shell}] \quad (2.5.26)$$

This is equivalent to the last term of (1.3.19).

Comparing the electron–electron repulsion in (2.5.20) with (2.4.15), we see that in the Hartree–Fock approximation the exchange–correlation hole is given by

$$\rho_{xc}^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = \rho_x^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2} \frac{|\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho(\mathbf{r}_1)} \quad [\text{closed shell}] \quad (2.5.27)$$

From (2.4.13) the pair correlation function is

$$h^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{4} \frac{|\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \quad [\text{closed shell}] \quad (2.5.28)$$

The “correlation” included here is among electrons of the same spin only, as again can be seen by noting in (2.5.9) that the spin integrations over the $\gamma_1(\mathbf{x}_1, \mathbf{x}_2)\gamma_1(\mathbf{x}_2, \mathbf{x}_1)$ factor give zero for contributions from different spin states for particles 1 and 2. The term *correlation* as defined in §1.4 is over and above this correlation already included in the single-determinant description, so we sometimes use the notation ρ_x^{HF} for the *exchange hole* of (2.5.28). Note that the sum rules of (2.4.12) and (2.4.14) are satisfied in Hartree–Fock theory:

$$\int \rho(\mathbf{r}_2) h^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \rho_x^{\text{HF}}(\mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (2.5.29)$$

This property is preserved for any approximate ρ_2 that is N -representable.

2.6 The N -representability of reduced density matrices

The necessary and sufficient conditions for a given first-order density matrix to be derivable from a mixed-state density operator were stated in

(2.3.30). In this section, we give the proof of this theorem and also briefly discuss the corresponding problem for the second-order density matrix.

Necessary conditions on Γ_1 and Γ_2 are conditions that they satisfy when they satisfy (2.3.19) for a proper Γ_N . Sufficient conditions are those that guarantee the existence of a Γ_N that reduces to this Γ_1 and/or Γ_2 . The set of Γ_1 or Γ_2 that simultaneously satisfies both necessary and sufficient conditions is called the set of N -representable Γ_1 or Γ_2 . Thus, if the energy (2.4.9) is minimized over sets Γ_1 and Γ_2 satisfying only necessary conditions (such sets are larger than the corresponding N -representable sets), an energy lower than the true energy—lower bound to the energy—can be obtained; if the energy is minimized over sets satisfying only sufficient conditions (such sets are smaller than the corresponding N -representable sets), an energy higher than the true energy is delivered—an upper bound to the energy. In the Hartree–Fock method, for example, the density matrix γ_1 satisfies the sufficient conditions (2.5.5) and (2.5.6); Hartree–Fock energies are consequently upper bounds for true energies. Lower-bound studies are rarer; they include pioneering works by Garrod and Percus (1964) and Garrod and Fusco (1976). Note that if one minimizes over *all* sets satisfying the sufficient conditions, the ground-state energy is obtained.

We now derive some necessary conditions on γ_1 and γ_2 imposed by N -representability—the so-called Pauli conditions (Coleman 1981). These are that if $|\psi_i\rangle$ is some normalized spin-orbital state and $|\psi_i\psi_j\rangle$ is a normalized 2×2 Slater determinantal state built from orthonormal ψ_i and ψ_j , then

$$0 \leq \langle \psi_i | \hat{\gamma}_1 | \psi_i \rangle \leq 1 \quad (2.6.1)$$

and

$$0 \leq \langle \psi_i\psi_j | \hat{\gamma}_2 | \psi_i\psi_j \rangle \leq 1 \quad (2.6.2)$$

or, in the coordinate representation,

$$0 \leq \iint d\mathbf{x}_1 d\mathbf{x}'_1 \psi_i^*(\mathbf{x}'_1) \gamma_1(\mathbf{x}'_1, \mathbf{x}_1) \psi_i(\mathbf{x}_1) \leq 1 \quad (2.6.3)$$

and

$$0 \leq \frac{1}{2} \iiint d\mathbf{x}_1 d\mathbf{x}'_1 d\mathbf{x}_2 d\mathbf{x}'_2 \det [\psi_i^*(\mathbf{x}'_1) \psi_j^*(\mathbf{x}'_2)] \gamma_2(\mathbf{x}'_1\mathbf{x}'_2, \mathbf{x}_1\mathbf{x}_2) \det [\psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_2)] \leq 1 \quad (2.6.4)$$

These results can be derived in various ways.

We follow Coleman (1981) and use the method of second quantization as described in Appendix C. For each member of an arbitrary orthonormal set $\{\psi_i\}$, there is a *creation operator* \hat{a}_i^+ and an *annihilation operator* \hat{a}_i . The corresponding creation and annihilation *field operators* are

defined as

$$\hat{\psi}^+(\mathbf{x}) = \sum_i \psi_i^*(\mathbf{x}) \hat{a}_i^+ \quad (2.6.5)$$

and

$$\hat{\psi}(\mathbf{x}) = \sum_i \psi_i(\mathbf{x}) \hat{a}_i \quad (2.6.6)$$

In terms of these, for a state $|\Psi\rangle$ the first- and second-order reduced density matrices γ_1 and γ_2 of (2.3.2) and (2.3.3) are given, respectively, by (see Appendix C)

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = \langle \Psi | \hat{\psi}^+(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | \Psi \rangle \quad (2.6.7)$$

$$\gamma_2(\mathbf{x}'_1 \mathbf{x}'_2, \mathbf{x}_1 \mathbf{x}_2) = \frac{1}{2} \langle \Psi | \hat{\psi}^+(\mathbf{x}_2) \hat{\psi}^+(\mathbf{x}_1) \hat{\psi}(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}'_2) | \Psi \rangle \quad (2.6.8)$$

We use these to establish, in turn, (2.6.1) and (2.6.2).

Inserting (2.6.7) into the integral in (2.6.3) and using (2.6.5) and (2.6.6), we find, if we take the set $\{\psi_j\}$ to include ψ_i as one of its members (which we can always do),

$$\begin{aligned} \langle \psi_i | \hat{\gamma}_1 | \psi_i \rangle &= \iint d\mathbf{x}_1 d\mathbf{x}'_1 \psi_i^*(\mathbf{x}'_1) \langle \Psi | \sum_i \psi_i^*(\mathbf{x}_1) \hat{a}_i^+ \sum_j \psi_j(\mathbf{x}'_1) \hat{a}_j | \Psi \rangle \psi_i(\mathbf{x}_1) \\ &= \langle \Psi | \hat{a}_i^+ \hat{a}_i | \Psi \rangle \end{aligned} \quad (2.6.9)$$

Here, the operator

$$\hat{N}_i = \hat{a}_i^+ \hat{a}_i \quad (2.6.10)$$

is the occupation number operator for the i th orbital. It is idempotent:

$$\hat{N}_i^2 = \hat{a}_i^+ \hat{a}_i \hat{a}_i^+ \hat{a}_i = \hat{a}_i^+ (1 - \hat{a}_i^+ \hat{a}_i) \hat{a}_i = \hat{N}_i \quad (2.6.11)$$

Thus \hat{N}_i is a projection operator. But the expectation value of any projection operator is always nonnegative and not greater than 1:

$$\langle \Psi | \hat{P}^2 | \Psi \rangle = \sum_j |\langle \Psi | \hat{P} | \Psi_j \rangle|^2 \leq \sum_j |\langle \Psi | \Psi_j \rangle|^2 = 1 \quad (2.6.12)$$

where $\{\Psi_j\}$ is any complete set.

Therefore the right-hand side of (2.6.9) is a nonnegative number less than or equal to 1, proving (2.6.1). We note in passing that the total number operator is

$$\hat{N} = \sum_i \hat{N}_i = \sum_i \hat{a}_i^+ \hat{a}_i \quad (2.6.13)$$

For the proof of (2.6.2), we need the quantity

$$\begin{aligned} \hat{\psi}(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_2) &= \sum_i \psi_i(\mathbf{x}_1) \hat{a}_i \sum_j \psi_j(\mathbf{x}_2) \hat{a}_j \\ &= \sum_j \sum_i \psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_2) \hat{a}_i \hat{a}_j \\ &= \sum_{i < j} [\psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_2) \psi_i(\mathbf{x}_1)] \hat{a}_i \hat{a}_j \\ &= \sum_{i < j} \det [\psi_i(\mathbf{x}_1) \psi_j(\mathbf{x}_2)] \hat{a}_i \hat{a}_j \end{aligned} \quad (2.6.14)$$

where the fact has been used that \hat{a}_i and \hat{a}_j anticommute (see Appendix C). Inserting (2.6.14) and its adjoint into (2.6.8) and then (2.6.4), and using the orthogonality and normalization property of the 2×2 determinants, we find

$$\begin{aligned} \langle \phi_i \phi_j | \hat{\gamma}_2 | \phi_i \phi_j \rangle &= \langle \Psi | \hat{a}_j^+ \hat{a}_i^+ \hat{a}_i \hat{a}_j | \Psi \rangle \\ &= \langle \Psi | \hat{N}_j \hat{N}_i | \Psi \rangle \end{aligned} \quad (2.6.15)$$

From the fact that the product of two projection operators is still a projection operator, we then see that $\langle \Psi | \hat{N}_j \hat{N}_i | \Psi \rangle$ in (2.6.15) is a nonnegative number less than or equal to 1. Equation (2.6.2) follows.

Equation (2.6.1) is equivalent to the requirement that the eigenvalues of $\hat{\gamma}_1$, the occupation numbers n_i of (2.3.12), fall in the range 0 to 1:

$$0 \leq n_i \leq 1 \quad (2.6.16)$$

Equation (2.6.3) is not a condition on the eigenvalues of $\hat{\gamma}_2$, however, since the eigenfunctions of $\hat{\gamma}_2$ are not in general 2×2 Slater determinants.

Leaving the analysis of the N -representability of $\hat{\gamma}_2$ aside, we complete the basic story of $\hat{\gamma}_1$ by asserting and proving that conditions (2.6.16) are not only necessary but also sufficient conditions for the ensemble- N -representability of a first-order reduced density matrix (Coleman 1963, 1981). Necessity has just been proved; it remains to prove sufficiency.

We need a simple lemma about vectors and convex sets. Recall from §2.3 that a set is convex if an arbitrary positively weighted average of any two elements in the set also belongs to the set. Define an *extreme element* of a convex set as an element E such that $E = p_1 Y_1 + p_2 Y_2$ implies that Y_1 and Y_2 are both multiples of E . Then the lemma states that the set \mathcal{L} of vectors $\mathbf{v} = (v_1, v_2, \dots)$ in a space of arbitrary but fixed dimension with $0 \leq v_i \leq 1$ and $\sum v_i = N$ is convex and its extreme elements are the vectors with N components equal to 1 and all other components equal to zero. That \mathcal{L} is convex is obvious. The condition on \mathcal{L} requires that each element has at least N positive components. Thus, a mean of any two vectors has more than N components unless the nonzero components of the original vectors are the same and all equal to 1. The vectors with N components equal to 1 are therefore extreme. No other type of vector is extreme, as any vector with more than N positive components can always be resolved into an average of several extreme elements.

Given this lemma, it is clear that any $\hat{\gamma}_1$ or $\hat{\Gamma}_1$ satisfying (2.6.16) is an element of a convex set whose extreme elements are those γ_1^0 (or Γ_1^0) that have N eigenvalues equal to 1 and the rest equal to zero. Each of these γ_1^0 (or $\hat{\Gamma}_1^0$), according to the discussion in §2.5, determines up to a phase a determinantal N -electron wave function and a unique corresponding pure-state density operator $\hat{\gamma}_N^0$. Some positively weighted sum of these γ_1^0

will be the Γ_N that reduces to the given $\hat{\gamma}_1$ (or $\hat{\Gamma}_1$) through (3.3.20). Thereby, sufficiency is proved.

2.7 Statistical mechanics

As was shown in §2.2, when a system is in a mixed state, rather than a pure state, it is mandatory to describe it with density operators. Such is the case for a system at some finite temperature, for the ignorance of the details of the interaction between system and surroundings makes defining an appropriate complete Hamiltonian impossible. There will be a probability distribution over accessible pure states of the form (2.2.7), with probability p_i for the accessible state $|\Psi_i\rangle$, in the ensemble density operator $\hat{\Gamma}$. The probabilities must be determined by a statistical-mechanical argument appropriate for each particular case (Gibbs 1931, Feynman 1972, McQuarrie 1976).

The key quantity to consider is the *entropy* of the probability distribution,

$$S = -k_B \sum_i p_i \ln p_i \quad (2.7.1)$$

$$= -k_B \text{Tr} (\hat{\Gamma} \ln \hat{\Gamma}) \quad (2.7.2)$$

The first formula is the definition, the second follows from the fact that the trace of an operator is the sum of its eigenvalues. The constant k_B is Boltzmann's constant.

First we consider the *canonical ensemble*, which is a mixture of pure states all having the same particle number N . Consequently

$$\hat{\Gamma}_N = \sum_i p_{Ni} |\Psi_{Ni}\rangle \langle \Psi_{Ni}| \quad (2.7.3)$$

We seek to determine the p_{Ni} by the maximum-entropy principle. At equilibrium, S will be a maximum subject to two constraints. The probabilities must sum to unity, to which we attach a Lagrange multiplier λ , and the expectation value of \hat{H}_N must equal the observed energy,

$$E = \text{tr} (\hat{\Gamma}_N \hat{H}) \quad (2.7.4)$$

to which we attach another Lagrange multiplier α . (The notation tr indicates a trace over N constant states only.) The variational principle thus is

$$\delta \{-k_B \text{tr} (\hat{\Gamma}_N \ln \hat{\Gamma}_N) + \alpha (\text{tr} \hat{\Gamma}_N \hat{H} - E) + \lambda (\text{tr} \hat{\Gamma}_N - 1)\} = 0 \quad (2.7.5)$$

One can carry out the variation either by varying both the p_{Ni} and $|\psi_{Ni}\rangle$ in (2.7.3), or more elegantly, by working with $\hat{\Gamma}_N$ itself. Doing the latter, use $\hat{\Gamma}_N = \hat{\Gamma}_N^0 + \delta \hat{\Gamma}_N$ in (2.7.5) and find

$$\text{tr} [\delta \hat{\Gamma}_N (-k_B \ln \hat{\Gamma}_N^0 + 1 + \alpha \hat{H} + \lambda)] = 0 \quad (2.7.6)$$

This gives, after determination of λ from the normalization condition on $\hat{\Gamma}_N^0$,

$$\hat{\Gamma}_N^0 = \frac{e^{-\beta\hat{H}}}{\text{tr}(e^{-\beta\hat{H}})} \quad (2.7.7)$$

where

$$\beta = \frac{-\alpha}{k_B} = \frac{1}{k_B\theta} \quad (2.7.8)$$

in which θ is the temperature. Note that the final $\hat{\Gamma}_N^0$ commutes with \hat{H}_N , in agreement with (2.2.18). That (2.7.7) corresponds to a maximum S can be checked readily.

These results can be reformulated as follows. Define the *Helmholtz free energy* A for the density operator $\hat{\Gamma}_N$ by

$$A[\hat{\Gamma}_N] \equiv \text{tr} \hat{\Gamma}_N \left(\frac{1}{\beta} \ln \hat{\Gamma}_N + \hat{H} \right) = E - \theta S \quad (2.7.9)$$

Then for all positive and unit trace $\hat{\Gamma}_N$,

$$A[\hat{\Gamma}_N^0] \leq A[\hat{\Gamma}_N] \quad (2.7.10)$$

where

$$A[\hat{\Gamma}_N^0] = -\frac{1}{\beta} \ln Z_N \quad (2.7.11)$$

with Z_N the *partition function*

$$Z_N = \text{tr} e^{-\beta\hat{H}} \quad (2.7.12)$$

One proof of (2.7.10) is given by Feynman (1972). Another is presented in §3.5.

Now we turn to the *grand-canonical-ensemble* approach. The system is allowed to have a more general $\hat{\Gamma}$ in which there are nonzero probabilities associated with different particle numbers, but an average number of particles equal to some observed number

$$\text{Tr}(\hat{\Gamma}\hat{N}) = N \quad (2.7.13)$$

The entropy must be maximized subject to constant energy (2.7.4) and constant particle number (2.7.13). The result is the formula for the equilibrium $\hat{\Gamma}^0$,

$$\hat{\Gamma}^0 = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\text{Tr} e^{-\beta(\hat{H}-\mu\hat{N})}} \quad (2.7.14)$$

where μ is the Lagrange multiplier for the constraint of (2.7.13) and is called the *chemical potential*.

Again there is a reformulation. Define the *grand potential* by

$$\Omega[\hat{\Gamma}] \equiv \text{Tr} \hat{\Gamma} \left(\frac{1}{\beta} \ln \hat{\Gamma} + \hat{H} - \mu\hat{N} \right) = E - \theta S - \mu N \quad (2.7.15)$$

Then for all positive and unit trace $\hat{\Gamma}$,

$$\Omega[\hat{\Gamma}^0] \leq \Omega[\hat{\Gamma}] \quad (2.7.16)$$

where

$$\Omega[\hat{\Gamma}^0] = -\frac{1}{\beta} \ln Z \quad (2.7.17)$$

and Z is the *grand partition function*

$$Z = \text{Tr} e^{-\beta(\hat{H} - \mu\hat{N})} \quad (2.7.18)$$

A somewhat involved proof of (2.7.16) may be found in a paper by Mermin (1965), who followed Gibbs (1931, p. 131). A much simpler proof is given in §3.6.

It is instructive to compare the three minimum principles we have now established: (1.2.3) for the ground-state energy, (2.7.10) for the equilibrium Helmholtz free energy, and (2.7.16) for the grand potential. The second extends the first to finite temperature within the same N -particle Hilbert space. The third also applies to a finite-temperature system but to the larger Fock space that is the product space of all the different N -constant Hilbert spaces. The density-functional theory described in the next chapter will be structured similarly, proceeding from the ground-state theory based on (1.2.3) to finite-temperature extensions based on (2.7.10) and (2.7.16). The zero-temperature limits of the finite-temperature theories are of special interest.