The electron–electron interaction V is diagonal in the coordinate representation and has the form

$$V(\mathbf{r}\sigma, \mathbf{r}'\sigma') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

We choose the coordinate representation with spin as the basis $|\alpha\rangle$ and $|\beta\rangle$, and we denote the Hartree-Fock eigenfunctions as

$$\langle \mathbf{r}\sigma | m\rangle = \psi_m(\mathbf{r}\sigma)$$

With this notation, the Hartree-Fock equations (22.36) are transcribed as

$$\boxed{\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi_m(\mathbf{r}\sigma) - \frac{Ze^2}{r}\psi_m(\mathbf{r}\sigma) + e^2\sum_{t=1}^{n}\sum_{\sigma'}\int \psi_t^*(\mathbf{r}'\sigma')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_t(\mathbf{r}'\sigma')\psi_m(\mathbf{r}\sigma)\, d^3r' \\ -e^2\sum_{t=1}^{n}\sum_{\sigma'}\int \psi_t^*(\mathbf{r}'\sigma')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_t(\mathbf{r}\sigma)\psi_m(\mathbf{r}'\sigma')\, d^3r' = \varepsilon_m\psi_m(\mathbf{r}\sigma) \end{aligned}} \tag{22.37}$$

These coupled nonlinear differential-integral equations constitute the most familiar realization of the Hartree-Fock theory. The first sum on the left-hand side (without the term $t = m$ if m is an occupied state) represents the average effect of the interaction between all the other electrons in occupied one-particle states. The last sum on the left-hand side is attributable to the exchange matrix elements of the interaction.

Exercise 22.10. Show that the configuration space wave function corresponding to the independent particle state (22.22) can be expressed as the *Slater determinant*

$$\psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_n\sigma_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_1(\mathbf{r}_1\sigma_1) & \psi_1(\mathbf{r}_2\sigma_2) & \cdots & \psi_1(\mathbf{r}_n\sigma_n) \\ \psi_2(\mathbf{r}_1\sigma_1) & \psi_2(\mathbf{r}_2\sigma_2) & \cdots & \psi_2(\mathbf{r}_n\sigma_n) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_n(\mathbf{r}_1\sigma_1) & \psi_n(\mathbf{r}_2\sigma_2) & \cdots & \psi_n(\mathbf{r}_n\sigma_n) \end{vmatrix} \tag{22.38}$$

5. *Quantum Statistics and Thermodynamics.* The many-body operator formalism of Chapter 21 is ideally suited for treating statistical ensembles of identical particles. Here we will derive the quantum distribution functions for a system of noninteracting particles in thermal equilibrium.

If ρ denotes the *density* (or *statistical*) operator for an ensemble with fixed values for the averages of $\mathcal{H}$ and N, statistical thermodynamics requires that the von Neumann entropy,

$$S = -k\,\text{trace}(\rho \ln \rho) \tag{22.39}$$

be made a maximum subject to the constraints

$$\langle N\rangle = \text{trace}(\rho N) = n, \qquad \langle \mathcal{H}\rangle = \text{trace}(\rho\mathcal{H}) = E, \qquad \text{trace}(\rho) = 1 \tag{22.40}$$

The entropy principle is based on the probability and information concepts introduced in Section 2 in the Appendix and Section 15.5. Except for the multiplication by Boltzmann's constant k, the entropy S is that defined in Eq. (15.128).

Using the Lagrangian multipliers α and β, we see that the variational principle takes the form

$$\delta(S - k\alpha\langle N\rangle - k\beta\langle\mathcal{H}\rangle) = 0 \tag{22.41}$$

The normalization constraint in (22.40) requires that the variations of the density operator be restricted to

$$\text{trace}(\delta\rho) = 0 \tag{22.42}$$

and, therefore,

$$\delta S = -k\,\text{trace}(\delta\rho \ln \rho + \delta\rho) = -k\,\text{trace}(\delta\rho \ln \rho)$$

Substituting all the variations into (22.41), we obtain

$$\text{trace}[\delta\rho(\ln \rho + \alpha N + \beta\mathcal{H})] = 0$$

which is consistent with (22.42) only if

$$\ln \rho + \alpha N + \beta\mathcal{H} = -\ln Z\, 1$$

where Z is a number. We thus arrive at the grand canonical form of the density operator:

$$\boxed{\rho = \frac{e^{-\alpha N - \beta\mathcal{H}}}{Z}} \tag{22.43}$$

The normalization condition gives us

$$\boxed{Z = \text{trace}\; e^{-\alpha N - \beta\mathcal{H}}} \tag{22.44}$$

which is called the *grand partition function*. The parameters α and β must be determined from the first two constraint conditions (22.40). By thermodynamic arguments, $\beta = 1/kT$ is a measure of the temperature and $\mu = -\alpha/\beta$ is identified as the chemical potential.

Exercise 22.11. Evaluate the entropy for the equilibrium state (22.43), and show that

$$-kT \ln Z = \langle\mathcal{H}\rangle - \mu\langle N\rangle - TS = E - TS - \mu n \tag{22.45}$$

which is the grand canonical potential (or generalized free energy), suitable for relating thermodynamic variables to the underlying microscopic description.[6]

For a system of noninteracting identical particles with one-particle energies ε_i, known in thermodynamics as a generalized *ideal gas*,

$$\mathcal{H} = \sum_i \varepsilon_i a_i^\dagger a_i = \sum_i \varepsilon_i N_i \tag{22.46}$$

The ensemble average of any physical quantity represented by an operator Q may be computed by application of the formula

$$\langle Q\rangle = \text{trace}\; \rho Q \tag{22.47}$$

[6]Callen (1985), Section 5.3, and Reif (1965), Section 6.6.

We apply this relation to the evaluation of the average occupation numbers N_i:

$$\langle N_i \rangle = \langle a_i^\dagger a_i \rangle = \text{trace}(e^{-\alpha N - \beta \mathcal{H}} a_i^\dagger a_i)/Z \tag{22.48}$$

Using Eqs. (21.31)–(21.33) and the identity (3.59), we find that

$$\text{trace}(e^{-\alpha N - \beta \mathcal{H}} a_i^\dagger a_i) = e^{-(\alpha + \beta \varepsilon_i)} \, \text{trace}(e^{-\alpha N - \beta \mathcal{H}} a_i a_i^\dagger) \tag{22.49}$$

Exercise 22.12. Verify Eq. (22.49).

If the commutation relations for bosons or anticomutation relations for fermions are used, we obtain (with the upper sign for bosons and the lower sign for fermions)

$$\text{trace}(e^{-\alpha N - \beta \mathcal{H}} a_i^\dagger a_i) = e^{-(\alpha + \beta \varepsilon_i)} \, \text{trace}[e^{-\alpha N - \beta \mathcal{H}}(1 \pm a_i^\dagger a_i)]$$

Combining this relation with (22.43), we obtain

$$\boxed{\langle N_i \rangle = \langle a_i^\dagger a_i \rangle = \frac{1}{e^{\alpha + \beta \varepsilon_i} \mp 1}} \tag{22.50}$$

which is the familiar formula for the distribution of particles with Bose-Einstein (− sign) and Fermi-Dirac (+ sign) statistics, respectively.

The connection with the more conventional method for deriving the distribution (22.50) is established by introducing the occupation numbers n_i as the eigenvalues of $N_i = a_i^\dagger a_i$ and the corresponding eigenstates $|n_1, n_2, \ldots n_i, \ldots\rangle$ as basis states of the ideal gas. In this representation, the grand partition function becomes

$$Z = \sum_{n_1, n_2, \ldots} \prod_i e^{-(\alpha + \beta \varepsilon_i) n_i} \tag{22.51}$$

The distribution (22.50) is recovered by computing

$$\langle N_i \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_i} \tag{22.52}$$

which follows from (22.44) and (22.48). The two kinds of quantum statistics are distinguished and their partition functions are different, because in the Bose-Einstein case the occupation numbers assume all nonnegative integers as eigenvalues, whereas for the Fermi-Dirac case, $n_i = 0, 1$ are the only possible values.

The derivation of $\langle N_i \rangle$, using operators rather than the occupation-number basis, is intended to exhibit as plainly as possible the connection between the commutation relations for bosons and the anticommutation relations for fermions and the − and + signs, respectively, which characterize the denominator of the two distribution laws.

The Maxwell-Boltzmann distribution,

$$\langle N_i \rangle = e^{-\alpha - \varepsilon_i / kT} \tag{22.53}$$

is an approximation for the quantum distributions (22.50), valid if $\langle N_i \rangle \ll 1$. This may be regarded as a low-density or high-temperature approximation.

Exercise 22.13. Using operator algebra, show that the square of the fractional deviation from the mean occupation number is

$$\frac{\langle (N_i - \langle N_i \rangle)^2 \rangle}{\langle N_i \rangle^2} = \frac{\langle N_i^2 \rangle - \langle N_i \rangle^2}{\langle N_i \rangle^2} = e^{\alpha + \beta \varepsilon_i} = \frac{1}{\langle N_i \rangle} \pm 1 \tag{22.54}$$

where the + sign pertains to Bose-Einstein statistics and the − sign to Fermi-Dirac statistics. Also consider the Maxwell-Boltzmann limit.

In the next chapter, the formalism developed here will be applied to the derivation of the Planck distribution for photons in thermal equilibrium.

Problems

1. Consider a system of identical bosons with only two one-particle basis states, $a^\dagger_{1/2}\Psi^{(0)}$ and $a^\dagger_{-1/2}\Psi^{(0)}$. Define the Hermitian operators x, p_x, y, p_y by the relations

$$a_{1/2} = \frac{1}{\sqrt{2\hbar}}\left(cx + i\frac{p_x}{c}\right), \qquad a_{-1/2} = \frac{1}{\sqrt{2\hbar}}\left(cy + i\frac{p_y}{c}\right)$$

where c is an arbitrary real constant, and derive the commutation relations for these Hermitian operators. Express the angular momentum operator (22.6) in terms of these "coordinates" and "momenta," and also evaluate $\mathcal{J}^2$. Relate $\mathcal{J}^2$ to the square of the Hamiltonian of an isotropic two-dimensional harmonic oscillator by making the identification $c = \sqrt{m\omega}$, and show the connection between the eigenvalues of these operators.

2. (a) Using the fermion creation operators $a^\dagger_{jm}$, appropriate to particles with angular momentum j, form the closed-shell state in which all one-particle states $m = -j$ to $+j$ are occupied.

   (b) Prove that the closed shell has zero total angular momentum.

   (c) If a fermion with magnetic quantum number m is missing from a closed shell of particles with angular momentum j, show that, for coupling angular momenta, the hole state may be treated like a one-particle state with magnetic quantum number $-m$ and an effective creation operator $(-1)^{j-m}a_{jm}$.

3. Consider the unperturbed states $a^\dagger_{nm_n} \cdots a^\dagger_{km_k} \cdots a^\dagger_{1m_1}|\mathbf{0}\rangle$ of n spin one-half particles, each occupying one of n equivalent, degenerate orthogonal orbitals labeled by the quantum number k, and with $m_k = \pm 1/2$ denoting the spin quantum number associated with the orbital k. Show that in the space of the 2^n unperturbed states a spin-independent two-body interaction may, in first-order perturbation theory, be replaced by the effective exchange (or *Heisenberg*) Hamiltonian

$$\mathcal{H}_{\text{eff}} = -\frac{1}{\hbar^2}\sum_{k\ell}\langle k\ell|V|\ell k\rangle \mathbf{S}_k \cdot \mathbf{S}_\ell + \text{const.}$$

where $\mathbf{S}_k$ is the *localized* spin operator

$$\mathbf{S}_k = \frac{\hbar}{2}\sum_{m_k m'_k} a^\dagger_{km_k}a_{km'_k}\langle m_k|\boldsymbol{\sigma}|m'_k\rangle$$

4. For a Fermi gas of free particles with Fermi momentum p_F, calculate the ground state expectation value of the pair density operator

$$\sum_{\sigma',\sigma''} \psi^\dagger_{\sigma'}(\mathbf{r}')\psi^\dagger_{\sigma''}(\mathbf{r}'')\psi_{\sigma''}(\mathbf{r}'')\psi_{\sigma'}(\mathbf{r}')$$

in coordinate space and show that there is a repulsive interaction that would be absent if the particles were not identical. Show that there is no spatial correlation between particles of opposite spin.