Quantum Mechanics

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VIII. Identical Particles

8.1 Permutation Symmetry and Symmetrization Postulate

8.1.1 Permutation Symmetry

Unlike in classical mechanics, particles in quantum mechanics are indistinguishable. Suppose Considering a two-particle system with particle 1 characterized by $|k'\rangle$ and particle 2 by $|k''\rangle$, all kets of form

$$c_1|k'\rangle|k''\rangle + c_2|k''\rangle|k'\rangle \tag{8.1}$$

lead to an identical set of eigenvalues when measuring is performed, which is known as **exchange degeneracy**.

Define the **permutation operator** P_{12} by

$$P_{12}|k'\rangle|k''\rangle = |k''\rangle|k'\rangle . \tag{8.2}$$

Clearly, we have

$$P_{21} = P_{12}, \quad P_{12}^2 = 1 . \tag{8.3}$$

The effect of P_{12} is interchanging 1 and 2.

For simplicity, we consider a specific case where the two-particle state ket is completely specified by the eigenvalues of a single observable A for each of the particles:

$$A_1|a'\rangle|a''\rangle = a'|a'\rangle|a''\rangle \tag{8.4}$$

and

$$A_2|a'\rangle|a''\rangle = a''|a'\rangle|a''\rangle . \tag{8.5}$$

Applying P_{12} to both sides of Eq. (8.4) and inserting $1 = P_{12}^{-1}P_{12}$, we have

$$P_{12}A_1P_{12}^{-1}P_{12}|a'\rangle|a''\rangle = a'P_{12}|a'\rangle|a''\rangle \Rightarrow P_{12}A_1P_{12}^{-1}|a''\rangle|a'\rangle = a'|a''\rangle|a'\rangle , \tag{8.6}$$

which is consistent with Eq. (8.5) only if

$$P_{12}A_1P_{12}^{-1} = A_2 , \tag{8.7}$$

which means that P_{12} must change the particle labels of observables.

The observables in the Hamiltonian of a system of two identical particles must appear symmetrically. For example,

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V_{\text{pair}}\left(|\mathbf{x}_1 - \mathbf{x}_2|\right) + V_{\text{ext}}\left(\mathbf{x}_1\right) + V_{\text{ext}}\left(\mathbf{x}_2\right). \tag{8.8}$$

Clearly, we have

$$P_{12} H P_{12}^{-1} = H\ , \tag{8.9}$$

so P_{12} is a constant of the motion. Due to Eq. (8.3), the allowed eigenvalues of P_{12} are +1 and -1. If the two-particle state ket is initially symmetrical (antisymmetrical), it remains so all the time. The eigenkets of P_{12} are selected as

$$\left|k'k''\right\rangle_{+} \equiv \frac{1}{\sqrt{2}}\left(\left|k'\right\rangle\left|k''\right\rangle + \left|k''\right\rangle\left|k'\right\rangle\right) \tag{8.10}$$

and

$$\left|k'k''\right\rangle_{-} \equiv \frac{1}{\sqrt{2}}\left(\left|k'\right\rangle\left|k''\right\rangle - \left|k''\right\rangle\left|k'\right\rangle\right). \tag{8.11}$$

Define the **symmetrizer** as

$$S_{12} \equiv \frac{1}{2}\left(1 + P_{12}\right), \tag{8.12}$$

and the **antisymmetrizer** as

$$A_{12} \equiv \frac{1}{2}\left(1 - P_{12}\right), \tag{8.13}$$

then we can have

$$\begin{aligned} &\begin{Bmatrix} S_{12} \\ A_{12} \end{Bmatrix}\left(c_1\left|k'\right\rangle\left|k''\right\rangle + c_2\left|k''\right\rangle\left|k'\right\rangle\right) \\ &= \frac{1}{2}\left(c_1\left|k'\right\rangle\left|k''\right\rangle + c_2\left|k''\right\rangle\left|k'\right\rangle\right) \pm \frac{1}{2}\left(c_1\left|k'\right\rangle\left|k''\right\rangle + c_2\left|k''\right\rangle\left|k'\right\rangle\right). \\ &= \frac{c_1 \pm c_2}{2}\left(\left|k'\right\rangle\left|k''\right\rangle \pm \left|k''\right\rangle\left|k'\right\rangle\right) \end{aligned} \tag{8.14}$$

8.1.1 Symmetrization Postulate

Half-integer-spin particles are fermions, and integer-spin particles are bosons. Fermions is antisymmetrical under the pair interchange, while bosons are symmetrical. Many identical fermions satisfy the **Fermi-Dirac** (F-D) **statistics** while bosons satisfy the **Bose-Einstein** (B-E) **statistics**. Fermions obey the **Pauli exclusion principle** that two fermions can not occupy the same state.

Consider two identical particles with only two states. For fermions, the only possible combined state is

$$\frac{1}{\sqrt{2}}\left(\left|k'\right\rangle\left|k''\right\rangle - \left|k''\right\rangle\left|k'\right\rangle\right). \tag{8.15}$$

For bosons, there are three possible states

$$|k'\rangle|k'\rangle,\quad |k''\rangle|k''\rangle,\quad \frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle+|k''\rangle|k'\rangle\right). \tag{8.16}$$

In contrast, for "classical" particles satisfying the **Maxwell-Boltzmann** (M-B) **statistics**, there are four independent states:

$$|k'\rangle|k''\rangle,\quad |k''\rangle|k'\rangle,\quad |k'\rangle|k'\rangle,\quad |k''\rangle|k''\rangle. \tag{8.17}$$

8.2 Two-Electron and Helium Systems

8.2.1 Two-Electron System

The base kets of two electrons may be specified by their positions $\mathbf{x}_1$, $\mathbf{x}_2$ and their spin-magnetic quantum numbers m_{s1} and m_{s2}. The wave function can be written as

$$\psi=\sum_{m_{s1}m_{s2}} C(m_{s1},m_{s2})\langle \mathbf{x}_1,m_{s1};\mathbf{x}_2,m_{s2}|\alpha\rangle. \tag{8.18}$$

If $\left[\mathbf{S}_{\text{tot}}^2,H\right]=0$, the energy eigenfunction is also an eigenfunction of $\mathbf{S}_{\text{tot}}^2$. The wavefunction can also be written as

$$\psi=\phi(\mathbf{x}_1,\mathbf{x}_2)\chi \tag{8.19}$$

with the spin function

$$\chi(m_{s1},m_{s2})=\begin{cases}\chi_{++}\\ \frac{1}{\sqrt{2}}(\chi_{+-}+\chi_{-+})\\ \chi_{--}\\ \frac{1}{\sqrt{2}}(\chi_{+-}-\chi_{-+})\end{cases}, \tag{8.20}$$

where χ_{+-} corresponds to $\chi\left(m_{s1}=\frac{1}{2},m_{s2}=-\frac{1}{2}\right)$, and vice versa. The first three are symmetrical triplet states, and the last one is antisymmetrical singlet.

We note

$$\langle \mathbf{x}_1,m_{s1};\mathbf{x}_2,m_{s2}|P_{12}|\alpha\rangle=\langle \mathbf{x}_2,m_{s2};\mathbf{x}_1,m_{s1}|\alpha\rangle. \tag{8.21}$$

Fermi-Dirac statistics thus requires

$$\langle \mathbf{x}_1,m_{s1};\mathbf{x}_2,m_{s2}|\alpha\rangle=-\langle \mathbf{x}_2,m_{s2};\mathbf{x}_1,m_{s1}|\alpha\rangle. \tag{8.22}$$

Clearly, P_{12} can be written as

$$P_{12}=P_{12}^{(\text{space})}P_{12}^{(\text{spin})}. \tag{8.23}$$

If the space part of the wave function is symmetrical (antisymmetrical), the spin part must be antisymmetrical (symmetrical).

Because

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \begin{cases} \dfrac{\hbar^2}{4}, & \text{triplet} \\ -\dfrac{3\hbar^2}{4}, & \text{singlet} \end{cases}, \tag{8.24}$$

we have

$$P_{12}^{(\text{spin})} = \frac{1}{2}\left(1 + \frac{4}{\hbar^2}\mathbf{S}_1 \cdot \mathbf{S}_2\right). \tag{8.25}$$

For the specific case where the mutual interaction between the two electrons can be ignored, the wave function for the energy eigenfunction ψ without spin dependence satisfying

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V_{\text{ext}}(\mathbf{x}_1) + V_{\text{ext}}(\mathbf{x}_2)\right]\psi = E\psi \tag{8.26}$$

is separable. Writing the solution to have the form $\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2)$ times the spin function, the space part must be written as a symmetrical and antisymmetrical combination:

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2) \pm \omega_A(\mathbf{x}_2)\omega_B(\mathbf{x}_1)\right], \tag{8.27}$$

where + is for a spin singlet and – is for a spin triplet. The probability

$$\begin{aligned} &p(\mathbf{x}_1, \mathbf{x}_2)\mathrm{d}^3x_1\mathrm{d}^3x_2 = \left|\phi(\mathbf{x}_1, \mathbf{x}_2)\right|^2 \mathrm{d}^3x_1\mathrm{d}^3x_2 \\ &= \frac{1}{2}\left\{\left|\omega_A(\mathbf{x}_1)\right|^2\left|\omega_B(\mathbf{x}_2)\right|^2 + \left|\omega_A(\mathbf{x}_2)\right|^2\left|\omega_B(\mathbf{x}_1)\right|^2 \pm 2\,\mathrm{Re}\left[\omega_A(\mathbf{x}_1)\omega_B(\mathbf{x}_2)\omega_A^*(\mathbf{x}_2)\omega_B^*(\mathbf{x}_1)\right]\right\}\mathrm{d}^3x_1\mathrm{d}^3x_2 \end{aligned} \tag{8.28}$$

The last term is known as the **exchange density**. Therefore, when the electrons are in a spin-triplet state, the probability of finding two electrons at the same point vanishes; when their spins are in a singlet state, there is enhanced probability of finding them at the same point.

8.2.2 The Helium Atom

The Schrödinger equation for a helium atom cannot be solved analytically, so we will apply the perturbation theory and the variational method to find the solution approximately.

The basic Hamiltonian is given by

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}, \tag{8.29}$$

where $r_1 \equiv |\mathbf{x}_1|, r_2 \equiv |\mathbf{x}_2|$, and $r_{12} \equiv |\mathbf{x}_1 - \mathbf{x}_2|$. Suppose the last term were absent, the space part of the wave function for the important case where one of the electrons is in the ground state and the other in an excited state is

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\psi_{100}(\mathbf{x}_1)\psi_{nlm}(\mathbf{x}_2) \pm \psi_{100}(\mathbf{x}_2)\psi_{nlm}(\mathbf{x}_1)\right]. \tag{8.30}$$

For the ground state, both electrons are in $n = 1$ and $l = 0$, so the space function must be symmetrical and only the spin singlet function is allowed. The wave function is then

$$\psi_{100}(\mathbf{x}_1)\psi_{100}(\mathbf{x}_2)\chi_{\text{singlet}} = \frac{Z^2}{\pi a_0^3}\exp\left[-Z(r_1 + r_2)/a_0\right]\chi \tag{8.31}$$

with $Z = 2$. The corresponding "unperturbed" ground-state energy is

$$E = 2 \times 4\left(-\frac{e^2}{2a_0} \right) = -108.8 \text{ eV}, \tag{8.32}$$

whose absolute value is about 30% larger than the experimental value.

Next, consider the last term in Eq. (8.29) as the perturbation. We obtain

$$\Delta_{(1s)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{(1s)^2} = \iint \frac{Z^6}{\pi^2 a_0^6} \exp\left[-2Z\left(r_1 + r_2 \right) / a_0 \right] \frac{e^2}{r_{12}} \mathrm{d}^3 x_1 \mathrm{d}^3 x_2 \ . \tag{8.33}$$

This integral can be performed in the spherical coordinates. Suppose $r_1 > r_2$, we have

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}} = \sum_{l=0}^{\infty} \frac{r_2^l}{r_1^{l+1}} P_l\left(\cos\gamma \right), \tag{8.34}$$

where γ is the angle between $\mathbf{x}_1$ and $\mathbf{x}_2$. Because

$$P_l\left(\cos\gamma \right) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}\left(\theta_1, \phi_1 \right) Y_l^m\left(\theta_2, \phi_2 \right), \tag{8.35}$$

The angular integration is trivial:

$$\int Y_l^m\left(\theta_i, \phi_i \right) \mathrm{d}\Omega_i = \frac{1}{\sqrt{4\pi}} \left(4\pi \right) \delta_{l0} \delta_{m0} . \tag{8.36}$$

It can be shown that the radial integration is

$$\begin{aligned} &\int_0^{\infty} \left[\int_0^{r_1} \frac{1}{r_1} \exp\left(-\left(2Z / a_0 \right)\left(r_1 + r_2 \right) \right) r_2^2 \mathrm{d}r_2 + \int_{r_1}^{\infty} \frac{1}{r_2} \exp\left(-\left(2Z / a_0 \right)\left(r_1 + r_2 \right) \right) r_2^2 \mathrm{d}r_2 \right] r_1^2 \mathrm{d}r_1 \\ &= \frac{5}{128} \frac{a_0^5}{Z^5} \end{aligned} . \tag{8.37}$$

Therefore, Eq. (8.33) can be integrated out to be

$$\Delta_{(1s)^2} = \left(\frac{Z^6 e^2}{\pi^2 a_0^6} \right) 4\pi \left(\sqrt{4\pi} \right)^2 \left(\frac{5}{128} \right) \left(\frac{a_0^5}{Z^5} \right) = \frac{5e^2}{2a_0} . \tag{8.38}$$

Adding this energy shift to Eq. (8.32), we get

$$E' = \left(-8 + \frac{5}{2} \right) \left(\frac{e^2}{2a_0} \right) \simeq -74.8 \text{ eV}, \tag{8.39}$$

which is much closer to the experimental value of -78.8 eV.

The calculated energy can be further optimized by using the variational method with $Z = 2$ as a variational parameter Z_{eff} because the electric charge felt by one electron is "screened" by the other electron. According to Eq. (8.31), the trial space wave function can be written as

$$\left\langle \mathbf{x}_1, \mathbf{x}_2 \middle| \tilde{0} \right\rangle = \left(\frac{Z_{\text{eff}}^3}{\pi a_0^3} \right) \exp\left[-Z_{\text{eff}}\left(r_1 + r_2 \right) / a_0 \right]. \tag{8.40}$$

The trail energy is then

$$\tilde{H} = \left\langle \tilde{0} \middle| \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} \middle| \tilde{0} \right\rangle - \left\langle \tilde{0} \middle| \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \middle| \tilde{0} \right\rangle + \left\langle \tilde{0} \middle| \frac{e^2}{r_{12}} \middle| \tilde{0} \right\rangle$$
$$= \left(Z_{\text{eff}}^2 - 2ZZ_{\text{eff}} + \frac{5}{8} Z_{\text{eff}} \right) \frac{e^2}{a_0} \quad . \tag{8.41}$$

The minimum of $\tilde{H}$ is located at

$$Z_{\text{eff}} = 2 - \frac{5}{16} = 1.6875 , \tag{8.42}$$

corresponding to the estimated energy value of -77.5 eV.

8.3 Multiparticle States

8.3.1 Non-Interacting Many-Body Systems

Two identical bosons without interactions can have their overall wave function written as

$$\psi_{\text{B}}(1,2) \equiv \psi_{\text{B}}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left[\phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) + \phi_2(\mathbf{x}_1) \phi_1(\mathbf{x}_2) \right], \tag{8.43}$$

where ϕ_1 and ϕ_2 are single-particle wave functions, and $\mathbf{x}_1$ and $\mathbf{x}_2$ are particle positions. By contrast, the overall wave functions for two identical fermions can be written as

$$\psi_{\text{F}}(1,2) \equiv \psi_{\text{F}}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left(\phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) - \phi_2(\mathbf{x}_1) \phi_1(\mathbf{x}_2) \right)$$
$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix} \quad . \tag{8.44}$$

For N identical fermions, the overall wave function can be written in form of the Slater determinant:

$$\psi_{\text{F}}(1, \cdots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ & \vdots & & \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix} . \tag{8.45}$$

The single-particle wave functions should satisfy the orthonormal condition:

$$\left\langle \phi_i \middle| \phi_j \right\rangle = \delta_{ij} . \tag{8.46}$$

Define the overall **exchange operator**

$$A = \frac{1}{\sqrt{N!}} \sum_{p=0}^{N-1} (\pm 1)^p P = \frac{1}{\sqrt{N!}} \left[1 \pm \sum_{ij} P_{ij} + \sum_{ijk} P_{ijk} \pm \cdots \right], \tag{8.47}$$

where "+" corresponds to bosons, and "-" corresponds to fermions, P_{ij} is the two-body exchange operator, and P_{ijk} is the three-body exchange operator. The overall wave function for non-interacting many-body identical particles can be expressed as

$$\psi = A\left[\phi_1(1)\phi_2(2)\cdots\phi_N(N)\right] = A\Pi, \tag{8.48}$$

where

$$\Pi \equiv \phi_1(1)\phi_2(2)\cdots\phi_N(N). \tag{8.49}$$

8.3.2 Second Quantization

Define a multiparticle state as

$$\left|n_1, n_2, \cdots, n_i, \cdots\right\rangle, \tag{8.50}$$

where n_i specify the number of particles with eigenvalue k_i for some operator, which span a **Fock space** assuming a basis of non-interacting states. The **vacuum state** is expressed as

$$\left|\mathbf{0}\right\rangle \equiv \left|0, 0, \cdots, 0, \cdots\right\rangle \tag{8.51}$$

and the single-particles state is

$$\left|k_i\right\rangle \equiv \left|0, 0, \cdots, n_i = 1, \cdots\right\rangle. \tag{8.52}$$

The **field operator** $a_i^\dagger$ increases by one the number of particles in state *i*:

$$a_i^\dagger \left|n_1, n_2, \cdots, n_i, \cdots\right\rangle \propto \left|n_1, n_2, \cdots, n_{i+1}, \cdots\right\rangle. \tag{8.53}$$

We *postulate* that

$$a_i^\dagger \left|\mathbf{0}\right\rangle = \left|k_i\right\rangle. \tag{8.54}$$

Because

$$\left\langle\mathbf{0}\right|a_i\left|k_i\right\rangle = \left\langle\mathbf{0}\right|\left[a_i a_i^\dagger\left|\mathbf{0}\right\rangle\right] = \left\langle k_i\right|k_i\rangle = 1, \tag{8.55}$$

we have

$$a_i\left|k_i\right\rangle = \left|\mathbf{0}\right\rangle, \tag{8.56}$$

which shows that a_i indeed acts as a particle annihilation operator with the following features:

$$\begin{aligned} &a_i\left|n_1, n_2, \cdots, n_i, \cdots\right\rangle \propto \left|n_1, n_2, \cdots, n_i - 1, \cdots\right\rangle \\ &a_i\left|\mathbf{0}\right\rangle = 0 \\ &a_i\left|k_j\right\rangle = \delta_{ij}\left|\mathbf{0}\right\rangle \end{aligned}. \tag{8.57}$$

Now consider the permutation symmetry. For a two-particle state,

$$a_i^\dagger a_j^\dagger\left|\mathbf{0}\right\rangle = \pm a_j^\dagger a_i^\dagger\left|\mathbf{0}\right\rangle, \tag{8.58}$$

where + sign is for bosons and – sign is for fermions. Extending to multiparticle states, we have

$$\left[a_i^\dagger, a_j^\dagger\right] = 0, \quad \left[a_i, a_j\right] = 0 \tag{8.59}$$

for bosons and

$$\left\{a_i^\dagger, a_j^\dagger\right\} = 0, \quad \left\{a_i, a_j\right\} = 0 \tag{8.60}$$

for fermions. For both bosons and anions, we can define the number operator

$$N = \sum_i a_i^\dagger a_i \tag{8.61}$$

to count the total number of identical particles.

Suppose the single-particle states $\left|k_i\right\rangle$ are eigenstates of an "additive" single-particle operator K, then in a multiparticle state

$$\left|\Psi\right\rangle = \left|n_1, n_2, \cdots, n_i, \cdots\right\rangle, \tag{8.62}$$

the corresponding multiparticle operator $\mathscr{K}$ has the eigenvalue of $\sum_i n_i k_i$. If we use the completeness relation to write

$$\left|k_i\right\rangle = \sum_j \left|l_j\right\rangle\left\langle l_j \middle| k_i\right\rangle, \tag{8.63}$$

then we may *postulate* that

$$a_i^\dagger = \sum_j b_j^\dagger \left\langle l_j \middle| k_i\right\rangle, \tag{8.64}$$

which implies that

$$a_i = \sum_j \left\langle k_i \middle| l_j\right\rangle b_j \ , \tag{8.65}$$

where $b_j^\dagger$ and b_j create and annihilate particles in the single-particle states $\left|l_j\right\rangle$. Then for the additive non-interacting single-particle operator, we have

$$\begin{aligned}
\mathscr{K} &= \sum_i k_i N_i = \sum_i k_i a_i^\dagger a_i \\
&= \sum_i k_i \sum_{mn} b_m^\dagger \left\langle l_m \middle| k_i\right\rangle\left\langle k_i \middle| l_n\right\rangle b_n \\
&= \sum_{mn} b_m^\dagger b_n \sum_i \left\langle l_m \middle| k_i\right\rangle k_i \left\langle k_i \middle| l_n\right\rangle \\
&= \sum_{mn} b_m^\dagger b_n \left\langle l_m \middle| \left[K \sum_i \left|k_i\right\rangle\left\langle k_i\right|\right] \middle| l_n\right\rangle \\
&= \sum_{mn} b_m^\dagger b_n \left\langle l_m \middle| K \middle| l_n\right\rangle
\end{aligned} \quad . \tag{8.66}$$

For the interacting case, let the symmetrical real matrix elements V_{ij} specify the two-particle eigenvalues for the interactions between particles in single-particle states $\left|k_i\right\rangle$ and $\left|k_j\right\rangle$. The corresponding operator is then second-quantized as

$$\mathscr{V} = \frac{1}{2}\sum_{i\neq j} V_{ij} N_i N_j + \frac{1}{2}\sum_i V_{ii} N_i \left(N_i - 1\right), \tag{8.67}$$

where the first term sums up all two-particle interactions, while the second term accounts for all "self-interactions" for particles in the same state with $n\left(n-1\right)/2$ ways. It can be rewritten as

$$\mathscr{V} = \frac{1}{2}\sum_{ij} V_{ij}\left(N_i N_j - N_i\delta_{ij}\right) = \frac{1}{2}\sum_{ij} V_{ij}\Pi_{ij}\ , \tag{8.68}$$

where the **pair distribution operator** $\Pi_{ij} \equiv N_i N_j - N_i\delta_{ij}$, which can also be expressed as

$$\begin{aligned}\Pi_{ij} &= a_i^\dagger a_i a_j^\dagger a_j - a_i^\dagger a_i\delta_{ij} = a_i^\dagger\left(\delta_{ij} \pm a_j^\dagger a_i\right)a_j - a_i^\dagger a_i\delta_{ij} \\ &= \pm a_i^\dagger a_j^\dagger a_i a_j = a_i^\dagger a_j^\dagger a_j a_i\end{aligned}\ . \tag{8.69}$$

Therefore, Eq. (8.67) can be rewritten as

$$\mathscr{V} = \frac{1}{2}\sum_{ij} V_{ij} a_i^\dagger a_j^\dagger a_j a_i\ . \tag{8.70}$$

We can use Eq. (8.65) to change its basis as

$$\mathscr{V} = \frac{1}{2}\sum_{mnpq}\langle mn|V|pq\rangle b_m^\dagger b_n^\dagger b_q b_p\ , \tag{8.71}$$

where

$$\langle mn|V|pq\rangle = \sum_{ij} V_{ij}\langle l_m|k_i\rangle\langle k_i|l_p\rangle\langle l_n|k_j\rangle\langle k_j|l_q\rangle\ . \tag{8.72}$$

8.4 Quantization of the Electromagnetic Field

8.4.1 Maxwell's Equations in Free Space

Maxwell's equations in Gaussian units without any charges or currents are

$$\begin{aligned}\nabla\cdot\mathbf{E} &= 0 \\ \nabla\cdot\mathbf{B} &= 0 \\ \nabla\times\mathbf{E} + \frac{1}{c}\frac{\partial\mathbf{B}}{\partial t} &= 0\ \cdot \\ \nabla\times\mathbf{B} - \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} &= 0\end{aligned} \tag{8.73}$$

Define a vector potential $\mathbf{A}(\mathbf{x},t)$ to have

$$\mathbf{B} = \nabla\times\mathbf{A}\ . \tag{8.74}$$

Choosing the Coulomb gauge

$$\nabla\cdot\mathbf{A} = 0\ , \tag{8.75}$$

we have

$$\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}\ . \tag{8.76}$$

Therefore, determining $\mathbf{A}(\mathbf{x},t)$ is equivalent to determining $\mathbf{E}(\mathbf{x},t)$ and $\mathbf{B}(\mathbf{x},t)$, which satisfies the wave equation

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = 0\ . \tag{8.77}$$

The set of solutions are

$$\mathbf{A}(\mathbf{x},t) = \mathbf{A}(\mathbf{k})\exp(\pm i\mathbf{k}\cdot\mathbf{x})\exp(\pm i\omega t)\ , \tag{8.78}$$

where $\omega \equiv \omega_k = kc$. The Coulomb gauge condition Eq. (8.75) implies that

$$\pm i\mathbf{k}\cdot\mathbf{A}(\mathbf{x},t)=0 \Rightarrow \mathbf{k}\cdot\mathbf{A}(\mathbf{k})=0, \tag{8.79}$$

which means that $\mathbf{A}(\mathbf{x},t)$ is perpendicular to the propagation direction $\mathbf{k}$, and the general solution to Eq. (8.77) can be in the form of

$$\mathbf{A}(\mathbf{x},t)=\sum_{\mathbf{k},\lambda}\hat{\mathbf{e}}_{\mathbf{k}\lambda}\mathbf{A}_{\mathbf{k},\lambda}(\mathbf{x},t), \tag{8.80}$$

where $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$ are unit vectors corresponding to two values for λ perpendicular to $\mathbf{k}$ and the Herimitan operator

$$\mathbf{A}_{\mathbf{k},\lambda}(\mathbf{x},t)=\mathbf{A}_{\mathbf{k},\lambda}\exp\left[-i(\omega_k t-\mathbf{k}\cdot\mathbf{x})\right]+\mathbf{A}^*_{\mathbf{k},\lambda}\exp\left[i(\omega_k t-\mathbf{k}\cdot\mathbf{x})\right]. \tag{8.81}$$

It is useful to take $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$ as directions of circular polarization written as

$$\hat{\mathbf{e}}_{\mathbf{k}\pm}=\mp\frac{1}{\sqrt{2}}\left(\hat{\mathbf{e}}^{(1)}_{\mathbf{k}}\pm i\hat{\mathbf{e}}^{(2)}_{\mathbf{k}}\right), \tag{8.82}$$

where $\hat{\mathbf{e}}^{(1)}_{\mathbf{k}}$ and $\hat{\mathbf{e}}^{(2)}_{\mathbf{k}}$ are linear unit vectors perpendicular to $\mathbf{k}$, and $\lambda=\pm$ denotes the polarization state. It is easy to show that

$$\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\hat{\mathbf{e}}^*_{\pm\mathbf{k}\lambda'}=\pm\delta_{\lambda\lambda'} \tag{8.83}$$

and

$$\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\times\hat{\mathbf{e}}_{\pm\mathbf{k}\lambda'}=\pm i\lambda\delta_{\lambda\lambda'}\hat{\mathbf{k}}\,. \tag{8.84}$$

The electric field $\mathbf{E}(\mathbf{x},t)$ can then be written down from Eq. (8.76) and the magnetic field $\mathbf{B}(\mathbf{x},t)$ can be written down from Eq. (8.74). The energy in the magnetic field is given by

$$\mathscr{E}=\frac{1}{8\pi}\int_V\left[\left|\mathbf{E}(\mathbf{x},t)\right|^2+\left|\mathbf{B}(\mathbf{x},t)\right|^2\right]\mathrm{d}^3x\,. \tag{8.85}$$

In a finite cubic volume $V=L^3$ with periodic boundary conditions applied, the wave vector

$$\mathbf{k}=(k_x,k_y,k_z)=\frac{2\pi}{L}(n_x,n_y,n_z), \tag{8.86}$$

where n_x,n_y,n_z are integers.

Using Eq. (8.76) with Eq. (8.80) and Eq. (8.81), we have

$$\mathbf{E}=\frac{i}{c}\sum_{\mathbf{k},\lambda}\omega_k\left[\mathbf{A}_{\mathbf{k},\lambda}\exp\left(-i(\omega_k t-\mathbf{k}\cdot\mathbf{x})\right)-\mathbf{A}^*_{\mathbf{k},\lambda}\exp\left(i(\omega_k t-\mathbf{k}\cdot\mathbf{x})\right)\right]\hat{\mathbf{e}}_{\mathbf{k}\lambda} \tag{8.87}$$

and

$$\mathbf{E}^*=-\frac{i}{c}\sum_{\mathbf{k}',\lambda'}\omega_{k'}\left[\mathbf{A}^*_{\mathbf{k}',\lambda'}\exp\left(i(\omega_{k'}t-\mathbf{k}'\cdot\mathbf{x})\right)-\mathbf{A}_{\mathbf{k}',\lambda'}\exp\left(-i(\omega_{k'}t-\mathbf{k}'\cdot\mathbf{x})\right)\right]\hat{\mathbf{e}}^*_{\mathbf{k}'\lambda'}\,. \tag{8.88}$$

Because

$$\int_V \exp\left[i\left(\mathbf{k}\mp\mathbf{k}'\right)\cdot\mathbf{x}\right]\mathbf{d}^3x = V\delta_{\mathbf{k},\pm\mathbf{k}'}, \tag{8.89}$$

combining with Eq. (8.83) to get

$$\begin{aligned}&\int_V \left|\mathbf{E}\left(\mathbf{x},t\right)\right|^2 \mathrm{d}^3x = \\ &\sum_{\mathbf{k},\lambda}\frac{\omega_k^2}{c^2}\left[\mathbf{A}^*_{\mathbf{k},\lambda}\mathbf{A}_{\mathbf{k},\lambda} + \mathbf{A}_{\mathbf{k},\lambda}\mathbf{A}^*_{\mathbf{k},\lambda} + \mathbf{A}^*_{\mathbf{k},\lambda}\mathbf{A}^*_{-\mathbf{k},\lambda}\exp\left(2i\omega_k t\right) + \mathbf{A}_{\mathbf{k},\lambda}\mathbf{A}_{-\mathbf{k},\lambda}\exp\left(-2i\omega_k t\right)\right]\end{aligned}. \tag{8.90}$$

The integration for $\left|\mathbf{B}\right|^2$ is similar, so we finally obtain

$$\mathscr{E} = \frac{V}{4\pi}\sum_{\mathbf{k},\lambda}\frac{\omega_k^2}{c^2}\left[\mathbf{A}^*_{\mathbf{k},\lambda}\mathbf{A}_{\mathbf{k},\lambda} + \mathbf{A}_{\mathbf{k},\lambda}\mathbf{A}^*_{\mathbf{k},\lambda}\right]. \tag{8.91}$$

8.4.2 Photons and Energy Quantization

For a many-body system composed of photons, an operator $a^\dagger_\lambda\left(\mathbf{k}\right)$ creates a photon with polarization λ and momentum $\hbar\mathbf{k}$, and $a_\lambda\left(\mathbf{k}\right)$ annihilates this photon. Because the energy of a photon is $\hbar\omega_k = \hbar ck$, the Hamiltonian is

$$H = \sum_{\mathbf{k},\lambda}\hbar\omega_k a^\dagger_\lambda\left(\mathbf{k}\right)a_\lambda\left(\mathbf{k}\right). \tag{8.92}$$

Photon is a boson with spin 1, and its polarization directions are the unit vectors given by Eq. (8.82). The rotation about the photon direction **k** through an angle ϕ for a circularly polarized electromagnetic wave is equivalent to the transformation

$$\hat{\mathbf{e}}^{(1)}_{\mathbf{k}} \to \hat{\mathbf{e}}^{(1)'}_{\mathbf{k}} = \cos\phi\hat{\mathbf{e}}^{(1)}_{\mathbf{k}} - \sin\phi\hat{\mathbf{e}}^{(2)}_{\mathbf{k}} \tag{8.93}$$

and

$$\hat{\mathbf{e}}^{(2)}_{\mathbf{k}} \to \hat{\mathbf{e}}^{(2)'}_{\mathbf{k}} = \cos\phi\hat{\mathbf{e}}^{(1)}_{\mathbf{k}} + \sin\phi\hat{\mathbf{e}}^{(2)}_{\mathbf{k}}, \tag{8.94}$$

which means that the rotation introduces a phase change $\exp\left(\mp i\phi\right)$ to $\hat{\mathbf{e}}_{\mathbf{k}\pm}$.

Eq. (8.92) can be rewritten as

$$\begin{aligned}H &= \frac{1}{2}\sum_{\mathbf{k},\lambda}\hbar\omega_k\left[a^\dagger_\lambda\left(\mathbf{k}\right)a_\lambda\left(\mathbf{k}\right) + a^\dagger_\lambda\left(\mathbf{k}\right)a_\lambda\left(\mathbf{k}\right)\right] \\ &= \frac{1}{2}\sum_{\mathbf{k},\lambda}\hbar\omega_k\left[a^\dagger_\lambda\left(\mathbf{k}\right)a_\lambda\left(\mathbf{k}\right) + a_\lambda\left(\mathbf{k}\right)a^\dagger_\lambda\left(\mathbf{k}\right) + 1\right]\end{aligned}. \tag{8.95}$$

This is consistent with the classical energy Eq. (8.91) with the definition of the operator

$$\mathbf{A}_{\mathbf{k},\lambda} = \sqrt{\frac{4\pi\hbar c^2}{2V\omega_k}}a_\lambda\left(\mathbf{k}\right) \tag{8.96}$$

differed by a "zero-point" energy called the **vacuum energy** with zero photons present:

$$E_0 = \frac{1}{2}\sum_{\mathbf{k},\lambda}\hbar\omega_k = \sum_{\mathbf{k}}\hbar\omega_k\ . \tag{8.97}$$

8.4.3 The Casimir Effect

The vacuum energy is able to exert a macroscopic force between conducting surfaces, which is called the **Casimir effect**. Supposing two large conducting plates are parallel in the *x*-*y* plane and separate by a distance *d* along the *z* axis, whose potential-energy function is

$$U(d) = E_0(d) - E_0(\infty). \tag{8.98}$$

Combining Eq. (8.97) with Eq. (8.86), we have

$$E_0(d) = \hbar \sum_{k_x,k_y,n} \omega_k = \hbar c \sum_{k_x,k_y,n} \sqrt{k_x^2 + k_y^2 + \left(\frac{n\pi}{d}\right)^2}\ . \tag{8.99}$$

Assume that the side length in the *x*-*y* plane $L \gg d$, the summations over k_x and k_y can be replaced by integrals:

$$E_0(d) = \hbar c \left(\frac{L}{\pi}\right)^2 \int_0^\infty \mathrm{d}k_x \int_0^\infty \mathrm{d}k_y \sum_n \sqrt{k_x^2 + k_y^2 + \left(\frac{n\pi}{d}\right)^2}\ . \tag{8.100}$$

The infinities can be handled by multiplying the integrand by a function $f(k)$, where $f(k) \to 1$ for $k \to 0$ and $f(k) \to 0$ for $k \to \infty$. Further introduce the polar coordinate $\rho = \sqrt{k_x^2 + k_y^2}$ with $\mathrm{d}k_x \mathrm{d}k_y = 2\pi\rho \mathrm{d}\rho$ and note that the integration limits in Eq. (8.100) corresponds to 1/4 of the (k_x, k_y)-plane, Eq. (8.98) becomes

$$\begin{aligned} U(d) &= 2\pi\hbar c \left(\frac{L}{\pi}\right)^2 \frac{1}{4} \int_0^\infty \rho \mathrm{d}\rho \times \\ &\left[\sum_n f\left(\sqrt{\rho^2 + \left(\frac{n\pi}{d}\right)^2}\right) \sqrt{\rho^2 + \left(\frac{n\pi}{d}\right)^2} - \frac{d}{\pi} \int_0^\infty \mathrm{d}k_z\, f\left(\sqrt{\rho^2 + k_z^2}\right) \sqrt{\rho^2 + k_z^2} \right]. \end{aligned} \tag{8.101}$$

Define a function

$$F(\kappa) \equiv \int_0^\infty \mathrm{d}x f\left(\frac{\pi}{d}\sqrt{x + \kappa^2}\right) \sqrt{x + \kappa^2} = \int_\kappa^\infty 2y^2 f\left(\frac{\pi}{d} y\right) \mathrm{d}y \tag{8.102}$$

and let $\rho^2 = \left(\frac{\pi}{d}\right)^2 x$, $k_z = \left(\frac{\pi}{d}\right)\kappa$, Eq. (8.101) becomes

$$U(d) = \frac{\pi^2 \hbar c}{4d^3} L^2 \left[\frac{1}{2} F(0) + \sum_{n=1}^\infty F(n) - \int_0^\infty F(\kappa) \mathrm{d}\kappa \right]. \tag{8.103}$$

For a function $F(x)$ defined over range $0 \le x \le N$, the trapezoidal rule gives

$$\int_0^N F(x)\mathrm{d}x \approx \frac{F(0)+F(N)}{2} + \sum_{i=1}^{N} F(i). \tag{8.104}$$

The Euler-Maclaurin summation formula tells us that

$$\frac{F(0)}{2} + \sum_{i=1}^{\infty} F(i) - \int_0^{\infty} F(x)\mathrm{d}x = -\frac{1}{12}F'(0) + \frac{1}{720}F'''(0) + \cdots. \tag{8.105}$$

For Eq. (8.102), because $F(x) \to 0$ as $x \to \infty$, we have

$$F'(y) = -2y^2 f\left(\frac{\pi}{d}y\right), \tag{8.106}$$

which gives $F'(0) = 0$. If we further assume that all derivatives of $f(k)$ go to zero as $k \to 0$, we have $F'''(0) = -4$ and Eq. (8.103) finally becomes

$$U(d) = \frac{\pi^2 \hbar c}{4d^3} L^2 \left(-\frac{4}{720}\right) = -\frac{\pi^2 \hbar c}{720 d^3} L^2. \tag{8.107}$$

So the Casmir force per unit area is

$$\mathscr{F}(d) = \frac{1}{L^2}\left(-\frac{\mathrm{d}U}{\mathrm{d}d}\right) = -\frac{\pi^2 \hbar c}{240 d^4}, \tag{8.108}$$

which shows that there is an attractive force between the plates due to the vacuum energy in the quantized electromagnetic field.