Lecture 3

Many Particle System

Spin and Statistics

Chapter 10

Many Particles

- Multiparticle Schrodinger Equation , (Wave Function)
- Independent Particles

  ↓

  Again seperation of variables
- Indentical Particles
- Exchange Symmetries and the Pauli Principle

  Example

The Total Spin of Two Electrons

Exchange Forces

- The Fermi Energy
- Degeneracy Pressure

Pictures

Pauli
Bose - Einstein
Fermi - Dirac

Bose Taylor et al. P. 315

Chapter 10

Many Particles

The multiparticle Schrodinger equation

$$H\,\psi(x_1, x_2, \cdots x_N, t) = i\hbar \frac{\partial}{\partial t} \psi(x_1, x_2, \cdots, x_N; t)$$

where

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \cdots + V(x_1, x_2, \cdots x_N)$$

$$\Rightarrow \Big[\Big(-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} - \cdots\Big) + V(x_1, x_2, \cdots x_N)\,\psi(x_1, x_2, \cdots x_N; t)$$

$$= i\hbar \frac{\partial}{\partial t} \psi(x_1, x_2, \cdots x_N; t)$$

$\psi(x_1, x_2, \cdots x_N; t) \longrightarrow$ multiparticle wave function.

$|\psi(x_1, x_2, \cdots x_N; t)|^2 \, dx_1 \, dx_2 \cdots dx_N$

→ probability of finding particle 1 in the range $(x_1, x_1 + dx_1)$
and particle 2 in the range $(x_2, x_2 + dx_2)$
and particle 3
⋮

For $V(x_1, x_2, \cdots x_N)$ independent of time, seperation of variable method may be used.

Ansatz $\psi(x_1, x_2, \cdots x_N, t) = u(x_1, x_2, \cdots x_N)\, e^{-iEt/\hbar}$

Substitute into the time-dependent Schrodinger equation

$$\Rightarrow \Big(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} - \cdots + V(x_1 \cdots x_N)\Big)\, u(x_1, x_2, \cdots x_N)$$

$$= E\, u(x_1, x_2, \cdots x_N)$$

↓

time independent Schrodinger equation
energy eigenvalue equation

Remarks:

- This clearly is a generalization of one particle Schrodinger equation.
- The equation is written in one dimension form for simplification

$$x_i \longrightarrow \vec{r}_i$$

$$\frac{\partial^2}{\partial x_i^2} \longrightarrow \nabla_i^2$$

- Spin can be included also.

The problem can be further simplified for independent, i.e.,

$$V(x_1, x_2, \cdots x_N) = V_1(x_1) + V_2(x_2) + \cdots + V_N(x_N)$$

The time independent Schrodinger equation becomes

$$\left[\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} + V_1(x_1)\right) + \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_2(x_2)\right) + \cdots\cdots \right] u(x_1, x_2, \cdots x_N)$$

$$= E\, u(x_1, x_2, \cdots, x_N)$$

Ansatz: $u(x_1, x_2, \cdots x_N) = u_1(x_1)\, u_2(x_2) \cdots u_N(x_N)$

- This ansatz comes from the fact that the probability of finding a particular particle somewhere is independent of the probabilities of finding particles anywhere else.
- This is essentially is to carry seperat of variable to the ultimate.

The problem is reduced to find $u_1(x_1), u_2(x_2), \cdots u(x_N)$

The results are

$$\left(-\frac{\hbar^2}{2m_1}\frac{d^2}{dx_1^2} + V_1(x_1)\right) u_1(x_1) = E_1 u_1(x_1)$$

$$\left(-\frac{\hbar^2}{2m_2}\frac{d^2}{dx_2^2} + V_2(x_2)\right) u_2(x_2) = E_2 u_2(x_2)$$

$$\vdots$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx_N^2} + V_N(x_N)\right) u_N(x_N) = E_N u_N(x_N)$$

and

$$E = E_1 + E_2 + \cdots + E_N$$

- The problem is reduced to solve N one-body problem (which we have learned how to solve.
- Not all H can be written as $H = \sum_i H_i$, but we shall try to approximate H by $H \simeq \sum_i \overline{H}_i$

Identical Particle

If two particles are not identical and $\psi(1,2)$ represents a state of a high energy electron and a low energy proton then $\psi(2,1)$, in which the roles of the two particles are reversed, would represent a high energy proton and low energy electron, an entirely different situation.

But if $\psi(1,2)$ are the wave function of two identical particles, for instance, two electrons

The indistinguishability of particles requires the states represented by $\psi(1,2)$ and $\psi(2,1)$ (with the roles of 1 and 2 reversed) must be physically indistinguishable

$$\Downarrow$$

$$H(1,2) = H(2,1)$$

$$|\psi(2,1)|^2 = |\psi(1,2)|^2$$

$$\Rightarrow \quad \psi(2,1) = e^{i\delta}\,\psi(1,2)$$

Among these possibilities

$$\psi(2,1) = \psi(1,2) \quad \rightarrow \quad \text{symmetric under } 1 \leftrightarrow 2$$

$$\psi(2,1) = -\psi(1,2) \quad \rightarrow \quad \text{anti-symmetric under } 1 \leftrightarrow 2$$

Postulate :

For identical bosons (particles with integer spin) the multiparticle wave function must be symmetric under exchange (of identical bosons)
any pair

$$\psi(1,2,\cdots i \cdots j \cdots) \underset{i\leftrightarrow j}{=} +\psi(1,2,\cdots j,\cdots i,\cdots)$$

i, j are identical bosons

For identical fermions (particles with half integral spins) the multiparticle wave function must be anti-symmetric under exchange of any pair of identical fermions.

$$\psi(1,2,\cdots i,\cdots j\cdots) \underset{i\leftrightarrow j}{=} -\psi(1,2,\cdots j,\cdots i,\cdots)$$

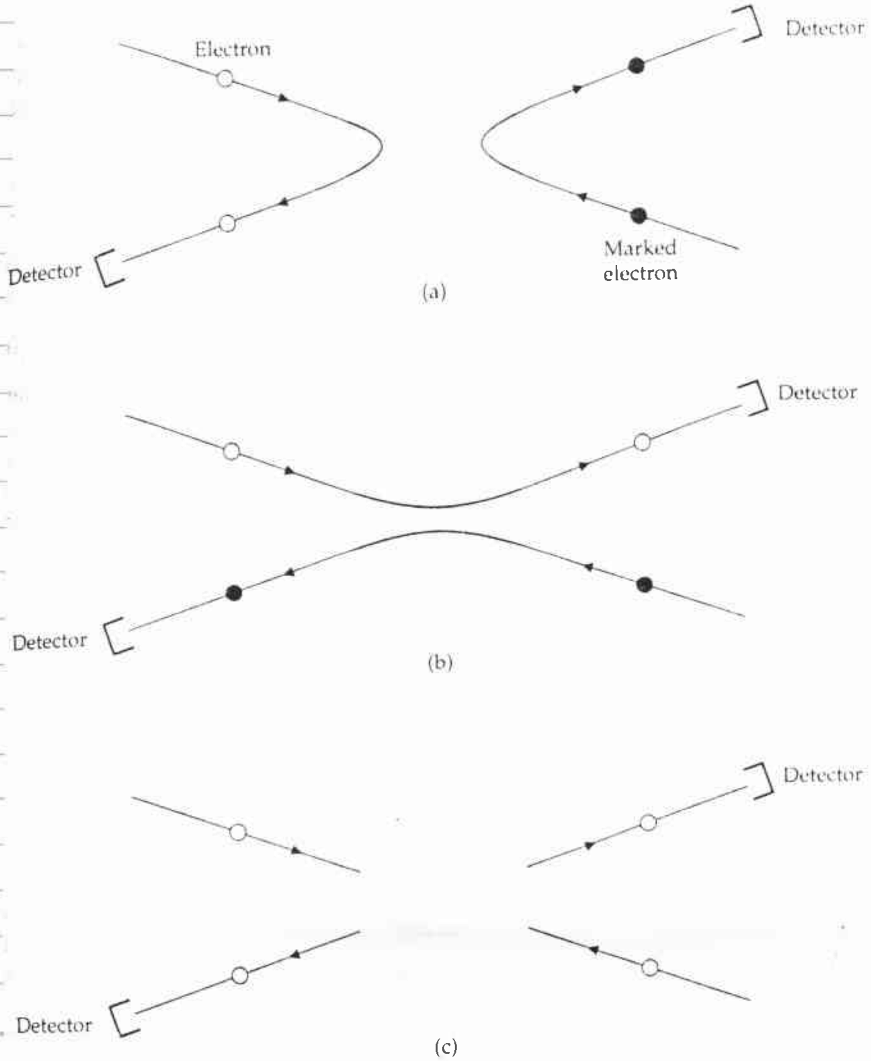
i, j are identical fermions

Identical Particles and Indistinguishability.

We say that two particles are identical if they have all the same intrinsic properties — same mass, same charge and same spin.

In classical mechanics, even identical particles are distinguishable in the sense that we could in principle keep track of which is which.
↓
follow the trajectory

In quantum mechanics, two identical particles are indistinguishable.
When the wavefunction overlaps, there is absolutely no way of distinguish two identical particles.



(a)

(b)

(c)

Consider two independent spin-zero bosons (with no interaction between them) in the same one dimensional potential infinite potential well.

$$H(1,2) = \frac{\vec{P}_1^2}{2\mu} + V(x_1) + \frac{\vec{P}_2^2}{2\mu} + V(x_2)$$

$$V(x) = \begin{cases} 0 & 0<x<L \\ \infty & \text{otherwise} \end{cases}$$

$$\left\{\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x_1} + V(x_1)\right] + \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x_2)\right]\right\} u(x_1,x_2) = E\,u(x_1,x_2$$

Ansatz $\quad u(x_1,x_2) = u(x_1)\,u(x_2)$

$$\Rightarrow u(x_2)\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx_1^2} + V(x_1)\right]u(x_1) + u(x_1)\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx_2^2} + V(x_2)\right]u(x_2$$

$$= E\,u(x_1)\,u(x_2)$$

$$\Rightarrow \underbrace{\frac{1}{u(x_1)}\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx_1^2} + V(x_1)\right]u(x_1)}_{\text{function of } x_1} = E - \underbrace{\frac{\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx_2^2} + V(x_2)\right]u(x_2)}{u(x_2)}}_{\text{function of } x_2}$$

$$= E_1$$

$$\Rightarrow \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx_1^2} + V(x_1)\right]\underbrace{u(x_1)}_{\text{the problem we have solved before.}} = E_1\,u(x_1)$$

$$u_n(x_1) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad \text{with} \quad E_{1,n} = \frac{n^2\hbar^2\pi^2}{2\ L^2}$$

and

$$\left[-\frac{\hbar^2}{2}\frac{d^2}{dx^2} + V(x_2)\right]u(x_2) = \underset{E-E_1}{\overset{}{E_2}}\,u(x_2)$$

$$u_m(x_2) = \sqrt{\frac{2}{L}}\sin\frac{m\pi x}{L} \qquad \text{with} \quad E_{2,m} = \frac{m^2\hbar^2\pi^2}{2\ L^2}$$

$u_m(x_1)\,u_n(x_2) = u_{m,n}(x_1,x_2)$ is the eigenfunction of the time-independent Schrodinger equation with eigenvalue $E = E_1 + E_2$

Spin can take integral and half integral (in unit of $\hbar$) values

Particles with integral spin values are called bosons, while those with half-integral spin are fermions.

e, p, n are fermions
π, K, γ are bosons.
α

Electrons are fermions since their spin is $\frac{1}{2}\hbar$, it is possible for electrons to form a "complete pair" in some materials.

The composite can have integral spin and the pair then behaves as a boson.

This change over from fermion to boson-like behavior is manifested in electrical properties of materials.

For example, when electrons behave as fermions, materials have finite resistance.
Under certain conditions, when electrons couple together to form pairs (called Cooper pairs), the material becomes a superconductor and loses its resistance completely.

$$u_{m,n}(x_1, x_2) = \frac{2}{L} \sin\frac{n\pi x_1}{L} \sin\frac{m\pi x_2}{L}$$

with eigenvalue $E = \dfrac{(m^2+n^2)\hbar^2\pi^2}{2\mu L^2}$

This wave function is not symmetric under $\underset{\underset{1}{\downarrow}}{x_1} \leftrightarrow \underset{\underset{2}{\downarrow}}{x_2}$

Here x_1, x_2 are the only label in 1 and 2

For identical bosons.

To satisfy the requirement of symmetric under $1 \leftrightarrow 2$

$$u_{mn}(x_1, x_2) \Rightarrow \frac{1}{\sqrt{N_A}}\left[u_m(x_1)\,u_n(x_2) + u_n(x_1)\,u_m(x_2)\right]$$

with $E = \dfrac{(m^2+n^2)\hbar^2\pi^2}{2\mu L^2}$

Consider two zero spin identical bosons interacting with a potential $V(|\vec{r}_1 - \vec{r}_2|)$

The time-independent Schrodinger equation has the form

$$H_{12} = \frac{\vec{p}_1^{\,2}}{2\mu} + \frac{\vec{p}_2^{\,2}}{2\mu} + V(|\vec{r}_1 - \vec{r}_2|)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 + V(|\vec{r}_1 - \vec{r}_2|)\right] u(\vec{r}_1, \vec{r}_2) = E\, u(\vec{r}_1, \vec{r}_2)$$

Introduce new variables

$\vec{R}$ and $\vec{r}$ (as we have done in Chapter 1)

$$\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2), \quad \vec{r} = \vec{r}_1 - \vec{r}_2$$

(Remembering $m_1 = m_2$)

It can be shown that

$$H = H_1(\vec{R}) + H_2(\vec{r})$$ (See Appendix A)

Note there is no cross term.

$H_1(\vec{R})$ is a free particle Hamiltonian

$\therefore$ Hamiltonian is seperable.

$$\Rightarrow \quad \psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{R})\,\Phi(\vec{r})$$

$\Phi(\vec{r})$ satisfies a Schrodinger equation with a central potential $V(r)$

The eigenfunction can be given by

$\Phi(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta, \phi)$ with eigenvalue $E_r \Rightarrow E^r_{n,\ell}$

Note: only for Coulomb potential $E^r_{n,\ell} \to \underset{\downarrow}{E^r_n}$

i.e., independent of ℓ

Now Bose statistics requires

$\psi(\vec{r}_1, \vec{r}_2)$ to be symmetric under $1 \leftrightarrow 2$

Under $1 \leftrightarrow 2$, $\vec{R} \to \vec{R}$, $\vec{r} \to -\vec{r}$

$\vec{r} \to -\vec{r}$ is spherical coordinate is

$r \to r$
$\theta \to \pi - \theta$
$\phi \to \pi + \phi$

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

$$\Rightarrow \quad Y_{\ell m}(\theta, \phi) \to Y_{\ell m}(\pi - \theta, \pi + \phi) = (-1)^\ell\, Y_{\ell m}(\theta, \phi)$$

$$\psi(\vec{r}_1, \vec{r}_2) = (-1)^\ell\, \psi(\vec{r}_2, \vec{r}_1)$$

In order the wave function to be symmetric

$\Rightarrow (-1)^\ell = 1 \Rightarrow \ell = 0, 2, 4, \cdots$

$\rho^0 \to \pi^0 \pi^0$

Spin of $\rho^0 = 1$

In the rest system of ρ^0, angular momentum conservation requires $\ell = 1$
(There is no spin to deal with)

However, bose statistics $\Rightarrow$ ℓ can be even only
$\Rightarrow \rho^0 \nrightarrow \pi^0 \pi^0$
($\rho^0 \to \pi^+ \pi^-$ conspicuously)

The Total Spin of Two Electrons

$\chi_+(1)$ → particle 1 has spin up. $S_{1z} = \frac{1}{2}\hbar$
$\chi_-(1)$ → particle 1 has spin down. $S_{z} = -\frac{1}{2}\hbar$
$\chi_+(2)$ → particle 2 has spin up $S_{2z} = \frac{1}{2}\hbar$
$\chi_-(2)$ → particle 2 has spin down. $S_{2z} = -\frac{1}{2}\hbar$

$\vec{S} = \vec{S}_1 + \vec{S}_2$

Two spin $\frac{1}{2}$ particles, such as two electrons

⇒ Total spin can be either 1 or 0

$S = 1$ $\quad S_z \quad \hbar,\ 0,\ -\hbar$
$\quad\quad\quad\ m_s \quad 1,\ 0,\ -1$

$S = 1,\ m_s = 1$ $\quad \chi_+(1)\chi_+(2)$
$\quad\quad\quad\ m_s = -1$ $\quad \chi_-(1)\chi_-(2)$

Note : they are both symmetric under $1 \leftrightarrow 2$

$m_s = 0$ can be formed by linear combination of
$\chi_+(1)\chi_-(2)$; $\chi_+(2)\chi_-(1)$

$S = 1,\ m_s = 0$ should have the same property under
interchange $1 \leftrightarrow 2$ ⇒ $\frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)]$

$$S = 1 \qquad \begin{array}{l} \chi_+(1)\chi_+(2) \\ \frac{1}{\sqrt{2}}(\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)) \\ \chi_-(1)\chi_-(2) \end{array}$$

$$S = 0 \qquad \frac{1}{\sqrt{2}}(\chi_+(1)\chi_-(2) - \chi_2(2)\chi_-(1))$$

Under $1 \leftrightarrow 2$
Spin wave function is symmetric for $S = 1$
anti-symmetric for $S = 0$

$S = 1$ triplet

$S = 0$ singlet

Two Electron System

The total wave function

$$\psi(1,2) = \psi(\vec{r}_1, \sigma_1 ; \vec{r}_2, \sigma_2)$$

= spatial wave function · spin wave function
Sy for $l = 0, 2, 4, \cdots$ Sy for $S = 1$
A for $l = 1, 3, 5$ A for $S = 0$

$\psi(1,2)$ must be anti-symmetric under $1 \leftrightarrow 2$

For singlet $l = 0, 2, 4, \cdots$
triplet $l = 1, 3, 5, \cdots$

$$(-1)^{l} \quad (-1)^{S+1} = (-1)$$

$\Rightarrow$ $l + S$ must be even.
sum up the above result.

Now we shall go back to the general N-body problem

N identical particle

$$\underset{\text{Hamiltonian}}{\underbrace{H(1, 2, \cdots N)}}$$

$$H(1, 2, \cdots i, \cdots j, \cdots N) = H(1, 2, \cdots j, \cdots i \cdots N)$$

↓

N particles are identity

For the case of independent particles

$$H(1, 2, \cdots N) = \sum_{i=1}^{N} H(i)$$

$H(i)$ ↓ the independent Hamiltonian for the ith particle

$$H(i) = \frac{p_i^2}{2m} + V(\vec{r}_i)$$

Solve $\quad H(i)\, \phi(i) = E\, \phi_i$

↓

essentially a one body problem

$\phi_\alpha(i) \quad \rightarrow$ eigenfunction

α all the quantum numbers need to specified state with corresponding Energy E_i

$$\Rightarrow \quad \psi_{\alpha_1 \alpha_2 \cdots \alpha_N}(1, 2 \cdots i \cdots j \cdots N) = \phi_{\alpha_1}(1)\, \phi_{\alpha_2}(2) \cdots \phi_{\alpha_i}(i)\, \phi_{\alpha_j}(j) \cdots \phi_{\alpha_N}(N)$$

is an eigenstate of $\quad H \psi = E \psi$

H ↓ total Hamiltonian

E ↳ total energy

$$E = E_{\alpha_1} + E_{\alpha_2} \cdots + E_{\alpha_N}$$

If we interchange $i \leftrightarrow j$

$$\psi_{\alpha_1 \alpha_2 \cdots \alpha_N}(1, 2, \cdots i, \cdots j, \cdots N) = \phi_{\alpha_1}(1) \cdots \phi_{\alpha_i}(j) \cdots \phi_{\alpha_j}(i) \cdots \phi_{\alpha_N}(N)$$

is also an eigenstate of $H\psi = E\psi$ with the same eigenvalue $E = E_{\alpha_1} + E_{\alpha_2} + \cdots + E_{\alpha_N}$

Bose-Einstein statistics requires the wavefunction to be symmetric under $i \leftrightarrow j$

$$\phi_{\alpha_1}(1)\,\phi_{\alpha_2}(2)\cdots\phi_{\alpha_i}(i)\cdots\phi_{\alpha_j}(j)\cdots\phi_{\alpha_N}(N)$$

+ all possible permutations
$\downarrow$
it is totally symmetric

Example (i) $\phi_n(1)\,\phi_m(2)$
$+ \phi_n(2)\,\phi_m(1)$ is clearly totally symmetric

$E = E_n + E_m$

(ii) $\phi_n(1)\,\phi_m(2)\,\phi_\ell(3)$
$+ \phi_n(1)\,\phi_m(3)\,\phi_\ell(2) + \phi_n(2)\,\phi_m(1)\,\phi_\ell(3) + \phi_n(2)\,\phi_m(3)\,\phi_\ell(1)$
$+ \phi_n(3)\,\phi_m(1)\,\phi_\ell(3) + \phi_m(3)\,\phi_n(2)\,\phi_\ell(1)$

clearly is a symmetric wave function.

Now Fermi-Dirac statistics requires the wavefunction to be anti-symmetric under $i \leftrightarrow j$

Fermi-Dirac statistics operates on identical fermions

We shall now add the spin m_s to our description

$\alpha_i \xrightarrow{} \{\alpha_i, m_s\}$
$\uparrow$
extension

$m_s = \pm\frac{1}{2}$ corresponds to the spin up and spin down

$\phi_{\alpha_1}(1)\,\phi_{\alpha_2}(2)\cdots\phi_{\alpha_N}(N)$ is an eigenfunction of H

with eigenvalue $E = E_{\alpha_1} + E_{\alpha_2} + \cdots E_{\alpha_N}$

Fermi-Dirac statistics requires the wave function to be anti-symmetric under $i \leftrightarrow j$

This can be done using Slater determinant.

$$\psi^{A}_{\alpha_1 \cdots \alpha_N}(1,2,\cdots N) = \begin{vmatrix} \phi_{\alpha_1}(1) & \phi_{\alpha_1}(2) & \cdots\cdots & \phi_{\alpha_1}(N) \\ \phi_{\alpha_2}(1) & \phi_{\alpha_2}(2) & \cdots\cdots & \phi_{\alpha_2}(N) \\ \vdots & & & \vdots \end{vmatrix}$$

Obviously, it is anti-symmetric under $i \leftrightarrow j$

Example α_1 $n\uparrow$

α_2 $n\downarrow$

$$\phi^{A} = \begin{vmatrix} \phi_{n\uparrow}(1) & \phi_{n\uparrow}(2) \\ \phi_{n\downarrow}(1) & \phi_{n\downarrow}(2) \end{vmatrix}$$

$$= \underbrace{\phi_{n\uparrow}(1)\phi_{n\downarrow}(2) - \phi_{n\uparrow}(2)\phi_{n\downarrow}(1)}_{\downarrow}$$

This is exactly the result we obtained before

Let us look at the three particle case discussed in the book

α_1 $u_{1\uparrow}$

α_2 $u_{1\downarrow}$

α_3 $u_{2\uparrow}$

$$\begin{vmatrix} u_{1\uparrow}(1) & u_{1\uparrow}(2) & u_{1\uparrow}(3) \\ u_{1\downarrow}(1) & u_{1\downarrow}(2) & u_{2\downarrow}(3) \\ u_{2\uparrow}(1) & u_{2\uparrow}(2) & u_{2\uparrow}(3) \end{vmatrix}$$

$$= u_{1\uparrow}(1) \begin{vmatrix} u_{1\downarrow}(2) & u_{1\downarrow}(3) \\ u_{2\uparrow}(2) & u_{2\uparrow}(3) \end{vmatrix}$$

$$- u_{1\uparrow}(2) \begin{vmatrix} u_{1\downarrow}(1) & u_{2\downarrow}(3) \\ u_{2\uparrow}(1) & u_{2\uparrow}(3) \end{vmatrix}$$

$$+ u_{1\uparrow}(3) \begin{vmatrix} u_{1\downarrow}(1) & u_{1\downarrow}(2) \\ u_{2\uparrow}(1) & u_{2\uparrow}(3) \end{vmatrix}$$

$$= u_{1\uparrow}(1)\, u_{1\downarrow}(2)\, u_{2\uparrow}(3) - u_{1\uparrow}(1)\, u_{1\downarrow}(3)\, u_{2\uparrow}(2)$$

$$- u_{1\uparrow}(2)\, u_{1\downarrow}(1)\, u_{2\uparrow}(3) + u_{1\uparrow}(2)\, u_{2\downarrow}(3)\, u_{2\uparrow}(1)$$

$$+ u_{1\uparrow}(3)\, u_{1\downarrow}(1)\, u_{2\uparrow}(3) - u_{1\uparrow}(3)\, u_{1\downarrow}(2)\, u_{2\uparrow}(1)$$

This is exactly the result given in the textbook.

For $\alpha_i = \alpha_j$, then the anti-symmetric wave function does not exist.

$\Rightarrow$ No more than one electron can have a given set of quantum numbers (including the spin quantum number

$\Rightarrow$ This is the Pauli exclusion principle.

分類：
編號：
總號：

Start from P. 12.   N particle identical.

Bose - Einstein statistics

$$H = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} + \underset{\frac{1}{2}kx_i^2}{\underset{\|}{V(x_i)}}\right) = \sum_{i=1}^{N} H_i$$

N harmonic oscillator

$$H_i \phi_n = E_n \phi_n$$

$\phi_{n_1}(x_1) \rightarrow$ first particles in n_1 state

$\phi_{n_1}(x_1)\,\phi_{n_2}(x_2)\cdots\phi_{n_N}(x_N)$

↓

is a solution of the Schrodinger equation. (eigenfunction)

with

For bosons, $i \leftrightarrow j$, the wave function must be symmetric

Example $N = 2$

$\phi_{n_1}(x_1)\,\phi_{n_2}(x_2)$

The first particle is at n_1 state with energy $E_{n_1} = (n_1+\frac{1}{2})\cdot\hbar\omega$

second particle is at n_2 state with energy $E_{n_2} = (n_2+\frac{1}{2})\cdot\hbar\omega$

$$\Rightarrow E_{tot} = (n_1+\tfrac{1}{2})\hbar\omega + (n_2+\tfrac{1}{2})\hbar\omega$$

Interchange $1 \leftrightarrow 2$

$$\Rightarrow \phi_{n_1}(x_2)\,\phi_{n_2}(x_1)$$

Clearly, it is not symmetric

$\phi_{n_1}(x_1)\,\phi_{n_2}(x_2)$ + all possible permutation

$\phi_{n_1}(x_1)\,\phi_{n_2}(x_2) + \phi_{n_1}(x_2)\,\phi_{n_2}(x_1)$

↓

clearly is symmetric under $1 \leftrightarrow 2$.

Three dimensional

$$H = \left(\sum_{i=1}^{N} \frac{\vec{p}^{\,2}}{2m} + V(r) \right) = \sum_{i=1}^{N} H_i$$

$$H_i \phi_n = E_n \phi_n$$

$$n \rightarrow \{n, l, m\}$$

$\phi_{n_1, l_1, m_1}(\vec{r}_1)$ the first particle is in a state $\{n_1, l_1, m_1\}$

$$\phi_{n_1, l_1, m_1}(\vec{r}_1) \phi_{n_2, l_2, m_2}(\vec{r}_2)$$

$\downarrow$

is not symmetric

$$\phi_{n_1, l_1, m_1}(\vec{r}_2) \phi_{n_2, l_2, m_2}(\vec{r}_1)$$

$\downarrow$

is the only possible permutation

$$\phi_{n_1, l_1, m_1}(\vec{r}_1) \phi_{n_2, l_2, m_2}(\vec{r}_2) + \phi_{n_1, l_1, m_1}(\vec{r}_2) \phi_{n_2, l_2, m_2}(\vec{r}_1)$$

is symmetric

Now we understand the meaning of

$$\phi_{\alpha_1}(1) \phi_{\alpha_2}(2) \cdots \phi_{\alpha_i}(i) \cdots \phi_{\alpha_j}(j) \cdots \phi_{\alpha_N}(N)$$

+ all possible permutation.

Of course, afterward, we have to normalize the wave function

Example : $N = 3$ case

The Fermi - Dirac Statistics

Notation in 10-13

Fermi - Dirac statistics

$i \leftrightarrow j$

the wave function change sign.

$\phi_{\alpha_i}(i) \longrightarrow \phi_{n_1, l_1, m_1, m_s}(\vec{r}_1, \vec{\sigma}_1)$

For $N = 2$

The anti-symmetric wave function

$$\psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_{n_1 l_1, m_1 m_{s_1}}(\vec{r}_1, \vec{\sigma}_1) & \phi_{n_1, l_1, m_1, m_{s_1}}(\vec{r}_2, \vec{\sigma}_2) \\ \phi_{n_2 l_2, m_2, m_{s_2}}(\vec{r}_1, \vec{\sigma}_1) & \phi_{n_2, l_2, m_2, m_{s_2}}(\vec{r}_2, \vec{\sigma}_2) \end{vmatrix}$$

$\downarrow$

Slater determinant

$1 \leftrightarrow 2$

exchange of column
determinant change sign.

$N = 3$

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{n_1, l_1, m_1, m_{s_1}}(\vec{r}_1, \vec{\sigma}_1) & \phi_{n_1, l_1, m_1, m_{s_1}}(\vec{r}_2, \vec{\sigma}_2) & \phi_{n_1 l_1 m_1 m_{s_1}}(\vec{r}_3, \vec{\sigma}_3) \\ \phi_{n_2 l_2 m_2, m_{s_2}}(\vec{r}_1, \vec{\sigma}_1) & \phi_{n_2, l_2, m_2, m_{s_2}}(\vec{r}_2, \vec{\sigma}_2) & \phi_{n_2 l_2, m_2, m_{s_2}}(\vec{r}_3, \vec{\sigma}_3) \\ \phi_{n_3 l_3 m_3, m_s}(\vec{r}_1, \vec{\sigma}_1) & \phi_{n_3, l_3, m_3, m_{s_3}}(\vec{r}_2, \vec{\sigma}_2) & \phi_{n_3, l_3, m_3, m_{s_3}}(\vec{r}_3, \vec{\sigma}_3) \end{vmatrix}$$

Under exchange $i \leftrightarrow j$ change sign

no four quantum numbers can be identical because then two rows would be identical

$$\Downarrow$$

ψ vanishes

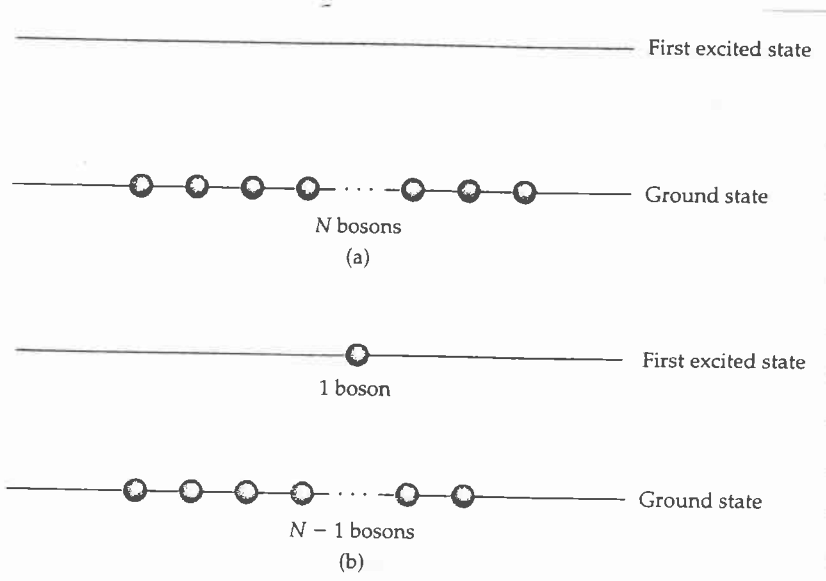
$\Rightarrow$ Pauli's exclusion principle

The Fermi Energy

Ground state for N bosons in an infinite well.

No restriction of Pauli exclusion principle.

$$E_g = N E_1$$



Average energy per particle

$$\frac{E_g}{N} = E_1$$

First excited state

$N-1$ bosons in ground state

1 boson in the first excited state.

The energy of this excited system is

$$(N-1) E_1 + E_2$$

For fermions, the exclusion principle is operative

$N \rightarrow$ taken to be even, $\frac{N}{2}$ is an integer.

$$E_g = E_1 [2(1^2) + 2(2^2) + \cdots + 2(\frac{N}{2})^2] = 2E_1 \sum_{j=1}^{N/2} j^2$$

$$[E_n = n^2 E_1]$$

$$\sum_{j=1}^{n} j^2 = \frac{1}{6} n(n+1)(2n+1)$$

If u_n can be written as $f(n)-f(n-1)$, then

$$S_N = \sum_{n=1}^{N} u_n = f(N) - f(0)$$

$\downarrow$

difference method.

Want to find $f(n)-f(n-1) \longrightarrow n^2$

Answer: $f(n) = n(n+1)(2n+1)$

$$f(n-1) = (n-1)n(2n-1)$$

$$f(n) - f(n-1) = n[2n^2+3n+1-2n^2+3n-1]$$

$$= 6n^2$$

$$u_n = \frac{1}{6} N(N+1)(2N+1)$$

$\downarrow$

$$\sum_{j=1}^{n} j^2 = \frac{1}{6} N(N+1)(2N+1)$$

As N large the sum $\sim \frac{1}{3}\left(\frac{N}{2}\right)^3$

$$E_g \cong 2E_1 \frac{(N/2)^3}{3} \simeq \frac{N^3}{12} E_1$$

$\downarrow$

$$\frac{E_g}{N} \simeq \frac{N^2}{12} E_1$$

$\downarrow$

average energy per particle in the ground state.

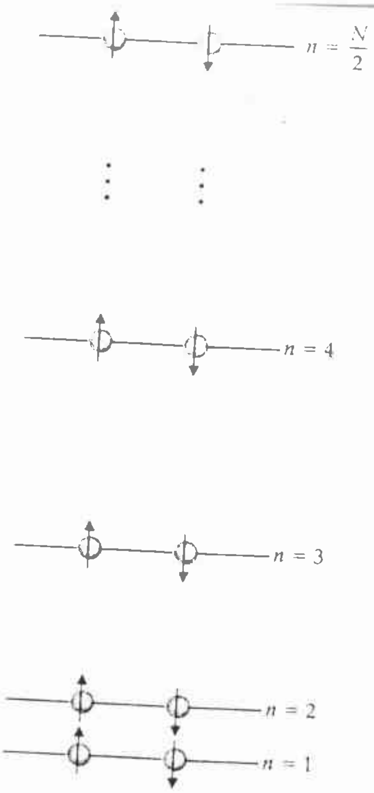
Please note the difference between the bosons and fermions.

The highest energy to be filled is known as the Fermi energy E_F

$$E_F = \frac{\pi^2\hbar^2\left(\frac{N}{2}\right)^2}{2mL^2} = \frac{\pi^2\hbar^2N^2}{8mL^2}$$

In one dimensional case $n_e = \frac{N}{L}$

$$\Rightarrow E_F = \frac{\pi^2\hbar^2}{8m} n_e^2$$



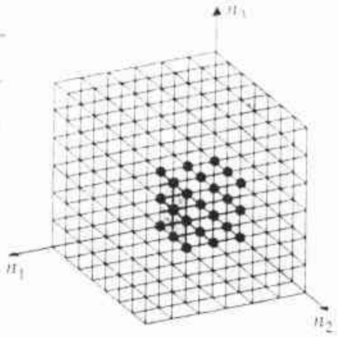
• Figure 10–7 The lowest energy, or ground, state for N fermions has at most two particles in each single-particle level, one with spin up and one with spin down. All the levels up to $n = N/2$ are filled.

Now we go into the three dimensional box (cubic)

$$E_{\{n_1, n_2, n_3\}} = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) = E_1 \cdot (n_1^2 + n_2^2 + n_3^2)$$

In the (n_1, n_2, n_3) space, there are

$\sim \frac{1}{8}\frac{4\pi R^3}{3}$ lattice points → integer n_1, n_2, n_3 with $n_1^2 + n_2^2 + n_3^2 \le R^2$



• Figure 10–8 The energy states in a three-dimensional well are labeled by a set of three integers. These integers can be depicted as sitting on the intersection points of a three-dimensional cubic lattice.

$$\frac{N}{2} = \frac{1}{8}\frac{4\pi R^3}{3}$$

$$R^2 = \frac{E_F}{E_1}$$

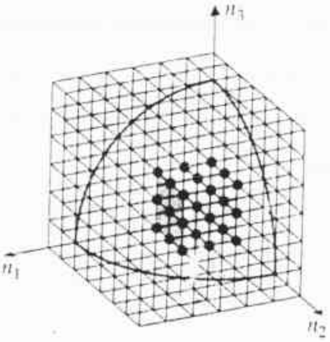
$$\Rightarrow \quad \frac{N}{2} = \frac{4}{8}\frac{\pi}{3}\left(\frac{E_F}{E_1}\right)^{3/2}$$

$$= \frac{\pi}{6}\left(\frac{E_F}{E_1}\right)^{3/2} \quad \Rightarrow \quad E_F = E_1\left(\frac{3N}{\pi}\right)^{2/3}$$

$$\Rightarrow \quad E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{L^3}\right)^{2/3}$$

$$n_f = \frac{N}{L^3}$$

$$\Rightarrow \quad E_f = \frac{\hbar^2}{2m}\left(3\pi^2 n_f\right)^{2/3}$$



• Figure 10–9 Because negative n-values for a three-dimensional well do not represent different states from those already labeled by the corresponding positive values, only positive values need be counted. This condition restricts us to one quadrant (one-eighth) of the full lattice. In other words, to find the points that correspond to the energy states and thus allow us to count the number of states with energy up to E, we restrict ourselves to points that lie within the octant that contains all positive coordinates of a sphere whose radius is proportional to E.

Total energy of the system

$$E_{tot} = \frac{\hbar^2\pi^2}{mL^2}\ \underset{\substack{\downarrow \\ \text{comes from the restriction to positive integers}}}{\frac{1}{8}} \int \vec{n}^2\, d^3\vec{n}$$

$$= \frac{\hbar^2\pi^2}{8mL^2}\ \underset{\substack{\downarrow \\ \text{angular integration.}}}{4\pi} \int_0^R n^4\, dn \qquad n^2 dn\, d\Omega = d^3\vec{n}$$

$$= \frac{\hbar^2\pi^3}{10mL^2} R^5$$

[Remembering $\frac{N}{2} = \frac{1}{8}\frac{4\pi}{3}R^3$]

$$\Rightarrow \quad E_{tot} = \frac{\hbar^2\pi^3}{10mL^2}\left(\frac{3N}{\pi}\right)^{5/3}$$

Using $\underset{\substack{\downarrow \\ \text{number density.}}}{n} = \frac{N}{L^3}$

$$\Rightarrow \quad E_{tot} = \frac{\hbar^2\pi^3}{10m}\left(\frac{3n}{\pi}\right)^{5/3} L^3$$

Remarks.

- The wave number k_F, defined by $E_f = \frac{\hbar^2 k_F^2}{2m}$

$$\Rightarrow \quad \underset{\substack{\parallel \\ \frac{2\pi}{\lambda_F}}}{k_F} = (3\pi^2 n)^{1/3}$$

$$\Rightarrow \quad \lambda_F = 2.03\, n^{-\frac{1}{3}}$$

$n^{-\frac{1}{3}} \sim$ interparticle spacing d

$$d \sim \frac{\lambda_F}{2}$$

$\Rightarrow$ Since the exclusion principle forbids two electrons with identical quantum numbers to be on top of each other

$\Rightarrow$ the closest that two electrons can get to each other is roughly half de Brogile wavelength ↔ Fermi energy.

If we keep a fixed number of electrons, then

$$E_{tot} = \frac{\hbar^2 \cdot \pi^2}{10m}\left(\frac{3N}{\pi}\right)^{5/3} V^{-2/3}$$

If N is large, it can be shown that the result is independent of the shape of the volume.

Degeneracy pressure

If the electron gas is compressed, the electrons are pushed closer to each other $\Rightarrow$ decrease the de Broglie wavelength $\Leftrightarrow$ increases the kinetic energy
$\Rightarrow$ the compression is resisted, and the pressure resisting the compression is called the degeracy pressure

$$P_{deg} = -\frac{\partial E_{tot}}{\partial V} = \frac{\hbar^2\pi^3}{15m}\left(\frac{3n}{\pi}\right)^{5/3}$$

The bulk modulus B of a material is defined by

$$B = V\frac{\partial p}{\partial V}$$

if $p = P_{deg}$, then $B = 5P_{deg}/3 = \frac{\hbar^2\pi^2}{9m}\left(\frac{3n}{\pi}\right)^{5/3}$

The use of a degenerate electron model for a metal gives the correct order of magnitude for the bulk modulus.

Example: for copper

$$n_e = 8.47\times10^{28} \text{ electron/m}^3$$

$\downarrow$

using above equation

$$\Rightarrow B = 6.4\cdot10^{10}\ N/m^2$$

Experimental result $\Rightarrow 14\times10^{10}\ N/m^2$

• Figure 10–4 Paul A. M. Dirac was one of the pioneers of quantum mechanics. He developed the quantum theory of radiation and did groundbreaking work in the creation of relativistic quantum mechanics. He predicted the existence of anti-matter. The French physicist Leon Brillouin, himself an important contributor, is in the background.

• Figure 10–3 The Italian-born American physicist Enrico Fermi (1901–1954) was both a brilliant theorist and an equally brilliant experimental physicist. Among his many accomplishments was his leadership in the construction of the first nuclear reactor. He is shown here on a hike with Niels Bohr in 1931.

• **Figure 10–2** Wolfgang Pauli was born in Vienna in 1900 and died in Zurich in 1958. He was one of the most brilliant theoretical physicists of this century.

Satyendranath Bose

(1894–1974, Indian)

Bose was born and educated in Calcutta, India. In a paper written in 1924 he derived the Planck formula for blackbody radiation by treating the photons as what we would now call bosons. This paper drew the attention of Einstein and secured an invitation for Bose to visit Europe, where he met Einstein, de Broglie, Born, and others. Einstein extended Bose's ideas, and the rules that govern bosons are now called Bose–Einstein statistics. We will see some of the dramatic consequences of these ideas in Chapter 13.

Astrophysical Applications

Stellar evolution (H. Bethe)

Stars start out as hydrogen gas, which "burns" by undergoing a succession of nuclear reactions

At some point the burning stops

⇒ then the only effects we have to worry about are

- gravitational force → work to compress the stellar matter
- degeneracy pressure of the electrons in the star, which works to hold the electrons, and with them all the stellar matter apart

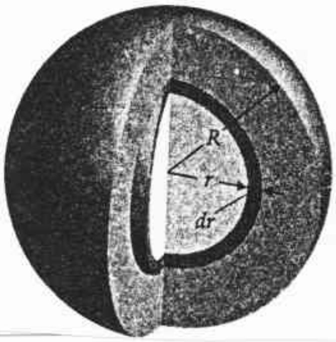


Figure 10–10 To find the gravitational potential energy of a uniform sphere of matter, we add up the separate contributions of thin spherical shells.

Gravitational pressure

$$dU = -\frac{G\,m\,dm}{r} = -G\,\frac{\frac{4\pi\rho r^3}{3}\cdot 4\pi\rho r^2 dr}{r}$$

$$= -\frac{16\pi^2 G\rho^2}{3} r^4 dr$$

$$U_g = -\frac{16\pi^2 G\rho^2}{3}\int_0^R r^4\,dr$$

$$= -\frac{16\pi^2 G\rho^2}{15} R^5$$

$$\rho = \frac{N m_p}{V}$$

m_p = mass of proton
N = number of nucleons

$$V = \frac{4\pi R^3}{3}$$

$$\Rightarrow\quad U_g = -\frac{3}{5}\left(\frac{4\pi}{3}\right)^{1/3} G\,(N m_p)^2 V^{-1/3}$$

$$\Rightarrow\quad P_g = -\frac{\partial U_g}{\partial V} = \frac{1}{5}\left(\frac{4\pi}{3}\right)^{1/3} G\,(N m_p)^2 V^{-4/3}$$

$$P_{deg} = \frac{6}{5}\left(\frac{\pi^4}{3}\right)^{1/3}\frac{\hbar^2}{2m_e}\left(\frac{N}{2}\right)^{5/3} V^{-5/3}$$

Equate $P_g = P_{deg}$

$$\Rightarrow\quad R = \left(\frac{81\pi^2}{128}\right)^{1/3}\frac{\hbar^2}{G m_p^2 m_e} N^{-\frac{1}{3}} \cong (1.15\cdot 10^{23}\,\mathrm{km})\,N^{-\frac{1}{3}}$$

For a star with the mass of the Sun.

$M_{sum} \sim 2 \times 10^{30}$ Kg ⇒ $N \simeq 1.2 \cdot 10^{57}$

After nuclear burning ⟶ white dwarfs

↓

gravitational pressure
balanced by degeneracy
pressure

[Note E_{tot} (degeneracy energy) $\sim \frac{1}{m}$

⇓

electrons plays the
dominant role.

For more massive (than the Sun) star
N → larger

↓

large the electrons' average energy

↓

electrons becomes relativistic

↓

pressures cannot balance

↓

the gravitational pressure
wins out.
the star continues to
collapse

↓

forcing all the particles
closer together
$e^- + p \to n + \nu$
↳ escape

⇒ neutron star

↓

degeneracy pressure due to neutron
balance the gravitational
pressure
$R \sim 10$ km.

For even more massive star, gravitational pressure dominate.

the degeneracy pressure even for neutrons

↓

gravitational collape
continues

↓

black hole

[Exchange force will be discussed in Chapter 11]

分類：
編號： 10-24
總號：

Hans Bethe

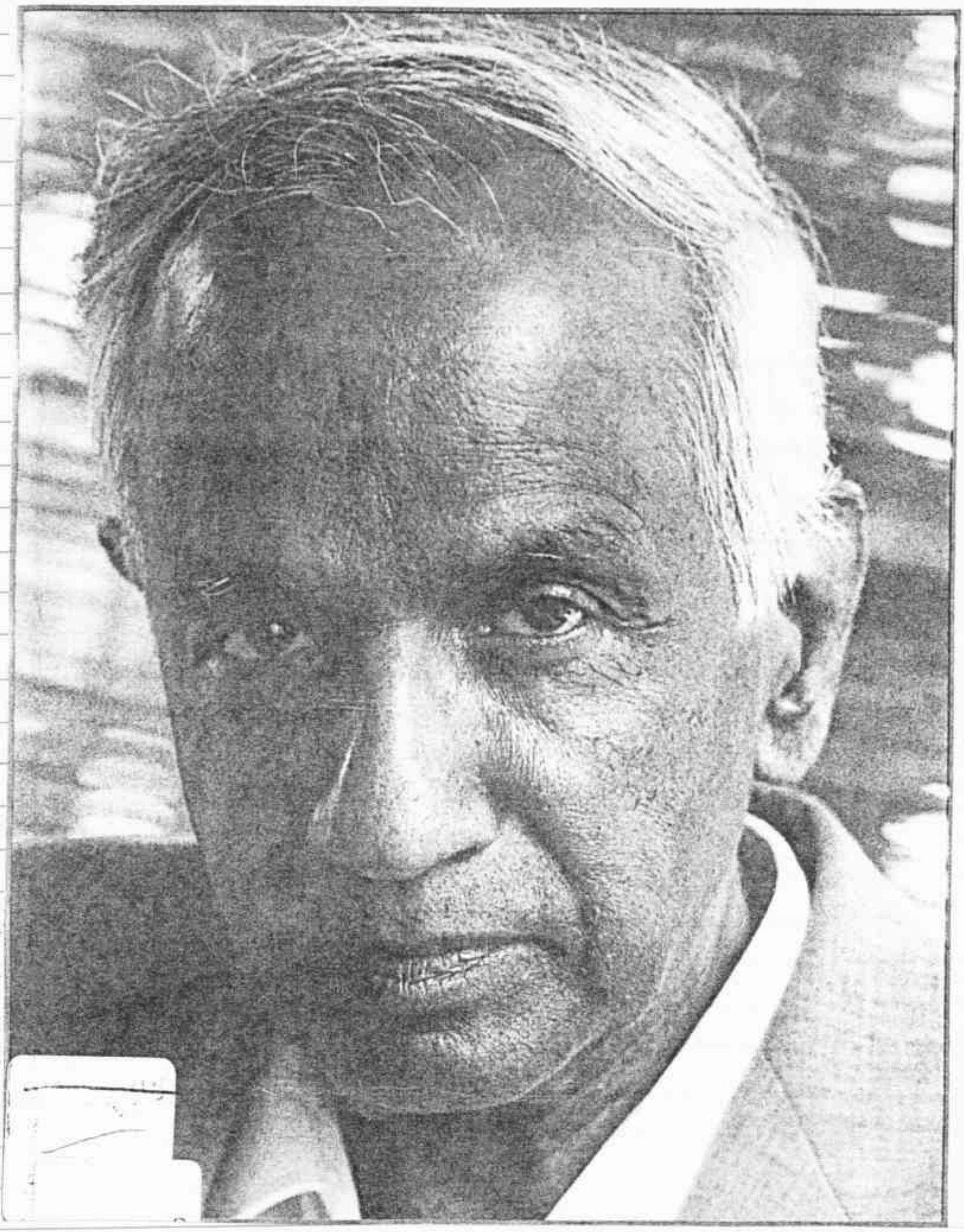
(Born 1906, German-American)

After postdoctoral work with Rutherford in Cambridge and Fermi in Rome, Bethe taught in Germany for a few years before coming to the United States in 1935. Among many contributions to atomic and nuclear physics, he is best known for finding the two nuclear cycles by which most stars get their energy. For this discovery, he won the 1967 Nobel Prize in physics.

分類：
編號： 10-25
總號：

CHANDRA

A Biography of S. Chandrasekhar



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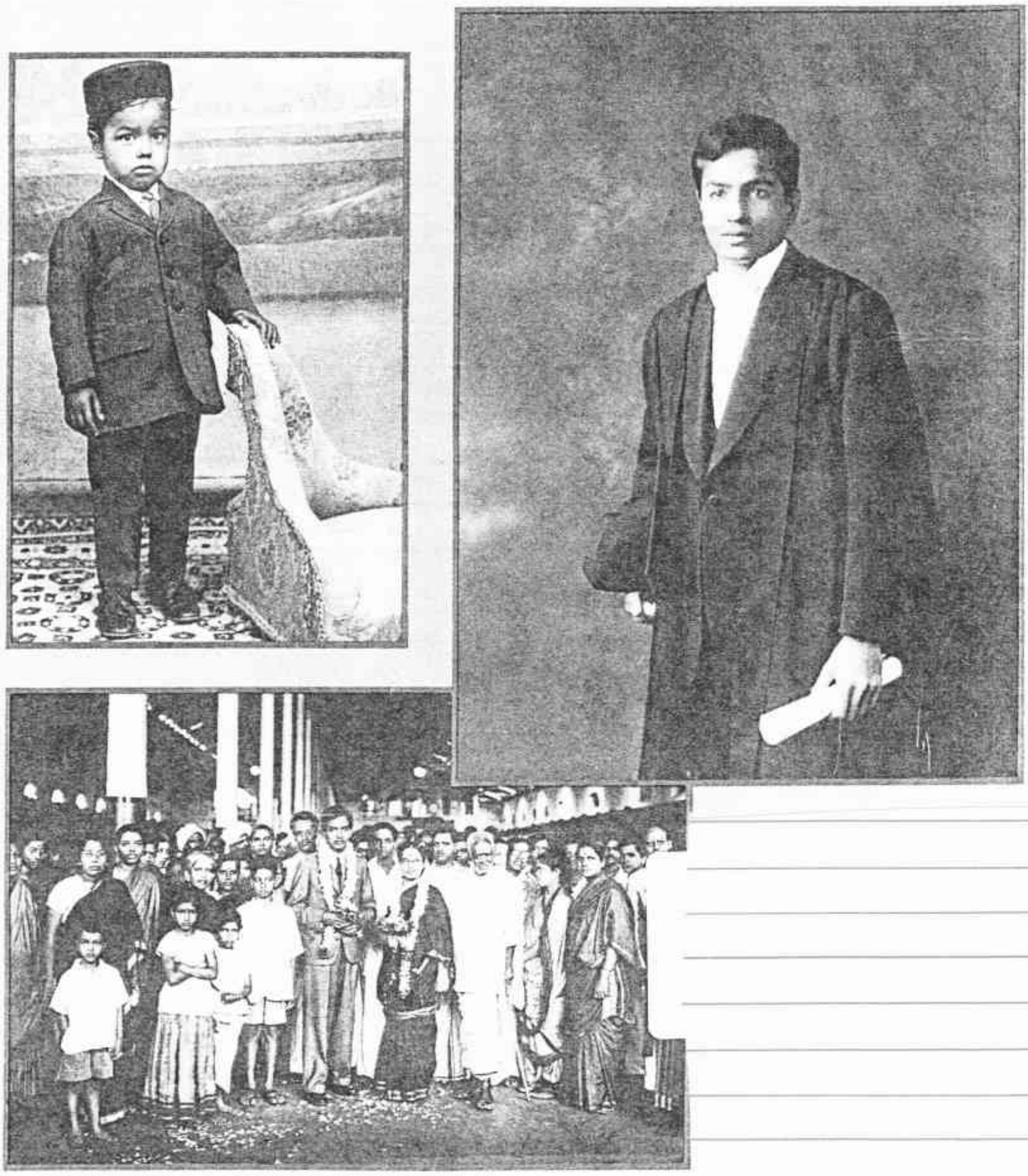
"I read *Chandra* from beginning to end with intense interest and pleasure."
—Freeman Dyson, author of *Disturbing the Universe* and *Infinite in All Directions*



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8

Identical Particles

Up to this point, we have dealt mainly with the motion of a single particle. We want to examine now how to describe systems with *many particles*. We shall focus on discussing systems of *identical* particles and examine how to construct their wave functions.

8.1 Many-Particle Systems

Most physical systems—nucleons, nuclei, atoms, molecules, solids, fluids, gases, etc.—involve many particles. They are known as *many-particle* or *many-body* systems. While atomic, nuclear and subnuclear systems involve intermediate numbers of particles ($\sim$ 2 to 300), solids, fluids and gases are truly many-body systems, since they involve very large numbers of particles ($\sim 10^{23}$).

8.1.1 Schrödinger Equation

How does one describe the dynamics of a system of N particles? This description can be obtained from a generalization of the dynamics of a single particle. The state of a system of N spinless particles (we ignore their spin for the moment) is described by a wave function $\Psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N, t)$, where $|\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)|^2 d^3r_1\, d^3r_2 \ldots d^3r_N$ represents the probability at time t of finding particle 1 in the volume element d^3r_1 centered about $\vec{r}_1$, particle 2 in the volume d^3r_2 about $\vec{r}_2$, ..., and particle N in the volume d^3r_N about $\vec{r}_N$. The normalization condition of the state is given by

$$\int d^3r_1 \int d^3r_2 \cdots \int |\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)|^2 d^3r_N = 1. \tag{8.1}$$

The wave function Ψ evolves in time according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = \hat{H} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t). \tag{8.2}$$

The form of $\hat{H}$ is obtained by generalizing the one-particle Hamiltonian $\vec{P}^2/(2m) + \vec{V}(\vec{r})$ to N

particles:

$$\hat{H} = \sum_{j=1}^{N} \frac{\hat{\vec{P}}_j^2}{2m_j} + \hat{V}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = -\sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \nabla_j^2 + \hat{V}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t), \qquad (8.3)$$

where m_i and $\hat{\vec{P}}_j$ are the mass and the momentum of the jth particle and $\hat{V}$ is the operator corresponding to the total potential energy.

The formalism of quantum mechanics for an N-particle system can be, in principle, inferred from that of a single particle. Operators corresponding to different particles commute; for instance, the commutation relations between the position and momentum operators are

$$[\hat{X}_j,\ \hat{P}_{x_k}] = i\hbar\delta_{jk}, \qquad [\hat{X}_j,\ \hat{X}_k] = [\hat{P}_{x_j},\ \hat{P}_{x_k}] = 0 \qquad (j, k = 1, 2, 3, \ldots, N), \qquad (8.4)$$

where $\hat{X}_j$ is the x-position operator of the jth particle, and $\hat{P}_{x_k}$ the x-momentum operator of the kth particle; similar relations can be obtained for the y and z components.

Stationary states

In the case where the potential $\hat{V}$ is *time independent*, the solutions of (8.2) are given by *stationary* states

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\, e^{-iEt/\hbar}, \qquad (8.5)$$

where E is the total energy of the system and ψ is solution to the time-independent Schrödinger equation $\hat{H}\psi = E\psi$, i.e.,

$$\left[-\sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \vec{\nabla}_j^2 + V(\vec{r}_1, \ldots, \vec{r}_N) \right] \psi(\vec{r}_1, \vec{r}_2,\ \ldots, \vec{r}_N) = E\ \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N). \qquad (8.6)$$

The properties of stationary states for a single particle also apply to N-particle systems. For instance, the probability density $\langle \psi \mid \psi \rangle$, the probability current density $\vec{j}$, and the expectation values of time-independent operators are conserved, since they do not depend on time:

$$\langle \Psi \mid \hat{A} \mid \Psi \rangle = \langle \psi \mid \hat{A} \mid \psi \rangle = \int d^3r_1 \int d^3r_2 \cdots \int \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \hat{A} \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\, d^3r_N. \qquad (8.7)$$

In particular, the energy of a stationary state is conserved.

Multi-electron atoms

For an illustration, let us consider an atom with Z electrons. If $\vec{R}$ is used to represent the position of the center of mass of the nucleus, the wave function of the atom depends on $3(Z+1)$ coordinates $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z, \vec{R})$, where $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z$ are the position vectors of the Z electrons. The time-independent Schrödinger equation for this atom, neglecting contributions from the spin–orbit correction, the relativistic correction and similar terms, is given by

$$\left[-\frac{\hbar^2}{2m_e} \sum_{i=1}^{Z} \vec{\nabla}_{r_i}^2 - \frac{\hbar^2}{2M} \vec{\nabla}_R^2 - \sum_{i=1}^{Z} \frac{Z e^2}{|\vec{r}_i - \vec{R}|} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z, \vec{R})$$
$$= E\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z, \vec{R}), \qquad (8.8)$$

where M is the mass of the nucleus and $-\hbar^2 \vec{\nabla}_R^2 / 2M$ is its kinetic energy operator. The term $-\sum_{i=1}^{Z} Ze^2/|\vec{r}_i - \vec{R}|$ represents the attractive Coulomb interaction of each electron with the nucleus and $\sum_{i>j} e^2/|\vec{r}_i - \vec{r}_j|$ is the repulsive Coulomb interaction between the ith and the jth electrons, $|\vec{r}_i - \vec{r}_j|$ is the distance separating them. As these (Coulomb) interactions are independent of time, the states of atoms are stationary.

We should note that the Schrödinger equations (8.2), (8.6) and (8.8) are all many-particle differential equations. As these equations cannot be separated into one-body equations, it is difficult, if not impossible, to solve them. For the important case where the N particles of the system do not interact—this is referred to as an *independent particle system*—the Schrödinger equation can be trivially reduced to N one-particle equations (Section 8.1.3); we have seen how to solve these equations exactly (chapters 4 and 6) and approximately (chapters 9 and 10).

8.1.2 Interchange Symmetry

Although the exact eigenstates of the many-body Hamiltonian (8.3) are generally impossible to obtain, we can still infer some of their properties by means of symmetry schemes. Let ξ_i represent the coordinates (position $\vec{r}_i$, spin $\vec{s}_i$, and any other internal degrees of freedom such as isospin, color, flavor) of the ith particle and let $\psi(\xi_1, \xi_2, \ldots, \xi_N)$ designates the wave function of the N-particle system.

We define a *permutation operator* (also called *exchange operator*) $\hat{P}_{ij}$ as an operator that, when acting on an N-particle wave function $\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)$, interchanges[1] the ith and the jth particles

$$\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N) = \psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N); \tag{8.9}$$

i and j are arbitrary ($i,\ j = 1, 2, \cdots, N$). Since

$$\begin{aligned} \hat{P}_{ji}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N) &= \psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) \\ &= \hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N), \end{aligned} \tag{8.10}$$

we have $\hat{P}_{ij} = \hat{P}_{ji}$. In general, permutation operators do not commute

$$\hat{P}_{ij}\hat{P}_{kl} \neq \hat{P}_{kl}\hat{P}_{ij} \qquad \text{or} \qquad [\hat{P}_{ij}, \hat{P}_{kl}] \neq 0 \qquad (ij \neq kl). \tag{8.11}$$

For instance, in the case of a four-particle state $\psi(\xi_1, \xi_2, \xi_3, \xi_4) = (3\xi_4/\xi_2\xi_3)e^{-i\xi_1}$, we have

$$\hat{P}_{12}\hat{P}_{14}\psi(\xi_1, \xi_2, \xi_3, \xi_4) = \hat{P}_{12}\psi(\xi_4, \xi_2, \xi_3, \xi_1) = \psi(\xi_2, \xi_4, \xi_3, \xi_1) = \frac{3\xi_1}{\xi_4\xi_3}e^{-i\xi_2}, \tag{8.12}$$

$$\hat{P}_{14}\hat{P}_{12}\psi(\xi_1, \xi_2, \xi_3, \xi_4) = \hat{P}_{14}\psi(\xi_2, \xi_1, \xi_3, \xi_4) = \psi(\xi_4, \xi_1, \xi_3, \xi_2) = \frac{3\xi_2}{\xi_1\xi_3}e^{-i\xi_4}. \tag{8.13}$$

Since two successive applications of $\hat{P}_{ij}$ leave the wave function unchanged,

$$\begin{aligned} \hat{P}_{ij}^2\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) &= \hat{P}_{ij}\psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) \\ &= \psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N), \end{aligned} \tag{8.14}$$

we have $\hat{P}_{ij}^2 = 1$, hence $\hat{P}_{ij}$ has two eigenvalues ± 1:

$$\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \pm\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N). \tag{8.15}$$

---

[1] L. E. Ballentine, *Quantum Mechanics: A Modern Development*, World Scientific, Singapore, 1998, Chapter 17.

The wave functions corresponding to the eigenvalue $+1$ are *symmetric* and those corresponding to -1 are *antisymmetric* with respect to the interchange of the pair $(i,\ j)$. Denoting these functions by ψ_s and ψ_a, respectively, we have

$$\psi_s(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \psi_s(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N), \tag{8.16}$$

$$\psi_a(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = -\psi_a(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N). \tag{8.17}$$

Example 8.1

Specify the symmetry of the following functions:

(a) $\psi(x_1, x_2) = 4(x_1 - x_2)^2 + \frac{10}{x_1^2+x_2^2}$

(b) $\phi(x_1, x_2) = -\frac{3(x_1-x_2)}{2(x_1-x_2)^2+7}$

(c) $\chi(x_1, x_2, x_3) = 6x_1x_2x_3 + \frac{x_1^2+x_2^2+x_3^2-1}{2x_2^3+2x_2^3+2x_3^3+5}$

(d) $\Phi(x_1, x_2) = \frac{1}{x_2+3}e^{-|x_1|}$

Solution

(a) The function $\psi(x_1, x_2)$ is symmetric, since $\psi(x_2, x_1) = \psi(x_1, x_2)$.

(b) The function $\phi(x_1, x_2)$ is antisymmetric, since $\phi(x_2, x_1) = -\phi(x_1, x_2)$. And ϕ is zero when $x_1 = x_2$: $\phi(x_1, x_1) = 0$.

(c) The function $\chi(x_1, x_2, x_3)$ is symmetric because

$$\begin{aligned} \chi(x_1, x_2, x_3) &= \chi(x_1, x_3, x_2) = \chi(x_2, x_1, x_3) = \chi(x_2, x_3, x_1) \\ &= \chi(x_3, x_1, x_2) = \chi(x_3, x_2, x_1). \end{aligned} \tag{8.18}$$

(d) The function $\Phi(x_2, x_1)$ is neither symmetric nor antisymmetric, since $\Phi(x_2, x_1) = \frac{1}{x_1+3}e^{-|x_2|} \neq \pm\Phi(x_1, x_2)$.

8.1.3 Systems of Distinguishable Noninteracting Particles

For a system of N noninteracting particles that are distinguishable—each particle has a different mass m_i and experiences a different potential $\hat{V}_i(\xi_i)$—the potential $\hat{V}$ is given by

$$\hat{V}(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) = \sum_{i=1}^{N} \hat{V}_i(\xi_i), \tag{8.19}$$

and the Hamiltonian of this system of N independent particles by

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_i}\nabla_i^2 + \hat{V}_i(\xi_i) \right], \tag{8.20}$$

where $\hat{H}_i = -\hbar^2\nabla_i^2/2m_i + \hat{V}_i(\xi_i)$ is the Hamiltonian of the ith particle, known as the single particle Hamiltonian. The Hamiltonians of different particles commute $[\hat{H}_i,\ \hat{H}_j] = 0$, since $[\hat{X}_i,\ \hat{X}_j] = [\hat{P}_i,\ \hat{P}_j] = 0$.

The Schrödinger equation of the N-particle system

$$\hat{H}\psi_{n_1,n_2,\cdots,n_N}(\xi_1,\xi_2,\cdots,\xi_N) = E_{n_1,n_2,\cdots,n_N}\psi_{n_1,n_2,\cdots,n_N}(\xi_1,\xi_2,\cdots,\xi_N), \tag{8.21}$$

separates into N one-particle equations

$$\left[-\frac{\hbar^2}{2m_i}\nabla_i^2 + \hat{V}_i(\xi_i)\right]\psi_{n_i}(\xi_i) = \varepsilon_{n_i}\psi_{n_i}(\xi_i) \tag{8.22}$$

with

$$E_{n_1,n_2,\cdots,n_N} = \varepsilon_{n_1} + \varepsilon_{n_2} + \cdots \varepsilon_{n_N} = \sum_{i=1}^{N}\varepsilon_{n_i} \tag{8.23}$$

and

$$\psi_{n_1,n_2,\cdots,n_N}(\xi_1,\xi_2,\cdots,\xi_N) = \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\cdots\psi_{n_N}(\xi_N) = \prod_{i=1}^{N}\psi_{n_i}(\xi_i). \tag{8.24}$$

We see that, when the interactions are neglected, the N-particle Schrödinger equation separates into N one-particle Schrödinger equations. The solutions of these equations yield the single-particle energies ε_{n_i} and states $\psi_{n_i}(\xi_i)$; the single-particle states are also known as the *orbitals*. The total energy is the sum of the single-particle energies and the total wave function is the product of the orbitals. The number n_i designates the set of all quantum numbers of the ith particle. Obviously, each particle requires one two or three-quantum numbers for its full description depending on whether the particles are moving in a one, two, or three dimensional space; if the spin were considered, we would need to add another quantum number. For instance, if the particles moved in a one-dimensional harmonic oscillator, n_i designate the occupation number of the ith particle. But if the particles were the electrons of an atom, then n_i would stand for four quantum numbers: the radial, orbital, and spin quantum numbers $N_i l_i m_{l_i} m_{s_i}$.

Example 8.2
Find the energy levels and wave functions of a system of four distinguishable spinless particles placed in an infinite potential well of size a. Use this result to infer the energy and the wave function of the ground state and the first excited state.

Solution
Each particle moves in a potential which is defined by $\hat{V}_i(x_i) = 0$ for $0 \le x_i \le a$ and $\hat{V}_i(x_i) = \infty$ for the other values of x_i. In this case the Schrödinger equation of the four-particle system:

$$\sum_{i=1}^{4}\left[-\frac{\hbar^2}{2m_i}\frac{d^2}{dx_i^2}\right]\psi_{n_1,n_2,n_3,n_4}(x_1,x_2,x_3,x_4) = E_{n_1,n_2,n_3,n_4}\psi_{n_1,n_2,n_3,n_4}(x_1,x_2,x_3,x_4), \tag{8.25}$$

separates into four one-particle equations

$$-\frac{\hbar^2}{2m_i}\frac{d^2\psi_{n_i}(x_i)}{dx_i^2} = \varepsilon_{n_i}\psi_{n_i}(x_i), \qquad i = 1,2,3,4, \tag{8.26}$$

with

$$\varepsilon_{n_i} = \frac{\hbar^2\pi^2 n_i^2}{2m_i a^2}, \qquad \psi_{n_i}(x_i) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_i\pi}{a}x_i\right). \tag{8.27}$$

The total energy and wave function are given by

$$E_{n_1,n_2,n_3,n_4} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2} + \frac{n_3^2}{m_3} + \frac{n_4^2}{m_4}\right), \tag{8.28}$$

$$\psi_{n_1,n_2,n_3,n_4}(x_1, x_2, x_3, x_4) = \frac{4}{a^2}\sin\left(\frac{n_1\pi}{a}x_1\right)\sin\left(\frac{n_2\pi}{a}x_2\right)\sin\left(\frac{n_3\pi}{a}x_3\right)\sin\left(\frac{n_4\pi}{a}x_4\right). \tag{8.29}$$

The ground state corresponds to the case where all four particles occupy their respective ground state orbitals, $n_1 = n_2 = n_3 = n_4 = 1$. The ground state energy and wave function are thus given by

$$E_{1,1,1,1} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3} + \frac{1}{m_4}\right), \tag{8.30}$$

$$\psi_{1,1,1,1}(x_1, x_2, x_3, x_4) = \frac{4}{a^2}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{\pi}{a}x_3\right)\sin\left(\frac{\pi}{a}x_4\right). \tag{8.31}$$

The first excited state is somewhat tricky. Since it corresponds to the next higher energy level of the system, it must correspond to the case where the particle having the largest mass occupies its first excited state while the other three particles remain in their respective ground states. For argument's sake, if the third particle were the most massive, the first excited state would correspond to the configuration $n_1 = n_2 = n_4 = 1$ and $n_3 = 2$; the energy and wave function of the first excited state would then be given by

$$E_{1,1,2,1} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{4}{m_3} + \frac{1}{m_4}\right), \tag{8.32}$$

$$\psi_{1,1,2,1}(x_1, x_2, x_3, x_4) = \frac{4}{a^2}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_3\right)\sin\left(\frac{\pi}{a}x_4\right). \tag{8.33}$$

Continuing in this way, we can obtain the entire energy spectrum of this system.

8.2 Systems of Identical Particles

8.2.1 Identical Particles in Classical and Quantum Mechanics

In classical mechanics, when a system is made of identical particles, it is possible to identify and distinguish each particle from the others. That is, although all particles have the same physical properties, we can "tag" each classical particle and follow its motion along a path. For instance, each particle can be colored differently from the rest, hence we can follow the trajectory of each particle separately at each time. *Identical classical particles, therefore, do not lose their identity; they are distinguishable.*

In quantum mechanics, however, identical particles are truly indistinguishable. The underlying basis for this is twofold. First, to describe a particle, we cannot specify more than

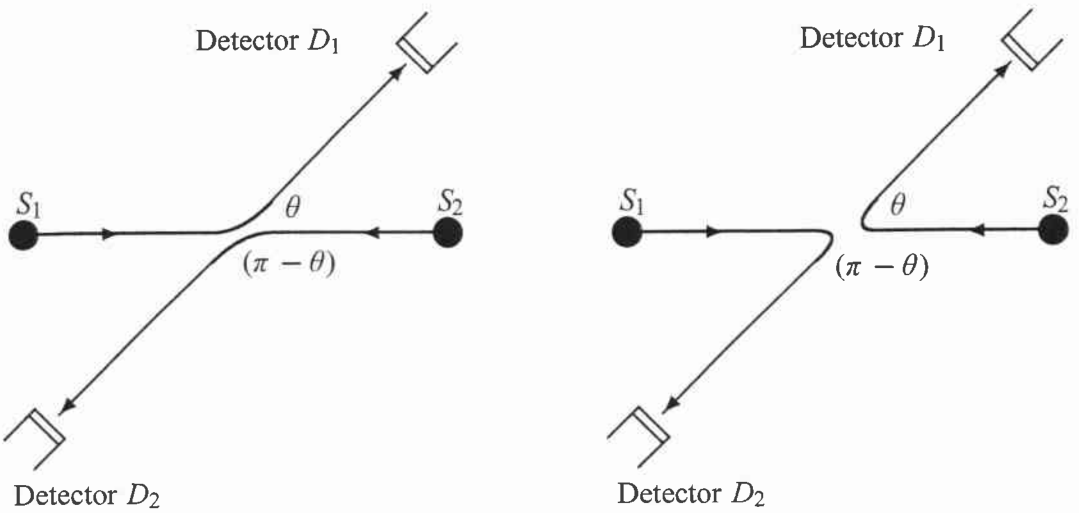

Figure 8.1 When scattering two *identical* particles in the center of mass frame, it is impossible to forcast with certitude whether the particles scatter according to the first process or to the second. For instance, we cannot tell whether the particle fired from source S_1 will make it to detector D_1 or to D_2.

a complete set of commuting observables. In particular, there exists no mechanism to tag the particles as in classical mechanics. Second, due to the uncertainty principle, the concept of the path of a particle becomes meaningless. Even if the position of a particle is exactly determined at a time, it is not possible to specify its coordinates at the next instant. Thus, *identical particles lose their identity (individuality) in quantum mechanics.*

To illustrate this, consider an experiment in which we scatter two identical particles. As displayed in Figure 8.1, after particles 1 and 2 (fired from the sources S_1 and S_2) have scattered, it is impossible to distinguish between the first and the second outcomes. That is, we cannot determine experimentally the identity of the particles that are collected by each detector. For instance, we can in no way tell whether it is particle 1 or particle 2 that has reached detector D_1. We can only say that a particle has reached detector D_1 and another has made it to D_2, but no information on their respective identities. There exists no experimental mechanism that allows us to follow the motion of each particle from the time it is fired out of the source till the time it reaches the detector. This experiment shows how *the individuality of a microscopic particle is lost the moment it is mixed with other similar particles.*

Having discussed the indistinguishability concept on a two-particle system, let us now study this concept on larger systems. For this, consider a system of N *identical* particles whose wave function is $\psi(\xi_1, \xi_2, \ldots, \xi_N)$.

The moment these N particles are mixed together, no experiment can determine which particle has the coordinates ξ_1, or which one has ξ_2, and so on. It is impossible to specify experimentally the identity of the particle which is located at ξ_1, or that located at ξ_2, and so on. The only measurements we can perform are those that specify the probability for a certain particle to be located at ξ_1, another at ξ_2, and so on, but we can never make a distinction as to which particle is which.

As a result, the probability remains unchanged by an interchange of the particles. For instance, an interchange of particles i and j will leave the probability density unaffected:

$$\left|\psi(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)\right|^2 = \left|\psi(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N)\right|^2, \quad (8.34)$$

hence

$$\psi(\xi_1,\ \xi_2,\ldots,\ \xi_i,\ldots,\ \xi_j,\ldots,\xi_N) = \pm\psi(\xi_1,\ \xi_2,\ldots,\ \xi_j,\ldots,\ \xi_i,\ldots,\xi_N). \tag{8.35}$$

This means that the wave function of a system of N identical particles is either symmetric or antisymmetric under the interchange of a pair of particles. We will deal with the implications of this result in Section 8.2.3. We will see that the sign in (8.35) is related to the spin of the particles: the negative sign corresponds to particles with half-odd-integral spin and the positive sign corresponds to particles with integral spin; that is, the wave functions of particles with integral spins are symmetric and the wave functions of particles with half-odd-integral spins are antisymmetric. In fact, experimental observations show that, in nature, particles come in two classes:

- Particles with *integral spin*, $S_i = 0,\ 1\hbar,\ 2\hbar,\ 3\hbar,\cdots$, such as photons, pions, alpha particles; these particles are called *bosons*.
- Particles with *half-odd-integral spin*, $S_i = \hbar/2,\ 3\hbar/2,\ 5\hbar/2,\ 7\hbar/2,\ldots$, such as quarks, electrons, positrons, protons, neutrons. These particles are called *fermions*.

That is, particles occurring in nature are either bosons or fermions.

Before elaborating more on the properties of bosons and fermions, let us present a brief outline on the interchange (permutation) symmetry.

8.2.2 Exchange Degeneracy

How does the interchange symmetry affect operators such as the Hamiltonian? Since the Coulomb potential, which results from electron–electron and electron–nucleus interactions,

$$V(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_Z) = -\sum_{i=1}^{Z}\frac{Z\,e^2}{|\vec{r}_i-\vec{R}|}+\sum_{i>j}\frac{e^2}{|\vec{r}_j-\vec{r}_j|} \tag{8.36}$$

is invariant under the permutation of any pair of electrons, the Hamiltonian (8.8) is also invariant under such permutations. This symmetry also applies to the orbital, spin and angular momenta of an atom. We may thus use this symmetry to introduce an another definition of the *identicalness* of particles: *The N particles of a system are said to be identical if the various observables of the system* (such as the Hamiltonian $\hat{H}$, the angular momenta, and so on) *are symmetrical when any two particles are interchanged.* If these operators were not symmetric under particle interchange, the particles would be distinguishable.

The invariance of the Hamiltonian under particle interchanges is not without physical implications: the eigenvalues of $\hat{H}$ are *degenerate*. The wave functions corresponding to all possible electron permutations have the same energy E: $\hat{H}\psi = E\psi$. This is known as the *exchange degeneracy*. For instance, the degeneracy associated with a system of two identical particles is equal to 2, since $\psi(\xi_1,\ \xi_2)$ and $\psi(\xi_2,\ \xi_1)$ correspond to the same energy E.

So the Hamiltonian of a system of N identical particles ($m_i = m$) is completely symmetric with respect to the coordinates of the particles:

$$\begin{aligned}\hat{H}(\xi_1,\ \ldots,\ \xi_i,\ \ldots,\ \xi_j,\ \ldots,\ \xi_N) &= \sum_{i=1}^{N}\frac{\vec{P}_i^2}{2m}+\hat{V}(\xi_1,\ \ldots,\ \xi_i,\ \ldots,\ \xi_j,\ \ldots,\ \xi_N)\\ &= \hat{H}(\xi_1,\ \ldots,\ \xi_j,\ \ldots,\ \xi_i,\ \ldots,\ \xi_N),\end{aligned} \tag{8.37}$$

because $\hat{V}$ is invariant under the permutation of any pair of particles $i \longleftrightarrow j$:

$$\hat{V}(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \hat{V}(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N). \tag{8.38}$$

This property can also be ascertained by showing that $\hat{H}$ commutes with the particle interchange operator $\hat{P}_{ij}$. If ψ is eigenstate to $\hat{H}$ with eigenvalue E, we can write

$$\begin{aligned} \hat{H}\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) &= \hat{H}\psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) \\ &= E\psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) = E\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) \\ &= \hat{P}_{ij}E\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \hat{P}_{ij}\hat{H}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N), \end{aligned} \tag{8.39}$$

or

$$[\hat{H}, \hat{P}_{ij}] = 0. \tag{8.40}$$

Therefore, $\hat{P}_{ij}$ is a *constant of the motion*. That is, if we start with a wave function that is symmetric (antisymmetric), it will remain so for all subsequent times. Moreover, since $\hat{P}_{ij}$ and $\hat{H}$ commute, they possess a complete set of functions that are joint eigenstates of both. As shown in (8.15) to (8.17), these eigenstates have definite parity, either symmetric or antisymmetric.

8.2.3 Symmetrization Postulate

We have shown in (8.35) that the wave function of a system of N identical particles is either symmetric or antisymmetric under the interchange of any pair of particles:

$$\psi(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \pm\psi(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N). \tag{8.41}$$

This result, which turns out to be supported by experimental evidence, is the very essence of the *symmetrization postulate* which stipulates that, in nature, the states of systems containing N identical particles are *either totally symmetric or totally antisymmetric* under the interchange of any pair of particles and that states with mixed symmetry do not exist. Besides that, this postulate states two more things:

- Particles with integral spins, or bosons, have symmetric states.
- Particles with half-odd-integral spins, or fermions, have antisymmetric states.

Fermions are said to obey *Fermi–Dirac statistics*, and bosons to obey *Bose–Einstein statistics*. So the wave function of a system of identical bosons is totally symmetric, and the wave function of a system of identical fermions is totally antisymmetric.

Composite Particles

The foregoing discussion pertains to identical particles that are "simple" or elementary such as quarks, electrons, positrons, muons, and so on. Let us now discuss the symmetry of systems of identical *composite* "particles" where each particle is composed of two or more identical elementary particles. For instance, alpha particles, which consist of nuclei that are composed of two neutrons and two protons each, are a typical example of composite particles. A system of N hydrogen atoms can also be viewed as a system of identical composite particles where each "particle" (atom) consists of a proton and an electron. Protons, neutrons, pions, etc., are themselves composite particles, because protons and neutrons consist of three quarks, and pions consist of two. *Quarks* are elementary spin $\frac{1}{2}$ particles.

Composite particles have spin. The spin of each composite particle can be obtained by adding the spins of its constituents. If the total spin of the composite particle is half-odd-integer, this particle behaves like a fermion, hence it obeys Fermi–Dirac statistics. If, on the other hand, its resultant spin is integer, it behaves like a boson and obeys Bose–Einstein statistics. In general, if the composite particle has an odd number of fermions, it is then a fermion, otherwise it is a boson. For instance, nucleons are fermions because they consist of three quarks; mesons are bosons because they consist of two quarks. For another illustrative example, let us consider the isotopes ^{4}He and ^{3}He of the helium atom: ^{4}He, which is called an alpha particle, is a boson for it consists of four nucleons (two protons and two neutrons), while ^{3}He is a fermion since it consists of three nucleons (one neutron and two protons). The hydrogen atom consists of two fermions (an electron and a proton), so it is a boson.

8.2.4 Constructing Symmetric and Antisymmetric Functions

Since the wave functions of systems of identical particles are either totally symmetric or totally antisymmetric, it is appropriate to study the formalism of how to construct wave functions that are totally symmetric or totally antisymmetric starting from unsymmetric functions. For simplicity, consider first a system of two identical particles. Starting from any normalized unsymmetric wave function $\psi(\xi_1, \xi_2)$, we can construct symmetric wave functions $\psi_s(\xi_1, \xi_2)$ as

$$\psi_s(\xi_1, \xi_2) = \frac{1}{\sqrt{2}}\Big[\psi(\xi_1, \xi_2) + \psi(\xi_2, \xi_1)\Big], \tag{8.42}$$

and antisymmetric wave functions $\psi_a(\xi_1, \xi_2)$ as

$$\psi_a(\xi_1, \xi_2) = \frac{1}{\sqrt{2}}\Big[\psi(\xi_1, \xi_2) - \psi(\xi_2, \xi_1)\Big], \tag{8.43}$$

where $1/\sqrt{2}$ is a normalization factor.

Similarly, for a system of three identical particles, we can construct ψ_s and ψ_a from an unsymmetric function ψ as follows:

$$\begin{aligned}\psi_s(\xi_1, \xi_2, \xi_3) &= \frac{1}{\sqrt{6}}\Big[\psi(\xi_1, \xi_2, \xi_3) + \psi(\xi_1, \xi_3, \xi_2) + \psi(\xi_2, \xi_3, \xi_1) \\ &\qquad + \psi(\xi_2, \xi_1, \xi_3) + \psi(\xi_3, \xi_1, \xi_2) + \psi(\xi_3, \xi_2, \xi_1)\Big], \qquad (8.44)\\ \psi_a(\xi_1, \xi_2, \xi_3) &= \frac{1}{\sqrt{6}}\Big[\psi(\xi_1, \xi_2, \xi_3) - \psi(\xi_1, \xi_3, \xi_2) + \psi(\xi_2, \xi_3, \xi_1) \\ &\qquad - \psi(\xi_2, \xi_1, \xi_3) + \psi(\xi_3, \xi_1, \xi_2) - \psi(\xi_3, \xi_2, \xi_1)\Big]. \qquad (8.45)\end{aligned}$$

Continuing this way, we can in principle construct symmetric and antisymmetric wave functions for any system of N identical particles.

8.2.5 Systems of Identical Noninteracting Particles

In the case of a system of N noninteracting identical particles, where all particles have equal mass $m_i = m$ and experience the same potential $\hat{V}_i(\xi_i) = \hat{V}(\xi_i)$, the Schrödinger equation of the system separates into N identical one-particle equations

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + \hat{V}(\xi_i)\right]\psi_{n_i}(\xi_i) = \varepsilon_{n_i}\psi_{n_i}(\xi_i). \tag{8.46}$$

Whereas the energy is given, like the case of a system of N distinguishable particles, by a sum of the single-particle energies $E_{n_1,n_2,\ldots,n_N} = \sum_{i=1}^N \varepsilon_{n_i}$, the wave function can no longer be given by a simple product $\psi_{n_1,n_2,\ldots,n_N}(\xi_1,\xi_2,\ldots,\xi_N) = \prod_{i=1}^N \psi_{n_i}(\xi_i)$ for at least two reasons. First, if the wave function is given by such a product, it would imply that particle 1 is in the state ψ_{n_1}, particle 2 in the state ψ_{n_2}, ..., and particle N in the state ψ_{n_N}. This, of course, makes no sense since all we know is that one of the particles is in the state ψ_{n_1}, another in ψ_{n_2}, and so on; since the particles are identical, there is no way to tell which particle is in which state. If, however, the particles were distinguishable, then their total wave function would be given by such a product as shown in (8.24). The second reason why the wave function of a system of identical particles cannot be given by $\prod_{i=1}^N \psi_{n_i}(\xi_i)$ has to do with the fact that such a product has, in general, no *definite* symmetry—a mandatory requirement for systems of N identical particles whose wave functions are either symmetric or antisymmetric. We can, however, extend the method of Section 8.2.4 to construct totally symmetric and totally antisymmetric wave functions from the single-particle states $\psi_{n_i}(\xi_i)$. For this, we are going to show how to construct symmetrized and antisymmetrized wave functions for systems of two, three, and N noninteracting identical particles.

8.2.5.1 Wave Function of Two-Particle Systems

By analogy with (8.17) and (8.43), we can construct the symmetric and antisymmetric wave functions for a system of two identical, noninteracting particles in terms of the single-particle wave functions as follows:

$$\psi_s(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2) + \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_1)\right] \tag{8.47}$$

$$\psi_a(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2) - \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_1)\right], \tag{8.48}$$

where we have supposed that $n_1 \neq n_2$. When $n_1 = n_2 = n$ the symmetric wave function is given by $\psi_s(\xi_1,\xi_2) = \psi_n(\xi_1)\psi_n(\xi_2)$ and the antisymmetric wave function is zero; we will deal later with the reason why $\psi_a(\xi_1,\xi_2) = 0$ whenever $n_1 = n_2$.

Note that we can rewrite ψ_s as

$$\boxed{\psi_s(\xi_1,\xi_2) = \frac{1}{\sqrt{2!}}\sum_P \hat{P}\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2),} \tag{8.49}$$

where $\hat{P}$ is the permutation operator, and where the sum is over all possible permutations (here we have only two possible ones). Similarly, we can write ψ_a as

$$\psi_a(\xi_1,\xi_2) = \frac{1}{\sqrt{2!}}\sum_P (-1)^P \hat{P}\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2), \tag{8.50}$$

where $(-1)^P$ is equal to +1 for an even permutation (i.e., when we interchange both ξ_1 and ξ_2 and also n_1 and n_2) and equal to -1 for an odd permutation (i.e., when we permute ξ_1 and ξ_2 but not n_1, n_2, and vice versa). Note that we can rewrite ψ_a of (8.48) in the form of a determinant

$$\boxed{\psi_a(\xi_1, \xi_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) \end{vmatrix}.} \tag{8.51}$$

8.2.5.2 Wave Function of Three-Particle Systems

For a system of three noninteracting identical particles, the symmetric wave function is given by

$$\psi_s(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \sum_P \hat{P} \psi_{n_1}(\xi_1) \psi_{n_2}(\xi_2) \psi_{n_3}(\xi_3) \tag{8.52}$$

or by

$$\begin{aligned} \psi_s(\xi_1, \xi_2, \xi_3) \quad & \frac{1}{\sqrt{3!}} \Big[\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\psi_{n_3}(\xi_3) + \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_3)\psi_{n_3}(\xi_2) \\ & + \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_1)\psi_{n_3}(\xi_3) + \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_3)\psi_{n_3}(\xi_1) \\ & + \psi_{n_1}(\xi_3)\psi_{n_2}(\xi_1)\psi_{n_3}(\xi_2) + \psi_{n_1}(\xi_3)\psi_{n_2}(\xi_2)\psi_{n_3}(\xi_1) \Big]. \end{aligned} \tag{8.53}$$

and the antisymmetric wave function is given by

$$\psi_a(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \sum_P (-1)^P \hat{P} \psi_{n_1}(\xi_1) \psi_{n_2}(\xi_2) \psi_{n_3}(\xi_3) \tag{8.54}$$

or, in the form of a determinant, by

$$\psi_a(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) & \psi_{n_1}(\xi_3) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) & \psi_{n_2}(\xi_3) \\ \psi_{n_3}(\xi_1) & \psi_{n_3}(\xi_2) & \psi_{n_3}(\xi_3) \end{vmatrix}. \tag{8.55}$$

If $n_1 = n_2 = n_3 = n$ we have $\psi_s(\xi_1, \xi_2, \xi_3) = \psi_n(\xi_1)\psi_n(\xi_2)\psi_n(\xi_3)$ and $\psi_a(\xi_1, \xi_2, \xi_3) = 0$.

8.2.5.3 Wave Function of Many-Particle Systems

We can generalize (8.52) and (8.55) and write the symmetric and antisymmetric wave functions for a system of N noninteracting identical particles as follows:

$$\psi_s(\xi_1, \xi_2, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \sum_P \hat{P} \psi_{n_1}(\xi_1) \psi_{n_2}(\xi_2) \cdots \psi_{n_N}(\xi_N), \tag{8.56}$$

$$\psi_a(\xi_1, \xi_2, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{n_1}(\xi_1) \psi_{n_2}(\xi_2) \cdots \psi_{n_N}(\xi_N), \tag{8.57}$$

or

$$\psi_a(\xi_1, \xi_2, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) & \cdots & \psi_{n_1}(\xi_N) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) & \cdots & \psi_{n_2}(\xi_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{n_N}(\xi_1) & \psi_{n_N}(\xi_2) & \cdots & \psi_{n_N}(\xi_N) \end{vmatrix}. \tag{8.58}$$

This $N \times N$ determinant, which involves one-particle states only, is known as the *Slater determinant*. An interchange of any pair of particles corresponds to an interchange of two columns of the determinant; this interchange introduces a change in the sign of the determinant. For even permutations we have $(-1)^P = 1$, and for odd permutations we have $(-1)^P = -1$.

The relations (8.56) and (8.58) are valid for the case where the numbers $n_1, n_2, \ldots, n_N$ are all different from one another. What happens if some, or all, of these numbers are equal? In the symmetric case, if $n_1 = n_2 = \ldots = n_N$ then ψ_s is given by

$$\psi_s(\xi_1, \xi_2, \ldots, \xi_N) = \prod_{i=1}^{N} \psi_n(\xi_i) = \psi_n(\xi_1)\psi_n(\xi_2)\cdots\psi_n(\xi_N). \tag{8.59}$$

When there is a multiplicity in the numbers $n_1, n_2, \ldots, n_N$ (i.e., when some of the numbers n_i occur more than once), we have to be careful and avoid double counting. For instance, if n_1 occurs N_1 times in the sequence $n_1, n_2, \ldots, n_N$, if n_2 occurs N_2 times, and so on, the symmetric wave function will be given by

$$\psi_s(\xi_1, \xi_2, \ldots, \xi_N) = \sqrt{\frac{N_1!N_2!\cdots N_n!}{N!}} \sum_P \hat{P} \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\cdots\psi_{n_N}(\xi_N); \tag{8.60}$$

the summation $\sum_P$ is taken only over permutations which lead to *distinct* terms and includes $N!/N_1!N_2!\cdots N_n!$ different terms. For example, in the case of a system of three independent, identical bosons where $n_1 = n_2 = n$ and $n_3 \neq n$, the multiplicity of n_1 is $N_1 = 2$, hence ψ_s is given by

$$\begin{aligned}\psi_s(\xi_1, \xi_2, \xi_3) &= \sqrt{\frac{2!}{3!}} \sum_P \hat{P} \psi_n(\xi_1)\psi_n(\xi_2)\psi_{n_3}(\xi_3) = \frac{1}{\sqrt{3}}\Big[\psi_n(\xi_1)\psi_n(\xi_2)\psi_{n_3}(\xi_3) \\ &\quad + \psi_n(\xi_1)\psi_{n_3}(\xi_2)\psi_n(\xi_3) + \psi_{n_3}(\xi_1)\psi_n(\xi_2)\psi_n(\xi_3)\Big]. \end{aligned} \tag{8.61}$$

Unlike the symmetric case, the antisymmetric case is quite straightforward: if, among the numbers $n_1, n_2, \ldots, n_N$, only two are equal, the antisymmetric wave function vanishes. For instance, if $n_i = n_j$, the ith and jth rows of the determinant (8.58) will be identical, hence the determinant vanishes identically. Antisymmetric wave functions, therefore, are nonzero only for those cases where all the numbers $n_1, n_2, \ldots, n_N$ are different.

8.3 The Pauli Exclusion Principle

As mentioned above, if any two particles occupy the same single-particle state, the determinant (8.58), hence the total wave function, will vanish since two rows of the determinant will be identical. We can thus infer that *in a system of N identical particles, no two fermions can occupy the same single-particle state at a time*; every single-particle state can be occupied by at most one fermion. This is the *Pauli exclusion principle*, which was first postulated in 1925 to explain the periodic table. It states that *no two electrons can occupy simultaneously the same (single-particle) quantum state on the same atom*; there can be only one (or at most one) electron occupying a state of quantum numbers $n_i l_i m_{l_i} m_{s_i}$: $\psi_{n_i l_i m_{l_i} m_{s_i}}(\vec{r}_i, \vec{S}_i)$. The exclusion principle plays an important role in the structure of atoms. It has a direct effect on the *spatial distribution* of fermions.

Boson condensation

What about bosons? Do they have any restriction like fermions? Not at all. There is no restriction on the number of bosons that can occupy a single state. Instead of the exclusion principle of fermions, bosons tend to condense all in the same state, the ground state; this is called *boson condensation*. For instance, all the particles of liquid ^{4}He (a boson system) occupy the same ground state. This phenomenon is known as *Bose–Einstein condensation*. The properties of liquid ^{3}He are, however, completely different from those of liquid ^{4}He, because ^{3}He is a fermion system.

Remark

We have seen that when the Schrödinger equation involves the spin, the wave function of a single particle is equal to the product of the spatial part and the spin part: $\Psi(\vec{r}, \vec{S}) = \psi(\vec{r})\chi(\vec{S})$. The wave function of a system of N particles, which have spins, is the product of the spatial part and the spin part:

$$\Psi(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2;\ \ldots;\ \vec{r}_N, \vec{S}_N) = \psi(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N). \tag{8.62}$$

This wave function must satisfy the appropriate symmetry requirements when the N particles are identical. In the case of a system of N identical bosons, the wave function must be symmetric, hence the spatial and spin parts must have the same parity:

$$\Psi_s(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2;\ \ldots;\ \vec{r}_N, \vec{S}_N) = \left\{ \begin{array}{l} \psi_a(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_a(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N) \\ \psi_s(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_s(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N). \end{array} \right. \tag{8.63}$$

In the case of a system of N identical fermions, however, the space and spin parts must have different parities, leading to an overall wave function that is antisymmetric:

$$\Psi_a(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2;\ \ldots;\ \vec{r}_N, \vec{S}_N) = \left\{ \begin{array}{l} \psi_a(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_s(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N) \\ \psi_s(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_a(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N); \end{array} \right. \tag{8.64}$$

Example 8.3 (Wave function of two identical, noninteracting particles)

Find the wave functions of two systems of identical, noninteracting particles: the first consists of two bosons, and the second of two spin $\frac{1}{2}$ fermions.

Solution

For a system of two identical, noninteracting bosons, (8.47) and (8.48) yield

$$\Psi_s(\vec{r}_1, \vec{S}_1; \vec{r}_2, \vec{S}_2) = \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} \left[\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) - \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right]\chi_a(\vec{S}_1,\ \vec{S}_2) \\ \left[\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) + \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right]\chi_s(\vec{S}_1,\ \vec{S}_2), \end{array} \right. \tag{8.65}$$

and for a system of two spin $\frac{1}{2}$ fermions

$$\Psi_a(\vec{r}_1, \vec{S}_1; \vec{r}_2, \vec{S}_2) = \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} \left[\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) - \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right]\chi_s(\vec{S}_1,\ \vec{S}_2) \\ \left[\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) + \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right]\chi_a(\vec{S}_1,\ \vec{S}_2), \end{array} \right. \tag{8.66}$$

where, from the formalism of angular momentum addition, there are three states (a triplet) that are symmetric, $\chi_s(\vec{S}_1, \vec{S}_2)$:

$$\chi_{triplet}(\vec{S}_1, \vec{S}_2) = \begin{cases} \left|\frac{1}{2}\ \frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\ \frac{1}{2}\right\rangle_2 \\ \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\ \frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle_2 + \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\ \frac{1}{2}\right\rangle_2 \right), \\ \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle_2, \end{cases} \tag{8.67}$$

and one state (a singlet) that is antisymmetric, $\chi_a(\vec{S}_1, \vec{S}_2)$:

$$\chi_{singlet}(\vec{S}_1, \vec{S}_2) = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\ \frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle_2 - \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\ \frac{1}{2}\right\rangle_2 \right). \tag{8.68}$$

8.4 The Exclusion Principle and the Periodic Table

Explaining the periodic table is one the most striking successes of the Schrödinger equation. When combined with the Pauli exclusion principle, the equation offers insightful information on the structure of multi-electron atoms.

In Chapter 6, we saw that the state of the hydrogen's electron, which moves in the spherically symmetric Coulomb potential of the nucleus, is described by four quantum numbers n, l, m_l and m_s: $\Psi_{nlm_lm_s}(\vec{r}) = \psi_{nlm_l}(\vec{r})\chi_{m_s}$, where $\psi_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta, \varphi)$ is the electron's wave function when the spin is ignored and $\chi_{m_s} = \left|\frac{1}{2},\ \pm\frac{1}{2}\right\rangle$ is the spin's state. This representation turns out to be suitable for any atom as well.

In a multi-electron atom, the average potential in which every electron moves is different from the Coulomb potential of the nucleus; yet, to a good approximation, it can be assumed to be spherically symmetric. We can therefore, as in hydrogen, characterize the electronic states by the four quantum numbers n, l, m_l and m_s, which respectively represent the principal quantum number, the orbital quantum number, the magnetic (or azimuthal) quantum number, and the spin quantum number; m_l represents the z-component of the electron orbital angular momentum and m_s the z-component of its spin.

Atoms have *shell structure*. Each atom has a number of major shells that are specified by the radial or principal quantum number n. Shells have subshells which are specified by the orbital quantum number l. Subshells in turn have subsubshells, called *orbitals*, specified by m_l; so *an orbital is fully specified by three quantum numbers n, l, m_l*, i.e., it is defined by $|nlm_l\rangle$. Each shell n therefore has $n - 1$ subshells corresponding to $l = 0, 1, 2, 3, \ldots, n - 1$, and in turn each subshell has $2l + 1$ orbitals (or subsubshells), since to $m_l = -l, -l + 1, -l + 2, \ldots, l - 2, l - 1, l$. As in hydrogen, individual electrons occupy single-particle states or orbitals; the states corresponding to the respective numerical values $l = 0, 1, 2, 3, 4, 5, \ldots$ are called s, p, d, f, g, h, ... states. Hence for a given n an s-state has 1 orbital ($m_l = 0$), a p-state has 3 orbitals ($m_l = -1, 0, 1$), a d-state has 5 orbitals ($m_l = -2, -1, 0, 1, 2$), and so on (Chapter 6). We will label the electronic states by nl where, as before, l refers to s, p, d, f, etc.; for example $1s$ corresponds to $(n, l) = (1, 0)$, $2s$ corresponds to $(n, l) = (2, 0)$, $2p$ corresponds to $(n, l) = (2, 1)$, $3s$ corresponds to $(n, l) = (3, 0)$, and so on.

How do electrons fill the various shells and subshells in an atom? If electrons were bosons, they would all group in the ground state $|nlm_l\rangle = |100\rangle$; we wouldn't then have the rich diversity of elements that exist in nature. But since electrons are identical fermions, they are

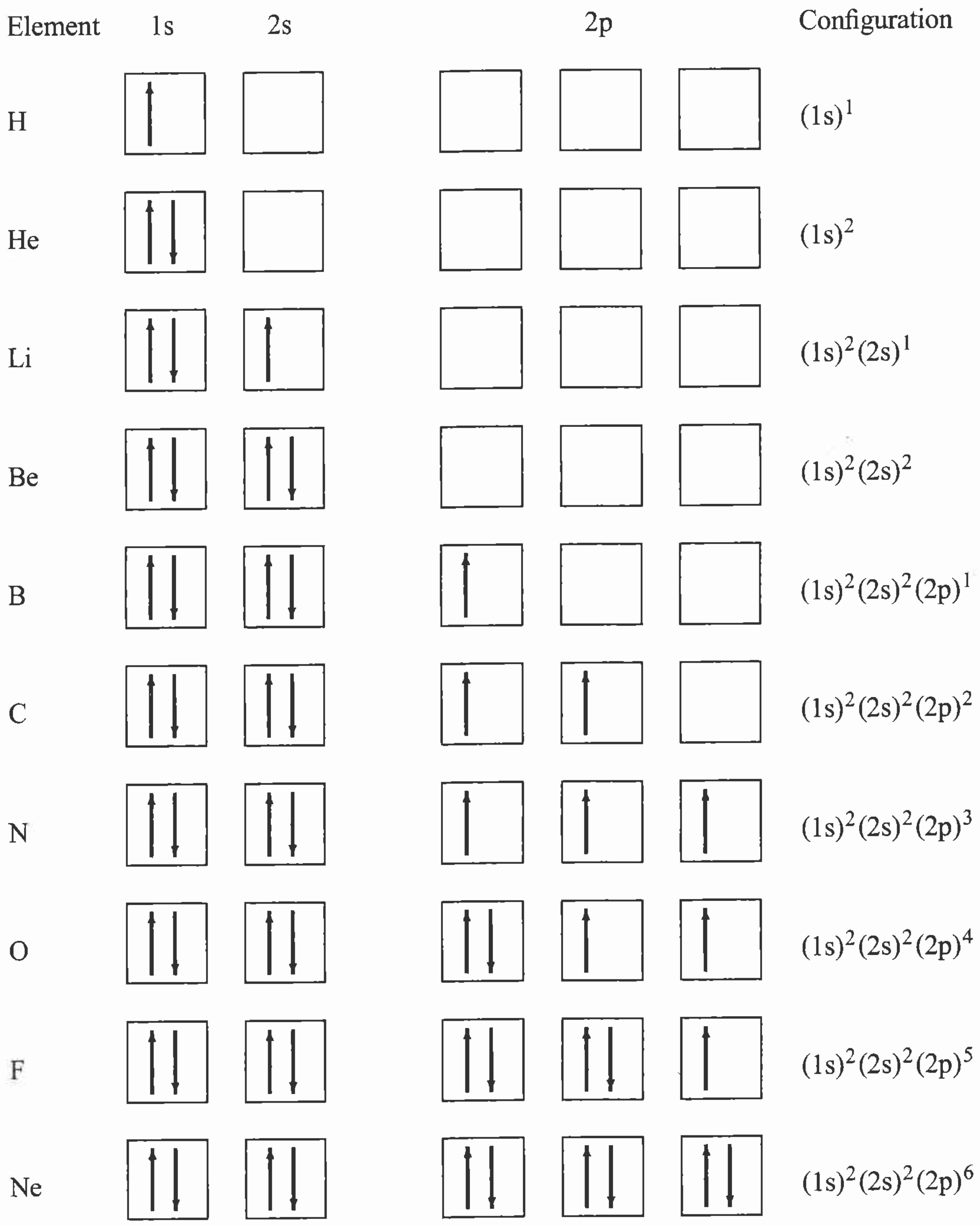

Figure 8.2 Filling orbitals according to the Pauli exclusion principle.

governed by the Pauli exclusion principle which states that *no two electrons can occupy simultaneously the same quantum state* $|nlm_lm_s\rangle$ *on the same atom.* Hence each orbital $|nlm_l\rangle$ can be occupied by two electrons *at most*: one having spin up $m_s = +\frac{1}{2}$, the other spin down $m_s = -\frac{1}{2}$. Hence, each state nl can accommodate $2(2l+1)$ electrons. So an s-state (i.e., $|n00\rangle$) can at most hold 2 electrons, a p-state (i.e., $|n1m_l\rangle$) at most 6 electrons, a d-state (i.e., $|n2m_l\rangle$) at most 10 electrons, an f-state (i.e., $|n3m_l\rangle$) at most 14 electrons, and so on (Figure 8.2).[2]

For an atom in the ground state, the *electrons fill the orbitals in order of increasing energy*; once a subshell is filled, the next electron goes into the vacant subshell whose energy is just above the previous subshell. When all orbitals in a major electronic shell are filled up, we get a *closed shell*; the next electron goes into the next major shell, and so on. By filling the atomic orbitals one after the other in order of increasing energy, one obtains all the elements of the periodic table (Table 8.1).

Elements $1 \le Z \le 18$

As shown in Table 8.1, the first period (or first horizontal row) of the periodic table has two elements, hydrogen H and helium He; the second period has 8 elements, lithium Li to neon Ne; the third period also has 8 elements, sodium Na to argon Ar; and so on. The orbitals of the 18 lightest elements, $1 \le Z \le 18$, are filled in order of increasing energy according to the sequence: 1s, 2s, 2p, 3s, 3p. The electronic state of an atom is determined by specifying the occupied orbitals or by what is called the *electronic configuration.* For example, hydrogen has one electron, its ground state configuration is $(1\text{s})^1$; helium He has two electrons: $(1\text{s})^2$; lithium Li has three electrons: $(1\text{s})^2(2\text{s})^1$; beryllium Be has four: $(1\text{s})^2(2\text{s})^2$, and so on.

Let us now say few words about how to determine the total angular momentum of an atom. For this, we need to calculate the total orbital angular momentum $\vec{L} = \sum_{i=1}^{Z} \vec{l}_i$, the total spin $\vec{S} = \sum_{i=1}^{Z} \vec{s}_i$, and then obtain total angular momentum by coupling $\vec{L}$ and $\vec{S}$, i.e., $\vec{J} = \vec{L} + \vec{S}$, where $\vec{l}_i$ and $\vec{s}_i$ are the orbital and spin angular momenta of individual electrons. As will be seen in Chapter 9, when the spin–orbit coupling is considered, the degeneracy of the atom's energy levels is partially lifted, introducing a splitting of the levels. The four numbers L, S, J and M are good quantum numbers, where $|L - S| \le J \le L + S$ and $-J \le M \le J$. So there are $2S + 1$ values of J when $L \ge S$ and $2L + 1$ values when $L < S$. Since the energy depends on J, the levels corresponding to an L and S split into $(2S + 1)$-multiplet. The issue now is to determine which one of these states has the lowest energy. Before studying this issue, let us introduce the spectroscopic notation according to which the state of an atom is labelled by ${}^{2S+1}L_J$ where, as before, the numbers $L = 0, 1, 2, 3, \ldots$ are designated by S, P, D, F, ... For example, since the total angular momentum of a beryllium atom is zero $J = 0$, because $L = 0$ (all electrons are in s-states, $l_i = 0$) and $S = 0$ (both electrons in the $(1\text{s})^2$ state are paired and so are the two electrons in the $(2\text{s})^2$ state), the ground state of beryllium can be written as ${}^1\text{S}_0$. This applies actually to all other closed shell atoms such as helium He, neon Ne, argon Ar, and so on; their ground states are all specified by ${}^1\text{S}_0$ (Table 8.1).

Let us now consider boron B: the closed shells 1s and 2s have $L = S = J = 0$. Thus the angular momentum of boron is determined by the 1p electron which has $S = 1/2$ and $L = 1$. A coupling of $S = 1/2$ and $L = 1$ yields $J = 1/2$ or $3/2$ leading therefore to two possible states:

$$ {}^2\text{P}_{1/2}, \qquad \text{or} \qquad {}^2\text{P}_{3/2}. \tag{8.69} $$

Which one has a lower energy?

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[2] R. Serway, C. J. Moses, and C. A. Moyer, *Modern Physics*, Saunders College Publishing, New York, 1989, p.238.

Table 8.1 Ground state electron configurations, spectroscopic description, and ionization energies for the first four rows of the Periodic Table. The brackets designate closed-shell elements.

Shell	Z	Element	Ground state configuration	Spectroscopic desctiption	Ionization energy (eV)
1	1	H	$(1s)^1$	$^2S_{1/2}$	13.60
	2	He	$(1s)^2$	$^1S_0$	24.58
2	3	Li	$[He](2s)^1 = (1s)^2(2s)^1$	$^2S_{1/2}$	5.39
	4	Be	$[He](2s)^2$	$^1S_0$	9.32
	5	B	$[He](2s)^2(2p)^1$	$^2P_{1/2}$	8.30
	6	C	$[He](2s)^2(2p)^2$	$^3P_0$	11.26
	7	N	$[He](2s)^2(2p)^3$	$^4S_{3/2}$	14.55
	8	O	$[He](2s)^2(2p)^4$	$^3P_2$	13.61
	9	F	$[He](2s)^2(2p)^5$	$^2P_{3/2}$	17.42
	10	Ne	$[He](2s)^2(2p)^6$	$^1S_0$	21.56
3	11	Na	$[Ne](3s)^1$	$^2S_{1/2}$	5.14
	12	Mg	$[Ne](3s)^2$	$^1S_0$	7.64
	13	Al	$[Ne](3s)^2(3p)^1$	$^2P_{1/2}$	5.94
	14	Si	$[Ne](3s)^2(3p)^2$	$^3P_0$	8.15
	15	P	$[Ne](3s)^2(3p)^3$	$^4S_{3/2}$	10.48
	16	S	$[Ne](3s)^2(3p)^4$	$^3P_2$	10.36
	17	Cl	$[Ne](3s)^2(3p)^5$	$^2P_{3/2}$	13.01
	18	Ar	$[Ne](3s)^2(3p)^6$	$^1S_0$	15.76
4	19	K	$[Ar](4s)^1$	$^2S_{1/2}$	4.34
	20	Ca	$[Ar](4s)^2$	$^1S_0$	6.11
	21	Sc	$[Ar](3d)^1(4s)^2$	$^2D_{3/2}$	6.54
	22	Ti	$[Ar](3d)^2(4s)^2$	$^3F_2$	6.83
	23	V	$[Ar](3d)^3(4s)^2$	$^4F_{3/2}$	6.74
	24	Cr	$[Ar](3d)^4(4s)^2$	$^7S_3$	6.76
	25	Mn	$[Ar](3d)^5(4s)^2$	$^6S_{3/2}$	7.43
	26	Fe	$[Ar](3d)^6(4s)^2$	$^5D_4$	7.87
	27	Co	$[Ar](3d)^7(4s)^2$	$^4F_{9/2}$	7.86
	28	Ni	$[Ar](3d)^8(4s)^2$	$^3F_4$	7.63
	29	Cu	$[Ar](3d)^{10}(4s)^1$	$^2S_{1/2}$	7.72
	30	Zn	$[Ar](3d)^{10}(4s)^2$	$^1S_0$	9.39
	31	Ga	$[Ar](3d)^{10}(4s)^2(4p)^1$	$^2P_{1/2}$	6.00
	32	Ge	$[Ar](3d)^{10}(4s)^2(4p)^2$	$^3P_0$	7.88
	33	As	$[Ar](3d)^{10}(4s)^2(4p)^3$	$^4S_{3/2}$	9.81
	34	Se	$[Ar](3d)^{10}(4s)^2(4p)^4$	$^3P_2$	9.75
	35	Br	$[Ar](3d)^{10}(4s)^2(4p)^5$	$^2P_{3/2}$	11.84
	36	Kr	$[Ar](3d)^{10}(4s)^2(4p)^6$	$^1S_0$	9.81

Consider another example, the carbon atom. Its ground state configuration $(1s)^2(2s)^2(2p)^2$ implies that its total angular momentum is determined by the two 2p electrons. The coupling of the two spins $s = 1/2$, as shown in equations (7.174) to (7.177), yields two values for their total spin $S = 0$ or $S = 1$; and, as shown in Problem 7.3 page 418, a coupling of two individual orbital angular momenta $l = 1$ yields three values for the total angular momenta $L = 0$, 1, or 2. But the exclusion principle dictates that the total wave function has to be antisymmetric, i.e., the spin and orbital parts of the wave function must have opposite symmetries. Since the singlet spin state $S = 0$ is antisymmetric, the spin triplet $S = 1$ is symmetric, the orbital triplet $L = 1$ is antisymmetric, the orbital quintuplet $L = 2$ is symmetric, and the orbital singlet $L = 0$ is symmetric, the following states are antisymmetric

$$ {}^1\text{S}_0, \qquad {}^3\text{P}_0, \qquad {}^3\text{P}_1, \qquad {}^3\text{P}_2, \qquad \text{or} \qquad {}^1\text{D}_2, \tag{8.70}$$

hence any one of these states can be the ground state of carbon. Again, which one of them has the lowest energy?

To answer this question and the question pertaining to (8.69), we may invoke *Hund's rules*: (a) The lowest energy level corresponds to the state with the largest spin S (i.e., the maximum number of electrons have unpaired spins), (b) Among the states with a given value of S, the lowest energy level corresponds to the state with the largest value of L, (c) For a subshell that is less than half full the the lowest energy state corresponds to $J = |L - S|$, and for a subshell that is more than half full the lowest energy state corresponds to $J = L + S$.

Hund's third rule answers the question pertaining to (8.69): since the 2p shell of boron is less than half full, the value of J corresponding to the lowest energy is given by $J = |L - S| = 1 - 1/2 = 1/2$, hence ${}^2\text{P}_{1/2}$ is the lower energy state.

To find which one of the states (8.70) has the lowest energy, Hund's first rule dictates that $S = 1$. Since the triplet $S = 1$ is symmetric, we need an antisymmetric spatial wave function; this is given by the spatial triplet $L = 1$. We are thus left with three possible choices: $J = 0$, 1, or 2. Hund's third rule precludes the values $J = 1$ and 2: since the 2p shell of carbon is less than half full, the value of J corresponding to the lowest energy is given by $J = |L - S| = 1 - 1 = 0$, hence ${}^3\text{P}_0$ is the lower energy state (Table 8.1). That is, the two electrons are in different spatial states or different orbitals (Figure 8.2). Actually, we could have guessed this result: since the Coulomb repulsion between the two electrons when they are paired together is much larger than when they are unpaired, the lower energy configuration corresponds to the case where the electrons are in different spatial states. The ground state configurations of the remaining elements, oxygen to argon, can be inferred in a similar way (Table 8.1).

Elements $Z \geq 18$

When the 3p shell is filled, one would expect to place the next electron in a 3d shell. But this doesn't take place due to the occurrence of an interesting effect: the 4s states have lower energy than the 3d states. Why? In a hydrogen atom the states 3s, 3p and 3d have the same energy ($E_3^{(0)} = -\mathcal{R}/3^2 = -1.51\,\text{eV}$, since $\mathcal{R} = 13.6\,\text{eV}$). But in multi-electron atoms, these states have different energy values. As l increases, the effective repulsive potential $\hbar^2 l(l+1)/2mr^2$ causes the d-state electrons to be thrown outward and the s-state electrons to remain closer to the nucleus. Being closer to the nucleus, the s-state electrons therefore feel the full attraction of the nucleus, whereas the d-state electrons experience a much weaker attraction. This is known as the *screening effect*, because the inner electrons, i.e., the s-state electrons, screen the nucleus, hence the outward electrons (the d-state electrons) do not experience the full attraction of the nucleus; they instead feel a weak effective potential. As a result, the energy of the 3d-state is larger than that of the 4s-state. The screening effect also causes the energy of the 5s-state to have a lower energy than the 4d-state, and so on. So for a given n, the energies E_{nl} increase as l increases; in fact, neglecting the spin–orbit interaction and considering relativistic corrections we will show in Chapter 9 (9.87) that the ground state energy depends on the principal and orbital quantum numbers n and l as $E_{nl}^{(0)} = Z^2 E_n^{(0)}\{1 + \alpha^2 Z^2[2/(2l+1) - 3/4n]/n\}$, where $\alpha = 1/137$ is the fine structure constant and $E_n^{(0)} = -\mathcal{R}/n^2 = -13.6\,\text{eV}/\text{n}^2$.

In conclusion, the periodic table can be obtained by filling the orbitals in order of increasing energy E_{nl} as follows (Table 8.1):

$$\boxed{1\text{s},\ 2\text{s},\ 2\text{p},\ 3\text{s},\ 3\text{p},\ 4\text{s},\ 3\text{d},\ 4\text{p},\ 5\text{s},\ 4\text{d},\ 5\text{p},\ 6\text{s},\ 4\text{f},\ 5\text{d},\ 6\text{p},\ 7\text{s},\ldots.} \qquad (8.71)$$

Remarks

The chemical properties of an element is mostly determined by the outermost shell. Hence elements with similar electron configurations of the outside shell have similar chemical properties. This is the idea behind the structure of the periodic table: it is arranged in a way that all elements in a column have similar chemical properties. For example the elements in the last column, helium, neon, argon, krypton, and so on, have the outer p-shell completely filled (except for helium whose outside shell is 1s). These atoms, which are formed when a shell or a subshell is filled, are very stable, interact very weakly with one another, and do not combine with other elements to form molecules or new compounds; that is, they are chemically inert. They are very reluctant to give up or to accept an electron. Due to these properties, they are called *noble gases*. They have a very low boiling point (around −200° C); note that each row of the periodic table corresponds to filling out a shell or subshell of the atom. There is a significant energy gap before the next level is encountered after each of these elements; as shown in Table 8.1, a large energy is required to ionize these elements; for instance, 24.58 eV is needed to ionize a helium atom.

Atoms consisting of a closed shell (or a rare gas configuration) plus an s-electron (or a valence electron), such as Li, Na, K, and so on, have the lowest binding energy; these elements are known as the alkali metals. In elements consisting of an alkali atom plus an electron, the second s-electron is more bound than the valence electron of the alkali atom because of the higher nuclear charge. As the p-shell is gradually filled (beyond the noble gas configuration), the binding energy increases initially (as in boron, carbon and nitrogen) till the fourth electron, then it begins to drop (Table 8.1). This is due to the fact that when the p-shell is less than half full all spins are parallel, hence all three spatial wave functions are antisymmetric. With the fourth electron (as in oxygen), two spins will be antiparallel or paired, hence the spatial wave function is not totally antisymmetric causing a drop in the energy. Note that elements with one electron more than or one electron less than noble gas configurations are the most active chemically, because they tend to easily give up or easily accept one electron.

Example 8.4

(a) Specify the total angular momenta corresponding to ^{4}G, ^{3}H and ^{1}D.

(b) Find the spectroscopic notation for the ground state configurations of aluminum Al ($Z = 13$) and scandium Sc ($Z = 21$).

Solution

(a) For the term ^{4}G the orbital angular momentum is $L = 4$ and the spin is $S = 3/2$, since $2S + 1 = 4$. The values of the total angular momentum corresponding to the coupling of $L = 4$ and $S = 3/2$ are given by $|4 - 3/2| \le J \le 4 + 3/2$. Hence we have $J = 5/2, 7/2, 9/2, 11/2$.

3. Quantum mechanics in postulational form

We are now prepared to present the basic postulates of quantum mechanics.

Complementarity postulates

Postulate I. The state of a physical system is represented by a vector (ket) in a linear vector space of infinitely many dimensions.

We shall make the following explanatory remarks:

(1) In view of the uncertainty relation, it is not possible to define, as in classical dynamics, the state of a system by specifying the coordinates and momenta of the particles at any given instant of time.

(2) A vector (ket) is to represent a state to allow the superposition of states. By hypothesis only the direction (not the *sense* such as the "arrow"), but not its length, defines a state. Thus multiplying a ket by any constant does not lead to a different state.

(3) The vector space of infinitely many dimensions is an abstract space, and not the configuration space nor the momentum space of the particles of a system.

(4) The changes of the state of a system are represented by changes in the ket. The Newtonian equations of motion are replaced by an equation for the change of the ket of a system.

Postulate II. All physical quantities ("observables") are represented by linear hermitian operators, which, acting on the state vector (ket), change the state of a system.

(1) Linearity is assumed for a linear theory in the state vectors to allow for superposition of state vectors.

(2) Hermitian operators are employed because hermitian operators have real eigenvalues. Real eigenvalues are needed on account of another basic postulate which connects the mathematical formalism (this and the preceding

postulate) with *physics*—the result of physical observations (see Probability Postulate in the following).

(3) The choice of the eigenvectors of an observable as the basis set of vectors immediately leads to the concepts of representations and transformation of representations. The requirement of invariance of the hermitian charactor of operators leads to unitary transformations.

(4) The transformation theory and the Probability Postulate (see IV below) build up Quantum Mechanics into a coherent system.

Postulate III. The hermitian operators for the coordinate q and the conjugate momentum (in the sense of classical dynamics) obey the commutation relation

$$pq - qp = \frac{\hbar}{i} 1. \tag{V-99}$$

(1) This relation, containing the Planck constant h, causes the system of quantum mechanics to have a fundamental break with classical physics.

(2) Together with the Probability Postulate (that connects the above mathematical formalism with physics), it leads to the uncertainty relation.

(3) In this sense, it may be regarded as the mathematical expression of the Einstein-de Broglie relations.

(4) It is a mathematical expression of the concept of complementarity.

(5) The commutation relation (V-99) may be taken to be a basic principle in quantum mechanics. The postulates I and II have been made for the construction of a mathematical system to cope with the non-classical commutation relation.

The above three postulates are essentially of a mathematical nature and have no real contact with the results of physical measurements. This contact is provided by the Probability Postulate.

Postulate IV. When a measurement is made of a physical quantity (represented by the hermitian operator Q) on a system in a state represented by a vector $|a\rangle$, the expectation value is given by

$$\langle Q \rangle = \langle a|Q|a\rangle, \tag{V-100}$$

(1) This postulate contains the main physical contents of the theory; for it makes theoretical statements of the result of experimental measurements.

(2) If $|a\rangle$ is an eigenstate of Q, say $|a\rangle = |q_k\rangle$, then the expectation value of the measurement is

$$\begin{aligned}\langle Q\rangle &= \langle q_k|Q|q_k\rangle = q_k\langle q_k|q_k\rangle \\ &= q_k, \end{aligned} \tag{V-101}$$

i.e., in this case, the measurement will definitely yield, with certainty, the eigenvalue q_k of Q.

(3) If $|a\rangle$ in (V-100) is an arbitrary state, it can be expanded in the complete set of eigenkets of Q,

$$|a\rangle = \sum_k\!\!\!\!\!\int |q_k\rangle\langle q_k|a\rangle \tag{V-102}$$

and

$$\langle a| = \sum_k\!\!\!\!\!\int \langle a|q_k\rangle\langle q_k|$$

and

$$\langle Q\rangle = \sum_k\!\!\!\!\!\int |\langle a|q_k\rangle|^2 q_k. \tag{V-103}$$

This states that the result of measurement is not a definite one of the eigenvalues, not an in-between value of the q_k's, but *one* of all the q_k's each of which may come out with a probability $|\langle a|q_k\rangle|^2$. The probabilities themselves are definite enough, as they are given by (V-103) but the theory does not tell which *one* of the q_k's will *actually* come out from the measurement.

(4) It is most important to note that the nature of this probability distribution

$$|\langle a|q_k\rangle|^2, \text{ for various } k,$$

is basically different from that in classical statistical physics. In the latter, probability is introduced, when dealing with an extremely large number of molecules, as a substitute for the exact knowledge which exits in principle. In quantum mechanics, even for one atom, a precise knowledge does *not* exist and probability is of an intrinsic nature.

For this reason, quantum mechanics differs from classical physics in a basic way.

(5) Then one may ask why such a probability concept is necessary. For one thing, since two non-commuting operators do not have simultaneous eigenkets, this probability postulate (employed in the derivation of the uncertainty relation) forms at least a *consistent* theory from the point of view of the *anschaulich* thought-experiments in Heisenberg's demonstration of the uncertainty relation on the Einstein-de Broglie relations.

(6) A much deeper and more difficult question is whether it is possible to assume the existence of "hidden variables" and the probability concept arises as the result of a sort of averaging over those hidden variables.[m] If this is the case, the probability will not be "intrinsic" but has the same classical meaning.

From the experimental point of view, when measurements are made, not on one atom, but on a large number of atoms, it is not possible to distinguish between the two kinds of probabilities. The question is a philosophical one—one concerning the nature of quantum mechanics. The concept of an intrinsic probability is repugnant to some philosophers of science; the most prominent ones have been Einstein, Planck and de Broglie. The question has been studied by von Neumann and the answer seems to be that an interpretation of probability in terms of hidden variables is inconsistent in the present system of quantum mechanics. We shall not go into this deep question, but refer to a review of critical studies by Belinfante.

The four postulates above have not included considerations regarding of the change of a system in time. For this, a separate postulate is furnished by the Schrödinger equation:

Postulate V. The change of the state of a physical system in time is governed by the equation

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}|a,t\rangle = H|a,t\rangle,$$

or

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial t} + H(q,p,t)\right)\Psi(q,t) = 0, \qquad \text{(V-104)}$$

where $\Psi(q,t)$ is the representative $\langle q,t|a,t\rangle$ of $|a,t\rangle$ in the q-representation.

(1) This equation is an independent postulate, unlike the Schrödinger equation for momentum, (V-64)

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial q} - p\right)\psi_p(q) = 0,$$

which can be derived from the commutation relation $pq - qp = \hbar/i$ on the transformation theory.

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[m] In the classical kinetic theory of gases, the "hidden variables" are the coordinates and momenta of the individual molecules. With these variables, the dynamical theory is a deterministic one; but on averaging over, and therefore suppressing, these variables, the theory works with probable values.

(2) In classical dynamics, the time variable t and the energy (Hamiltonian) H formally behave as a pair of canonical conjugate variables $(t, -H)$. It might then be thought that, analogously to (q, p), a commutation relation

$$Ht - tH = -\frac{\hbar}{i}1 \tag{V-105}$$

exists, and if so, then one may have a time representation in which the hermitian operators are:

$$t, \qquad H = -\frac{\hbar}{i}\frac{\partial}{\partial t}, \tag{V-106}$$

and an energy representation in which the hermitian operators are

$$H, \qquad t = \frac{\hbar}{i}\frac{\partial}{\partial E}. \tag{V-107}$$

But if two hermitian operators H and t exist that satisfy the commutation relation (V-105), it can be proved that, if E_a, ψ_a are the eigenvalue and eigenvector of H

$$H\psi_a = E_a\psi_a,$$

then

$$H(e^{i\varepsilon t/\hbar}\psi_a) = (E_a - \varepsilon)(e^{i\varepsilon t/\hbar}\psi_a), \tag{V-108}$$

i.e., $E_a - \varepsilon$ is the eigenvalue of H, for arbitrary, real value of ε, with the eigenvector $e^{i\varepsilon t/\hbar}\psi_a$.[n] As ε is real and arbitrary, it follows that H has a continuous spectrum of eigenvalues extending from $-\infty$ to $+\infty$. But this is not true of systems in general; in fact negative infinite total energy is unphysical. Also systems exist whose energy spectrum is not continuous.

Thus no hermitian operator t exists which satisfies a commutation relation like (V-105).[o] For this reason, it is not possible to derive the relations (V-106), (V-107) from a relation like (V-105).

The Schrödinger equation (V-104) must then be based on a different line of arguments.

In Sec. 2, (V-98), it is seen that

$$i\hbar\frac{d}{dt} = \text{a hermitian operator.}$$

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[n] See Prob. 7 at the end of Chap. 2, Sec. 2. Also (V-91a).

[o] This was pointed out by W. Pauli in his article in *Handbuch der Physik*, Bd. 24, 2nd ed. (Springer-Verlag, Heidelberg, 1933).

Hence it is reasonable to *postulate* (V-106)[p]

$$H = -\frac{\hbar}{i}\frac{\partial}{\partial t} \tag{V-109}$$

and hence the Schrödinger equation (V-104).

(3) The Schrödinger equation (V-104)

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial t} + H\right)\Psi(q, t) = 0$$

is a first-order differential equation in t, but second-order with respect to x, y, z. Thus its form is not Lorentz covariant. Attempts to have a relativistic wave equation have been made.[q] These are the Klein-Gordan equation and the Dirac equation.

(4) An argument for an equation which is of the first order in $\partial/\partial t$ is as follows. From the normalization

$$\int \Psi^*(q, t)\Psi(q, t)\,dq = 1,$$

one has

$$\int \left(\Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi\right) dq = 0. \tag{V-110}$$

To solve an initial value problem of an equation of first order in $\partial/\partial t$, one has to specify Ψ at $t = t_0$. For a second order in $\partial/\partial t$, it is necessary to specify Ψ and $\partial\Psi/\partial t$ at $t = t_0$, but (V-110) does not allow arbitrary Ψ and $\partial\Psi/\partial t$.

(5) The Schrödinger equation (V-104) determines $\Psi(q, t)$ in the course of time completely deterministically, and hence the probability $|\Psi(q, t)|^2$, but only the *probability* distribution, and not the actual outcome of an experiment! One may say that quantum mechanics is a "causal theory of probabilities".

(6) There are "constants of motion" of the Schrödinger equation. For example, take a system with central symmetry, i.e., the Hamiltonian H is invariant under parity operation (inversion with respect to a center, see Chap. 3, Sec. 4, (3), (III-115)–(III-120)) If at an instant t_0 the parity of the state of the system is *even*, the parity will remain *even* in time, if the system is not perturbed by external fields, such as electromognetic fields.

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[p] This is the view of Dirac in *The Principles of Quantum Mechanics*, Sec. 27, 4th Ed. (Clarendon Press, Oxford, 1958).

[q] See references to Schrödinger, Klein, Gordon, de Broglie and Fock at the end of Sec. 3 of Chap. 3.

As another example, take an atom with two electrons, such as helium, whose Hamiltonian is symmetric with respect to the interchange of the two electrons. The space part (i.e., without the spins) of the wave function of the two electrons may be symmetric or antisymmetric with respect to this interchange, (although the total wave function including both the space and the spin parts must be antisymmetric, according to Pauli's principle, which constitutes another independent postulate). If at one instant the state is symmetric, this symmetry will remain unchanged in time when the state changes in accordance with the Schrödinger equation, provided the system is not perturbed by external fields affecting the electron spins.

Such "constants of motions" are essentially the consequence of the symmetry properties of the system.

(7) For systems whose Hamiltonian H is not explicitly a function of time, then the assumption of the form

$$\Psi(q,t) = \psi_n(q)\exp\left(-\frac{iE_n t}{\hbar}\right) \tag{V-111}$$

leads to the time-independent Schrödinger equation

$$(H(q,p) - E_n)\psi_n(q) = 0. \tag{V-112}$$

We have seen a few examples of this equation in Chap. 3.

In subsection (6) above, we mentioned that for a system containing identical particles, there is the question of the symmetry of the state vector, or its representative $\psi(q_1, q_2, q_3, \ldots)$ in coordinate representation. This question arises as follows: Take a system containing two identical particles (for example, electrons), and let us denote them simply by the indices 1 and 2. The Schrödinger equation is

$$(H(1,2) - E)\psi(1,2) = 0.$$

Let P be the operator interchanging the two identical particles. Hence in general

$$P^2\psi(1,2) = \psi(1,2),$$

so that the eigenvalue of P^2 is 1, and those of P are ± 1, and corresponding to them, the function $\psi(1,2)$ is either symmetric with respect to P, i.e.,

$$P\psi_s(1,2) = \psi_s(1,2),$$

or antisymmetric, i.e.,

$$P\psi_a(1,2) = -\psi_a(1,2).$$

Both ψ_s, ψ_a are solutions of the Schrödinger equation because

$$PH(1,2) = H(2,1) = H(1,2).$$

The question is: Does nature allow both kinds of solutions?

The answer to this question came, paradoxically, before the question was asked, i.e., before quantum mechanics was born. For the electrons in atoms, Pauli postulated, the exclusion principle early in 1925. The connection with the symmetry of the wave function was first given by Dirac (1926). This principle can now be stated as follows.

Postulate VI. For a system of identical particles of *half-odd-integral* spin (such as electrons, muons, protons, neutrons), the wave function is *antisymmetric* with respect to the interchange of two particles. For identical particles of *integral spin* (such as pions, deuterons, α-particles), the ψ is *symmetric* with respect to the interchange of two particles.

This principle (including the Pauli principle) really, so to speak, does not belong to the group of postulates that form the system of quantum mechanics. It is directly related to the statistics—the Fermi-Dirac and the Bose-Einstein statistics. The relationship among the symmetry, the spin and the statistics is regarded as a profound law of nature.