

Dr. M.H. Shahnas

Quantum Mechanics-II

Useful Book : Quantum Mechanics
Stephen Gasiorowicz

Chapter 8

N-Particle System

$$\Psi(x_1, x_2, \dots, x_N)$$

$$\int \dots \int dx_1 dx_2 \dots dx_N |\Psi(x_1, x_2, \dots, x_N)|^2 = 1 \quad (1)$$

$|\Psi(x_1, x_2, \dots, x_N)|^2$: The probability density for finding particle 1 at x_1, \dots , particle N at x_N .

$$i\hbar \frac{\partial}{\partial t} \Psi(x_1, \dots, x_N, t) = H \Psi(x_1, \dots, x_N, t) \quad (2)$$

where $H = \sum_{i=1}^N \frac{p_i^2}{2m_i} + V(x_1, x_2, \dots, x_N) \quad (3)$

$$H = -\hbar^2 \left(\frac{1}{2m_1} \frac{\partial^2}{\partial x_1^2} + \dots + \frac{1}{2m_N} \frac{\partial^2}{\partial x_N^2} \right) + V(x_1, \dots, x_N) \quad (4)$$

$$[p_i, x_j] = \frac{\hbar}{i} \delta_{ij} \quad (5) \quad i, j: \text{particle indices}$$

If External fields = 0 (like E, B, Φ, \dots)

$$\rightarrow V = V(x_1 - x_2, x_1 - x_3, \dots, x_{N-1} - x_N) \quad (6)$$

relative coords.

(Relative distances)
Not absolute distances
measured from an origin.

External Field = 0

(No origin is determined)



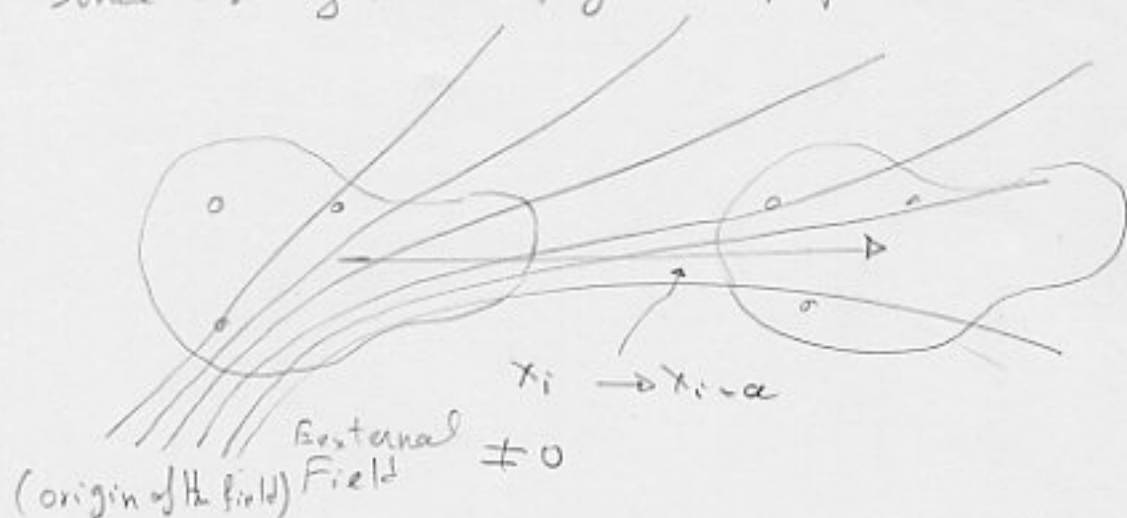
No change in the physical properties

$$x_i \xrightarrow{tr} x_i + a$$

(7)

Because in the absence of any external agency, the displacement of the whole system should not change any physical properties of the system (Physical quantities invariance under $x_i \xrightarrow{tr} x_i + a$)

But if there exists an external field, there may occur some changes in the physical properties.

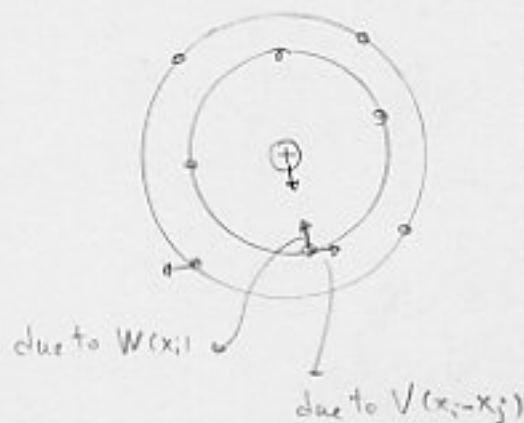


For two-body forces;

$$V = \sum_{i>j} V(x_i - x_j) \quad (8)$$

In atom;

$$V = \sum_{i=1}^N W(x_i) + \sum_{i>j} V(x_i - x_j) \quad (9)$$



In classical mechanics:

$$\text{If } \vec{F}_{\text{external}} = 0 \quad \rightarrow \quad P = \text{const.} \quad (10)$$

$$\text{Because: } m_i \frac{d^2 x_i}{dt^2} = - \frac{\partial}{\partial x_i} V(x_1, x_2, \dots, x_{N-1}, x_N) \quad (11)$$

$$\rightarrow \frac{d}{dt} \sum_i m_i \frac{dx_i}{dt} = - \sum_i \frac{\partial}{\partial x_i} V(x_1, x_2, \dots, x_{N-1}, x_N) \quad (12)$$

$$\text{But } \sum_i \frac{\partial}{\partial x_i} V(x_1, x_2, \dots, x_{N-1}, x_N) = 0 \quad (13)$$

Because for example, if $V = a(x_1 - x_2)^n$

$$\text{then } \frac{\partial}{\partial x_1} V = - \frac{\partial}{\partial x_2} V \text{ and so, ...}$$

$$\rightarrow P = \sum_i m_i \frac{dx_i}{dt} = \text{const.} \quad (14)$$

In Q.M. the same conclusion holds. We shall demonstrate it by using the invariance of H under the tr. (7).

$$H U_E(x_1, x_2, \dots, x_N) = E U_E(x_1, x_2, \dots, x_N) \quad (15)$$

In the absence of any external field;

$$H U_E(x_1+a, x_2+a, \dots, x_N+a) = E U_E(x_1+a, x_2+a, \dots, x_N+a) \quad (16)$$

Now let $a = \text{infinitesimal}$

$$\begin{aligned}
 U(x_1+a, x_2+a, \dots, x_N+a) &\approx U(x_1, \dots, x_N) + a \frac{\partial}{\partial x_1} U(x_1, \dots, x_N) + \\
 &+ a \frac{\partial}{\partial x_2} U(x_1, \dots, x_N) + \dots \approx U(x_1, \dots, x_N) + a \sum_i \frac{\partial}{\partial x_i} U(x_1, \dots, x_N)
 \end{aligned}
 \quad (17)$$

Subtracting (15) from (16);

$$\begin{aligned}
 a H \left(\sum_{i=1}^N \frac{\partial}{\partial x_i} \right) U_E(x_1, \dots, x_N) &= a E \left(\sum_{i=1}^N \frac{\partial}{\partial x_i} \right) U_E(x_1, \dots, x_N) \\
 &= a \left(\sum_{i=1}^N \frac{\partial}{\partial x_i} \right) E U_E(x_1, \dots, x_N) = a \left(\sum_{i=1}^N \frac{\partial}{\partial x_i} \right) H U_E(x_1, \dots, x_N)
 \end{aligned}
 \quad (18)$$

Define $P = \frac{\hbar}{i} \sum_{i=1}^N \frac{\partial}{\partial x_i} \equiv \sum_{i=1}^N P_i$ (19)

$$\rightarrow (HP - PH) U_E(x_1, \dots, x_N) = 0 \quad (20)$$

Since $\{U_E(x_1, \dots, x_N)\}$: complete set

$$(20) \rightarrow (HP - PH) \psi(x_1, \dots, x_N) = 0 \quad \forall \psi \quad (21)$$

$$\rightarrow (HP - PH) = 0 \quad \rightarrow [H, P] = 0 \quad (22)$$

Note that;

$$e^{+iHt/\hbar} [H, P] e^{-iHt/\hbar} = 0 \quad \rightarrow [H, P(t)] = 0 \quad (23)$$

$$\frac{dP(t)}{dt} = \frac{i}{\hbar} [H, P(t)] = 0 \quad \rightarrow \frac{dP(t)}{dt} = 0 \quad (24)$$

P : const. of motion

Two-particle system:

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} \quad \text{for two noninteracting particles} \quad (25)$$

$P(x_1, x_2) = P(x_1) P(x_2)$: The probability of one at x_1 and the other at x_2 (26)

↓
independent probabilities

$$\left(-\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} \right) \psi(x_1, x_2) = E \psi(x_1, x_2) \quad (27)$$

$$\psi(x_1, x_2) = \varphi_1(x_1) \varphi_2(x_2) \quad \text{(we expect)} \quad (28)$$

from (26)

$$(28) \xrightarrow{\text{in}} (27) \rightarrow \underbrace{-\left(\frac{\hbar^2}{2m_1}\right) \left(\frac{d^2 \varphi_1(x_1)}{dx_1^2}\right)}_{\varphi_1(x_1)} + \underbrace{-\left(\frac{\hbar^2}{2m_2}\right) \left(\frac{d^2 \varphi_2(x_2)}{dx_2^2}\right)}_{\varphi_2(x_2)} = E \psi \quad (29)$$

indep

$$\rightarrow E = E_1 + E_2 \quad (30)$$

$$\rightarrow \begin{cases} -\frac{\hbar^2}{2m_1} \frac{d^2 \varphi_1(x_1)}{dx_1^2} = E_1 \varphi_1(x_1) \\ -\frac{\hbar^2}{2m_2} \frac{d^2 \varphi_2(x_2)}{dx_2^2} = E_2 \varphi_2(x_2) \end{cases} \quad (31)$$

$$\rightarrow \varphi_1(x_1) \sim e^{ik_1 x_1} \quad \varphi_2(x_2) \sim e^{ik_2 x_2} \quad (32)$$

$$\psi(x_1, x_2) = C e^{i(k_1 x_1 + k_2 x_2)} \quad (33)$$

$$\text{when } k_1^2 = \frac{2m_1 E_1}{\hbar^2} \quad k_2^2 = \frac{2m_2 E_2}{\hbar^2} \quad (34)$$

In the presence of $V = V(x_1, -x_2)$;

$$(25) \quad \text{changes} \rightarrow \left(-\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} \right) \psi(x_1, x_2) + V(x_1, -x_2) \psi(x_1, x_2) = E \psi(x_1, x_2) \quad (4.3)$$

$$\text{Using} \quad \begin{cases} u = x_1, -x_2 \\ X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} = \frac{\mu}{m_2} x_1 + \frac{\mu}{m_1} x_2 \end{cases} \quad (4.4)$$

$$\rightarrow \begin{cases} x_1 = X + \frac{\mu}{m_1} u \\ x_2 = X - \frac{\mu}{m_2} u \end{cases} \quad (4.5)$$

$$\rightarrow \left(-\frac{\hbar^2}{2(m_1+m_2)} \frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial u^2} + V(X) \right) \psi(u, X) = E \psi(u, X) \quad (4.6)$$

where we have used;

$$\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial u} \frac{\partial u}{\partial x_1} + \frac{\partial \psi}{\partial X} \frac{\partial X}{\partial x_1} = \frac{\partial \psi}{\partial u} (1) + \frac{\partial \psi}{\partial X} \frac{\mu}{m_2} \quad (4.7)$$

$$\begin{aligned} \frac{\partial^2 \psi}{\partial x_1^2} &= \frac{\partial}{\partial x_1} \left[\frac{\partial \psi}{\partial u} + \frac{\partial \psi}{\partial X} \frac{\mu}{m_2} \right] = \frac{\partial}{\partial x_1} \left[\frac{\partial \psi}{\partial u} + \frac{\partial \psi}{\partial X} \frac{\mu}{m_2} \right] \frac{\partial u}{\partial x_1} + \\ &+ \frac{\partial}{\partial x_1} \left[\frac{\partial \psi}{\partial u} + \frac{\partial \psi}{\partial X} \frac{\mu}{m_2} \right] \frac{\partial X}{\partial x_1} = \frac{\partial^2 \psi}{\partial u^2} + \frac{\mu}{m_2} \frac{\partial^2 \psi}{\partial u \partial X} + \frac{\partial^2 \psi}{\partial X \partial u} \frac{\mu}{m_2} \\ &+ \left(\frac{\mu}{m_2} \right)^2 \frac{\partial^2 \psi}{\partial X^2} = \frac{\partial^2 \psi}{\partial u^2} + \left(\frac{\mu}{m_2} \right)^2 \frac{\partial^2 \psi}{\partial X^2} + \frac{2\mu}{m_2} \frac{\partial^2 \psi}{\partial u \partial X} \end{aligned} \quad (4.8)$$

$$\text{Similarly, } \frac{\partial^2 \psi}{\partial x_2^2} = \frac{\partial^2 \psi}{\partial u^2} + \left(\frac{\mu}{m_1} \right)^2 \frac{\partial^2 \psi}{\partial X^2} - \frac{2\mu}{m_1} \frac{\partial^2 \psi}{\partial u \partial X}$$

$$\psi(u, X) = e^{iKX} \Phi(u) \quad (4.9)$$

Remark: Note that $\Phi(u)$ is different from e^{iKu} because of $V(u)$.

$$\rightarrow -\frac{\hbar^2}{2\mu} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) = E \Psi(x) \quad \left(\begin{array}{l} \text{one-particle Schrödinger} \\ \text{equ. with reduced mass } \mu \end{array} \right) \quad (50)$$

$$E = E - \frac{\hbar^2 k^2}{2M} \quad (51)$$

Identical Particles:

The electrons are indistinguishable. If this were not so, then the spectrum of an atom, say, helium, would vary from experiment to experiment, depending on what kind of electrons were contained in it.

This is purely quantum mechanical property.

In Cl. M. it is possible to follow the orbits of all particles (in principle) so that they are never really indistinguishable.

The spin has a further effect on the consequences of indistinguishability which we will discuss next.

$$H(1,2) = H(2,1) \quad \text{for identical particles} \quad (52)$$

1, 2: includes all deg. of freedom including spin

For example;

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(x_1, x_2) \quad \text{for 2-particle system} \quad (53)$$

$$\text{with } V(x_1, x_2) = V(x_2, x_1) \quad (54)$$

$$\Psi(1, 2, \dots, N) \equiv \Psi(x_1, \sigma_1; x_2, \sigma_2, \dots, x_N, \sigma_N) \quad \text{The wave func. for } N \text{ identical particles} \quad (55)$$

For two-particle systems:

$$H(1, 2) \mathcal{U}_E(1, 2) = E \mathcal{U}_E(1, 2) \quad (56)$$

Since the labeling does not matter, we may write this as:

$$H(2, 1) \mathcal{U}_E(2, 1) = E \mathcal{U}_E(2, 1) \quad (57)$$

On the other hand, using (52);

$$H(1, 2) \mathcal{U}_E(2, 1) = E \mathcal{U}_E(2, 1) \quad (58)$$

Now we introduce; P_{12} : exchange op.

$$P_{12} \Psi(1, 2) = \Psi(2, 1)$$

$$(58) \rightarrow H P_{12} \mathcal{U}_E(1, 2) = E \mathcal{U}_E(2, 1) \\ = E P_{12} \mathcal{U}_E(1, 2) = P_{12} E \mathcal{U}_E(1, 2) = P_{12} H \mathcal{U}_E(1, 2) \quad (59)$$

$$\rightarrow [H, P_{12}] = 0 \quad (60)$$

$\rightarrow P_{12}$: comm of motion

$$\text{Also: } (P_{12})^2 \Psi(1, 2) = \Psi(1, 2) \quad (61)$$

$$\text{The eigenvalues of } P_{12} = \pm 1 \quad (62)$$

2 - Systems consisting of identical particles of integral spin (spin 0, 1, 2, ...) are described by symmetric wave functions. (Bosons), They are said to obey Bose-Einstein statistics.

Ex. -

$$\Psi^{(A)}(1,2,3) = \frac{1}{\sqrt{6}} \left[\Psi(1,2,3) - \Psi(2,1,3) + \Psi(2,3,1) - \Psi(3,2,1) + \Psi(3,1,2) - \Psi(1,3,2) \right] \quad (64)$$

$$\Psi^{(S)}(1,2,3) = \frac{1}{\sqrt{6}} \left[\Psi(1,2,3) + \Psi(2,1,3) + \Psi(2,3,1) + \Psi(3,2,1) + \Psi(3,1,2) + \Psi(1,3,2) \right] \quad (65)$$

Special Case:

N - noninteracting fermions;

They don't interact with each other but, do interact with a common potential;

$$H = \sum_{i=1}^N H_i \quad (66)$$

$$H_i = \frac{p_i^2}{2m} + V(x_i) \quad (67)$$

$$H_k U_{E_k}(x_k) = E_k U_{E_k}(x_k) \quad (68)$$

$U_{E_k}(x_k)$: eigenstates of the one-particle pot.

$$H U_E(1, 2, \dots, N) = E U_E(1, 2, \dots, N) \quad (69)$$

$$U_E(1, 2, \dots, N) = U_{E_1}(x_1) U_{E_2}(x_2) \dots U_{E_N}(x_N) \quad (70)$$

where $E_1 + E_2 + \dots + E_N = E$ (71)

In (70) x_i : includes space and spin degs. of freedom.

For two-particle system;

$$U^{(A)}(1, 2) = \frac{1}{\sqrt{2}} [U_{E_1}(x_1) U_{E_2}(x_2) - U_{E_1}(x_2) U_{E_2}(x_1)] \quad (72)$$

With 3-particles;

$$U^{(A)}(1, 2, 3) = \frac{1}{\sqrt{6}} [U_{E_1}(x_1) U_{E_2}(x_2) U_{E_3}(x_3) - U_{E_1}(x_2) U_{E_2}(x_1) U_{E_3}(x_3) \\ + U_{E_1}(x_2) U_{E_2}(x_3) U_{E_3}(x_1) - U_{E_1}(x_3) U_{E_2}(x_2) U_{E_3}(x_1) \\ + U_{E_1}(x_3) U_{E_2}(x_1) U_{E_3}(x_2) - U_{E_1}(x_1) U_{E_2}(x_3) U_{E_3}(x_2)] \quad (73)$$

$$U^{(A)}(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{E_1}(x_1) & \psi_{E_1}(x_2) & \dots & \psi_{E_1}(x_N) \\ \psi_{E_2}(x_1) & \psi_{E_2}(x_2) & \dots & \psi_{E_2}(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{E_N}(x_1) & \psi_{E_N}(x_2) & \dots & \psi_{E_N}(x_N) \end{vmatrix} \quad (74)$$

$i \leftrightarrow j$ involves the interchange of two columns
 (indices of the particles) \rightarrow this changes the sign

For example $1 \leftrightarrow 2$

$$U^{(A)}(2, 1, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{E_1}(x_2) & \psi_{E_1}(x_1) & \dots & \psi_{E_1}(x_N) \\ \psi_{E_2}(x_2) & \psi_{E_2}(x_1) & \dots & \psi_{E_2}(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{E_N}(x_2) & \psi_{E_N}(x_1) & \dots & \psi_{E_N}(x_N) \end{vmatrix} \quad (75)$$

$$\rightarrow U^{(A)}(1, 2, \dots, N) = -U^{(A)}(2, 1, \dots, N) \quad (76)$$

Now if $E_k = E_l \rightarrow$ two lines are the same
 (we assume $E_k = E_l$ and $\alpha_k = \alpha_l$)

Since the interchange of two rows \rightarrow changes the sign of the det.

$$\rightarrow \det = 0 \rightarrow U^{(A)}(1, 2, \dots, N) = 0 \quad (77)$$

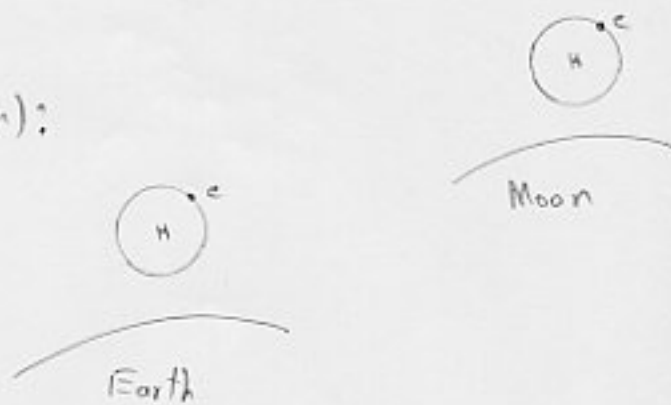
→ The requirement of antisymmetry introduces an effective interaction between two fermions;

Two particles in the same state tend to stay away from each other, since the joint wave func. vanishes when their separation goes to zero.

Thus even noninteracting particles behave as if there were a repulsive interaction between them.

Pauli Exclusion principle (restricted version):

The state of given energy, ang. mom., parity, ... can be occupied by two electrons (spin $\frac{1}{2}$ particles) (of opposite spin variables) but by no more than two electrons



Remark: No two electrons can be in the same quantum state.

Question: Consider two H-Atoms in their ground states, one on the moon and the other one on the earth.

Must the two electrons be in opposite spin states?

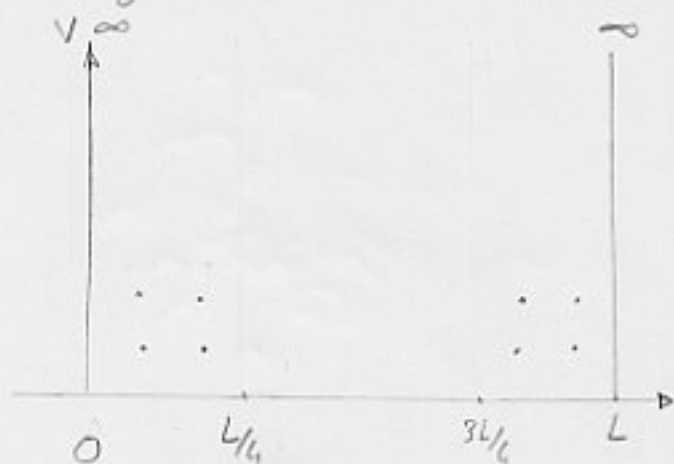
To answer this question one must specify (in general);

- i) Spin orientation of the electrons
- ii) Whether they are in the ground state of their respective atoms or not.
- iii) The energy of the atoms.

How well do we know these?

Ex. - Consider the atoms are localized in $0 \leq x \leq L/4$ and

$3L/4 \leq x \leq L$ respectively.



In chap. 4 for a particle in box we obtained;

$$E_n^{(-)} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad E_n^{(+)} = \frac{(n - \frac{1}{2})^2 \pi^2 \hbar^2}{2ma^2} \quad n = 1, 2, 3, \dots$$

here $E_n^{(\pm)} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (78)$

(Remember the wave func. must vanish at $x=0, L$
sol $\rightarrow \sin kx$ only)

$$E = \frac{p^2}{2m} \quad (79)$$

$$(78)(79) \Rightarrow p = \frac{\hbar n \pi}{L} \quad (80)$$

Remark: Note that for classical particles ($m = \text{large}$) we have localized wave func (ψ), (i.e. $\psi = \sum a_n \sin k_n x$)
So E and ΔE are different from eqns (78) and (82).

$\Delta p \Delta x \gtrsim \hbar \rightarrow \Delta p \Delta x \sim \hbar k$ (can be proved using the wave-func.)

$$\Delta p \sim \frac{\hbar k}{\Delta x} \sim \frac{\hbar k}{L} \quad (81)$$

$$\Delta E \approx \frac{p \Delta p}{m} = \left(\frac{\hbar n \pi}{L}\right) \left(\frac{\hbar k}{L}\right) \frac{1}{m} = \frac{\hbar^2 n \pi^2}{m L^2} \quad (82)$$

This however is larger than;

$$E_n - E_{n-1} \approx \frac{\hbar^2 n^2 \pi^2}{m L^2} \quad (83)$$

$$\Delta E > E_n - E_{n-1} \quad \text{for } n > 1 \quad (84)$$

In fact for atoms separated by 1 meter, moving with 10^6 cm/sec
 $\rightarrow n \sim 10^{11}$ (classical limit)

Note that (80) $\rightarrow n = \frac{PL}{\hbar n} = \frac{m v L}{\hbar n}$ (85)
 { comp of the other atoms }
 $n \sim 10^{11}$
 (the electrons of some atoms)
 (Because of large separation, the electrons are indifferent quantum states, so they may or may not be in the same spin state)

\rightarrow So that there is no possibility that in a macroscopic situation there will be conflict with classical intuition.

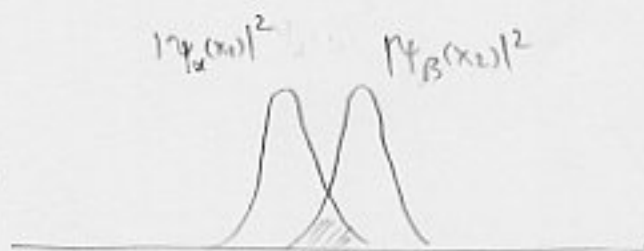
In fact, if the two atoms are labeled A and B, the question is whether there is a difference between using the wave func.

$$\psi_A(x_1) \psi_B(x_2) \quad (86)$$

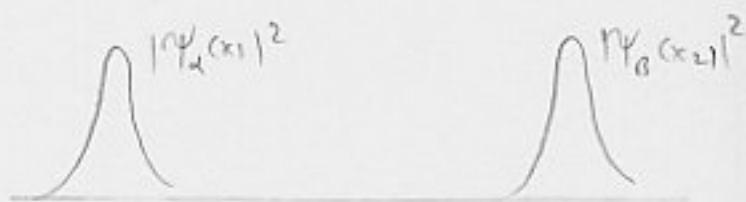
$$\text{and } \frac{1}{\sqrt{2}} [\psi_A(x_1) \psi_B(x_2) - \psi_A(x_2) \psi_B(x_1)]$$

to describe the two electron state?

i) If the two electrons are close ($n \sim 1$),
the results calculated with uncorrelated
wave functions and antisymmetrized wave functions
are different



ii) But the results are the same
if they are far enough ($n \rightarrow \infty$)



} Remark (c: see P(170))

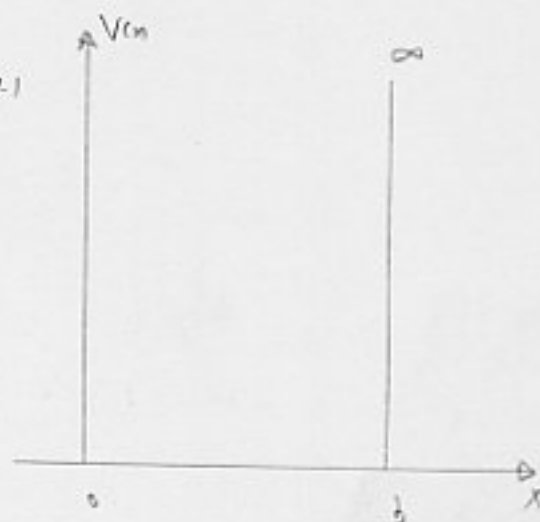
The ground state of N -Fermions and N -Bosons:
(both non-interacting)

Consider the infinite pot. box, $V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < b \\ \infty & b < x \end{cases}$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x) \quad (87)$$

$$\Rightarrow \psi_n(x) = \sqrt{\frac{2}{b}} \sin\left(\frac{n\pi x}{b}\right) \quad n=1, 2, 3, \dots \quad (88)$$

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mb^2} \quad (89)$$



For N non-interacting bosons, the ground state has all the particles in the $n=1$ state

$$E = N \frac{\hbar^2 n^2}{2mb^2} \quad \rightarrow \quad \frac{E}{N} = \frac{\hbar^2 n^2}{2mb^2} \quad (90)$$

For N non-interacting fermions, only 2-electrons can go into each of the states $n=1, 2, 3, \dots$

\rightarrow $\frac{N}{2}$ of states are filled by N fermions;

$$E = 2 \sum_{n=1}^{N/2} \frac{\hbar^2 n^2}{2mb^2} = \frac{\hbar^2}{mb^2} \frac{N^3}{24} \quad (91)$$

when we have used;

$$\sum_{n=1}^{N/2} n^2 \approx \int_1^{N/2} n^2 dn \approx \frac{1}{3} \left(\frac{N}{2}\right)^3 \quad \text{for } n \rightarrow \text{large} \quad (92)$$

$$\rightarrow \frac{E}{N} = \frac{\hbar^2 n^2}{24mb^2} N^2 \quad (93)$$

↑
grows with N^2

Therefore; for a given E ;

$N \sim E$ number of bosons

$N \sim E^{1/3}$ " = fermions

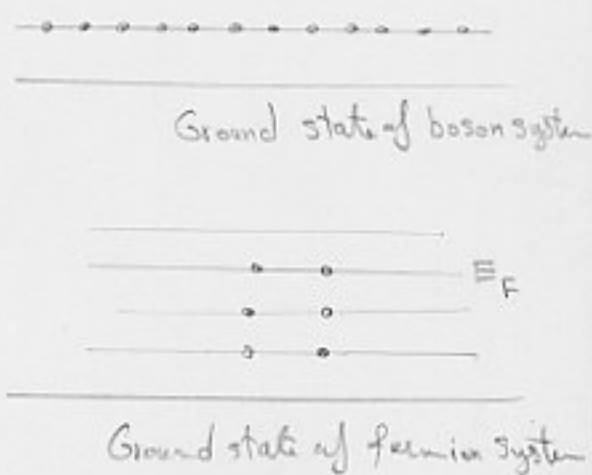
The highest level to be filled in the fermion case has $n = \frac{N}{2}$

$$\rightarrow E_F = \frac{\hbar^2 n^2 N^2}{8mb^2} \quad (94)$$

In terms of the density of fermions:

$$\rho = \frac{N}{b} \quad (\text{in one-dim})$$

$$\rightarrow E_F = \frac{\hbar^2 n^2}{8m} \rho^2$$



Remark! (From P 168):

The wave func. of two-electrons: Either $\psi = \psi_+ \chi_{S_{up}}$ or $\psi = \psi_- \chi_{S_{up}}$

$$\text{where } \psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{\alpha}(x_1) \psi_{\beta}(x_2) \pm \psi_{\alpha}(x_2) \psi_{\beta}(x_1))$$

The probability of observing electron 1 in d^3x_1 around x_1 and electron 2 in d^3x_2 around x_2 is given by:

$$P_{\pm} \approx \frac{1}{2} [|\psi_{\alpha}(x_1)|^2 |\psi_{\beta}(x_2)|^2 + |\psi_{\alpha}(x_2)|^2 |\psi_{\beta}(x_1)|^2 \pm 2 \text{Re}(\psi_{\alpha}(x_1) \psi_{\beta}(x_2) \psi_{\alpha}^*(x_2) \psi_{\beta}^*(x_1))]$$

$$P_{-} |_{x_1=x_2} = 0 \quad P_{+} |_{x_1=x_2} = \text{large}$$

↑
exchange term
 $d^3x_1 d^3x_2$

If the separation of the two electrons is large, then

$$\text{exchange term} \approx 0 \quad \rightarrow \quad P_{\pm} \approx |\psi_{\alpha}(x_1)|^2 |\psi_{\beta}(x_2)|^2$$