呂浩宇

General Physics (II) Quantum Physics

思考策略：先看熟悉之簡單問題，再用以猜複雜情形之物理系統行為

Degenerate energy levels : free-electron in a 3D infinite potential well

邊界以內的部分滿足 Schrödinger equation： 依命題 $(V(x,y,z,t)=0)$

$$i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z,t)$$

, to find energy eigen states 能量本徵態

separation of variable： $\Psi(x,y,z,t) = U(t)\psi(x,y,z)$

$$\Rightarrow \psi\, i\hbar\frac{\partial U}{\partial t} = U\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi\right)$$

左右同除 $U\psi$

$$\Rightarrow i\hbar\frac{1}{U}\frac{\partial U}{\partial t} = \underbrace{\frac{-1}{\psi}\left(\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi\right) = E}$$

常數，詮釋為總能量

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

: 3D time-independent Schrödinger equation

繼續做 separation of variable

觀察能階之 degeneracy

令 $\psi(x,y,z) = X(x)Y(y)Z(z)$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)XYZ = EXYZ$$

左右同除 XYZ

$$\Rightarrow \underbrace{-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\partial^2}{\partial x^2}X}_{\text{只有 } x \text{ dependence, 必須為常數 } E_x} \underbrace{-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\partial^2}{\partial y^2}Y}_{\text{只有 } y \text{ dependence, 必須為常數 } E_y} \underbrace{-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{\partial^2}{\partial z^2}Z}_{\text{只有 } z \text{ dependence, 必須為常數 } E_z} = E$$

$\Rightarrow$

(1) $E = E_x + E_y + E_z$ ：總能量為各個自由度所貢獻的能量之總合

(2)
- i) $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}X = E_x X$
- ii) $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}Y = E_y Y$
- iii) $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}Z = E_z Z$

$\rightarrow$ 在三個空間維度，皆分別為一維無限深位能井問題

(generalized 到自由度更高的問題之後，描述系統所需要的量子數越多)

$\downarrow$

quantum numbers
$$\begin{cases} n_x = 1, 2, 3, 4, 5, 6, \ldots \\ n_y = 1, 2, 3, 4, 5, 6, \ldots \\ n_z = 1, 2, 3, 4, 5, 6, \ldots \end{cases}$$

$\Downarrow$

$$E_{xn} = \frac{\hbar^2}{2m}\left(\frac{n_x\pi}{L_x}\right)^2,\quad E_{yn} = \frac{\hbar^2}{2m}\left(\frac{n_y\pi}{L_y}\right)^2,\quad E_{zn} = \frac{\hbar^2}{2m}\left(\frac{n_z\pi}{L_z}\right)^2$$

能階

$$E = \frac{\hbar^2}{2m}\pi^2\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

若 $L_x = L_y$，則不同組合之 n_x 與 n_y 可給出相同的能量 E，如 $(n_x=1,\ n_y=2)$ 與 $(n_y=1,\ n_x=2)$ 為相同總能量 E 之不同狀態。此情形稱能階為 degenerate

若 $L_x = L_y = L_z$，在量子數很大的情形，可以 n_r^2 及其它量子數來表示系統狀態

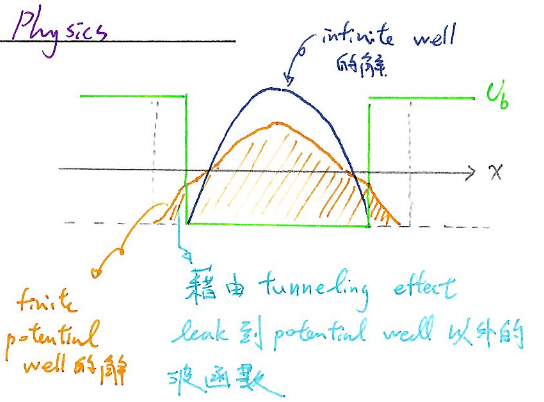
其它量子數：描述系統在徑向以外之方向的運動

$n_r^2 = n_x^2 + n_y^2 + n_z^2$ —— 徑向自由度與總能量之關係

$n_x, n_y, n_z < n_r$

呂詰宇

A generalization to 3D finite potential well



在知道波函數 $\psi(x, y, z)$ 的情形下，
系統的能量僅跟 ψ 的空間二次微分及(已知)
的 potential 有關。

可預期由三維的 infinite well generalized 到
有限的 potential 之情形，系統仍可由差不多的
quantum numbers 的組合來描述。 ⟶ 能階仍為不連續。

唯因波函數可藉由 tunneling effect leak 到 potential well 外面，
對於同樣的量子數，finite well 可等效地被視為一更寬的 potential well，
故能量較 infinite well 在同樣量子數之情形低。

想像 potential well 慢慢變形，由正/長方形的三維
potential well 漸漸地變成三維球對稱的
potential well.

預期：

1. 仍有一與徑方方向運動相關的量子數 (n_r) 與系統總能量極為相關
2. 亦有用以描述其它方向運動之量子數，且亦與系統之總能量相關。
3. 與 3 維 infinite square/rectangular 之情形類似，系統能階 degenerate

   物理上應理解為，在 potential 為球對稱的情形下，能量僅與運動之"程度"有關，而與運動之方向無關

4. 與 3 維 infinite square/rectangular 類似，$E \propto \frac{1}{n^2}$

   → 主量子數：為描述波函數在徑向之行為之量子數與描述波函數在其它方向之行為之量子數之某種組合

描述氫原子儀之電子所需之量子數： $E = -\frac{1}{2} m_e c^2 (Z\alpha)^2 \frac{1}{n^2}$

- n_r ; radial QN (徑向行為)
- l : angular momentum QN (其它方向行為)
  ↳ 只描述運動之程度，無關方向
- m: orbital magnetic QN (只描述運動之方向，與程度無關，故與能量無關。
  選取方向之自由度造成能階 degenerate
- principal QN: $n \equiv n_r + l + 1$
  $n = 1, 2, 3, \ldots$

  l 絕對值必須小於 n 且為正整數： $l = 0, 1, 2, \ldots, n-1$
- S_z: spin QN: $\pm\frac{1}{2}\hbar$ 电子自旋，描述電子內稟角動量，無古典對應。

呂浩宇

System with Many Particles (Boson, Fermion, Pauli exclusion principle)

wave function for N particles: $\psi(\underbrace{x_1}_{\text{position variable of the }i\text{th particle}}, x_2, x_3, \cdots, x_N; t)$

$|\psi(x_1, x_2, \cdots; t)|^2 dx_1 dx_2 \cdots dx_N$: the probability of finding particle 1 in the range (x_1, x_1+dx_1), particle 2 in the range (x_2, x_2+dx_2) and so forth.

Schrödinger equation: $$i\hbar \frac{\partial \Psi(x_1, x_2, \cdots; t)}{\partial t} = H\Psi(x_1, x_2, \cdots; t)$$

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

A. Independent Particles

N particles which do not interact with each other, and are subject to external potential that are only relevant to individual of them:

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

$$\Psi(x_1, x_2, \cdots; t) = \psi(x_1)\psi(x_2)\psi(x_3)\cdots\psi(x_N)\, e^{-iEt/\hbar}$$

物理意義: particle 1 出現在 x_1 且 particle 2 出現在 x_2 的机率等於 particle 1 出現在 x_1 的机率乘以 particle 2 出現在 x_2 的机率, … 等.

B. Identical Particles (this discussion is based on the case with only 2 particles for simplicity; the conclusion can be generalized to many electrons.)

All electrons are identicle.

fundamentally, we are not allowed to distinguish two electrons.

We can say: one electron is at x_1, another electron is at x_2.

We are not permitted to make the statement: electron 1 is at x_1, electron 2 is at x_2

$V(x_1, x_2) = V(x_2, x_1)$: if we inter-change these two electrons, the potential energy is the same, such that we cannot distinguish these two electrons based on the potential.

若我們將 wave function 簡單寫作 $\psi(x_1, x_2) = \overbrace{U_m(\underbrace{x_1}_{\text{electron 1 之 position variable}})}^{\text{QN 為 m 之 energy eigen state}}\,\overbrace{U_n(x_2)}^{\text{QN 為 n 之 energy eigen state.}}$,則形同說電子 1 在 mth state,電子 2 在 nth state.

這件事在量子力学中是 fundamentally 不被允許的

$\Downarrow$

symmetrized wave function: $\frac{1}{\sqrt{2}}[U_m(x_1)U_n(x_2) + U_m(x_2)U_n(x_1)] \equiv \psi_S \rightarrow$ Bosonic

Anti-symmetrized wave function: $\frac{1}{\sqrt{2}}[U_m(x_1)U_n(x_2) - U_m(x_2)U_n(x_1)] \equiv \psi_A \rightarrow$ fermonic

此形式造成無古典對應之 "exchange forces"

$\psi_S(x_1, x_2) = \psi_S(x_2, x_1)$
兩電子交換,波函數之形式完全不變

$\psi_A(x_1, x_2) = -\psi_A(x_2, x_1)$
兩電子交換,波函數只差一個負号

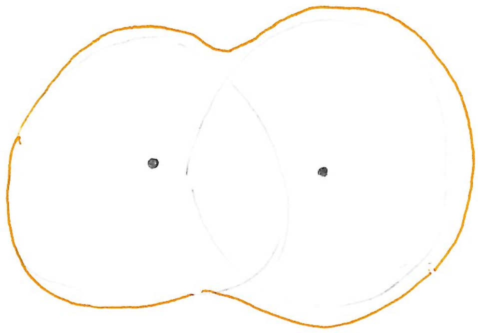
由於机率只與波函數的平方有關,此二種形式之波函數皆滿足使得兩電子無法被區分之要求.

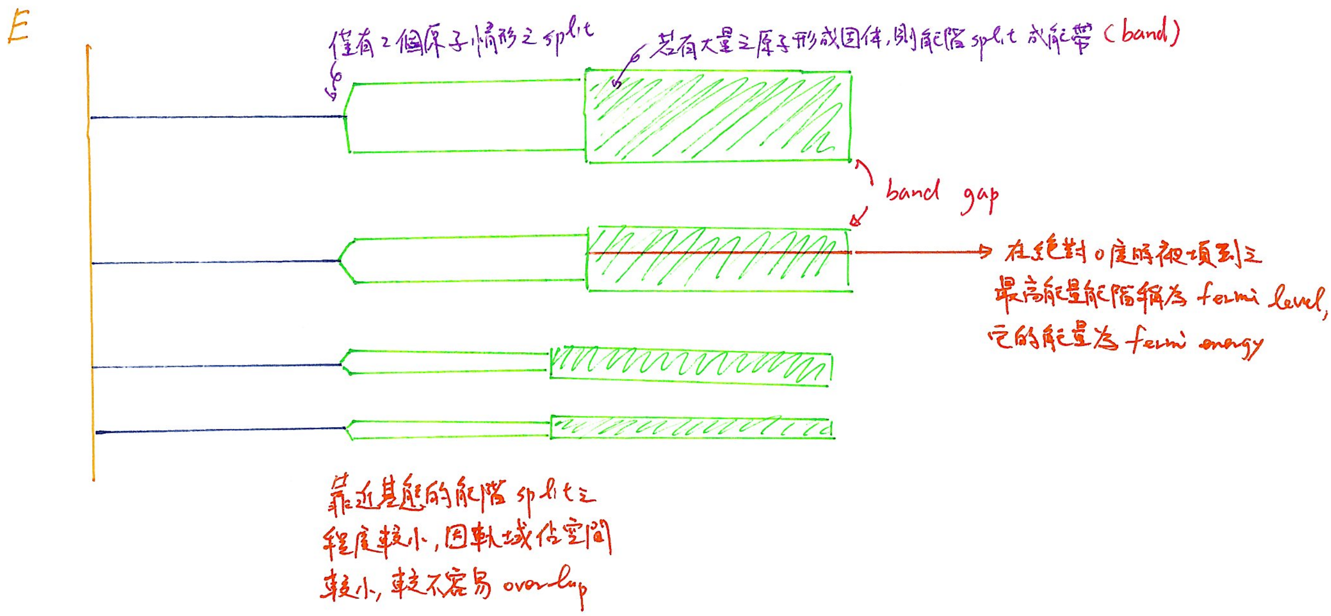
$\Longrightarrow$ if $m = n$, then $\psi_A = 0 \Rightarrow$ electrons can not have the same quantum number.
Pauli exclusion principle.

呂浩宇

Energy levels in a crystalline solid

當兩個原子靠近到它們外層電子的軌域在空間上重疊，我們便不能說個別電子是繞著哪一個原子。此時稱此系統為双原子系統，其電子數為單一原子系統之兩倍，能階由單原子能階 split 成高低能階 以滿足 Pauli exclusion principle





valence band : the highest filled band.
conduction band : the highest, not completely filled band.

Semiconductor : material that has a very narrow gap between the conduction and valence band, such that it is possible to stochastically excite some electrons from conduction to valence band in room temperature.
形成價帶中的一個電洞與導帶中的一個電子，兩者皆可導电.

Insulators do not have conduction band. And the energy between the valence band and the vacant band just above the valence band is very large. In this case, under the external E-field, the electrons cannot gain averaged kinetic energy since all energy levels in the valence band are filled while there is no way to hop to the higher energy band.

可藉由 dopping 增加 charge carrier 之密度.
導帶中電子增加者為 n-type 半導体
價帶中電洞增加者為 p-type 半導体