Wavefunct° for N particle system: $\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$

where $|\Psi|^2 d^3\underline{r}_1\, d^3\underline{r}_2 \cdots d^3\underline{r}_N$

Normalisat° $\int\int\int |\Psi|^2 d^3\underline{r}_1\, d^3\underline{r}_2 \cdots d^3\underline{r}_N = 1$

Momentum operator : $\hat{p}_i = -i\hbar\nabla_i$

For all N particles $\hookrightarrow$ $\hat{p} = \sum_{i=1}^{N} \hat{p}_i$

$[\hat{p}_{x_i}, \hat{x}_j] = -i\hbar\delta_{ij}$

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2 + \underbrace{V(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)}_{\text{general potential energy}}$$

general potential energy depends → interact° / → external field

 Two interacting particles with no external field

Potential energy only depends on separat° btw particles

$V(\underline{r}_1, \underline{r}_2) = V(\underline{r})$

$\underline{r} = \underline{r}_1 - \underline{r}_2$

Hamitonian $\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(\underline{r}_1, \underline{r}_2)$

Treat centre-of-mass & relative mot° separately

Centre of mass coordinate $\underline{R} = \frac{m_1\underline{r}_1 + m_2\underline{r}_2}{m_1 + m_2}$

$= \frac{m_1}{M}\underline{r}_1 + \frac{m_2}{M}\underline{r}_2$

$M = m_1 + m_2$

Velocity centre of mass $\underline{V} = \frac{d\underline{R}}{dt} = \frac{m_1}{M}\underline{V}_1 + \frac{m_2}{M}\underline{V}_2$

Momentum of centre of mass $\underline{P} = M\underline{V} = \underline{p}_1 + \underline{p}_2$

For relative mot°: particle of reduced mass $\mu = \frac{m_1 m_2}{M}$

velocity $\underline{v} = \frac{d\underline{r}}{dt} = \underline{V}_1 - \underline{V}_2$

momentum $\underline{p} = \mu\underline{v} = \frac{m_1 m_2}{M}\left(\underline{V}_1 - \underline{V}_2\right) = \frac{m_2\underline{p}_1 - m_1\underline{p}_2}{M}$

$$\begin{cases} \underline{p}_1 = \underline{p} + \frac{m_1}{M}\underline{P} \\ \underline{p}_2 = -\underline{p} + \frac{m_2}{M}\underline{P} \end{cases}$$

Hamiltonian $\hat{H} = \frac{m_1 + m_2}{2M^2}\hat{\underline{P}}^2 + \frac{1}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\hat{\underline{p}}^2 + V(r)$

$$= \frac{\hat{\underline{P}}^2}{2M} + \frac{\hat{\underline{p}}^2}{2\mu} + V(\underline{r})$$

$$\hat{H} = \hat{H}_{cm} + \hat{H}_{rel}$$

$$\hat{H}_{cm} = \frac{-\hbar^2}{2M}\nabla_R^2 \qquad \hat{H}_{rel} = \frac{-\hbar^2}{2\mu}\nabla_r^2 + V(\underline{r})$$

$$\Downarrow$$

$$\phi(\underline{R}, \underline{r}) = U(\underline{R})\,u(\underline{r})$$

Example separates into 2 TISEs

$\swarrow$ Centre of mass

$$\frac{-\hbar^2}{2M}\nabla_R^2 U = E_R U$$

for free particle of mass

$\searrow$ particle of reduced mass μ moving with potential $V(\underline{r})$

$$\frac{-\hbar^2}{2\mu}\nabla_r^2 u + V(\underline{r})u = E_r u$$

for a particle of mass μ

in potential $V(r)$

Total E : $E = E_R + E_r$

Example: Central potentials

$V(r)$ ∝ distance origin

3D Schröd eqt° => separates nicely in spherical polar coords $\underline{r} = (r, \theta, \phi)$

The TISE becomes

$$-\frac{\hbar^2}{2\mu}\left[\underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2}}_{\nabla^2 u \text{ in spherical polars}}\right]+V(r)\,u=E\,u$$

Potential energy V is a function of r only

We look for separable solut°s of the form

$$u(r,\theta,\phi) = \underbrace{R(r)}_{\text{radial coord}} \times \underbrace{Y(\theta,\phi)}_{\text{angular coord}}$$

Substitute (2) into (1), multiply by r^2 and divide through by u:

$$\left[\underbrace{-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+r^2V(r)-r^2E}_{\text{function of } r \text{ only}}\right] - \frac{\hbar^2}{2\mu}\left[\underbrace{\frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}}_{\text{function of } \theta,\phi \text{ only}}\right]=0$$

Each bracket must be cnst

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(V(r)+\frac{\hbar^2\lambda}{2\mu r^2}\right)R = ER$$

$$-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \lambda Y$$

angular momentum operator $\hat{L}^2$

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$\hat{L}^2|Y_{\ell m}(\theta,\phi)\rangle = \ell(\ell+1)\hbar^2|Y_m(\theta,\phi)\rangle$$

$$\Downarrow$$

angular parts of wavef° must be spherical harmonics

$$\boxed{\lambda = \ell(\ell+1)}$$

$\downarrow$ becomes

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)R = ER}$$

Notes:

- All $\overbrace{\text{central potentials}}^{\text{only } V(r)}$ have their angular solut°s given by spherical harmonics.

  Radial dependence found solving

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)R = ER}$$

- Energy eigenvals also given by $\uparrow$

  $\propto \ell$

~~α~~ m

- Solut°s given ℓ & different m are degenerate

$\uparrow$ $\propto$ tot angular momentum

Hydrogen atom

Electrostatic potential energy btw electron & proton

$$V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

$$\boxed{n > \ell \ \& \ |m| \leq \ell}$$

Energy eigenvals

$$E_n = -\frac{1}{n^2}\left(\frac{\mu e^2}{32\pi^2\varepsilon_0^2 \hbar^2}\right) \quad [eV]$$

n : radial qntum n°

ℓ, m : angular momentum n°

→ $n=1, \ell=0, m=0$.

$$R(r) \propto \exp(-r/a_0)$$

Bohr radius : $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$

$$Y_{00} = \sqrt{\frac{1}{4\pi}} \quad \boxed{\text{1s orbital}}$$

Degenerate eigenf°s

$$u_{100}(r, \theta, \phi) = A\exp(-r/a_0)$$

Find normalisat° cnst A :

$$\iiint |u(r,\theta,\phi)|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi = 1$$

Eigenvalue $E_1 = -13.6$ eV

$\rightarrow$ $\underline{n = 2,\ l = 1,\ m = -1, 0, 1}$

$$R(r) \propto r \exp(-r/2a_0)$$

$$\left.\begin{array}{l} Y_{10} = \sqrt{\dfrac{3}{4\pi}} \cos\theta \\[2em] Y_{1\pm1} = \mp\sqrt{\dfrac{3}{8\pi}} \sin\theta \exp(\pm i\phi) \end{array}\right\} \boxed{\text{p orbitals}}$$

Degenerate eigenf°s

$$u_{21-1}(r,\theta,\phi) = Ar\exp(-r/2a_0)\sin\theta\exp(-i\phi)$$

$$u_{210}(r,\theta,\phi) = Ar\exp(-r/2a_0)\cos\theta$$

$$u_{211}(r,\theta,\phi) = Ar\exp(-r/2a_0)\sin\theta\exp(+i\phi)$$

Eigenvalue $E_2 = -13.6/4$ eV

Two distinguishable non-interacting particles in an external field

Particles are independent: no interact°

Potential E: $V(\underline{r}_1, \underline{r}_2) = V_1(\underline{r}_1) + V_2(\underline{r}_2)$

Hamiltonian: $\hat{H} = -\dfrac{\hbar^2}{2m_1}\nabla_1^2 - \dfrac{\hbar^2}{2m_2}\nabla_2^2 + V_1(\underline{r}_1) + V_2(\underline{r}_2)$

Using separat° of vars: $\phi(\underline{r}_1, \underline{r}_2) = u_a(\underline{r}_1)\, u_b(\underline{r}_2)$

u_a: state a, particle 1

u_b: state b, particle 2

Two particle TISE becomes $\hat{H}\phi = E\phi$:

$$\left[-\frac{\hbar^2}{2m_1}\frac{1}{u_a}\nabla_1^{\,2}u_a + \frac{1}{u_a}V_1(\underline{r}_1)u_a\right] + \left[-\frac{\hbar^2}{2m_2}\frac{1}{u_b}\nabla_2^{\,2}u_b + \frac{1}{u_b}V_2(\underline{r}_2)u_b\right] = E$$

each bracket $\propto$ one var (a/b)

= cnst

Σ cnsts $= \underbrace{E_1 + E_2} = E_{TOT}$

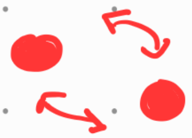
Problem separates into 2 separate TISEs

$$-\frac{\hbar^2}{2m_1}\nabla_1^{\,2}u_a + V_1(\underline{r}_1)u_a = E_1 u_a$$

$$-\frac{\hbar^2}{2m_2}\nabla_2^{\,2}u_b + V_2(\underline{r}_2)u_b = E_2 u_b$$

where $E = E_1 + E_2$

Indistinguishable particles



Two identical particles $\Rightarrow$ indistinguishable

✓ represents physical observable

Hermitian operator must remain unchanged regardless of particle labels: $\hat{A}(1,2) = \hat{A}(2,1)$

Particle exchange operator $\hat{P}$

Particle Exchange Operator $\hat{P}_{12}$

not the same as parity operator

A4!

If α is the corresponding eigenvalue

$$\hat{A}(1,2)\phi(1,2) = \alpha\phi(1,2) \qquad (2)$$

Swopping labels should have no effect

$$\hat{A}(2,1)\phi(2,1) = \alpha\phi(2,1) \qquad (3)$$

Applying $\hat{P}_{12}$ to (2)

$$\begin{aligned}\hat{P}_{12}\hat{A}(1,2)\phi(1,2) &= \alpha\hat{P}_{12}\phi(1,2) \\ &= \alpha\phi(2,1) \\ &= \hat{A}(2,1)\phi(2,1) && \boxed{\text{using (3)}} \\ &= \hat{A}(1,2)\hat{P}_{12}\phi(1,2) && \boxed{\text{using (1)}}\end{aligned}$$

So

$$\hat{P}_{12}\hat{A}(1,2)\phi(1,2) - \hat{A}(1,2)\hat{P}_{12}\phi(1,2) = 0$$

i.e., the commutation relation

$$\boxed{\left[\hat{P}_{12}, \hat{A}(1,2)\right] = 0} \qquad (4)$$

Hence, $\hat{P}_{12}$ is compatible with any Hermitian operator $\hat{A}(1,2)$. An eigenfunction $\phi(1,2)$ of $\hat{A}(1,2)$ must therefore be a solution of the eigenvalue equation

$$\hat{P}_{12}\phi(1,2) = p\phi(1,2) \qquad (5)$$

where p is the eigenvalue. So

$$\boxed{\begin{aligned}\phi(1,2) &= \hat{P}_{12}\phi(2,1) \\ &= p\phi(2,1) && \boxed{\text{using (5)}} \\ &= p\hat{P}_{12}\phi(1,2) \\ &= p^2\phi(1,2) && \boxed{\text{using (5)}} \\ \therefore p^2 &= 1 \Rightarrow p = \pm 1\end{aligned}}$$

symmetric eigenf°

Hence $\boxed{\phi(1,2) = \pm\phi(2,1)}$

antisymmetric eigenf°

$\hat{P}_{12}$ & $\hat{A}(1,2)$ share common set eigenf° $\Rightarrow$ $\hat{P}_{12}$ does not change the system anti/-symmetric state.

Every particle is either anti/-symm : never mixed symmetry

Symmetric	Anti-symmetric
bosons	fermions
0 / integer spin ($s = 0, 1, 2$)	($s = 1/2, 3/2, \dots$)
Bose-Einstein states	Fermi-Dirac statistics

photons, phonons, pi-mesons, cooper pairs   electrons, protons, neutrons

symmetric

$$\boxed{u_+(1,2) = \frac{1}{\sqrt{2}}\left[u_a(1)u_b(2) + u_a(2)u_b(1)\right]}$$

and   normalisation

$$\boxed{u_-(1,2) = \frac{1}{\sqrt{2}}\left[u_a(1)u_b(2) - u_a(2)u_b(1)\right]}$$

antisymmetric

Note change of notation for simplicity of representation

a and *b* label the particle states; 1 and 2 label the particles

- As required

$$u_+(2,1) = \frac{1}{\sqrt{2}}\left[u_a(2)u_b(1) + u_a(1)u_b(2)\right]$$
$$= u_+(1,2)$$

and

$$u_-(2,1) = \frac{1}{\sqrt{2}}\left[u_a(2)u_b(1) - u_a(1)u_b(2)\right]$$
$$= -u_-(1,2)$$

- If two fermions tried to occupy the same state such that $u_a = u_b$

$$u_-(1,2) = \frac{1}{\sqrt{2}}\left[u_a(1)u_a(2) - u_a(2)u_a(1)\right]$$
$$= 0$$

i.e. the state does not exist.

This is the Pauli exclusion principle: two fermions cannot exist in the same single particle state (Noble Prize 1945). The principle is the cornerstone of atomic and molecular physics and chemistry

The occupation of a fermion state is either zero or unity – Fermi-Dirac statistics

(½) (½) Two non-interacting indistinguishable spin ½ fermᵒs

$\underline{S} = S_1 + S_2$ spin matrices

$\uparrow\uparrow \therefore S = 1$

$\uparrow\downarrow \therefore S = 0$

Spin eigenfᵒs denoted by $\chi_{SM_s}(1,2)$

$$\hat{S}^2 \chi_{SM_s}(1,2) = S(S+1)\hbar^2 \chi_{SM_s}(1,2)$$
$$\hat{S}_z \chi_{SM_s}(1,2) = M_s \hbar \chi_{SM_s}(1,2)$$

Spin magnetic quantum n°: $M_s = -S, -S+1, \dots, S$

Total spin operator $\hat{S}^2 = (\hat{S}_1 + \hat{S}_2)\cdot(\hat{S}_1 + \hat{S}_2)$

$$= S_1^2 + S_2^2 + 2\underbrace{\hat{S}_1 \cdot \hat{S}_2}$$

$$\hat{S}_1 \cdot \hat{S}_2 = \hat{S}_{x_1}\hat{S}_{x_2} + \hat{S}_{y_1}\hat{S}_{y_2} + \hat{S}_{z_1}\hat{S}_{z_2}$$

$$= \hat{S}_x + \hat{S}_y + \hat{S}_z$$

Eigenf° for two ferm°s with spin $s_i = 1/2 \ (i=1,2)$

by $\alpha_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ & $\beta_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

s.t $\hat{S}_{z_i}\alpha_i = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$= \frac{\hbar}{2}\alpha_i$

$\hat{S}_{z_i}\beta_i = -\frac{\hbar}{2}\beta_i$

$S=1 \Rightarrow 3$ spin eigenf°s $M_s = -1, 0, 1$

$\chi_1(1,2) = \alpha\alpha_2$ $\quad M=-1$

$\chi_{1-1}(1,2) = \beta_1\beta_2$ $\quad M=0$

$\chi_{10}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \alpha\beta_1]$ $\quad M=1$

$S=0 \Rightarrow 1$ spin eigenf° $M_s = 0$

$$\chi_{00}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \alpha_2\beta_1]$$

Two particle syst identical 1/2 ferm$^\circ$s

overall space & spin dependent eigenf$^\circ$s

$$\phi(1,2) = \underbrace{u(1,2)}_{\text{spatiall dep component}} \, \underbrace{\chi(1,2)}_{\text{Spin dep com}}$$

2 ways generating antisymmetric eigenf$^\circ$ $\phi(1,2)$ required for ferm$^\circ$s

① $\uparrow\uparrow$ Triplet state

$u(1,2)$ antisymmetric

$\chi(1,2)$ symmetric

$\leftarrow$ ½ ½ $\rightarrow$

repel each other at short separat$^\circ$s

$\underbrace{}$

property anti-symm space eigenf$^\circ$

$$u_-(1,2) = \frac{1}{\sqrt{2}}\left[u_a(1)\,u_b(2) - u_a(2)\,u_b(1)\right]$$

with

$$\chi_{11}(1,2) = \alpha_1\alpha_2$$

$$\chi_{1-1}(1,2) = \beta_1\beta_2$$

$$\chi_0(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_1\beta_2 + \alpha_2\beta_1\right]$$

$\underline{r}_1 \approx \underline{r}_2 \qquad u_a(1)\,u_b(2) \approx u_a(2)\,u_b(1) \quad \Rightarrow \quad u_-(1,2) \approx 0$

$\phi(1,2) \approx 0$

ferm°s with aligned spins have a small probability of being found in the same reg° of space

↑↓ Singlet state

½ → ← ½
attract each other in short separat°

$u(1,2)$ symmetric
$\chi(1,2)$ antisymmetric

$$u_+(1,2) = \frac{1}{\sqrt{2}}\left[u_a(1)\,u_b(2) + u_a(2)\,u_b(1)\right]$$

with $\chi_{00}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_1\beta_2 - \alpha_2\beta_1\right]$

$r_1 \approx r_2 \quad \phi(1,2) \neq 0 \Rightarrow$ ferm°s with anti-parallel spins have a larger probability of being found in the same reg° of space

Spin ½ ferm°s move under influence of a force α spin
EXCHANGE FORCE

Example

Consider two non-interacting spin ½ fermions in a 1D infinite square well potential.

If the spins are parallel, the total spin $S = 1$. The space and spin dependent eigenfunction

$$\phi(1,2) = u_-(1,2)\,\chi_{1M_S}(1,2)$$

$S = 1$

where

$$u_-(1,2) = \frac{1}{\sqrt{2}}\left[u_a(1)u_b(2) - u_a(2)u_b(1)\right].$$

$$\phi(1,2) = u_+(1,2)\,\chi_{00}(1,2)$$

with $a = b = 1$

normalisation constant when $a = b$ (see problems sheet)

$$u_+(1,2) = \frac{1}{2}\left[u_1(x_1)u_1(x_2) + u_1(x_2)u_1(x_1)\right]$$
$$= u_1(x_1)u_1(x_2)$$

i.e. the state exists. The Hamiltonian

$$\hat{H} = \hat{T}_1 + \hat{T}_2$$

$V(x_i) = 0$ in the potential well, no interaction between particles

where

If the fermions try to occupy the same state with $a=b$, then $u_{-}(1,2)=0$. The ground state does not correspond $a=b=1$ because this state does not exist. For ground state, see problems sheet

If the spins are antiparallel, the total spin $S=0$. The space and spin eigenfunction for the ground state

$$\hat{T}_i = -\frac{\hbar^2}{2m}\frac{d^2}{dx_i^2}$$

and

Ground state energy eigenvalue for single particle state

$$\hat{T}_i u_1(x_i) = E_1 u_1(x_i)$$

TISE for $V(x_i)=0$

TISE for the two-particle system

$$\begin{aligned}
\hat{H}\phi(1,2) &= \left(\hat{T}_1+\hat{T}_2\right)\phi(1,2)\\
&= \chi_{00}\left\{\left[\hat{T}_1 u_1(x_1)\right]u_1(x_2)+u_1(x_1)\left[\hat{T}_2 u_1(x_2)\right]\right\}\\
&= 2E_1\chi_{00}u_1(x_1)u_1(x_2)\\
&= 2E_1\phi(1,2)
\end{aligned}$$

So, the ground state corresponds to $a=b=1$, and the ground state energy is $2E_1$