

Section 3. Many particle systems

- As discussed in section 1.8, if the potential energy is not time dependent, then all information about the particle state can be obtained by solving the TISE
- How do we write the TISE for systems containing more than one particle?
- Illustrate with examples of two-particle systems
- Discuss the consequences of the indistinguishability of identical particles
- Fermions and bosons and symmetry of the wavefunction.
- Pauli exclusion principle

3.1 Wavefunction and operators

- Wavefunction for an N particle system (ignoring spin)

$$\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$$

where

$$|\Psi|^2 d^3 \underline{r}_1 d^3 \underline{r}_2 \dots d^3 \underline{r}_N$$

is the probability that particle 1 is in volume element $d^3 \underline{r}_1$ at \underline{r}_1 *and* particle 2 is in volume element $d^3 \underline{r}_2$ at \underline{r}_2 *...* *and* particle N is in volume element $d^3 \underline{r}_N$ at \underline{r}_N

Normalisation: $\int \int \int |\Psi|^2 d^3 \underline{r}_1 d^3 \underline{r}_2 \dots d^3 \underline{r}_N = 1$

- Momentum operator for single particle i

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

For all N particles

$$\hat{p} = \sum_{i=1}^N \hat{p}_i$$

- Operators describing single particle observables commute when they refer to different particles e.g.

x component of
momentum for
particle i

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

x component of
position for particle j

- The Hamiltonian

$$\hat{H} = -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$$

In general potential energy $V(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$ will depend on (i) **interaction** between particles and (ii) presence of an **external field**

3.2 Two interacting particles, no external field

- The potential energy depends only on the separation between the particles

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

where $\underline{r} = \underline{r}_1 - \underline{r}_2$. The two particle Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(\underline{r}_1, \underline{r}_2) \quad (1)$$

- As in classical mechanics, **treat the centre-of-mass and relative motion separately**

Centre of mass coordinate is given by

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

where total mass $M = m_1 + m_2$. Velocity of 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

$$\underline{P} = M\underline{V} = \underline{p}_1 + \underline{p}_2 \quad (2)$$

For relative motion, particle of

reduced mass $\mu = \frac{m_1 m_2}{M}$

with coordinate $\underline{r} = \underline{r}_1 - \underline{r}_2$ has velocity

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

Momentum

$$\begin{aligned}\underline{p} &= \mu \underline{v} = \frac{m_1 m_2}{M} \underline{v}_1 - \underline{v}_2 \\ &= \frac{m_2 \underline{p}_1 - m_1 \underline{p}_2}{M}\end{aligned}\tag{3}$$

Solving (2) and (3) gives

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

- So the Hamiltonian operator in (1) becomes

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

Or

$$\hat{H} = \hat{H}_{\text{CM}} + \hat{H}_{\text{rel}}$$

where

$$\hat{H}_{\text{CM}} = -\frac{\hbar^2}{2M} \nabla_R^2$$

centre of mass
motion

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

relative motion

We have used $\hat{P} = -i\hbar\nabla_R$ and $\hat{p} = -i\hbar\nabla_r$ where the gradient operators ∇_R and ∇_r are with respect to the vectors \underline{R} and \underline{r} , respectively.

- We can use the separation of variables method and write

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

The problem separates into 2 TISEs, one for the centre of mass

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

TISE for a free particle of mass M

and one for a particle of reduced mass μ moving in the potential $V(\underline{r})$

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

TISE for a particle of mass μ in the potential $V(\underline{r})$

where the total energy $E = E_R + E_r$.

Example: Central potentials

- If the potential energy $V(\underline{r})$ depends only on the distance from the origin, then the 3D Schrodinger equation separates nicely in spherical polar coordinates $\underline{r} = (r, \theta, \phi)$

- The TISE becomes

$\nabla^2 u$ in spherical
polars



$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \phi^2} \right] + V(r) u = E u \quad (1)$$

Potential energy V is a function of r only

- We look for **separable** solutions of the form

$$u(r, \theta, \phi) = R(r) \times Y(\theta, \phi) \quad (2)$$

R is a function only of the radial coordinate

Y is a function only of the angular coordinates.
The use of the symbol Y is not an accident!

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

function of r only

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

function of θ, ϕ only

- The first bracket depends only on r and the second bracket depends only on θ and ϕ , but

the whole equation holds at every point in space. Therefore, **each bracket must be a constant**. We call the second bracket $-\lambda$, which gives:

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(V(r) + \frac{\hbar^2 \lambda}{2\mu r^2} \right) R = E R \quad (3)$$

$$-\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = \lambda Y \quad (4)$$

- In section 2.3 we saw that the angular momentum operator \hat{L}^2 in spherical polars is

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (5)$$

and its eigenfunctions are spherical harmonics

$$\boxed{\hat{L}^2 |Y_{\ell m}(\theta, \phi)\rangle = \ell(\ell + 1) \hbar^2 |Y_{\ell m}(\theta, \phi)\rangle} \quad (6)$$

By comparing (4), (5) and (6), we can see that the **angular parts of the wavefunction must be spherical harmonics and that $\lambda = \ell(\ell + 1)$**

The angular momentum quantum numbers ℓ and m characterise the angular parts of the wavefunction

The radial equation (3) becomes

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} \right) R = E R \quad (7)$$

Notes

i.e. $V(r)$ only

- **All** central potentials have their angular solutions given by spherical harmonics. The radial dependence is found by solving (7)
- The energy eigenvalues are also given by (7). They depend on ℓ but do not depend on m .
- Solutions with a given ℓ value (which fixes the total angular momentum), but different m values (i.e. different L_z components) are degenerate

Case of the Hydrogen atom

For the H atom $V(r)$ is the electrostatic potential energy between an electron and a proton

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

and (7) can be solved to find $R(r)$, which leads to the introduction of a new quantum number n ($= 1, 2, 3\dots$).

$$n, \ell, m \text{ satisfy } n > \ell \text{ and } |m| \leq \ell.$$

The energy eigenvalues

$$E_n = -\frac{1}{n^2} \left(\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \right)$$

depend only on n . The H atom is a special case in this respect. For most central potentials, the energy depends on both n and ℓ .

- For $n = 1, \ell = 0, m = 0$,

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

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Bohr radius

Also $Y_{00} = \sqrt{\frac{1}{4\pi}}$

s orbital

So

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

Note labelling

n : radial quantum number

ℓ, m : angular momentum quantum numbers

To find the normalisation constant A we require

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

Eigenvalue $E_1 = -13.6 \text{ eV}$

- For $n = 2$, $\ell = 1$, $m = -1, 0, 1$

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

Also

$$\left. \begin{aligned} Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta \\ Y_{1\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i\phi) \end{aligned} \right\} \boxed{p \text{ orbitals}}$$

So the degenerate eigenfunctions

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

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

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

Eigenvalue: $E_2 = -13.6/4 \text{ eV}$

3.3 Two distinguishable non-interacting particles in an external field

- The particles are **independent** because they do not interact. Potential energy

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

- So the Hamiltonian

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

- Use the separation of variables method and write

State a occupied by particle 1

$$\phi(\underline{r}_1, \underline{r}_2) = u_a(\underline{r}_1) u_b(\underline{r}_2)$$

State b occupied by particle 2

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

- The two particle TISE $\hat{H}\phi = E\phi$ becomes

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

Each bracket is a function of only one variable, but the whole equation holds for every point in space. **Therefore, each bracket must be a constant, and the sum of these constants must be E . Call these constants E_1 and E_2**

The problem separates into 2 separate TISEs

$$\begin{aligned} -\frac{\hbar^2}{2m_1} \nabla_1^2 u_a + V_1(\underline{r}_1) u_a &= E_1 u_a \\ -\frac{\hbar^2}{2m_2} \nabla_2^2 u_b + V_2(\underline{r}_2) u_b &= E_2 u_b \end{aligned} \tag{1}$$


where $E = E_1 + E_2$

3.4 Indistinguishable particles

- **Identical particles** cannot be distinguished in any physical measurement and are therefore **indistinguishable**
- A **Hermitian** operator, representing a physical observable, must remain unchanged if the particle labels are interchanged i.e.

$$\hat{A}(1,2) = \hat{A}(2,1) \quad (1)$$

Not the same as the parity operator



- Introduce the **particle exchange operator** \hat{P}_{12} .

When \hat{P}_{12} acts on an eigenfunction $\phi(1,2)$ of $\hat{A}(1,2)$, the labels 1 & 2 are interchanged

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

If α is the corresponding eigenvalue

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

Swapping labels should have no effect

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

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

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

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

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

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

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

where p is the eigenvalue. So

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

$$= p\phi(2,1)$$

using (5)

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

$$= p^2\phi(1,2)$$

using (5)

$$\therefore p^2 = 1 \Rightarrow p = \pm 1$$

- From the definition of \hat{P}_{12}

$$\begin{aligned}\phi(1,2) &= \hat{P}_{12}\phi(2,1) \\ &= p\phi(2,1)\end{aligned}$$

using (5)

Hence

$$\phi(1,2) = \pm\phi(2,1)$$

Eigenfunction is **symmetric** if there is no change of sign on particle interchange (+ sign)

Eigenfunction is **antisymmetric** if there is change of sign on particle interchange (− sign)

- From (4), \hat{P}_{12} and the Hermitian operator $\hat{A}(1,2)$ share a **common set** of eigenfunctions.

So, if a system starts in a symmetric (antisymmetric) state, the application of \hat{P}_{12} will not change that state, i.e., it will **remain** symmetric (antisymmetric) for all time

- Turns out that **every particle is described by either a symmetric or antisymmetric wavefunction**. It is an empirical fact that mixed symmetry does not occur

- Particles with **symmetric** wavefunctions are called **bosons**. Bosons have zero or integer spin ($s = 0, 1, 2, \dots$). They obey **Bose-Einstein statistics**. Examples include photons, phonons, pi-mesons, Cooper pairs

- Particles with **antisymmetric** wavefunctions are called **fermions**. Fermions have half-integer spin ($s = 1/2, 3/2, \dots$). They obey **Fermi-Dirac statistics**. Examples include electrons, protons, neutrons

3.5 Two non-interacting indistinguishable particles in an external field

- In section 3.3, we considered the TISE for two non-interacting distinguishable particles in an external field. For particle 1 in state a with eigenfunction $u_a(\underline{r}_1)$ and particle 2 in state b with eigenfunction $u_b(\underline{r}_2)$ we found solutions of the form $u_a(\underline{r}_1)u_b(\underline{r}_2)$
- For two non-interacting **indistinguishable** particles, $m_1 = m_2$, the kinetic energy operators must remain unchanged on particle label exchange

$$-\frac{\hbar^2}{2m_1}\nabla_1^2 = -\frac{\hbar^2}{2m_2}\nabla_2^2$$

and the potential energy operators must remain unchanged on particle label exchange

$$V_1(\underline{r}_i) = V_2(\underline{r}_i) \text{ for } i = 1 \text{ or } 2$$

i.e., equations (1) in section 3.3 become identical and have the same set of eigenvalues and eigenfunctions

- Need to look for solutions of the TISE that have the appropriate **symmetry** with respect to particle exchange. These are **linear combinations** of $u_a(\underline{r}_1)u_b(\underline{r}_2)$ and $u_a(\underline{r}_2)u_b(\underline{r}_1)$

symmetric

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

and

normalisation

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

antisymmetric

Note change of notation for simplicity of representation

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

• As required

$$\begin{aligned} u_+(2,1) &= \frac{1}{\sqrt{2}} [u_a(2)u_b(1) + u_a(1)u_b(2)] \\ &= u_+(1,2) \end{aligned}$$

and

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

$$= -u_{-}(1,2)$$

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

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

$$= 0$$

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

- For bosons, $u_+(1,2) \neq 0$ if $u_a = u_b$, i.e., the state exists. There is **no limit** on the number of particles that can occupy the same quantum state – **Bose-Einstein** statistics

At low temperatures, a system of bosons (e.g. liquid ^4He) exhibits a tendency for **all particles to occupy the same ground state**. This is the phenomenon of **Bose-Einstein condensation** (Nobel Prize in Physics 2001)

3.6 Two non-interacting indistinguishable spin $\frac{1}{2}$ fermions

- In general, the spin of particles cannot be ignored
- If \hat{S}_i is the operator for a fermion with spin $s_i = 1/2$ ($i = 1, 2$), the operator for the total spin

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

\hat{S}_i acts only on particle i

- Expect that the net spin of the system is either $S = s_1 + s_2 = 1$ (spins parallel $\uparrow\uparrow$) or $S = s_1 - s_2 = 0$ (spins antiparallel $\uparrow\downarrow$)
- If the spin eigenfunctions are denoted by $\chi_{SM_S}(1,2)$, expect that (see Section 2.2)

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

$$\hat{S}_z \chi_{SM_S}(1,2) = M_S \hbar \chi_{SM_S}(1,2)$$

where the ‘spin magnetic quantum number’
 $M_s = -S, -S + 1, \dots, S$

The total spin operator

$$\begin{aligned}\hat{S}^2 &= (\hat{S}_1 + \hat{S}_2) \bullet (\hat{S}_1 + \hat{S}_2) \\ &= \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \bullet \hat{S}_2\end{aligned}$$

where

$$\begin{aligned}\text{For two vectors } \underline{S}_1 \text{ and } \underline{S}_2, \\ \underline{S}_1 \bullet \underline{S}_2 &= S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2}\end{aligned}$$

$$\hat{S}_1 \bullet \hat{S}_2 = \hat{S}_{x1}\hat{S}_{x2} + \hat{S}_{y1}\hat{S}_{y2} + \hat{S}_{z1}\hat{S}_{z2}$$

The z component of the total spin operator

$$\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$$

$$\hat{S}_{zi} \text{ acts only on particle } i$$

- Represent the eigenfunctions for two fermions with spin $s_i = 1/2$ ($i = 1, 2$) by

$$\alpha_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \beta_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

such that

$$\hat{S}_{zi}\alpha_i = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \alpha_i$$

$$\hat{S}_{zi}\alpha_i = \frac{\hbar}{2}\alpha_i \quad \text{and} \quad \hat{S}_{zi}\beta_i = -\frac{\hbar}{2}\beta_i$$

Example

For a two-particle state such as $\alpha_1\alpha_2$, the subscripts refer to different electrons. So

$$\hat{S}_{z1}\alpha_1\alpha_2 = \left(\hat{S}_{z1}\alpha_1\right)\alpha_2 = \frac{\hbar}{2}\alpha_1\alpha_2$$

and

$$\hat{S}_{z2}\alpha_1\alpha_2 = \alpha_1\left(\hat{S}_{z2}\alpha_2\right) = \frac{\hbar}{2}\alpha_1\alpha_2$$

- For $S = 1$, expect three spin eigenfunctions corresponding to $M_S = -1, 0, 1$

These states are given by the symmetric combinations

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

$$M_S = 1$$

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

$$M_S = -1$$

$$\chi_{10}(1, 2) = \frac{1}{\sqrt{2}}[\alpha_1 \beta_2 + \alpha_2 \beta_1]$$

$$M_S = 0$$

Check: For $\chi_{11}(1, 2)$,

$$\begin{aligned}\hat{S}^2 \chi_{11}(1, 2) &= (\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2) \chi_{11}(1, 2) \\ &= 2\hbar^2 \chi_{11}(1, 2) = S(S+1)\hbar^2 \chi_{11}(1, 2) \\ &\Rightarrow S = 1\end{aligned}$$

$$\begin{aligned}\hat{S}_z \chi_{11}(1, 2) &= (\hat{S}_{z1} + \hat{S}_{z2}) \chi_{11}(1, 2) \\ &= \hbar \chi_{11}(1, 2) = M_S \hbar \chi_{11}(1, 2) \\ &\Rightarrow M_S = 1\end{aligned}$$

See problems sheet

- For $S = 0$, expect one spin eigenfunction corresponding to $M_S = 0$

The state is given by the antisymmetric combination

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

Check

$$\begin{aligned}\hat{S}^2 \chi_{00}(1,2) &= (\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2) \chi_{00}(1,2) \\ &= 0 \chi_{00}(1,2) = S(S+1)\hbar^2 \chi_{00}(1,2) \\ &\Rightarrow S = 0\end{aligned}$$

$$\begin{aligned}\hat{S}_z \chi_{00}(1,2) &= (\hat{S}_{z1} + \hat{S}_{z2}) \chi_{00}(1,2) \\ &= 0 \chi_{00}(1,2) = M_S \chi_{00}(1,2) \\ &\Rightarrow M_S = 0\end{aligned}$$

See problems sheet

- For a two-particle system of identical spin 1/2 fermions, write the overall space and spin dependent eigenfunctions as

$$\phi(1,2) = \overbrace{u(1,2)}^{\text{spatially dependent component}} \underbrace{\chi(1,2)}_{\text{spin dependent component}}$$

- There are two ways of generating the **antisymmetric** eigenfunctions $\phi(1,2)$ required for fermions

- Triplet state $\uparrow\uparrow$

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

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

with

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

or

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

or

$$\chi_{10}(1,2) = \frac{1}{\sqrt{2}} [\alpha_1\beta_2 + \alpha_2\beta_1]$$

As above

If $\underline{r}_1 \approx \underline{r}_2$, then $u_a(1)u_b(2) \approx u_a(2)u_b(1)$ such that $u_-(1,2) \approx 0$ and $\phi(1,2) \approx 0 \Rightarrow$ **fermions with aligned spins have a small probability of being found in the same region of space**

- Singlet state $\uparrow\downarrow$

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

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

with

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

As above

If $\underline{r}_1 \approx \underline{r}_2$, $\phi(1,2) \neq 0 \Rightarrow$ fermions with anti-parallel spins have a larger probability of being found in the same region of space

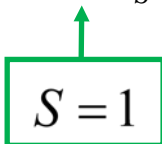
- Two spin $\frac{1}{2}$ fermions in a triplet state act as if they repel each other at short separations. This is not e.g. the Coulomb repulsion because we have assumed that the fermions do not interact. It is a property of the anti-symmetric space eigenfunctions
- Two spin $\frac{1}{2}$ fermions in a singlet state act as if they attract each other at short separations
- So the spin $\frac{1}{2}$ fermions move under the influence of a force whose sign (repulsive or attractive) depends on the relative orientation of their spins. This is the exchange force
- He atom provides the simplest realistic system where the question of particle identity plays an important role

Example

Consider two non-interacting spin $\frac{1}{2}$ fermions in a 1D infinite square well potential.

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

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

where 

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

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

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

with $a = b = 1$

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

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

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

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

Ground state energy eigenvalue
for single particle state

and

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

TISE for $V(x_i) = 0$

TISE for the two-particle system

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

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

