

The Zeeman Effect

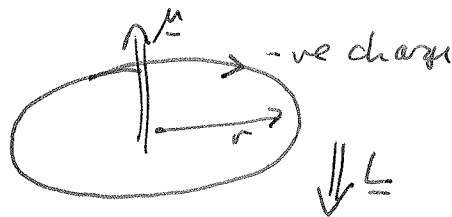
We've identified the various energy levels in the hydrogen spectrum with different values of j . However to be sure that these identifications are correct it would be interesting to be able to measure the degeneracy of these states. For example a $j = \frac{1}{2}$ level should have degeneracy 2 corresponding to $m_j = \pm \frac{1}{2}$. To do this we have to pick out a particular spatial direction as special - for example by applying an external magnetic field (remember your earlier discussions of the Stern-Gerlach experiment with JMR). If the magnetic field applied is weak (we'll see what this means quantitatively in a minute) this leads to the Zeeman effect.

To study this effect we need to know the interaction energy between the electron and the external \underline{B} field. There are two contributions:

- 1) Spin we've already seen that the electron has a magnetic dipole moment due to its intrinsic spin of

$$\underline{\mu}_{\text{spin}} = -\frac{e}{2m_e} g_s \underline{S}$$

- 2) Orbital motion of the electron produces a magnetic dipole moment



$$\text{magnitude} = I \times \text{area} = \frac{e v \pi r^2}{2\pi r} = \frac{e}{2m_e} (m_e v r)$$

↑
magnitude of \underline{L}

$$\underline{\mu}_{\text{orbital}} = -\frac{e}{2m_e} \underline{L}$$

So altogether the interaction Hamiltonian with the external \underline{B} field is

$$h = -\underline{B} \cdot \left(-\frac{e}{2m_e} (\underline{L} + 2\underline{S}) \right)$$

$$= \frac{e}{2m_e} \underline{B} \cdot (\underline{L} + 2\underline{S}) \quad \left(\text{as usual we've put } g_s = 2 \right)$$

(3)

So we take the real hydrogen atom whose states are

$$|n, j, l, m_j\rangle \quad \text{with} \quad E_{nj} = -\frac{\alpha^2 mc^2}{2n^2} + \Delta E_{nj}^{FS}$$

and apply a small magnetic field so that h is a small perturbation

1. The ground state

This is $|1, \frac{1}{2}, 0, \pm \frac{1}{2}\rangle$ ie has degeneracy 2.

$$\langle 1, \frac{1}{2}, 0, m_j' | h | 1, \frac{1}{2}, 0, m_j \rangle$$

$$= \frac{eB}{2m_e} \langle 1, \frac{1}{2}, 0, m_j' | L_z + 2S_z | 1, \frac{1}{2}, 0, m_j \rangle$$

(where we've set the B field to be along the z direction)

The part involving L_z vanishes because $l=0$ (and the wavefunctions are spherically symmetric) so we get

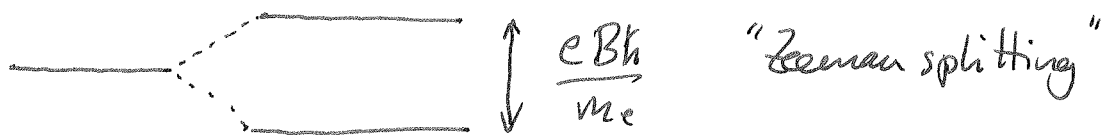
$$= \frac{eB}{2m_e} \cdot 2 \cdot \hbar \cdot m_j \delta_{m_j' m_j}$$

and the off-diagonal matrix elements are zero - we can use non-degenerate PT straight away to get

$$\Delta E_{m_j}^{Z(\text{Zeeman})} = \frac{eB\hbar}{m_e} \left(\pm \frac{1}{2} \right) \quad \text{for } m_j = \pm \frac{1}{2}$$

Thus the two degenerate states are split by the application of the B field

(4)



Clearly this will be a good result provided that the splitting is much less than the energy difference from the

1st excited state i.e. $\frac{eB\hbar}{m_e} \ll mc^2\alpha^2$

2. Excited states $j = \frac{1}{2}, l = 0$

these are $|n, \frac{1}{2}, 0, \pm\frac{1}{2}\rangle$ and the argument goes as above and we get

$$\Delta E_{m_j}^Z = \frac{eB\hbar}{m_e} (\pm\frac{1}{2}) \quad \text{again.}$$

but for a this to be a good approx. now need $\Delta E \ll \Delta E^{FS}$, $B \ll 1T$

3. Excited states ~~$j = \frac{1}{2}$~~ $l \neq 0$

cannot drop L_z and

These have $l \neq 0$ and so now we have to deal with matrix elements

$$\langle n, j', l', m_j' | L_z + 2S_z | n, j, l, m_j \rangle$$

The states are eigenstates of $J_z = L_z + S_z$ with eigenvalue m_j

but unfortunately not of $L_z + 2S_z$. You'll deal with

this problem in more detail next year. For now let's

(5)

Be content with looking at the first excited state in which case we know that $l=1$.

We can see that

$$[J_z, L_z + 2S_z] = 0$$

so if we take the matrix element

$$\langle n, j', l, m_j' | \left[\begin{array}{c} \leftarrow J_z (L_z + 2S_z) \\ - (L_z + 2S_z) \overrightarrow{J_z} \end{array} \right] | n, j, l, m_j \rangle = 0$$

$$(m_j' - m_j) \langle n, j', l, m_j' | L_z + 2S_z | n, j, l, m_j \rangle = 0$$

so the matrix element is zero unless $m_j = m_j'$.

The states with different j ~~are~~ (in this case $\frac{1}{2}$ and $\frac{3}{2}$) are non-degenerate so we can use non-degenerate P.T.

$$\underline{j = \frac{3}{2} \quad m_j = +\frac{3}{2}}$$

In this case \underline{L} and \underline{S} are aligned $L_z = +1 \hbar$
 $S_z = +\frac{1}{2} \hbar$

$$\text{so } \Delta E_{m_j = \pm \frac{3}{2}}^2 = \frac{eB\hbar}{m_e} \cdot 2 \times \pm 1$$

⑥

$j = \frac{3}{2} \quad m_j = \frac{1}{2}$ and $j = \frac{1}{2} \quad m_j = \frac{1}{2}$

Now the J^2, J_z eigenstates are linear superpositions

$$|3/2, 1/2\rangle = \sqrt{\frac{2}{3}} |1,0\rangle |1/2, 1/2\rangle + \sqrt{\frac{1}{3}} |1,1\rangle |1/2, -1/2\rangle$$

\uparrow \uparrow
 L S

and $|\frac{3}{2}, \frac{1}{2}\rangle = \sqrt{\frac{1}{3}} |1,0\rangle |1/2, 1/2\rangle - \sqrt{\frac{2}{3}} |1,1\rangle |1/2, -1/2\rangle$

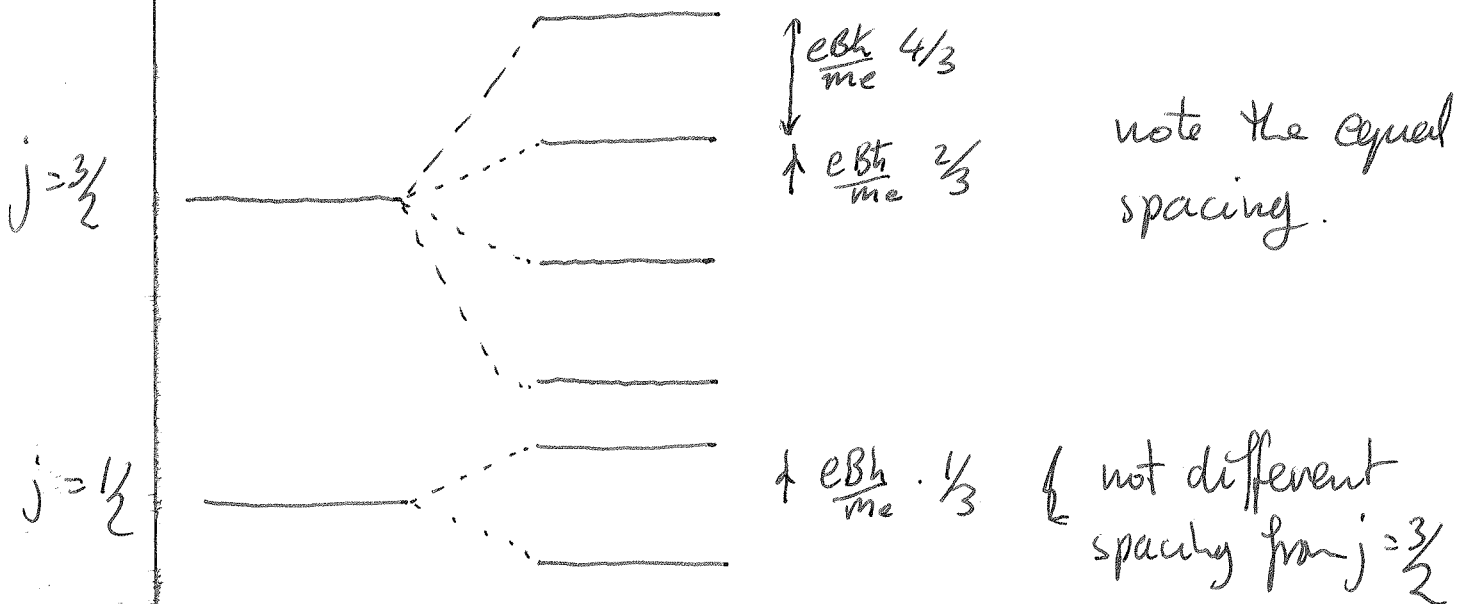
These coefficients are calculable but you can look them up

Now $L_z + 2S_z$ kills the second state on the r.h.s

so we get

$$j = \frac{3}{2} \quad \Delta E_{m_j = \pm 1/2}^z = \frac{eB\hbar}{m_e} \cdot \frac{2}{3} \times \pm 1$$

$$j = \frac{1}{2} \quad \Delta E_{m_j = \pm 1/2}^z = \frac{eB\hbar}{m_e} \cdot \frac{1}{3} \times \pm 1$$



Helium I

The Helium atom has two electrons and a nucleus with charge $+2e$ and mass about $4m_p$. As for hydrogen we'll start by ignoring everything except the Coulomb forces, and assuming that the nucleus is infinitely massive (a much better approx. here than it was for hydrogen). So the Hamiltonian is

$$\begin{aligned}
 H &= \frac{p_1^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0 r_1} &= H_1 &\leftarrow \text{K.E. and P.E. for 1st electron} \\
 &+ \frac{p_2^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0 r_2} &= H_2 &\leftarrow \text{K.E. and P.E. for 2nd electron} \\
 &+ \frac{e^2}{4\pi\epsilon_0 |\underline{r}_1 - \underline{r}_2|} &= H_{12} &\leftarrow \text{repulsion between the two electrons}
 \end{aligned}$$

The repulsion term makes life complicated. One would guess that it's magnitude will be similar to the two central Coulomb terms and the Schrodinger equation is not separable. In fact problems of this sort are not exactly solvable.

Note that the coordinates of each particle appear in H .

The wavefunction is now

$$\Psi(\underline{r}_1, \underline{r}_2, t) = \Phi(\underline{r}_1, \underline{r}_2) e^{-iEt/\hbar}$$

and the ^{time indep} Schrodinger equation is a partial differential equation in six coordinates!

A Crude Approximation

Let's ignore the repulsion term temporarily. Then it's clear that each electron is independently in a central potential of charge $+2e$ and will have hydrogen like states labelled by n, l, m . So the state for both electrons will be (ignoring spin for a moment)

$$|n_1, l_1, m_1; n_2, l_2, m_2\rangle = |n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle$$

and this is an eigenstate of $H = H_1 + H_2$

$$\begin{aligned} (H_1 + H_2) |n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle &= (H_1 |n_1, l_1, m_1\rangle) |n_2, l_2, m_2\rangle + |n_1, l_1, m_1\rangle (H_2 |n_2, l_2, m_2\rangle) \\ &= (E_{n_1} + E_{n_2}) |n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle \\ &= -\frac{m_0 c^2}{2} (2\alpha)^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) |n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle \end{aligned}$$

because central potential is $2e$ now

So the ground state will have energy

$$E_{11} = -\frac{m_0 c^2}{2} \alpha^2 \cdot 8 = -108.8 \text{ eV}$$

↑
Hydrogen
ionization
energy

The ionization energy is the difference between this energy and $E_{1, \infty} = -54.4 \text{ eV}$
 one electron left in g.s. \swarrow
 \nwarrow other electron pushed out

ie the ionization energy for Helium according to this calculation is 54.4 eV. Experimentally it is 24.6 eV so the discrepancy is large.

This must be accounted for by the repulsion term whose magnitude we can easily estimate to be

$$\sim \frac{e^2}{4\pi\epsilon_0 a_{\text{He}}} \quad a_{\text{He}} = \frac{1}{2} a \quad \left\{ \begin{array}{l} \text{Bohr radius for} \\ \text{Hydrogen} \end{array} \right.$$

\swarrow effect of central charge $2e$

$$\sim 2 \frac{e^2}{4\pi\epsilon_0 a}$$

$$\sim 4 |E_1| \quad \left\{ \begin{array}{l} \text{ground state energy for Hydrogen} \end{array} \right.$$

$$\sim 54 \text{ eV}!$$

So we see that the effect of the repulsion is going to be

to add a large positive amount to E_{11} for the true ground state energy of He.

It's clear that this contribution is going to be so large that perturbation theory will not be reliable. On the other hand this is real physics and obviously we would like to understand the He ionisation energy better than this. We need another way of calculating the effect of the repulsion.

B The Variational Principle

This is based on the observation that if $|\psi\rangle$ is any normalizable state then the ground state energy satisfies

$$E_0 \leq \langle \psi | H | \psi \rangle$$

This is easy to prove because completeness of states allows us to write

$$|\psi\rangle = \sum_n a_n |n\rangle \quad H|n\rangle = E_n |n\rangle$$

$$\text{so } 1 = \langle \psi | \psi \rangle = \sum_n |a_n|^2$$

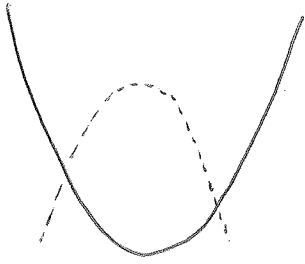
$$E_T = \langle \psi | H | \psi \rangle$$

$$= \langle \psi | \sum_n a_n E_n |n\rangle = \sum_n E_n |a_n|^2$$

$$\text{and } E_T - E_0 = \sum_n (E_n - E_0) |a_n|^2 \geq 0$$

So how do we use this? Let's use the SHO as an example.

example. $H = \frac{p^2}{2m} + \frac{1}{2} kx^2$



guess a form for the g.s. wave fn

eg. $\psi = C(a^2 - x^2) \quad -a < x < a$
 $= 0$ otherwise.

a is unknown - our aim is to find the best choice.
 First normalize ψ .

$$1 = \int_{-a}^a dx \ C^2 (a^2 - x^2)^2 \left[= C^2 \left(a^4 2a - 2a^2 \cdot \frac{2a^3}{3} + 2 \frac{a^5}{5} \right) \right]$$

$$= C^2 2a^5 \left(1 - \frac{2}{3} + \frac{1}{5} \right)$$

$$= C^2 \frac{16}{15} a^5$$

Then compute

$$\langle H \rangle_{\psi} = C^2 \int_{-a}^a (a^2 - x^2) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right) (a^2 - x^2) dx$$

Let $x = ay$

$$\langle H \rangle_{\psi} = C^2 a^5 \int_{-1}^1 dy (1 - y^2) \left(-\frac{\hbar^2}{2ma^2} \frac{d^2}{dy^2} + \frac{1}{2} ka^2 y^2 \right) (1 - y^2)$$

$$= C^2 a^5 \int_{-1}^1 dy \left\{ 2(1 - y^2) \frac{\hbar^2}{2ma^2} + \frac{1}{2} ka^2 y^2 (1 - y^2)^2 \right\}$$

$$= C^2 a^5 \left(\frac{4}{3} \frac{\hbar^2}{ma^2} + \frac{8}{3 \cdot 5 \cdot 7} ka^2 \right)$$

$$= \frac{5}{4} \left(\frac{\hbar^2}{ma^2} + \frac{2}{35} ka^2 \right)$$

Now we minimize this w.r.t. a^2 so

$$\left[\begin{array}{l} -\frac{\hbar^2}{m a^4} + \frac{2}{35} k = 0, \quad a^2 = \frac{35}{2} \frac{\hbar^2}{k m} \\ \text{which gives} \quad a^2 = \sqrt{\frac{35}{2}} \frac{\hbar}{\sqrt{k m}} \end{array} \right]$$

$$\begin{aligned} \text{so } \min \langle H \rangle_{\psi} &= \frac{5}{4} \left(\frac{\hbar^2}{m} \sqrt{\frac{2}{35}} \frac{\sqrt{k m}}{\hbar} + \sqrt{\frac{2}{35}} \frac{k \hbar}{\sqrt{k m}} \right) \\ &= \hbar \sqrt{\frac{k}{m}} \cdot \frac{5}{2} \cdot \sqrt{\frac{2}{35}} \\ &= \hbar \omega \times 0.598 \end{aligned}$$

This is not too bad; the real answer is of course $\frac{1}{2} \hbar \omega$ and our trial wavefunction was pretty crude.

C Screening

Now back to He. One way of looking at it is this.

In the crude approximation each electron always sees the full nuclear charge

$+2e$ \oplus \oplus nuclear charge $Z=2$

and has radial wave function in the ground state $e^{-Zr/a} \frac{1}{\sqrt{4\pi}} \frac{2}{(a/Z)^3}$

However, some of the time the other electron ~~is~~ lies closer to the nucleus and partially screens the charge; so the electron we're looking at actually "sees" a nuclear charge $Z_{\text{eff}} < 2$. This suggests that a good trial wave function would be

$$\psi = \left(\frac{1}{\sqrt{4\pi}} \frac{2}{(a/Z_{\text{eff}})^3} \right) e^{-Z_{\text{eff}}r/a} e^{-Z_{\text{eff}}r/a}$$

We should compute $E_T = \langle \psi | H | \psi \rangle$ and then vary Z_{eff} to find the lowest value of E_T .

we can write

$$H = \frac{p_1^2}{2m} - \frac{Z_{eff} e^2}{4\pi\epsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Z_{eff} e^2}{4\pi\epsilon_0 r_2}$$

$$+ \frac{e^2}{4\pi\epsilon_0 |\underline{r}_1 - \underline{r}_2|} + \frac{(Z_{eff}-2)e^2}{4\pi\epsilon_0 r_1} + \frac{(Z_{eff}-2)e^2}{4\pi\epsilon_0 r_2}$$

Our trial wavefn is an eigenfn of the first line. Letting E_R be the ionization energy of Hydrogen the first line gives us a contribution to $\langle \psi | H | \psi \rangle$ of

$$- 2 \cdot Z_{eff}^2 E_R$$

The last two terms on the second line give us a contribution

$$2 \cdot \frac{(Z_{eff}-2)e^2}{4\pi\epsilon_0} \cdot 4 \left(\frac{Z_{eff}}{a}\right)^3 \int_0^\infty dr \frac{r^2}{r} e^{-2Z_{eff}r/a}$$

$$= 2 \cdot \frac{(Z_{eff}-2)e^2}{4\pi\epsilon_0} \frac{Z_{eff}}{a} = 4 \cdot Z_{eff} (Z_{eff}-2) E_R$$

and the first term on the second line gives

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{16\pi^2} \left(2 \frac{Z_{eff}^3}{a^3}\right)^2 \int d^3\underline{r}_1 d^3\underline{r}_2 \frac{e^{-2Z_{eff}r_1/a} e^{-2Z_{eff}r_2/a}}{|\underline{r}_1 - \underline{r}_2|}$$

first rescale $r = a/2Z_{eff} \rho$ then we get

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{16\pi^2} \frac{Z_{eff}^6}{a^6} \left(\frac{a}{2Z_{eff}}\right)^5 \int d^3\rho_1 d^3\rho_2 \frac{e^{-\rho_1 - \rho_2}}{|\rho_1 - \rho_2|}$$

$$= 2E_R Z_{eff} \cdot \frac{16}{2^5} \frac{1}{16\pi^2} \int \frac{d^3p_1 d^3p_2 e^{-p_1 - p_2}}{|p_1 - p_2|}$$

$$= E_R Z_{eff} \cdot \frac{1}{16\pi^2} \int d\Omega_1 p_1^2 dp_1 \frac{d\Omega_2 \sin\theta_2 d\theta_2 dp_2 e^{-p_1 - p_2}}{\sqrt{p_1^2 + p_2^2 - 2p_1 p_2 \cos\theta_2}}$$

$$= E_R Z_{eff} \cdot \frac{1}{2} \int \frac{p_1^2 dp_1 p_2^2 dp_2 e^{-p_1 - p_2}}{p_1 p_2} \left[(p_1^2 + p_2^2 - 2p_1 p_2 \cos\theta_2)^{1/2} \right]_0^\pi$$

$$= E_R Z_{eff} \cdot \frac{1}{2} \int p_1 dp_1 p_2 dp_2 e^{-p_1 - p_2} \left(p_1 + p_2 - |p_1 - p_2| \right)$$

$$\begin{array}{ll} 2p_2 & \text{if } p_2 < p_1 \\ 2p_1 & \text{if } p_2 > p_1 \end{array}$$

now just a sum of two ordinary double integrals. Answer is $\frac{5}{4} \cdot 2$

$$= \cancel{E_R} Z_{eff}$$

$$= E_R Z_{eff} \frac{5}{4}$$

So altogether we have

$$E_T = -2E_R \left(Z_{eff}^2 - 2Z_{eff}(Z_{eff} - 2) - \frac{5}{8} Z_{eff} \right)$$

minimizing this we find $Z_{eff} = 2 - \frac{5}{16}$

this is the effect of screening

and

$$E_T = -77.5 \text{ eV}$$

which compares well with $-24.6 - 54.4 = -79 \text{ eV}$ total ionisation energy
 1st electron 2nd electron

Exchange Symmetry

So far in discussing Helium we have ignored the fact, which you already know, that identical electrons cannot occupy the same quantum state — this is the Pauli Exclusion Principle.

This is a special case of a more general exchange principle which states

1. Wave functions, or states, of identical bosons — particles with integer spin = 0, 1, 2, ... — must be symmetric under the exchange of particles.
2. Wave functions, or states, of identical fermions — particles with half-integer spin = $\frac{1}{2}$, $\frac{3}{2}$, ... — must be antisymmetric under the exchange of particles.

Where does this come from? Consider a state

of two identical particles
 $|1, 2\rangle$ ← labels of particles

and swap the labels

$$S |1,2\rangle = |2,1\rangle$$

\nearrow
operator that swaps labels.

Now the particles are identical so we cannot tell the difference between the state $|1,2\rangle$ and the state $|2,1\rangle$ - there is absolutely no measurement we can make which will

come out different for these two states. It

follows that $|2,1\rangle$ and $|1,2\rangle$ must be the same up to a constant phase factor.

We can find out what that factor is by acting with S again

$$S^2 |1,2\rangle = S |2,1\rangle = |1,2\rangle$$

so the eigenvalues of S^2 are 1 and hence

the eigenvalues of S are either

+1 state symmetric under exchange

-1 state anti-symmetric under exchange.

Ultimately it is then an experimental question as to which particle types have which symmetry

Now let's look at some examples.

A Two spin-0 bosons trapped in an SHO potential

The lowest energy state possible for two particles is when they are both in the ground state so it has wavefunction

$$\Phi(x_1, x_2) = \phi_0(x_1) \phi_0(x_2) \quad E_{00} = \hbar\omega\left(\frac{1}{2} + 0 + \frac{1}{2} + 0\right) = \hbar\omega$$

Note that under $1 \leftrightarrow 2$

$$\begin{aligned} \Phi(x_1, x_2) &\rightarrow \phi_0(x_2) \phi_0(x_1) = \phi_0(x_1) \phi_0(x_2) \\ &= \Phi(x_1, x_2) \end{aligned}$$

so Φ is symmetric. Therefore it \longrightarrow

obeys the EP. When we look at the first excited state there seem to be two possibilities

$$\begin{array}{ll} \phi_0(x_1) \phi_1(x_2) & E_{01} = \hbar\omega(0 + \frac{1}{2} + 1 + \frac{1}{2}) \\ \text{or } \phi_0(x_2) \phi_1(x_1) & = 2\hbar\omega \end{array}$$

~~B~~ \otimes

but neither of these is symmetric under $1 \leftrightarrow 2$; only the combination

$$(\phi_0(x_1) \phi_1(x_2) + \phi_0(x_2) \phi_1(x_1)) / \sqrt{2}$$

is allowed. So in fact the first excited state is not degenerate (unlike the case of two different spin 0 bosons when both the wave functions \otimes are allowed).

Second excited state is a similar story. Now

$$\phi_1(x_1) \phi_2(x_2) \quad \checkmark$$

$$\phi_0(x_1) \phi_2(x_2)$$

$$\phi_0(x_2) \phi_2(x_1)$$

} sum is symmetric

all have energy $3\hbar\omega$ but only two combinations are symmetric.

B Two spin-1/2 fermions in an SHO potential

Now the wave-fn is a product of space dependent and spin dependent pieces. For the ground state

$$\phi_0(x_1) \phi_0(x_2)$$

is necessarily symmetric so the spin part must be

$$\left(\begin{array}{c} | \uparrow \rangle \\ \uparrow \\ \text{particle 1} \end{array} | \downarrow \rangle - | \downarrow \rangle | \uparrow \rangle \right) / \sqrt{2} \quad \underline{\text{antisymmetric}}$$

particle 2

This has $S_z = 0$ and $S = 0$ (see JMR's notes). So the ground state is

$$| 0 \rangle | 0 \rangle \left(\begin{array}{c} | \uparrow \rangle | \downarrow \rangle \\ \text{particle 2 spin} \\ | \downarrow \rangle | \uparrow \rangle \end{array} \right) / \sqrt{2}$$

particle 1 space particle 2 space particle 1 spin

For the 1st excited state we have two possibilities

symmetric space \times antisymmetric spin

$$\left(| 0 \rangle | 1 \rangle + | 1 \rangle | 0 \rangle \right) / \sqrt{2} \quad \left(| \uparrow \rangle | \downarrow \rangle - | \downarrow \rangle | \uparrow \rangle \right) / \sqrt{2} \quad S=0$$

or antisym space \times symmetric spin

$$\left(| 0 \rangle | 1 \rangle - | 1 \rangle | 0 \rangle \right) / \sqrt{2} \quad \left\{ \begin{array}{l} | \uparrow \rangle | \uparrow \rangle \\ (| \uparrow \rangle | \downarrow \rangle + | \downarrow \rangle | \uparrow \rangle) / \sqrt{2} \\ | \downarrow \rangle | \downarrow \rangle \end{array} \right. \quad S=1$$

Note that the Pauli Principle follows from the antisymmetry — an antisymmetric state formed from an arbitrary state

$$(|n, m\rangle - |m, n\rangle) / \sqrt{2}$$

$$\begin{array}{cc} \uparrow & \uparrow \\ p_{1l1} & p_{1l2} \end{array}$$

will automatically vanish if $m = n$.