

Further Quantum Mechanics: Problem Set 3.

Trinity term weeks 1-3

Qu 1. A particle with mass m , charge q and momentum \hat{p} moves in a magnetic field described by the vector potential \mathbf{A} . The Hamiltonian is

$$H = \frac{1}{2m} (\hat{p} - q\mathbf{A})^2.$$

The wavefunction $\psi(\mathbf{r}, t)$ satisfies the time-dependent Schrödinger equation with this Hamiltonian, and the probability density $\rho \equiv |\psi(\mathbf{r}, t)|^2$ obeys the continuity equation

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{j}.$$

$$\begin{aligned} \hat{H}\psi &= i\hbar \frac{\partial \psi}{\partial t} \\ \hat{H}\psi^* &= -i\hbar \frac{\partial \psi^*}{\partial t} \end{aligned}$$

Show from the time-dependent Schrödinger equation that

$$\mathbf{j} = \frac{\hbar}{2im} \{\psi^* \nabla \psi - \psi \nabla \psi^*\} - \frac{q}{m} |\psi|^2 \mathbf{A}.$$

The particle moves in the x - y plane with a uniform magnetic field in the z -direction, represented by

$$\mathbf{A} = \frac{B}{2} (-y, x, 0).$$

Show that the function

$$\varphi(x, y) = \exp(-[x^2 + y^2]/4\ell_B^2)$$

is an eigenfunction for a suitably chosen value for ℓ_B . Find this value of ℓ_B and the energy. Evaluate \mathbf{j} for this state. Discuss the physical significance of your results.

Qu 2. The Hamiltonian for a hydrogen atom in a uniform magnetic field with flux density B along z is approximately

$$H = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar e}{2m} (BL_z + \sigma_z) \quad ? \quad \text{LBS?}$$

where $\hbar L_z$ and $(\hbar/2)\sigma_z$ are operators representing respectively the z -components of the orbital and spin angular momentum of the electron.

$$2S = \frac{\hbar}{2} \sigma_z \quad B$$

Discuss how the terms involving B arise. What is the justification for omitting a term in B^2 ?

What quantum numbers label eigenstates of this Hamiltonian?

Draw a diagram showing the energies of a representative selection of these eigenstates as a function of magnetic field.

(Questions 3 and 4 are adapted from Shankar)

Qu 3. A system has n non-degenerate energy levels that may each be occupied by a single particle. These states account for all the degrees of freedom of the particle – both orbital and (if relevant) spin. These levels are occupied by a number p of similar non-interacting particles. How many distinct states are there for the p -particle system in the following cases:

- (i) if the particles are distinguishable;
- (ii) if the particles are identical fermions and $p = n$;
- (iii) if the particles are identical bosons and $p = n = 2$;
- (iv) if the particles are identical bosons and $p = n = 3$?

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12121

Qu 4. Consider two identical, non-interacting particles, each of mass m , with coordinates x_1, x_2 . They are confined to a box of length L , so that $0 \leq x_1, x_2 \leq L$.

Suppose the particles are identical spin-zero bosons. What is the wavefunction $\psi(x_1, x_2)$ if the system is in an eigenstate with total energy: (i) $\hbar^2\pi^2/mL^2$, or (ii) $5\hbar^2\pi^2/2mL^2$?

Suppose alternatively that the particles are identical spin-half fermions: for the same values of total energy write down a complete set of possible wavefunctions, as products of space and spin factors. ?

Qu 5. He: ionisation energy. The ionization energy is the energy required to remove one electron from an atom or ion in its ground state, leaving it in the ground state of the next higher ionization stage. (The energy is often quoted in eV and referred to as an ionization potential.)

If we make the (poor) approximation of ignoring the electron-electron repulsion altogether, what value (in eV) is obtained for the ionization potential of the ground state in helium? How much additional energy would then be required to remove the second electron? Assuming these estimates have been made as accurately as reasonably possible within their respective assumptions, state the degree of accuracy of each of these two results (i.e. how close they may be expected to be to the true first and second ionization energies for helium.)

To do better, use the variational method. Using hydrogen-like wavefunctions for both electrons: $\psi_{1s} = \sqrt{Z^3/\pi a_0^3} \exp(-Zr/a_0)$, show that

$$\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle = \frac{2Z}{a_0}.$$

Using also $\langle p_1^2 + p_2^2 \rangle = 2Z^2\hbar^2/(a_0^2)$ and $\langle 1/r_{12} \rangle = 5Z/(8a_0)$, show that the mean energy as a function of an effective nuclear charge Z is

$$E(Z) = -2E_R (4Z - Z^2 - 5Z/8).$$

Complete the variational procedure, and hence obtain an upper limit for the ground state energy, and a lower limit for the ionization energy of helium.

Qu 6. Two of the energy levels in Helium have the standard notation $1s2s^1S_0$ and $1s2s^3S_1$. Explain every part of this notation. The difference in the notation for the two levels stresses a difference in the spin part of the wavefunction, but the spatial part is also different: what is the important distinguishing feature between the two spatial wavefunctions?

To: Felix Tennie

Further Quantum Mechanics 3

Ziyan Li

$$1. \hat{H} = \frac{1}{2m} (\hat{p} - q\hat{A})^2 = \frac{\hat{p}^2}{2m} - \frac{q}{2m} (\hat{p} \cdot \hat{A} + \hat{A} \cdot \hat{p}) + \frac{q^2 A^2}{2m}$$

$$\text{TDSE} \quad \hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}, \quad \hat{p} = -i\hbar \nabla$$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + \frac{i\hbar q}{2m} (\nabla \cdot (A\psi) + A \cdot \nabla \psi) + \frac{q^2 A^2}{2m} \psi \quad (1)$$

$$\psi^* (1) \Rightarrow i\hbar \psi^* \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \psi^* \nabla^2 \psi + \frac{i\hbar q}{2m} (\psi^* \nabla \cdot (A\psi) + \psi^* A \cdot \nabla \psi) + \frac{q^2 A^2}{2m} \psi^* \psi \quad (2)$$

Complex conjugate of (2) \Rightarrow

$$-i\hbar \psi \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \psi \nabla^2 \psi^* - \frac{i\hbar q}{2m} (\psi \nabla \cdot (A\psi^*) + \psi A \cdot \nabla \psi^*) + \frac{q^2 A^2}{2m} \psi \psi^* \quad (3)$$

$$(2) - (3) \Rightarrow$$

$$i\hbar \left(\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right) = -\frac{\hbar^2}{2m} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*)$$

$$+ \frac{i\hbar q}{2m} (\psi^* \nabla \cdot (A\psi) + \psi^* A \cdot \nabla \psi + \psi \nabla \cdot (A\psi^*) + \psi A \cdot \nabla \psi^*) + \frac{q^2 A^2}{2m} (\psi^* \psi - \psi \psi^*) \quad (4)$$

Examine each part of (4)

$$\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} = \frac{\partial}{\partial t} (\psi^* \psi) = \frac{\partial |\psi|^2}{\partial t} = \frac{\partial \rho}{\partial t} \quad (5)$$

Consider scalar ϕ and vector \underline{F}

$$\underline{\nabla} \cdot (\phi \underline{F}) = \partial_i (\phi F)_i = \partial_i (\phi F_i) = \phi \partial_i F_i + (\partial_i \phi) F_i$$

$$= \phi (\underline{\nabla} \cdot \underline{F}) + (\underline{\nabla} \phi) \cdot \underline{F}$$

$$\rightarrow \psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* = \psi^* (\underline{\nabla} \cdot \underline{\nabla} \psi) - \psi (\underline{\nabla} \cdot \underline{\nabla} \psi^*)$$

$$= (\psi^* (\underline{\nabla} \cdot \underline{\nabla} \psi) + \underline{\nabla} \psi \cdot \underline{\nabla} \psi^*) - (\psi (\underline{\nabla} \cdot \underline{\nabla} \psi^*) + \underline{\nabla} \psi^* \cdot \underline{\nabla} \psi)$$

$$= \underline{\nabla} \cdot (\psi^* \underline{\nabla} \psi) - \underline{\nabla} \cdot (\psi \underline{\nabla} \psi^*)$$

$$= \underline{\nabla} \cdot (\psi^* \underline{\nabla} \psi - \psi \underline{\nabla} \psi^*) \quad \textcircled{5}$$

$$\rightarrow \nabla \cdot (\psi^* \underline{A} \psi) + \cancel{\psi^* \underline{A} \psi} \psi^* \underline{A} \cdot (\underline{\nabla} \psi) + \psi \underline{\nabla} \cdot (\underline{A} \psi^*) + \psi \underline{A} \cdot (\underline{\nabla} \psi^*)$$

$$= \psi^* \psi (\underline{\nabla} \cdot \underline{A}) + \psi^* \underline{A} \cdot (\underline{\nabla} \psi) + \psi^* \underline{A} \cdot (\underline{\nabla} \psi)$$

$$+ \psi \psi^* \underline{\nabla} \cdot \underline{A} + \psi \underline{A} \cdot (\underline{\nabla} \psi^*) + \psi \underline{A} \cdot (\underline{\nabla} \psi^*)$$

$$= 2 (\psi^* \psi (\underline{\nabla} \cdot \underline{A}) + \psi^* \underline{A} \cdot (\underline{\nabla} \psi) + \psi \underline{A} \cdot (\underline{\nabla} \psi^*))$$

$$= 2 (\psi^* \psi (\underline{\nabla} \cdot \underline{A}) + \underline{A} \cdot \underline{\nabla} (\psi^* \psi))$$

$$= 2 \underline{\nabla} \cdot (\psi^* \psi \underline{A}) = 2 \underline{\nabla} \cdot (|\psi|^2 \underline{A}) \quad \textcircled{7}$$

Substitute $\textcircled{5}$, $\textcircled{6}$, $\textcircled{7}$ into $\textcircled{4}$ we get

$$i\hbar \frac{\partial \rho}{\partial t} = -\frac{\hbar^2}{2m} \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*) + \frac{i\hbar q}{2m} \cdot 2 \cdot \nabla \cdot (\psi^* \underline{A})$$

$$\rightarrow \frac{\partial \rho}{\partial t} = -\nabla \cdot \left\{ \frac{\hbar^2}{2im} [\psi^* \nabla \psi - \psi \nabla \psi^*] - \frac{q}{m} |\psi|^2 \underline{A} \right\}$$

$$\therefore \frac{\partial \rho}{\partial t} = -\nabla \cdot \underline{j}$$

$$\therefore \underline{j} = \frac{\hbar^2}{2im} [\psi^* \nabla \psi - \psi \nabla \psi^*] - \frac{q}{m} |\psi|^2 \underline{A} \quad \text{(Q.E.D.)}$$

For $\underline{A} = \frac{B}{2} (-y, x, 0)$. $A_x = -\frac{By}{2}$, $A_y = \frac{Bx}{2}$, $A_z = 0$

trial solution $\psi(x, y) = \exp(-[x^2 + y^2]/4l_B^2)$

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{1}{4l_B^4} (x^2 + y^2) \exp(-(x^2 + y^2)/4l_B^2)$$

$$= \frac{1}{4l_B^2} \exp(-(x^2 + y^2)/4l_B^2)$$

$$\nabla \psi = \left(\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, 0 \right)$$

$$= (-x, -y, 0) \left(\frac{1}{2l_B^2} \right) \exp(-(x^2 + y^2)/4l_B^2)$$

$$\underline{A} \cdot \nabla \psi = \frac{xyB}{4l_B^2} (1, -1, 0) \exp(-(x^2 + y^2)/4l_B^2)$$

$$\frac{xyB}{4l_B^2} \exp(-(x^2 + y^2)/4l_B^2) (xy - xy) = 0$$

$$\psi = \frac{B}{2} (-y, x, 0) \exp(-\frac{x^2+y^2}{4l_B^2})$$

$$\begin{aligned} \nabla \cdot (\psi) &= \frac{\partial(\psi)_x}{\partial x} + \frac{\partial(\psi)_y}{\partial y} \\ &= \frac{B}{2} (-y) \left(-\frac{x}{2l_B^2} e^{-\frac{x^2+y^2}{4l_B^2}} \right) + \frac{B}{2} (x) \left(-\frac{y}{2l_B^2} e^{-\frac{x^2+y^2}{4l_B^2}} \right) \\ &= 0 \end{aligned}$$

$$\Delta^2 \psi = \cancel{(x^2+y^2) \frac{B^2}{4}} (x^2+y^2) \frac{B^2}{4} \exp(-\frac{x^2+y^2}{4l_B^2})$$

$$\therefore \cancel{\nabla^2 \psi = E \psi}$$

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m} \left(\frac{1}{4l_B^2} (x^2+y^2) \right) - \frac{\hbar^2}{2m} \left(\frac{-1}{l_B^2} \right) + \frac{q^2 B^2}{4(2m)} \right] \psi$$

$$= \left[\frac{1}{4} (q^2 B^2 - \frac{\hbar^2}{l_B^2}) (x^2+y^2) + \frac{\hbar^2}{2ml_B^2} \right] \psi$$

$$\therefore \text{When } q^2 B^2 - \frac{\hbar^2}{l_B^2} \Rightarrow \boxed{l_B = \sqrt{\frac{\hbar}{qB}}}, \text{ the}$$

coefficient in front of ψ is constant and is equal to

$$\frac{\hbar^2}{2ml_B^2} = \frac{\hbar^2}{2m} \frac{qB}{\hbar} = \cancel{\frac{\hbar qB}{2m}} \frac{\hbar qB}{2m}$$

$$\therefore \text{energy level } E_0 = \boxed{\frac{\hbar qB}{2m}}$$

\rightarrow in this case ψ is an eigenfunction of \hat{H}

$$\therefore \underline{j} = \frac{\hbar}{2im} \{ \psi^* \nabla \psi - \psi \nabla \psi^* \} - \frac{q}{m} |\psi|^2 \underline{A}$$

and $\psi(x, y) = \exp(-x^2 + y^2 / 4l_B^2)$ is real

$$\therefore \psi^* = \psi$$

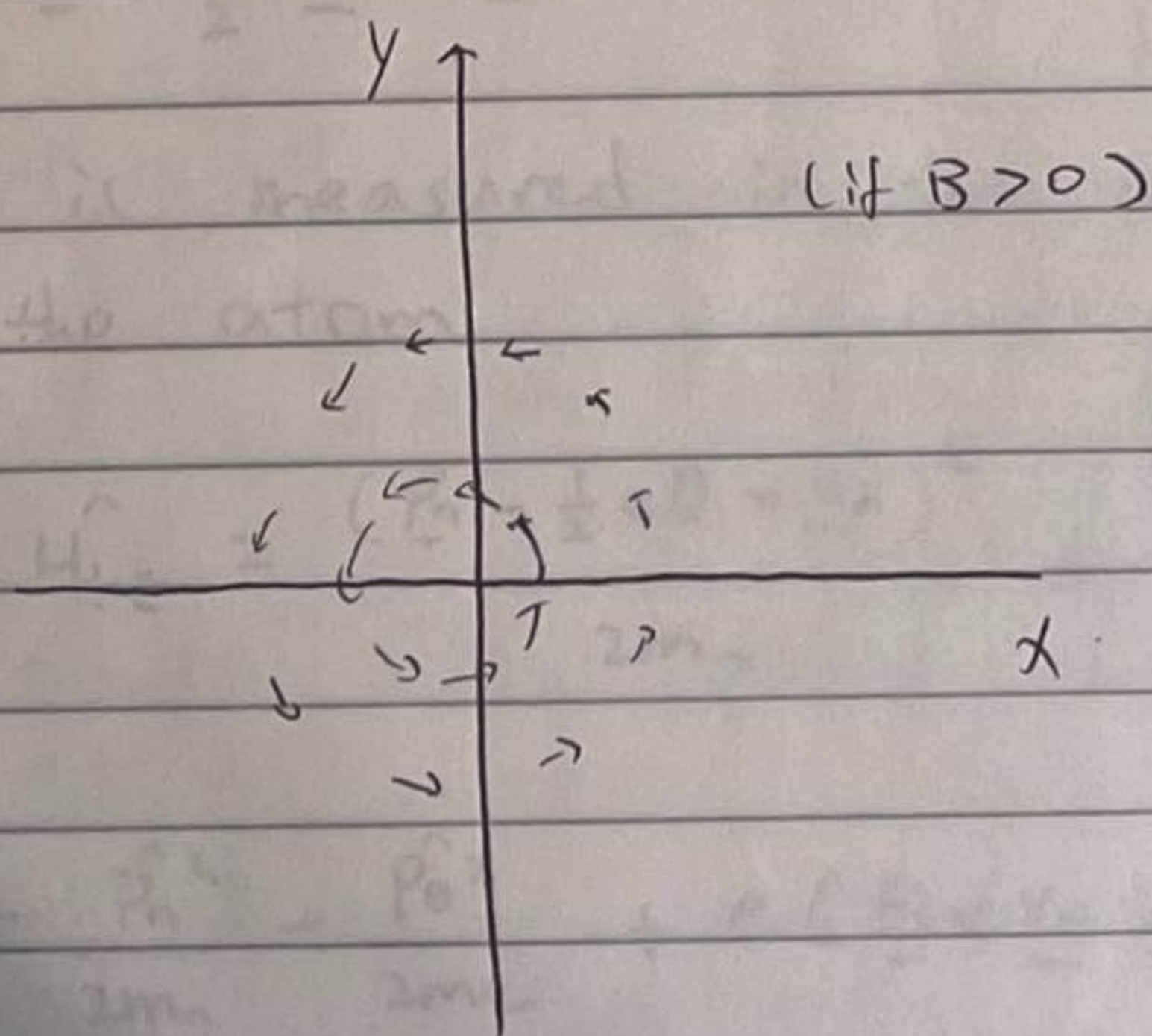
$$\therefore \underline{j} = -\frac{q}{m} |\psi|^2 \underline{A}$$

$$= -\frac{q}{m} \exp(-x^2 + y^2 / 4l_B^2) \times \frac{B}{2} (-y, x, 0)$$

let $R = \sqrt{x^2 + y^2}$, $\hat{e}_\phi = (-\sin\theta, \cos\theta, 0)$, then

$$\begin{aligned} \underline{A} &= (-y, x, 0) = R \left(-\frac{y}{R}, \frac{x}{R}, 0 \right) \\ &= R (-\sin\theta, \cos\theta, 0) = R \hat{e}_\phi \end{aligned}$$

$$\rightarrow \underline{j} = \boxed{-\frac{q}{m} e^{-R^2/4l_B^2} \frac{B}{2R} \hat{e}_\phi}$$



If $B > 0$ current runs counterclockwise

if $B < 0$ current runs clockwise

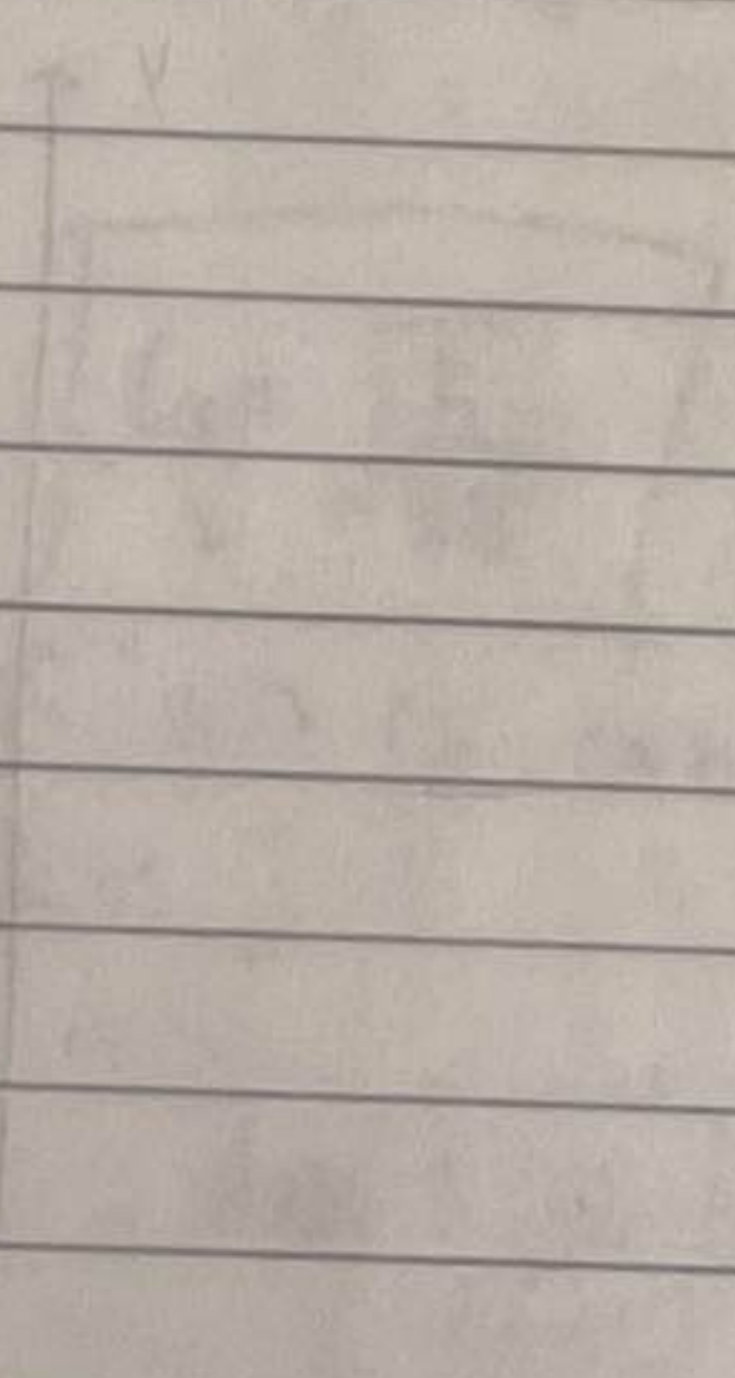
around the gyrocentre $(x, y) = (0, 0)$

This resembles the classical picture in which ~~the current~~ a charged particle goes into ~~a~~ a magnetic field and undergoes circular (or helical) motion

$$A^2(\mathbf{r}) \frac{p}{\hbar} = \dots$$

$$\frac{d\mathbf{r}}{dt} = \frac{1}{\hbar} \nabla \phi$$

$$\frac{d\mathbf{r}}{dt} = \frac{1}{\hbar} \nabla \left(\frac{1}{2} m v^2 + \dots \right)$$



If B_{z0} current runs counter-clockwise
 If B_{z0} current runs clockwise
 around the z-axis

2. The Hamiltonian in a magnetic field for a charged particle is

$$\hat{H} = \frac{1}{2m} (\hat{\underline{P}} - Q\hat{\underline{A}})^2$$

Apply this formula to the ~~proton~~^{nucleus} and electron in the hydrogen atom:

the kinetic energy part of the Hamiltonian is

$$\hat{H}_{KE} = \frac{1}{2m_n} (\hat{\underline{P}}_n - e\hat{\underline{A}})^2 + \frac{1}{2m_e} (\hat{\underline{P}}_e + e\hat{\underline{A}})^2$$

\therefore the magnetic field \underline{B} is uniform so

we choose the vector potential to be

$$\underline{A} = \frac{1}{2} \underline{B} \times \underline{x} \quad (\text{so } \underline{B} = \nabla \times \underline{A})$$

\underline{x} is measured in the centre of mass coordinate of the atom.

$$\rightarrow \hat{H}_{KE} = \frac{(\hat{\underline{P}}_n - \frac{1}{2} e \underline{B} \times \underline{x}_n)^2}{2m_n} + \frac{(\hat{\underline{P}}_e + \frac{1}{2} e \underline{B} \times \underline{x}_e)^2}{2m_e}$$

$$= \frac{\hat{P}_n^2}{2m_n} + \frac{\hat{P}_e^2}{2m_e} + e \left(\underline{B} \times \underline{x}_e \cdot \frac{\hat{\underline{P}}_e}{2m_e} - \underline{B} \times \underline{x}_n \cdot \frac{\hat{\underline{P}}_n}{2m_n} \right) + O(|B|^2) \quad (1)$$

the terms of order $|B|^2$ can be neglected because when the field is weak enough for the $O(|B|)$ to be small compare to

the terms in the gross-structure Hamiltonian,
 (for ~~as~~ we want to use perturbation theory,
 the $O(|B|^2)$ terms must be negligible

Also: $\nabla \hat{p} \cdot \underline{B} \times \underline{x} = \underline{B} \times \underline{x} \cdot \nabla \hat{p}$ (we have used)

this is because $\underline{B} \times \underline{x} = \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix} \times \begin{pmatrix} x \\ y \\ z \end{pmatrix}$
 $= \begin{pmatrix} B_y z - B_z y \\ B_z x - B_x z \\ B_x y - B_y x \end{pmatrix}$

this is because

$\therefore \underline{B} \times \underline{x} = \epsilon_{ijk} B_j x_k$

$[\hat{p}_i, (\underline{B} \times \underline{x})_j] = [\hat{p}_i, \epsilon_{ijk} B_j x_k]$

$= \epsilon_{ijk} ([\hat{p}_i, B_j] x_k + B_j [\hat{p}_i, x_k])$

$\because B_j$ is constant $\therefore [\hat{p}_i, B_j] = 0$

$[\hat{p}_i, x_k] = -i\hbar \delta_{ik} \quad \therefore i \neq k \quad \therefore [\hat{p}_i, x_k] = 0$

\rightarrow we can safely write equation ①

\therefore The perturbation caused by the magnetic field is

$\hat{H}_B = e\underline{B} \cdot \left(\underline{x}_e \times \frac{\hat{p}_e}{2m_e} - \underline{x}_n \times \frac{\hat{p}_n}{2m_n} \right)$

Define $\underline{X} \equiv \frac{m_e \underline{x}_e + m_n \underline{x}_n}{m_e + m_n}$, $\underline{r} \equiv \underline{x}_e - \underline{x}_n$

then $\underline{x}_e = \underline{X} + \frac{m_n}{m_e + m_n} \underline{r}$, $\underline{x}_n = \underline{X} - \frac{m_e}{m_e + m_n} \underline{r}$

$$\frac{\partial}{\partial \underline{x}_e} = \frac{\partial \underline{X}}{\partial \underline{x}_e} \cdot \frac{\partial}{\partial \underline{X}} + \frac{\partial \underline{r}}{\partial \underline{x}_e} \cdot \frac{\partial}{\partial \underline{r}} = \frac{m_e}{m_e + m_n} \frac{\partial}{\partial \underline{X}} + \frac{\partial}{\partial \underline{r}}$$

$$\therefore \hat{P}_e = -i\hbar \frac{\partial}{\partial \underline{x}_e}, \quad \hat{P}_n = -i\hbar \frac{\partial}{\partial \underline{x}_n}, \quad \hat{P}_X = -i\hbar \frac{\partial}{\partial \underline{X}}, \quad \hat{P}_r = -i\hbar \frac{\partial}{\partial \underline{r}}$$

$$\therefore \hat{P}_e = \frac{m_e}{m_e + m_n} \hat{P}_X + \hat{P}_r, \quad \hat{P}_n = \frac{m_n}{m_e + m_n} \hat{P}_X - \hat{P}_r$$

$$\rightarrow \hat{H}_B = \frac{1}{2} e \underline{B} \cdot \left(\frac{\underline{x}_e \times \hat{P}_e}{m_e} - \frac{\underline{x}_n \times \hat{P}_n}{m_n} \right)$$

$$= \frac{1}{2} e \underline{B} \cdot \left\{ \left(\underline{X} + \frac{m_n}{m_e + m_n} \underline{r} \right) \times \left(\frac{1}{m_e + m_n} \hat{P}_X + \frac{1}{m_e} \hat{P}_r \right) \right.$$

$$\left. - \left(\underline{X} - \frac{m_e}{m_e + m_n} \underline{r} \right) \times \left(\frac{1}{m_e + m_n} \hat{P}_X - \frac{1}{m_n} \hat{P}_r \right) \right\}$$

$$= \frac{1}{2} e \underline{B} \cdot \left\{ \left(\frac{1}{m_e} + \frac{1}{m_n} \right) \underline{X} \times \hat{P}_r + \frac{1}{m_e + m_n} \underline{r} \times \hat{P}_X \right.$$

$$\left. + \frac{m_n/m_e - m_e/m_n}{m_e + m_n} \underline{r} \times \hat{P}_r \right\}$$

We require matrix element of \hat{H}_B to be

$$\langle n' \underline{r}' | \hat{P}_X | n \underline{r} \rangle \quad \text{where state}$$

$|P_X\rangle |n \underline{r}\rangle$ consists of the momentum

eigenstate of centre of mass $\rightarrow |P_X\rangle$,
and the usual ~~hydro~~ rest frame

hydrogen eigenstate $|n\ell m\rangle$. We want to be in the rest frame of the centre of mass of the atom.

Because of uncertainty principle we cannot require $\underline{x} = 0$ and $\underline{P}_x = 0$ at the same time, but we can require

$$\langle \underline{x} \rangle = 0 \quad \text{and} \quad \langle \underline{P}_x \rangle = 0 \quad \text{for all eigenstates } |P_x\rangle$$

Consequently the terms involving $\underline{x} \times \underline{P}_r$ and $\underline{r} \times \underline{P}_x$ vanish when taking matrix elements against $|P_x\rangle |n\ell m\rangle$

\therefore we can write H_B with the only term that actually contributes to the matrix elements

$$\begin{aligned} \rightarrow \hat{H}_B &= \frac{1}{2} e \underline{B} \cdot \frac{m_n/m_e - m_e/m_n}{m_e + m_n} \underline{r} \times \underline{P}_r \\ &= \frac{1}{2} e \underline{B} \cdot \frac{m_n^2 - m_e^2}{(m_n + m_e)m_n m_e} \underline{r} \times \underline{P}_r = \frac{e(m_n - m_e)}{2m_e m_n} \underline{B} \cdot \underline{r} \times \underline{P}_r \\ &\approx \frac{e\hbar}{2m} \underline{B} \cdot \underline{L} \quad (\hbar \underline{L} = \underline{r} \times \underline{P}_r) \end{aligned}$$

We can also add the Zeeman spin

Hamiltonian to the original Hamiltonian

$$H_{Zsh} = \frac{e\hbar}{m_e} \underline{S} \cdot \underline{B} = \frac{e\hbar}{2m_e} \underline{\sigma} \cdot \underline{B}$$

If we orient the ~~xyz~~ coordinates so \underline{B} is along z , then

$$H_B = \frac{e\hbar}{2m_e} B L_z, \quad H_{Zsh} = \frac{e\hbar}{2m_e} B \sigma_z$$

→ Add to the original Hydrogen Hamiltonian we have

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar e}{2m} B (L_z + \sigma_z)$$

→ Quantum numbers labelling this Hamiltonian

are n, l, m_l, s, m_s . State $|n, l, m_l, s, m_s\rangle = |n, l, m_l\rangle |s, m_s\rangle$

$$\hat{H} = \hat{H}_{gross} + \frac{\hbar e}{2m} B (\hat{L}_z + \hat{\sigma}_z)$$

→ $z=1$ in this case.

$$\hat{H} |n, l, m_l\rangle |s, m_s\rangle = \left(-\frac{\hbar^2 R^2}{n^2} + \frac{\hbar e}{2m} B m_l + \frac{\hbar e}{2m} B (2m_s) \right) |n, l, m_l\rangle |s, m_s\rangle$$

$$\hat{H}_{gross} |n, l, m_l\rangle = E_{gross} |n, l, m_l\rangle$$

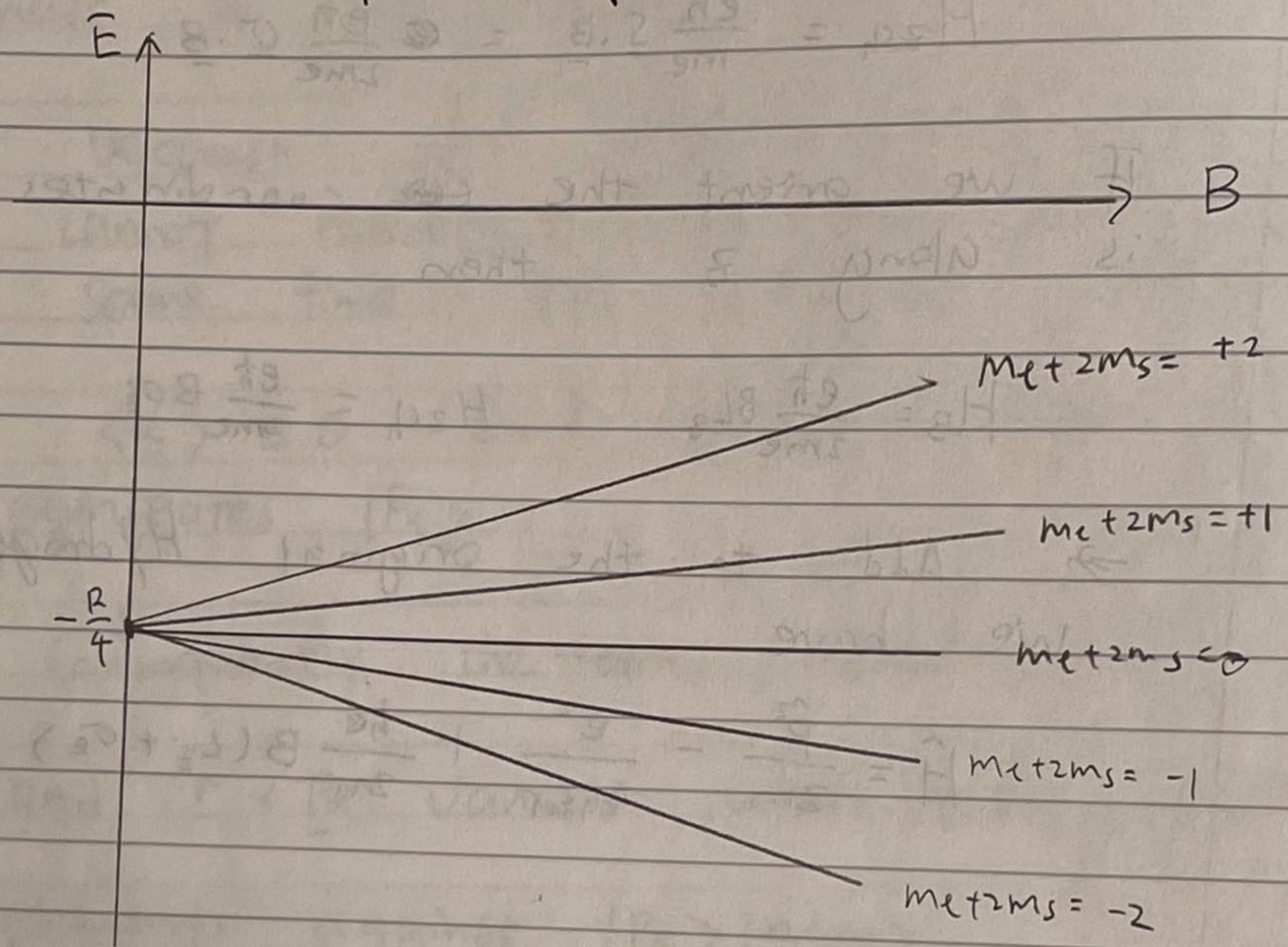
$$\hat{L}_z |n, l, m_l\rangle = m_l \hbar |n, l, m_l\rangle$$

$$\frac{\hbar}{2} \hat{\sigma}_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle$$

$$\rightarrow \hat{\sigma}_z |s, m_s\rangle = 2m_s |s, m_s\rangle$$

$$\rightarrow E = \bar{E}_{\text{gross}} + \frac{\hbar e}{2m} B (m_l + 2m_s)$$

$\hat{\uparrow}$ independent of B



If $n=2$

$$l=1 \rightarrow m_l = -1, 0, 1$$

$$s = \frac{1}{2} \rightarrow m_s = -\frac{1}{2}, \frac{1}{2}$$

$$m_l + 2m_s = -2, -1, 0, 1, 2$$

$$\bar{E}_{\text{gross}} = -\frac{R}{n^2} = -\frac{R}{4}$$

3. (i) distinguishable particles

Since the n energy levels are non-degenerate

Each particle has n distinct states available for it to occupy

There are P distinct particles

→ total number of states of the system

$$= \cancel{P^n} = n^P \quad \checkmark$$

(ii) identical fermions, $P=n$

fermions have to obey the Pauli exclusion principle

No ~~two~~ more than one fermions can be in the same quantum state.

∴ n states available for $P=n$ particles

∴ only $\boxed{1}$ single state available for

the entire system

(general formula for fermions is $\frac{n!}{P!(n-P)!}$)

(iii) identical bosons $p=n=2$

particles are indistinguishable but ~~can occupy~~
one state can have more than one particles.

Possibilities : (E_1, E_2 are energies)

① 1 in E_1 , 1 in E_2

② both in E_1

③ both in E_2

∴ 3 distinct states ✓

(iv) possibilities

① all three in E_1

② 2 in E_1 , 1 in E_2

③ 2 in E_1 , 1 in E_3

④ 1 in E_1 , 2 in E_2

⑤ 1 in E_1 , 1 in E_2 , 1 in E_3

⑥ 1 in E_1 , 2 in E_3

⑦ all 3 in E_2

⑧ 2 in E_2 , 1 in E_3

⑨ 1 in E_2 , 2 in E_3

⑩ all 3 in E_3 ✓

∴ 10 distinct states

(general formula for bosons is $\frac{(n+p-1)!}{p!(n-1)!}$)

4. → Because the particles are non-interacting, we can express the combined state of the system as superposition of products of the eigenstates of particles 1 and 2 individually in the box.

→ The eigenstates of combined system is formed by the products of the eigenstates of the particles 1 and 2.

→ And the energy eigenvalues are the sum of the ~~the~~ individual energies of particles 1 and 2.

We know from particle in a box :

$$\Psi_{n_1}(x_1) = \sqrt{\frac{2}{L}} \sin\left(\frac{n_1 \pi x_1}{L}\right) \rightarrow E_1 = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2$$

$$\Psi_{n_2}(x_2) = \sqrt{\frac{2}{L}} \sin\left(\frac{n_2 \pi x_2}{L}\right) \rightarrow E_2 = \frac{\hbar^2 \pi^2}{2mL^2} n_2^2$$

Combined eigenstate :

$$\Psi_{n_1, n_2}(x_1, x_2) = \frac{2}{L} \sin\left(\frac{n_1 \pi x_1}{L}\right) \sin\left(\frac{n_2 \pi x_2}{L}\right)$$

→ The corresponding energy is

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2)$$

Bosons \circ (spin 0 Bosons)

(i) If $E = \frac{\hbar^2 \pi^2}{mL^2} \approx$, then we have

$n_1 = n_2 = 1$ is the only ~~possibility~~ possibility

$$\cancel{\psi_{(1,1)}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_1(x_1) \psi_1(x_2) + \psi_1(x_2) \psi_1(x_1))}$$

\approx The system has wavefunction:

$$\psi_{(1,1)}(x_1, x_2) = \psi_1(x_1) \psi_1(x_2)$$

$$\cancel{= \frac{2}{L} \sin^2 \left(\frac{\pi x}{L} \right)}$$

$$= \boxed{\frac{2}{L} \sin\left(\frac{\pi x_1}{L}\right) \sin\left(\frac{\pi x_2}{L}\right)}$$

(ii) If $E = \frac{5\hbar^2 \pi^2}{2mL^2}$, then we have ~~an~~ a

~~(n₁, n₂) =~~ ~~antisymmetrical~~ superposition of

$(n_1, n_2) = (1, 2)$ and $(n_1, n_2) = (2, 1)$ because

$$n_1^2 + n_2^2 = 5$$

$$\rightarrow \psi_{(1,2)}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_1(x_1) \psi_2(x_2) + \psi_2(x_1) \psi_1(x_2))$$

$$\rightarrow \psi_{(1,2)}(x_1, x_2) = \boxed{\frac{\sqrt{2}}{L} \left(\sin\frac{\pi x_1}{L} \sin\frac{2\pi x_2}{L} + \sin\frac{2\pi x_1}{L} \sin\frac{\pi x_2}{L} \right)}$$

For spin $-\frac{1}{2}$ Fermions \circ :

the total wavefunction ~~is~~ should be antisymmetric with respect to the exchange of particles 1 and 2

So there are two cases

① space factor ~~is~~ antisymmetric, spin factor symmetric

So 3 possible sets :

$$\psi_{(1,2, \frac{1}{2})}(x_1, x_2) = \frac{\sqrt{2}}{L} \left(\sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} - \sin \frac{\pi x_2}{L} \sin \frac{2\pi x_1}{L} \right) \otimes (|\uparrow_1\rangle |\uparrow_2\rangle)$$

spin up
/ \

or

$$= \frac{\sqrt{2}}{L} \left(\sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} - \sin \frac{\pi x_2}{L} \sin \frac{2\pi x_1}{L} \right) \otimes \frac{1}{\sqrt{2}} (|\uparrow_1\rangle |\downarrow_2\rangle + |\uparrow_2\rangle |\downarrow_1\rangle)$$

or

$$= \frac{\sqrt{2}}{L} \left(\sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} - \sin \frac{\pi x_2}{L} \sin \frac{2\pi x_1}{L} \right) \otimes (|\downarrow_1\rangle |\downarrow_2\rangle)$$

② space factor symmetric, spin factor antisymmetric

only 1 possibility :

$$\psi_{(1,2, \frac{1}{2})}(x_1, x_2) =$$

$$\frac{\sqrt{2}}{L} \left(\sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} + \sin \frac{\pi x_2}{L} \sin \frac{2\pi x_1}{L} \right)$$

$$\otimes \frac{1}{\sqrt{2}} (|\uparrow_1\rangle |\downarrow_2\rangle - |\uparrow_2\rangle |\downarrow_1\rangle)$$

5. Ignoring the electron - electron repulsion, the energy of ground state of He atom is

$$E_0 = -Z^2 R \left(\frac{1}{n^2} + \frac{1}{n^2} \right) = -(2)^2 R \left(\frac{1}{1} + \frac{1}{1} \right) = -8R$$
$$= -8(13.6 \text{ eV}) = -108.8 \text{ eV}$$

the energy of ground state of He^+ ion is

$$E_0' = -\frac{Z^2 R}{n^2} = -\frac{(2)^2 R}{1} = -4R = -54.4 \text{ eV}$$

\therefore first ionization energy is the difference between two ground states above:

$$\Delta E_1 = E_0' - E_0 = \boxed{54.4 \text{ eV}}$$

Second ionization energy is simply the binding energy of He^+ as there is only 1 electron left.

$$\Delta E_2 = \boxed{54.4 \text{ eV}}$$

True ground state energy of He atom is ~~-79.0 eV~~
about -79.0 eV

$$\rightarrow \tilde{\Delta E}_1 = 79.0 \text{ eV} - 54.4 \text{ eV} = 24.6 \text{ eV}$$

The actual value of second ionization energy is still the binding energy

$$\therefore \tilde{\Delta E}_2 = 54.4 \text{ eV}$$

We see that $\Delta E_1 \sim 2.21 \Delta \tilde{E}_1$, but $\Delta E_2 \approx \Delta \tilde{E}_2$

The ~~first~~ degree of accuracy of ~~first~~ estimation of first ionization energy is very low ~~because~~ because ~~the~~ we fail to consider the effect of the electron-electron repulsion.

The degree ~~of~~ of accuracy of second ionization energy is high ^(~ 1) because in removing the second electron, there is only 1 electron in the system and there is no electron-electron ~~repul~~ repulsion that needs consideration.

The variational method :

$$\begin{aligned} \left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle &= \iint dr_1 dr_2 r_1^2 r_2^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \left(\frac{Z^3}{\pi a_0^3} \right)^2 \exp(-Zr_1/a_0) \\ &\quad \times \int d\theta_1 \sin\theta_1 \int d\phi_1 \int d\theta_2 \sin\theta_2 \int d\phi_2 \times \exp(-Zr_2/a_0) \\ &= \iint dr_1 dr_2 r_1 r_2 (r_1 + r_2) \left(\frac{Z^3}{\pi a_0^3} \right)^2 \exp(-Z(r_1 + r_2)/a_0) \times (4\pi)^2 \\ &= \left(\frac{4Z^3}{\pi a_0^3} \right)^2 \int_{r_2=0}^{r_2=\infty} \int_{r_1=0}^{r_1=\infty} dr_1 dr_2 r_1 r_2 (r_1 + r_2) \exp(-Z(r_1 + r_2)/a_0) \end{aligned}$$

let $u = r_1 r_2$, $v = r_1 + r_2$ then

$$du dv = \left| \frac{\partial(u, v)}{\partial(r_1, r_2)} \right| dr_1 dr_2$$

$$= \frac{16Z^6}{a_0^6} \int_{r_2=0}^{r_2=\infty} \int_{r_1=0}^{r_1=\infty} dr_1 dr_2 r_1 r_2 (r_1 + r_2) e^{-2Z(r_1+r_2)/a_0}$$

$$= \frac{16Z^6}{a_0^6} \int_0^\infty dr_1 r_1 \int_0^\infty dr_2 r_2 (r_1 + r_2) e^{-2Z(r_1+r_2)/a_0}$$

$$= \frac{16Z^6}{a_0^6} \int_0^\infty dr_1 r_1 e^{-2Zr_1/a_0} \int_0^\infty dr_2 r_2 (r_1 + r_2) e^{-2Zr_2/a_0}$$

$$\Rightarrow \int_0^\infty dr_2 r_2 (r_1 + r_2) e^{-2Zr_2/a_0}$$

$$= \int_0^\infty dr_2 r_2^2 e^{-2Zr_2/a_0} + r_1 r_2 e^{-2Zr_2/a_0}$$

$$= \left[-\left(\frac{a_0}{2Z}\right) r_2^2 e^{-2Zr_2/a_0} - 2r_2 \left(\frac{a_0}{2Z}\right)^2 e^{-2Zr_2/a_0} - 2\left(\frac{a_0}{2Z}\right)^3 e^{-2Zr_2/a_0} \right]_0^\infty$$

$$+ r_1 \left[r_2 - \left(\frac{a_0}{2Z}\right) r_2 e^{-2Zr_2/a_0} - \left(\frac{a_0}{2Z}\right)^2 e^{-2Zr_2/a_0} \right]_0^\infty$$

$$= 2\left(\frac{a_0}{2Z}\right)^3 + r_1 \left(\frac{a_0}{2Z}\right)^2$$

$$\Rightarrow \int_0^\infty dr_1 r_1 e^{-2Zr_1/a_0} \left(2\left(\frac{a_0}{2Z}\right)^3 + r_1 \left(\frac{a_0}{2Z}\right)^2 \right)$$

$$= 2\left(\frac{a_0}{2Z}\right)^3 \int_0^\infty dr_1 r_1 e^{-2Zr_1/a_0} + \left(\frac{a_0}{2Z}\right)^2 \int_0^\infty dr_1 r_1^2 e^{-2Zr_1/a_0}$$

$\underbrace{\hspace{10em}}_{\left(\frac{a_0}{2Z}\right)^2} \qquad \underbrace{\hspace{10em}}_{2\left(\frac{a_0}{2Z}\right)^3}$

$$= 4 \left(\frac{a_0}{2z} \right)^5$$

$$\therefore \left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle = 16 \frac{z^6}{a_0^6} \times 4 \times \frac{a_0^5}{32 z^5}$$

$$= \frac{2z}{a_0} \quad \text{Q.E.D.}$$

The Hamiltonian for Helium is

$$\hat{H} = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{-2}{r_1} + \frac{-2}{r_2} + \frac{1}{r_{12}} \right)$$

The mean energy obtained using the hydrogen like wavefunction as trial function is

$$\langle E \rangle = E(z) = \frac{1}{2m_e} \langle p_1^2 + p_2^2 \rangle - \frac{2e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle + \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_{12}} \right\rangle$$

$$= \frac{1}{2m_e} \left(\frac{2z^2 \hbar^2}{a_0^2} \right) - \frac{2e^2}{4\pi\epsilon_0} \cdot \frac{2z}{a_0} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{5z}{8a_0} \right)$$

$$\therefore a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \quad \therefore E_R = \frac{\hbar^2}{2m_e a_0^2} = \frac{e^2}{8\pi\epsilon_0 a_0} = 13.6 \text{ eV}$$

$$\therefore \langle E \rangle = \left(\frac{\hbar^2}{2m_e a_0^2} \right) \cdot (2) \cdot z^2 - \left(\frac{e^2}{8\pi\epsilon_0 a_0} \right) \cdot (2) \cdot (4z) + \left(\frac{e^2}{8\pi\epsilon_0 a_0} \right) \cdot (2) \cdot \left(\frac{5}{8} z \right)$$

$$\rightarrow \langle E \rangle = -2E_R \left(4z - z^2 - \frac{5z}{8} \right) \quad (\text{QED})$$

$$\therefore \langle E \rangle = -2E_R$$

$$E(z) = -2E_R \left(\frac{27}{8}z - z^2 \right)$$

Using variational principle; the true ground state energy of Helium is

$$E_{\text{He}} \leq E(z)_{\text{min}} = E(z) \Big|_{\frac{dE(z)}{dz} = 0}$$

$$\text{Set } 0 = \frac{dE(z)}{dz} \Rightarrow \text{gives } \frac{27}{8} = 2z \quad \therefore z = \frac{27}{16}$$

$$\therefore E(z)_{\text{min}} = -2E_R \left(\left(\frac{27}{8}\right)\left(\frac{27}{16}\right) - \left(\frac{27}{16}\right)^2 \right)$$

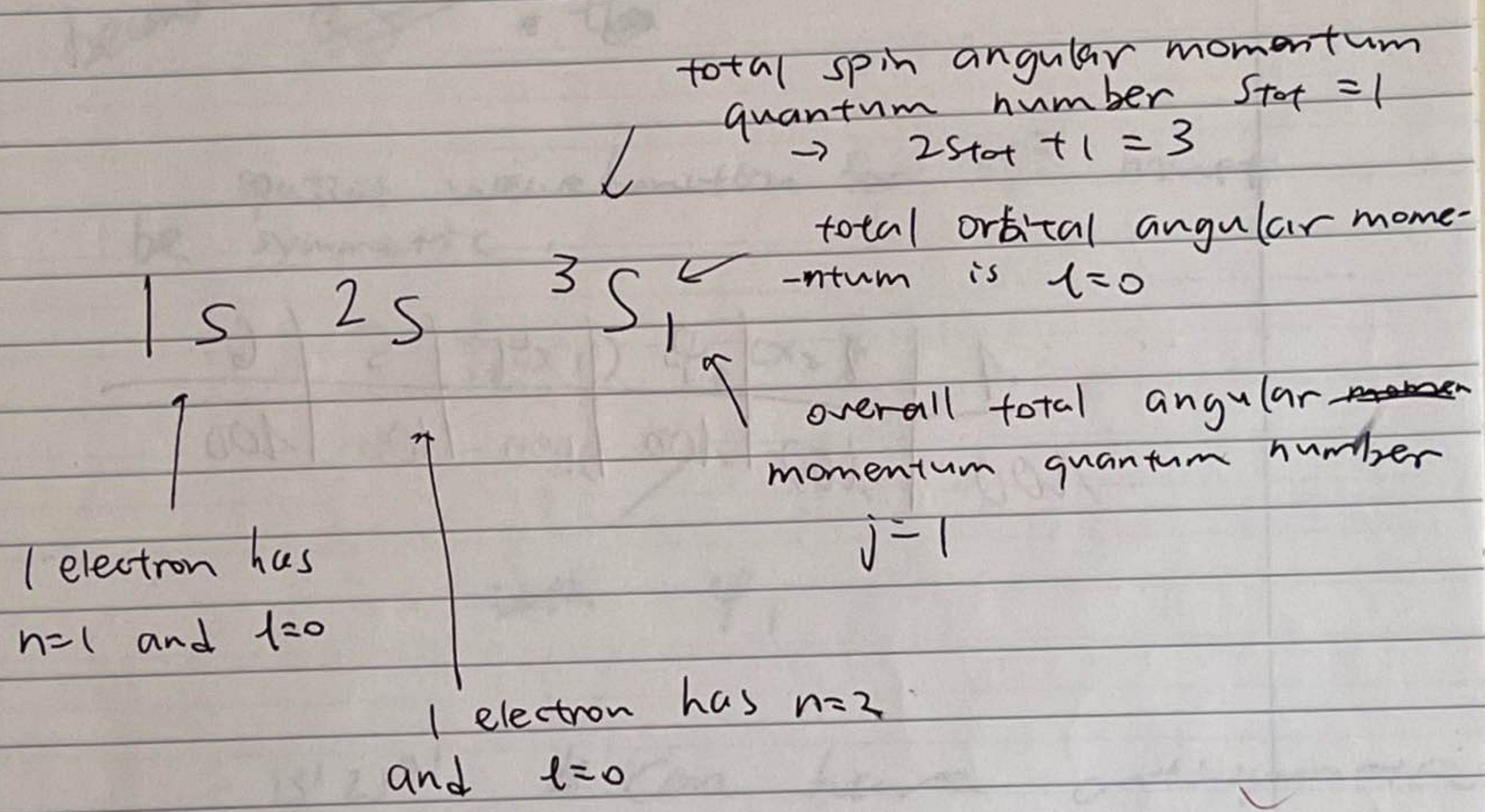
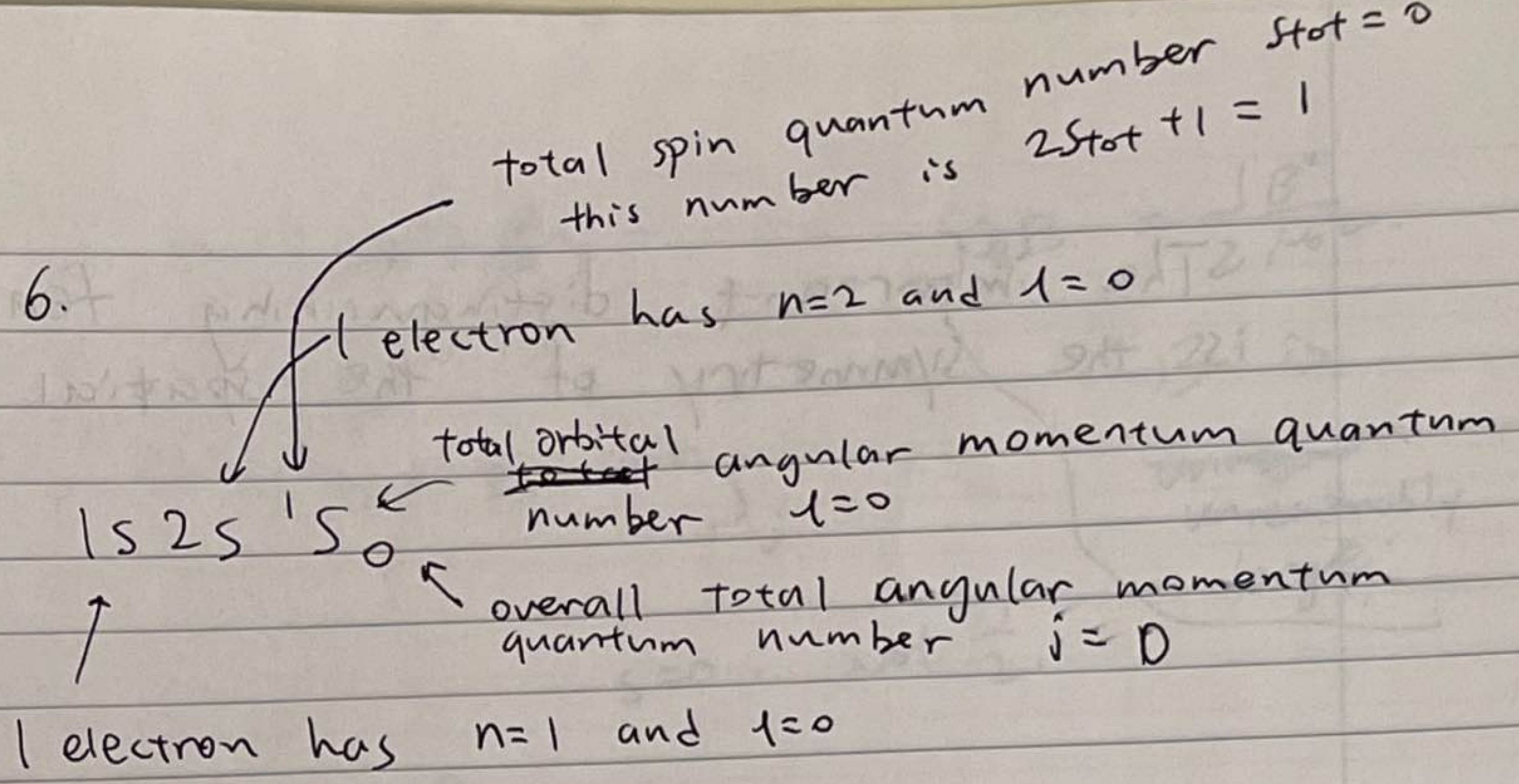
$$= \frac{-729}{128} E_R = \boxed{-77.5 \text{ eV}}$$

This is the upper limit for ground state energy

The lower limit for first ionisation energy is then given by

$$\Delta E_{\text{min}} = 77.5 \text{ eV} - 54.4 \text{ eV} = \boxed{23.1 \text{ eV}}$$

6.



\rightarrow $1s2s^1s_0$ corresponds to ~~two~~ two ~~wave~~ electrons in a spin ~~+~~ singlet state \Rightarrow spin wavefunction is antisymmetric $\Rightarrow \therefore$ electrons are fermions which means overall wavefunction is antisymmetric $\Rightarrow \therefore$ The spatial wavefunction is symmetric

\rightarrow $1s2s^3s_1$ corresponds to two electrons in a spin triplet state \Rightarrow spin wavefunction is symmetric $\Rightarrow \therefore$ Spatial wavefunction is antisymmetric

The important distinguishing feature is the symmetry of the spatial wavefunctions

1	2	3	4	5	6
100	100	100	100	100	100

$$u = \frac{1}{2}(\epsilon_0 \hbar^2 + \frac{B^2}{\mu_0})$$

$$N_B B. = \frac{1}{2} \frac{B^2}{\mu_0}$$

eg

1s² 2s² 2p⁶ 3s² 2st¹ }_j

B is

~~unreasonably~~
unreasonably large

s=0, not 1/2.

because ~~the~~ ~~the~~

spatial wavefunction for 3s² must be symmetric,

$$\psi_1(x_1) \psi_2(x_2) \dots$$

both ψ_1

1s² 2s² can have antisymmetric spatial wavefunctions.

$$\frac{1}{\sqrt{2}} (\psi_1(x_1) \psi_2(x_2) - \psi_1(x_2) \psi_2(x_1))$$

$$e^{i\theta \cdot L} |4\rangle = |4\rangle$$

$$e^{i\theta \cdot L} = I \quad L=0$$

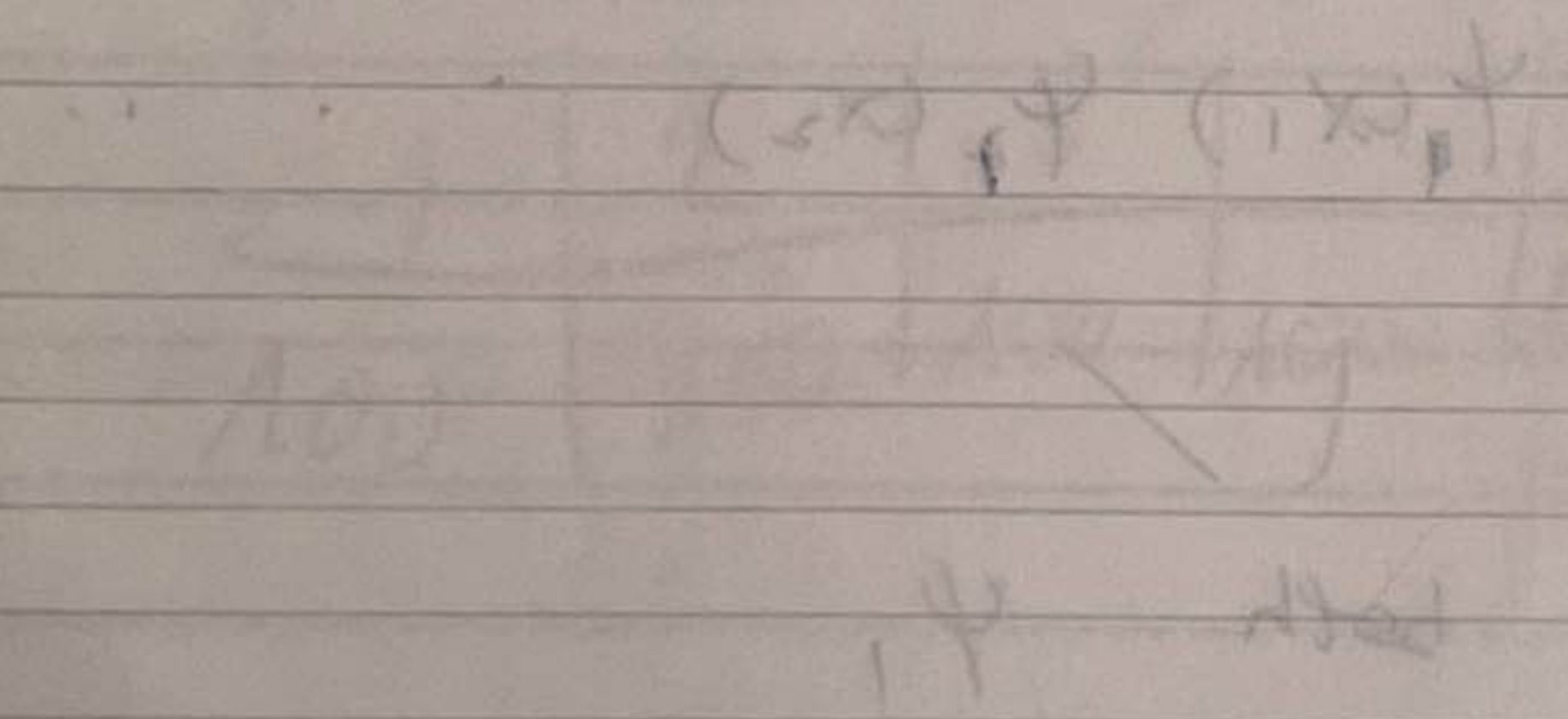
→ spherically symmetric (fully filled)

and half filled shells) have

zero orbital angular momentum

$$l=0$$

orbital wavefunction for $3d^5$ is spherically symmetric.



$$\frac{1}{\sqrt{2}} (\psi_{1,0} + \psi_{1,0})$$

$$|M_J| = |M_L|$$

$$I = 0$$

spherically symmetric (half filled)