Further Quantum Mechanics

Direct continuation of Quantum Mechanics course. Division of material between courses not significant.

Three main themes

1. Topics in basic theory
2. Approximation methods
3. Aspects of atomic physics

Detailed reading suggestions on course webpage.
Hand written notes on Weblearn as course progresses.

Quantum Mechanics of Charged Particles in Magnetic fields

How to write down Hamiltonian?

Know this for systems where forces are gradient of potential energy — doesn't cover Lorentz force.

In principle

- Take classical Hamiltonian & replace coordinates & momenta with operators
- Get classical Hamiltonian from Lagrangian
- Pick Lagrangian to give correct equation of motion

Will take short-cut

State quantum Hamiltonian

Check equation of motion

Result

$$H = \frac{1}{2m}\left(\hat{\underline{p}} - q\underline{A}\right)^2 + q\phi$$

for pcle of mass m and charge q in EM field described by vector & scalar potentials $\underline{A}$ & ϕ.

Recall from EM lecs

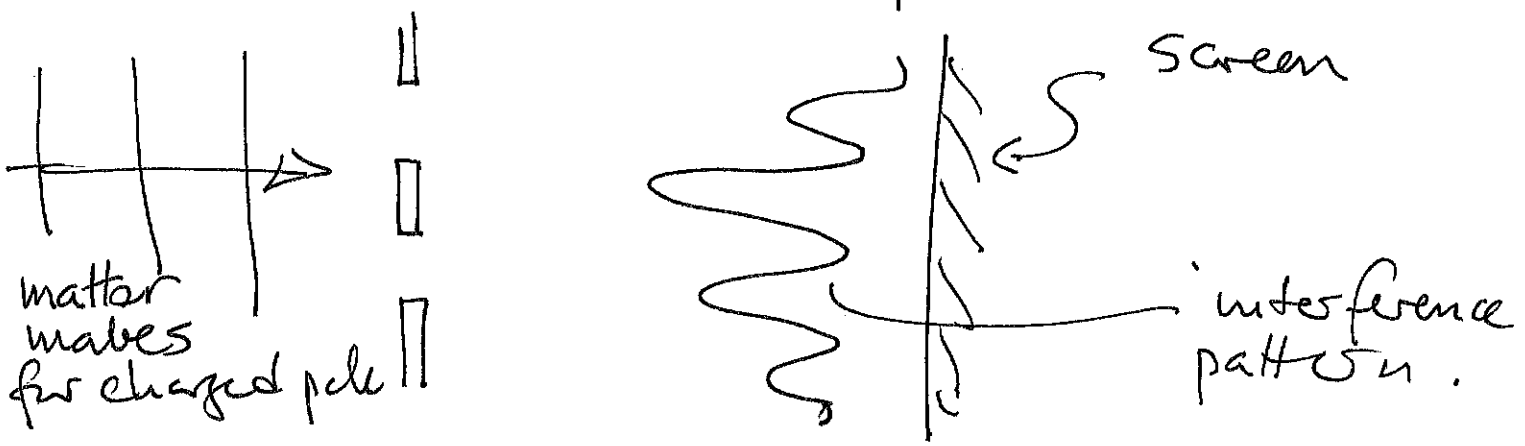
$$\underline{B} = \underline{\nabla} \times \underline{A}$$

$$\underline{\mathcal{E}} = -\underline{\nabla}\phi - \partial_t \underline{A}$$

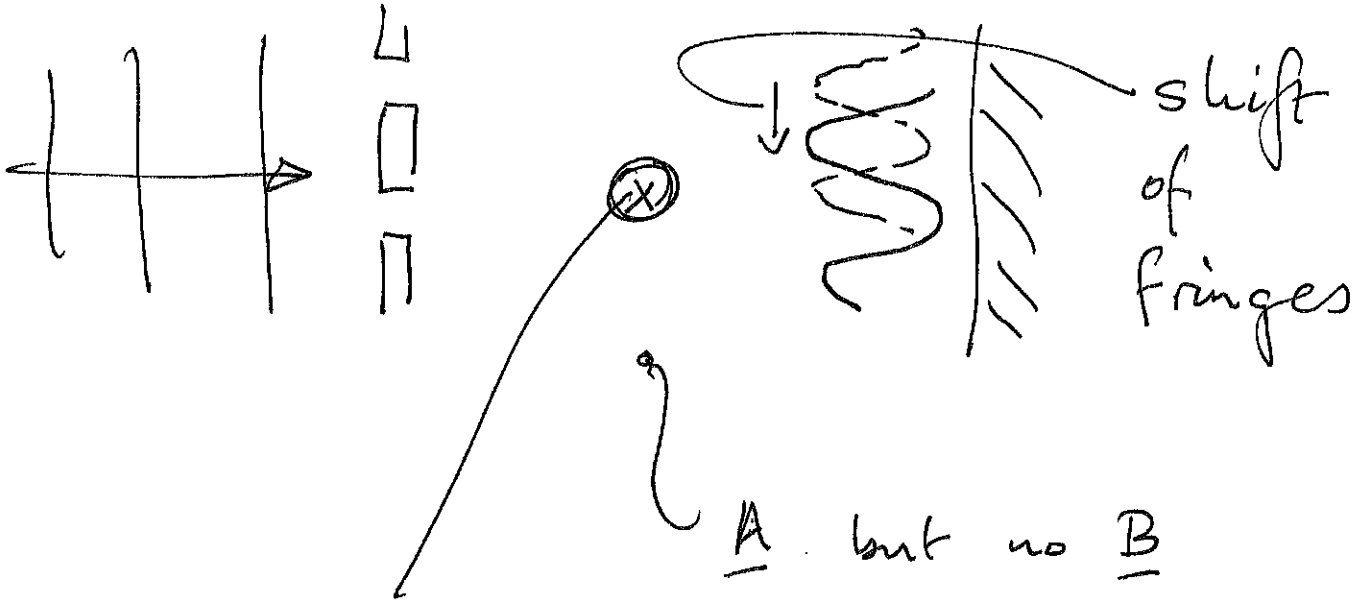
Aharonov-Bohm effect

Surprising feature of Hamiltonian: involves $\underline{A}$ & not just $\underline{B}$. Does this mean $\underline{A}$ is "real"?

Consider interference expt:



Add flux tube, shielded from waves



Cannot have $\underline{A} = 0$ outside flux tube because Stokes' theorem says

$$\oint_{\mathcal{C}} \underline{A} \cdot d\underline{l} = \int_{S} \mathrm{curl}\,\underline{A} \cdot d\underline{S} = \underline{\Phi}$$

$\mathcal{C}$ enclosing tube; S surface bounded by $\mathcal{C}$; $\underline{\Phi}$ flux thro' tube

Interference is affected by $\underline{A}$

$\Rightarrow$ Vector potential is "real", just like $\underline{B}$-field.

Gauge transformations in EM & QM

Significance of vector potential leads to possible problem: know from EM that potentials ϕ & $\underline{A}$ are not unique, since we can make a gauge transformation

$$\underline{A} \rightarrow \underline{A}' = \underline{A} + \underline{\nabla} \chi$$

$$\phi \rightarrow \phi' = \phi - \partial_t \chi$$

without changing the fields

$$\underline{B} = \underline{\nabla} \times \underline{A} = \underline{\nabla} \times \underline{A}'$$

$$\underline{E} = -\underline{\nabla}\phi - \partial_t \underline{A} = -\underline{\nabla}\phi' - \partial_t \underline{A}'$$

Apparent problem

Hamiltonian depends on gauge

Solution

Wavefunction is also changed ~~by~~ under gauge transformation – but only by phase, so that ~~eg~~ physical quantities (eg $|\psi|^2$) invariant

Given soln to TDSE

$$i\hbar\,\partial_t\psi = H\psi$$

with $H = \frac{1}{2m}\left(\hat{p} - q\underline{A}\right)^2 + q\phi$

Do gauge transformation

$$H \to H' = \frac{1}{2m}\left(\hat{p} - q\underline{A}'\right)^2 + q\phi$$

Claim: satisfy new TDSE if we also transform ψ

$$\boxed{\psi \to \psi' = e^{iq\chi/\hbar}\,\psi}$$

Check

On lhs get extra term:

$$i\hbar\,\partial_t\psi' = e^{iq\chi/\hbar}\left(i\hbar\,\partial_t\psi - q(\partial_t\chi)\,\psi\right)$$

On rhs get extra terms:

(1) $q\phi\psi \longrightarrow q(\phi - \partial_t\chi)\,e^{iq\chi/\hbar}\,\psi$

└ cancels with lhs

(2) $\frac{1}{2m}\left(\hat{p} - q\underline{A}\right)^2\psi \longrightarrow \frac{1}{2m}\left(-i\hbar\underline{\nabla} - q\underline{A} - q\underline{\nabla}\chi\right)^2 e^{iq\chi/\hbar}\,\psi$

$= \frac{1}{2m}\,e^{iq\chi/\hbar}\left(-i\hbar\underline{\nabla} - q\underline{A} - q\underline{\nabla}\chi + q\underline{\nabla}\chi\right)^2\psi$ (cancel)

Check that form of H is reasonable

Calculate eqn of motion for avges & compare with classical version

Recall

$$\frac{d}{dt}\langle Q\rangle = -\frac{1}{i\hbar}\langle [H,Q]\rangle$$

& hence also

$$\frac{d^2}{dt^2}\langle Q\rangle = \left(\frac{1}{-i\hbar}\right)^2\langle [H,[H,Q]]\rangle$$

Set $Q = x_k$ & calculate velocity & acceleration for ptcle in EM field

Useful relation

$$[P^2,Q] = P^2Q - QP^2$$

$$= P([P,Q]+QP) - ([Q,P]+PQ)P$$

$$= P[P,Q] + [P,Q]P$$

With our form for H

$$[H, x_k] = \frac{1}{2m}\left[(\hat{\underline{p}} - q\underline{A})^2, x_k\right]$$

$$= -\frac{i\hbar}{m}(p_k - qA_k)$$

So velocity is

$$\frac{d}{dt}\langle x_k\rangle = \frac{1}{m}\langle (p_k - qA_k)\rangle$$

Also have

$$\left[H,[H,x_k]\right] = -\frac{i\hbar}{m}\left\{\frac{1}{2m}\sum_\ell\left[(\hat{p}_\ell - qA_\ell)^2, (p_k - qA_k)\right]\right.$$

$$\left. + \left[q\phi, (p_k - qA_k)\right]\right\}$$

$$= \frac{(-i\hbar)^2}{m}\left\{\frac{q}{m}\sum_\ell(\hat{p}_\ell - qA_\ell)\left(\frac{\partial A_\ell}{\partial x_k} - \frac{\partial A_k}{\partial x_\ell}\right) - q\frac{\partial\phi}{\partial x_k}\right\}$$

so

$$\boxed{m\frac{d^2}{dt^2}\langle x_k\rangle = \left\langle \frac{q}{m}\sum_\ell(\hat{p}_\ell - qA_\ell)\left(\frac{\partial A_\ell}{\partial x_k} - \frac{\partial A_k}{\partial x_\ell}\right) - q\frac{\partial\phi}{\partial x_k}\right\rangle}$$

— as expected

Lorentz force

electric force

Recall $\underline{v}\times\underline{B} \equiv v\times(\nabla\times\underline{A})$

& $\underline{a}\times(\underline{b}\times\underline{c}) = \underline{b}(\underline{a}\cdot\underline{c}) - \underline{c}(\underline{a}\cdot\underline{b})$

Probability current

Expression is changed in presence of non-zero vector potential

Recall the derivation

Continuity equation $\partial_t \rho = -\underline{\nabla} \cdot \underline{J}$

+ definition $\rho = |\psi|^2$

so $\partial_t \rho = \left(\psi^* \partial_t \psi + \psi \partial_t \psi^* \right)$

$= \frac{1}{i\hbar} \left(\psi^* H\psi - \psi (H\psi)^* \right)$ from TDSE

Now we have

$$H = \frac{1}{2m} \left(-i\hbar \underline{\nabla} - q\underline{A} \right)^2 + q\phi$$

so

$$\partial_t \rho = \frac{1}{2im\hbar} \left\{ -\hbar^2 \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \right) \right.$$

$$\left. + i\hbar q \left(\psi^* \left[\underline{A} \cdot \underline{\nabla} \psi + \underline{\nabla} \cdot (\underline{A} \psi) \right] + \psi \left[\underline{A} \cdot (\underline{\nabla} \psi)^* + \underline{\nabla} \cdot (\underline{A} \psi^*) \right] \right) \right\}$$

From this we see that

$$\boxed{\underline{J} = \frac{\hbar}{2im} \left(\psi^* \underline{\nabla} \psi - \psi \underline{\nabla} \psi^* \right) - \frac{q}{m} |\psi|^2 \underline{A}}$$

Charged pcles in uniform magnetic field

Recall classical result



Acceleration = Lorentz force

$$\frac{mv^2}{r} = qBv \Rightarrow \omega \equiv \frac{v}{r} = \frac{qB}{m}$$

Analogous to SHO since frequency indept. of amplitude.

Quantum version

Need to pick gauge.

Take $\underline{A} = B(0, x, 0)$

Then $\underline{\nabla} \times \underline{A} = (0, 0, B)$

For motion in xy plane

$$H = \frac{1}{2m}\left\{(-i\hbar\partial_x)^2 + (-i\hbar\partial_y - qBx)^2\right\}$$

Solve TISE using sep^n of vbles

try $\psi(x,y) = e^{iky}\varphi(x)$

then

$$E\varphi(x) = \frac{1}{2m}\left\{(-i\hbar\partial_x)^2 + \underbrace{(\hbar k - qBx)^2}_{(qB)^2(x-x_0)^2}\right\}\varphi(x)$$

with $x_0 = \frac{\hbar k}{qB} \equiv \ell_B^2 k$

where $\ell_B = \left(\frac{\hbar}{qB}\right)^{1/2}$ mag length

This is a displaced SHO with "spring const" $\frac{(qB)^2}{m}$

and hence frequency

$$\left(\frac{\text{spring const}}{\text{mass}}\right)^{1/2} = \left(\frac{(qB)^2}{m^2}\right)^{1/2} = \frac{qB}{m}$$

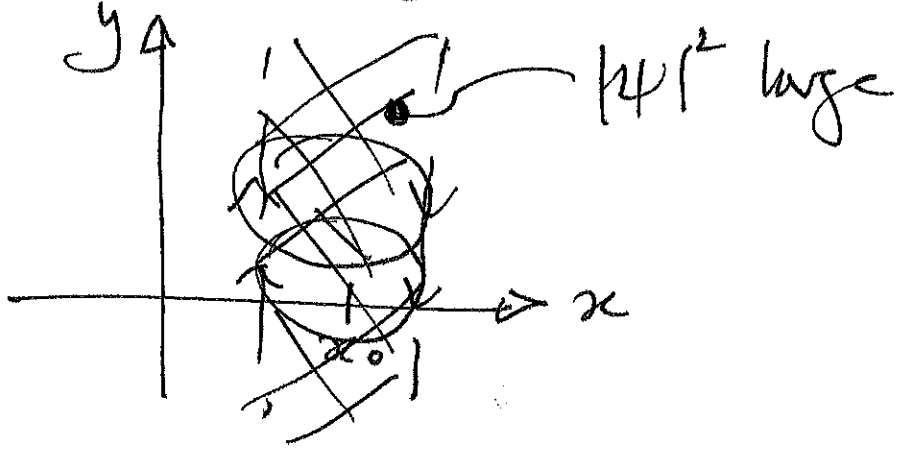
So energy levels are

$$E = (n+\tfrac{1}{2})\hbar\omega_c \qquad \text{with } \omega_c = \frac{qB}{m}$$

("Landau levels")

Eigenfunctions

Superposition of orbits



Calculate current

$$J = \frac{\hbar}{2im}\left(\psi^* \nabla\psi - \psi \nabla\psi^*\right) - \frac{q}{m}|\psi|^2 A$$

with $\psi = e^{iky}\varphi(x)$ (φ real) & $A = B(0, x, 0)$

$$J_x = 0 \quad \& \quad J_y = \frac{\hbar k}{m} - \frac{qB}{m}x = -\frac{qB}{m}(x - x_0)$$

— consistent with picture & superposition of orbits

States in Landau level?

Consider system $L_x \times L_y$ periodic in y

$$k = \frac{2\pi}{L_y} \times m \quad \text{(} m \text{ integer)}$$

so $$x_0 = 2\pi \frac{\ell_B^2}{L_y} \times m$$

but $0 < x_0 < L_x$ so $0 < m < \frac{L_x L_y}{2\pi \ell_B^2}$

So (# states in Landau level) $\propto$ (area of system)

Perturbation theory

Not all problems are exactly solvable
— need approximate solutions

Often want consequences of small change in system

Time-independent perturbation theory

Generic Problem

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

λ: small a dimensionless

$\hat{V}$: perturbation

$\hat{H}_0$: (unperturbed Hamiltonian

Assume we know everything about unperturbed problem

$$\hat{H}_0 |n\rangle = E_n |n\rangle$$

$$\langle n | m \rangle = \delta_{n,m}$$

Aim Solve TISE as power series in λ

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

with $|\psi\rangle = |n\rangle + \lambda|\delta\psi_n^{(1)}\rangle + \dots$

$$E = E_n + \lambda \delta E_n^{(1)} + \lambda^2 \delta E_n^{(2)}$$

NB notation: $\delta E_n^{(2)}$ — (2) ← order in λ; n ← label for level

Substitute into TISE

$$(\hat{H}_0 + \lambda\hat{V})(|n\rangle + \lambda|\delta\psi_n^{(1)}\rangle + \dots)$$

$$= (E_n + \lambda\delta E_n^{(1)} + \lambda^2 \delta E_n^{(2)} + \dots)(|n\rangle + \lambda|\delta\psi_n^{(1)}\rangle + \dots)$$

Separate each order in λ

since Eqn holds for range of λ, must have equality order-by-order

(λ^0) $\hat{H}_0|n\rangle = E_n|n\rangle$

(λ^1) $\hat{V}|n\rangle + \hat{H}_0|\delta\psi_n^{(1)}\rangle$

$$= E_n|\delta\psi_n^{(1)}\rangle + E_n^{(1)}|n\rangle$$

λ^2

$$H_0|\delta\psi_n^{(2)}\rangle + \hat{V}|\delta\psi_n^{(1)}\rangle$$

$$= \delta E_n^{(2)}|n\rangle + \delta E_n^{(1)}|\delta\psi_n^{(1)}\rangle + E_n|\delta\psi_n^{(2)}\rangle$$

etc

To get δE's & $|\delta\psi\rangle$'s

Take $\langle n|$ × (Eqn at $\mathcal{O}(\lambda^1)$)

$$\langle n|\hat{V}|n\rangle = \underbrace{\langle n|(E_n - H_0)}_{\text{zero}}|\delta\psi_n^{(1)}\rangle + \delta E_n^{(1)}\underbrace{\langle n|n\rangle}_{1}$$

so

$$\boxed{\delta E_n^{(1)} = \langle n|\hat{V}|n\rangle}$$

Very useful result!

What about $|\delta\psi_n^{(1)}\rangle$?

Take $\langle m|$ × (Eqn at $\mathcal{O}(\lambda^1)$) $\quad (m \neq n)$

$$\langle m|\hat{V}|n\rangle = \underbrace{\langle m|(E_n - H_0)}_{(E_n - E_m)\langle m|}|\delta\psi_n^{(1)}\rangle + \delta E_n^{(1)}\underbrace{\langle m|n\rangle}_{\text{zero}}$$

$$= (E_n - E_m)\langle m|\delta\psi_n^{(1)}\rangle$$

so

$$\langle m | \delta\psi_n^{(1)} \rangle = \frac{\langle m | \hat{V} | n \rangle}{E_n - E_m}$$

and hence

$$|\delta\psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle m|\hat{V}|n\rangle}{E_n - E_m} |m\rangle$$

NB requires E_n to be non-degenerate

Aside What about normalisation of $|\psi\rangle$?

$$\langle\psi|\psi\rangle = \left(\langle n| + \lambda \langle \delta\psi_n^{(1)}| + \ldots\right)\left(|n\rangle + \lambda |\delta\psi_n^{(1)}\rangle + \ldots\right)$$

$$= \langle n|n\rangle + \lambda\left\{\langle \delta\psi_n^{(1)}|n\rangle + \text{c.c.}\right\} + \mathcal{O}(\lambda^2)$$

so pick $\langle n | \delta\psi_n^{(1)} \rangle = 0$

– consistent with above expression

Second-order change in energy

Take $\langle n| \times$ (Eqn at $\mathcal{O}(\lambda^2)$)

$$\langle n|\hat{V}|\delta\psi_n^{(1)}\rangle = \delta E_n^{(2)}\underbrace{\langle n|n\rangle}_{1} + \delta E_n^{(1)}\underbrace{\langle n|\delta\psi_n^{(1)}\rangle}_{\text{zero}} + \underbrace{\langle n|(E_n - H_0)}_{\text{zero}}|\delta\psi_n^{(2)}\rangle$$

$|\delta\psi_n^{(1)}\rangle$: now known

So

$$\delta E_n^{(2)} = \sum_{\substack{m \\ m\neq n}} \frac{|\langle n|\hat{V}|m\rangle|^2}{E_n - E_m}$$

Again need E_n non-degenerate

Note ground state shift always negative

Degenerate perturbation theory

What happens if several states have same energy?

Appear to find infinite $|\delta\psi^{(1)}\rangle$ from arbitrarily small λ

In fact, just need to make right choice of basis states

Degeneracy + choice of basis

Suppose $|1\rangle, |2\rangle \ldots |n\rangle$ degenerate (i.e. $E_1 = E_2 = \ldots = E_n$) & orthonormal $\langle n|m\rangle = \delta_{n,m}$

Then we can equally well choose as eigenstates of H_0 a different linear combination: $|1'\rangle, |2'\rangle \ldots |n\rangle$

with $$|l'\rangle = \sum_{m=1}^{n} U_{l'm} |m\rangle$$

$U_{l'm}$ ← $n \times n$ unitary matrix

If $\hat{H}_0 |l\rangle = E|l\rangle$ for $l = 1 \ldots n$

then $\hat{H}_0 |l'\rangle = E|l'\rangle$ as well

Also

$$\langle k'|\ell'\rangle = \sum_{pm} U^*_{k'p} U_{\ell' m} \underbrace{\langle p|m\rangle}_{\delta_{pm}}$$

$$= \sum_m U_{\ell' m} U^+_{mk'} = (UU^+)_{\ell' k'}$$

$$= \delta_{\ell', k'}$$

Use basis choice to remove degeneracy in $|\delta\psi\rangle$

- Pick U so that $\langle \ell'|\hat{V}|n'\rangle$ is diagonal with degenerate subspace

Then in

$$|\delta\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle m|\hat{V}|n\rangle}{E_n - E_m} |m\rangle$$

"$\sum_{m\neq n}$" is replaced by "$\sum_{E_m \neq E_n}$"

Now previous results hold

$$\delta E_{\ell'}^{(1)} = \langle \ell'|\hat{V}|\ell'\rangle$$

etc

Illustration 1

$$\hat{H}_0 = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \quad \& \quad \hat{V} = \begin{pmatrix} V_1 & \cdot \\ \cdot & V_2 \end{pmatrix}$$

Then $|1\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $\quad E_1 = \epsilon_1$

$|2\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ $\quad E_2 = \epsilon_2$

Find

$$\delta E_1^{(1)} = \langle 1|\hat{V}|1\rangle = (1,0)\begin{pmatrix} V_1 & \cdot \\ \cdot & V_2 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = V_1$$

$$|\delta\psi_1^{(1)}\rangle = \frac{\langle 2|\hat{V}|1\rangle}{E_1 - E_2}$$

but $\langle 2|\hat{V}|1\rangle = (0,1)\begin{pmatrix} V_1 & \cdot \\ \cdot & V_2 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$$= (0,1)\begin{pmatrix} V_1 \\ 0 \end{pmatrix}$$

$$= 0$$

So Eigenvalue of $\hat{H}_0 + \lambda\hat{V}$

is $\epsilon_1 + \lambda V_1 + \mathcal{O}(\lambda^2)$

Eigenvector is $\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \mathcal{O}(\lambda^2)$

(will put $\lambda = 1$ from now on)

Illustration 2

$\hat{H}_0$ as before, but now $\hat{V} = \begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix}$

$$\delta E_1^{(1)} = \langle 1|\hat{V}|1\rangle = (1,0)\begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= (1,0)\begin{pmatrix} 0 \\ v \end{pmatrix} = 0$$

Also $\langle 2|\hat{V}|1\rangle = (0,1)\begin{pmatrix} 0 \\ v \end{pmatrix} = v$

so $\delta E_1^{(2)} = \dfrac{|\langle 2|\hat{V}|1\rangle|^2}{E_1 - E_2} = \dfrac{v^2}{\epsilon_1 - \epsilon_2}$

and $|\delta\psi_1^{(1)}\rangle = \dfrac{\langle 2|\hat{V}|1\rangle}{E_1 - E_2}|2\rangle = \dfrac{v}{\epsilon_1 - \epsilon_2}|2\rangle$

Check

$$\begin{vmatrix} \epsilon_1 - E & \lambda v \\ \lambda v & \epsilon_2 - E \end{vmatrix} = (\epsilon_1 - E_*)(\epsilon_2 - E) - \lambda^2 v^2 = 0$$

$$E^2 - (\epsilon_1 + \epsilon_2)E + \epsilon_1\epsilon_2 - \lambda^2 v^2 = 0$$

$$E = \frac{\epsilon_1 + \epsilon_2}{2} \pm \frac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4\lambda^2 v^2}$$ with +ve sign

$$= \frac{\epsilon_1 + \epsilon_2}{2} \pm \frac{\epsilon_1 - \epsilon_2}{2}\left[1 + \frac{4\lambda^2 v^2}{(\epsilon_1 - \epsilon_2)^2}\right]^{1/2} \simeq \epsilon_1 + \frac{\lambda^2 v^2}{\epsilon_1 - \epsilon_2}$$

Illustration 3 – degenerate case

As for (2) but with $\epsilon_1 = \epsilon_2$

Recall: should take linear combination of $|1\rangle$ & $|2\rangle$ to diagonalise $\hat{V}$.

$$|1'\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \cong \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$$

$$|2'\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) \cong \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

$$\hat{V}|1'\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}v & v\\ v & v\end{pmatrix}\begin{pmatrix}1\\1\end{pmatrix} = v|1'\rangle$$

$$\hat{V}|2'\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}v & v\\ v & v\end{pmatrix}\begin{pmatrix}1\\-1\end{pmatrix} = -v|2'\rangle$$

So $\delta E^{(1)}_{1'} = v$ & $\delta E^{(1)}_{2'} = -v$

Check against exact result

$$E = \frac{\epsilon_1+\epsilon_2}{2} \pm \frac{\sqrt{(\epsilon_1-\epsilon_2)^2 + 4\lambda^2 v^2}}{2}$$

If $\epsilon_1 = \epsilon_2$ NVE

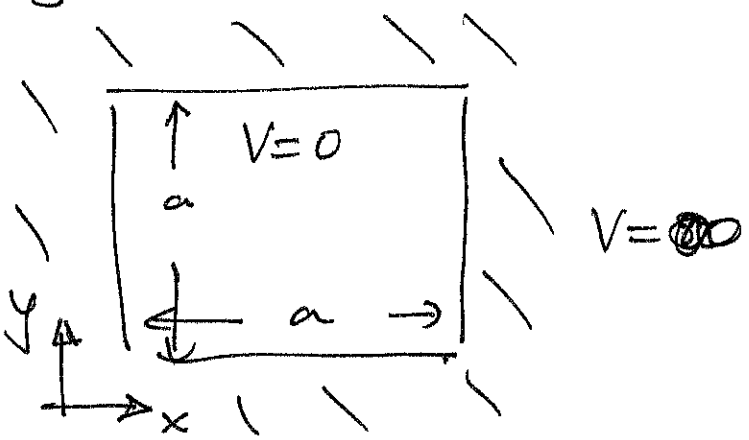
$$E = \epsilon_1 \pm \lambda v \qquad \text{ok}$$

Aside

Qu: how does degeneracy arise?

Ans: symmetry

Eg pcle in square box



Eigenfunctions

$$\psi_{lm}(x,y) = \sin(k_x x)\sin(k_y y)$$

$$k_x = \frac{l\pi}{a} \qquad k_y = \frac{m\pi}{a}$$

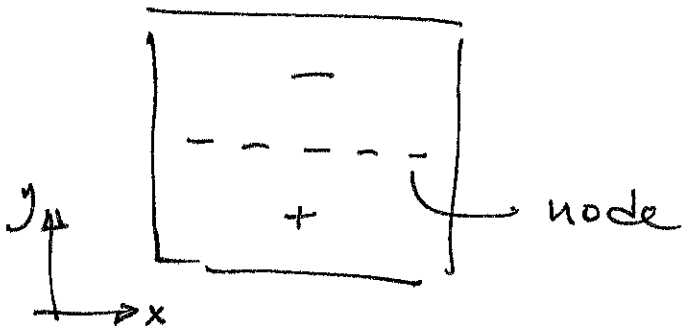
$$l, m = 1, 2, \ldots$$

$$E_{lm} = \frac{\hbar^2 \pi^2}{2ma^2}(l^2 + m^2)$$

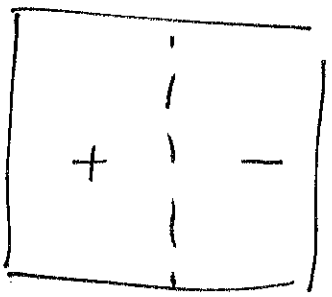
Ground state $l = m = 1$ unique

1st excited state $l=1, m=2$ or $l=2, m=1$ } degenerate

In pictures



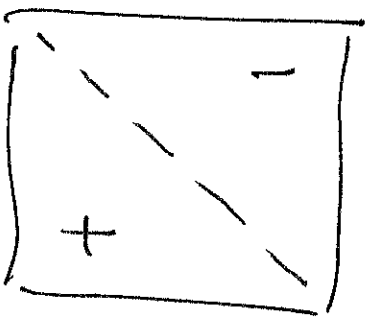
$l=1, m=2$



$l=2, m=1$

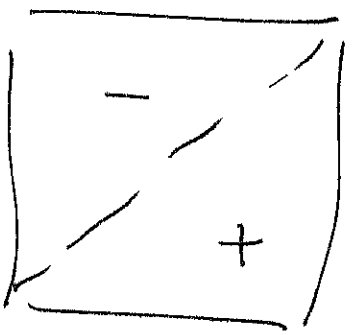
New linear combinations

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



or

$$\frac{1}{\sqrt{2}}\left(\psi_{1,2}-\psi_{2,1}\right)$$



Magnetic fields in atomic physics
– application of perturbation theory

Physical idea

Orbiting charge ≡ current loop
– generates magnetic moment $\underline{\mu}$

Energy in field depends on orientation

$$\Delta E = -\underline{\mu} \cdot \underline{B}$$

Two possibilities

(1) Moment exists before field is applied

Energy splitting ΔE called Zeeman effect

Alignment of moments in the field direction called paramagnetism

(2) Moment is induced by field

$$\underline{\mu} = \chi \underline{B}$$

Moment opposite to $\underline{B}$ so $\chi < 0$ (Lenz's law). Diamagnetism

$$\chi = A \frac{1}{2} \frac{d^2 E}{dB^2}$$

$$\Delta E = -\int_0^B \chi \underline{B}' \cdot d\underline{B}' = -\frac{1}{2}\chi B^2$$

so $\chi = -$ $\partial^2 E / \partial B^2$

Convenient choice for $\underline{A}$ to represent uniform $\underline{B}$

$$\underline{A} = \frac{1}{2}\underline{B}\times\underline{r} \quad \Rightarrow$$

take $\underline{B} = B\hat{z} \Rightarrow \underline{A} = \frac{B}{2}(-y, x, 0)$

then $\underline{\nabla}\times\underline{A} = (0, 0, B)$

Perturbation is

$$\hat{V} = -\frac{q}{m}\underline{p}\cdot\underline{A} + \frac{q^2}{2m}\underline{A}^2$$

$$= -\frac{q}{2m}\underline{B}\cdot(\underline{r}\times\underline{p}) + \frac{q^2B^2}{8m}(x^2+y^2)$$

$$= -\frac{q}{2m}\underline{B}\cdot\underline{L} + \frac{q^2B^2}{8m}(x^2+y^2)$$

(as expected from classical calculation

Consequences depend on atomic state

(A) Diamagnetic response

Suppose atom has angular momentum quantum number $\ell = 0$ — then $m = 0$

so $\langle \underline{B}\cdot\underline{L}\rangle = B\langle L_z\rangle = 0$

So first-order perturbation theory gives

$$\delta E_n^{(1)} = \langle n|\hat{V}|n\rangle = \frac{q^2B^2}{8m}\langle x^2+y^2\rangle$$

and

$$\chi = -\frac{d^2E}{dB^2} = -\frac{q^2}{4m}\underbrace{\langle x^2+y^2\rangle}_{\frac{2}{3}r^2} = -\frac{q^2}{6m}\langle r^2\rangle$$

cf Electromagnetism – see Prof Terquem's notes Eq (3.10).

Aside: should also consider B^2 term from $-q\underline{B}\cdot\hat{\underline{L}}$ treated at second order. But this is zero if $\underline{L}(n)=0$.

(B) Zeeman Effect

Consider state with $l \neq 0$

Then have degeneracy from rotational symmetry.

Recall quantum #'s for atomic states

$|n, l, m\rangle$ — z-cpt of angular momentum: $-l \le m \le l$

l — total angular momentum $l = 0, 1 \ldots n-1$

n — principal — fixes energy $n = 1, 2 \ldots$

Degenerate perturbation theory:

Should find basis in which

$$\hat{V} = -\frac{qB}{2m}\hat{L}_z$$

is diagonal.

Easy! We are already using this basis!

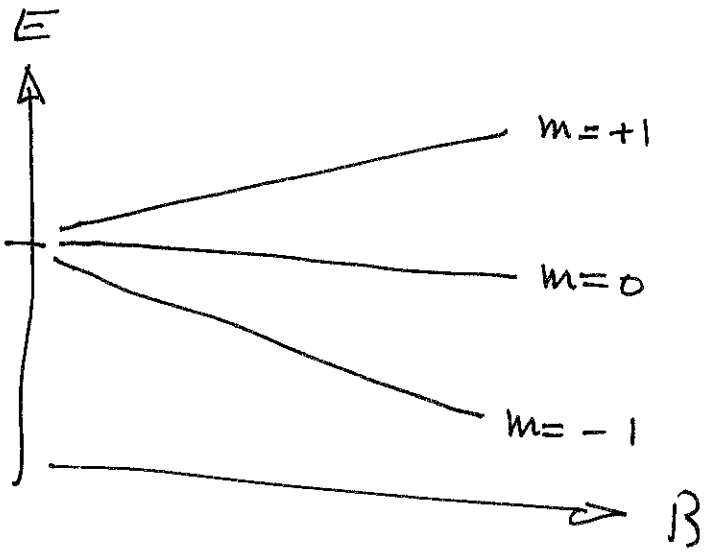
Have

$$L_z |n,\ell,m\rangle = \hbar m |n,\ell,m\rangle$$

so $$\langle n_1,\ell_1,m_1 | \hat{V} | n_2,\ell_2,m_2\rangle = -\frac{qB\hbar}{2m_e} m \times \delta_{n_1,n_2}\delta_{\ell_1,\ell_2}\delta_{m_1,m_2}$$

and

$$\boxed{\delta E^{(1)}_{n\ell m} = -\frac{qB\hbar}{2m_e} m}$$



Eg $\ell = 1$

$m = -1, 0, 1$

(omitting spin effects)

Similar relation between spin angular momentum and magnetic moment but with different proportionality factor

Parameterise this using "g-factor"

$$\underline{\mu} = -g\frac{qB}{2m}\hat{\underline{S}}$$

Electric fields in atomic physics: Stark effect

Two cases:

① Atom with electric dipole moment $\underline{p}$
- energy depends on orientation relative to field

$$\Delta E = -\underline{p}\cdot\underline{\mathcal{E}}$$

② Atom initially unpolarised

then $\underline{p} = \chi\underline{\mathcal{E}}$ ← atomic electric polarisability

$$\Delta E = -\int_0^{\mathcal{E}} \underline{p}\cdot d\underline{\mathcal{E}}' = -\frac{1}{2}\chi\mathcal{E}^2$$

QM calculation

$$\hat{H}_0 = -\frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0\hat{r}}$$

$$\hat{V} = e\mathcal{E}z = e\mathcal{E}r\cos\theta$$

Eigenstates of $\hat{H}_0$ are $|n,\ell,m\rangle$

$$E_n = -\frac{R}{n^2}$$ ← Rydberg

Recall form of hydrogenic wavefunctions

$$\langle r, \theta, \phi | n, \ell, m \rangle = Y_{\ell m}(\theta, \phi) R_{n,\ell}(r)$$

with $Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$

$$Y_{1,\pm 1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi}$$

$$Y_{1,0}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

Ground state Stark shift

First order

$$\langle 1,0,0 | \hat{V} | 1,0,0 \rangle \propto \int_0^{\pi} \sin\theta \, d\theta \, \cos\theta = \frac{1}{2}\left[\sin^2\theta\right]_0^{\pi} = 0$$

$\cos\theta$ — from $\hat{V}$

$\sin\theta \, d\theta$ — from volume element

so $\delta E_1^{(1)} = 0$

Second order

Need $\langle 1,0,0 | \hat{V} | n, \ell, m \rangle$

Only non-zero for $m = 0$ & $\ell = 1$

In this case

$$\propto \int_0^{\pi} \underbrace{\sin\theta \, d\theta}_{\text{volume element}} \times \cos\theta \times \cos\theta = \left[-\frac{\cos^3\theta}{3}\right]_0^{\pi} = \frac{2}{3}$$

$\cos\theta$ from $\hat{V}$; $\cos\theta$ from $Y_{1,0}$

So

$$\delta E_1^{(2)} = -\sum_{n=2}^{\infty} \frac{|\langle 1,0,0|\hat{V}|n,1,0\rangle|^2}{R_\infty\left(1/1^2 - 1/n^2\right)}$$

$$= -\frac{e^2\mathcal{E}^2 a_0^2}{R} \times \# \quad \# = 9/4$$

Interpretation: ground state is unpolarised - because spherically symmetric

Electric field induces dipole moment

Dipole aligns with field - lowers energy

Stark effect for hydrogen in $n=2$ level

Four degenerate states

$$|2,0,0\rangle \;,\; |2,1,0\rangle \;,\; |2,1,1\rangle \text{ \& } |2,1,-1\rangle$$

Must construct 4×4 matrix with elements

$$\langle 2,\ell,m|\,\hat{V}\,|2,\ell',m'\rangle$$

Integral on ϕ is

$$\int_0^{2\pi} e^{-im\phi}\, e^{+im'\phi}\, d\phi = \begin{cases} 2\pi & m=m' \\ 0 & m\neq m' \end{cases}$$

Integral on Θ

Zero for $l = l'$

since $[Y_{lm}(\theta, \phi)]^2$ even under $\theta \to \pi - \theta$

while $\cos\theta$ is odd under $\theta \to \pi - \theta$

So only non-zero terms are

$\langle 2, 0, 0 | \hat{V} | 2, 1, 0 \rangle$ and conjugate

$= -3e\mathcal{E}a_0$

$\equiv v$

See Qu 6.8 of Blundell's problem sets

So matrix

$$\langle 2, l, m | \hat{V} | 2, l', m' \rangle$$

is

	$l=0, m=0$	$l=1, m=0$	$l=1, m=-1$	$l=1, m=+1$
$l=0, m=0$	0	v	0	0
$l=1, m=0$	v	0	0	0
$l=1, m=-1$	0	0	0	0
$l=1, m=+1$	0	0	0	0

Should transform basis to diagonalise this matrix

Note that $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

& $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = -\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

So e-vectors of 4×4 matrix are

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \text{ & } \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

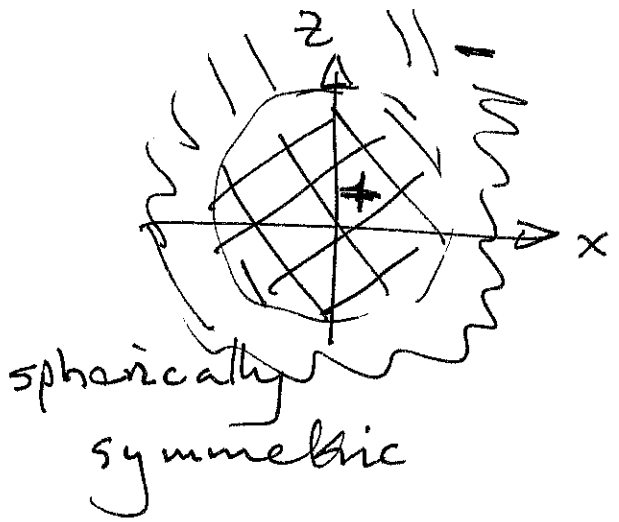
Energy levels are $-\frac{R}{2^2} + U$, $-\frac{R}{2^2} - U$

& $-\frac{R}{2^2}$ (twice)

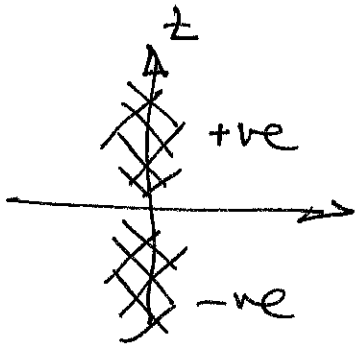
<u>Wavefunctions</u>

Probability densities

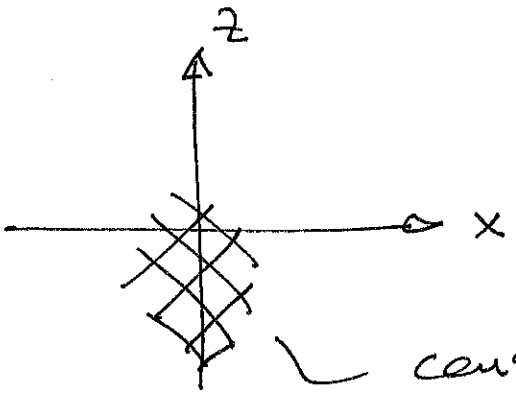
$\langle \underline{r} | 2,0,0 \rangle$



$\langle \underline{r} | 2,1,0 \rangle$



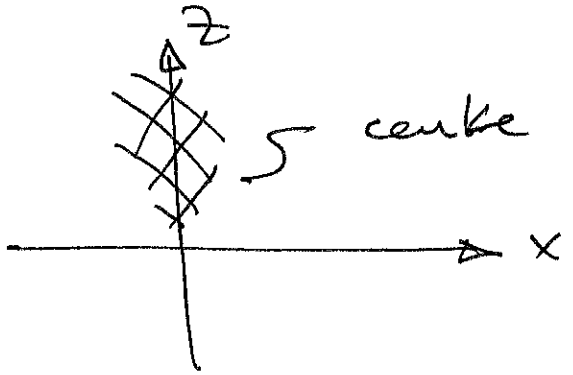
$\langle \underline{r} | \{ |2,0,0\rangle + |2,1,0\rangle \}$



centre at -ve z

lower in energy
for ξ-field in +ve $\hat{z}$-dirn
(electron charge -ve!)

$\langle r | \{ |2,0,0\rangle - |2,1,0\rangle \}$



centre at +ve z

higher in
energy

Variational Method

Alternative to perturbation theory, not restricted to small $\hat{V}$. Most useful for ground-state energies & wavefunctions.

Idea Guess approximate wavefn
Always gives upper bound
to ground state energy

Theorem $\hat{H}|n\rangle = E_n|n\rangle \qquad E_0 \leq E_1 \leq E_2 \cdots$

Any state $|\psi\rangle = \sum_n c_n |n\rangle$ with $\sum_n |c_n|^2 = 1$

Use $|\psi\rangle$ to estimate ground state energy

$$\langle\psi|\hat{H}|\psi\rangle = \sum_{n,m} c_m^* c_n \langle m|\hat{H}|n\rangle$$

$$= \sum_n |c_n|^2 E_n$$

$$= E_0 \underbrace{\sum_n |c_n|^2}_{1} + \underbrace{\sum_n |c_n|^2 (E_n - E_0)}_{\geq 0}$$

so $\boxed{\langle\psi|\hat{H}|\psi\rangle \geq E_0}$

Practical use

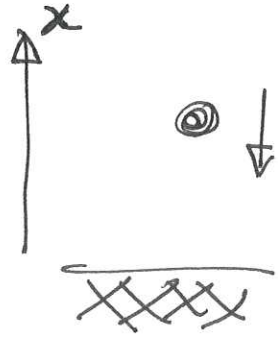
Take $|\psi\rangle$ with adjustable parameters

Vary parameters to minimise $\langle\psi|\hat{H}|\psi\rangle$

Get upper bound on E_0 and approximate $|0\rangle$.

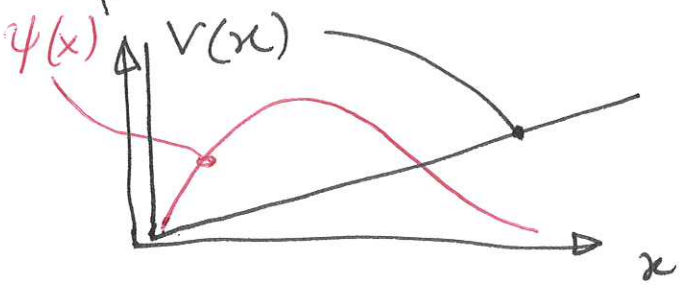
Example

Quantum bouncing ball



$$V(x) = \begin{cases} \infty & x < 0 \\ mgx & x > 0 \end{cases}$$

Expect



Try

$$\psi(x) = \begin{cases} 0 & x < 0 \\ Nxe^{-ax} & x > 0 \end{cases}$$

adjustable

Will need integrals

$$\int_0^\infty x^n e^{-bx}\,dx = b^{-(n+1)} \int_0^\infty s^n e^{-s}\,ds = n!\, b^{-(n+1)}$$

$bx = s$

① Find normalisation

$$1 = \int_0^\infty |\psi(x)|^2 dx = N^2 \int_0^\infty x^2 e^{-2ax} dx$$

$$= N^2 \frac{2}{(2a)^3}$$

$$\boxed{N^2 = 4a^3}$$

② Find $\langle \hat{H} \rangle$

(a) $\langle PE \rangle = \int_0^\infty |\psi(x)|^2 V(x)$

$$= N^2 mg \int_0^\infty x\, x^2 e^{-2ax} dx$$

$$= 4a^3 mg \frac{3!}{(2a)^4} = \frac{3mg}{2a}$$

(b) $\langle KE \rangle = -\frac{\hbar^2}{2m} \int_0^\infty \psi(x) \frac{d^2\psi}{dx^2} dx$

$$= -\frac{\hbar^2}{2m} N^2 \int_0^\infty x(a^2x - 2a) e^{-2ax} dx$$

$$= -\frac{\hbar^2}{2m} 4a^3 \left(\frac{2a^2}{(2a)^3} - \frac{2a}{(2a)^2} \right)$$

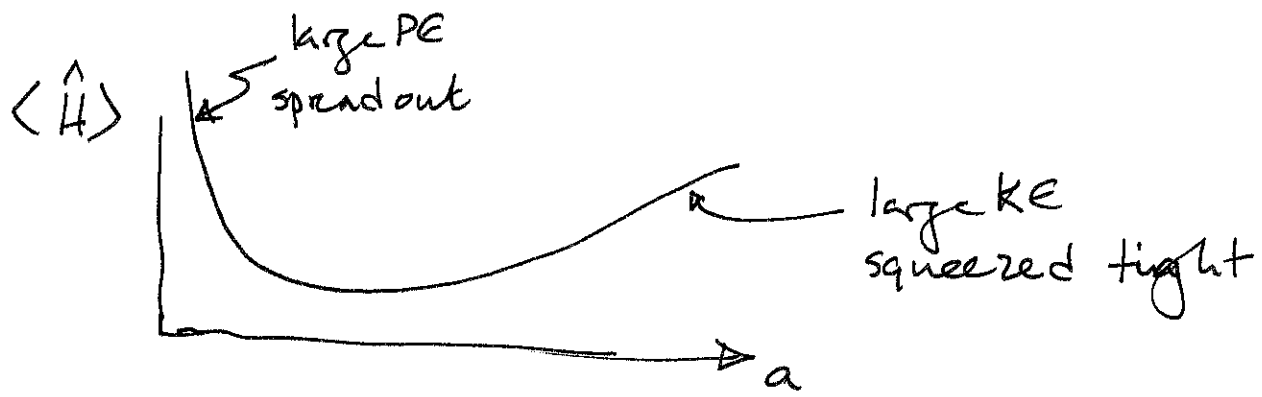
$$= -\frac{\hbar^2 a^2}{m} \left(\frac{1}{2} - 1 \right) = \frac{\hbar^2 a^2}{2m}$$

$$\boxed{\frac{d\psi}{dx} = N(1-ax)e^{-ax}}$$

$$\boxed{d^2\psi/dx^2 = N(a^2x - 2a)e^{-ax}}$$

So

$$\langle \hat{H} \rangle = \frac{\hbar^2 a^2}{2m} + \frac{3mg}{2a}$$



Minimise

$$\frac{\partial \langle \hat{H} \rangle}{\partial a} = 0$$

$$\frac{\hbar^2 a}{m} - \frac{3mg}{2a^2} = 0$$

$$a = \left(\frac{3m^2 g}{2\hbar^2} \right)^{1/3}$$

$$E_0 \leq \underbrace{\left(\frac{3}{2}\right)^{5/3}}_{1.965} \left(\hbar^2 m g^2\right)^{1/3}$$

Exact answer (Airey functions) 1.856...

Further application of variational approach: proof of virial theorem

Consider particle in power-law potential

$$V(r) = V_0 r^n \qquad \text{eg SHO, } n=2 \text{ ; Coulomb, } n=-1.$$

How do PE & KE compare?

Suppose exact eigenstate is $\psi(\underline{r})$

Consider variational state $\psi(a\underline{r})$

$$\langle PE \rangle_{var} = \frac{\int d^d\underline{r} \; |\psi(a\underline{r})|^2 V_0 r^n}{\int d^d\underline{r} \; |\psi(a\underline{r})|^2}$$

change variables: $\underline{R} = a\underline{r}$

$$\langle PE \rangle_{var} = a^{-n} \frac{\int d^d\underline{R} \; |\psi(\underline{R})|^2 V_0 R^n}{\int d^d\underline{R} \; |\psi(\underline{R})|^2} = a^{-n} \langle PE \rangle_{exact}$$

Likewise $\langle KE \rangle_{var} = a^2 \langle KE \rangle_{exact}$

so $\langle H \rangle_{var} = a^2 \langle KE \rangle_{exact} + a^{-n} \langle PE \rangle_{exact}$

At minimum $2a \langle KE \rangle_{exact} - n a^{-(n+1)} \langle PE \rangle_{exact} = 0$

But we know $a = 1$ is optimal, so $\langle KE \rangle_{exact} = \frac{n}{2} \langle PE \rangle_{exact}$

SHO : $\langle KE \rangle = \langle PE \rangle$

Coulomb : $\langle KE \rangle = -\frac{1}{2} \langle PE \rangle$

WKB approximation

Way to study quantum problems in semiclassical limit: (quantum wavelength) $\ll$ (scale in $V(r)$)

Limited to 1D or radial problems in 3D with spherical symmetry

Recall 1D QM

Ptcle with total energy E
Pot energy V (indept of x for now)

$$\psi = A e^{ikx}$$

$$\frac{\hbar^2 k^2}{2m} = E - V \Rightarrow k = \frac{\sqrt{2m(E-V)}}{\hbar}$$

Probability current

$$j = \frac{\hbar}{2im}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right) = \frac{\hbar k}{m} |A|^2$$

What if $V \to V(x)$ (but slowly varying) ?

Guess $\quad k \to k(x) = \dfrac{\sqrt{2m(E - V(x))}}{\hbar}$

$$A \to A(x) \propto \frac{1}{\sqrt{k(x)}}$$

so that j is constant

$\left(|\psi|^2 \propto \frac{1}{\text{speed}}\right)$

Derivation

Write $\quad \psi(x) = A(x)\, e^{i\int^x k(x')\,dx'}$ $\quad A, k$ real

Substitute into TISE to find $A(x)$ & $k(x)$

Recall that $\quad \dfrac{d}{dx}\int^x k(x')\,dx' = k(x)$

$$\frac{d\psi}{dx} = \left[A'(x) + ik(x)A(x)\right] e^{i\int^x k(x')dx'}$$

$$\frac{d^2\psi}{dx^2} = \left[A''(x) + 2ik(x)A'(x) + ik'(x)A(x) - k^2(x)A(x)\right] \times e^{i\int^x k(x')dx'}$$

so

$$\frac{\hbar^2}{2m}\left[k^2(x)A(x) + i\left(2k(x)A'(x) + k'(x)A(x)\right) - A''(x)\right] = \left[E - V(x)\right]A(x)$$

single derivative: quite small

double derivative: v. small

not small even if $V(x)$ const.

zero if $V(x)$ constant so small if $V(x)$ is slowly varying

leading approximation

$$k(x) = \frac{\sqrt{2m[E - V(x)]}}{\hbar}$$

next approximation

$$2k(x)A'(x) + k'(x)A(x) = 0$$

so $$\frac{1}{A(x)}\frac{dA(x)}{dx} = -\frac{1}{2}\frac{1}{k(x)}\frac{dk(x)}{dx}$$

$$\ln[A(x)] = -\frac{1}{2}\ln[k(x)] + C$$

$$A(x) \propto \frac{1}{\sqrt{k(x)}}$$ as anticipated

Physical picture

slowly varying potential: pde's wavelength changes but without backscattering.

varying $A(x)$ ≡ large $|\psi(x)|^2$ where pde is slow

Classically forbidden region

$$\psi(x) \propto \frac{1}{\sqrt{\lambda(x)}}\, e^{-\int^{x}\lambda(x')\,dx'}$$

$$\lambda(x) = \frac{\sqrt{2m(V(x) - E)}}{\hbar}$$ real if $V(x) > E$

Matching region

Classical turning point: suppose $V(x) = E$ at $x = x_c$. Then $k(x)$ & $\lambda(x)$ go to zero as x approaches x_c

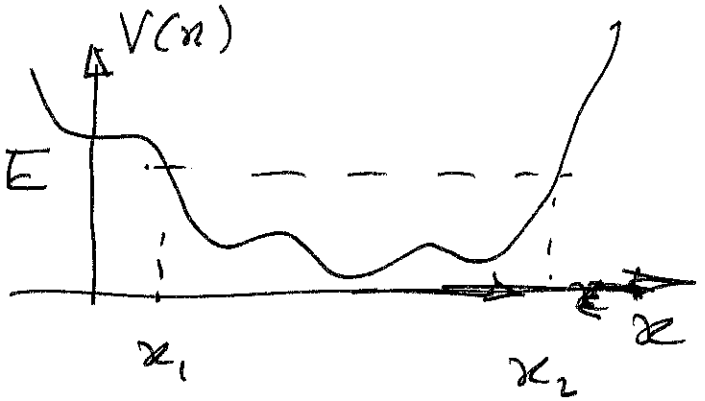
If $V(x)$ is smooth, can Taylor-expand

$$V(x) \simeq V(x_c) + (x - x_c) V'(x_c)$$

and match WKB solutions on each side of x_c. Details beyond scope of course.

Bound states

whole number of $\frac{1}{2}$-wavelengths between classical turning points



$$\int_{x_1}^{x_2} k(x)\, dx = n\pi + \text{const} = \left(n + \tfrac{1}{2}\right)\pi$$

depends on matching region

$\Rightarrow$ hence E_n for n large.

Example Simple Harmonic Oscillator

$$V(x) = \tfrac{1}{2} k x^2$$

Classical turning points $\pm x_c$

$$E = \tfrac{1}{2} k x_c^2$$

$$k(x) = \frac{\sqrt{2m[E - V(x)]}}{\hbar} = \frac{\sqrt{mk(x_c^2 - x^2)}}{\hbar}$$

so

$$(n + \tfrac{1}{2})\pi = \int_{-x_c}^{x_c} k(x)\, dx \qquad \text{let } x = x_c s$$

$$= \frac{\sqrt{mk x_c^2}}{\hbar} x_c \underbrace{\int_{-1}^{1} (1 - s^2)^{1/2}\, ds}$$

$s = \sin\theta \qquad ds = \cos\theta\, d\theta$

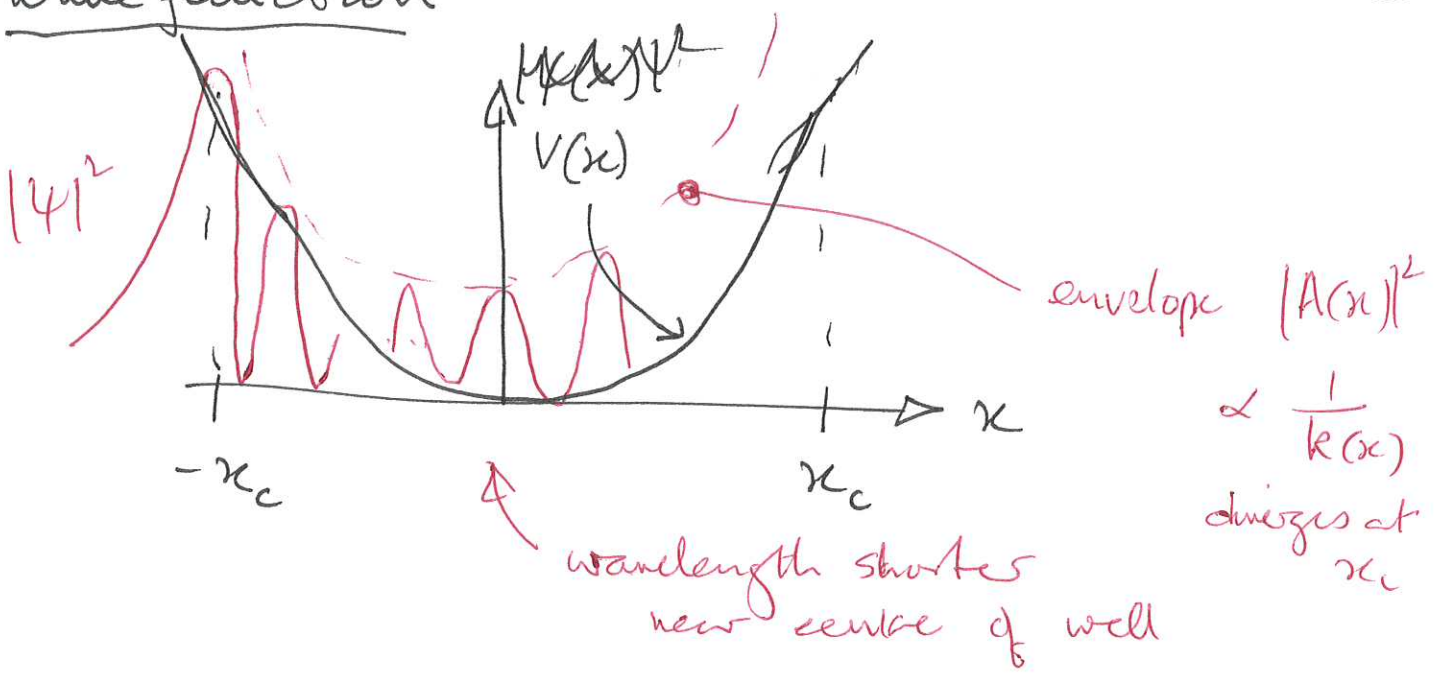
$$\int_{-\pi/2}^{\pi/2} \cos^2\theta\, d\theta = \frac{\pi}{2}$$

so $$(n + \tfrac{1}{2})\pi = \frac{\sqrt{mk}}{\hbar} x_c^2 \frac{\pi}{2}$$

and $$x_c^2 = 2 \frac{\hbar}{\sqrt{mk}} (n + \tfrac{1}{2})$$

hence $$E = \tfrac{1}{2} k x_c^2 = \hbar \sqrt{\frac{k}{m}} (n + \tfrac{1}{2}) = \hbar\omega (n + \tfrac{1}{2})$$

Wave function



— see slide.

Second Example: WKB & tunnelling – α decay

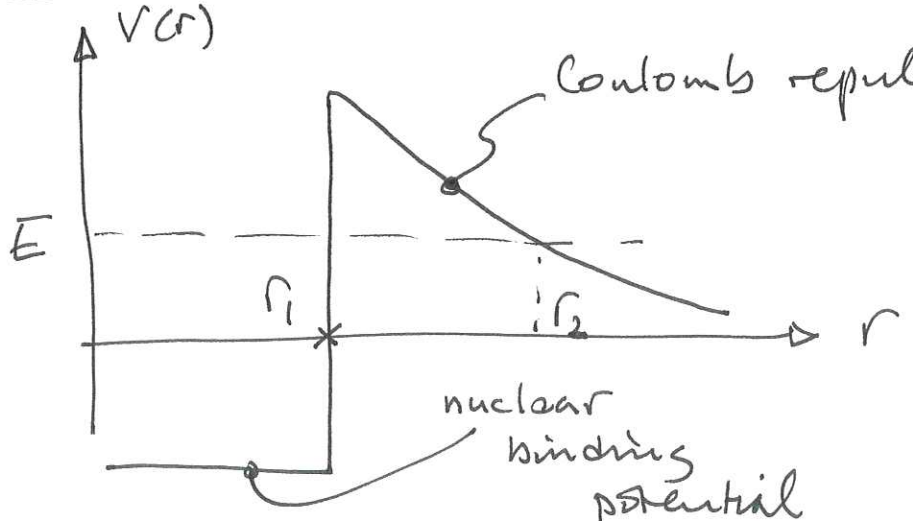
Eg $^{238}U \longrightarrow {}^{234}Th + \alpha$ ($2n + 2p$)

½-life of ^{238}U is $\sim 5 \times 10^9$ years

but ^{232}U has ½-life of only 70 years

– Why?

Potential seen by α-pcle



α-pcle tunnels through classical barrier between r_1 & r_2

Inside barrier

$$\lambda(r) = \frac{\sqrt{2m(V(r)-E)}}{\hbar}$$

$$V(r) = \frac{2Ze^2}{4\pi\varepsilon_0 r} \qquad E = V(r_2)$$

Treat as 1D

$$\psi(r_2) = \psi(r_1)\, e^{-\int_{r_1}^{r_2}\lambda(r)\,dr}$$

$$\int_{r_1}^{r_2}\lambda(r) \propto \int_{r_1}^{r_2}\left(\frac{1}{r}-\frac{1}{r_2}\right)^{1/2}dr \simeq \int_{r_1}^{r_2}\left(\frac{1}{r}\right)^{1/2}dr \simeq 2r_2^{1/2}$$

$$\propto E^{-1/2}.$$

Decay rate ~ (attempt frequency) × (escape probability)

$$\sim \frac{\text{velocity}}{\text{nuclear size}} \times |\psi(r_2)|^2 / |\psi(r_1)|^2$$

$$\propto \exp\left(-\text{const} \times E^{-1/2}\right)$$

so lifetime $\propto \exp\left(\text{const} \times E^{-1/2}\right)$

See graph: vary E by considering different isotopes. Variation in $\frac{1}{2}$-life from 5×10^{9} yrs to 10^{-4} yrs.

Approximations for quantum problems with time-dependent Hamiltonians

Example : atom in light beam

Want to solve TDSE

$$i\hbar\, \partial_t |\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$$

If $\hat{H}$ is constant can use separation of variables to show general solution is

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar}|n\rangle$$

But if $\hat{H}$ varies with time, c_n, E_n & $|n\rangle$ all become time-dependent.

Overview

Three alternative simplifications

(1) Sudden $\hat{H}(t)$ changes quickly between initial + final forms

(2) Adiabatic $\hat{H}(t)$ changes slowly

(3) Perturbative : $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ ← small

NB fast/slow must be compared with intrinsic frequency

Sudden approximation

$$H(t) = \begin{cases} H_i & t < 0 \\ H_f & t > 0 \end{cases}$$

simple to treat because TDSE is first order.

For $t > 0$ have

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} |n\rangle$$

where $H_f|n\rangle = E_n|n\rangle$

and $c_n = \langle n|\psi(t=0^-)\rangle$

Example

Particle in a box

Initially in ground state

Expand box suddenly

Probability still to be in ground state?

$$H_i = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_i(x)$$

$$H_f = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_f(x)$$

$$V_i(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases} \qquad V_f(x) = \begin{cases} 0 & 0 < x < 2a \\ \infty & \text{otherwise} \end{cases}$$

Initially in ground state

$$\langle x | \psi(t=0^-) \rangle = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{\pi x}{a}\right)$$

Ground state wavefn in box of side $2a$ is

$$\langle x | n=1 \rangle = \left(\frac{1}{a}\right)^{1/2} \sin\left(\frac{\pi x}{2a}\right)$$

so

$$C_1 = \frac{\sqrt{2}}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi x}{2a}\right)$$

Use $\sin A \sin B = \frac{1}{2}\left[\cos(A-B) - \cos(A+B)\right]$

$$C_1 = \frac{1}{a\sqrt{2}} \int_0^a \left[\cos\left(\frac{\pi x}{2a}\right) - \cos\left(\frac{3\pi x}{2a}\right)\right] dx$$

$$= \frac{1}{a\sqrt{2}} \left[\frac{2a}{\pi} \sin\left(\frac{\pi x}{2a}\right) - \frac{2a}{3\pi} \sin\left(\frac{3\pi x}{2a}\right)\right]_0^a$$

$$= \frac{4\sqrt{2}}{3\pi}$$

So prob to remain in gnd state is

$$|C_1|^2 = \frac{32}{9\pi^2} = 0.360$$

Also non-zero probabilities $|C_n|^2$ for $n > 1$ to be in excited states

Adiabatic limit

$H(t)$ changes slowly

For each time t, $H(t)$ has set of eigenstates: "instantaneous eigenstates"

Theorem: if system starts in instantaneous eigenstate, it remains in the eigenstate as $H(t)$ changes.

(proof next lecture)

In previous example:

If box size increases slowly

pole remains exactly in gnd state

zero probability of transition to excited state.

Energy in time-dependent problems

Avge energy of quantum system

$$E(t) = \langle \psi(t) | \hat{H}(t) | \psi(t) \rangle$$

Time dependence?

$$\partial_t E(t) = \left(\partial_t \langle \psi | \right) \hat{H} | \psi \rangle + \langle \psi | \hat{H} \left(\partial_t | \psi \rangle\right) + \langle \psi | \left(\partial_t \hat{H}\right) | \psi \rangle$$

We know (TDSE)

$$\partial_t |\psi\rangle = \frac{1}{i\hbar} \hat{H} |\psi\rangle$$

& $$\partial_t \langle\psi| = -\frac{1}{i\hbar} \langle\psi| \hat{H}$$

so $$\partial_t E(t) = \langle\psi| (\partial_t \hat{H}) |\psi\rangle$$

Energy of quantum system is not conserved if $\partial_t \hat{H} \neq 0$ — work is done on/by surroundings.

Consider slowly expanded box (length L)

In instantaneous ground state

$$E = \frac{\hbar^2 \pi^2}{8 m L^2}$$

$$\Delta E = -\frac{2E}{L} \Delta L$$

Force (pressure) of pde on wall is $F = \frac{2E}{L}$.

Classical calculation

$$\text{Force} = \text{Rate of change of momentum} = \frac{2mv}{2L/v} = 2 \times \frac{\frac{1}{2} m v^2}{L}$$

($2mv$: per reflection; $2L/v$: time between bounces)

Summarise

In this example (not always)

Sudden change in box length → no alteration in energy of quantum system

adiabatic change in box length → quantum system does work on moving wall of box & looses energy

(Proof) of adiabatic theorem

Instantaneous eigenstates

$$\hat{H}(t)\,|n(t)\rangle = E_n(t)\,|n(t)\rangle$$

Use these to write wavefn

$$|\psi(t)\rangle = \sum_n c_n(t) \exp\left(-\tfrac{i}{\hbar}\int^t E_n(t')\,dt'\right) |n(t)\rangle$$

① Substitute into TDSE

$$i\hbar\,\partial_t|\psi(t)\rangle =$$

$$= \sum_n \exp(\quad)\left\{\left(i\hbar\,\partial_t c_n + c_n E_n(t)\right)|n(t)\rangle + i\hbar c_n\,\partial_t|n(t)\rangle\right\}$$

$$\hat{H}(t)|n(t)\rangle = \sum \exp(\quad)\, c_n E_n(t)\,|n(t)\rangle$$

② Act with $\langle m(t)|$ to pick out one term & Multiply by $\frac{1}{i\hbar}\exp\left(+\frac{i}{\hbar}\int^t E_m(t')\,dt'\right)$

$$\partial_t c_m(t) = -\sum_n c_n(t)\, e^{\frac{i}{\hbar}\int^t [E_m(t') - E_n(t')]\,dt'} \times \langle m(t)|\frac{d}{dt}|n(t)\rangle$$

Can get $\langle m(t)|\frac{d}{dt}|n(t)\rangle$ from time-independent perturbation theory.

Under $t \to t + \Delta t$

$$\hat{H}(t) \to \hat{H}(t) + \Delta t \cdot \partial_t \hat{H}(t)$$

so $|n(t)\rangle \to |n(t)\rangle + \sum_{\substack{m \\ m\neq n}}{}' |m\rangle \frac{\langle m|\hat{V}|n\rangle}{E_n - E_m}$

where $\hat{V} = \Delta t \cdot \partial_t \hat{H}(t)$

so $$\langle m(t)|\frac{d}{dt}|n(t)\rangle = \frac{\langle m(t)|\frac{d\hat{H}}{dt}|n(t)\rangle}{E_n(t) - E_m(t)}$$

so

$$\partial_t c_m(t) = -\sum_{\substack{n \\ n\neq m}}{}' c_n(t) e^{\frac{i}{\hbar}\int^t (E_m(t') - E_n(t'))\,dt'} \times \frac{\langle m(t)|\partial_t \hat{H}(t)|n(t)\rangle}{E_n(t) - E_m(t)}$$

Want to integrate this in time

If change is slow $\partial_t \hat{H}(t)$ is small

But change takes long time

— do effects build up?

Suppose $\hat{H}(t)$ changes on timescale T

Write $s = t/T$

$s = 0$ at start

$s = 1$ at end

$$\frac{d}{dt} = \frac{1}{T}\frac{d}{ds}$$

$$\hat{H}(t/T) \equiv \hat{H}(s)$$

Then

$$\frac{dC_m}{ds} = -\sum_n{}' C_n(s)\, e^{\frac{i}{\hbar} T \int^s [E_m(s') - E_n(s')]\, ds'} \times \frac{\langle m(s) | \frac{d\hat{H}}{ds} | n(s) \rangle}{E_n(s) - E_m(s)}$$

$$C_m(1) + C_m(0) + \int_0^1 \frac{dC_m}{ds}\, ds$$

but $e^{i\frac{T}{\hbar}\int \ldots}$ $\Rightarrow$ rapid oscillations when T is large

$\Rightarrow$ large to zero.

So $C_m(1) = C_m(0)$ as $T \to \infty$

Applications

① Cosmic microwave background radiation

cf pcle in expanding box

300,000 yrs after 'big bang'

Photons with energies $\sim 13.6\,eV$

Now with energy $2.7\,K$

② Molecular / solid vibrations

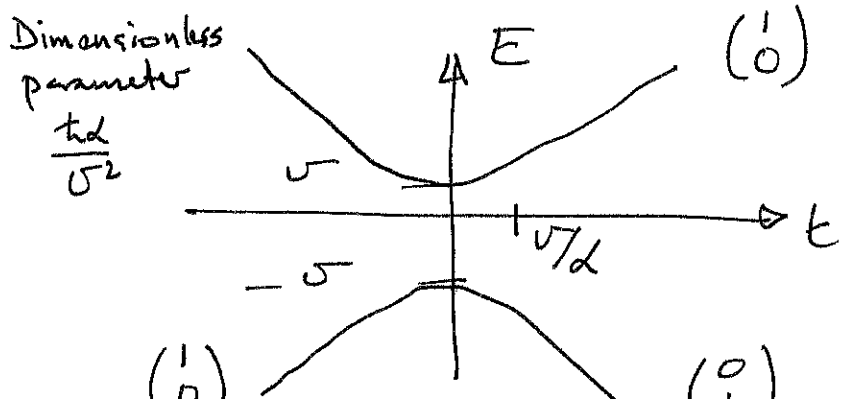
'Electron glue' remains in instantaneous ground state as nuclei move.

The Landau–Zener Problem

World's simplest time-dependent Hamiltonian

$$H = \begin{pmatrix} \alpha t & v \\ v & -\alpha t \end{pmatrix}$$

$$E = \sqrt{(\alpha t)^2 + v^2}$$



Start system in $\begin{pmatrix}1\\0\end{pmatrix}$ for $t \to -\infty$

Then as $t \to +\infty$

Adiabatic limit α small $\psi \sim \begin{pmatrix}0\\1\end{pmatrix}$

Fast limit

Time-dependent perturbation theory

Suppose time-dependent part of $\hat{H}$ is small

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

($\hat{H}_0$: time-independent; $\hat{V}(t)$: small)

Try $$|\psi(t)\rangle = \sum_n c_n(t)\, e^{-iE_n t/\hbar} |n\rangle$$

(E_n: evalues, $|n\rangle$: estates of $\hat{H}_0$)

- Always possible
- Time-dependence of $c_n(t)$ due to $\hat{V}(t)$

TDSE becomes

$$\sum_n e^{-iE_n t/\hbar} \left\{ i\hbar \left[\partial_t c_n(t)\right] + E_n c_n(t) \right\} |n\rangle$$

$$= \sum_n e^{-iE_n t/\hbar} c_n(t) \left\{ \hat{H}_0 |n\rangle + \hat{V}(t)|n\rangle \right\}$$

Take $\langle m| \ldots$ to pick out one term on LHS & multiply by $\frac{1}{i\hbar} e^{+iE_n t/\hbar}$

$$\partial_t c_m(t) = \frac{1}{i\hbar} \sum_n e^{i(E_m - E_n)t/\hbar} \langle m|\hat{V}(t)|n\rangle\, c_n(t)$$

So far no approximation

— but have many coupled differential eqns

Perturbative expansion

Suppose system is initially ($t=0$) in state "i"
Want probability for transition to final state "f".

At zeroth order in $\hat{V}(t)$ $\quad C_n(t) = \delta_{n,i}$

— substitute this in rhs

Then at first order in $\hat{V}(t)$

$$\partial_t C_f(t) = \frac{1}{i\hbar} \langle f | \hat{V}(t) | i \rangle \, e^{i(\epsilon_f - \epsilon_i)t/\hbar}$$

with initial condition $C_f(t=0) = 0$

so

$$C_f(t) = \frac{1}{i\hbar} \int_0^t dt' \langle f | \hat{V}(t') | i \rangle \, e^{i(\epsilon_f - \epsilon_i)t'/\hbar} dt'$$

$$+ \quad \Theta(\hat{V}^2(t))$$

write $\quad \dfrac{\epsilon_f - \epsilon_i}{\hbar} \equiv \omega_{fi}$

Perturbation periodic in time

often (eg atom + light) interested in

$$\hat{V}(t) = \hat{V}\, e^{-i\omega t}$$

↳ indept of time

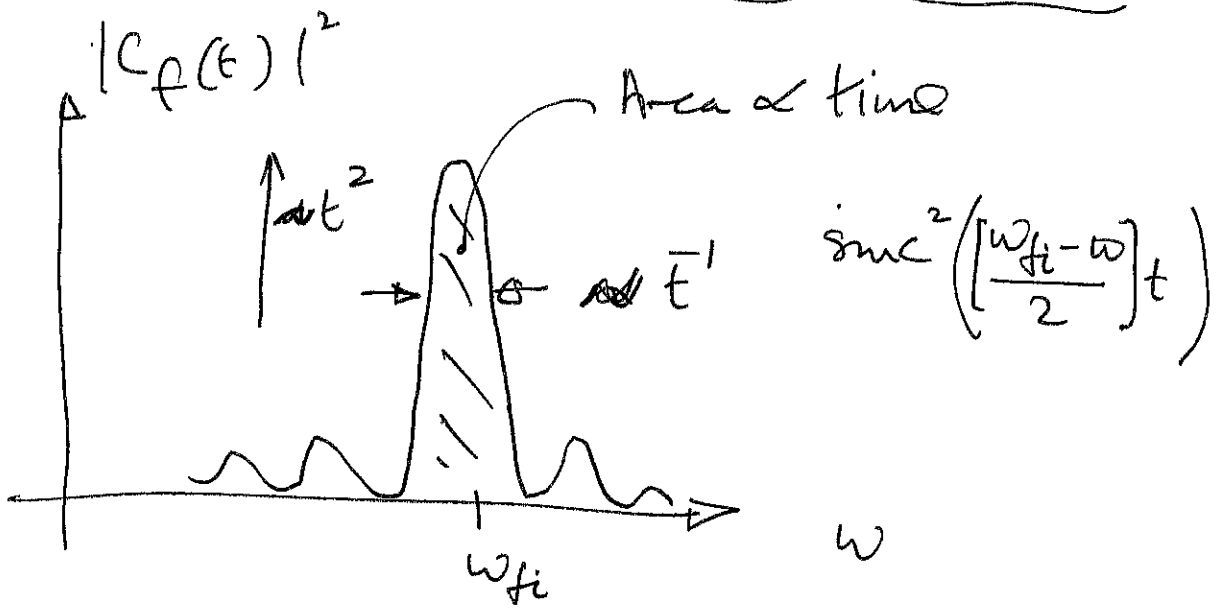
Then

$$c_f(t) = -\frac{1}{i\hbar} \langle f|\hat{V}|i\rangle \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega}$$

or

$$|c_f(t)|^2 = \frac{1}{\hbar^2} |\langle f|\hat{V}|i\rangle|^2 \frac{\sin^2\left(\left[\frac{\omega_{fi}-\omega}{2}\right]t\right)}{\left[(\omega_{fi}-\omega)/2\right]^2}$$

How does transition probability depend on ω & t?



$$\int_{-\infty}^{\infty} d\omega \; \frac{\sin^2\left(\left[\frac{\omega_{fi}-\omega}{2}\right]t\right)}{\left(\left[\omega_{fi}-\omega\right]/2\right)^2}$$

$$x = \left[\frac{\omega_{fi}-\omega}{2}\right]t$$

$$dx = -\frac{t}{2}\,d\omega$$

$$= 2t \underbrace{\int_{-\infty}^{\infty} dx \; \frac{\sin^2 x}{x^2}}$$

π — see complex analysis short optic

So can summarise result as

Transition rate $i \to f$ is

$$\boxed{\frac{2\pi}{\hbar^2}\,|\langle f|\hat{V}|i\rangle|^2\,\delta(\omega_{fi}-\omega)}$$

NB time-dependence $\hat{V}(t) = \hat{V}\,e^{i\omega t}$

gives $\omega_{fi} = \omega$ i.e. $E_f - E_i = \hbar\omega$

— transition up in energy.

Opposite time-dependence $\hat{V}(t) = \hat{V}\,e^{+i\omega t}$

gives $\omega_{fi} = -\omega$ i.e. $E_f - E_i = -\hbar\omega$

— transition down in energy

Fermi Golden Rule

δ-fn is awkward: need a physical reason to integrate over $\omega_{fi} - \omega$.

Two possibilities

① Discrete E_f & E_i so fixed ω_{fi} but range of drive frequencies ω with density $\rho(\omega)$

eg atom under illumination that is not perfectly monochromatic

Integrate on ω

$$\text{Transition rate} = \frac{2\pi}{\hbar^2} |\langle f|\hat{V}|i\rangle|^2 \rho(\omega_{fi})$$

② Continuous range of final states (but fixed ω). Let density be $g(E_f)$

Integrate on E_f

$$g(E_f)\, dE_f = g(E_f)\, \hbar\, d\omega_{fi}$$

$$\text{Transition rate} = \frac{2\pi}{\hbar} |\langle f|\hat{V}|i\rangle|^2 g(E_f)$$

Radiative transitions

Important application of results for time-dependent perturbation theory

Transitions between atomic energy levels induced by light

What is $\hat{V}$ in this case?

Interaction between light & electron in atom due to electric & magnetic forces

Electron speed $\ll c$ $\Rightarrow$ electric forces dominate

Light wavelength $\ll$ size of atom

$\Rightarrow$ electric field $\approx$ constant across ~~[illegible]~~ atom

Together: "dipole approximation".

In principle light described in terms of scalar & vector potentials. Will just use scalar potential appropriate for uniform oscillating electric field.

If electric field is along $\hat{z}$

$$\hat{V} = e\mathcal{E}\hat{z}$$

So transition rate $i \to f$ is given by

$$\frac{2\pi}{\hbar^2} e^2 \mathcal{E}^2 |\langle f|z|i\rangle|^2 g(\omega_{fi})$$

NB This gives rate of absorption and of stimulated emission (i.e. caused by incident light).

There is also spontaneous emission by atoms that are initially in an excited state.

To describe this, need to treat light quantum mechanically (as well as atom).

[Essentially: zero-pt fluctuations of EM-field have similar effect to oscillating field of incident light.]

Selection Rules

Not sufficient that $W = W_{fi}$ for transition to happen.

Whether it does is controlled by 'selection rules'.

Two ways to think about this:

(1) Conservation of angular momentum

Same for (initial atomic state + photon) and (final atomic state).

(2) Matrix element

Is $\langle f | \hat{V} | i \rangle$ non-zero?

Via Conservation of angular momentum

Recall rules for addition of angular momentum in QM

Two objects with quantum numbers l_1 & l_2 for total angular momentum operators & m_1 & m_2 for z-cpt.

Combined system has quantum numbers l, m with: $|l_1 - l_2| \leq l \leq |l_1 + l_2|$ & $m = m_1 + m_2$

Here

System (1) is atom in initial state

Quantum numbers ℓ_i & m_i

System (2) is photon

Photon has $\ell_{photon} = 1$

& $m_{photon} = \pm 1$ along axis of travel

Combined system is atom in final state

Quantum numbers ℓ_f & m_f

Conclude

(a) $|\ell_i - 1| \leq \ell_f \leq |\ell_i + 1|$

(b) $m_f = m_i \pm 1$ if photon travels along $\hat{z}$-axis (i.e. quantisation axis)

or $m_f = m_i, m_i \pm 1$ for general propagation direction

Via Matrix elements

$\langle f | \hat{z} | i \rangle$ is triple integral

— on r, θ & ϕ.

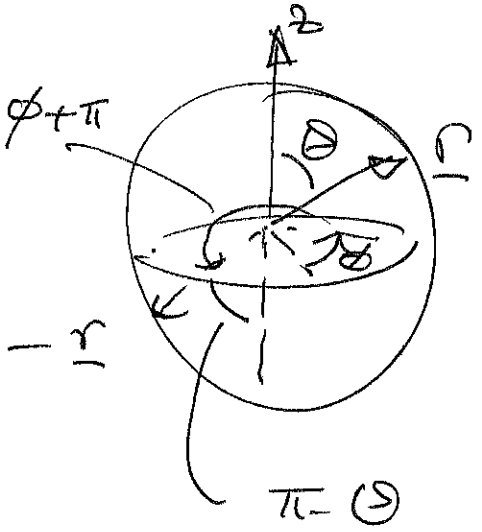
Important parts are angular ones.

Non-zero only if $l_f = l_i \pm 1$

(so $l_f = l_i$ is forbidden).

Can see this by considering effect of parity operation : $\underline{r} \to -\underline{r}$

or $\begin{cases} r \to r \\ \theta \to \pi - \theta \\ \phi \to \phi + \pi \end{cases}$



Effect of inversion on spherical harmonics

$$Y_{lm}(\pi-\theta, \phi+\pi) = (-1)^l Y(\theta,\phi)$$

Examples

$$Y_{0,0} = \text{const}$$

$$Y_{1,1} \propto \sin\theta\, e^{i\phi}$$

$$Y_{1,0} \propto \cos\theta$$

Consider change of variables in calculation of $\langle f|\hat{z}|i\rangle = (-1)^{l_f+l_i+1}\langle f|\hat{z}|i\rangle$

Either $l_f + l_i + 1$ is even or $\langle f|\hat{z}|i\rangle = 0$

Consider also integral on ϕ

$$\langle f|V|i\rangle \propto \int_0^{2\pi} d\phi \; e^{-im_f\phi} \times \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} e^{+im_i\phi}$$

according to polarisation of incident light

In spherical polars

$$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = \begin{Bmatrix} r\sin\theta\cos\phi \\ r\sin\theta\sin\phi \\ r\cos\theta \end{Bmatrix}$$

so terms in $e^{\pm i\phi}$ for photon propagating along $\hat{z}$

$$\Rightarrow \quad m_f = m_i \pm 1 \quad \text{in this case}$$

Summary (electric dipole transitions)

$$\Delta l = \pm 1$$

$$\Delta m = 0, \pm 1$$

but $\Delta m = \pm 1$ for photon propagating along $\hat{z}$

No coupling to spin, so initial & final spin states are identical

Identical Particles

Principles

'Identical' has much stronger meaning in QM than classically

(Initial configuration) $\xrightarrow{\text{dynamics}}$ (Final configuration)

Classically: can always follow trajectories & know which initial pcle moved to which final position

So classically 'identical' means same law of motion, but can tell which pcle is which

Quantum mechanically: cannot follow trajectories without changing behavior of two-slits interference

Cf Statistical mechanics course

Practicalities

From one pcl to N pcles

$$\psi(\underline{r}) \longrightarrow \psi(\underline{r}_1, \underline{r}_2 \cdots \underline{r}_N)$$

$$|\psi(\underline{r}_1 \cdots \underline{r}_N)|^2 \, d^3\underline{r}_1 \cdots d^3\underline{r}_N$$

gives prob density to find pcle 1 in vol $d^3\underline{r}_1$ near $\underline{r}_1$ ... & pcle N in vol $d^3\underline{r}_N$ near $\underline{r}_N$.

Consider N=2

$$|\psi(\underline{r}_1, \underline{r}_2)|^2 = |\psi(\underline{r}_2, \underline{r}_1)|^2$$

if pcles identical.

Define exchange operator P_{12} swaps 1 & 2

$$P_{12} \, \psi(\underline{r}_1, \underline{r}_2) = \psi(\underline{r}_2, \underline{r}_1)$$

$$= e^{i\alpha} \psi(\underline{r}_1, \underline{r}_2) \qquad \alpha \text{ real}$$

Then

$$(P_{12})^2 \psi(\underline{r}_1, \underline{r}_2) = P_{12} \psi(\underline{r}_2, \underline{r}_1) = \psi(\underline{r}_1, \underline{r}_2)$$

so $(e^{i\alpha})^2 = 1 \quad \Rightarrow \quad e^{i\alpha} = \pm 1$.

Observational fact

Two types of pcle

fermions $\quad \hat{\mathcal{O}}^{\alpha} = -1$

bosons $\quad \hat{\mathcal{O}}^{\alpha} = +1$

From relativistic quantum field theory, spin-statistics theorem:

fermions — half odd integer spin

bosons — integer spin

Building wavefns of correct symmetry

Two-particle system

Consider eigenstates of Hamiltonian

In general $H = H_1 + H_2 + H_{12}$

H_1: pcle 1, H_2: pcle 2, H_{12}: interacting

e.g. ($d=3$)

$$H_k = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2}\right) + V(\underline{r}_k)$$

$k = 1$ or 2

$$H_{12} = V(\underline{r}_1 - \underline{r}_2)$$

Want to solve

$$H\psi(\underline{r}_1, \underline{r}_2) = E\psi(\underline{r}_1, \underline{r}_2)$$

Try separation of variables – OK if $H_{12} = 0$

$$\psi(\underline{r}_1, \underline{r}_2) = \varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2)$$

substitute into TISE & divide by ψ

$$\frac{1}{\varphi_1(\underline{r})} H_1 \varphi_1(\underline{r}_1) + \frac{1}{\varphi_2(\underline{r}_1)} H_2 \varphi_2(\underline{r}_2) = E$$

Provided there is no term $\frac{1}{\varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2)} H_{12}\varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2)$

we can say each term is constant, so

$$H_1\varphi_1(\underline{r}_1) = E_1\varphi_1(\underline{r}_1)$$
$$H_2\varphi_2(\underline{r}_2) = E_2\varphi_2(\underline{r}_2) \quad \& \quad E = E_1 + E_2$$

This solves PDE but is not end of story

In general $\varphi_1(\underline{r}_2)\varphi_2(\underline{r}_1) \neq e^{i\alpha}\varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2)$

[Exception: if $\varphi_1(\underline{r}) = \varphi_2(\underline{r})$, in which case $e^{i\alpha} = 1$]

Recall Sep^n of vbles – general sol^n is superposition of terms with product form

Here: need to symmetrise or antisymmetrise

Bosons

$$\psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}} \left\{ \varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2) + \varphi_2(\underline{r}_1)\varphi_1(\underline{r}_2) \right\}$$

Fermions

$$\psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}} \left\{ \varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2) - \varphi_2(\underline{r}_1)\varphi_1(\underline{r}_2) \right\}$$

Both are eigenfunctions of $H_1 + H_2$ with energy $E = E_1 + E_2$

Pauli exclusion principle

If states $\varphi_1(\underline{r})$ & $\varphi_2(\underline{r})$ are the same, the antisymmetrised $\psi(\underline{r}_1, \underline{r}_2)$ vanishes

– two identical fermions cannot occupy same quantum state.

Counting states in statistical physics

Consides two different orbitals that can be occupied by two pcles

Distinguishable pcles

4 possible states

$\varphi_1(\underline{r}_1)\ \varphi_1(\underline{r}_2)$ both in state 1

$\varphi_2(\underline{r}_1)\ \varphi_2(\underline{r}_2)$ both in state 2

$\varphi_1(\underline{r}_1)\ \varphi_2(\underline{r}_2)$ { pcle 1 in state 1 / pcle 2 in state 2

$\varphi_2(\underline{r}_1)\ \varphi_1(\underline{r}_2)$ { pcle 1 in state 2 / pcle 2 in state 1

Identical bosons

3 possible states

– symmetrise last two

Identical fermions

1 allowed state

– exclude first two

antisymmetrise last two

More generally

Specify distinct states of non-interacting system by # ptcles in each orbital (cf Gibbs paradox)

Make wavefn by symmetrising (bosons) or antisymmetrising (fermions).

Examples

3 identical bosons: two in orbital $\varphi_1(\underline{r})$ & one in orbital $\varphi_2(\underline{r})$

$$\psi(\underline{r}_1,\underline{r}_2,\underline{r}_3) = \frac{1}{\sqrt{3}}\{\varphi_1(\underline{r}_1)\varphi_1(\underline{r}_2)\varphi_2(\underline{r}_3) + \varphi_1(\underline{r}_2)\varphi_1(\underline{r}_3)\varphi_2(\underline{r}_1) + \varphi_1(\underline{r}_1)\varphi_1(\underline{r}_3)\varphi_2(\underline{r}_2)\}$$

N identical fermions in orbitals $\varphi_1(\underline{r}_1)\ldots\varphi_N(\underline{r})$

$$\psi(\underline{r}_1,\underline{r}_2\ldots\underline{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(\underline{r}_1) & \varphi_2(\underline{r}_1) & \cdots & \varphi_N(\underline{r}_1) \\ \varphi_1(\underline{r}_2) & \varphi_2(\underline{r}_2) & \cdots & \\ & & & \\ \varphi_1(\underline{r}_N) & \cdots & & \varphi_N(\underline{r}_N) \end{vmatrix}$$

'Slater determinant'

Product spaces

Suppose we have basis states $\{|x_1\rangle\}$ for pcle 1 and $\{|x_2\rangle\}$ for pcle 2.

Can write as basis for product space

$$|x_1, x_2\rangle = |x_1\rangle \otimes |x_2\rangle$$

"times" (direct product)

Need to define

① Scalar product

If $|y_1, y_2\rangle = |y_1\rangle \otimes |y_2\rangle$

then $\langle y_1, y_2 | x_1, x_2\rangle = \langle y_1|x_1\rangle \cdot \langle y_2|x_2\rangle$

② Action of opcalrs

If H_1 involves only coords of 1st pcle

$$H_1 |x_1\rangle = |z_1\rangle$$

Then $H_1 \otimes \mathbb{1}$ acts on $|x_1, x_2\rangle$

$$(H_1 \otimes \mathbb{1})\, |x_1\rangle \otimes |x_2\rangle = |z_1\rangle \otimes |x_2\rangle$$

General state in product space is superposition $\sum_{i,j} A_{ij} |x_i\rangle \otimes |y_j\rangle$

Aside orbital & spin wavefns

similar notation is useful in 1-ptcle problem to discuss orbital & spin degrees of freedom

in hydrogen atom

Eg "electron is in $n=1$ state with spin up"

"$n=1$ state" means orbital wavefn

$$\varphi(r,\theta,\phi) = N e^{-r/a_0}$$

"spin up" means spin wavefn

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

in basis where $S^z = \frac{\hbar}{2}\sigma^z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Combine these by writing

$$\varphi(r,\theta,\phi) \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

as full wavefunction

operator on coords eg $\hat{p}_z \otimes \mathbb{1}$

operator on spin eg $\mathbb{1} \otimes \sigma_z$

symmetrised basis states for multi-particle system

$$|x_1, x_2\rangle = \frac{1}{\sqrt{2}} \{ |x_1\rangle \otimes |x_2\rangle + |x_2\rangle \otimes |x_1\rangle \}$$

– for bosons

$$|x_1, x_2\rangle = \frac{1}{\sqrt{2}} \{ |x_1\rangle \otimes |x_2\rangle - |x_2\rangle \otimes |x_1\rangle \}$$

– for fermions

Simple Example

Two particles in 1D box

coordinates $x, y \in [0, L]$

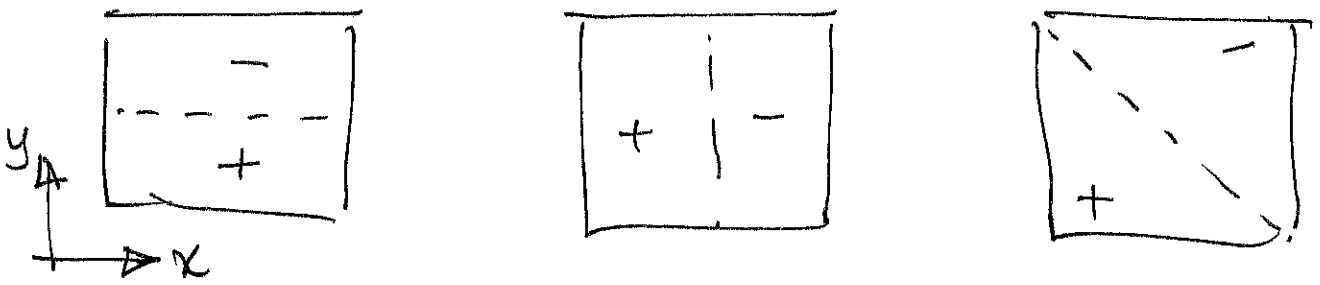
single-pcle wavefns

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

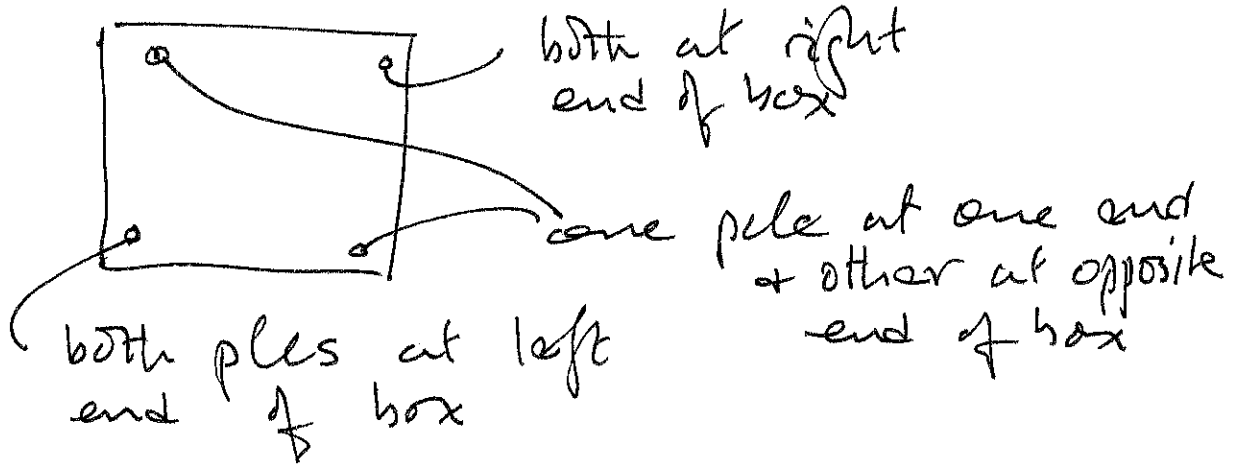
consider state for two bosons with $(n_1, n_2) = (1, 2)$

$$\psi(x,y) = \frac{\sqrt{2}}{L} \left(\sin\frac{\pi x}{L} \sin\frac{2\pi y}{L} + \sin\frac{2\pi x}{L} \sin\frac{\pi y}{L} \right)$$

1st term 2nd term $\psi(x,y)$



Meaning of coords?



bosons bunch together — more likely both to be at same end than at opp ends.

<u>What about fermions?</u>

Choose basis states of form

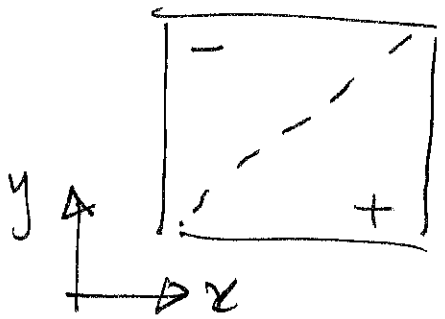
$$|\psi\rangle = |\text{space part}\rangle \otimes |\text{spin part}\rangle$$

Make $|\psi\rangle$ antisymmetric if one factor is antisymmetric & other is symmetric

If |spin part⟩ is symmetric then |space part⟩ must be antisymmetric

In our example

$$\psi(x,y) = \frac{\sqrt{2}}{L}\left(\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L} - \sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\right)$$



$|\psi|^2$ is max when ptcles are at opposite ends of box.

More generally: $\psi(x,y) = -\psi(y,x)$ implies $\psi(x,x) = 0$ so fermions avoid each other (if in symmetric spin state).

<u>Consider spin wavefns for two $s=\frac{1}{2}$ ptcles in more detail</u>

Single ptcle basis states $|\uparrow\rangle$ & $|\downarrow\rangle$
eigenstates of S^2 with e-values $\pm\frac{1}{2}\hbar$

Have $2\times 2 = 4$ two-ptcle states.

Form symmetric/antisymmetric combinations

$|\uparrow_1\rangle \otimes |\uparrow_2\rangle$

$\frac{1}{\sqrt{2}}\{|\uparrow_1\rangle \otimes |\downarrow_2\rangle + |\downarrow_1\rangle \otimes |\uparrow_2\rangle\}$

$|\downarrow_1\rangle \otimes |\downarrow_2\rangle$

– all symmetric

and

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

– antisymmetric

What is physical significance of different combinations?

Recall rules for addition of angular mmtm

$$|l_1 - l_2| \leq l_{tot} \leq [l_1 + l_2]$$

& $l^z_{tot} = 0, \pm 1 \ldots \pm l_{tot}$

Here $s_1 = s_2 = 1/2$

so $s_{tot} = 0$ or 1

$s^z_{tot} = 0, \pm 1$ if $s_{tot} = 1$

$s^z_{tot} = 0$ if $s_{tot} = 0$

See that $s^z_{tot} = +1$ for $|\uparrow_1\rangle \otimes |\uparrow_2\rangle$

& other two symmetric states have $s^z_{tot} = 0, -1$

In fact spin symmetric state has $S_{tot} = 1$
so implies antisymmetric spatial state

antisymmetric spin state has $S_{tot} = 0$
so implies symmetric spatial state

Exchange interactions

If there is an interaction potential between pcles, the energies of different spin states are split even though there are no spin-dependent forces

Calculate energy shift ΔE due to interaction $V(\underline{r}_1 - \underline{r}_2)$ using first-order perturbation theory

$$\Delta E = \iint d^3\underline{r}_1 \, d^3\underline{r}_2 \, |\psi(\underline{r}_1, \underline{r}_2)|^2 \, V(\underline{r}_1 - \underline{r}_2)$$

$$\psi(\underline{r}_1 \underline{r}_2) = \frac{1}{\sqrt{2}} \left\{ \varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2) \pm \varphi_2(\underline{r}_1)\varphi_1(\underline{r}_2) \right\}$$

$+$ for $S_{tot} = 0$
$-$ for $S_{tot} = 1$

$$\Delta E = \Delta E_{Direct} \pm \Delta E_{Exchange}$$

$$\Delta E_{Direct} = \int |\varphi_1(\underline{r}_1)\,\varphi_2(\underline{r}_2)|^2\, V(\underline{r}_1 - \underline{r}_2)\, d^3\underline{r}_1\, d^3\underline{r}_2$$

$$\Delta E_{Exchange} = \int \varphi_1^*(\underline{r}_1)\,\varphi_2^*(\underline{r}_2)\,\varphi_2(\underline{r}_1)\,\varphi_1(\underline{r}_2)\, V(\underline{r}_1 - \underline{r}_2)\, d^3\underline{r}_1\, d^3\underline{r}_2$$

If $V(\underline{r}_1 - \underline{r}_2)$ is maximum for $\underline{r}_1 \simeq \underline{r}_2$ typically have $\Delta E_{Exchange} > 0$

so lowest energy state has spins parallel

Origin of magnetism

Composite systems

Suppose we have two identical ptcles, each made up of N_F fermions & N_B bosons

Exchange of ptcle positions generates factor $(-1)^{N_F}$

So if N_F is odd, composite ptcles are fermions

If even, they are bosons (Cf addition of ang mntm)

Example: He

Two isotopes both superfluid at low T

^3He 1n +2p +2e fermion $T_s = 2.5 \times 10^{-3}$ k

^4He 2n +2p +2e boson $T_s = 2.1$ k

Electronic States of He

Simplest 'many' ptcle system

2 electrons + nucleus ← represents as static potl.

Hamiltonian

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\underline{r}_1 - \underline{r}_2|}$$

$\equiv$ Kinetic energy + Coulomb energy

nucleus – electron & electron – electron

Cannot solve exactly since no sep^n of vbles – need approximations and/or numerical sol^n.

Recall sol^n for single ptcle in Coulomb potl

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

States labelled by n, ℓ, m & m_s

$$\text{Energy} = -Z^2 R \times \frac{1}{n^2}$$

↳ Rydberg $\simeq 13.6$ eV

He Gnd state

simplest approx

Ignore e-e interaction

Then lowest energy state has

$n_1 = n_2 = 1$

so $\ell_1 = \ell_2 = 0$

$m_1 = m_2 = 0$

& $m_{s1} = +\frac{1}{2}$, $m_{s2} = -\frac{1}{2}$

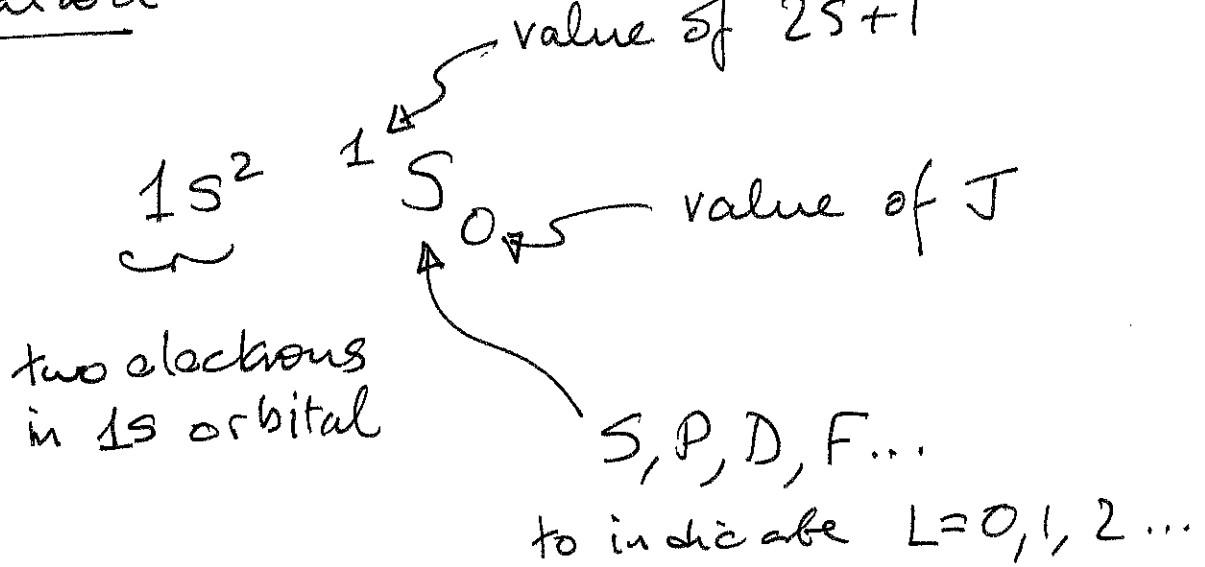
Electrons in singlet state with $S_{tot} = 0$

Also consider $\underline{L} = \underline{\ell}_1 + \underline{\ell}_2$

Clear that $L = 0$

Finally $\underline{J} = \underline{L} + \underline{S}$ clear that $J = 0$

Notation



Ground state energy

Ignoring e-e interactions

$$E = -\frac{Z^2}{4}R \quad \text{for electron with } n=1$$

So gnd state energy is

$$-4R \times 2$$
$$= -8 \times 13.6\ eV$$
$$= -108.8\ eV$$

Correction due to e-e repulsion?

Use 1st order perturbation theory

$$\Delta E = \langle 0 | \frac{e^2}{4\pi\varepsilon_0 |\underline{r}_1 - \underline{r}_2|} | 0 \rangle$$

$$(\varphi_{1s}(r_1)\, \varphi_{1s}(r_2))$$

Clearly +ve a $\Theta(R)$.

Calculate integral (see Binney + Skinner)

$$\Delta E = \frac{5}{2}R$$

So improved estimate is

$$E = -8R + \frac{5}{2}R = -\frac{11}{2}R = -74.8\ eV$$

Experiment: $-79.0\ eV$ — reasonable agreement

Measure via ionisation energies

$$He \xrightarrow[\text{energy}]{\text{1st ionisation}} He^+ + e^- \xrightarrow[\text{energy}]{\text{2nd ionisation}} He^{2+} + 2e^-$$

What about ground state energy of He^+?

Now have problem that is accurately hydrogenic

$$E_{He^+} = -4 \times 13.6\,eV = -54.4\,eV$$

so 2nd ionisation energy is $+54.4\,eV$

1st ionisation energy is approximately

$$-4R - \left(-\frac{11}{2}R\right) = \frac{3}{2}R$$

$$= 20.4\,eV$$

Remaining electron <u>shields</u> nuclear charge

First excited state of He

Return to non-interacting picture

$$E = -4R\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

quantum numbers for two electrons

1st excited state: pick $n_1 = 1$ & $n_2 = 2$

Configuration $1s^1\,2s^1$

[continued] Configuration $1s^1 2s^1$

so total angular mntm $L = 0$

but now have singlet & triplet states

so $(2S+1) = 1$ or 3

and $J = 0$ or 1

so have states with $^1S_0$ & $^3S_1$

Effect of e-e interactions?

From first-order perturbation theory

$$\Delta E = \Delta E_{Direct} \pm \Delta E_{Exchange}$$

(+ : singlet, − : triplet)

$$\Delta E_{Direct} = \iint d^3\underline{r}_1\, d^3\underline{r}_2\, |\varphi_{1s}(r_1)\,\varphi_{2s}(r_2)|^2 \frac{e^2}{4\pi\varepsilon_0|\underline{r}_1 - \underline{r}_2|}$$

$$\Delta E_{Exchange} = \iint d^3\underline{r}_1\, d^3\underline{r}_2\, \varphi_{1s}(r_1)\,\varphi_{2s}(r_2)\,\varphi_{1s}(r_2)\,\varphi_{2s}(r_1) \times \frac{e^2}{4\pi\varepsilon_0|\underline{r}_1 - \underline{r}_2|}$$

$\Delta E_{Exchange} > 0$ because $\frac{1}{|\underline{r}_1 - \underline{r}_2|}$ is largest when $\underline{r}_1 \cong \underline{r}_2$ and in this case

$$\varphi_{1s}(r_1)\,\varphi_{2s}(r_2)\,\varphi_{1s}(r_2)\,\varphi_{2s}(r_1)$$

is positive.

Calculation with this approx gives

$$\Delta E_{Exchange} = 1.2\ eV$$

Experiment

$$\Delta E_{Exchange} = 0.4\ eV$$

Right sign but poor estimate

Simple argument for why triplet is lower in energy

triplet $\Rightarrow$ spins symmetric + spatial wavefn antisymmetric

antisym $\Rightarrow |\psi(\underline{r}_1, \underline{r}_2)|^2 = 0$ if $\underline{r}_1 = \underline{r}_2$

$\Rightarrow$ electrons avoid each other.

$\Rightarrow$ lower Coulomb energy

More nuanced view

perturbation not small

KE as well as PE altered

Avge Energy of Singlet + Triplet

$$E = -4R\left(\frac{1}{1^2} + \frac{1}{2^2}\right) + E_{Direct}$$

$$= -68\ eV + \underbrace{11.4\ eV}_{0.8R}$$

so much smaller than for $1s^2$ state

because 2nd electron is at different radius from 1st

Higher excited states

Have discussed $1s^1 2s^1$

i.e. $n_1 = 1$, $n_2 = 2$, $\ell_1 = \ell_2 = 0$

But with $n_2 = 2$ can also have $\ell_2 = 1$

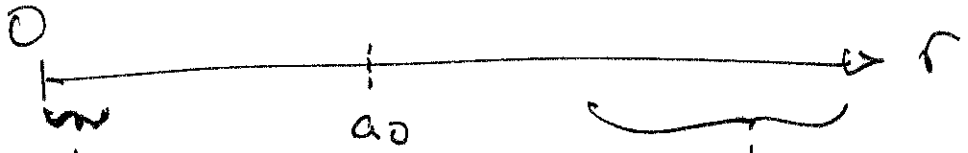
i.e. $1s^1 2p^1$

Energy?

For Coulomb potential & single pcle, energy depends only on n & not on ℓ

No longer true with more than one electron

Consider potential seen by "second" electron



Coulomb with $Z = 2$

Coulomb with $Z = 1$ since charge of "first" electron partially cancels nuclear charge

Binding energy is reduced as Z_{eff} decreases

Electrons with given n are further on avge from nucleus if ℓ is larger

So $1s^1 2p^1$ is higher in energy than $1s^1 2s^1$

$1s^1 2p^1$ is called a configuration

Have several states with this configuration

$L = 1 \Rightarrow P$

either $S = 0 \Rightarrow J = 1$

or $S = 1 \Rightarrow J = 0, 1$ or 2

So

$1s^1 2p^1\ {}^1P_1$ } higher in energy

$1s^1 2p^1\ {}^3P_0$

$1s^1 2p^1\ {}^3P_1$ } lower in energy because of exchange

$1s^1 2p^1\ {}^3P_2$

Many electron atoms

Eigenstates in Coulomb potential + Pauli exclusion principle + the periodic table

Recall periodic table

H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

Count states in Coulomb potential

$n=1$ $\ell=0$ $m=0$ $m_s=\pm\frac{1}{2}$ 2 states H, He

$n=2$ $\ell=0$ $m=0$ $m_s=\pm\frac{1}{2}$
$\ell=1$ $m=0,\pm1$, $m_s=\pm\frac{1}{2}$ } 8 states

$n=3$ $\ell=0$ $m=0$ $m_s=\pm\frac{1}{2}$
$\ell=1$ $m=0,\pm1$ $m_s=\pm\frac{1}{2}$
$\ell=2$ $m=0,\pm1,\pm2$ $m_s=\pm\frac{1}{2}$ } 18 states

Does this explain everything?

— no

① 4s occupied before 3d

② Ionisation energies — see below

Electronic structure of atoms in 1st two periods

H	$1s^1$	$^2S_{1/2}$	
He	$1s^2$	$^1S_0$	
Li	$1s^2 2s^1$	$^2S_{1/2}$	
Be	$1s^2 2s^2$	$^1S_0$	
B	$1s^2 2s^2 2p^1$	^2P_J	$J = 1/2, 3/2$
C	$1s^2 2s^2 2p^2$	^3P_J	$J = 0, 1, 2$
N	$1s^2 2s^2 2p^3$	$^4S_{3/2}$	
O	$1s^2 2s^2 2p^4$	^3P_J	$J = 0, 1, 2$
F	$1s^2 2s^2 2p^5$	^2P_J	$J = 1/2, 3/2$
Ne	$1s^2 2s^2 2p^6$	$^1S_0$	

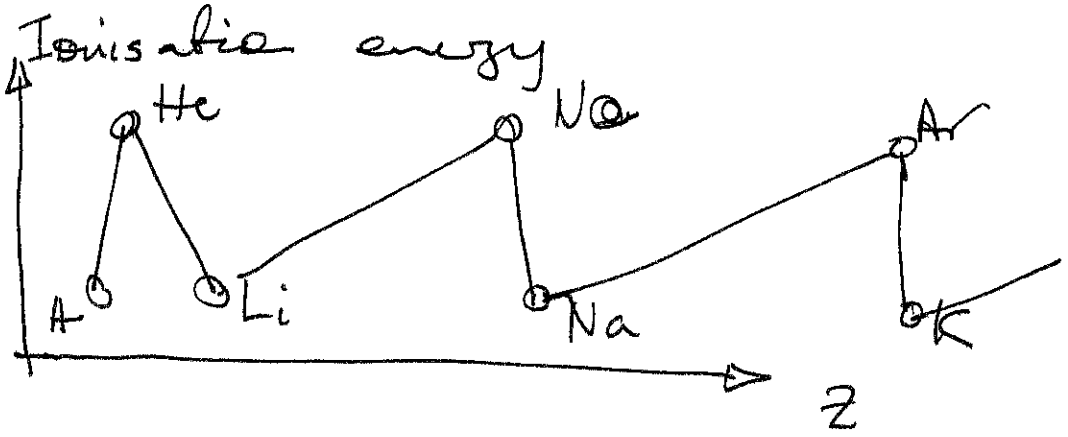
Hund's rules (to minimise Coulomb repulsion between electrons)

① Take highest spin state allowed by Pauli exclusion principle

② Take highest L with this spin

In lecture: (1) Give all configurations
(2) Give ground state for H – B
(3) Discuss N in detail
(4) Give F & Ne
(5) Give Hund's rules (6) Fill in rest

Consider Ionisation energy vs Z



Ionisation energy $\sim \frac{Z_{eff}^2 R}{n^2}$

Z_{eff}^2 ← increases slowly with Z for fixed n

n^2 ← jumps with Z

Outer electron sees effective charge close to $Z_{eff} = 1$ but screening less effective as Z increases within each row of periodic table.

Classical uncertainty & density matrices

Needed to discuss of MRI scanners & quantum computers

QM vs stat phys

Two types of averaging

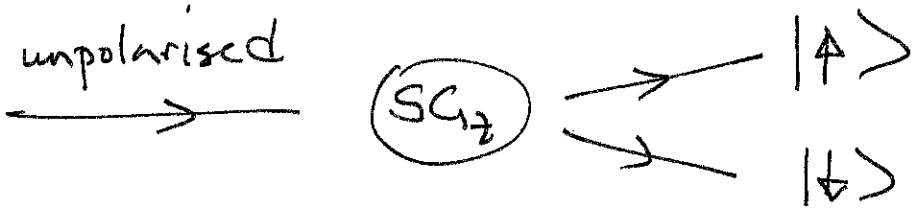
QM $\langle A \rangle = \langle \chi | \hat{A} | \chi \rangle$

Stat Phys $[A]_{Av} = \sum_n p_n A_n$

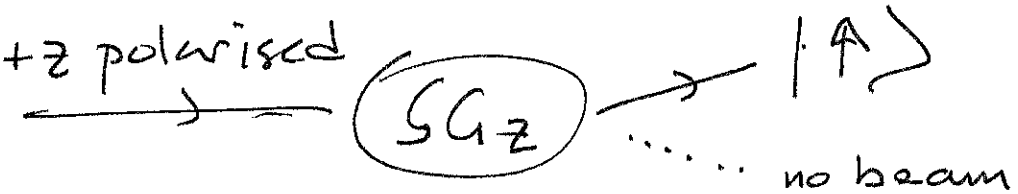
Sometimes need to combine both.

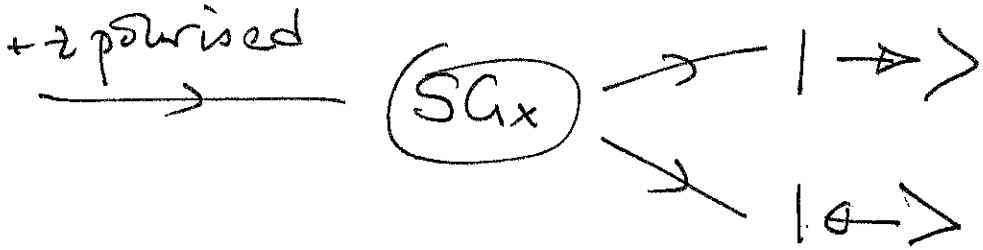
Example with Stern-Gerlach beam splitters

Compare four experiments with $s = \frac{1}{2}$ atoms









Problem How to represent difference between polarised & unpolarised beams

NB unpolarised $\neq C_+ |\uparrow\rangle + C_- |\downarrow\rangle$

because any choice of relative phase introduces coherence: eg $C_+ = C_- = \frac{1}{\sqrt{2}} \Rightarrow |\rightarrow\rangle$

Consider stat phys averaging in detail

$$[A]_{av} = \sum_n p_n A_n = \sum_n p_n \langle n | \hat{A} | n \rangle$$

Suppose we want to use different basis eg $\{|\alpha\rangle\}$ in place of $\{|n\rangle\}$

Use $\mathbb{1} = \sum_\alpha |\alpha\rangle\langle\alpha|$

Then

$$[A]_{av} = \sum_{\alpha,\beta} \sum_n p_n \langle n|\alpha\rangle \langle\alpha|\hat{A}|\beta\rangle\langle\beta|n\rangle$$

$$\equiv \sum_{\alpha\beta} \sum_n \underbrace{\langle\beta|n\rangle p_n \langle n|\alpha\rangle}_{\hat{\rho}_{\beta\alpha}} \underbrace{\langle\alpha|\hat{A}|\beta\rangle}_{\hat{A}_{\alpha\beta}}$$

$$= \mathrm{Tr}\left[\hat{\rho}\hat{A}\right]$$

so define density operator $\hat{\rho} = \sum_n |n\rangle p_n \langle n|$

with matrix elements

$$\hat{\rho}_{\beta\alpha} = \langle \beta | \hat{\rho} | \alpha \rangle$$ is for any other operator

Includes QM expectation value since

if $p_n = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$

then $\hat{\rho} = |m\rangle\langle m|$

and $\mathrm{Tr}\left[\hat{\rho}\hat{A}\right] = \sum_\ell \langle \ell | m \rangle \langle m | \hat{A} | \ell \rangle = \langle \ell | \hat{A} | \ell \rangle$

as expected

General properties (cut if short of time)

① $\mathrm{Tr}\left[\hat{\rho}\right] = \left[\mathbb{1}\right]_{ar} = 1$

② For pure state

$$(\hat{\rho})^2 = \sum_{n,m} |n\rangle p_n \langle n|m\rangle p_m \langle m|$$

$$= \sum_n |n\rangle p_n^2 \langle n| = \hat{\rho} \quad \text{if } p_n = 0 \text{ or } 1 \text{ for all } n$$

③ Time evolution

If p_n's constant, use $\begin{cases} i\hbar\, \partial_t |n\rangle = \hat{H}|n\rangle \\ -i\hbar\, \partial_t \langle n| = \langle n|\hat{H} \end{cases}$

so

$$i\hbar\, \partial_t \hat{\rho} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} = \left[\hat{H}, \hat{\rho}\right] = -\left[\hat{\rho}, \hat{H}\right]$$

Note that this is opposite to time-dependance of observables

$$i\hbar \partial_t \langle\psi|\hat{A}|\psi\rangle = \langle\psi|\hat{A}\hat{H}|\psi\rangle - \langle\psi|\hat{H}\hat{A}|\psi\rangle$$

$$= \langle\psi|[\hat{A},\hat{H}]|\psi\rangle$$

(provided $\partial_t \hat{A} = 0$)

Return to SG beams

Recall some basics

$$\hat{S}_z = \frac{\hbar}{2}\sigma_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{S}_x = \frac{\hbar}{2}\sigma_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Notation

$$\sigma_z|\uparrow\rangle = |\uparrow\rangle \quad \text{and} \quad \sigma_z|\downarrow\rangle = -|\downarrow\rangle$$

$$\sigma_x|\rightarrow\rangle = |\rightarrow\rangle \quad \text{and} \quad \sigma_x|\leftarrow\rangle = -|\leftarrow\rangle$$

In our basis

$$|\uparrow\rangle \sim \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad + \quad |\downarrow\rangle \sim \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$|\rightarrow\rangle \sim \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad |\leftarrow\rangle \sim \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Density matrix for unpolarised beam

$$\hat{\rho}_{unpol} = \sum_n p_n |n\rangle\langle n|$$

$$= \frac{1}{2}\left(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\right)$$

$$= \frac{1}{2}\,\mathbb{1}$$

Density matrix for +z polarised beam

$$\hat{\rho}_{+z} = |\uparrow\rangle\langle\uparrow|$$

In z-basis

$$\hat{\rho}_{+z} = \begin{pmatrix} \langle\uparrow|\hat{\rho}_{+z}|\uparrow\rangle & \langle\uparrow|\hat{\rho}_{+z}|\downarrow\rangle \\ \langle\downarrow|\hat{\rho}_{+z}|\uparrow\rangle & \langle\downarrow|\hat{\rho}_{+z}|\downarrow\rangle \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

For +x polarised beam

$$\hat{\rho}_{+x} = |\rightarrow\rangle\langle\rightarrow|$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$ in z-basis

Observables in SG expt

For SG_z $\quad \hat{A}_\uparrow = \frac{1}{2}(1+\sigma_z) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$

eigenvalues: 1 if up, 0 if down
Gives intensity in up beam

likewise $\hat{A}_\downarrow = \frac{1}{2}(1-\sigma_z) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$

For SG_x $\quad \hat{A}_\rightarrow = \frac{1}{2}(1+\sigma_x) = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$

$\hat{A}_\leftarrow = \frac{1}{2}(1-\sigma_x) = \frac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$

Now calculate

Unpolarised beam

$$\mathrm{Tr}\left[\hat{\rho}_{unpol}\,\hat{A}_*\right] = \frac{1}{2}\mathrm{Tr}\left[\hat{A}_*\right] = \frac{1}{2} \quad \text{in all cases}$$

($*$ = $\uparrow, \downarrow, \rightarrow$ or $\leftarrow$)

z-polarised beam

$$\mathrm{Tr}\left[\hat{\rho}_{+z}\,\hat{A}_\uparrow\right] = \mathrm{Tr}\left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\cdot\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\right] = 1$$

$$\mathrm{Tr}\left[\hat{\rho}_{+z}\,\hat{A}_\downarrow\right] = \mathrm{Tr}\left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\cdot\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}\right] = 0$$

$$\mathrm{Tr}\left[\hat{\rho}_{+z}\,\hat{A}_\rightarrow\right] = \frac{1}{2}\mathrm{Tr}\left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\cdot\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}\right] = \frac{1}{2}$$

x - polarised beam

$$\mathrm{Tr}\left[\hat{\rho}_{+x}\,\hat{A}_{\uparrow}\right] = \frac{1}{2}\mathrm{Tr}\left[\begin{pmatrix}1&1\\1&1\end{pmatrix}\begin{pmatrix}1&0\\0&0\end{pmatrix}\right] = \frac{1}{2}$$

$$\mathrm{Tr}\left[\hat{\rho}_{+x}\,\hat{A}_{\rightarrow}\right] = \frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix}1&1\\1&1\end{pmatrix}\begin{pmatrix}1&1\\1&1\end{pmatrix}\right] = 1$$

$$\mathrm{Tr}\left[\hat{\rho}_{+x}\,\hat{A}_{\leftarrow}\right] = \frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix}1&1\\1&1\end{pmatrix}\begin{pmatrix}1&-1\\-1&1\end{pmatrix}\right] = 0$$

— as desired

So density matrix gives way to represent both quantum and statistical (classical) uncertainty in same framework.