Notes on Further Quantum Mechanics

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1 Charged Particle Motion in Magnetic Field

1.1 Hamiltonian and Magnetic Field

The Hamiltonian of a charged particle in a electromagnetic field:

$$H = \frac{1}{2m}\left|\left|\boldsymbol{p} - q\boldsymbol{A}\right|\right|^2 + q\varphi \tag{1}$$

where $\boldsymbol{A}$ is the vector potential and φ is the electrostatic potential.

Recall from EM lectures:

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} \qquad\qquad \boldsymbol{E} = -\boldsymbol{\nabla}\varphi - \frac{\partial \boldsymbol{A}}{\partial t} \tag{2}$$

Aharonov-Bohm Effect: the Hamiltonian H involves $\boldsymbol{A}$ instead of $\boldsymbol{B}$. Does it mean $\boldsymbol{A}$ is "real"?

- Theory & Experiment: $\boldsymbol{A} \neq 0 \Rightarrow$ the fringes are shifted in the interference experiment.

The vector potential is "real" in Quantum Mechanics!

There is a problem with gauge transformation.We know from EM that $\boldsymbol{A}$ and φ are not uniquely determined. The fields $\boldsymbol{E}$ and $\boldsymbol{B}$ are unchanged under the transformation:

$$\boldsymbol{A} \mapsto \boldsymbol{A}' + \boldsymbol{\nabla}\chi \qquad\qquad \varphi \mapsto \varphi' - \frac{\partial \chi}{\partial t} \tag{3}$$

where χ is an arbitrary smooth scalar field. We see that H depends explicitly on the choice of χ.

Solution: The eigenstates $|\psi\rangle$ also depend on χ, but only via a phase, which has no effect on physical quantities. That is, $||\psi||^2$ is independent of χ.

$$|\psi\rangle \mapsto |\psi'\rangle := \mathrm{e}^{\mathrm{i}q\chi/\hbar}\,|\psi\rangle \tag{4}$$

Check that TDSE is satisfied under gauge transformations.

1.2 Probability Current

The continuity equation

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J} \tag{5}$$

For probability density, $\rho = ||\psi||^2$. We have

$$\frac{\partial \rho}{\partial t} = \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} = \frac{1}{\mathrm{i}\hbar} \left(\psi^* H \psi - \psi H \psi^* \right) \tag{6}$$

from TDSE.

If we substitute the Hamiltonian from Equation 1 into the expression, we obtain

$$\frac{\partial \rho}{\partial t} = -\frac{\mathrm{i}}{2m} \left(-\hbar \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \right) + \mathrm{i}q \left(\psi^* \left(\boldsymbol{A} \cdot \boldsymbol{\nabla} \psi + \psi \boldsymbol{\nabla} \cdot \boldsymbol{A} \right) - \psi \left(\boldsymbol{A} \cdot \boldsymbol{\nabla} \psi^* + \psi^* \boldsymbol{\nabla} \cdot \boldsymbol{A} \right) \right) \right) \tag{7}$$

The probability current is shifted by $\boldsymbol{A}$:

$$\boldsymbol{J} = -\frac{\mathrm{i}\hbar}{2m} \left(\psi^* \boldsymbol{\nabla} \psi - \psi \boldsymbol{\nabla} \psi^* \right) - \frac{q}{m} ||\psi||^2 \boldsymbol{A} \tag{8}$$

1.3 Charged Particles in Uniform Magnetic Field

In classical situation, a charged particle in a uniform magnetic field undergoes circular motion, which can be characterized by the speed v and radius r. The angular frequency $\omega = qB/m$, which is independent of v and r, as in the case of harmonic oscillation.

Now we consider the quantum mechanical situation. Let $\boldsymbol{B} = B\boldsymbol{e}_z$. We pick the gauge

$$\boldsymbol{A} = Bx\boldsymbol{e}_y \tag{9}$$

The Hamiltonian

$$H = \frac{1}{2m} \left(\left(-\mathrm{i}\hbar \frac{\partial}{\partial x} \right)^2 + \left(-\mathrm{i}\hbar \frac{\partial}{\partial y} - qBx \right)^2 \right) \tag{10}$$

We can solve TISE via seperation of variables. We seek solutions of the form

$$\psi(x, y) = \mathrm{e}^{\mathrm{i}ky} \phi(x) \tag{11}$$

Substitute in the TISE:

$$\mathrm{e}^{\mathrm{i}ky} \left(\left(-\mathrm{i}\hbar \frac{\partial}{\partial x} \right)^2 + (\hbar k - qBx)^2 \right) \phi(x) = E \mathrm{e}^{\mathrm{i}ky} \phi(x) \tag{12}$$

The term p_x^2 acts like kinetic energy, and the term $(\hbar k - qBx)^2$ acts like potential energy. In particular, $x - \hbar k/qB$ is a one-dimensional simple harmonic oscillator. The length scale is $\ell_B = \sqrt{\hbar/qB}$. The frequency of the oscillator is qB/m, which coincides with the classical situation.

The energy levels are

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) = \frac{\hbar qB}{m} \left(n + \frac{1}{2} \right) \tag{13}$$

which are called **Landau levels**.

We can calculate the probability current:

$$J_y = \frac{qB}{m}\left(\frac{\hbar k}{qB} - x\right)||\psi||^2 \tag{14}$$

Since E_n is independent of the wavenumber k, there are degenercies at each energy level. The result is not surprising as we can regard it as the superposition of classical circular orbits with different centers.

We can think of a system of size $L_x \times L_y$ with periodic boundary conditions at least in the y-direction. Therefore

$$k \in \frac{2\pi}{L_y}\mathbb{Z} \tag{15}$$

Center of the state:

$$x_0 = \frac{\hbar}{qB} \cdot \frac{2\pi}{L_y} \cdot r \tag{16}$$

Then

$$0 \leqslant x_0 \leqslant L_x \quad \Rightarrow \quad 0 \leqslant r \leqslant L_x L_y \frac{qB}{m}\frac{1}{2\pi} = \frac{\text{Area}}{2\pi\ell_B^2} \tag{17}$$

2 Time-Independent Perturbation Theory

We wish to solve the time-independent Schrödinger equation with an asymptotic method.

Consider the Hamiltonian

$$H = H_0 + \lambda V \tag{18}$$

where H_0 is a Hamiltonian that we know how to solve and λ is a small coefficient. Suppose that we have an orthonormal complete set of eigenstates of H_0:

$$H_0 |n\rangle = E_n |n\rangle \tag{19}$$

We try to solve TISE of H as power series expansion of λ:

$$(H_0 + \lambda V)\left(|n\rangle + \lambda\left|\delta\psi_n^{(1)}\right\rangle + O(\lambda^2)\right) = (E_n + \lambda\delta E_n^{(1)} + \cdots)\left(|n\rangle + \lambda\left|\delta\psi_n^{(1)}\right\rangle + \cdots\right) \tag{20}$$

Seperating the equation into powers of λ, notice the the coefficient of λ^0 is automatically satisfied. The coefficient of λ^1:

$$H_0\left|\delta\psi_n^{(1)}\right\rangle + V|n\rangle = \delta E_n^{(1)}|n\rangle + E_n\left|\delta\psi_n^{(1)}\right\rangle \tag{21}$$

Acting the bra $\langle n|$ at both sides of Equation 21:

$$\langle n|(E_n - H_0)\left|\delta\psi_n^{(1)}\right\rangle + \langle n|V|n\rangle = \langle n|\delta E_n^{(1)}|n\rangle \tag{22}$$

which implies that

$$\delta E_n^{(1)} = \langle n|V|n\rangle \tag{23}$$

Acting the bra $\langle m|$ $(m \neq n)$ at both sides of Equation 21:

$$\langle m|(E_n - H_0)\left|\delta\psi_n^{(1)}\right\rangle + \langle m|V|n\rangle = \langle m|\delta E_n^{(1)}|n\rangle \tag{24}$$

which implies that

$$\left\langle m \left| \delta\psi_n^{(1)} \right\rangle = \frac{\langle m| V |n\rangle}{E_n - E_m} \tag{25}$$

Next we think about the normalization of the state:

$$1 = \left(\langle n| + \lambda \left\langle \delta\psi_n^{(1)} \right| + O(\lambda^2)\right) \left(|n\rangle + \lambda \left|\delta\psi_n^{(1)}\right\rangle + O(\lambda^2)\right) \tag{26}$$

$$= 1 + 2\lambda \,\mathrm{Re}\left\langle \delta\psi_n^{(1)} \right| n\rangle + O(\lambda^2) \tag{27}$$

Therefore we pick

$$\left\langle \delta\psi_n^{(1)} \right| n\rangle = 0 \tag{28}$$

Now, assuming that H_0 has no degenercies in the energy levels, we can expand $\left|\delta\psi_n^{(1)}\right\rangle$ in the basis of $|n\rangle$:

$$\left|\delta\psi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{\langle m| V |n\rangle}{E_n - E_m} |m\rangle \tag{29}$$

We can calculate the second order approximation. The coefficient of λ^2:

$$H_0 \left|\delta\psi_n^{(2)}\right\rangle + V \left|\delta\psi_n^{(1)}\right\rangle = \delta E_n^{(2)} |n\rangle + \delta E_n^{(1)} \left|\delta\psi_n^{(1)}\right\rangle + E_n \left|\delta\psi_n^{(2)}\right\rangle \tag{30}$$

Acting the bra $\langle n|$ at both sides of Equation 30:

$$\langle n| V \left|\delta\psi_n^{(1)}\right\rangle = \langle n| (E_n - H_0) \left|\delta\psi_n^{(2)}\right\rangle + \langle n| \delta E_n^{(1)} \left|\delta\psi_n^{(1)}\right\rangle + \langle n| \delta E_n^{(2)} |n\rangle \tag{31}$$

which implies that

$$\delta E_n^{(2)} = \langle n| V \left|\delta\psi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{|\langle n| V |m\rangle|^2}{E_n - E_m} \tag{32}$$

Notes on Further Quantum Mechanics

Part I : Approximation Methods

Part II : Atomic Physics

Part III : Density Operators

Degenerate Perturbation.

In QM, symmetry → degenerecy in energy

E.G. 2D infinite square well.

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

$\Rightarrow E_{1,2} = E_{2,1}$. consequence of symmetry

Have freedom in choice of eigenstates.

$\{|\psi_1\rangle, \cdots, |\psi_n\rangle\}$ orthonormal basis of $\ker(\hat{\mathcal{H}}_0 - E\hat{id})$

$\{|\varphi_1\rangle, \cdots, |\varphi_n\rangle\}$ another orthonormal basis

then $|\varphi_e\rangle = U_{em}|\psi_m\rangle$

where U_{em} is a unitary matrix.

In perturbation theory, choose the basis such that

$\langle n'|V|m'\rangle = 0$ whenever $E_{m'} = E_{n'}$ $(m' \neq n')$

i.e. diagonalize $\langle n|V|m\rangle$ in the eigenspace !

Magnetic fields in atomic physics

Physical idea:

orbiting charge → current loop → magnetic moment $\vec{\mu}$

Energy depends on orientation $\Delta E = -\vec{B}\cdot\vec{\mu}$

Two types of material:

① Paramagnetism: $\vec{\mu}$ exists at $\vec{B}=0$. $\vec{\mu}$ aligns with $\vec{B}$.

② Diamagnetism: $\vec{\mu}$ produced by $\vec{B}$

$$\vec{\mu} = \chi_m \vec{H} = \frac{\chi_m}{\mu_0}\vec{B} \qquad \chi_m: \text{susceptibility}$$

Lenz's Law: $\chi_m < 0$.

$$\Delta E = -\int_0^{\vec{B}} \chi_m \vec{B}'\cdot d\vec{B}' = -\frac{1}{2}\chi_m B^2.$$

$$\Rightarrow \chi_m = -\frac{1}{\mu_0}\frac{\partial^2 \Delta E}{\partial B^2}$$

Classical view:

particle q, m, orbiting with radius r, speed v

$\Rightarrow$ Angular momentum $L = mvr$

Magnetic moment $\mu = IA = \frac{qv}{2\pi r}\cdot\pi r^2 = \frac{q}{2m}L$

$$\vec{\mu} = \frac{q}{2m}\vec{L}$$

Quantum calculation:

$$H = \frac{1}{2m}(\vec{p} - q\vec{A})^2 - \frac{q^2}{4\pi\varepsilon_0 r} \quad \text{(Coulomb interaction)}$$

$$= \underbrace{\frac{1}{2m}p^2 - \frac{q^2}{4\pi\varepsilon_0 r}}_{H_0} \underbrace{- \frac{q}{m}\vec{p}\cdot\vec{A} + \frac{q^2}{2m}\|\vec{A}\|^2}_{\text{perturbation}}$$

check: $\vec{p}$ and $\vec{A}$ commutes

Convenient form of $\vec{A}$ (uniform $\vec{B}$): $\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$

Take $\vec{B} = B\hat{z}$. Then $\vec{A} = \frac{1}{2}B(-y, x, 0)$

Perturbation : $V = -\frac{q}{m}\vec{p}\cdot\vec{A} + \frac{q^2}{2m}\|\vec{A}\|^2$

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

$= \underbrace{-\frac{q}{2m}\vec{B}\cdot\vec{L}}_{\text{classical part}} + \underbrace{\frac{q^2B^2}{8m}(x^2+y^2)}_{O(B^2),\ \text{negligible}}$

Consequences depend on atomic states:

a) Diamagnetic response.

Unperturbed atom : $L = 0$

$\delta E_n^{(1)} = \langle n|V|n\rangle \propto \vec{B}\cdot\langle n|\vec{L}|n\rangle = 0$ (neglect $O(B^2)$)

1st order perturbed energy is zero ! ↙

using 1st order perturbation on B^2 term :

$\delta E_n^{(1)} = \frac{q^2B^2}{8m}\langle n|(x^2+y^2)|n\rangle = \frac{q^2B^2}{12m}\langle n|r^2|n\rangle$

Then $\chi_m = -\frac{q^2}{6m\mu_0}\langle r^2\rangle_n$

NB : using 2nd order perturbation theory on B term

also get B^2 in energy

$\delta E_n^{(2)} = \sum_{m\neq n}\frac{|\langle n|V|m\rangle|^2}{E_n - E_m} = 0$ if $\vec{L}|n\rangle = 0$.

b) Pre-existing atomic magnetic moment

"Zeeman effect"

Consider atomic state with non-zero angular momentum

i.e. $l \neq 0$

Have degeneracy. (symmetry in the directions)

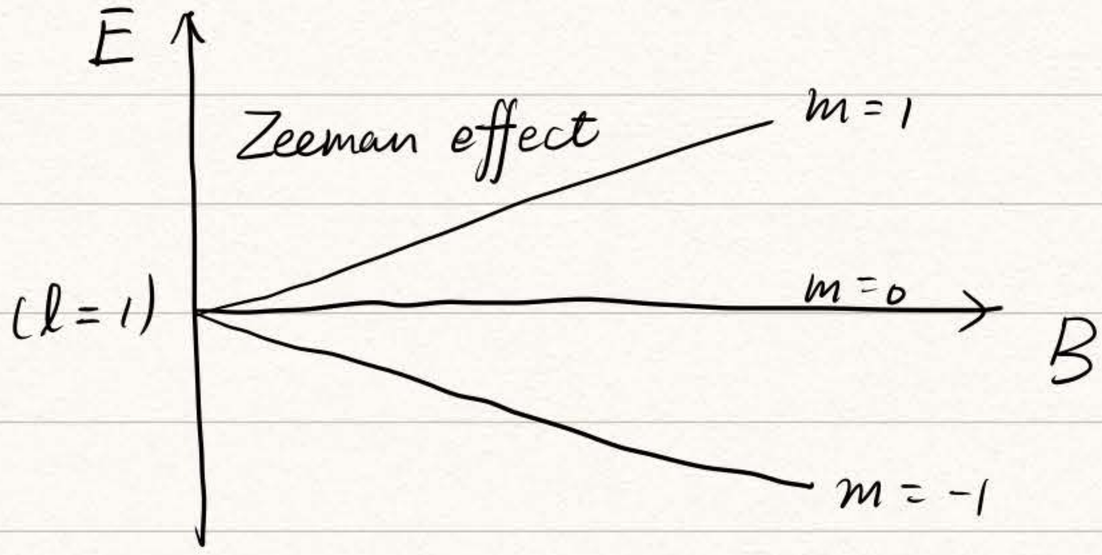
State: $|n, l, m\rangle$ — m: angular momentum $\hat{L}_z$; n: energy; l: angular momentum ($\hat{L}^2$)

Fix n, l. Degeneracy: $-l \le m \le l$

Choose the basis states in which V is diagonalized.

$V = -\frac{q}{2m_e} B L_z$. already diagonal ~

$\delta E_n^{(1)} = \langle n|V|n\rangle = -\frac{qB}{2m_e}\langle n|L_z|n\rangle = -\frac{q\hbar}{2m_e} B m$ ← quantum No.



Similar effect with intrinsic angular momentum (spin)

$\Delta E = g \frac{e\hbar}{2m} B m_s$ ← spin quantum number

↑ "g-factor" from relativistic QM

Electric field in atomic physics : "Stark effect"

Two cases :

① Atom with electric dipole moment $\vec{p}$

energy depends on orientation relative to electric field

$\Delta E = -\vec{p} \cdot \vec{\mathcal{E}}$ ← electric field.

② Atom initially unpolarized. $\vec{p} = \chi_e \vec{\mathcal{E}}$ χ_e : polarizability

$\Delta E = -\int_0^{\vec{\mathcal{E}}} \chi_e \vec{\mathcal{E}}' \cdot d\vec{\mathcal{E}}' = -\frac{1}{2}\chi_e \mathcal{E}^2$

QM calculation

$H_0 = \frac{p^2}{2m} - \frac{e}{4\pi\varepsilon_0 r}$, $V = e\mathcal{E}z$

Eigenstates of H_0 : $|n, l, m\rangle$, $E_n = -\frac{R}{n^2}$ ← Rydberg constant

Wave functions:

$\psi_{n,l,m}(r, \theta, \varphi) = Y_{l,m}(\theta, \varphi) R_{n,l}(r)$

with $Y_{0,0}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}$, $Y_{1,\pm1}(\theta, \varphi) = \mp\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{\pm i\varphi}$

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

Ground state Stark shift

1st order : $\delta E^{(1)} = \langle 1,0,0|V|1,0,0\rangle$

$\propto \int_0^{\pi} \sin\theta \cos\theta \, d\theta = 0$

2nd order : Need to compute $\langle 1,0,0|V|n,l,m\rangle$

$\int_0^{2\pi} *(\varphi)\, d\varphi = 0$ unless $m = 0$.

$\int_0^{\pi} *(\theta)\, d\theta = 0$ unless $l = 1$

If $l = 1$ $\int_0^{\pi} \sin\theta \cdot \cos\theta \cdot \cos\theta \, d\theta = \frac{2}{3}$.

↑ Jacobian ↑ perturbation ↑ $Y_{1,1}$

Therefore $\delta E_n^{(2)} = \sum_{n \neq 1} \frac{|\langle 1,0,0|V|n,1,0\rangle|^2}{E_1 - E_n}$

$$= -\sum_{n\geq 2}\left(R\left(1-\frac{1}{n^2}\right)\right)^{-1} e^2\mathcal{E}^2 a_0^2 \left|\langle 1,0,0|\frac{r}{a_0}|n,1,0\rangle\right|^2$$

$$= -\frac{e^2\mathcal{E}^2 a_0^2}{R}\underbrace{\sum_{n\geq 2}\frac{\left|\langle 1,0,0|\frac{r}{a_0}|n,1,0\rangle\right|^2}{1-1/n^2}}$$

physical parameters ↓ ; purely numerical factor ; ↑ Bohr radius

Stark effect for hydrogen in $n=2$ state

Four degenerate states : $|2,0,0\rangle, |2,1,1\rangle, |2,1,0\rangle, |2,1,-1\rangle$.

Construct $M \in \mathbb{R}^{4\times 4}$ with entries in these states :

$\langle 2,\ell,m|V|2,\ell',m'\rangle$:

φ dependence $\int_0^{2\pi} e^{i(m'-m)\varphi}\, d\varphi = 0$ unless $m = m'$

θ dependence $\int_0^{\pi} \cdots (\theta)\, d\theta = 0$ for $\ell = \ell'$

since $Y_{\ell,m}(\theta,\varphi)^2$ is invariant under $\theta \mapsto \pi - \theta$

Only non-zero elements are

$\langle 2,0,0|V|2,1,0\rangle$, $\langle 2,1,0|V|2,0,0\rangle$.

(Calculation in problem sheet 2)

$\langle 2,0,0|V|2,1,0\rangle = -3e\mathcal{E}a_0 =: v$

M is given by

$$M = \begin{pmatrix} 0 & -3e\mathcal{E}a_0 & 0 & 0 \\ -3e\mathcal{E}a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

↑ $|2,0,0\rangle$ ↑ $|2,1,0\rangle$ ↑ $|2,1,1\rangle$ ↑ $|2,1,-1\rangle$

Diagonalize M : eigenstates : $\frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle)$: $-3e\mathcal{E}a_0$

$\frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle)$: $3e\mathcal{E}a_0$

$|2,1,1\rangle$, $|2,1,-1\rangle$: 0 .

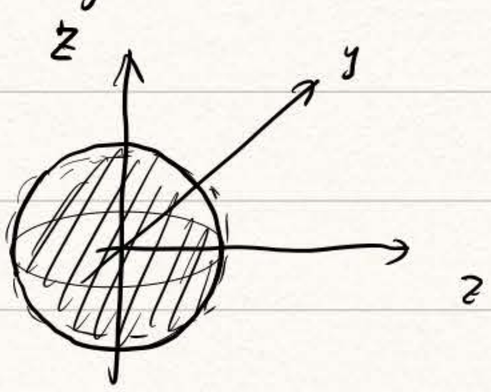
$E = -\frac{R}{2^2} + v$ dipole opposite to $\vec{\mathcal{E}}$

$E = -\frac{R}{2^2} - v$ dipole aligned with $\vec{\mathcal{E}}$

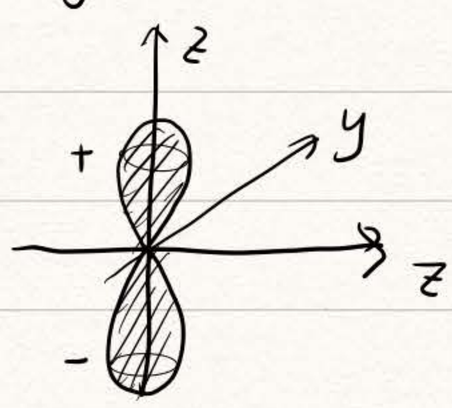
$E = 0$ dipole perpendicular to $\vec{\mathcal{E}}$.

Wave functions:

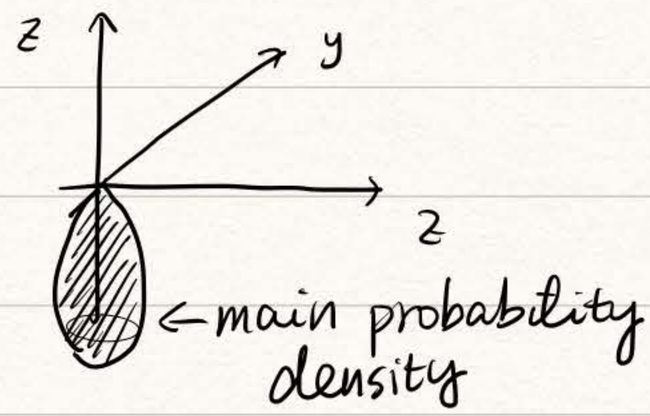
$\langle x,y,z|2,0,0\rangle$



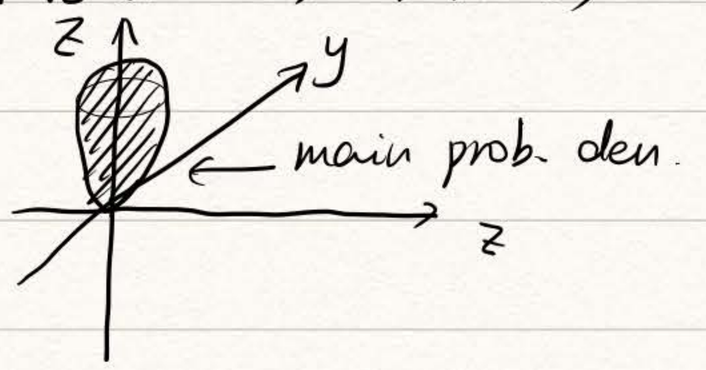
$\langle x,y,z|2,1,0\rangle$



$\langle x,y,z|\frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle)$



$\langle x,y,z|\frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle)$



Variational Method

- Alternative to perturbation theory. Not restricted to small V.
  Most useful for bound states.
- Guess approx. form for wave function (with adjustable parameters)
- Gives upper bound to ground state energy.

Def. Suppose that we have Hamiltonian H and unknown energies / eigenstates : $H|n\rangle = E_n|n\rangle$

We define the trial wave function : $|\psi\rangle = \sum_n c_n|n\rangle$

Estimate for energy of trial state :

$$\langle\psi|H|\psi\rangle = \sum_{n,m} c_m^* c_n \langle m|H|n\rangle = \sum_n |c_n|^2 E_n$$

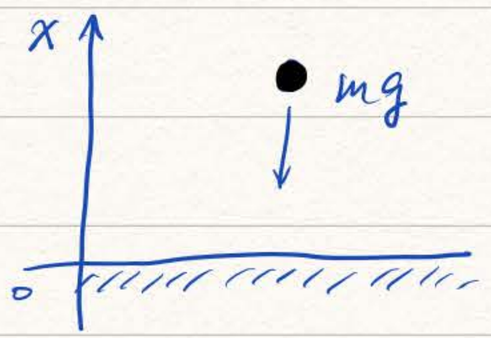
$$= \sum_n |c_n|^2 E_0 + \sum_n |c_n|^2 (E_n - E_0)$$

If $|\psi\rangle$ is normalized, then $\sum_n |c_n|^2 = 1$. Since $E_n - E_0 \geq 0$,

we have : $\boxed{\langle\psi|H|\psi\rangle \geq E_0}$

Example : quantum bouncing ball

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



Try $\psi(x) = \begin{cases} 0, & x < 0 \\ Nxe^{-ax}, & x > 0 \end{cases}$ a is the adjustable parameter

Find normalization :

$$1 = N^2 \int_0^\infty x^2 e^{-2ax}\, dx = N^2 \cdot (2a)^{-3} 2! \Rightarrow N^2 = 4a^3$$

Find $\langle\psi|H|\psi\rangle$:

$$\langle\psi|V|\psi\rangle = N^2 \int_0^\infty mgx \cdot x^2 e^{-2ax}\, dx$$

$$= 4a^3 mg \frac{1}{(2a)^4} 3! = \frac{3mg}{2a}$$

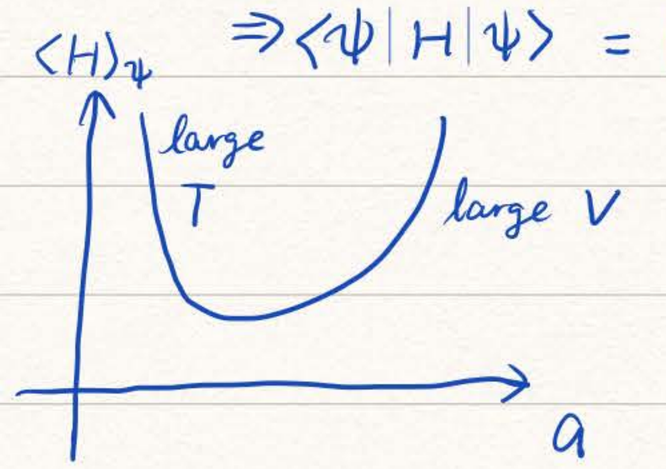
$$\langle\psi|\frac{p^2}{2m}|\psi\rangle = \frac{a^2\hbar^2}{2m}$$

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

Minimize $\langle\psi|H|\psi\rangle$: $\frac{\partial}{\partial a}\langle\psi|H|\psi\rangle = 0$

$$\Rightarrow -\frac{3mg}{2a^2} + \frac{a\hbar^2}{m} = 0 \Rightarrow a = \left(\frac{3m^2g}{2\hbar^2}\right)^{\frac{1}{3}}$$

$$\Rightarrow \langle\psi|H|\psi\rangle = \left(\frac{3}{2}\right)^{\frac{2}{3}}(\hbar^2mg^2)^{\frac{1}{3}} \geq E_0.$$



Virial Theorem

Applies to power law potential $V(r) \propto r^n$

e.g. $n = 2$: harmonic oscillator $n = -1$: Coulomb interaction

How do KE & PE compare ?

Suppose that the exact ground state wave function is $\psi(\vec{r})$.

Trial wave function : $\varphi(\vec{r}) = \psi(a\vec{r})$

$$\langle V\rangle_\varphi = \frac{\int d^3\vec{r}\,|\psi(a\vec{r})|^2 V_0 r^n}{\int d^3\vec{r}\,|\psi(a\vec{r})|^2} = a^{-n}\frac{\int d^3\vec{R}\,|\psi(\vec{R})|^2 V_0 R^n}{\int d^3\vec{R}\,|\psi(\vec{R})|^2}$$

$$= a^{-n}\langle V\rangle_\psi$$

Similarly, $\langle\frac{p^2}{2m}\rangle_\varphi = a^2\langle\frac{p^2}{2m}\rangle_\psi$

$$\Rightarrow \langle H\rangle_\varphi = a^{-n}\langle V\rangle_\psi + a^2\langle\frac{p^2}{2m}\rangle_\psi$$

$$\frac{\partial}{\partial a}\langle H\rangle_\varphi = 0 \Rightarrow -na^{-n-1}\langle V\rangle_\psi + 2a\langle\frac{p^2}{2m}\rangle_\psi = 0$$

We know that it is satisfied when $a = 1$

$$\Rightarrow \boxed{\langle\frac{p^2}{2m}\rangle_\psi = \frac{n}{2}\langle V\rangle_\psi} \quad \text{(Virial Theorem)}$$

WKB Approximation

Way to study quantum problem in the semi-classical limit

quantum wavelength $\ll$ scale on which $V(r)$ varies.

→ limited to 1D problem

Particle with energy E moving in uniform potential V

Wave function $\psi = Ae^{ikx} \Rightarrow \frac{\hbar^2 k^2}{2m} + V = E$

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

Probability current $j = \frac{\hbar}{2im}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)$

$$= \frac{\hbar}{2im} |A|^2 k$$

What if $V = V(x)$ but varies very slowly

Guess : $k \mapsto k(x) = \frac{\sqrt{2m(E-V(x))}}{\hbar}$

j is conserved. (independent of x)

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

Derivation from TISE :

Write $\psi(x) = A(x) e^{i\int_0^x k(x')dx'}$. A, k are real

Substitute into TISE :

$$\frac{d}{dx}\psi(x) = \left(A'(x) + iA(x)k(x)\right) e^{i\int_0^x k(x')dx'}$$

$$\frac{d^2}{dx^2}\psi(x) = \left(A''(x) + iA'(x)k(x) + iA(x)k(x) - A(x)k(x)^2\right) e^{i\int_0^x k(x')dx'}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(A'' + 2iA'k + iAk' - Ak^2\right) = (E-V)A$$

A'': very small; $2iA'k + iAk'$: quite small; $-Ak^2$: not small

Equating the terms :

Not small : $\frac{\hbar^2 k(x)^2}{2m} = E - V(x). \Rightarrow k(x) = \frac{\sqrt{2m(E-V(x))}}{\hbar}$

Quite small : $2\frac{dA}{dx}k + A\frac{dk}{dx} = 0$

$$\Rightarrow 2\int \frac{dA}{A} = -\int \frac{dk}{k}$$

$$\Rightarrow A(x) \propto k(x)^{-\frac{1}{2}}$$

In the classically forbidden region : $E < V(x)$.

$$\psi(x) \propto \frac{1}{\sqrt{\lambda(x)}} e^{-\int_0^x \lambda(x')dx'} \qquad \lambda(x) = \frac{\sqrt{2m(V(x)-E)}}{\hbar}$$

Classical turning points : $x = x_e$ $V(x_e) = E$. $k(x_e), \lambda(x_e) = 0$

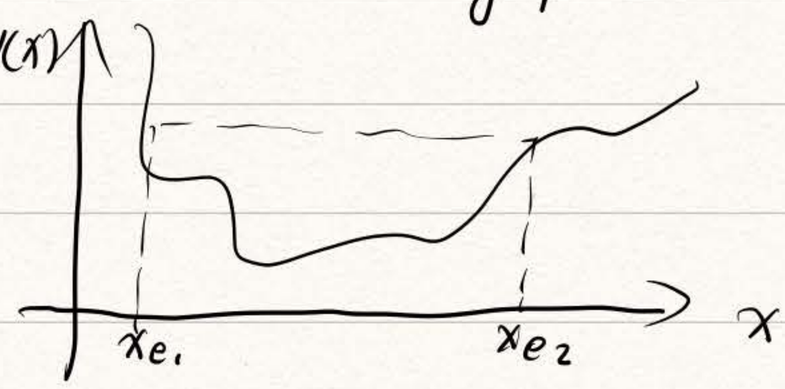
Bound states

Energies fixed by $\frac{n\lambda}{2}$ between classical turning points

$$\int_{x_{e_1}}^{x_{e_2}} k(x')dx' = n\pi + \text{const}$$

usually $\frac{1}{2}$

$\Rightarrow E_n$ for large n



Example : Simple harmonic oscillator

$$V(x) = \frac{1}{2}gx^2.$$

Classical turning points : $\pm x_e \Rightarrow E = \frac{1}{2}gx_e^2$

$$k(x) = \frac{\sqrt{2m(E-V(x))}}{\hbar} = \frac{\sqrt{mg}}{\hbar}(x_e^2 - x^2)^{\frac{1}{2}}$$

Energy levels : $\frac{\sqrt{mg}}{\hbar}\int_{-x_e}^{x_e}(x_e^2-x^2)^{\frac{1}{2}}dx = (n+\frac{1}{2})\pi$

$$\Rightarrow \frac{\sqrt{mg}}{\hbar}x_e^2\underbrace{\int_{-1}^{1}\sqrt{1-s^2}\,ds}_{\pi/2} = (n+\frac{1}{2})\pi$$

$$\Rightarrow \frac{\sqrt{mg}}{\hbar}\cdot\frac{x_e^2}{2} = n+\frac{1}{2}$$

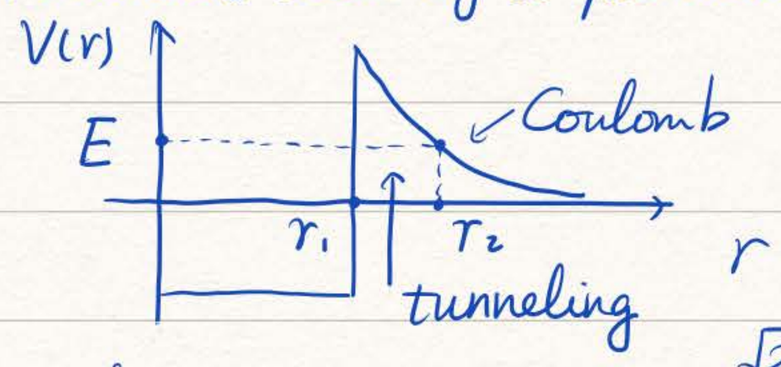
$$\Rightarrow E_n = \frac{1}{2}gx_e^2 = (n+\frac{1}{2})\cdot\frac{\hbar}{\sqrt{mg}}\cdot g = (n+\frac{1}{2})\hbar\sqrt{\frac{g}{m}}$$

$$= (n+\frac{1}{2})\hbar\omega$$

Example : WKB & tunneling & decay

$^{238}U \longrightarrow {}^{234}Th + {}^{4}He$ (α decay)

Potential seen by α-particle :



Inside the barrier : $\lambda(r) = \frac{\sqrt{2m(V(r)-E)}}{\hbar}$ $V(r) = \frac{2Ze^2}{4\pi\varepsilon_0 r}$

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

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

where $\int_{r_1}^{r_2} \lambda(r)\,dr \propto \int_{r_1}^{r_2} \left(\frac{1}{r} - \frac{1}{r_2}\right)^{\frac{1}{2}} dr \approx \int_{r_1}^{r_2} r^{-\frac{1}{2}}\, dr \approx 2\sqrt{r_2}$

(for $r \ll r_2$) ?

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

$$\Rightarrow \psi(r_2) \approx \psi(r_1)\, e^{-\text{const}\cdot E^{-1/2}}$$

Decay rate $\approx$ Attempt rate $\times$ Escape probability

$$\approx \frac{\text{speed}}{\text{diameter}} \times \left|\frac{\psi(r_2)}{\psi(r_1)}\right|^2$$

$\Rightarrow$ Life time $\propto e^{\text{const}\cdot E^{-1/2}}$

^{238}U : 5×10^9 years ^{232}U : 70 years.

Approximation methods for time-dependent Hamiltonians

TDSE : $i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$

If $\hat{H}$ is time-independent, then $|\psi(t)\rangle = \sum_n c_n e^{-\frac{iE_n}{\hbar}t}|n\rangle$.

If $\hat{H} = \hat{H}(t)$, then c_n, E_n & $|n\rangle$ all depend on time

Possible simplifications :

① Sudden change of $\hat{H}(t)$ between initial & final forms

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

Intrinsic time scale : frequency $\omega = \frac{E_n - E_m}{\hbar}$

③ Perturbative change : $\hat{H}(t) = \hat{H}_0 + \delta\hat{H}(t)$.

Sudden approximation :

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

(simple because TDSE is 1st order in t)

For $t > 0$:

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

where $c_n = \langle n|\psi(0-)\rangle$ $\quad (\psi(0-) = \lim_{t\to 0^-}\psi(t))$

Example : Particle in a box in ground state initially

Expand the box suddenly. $\mathbb{P}(|\psi(0+)\rangle = |0\rangle) = ?$

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

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

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

Initial ground state: (of H_i)

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

Ground state of H_f:

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

The probability $\mathbb{P} = |\langle 1|\psi(0^-)\rangle|^2$

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

$$= \left|\frac{4\sqrt{2}}{3\pi}\right|^2 = \frac{32}{9\pi^2}$$

$\Rightarrow$ Also some probability to be excited into higher states.

Adiabatic limit:

For each t, $\hat{H}(t)$ has instantaneous eigenstates

Adiabatic Theorem: Instantaneous eigenstates:

$\hat{H}(t)|n(t)\rangle = E_n(t)|n(t)\rangle$. $\{|n(t)\rangle\}$ forms a basis of the Hilbert space $\mathcal{H}$. We can use these states to write.

$$|\psi(t)\rangle = \sum_n c_n(t)\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right)|n(t)\rangle.$$

If $\hat{H}(t)$ changes slowly, then $|c_n(t)|^2 = |c_n(0)|^2$ for all $t > 0$.

Proof: Substitute into TDSE:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \sum_n \exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right)$$

$$\| \qquad \left(\left(i\hbar\frac{\partial c_n}{\partial t} + c_n E_n\right)|n(t)\rangle + i\hbar c_n(t)\frac{\partial}{\partial t}|n(t)\rangle\right)$$

$$\hat{H}(t)|\psi(t)\rangle = \sum_n \exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right) c_n(t)E_n(t)|n(t)\rangle$$

$$\Rightarrow \sum_n \exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right)\left(i\hbar\frac{\partial c_n}{\partial t}|n(t)\rangle + i\hbar c_n(t)\frac{\partial}{\partial t}|n(t)\rangle\right) = 0$$

Taking $\langle m(t)|\exp\left(\frac{i}{\hbar}\int_0^t E_m(t')\,dt'\right)$

$$\frac{\partial c_m}{\partial t} = -\sum_n c_n(t)\langle m(t)|\frac{\partial n}{\partial t}\rangle \exp\left(\frac{i}{\hbar}\int_0^t (E_m(t) - E_n(t'))\,dt'\right)$$

The term $\langle m(t)|\frac{\partial n}{\partial t}(t)\rangle$ can be obtained from time-independent

perturbation theory :

Under $t \mapsto t+\Delta t$, $\hat{H}(t) \longmapsto \hat{H}(t) + \Delta t \frac{\partial}{\partial t}\hat{H}(t)$.

So $|n(t)\rangle \mapsto |n(t)\rangle + \sum_{\ell \neq n} |\ell(t)\rangle \cdot \frac{\langle \ell(t)|\hat{V}|n(t)\rangle}{E_\ell(t) - E_n(t)}$ where $\hat{V} = \Delta t \frac{\partial}{\partial t}\hat{H}(t)$

$$\Rightarrow \left|\frac{\partial n}{\partial t}(t)\right\rangle = \sum_{\ell \neq n} |\ell(t)\rangle \frac{\langle \ell(t)|\partial_t \hat{H}|n(t)\rangle}{E_n(t) - E_\ell(t)}$$

Hence $$\frac{\partial c_m}{\partial t} = -\sum_{n \neq m} c_n(t) \exp\left(\frac{i}{\hbar}\int_0^t (E_m(t') - E_n(t'))\,dt'\right) \frac{\langle m(t)|\partial_t H|n(t)\rangle}{E_n(t) - E_m(t)}$$

Suppose that $\hat{H}$ changes over time interval T.

Let $s = \frac{t}{T} \Rightarrow \frac{d}{dt} = \frac{1}{T}\frac{d}{ds}$

$$\Rightarrow \frac{\partial c_m}{\partial s} = -\sum_{n \neq m} c_n(s) \exp\left(\frac{iT}{\hbar}\int_0^s (E_m(s') - E_n(s'))\,ds'\right) \frac{\langle m(s)|\partial_s H|n(s)\rangle}{E_n(s) - E_m(s)}$$

Integral over s :

$$c_m(s=1) = c_m(s=0) + \int_0^1 ds' \frac{\partial c_m}{\partial s}(s')$$

If T is large. $\frac{\partial c_m}{\partial s}$ oscillates rapidly.

As a result, $\int_0^1 ds' \frac{\partial c_m}{\partial s}(s') \to 0$

We conclude that $|c_m(s)|^2 = |c_m(0)|^2$ for $T \to \infty$. ▨

$\int f(x) e^{iTx} \to 0$ as $T \to \infty$

↑ (Riemann-Lebesgue Lemma)

Example : Particle in a box in ground state initially

Expand the box slowly.

The particle in ground state has zero probability to be excited into higher states !

Energy in time-dependent systems

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

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

$$+ \langle \psi(t)|\frac{\partial \hat{H}}{\partial t}|\psi(t)\rangle$$

By TDSE : $\frac{\partial}{\partial t}\langle \psi(t)| = -\frac{1}{i\hbar}\langle \psi(t)|\hat{H}(t)$;

$$\frac{\partial}{\partial t}|\psi(t)\rangle = \frac{1}{i\hbar}\hat{H}(t)|\psi(t)\rangle$$

The two terms cancel !

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

Example : Particle in a box of length L.

The energy $E = \frac{\hbar^2\pi^2}{8mL^2}$

Changes L slowly $\Rightarrow \Delta E = -\frac{2E}{L}\Delta L$

↳ Force exerted by the particle on the box : $F = \frac{2E}{L}$

↳ Classically, $F = \frac{dp}{dt} = \frac{2mv}{2L/v} = \frac{2T}{L}$.

consistent with the quantum result.

Summary : { sudden change : no change in energy ;
adiabatic change : no change in state .

Applications

① Cosmic microwave background radiation

photos in expanding universe $\tilde{\Rightarrow}$ particles in expanding box.

② Molecular / Solid vibrations

Time-dependent perturbation theory

Suppose that the time dependent part of $\hat{H}$ is small:

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

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

where E_n are energy levels of $\hat{H}_0$, $|n\rangle$ are eigenstates of $\hat{H}_0$.

This is always possible. $c_n(t)$ is due to $\hat{V}(t)$.

Substitute into TDSE:

$$\sum_n e^{-\frac{iE_n}{\hbar}t}\left(i\hbar\frac{\partial c_n}{\partial t} + E_n c_n(t)\right)|n\rangle = \sum_n e^{-\frac{iE_n}{\hbar}t} c_n(t)\left(E_n + \hat{V}(t)\right)|n\rangle$$

Taking $\langle m| \frac{1}{i\hbar} e^{\frac{iE_m}{\hbar}t}$:

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

Perturbative expansion: Suppose that system initially is in the state $|i\rangle$, We want the probability of transition to $|m\rangle$.

At 0^{th} order of $\hat{V}(t)$: $c_n(t) = \delta_{i,m}$.

Put this into RHS of TDSE:

$$\frac{\partial c_m}{\partial t} = \frac{1}{i\hbar} e^{i(E_m - E_i)t/\hbar} \langle m|\hat{V}|i\rangle$$

Let $\omega_{m,i} = \frac{E_m - E_i}{\hbar}$. Integrate the expression:

$$c_m(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i\omega_{m,i}t'} \langle m|\hat{V}(t)|i\rangle \leftarrow \underline{1^{st} \text{ order approximation}} + O(\hat{V}^2)$$

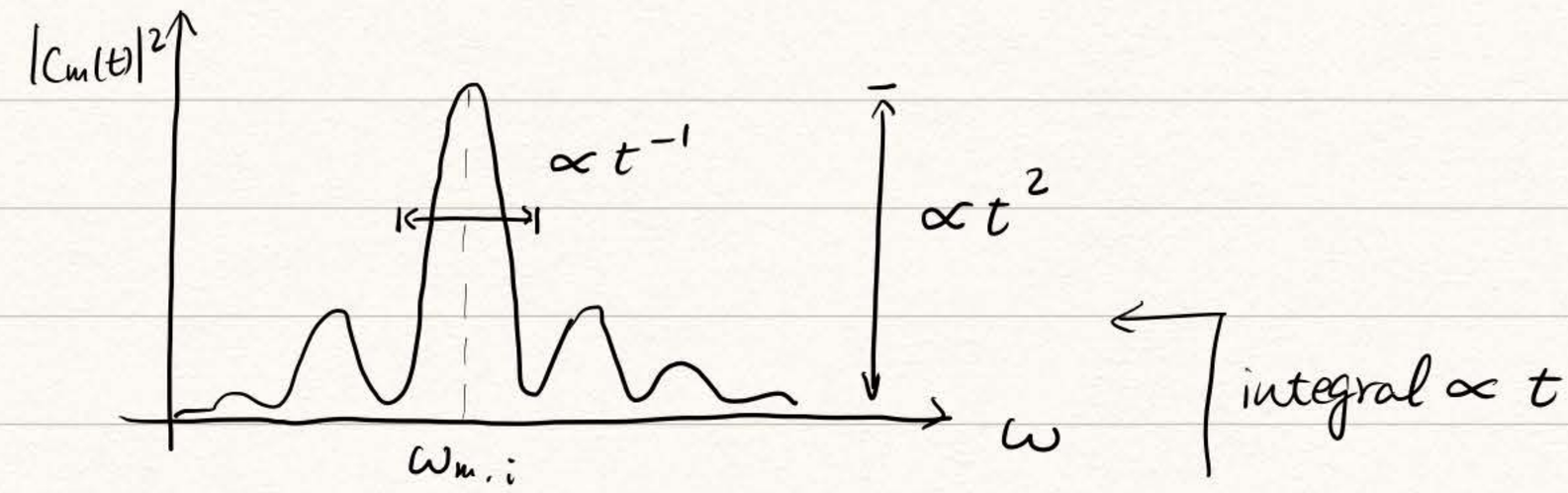
Perturbation periodic in time:

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

$$\Rightarrow c_m(t) = \frac{1}{\hbar}\langle m|\hat{V}|i\rangle \frac{e^{i(\omega_{m,i} - \omega)t} - 1}{\omega_{m,i} - \omega}$$

$$\Rightarrow |c_m(t)|^2 = \frac{1}{\hbar^2}|\langle m|\hat{V}|i\rangle|^2 \cdot \frac{\sin^2\left(\frac{1}{2}(\omega_{m,i} - \omega)t\right)}{\left(\frac{1}{2}(\omega_{m,i} - \omega)\right)^2}$$

Transition probability depends on t & ω:



Let $\frac{\omega_{m,i}-\omega}{2}t = s$. $I = 2t\int_{-\infty}^{\infty} ds \frac{\sin^2 s}{s^2} = 2\pi t$

Transition rate from $|i\rangle$ to $|m\rangle$: $\frac{2\pi}{\hbar^2}|\langle i|\hat{V}|m\rangle|^2 \delta(\omega-\omega_{m,i})$

NB : $\hat{V}(t) = \hat{V}e^{-i\omega t}$: $\omega > 0 \Rightarrow E_m > E_i$

Fermi's golden rule :

Physical reason for integrating a δ-function .

Possibilities :

① $\omega_{m,i}$ fixed, perturbation has range of frequencies with density $\rho(\omega)$

The transition rate : $\frac{2\pi}{\hbar^2}|\langle m|\hat{V}|i\rangle|^2 \rho(\omega_{m,i})$

② Continuous range of $\omega_{m,i}$ available

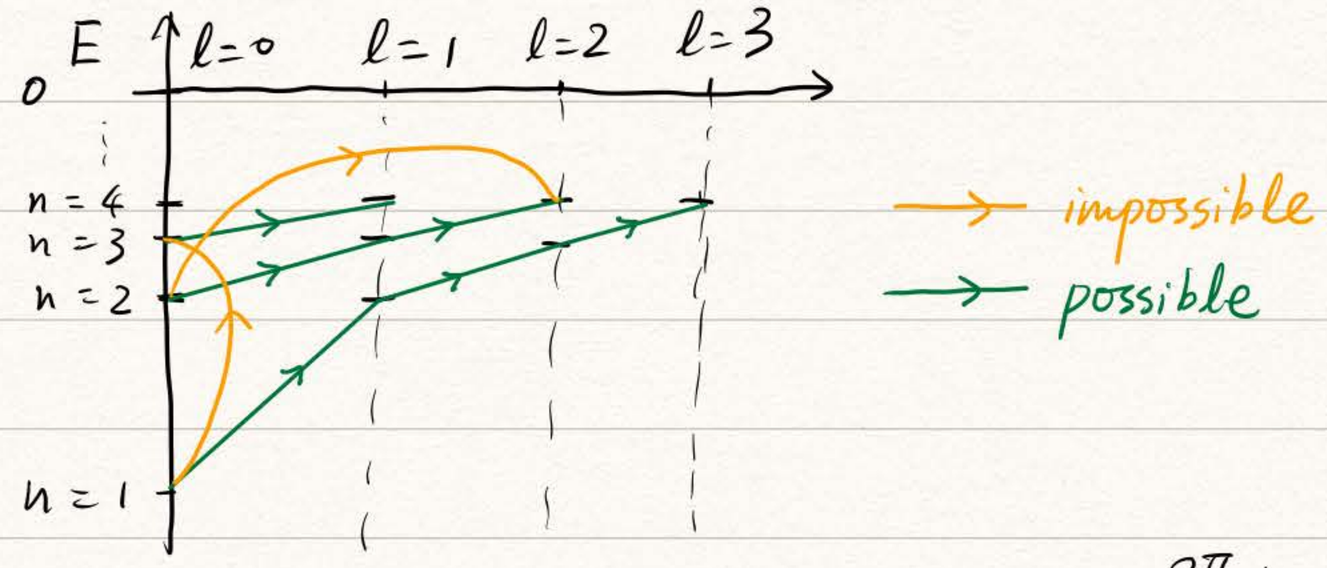
Density of states in energy $g(E_m)$

$\Rightarrow$ The transition rate : $\frac{2\pi}{\hbar^2}|\langle m|\hat{V}|i\rangle|^2 g(E_m)$, $E_m = E_i + \hbar\omega$

Radiative transitions in atomic physics

Transitions between atomic energy levels induced by light

In a hydrogen-like atom :



By Fermi's golden rule, the transition rate is $\frac{2\pi}{\hbar^2}|\langle m|\hat{V}|i\rangle|^2 \rho(\omega_{m,i})$

Electron speed $\ll c$ $\Rightarrow$ electric force from EM radiation dominates

Constant electric field over size of atom ($\lambda \gg a_0$)

"Dipole approximation"

We can just consider the scalar potential $\hat{V} = e\mathcal{E}z$

Transitive rate : $\frac{2\pi}{\hbar^2} e^2\mathcal{E}^2 |\langle m|\hat{z}|i\rangle|^2 \rho(\omega_{m,i})$

This describes ① absorption ② stimulated emission

does not describes ③ spontaneous emission

Why ? EM Theory is classical but QM is not

↳ Needs quantization of the field

Selection rules

$\omega = \omega_{m,i}$ is not sufficient to have transition.

Two approaches :

① Conservation of angular momentum

② Consider the non-zero matrix element $\langle m|\hat{z}|i\rangle$.

① Conservation of angular momentum:

Consider a composite system with quantum number l_1, m_1 and l_2, m_2. The combined system has quantum numbers:

$m = m_1 + m_2$; $|l_1 - l_2| \leq l \leq l_1 + l_2$

Part 1: atom in intial state l_i, m_i

Part 2: photon $l = 1$, $m = \pm 1$ along direction of propagation

$\Rightarrow |l_i - 1| \leq l_m \leq |l_i + 1|$

If light propagates along $\vec{e}_z$, $m_m = m_i \pm 1$

for general directions, $m_m = m_i \pm 1$ or m_i

② From matrix elements:

Selection rules from angular integrals (θ, φ)

$\Rightarrow \langle m|\hat{V}|i\rangle$ is non-zero only if $l_m = l_i \pm 1$

We can show this by considering the parity operation $\vec{r} \mapsto -\vec{r}$.

Then $r \mapsto r$, $\theta \mapsto \pi - \theta$, $\varphi \mapsto \varphi + \pi$.

Effect on spherical harmonics: $Y_{l,m}(\theta, \varphi) \mapsto (-1)^l Y_{l,m}(\theta, \varphi)$

$\Rightarrow \langle m|\hat{z}|i\rangle = (-1)^{l_m + l_i + 1} \langle m|\hat{z}|i\rangle$

$\Rightarrow$ either $l_m + l_i + 1 \in 2\mathbb{Z}$ or $\langle m|\hat{z}|i\rangle = 0$.

Integration over φ:

$$\langle m|\hat{z}|i\rangle \propto \int_0^{2\pi} d\varphi\, e^{i(m_i - m_m)\varphi} \cdot \left\{ \begin{matrix} \hat{x} \\ \hat{y} \end{matrix} \right\} e^{\pm i\varphi}$$
$$\hat{z} \to 1$$

$\Rightarrow m_m = m_i \pm 1$ or m_i

Summary : $\Delta \ell = \pm 1$

$$\Delta m = \begin{cases} 0, \pm 1 & \text{general direction} \\ \pm 1 & \text{direction of propagation} \end{cases}$$

Spin is unchanged.

Idential particles in quantum mechanics

Quantum mechanically, we cannot tell which particle in initial state goes to the given particles in final states.

Practicalities

For a system of N particles:

Wave function $\psi = \psi(\vec{r}_1, \cdots, \vec{r}_N)$

→ (Joint) probability density: $|\psi(\vec{r}_1, \cdots, \vec{r}_N)|^2$

Consider the case $N = 2$:

Define exchange operator $\hat{P}_{1,2}: \psi(\vec{r}_1, \vec{r}_2) \longmapsto \psi(\vec{r}_2, \vec{r}_1)$

Suppose that $\hat{H}$ is the Hamiltonian for 2 identical particles.

Then: $$\boxed{[\hat{P}_{1,2}, \hat{H}] = 0}$$

We can find simultaneous eigenstates of $\hat{P}_{1,2}$ and $\hat{H}$.

Consider these eigenstates, we have:

$$|\psi(\vec{r}_1, \vec{r}_2)|^2 = |\psi(\vec{r}_2, \vec{r}_1)|^2 \quad \text{(probability density unchanged)}$$

$$\Rightarrow \hat{P}_{1,2}\psi(\vec{r}_1, \vec{r}_2) = e^{i\alpha}\psi(\vec{r}_2, \vec{r}_1), \text{ for } \alpha \in \mathbb{R}$$

But $\hat{P}_{1,2}^2 \psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1, \vec{r}_2) \Rightarrow \hat{P}_{1,2}^2 = id \Rightarrow e^{2i\alpha} = 1$

$$\Rightarrow e^{i\alpha} = \begin{cases} +1, & \text{"bosons"} \quad \text{e.g. photons} \\ -1 & \text{"fermions"} \quad \text{e.g. electrons} \end{cases}$$

In relativistic QFT, bosons have integer spin; fermions have

half-integer spin.

Building wave functions with correct symmetry

Consider eigenstates of $\hat{H}$ for $N=2$:

In general $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{1,2}$

Example. 3D TISE:

$H_1 = -\frac{\hbar^2}{2m}\nabla_1^2 + V(\vec{r}_1)$, $H_2 = -\frac{\hbar^2}{2m}\nabla_2^2 + V(\vec{r}_2)$

$H_{1,2} = U(\vec{r}_1 - \vec{r}_2)$

TISE: $\hat{H}\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$

Try separation of variables in the case $\hat{H}_{1,2} = 0$:

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

Substitute into TISE: $\begin{cases} \hat{H}_1\varphi(\vec{r}_1) = E_1\varphi(\vec{r}_1) \\ \hat{H}_2\varphi(\vec{r}_2) = E_2\varphi(\vec{r}_2) \end{cases}$ $(E = E_1 + E_2)$

→ No symmetry in $\vec{r}_1$ & $\vec{r}_2$. Not eigenstate of $\hat{P}_{1,2}$

The eigenstate is

$$\psi(\vec{r}_1, \vec{r}_2) = \begin{cases} \frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_1(\vec{r}_2)\right) & \text{for bosons} \\ \frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_1(\vec{r}_2)\varphi_1(\vec{r}_2)\right) & \text{for fermions} \end{cases}$$

(both eigenstate of $\hat{H}$ and $\hat{P}_{1,2}$).

Pauli exclusion principle

For fermions, $\psi(\vec{r}_1, \vec{r}_2) = 0$ if φ_1 and φ_2 are the same function

We cannot put two fermions into the same quantum state!

Counting quantum states (repeating in stat. mech.)

Consider two orbitals φ_1, φ_2 occupied by two particles.

Distinguishable: 4 different states.

① $\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)$ ② $\varphi_2(\vec{r}_1)\varphi_2(\vec{r}_2)$ ③ $\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)$ ④ $\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)$

Identical bosons: 3 different states:

① $\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)$ ② $\varphi_2(\vec{r}_1)\varphi_2(\vec{r}_2)$

③ $\frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1) + \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\right)$

Identical fermions: 1 state. $\frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\right)$

More generally, given states of system with many particles.

{ can have arbitrarily many bosons in the same state;
  can have only 0 or 1 fermion in a state.

Product state

Suppose that we have states $|\psi_1\rangle$ for particle 1 and $|\psi_2\rangle$ for particle 2. We write the product state

$|\psi_1, \psi_2\rangle := |\psi_1\rangle \otimes |\psi_2\rangle$ (tensor product of vectors)

Inner product: $\langle \phi_1, \phi_2 | \psi_1, \psi_2 \rangle := \langle \phi_1 | \psi_1 \rangle \cdot \langle \phi_2 | \psi_2 \rangle$.

Suppose that $\hat{H}_1$ acts on $|\psi_1\rangle$, then

$$(\hat{H}_1 \otimes i\hat{d})|\psi_1, \psi_2\rangle = (\hat{H}_1|\psi_1\rangle) \otimes (i\hat{d}|\psi_2\rangle) = \hat{H}_1|\psi_1\rangle \otimes |\psi_2\rangle$$

(usually $\hat{H}_1 \otimes i\hat{d}$ is identified with $\hat{H}_1$)

General state in superposition: $\sum_{x,y} A_{x,y}|x, y\rangle$.

Symmetrized basis states

For bosons, $|\psi_1, \psi_2\rangle = \frac{1}{\sqrt{2}}\left(|\psi_1\rangle \otimes |\psi_2\rangle + |\psi_2\rangle \otimes |\psi_1\rangle\right)$

For fermions, $|\psi_1, \psi_2\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle \otimes |\psi_2\rangle - |\psi_2\rangle \otimes |\psi_1\rangle)$

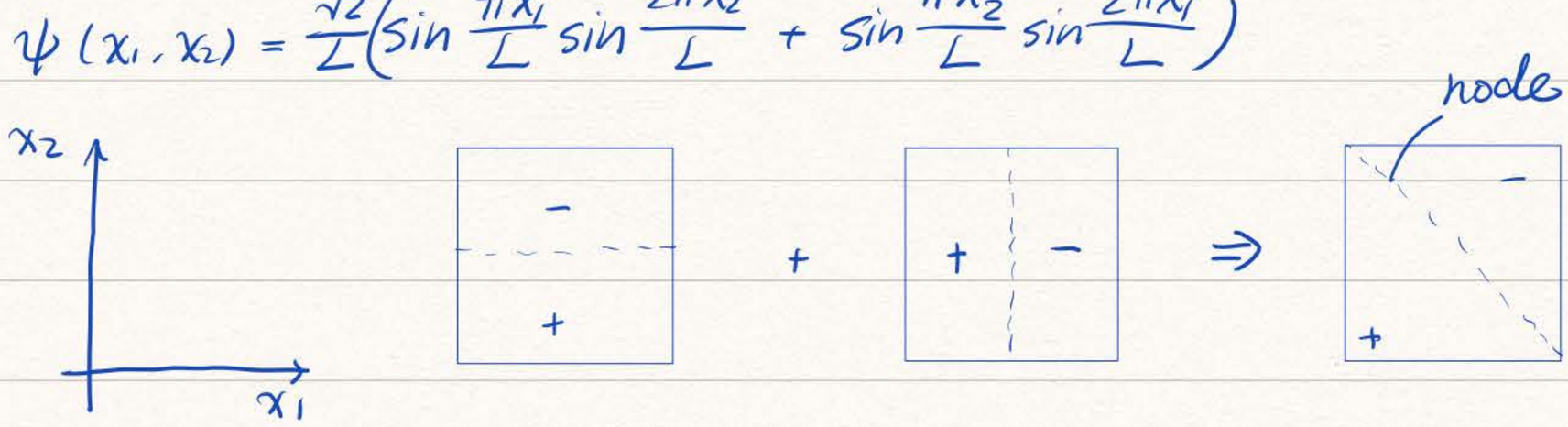
Example. Two-particle system in a 1D box of length L.

We know the single particle wave functions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}.$$

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

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



We find that bosons are more likely to be at the same end.

In kinetic theory, the motion of identical particles are correlated even if they have no interactions!

Choose basis states of the form:

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

anti-sym { sym / anti-sym or anti-sym / sym

Consider spin wave function for two spin-$\frac{1}{2}$ particles.

Possible states:

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

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

Addition of angular momenta:

$$\text{spin-}\tfrac{1}{2} \oplus \text{spin-}\tfrac{1}{2} \Rightarrow \text{total spin} = \begin{cases} 1 & \text{symmetric} \\ 0 & \text{anti-symmetric} \end{cases}$$

Symmetric : "triplet states" Anti-symmetric : "singlet states"

Exchange interactions

If there is an interaction potential, then the energies of spin states are different even though there is no direct coupling between spins.

Calculate energy change ΔE due to $V(\vec{r}_1 - \vec{r}_2)$ using 1st order pertubation theory :

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

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

$$\Rightarrow \Delta E = \Delta E_{direct} + \Delta E_{exchange}$$

where : $\Delta E_{direct} = \iint |\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)|^2 V(\vec{r}_1 - \vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2$

$$\Delta E_{exchange} = \iint \varphi_1^*(\vec{r}_1)\varphi_2(\vec{r}_1)\varphi_2^*(\vec{r}_2)\varphi_1(\vec{r}_2)\, V(\vec{r}_1 - \vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 .$$

Repulsive interaction $\Rightarrow$ lower energy if $S_{total} = 1$ i.e. spin aligned

Composite Systems

Suppose that we are two identical particles, each composed of N_F fermions & N_B bosons.

Exchanging particle coordinates, wave function changes :

$$(-1)^{N_F} \cdot (+1)^{N_B}$$

$\Rightarrow$ Composite is $\begin{cases} \text{fermion}, & \text{if } N_F \text{ is odd} \\ \text{boson}, & \text{if } N_B \text{ is even} \end{cases}$

(consistent with addition of spin)

Example. Helium.

He has two isotopes:

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

^4He : $2n + 2p + 2e$ (boson) $T_s = 2.1 K$

Both ^3He & ^4He are superfluids at low T.

Electronic states of He

This is the simplest many-particle system.

The Hamiltonian:

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

↑ kinetic energy ↑ electron-nucleus ↑ electron-electron

We cannot solve TISE exactly.

Recall that for hydrogen-like atoms,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}.$$

The eigenstates are labelled by quantum numbers:

n	ℓ	m	m_s
↑	↑	↑	↑
energy	total $\hat{L}$	$\hat{L}_z$	spin

The energy $E_n = -\frac{Z^2R}{n^2}$. $R \approx 13.6\,eV$.

Helium ground state

Simplest approximation: ignore e-e repulsion.

The lowest energy state:

$n_1 = n_2 = 1$, $\ell_1 = \ell_2 = 0$, $m_1 = m_2 = 0$, $\underline{m_{s1} = +\frac{1}{2},\ m_{s2} = -\frac{1}{2}}$

Pauli exclusion.

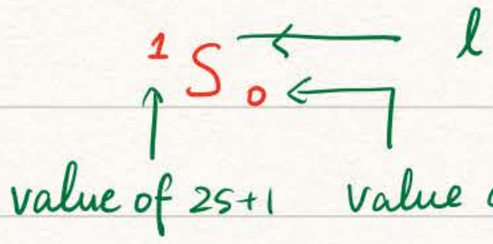
Also consider total angular momentum:

$$\vec{L} = \vec{L}_1 + \vec{L}_2 = 0. \quad \vec{S} = \vec{S}_1 + \vec{S}_2 = 0. \quad \vec{J} = \vec{L} + \vec{S} = 0$$

Notation (convention in chemistry):

$1s^2$ ← total electrons in orbital.

n ↑ ℓ ↑ ($\ell = 0, 1, 2, 3 \mapsto s, p, d, f$)



Ground state energy : $E_0 = -4R \times 2 = -108.8\,eV$

Correction from e-e repulsion from 1st order perturbation theory :

$$\Delta E_0 = \langle 0 | \frac{e^2}{4\pi\varepsilon_0} \|\vec{r}_1 - \vec{r}_2\|^{-1} | 0 \rangle$$

Calculate the integral (see Binney & Skinner)

$$\Delta E_0 = \frac{5}{2} R$$

$\Rightarrow$ Ground state energy $E_0 = -4R \times 2 + \frac{5}{2}R = -\frac{11}{2}R = -74.8\,eV$

(Experimental value $-79\,eV$)

Measurement via ionization

$$He \longrightarrow He^+ + e^- \longrightarrow He^{2+} + 2e^-$$

(1^{st} ionization) + (2^{nd} ionization) = − ground state energy

He^+ is hydrogen-like, $E_{He^+} = -4R \times 2 = -54.4\,eV$

We deduce that the 1^{st} ionization energy is $(4 - \frac{5}{2})R = 20.4\,eV$

1^{st} ionization energy < 2^{nd} ionization energy :

Shielding effect of the 2^{nd} electron.

First excited state of He

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

1^{st} excited state : $n_1 = 1$, $n_2 = 2$.

The configuration is $1s^1 2s^1$

$l_1 = l_2 = 0 \Rightarrow l = 0$

There are two choices of spin : $^1S_0$ or $^3S_1$

either symmetric or anti-symmetric spatial wave functions

Correction from e-e repulsion :

$$\Delta E = \Delta E_{direct} \pm \Delta E_{exchange} \quad (+ : \text{singlet} \; ; \; - : \text{triplet})$$

$$\Delta E_{direct} = \iint |\varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)|^2 \frac{e^2}{4\pi\varepsilon_0} \|\vec{r}_1 - \vec{r}_2\|^{-1} d\vec{r}_1 d\vec{r}_2$$

$$\Delta E_{exchange} = \iint \varphi_{1s}(\vec{r}_1)\varphi_{2s}(\vec{r}_2)\varphi_{1s}(\vec{r}_2)\varphi_{2s}(\vec{r}_2) \frac{e^2}{4\pi\varepsilon_0} \|\vec{r}_1 - \vec{r}_2\|^{-1} d\vec{r}_1 d\vec{r}_2$$

We expect that $\Delta E_{exchange} > 0$ for $\vec{r}_1 \approx \vec{r}_2$.

So spins are aligned in lower energy state.

Calculation of integral gives $\Delta E_{exchange} = 12eV$

but in experiment it is $0.4eV$. Bad approximation !
(because perturbation is not small)

Simple argument :

$S_{total} = 1$. spins parallel + Pauli exclusion

$\Rightarrow$ electrons avoid each other in space

$\Rightarrow$ lower Coulomb energy

Average of singlet & triplet states :

$$E = -4R\left(\frac{1}{1^2} + \frac{1}{2^2}\right) + \underbrace{\Delta E_{direct}}_{0.8\,R}$$

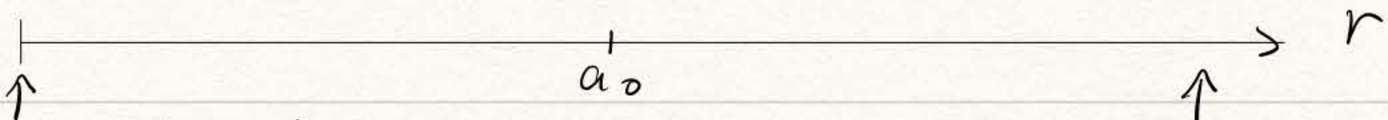
$\frac{\Delta E_{direct}}{E}$ is much smaller than that in ground state.

— the other electron partially screen nuclear charge

Higher excited states

$1s^1 2p^1$: degenerate with $1s^1 2s^1$ if neglecting e-e repulsion.

The potential seen by "2nd" electron :



see full nuclear charge — see $Z_{eff} = 1$

In fact energy of $1s^1 2p^1$ is higher than $1s^1 2s^1$

Lowest two excited states :

$1s^1 2s^1$ $^3S_1$ lower $1s^1 2s^1$ $^1S_0$ higher

Next configuration :

$1s^1 2p^1$ $^3P_0$, $1s^1 2p^1$ $^3P_1$, $1s^1 2p^1$ $^3P_2$, $1s^1 2p^1$ $^1P_1$

lower — higher

Many electron atoms

Eigenstates in Coulomb potential + Pauli exclusion

$\Longrightarrow$ Periodic table ~

First row : $n=1,\ \ell=0,\ m=0,\ m_s=\pm\frac{1}{2}$

2 states : H , He

Second row : $n=2,\begin{cases}\ell=0,\ m=0,\ m_s=\pm\frac{1}{2}\\ \ell=1,\ m=0,\pm1,\ m_s=\pm\frac{1}{2}\end{cases}$

8 states : Li $\rightarrow$ Ne

$n=3\begin{cases}\ell=0,\ m=0,\ m_s=\pm\frac{1}{2}\\ \ell=1,\ m=0,\pm1,\ m_s=\pm\frac{1}{2}\\ \ell=2,\ m=0,\pm1,\pm2,\ m_s=\pm\frac{1}{2}\end{cases}$

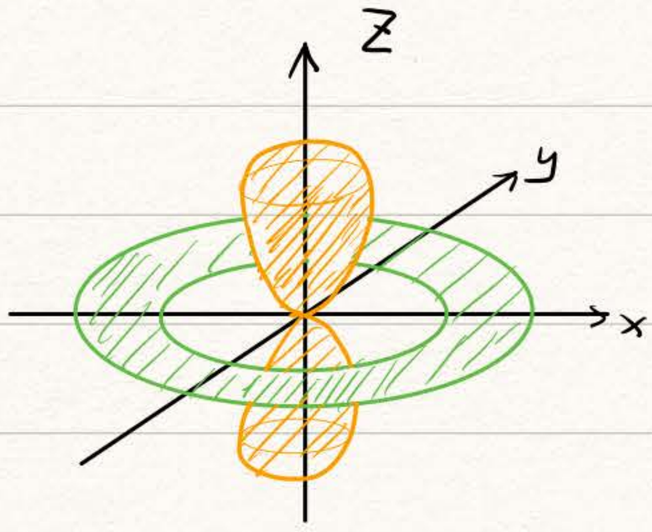
18 states : Third row Na $\rightarrow$ Ar Transition metals Sc $\rightarrow$ Zn

Issues :

① We fill up 4s before 3d !!!

② Ionization energy v.s. atomic number

Electronic structure in first two rows



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 : $1s^2 2s^2 2p^1\ \ ^2P_J$ $\rightarrow (J=\frac{1}{2}$ or $\frac{3}{2})$

C : $1s^2 2s^2 2p^2\ \ ^3P_J$ $\rightarrow (J=0,1,2)$ 2p : ↑ ↑ _

(which state has lower energy will be discussed in 3rd year course)

N : $1s^2 2s^2 2p^3$ → $^4S_{3/2}$ 2p : ↑ ↑ ↑ ←

O : $1s^2 2s^2 2p^4$ → ^3P_J ($J = 0, 1, 2$)

F : $1s^2 2s^2 2p^5$ → ^2P_J ($J = \frac{1}{2}$ or $\frac{3}{2}$)

Ne : $1s^2 2s^2 2p^6$ → $^1S_0$

3 electrons in 2p orbitals. ($l = 1$, $m = 0, \pm 1$)

Lowest Coulomb energy if spins parallel

Pauli exclusion ⇒ 1 electron in each $m = 0, \pm 1$.

⇒ Total orbital angular momentum 0.

Hund's Rules: To minimize Coulomb energy,

① Take highest possible total spin allowed by Pauli exclusion

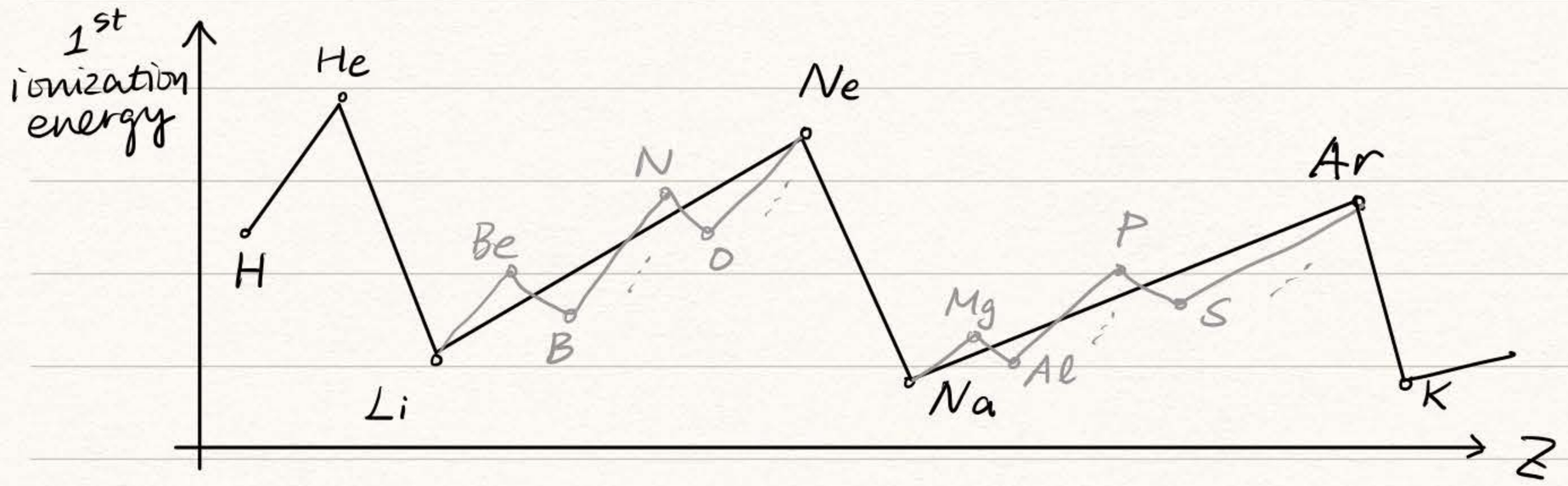
② Take highest possible L consistent with ①.

1st ionization energy v.s. atomic number

$Z \rightarrow Z_{eff}$ Nuclear charge screened by inner electrons.

$$E = -\frac{R}{n^2} Z_{eff}^2$$

↑ jump at the end of each row



Classical uncertainty & density matrices

Quantum Mechanics v.s. Statiscal Mechanics

Two types of averages :

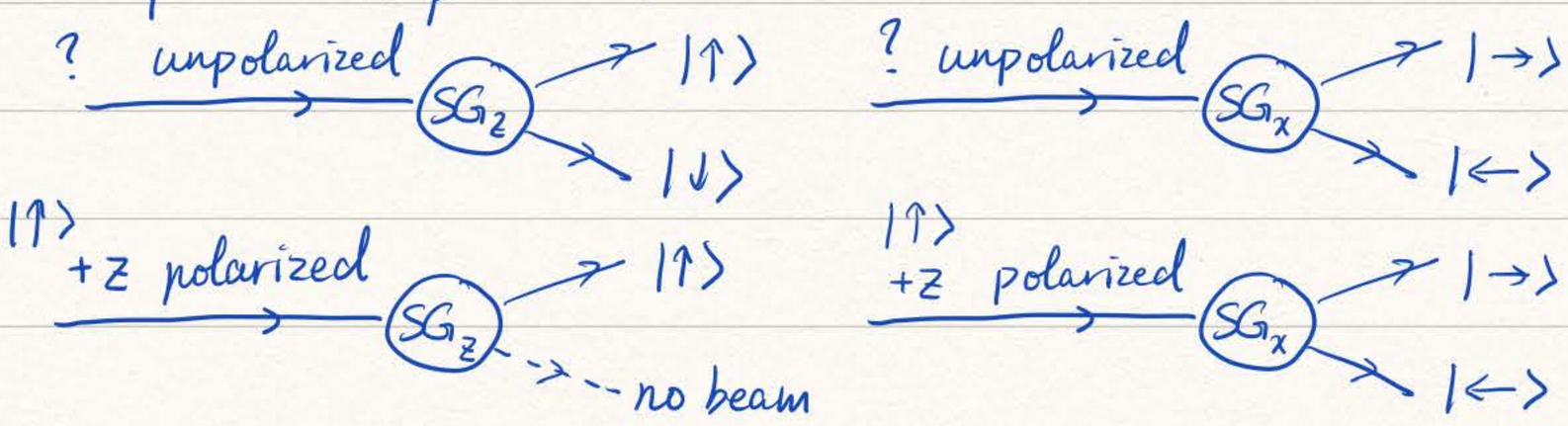
QM : $\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle$

SM : $[A]_{av} = \sum_n p_n A_n$

Sometimes we need to combine these two ways.

Example. Stern-Gerlach experiment.

Compare 4 experiments



How to represent unpolarized beam in QM ?

N.B. unpolarized $\neq c_1|\uparrow\rangle + c_2|\downarrow\rangle$

any choice of c_1 & c_2 gives a specific polarization.

Consider SM average :

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

Rewrite $\langle n|\hat{A}|n\rangle$ using some different orthonormal basis $\{|\alpha\rangle\}$.

Use $\hat{id} = \sum_\alpha |\alpha\rangle\langle\alpha|$

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

$$= \sum_{\alpha,\beta} \underbrace{\left(\sum_n \langle\beta|n\rangle p_n \langle n|\alpha\rangle\right)}_{\langle\beta|\hat{\rho}|\alpha\rangle} \langle\alpha|\hat{A}|\beta\rangle = tr(\hat{\rho}\hat{A})$$

We define $\hat{\rho} = \sum_n |n\rangle p_n \langle n|$ with elements $\langle \beta|\hat{\rho}|\alpha\rangle = \sum_n \langle \beta|n\rangle p_n \langle n|\alpha\rangle$

This reduces to QM average if $p_n = \delta_{nm}$

$\hat{\rho}$ is called the *density matrix*.

The eigenvalues of $\hat{\rho}$ are p_n. $0 \le p_n \le 1$. $\sum_n p_n = 1 \Rightarrow tr\,\hat{\rho} = 1$

- $\hat{\rho}$ represents the pure state if and only if $\hat{\rho}^2 = \hat{\rho}$.

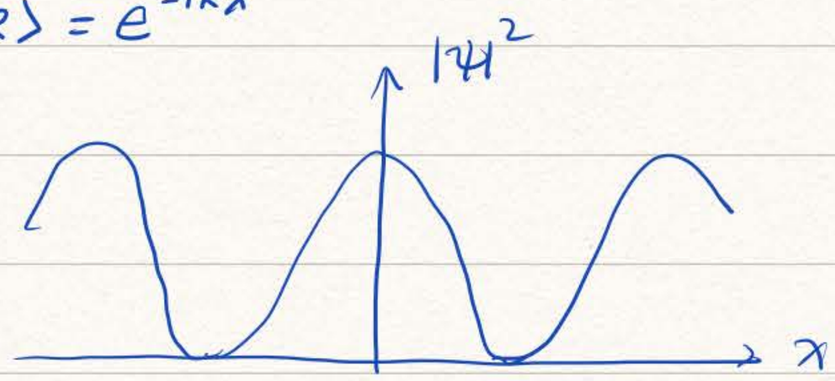
Example. Two particle beams in 1D with opposite momenta $\pm\hbar k$

$\langle x|k\rangle = e^{ikx}$, $\langle x|-k\rangle = e^{-ikx}$

Coherent version:

$|\psi\rangle = \frac{1}{\sqrt{2}}(|k\rangle + |-k\rangle)$

$\Rightarrow |\langle x|\psi\rangle|^2 = 2\cos^2 kx$



Density matrix $\hat{\rho} = |\psi\rangle\langle\psi| = \frac{1}{2}(|k\rangle\langle k| + |k\rangle\langle -k| + |-k\rangle\langle k| + |-k\rangle\langle -k|)$

$\Rightarrow tr(\hat{\rho}\hat{x}) = \frac{1}{2} tr\left(|x\rangle\langle x|(|k\rangle\langle k| + |k\rangle\langle -k| + |-k\rangle\langle k| + |-k\rangle\langle -k|)\right)$

$= \frac{1}{2}(1 + 1 + e^{2ik} + e^{-2ik}) = 1 + \cos 2kx = 2\cos^2 kx$

(as expected)

Incoherent version:

Density matrix $\hat{\rho} = \frac{1}{2}(|k\rangle\langle k| + |-k\rangle\langle -k|)$

$\Rightarrow tr(\hat{\rho}\hat{x}) = \frac{1}{2}(1+1) = 1$ No interference fringes.

Example. Stern-Gerlach experiments again.

Pauli matrices:

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\hat{\sigma}_z|\uparrow\rangle = |\uparrow\rangle$, $\hat{\sigma}_z|\downarrow\rangle = -|\downarrow\rangle$, $\hat{\sigma}_x|\rightarrow\rangle = |\rightarrow\rangle$, $\hat{\sigma}_x|\leftarrow\rangle = -|\leftarrow\rangle$

Spinors: $|\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$, $|\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix} \Rightarrow |\rightarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$, $|\leftarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

For unpolarized beam, density matrix:

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

$$= \frac{1}{2}\left(\begin{pmatrix}1\\0\end{pmatrix}(1\ 0) + \begin{pmatrix}0\\1\end{pmatrix}(0\ 1)\right) = \begin{pmatrix}\frac{1}{2} & 0\\ 0 & \frac{1}{2}\end{pmatrix} = \frac{1}{2}\hat{id}$$

For polarized beam, density matrix:

$$\hat{\rho}_{+z} = |\uparrow\rangle\langle\uparrow| = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}$$

Observables in SG:

For SG_z, $\hat{A}_{+z} = \frac{1}{2}(\hat{id} + \hat{\sigma}_z) = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}$

eigenvalue 1 with $|\uparrow\rangle$, 0 with $|\downarrow\rangle$

$$\hat{A}_{-z} = \frac{1}{2}(\hat{id} - \hat{\sigma}_z) = \begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}$$

For SG_x, $\hat{A}_{+x} = \frac{1}{2}(\hat{id} + \hat{\sigma}_x) = \frac{1}{2}\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}$

$$\hat{A}_{-x} = \frac{1}{2}(\hat{id} - \hat{\sigma}_z) = \frac{1}{2}\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}$$

$+z$-polarized beam:

$tr(\hat{\rho}_{+z}\hat{A}_{+z}) = 1$ $\quad tr(\hat{\rho}_{+z}\hat{A}_{-z}) = 0$

$tr(\hat{\rho}_{+z}\hat{A}_{+x}) = \frac{1}{2}$ $\quad tr(\hat{\rho}_{+z}\hat{A}_{+x}) = \frac{1}{2}$

Unpolarized beam:

$tr(\hat{\rho}_0\hat{A}_*) = \frac{1}{2}tr(\hat{id}\hat{A}_*) = \frac{1}{2}$ for $\hat{A}_*$ measuring any directions.