

Quantum kinetics

Reading:

- ▶ Kasap: 3.7
- ▶ Griffiths QM: 9.1 - 9.2

Operators and expectation values

- ▶ $|\psi(\vec{r})|^2$ probability distribution of \vec{r}
- ▶ Average value of \vec{r} :

$$\langle \vec{r} \rangle \equiv \int d\vec{r} |\psi(\vec{r})|^2 \vec{r}$$

Expectation value of operator \vec{r} in state with wavefunction ψ

$$\langle \psi | \vec{r} | \psi \rangle \equiv \int d\vec{r} \psi^*(\vec{r}) \vec{r} \psi(\vec{r})$$

- ▶ Expectation value of r^2 :

$$\langle r^2 \rangle \equiv \langle \psi | r^2 | \psi \rangle \equiv \int d\vec{r} \psi^*(\vec{r}) r^2 \psi(\vec{r})$$

- ▶ Uncertainty in x , $\Delta x \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

Momentum operator

- ▶ For a free particle with momentum $\vec{p} = \hbar\vec{k}$, $\psi = e^{i\vec{k}\cdot\vec{x}}/\sqrt{L}$
- ▶ Consider expectation value of gradient

$$\begin{aligned}
 \langle\psi|\nabla|\psi\rangle &\equiv \int d\vec{r} \psi^*(\vec{r}) \nabla \psi(\vec{r}) \\
 &= \frac{1}{L} \int d\vec{r} e^{-i\vec{k}\cdot\vec{x}} \nabla e^{i\vec{k}\cdot\vec{x}} \\
 &= \frac{1}{L} \int d\vec{r} e^{-i\vec{k}\cdot\vec{x}} i\vec{k} e^{i\vec{k}\cdot\vec{x}} \\
 &= i\vec{k}
 \end{aligned}$$

- ▶ Momentum operator \hat{p} defined by $\langle\vec{p}\rangle = \langle\psi|\hat{p}|\psi\rangle$
- ▶ So the momentum operator is

$$\hat{p} = -i\hbar\nabla$$

Hamiltonian operator

- ▶ If we define the Hamiltonian operator as

$$\hat{H} \equiv \frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) = \frac{\hat{p}^2}{2m} + V(\vec{r})$$

the Schrodinger equation becomes $\hat{H}\psi = E\psi$

- ▶ Expectation value of the Hamiltonian is $\langle \psi | \hat{H} | \psi \rangle = E$
- ▶ What about time dependence? Remember $\psi(\vec{r}, t) = \psi(\vec{r})e^{-iEt/\hbar}$

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &\equiv \int d\vec{r} \psi^*(\vec{r}, t) \hat{H} \psi(\vec{r}, t) \\ &= \int d\vec{r} \psi^*(\vec{r}) e^{iEt/\hbar} \hat{H} \psi(\vec{r}) e^{-iEt/\hbar} \\ &= \int d\vec{r} \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) \\ &= \int d\vec{r} \psi^*(\vec{r}) E \psi(\vec{r}) \\ &= E \end{aligned}$$

Time dependence due to perturbations

- ▶ Let Hamiltonian \hat{H} have two eigenstates $H\psi_1 = E_1\psi_1$ and $H\psi_2 = E_2\psi_2$
- ▶ Eigenstates are orthogonal $\int \psi_1^* \psi_2 = 0$ and complete: any $\psi = c_1\psi_1 + c_2\psi_2$
- ▶ Say apply electric field $\vec{E}e^{-i\omega t}$, changes Hamiltonian to $\hat{H} + \hat{H}'e^{-i\omega t}$ with $\hat{H}' = -e\vec{E} \cdot \vec{r}$
- ▶ Time-dependent Schrodinger equation $(\hat{H} + \hat{H}'e^{-i\omega t})\psi = i\hbar\frac{\partial\psi}{\partial t}$
- ▶ Substitute expansion $\psi(t) = c_1(t)e^{-iE_1t/\hbar}\psi_1 + c_2(t)e^{-iE_2t/\hbar}\psi_2$

$$\begin{aligned} (\hat{H} + \hat{H}'e^{-i\omega t})(c_1e^{-iE_1t/\hbar}\psi_1 + c_2e^{-iE_2t/\hbar}\psi_2) \\ = (i\hbar\dot{c}_1 + E_1c_1)e^{-iE_1t/\hbar}\psi_1 + (i\hbar\dot{c}_2 + E_2c_2)e^{-iE_2t/\hbar}\psi_2 \end{aligned}$$

- ▶ Rewrite using eigenvalues of \hat{H}

$$\begin{aligned} c_1e^{-i(E_1+\hbar\omega)t/\hbar}\hat{H}'\psi_1 + c_2e^{-i(E_2+\hbar\omega)t/\hbar}\hat{H}'\psi_2 \\ = i\hbar\dot{c}_1e^{-iE_1t/\hbar}\psi_1 + i\hbar\dot{c}_2e^{-iE_2t/\hbar}\psi_2 \end{aligned}$$

Time dependence due to perturbations (contd.)

- ▶ Equation in terms of expansion $\psi(t) = c_1(t)e^{-iE_1t/\hbar}\psi_1 + c_2(t)e^{-iE_2t/\hbar}\psi_2$

$$\begin{aligned} c_1e^{-i(E_1+\hbar\omega)t/\hbar}\hat{H}'\psi_1 + c_2e^{-i(E_2+\hbar\omega)t/\hbar}\hat{H}'\psi_2 \\ = i\hbar\dot{c}_1e^{-iE_1t/\hbar}\psi_1 + i\hbar\dot{c}_2e^{-iE_2t/\hbar}\psi_2 \end{aligned}$$

- ▶ Now integrate equation $\int \psi_2(\vec{r}, t)^*$ to get

$$c_1\langle\psi_2|\hat{H}'|\psi_1\rangle e^{i(E_2-E_1-\hbar\omega)t/\hbar} + c_2\langle\psi_2|\hat{H}'|\psi_2\rangle e^{-i\omega t} = i\hbar\dot{c}_2$$

- ▶ If we start at $t = 0$ in state ψ_1 i.e. $c_1(0) = 1$, $c_2(0) = 0$, then at $t = 0$

$$i\hbar\dot{c}_2 = \langle\psi_2|\hat{H}'|\psi_1\rangle e^{i(E_2-E_1-\hbar\omega)t/\hbar}$$

which is the rate at which state ψ_2 starts appearing

- ▶ $c_2(t)$ oscillates in time with zero average value as long as $E_2 \neq E_1 + \hbar\omega$ (Energy conservation)
- ▶ If $E_2 = E_1 + \hbar\omega$, then $c_2(t)$ grows in time

Fermi's Golden rule

- ▶ Upon applying a perturbation Hamiltonian $H' e^{i\omega t}$,

$$\Gamma_{1 \rightarrow 2} = \frac{2\pi}{\hbar} |\langle \psi_2 | \hat{H}' | \psi_1 \rangle|^2 \delta(E_2 - (E_1 + \hbar\omega))$$

is the rate of transitioning from ψ_1 to ψ_2

- ▶ More generally,

$$\Gamma_i = \frac{2\pi}{\hbar} \sum_f |\langle \psi_f | \hat{H}' | \psi_i \rangle|^2 \delta(E_f - (E_i + \hbar\omega))$$

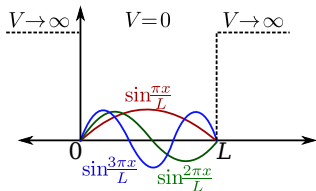
is the rate of transitioning out of initial state ψ_i

- ▶ Fundamental equation of 'quantum kinetics'
(say analogous to Arrhenius equation)

Example: particle in a box absorption spectrum

- ▶ States with discrete energies and (normalized) wavefunctions:

$$E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2}, \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$



- ▶ Starting at $n = 1$, apply EM field $-e\mathcal{E}xe^{-i\omega t}$
- ▶ Absorb photons and go to higher n
- ▶ Will excitations occur to all n with equal probability?
- ▶ Matrix element for transition:

$$\langle \psi_n | (-e\mathcal{E}x) | \psi_1 \rangle \equiv -e\mathcal{E} \int_0^L dx \psi_n^*(x) x \psi_1(x) = \frac{-4e\mathcal{E}Ln}{\pi^2(n^2 - 1)^2} [1 - (-1)^{n-1}]$$

- ▶ Transition (absorption) rate:

$$\Gamma = \frac{2\pi}{\hbar} \sum_{\text{even } n} \delta(E_n - E_1 - \hbar\omega) \left| \frac{-8e\mathcal{E}Ln}{\pi^2(n^2 - 1)^2} \right|^2$$

- ▶ Selection rule: transitions from $n = 1$ only to even n

Orbital angular momentum

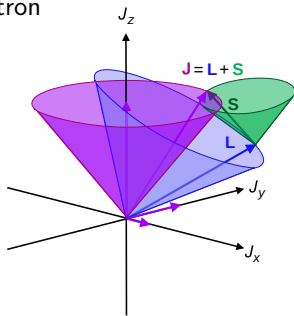
- ▶ Classical picture: electrons revolving around nuclei with $\vec{L} = \vec{r} \times \vec{p}$
- ▶ In quantum picture, $\hat{L} = \vec{r} \times \hat{p} = -i\hbar\vec{r} \times \nabla$
- ▶ In particular $\hat{L}_z = -i\hbar(x\partial_y - y\partial_x) = -i\hbar\partial_\phi$
- ▶ In atomic orbitals, angular dependence $Y_{lm_l}(\theta, \phi) = P_l^{m_l}(\cos\theta)e^{im_l\phi}$
- ▶ Azimuthal angular momentum $\langle \hat{L}_z \rangle = m_l\hbar$
- ▶ Account for all directions, magnitude of angular momentum

$$\langle \hat{L}^2 \rangle = l(l+1)\hbar^2$$

- ▶ Number of projections quantized to $2l+1$ (number of allowed m_l)

Spin angular momentum

- ▶ Electrons have spin $s = 1/2$
- ▶ Corresponding $m_s = \pm 1/2$ ($2 = 2s + 1$ values)
- ▶ Projected angular momentum $S_z = m_s \hbar$
- ▶ Angular momentum magnitude $S^2 = s(s + 1)\hbar^2$
- ▶ Both orbital and spin angular momentum for electron
- ▶ Total angular momentum $\vec{J} = \vec{L} + \vec{S}$
- ▶ Also quantized, with quantum numbers j, m_j
- ▶ $j = |l - s|$ to $l + s$ in increments of 1
- ▶ $m_j = -j, -j + 1, \dots, +j$
- ▶ Projected angular momentum $J_z = m_j \hbar$
- ▶ Angular momentum magnitude $J^2 = j(j + 1)\hbar^2$



Angular momentum consequence: magnetic moments

- ▶ Consider particle with charge q and mass m moving with speed v in circle of radius r
- ▶ Angular momentum $L = mvr$
- ▶ Current $I = \frac{qv}{2\pi r}$
- ▶ Magnetic moment $\mu = \frac{1}{2} \oint \vec{r} \times d\vec{l} I = \frac{1}{2} r (2\pi r) \frac{qv}{2\pi r} = qvr/2$
- ▶ Classical particle $\mu = \frac{q}{2m} L$
- ▶ Exactly true for orbital angular momentum

$$\mu_z = \frac{-e}{2m} m_l \hbar = -m_l \mu_B$$

where $\mu_B \equiv \frac{e\hbar}{2m}$ is the Bohr magneton

- ▶ What about spin?

$$\mu_z = -g_e m_s \mu_B$$

where $g_e \approx 2.0023 = 2 + \frac{e^2}{4\pi\epsilon_0\hbar c} + \dots$ is called the gyromagnetic ratio (Relativity $\Rightarrow g_e = 2$, rest quantum correction)

Angular momentum conservation: selection rules

- ▶ Light absorption: photon excites electron from lower state nlm_l to higher state $n'l'm'_l$
- ▶ Dominant electron-photon interaction through electric field \Rightarrow involves only L of electron (not S)
- ▶ Initial angular momentum $s = 1$ in photon and l of electron
 $\Rightarrow j = l - 1, \dots, l + 1$
- ▶ Projection $m_j = m_s + m_l = m_l - 1, \dots, m_l + 1$
- ▶ Angular momentum conservation (l', m'_l) must equal (j, m_j)
- ▶ Process allowed only if $\Delta l = 0, \pm 1$ and $\Delta m_l = 0, \pm 1$
- ▶ More careful analysis $\Delta l = 0$ disallowed (because $\langle \psi_2 | \hat{H}' | \psi_1 \rangle = 0$),
 $\Rightarrow \Delta l = \pm 1$ and $\Delta m_l = 0, \pm 1$