MTLE-6120: Advanced Electronic Properties of Materials

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 $\vec{r}$:

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

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

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

- Expectation value of r^2:

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

- 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

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

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

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

Hamiltonian operator

- If we define the Hamiltonian operator as

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

  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 $\psi(\vec{r},t) = \psi(\vec{r})e^{-iEt/\hbar}$

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

Time depending 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 $\vec{\mathcal{E}} e^{-i\omega t}$, changes Hamiltonian to $\hat{H} + \hat{H}' e^{-i\omega t}$ with $\hat{H}' = e\vec{\mathcal{E}} \cdot \vec{r}$
- Time-dependent Schrodinger equation $(\hat{H} + \hat{H}' e^{-i\omega t})\psi = i\hbar \frac{\partial \psi}{\partial t}$
- Substitute expansion $\psi(t) = c_1(t) e^{-iE_1 t/\hbar}\psi_1 + c_2(t) e^{-iE_2 t/\hbar}\psi_2$

$$(\hat{H} + \hat{H}' e^{-i\omega t})(c_1 e^{-iE_1 t/\hbar}\psi_1 + c_2 e^{-iE_2 t/\hbar}\psi_2) \\ = (i\hbar\dot{c}_1 + E_1 c_1) e^{-iE_1 t/\hbar}\psi_1 + (i\hbar\dot{c}_2 + E_2 c_2) e^{-iE_2 t/\hbar}\psi_2$$

- Rewrite using eigenvalues of $\hat{H}$

$$c_1 e^{-i(E_1+\hbar\omega)t/\hbar}\hat{H}'\psi_1 + c_2 e^{-i(E_2+\hbar\omega)t/\hbar}\hat{H}'\psi_2 \\ = i\hbar\dot{c}_1 e^{-iE_1 t/\hbar}\psi_1 + i\hbar\dot{c}_2 e^{-iE_1 2/\hbar}\psi_2$$

Time dependence due to perturbations (contd.)

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

$$c_1e^{-i(E_1+\hbar\omega)t/\hbar}\hat{H}'\psi_1 + c_2e^{-i(E_2+\hbar\omega)t/\hbar}\hat{H}'\psi_2$$
$$= i\hbar\dot{c}_1e^{-iE_1t/\hbar}\psi_1 + i\hbar\dot{c}_2e^{-iE_12/\hbar}\psi_2$$

- 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 $H'e^{i\omega t}$,

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

is the rate of transitioning from ψ_1 to ψ_2

- More generally,

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

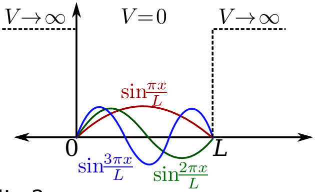
is the rate of transitioning out of initial state ψ_i

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

Example: particle in a box absorption spectrum

- States with discrete energies and (normalized) wavefunctions:

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



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

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

- 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

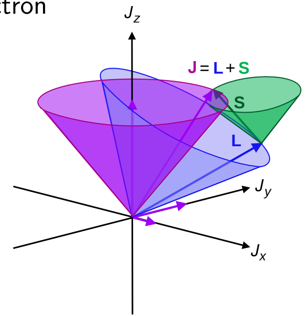
- Classical picture: electrons revolving around nuclei with $\vec{L} = \vec{r} \times \vec{p}$
- In quantum picture, $\hat{\vec{L}} = \vec{r} \times \hat{\vec{p}} = -i\hbar\vec{r} \times \nabla$
- In particular $\hat{L}_z = -i\hbar(x\partial_y - y\partial_x) = -i\hbar\partial_\phi$
- In atomic orbitals, 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
- $m_j = -j, -j+1, \ldots, +j$
- 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 $\mu = \frac{1}{2}\oint \vec{r} \times \mathrm{d}\vec{l} I = \frac{1}{2} r(2\pi r)\frac{qv}{2\pi r} = qvr/2$
- 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 $g_e \approx 2.0023 = 2 + \frac{e^2}{4\pi\epsilon_0 \hbar c} + \cdots$ 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 $\Rightarrow j = l - 1, \ldots, l + 1$
- Projection $m_j = m_s + m_l = m_l - 1, \ldots, m_l + 1$
- 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 $\Delta m_l = 0, \pm 1$