Fermi’s Golden Rule

Some QM basics

Time dependent Schrödinger equation:

$$\boxed{i\hbar\frac{\partial|\psi(\mathbf{r},\mathrm{t})\rangle}{\partial t}=\widehat{H}_0|\psi(\mathbf{r},\mathrm{t})\rangle}$$

For a stationary system, $|\psi(\mathbf{r},\mathrm{t})\rangle = e^{-iEt/\hbar}\cdot|\psi(\mathbf{r})\rangle$. Plugging this expression into the Schrödinger equation, we obtain:

$$i\hbar\frac{\partial|\psi\rangle}{\partial t}=-i\hbar\frac{iE}{\hbar}e^{-iEt/\hbar}\cdot|\psi(\mathbf{r})\rangle=e^{-iEt/\hbar}\cdot\widehat{H}_0|\psi(\mathbf{r})\rangle$$

or

$$\boxed{\widehat{H}_0|\psi(\mathbf{r})\rangle=E|\psi(\mathbf{r})\rangle}$$

This is the time independent Schrödinger equation. Note that $\mathbf{r}$ denotes multiple coordinates (spatial, spin etc.)

$|\varphi\rangle$…state function (ket)

$\langle\psi|$…state function (bra)

$\langle\psi|\varphi\rangle$…projection (scalar product)

$\widehat{H}|\varphi\rangle$ = E $|\varphi\rangle$ … Eigenvalue, Eigenvector equation

$\langle n|m\rangle=\delta_{nm}$ …Orthonomal basis

$|\varphi\rangle=\sum_n c_n|n\rangle$ with $c_n=\langle n|\varphi\rangle$

$\langle\varphi|\widehat{H}|\varphi\rangle$ … expectation value

1.3.2 Derivation of Fermi’s golden rule

The famous rate equation was first derived by Dirac and the name “golden rule" was given by Fermi in view of its instrumental role in his theory of Beta decay. Later it was realized that the rule can be used to calculate transition rates or cross sections of various processes, such as tunneling processes, light-matter interaction, conduction in solids. In this course, we will use it to determine the rates of some electron and energy transfer processes.

We consider a quantum mechanical system, that goes from an initial Eigenstate $|\psi_i\rangle$ to a final state $|\psi_f\rangle$ under the influence of an external stimulus (force). We are interested in the probability $P_{i\to f}$ of this transition to happen and finally derive the rate $\Gamma = \partial P/\partial t$.

The time dependence of any quantum system is given by the time dependent Schrödinger equation:

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = (\hat{H}_0+\lambda\hat{V})|\psi\rangle \qquad (1)$$

$\hat{H}_0$ is the Hamiltonian of the unperturbed system (i.e. at t<0) and $|\psi_i\rangle$ is an eigenstate with eigenenergy E_i. $\hat{H}_0$ has a quasi-continuum $\{|\mathrm{n}\rangle\}$ and $|\psi_f\rangle$ is one of these states with energy E_f. $\hat{V}$ is a perturbation that is turned on at $t = 0$ and which couples $|\psi_i\rangle$ and $|\psi_f\rangle$ and possibly also states within the continuum band too. λ is a control parameter that will be used to track the order of the perturbation. It will be set to one at the end.

The initial condition is that $|\psi(t=0)\rangle = |\psi_i\rangle$. We can expand the wave function $|\psi(t;\lambda\rangle$ as a power series of λ:

$$|\psi(t;\lambda\rangle = \sum_{s=0}^{\infty} \lambda^s |\psi_s(\mathrm{t})\rangle \qquad (2)$$

$|\psi_s(\mathrm{t})\rangle$ must obey the same initial condition as above; $|\psi_0(0)\rangle = |\psi_i\rangle$ and $|\psi_s(0)\rangle=0$ for s≥ 1. Inserting (2) into (1) and equating the coefficients of the powers λ gives:

λ^0:

$$i\hbar\frac{\partial|\psi_0(t)\rangle}{\partial t} = \hat{H}_0|\psi_0(t)\rangle \qquad (3)$$

λ^1(first order):

$$i\hbar\frac{\partial|\psi_1(t)\rangle}{\partial t} = \hat{H}_0|\psi_1(t)\rangle + \hat{V}|\psi_0(t)\rangle \qquad (4)$$

From (3) we get:

$$|\psi_0(t) = e^{-iE_i t/\hbar}|\psi_i\rangle \qquad (5)$$

Substituting (5) into (4) and projecting both sides onto $|\mathrm{n}\rangle$, we get :

$$i\hbar\frac{\partial}{\partial t}\langle n|\psi_1(t)\rangle = E_n\langle n|\psi_1(t)\rangle + \langle n|\hat{V}|\psi_i\rangle e^{-iE_i t/\hbar} \qquad (6)$$

The solution of differential equation (5) is:

$$\langle n|\psi_1(t)\rangle = \langle n|\hat{V}|\psi_i\rangle \frac{1-e^{i(E_n-E_i)t/\hbar}}{E_n-E_i} e^{-iE_i t/\hbar} \qquad (7)$$

The probability of finding the system in state $|n\rangle$ after time t is therefore :

$$P_n = |\langle n|\psi_1(t)\rangle|^2 = \left|\langle n|\hat{V}|\psi_i\rangle\right|^2 \left|\frac{1}{e^{-i(E_n-E_i)t/2\hbar}}\left(e^{i(E_n-E_i)t/2\hbar} - e^{-i(E_n-E_i)t/2\hbar}\right)\frac{1}{E_n-E_i}\right|^2 \cdot 1 \qquad (8)$$

$$= \left|\langle n|\hat{V}|\psi_i\rangle\right|^2 \frac{4\cdot sin^2\left((E_n-E_i)t/2\hbar\right)}{(E_n-E_i)^2} = \frac{2t}{\hbar}\left|\langle n|\hat{V}|\psi_i\rangle\right|^2 \frac{sin^2\left((E_n-E_i)t/2\hbar\right)}{(E_n-E_i)^2 t/2\hbar}$$

The final state $|\psi_f\rangle$ is within the manifold $\{|n\rangle\}$ and therefore the probability P for the transition has to sum over the final states of interests:

$$P_{i\to f} = \sum_n |\langle n|\psi_1(t)\rangle|^2 = \frac{2t}{\hbar}\sum_n \left|\langle n|\hat{V}|\psi_i\rangle\right|^2 \frac{sin^2\left((E_n-E_i)t/2\hbar\right)}{(E_n-E_i)^2\, t/2\hbar} \qquad (9)$$

We see that the weight function $\frac{sin^2\left((E_n-E_i)t/2\hbar\right)}{(E_n-E_i)^2 t/2\hbar}$ width scales with 1/t, while its height scales with t.

One can show that in the limit of t → ∞ $\frac{\sin^2\left((E_n-E_i)t/2\hbar\right)}{(E_n-E_i)^2 t/2\hbar}$-> $\pi \cdot \delta(E_n - E_i)$. As a matter of fact, a very good approximation to the δ – function is already obtained at small times. We also assume that $\langle n|\hat{V}|\psi_i\rangle$ does not vary much with time in the limit of small $(E_n - E_i)$. The same is true for the density of states that we take as $\rho(E_f)$. In this approximation we obtain:

$$P_{i\to f} = \frac{2\pi t}{\hbar}\left|\langle n|\hat{V}|\psi_i\rangle\right|^2 \rho(E_f)$$

We then get the Fermi golden rule by taking the derivative with time:

$$\Gamma_{i\to f} = \frac{\partial P_{i\to f}}{\partial t} = \frac{2\pi}{\hbar}\left|\langle n|\hat{V}|\psi_i\rangle\right|^2 \rho(E_f)$$

The golden rule is not valid for all times. In order that the central bump of the weight function falls within the group of final states we are looking at the spread of energy $\Delta\varepsilon = E_f - E_i$ should be comparable to 2π $\hbar$/t or t > 2π $\hbar$/ $\Delta\varepsilon$. On the other hand, the time must be short enough so that many states fall within the bump, i.e. the level spacing $\delta\varepsilon$ must be small compared with 2π $\hbar$/t or t<< 2π $\hbar/\delta\varepsilon$ (also expressed as t<< 2π $\hbar\rho(E_f)$).

Application of Fermi’s Golden Rule

Absorption and luminescence

$\hat{V}(t) = \boldsymbol{\mu E}(\boldsymbol{t})$ $\boldsymbol{\mu}$ is the dipole operator and $\boldsymbol{E}(\boldsymbol{t})$ the oscillating electrical field of the photon

FRET

$\hat{V}(t) = \frac{3(\boldsymbol{\mu_A}\widehat{r)}(\boldsymbol{\mu_D}\widehat{r)}-\boldsymbol{\mu_A}\boldsymbol{\mu_D}}{r^3}$ $\boldsymbol{\mu_A}$ and $\boldsymbol{\mu_D}$ are the transition dipole moment operators of acceptor and donor, respectively.

Electron transfer

$\hat{V}(t) = J_0 e^{-\beta(R-R_0)}(|A\rangle\langle D| + |D\rangle\langle A|)$ where $J_0 e^{-\beta(R-R_0)}$is the coupling matrix element and $|A\rangle$ and $|D\rangle$ are the representing the states (electronic and nuclear) of the acceptor and donor, respectively