Fermi's Golden Rule for bound-continuum transitions

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1 Notational details, definition of functions

Define the inprodukt between two functions $\phi(x)$ and $\psi(x)$ as

$$\langle\phi|\psi\rangle = \int \mathrm{d}x\phi^*(x)\psi(x), \tag{1}$$

the function $\varphi_x(x)$ as

$$\varphi_x(x') \equiv \delta(x - x'), \tag{2}$$

and the shorthand notation $|x\rangle \equiv |\phi_x\rangle$. Then, for arbitrary function ψ

$$\langle x|\psi\rangle = \int \mathrm{d}x'\varphi_x^*(x')\psi(x') = \psi(x). \tag{3}$$

The $|x\rangle$ are orthonormal

$$\langle x|x'\rangle = \varphi_{x'}(x) = \delta(x - x') \tag{4}$$

and form a complete basis of the Hilbert space, since for arbitrary ϕ and ψ

$$\int \mathrm{d}x\langle\phi|x\rangle\langle x|\psi\rangle = \int \mathrm{d}x\langle x|\phi\rangle^*\langle x|\psi\rangle = \int \mathrm{d}x\phi(x)^*\psi(x) = \langle\phi|\psi\rangle, \tag{5}$$

so that $\int \mathrm{d}x|x\rangle\langle x| = \hat{1}$.

Define the functions $|k\rangle$ by their coordinate representation:

$$\langle x|k\rangle = \frac{1}{\sqrt{2\pi}}e^{ikx}. \tag{6}$$

These functions are orthonormal due to

$$\langle k|k'\rangle = \int \mathrm{d}x\langle k|x\rangle\langle x|k'\rangle = \int \mathrm{d}x\langle x|k\rangle^*\langle x|k'\rangle = \frac{1}{2\pi}\int \mathrm{d}xe^{i(k'-k)x} = \delta(k - k'). \tag{7}$$

Furthermore, they also form a basis for the Hilbert space, since

$$\begin{aligned}\int \mathrm{d}k|k\rangle\langle k| &= \int \mathrm{d}k \int \mathrm{d}x|x\rangle\langle x|k\rangle \int \mathrm{d}x'\langle k|x'\rangle\langle x'| \\ &= \frac{1}{2\pi}\int \mathrm{d}k \int \mathrm{d}x \int \mathrm{d}x'|x\rangle e^{ik(x-x')}\langle x'| \\ &= \int \mathrm{d}x \int \mathrm{d}x'|x\rangle\delta(x-x')\langle x'| = \int \mathrm{d}x|x\rangle\langle x| = \hat{1}. \end{aligned} \tag{8}$$

And finally, the $|k\rangle$ are eigenkets of the momentum operator $\hat{p}$. Postulate $[\hat{x},\hat{p}] = i\hbar\hat{1}$, then $\langle x|[\hat{x},\hat{p}]x'\rangle = (x-x')\langle x|\hat{p}x'\rangle = i\hbar\langle x|x'\rangle = i\hbar\delta(x-x')$, which has as solution $\langle x|\hat{p}x'\rangle = -i\hbar\nabla\delta(x-x')$. Then

$$\begin{aligned}\langle x|\hat{p}k\rangle &= \int \mathrm{d}x'\langle x|\hat{p}x'\rangle\langle x'|k\rangle = -\frac{i\hbar}{\sqrt{2\pi}}\int \mathrm{d}x'[\nabla\delta(x-x')]e^{ikx'} \\ &= -\frac{i\hbar}{\sqrt{2\pi}}\int \mathrm{d}x'\delta(x-x')\nabla e^{ikx'} = \frac{\hbar k}{\sqrt{2\pi}}\int \mathrm{d}x'\delta(x-x')e^{ikx'} = \frac{\hbar k}{\sqrt{2\pi}}e^{ikx} \\ &= \hbar k\langle x|k\rangle, \end{aligned} \tag{9}$$

and since the $|x\rangle$ form a complete basis, we can write $\hat{p}|k\rangle = \hbar k|k\rangle$.

Extending this to three dimensions, we define

$$|\mathbf{r}\rangle \equiv |x\rangle|y\rangle|z\rangle, \tag{10}$$

and similarly

$$|\mathbf{k}\rangle \equiv |k_x\rangle|k_y\rangle|k_z\rangle. \tag{11}$$

Hence, we get

$$\langle\mathbf{r}|\mathbf{r}'\rangle = \langle x|x'\rangle\langle y|y'\rangle\langle z|z'\rangle = \delta(x-x')\delta(y-y')\delta(z-z') = \delta(\mathbf{r}-\mathbf{r}') \tag{12}$$

and

$$\langle\mathbf{r}|\mathbf{k}\rangle = \langle x|k_x\rangle\langle y|k_y\rangle\langle z|k_z\rangle = \frac{1}{\sqrt{8\pi^3}}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{13}$$

The $|\mathbf{k}\rangle$ form of course again a complete space, since

$$\int \mathrm{d}\mathbf{k}|\mathbf{k}\rangle\langle\mathbf{k}| = \int \mathrm{d}k_x|k_x\rangle\langle k_x| \int \mathrm{d}k_y|k_y\rangle\langle k_y| \int \mathrm{d}k_z|k_z\rangle\langle k_z| = \hat{1}\hat{1}\hat{1} = \hat{1}. \tag{14}$$

The three dimensional $|\mathbf{k}\rangle$ are of course eigenfunctions of the momentum operator in all directions

$$\hat{p}_\alpha|\mathbf{k}\rangle = \hbar k_\alpha|\mathbf{k}\rangle \;\; \alpha = x,y,z \quad \Rightarrow \quad \hat{\mathbf{p}}|\mathbf{k}\rangle = \hbar\mathbf{k}|\mathbf{k}\rangle. \tag{15}$$

In spherical coordinates (k,ϕ_k,θ_k) the volume element $\mathrm{d}\mathbf{k} = k^2\mathrm{d}k\mathrm{d}\hat{\mathbf{k}}$, and since

$$E_k = \frac{\hbar^2k^2}{2\mu} \Rightarrow \mathrm{d}E_k = \left(\frac{\mathrm{d}E_k}{\mathrm{d}k}\right)\mathrm{d}k = \frac{\hbar^2k}{\mu}\mathrm{d}k \Rightarrow k^2\mathrm{d}k = \frac{\mu k}{\hbar^2}\mathrm{d}E_k, \tag{16}$$

the completeness condition reads

$$\int \mathrm{d}E_k \mathrm{d}\hat{\mathbf{k}} \frac{\mu k}{\hbar^2} |\mathbf{k}\rangle\langle\mathbf{k}| = \hat{1}. \tag{17}$$

Thus, if we define

$$|\hat{\mathbf{k}}E_k\rangle \equiv \sqrt{\frac{\mu k}{\hbar^2}} |\mathbf{k}\rangle, \tag{18}$$

we have an energy normalized function, for which

$$\int \mathrm{d}E_k \mathrm{d}\hat{\mathbf{k}} |\hat{\mathbf{k}}E_k\rangle\langle\hat{\mathbf{k}}E_k| = \hat{1}, \tag{19}$$

and

$$\begin{aligned} \langle\hat{\mathbf{k}}E_k|\hat{\mathbf{k}}'E_k'\rangle &= \frac{\mu\sqrt{kk'}}{\hbar^2}\langle\mathbf{k}|\mathbf{k}'\rangle = \frac{\mu\sqrt{kk'}}{\hbar^2}\delta(\mathbf{k}-\mathbf{k}') \\ &= \frac{\mu\sqrt{kk'}}{\hbar^2}\frac{1}{k^2}\delta(k-k')\delta(\hat{\mathbf{k}}-\hat{\mathbf{k}}') \\ &= \frac{\mu\sqrt{kk'}}{\hbar^2 k^2} 2k'\delta(k^2-k'^2)\delta(\hat{\mathbf{k}}-\hat{\mathbf{k}}') \\ &= \frac{k'\sqrt{k'}}{k\sqrt{k}}\delta(E_k-E_k')\delta(\hat{\mathbf{k}}-\hat{\mathbf{k}}') \end{aligned} \tag{20}$$

Of course, the energy normalized functions are also eigenfunctions of the three dimensional momentum operator:

$$\hat{\mathbf{p}}|\hat{\mathbf{k}}E_k\rangle = \hbar\mathbf{k}|\hat{\mathbf{k}}E_k\rangle. \tag{21}$$

2 Scattering wave function

Consider a time-dependent Hamiltonian

$$\hat{H}(t) = \hat{T} + \hat{V}(t), \tag{22}$$

where the time dependency is caused solely by the pertubation $\hat{V}(t)$. Assume the system is initially in a bound eigenstate of $\hat{T}$:

$$\hat{T}|i\rangle = \hbar\omega_i|i\rangle. \tag{23}$$

The energy normalized continuum functions $|\hat{\mathbf{k}}E_k\rangle$ are also eigenfunctions of $\hat{T}$, since

$$\hat{T}|\hat{\mathbf{k}}E_k\rangle = \frac{\hat{p}^2}{2\mu}|\hat{\mathbf{k}}E_k\rangle = \frac{\hbar^2 k^2}{2\mu}|\hat{\mathbf{k}}E_k\rangle \equiv \hbar\omega_k|\hat{\mathbf{k}}E_k\rangle. \tag{24}$$

Define the time-dependent kets $|i;t\rangle$ and $|\hat{\mathbf{k}}E_k;t\rangle$ by the time evolution of $|i\rangle$ and $|\hat{\mathbf{k}}E_k\rangle$:

$$|i;t\rangle \equiv e^{-i\omega_i t}|i\rangle \quad \text{and} \quad |\hat{\mathbf{k}}E_k;t\rangle \equiv e^{-i\omega_k t}|\hat{\mathbf{k}}E_k\rangle \tag{25}$$

The total wave function $|\psi(t)\rangle$ must obey the Schrödinger equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle. \tag{26}$$

Define the new kets $|\widetilde{\psi}(t)\rangle$ by propagating the total wave function back in time with $\hat{T}$:

$$|\widetilde{\psi}(t)\rangle \equiv e^{i\hat{T}t/\hbar}|\psi(t)\rangle. \tag{27}$$

Then

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\widetilde{\psi}(t)\rangle = e^{i\hat{T}t/\hbar}(-\hat{T})|\psi(t)\rangle + e^{i\hat{T}t/\hbar}\hat{H}(t)|\psi(t)\rangle = e^{i\hat{T}t/\hbar}\hat{V}(t)e^{-i\hat{T}t/\hbar}|\widetilde{\psi}(t)\rangle \tag{28}$$

Integrating both sides from 0 to t gives

$$i\hbar(|\widetilde{\psi}(t)\rangle - |\widetilde{\psi}(0)\rangle) = \int_0^t e^{i\hat{T}t'/\hbar}\hat{V}(t')e^{-i\hat{T}t'/\hbar}|\widetilde{\psi}(t')\rangle\mathrm{d}t', \tag{29}$$

and since $|\widetilde{\psi}(0)\rangle) = |\psi(0)\rangle = |i\rangle$

$$|\widetilde{\psi}(t)\rangle = |i\rangle - \frac{i}{\hbar}\int_0^t e^{i\hat{T}t'/\hbar}\hat{V}(t')e^{-i\hat{T}t'/\hbar}|\widetilde{\psi}(t')\rangle\mathrm{d}t'. \tag{30}$$

Using first order pertubation theory, the ket $|\widetilde{\psi}(t')\rangle$ is replaced by its initial value $|i\rangle$, so that the scattering part of the wave function is given by

$$|\psi^{(1)}(t)\rangle = e^{-i\hat{T}t/\hbar}\int_0^t e^{i\hat{T}t'/\hbar}\hat{V}(t')e^{-i\hat{T}t'/\hbar}|i\rangle\mathrm{d}t' \tag{31}$$

We can expand the scattering wave function in terms of the energy normalized functions $|\hat{\mathbf{k}}E_k;t\rangle$ as

$$|\psi^{(1)}(t)\rangle = \int \mathrm{d}E_k\mathrm{d}\hat{\mathbf{k}}f_{\hat{\mathbf{k}}E_k}(t)|\hat{\mathbf{k}}E_k;t\rangle, \tag{32}$$

and since

$$\begin{aligned}\langle\hat{\mathbf{k}}E_k;t|\psi^{(1)}(t)\rangle &= \int \mathrm{d}E'_k\mathrm{d}\hat{\mathbf{k}}'f_{\hat{\mathbf{k}}'E'_k}(t)\langle\hat{\mathbf{k}}E_k;t|\hat{\mathbf{k}}'E'_k;t\rangle \\ &= \int \mathrm{d}E'_k\mathrm{d}\hat{\mathbf{k}}'f_{\hat{\mathbf{k}}'E'_k}(t)\frac{k'\sqrt{k'}}{k\sqrt{k}}\delta(E_k - E'_k)\delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = f_{\hat{\mathbf{k}}E_k}(t),\end{aligned} \tag{33}$$

the expansion coefficents are given by

$$\begin{aligned} f_{\hat{\mathbf{k}}E_k}(t) &= -\frac{i}{\hbar}\int_0^t \langle \hat{\mathbf{k}}E_k;t|e^{-i\hat{T}t/\hbar}e^{i\hat{T}t'/\hbar}\hat{V}(t')e^{-i\hat{T}t'/\hbar}i\rangle \mathrm{d}t' \\ &= \int_0^t \langle e^{-i\omega_k t}\hat{\mathbf{k}}E_k|e^{-i\hat{T}t/\hbar}e^{i\hat{T}t'/\hbar}\hat{V}(t')e^{-i\omega_i t'}i\rangle \mathrm{d}t' \\ &= \int_0^t \langle e^{-i\hat{T}t'/\hbar}e^{i(\hat{T}-\hbar\omega_k)t/\hbar}\hat{\mathbf{k}}E_k|\hat{V}(t')e^{-i\omega_i t'}i\rangle \mathrm{d}t' \\ &= \int_0^t e^{i(\omega_k-\omega_i)t'}\langle \hat{\mathbf{k}}E_k|\hat{V}(t')i\rangle \mathrm{d}t'. \end{aligned} \tag{34}$$

In the electric dipole approximation, the perturbation is given by

$$\hat{V}(t) = E_0\mathbf{e}\cdot\hat{\boldsymbol{\mu}}\cos\omega t = \frac{E_0}{2}\mathbf{e}\cdot\hat{\boldsymbol{\mu}}(e^{i\omega t}+e^{-i\omega t}), \tag{35}$$

so that the expansion coefficients become

$$\begin{aligned} f_{\hat{\mathbf{k}}E_k}(t) &= -\frac{iE_0}{2\hbar}\langle \hat{\mathbf{k}}E_k|\mathbf{e}\cdot\hat{\boldsymbol{\mu}}i\rangle \int_0^t e^{i(\omega_{ki}+\omega)t'} + e^{i(\omega_{ki}-\omega)t'}\mathrm{d}t' \\ &= -\frac{E_0}{2\hbar}\langle \hat{\mathbf{k}}E_k|\mathbf{e}\cdot\hat{\boldsymbol{\mu}}i\rangle \left[\frac{e^{i(\omega_{ki}+\omega)t}-1}{\omega_{ki}+\omega} + \frac{e^{i(\omega_{ki}-\omega)t}-1}{\omega_{ki}-\omega}\right]. \end{aligned} \tag{36}$$

Applying the rotating wave approximation, only the second (resonant) term contributes, so that

$$\begin{aligned} f_{\hat{\mathbf{k}}E_k}(t) &= -\frac{E_0}{2\hbar}\langle \hat{\mathbf{k}}E_k|\mathbf{e}\cdot\hat{\boldsymbol{\mu}}i\rangle \frac{e^{i(\omega_{ki}-\omega)t}-1}{\omega_{ki}-\omega} \\ &= \frac{E_0 t}{2i\hbar}\langle \hat{\mathbf{k}}E_k|\mathbf{e}\cdot\hat{\boldsymbol{\mu}}i\rangle \frac{e^{i(\omega_{ki}-\omega)t/2}-e^{-i(\omega_{ki}-\omega)t/2}}{2i(\omega_{ki}-\omega)t/2}e^{i(\omega_{ki}-\omega)t/2} \\ &= \frac{E_0 t}{2i\hbar}\langle \hat{\mathbf{k}}E_k|\mathbf{e}\cdot\hat{\boldsymbol{\mu}}i\rangle \operatorname{sinc}[(\omega_{ki}-\omega)t/2]e^{i(\omega_{ki}-\omega)t/2}. \end{aligned} \tag{37}$$

3 Photodissociation cross section

The transition probability per energy interval $P_{\hat{\mathbf{k}}E_k}(t)$ for a transition from the initial state to a scattering state $|\hat{\mathbf{k}}E_k;t\rangle$ is given by

$$\begin{aligned} P_{\hat{\mathbf{k}}E_k}(t) &= |\langle \hat{\mathbf{k}}E_k;t|\psi(t)\rangle|^2 = |f_{\hat{\mathbf{k}}E_k}(t)|^2 \\ &= \frac{E_0^2 t^2}{4\hbar^2}|\langle \hat{\mathbf{k}}E_k|\mathbf{e}\cdot\hat{\boldsymbol{\mu}}i\rangle|^2 \operatorname{sinc}^2[(\omega_{ki}-\omega)t/2]. \end{aligned} \tag{38}$$

Using the following representation for the δ function

$$\delta(x) = \lim_{t\to\infty}\frac{t}{\pi}\operatorname{sinc}^2[xt], \tag{39}$$

we get that the transition probability for large enough t is given by

$$P_{\hat{\mathbf{k}}E_k}(t) = \frac{\pi E_0^2 t}{2\hbar^2} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2 \delta(\omega_{ki} - \omega). \tag{40}$$

The transition rate $k_{\hat{\mathbf{k}}E_k}$ is the time derivative of the transition probability, so that

$$k_{\hat{\mathbf{k}}E_k} = \frac{\pi E_0^2}{2\hbar^2} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2 \delta(\omega_{ki} - \omega). \tag{41}$$

Note that within this approximate model the transition rate is constant in time.

Consider a thin slice of area A and width $\mathrm{d}z$ in the sample. The molecule density is ρ, so that the number of molecules in the slice is $\rho A \mathrm{d}z$. The energy absorption per dissociating molecule is $\hbar\omega_{ki}$, and the number of absorbing molecules per time slice $\mathrm{d}t$ is $k_{\hat{\mathbf{k}}E_k}\mathrm{d}t$, so that the total energy change $\mathrm{d}S$ in the slice is given by

$$\mathrm{d}S = -\rho A \mathrm{d}z k_{\hat{\mathbf{k}}E_k} \mathrm{d}t \hbar\omega_{ki}. \tag{42}$$

By definition this is equal to the the volume of the slice, times the change in energy density $\mathrm{d}W$, so that

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -\rho \frac{\pi E_0^2 \omega_{ki}}{2\hbar} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2 \delta(\omega_{ki} - \omega), \tag{43}$$

and since $W = E_0^2/2\epsilon_o$ this is

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -\rho \frac{\pi W \omega_{ki}}{\hbar\epsilon_0} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2 \delta(\omega_{ki} - \omega). \tag{44}$$

Using the relations

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\mathrm{d}I}{\mathrm{d}z} \quad \text{and} \quad W = \frac{I}{c}, \tag{45}$$

where c is the speed of the moving photon, we get

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -\rho \frac{\pi \omega_{ki}}{\hbar\epsilon_0 c} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2 \delta(\omega_{ki} - \omega) I \tag{46}$$

so that the photodissociation cross section $\sigma(\omega)$ would be

$$\sigma(\omega) = \frac{\pi \omega_{ki}}{\hbar\epsilon_0 c} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2 \delta(\omega_{ki} - \omega). \tag{47}$$

However, since excitation with an exact energy difference $\hbar\omega$ is impossible, we integrate over E_k to get the partial photodissociation cross section for a transition in direction $\hat{\mathbf{k}}$:

$$\sigma(\omega) = \frac{\pi \omega}{\epsilon_0 c} |\langle \hat{\mathbf{k}} E_k | \mathbf{e} \cdot \hat{\boldsymbol{\mu}} i \rangle|^2. \tag{48}$$