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Fermi's Golden Rule

Ronald Lovett
Washington University in St. Louis

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References

Quantum Mechanics, E. Merzbacher, Chapter 18 (Chem QC174.1 M36).

A bound state coupled to unbound states

Consider a system that – at a certain level of approximation – consists of a single bound (localized) state ψ of energy $\approx \hbar\nu$ and a 'ladder' of unbound (non-localized) states ϕ_n of energy $\approx n\hbar\omega,\ n = 0, \pm 1, \pm 2, \ldots$ (see the Fig. 1 below). The energy step $\hbar\omega$ in the ladder is small. The functions $\psi, \{\phi_n\}$ form an orthonormal basis set for this system.

The functions $\psi, \{\phi_n\}$ only *approximate* energy eigenfunctions of the system. Actually there is a small "coupling" between the ψ and ϕ_n states. If the 'coupling' between the bound and unbound states is independent of n, then the effect of the real Hamiltonian on these functions is

$$\hat{H}\psi = \hbar\nu\,\psi + V \sum_{n=-\infty}^{\infty} \phi_n, \tag{1}$$

$$\hat{H}\phi_n = n\hbar\omega\,\phi_n + V^*\psi, \qquad \text{all } n. \tag{2}$$

Using $\psi, \{\phi_n\}$ as a basis set, the actual state of the system can be represented

$$\Psi(t) = a(t)\,e^{-i\nu t}\,\psi + \sum_n c_n(t)\,e^{-in\omega t}\,\phi_n \tag{3}$$

with the time evolution of $a(t), \{c_n(t)\}$ fixed by

$$\dot{a}(t) = \frac{V^*}{i\hbar} \sum_n c_n(t)\,e^{i(\nu - n\omega)t} \tag{4}$$

$$\dot{c}_n(t) = \frac{V}{i\hbar}\,a(t)\,e^{-i(\nu - n\omega)t}. \tag{5}$$

Decay out of $\Psi(0) = \psi$

If the system starts at time $t = 0$ in state ψ, then $a(t)$, $\{c_n(t)\}$ are fixed by

$$\begin{aligned}
\dot{a}(t) &= -\frac{|V|^2}{\hbar^2} \sum_n e^{i(\nu - n\omega)t} \int_0^t d\tau\, e^{-i(\nu - n\omega)\tau}\, a(\tau), \\
a(0) &= 1, \\
c_n(t) &= -\frac{iV}{\hbar} \int_0^t d\tau\, e^{-i(\nu - n\omega)\tau}\, a(\tau).
\end{aligned} \tag{6}$$

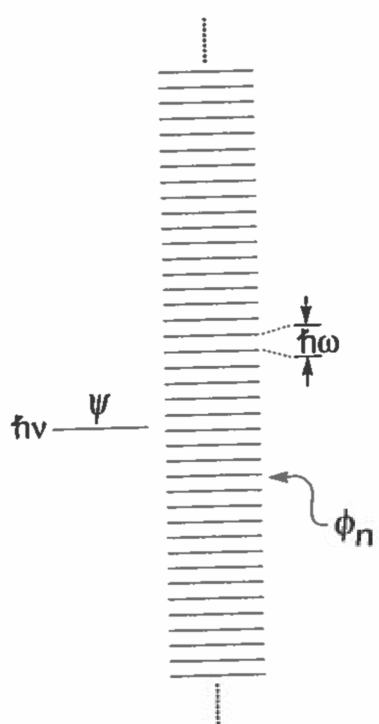
Since

$$S(x) = \lim_{N\to\infty} \frac{1}{2\pi} \sum_{n=-N}^{N} e^{inx} = \sum_{k=-\infty}^{\infty} \delta(x - 2\pi k),$$

the differential-integral equation for $a(t)$ can be written

$$\begin{aligned}
\dot{a}(t) &= -\frac{2\pi|V|^2}{\hbar^2} \int_o^t d\tau a(\tau) e^{i\nu(t-\tau)} S(\omega(t-\tau)) \\
&= -\frac{2\pi|V|^2}{\hbar^2\omega} \Big\{ \frac{1}{2} a(t) + \sum_{1 \le k < \omega t/2\pi} e^{2\pi i\nu k/\omega} a(t - \frac{2\pi k}{\omega}) \Big\}.
\end{aligned} \tag{7}$$

Fig. 1 The level diagram for this system



Problem Set #7

1. Assume that ψ, $\{\phi_n\}$ form an orthonormal basis set. Show that, given (1), the coefficient of ψ in (2) *had* to be V^*. What will $\Psi(t)$ look like if $V = 0$? Give a physical interpretation for the time evolution of $|a(t)|^2$, $\{|c_n(t)|^2\}$. Show that equations (1) – (3) $\Longrightarrow$ (4) and (5).

2. By what sequence of steps can $\Psi(t)$ be determined from the system of equations in (6)?

3. Suppose that (in atomic units),

$$V = 0.1$$

$$\omega = 0.2\,\pi$$

$$\nu = 5$$

Make plots of $|a(t)|^2$ and $\log_{10}|a(t)|^2$ vs. t for $0 \le t \le 6\pi/\omega$. Use animation to show how the function of $n\hbar\omega$, $|c_n(t)|^2$, varies with time for $0 \le t \le 2\pi/\omega$.

Log[10, x] will give $log_{10}(x)$. The proceedure DSolve[f' [t] + c f [t] == E^t,f [t],t] will return the solution to $f'(t) + cf(t) = e^t$ (writing C[1] for the constant of integration). DSolve[{f' [t] + c f [t] == E^t, f [0]==1},f [t],t] will return the solution to $f'(t) + cf(t) = e^t$ which satisfies the boundary condition $f(0) = 1$.

4. Which states in the 'ladder' contribute to the decay out of ψ? How important is the assumption that the coupling is independent of n? If $\rho = 1/\hbar\omega$ is the *density of states* in the 'ladder', express the decay rate for the occupancy of ψ in terms of ρ, V and physical constants.