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Fermi's Golden Rule

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Fermi's Golden Rule

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 ψ , $\{\phi_n\}$ form an orthonormal basis set for this system.

The functions ψ , $\{\phi_n\}$ 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

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

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

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

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

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

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

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

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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

$$\dot{a}(t) = -\frac{|V|^2}{\hbar^2} \sum_n e^{i(\nu - n\omega)t} \int_0^t d\tau \, e^{-i(\nu - n\omega)\tau} \, a(\tau),$$

$$a(0) = 1,$$

$$c_n(t) = -\frac{iV}{\hbar} \int_0^t d\tau \, e^{-i(\nu - n\omega)\tau} \, a(\tau).$$
(6)

Since

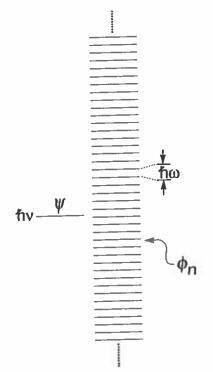
$$S(x) = \lim_{N \to \infty} \frac{1}{2\pi} \sum_{n=-N}^{N} e^{inx} = \sum_{k=-\infty}^{\infty} \delta(x - 2\pi k),$$

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

$$\dot{a}(t) = -\frac{2\pi |V|^2}{\hbar^2} \int_0^t d\tau a(\tau) e^{i\nu(t-\tau)} S(\omega(t-\tau))$$

$$= -\frac{2\pi |V|^2}{\hbar^2 \omega} \left\{ \frac{1}{2} a(t) + \sum_{1 \le k < \omega t/2\pi} e^{2\pi i\nu k/\omega} a(t - \frac{2\pi k}{\omega}) \right\}.$$
 (7)

Fig. 1 The level diagram for this system



due 11 March 2013 Fermi's Golden Rule

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] + cf[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] + cf[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.

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