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Transition Probability due to Random Perturbations

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The subject of transition probabilities induced by random perturbations is treated. The expression for average transition rates between two energy levels is derived for the general case when the frequency spectrum of the perturbation and the distribution of the energy levels have comparable widths. The general expression takes an especially simple form for the special cases where the frequency bandwidth of the perturbation Hamiltonian is either much larger or much smaller than that of the energy level distribution. The formulas are applied, by way of illustration, to a number of physical problems.

INTRODUCTION

THIS paper attempts to present, from a unified point of view, the effect of random perturbations on transitions between two energy levels. It is shown that the degree of randomness of a given perturbation is characterized by Ω_1/Ω_0 , the ratio of the spectral bandwidth of the perturbation to the width of the energy level distribution. The theory has a strong bearing on the case of motional narrowing of resonance lines, which has been studied in detail by Bloembergen *et al.*¹ Some of the features of the motional narrowing theory are rederived as a special case.

THEORY

The starting point for first-order time-dependent perturbation theory is usually the equation²

$$a_k(t) = (i\hbar)^{-1} \int_0^t H_{km}'(t') e^{i\omega_{km}t'} dt', \quad (1)$$

where $|a_k(t)|^2$ is the probability of finding the system at time t in an energy state E_k , if at $t=0$ when the perturbation is turned on it is known to possess the energy E_m . $H_{km}'(t)$ is the matrix element of the perturbation Hamiltonian connecting the two states, and $\omega_{km} = (E_k - E_m)/\hbar$.

If E_k and E_m are not sharp well-defined energy levels, we must introduce a distribution function $\rho(\omega_{km})$, where $\rho(\omega)d\omega = g(E)dE$ is the probability of finding the energy difference ω_{km} within the range $\omega \pm \frac{1}{2}d\omega$. The total transition probability per unit time to this group of

states is

$$w(t) = \frac{d}{dt} \sum_k |a_k(t)|^2 \rightarrow \frac{d}{dt} \int_{-\infty}^{\infty} \rho(\omega_{km}) d\omega_{km} |a_k(t)|^2, \quad (2)$$

where

$$\int_{-\infty}^{\infty} \rho(\omega_{km}) d\omega_{km} = 1.$$

Consider now a case in which the perturbation $H_{km}'(t)$ is a random stationary process. (An example would be the effects of thermal vibrations of a crystal lattice at the site of a single atom.) From (1) it follows that there will be statistical fluctuations in w so that we may define an average transition probability per unit time as

$$\begin{aligned} \langle w \rangle &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T w(t) dt \\ &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \frac{d}{dt} \int_{-\infty}^{\infty} \rho(\omega_{km}) d\omega_{km} |a_k(t)|^2, \end{aligned} \quad (3)$$

where (2) was used. This reduces to

$$\langle w \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-\infty}^{\infty} \rho(\omega_{km}) d\omega_{km} |a_k(T)|^2. \quad (4)$$

Utilizing Eq. (1) we note that

$$\begin{aligned} \frac{|a_k(T)|^2}{T} &= \frac{1}{\hbar^2 T} \int_0^T \int_0^T H_{km}'(t') \\ &\quad \times H_{km}'^*(t'') e^{i\omega_{km}(t'-t'')} dt' dt''. \end{aligned}$$

By changing variables so that $t'' - t' = \tau$ and $t' = t$, we

¹ N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).

² See, for instance, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 197.

may show that this reduces to

$$\frac{|a_k(T)|^2}{T} = \frac{1}{\hbar^2 T} \left\{ \int_{-T}^0 d\tau e^{-i\omega_{km}\tau} \int_{-\tau}^T H_{km}'(t) H_{km}'^*(t+\tau) dt \right. \\ \left. + \int_0^T d\tau e^{-i\omega_{km}\tau} \times \int_0^{T-\tau} H_{km}'(t) H_{km}'^*(t+\tau) dt \right\}. \quad (5)$$

Now let the spectral density function be

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} R(\tau) e^{-i\omega\tau} d\tau, \quad (6)$$

where $R(\tau)$ is the auto-correlation function of the perturbation Hamiltonian defined by

$$R(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T H_{km}'(t) H_{km}'^*(t+\tau) dt. \quad (7)$$

Utilizing (6) and (7), Eq. (5) becomes as $T \rightarrow \infty$:

$$\lim_{T \rightarrow \infty} \frac{|a_k(T)|^2}{T} = \frac{2\pi}{\hbar^2} P(\omega).$$

If now we interchange the limit and integral order in (4), we find

$$\langle w \rangle = \frac{2\pi}{\hbar^2} \int_{-\infty}^{\infty} \rho(\omega) P(\omega) d\omega, \quad (8)$$

for the average total transition probability per second for random perturbations. This is our main starting point.

The spectral distribution function $P(\omega)$ and the distribution function for the energies $\rho(\omega)$ may have comparable widths or widths differing by orders of magnitude. We take these cases up one by one.

Case 1

If $\rho(\omega)$ is many times wider than $P(\omega)$, we may replace $P(\omega)$ in Eq. (8) by $\langle |H_{km}'(t)|^2 \rangle \delta(\omega - \omega_0)$, where ω_0 is the center frequency of the spectral distribution function $P(\omega)$. This leads to

$$\langle w \rangle = (2\pi/\hbar^2) \rho(\omega_0) \langle |H_{km}'(t)|^2 \rangle \\ = (2\pi/\hbar) g(E) \langle |H_{km}'(t)|^2 \rangle, \quad (9)$$

since $g(E)dE = \rho(\omega)d\omega$. This is Fermi's "Golden Rule No. 2" and is the form most often encountered, since it corresponds, in the limit, to the case of harmonic perturbation.

Case 2

If $\rho(\omega)$ is very narrow compared with $P(\omega)$, Eq. (8) becomes

$$\langle w \rangle = (2\pi/\hbar^2) P(\omega_0), \quad (10)$$

where ω_0 is the center frequency of the narrow energy level distribution $\rho(\omega) = \delta(\omega - \omega_0)$. The application of Eq. (10) is illustrated by the following example, viz., the radiation lifetime of a spin in a cavity.

Imagine an isolated spin with $S = \frac{1}{2}$ placed inside a microwave cavity and subjected to a steady magnetic field H_0 . The problem is to calculate the lifetime of the spin in an excited state ($S = \frac{1}{2}$) before undergoing a spontaneous transition to the state $S = -\frac{1}{2}$. If the dimensions of the cavity are comparable to the wavelength corresponding to the resonance frequency of the spin, $\omega = \gamma H_0$, the spontaneous emission lifetime is much smaller than the free-space lifetime. This is due to the increased radiation density of the "zero-field vibrations."¹

The perturbation Hamiltonian is

$$H'(t) = \frac{1}{2} \gamma \hbar S^+ h_1(t), \quad (11)$$

where $S^+ = S_x + iS_y$, and $h_1(t)$ is the effective rf field due to the zero-field vibrations of the single cavity mode "on speaking terms" with the spin. Since

$$R(0) = \int_{-\infty}^{\infty} P(\omega) d\omega = \langle |H_{km}'(t)|^2 \rangle, \quad (12)$$

we have by (11)

$$\int_{-\infty}^{\infty} P(\omega) d\omega = \frac{\gamma^2 \hbar^2}{4} \langle h_1^2(t) \rangle = \frac{\pi \omega_0 P(\omega_0)}{2Q}, \quad (13)$$

where we assumed the energy distribution in the cavity to be Lorentzian with a width ω_0/Q , Q being the loaded quality factor of the cavity. We also made use of the matrix elements $\langle \frac{1}{2} | S^+ | -\frac{1}{2} \rangle = 1$. The rf field $h_1(t)$ is calculated by assuming the total stored energy in the cavity to be equal to the zero-field vibration energy $\hbar\omega/2$, which yields

$$\langle [h_1(t)]^2 \rangle = 2\pi \hbar \omega / V_c, \quad (14)$$

where V_c is the volume of the cavity. Equations (13) and (14) yields

$$P(\omega_0) = \pi^2 \hbar^3 Q / V_c, \quad (15)$$

which when substituted in Eq. (10) leads to a lifetime τ ,

$$\tau = \langle w \rangle^{-1} = V_c / (2\pi \gamma^2 \hbar Q). \quad (16)$$

This is the desired result.³

Case 3

If neither of the extreme conditions treated as cases 1 and 2 prevails, i.e., when $\rho(\omega)$ and $P(\omega)$ have comparable frequency bandwidth (which overlap), the exact forms of $\rho(\omega)$ and $P(\omega)$ have to be known before the integration in Eq. (8) for the average transition probability rate $\langle w \rangle$ can be carried out. The exact form as-

³ We did not specify the placement of the sample or the resonance mode utilized. This could change the numerical factor in Eq. (16).

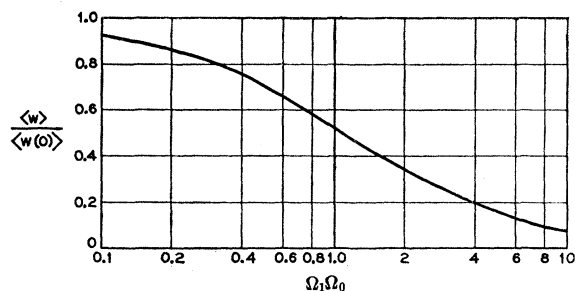


FIG. 1. Normalized transition probability $\langle w \rangle / \langle w(0) \rangle$ as a function of the ratio Ω_1 / Ω_0 , which is the ratio of the width of the perturbation Hamiltonian spectral function to that of the energy-level distribution.

sumed will depend on the problem treated. One reasonable assumption which may obtain in many cases is to take $P(\omega)$ as a Lorentzian function, with width Ω_1 , centered, about ω_0 :

$$P(\omega) = \frac{\langle |H_{km}'(t)|^2 \rangle}{\pi} \frac{\Omega_1}{\Omega_1^2 + (\omega - \omega_0)^2}, \quad (17)$$

and to assume that the energy level distribution is given by a Gaussian of width Ω_0 centered about ω_0 .

$$\rho(\omega) = [\Omega_0(2\pi)^{1/2}]^{-1} \exp[-(\omega - \omega_0)^2 / 2\Omega_0^2]. \quad (18)$$

Note that $P(\omega)$ satisfies Eq. (12) and that $\rho(\omega)$ is normalized to unity. Substituting Eqs. (17) and (18) in Eq. (8) and performing the integration leads to

$$\langle w \rangle = (2\pi)^{1/2} \frac{\langle |H_{km}(t)|^2 \rangle}{\hbar^2 \Omega_0} \exp\left[\frac{1}{2}(\Omega_1/\Omega_0)^2\right] \operatorname{erfc}\left(\frac{\Omega_1}{\sqrt{2}\Omega_0}\right), \quad (19)$$

where

$$\operatorname{erfc}x = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt.$$

We may find it advantageous to define

$$\langle w(0) \rangle = \langle w \rangle_{\Omega_1/\Omega_0=0} = (2\pi)^{1/2} \langle |H_{km}'(t)|^2 \rangle / \hbar^2 \Omega_0, \quad (20)$$

and then rewrite Eq. (19) in a form in which $\langle w \rangle$ is a function of Ω_1/Ω_0

$$\langle w \rangle = \langle w(0) \rangle \exp\left[\frac{1}{2}(\Omega_1/\Omega_0)^2\right] \operatorname{erfc}\left(\frac{\Omega_1}{\sqrt{2}\Omega_0}\right). \quad (21)$$

Note that $\langle w(0) \rangle$ is the same transition probability considered in case 1. The equality of Eq. (9) and Eq. (20)

can be shown by the use of Eq. (18). $\langle w(0) \rangle$ is thus the average transition probability rate for the case of harmonic perturbation. Equation (21) shows how $\langle w \rangle$ decreases as the perturbation becomes less harmonic, i.e., as the bandwidth Ω_1 of the spectral density function starts increasing. It also provides us with a criterion for the harmonicity of the perturbation, $(\Omega_1/\Omega_0)^2 \ll 1$. The function $\langle w \rangle / \langle w(0) \rangle$ is plotted in Fig. 1 with Ω_1/Ω_0 as the abscissa. In conclusion we will illustrate the application of Eq. (21) in a specific example, viz., motional narrowing in nuclear magnetic resonance.

The observed linewidth $\Delta\omega$, measured in nuclear magnetic resonance (NMR) experiments in liquids, narrows with increasing temperature. This observation has been explained by Bloembergen, Purcell, and Pound⁴ (B.P.P.). They showed that the observed linewidth is related to the time τ between mutual spin flips by $\Delta\omega = \tau^{-1}$. At high temperatures the center of gravity of the spectral function of the dipolar perturbation is shifted toward higher frequencies which, by conservation of energy, are less effective in flipping spins. This leads to a longer τ or, equivalently, to a narrower line.

Although our theory is capable of yielding quantitative information we shall merely illustrate how the ratio $\Delta\omega / [\Delta\omega]_{T=0}$ is derived. The spectral density function used by B.P.P. is

$$P(\omega) = \frac{\langle |H_{km}'(t)|^2 \rangle}{\pi} \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \quad (22)$$

which implies the autocorrelation function

$$R(\tau) = \langle |H_{km}'(t)|^2 \rangle e^{-|\tau|/\tau_c}, \quad (23)$$

where τ_c is the "coherence" time of $H_{km}'(t)$.

A comparison of Eq. (22) with Eq. (17) shows that with the substitution

$$\omega_0 = 0, \quad \Omega_1 = \tau_c^{-1},$$

and bearing in mind that $\langle w \rangle = 1/\tau = \Delta\omega$, Eq. (21) can be applied directly to this example, i.e.,

$$\Delta\omega / (\Delta\omega)_{T=0} = \exp\left[\frac{1}{2}(\Omega_1/\Omega_0)^2\right] \operatorname{erfc}(\Omega_1/\sqrt{2}\Omega_0).$$

$\Omega_1 = \tau_c^{-1} \propto T$, so that in Fig. 1, the abscissa is proportional to temperature and the graph shows the narrowing of the NMR absorption line with increasing temperature.

⁴ N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).