

Parametric dipolar resonance

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Abstract

A new type of resonance, which we call parametric resonance, is described, concerning the rotation (precession) of electric dipoles about fixed (quenched) positions determined by internal electric fields. Most likely, it is expected to occur in polar (paraelectric) solids and liquids. The resonance appear under the action of an external radio-frequency field of frequency $\omega = 2\omega_0$, where, for typical situations, ω_0 is a frequency of the order $\geq 10^{12} s^{-1}$.

The interaction of the electromagnetic field with matter developed along the years in valuable techniques of investigating the quantum behaviour of material samples; these techniques are known as (various) spectroscopies. First, the Thomson scattering of radiation by material dipoles evolved in sophisticated scattering techniques, like Raman or Brillouin scattering in condensed matter. Next, the resonant Rayleigh scattering (fluorescence scattering) led to optical spectroscopy, which unleashed the birth of Quantum Mechanics. Spectroscopies related to electronic transitions as well as molecular vibrations and rotations have been gradually developed, associated with the resonant response of electric dipoles. At the beginning of the second half of the 20th century the atomic, molecular and nuclear magnetic moments have been brought into play, and the famous magnetic resonances (nuclear magnetic resonance, electron spin resonance, paramagnetic resonance, ferromagnetic resonance, nuclear quadrupole resonance, etc) have been established. The solid state and materials physics includes today various spectroscopies, all of them based on the resonance phenomenon, which bring valuable information about the structure of the condensed matter.¹

We describe here a spectroscopy technique, based on the well-known parametric resonance phenomenon, which may appear as new. It applies to electric dipoles (paraelectric matter) coupled to electric fields; the combination of fields consists of a constant, uniform field and a radio-frequency field.

Consider a constant, uniform electric field $\mathbf{E}_0 = E_0(0, 0, 1)$ oriented along the z -axis; the potential energy of an electric dipole $\mathbf{d} = d(\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$ of arbitrary orientation is $U = -dE_0 \cos \theta$. The hamiltonian of rotation in this field is given by

$$H = \frac{1}{2}I(\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta) - dE_0 \cos \theta \quad , \quad (1)$$

where I is the moment of inertia of the dipole, considered as a spherical pendulum (spherical top). The equation of motion

$$I \frac{d}{dt}(\dot{\varphi} \sin^2 \theta) = 0 \quad (2)$$

¹There is a vast literature on the subject, so that any specific reference is both impossible and pointless.

indicates that the component L_z of the angular momentum is conserved, $\dot{\varphi} \sin^2 \theta = L_z/I$; consequently, an effective potential function

$$U_{eff} = \frac{L_z^2}{2I \sin^2 \theta} - dE_0 \cos \theta \quad (3)$$

occurs in the hamiltonian. Consider that the dipole energy dE_0 is much greater than the rotation energy L_z^2/I , which is of the order of the temperature T . For typical value $d = 10^{-18} esu$ and temperature $T = 300K \simeq 4 \times 10^{-14} erg$ this condition requires an electric field $E_0 \gg T/d = 4 \times 10^4 statvolt/cm \simeq 1.6 \times 10^9 V/m$. This is a high electric field, which may appear as an internal field in polar condensed matter. For instance, the electric field created by an electron charge at distance $1 \text{ \AA} = 10^{-8} cm$ is $4.8 \times 10^{-10}/10^{-16} = 4.8 \times 10^6 statvolt/cm$. In this case, the effective potential given by equation (3) has a minimum value for $\theta_0 \simeq (L_z^2/IdE_0)^{1/4} \simeq (T/dE_0)^{1/4} \ll 1$ and it can be expanded in powers of $\delta\theta = \theta - \theta_0$ around this minimum value as

$$U_{eff} \simeq -dE_0 + 2dE_0\delta\theta^2 ; \quad (4)$$

the hamiltonian given by equation (1) becomes

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2\delta\theta^2 - dE_0 , \quad (5)$$

where $\omega_0 = 2\sqrt{dE_0/I}$ is sometimes known as Rabi's frequency; according to our condition of high field, we have $\omega_0 \gg 10^{12} s^{-1}$. Therefore, the dipoles are quenched in the internal electric field, where they execute small oscillations. The angle φ rotates freely with the frequency $\dot{\varphi} \simeq L_z/I \sin^2 \theta_0 = \frac{1}{2}\omega_0$ ($\varphi = \frac{1}{2}\omega_0 t$).

Consider an external radio-frequency field $\mathbf{E}(t) = E(t)(\sin \alpha, 0, \cos \alpha)$, $E(t) = E \cos \omega t$, which makes an angle α with the z -axis; its interaction with the dipole is

$$H_{int} = -dE(t)(\sin \alpha \sin \theta \cos \varphi + \cos \alpha \cos \theta) , \quad (6)$$

which provides two relevant interaction hamiltonians:

$$H_{1int} = -\frac{1}{2}dE \sin \alpha \left[\cos(\omega + \frac{1}{2}\omega_0)t + \cos(\omega - \frac{1}{2}\omega_0)t \right] \delta\theta , \quad (7)$$

$$H_{2int} = \frac{1}{2}dE \cos \alpha \cos \omega t \cdot \delta\theta^2 .$$

The interaction hamiltonian H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$ with the resonance frequency $\Omega = \frac{1}{2}\omega_0, \frac{3}{2}\omega_0$. In general, for an interaction $H_{int} = h \cos \omega t$, the rate of transition between two states n and $n+s$, with energies E_n, E_{n+s} is

$$\frac{\partial |c_{n+s,n}|^2}{\partial t} = \frac{\pi}{2\hbar^2} |h_{n+s,n}|^2 \delta(\omega_{n;s} - \omega) \quad (8)$$

in the first order of the perturbation theory, where $\omega_{n;s} = (E_{n+s} - E_n)/\hbar$. For H_{1int} we get

$$\frac{\partial |c_{n+1,n}|^2}{\partial t} = \frac{\pi}{16\hbar I \omega_0} d^2 E^2 (n+1) \sin^2 \alpha \delta(\omega - \Omega) \quad (9)$$

and the absorbed power

$$\begin{aligned} P &= \hbar \Omega \frac{\partial |c_{n+1,n}|^2}{\partial t} = \frac{\pi}{16I\omega_0} d^2 E^2 \Omega (n+1) \sin^2 \alpha \delta(\omega - \Omega) = \\ &= \frac{1}{16I\omega_0} d^2 E^2 \Omega (n+1) \sin^2 \alpha \frac{\alpha}{(\omega - \Omega)^2 + \alpha^2} , \quad \alpha \rightarrow 0^+ , \end{aligned} \quad (10)$$

which is a typical resonance curve. In order to compute the mean power the thermal weights $e^{-\beta\hbar\omega_0 n} / \sum e^{-\beta\hbar\omega_0 n}$ should be introduced, where $\beta = 1/T$ is the inverse of the temperature T ; since $\beta\hbar\omega_0 \gg 1$, only the lowest states n are excited by interaction.

The harmonic-oscillator hamiltonian given by equation (5) and the interaction hamiltonian H_{2int} given by equation (7),

$$H' = H + H_{2int} = \frac{1}{2}I\dot{\theta}^2 + \frac{1}{2}I\omega_0^2(1 + h \cos \omega t)\delta\theta^2, \quad (11)$$

where $h = \frac{E}{2E_0} \cos \alpha$, leads to the classical equation of motion

$$\delta\ddot{\theta} + \omega_0^2(1 + h \cos \omega t)\delta\theta = 0, \quad (12)$$

which is the well-known equation of parametric resonance (Mathieu's equation). As it is well known, beside periodic solutions, the classical equation (12) has also aperiodic solutions, which may grow indefinitely with increasing time; these are (parametrically) resonant solutions, which occur for ω in the neighbourhood of $2\omega_0/n$, $n = 1, 2, 3, \dots$. As we can see immediately, the solutions of equation (12) are determined by the initial conditions $\delta\theta(t=0)$ and $\delta\dot{\theta}(t=0)$ (as for any homogeneous equation). Since fluctuations generate vanishing initial conditions, the classical solutions of equation (12) are vanishing.

The quantum-mechanical dynamics is different. The interaction hamiltonian H_{2int} produces transitions between the harmonic-oscillator states n and $n + 2$ (due to the matrix elements of $\delta\theta^2$). These transitions have frequency $2\omega_0$, in accordance with the classical dynamics. The transition rate is

$$\frac{\partial |c_{n+2,n}|^2}{\partial t} = \frac{\pi\hbar^2}{128}\omega_0^2(n+1)(n+2)\delta(2\omega_0 - \omega) \quad (13)$$

and the absorbed power

$$\begin{aligned} P &= 2\hbar\omega_0 \frac{\partial |c_{n+2,n}|^2}{\partial t} = \frac{\pi\hbar^2}{64}\hbar\omega_0^3(n+1)(n+2)\delta(2\omega_0 - \omega) \simeq \\ &\simeq \frac{\hbar^2}{64}\hbar\omega_0^3(n+1)(n+2)\frac{\alpha}{(2\omega_0 - \omega)^2 + \alpha^2}, \quad \alpha \rightarrow 0^+, \end{aligned} \quad (14)$$

where we may put $n = 0$. The intensity given by equation (14) is small, because, especially, the factor $(E/E_0)^2$.

The parametric resonance disappears for $\alpha = \frac{\pi}{2}$, *i.e.* for the applied radio-frequency field \mathbf{E} at right angle with the quenching field \mathbf{E}_0 . The quenching field may occur, very likely, in (polar) solids; the effect of the parametric resonance depends on the orientation of the crystal; in amorphous samples the absorption is averaged over angles α ($\overline{\cos^2 \alpha} = \frac{1}{3}$). The parameter α in equation (14), which gives the width of the absorption line, is a damping parameter; in solids it originates, very likely, in the dipolar interaction. Since the dipolar interaction is taken mainly in the quenching effect we may expect a small damping, and, consequently, a rather sharp resonance line. In liquids, beside the random distribution of the dipoles (and the average over angle α), we may expect the usual motional narrowing of the line. In gases the quenching field is weak, and the parametric resonance is not expected to occur.

Consider now the opposite case, when the field E_0 is weak, such that $dE_0 \ll L_z^2/I$. The effective potential U_{eff} given by equation (3) has a minimum value for $\theta \simeq \frac{\pi}{2}$ and the hamiltonian given by equation (1) reduces to

$$H \simeq \frac{1}{2}I\dot{\theta}^2 + \frac{1}{2}I\omega_0^2\theta^2, \quad (15)$$

where $\tilde{\theta} = \theta - \frac{\pi}{2}$ and $\omega_0 = L_z/I$; the field E_0 brings only a small correction to the $\pi/2$ -shift in θ , while its contribution to the hamiltonian is a second-order effect. The angle φ moves freely with angular velocity $\dot{\varphi} = \omega_0$. The quantized φ -motion gives $L_z = \hbar m$, m any integer, such that $\omega_0 = \frac{\hbar}{I}m$; the lowest value of this frequency is $\hbar/I \simeq 10^{11} - 10^{12} s^{-1}$ for typical values $I = 10^{-39} - 10^{-38} g \cdot cm^2$ ($10^4 - 10^5$ electronic mass for the molecular mass, $10^{-8} cm$ for the molecular diameter). We can see that the molecular rotations are described by a set of harmonic oscillators with frequencies $\omega_0 = \frac{\hbar}{I}m$, beside the φ -precession. The energy quanta are $\hbar\omega_0 = \frac{\hbar^2}{I}m$, with the lowest value $\frac{\hbar^2}{I} = 1K - 10K$.

The interaction hamiltonian given by equation (6) leads to two relevant interactions

$$H_{1int} = dE \cos \alpha \cos \omega t \cdot \tilde{\theta} , \quad (16)$$

$$H_{2int} = \frac{1}{4}dE \sin \alpha [\cos(\omega + \omega_0)t + \cos(\omega - \omega_0)t] \cdot \tilde{\theta}^2 .$$

The interaction H_{1int} produces transitions between the harmonic-oscillator states n and $n + 1$, with an absorbed power

$$P = \frac{\pi}{4I}d^2E^2(n+1) \cos^2 \alpha \delta(\omega_0 - \omega) . \quad (17)$$

At low temperatures ($\hbar^2/I \gg T$), only a few states contribute to the absorbed power, such that we may put $n = 0$ in equation (17) and sum over a few values of m in $\delta(\omega_0 - \omega) = \delta(\hbar m/I - \omega)$.

The interaction hamiltonian H_{2int} given by equation (16) produces parametric resonance with frequencies $\Omega = \omega_0, 3\omega_0$. The absorbed power is

$$P = \frac{\pi \hbar \Omega}{128I^2\omega_0^2}d^2E^2(n+1)(n+2) \sin^2 \alpha \delta(\Omega - \omega) . \quad (18)$$

It is worth noting that low fields E_0 have, practically, no effect upon the motion, such that we are left with free rotations, with the hamiltonian $H = L^2/2I$, energy levels $E_l = \hbar^2 l(l+1)/2I$, $l = 0, 1, 2, \dots$, and eigenfunctions Y_{lm} (spherical harmonics). The interaction hamiltonian

$$H_{int} = -dE(\sin \alpha \sin \theta \cos \varphi + \cos \alpha \cos \theta) \cos \omega t \quad (19)$$

generates transitions according to the matrix elements of $\sin \theta \cos \varphi$ and $\cos \theta$. Since the rotations are free, we may take E directed along the z -axis, *i.e.* we may put $\alpha = 0$. The matrix elements of $\cos \theta$ are given by

$$(\cos \theta)_{l+1,m;l,m} = C_{lm} = -i \sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}} . \quad (20)$$

We get the absorbed power

$$P = \frac{\pi}{2\hbar}d^2E^2 |C_{lm}|^2 \omega_l \delta(\omega_l - \omega) , \quad (21)$$

where $\omega_l = \hbar(l+1)/I$, $l = 0, 1, 2, \dots$ and the mean absorbed power

$$\bar{P} = \frac{\pi}{2\hbar}d^2E^2 C \sum_{ml} |C_{lm}|^2 e^{-\beta \hbar^2 l(l+1)/2I} \omega_l \delta(\omega_l - \omega) ; \quad (22)$$

C is the normalization constant of the thermal distribution,

$$C \sum_l (2l+1) e^{-\beta \hbar^2 l(l+1)/2I} = 1 . \quad (23)$$

We can see that we have resonances for $\omega = \omega_l$, as in the case of the harmonic-oscillator approximation, and the mean powers are similar in both cases, providing we limit ourselves to the lowest-energy harmonic-oscillator states.

It is worth noting that, although a weak field has practically no influence on the rotation, it has an influence on the statistical behaviour. Indeed, the hamiltonian of rotations

$$H = \frac{1}{2}I(\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta) \quad (24)$$

can also be written as

$$H = \frac{1}{2I}P_\theta^2 + \frac{1}{2I \sin^2 \theta}P_\varphi^2 \quad (25)$$

with the momenta (angular momenta) $P_\theta = I\dot{\theta}$ and $P_\varphi = I\dot{\varphi} \sin^2 \theta$. The classical statistical distribution is

$$\text{const} \cdot dP_\theta dP_\varphi d\theta e^{-\beta P_\theta^2/2I} e^{-\beta P_\varphi^2/2I \sin^2 \theta} , \quad (26)$$

or, integrating over momenta, $\frac{1}{2} \sin \theta d\theta$. In the presence of the field we have the distribution $\simeq \frac{1}{2} \sin \theta d\theta \cdot e^{\beta dE_0}$ (since $\beta dE_0 \ll 1$), which leads, for example, to $\overline{\cos \theta} = \beta dE_0/3$. In the quantum regime, where $T \ll \hbar^2/I$, the interaction $-dE_0 \cos \theta$ brings a second-order contribution to the energy levels $E_l = \hbar^2 l(l+1)/2I$, the matrix elements of $\cos \theta$ are modified to $\widetilde{(\cos \theta)}_{lm,lm}$ in the first-order of the perturbation theory, and the mean value is given by $\overline{\cos \theta} = \sum \widetilde{(\cos \theta)}_{lm,lm} \Delta(\beta E_l) e^{-\beta E_l} / \sum e^{-\beta E_l}$.