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Quasi-classical dynamics: harmonic-oscillator approximation to some quantum-mechanical systems, especially in condensed matter

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Abstract

The Heisenberg time-dependence of quantum-mechanical operators is analyzed within the quasi-classical approximation, where the quanta of action \hbar (Planck's constant) is much smaller than the relevant amounts of mechanical action. It is shown that such a circumstance can provide an approximation by harmonic oscillators to some quantum-mechanical systems, especially in condensed matter. The accuracy of the approximation is assessed by estimating the mean power absorbed from an external time-dependent force; both classically and quantum-mechanically this power exhibits a typical resonance behavior. It is shown that the mean power obtained by means of the harmonic-oscillator approximation is the variation with respect to the quantum number of the total mean power. In most simple cases the difference between the exact result and the approximate one resides in a numerical factor. A few examples are given for simple quantum-mechanical systems (rigid planar and spatial rotator endowed with an electric dipole moment under the action of an electric field), as well as the nuclear magnetic and quadrupole resonances.

Introduction. It is well known that the quasi-classical approximation works in Quantum Mechanics whenever the quanta of action \hbar (Planck's constant) is much smaller than the relevant amounts of mechanical action; this implies high quantum numbers. The energy levels of the hydrogen atom become dense for high values of the quantum number and can be approximated by the energy provided by the Classical Mechanics. This is the well-known Bohr's principle of correspondence.[1]-[3] When the de Broglie's wavelength is much smaller than the relevant spatial dimensions and does not vary too much, then the wavefunction may be approximated by a quasi-plane wave and the motion may have a trajectory, very much alike the geometrical-optics approximation for waves. This is known as the quasi-classical approximation (or the Jeffrey-Wentzel-Kramers-Brillouin - JWKB - approximation).[4]-[10] A superposition of such plane waves gives a wavepacket which simulates spatial localization (classical limit).[11, 12] In the quasi-classical limit $\hbar \to 0$ the quantum-mechanical commutator reproduces the corresponding classical Poisson brackets.[13]

Another, less known, aspect of the quasi-classical approximation is described here, which arises from the Heisenberg's time-dependence of the quantum-mechanical operators.[14, 15] It leads to an approximation by classical harmonic oscillators of some quantum-mechanical systems, especially in condensed matter; such an approximation may be called a quasi-classical dynamics.

Quasi-classical dynamics. Quantum systems. Let O be a dynamical variable of a quantummechanical motion governed by a hamiltonian H (independent of time); its equation of motion is $\dot{O} = (i/\hbar)[H, O]$, or $\dot{O}_{mn} = (i/\hbar)(E_m - E_n)O_{mn}$, where O_{mn} are the matrix elements for the states m, n with energies E_m, E_n ; we assume $O_{mn} \neq 0$ for $m \neq n$. For large values of the energy levels E_m and the quantum number m the energy levels are "densely distributed", in the sense that $\Delta E_m/E_m = (E_m - E_n)/E_m \ll 1$ for any finite difference $\Delta E_m = E_m - E_n$; according to Bohr's correspondence principle, in this case we are approaching the (quasi-) classical limit. Moreover, under the same conditions, the matrix elements O_{mn} depend weakly on m and may fall abruptly to zero with increasing |m - n| (due to the rapid oscillations of the wavefunctions with large quantum numbers); according to the equation of motion, the matrix elements O_{mn} are approximated by the Fourier components O_{n-m} of the classical quantity O(t). We write n = m+s, $\omega_n = E_n/\hbar = \omega_{m+s} = \omega_m + s(\partial \omega_m/\partial m) + \dots$ and $O_{mn} = O_{m,m+s} \simeq O_s$ for small values of s (in comparison with $m, s \ll m$). For a superposition $\psi = \sum_m c_m \varphi_m e^{-i\omega_m t}$ of wavefunctions $\varphi_m e^{-i\omega_m t}$, the mean value of the variable O is

$$\overline{O} = \sum_{mn} c_m^* c_n O_{mn} e^{i(\omega_m - \omega_n)t} \simeq \sum_{ms} c_m^* c_m O_s e^{-is(\partial \omega_m / \partial m)t} \simeq \sum_s O_s e^{-i\omega_s t} \quad , \tag{1}$$

which is the Fourier transform of the classical quantity O(t) with frequencies $\omega_s = s(\partial \omega_m / \partial m)$. The equation of motion for one component reads

$$\dot{O}_s = -i\omega_s O_s \quad , \tag{2}$$

for a fixed m.

The nature and meaning of this equation require a few clarifications. First, we note the approximate character of the equation (2), as a result of the approximations involved in deriving equation (1). Equation (2) is an approximation for the classical equation of motion of the classical quantity O. Indeed, on one hand it retains partially the quantum-mechanical character of the motion through $\omega_s = (E_{m+s} - E_m)/\hbar$ and the presence of m in O_s (not written explicitly); on the other hand, it refers to a motion which changes the energy $(E_m \neq E_{m+s})$, while the classical motion proceeds with the conservation of the energy. For such reasons, we call equation (2) the quasi-classical equation of motion. For instance, writing $O_s = O_s^{(1)} + iO_s^{(2)}$, we have $\dot{O}_s^{(1)} = \omega_s O_s^{(2)}$, $\dot{O}_s^{(2)} = -\omega_s O^{(1)}$ and $\ddot{O}_s^{(1)} = -\omega_s^2 O_s^{(1)}$, $\ddot{O}_s^{(2)} = -\omega_s^2 O_s^{(2)}$; the classical quantity is either $O_s^{(1)}$ or $O_s^{(2)}$ (O is a real quantity); the classical equations of motion can be represented as $\dot{O}_s^{(1)} = \partial H/\partial P$, $\dot{P} = -\partial H/\partial O_s^{(1)}$, $\ddot{O}_s^{(1)} = (\partial/\partial t)(\partial H/\partial P)$, where P is a generalized momentum and $(\partial/\partial t)(\partial H/\partial P)$ acts as a generalized force (and similar equations for $O_s^{(2)}$); in general, the generalized force $(\partial/\partial t)(\partial H/\partial P)$ differs from the harmonic-oscillator force $-\omega_s^2 O_s^{(1)}$. For the particular case of a harmonic oscillator with eigenfrequency ω_0 the quasi-classical equation of motion is formally the same as the classical equation of motion, but the former assumes in addition $\hbar\omega_0 = E_{m+1} - E_m$, *i.e.* the quantum-mechanical condition for the quantization of the energy. The quantum-mechanical motion governed by the commutator with the hamiltonian is equivalent in the (quasi-) classical limit $\hbar \to 0$ with the classical motion governed by the Poisson brackets, though the quasi-classical motion is associated with the quantum jumps (change of energy), while the classical motion refers to a given orbit (which implies the energy conservation). In the classical limit $\hbar \to 0$ the quantum jumps disappear and we are left with a classical motion; but the classical equation of motion is not necessarily the equation of motion of a harmonic oscillator. It is a remarkable property of the Quantum Mechanics that the quantum-mechanical motion of any dynamical variable can be approximated, within certain limitations as those pointed out here, by a harmonic-oscillator motion in the quasi-classical limit, as indicated by equation (2).

The quasi-classical equation of motion (2) implies that the motion is governed by a harmonicoscillator effective hamiltonian

$$H_{eff} = \frac{1}{2M} P_s^2 + \frac{1}{2} M \omega_s^2 O_s^2 \quad , \tag{3}$$

where P_s is the canonical-conjugate momentum for the "coordinate" O_s and M is a "mass" parameter.

In the presence of a time-dependent, external interaction given by a hamiltonian $H_{int}(t) = h \cos \omega t$, the change in time of the quantity O_s acquires a new contribution, which we write as \dot{O}^{cl} ; equation (2) becomes

$$\dot{O}_s = -i\omega_s O_s + \dot{O}^{cl} ; \qquad (4)$$

the new term \dot{O}^{cl} denotes that part of the time derivative of the classical quantity O, denoted O^{cl} , which arises from the external interaction. At this moment, we may drop out the suffix s in equation (4) and denote $\omega_0 = \omega_s$. With $O = O^{(1)} + iO^{(2)}$ we get from equation (4) $\dot{O}^{(1)} = \omega_0 O^{(2)} + \dot{O}^{cl}$, $\dot{O}^{(2)} = -\omega_0 O^{(1)}$ and

$$\ddot{O}^{(1)} + \omega_0^2 O^{(1)} = [(\partial/\partial t) \dot{O}^{cl}]_{int} ; \qquad (5)$$

the suffix *int* in equation (5) indicates that we retain only the contribution of the external interaction. Equation (5) is the equation of motion of a harmonic oscillator under the action of a generalized force $[(\partial/\partial t)\dot{O}^{cl}]_{int}$; a similar equation is obtained for $O^{(2)}$; we may drop out the labels (1), (2) and write simply

$$\ddot{O} + \omega_0^2 O = [(\partial/\partial t)\dot{O}^{cl}]_{int} .$$
(6)

We are interested in the particular solution of equation (6), which is generated by the interaction. Within the quasi-classical dynamics the interaction produces small effects, so that we may denote δO the particular solution of equation (6); it is the variation of the quantity O for small changes $s \ll m$ in the quantum numbers m; equation (6) becomes

$$\delta \ddot{O} + \omega_0^2 \delta O = [(\partial/\partial t) \dot{O}^{cl}]_{int} ; \qquad (7)$$

if present in the *rhs* of this equation, δO should be neglected there, in order to preserve the perturbation character of the interaction. A damping term can be introduced in equation (7) (the coefficient α), which becomes

$$\delta \ddot{O} + \omega_0^2 \delta O + 2\alpha \delta \dot{O} = (\partial/\partial t) (\dot{O}^{cl})_{int} , \qquad (8)$$

where $\alpha \to 0^+$; multiplying by δO we get a conservation law,

$$\frac{d}{dt}\left(\frac{1}{2}(\delta\dot{O})^2 + \frac{1}{2}\omega_0^2(\delta O)^2\right) + 2\alpha(\delta\dot{O})^2 = \delta\dot{O}[(\partial/\partial t)\dot{O}^{cl}]_{int} \quad , \tag{9}$$

which is related to the energy conservation.

The calculation of the generalized force $[(\partial/\partial t)\dot{O}^{cl}]_{int}$ is carried out by means of the Poisson brackets. For the classical dynamics of the variable O we have $\dot{O} = \{O, H_{eff}\} + \{O, H_{int}\}$ and

$$(\partial/\partial t)O = \{\{O, H_{eff}\}, H_{eff}\} + \{\{O, H_{eff}\}, H_{int}\} + \{\{O, H_{int}\}, H_{eff}\} + \{\{O, H_{int}\}, H_{int}\};$$

$$(10)$$

the first term in the *rhs* of equation (10) must be left aside since it does not contain the interaction; similarly, the last term in equation (10) must be left aside, since we limit ourselves to the first order of the perturbation theory in H_{int} ; therefore, we get

$$(\partial/\partial t)(O^{cl})_{int} = \{\{O, H_{eff}\}, H_{int}\} + \{\{O, H_{int}\}, H_{eff}\}$$
(11)

for the generalized force appearing in equation (7). We note that the effective hamiltonian H_{eff} is used in equation (11), and not the classical counterpart of the original hamiltionian H, in order to preserve the consistency of the quasi-classical approximation. For special forms of the interaction hamiltonian the generalized force given by equation (11) may contain O and P generated by H_{eff} (or expressions containing such O and P); let us denote them by O_0 and P_0 . The classical behaviour of these quantities implies undetermined constants (arising from initial conditions), beside a time dependence. If the external interaction proceeds at a slower time scale than the the motion of these quantities, we may take the time average of the classical O_0 and P_0 . In condensed matter at thermal equilibrium O_0 and P_0 can be determined by their thermal averages. We may also take approximately for O_0 and P_0 the mean values for the quantum state m. All these procedures introduce an additional approximate character in the solution of the quasi-classical equation (8). It is also worth stressing the fact that there might be cases (like the motion of the magnetization in condensed matter) where we have equations of motion but not necessarily a (classical) hamiltonian formalism; in that case the time derivative $\partial/\partial t$ in equation (7) retains only its basic meaning, that of a derivative with respect to the time.

Assuming that h depends only on O in $H_{int}(t) = h \cos \omega t$ and using the hamiltonian given by equation (3) we get

$$\dot{O}^{cl} = P/M$$
 and

$$[(\partial/\partial t)\dot{O}^{cl}]_{int} = (\dot{P}/M)_{int} = -(\partial H_{int}/\partial O)/M = -(1/M)(\partial h/\partial O)\cos\omega t ; \qquad (12)$$

equation (8) becomes

$$\delta\ddot{O} + \omega_0^2 \delta O + 2\alpha \delta\dot{O} = -\frac{1}{M} \cdot \frac{\partial h}{\partial O} \cos \omega t \tag{13}$$

with solution

$$\delta O = a \cos \omega t + b \sin \omega t \quad , \tag{14}$$

where

$$a = \frac{1}{M} \cdot \frac{\partial h}{\partial O} \cdot \frac{\omega^2 - \omega_0^2}{(\omega^2 - \omega_0^2)^2 + 4\omega^2 \alpha^2} \simeq \frac{1}{2M\omega_0} \cdot \frac{\partial h}{\partial O} \cdot \frac{\omega - \omega_0}{(\omega - \omega_0)^2 + \alpha^2} ,$$

$$b = -\frac{1}{M} \cdot \frac{\partial h}{\partial O} \cdot \frac{2\omega\alpha}{(\omega^2 - \omega_0^2)^2 + 4\omega^2 \alpha^2} \simeq -\frac{1}{2M\omega_0} \cdot \frac{\partial h}{\partial O} \cdot \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} ,$$
(15)

for ω near ω_0 . The mean "power" dissipated (absorbed) by the oscillator is

$$\delta P_{osc} = M \overline{\delta \dot{O}[(\partial/\partial t)\dot{O}^{cl}]_{int}} =$$

$$= M \overline{(-a\omega\sin\omega t + b\omega\cos\omega t)[-(1/M)(\partial h/\partial O)\cos\omega t)]} =$$

$$= -\frac{1}{2}b\omega\frac{\partial h}{\partial O} \simeq \frac{(\partial h/\partial O)^2}{4M} \cdot \frac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \to \frac{\pi(\partial h/\partial O)^2}{4M}\delta(\omega_0 - \omega)$$
(16)

(for $\alpha \to 0^+$). As a function of ω , this is a typical resonance curve. As we shall see immediately, δP_{osc} is only the variation of the mean absorbed power with respect to the quantum numbers, as a consequence of the small effects produced by the classical interaction.

Indeed, it is worth comparing this result with the quantum-mechanical theory of perturbation. Let

$$\psi = \varphi_n e^{-\frac{i}{\hbar}E_n t} + \sum_k' c_{kn} \varphi_k e^{-\frac{i}{\hbar}E_k t}$$
(17)

be the wavefunction produced to the first order of the perturbation theory by the interaction $H_{int}(t) = h \cos \omega t$; from the Schrödinger equation $i\hbar \partial \psi / \partial t = (H + H_{int})\psi$ we get

$$i\hbar\dot{c}_{kn} = \frac{1}{2}h_{kn}\left[e^{i(\omega_{kn}+\omega)t+\alpha t} + e^{i(\omega_{kn}-\omega)t+\alpha t}\right] \quad , \tag{18}$$

where the interaction is introduced adiabatically $(\alpha \rightarrow 0^+)$; hence,

$$c_{kn} = -\frac{h_{kn}}{2\hbar} \left[\frac{e^{i(\omega_{kn}+\omega)t+\alpha t}}{\omega_{kn}+\omega-i\alpha} + \frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha} \right] .$$
(19)

The transition from the state n to the state k with the absorption of the quanta of energy $\hbar\omega_{kn} = E_k - E_n$ corresponds to the coefficient

$$c_{kn} \simeq -\frac{h_{kn}}{2\hbar} \cdot \frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha} ; \qquad (20)$$

it produces

$$R = \frac{\partial |c_{kn}|^2}{\partial t} = \frac{|h_{kn}|^2}{2\hbar^2} \cdot \frac{\alpha}{(\omega_{kn} - \omega)^2 + \alpha^2} \to \frac{\pi |h_{kn}|^2}{2\hbar^2} \delta(\omega_{kn} - \omega)$$
(21)

transitions per unit time and absorbs (dissipates) a power

$$P = \frac{|h_{kn}|^2}{2\hbar} \omega_{kn} \frac{\alpha}{(\omega_{kn} - \omega)^2 + \alpha^2} \to \frac{\pi |h_{kn}|^2}{2\hbar} \omega_{kn} \delta(\omega_{kn} - \omega) .$$
(22)

We set $n \to m$ and $k \to m + s$ and get

$$P = \frac{|h_s|^2}{2\hbar} \omega_0 \frac{\alpha}{(\omega_0 - \omega)^2 + \alpha^2} \to \frac{\pi |h_s|^2}{2\hbar} \omega_0 \delta(\omega_0 - \omega) .$$
(23)

We compare δP given by equation (23) with δP_{osc} given by equation (16); for these two quantities be equal we should have

$$\delta\left(\frac{|h_s|^2}{2\hbar}\omega_0\right) = \frac{(\partial h/\partial O)^2}{4M} ; \qquad (24)$$

such an equality is not fulfilled in general; it gives the deviation of the quasi-classical approximation (based on harmonic oscillators) from the quantum-mechanical dynamics. Equation (24) is satisfied for a harmonic oscillator, as expected; indeed, we have

$$\delta\left(\frac{|h_s|^2}{2\hbar}\omega_0\right) = \frac{h_s\delta h_s}{\hbar}\omega_0 = \frac{h_s(\partial h_s/\partial O)\delta O}{\hbar}\omega_0 = \frac{(\partial h/\partial O)^2}{4M} , \qquad (25)$$

or

$$h\delta O = \frac{\hbar}{4M\omega_0} (\partial h/\partial O) \quad , \tag{26}$$

where we dropped out the suffix s and assumed a constant ω_0 . Equation (26) can also be written as

$$h\delta O = \frac{\hbar}{4M\omega_0 s} \cdot \frac{\partial h}{\partial O} \delta n \; ; \tag{27}$$

for $h = f_r O^r$ we get $O = \sqrt{(\hbar r/2M\omega_0 s)n}$ from equation (27), which, for r = s = 1, is the matrix element of the displacement operator for a harmonic oscillator with mass M and frequency ω_0 . For h = fO, we get $\delta P_{osc} = (\pi f^2/4M)\delta(\omega_0 - \omega)$ from equation (16) and $P_{osc} = (\pi f^2/4M)n\delta(\omega_0 - \omega)$,

which coincides with equation (23) for large n. This is precisely the result obtained by means of the first-order theoretical-perturbation calculation using the effective harmonic-oscillator hamiltonian given by equation (3) and the interaction hamiltonian $H_{int} = fO \cos \omega t$ in the limit of large n. In general, for interactions of the form h = fO, we get from equation (24) $\delta(O^2\omega_0) = \hbar/2M$, or $\delta(O\dot{O}) = \hbar/2M$, $\delta(OP) = \hbar/2$, which corresponds to the uncertainty relations $\delta P\delta O \simeq \hbar/2$. As we shall see from examples below, for most simple cases the difference between P and P_{osc} is only a numerical factor of the order of the unity.

Similarly, the mean value of an operator O for the wavefunction ψ given by equation (17) is

$$\overline{O} = O_{nn} + \sum_{k}^{\prime} \left(c_{kn} O_{kn}^* e^{-i\omega_{kn}t} + c_{kn}^* O_{kn} e^{i\omega_{kn}t} \right) \quad ; \tag{28}$$

hence, we may see that the change brought about by the interaction in the (quasi-) classical matrix elements of an operator are included in

$$\frac{\hbar}{2\hbar}O\left(\frac{e^{-i\omega t}}{\Delta\omega + i\alpha} + c.c.\right) = \frac{\hbar}{\hbar}O\frac{\Delta\omega \cdot \cos\omega t - \alpha\sin\omega t}{(\Delta\omega)^2 + \alpha^2} \quad , \tag{29}$$

where $\Delta \omega = \omega_0 - \omega$, the interaction has been removed adiabatically from t to $t \to \infty$ (in accordance with the relaxation term in the harmonic-oscillator equation) and irrelevant phase factors have been left aside. Now we compare the variation of this change with the classical solution given by equation (14),

$$2\frac{h}{\hbar}\delta O = \frac{(\partial h/\partial O)}{2M\omega_0} \quad , \tag{30}$$

which is identical with equation (26) (the factor 2 in the *lhs* of equation (30) comes from the fact that the final state k is both n + s and n - s).

Example 1. Planar rotator. Consider a dipole **d**, consisting of a charge q with mass m, which can rotate freely in plane at a distance l form its axis (plane rotator); since $\mathbf{l} = l(\cos \varphi, \sin \varphi)$ and $\dot{\mathbf{l}} = l\dot{\varphi}(-\sin \varphi, \cos \varphi)$, we get the hamiltonian

$$H = \frac{1}{2}ml^2\dot{\varphi}^2 = \frac{1}{2ml^2}L^2 \quad , \tag{31}$$

where $L = ml^2 \dot{\varphi}$ is the angular moment and $I = ml^2$ is the moment of inertia. Since $L = -i\hbar \frac{\partial}{\partial \varphi}$, we get the wavefunctions $\psi_l = \frac{1}{\sqrt{2\pi}} e^{il\varphi}$ and the energy levels $E_l = \hbar^2 l^2/2I$, l = 0, 1, 2, ... (l denotes here both the quantum number and the dipole length); the matrix elements of the dipole moment **d** involve only states l and $l \pm 1$, with the frequency $\omega_{l\pm 1,l} = (E_{l\pm 1} - E_l)/\hbar = \frac{\hbar}{I} (\pm l + \frac{1}{2})$.

The angle φ is not a dynamical variable, so it is not suitable for a quasi-classical dynamics (though for large l there exists the classical limit, in the sense that φ can be localized by wavepackets with a high accuracy). Indeed, from the commutation relation $[L, \varphi] = -i\hbar$ we get $(l - l')\varphi_{ll'} = -i\delta_{ll'}$, and $\varphi_{ll'} = 0$ for $l \neq l'$, while φ_{ll} is undetermined. This result can be verified directly on the matrix elements

$$\varphi_{ll'} = \frac{1}{2\pi} \int d\varphi \cdot \varphi e^{i(l'-l)\varphi} = \frac{\partial}{\partial [i(l'-l)]} \frac{1}{2\pi} \int d\varphi e^{i(l'-l)\varphi} = 0 \ , \ l \neq l' \ ; \tag{32}$$

similarly, $\dot{\varphi} = (i/\hbar)[H, \varphi] = L/I$, $\dot{\varphi}_{ll'} = (i/\hbar)(E_l - E_{l'})\varphi_{ll'} = (\hbar l/I)\delta_{ll'}$ and $\dot{\varphi}_{ll'} = 0$ for $l \neq l'$; the classical motion proceeds with $\dot{\varphi} = L/I = const.^1$

¹The direct calculation by parts of the integral in equation (32) requires the dismissal of the "surface" term, according to the rules of the Quantum Mechanics regarding orthogonal sets of eigenfunctions (see, for instance, Ref. [16]).

The projection of the dipole on an axis can play the role of a dynamical variable. Such an axis can be provided by an external electric field $\mathbf{E}(t) = \mathbf{E} \cos \omega t$. The orientation of the rotator is given by the direction of its angular momentum \mathbf{L} . In a local reference frame we may take \mathbf{L} directed along the z axis; then, the electric field has the components $\mathbf{E} = E(\sin \theta, 0, \cos \theta)$ and the dipole can be written as $\mathbf{d} = d(\cos \varphi, \sin \varphi, 0)$. The interaction hamiltonian reads

$$H_{int}(t) = -\mathbf{d}\mathbf{E}\cos\omega t = -dE\sin\theta\cos\varphi\cos\omega t \;; \tag{33}$$

we take $x = l \cos \varphi$ as a dynamical variable and write the interaction hamiltonian as

$$H_{int}(t) = -(dE/l)x\sin\theta\cos\omega t = -qEx\sin\theta\cos\omega t .$$
(34)

We can see that the matrix elements $x_{ll'}$ are non-vanishing for $l' = l \pm 1$; therefore we can write $\ddot{x}_s + \omega_s^2 x_s = 0$, where s = 1 and $\omega_s = (\hbar/I)(l + 1/2) \simeq (\hbar/I)l$ for $l \gg 1$ (indeed, we need $\hbar\omega_s/E_l = 2l + 1 \gg 1$, in order to have energy levels densely distributed). It is worth noting that $\omega_s = (\hbar/I)l = L/I$ is the classical frequency in $x = l\cos(Lt/I)$ and, indeed, $\ddot{x} + (L/I)^2 x = 0$. We drop out the label s in x_s and denote $\omega_0 = (\hbar/I)l$ with a fixed l; therefore, the corresponding quasi-classical equation of motion reads $\ddot{x} + \omega_0^2 x = 0$ (also, we use x instead of δx). The force acting upon this harmonic oscillator is $(dE/l)\sin\theta\cos\omega t$, so that we have the quasi-classical equation of motion

$$\ddot{x} + \omega_0^2 x = \frac{qE}{m} \sin\theta \cos\omega t .$$
(35)

The mean absorbed power is

$$\delta P_{osc} = \overline{qE\dot{x}\sin\theta\cos\omega t} = \frac{1}{2}qEb\omega\sin\theta = \frac{q^2E^2\sin^2\theta}{4m}\frac{\alpha}{(\omega-\omega_0)^2 + \alpha^2} .$$
(36)

According to equation (23) the power absorbed by quantum-rotation jumps is given by

$$P = \frac{\pi d^2 E^2 \sin^2 \theta}{8\hbar} \omega_0 \delta(\omega_0 - \omega) ; \qquad (37)$$

since $\omega_0 = (\hbar/I)l$ we can see that $\delta P = (\pi q^2 E^2 \sin^2 \theta / 8m)\delta(\omega_0 - \omega)$, which differs from δP_{0sc} given by equation (36) by a factor 1/2. Such a discrepancy reflects the deviation of the quasi-classical approximation, based on harmonic oscillators, from the original dynamics.

It is worth noting that for large l we are in the classical limit, with the hamiltonian $L^2/2I - dE \sin \theta \cos \varphi \cos \omega t$; the equation of motion reads

$$\ddot{\varphi} = -\frac{dE}{I}\sin\theta\sin\varphi\cos\omega t \; ; \tag{38}$$

we solve this equation by perturbation theory, with a series $\varphi = \varphi_0 + \lambda \varphi_1 + ...$, where $\lambda = dE \sin \theta / I \ll 1$. With convenient initial conditions we get

$$\varphi = \omega_0 t + \frac{\lambda}{2} \left[\frac{\sin(\omega_0 + \omega)t - (\omega_0 + \omega)t}{(\omega_0 + \omega)^2} + \frac{\sin(\omega_0 - \omega)t - (\omega_0 - \omega)t}{(\omega_0 - \omega)^2} \right] + \dots , \qquad (39)$$

which indicates a rotation with small oscillations. As expected, this classical solution is fundamentally different from the quantum-mechanical jumps and from the quasi-classical approximation. A friction term can be included in φ_0 (with the coefficient α such as $\alpha\lambda \ll 1$), with a similar conclusion. **Example 2. Spherical pendulum.** The spherical pendulum (spatial, rigid rotator, spherical top) consists of a point of mass M which rotates freely in space at the end of a radius $\mathbf{l} = l(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, as described by the hamiltonian

$$H = \frac{1}{2}M\dot{\mathbf{l}}^2 = \frac{1}{2}Ml^2(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) ; \qquad (40)$$

if the point has a charge q, it is a dipole $\mathbf{d} = q\mathbf{l}$ which can couple to an external electric field $\mathbf{E}\cos\omega t$, with an interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$. We take the electric field directed along the z-axis.

As it is well known, the angular momentum $\mathbf{L} = M\mathbf{l} \times \dot{\mathbf{l}}$ has the components $L_x = Ml^2(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$, $L_y = Ml^2(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, $L_z = Ml^2\dot{\varphi}\sin^2\theta$ and the hamiltonian can be written as

$$H = \frac{1}{2I}L^2 \quad , \tag{41}$$

where $I = Ml^2$ is the moment of inertia. The eigenfunctions are the spherical harmonics Y_{lm} with the eigenvalues $\hbar^2 l(l+1)$, l = 0, 1, ... The z-component of the angular momentum is $L_z = -i\hbar \frac{\partial}{\partial \varphi}$, with the same eigenfunctions Y_{lm} , $L_z Y_{lm} = \hbar m Y_{lm}$, m = -l, -l + 1, ...l. The energy levels of the spherical pendulum are $E_l = \frac{\hbar^2}{2I} l(l+1)$; they are degenerate with respect to the quantum number m, which takes 2l + 1 values. (l denotes here both the length of the dipole and the quantum number of the angular momentum).

The angles φ and θ do no admit a quasi-classical approximation, in the sense discussed here for dynamical variables (this is a typical situation for the free motion). Indeed, the matrix elements $\varphi_{lm,lm'}$ are vanishing for $m \neq m'$, while the matrix elements $\theta_{l,m;l+s,m}$ do not fall off rapidly with increasing s.

We can take $z = l \cos \theta$ as a quasi-classical variable with s = 1, corresponding to transitions from l to l + 1; the generalized force is

$$(\partial/\partial t)(\dot{z}^{cl}) = \frac{qE}{M}\cos\omega t \tag{42}$$

and the equation of motion reads

$$\ddot{z} + \omega_0^2 z = \frac{qE}{M} \cos \omega t .$$
(43)

The mean absorbed power is given by

$$\delta P_{osc} = \frac{1}{2} q E b \omega_0 = \frac{q^2 E^2}{4M} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \quad , \tag{44}$$

which should be multiplied by $2l + 1 \simeq 2l$ in order to account for the degeneracy; we get $\delta P_{osc} = (\pi q^2 E^2/2M) l \delta(\omega_0 - \omega)$.

The transition rate of quantum jumps for $\omega_0 = (E_{l+1} - E_l)/\hbar = (\hbar/I)(l+1)$ is

$$\frac{\partial |c_{lm}|^2}{\partial t} = \frac{\pi d^2 E^2}{2\hbar^2} \left| (\cos \theta)_{lm} \right|^2 \delta(\omega_0 - \omega) \quad , \tag{45}$$

where [10]

$$(\cos\theta)_{lm} = (\cos\theta)_{l+1,m;l,m} = -i\sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}};$$
(46)

the absorbed power is

$$P = \hbar\omega_0 \sum_{m=-l}^{l} \frac{\partial |c_{lm}|^2}{\partial t} = \frac{\pi d^2 E^2}{2\hbar} \omega_0 \sum_{m=-l}^{l} |(\cos\theta)_{lm}|^2 \,\delta(\omega_0 - \omega) = \frac{d^2 E^2}{6\hbar} \omega_0 (l+1) \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} = \frac{d^2 E^2}{6I} (l+1)^2 \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \,.$$
(47)

We can see that $\delta P = (\pi d^2 E^2/3I) l \delta(\omega_0 - \omega)$ (for $l \gg 1$), which differs from δP_{osc} given above by a factor 2/3.

We may consider the classical limit of the motion, corresponding to large values of $m \simeq l \gg 1$; in this case the φ -motion is in the classical limit (for large m and $\hbar \to 0$ the component L_z remains finite) and the associated Legendre polynomials P_{lm} in the spherical harmonics Y_{lm} are localized near the equator; indeed, $P_{ll} \sim \sin^l \theta$. For small variations $\delta \theta$ around $\pi/2$ we have $\delta \theta \simeq \sin \delta \theta = \cos(\pi/2 - \delta \theta) = \cos \theta$, so we have to take the matrix elements of $\cos \theta$, which are different from zero for $l' = l \pm 1$. Consequently, we take $\delta \vartheta$ for O in the quasi-classical equation, s = 1 and $\omega_0 = (E_{l+1} - E_l)/\hbar \simeq (\hbar/I)l$, for a fixed $l \gg 1$; in addition, $\cos \theta$ in the interaction hamiltonian may be approximated by $\delta \theta$, where $\delta \theta$ is the new quasi-classical variable θ_s ; the equation of quasi-classical motion is

$$\ddot{\theta}_s + \omega_0^2 \theta_s = -\frac{dE}{I} \cos \omega t \ . \tag{48}$$

The mean absorbed power is given by

$$\delta P = -dE\overline{\dot{\theta}_s \cos \omega t} = -\frac{1}{2}dEb\omega \simeq \frac{d^2 E^2}{4I} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \quad , \tag{49}$$

which coincides with equation (44) and the m = l-component of δP in equation (47), as expected (up to the degeneracy factor).

Extension to some problems in condensed matter. In condensed matter the energy levels have a limited meaning, as a consequence of the interaction between the atomic constituents. A coarse graining is meaningful in this case, which consists in taking a number N of atomic constituents, labelled by i = 1, 2, ...N, around each point in the sample, such that $N \gg 1$, but N is still much smaller than the total number of atomic constituents in the sample. The coarse graining implies averages of the type $O = (1/N) \sum_{i=1}^{N} O_i$ for any physical quantity O, so that any change δO is of the order $\delta O \sim \delta O_i/N$ (for an incoherent motion, like in "normal" condensed matter), or $\delta O/\delta O_i \sim 1/N \ll 1$; therefore, the quantum states (and the energy levels) are densely distributed and the quasi-classical approximation can be applied. Moreover, the quantummechanical states for each atomic constituent i are usually limited in number (like magneticmoment states, for instance), so that the comparison between the quasi-classical approximation and the quantum-mechanical computations involve small quantum numbers; in this case δO is practically O, and P_{osc} is practically P, up to numerical factors of the order of unity. Usually, the (normal) condensed matter is at finite temperatures, which implies both direct and reverse quantum transitions (jumps). Making use of equation (22), the temperature-dependent power can be written as

$$P_{th} = \frac{\pi}{2\hbar} \omega_0 \left(\sum'_n\right) \times \left[\sum_{m(n)} |h_{n+s,n}(m)|^2 e^{-\beta E_n} - \sum_{m(n+s)} |h_{n,n+s}(m)|^2 e^{-\beta E_{n+s}}\right] \delta(\omega_0 - \omega)/Z \quad ,$$

$$(50)$$

where (\sum_{n}') stands for the summation over those states n which are separated by the same frequency ω_0 from states n + s; $\sum_{m(n)}$ indicates a summation over possible degenerate states

labelled by m(n) for n (and m(n+s) for n+s), which may affect the matrix elements of the interaction hamiltonian h; $\beta = 1/T$ is the reciprocal of the temperature T; and

$$Z = \sum_{n} \sum_{m(n)} e^{-\beta E_n} \tag{51}$$

is the partition function. In the quasi-classical approximation equation (50) can be written approximately as

$$P_{th} = \left(\sum_{n}^{\prime}\right) \frac{\pi |h_{s}|^{2}}{2\hbar} \omega_{0}(\beta \hbar \omega_{0}) f(n) e^{-\beta E_{n}} \delta(\omega_{0} - \omega) / Z =$$

$$= \left(\sum_{n}^{\prime}\right) P(n)(\beta \hbar \omega_{0}) f(n) e^{-\beta E_{n}} / Z \quad , \qquad (52)$$

where $|h_s|^2 f(n)$ is the approximate result of the summation $\sum_{m(n)} |h_{n+s,n}(m)|^2$ and $\beta \hbar \omega_0$ was assumed to be much smaller than unity. In equation (52) P_{osc} may be used approximately for P(n), according to the discussion above. For the particular case of a harmonic oscillator there is no degeneracy and summation in equation (52) extends over all the states $(P(n) \sim n)$. The partition function is $Z = \sum_{n=0} e^{-\beta \hbar \omega_0 n} \simeq 1/\beta \hbar \omega_0$ and $\sum_{n=0} n e^{-\beta \hbar \omega_0 n} = 1/(\beta \hbar \omega_0)^2$, so that P_{th} is independent of temperature.

Example 3. Nuclear magnetic resonance. We consider the motion of a magnetic moment $\overrightarrow{\mu}$ in a constant (static) and uniform magnetic field \mathbf{H}_0 directed along the z-axis (the longitudinal field) and an oscillating magnetic field $\mathbf{H}(t) = \mathbf{H} \cos \omega t$, directed along the x-axis (the transverse field), where ω is the oscillation frequency. The interaction hamiltonian can be written as

$$H_{int} = -\overrightarrow{\mu} [H_0 \mathbf{e}_z + H(t) \mathbf{e}_x] \quad , \tag{53}$$

where $\mathbf{e}_{x,z}$ are the corresponding unit vectors. The Larmor equation $\dot{\overrightarrow{\mu}} = \gamma \overrightarrow{\mu} \times [H_0 \mathbf{e}_z + H(t) \mathbf{e}_x]$ reads

$$\mu_x = \gamma \mu_y H_0 ,$$

$$\dot{\mu}_y = -\gamma \mu_x H_0 + \gamma \mu_z H \cos \omega t ,$$

$$\dot{\mu}_z = -\gamma \mu_y H \cos \omega t ,$$
(54)

where γ is the gyromagnetic factor.

The magnetic moment in the equations written above is a quantum-mechanical operator; it is related by the quantum-mechanical operator of the angular momentum **J** (spin) by $\vec{\mu} = g\mu_B \mathbf{J} =$ $\gamma \hbar \mathbf{J}$, where g is a Lande factor, μ_B is a Bohr magneton (atomic or nuclear) and γ is a gyromagnetic factor (the magnetic moment of a particle, or ensembly of particles, is given by $\mu = g\mu_B J = \gamma \hbar J$; it is convenient to use a suffix for this magnetic moment, and write, for instance, $\mu_p = g\mu_B J = \gamma \hbar J$, where the suffix p stands for "particle", in order to distinguish it from the magnitude $[(\vec{\mu})^2]^{1/2}$ of the operator $\overrightarrow{\mu}$). Making use of the commutation relations $[J_i, J_j] = i\varepsilon_{ijk}J_k$ of the operators of the angular momentum, the Larmor equations of motion written above are obtained from the quantum-mechanical equation of motion $\overrightarrow{\mu} = (i/\hbar)[H_{int}, \overrightarrow{\mu}]$. The interaction $-\overrightarrow{\mu}\mathbf{H}_0 = -\mu_z H_0 =$ $-\gamma \hbar J_z H_0$ splits the degenerate level according to $-\gamma \hbar m_z H_0$, where $m_z = -J, -J + 1, ...J$ is the quantum number of the component J_z ; it is convenient to introduce the frequency $\omega_0 = \gamma H_0$ and write the energy levels as $-\hbar\omega_0 m_z$. The states labelled by m_z are eigenstates of the operator J_z and μ_z ; for each of these states J_z and μ_z are constant, while $\mu_{x,y}$ (and $J_{x,y}$) are undetermined; the mean value of $\mu_{x,y}$ (and $J_{x,y}$) over any state m_z is vanishing. The interaction $-\overrightarrow{\mu}\mathbf{H}(t) = -\gamma\hbar J_x H(t)$ produces transitions between the states m_z and $m_z \pm 1$, so it mixes up such states; consequently, we measure mean (average) values (expectation values) of the operators $\overrightarrow{\mu} = (\mu_x, \mu_y, \mu_z)$.

Therefore, we take the average of the magnetic moment over the quantum motion in equations (54) (quantum-mechanical averages); this means that we can replace the operator $\vec{\mu} = \gamma \hbar \mathbf{J}$ by its average, denoted $\vec{\mu}_{av}$ and given by

$$\overrightarrow{\mu_{av}} = \sum_{\sigma\sigma'} \int d\mathbf{r} \psi^*_{\sigma'} (\overrightarrow{\mu})_{\sigma'\sigma} \psi_{\sigma} \quad , \tag{55}$$

where ψ_{σ} is the spinor corresponding to the angular momentum \mathbf{J} ; $\overrightarrow{\mu_{av}}$ is now a classical variable which can be measured. It is this quantity which is often viewed as the magnetic moment, especially for ensemblies of particles (a similar average \mathbf{J}_{av} can be introduced for the angular momentum, so we can preserve the equation $\overrightarrow{\mu_{av}} = \gamma \hbar \mathbf{J}_{av}$; we note that equations (55) define also a density of magnetic moment (magnetization). For a sample of condensed matter $\overrightarrow{\mu_{av}}$ can carry a position label \mathbf{r}_i , denoting the position of the *i*-th particle with this magnetic moment; in a course-graining average, specific to the continuum models of matter, the label \mathbf{r}_i , may become the continuous, local position **r**, so that the corresponding average magnetic moment $\overrightarrow{\mu_{av}}$ may be a function $\overline{\mu_{av}}(t, \mathbf{r})$ of the time t and position \mathbf{r} . Moreover, the measurable quantities in condensed matter are statistical averages, so that we may assume that we have a local thermodynamic equilibrium and $\overrightarrow{\mu_{av}}(t,\mathbf{r})$ is also averaged over such a statistical distribution, which can be written as $\overrightarrow{\mu_{av}}$. If we are not interested in the spatial variations (which may imply diffusion of the moments), we may leave aside the r-dependence; for simplification we may also leave aside the average bars and the suffix av, and write simply $\vec{\mu}$ for this classical quantity; in fact, it is more convenient to use the magnetization \mathbf{M} (the magnetic moment of the unit volume, accordingly averaged), which obeys the equations of motion

$$M_x = \gamma M_y H_0 ,$$

$$\dot{M}_y = -\gamma M_x H_0 + \gamma M_z H \cos \omega t , \qquad (56)$$

$$\dot{M}_z = -\gamma M_y H \cos \omega t ,$$

derived from equations (55) by the succession of averages described above (quantum-mechanical, coarse-graining, statistical). We consider here the particular situation of magnetic moments associated with atomic nuclei, but the procedure described above is more general and can also be applied to other magnetic moments. The average procedure described here for the magnetic moments in condensed matter is the quasi-classical approximation as presented in this paper.

At thermal equilibrium the statistical average of the magnetization is zero; applying the magnetic field \mathbf{H}_0 an interaction $-\overrightarrow{\mu} \mathbf{H}_0$ appears, which restores the thermal equilibrium with a non-zero average magnetic moment directed along the longitudinal field \mathbf{H}_0 . Since the interaction energy μH_0 is much smaller than the temperature T, we may use the distribution $\sim e^{\overrightarrow{\mu} \mathbf{H}_0/T}$ of the classical statistics; we get the statistical average of the magnetic moment $\overline{\mu_z} = \mu^2 H_0/3T$ and the longitudinal magnetization $M_0 = n\overline{\mu}_z = n\mu^2 H_0/3T$, where n is the density of particles; the transverse components of the magnetization are vanishing $(M_{x,y} = 0)$; here μ is the "magnetic moment of the particle" ($\mu = \mu_p = \gamma \hbar J$). As it is well known, this is the Curie-Langevin-Debye law.[17]-[20] The relaxation of the longitudinal magnetization is governed by the kinetic equation

$$\frac{dM_z}{dt} = \alpha_1 (M_0 - M_z) \quad , \tag{57}$$

where α_1 is a (longitudinal) damping coefficient; the solution is $M_z = M_0(1 - e^{-\alpha_1 t})$, for zero initial magnetization. The average transverse magnetization is vanishing; if, by external means, we take

the transverse magnetization out of equilibrium $(M_{x,y0} \neq 0 \text{ initially})$, it will relax according to

$$\frac{dM_x}{dt} = -\alpha_2 M_x , \quad \frac{dM_y}{dt} = -\alpha_2 M_y , \quad (58)$$

where α_2 is a transverse damping coefficient. The solution is $M_{x,y} = M_{x,y0}e^{-\alpha_2 t}$ (for more details regarding the relaxation coefficients, see, for instance, Ref. [21]). Including these damping coefficients equations (56) become

$$M_x = \gamma M_y H_0 - \alpha_2 M_x ,$$

$$\dot{M}_y = -\gamma M_x H_0 + \gamma M_z H \cos \omega t - \alpha_2 M_y ,$$

$$\dot{M}_z = -\gamma M_y H \cos \omega t - \alpha_1 (M_z - M_0) ;$$

(59)

for small values of the field H we may put approximately $M_z \simeq M_0$ in these equations and neglect the time-dependence of the longitudinal component M_z of the magnetization; then, equations (59) can be approximated by

$$\dot{M}_x \simeq \gamma M_y H_0 - \alpha_2 M_x , \qquad (60)$$
$$\dot{M}_y \simeq -\gamma M_x H_0 + \gamma M_0 H \cos \omega t - \alpha_2 M_y , \dot{M}_x \simeq \omega_0 M_y - \alpha_2 M_x ,$$

or

$$\dot{M}_x \simeq \omega_0 M_y - \alpha_2 M_x ,$$

$$\dot{M}_y \simeq -\omega_0 M_x + \omega_m H \cos \omega t - \alpha_2 M_y ,$$
(61)

where $\omega_0 = \gamma H_0$ and $\omega_m = \gamma M_0$. These equations can be transformed into

$$\ddot{M}_x + \omega_0^2 M_x + \alpha_2 \dot{M}_x = \omega_0 \omega_m H \cos \omega t ,$$

$$\ddot{M}_y + \omega_0^2 M_y + \alpha_2 \dot{M}_y = -\omega \omega_m H \sin \omega t ,$$
(62)

for $\alpha_2 \ll \omega_0, \omega_m$, which are equations of motion of damped harmonic oscillators, in accordance with their quasi-classical nature. The particular solution of equations (61) is given by

$$M_x = a \cos \omega t + b \sin \omega t ,$$

$$M_y = \frac{-a\omega + b\alpha_2}{\omega_0} \sin \omega t + \frac{b\omega + a\alpha_2}{\omega_0} \cos \omega t ,$$
(63)

where

$$a = -\omega_0 \omega_m H \frac{\omega^2 - \omega_0^2 - \alpha_2^2}{(\omega^2 - \omega_0^2 - \alpha_2^2)^2 + 4\omega^2 \alpha_2^2} ,$$

$$b = \omega_0 \omega_m H \frac{2\omega \alpha_2}{(\omega^2 - \omega_0^2 - \alpha_2^2)^2 + 4\omega^2 \alpha_2^2} .$$
(64)

We can simplify these solutions by using $\alpha_2 \ll \omega_0$, ω_m and assuming ω close to ω_0 . We get

$$M_x \simeq a \cos \omega t + b \sin \omega t$$
, $M_y \simeq -a \sin \omega t + b \cos \omega t$, (65)

where

$$a \simeq -\frac{1}{2}\omega_m H \frac{\omega - \omega_0}{(\omega - \omega_0)^2 + \alpha_2^2} , \ b \simeq \frac{1}{2}\omega_m H \frac{\alpha_2}{(\omega - \omega_0)^2 + \alpha_2^2} .$$
 (66)

These solutions are obtained also from the oscillator equations (62) with $\alpha_2 \rightarrow \alpha_2/2$ in equations (66). From equations (63) we can see that the magnetization performs a Larmor precession about the z-axis with frequency ω (the frequency of the external field); the transverse magnetization rotates with constant magnitude $M_x^2 + M_y^2 = a^2 + b^2 \simeq (\omega_m H/2\alpha_2)^2$. The power absorbed from the field and dissipated by the motion of the transverse magnetization can be obtained from equations (62), through

$$\frac{d}{dt}\left(\frac{1}{2}\dot{M}_x^2 + \frac{1}{2}\omega_0^2 M_x^2\right) + \alpha_2 \dot{M}_x^2 = \omega_0 \omega_m H \dot{M}_x \cos \omega t , \qquad (67)$$

We get

$$P_{osc} = \overline{H\dot{M}_x \cos \omega t} = \frac{1}{2}Hb\omega = \frac{1}{4}\omega_m H^2 \frac{\omega\alpha_2}{(\omega - \omega_0)^2 + \alpha_2^2} ; \qquad (68)$$

or

$$P_{osc} = \frac{\pi}{4} \omega_m \omega_0 H^2 \delta(\omega - \omega_0) \ , \ \alpha_2 \to 0^+ \ (\alpha_2 \ll \omega_0) \ . \tag{69}$$

These are typical solutions of damped harmonic oscillators exhibiting resonance for $\omega = \omega_0$. This is the typical solution of the magnetic resonance.[22]-[24] As it is well known, equations (59) and (60) are called Bloch equations.[25]

Let us calculate now the power absorbed in magnetic resonance by quantum-mechanical transitions $m_z \rightarrow m_z \pm 1$ caused by the interaction hamiltonian $H_{int}(t) = -\gamma \hbar I_x H \cos \omega t$ (we denote the nuclear spin by **I**); each of these transitions proceeds with the absorption or emission of the quanta of energy $\hbar \omega_0$; these transitions release and absorb energy, and we are interested in the net energy absorption rate per unit time.

In the presence of the longitudinal field \mathbf{H}_0 the energy levels are given by $-\gamma \hbar H_0 m_z = -\hbar \omega_0 m_z$; the lowest energy level has $m_z = I$ and the highest energy level has $m_z = -I$. The energy absorption proceeds from m_z to $m_z - 1$, where $m_z = I$, I - 1, $\dots - I + 1$, with the rate

$$\frac{\partial |c_{m_z-1}|^2}{\partial t} = \frac{1}{2} \gamma^2 H^2 |(I_x)_{m_z-1,m_z}|^2 \frac{\alpha}{(\omega-\omega_0)^2 + \alpha^2} ; \qquad (70)$$

the energy emission implies transitions from m_z to $m_z + 1$, where $m_z = I - 1$, I - 2, $\dots - I$; the rate of these transitions is given by

$$\frac{\partial |c_{m_z+1}|^2}{\partial t} = \frac{1}{2} \gamma^2 H^2 |(I_x)_{m_z+1,m_z}|^2 \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} ; \qquad (71)$$

the matrix elements of the spin component I_x are[10]

$$(I_x)_{m_z-1,m_z} = \frac{1}{2} [(I+m_z)(I-m_z+1)]^{1/2} ,$$

$$(I_x)_{m_z+1,m_z} = \frac{1}{2} [(I-m_z)(I+m_z+1)]^{1/2} .$$
(72)

The transition rates must be weighted by the statistical distribution $e^{\beta \hbar \omega_0 m_z} / \sum_{m_z} e^{\beta \hbar \omega_0 m_z}$, so that the net transition rate is given by

$$R = \frac{\overline{\partial |c_{m_z-1}|^2}}{\partial t} - \frac{\overline{\partial |c_{m_z+1}|^2}}{\partial t} =$$

$$= \frac{1}{2} \gamma^2 H^2 \overline{|I_x|^2} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \quad , \qquad (73)$$

where

$$\overline{|I_x|^2} = \left[\sum_{m_z=I}^{-I+1} |(I_x)_{m_z-1,m_z}|^2 - \sum_{m_z=I-1}^{-I} |(I_x)_{m_z+1,m_z}|^2\right] e^{\beta\hbar\omega_0 m_z} / \sum_{m_z=I}^{-I} e^{\beta\hbar\omega_0 m_z} = \frac{1}{4} \left[\sum_{m_z=I}^{-I+1} (I^2 + I + m_z - m_z^2) - \sum_{m_z=I-1}^{-I} (I^2 + I - m_z - m_z^2)\right] e^{\beta\hbar\omega_0 m_z} / \sum_{m_z=I}^{-I} e^{\beta\hbar\omega_0 m_z}$$
(74)

(here, the net emission rate is equal with the net absorption rate, R in equation (73) being, in fact, |R|); the rearrangement of the summations in equation (74) lead to

$$\overline{|I_x|^2} = \frac{1}{2} \sum_{m_z - I}^{I} m_z e^{\beta \hbar \omega_0 m_z} / \sum_{m_z = -I}^{I} e^{\beta \hbar \omega_0 m_z} = \frac{1}{2} \overline{m_z} \quad , \tag{75}$$

where $\overline{m_z}$ is the thermal average of the quantum number m_z . For $\beta \hbar \omega_0 \ll 1$ we get $\overline{m_z} = \hbar \omega_0 I(I+1)/3T$ (and $\overline{m_z^2} = I(I+1)/3$); we note that the average magnetic moment directed along the z-axis is $\gamma \hbar \overline{m_z} = \gamma^2 \hbar^2 H_0 I(I+1)/3T$ while the same average calculated with the classical statistics is $\mu^2 H_0/3T = \gamma^2 \hbar^2 H_0 I^2/3T$ (as given above); in the quantum-mechanical statistics I^2 is replaced by I(I+1), as expected. Inserting $\overline{|I_x|^2}$ given by equation (75) in equation (73) we get the net absorption rate

$$R = \frac{1}{4}\gamma^2 H^2 \overline{m_z} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2}$$
(76)

and the power absorbed per unit volume

$$P = n\hbar\omega_0 R = \frac{1}{4}n\hbar\omega_0\gamma^2 H^2 \overline{m_z} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \quad , \tag{77}$$

or

$$P = \frac{1}{4} \gamma \omega_0 M_0 H^2 \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} = \frac{1}{4} \omega_m \omega_0 H^2 \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \quad , \tag{78}$$

since $n\gamma\hbar\overline{m_z}$ is the magnetization M_0 along the z-axis (and $\omega_m = \gamma M_0$). This equation should be compared with the equation (68) which gives the absorbed power per unit volume within the classical treatment; we can see that they are the same (near the resonance, with $\alpha = \alpha_2$, up to I^2 replaced by I(I + 1) in magnetization and ω_m). We note that the perturbation is applied here adiabatically (for a long time), which warrants the attaining of the thermal equilibrium.

Example 4. Nuclear quadrupole resonance. It may happen that the structure of the quantum states of the magnetic moment (spin) is not governed by an external field, as H_0 in the case of the magnetic resonance described above, but it is produced by local interactions of the magnetic moments with their environment. For instance, the hyperfine interaction acts in the case of paramagnetic (spin) resonance, the quadrupole interaction determines the nuclear quadrupole resonance, etc. In such cases the direct application of the averages technique in the equations of motion of the magnetic moment described above is not convenient, since these equations depend also on external degrees of freedom, or a non-linear. First, we should take into account the effect of the local interaction with the surrounding medium. The quantum nature of the condensed matter has certain particularities, which may allow a quasi-classical description.

In normal condensed matter the wavefunctions and energy levels have a limited validity, due, on one side, to the large number of states densely distributed in energy, to the natural uncertainties arising from internal, residual interactions and, on the other side, to the inevitable interaction with the external world, which makes practically impossible the preparation of a pure quantum state. In fact, mixed states described by the density matrix, or thermodynamic states described by the statistical matrix are appropriate for condensed matter, exhibiting, to a large extent, a classical behaviour. These particularities also provide the basis for a quasi-classical dynamics in some cases in condensed matter. (This is true for usual conditions, which define a "normal" condensed matter. At low temperatures, we may encounter quantum states for condensed matter, like superfluidity, superconductivity, ferromagnetism, etc).

The nuclear magnetic moments in solids are affected by the interaction with the surrounding ions, which generate high gradients of electric field. Consequently, a quadrupole interaction

$$V_2 = \frac{1}{6} \sum_{ij} Q_{ij} V_{ij} , \quad V_{ij} = \frac{\partial^2 \Phi}{\partial x_{ai} \partial x_{aj}}$$
(79)

acts on the nuclear magnetic moments, where Q_{ij} is the tensor of the quadrupole moment, Φ is the electric potential at the location of the magnetic moment, a denotes the surrounding ions and i, jare cartesian coordinates. This interaction splits the degeneracy of the energy levels with respect to the magnetic quantum number m (and shifts the energy levels), such that transitions between such levels may be induced by an external time-dependent magnetic field (the energy levels can depend on the temperature). These transitions have a resonance character, and are known as the nuclear quadrupole resonance.[26]-[29] (The resonance frequencies are in the radiofrequency range. The nuclear quadrupole resonance does not appear for nuclear spins I = 0, 1/2, which give a vanishing quadrupole moment. The average of the quadrupole interaction with respect to the molecular motion leads to a very weak effective interaction in liquids, so that the nuclear quadrupole resonance is not observed in liquids, or in gases, where the interaction is very weak).

Let us consider a sample of condensed matter consisting of atomic constituents (not necessarily identical), like atoms, ions, molecules, spins, magnetic moments, etc (at rest, as in solids, or in motion as in liquids, gases, etc). As independent entities, each of these atomic constituents has its own (quantum) dynamics, defined by stationary states and energy levels. Some of these states may be degenerate, as, for instance, the spin states associated with various spatial orientations of the spin (the spatial degeneray). The local interaction occurring in condensed matter, between these atomic constituents, or between them and their environment lead to changes in these quantum states, or to generation of new quantum states, as, for instance, those occurring by the removal of the degeneracies. Let us consider a collection of N such "quatum systems" labelled by i = 1, 2...N, each with a set of quantum states labelled by quantum numbers n_i and energy ε_{n_i} , such as the total energy of the collection is $E_n = \varepsilon_{n_1} + \varepsilon_{n_2} + \ldots + \varepsilon_{n_N}$; it is convenient to denote the states of the collection by $n = (n_1, n_2, ..., n_N)$. Now we see that another energy $E_{n'}$ is obtained by changing at least by a unity at least one of the quantum numbers n_i , for instance $E_{n'} = \varepsilon_{n_1} + \ldots + \varepsilon_{n'_i} + \ldots + \varepsilon_{n_N}$, where $n'_i = n_i \pm 1$. Such a change implies a small difference in energy, $E_{n'} - E_n$ in comparison with the energies $E_{n,n'}$, providing $N \gg 1$. If the dynamics is such as the change in energy proceeds in time Δt , then $E_{n'} - E_n$ is of the order $\hbar/\Delta t$, where \hbar is Planck's constant. This indicates a change in the mechanical action of the order \hbar , which is much smaller that the mechanical action associated to the whole set of N systems. Consequently, we may adopt a quasi-classical description for the dynamics of the assembly of N systems. Moreover, we may take such assemblies in the vicinity of any position in the sample, and take the average of the physical quantities over such coarse-graining structures; the number N of systems in each assembly is much larger than unity, but still sufficiently small at the macroscopic scale as to allow the definition of a coarse-graining averaged model (possibly continuous) for the macroscopic sample. The physical quantities defined in this manner are classical quantities wich obey a (quasi-) classical dynamics.

If the perturbation hamiltonian is given by $H_{int}(t) = -\overrightarrow{\mu} \mathbf{H} \cos \omega t$, where $\overrightarrow{\mu}$ is the (quasi-) classical magnetic moment, the quasi-classical dynamics for a frequency $\omega_s = \omega_0$ is governed by

the quasi-classical equations of motion

$$\dot{\overrightarrow{\mu}} = -i\omega_0 \,\overrightarrow{\mu} + \gamma \,\overrightarrow{\mu^{cl}} \times \mathbf{H} \cos \omega t \quad , \tag{80}$$

where γ is the gyromagnetic factor; in this equation $\overrightarrow{\mu}$ is the magnetic moment generated by the magnetic field $\mathbf{H} \cos \omega t$ (particular solution) and $\overrightarrow{\mu^{cl}}$ may have a non-vanishing part $\overrightarrow{\mu_0}$ generated by the statistical distribution over the states whose energies are denoted $\hbar\omega(m)$; $\hbar\omega_0$ is one of the differences $\hbar\omega(m') - \hbar\omega(m)$, according to the selection rules; it is these contributions $\overrightarrow{\mu_0}$ which are retained in $\overrightarrow{\mu^{cl}}$. Equations (80) for the real part of the moment $\overrightarrow{\mu}$ become

$$\ddot{\vec{\mu}} + \omega_0^2 \vec{\mu} = -\gamma \omega \vec{\mu_0} \times \mathbf{H} \sin \omega t .$$
(81)

We may assume that the thermal average of the magnetic moment is vanishing in the absence of the interaction,

$$\overline{\overrightarrow{\mu_0}} = \sum \overline{\mu_0} e^{-\beta H} / \sum e^{-\beta H} = 0 \quad , \tag{82}$$

where $\beta = 1/T$ is the inverse of the temperature T. In the presence of the interaction which produces the energy levels $\hbar\omega(m)$ the mean value of the magnetic moment is

$$\overline{\overrightarrow{\mu_0}} = \sum \overline{\mu_0} e^{-\beta H - \beta \hbar \omega(m)} / \sum e^{-\beta H - \beta \hbar \omega(m)} \simeq -\beta \hbar \overline{\overrightarrow{\mu_0}} \omega(m) \quad , \tag{83}$$

for $\beta \hbar \omega(m) \ll 1$; it is differences of the type $\hbar \omega(m') - \hbar \omega(m)$ which matters in this mean value, so we may write conveniently $\overrightarrow{\mu_0}\omega(m) = \mathbf{c}\mu\omega_0$, where **c** is an undetermined numerical vectorial coefficient directed along the mean magnetization (magnetic moment $\overline{\mu_0}$) and μ is the magnetic moment. Now, equations (81) can be written for magnetization (including damping) as

$$\ddot{\mathbf{M}} + \omega_0^2 \mathbf{M} + 2\alpha \dot{\mathbf{M}} = \omega \omega_m \mathbf{c} \times \mathbf{H} \sin \omega t \quad , \tag{84}$$

where $\omega_m = \gamma n \mu (\hbar \omega_0 / T)$, *n* being the density of magnetic moments; $\mathbf{M}_0 = n \beta \hbar \mu \omega_0 \mathbf{c} = (\omega_m / \gamma) \mathbf{c}$ is a static magnetization. We can see now that the situation is very much similar with the nuclear magnetic resonance; in fact, the classical equations (84) apply also to the nuclear magnetic with $\mathbf{c} = \mathbf{e}_z$. We note the occurrence of the vector \mathbf{c} in the nuclear quadrupole resonance, which indicates the anisotropy of the magnetization.

The (particular) solution of equations (84) is

$$\mathbf{M} = \mathbf{c} \times \mathbf{H}(a\sin\omega t + b\cos\omega t) \quad , \tag{85}$$

where

$$a = -\frac{1}{2}\omega_m \frac{\omega - \omega_0}{(\omega - \omega_0)^2 + \alpha^2} , \ b = -\frac{1}{2}\omega_m \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2}$$
(86)

(for ω near the resonance frequency ω_0); the absorbed (mean) power (per unit volume) is given by

$$P = \overline{(\mathbf{c} \times \mathbf{H})\dot{\mathbf{M}}\sin\omega t} = -\frac{1}{2}\omega_0 b(\mathbf{c} \times \mathbf{H})^2 = \frac{1}{4}\omega_m \omega_0 (\mathbf{c} \times \mathbf{H})^2 \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} .$$
(87)

The magnetization induced by the external field $\mathbf{H} \cos \omega t$ performs a rotation about \mathbf{H} in the plane perpendicular to \mathbf{H} and \mathbf{c} with the angular frequency ω . The power computed by means of the quantum transitions of the interaction hamiltonian $H_{int}(t) = -\overrightarrow{\mu} \mathbf{H} \cos \omega t$ coincides with the absorbed power given by equation (87), providing the numerical vector \mathbf{c} is determined from the matrix elements of the magnetic moment $\overrightarrow{\mu}$ (the thermal average of the transition rate being taken). We emphasize again that the considerations made above assume the thermal equilibrium

which requires times longer than the damping (relaxation) times; for short pulses of the external field the magnetization suffers a sudden nutation and precession; the mean value can be computed by means of the perturbation theory; it is of the order $n\mu$ multiplied by a reduction factor $|H_{int}|/\hbar\Delta\omega \simeq \gamma H/\Delta\omega$, where $\Delta\omega$ is the bandwidth generated by the pulse (the inverse of the duration of the pulse); this estimation may be taken as M_0 in the damped free-oscillation solution (free induction) of the harmonic oscillator equation.

The quadrupole interaction V_2 exhibits, in general, an anisotropy; its diagonalization, which leads to eigenfrequencies denoted by ω_0 in the quasi-classical approximation, defines an ellipsoid (the principal axes of the quadratic form); the external radiofrequency field **H** may have an arbitrary orientation with respect to these axes, as expressed by the vectorial product $\mathbf{c} \times \mathbf{H}$ in equation (85). If the sample is an amorphous solid, or it is impurified, or it is a powder, etc, an average must be taken over the orientations of the sample, as given by $\overline{\sin^2 \theta}$ in the equation for the absorbed power, where θ is the angle between **H** and **c**.

An external, uniform magnetic field H_0 can be applied in NQR experiments; it produces energy levels $\hbar\omega(m) = \gamma \hbar m H_0$, which combine now with the energy levels produced by the quadrupole interaction V_2 to give the frequencies ω_0 .

Discussion and conclusions. The time dependence of the quantum-mechanical operators (Heisenberg representation) has been investigated here in the quasi-classical approximation, where the energy levels are densely distributed. It has been shown, in these circumstances, that physical quantities behave approximately as classical harmonic oscillators, with eigenfrequencies given by the difference in energy levels. Under the action of a time-dependent external field these classical oscillators absorb (dissipate) energy, which approximates the variation, with respect to the quantum numbers, of the energy absorbed in quantum-mechanical transitions. Two examples of simple quantum-mechanical systems are given in this respect (planar and spatial rigid rotators endowed with an electric dipole moment), which may serve to further enlighten the details of the approximation involved. In condensed matter the coarse graining average provides a natural means for the quasi-classical approximation. This approximation has been illustrated here for magnetic resonance and the nuclear quadrupole resonance. The quasi-classical equations of motion presented in this paper may shed further light upon the relationship between Quantum Mechanics and Classical Mechanics.

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