

Quasi-classical dynamics in condensed matter

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Abstract

It is shown that motion in normal condensed matter is a quasi-classical motion, governed, in general, by classical quasi-particles. It is also shown that the response of condensed matter to an external perturbation is similar to the response of classical harmonic oscillators driven by external fields. The quasi-classical limit of the transition rate is derived, as well as the absorption power and the quasi-classical equations of motion for an arbitrary physical quantity, for a periodic external perturbation; all these quantities exhibit a typical resonant behaviour of harmonic oscillators with characteristic frequencies (eigenfrequencies) determined by the underlying quantum dynamics. It is also shown that the response to an external perturbation at finite temperatures is that of a resonating harmonic oscillator.

Consider a sample of condensed matter consisting of composite particles (*e.g.* molecules, molecular structures, atomic nuclei, fine grains, etc). In many cases these particles move around fixed positions, as in solids, or move along classical trajectories, as in classical liquids or gases, such as, when identical, their motion is not entangled and we may consider them as being discernable. We assume that the particles are endowed with an internal dynamics, given in terms of generalized coordinates x_i , $i = 1, 2, \dots, N$ (spin included), a hamiltonian $H = \sum_{i=1}^N h_i(x_i)$ and wavefunctions $\varphi_{n_i}(x_i)$, $h_i \varphi_{n_i}(x_i) = \varepsilon_{n_i} \varphi_{n_i}(x_i)$, where N is the particle number and ε_{n_i} are the particle energies; the coordinates x_i may denote a vector associated to the i -th particle, like for translations, rotations or vibrations in the three-dimensional space, n_i denoting the corresponding quantum numbers. We assume that each particle has its own internal motion, independent of the motion of other particles, such that the total energy is $E_{\mathbf{n}} = \sum_{i=1}^N \varepsilon_{n_i}$ and the wavefunctions of the assembly of N particles can be written as $\varphi_{\mathbf{n}}(x_1, \dots, x_N) = \varphi_{\mathbf{n}}(\mathbf{x}) = \prod_{i=1}^N \varphi_{n_i}(x_i)$, where $\mathbf{n} = (n_1, n_2, \dots, n_N)$ and $\mathbf{x} = (x_1, x_2, \dots, x_N)$; since the internal coordinates are disentangled from each other, there is no need for symmetrization when particles are identical.

The number N can be the number of particles in the sample, but we can also consider an arbitrary position \mathbf{r} in the sample and $N(\mathbf{r}, t)$ particles around this position at one moment of time t ; then, the energy $E_{\mathbf{n}}$, the wavefunctions $\varphi_{\mathbf{n}}$ and the dimension of the vector \mathbf{n} depend on \mathbf{r} and t through $N(\mathbf{r}, t)$. An average over all these particles around any position \mathbf{r} at any moment of time t provides a continuum model of matter; within such a model the physical properties depend on the position \mathbf{r} and the time t . This is one of the basic assumption of all the classical physics, like elasticity, fluids, electromagnetism, statistical physics, etc.

Consider two vectors $\mathbf{n} = (n_1, \dots, n_i, \dots, n_N)$ and $\mathbf{n}' = (n_1, \dots, n'_i, \dots, n_N)$ which differ by two values n_i, n'_i of the quantum number of the i -th particle. For any reasonable difference $n'_i - n_i$ and N very large

($N \gg 1$) the two vectors \mathbf{n} and \mathbf{n}' differ slightly from each other; this holds also for the energies $E_{\mathbf{n}}$, $E_{\mathbf{n}'}$ and for the wavefunctions $\varphi_{\mathbf{n}}$, $\varphi_{\mathbf{n}'}$. For $N \gg 1$ there exists a large number of states \mathbf{n} (which grows exponentially with N), many of them degenerate, which are densely distributed in energy and wavefunctions. For instance, we can represent the energy as $E_{\mathbf{n}} = \sum_{i=1}^N \varepsilon_{n_i} = N\bar{\varepsilon}_{n_i}$ and the energy variation as $\delta E_{\mathbf{n}} = \delta \bar{\varepsilon}_{n_i}$ for some n_i , and we have $\delta E_{\mathbf{n}}/E_{\mathbf{n}} < 1/N \ll 1$ for $N \gg 1$. In quantum processes, the uncertainty $\delta E_{\mathbf{n}}$ in energy and the uncertainty δt in time duration are related through $\delta E_{\mathbf{n}}\delta t \simeq \hbar$, while $\Delta E_{\mathbf{n}} = N\delta E_{\mathbf{n}}$ and $\Delta E_{\mathbf{n}}\delta t \simeq N\hbar \gg 1$, which shows that the averaging process over a macroscopic number of particles leads to a classical dynamics. A similar "classical" uncertainty relation holds also for momentum and coordinate, as a consequence of the "coarse graining" procedure of "macroscopic" average described here.

Under these circumstances the relevant wavefunctions are superpositions of the type

$$\psi_{\mathbf{n}_0}(\mathbf{x}, t) = \int d\mathbf{n} \varphi_{\mathbf{n}}(\mathbf{x}) e^{-\frac{i}{\hbar} E_{\mathbf{n}} t} = \int d\mathbf{n} c_{\mathbf{n}}(\mathbf{x}) e^{i[\Phi_{\mathbf{n}}(\mathbf{x}) - \omega_{\mathbf{n}} t]} \quad , \quad (1)$$

where we introduced the modulus $c_{\mathbf{n}}(\mathbf{x})$ and the phase $\Phi_{\mathbf{n}}(\mathbf{x})$ of the wavefunctions $\varphi_{\mathbf{n}}(\mathbf{x})$, and denoted by $\omega_{\mathbf{n}} = E_{\mathbf{n}}/\hbar$ the frequency corresponding to the energy $E_{\mathbf{n}}$; the integration in equation (1) extends over a large domain around an arbitrary value \mathbf{n}_0 of the quantum numbers. Since the quantities in equation (1) are slowly varying functions of \mathbf{n} we may use the series expansions

$$\begin{aligned} c_{\mathbf{n}} &= c^{(0)} + \mathbf{s}c^{(1)} + s_i s_j c^{(2)} + \dots \quad , \\ \Phi_{\mathbf{n}} &= \Phi^{(0)} + \mathbf{s}\Phi^{(1)} + s_i s_j \Phi_{ij}^{(2)} + \dots \quad , \\ \omega_{\mathbf{n}} &= \omega^{(0)} + \mathbf{s}\omega^{(1)} + s_i s_j \omega_{ij}^{(2)} + \dots \quad , \end{aligned} \quad (2)$$

where $\mathbf{s} = \mathbf{n} - \mathbf{n}_0$. Equation (1) becomes

$$\psi_{\mathbf{n}_0}(\mathbf{x}, t) \simeq e^{i[\Phi^{(0)}(\mathbf{x}) - \omega^{(0)} t]} \int d\mathbf{s} [c^{(0)}(\mathbf{x}) + \dots] e^{i\mathbf{s}[\Phi^{(1)}(\mathbf{x}) - \omega^{(1)} t] + i s_i s_j [\Phi_{ij}^{(2)} - \omega_{ij}^{(2)} t]} \quad , \quad (3)$$

and, in the first approximation, we get

$$\begin{aligned} \psi_{\mathbf{n}_0}(\mathbf{x}, t) &\simeq c^{(0)}(\mathbf{x}) e^{i[\Phi^{(0)}(\mathbf{x}) - \omega^{(0)} t]} \int d\mathbf{s} e^{i\mathbf{s}[\Phi^{(1)}(\mathbf{x}) - \omega^{(1)} t]} \simeq \\ &\simeq (2\pi)^N c^{(0)}(\mathbf{x}) e^{i[\Phi^{(0)}(\mathbf{x}) - \omega^{(0)} t]} \delta(\Phi^{(1)}(\mathbf{x}) - \omega^{(1)} t) \quad ; \end{aligned} \quad (4)$$

we can see that the wavefunction superposition is a localized wavepacket with a classical trajectory given by $\Phi^{(1)}(\mathbf{x}) - \omega^{(1)} t = \text{grad}_{\mathbf{n}} \Phi(\mathbf{x}) - \omega^{(1)} t = 0$. Due to the large number of particles, the local, (free) internal motion in condensed matter is a classical motion. For instance, if the coordinates \mathbf{x} are the angles of free rotations with angular frequency ω , then the phase is $\Phi_{\mathbf{l}} = \mathbf{l}\mathbf{x}$, the energy is $E_{\mathbf{l}} = \frac{1}{2} \hbar \mathbf{l} \omega$, the derivatives in the expansions given by equations (2) are taken with respect to the components of the vector $\mathbf{l} = (\mathbf{l}_1, \mathbf{l}_2, \dots, \mathbf{l}_N)$, where \mathbf{l} is the angular momentum, and the equations of motion are the classical equations $\mathbf{x} = \omega t$ of free rotations. If the internal motion consists of vibrations, then the wavepacket does not propagate, but, instead, it reduces to a local, classical vibration; if the internal motion is rotation of electric dipoles or magnetic moments, it reduces to classical motion of spatial rotators; if the internal motion is that of electric charges and currents in atomic nuclei, then, in condensed matter, it reduced to classical motion of local charges and currents; etc.

As it is well known, the next-order approximation to equation (3) involves the quadratic terms in s_i which leads to (imaginary) gaussians with pre-factors proportional to $t^{-N/2}$ at least. For

increasing time the gaussians oscillate rapidly and the wavepacket flattens, gets delocalized, and, consequently, has a finite lifetime (and a mean free path if propagating). In this context, we may speak of classical quasi-particles which govern the internal motion in condensed matter; apart from finite lifetimes and mean free paths, the quasi-particles are characterized by arbitrary vectors \mathbf{n}_0 around which the wavepackets are constructed. In the first approximation, the wavefunctions of the quantum states which form the quasi-particles can be written as

$$\chi_{\mathbf{n}_0,s}(\mathbf{x}, t) \simeq c^{(0)}(\mathbf{x}) e^{i[\Phi^{(0)}(\mathbf{x}) - \omega^{(0)}t]} \cdot e^{is[\Phi^{(1)}(\mathbf{x}) - \omega^{(1)}t]} \quad (5)$$

(up to a normalization constant), where $c^{(0)}$, $\Phi^{(0)}$, $\Phi^{(1)}$, $\omega^{(0)}$ and $\omega^{(1)}$ depend slightly on \mathbf{n}_0 . A particular situation in this context is offered by the harmonic oscillators whose wavefunctions are real and the frequencies are linear in the quantum numbers. A superposition of such wavefunctions yields an oscillating (vibrating) localized wavepacket; however, it is important to realize that there still exists the continuum of states and energies for a macroscopic set of such N oscillators.

It is easy to see that the above considerations can be extended to interacting internal motions as well as to the external motion of the particles in (normal) condensed matter. Indeed, around any arbitrary position in a condensed matter sample we consider N particles described by a wavefunction $\varphi_{\mathbf{n}}(\mathbf{x}) = \varphi_{n_1 n_2 \dots n_N}(x_1, x_2, \dots x_N)$ with an energy $E_{\mathbf{n}} = E_{n_1 n_2 \dots n_N}$, where the quantum numbers $n_1, n_2, \dots n_N$ are allowed to take values in a reasonably large range. Under such conditions we have a large multitude of quantum states, most of them degenerate, densely distributed in energy and wavefunctions; such states form quasi-particle wavepackets whose motion, like (limited) free translations and rotations in the case of "external" motion, turns out to be a classical motion. All what is necessary for such a picture to hold is the existence of individual quantum numbers $n_1, n_2, \dots n_N$; it is not necessary to have individual wavefunctions φ_{n_i} , nor energy levels ε_{n_i} , $i = 1, 2, \dots N$, and, moreover, the symmetrization of the wavefunction for identical particles does not produce any difficulty. Consequently, the description may apply to both internal and external interacting motion of individual particles with individual quantum numbers.

Usually, the interaction between the internal degrees of freedom or the interaction between particles in their motion relative to one another in condensed matter leads to (quantum) elementary excitations, which are either quasi-particles, like quasi-electrons, polarons, etc, or collective, correlated elementary excitations like phonons, magnons, plasmons, etc. When localized, we may form locally sets of N quasi-particles and apply the above formalism of "coarse graining", which leads to a classical dynamics. When delocalized, and labelled by wavevectors \mathbf{k} , we can form superpositions of such \mathbf{k} -quasi-particles, which again leads to localized wavepackets and a classical dynamics. The collective excitations are usually propagating waves labelled by wavevectors \mathbf{k} (or global vibrations like the volume plasmons); usually, each of these \mathbf{k} -wave obeys a harmonic-oscillator dynamics, with quantum numbers $n_{\mathbf{k}}$. We can form sets of such \mathbf{k} -waves, say $\mathbf{k}_1, \mathbf{k}_2, \dots \mathbf{k}_N$, in the vicinity of some \mathbf{k} , and consider harmonic-oscillator states labelled by $n_{\mathbf{k}_1}, n_{\mathbf{k}_2}, \dots n_{\mathbf{k}_N}$, which lead again to a classical dynamics; this time, the classical quasi-particles are localized in the \mathbf{k} -space (and delocalized in the direct space, *i.e.* they retain, in general, their wavelike character; a more appropriate term for them might be classical "quasi-waves"). The wavepackets for harmonic oscillators are, in general, oscillating (vibrating, not propagating) wavepackets, but what is essential in this picture is the fact that there exist energies $E_{n_{k_1} \dots n_{k_N}} = \hbar(\omega_{k_1} n_{k_1} + \omega_{k_N} n_{k_N})$ which are densely distributed over the states n_{k_1}, n_{k_N} and, similarly, densely-distributed wavefunctions.

A notable exception from the picture described above is provided by the quantum condensed matter ("condensates"), *i.e.* quantum "liquids" like superfluids, superconductors, ferromagnetics, etc, where the particles condense macroscopically on a single quantum state (or a few), at low temperature. The adjective "normal" is used to differentiate the usual condensed matter from

the quantum condensed matter. 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.

An arbitrary physical quantity $F(\mathbf{x})$ can be defined as a local one-particle operator $F(\mathbf{x}) = \sum_{i=1}^N f_i(x_i)$ for the set of N particles discussed above and a density $F(\mathbf{x})/N$ can be employed. Suitable extensions, like two-particle operators, can be introduced similarly. Consider an external field which couples to condensed matter, like, for instance, the coupling of the electromagnetic, electric or magnetic fields to electric charges and currents, electric dipoles, or, respectively, magnetic moments.

An external perturbation $h(x, t)$ changes the unperturbed wavefunctions $\psi_n(x, t) = g_n \varphi_n(x) e^{-\frac{i}{\hbar} E_n t}$ into perturbed wavefunctions

$$\tilde{\psi}_n = \tilde{g}_n \varphi_n(x) e^{-\frac{i}{\hbar} E_n t} + \sum_k' c_{kn} \varphi_k e^{-\frac{i}{\hbar} E_k t} , \quad (6)$$

where the prime over summation means $k \neq n$; in order to simplify the notation we write simply n instead of bold \mathbf{n} for the state label and, for technical reasons, we introduce the weights g_n , $\sum_n |g_n|^2 = 1$, which help us get the density matrix. Indeed, the mean value

$$\bar{F} = \sum_{nm} (\psi_n, F \psi_m) = \sum_{nm} g_n^* g_m F_{nm} e^{i\omega_{nm} t} \quad (7)$$

of an arbitrary physical quantity F , where $\hbar\omega_{nm} = E_n - E_m$, shows that $g_n^* g_m \rightarrow \rho_{mn}$ is a representation (of pure states) for the density matrix ρ_{mn} . The statistical matrix $w_n = e^{-\beta E_n} / \sum_n e^{-\beta E_n}$, where $\beta = 1/T$ is the inverse of the temperature T , is diagonal (in the energy representation) and corresponds to $g_n^* g_n \rightarrow \rho_{nn} \rightarrow w_n$ ($\sum_n e^{-\beta E_n}$ is the free energy). The Schrodinger equation $i\hbar \frac{\partial \tilde{\psi}}{\partial t} = (H + h)\tilde{\psi}$ leads to

$$i\hbar \dot{\tilde{g}}_n = \tilde{g}_n h_{nn}(t) + \sum_k' c_{kn} h_{nk}(t) e^{i\omega_{nk} t} , \quad (8)$$

$$i\hbar \dot{c}_{kn} = \tilde{g}_n h_{kn} e^{i\omega_{kn} t} + \sum_{k'}' c_{k'n} h_{kk'} e^{i\omega_{kk'} t} ,$$

and, in the first order of the perturbation theory, we have

$$\tilde{g}_n = g_n e^{-\frac{i}{\hbar} \int^t dt' h_{nn}(t')} \simeq g_n \left[1 - \frac{i}{\hbar} \int^t dt' h_{nn}(t') \right] \quad (9)$$

and

$$i\hbar \dot{c}_{kn} = g_n e^{i\omega_{kn} t} h_{kn}(t) . \quad (10)$$

We can see that

$$(\tilde{\psi}_n, \tilde{\psi}_n) = g_n^2 , \quad (11)$$

$$(\tilde{\psi}_n, \tilde{\psi}_m) = \tilde{g}_n^* c_{nm} + \tilde{g}_m c_{mn}^* , \quad n \neq m ,$$

which shows that unitarity $\sum_n g_n^2 = 1$ is preserved (the normalization is $\sum_n (\psi_n, \psi_n) = \sum |g_n|^2 = 1$); we shall see below that the orthogonality $(\tilde{\psi}_n, \tilde{\psi}_m) = 0$, for $n \neq m$, is also preserved.

We introduce the perturbation slowly from $t = -\infty$ ("adiabatically") and get the coefficients

$$c_{kn} = -\frac{i}{\hbar} g_n \int_{-\infty}^t dt' e^{i\omega_{kn}t' + \alpha t'} h_{kn}(t') , \quad (12)$$

where $\alpha \rightarrow 0^+$; for a periodic perturbation $h(t) = h \cos \omega t$

$$c_{kn} = -\frac{g_n h_{kn}}{2\hbar} \left[\frac{e^{i(\omega_{kn} + \omega)t + \alpha t}}{\omega_{kn} + \omega - i\alpha} + \frac{e^{i(\omega_{kn} - \omega)t + \alpha t}}{\omega_{kn} - \omega - i\alpha} \right] . \quad (13)$$

The coefficient c_{kn} gives the probability for the transition $n \rightarrow k$; obviously, for $\omega_{kn} > 0$ the second term in equation (13) brings the main contribution ($\omega > 0$); for $\alpha \rightarrow 0$ we get

$$c_{kn} = -\frac{g_n h_{kn}}{2\hbar} \cdot 2\pi i \delta(\omega_{kn} - \omega) \quad (14)$$

and the transition probability per unit time (the rate of transition)

$$|c_{kn}|^2 / t = \frac{2\pi}{\hbar} |g_n|^2 |h_{kn}/2|^2 \delta(E_k - E_n - \hbar\omega) \quad (15)$$

which is the famous Fermi's "golden rule" ($\delta(\omega = 0) = t/2\pi$). Up to the weights g_n, g_k , an equal rate holds for the transition from the state k to the state n (which is an illustration of the principle of detailed balancing), the net balance depending on the original populations of states,

$$\frac{\partial |c_{kn}|^2}{\partial t} - \frac{\partial |c_{nk}|^2}{\partial t} = \frac{2\pi}{\hbar} (|g_n|^2 - |g_k|^2) |h_{kn}/2|^2 \delta(E_k - E_n - \hbar\omega) . \quad (16)$$

Making use of equation (13) we get immediately $w_m c_{mn}^* = -w_n c_{nm}$, *i.e.* the orthogonality equation (11) ($\tilde{\psi}_n, \tilde{\psi}_m) = 0$ for $n \neq m$).

In view of the slow variation with the state labels we may write $\omega_{kn} \simeq \mathbf{s}\omega^{(1)} = \omega_s$ in equation (14) and $h_{kn} \simeq h_s$, where $\mathbf{k} = \mathbf{n} + \mathbf{s}$; we may limit ourselves to the lowest ω_s . For calculating the matrix elements h_{kn} we may use the wavefunctions given by equation (5), such as $h_s = N\bar{h}_s$, \bar{h}_s being an average over the N particles ($h(x) = \sum_{i=1}^N h_i(x_i)$). The coefficient c_{kn} becomes

$$c_{kn} \simeq c_{n;s} = -\frac{i}{\hbar} g_n [2\pi (N\bar{h}_s/2) \delta(\omega_s - \omega)] ; \quad (17)$$

we can see that the temporal Fourier transform of the external interaction is included in the bracket in equation (17), corresponding to the characteristic frequency ω_s . The coefficient c_{kn} governs the response of the condensed matter sample to the external field. Usually, the weights g_n correspond to the statistical weights $w_n = e^{-\beta E_n} / \sum_n e^{-\beta E_n}$, which, for energies small in comparison with the temperature, can be approximated by $1/N$; making use of equation (16), where we retain only the $|g_n|^2$ -term, and leaving aside other weights and multiplicities we can write down the energy absorbed per unit time from the external field as

$$\frac{2\pi}{\hbar} N |\bar{h}_s/2|^2 \omega \delta(\omega_s - \omega) = \frac{1}{\hbar} N |\bar{h}_s/2|^2 \frac{2\alpha\omega}{(\omega - \omega_s)^2 + \alpha^2} , \quad \alpha \rightarrow 0 , \quad (18)$$

which is a typical resonance absorption. Equation (18) shows that the response of the assembly of N particles to an external field proceeds by the classical motion of harmonic oscillators with frequency ω_s .

For instance, an electric field E coupled to the displacement u of charges q with mass m gives a hamiltonian $\bar{h} = qEu \cos \omega t$; the quantization yields $u = \sqrt{\hbar/2m\omega_s}(a + a^+)$, and we can see that u_s corresponds to transitions $n = 0 \rightarrow n = 1$, where n is the quanta number; therefore, we have $u_s = \sqrt{\hbar/2m\omega_s}$ ($2m\omega_s u_s^2/\hbar$ is the oscillator strength) and, from equation (18), the power absorption

$$P = \frac{q^2 E^2}{4m} \frac{\alpha}{(\omega - \omega_s)^2 + \alpha^2} \quad (19)$$

per particle. This is indeed the power absorption of a classical oscillator with the equation of motion

$$m\ddot{u}_s + m\omega_s^2 u_s + m\gamma\dot{u}_s = qE \cos \omega t \quad , \quad (20)$$

where

$$u_s = \frac{qE}{2m\omega_s} \frac{\omega_s - \omega}{(\omega_s - \omega)^2 + \alpha^2} \cos \omega t + \frac{qE}{2m\omega_s} \frac{\alpha}{(\omega_s - \omega)^2 + \alpha^2} \sin \omega t \quad ; \quad (21)$$

where $\alpha = \gamma/2$; from equation (20) we get

$$\frac{d}{dt} \left(\frac{1}{2} m \dot{u}_s^2 + \frac{1}{2} m \omega_s^2 u_s^2 \right) + m\gamma\dot{u}_s^2 = qE\dot{u}_s \cos \omega t \quad (22)$$

and the (average) absorbed power

$$P = m\gamma \overline{\dot{u}_s^2} = \frac{q^2 E^2}{4m} \frac{\alpha}{(\omega - \omega_s)^2 + \alpha^2} \quad , \quad (23)$$

which coincides with equation (19).

The matrix elements of an arbitrary quantity F between perturbed states given by equation (6) are

$$\begin{aligned} \tilde{F}_{nm} &= (\tilde{\psi}_n, F \tilde{\psi}_m) = \\ &= \tilde{g}_n^* \tilde{g}_m e^{i\omega_{nm}t} F_{nm} + \sum_k' [\tilde{g}_n^* F_{nk} c_{km} e^{i\omega_{nkt}} + \tilde{g}_m F_{km} c_{kn}^* e^{i\omega_{kmt}}] \quad , \end{aligned} \quad (24)$$

or, by making use of the coefficients given by equation (13),

$$\begin{aligned} \tilde{F}_{nm} &= g_n^* g_m \left[1 - \frac{i}{\hbar} \int^t dt' (h_{mm} - h_{nn}) \right] e^{i\omega_{nm}t} F_{nm} - \\ &- g_n^* g_m \frac{e^{i\omega_{nm}t}}{2\hbar} \sum_k' \left[\frac{F_{nk} h_{km}}{\omega_{km} + \omega - i\alpha} + \frac{h_{nk} F_{km}}{\omega_{kn} - \omega + i\alpha} \right] e^{i\omega t} - \\ &- g_n^* g_m \frac{e^{i\omega_{nm}t}}{2\hbar} \sum_k' \left[\frac{F_{nk} h_{km}}{\omega_{km} - \omega - i\alpha} + \frac{h_{nk} F_{km}}{\omega_{kn} + \omega + i\alpha} \right] e^{-i\omega t} \quad , \end{aligned} \quad (25)$$

where

$$1 - \frac{i}{\hbar} \int^t dt' (h_{mm} - h_{nn}) = 1 - \frac{i}{\hbar\omega} (h_{mm} - h_{nn}) \sin \omega t \quad ; \quad (26)$$

we can see the occurrence of the (unperturbed) density matrix $g_n^* g_m \rightarrow \rho_{mn}$.

According to equation (25) the evolution of a quantity F associated to two states n and m proceeds by transitions which involve intermediate states labelled by k ("indirect processes"). In view of the continuum of states in condensed matter the main contribution comes from those k -states lying in the vicinity of the n, m -states ("direct processes"). We write

$$\begin{aligned} \omega_{km} &= \omega_{nm} + \omega_{kn} = \omega_{nm} + (\mathbf{k} - \mathbf{n})\omega_{1n} + \dots \quad , \\ \omega_{kn} &= \omega_{mn} + \omega_{km} = -\omega_{nm} + (\mathbf{k} - \mathbf{m})\omega_{1m} + \dots \end{aligned} \quad (27)$$

and neglect the $\omega_{1n,m}$ -terms in equation (25); we get

$$\begin{aligned} \tilde{F}_{nm} &\simeq g_n^* g_m \left[1 - \frac{i}{\hbar\omega} (h_{mm} - h_{nn}) \sin \omega t \right] e^{i\omega_{nm}t} F_{nm} - \\ &- g_n^* g_m \frac{1}{2\hbar} [F, h]_{nm} \left[\frac{e^{i(\omega_{nm}+\omega)t}}{\omega_{nm}+\omega} + \frac{e^{i(\omega_{nm}-\omega)t}}{\omega_{nm}-\omega} \right] , \end{aligned} \quad (28)$$

or

$$\begin{aligned} \tilde{F}_{nm} &\simeq g_n^* g_m \left[1 - \frac{i}{\hbar} (h_{mm} - h_{nn}) \cos \omega t \right] e^{i\omega_{nm}t} F_{nm} + \\ &+ g_n^* g_m \left[1 - \frac{i}{\hbar\omega} (h_{mm} - h_{nn}) \sin \omega t \right] i\omega_{nm} e^{i\omega_{nm}t} F_{nm} + \\ &+ g_n^* g_m \frac{i}{\hbar} e^{i\omega_{nm}t} [h(t), F]_{nm} . \end{aligned} \quad (29)$$

Leaving aside the weight factors we can write

$$\dot{\tilde{F}}_{nm} \simeq i\omega_{nm} e^{i\omega_{nm}t} F_{nm} + \frac{i}{\hbar} e^{i\omega_{nm}t} [h(t), F]_{nm} \quad (30)$$

for the quasi-classical motion of a quantity F in condensed matter subjected to a perturbation h ; this equation can be obtained directly from Schrodinger's equation $i\hbar \frac{\partial \psi}{\partial t} = [H + h(t)]\psi$, by taking the matrix elements $(\psi', F\psi)$ within the approximation used above. Indeed, we get

$$i\hbar \frac{\partial}{\partial t} (\psi', F\psi) = (\psi', [F, H + h(t)]\psi) , \quad (31)$$

or, with $\psi = e^{-\frac{i}{\hbar}Ht}\Phi$,

$$\frac{\partial}{\partial t} (\Phi', e^{\frac{i}{\hbar}Ht} F e^{-\frac{i}{\hbar}Ht} \Phi) = \frac{i}{\hbar} (\Phi', e^{\frac{i}{\hbar}Ht} [H, F] e^{-\frac{i}{\hbar}Ht} \Phi) + \frac{i}{\hbar} (\Phi', e^{\frac{i}{\hbar}Ht} [h(t), F] e^{-\frac{i}{\hbar}Ht} \Phi) . \quad (32)$$

Making use of equation (6) we get

$$\Phi_n = \varphi_n + \sum_k^l c_{kn} \varphi_k \quad (33)$$

for $g_n = 1$ and

$$\begin{aligned} \frac{i}{\hbar} (\Phi_n, e^{\frac{i}{\hbar}Ht} [H, F] e^{-\frac{i}{\hbar}Ht} \Phi_m) &= i\omega_{nm} e^{i\omega_{nm}t} F_{nm} - \frac{i}{2\hbar} e^{i\omega_{nm}t} \sum_k' \left[\frac{\omega_{nk} F_{nk} h_{km}}{\omega_{km} + \omega - i\alpha} + \frac{\omega_{km} F_{km} h_{nk}}{\omega_{kn} - \omega + i\alpha} \right] e^{i\omega t} - \\ &- \frac{i}{2\hbar} e^{i\omega_{nm}t} \sum_k' \left[\frac{\omega_{nk} F_{nk} h_{km}}{\omega_{km} - \omega - i\alpha} + \frac{\omega_{km} F_{km} h_{nk}}{\omega_{kn} + \omega + i\alpha} \right] e^{-i\omega t} ; \end{aligned} \quad (34)$$

for k close to n in terms containing ω_{km} and for k close to m in terms containing ω_{kn} the quantity given by equation (34) in brackets is zero; from equation (32) we are left with

$$\frac{\partial}{\partial t} (\Phi_n, e^{\frac{i}{\hbar}Ht} F e^{-\frac{i}{\hbar}Ht} \Phi_m) \simeq i\omega_{nm} e^{i\omega_{nm}t} F_{nm} + \frac{i}{\hbar} (\varphi_n, e^{\frac{i}{\hbar}Ht} [h(t), F] e^{-\frac{i}{\hbar}Ht} \varphi_m) , \quad (35)$$

which is equation (30) for $g_n = 1$.

In equation (30) we can absorb the exponential factors $e^{i\omega_{nm}t}$ in F_{nm} , which becomes now time-dependent; in addition, we may limit ourselves to states lying close to n or m in the commutator, such as equation (30) can be written now as

$$\dot{F}_{nm} \simeq i\omega_{nm} F_{nm} + \frac{i}{\hbar} [h(t), F]_{nm} , \quad (36)$$

where we recognize the equation of motion $\dot{F} = \frac{i}{\hbar}[H + h(t), F]$. Moreover, since the evolution of a classical quantity is governed by Poisson's bracket $\dot{F} = \{H, F\} = \frac{\partial F}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial F}{\partial p} \frac{\partial H}{\partial q}$, where q and p are the canonical coordinate and, respectively, momentum, writing $p = -i\hbar \frac{\partial}{\partial q}$, we get

$$\begin{aligned} F = \{H, F\} &= \frac{\partial H}{\partial p} \frac{\partial F}{\partial q} - \frac{\partial F}{\partial p} \frac{\partial H}{\partial q} = \frac{i}{\hbar} \left[\frac{\partial H}{\partial p} (pF) - \frac{\partial F}{\partial p} (pH) \right] = \\ &= \frac{i}{\hbar} [(\Delta H)F - (\Delta F)H] = \frac{i}{\hbar} [HF - FH] = \frac{i}{\hbar} [H, F] ; \end{aligned} \quad (37)$$

therefore, we can write equation (36) as

$$\dot{F}_{nm} \simeq i\omega_{nm}F_{nm} + \{h(t), F\} = i\omega_{nm}F_{nm} + \left(\frac{\partial F}{\partial t} \right)_{cl;h} , \quad (38)$$

which indicates a classical dynamics for F ; we can pass now to the classical description, and prefer to use $\omega_{nm} \simeq -\omega_s$; we get

$$\dot{F} \simeq -i\omega_s F + \left(\frac{\partial F}{\partial t} \right)_{cl;h} , \quad \ddot{F} + \omega_s^2 F = \left(\frac{\partial^2 F}{\partial t^2} \right)_{cl;h} , \quad (39)$$

which is the equation of motion for a harmonic oscillator with the characteristic frequency ω_s , driven by an external (generalized) force generated by the perturbation $h(t)$.

From equation (24) we find the mean value

$$\begin{aligned} \bar{F} &= \sum_{nm} (\tilde{\psi}_n, F \tilde{\psi}_m) = \\ &= \sum_{nm} [\tilde{g}_n^* \tilde{g}_m + \sum_k' (\tilde{g}_n^* c_{mk} + \tilde{g}_m c_{nk}^*)] e^{i\omega_{nm}t} F_{nm} , \end{aligned} \quad (40)$$

hence the perturbed density matrix

$$\begin{aligned} \tilde{\rho}_{mn} &= \rho_{mn} \left[1 - \frac{i}{\hbar} \int^t dt' (h_{mm} - h_{nn}) \right] - \\ &- \frac{1}{2\hbar} \sum_k' \rho_{kn} h_{mk} \left[\frac{e^{i(\omega_{mk} + \omega)t}}{\omega_{mk} + \omega - i\alpha} + \frac{e^{i(\omega_{mk} - \omega)t}}{\omega_{mk} - \omega - i\alpha} \right] + \\ &+ \frac{1}{2\hbar} \sum_k' \rho_{mk} h_{kn} \left[\frac{e^{i(\omega_{kn} + \omega)t}}{\omega_{kn} + \omega - i\alpha} + \frac{e^{i(\omega_{kn} - \omega)t}}{\omega_{kn} - \omega - i\alpha} \right] ; \end{aligned} \quad (41)$$

indeed, this is the equation of motion $\dot{\tilde{\rho}} = \frac{i}{\hbar} [\rho, e^{\frac{i}{\hbar} H t} h(t) e^{-\frac{i}{\hbar} H t}]$ for the density matrix. For a diagonal unperturbed density matrix we get $\bar{F} = \sum_{nm} \tilde{\rho}_{mn} F_{nm}$ and

$$\begin{aligned} \tilde{\rho}_{mn} &= \rho_{mm} \delta_{mn} + \\ &+ \frac{1}{2\hbar} (\rho_{mm} - \rho_{nn}) h_{mn} \left[\frac{e^{i\omega t}}{\omega_{mn} + \omega - i\alpha} + \frac{e^{-i\omega t}}{\omega_{mn} - \omega - i\alpha} \right] . \end{aligned} \quad (42)$$

Using the statistical matrix $\rho_{mm} = w_m = e^{-\beta E_m} / \sum_m e^{-\beta E_m}$ we can compute the quasi-classical response

$$\delta \bar{F} = \sum_{ms} \beta \omega_s w_m \frac{\omega_s \cos \omega t + i\omega \sin \omega t}{\omega^2 - \omega_s^2 - 2i\alpha \omega_s} h_s F_s \quad (43)$$

of a quantity F due to the external perturbation for densely-distributed states $\mathbf{n} = \mathbf{m} + \mathbf{s}$; since $\omega_{-s} = -\omega_s$ we get

$$\delta \bar{F} = \beta \frac{2(\omega^2 - \omega_s^2) \omega_s^2 \cos \omega t - 4\alpha \omega \omega_s^2 \sin \omega t}{(\omega^2 - \omega_s^2)^2 + 4\alpha^2 \omega_s^2} h_s F_s . \quad (44)$$

where we must change the sign of α in order to account for damping. Comparing with equation (21) we can see that the response is that of a harmonic oscillator acted by an external periodic perturbation.

In conclusion, one may say that a "coarse graining", *i.e.* a (local) "macroscopic" average, in (normal) condensed matter leads to a classical description of both internal and external motion. In general, classical quasi-particles are relevant for such a motion, localized either in the direct space (for quantum quasi-particles) or in the \mathbf{k} -space for collective (wavelike) excitations. The coupling and the response of the normal condensed matter to external fields is described in terms of classical harmonic oscillators, the only remnants of the quantum nature being characteristic frequencies and oscillator strengths. The quasi-classical limit of the transition rate, absorbed power, equation of motion of arbitrary quantities, density and statistical matrices have been derived, all exhibiting typical features of resonant dynamics of harmonic oscillators.