Perturbation-theory calculations of two-quantum relaxation processes

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The causes for the discrepancies between the transition rates in the balance equations for atomic level populations and the transition probabilities per unit time calculated with the usual perturbation-theory formulas are investigated. It is shown that the structure of the probability for a two-quantum transition from a level n to a level k, involving an intermediate level m (to which a real transition from the initial level is possible), is such that it can be incorporated into the standard perturbation-theory formula only for times considerably exceeding the lifetime γ_m^{-1} of the mth level. In this case "resonance" contributions to the transition probability have time to develop. For times $t \ll \gamma_m^{-1}$ the "resonance" contributions are negligible.

1. A detailed analysis of the behavior of an atom with discrete energy levels, interacting with a phonon field which is in thermal equilibrium at constant temperature T, leads to the following balance equations for the population of atomic levels[1]:

$$d\sigma_i/dt = \sum_j [(\sigma_j - \sigma_j^0) W_{ji} - (\sigma_i - \sigma_i^0) W_{ij}] \tag{1}$$

where σ_j^0 is the equilibrium value of population. In the first-order approximation in interaction V the relaxation parameters W_{ij} are in full accord with the transition probabilities per unit time given by the perturbation theory. For simplicity we confine ourselves to a system with three consecutive levels k, n, and m.

Deviations from the standard perturbation theory appear already when we consider two-phonon transitions, if the total splitting of the levels k, n, and m does not exceed the Debye energy. A calculation of the transition probability per unit time between the levels n and k with absorption of one phonon (λ) and emission of another (σ) by using the formula[2]

$$w_{nk} = 2\pi\hbar^{-2} \sum_{\lambda\sigma} |U_{k\lambda\sigma,n}(E_{k\lambda\sigma})|^2 \delta(E_{k\lambda\sigma} - E_n) \tag{2}$$

(here $\hat{U}(\omega)$ is the Laplace transform of the time-development operator $\hat{S}$ of the system, $\psi(t) = S(t)\psi(0)$, see (8) below) leads to the conclusion that the essential contribution to the probability is due to the "resonance" phonons with frequencies $\omega_\lambda \approx \omega_{mn}$, and $\omega_\sigma \approx \omega_{mk}$[3,4]. However, the contribution of these phonons to the relaxation parameters of (1), calculated in the same approximation proves to be negligible[1,5].

An apparent contradiction arises here because

$$w_{nk} = d\sigma_k/dt \tag{3}$$

for the time intervals

$$w_{nk}^{-1} \gg t \gg \omega_{nk}^{-1} \tag{3a}$$

at the initial condition $\sigma_n(0) = 1$; under this condition and at small times, Eq. (1) assumes the same form (3):

$$W_{nl} = d\sigma_l/dt, \quad l = m,\ k, \tag{4}$$

if the detailed-balancing conditions $\sigma_j^0 W_{ji} = \sigma_i^0 W_{ij}$ are fulfilled. To clarify the situation it is necessary to compare more carefully the conditions for the validity of (1) with those for the applicability of (2). Such an analysis is interesting also from the point of view of the general theory of quantum transitions.

2. The balance equations (1) are obtained by averaging the equation for the density matrix of an atom and the phonon field over the phonon states. The thermal-equilibrium assumption for the phonons means that during the time $\tau_c \equiv \omega_c^{-1}$ of the relaxation of excitations in the phonon system the atom experiences no marked changes, i.e.

$$W_{ij}\tau_c \ll 1. \tag{5}$$

In the general case τ_c must be understood to be the longest lifetime of the phonons involved in the relaxation. For the validity of (1) it is moreover necessary that the levels m, n, and k were sufficiently well resolved, i.e. that the widths of these levels, which we can estimate by using W_{ij}, were much less than the corresponding splittings.

The above conditions can be jointly represented by the inequalities:

$$W_{ij} \ll \omega_c,\ |\omega_{ij}|. \tag{6}$$

It is clear now that (1) can be reduced to (4) with the initial condition $\sigma_n(0) = 1$ for the times t satisfying

$$W_{ij}^{-1} \gg t \gg \tau_c,\ |\omega_{ij}|^{-1}. \tag{7}$$

It might be well to note that these inequalities involve all the relaxation parameters W_{ij} and not just W_{nk} or W_{nm}.

3. Now let us analyze the derivation of (2) and (3). According to Heitler[2] the amplitude of the state N of the whole system atom plus phonons, which was initially in the state 0, at the time t is given by

$$b_N(t) = \frac{i}{2\pi\hbar} \int_{-\infty+i\varepsilon}^{\infty+i\varepsilon} \exp[i(\omega_N - \omega)t] \frac{U_{N0}(\omega)\, d\omega}{(\omega - \omega_N)[\omega - \omega_0 + {}^1/_2 i\Gamma(\omega)]}, \tag{8}$$

where $E_N = \hbar\omega_N$ is the energy of the state N,

$$-\frac{i}{2}\hbar\Gamma(\omega) = V_{00} + \sum_{M \neq 0} \frac{V_{0M} U_{M0}(\omega)}{\hbar(\omega - \omega_M)}, \tag{9}$$

and V is the energy of the atom-phonon interaction. The real part of Γ determines the width of the initial level of the atom.

Evidently, without additional restrictions (8) can be rewritten in the form

$$b_N(t) = \frac{U_{N0}(\omega_N)}{\hbar(\omega_N - \omega_0')} + \frac{U_{N0}(\omega_0')}{\hbar(\omega_0' - \omega_N)} \exp[i(\omega_N - \omega_0')t], \quad \omega_0' = \omega_0 - {}^1/_2 i\Gamma, \tag{10}$$

which in the limit as $\Gamma \to 0$ and $t \to \infty$ yields (2) and (3), provided only that the matrix $\hat{U}(\omega)$ itself has no singularities. However, this is not the case when the processes like resonance fluorescence are studied.

Indeed, let the Hamiltonian for the interaction between the atom and the phonons be

$$V=\sum_\alpha V^\alpha Q^\alpha, \tag{11}$$

where the operators V^α act only on the atomic states, and Q^α are linear in the lattice variables. The equation for the matrix $\hat{U}$, which is the Laplace transform of the Schrödinger equation, is

$$U_{N0}(\omega)=\langle N|V|0\rangle+\sum_{M\neq0}\frac{\langle N|V|M\rangle U_{M0}(\omega)}{\omega-\omega_M}, \tag{12}$$

In the case when the final state differs from the initial state by two phonons ($N = k\lambda\sigma$) its approximate solution is given by[4]

$$U_{k\lambda\sigma,n}=\frac{\langle k\lambda\sigma|V|m\lambda\rangle\langle m\lambda|V|n\rangle}{\omega-\omega_{m\lambda}+{}^1/{}_2 i\gamma_m}+\frac{\langle k\lambda\sigma|V|m\sigma\rangle\langle m\sigma|V|n\rangle}{\omega-\omega_{m\sigma}}, \tag{13}$$

where

$$\frac{1}{2}\gamma_m(\omega)=i\sum_{p=k,n;\sigma}\frac{\langle m\lambda|V|p\lambda\sigma\rangle\langle p\lambda\sigma|V|m\lambda\rangle}{\omega-\omega_{p\lambda\sigma}}. \tag{14}$$

We see that the term

$$\frac{\langle k\lambda\sigma|V|m\lambda\rangle\langle m\lambda|V|n\rangle\exp[i(\omega_{k\lambda\sigma}-\omega_{m\lambda}+{}^1/{}_2 i\gamma_m)t]}{(\omega_{m\lambda}-\omega_{k\lambda\sigma}-{}^1/{}_2 i\gamma_m)(\omega_{m\lambda}-\omega_n+{}^1/{}_2 i(\Gamma-\gamma_m))}. \tag{15}$$

appears in addition to the right-hand side of the expression (10) for $b_N(t)$. (The pole $\omega = \omega_{m\sigma}$ need not be considered since the corresponding term vanishes at $t \gg \omega_{mk}^{-1}$.) In order to be able to neglect this term in calculating $d|b_{k\lambda\sigma}|^2/dt$, i.e. to obtain the usual result (2), the following additional condition must be fulfilled

$$\operatorname{Re}\gamma_m t\gg1. \tag{16}$$

But the quantity $\operatorname{Re}\gamma_m$ (in the following we shall omit the real part symbols) measures the broadening at the intermediate level m, and the above condition therefore requires sufficiently large width of this level, at any rate such that $\gamma_m \gg \Gamma$.

Thus the whole set of conditions for the validity of the relations (2) and (3), when applied to processes like resonance fluorescence, appears as follows:

$$\Gamma^{-1}\gg t\gg\gamma_m^{-1},\ |\omega_{ij}|^{-1}. \tag{17}$$

These conditions differ substantially from those (7) for the equation (4), and hence there is no reason to expect the identity of content of (3) and (4).

4. If we now calculate the transition probability per unit time under the constraint (7) on time t, which is possible if the breadth of m is small compared to all the other splittings, we must obtain an expression free from contributions of the "resonance" phonons. This is interesting enough to at least sketch the calculation. It is obvious that the contribution of (15) must now be taken into account, and after some simple algebra we obtain the following expression for the transition probability:

$$\frac{d}{dt}|b_{k\lambda\sigma}|^2=-\frac{i|A|^2}{\omega_1+i\Gamma}\left\{e^{-2\Gamma t}\left|\frac{e^{i(\omega_2-i\varepsilon)t}-1}{\omega_2-i\varepsilon}\right|^2\right.$$
$$\left.-e^{-i(\omega_1-i\Gamma)t}\frac{1-e^{i(\omega_2+i\varepsilon)t}}{\omega_2+i\varepsilon}\frac{1-e^{-i(\omega_2-\omega_1-i\gamma)t}}{\omega_2-\omega_1-i\gamma}\right\}+\text{c.c.} \tag{18}$$

Here

$$\varepsilon=\gamma-\Gamma,\quad A=\langle k\lambda\sigma|V|m\lambda\rangle\langle m\lambda|V|n\rangle,$$
$$\omega_1=\omega_{kn}+\omega_\sigma-\omega_\lambda,\quad \omega_2=\omega_{mn}-\omega_\lambda$$

and the factor 1/2 at γ and Γ is omitted for brevity. We have also omitted the second terms in the expression (13) for $U_{k\lambda\sigma,n}$ because they add no singularities to the calculation of the resonance fluorescence processes, and their contributions are small in the resonance phonons region.

In order to get the total probability of the atomic transition n → k, the expression (18) must be averaged over the propagation directions of the phonons, and over their polarizations and frequencies. Since the calculations are carried out at small Γ one can use the following approximation (see[2]):

$$\frac{1}{\omega_1+i\Gamma}\approx\frac{P}{\omega_1}-i\pi\delta(\omega_1),\quad \frac{e^{-i\omega_1 t}}{\omega_1+i\Gamma}\approx-2\pi i\delta(\omega_1), \tag{19}$$

where P stands for the principal value, and (18) reduces to

$$\frac{d}{dt}|b_{k\lambda\sigma}|^2=2\pi|A|^2\left|\frac{e^{i(\omega_2+i\gamma)t}-1}{\omega_2+i\gamma}\right|^2\delta(\omega_1). \tag{20}$$

The novelty of this expression compared to the usual formula (2) is the presence of the exponent. As a result the integration of (20) over ω_2 contains no singularities however small γ be.

Thus, we come to a conclusion that at times γ^{-1}, $\Gamma^{-1} \gg t \gg |\omega_{ij}^{-1}|$ the contribution of the resonance phonons to the atomic transition probability from state n to state k is negligible. This contribution becomes essential only at large times $\Gamma^{-1} \gg t \gg \gamma^{-1}$, $|\omega_{ij}|^{-1}$. The latter inequalities are possible only in the case when the width of the intermediate level much exceeds that of the initial level. However, this is precisely the case when the processes like resonance fluorescence are dominant in the spin-lattice relaxation. In the study of these relaxation processes the balance equation approach cannot be regarded as entirely equivalent to the quantum-mechanical perturbation theory, but under the same conditions they both lead to the same results.

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