

## On relaxation times

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**Abstract.** The physical background of the relation  $T_2 = 2T_1$  between the transverse and longitudinal relaxation times in atomic and molecular spectroscopy is discussed.

In a recent paper [1] we reported the relationship  $T_2 = 2T_1$  for the characteristic times  $T_1$  of ‘longitudinal’ relaxation of the diagonal elements of the density matrix and the ‘transverse’ relaxation times  $T_2$  of the off-diagonal elements of the density matrix of a quantum system with two nondegenerate energy levels (see also Ref. [2]). The times  $T_1$  and  $T_2$  describe, respectively, the free relaxation of the level population difference to the equilibrium value and the free relaxation of the polarization to the zero value. The calculation was performed for two exactly solvable models of collision and field relaxation for the limiting case of weak relaxation perturbations.

This almost self-evident result, however, disagrees with the widespread notion that the baseline for simple physical situations (a ‘zero approximation’ of a sort for the analysis of the more complicated spectroscopic models) is the relationship  $T_1 = T_2$ . It is this case that is usually analyzed as an instructive example [3], or used for getting various estimates.

The issue is by no means purely academic. The analysis of experimental data in optical and microwave spectroscopy always involves if only the discussion of the possible causes of discrepancies between the measurement results and those found by calculations for a refined two-level model. Such causes include the degeneration of the excited level, the commencement of the regime of ‘strong collisions’ at high temperatures, the properties of the buffer gas, etc. It goes without saying that physically justified assumptions leading to reasonable estimates can only rely on sound knowledge of the properties of a simplified physico-mathematical model. We are not aware of any methodologically reliable direct measurements of the ratio  $T_2/T_1$  under standard conditions, but a comparative analysis of the vast body of concomitant scientific literature goes beyond the scope of this brief letter.

Consider a quantum system with two energy levels  $E_1$  and  $E_2$ . If it is subjected to a periodic electric field with cyclic frequency  $\omega$ , then the relaxation equations for the density matrix  $\langle n|\rho|m\rangle$  after conventional simplifications [4] reduce to

the standard form

$$\frac{d}{dt}\langle 1|\rho|2\rangle - i\frac{V}{2}r \exp(i\epsilon t) = -\frac{\langle 1|\rho|2\rangle}{T_2}, \quad (1)$$

$$\frac{dr}{dt} + 2V \operatorname{Im}[\langle 1|\rho|2\rangle \exp(-i\epsilon t)] = -\frac{r-r_0}{T_1}, \quad (2)$$

where  $r = \langle 1|\rho|1\rangle - \langle 2|\rho|2\rangle$ ,  $\epsilon = \omega - \omega_0$ ,  $\omega_0 = E_2 - E_1$ , and  $V$  is the energy amplitude of perturbation brought in by the exciting field (we use the system of units in which  $\hbar = 1$ ). The equilibrium value of the difference  $r_0$  between relative populations of the ground state and the excited state depends on the energy temperature  $\theta$  in the usual way:  $r_0 = \tanh(\omega_0/2\theta)$ .

For calculation of the shape of the absorption line in the quasi-stationary regime we introduce the variable  $\tilde{\rho} = \langle 1|\rho|2\rangle \exp(-i\epsilon t)$ , whose imaginary part is a convenient dimensionless function characterizing the rate of absorption of the field energy. Straightforward algebra under the assumption of weak saturation  $V^2 T_1 T_2 \ll 1$  leads to the simple formula

$$\operatorname{Im} \tilde{\rho} = \frac{VT_2 r_0}{2(1 + \epsilon^2 T_2^2)}. \quad (3)$$

We see that when the field is weak enough, the absorption line has a Lorentzian shape, and its width is determined by the time of transverse relaxation  $T_2$ .

The physical meaning of the parameters  $T_1$  and  $T_2$  becomes evident when we consider the free relaxation of variables  $r$  and  $\langle 1|\rho|2\rangle$  at  $V = 0$ . For this situation, from Eqns (1) and (2) one finds

$$r(t) = r(0) \exp\left(-\frac{t}{T_1}\right) + r_0 \left[1 - \exp\left(-\frac{t}{T_1}\right)\right], \quad (4)$$

$$\langle 1|\rho(t)|2\rangle = \langle 1|\rho(0)|2\rangle \exp\left(-\frac{t}{T_2}\right). \quad (5)$$

After recalculation from a single atom to a unit of gas volume, these variables characterize the density of the excitation energy and the amplitude of polarization of the medium, respectively.

Indeed, in the appropriately selected representation, the matrix of the electric dipole moment can be written in the form

$$\langle n|D|m\rangle = d_0 \begin{pmatrix} 0 & \exp(-i\omega_0 t) \\ \exp(i\omega_0 t) & 0 \end{pmatrix}, \quad (6)$$

where  $d_0$  is the numerical constant of an elementary dipole for atoms of a given sort. The dipole moment of the atom is calculated as the mean value of the relevant operator

$$\begin{aligned} \langle D(t) \rangle &= \operatorname{Sp} \hat{\rho} \hat{D} = \sum_{n,m} \langle n|\rho|m\rangle \langle m|D|n\rangle \\ &= d_0 [\langle 1|\rho(t)|2\rangle \exp(i\omega_0 t) + \text{c. c.}] \sim \exp\left(-\frac{t}{T_2}\right). \end{aligned} \quad (7)$$

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Thus, the parameters  $T_1$  and  $T_2$  are the characteristic times taken by the density of energy and the amplitude of polarization to freely relax to their equilibrium and zero values, respectively.

The relation  $T_1 = 2T_2$  is not a specifically quantum relation. Consider, for example, a medium of charged dissipative oscillators, employed in the elementary theory of dispersion. In this case the above relation is self-evident. It simply derives from the fact that the energy is a quadratic function of the canonical variables, whereas the polarization is a linear function of the oscillator coordinates.

The quantum version of this relation is not our invention. In the book of W Heitler [5], the perturbation theory was used for calculating the Lorentzian shape of the absorption–emission line for a two-level atom in the presence of radiation friction:

$$L(\omega) = \frac{1}{(\omega - \omega_0)^2 + \gamma^2/4}, \quad (8)$$

where  $\gamma = 1/T_1$  is the inverse time of the atom's stay in the excited state. Comparison of Eqns (8) and (3) reveals that the relation  $T_2 = 2T_1$  holds in this case too.

It looks like the arguments developed above leave no place for doubt; nevertheless, the belief in the ‘priority’ of the relation  $T_2 = T_1$  is quite common. The most obvious ground for this belief is the customary resort to the semiphenomenological Kubo equation for the density matrix [6, 7]. As applied to the two-level model under consideration, this equation can be written in the form

$$\frac{d}{dt} \langle n|\rho|m \rangle + i \langle n|[V, \rho]|m \rangle = -\frac{\langle n|\rho|m \rangle - \langle n|\rho_0|m \rangle}{\tau}, \quad (9)$$

where  $\hat{V}$  is the operator of perturbation by the exciting field, and  $\langle n|\rho_0|m \rangle = Z^{-1} \exp(-E_n/\theta) \delta_{nm}$  is the equilibrium density matrix.

According to Eqn (9), the diagonal and off-diagonal elements of the density matrix in the absence of an external field relax to equilibrium with one and the same characteristic time  $\tau = T_1 = T_2$ . As a first estimate, the value of  $\tau$  is usually taken equal to the free running time. Then, based on the results of correlation between calculated results and those of the spectroscopic experiment, this value usually has to be made several times larger.

In all likelihood, the traditional trust in the Kubo equation rests on its being structurally similar to the Boltzmann kinetic equation in the  $\tau$ -approximation [7]:

$$\frac{\partial f}{\partial t} = \sum_{k=1}^3 \left( v_k \frac{\partial f}{\partial x_k} + \frac{F_k}{m} \frac{\partial f}{\partial v_k} \right) = -\frac{f - f_0}{\tau}, \quad (10)$$

where  $f(x_k, v_k)$  is the one-particle distribution function,  $x_k$  and  $v_k$  are the components of coordinates and velocities, and  $\mathbf{F}(x_k, v_k)$  is the macroscopic field of force. The function  $f_0$  is the locally equilibrium biased Maxwell distribution with respect to velocities, normalized to the local density of the weakly nonequilibrium gas.

Equation (10), notwithstanding the obviously phenomenological nature of its relaxation term, correctly describes the relation between viscosity and thermal conductivity of a gas medium and allows the formulation of the equations of macroscopic gas dynamics. Applied to an electron gas in plasma, this equation permits the study of the behavior of

complex conductivity, spatial dispersion of waves, etc. In short, this equation is relevant to a broad class of atomic, molecular and electron processes, and its validity has more than once been proven by experiment.

Compared to that, the repute of the Kubo equation has much less substance behind it, and is mostly based on the outward analogy and seeming simplicity. Sometimes thrown in is the formally treated principle of correspondence between quantum and classical equations. We believe that application of this principle to phenomenological mathematical constructions is not sufficiently justified. As shown above, a microphysical treatment of the principle of correspondence leads to a different result.

Of course, the final arbiter is the ‘pure’ experiment. Paradoxically, the staging of such an experiment is prevented by the *a priori* anticipation of the result  $T_2 = T_1$  by many experimenters within the available accuracy, given that it is not that simple to ensure the ‘purity’ of the experiment. One has to select a spectroscopic object with a nondegenerate quantum transition, make sure that the relaxation perturbations are small, and generate the exciting pulses with perfectly steep fronts.

However, the theoretical arguments developed above convince us that the result of such an experiment will most likely be  $T_2/T_1 \approx 2$ . This allows us to formulate the following preliminary conclusions:

- (1) the relationship  $T_2 = 2T_1$  is basic for simple models of relaxation;
- (2) the Kubo equation gives an exaggerated rate of transverse relaxation;
- (3) formal nonphysical application of the principle of correspondence may be misleading.

We hope that this brief analysis will help the readers to avoid misconceptions which, multiplied by the human factor, may be quite impeding to the progress of science.

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