# RELAXATION IN A DISCRETE SPECTRUM IN THE APPROXIMATION OF INSTANTANEOUS COLLISIONS

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## Abstract

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# RELAXATION IN A DISCRETE SPECTRUM IN THE APPROXIMATION OF INSTANTANEOUS COLLISIONS

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The calculation of transition probabilities and phase shifts that broaden spectral lines is usually based on consideration of an individual collision with subsequent averaging over impact parameters ($^1$). At the same time, the full information about the behavior of the system under the simultaneous action of external fields and numerous collisions replacing one another can be obtained only if one has a kinetic equation for the density matrix $\rho$ representing the system. Such an equation was obtained ($^2$) under the assumption that all collisions are instantaneous and that each completely restores the equilibrium disturbed during the free-flight time $\tau_0$: $\rho$ passes into

$$\rho_0 = \frac{1}{z} \exp\left[-\frac{\hat{H}_0}{kT}\right].$$

In fact, a single collision is not always sufficient to restore the equilibrium population of the levels or to destroy the phase correlation between them. In addition, the phenomenological introduction of $\tau_0$ does not make it possible to establish a connection between the kinetic theory and the microscopic calculation of the relaxation parameters, or to reflect the specificity of the action of a collision on different terms. It turns out that this deficiency is not fundamental. A kinetic equation for $\rho(t)$ will be derived below under the sole condition $\tau_c \ll \tau_0$ ($\tau_c$ is the collision time). This makes it possible to give a correct statistical-microscopic definition of all relaxation parameters and frequency shifts appearing in the equation. If necessary, the method for calculating relaxation times and shifts can be developed in such a way as to take into account the reaction of the particle participating in the collision.

1. If a gas molecule (atom) is subjected simultaneously to the action of fields ($\hat{H}_0$) and collisions ($\hat{V}$), then its Hamiltonian is $\hat{H} = \hat{H}_0 + \hat{V}$. Since collisions are short, their duration can be neglected on the scale of $\tau_0$, and changes in the state of the system can be taken into account—so

far formally—by a certain operator which, acting on an arbitrary density matrix, transforms it exactly as the collision itself (averaged over all its parameters) does:

$$\hat{P}\rho(t_i - 0) = \rho(t_i + 0),$$

where $t_i$ is the instant of collision. In the intervals between collisions $\hat{H} = \hat{H}_0$, and

$$\rho(t) = \hat{S}_0(t, t_i)\rho(t_i + 0)\hat{S}_0^{-1}(t, t_i),$$

where $\hat{S}_0(t, t_i)$ is the unitary transformation from one instant of time to another:

$$i\hbar \frac{d\hat{S}_0}{dt} = \hat{H}_0 \cdot \hat{S}_0. \tag{1}$$

Suppose that in the interval $(0, \tau)$ the molecule which we are following has undergone $k$ collisions at successive instants of time $t_1, t_2, \dots, t_k$. Then at the instant $\tau$ its matrix will be

$$\rho(\tau, t_k, \dots, t_1) = \hat{S}_0(\tau, t_k)\,[\hat{P}\rho(t_k, t_{k-1}, \dots, t_1)]\,\hat{S}_0^{-1}(\tau, t_k), \tag{2}$$

where the probability of this event is

$$dW(\tau, t_k, \dots, t_1) = \frac{1}{\tau_0^k} \exp\left(-\frac{\tau}{\tau_0}\right) dt_1 dt_2, \dots, dt_k. \tag{3}$$

The quantity $\rho$ depends both on the positions of the $t_i$ and on their number; therefore its mean value is obtained by integrating over all $t_i$ from 0 to $t_{i+1}$ and summing over all $k$, including also the case in which there are no collisions at all in the interval $(0, \tau)$ $(k = 0)$:

$$\bar{\rho} = \exp\left(-\frac{\tau}{\tau_0}\right) \hat{S}_0(\tau, 0)\rho(0)\hat{S}_0^{-1}(\tau, 0) +$$

$$+ \exp\left(-\frac{\tau}{\tau_0}\right) \sum_{k=0}^{\infty} \frac{1}{\tau_0^k} \int_0^{\tau} dt_k \int_0^{t_k} dt_{k-1} \dots \int_0^{t_2} dt_1 \rho(\tau, t_k, \dots, t_1). \tag{4}$$

Multiplying both sides of this equality by $\frac{1}{\tau_0} \exp \frac{\tau}{\tau_0} \hat{S}_0(t, \tau)$ on the right and by $\hat{S}_0^{-1}(t, \tau)$ on the left, and integrating over $\tau$ from 0 to $t$, one may observe that the same sum as in (4) is obtained on the right-hand side, but with the new argument $t$. Eliminating it with the aid of (4), we find the integral equation

$$\bar{\rho}(t) = \exp\left(-\frac{t}{\tau_0}\right)\hat{S}_0(t,0)\rho(0)\hat{S}_0^{-1}(t,0) +$$

$$+\frac{1}{\tau_0}\int_0^t \exp\left[-\frac{t-\tau}{\tau_0}\right]\hat{S}_0(t,\tau)\hat{P}\bar{\rho}(t)\hat{S}_0^{-1}(t,\tau)d\tau. \tag{5}$$

The equation used as the basis for the calculation of Karpus and Schwinger (2) is an asymptotic approximation to the present one (for $t \to \infty$) in the special case when each impact leads to complete restoration of equilibrium ($\hat{P}\rho = \rho_0$). Differentiating (5) with respect to $t$, taking (1) into account, and then eliminating the integral term with the aid of (5), we find

$$\frac{d\bar{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}_0, \bar{\rho}] - \frac{1-\hat{P}}{\tau_0}\bar{\rho} = -\frac{i}{\hbar}[\hat{H}_0, \bar{\rho}] - \hat{G}\bar{\rho}. \tag{6}$$

In this differential form the kinetic equation is quite suitable for application; it is only necessary to give a precise meaning to the operator $\hat{P}$.

2. According to the definition of the operator $\hat{P}$ given above, it must instantaneously produce the same transformation of $\rho$ as a collision is able to perform during the time $\sim \tau_c$. Therefore

$$\hat{S}_0(\tau_c,0)\hat{P}\rho\hat{S}_0^{-1}(\tau_c,0) = \hat{S}(\tau_c,0)\rho\hat{S}^{-1}(\tau_c,0), \quad \hat{P}\rho = \hat{S}_0^{-1}\hat{S}\rho\hat{S}^{-1}\hat{S}_0 = \hat{S}^{\times}\rho\hat{S}^{\times -1}, \tag{7}$$

where $\hat{S}^{\times} = \hat{S}_0^{-1}\hat{S}$ is the unitary transformation corresponding to the full Hamiltonian $\hat{H}$ in the interaction representation

$$i\hbar\frac{d}{dt}\hat{S}^{\times} = \hat{V}^{\times}\hat{S}^{\times}, \qquad \hat{V}^{\times} = \hat{S}_0^{-1}\hat{V}\hat{S}_0. \tag{8}$$

Writing (7) out in elements, we obtain

$$\sum_{k,l} S^{\times}_{ik}\rho_{kl}S^{\times -1}_{lm} = \mathrm{Tr}\,\hat{P}^{im}\rho \quad \text{or} \quad P^{im}_{lk} = S^{\times}_{ik}(+\infty,-\infty)S^{\times -1}_{lm}(+\infty,-\infty). \tag{9}$$

The infinite arguments in the transformation $S^{\times}$ do not mean abandoning the approximation of instantaneity; we calculate the full effect of the perturbation by the collision, counting from the infinitely distant moment when it began, up to the time when it has completely ended, but then

we assign it entirely to the moment when the approach of the particles was maximal.

Classifying all collisions according to this single feature—by the coincidence of the instant of closest approach—we obtain an ensemble in which both the flight velocities $v$ and the impact parameters $r$ may be quite different. To obtain the operator $\hat{P}$ appearing in (6), we must average $\hat{P}$ over these parameters. The distribution in $r$ is evidently $dW(r) = 2\pi r\,dr/\sigma$, where $\sigma$ is the total target area. This contains a certain ambiguity—the same as in $\tau_0 = [n\sigma\bar{v}]^{-1}$, but it is precisely this ambiguity that is eliminated from

$$\hat{G} = \frac{1}{\tau_0}[1-\hat{\bar{P}}] = n\sigma\bar{v}\left[\int_0^{r_0}\frac{2\pi r\,dr}{\sigma} - \int_0^{r_0}\hat{P}(r)\frac{2\pi r\,dr}{\sigma}\right] = 2\pi n\bar{v}\int_0^{r_0}[1-\hat{P}(r)]\,r\,dr, \tag{10}$$

after which the target radius $r_0$ ($\sigma = \pi r_0^2$) may without hesitation be allowed to tend to $\infty$. It is noteworthy that, under such a limiting transition, both the operator $\hat{P}$ itself and $\tau_0$ would go to 0, and only their ratio

$$\hat{G}^{im} = 2\pi n\int_0^{\infty} dW(v)\cdot\int_0^{\infty}[1-\hat{P}^{im}(r,v)]\,r\,dr, \qquad G_{lk}^{im} = [G_{kl}^{mi}]^* \tag{11}$$

remains a well-defined quantity. The averaging over the velocity distribution $dW(v)$ can often be omitted by replacing $v$ by $\bar{v}$.

3. It is now useful to rewrite equation (6) in the form

$$\frac{d\bar{\rho}_{im}}{dt} = -\frac{i}{\hbar}[\hat{H}_0,\bar{\rho}]_{im} - \operatorname{Tr}\hat{G}^{im}\bar{\rho}, \tag{12}$$

since the relaxation operator $G$ is not self-adjoint, not unitary, and is not even a single operator, but a set of operators in the ordinary sense of the word. To each element $\rho_{im}$ there corresponds its own operator $\hat{G}^{im}$, which each time mixes the matrix elements among themselves in a different way. Since $\hat{G}$ is a constant operator, its imaginary part determines the shift of the corresponding terms, while its real part determines the relaxation parameters specifying the rate of exponential approach of the system to equilibrium.

For the formalism developed here it is essential that the motion of the colliding atoms be described classically. But this in no way prevents one from quantizing the electronic states not only of the atom under consideration, but also of the incident atom, taking into account the recoil produced by the interaction. This, in any case, can be done if the atoms under consideration are dissolved in others whose state is not substantially disturbed by the acting radiation, i.e., at any moment remains at equilibrium. Then, calculating the two-particle transformation $S_{im,rs}$ (the indices $r, s$ refer to the perturbing atom), we must, in determining the operator $\hat{P}$, average over the states of the second particle, i.e., over $\rho_{rs}^0$,

$$P_{lk}^{im} = \sum_{r,s} S_{ik,rs}^{*}(+\infty,-\infty)\frac{\exp(-E_s/kT)}{z}S_{lm,sr}^{*-1}(+\infty,-\infty). \qquad (13)$$

Only owing to this refinement do transitions from upper levels to lower ones and in the reverse direction cease to be equiprobable, and thermal equilibrium is established in the system.

It is noteworthy that the form of equation (12) remains unchanged, regardless of whether the collision produces a strong or a weak action. It is simply that in the first case (2) the relaxation times do not depend on the perturbation and are equal to $1/\tau_0$, while in the second (3) they are proportional to $\hat{V}^2$, as in the usual perturbation theory (4).

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*Note: Figure translations are in progress. See original paper for figures.*

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