KINETIC DESCRIPTION OF QUANTUM SYSTEM RELAXATION

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Based on the Feynman path integral method the molecular relaxation (for molecules in a bath interacting with an electromagnetic field) is described in such a way that the phenomenological constant appears in the Schrodinger equation itself.

The relaxation problem for a quantum system interacting with a field has always been of great importance for atmospheric optics.[1] In linear spectroscopy it is the spectral line width and shift that are associated with the relaxation and the analysis of damping of quantum states has already become a concrete task. In the case of a strong field the situation is different. A great number of problems including those pertaining to the atmospheric gases are being solved using model versions (see, for example, Refs. 2—7). At the same time these questions are important for assessment of prospects for nonlinear spectroscopy methods and require efficient tools of analysis.

A virtually exact description of the interaction between an isolated system and a resonant field in terms of the evolution operator is well known.[8] The introduction of other Interactions, however (say, molecular collisions), that, in fact, are responsible, for the relaxation, makes the problem very complicated (see, for example, Ref. 9). The difficulties can be avoided but at the cost of considerable concessions of physical character (using, for instance, the strong collision model,[10] where the saturation effect is described in terms of the relaxation time alone). In considering the field-matter interaction in terms of the matrix density formalism the relaxation constants appear immediately in the appropriate kinetic equations, but it becomes impossible to obtain solutions similar to those given in Ref. 8.

The central idea of the present paper is to discuss the feasibility of introducing the relaxation constants directly into the Schrodinger equation relying upon the possibility of combining the advantages of the two approaches mentioned above. The way suggested here is clearly heuristic and requires an appropriate substantiation and test verification.

We start from the path integral method.[14] It has been assumed in Refs. 15—16 that possible alternative paths have a limited length l because of the relativistic condition $l < c\tau$ (c is the velocity of light, τ is time). In other words it is proposed to write

$$\psi(r,t+\tau) = \int\limits_{-\infty}^{\infty} K(r,r_1,t,\tau)\psi(r_1,t)\mathrm{d}^3r_1, \tag{1}$$

where

$$K(r,r_1,t,\tau) = K_0(r,r_1,t,\tau)f(r-r_1,\tau). \tag{2}$$

Here $\psi(r, t)$ is the particle wave function at a time t (moments t and $t + \tau$ are close enough), K_0 is a conventional propagator to be discussed below, and f is the weighting function introduced for a mathematical realization of the assumption of limited l.

Generally speaking, the introduction of the weighting function seems to be redundant since from the formal point of view for $l > c\tau$ the exact relativistic propagator is converted from the oscillating function into the exponentially decreasing function. However, the presence of $f(r - r_1, \tau) = f(\kappa, \tau)$ in Eq. (1) leads to the salient features that can be used for introducing the relaxation into the equation for ψ.

It was shown in Ref. 15 that the presence of the weighting function in Eq. (1) leads to the appearance of a non—Hermitonian term in the Hamiltonian which causes the damping of $\psi(t)$. Now we suggest that this fact be interpreted in the sense that the limitation of the path length works as statistical noise which is the physical reason for relaxation. Proceeding with this interpretation we will assume that f is related to a random change in the path direction. If the change is of Markovian character, then

$$f(\kappa,\tau) = \exp\left[-\frac{1}{\tau}\left(\frac{\kappa_x^2}{D_x} + \frac{\kappa_y^2}{D_y} + \frac{\kappa_z^2}{D_z}\right)\right], \tag{3}$$

where D_x, D_y, D_z are some "diffusion coefficients" of the end points of the paths along the chosen directions in the bath.

Discrimination of paths by means of Eq. (3) allows us to account for the effect of the environment on the ψ—function of the particle, since the summation of the alternative probability amplitudes takes into account both their phases, which are primarily caused by the regular external fields and "the intensity", which depends on the effect of random factors.

For a particle in the electromagnetic field the propagator K_0 can be written to within the normalization constant B:

$$K_0(r,r_1,t,\tau) = B\exp\left[\frac{i}{h}\tau L\left(\frac{r_1+r}{2},\frac{r_1-r}{\tau},t+\frac{\tau}{2}\right)\right], \tag{4}$$

where

$$L\left(\frac{r_1+r}{2},\frac{r_1-r}{\tau},t+\frac{\tau}{2}\right) = \frac{m(r_1+r)^2}{2\tau^2} - e\varphi\left(\frac{r_1+r}{2},t+\frac{\tau}{2}\right) + \\ + \frac{e}{c\tau}\left((r_1+r)A\left(\frac{r_1+r}{2},t+\frac{\tau}{2}\right)\right) \tag{5}$$

(e and m are the particle charge and mass and $\varphi(r, t)$ and $A(r, t)$ are scalar and vector potentials of the external field).

Taking $D_x = D_y = D_z = D$ in Eq. (3) and using standard manipulations one can readily arrive at the Schrodinger equation

$$ih\frac{\partial\psi}{\partial t} = \frac{1}{1+i\alpha}\left[\frac{1}{2m}\left(P - \frac{e}{c}A\right)^2\psi\right] + e\varphi\psi \tag{6}$$

with $\alpha = (2h/mD) > 0$.

The fact that the changes in Eq. (6) due to Eq. (3) have touched upon the kinetic energy operator seems fairly reasonable: the higher the velocity, the larger is the volume size where the particle can be found for a given time and, accordingly, the greater is the collision probability and the probability for the state of the system to change.

The previously mentioned non—Hermitian character of the Hamiltonian in Eq. (6) naturally results in the nonconservat ion_ of the wave function normalization. Uhile this circumstance is quite acceptable in the treatment of unstable particles[15] (incidentally, this property of Eq. (6) illustrates a certain flexibility of the proposed procedure), the application of this equation to stable systems implies additional modificat ion.

To derive an equation which is appropriate for the description of molecules whose lifetime is much longer than the time of damping of the excited quantum states, we will supplement $K(r, r_1, t, \tau)$. In so doing, we will take into account that Eq. (3) represents a stable distribution[17] and, therefore, together with Eq. (4) preserves the most important group properties of the propagator. It is reasonable, on that ground, to make changes in the Lagrangian, the more so because it is determined to within the total derivative with respect to time. Thus ue will supplement Eq. (5) with a functional of the wave function $\Phi(\psi(r, t))$, assuming it to be dependent solely of time and requiring that the ψ—function satisfy both Eq. (1) and the normalization condition

$$\int_{-\infty}^{\infty}|\psi(r,t+\tau)|^2\,\mathrm{d}^3r = \int_{-\infty}^{\infty}|\psi(r,t)|^2\,\mathrm{d}^3r + O(\tau^2). \tag{7}$$

The corresponding computations show that the simplest function will have the form

$$\Phi(\psi(r,t)) = -\frac{i\alpha}{1+\alpha^2} < \psi\left|\frac{1}{2m}\left(P - \frac{e}{c}A\right)^2\right|\psi > / < \psi|\psi >. \tag{8}$$

The conventional procedure with the propagator using Eq. (8) yields an integro—differential equation (instead of Eq. 6)) for the evolution of the system in the electromagnetic field with the Markovian perturbation of the form

$$ih\frac{\partial\psi}{\partial t} = \frac{1-i\alpha}{1+\alpha^2}\cdot\frac{1}{2m}\left(P - \frac{e}{c}A\right)^2\psi + e\varphi\psi - \Phi((\psi(r,t))\psi. \tag{9}$$

Thus it follows from most general considerations that the behavior of the stable quantum system interacting with a bath can be described by a nonlinear equation (the term $<\psi|\psi>$ in Eq. (8) is naturally taken to be unity). In general case, the problem of determining the wave function which satisfies Eq. (9) is rather complicated, and a simple substitution shows that one of the possible solutions is as follows:

$$\psi = \frac{\psi_1}{\left(<\psi_1|\psi_1>\right)^{1/2}}, \tag{10}$$

where ψ_1 is a function which satisfies Eq. (6) (some solutions of Eq. (6) can be found in Ref. 16). Incidentally, the substitution (10) reveals the pragmatic sense of the entire renormalization procedure leading from Eq. (6) to Eq. (9).

The generalization of Eq. (9) to the case in which "diffusion coefficients" are different along he different axes is trivial. Let $x_1 = x$, $x_2 = y$, $x_3 = z$, $D_k = D_{xk}$, $A_k = A_{xk}$, $P_k = -ih\frac{\partial}{\partial x_k}$, and $\alpha = 2h/mD_k$. Then we have

$$ih\frac{\partial\psi}{\partial t} = \left(\sum_{k=1}^{3}\left[\frac{1-i\alpha_k}{1+\alpha_k^2}T_k + \frac{i\alpha_k}{1+\alpha_k^2} < \psi|T_k|\psi >\right]\right)\psi + e\varphi\psi, \tag{11}$$

where the following notation is introduced

$$T_k = \frac{1}{2m}\ P_k^2 - \frac{e}{mc}A_kP_k + \frac{ihe}{2mc}\frac{\partial A_k}{\partial x_k} + \frac{e^2}{2mc^2}A_k^2. \tag{12}$$

Equations (9) and (12) are written to illustrate the idea for a single particle. Consequently, they include a small number of phenomenological parameters, which may be insufficient for the calculations of concrete systems. In addition, it should be noted that a standard derivation of the evolution operator proceeding from Eqs. (9) and (12) is faced with certain difficulties, in particular, due to the dependence of the evolution operator on the initial state of the quantum system caused by the nonlinearity of the starting relations. If we are to take into consideration the above circumstances, we will pass over from Eq. (12) to a more general equation. First of all, account should be taken of the fact that in a system, which consists of a great number of particles (an atom or a molecule), it is sufficient to include the interaction between electrons in the potential energy operator. As a result, the kinetic part of the Lagrangian can be written as an additive function with each term corresponding to an individual particle. In addition the particles of the molecule can interact with the bath in different ways. Therefore, each particle will be associated with its weighting function characterized by its coordinates and "diffusion coefficients". Then, proceeding to the problem of many particles in Eqs. (1)–(5) we can write

$$ih\frac{\partial\psi}{\partial t} = \left(\sum_{k=1}^{N}\left[\frac{1}{1+i\alpha_k^2}\left(\widehat{P}_k - \frac{e}{c}A\right)^2\right]\right)\psi + U\psi. \tag{13}$$

In Eq. (13) the summation is taken over all the electrons, $\widehat{P}_k$ is the momentum operator for the kth particle, and $\alpha = 2h/mD_k$ (taking $D_{kx} = D_{ky} = D_{kz} = D_k$). Both Eq. (13) and the juxtaposed equation for "a normalized function"

$$ih\frac{\partial\psi}{\partial t} = \left(\sum_{k=1}^{N}\left[\frac{1}{1+i\alpha_k}\left(\widehat{P}_k - \frac{e}{c}A\right)^2 + \right.\right.$$
$$\left.\left. + \frac{i\alpha_k}{1+i\alpha_k^2} < \psi\left|\left(P_k - \frac{e}{c}A\right)^2\right|\psi >\right)\psi + U\psi \tag{14}$$

have formally the same structure as Eqs. (6) and (11), but may contain a far greater number of variable parameters (evidently some of them can be taken identical if necessary).

Now we will proceed to the dipole approximation in Eq. (14). It can be done if we represent the wave function in the form of the product[8,18]

$$\psi(r,t) = \exp\left[\frac{i}{hc}A(P,t)\sum_k er_k\right]\psi(r,t), \qquad (15)$$

where $A(R,\ t)$ is the vector potential defined in the center of mass of the molecule. A little manipulation yields

$$ih\frac{\partial\psi}{\partial t} = \sum_k\left(\frac{1}{1+i\alpha_k}P_k^2 + \frac{i\alpha_k}{1+i\alpha_k^2}<\psi|P_k^2|\psi>\right)\psi + U\psi + V\psi, (16)$$

where $V = d\cdot E(R,\ t)$ is the perturbation operator, d is the dipole moment, and $E = -\dfrac{1}{c}\dfrac{\partial A}{\partial t}$ is the electric field. Equation (16) can be approximately replaced by

$$ih\frac{\partial\psi}{\partial t} = \Pi(H_0 - U)\psi + \frac{1}{2}<\psi|(\Pi^* - \Pi)(H_0 - U)|\psi>\psi +$$
$$+U\psi + V\psi, \qquad (17)$$

where H_0 is the Hamiltonian of the unperturbed molecule and Π is the superoperator with the diagonal matrix elements

$$\Pi_{jj}= 1 / (1 + i\alpha_j), \qquad (18)$$

which introduces the appropriate relaxation constant related to α_j for each energy level. Similarly, Eq. (13) is replaced by

$$ih\frac{\partial\psi}{\partial t} = \Pi(H_0 - U)\psi + U\psi + V\psi, \qquad (19)$$

The above equations, especially Eq. (19) with the normalization condition (10) enables us to examine the behavior of the molecule under the effect of statistical perturbation in the electromagnetic field, using standard methods for the solution of the Schrodinger equation. In particular, the problem can be divided into two parts: first, the unnormalized basic wave functions are to be found for the state of molecule in the bath by solving the equation

$$ih\frac{\partial\psi}{\partial t} = \Pi(H_0 - U)\psi + U\psi \qquad (20)$$

and then the effect of radiation is to be accounted for. This is what we need. Thus the problem formulated in this paper appears to be solved to a considerable extent. We have derived equations which are, as a matter of fact, the Schrodinger equations but written for the wave functions averaged over the bath states, and, hence, the relaxation processes should be taken into account. The behavior of a two−level system in a strong harmonic field and its relaxation after the field has been switched off was verified by means of Eqs. (19) and (10) to give correct results, i.e., oscillations of the level populations with the Rabi frequency and their damping according to the exponential or (depending on the conditions) bi-exponent ial law of free polarization (as observed in a number of experiments[3]).

In proceeding to the evolution operator $\hat{g}\ (t,\ t_0)$ of a quantum system interacting with the bath the resulting equation is to have a formal structure slightly different from Eq. (17) because Eqs. (16) and (17) are nonlinear as previously

$$ih\frac{\partial\hat{g}}{\partial t} = \Pi(H_0-U)\ \hat{g} + U\hat{g} + \Pi_1\hat{g}, \qquad (21)$$

where Π_1 is a nonlinear superoperator in $\hat{g}$ which satisfies not only Eq. (21) but the operator relation

$$\hat{g}^*([\Pi(H_0 - U)] - [\Pi(H_0 - U)^*)\hat{g} = \hat{g}^*(\Pi_1\hat{g}) - (\Pi_1\hat{g}^*)\hat{g}. (22)$$

In conclusion it should be noted that even though the equations proposed in this paper have been derived using the Gaussian weighting function, the assumption of the Markovian character of the perturbation is not necessary. The only restriction imposed on $f(\kappa,\ \tau)$ is the requirement that the propagator (2) be a group element for small τ. This fact gives us the possibility by a special choice of the weighting function to describe not only the relaxation of different subsystems of quantum ensembles but also their interaction in turns of the bath, for example, the mutual effect of electronic and rotational−vibrational terms of molecules.

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