

## Quantum Theory of Dielectric Relaxation\*

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The statistical behavior of a system coupled to a reservoir at temperature  $T$  is discussed, with the assumption that the interactions are impulsive. Kinetic equations are written for the classical distribution function and quantum density operator. The class of operators admitted leads to a proper description of the irreversible behavior of the system, but the construction of the collision operator for a given Hamiltonian of system and reservoir is not treated. Application is made to the quantum theory of dielectric relaxation, with the further assumption that the position coordinates of the system are unchanged by collisions. An explicit solution is found for the behavior in an external alternating field, of a two-dimensional dipole of moment of inertia  $I$ , subject to strong collisions with the reservoir. For low collision frequency  $1/\tau$ , discrete rotational lines of width  $1/\tau$  are found, while at high collision frequencies there is a continuous Debye spectrum with relaxation time  $\tau^* = (1/\tau)/(I/kT)$ . At intermediate collision times, the absorption and dispersion are governed by an interplay of quantum and inertial effects.

### 1. INTRODUCTION

IN this note, we examine some aspects of the quantum theory of a system interacting impulsively with a reservoir. The meaning of "impulsive" is as follows: the system evolves under the influence of its own Hamiltonian, except for infinitesimal time intervals when the state is abruptly changed by interactions with the reservoir. For the classical theory, general properties of this model, such as the approach to equilibrium, the free-energy production, etc., have been studied.<sup>1</sup> Here we will be concerned with the corresponding quantum theory and its particular application to the theory of dielectric relaxation. The approach will be to postulate quantum equations corresponding to given classical models.

The problem of the quantum theory of dielectric relaxation is to describe mathematically the transition from the low-pressure rotational line spectrum of a polar gas to the continuous Debye spectrum at high pressures, or in the liquid state. The nature of this transition will depend on the detailed interactions between the absorbing molecule and its neighbors. However, for the case of a dilute solution of polar molecules in a nonpolar solvent the situation is particularly simple. A classical theory of dielectric relaxation appropriate to this case was developed.<sup>2</sup> It was argued that the short-range character of the intermolecular forces implies that collisions are of small duration compared to resonant period, applied-field period, and time between collisions. Since there is a limited amount of energy available ( $\approx kT$ ), we may use models in which the dipolar coordinates are unchanged at collisions,

while the velocities are changed. These models are special cases of the general impulsive model of reference 1.

In the present note, we postulate quantum theories for both the general impulsive model, and the more special no-position-change case. We obtain a conceptual unification of the low- and high-pressure limits, which may provide guidance in the design of experiments. Our considerations are, however, schematic in that no attempt is made to treat the Hamiltonian of system plus reservoir by an impulsive approximation, and to integrate over reservoir variables. This has been accomplished for the case where the system-reservoir interaction can be treated appropriately by perturbation theory.<sup>3</sup>

### 2. CLASSICAL THEORY OF DIELECTRIC RELAXATION

We outline first the features of a general classical theory of relaxation. The pattern of presentation will be followed in the quantum theory. A general system is described by a distribution function  $u(x,t)$ , where  $x$  is a point in the phase space  $(p_i, q_i)$  of the system. When there is an impulsive interaction with a reservoir at temperature  $T$ , the distribution function obeys the integrodifferential Eq. (1).

$$\begin{aligned} \partial u / \partial t + \{u, H\} &= \int \{K(x, x')u(x', t) - K(x', x)u(x, t)\} dx' \\ &= \delta u / \delta t, \end{aligned} \quad (1)$$

where  $K(x, x')$  is the probability per unit time that a system at the point  $x'$  jumps to the point  $x$  by collision with the reservoir. The symmetry property

$$\begin{aligned} K(x, x') &= L(x, x')e^{\beta H(x')}, \\ L(x', x) &= L(x, x'), \quad \beta = 1/kT \end{aligned} \quad (2)$$

assures detailed balancing at equilibrium. If the Hamil-

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<sup>1</sup> P. G. Bergmann and J. L. Lebowitz, *Phys. Rev.* **99**, 578 (1955).

<sup>2</sup> E. P. Gross, *Phys. Rev.* **97**, 395 (1955); *J. Chem. Phys.* **23**, 1415 (1955).

<sup>3</sup> F. Bloch, *Phys. Rev.* **102**, 104 (1956); A. Redfield (to be published); K. Tomita (to be published).

tonian  $H$  is time-independent, the system approaches a canonical distribution in the course of time, and the free energy decreases monotonically.

The derivation of Eqs. (1) invokes conservation of energy of system plus reservoir at an instantaneous collision. The reservoir is assumed to be permanently in a canonical distribution, and an assumption of microscopic reversibility is made.  $K(x, x')$  is independent of the state of the system.

In the theory of relaxation we are interested in the case where  $H$  is time-dependent, as for example  $H = H_0(p, q) + E_0 \cos \omega t - V(q)$ . The conservation argument leads again to (1) and (2) with  $H$  now the instantaneous time-dependent Hamiltonian. If we assume as in reference 2 that the position coordinates are not changed by collisions, we have

$$K(x, x') = K'(x, x') \delta(q - q').$$

The models of Fröhlich and Van Vleck and Weisskopf<sup>4</sup> involve position changes at collision, but are of the general type (1) with  $H$  the instantaneous Hamiltonian.

The formulation and solution of equations with appropriate collision kernels, satisfying the above requirements, yields a classical theory of resonance and relaxation. Here we have done justice to the intuitive meaning of impulsive. We may note that the treatment of the system-reservoir interaction by perturbation theory yields similar equations (with the instantaneous Hamiltonian) under certain circumstances (see reference 3). In reference 2 particular kernels were postulated. These appear reasonable, but of course to be sure that a kernel is physically satisfactory, it must be derived from some definite Hamiltonian of system plus reservoir. We do not treat this problem.

The general theory of dielectric relaxation employs distribution functions in the full phase space  $(p_i, q_i)$  of the system, rather than only in the configuration space  $(q_i)$ , as is the case for the Debye theory. One obtains inertial corrections, and also a detailed physical picture of the transfer of energy and angular momentum from the applied field through the system of dipoles to the reservoir. Because of the nature of classical mechanics a theory of line structure at low pressures requires a quantum generalization.

### 3. QUANTUM COLLISION KERNELS

The statistical properties of the system are now described by a Hermitian density operator  $\rho$  of trace unity. The expectation value of an observable  $G$  is  $\text{tr}(G\rho)$ . For a system with Hamiltonian  $H$ , the equation governing the time behavior of  $\rho$  is

$$\frac{\partial \rho}{\partial t} + \frac{i}{\hbar} [H, \rho] = \frac{\delta \rho}{\delta t} \quad (3)$$

The left-hand side is the quantum analog of the Liouville equation, and specifies the change of  $\rho$  arising from the action of the Hamiltonian. The right-hand side treats the effects of the interaction with the reservoir. In a representation where the system coordinates  $q$  are diagonal, we write

$$\left( q \left| \frac{\delta \rho}{\delta t} \right| q' \right) = \sum_{q'', q'''} (qq' | Q(t) | q''q''') (q'' | \rho(t) | q'''). \quad (4)$$

An operator  $Q$  with four continuous indices is needed because a collision changes the general matrix element  $\rho(q, q', t)$ ; there are contributions from all points  $(q'', q''')$ . The collisions are instantaneous, i.e.,  $t$  is the only time in the collision kernel. Following the pattern of the classical theory, we impose the following conditions on the kernel  $Q$ :

(1)  $Q$  must be such that  $\delta \rho / \delta t = Q\rho$  is Hermitian and  $\text{tr}(\delta \rho / \delta t) = 0$ . Then, the normalization and Hermiticity of  $\rho$  are preserved in the course of time. These requirements can be satisfied in a general matrix representation by writing [in analogy to reference 1, Eq. (3.1)]

$$\frac{\delta \rho}{\delta t} = \sum_{z, z'} \{ K(s, s' | z, z') \rho(z', z) - \frac{1}{2} K(z, z | s, z') \rho(z', s') - \frac{1}{2} K(z, z | s' z') \rho(z' s) \}. \quad (5)$$

The operator  $K(s, s' | z, z')$  must be Hermitian in both sets of indices and positive-definite. Thus

$$\sum_{ss'} \sum_{zz'} A(s, s') K(s', s | z, z') B(z', z) \geq 0,$$

when  $A$  and  $B$  are positive matrices.

(2)  $Q\rho_0 = 0$ , where  $\rho_0 = e^{-\beta H_0} / \text{tr} e^{-\beta H_0}$ ,  $\beta = 1/kT$ ,  $k$  is Boltzmann's constant,  $T$  is the reservoir temperature, and  $H_0$  is a time-independent Hamiltonian. In addition,  $Q$  must give a proper account of the approach to this equilibrium. The symmetry conditions on  $K(s, s' | z, z')$  which are equivalent to those in the classical theory, [see reference 1, Eqs. (2.2) and (2.4)], are

$$K(s', s | z, z') = \frac{1}{2} \sum_y L(s', s | z, y) e^{\beta H}(y, z') + \frac{1}{2} \sum_y L(s', s | y, z') e^{\beta H}(z', y). \quad (6)$$

These conditions can be shown to lead to a monotonic decrease in the free energy.

The analog of the classical condition of no position change during a collision here takes the form

(3)  $(q | \delta \rho / \delta t | q) = 0$ ; i.e., the diagonal elements of  $\delta \rho / \delta t$  in a coordinate representation vanish. Then the expectation value of any operator  $F$  which is a function of position alone, is unchanged by collision. Thus

$$\begin{aligned} \text{tr} \left( F \frac{\delta \rho}{\delta t} \right) &= \sum_{q, q'} f(q) \delta(q' - q) \left( q' \left| \frac{\delta \rho}{\delta t} \right| q' \right) \\ &= \sum_q f(q) \left( q \left| \frac{\delta \rho}{\delta t} \right| q \right) = 0. \end{aligned}$$

<sup>4</sup> J. H. Van Vleck and V. Weisskopf, *Revs. Modern Phys.* **17**, 227 (1945); H. Fröhlich, *Nature* **157**, 478 (1946), and *Theory of Dielectrics* (Clarendon Press, Oxford, 1949).

This implies that

$$(qq|Q|q''q''')=0 \text{ for all } q, q'', q'''. \quad (7)$$

The approach of Karplus and Schwinger<sup>5</sup> to the theory of microwave line shape (and dielectric relaxation) is based on the assumption

$$\frac{\delta p}{\delta t} = -\frac{p}{\tau} + \frac{1}{\tau} p_{\text{eq}}; \quad p_{\text{eq}} = e^{-\beta H(t)} / \text{tr}(e^{-\beta H}), \quad (8)$$

where  $\tau$  is the constant collision time. This is a quantum analog of reference 4 where ( $u \equiv f$ )

$$\frac{\delta f}{\delta t} = -\frac{f}{\tau} + \frac{f_{\text{eq}}}{\tau}, \quad f_{\text{eq}} = \frac{e^{-\beta H(t)}}{\int e^{-\beta H} d p d q}. \quad (9)$$

These models satisfy (1) and (2) but not (3). For the general theory of the response to time dependent fields, we postulate that the instantaneous Hamiltonian is to be used in the kernels. In all theories the presence of the instantaneous Hamiltonian ensures that if the value of the applied field is abruptly altered, the system ultimately comes to the proper new equilibrium.

In the present work we are interested in quantum kernels that yield the same results as the kernels of reference 2 when  $\hbar \rightarrow 0$ . With the density operator formalism, the connection between classical and quantum kernels is usually not as transparent as for Eqs. (8) and (9). The reason is that we give preference to the coordinate representation with the statement that the position is unchanged by collisions. A closer correspondence results when the Wigner distribution,<sup>6</sup>  $f_w(p, q, t)$  is used to describe the evolution of a quantum ensemble.

Appropriate quantum kernels are suggested by requiring that the Wigner distribution satisfy an integrodifferential equation with a stochastic kernel which is the same as that obeyed by the classical distribution function. Then one expresses the Wigner function in terms of the density matrix. There are, however, technical points connected with conditions for the Wigner function to represent a physical system, and its meaning when the coordinate range is not  $-\infty$  to  $+\infty$ . We have used it only to suggest kernels for the density operator appropriate for strong collisions, Brownian motion, etc. In the following section we work out the theory of the electrical response of a two-dimensional dipole for one such kernel. The physical situation described is a strong-collision case arising from short-range forces between dipolar and nondipolar molecules.

### Solution for Two-Dimensional Dipole

We study a particular expression for  $\delta p / \delta t$  which is closely related to the classical strong-collision model<sup>2</sup>

<sup>5</sup> R. Karplus and J. Schwinger, *Phys. Rev.* **73**, 1020 (1948).

<sup>6</sup> E. P. Wigner, *Phys. Rev.* **40**, 739 (1932); T. Takabayasi, *Progr. Theoret. Phys. Japan* **11**, 341 (1954).

in which the system has a Maxwellian velocity distribution after impact.

$$\frac{\delta p}{\delta t}(q, q', t) = -\frac{p}{\tau}(q, q') + \frac{p_{\text{eq}}(q, q')}{2\tau} \left[ \frac{p(q, q)}{p_{\text{eq}}(q, q)} + \frac{p(q', q')}{p_{\text{eq}}(q', q')} \right]. \quad (10)$$

$\tau$  is a collision time, and  $p_{\text{eq}}(t)$  represents the equilibrium density operator appropriate to the instantaneous value of the time-dependent Hamiltonian  $H(t)$ . The term in the square bracket is symmetric so that it maintains the Hermitian character of  $\delta p / \delta t$  in the course of time. The classical expression for the strong collision model was

$$\frac{\delta f}{\delta t}(q, p, t) = -\frac{f(q, p, t)}{\tau} + \frac{1}{\tau} n(q, t) F(p), \quad (11)$$

where  $n(q, t)$  is the number density and  $F(p)$  the Maxwellian velocity distribution. The first terms of the classical and quantum expressions are direct analogs. In the second terms,  $p(q, q)$  is the analog of  $n(q)$ .

We now examine the question of the absorption and dispersion of radiation by a system obeying Eqs. (1) and (4). We write

$$H(t) = H_0 + V(t) = H_0 - \mathbf{u}_{\text{op}} \cdot \mathbf{E}_0 \text{Re } e^{i\omega t}, \quad (12)$$

where  $H_0$  is the Hamiltonian of the system,  $V(t)$  the interaction with the electric field  $E_0 \cos \omega t$ .  $\mathbf{u}_{\text{op}}$  is the dipole moment operator of the system. Our goal is to compute the expectation value of the dipole moment operator<sup>5</sup> (polarization)

$$M(t) = \text{tr}[p(t)\mathbf{u}_{\text{op}}], \quad (13)$$

to the first power in  $E_0$  (nonsaturation region). With  $p = p_{\text{eq}}(t) + D$ , we find to this approximation

$$\begin{aligned} \frac{\partial D}{\partial t} + \frac{i}{\hbar} [H_0, D] \\ = -\frac{\partial p_{\text{eq}}}{\partial t} - \frac{D}{t} + \frac{p_0(q, q')}{2t} \left[ \frac{D(q, q)}{p_0(q, q)} + \frac{D(q', q')}{p_0(q', q')} \right], \end{aligned} \quad (14)$$

where

$$p_0 = e^{-H_0/kT} / \text{tr}(e^{-H_0/kT}).$$

Further investigation is most convenient in a scheme where  $H_0$  is diagonal. We introduce

$$H_0 \psi_n(q) = E_n \psi_n(q); \quad \psi_n(q) \equiv (n/q), \quad (15)$$

and use relations of the type<sup>7</sup>

$$(n|D|m) = \sum_{qq'} (n|q)(q|D|q')(q'|m), \quad (16)$$

$$\sum_q (n|q)(q|m) = \delta_{nm}; \quad \sum_n (q|n)(n|q') = \delta(q-q').$$

<sup>7</sup> P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, London, 1947).

For the two-dimensional dipole, we are interested in the component of  $\mathbf{u}_{op}$  along the direction of the field  $E_0$  ( $z$  axis). Then

$$\begin{aligned}
 (\mu_{op})_z(q, q') &= \mu \cos q \delta(q - q'), \\
 \langle n | q \rangle &= (1/2\pi) e^{inq}, \quad \langle n | \mu_{op} | m \rangle = \frac{1}{2} \mu \{ \delta_{n, m+1} + \delta_{n, m-1} \}, \\
 p_0(q', q) &= \sum_n e^{-\beta E_n} \psi_n^*(q) \psi_n(q') / \sum_q \sum_k e^{-\beta E_k} |\psi_k(q)|^2 \\
 &= \sum_{n=-\infty}^{+\infty} e^{-\beta E_n} e^{in(q'-q)} / 2\pi \sum_k e^{-\beta E_k}, \\
 p_m^0 &\equiv e^{-\beta E_m} / \sum_k e^{-\beta E_k}, \\
 E_k &= \hbar^2 k^2 / 2I,
 \end{aligned}
 \tag{17}$$

where  $I$  is the moment of inertia,

$$\begin{aligned}
 \langle n | p_{eq} | m \rangle &= p_m^0 \delta_{mn} + \left( \frac{p_m^0 - p_n^0}{\hbar w_{mn}} \right) V_{mn}(t) - T_{nm} \\
 &\equiv \left( n \left| \frac{\partial p_{eq}}{\partial t} \right| m \right) = \frac{\mu E_0}{2} \left( \frac{p_m^0 - p_n^0}{\hbar w_{mn}} \right) \\
 &\quad \times i w e^{i w t} \{ \delta_{m, n+1} + \delta_{m, n-1} \}.
 \end{aligned}
 \tag{18}$$

Then one finds,

$$\frac{\partial D_{nm}}{\partial t} + i w_{nm} D_{nm} + \frac{D_{nm}}{\tau} - \frac{(p_n^0 + p_m^0)}{2\tau} \sum_k D_{k+n-m, k} = T_{nm}.
 \tag{19}$$

The only terms which do not vanish for long times are  $D_{n, n\pm 1}$ .

Introduce

$$\sigma_{nm} = (1/\tau) + i w_{nm} + i w.$$

We form the sums  $\sum_m D_{m\pm 1, m}$ :

$$\sum_m D_{m\pm 1, m} = \sum_m \frac{T_{m\pm 1, m}}{\sigma_{m\pm 1, m}} \left/ \left( 1 - \sum_k \frac{p_k^0 + p_{k\pm 1}^0}{2\tau \sigma_{k\pm 1, k}} \right) \right. .
 \tag{20}$$

The complex polarization  $\mathbf{M}(t)$  is given by

$$\begin{aligned}
 \mathbf{M}(t) &= \sum_{nm} p_{nm}(\mathbf{u}_{op})_{mn} \\
 &= \sum_{nm} (p_{eq})_{nm}(\mathbf{u}_{op})_{mn} + \frac{\mu}{2} \sum_{n=-\infty}^{\infty} \{ D_{n+1, n} + \text{c.c.} \}.
 \end{aligned}
 \tag{21}$$

We obtain the result

$$M(t) = -\frac{\mu^2 E_0}{2} \sum_n \frac{(p_{n+1}^0 - p_n^0)}{\hbar w_{n+1, n}} + \frac{\mu}{2} \sum_n \{ D_{n+1, n} + \text{c.c.} \}.
 \tag{22}$$

This result is very close in form to the classical formula of reference 2. The integration over the continuous range of dipolar angular velocities is here replaced by a discrete sum over the quantum number  $k$ . The frequencies  $w_{k+1, k} = (\hbar/8\pi I)(2k+1)$  give rise to a sum which differs only slightly from the integral when  $w_{k+1, k} \ll 1/\tau$ . Since  $1/\tau$  is independent of  $k$ , at any given pressure this condition may be satisfied by the low-lying rotational lines, which then have their individual line structure destroyed. The lines of higher  $k$  values may still be resolved.

If the collision frequency  $1/\tau$  is small compared to  $w$  and  $w_{1, 0}$ , formula (14) shows the characteristic quantum line structure, with width  $1/\tau$ . This is clear for the numerator. For the denominator only one term in the sum is appreciable, so that the sum is small of the order of 1 divided by the number of levels excited at thermal equilibrium. In general the result shows the interplay of quantum line effects, classical inertial effects and the transition to the Debye shape at high pressures [relaxation time  $\tau^* = (1/\tau)(I/kT)$ ].

Similar results are obtained for quantum generalizations of the other models of reference 2. The solutions for systems other than the two-dimensional dipole are, however, not easy to obtain in explicit form for the entire range of pressures.