Kinetic equations are deduced for the density matrix describing the relaxation in a two-level system interacting with a heat reservoir. It is assumed that the frequency of transition between the levels is small relative to the characteristic frequency of fluctuation in the reservoir; the interaction may be of any strength. The equations are used to discuss the relaxation in such a system.

Many problems in chemistry and physics involve theoretical consideration of relaxation in a system with two stationary states. Examples are cis-trans isomerization by interaction with a heat reservoir and molecular interaction during energy exchange between an unpaired electron in a radical and the surrounding medium. The potential of such a system may be approximated by a double potential well with only two states, these being close either because the potential has low asymmetry or because the tunnel splitting is small (symmetric potential). The relaxation is clearly closely related to the line shape for the transition between these states. The general problem is that of correlating the relaxation kinetics with the shape of the spectral lines.

The question can be discussed in general terms from the solution of the relaxation equation for the density matrix. The diagonal elements of the density matrix in the relaxation equations are unrelated to the nondiagonal ones if the frequency of transition between the levels is large relative to the characteristic frequency of the fluctuations in the heat reservoir and if the interaction with the reservoir is weak. The relaxation of the populations (the feature of interest in chemical kinetics) is then virtually independent of the relaxation in the nondiagonal elements (which govern the line shape). Then the derivation of the relaxation is well-known, as are the general properties of the solution [1, 6]. Another limiting case is that when the interaction is not weak and the transition frequency is small relative to the characteristic one.

Here we consider a symmetrical double well for simplicity; we consider only the connection between each pair of states arising when the degeneracy is removed by the tunnel effect (see the upper part of Fig. 1). The Hamiltonian for the split pair may be put as

\[ H = \hbar \left( \omega_x s_x + \omega_z s_z \right), \]

in which \( s_x \) and \( s_z \) are Pauli matrices, \( \omega_x \) and \( \omega_z \) being random functions of time that approximate the action of the reservoir. The problem is then the quantum analog of the classical model for passage over a potential barrier in response to a random force, which Kramers [2] discussed in relation to the diffusion theory of reactions. Here we can determine the mean time for transition from one well to another for any value of the coupling to the reservoir (this coupling is analogous to the \( a \) of Kramers’s theory). Two models for the reservoir are possible, namely gas and liquid.

**Gas Model**

The time history is described by the matrix for the density \( Q \) which satisfies

\[ i \frac{dQ}{dt} = [H, Q], \]

in which \( H \) is a time-dependent hamiltonian. The matrix for \( Q \) may be expanded in terms of Pauli spin matrices \( s \) as

\[ Q = \frac{1}{2} I + Xs_x + Ys_y + Zs_z, \]

in which \( X, Y, \) and \( Z \) are functions of time; they are found from the system derived by substituting (3) and (1) into (2):

\[ \dot{X} = -\left[ \omega + \omega_x(t) \right] Y, \]
\[ \dot{Y} = \left[ \omega + \omega_z(t) \right] X - \omega_x(t) Y, \]
\[ \dot{Z} = \omega_x(t) Y. \]

Here \( \omega_x(t) \) and \( \omega_z(t) \) are random functions. We use the statistical features of these to find \( X, Y, \) and \( Z \) as functions of
time during intervals \( \tau \) substantially exceeding the correlation times of \( \omega_X(t) \) and \( \omega_z(t) \). In the interaction representation we have

\[
X_0 = Z, \quad X_\pm = \frac{1}{\sqrt{2}} \left( X \pm iY \right) \exp (\mp i\omega t),
\]

\[
\omega^\pm = \frac{1}{\sqrt{2}} \omega_x(t) \exp (\mp i\omega t),
\]

the system equivalent to (4) being

\[
\dot{X} = i\Omega(t) X,
\]

\[
\begin{pmatrix}
X_+ \\
X_-
\end{pmatrix}, \quad \Omega(t) = \begin{pmatrix}
\omega_z, & 0, & -\omega_+ \\
0, & -\omega_z, & \omega- \\
-\omega_-, & \omega+, & 0
\end{pmatrix}.
\]

Here \( \Omega \) is dependent on time, in general. The specific features of molecular interaction in a gas appear as the fact that \( \Omega(t) \) differs from zero only during collisions, whose characteristic time is \( \tau_\text{c} \); between these (characteristic time \( \tau_\text{c} \)) \( \omega(t) = 0 \). The tunneling period \( \tau_\text{t} \approx 1/\omega \) is typically much larger than \( \tau_\text{c} \) \( \tau_\text{c} \) is about \( 10^{-12} \) sec, whereas \( \omega \) for the inversion of \( \text{NH}_3 \) is \( 2.4 \times 10^{10} \) sec \(^{-1} \), for example, so we may assume as follows in solving (6):

\[
\tau_0 \ll \tau_\text{t}, \quad \omega \tau_0 \ll 1.
\]

We also assume that \( \omega(t) \) for collision \( i \) may be put as

\[
\Omega_i(t) = f(t) \Omega_0^i,
\]

in which \( \Omega_0^i \) is a matrix independent of time, but whose elements \( \omega_X \) and \( \omega_z \) are functions of \( t \) (by \( t \) we may understand the set of parameters characterizing collisions of a pair of particles, such as the velocities at infinity); \( f(t) \) is a nonmatrix time function. The precise physical significance of (8) is discussed below. The solution to (6) may be put formally as an infinite series:

\[
X(t + \tau) - X(t) = \sum_{n=0}^{\infty} \int_{t}^{t+\tau} \int_{t}^{t+\tau} \int_{t}^{t+\tau} \Omega(t_1) dt_1 \Omega(t_2) dt_2 \cdots \Omega(t_n) dt_n. \tag{9}
\]

Then (7) is used to choose a time \( \tau \) such that \( \tau_0 \ll \tau \ll \tau_\text{t} \); then the \( \Omega^\tau(t) \) of (9) can be the \( \Omega^\tau_k(t) \) corresponding to a collision with parameter \( k \) that occurs between times \( t \) and \( t + \tau \); (8) shows that the \( \Omega^\tau_k(t) \) commute pairwise so the series of (9) converges and gives

\[
B = \exp[i\Omega_k \tau_0] - 1,
\]

in which \( \tau_0 = \int f(t) dt \). The collisions are uncorrelated and the probability of a collision in time \( \tau \) is \( \tau/\tau_\text{c} \), so the average of (9) gives

\[
\langle X(t + \tau) \rangle - \langle X(t) \rangle = \langle \exp (i\Omega_k \tau_0) - 1 \rangle \frac{\tau}{\tau_\text{c}} \langle X(t) \rangle. \tag{10}
\]

\( B \) can be found quite simply, because (6) has definite symmetry. We omit intermediate steps; the final result is

\[
B = \frac{1 - \cos \omega_0 \tau_0}{\omega_0^2} \left| \begin{array}{ccc}
\omega_z^2 + \frac{\omega_z^2}{2}, & -\frac{\omega_z^2}{2} \phi_+^\tau_\text{c}(\tau), & -\frac{\omega_z \omega_x}{\sqrt{2}} \phi_+^\tau_\text{c}(\tau) \\
-\frac{\omega_z^2}{2} \phi_-^\tau_\text{c}(\tau), & \omega_z^2 + \frac{\omega_z^2}{2}, & -\frac{\omega_z \omega_x}{\sqrt{2}} \phi_-^\tau_\text{c}(\tau) \\
-\frac{\omega_z \omega_x}{\sqrt{2}} \phi_-^\tau_\text{c}(\tau), & -\frac{\omega_z \omega_x}{\sqrt{2}} \phi_+^\tau_\text{c}(\tau), & \omega_z^2
\end{array} \right|. \tag{11}
\]