FEATURE ARTICLE

Tunneling of Molecules in Low-Temperature Media: An Elementary Description

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We discuss the influence of the environment on the tunneling of molecules at low temperature, using elementary quantum mechanics. We show that even in the gas phase dephasing processes can render the tunneling incoherent and that the tunneling rate due to dephasing is often enormously decreased relative to the unperturbed period. In addition to these effects, in the condensed phase, a renormalization of the effective tunneling matrix element occurs.

I. Introduction

One of the earliest problems of molecular quantum mechanics was the nature and stability of chiral molecules.¹ Since electromagnetic forces conserve parity, it was realized that, in its simplest form, the behavior of chiral molecules could be represented as the motion of a particle in a symmetric double well potential V(q) with the coordinate representing the degree of chirality or handedness. The positions of the minima $(\pm q_0)$ are the equilibrium positions of the left-handed and right-handed molecules, respectively. The eigenstates of the Hamiltonian for this one-dimensional system

$$H = T + V(q) \tag{1}$$

namely

$$H\psi_n(q) = \epsilon_n \psi_n(q) \tag{2}$$

are eigenstates of parity as long as the barrier is neither infinitely high nor infinitely wide. Thus, states with a definite handedness must be coherent superpositions of the eigenstates and hence are nonstationary states. When only the lowest two eigenstates $(\psi_{\pm}(q))$ are important in a description of the system, then the "localized" or handed states may be written as

$$\psi_{\rm L}(q) = \frac{1}{2^{1/2}} (\psi_{+}(q) + \psi_{-}(q)) \tag{3a}$$

$$\psi_{\mathbf{R}}(q) = \frac{1}{2^{1/2}}(\psi_{+}(q) - \psi_{-}(q))$$
 (3b)

Hence, if the system is prepared at t = 0 in $\psi_{L}(q)$, the measurement of any handed property (including the position of the particle), will yield a result proportional to $\cos 2\delta t$, where 2δ is the energy splitting between ψ_+ and ψ_- . We call δ the tunneling matrix element. Its magnitude ranges from hundreds of hertz to the inverse of the lifetime of the universe, and thus its existence has been ignored except as a particularly visual manifestation of tunneling and the two-state model. The stability of handedness, when considered in a strictly one-dimensional model, was always justified by the smallness of δ .

The discovery that weak neutral currents imply the violation of parity at the level of nonrelativistic quantum mechanics² has renewed interest in the tunneling of handed molecules.³ This parity violation may modify V(q) through the addition of a small antisymmetric potential $\epsilon(q)$, which is determinable from electronic structure calculations. The total potential is now $V(q) + \epsilon(q)$, and thus the chiral molecule can be represented as moving in a slightly asymmetric double well with the difference in energies of the minima being 2ϵ . Of course, which handedness is lower depends on the molecule and (within the Born-Oppenheimer approximation) the state of the molecule.⁴

The dynamics of the chiral molecule in the two-state approximation is changed dramatically by this change in the potential. Ignoring the negligible changes in the shape of the wave functions in each well, a molecule prepared on the left at t = 0 will have handed properties that change in time as

property(t)
$$\propto \frac{\epsilon^2 + \delta^2 \cos 2(\epsilon^2 + \delta^2)^{1/2} t}{\epsilon^2 + \delta^2}$$
 (4)

Note that ϵ is a manifestation of the properties of the wave functions at $\pm q_0$, its magnitude is on the order of hertz, and it is independent of tunneling. Thus although ϵ is small, it may swamp the effects of tunneling. This represents the coherent competition between localization (ϵ) and tunneling (δ). Note that, if the tunneling dynamics of an isolated handed molecule prepared in a time short compared to its period could be measured, a unique confluence of high-energy and chemical dynamic processes could be measured. In addition, such a measurement would provide a confirmation of parity nonconservation in molecules in a manner complementary to spectroscopic measurements that have been proposed.

In the previous paragraph, we emphasized the word isolated. The processes that we have discussed involve the ratios of small numbers in systems perturbed from exact degeneracy. Clearly, omnipresent environmental effects may qualitatively change the dynamics. In the rest of this paper, we examine how this comes about. We shall consider both gas-phase environments as well as condensed matter. Throughout this paper we shall usually assume that the effect of static fields may be removed. In addition, we will also assume that what may be called "inhomogeneous incoherence"-those effects caused by a preparation time scale

⁽¹⁾ Hund, F. Z. Phys. 1927, 43, 805. A very recent discussion of this issue and many of those that follow, albeit in an entirely different manner, may be found in: Goldanskii, V. I.; Kunz'min, V. V. Z. Phys. Chem. (Leipzig) 1988, 269, 216.

⁽²⁾ For a recent textbook discussion of these issues see: Commins, E. D.; Bucksbaum, P. H. Weak Interactions of Leptons and Quarks; Cambridge University Press: Cambridge, UK, 1983; Chapter 9.
(3) Harris, R. A.; Stodolsky, L. Phys. Lett. 1978, 18B, 313.

⁽⁴⁾ Letokhov, V. Phys. Lett. 1975, 53A, 275.

on the order of or greater than an oscillation period of an isolated molecule ignoring parity violations need not be considered. In practice, these problems may present the greatest experimental difficulty.

Finally, we should point out that although we speak of handedness and chirality, the general considerations we consider are applicable to symmetric and slightly asymmetric double well potentials of all kinds. In some specific discussions later on, we use the effect of the parity operator on the S matrix to make statements about the relaxation rates; these discussions will not apply to a general double well potential unless some other symmetry element is operative in that case which plays the role of parity in the chiral case.

In section II, we define some notation and make some general remarks on the effect of fluctuations on tunneling. In section III, we present a crude model for the effect of dephasing on tunneling, and in section IV we discuss in more detail a collisional model for the dynamics. Finally, in section V, we discuss the effect of a condensed phase on tunneling in the simplest spin-boson model.

II. The Coupling of a Double Well Potential to a Medium: General Considerations

Consider the coupling of the double well coordinate to another system. The latter be the other degrees of freedom in the molecule itself. Such an interaction occurs when normally decoupled degrees of freedom (in the isolated molecule) are recoupled due to the interaction between the molecule and a medium. We shall consider this situation in some detail when the molecule is in a gas. In this case, the new degree of freedom is rotation. When the molecule is in a condensed phase such as a solid, rotational motion is often severely hindered; in that case other degrees of freedom may become important.

The explicit form the potential energy of interaction takes varies with the system and medium. Suppose we call this potential V(q,Q), where the variable Q denotes all the other degrees of freedom. In the two-state limit we must be careful to distinguish the gas-phase interactions from the condensed-phase interaction. In the former case, we consider the *isolated-molecule* two-state system as the starting point and ignore the role collisions may have on the molecular double well itself. In the condensed phase, the equilibrium positions of the molecules of the medium may change the shape of the double well potential sufficiently so that we must redefine the starting point as the effective double well potential (or effective two-state system) in the medium. In this case, however, we need only change the magnitudes of δ and ϵ . We may therefore take the two-level system as a general starting point for our discussion.

Given this, we may write the most general potential for the two-state model as⁵

$$V(q,Q) = V_0(Q)\mathbf{1} + \mathbf{V}_1(Q)\cdot\boldsymbol{\sigma}$$
(5)

where we use the notation

$$\sigma = \hat{e}_x \sigma_x + \hat{e}_y \sigma_y + \hat{e}_z \sigma_z \tag{6a}$$

and

$$\sigma_{z}|L\rangle = |L\rangle \qquad \sigma_{z}|R\rangle = -|R\rangle \tag{6b}$$

The potentials $V_i(Q)$ are given by

$$V_0(Q) = \frac{1}{2} \left[\int dq \ \psi_L(q) \ V(q,Q) \ \psi_L(q) + \int dq \ \psi_R(q) \ V(q,Q) \ \psi_R(q) \right]$$

$$\equiv \frac{1}{2} [\langle L|\mathcal{V}|L\rangle_{q} + \langle R|\mathcal{V}|R\rangle_{q}]$$
(7)

and

$$V_{z}(Q) = \frac{1}{2} [\langle L|V|L \rangle_{q} - \langle R|V|R \rangle_{q}]$$
(8)

and

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$$V_{x}(Q) = \frac{i}{2} [\langle L|V|R \rangle_{q} + \langle R|V|L \rangle_{q}]$$
(9a)

$$V_{y}(Q) = \frac{i}{2} [\langle \mathbf{L} | \mathcal{V} | \mathbf{R} \rangle_{q} - \langle \mathbf{R} | \mathcal{V} | \mathbf{L} \rangle_{q}]$$
(9b)

remembering that, in a condensed medium, ψ_L and ψ_R incorporate static effects of other modes. We see that, in this representation, V_x and V_y differ greatly from V_0 and V_z . If V(q,Q) is a local operator, then V_0 and V_z depend on the wave functions in each well, while V_x and V_y depend on the overlap of the wave functions in the barrier region. Thus V_z and V_0 can be taken to be significantly larger than V_x and V_y . There may be situations where this is not the case. For example, if the higher levels in the double well become important, one can imagine still treating the system as a two-level system by transforming the Hamiltonian so that the effect of the higher states is manifested by a nonlocal potential. In this case, it may turn out that V_x and V_y can be larger than δ and must therefore be taken into account.

We can think about V_0 and V_z as medium-dependent fluctuations in the depths of the left- and right-hand sides of the double well potential and V_x and V_y as medium-dependent fluctuations in the barrier of the double well. (We say fluctuations because the average or static part of these terms can simply be added to the isolated molecule potential.) For most of the remainder of this article we shall assume that the potential is given by

$$V(q,Q) = V_0 1 + V_z \sigma_z$$
 (10)

By causing fluctuations in the well depths, this potential acts as a dynamic version of the parity-violating potential ($\epsilon \sigma_z$). The effect of V is to promote localization (i.e., its eigenstates are |L) and |R)) while the effect of δ is to promote delocalization; hence we have again a competition between the delocalization through tunneling and localization through parity violation and interaction with a medium. Note that the term $V_x \sigma_x$ is a term that can either enhance or suppress tunneling depending on its sign relative to that δ . When V_x becomes large, this will signal the decreasing validity of the two-state model.

III. The Crudest Theory of Dephasing^{4,6}

In the previous section we pointed out that, in the absence of weak interactions, the dynamics of a molecule in a medium which couples to the molecule via a potential given by (10) exhibits the competition between delocalization $(\delta \sigma_x)$ and localization V. In certain limits this is known as "pure dephasing" since delocalization is represented as a coherence of $|L\rangle$ and $|R\rangle$ and localization represents incoherence.

We can exhibit this competition by a very simple model called "collision interruptus". Imagine the handed molecule subjected to random collisions in a gaseous, parity-neutral medium. The mean time between collisions is $\tau_{\rm c}$, and the duration of a collision is $\tau_{\rm c}$. In the extreme case of dephasing we consider

$$\delta^{-1} \gg \tau \gg \tau_{\rm c} \tag{11}$$

We think of the molecule as freely tunneling for a time τ (by freely tunneling we mean acting under the Hamiltonian of the isolated molecule) and then undergoing a perfect dephasing collision for a time τ_c . By a perfect dephasing collision, we mean a collision in which the coherence is completely interrupted and then the system begins freely tunneling again, but starting from the condition after the collision. Quantitatively, we take the density matrix of the system to be

$$\rho(t) = \frac{1}{2} [1 + \mathbf{P}(t) \cdot \boldsymbol{\sigma}]$$
(12)

Suppose initially, the system is on the left; then

$$\rho(0) = \frac{1}{2}(1 + \sigma_z) \tag{13}$$

i.e.

$$P_z(0) = 1, P_x(0) = 0 = P_v(0)$$
 (14)

After a time τ , we will have

⁽⁵⁾ See Cohen-Tannoudji, C.; Diu, B.; Laloe, F. *Quantum Mechanics*; Wiley: New York, 1977; Vol. I, for a good discussion of the two-state approximation and tunneling in a double well.

⁽⁶⁾ Simonius, M. Phys. Rev. Lett. 1978, 26, 980.

$$P_z(\tau) = \cos 2\delta\tau \qquad (15a)$$

$$P_x(\tau) = 0 \tag{15b}$$

$$P_{\nu}(\tau) = \sin 2\delta\tau \tag{15c}$$

By our previous arguments, a concomitant of the delocalization in L and R ($P_z(\tau)$ ceasing to be 1), there is a buildup in phase coherence in the density matrix component $P_y(\tau)$ (which grows from 0). Now, suppose at time τ there is a perfect collision (lasting a time τ_c), in which the system is localized by the interaction. Thus after the collision P_y is again 0, but P_z is cos $2\delta\tau$. Now the system begins to tunnel freely again beginning from this initial condition. After N such events

$$P_{z} = (\cos 2\delta\tau)^{N} \simeq (1 - 2\delta^{2}\tau^{2})^{N} = e^{-2(\delta^{2}\tau)N\tau}$$
(16)

Now $N\tau = t$, the time after N events, so that

$$P_z = e^{-Rt} \tag{17}$$

where the relaxation rate is given by

$$R \approx 2\delta^2 \tau \tag{18}$$

Thus

$$R^{-1} \gg \delta^{-1} \gg \tau \tag{19}$$

and pure dephasing acts to stabilize the handed molecule on a time scale much longer than the tunneling period, and also much longer than the time scale between collisions.

The crude model discussed above is instructive in two respects. First, we can see how pure dephasing may stabilize handedness on a time scale long compared to the tunneling period, indeed on a macroscopic time scale. Second, we note that whatever time development occurs, occurs in such a way that $P_z(t)$ shrinks in size.

IV. The Dilute Gas Limit⁷

In order to construct a quantitative version of the extreme dephasing model described in the previous section, let us consider how a single collision may induce incoherence into the density matrix of the tunneling degree of freedom of the molecule. Suppose that before a collision (with a gas atom) the overall wave function is

$$|\Psi_{\mathbf{B}}\rangle = |\Phi\rangle(c_{\mathbf{L}}|\mathbf{L}\rangle + c_{\mathbf{R}}|\mathbf{R}\rangle) \tag{20}$$

where $|\Phi\rangle$ contains the relative coordinate between atom and molecule as well as any other molecular degrees of freedom, assumed the same for both left and right states. The density operator is then

$$D_{\rm B} = |\Psi_{\rm B}\rangle \langle \Psi_{\rm B}| \tag{21}$$

and the reduced density operator for the tunneling degree of freedom is

$$p_{\rm B} = {\rm Tr}' D_{\rm B} \tag{22}$$

where Tr' means the trace over all degrees of freedom except the tunneling coordinate. In matrix form in the $|L\rangle$, $|R\rangle$ representation

$$\rho_{\rm B} = \begin{pmatrix} |c_{\rm L}|^2 & c_{\rm L}c_{\rm R}^* \\ c_{\rm R}c_{\rm L}^* & |c_{\rm R}|^2 \end{pmatrix}$$
(23)

and clearly

$$\rho_{\rm B}{}^2 = \rho_{\rm B} \tag{24}$$

We now assume a collision occurs where the duration of the collision, τ_c , is so short that we can talk about the wave function after the collision, Φ_A , being described by an S matrix. The most general form for the S matrix is

$$\mathbf{S} = S_0 \mathbf{1} + \mathbf{S} \cdot \boldsymbol{\sigma} \tag{25}$$

where S_0 and S_i are operators in the space of all degrees of freedom

except the tunneling coordinate. If the collision cannot induce transitions between $|L\rangle$ and $|R\rangle$, then

$$S = S_0 \mathbf{1} + S_1 \sigma_z \equiv S_L |L\rangle \langle L| + S_R |R\rangle \langle R|$$
(26)

The properties of unitarity of the S matrix demand that

$$S^{+}S = 1 = S_{0}^{+}S_{0}\mathbf{1} + S_{1}^{+}S_{1}\mathbf{1} + S_{1}^{+}S_{0}\sigma_{z} + S_{0}^{+}S_{1}\sigma_{z} \quad (27)$$

so that

$$S_0^+ S_0 + S_1^+ S_1 = 1 \tag{28}$$

and

$$S_0^+ S_1 + S_1^+ S_0 = 0 (29)$$

or, more simply,

$$S_{\rm L}^+ S_{\rm L} = 1 \tag{30}$$

$$S_{\rm R}^+ S_{\rm R} = 1 \tag{31}$$

That is, the S matrices for L and R scattering are separately unitary; however $S_L^+S_R$ is an operator whose norm can range from 0 to 1.

With the above in mind, let us calculate the state $|\Psi_A\rangle$ from $|\Psi_B\rangle$. By definition

$$|\Psi_{\rm A}\rangle = {\rm S}|\Psi_{\rm B}\rangle \tag{32}$$

or

$$|\Psi_{\rm A}\rangle = c_{\rm L}|L\rangle S_{\rm L}|\Phi\rangle + c_{\rm R}|R\rangle S_{\rm R}|\Phi\rangle \tag{33}$$

and the reduced density matrix of the tunneling degree of freedom is

$$\rho_{\mathbf{A}} = \begin{pmatrix} |c_{\mathbf{L}}|^2 & c_{\mathbf{L}}c_{\mathbf{R}}^* \langle \Phi | S_{\mathbf{R}}^+ S_{\mathbf{L}} | \Phi \rangle \\ c_{\mathbf{R}}c_{\mathbf{L}}^* \langle \Phi | S_{\mathbf{L}}^+ S_{\mathbf{R}} | \Phi \rangle & |c_{\mathbf{R}}|^2 \end{pmatrix}$$
(34)

From these equations, the dephasing role of the S matrix becomes clear. The difference in populations of L and R is clearly

$$P_{\rm L} - P_{\rm R} = |c_{\rm L}|^2 - |c_{\rm R}|^2 \tag{35}$$

which is unchanged in the collision. However, the density matrix elements which regulate the phase of ρ , namely, ρ_{LR} and ρ_{RL} , do change:

$$(\rho_{\rm A})_{\rm LR} = (\rho_{\rm B})_{\rm LR} \langle \Phi | S_{\rm R}^+ S_{\rm L} | \Phi \rangle \tag{36}$$

and

$$(\rho_{\mathsf{A}})_{\mathsf{R}\mathsf{I}} = (\rho_{\mathsf{B}})_{\mathsf{R}\mathsf{I}} \langle \Phi | S_{\mathsf{I}}^{\dagger} S_{\mathsf{R}} | \Phi \rangle \tag{37}$$

Since S_L and S_R are unitary operators, we have

$$|\langle \Phi | S_{\mathrm{L}}^{+} S_{\mathrm{R}} | \Phi \rangle| \leq 1 \tag{38}$$

Thus ρ_{LR} is constant or decreases during a collision, and incoherence increases during a collision.

We are now able to derive a set of homogeneous Bloch equations under the assumption that collisions occur at a uniform rate. Let us define a rate, or damping parameter, loosely as

$$\lambda \equiv [\langle \phi | S_{L}^{+} S_{R} | \phi \rangle - 1] (\text{number of collisions per second}) \rangle \quad (39)$$

where the outer brackets indicate certain averaging processes to be made more precise later. From (36) and (39), we have

$$\rho_{LR} \to \rho_{LR} + \lambda \rho_{LR} \, \mathrm{d}t \tag{40}$$

and

$$\rho_{\rm RL} \to \rho_{\rm RL} + \lambda^* \rho_{\rm RL} \, \mathrm{d}t \tag{41}$$

where we have allowed λ to be complex in general. In the limit of dt short compared to the time between collisions, but long compared to the duration of a collision, we may write

$$\left(\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t}\right)_{\mathrm{free}} + \left(\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t}\right)_{\mathrm{collisions}} \tag{42}$$

Now

⁽⁷⁾ Harris, R. A.; Stodolsky, L. Phys. Lett. 1982, 116B, 464; J. Chem. Phys. 1981, 74, 2145.

$$\left(\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t}\right)_{\mathrm{free}} = (2\delta\hat{e}_x + 2\epsilon\hat{e}_z) \times \mathbf{P}(t) \tag{43}$$

from the equations of motion of P(t) from tunneling and static asymmetry. From (42) and (43) we have

$$\left(\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t}\right)_{\mathrm{coll}} = \lambda'(\hat{e}_x P_x + \hat{e}_y P_y) + \lambda''\hat{e}_x \times \mathbf{P}$$
(44)

where λ' and λ'' are the real and imaginary parts of λ . The overall rate of change of **P** can then be written

$$\left(\frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t}\right) = \mathbf{V} \times \mathbf{P} - \lambda' \mathbf{P}_{\mathrm{T}}$$
(45)

where

$$\mathbf{V} = 2\delta\hat{e}_x + (2\epsilon + \lambda'')\hat{e}_z \tag{46}$$

and

$$\mathbf{P}_{\mathrm{T}} = \hat{e}_{x} P_{x} + \hat{e}_{y} P_{y} \tag{47}$$

Equation 45 is the Bloch equation in vector form; it does, however, suffer from the deficiency that the predicted equilibrium solution is equal probabilities in $|L\rangle$ and $|R\rangle$, irrespective of the energy asymmetry. If detailed balance is taken into account, the Bloch equations will have the correct infinite time solutions. In the gas phase where $\beta \epsilon \ll 1$ ($\beta = (k_B T)^{-1}$), this difference is of no importance. In the condensed phase, care must be taken to ensure the correct low-temperature behavior.

Before discussing the solutions to the Bloch equations, we may quantify our definition of λ and examine the meaning of λ' and λ'' . We consider the dilute gas limit and assume the other degrees of freedom act solely as a thermal bath. From standard scattering theory, we obtain the result

$$\lambda = \sum_{J} \sum_{i} w^{J}(i) \frac{n v_{i} \pi}{k_{i}^{2}} \sum_{f} \frac{(2J+1)}{(2J_{i}+1)(2J_{f}+1)} [1 - (S_{\text{Lif}}^{J})^{+} S_{\text{Rif}}^{J}]$$
(48)

Here, i and f refer to all initial and final states of the molecule including relative momentum, but excluding total angular momentum J. The probability of finding the colliding system in states i with total angular momentum J is $w^{J}(i)$. v_{i} is the relative velocity in the initial state, k_{i} the relative wave vector, and n the number density of the colliding species.

The real part of λ (λ') plays the role of a damping parameter, ubiquitous in kinetic or Bloch type equations. The meaning of λ'' is less clear, but since it adds to the asymmetry (2ϵ) in (46), we see that it is a collision-induced energy asymmetry. If the medium that interacts with the molecule is parity neutral, we then expect λ'' to be zero. Now, from (36) and (37), we see that λ'' is zero if

$$\operatorname{Tr} \rho' S_{\mathrm{L}}^{+} S_{\mathrm{R}} = \operatorname{Tr} \left(\rho' S_{\mathrm{L}}^{+} S_{\mathrm{R}} \right)^{*} \tag{49}$$

or

$$\operatorname{Tr} \rho' S_{\mathrm{I}}^{+} S_{\mathrm{R}} = \operatorname{Tr} \rho' S_{\mathrm{R}}^{+} S_{\mathrm{I}}$$
(50)

where ρ' is the density matrix for all the other degrees of freedom before a collision. The total parity operator, P, can be written as a parity operator P' operating on the other degrees of freedom multiplied by σ_x :

$$P = P'\sigma_x \tag{51}$$

Under parity, we then have

$$S_{\rm R} = P'S_{\rm L}P' \tag{52}$$

$$\operatorname{Tr} \rho' S_{1}^{+} S_{P} = \operatorname{Tr} \rho' P' S_{P}^{+} P' P' S_{1} P'$$
(53)

or

$$\operatorname{Tr} (P'\rho'P')S_{\mathrm{R}}^{+}S_{\mathrm{L}} = \operatorname{Tr} \rho'S_{\mathrm{L}}^{+}S_{\mathrm{R}}$$
(54)

i.e., if all the other degrees of freedom have no parity sense, then $\lambda^{\prime\prime}=0.$

When the handed molecule is in a spinless atomic gas, the role that angular momentum and parity conservation play in evaluating λ' merits discussion. The relevant degrees of freedom here are the relative kinetic energy, the relative angular momentum, and the rotational energy and angular momentum of the molecule, an asymmetric top. We neglect vibrations as being too high in excitation energy to contribute.

Let us represent λ as (see (39))

$$\lambda \propto \operatorname{Tr} \rho'(S_{\mathrm{L}}^{+}S_{\mathrm{R}} - 1)$$
(55)

Using the parity operator, $P = P'\sigma_x$, and the unitarity of S_R , we may write this as

$$\lambda \propto \operatorname{Tr} \rho'[P'S_{R}^{*}P'S_{R} - S_{R}^{*}S_{R}]$$
(56)

or

$$\lambda \propto \operatorname{Tr} \left\{ \rho'[P'S_{\mathsf{R}}^{\dagger}P' - S_{\mathsf{R}}^{\dagger}]S_{\mathsf{R}} \right\}$$
(57)

Consider a given term in (57) involving the relative angular momentum, l,

$$I_{ll'} \equiv (\langle l|P'S_{\mathbf{R}}P'|l'\rangle - \langle l|S_{\mathbf{R}}|l'\rangle)\langle l'|S_{\mathbf{R}}|l\rangle$$
(58)

where we have ignored all other labels. Since $P(l) = (-1)^{l} |l\rangle$

$$I_{ll'} \propto ((-1)^{l+l'} - 1)$$
 (59)

Hence, $I_{ll'}$ vanishes when l + l' is even; i.e., $|l\rangle$ and $|l'\rangle$ must have opposite parity to contribute to λ . We now apply the overall parity operator to the S matrix itself. Note that the parity operator P'is *either* that operating on the relative coordinate *or* that operating on the rotational coordinate, so that the total parity operator can be taken as the product of these two. In the representation diagonal in J and M, we then have

$$\langle ljm|S_{\rm L}^{JM}|l'j'm'\rangle = \langle ljm|P_{\rm rel}P_{\rm rot}S_{\rm L}^{JM}P_{\rm rot}P_{\rm rel}|l'j'm'\rangle \quad (60)$$

so that

$$(-1)^{l+l'+jpj'+m+m'} = 1$$
(61)

Here the states $|ljm\rangle$ are eigenstates of parity. Note that the allowed values of the pair l,j are fixed by conservation of angular momentum. Equations 59 and 61 imply that, in order to contribute to $\lambda', j + j' + m + m'$ must be odd. Since the energy levels of an asymmetric top with different values of the pair (j,m) are not degenerate, we come to the result that only *inelastic* processes contribute to λ . This plus the opposite parity of l and l' allow two important conclusions. First, the relaxation rate is due to the quantum mechanical interference of partial waves, and second, if inelastic collisions do not contribute because of the temperature or masses, λ will be zero. Hence, unlike the usual case, very delicate processes are necessary to have a nonvanishing λ for gas-phase relaxation of handedness.

Before going on to condensed-media problems, we briefly exhibit the above conclusion using a simple one-dimensional model. Here, of course, the angular momentum restriction does not apply, but parity and energy consideration play important roles.

In one dimension S_L and S_R are determined by solving the Schrödinger equations describing elastic scattering from particles localized in the left and right wells of a double well centered at the origin. In the two-state model, the interaction of an atom with a particle in, e.g., the left wall is a simple potential in the atomic degree of freedom localized at q = -a where -a is the position of the minimum in the left-hand well. Thus we are led to the two Schrödinger equations:

$$H_{\rm L}\psi_{\rm L} \equiv [p^2/2m + V(q+a)]\psi_{\rm L}(q) = E\psi_{\rm L}(q)$$
(62)

and

$$H_{\rm R}\phi_{\rm R} \equiv [p^2/2m + V(q-a)]\psi_{\rm R}(q) = E\psi_{\rm R}(q) \qquad (63)$$

where V(q) is the interaction of the atom and a particle localized at the origin. Because we are simulating the three-dimensional problem, we assume V(q) is finite. Thus, we are not considering in any sense collinear scattering. In passing we note that, in order for parity to be conserved, we must have

$$V(q) = V(-q) \tag{64}$$

The scattering solutions of (62) and (63) determine S_L and S_R , respectively.

The scattering states in one dimension are discussed in the literature. Both ψ_L and ψ_R can be derived from the solution ψ of the unshifted scattering problem.

$$H\psi \equiv [p^2/2m + V(q)]\psi = E\psi \tag{65}$$

The continuous spectrum of H is double degenerate, so that we will label ψ by two quantum numbers: the energy E and a quantum number μ which takes only two values, ± 1 . The scattering wave functions are defined with the following boundary conditions:

$$\psi_{E}^{(\mu)}(q) = \exp(i\mu kq) + R_{\mu} \exp(-i\mu kq), \quad q \to -\infty$$
$$= T_{\mu} \exp(i\mu q), \quad q \to -\infty \tag{66}$$

where

$$E = h^2 k^2 / 2m \tag{67}$$

and T_{μ} and R_{μ} are the transmission and reflection amplitudes, respectively. (*R* here should not be confused with the label *R* in $S_{\rm R}$ and $\psi_{\rm R}$, which stands for "right".) The one-dimensional *S* matrix that corresponds to $\psi^{(\mu)}(q)$ is

$$\boldsymbol{S} = \begin{pmatrix} T_{-1} & R_{-1} \\ R_1 & T_1 \end{pmatrix} \tag{68}$$

Due to the reflection symmetry of the Hamiltonian, $T_{-1} = T_1$ and $R_{-1} = R_1$, so that from now on we will denote T_{-1} and T_1 by T, and R_{-1} and R_1 by R.

It is an exercise in 1D scattering theory to show that

$$S_{\rm L}^{+}S_{\rm R} = \begin{pmatrix} |T|^2 + \gamma^2 |R|^2 & \gamma^* R T^* + \gamma R^* T \\ \gamma^* R^* T + \gamma R T^* & |T|^2 + \gamma^{*2} |R|^2 \end{pmatrix}$$
(69)

where $\gamma = \exp(2ika)$.

The overlap matrix $S_L^+ S_R$ clearly expresses the quantum-mechanical nature of the relaxation process. The nonvanishing of the relaxation rate λ is due to the simple interference in the scattering of the double well. The amplitudes of the scattering from each well are simply phase shifted from one another. With a small amount of effort one may show that λ is given by

$$\lambda = \rho \langle \nu \rangle G(\nu) \tag{70}$$

where ρ is the density of the scatterers, and $\langle \nu \rangle$ is the average speed:

$$\langle \nu \rangle = (h/mZ) \int_0^\infty k \exp(-\beta h^2 k^2/2m) \, \mathrm{d}k$$

= $(h\beta Z)^{-1} = (2/\pi m\beta)^{-1}$ (71)

The function G(v) is given by

$$G(\nu) = 4\nu \int_0^\infty x \, \exp(-\nu x^2) \, \sin^2 x |R|^2 \, \mathrm{d}x \tag{72}$$

where $x = 2ak = \Delta k$, and

$$\nu = \beta h^2 / 2m\Delta^2 \tag{73}$$

is the only significant dynamical parameter in the one-dimensional model. (There may be additional parameters in the problem stemming from V(q).) In (70), $\rho(\nu)$ is essentially the geometric factor (corresponding to ideal reflection, $|R|^2 = 1$). The effect of the interference between the waves that are scattered from the particles localized in the left and right wells is embedded in the function $G(\nu)$.

Because V(q) is taken to be finite, classically, $|R|^2$ behaves as

$$|R|^2 = 1, \quad x < x_c$$

= 0, $x > x_c$ (74)

where $x_c = (\Delta/h)(2mE_c)^{1/2}$ and E_c is the energy that is necessary to surmount the potential barrier. In fact, (74) is a good approximation to the quantum-mechanical reflection coefficient as well, so that we can derive the general behavior of $G(\nu)$ by using the classical reflection coefficient. Denoting the "classical" interference term for G_{cl} , we get

$$\lambda \propto \nu^{-3/2}, \quad \nu x_{\rm c} \gg 1$$

$$\propto \nu^{1/2}, \quad \nu x_{\rm c} \ll 1 \tag{75}$$

Thus, λ exhibits a maximum as a function of temperature and tends to zero at both low and high temperatures.

Extreme quantum-mechanical behavior can be simulated by considering the scattering by a δ function. In this case

$$|R|^2 = \eta^2 / (\eta^2 + x^2) \tag{76}$$

where η is a dimensionless constant. This reflection coefficient gives rise to

$$G_{\delta}(\eta,\nu) = 4\eta^{2}\nu \int_{0}^{\infty} x \exp(-\nu x^{2}) \sin^{2} x \frac{dx}{x^{2} + \lambda^{2}}$$
(77)

It may be shown that G_{δ} also vanishes in the limits $\nu \to 0$, ∞ although the asymptotic behavior at $\nu \to 0$ is different from that of (77) for the classical case.

Since (74) will be a good approximation for the reflection coefficient in most cases (the δ function being an extreme exception), $G_{\rm el}$ may be a more or less universal function. However, appreciable deviations can occur if V has a length scale that matches the distance between the wells Δ . This one-dimensional model is very similar to the two-slit problem in which only a thermally averaged phase remains.

The important conclusion of this one-dimensional model is that λ does not have a monotonic behavior as a function of temperature. This result, as we argued above, is due to the severe restrictions parity and energy conservation imply and thus should be generally valid. With this in mind we conclude our discussion of the gas-phase problem by examining the relation of the "collision interruptus" model of section III to the solutions of the Bloch equations.

Consider the simple case of no asymmetry so that $\epsilon = \lambda'' = 0$. In this case the variable P_x is uncoupled from P_z and P_y , so we have

$$\frac{\mathrm{d}P_z}{\mathrm{d}t} = 2\delta P_y \tag{78}$$

$$\frac{\mathrm{d}P_y}{\mathrm{d}t} = -2\delta P_z - \lambda' P_y \tag{79}$$

which can be put into the form of a damped harmonic oscillator equation

$$\frac{\mathrm{d}^2 P_z}{\mathrm{d}t} + \lambda' \frac{\mathrm{d}P_z}{\mathrm{d}t} + (2\delta)^2 P_z = 0 \tag{80}$$

when λ' is smaller than 4δ , P_z undergoes damped oscillations to the equilibrium, $P_z = 0$. When $\lambda' \gg 4\delta$, we have

$$P_{z}(t) = P_{z}(0) \left\{ e^{-(2\delta)^{2}t/\lambda'} + \frac{(2\delta)^{2}}{\lambda'} e^{-\lambda' t} \right\}$$
(81)

so that

$$P_z(t) \simeq P_z(0)e^{-Rt} \tag{82}$$

where the rate R is

$$R = (2\delta)^2 / \lambda' \tag{83}$$

in full agreement with the "collision interruptus" model (with $\tau^{-1} = \lambda'$).

We call this model "racemization by dephasing". While high-temperature racemization follows an Arrhenius law, this model clearly does not, unless λ' is proportional to $\exp(E/k_BT)$. Note that if $\lambda' \gg (2\delta)$, the handedness of the molecule may be

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stabilized on a time scale enormously long compared to the period δ . In addition, on kinetic theory grounds we expect λ' to decrease as temperature decreases; hence R may increase as temperature decreases, until the oscillations become underdamped. Similarly as the collision rate increases, λ' increases and the rate decreases. This paradoxical behavior is characteristic of dephasing as opposed to kinetic racemization.

There is another, intuitive way of describing what happens in terms of the mean position of the double well coordinate defined as

$$q = |L\rangle\langle L|q|L\rangle\langle L| + |R\rangle\langle R|q|R\rangle\langle R|$$
(84)

Since

$$-\langle \mathbf{L}|q|\mathbf{L}\rangle = +\langle \mathbf{R}|q|\mathbf{R}\rangle = q_0 \tag{85}$$

we have

$$q = q_0[|\mathbf{R}\rangle\langle\mathbf{R}| - |\mathbf{L}\rangle\langle\mathbf{L}|] = -q_0\sigma_z \tag{86}$$

Similarly, from the Heisenberg equations of motion

$$\dot{q} = -q_0(2\delta)\sigma_y \tag{87}$$

Thus far, we have neglected fluctuations; when these are included we find

$$\langle q(t) \rangle = -q_0 P_z(t) \tag{88}$$

and so the equation of motion of $\langle q(t) \rangle$ is that of a damped oscillator

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle q(t)\rangle + \lambda' \frac{\mathrm{d}\langle q(t)\rangle}{\mathrm{d}t} + (2\delta)^2\langle q(t)\rangle = 0 \tag{89}$$

with general initial conditions

$$\langle q(0) \rangle = -q_0 P_z(0) \tag{90}$$

$$\langle \dot{q}(0) \rangle = -2\delta q_0 P_y(0) \tag{91}$$

The slow relaxation to equilibrium as expressed earlier now becomes manifested in the well-known second relaxation time of an overdamped harmonic oscillator, displaced from the origin, with no significant initial velocity. (The role of initial velocity is to modify the transient.) We shall see that the ideas presented here as far as $P_z(t)$ or $\langle q(t) \rangle$ obeying a damped oscillator equation will persist in a condensed medium. The values of δ and λ will be modified significantly, however. The dephasing aspect of the problem remains unchanged.⁸

What happens when ϵ is not zero? Nothing much in the gas phase, as long as $\beta \epsilon \ll 1$. In the equations of motion, all three components of $\mathbf{P}(t)$ are coupled and so, strictly speaking, the population difference $P_z(t)$ no longer satisfies a damped oscillator equation. In the overdamped limit, we find

$$P_{z}(t) = P_{z}(0) \exp\left\{-\frac{(2\delta)^{2}t}{\lambda'}\left[1 + \frac{\{(2\epsilon)^{2} + (2\delta)^{2} + (\lambda'')^{2}\}}{\lambda'^{2}}\right]\right\}$$
(92)

so that in this limit, the asymmetry changes the rate by at most a small numerical factor.

V. Tunneling System in a Condensed Phase

A. Renormalization of Tunneling Matrix Element. We now turn to the dynamics of a particle in a double well potential when placed in a condensed phase.⁹ Although many of the issues mentioned in the preceding sections are also important here, a new issue arises when the coupling is strong: the renormalization of the tunneling matrix element, δ , due to the coupling. This possibility exists because the medium is always present; the idea of a collision loses its meaning. The simplest representation of a condensed phase relevant to chemical systems (as well as many others) is, of course, a collection of harmonic oscillators. When the oscillators couple linearly to the double well, the result is the ubiquitous spin-boson model studied at great length by many and, in particular recently, by Leggett and his co-workers. The results of their labors may be found in the massive article found in *Reviews of Modern Physics.*⁹ Our discussion follows a more traditional approach and in a way is closely related to the gas-phase theory.¹⁰ The theory proceeds in two steps. First, we examine what happens to the tunneling frequency when the system is in equilibrium. The spin-boson Hamiltonian is given by (in the |L), |R) representation)

$$H = \delta \sigma_x + \frac{1}{2} \sum_i (p_i^2 + \omega_i^2 q_i^2) + \sum_i g_i q_i \sigma_z$$
(93)

Here we have assumed that the asymmetry ϵ is zero; if there is an asymmetry, we add a term $\epsilon \sigma_z$.

The eigenfunctions of this Hamiltonian can easily be found in two limiting cases: (i) If $g_i = 0$ for all *i*, then the eigenvalues (neglecting zero-point energies) are $\pm \delta + \sum_i \nu_i \omega_i$, where ν_i are integers, and the eigenvectors are $|\pm\rangle = 1/2^{1/2}(|L\rangle \pm |R\rangle) \times |\{\nu_j\}\rangle$. (ii) If $\delta = 0$, then the eigenvectors are displaced oscillators whose displacements depend on whether the particle is in the left well $(|L\rangle)$ or right well $(|R\rangle)$. These latter states can be represented as

$$|\mathbf{A};\nu_{j}\rangle \equiv \exp\left[\pm i\left\{\sum_{j}\frac{p_{j}g_{j}}{\omega_{j}^{2}}\right\}\right]|\mathbf{A}\rangle|\{\nu_{j}\}\rangle$$
(94)

where $|\{v_j\}\rangle$ is an eigenstate of the uncoupled harmonic oscillator Hamiltonian and A is either L or R.

When neither of these conditions is met, the eigenstates of this Hamiltonian are not known. In this case, we might try standard perturbation theory or a variational-perturbation method. The latter procedure turns out to be both accurate and instructive, so we adopt this approach. The simple variational method we use is, of course, not exact and can be improved in a variety of ways.¹⁰ However, it is a straightforward procedure to describe the main qualitative features of the dynamics. For the infrared divergent case, in which subtle transitions occur, the variational method is only a good zero-order guide to the behavior. For the nondivergent cases, we expect it to be better. To begin we consider the zero temperature case.

The key physical idea is that each harmonic model will be displaced on average an amount which depends on δ , g_j , and ω_j . For large frequency, ω_j , the harmonic mode will be able to follow the tunneling particle exactly, so that if the tunneling particle is on the left, the mode will be fully displaced to its left equilibrium position and similarly for the right side. For small ω_j , however, the mode will be "sluggish" and unable to follow the tunneling particle, so that the displacement of that mode will be substantially reduced. Since the effective tunneling matrix element, δ_{eff} , will be δ multiplied by a product of Franck-Condon overlap factors (one for each mode), δ_{eff} will depend sensitively on the spectral distribution of frequencies (ω_i), the coupling constants (g_i), and δ itself. We are then led to taking simple approximate forms for the trial wave functions based on our knowledge of the form of the eigenfunctions when $\delta = 0$:

$$\tilde{\mathbf{L}};\nu_{j}\rangle = \exp\left\{i\sum_{j}\frac{f_{j}p_{j}}{\omega_{j}^{2}}\right\}|\langle\nu_{j}\rangle\rangle|\mathbf{L}\rangle$$
(95)

$$|\tilde{\mathbf{R}};\nu_{j}\rangle = \exp\left\{-i\sum_{j}\frac{f_{j}p_{j}}{\omega_{j}^{2}}\right\}|\{\nu_{j}\}\rangle|\mathbf{R}\rangle$$
(96)

Here we have displaced each oscillator by a fraction (f_j/g_j) of the full amount it would be displaced if $\delta = 0$. Using these trial

⁽⁸⁾ Harris, R. A.; Silbey, R. J. Chem. Phys. 1983, 78, 7330.

⁽⁹⁾ See Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. *Rev. Mod. Phys.* **1987**, *59*, 1, for an extensive discussion of the functional integral approach applied to this problem. In addition, this paper contains a definitive list of references for the spin-boson problem.

⁽¹⁰⁾ Silbey, R.; Harris, R. A. J. Chem. Phys. 1984, 80, 2615. Harris, R. A.; Silbey, R. J. Chem. Phys. 1985, 83, 1069.

 ⁽¹¹⁾ Carmeli, B.; Chandler, D. J. Chem. Phys. 1985, 90, 3400. Gross, E.
 P. Preprints, 1988.

functions, we can find the matrix elements of H; assuming that only the zero quantum ($\nu_j = 0$) states (the ground states) need be considered at T = 0, we find (neglecting zero-point energy)

$$\langle \tilde{L}; \{0_j\} | H| \tilde{L}; \{0_j\} \rangle = + \sum_j \frac{(f_j^2 - 2f_j g_j)}{\omega_j^2}$$
 (97)

$$\langle \tilde{\mathbf{R}}; \{\boldsymbol{0}_j\} | \boldsymbol{H} | \tilde{\mathbf{R}}; \{\boldsymbol{0}_j\} \rangle = + \sum_j \frac{(f_j^2 - 2f_j \boldsymbol{g}_j)}{\omega_j^2}$$
(98)

$$\langle \tilde{\mathbf{L}}; \{0_j\} | \boldsymbol{H} | \tilde{\mathbf{R}}; \{0_j\} \rangle = \delta \exp\left\{-\sum_j \frac{f_j^2}{\omega_j^3}\right\} \equiv \delta_{\text{eff}}$$
(99)

The lower eigenvalue of the two-dimensional matrix representing the Hamiltonian is then

$$\tilde{E} = -|\delta_{\text{eff}}| + \sum_{j} \left\{ \frac{(f_j^2 - 2f_j g_j)}{\omega_j^2} \right\}$$
(100)

we may now minimize this energy with respect to variations of the f_j . Taking the derivative of \tilde{E} with respect to f_j , we find

$$f_j = g_j (1 + 2|\delta_{\text{eff}}|/\omega_j)^{-1}$$
 (101a)

This result agrees with the qualitative arguments we made before. If the frequency of the mode, ω_j , is large compared to the effective tunneling matrix element $(|\delta_{eff}|)$, then $f_j \simeq g_j$, and so the mode is fully displaced wherever the tunneling particle is. That is, this mode tracks the tunneling particle as it moves. If however ω_j is small compared to the effective tunneling matrix element $|\delta_{eff}|$, then $f_j \approx g_j(\omega_j/2|\delta_{\text{eff}}|) \ll g_j$. Thus this mode cannot track the tunneling particle very well, and its displacement is quite small. For many systems of interest, the most important modes are relatively high frequency compared to the tunneling matrix element. After all, the vibrational modes of common molecules have frequencies of a few hundred cm⁻¹ or higher, while tunneling matrix elements are usually smaller than 1 cm⁻¹. However, when the tunneling system is put in a condensed phase, the latter has vibrational or other modes with very low frequencies. We must be extremely careful in treating the dynamics of these modes in particular when these interact with the tunneling particle. It turns out, as we shall see, that the important measure of the interaction between the tunneling particle and the thermal bath is given by

$$J(\omega) = \sum_{j} \frac{g_i^2}{\omega_j} \delta(\omega - \omega_j)$$
(102)

Notice that if g_j^2 is a function of ω_j only (i.e., $g_j^2 = g^2(\omega_j)$, then

$$J(\omega) = \frac{g^2(\omega)}{\omega}\rho(\omega)$$
(103)

where $\rho(\omega)$ is the density of states of the harmonic modes in the thermal bath as frequency ω .

The effect of the modes on the effective tunneling matrix can be rather large. Consider the formula for δ_{eff} :

$$\delta_{\text{eff}} = \delta \exp[-\{\sum_{j} f_j^2 / \omega_j^3\}]$$
(104)

The exponential is, as we have stressed, the product of Franck-Condon factors for the modes. For the high-frequency modes $f_j \approx g_j$ and the Franck-Condon factor for that mode is a $e^{-g_j^2/\omega_j^2} < 1$. For the low-frequency modes, the result is more complex. Consider what would happen if $f_j = g_j$ (note this is not the variational solution) for all modes: the total Franck-Condon factor in this case is

$$\exp\left[-\left\{\sum_{j} g_{j}^{2} / \omega_{j}^{3}\right\}\right] = \exp\left[-\int_{0}^{\omega_{c}} J(\omega) / \omega^{2} d\omega\right] \quad (105)$$

This formula shows how the Franck-Condon factor (and ultimately the dynamics of the two-level system) depends on $J(\omega)$, the spectral density. Notice that if $J(\omega)$ varies as ω^{α} near $\omega =$ 0, and if $\alpha \leq 1$, the integral diverges and the total Franck-Condon factor is zero. This implies that the amplitude for tunneling, δ_{eff} , becomes zero (at T = 0) and the two states $|L\rangle$ and $|R\rangle$ are degenerate; i.e., the symmetry has been broken. For the optical isomer example, this would imply that the isomers are stable (at this level of approximation); i.e., they never interconvert by tunneling, at least to this order.

We have already indicated a difficulty with this argument: the low-frequency modes in the bath cause the divergence in the integral, but these modes are those which are sluggish and do not displace as fully as they can (i.e., $f_j \neq g_j$ for these modes). If we now compute the Franck-Condon factor and δ_{eff} for the variational wave functions using (101a) for f_j , we find

$$\delta_{\text{eff}} = \delta \exp\left[-\sum_{j} \frac{g_{j}^{2}/\omega_{j}}{\left(1 + \frac{2|\delta_{\text{eff}}|}{\omega_{j}}\right)^{2}}\right]$$
(106a)
$$= \delta \exp\left[-\int_{0}^{\omega_{\text{c}}} \frac{J(\omega) \, d\omega}{(\omega + 2|\delta_{\text{eff}}|)^{2}}\right]$$
(106b)

This is a self-consistent equation for δ_{eff} , which can be solved by iteration or, in certain, cases, by analytic means.

We will consider the cases $J(\omega) = \eta_{\alpha}\omega^{\alpha}$ for $\alpha = 1$ and 3. Consider $\alpha = 3$, which corresponds to the coupling constant and density of states for three-dimensional phonons interacting with a localized system. In this case

$$\delta_{\text{eff}} = \delta \, \exp\left[-\eta_3 \left\{ \int_0^{\omega_{\text{c}}} \frac{\omega^3 \, \mathrm{d}\omega}{[\omega + 2|\delta_{\text{eff}}|]^2} \right\} \right] \tag{107}$$

The integrand goes to zero as $\omega \rightarrow 0$ quickly enough, so that for δ/ω_c small, we have

$$\delta_{\rm eff} \simeq \delta \, \exp[-[\eta_3 \omega_{\rm c}^2/2]] \tag{108}$$

From the form of the variational energy ((100)), we have

$$\tilde{E} \simeq -|\delta_{\text{eff}}| - \frac{1}{2} \int_0^{\omega_c} \frac{d\omega J(\omega)}{\omega} = -|\delta_{\text{eff}}| - \frac{1}{6} \eta_3 \omega_c^3 \quad (109)$$

The latter term is the potential energy decrease due to the displacement of all the oscillators. For this case then, we find that the low-frequency modes play little role in the tunneling dynamics and the high-frequency modes act to diminish the tunneling matrix element by introducing a small Franck-Condon factor. As the coupling to the bath increases (η_3 gets larger), the tunneling matrix element δ_{eff} becomes smaller, but never becomes zero until $\delta_3 \rightarrow \infty$.

Now consider the Ohmic case, $J(\omega) = \eta_1 \omega$. As we pointed out above, this can lead to $\delta_{\text{eff}} = 0$ if all $f_j = g_j$. The variational equation for δ_{eff} is now

$$\delta_{\text{eff}} = \delta \exp\left[-\eta_1 \int_0^{\omega_c} \frac{\omega \, \mathrm{d}\omega}{[\omega + 2|\delta_{\text{eff}}|]^2}\right]$$
(110)

$$\simeq \delta \left(\frac{2|\delta_{\rm eff}|}{\omega_{\rm c}} \right)^{\eta_1} \tag{111}$$

So the self-consistent solution is either $|\delta_{eff}| = 0$ or

$$\delta_{\rm eff} = \delta \left(\frac{2|\delta_{\rm eff}|}{\omega_{\rm c}} \right)^{\eta_1/(1-\eta_1)} \tag{112}$$

It is easy to see that for $\eta_1 < 1$ the latter is on the lower energy solution to the variational problem, while for $\eta_1 > 1$ the former is the lower energy solution. Thus the variational calculation predicts that as the coupling to the bath increases (η gets larger) from zero, the effective tunneling matrix element becomes smaller and smaller and goes to zero for a finite coupling to the bath (η_1) = 1). Note that the potential energy due to the displacement of the modes which is given by

$$\sum_{j} (f_j^2 - 2f_j g_j) / \omega_j^2 = -\int_0^{\omega_c} \frac{J(\omega)}{\omega} \frac{(1 - 2\delta_{\text{eff}} / \omega)}{(1 + 2\delta_{\text{eff}} / \omega)^2} d\omega$$
$$\simeq -\eta_1 \omega_c \qquad (113)$$

does not become infinite even for $\delta_{eff} = 0$.

For temperatures above 0 K, we can calculate an upper bound on the free energy with the same set of states and find the renormalized tunneling matrix element by minimizing the free energy with respect to f_j again. This procedure leads to a temperature-dependent δ_{eff} .

The only differences between 0 K and finite temperature are the weighting of oscillator frequencies by the ubiquitous $\coth \beta \omega/2$ and the concomitant realization that the ground state of the two-state system is not 100% populated. These facts are expressed in the equation for the renormalized frequency and shifted oscillator amplitude, namely,

$$\delta_{\rm eff} = \delta \, \exp[-2\sum_{l} f_l^2 \omega_l^{-2} \, \coth \, (\beta \omega_l/2)] \equiv \delta e^{-2F} \quad (106c)$$

and

$$f_l = g_l (1 + 2\delta_{\text{eff}} \omega_l^{-1} \coth (\beta \omega_l/2) \tanh \beta \delta_{\text{eff}}^{-1} \quad (101b)$$

In terms of the coupling density of states, the equation for F may be written as

$$F = \int_0^{\omega_c} \frac{J(\omega) \coth (\beta \omega/2)}{[\omega + 2\delta_{\text{eff}} \coth (\beta \omega/2) \tanh \beta \delta_{\text{eff}}]^2} \, d\omega$$

We see explicitly in these equations how sluggish versus quick modes are scaled by β .

B. Tunneling Dynamics. We now turn to a calculation of the dynamics of the tunneling particle based on this variational procedure. Since the set of states that we have used to find the effective tunneling matrix elements ((99)) can be generated by a unitary transformation U of the noninteracting states, with

$$U = \exp\left(i\sum_{j} \frac{f_{j} p_{j}}{\omega_{j}^{2}} \sigma_{z}\right)$$
(114)

we can transform the original Hamiltonian with this U:

$$\tilde{H} = U^{-1} H U$$

$$= \delta\{|L\rangle \langle R| \ e^{\sum_{j} f_{j} p_{j} / \omega_{j}^{2}} + hc\} + \frac{1}{2} \sum_{j} (p_{j}^{2} + \omega_{j}^{2} q_{j}^{2}) + \sum_{j} (g_{j} - f_{j}) q_{j} \sigma_{z} + \sum_{j} (f_{j}^{2} - 2f_{j} g_{j} / \omega_{j}^{2}) \ (115)$$

If we average the terms containing the remaining tunneling boson interactions over the harmonic bath, we find, after adding and subtracting this average

$$\tilde{H} = \delta_{\text{eff}}\sigma_z + \frac{1}{2}\sum_j (p_j^2 + \omega_j^2 q_j^2) + \sum_j (f_j^2 - 2g_j f_j) / \omega_j^2 + \delta\{|L\rangle\langle R|\theta + |R\rangle\langle L|\theta^+\} + \sum_j (g_j - f_j)q_j\sigma_z$$
(116)

with

$$\theta = \exp(\sum_{j} i 2f_j p_j / \omega_j^2) - e^{-2\sum f_j^2 / \omega_j^3}$$
(117)

The first three terms in H are those which give the upper bound on E (or A at finite T) while the last two terms are *fluctuations* of the boson-tunneling particle interactions due to the thermal bath. Here, we are implicitly assuming that the boson bath remains close to the equilibrium defined by the average interaction to the tunneling particle. It is instructive to examine H in this light. Notice that if $f_j = 0$, i.e., the best displacement for all the bosons is no displacement, then the fluctuations are proportional to σ_x ; i.e., they are population relaxation in the L, R representation or dephasing in the eigenstate (\pm) representation. If however f_j = g_j , i.e., all the oscillators are displaced fully, then the fluctuations are in the tunneling matrix element term and are population relaxation in the \pm representation (or dephasing in the L, R representation). On the basis of the arguments presented above, we would say that in a qualitative sense the high-frequency modes $(\omega_j \gg \delta_{\text{eff}})$ cause fluctuations in the tunneling matrix element, while the low-frequency modes cause fluctuations in the L-R energy difference. Of course, this is based on the transformed states which already include the major part of the interaction.

We may now calculate the effect of these fluctuations on the tunneling dynamics by treating these terms to second order in perturbation theory. The most straightforward procedure is to calculate the reduced density matrix, ρ_{red} , defined as

$$\rho_{\rm red}(t) = {\rm Tr}_{\rm bath} \,\rho(t) \tag{118}$$

where $\rho(t)$ is the density matrix for the entire system, tunneling particle plus all the bosons. The reduced density matrix is still an operator in the two-level system space with matrix elements defined as

$$P_{z} = \langle L | (\rho_{red}) | L \rangle - \langle R | \rho_{red} | R \rangle$$

$$P_{x} = \langle L | \rho_{red} | R \rangle + \langle R | \rho_{red} | L \rangle$$

$$P_{y} = i [\langle L | \rho_{red} | R \rangle - \langle R | \rho_{red} | L \rangle]$$
(119)

The standard Redfield theory for the reduced density matrix of a system weakly interacting with a bath allows us to calculate the equations of motion of P_z , P_y , and P_x . We find at temperature $T = (k\beta)^{-1}$

$$\dot{P}_{z} = 2\delta_{\text{eff}}P_{y} - \gamma_{1}P_{z}$$

$$\dot{P}_{y} = -2\delta_{\text{eff}}P_{z} - \gamma_{2}P_{y}$$

$$r_{x} = +\Gamma(1 - A) - \Gamma(1 + A)P_{x}$$
(120)

where $A = \exp(-2\beta |\delta_{eff}|)$, and

Þ

$$\gamma_2 = \Gamma_{\rm PD} + (1+A) \int_{-\infty}^{+\infty} e^{-i2\delta_{\rm eff}t} \langle V_0(t)V_0 \rangle \, dt \quad (121)$$

$$\gamma_1 = \Gamma_{\rm PD} + (1+A) \int_{-\infty}^{+\infty} e^{-i2\delta_{\rm eff}t} \langle V_{\rm LR}''(t) V_{\rm LR}'' \rangle \,\mathrm{d}t \qquad (122)$$

$$\Gamma_{\rm PD} = \frac{1}{2} \int_{-\infty}^{+\infty} \langle V_{\rm LR}'(t) V_{\rm LR}' \rangle \, \mathrm{d}t \qquad (123)$$

$$\Gamma = \int_{-\infty}^{+\infty} dt \ e^{-i2\delta_{\text{eff}}t} \{ \langle V_0(t)V_0 \rangle + \langle V_{\text{LR}}''(t)V_{\text{LR}}'' \rangle \}$$
(124)

and

$$V_{0} = \sum_{j} (g_{j} - f_{j})q_{j}$$
(125)

$$V_{\rm LR}' = \frac{\delta}{2}(\theta + \theta^+) \tag{126}$$

$$V_{\rm LR}^{\prime\prime} = \frac{\delta}{2i}(\theta - \theta^+) \tag{127}$$

These rather formidable expressions simplify when $g_j = f_j$ ($V_0 = 0$) or when $f_j = 0$ ($V_{LR}' = V_{LR}'' = 0$). The equation of motion for P_z can be seen to be that of a damped harmonic oscillator with complex frequency given by

$$U = -i\left(\frac{\gamma_1 + \gamma_2}{2}\right) \pm \left\{-\left(\frac{\gamma_1 - \gamma_2}{2}\right)^2 + 4\delta_{\text{eff}}^2\right\}^{1/2} (128)$$

In the very weak coupling limit, $f_j = 0$, thus $\gamma_1 = 0$, and

$$\dot{P}_{z} = 2\delta_{\text{eff}}P_{y}$$

$$\dot{P}_{x} = (1 - A)\Gamma - (1 + A)\Gamma P_{x}$$

$$\dot{P}_{y} = 2\delta_{\text{eff}}P_{z} - \gamma_{2}P_{y}$$
(129)

in agreement with (78) and (79). Note however that the equation of motion of P_x is different in the present case, because it allows for the Boltzmann distribution (in the \pm representation) at equilibrium.

In the limit that $f_j \neq 0$, then $\gamma_1 \neq 0$, and the equations of motion P_i differ from (129). This is due to the coupling of the

bath to the tunneling particle which is taken into account by the unitary transformation, U. That is, the viewpoint is that the tunneling particle now has a cloud of bosons surrounding it, and which it must carry as it tunnels. The scattering by the bath is now different from in the very weak coupling limit, and this is realized by the new form of the equations of motion. Notice that the manner in which the coupling to the bath enters the damping is quite complex now. For example, the complex frequency of the damped oscillator has the bath coupling in $\delta_{\rm eff}$ as well as γ_1 and γ_2 . As the coupling to the bath increases so that f_i becomes closer to g_j , then δ_{eff} gets smaller, and in addition, $\gamma_1 - \gamma_2$ becomes smaller (i.e., $V_0 \rightarrow 0$ and a detailed study of $\langle V_{LR}''(t) V_{LR}'' \rangle$ shows that it too becomes small). In this limit then, the damping is due largely to the term $(\gamma_1 + \gamma_2)/2$ in U and not to the relative values of δ_{eff} and $(\gamma_1 - \gamma_2)$ in the square root. From the definition of $\Gamma_{\rm PD}$, one can see that $\Gamma_{\rm PD}$ (and γ_1 and γ_2) is proportional to $\delta_{\rm eff}^2$ in this limit, so that the decay of P_z is approximately proportional to $\delta_{eff}^2 \tau_c$, where τ_c is the characteristic decay time of the correlation function in the definition of Γ_{PD} . This agrees with the strong coupling limit discussed above.

C. The Asymmetric Double Well. Essentially negligible modification of the theory of the previous two sections is necessary when the double well possesses an intrinsic asymmetry.

The unitary transformation, U, commutes with the asymmetry $\epsilon \sigma_z$ and hence still diagonalizes the Hamiltonian in the limit of no tunneling. The resulting equation for $\{f_i\}$ and δ_{eff} is of course modified by the presence of $\epsilon \sigma_z$; namely, (101b) now reads

$$f_i = g_i \left\{ 1 + \frac{2\delta_{\text{eff}}^2 \coth\left(\beta\omega_i/2\right) \tanh\beta(\epsilon^2 + \delta_{\text{eff}}^2)^{1/2}}{\omega_i(\delta_{\text{eff}}^2 + \epsilon^2)^{1/2}} \right\}$$
(130)

The self-consistent equation for δ_{eff} is a simple generalization of (106), namely

$$\delta_{\text{eff}} = \delta \exp\left[-\frac{1}{\pi} \int_{0}^{\infty} d\omega J(\omega) \coth\left(\frac{\beta\omega}{2}\right) \times \left\{\frac{\omega + 2\delta_{\text{eff}}^{2} \coth\left(\beta\omega/2\right) \tanh\beta(\epsilon^{2} + \delta_{\text{eff}})^{1/2}}{(\delta_{\text{eff}}^{2} + \epsilon^{2})^{1/2}}\right\}^{-2}\right] (131)$$

Clearly if $\delta_{\text{eff}} \gg \epsilon$, ϵ plays a totally insignificant role. So we assume $\epsilon \gg \delta_{\text{eff}}$

$$\delta_{\text{eff}} \simeq \delta \exp\left[-\frac{1}{\pi} \int_0^\infty d\omega \ J(\omega) \ \coth\left(\frac{\beta\omega}{2}\right) \times \left[\omega + \frac{2}{\epsilon} \delta_{\text{eff}}^2 \ \coth\left(\beta\omega/2\right) \ \tanh\beta\epsilon\right]^2\right] (132)$$

For $T \gg \epsilon$ and $T > \omega_i$ (for the ω_i of importance, which are near $\omega_i = 0$), we find

$$\delta_{\rm eff} = \delta \, \exp\left[-\frac{1}{\pi} \int_0^\infty d\omega \, J(\omega) \frac{\omega}{(\omega^2 + 4\delta_{\rm eff}^2)^2}\right] \quad (133)$$

When $J(\omega) = \eta \omega e^{-\omega/\omega_c}$ (Ohmic case)

$$\delta_{\rm eff} \simeq \delta \, \exp\left[-\frac{2\eta}{\beta\pi} \int_0^\infty \frac{\omega^2 e^{-\omega/\omega_{\rm c}}}{(\omega^2 + 4\delta_{\rm eff})^2}\right] \tag{134}$$

the only solution to this equation is $\delta_{eff} = 0$. Thus the breaking of the symmetry on a level large compared to δ_{eff} completely suppresses the tunneling.

We now assume that $J(\omega) \sim \gamma \omega^3 e^{-\omega/\omega_c}$ for the case of a Debye-like spectrum. Here

$$\delta_{\rm eff} \simeq \delta \, \exp\left[-\frac{2\gamma}{\beta\pi} \int_0^\infty e^{-\omega/\omega_{\rm c}} \frac{\omega^4 \, \mathrm{d}\omega}{(\omega^2 + 4\delta_{\rm eff}^2)^2}\right] \tag{135}$$

We see that the solution of this equation is a $\delta_{eff} > 0$.

When $T \ll \epsilon$, we have $(T > \omega_i \text{ of interest})$

$$\delta_{\rm eff} = \delta \, \exp\left[-\frac{2}{\beta} \int d\omega \, \frac{\omega \, J(\omega)}{(\omega^2 + 4\delta_{\rm eff}^2 T/\epsilon)^2}\right] \quad (136)$$

Here δ_{eff} is again 0 for all but the lowest temperatures for the Ohmic case $(J(\omega) \sim \omega)$ and also for $J(\omega) \sim \omega^2$). We must turn to dynamics to obtain a fuller picture of what is happening.

We shall assume that $\delta^2/\epsilon \ll 1$ irrespective of the form of $J(\omega)$. We see that $f_i \approx g_i$ for almost all modes. Accordingly, an analysis equivalent to that of the previous section gives rise to a master equation for $P_z(t)$

$$\dot{P}_{z}(t) = -[1 + e^{-2\beta\epsilon}]\Gamma P_{z} - [1 - e^{-2\beta\epsilon}]\Gamma$$
(137)

Since $|L\rangle$ has a higher zero-order energy than $|R\rangle$, the decay rate of P_z is directly related to the population relaxation rate Γ , given by the golden rule

ı

$$\Gamma = \int_{-\infty}^{\infty} d\tau \ e^{-2i\epsilon t} \langle V_{LR}(\tau) \ V_{RL}(0) \rangle$$
(138)

where

$$V_{\rm LR} = \delta X - \delta_{\rm eff} \tag{139}$$

with the operator X given by

$$X = \exp(\sum_{j} 2ig_{j}P_{j}/\omega_{j}^{2})$$
(140)

What we have here is nothing more than the old-fashioned emission rate between Born-Oppenheimer states separated by a gap 2ϵ . We shall consider the low- and high-*T* limits of Γ . The explicit expression for Γ in terms of $J(\omega)$ is well-known from polaron theory.

$$\Gamma = \frac{1}{2} \delta^2 \int_{-\infty}^{\infty} d\tau \ e^{-i2\epsilon\tau} [e^{\phi(\tau)} - 1] e^{-\phi(0)}$$
(141)

where

$$\phi(\tau) = \frac{4}{\pi} \int_0^\infty d\omega \, \frac{J(\omega)}{\omega^2} \left[i \sin \omega \tau + \cos \omega \tau \coth \frac{\beta \omega}{2} \right]$$
(142)

In the high-T limit $\phi(\tau) - \phi(0)$ is related to the memory function $K(\tau)$ associated with the classical double well coupled to an oscillator

$$K(\tau) = \int_0^{\infty} \frac{\cos \omega \tau}{\omega} J(\omega) \, d\omega \qquad (143)$$

$$\phi(\tau) - \phi(0) = \frac{4i}{\pi} \int_0^{\tau} dt' K(t') - \frac{8}{\beta \pi} \int_0^{\tau} dt_1 \int_0^{t_1} dt_2 K(t_2)$$
(144)

Of course, under those circumstances for which only the short-time behavior of $\phi(\tau)$ is important, e.g., where $K(\tau)$ has a short correlation time

$$\phi(\tau) - \phi(0) = \frac{4i}{\pi} \alpha \tau - \frac{4}{\beta \pi} \alpha \tau^2$$
(145)

where $\alpha = \int_0^{\infty} J(\omega)/\omega \, d\omega$. This yields for Γ the classical Arrhenius behavior:

$$\Gamma = \frac{\delta^2 \pi}{4} \left(\frac{1}{\alpha k_{\rm B} T} \right)^{1/2} \exp \left[-\frac{4\pi}{\alpha k_{\rm B} T} \left(\epsilon + \frac{2}{\pi^{\alpha}} \right)^2 \right] \quad (146)$$

At low temperatures, the precise form of the cutoff in $J(\omega)$ enters. Using the exponential form which has been used throughout this section, and leaving out the well-known but delicate details, we find for *Ohmic* $J(\omega)$

$$\Gamma = \frac{\delta^2}{\omega_{\rm c}} \frac{\pi}{\gamma(4\eta/\pi)} \left(\frac{2\epsilon}{\omega_{\rm c}}\right)^{(4\eta/\pi)-1} \left[1 + \frac{\pi^2}{6} \left(\frac{1}{2\beta}\right)^2 \left(\frac{4\eta}{\pi}\right) \times \left(\frac{4\eta}{\pi} - 1\right) \left(\frac{4\eta}{\pi} - 2\right) + O(\beta^{-4})\right] (147)$$

where $\gamma(x)$ is the gamma function, agreeing with Leggett et al.⁹

VI. Conclusions

There are a number of conclusions that may be reached from our study of the influence of a medium on the tunneling in a double well. First, static and dynamic asymmetries are additive in their effects, in both the binary collision, dilute gas, and the harmonic oscillator medium cases. Second, the role of a small asymmetry of the wells in the tunneling dynamics is only quantitative at finite temperature as long as one is not in a region where the tunneling amplitude δ_{eff} vanishes. When δ_{eff} is zero as in the Ohmic density of states case at $\alpha > 1$, the low-temperature tunneling dynamics of the asymmetric well is qualitatively different from that of the symmetric well.

In the symmetric case at T = 0, the localization is total in the renormalized golden rule limit, but absolutely symmetric. That is, if the system begins in $|L\rangle$ it stays in $|L\rangle$ forever. Similarly, if it begins in $|R\rangle$ it stays in $|R\rangle$ forever. In a sense we must say that localization really is not symmetry breaking. Any incoherent mixture of $|L\rangle$ and $|R\rangle$ could be created. It is just that their mirrors would be equally probable and stay in the original conditions forever. As T is raised, there will be incoherent tunneling from $|L\rangle$ and $|R\rangle$ and vice versa.

When the wells are *asymmetric*, there is a golden rule rate that is spontaneous emission (plus induced emission at higher temperatures) for a transition from the higher energy well to the lower energy well, and induced emission backward, exactly like the Einstein A and B coefficients. Like the symmetric case $\delta_{eff} = 0$ has rendered everything incoherent, but the broken symmetry has created populations that incoherently tunnel into one another via the transformed interaction. At zero temperature, since only spontaneous emission can occur, the higher energy state alone decays, and the lower state is stable forever. Thus, the medium has truly broken the mirror symmetry; for in the absence of the medium, even through the tunneling is asymmetric, the mirror tunneling is identical. At zero temperature in the asymmetric well, when $\delta_{\text{eff}} = 0$, the medium has truly destroyed the mirror.

For many physical systems of interest to physical chemists and condensed matter physicists, the bath is not Ohmic; thus, the behavior of the dynamics of a tunneling system interacting with a bath is relatively straightforward. The methods we have reviewed in this paper provide a good description of this behavior.

We stress that there are a number of other methods that may be used to derive the results presented here. In addition, the systems for which these methods and concepts are applicable range from high-energy processes¹² to macroscopic quantum mechanics¹³ to good old fashioned NMR.¹⁴

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ARTICLES

Ab Initio SCF Studies of the Electronic Structures of Halogen Nitrates. 2. FNO_x (x = 1, 2, 3)

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Self-consistent field calculations have been performed on the compounds FNO_x (x = 1, 2, 3) using 4-31G, 6-31G*/MP2, and PDZ/MP2 basis sets. Dipole moments, Koopmans' ionization potentials, and predicted geometries are reported. The predicted relative stability for FNO₂ isomers is $FNO_2 > c$ -FONO > t-FONO. FONO₂ is predicted to only slightly prefer a planar configuration in agreement with experiment. The FONO₂ isomer is more stable than FOONO by about 40 kcal/mol.

Introduction

The halogens play an important role in the chemistry of the atmosphere. In most investigations, chlorine has been the center of attention since it is the catalyst of the well-known ClO ozone depletion cycle

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O_3 \rightarrow Cl + 2O_2$$

$$2O_3 \rightarrow 3O_2$$

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However, it is evident from atmospheric measurements¹ that fluorine, bromine, and iodine may also be important in atmospheric chemistry. Bromine is predicted to play an important role in the chemistry of the stratospheric antarctic ozone hole.^{1,2} A primary constituent of the oceanic troposphere is CH_3I , which yields the iodine atom upon photolysis by the sun.³ It is well-known that Cl and ClO react with several nitrogen oxides to produce ClNO,

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