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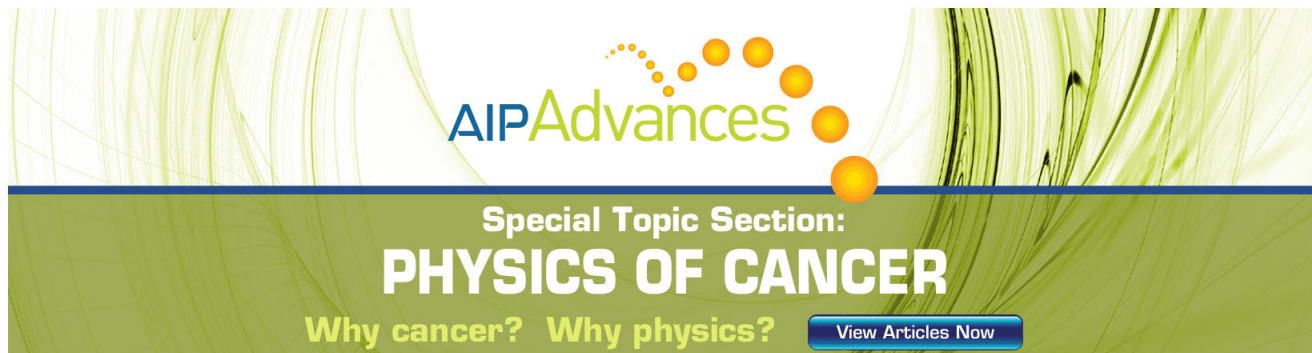
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# On the stabilization of optical isomers through tunneling friction

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A handed molecule may be represented as a particle in a symmetric double well. When placed in contact with a low temperature medium, the mean position of the particle obeys an equation of motion identical to a damped harmonic oscillator. The standard relaxation theory is used to relate the damping to classical friction, in agreement with recent path integral methods; however, no renormalization of the tunneling matrix element occurs. The stability of handedness is explained in terms of the damped oscillator.

The dynamics of a handed molecule may be usefully represented as the motion of a simple particle in a slightly asymmetric double well. Asymmetric because of the fundamental parity nonconservation.<sup>1</sup> The dynamical manifestation of the parity violation is a stabilization of the handed forms of the molecule at a low level of excitation in the double well. This stabilization comes about through a suppression of the amplitude of oscillation from one handed form to the other.<sup>2</sup>

When the above mentioned molecule is placed in an optically neutral environment, limiting theoretical calculations have shown that the handed or localized states may be stable on time scales enormously long compared to the tunneling frequency.<sup>2-6</sup> In addition, the effect of the asymmetry of the double well is entirely wiped out.

The theoretical models to describe this model range from the quantum collision in a dilute gas to classical fluctuations in an arbitrary medium. Very recently, path integral methods have shown similar effects in a low temperature tunneling system where the effect of the medium would be ordinary friction if the particle was above the barrier in the double well.<sup>7-9</sup>

In this note, we would like to show that all these models are approximately equivalent. We shall point out that the stabilization of handedness is subject to an extremely simple and physical interpretation, which we shall denote as "tunneling friction."<sup>7,8</sup> The meaning of this phrase will become more clear in the subsequent development.

We begin with a particle confined in a symmetric double well potential interacting with a medium. As usual, the total Hamiltonian is given by

$$H = H_B + H_w + V, \quad (1)$$

where  $H_B$  is the bath Hamiltonian,  $H_w$  is the Hamiltonian of the double well, and  $V$  is the coupling. In this paper, we will assume that the temperature is low enough so that we need only consider the lowest two quantum states of the double well; however, we will also assume later that the temperature is *larger than the splitting of those two*

levels induced by the tunneling matrix element. In this limit, the two state model of the double well is adequate. Thus, in the left-right basis,

$$H = \delta\sigma_x. \quad (2)$$

The most general form of  $V$  in the two state model is

$$V = V_0\mathbf{1} + V_1 \cdot \sigma \quad (3)$$

where  $V_0$  and  $V_1$  are quantum mechanical operators depending on the coordinates of the medium. When the temperature is low, the medium can neither knock the particle over the double well nor through it, hence, we may approximate  $V$  by

$$V = V_0\mathbf{1} + V_1\sigma_x. \quad (4)$$

Thus the total Hamiltonian in the spin representation, left-right basis, is

$$H = H_B + \delta\sigma_x + V_0\mathbf{1} + V_1\sigma_x. \quad (5)$$

We are now ready to pose and answer the question: if the particle is on the left-hand side of the well at  $t = 0$ , and the medium is in thermal equilibrium, what is the state of the particle as a function of time? In order to answer this, we must determine the equation of motion of a two level density matrix or, in other words, determine the equation of motion of the polarization vector  $\mathbf{P}(t)$ , where

$$\mathbf{P}(t) = \text{Tr } \rho(t)\sigma, \quad (6)$$

where  $\rho(t)$  is the full density matrix of the two level system plus bath given by

$$\rho(t) = \exp(-iHt) \rho_B (1 + \sigma_x) / 2 \exp(-iHt), \quad (7)$$

where we have set  $\hbar = 1$ .

The equations of motion for  $\mathbf{P}(t)$  may readily be derived from the simple relaxation theory of Nitzan and Silbey<sup>10</sup> which is valid in the weak coupling short correlation time limit. The short correlation time limit and very strongly interacting gas phase limit may also be intuitively derived in this manner, or more rigorously by other methods. These methods are clearly explained elsewhere.<sup>4</sup>

The equations of motion for  $\mathbf{P}(t)$  in terms of its components are

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$$\begin{aligned} \dot{P}_x(t) &= 2i \int_0^\infty \langle [V_0(\tau), V_1(0)] \rangle d\tau P_y(t) \\ &\quad - 2 \int_0^\infty d\tau \langle [V_1(\tau), V_1(0)]_* \rangle \cos 2\delta\tau P_x(t) \\ &\quad - 2i \int_0^\infty d\tau \langle [V_1(\tau), V_1(0)] \rangle \sin 2\delta\tau, \end{aligned} \quad (8)$$

$$\begin{aligned} \dot{P}_y(t) &= -2\delta P_x(t) + \int_0^\infty d\tau \langle [V_0(\tau), V_1(0)] \rangle P_x(t) \\ &\quad - 2 \int_0^\infty d\tau \langle [V_1(\tau), V_1(0)]_* \rangle \cos 2\delta\tau P_y(t) \\ &\quad - 2 \int_0^\infty d\tau \sin 2\delta\tau \langle [V_1(\tau), V_1(0)]_* \rangle P_x(t), \end{aligned} \quad (9)$$

$$\dot{P}_x(t) = 2\delta P_y(t). \quad (10)$$

In the above, the symbol  $[ , ]_*$  is the anticommutator, and the average is over the bath in thermal equilibrium. As usual, we have extended the finite limits of integration to infinity, which is fully consistent with the initial assumptions. Note that the medium has been treated explicitly quantum mechanically and that these equations are correct at all temperatures such that the weak coupling, short correlation time assumptions hold. We do not consider corrections to those assumptions here.

We assume the medium is parity neutral, i. e., has no parity sense. In mathematical terms, this assumption implies

$$[\rho_B, \sigma_B] = 0 \quad (11)$$

for all temperatures considered here, where  $\sigma_B$  is the parity operator of the medium. Since the overall parity operator is

$$\sigma = \sigma_B \sigma_x, \quad (12)$$

then  $V_0$  is parity even and  $V_1$  is parity odd. Therefore,

$$[V_0(t), V_1(0)] = 0. \quad (13)$$

Because of this, the Bloch equations simplify greatly. The absence of a parity sense leads to a decoupling of the equation for  $P_x(t)$  from the other components of  $\mathbf{P}(t)$ , so that

$$\dot{P}_x = -\lambda P_x + \gamma, \quad (14)$$

where the complex parameter  $\lambda$  takes the form

$$\lambda \equiv \lambda' + i\lambda'' = 2 \int_0^\infty d\tau \exp(i2\delta\tau) \langle [V_1(\tau), V_1(0)]_* \rangle \quad (15)$$

and the inhomogeneous term  $\gamma$  is

$$\gamma = 2i \int_0^\infty d\tau \sin 2\delta\tau \langle [V_1(\tau), V_1(0)] \rangle. \quad (16)$$

Equation (14) is the standard rate equation which describes the approach to statistical equilibrium. We defer further discussion of this equation until we have discussed the equation of motion for  $P_y(t)$  and  $P_x(t)$ . The two equations are

$$\dot{P}_y = -2\delta P_x - \lambda' P_y - \lambda'' P_x \quad (17)$$

and

$$\dot{P}_x = 2\delta P_y. \quad (18)$$

We see that  $\lambda'$  plays the role of a damping parameter and  $\lambda''$  shifts the natural tunneling frequency. The Bloch equations, (14), (17), and (18) are somewhat more general than those derived by the classical fluctuation method and both more and less general than those derived from the quantum mechanical gas phase equations, as well as the phenomenological fluctuation theory present in the same work. The equations are more general than those determined from the classical fluctuation theory for two reasons: (a) the averages are quantum mechanical, a consideration which is crucial in an atomic gas phase medium and (b) the correlation functions are not necessarily proportional to delta functions. In the delta function correlation function (the zero correlation time) limit,  $\lambda''$  vanishes as does  $\gamma$ . Both the S matrix gas phase theory and the phenomenological theory have essentially used condition b. The S matrix theory is more general than that presented here, because in a dilute gas, we need not assume weak coupling to derive the result. In addition, the phenomenological theory is entirely general within the short correlation time framework. Finally, it is known that for delta function Gaussian correlations, the equations derived here are exact; in all that follows we shall neglect the terms  $\lambda''$  and  $\gamma$ .

The description of the dynamics of the handed molecule in terms of the polarization vector  $\mathbf{P}(t)$  is entirely natural given the approximation of the double well as a two state system. There is an alternative way of looking at the behavior of the particle in the double well, which is not only intuitively useful but necessary for the proper incorporation of classical friction.

Classical friction is felt by the mean position of the  $a$  particle in a potential. Hence we must determine the equation of motion of the mean position of the particle in the double well from the Bloch equations. In order to do this, we must first determine the operator representing position. In the two state model,

$$q = |r\rangle \langle r|q\rangle \langle r| + |l\rangle \langle l|q\rangle \langle l|. \quad (19)$$

But,

$$\langle l|q|l\rangle = -\langle r|q|r\rangle = -q, \quad (20)$$

where  $q_0$  is the minimum of the right-hand well. Thus,

$$q = -q_0 \sigma_x. \quad (21)$$

From the Heisenberg equations of motion we easily find the velocity operator  $\dot{q}$  to be

$$\dot{q} = -q_0 2\delta \sigma_y. \quad (22)$$

We may now find the equation of motion of  $\langle q(t) \rangle$  since we know that

$$\langle \dot{q}(t) \rangle = -q_0 P_x(t). \quad (23)$$

This equation of motion is a classical damped harmonic oscillator,

$$d^2 \langle q(t) \rangle / dt^2 + \lambda' d \langle q(t) \rangle / dt + (2\delta)^2 \langle q(t) \rangle = 0, \quad (24)$$

whose most general initial conditions are

$$\langle q(0) \rangle = -q_0 P_x(0) \quad (25)$$

and

$$\langle \dot{q}(0) \rangle = -2\delta q_0 P_y(0). \quad (26)$$

Although all we have done is rewrite the Bloch equations in their circular form, the change in interpretation is profound. Subject to the conditions outlined at the beginning of the paper, the mean position of a particle in the double well behaves like a damped harmonic oscillator. The initial condition of localization in, e.g., the left-hand side means simply that at  $t=0$  the mean position of the oscillator is displaced from equilibrium by an amount  $-q_0$ . The initial velocity is just proportional to the degree of coherence initially present in  $P_y(0)$ . The equation of motion for  $P_x(t)$  retains its two level origin.

We are now in a position to relate  $\lambda'$ , which we shall denote as  $\lambda$ , to the classical friction through the Leggett, Bray, and Moore models.<sup>7,8</sup>

We assume that the bath is just a collection of harmonic modes,

$$H_B = (1/2) \sum_i \omega_i \{a_i^\dagger a_i + (1/2)\}. \quad (27)$$

The coupling will be taken to be linear in the bath coordinates, which is the simplest parity conserving interaction,

$$V = -q_0 \sum_i X_i C_i. \quad (28)$$

In order to determine  $\lambda$  we must calculate the fluctuation

$$S_i(\omega) = (1/2) \int_{-\infty}^{+\infty} dt \exp(i\omega t) \langle [X_i(t), X_i(0)]_+ \rangle \quad (29)$$

since

$$\lambda = q_0 \sum_i C_i^2 S_i(2\delta). \quad (30)$$

If we invoke the fluctuation-dissipation theorem, then

$$\lambda = q_0 \sum_i C_i^2 \coth \beta \delta \cdot \chi''(2\delta), \quad (31)$$

where

$$\beta = (1/k_B T). \quad (32)$$

We may determine  $\chi''$  by elementary commutator algebra, to obtain

$$\chi''(2\delta) = (\pi/2m_l \omega_l) \{ \delta(2\delta - \omega_l) - \delta(2\delta + \omega_l) \}, \quad (33)$$

where  $m_l$  is the mass of the  $l$ th mode.

We now invoke the assumption that  $kT \gg 2\delta$  in order to arrive at the final form.

$$\lambda = (q_0^2 \pi / 2\beta \delta) \sum_i (C_i^2 / m_i \omega_i) \delta(2\delta - \omega_i). \quad (34)$$

In the units of Bray and Moore,

$$C_i = C_i / \hbar. \quad (35)$$

The expression for the classical friction may now be assumed, giving

$$\lambda = q_0^2 \eta / \beta \hbar^2, \quad (36)$$

where  $\eta$  is the classical friction constant,

$$\eta = \frac{\pi}{2} \sum_i (C_i^2 / 2m_i \omega_i^2) \delta(2\delta - \omega_i). \quad (37)$$

The results of Bray and Moore follow with one limitation: their  $\delta$  is renormalized and, in fact, approaches zero at  $T=0$ . This effect is not predicted by our work; in fact, the renormalization of  $\delta$  predicted by our model is in the opposite direction. It is not clear whether this discrepancy is due to the use of the two state model (which should be valid in weak coupling) or perhaps to the approximation of the path integral in Bray and Moore.<sup>8</sup>

The phrase "tunneling friction," should by now be clear even if cannot be directly related to classical friction. The competition between the medium and the tunneling does not destroy the tunneling, but in the limit of overdamping renders it incoherent. This incoherent tunneling, as has been previously emphasized, enormously stabilizes the handed forms of the molecule. The particle is essentially trapped in the well for macroscopic times.

This trapping is familiar behavior for an overdamped oscillator. When such an oscillator is displaced from equilibrium to a point  $-q_0$  with zero initial velocity, it will drift towards a position  $-q_0/e$  from equilibrium in a time  $[\lambda/(2\delta)^2]$ , which is enormously long compared to the natural period of the oscillator. This slow drift towards equilibrium is, of course, equivalent to the shrinkage of the population difference of the two optical isomers discussed earlier. Concomitantly, any initial parity in the molecule  $P_x(0)$  will decay rapidly to zero in a  $1/e$  time of  $1/\lambda$ . The latter is the well known  $T_2$  while the former is  $T_1$  in analogy to magnetic resonance. Another physical system which is analogous to that considered in this paper is an excited state system consisting of two molecules, i.e., a dimer, which is coupled to a phonon bath. In this case, the two level electronic system consists of the two lowest excited electronic states of the dimer and the coupling to the phonons is usually taken to be linear in the phonon coordinate. The equations of motion for this and for related systems have been derived and studied by Haken and Strobl,<sup>11</sup> Rackovsky and Silbey,<sup>12</sup> Abram and Silbey,<sup>13</sup> Rahman, Kenkre and Knox,<sup>14</sup> and Wertheimer and Silbey.<sup>15</sup> In the most common examples of this system,  $\delta$  is not small compared  $\lambda$  to and thus the oscillator is not overdamped. In addition, the term  $\gamma$  is not negligible since it is the term which gives Boltzmann equilibrium between the two states ( $|l\rangle \pm |r\rangle$ ).

In conclusion, we have examined the low temperature behavior of a chiral molecule as represented by a particle in a double well potential coupled to a medium. By low temperatures, we mean low enough to treat only the lowest pair of states in the well; as pointed out above, the temperature must be large<sup>8</sup> compared to the tunneling induced splitting in order for certain of the approximations to be valid. To a large degree independent of the medium, the mean position of the particle in the well obeys the equation of motion of a damped harmonic oscillator. When this oscillator is overdamped and the initial conditions of oscillator reflects localization (i.e., an initial handed condition), then the localized state is essentially stabilized forever.

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