

## Multistate transitions and quantum oscillations of optical activity

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We consider the effects of multistate transitions on the tunneling racemization of chiral molecules. This requires going beyond simple two-state models of enantiomers and to include transitions within a multiple-level quantum-mechanical system. We derive an *effective* two-level description which accounts for transitions from the enantiomers to an arbitrary number of excited states as an application of the Weisskopf-Wigner approximation scheme. Modifications to the optical activity from these additional states are considered in general terms under the assumption of *CPT* invariance and then under *T* invariance. Some formal dynamical analogies between enantiomers and the neutral *K*-meson system are discussed.

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### I. INTRODUCTION

The effects of parity violation in the two-level approximation for the quantum dynamics of a pair of strictly isolated molecular enantiomers [1] was considered some years ago by Harris and Stodolsky (HS) [2]. Based on this model, they pointed out the interesting possibility that tunneling should exist leading to oscillations in the optical activity (OA). They argued moreover that such a system should be sensitive to extremely small energies and could be used to observe the presence of the weak interaction via oscillations of the optical activity about a nonzero value. Their basic idea continues to motivate detailed proposals for measuring the optical activity [3], a highly nontrivial pursuit. In this vein, it is also worth mentioning the many varied independent experimental efforts and proposals aimed at detecting parity violation (PV) in chiral molecules. These techniques include vibrational-rotational [4], electronic [5–7], Mössbauer [8], and nuclear magnetic resonance (NMR) spectroscopy [9]. Proposals for measuring the PV energy difference in crystallization [10] and in solubility experiments [11] have also been considered. To date, however, no effects of parity violation in chiral molecules have been experimentally observed. The challenge has been taken up recently by a multidisciplinary consortium to employ high-resolution laser spectroscopy for a *first* observation of PV in chiral molecules [12].

Returning to the HS scheme, they also recognized that obstacles to the observation and detection of these chiral oscillations in the OA will come from interactions with the surrounding medium such as collision effects, thus tending to induce relaxation phenomena [13]. Radiative processes, fundamental interactions with the radiation field, are also important and their inclusion necessarily implies adopting a complex *multilevel* treatment [14]. Indeed, the effects of both collisional and radiative processes can be *simulated* approximately by *phenomenologically* adding complex energies  $E_k - \frac{i}{2}\Gamma_k$ , to the Hamiltonian spectrum, where  $\Gamma_k$  denotes a decay width [15]. Apart from effects of collisions between the enantiomers and a background medium (i.e., gas, liquid, or solid), the double-well model implies a tower of excited

electronic-vibrational states for the chiral molecules [16], and transitions between these states, induced by an external field, is expected to modify the fundamental oscillation period and amplitude of the OA of the ground-state enantiomers. These considerations would seem to invalidate the simplest two-state HS description. It is clear that the multistate nature of real molecules should be taken into account in order to obtain a more accurate description [15].

Motivated by the above-mentioned considerations, we probe somewhat further in the quantum-mechanical model of HS. Therefore our objective in this paper is to consider a multistate approach applied to the racemization problem and demonstrate that an *effective* two-level Hamiltonian description can be derived from perturbation theory, thus legitimizing this description. We derive the explicit form of the energy spectrum of the reduced two-level system in terms of the appropriate interaction Hamiltonian. Our aim is to keep the discussion as general as possible, thus our basic assumption is the existence of a Hermitian interaction Hamiltonian responsible for inducing the transitions from the chiral molecules to higher (e.g., electronic, vibrational, and/or rotational) levels. Given this interaction, we then adapt straightforwardly the Weisskopf-Wigner (WW) approximation scheme [17], originally used for solving the linewidth problem in atomic transitions [18], to the case of chiral molecules treated as a complex multistate quantum-mechanical system. The effect of transitions is twofold: on the one hand, they lead to corrections to the enantiomer mass matrix, thus lifting the enantiomeric mass degeneracy and hence yielding corrections to the oscillation period; and on the other, they also *in principle* allow for effects of decay channels of the enantiomers. However, in the context of real molecules, such energy-conserving *decay channels* are most likely absent, as these would entail the fragmentation or dissociation of the enantiomers into smaller molecular units. This notwithstanding, the WW approach convincingly establishes a formal analogy between the *dynamics* of the racemization of molecular enantiomers and the interference and decay effects predicted [19] and observed [20,21] in the neutral kaon system of elementary particle physics. These are both examples of multiple-level quantum systems with oscillations, although the underlying physics in each system (chiral molecules, *K* mesons) is of course radically different.

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We give a brief overview of the simplest Harris-Stodolsky two-state approach in Sec. II. Motivated by the multilevel nature of real molecules pointed out above, we approach this problem by applying the Weisskopf-Wigner approximation scheme in Sec. III. This permits one to derive an effective two-level description which takes into account transitions to an arbitrary number of multiple excited states. The “end” result is expressed as a compact  $2 \times 2$  mass matrix which acts in the space of the two enantiomers. The associated eigenvalues and eigenvectors depend on whether one assumes the putative interaction Hamiltonian is *CPT* or *T* invariant, and these invariance principles also effect the final form of the OA and the oscillation period. Our goal here is to derive an effective Hamiltonian description for the *transitions* to and from multiple levels, not a study *per se* of the effects that PV may itself lead to [22–29], although these can be included in principle as part of the overall perturbation. Dynamical analogies between enantiomers and the neutral *K*-meson system [16,30,31] are discussed in Sec. IV. We comment on the novelty of the approach developed in the Discussion, and contrast it briefly to other current theoretical works. The WW method is summarized in the Appendix.

## II. HARRIS-STODOLSKY TWO-STATE MODEL

The Hamiltonian  $H$  describing the dynamics of a pair of strictly isolated chiral molecules  $|L\rangle, |R\rangle$  is [2]

$$H = E_0 \mathbf{1} + \delta \sigma_x + \epsilon \sigma_z = H_0 + \epsilon \sigma_z, \quad (1)$$

where  $\delta = \langle L|H_0|R\rangle$  is a parameter related to barrier height and  $\epsilon$  is the energy shift due to parity violation. For  $\epsilon = 0$ , the eigenvectors  $|+\rangle = (|L\rangle + |R\rangle)/\sqrt{2}$  and  $|-\rangle = (|L\rangle - |R\rangle)/\sqrt{2}$  are states of definite parity:  $P|+\rangle = |+\rangle$  and  $P|-\rangle = -|-\rangle$ . The eigenvalues are given by  $E_{\pm} = E_0 \pm \delta$ , and level splitting is due to tunneling alone. The system wave function obeys  $i\hbar \frac{d|\Psi\rangle}{dt} = H|\Psi\rangle$ , and in terms of the parity basis, the general time-dependent solution is given by

$$|\Psi(t)\rangle = ae^{-i(E_0+\delta)t/\hbar}|+\rangle + be^{-i(E_0-\delta)t/\hbar}|-\rangle, \quad (2)$$

where the values of  $a, b$  incorporate the initial condition  $|\Psi(0)\rangle$ . Thus, if we prepare the system to be initially in the chiral state  $|L\rangle$ , then  $a = b = 1/\sqrt{2}$ , and at any later time  $t \geq 0$  the wave function is given by

$$|\Psi(t)\rangle = e^{-iE_0t/\hbar} [\cos(\delta t/\hbar)|L\rangle - i \sin(\delta t/\hbar)|R\rangle]. \quad (3)$$

Then  $P_L(t) = |\langle L|\Psi(t)\rangle|^2 = \cos^2(\frac{\delta t}{\hbar})$  and  $P_R(t) = |\langle R|\Psi(t)\rangle|^2 = \sin^2(\frac{\delta t}{\hbar})$  are the probabilities for the system to be in chiral state  $L$  or to make a transition to the state  $R$  at time  $t$ , respectively. Note that  $P_L(t) + P_R(t) = 1$ . The optical activity is given by [2]

$$\begin{aligned} \Theta(t) &= \Theta_{\max}[P_L(t) - P_R(t)] \\ &= \Theta_{\max} \cos \frac{2\delta t}{\hbar}. \end{aligned} \quad (4)$$

For parity violation,  $|\epsilon| > 0$ , and the eigenvalues are  $E_{1,2} = E_0 \pm (\delta^2 + \epsilon^2)^{1/2}$  and the associated eigenstates are given by  $|\Psi_1\rangle = \cos \phi |L\rangle + \sin \phi |R\rangle$  and  $|\Psi_2\rangle = -\sin \phi |L\rangle + \cos \phi |R\rangle$ , with mixing angle defined via  $\cot 2\phi = \frac{\epsilon}{\delta}$  [2]. If

the system is initially prepared to be in the chiral state  $|L\rangle$ , then at any later time its wave function is given by

$$\begin{aligned} |\Psi(t)\rangle &= e^{-iE_0t/\hbar} [(\cos^2 \phi e^{-i\Delta t/\hbar} + \sin^2 \phi e^{+i\Delta t/\hbar})|L\rangle \\ &\quad + \cos \phi \sin \phi (e^{-i\Delta t/\hbar} - e^{+i\Delta t/\hbar})|R\rangle], \end{aligned} \quad (5)$$

where  $\Delta \equiv (\delta^2 + \epsilon^2)^{1/2}$ . The probability to make a transition to a state  $|R\rangle$  is therefore given by

$$\begin{aligned} P_R(t) &= |\langle R|\Psi(t)\rangle|^2 \\ &= 4 \sin^2 \phi \cos^2 \phi \sin^2(\sqrt{\epsilon^2 + \delta^2}t/\hbar) \\ &= \frac{\delta^2}{\epsilon^2 + \delta^2} \sin^2(\sqrt{\epsilon^2 + \delta^2}t/\hbar). \end{aligned} \quad (6)$$

The probability to be in the state  $|L\rangle$  is

$$\begin{aligned} P_L(t) &= |\langle L|\Psi(t)\rangle|^2 \\ &= \cos^2 \frac{\Delta t}{\hbar} + \cos^2 2\phi \sin^2 \frac{\Delta t}{\hbar}, \\ &= \cos^2 \frac{\Delta t}{\hbar} + \frac{\epsilon^2}{\delta^2 + \epsilon^2} \sin^2 \frac{\Delta t}{\hbar}. \end{aligned} \quad (7)$$

Once again, we have  $P_L(t) + P_R(t) = 1$ . The corresponding optical activity (OA) is then calculated to be

$$\begin{aligned} \Theta(t) &= \Theta_{\max}[P_L(t) - P_R(t)] \\ &= \Theta_{\max} \frac{\epsilon^2 + \delta^2 \cos(2\Delta t/\hbar)}{\delta^2 + \epsilon^2}. \end{aligned} \quad (8)$$

This latter formula is the starting point for recent proposals for measuring the parity-violating energy difference  $\epsilon$  between enantiomers [3].

## III. MULTILEVEL PROBLEM: TRANSITIONS TO MANY STATES

We start with a mass degenerate pair  $|L\rangle, |R\rangle$  of chiral enantiomers:  $m_L = m_R \equiv m$ , considered as ground states of a Hamiltonian  $H_0$ . We then include transitions from these states to other eigenstates or levels of  $H_0$  induced by external fields (radiation, thermal effects, etc.). The problem we thus consider is the time evolution of a state initially prepared as a superposition of  $|L\rangle$  and  $|R\rangle$ . We regard the potential well barrier, the parity-violating energy difference  $\epsilon$  as part of the overall perturbation  $H_1$ . So we decompose  $H_1 = \delta \sigma_x + \epsilon \sigma_z + H_2$ , where the first two terms act only within the two-dimensional subspace of the ground-state enantiomers, and  $H_2$  induces transitions from these to the other (electronic-vibrational) levels. These specific considerations show up only at the stage where we display the explicit matrix elements of the effective two-level Hamiltonian. The following analysis is, however, independent of the explicit form of the overall perturbation  $H_1$ .

### A. Mass matrix

We have a system described by the Schrödinger wave function  $|\Psi(t)\rangle$  whose time evolution is given by ( $\hbar = 1$ ):

$$i \frac{d}{dt} |\Psi(t)\rangle = (H_0 + H_1) |\Psi(t)\rangle. \quad (9)$$

We write the full Hamiltonian  $H = H_0 + H_1$ , here  $|L\rangle$  and  $|R\rangle$  are the two degenerate discrete eigenstates of  $H_0$ , that is, a pair of mirror-image enantiomers, and the perturbation  $H_1$  induces transitions from these states to other (possibly unbound) eigenstates  $|k\rangle$  of  $H_0$  and possibly also between  $|L\rangle$  and  $|R\rangle$ . The problem to solve is the time evolution of a state initially prepared as a superposition of the two degenerate chiral states. In terms of the interaction representation, the state vector

$$|\psi(t)\rangle = e^{iH_0 t} |\Psi(t)\rangle \quad (10)$$

satisfies the equation

$$i \frac{d}{dt} |\psi(t)\rangle = e^{iH_0 t} H_1 e^{-iH_0 t} |\psi(t)\rangle = H_1' |\psi(t)\rangle, \quad (11)$$

so that the time dependence of  $|\psi(t)\rangle$  arises solely from the perturbation term  $H_1$ . We expand the interaction representation wave function in terms of the complete set of eigenstates:

$$|\psi(t)\rangle = a(t)|L\rangle + b(t)|R\rangle + \sum_k c_k(t)|k\rangle, \quad (12)$$

subject to the initial conditions  $a(0) = a_0, b(0) = b_0$ , and  $c_k(0) = 0$ . Then Eq. (11) leads to the following set of coupled equations for the probability amplitudes:

$$i \frac{da(t)}{dt} = \langle L|H_1|L\rangle a(t) + \langle L|H_1|R\rangle b(t) + \sum_k \langle L|H_1'|k\rangle c_k(t), \quad (13)$$

$$i \frac{db(t)}{dt} = \langle R|H_1|L\rangle a(t) + \langle R|H_1|R\rangle b(t) + \sum_k \langle R|H_1'|k\rangle c_k(t), \quad (14)$$

$$i \frac{dc_k(t)}{dt} = \langle k|H_1'|L\rangle a(t) + \langle k|H_1'|R\rangle b(t) + \sum_j \langle k|H_1'|j\rangle c_j(t). \quad (15)$$

We may omit the prime on  $H_1$  for the matrix elements taken within the  $|L\rangle, |R\rangle$  subspace in Eqs. (13) and (14), since these are assumed to be degenerate in mass. Applying the Weisskopf-Wigner [17] approximation procedure to this multilevel system yields the *effective* two-level quantum-mechanical description [see Eq. (A14)]

$$i \frac{d}{dt} \Phi = (\mathbf{M} - i\mathbf{\Gamma})\Phi. \quad (16)$$

The Hermitian mass and decay matrices  $\mathbf{M} = \mathbf{M}^\dagger$  and  $\mathbf{\Gamma} = \mathbf{\Gamma}^\dagger$  have the explicit matrix elements at order  $O(H_1^2)$

$$M_{\alpha\beta} = m\delta_{\alpha\beta} + \langle \alpha|H_1|\beta\rangle - \text{P} \sum_k \frac{\langle \alpha|H_1|k\rangle \langle k|H_1|\beta\rangle}{E_k - m}, \quad (17)$$

and

$$\Gamma_{\alpha\beta} = 2\pi \sum_k \langle \alpha|H_1|k\rangle \langle k|H_1|\beta\rangle \delta(E_k - m), \quad (18)$$

where the indices  $\alpha, \beta$  stand for the states  $L$  or  $R$ .

The only assumptions that go into obtaining the result in Eqs. (16)–(18) are that the dynamics is determined by the

time-dependent Schrödinger equation, the higher order terms  $O(H_1^3)$  are neglected, and that the Hamiltonian  $H$  is Hermitian (see the Appendix for details). This result allows for the possibility of energy-conserving decay channels through the decay matrix  $\mathbf{\Gamma}$ . Assuming that the chiral enantiomers are not *unstable*, there will be no decay, that is, no fragmentation nor dissociation of the enantiomers into other molecular species. Barring this possibility, there will be no contribution from Eq. (18) because  $E_k > m$ . One might nevertheless be tempted to think that  $\mathbf{\Gamma}$  could automatically account for effects of elastic collisions. Indeed, the full operator structure  $\mathbf{M} - i\mathbf{\Gamma}$  of the right-hand side of Eq. (16) implies complex energies for the spectrum and is reminiscent of the terms that are added *phenomenologically* to the molecular Hamiltonian as a way of simulating approximately the effects of collisions and radiative effects [14]. However, its inclusion would imply exponential decay in the probabilities  $P_L(t), P_R(t)$  themselves, as well of course in the optical activity  $\sim (P_L - P_R)$ , so that, e.g.,  $P_L(t), P_R(t) \rightarrow 0$  as time increases, whereas collisional effects yield instead  $P_L(t), P_R(t) \rightarrow \frac{1}{2}$  [32]. Henceforth, we set  $\mathbf{\Gamma} = 0$  in the remainder of this paper.

## B. Eigenvalues and eigenvectors: CPT and T invariance

The underlying assumed invariance affects the form of the eigenvalues and eigenvectors of Eq. (16), and it is therefore of interest to consider independently the implications of first *CPT* and then *T* invariance. The former applies only for the case of the so-called *CP* enantiomers, which require the existence of mirror image molecules composed of *antiparticles* [16], that is, the *CP* partner of  $|L\rangle$  is  $|\bar{R}\rangle$ , the anti-right-handed molecule; whereas the *CP* partner of  $|R\rangle$  is  $|\bar{L}\rangle$ , the anti-left-handed molecule.

Thus the solution of the eigenvalue problem

$$\mathbf{M}\Psi_\pm = \lambda_\pm \Psi_\pm, \quad (19)$$

assuming *CPT* invariance, so that  $M_{11} = M_{22}$  (and  $\Gamma_{11} = \Gamma_{22}$ ) [20], is given by [19]

$$|\Psi_\pm\rangle = \begin{pmatrix} p \\ \pm p^* \end{pmatrix} \frac{1}{\sqrt{2|p|^2}}, \quad (20)$$

where

$$\lambda_\pm = M_{11} \pm |M_{12}|, \quad (21)$$

and  $p$  is the complex number

$$p^2 = M_{12}. \quad (22)$$

From Eq. (20), and in terms of the *CP* enantiomers, we have

$$|L\rangle = \frac{e^{i\alpha}}{\sqrt{2}} (|\Psi_+\rangle + |\Psi_-\rangle), \quad (23)$$

$$|\bar{R}\rangle = \frac{e^{i\alpha}}{\sqrt{2}} (|\Psi_+\rangle - |\Psi_-\rangle), \quad (24)$$

where  $e^{-i\alpha} = p/|p|$ .

If on the other hand we assume only  $T$  invariance, then  $M_{12}^* = M_{12}$  [20], and in this case the eigenvalues and eigenvectors of Eq. (19) are given by [16]

$$\lambda_{\pm} = \frac{1}{2}(M_{11} + M_{22}) \pm \frac{1}{2}[(M_{11} - M_{22})^2 + 4M_{12}^2]^{1/2}, \quad (25)$$

$$|\Psi_{+}\rangle = \cos \phi |L\rangle + \sin \phi |R\rangle, \quad (26)$$

$$|\Psi_{-}\rangle = -\sin \phi |L\rangle + \cos \phi |R\rangle, \quad (27)$$

$$\text{where } \cot 2\phi = \frac{(M_{11} - M_{22})}{2|M_{12}|}.$$

### C. Corrections to the optical activity

Now we can determine how the inclusion of multiple states affects the optical activity with respect to the simplest HS model. We prepare the state to be initially  $|L\rangle$  and assume first only  $T$  invariance. Using Eqs. (25)–(27), we find the wave function at any time is given by

$$|\Psi(t)\rangle = (\cos^2 \phi e^{-i\lambda_{+}t} + \sin^2 \phi e^{-i\lambda_{-}t})|L\rangle + \sin \phi \cos \phi (e^{-i\lambda_{+}t} - e^{-i\lambda_{-}t})|R\rangle. \quad (28)$$

Following a sequence of steps similar to those in Sec. II, we can evaluate the probabilities  $P_L, P_R$  and the optical activity in the presence of multistate transitions. The probabilities to be in state  $|L\rangle$  or  $|R\rangle$  at any time  $t \geq 0$  are given by

$$P_L(t) = \cos^2(\Delta t) + \frac{(M_{11} - M_{22})^2}{4\Delta^2} \sin^2(\Delta t), \quad (29)$$

$$P_R(t) = \frac{M_{12}^2}{\Delta^2} \sin^2(\Delta t). \quad (30)$$

We find that

$$\Theta(t) = \Theta_{\max} \frac{\frac{1}{4}(M_{11} - M_{22})^2 + M_{12}^2 \cos(2\Delta t/\hbar)}{\Delta^2}, \quad (31)$$

where the explicit matrix elements  $M_{\alpha\beta}$  are given by Eq. (17) and  $\Delta = \frac{1}{2}[(M_{11} - M_{22})^2 + 4M_{12}^2]^{1/2}$ .

When  $CPT$  invariance holds,  $M_{11} = M_{22}$ , and then the optical activity is given by

$$\Theta(t) = \Theta_{\max} \cos(2\Delta t/\hbar), \quad (32)$$

where now,  $\Delta = |M_{12}|$ . If we denote the oscillation periods  $\tau_{CPT}$  and  $\tau_T$  when  $CPT$  or  $T$  invariance is imposed, then we have the general result that

$$\tau_{CPT} > \tau_T, \quad (33)$$

so that the oscillation period in the case of the hypothetical  $CP$  enantiomers is *longer* than that for the  $P$  enantiomers, for a given interaction Hamiltonian  $H_1$ .

The time-average optical activity for the case of  $P$  enantiomers is

$$\left\langle \frac{\theta(t)}{\theta_{\max}} \right\rangle_t = \frac{\frac{1}{4}(M_{11} - M_{22})^2}{\frac{1}{4}(M_{11} - M_{22})^2 + M_{12}^2}. \quad (34)$$

If  $CPT$  invariance is assumed, then the time-average of Eq. (32) is zero:

$$\left\langle \frac{\theta(t)}{\theta_{\max}} \right\rangle_t = 0. \quad (35)$$

As mentioned earlier, we write  $H_1 = \delta\sigma_x + \epsilon\sigma_z + H_2$ , where the first two terms act only within the two-dimensional subspace of the enantiomers  $|L\rangle, |R\rangle$ , and  $H_2$  induces transitions from these to the other levels  $|k\rangle$ , thus we evaluate

$$M_{\alpha\beta} = m\delta_{\alpha\beta} + \langle \alpha | \delta\sigma_x + \epsilon\sigma_z | \beta \rangle - P \sum_k \frac{\langle \alpha | H_2 | k \rangle \langle k | H_2 | \beta \rangle}{E_k - m}. \quad (36)$$

If we shut off the perturbation  $H_2$ , then from Eq. (17) it is easy to check that Eq. (31) reduces to the optical activity of the isolated two-state system, Eq. (8). By the same token, Eq. (32) reduces to Eq. (4) in this same limit.

Note that since  $\mathbf{M}$  is Hermitian,  $P_L(t) + P_R(t) = 1$  continues to hold, even allowing for transitions to the other states  $|k\rangle$ . If  $\mathbf{\Gamma}$  were not vanishing, then these probabilities would decay exponentially in time.

### IV. FORMAL ANALOGIES TO THE $K$ -MESON SYSTEM

In the context of symmetry breaking in physics, Wigner pointed out some time ago a strictly formal analogy between  $K$  mesons and chiral molecules [31]. The neutral  $K^0$  meson and its antiparticle  $\bar{K}^0$  are related by the combined operations of charge conjugation and parity ( $CP$ ):  $|\bar{K}^0\rangle = CP |K^0\rangle$  [20]. From this, one defines superpositions [33]  $|K_1\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle + |\bar{K}^0\rangle)$  and  $|K_2\rangle = \frac{1}{\sqrt{2}}(|K^0\rangle - |\bar{K}^0\rangle)$  that are eigenstates of  $CP$ :  $CP |K_1\rangle = |K_1\rangle$  and  $CP |K_2\rangle = -|K_2\rangle$ . The chiral molecules are interrelated by the parity operation:  $|L\rangle = P|R\rangle, |R\rangle = P|L\rangle$ , and the eigenstates of definite parity are the mixtures  $|+\rangle = \frac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$  and  $|-\rangle = \frac{1}{\sqrt{2}}(|L\rangle - |R\rangle)$ , as  $P|+\rangle = |+\rangle$  and  $P|-\rangle = -|-\rangle$ . These algebraic relationships led Wigner to propose a formal analogy between neutral kaons and enantiomers, namely, the state-vector associations ( $\leftrightarrow$ )

$$|L\rangle \leftrightarrow |K^0\rangle, \quad (37)$$

$$|R\rangle \leftrightarrow |\bar{K}^0\rangle, \quad (38)$$

$$|+\rangle \leftrightarrow |K_1\rangle, \quad (39)$$

$$|-\rangle \leftrightarrow |K_2\rangle. \quad (40)$$

This analogy can be made more encompassing by extending these relationships to the dynamic level. The kaons are eigenstates of the strong  $H_{st}$  and electromagnetic  $H_{\gamma}$  interactions:  $(H_{st} + H_{\gamma})|K^0\rangle = m_K|K^0\rangle$  and  $(H_{st} + H_{\gamma})|\bar{K}^0\rangle = m_K|\bar{K}^0\rangle$  and are degenerate in mass. The weak interaction  $H_{\text{weak}}$  connects  $K^0$  and  $\bar{K}^0$  with other continuum states, which causes the various decay modes and removes their degeneracy. The Schrödinger equation (9) describes the time evolution of a neutral kaon system, within the two-level approach in Eqs. (16)–(18). For this, one makes the specific identifications

$$H_0 = H_{st} + H_{\gamma}, \quad (41)$$

$$H_1 = H_{\text{weak}}, \quad (42)$$

where now the indices  $\alpha, \beta$  stand for the states  $K^0$  or  $\bar{K}^0$  and  $m = m_K = m_{\bar{K}}$  [19–21, 34]. Due to kaon decays, the decay matrix  $\mathbf{\Gamma}$  is nonzero. The eigenvalue problem for  $(\mathbf{M} - i\mathbf{\Gamma})$  has been worked out in full detail [19]. The eigenvalues have



real and imaginary parts, and these can be expressed as  $m_{1,2} - \frac{i}{2}\gamma_{1,2}$  [20]. So if we prepare a state which is initially pure  $K^0$ , at any later time the probability to find a  $\bar{K}^0$  is [21] ( $\hbar = 1$ )

$$P(\bar{K}^0, t) = \frac{1}{4} [e^{-\gamma_1 t} + e^{-\gamma_2 t} - 2e^{-(\gamma_1 + \gamma_2)t} \cos(m_2 - m_1)t], \quad (43)$$

$$= \cos^2 \frac{(m_2 - m_1)t}{2}, \quad (\gamma_{1,2} \rightarrow 0), \quad (44)$$

which describe decaying meson oscillations. In the limit of zero decay (second line) these would become pure oscillations and thus formally similar to the chiral oscillations derived above. These considerations raise Wigner's static analogy relating state vectors to a *dynamic* one, between effective two-level Schrödinger equations, oscillations in the transition probability between  $L$  and  $R$ , Eq. (6), and the strangeness oscillations of the neutral kaon system.

We must point out, however, that the consideration given to a two-state model involving  $CP$  enantiomers in Secs. III B and III C is strictly a mathematical illustration only and can never be realized experimentally. This is because such molecule-antimolecule transformations would require a huge violation of baryon number conservation [30]. This problem does not arise in the  $K$ -meson system because mesons have baryon number zero (mesons are not baryons!)

## V. DISCUSSION

A number of criticisms of the simplest two-state HS model have been marshalled in the past: namely, that it could only apply at exceedingly low temperatures, that it neglects the radiation field, and that it does not account for collisions. It has been suggested that perhaps the most serious problem arises from the multistate nature of real molecules [14]. It is the latter objection which motivates the work presented here, providing us the incentive to consider the multistate nature in a fairly general way. One aspect (and only one) of this complex problem is the influence of transitions to a tower of excited (electronic-vibrational) states of enantiomers induced by an appropriate external field or perturbation. In this situation, results from Weisskopf-Wigner perturbation theory demonstrate that we can continue to employ an *effective* two-state description, where the influence of the tower of multiple states is accounted for by the matrix elements of the effective Hamiltonian or mass matrix acting in the subspace of the two enantiomers. The effects that multiple states have on the racemization and optical activity can then be worked out in terms of the explicit matrix elements of the specific interaction responsible for these transitions. The importance of assuming  $CPT$  or  $T$  invariance is underscored here. These results hold generally. The main result is that a two-state approach remains valid, because the inclusion of the multiple states can be included in an effective Hamiltonian description. An approach such as this may prove useful for interpreting proposed spectroscopic measurements of molecular parity violation, such as represented in Fig. 1 of Ref. [35], involving transitions to excited levels.

In comparison to the general results obtained here, much of the theoretical work has focused on the explicit calculations of the parity-violating energy difference in chiral

molecules; see [35] for a recent review. These involve *ab initio* computations of the PV interactions employing techniques such as nonrelativistic and relativistic (Dirac)-Hartree-Fock and multiconfigurational self-consistent (MCSCF) levels, as well as density functional theory (DFT) [22–29]. There the primary objective is the (numerical) evaluation of effective parity-violating Hamiltonians which requires using many-body quantum-mechanical wave functions, to account for the multiple nuclei and electrons [35] involved. In these investigations, the dominant contribution to the parity-violating energy difference between enantiomers  $E_{pv}$  is calculated from matrix elements connecting the ground-state singlet with excited triplet states. Thus, it should be possible to employ an effective two-level description in these more complex theoretical approaches as well.

Regarding collisional effects, a two-level approach has been used to describe how racemization depends on the interaction of the enantiomers with the environment [32]. This might suggest that both the multistate nature of real molecules and collisional effects with the surrounding medium might be able to be combined in an overall effective two-level description.

Finally, we have also further developed the formal dynamical analogies between the system of enantiomers and the kaon system. The unifying framework is provided by the WW perturbation theory. We note that a formal comparison between chiral molecules and neutrinos was recently invoked to derive properties of the oscillations between isolated enantiomers in a two-level HS-type approximation [36].

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## APPENDIX : REDUCTION FROM MULTILEVEL TO A TWO-STATE SYSTEM

The main steps of the Weisskopf-Wigner (WW) time-dependent perturbation theory [17–19] and Appendix A of Ref. [21] are reviewed and adapted here to a doublet of mass-degenerate enantiomers. We emphasize that the WW method is general and provides a way to reduce an *a priori* multiple-level quantum system to an effective two-level system, independent of the actual form of the specific Hermitian Hamiltonians involved.

To derive Eq. (16) from Eqs. (13)–(15), introduce the two-component column vectors

$$\phi(t) = \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}, \quad \mathbf{C}_k = \begin{pmatrix} \langle k|H_1|L \rangle \\ \langle k|H_1|R \rangle \end{pmatrix}, \quad (A1)$$

then the first WW approximation consists in truncating the solution of the Eqs. (13)–(15) to second order in  $H_1$ . This

implies they can be written as follows by using  $\langle k|H_1^L|L\rangle = e^{iw_k t} \langle k|H_1|L\rangle$ ,  $\langle k|H_1^R|R\rangle = e^{iw_k t} \langle k|H_1|R\rangle$ :

$$i \frac{d\boldsymbol{\phi}(t)}{dt} = \mathbf{h}\boldsymbol{\phi}(t) + \sum_k \mathbf{C}_k^* e^{-iw_k t} c_k(t), \quad (\text{A2})$$

$$i \frac{dc_k(t)}{dt} = \mathbf{C}_k^T \boldsymbol{\phi}(t) e^{iw_k t}, \quad (\text{A3})$$

where  $w_k = E_k - m$  ( $m_L = m_R \equiv m$ ), and  $\mathbf{h}$  is the submatrix of  $H_1$  in the two-state subspace:

$$\mathbf{h} = \begin{pmatrix} \langle L|H_1|L\rangle & \langle L|H_1|R\rangle \\ \langle R|H_1|L\rangle & \langle R|H_1|R\rangle \end{pmatrix}. \quad (\text{A4})$$

Solve Eq. (A3) for  $c_k$  and substitute these solutions back into Eq. (A2). The resultant equation for  $\boldsymbol{\phi}(t)$  can be solved in closed form via a Laplace transform [21] and yields

$$\boldsymbol{\phi}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dy \frac{e^{(iy+\epsilon)t}}{y - i\epsilon + \mathbf{W}(iy + \epsilon)} \boldsymbol{\phi}_0, \quad (\text{A5})$$

where  $\boldsymbol{\phi}_0 = \boldsymbol{\phi}(0)$  is the initial condition, and

$$\mathbf{W}(s) = \mathbf{h} - \sum_k \frac{\mathbf{D}_k}{w_k - is}, \quad \mathbf{D}_k = \mathbf{C}_k^* \mathbf{C}_k^T. \quad (\text{A6})$$

Up to this point, the solution Eq. (A5) is exact to  $O(H_1^2)$ . If we regard the perturbation  $H_1$  as small, then the second-order contribution to the matrix  $\mathbf{W}$  should receive its main contribution to the integral from the neighborhood of  $y = 0$ . The second WW approximation consists in replacing  $\mathbf{W}$  by its value at  $y = 0$ , which leads to the integral

$$\boldsymbol{\phi}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dy e^{iyt} \left[ y + \mathbf{h} - \mathbf{P} \sum_k \frac{\mathbf{D}_k}{w_k} - i\pi \sum_k \delta(w_k) \mathbf{D}_k \right]^{-1} \boldsymbol{\phi}_0, \quad (\text{A7})$$

and which follows from the identity (P denotes the Cauchy principal part) [18]

$$\lim_{\sigma \rightarrow 0} \frac{1}{x \pm i\sigma} = \mathbf{P} \frac{1}{x} \mp i\pi \delta(x). \quad (\text{A8})$$

Evaluating the integral Eq. (A7) yields the general solution

$$\boldsymbol{\phi}(t) = e^{-i\mathbf{W}_0 t} \boldsymbol{\phi}_0, \quad (\text{A9})$$

where

$$\mathbf{W}_0 = \mathbf{h} - \mathbf{P} \sum_k \frac{\mathbf{D}_k}{w_k} - i\pi \sum_k \delta(w_k) \mathbf{D}_k. \quad (\text{A10})$$

The time dependence in the interaction representation of the two-level wave function in the WW approximation is given by

$$i \frac{d}{dt} \boldsymbol{\phi}(t) = \mathbf{W}_0 \boldsymbol{\phi}(t). \quad (\text{A11})$$

Returning now to the Schrödinger representation  $\boldsymbol{\Phi} = e^{-iH_0 t} \boldsymbol{\phi}$ ,

$$i \frac{d}{dt} \boldsymbol{\Phi} = (H_0 + e^{-iH_0 t} \mathbf{W}_0 e^{iH_0 t}) \boldsymbol{\Phi}, \quad (\text{A12})$$

$$= (H_0 + \mathbf{W}_0) \boldsymbol{\Phi}, \quad (\text{A13})$$

$$= (\mathbf{M} - i\boldsymbol{\Gamma}) \boldsymbol{\Phi}. \quad (\text{A14})$$

Here

$$\mathbf{M} = m\mathbf{1} + \mathbf{h} - \mathbf{P} \sum_k \frac{\mathbf{D}_k}{w_k}, \quad (\text{A15})$$

and

$$\boldsymbol{\Gamma} = 2\pi \sum_k \delta(w_k) \mathbf{D}_k, \quad (\text{A16})$$

are known as the mass and decay matrices, respectively. Since the two-level subsystem is degenerate,  $H_0 = m\mathbf{1}$  and so  $[e^{-iH_0 t}, \mathbf{W}_0] = 0$ .

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- [1] F. Hund, *Z. Phys.* **43**, 805 (1927).
  - [2] R. A. Harris and L. Stodolsky, *Phys. Lett. B* **78**, 313 (1978).
  - [3] P. Bargeño, I. Gonzalo, and R. Pérez de Tudela, *Phys. Rev. A* **80**, 012110 (2009).
  - [4] V. S. Letokhov, *Phys. Lett. A* **53**, 275 (1975).
  - [5] M. Quack, *Chem. Phys. Lett.* **132**, 147 (1986).
  - [6] R. Berger, M. Gottselig, M. Quack, and M. Willeke, *Angew. Chem. Int. Ed.* **40**, 4195 (2001).
  - [7] R. Berger, *PhysChemChemPhys* **5**, 12 (2003).
  - [8] I. B. Khriplovich, *Sov. Phys. JETP* **52**, 177 (1980).
  - [9] A. L. Barra, J. B. Robert, and L. Wiesenfeld, *Phys. Lett. A* **115**, 443 (1986).
  - [10] L. Keszthelyi, *J. Biol. Phys.* **20**, 241 (1994).
  - [11] M. Shinitzky, F. Nudelman, Y. Barda, R. Haimovitz, E. Chen, and D. W. Deamer, *Orig. Life. Evol. Biosph.* **32**, 285 (2002).
  - [12] B. Darquié, C. Stoeffler, A. Shelkovich, C. Daussy, A. Amy-Klein, C. Chardonnet, S. Zrig, L. Guy, J. Crassous, P. Soulard, P. Asselin, T. R. Huet, P. Schwerdtfeger, R. Bast, and T. Saue, *Chirality* **22**, 870 (2010).
  - [13] R. A. Harris and L. Stodolsky, *J. Chem. Phys.* **74**, 2145 (1981).
  - [14] M. Quack, *Angew. Chem. Int. Ed.* **28**, 571 (1989).
  - [15] M. Quack, *Adv. Chem. Phys.* **50**, 395 (1982).
  - [16] L. D. Barron, *Chem. Soc. Rev.* **15**, 189 (1986).
  - [17] V. F. Weisskopf and E. P. Wigner, *Z. Phys.* **63**, 54 (1930); **65**, 18 (1930).
  - [18] W. Heitler, *The Quantum Theory of Radiation* (Dover, New York, 1984).
  - [19] T. D. Lee, R. Oehme, and C. N. Yang, *Phys. Rev.* **106**, 340 (1957).
  - [20] T. D. Lee, *Particle Physics and Introduction to Field Theory* (Harwood Academic, New York, 1990).
  - [21] P. K. Kabir, *The CP Puzzle* (Academic, London, 1968).
  - [22] A. Bakasov, T. K. Ha, and M. Quack, *J. Chem. Phys.* **109**, 7263 (1998).
  - [23] P. Lazzarotti and R. Zanasi, *Chem. Phys. Lett.* **279**, 349 (1997).
  - [24] J. K. Laerdahl and P. Schwerdtfeger, *Phys. Rev. A* **60**, 4439 (1999).

- [25] J. Thyssen, J. K. Laerdahl, and P. Schwerdtfeger, *Phys. Rev. Lett.* **85**, 3105 (2000).
- [26] R. Berger, N. Langermann, and C. van Wüllen, *Phys. Rev. A* **71**, 042105 (2005).
- [27] R. Berger and C. van Wüllen, *J. Chem. Phys.* **122**, 134316 (2005).
- [28] P. Schwerdtfeger, T. Saue, J. N. P. van Stralen, and L. Visscher, *Phys. Rev. A* **71**, 012103 (2005).
- [29] A. C. Hennum, T. Helgaker, and W. Klopper, *Chem. Phys. Lett.* **354**, 274 (2002).
- [30] L. D. Barron, *Chem. Phys. Lett.* **221**, 311 (1994).
- [31] E. P. Wigner, *Sci. Am.* **213**, 28 (1965).
- [32] M. Cattani, *J. Quant. Spectrosc. Radiat. Transfer* **46**, 507 (1991); **52**, 831 (1994); *Nuovo Cimento D* **17**, 1083 (1995); M. Cattani and J. M. F. Bassalo, *J. Quant. Spectrosc. Radiat. Transfer* **69**, 107 (2001).
- [33] M. Gell-Mann and A. Pais, *Phys. Rev.* **97**, 1387 (1955).
- [34] R. G. Sachs, *The Physics of Time Reversal* (University of Chicago Press, Chicago, 1987).
- [35] M. Quack, J. Stohner, and M. Willeke, *Annu. Rev. Phys. Chem.* **59**, 741 (2008).
- [36] P. Bargaño, R. Pérez de Tudela, and I. Gonzalo, *Int. J. Quantum Chem.* **111**, 430 (2011).