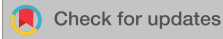


RESEARCH ARTICLE | DECEMBER 15 1997

Control of molecular chirality

Jiushu Shao; Peter Hänggi



J. Chem. Phys. 107, 9935–9941 (1997)

<https://doi.org/10.1063/1.475296>



Nanotechnology &
Materials Science



Optics &
Photonics



Impedance
Analysis



Scanning Probe
Microscopy



Sensors



Failure Analysis &
Semiconductors



Unlock the Full Spectrum.
From DC to 8.5 GHz.

Your Application. Measured.

[Find out more](#)



Control of molecular chirality

Jiushu Shao and Peter Hänggi

Institut für Physik, Universität Augsburg, Memminger Strasse 6, D-86135 Augsburg, Germany

(Received 19 June 1997; accepted 5 September 1997)

We present a theoretical study of controlling molecular chirality in chemical reactions by circularly polarized fields. A theory of absolute asymmetric synthesis is formulated by standard perturbation theory. An estimation of the chiral polarization of the product is provided. We show that an unstable chiral configuration can be described as a spin one-half particle. The circularly polarized field with well adjusted parameters is applied to stabilize chiral molecules (destruction of quantum coherence in the two-level system). © 1997 American Institute of Physics. [S0021-9606(97)01846-1]

I. INTRODUCTION

The Hamiltonian of molecules when described within the framework of quantum electrodynamics is parity invariant. However, the existing configuration (state) of some kind of molecules, so-called chiral molecules does not exhibit parity symmetry at all. This symmetry breaking effect and the closely related biological homochirality have puzzled biologists, chemists and physicists for over 150 years.¹⁻³ There are three fundamental problems: 1) why are the chiral configurations – once prepared – stable for a long time? 2) why are superpositions of stable chiral states not (yet) observed?² 3) why are (*L*)-amino-acids and (*D*)-sugars ubiquitous in the biochemistry of living organisms?^{3,4}

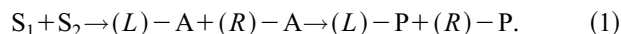
At the inception of quantum mechanics, Hund proposed a simple theory to explain the stability of chiral molecules.⁵ His idea can be formulated as a problem of quantum tunneling in a one-dimensional double-well system. The two chiral configurations correspond to the two localized states in the potential wells and the change of configurations corresponds to tunneling from one well to the other. One can show that the coherent tunneling time has a very wide range, from sub-picosecond to the age of the universe, depending on the mass of the particle and the feature of the potential. If the molecule has a heavy effective mass and the potential has a high and wide barrier, then the coherent tunneling time is long and *vice versa*. In the former case the molecule has two stable chiral configurations which are two distinct chemical identities. In the latter case the molecule, the substituted ammonia NHDT say, does not have stable chiral states. In fact, it does not possess spatially localized configurations. Note that this kind of instability is essential to realize the operation of an ammonia maser.⁶ By unstable we mean that the pair of enantiomers of a chiral molecule interconvert into each other very quickly via quantum coherence. We should point out that the problem of isolating the chiral degree of freedom from the manifold of molecular dynamics is subtle, especially for complicated molecules. Further, recognizing that a chiral molecule must be three-dimensional, we see that information about the molecular structure is incomplete in Hund's theory.⁷

The second problem is essentially related to the sort of Schrödinger's cat.⁸ Obviously, quantum mechanics does not provide an answer for the isolated molecular system. Many

efforts have been made to take into account the influence of an environment.^{2,9-11} Unfortunately, a satisfactory answer is still not available.

The third problem is the so-called puzzle of biological homochirality. It is more complicated, and may present a key to unravel the mystery of the origin of life.¹² One interesting idea concerns the role of weak interactions. Because the weak interaction violates the parity symmetry, it does make one of the two configurations of a chiral molecule more stable. In fact, theoretical calculations show that (*L*)-amino-acids and (*D*)-sugars which are predominant in the biological world do have smaller energies than their corresponding enantiomers.¹³ However, the energy difference is so small that thus far it could not be detected experimentally.

In this paper we focus on the practical aspect of molecular chirality. That is, we intend to control molecular chirality by external fields. In particular, we shall explain how to make a chemical reaction chiral-selective by employing *circularly polarized fields* (CPF). Two kinds of chemical reactions are related to the controlling scheme.¹⁴ One is the prochiral reaction in which the chiral configurations are stable. A simple reaction mechanism is that the achiral substrates S_1 and S_2 change into the chiral product P through the chiral activated complex A , namely

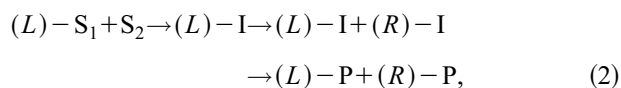


Here, in order to be consistent with the former theoretical investigations of control of tunneling¹⁵⁻²⁰ we use the physicist's notations (*L*) and (*R*) to represent the chemist's two chiral configurations.²¹ Note that the (thermodynamic) interconversion process between (*L*) - P and (*R*) - P is not explicitly presented in the mechanism. Obviously, in the absence of any external chiral physical influence one gets racemic products. To have a chiral-selective reaction one must resolve or stabilize *one* enantiomer of the activated complex or the product by using some sort of chiral fields.²² This is termed *absolute asymmetric synthesis* (AAS).

Up to present days, asymmetric synthesis through chemical reactions is still a fine art and very expensive. A successful AAS is undoubtedly one of the most ambitious objectives for chemistry. AAS is not only invaluable in chemistry and chemical industry, but also helpful to understanding the origin of life. Chemists have repeatedly verified AAS with testable positive results.^{1,3} The external physical

fields they used are diversified: From circularly polarized radiations to spinning vessels and gravity. We should point out that the concept of AAS stems from physical intuition, namely a chiral field interacts differently with the two enantiomers of a chiral molecule. The underlying chemical concept is the diastereomeric relationship. To design AAS one should address two questions: which fields are chiral and how do they affect the chiral polarization of the product? An elegant answer to the first question has been provided by Barron.^{1,23} From the consideration of symmetry he was able to delineate *true* or time reversal (T -invariant) chirality from *false* or T -noninvariant chirality and concluded that only under a truly chiral influence will the energy of a chiral molecule be different from that of its mirror image.^{1,23} Although we can not give a general answer to the second question, we will present a first quantitative treatment for AAS in the influence of the circularly polarized light.

The other chemical reactions we are interested in are those that have no enantioselectivity under ordinary lab conditions. We suppose that one of the substrate is a pure enantiomer and that the reaction evolves through an *unstable* chiral intermediate. The reaction mechanism may simply be written as



where the second step is a very fast racemization process via quantum coherence. The chiral polarization C of the product may approximately estimated as

$$C \equiv \frac{[(L) - P] - [(R) - P]}{[(L) - P] + [(R) - P]} \approx \frac{[\overline{(L) - I}] - [\overline{(R) - I}]}{[\overline{(L) - I}] + [\overline{(R) - I}]}, \quad (3)$$

where $[X]$ denotes the concentration of X and $\overline{[X]}$ the time-averaged value of $[X]$. Without suitable driving fields the chiral polarization C is vanishingly small. Our aim with this work is to stabilize the intermediate $(L) - I$ by employing appropriate fields in order to obtain a product with a finite chiral polarization.

Section II gives an elementary description of AAS by CPF control. A rough estimation rules out the possibility of AAS by CPF resulting from natural sources. In Sec. III, a two-state theory of the unstable chiral molecule is put forward. It is shown that the two chiral configurations with an electric transition dipole moment are mathematically equivalent to a spin-1/2 system. Suppression of quantum coherence of two-level systems by the CPF control is discussed in Sec. IV. A summary and conclusions are presented in Sec. V.

II. ABSOLUTE ASYMMETRIC SYNTHESIS BY CIRCULARLY POLARIZED LIGHT

We consider the prochiral reaction described above in Eq. (1). The chiral polarizability C is a characteristic quantity which describes the product composition. It depends on the relative reaction rate and the (thermodynamic) interconversion rate between the two enantiomers of the product. According to the general theory, if C is predominantly de-

termined by the relative reaction rate, then the reaction is said to be controlled by kinetics. Otherwise, if C is predominantly hinged on the interconversion rate, then we have a thermodynamically controlled reaction.¹⁴ In the former case the chiral polarization C is dependent on the relative stability of $(L) - A$ and $(R) - A$; likewise, in the latter case C is dependent on the relative stability of $(L) - P$ and $(R) - P$. In both cases it is necessary to calculate the interaction energy between the chiral configuration and the optical field in order to evaluate the chiral polarizability C .

We treat the molecule plus the CPF by the semiclassical method. The Born-Oppenheimer approximation is adopted to define the *molecular structure*.²⁴ Therefore, the whole Hilbert space in the quantum treatment is separated into two subspaces, one is the electronic and the other is the nuclear. For a chiral state, being associated with a stable nuclear configuration, only the dynamics of the electrons is relevant. Concerning the interaction between the molecule and the field, the electric dipole and magnetic dipole field interactions are sufficient for our purposes. The Hamiltonian of the system thus reads

$$H(t) = H_0 - \boldsymbol{\mu} \cdot \mathbf{E}^\pm(t) - \mathbf{m} \cdot \mathbf{B}^\pm(t), \quad (4)$$

where H_0 is the Born-Oppenheimer Hamiltonian of the chiral state, $\boldsymbol{\mu}$ and \mathbf{m} are the electric and magnetic dipole moment operators and $\mathbf{E}^\pm(t)$ and $\mathbf{B}^\pm(t)$ are the circularly polarized electric and magnetic fields, namely

$$\mathbf{E}^\pm(t) = 2E(\mathbf{i} \cos \omega t \pm \mathbf{j} \sin \omega t);$$

$$\mathbf{B}^\pm(t) = 2B(\pm \mathbf{i} \sin \omega t - \mathbf{j} \cos \omega t),$$

with \mathbf{i} and \mathbf{j} being the unit vectors in the x -axis and y -axis. Superscripts L and R will be tagged in H_0 for the corresponding enantiomers later.

Suppose that the wave functions of H_0 are known: $H_0|\psi_n\rangle = \epsilon_n|\psi_n\rangle$. Let the system start from one enantiomer that is the electronic ground state of H_0 . Because the available macroscopic electromagnetic field is much weaker as compared to the microscopic counterpart, the interaction term $H^\pm(t) \equiv -\boldsymbol{\mu} \cdot \mathbf{E}^\pm(t) - \mathbf{m} \cdot \mathbf{B}^\pm(t)$ presents a small perturbation to H_0 . Therefore, standard perturbation theory can be invoked for the calculation of the interaction energy.^{25,26} Setting $\hbar = 1$ in the following, the wave function can be written as

$$|\Psi(t)\rangle = \sum_n a_n(t) \exp(-iE_n t) |\psi_n\rangle.$$

Inserting $|\Psi(t)\rangle$ into the Schrödinger equation, $i\partial|\Psi(t)\rangle/\partial t = H(t)|\Psi(t)\rangle$, one obtains

$$a_k(t) = a_k(0) - i \sum_n \int_0^t a_n(t) H_{kn}^\pm(t) \exp(i\omega_{kn} t) dt,$$

where $\omega_{kn} = E_k - E_n$ are the Bohr frequencies, and $H_{kn}^\pm(t) = \langle \psi_k | H^\pm(t) | \psi_n \rangle$. Switching on the field adiabatically and employing the first-order time-dependent perturbation theory, we obtain²⁵

$$\begin{aligned}
a_k(t) &= -i \lim_{\eta \rightarrow 0^+} \int_{-\infty}^t H_{k0}^\pm(t) \exp[(i\omega_{k0} + \eta)t] \\
&\quad + \mu_{y,0n} m_{x,n0} \sin(2\omega t) \Bigg\}. \quad (7) \\
&= (E\mu_{x,k0} - Bm_{y,k0}) \left[\frac{e^{i(\omega + \omega_{n0})t}}{\omega + \omega_{n0}} - \frac{e^{-i(\omega - \omega_{n0})t}}{\omega - \omega_{n0}} \right] \\
&\quad \mp i(E\mu_{y,k0} + Bm_{x,k0}) \left[\frac{e^{i(\omega + \omega_{n0})t}}{\omega + \omega_{n0}} + \frac{e^{-i(\omega - \omega_{n0})t}}{\omega - \omega_{n0}} \right]
\end{aligned}$$

for $k \neq 0$. Because all the unperturbed wave functions may be taken to be real, the matrix elements of the electric transition dipole moment $\langle \psi_l | \boldsymbol{\mu} | \psi_n \rangle = \langle \psi_l | e \sum_j \mathbf{r}_j | \psi_n \rangle$ are real and that of the magnetic transition dipole moment $\langle \psi_l | \mathbf{m} | \psi_n \rangle = \langle \psi_l | -i \sum_j \mathbf{r}_j \times \nabla_j | \psi_n \rangle$ are imaginary.²⁶ The expectation value of the energy reads

$$\begin{aligned}
\mathcal{E}(t) &= \langle \Psi(t) | H(t) | \Psi(t) \rangle \\
&= E_0 - \boldsymbol{\mu}_{00} \cdot \mathbf{E}^\pm(t) \\
&\quad - 2 \operatorname{Re} \left\{ \sum_{n \neq 0} \frac{\omega_{n0}}{\omega_{n0}^2 - \omega^2} \boldsymbol{\mu}_{n0} \cdot \mathbf{E}^\pm(t) \boldsymbol{\mu}_{0n} \cdot \mathbf{E}^\pm(t) \right\} \\
&\quad + 2 \operatorname{Im} \left\{ \sum_{n \neq 0} \frac{1}{\omega_{n0}^2 - \omega^2} \mathbf{m}_{n0} \cdot \dot{\mathbf{B}}^\pm(t) \boldsymbol{\mu}_{0n} \cdot \mathbf{E}^\pm(t) \right\}, \quad (5)
\end{aligned}$$

where $\dot{\mathbf{B}}^\pm(t) = \partial \mathbf{B}^\pm(t) / \partial t$.

Because the pair of enantiomers of a chiral molecule are mirror images of each other, their Hamiltonians H_0^L and H_0^R are interchangeable by applying a parity transformation, i.e. $H_0^L = \mathcal{P} H_0^R \mathcal{P}^{-1}$ where \mathcal{P} is the parity operator. H_0^L and H_0^R have the same eigenenergies and their eigenfunctions are related by $|\psi_n^L\rangle = \mathcal{P} |\psi_n^R\rangle$. Moreover, we have $\boldsymbol{\mu}_{ln}^L = \boldsymbol{\mu}_{ln}^R$ and $\mathbf{m}_{ln}^L = -\mathbf{m}_{ln}^R$. Using Eq. (5), we readily evaluate the energy difference between the two enantiomers, i.e.

$$\begin{aligned}
\Delta(t) &\equiv \mathcal{E}^L(t) - \mathcal{E}^R(t) \\
&= 4 \operatorname{Im} \left\{ \sum_{n \neq 0} \left[\frac{1}{\omega_{n0}^2 - \omega^2} \boldsymbol{\mu}_{0n} \cdot \mathbf{E}^\pm(t) \mathbf{m}_{n0} \cdot \dot{\mathbf{B}}^\pm(t) \right] \right\} \\
&= \pm 8EB\omega \operatorname{Im} \left\{ \sum_{n \neq 0} \frac{1}{\omega_{n0}^2 - \omega^2} [2\mu_{x,0n} m_{x,n0} \cos^2 \omega t \right. \\
&\quad + 2\mu_{y,0n} m_{y,n0} \sin^2 \omega t \pm (\mu_{x,0n} m_{y,n0} \\
&\quad \left. + \mu_{y,0n} m_{x,n0}) \sin(2\omega t) \right\}. \quad (6)
\end{aligned}$$

Note that molecules under study are freely rotating. The rotational averages of the products $\mu_{x,0n} m_{y,n0}$ and $\mu_{y,0n} m_{x,n0}$ are the same, yielding $R_{n0}/3$, where $R_{n0} = \operatorname{Im}(\boldsymbol{\mu}_{0n} \mathbf{m}_{n0})$ is the rotational strength.^{26,27} Taking this into account, we arrive at the key result,

$$\Delta(t) = \pm 8EB\omega \operatorname{Im} \left\{ \sum_{n \neq 0} \frac{1}{\omega_{n0}^2 - \omega^2} \left[\frac{2}{3} R_{n0} \pm (\mu_{x,0n} m_{y,n0} \right. \right.$$

Some conclusions can be drawn directly from this expression: 1) $\Delta(t)$ is a periodic function of time; 2) $\Delta(t) = 0$ if the external field is static ($\omega = 0$), which is a dynamic proof of the de Gennes theorem stating the impossibility of AAS in a static electric and/or a magnetic field;²⁸ 3) $\Delta(t)$ vanishes at very high frequency.

Suppose that the driving period is much shorter than the time duration of the physical processes we are interested in. The time-dependent energy difference $\Delta(t)$ may then be replaced by its time-averaged value, i.e.

$$\bar{\Delta} \equiv \frac{\omega}{\pi} \int_0^{\pi/\omega} \Delta(t) dt = \pm \frac{16}{3} EB\omega \sum_{n \neq 0} \frac{R_{n0}}{\omega_{n0}^2 - \omega^2}. \quad (8)$$

This formula will be used for the evaluation of the chiral polarization in the following. Note that it needs some modifications at resonance, which is not the subject of present paper.

We are now ready to evaluate the chiral polarization C from first principles. Under thermodynamic control, C is determined by the relative concentration of the two enantiomers of the product in equilibrium. Thus using the Boltzmann statistics, we find

$$\begin{aligned}
C &= \frac{[(L) - P] / [(R) - P] - 1}{[(L) - P] / [(R) - P] + 1} \\
&\approx \frac{\exp(-\beta \bar{\Delta}_P) - 1}{\exp(-\beta \bar{\Delta}_P) + 1} \\
&= \tanh \left(-\frac{1}{2} \beta \bar{\Delta}_P \right), \quad (9)
\end{aligned}$$

where $\beta = 1/k_B T$ with k_B being Boltzmann's constant and T temperature. $\bar{\Delta}_P = \overline{\mathcal{E}_P^L(t) - \mathcal{E}_P^R(t)}$ is the time-averaged energy difference between the pair of enantiomers of the product, (L)–P and (R)–P. It is calculated according to Eq. (8).

Let us next consider kinetic control: The general kinetic equations of the reaction read

$$\frac{d[(L, R) - P(t)]}{dt} = k_{L,R} [S_1(t)]^{\nu_1} [S_2(t)]^{\nu_2}$$

and

$$\frac{d[S_1(t)]}{dt} = \frac{d[S_2(t)]}{dt} = -(k_L + k_R) [S_1(t)]^{\nu_1} [S_2(t)]^{\nu_2},$$

where $\nu_1 + \nu_2$ is the order of the rate law and $k_{L,R}$ are the rate constants. To derive C we only need the first equation. A simple integration yields

$$[(L, R) - P(t)] = k_{L,R} \int_0^t dt [S_1(t)]^{\nu_1} [S_2(t)]^{\nu_2}.$$

Therefore, we obtain for the chiral polarization

$$C = \frac{k_L/k_R - 1}{k_L/k_R + 1}. \quad (10)$$

Although the concentrations of both enantiomers increase as time goes on, their ratio does not change with respect to

time. So, the chiral polarization C is time independent. The absolute of the RHS, i.e. $|C|$ is called the advantage factor in Ref. 3.

From classical transition state theory we know^{29,30}

$$k_{L,R} = \kappa \frac{k_B T}{2\pi} e^{-\beta \Delta G_{L,R}},$$

where κ is the transmission coefficient and ΔG the difference in the Gibbs free energy between the activated complex A and the substrate molecules. Thus we have

$$\frac{k_L}{k_R} = \exp(-\beta \overline{\Delta}_A). \quad (11)$$

Inserting Eq. (11) into Eq. (10), we obtain

$$C = \tanh\left(-\frac{1}{2}\beta \overline{\Delta}_A\right), \quad (12)$$

being similar to the result of thermodynamic control given in Eq. (9). We see that the chiral polarization C depends on two factors, namely temperature T and the chiral feature of the activated complex which is characterized by $\overline{\Delta}_A$. At low temperatures and with a large $|\overline{\Delta}_A|$, a product with a large chiral polarization will be achieved and *vice versa*. Although the activated complex A is assumed to be chiral, it may happen that A possesses a configuration deviating not much from that of the achiral reactants. In this case, $\overline{\Delta}_A$ and consequently C are expected to be small. It seems that Eq. (9) yields an upper limit for the chiral polarization.

Let us put forward an estimation for C . The incident frequency ω is assumed to be close to one transition frequency of the molecule ω_{n0} , which gives the major contribution to $\overline{\Delta}$. Hence Eq. (8) becomes

$$\overline{\Delta} = \pm \frac{16}{3} EB \omega \frac{R_{n0}}{\omega_{n0}^2 - \omega^2}. \quad (13)$$

The electric dipole moment is approximated by ea_0 , where a_0 is the Bohr radius of a ground state hydrogen atom. Similarly, the magnetic dipole moment is represented by the Bohr magneton $e/2mc$.³¹ We then obtain $R_{n0} = 7.5 \times 10^{-19} \text{ C m T}^{-1} \text{ s}^{-1}$. From the quantum theory of optical activity, we observe that $\omega^2(\omega_{n0}^2 - \omega^2)^{-1}$ has the magnitude of unity.^{26,27} This yields $\overline{\Delta} = \pm 16EBR_{n0}/3\omega$. If the CPF control is performed with a red light ($\omega \approx 3.14 \times 10^{15} \text{ s}^{-1}$) at field strengths $E \approx 200 \text{ V m}^{-1}$ and $B = 6.5 \times 10^{-7} \text{ T}$ (the electromagnetic field from strong solar radiation), we obtain $\overline{\Delta} = \pm 1.7 \times 10^{-37} \text{ J}$. This is too small to result in a nonvanishing C at finite temperatures. Thus, our observation excludes the possibility of AAS under natural conditions. For strong CPF control, i.e. $E = 2.0 \times 10^7 \text{ V m}^{-1}$ and $B = 2 \text{ T}$, we obtain $\overline{\Delta} = \pm 5.1 \times 10^{-26} \text{ J}$. At room temperature $T = 300$, one thus finds $|\overline{C}| = 1.3 \times 10^{-6}$, which is still far too small from a practical point of view.

A better estimation is based on the rotation angle θ , which is the angle the plane of polarization rotates when a

linearly polarized light passes through the chiral medium.^{26,27} θ can be evaluated according to the Rosenfeld formula,^{26,27} i.e.

$$\theta = \mathcal{N} l \frac{2}{3} \mu_0 \sum_{n \neq 0} \frac{\omega^2 R_{n0}}{\omega_{n0}^2 - \omega^2}, \quad (14)$$

where \mathcal{N} is the number density of the molecule, l is the sample length that the light passes through and μ_0 is the vacuum permeability. Comparing to Eq. (8), we find

$$\overline{\Delta} = \pm \frac{8EB\theta}{\mathcal{N} l \mu_0 \omega}. \quad (15)$$

In a typical experimental setup one has $l = 0.1 \text{ m}$, $\mathcal{N} = 6.0 \times 10^{26} \text{ m}^{-3}$. Let us assume a large angle of rotation $\theta = 4\pi$. One can show that using the same electromagnetic field strengths as above, similar results for C emerge.

In conclusion, we have been able to evaluate the chiral polarization of the product in AAS driven by the circularly polarized light. It is shown that AAS produces a negligible chiral polarization even if the light is very strong.³²

Let us consider the other kind of reactions (cf. Eq. (2)). As we stressed above, the chiral state of the intermediate is unstable, i.e. the enantiomers interconvert coherently. Thus the foregoing discussions based on the Born-Oppenheimer approximation are no longer valid. It would be extremely difficult to develop a full quantum theory treating the motion of electrons and the motion of nuclei in a molecule on the same footing.³³ Fortunately, we shall focus on the simple case where the essential physics is the interconversion dynamics of the two ‘‘chiral’’ states. As a consequence, the unstable chiral molecule may be described as a two-state system. This idea will be further explored in the next section.

III. TWO-STATE MODEL OF (UNSTABLE) CHIRAL MOLECULES

Although the magnetic interaction is essential in discussing (stable) molecular chirality, it is very weak compared to electric interaction, it thus can be neglected for achiral or unstable chiral molecules. Our model for the two chiral configurations will be based on a two-level system (TLS) with an electric transition dipole moment μ . We shall establish the Hamiltonian for such a model subject to a general electric field \mathbf{E} .

Suppose the energy difference between the eigenstates of the TLS is Δ_0 . In the absence of external fields, the system can – equivalently – be regarded as a spin-1/2 particle (with a gyromagnetic factor $g=2$) in a magnetic field along the z -direction. Applying a static electric field \mathbf{E} to the system is then formally equivalent to switching on a magnetic field in the x -direction for the spin. Taking μ for the magnetic transition dipole moment of the spin, we find the effective magnetic field: $B_x = E$ and $B_z = \Delta_0/2\mu$. The effective Hamiltonian reads therefore

$$H = -\frac{1}{2} \Delta_0 \sigma^z - \mu E \sigma^x, \quad (16)$$

where σ are the Pauli matrices. The Hamiltonian has two energy eigenvalues: $\mp\sqrt{\Delta_0^2 + \mu^2 E^2}$. The two ‘‘chiral’’ states representing the pair of enantiomers are

$$|L\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

and

$$|R\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle),$$

where $|1\rangle$ and $|2\rangle$ represents the ground and the excited states of the corresponding TLS. Note that the z -axis has an unspecified direction in the system. One can choose an arbitrary direction in the plane formed by the other two axes for \mathbf{E} , which does not change the physics. Therefore, the eigenenergies are in general expected to be $\mp\sqrt{\Delta_0^2 + \mu^2(E_x^2 + E_y^2)}$. Because the eigenvalues for a general 2×2 Hermitian Hamiltonian (H_{ij}) are

$$\frac{H_{11} + H_{22}}{2} \mp \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + |H_{12}|^2},$$

we obtain $H_{11} = -\Delta_0/2$, $H_{22} = \Delta_0/2$, and $|H_{12}|^2 = \mu^2(E_x^2 + E_y^2)$. Supposing the interaction term is linear in E_x and E_y as it is in Eq. (16), we find the complex-valued interaction matrix elements, $H_{12} = -\mu(E_x - iE_y)$ and $H_{21} = -\mu(E_x + iE_y)$, up to an arbitrary phase. Therefore, the Hamiltonian of the two-level system in a general static electric field \mathbf{E} reads

$$H = -\frac{1}{2}\Delta_0\sigma^z - \mu E_x\sigma^x - \mu E_y\sigma^y. \quad (17)$$

Therefore, the interconversion dynamics of the two ‘‘chiral’’ configurations is nicely described by quantum coherence of an equivalent spin 1/2 system. One can show that the Hamiltonian keeps the same form even if the electric field is time dependent.

IV. LOCALIZATION BY CIRCULARLY POLARIZED FIELD CONTROL

Return to the problem of enantioselective control (refer to Eq. (2)). According to Sec. III the chiral intermediate (I) may be described as a two-state electric dipole moment. Our task is to block quantum coherence between the chiral states by monochromatic electric fields. Viewed in terms of Hund’s theory (not exact, but physically illustrative), controlling molecular chirality then amounts to realizing localization. For the linearly polarized driving field with well adjusted frequency and strength, the coherent destruction of tunneling (localization) has been discovered by Hänggi and co-workers.¹⁵ Their results may be applied directly to our context. However, in order to gain more physical insights we will employ CPF control, which allows us to work out analytical results. It turns out that good localization can also be achieved if the applied circularly polarized field satisfies certain conditions, as described below.

The Hamiltonian is

$$H(t) = -\frac{1}{2}\Delta_0\sigma^z + \frac{1}{2}V_0(\sigma^+ e^{i\omega t} + \sigma^- e^{-i\omega t}), \quad (18)$$

where $V_0 = -\mu E$ (see Eq. (4) with \mathbf{E}^- being applied) and $\sigma^\pm = \sigma^x \pm i\sigma^y$. This model is exactly solvable, a known fact since the pioneering work by Rabi and Schwinger.³⁵ It should be stressed that the problem we are addressing is on quantum coherence while former studies focused on the transition between the eigenstates. The quantity of interest is $P_L(t)$, the probability of the system to be found in the left state (L). Given $P_L(t)$, the chiral polarization is obtained through $C(t) = 2P_L(t) - 1$.

In the following we consider for control solely driving fields with zero average bias, i.e. with $\omega \neq 0$. Put differently, we do not consider the limit of static fields, $\omega = 0$. The latter situation describes a biased two-level system for which one localized state has less energy than the other and it is naturally favored. Moreover, strong static fields are difficult to realize in practice.

Consider again the Schrödinger equation $i\partial|\psi(t)\rangle/\partial t = H(t)|\psi(t)\rangle$. Using a gauge transformation $|\psi'(t)\rangle = \mathcal{U}|\psi(t)\rangle$, where $\mathcal{U} = \exp(-i\omega t\sigma^z/2)$, we find³⁴

$$i\frac{\partial|\psi'(t)\rangle}{\partial t} = i\frac{\partial\mathcal{U}}{\partial t}|\psi(t)\rangle + i\mathcal{U}\frac{\partial|\psi(t)\rangle}{\partial t} = \tilde{H}|\psi'(t)\rangle, \quad (19)$$

where

$$\tilde{H} = \mathcal{U}H\mathcal{U}^\dagger + i\frac{\partial\mathcal{U}}{\partial t}\mathcal{U}^\dagger = -\left(\frac{\Delta_0}{2} - \frac{\omega}{2}\right)\sigma^z + V_0\sigma^x$$

is now *time independent*. The eigenenergies of \tilde{H} are $\tilde{\epsilon}_\pm = \pm\tilde{\epsilon}$, where $\tilde{\epsilon} = \sqrt{(\Delta_0 - \omega)^2/4 + V_0^2}$. The corresponding eigenfunctions read

$$|+\rangle = c_1|L\rangle + c_2|R\rangle$$

and

$$|-\rangle = c_2|L\rangle - c_1|R\rangle,$$

where

$$c_1 = \frac{1}{\sqrt{2}} \frac{V_0 + (\Delta_0 - \omega)/2 + \tilde{\epsilon}}{\sqrt{[(\Delta_0 - \omega)/2 + \tilde{\epsilon}]^2 + V_0^2}}$$

and

$$c_2 = \frac{1}{\sqrt{2}} \frac{V_0 - (\Delta_0 - \omega)/2 - \tilde{\epsilon}}{\sqrt{[(\Delta_0 - \omega)/2 + \tilde{\epsilon}]^2 + V_0^2}}.$$

Note that $|\psi'(t)\rangle = \exp(-i\tilde{\epsilon}t)(|+\rangle + \exp(i\tilde{\epsilon}t)\langle -|\psi(0)\rangle|-\rangle)$ and $|\psi(t)\rangle = \mathcal{U}^\dagger|\psi'(t)\rangle$. The wave function $|\psi(t)\rangle = c_L(t)|L\rangle + c_R(t)|R\rangle$ can explicitly be derived. In the basis of localized states $|L\rangle$ and $|R\rangle$ we can write

$$\begin{pmatrix} c_L(t) \\ c_R(t) \end{pmatrix} = \mathbf{A}(t) \begin{pmatrix} c_L(0) \\ c_R(0) \end{pmatrix},$$

where $\mathbf{A}(t)$ acts as the propagator. After some algebra, we obtain

$$\mathbf{A}(t) = \begin{pmatrix} a(t) - ib(t) & -c(t) + id(t) \\ c(t) + id(t) & a(t) + ib(t) \end{pmatrix}, \quad (20)$$

where

$$a(t) = \cos(\Omega t/2)\cos(\omega t/2) + \cos\theta \sin(\Omega t/2)\sin(\omega t/2),$$

$$b(t) = \sin\theta \sin(\Omega t/2)\cos(\omega t/2),$$

$$c(t) = \sin\theta \sin(\Omega t/2)\sin(\omega t/2),$$

$$d(t) = \cos(\Omega t/2)\sin(\omega t/2) - \cos\theta \sin(\Omega t/2)\cos(\omega t/2),$$

with $\Omega = \sqrt{(\Delta_0 - \omega)^2 + 4V_0^2}$ being the Rabi frequency, and $\tan\theta = 2V_0/(\Delta_0 - \omega)$. The lifetime of the system is assumed to be much longer than the coherent tunneling period $2\pi/\Delta_0$.

Next we study the time evolution of the driving dynamics for a given initial preparation in the left state, i.e. $c_L(0) = 1$, yielding $P_L(0) = |c_L(0)|^2 = 1$. A necessary condition for complete localization is localization at multiples of the driving period $t = n2\pi/\omega$ (stroboscopic localization). For this to occur the propagator \mathbf{A} has to satisfy the following condition: It must have the same period as that of the external field.^{15,18} This requirement leads to the condition of $\Omega = n\omega$ (n positive integers) with $\omega = \Delta_0$ excluded (resonance condition). One can check that no stroboscopic localization shows up at resonance $\omega = \Delta_0$. In the case of strong off-resonance $\omega \neq \Delta_0$, $\omega \gg \Delta_0$, the time-average of $P_L(t) = |c_L(t)|^2$ is

$$\overline{P_L} = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} dt [a^2(t) + b^2(t)],$$

which for $\Omega = n\omega$ reduces to

$$\overline{P_L} = \frac{1}{2} + \frac{\sin(2n\pi)}{4\pi(n^2 - 1)} (n \cos^2\theta + \cos\theta). \quad (21)$$

One immediate result is that $\overline{P_L} = 1/2$ for all $n > 1$. That is, the system is always delocalized if the Rabi frequency equals a higher multiple $n\omega$, $n = 2, 3, \dots$, of the driving frequency. For $n = 1$ we find a relationship between the period and the amplitude of the acting field. This off-resonance condition reads

$$\omega = \frac{\Delta_0^2 + 4V_0^2}{2\Delta_0} > 0, \quad (22)$$

which must be satisfied to reach localization. Imposing this condition on the applied field, we find for optimal localization ($n = 1$)

$$\overline{P_L} = \frac{1 + x^2 + 2x^4}{2(1 + x^2)^2}, \quad (23)$$

where $x = 2V_0/\Delta_0$. The resulting chiral polarization is

$$C = \frac{x^4 - x^2}{(1 + x^2)^2}. \quad (24)$$

Very large chiral polarization (near unity) can be obtained through large x , which amounts to a strong field with a corresponding high frequency, cf. Eq. (22). From the expression in Eq. (24) we see that C easily attains the saturation value 1.

Thus, even a moderate strong field can lead to a large chiral polarization C . For instance, setting $V_0 = 2\Delta_0$ and $\omega = 17\Delta_0/2$, we obtain $C > 0.83$.

It is interesting to note that C becomes *negative* if $0 < x < 1$. In this case, the (*R*)-enantiomer slightly dominates in the product although the reactant is in the (*L*)-form! The minimum of C is

$$C^{\min} = -\frac{1}{8},$$

which corresponds to

$$\omega^{\min} = \frac{2}{3}\Delta_0, \quad V_0^{\min} = \frac{1}{2\sqrt{3}}\Delta_0.$$

The Floquet theory may help us have a better understanding of localization.^{15,34} In our model the quasienergies are well known.³⁴ They are evaluated to be

$$\epsilon_{\pm, n} = \tilde{\epsilon}_{\pm} + \left(\frac{1}{2} + n\right)\omega, n = 0, \pm 1, \pm 2, \dots$$

Recognizing that $\tilde{\epsilon}_{\pm} = \pm\Omega/2$, we find that the localization condition $\Omega = \omega$ is equivalent to $\epsilon_{+, 0} \equiv (\Omega + \omega)/2 = \epsilon_{-, 1} \equiv (-\Omega + 3\omega)/2$. The latter is nothing but level-crossing between the corresponding dressed states.

Three further remarks are in order. First, localization depends on the helicity of the driving field, i.e. the sign of frequency ω is strictly *positive*, cf. Eq. (22). In our case only the *clockwise* circularly polarized electric field (i.e. $\mathbf{E}^-(t)$) may be applied to stabilize the chiral state. Second, all discussions are also valid for the system evolving from the right state. Therefore, *one cannot get a finite chiral polarization from an eigenstate*. Third, we must prepare an initial condition corresponding to a pure chiral state. If the reaction we attempt to control produces such (unstable) intermediates that keep their chiral configurations for sufficient long time, the initial condition used in this work can, in principle, be realized at the early stage of the reaction, see Eq. (2). Otherwise, to resolve a pure chiral state from a racemic mixture one may invoke a “chiral mirror” scheme of the type presented in Ref. 32. The underlying idea is that two chiral configurations experience different forces in a circularly polarized field (cf. the discussion in Sec. II and Ref. 32).

V. SUMMARY AND CONCLUSIONS

In this paper we have shown how to use circularly polarized fields to control molecular chirality in chemical reactions. Resorting to standard first-order perturbation theory, we have been able to calculate the interaction energy between molecules and electromagnetic fields. With these results we have derived a formula by which one can evaluate the chiral polarization in absolute asymmetric synthesis driven by a circularly polarized light. A relationship between the chiral polarization and the rotation angle is established. Rough estimations show that absolute asymmetric synthesis is rarely possible in nature.

Similar to Feynman's explanation of the physics of an ammonia maser, we have suggested a two-state model of *unstable* chiral molecules. Unlike Hund's theory of one-dimensional quantum tunneling, the spatial information of the molecule is considered in this model. It is demonstrated that an unstable chiral molecule in presence of an electric transition dipole moment can equivalently be treated as a spin-1/2 particle. Destruction of quantum coherence (localization) by the circularly polarized electric field control is discovered within this approach. Hence, enantioselective reaction may be achieved by applying the proposed field control. Because the aim of this work has been to convey the concept of controlling molecular chirality by external time-dependent fields, simple reaction mechanisms are assumed; moreover, we neglected environmental dissipation effects, which in the gas phase are weak.

ACKNOWLEDGMENTS

J.S. would like to thank W.H.E. Schwarz for useful discussions. This work was supported by the Alexander von Humboldt-Stiftung, the National Natural Science Foundation of China, and the Deutsche Forschungsgemeinschaft (P.H.) via the Schwerpunktprogramm "Zeitabhängige Phänomene und Methoden in Quantensystemen der Physik und Chemie" (Az. HA 1517/14-2).

- ¹L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, London, 1982); Chem. Soc. Rev. **15**, 189 (1986); and references therein.
- ²A. Amann in *Large-Scale Molecular Systems*, edited by W. Gans, A. Blumen, and A. Amann (Plenum, New York, 1991), pp. 3–30, and references therein.
- ³V. I. Gol'danskii and V. V. Kuz'min, Sov. Phys. Usp. **32**, 1 (1989); V. A. Avetsov and V. I. Gol'danskii, *ibid.* **39**, 819 (1996).
- ⁴S. F. Mason, Nature (London) **311**, 1 (1984).
- ⁵F. Hund, Z. Phys. **43**, 805 (1927).
- ⁶R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, Massachusetts, 1965), Vol. III, Chap. 8.
- ⁷This by no means belittles the importance of Hund's theory. We are also aware that the Hund theory has been used to successfully illustrate new physical effects of chiral molecules. For instance, concerning preparation of superposition state, see J. Cina and R. A. Harris, J. Chem. Phys. **100**, 2531 (1994); concerning the coherent stereomutation, see R. Marquardt and M. Quack, Z. Phys. D **36**, 229 (1996).
- ⁸E. Schrödinger, Naturwissenschaften **23**, 807,823,844 (1935).
- ⁹P. Pfeifer in *Energy Storage and Redistribution in Molecules*, edited by J. Hinze (Plenum, New York, 1983), pp. 315–326.
- ¹⁰R. Silbey and R. A. Harris, J. Phys. Chem. **93**, 7062 (1989).
- ¹¹D. Giulini, E. Joos, C. Kiefer, J. Kupsch, I.-O. Stamatescu, and H. D. Zeh, *Decoherence and the Appearance of a Classical World in Quantum Theory* (Springer, Berlin, 1996), Chap. 3, and references therein.
- ¹²*Chemical Evolution: Origin of Life*, edited by C. Pannamperuma and J. Chela-Flores (Deepak, Hampton, Virginia, 1993).
- ¹³S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations* (Cambridge University Press, Cambridge, 1982), Chap. 11; S. F. Mason and G. E. Tranter, Mol. Phys. **53**, 1091 (1984); G. E. Tranter, Nature (London) **318**, 172 (1985).
- ¹⁴Cf. F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry*, 3rd ed. (Plenum, New York, 1990), for stereochemistry in chemical reactions.
- ¹⁵F. Grossmann, P. Jung, T. Dittrich, and P. Hänggi, Z. Phys. B **84**, 315 (1991); F. Grossmann, T. Dittrich, P. Jung, and P. Hänggi, Phys. Rev. Lett. **67**, 516 (1991); F. Grossmann, T. Dittrich, and P. Hänggi, Physica B **175**, 293 (1991); F. Grossmann and P. Hänggi, Europhys. Lett. **18**, 571 (1992).
- ¹⁶R. Bavli and H. Metiu, Phys. Rev. Lett. **69**, 1986 (1992); Phys. Rev. A **47**, 3299 (1993).
- ¹⁷M. Morillo and R. I. Cukier, J. Chem. Phys. **98**, 4548 (1993); R. I. Cukier and M. Morillo, Chem. Phys. **183**, 375 (1994).
- ¹⁸L. Wang and J. Shao, Phys. Rev. A **49**, R637 (1994); H. Cheng, M.-L. Ge, and J. Shao, Phys. Lett. A **191**, 1 (1994).
- ¹⁹Y. Dakhnovskii, Phys. Rev. B **49**, 4649 (1994); Y. Dakhnovskii and R. D. Coalson, J. Chem. Phys. **103**, 2908 (1995); Y. Dakhnovskii, D. G. Evans, H. J. Kim, and R. D. Coalson, *ibid.* **103**, 5461 (1995).
- ²⁰D. E. Makarov and N. Makri, Phys. Rev. E **52**, 5863 (1995); N. Makri, J. Chem. Phys. **106**, 2286 (1997).
- ²¹Chemists use the Cahn-Ingold-Prelog convention *R* and *S* to specify the two chiral configurations. Fisher convention *D* and *L* are also used in the chemistry of amino acids and sugars. See Ref. 14.
- ²²For recent experimental studies, see, for instance, W. J. Bernstein, M. Calvin, and O. Buchardt, J. Am. Chem. Soc. **94**, 494 (1972); **95**, 527 (1973); C. A. Mead, A. Moscovitz, H. Wynberg, and F. Meuwese, Tetrahedron Lett., 1063 (1977); W. Rhodes and R. C. Dougherty, J. Am. Chem. Soc. **100**, 6247 (1978); R. C. Dougherty, *ibid.* **102**, 380 (1980); G. Kaupp and H. Haak, Angew. Chem. **105**, 727 (1993); G. Kaupp and R. Marquardt, *ibid.* **106**, 1527 (1994).
- ²³L. D. Barron, Science **266**, 1491 (1994).
- ²⁴The terminology of molecular structures used within the chemical community is a classical concept. It is not trivial to obtain a rigorous formulation of this concept in the framework of quantum mechanics. See, for instance, R. G. Woolley, Adv. Phys. **25**, 27 (1976).
- ²⁵G. Baym, *Lectures on Quantum Mechanics* (Addison-Wesley, Reading, Massachusetts, 1969).
- ²⁶P. W. Atkins, *Molecular Quantum Mechanics*, 2nd ed. (Oxford University Press, Oxford, 1983), Chap. 13.
- ²⁷D. J. Caldwell and H. Eyring, *The Theory of Optical Activity* (Wiley, New York, 1971); E. Charney, *The Molecular Basis of Optical Activity* (Wiley, New York, 1979).
- ²⁸P. G. de Gennes, C. R. Acad. Sci. Paris, Ser. B **270**, 891 (1970).
- ²⁹See, for instance, H. Eyring, S. H. Lin, and S. M. Lin, *Basic Chemical Kinetics* (Wiley, New York, 1980).
- ³⁰P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
- ³¹E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937); M. P. Silverman, *More Than One Mystery* (Springer, New York, 1995), Chap. 6.
- ³²Although the difference in interaction energies for the pair of enantiomers and a circularly polarized light is too small to drive (useful) AAS, it can be utilized to resolve the racemic sample of a chiral compound in the gas phase. See the discussion by J. Kucirka and A. G. Shekhtman, Phys. Lett. A **221**, 273 (1996).
- ³³The related dynamics is nonadiabatic transition. See, for instance, H. Nakamura, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Marcel Dekker, New York, 1996), Chap. 12.
- ³⁴P. Hänggi, in: T. Dittrich, P. Hänggi, G.-L. Ingold, B. Kramer, G. Schön, and W. Zwirger, *Quantum Transport and Dissipation*, (VCH, Weinheim, 1997), Chap. 5.
- ³⁵I. I. Rabi, Phys. Rev. **51**, 625 (1937); J. Schwinger, *ibid.* **51**, 648 (1937).