

## Vacuum-Induced Symmetry Breaking of Chiral Enantiomer Formation in Chemical Reactions

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A material with symmetry breaking inside can transmit the symmetry breaking to its vicinity by vacuum electromagnetic fluctuations. Here, we show that vacuum quantum fluctuations proximate to a parity-symmetry-broken material can induce a chirality-dependent spectral shift of chiral molecules, resulting in a chemical reaction process that favors producing one chirality over the other. We calculate concrete examples and evaluate the chirality production rate with experimentally realizable parameters, showing the promise of selecting chirality with symmetry-broken vacuum quantum fluctuations.

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**Introduction.**—The notion of chirality (or handedness) dates back to the year 1848 when Louis Pasteur noticed two types of crystals, each one a mirror image of the other. Since then, the ubiquitous existence of chirality has been recognized and appreciated in different areas ranging from fundamental physics to chemistry and biology. One of the most promising endeavors is to explain the origin of molecular handedness in nature [1].

Chemists often refer to mirror-image molecules as *L* enantiomers and *D* enantiomers, where *L* and *D* conventionally stand for left- and right-handedness. When chiral molecules are synthesized from achiral building blocks, equal amounts of the *L* and *D* enantiomers are usually produced in the absence of external influences. Therefore, chirality selection in chemical reactions remains an important but painstakingly difficult task [2].

The most common approach to selecting chirality in chemistry is by using a chiral catalyst in a sophisticated procedure [3,4]. However, it is difficult to identify the appropriate chiral catalyst for a specific chemical reaction. Additional methods involve employing external influences, such as static EM fields or circularly polarized radiation, to discriminate chirality [5–18]. The efficiency of these approaches depends on specific circumstances [2] and typically does not exceed the efficiency of the catalytic approach [19,20]. Therefore, the quest for a universal and more efficient method to select chirality is of great practical importance.

Vacuum quantum fluctuations are a promising candidate for selecting chirality in chemical reactions. At first glance, it would appear impossible, since a vacuum, by definition, contains nothing and would not affect chemical reactions. However, quantum fluctuations in the vacuum have successfully explained many famous phenomena, such as the

anomalous magnetic moment [21], Lamb shift [22,23], and Casimir forces [24–27]. In particular, quantum-fluctuation-related effects could be enhanced or modified by confining light modes in a small cavity [28–31]. Indeed, physicists have come to appreciate using quantum fluctuations in cavities to tailor the properties of materials or molecules [32,33]. For example, quantum fluctuations in cavities can mediate interactions between electrons, leading to the enhancement of superconductivity [34–38], the breakdown of the quantization of Hall conductance [39–41], or new phases of matter [42–48]. Furthermore, pioneering works have shown that quantum fluctuations in cavities can modify activation barriers and even affect chemical reaction rates significantly [49–55].

However, quantum fluctuations in the vacuum (or a trivial cavity) preserve parity symmetry (PS) and are unable to induce an access of chirality in chemical reactions. Incorporating PS breaking into the quantum fluctuations is essential for selecting chirality. Several studies have demonstrated the influence of symmetry breaking on phenomena induced by quantum fluctuations, such as chirality-dependent Casimir forces [56–65], dissipationless Casimir viscosity [66], and band gap generation [67–70]. To highlight the combined power of the symmetry breaking and quantum fluctuations, Wilczek and one of us proposed a general framework, showing that symmetry breaking can be transmitted from materials to their vicinity via vacuum quantum fluctuations. The vacuum in proximity to a symmetry-broken material is referred to as its quantum atmosphere [71].

In this Letter, we show that the quantum fluctuations proximate to a PS-broken material can induce a notable energy difference between a chiral molecule and its mirror-image enantiomer. The energy difference shifts the



FIG. 1. A pair of enantiomers (red and blue colors refer to opposite chirality) immersed in PS-broken quantum fluctuations proximate to a Pasteur material (a) and in a gyrotropic cavity (b).

activation barrier in chemical reactions, resulting in an excess of one particular chirality over the other. We propose two setups for exploring this effect: one involving a Pasteur material and the other utilizing a gyrotropic cavity (Fig. 1). Notice that gyrotropic cavities, which permit the existence of only one circular polarization of photonic mode, have been realized experimentally using patterned chiral mirrors [72–74], spin-orbital coupled materials [75], and topological photonic materials [76,77].

The Letter is organized as follows: We first review the theoretical model of chiral molecules based on the Born-Oppenheimer (BO) approximation [78]. Second, we identify a chiral energy shift that can characterize chiral ensembles in a PS-broken vacuum. Through first-principles calculation, we uncover a sizable energy disparity of a pair of enantiomers. Finally, we evaluate the chemical reaction rate and obtain a notable chirality production rate, amply illustrating the selective power of symmetry-broken quantum fluctuations.

*BO approximation and the model of chiral molecules.*—The Hamiltonian of a molecule contains three parts: the energy of nucleus, the energy of electrons, and the interaction energy between the electrons and the nucleus:

$$\hat{H}_{\text{mol}} = \hat{T}_n + \hat{V}_n(\hat{\mathbf{R}}) + \hat{T}_{\text{el}} + \hat{V}_{\text{el}}(\hat{\mathbf{r}}) + \hat{V}_{n\text{-el}}(\hat{\mathbf{R}}, \hat{\mathbf{r}}). \quad (1)$$

Here,  $\hat{T}$  and  $\hat{V}$  denote the kinetic energy and Coulomb interactions, respectively; subindices  $n$  and  $\text{el}$  represent nucleus and electrons, respectively; variables  $\{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_1}\}$  and  $\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_2}\}$  stand for the positions of  $N_1$  nucleus and  $N_2$  electrons, respectively.

BO approximation is based on the fact that the kinetic energy of electrons is much larger than the nucleus. The energy-scale separation allows one to treat the electron movement first while the nuclear positions are regarded as fixed parameters. According to this scenario, the BO approximation is a two-step procedure [78,79]: (i) Solve the electronic Hamiltonian  $\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{el}} + \hat{V}_{n\text{-el}}(\mathbf{R}, \hat{\mathbf{r}})$ , whose  $i$ th eigenenergy and eigenstate are functions of  $\mathbf{R}$ , denoted as  $E_{\text{el},i}(\mathbf{R})$  and  $|\phi_i(\mathbf{R})\rangle$  ( $i = 0, 1, 2, \dots$ ), respectively. (ii) Promoting  $\mathbf{R}$  to be an operator yields an  $\hat{\mathbf{R}}$ -dependent electronic Hamiltonian  $\hat{H}_{\text{el}}(\hat{\mathbf{R}}) = \sum_i E_{\text{el},i}(\hat{\mathbf{R}}) |\phi_i(\hat{\mathbf{R}})\rangle \langle \phi_i(\hat{\mathbf{R}})|$ . The potential energy surface (PES) for the  $i$ th electronic energy level is defined as

$$\hat{V}_i(\hat{\mathbf{R}}) \equiv \hat{V}_n(\hat{\mathbf{R}}) + E_{\text{el},i}(\hat{\mathbf{R}}) |\phi_i(\hat{\mathbf{R}})\rangle \langle \phi_i(\hat{\mathbf{R}})|. \quad (2)$$

Because of the well-separated PESs, the transition between different PESs can be ignored, and the effective Hamiltonian for the  $i$ th PES reduces to  $\hat{H}_{\text{mol}}^{(i)} = \hat{T}_n(\hat{\mathbf{R}}) + \hat{V}_i(\hat{\mathbf{R}})$ . We will focus on the shift of the ground-state PES of a chiral molecule induced by PS-broken quantum fluctuations.

To characterize chiral molecules, we introduce a parity operator  $\mathcal{J}_P$  and a rotation operator  $\mathcal{J}_R$ . For a chiral molecule, any rotation of nuclear configurations could not bring the electronic Hamiltonian identical to its enantiomer, i.e.,  $\hat{H}_{\text{el}}(\mathcal{J}_R \hat{\mathbf{R}}) \neq \hat{H}_{\text{el}}(\mathcal{J}_P \hat{\mathbf{R}})$  for all  $\mathcal{J}_R \in \text{SO}(3)$ . By contrast, for achiral molecules, there always exists a rotation operation that can bring the electronic Hamiltonian identical to its parity counterpart.

*Energy shift of chiral molecules in vacuum.*—We consider a molecule interacting with a nearby symmetry-broken material through vacuum quantum EM fluctuations. Within the BO approximation, and the total Hamiltonian consists the electronic Hamiltonian  $\hat{H}_{\text{el}}$  of the molecule, the vacuum EM Hamiltonian  $\hat{H}_{\text{em}}$ , the electron-EM interaction  $\hat{H}_{\text{el-em}}$ , and the material-EM interaction  $\hat{H}_{\text{mat-em}}$ :

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{el-em}} + \hat{H}_{\text{em}} + \hat{H}_{\text{mat-em}}. \quad (3)$$

Tracing out the material degrees of freedom  $|\psi_{\text{mat}}\rangle$  yields an effective Hamiltonian  $H_{\text{sb}}$  that embodies the symmetry-breaking information of the material:

$$\hat{H}_{\text{sb}} = \hat{H}_{\text{em}} + \text{Tr}_{\text{mat}}(\hat{H}_{\text{mat-em}}), \quad (4)$$

where  $\text{Tr}_{\text{mat}}$  denotes the trace of the matrix with respect to the states of the material. Since  $\hat{H}_{\text{sb}}$  encodes all the material's influence on the vacuum EM fields, a simplified Hamiltonian can be employed to address the interaction between the molecules and the symmetry-broken material:

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{el-em}} + \hat{H}_{\text{sb}}. \quad (5)$$

When considering the interactions between molecules and EM fields, the important Fourier components of EM fields are those whose frequencies are on the order of atomic frequencies or less. Since the corresponding wavelength is much larger than the size of the molecule, one could employ the interaction Hamiltonian in a multipolar coupling scheme and long-wavelength approximation, describing the interaction of a molecule with the EM fields:  $\hat{H}_{\text{el-em}} = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}} - \hat{\mathbf{m}} \cdot \hat{\mathbf{B}}$ , where  $\hat{\mathbf{d}}$  and  $\hat{\mathbf{m}}$  denote the electric and magnetic dipoles of the molecule, respectively. This multipolar coupling Hamiltonian has been extensively studied in the literature [56–58,80,81]. Electromagnetic quantum fluctuations renormalize the electronic energy levels, yielding a shift of the ground-state energy (we use the unit  $\hbar = c = 1$ )

$$\Delta E_0 = -\sum_{i,I,F} p(I) \frac{|\langle \phi_i, F | \hat{\mathbf{d}} \cdot \hat{\mathbf{E}} + \hat{\mathbf{m}} \cdot \hat{\mathbf{B}} | \phi_0, I \rangle|^2}{E_{i0} + \Omega_{FI}}.$$

Here,  $|\phi_i, I\rangle \equiv |\phi_i(\mathbf{R})\rangle \otimes |I\rangle$  is the direct product state of the  $i$ th PES's state  $|\phi_i(\mathbf{R})\rangle$  and the photonic state  $|I\rangle$ .  $p(I) = e^{-\beta E_I}/Z_{\text{ph}}$  is the thermal probability of the initial photonic state  $|I\rangle$ .  $E_{i0}$  is the energy gap between the  $i$ th PES and the lowest PES.  $\Omega_{FI} = \Omega_F - \Omega_I$  is the energy gap between the photonic states  $|F\rangle$  and  $|I\rangle$ .

The ground-state energy shift includes two parts: The first contribution

$$\Delta E_0^{\text{ach}} = -\sum_{i,I,F} p(I) \frac{|\mathbf{d}_{0i} \cdot \mathbf{E}_{IF}|^2 + |\mathbf{m}_{0i} \cdot \mathbf{B}_{IF}|^2}{E_{i0} + \Omega_{FI}} \quad (6)$$

is achiral, because it remains invariant under a parity operation (i.e.,  $\mathbf{m} \rightarrow \mathbf{m}$  and  $\mathbf{d} \rightarrow -\mathbf{d}$ ). By contrast, the second contribution

$$\Delta E_0^{\text{ch}} = -\sum_{i,I,F} p(I) \frac{2\text{Re}[(\mathbf{d}_{0i} \cdot \mathbf{E}_{IF})(\mathbf{m}_{0i} \cdot \mathbf{B}_{FI})]}{E_{i0} + \Omega_{FI}} \quad (7)$$

reverses its sign under the parity operation and is called *chiral energy shift*. The transition matrices are defined as  $\mathbf{d}_{0i} = \langle \phi_0 | \hat{\mathbf{d}} | \phi_i \rangle$ ,  $\mathbf{m}_{0i} = \langle \phi_i | \hat{\mathbf{m}} | \phi_0 \rangle$ ,  $\mathbf{E}_{IF} = \langle I | \hat{\mathbf{E}} | F \rangle$ , and  $\mathbf{B}_{FI} = \langle F | \hat{\mathbf{B}} | I \rangle$ .

The chiral energy shift arises for a molecule (regardless of being chiral or not) with finite electronic and magnetic dipoles. However, to calculate the average chiral energy shift of an isotropic ensemble (liquid or gas), one should integrate over all orientations. And that makes the key difference: The average chiral energy shift vanishes for achiral ensembles but remains finite for chiral ensembles (see the proof [82]):

$$\langle \Delta E_0^{\text{ch}} \rangle = -\sum_{i,I,F} \frac{2p(I)\text{Re}[\mathcal{R}_{i0}(\mathbf{E}_{IF} \cdot \mathbf{B}_{FI})]}{3(E_{i0} + \Omega_{FI})}, \quad (8)$$

where  $\mathcal{R}_{i0} \equiv (\mathbf{d}_{0i} \cdot \mathbf{m}_{i0})$ , the imaginary part of which is called rotatory strength [90,91]. In what follows, we will evaluate the chiral energy shift of chiral molecules induced by two types of PS-broken quantum fluctuations.

*Chiral molecules above a Pasteur material.*—The EM response of a Pasteur material is governed by the constitutive relations  $\mathbf{D} = \epsilon \mathbf{E} - i\kappa \mathbf{H}$  and  $\mathbf{B} = \mu \mathbf{H} + i\kappa \mathbf{E}$ , where, following Landau's convention,  $\mathbf{D}$  and  $\mathbf{B}$  ( $\mathbf{E}$  and  $\mathbf{H}$ ) are called electric and magnetic induction (field);  $\epsilon = \epsilon_r \epsilon_0$  ( $\mu = \mu_r \mu_0$ ) are the permittivity (permeability) of the Pasteur material [92]; the parameter  $\kappa$  characterizes the strength of PS breaking. While the Casimir-Polder forces between a chiral molecule and a Pasteur material have been nicely investigated [58], we focus on the spectral change.

We can alternatively express Eq. (8) in terms of Green's functions [82]:

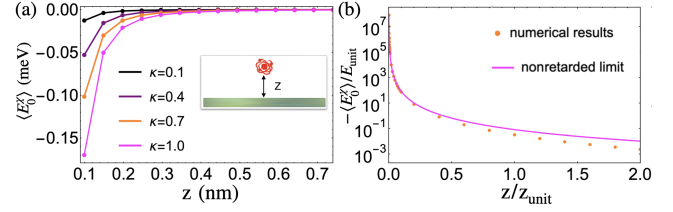


FIG. 2. (a) Numerically calculation of average chiral energy shift for different parameter  $\kappa$ . We set  $E_{10} = 2$  eV and  $\text{Im}\mathcal{R}_{10} = 0.1ea_0\mu_B$  with  $a_0$  and  $\mu_B$  the Bohr radius and Bohr magnetic moment, respectively. (b) The analytical nonretarded result works for  $z \ll z_{\text{unit}} = 1/E_{10}$ ; the energy unit is defined as  $E_{\text{unit}} = \mu_0 \text{Im}\mathcal{R}_{10} E_{10}^3 / 3\pi^2$ ;  $\kappa = 0.4$ . We set  $\epsilon_r = \mu_r = 1$ .

$$\langle \Delta E_0^{\text{ch}} \rangle = \frac{2\mu_0}{3\pi} \sum_i \text{Im}\mathcal{R}_{i0} \int_0^{+\infty} \frac{\xi^2 d\xi}{E_{i0}^2 + \xi^2} \text{Tr} \nabla \times \mathbf{G}(i\xi) \quad (9)$$

with  $\mathbf{G}$  the Green's function of EM fields, which includes the free-space contribution  $\mathbf{G}_{\text{free}}$  and the symmetry-breaking contribution from Pasteur material  $\mathbf{G}_{\text{sb}}$ . Similar formulas Eqs. (6), (7), and (9) have been used to derive chiral-surface-molecule interactions and chiral-surface-mediated interactions previously [58,59]. While the free-space contribution embodies no symmetry-breaking information and leads to identical energy shift for enantiomers, the symmetry-breaking contribution differentiates chiral enantiomers. One can obtain  $\mathbf{G}_{\text{sb}}$  from the reflection coefficients of the Pasteur plate, namely,  $r_{ss}$ ,  $r_{sp}$ ,  $r_{ps}$ , and  $r_{pp}$ , where the subindices indicate the polarization of the incoming and reflected EM wave [82]. We numerically calculate the distance-dependent energy shift and compare it with the analytical nonretarded limit  $[\mu_0(r_{sp} - r_{ps})/48i\pi z^3] \text{Im}\mathcal{R}_{eg}$  (Fig. 2). Here,  $z$  is the distance between the chiral molecule and Pasteur plate, and  $\text{Im}\mathcal{R}_{10}$  is the rotatory strength considering the molecular ground state and its first excited state.

*Chiral molecules in gyrotropic cavities.*—We study chiral molecules in a PS-broken gyrotropic cavity. The Hamiltonian for the cavity photonic modes reads  $\hat{H}_{qa} = \sum_n \Omega_n (\hat{a}_n^\dagger \hat{a}_n + \frac{1}{2})$ , where  $\hat{a}_n^\dagger$  is the creation operator of a photonic mode  $n$  and frequency  $\Omega_n$ . In terms of creation and annihilation operators, the vector potential is

$$\hat{\mathbf{A}}(\mathbf{r}) = \sum_n g_n [\mathbf{A}_n(\mathbf{r}) \hat{a}_n + \mathbf{A}_n^*(\mathbf{r}) \hat{a}_n^\dagger], \quad (10)$$

where the coupling strength  $g_n = \sqrt{1/2\epsilon_0 \Omega_n V_{\text{eff}}}$  and  $\mathbf{A}_n(\mathbf{r}) = e^{i\mathbf{k}_n \cdot \mathbf{r}} \hat{\mathbf{e}}$  represents the EM wave of polarization  $\hat{\mathbf{e}}$ . We assume a general polarization  $\hat{\mathbf{e}} = \hat{\mathbf{e}}_R + i\hat{\mathbf{e}}_I$  with real  $\hat{\mathbf{e}}_R$  and  $\hat{\mathbf{e}}_I$ , which encodes the symmetry-broken information. Substituting the EM fields operators (Coulomb gauge)

$$\begin{aligned} \hat{\mathbf{E}}(\mathbf{r}) &= i \sum_n g_n \Omega_n [\mathbf{A}_n(\mathbf{r}) \hat{a}_n - \mathbf{A}_n^*(\mathbf{r}) \hat{a}_n^\dagger] \quad \text{and} \\ \hat{\mathbf{B}}(\mathbf{r}) &= i \sum_n g_n [\nabla \times \mathbf{A}_n(\mathbf{r}) \hat{a}_n + \nabla \times \mathbf{A}_n^*(\mathbf{r}) \hat{a}_n^\dagger] \end{aligned} \quad (11)$$

into Eq. (8) yields the chiral energy shift [82]

$$\langle \Delta E_0^x \rangle = \sum_n \frac{4g_n^2 \Omega_n^2}{3} \hat{\mathbf{e}}_k \cdot (\hat{\mathbf{e}}_R \times \hat{\mathbf{e}}_I) \sum_i \frac{\text{Im}\mathcal{R}_{i0}}{E_{i0} + \Omega_n}. \quad (12)$$

Here, the factor  $\hat{\mathbf{e}}_k \cdot (\hat{\mathbf{e}}_R \times \hat{\mathbf{e}}_I)$  flips sign under parity operation and implies the chirality of the cavity mode.  $\hat{\mathbf{e}}_k \cdot (\hat{\mathbf{e}}_R \times \hat{\mathbf{e}}_I) = \pm \frac{1}{2}$  for a right(left)-handed circularly polarized mode, whereas it vanishes in a linearly polarized one. Let us estimate the magnitude of the chiral energy shift with promising experimental parameters. Considering two-level systems (ground state  $|g\rangle$  and excited state  $|e\rangle$ ), we estimate the chiral energy shift in a left-handed gyrotropic cavity:

$$\langle \Delta E_0^x \rangle = -\frac{4\pi\alpha}{3} \sum_n \left( \frac{\text{Im}\mathcal{R}_{eg}}{ea_0\mu_B} \right) \left( \frac{a_0^3}{V_{\text{eff}}} \right) \frac{\Omega_n}{\Delta E + \Omega_n} E_{\text{Ryd}}, \quad (13)$$

where  $\alpha$ ,  $a_0$ , and  $\mu_B$  are the fine structure constant, Bohr radius, and Bohr magnetic moment, respectively.  $\Delta E$  denotes the electronic energy gap;  $\Omega_n$  is the frequency of the  $n$ th photonic mode;  $E_{\text{Ryd}}$  is the Rydberg energy;  $\text{Im}\mathcal{R}_{eg}$  is the molecular rotatory strength, and the effective mode volume of a cavity is defined as the ratio between the total field energy in the cavity divided by the field energy density at the molecular position, i.e.,  $V_{\text{eff}} = \int_V d^3r \epsilon(\mathbf{r}) |\mathbf{E}(\mathbf{r})|^2 / \epsilon_0 |\mathbf{E}(\mathbf{r}_m)|^2$ . Setting  $\text{Im}\mathcal{R}_{eg} \approx 0.1ea_0\mu_B$ ,  $\Delta E \approx 2$  eV,  $\Omega_n = 0.1n$  eV (ten modes  $n = 1, 2, \dots, 10$ ), and the smallest effective volume reachable in experiments  $V_{\text{eff}} \approx 0.2$  nm<sup>3</sup>, we obtain an experimental detectable chiral energy shift  $\delta E_0^x \approx -0.06$  meV.

*Collective enhancement.*—Here, we explore how the chiral energy shift can be enhanced by collective effects. For this analysis, it is important to identify two types of terms in Eq. (7), commonly called the Debye term ( $i = 0$ ) and the London term ( $i \neq 0$ ). While both terms contribute to the measurable spectral shift, only the Debye term can benefit from collective effect in a polarized ensemble of molecules (see below). Similar to Eq. (7), we calculate the Debye part of the chiral energy shift of all  $N$  molecules at zero temperature [82]:

$$\begin{aligned} \Delta E_{0,N}^x|_{\text{Debye}} &= -\sum_n \frac{2\text{Re} \left[ \left( \sum_{j=1}^N \mathbf{d}_{00}^{(j)} \cdot \mathbf{E}_{n,01}^{(j)} \right) \left( \sum_{j=1}^N \mathbf{m}_{00}^{(j)} \cdot \mathbf{B}_{n,10}^{(j)} \right) \right]}{\Omega_n} \\ &= -N^2 \sum_n \frac{2\text{Re}[(\mathbf{d}_{00} \cdot \mathbf{E}_{n,01})(\mathbf{m}_{00} \cdot \mathbf{B}_{n,10})]}{\Omega_n}, \end{aligned} \quad (14)$$

where  $n$  labels the cavity modes and  $(j)$  represents the physical quantities of the  $j$ th molecule. The second equality follows that the molecules are polarized:  $\mathbf{d}_{00}^{(j)} \cdot \mathbf{E}_{n,01}^{(j)} = \mathbf{d}_{00} \cdot \mathbf{E}_{n,01}$ ,  $\mathbf{m}_{00}^{(j)} \cdot \mathbf{B}_{n,10}^{(j)} = \mathbf{m}_{00} \cdot \mathbf{B}_{n,10}$ . (A similar derivation was also given in [52].) Modeling chiral cavity modes the same as before, the Debye term per molecule is

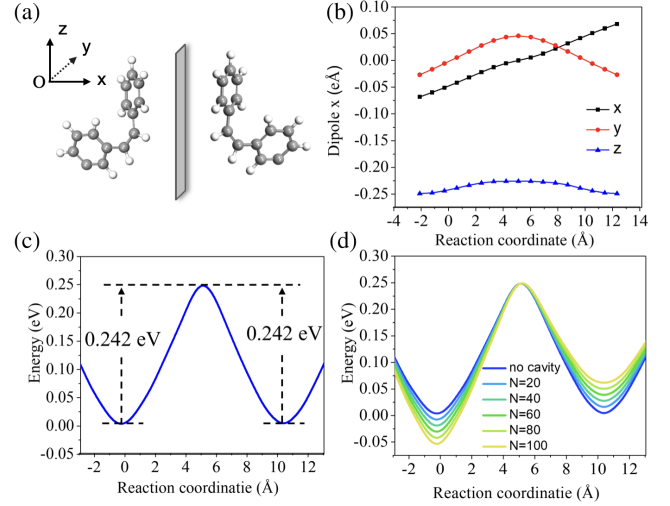


FIG. 3. (a) Atomic structure of a chiral molecule and its enantiomer. Gray and white balls represent carbon and hydrogen atoms, respectively. (b) DFT calculated electric dipole as a function of the reaction coordinate. The reaction coordinate is defined as a certain average of nuclei displacement, which captures the change of molecular configuration. The reaction coordinate is defined as a certain average displacement of nucleus, capturing the change of molecular configuration. (c) Bare molecular PES. The barrier is symmetric for left-handed and right-handed molecules. (d) Molecular PES versus the reaction coordinate induced by chiral energy shift [see Eq. (16)]. Different colors correspond to different numbers of molecules.

$$\begin{aligned} \Delta E_0^x|_{\text{Debye}} &= -N \sum_n \frac{2\text{Re}[(\mathbf{d}_{00} \cdot \mathbf{E}_{n,01})(\mathbf{m}_{00} \cdot \mathbf{B}_{n,10})]}{\Omega_n} \\ &= -N \sum_n g_n^2 \Omega_n (d_{00,x} m_{00,y} - d_{00,y} m_{00,x}). \end{aligned} \quad (15)$$

To illustrate the opposite energy shift for a pair of enantiomers, we consider a concrete example—an ensemble of chiral molecules named hydrogen-missing helicene [Fig. 3(a)]. Using density functional theory (DFT), we calculate the ground-state electric dipole moment of this molecule as it undergoes a transition from left-handed to right-handed configuration [82] [Fig. 3(b)]. Enantiomers are mirror images of each other across the  $y$ - $z$  plane, resulting in dipole moments of  $(\pm d_{00,x}, d_{00,y}, d_{00,z})$ . The ground-state magnetic moment arises from an unpaired electron, which can be polarized in the  $y$  direction. Consequently, the pair of enantiomers experience opposite chiral energy shifts (note that the London term does not scale with  $N$  and can be ignored here [82]):

$$\Delta E_0^x \approx \Delta E_0^x|_{\text{Debye}} = \mp N \sum_n g_n^2 \Omega_n d_{00,x} m_{00,y}. \quad (16)$$

Using the same parameters as given below Eq. (13) except with  $\mathbf{d}_{00} = 0.2ea_0\mathbf{e}_x$  and  $\mathbf{m}_{00} = \mu_B\mathbf{e}_y$ , we find the magnitude  $\mp N \times 0.92$  meV. Our DFT calculations in Fig. 3(d) show that the chiral energy shift in a cluster of 100 molecules can be significantly enhanced. We have not

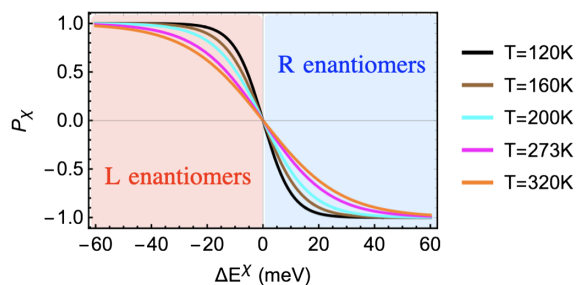


FIG. 4. Chirality-selective rate as a function of the chiral energy shift at different temperatures. Upon reversing the chiral energy shift, opposite chirality is selected.

considered the effect of intermolecular interactions [56,57,65], which may influence the collective enhancement quantitatively by either strengthening or weakening the molecular alignment.

Finally, we evaluate the impact of chiral energy shift in chemical reactions. According to the collision theory, chemical reaction rates depends on the activation energy  $E_a$ —a minimum amount of energy that the reactants need to overcome to form products. The chemical reaction rates can be approximately calculated by the Arrhenius equation  $k = A \exp(-\beta E_a)$  ( $k$  is the rate constant and  $E_a$  is the activation energy) [93]. We define a *chirality-selective rate* to characterize the reaction-rate difference between chiral enantiomers [82]:

$$P_\chi = \frac{k_L - k_R}{k_L + k_R} = \frac{1 - \exp(-2\beta\Delta E_0^\chi)}{1 + \exp(-2\beta\Delta E_0^\chi)} \quad (17)$$

with  $k_L$  ( $k_R$ ) denoting the chemical reaction rates for the  $L$  ( $R$ ) enantiomer. In Supplemental Material [82], we use transition state theory to justify the above result. One could tune the sign of the chiral energy shift to select desired chirality in chemical reactions (see Fig. 4).

*Summary.*—We studied the effect of quantum fluctuations on the spectra of chiral molecules. Our research demonstrates that PS-broken quantum fluctuations can induce a chirality-dependent shift in the ground-state energy. We predicted a significant rate of chirality selection for chiral enantiomers in a gyrotropic cavity. Since chirality selection is related to the rotational strength or the ground-state dipole moments (generally nonzero), our findings have broad applicability and are not limited to any specific molecular model. We remark that our logic, content, and proposals differ fundamentally from the recent papers discussing chirality discrimination [94,95].

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