Static nonlinear Schrödinger equations for the achiral-chiral transitions of polar chiral molecules

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In the mean-field theory, the stabilization of polar chiral molecules is understood as a quantum phase transition where the mean-field ground state of molecules changes from the achiral eigenstate of the molecular Hamiltonian to one of the degenerated chiral states as the increase of the intermolecular interaction. Starting from the many-body Hamiltonian of the molecular gases with electric dipole-dipole interactions, we give the *static* nonlinear Schrödinger equations without free parameters to explore the achiral-chiral transitions of polar chiral molecules. We find that the polar chiral molecules of different species can be classified into two categories: At the critical point for the achiral-chiral transition, the mean-field ground state changes continuously in one category and changes discontinuously in the other category. We further give the mean-field phase diagram of the achiral-chiral transitions for both two categories.

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I. INTRODUCTION

The stabilization of chiral molecules is an old but important problem in molecular quantum mechanics. According to quantum theory, the molecules might be expected to stay in the ground state $|+\rangle$ of the parity-invariant molecular Hamiltonian in the space of the chirality (related vibrational) degree of freedom. However, chiral molecules commonly stay stably in the localized left-handed state $|L\rangle$ or right-handed state $|R\rangle$, which are respectively the symmetric and antisymmetric superpositions of the ground state $|+\rangle$ and the first excited state $|-\rangle$ of the parity-invariant molecular Hamiltonian. The left- and right-handed states are chiral in the sense that $|L\rangle = \hat{\mathcal{T}}|R\rangle$ with the parity operator $\hat{\mathcal{T}}$. This stabilization problem of chiral molecules has been explained previously with the exceedingly long tunneling time [1] between $|L\rangle$ and $|R\rangle$ and/or introducing party-violating terms [2–7] in the molecular Hamiltonian, by considering the single molecule as an isolated system. Later it is found that the above mechanisms are not sufficient to explain the observed stabilization of some kinds of chiral molecules [8–16].

In fact, isolated molecules do not exist in nature. The effects of the environment must be taken into consideration in realistic physical systems. The intermolecular interaction is one of the effects of the environment attributing to the stabilization of chiral molecules [8–12]. Many approaches have been proposed to quantitatively deal with the effect of the intermolecular interaction, where the most well-known ones are the mean-field theory [13,17,18] and the decoherence theory [14,15,19–23]. There are also proposals combining both the mean-field and the decoherence theories to study the stabilization of chiral molecules [16,24]. According to the mean-field theory, the stabilization of chiral molecules is the result of a quantum phase transition from an achiral phase to a chiral phase [17,18], namely, the achiral-chiral transition. According to the decoherence theory, the stabilization of chiral molecules can be understood [14] in analogy to the quantum Zeno effect [25] when the environment behaves as continuously monitoring the molecular state.

Using the mean-field theory, Jona-Lasinio and coworkers [17,18] introduced an ingenious model in the chirality degree of freedom to explore the static and time-dependent problems of polar chiral molecules of $\mathcal{C}_2$ symmetry, which have *zero* permanent electric dipole momentum in an achiral state and *nonzero* permanent electric dipole momentum in a chiral state. They quantitatively describe, without free parameters, the effect of the intermolecular interaction in the stabilization of chiral molecules by giving simply the effective interaction between the ith and jth molecules as the form $\sigma_i^z\sigma_j^z$ with σ^z given in the basis $\{|L\rangle, |R\rangle\}$. However, this form of the effective interaction is not sufficient to describe polar chiral molecules of $\mathcal{C}_1$ symmetry [16], which have *nonzero* permanent electric dipole momentums in both an achiral state and a chiral state. Thus, such chiral molecules have *nonzero* interaction energy in an achiral state according to Keesom's theory [26].

In this paper, we reinvestigate the stabilization of the polar chiral molecules by means of mean-field theory directly from the standard form of the electric dipole-dipole interactions. Since the dipole-dipole interactions are directly related to the positions and orientations of the molecules, the many-body state of the system in the spatial (position) and rotational (orientation) degrees of freedom is considered thoroughly via assuming that the two-particle density follows the Bolztmann distribution [27] with respect to the electric dipole-dipole interaction. Summing over all possible molecular distances and all possible dipole orientations with the help of the Bolztmann distribution and using the standard method of Lagrange multipliers, we arrive our static nonlinear Schrödinger equations in the space of the chirality degree of freedom.

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Self-consistently solving the nonlinear eigenvalue problem, we find that the polar chiral molecules can be classified into two categories. In one category, the mean-field ground state changes continuously from the achiral ground state of the parity-invariant molecular Hamiltonian to one of two degenerated chiral states with the increase of the intermolecular interaction. In the other category, the mean-field ground state changes discontinuously from the achiral ground state to one of the two degenerated chiral ones. In contrast, only the continuous transitions have been predicted in previous works [17,18].

II. MODEL

A. Many-body Hamiltonian

Without taken the kinetic and rotational energies of single molecules into consideration [13,14,16–18,20,22,23], the many-body Hamiltonian for the system of N molecules is

$$\hat{H}=\sum_{i=1}^{N}\left(-\frac{\omega}{2}|L\rangle_{ii}\langle R|+\text{H.c.}\right)+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\hat{V}_{ij}, \tag{1}$$

where the first term is the parity-invariant molecular Hamiltonian given in the basis $\{|L\rangle,|R\rangle\}$ and the second term describes the standard electric dipole-dipole interaction between the ith and jth molecules located at $\boldsymbol{r}_i^s$ and $\boldsymbol{r}_j^s$ with the form

$$\hat{V}_{ij}=\frac{\hat{\boldsymbol{\mu}}^{s,i}\cdot\hat{\boldsymbol{\mu}}^{s,j}-3\big(\hat{\boldsymbol{\mu}}^{s,i}\cdot\boldsymbol{r}_{ij}^s\big)\big(\hat{\boldsymbol{\mu}}^{s,j}\cdot\boldsymbol{r}_{ij}^s\big)r_{ij}^{-2}}{4\pi\varepsilon_0 r_{ij}^3}. \tag{2}$$

Here $\hat{\boldsymbol{\mu}}^{s,i}$ is the electric dipole operator of the ith molecule in the space-fixed frame, the notation "s" indicates the space-fixed frame, and $r_{ij}=|\boldsymbol{r}_{ij}^s|$. $\boldsymbol{r}_{ij}^s$ $(\equiv\boldsymbol{r}_i^s-\boldsymbol{r}_j^s)$ can be expressed as

$$\boldsymbol{r}_{ij}^s=r_{ij}\sum_{\sigma=0,\pm1}\sqrt{\frac{4\pi}{3}}Y_{1\sigma}\big(\tilde{\Omega}_{\boldsymbol{r}_{ij}^s}\big)\boldsymbol{e}_\sigma^s, \tag{3}$$

where $\tilde{\Omega}_{\boldsymbol{r}^s}=(\alpha_{\boldsymbol{r}^s},\beta_{\boldsymbol{r}^s})$ are the solid angles of $\boldsymbol{r}^s$ and $Y_{1\sigma}$ are the spherical harmonics. Here $\boldsymbol{e}_0^s=\boldsymbol{e}_Z$ and $\boldsymbol{e}_{\pm1}^s=(\mp\boldsymbol{e}_X-i\boldsymbol{e}_Y)/\sqrt{2}$ with the coordinations in the space-fixed frame (X,Y,Z).

The components of the electric dipole operator $\hat{\boldsymbol{\mu}}^s$ of a general chiral molecule in the space-fixed frame can be obtained by a rotation from the molecular frame [28] via

$$\hat{\mu}_\sigma^s=\sum_{\sigma'=0,\pm1}D_{\sigma\sigma'}^{1*}(\alpha,\beta,\gamma)\hat{\mu}_{\sigma'}^m \tag{4}$$

with $\hat{\mu}_0^s=\hat{\mu}_Z^s$ and $\hat{\mu}_{\pm1}^s=(\mp\hat{\mu}_X^s-i\hat{\mu}_Y^s)/\sqrt{2}$. The index "$m$" indicates the molecular frame and "$*$" denotes taking conjugate complex. D^1 is the rotation matrix in three dimensions. Here $\Omega=(\alpha,\beta,\gamma)$ are the Euler angles denoting the orientation of the molecule. $\hat{\mu}_{\sigma'}^m$ are the components of the electric dipole $\hat{\boldsymbol{\mu}}^m$ in the molecular frame with $\hat{\mu}_0^m=\hat{\mu}_z^m$ and $\hat{\mu}_{\pm1}^m=(\mp\hat{\mu}_x^m-i\hat{\mu}_y^m)/\sqrt{2}$. Here x, y, and z are, respectively, the principal (inertial) axes of the molecule in the molecular frame.

B. Static nonlinear Schrödinger equations

We assume the N-molecule $(N\gg1)$ system is described by the density matrix

$$\rho=\rho_{sr}\big(\boldsymbol{r}_1^s,\ldots,\boldsymbol{r}_N^s;\Omega_1,\ldots,\Omega_N;\lambda_1,\ldots,\lambda_N\big)\otimes\prod_{i=1}^{N}|\lambda_i\rangle\langle\lambda_i|, \tag{5}$$

where ρ_{sr} describes the density matrix of the system in the spatial and rotational degrees of freedom with $\boldsymbol{r}_i^s$ and Ω_i denoting the position and orientation of the ith molecule. Indeed, a molecule in general has many vibrational degrees of freedom. We refer to only the one relating to the two chiral states (called the chirality degree of freedom) and assume that all other vibrational degrees of freedom are frozen. Since the electric dipole-dipole interactions couple the chirality, spatial, and rotational degrees of freedom, it is natural that ρ_{sr} is dependent on the states of molecules in the chirality degree of freedom $|\lambda_i\rangle$. With the framework of mean-field theory, we replace the state in the chirality degree of freedom $|\lambda_i\rangle$ with a mean-field state of

$$|\lambda\rangle=\varphi_{\lambda,L}|L\rangle+\varphi_{\lambda,R}|R\rangle. \tag{6}$$

Correspondingly, we will use $\rho_{sr}(\boldsymbol{r}_1^s,\ldots,\boldsymbol{r}_N^s;\Omega_1,\ldots,\Omega_N;\lambda)$ to replace $\rho_{sr}(\boldsymbol{r}_1^s,\ldots,\boldsymbol{r}_N^s;\Omega_1,\ldots,\Omega_N;\lambda_1,\ldots,\lambda_N)$.

Then the energy of the system, $E\equiv\mathrm{Tr}(\rho\hat{H})$, can be expressed as

$$E\simeq-N\frac{\omega}{2}(\varphi_{\lambda,L}^*\varphi_{\lambda,R}+\text{c.c.})+\frac{N(N-1)}{2}g(\lambda), \tag{7}$$

where the mean-field two-particle interaction energy is

$$g(\lambda)\equiv\mathrm{Tr}(\rho_{sr}\hat{V}_{12})=\mathrm{Tr}(\rho_{sr}\langle\lambda,\lambda|\hat{V}_{12}|\lambda,\lambda\rangle). \tag{8}$$

Here $|\lambda,\lambda\rangle=|\lambda_1\rangle\otimes|\lambda_2\rangle$ with $|\lambda_{1,2}\rangle=|\lambda\rangle$, and $V_{12}(\lambda)\equiv\langle\lambda,\lambda|\hat{V}_{12}|\lambda,\lambda\rangle$ is an operator in the space of the spatial and rotational degrees of freedom. Explicitly, we have

$$V_{12}(\lambda)=-\frac{1}{4\pi\varepsilon_0 r_{12}^3}\sum_{\sigma_1',\sigma_2'=0,\pm1}\mu_{\lambda,\sigma_1'}^m\big(\hat{\mu}_{\lambda,\sigma_2'}^m\big)^*\left[\sum_{\sigma_1,\sigma_2=0,\pm1}4\pi D_{\sigma_1\sigma_2'}^1(\Omega_2)D_{\sigma_1\sigma_1'}^{1*}(\Omega_1)Y_{1\sigma_1}\big(\tilde{\Omega}_{\boldsymbol{r}_{12}^s}\big)Y_{1\sigma_2}^*\big(\tilde{\Omega}_{\boldsymbol{r}_{12}^s}\big)-\sum_{\sigma=0,\pm1}D_{\sigma\sigma_1'}^{1*}(\Omega_1)D_{\sigma\sigma_2'}^1(\Omega_2)\right] \tag{9}$$

with $\mu_{\lambda,\sigma'}^m\equiv\langle\lambda|\hat{\mu}_{\sigma'}^m|\lambda\rangle$.

Further the mean-field two-particle interaction energy approximates to

$$g(\lambda)=\mathrm{Tr}_{\{1,2\}}\big[V_{12}(\lambda)\rho_{12}^{sr}(\boldsymbol{r}_1,\boldsymbol{r}_2;\Omega_1,\Omega_2;\lambda)\big] \tag{10}$$

with the two-particle density matrix

$$\rho_{12}^{sr}(\boldsymbol{r}_1,\boldsymbol{r}_2;\Omega_1,\Omega_2;\lambda)\equiv\mathrm{Tr}_{\{3,\ldots,N\}}[\rho_{sr}], \tag{11}$$

where $\mathrm{Tr}_{\{1,2\}}$ means an integral over $\boldsymbol{r}_1^s$, $\boldsymbol{r}_2^s$, Ω_1, and Ω_2, and $\mathrm{Tr}_{\{3,\ldots,N\}}$ means an integral over all coordinates and Euler angles except $\boldsymbol{r}_1^s$, $\boldsymbol{r}_2^s$, Ω_1, and Ω_2.

The two-particle density matrix can be approximately written as [27]

$$\rho_{12}^{sr}(\boldsymbol{r}_1,\boldsymbol{r}_2;\Omega_1,\Omega_2) \simeq \frac{1}{\mathcal{Z}}\exp\left[-\frac{V_{12}(\lambda)}{k_BT}\right] \tag{12}$$

with the Boltzmann constant k_B and the normalization constant $\mathcal{Z}$. Here we have assumed the Boltzmann distribution of the two-particle density in the spatial and rotational degrees of freedom [27]. Since V_{12} and ρ_{12}^{sr} are functions of $\boldsymbol{r}_{12}^s$, we make variable substitution as $\int d^3\boldsymbol{r}_1^s d^3\boldsymbol{r}_2^s\cdots = \int d^3\boldsymbol{r}_1^s d^3\boldsymbol{r}_{12}^s\cdots$ and integrate over $\boldsymbol{r}_1^s$ first. Then we can get

$$g(\lambda) = \frac{1}{\mathcal{V}}\int d^3\boldsymbol{r}_{12}^s\, d\Omega_1\, d\Omega_2 V_{12}\rho_{12}^{sr} \tag{13}$$

with the volume of the gas $\mathcal{V}$. Assuming $V_{12}/(k_BT) \ll 1$ and applying the Taylor expansion to $g(\lambda)$, we have

$$\begin{aligned} g(\lambda) &= -\frac{512\pi^5}{3}\frac{1}{\mathcal{Z}}\frac{\mathcal{V}}{k_BT}\int_{r_{12}>d} r_{12}^2 dr_{12}\frac{|\boldsymbol{\mu}_\lambda^m|^4}{\left(4\pi\varepsilon_0 r_{12}^3\right)^2} \\ &= -\frac{1}{N}\frac{P|\boldsymbol{\mu}_\lambda^m|^4}{18\pi(\varepsilon_0k_BT)^2d^3} \end{aligned} \tag{14}$$

with P the pressure of the gas and d the molecular collision diameter. We have used $\int d^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2\, d\Omega_1\, d\Omega_2 V_{12} = 0$, $\mathcal{Z} \simeq 64\pi^4\mathcal{V}^2$ and the approximation of ideal gas $P\mathcal{V} \simeq Nk_BT$. We note that $|\boldsymbol{\mu}_\lambda^m|^4/(4\pi\varepsilon_0 r_{12}^3)^2$ is the Van der Waals potential between two electric dipoles, namely, the Keesom interaction [26].

The average energy of a molecule in the system, $\varepsilon(\lambda) \equiv E/N$, is approximately given as

$$\varepsilon(\lambda) = -\frac{\omega}{2}(\varphi_{\lambda,L}^*\varphi_{\lambda,R} + \text{c.c.}) - \frac{P|\boldsymbol{\mu}_\lambda^m|^4}{36\pi(\varepsilon_0k_BT)^2d^3} \tag{15}$$

by neglecting the terms of order $1/N$ in the large N limit.

For a pair of left- and right-handed chiral states $|L\rangle$ and $|R\rangle$, we have $\boldsymbol{\mu}_L^m \equiv \langle L|\hat{\boldsymbol{\mu}}^m|L\rangle$ and $\boldsymbol{\mu}_R^m \equiv \langle R|\hat{\boldsymbol{\mu}}^m|R\rangle$. It is well known that their components satisfy [29–36]

$$\mu_{L,x}^m\mu_{L,y}^m\mu_{L,z}^m = -\mu_{R,x}^m\mu_{R,y}^m\mu_{R,z}^m. \tag{16}$$

1. Polar chiral molecules of $\mathcal{C}_1$ symmetry

For polar chiral molecules of $\mathcal{C}_1$ symmetry whose three components of the electric-dipole along the three principle axes are *nonzero*, we can assume that the components obey [37,38]

$$\begin{aligned} \mu_{L,x}^m &= \mu_{R,x}^m = \mu_x^m \neq 0, \\ \mu_{L,y}^m &= \mu_{R,y}^m = \mu_y^m \neq 0, \\ \mu_{L,z}^m &= -\mu_{R,z}^m = \mu_z^m \neq 0. \end{aligned} \tag{17}$$

With Eq. (17), we have

$$\begin{aligned} \mu_{\lambda,\pm1}^m &\equiv \langle\lambda|\hat{\mu}_{\pm1}^m|\lambda\rangle = \frac{\mp\mu_x^m - i\mu_y^m}{\sqrt{2}}, \\ \mu_{\lambda,0}^m &\equiv \langle\lambda|\hat{\mu}_0^m|\lambda\rangle = \mu_z^m(|\varphi_{\lambda,L}|^2 - |\varphi_{\lambda,R}|^2). \end{aligned} \tag{18}$$

By means of Eqs. (15) and (18) and the condition $|\varphi_{\lambda,L}|^2 + |\varphi_{\lambda,R}|^2 = 1$, we can get the static nonlinear Schrödinger equations for the system in the space of the chirality degree of freedom via the method of Lagrange multipliers as

$$\begin{aligned} -\frac{\omega}{2}\varphi_{\lambda,L} + US_z^3(\lambda)\varphi_{\lambda,R} + GS_z(\lambda)\varphi_{\lambda,R} &= \eta\varphi_{\lambda,R}, \\ -\frac{\omega}{2}\varphi_{\lambda,R} - US_z^3(\lambda)\varphi_{\lambda,L} - GS_z(\lambda)\varphi_{\lambda,L} &= \eta\varphi_{\lambda,L}, \end{aligned} \tag{19}$$

where the eigenvalue η is the chemical potential, and

$$S_z(\lambda) \equiv |\varphi_{\lambda,L}|^2 - |\varphi_{\lambda,R}|^2, \tag{20}$$

$$U = \frac{\left(\mu_z^m\right)^4P}{36\pi(\varepsilon_0k_BT)^2d^3}, \tag{21}$$

$$G = \frac{\left(\mu_z^m\mu_\perp^m\right)^2P}{36\pi(\varepsilon_0k_BT)^2d^3} \tag{22}$$

with $\mu_\perp^m \equiv \sqrt{(\mu_x^m)^2 + (\mu_y^m)^2}$.

For polar chiral molecules of $\mathcal{C}_1$ symmetry in an achiral state ($\varphi_{\lambda,L} = \pm\varphi_{\lambda,R}$), they have *nonzero* components of the permanent electric dipole momentum, $\mu_{\lambda,\pm1}^m \neq 0$. This means the two-particle interaction energy is *nonzero*. In contrast, one would obtain *zero* two-particle interaction energy for polar chiral molecules of $\mathcal{C}_1$ symmetry in an achiral state according to the model in Refs. [17,18]. This contradicts the Keesom's theory [26], where the two-particle interaction energy for polar chiral molecules of $\mathcal{C}_1$ symmetry in an achiral state is *nonzero*. Thus, the model in Refs. [17,18] is not available for polar chiral molecules of $\mathcal{C}_1$ symmetry, as also pointed out in Ref. [16].

2. Polar chiral molecules of $\mathcal{C}_2$ symmetry

For polar chiral molecules of $\mathcal{C}_2$ symmetry, only one of the three components of the electric-dipole along the three principle axes is *nonzero*. In the problem of the stabilization of polar chiral molecules, the polar chiral molecules of $\mathcal{C}_2$ symmetry can be considered as a special case of polar chiral molecules of $\mathcal{C}_2$ symmetry. We can assume that the components obey [39]

$$\begin{aligned} \mu_{L,x}^m &= \mu_{R,x}^m = \mu_x^m = 0, \\ \mu_{L,y}^m &= \mu_{R,y}^m = \mu_y^m = 0, \\ \mu_{L,z}^m &= -\mu_{R,z}^m = \mu_z^m \neq 0. \end{aligned} \tag{23}$$

Then we have

$$\begin{aligned} \mu_{\lambda,\pm1}^m &\equiv \langle\lambda|\hat{\mu}_{\pm1}^m|\lambda\rangle = 0, \\ \mu_{\lambda,0}^m &\equiv \langle\lambda|\hat{\mu}_0^m|\lambda\rangle = \mu_z^m(|\varphi_{\lambda,L}|^2 - |\varphi_{\lambda,R}|^2) \end{aligned} \tag{24}$$

and get the static nonlinear Schrödinger equations in the space of the chirality degree of freedom as

$$\begin{aligned} -\frac{\omega}{2}\varphi_{\lambda,L} + US_z^3(\lambda)\varphi_{\lambda,R} &= \eta\varphi_{\lambda,R}, \\ -\frac{\omega}{2}\varphi_{\lambda,R} - US_z^3(\lambda)\varphi_{\lambda,L} &= \eta\varphi_{\lambda,L}. \end{aligned} \tag{25}$$

In fact, Eq. (25) is the special case of Eq. (19) when $G = 0$.

In Refs. [17,18], the nonlinear terms are proportional to $S_z(\lambda)$ since they have used the effective interaction of the form $\sigma_i^z\sigma_j^z$ to describe the electric dipole-dipole interactions. However, we obtain a different form of nonlinear Schödinger equations (25) with the nonlinear terms proportional to $S_z^3(\lambda)$ by using the standard form of the electric dipole-dipole interactions.

We would like to remark that the very central point of this paper is the appearance of the term $|\boldsymbol{\mu}_\lambda^m|^4$ in Eq. (14), where $|\boldsymbol{\mu}_\lambda^m|^2$ will be introduced twice in the mean-field two-particle interaction energy. For the first time, it is introduced in $V_{12}(\lambda)$ of Eq. (9), which gives the mean-field two-particle interaction energy of two orientated molecules of Euler angler Ω_1 and Ω_2. For the second time, it is introduced in making the sum over all possible Ω_1 and Ω_2 in Eq. (13) via assuming the Boltzmann distribution of the two-particle density in Eq. (12). It is the appearance of $|\boldsymbol{\mu}_\lambda^m|^4$ in Eq. (14) that induces the nonlinear terms proportional to $S_z^3(\lambda)$ in our nonlinear Schödinger equations (19) and (25).

III. ACHIRAL-CHIRAL TRANSITION

Starting from the many-body Hamiltonian (1), we have obtained the static nonlinear Schrödinger equations for all the polar chiral molecules with inversion symmetry in the space of the chirality degree of freedom. In the following, we will explore the achiral-chiral transitions via solving the nonlinear eigenvalue problem associated with Eq. (19). The coefficients $\varphi_{\lambda,L}$ and $\varphi_{\lambda,R}$ can be chosen real. With Eq. (19), we have

$$S_z(\lambda)\{4\varphi_{\lambda,L}\varphi_{\lambda,R}[US_z^2(\lambda)+G]-\omega\}=0. \tag{26}$$

Once the solutions are found, the corresponding eigenvalues (chemical potential) are given by

$$\eta=-\omega\varphi_{\lambda,L}\varphi_{\lambda,R}-US_z^4(\lambda)-GS_z^2(\lambda). \tag{27}$$

There are always two solutions to Eq. (26) when $S_z(\lambda)=0$. Up to an irrelevant sign, these two solutions correspond to the achiral eigenstates

$$|\pm\rangle=\frac{1}{\sqrt{2}}(|L\rangle\pm|R\rangle) \tag{28}$$

with the corresponding eigenvalues $\eta_\pm=\mp\omega/2$. They are, respectively, the ground and first excited eigenstates of the parity-invariant molecular Hamiltonian.

We note that $\mathcal{G}\equiv G/U=(\mu_\perp^m/\mu_z^m)^2$ is determined by the species of polar chiral molecules, and thus it can not be given arbitrarily. For the polar chiral molecules of $\mathcal{C}_2$ symmetry, $\mathcal{G}=0$. For the polar chiral molecules of $\mathcal{C}_1$ symmetry, $\mathcal{G}\neq 0$. For example, $\mathcal{G}\simeq 2.7$ for propylene oxide [40] and $\mathcal{G}\simeq 0.46$ for solketal [34]. For convenience of discussion in the following, we will use $\mathcal{G}$ as a tunable parameter.

For a given value of $\mathcal{G}$, there will be further chiral solutions to Eq. (26) when f ($\equiv\omega/U$) is smaller than a critical value f_{cr} as shown in Fig. 1. The corresponding chiral states have lower energies than the achiral state $|+\rangle$. The decrease of f will give rise to the achiral-chiral transition. Changing $\mathcal{G}$, we find that the achiral-chiral transitions can be divided into two categories: In category (I) the mean-field ground state changes continuously from the achiral state $|+\rangle$ to a chiral state with the decrease of f; in category (II) the mean-field ground state changes discontinuously at the critical point of f_{cr}.

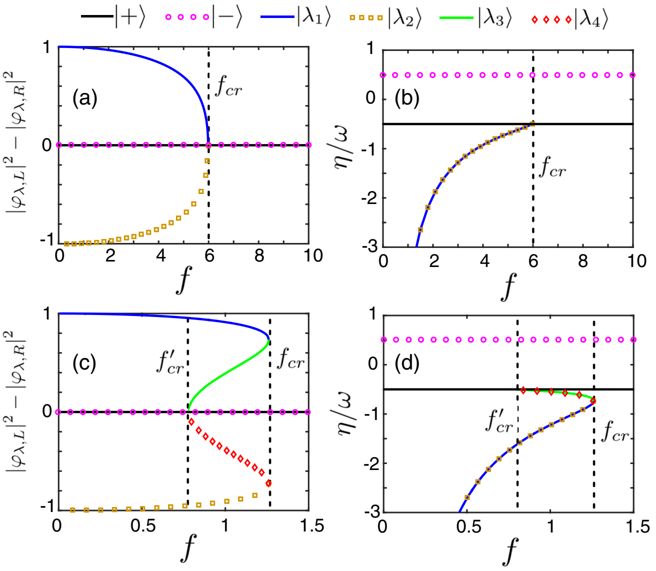

FIG. 1. Achiral-chiral transitions. (a, b) The achiral-chiral transition in category (I) with $\mathcal{G}=3$. (c, d) The achiral-chiral transition in category (II) with $\mathcal{G}=0.4$. Here $|\pm\rangle$ are the two achiral eigenstates. The other possible eigenstates $|\lambda_1\rangle$, $|\lambda_2\rangle$, $|\lambda_3\rangle$, and $|\lambda_4\rangle$ are chiral in the sense $|\lambda_1\rangle=\hat{\mathcal{T}}|\lambda_2\rangle$ and $|\lambda_3\rangle=\hat{\mathcal{T}}|\lambda_4\rangle$ with the parity operator $\hat{\mathcal{T}}$. Here we have $f\equiv\omega/U$ and $\mathcal{G}\equiv G/U$.

In Figs. 1(a) and 1(b), we choose $\mathcal{G}=3$ to show the typical behaviors of the achiral-chiral transitions in category (I). When f decreases from the region $f>f_{cr}$ to the region $f<f_{cr}$, the mean-field ground state will change continually from the achiral state $|+\rangle$ to one of the two degenerated chiral states $|\lambda_1\rangle$ and $|\lambda_2\rangle$. They are chiral in the sense [18] that $|\lambda_1\rangle=\hat{\mathcal{T}}|\lambda_2\rangle$ with the parity operator $\hat{\mathcal{T}}$. In the limit $f\ll 1$ ($\omega\ll U$), we find that $|\lambda_1\rangle$ and $|\lambda_2\rangle$ approach the localized states $|L\rangle$ and $|R\rangle$, respectively. In category (II) the typical behaviors are shown in Figs. 1(c) and 1(d) with $\mathcal{G}=0.4$. When f decreases from the region $f>f_{cr}$ to the region $f<f_{cr}$, the mean-field ground state jumps from the achiral state $|+\rangle$ to one of the degenerated chiral states $|\lambda_1\rangle$ and $|\lambda_2\rangle$ at the critical point. We find that there are two additional higher-energy chiral solutions $|\lambda_3\rangle$ and $|\lambda_4\rangle$ with $|\lambda_3\rangle=\hat{\mathcal{T}}|\lambda_4\rangle$ in the region $f'_{cr}<f<f_{cr}$ in the case of $\mathcal{G}=0.4$.

In Fig. 2 we give phase diagram in the ($\mathcal{G}$-f) plane to show how f_{cr} and f'_{cr} vary with $\mathcal{G}$. The line of $f_{cr}(\mathcal{G})$ divides the plane into the upper and lower halves. The achiral states $|\pm\rangle$ are always the mean-field eigenstates of the system with eigenvalues $\eta_\pm=\mp\omega/2$. In the lower half plane, the system has two degenerated chiral eigenstates $|\lambda_1\rangle$ and $|\lambda_2\rangle$ with lower eigenvalues than $|\pm\rangle$. In the area surrounded by $f'_{cr}(\mathcal{G})$, $f_{cr}(\mathcal{G})$, and the f axis, there are further two degenerated chiral eigenstates $|\lambda_3\rangle$ and $|\lambda_4\rangle$ whose eigenvalues are lower than that of $|\pm\rangle$ but higher than that of $|\lambda_1\rangle$ and $|\lambda_2\rangle$. The intersection of the lines of $f_{cr}(\mathcal{G})$ and $f'_{cr}(\mathcal{G})$ give the critical value $\mathcal{G}_{cr}=2$ labeled with the vertical black dashed line. It divides the achiral-chiral transitions into categories (I) and (II). In category (I) where $\mathcal{G}\geqslant\mathcal{G}_{cr}$, the mean-field ground state changes continuously from the achiral state $|+\rangle$ to one of the two degenerated chiral states $|\lambda_1\rangle$ and $|\lambda_2\rangle$ with the decrease of f. In category (II) where $\mathcal{G}<\mathcal{G}_{cr}$, the

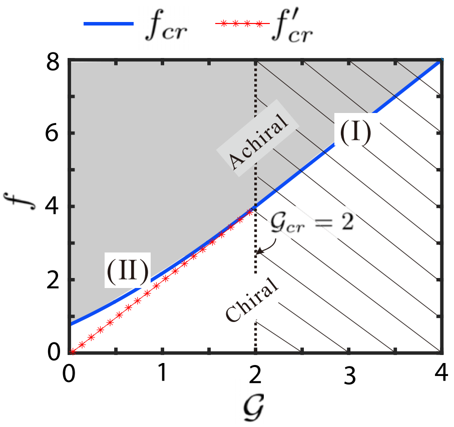

FIG. 2. Phase diagram of the achiral-chiral transitions in the ($\mathcal{G}$-f) plane. The line of f_{cr} divides the plane into upper and lower halves, where the mean-field ground states are the achiral and chiral states, respectively. The intersection of the lines of f_{cr} and f'_{cr} gives $\mathcal{G}_{cr} = 2$. It divides the achiral-chiral transitions into categories (I) and (II). In category (I) where $\mathcal{G} \geqslant \mathcal{G}_{cr}$, the achiral-chiral transitions present typical behaviours as shown in Figs. 1(a) and 1(b). In category (II) where $\mathcal{G} < \mathcal{G}_{cr}$, the achiral-chiral transitions present typical behaviours as shown in Figs. 1(c) and 1(d).

mean-field ground state changes discontinuously at the critical point.

As we have pointed out, $\mathcal{G}$ is determined by the species of polar chiral molecules. Different species of polar chiral molecules of $\mathcal{C}_1$ symmetry can be classified with the help of Fig. 2 in two categories. Here we take propylene oxide and solketal as examples. They are polar chiral molecules of $\mathcal{C}_1$ symmetry. Propylene oxide with $\mathcal{G} \simeq 2.7$ can be classified into category (I) where the mean-field ground state changes continuously at the critical point. Solketal with $\mathcal{G} \simeq 0.46$ can be classified into category (II) where the mean-field ground state changes discontinuously at the critical point.

IV. SUMMARY

Starting from the many-body Hamiltonian of the gases of polar chiral molecules with electric dipole-dipole interactions of standard form, we have given the static nonlinear Schrödinger equations in the space of the chirality degree of freedom to explore the achiral-chiral transitions. Our approach can be applied to polar chiral molecules of both $\mathcal{C}_1$ and $\mathcal{C}_2$ symmetry without free parameters. For the achiral-chiral transitions, we have given the mean-field phase diagram in the ($\mathcal{G}$-f) plane. We find that, for polar chiral molecules with $\mathcal{G} = (\mu_\perp^m/\mu_z^m)^2 > 2$ the mean-field ground state changes continuously from the achiral state $|+\rangle$ to one of the two degenerated chiral state $|\lambda_1\rangle$ and $|\lambda_2\rangle$ with the decrease of f, for polar chiral molecules with $\mathcal{G} < 2$ the mean-field ground state changes discontinuously. This is different from the results predicted with the models in Refs. [13,17,18], where the mean-field ground state always changes continuously. It is worth noting that our discussions based on the molecular electric dipole-dipole interactions are not available to the nonpolar chiral molecules, i.e., molecules that belong to the D_n point groups [41,42].

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