Quantum theory of chiral interactions in cholesteric liquid crystals

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The effective chiral interaction between molecules arising from long-range quantum interactions between fluctuating charge moments is analyzed in terms of a simple model of chiral molecules. This model is based on the approximations that (a) the dominant excited states of a molecule form a band whose width is small compared to the average energy of excitation above the ground state and (b) biaxial orientational correlation between adjacent molecules can be neglected. Previous treatments of quantum chiral interactions have been based on a multipole expansion of the effective interaction energy within second-order perturbation theory. We consider a system consisting of elongated molecules and, although we invoke the expansion in terms of coordinates transverse to the long axis of constituent molecules, we treat the longitudinal coordinate exactly. Such an approximation is plausible for molecules in real liquid crystals. The macroscopic cholesteric wave vector $\mathbf{Q}$ ($Q=2\pi/P$, where P is the pitch) is obtained via $Q=h/K_2$, where K_2 is the Frank elastic constant for twist and h is the torque field which we calculate from the effective chiral interaction $\kappa_{IJ}\mathbf{a}_I\times\mathbf{a}_J\cdot\mathbf{R}_{IJ}$, where the unit vector $\mathbf{a}_I$ specifies the orientation of molecule I and $\mathbf{R}_{IJ}$ is the displacement of molecule I relative to molecule J. We identify two distinct physical limits depending on whether one or both of the interacting molecules are excited in the virtual state. When both molecules are excited, we regain the R_{IJ}^{-8} dependence of κ_{IJ} on intermolecular separation found previously by Van der Meer *et al.* [J. Chem. Phys. **65**, 3935 (1976)]. The two-molecule, unlike the one-molecule term, can be interpreted in terms of a superposition of pairwise interactions between individual atoms (or local chiral centers) on the two molecules. Contributions to κ_{IJ} when one molecule is excited in the virtual state are of order R_{IJ}^{-7} for helical molecules which are assumed not to have a global dipole moment, but whose atoms possess a dipole moment. It is shown that for a helical molecule Q can have either the same or the opposite sign as the chiral pitch of an individual molecule, depending on the details of the anisotropy of the atomic polarizability. The one-molecule mechanism can become important when the local atomic dipoles become sizable, although biaxial correlations (ignored here) should then be taken into account. Our results suggest how the architecture of molecular dipole moments might be adjusted to significantly influence the macroscopic pitch. [S1063-651X(99)12303-1]

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I. INTRODUCTION

In the cholesteric liquid crystalline phase [1,2], anisotropic mesogens align on average along a local unit director $\mathbf{n}(\mathbf{r})$ that rotates in a helical fashion about a uniform pitch axis. The pitch P of this helix ranges from a few tenths of a micron to 10 or more microns. In fact, solutions of the viruses fd and tobacco mosaic virus (TMV), as well as DNA, have even much larger pitches [3,4]. Because the pitch is usually large compared to the intermolecular separation, these systems are locally essentially indistinguishable from nematics and consequently they are often referred to as chiral nematics (CN's). The pitch wave number $Q=2\pi/P$ can even pass through zero as a function of temperature [1,2]. The helical structure of a cholesteric phase must result from the molecular chirality of some or all of its constituent mesogens. Achiral mesogens form an achiral nematic rather than a chiral nematic phase. Phenomenologically, the explanation of the twist of the cholesteric phase is straightforward: chiral mesogens must lead to a chiral term $h\mathbf{n}\cdot\boldsymbol{\nabla}\times\mathbf{n}$ in the long-wavelength free energy density that favors twist. This tendency to twist is resisted by a twist elastic energy density $\frac{1}{2}K_2(\mathbf{n}\cdot\boldsymbol{\nabla}\times\mathbf{n})^2$, where K_2 is the Frank elastic constant for twist. If the pitch axis coincides with the z direction, then in the equilibrium configuration one has

$$\mathbf{n}(\mathbf{r})=(\cos Qz,\sin Qz,0), \tag{1}$$

with

$$Q\equiv 2\pi/P=h/K_2. \tag{2}$$

(Our definition of Q is such that positive Q corresponds to right-handed macroscopic chirality [5]). The magnitude of K_2, which has units of energy per unit length, is estimated with good accuracy by dimensional analysis. The characteristic energy is of the order of the thermal energy, $k_BT\sim k_BT_{NI}$ where k_B is the Boltzmann constant, T is the temperature, and T_{NI} is the isotropic-to-nematic transition temperature. The characteristic length is a molecular length L, so that $K_2\sim k_BT/L$. A similar dimensional analysis for the torque field h, which has units of energy/(length^2), would predict $h\sim k_BT/L^2$ and $P\sim L$. This is a far tighter pitch than is observed in any cholesteric. This reasoning indicates that an explanation of the magnitude of h requires considering a detailed model of the cholesteric. The chiral structure of cholesterics also raises some technological issues. It would be very desirable to be able to ''engineer'' molecules that have specific values of h and thus P or more generally that have a specific temperature dependence for h. To realize this goal, it is necessary to understand how variations in molecular architecture and electronic structure influence h. As a first step in dealing with these issues of fundamental and applied science, this paper will address some aspects of the calculation of h from a molecular model.

In fact, the calculation of h is highly nontrivial. It involves the rather complex interactions between mesogens and the orientational correlations they induce. If there are chiral mesogens, there are chiral interactions, and h is nonzero; otherwise, h is zero. One typically identifies three types of interactions between molecules [6]: (1) long-range attractive dispersion (van der Waals) interactions, (2) short-range repulsive interactions, whose origin is the Pauli principle, and (3) direct Coulomb interactions, which take the form of dipolar, quadrupolar, etc. interactions between electrically neutral mesogens. The latter interactions are of secondary importance in many chiral and achiral liquid crystals and will be ignored here. Initially Straley [7] proposed that the macroscopic chirality of CN's could be understood qualitatively in terms of the packing of screws. These short-range repulsive forces were modeled as hard-core or steric potentials [8–10,19], reflecting molecular shape, that contribute to the entropy but not the internal energy. For spherical atoms, the repulsive and dispersion forces can be combined in a single effective potential such as the Lennard-Jones 6–12 central-force potential. More generally, interactions between achiral molecules can be modeled as sums over central-force effective potentials between pairs of atoms or mass points on different molecules [11]. There are chiral versions of both dispersion and short-range repulsive forces. Chiral dispersion forces were first analyzed by Goossens [12] and later more systematically by others [6,13,14]. They found that the dominant chiral interaction between chiral mesogens, calculated in the limit of center-of-mass separation R much larger than any molecular dimension L, was proportional to R^{-7} and to the product of dipolar and quadrupolar molecular matrix elements. Various somewhat *ad hoc* chiral intermolecular interactions, some based on implementing models equivalent to threaded rods [15–18], others on surface-nematic interactions of chiral dopants [19], have been introduced mostly as input to simulations of chiral systems. Models for flexible mesogens have also been treated [20].

A chiral molecule is one that cannot be rotated into coincidence with its mirror image [21]. Chiral molecules cannot be uniaxial: at minimum, their description requires an orthonormal triad of vectors rather than a single vector. A microscopic description of chiral interactions involves the complete orthonormal triad of axes emblazoned on each of the two interacting molecules. However, as we have mentioned, apart from very small corrections arising from slow local twist, the cholesteric phase is locally uniaxial. It is, therefore, natural to seek effective chiral interactions between effectively uniaxial molecules. If a molecule J of arbitrary shape is spun about some axis $\mathbf{a}_J$, it becomes on average uniaxial with respect to this axis. Thus, general pair interactions between molecules I and J in a chiral nematic can be reduced to uniaxial pair interactions by averaging over independent rotations of each member of the pair about the local nematic director. The resulting potential is only approximate in that it ignores orientational correlations between molecules in the plane perpendicular to $\mathbf{a}_I$ and $\mathbf{a}_J$. In practice, one usually averages over independent rotations of each molecule about its body axis $\mathbf{a}$, rather than the more correct average over rotations about the local nematic director. We mention that it is known that the chiral part of central-force potentials (such as hard-body interactions) vanishes when such correlations are neglected [22,23]. However, dispersion contributions to the chiral interaction do not require nonzero orientational correlations between molecules. As discussed in Appendix A and as has been found by several previous authors [13,14], the long-range dispersion interaction survives this independent rotation procedure to produce an effective chiral potential between effectively uniaxial mesogens of the form

$$E_{IJ}(\mathbf{a}_I,\mathbf{a}_J,\mathbf{R}_{IJ})=(\mathbf{a}_I\times\mathbf{a}_J\cdot\mathbf{R}_{IJ})\kappa_{IJ}, \tag{3}$$

where $\mathbf{R}_{IJ}$ is the displacement of the center of molecule I relative to the center of molecule J and only terms in κ_{IJ} which are odd in both $\mathbf{a}_I$ and $\mathbf{a}_J$ are retained. The effective interaction of Eq. (3) arises between two chiral molecules as well as between a chiral molecule and an achiral one.

Our derivation of the effective chiral interaction differs from previous ones [13,14] in two important respects. First, previous calculations of this interaction are based on a multipole expansion in the variable $\mathbf{r}_i/R_{IJ}$, where $\mathbf{r}_i$ is the coordinate of the ith charge of molecule I relative to the center of molecule I. Strictly speaking, the multipole expansion only applies when $\mathbf{R}_{IJ}\equiv\mathbf{R}$ is large compared to any dimension of the molecules. This expansion does not apply to pairs of molecules whose separation is less than their length but greater than their width. We develop a modified multipole expansion in which coordinates transverse to long molecular axes are treated as small parameters. Second, the results of previous calculations are expressed in terms of electric dipole and quadrupole matrix elements of the entire molecule. But in a long molecule, typical of those comprising liquid crystals, we expect the electronic states to be strongly localized [24]. Accordingly, it seems more useful to express results in terms of matrix elements within atoms or local complexes. In so doing, it is natural to assume the relevant excited state can be reached from the ground state by matrix elements of the dipole moment operator. Then, the quadrupole moment operator is easily related to the dipole moment operator, with the result that the only matrix elements appearing in the present paper are those of the dipole moment operator between local atomic states. In common with previous treatments, we will neglect the effects of biaxial correlations between interacting molecules. Accordingly, we will evaluate κ_{IJ} by averaging each molecule independently over spinning about its long axis. In future [25] we plan to discuss how the chiral interaction between helical molecules depends on the angles describing rotation about their longest body axis.

We may summarize briefly the results of this program. Although we do not expand in powers of the longitudinal coordinates of the charges in each molecule, our results are formally not very different from the previous ones [13,14]. However, by expressing the results in terms of matrix elements of localized atomic orbitals, we identify two distinct physical mechanisms. The first is the dipole-quadrupole interaction previously identified. The second is one involving a three-body interaction between two local atomic dipole moments on one molecule and a local anisotropic polarizability of the second molecule. This second interaction, formally present in previous work, can dominate the first one in certain situations. Furthermore, our approach allows us to discuss how these interactions depend on the length of the mol-

ecule. For a helical molecule we find that the contribution to κ_{IJ} due to the first mechanism is proportional to L^2/R^8 for $L \ll R$ and to L/R^7 for $L \gg R$. Results for the three-body interaction are more complicated [see Eq. (65)]. In both cases, the magnitude of the pitch arising from these interactions in a concentrated system of helical molecules with polarizability corresponding to a dielectric constant of about 1.3 would be 10 μm. This is a larger pitch than one observes for most concentrated cholesterics. It is possible that this discrepancy is due to some of the simplifying assumptions in our calculations, most probably our disregard of biaxial correlations between molecules [25]. Alternatively, it is possible that the pitch of most cholesterics is determined by steric rather than by quantum interactions. Elsewhere we will apply the approach of the present paper to obtain the quantum contributions to K_2 [25].

Briefly, this paper is organized as follows. In Sec. II we give an overview of the calculation of the torque field h from which the macroscopic chiral pitch can be determined. In Sec. III we derive a rather general expression for the strength of the chiral interaction between molecules in terms of matrix elements of the dipole moment operators of atoms between the ground state and excited states localized on atoms. The contribution to this effective chiral interaction from virtual states in which both molecules are excited is treated in Sec. IV and that in which only one molecule is excited is treated in Sec. V. Numerical estimates of the pitch for a system of helical molecules are given which show that the quantum mechanism when both molecules are excited is unlikely to explain the observed pitch of most cholesterics. Our results and conclusions are summarized in Sec. VI.

II. OVERVIEW OF CALCULATION

In this section we give an overview and a summary of the results of the calculation, given in the next section, of the chiral interaction between molecules. Recently [22] a systematic formulation was given that expresses the macroscopic pitch of a CN in terms of microscopic interactions between molecules. Such a formulation is required in cases where it is either necessary or desirable to include orientational correlations between interacting molecules. It was shown that for central-force interactions between atoms on different molecules, a nonzero effective chiral interaction between molecules could only be obtained when orientational correlations, specifically biaxial correlations, between molecules were taken into account. In contrast, in the present paper we will see that the quantum interactions between molecules are not of this type. Thus, in the present context, it is permissible to use a simpler and more traditional approach in which each molecule is characterized by the orientation of its long axis, specified by the unit vector **a**. We will then evaluate the chiral interaction energy between molecules I and J written in Eq. (3). This interaction energy is evaluated within what we will call the ''uniaxial'' approximation in which we independently average over the orientations of the two molecules when **a** is specified for each molecule. In order to calculate the macroscopic chiral pitch it is only necessary to evaluate the chiral part of this interaction, i.e., the part of the form written in Eq. (3). This interaction energy can then be added to whatever phenomenological interaction one is using to describe the nematic phase which would result in the absence of chiral interactions.

To make contact with a continuum theory, one introduces a local order parameter tensor via

$$Q_{\alpha\beta}(\mathbf{r}) = a_\alpha(\mathbf{r}) a_\beta(\mathbf{r}) - \tfrac{1}{3}\delta_{\alpha\beta}. \tag{4}$$

When thermally averaged, this tensor becomes the usual de Gennes–Maier–Saupe order parameter [26,1]. In the long-wavelength limit, the chiral interaction E_{IJ} leads to a continuum interaction of the form

$$E_{\rm int} = \gamma' \int d\mathbf{r} \epsilon_{\alpha\beta\gamma} Q_{\alpha\delta}(\mathbf{r}) \nabla_\beta Q_{\gamma\delta}(\mathbf{r}), \tag{5}$$

where Greek indices label Cartesian components, $\delta_{\alpha\beta}$ is the Kronecker delta, $\epsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor, the repeated-index summation convention is understood, and the constant γ' is the macroscopic analog of κ_{IJ}. If we express $\mathbf{Q}$ in terms of the director $\mathbf{n}(\mathbf{r})$ as

$$\langle Q_{\alpha\beta} \rangle_T = S(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), \tag{6}$$

where $\langle\ \rangle_T$ indicates a thermal average, then the above chiral interaction leads to the familiar Frank free energy in the presence of macroscopic chiral twist (but neglecting splay and bend distortions) as [5]

$$F = \tfrac{1}{2} K_2 \int d\mathbf{r} [\mathbf{n}(\mathbf{r}) \cdot \nabla \times \mathbf{n}(\mathbf{r})]^2 + h \int d\mathbf{r} \mathbf{n}(\mathbf{r}) \cdot \nabla \times \mathbf{n}(\mathbf{r}), \tag{7}$$

where, within mean-field theory, $h = \gamma' S^2$. The main goal of the present paper is to obtain h from a microscopic model. In particular, we will obtain h from an evaluation of κ_{IJ} in Eq. (3). As we have seen in Eqs. (1) and (2), a determination of h leads immediately to the determination of the macroscopic chiral wave vector $\mathbf{Q}$. In addition, the chiral properties of an isotropic liquid consisting of chiral molecules, such as the rotary power, are also related to κ_{IJ}.

The interaction between molecules we are going to study is the generalization, for chiral molecules, of the attractive $1/R^6$ term in the van der Waals potential between neutral spherical atoms. This calculation is based on a quantum mechanical treatment of the total Coulomb interaction $\mathcal{H}_{IJ}$ between charges on the two interacting molecules, I and J:

$$\mathcal{H}_{IJ} = \sum_{i \in I} \sum_{j \in J} \frac{q_i q_j}{R_{ij}}, \tag{8}$$

where $i \in I$ indicates that the sum is over all charges q_i, both electronic and nuclear, in molecule I and R_{ij} is the displacement of q_i relative to q_j. In this calculation we neglect any biaxial correlations between the orientations of the two molecules. Within this assumption it has been shown [22] that central-force interactions [like those of Eq. (8) when taken in first-order perturbation theory] cannot lead to any chiral interactions. Therefore, we consider the effect of $\mathcal{H}_{IJ}$ within second-order perturbation theory. The effective interaction between molecules I and J is then

$$E_{IJ} = E_{IJ}(\hat{\omega}_I, \hat{\omega}_J, \mathbf{R}_{IJ}) = \left\langle 0 \left| \mathcal{H}_{IJ} \frac{\mathcal{P}}{\mathcal{E}} \mathcal{H}_{IJ} \right| 0 \right\rangle, \tag{9}$$

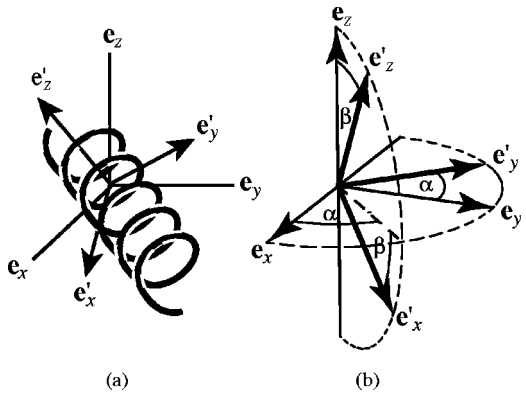

FIG. 1. Left: molecule-fixed coordinate system, defined by the unit vectors $\mathbf{e}'_\mu$. Right: definition of the Euler angles α, β, and γ which take the space-fixed axes $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ into the molecule-fixed axes, $\mathbf{e}'_x$, $\mathbf{e}'_y$, and $\mathbf{e}'_z$. Note that α and β are the usual spherical angles which specify the orientation of the long axis of the molecule, $\mathbf{e}'_z$, with respect to the space-fixed axes. The third Euler angle γ, not shown here, is the angle of rotation about the z' axis which brings the x and y axes in coincidence with the x and y axes fixed in the body (respectively, $\mathbf{e}'_x$ and $\mathbf{e}'_y$).

where $\mathcal{E}=E_0-\mathcal{H}_0$, with E_0 the energy of the ground state $|0\rangle$, $\mathcal{H}_0$ the unperturbed Hamiltonian describing noninteracting molecules, and $\mathcal{P}$ a projection operator that excludes the ground state. Here we have indicated that E_{IJ} depends on $\hat{\omega}_I$ (and $\hat{\omega}_J$) which denotes the triad of Euler angles (see Fig. 1) needed to specify the orientation of the Ith(Jth) molecule and on $\mathbf{R}_{IJ}$. Both $\mathbf{R}_{IJ}$ and $\mathbf{r}_i$, the position of the ith charge in molecule I relative to the center of the molecule, may be expressed with respect to coordinate axes, $\mathbf{e}_\mu$, fixed in space, as shown in Fig. 2:

$$\mathbf{R}_I=R_{I\mu}\mathbf{e}_\mu, \quad \mathbf{r}_i=r_{i\mu}\mathbf{e}_\mu. \tag{10}$$

We now must average this interaction energy over the orientations of the two molecules, when the long axes of molecules I and J are fixed to lie along the unit vectors $\mathbf{a}_I$ and $\mathbf{a}_J$, respectively, and correlations between the orientations of the two molecules are neglected. To carry out this

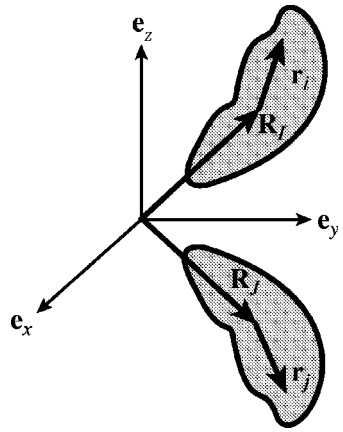

FIG. 2. Space-fixed coordinate system, showing the displacement $\mathbf{R}_I$ of the Ith molecule and the displacement $\mathbf{r}_i$ of the ith charge of the I molecule relative to the center of the molecule.

average we introduce axes specified by unit vectors $\mathbf{e}'_{I\mu}$ emblazoned on the Ith molecule, as shown in Fig. 1, so that

$$\mathbf{r}_i=r'_{i\mu}\mathbf{e}'_{I\mu}. \tag{11}$$

Previously Van der Meer *et al.* [13] carried out this averaging within the multipole expansion. However, since we wish to treat long molecules of the type usually constituting liquid crystals, we do not make the usual multipole expansion, but rather expand only in terms of transverse coordinates of the molecule. Thus we set

$$\mathbf{r}_i=z'_i\mathbf{a}_I+\boldsymbol{\rho}_i, \tag{12}$$

where $\boldsymbol{\rho}_i\cdot\mathbf{a}_I=0$. [Throughout, atom i (j) is assumed to be in molecule I (J).] Thus z'_i and $\boldsymbol{\rho}_i$ are the coordinates of the ith charge of molecule I relative to the center of the molecule, respectively, longitudinal and transverse to the long axis of the molecule aligned along $\mathbf{a}_I=\mathbf{e}'_z$. Now we expand E_{IJ} in powers of $\boldsymbol{\rho}$ and perform the orientational average over powers of $\boldsymbol{\rho}$ (indicated by $[\,]_{\rm av}$) using, e.g.,

$$\begin{aligned}[(\rho_i)_\alpha(\rho_{i'})_\beta]_{\rm av}&=\tfrac{1}{2}(x'_ix'_{i'}+y'_iy'_{i'})(\delta_{\alpha,\beta}-a_\alpha a_\beta)\\&\quad+\tfrac{1}{2}\epsilon_{\alpha\beta\gamma}a_\gamma(x'_iy'_{i'}-y'_ix'_{i'})\\&=\tfrac{1}{2}r'_{i\mu}r'_{i'\mu}(\delta_{\alpha,\beta}-a_\alpha a_\beta)\\&\quad+\tfrac{1}{2}\epsilon_{\mu\nu z}r'_{i\mu}r'_{i'\nu}\epsilon_{\alpha\beta\gamma}a_\gamma,\end{aligned} \tag{13}$$

where μ and ν run over only transverse (x, y) coordinates and $a_\gamma\equiv(\mathbf{a}_I)_\gamma$. Thereby we find that

$$[E_{IJ}]_{\rm av}=(\mathbf{a}_I\times\mathbf{a}_J\cdot\mathbf{R}_{IJ})\kappa_{IJ}(\mathbf{a}_I,\mathbf{a}_J,\mathbf{R}_{IJ})+\cdots. \tag{14}$$

Here we have written the term responsible for the chiral interaction between molecules I and J and have discarded the nonchiral terms (represented by $\cdots$).

The expressions for κ_{IJ} in its most general form are not very enlightening, although they do display the appropriate symmetry to vanish for molecules which are not chiral. To gain some insight into the meaning of these results we have had recourse to a model of the excited states, which appear in second-order perturbation theory. Our first assumption is that the important excited states consist of dipolar fluctuations from the ground state. In other words, these states are taken to be the three atomic p states $|\mu_i\rangle$ on atom i. The second assumption is that δ, the width in energy of the band of excited states obtained by allowing these excitations to occur on any atom, is small compared to their energy E relative to the ground state. This assumption allows us to take the virtual intermediate states to be strictly localized to individual atoms [24]. Nonlocal effects give rise to corrections of relative order, δ/E. Under these assumptions, our results may be summarized as follows. Contributions to κ_{IJ} can be classified into two types, depending on whether one or both molecules in the intermediate state are in an excited state. These are denoted $\kappa_{IJ}^{(1)}$ and $\kappa_{IJ}^{(2)}$, and will be referred to as ''one-molecule'' and ''two-molecule'' terms, respectively. Our results are conveniently written in terms of the definition $\kappa_{IJ}^{(n)}=\frac{1}{2}[\tilde{\kappa}_{IJ}^{(n)}+\tilde{\kappa}_{JI}^{(n)}]_{\mathbf{a}}$, where, for any function f of $\mathbf{a}_I$ and $\mathbf{a}_J$,

$$[f]_{\mathbf{a}}=\tfrac{1}{4}[f(\mathbf{a}_I,\mathbf{a}_J)-f(-\mathbf{a}_I,\mathbf{a}_J)-f(\mathbf{a}_I,-\mathbf{a}_J)+f(-\mathbf{a}_I,-\mathbf{a}_J)]. \tag{15}$$

Then

$$\tilde{\kappa}_{IJ}^{(2)}=\sum_{i\in I,j\in J} M_{ij}S_{ij}, \tag{16}$$

where

$$S_{ij}=[\mathbf{a}_I\cdot\mathbf{a}_J-2(\mathbf{a}_I\cdot\overline{\mathbf{D}}_{ij})(\mathbf{a}_J\cdot\overline{\mathbf{D}}_{ij})/\overline{D}_{ij}^2]\overline{D}_{ij}^{-8}, \tag{17}$$

$$M_{ij}=3e^4\Bigg\{\sum_{\mu,\nu} E_{\nu\mu}(i,j)^{-1}[\overline{y}_j'\langle 0|\Delta z_j'|\mu_j\rangle\langle\mu_j|\Delta x_j'|0\rangle -\overline{x}_j'\langle 0|\Delta z_j'|\mu_j\rangle\langle\mu_j|\Delta y_j'|0\rangle][2\langle 0|\Delta z_i'|\nu_i\rangle^2 -\langle 0|\Delta x_i'|\nu_i\rangle^2-\langle 0|\Delta y_i'|\nu_i\rangle^2]\Bigg\}, \tag{18}$$

where the sums over i and j now run only over electrons, $\overline{\mathbf{r}}_j'$ is the expectation value of $\mathbf{r}_j'$ in the ground state, i.e., it is the center of the atom associated with charge j, $\Delta\mathbf{r}_j'=\mathbf{r}_j'=\overline{\mathbf{r}}_j'$, and

$$\overline{\mathbf{D}}_{ij}=\mathbf{R}_{IJ}+\overline{z}_i'\mathbf{a}_I-\overline{z}_j'\mathbf{a}_J. \tag{19}$$

Also $|\mu_j\rangle$ denotes the state when all atoms are in their ground state except for atom j, which is in the excited p state labeled μ, which has energy $E_\mu(j)$ relative to the ground state and $E_{\nu\mu}(i,j)=E_\nu(i)+E_\mu(j)$. Here $\langle\mu_j|\Delta\mathbf{r}_j|0\rangle$ is nonzero only when j refers to an electronic charge. We also find that

$$\tilde{\kappa}_{IJ}^{(1)}=3\sum_{ii'j}[p_{ix}'p_{i'y}'-p_{i'x}'p_{iy}']\frac{(\overline{\mathbf{D}}_{i'j}\cdot\mathbf{a}_J)}{\overline{D}_{ij}^3\overline{D}_{i'j}^5}e^2\sum_\mu E_\mu(j)^{-1} \times[2\langle\mu_j|\Delta z_j'|0\rangle^2-\langle\mu_j|\Delta x_j'|0\rangle^2-\langle\mu_j|\Delta y_j'|0\rangle^2], \tag{20}$$

where the sums over i and i' are over atoms and $\mathbf{p}_\alpha'$ is the α component of the dipole moment vector in the ground state evaluated in the molecule-fixed coordinate system. (For this calculation a local dipole moment was assumed, but this does not necessarily imply the existence of a dipole moment of the molecule as a whole.) Note that the above expressions, since they have already been averaged over rotations about the long axis, are invariant with respect to rotation of each molecule about its long axes parallel to $\mathbf{e}_z'$.

Our result for $\kappa_{IJ}^{(2)}$ is closely related to that previously obtained by Van der Meer *et al.* [13] and by Kats [14]. To obtain a form close to that obtained by Kats, we write

$$M_{ij}=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\sigma'(j;\omega+i0^+)\gamma'(i;-\omega+i0^+)d\omega, \tag{21}$$

where

$$\sigma'(j;\omega)=e^2\sum_\mu(\langle 0|y_j'z_j'|\mu_j\rangle\langle\mu_j|x_j'|0\rangle-\langle 0|x_j'z_j'|\mu_j\rangle \times\langle\mu_j|y_j'|0\rangle)/[\omega-E_\mu(j)], \tag{22}$$

$$\gamma'(i;\omega)=e^2\sum_\nu(2\langle 0|z_i'|\nu_j\rangle^2-\langle 0|x_i'|\nu_j\rangle^2-\langle 0|y_i'|\nu_j\rangle^2)/ \times[\omega-E_\nu(i)] =\alpha_{zz}'(i;\omega)-\tfrac{1}{2}\alpha_{xx}'(i;\omega)-\tfrac{1}{2}\alpha_{yy}'(i,\omega), \tag{23}$$

where $\alpha_{\mu\nu}'$ is the μ-ν component of the polarizability tensor with respect to the molecular frame. Here $\gamma'(\omega)$ is the anisotropy of the polarizability and $\sigma'(\omega)$ is the higher-order quadrupole-dipole response function (which Kats calls the gyrotropy), both taken in the molecular frame, as indicated by prime superscripts. Here these quantities are given by a sum over the corresponding properties for the individual atoms. We assume that the relevant excited states are localized p states, in which case the gyrotropy can be related to the polarizability:

$$\sigma'(j;\omega)=e^2\sum_\mu(\overline{y}_j'\langle 0|z_j'|\mu_j\rangle\langle\mu_j|x_j'|0\rangle-\overline{x}_j'\langle 0|z_j'|\mu_j\rangle \times\langle\mu_j|y_j'|0\rangle)/[\omega-E_\mu(j)] =\tfrac{1}{2}\overline{y}_j'\alpha_{zx}(j;\omega)-\tfrac{1}{2}\overline{x}_j'\alpha_{yz}(j;\omega). \tag{24}$$

In addition the factor S_{ij} depends on the z' component of the position of the ith atom, whereas in the bare multipole expansion used by Van der Meer *et al.* and Kats, only $\mathbf{R}_{IJ}$ appears. Because we do not include the z' coordinate within the multipole approximation, we can treat long molecules in an appropriate way, as is reflected in the sum over atoms of S_{ij}. One sees that the chirality of the molecule is incorporated in σ', which vanishes if the molecule has a mirror plane [27]. In $\tilde{\kappa}_{IJ}^{(1)}$, the chirality of the molecule I is incorporated in terms like

$$\tau'\equiv\sum_{ii'}[p_{ix}'p_{i'y}'-p_{i'x}'p_{iy}'][\overline{z}_i'-\overline{z}_{i'}']. \tag{25}$$

In the case of classical interactions, it was not possible to construct a third rank tensor of the mass moments which was zero for achiral molecules and nonzero for chiral molecules [22], because such a mass moment tensor was symmetric under interchange of any pair of its three indices. Here, however, one sees that σ' and τ' are x,y,z elements of tensors that are not symmetric in all indices and that, therefore, can be used as an indicator of chirality.

It is interesting to evaluate these expressions for some specific geometry of a chiral molecule. For this purpose we treat in some detail a helical molecule, patterned after DNA. Then we introduce local atomic coordinates whose axes coincide with the axes defined by the local excited p states. We assume that these axes, shown in Fig. 3, are identical to those of the tangent, the normal, and the binormal unit vectors,

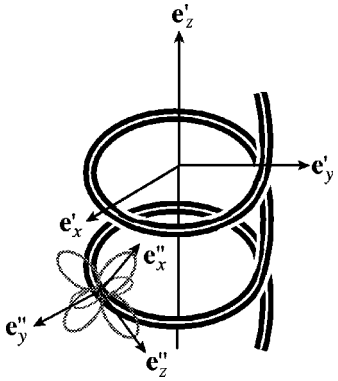

FIG. 3. Local atomic coordinate system, defined by the unit vectors $\mathbf{e}''_\mu$, showing that the local excited p states define the orientation of the local axes. Here $\mathbf{e}''_z$ is the unit vector tangent to the helix, the unit normal $\mathbf{e}''_x$ lies along the radius of curvature, and the binormal unit vector $\mathbf{e}''_y$ is the third member of the triad of mutually perpendicular unit vectors.

which we call $\mathbf{e}''_\mu$, with μ, respectively, z, x, and y, so that we can relate the $\alpha'_{\mu,\nu}$ to its components $\alpha''_{\mu,\mu}$ in the local atomic frame as

$$\alpha'_{\gamma\delta}(j)=2e^2\sum_\mu E_\mu(j)^{-1}\langle\mu_j|r''_{j\mu}|0\rangle^2(\mathbf{e}''_{j\mu}\cdot\mathbf{e}'_\gamma)(\mathbf{e}''_{j\mu}\cdot\mathbf{e}'_\delta)$$
$$=(\mathbf{e}''_{j\mu}\cdot\mathbf{e}'_\gamma)(\mathbf{e}''_{j\mu}\cdot\mathbf{e}'_\delta)\alpha''_{\mu\mu}(j). \quad (26)$$

One should note the following general points in connection with our results. First, the result in Eq. (16) shows that $\kappa_{IJ}^{(2)}$ can be viewed as arising from a superposition of interactions between local centers of chirality on one molecule with centers of anisotropic polarizability on another molecule. As is well known [13], this result implies that chirality can be induced by the interaction between a chiral molecule and an achiral one that has a local center of anisotropic polarizability. In contrast, the result in Eq. (20) is a three-body interaction between two local dipoles on one molecule (combined with resulting chiral strength τ') with a local anisotropic polarizability of the second molecule. Finally, we mention that it is interesting to generalize these results to a flexible polymer the orientation of whose backbone may vary appreciably over its length.

III. CHIRALITY FROM INTERMOLECULAR INTERACTIONS

We now turn to the calculation of κ_{IJ}. For this purpose we give a brief discussion of how the average over orientations is to be done. In general, the orientation of the Ith molecule is specified by the three Euler angles α_I,β_I, and γ_I, for which we adopt the definition of Rose [28], as is illustrated in Fig. 1. In particular, α_I and β_I are taken to specify the orientation of the long axis of the molecule. So we write

$$\mathbf{a}_I=\sin\beta_I\cos\alpha_I\mathbf{e}_x+\sin\beta_I\sin\alpha_I\mathbf{e}_y+\cos\beta_I\mathbf{e}_z. \quad (27)$$

Within the spirit of mean-field theory we should average the interaction energy between molecules I and J over the single-molecule orientational distribution function appropriate to a nematic, which locally is a good description of the CN. For molecule I this average should be taken subject to its long axis being specified by the fixed value of $\mathbf{a}_I$. The single-molecule orientation distribution function $\rho(\hat{\omega}_I)$ must be independent of α_I and also should be invariant under $\mathbf{a}\rightarrow-\mathbf{a}$. Specifically, correlations between β_I and γ_I are allowed [29], as is discussed in Appendix B. For any function of molecular orientation $f(\hat{\omega})$ this average is

$$[f(\hat{\omega})]_{\rm av}=\frac{1}{2\pi}\int\rho(\hat{\omega}_I)f(\hat{\omega}_I)d\gamma_I d\alpha_I\Big/\int\rho(\hat{\omega}_I)d\gamma_I. \quad (28)$$

However, when the molecule is not strongly biaxial, or when the molecule is perfectly aligned along the nematic direction, the assumption that $\rho(\hat{\omega})$ is independent of γ_I, as is usually done [13,14], is sufficient. This approximation, which we call the uniaxial approximation, will be used in this paper. In addition, to preserve invariance under $\mathbf{a}_I\rightarrow-\mathbf{a}_I$, we will also project out of the calculation terms in κ_{IJ} that are even in $\mathbf{a}_I$ and in $\mathbf{a}_J$. This step can be done at the end of the calculation using Eq. (15).

Our calculation of κ_{IJ}, like previous ones [13,14], is analogous to that of the well-known R^{-6} interactions between widely separated neutral atoms. Quantum fluctuations involving dipole moments in excited states are treated within second-order perturbation theory. Short-range quantum repulsion is often treated in an *ad hoc* fashion via a classical central-force interaction between atoms but this effect will not be discussed here. We take the interaction Hamiltonian $\mathcal{H}_{IJ}$ for molecules I and J to arise from the Coulomb interaction between the ith charge on molecule I, denoted q_i, and its counterpart on molecule J. Thus we write

$$\mathcal{H}_{IJ}=\sum_{i\in I}\sum_{j\in J}\frac{q_iq_j}{|\mathbf{R}_{IJ}+\mathbf{r}_i-\mathbf{r}_j|}. \quad (29)$$

We use Eq. (12) to write

$$\mathcal{H}_{IJ}=\sum_{i\in I}\sum_{j\in J}\frac{q_iq_j}{D_{ij}}\left[1+\frac{2}{D_{ij}^2}\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}+\frac{1}{D_{ij}^2}\boldsymbol{\rho}_{ij}^2\right]^{-1/2}, \quad (30)$$

where $\boldsymbol{\rho}_{ij}=\boldsymbol{\rho}_i-\boldsymbol{\rho}_j$ and

$$\mathbf{D}_{ij}=\mathbf{R}_{IJ}+z'_i\mathbf{a}_I-z'_j\mathbf{a}_J. \quad (31)$$

Note that $\mathbf{D}_{ij}$ is evaluated for $\boldsymbol{\rho}_i=\boldsymbol{\rho}_j=0$.

We now expand with respect to transverse coordinates to obtain

$$\mathcal{H}_{IJ}=\sum_{i\in I,j\in J}\frac{q_iq_j}{D_{ij}}\left[1-\frac{1}{D_{ij}^2}\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}-\frac{\boldsymbol{\rho}_{ij}^2}{2D_{ij}^2}+\frac{3[\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}]^2}{2D_{ij}^4}\right.$$
$$-\frac{5[\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}]^3}{2D_{ij}^6}+\frac{3[\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}]}{2D_{ij}^4}\boldsymbol{\rho}_{ij}^2+\frac{3\boldsymbol{\rho}_{ij}^4}{8D_{ij}^4}$$
$$\left.-\frac{15}{4}\frac{[\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}]^2}{D_{ij}^6}\boldsymbol{\rho}_{ij}^2+\frac{35}{8}\frac{[\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}]^4}{D_{ij}^8}+O\left(\frac{1}{D_{ij}^5}\right)\right]. \quad (32)$$

Note that this expansion is valid if the charge distributions of the two molecules do not overlap one another. Strictly speaking, the validity of our treatment requires satisfying this condition for all configurations with nonnegligible weight in the partition function.

We now consider an evaluation of the interaction energy between two molecules treating $\mathcal{H}_{IJ}$ via perturbation theory. The first term is the ground-state expectation value of the Coulomb interaction between atoms on different molecules. If we neglect biaxial correlations between orientations of adjacent molecules and we simply average this interaction over the uncorrelated rotations of the two molecules, subject to their long axes being fixed, then we find the resulting interaction to be completely achiral [22]. Accordingly, to obtain an effective chiral interaction from $\mathcal{H}_{IJ}$ when such biaxial correlations are neglected, it is necessary to evaluate the energy of interaction within second-order perturbation theory, whereby

$$E_{IJ}=-\sum_{n_I,n_J}{}' \frac{|(\mathcal{H}_{IJ})_{n_I,n_J;0,0}|^2}{E_{n_In_J}}, \tag{33}$$

where the sums are over states $|n_I\rangle(|n_J\rangle)$ of molecule I (J) and the prime indicates exclusion of the term when both molecules are in their ground state. Here $E_{n_In_J}$ is the energy (relative to the ground state) of the state when molecules I and J are in states $|n_I\rangle$ and $|n_J\rangle$, respectively.

The obvious step of substituting the expansion of Eq. (32) into Eq. (33) leads to rather complicated algebra. We now classify terms according to their order in R_{IJ}^{-1}. Since we do not assume the length L of the molecules to be much less than the separation R_{IJ} between molecules, in counting powers of R_{IJ} we consider $L/R_{IJ}\sim 1$. As we shall see, $E_{IJ}\sim R_{IJ}^{-p}$ [30], where $p=7$ for two-molecule terms and $p=6$ for one-molecule terms. Accordingly, we drop all contributions which are of order R_{IJ}^{-p} with $p>7$. Also, we drop contributions which are proportional to odd powers of $\boldsymbol{\rho}$, since these will vanish when we average over rotation about the long axis of the molecules. Thereby we obtain

$$\begin{aligned}[E_{IJ}]_{\rm av}&=-\left[\sum_{n_I,n_J}{}' \frac{|(\mathcal{H}_{IJ})_{n_In_J;00}|^2}{E_{n_In_J}}\right]_{\rm av}\\ &=-\sum_{i,i'\in I}\sum_{j,j'\in J}\sum_{n_I,n_J}{}' [\mathcal{E}_{ij;i'j';n}]_{\rm av}\frac{q_iq_{i'}q_jq_{j'}}{E_{n_In_J}},\end{aligned} \tag{34}$$

where n is shorthand for n_I,n_J and

$$\begin{aligned}\mathcal{E}_{ij;i'j';n}=&\left[\frac{1}{D_{ij}}\right]_{0n}\left[\frac{1}{D_{i'j'}}\right]_{n0}-\left[\frac{\boldsymbol{\rho}_{ij}^2}{D_{ij}^3}\right]_{0n}\left[\frac{1}{D_{i'j'}}\right]_{n0}+\left[\frac{3(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij})^2}{D_{ij}^5}\right]_{0n}\left[\frac{1}{D_{i'j'}}\right]_{n0}+\frac{1}{4}\left[\frac{\rho_{ij}^2}{D_{ij}^3}\right]_{0n}\left[\frac{\rho_{i'j'}^2}{D_{i'j'}^3}\right]_{n0}\\ &+\left[\frac{\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}}{D_{ij}^3}\right]_{0n}\left[\frac{\boldsymbol{\rho}_{i'j'}\cdot\mathbf{D}_{i'j'}}{D_{i'j'}^3}\right]_{n0}-\frac{3}{2}\left[\frac{(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij})^2}{D_{ij}^5}\right]_{n0}\left[\frac{\boldsymbol{\rho}_{i'j'}^2}{D_{i'j'}^3}\right]_{0n}+\frac{9}{4}\left[\frac{(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij})^2}{D_{ij}^5}\right]_{n0}\left[\frac{(\boldsymbol{\rho}_{i'j'}\cdot\mathbf{D}_{i'j'})^2}{D_{i'j'}^5}\right]_{0n}\\ &-3\left[\frac{(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij})\boldsymbol{\rho}_{ij}^2}{D_{ij}^5}\right]_{n0}\left[\frac{\boldsymbol{\rho}_{i'j'}\cdot\mathbf{D}_{i'j'}}{D_{i'j'}^3}\right]_{0n}+5\left[\frac{\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij}}{D_{ij}^3}\right]_{n0}\left[\frac{(\boldsymbol{\rho}_{i'j'}\cdot\mathbf{D}_{i'j'})^3}{D_{i'j'}^7}\right]_{0n}\\ &+\left[\frac{3\boldsymbol{\rho}_{ij}^4}{4D_{ij}^5}-\frac{15\boldsymbol{\rho}_{ij}^2}{2D_{ij}^7}(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij})^2+\frac{35(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}_{ij})^4}{4D_{ij}^9}\right]_{n,0}\left[\frac{1}{D_{i'j'}}\right]_{0,n}.\end{aligned} \tag{35}$$

When one averages over independent rotations of the two molecules about their long axes, using Eq. (13), one sees that the first two lines of Eq. (35) do not lead to a chiral interaction.

We imagine the virtual states $\{n\}$ in Eq. (35) to be a linear combination of excited atomic p states. Accordingly, all matrix elements can be chosen to be real. Also, in this model we take no explicit account of exchange and correlation effects beyond what is included in self-consistent atomic orbitals. Thus, it is permissible to label electrons according to their atomic location. Then, for the matrix element of an arbitrary function f of $\mathbf{r}_i$ we can write

$$\begin{aligned}\langle n_i|f(\mathbf{r}_i)|0\rangle=&\boldsymbol{\nabla}'_\alpha f(\mathbf{r})|_{\mathbf{r}_i=\overline{\mathbf{r}}}\langle n_i|\Delta r'_{i\alpha}|0\rangle\\ &+O(\langle n_i|\Delta\mathbf{r}'_{i\alpha}\Delta\mathbf{r}'_{i\beta}|0\rangle),\end{aligned} \tag{36}$$

where $\Delta\mathbf{r}_i=\mathbf{r}_i-\langle 0|\mathbf{r}_i|0\rangle\equiv\mathbf{r}_i-\overline{\mathbf{r}}_i$. To leading order in $1/R_{IJ}$ we have

$$\begin{aligned}\langle n_i|D_{ij}^{-1}|0\rangle&=-\langle n_i|\Delta z'_i|0\rangle(\mathbf{a}_I\cdot\overline{\mathbf{D}}_{ij})\overline{D}_{ij}^{-3},\\ \langle n_in_j|D_{ij}^{-1}|0\rangle&=-\langle n_in_j|\Delta z'_i\Delta z'_j|0_i0_j\rangle[3(\mathbf{a}_I\cdot\overline{\mathbf{D}}_{ij})(\mathbf{a}_J\cdot\overline{\mathbf{D}}_{ij})\\ &\quad-\mathbf{a}_I\cdot\mathbf{a}_J\overline{D}_{ij}^2]\overline{D}_{ij}^{-5},\end{aligned} \tag{37}$$

where $|n_in_j\rangle$ is the state (whose energy relative to the ground state is $E_{n_in_j}$) in which atom i is in excited state $|n_i\rangle$, atom j is in state $|n_j\rangle$, and all other atoms are in their ground state and $\overline{\mathbf{D}}_{ij}$ was defined in Eq. (19). Thus $[D_{ij}^{-1}]_{0,n}$ is of order at least R_{IJ}^{-2} for single-molecule terms and of order at least R_{IJ}^{-3} for two-molecule terms. This argument shows that the last

line of Eq. (35) does not contribute at leading order in $1/R_{IJ}$ and that we have only to deal with the second and third lines of this equation.

We now carry out the average over the orientations of molecules I and J subject to their long axes being fixed to be, respectively, along $\mathbf{a}_I$ and $\mathbf{a}_J$, using Eq. (13) and we keep only chiral terms of the form written in Eq. (3). This procedure is algebraically extremely complicated. However, the fact that the relevant excited states are undoubtedly strongly localized leads to drastic simplifications. Accordingly, we will evaluate Eq. (35) within a model in which each molecule has a narrow band of excited states. If we set $\kappa_{IJ} = \frac{1}{2}[\tilde{\kappa}_{IJ} + \tilde{\kappa}_{JI}]$, then the chiral terms which arise from performing the orientational average (see Appendix C) lead to the result

$$\begin{aligned}\tilde{\kappa}_{IJ} = \sum_{i,i',j,j'} \sum_{n}{}' \frac{q_i q_j q_{i'} q_{j'}}{E_{n_I n_J}} \Bigg\{ 2\Bigg[\left(\frac{y_i'}{D^3}\right)_{n0} \left(\frac{x_{i'}' z_{j'}'}{D'^3}\right)_{0n} \\ - \left(\frac{x_i'}{D^3}\right)_{n0} \left(\frac{y_{i'}' z_{j'}'}{D'^3}\right)_{0n} \Bigg] \\ - 3\Bigg[\left(\frac{x_i' x_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{x_{i'}' y_{j'}'}{D'^3}\right)_{0n} \\ - \left(\frac{x_i' y_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{x_{i'}' x_{j'}'}{D'^3}\right)_{0n} \\ + \left(\frac{y_i' x_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{y_{i'}' y_{j'}'}{D'^3}\right)_{0n} \\ - \left(\frac{y_i' y_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{y_{i'}' x_{j'}'}{D'^3}\right)_{0n} \Bigg] \Bigg\} + \cdots, \end{aligned} \tag{38}$$

where now n is shorthand for n_i, n_j, $\mathbf{D} \equiv \mathbf{D}_{ij}$, $\mathbf{D}' \equiv \mathbf{D}_{i'j'}$, and the dots represent terms we dropped which do not contribute within the approximation we invoke in which the relevant excited states are strictly localized. (However, our results can be generalized to allow the excited states to extend over a small complex of atoms, if one simply lets the indices label electrons in complexes rather than those on atoms.) For localized excited states, all matrix elements are diagonal in their site indices. Nonlocal corrections to our results will be small in the parameter t/E, where t is a hopping matrix element which sets the scale of the width of the band of excited states and E is a typical energy of the excited states relative to the ground state [24]. However, it is important to check that these nonlocal corrections are not proportional to a lower power of $1/R_{IJ}$ than the local ones we keep. An analysis of the relative importance of nonlocal terms is given in Appendix D, where we show explicitly (albeit only for typical terms when both molecules are excited in the virtual state) that nonlocal contributions to the chiral interaction occur at the same order in $1/R_{IJ}$ as do the local ones, but they are smaller by a factor of order t/E. This result justifies our subsequent neglect of nonlocal effects.

If both molecules are in excited states in the virtual state "n," we may set $i = i'$ and $j = j'$. If only one molecule, say the Ith one, is excited in the virtual state, then j and j' may be different. We will consider these two cases in the next two sections.

IV. TWO-MOLECULE TERMS

In this section we carry the sum in Eq. (38) over excited states $|i,n;j,m\rangle$, in which molecule I is in state $|i_n\rangle$ with its ith atom excited to its nth state and molecule J is in state $|j_m\rangle$ with its jth atom excited to its mth state. Because we are dealing with localized states, these virtual states are obtained from the ground state only by interactions involving electronic charges on atoms i of molecule I and j of molecule J. Thus we no longer need consider here the presence of positive nuclear charges. Neglecting contributions of relative order (t/E) (as discussed in Appendix D), we may set $i = i'$ and $j = j'$ in Eq. (38), so that the contribution from virtual states in which both molecules are excited, indicated by the superscript (2), is

$$\begin{aligned}\tilde{\kappa}_{IJ}^{(2)} = \sum_{ij} \sum_{n}{}' \frac{e^4}{E_{n_I n_J}} \Bigg\{ 2\Bigg[\left(\frac{y_i'}{D^3}\right)_{0n} \left(\frac{x_i' z_j'}{D^3}\right)_{n0} \\ - \left(\frac{x_i'}{D^3}\right)_{n0} \left(\frac{y_i' z_j'}{D^3}\right)_{0n} \Bigg] - 3\Bigg[\left(\frac{x_i' x_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{x_i' y_j'}{D^3}\right)_{0n} \\ - \left(\frac{x_i' y_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{x_i' x_j'}{D^3}\right)_{0n} \\ + \left(\frac{y_i' x_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{y_i' y_j'}{D^3}\right)_{0n} \\ - \left(\frac{y_i' y_j' (\mathbf{D}\cdot\mathbf{a}_I)}{D^5}\right)_{n0} \left(\frac{y_i' x_j'}{D^3}\right)_{0n} \Bigg] \Bigg\}. \end{aligned} \tag{39}$$

We now evaluate this expression using the procedure of Eq. (36). To illustrate the calculation for the first two terms of Eq. (39) we write

$$\begin{aligned} T_1 &\equiv (y_i' D^{-3})_{0n} [x_i' (\overline{z_j'} + \Delta z_j') D^{-3}]_{n0} \\ &\quad - (x_i' D^{-3})_{0n} [y_i' (\overline{z_j'} + \Delta z_j') D^{-3}]_{n0} \\ &= (y_i' D^{-3})_{0n} [x_i' (\Delta z_j') D^{-3}]_{n0} \\ &\quad - (x_i' D^{-3})_{0n} [y_i' (\Delta z_j') D^{-3}]_{n0}. \end{aligned} \tag{40}$$

Expanding the other matrix elements in accord with Eq. (36) and recalling that both molecules are excited in the virtual state, we obtain

$$\begin{aligned} (y_i' D^{-3})_{0n} &= (\Delta \mathbf{r}_{i\alpha}' \Delta z_j')_{0n} \boldsymbol{\nabla}_{i\alpha}' \boldsymbol{\nabla}_{jz}' (\overline{y_i'} \overline{D}^{-3}) \\ &= (\Delta y_i' \Delta z_j')_{0n} \boldsymbol{\nabla}_{jz}' \overline{D}^{-3} \\ &\quad + (\Delta z_i' \Delta z_j')_{0n} \overline{y_i'} [\boldsymbol{\nabla}_{iz}' \boldsymbol{\nabla}_{jz}' \overline{D}^{-3}]. \end{aligned} \tag{41a}$$

Here we have dropped matrix elements like $(\Delta r'_{i\alpha}\Delta r'_{i\beta})_{0n}$ which involve higher than dipole excitations and would therefore vanish for the p symmetry we have assumed for the low-lying excited states. In any event, since $\Delta\mathbf{r}\sim a_0$, the Bohr radius, this term would be smaller than those we keep by a factor of order (a_0/R). To write the second line, one notes that D depends on $\mathbf{r}'_i$ and $\mathbf{r}'_j$ only through z'_i and z'_j. Similar relations hold for the other terms in T_1, e.g.,

$$(x'_i\Delta z'_j D^{-3})_{n0}=(\Delta x'_i\Delta z'_j)_{n0}\overline{D^{-3}}+\overline{x'_i}(\Delta z'_i\Delta z'_j)_{n0}\boldsymbol{\nabla}'_{iz}\overline{D^{-3}}, \tag{41b}$$

$$(x'_i D^{-3})_{0n}=(\Delta x'_i\Delta z'_j)_{0n}\boldsymbol{\nabla}'_{jz}\overline{D^{-3}} +\overline{x'_i}(\Delta z'_i\Delta z'_j)_{0n}\boldsymbol{\nabla}'_{iz}\boldsymbol{\nabla}'_{jz}\overline{D^{-3}}, \tag{41c}$$

$$(y'_i\Delta z'_j D^{-3})_{n0}=(\Delta y'_i\Delta z'_j)_{n0}\overline{D^{-3}}+\overline{y'_i}(\Delta z'_i\Delta z'_j)_{n0}\boldsymbol{\nabla}'_{iz}\overline{D^{-3}}. \tag{41d}$$

Thereby for the first two terms of Eq. (39) we obtain

$$\begin{aligned}T_1=&[\overline{x'_i}(\Delta y'_i\Delta z'_j)_{0n}(\Delta z'_i\Delta z'_j)_{n0}\\&-\overline{y'_i}(\Delta x'_i\Delta z'_j)_{0n}(\Delta z'_i\Delta z'_j)_{n0}]\\&\times[(\boldsymbol{\nabla}'_{zi}\overline{D^{-3}})(\boldsymbol{\nabla}'_{zj}\overline{D^{-3}})-\overline{D^{-3}}(\boldsymbol{\nabla}'_{zi}\boldsymbol{\nabla}'_{zj}\overline{D^{-3}})].\end{aligned} \tag{42}$$

Treating the other terms in Eq. (39) similarly, we obtain

$$\begin{aligned}\tilde{\kappa}^{(2)}_{IJ}=3\sum_{i,j}\,&(e^4/\overline{D^8_{ij}})[\mathbf{a}_I\cdot\mathbf{a}_J-2(\mathbf{a}_I\cdot\overline{\mathbf{D}}_{ij})(\mathbf{a}_J\cdot\overline{\mathbf{D}}_{ij})/\overline{D^2_{ij}}]\\&\times\Bigg\{\sum_{\mu,\nu}E_{\nu\mu}(i,j)^{-1}[\overline{y'_j}\langle 0_j|\Delta z'_j|\mu_j\rangle\langle\mu_j|\Delta x'_j|0\rangle\\&-\overline{x'_j}\langle 0|\Delta z'_j|\mu_j\rangle\langle\mu_j|\Delta y'_j|0\rangle][2\langle 0|\Delta z'_i|\nu_i\rangle^2\\&-\langle 0|\Delta x'_i|\nu_i\rangle^2-\langle 0|\Delta y'_i|\nu_i\rangle^2]\Bigg\},\end{aligned} \tag{43}$$

where μ and ν range over the labels x, y, and z of the local atomic excited p states and $E_{\nu\mu}(i,j)$ is the energy of the virtual state relative to the ground state. (In principle, this energy can depend on the positions of the excited atoms. However, in our simplified treatment we will neglect such dependence.) In addition note that the expression given above for $\tilde{\kappa}^{(2)}_{IJ}$ must be averaged with respect to up and down directions of Ith and Jth molecules, as in Eq. (15). If the excited states have a degeneracy with respect to spin, then the sum over μ and ν should be extended to include a sum over spin indices. However, since singlet-triplet transitions are nearly forbidden, the multiplicity due to spin does not affect our results. Thus we obtain the result written in Eq. (16).

As discussed in the preceding section, our result is similar to that given by Van der Meer *et al.* [13] and Kats [14]. The important new aspect of Eq. (43) is that $\kappa^{(2)}_{IJ}$ is expressed as a sum of contributions from pairs of atoms, one on each molecule. This formulation is consistent with the concept of local chiral centers [31]. For $L\ll R$ our expression for $\kappa^{(2)}_{IJ}$ based on Eq. (43), when written in the form of Eq. (16), reduces to that of Van der Meer *et al.* [13] and Kats [14] when M_{ij} does not depend on i and j. However, when L is not much less than R, the fact that S_{ij} involves an average over distances between atoms (rather than simply the distance between the centers of mass of the two molecules), leads to very different results. In any case, it is important to realize that M_{ij} should be evaluated with respect to localized states, as is done here.

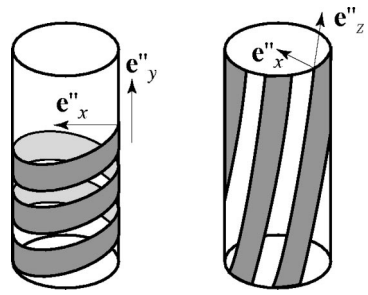

FIG. 4. Locally defined principal axes for weakly chiral molecules with large q (left) and small q (right). Note that the axis nearly collinear with the long axis of the molecule is the y axis for large q and the z axis for small q. In Eqs. (48a) and (48b) the anisotropy of the polarizability needed is with respect to the long axis of the molecule.

A. Helical molecule

In this subsection we give a concrete evaluation of the above expression for two identical helical molecules. In the above formulas, position operators are given in the coordinate system fixed in the molecule while matrix elements are taken with respect to atomic p states which are referred to the principal axes locally defined for each atom of a molecule. Let us introduce the parametric representation of coordinates of an atom on a helical molecule:

$$z'=s,\quad x'=a\cos(qs),\quad y'=a\sin(qs), \tag{44}$$

where q, the chiral wave vector of the helix, is defined so that a right-handed molecule [32] has q positive. The locally defined principal axes for the ith atom at $z'=s$ are chosen in the following way (see Fig. 3):

$$\begin{aligned}\mathbf{e}''_{ix}&=\cos(qs)\mathbf{e}'_x+\sin(qs)\mathbf{e}'_y,\\ \mathbf{e}''_{iy}&=c[-\sin(qs)\mathbf{e}'_x+\cos(qs)\mathbf{e}'_y-aq\mathbf{e}'_z],\\ \mathbf{e}''_{iz}&=c[-aq\sin(qs)\mathbf{e}'_x+aq\cos(qs)\mathbf{e}'_y+\mathbf{e}'_z],\end{aligned} \tag{45}$$

where $c^2=[1+(aq)^2)]^{-1}$. Here $\mathbf{e}''_{iz}$ is the tangent vector to the helix at $z'=s$, $\mathbf{e}''_{ix}$ is a unit vector along the radius of curvature at $z'=s$, and $\mathbf{e}''_{iy}$ is the unit vector along the binormal or the third orthogonal direction [33]. We assume that the principal axes for excited p states coincide with these principal geometric directions. If we write $\mathbf{e}''_{i\mu}=\mathcal{O}_{i;\mu\nu}\mathbf{e}'_{i\nu}$, then the inverse transformation is $\mathbf{e}'_{i\nu}=\mathcal{O}_{i;\mu\nu}\mathbf{e}''_{i\mu}$.

Note that the local axes are defined so that the matrix elements in Eq. (43) are

$$\langle\mu_i|\Delta\mathbf{r}'_\nu|0\rangle=\mathcal{O}_{i;\rho\nu}\langle\mu_i|\Delta\mathbf{r}''_\rho|0\rangle, \tag{46}$$

where $\langle \mu_i|\Delta \mathbf{r}_\rho''|0\rangle$ is nonzero only if $\rho=\mu$. Thus, in terms of local atomic coordinates we may evaluate Eq. (18) to obtain

$$\begin{aligned}M_{ij}=&3e^4c^2a^2q[\langle x_i|\Delta x_i''|0\rangle^2(\langle z_j|\Delta z_j''|0\rangle^2/E_{xz}\\&-\langle y_j|\Delta y_j''|0\rangle^2/E_{xy})+c^2[1-2a^2q^2]\\&\times\langle y_i|\Delta y_i''|0\rangle^2(\langle z_j|\Delta z_j''|0\rangle^2/E_{yz}-\langle y_j|\Delta y_j''|0\rangle^2/E_{yy})\\&+c^2[2-a^2q^2]\langle z_i|\Delta z_i''|0\rangle^2(\langle y_j|\Delta y_j''|0\rangle^2/E_{zy}\\&-\langle z_j|\Delta z_j''|0\rangle^2/E_{zz})].\end{aligned}\tag{47}$$

This quantity cannot depend on the locations of sites i and j because it is invariant against rotation about the long axis of the molecule and all locations on the helix are equivalent once end effects are neglected. Thus, neglecting end effects, we obtain the limiting results,

$$M_{ij}\equiv M\approx\begin{cases}6e^4a^2q\left[\left\langle y|\Delta y''|0\right\rangle^2\left(\dfrac{\langle z|\Delta z''|0\rangle^2}{E_{zy}}-\dfrac{\langle x|\Delta x''|0\rangle^2}{2E_{xy}}-\dfrac{\langle y|\Delta y''|0\rangle^2}{2E_{yy}}\right)\right.\\\left.-\langle z|\Delta z''|0\rangle^2\left(\dfrac{\langle z|\Delta z''|0\rangle^2}{E_{zz}}-\dfrac{\langle x|\Delta x''|0\rangle^2}{2E_{xz}}-\dfrac{\langle y|\Delta y''|0\rangle^2}{2E_{yz}}\right)\right], & (aq)^2\ll 1,\quad (48a)\\6\dfrac{e^4}{q}\left[\langle y|\Delta y''|0\rangle^2\left(\dfrac{\langle y|\Delta y''|0\rangle^2}{E_{yy}}-\dfrac{\langle x|\Delta x''|0\rangle^2}{2E_{xy}}-\dfrac{\langle z|\Delta z''|0\rangle^2}{2E_{zy}}\right)\right.\\\left.-\langle z|\Delta z''|0\rangle^2\left(\dfrac{\langle y|\Delta y''|0\rangle^2}{E_{yz}}-\dfrac{\langle x|\Delta x''|0\rangle^2}{2E_{xz}}-\dfrac{\langle z|\Delta z''|0\rangle^2}{2E_{zz}}\right)\right], & (aq)^2\gg 1.\quad (48b)\end{cases}$$

In both limits, the molecule is only weakly chiral, as we illustrate in Fig. 4. (To measure chiral strength the criterion of Ref. [22] may be invoked.)

Now let us consider $\kappa_{IJ}^{(2)}$ as a function of the molecular length L. For simplicity we assume that the molecules are aligned exactly along their local nematic directions. Also we simplify the calculation by considering only the case when $\mathbf{R}_{IJ}$ is perpendicular to $\mathbf{a}_I$. Thus we will set

$$\mathbf{a}_I\cdot\mathbf{a}_J=1,\quad (\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I)(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_J)=(\overline{z_j}-\overline{z_i})^2,$$
$$\overline{D_{ij}^2}=R^2+(\overline{z_i}-\overline{z_j})^2.\tag{49}$$

Then

$$\begin{aligned}\kappa_{IJ}^{(2)}=&M\sum_{ij}\ (1/\overline{D_{ij}^8})[\mathbf{a}_I\cdot\mathbf{a}_J-2(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I)(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_J)/\overline{D_{ij}^2}]\\=&\frac{N^2M}{L^2}\int_{-L/2}^{L/2}\int_{-L/2}^{L/2}dz_Idz_J\frac{R^2-(z_I-z_J)^2}{[R^2+(z_I-z_J)^2]^5}\\=&\frac{\rho^2M}{R^6}\left[\frac{15L}{32R}\tan^{-1}\left(\frac{L}{R}\right)+\frac{L^2(51R^4+72R^2L^2+29L^4)}{96(R^2+L^2)^3}\right],\end{aligned}\tag{50}$$

where N is the number of atoms in a molecule and $\rho=N/L$ is the number of atoms per unit length in the molecule. For this simple calculation the average of Eq. (15) is superfluous, so that $\kappa_{IJ}^{(2)}=\tilde{\kappa}_{IJ}^{(2)}$. The asymptotic result for $L\ll R$ that $\kappa_{IJ}^{(2)}\sim R^{-8}$ can be seen in previous calculations [13,14]. However, even in this limit, the fact that $\kappa_{IJ}^{(2)}$ is proportional to L^2 is not apparent from the previous results. To our knowledge, our result that $\kappa_{IJ}^{(2)}\sim L/R^7$ for $L\geqslant R$ is a new one.

The macroscopic chiral wave vectors $\mathbf{Q}$ and $\mathbf{R}$ are both taken perpendicular to the nematic direction. For $QR_{IJ}\ll 1$, we have $\mathbf{a}_I\times\mathbf{a}_J\cdot\mathbf{R}_{IJ}=-QR^2\cos^2\phi_R$, where ϕ_R is the angle between $\mathbf{R}_{IJ}$ and $\mathbf{Q}$. Then the chiral energy per molecule from virtual states with two molecules excited, $\mathcal{E}^{(2)}$, is given by

$$\begin{aligned}\mathcal{E}^{(2)}\equiv&\tfrac{1}{2}\sum_J\ \langle E_{IJ}\rangle=-\tfrac{1}{2}\sum_J\ QR^2\cos^2\phi_R\kappa_{IJ}^{(2)}\\=&-\tfrac{1}{4}\gamma M\rho^2(QR)\frac{1}{R^5}\left[\frac{15L}{32R}\tan^{-1}\left(\frac{L}{R}\right)\right.\\&\left.+\frac{L^2(51R^4+72R^2L^2+29L^4)}{96(R^2+L^2)^3}\right].\end{aligned}\tag{51}$$

In obtaining this result we approximated the sum over J by a sum over γ nearest neighbors in the plane as specified in Eq. (49), so that $\cos^2\phi_R\to\frac{1}{2}$. From the discussion in Appendix E we are led to believe that the result of Eq. (51) will not be seriously modified by taking a more realistic distribution of nearest neighboring molecules. We identify this result with the contribution to the torque field h in the Frank free energy from virtual states with two molecules excited:

$$\begin{aligned}h^{(2)}=&-\frac{\mathcal{E}^{(2)}}{\Omega Q}=\frac{\gamma M\rho^2L}{4\Omega R^5}\left[\frac{15}{32}\tan^{-1}\left(\frac{L}{R}\right)\right.\\&\left.+\frac{LR(51R^4+72R^2L^2+29L^4)}{96(R^2+L^2)^3}\right]\end{aligned}\tag{52a}$$

$$=\frac{\gamma M\rho^2L^2}{4R^9},\quad L\ll R\tag{52b}$$

$$\approx \frac{15\pi\gamma M\rho^2}{256R^7}, \quad L \geqslant R, \tag{52c}$$

where we took the volume per molecule, Ω, to be $\Omega = LR^2$ for $L \geqslant R$ and R^3 for $L \ll R$. For $L \ll R, h^{(2)} \propto (L^2/R^9)$, consistent with the previous results of Refs. [13,14], whereas for $L \geqslant R, h^{(2)} \propto 1/R^7$.

B. Numerical estimate of the macroscopic pitch

Now we want to estimate the value of the pitch using the result for $\mathcal{E}$ obtained above. Intuitively one expects that the polarizability tensor will have its largest component tangent to the helix and that the anisotropy of the polarizability in the plane perpendicular to the tangent will be small. Essentially, we will attribute the anisotropy of the polarizability to the anisotropy in the excitation energy E_α. Therefore, somewhat arbitrarily, we will take all the matrix elements like $|\langle \mu | \Delta r''_\alpha | 0 \rangle|$, where $\mu = x,y,z$, to have the same value, a_a, where a_a is of order the radius of an atom. We therefore parametrize the excitation energies in Eq. (47) as

$$E_x/E = 1 + \tfrac{1}{3}\delta + \eta, \quad E_y/E = 1 + \tfrac{1}{3}\delta - \eta, \quad E_z/E = 1 - \tfrac{2}{3}\delta, \tag{53}$$

where E is the average excitation energy. Within our assumption of constant matrix elements the parameters δ and η characterize the anisotropy of the excitation energy and through it the anisotropy of the atomic polarizability. When this anisotropy is small, we find that

$$M = -\frac{3e^4 a_a^4 a}{2E}\left(\frac{aq}{1+a^2q^2}\right)(\delta - \eta)\Psi(aq) \equiv -\frac{3e^4 a_a^4 a}{2E} G(\delta, \eta, aq), \tag{54}$$

where

$$\Psi(aq) = \frac{\delta - \frac{1}{2}(aq)^2(\delta - 3\eta)}{(1+a^2q^2)} \tag{55}$$

and

$$G(\delta, \eta, aq) = \left(\frac{aq(\delta - \eta)}{1+a^2q^2}\right)\Psi(aq). \tag{56}$$

The corresponding results for $\kappa_{IJ}^{(2)}$ are

$$\kappa_{IJ}^{(2)} = -\frac{3e^4 a_a^4 a\rho^2 L^2}{2ER^8} G(\delta, \eta, aq), \quad L \ll R \tag{57a}$$

$$\approx -\frac{45\pi e^4 a_a^4 a\rho^2 L}{128ER^7} G(\delta, \eta, aq), \quad L \geqslant R. \tag{57b}$$

Thus M is quadratic in the anisotropy of the polarizability and

$$h^{(2)} = -\frac{3\gamma e^4 a_a^4 a\rho^2 L^2}{8ER^9} G(\delta, \eta, aq), \quad L \ll R \tag{58a}$$

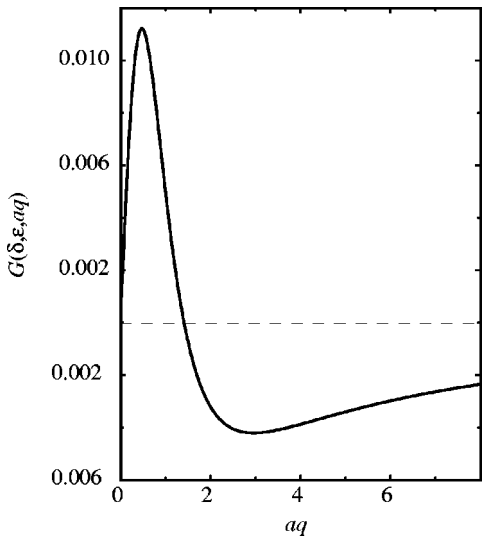

FIG. 5. The function $G(\delta, \eta, aq) = [aq/(1+a^2q^2)](\delta - \eta)\Psi(aq)$ versus aq for $\delta = \frac{1}{5}$ and $\eta = 0$.

$$\approx -\frac{45\pi\gamma e^4 a_a^4 a\rho^2}{512ER^7} G(\delta, \eta, aq), \quad L \geqslant R. \tag{58b}$$

This conclusion is a natural one: surely the torque field must disappear when the anisotropy of the polarizability is turned off. Also, when $E_z = E_y$ (i.e., when $\delta = \eta$), the chiral constant σ' vanishes. To see that note that when $E_z = E_y$, one of the principal axes for each atom can be taken to be perpendicular to the axis of the helix, in which case the matrix elements appearing in σ' are invariant with respect to the mirror operation $z' \to -z'$. To illustrate the dependence of $h^{(2)}$ on the molecular chiral wave vector q, we show in Fig. 5 $G(\delta, \eta, aq)$ versus aq for fixed values of δ and η. There one sees that $h^{(2)}$ is maximal for aq of order unity and decreases rapidly away from this maximum. Of course, an experimental test of this dependence is difficult since varying q at constant ρ involves structural changes in a molecule. To treat small chirality we take $aq = 1/3$ (or $aq = 3$) and we set $a_a = 1$ Å, $E = 8$ eV (these parameters correspond to an atomic polarizability $\alpha = 2e^2 a_a^2/E = 27a_0^3$), $a = 7.5$ Å, $\gamma = 6$, $L = 200$ Å, $R = 20$ Å, $\rho = 3$ Å^{-1}, $\delta = 1/5$, and $\eta = 0$. With the volume per molecule, $\sim LR^2$, the chosen values of the parameters correspond to volumetric density of molecules of about 40% and a dielectric constant, $\epsilon = 1 + 4\pi\alpha\rho L/\Omega \approx 1.3$. Then the torque field is approximately $h = 4.5 \times 10^{-4}$ (dyn/cm). If now one takes the Frank constant K_2 to be 10^{-7} dyn, then the macroscopic pitch of the liquid crystal will be $P = 2\pi/Q = 2\pi K_2/h = -14$ μm (or 28 μm for $aq = 3$). If we had taken $\delta = 3/10$ and $\eta = 0$, then the pitch would be -4.5 μm (or 9.0 μm for $aq = 3$).

It may be seen that the computed pitch is longer than one usually finds experimentally for a system consisting of molecules of the above size. There are two possible explanations for this discrepancy. First of all, our approximations, although improved over previous ones, may still not be sufficiently accurate. For example, two helices of radius 7.5 Å at a center-to-center separation of 20 Å have their nearest groups separated by only 5 Å. Under these conditions, the expansion in terms of even the transverse coordinates of the

atoms may not be rapidly convergent. The second possible reason for the discrepancy between calculated and observed pitches would be that an explanation of the pitch of cholesterics requires consideration of steric interactions. We are presently considering how our arguments might be improved to discriminate between these two explanations.

If one can find molecules for which quantum chiral interactions considered in this section are dominant, then the following remarks are relevant. Notice that for helical molecules the torque field h can have either sign in both the large q and small q limit, depending on the signs of $(\delta-\eta)$ and $(\delta-3\eta)$. This is in contrast to the situation for steric interactions, for which it is believed [34] that the contribution to h from the repulsive (i.e., steric) chiral interaction between molecules is negative for small q and is positive for large q. Helical molecules which do not follow the sign prediction for h due to repulsive steric interactions might constitute examples of molecules for which the quantum dispersion forces dominate the chiral interactions. In general, the density dependence of the quantum and steric contributions to h will be different. Thus, if these two mechanisms compete, it is likely that the sign of h could depend on the density.

V. ONE-MOLECULE TERMS

In the model of a molecule considered before we supposed it to consist of He-like atoms. In reality one would expect the outer electronic shell of atoms to be deformed by the interaction with nearest neighbors. In general, constituent atoms or complexes will possess a dipole moment. Hence it is of interest to consider the situation when one of the molecules is in its ground state in the virtual state of a two-molecule system. Up to now this case was ignored, although, as we shall see, it may play a significant, if not dominant role.

From Eq. (38) we obtain the following expression for the additional contribution, denoted $\kappa_{IJ}^{(1)}$, to κ_{IJ} from virtual states in which only one molecule is excited. We still invoke the approximation of localized excited states [24]. But then terms in which only molecule J is excited require evaluation of $\mathcal{E}_{ij;i'j'n}$ with $j=j'$, but i and i' are arbitrary and similarly when only molecule I is excited. For a molecule in the excited state we use the same approximation as before, again expanding the denominator with respect to $\Delta\mathbf{r}$ to get a nonzero matrix element. For the molecule which remains in its ground state in the virtual state, one has to include both signs of charge at each site. Thus (see Appendix F) we find that

$$\tilde{\kappa}_{IJ}^{(1)}=6\sum_{i,i'\in I;j\in J}e^2q_iq_{i'}(\overline{x_i'}\,\overline{y_{i'}'}-\overline{x_{i'}'}\,\overline{y_i'})\frac{(\overline{\mathbf{D}}_{i'j}\cdot\mathbf{a}_J)}{\overline{D}_{ij}^3\overline{D}_{i'j}^5}$$
$$\times\sum_\mu E_\mu(j)^{-1}(\langle\mu_j|\Delta z_j'|0\rangle^2-\tfrac{1}{2}\langle\mu_j|\Delta x_j'|0\rangle^2$$
$$-\tfrac{1}{2}\langle\mu_j|\Delta y_j'|0\rangle^2). \tag{59}$$

In Eq. (59) we sum i and i' over all the charges in a given atom, in which case $q_i\overline{x_i'}$ is replaced by p_{xi}', where $\mathbf{p}_i$ is now the expectation value of the dipole moment of the ith atom, in its ground state, so that i and i' from now on refer to atoms, whereas j will still label electronic charges. Then the preceding equation can be reduced to

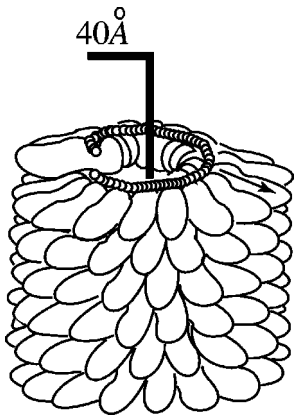

FIG. 6. TMV, adapted from Ref. [35]. We indicate a possible axis along which the dipole moment of each complex might be oriented. In the situation shown here, the largest component of the dipole moment of the complex is radial.

$$\tilde{\kappa}_{IJ}^{(1)}=6\sum_{ii'j}[p_{ix}'p_{i'y}'-p_{i'x}'p_{iy}']\frac{(\overline{\mathbf{D}}_{i'j}\cdot\mathbf{a}_J)}{\overline{D}_{ij}^3\overline{D}_{i'j}^5}$$
$$\times e^2\sum_\mu E_\mu(j)^{-1}[\langle\mu_j|\Delta z_j'|0\rangle^2-\tfrac{1}{2}\langle\mu_j|\Delta x_j'|0\rangle^2$$
$$-\tfrac{1}{2}\langle\mu_j|\Delta y_j'|0\rangle^2] \tag{60a}$$
$$\equiv W_1W_2, \tag{60b}$$

where W_1 is the factor on the first line of Eq. (60a) and W_2 that on the second and third lines of this equation. In writing this result we assumed that for typical atoms i one has $p_{ix}\overline{z_{i'}}\gg p_{iz}\overline{x_{i'}}$. Once again, in this expression one has to carry out averaging with respect to independent up and down orientations of both molecules. But this average turns out to be superfluous for the model of a helical molecule which was introduced above.

As in Eq. (45), we introduce components of the atomic dipole moment with respect to the principal axes of the atom, in which case we have

$$p_x'=p_x''\cos(qs)-cp_y''\sin(qs)-caqp_z''\sin(qs),$$
$$p_y'=p_x''\sin(qs)+cp_y''\cos(qs)+caqp_z''\cos(qs), \tag{61}$$
$$p_z'=-caqp_y''+cp_z''.$$

The component p_x'' is essentially the radial component of the atomic dipole moment and is nonzero for helical geometry. For instance, for the molecule TMV, shown in Fig. 6 [35], this radial component may be appreciable. In such a case we write

$$\wp_{ii'}^2\equiv p_{ix}'p_{i'y}'-p_{i'x}'p_{iy}'$$
$$=[p_x''^2+c^2(p_y''+aqp_z'')^2]\sin[q(s_{i'}-s_i)] \tag{62a}$$
$$\equiv\wp_0^2\sin[q(s_{i'}-s_i)]. \tag{62b}$$

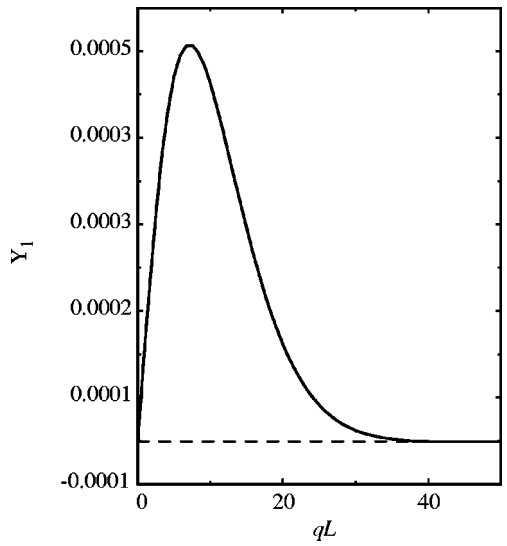

FIG. 7. $Y_1(qL,L/R)=\Psi(aq)X_1(qL,L/R)$, with $\Psi(aq)$ and $X_1(\tilde{q},\tilde{L})$ defined in Eqs. (55) and (63), respectively, versus qL for $L=200$ Å, $R=20$ Å, $\rho=3$ Å^{-1}, $\delta=1/5$, and $\eta=0$. According to Eq. (68) the quantity plotted gives the dependence of the torque field $h^{(1)}$ on the chiral wave vector of a molecule q. Note that the molecule is achiral if either $q\to 0$ or $q\to\infty$.

We now substitute this form into Eq. (60a) and assume perfect alignment as in Eq. (49). Then the summand is symmetrized and we write $W_1=\wp_0^2 X_1 L/R^8$, with

$$X_1(\tilde{q},\tilde{L})=3\sum_{ii'j}\left[\frac{1-\tilde{L}^2[\tilde{s}_j{}^2+\tilde{s}_i\tilde{s}_{i'}-\tilde{s}_j(\tilde{s}_i+\tilde{s}_{i'})]}{[1+\tilde{L}^2(\tilde{s}_j-\tilde{s}_i)^2]^{5/2}[1+\tilde{L}^2(\tilde{s}_j-\tilde{s}_{i'})^2]^{5/2}}\right]\times(\tilde{s}_{i'}-\tilde{s}_i)\sin[\tilde{q}(\tilde{s}_{i'}-\tilde{s}_i)], \tag{63}$$

where $\tilde{s}=s/L,\tilde{q}=qL$, and $\tilde{L}=L/R$. To evaluate W_2 we again invoke the model of Eq. (53), in which case, for small anisotropy, Eqs. (26) and (44) enable us to write

$$\begin{aligned}W_2&\equiv e^2\sum_\mu E_\mu^{-1}[\langle\mu_j|\Delta z_j'|0\rangle^2-\tfrac{1}{2}\langle\mu_j|\Delta x_j'|\rangle^2-\tfrac{1}{2}\langle\mu_j|\Delta y_j'|\rangle^2]\\&=e^2\left[-\frac{\langle x|\Delta x''|0\rangle^2}{2E_x}+\frac{\langle y|\Delta y''|0\rangle^2}{2E_y}\frac{2(aq)^2-1}{1+(aq)^2}+\frac{\langle z|\Delta z''|0\rangle^2}{2E_z}\frac{2-(aq)^2}{1+(aq)^2}\right]\\&=\frac{e^2a_a^2}{E}\Psi(aq),\end{aligned} \tag{64}$$

where $\Psi(aq)$ is defined in Eq. (55). Using the asymptotic evaluations in Appendix G, we thus have the results

$$\tilde{\kappa}_{IJ}^{(1)}=\begin{cases}\dfrac{e^4a_a^2d^2L^4\rho^3}{ER^8}\Psi(aq)\phi(\frac{1}{2}qL), & a\ll L\ll R \quad (65a)\\[2ex]\dfrac{8e^4a_a^2d^2\rho^3qL}{ER^4}\Psi(aq)I_1^2(qR), & L\gg R \quad (65b)\end{cases}$$

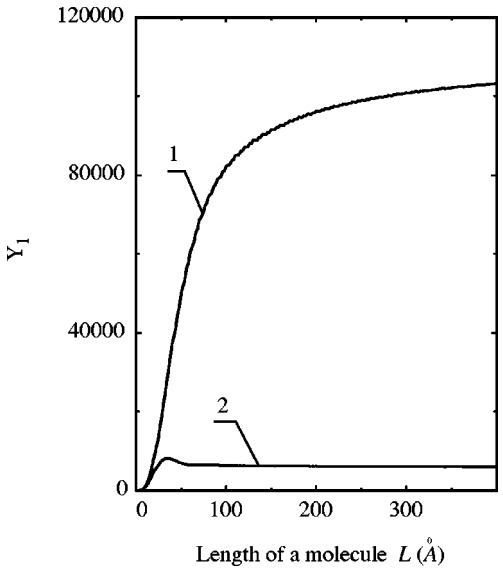

FIG. 8. The factor $Y_1\equiv\Psi(aq)X_1(qL,L/R)$ as a function of L for two values of the molecule wave number $q=0.0444$ Å^{-1} (plot 1) and $q=0.1333$ Å^{-1} (plot 2) with $R=20$ Å, $a=7.5$ Å, $\delta=0.2$, and $\eta=0$. According to Eq. (68) when $L\gg R$ (so that $\Omega=LR^2$) the quantity plotted gives the dependence of the torque field $h^{(1)}$ on the length L of a molecule.

where d is the effective size of the dipole moment: $\wp_0=ed$,

$$\phi(x)=-(3/2)(d/dx)[(\sin x)/x]^2, \tag{66}$$

and

$$I_n(qR)=\int_0^\infty e^{-(1/2)[x^2+(qR/x)^2]}x^n dx. \tag{67}$$

Now we evaluate h following the procedure of Eq. (51) in terms of the chiral energy per molecule $\mathcal{E}^{(1)}$ due to one-molecule effects:

$$h^{(1)}=-\frac{\mathcal{E}^{(1)}}{\Omega Q}=\frac{\gamma R^2}{4\Omega}W_1W_2=\left(\frac{\gamma e^4a_a^2d^2L}{4ER^6\Omega}\right)\Psi(aq)X_1(\tilde{q},\tilde{L}). \tag{68}$$

Using the evaluations of Appendix G, we obtain the asymptotic results,

$$h^{(1)}=\begin{cases}\dfrac{\gamma e^4a_a^2d^2L^4\rho^3}{4ER^9}\Psi(aq)\phi(\frac{1}{2}qL), & a\ll L\ll R \quad (69a)\\[2ex]\dfrac{2\gamma e^4a_a^2d^2\rho^3q}{ER^4}\Psi(aq)I_1^2(qR), & L\gg R. \quad (69b)\end{cases}$$

Here again we see from the appearance of $\Psi(aq)$ that chirality requires a nonzero anisotropy of the polarizability characterized by δ and η. Since the factor $\Psi(aq)$ also appears in Eq. (58), we see that the critical value (if any) where h changes sign as q is varied is only determined by the geometry, at least within our simple model. For concentrated systems, the limit $L\gg R$ is the most relevant and for this case Fig. 7 shows how $h^{(1)}$ depends on the molecular chirality q,

when the length of the molecules and the density of atoms ρ are fixed. Note that the variation of $h^{(1)}$ with the molecular chirality q strongly depends on details of molecular geometry since only a fixed number of atoms is allowed on a helical thread. Figure 7 shows that for aq of order unity or less, where $h^{(1)}$ is appreciable and may give a short pitch, $h^{(1)}$ is positive, whereas for steric interactions h is believed to be negative for small q [7,34]. Since increasing the density probably causes steric interactions to dominate, it is possible that the combination of these two mechanisms could cause h to change sign as a function of density or temperature [36]. In Fig. 8 we show the behavior of the quantity $Y_1 \equiv \Psi(aq) X_1(\tilde{q},\tilde{L})$ as a function of L for $R=20$ Å, $\rho = 3$ Å^{-1}, $\delta = 1/5$, and $\eta = 0$ for two fixed values of the molecular chiral wave vector, q. In particular, it is noteworthy that for large L, Y_1 (and therefore $h^{(1)}$) is independent of L. To get some idea of the relative importance of $h^{(1)}$ and $h^{(2)}$, consider their ratio:

$$r \equiv \frac{h^{(1)}}{h^{(2)}} = \begin{cases} -\left(\dfrac{2L^2 d^2 \rho}{3a_a^2 a}\right)\left(\dfrac{1+a^2q^2}{aq}\right)(\delta-\eta)^{-1}\phi(\tfrac{1}{2}qL), \quad L \ll R & \text{(70a)} \\ -\left(\dfrac{1024R^3 d^2 \rho}{45\pi a_a^2 a^2}\right)(1+a^2q^2)(\delta-\eta)^{-1} I_1^2(qR), \quad L \gg R. & \text{(70b)} \end{cases}$$

One sees that even with d/a_a as small as 0.03, this ratio can easily be of order unity.

To numerically estimate the pitch arising from the considered interaction we will take parameters of a system and constituent molecules chosen in the preceding section. Then, if $aq = 1/3$ one finds $h^{(1)} = 0.5(d/a_0)^2$ dyn/cm. If molecules possess a local dipole moment, the resulting dipolar interactions may lead to strong biaxial correlations between neighboring molecules. Using the evaluation of the dipolar interaction energy in terms of the integral analyzed in Appendix G, we estimate the order of magnitude of the dipole-dipole interaction to be $V_{dd} \approx (d/a_0)^2 10^5$ K. So if we suppose that the biaxial correlations due to dipole-dipole interaction among molecules is negligible when it is less than 100 K then one must have $(d/a_0)^2 < 10^{-3}$. At the upper limit of validity of our calculations $(d/a_0)^2 = 10^{-3}$ and the macroscopic pitch due to $h^{(1)}$ will be $P^{(1)} = 2\pi K_2 / h^{(1)} = 12.5$ μm. As the density of local dipoles is increased, the macroscopic pitch becomes smaller. For instance, if we set $d/a_0 = 1/3$, we get a pitch of order 0.1 μm, although this estimate will be significantly modified by biaxial correlations, which have been neglected in our treatment. Since $h^{(1)} \sim \rho^3$ and the dipole-dipole interaction is proportional to ρ^2, it is conceivable that for much larger molecules $h^{(1)}$ could be significant without the dipoles being large enough to induce long-range biaxial order. Finally, when aq is larger than unity (as for TMV), this mechanism leads to a very large pitch for almost any choice of parameters. As mentioned in Sec. IV B, it is possible that larger values of the pitch would be obtained if the role of the transverse were treated exactly rather than by an expansion.

VI. CONCLUSION

Here we put our work into the context of current research and record our conclusions.

(1) We introduced a simple model of localized polar excited states that enabled us to make an explicit calculation of the chiral interaction, $\kappa_{IJ} \mathbf{a}_I \times \mathbf{a}_J \cdot \mathbf{R}_{IJ}$, between molecules I and J due to quantum charge fluctuations analogous to those responsible for the R^{-6} dispersion interaction between neutral atoms. We identified two distinct physical effects depending on whether one or both molecules were excited in the virtual state of the two-molecule system. In implementing this calculation we used a modified multipole expansion in which only coordinates transverse to the long axis of the molecule were expansion parameters, so that we could treat long molecules which usually are the building blocks of liquid crystals. The contribution $\kappa_{IJ}^{(2)}$ to κ_{IJ} from virtual states with both molecules excited has a form similar to that found by Van der Meer *et al.* [13] and Kats [14]. For a helical molecule of length L we find that $\kappa_{IJ}^{(2)} \propto L^2/R^8$ for $L \ll R$ and $\kappa_{IJ}^{(2)} \propto L/R^7$, for $L \gg R_{IJ}$. The contribution $\kappa_{IJ}^{(1)}$ to κ_{IJ} from virtual states with only one molecule excited is usually only dominant when the local atomic dipole moments are large enough to give rise to significant (possibly long-range) biaxial correlations. Both mechanisms give rise to a chiral interaction between a chiral molecule and an achiral one that has a local anisotropic polarizability. Our formulation leads to numerical estimates of the pitch which are larger than that found in many cholesterics. Whether this discrepancy is an artifact of the expansion in transverse coordinates along with a disregard of biaxial correlations between molecules or is an indication that steric rather than quantum interactions are the microscopic origin of macroscopic chirality is not clear at present. The role of biaxial correlations between molecules is considered elsewhere [25].

(2) We evaluated κ_{IJ} and the torque field h for helical molecules as a function of the wave vector q which describes the chiral structure of an individual molecule. We found that the sign of h depends on the details of the anisotropy of the local atomic polarizability. For instance, for $(aq)^2 \ll 1$, the sign of $h^{(1)}$ (the contribution to h from virtual states in which only one molecule is excited) has the same sign as δ, the local anisotropy of the polarizability. One expects δ to be positive because presumably the polarizability along the tangent of the helix is larger than that along perpendicular directions. This sign of $h^{(1)}$ is opposite to that expected from steric interactions [34]. As for steric interactions, one expects

$h^{(1)}$ to change sign as q is increased, but our calculations indicate that this only happens when $h^{(1)}$ is so small that it is hardly likely to be the dominant mechanism for macroscopic chirality. When δ is positive and large, the sign of the two-molecule contributions to h is negative for small aq and positive for large aq, just as expected for steric interactions. However, our calculations indicate that normally $h^{(2)}$ is not significant.

(3) Here we calculated the effective chiral interactions by averaging the orientation of the molecule over configurations with the long axis fixed. Even within mean-field theory, wherein each molecule is described by a single-molecule orientational distribution function of the three Euler angles, the only required symmetry in the locally nematic state is that it be invariant against rotations about the nematic axis. As discussed in Appendix B, this requirement still permits biaxial contributions to the orientational probability distribution which we neglected.

(4) These calculations suggest some general observations. First of all, the interaction from virtual states with two molecules excited gives rise to a two-point chiral interaction in the form of an integral over the long axis of each molecule. This result gives a formal justification for introduction of a chiral interaction between ''chiral centers'' on one molecule with a center of local anisotropic polarizability on another molecule. However, this same characterization does *not* apply to the mechanism involving local permanent atomic dipole moments. The dipolar mechanism leads to an intrinsically three-point chiral interaction of a type which, as far as we know, has not yet been proposed. It would be interesting to observe such an interaction for helical molecules which have a local radial dipole moment.

(5) Our calculations can potentially be generalized in several directions. For instance, there seems to be no reason why our results cannot be taken over immediately to discuss the interaction between flexible polymers. There the average over spinning (within a tube surrounding the convoluted polymer shape) can still be taken. Then in Eq. (16) one would replace $\mathbf{a}_I$ by its local value at atom i. Our calculations can also be applied to liquid crystal systems containing a mixture of chiral and achiral molecules. There one has two types of interactions to consider. The first of these is the interaction between adjacent chiral and achiral molecules to which the results of this paper apply directly. The second is the interaction between more widely separated pairs of chiral molecules. For this interaction, our result for κ_{IJ} ought to be multiplied by ϵ^{-2}, where ϵ is the static dielectric constant.

ACKNOWLEDGMENTS

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APPENDIX A: QUANTUM AND CLASSICAL AVERAGING

The energy of interaction of molecules I and J averaged over their rotational motion when expressed in terms of a multipole expansion is of the form

$$[U_{IJ}]_{\rm av}=\sum_{M\{\alpha\},N,\{\beta\}}\Lambda_{\alpha_1,\alpha_2,\ldots,\alpha_n;\beta_1,\beta_2,\ldots,\beta_m}(I,J)\times[M_{\alpha_1,\alpha_2,\ldots,\alpha_n}(\rho_I)]_{\rm av}[N_{\beta_1,\beta_2,\ldots,\beta_m}(\rho_J)]_{\rm av}, \tag{A1}$$

where $[\ ]_{\rm av}$ indicates an average over orientations and $\mathbf{M}$ and $\mathbf{N}$ are tensors of arbitrary rank which are functionals of a density on the molecule in question. For classical two-body interactions these tensors are multipole moments of the form

$$M_{\alpha_1,\alpha_2,\ldots,\alpha_n}(\rho_I)=\int d\mathbf{r}\rho_I(\mathbf{r})r_{\alpha_1}r_{\alpha_2}\ldots,r_{\alpha_n}. \tag{A2}$$

For classical two-body interactions these tensors are thus linear functions of the density, so that the orientational average of the tensor is the same as the tensor evaluated for the orientationally averaged density:

$$[M_{\alpha_1,\alpha_2,\ldots,\alpha_n}(\rho)]_{\rm av}=M_{\alpha_1,\alpha_2,\ldots,\alpha_n}([\rho]_{\rm av}). \tag{A3}$$

This means that classically the interaction averaged over the orientational motion of molecule I, say, is the same as the interaction would be for a molecule having the average (over orientations) shape. Thus, classically, spinning a chiral molecule leads to two-body interactions characteristic of a uniaxial, i.e., achiral molecule. Quantum mechanically, the situation is different, because in second-order perturbation theory the tensor $\mathbf{M}$, say, in Eq. (A1) is a bilinear function of the density $\rho(I)$ of the form

$$M_{\alpha_1,\alpha_2,\ldots,\alpha_n}=\int\rho(\mathbf{r})d\mathbf{r}\int d\mathbf{r}'\rho(\mathbf{r}')T(\mathbf{r},\mathbf{r}')\times r_{\alpha_1}\cdots r_{\alpha_k}r'_{\alpha_{k+1}}\cdots r'_{\alpha_n}, \tag{A4}$$

where $T(\mathbf{r},\mathbf{r}')$ depends on the spatial correlations of the important excited states, and Eq. (A3) is incorrect. In other words, the nonlinear fluctuation of the electric field of a molecule due to quantum fluctuations has a chiral component that survives an average over rotations and thereby distinguishes between right-handed and left-handed molecules.

APPENDIX B: BIAXIAL ORIENTATIONAL CORRELATIONS

If the Euler angles are taken to represent the orientation of the molecule with reference to axes fixed in space such that the z axis coincides with the axis of nematic order, then the probability distribution for the orientation of a single molecule must be independent of α. If the distribution is also independent of γ, then it means that for each value of β, the molecule spins with equal probability through all angles about its long axis. However, if we have correlations between β and γ, we can have a distribution like that describing the orientation of the moon in which $\gamma-\beta$ assumes a fixed value. For a molecule, this distribution is depicted in Fig. 9.

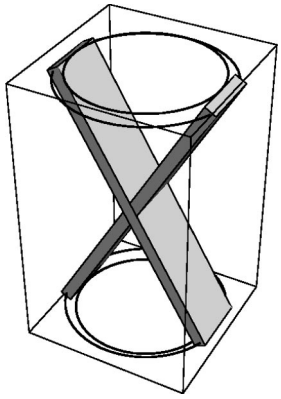

FIG. 9. Distribution for which $\gamma-\beta$ is fixed.

APPENDIX C: ORIENTATIONAL AVERAGES

In this appendix we evaluate the orientational averages (indicated by brackets, $[\ ]_{\rm av}$) of the terms in Eq. (35). In this calculation, we should keep in mind that we only need keep terms which include one antisymmetric tensor. Also only averages of even numbers of powers of components of $\boldsymbol{\rho}_i$ are nonzero. Finally, terms obtained by interchanging the indices i and j (labeling atoms on different molecules) can be included implicitly. With these understandings we use Eq. (13) to write

$$\begin{aligned}T_1 &\equiv [(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}D^{-3})_{n0}(\boldsymbol{\rho}_{ij}\cdot\mathbf{D}D^{-3})_{0n}]_{\rm av}\\ &=2[(\rho_{i\alpha}D_\alpha D^{-3})_{n0}(\rho_{i\beta}D_\beta D^{-3})_{0n}]_{\rm av}\\ &=\epsilon_{\alpha\beta\gamma}a_{I\gamma}\epsilon_{\mu\nu z}(r'_{i\mu}D_\alpha D^{-3})_{n0}(r'_{i\nu}D_\beta D^{-3})_{0n}\\ &=[\mathbf{R}\times\mathbf{a_I}\cdot\mathbf{a}_J][(r'_{i\mu}z_jD^{-3})_{n0}(r'_{i\nu}D^{-3})_{0n}\\ &\quad-(r'_{i\mu}D^{-3})_{n0}(r'_{i\nu}z_jD^{-3})_{0n}]\epsilon_{\mu\nu z}\\ &=2[\mathbf{R}\times\mathbf{a_I}\cdot\mathbf{a}_J](r'_{i\mu}z'_jD^{-3})_{n0}(r'_{i\nu}D^{-3})_{0n}\epsilon_{\mu\nu z}.\end{aligned}\tag{C1}$$

In terms involving four powers of transverse components, contributions at the order in R_{IJ}^{-1} which we need require that two components refer to atom i and two to atom j. Thus

$$\begin{aligned}T_2 &\equiv -\tfrac{3}{2}[([\boldsymbol{\rho}_{ij}\cdot\mathbf{D}]^2D^{-5})_{n0}(\rho_{ij}^2D^{-3})_{0n}]_{\rm av}\\ &=-3[([\boldsymbol{\rho}_i\cdot\mathbf{D}]^2D^{-5})_{n0}(\rho_j^2D^{-3})_{0n}]_{\rm av}\\ &\quad-6[([\boldsymbol{\rho}_i\cdot\mathbf{D}][\boldsymbol{\rho}_j\cdot\mathbf{D}])_{n0}([\boldsymbol{\rho}_i\cdot\boldsymbol{\rho}_j]D^{-3})_{0n}]_{\rm av}.\end{aligned}\tag{C2}$$

The first term gives rise to no antisymmetric terms and can be dropped. The second term leads to

$$\begin{aligned}T_2 &\equiv -3[(r'_{i\mu}D_\alpha\rho_{j\beta}D_\beta D^{-5})_{n0}(r'_{i\mu}\rho_{j\alpha}D^{-3})_{0n}]_{\rm av}\\ &\quad+3[(r'_{i\mu}D_\alpha a_{I\alpha}\rho_{j\beta}D_\beta D^{-5})_{n0}(r'_{i\mu}a_{I\gamma}\rho_{j\gamma}D^{-3})_{0n}\\ &\quad-3\epsilon_{\mu\nu z}\epsilon_{\alpha\beta\rho}a_{I\rho}\langle(r'_{i\mu}D_\alpha\rho_{j\beta}D_\beta D^{-5})_{n0}(r'_{i\nu}\rho_{j\gamma}D^{-3})_{0n}]_{\rm av}.\end{aligned}\tag{C3}$$

The first term gives zero antisymmetric contribution. The second and third terms give identical contributions. So

$$T_2=3[\mathbf{R}\times\mathbf{a_I}\cdot\mathbf{a}_J](r'_{i\mu}r'_{j\nu}[\mathbf{D}\cdot\mathbf{a}_I]D^{-5})_{n0}(r'_{i\mu}r'_{j\tau}D^{-3})_{0n}\epsilon_{\nu\tau z}.\tag{C4}$$

Likewise, keeping only relevant terms, we write

$$\begin{aligned}T_3 &\equiv \tfrac{9}{4}[([\boldsymbol{\rho}_{ij}\cdot\mathbf{D}]^2D^{-5})_{n0}([\boldsymbol{\rho}_{ij}\cdot\mathbf{D}]^2D^{-5})_{0n}]_{\rm av}\\ &=[\tfrac{9}{2}([\boldsymbol{\rho}_i\cdot\mathbf{D}]^2D^{-5})_{n0}([\boldsymbol{\rho}_j\cdot\mathbf{D}]^2D^{-5})_{0n}+9([\boldsymbol{\rho}_i\cdot\mathbf{D}]\\ &\quad\times[\boldsymbol{\rho}_j\cdot\mathbf{D}]D^{-5})_{n0}([\boldsymbol{\rho}_i\cdot\mathbf{D}][\boldsymbol{\rho}_j\cdot\mathbf{D}]D^{-5})_{0n}]_{\rm av}.\end{aligned}\tag{C5}$$

The first term leads to zero antisymmetric contribution. In the second term there are two equal contributions, one from taking the antisymmetric term in the average over $\boldsymbol{\rho}_i$, the other from the antisymmetric term in the average over $\boldsymbol{\rho}_j$. So we write

$$\begin{aligned}T_3 &=9\epsilon_{\mu\nu z}[(r'_{i\mu}\rho_{j\beta}D_\alpha D_\beta D^{-5})_{n0}\\ &\quad\times(r'_{i\nu}\rho_{j\delta}D_\gamma D_\delta D^{-5})_{0n}\epsilon_{\alpha\gamma\rho}a_{I\rho}]_{\rm av}\\ &=\tfrac{9}{2}\epsilon_{\mu\nu z}(r'_{i\mu}r'_{j\tau}D_\alpha D_\beta D^{-5})_{n0}(r'_{i\nu}r'_{j\tau}D_\gamma D_\delta D^{-5})_{0n}\\ &\quad\times\epsilon_{\alpha\gamma\rho}a_{I\rho}(\delta_{\beta\delta}-a_{J\beta}a_{J\delta}).\end{aligned}\tag{C6}$$

Then, using the symmetry between the two matrix elements, we have

$$\begin{aligned}T_3 &=9[\mathbf{R}\times\mathbf{a_I}\cdot\mathbf{a}_J](r'_{i\mu}r'_{j\nu}D_\alpha D^{-5})_{n0}\\ &\quad\times(r'_{i\mu}r'_{j\tau}D_\gamma D_\delta z'_iD^{-5})_{0n}\epsilon_{\nu\tau z}(\delta_{\alpha\gamma}-a_{I\alpha}a_{I\gamma}).\end{aligned}\tag{C7}$$

We set $z'_i=\overline{z'_i}+\Delta z'_i$. The term in $\overline{z'_i}$ vanishes. Thus

$$\begin{aligned}T_3 &=9\mathbf{R}\times\mathbf{a_I}\cdot\mathbf{a}_J\overline{r'_{i\mu}}(r'_{i\mu}r'_{j\nu}D_\alpha D^{-5})_{n0}\\ &\quad\times(r'_{j\tau}D_\gamma D_\delta(\Delta z'_i)D^{-5})_{0n}\epsilon_{\nu\tau z}(\delta_{\alpha\gamma}-a_{I\alpha}a_{I\gamma}).\end{aligned}\tag{C8}$$

The matrix elements are symmetric functions of μ and τ. So the antisymmetry of the ϵ tensor causes this term to vanish. At higher order in R_{IJ}^{-1} there would be nonzero contributions from this term. But at the order we consider there are none.

The remaining terms in Eq. (35) vanish for reasons similar to those which made T_3 vanish. So the only contributions that survive are those written in Eq. (38).

APPENDIX D: NONLOCAL EFFECTS

In this appendix we discuss nonlocal corrections contained in Eq. (38) from terms where $i\neq i'$ and/or $j\neq j'$. Rather than give a general argument, we will illustrate the nature of the argument by considering specifically the nonlocal corrections to the first term in Eq. (38). For this purpose we assume that the ''unperturbed'' energies $E_{n_in_j}$ can be obtained from a Hamiltonian of the form

$$\mathcal{H}=\mathcal{H}_0+V_{\rm hop}\equiv\mathcal{H}_0+\sum_{i,j;\alpha,\beta}|i\alpha\rangle t_{ij}^{\alpha\beta}\langle j\beta|,\tag{D1}$$

where $\mathcal{H}_0$ is completely local:

$$\mathcal{H}_0=\sum_{i\alpha}|i\alpha\rangle E_i^\alpha\langle i\alpha|.\tag{D2}$$

We assume the states to be strongly localized so that $|t_{ij}^{\alpha\beta}| \ll E_i^\alpha$ for all indices.

Now we consider the contribution T_0 to $\kappa_{IJ}=\frac{1}{2}[\tilde{\kappa}_{IJ}+\tilde{\kappa}_{JI}]$ from the first line of Eq. (38). Thus we write

$$T_0=-e^4\left[\left\langle 0\left| r_{i\alpha}D_{ij}^{-3}\frac{1}{\mathcal{E}}r_{i'\beta}z_{j'}D_{i'j'}^{-3}\right|0\right\rangle - \left\langle 0\left| r_{i\alpha}z_jD_{ij}^{-3}\frac{1}{\mathcal{E}}r_{i'\beta}D_{i'j'}^{-3}\right|0\right\rangle\right]\epsilon_{\alpha\beta z}. \quad \text{(D3)}$$

In this appendix all coordinates are taken relative to axes fixed in the molecule. Thus, r_i^μ here denotes what we called $(\mathbf{r}')_i^\mu$ in the notation of Eq. (11). For simplicity we consider here only the contribution from virtual states in which both molecules are excited. In that case, the sums are only over electrons.

Now we expand the matrix elements according to Eq. (36), as was done in Eq. (41). Thereby we get the corresponding contribution $\delta\kappa_{IJ}$ as

$$\begin{aligned}\delta\kappa_{IJ}=&\left\langle 0\left|\Delta r_{i\xi}\Delta r_{j\eta}\frac{1}{\mathcal{E}}\Delta r_{i'\sigma}\Delta r_{j\tau}\right|0\right\rangle[(\nabla_{i\xi}\nabla_{j\eta}\overline{r}_{i\mu}\overline{D}_{ij}^{-3})\\ &\times(\nabla_{i'\sigma}\nabla_{j'\tau}\overline{z}_{j'}\overline{r}_{i'\nu}\overline{D}_{i'j'}^{-3})-(\nabla_{i\xi}\nabla_{j\eta}\overline{r}_{i\mu}\overline{z}_j\overline{D}_{ij}^{-3})\\ &\times(\nabla_{i'\sigma}\nabla_{j'\tau}\overline{r}_{i'\nu}\overline{D}_{i'j'}^{-3})]\epsilon_{\mu\nu z}\\ =&\left\langle 0\left|\Delta r_{i\xi}\Delta r_{j\eta}\frac{1}{\mathcal{E}}\Delta r_{i'\sigma}\Delta r_{j\tau}\right|0\right\rangle[(\delta_{\xi\mu}\nabla_{j\eta}\overline{D}_{ij}^{-3}\\ &+\overline{r}_{i\mu}\nabla_{i\xi}\nabla_{j\eta}\overline{D}_{ij}^{-3})(\delta_{\sigma\nu}\delta_{\tau z}\overline{D}_{i'j'}^{-3}+\delta_{\sigma\nu}\overline{z}_j\nabla_{j'\tau}\overline{D}_{i'j'}^{-3},\\ &+\delta_{\tau z}\overline{r}_{i'\nu}\nabla_{j'\tau}\overline{D}_{i'j'}^{-3})-(\delta_{\xi\mu}\delta_{\eta z}\overline{D}_{ij}^{-3}+\delta_{\xi\mu}\overline{z}_j\nabla_{j\eta}\overline{D}_{ij}^{-3}\\ &+\delta_{\eta z}\overline{z}_j\nabla_{i\xi}\overline{D}_{ij}^{-3})(\delta_{\sigma\nu}\nabla_{j'\tau}\overline{D}_{i'j'}^{-3},\\ &+\overline{r}_{i'\nu}\nabla_{i'\sigma}\nabla_{j'\tau}\overline{D}_{i'j'}^{-3})]\epsilon_{\mu\nu z}. \end{aligned} \quad \text{(D4)}$$

Here we dropped terms of order $1/R_{IJ}^9$. In evaluating the gradients, note that D_{ij} depends on $\mathbf{r}_i(\mathbf{r}_j)$ only via $z_i(z_j)$. Thus $\nabla_{i\xi}\nabla_{j\eta}\overline{D}_{ij}^{-3}$ is only nonzero for $\xi=\eta=z$.

The terms of greatest interest are those of order $1/R_{IJ}^7$, because such terms are of potentially lower order than the local terms we kept of order $1/R_{IJ}^8$. These leading-order terms are

$$\begin{aligned}\delta\kappa_{IJ}=&\left\langle 0\left|\Delta r_{i\mu}\Delta r_{jz}\frac{1}{\mathcal{E}}\Delta r_{i'\nu}\Delta r_{jz}\right|0\right\rangle(\overline{D}_{i'j'}^{-3}\nabla_{jz}\overline{D}_{ij}^{-3}\\ &-\overline{D}_{ij}^{-3}\nabla_{j'z}\overline{D}_{i'j'}^{-3})\epsilon_{\mu\nu z}\equiv\left\langle 0\left|\Delta r_{i\mu}\Delta r_{jz}\frac{1}{\mathcal{E}}\Delta r_{i'\nu}\Delta r_{jz}\right|0\right\rangle\\ &\times[f(z_i,z_j,z_{i'},z_{j'})-f(z_{i'},z_{j'},z_i,z_j)], \end{aligned} \quad \text{(D5)}$$

where $f\sim 1/R_{IJ}^7$. Note that when the states are localized, i.e., when $i=i'$ and $j=j'$, the factor in large square brackets vanishes. Now consider expanding $\mathcal{E}$ as in Eq. (D1), so that

$$\frac{1}{\mathcal{E}}=\frac{1}{E_0-\mathcal{H}_0}+\frac{1}{E_0-\mathcal{H}_0}V_{\rm hop}\frac{1}{E_0-\mathcal{H}_0}+\frac{1}{E_0-\mathcal{H}_0}V_{\rm hop}\frac{1}{E_0-\mathcal{H}_0}V_{\rm hop}\frac{1}{E_0-\mathcal{H}_0}+\cdots, \quad \text{(D6)}$$

where $E_0-\mathcal{H}_0\sim E$, where E, the typical excitation energy, is much larger than t, a typical hopping matrix element. This equation implies that when it requires m hops for an electron to move from site i to site i' and n hops for an electron to move from site j to site j', then the matrix element will be of relative order $(t/E)^{(m+n)}$. Thus

$$\begin{aligned}\Delta f\equiv& f(z_i,z_j,z_{i'},z_{j'})-f(z_{i'},z_{j'},z_i,z_j)\\ &\sim(t/E)\nabla f\sim(t/E)(z_i-z_{i+1})/R_{IJ}^8. \end{aligned} \quad \text{(D7)}$$

We see that the ratio of this nonlocal contribution to the local contribution of Eq. (38) is of order $\Delta f/(r_\perp/R_{IJ}^8)$, where $r_\perp$ is a typical value of $\overline{x_i}$ or $\overline{y_i}$. This ratio is thus of order $(t/E)\times(z_{i+1}-z_i)/r_\perp$. Normally $(z_{i+1}-z_i)/r_\perp$ is of order unity, so indeed the nonlocal contributions are of relative order t/E and can reasonably be neglected.

APPENDIX E: POSITIONAL CORRELATIONS

In this appendix we consider how energy of interaction for the system of molecules is effected by the relative distribution of molecules. A simple way to address this issue is to evaluate the chiral interaction as a function of $Z_{IJ}\equiv Z$, the z component of $\mathbf{R}_{IJ}$. We assume that it suffices to do this for helical molecules, in which case the calculations can be done explicitly. Previously we had set $Z=0$ and had considered the contribution to the torque field from a shell of six neighbors taken to lie in the equatorial plane. Here we show numerically that this approximation is quite reasonable. We study the dependence of $S_{IJ}\equiv\Sigma_{ij}S_{ij}$ on Z_{IJ}. We still assume perfect nematic order, so that $\mathbf{a}_I=\mathbf{a}_J=e_z$. Then the sum in Eq. (50) becomes

$$S_{IJ}(Z)=\sum_{ij}[R^2+(Z+z_i-z_j)^2]^{-5}[R^2-(Z+z_i-z_j)^2], \quad \text{(E1)}$$

and we see that

$$\frac{\kappa_{IJ}^{(2)}(Z)}{\kappa_{IJ}^{(2)}(0)}=\frac{S_{IJ}(Z)}{S_{IJ}(0)}. \quad \text{(E2)}$$

For the one-molecule terms we similarly note that the Z dependence in Eq. (59) is reproduced by writing

$$\begin{aligned}\tilde{\kappa}_{IJ}^{(1)}(Z)\propto&\sum_{ii'j}q_iq_{i'}(\overline{x_i'}\overline{y_{i'}'}-\overline{x_{i'}'}\overline{y_i'})\frac{(\overline{\mathbf{D}}_{i'j}\cdot\mathbf{a}_J)}{\overline{D}_{ij}^3\overline{D}_{i'j}^5}\\ =&\sum_{ii'j}\frac{\wp_0^2(Z+\overline{z_{i'}'}-\overline{z_j'})\sin[q(\overline{z_{i'}'}-\overline{z_i'})]}{[R^2+(Z+\overline{z_i'}-\overline{z_j'})^2]^{3/2}[R^2+(Z+\overline{z_{i'}'}-\overline{z_j'})^2]^{5/2}}, \end{aligned} \quad \text{(E3)}$$

in the notation of Eqs. (59) and (60).

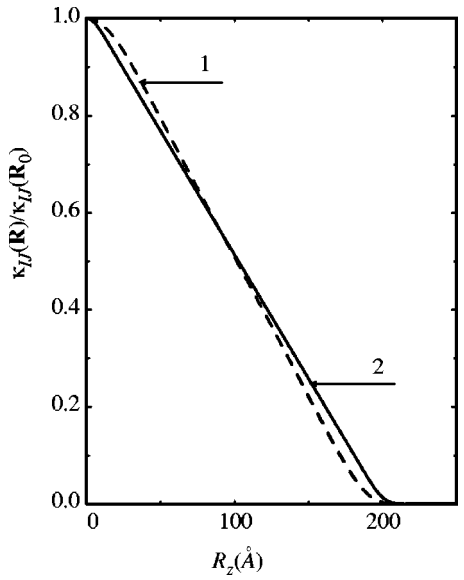

FIG. 10. The ratio $\kappa_{IJ}^{(n)}(Z)/\kappa_{IJ}^{(n)}(0)$, where Z is the z component of $\mathbf{R}_{IJ}$ for molecules of length $L=200$ Å and intermolecular separation $R=20$ Å. For $n=1$ we show essentially indistinguishable curves for $q=0.0444$ $(\text{Å})^{-1}$ and for $q=0.1333$ $(\text{Å})^{-1}$. For $n=2$ this ratio does not depend on q.

These results allow us to compute the ratio $\kappa_{IJ}^{(n)}(Z)/\kappa_{IJ}^{(n)}(0)$ which is shown in Fig. 10 for $n=1$ and $n=2$. This result is representative of the situation for a wide range of parameters. As one might expect, the contribution to the torque field decreases strongly as $|Z|/L$ increases towards unity. Accordingly, the approximation of including only the effect of equatorial neighbors is a good one.

APPENDIX F: CONTRIBUTIONS TO $H^{(1)}$

In this appendix we discuss the evaluation of the one-molecule contributions to $\tilde{\kappa}_{IJ}$. We consider the terms in the last two lines of Eq. (38). We will analyze the one-molecule contributions which arise when $i=i'$ but j and j' are in general different. In the intermediate excited state only atom i is in an excited state. Atoms j and j' remain in their ground states. Calling this term T we write

$$T=-3\sum_{i,j,j'} e^2 q_j q_{j'} \left\langle 0 \left| x_i' y_{j'}' D_{ij'}^{-3} \frac{1}{\mathcal{E}} x_i' x_j' \mathbf{D}_{ij}\cdot\mathbf{a}_I D_{ij}^{-5} \right| 0 \right\rangle + \cdots, \tag{F1}$$

where the dots denote the three additional terms required to make the expression be rotationally invariant. (These can be reconstructed at the end of the calculation.) Using the expansion of Eq. (36) we have

$$\begin{aligned} T=&-3e^2\sum_{ijj'} q_j q_{j'} \left\langle 0 \left| [\Delta x_i' \overline{D}_{ij'}^{-3} \right.\right. \\ &+\overline{x_i'}\Delta z_i'(\boldsymbol{\nabla}_{iz} D_{ij'}^{-3})]\overline{y_{j'}'}\frac{1}{\mathcal{E}}\{\Delta x_i' \mathbf{D}_{ij}\cdot\mathbf{a}_I D_{ij}^{-5} \\ &\left.\left. +\overline{x_i'}\Delta z_i' \boldsymbol{\nabla}_{iz}[(\mathbf{D}_{ij}\cdot\mathbf{a}_I)D_{ij}^{-5}]\}\overline{x_j'} \right| 0 \right\rangle + \cdots \\ \approx&-3e^2\sum_{ijj'} q_j q_{j'} \left\langle 0 \left| \Delta x_i' \frac{1}{\mathcal{E}} \Delta x_i' \right| 0 \right\rangle \overline{x_j' y_{j'}'} \overline{D}_{ij'}^{-3} \\ &\times(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I)\overline{D}_{ij}^{-5}+\cdots. \end{aligned} \tag{F2}$$

Now we carry the sum over j (j') over the charges that comprise the dipole moment $\mathbf{p}_j(\mathbf{p}_{j'})$ on atom j (j') to get

$$\begin{aligned} T=&-3e^2\sum_{ijj'} \left\langle 0 \left| \Delta x_i' \frac{1}{\mathcal{E}} \Delta x_i' \right| 0 \right\rangle [p_{yj'}' \overline{D}_{ij'}^{-3} \\ &+p_{zj'}'\overline{y_{j'}'}(\boldsymbol{\nabla}_{j'z} D_{ij'}^{-3})]\{p_{xj}'(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I)\overline{D}_{ij}^{-5} \\ &+p_{zj}'\overline{x_j'}\boldsymbol{\nabla}_{jz}[(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I)D_{ij}^{-5}]\}+\cdots \\ \approx&-3e^2\sum_{ijj'} \left\langle 0 \left| \Delta x_i' \frac{1}{\mathcal{E}} \Delta x_i' \right| 0 \right\rangle p_{yj'}' p_{xj}' \overline{D}_{ij'}^{-3} \\ &\times(\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I)D_{ij}^{-5}+\cdots, \end{aligned} \tag{F3}$$

where now j and j' refer to atoms. Restoring the additional terms to preserve rotational invariance we obtain

$$\begin{aligned} T=&-3e^2\sum_{ijj'} \left[\left\langle 0 \left| \Delta x_i' \frac{1}{\mathcal{E}} \Delta x_i' \right| 0 \right\rangle + \left\langle 0 \left| \Delta y_i' \frac{1}{\mathcal{E}} \Delta y_i' \right| 0 \right\rangle \right] \\ &\times[p_{yj'}' p_{xj}' - p_{xj'}' p_{yj}'] \overline{D}_{ij'}^{-3} (\overline{\mathbf{D}}_{ij}\cdot\mathbf{a}_I) D_{ij}^{-5}. \end{aligned} \tag{F4}$$

When the indices are relabeled, this result reproduces part of Eq. (59).

APPENDIX G: EVALUATION OF INTEGRALS IN SEC. V

In this appendix we evaluate the integral X_1 in Eq. (63) and an integral needed to evaluate the dipolar interaction energy between two long helices.

Consider the asymptotic evaluation of Eq. (63), first, in the limit $L \gg R$. End effects can be shown to be negligible, in which case the final summation (over $\tilde{s}_j$) introduces a factor of N and one sets $s_j=0$. Also we consider only the continuum limit in which the sums are replaced by integrals. One can show that correct to leading order in $\tilde{L}^{-1}$, the limits on the integrals can be extended to $\pm\infty$. Thus we have the asymptotic result

$$\begin{aligned} X_1(\tilde{q},\tilde{L}) \sim& 3N^3 \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds' \left[\frac{1-\tilde{L}^2 s s'}{(1+\tilde{L}^2 s^2)^{5/2}(1+\tilde{L}^2 s'^2)^{5/2}} \right] \\ &\times(s'-s)\sin[qL(s'-s)]. \end{aligned} \tag{G1}$$

For each of the two factors in the denominator we introduce the representation

$$p^{-5/2} = \frac{1}{(3\sqrt{2\pi})} \int_{-\infty}^{\infty} x^4 e^{-(1/2)px^2} dx. \tag{G2}$$

Then the integrations over s and s' can be done analytically and eventually one finds that

$$X_1(\tilde{q},\tilde{L}\to\infty) = 8(\rho R)^3 (qR) I_1^2(qR), \tag{G3}$$

where I_1 is defined in Eq. (67) of the text.

The limit $\tilde{L}\to 0$ is trivial. We find that

$$X_1(\tilde{q},\tilde{L}\to 0)=N^3\phi(\tfrac{1}{2}qL), \tag{G4}$$

where $\phi(x)=-(3/2)(d/dx)[(\sin x)/x]^2$.

Finally we evaluate the dipolar interaction energy E_{dd} between two long helical molecules, *a* and *b*, separated by a distance *R* along the *x* axis. We assume that the radius of the helix is much less than *R*. In this limit, in terms of the atomic dipole moments we write

$$\begin{aligned}E_{dd}=\rho^2\int_{-L/2}^{L/2}dz_a\int_{-L/2}^{L/2}dz_b[R^2+z_{ab}^2]^{-3/2}\Big\{&[p_x''\cos(qz_a+\phi_a)-c\tilde{p}_y''\sin(qz_a+\phi_a)][p_x''\cos(qz_b+\phi_b)\\&-c\tilde{p}_y''\sin(qz_b+\phi_b)]\left[1-\frac{3R^2}{R^2+z_{ab}^2}\right]+[p_x''\sin(qz_a+\phi_a)+c\tilde{p}_y''\cos(qz_a+\phi_a)][p_x''\sin(qz_b+\phi_b)\\&+c\tilde{p}_y''\cos(qz_b+\phi_b)]\Big\},\end{aligned} \tag{G5}$$

where $\tilde{p}_y''=p_y''+aqp_z''$, $\phi_a(\phi_b)$ is the angle of rotation of molecule *a* (*b*) about its long axis, and $z_{ab}=z_a-z_b$. Here we did not include terms involving p_z' which either are independent of both angles ϕ_a and ϕ_b or vanish in the limit $L\to\infty$. In that limit we only need to keep terms which depend on z_{ab}, in which case we have

$$E_{dd}=\tfrac{1}{2}\rho^2\wp_0^2L\int_{-\infty}^{\infty}\cos(qz_{ab}+\phi_{ab})\left[\frac{2z_{ab}^2-R^2}{(R^2+z_{ab}^2)^{5/2}}\right]dz_{ab}, \tag{G6}$$

where $\phi_{ab}=\phi_a-\phi_b$. Using Eq. (G2) we obtain the final result

$$E_{dd}=-L\rho^2\wp_0^2q^2I_{-1}\cos\phi_{ab}\equiv-\tfrac{1}{2}V_{dd}\cos\phi_{ab}. \tag{G7}$$

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