The contribution of the Chirality-Induced Spin Selectivity (CISS) effect to the dispersion interaction between chiral molecules

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ABSTRACT
Dispersion interactions are one of the components of van der Waals forces, which play a key role in the understanding of intermolecular interactions in many physical, chemical and biological processes. The theory of dispersion forces was developed by London in the early years of quantum mechanics. However, it was only in the 1960s that it was recognized that for molecules lacking an inversion center such as chiral and helical molecules, there are chirality-sensitive corrections to the dispersion forces proportional to the rotatory power known from the theory of circular dichroism and with the same distance scaling law $R^{-6}$ as the London energy. The discovery of the Chirality-Induced Spin Selectivity (CISS) effect in recent years has led to an additional twist in the study of chiral molecular systems, showing a close relation between spin and molecular geometry. Motivated by it, we propose in this investigation that there may exist additional contributions to the dispersion energy related to intermolecular, induced spin-orbit (ISOC) interactions. Within a second-order perturbative approach, these forces manifest as an effective intermolecular spin-spin exchange interaction. Although they are weaker than the standard London forces, the ISOC interactions turn out to be nevertheless not negligible and display the same $R^{-6}$ distance scaling. Our results suggest that classical force field descriptions of van-der-Waals interactions may require additional modifications to include the effects discussed here.

I. INTRODUCTION
Dispersion forces, together with Keesom and Debye forces, are the three pillars building the van-der-Waals (vdW) interactions, which are ubiquitous in physics, chemistry and biology, and of fundamental importance for understanding weak intermolecular interactions. While Keesom and Debye forces can be explained within classical physics, only the advent of the quantum theory allowed to introduce and rationalize dispersion forces. In fact, the quantum mechanical theory of dispersion interactions was developed by London already in the early years of quantum mechanics. Their approach was based on a second-order perturbation treatment describing the interaction between fluctuating dipole moments in a pair of interacting molecules at distance $R$, and it naturally led to an attractive contribution to the potential energy with an $R^{-6}$ distance dependence. Meanwhile, very sophisticated methodological developments have taken place to account for vdW interactions in the modelling of physical systems, see e.g. 7,8,9. Interestingly, slightly earlier than the work by London and
Eisenchitz, Rosenfeld\textsuperscript{10} formulated, also based on a perturbative treatment, a theoretical framework to describe natural optical activity. The Rosenfeld equation provided the basis for quantifying experiments in optical circular dichroism. It relates the difference in absorption of right- and left circularly polarized light crossing a sample of randomly oriented molecules to the imaginary part of a product of transition matrix elements of the electric dipole and the magnetic dipole operators: \( \text{Im} \left[ \langle 0 | \mu_e | n \rangle \langle n | \mu_m | 0 \rangle \right] \). This so-called rotatory power can be shown to be non-vanishing only for chiral molecules and it changes sign when going from one enantiomer to the other, since under an inversion operation, the dipole moment operator behaves as a polar vector while the magnetic moment operator behaves as an axial vector.\textsuperscript{11}

A natural question which may arise is whether the interaction between chiral molecules—in particular dispersive interactions—may allow for chiral discrimination. Theoretical research in this direction started as early as in the 1960s by Craig, Power, and Thirunamachandran,\textsuperscript{12,13} and has been continued mostly in the works by Woolley,\textsuperscript{14,15,16} Barron,\textsuperscript{11,17} and Salam.\textsuperscript{18,19,20,21} Methodologically, these investigations use either second-order perturbation theory (as in London’s paper) or so-called molecular quantum electrodynamics (mQED). The latter approach describes dispersion forces via the exchange of virtual photons and allows to obtain general expressions describing not only non-retarded dispersion interactions (with the \( R^6 \) power law behavior), but also the retarded Casimir-Polder interactions (scaling as \( R^8 \)). A fundamental result of all these studies is that there exists a contribution to dispersion forces, which is chirality-sensitive, and it involves a susceptibility tensor closely related to the rotatory power introduced by Rosenfeld.

Also associated to chiral molecules is the recently discovered Chirality-Induced Spin Selectivity (CISS) effect.\textsuperscript{22,23} The CISS effect suggests a non-trivial connection between spin and geometry in chiral molecules and it has been extensively demonstrated in a very broad class of molecular systems and under very different experimental conditions.\textsuperscript{24,25,26,27,28,29,30,31,32,33,34} Theoretically, also a large number of studies based on model Hamiltonian\textsuperscript{35,36,37,38,39,40,41,42,43,44,45,46,47} and, more recently, first-principle\textsuperscript{48,49,50,51} approaches has been presented. A common starting point in the vast majority of the presented models so far is the presence of a specific spin-orbit coupling contribution connected with the helical geometry (either postulated or obtained through a coarse-graining procedure). Still, the ultimate origin of the CISS effect remains a matter of intense debate, see e.g. the recent discussions in Refs.\textsuperscript{44,52,53}

Can CISS-related interactions provide also a contribution to the interaction energy between chiral molecules? A hint that this might be the case was presented in the combined experimental-theoretical study by Kumar et al.\textsuperscript{28}, where a Density-Functional calculation revealed a chirality-sensitive energy contribution for the interaction between a pair of molecules, which turned out to be less repulsive for the homochiral pair than for the heterochiral one. The implications of these results could be crucial for the treatment of e.g. intermolecular interactions and biological recognition.\textsuperscript{32} The obtained contribution had, however, its origin in electronic exchange effects (see also Ref.\textsuperscript{49} for a study of exchange interactions in arrays of helical molecules). Exchange interactions and the associated antisymmetrization of the electronic wave functions are, nevertheless, in general negligible for both non-retarded (London) and retarded (Casimir-Polder) ranges, and a more phenomenological approach may be required to include the influence of the CISS effect in this range. More recently, San Sebastian et al.\textsuperscript{30} demonstrated enantiospecific response in Nuclear Magnetic Resonance experiments for a class of optically active metal–organic frameworks. Although no full theoretical description was developed in the paper, it was nevertheless suggested that besides the well-known \( J-J \) coupling required to describe spin-spin interactions in NMR setups, an additional contribution might be needed to account for chirality-induced electron spin polarization. This contribution would have the form of a generic Rashba-
like term describing spin-orbit coupling mediated by a chiral electric field, an idea originally introduced in Refs. 54, 55; in the context of model Hamiltonians.

Inspired by these studies, we suggest here a novel contribution to dispersion forces mediated by induced spin-orbit interactions between helical molecules. The approach is largely phenomenological, since we are not aiming at this stage at a microscopic derivation of the model. We rather assume that the electric field generated by a fluctuating dipole in one molecule can act as the source of a spin-orbit coupling contribution in the second molecule, the same holding for the second molecule. This is similar to the Rashba-like term suggested in Ref. 10, which thus takes into account the contribution of the CISS effect in our model.

To simplify the problem, we will work only within the dipole approximation and do not include higher-order multipole moments of the helical molecules. 3 Only the so called near-zone will be addressed, for which the distance between the molecules \( R \ll \frac{\lambda}{\epsilon} \), with \( \lambda \) being the reduced wavelength of a typical electronic transition. In this region, a second order perturbation treatment using static dipole-dipole interactions yields the same results as with the more general and powerful method of molecular quantum electrodynamics, which requires going to fourth order perturbation theory and a very careful diagrammatic analysis. 18 Moreover, a standard mQED treatment including spin-orbit interaction does not seem straightforward at this stage, since the Hamiltonians used in mQED are intrinsically non-relativistic, and it is not yet evident how to derive in a consistent way the corresponding spin-orbit coupling terms, allowing to formulate a consistent diagrammatic description.

Being aware of these limitations, we will, therefore, postulate that in the near-zone regime the mutual interaction between helical molecules will not only lead to the already known dipole-dipole dispersion forces, but that the electric dipole field of each molecule can lead to a spin-orbit coupling energy term in the other molecule’s Hamiltonian. We find that there is a small, but non-negligible correction to the London dispersion energy arising from these interactions, displaying at the level of the dipole approximation an \( R^6 \) scaling. Moreover, within a perturbative approach, this intermolecular spin-orbit (ISOC) interaction can be mapped onto an effective generalized anisotropic Heisenberg-like Hamiltonian describing spin-spin exchange interactions. As mentioned above, the CISS contribution in our model is included through this ISOC, i.e. the electric field generated by one of the two molecules acts as the effective field that triggers the CISS response in the other molecule. To further proceed, we adopt a heuristic point of view associating triplet energies to homochiral interactions and singlet energies to heterochiral ones, which is in the spirit of the commonly accepted qualitative explanation of the CISS effect. 27, 28, 56

As an additional test of the consistency of our results we have performed Density-Functional based calculations of the interaction energy of a system consisting of two hexa-helicene molecules. A general symmetry analysis 11 indicates that a key element in the onset of chiral discrimination is its dependence on the breaking of space inversion symmetry. This implies that the description of chiral molecules must include in general both the electric and magnetic susceptibility tensors; it also implies that the results must be either absent or be considerably weaker for linear molecules having a center of inversion. In addition to these general considerations, the results of our calculations provide strong support for our model, since the chiral discrimination effect, leading to different interaction energies for homochiral and heterochiral pairs, is non-zero only if the DFT calculations include a dispersion term. This result by itself is, however, not enough to clarify the separate contribution of the CISS effect to the van der Waals interactions, which is the central subject of our contribution.
Despite the limitations of our approach, we believe that our results point to the potential relevance of spin-related interactions between helical molecules within the van-der-Waals interaction range, and the fact that the CISS contribution has the same distance dependence as the ordinary term based on London theory, but it now includes the fundamental result that this interaction depends on intermolecular relative spin orientation. Our results can therefore be of interest in addressing the chiral discrimination component of intermolecular interactions in biological systems, where chiral structures are ubiquitous, as well as the interplay between the magnetic response arising from the CISS effect and the modified form of vdW interactions we are suggesting here.

In the next section we will describe briefly the Density-Functional calculations (Sec. II.A) before presenting our model Hamiltonian for the ISOC (Sec. II.B) and analyzing it in second order degenerate perturbation theory (Sec. II.C). In Sec. II.D, the electron-on-a-helix model is introduced for calculating the relevant electrical transition dipole moments. The results are then presented in Sec. III.A-C. A summary of the results and an outlook of open issues is finally provided in Sec. IV.

II. INDUCED INTERMOLECULAR SPIN-ORBIT COUPLING IN CHIRAL MOLECULES

A. Preliminary: A Density-Functional-Theory based calculation of chiral discrimination energies

Before introducing our proposed model for intermolecular induced spin-orbit coupling (ISOC), we have carried out a standard atomistic DFT calculation including van der Waals interactions for a homo- and a heterochiral molecular pair in order to obtain a first insight into the orders of magnitude of the energetic differences of the D-D pair when compared with a D-L pair in the absence of spin-related effects. We have chosen helicene as a simple carbon-based model molecular system, which does not have a sizeable permanent dipole moment in the ground state, so that the main contribution to vdW interactions is expected to arise from dispersion interactions.

We have carried out two types of calculations: (i) for D-D and D-L pairs while enforcing their helical axis to be parallel to each other without further optimization of the relative orientation or intermolecular separation (see Figure S0 in the supplementary material section); (ii) full structural optimization with a search of the local minima for D-D and D-L configurations (see Figures S1 and S2 in the supplementary material section, where also additional technical details of the DFT calculations are provided). In this latter case the structural minimization procedure results in final structures displaying a difference in relative orientation between the enantiomers in the D-L case compared to the D-D case.

In approach (i) we obtained an energy difference $\Delta E_{ch} = E_{DD} - E_{DL}$ between D-D and D-L arrangements of $\Delta E_{ch} = -0.24$ eV, indicating that the D-D configuration has a smaller energy than the D-L one. In contrast, the approach (ii) yields $\Delta E_{ch} = +0.35$ eV, i.e. the D-L conformation is energetically preferred, which is clearly related to the larger degree of orientational freedom allowed in this second calculation. In any case, these energies can be considered as a measure of the “discrimination power” of a DFT calculation including dispersion interactions. Although at the range of the obtained typical equilibrium distances (~2.9-3.5 Å, similar for the D-D and D-L cases) electronic exchange interactions may still play a role, we have found out that the major contribution to the discriminative interactions is provided by the dispersion interactions. In fact, we have, in case (ii), artificially switched off dispersion contributions, and found that the value of $\Delta E_{ch}$ goes down by roughly a factor of 10 to ~27 meV.
As already stressed in the Introduction, these DFT calculations clearly indicate that chiral discrimination
is absent if dispersion forces are not explicitly included. However, this leaves unanswered the question
as to whether there is a separate contribution arising from the CISS effect. The general question of
separating exchange and spin-orbit contributions in a many-body description is an intricate one because
these terms are not independent due to symmetry constraints on the wave function and the Hamiltonian
itself. These considerations are especially important for our understanding of spin polarization
phenomena in chiral systems, and justify the use of model calculations, like the one considered here,
which can shed light on this important topic. In what follows, we will show that to second order in the
spin-orbit coupling an effective intermolecular spin-spin interaction emerges, which can contribute to
the discriminatory power between enantiomers.

B. The model Hamiltonian

Assuming that retardation effects do not play any role in the relevant separation ranges between
molecules \(R\ll\hbar\), we can use static potentials within the dipole approximation (to lowest order) and
write for the proposed spin-orbit interaction operator the following expression (we are going to use all
along the Einstein sum convention for Greek indices):

\[
H = H_0^A + H_0^B + H_{\text{int}},
\]

\[
H_{\text{int}} = H_{\text{ex-A}} + H_{\text{ex-B}} = \lambda_{SO} \sigma_B \left( p(B) \times \vec{E}_A(R) \right) + \lambda_{SO} \sigma_A \left( p(A) \times \vec{E}_B(R) \right),
\]

\[
E_{j=A,B,\alpha}(R) = -\frac{1}{4\pi\varepsilon_0} \frac{\mu_\beta(j)}{R^3} (\delta_{\alpha\beta} - 3 \hat{r}_\alpha \cdot \hat{r}_\beta) = -\frac{1}{4\pi\varepsilon_0} T_{\alpha\beta} \mu_\beta(j).
\]

\(H_0^A\) and \(H_0^B\) are zero-order non-interacting single-particle Hamiltonians, which will be specified later
on. \(\mu_\beta(j)\) is the \(\beta\) component of the dipole moment operator of molecule \(j=A,B\), \(r_\alpha = R_\alpha / R\), and
\(R = |R_A - R_B|\) is the distance between molecules \(A\) and \(B\). Using the Levy-Civita tensor, the interaction
part can be written as:

\[
H_{\text{int}} = -\frac{\lambda_{SO}}{4\pi\varepsilon_0} \sum_{j=A,B} \sum_{\alpha=A,B} e_{\alpha\beta\gamma} \sigma_\alpha(\gamma) p_\beta(l) T_{\alpha\beta} \mu_\beta(j).
\]

It is important to notice at this point that the coupling strength \(\lambda_{SO}\) may be in general different from the
bare relativistic coupling \(\epsilon \hbar / (2mc)^2\), and can involve in a non-trivial way electronic matrix
elements, see e.g.. Moreover, it does not need to be in general equal in both summands of Eq. (1)
if the molecules are different. Hence, we leave it as an open parameter and provide later on a rough
estimate of its possible orders of magnitude. Moreover, notice that no symmetrization of the Hamiltonian
is required to make it Hermitian, since the momentum operator acts on different degrees of freedom as
the \(T\)-tensor. Finally, we do not consider the molecules to possess a permanent dipole moment, which
would lead to additional corrections arising from induction forces. Such contributions can be treated
separately. The model describes, thus, how a fluctuating dipolar field on one molecule induces not only
a fluctuating dipole on the other molecule, but also a spin-orbit field.

C. Degenerate perturbation theory
In the lowest-level approximation we will assume that the zero-order wave functions originate from a (helical) molecule without intrinsic spin-orbit interactions, i.e. spin-orbit coupling in a molecule arises only through the influence of the other molecule as previously mentioned. This is a reasonable, though simplified, starting point, since we are not addressing here issues related to spin transport and the resulting spin polarization in helical systems, which require the inclusion of intramolecular spin-orbit and, most likely, exchange effects. How to account for CISS-related effects will be discussed later on.

In the absence of the spin degrees of freedom, a standard second order perturbative approach would be sufficient as commonly used to derive the London dispersion energy. However, in our case each molecular energy eigenvalue in zero order is twofold degenerate because of spin. This implies that for the two interacting molecules there is a fourfold spin degeneracy for each energy eigenvalue $E_{nm} = E_n(A) + E_m(B)$. Within each of these subspaces we can define a tensor product basis of the form $(\uparrow \uparrow), (\uparrow \downarrow), (\downarrow \uparrow), (\downarrow \downarrow)$. The first spin component refers to molecule A, the second one to molecule B.

Now, it turns out that perturbative corrections which are first order in the spin-orbit coupling strength from Eq. (1) identically vanish, since the matrix elements of the momentum operator over the ground state are zero, i.e.: $\langle 0_A \uparrow, 0_B \uparrow | H_{\text{int}} | 0_A \uparrow, 0_B \uparrow \rangle = - \delta_{\alpha \beta} \langle \uparrow | \sigma_{\alpha}(B)| \uparrow \rangle \langle 0_B | p_{\beta}(B) | 0_B \rangle T_{\rho \sigma} \langle 0_A | \mu_{\rho}(A) | 0_A \rangle = 0$.

This is in contrast to the standard dipole-dipole forces, which contain directly the product of dipole matrix elements and hence can give a nonzero contribution in the ground state, if the molecules possess permanent dipole moments. As a result, we need to use second-order degenerate perturbation theory. Here, the secular matrix for the perturbation $H_{\text{int}}$ needs to be built within each fourfold degenerate spin subspace of the Hilbert space of the interacting molecules, $H = H_A \otimes H_B$, using the previously introduced spinor basis. The obtained eigenvalues of the 4x4 secular matrix will provide the required energy corrections to the non-interacting ground state of the two molecules to second order in the spin-orbit coupling strength.

A typical matrix element will, therefore, look like:

\[
\langle n_{A,y}, m_{B,x} | H_{\text{int}} | 0_{A,y}, 0_{B,x} \rangle = \sum_{\omega_{n0}, \omega_{m0}} \frac{1}{\omega_{n0} + \omega_{m0}} \left\langle 0_{A,y}, 0_{B,x} | H_{\text{int}} | n_{A,y}, m_{B,x} \rightangle \langle n_{A,y}, m_{B,x} | H_{\text{int}} | 0_{A,y}, 0_{B,x} \rangle.
\]

We have used the simplified notation $\langle n_{A,y}, m_{B,x} \rangle = \langle n_{A,y} \rangle \otimes \langle m_{B,x} \rangle$, and $\omega_{n0} = E_n(A) - E_0(A)$.

After a lengthy but straightforward calculation, we obtain the following tensor representation of the second-order energy correction (using Einstein’s sum convention):

\[
W^{(2)}(R) = 1_A \otimes \sigma_{\alpha} B^A_{\alpha p} \sigma_{\beta} B^B_{\beta p} + \sigma_{\alpha} A^A_{\alpha p} \sigma_{\beta} A^B_{\beta p} \otimes 1_B + \epsilon_{\alpha \beta \gamma} \{ 1_A \otimes \sigma_{\xi} B^A_{\alpha p} + Q_{\alpha p}^{AB} \sigma_{\xi} A^A_{\alpha p} \otimes 1_B \} + \sigma_{\alpha} A^A_{\alpha p} \otimes \sigma_{\beta} B^B_{\beta p} (K_{\alpha p}^{BA} + K_{\alpha p}^{AB}).
\]
In the second row, the first term is diagonal in spin space while the third one has the form of a generalized spin-spin contribution with effective spin-exchange coupling \( J_{ab} = K_{ab}^{RA} + K_{ab}^{AB} \). The middle term can be rewritten as an effective magnetic Zeeman-like interaction acting separately on the A- and B-subspaces:

\[
i \varepsilon_{ab} \mathbf{Q}_{ab}^{RA} = i l_A \otimes \mathbf{\sigma}_x \mathbf{Q}_{ab}^{RA} = i l_A \otimes \mathbf{\sigma}_x \mathbf{B}_z = i l_A \otimes \mathbf{\sigma}_x \cdot \mathbf{b}^{RA}.
\]

(5)

This leads to the more compact expression:

\[
W^{(2)}(R) = l_A \otimes l_B (\mathbf{Q}_{aa}^{RA} + \mathbf{Q}_{aa}^{AB}) + i [l_A \otimes \mathbf{\sigma}_x \cdot \mathbf{b}^{RA} + \mathbf{\sigma}_x \cdot \mathbf{b}^{AB} \otimes l_B] + J_{ab} \mathbf{\sigma}_a \otimes \mathbf{\sigma}_b.
\]

(6)

which is the central result of our investigations.

In Eq. (4) we have introduced the tensor:

\[
\mathbf{Q}_{ab}^{RA} = -\left( \frac{\lambda_{SO}}{4\pi e_0} \right)^2 \mathbf{e}_{\alpha \gamma} \mathbf{e}_{\beta \gamma} T_{\gamma \rho} T_{\gamma' \rho'} \sum_{n,m=0} \frac{1}{\omega_{n0} + \omega_{m0}} p_c^{\text{on}}(B) \mu_{\rho}^{\text{on}}(A) p_{\rho}^{\text{on}}(B) \mu_{\rho}^{\text{on}}(A) =
\]

(7)

\[
= -\left( \frac{\lambda_{SO}}{4\pi e_0} \right)^2 \frac{m_e}{e\hbar} \mathbf{e}_{\alpha \gamma} \mathbf{e}_{\beta \gamma} T_{\gamma \rho} T_{\gamma' \rho'} \sum_{n,m=0} \frac{\omega_{n0}^2}{\omega_{n0} + \omega_{m0}} \mu_c^{\text{on}}(B) \mu_{\rho}^{\text{on}}(A) \mu_{\rho}^{\text{on}}(A) =
\]

\[
= -\left( \frac{\lambda_{SO}}{4\pi e_0} \right)^2 \frac{m_e}{e\hbar} \mathbf{e}_{\alpha \gamma} \mathbf{e}_{\beta \gamma} T_{\gamma \rho} T_{\gamma' \rho'} \int_0^\infty \frac{du}{2\pi} \left\{ 2 \sum_{n,m=0} \frac{\omega_{n0}^3}{u^2 + \omega_{m0}^2} \mu_c^{\text{on}}(B) \mu_{\rho}^{\text{on}}(B) \right\} \left( 2 \sum_{n=0} \frac{\omega_{n0}}{u^2 + \omega_{n0}^2} \mu_{\rho}^{\text{on}}(A) \mu_{\rho}^{\text{on}}(A) \right)
\]

\[
= -\lambda_{SO}^2 \mathbf{e}_{\alpha \gamma} \mathbf{e}_{\beta \gamma} T_{\gamma \rho} T_{\gamma' \rho'} \int_0^\infty \frac{du}{2\pi} \Gamma^{\beta \rho}(iu) \alpha_{\rho\rho}(iu).
\]

The second row in Eq. (7) is obtained by using the general relation:

\[
\langle n | p_\alpha | m \rangle = \frac{i \hbar}{\omega} (E_n - E_m) \langle n | \mathbf{e}_\alpha | m \rangle = -\frac{i \hbar}{\omega} \omega_{mn} \langle n | \mu_\alpha | m \rangle,
\]

to express the momentum matrix elements in terms of dipole matrix elements. In the third row, we have used the identity:

\[
\frac{1}{a+b} = \frac{2}{\pi} \int_0^\infty \frac{du}{(a^2 + u^2)(b^2 + u^2)}.
\]

to define the two susceptibility tensors of the last row of Eq. (7). In a similar way the \( \mathbf{K} \)-tensor in Eq. (4) is given by:
$K_{\alpha\beta}^{RA} = \left( \frac{\lambda_{SO}}{4\pi e_0} \right)^2 \epsilon_{\alpha\gamma\delta} \epsilon_{\beta\gamma\nu} T^\gamma_{\gamma,\gamma'} T^\nu_{\nu,\gamma'} \sum_{n,m=0} \frac{1}{\omega_{a0} + \omega_{n0}} p_{\epsilon0}^{(n)}(A) \mu_{\mu0}^{(n)}(B) \mu_{\nu0}^{(n)}(A) = \frac{\lambda_{SO}}{4\pi e_0} \left( \frac{m_e}{e \hbar} \right)^2 \epsilon_{\alpha\gamma\delta} \epsilon_{\beta\gamma\nu} T^\gamma_{\gamma,\gamma'} T^\nu_{\nu,\gamma'} \sum_{n,m=0} \frac{\omega_{a0}\omega_{n0}}{\omega_{a0} + \omega_{n0}} \mu_{\epsilon0}^{(n)}(A) \mu_{\mu0}^{(n)}(B) \mu_{\nu0}^{(n)}(A) = \frac{\lambda_{SO}^2}{4\pi e_0} \epsilon_{\alpha\gamma\delta} \epsilon_{\beta\gamma\nu} T^\gamma_{\gamma,\gamma'} T^\nu_{\nu,\gamma'} \int_0^\infty \frac{d\epsilon_{\alpha\gamma\delta} \epsilon_{\beta\gamma\nu} T^\gamma_{\gamma,\gamma'} T^\nu_{\nu,\gamma'}}{2\pi} \pi^B_{\mu\nu}(iu) \Pi_{\gamma'}^{(A)}(iu)$. 

Due to $Q^{BA} = (Q^{BA})^\dagger$ and $K^{BA} = (K^{BA})^\dagger$ the $Q$- and $J$-tensors are Hermitian. However, if the $Q$-tensor is real, the contribution arising from Eq. (5) identically vanishes, since there will be terms with the following form: $\epsilon_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} Q^{BA}_{\alpha\beta\gamma} = \epsilon_{\alpha\beta\gamma} Q^{BA}_{\alpha\beta\gamma} - \epsilon_{\alpha\beta\gamma} Q^{BA}_{\alpha\beta\gamma} = (\epsilon_{\alpha\beta\gamma} - \epsilon_{\alpha\beta\gamma}) Q^{BA}_{\alpha\beta\gamma} = 0$. On the other hand, if the zero-order Hamiltonian has complex eigenstates (e.g. by considering intra-molecular spin-orbit interactions), then the $Q$-tensor is not real and the expression in Eq. (5) does not necessarily vanish. In this study we will only consider the case of real wave functions and, hence, the SOC energy correction to the dispersion interaction adopts the simpler form:

$W^{[2]}(R) = 1_A \otimes 1_B (Q_{\alpha\alpha}^{BA} + Q_{\alpha\alpha}^{AB}) + J_{\alpha\beta} \sigma_\alpha^A \otimes \sigma_\beta^B$. 

In the last row of Eqs. (7) and (8) we have introduced atomic units to obtain a single effective coupling constant $\lambda_{eff}$. Expressing the energy scale in units of $\hbar^2 / m_e a_B^2$ and length scales in Bohr radii $a_B$, we have $(\lambda_{SO}$ has dimensions of C s kg$^{-1}$):

$\lambda_{eff} = \frac{\hbar \lambda_{SO}}{ea_B^2} = 2.34 \times 10^9 \times \lambda_{SO}$. 

If the full susceptibility tensors are considered as in Eqs. (7) and (8), then only numerical expressions can be obtained for the roots of the secular equation and, therefore, an underlying model is needed for the zero-order Hamiltonian. We will therefore first discuss the isotropic limit, which allows for an explicit analytical solution of the roots of the secular matrix. In the supplementary information we show, by exploiting the Unsöld approximation,38 that the spin-spin exchange term in Eq. (9) can be related to the square dipole fluctuations in the ground state of the respective molecules.

**Degenerate perturbation theory in the isotropic case.** Although Eq. (9) already provides a basis for the calculations, to further simplify the expressions we will assume that the susceptibility tensors are isotropic (this is, of course, a strong simplification for a molecular system with helical symmetry, which will be lifted later on in this study). Thus, e.g.

$\alpha_{j,j'}^{\gamma-A,B}(iu) = \delta_{j,j'} \frac{2}{\sum_{n=m} \frac{\omega_{a0}}{n+2} \omega_{a0} (j) \mu_{\mu0}^{(n)}(j) = \delta_{j,j'} \frac{2}{\sum_{n=m} \frac{\omega_{a0}}{n+2} + (\omega_{a0})^2} | \langle 0 | \mu_{\gamma-A,B} | n \rangle |^2$, 

and similar for the other tensors. In this way the $Q$- and $K$-tensors reduce to:
\[ Q_{\alpha\beta}^{\text{RA}} = -\lambda_{\alpha\beta}^{2} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ \delta_{\alpha\gamma} - \frac{1}{2} \delta_{\gamma\alpha} \right] T_{\gamma\rho} T_{\rho\gamma} \]

\[ = -\lambda_{\alpha\beta}^{2} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ \delta_{\alpha\gamma} - \frac{1}{2} \delta_{\gamma\alpha} \right] T_{\gamma\rho} T_{\rho\gamma} \]

\[ = -\lambda_{\alpha\beta}^{2} \frac{1}{R^6} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ \delta_{\alpha\gamma} - \frac{1}{2} \delta_{\gamma\alpha} \right] T_{\gamma\rho} T_{\rho\gamma} \]

\[ = -\lambda_{\alpha\beta}^{2} \frac{1}{R^6} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ \delta_{\alpha\gamma} - \frac{1}{2} \delta_{\gamma\alpha} \right] T_{\gamma\rho} T_{\rho\gamma} \]

and

\[ K_{\alpha\beta}^{\text{RA}} = -\lambda_{\alpha\beta}^{2} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ \delta_{\alpha\gamma} - \frac{1}{2} \delta_{\gamma\alpha} \right] T_{\gamma\rho} T_{\rho\gamma} \]

\[ = -\lambda_{\alpha\beta}^{2} \frac{1}{R^6} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ 4\delta_{\alpha\gamma} - 6\delta_{\gamma\alpha} \right] \]

\[ = -\lambda_{\alpha\beta}^{2} \frac{1}{R^6} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ 4\delta_{\alpha\gamma} - 6\delta_{\gamma\alpha} \right] \]

\[ = -\lambda_{\alpha\beta}^{2} \frac{1}{R^6} \int \frac{du}{2\pi} \frac{u}{u^2 + 1} \left[ 4\delta_{\alpha\gamma} - 6\delta_{\gamma\alpha} \right] \]

To proceed, we will assume a fixed relative spatial orientation of the two molecules. Hence, without loss of generality (due to the isotropy of the problem, there is no preferred orientation), we choose \( \vec{R} = (R,0,0) \) to obtain:

\[ T = \frac{1}{R^6} \begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

As a result of the previous simplifications, we get (for isotropic susceptibility tensors it holds that \( K_{\alpha\beta}^{\text{RA}} = K_{\alpha\beta}^{\text{AB}} \) but \( Q_{\alpha\beta}^{\text{RA}} \neq Q_{\alpha\beta}^{\text{AB}} \) as far as the molecules are different):

\[ W^{(2)}(R) = 12 \left[ Q^{\text{RA}}(R) + Q^{\text{AB}}(R) \right] \frac{1}{R^6} \]

(14)

\[ = 12 \left[ Q^{\text{RA}}(R) + Q^{\text{AB}}(R) \right] \frac{1}{R^6} \]

Notice that the isotropy of the susceptibility tensors does not imply isotropy in spin space. Hence, the spin-spin interaction term is not fully symmetric in \( x, y, \) and \( z \). This is similar to a two-site Heisenberg model. Once we obtain the eigenvalues of the secular matrix, the obtained spin-dependent energy corrections should be added to the standard London result for the dispersion interactions as given by:

\[ W^{(2)}_{\text{London}} = -\frac{1}{(4\pi\varepsilon_0)^2} \sum_{n,m=0}^\infty \frac{1}{\omega_n + \omega_m} \mu_n^\alpha (A) \mu_m^\beta (A) \mu_n^\gamma (B) \mu_m^\rho (B) \]

(15)

\[ = -\frac{1}{2\pi} \int_0^\infty \frac{du}{u^2 + 1} \left[ \delta_{\alpha\gamma} (iu) \delta_{\beta\rho} (iu) \right] = -\frac{1}{2\pi} \int_0^\infty \frac{du}{u^2 + 1} \left[ \delta_{\alpha\gamma} (iu) \right] \]

which reduces to (in atomic units):

\[ W^{(2)}_{\text{London}} (R) = -\frac{12}{\pi} \frac{1}{R^6} \times \frac{1}{u^2 + 1} \int_0^\infty \frac{du}{u^2 + 1} \alpha^\alpha (iu) \alpha^\beta (iu), \]

(16)
after considering the isotropic case. This latter expression will be used as a reference for the remaining of the paper, for both isotropic and anisotropic cases. This will help to better highlight the influence of the spin-spin interactions in the dispersion energy and its dependence on molecular chirality in later sections.

D. Model of an electron on a helix

The results obtained so far did not assume any specific underlying model for the zero-order Hamiltonian. To further proceed and obtain numerical results for the various response tensors previously defined, we formulate a minimal microscopic model for a helical system. Such a model will also allow to consider the dependence on the geometrical parameters of the helix, radius and pitch. On the contrary, the inclusion of intramolecular contributions to the CISS effect in the zero-order Hamiltonian would require the consideration of, at least, intramolecular spin-orbit coupling. This will, however, considerably increase the complexity of the model, since the zero-order spinors will not factorize into the product of a spinor and a spatial wave function as in the previous derivations. Such contributions will, therefore, not be considered in what follows.

Our further analysis will be based on a simple electron-on-a-helix model with Hamilton operator given by: 

$$H = -(\hbar^2 / 2m) \partial^2 / \partial s^2,$$

where $s$ is the arc length along the helix. This model is equivalent to Tinoco’s model, and clearly yields the same eigenfunctions. Using open-end boundary conditions, the wave functions are simply given by: 

$$\Psi_n(s) = \sqrt{2/L} \sin(k_n s),$$

where $L$ is the length of the helix given by $L = KL_0 = K \sqrt{b^2 + 4\pi^2 R^2}$ ($K$ is the number of turns of the helix), and the wave vector $k_n = \pi n / L$.

Using these wave functions, the dipole matrix elements for a helix whose axis is parallel to the $z$-axis in a local coordinate system can be computed as:

$$\mu_{nm} = 0,$$

$$\mu_{2m} = \frac{8}{\pi} s_n k_n R_n \frac{mn[(-1)^{m+n} - 1]}{[(m-n)^2 - 4K^2][(m+n)^2 - 4K^2]},$$

$$\mu_{3m} = \frac{4}{\pi^2} k_n |b| \frac{mn[(-1)^{m+n} - 1]}{(m^2 - n^2)^2},$$

$$\mu_{nm} = (\pm R/2, 0, 0) \text{ for } 2K = m \pm n, m \geq n,$$

with $s_n = \pm 1$ denoting the helix chirality. We obtain then for products of the dipole moment matrix elements (notice that the ground state “0” corresponds in this model to the $n=1$ quantum number):

$$\mu_{m1} \mu_{n1}^* = 16[1 + (-1)^{m+n}]^2 (Km)^2 \times$$

$$\begin{pmatrix}
0 & 0 & 0 \\
0 & \frac{4R_n^3}{\pi^2} \frac{(m-n)^2 - 4K^2}{[(m-1)^2 - 4K^2][(m+1)^2 - 4K^2]} & \frac{4R_n^3}{\pi^2} \frac{(m+n)^2 - 4K^2}{[(m+1)^2 - 4K^2][(m-1)^2 - 4K^2]} \\
0 & \frac{2s_n |b| R_n}{\pi^2} \frac{(m-n)^2 - 4K^2}{[(m-1)^2 - 4K^2][(m+1)^2 - 4K^2]} & \frac{2s_n |b| R_n}{\pi^2} \frac{(m+n)^2 - 4K^2}{[(m+1)^2 - 4K^2][(m-1)^2 - 4K^2]} \\
0 & \frac{2s_n |b| R_n}{\pi^2} \frac{(m-n)^2 - 4K^2}{[(m-1)^2 - 4K^2][(m+1)^2 - 4K^2]} & \frac{b^2}{\pi^4} \frac{1}{(m^2 - 1)^2}
\end{pmatrix},$$

(18)
for \( m \neq 2K + 1 \) and \( m \neq 2K - 1 \). For \( m = 2K + 1 \) or \( m = 2K - 1 \), we obtain:

\[
\mu^m_{\alpha m} \mu^m_{\beta m} = \frac{R^2}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\]

Notice that the influence of the helicity will appear only in the off-diagonal components of the susceptibility tensors. Hence, within the isotropic approximation only a dependence of radius and pitch of the helix will survive, but no helicity dependence. For the isotropic case, see Eq. (15), we will adopt the following form for the product of the dipole matrix elements:

\[
\mu^m_{\alpha m} \mu^m_{\beta m} = \delta_{\alpha\beta} 16[1 + (-1)^m]^2 (Km)^2 \times 
\frac{1}{3} \left\{ \frac{4R^2 / \pi^2}{[(m-1)^2 - 4K^2] [(m+1)^2 - 4K^2]} + \frac{b^2 / \pi^4}{(m^2 - 1)^2} \right\} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},
\]

\[
\mu^m_{\alpha m} \mu^m_{\beta m} = \delta_{\alpha\beta} \frac{R^2}{12} \text{ for } m = 2K \pm 1.
\]

Later on in this study, we will include the full tensors for the sake of comparison and thus, a natural dependence on the enantiomer type will result. We also mention that this model can be extended to include transversal degrees of freedom due to a finite size confinement potential. However, as long as no transitions between the transversal states are considered, the previous results remain valid.\(^{12}\)

### E. Dispersion potential

For the numerical evaluation we will use a simple Lennard-Jones type of potential to include the induced spin-orbit related corrections to the dispersion interactions:

\[
V_{LL,\sigma}(R) = -\frac{C_0}{R^{12}} \left( C_{\text{London}}^{\text{iso}} + W_{SO,\sigma}^j \right),
\]

The constant \( C_0 \) is arbitrary and only controls the repulsive part of the potential. The index \( j = \text{iso, aniso} \) labels the two different cases to be discussed in the next section. The coefficient \( C_{\text{London}}^{\text{iso}} \) relates to the standard London dispersion interaction via Eq. (16) (see the remark at the end of Sec. II.C). Finally, the spin-dependent energy corrections \( W_{SO,\sigma}^j \) include the influence of the ISOC and can be related to the CISS effect as it will be discussed in the next section. Notice that \( C_{\text{London}}^{\text{iso}} \) contains a dependence on the helical parameters radius and pitch, but it does not depend on the molecular chirality.
III. RESULTS

A. Parameter estimation

As previously mentioned, the bare relativistic spin-orbit parameter \( \lambda_{SO} \) does not need to be identical with our coupling strength \( \lambda_{SO} \). Assuming typical length scales in a molecule of \( \sim 1 \text{nm} \) and potential gradients (related to the intramolecular electrostatic potential) of \( \sim 1 \text{eV/nm} \), we can obtain values of \( \lambda_{SO} \approx 0.009 \text{meV} \), if we set \( \lambda_{eff} = 30 \) in Eq. (10). This order of magnitude for the spin-orbit energy scale is smaller than the typical atomic values for light atoms such as carbon, but still much larger than the scales of the bare relativistic coupling.

We can also provide a rough order of magnitude estimate of the ratio \( W_{SO,iso}^{(2)} / W_{London}^{(2),iso} \) for the isotropic case, see Eqs. (12) and (13) as well as Eqs. (27) and (28) in the next section. For simplicity, we only consider the triplet ground state energy from Eq. (26). To further proceed with the estimation, we assume that only the lowest excitation energy is contributing to the sums in the corresponding susceptibility tensors. Taking as a reference the model Hamiltonian of the electron-on-a-helix, the lowest non-vanishing contribution appears for the transition \( n=1 \rightarrow n=2 \) (see Eq. (19), noticing that \( n=1 \) corresponds to the ground state “0”). Based on this, we obtain (keeping atomic units, so that \( b \) and \( R_0 \) are given in Bohr radii and for \( K=1 \)):

\[
\frac{W_{SO}^{(2),iso}}{W_{London}^{(2),iso}} \approx 33\pi^2 \omega_{21}^2 = 33\pi^5 \left( \frac{\lambda_{eff}}{R_0^2} \right)^2 = 33\pi^4 \left( \frac{\lambda_{eff}}{b^2 + 4\pi^2 R_0^2} \right)^2 .
\]  

\( (21) \)

Assuming \( b=R_0=\rho \), one first gets:

\[
\frac{W_{SO}^{(2),iso}}{W_{London}^{(2),iso}} = 6.16 \times \left( \frac{\lambda_{eff}}{\rho^2} \right)^2 .
\]

Taking \( \rho \approx 1 \text{nm}=18.9 a_B \) and \( \lambda_{eff} = 30 \) leads to the following estimate:

\[
\frac{W_{SO}^{(2),iso}}{W_{London}^{(2),iso}} \sim 5.7 \times 10^{-2},
\]

which is small but non-negligible and it can be made larger if \( \lambda_{eff} \), and hence the physical \( \lambda_{SO} \), turns out to be larger. Thus, \( \lambda_{eff} = 100 \) gives a ratio of 0.38. Obviously, this latter value may represent an overestimation of the coupling strength, but highlights the possible range of the interaction strength. More quantitative estimates will require a detailed atomistic approach; our results suggest, nevertheless, that the corrections to the dispersion energy found here can play a non-negligible role.

The value of \( \lambda_{eff} \) may be further reduced if we assume the presence of a gap in the eigenvalue spectrum as a way of mimicking a large HOMO-LUMO gap. In this case, the excitation energies of the electron-on-the-helix Hamiltonian will be given (in a.u.) by the expression: \( \omega_{n1} = \Delta_{H-L} + \pi^2 (n^2 - 1)/L^2 \). By
carrying out the same approximations as in the previous paragraphs of this section and under the assumption that $3\pi^2/(\Delta_{H-L}L^2) \ll 1$, we obtain now that the ratio of the London to the SO contributions is of the form:

$$\frac{W^{(2),\text{iso}}_{SO}}{W^{(2),\text{iso}}_{\text{London}}} = 2\Delta_{H-L}^2\lambda_{\text{eff}}^2,$$

(22)

As a result, for a value of $\Delta_{H-L} = 2 \text{ eV} = 0.073 \text{ a.u.}$, it is enough to have $\lambda_{\text{eff}} = 10$ to obtain a ratio $W^{(2),\text{iso}}_{SO}/W^{(2),\text{iso}}_{\text{London}} \approx 7 \times 10^{-2}$. This point may play a role in more realistic electronic structure calculations for helical systems, which display a qualitatively different electronic spectrum as that obtained with our simple model and possess HOMO-LUMO gaps in the order of magnitude given above.

**B. Isotropic case**

We proceed now to discuss in more detail the intermolecular interactions, first addressing the simpler isotropic case. At this approximation level we cannot address the issue of homo- vs. heterochiral energetic discrimination. Indeed, as a result of Eq. (18) the only helicity, i.e. enantiomer, dependence of the underlying electron-on-a-helix model appears in the off-diagonal terms of the different response tensors and can, therefore, not be caught by an isotropic approximation as obtained in Eq. (19). The absence of spin-dependent interactions in the zero-order Hamiltonian, on the other side, makes it also difficult to introduce intra-molecular contributions to the CISS effect into the formalism, which might naturally lead to different interaction strengths between equal and different enantiomers.  

Therefore, at this place we resort to a heuristic argument to help in the choice of the ground states for homo- and heterochiral cases when computing the corrections to the dispersion energies within the isotropic approximation. For this, we will rely on the qualitative picture of the CISS effect, mostly presented in the experimental literature, see. e.g.  

28, 56, 27 and which, in our current discussion, would be stated as follows: the fluctuating electric dipole moments in the interacting molecules are accompanied by fluctuations in the spin density, which will - for the specific case of helical molecules with their helical axes aligned parallel to each other - energetically favor a ferro (triplet)-alignment for homo-chiral pairs and antiferro (singlet)-alignment for heterochiral pairs. Since our choice of spin basis is defined up to an orthogonal transformation, we can use instead of the original spinor basis $|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle$ a singlet-triplet basis obtained with the transformation matrix:

$$O = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\
0 & 0 & -1 & 0
\end{pmatrix},$$

which leads to the new basis:
\[ |S\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right). \]  
\[ |T_1\rangle = |\uparrow\uparrow\rangle, \quad |T_2\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right), \quad |T_3\rangle = |\downarrow\downarrow\rangle. \]  

We can now project Eq. (14) on the singlet and triplet states separately, mimicking the fact of having molecules with either different or the same chirality, respectively. The projection on the singlet state gives the correction:

\[ W_{S}^{(2),iso} = \langle S | W_{S}^{(2),iso} (R) | S \rangle = 12(Q^{BA}(R) + Q^{AB}(R)) - 12K(R), \]  

and for the triplet

\[ W_{T}^{(2),iso} = \langle T | W_{T}^{(2),iso} (R) | T \rangle = 12(Q^{BA}(R) + Q^{AB}(R)) + 4K(R) \begin{pmatrix} 2 & 0 & -3 \\ -3 & 0 & 2 \end{pmatrix}. \]  

From where the eigenvalues immediately follow as:

\[ W_{T}^{(2),iso} = 12(Q^{BA}(R) + Q^{AB}(R)) + \begin{cases} -4K(R) & \text{for } |T_+\rangle = \frac{1}{\sqrt{2}} (|T_1\rangle + |T_3\rangle) \text{ and } |T_-\rangle = |T_2\rangle \\ 20K(R) & \text{for } |T_0\rangle = \frac{1}{\sqrt{2}} (|T_1\rangle - |T_3\rangle) \end{cases} \]  

For identical molecules A=B,

\[ Q(R) = -\lambda_{eff}^2 \frac{1}{R^6} \int_0^{2\pi} \frac{du}{2\pi} \Gamma(iu)\alpha(iu), \]

\[ K(R) = -\lambda_{eff}^2 \frac{1}{R^6} \int_0^{2\pi} \frac{du}{2\pi} \Pi(iu)\Pi(iu). \]

Since both \( Q(R) \) and \( K(R) \) turn out to be negative, it follows that the homochiral case corresponding to the triplet ground state \( W_{T_0}^{(2),iso} \) has a lower energy than the heterochiral case \( W_{S}^{(2),iso} \). One can make in this case a very rough estimate of the triplet-singlet energetic separation by considering a single transition in the calculation of the polarizability tensors, similar to the treatment of Sec. III.A). First, the triplet-singlet difference \( \Delta_{T-S} \) can be written, using Eqs. (24), and (26) in the following way:

\[ \Delta_{T-S} = -36 |K(R)|. \]  

Including only the transition \( n=1 \rightarrow n=2 \), one obtains the estimate (for one helix turn \( K=1 \)):

\[ \Delta_{T-S}(R) = -36 \frac{\lambda_{eff}^2}{R^3} \frac{3\pi^2}{L^2} s_1^2 ((1 + s_2 (b / R)^2)^2 = -9 \frac{\lambda_{eff}^2}{R^3} \frac{s_1^2 (1 + s_2 b_0^2)^2}{1 + (b_0 / 2\pi)^2}. \]
where \( s_1 = 1.51, s_2 = 0.63 \) are numerical constants and \( b_0 = b / R_0 \).

The numerical results for the isotropic case are shown in Figure 1. The separation between the two (identical) molecules has been scaled by their radius, while the interaction energy is scaled by the minimum \( E_{\text{min}} = V_{\text{LJ}}(R = R_{\text{min}}, \lambda_{\text{eff}}) \) of the Lennard-Jones potential for \( \lambda_{\text{eff}} = 0 \). This corresponds to a value of \( E_{\text{min}} = 0.38 \text{ a.u.} = 10.3 \text{ eV} \). At this place we remark that to obtain reasonable orders of magnitude of the interaction energies, in the range of few eV, it turns out to be necessary to use rather small helical parameters \( R \) and \( b \), of the order of few Ångströms. This is related to the simplicity of the electron-on-a-helix model, where the energy eigenvalues scale with the inverse square of the helix length \( L \) (similar to the simple particle-in-a-box model). For larger helical parameters in the order of 1 nm the energy differences are in the order of few meV, leading to an artificial increase of the interaction energy. This seems to be an artifact of the model, which will not be present, in general, in realistic molecular systems, but it does not affect the main qualitative features of the following discussion.

Figure 1(a) shows the Lennard-Jones potential as defined by Eq. (20) for different values of the effective dimensionless spin-orbit coupling parameter \( \lambda_{\text{eff}} \) for the triplet ground state \( |T_0\rangle \), corresponding to the homochiral case, as previously discussed, to highlight the influence of the ISOC. The connecting vector of the two helices lies along the x-axis, \( e_x = (1,0,0) \). Since both the London contribution and the spin-orbit mediated correction are negative (attractive), the equilibrium position of the LJ-potential is slightly shifted to shorter distances depending on the strength of \( \lambda_{\text{eff}} \). This latter behavior will remain also for the more general anisotropic situation. In Figure 1(b) we show the difference \( \Delta_{T-S}^\text{TS} \) as a function of the scaled intermolecular separation for different values of \( \lambda_{\text{eff}} \). As suggested by the simple analytical estimation in Eq. (29), increasing \( \lambda_{\text{eff}} \) leads to an increase in the energetic separation between triplet and singlet, implying a stronger attractive interaction in the homochiral (triplet) situation than in the heterochiral case. This result is in line with the conclusion of Ref.\(^{28}\), which was however obtained using a full DFT calculation including also electronic exchange effects not dealt with in our study. Figure 1(c) shows \( \Delta_{T-S} \) as a function of the molecular pitch. Here, increasing the pitch of the helices also leads to an increasing energetic separation between triplet and singlet states, which can also be seen in Eq. (29), since the denominator \( 1 + (b_0 / 2\pi)^2 = 1 + 0.025b_0^2 \) is much smaller than the numerator and thus \( \Delta_{T-S} \sim (1 + s_2 b_0^2)^2 \).
Figure 1. Influence of induced intermolecular spin-orbit interactions on the dispersion forces modelled with a Lennard-Jones (LJ) type of potential for the isotropic case. For all cases we have chosen the helical parameters $R_0=b=0.4$ nm. (a) LJ-potential including the London dispersion contribution and the spin-dependent contributions arising from the solution of the secular equation. Different colors correspond to different strengths of the effective SOC parameter $\lambda_{\text{eff}}$. For simplicity, only the homochiral situation is shown. The vertical dashed line is only a guide for the eye. (b) Energy difference $\Delta_{T-S}$ between triplet (homochiral) and singlet (heterochiral) cases for varying $\lambda_{\text{eff}}$. With increasing $\lambda_{\text{eff}}$ the enantiomers in the triplet state experience a less repulsive interaction. The inset shows typical LJ curves for singlet and triplet states and for $\lambda_{\text{eff}} = 30$. (c) Energy difference $\Delta_{T-S}$ between triplet and singlet cases as a function of distance for different scaled helical pitch values $b/R_0$ and $\lambda_{\text{eff}} = 30$. Increasing the pitch also leads to an increasing energetic distance between homo- and heterochiral situations. Intermolecular separations are scaled with the helix radius and the energy with the minimum of the London dispersion energy $E_{\text{LJ min}}(R_0, 0) = 0.038$ a.u.

C. Anisotropic case

If we keep the full anisotropy of the problem, the results are very difficult to interpret due to the strong mixing of the original spinor basis, and a more refined theoretical formulation with a realistic zero order Hamiltonian may be in place. Since this goes beyond the scope of this investigation, we will introduce some simplifications in Eq. (9) regarding the spin exchange interaction term as given by the $J$-tensor: (i) for the diagonal components, we assume only two effective coupling parameters $J_{zz}$ and $J_{\perp} = (J_{xx} + J_{yy})/2$, while (ii) for the off-diagonal coupling we introduce the approximation $J_0 = (J_{xy} + J_{yz} + J_{zx})/3$. Thus, Eq. (9) reduces to the simpler expression:

$$W^{(2),\text{aniso}}(R) = 1_A \otimes 1_B (Q^{AA}_{\alpha\beta} + Q^{BB}_{\alpha\beta}) + J_{\perp} (\sigma^A_x \otimes \sigma^B_x + \sigma^A_y \otimes \sigma^B_y) + J_{zz} \sigma^A_z \otimes \sigma^B_z$$

$$+ J_0 (\sigma^A_x \otimes \sigma^B_y + \sigma^A_y \otimes \sigma^B_x + \sigma^A_x \otimes \sigma^B_z + \sigma^A_y \otimes \sigma^B_z + \sigma^A_z \otimes \sigma^B_x + \sigma^A_z \otimes \sigma^B_y). \tag{30}$$

Notice that in contrast to the isotropic case and despite the previous simplifications, we still have now a helicity-dependence in the $J$-tensor arising from the off-diagonal components of the dipole moment matrix elements in Eq. (18). Along similar lines as for the isotropic case, we introduce now the singlet-triplet basis previously defined to obtain the following matrix representation of the interaction energy:
This result shows that the singlet and triplet sectors are also decoupled (this even holds for the full expression in Eq. (9), although we only discuss here the simplified case). As a result, we can treat the two subspaces separately. The choice of the ground state will be carried out in a slightly different way as for the isotropic case: we evaluate namely the singlet energy for $s_A = s_B = 1$ (same enantiomers) and $s_A = -s_B = 1$ (different enantiomers) and chose the state with the lowest energy. The same is then done for the triplet states. Finally, we use as a reference for the London energy the isotropic limit from Eq. (16) to have a clear dependence on chirality exclusively related to the spin-dependent part, since in the general anisotropic case the London contribution also becomes chirality-dependent (this corresponds within our model to the DFT calculations presented in Sec. II.A).

In Figure 2 the corresponding results are shown when choosing the connecting line between the molecules along the (a) x-axis $R = R(1,0,0)$, (b) y-axis $R = R(0,1,0)$, and (c) $R = (R/\sqrt{2})(1,1,0)$. In general, the energy difference $\delta E_j = E^\text{hetero}_j - E^\text{homo}_j$ ($j=$singlet, triplet) is sensitively dependent on the relative orientation and it ranges roughly from 0.1 eV ($\delta E^\text{triplet}_j$ in panel (c)) to up to 1 eV ($\delta E^\text{triplet}_j$ in panel (b)). In general, the results in the anisotropic case turn out to be more sensitive to the parameter choice, so that a detailed study with a more realistic Hamiltonian is required, also to clarify how strong the orientation dependence of the results is.

![Figure 2](image_url)

**Figure 2. Directional dependence of the induced intermolecular spin-orbit interaction for the anisotropic case.** All curves are generated by using the Lennard-Jones potential of Eq. (20). For all cases we have chosen the helical parameters $R=b=0.4$ nm and $\lambda_{eff} = 30$. Panels (a)-(c) correspond to the separation vector between the two molecules directed along the x-, y-, and $(1/\sqrt{2})(1,1,0)$-directions. We plot for each spin configuration (singlet vs. triplet) the energies of the homo- and heterochiral situations (see the text for details). Intermolecular separations are scaled with the helix radius and the energy with the minimum of the London dispersion energy at the minimum $E^\text{min}_{LJ} = V_{LJ}(R = R_{min}, \lambda_{eff} = 0) = 0.03$ a.u.

Clearly, a more realistic atomistic calculation involving the true helical structure will be ultimately needed to further clarify specific quantitative details of the intermolecular interactions as well as the conditions under which isotropic and anisotropic limits may become experimentally relevant.\textsuperscript{11} Despite the involved approximations used to arrive at the previous results, the cases discussed in Figures 1 and
illustrate that the introduction of the CISS effect can lead to a selection of the relevant ground states for homo- and heterochiral situations and thus, to an additional chirality discriminating contribution to the dispersion forces as far as the involved molecular systems have the same chemical composition and a fixed spatial orientation. If the molecules belong to two different chemical species, \( A \neq B \), then a clear statement may be more difficult to achieve and it will require a full atomistic calculation.

One should also notice that our results are valid only in the van-der-Waals region of the potential energy surface, i.e. where second order perturbation theory and the neglect of electronic exchange effects (antisymmetrization of the wave function) is justified. Thus, any quantitative effects shown in Figures 1 and 2 below the equilibrium distance are clearly not physically relevant.

## IV. CONCLUSIONS

In conclusion, we have discussed the consequences of assuming the presence of mutually induced spin-orbit coupling in helical molecules in the near-zone range, i.e. where electronic exchange effects can be neglected. Our results show a non-negligible spin-dependent correction to the standard London dispersion forces, which has the form of a generalized Heisenberg Hamiltonian with a spin-spin exchange interaction term scaling with \( R^{-6} \), in a similar way as the London dispersion energy. A rough estimate provided a ratio of the obtained SOC-dependent contribution to the London dispersion energy in the range 0.1 – 0.01 depending on the chosen parameters, see Sec. III.A. The CISS effect was taken into account through a heuristic argument relating the obtained triplet ground states to homochiral situations and singlet ground states to heterochiral situations, in the spirit of the commonly accepted qualitative picture of the CISS effect.

In the light of the results obtained here, it can be speculated whether the spin-dependent correction terms to the dispersion interaction may also provide an additional contribution – besides the intrinsic spin-orbit terms commonly assumed in the models so far – to the description of the CISS effect and the related spin selectivity for transport studies in self-assembled monolayers, where intermolecular interactions cannot be neglected and the relative molecular orientations are nearly fixed in space.

We remark that in general terms, besides the proposed spin-orbit mediated dispersion terms and the electric dipole-dipole interactions leading to the London dispersion, there are also magnetic dipole-dipole interactions, which should be included in a complete calculation of dispersion forces for chiral molecules.\(^{11,60}\). Additionally, contributions from quadrupole terms may also be required, since they are known to play a role in chiral molecules.\(^{11}\) The DFT calculations presented in the supplementary material suggest, in fact, that contributions of higher order, scaling as \( R^{-8} \), can yield a significant contribution to the dispersion energy.

Concerning possible corrections to the chirality discriminating intermolecular interactions involving the rotatory power (RP),\(^{12,19,60}\) one may wonder if, within 2\(^{nd}\) order perturbation theory, mixed SOC-magnetic terms may yield additional corrections to these terms, i.e. contributions with the generic form \( \langle H_{SO} \rangle \langle H_{mag-dip-dip} \rangle \). Such terms would also involve products of transition matrix elements of electrical and magnetic dipole moments, similar to the RP. A very preliminary calculation shows that, indeed, a possible correction to the RP-related terms\(^{12,19,60}\) can play a role and it scales roughly as (in atomic units) \( \alpha^2 \lambda_{\text{eff}} \langle \omega \rangle \) with \( \alpha = 1/137 \) being the fine structure constant, and \( \langle \omega \rangle \) is a typical excitation energy.
scale. Since the standard RP contribution scales as $\alpha^2$, the leading correction to it will be proportional to $\lambda_{\text{eff}} \langle \omega \rangle$. An in-depth study of this issue will be the topic of a separate study.

Our investigation represents a very first step towards a more extensive quantitative analysis of induced intermolecular spin-dependent interactions between chiral molecules. From a more formal point of view, it might be of interest to elucidate how to consistently formulate the problem in the frame of molecular quantum electrodynamics, which would allow for a systematic derivation of spin-orbit mediated corrections within both the London and the Casimir-Polder ranges. A more general theory should also take into account exchange effects in helical molecules at shorter ranges. Finally, it will be desirable to address the relevance of the corrections derived in this investigation to real molecular systems via an extension of available parametrizations for vdW interactions.

SUPPLEMENTARY MATERIAL

The Supplementary Material includes few additional details of the analytical calculations presented in the main text as well as details of the Density-Functional-Theory calculations on helicene enantiomers.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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