Medium-assisted van der Waals dispersion interactions involving chiral molecules

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Abstract
The van der Waals dispersion interaction between two chiral molecules in the presence of arbitrary magnetoelectric media is derived using perturbation theory. To be general, the molecular polarisabilities are assumed to be of electric, paramagnetic and diamagnetic natures, and the material environment is considered to possess a chiral electromagnetic response. The derived expressions of electric dipole polarisable–chiral, magnetic dipole susceptible–chiral, and diamagnetic susceptible–chiral, and chiral–chiral interaction potentials when added to the previously obtained contributions in the literature, form a complete set of dispersion interaction formulas. We present them in a unified form making use of electric–magnetic duality. As an application, the case of two anisotropic molecules embedded in a bulk magnetoelectric medium is considered, where we derive the retarded and non-retarded limits with respect to intermolecular distance.

1. Introduction
The non-superposability of an object on its mirror image classifies it as chiral. A familiar example is provided by the left and right hands. Molecules that are chiral lack an improper axis of rotation, exist as enantiomeric pairs, and exhibit optical activity [1–5], that is, they are able to rotate the plane of polarisation of light either to the left or to the right, and are so termed laevorotatory or dextrorotatory. Other manifestations of molecular handedness include differential absorption (circular dichroism) [6] and differential scattering (Rayleigh and Raman) [7] of circularly polarised light, their nonlinear analogues [8], as well as other chiroptical spectroscopies that depend quadratically or on higher powers of the strengths of electromagnetic fields, such as sum-frequency and second-harmonic generation [9–11]. Many of these phenomena have also been predicted to occur when the incident radiation is of the structured type [12–19].

Because chiral compounds possess reduced or no elements of symmetry, selection rules normally in operation that are used to determine whether spectroscopic transitions are allowed or forbidden are considerably relaxed, or no longer apply. This enables multipole moments such as the magnetic dipole and electric quadrupole to feature to leading order in chiroptical processes, in addition to the usually dominant electric dipole moment. Accounting from the outset for both the charge and current density distributions of a collection of protons and electrons that form atoms and molecules is therefore necessary. Furthermore, Maxwell’s equations are needed to describe intrinsic electromagnetic effects due to the sources, as well as those arising from any applied radiation fields. Due to the microscopic nature of such elementary charged particles, both radiation and matter ought to be treated rigorously subject to the laws of quantum mechanics [20]. Hence the theory of molecular QED [21–23] naturally lends itself as the obvious means by
which to investigate fundamentally the interactions between photons and electrons, and any effects due to the handedness of molecules.

Non-relativistic QED theory in the Coulomb gauge has not only been successfully applied to a whole host of linear and nonlinear optical processes, but also permits inter-particle interactions to be studied using the same formalism. Well-known examples include resonant transfer of electronic excitation energy [21, 22, 24–27], and dispersion forces between two and three atoms or molecules [21, 22, 28–33]. For interactions between enantiomers, be they chemically identical or distinct species, both energy transfer and the dispersion energy shift are discriminatory and depend upon the handedness of the molecules [34–41]. According to QED theory, the interaction between particles is mediated by the exchange of virtual photons—by definition unobservable but permitted by the time–energy uncertainty principle [42, 43]. In the case of migration of energy, a single virtual photon is responsible for conveying energy from an excited donor moiety to an unexcited acceptor entity. This compares with the dispersion force, which is understood to arise from the exchange of two virtual photons.

In the presence of an environment, the mediating photons are no longer free-space light quanta associated with the vacuum electromagnetic field but become modified by the medium. One approach for dealing with this is to affect a scheme in which the radiation field and the surrounding environment are quantised, resulting instead in medium-assisted photons. This formed the basis for the construction of a macroscopic QED theory in which a magnetoelectric medium is accounted for and described by frequency dependent electric permittivity and magnetic permeability functions [44–48]. As in molecular QED, its macroscopic counterpart has been cast in terms of minimal- and multipolar-coupling frameworks; it has been applied with great advantage to the calculation of Casimir, Casimir–Polder, and van der Waals forces. For the last type of interaction, this has specifically included the evaluation of pair dispersion potentials in a magnetoelectric medium involving atoms or molecules that are either electrically polarisable or paramagnetically and diamagnetically susceptible, and their behavior has been examined as a function of interparticle separation distance in the non-retarded and retarded coupling regimes [49, 50].

Within the context of interactions involving optically active species, up to now macroscopic QED has only been employed to study Casimir–Polder forces [51, 52], i.e. between a microscopic particle and a macroscopic object, and the van der Waals dispersion energy between an electrically polarisable molecule and a chiral molecule. While it is known that the last mentioned potential vanishes in free space for an isotropic pair of interacting molecules, it was shown recently that a non-zero energy shift arises by specifically choosing the environment to be a chiral plate [53]. Not only is the energy finite, but its magnitude and sign may even be controlled and its behavior studied for particular configurations of the chiral molecules and the achiral molecule relative to the chiral plate. For instance, there is maximal enhancement of the interaction when the two particles are aligned parallel to the plate but are each separated a large distance from it. This offers a realistic possibility for the separation of enantiomers, complementing a recent proposal exploiting parity violation in the Casimir–Polder potential when a beam of chiral molecules passes through a pair of chiral mirrors [54].

In the present work, we develop a general and complete macroscopic QED theory for the van der Waals dispersion interaction between two molecules with arbitrary linear dipolar response that may or may not be chiral and are described by their electric polarisability, para- and diamagnetic susceptibility, and mixed electric–magnetic dipole (chiral) susceptibility in a magnetoelectric medium. Even though the electric quadrupole ($Q$) is of the same order of magnitude as the magnetic dipole moment ($m$), and is often accounted for when considering chiroptical phenomena or discriminatory interactions, the former contribution is not included below, with attention being limited to dipolar contributions and the diamagnetic coupling. This is reasonable on three grounds: firstly, comparison will be made with dispersion energy shifts calculated in free space for which contributions dependent upon the mixed electric dipole–quadrupole ($dQ$) polarisability vanish for freely tumbling molecules, and secondly, inclusion of the electric quadrupole interaction term gives rise to a large number of additional contributions to the dispersion potential which are of the same order as those to be presented, such as $dd–dQ$, $dQ–dQ$, $dd–QQ$, etc, energy shifts, but none of which exhibit discriminatory effects for isotropic systems. Thirdly, the electric-, magnetic-dipole, and chiral interactions conceptually form a closed set with respect to duality (see section 4 below), in which the different contributions can be viewed as an expansion in powers of the fine structure constant (see section 6). By contrast, an inclusion of higher-order multipoles corresponds to an expansion in terms of the molecular size. Fourth-order diagrammatic perturbation theory is employed to compute the interaction energy, and explicit contributions involving one or two chiral species are extracted. On inserting the Green’s tensor for a homogeneous medium, it is found that the results obtained for free space reduce to those previously derived using molecular QED [22].

The paper is organized as follows. The basic formalism for QED in the presence of chiral magnetoelectric media together with the introduction of molecule–field interaction Hamiltonians are given.
in section 2. In section 3 the derivation of electric–chiral, paramagnetic–chiral, and chiral–chiral van der Waals dispersion potentials are presented via fourth order perturbation theory, followed by the diamagnetic–chiral interaction for which the third order perturbation theory is applied. A unified form of the formulas of various dispersion interaction potentials is derived in section 4 using the electric–magnetic duality. As an application of the obtained formulas, the interaction between two anisotropic molecules embedded in a homogeneous magnetoelectric media is computed in section 5 where also the retarded and non-retarded limits of intermolecular distances are considered. A summary and concluding remarks are provided in section 6.

2. Basic formalism

The Hamiltonian of a system comprised of two molecules A and B in the presence of a quantised electromagnetic field is given as

\[ \hat{H} = \hat{H}_F + \sum_{A'=A,B} \hat{H}_{A'} + \sum_{A'=A,B} \hat{H}_{A'F}, \]

where \( \hat{H}_F, \hat{H}_{A'}, \) and \( \hat{H}_{A'F} \) denote, respectively, field, molecule, and molecule–field interaction Hamiltonians. In terms of fundamental photonic annihilation and creation operators, \( \hat{f}_\lambda \) and \( \hat{f}_\lambda^\dagger \), the field Hamiltonian reads [46]

\[ \hat{H}_F = \sum_{\lambda=e,m} \int d^3r \int_0^\infty d\omega \hbar \omega \hat{f}_\lambda (r, \omega) \cdot \hat{f}_\lambda^\dagger (r, \omega) \]

with \( \lambda \) referring to the electric (\( \lambda = e \)) or magnetic (\( \lambda = m \)) nature of the noise source. These operators obey the following commutation relations:

\[ [\hat{f}_\lambda (r, \omega), \hat{f}_\lambda^\dagger (r', \omega')] = 0, \]

\[ [\hat{f}_\lambda (r, \omega), \hat{f}_\lambda^\dagger (r', \omega')] = i \hbar \lambda \delta (r - r') \delta (\omega - \omega'), \]

with \( I \) being the identity matrix. It should be borne in mind that while we will use ‘photon’ to describe bosonic excitations, these are medium-dressed photons, more appropriately termed ‘polaritons’.

The ground-state of the field \( \{0\} \) is defined by

\[ \hat{f}_\lambda (r, \omega) \{0\} = 0, \quad \forall r, \omega, \lambda \]

and the excited photonic states are defined by repeated application of the creation operator to the ground-state. For example, for single- and two-photon excited states,

\[ |\lambda (r, \omega)\rangle = \hat{f}_\lambda^\dagger (r, \omega) \{0\}, \]

\[ |\lambda (r, \omega), \lambda' (r', \omega')\rangle = \frac{1}{\sqrt{2}} \hat{f}_\lambda^\dagger (r, \omega) \hat{f}_{\lambda'}^\dagger (r', \omega') \{0\}. \]

The molecular Hamiltonian may be written in terms of unperturbed molecular eigenenergies and eigenstates as

\[ \hat{H}_{A'} = \sum_k E_k^{A'} |k^{A'}\rangle \langle k^{A'}|, \quad A' = A, B. \]

In the multipolar coupling scheme, the molecule–field interaction Hamiltonian takes the form [50]

\[ \hat{H}_{A'F} = -\hat{d}_{A'} \cdot \hat{E}(r_{A'}) - \hat{m}_{A'} \cdot \hat{B}(r_{A'}) - \frac{1}{2} \hat{B}(r_{A'}) \cdot \hat{\beta}_{A'}^D \cdot \hat{B}(r_{A'}), \]

with \( \hat{d}_{A'} \) and \( \hat{m}_{A'} \) being, respectively, electric and magnetic dipole moment operators of the molecule \( A' \) and \( \hat{\beta}_{A'}^D \) is its operator-valued diamagnetisability tensor

\[ \hat{\beta}_{A'}^D = -\sum_{\alpha \in A'} \frac{q^2_\alpha}{4m_\alpha} (\vec{r}_\alpha^2 I - \vec{r}_\alpha \vec{r}_\alpha), \]
where $q_α$ and $m_α$ are, respectively, the electric charge and mass of the particle $α$, and $\hat{r}_α$ is its position vector relative to the center of mass of the molecule. The electric and magnetic fields can be expressed as linear combinations of the fundamental photonic operators. To this end, we introduce $\mathcal{R}_{λ,λ'}(r, ω)$ ($λ, λ' = e, m$) as the $3 \times 3$ blocks of the $6 \times 6$ tensor $\mathcal{R}(r, ω)$,

$$\mathcal{R} = \begin{pmatrix} \mathcal{R}_{ee} & \mathcal{R}_{em} \\ \mathcal{R}_{me} & \mathcal{R}_{mm} \end{pmatrix},$$

which is the response tensor of the magnetoelastic material environment [51] defined, for locally responding media, according to

$$\mathcal{R} \cdot \mathcal{R}^T = \begin{pmatrix} \varepsilon_0 \text{Im}(\varepsilon - \kappa^T \cdot \mu^{-1} \cdot \kappa) & -i\sqrt{\varepsilon_0 \mu_0} \text{Im}(\kappa^T \cdot \mu^{-1}) \\ i\sqrt{\varepsilon_0 \mu_0} \text{Im}(\mu^{-1} \cdot \kappa) & -\frac{1}{\mu_0} \text{Im}(\mu^{-1}) \end{pmatrix}.$$  \hspace{1cm} (12)

In equation (12) $\varepsilon = \varepsilon(r, ω)$ and $\mu = \mu(r, ω)$ are, respectively, the relative electric permittivity and magnetic permeability tensors of the media, and $\kappa = \kappa(r, ω)$ is the chirality tensor responsible for the contribution of an electric effect to a magnetic response and vice versa. The electric and magnetic fields are given as

$$E(r) = \sum_{λ=e,m} \int d^3r' \int_0^∞ dω \mathbf{G}_λ(r, r', ω) \cdot \mathbf{f}_λ(r', ω) + \text{H.c.},$$

$$B(r) = \sum_{λ=e,m} \int d^3r' \int_0^∞ \frac{dω}{ω} \nabla × \mathbf{G}_λ(r, r', ω) \cdot \mathbf{f}_λ(r', ω) + \text{H.c.},$$

where $\mathbf{G}_e$ and $\mathbf{G}_m$ are the mode tensors introduced in terms of the Green tensor $\mathbf{G}$,

$$\mathbf{G}_λ(r, r', ω) = -iμ_0ω\sqrt{\frac{ℏ}{π}} \left[ iω \mathbf{G}(r, r', ω) \cdot \mathcal{R}_{λe}(r', ω) + \mathbf{G}(r, r', ω) \times \frac{\nabla'}{ω} \cdot \mathcal{R}_{λm}(r', ω) \right],$$  \hspace{1cm} (15)

with $\nabla'$ denoting differentiation from the left. The Green tensor $\mathbf{G}(r, r', ω)$ obeys the differential equation [51]

$$\nabla × \mu^{-1} \cdot \nabla × \mathbf{G} + \frac{ω}{c} \nabla × \mu^{-1} \cdot \kappa \cdot \mathbf{G} + \frac{ω}{c} \kappa^T \cdot \mu^{-1} \cdot \nabla × \mathbf{G} - \frac{ω^2}{c^2} (\varepsilon - \kappa^T \cdot \mu^{-1} \cdot \kappa) \cdot \mathbf{G} = \mathbf{l}δ(r - r'),$$

$$T^e = T^m.$$ \hspace{1cm} (16)

All geometric and magnetoelastic properties of the environment are taken into account via $\varepsilon(r, ω)$, $\mu(r, ω)$, and $\kappa(r, ω)$. Furthermore, the Green tensor obeys the Schwarz reflection principle

$$\mathbf{G}(r, r', ω) = \mathbf{G}^*(r, r', ω^*),$$

Onsager reciprocity

$$\mathbf{G}(r, r', ω) = \mathbf{G}^T(r', r, ω),$$

and a useful integral relation [55, 56]

$$\sum_{λ=e,m} \int d^3\mathbf{s} \mathbf{G}_λ(r, s, ω) \cdot \mathbf{G}^T_λ(r', s, ω) = \frac{ℏμ_0ω^2}{π} \text{Im} \mathbf{G}(r, r', ω).$$  \hspace{1cm} (19)

These properties will be used in the evaluation of matrix elements appearing in perturbation formulas.

3. Interaction potential

For ground-state molecules the van der Waals dispersion interaction is mediated by two virtual-photon exchanges between the molecules accompanied by internal transitions. In achiral molecules the molecular eigenstates are also the eigenstates of the parity operator. Hence, the resulting expression for the interaction potential is obtained such that every molecule may be considered as a superposition of an electric dipole polarisable, a magnetic dipole susceptible, and a diamagnetic susceptible molecule, for which the molecular transitions are, respectively, electric, paramagnetic, or diamagnetic type only [see reference [50]) and will be briefly referred to as electric, paramagnetic, and diamagnetic molecules afterwards. For chiral molecules,
Figure 1. Two-virtual photon exchange diagrams contributing to the van der Waals dispersion potential. The various intermediate states required in equation (20) are readily obtained.

however, each molecular transition may possess interdependent electric and magnetic dipole moments and additional higher multipole moments. This leads to an additional chiral contribution to the interaction potential, to which the rest of this section is devoted.

In order to calculate the interaction energy between two ground-state molecules A and B in the presence of a medium-assisted electromagnetic field we use perturbation theory. To do so, we consider the sum of the field and molecular Hamiltonians as unperturbed Hamiltonian, and the sum of the molecule–field interaction Hamiltonians, $\hat{H}_{AB} + \hat{H}_{BE} \equiv \hat{H}_{\text{int}}$, as perturbation. The electric or paramagnetic transitions in the molecules depend linearly on the electric and magnetic fields, respectively, and are associated with the absorption or emission of a single virtual photon, while the diamagnetic coupling involves a two-photon transition. Hence, in the calculation of the energy shift, different orders of perturbation theory are required for diamagnetic molecules in comparison to electric and paramagnetic ones.

3.1. Electric–chiral, paramagnetic–chiral, and chiral–chiral interactions

The lowest order perturbation leading to the interaction potential, involving an electric, paramagnetic, or a chiral molecule that interacts with a second species which is chiral via two virtual photon exchange is the fourth order [49, 50],

$$U(r_A, r_B) = - \sum_{I,II,III \neq 0} \frac{\langle 0 | \hat{H}_{\text{int}} | III \rangle \langle III | \hat{H}_{\text{int}} | II \rangle \langle II | \hat{H}_{\text{int}} | I \rangle \langle I | \hat{H}_{\text{int}} | 0 \rangle}{(E_{III} - E_0)(E_{II} - E_0)(E_{I} - E_0)},$$

(20)

with the ground state of the total system denoted by $|0\rangle \equiv |0_A\rangle |0_B\rangle |\{0\}\rangle$. The numerator is comprised of multiplication of four matrix elements, each corresponding to an event in which one of the molecules undergoes a transition accompanied by emission or absorption of a virtual photon. The photon emitted by one of the molecules has to be absorbed by the other to contribute to the coupling between molecules. In order to take into account a complete set of intermediate states in calculating the right hand side of equation (20), one may use a diagrammatic language depending on the time-ordered sequence of the propagation of two virtual photons, as sketched in figure 1. In this and subsequent time-ordered diagrams, time flows vertically upward while the horizontal axis represents relative spatial displacement of particles A and B. The solid vertical line signifies the state of the molecule while the wavy line depicts the propagation of a virtual photon of a specified mode. The intersection of wavy and solid lines corresponds to coupling between radiation and matter through the relevant multipole moment and Maxwell field operator and which is illustrated by the dot in the figure. In every single diagram shown, each molecule undergoes two transitions, from the ground state to an excited state and back.
interaction Hamiltonians reduce to
\[ r \]

Let us consider an (achiral) electric molecule A and a chiral molecule B located respectively at positions \( r_A \) and \( r_B \) in the presence of an arbitrary arrangement of magnetoelectric media. The molecule–field interaction Hamiltonians reduce to
\[
\hat{H}_{AF} = -\vec{d}_A \cdot \vec{E}(r_A),
\]
\[
\hat{H}_{BF} = -\vec{d}_B \cdot \vec{E}(r_B) - \vec{m}_B \cdot \vec{B}(r_B).
\]

We first calculate the contribution from every single diagram in figure 1 in the right hand side of equation (20). For example, for diagram (1) in figure 1, the respective intermediate states read as follows:
\[
|I\rangle = |m_A\rangle |0_B\rangle |1_{\lambda_A}(r_1, \omega_1)\rangle,
\]
\[
|II\rangle = |0_A\rangle |0_B\rangle |1_{\lambda_B}(r_2, \omega_2), 1_{\lambda_A}(r_3, \omega_3)\rangle,
\]
\[
|III\rangle = |0_A\rangle |l_B\rangle |1_{\lambda_B}(r_4, \omega_1)\rangle,
\]

where \( |m_A\rangle \) and \( |l_B\rangle \) denote excited molecular states. The denominator is equal to
\[
h^3(\omega_A^m + \omega_1)(\omega_2 + \omega_3)(\omega_B^m + \omega_4)\]

with \( \omega_A^m = (E_{A'} - E_A^0)/\hbar \) denoting the transition frequency of molecule A'. Substitution of equation (21) together with equation (13) for the electric field operator, making use of the definitions (6) and (7) for single- and two-photon states of the electromagnetic field, and applying the commutation relations (3) and (4), we find
\[
\langle I|\hat{H}_{AF}|0\rangle = -\frac{1}{\sqrt{2}} \left[ d_A^{\alpha \mu} \cdot G_{\lambda_A}(r_A, r_1, \omega_1) \right]_{\lambda_1} \delta^{(31)},
\]
\[
\langle II|\hat{H}_{AF}|I\rangle = -\frac{1}{\sqrt{2}} \left[ d_A^{\alpha \mu} \cdot G_{\lambda_B}(r_A, r_2, \omega_2) \right]_{\lambda_2} \delta^{(33)} - \frac{1}{\sqrt{2}} \left[ d_B^{\beta \nu} \cdot G_{\lambda_A}(r_A, r_3, \omega_3) \right]_{\lambda_3} \delta^{(21)},
\]

where \( d_A^{\alpha \mu} = (i\hbar \delta_{\alpha \beta}) \) is the transition electric dipole moment, and we have introduced the short-hand notation \( \delta^{(\alpha \beta)} = \delta(r_A - r_B) \delta(\omega_A - \omega_B) \delta_{\lambda_1 \lambda_2} \delta_{\lambda_2 \lambda_3} \). The two photons present in state |II⟩ are to be absorbed by the chiral molecule B. Diagram (1) refers to two cases of (1)a and (1)b as shown in figure 2, differing in the time-ordering of the electric–dipole and magnetic–dipole transitions in the chiral molecule B. Restricting our attention to case (1)a, similar to equations (24) and (25) we obtain
\[
\langle III|\hat{H}_{BF}|II\rangle = -\frac{1}{\sqrt{2}} \left[ d_B^{\beta \nu} \cdot G_{\lambda_B}(r_B, r_2, \omega_2) \right]_{\lambda_2} \delta^{(24)} - \frac{1}{\sqrt{2}} \left[ d_B^{\beta \nu} \cdot G_{\lambda_B}(r_B, r_3, \omega_3) \right]_{\lambda_3} \delta^{(24)},
\]
\[
\langle 0|\hat{H}_{BF}|III\rangle = -\frac{1}{\sqrt{2}} \left[ m_B^{\beta \nu} \cdot \nabla_B \times G_{\lambda_B}(r_B, r_4, \omega_4) \right]_{\lambda_4} \delta^{(24)},
\]

The chirality contribution of a molecule to the interaction potential comes from processes in which an electric upward transition in the molecule is followed by a magnetic downward one in the same molecule, or vice versa. To this order of multipole approximation it can be decomposed into three parts: electric–chiral, paramagnetic–chiral, and chiral–chiral, each of which is examined below.

3.1.1. Electric–chiral interaction.

Let us consider an (achiral) electric molecule A and a chiral molecule B located respectively at positions \( r_A \) and \( r_B \) in the presence of an arbitrary arrangement of magnetoelectric media. The molecule–field interaction Hamiltonians reduce to

\[
\hat{H}_{AF} = -\vec{d}_A \cdot \vec{E}(r_A),
\]
\[
\hat{H}_{BF} = -\vec{d}_B \cdot \vec{E}(r_B) - \vec{m}_B \cdot \vec{B}(r_B).
\]

We first calculate the contribution from every single diagram in figure 1 in the right hand side of equation (20). For example, for diagram (1) in figure 1, the respective intermediate states read as follows:

\[
|I\rangle = |m_A\rangle |0_B\rangle |1_{\lambda_A}(r_1, \omega_1)\rangle,
\]
\[
|II\rangle = |0_A\rangle |0_B\rangle |1_{\lambda_B}(r_2, \omega_2), 1_{\lambda_A}(r_3, \omega_3)\rangle,
\]
\[
|III\rangle = |0_A\rangle |l_B\rangle |1_{\lambda_B}(r_4, \omega_1)\rangle,
\]

where \( |m_A\rangle \) and \( |l_B\rangle \) denote excited molecular states. The denominator is equal to

\[
h^3(\omega_A^m + \omega_1)(\omega_2 + \omega_3)(\omega_B^m + \omega_4)\]

with \( \omega_A^m = (E_{A'} - E_A^0)/\hbar \) denoting the transition frequency of molecule A'. Substitution of equation (21) together with equation (13) for the electric field operator, making use of the definitions (6) and (7) for single- and two-photon states of the electromagnetic field, and applying the commutation relations (3) and (4), we find

\[
\langle I|\hat{H}_{AF}|0\rangle = -\frac{1}{\sqrt{2}} \left[ d_A^{\alpha \mu} \cdot G_{\lambda_A}(r_A, r_1, \omega_1) \right]_{\lambda_1} \delta^{(31)},
\]
\[
\langle II|\hat{H}_{AF}|I\rangle = -\frac{1}{\sqrt{2}} \left[ d_A^{\alpha \mu} \cdot G_{\lambda_B}(r_A, r_2, \omega_2) \right]_{\lambda_2} \delta^{(33)} - \frac{1}{\sqrt{2}} \left[ d_B^{\beta \nu} \cdot G_{\lambda_A}(r_A, r_3, \omega_3) \right]_{\lambda_3} \delta^{(21)},
\]

where \( d_A^{\alpha \mu} = (i\hbar \delta_{\alpha \beta}) \) is the transition electric dipole moment, and we have introduced the short-hand notation \( \delta^{(\alpha \beta)} = \delta(r_A - r_B) \delta(\omega_A - \omega_B) \delta_{\lambda_1 \lambda_2} \delta_{\lambda_2 \lambda_3} \). The two photons present in state |II⟩ are to be absorbed by the chiral molecule B. Diagram (1) refers to two cases of (1)a and (1)b as shown in figure 2, differing in the time-ordering of the electric–dipole and magnetic–dipole transitions in the chiral molecule B. Restricting our attention to case (1)a, similar to equations (24) and (25) we obtain

\[
\langle III|\hat{H}_{BF}|II\rangle = -\frac{1}{\sqrt{2}} \left[ d_B^{\beta \nu} \cdot G_{\lambda_B}(r_B, r_2, \omega_2) \right]_{\lambda_2} \delta^{(24)} - \frac{1}{\sqrt{2}} \left[ d_B^{\beta \nu} \cdot G_{\lambda_B}(r_B, r_3, \omega_3) \right]_{\lambda_3} \delta^{(24)},
\]
\[
\langle 0|\hat{H}_{BF}|III\rangle = -\frac{1}{\sqrt{2}} \left[ m_B^{\beta \nu} \cdot \nabla_B \times G_{\lambda_B}(r_B, r_4, \omega_4) \right]_{\lambda_4} \delta^{(24)},
\]
Note that $\hat{H}_{\text{EC}}$ is substituted by $-\mathbf{d}_B \cdot \mathbf{E}(r_B)$ and $-\mathbf{m}_B \cdot \mathbf{B}(r_B)$, respectively, for the first and second photon absorptions in molecule B.

Next we substitute these matrix elements into equation (20). The summation present in equation (20) runs over discrete variables of molecular states $m$, $l$, electric or magnetic nature of the noise source $\lambda$, spatial components $i$, as well as continuous variables of frequency and position. Making use of the integral relation (19) leads to the contribution coming from case (1)a to the fourth-order energy shift as

$$ U_{\text{EC}}^{1a} = -\frac{\mu_0^2}{\hbar \pi^2} \sum_{m,l,\lambda,0} \int_0^\infty \frac{d\omega_1}{\omega_1} \int_0^{\omega_1} d\omega_2 \frac{N_{\text{EC}}(\omega_1,\omega_2)}{D_1(\omega_1,\omega_2)} $$

where

$$ N_{\text{EC}}(\omega_1,\omega_2) = -\frac{1}{\omega_2} \text{tr} \left[ d_A^{m0} d_A^{m} \cdot \text{Im} \mathbf{G}(r_A, r_B, \omega_1) \cdot d_B^{n0} m_B^{n} \cdot \nabla_B \times \text{Im} \mathbf{G}(r_B, r_A, \omega_2) \right], $$

$$ D_1(\omega_1,\omega_2) = (\omega_1^m + \omega_1)(\omega_1 + \omega_2)(\omega_1^m + \omega_2). $$

In writing equation (29) we have used Lloyd’s theorem which allows us to assume that the matrix elements of the electric dipole operator are real-valued while those of the magnetic dipole operator are taken to be pure imaginary; $d_A^{m0} = d_A^{m0}^*, m_B^{n0} = -m_B^{n0}$ [57].

The contribution from diagram (1)b can be obtained in a similar manner and the only difference compared with that of (1)a is found to be that $N(\omega_1,\omega_2)$ is replaced by $N(\omega_2,\omega_1)$. That is,

$$ U_{\text{EC}}^{1b} = U_{\text{EC}}^{1a} + U_{\text{EC}}^{1b} = -\frac{\mu_0^2}{\hbar \pi^2} \sum_{m,l,\lambda,0} \int_0^\infty \frac{d\omega_1}{\omega_1} \int_0^{\omega_1} d\omega_2 \frac{N_{\text{EC}}(\omega_1,\omega_2)}{D_1(\omega_1,\omega_2)} $$

$$ = -\frac{\mu_0^2}{\hbar \pi^2} \sum_{m,l,\lambda,0} \int_0^{\omega_1} d\omega_1 \int_0^{\omega_2} d\omega_2 \frac{N_{\text{EC}}(\omega_1,\omega_2)}{D_1(\omega_1,\omega_2)} \left[ \frac{1}{D_1(\omega_1,\omega_2)} + \frac{1}{D_1(\omega_1,\omega_2)} \right]. $$

For all other diagrams in figure 1 the result is seen to be obtained similarly to diagram (1). Summing over all contributions leads to (see appendix A)

$$ U_{\text{EC}}(r_A, r_B) = \frac{\mu_0^2}{\hbar \pi^2} \sum_{m,l,\lambda,0} \frac{4\omega_1^m}{\omega_1^m + \omega_B^l} \int_0^{\omega_1} d\omega_1 \int_0^{\omega_2} d\omega_2 \frac{N_{\text{EC}}(\omega_1,\omega_2)}{D_1(\omega_1,\omega_2)} $$

$$ \times \text{tr} \left[ d_A^{m0} d_A^{m} \cdot \text{Im} \mathbf{G}(r_A, r_B, \omega_1) \cdot d_B^{n0} m_B^{n} \cdot \nabla_B \times \text{Im} \mathbf{G}(r_B, r_A, \omega_2) \right] $$

$$ \times \left[ \frac{1}{(\omega_1^m + \omega_2)(\omega_B^l + \omega_2)} - \frac{1}{(\omega_1^m + \omega_1)(\omega_B^l + \omega_1)} \right] \left( \frac{1}{\omega_2} - \frac{1}{\omega_1} \right). $$

Equation (32) can be simplified, first, by performing one of the frequency integrals and then rewriting the remaining integral in terms of imaginary frequency $\omega = i\xi$ (see appendix B) to yield

$$ U_{\text{EC}}(r_A, r_B) = -\frac{4\mu_0^2}{\hbar \pi} \int_0^{\infty} d\xi \xi^3 \int_0^{\infty} d\xi \xi^3 \frac{\xi^m}{(\omega_A^m)^2 + \xi^2} \frac{\xi^m}{(\omega_B^l)^2 + \xi^2} $$

$$ \times \text{tr} \left[ d_A^{m0} d_A^{m} \cdot \mathbf{G}(r_A, r_B, i\xi) \cdot d_B^{n0} m_B^{n} \cdot \nabla_B \times \mathbf{G}(r_B, r_A, i\xi) \right]. $$

This formula can be written as

$$ U_{\text{EC}}(r_A, r_B) = \frac{\hbar \pi}{4} \int_0^{\infty} d\xi \xi \text{tr} \left[ \alpha_A(i\xi) \cdot \mathbf{G}(r_A, r_B, i\xi) \cdot \chi^{em}_B(i\xi) \cdot \nabla_B \times \mathbf{G}(r_B, r_A, i\xi) \right], $$

where $\alpha(\omega)$ and $\chi^{em}(\omega)$ are, respectively, electric polarisability and chiral polarisability of the molecules, given as

$$ \alpha_A(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{2}{\hbar} \sum_m \frac{\omega_A^m d_A^{m0} d_A^{m}}{(\omega_A^m)^2 - \omega^2 - i\epsilon}, $$

$$ \chi^{em}_B(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{2}{\hbar} \sum_m \frac{\omega_B^{m0} m_B^{m}}{(\omega_B^m)^2 - \omega^2 - i\epsilon}. $$
The quantity $\chi^{\text{em}}(\omega)$ is related to the dynamic mixed electric–magnetic dipole polarisability, which is usually labeled $G(\omega)$ when examining chiroptical response in molecular QED theory [21, 22]. Equation (34) agrees with the corresponding result given in reference [53] where the calculation was based upon second-order perturbation theory by introducing an effective two-photon interaction Hamiltonian.

3.1.2. Paramagnetic–chiral interaction.
To isolate the energy shift between a magnetic dipole susceptible molecule and a chiral one, the electric dipole of $A$ is replaced by a magnetic dipole moment, so that the interaction Hamiltonian of molecule $A$ becomes

$$\hat{H}_{AF} = -\hat{m}_A \cdot \mathbf{B}(r_A),$$

while that of molecule $B$ is again given by equation (22). Following the same procedure as in obtaining the electric–chiral potential, first, we restrict our attention to case (1) in figure 1, which in turn splits into two cases (1)a and (1)b shown in figure 3 for the paramagnetic–chiral interaction. For case (1)a in figure 3, it can be seen easily that the intermediate states and the denominator remain unchanged, the matrix elements following equation (20) and making use of the integral relation (19) lead to the

$$\langle I | \hat{H}_{AF} | 0 \rangle = \left[ \frac{1}{\omega_1} m_A^{(0)} \cdot \nabla_A \times G_{A_1}^*(r_A, r_1, \omega_1) \right]_{i_1},$$

(38)

$$\langle II | \hat{H}_{AF} | I \rangle = \frac{1}{\sqrt{2}} \left[ \frac{1}{\omega_2} m_A^{(0)} \cdot \nabla_A \times G_{A_2}^*(r_A, r_2, \omega_2) \right]_{i_2} + \frac{1}{\sqrt{2}} \left[ \frac{1}{\omega_3} m_B^{(0)} \cdot \nabla_A \times G_{B_3}^*(r_A, r_3, \omega_3) \right]_{i_3} \delta^{(21)}.$$

(39)

Substitution of these into equation (20) and making use of the integral relation (19) leads for the contribution of diagram (1)a in figure 3, again, to equation (28) with $N_{EC}(\omega_1, \omega_2)$ being replaced by

$$N_{PC}(\omega_1, \omega_2) = -\frac{i}{\omega_1 \omega_2^3} \text{tr} \left[ m_A^{(0)} m_A^{(m)} \cdot \nabla_A \times \mathbf{G}(r_A, r_B, \omega_2) \times \widehat{\nabla}_B \cdot m_B^{(0)} d_B^{(l)} \cdot \text{Im} \mathbf{G}(r_B, r_A, \omega_1) \times \widehat{\nabla}_A \right].$$

(40)

The contribution of diagram (1)b in figure 3 also results in equation (40) with $N_{PC}(\omega_1, \omega_2)$ being replaced by $N_{PC}(\omega_2, \omega_1)$. Taking into account the contribution from all other diagrams in figure 1 we obtain (see appendix C)

$$U_{PC}(r_A, r_B) = \frac{\mu_0^2}{\hbar^2 \pi} \sum_{m,l \neq 0} \frac{4 \omega_A^{(m)}}{\omega_A^{(m)} + \omega_B^{(l)}} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \omega_1 \omega_2 \times \text{tr} \left[ m_A^{(0)} m_A^{(m)} \cdot \nabla_A \times \mathbf{G}(r_A, r_B, \omega_2) \times \widehat{\nabla}_B \cdot m_B^{(0)} d_B^{(l)} \cdot \text{Im} \mathbf{G}(r_B, r_A, \omega_1) \times \widehat{\nabla}_A \right] \times \left[ \frac{1}{\omega_A^{(m)} + \omega_1 + \omega_2} - \frac{1}{\omega_A^{(m)} + \omega_1} \right] \left( \frac{1}{\omega_2 + \omega_1} + \frac{1}{\omega_2 - \omega_1} \right).$$

(41)
At this stage, in order to present the result in a more convenient form, we may first use the definition (B.3) and the identity (B.5) to perform one of the frequency integrals, and then use complex analysis to write the remaining integral in terms of imaginary frequency as outlined in appendix A. Doing so, we end up with

\[
U_{\text{PC}}(r_A, r_B) = \frac{\hbar \mu_0^2}{\pi} \int_0^{\infty} d\xi \frac{2}{\omega} \sum_m \frac{\omega_m^A \omega_m^B \omega_m^p}{(\omega_m^A)^2 - \omega^2 - i\epsilon\omega},
\]

where the paramagnetic susceptibility tensor \(\beta_m^A(\omega)\) and the chiral polarisability \(\chi_m^\text{me}_B(\omega)\) are defined as

\[
\beta_m^A(\omega) = \lim_{\epsilon \to 0^+} \frac{2}{\hbar^2} \sum_{\omega_m^A} \frac{\omega_m^A \omega_m^B \omega_m^p}{(\omega_m^A)^2 - \omega^2 - i\epsilon\omega},
\]

\[
\chi_m^\text{me}_B(\omega) = \lim_{\epsilon \to 0^+} \frac{2}{\hbar^2} \sum_{\omega_m^B} \frac{\omega_m^B \omega_m^p}{(\omega_m^B)^2 - \omega^2 - i\epsilon\omega}.
\]

3.1.3. Chiral–chiral interaction.

In order to calculate the chiral–chiral contribution to the intermolecular potential, the molecule–field interaction Hamiltonians that have to be considered are

\[
\hat{H}_{A'F} = -\hat{d}_{A'} \cdot \hat{E}(r_{A'}) - \hat{m}_{A'} \cdot \hat{B}(r_{A'}), \quad A' \in \{A, B\}
\]

as in each molecule, one of the two opposite transitions (mentioned before) have to be considered of an electric nature with the other being considered a magnetic transition. Hence, every single diagram in figure 1 splits into four additional time-orderings. As an example, figure 4 shows the resulting split of diagram (1).

Let’s consider, first, diagram (1)a from figure 4. A calculation similar to the one outlined above equation (24), leads to the matrix elements \(\langle I|\hat{H}_{A'F}|0\rangle, \langle II|\hat{H}_{A'F}|I\rangle, \langle III|\hat{H}_{A'F}|II\rangle, \text{ and } \langle 0|\hat{H}_{A'F}|III\rangle\) given, respectively, by equations (24), (26), (27) and (39). Substitution of these matrix elements in equation (20), leads to

\[
U_{\text{CC}}^{(1)a} = \frac{\mu_0^2}{\pi \hbar^2} \sum_{m,l \neq 0} \int_0^{\infty} d\omega_1 \int_0^{\infty} d\omega_2 \int_0^{\infty} d\omega_3 \frac{N_{\text{CC}}^{(1)a}(\omega_1, \omega_2)}{D_1(\omega_1, \omega_2)},
\]

where

\[
N_{\text{CC}}^{(1)a}(\omega_1, \omega_2) = \frac{1}{\omega_1^2} \text{tr} \left[ d_{m_A}^{\text{ol}} m_A^{\text{ol}} \cdot \nabla_A \times \text{Im} \left( \mathbf{G}(r_A, r_B, \omega_2) \times \nabla_B \cdot m_B^{\text{ol}} d_B^{\text{ol}} \cdot \text{Im} \left( \mathbf{G}(r_B, r_A, \omega_1) \right) \right) \right].
\]

The contributions \(U_{\text{CC}}^{(1)b}, U_{\text{CC}}^{(1)c}, \text{ and } U_{\text{CC}}^{(1)d}\) are found to have the same form as the right hand side of equation (46), with \(N_{\text{CC}}^{(1)b}, N_{\text{CC}}^{(1)c}, \text{ and } N_{\text{CC}}^{(1)d}\) where

\[
N_{\text{CC}}^{(1)b}(\omega_1, \omega_2) = \frac{1}{\omega_2} \text{tr} \left[ d_{m_A}^{\text{ol}} m_A^{\text{ol}} \cdot \nabla_A \times \text{Im} \left( \mathbf{G}(r_A, r_B, \omega_2) \cdot d_B^{\text{ol}} m_B^{\text{ol}} \cdot \nabla_B \times \text{Im} \left( \mathbf{G}(r_B, r_A, \omega_1) \right) \right) \right],
\]

\[
N_{\text{CC}}^{(1)c}(\omega_1, \omega_2) = N_{\text{CC}}^{(1)b}(\omega_2, \omega_1), \quad N_{\text{CC}}^{(1)d}(\omega_1, \omega_2) = N_{\text{CC}}^{(1)a}(\omega_2, \omega_1).
\]
Using these, the contribution of diagram (1) in figure 1 to the chiral–chiral interaction potential becomes

\[ U_{\text{CC}}^{(1)} = -\frac{\hbar^2}{\pi} \sum_{m, l \neq 0} \int_0^\infty \frac{d\omega_1}{\pi} \int_0^\infty \frac{d\omega_2}{\pi} \omega_1^2 \omega_2^2 \left[ N_{1\text{c}}^2(\omega_1, \omega_2) + N_{1\text{b}}(\omega_1, \omega_2) \right] \left[ \frac{1}{D_1(\omega_1, \omega_2)} + \frac{1}{D_1(\omega_2, \omega_1)} \right]. \]

(49)

By calculating the contribution of all other diagrams in figure 1 in a similar manner and summing them up, we obtain (see appendix D) the chiral–chiral interaction potential as

\[ U_{\text{CC}}(r_A, r_B) = -\frac{\hbar^2}{\pi} \int_0^\infty \frac{d\xi}{\pi} \xi^2 \left\{ \text{tr} \left[ \chi_{\text{em}}^A(\xi) \cdot \nabla A \times \mathbf{G}(r_A, r_B, \xi) \cdot \mathbf{G}(r_B, r_A, \xi) \] \right. \nonumber \]

\[ + \left. \text{tr} \left[ \chi_{\text{em}}^A(\xi) \cdot \nabla A \times \mathbf{G}(r_A, r_B, \xi) \cdot \chi_{\text{em}}^B(\xi) \cdot \nabla B \times \mathbf{G}(r_B, r_A, \xi) \right] \right\}. \]

(50)

3.2. Diamagnetic–chiral interaction

While obtaining the formula of interaction potentials so far required fourth-order perturbation theory, the diamagnetic–chiral interaction potential is obtained via third-order perturbation theory (cf. reference [50]),

\[ U_{\text{DC}}(r_A, r_B) = \sum_{I, II \neq 0} \frac{\langle 0|\hat{H}_{\text{int}}|II \rangle \langle II|\hat{H}_{\text{int}}|I \rangle \langle I|\hat{H}_{\text{int}}|0 \rangle}{(E_{II} - E_0)(E_I - E_0)}, \]

(51)

The underlying reason is that the diamagnetic molecule–field interaction is a two–photon process. The two photons are exchanged with the chiral molecule to participate in the two–molecule interaction. To perform the calculation, we replace the paramagnetic molecule A in the preceding section with a diamagnetic one. That is

\[ \hat{H}_{\text{AF}} = -\frac{1}{2} \hat{B}(r_A) \cdot \hat{\beta}_{\text{A}}^D \cdot \hat{B}(r_A), \]

(52)

with \( \hat{\beta}_{\text{A}}^D \) defined in equation (10), and \( \hat{H}_{\text{BF}} \) was given by equation (22). The complete set of intermediate states that are involved in the perturbation formula (51) can be taken into account by the diagrams given in figure 5 (see reference [50]).

Each one of the three diagrams in figure 5 is split, as shown in figure 6, into two cases depending on whether the first transition occurring in the chiral molecule B is of electric type or magnetic type, labeled by a or b, respectively, as shown in figure 6.

Let’s consider first diagram (1) in figure 5. The corresponding intermediate states are given as follows

\[ |I\rangle = |0_A\rangle |0_B\rangle |1_{\lambda_{1\text{a}}}(r_1, \omega_1), 1_{\lambda_{2\text{a}}}(r_2, \omega_2)\rangle, \]

\[ |II\rangle = |0_A\rangle |0_B\rangle |1_{\lambda_{1\text{b}}}(r_3, \omega_3)\rangle. \]

(53)

To determine the corresponding matrix elements present in the numerator of equation (51), diagram (1)a or (1)b in figure 6 have to be distinguished. For the former one finds
The contributions from each diagram, Dia in Using these for matrix elements in equation (51), the implicitly included summations over integrals can be performed on making use of the integral relation (19) to lead to the contribution from diagram (1)a in figure 6 as Figure 6. (1a) from figure 5 being split into two cases depending on the sequence of the transitions in the chiral molecule B.

\[
\langle I | \hat{H}_{\text{int}} | 0 \rangle = -\frac{1}{2} \beta^0_{\alpha\beta}(1,1,1) \langle r_1, \omega_1, 1, \lambda_1 \mid B_{\alpha}(r_1) \beta_{\beta}(r_1) \rangle \{0\}.
\]

\[
= \frac{\beta^0_{\alpha\beta}}{\sqrt{2\omega_1\omega_2}} \left[ \nabla_A \times G_{\lambda_1}(r_1, r_1, \omega_1) \right]_{\alpha i} \left[ \nabla_A \times G_{\lambda_2}(r_2, r_2, \omega_2) \right]_{\beta i},
\]

(54)

\[
\langle II | \hat{H}_{\text{int}} | I \rangle = \langle 0 | \{ l_B \mid (1,1,1)(r_3, \omega_3) \} - \hat{d}_B \cdot \hat{E}(r_3) \rangle \{0\} \langle 0 | (1,1,1)(r_1, \omega_1, 1, \lambda_1 \mid B_{\alpha}(r_1) \beta_{\beta}(r_2, \omega_2) \rangle \}

\]

\[
= -\frac{d^0_B}{\sqrt{2}} \left[ \nabla_{A} \times G_{\lambda_1}(r_1, r_1, \omega_1) \right]_{\gamma i} \delta^{(32)} - \frac{d^0_B}{\sqrt{2}} \left[ \nabla_{B} \times G_{\lambda_2}(r_2, r_2, \omega_2) \right]_{\gamma i} \delta^{(31)},
\]

(55)

\[
\langle 0 | \hat{H}_{\text{int}} | II \rangle = \langle 0 \mid -\frac{1}{2} m_B \cdot \hat{B}(r_3) \rangle |II\rangle = -\frac{m_B}{\omega_3} \left[ \nabla_{A} \times G_{\lambda_1}(r_3, r_3, \omega_3) \right]_{\gamma i},
\]

(56)

with the respective denominator in equation (51) being \(h^2(\omega_3 + \omega_B(\omega_1 + \omega_2))\). After substituting these matrix elements in equation (51), the implicitly included summations over \(\lambda_1 (j = e, m)\) and position integrals can be performed on making use of the integral relation (19) to lead to the contribution from diagram (1)a in figure 6 as

\[
U_{DC}^{(a)} = \frac{\beta^0_{\alpha\beta}}{\pi^2} \sum_{j} \int_{0}^{\infty} d\omega_1 \int_{0}^{\infty} d\omega_2 D_{1a}(\omega_1, \omega_2)
\]

\[
\times \text{tr} \left\{ \beta^0 \cdot \nabla_{A} \times \text{Im} \left[ G(r_3, r_3, \omega_3) \right] \nabla_{A} \cdot m^0_B \right\},
\]

(57)

where

\[
D_{1a}(\omega_1, \omega_2) = \frac{\omega_2}{(\omega_1 + \omega_2)(\omega_B^2 + \omega_2)}.
\]

(58)

The contributions from each diagram, \(U_{DC}^{(b)}\), can be obtained similarly. It is found that the only difference is in \(D_{1a}^{(b)}(\omega_1, \omega_2)\) as listed below:

\[
D_{1b} = D_{3a} = \frac{-\omega_1}{(\omega_1 + \omega_2)(\omega_B^2 + \omega_1)}, \quad D_{2a} = D_{2b} = \frac{-\omega_1}{(\omega_B^2 + \omega_1)(\omega_B^2 + \omega_2)}, \quad D_{3b} = D_{1a}.
\]

(59)

Using these for \(U_{DC}^{(b)}\) and summing up the resulting expressions, as shown in appendix E, leads to the diamagnetic–chiral interaction potential as

\[
U_{DC}(r_A, r_B) = \frac{\hbar \mu_B^0}{\pi} \int_{0}^{\infty} d\xi \xi \text{tr} \left\{ \beta^0 \cdot \nabla_A \times \left[ G(r_3, r_3, i\xi) \right] \nabla_{A} \cdot \chi^0_{\alpha\gamma}(i\xi) \cdot \text{Im} \left[ G(r_3, r_3, i\xi) \right] \nabla_{A} \right\}.
\]

(60)

It is worth noting that the formula for the diamagnetic–chiral interaction potential and that for the paramagnetic–chiral energy shift, equations (42) and (60), despite being obtained from different orders of
perturbative calculations, have exactly the same structural form. These may be summed in a single formula by substitution of $\beta^e(\omega) + \beta^m \rightarrow \beta(\omega)$ to give an overall magnetic–chiral interaction:

$$U_{MC}(r_A, r_B) = \frac{\hbar r_0^2}{\pi} \int_0^\infty d\xi \text{tr} \left\{ \beta_A(i\xi) \cdot \left[ \nabla_A \times \mathbf{G}(r_A, r_B, i\xi) \times \vec{\nabla}_B \right] \right\} \cdot \mathbf{\chi}^{me}_B(i\xi) \cdot \left[ \mathbf{G}(r_B, r_A, i\xi) \times \vec{\nabla}_A \right] .$$

Including both paramagnetic and diamagnetic contributions in equation (61) ensures that the result is gauge invariant [15]. The chiral polarisabilities of the two enantiomers of a chiral molecule oppose each other in algebraic sign. This results in a discriminatory vdW dispersion interaction for the two enantiomers as it can be seen from the expressions obtained, equations (34), (42), (50) and (60), where a sign change emerges as a chiral molecule is replaced by its enantiomer.

### 4. Duality invariance

The formulas for various contributions to the vdW dispersion interaction given so far in this paper with one or both ground-state molecules being chiral, complete the formulas given for non-chiral species in literature (see references [49, 50, 58]). In this section we gather all contributions and discuss their symmetry with respect to the duality of electric and magnetic fields.

As a preparation, we note that all vdW interactions presented in this paper except for the diamagnetic one derive from the linear interaction

$$\hat{H}_{\text{vdW}} = -\sum_{\lambda} \mathbf{d}^\lambda \cdot \mathbf{E}(r_{\lambda'}) - \mathbf{m}^\lambda \cdot \mathbf{B}(r_{\lambda'}).$$

Recall that for $r_{\lambda'}$ in free space, the electric and magnetic fields featuring in this interaction obey duality invariance [59, 60]: when combining a known solution to the Maxwell equation into a dual pair $E_\lambda$ ($\lambda = e, m$) with $E_e = E, E_m = iB$, then applying a rotation in this two-dimensional duality space

$$\begin{pmatrix} E_e^\prime \\ E_m^\prime \end{pmatrix} = D(\theta) \begin{pmatrix} E_e \\ E_m \end{pmatrix}, \quad D(\theta) = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}$$

generates a new solution to the Maxwell equations. It follows immediately that the linear interaction Hamiltonian above can be written in duality-invariant form

$$\hat{H}_{\text{vdW}} = -\sum_{\lambda} \mathbf{d}^\lambda \cdot \mathbf{E}_\lambda(r_{\lambda'}).$$

by introducing a dual pair vector of molecular dipoles $\mathbf{d}^\lambda$ with $d^e = d, d^m = m/c$ and positing that such an upper-index dual pair vector transforms with $D^T(\theta) = D^{-1}(\theta)$ under a duality rotation.

If we now calculate the vdW potential arising from this molecule–field interaction using dual-pair notation, then we arrive at a total interaction

$$U(r_A, r_B) = \sum_{\lambda_1,\lambda_2,\lambda_3,\lambda_4 = e,m} U_{\lambda_1\lambda_2\lambda_3\lambda_4}$$

with

$$U_{\lambda_1\lambda_2\lambda_3\lambda_4}(r_A, r_B) = -\frac{\hbar}{2\pi c^2} \int_0^\infty d\xi \text{tr} \left[ \alpha_{\lambda_1\lambda_2}(i\xi) \cdot \mathbf{G}_{\lambda_1\lambda_3}(r_A, r_{\lambda_1}, i\xi) \cdot \alpha_{\lambda_3\lambda_4}(i\xi) \cdot \mathbf{G}_{\lambda_4\lambda_2}(r_{\lambda_4}, r_A, i\xi) \right].$$

which is duality-invariant given that both molecules are situated in a free-space region. Here, we have introduced Green tensor components in duality space:

$$\mathbf{G}_{ee}(r, r', \omega) \equiv \frac{i\omega}{c} \mathbf{G}(r, r', \omega) \left( -\frac{i\omega}{c} \right),$$

$$\mathbf{G}_{em}(r, r', \omega) \equiv \frac{i\omega}{c} \mathbf{G}(r, r', \omega) \times \left( -\vec{\nabla}' \right),$$

$$\mathbf{G}_{me}(r, r', \omega) \equiv \vec{\nabla} \times \mathbf{G}(r, r', \omega) \left( -\frac{i\omega}{c} \right),$$

$$\mathbf{G}_{mm}(r, r', \omega) \equiv \vec{\nabla} \times \mathbf{G}(r, r', \omega) \times \left( -\vec{\nabla}' \right),$$

which emerge from expectation values $\langle \vec{E}, \vec{E}' \rangle$ and transform via $D(\theta)$ as well as polarisabilities.
\[ \alpha^\text{em}(\omega) \equiv \alpha(\omega), \quad (71) \]
\[ \alpha^\text{me}(\omega) \equiv \chi^\text{em}(\omega)/\epsilon, \quad (72) \]
\[ \alpha^\text{me}(\omega) \equiv \chi^\text{me}(\omega)/\epsilon, \quad (73) \]
\[ \alpha^\text{mm}(\omega) \equiv \beta(\omega)/\epsilon^2 \quad (74) \]

which transform via \( D^T(\theta) \). Equations (65) and (66) give the most general vdW potential of two molecules with dipole polarisabilities, magnetisabilities, and electromagnetic cross-polarisabilities within an arbitrary bi-anisotropic environment. By virtue of \( \beta(\omega) = \beta'(\omega) + \beta'' \), this includes molecules with both paramagnetic and diamagnetic responses. The general potential is duality invariant, provided that both molecules are situated in free-space regions. For molecules in media, duality-invariance can be ensured by using the real-cavity model where the molecules are surrounded by small free-space cavities [61].

The interactions considered in the previous sections emerge by identifying \( E = ee, M = mm, C = em + me \):

\[ U_{EE} = U_{eene}, \quad U_{EM} = U_{eemn}, \quad U_{ME} = U_{mme}, \quad U_{MM} = U_{mmme} \quad (75) \]
\[ U_{EC} = U_{eeem} + U_{eme}, \quad U_{MC} = U_{mmem} + U_{memn}, \quad (76) \]
\[ U_{CE} = U_{eeme} + U_{mee}, \quad U_{CM} = U_{mmme} + U_{memn}, \quad (77) \]
\[ U_{CC} = U_{eemm} + U_{mme} + U_{mem} \quad (78) \]

where for chiral responses, one may use Lloyd’s theorem \( \chi^\text{me} = -\chi^\text{em}^\top \) (compare equations (36) and (44)) [57].

The duality invariance with \( \theta = \pi/2 \) can be exploited for molecules with electric, chiral, and paramagnetic responses by replacing \( \alpha \leftrightarrow \beta/\epsilon^2 \) and \( \chi^\text{em} \leftrightarrow -\chi^\text{me} \), thus generating new potentials from previously calculated results. For instance, this explains why \( U_{EE} \) and \( U_{MM} \) in free space are so strikingly similar and the same holds for \( U_{EC} \) and \( U_{MC} \). For diamagnetic molecules, this transformation applies only formally, since the diamagnetic magnetisability is negative, in contrast to the electric polarisability from which it is obtained via the transformation.

One may be tempted to generate chiral potentials from electric or magnetic ones by applying a duality transformation \( \theta = \pi/2 \). However, as noted in references [48, 62], such a transformation will generate nonreciprocal cross-polarisabilities which do not obey Lloyd’s theorem and hence do not correspond to chiral molecules, but instead charge-parity violating ones. For instance, starting from a purely electric isotropic molecule of polarisability \( \alpha \), the transformed molecule will exhibit cross-polarisabilities \( \chi^\text{em}/\epsilon = \chi^\text{me}/\epsilon = \alpha/4 \) which clearly violate Lloyd’s theorem. This is why vdW potentials involving chiral molecules have a distance dependence which is quite distinct from the known dependences for electric and magnetic molecules. We will see this explicitly below when studying bulk-media examples.

5. Interactions in homogeneous magnetoelectric media

As a simple application of the obtained formulas, we may consider two molecules located in a homogeneous magnetoelectric medium for which it can easily be verified that the chirality contribution vanishes in the case of isotropic molecules unless both molecules are chiral i.e. after performing a rotational average. Hence, for the sake of generality we consider anisotropic molecules and treat the case of isotropic molecules as specific examples. For notational convenience we replace, in what follows, \( \chi^\text{em} \) with \( \chi \) and use the fact that \( \chi^\text{me} = -\chi^\text{em}^\top = -\chi^\top \).

5.1. Electric–chiral interaction

The Green’s tensor \( G^{(b)}(r_A, r_B, i\xi) \) of a dispersive homogeneous bulk magnetoelectric media with relative electric permittivity \( \varepsilon(\omega) \) and magnetic permeability \( \mu(\omega) \) reads [46]

\[ G^{(b)}(r_A, r_B, i\xi) = \frac{\mu(i\xi)}{4\pi} \left( 1 - \frac{1}{k^2} \nabla_A \nabla_A \right) \frac{e^{-ikR}}{R} = \frac{\mu(i\xi)e^{-ikR}}{4\pi k^2 R^2} \left[ f(kR)I - g(kR) \frac{RR}{R^2} \right], \quad (79) \]

where \( k = n(i\xi)/c \) with \( n(i\xi) = \sqrt{\varepsilon(i\xi)\mu(i\xi)} \) being the refractive index, \( R = |R|, R = r_A - r_B \), and
f(x) = 1 + x + x^2, 
\quad g(x) = 3 + 3x + x^2.  
\quad (80)

Using this tensor together with the required derivative

\[ \nabla_B \times \mathbf{G}^{(b)}(r_B, r_A, i\xi) = \frac{\mu(i\xi)}{4\pi} \nabla_B \left( \frac{e^{-iR}}{R} \right) \times \mathbf{I} = \frac{\mu(i\xi)e^{-iR}}{4\pi R^3} (1 + kR) \mathbf{R} \times \mathbf{I} \quad (81) \]

in equation (34) for an electric molecule A and a chiral molecule B, results in

\[ U_{EC}(R) = \frac{\hbar \mu_0^2}{16\pi^3 \varepsilon_0^2} e^{q} \tilde{q} \int_0^\infty d\xi ~ \xi^\alpha n^3(i\xi) \mu^2(i\xi) e^{-2ni\xi R_{\lambda\lambda} / c} \alpha_{\lambda\lambda}^{\mu}(i\xi) \chi_0^{\mu}(i\xi) \]

\[ \times \left[ \frac{c^2(\delta_{\mu\nu} - R_{\mu\nu})}{n^2(i\xi) R^2 \xi^2} + \frac{2c^2}{n^2(i\xi) R^2 \xi^3} + \frac{2c^2}{n^2(i\xi) R^4 \xi^4} + \frac{c^2(\delta_{\mu\nu} - 3R_{\mu\nu})}{n^2(i\xi) R^2 \xi^3} \right] \quad (82) \]

with \( \tilde{R} = R / R \). In the case of isotropic molecules, for which \( \alpha \) and \( \chi \) are diagonal matrices, it can be seen easily that the interaction potential vanishes.

In the retarded limit of intermolecular separation (\( R \gg c / \omega_{\text{min}} \) with \( \omega_{\text{min}} \) being the smallest of molecular transition frequencies as well as medium characteristic frequencies), \( \alpha \) and \( \chi \) in equation (82) can be replaced by their static values \( \alpha(0) \) and \( \chi(0) \),

\[ \alpha_{\lambda\lambda}(0) = \frac{2}{\hbar} \sum_m \frac{d_m^{\mu\alpha} d_m^{\nu\beta}}{\omega_A^{\mu\nu}} \equiv \alpha_{\lambda\lambda}, \quad \lim_{\xi \to 0} \chi_0^{\mu}(i\xi) = -\frac{2i}{\hbar} \xi \sum_i \frac{d_{\mu i}^{\nu} n_{\nu i}^{\nu}}{(\omega_0)^2} \equiv \xi \chi_{\lambda\lambda}^{\mu}. \quad (83) \]

Performing the remaining integral leads to

\[ U_{EC}^{\mu}(R) = \frac{7\hbar \mu_0^2 c^2 (0)}{128\pi^3 \varepsilon_0^2 n^2(0) R^6} e^{q} \tilde{q} \int_0^\infty d\xi ~ \xi^\alpha n^3(i\xi) \mu^2(i\xi) e^{-2ni\xi R_{\lambda\lambda} / c} \alpha_{\lambda\lambda}^{\mu}(i\xi) \chi_{\lambda\lambda}^{\mu}(i\xi). \quad (84) \]

In the opposite limit of non-retarded coupling (\( R \ll c / \omega_{\text{max}} \) with \( \omega_{\text{max}} \) being the largest of molecular transition frequencies as well as medium characteristic frequencies) the exponential factor in equation (82) tends to unity and the last term in the square brackets gives the main contribution. In this limit

\[ U_{EC}^{\mu}(R) = \frac{\hbar \mu_0^2 c^2}{16\pi^3 \varepsilon_0^2 R^6} e^{q} \tilde{q} \int_0^\infty d\xi ~ \xi^\alpha n^3(i\xi) \mu^2(i\xi) e^{-2ni\xi R_{\lambda\lambda} / c} \alpha_{\lambda\lambda}^{\mu}(i\xi) \chi_{\lambda\lambda}^{\mu}(i\xi). \quad (85) \]

5.2. Magnetic–chiral interaction

The interaction potential of a magnetic molecule A and a chiral molecule B in a bulk media may be written by direct calculation of the required derivatives of the Green’s tensor,

\[ \nabla_A \times \mathbf{G}^{(b)}(r_A, r_B, i\xi) \times \tilde{\nabla}_B = n^2(i\xi) \frac{c^2}{\varepsilon_2} \mathbf{G}^{(b)}(r_A, r_B, i\xi), \quad (86) \]

and

\[ \mathbf{G}^{(b)}(r_B, r_A, i\xi) \times \tilde{\nabla}_A = -\nabla_B \times \mathbf{G}^{(b)}(r_B, r_A, i\xi), \quad (87) \]

together with equation (81), and using them in equation (61). The result is

\[ U_{MC}(R) = \frac{\hbar \mu_0^2 c^2}{16\pi^3 \varepsilon_0^2 q} \int_0^\infty d\xi ~ \xi^\alpha n^3(i\xi) \mu^2(i\xi) e^{-2ni\xi R_{\lambda\lambda} / c} \alpha_{\lambda\lambda}^{\mu}(i\xi) \chi_{\lambda\lambda}^{\mu}(i\xi) \]

\[ \times \left[ \frac{c^2(\delta_{\mu\nu} - R_{\mu\nu})}{n^2(i\xi) R^2 \xi^2} + \frac{2c^2}{n^2(i\xi) R^2 \xi^3} + \frac{2c^2}{n^2(i\xi) R^4 \xi^4} + \frac{c^2(\delta_{\mu\nu} - 3R_{\mu\nu})}{n^2(i\xi) R^2 \xi^3} \right] \quad (88) \]

Similar to the electric–chiral interaction potential in bulk media, the magnetic–chiral one vanishes for isotropic molecules by orientational averaging.
In the retarded limit, the result is obtained through a similar manner as for the electric–chiral interaction potential, as

$$U_{MC}^{\text{r}}(R) = \frac{7\mu_0^2}{128\pi^3 n^3(0) R^6} \epsilon_{pq} \tilde{R}_{q}(5\delta_{p} - 9\tilde{R}_{p}) \beta_{A}^{\text{p}} \chi_{B}^{\text{r}},$$  

(89)

where

$$\beta_{A} = \beta_{A}^{0} + \beta_{A}^{\text{p}}(0) = \beta_{A}^{0} + \frac{2}{\hbar} \sum_{m} \frac{m_{A}^{\text{m}} m_{B}^{\text{m}}}{\omega_{A}^{m}}.$$  

(90)

In the non-retarded limit, the diamagnetic–chiral and paramagnetic–chiral interactions have to be treated separately because of the frequency-independent nature of the diamagnetisability. For the paramagnetic–chiral interaction, through a similar discussion for electric–chiral contribution that led to equation (84), we obtain

$$U_{MC}^{\text{n}}(R) = \frac{h\mu_0^2}{16\pi^3 R^7} \epsilon_{pq} \tilde{R}_{q}(\delta_{p} - 3\tilde{R}_{p}) \int_{-\infty}^{\infty} d\xi \mu_0^2 \langle i\xi \rangle \beta_{A}^{\text{p}}(i\xi) \chi_{B}^{\text{r}}(i\xi).$$  

(91)

For the diamagnetic–chiral interaction, in the non-retarded limit, approximating the exponential factor to unity results in a divergent integral because, on the contrary to the retarded limit, the major contribution to the frequency integral comes from frequencies much greater than $c/\omega_{\text{max}}$. Hence, the magnetoelectric properties of the media can be replaced by those of free-space and the chiral polarisability, equation (36), approximates to

$$\chi_{B}^{\text{p}}(\omega) = \frac{2}{\hbar\omega} \sum_{l} d_{l}^{0} m_{B}^{l}.$$  

(92)

Using equation (92) in equation (88) together with $\beta \to \beta^{\text{p}}$, results in

$$U_{MC}^{\text{n}}(R) = -\frac{5\mu_0^2}{64\pi^3 R^7} \epsilon_{pq} \tilde{R}_{q} \beta_{A}^{\text{p}}(0) \sum_{m} (d_{m}^{0} m_{B}^{m})^{r}.$$  

(93)

5.3. Chiral–chiral interaction

The contribution from the chirality of two molecules A and B to the vdW interaction potential in a bulk magnetoelectric media can be obtained by making use of equations (81) and (86) for the required derivatives of the Green’s tensor in equation (50), together with equations (79) and (80). This leads to

$$U_{CC}^{\text{r}}(R) = \frac{h\mu_0^2}{16\pi^3} \int_{0}^{\infty} d\xi \xi^{6} n^{2}(i\xi) \mu^{2}(i\xi) e^{-2m(i\xi) R / \varepsilon_{A}(i\xi)} \chi_{A}^{\text{r}}(i\xi) \chi_{B}^{\text{r}}(i\xi)$$

$$\times \left\{ \frac{c^6}{n^2(i\xi) R^4 \xi^4} + \frac{2c^3}{n^2(i\xi) R^2 \xi^2} \right\} \left( \delta_{p} - 3\tilde{R}_{p} \right)$$

$$+ \frac{c^4}{n^2(i\xi) R^2 \xi^2} \left[ 3\delta_{q} \delta_{p} - 7\delta_{q} \tilde{R}_{p} - \delta_{q} \tilde{R}_{p} \right] + 15\tilde{R}_{p} \tilde{R}_{p} \tilde{R}_{q} + c_{q} c_{p} c_{q} c_{p}$$

$$+ \frac{c^3}{n^2(i\xi) R \xi} \left[ 6\delta_{q} \delta_{p} - 4\delta_{q} \tilde{R}_{p} - \delta_{q} \tilde{R}_{p} \right] + 6\tilde{R}_{p} \tilde{R}_{p} \tilde{R}_{q} + 2c_{q} c_{p} c_{q} c_{p}$$

$$+ \frac{c^2}{n^2(i\xi)} \left[ \delta_{q} \delta_{p} - \delta_{q} \tilde{R}_{p} - \delta_{q} \tilde{R}_{p} \right] + 6\tilde{R}_{p} \tilde{R}_{p} \tilde{R}_{q} + c_{q} c_{p} c_{q} c_{p} \right\}.$$  

(94)

It is worth noting that in the case of isotropic molecules in free space, for which $\chi_{A}^{\text{r}} = \chi_{A} e^{i\delta_{p}}$ and $\varepsilon = \mu = 1$, equation (94) after changing the integration variable according to $\eta = \xi / c$ reduces to

$$U_{CC}^{\text{r}}(R) = \frac{h\mu_0^2}{8\pi^3 R^6} \int_{0}^{\infty} d\eta e^{-2\eta R (\chi_{A}(i\eta \varepsilon) \chi_{B}(i\eta \varepsilon) + 3 + 6\eta R + 4\eta^2 R^2),}$$  

(95)

in agreement with references [37–39, 63]. As stated above, this interaction cannot be obtained from the well-known electric–electric potential by means of a duality transformation.
Returning to the bulk-medium case, we note that in the retarded intermolecular separation, the chiral polarisabilities in equation (94) can be replaced by their static limits. Calculation of the remaining integral results in

\[
U_{CC}(R) = \frac{\hbar \mu_e^2}{128 \pi^3 \sigma^2(0)^2 R^2} \chi^\alpha_A(0) \chi^\beta_B(0) \left( 101 \delta_{q} \delta_{j} - 171 \delta_{q} \delta_{i} \bar{R}_{j} \bar{R}_{p} - 171 \delta_{p} \delta_{i} \bar{R}_{j} \bar{R}_{q} + 297 \bar{R}_{j} \bar{R}_{p} \bar{R}_{q} + 81 \epsilon_{\mu \nu \rho} \epsilon_{qj} \bar{R}_{\mu} \right),
\]

where \( \chi^\alpha_A \) is defined according to equation (83).

In the opposite limit of non-retarded intermolecular distances, we may set the exponential factor in equation (94) to unity and retain only the term proportional to \( \frac{1}{R^6} \) in the curly brackets. This leads to

\[
U_{CC}(R) = \frac{\hbar \mu_e^2}{16 \pi^2 R^6} \left( \delta_{q} - 3 \bar{R}_{j} \bar{R}_{q} \right) \left( \delta_{p} - 3 \bar{R}_{i} \bar{R}_{p} \right) \int_0^{\infty} d\xi \frac{1}{\xi^{\mu}(i\xi) \chi^\alpha_A(i\xi) \chi^\beta_B(i\xi)}. \]

### 6. Conclusion

In this paper a general expression for the van der Waals dispersion interaction potential between two ground-state molecules in the presence of arbitrary magnetoelectric media is derived making use of perturbation theory. The result for the diamagnetic–chiral interaction potential is seen to have the same perturbative calculations. The formulas obtained in this paper, together with those found in earlier studies (e.g. references [49, 50, 58]) form a complete set of formulas for the van der Waals interaction potentials for molecules with electric, paramagnetic, and diamagnetic polarisabilities, applicable for chiral and anisotropic molecules and for arbitrary ranges of intermolecular separations as well as allowing for a possible chirality of the surrounding media. The formulas of various contributions to the full dispersion interaction have been brought into a unified form by taking advantage of electric–magnetic duality.

As an application of the obtained formulas, the interaction potential for two anisotropic chiral molecules embedded in a homogeneous magnetoelectric medium has been evaluated. The retarded and non-retarded limits of intermolecular separations are obtained and their corresponding distance power laws are summarized in table 1. Noting that the case of free space may be considered as a limit for bulk magnetoelectric media with \( \epsilon = \mu = 1 \), it is seen that the distance power laws would be the same and the corresponding references in literature are given in the table.

| Interaction component | Retarded limit | Non-retarded limit |
|-----------------------|---------------|-------------------|
| Electric–electric [49]| \(-R^{-7}\)    | \(-R^{-6}\)       |
| Electric–paramagnetic [58]| \(+R^{-7}\)   | \(+R^{-4}\)       |
| Electric–diamagnetic [50]| \(-R^{-7}\)   | \(-R^{-4}\)       |
| Electric–chiral [64]  | \(\pm R^{-8}\) | \(\pm R^{-3}\)    |
| Paramagnetic–paramagnetic [58]| \(-R^{-7}\)   | \(-R^{-6}\)       |
| Paramagnetic–diamagnetic [50]| \(+R^{-7}\)   | \(+R^{-4}\)       |
| Paramagnetic–chiral [64] | \(\pm R^{-8}\) | \(\pm R^{-3}\)    |
| Diamagnetic–diamagnetic [50]| \(-R^{-7}\)   | \(-R^{-6}\)       |
| Diamagnetic–chiral [65] | \(\pm R^{-8}\) | \(\pm R^{-6}\)    |
| Chiral–chiral [65]    | \(\pm R^{-9}\) | \(\pm R^{-6}\)    |
potential in second-order perturbation theory. The same is true for the magnetic near field due to a magnetic dipole, so we find the same scaling for the paramagnetic–paramagnetic and chiral–chiral potentials. However, the magnetic near field of an electric dipole scales as $1/R^2$ and vice versa, so that mixed electric–magnetic coupling reduces the inverse power of $R$ by one. We hence arrive at $1/R^3$ for the electric–chiral and paramagnetic–chiral potentials and $1/R^4$ for the electric–paramagnetic one. This reasoning and the resulting power laws remain largely valid when considering dia- instead of paramagnetic molecules. The only exception is the diamagnetic–chiral case where the nondispersive nature of the diamagnetic response leads to an anomalous $1/R^2$ scaling that deviates from the $1/R^3$ paramagnetic–chiral potential.

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**Appendix A. Calculation of equation (32) for the chiral–electric potential**

Taking into account the contributions from all diagrams in figure 1 to equation (20) for the electric–chiral interaction leads to

$$U_{EC} = \sum_{i=1}^{12} U_{EC}^i = -\frac{\mu_0}{\hbar \pi^2} \sum_{m,\neq 0} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \omega_1^2 \omega_2^2 N_{EC}(\omega_1, \omega_2) \left[ D_{EC}^\alpha(\omega_1, \omega_2) + D_{EC}^\beta(\omega_2, \omega_1) \right],$$  \hspace{1cm} (A.1)

where

$$D_{EC}^\alpha(\omega_1, \omega_2) = \pm \left( \frac{1}{D_1} - \frac{1}{D_2} + \frac{1}{D_3} - \frac{1}{D_9} - \frac{1}{D_{11}} - \frac{1}{D_{12}} \right) + \frac{1}{D_4} - \frac{1}{D_5} + \frac{1}{D_6} + \frac{1}{D_7} + \frac{1}{D_8} + \frac{1}{D_{10}}$$  \hspace{1cm} (A.2)

with $D_i$ denoting the energy denominator for case $(i)$ as listed in table A1. It is not difficult to show that

$$D_{EC}^\alpha(\omega_1, \omega_2) + D_{EC}^\beta(\omega_2, \omega_1) = \frac{4\omega^m}{\omega^m + \omega^l} \left[ \frac{1}{(\omega^m + \omega^l)(\omega^l + \omega^2)} - \frac{1}{(\omega^m + \omega^1)(\omega^l + \omega^2)} \right]$$

$$\times \left( \frac{1}{\omega^2 + \omega^1} - \frac{1}{\omega^2 - \omega^1} \right)$$  \hspace{1cm} (A.3)

(cf. reference [21]). Making use of equation (A.3) in equation (A.1) leads to equation (32).

**Appendix B. Calculation of equation (33) for the chiral–electric potential**

In equation (32) we encounter a double integral in the form of

$$\int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \omega_1^2 \omega_2^2 \text{Im} \left[ G_{\alpha}(\omega_1) \text{Im} \left[ G_{\beta}(\omega_2) \left( \frac{1}{\omega_2 + \omega_1} - \frac{1}{\omega_2 - \omega_1} \right) \right] \right] \equiv \mathcal{I}_i, \hspace{1cm} i = 1, 2$$  \hspace{1cm} (B.1)

where $G_{\alpha}$ and $G_{\beta}$ denote typical matrix elements of the Green tensor. In order to calculate $\mathcal{I}_1$, the integral over $\omega_2$,

$$\int_0^\infty d\omega_2 \omega_2 \text{Im} \left[ G_{\beta}(\omega_2) \left( \frac{1}{\omega_2 + \omega_1} - \frac{1}{\omega_2 - \omega_1} \right) \right] \equiv g^{(1)}_\beta(\omega_1)$$  \hspace{1cm} (B.2)

is to be performed first, for which we introduce its more general form as
Table A1. The energy denominators corresponding to the diagrams in figure 1.

| Diagram | Energy denominator $D_i$ |
|---------|--------------------------|
| (1)     | $D_1 = (\omega_1^\alpha + \omega_1)(\omega_1 + \omega_2)(\omega_1 + \omega_2)$ |
| (2)     | $D_2 = (\omega_1^\alpha + \omega_1)(\omega_2 + \omega_2)(\omega_1 + \omega_2)$ |
| (3)     | $D_3 = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_2 + \omega_2)$ |
| (4)     | $D_4 = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_1 + \omega_2)$ |
| (5)     | $D_5 = (\omega_1^\alpha + \omega_1)(\omega_1 + \omega_1)(\omega_1 + \omega_2)$ |
| (6)     | $D_6 = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_1 + \omega_2)$ |
| (7)     | $D_7 = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_1 + \omega_2)$ |
| (8)     | $D_8 = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_1 + \omega_2)$ |
| (9)     | $D_9 = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_1 + \omega_2)$ |
| (10)    | $D_{10} = (\omega_1^\alpha + \omega_1)(\omega_1^\alpha + \omega_2)(\omega_1 + \omega_2)$ |
| (11)    | $D_{11} = (\omega_1^\alpha + \omega_1)(\omega_1 + \omega_2)(\omega_1 + \omega_2)$ |
| (12)    | $D_{12} = (\omega_1^\alpha + \omega_1)(\omega_1 + \omega_2)(\omega_1 + \omega_2)$ |

\[
g^{(n)}(\omega) = \int_0^\infty d\omega' \omega'^n \text{Im} G(\omega') \left( \frac{1}{\omega' + \omega} + \frac{(-1)^n}{\omega' - \omega} \right), \quad (B.3)
\]

for real $\omega$ and non-negative integer $n$. The Schwartz reflection principle, equation (17), implies that for real $\omega$ the imaginary part of the Green tensor is an odd function of $\omega$. Using this, it is easy to show that the integrand in equation (B.3) is an even function of $\omega'$, and we may write

\[
g^{(n)}(\omega) = \frac{1}{2} \text{Im} \int_{-\infty}^\infty d\omega' \omega'^n G(\omega') \left( \frac{1}{\omega' + \omega} + \frac{(-1)^n}{\omega' - \omega} \right). \quad (B.4)
\]

This integral can be evaluated using contour integral techniques by drawing an infinitely large semicircle in the upper half of the complex frequency plane (where the Green’s function is analytic as a response function [55]) to the real axis, and making use of the Cauchy formula. This leads to

\[
g^{(n)}(\omega) = \frac{\pi}{2} (-\omega)^n [G(\omega) + G^*(\omega)]. \quad (B.5)
\]

Using equation (B.2) together with equation (B.5) in equation (B.1) results in

\[
I_1 = \frac{\pi i}{4} \int_0^\infty d\omega' \omega'^3 \left[ G_1(\omega) - G_1^*(\omega) \right] \left[ G_2(\omega) + G_2^*(\omega) \right] 
= \frac{\pi i}{4} \int_0^\infty d\omega' \omega'^3 \left[ G_1(\omega)G_2(\omega) - G_1^*(\omega)G_2^*(\omega) \right] 
+ \frac{\pi i}{4} \int_0^\infty d\omega' \omega'^3 \left[ G_1(\omega)G_2^*(\omega) - G_1^*(\omega)G_2(\omega) \right]. \quad (B.6)
\]

The double integral $I_2$ defined by equation (B.1) can be treated similarly to obtain

\[
I_2 = \frac{\pi i}{4} \int_0^\infty d\omega' \omega'^3 \left[ G_1(\omega)G_2(\omega) - G_1^*(\omega)G_2^*(\omega) \right] 
+ \frac{\pi i}{4} \int_0^\infty d\omega' \omega'^3 \left[ G_2(\omega)G_3(\omega) - G_2^*(\omega)G_3^*(\omega) \right], \quad (B.7)
\]

hence, for $I_2 - I_1$ appearing in equation (32), we end up with

\[
I_2 - I_1 = -\frac{\pi i}{2} \int_0^\infty d\omega' \omega'^3 \left[ G_1(\omega)G_2(\omega) - G_1^*(\omega)G_2^*(\omega) \right]. \quad (B.8)
\]

For the second term in the square brackets we may change the variable as $\omega \to -\omega$ and make use of the Schwartz reflection principle to rewrite equation (B.8) in the form
\[ I_2 - I_1 = -\frac{\pi i}{2} \left\{ \int_{0}^{\infty} \frac{d\omega \omega^3 G_{\alpha}(\omega) G_{\beta}(\omega)}{(\omega^m + \omega)(\omega^b + \omega)} + \int_{-\infty}^{0} \frac{d\omega \omega^3 G_{\alpha}(\omega) G_{\beta}(\omega)}{(\omega^m - \omega)(\omega^b - \omega)} \right\}. \] (B.9)

Again, using the fact that both of the integrands are analytic in the upper half of the complex frequency plane including the real axis, we may replace the integration path in the first(second) integral by a quarter-circle in the first(second) quadrant together with the positive imaginary axis \((\omega = i\xi)\). The contribution from the quarter circle vanishes due to the limiting behavior of the Green tensor for large frequencies, and we are left with

\[ I_2 - I_1 = -\pi(\omega^m_A + \omega^b_B) \int_{0}^{\infty} d\xi \frac{\xi^4 G_{\alpha}(i\xi) G_{\beta}(i\xi)}{[(\omega^m_A)^2 + \xi^2][(\omega^b_B)^2 + \xi^2]}. \] (B.10)

Using this, leads from equation (32) to equation (33).

**Appendix C. Calculation of equation (41) for the paramagnetic–chiral potential**

\[ U_{PC}(r_A, r_B) = -\frac{\mu_0}{\hbar^2} \sum_{m, j, l=0}^{\infty} \int_{0}^{\infty} d\omega_1 \int_{0}^{\infty} d\omega_2 \omega_1^2 \omega_2^2 N_{PC}(\omega_1, \omega_2)[D_{PC}^+(\omega_1, \omega_2) + D_{PC}^-(\omega_2, \omega_1)], \] (C.1)

where

\[ D_{PC}^\pm(\omega_1, \omega_2) = \pm \left( \frac{1}{D_1} - \frac{1}{D_2} + \frac{1}{D_3} - \frac{1}{D_4} - \frac{1}{D_5} - \frac{1}{D_6} - \frac{1}{D_7} - \frac{1}{D_8} - \frac{1}{D_{10}} \right). \] (C.2)

By a straightforward algebra it can be shown that

\[ D_{PC}^+(\omega_1, \omega_2) + D_{PC}^-(\omega_2, \omega_1) = \frac{4\omega^m_A}{\omega^m_A + \omega^b_B} \left[ \frac{1}{(\omega^m_A + \omega_2)(\omega^b_B + \omega_2)} - \frac{1}{(\omega^m_A + \omega_1)(\omega^b_B + \omega_1)} \right] \times \left( \frac{1}{\omega_2 + \omega_1} + \frac{1}{\omega_2 - \omega_1} \right). \] (C.3)

Substituting equations (40) and (C.3) into equation (C.1) leads to equation (41).

**Appendix D. Calculation of equation (50) for the chiral–chiral potential**

By calculating the contribution of all other diagrams in figure 1 similar to that of diagram (1) and summing them up, we obtain

\[ U_{CC} = -\frac{\mu_0}{\hbar^2} \sum_{m, j, l=0}^{\infty} \int_{0}^{\infty} d\omega_1 \int_{0}^{\infty} d\omega_2 \omega_1^2 \omega_2^2 \left\{ N_{CC}^{(a)}(\omega_1, \omega_2)[D^-(\omega_1, \omega_2) + D^-(\omega_2, \omega_1)] \right\} 
+ N_{CC}^{(b)}(\omega_1, \omega_2)[D^+(\omega_1, \omega_2) + D^+(\omega_2, \omega_1)] \] (D.1)

with

\[ D^\pm(\omega_1, \omega_2) = \frac{1}{D_1} - \frac{1}{D_2} + \frac{1}{D_3} + \frac{1}{D_4} - \frac{1}{D_5} + \frac{1}{D_6} - \frac{1}{D_7} + \frac{1}{D_8} + \frac{1}{D_{10}} \pm \left( \frac{1}{D_4} - \frac{1}{D_5} - \frac{1}{D_6} - \frac{1}{D_7} + \frac{1}{D_8} + \frac{1}{D_{10}} \right). \] (D.2)

After some straightforward algebra, it can be shown that

\[ D^+(\omega_1, \omega_2) + D^+(\omega_2, \omega_1) = \frac{4\omega^m_A}{\omega^m_A + \omega^b_B} F_{\pm}(\omega_1, \omega_2), \] (D.3)

where \( F_{\pm}(\omega_1, \omega_2) = f_{\pm}(\omega_1, \omega_2) + f_{\pm}(\omega_2, \omega_1) \) with

\[ f_{\pm}(\omega_1, \omega_2) = \frac{\omega_1}{(\omega^m_A + \omega_1)(\omega^b_B + \omega_1)} \left( \frac{1}{\omega_1 + \omega_2} \pm \frac{1}{\omega_1 - \omega_2} \right). \] (D.4)

Upon making use of equations (47) and (48), equation (D.1) becomes
In order to determine the diamagnetic–chiral interaction potential, equation (57) has to be added to other portions for those $D_{(a)}$ is replaced by $D_{\omega(b)}$ given by equation (59). Doing this yields

$$U_{DC} = \frac{4\mu_0^2}{\pi^2} \sum_{m,l} \frac{1}{\omega^2 + \omega_l^2} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \omega_1 \omega_2 \left\{ \omega_1^2 \left[ J_1(\omega) \cdot \tilde{\nabla}_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \cdot m_A^m \cdot m_B^l \right] + \omega_1 \omega_2 \left[ \omega_1 \omega_2 \cdot \tilde{\nabla}_B \cdot m_A^m \cdot \nabla_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \right] F_+ \right\}.$$  (D.5)

Now, in order to write the result in a compact form, we follow a similar procedure as for obtaining equations (34) and (42).

### Appendix E. Calculation of equation (60) for the diamagnetic–chiral potential

In order to determine the diamagnetic–chiral interaction potential, equation (57) has to be added to other portions for those $D_{(a)}$ is replaced by $D_{\omega(b)}$ given by equation (59). Doing this yields

$$U_{DC} = \frac{4\mu_0^2}{\pi^2} \sum_{m,l} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \frac{\omega_1^2 \omega_2}{(\omega_1 + \omega_2)(\omega_1 + \omega_2)} \left\{ \omega_1 \omega_2 \left[ J_1(\omega) \cdot \tilde{\nabla}_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \cdot m_A^m \cdot m_B^l \right] + \omega_1 \omega_2 \left[ \omega_1 \omega_2 \cdot \tilde{\nabla}_B \cdot m_A^m \cdot \nabla_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \right] F_+ \right\}.$$  (E.1)

This may be written as

$$U_{DC} = \frac{4\mu_0^2}{\pi^2} \sum_{m,l} \int_0^\infty d\omega_1 \frac{\omega_1}{(\omega_1 + \omega_2)} \left\{ \omega_1 \omega_2 \left[ J_1(\omega) \cdot \tilde{\nabla}_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \cdot m_A^m \cdot m_B^l \right] + \omega_1 \omega_2 \left[ \omega_1 \omega_2 \cdot \tilde{\nabla}_B \cdot m_A^m \cdot \nabla_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \right] F_+ \right\}.$$  (E.2)

with

$$J_1(\omega) = \int_0^\infty d\omega_2 \frac{\omega_2}{(\omega + \omega_2)(\omega_1 + \omega_2)} \left[ \omega_1 \omega_2 \cdot \tilde{\nabla}_B \cdot \mathbf{G}(r_A, r_B, \omega_2) \right].$$  (E.3)

The Green’s tensor being analytic in the upper half of the complex frequency plane, facilitates rewriting $J_1(\omega)$ in terms of the imaginary frequency $\omega \rightarrow i\xi$ as

$$J_1(\omega) = \left[ \frac{\omega_2}{(\omega + \omega_2)(\omega_1 + \omega_2)} \right] \mathbf{G}(r_A, r_B, \omega_2) = \int_0^\infty d\xi \frac{\omega_2}{(\omega + \omega_2)(\omega^2 + \xi^2)} \left[ \omega_2 \cdot \tilde{\nabla}_B \cdot \mathbf{G}(r_A, r_B, i\xi) \right].$$  (E.4)

In the second line we have used the fact that the Green tensor is real-valued for imaginary frequency due to the Schwartz reflection principle, equation (17). Using equation (E.4) in (E.2) gives

$$U_{DC} = \frac{4\mu_0^2}{\pi^2} \sum_{m,l} \int_0^\infty d\xi \frac{1}{(\omega_1^2 + \xi^2)} \left[ \omega_1 \omega_2 \left[ J_1(\omega) \cdot \tilde{\nabla}_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \cdot m_A^m \cdot m_B^l \right] + \omega_1 \omega_2 \left[ \omega_1 \omega_2 \cdot \tilde{\nabla}_B \cdot m_A^m \cdot \nabla_A \times \mathbf{G}(r_A, r_B, \omega_1) \times \tilde{\nabla}_B \right] F_+ \right\}.$$  (E.5)

with

$$J_2 = \left[ \frac{\omega}{(\omega^2 + \xi^2)} \right] \mathbf{G}(r_B, r_A, \omega).$$  (E.6)

At this stage, noting that the integrand in (E.6) has a simple pole at $\omega = i\xi$ in the upper half of the complex frequency plane, we may use contour integral techniques to replace the integration path with the positive part of the imaginary axis and excluding the pole by applying an infinitesimal halfcircle around it. Doing so, we find
\[
\int_{0}^{\infty} \frac{d\omega \omega}{(\omega^2 + \xi^2)} G(r_B, r_A, \omega) = -P\int_{0}^{\infty} \frac{d\nu (-\nu^2 + \xi^2)}{\nu^2} G(r_B, r_A, i\nu) + \frac{i\pi}{2} G(r_B, r_A, i\xi). \tag{E.7}
\]

Hence, the right hand side of equation (E.6) reduces to \((\pi/2)G(r_B, r_A, i\xi)\). Using this in equation (E.5) results in

\[
U_{DC} = -\frac{2\mu_0^2}{\pi} \sum_i \int_{0}^{\infty} \frac{d\xi \xi^2}{(\omega_B^2 + \xi^2)} \text{tr} \left\{ \beta_A^0 \cdot \nabla_A \times \mathbf{G}(r_A, r_B, i\xi) \times \nabla_B \cdot \mathbf{m}_B^{d_B^{ii}} - \left[ \mathbf{G}(r_B, r_A, i\xi) \times \nabla_A \right] \right\}. \tag{E.8}
\]

Finally, the summation over \(i\) in the right hand side can be replaced in terms of the chiral polarisability defined by equation (44),

\[
\sum_i \frac{m_B^{d_B^{ii}} g^{ii}}{(\omega_B^2 + \xi^2)} = \frac{-\hbar}{2 \xi} \chi^{\mu\nu}_{0}(i\xi), \tag{E.9}
\]

which leads to equation (60).

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