Body-assisted dispersion potentials of diamagnetic atoms

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We derive Casimir–Polder and van der Waals potentials of one or two atoms with diamagnetic properties in an arbitrary environment of magnetoelectric bodies. The calculations are based on macroscopic quantum electrodynamics and leading-order perturbation theory. For the examples of an atom and a perfect mirror and two atoms in free space we show that diamagnetic dispersion potentials have the same sign as their electric counterparts, but can exhibit quite different distance dependences.

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I. INTRODUCTION

The issue of electrodynamics in magnetodielectrics is a long-standing one [1]. These range from the form and propagation of Maxwell fields in such media, to their absorption and emission characteristics, as well as to the numerous other optical properties that they exhibit. One curious aspect, recently confirmed by fabrication of periodic arrays of thin metallic wires [2–4], is the existence of left-handed materials, so-called because the electric, magnetic and direction of propagation vectors form a left-handed triad, resulting in a metamaterial with negative refractive index. Another interesting aspect is the nature of inter-particle interactions in media with electrical permittivity, magnetic permeability, or both. This has its origins in the work of Casimir [5], subsequently spawning a wide variety of related phenomena categorized under Casimir-like effects [6–9], and including the Casimir–Polder (CP) dispersion potential [10].

The understanding and computation of van der Waals forces (vdW) for chemical, physical and biological systems is of fundamental importance and widespread interest as they manifest in vacuum, gaseous or condensed phases. These vary from semi-classical treatments yielding the London dispersion formula, to quantum field theoretic approaches where radiative effects are properly accounted for and result in Casimir energy shifts. Perhaps the best-known example of a fundamental theory that automatically includes retardation is quantum electrodynamics (QED). Two often-used versions include macroscopic [11,12] and microscopic [13,14] QED, their prefixes aptly describing their general range of applicability.

In the former variant, the body-assisted electromagnetic field is evaluated by quantizing the radiation field and the dispersive and absorptive medium. This enables the body-induced atomic energy shift to be computed, which is interpreted as the potential of the force. From this, pair and many-body interaction energies can also be calculated. This has been successfully carried out for both electrically polarizable [12] and paramagnetically susceptible systems [18]. Effects of an intermediate medium can also be accounted for [18,20].

Microscopic Coulomb gauge QED constructed via quantization of the free electromagnetic field has also been used successfully to evaluate atom–field and atom–atom interactions in a vacuum. In the latter situation this has included re-calculation of the CP potential, and its extension to higher multipole moment contributions, such as magnetic dipole, electric quadrupole and diamagnetic couplings [21–27]. Unexpected results ensue such as the discriminatory nature of the interaction between two chiral (optically active) molecules; the repulsive form of the ground state dispersion energy shift between an electrically polarizable atom and a paramagnetically susceptible one; and that in the near-zone, the electric–diamagnetic contribution to this potential is larger than the corresponding limit arising from the electric–paramagnetic term [23].

In this paper a systematic study is performed on the CP potentials of a diamagnetic atom and its vdW potentials with another, and with an atom that is either electrically or paramagnetically polarizable in a medium comprised of magnetodielectric bodies using macroscopic QED theory. Interest in contributions arising from dia-
magnetic coupling has been due to their importance when computing highly accurate potentials for alkali metal atom dimers [28], where it has been found that the electric–diamagnetic and paramagnetic–diamagnetic terms can be larger than the electric–paramagnetic and paramagnetic–paramagnetic energy shifts. The article is organized as follows. Section II briefly describes the quantized body-assisted Maxwell field operators in the medium, their expression in terms of the Green’s-function solution of the Helmholtz equation, and the writing of the total system Hamiltonian. Electric and total magnetic contributions to the single atom CP shift, and for an atom placed in front of a perfectly reflecting mirror are obtained in Sec. III. Presented in Sec. IV are diagrammatic perturbation theory results for the dispersion pair potential when at least one of the atoms is diamagnetic. Corresponding free-field interaction energies are also given, and these are briefly compared with results obtained via microscopic QED. In all of the cases examined, the asymptotic limits of the energy shift in the near- and far-zones corresponding to non-retarded and retarded regimes are found, and compared with previously obtained limiting forms for electric, paramagnetic, and electric-paramagnetic interactions. A short summary is given in Sec. V.

II. QUANTISATION SCHEME

Consider one or two atoms (or molecules) with internal Hamiltonians ($\xi = A, B$)

$$\hat{H}_\xi = \sum_n E^n_\xi |n_\xi\rangle \langle n_\xi|$$

which are placed at positions $r_\xi$ within an arbitrary arrangement of linearly, locally and isotropically responding magnetoelectric bodies, described by a Kramers-Kronig consistent permittivity $\varepsilon(r, \omega)$ and permeability $\mu(r, \omega)$. Upon introducing bosonic variables $\hat{f}^\dagger_\lambda(r, \omega)$ and $\hat{f}_\lambda(r, \omega)$, which are creation and annihilation operators for the elementary electric ($\lambda = e$) and magnetic ($\lambda = m$) excitations of the system of bodies and electromagnetic field and obey the bosonic commutation relations

$$[\hat{f}_\lambda(r, \omega), \hat{f}^\dagger_{\lambda'}(r', \omega')] = \delta(r - r')\delta_{\lambda\lambda'} \delta(\omega - \omega')$$

and

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

the body–field Hamiltonian takes the form [12]

$$\hat{H}_F = \sum_{\lambda = e, m} \int d^3r \int_0^\infty d\omega \hat{\hbar}\omega \hat{f}^\dagger_\lambda(r, \omega) \cdot \mathbf{f}_\lambda(r, \omega).$$

The ground-state of $\hat{H}_F$ can obviously be defined by

$$\mathbf{f}_\lambda(r, \omega) |0\rangle = 0 \quad \forall \lambda, r, \omega.$$  (5)

Within the multipolar coupling scheme, the interaction of each atom with the body-assisted electromagnetic field is given by [20]

$$\hat{H}_{\xi F} = \hat{H}_{\xi F}^e + \hat{H}_{\xi F}^m + \hat{H}_{\xi F}^d.$$  (6)

Here the three terms are the electric, paramagnetic and diamagnetic interactions,

$$\hat{H}_{\xi F}^e = -\hat{\mathbf{\mu}}_{\xi} \cdot \mathbf{E}(r_\xi),$$

$$\hat{H}_{\xi F}^m = -\hat{\mathbf{m}}_{\xi} \cdot \mathbf{B}(r_\xi),$$

$$\hat{H}_{\xi F}^d = \sum_{\alpha \in \xi} \frac{q^2}{8\pi\varepsilon_0|\mathbf{r}_\alpha - \mathbf{r}_\alpha|} \left(\hat{r}_\alpha \times \hat{\mathbf{B}}(r_\xi)\right)^2,$$

with $\hat{\mathbf{\mu}}_{\xi}$ and $\hat{\mathbf{m}}_{\xi}$ being the respective atomic electric and magnetic dipole operators and $q_\alpha$, $m_\alpha$ and $\mathbf{r}_\alpha$ denoting the charges, masses and positions relative to the center of mass of the particles contained in the atoms. Note that electric quadrupole and even octupole contributions can easily be included in the formalism; they have recently been shown to affect the CP potential of Rydberg atoms close to surfaces [30].

Introducing the atomic diamagnetisability operator as

$$\beta^d_{\xi} = -\sum_{\alpha \in \xi} \frac{q^2}{8\pi\varepsilon_0|\mathbf{r}_\alpha|^3} (\hat{r}_\alpha^2 \mathbf{I} - \hat{\mathbf{r}}_\alpha \hat{\mathbf{r}}_\alpha^2),$$

and using the identity $[a \times b]^2 = b \cdot (a^2 I - aa \cdot b)$, the diamagnetic interaction Hamiltonian may be cast in the form

$$\hat{H}_{\xi F}^d = -\frac{1}{2} \hat{\mathbf{B}}(r_\xi) : \beta^d_{\xi} : \hat{\mathbf{B}}(r_\xi).$$  (11)

The ground-state diamagnetisability of an atom is given by the expectation value

$$\beta^d_{\xi} \equiv \langle \beta^d_{\xi} \rangle = -\sum_{\alpha \in \xi} \frac{q^2}{6\pi m_\alpha} \langle 0|\hat{r}_\alpha^2 \mathbf{I} - \hat{\mathbf{r}}_\alpha \hat{\mathbf{r}}_\alpha|0\rangle_{\xi}$$

$$=-\sum_{\alpha \in \xi} \frac{q^2}{6m_\alpha} \langle \hat{r}_\alpha^2 \rangle \mathbf{I} \equiv \beta^d_{\xi} \mathbf{I},$$  (12)

where the second line holds for isotropic atoms.

The total Hamiltonian of the atom(s) interacting with the electromagnetic field in the presence of the bodies takes the form

$$\hat{H} = \sum_{\xi = A, B} \hat{H}_\xi + \hat{H}_F + \sum_{\xi = A, B} \hat{H}_{\xi F}.$$  (13)

The electric and magnetic field operators can be expanded in terms of the bosonic operators $\hat{f}_\lambda(r, \omega)$ and $\hat{f}_\lambda(r, \omega)$ as

$$\hat{\mathbf{E}}(r) = \sum_{\lambda = e, m} \int d^3r' \int_0^\infty d\omega \mathbf{G}_\lambda(r, r', \omega) \cdot \hat{f}_\lambda(r', \omega) + \text{H.c.},$$  (14)

$$\hat{\mathbf{B}}(r) = \sum_{\lambda = e, m} \int d^3r' \int_0^\infty d\omega \frac{\nabla \times \mathbf{G}_\lambda(r, r', \omega)}{\omega} \cdot \hat{f}_\lambda(r', \omega) + \text{H.c.}$$  (15)
The expansion coefficients $G_\lambda$ are related to the classical Green tensor $G$ by
\begin{equation}
G_e(r, r', \omega) = i \frac{\omega^2}{c^2} \sqrt{\frac{\hbar}{\pi \varepsilon_0}} \text{Im} \varepsilon(r', \omega) G(r, r', \omega),
\end{equation}
\begin{equation}
G_m(r, r', \omega) = i \frac{\omega^2}{c^2} \sqrt{\frac{\hbar}{\pi \mu_0}} \frac{\mu(r', \omega)}{|\mu(r', \omega)|^2} [\nabla' \times G(r', r, \omega)]^T;
\end{equation}
and the Green tensor is the unique solution to the Helmhotz equation
\begin{equation}
[\nabla \times \frac{1}{\mu(r, \omega)} \nabla \times - \frac{\omega^2}{c^2} \varepsilon(r, \omega)] G(r, r', \omega) = \delta(r - r')
\end{equation}
together with the boundary condition
\begin{equation}
G(r, r', \omega) \to 0 \quad \text{for} \ |r - r'| \to \infty.
\end{equation}
Just like the permittivity and permeability, the Green tensor is an analytic function in the upper half of the complex frequency plane and fulfils the Schwarz reflection principle
\begin{equation}
G(r, r', -\omega^*) = G^*(r, r', \omega).
\end{equation}
In addition, it obeys the Onsager–Lorentz reciprocity
\begin{equation}
G(r', r, \omega) = G^T(r, r', \omega)
\end{equation}
and the useful integral relation
\begin{equation}
\sum_{\lambda = e, m} \int d^3 s \ G_\lambda(r, s, \omega) \cdot G_\lambda^T(r', s, \omega) = \frac{\hbar \mu_0}{\pi} \omega^2 \text{Im} \ G(r, r', \omega)
\end{equation}
holds.

III. CASIMIR–POLDER POTENTIAL OF A SINGLE ATOM

In this section, we calculate the CP force on a single atom in the presence of magnetoelectric bodies, discarding the label $A$ wherever possible. According to Casimir and Polder, the force can be derived from the associated CP potential $U(r_A)$
\begin{equation}
F = -\nabla U(r_A),
\end{equation}
which in turn can be identified as the position-dependent part of the energy shift $\Delta E$ due to the atom–field coupling
\begin{equation}
U(r_A) = \Delta E(r_A).
\end{equation}

A. Perturbation theory

We assume the atom–field system to be prepared in the uncoupled ground state $|0_A\rangle |0\rangle$ and calculate the energy shift due to the atom–field coupling within leading-order perturbation theory. Let us first study a purely diamagnetic atom, whose CP potential is due to the first-order energy shift associated with the diamagnetic part of the atom–field interaction $11$.
\begin{equation}
\Delta E = \langle \{0\} | \langle 0_A | - \frac{1}{2} \hat{B}(r_A) \cdot \hat{\beta} \cdot \hat{B}(r_A) | 0_A \rangle \{0\} \rangle.
\end{equation}
Normally, CP energy shifts only arise in second order perturbation theory. However, due to the diamagnetic interaction Hamiltonian being quadratic in the magnetic induction field, already the first perturbation order contributes. It can be easily evaluated by using the magnetic-field expression $15$, the bosonic commutation relations $22$ and $23$, and the integral relation $22$, resulting in
\begin{equation}
\Delta E = \frac{\hbar \mu_0}{2\pi} \int_0^{\infty} d\omega \text{tr} [\hat{\beta} \cdot \text{Im} G_{mm}(r_A, r_A, \omega)]
\end{equation}
with
\begin{equation}
G_{mm}(r, r', \omega) = \nabla \times G(r, r', \omega) \times \nabla'.
\end{equation}
For an atom in a free-space region, the CP potential can be extracted from this energy shift by separating the Green tensor into its bulk and scattering parts,
\begin{equation}
G(r, r', \omega) = G^{(0)}(r, r', \omega) + G^{(1)}(r, r', \omega),
\end{equation}
and discarding the constant energy shift associated with the translationally invariant bulk part by making the replacement $G \mapsto G^{(1)}$. The result can be simplified by converting the integral over real frequencies to another along the imaginary axis in the complex frequency plane. To this end, we first write
\begin{equation}
\int_0^{\infty} d\omega \text{Im} G(r, r', \omega) = \text{Im} \int_0^{\infty} d\omega G(r, r', \omega).
\end{equation}
The integral on the right hand side can be replaced by an integral along the positive imaginary axis ($\omega \mapsto i\xi$) plus a vanishing integral along infinite quarter-circles via Cauchy’s theorem. Using the fact that $G(i\xi)$ is real-valued for a real $\xi$, as can be inferred from Schwarz reflection principle $20$, one finds
\begin{equation}
U_d(r_A) = \frac{\hbar \mu_0}{2\pi} \int_0^{\infty} d\xi \text{tr} [\hat{\beta} \cdot G_{mm}^{(1)}(r_A, r_A, i\xi)]
\end{equation}
\begin{equation}
= \frac{\hbar \mu_0}{2\pi} \int_0^{\infty} d\xi \beta^d \text{tr} G_{mm}^{(1)}(r_A, r_A, i\xi).
\end{equation}
The second line in Eq. $30$ holds for isotropic atoms. For an atom with an additional nontrivial electric and paramagnetic response, the respective electric and paramagnetic interactions in the coupling Hamiltonian $9$
also need to be taken into account. As shown previously, they give rise to second-order energy shifts such that the electric and paramagnetic CP potentials are given by

\[ U_e(r_A) = \frac{\hbar}{2\pi\varepsilon_0} \int_0^\infty d\xi \text{tr} \left[ \alpha(i\xi) \mathbf{G}^{(1)}_{ee}(r_A, r_A, i\xi) \right] \]

\[ = \frac{\hbar}{2\pi\varepsilon_0} \int_0^\infty d\xi \alpha(i\xi) \text{tr} \mathbf{G}^{(1)}_{ee}(r_A, r_A, i\xi), \]  

(31)

\[ U_p(r_A) = \frac{\hbar\mu_0}{4\pi} \int_0^\infty d\xi \text{tr} \left[ \beta^p(i\xi) \mathbf{G}^{(1)}_{mm}(r_A, r_A, i\xi) \right] \]

\[ = \frac{\hbar\mu_0}{4\pi} \int_0^\infty d\xi \beta^p(i\xi) \text{tr} \mathbf{G}^{(1)}_{mm}(r_A, r_A, i\xi) \]  

(32)

with

\[ \mathbf{G}_{ee}(r, r, \omega) = -\frac{\omega^2}{c^2} \mathbf{G}(r, r, \omega) \]  

(33)

and

\[ \alpha(\omega) = \lim \frac{\omega^3}{\hbar} \sum_k \frac{\omega_k^4}{(\omega_k^2)^2 - \omega^2 - \omega \epsilon} \]

\[ = \lim \frac{\omega^3}{\hbar} \sum_k \frac{\omega_k^4}{(\omega_k^2)^2 - \omega^2 - \omega \epsilon} = \alpha(\omega)I, \]  

(34)

\[ \beta^p(\omega) = \lim \frac{\omega^3}{\hbar} \sum_k \frac{\omega_k^4}{(\omega_k^2)^2 - \omega^2 - \omega \epsilon} = \beta^p(\omega)I \]  

(35)

\[ [\omega^2_k = (E^2_k - E^0_k)/\hbar, \mu^0_k = (0|\mu_A|k), m^0_k = (0|m_A|k)] \]

denoting the polarisability and paramagnetisability of the atom, respectively. Introducing the total magnetisability

\[ \beta(\omega) = \beta^p(\omega) + \beta^d \]

\[ = [\beta^p(\omega) + \beta^d]I = \beta(\omega)I, \]  

(36)

the magnetic part of the CP potential reads

\[ U_m(r_A) = U_p(r_A) + U_d(r_A) \]

\[ = \frac{\hbar\mu_0}{4\pi} \int_0^\infty d\xi \text{tr} \left[ \beta(i\xi) \mathbf{G}^{(1)}_{mm}(r_A, r_A, i\xi) \right] \]

\[ = \frac{\hbar\mu_0}{4\pi} \int_0^\infty d\xi \beta(i\xi) \text{tr} \mathbf{G}^{(1)}_{mm}(r_A, r_A, i\xi) \]  

(37)

and the total CP potential is given by

\[ U(r_A) = U_e(r_A) + U_m(r_A). \]  

(38)

We have thus generalised previous results for the CP potential of an atom with electric and paramagnetic properties to one that also exhibits nontrivial diamagnetic properties. It is found that despite the different interaction terms and perturbative orders (first order instead of second order), the extension to a diamagnetic atom can be obtained formally by including the diamagnetic contribution in the magnetisability, \( \beta^p(\omega) \mapsto \beta^p(\omega) + \beta^d \). In particular, the local-field corrected potentials for atoms embedded in a medium as derived in Ref. [18] remain valid with this replacement.

By introducing \( \alpha^2(\omega) = \alpha(\omega), \alpha^m(\omega) = \beta(\omega)/\epsilon^2 \), the electric and magnetic parts of the CP potential can be given in the compact notation

\[ U^\lambda(r_A) = \frac{\hbar}{2\pi\varepsilon_0} \int_0^\infty d\xi \text{tr} \left[ \alpha^\lambda(i\xi) \mathbf{G}^{(1)}_{\lambda\lambda}(r_A, r_A, i\xi) \right] \]

\[ = \frac{\hbar}{2\pi\varepsilon_0} \int_0^\infty d\xi \alpha^\lambda(i\xi) \text{tr} \mathbf{G}^{(1)}_{\lambda\lambda}(r_A, r_A, i\xi) \]  

(39)

(\( \lambda = e, m \)).

There are two important differences between the diamagnetic and the paramagnetic magnetisabilities which will have an impact on the associated potentials. Firstly, the diamagnetisability has an opposite sign with respect to the paramagnetisability, which is a consequence of the Lenz rule. Secondly, in contrast to the paramagnetisability which obeys the usual Kramers–Kronig relations, the diamagnetisability is independent of frequency.

### B. Application: Atom in front of a perfectly reflecting mirror

Let us consider an isotropic atom at distance \( z_A \) from a perfectly reflecting planar mirror. The magnetoelectric properties of the mirror are characterised by \( \varepsilon = \infty \) (\( \mu = \infty \)) for a perfectly conducting (infinitely permeable) plate. The Green tensor reads [31]

\[ \mathbf{G}^{(1)}(r, r', i\xi) = \pm \frac{1}{8\pi^2} \int \frac{d^2q}{b} \phi(q + \mathbf{r} - q - \mathbf{r}') (\mathbf{e}_p^+ e_p^- - \mathbf{e}_s \mathbf{e}_s) \]  

(40)

\( (q = q \pm ib \mathbf{e}_z, q \perp \mathbf{e}_z, q = |q|, b = \sqrt{q^2 + \epsilon^2/c^2}) \) with the upper (lower) sign corresponding to a perfectly conducting (infinitely permeable) plate and the polarisation vectors \( \mathbf{e}_s \) and \( \mathbf{e}_p \) being defined by \( (\mathbf{e}_q = q / q) \)

\[ \mathbf{e}_s = e_q \mathbf{e}_z, \quad \mathbf{e}_p^\pm = \frac{C}{\xi - iq \mathbf{e}_z} \pm be_q . \]  

(41)

Evaluating the double curl of the Green tensor, we find that \( \mathbf{G}^{(1)}_{mm}(r, r', i\xi) \) is equal to \(-\xi^2 c^{-2} \mathbf{G}^{(1)}_{rr}(r, r', i\xi) \). Substituting this into Eq. [30] and carrying out the \( q \)-integral, one finds

\[ U_d(z_A) = \frac{\pm \hbar\mu_0 \beta d / 4\pi^2 \varepsilon^2}{\varepsilon^2} \int_0^\infty d\xi e^{-2z_A \xi/c} \]

\[ \times \left( 1 + 2 \frac{\varepsilon^2 \zeta^2}{c^2} + 2 \frac{\varepsilon^2 \zeta^2}{c^2} \right). \]  

(42)

After performing the \( \zeta \)-integral, we find an attractive (repulsive) CP potential

\[ U_d(z_A) = \pm \frac{3\hbar\mu_0 \beta d}{32\pi^2 \varepsilon^2} = \pm \frac{3\hbar\mu_0 \epsilon}{32\pi^2 \varepsilon^2} \sum_{\alpha \in A} \frac{q^2}{6m_\alpha} \left( \hat{p}_\alpha^2 \right). \]  

(43)
of a diamagnetic atom in front of a perfectly conducting (permeable) plate. It is given by a single $1/z_A^4$ power law.

In Table I we compare this result with the known findings for electric and paramagnetic atoms. We recall that electric and paramagnetic atoms interact with conducting and permeable plates according to an 'equals-attract, opposites-repel' rule: An electric plate attracts electric atoms while repelling (para)magnetic atoms, with corresponding results for a (para)magnetic plate. In contrast to this, diamagnetic potentials carry a sign that is opposite to their paramagnetic counterparts. This is due to the Lenz rule as encoded in the minus sign in the diamagnetic magnetisability $\mu_d$. The diamagnetic CP potential thus has the same sign as the corresponding electric potential.

Another difference is the fact that the wavelengths of electric and paramagnetic dipole transitions divide the CP potential into two asymptotic regimes: the non-retarded regime of distances smaller than these wavelengths and the opposite, retarded regime. The CP potential follows two distinct $1/z_A^4$ and $1/z_A^2$ power laws in these regimes, respectively. On the other hand, the frequency-independent diamagnetic magnetisability lacks an intrinsic length scale. As a result, the CP interaction with a perfectly reflecting plate follows a retarded $1/z_A^2$ power law at all distances.

IV. TWO-ATOM VAN DER WAALS INTERACTION

Similar to the single-atom case, the body-assisted vdW force between two atoms can be derived from the two-atom vdW potential $U(r_A,r_B)$, which is that part of the energy shift depending on the positions of both atoms,

$$U(r_A,r_B) = \Delta E(r_A,r_B). \tag{44}$$

A. Perturbation theory

Again, we assume the atom–field system to be in its uncoupled ground-state $|0_A\rangle|0_B\rangle\{0\}$, but now we have to calculate the leading-order two-atom energy shift. We begin with two purely diamagnetic atoms, in which case the vdW potential follows from the second-order energy shift

$$\Delta_2 E = \sum_{\phi \neq 0} \frac{\langle 0|\hat{H}_{AF}^d + \hat{H}_{BF}^d|\phi\rangle \langle \phi|\hat{H}_{AF}^d + \hat{H}_{BF}^d|0 \rangle}{E_0 - E_\phi}. \tag{45}$$

Note that the first order energy shift just leads to the sum of two diamagnetic CP potentials as discussed in the previous Sect. III A. Due the diamagnetic interaction Hamiltonian being quadratic in the fields, the vdW shift already appears in second order perturbation theory rather than in fourth order as for electric and paramagnetic dipole transitions.

The numerator of the term in Eq. (45), when read from right to left, represents processes in which the system starts from its ground state, goes to a state $|\phi\rangle$ due to a first atom–field interaction, and finally returns to its ground state in the course of a second interaction. As the interaction Hamiltonian is quadratic in the magnetic field, the intermediate state $|\phi\rangle$ must involve the field in its ground state or exhibit two field excitations (photons). Only the latter case leads to a genuine two-atom interaction,

$$|\phi\rangle = |0_A\rangle|0_B\rangle|1_{\lambda i}(r,\omega),1_{\lambda' j'}(r',\omega')\rangle \tag{46}$$

with the two-photon state being defined by

$$|1_{\lambda i}(r,\omega),1_{\lambda' j'}(r',\omega')\rangle = \frac{1}{\sqrt{2}} f_{\lambda i}(r',\omega') f_{\lambda' j'}(r,\omega)|\{0\}\rangle. \tag{47}$$

The photons must have been emitted by one of the atoms and then absorbed by the other. This is schematically illustrated in Fig. II, where the solid lines and the dashed lines represent the atoms and the photons, respectively (where time progresses in the upwards direction). Note that the formal sum in Eq. (45) involves sums over $\lambda, \lambda'$, $i, i'$ as well as integrals over $r, r', \omega$ and $\omega'$. We begin with the contribution $\Delta_2 E_{(i)}$ to the energy shift corresponding to Fig. II(i), where atom $A$ emits two photons and atom $B$ absorbs them, i.e., where the second matrix element in the perturbative energy shift (45) is due to the diamagnetic interaction of atom $A$ and the first one is due to that of atom $B$. The required two-photon emission matrix element for atom $A$ takes the form

$$\langle \phi|\hat{H}_{AF}^d|0\rangle = \frac{-\beta_{Ajk}}{2\sqrt{2}} \times \langle \{0\}|\hat{f}_{\lambda i'}(r',\omega') f_{\lambda i}(r,\omega) \hat{B}_j(r_A) \hat{B}_k(r_A)|\{0\}\rangle, \tag{48}$$

where Eqs. (11), (40), and (47) have been used. The two-photon absorption matrix element $\langle 0|\hat{H}_{BF}^d|\phi\rangle$ can be obtained by taking the complex conjugate of the above and

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Contributions to the vdW interaction of two diamagnetic atoms.}
\end{figure}
TABLE I: Signs and asymptotic power laws of the ground-state CP potential of an electric, para- or diamagnetic atom with a perfectly reflecting plate.

| Plate → | Perfectly conducting | Infinitely permeable |
| --- | --- | --- |
| Atom ↓ Limit → | Retarded | Nonretarded | Retarded | Nonretarded |
| Electric | $-\frac{1}{z_A}$ | $-\frac{1}{z_A}$ | $+\frac{1}{z_A}$ | $+\frac{1}{z_A}$ |
| Paramagnetic | $+\frac{1}{z_A}$ | $+\frac{1}{z_A}$ | $-\frac{1}{z_A}$ | $-\frac{1}{z_A}$ |
| Diamagnetic | $-\frac{1}{z_A}$ | | $+\frac{1}{z_A}$ |

replacing the labels $A$ by $B$. After substituting Eq. (15) for the magnetic field and making use of the commutation relations (22) and (23), the respective term in Eq. (45) reads

$$\frac{\langle 0 | \hat{H}^d_{EF} | \phi \rangle \langle \phi | \hat{H}^d_{EF} | 0 \rangle}{E_0 - E_\phi} = \frac{-1}{2\omega^2 + \hbar^2} \times \text{tr} \left\{ \beta^d_A \left[ \nabla_A \times G_\phi(r_A, r, \omega') \cdot G^\dagger_B(r_B, r, \omega) \times \nabla_B \right] \ight. \\
\left. \times \beta^d_B \left[ \nabla_B \times G_\phi(r_B, r', \omega') \cdot G^\dagger_A(r_A, r', \omega') \times \nabla_A \right] \right\}. \quad (49)$$

At this stage, performing the integrals over $r$ and $r'$ included in Eq. (45) by means of the integral relation (22) results in

$$\Delta_2 E_{(i)} = -\frac{\hbar^2 \mu_0}{2\pi^2} \int_0^\infty \frac{d\omega}{\omega} \int_0^\infty \frac{d\omega'}{\omega + \omega'} \times \text{tr} \left[ \beta^d_A \text{Im} G_{mm}(r_A, r_B, \omega) \cdot \beta^d_B \text{Im} G_{mm}(r_B, r_A, \omega') \right]. \quad (50)$$

[Recall Eq. (27)]. It can easily be seen that the contribution (ii) as depicted in Fig. (i) is exactly the same. We hence find

$$U_{dd}(r_A, r_B) = -\frac{\hbar^2 \mu_0^2}{\pi^2} \int_0^\infty \frac{d\omega}{\omega} \int_0^\infty \frac{d\omega'}{\omega + \omega'} \times \text{tr} \left[ \beta^d_A \text{Im} G_{mm}(r_A, r_B, \omega) \cdot \beta^d_B \text{Im} G_{mm}(r_B, r_A, \omega') \right]. \quad (51)$$

As for the single-atom potential, the result can be simplified via contour-integral techniques. We first write

$$\int_0^\infty \frac{d\omega'}{\omega + \omega'} \text{Im} G_{mm}(\omega') = \text{Im} \int_0^\infty \frac{d\omega'}{\omega + \omega'} G_{mm}(\omega')$$

and use the fact that the Green tensor is analytic in the upper half of the complex frequency plane including the real axis. Hence, we may replace the integral with an integral along the positive imaginary frequency axis and use the Schwarz reflection principle (20) to obtain

$$\int_0^\infty \frac{d\omega'}{\omega + \omega'} \text{Im} G_{mm}(\omega') = \int_0^\infty \frac{d\xi}{\omega + \omega'} G_{mm}(\xi). \quad (53)$$

Substituting this result into Eq. (51), we next evaluate the integral over $\omega$,

$$\int_0^\infty d\omega \frac{\text{Im} G_{mm}(\omega)}{\omega^2 + \xi^2} = \text{Im} \int_0^\infty d\omega \frac{\omega G_{mm}(\omega)}{\omega^2 + \xi^2} \quad (54)$$

The integrand in the right hand side has a simple pole at $\omega = i\xi$ in the upper half of the complex frequency plane. Again using Cauchy’s theorem, we transform this integral into a principal value integral along the positive imaginary axis, an integral along an infinitesimal half circle around the pole, and a (vanishing) integral along an infinite quarter circle. The first integral is real, while the second integral results in $i\pi G_{mm}(i\xi)$, so that

$$\int_0^\infty d\omega \frac{\text{Im} G_{mm}(\omega)}{\omega^2 + \xi^2} = \text{Im} \left[ \int_0^\infty d\omega \frac{\omega G_{mm}(i\omega)}{\omega^2 - \xi^2} + \frac{i\pi}{2} G_{mm}(i\xi) \right]$$

$(P$: principal value). After substituting this result together with Eq. (55) into Eq. (15), we find the CP potential of two diamagnetic atoms,

$$U_{dd}(r_A, r_B) = -\frac{\hbar^2 \mu_0^2}{\pi^2} \int_0^\infty d\xi \times \text{tr} \left[ \beta^d_A G_{mm}(r_A, r_B, i\xi) \cdot \beta^d_B G_{mm}(r_B, r_A, i\xi) \right]$$

$$= -\frac{\hbar \mu_0^2}{2\pi} \int_0^\infty d\xi \beta^d_A \beta^d_B \times \text{tr} \left[ G_{mm}(r_A, r_B, i\xi) \cdot G_{mm}(r_B, r_A, i\xi) \right] \quad (56)$$

where the second equality holds for isotropic atoms.
Let us consider next the interaction of a diamagnetic atom $A$ with an electric atom $B$. It can be seen easily that the leading two-atom energy shift is of third order in this case,

$$\Delta_3 E = \frac{1}{\pi^2} \int_0^\infty \frac{d\omega'}{(\omega' + \omega)^2} \sum_{\lambda} G_{\lambda B}(r_{AB}) \cdot \mathbf{B}(r_{AB}) - \hat{\mathbf{B}}(r_{AB}) \cdot \mathbf{E}(r_{AB}).$$

The relevant intermediate states $|\phi\rangle$ and $|\psi\rangle$ can easily be determined with the help of the diagrams in Fig. 2. Let us begin with diagram (i) which correspond to the the case where atom $A$ emits two photons and atom $B$ absorbs them one after another, so the relevant intermediate states are

$$|\phi\rangle = |0_A\rangle|0_B\rangle|1_A(r,\omega),1_B(r',\omega')\rangle,$$

$$|\psi\rangle = |0_A\rangle|n_B\rangle|1_A(r,\omega),1_B(r',\omega')\rangle.$$

In the two-photon emission matrix element, $\hat{\mathcal{H}}_{\text{int}}$ has to be replaced by $\hat{\mathcal{H}}_{\text{int}}^{d}$. This leads, as outlined below Eq. (48), to

$$\langle \phi | \hat{\mathcal{H}}_{\text{int}}^{d} | 0 \rangle = \frac{-1}{\sqrt{2\omega}} \mathbf{G}_{\lambda}(r_{AB},\omega) \cdot \mathbf{B}(r_{AB}) \cdot \mathbf{G}_{\lambda}(r_{AB},r',\omega'),$$

while in the two other matrix elements, $\hat{\mathcal{H}}_{\text{int}}$ has to be replaced with $\hat{\mathcal{H}}_{\text{int}}^{c}$. This yields

$$\langle \psi | - \mu_B \cdot \mathbf{E}(r_{AB}) | \phi \rangle = \frac{-1}{\sqrt{2}} \left\{ \mu^0_B \cdot \mathbf{G}_{\lambda}(r_{AB},\omega) \right\}_{r',r''} \delta(r-r')\delta(\omega'-\omega'') + \mu^0_B \cdot \mathbf{G}_{\lambda}(r_{AB},\omega') \right\}_{r',r''} \delta(\omega'-\omega''),$$

where the expression (44) for the electric field, as well as the commutation relations (2) and (3) have been used. Substitution of these matrix elements into Eq. (57) and performing the integrals over $r$, $r'$, and $r''$ using the integral relation (22), we find the contribution of diagram (i) to the energy shift to be

$$\Delta_3 E_{(i)} = \frac{\mu^2_B}{\pi^2} \int_0^\infty \frac{d\omega'}{(\omega' + \omega)^2} \sum_{\lambda} \left[ \mathbf{d}^{\text{in}}_{\lambda} \cdot \mathbf{K}^T(r_{AB},r_B,\omega) \cdot \beta_{\lambda} \cdot \mathbf{K}(r_B,r_{AB},\omega) \cdot \mathbf{d}^{\text{out}}_{\lambda} \right],$$

where

$$\mathbf{K}(r_B,r',\omega) = \nabla \times \mathbf{G}(r_B,r',\omega).$$

The contribution to the energy shift from diagrams (ii) and (iii) result in terms similar to Eq. (63), except that the energy denominator $(\omega + \omega')(\omega_B' + \omega)$ has to be replaced with $(-\omega_B + \omega'(\omega_B' + \omega))$ for diagram (ii) and with $(\omega + \omega')(\omega_B' + \omega)$ for diagram (iii). Summing all contributions, we find

$$\Delta_3 E = \frac{\mu^2_B}{\pi^2} \int_0^\infty \frac{d\omega'}{(\omega' + \omega)^2} \sum_{\lambda} \left[ \mathbf{d}^{\text{in}}_{\lambda} \cdot \mathbf{K}^T(r_{AB},r_B,\omega) \cdot \beta_{\lambda} \cdot \mathbf{K}(r_B,r_{AB},\omega) \cdot \mathbf{d}^{\text{out}}_{\lambda} \right].$$

By transforming the $\omega'$ integral by means of contour-integral to run along the positive imaginary axis,

$$\int_0^\infty \frac{d\omega'}{(\omega' + \omega)(\omega_B' + \omega)} = \int_0^\infty d\xi \frac{\xi^2(\omega_B' + \omega)}{(\omega^2 + \xi^2)(\omega_B'^2 + \xi^2)},$$

and then performing the $\omega$ integral in the way explained above Eq. (55), one obtains

$$U_{\text{vdW}}(r_{AB},\omega_B) = \frac{\mu^2_B}{2\pi} \int_0^\infty d\xi \frac{\xi^2}{(\omega_B^2 + \xi^2)} \left[ \mathbf{K}(r_{AB},r_B,\omega_B) \cdot \mathbf{K}^T(r_B,r_{AB},\omega_B) \right] \cdot \mathbf{d}^{\text{in}}_{\lambda} \cdot \mathbf{G}(r_B,r_{AB},\omega_B) \cdot \mathbf{d}^{\text{out}}_{\lambda},$$

where the definition (43) has been used and the second equality holds for isotropic atoms. Our result (63) for the vdW potential of a diamagnetic atom $A$ with an electric atom $B$ may be written in the form ($\beta_{\lambda} = \alpha^2_{\lambda} g_B$)

$$U_{\text{vdW}}(r_{AB},\omega_B) = -\frac{\hbar}{2\pi} \int_0^\infty d\xi \left[ \mathbf{G}_{\text{me}}(r_{AB},r_B,\omega_B) \cdot \mathbf{C}(\omega_B) \cdot \mathbf{G}_{\text{me}}(r_B,r_{AB},\omega_B) \right] \cdot \mathbf{d}^{\text{in}}_{\lambda} \cdot \mathbf{G}(r_B,r_{AB},\omega_B) \cdot \mathbf{d}^{\text{out}}_{\lambda},$$

where

$$\mathbf{C}(\omega_B) = \frac{\omega_B}{\pi^2} \left( \frac{\mu^2_B}{\omega_B^2} \cdot \mathbf{B}(r_{AB}) \cdot \mathbf{E}(r_{AB}) \right).$$
where
\[ G_{me}(r, r', \omega) = \frac{i\omega}{c} \mathbf{K}(r, r', \omega) = \frac{i\omega}{c} \nabla \times \mathbf{G}(r, r', \omega), \quad (70) \]
\[ G_{em}(r, r', \omega) = -\frac{i\omega}{c} \mathbf{K}^T(r', r, \omega) = \frac{i\omega}{c} \mathbf{G}(r, r', \omega) \times \overset{\leftrightarrow}{\nabla}. \quad (71) \]

Obviously, the interaction between an electric atom \( A \) with a diamagnetic atom \( B \) is given by the right hand side of Eq. (68) with the labels \( A \) and \( B \) being interchanged. The vdW potential of a diamagnetic atom \( A \) (where \( \lambda \lambda \neq e, m \)) is given by the right hand side of Eq. (79) with \( \beta' = \beta' \). The complete vdW potential of two atoms with nontrivial electric, para- and diamagnetic properties can thus be given as
\[ U(r_A, r_B) = \sum_{\lambda, \lambda'} \sum_{m, m'} U_{\lambda \lambda'}(r_A, r_B) \]
\[ \times \text{tr}[\alpha_{\lambda'}^d \mathbf{G}_{mm}(r_A, r_B, i\xi) \cdot \alpha_B^p(i\xi) \cdot \mathbf{G}_{mm}(r_B, r_A, i\xi)] \]
\[ = -\frac{\hbar}{c} \int_0^\infty \mathrm{d} \xi \int_0^\infty \mathrm{d} \tilde{\xi} \alpha_{\lambda'}^d(\xi) \cdot \alpha_B^p(i\xi) \cdot \mathbf{G}_{mm}(r_B, r_A, i\xi) \]
\[ \times \text{tr}[\mathbf{G}_{mm}(r_A, r_B, i\xi) \cdot \mathbf{G}_{mm}(r_B, r_A, i\xi)]. \quad (72) \]

We have thus generalised the body-assisted vdW potential to allow for two paramagnetic atoms \[ 18 \], we again observe that the generalization can be achieved by replacing the paramagnetisability of each atom with the total magnetisability, \( \beta' \) \( \rightarrow \) \( \beta'(\omega) + \beta'' \). The complete vdW potential of two atoms with nontrivial electric, para- and diamagnetic properties can thus be given as
\[ U(r_A, r_B) = \sum_{\lambda, \lambda'} \sum_{m, m'} U_{\lambda \lambda'}(r_A, r_B) \]
\[ \times \text{tr}[\alpha_{\lambda'}^d(\xi) \cdot \mathbf{G}_{\lambda \lambda}(r_A, r_B, \alpha_B^p(\xi) \cdot \mathbf{G}_{\lambda \lambda}(r_B, r_A, \xi)] \]
\[ = -\frac{\hbar}{c} \int_0^\infty \mathrm{d} \xi \int_0^\infty \mathrm{d} \tilde{\xi} \alpha_{\lambda'}^d(\xi) \cdot \alpha_B^p(\xi) \cdot \mathbf{G}_{\lambda \lambda}(r_B, r_A, \xi) \]
\[ \times \text{tr}[\mathbf{G}_{\lambda \lambda}(r_A, r_B, \xi) \cdot \mathbf{G}_{\lambda \lambda}(r_B, r_A, \xi)]. \quad (74) \]

Again, this implies that previous results for local-field corrected vdW potentials \[ 18 \] remain valid for diamagnetic atoms.

**B. Application: Two atoms in free space**

As the simplest example for the two-atom interaction, let us consider two isotropic atoms \( A \) and \( B \) interacting with each other in free space. The Green tensor reads (see e.g. Ref. [12])
\[ \mathbf{G}^{(0)}(r_A, r_B, i\xi) = \frac{c^2}{4\pi^2 \xi^2} \int [f(l\xi/c) - g(l\xi/c)(\xi)e_l] e^{-l\xi/c} \]
\[ \times \mathbf{G}(r_A - r_B, l, \xi) \]
\[ \times \mathbf{G}(r_A - r_B, l, \xi) \quad (75) \]

Evaluating the curls as contained in definitions (27), (70) and (71), one easily finds
\[ \mathbf{G}^{(0)}_{mm}(r_A, r_B, i\xi) = \mathbf{G}^{(0)}_{mm}(r_A, r_B, i\xi) \]
\[ = \frac{\xi^2}{c^2} \mathbf{G}^{(0)}(r_A, r_B, i\xi), \quad (77) \]
\[ \mathbf{G}^{(0)}_{me}(r_A, r_B, i\xi) = -\mathbf{G}^{(0)}_{me}(r_A, r_B, i\xi) \]
\[ = \frac{\xi}{4\pi^2 e^2} (1 + 2\xi^2) e^{-l\xi/c} e_l \times e_l \quad (78) \]

Substituting these into Eqs. (74) and (73) we obtain a total free-space vdW potential
\[ U(r_A, r_B) = U(l) = \frac{\mu_0^2}{16\pi^3} \]
\[ \times \left\{ -\frac{1}{l^3} \int_0^\infty \mathrm{d} \xi \left[ c^4 l (l\xi) \alpha_B^p(i\xi) + \beta_A^p(i\xi) \beta_B^p(i\xi) \right] h_1(l\xi/c) \right\} \]
\[ + \frac{1}{l^3} \int_0^\infty \mathrm{d} \xi \left[ c^2 l (l\xi) \beta_A^p(i\xi) \beta_B^p(i\xi) + \beta_A^p(i\xi) \alpha_B^p(i\xi) \right] h_2(l\xi/c) \}, \quad (79) \]
\[ \text{where} \]
\[ h_1(x) = (3 + 6x + 4x^2 + 2x^3 + x^4) e^{-2x}, \quad (80) \]
\[ h_2(x) = (1 + 2x + x^2) e^{-2x}. \quad (81) \]

As expected from the results of Sect. [IV.A] this result has the same form as the previously derived potential between electric and paramagnetic atoms \[ 18 \], except that here the total magnetisability appears in place of the paramagnetic one.

It is of particular interest to inspect the behaviour of the interaction potential in the nonretarded/retarded limits, where the atom–atom separation is small/large compared to the respective atomic wavelengths. We focus here on the contribution of the atomic magnetisabilities to the potential, given by Eq. (79) with \( \beta(i\xi) \rightarrow \beta'' \). The interaction potential between a diamagnetic atom \( A \) and an electric atom \( B \), using the explicit expression for the polarisability \[ 54 \] in Eq. (79), is found to be an attractive potential in the form
\[ U_{de}(l) = -\frac{\mu_0^2 |\beta''|}{24\pi^2 \eta^2} \sum_k \omega_B^k |\mu_B^k|^2 \int_0^\infty \mathrm{d} \xi \frac{\xi^2}{\xi^2 + \omega_B^k} h_2(l\xi/c) \quad (82) \]
To achieve the limiting cases mentioned above, we note that in the $\xi$-integral, $\omega_0^2/k^3 \ll \xi$ does not hold in the non-retarded (retarded) limit. This leads to a $l^{-5}$-dependent and a $l^{-7}$-dependent potential for the nonretarded and retarded limits, respectively, as follows

$$U_{\text{de}}^{\text{n.r.}}(l) = -\frac{5\mu_0^2 c^3 |\beta_A|}{96\pi^2 l^4} \sum_k \frac{\omega_0^2 |\mu_B^k|^2}{\omega_B^k},$$

(83)

$$U_{\text{de}}^{\text{r}}(l) = -\frac{7\mu_0^2 c^3 |\beta_A|}{96\pi^2 l^7} \sum_k \frac{|\mu_B^k|^2}{\omega_B^k},$$

(84)

The diamagnetic–paramagnetic part of the two-atom interaction in free space is seen to be repulsive. It reads

$$U_{dp}(l) = \frac{\mu_0^2 |\beta_A|}{24\pi^2 l^6} \sum_k \frac{\omega_B^k |\mu_B^k|^2}{\omega_0^2} \int_0^\infty \frac{d\xi}{\xi^2 + \omega_B^k} \xi h_1(\xi/c),$$

(85)

where Eq. (85) is used for the paramagneticizability of atom B. For the nonretarded limit Eq. (85) exhibits a $l^{-6}$-dependence,

$$U_{dp}^{\text{n.r.}}(l) = \frac{\mu_0^2 |\beta_A|}{16\pi^2 l^6} \sum_k \frac{|\mu_B^k|^2}{\omega_0^2},$$

(86)

while in the retarded limit it tends to a $l^{-7}$-dependent potential,

$$U_{dp}^{\text{r}}(l) = \frac{23\mu_0^2 c^3 |\beta_A|}{96\pi^2 l^7} \sum_k \frac{|\mu_B^k|^2}{\omega_B^k} = \frac{23\mu_0^2 c^3 |\beta_A|}{64\pi^2 l^7} |\beta_B^d(0)|.$$  

(87)

Finally, the diamagnetic–diamagnetic two-atom interaction in free space shows a unique attractive $l^{-7}$-dependence for any arbitrary range of atom–atom separation, due to the frequency-independence of diamagnetisabilities. As can be obtained from Eq. (87), it is given by

$$U_{dd}(l) = -\frac{23\mu_0^2 c^3}{64\pi^2 l^7} |\beta_A^d| |\beta_B^d|.$$  

(88)

In Table I we compare the signs and asymptotic power law of the vdW potentials involving diamagnetic atoms with the known results for purely electric or paramagnetic atoms.13 We observe that the replacement of a paramagnetic atom with a diamagnetic one leads to a sign change of the vdW interaction as predicted by the Lenz rule. In addition, the frequency-independence of the diamagnetic magnetisability leads to new asymptotic power laws, e.g., $1/l^5$ for the nonretarded electric–diamagnetic interaction. This result is in between the $1/l^6$ and $1/l^4$ asymptotes found for the electric–electric and electric–paramagnetic cases.

C. Comparison with Microscopic QED

It is instructive to compare the results obtained in this section for the vdW dispersion interaction between atoms in free space when either one or both species is diamagnetic using body-assisted fields, with that derived using microscopic QED. In this second approach it is common to use the well-established molecular QED theory 12,16. For two mutually interacting particles A and B in vacuum coupled to the radiation field, the total Hamiltonian is written in the form of Eq. (13) with $H_\xi$ given by Eq. (11). In the multipolar coupling scheme, the Hamiltonian operator for the free electromagnetic field is expressed as

$$\hat{H}_F = \frac{1}{2} \int d^3 r \left[ \frac{1}{\varepsilon_0} \hat{E}^2(r) + \frac{1}{\mu_0} \hat{B}^2(r) \right] = \sum_{k,\lambda} \left[ \hat{a}^{(\lambda)}(\mathbf{k}) \hat{a}^{(\lambda\dagger)}(\mathbf{k}) + \frac{1}{2} \right] \hbar \omega,$$

(89)

where $\hat{d}(r)$ and $\hat{b}(r)$ are second quantized microscopic electric displacement and magnetic field operators, respectively. They are commonly written as a mode sum in terms of vacuum boson annihilation and creation operators $\hat{a}^{(\lambda)}(\mathbf{k})$ and $\hat{a}^{(\lambda\dagger)}(\mathbf{k})$ for a photon of wave vector $\mathbf{k}$, polarization index $\lambda$, and circular frequency $\omega = ck$, as in the second equality of Eq. (89). Analogous to Eq. (6) with Eqs. (7)–(9), the atom–field coupling Hamiltonian for the dispersion interactions of interest is

$$\hat{H}_{\xi F} = -\varepsilon_0^{-1} \mu_\xi \hat{d}(\mathbf{r}_\xi) - m_\xi \hat{b}(\mathbf{r}_\xi) + \sum_{\alpha,\xi} \frac{q_\alpha^2}{8m_\alpha} \left[ \hat{\mathbf{r}}_\alpha \times \hat{b}(\mathbf{r}_\xi) \right]^2,$$

(90)

It is worth noting the explicit appearance in the last two expressions of the electric displacement field operator. This is a direct consequence of adopting the multipolar framework, where the field momentum canonically conjugate to the vector potential is proportional to $\hat{d}(r)$ instead of to the electric field itself. This is a common feature of the microscopic and macroscopic approaches. In the latter, the quantised field $\hat{E}(r)$ also refers to the Power–Zienau transformed electric field operator that has to be regarded as displacement field with respect to the atomic polarisation 12.

Dispersion potentials between a diamagnetic atom and an electrically polarizable and a magnetically susceptible atom, and between two diamagnetic atoms may be computed in a manner similar to that already detailed. As before, the last interaction is obtained via second-order perturbation theory and is depicted in Fig. 1, while the former two occur in third-order and are described by Fig. 2. Matrix elements are evaluated using unperturbed product atom–field states $|n_\xi \rangle m(\mathbf{k},\lambda) = |n_\xi \rangle m(\mathbf{k},\lambda)$ where a number state representation is used to signify the number of photons present, in this case $m$.

As expected, results identical to Eqs. (62), (63) and (64) are found for the vdW dispersion potentials between a diamagnetic and an electric atom, a diamagnetic and a paramagnetic one, and between two diamagnetic atoms, valid for the entire range of separation distance vector $l$ beyond wave function overlap of the two centres and
TABLE II: Signs and asymptotic power laws of ground-state vdW potentials of electric, para- or diamagnetic atoms in free space.

| Atom A $\rightarrow$ | Electric | Paramagnetic | Diamagnetic |
|----------------------|----------|--------------|-------------|
| Atom B $\downarrow$ Limit $\rightarrow$ Retarded | Nonret. | Retarded | Nonret. | Retarded | Nonret. |
| Electric             | $-\frac{1}{l^7}$ | $-\frac{1}{l^7}$ | $+\frac{1}{l^7}$ | $+\frac{1}{l^7}$ | $-\frac{1}{l^7}$ | $-\frac{1}{l^7}$ |
| Paramagnetic         | $+\frac{1}{l^7}$ | $+\frac{1}{l^7}$ | $-\frac{1}{l^7}$ | $-\frac{1}{l^7}$ | $+\frac{1}{l^7}$ | $+\frac{1}{l^7}$ |
| Diamagnetic          | $-\frac{1}{l^7}$ | $-\frac{1}{l^7}$ | $+\frac{1}{l^7}$ | $+\frac{1}{l^7}$ | $-\frac{1}{l^7}$ |

We have calculated CP and vdW potentials of atoms with nontrivial diamagnetic properties in the presence of arbitrary magnetoelectric bodies on the basis of macroscopic QED and leading-order perturbation theory. The nonlinear interaction generating the diamagnetic interaction is quite different from the paramagnetic coupling and it leads to different perturbative orders. Nevertheless, we have found that diamagnetic atomic properties lead to dispersion potentials which formally resemble those of paramagnetic atoms where the diamagnetic magnetisability appears in place of the paramagnetic one. We have explicitly shown this correspondence for one- and two-atom potentials, but it is expected to hold for multi-atom vdW potentials as well.

However, the fact that the diamagnetic magnetisability is negative and frequency-independent leads to diamagnetic potentials that differ in signs and power laws from their paramagnetic counterparts. Diamagnetic dispersion interactions carry the same sign as the well-known electric potentials, which implies that diamagnetism alone cannot be used to realise repulsive potentials. The unique power laws resulting from the frequency-independence imply that diamagnetic potentials have their strongest influence at short range.

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