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Casimir-Polder long-range interaction potentials between alkali-metal atoms

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A complete description of the multipolar Casimir-Polder effects between two alkali-metal atoms in the ground state is presented. We give both general and particular expressions for the electric-electric, electric-magnetic, magnetic-magnetic, diamagnetic-electric, and diamagnetic-magnetic two-photon multipole processes, many of which have not been discussed previously in literature, to our knowledge. The asymptotic behavior of the Casimir-Polder potential is studied in terms of the K_7, K_9, and K_{11} long-range coefficients. We have established the range of validity of the Casimir-Polder potential by analyzing the first-order correction to the energy given by the matrix element of the contact interaction term between the atomic charge distributions. Numerical values for the Casimir-Polder long-range interaction potentials for both homonuclear and heteronuclear alkali-metal dimers are presented. Comparisons with previous analytical and numerical results are included. [S1050-2947(99)03102-9]

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I. INTRODUCTION

Fifty years ago, Casimir and Polder (CP) [1] pointed out that the true asymptotic behavior of the long-range interaction potential between two neutral spherically symmetric atoms is proportional to $1/R^7$, rather than to $1/R^6$ as given by the London–van der Waals (LvdW) dispersion theory. The CP result is a direct consequence of the retardation effects (in the electric dipole interaction approximation). Moreover, the CP expression of the interaction potential between two identical atoms in the ground state [1] reduces, in the limit of small values of R, to the well-known LvdW electric dipole interaction.

Since the pioneering work of CP [1], substantial theoretical efforts have been devoted to this problem. These investigations have resulted in an improved understanding of the CP effect [2–15]. Generalizations to multipolar interactions among atoms [16–21] and molecules [22–26] have been also made. Detailed numerical evaluations of the CP interaction have been presented for various atomic systems [27–33]. It is now widely appreciated that the retardation effects may be well understood in the framework of quantum electrodynamics as a two-photon exchange coupling between atomic and molecular systems. Until now, virtually all theoretical investigations of the retarded electric-multipolar interaction between two neutral atoms in the ground state were limited to contributions which, in the limit of small values of R, reduce precisely to the LvdW electric multipole interactions (quadrupole-dipole, quadrupole-quadrupole, and dipole-octupole).

Recently, Salam and Thirunamachandran [26] pointed out that the electric (dipole,dipole)-(octupole,octupole) interaction leads to a new contribution given by the case where one of the atoms undergoes two octupole transitions through P intermediate states. This contribution is in addition to that involving F intermediate states (which in the limit of small values of R is given by the dipole-octupole contribution to the C_{10} dispersion coefficient). This new term, involving P intermediate states, has no counterpart in the LvdW formalism. Moreover, it may be viewed in the limit of small values of R, as a correction proportional to α^4 to the C_6 dispersion coefficient, while in the limit $R\to\infty$ it behaves as $1/R^{11}$. Similar to this term, many other terms generated, for instance, by the (dipole,octupole)-(dipole,dipole) interaction, (dipole,octupole)-(octupole,dipole) interaction, etc., are present in a complete description of the multipolar CP effect. None of them have counterparts in a LvdW formalism, and none have been discussed in literature so far. In addition to the above mentioned electric-electric (e-e) multipolar interactions there are also contributions from electric-magnetic (e-m), magnetic-magnetic (m-m), diamagnetic-electric (d-e), and diamagnetic-magnetic (d-m) multipolar interactions. The last one, the d-m interaction, has to our knowledge not been studied before. For e-m, m-m, and d-e interactions, the dipole-dipole contributions have been studied in the general context of long-range intermolecular forces [4,9,10,19,24]. Important results have been also obtained for the case of two hydrogen atoms [8] by including hyperfine interactions. In general, one may conclude that the CP interaction potential, including all multipolar interactions, behaves in the limit $R\to\infty$ as

$$V(R)=-\frac{K_7}{R^7}-\frac{K_9}{R^9}-\frac{K_{11}}{R^{11}}-\cdots, \tag{1.1}$$

where K_7, K_9, and K_{11} have been the long-range coefficients, while in the limit of small values of R it behaves as

$$V(R)=-\frac{C_6}{R^6}-\frac{C_8}{R^8}-\frac{C_{10}}{R^{10}}-\cdots, \tag{1.2}$$

where the C_6, C_8, and C_{10} coefficients are, up to corrections of order α^2, α^4, etc. (α is the fine structure constant), the dispersion coefficients.

While the dispersion coefficients C have been well studied, the long-range coefficients K are not as well known, and the complete form of the multipolar CP interaction potential is missing. We have undertaken this investigation in light of recent advances in ultracold atomic physics. Although the retardation effects are small in comparison to the dispersion forces, they may be important in describing atomic processes at very low temperature.

Our entire analysis of the multipolar CP interaction will be focused on the particular case of alkali-metal atoms, although an extension to other families of atoms and molecules is obvious. We will systematically investigate all two-photon e-e, e-m, m-m, d-e, and d-m multipolar processes. Special attention will be directed toward processes which in the limit $R\rightarrow\infty$ contribute to the K_7, K_9, and K_{11} long-range coefficients. We intend to establish expressions for the long-range interaction potentials between alkali-metal atoms suitable for explicit numerical evaluations. We choose to describe the alkali-metal atoms by single-active electron model potentials [34], since the core excitation processes are unlikely to be important in the description of the long-range atomic interactions (no overlapping between the atomic charge distributions is assumed). We also neglect the interaction between electronic and nuclear spins. These hyperfine interactions may become relatively important in describing magnetic interactions [8] and their consequences will be discussed elsewhere. We adopt the Power-Zienau-Woolley (PZW) representation [2,35–38] for the long-range interaction Hamiltonian in a multipolar expansion form,

$$\begin{aligned} H=&\frac{p_1^2}{2}+V_A(r_1)+\sum_n Q^{(n)}(\vec{R}_A,\vec{r}_1)+\alpha\sum_n M^{(n)}(\vec{R}_A,\vec{r}_1)\\ &+\alpha^2\sum_{n,m} D^{(n,m)}(\vec{R}_A,\vec{r}_1)+\frac{p_2^2}{2}+V_B(r_2)\\ &+\sum_n Q^{(n)}(\vec{R}_B,\vec{r}_2)+\alpha\sum_n M^{(n)}(\vec{R}_B,\vec{r}_2)\\ &+\alpha^2\sum_{n,m} D^{(n,m)}(\vec{R}_B,\vec{r}_2)+\mathcal{V}(\vec{R},\vec{r}_1,\vec{r}_2)+H_R, \end{aligned} \tag{1.3}$$

where

$$\begin{aligned} Q^{(n)}(\vec{R},\vec{r})=&\frac{i^{n+1}}{(n+1)!}\sum_{\vec{k}\lambda}\left(\frac{2\pi\omega}{L^3}\right)^{1/2}(\vec{r}\cdot\hat{e}_{\vec{k}\lambda})(\vec{r}\cdot\vec{k})^n\\ &\times[a_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{R}}+(-1)^{n+1}\text{H.c.}] \end{aligned} \tag{1.4}$$

are the electric multipoles;

$$M^{(n)}(\vec{R},\vec{r})=\vec{L}\cdot\vec{\mathcal{M}}^{(n)}+\vec{\mathcal{M}}^{(n)}\cdot\vec{L}, \tag{1.5}$$

with

$$\begin{aligned} \vec{\mathcal{M}}^{(n)}(\vec{R},\vec{r})=&\frac{i^{n+1}}{2(n+2)n!}\sum_{\vec{k}\lambda}\left(\frac{2\pi\omega}{L^3}\right)^{1/2}\hat{b}_{\vec{k}\lambda}(\vec{r}\cdot\vec{k})^n\\ &\times[a_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{R}}+(-1)^{n+1}\text{H.c.}], \end{aligned} \tag{1.6}$$

are the magnetic multipoles,

$$D^{(n,m)}(\vec{R},\vec{r})=2(\vec{\mathcal{M}}^{(n)}\times\vec{r})\cdot(\vec{\mathcal{M}}^{(m)}\times\vec{r}); \tag{1.7}$$

are the diamagnetic multipoles;

$$\mathcal{V}(\vec{R},\vec{r}_1,\vec{r}_2)=4\pi\vec{r}_1\cdot\vec{r}_2\int_0^1\int_0^1 d\xi_1 d\xi_2\,\delta(\vec{R}-\xi_1\vec{r}_1+\xi_2\vec{r}_2), \tag{1.8}$$

is the contact interaction term between the two atomic charge distributions; and H_R is the free radiation field Hamiltonian. $a_{\vec{k}\lambda\dagger}$ and $a_{\vec{k}\lambda}$ are the photon creation and annihilation operators, $\hat{e}_{\vec{k}\lambda}$, where $\lambda=1$ and 2 are the polarization vectors, $\hat{b}_{\vec{k}\lambda}=\hat{e}_{\vec{k}\lambda}\times\hat{k}$, $\vec{R}_A$ and $\vec{R}_B$ are the position vectors of the nucleus relative to the laboratory frame, $\vec{R}=\vec{R}_A-\vec{R}_B$ is the internuclear vector, and $\vec{r}_1$ and $\vec{r}_2$ are the position vectors of the electrons relative to the nucleus. As usual, the radiation field satisfies periodic boundary conditions at the sides of a cube of edge L. Later L will be made infinite and the sum over the discrete values of $\vec{k}$ will be replaced by an integral over $\vec{k}$ according to $(2\pi/L)^3\Sigma_{\vec{k}}\rightarrow\int d\vec{k}$. We use the atomic units ($e=m_e=\hbar=1$).

Since we are interested in studying the long-range part of the interaction potential, no overlapping between the atomic charge distributions is assumed. Thus the contact interaction term $\mathcal{V}$ in Eq. (1.3) may be neglected. The long-range inter-

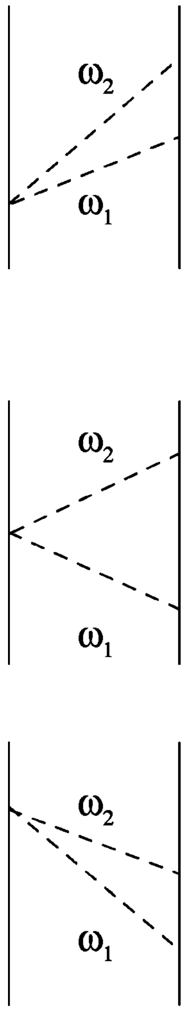

FIG. 1. Three topologically distinct two-photon diamagnetic-electric (diamagnetic-magnetic) diagrams. The other three may be obtained by a mirror inversion.

action potential may be determined by perturbatively solving the eigenvalue problem for Eq. (1.3), where the perturbation is given by the sums of electric, magnetic, and diamagnetic multipoles. The order of relevant multipoles which enter in our final computation will be decided in the perturbation procedure by our desire to evaluate only terms contributing in the large separation limit to the K_7, K_9, and K_{11} long-range coefficients. The perturbation procedure is carried out up to the fourth order, retaining all terms proportional to e^4. In atomic units, $e=1$ and so the electronic charge is not a visible quantity in our notations. However, one should bear in mind that in Eq. (1.3) the electric and magnetic multipoles are multiplied by e while the diamagnetic multipoles are multiplied by e^2. Furthermore, only R-dependent terms will be considered. Other terms, such as those contributing to the atomic self-energies, were eliminated, since the interaction potential between atoms is given by the difference of the interaction energies at a given R and at infinity. The two-photon exchange processes between atoms are described in terms of time-ordered diagrams. One may notice that there are no contributions proportional to e, e^2, and e^3, and there are no contributions from the first and second order of perturbation. The d-e and d-m processes (which occur in the third order of perturbation) are presented in Sec. II. The e-e, e-m, and m-m multipolar interactions (which occur in the fourth order of perturbation) are presented in Sec. III. The complete picture of the two-photon interactions which enter in our final description of the CP long-range interaction potential is presented in Sec. IV. Section V presents a simple criterion for establishing the long-range domain of the two-atom interaction (the minimum value of R for which the interaction potential is well approximated by the CP expression alone). This criterion is based on the analyses of the first-order perturbation matrix element of the contact interaction between atomic charge distributions. It is intended to substitute the LeRoy radius criterion [39] in a more rigorous way. The numerical results and discussions are presented in Sec. VI. A detailed quantitative analysis of different processes involved in the CP long-range expression of the interaction potential is carried out for the particular case of two interacting potassium atoms. Numerical results for the long-range interaction potentials are presented for all alkali-metal dimers, including the heteronuclear cases. Discussions about the range of validity of the LvdW dispersion form of the interaction potential are also included. Section VII presents our conclusions.

II. DIAMAGNETIC-ELECTRIC AND DIAMAGNETIC-MAGNETIC MULTIPOLAR INTERACTIONS

d-e and d-m multipolar couplings between atoms occur in the third order of perturbation by matrix elements containing one diamagnetic multipole $D^{(n,m)}$ [Eq. (1.7)], and two electric [Eq. (1.4)], or two magnetic [Eq. (1.5)], multipoles, respectively. These matrix elements may be represented by two-photon time-ordered diagrams, where the diamagnetic vertex is a two-photon vertex. There are six topological distinct diagrams in total. Three of them are presented in Fig. 1. The other three are similar, but with the diamagnetic vertex owned by the other atom (mirror symmetry). We analyze all multipolar interactions which contribute to the K_7, K_9, and K_{11} long-range coefficients. We start by establishing the general expression of the d-e (d-m) interaction involving one (p_1,p_2)-order diamagnetic multipole and two (q_1,q_2)-order electric (magnetic) multipoles. For convenience, we denote the electric multipoles (of order q) by letters (q) and the multipoles (of order p) which involve magnetic interactions by underscored letters (p). Consequently, a diamagnetic multipole of order p_1+p_2 will be denoted by $(\underline{p}_1,\underline{p}_2)$.

A. Diamagnetic-electric interaction

The three diagrams from Fig. 1, with the first photon emitted (absorbed) in a p_1 diamagnetic mode by the first atom and absorbed (emitted) via a q_1 electric multipole transition by the second atom, have similar expressions and they may be studied together. The sum of their contributions is given by

$$f_{\underline{p}_1+\underline{p}_2q_1q_2}=\frac{(-1)^{q1+q2}i^{p_1+p_2+q_1+q_2}\alpha^2}{2(p_1+2)p_1!(p_2+2)p_2!(q_1+1)!(q_2+1)!}\langle r^{p_1+p_2+2}\rangle$$
$$\times\sum_{n_2l_2}\sum_{\vec{k}_1\vec{k}_2}\frac{2\pi\omega_1}{L^3}\frac{2\pi\omega_2}{L^3}k_1^{p_1+q_1}k_2^{p_2+q_2}e^{i\vec{k}_1\cdot\vec{R}}e^{i\vec{k}_2\cdot\vec{R}}\frac{1}{D_{n_2l_2}}(n_g0|r^{q_2+1}|n_2l_2)(n_2l_2|r^{q_1+1}|n_g0)$$
$$\times\sum_{\lambda_1\lambda_2m_2}\langle 00|(\hat{e}_2\cdot\hat{r})(\hat{k}_2\cdot\hat{r})^{q_2}|l_2m_2\rangle\langle l_2m_2|(\hat{e}_1\cdot\hat{r})(\hat{k}_1\cdot\hat{r})^{q_1}|00\rangle$$
$$\times\langle 00|[\hat{b}_1\cdot\hat{b}_2-(\hat{b}_1\cdot\hat{r})(\hat{b}_2\cdot\hat{r})](\hat{k}_1\cdot\hat{r})^{p_1}(\hat{k}_2\cdot\hat{r})^{p_2}|00\rangle, \tag{2.1}$$

where the electronic radial and angular parts were factored and

$$\frac{1}{D_{nl}}=\frac{1}{\Delta_{nl}+\omega_1}\left[\frac{1}{\omega_1+\omega_2}-\frac{1}{\omega_1-\omega_2}\right]+\frac{1}{\Delta_{nl}+\omega_2}\left[\frac{1}{\omega_1+\omega_2}+\frac{1}{\omega_1-\omega_2}\right], \tag{2.2}$$

where $\Delta_{nl}=E_{nl}-E_{n_g0}$ is the atomic excitation energy from the ground state to the nl energy level. We have used the short notation $\hat{e}_{1(2)}$ for $\hat{e}_{\vec{k}_{1(2)}\lambda_{1(2)}}$ and $\hat{b}_{1(2)}$ for $\hat{b}_{\vec{k}_{1(2)}\lambda_{1(2)}}$. The radial matrix elements are denoted by $(\ |\ |\ )$, while the angular matrix elements are denoted by $\langle\ |\ |\ \rangle$. The atomic states are denoted by $|nlm\rangle$, where $|n_g00\rangle$ is the ground state. $\langle r^n\rangle$

denotes the radial matrix element $(n_g0|r^n|n_g0)$ (the average of r^n in the ground state). We note that $f_{\underline{p}_1+\underline{p}_2q_1q_2}$ is zero if p_1+p_2 or q_1+q_2 are odd quantities, according to the atomic multipole transition selection rules (since the initial and final atomic states are identical). We start the computation of $f_{\underline{p}_1+\underline{p}_2q_1q_2}$ by analyzing the triple sum over photon polarizations λ_1 and λ_2 and the atomic magnetic quantum number m_2 from Eq. (2.1). It may be rewritten as

$$T^{DE}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_1\cdots s_{p_1}}[\delta_{i_0j_0}\mathcal{Q}^{(p_2+q_2+1)}_{t,i_1\cdots i_{q_2},r_1\cdots r_{p_2}}(\hat{k}_2)\mathcal{Q}^{(p_1+q_1+1)}_{t,j_1\cdots j_{q_1},s_1\cdots s_{p_1}}(\hat{k}_1)-\mathcal{Q}^{(p_2+q_2+1)}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2}}(\hat{k}_2)\mathcal{Q}^{(p_1+q_1+1)}_{j_0\cdots j_{q_1},s_1\cdots s_{p_1}}(\hat{k}_1)]$$
$$-\epsilon_{j_0r_0t_2}\epsilon_{j_0s_0t_1}T^{DE}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\mathcal{Q}^{(p_2+q_2+1)}_{t_2,i_1\cdots i_{q_2},r_1\cdots r_{p_2}}(\hat{k}_2)\mathcal{Q}^{(p_1+q_1+1)}_{t_1,j_1\cdots j_{q_1},s_1\cdots s_{p_1}}(\hat{k}_1), \tag{2.3}$$

where

$$\mathcal{Q}^{(p+q)}_{i_1\cdots i_p,j_1\cdots j_q}(\hat{k})=\hat{k}_{i_1}\cdots\hat{k}_{i_p}\hat{k}_{j_1}\cdots\hat{k}_{j_q} \tag{2.4}$$

is a tensor of order $p+q$, with $\hat{k}_i$ the ith Cartesian component of the $\hat{k}$ unit vector, and

$$T^{DE}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_1\cdots s_{p_1}}=\mathcal{D}^{(00)(00)}_{r_1\cdots r_{p_2},s_1\cdots s_{p_1}}\sum_{m_2}\mathcal{D}^{(00)(l_2m_2)}_{i_0\cdots i_{q_2}}\mathcal{D}^{(l_2m_2)(00)}_{j_0\cdots j_{q_1}} \tag{2.5}$$

is a tensor of order $p_1+p_2+q_1+q_2+2$, where

$$\mathcal{D}^{(l_1m_1)(l_2m_2)}_{i_1\cdots i_n}=\langle l_1m_1|\mathcal{Q}^{(n)}_{i_1\cdots i_n}(\hat{r})|l_2m_2\rangle \tag{2.6}$$

is a tensor of order n. In Eq. (2.3) the Einstein summation convention over repeated indices is assumed. ϵ_{ijk} is the total antisymmetric unit tensor. Replacing the sum over the discrete values of $\vec{k}_1$ and $\vec{k}_2$ by integrals in Eq. (2.1), the integration over the directions of $\vec{k}_1$ and $\vec{k}_2$ may be formally computed by introducing the quantity:

$$\mathcal{P}^{(n)}_{i_1\cdots i_n}(\alpha\omega R)\equiv\frac{1}{2\pi}\int d\Omega_{\vec{k}}\mathcal{Q}^{(n)}_{i_1\cdots i_n}(\hat{k})e^{i\vec{k}\cdot\vec{R}}, \tag{2.7}$$

where $\mathcal{P}^{(n)}$ is a tensor of order n which depend on $\alpha\omega R$ (in a.u., $k=\alpha\omega$). It can by shown that $\mathcal{P}^{(n)}$ has the structure

$$\mathcal{P}^{(n)}_{i_1\cdots i_n}(u)=e^{iu}\Theta^{(n)}_{i_1\cdots i_n}\left(\frac{1}{iu}\right)+\text{c.c.}, \tag{2.8}$$

where $\Theta^{(n)}_{i_1\cdots i_n}$ is a polynomial of order n with real coefficients. Then the integrals over ω_1 and ω_2 may be rotated into the complex plane along the imaginary axis. In doing this, one may notice that one of the integrals disappears in favor of the residue of the integrand at the simple pole $\omega_1=\omega_2$ [see Eq. (2.2)]. After some algebraic transformations, the final expression of $f_{\underline{p}_1+\underline{p}_2q_1q_2}$ is given by

$$f_{\underline{p}_1+\underline{p}_2q_1q_2}=-\frac{\alpha}{2\pi}\frac{\mathcal{K}_{\underline{p}_1\underline{p}_2q_1q_2}}{R^{p_1+p_2+q_1+q_2+7}}\langle r^{p_1+p_2+2}\rangle$$
$$\times\sum_l\int_0^\infty du\,u^{p_1+p_2+q_1+q_2+6}\mathcal{R}^l_{q_1+1q_2+1}\left(i\frac{u}{\alpha R}\right)e^{-2u}\{T^{DE}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_1\cdots s_{p_1}}$$
$$\times[\delta_{i_0j_0}\Theta^{(p_2+q_2+1)}_{t,i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+1)}_{t,j_1\cdots j_{q_1},s_1\cdots s_{p_1}}-\Theta^{(p_2+q_2+1)}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+1)}_{j_0\cdots j_{q_1},s_1\cdots s_{p_1}}]$$
$$-\epsilon_{i_0r_0t_2}\epsilon_{j_0s_0t_1}T^{DE}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\Theta^{(p_2+q_2+1)}_{t_2,i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+1)}_{t_1,j_1\cdots j_{q_1},s_1\cdots s_{p_1}}\}, \tag{2.9}$$

where the argument of the Θ polynomials is $-1/u$ and

$$\mathcal{K}_{\underline{p}_1\underline{p}_2q_1q_2}=[(p_1+2)p_1!(p_2+2)p_2!(q_1+1)!(q_2+1)!]^{-1}, \tag{2.10}$$

$$\mathcal{R}^l_{pq}(i\omega)=\text{Re}[(n_g0|r^pg_l(i\omega)r^q|n_g0)], \tag{2.11}$$

where g_l is the radial Green's function for angular momentum l. To this end, specific expressions of $f_{\underline{p}_1+\underline{p}_2q_1q_2}$, for given values of p_1, p_2, q_1, and q_2, may be obtained using MATHEMATICA, since both the T^{DE} tensor [Eq. (2.5)], and the Θ polynomials [Eq. (2.8)], may be easily generated. The summation over l in Eq. (2.9) involves only a finite number of terms, and the actual relevant values of l may be established at the outset by analyzing the selection rules of atomic multipole transitions. In the limit $R\to\infty$ the $f_{\underline{p}_1+\underline{p}_2q_1q_2}$ quantities behave as $1/R^{p_1+p_2+q_1+q_2+7}$ with the full expression given by Eq. (2.9) with $\mathcal{R}^{l}_{q_1+1q_2+1}$ evaluated at $u=0$. Then, only the $f_{\underline{0}+\underline{0}00}$ term will contribute to the K_7 coefficient. It is given by

$$f_{\underline{0}+\underline{0}00}=-\frac{\alpha}{18\pi R^7}\langle r^2\rangle\int_0^\infty du\,u^2\mathcal{R}^{1}_{11}\left(-i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2. \tag{2.12}$$

In the limit $R\to\infty$, it becomes

$$f_{\underline{0}+\underline{0}00}=-\frac{7\alpha}{72\pi R^7}\langle r^2\rangle\mathcal{R}^{1}_{11}(0). \tag{2.13}$$

For the K_9 coefficient we have to consider all terms which satisfy the conditions $p_1+p_2+q_1+q_2=2$, $p_1+p_2=\text{even}$, and $q_1+q_2=\text{even}$. They are $f_{\underline{1}+\underline{1}00}$, $f_{\underline{2}+\underline{0}00}=f_{\underline{0}+\underline{2}00}$, $f_{\underline{0}+\underline{0}11}$, and $f_{\underline{0}+\underline{0}20}=f_{\underline{0}+\underline{0}02}$. The equalities are due to the general symmetry $f_{\underline{p}_1+\underline{p}_2q_1q_2}=f_{\underline{p}_2+\underline{p}_1q_2q_1}$. This is a result of the fact that the set of diagrams which contribute to the expression of $f_{\underline{p}_2+\underline{p}_1q_2q_1}$ may be obtained from the set of diagrams corresponding to $f_{\underline{p}_1+\underline{p}_2q_1q_2}$ by interchanging the label of the photon lines. Finally, we have

$$f_{\underline{1}+\underline{1}00}=-\frac{\alpha}{405\pi R^9}\langle r^4\rangle\int_0^\infty du\,u^2\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}\times(21+42u+35u^2+14u^3+4u^4), \tag{2.14}$$

$$f_{\underline{2}+\underline{0}00}=-\frac{\alpha}{180\pi R^9}\langle r^4\rangle\int_0^\infty du\,u^4\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2, \tag{2.15}$$

$$f_{\underline{0}+\underline{0}11}=-\frac{\alpha}{360\pi R^9}\langle r^2\rangle\int_0^\infty du\,u^2\mathcal{R}^{2}_{22}\left(i\frac{u}{\alpha R}\right)e^{-2u}\times(3+3u+u^2)^2, \tag{2.16}$$

$$f_{\underline{0}+\underline{0}20}=-\frac{\alpha}{540\pi R^9}\langle r^2\rangle\int_0^\infty du\,u^4\mathcal{R}^{1}_{31}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2. \tag{2.17}$$

In the asymptotic limit, $R\to\infty$, the f terms have the following expressions:

$$f_{\underline{1}+\underline{1}00}=-\frac{32\alpha}{135\pi R^9}\langle r^4\rangle\mathcal{R}^{1}_{11}(0), \tag{2.18}$$

$$f_{\underline{2}+\underline{0}00}=-\frac{9\alpha}{160\pi R^9}\langle r^4\rangle\mathcal{R}^{1}_{11}(0), \tag{2.19}$$

$$f_{\underline{0}+\underline{0}11}=-\frac{33\alpha}{320\pi R^9}\langle r^2\rangle\mathcal{R}^{2}_{22}(0), \tag{2.20}$$

$$f_{\underline{0}+\underline{0}20}=-\frac{3\alpha}{169\pi R^9}\langle r^2\rangle\mathcal{R}^{1}_{31}(0). \tag{2.21}$$

For the K_{11} coefficient we have to consider all terms satisfying the condition $p_1+p_2+q_1+q_2=4$, with p_1+p_2 and q_1+q_2 even quantities. They are $f_{\underline{4}+\underline{0}00}=f_{\underline{0}+\underline{4}00}$, $f_{\underline{3}+\underline{1}00}=f_{\underline{1}+\underline{3}00}$, $f_{\underline{2}+\underline{2}00}$, $f_{\underline{2}+\underline{0}20}=f_{\underline{0}+\underline{2}02}=f_{\underline{2}+\underline{0}02}=f_{\underline{0}+\underline{2}20}$, $f_{\underline{2}+\underline{0}11}=f_{\underline{0}+\underline{2}11}$, $f_{\underline{1}+\underline{1}20}=f_{\underline{1}+\underline{1}02}$, $f_{\underline{1}+\underline{1}11}$, $f_{\underline{0}+\underline{0}40}=f_{\underline{0}+\underline{0}04}$, $f_{\underline{0}+\underline{0}31}=f_{\underline{0}+\underline{0}13}$, and $f_{\underline{0}+\underline{0}22}$. Their expressions are given by

$$f_{\underline{4}+\underline{0}00}=-\frac{\alpha}{5040\pi R^{11}}\langle r^6\rangle\int_0^\infty du\,u^6\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2, \tag{2.22}$$

$$f_{\underline{3}+\underline{1}00}=-\frac{\alpha}{9450\pi R^{11}}\langle r^6\rangle\int_0^\infty du\,u^4\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(33+66u+55u^2+22u^3+6u^4), \tag{2.23}$$

$$f_{\underline{2}+\underline{2}00}=-\frac{\alpha}{10080\pi R^{11}}\langle r^6\rangle\int_0^\infty du\,u^2\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(450+900u+810u^2+420u^3+139u^4+38u^5+9u^6), \tag{2.24}$$

$$f_{\underline{2}+\underline{0}20}=-\frac{\alpha}{5400\pi R^{11}}\langle r^4\rangle\int_0^\infty du\,u^6\mathcal{R}^{1}_{31}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2, \tag{2.25}$$

$$f_{\underline{2}+\underline{0}11}=-\frac{\alpha}{3600\pi R^{11}}\langle r^4\rangle\int_0^\infty du\, u^4\mathcal{R}_{22}^{2}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+3u+u^2)^2, \tag{2.26}$$

$$f_{\underline{1}+\underline{1}20}=-\frac{\alpha}{12150\pi R^{11}}\langle r^4\rangle\int_0^\infty du\, u^4\mathcal{R}_{31}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(21+42u+35u^2+14u^3+4u^4), \tag{2.27}$$

$$f_{\underline{1}+\underline{1}11}=-\frac{\alpha}{8100\pi R^{11}}\langle r^4\rangle\int_0^\infty du\, u^2\mathcal{R}_{22}^{2}\left(i\frac{u}{\alpha R}\right)e^{-2u}(495+990u+891u^2+462u^3+147u^4+30u^5+4u^6), \tag{2.28}$$

$$f_{\underline{0}+\underline{0}40}=-\frac{\alpha}{25200\pi R^{11}}\langle r^2\rangle\int_0^\infty du\, u^6\mathcal{R}_{51}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2, \tag{2.29}$$

$$f_{\underline{0}+\underline{0}31}=-\frac{\alpha}{10080\pi R^{11}}\langle r^2\rangle\int_0^\infty du\, u^4\mathcal{R}_{42}^{2}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+3u+u^2)^2. \tag{2.30}$$

In the expression of $f_{\underline{0}+\underline{0}22}$ [Eq. (2.9)], l is allowed to take two values 1 and 3. Thus we write its expression as $f_{\underline{0}+\underline{0}22}=f^P_{\underline{0}+\underline{0}22}+f^F_{\underline{0}+\underline{0}22}$, where $f^P_{\underline{0}+\underline{0}22}$ is the contribution for $l=1$ and $f^F_{\underline{0}+\underline{0}22}$ is the contribution for $l=3$. Then we have

$$f^P_{\underline{0}+\underline{0}22}=-\frac{\alpha}{16200\pi R^{11}}\langle r^2\rangle \times\int_0^\infty du\, u^6\mathcal{R}_{33}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2, \tag{2.31}$$

$$f^F_{\underline{0}+\underline{0}22}=-\frac{\alpha}{14175\pi R^{11}}\langle r^2\rangle \times\int_0^\infty du\, u^2\mathcal{R}_{33}^{3}\left(i\frac{u}{\alpha R}\right)e^{-2u}(15+15u+6u^2+u^3). \tag{2.32}$$

In the asymptotic limit, $R\to\infty$, these terms become

$$f_{\underline{4}+\underline{0}00}=-\frac{11\alpha}{448\pi R^{11}}\langle r^6\rangle\mathcal{R}_{11}^{1}(0), \tag{2.33}$$

$$f_{\underline{3}+\underline{1}00}=-\frac{101\alpha}{170\pi R^{11}}\langle r^6\rangle\mathcal{R}_{11}^{1}(0), \tag{2.34}$$

$$f_{\underline{2}+\underline{2}00}=-\frac{363\alpha}{896\pi R^{11}}\langle r^6\rangle\mathcal{R}_{11}^{1}(0), \tag{2.35}$$

$$f_{\underline{2}+\underline{0}20}=-\frac{11\alpha}{480\pi R^{11}}\langle r^4\rangle\mathcal{R}_{31}^{1}(0), \tag{2.36}$$

$$f_{\underline{2}+\underline{0}11}=-\frac{143\alpha}{1600\pi R^{11}}\langle r^4\rangle\mathcal{R}_{22}^{2}(0), \tag{2.37}$$

$$f_{\underline{1}+\underline{1}20}=-\frac{49\alpha}{675\pi R^{11}}\langle r^4\rangle\mathcal{R}_{31}^{1}(0), \tag{2.38}$$

$$f_{\underline{1}+\underline{1}11}=-\frac{209\alpha}{450\pi R^{11}}\langle r^4\rangle\mathcal{R}_{22}^{2}(0), \tag{2.39}$$

$$f_{\underline{0}+\underline{0}40}=-\frac{11\alpha}{2240\pi R^{11}}\langle r^2\rangle\mathcal{R}_{42}^{2}(0), \tag{2.40}$$

$$f_{\underline{0}+\underline{0}31}=-\frac{143\alpha}{4480\pi R^{11}}\langle r^2\rangle\mathcal{R}_{42}^{2}(0), \tag{2.41}$$

$$f^P_{\underline{0}+\underline{0}22}=-\frac{11\alpha}{1440\pi R^{11}}\langle r^2\rangle\mathcal{R}_{33}^{1}(0), \tag{2.42}$$

$$f^F_{\underline{0}+\underline{0}22}=-\frac{143\alpha}{1260\pi R^{11}}\langle r^2\rangle\mathcal{R}_{33}^{3}(0). \tag{2.43}$$

B. Diamagnetic-magnetic interaction

The general expression for the d-m interaction involving a (p_1,p_2)-order diamagnetic multipole [Eq. (1.7)], and two q_1 and q_2 magnetic multipoles, Eq. (1.5), may be obtained following a procedure similar to that discussed in Sec. II A for the d-e interaction. The final expression for the $f_{\underline{p}_1+\underline{p}_2\underline{q}_1\underline{q}_2}$ term (the sum of the contribution of diagrams from Fig. 1, but with q_1 and q_2 magnetic multipole vertexes) is given by

$$
\begin{aligned}
f_{\underline{p}_1+\underline{p}_2\underline{q}_1\underline{q}_2} = & -\frac{\alpha^3}{8\pi}\frac{\mathcal{K}_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}}{R^{p_1+p_2+q_1+q_2+7}}\langle r^{p_1+p_2+2}\rangle\sum_l\int_0^\infty du\, u^{p_1+p_2+q_1+q_2+6}\mathcal{R}^l_{p_1p_2}\left(i\frac{u}{\alpha R}\right)e^{-2u}\{T^{DM}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_1\cdots s_{p_1}}\\
& \times[\delta_{i_0j_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}-\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},i_0,s_1\cdots s_{p_1}}\\
& -\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},j_0,r_1\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}+\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},t,r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},t,s_1\cdots s_{p_1}}]\\
& -T^{DM}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}[\delta_{i_0r_0}\delta_{j_0s_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}\\
& -\delta_{i_0r_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}-\delta_{j_0s_0}\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}\\
& +\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}]\},
\end{aligned}
\tag{2.44}
$$

where

$$
\mathcal{K}_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}=[(p_1+2)p_1!(p_2+2)p_2! \times(q_1+2)q_1!(q_2+2)q_2!]^{-1},
\tag{2.45}
$$

and

$$
T^{DM}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_1\cdots s_{p_1}} =\mathcal{D}^{(00)(00)}_{r_1\cdots r_{p_2},s_1\cdots s_{p_1}}\sum_m \mathcal{L}^{(00)(lm)}_{i_0\cdots i_{q_2}}\mathcal{L}^{(lm)(00)}_{j_0\cdots j_{q_1}},
\tag{2.46}
$$

is a tensor of order $p_1+p_2+q_1+q_2+2$ and

$$
\mathcal{L}^{(l_1m_1)(l_2m_2)}_{i_0\cdots i_n}=\langle l_1m_1|\{L_{i_0},\mathcal{Q}^{(n)}_{i_1\cdots i_n}(\hat{r})\}|l_1m_1\rangle
\tag{2.47}
$$

is a tensor of order $n+1$, where L_i is the ith Cartesian component of the atomic orbital angular momentum $\vec{L}$ and $\{,\}$ denotes the anticommutator. In the asymptotic limit, $f_{\underline{p}_1+\underline{p}_2\underline{q}_1\underline{q}_2}$ behaves as $1/R^{p_1+p_2+q_1+q_2+7}$, where the full expression is given by Eq. (2.44) for $\mathcal{R}^l_{p_1p_2}$ evaluated at $u=0$. We mention that the $f_{\underline{p}_1+\underline{p}_2\underline{q}_1\underline{q}_2}$ terms are zero if $q_1=0$ or $q_2=0$, since the $\mathcal{L}^{(00)(lm)}_{i_0}$ tensor is zero and so are the corresponding T^{DE} tensors. Thus there is no contribution in $1/R^7$ from the d-m interaction in the asymptotic limit. For the K_9 coefficient only one term $f_{\underline{0}+\underline{011}}$ contributes. It has the following expression:

$$
f_{\underline{0}+\underline{011}}=-\frac{\alpha^3}{648\pi R^9}\langle r^2\rangle\int_0^\infty du\, u^4\mathcal{R}^1_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2.
\tag{2.48}
$$

In the limit $R\to\infty$, it is given by

$$
f_{\underline{0}+\underline{011}}=-\frac{\alpha^3}{64\pi R^9}\langle r^2\rangle\mathcal{R}^1_{11}(0).
\tag{2.49}
$$

For the K_{11} coefficient, the contributing terms satisfy the conditions $p_1+p_2+q_1+q_2=4$, $p_1+p_2=$even, $q_1+q_2=$even, $q_1\geqslant1$, and $q_2\geqslant1$. They are $f_{\underline{2}+\underline{011}}$, $f_{\underline{1}+\underline{111}}$, $f_{\underline{0}+\underline{031}}=f_{\underline{0}+\underline{013}}$, and $f_{\underline{0}+\underline{022}}$, and their expressions are given by

$$
f_{\underline{2}+\underline{011}}=-\frac{\alpha^3}{6480\pi R^9}\langle r^4\rangle\int_0^\infty du\, u^6\mathcal{R}^1_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2,
\tag{2.50}
$$

$$
f_{\underline{1}+\underline{111}}=-\frac{\alpha^3}{14580\pi R^9}\langle r^4\rangle\int_0^\infty du\, u^4\mathcal{R}^1_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u} \times(21+42u+35u^2+14u^3+4u^4),
\tag{2.51}
$$

$$
f_{\underline{0}+\underline{031}}=-\frac{\alpha^3}{10800\pi R^9}\langle r^2\rangle \times\int_0^\infty du\, u^6\mathcal{R}^1_{31}\left(i\frac{u}{\alpha R}\right)e^{-2u}(1+u)^2,
\tag{2.52}
$$

$$
f_{\underline{0}+\underline{022}}=-\frac{\alpha^3}{3840\pi R^9}\langle r^2\rangle \times\int_0^\infty du\, u^4\mathcal{R}^2_{22}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+3u+u^2)^2.
\tag{2.53}
$$

In the asymptotic limit, $R\to\infty$, these become

$$
f_{\underline{2}+\underline{011}}=-\frac{11\alpha^3}{576\pi R^{11}}\langle r^4\rangle\mathcal{R}^1_{11}(0),
\tag{2.54}
$$

$$
f_{\underline{1}+\underline{111}}=-\frac{49\alpha^3}{810\pi R^{11}}\langle r^4\rangle\mathcal{R}^1_{11}(0),
\tag{2.55}
$$

$$
f_{\underline{0}+\underline{031}}=-\frac{11\alpha^3}{960\pi R^{11}}\langle r^2\rangle\mathcal{R}^1_{31}(0),
\tag{2.56}
$$

$$
f_{\underline{0}+\underline{022}}=-\frac{429\alpha^3}{5120\pi R^{11}}\langle r^2\rangle\mathcal{R}^2_{22}(0).
\tag{2.57}
$$

We note that the contribution of the d-m terms is α^2 times smaller than that of the d-e terms.

III. ELECTRIC-ELECTRIC, ELECTRIC-MAGNETIC, AND MAGNETIC-MAGNETIC INTERACTIONS

The e-e, e-m, and m-m multipolar coupling between two atoms in the ground state occur in the fourth order of perturbation as a result of two-photon exchange. The perturbation matrix elements involving four electric and magnetic multipoles operators may be represented by two-photon time-ordered diagrams. There are 12 topologically distinct diagrams in total. Six of them are presented in Fig. 2. The other six are the mirror symmetric versions of those from Fig. 2. As in Sec. II we will investigate all diagrams which contribute to the K_7, K_9, and K_{11} long-range coefficients. Thus, we start by studying the general expressions for e-e, e-m, and m-m multipole interactions[1].

A. Electric-electric interactions

In this case, the vertexes of all twelve diagrams (six of which are presented in Fig. 2) correspond to electric multipoles. One may easily show that the twelve diagrams which involve p_1-, p_2-, q_1-, and q_2-order electric multipoles, such that the first photon is emitted and absorbed as a result of p_1 and q_1 electric multipole atomic transitions, and where the first atom is experiencing only p_1 and p_2 electric multipolar transitions, have similar expressions and they may be studied together. The sum of their contribution is given by

$$\begin{aligned}
f_{p_1p_2q_1q_2} = & -\frac{(-1)^{q_1+q_2} i^{p_1+p_2+q_1+q_2}}{(p_1+1)!(p_2+1)!(q_1+1)!(q_2+1)!} \\
& \times \sum_{n_1l_1n_2l_2} \sum_{\vec{k}_1\vec{k}_2} \frac{2\pi\omega_1}{L^3} \frac{2\pi\omega_2}{L^3} k_1^{p_1+q_1} k_2^{p_2+q_2} e^{i\vec{k}_1\cdot\vec{R}} e^{i\vec{k}_2\cdot\vec{R}} \\
& \times \frac{1}{D_{n_1l_1n_2l_2}} (n_g 0|r^{q_2+1}|n_2l_2)(n_2l_2|r^{q_1+1}|n_g0)(n_g0|r^{p_2+1}|n_2l_2)(n_2l_2|r^{p_1+1}|n_g0) \\
& \times \sum_{\lambda_1\lambda_2m_1m_2} \langle 00|(\hat{e}_2\cdot\hat{r})(\hat{k}_2\cdot\hat{r})^{q_2}|l_2m_2\rangle\langle l_2m_2|(\hat{e}_1\cdot\hat{r})(\hat{k}_1\cdot\hat{r})^{q_1}|00\rangle \\
& \times \langle 00|(\hat{e}_2\cdot\hat{r})(\hat{k}_2\cdot\hat{r})^{p_2}|l_1m_1\rangle\langle l_1m_1|(\hat{e}_1\cdot\hat{r})(\hat{k}_1\cdot\hat{r})^{p_1}|00\rangle,
\end{aligned} \tag{3.1}$$

where the electronic radial and angular part have been factored, and where

$$\begin{aligned}
\frac{1}{D_{n_1l_1n_2l_2}} = & -\frac{2}{\Delta_{n_1l_1}^2 - \Delta_{n_2l_2}^2} \left\{ \frac{\Delta_{n_2l_2}}{\Delta_{n_1l_1}+\omega_1} \left(\frac{1}{\omega_1+\omega_2} - \frac{1}{\omega_1-\omega_2} \right) - \frac{\Delta_{n_1l_1}}{\Delta_{n_2l_2}+\omega_2} \left(\frac{1}{\omega_1+\omega_2} + \frac{1}{\omega_1-\omega_2} \right) \right. \\
& \left. + \frac{\Delta_{n_2l_2}}{\Delta_{n_1l_1}+\omega_2} \left(\frac{1}{\omega_1+\omega_2} + \frac{1}{\omega_1-\omega_2} \right) - \frac{\Delta_{n_1l_1}}{\Delta_{n_2l_2}+\omega_1} \left(\frac{1}{\omega_1+\omega_2} - \frac{1}{\omega_1-\omega_2} \right) \right\}.
\end{aligned} \tag{3.2}$$

Similar notations to those in Eq. (2.1) have been adopted. As in Sec. II we start the analysis of the $f_{p_1p_2q_1q_2}$ terms by rewriting the sum from Eq. (3.1) over the photon polarizations λ_1 and λ_2 and atomic magnetic quantum numbers m_1 and m_2 according to

$$\begin{aligned}
T^{EE}_{i_0\cdots i_{p_2},r_0\cdots r_{q_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}} & [\delta_{i_0r_0}\delta_{j_0s_0} \mathcal{Q}^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}(\hat{k}_2) \mathcal{Q}^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}(\hat{k}_1) \\
& - \delta_{i_0r_0} \mathcal{Q}^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}(\hat{k}_2) \mathcal{Q}^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}(\hat{k}_1) - \delta_{j_0s_0} \mathcal{Q}^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}(\hat{k}_2) \mathcal{Q}^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}(\hat{k}_1) \\
& + \mathcal{Q}^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}(\hat{k}_2) \mathcal{Q}^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}(\hat{k}_1)],
\end{aligned} \tag{3.3}$$

---

[1] An alternative expression for the e-e multipolar interaction was presented in Ref. [26]. However, our general expression of the e-e multipolar interaction is different and suitable for final numerical computation.

where

$$T^{EE}_{i_0\cdots i_{p_2},r_0\cdots r_{q_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}=\sum_{m_1m_2}\mathcal{D}^{(00)(l_2m_2)}_{i_0\cdots i_{q_2}}\mathcal{D}^{(l_2m_2)(00)}_{r_0\cdots r_{p_2}}\mathcal{D}^{(00)(l_1m_1)}_{j_0\cdots j_{q_1}}\mathcal{D}^{(l_1m_1)(00)}_{s_0\cdots s_{p_1}} \tag{3.4}$$

is a tensor of order $p_1+p_2+q_1+q_2+4$. The tensors $\mathcal{Q}$, from Eq. (3.3), and $\mathcal{D}$, from Eq. (3.4), are defined by Eqs. (2.4) and (2.6), respectively. Replacing the sum over the discrete values of $\vec{k}_1$ and $\vec{k}_2$ by integrals, the integral over the directions of $\vec{k}_1$ and $\vec{k}_2$ may be computed formally in terms of the $\mathcal{P}$ tensors defined by Eq. (2.7). Finally the double integral over ω_1 and ω_2 may be rotated into the complex plane along the imaginary axis. In doing so, one may notice that one of the integral will disappear in favor of the residue of the integrand at the simple pole $\omega_1=\omega_2$ [see Eq. (3.2)]. The final expression of the $f_{p_1p_2q_1q_2}$ term is given (after some algebraic transformations) by

$$\begin{aligned}f_{p_1p_2q_1q_2}=&-\frac{2}{\pi\alpha}\frac{\mathcal{K}_{p_1p_2q_1q_2}}{R^{p_1+p_2+q_1+q_2+7}}\sum_{l_1l_2}\int_0^\infty du\, u^{p_1+p_2+q_1+q_2+6}\mathcal{R}^{l_1}_{p_1+1p_2+1}\left(i\frac{u}{\alpha R}\right)\\&\times\mathcal{R}^{l_2}_{q_1+1q_2+1}\left(i\frac{u}{\alpha R}\right)e^{-2u}T^{EE}_{i_0\cdots i_{p_2},r_0\cdots r_{q_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\\&\times[\delta_{i_0r_0}\delta_{j_0s_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}-\delta_{i_0r_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\\&-\delta_{j_0s_0}\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}+\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}],\end{aligned} \tag{3.5}$$

where the Θ polynomials are defined by Eq. (2.8), and they enter into Eq. (3.5) with argument $-1/u$. The $\mathcal{R}$ quantities are defined in Eq. (2.11). The summations over l_1 and l_2 involve only a finite number of terms. Actually, significant values of l_1 and l_2 may be established at the outset by analyzing the selection rules for the electric multipole atomic transitions. We note that the $f_{p_1p_2q_1q_2}$ terms are zero unless $p_1+p_2+q_1+q_2$ is an even quantity. This is a result of the fact that the atomic initial and final states are identical. One may also note that $f_{p_1p_2q_1q_2}=f_{p_2p_1q_2q_1}$, since the 12 diagrams involved in the latter term may be obtained from the diagrams involved in the first term by interchanging the photon labels. In the special case of identical atoms we also have $f_{p_1p_2q_1q_2}=f_{q_1q_2p_1p_2}$. To this end, explicit expressions of $f_{p_1p_2q_1q_2}$ for particular values of p_1, p_2, q_1, and q_2 may be easily obtained from Eq. (3.5) by using MATHEMATICA. In the limit $R\to\infty$, the $f_{p_1p_2q_1q_2}$ term behaves as $1/R^{p_1+p_2+q_1+q_2+7}$ with the full expression given by Eq. (3.5) for $\mathcal{R}$ evaluated at $u=0$. Thus for the K_7 coefficient only the f_{0000} term contributes. It has the expression

$$\begin{aligned}f_{0000}=&-\frac{4}{9\pi\alpha R^7}\int_0^\infty du\left[\mathcal{R}^1_{11}\left(i\frac{u}{\alpha R}\right)\right]^2\\&\times e^{-2u}(3+6u+5u^2+2u^3+u^4),\end{aligned} \tag{3.6}$$

which in the limit $R\to\infty$ becomes

$$f_{0000}=-\frac{23}{9\pi\alpha R^7}[\mathcal{R}^1_{11}(0)]^2. \tag{3.7}$$

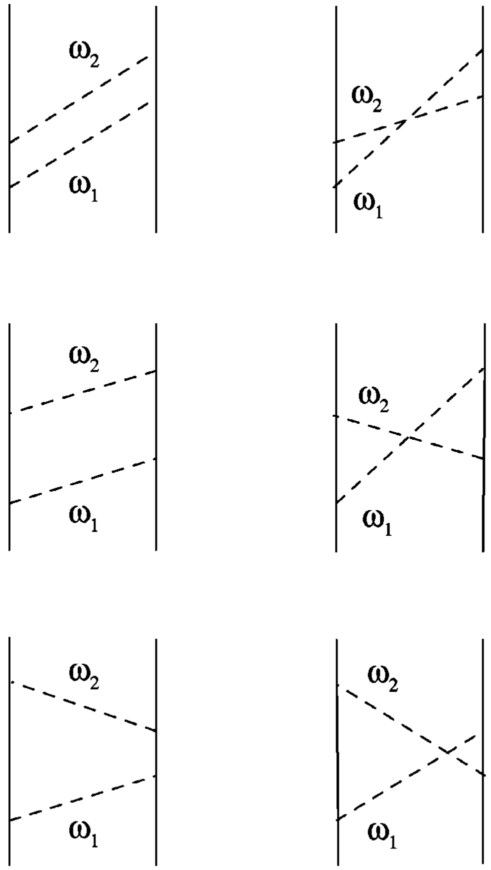

FIG. 2. Six topologically distinct two-photon electric-electric (electric-magnetic, and magnetic-magnetic) diagrams. The other six may be obtained by mirror inversion.

For the K_9 coefficient, terms for which $p_1+p_2+q_1+q_2=2$ contribute when p_1+p_2 and q_1+q_2 are even quantities. They are $f_{1100}=f_{0011}$ and $f_{2000}=f_{0200}=f_{0020}=f_{0002}$. Their expressions are given by

$$f_{1100}=-\frac{1}{45\pi\alpha R^9}\int_0^\infty du\,\mathcal{R}_{22}^{2}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{11}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}\times(90+180u+162u^2+84u^3+27u^4+6u^5+u^6), \tag{3.8}$$

$$f_{2000}=-\frac{2}{135\pi\alpha R^9}\int_0^\infty du\,u^2\mathcal{R}_{31}^{1}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{11}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}\times(3+6u+5u^2+2u^3+u^4). \tag{3.9}$$

In the limit $R\to\infty$, Eqs. (3.8) and (3.9) become

$$f_{1100}=-\frac{177}{40\pi\alpha R^9}\mathcal{R}_{22}^{2}(0)\mathcal{R}_{11}^{1}(0), \tag{3.10}$$

$$f_{2000}=-\frac{43}{180\pi\alpha R^9}\mathcal{R}_{31}^{1}(0)\mathcal{R}_{11}^{1}(0). \tag{3.11}$$

For the K_{11} coefficient, terms for which $p_1+p_2+q_1+q_2=4$ contribute, when p_1+p_2 and q_1+q_2 are even quantities. They are $f_{4000}=f_{0400}=f_{0040}=f_{0004}$, $f_{3100}=f_{1300}=f_{0031}=f_{0013}$, $f_{2200}=f_{0022}$, $f_{2020}=f_{0202}=f_{0220}=f_{2002}$, $f_{1102}=f_{1120}$, and f_{1111}. We note that for f_{2200} there are two possible values for l_1 [in the sum from Eq. (3.5)]: 1 and 3. Thus we split the f_{2200} term as $f_{2200}=f_{2200}^{P}+f_{2200}^{F}$, where f_{2200}^{P} corresponds to $l_1=1$ and f_{2200}^{F} corresponds to $l_1=3$. The expressions of the above f terms are given by

$$f_{4000}=-\frac{1}{3150\pi\alpha R^{11}}\int_0^\infty du\,u^4\mathcal{R}_{51}^{1}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{11}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+6u+5u^2+2u^3+u^4), \tag{3.12}$$

$$f_{3100}=-\frac{1}{1260\pi\alpha R^{11}}\int_0^\infty du\,u^2\mathcal{R}_{42}^{2}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{11}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(90+180u+162u^2+84u^3+27u^4+6u^5+u^6), \tag{3.13}$$

$$f_{2200}^{P}=-\frac{1}{2025\pi\alpha R^{11}}\int_0^\infty du\,u^4\mathcal{R}_{33}^{1}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{11}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+6u+5u^2+2u^3+u^4), \tag{3.14}$$

$$f_{2200}^{F}=-\frac{1}{14175\pi\alpha R^{11}}\int_0^\infty du\,\mathcal{R}_{33}^{3}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{11}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}\times(4725+9450u+8775u^2+4950u^3+1863u^4+486u^5+90u^6+12u^7+u^8), \tag{3.15}$$

$$f_{2020}=-\frac{1}{2025\pi\alpha R^{11}}\int_0^\infty du\,u^4\left[\mathcal{R}_{31}^{1}\left(i\frac{u}{\alpha R}\right)\right]^2e^{-2u}(3+6u+5u^2+2u^3+u^4), \tag{3.16}$$

$$f_{1102}=-\frac{1}{1350\pi\alpha R^{11}}\int_0^\infty du\,u^2\mathcal{R}_{22}^{2}\left(i\frac{u}{\alpha R}\right)\mathcal{R}_{31}^{1}\left(i\frac{u}{\alpha R}\right)e^{-2u}(90+180u+162u^2+84u^3+27u^4+6u^5+u^6), \tag{3.17}$$

$$f_{1111}=-\frac{1}{900\pi\alpha R^{11}}\int_0^\infty du\left[\mathcal{R}_{22}^{2}\left(i\frac{u}{\alpha R}\right)\right]^2e^{-2u}(5040+10080u+9360u^2+5280u^3+1983u^4+510u^5+89u^6+10u^7+u^8). \tag{3.18}$$

In the limit $R\to\infty$, they become

$$f_{4000}=-\frac{71}{1400\pi\alpha R^{11}}\mathcal{R}_{51}^{1}(0)\mathcal{R}_{11}^{1}(0), \tag{3.19}$$

$$f_{3100}=-\frac{319}{560\pi\alpha R^{11}}\mathcal{R}_{42}^{2}(0)\mathcal{R}_{11}^{1}(0), \tag{3.20}$$

$$f_{2200}^{P}=-\frac{71}{900\pi\alpha R^{11}}\mathcal{R}_{33}^{1}(0)\mathcal{R}_{11}^{1}(0), \tag{3.21}$$

$$f_{2200}^{F}=-\frac{10582}{1575\pi\alpha R^{11}}\mathcal{R}_{33}^{3}(0)\mathcal{R}_{11}^{1}(0), \tag{3.22}$$

$$f_{2020}=-\frac{71}{900\pi\alpha R^{11}}[\mathcal{R}_{31}^{1}(0)]^2, \tag{3.23}$$

$$f_{1102}=-\frac{319}{600\pi\alpha R^{11}}\mathcal{R}^{2}_{22}(0)\mathcal{R}^{1}_{21}(0), \tag{3.24}$$

$$f_{1111}=-\frac{5591}{400\pi\alpha R^{11}}[\mathcal{R}^{2}_{22}(0)]^{2}. \tag{3.25}$$

B. Electric-magnetic interactions

The e-m interaction terms are given by the same 12 diagrams (see Fig. 2), but now two of the vertexes represent electric multipoles and the other two magnetic multipoles. The computation of the e-m interaction diagrams is similar to that for the e-e case. Therefore, only the final results are presented here. We note that only the processes where the electric multipole transitions are experienced by the same atom give a nonzero contribution. Other processes, where the atoms experience a magnetic multipolar transition followed by an electric one, or vice versa, cancel each other out, so that the overall contribution of these diagrams is zero. Thus by e-m interaction terms we refer only to the case where one of the atoms is emitting or absorbing photons as a result of electric multipolar transitions and the other atom is absorbing or emitting photon as a result of magnetic multipolar transitions. The sum of the corresponding 12 diagrams (in which the first atom experiences only magnetic transitions) is denoted by $f_{\underline{p}_1\underline{p}_2q_1q_2}$, where the underscore marks the magnetic multipoles. Its general expression is given by

$$f_{\underline{p}_1\underline{p}_2q_1q_2}=-\frac{\alpha}{2\pi}\frac{\mathcal{K}_{\underline{p}_1\underline{p}_2q_1q_2}}{R^{p_1+p_2+q_1+q_2+7}}\sum_{l_1l_2}\int_0^{\infty}du\,u^{p_1+p_2+q_1+q_2+6}\mathcal{R}^{l_1}_{p_1p_2}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{l_2}_{q_1+1q_2+1}\left(i\frac{u}{\alpha R}\right)$$
$$\times e^{-2u}T^{EM}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\Theta^{(p_2+q_2+1)}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+1)}_{j_0\cdots j_{q_1},s_1\cdots s_{p_1}}, \tag{3.26}$$

where the $\mathcal{R}$ quantities are defined by Eq. (2.11), the $\mathcal{K}_{\underline{p}_1\underline{p}_2q_1q_2}$ coefficient is defined by Eq. (2.10), the Θ polynomial, which enter in Eq. (3.26) with argument $-1/u$ are defined by Eq. (2.8), and

$$T^{EM}_{i_0\cdots i_{q_2},r_1\cdots r_{p_2},j_0\cdots j_{q_1},s_1\cdots s_{p_1}}=\epsilon_{i_0r_0t_1}\epsilon_{j_0s_0t_2}\sum_{m_1m_2}\mathcal{D}^{(00)(l_2m2)}_{t_1i_1\cdots i_{q_2}}\mathcal{D}^{(l_2m2)(00)}_{t_2j_1\cdots j_{q_1}}\mathcal{L}^{(00)(l_1m_1)}_{r_0\cdots r_{p_2}}\mathcal{L}^{(l_1m_1)(00)}_{s_0\cdots s_{p_1}}, \tag{3.27}$$

is a tensor of order $p_1+p_2+q_1+q_2+2$ with $\mathcal{D}$ and $\mathcal{L}$ tensors defined by Eqs. (2.6) and (2.47), respectively. In the limit $R\to\infty$ the $f_{\underline{p}_1\underline{p}_2q_1q_2}$ term behaves as $1/R^{p_1+p_2+q_1+q_2+7}$, where the full expression is also given by Eq. (3.26), but for $\mathcal{R}$ evaluated at $u=0$. We note that $f_{\underline{p}_1\underline{p}_2q_1q_2}$ is zero if $p_1=0$ or $p_2=0$, since $\mathcal{L}^{(00)(lm)}_{i_0}$ is zero and so is T^{EM}. Also, p_1+p_2 and q_1+q_2 must be even quantities, since the initial and final atomic states are identical. Therefore, there is no e-m contributions to the K_7 coefficient. The first nonzero e-m contribution is given by the $f_{\underline{11}00}$ term to the K_9 coefficient. It has the expression

$$f_{\underline{11}00}=-\frac{\alpha}{81\pi R^{9}}\int_0^{\infty}du\,u^{2}\left[\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)\right]^{2}(3+6u+5u^{2}+2u^{3}+u^{4}), \tag{3.28}$$

which in the limit $R\to\infty$ becomes

$$f_{\underline{11}00}=-\frac{43\alpha}{81\pi R^{9}}[\mathcal{R}^{1}_{11}(0)]^{2}. \tag{3.29}$$

For the K_{11} coefficient, terms which satisfy the conditions $p_1+p_2+q_1+q_2=4$, p_1+p_2 and q_1+q_2 are even quantities, and $p_1\geqslant 1$ and $p_2\geqslant 1$ contribute. These terms are $f_{\underline{31}00}=f_{\underline{13}00}$, $f_{\underline{22}00}$, $f_{\underline{11}20}=f_{\underline{11}02}$, and $f_{\underline{11}11}$. They have the following expressions:

$$f_{\underline{31}00}=-\frac{\alpha}{1350\pi R^{11}}\int_0^{\infty}du\,u^{4}\mathcal{R}^{1}_{31}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+6u+5u^{2}+2u^{3}+u^{4}), \tag{3.30}$$

$$f_{\underline{22}00}=-\frac{\alpha}{720\pi R^{11}}\int_0^{\infty}du\,u^{2}\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{2}_{22}\left(i\frac{u}{\alpha R}\right)e^{-2u}(90+180u+162u^{2}+84u^{3}+27u^{4}+6u^{5}+u^{6}), \tag{3.31}$$

$$f_{\underline{11}20}=-\frac{\alpha}{2430\pi R^{11}}\int_0^{\infty}du\,u^{4}\mathcal{R}^{1}_{31}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)e^{-2u}(3+6u+5u^{2}+2u^{3}+u^{4}), \tag{3.32}$$

$$f_{\underline{11}11}=-\frac{\alpha}{1620\pi R^{11}}\int_0^{\infty}du\,u^{2}\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{2}_{22}\left(i\frac{u}{\alpha R}\right)e^{-2u}(90+180u+162u^{2}+84u^{3}+27u^{4}+6u^{5}+u^{6}). \tag{3.33}$$

In the limit $R\to\infty$, they become

$$f_{\underline{3}100}=-\frac{71\alpha}{1296\pi R^{11}}\mathcal{R}^{1}_{11}(0)\mathcal{R}^{1}_{31}(0), \tag{3.34}$$

$$f_{\underline{2}200}=-\frac{319\alpha}{320\pi R^{11}}\mathcal{R}^{1}_{11}(0)\mathcal{R}^{2}_{22}(0), \tag{3.35}$$

$$f_{\underline{1}120}=-\frac{71\alpha}{1080\pi R^{11}}\mathcal{R}^{1}_{11}(0)\mathcal{R}^{1}_{31}(0), \tag{3.36}$$

$$f_{\underline{1}111}=-\frac{319\alpha}{720\pi R^{11}}\mathcal{R}^{1}_{11}(0)\mathcal{R}^{2}_{22}(0). \tag{3.37}$$

C. Magnetic-magnetic interactions

The m-m interaction is described by the same 12 topologically distinct diagrams (see Fig. 2) involved in the description of the e-e interaction, but now all four vertexes are given by magnetic multipoles. The sum of the twelve diagrams involving $p_1,\ p_2,\ q_1$, and q_2 magnetic multipoles takes the following expression:

$$\begin{aligned}f_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}=&-\frac{\alpha^3}{8\pi}\frac{\mathcal{K}_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}}{R^{p_1+p_2+q_1+q_2+7}}\sum_{l_1l_2}\int_0^\infty du\,u^{p_1+p_2+q_1+q_2+6}\mathcal{R}^{l_1}_{p_1p_2}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{l_2}_{q_1q_2}\left(i\frac{u}{\alpha R}\right)e^{-2u}\\&\times T^{MM}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}[\delta_{i_0r_0}\delta_{j_0s_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}-\delta_{i_0r_0}\Theta^{(p_2+q_2)}_{i_1\cdots i_{q_2},r_1\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\\&-\delta_{j_0s_0}\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}\Theta^{(p_1+q_1)}_{j_1\cdots j_{q_1},s_1\cdots s_{p_1}}+\Theta^{(p_2+q_2+2)}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2}}\Theta^{(p_1+q_1+2)}_{j_0\cdots j_{q_1},s_0\cdots s_{p_1}}],\end{aligned} \tag{3.38}$$

where the $\mathcal{R}$ matrix elements are given by Eq. (2.11), the coefficient $\mathcal{K}_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}$ is given by Eq. (2.45), and

$$\begin{aligned}&T^{MM}_{i_0\cdots i_{q_2},r_0\cdots r_{p_2},j_0\cdots j_{q_1},s_0\cdots s_{p_1}}\\&\quad=\sum_{m_1m_2}\mathcal{L}^{(00)(l_2m_2)}_{i_0\cdots i_{q_2}}\mathcal{L}^{(l_2m_2)(00)}_{j_0\cdots j_{q_1}}\mathcal{L}^{(00)(l_1m_1)}_{r_0\cdots r_{p_2}}\mathcal{L}^{(l_1m_1)(00)}_{s_0\cdots s_{p_1}}\end{aligned} \tag{3.39}$$

is a tensor of $p_1+p_2+q_1+q_2+4$ order, with the $\mathcal{L}$ tensors defined by Eq. (2.47). The polynomial Θ are defined by Eq. (2.8), and they enter into Eq. (3.38) with argument $-1/u$. We note that $f_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}$ is zero if any of $p_1,\ p_2,\ q_1$, and q_2 is zero, since the $\mathcal{L}^{(00)(lm)}_{i_0}$ tensor is zero and so is T^{MM}. Also, p_1+p_2 and q_1+q_2 must be even quantities, according to the magnetic multipole selection rules, since the initial and final atomic states are identical. In the asymptotic limit the $f_{\underline{p}_1\underline{p}_2\underline{q}_1\underline{q}_2}$ term behaves as $1/R^{p_1+p_2+q_1+q_2+7}$, while the full expression is given by Eq. (3.38) for $\mathcal{R}$ evaluated at $u=0$. Thus the m-m interaction will make no contributions to the K_7 and K_9 coefficients, since in these cases at least one of the indices $p_1,\ p_2,\ q_1$, and q_2 is zero. The contribution to the K_{11} coefficient is given by $f_{\underline{1111}}$. The explicit expression of $f_{\underline{1111}}$ is given by

$$\begin{aligned}f_{\underline{1111}}=&-\frac{\alpha^3}{2916\pi R^{11}}\int_0^\infty du\,u^4\left[\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)\right]^2\\&\times e^{-2u}(3+6u+5u^2+2u^3+u^4),\end{aligned} \tag{3.40}$$

which in the limit $R\to\infty$ becomes

$$f_{\underline{1111}}=-\frac{71\alpha^3}{1296\pi R^{11}}[\mathcal{R}^{1}_{11}(0)]^2. \tag{3.41}$$

IV. CASIMIR-POLDER POTENTIAL

The final expression of the CP long-range interaction potential is obtained by adding all e-e, e-m, m-m, d-e, and d-m multipolar contributions. In Table I we present all distinct f terms, together with their multiplicity factors, which enter in the final expression of the CP potential, grouped according to their asymptotic behavior. Their explicit expressions were presented in Secs. II and III. The multiplicity factors come from the number of equivalences for each f term. For example, as we mentioned in Sec. III, since $f_{1100}=f_{0011}$, in Table I we report only the f_{1100} term with multiplicity 2. All e-m, d-e, and d-m terms enter with an even multiplicity, since the electric multipole transitions, in the first case, and the diamagnetic multipole transition, in the latter two cases, may occur in the first or second atom. Relative to the e-e interactions, the contributions of the e-m and d-e interactions are of order α^2, while the contributions of the m-m and d-m

TABLE I. The f terms, together with their multiplicity, which enter into the final expression of the Casimir-Polder long-range potential. In the left column we indicate the asymptotic behavior in terms of $1/R$ powers.

	e-e	e-m	d-e	m-m	d-m
$1/R^7$	f_{0000}		$2f_{\underline{0}+\underline{0}00}$		
$1/R^9$	$2f_{1100}$ $4f_{2000}$	$2f_{\underline{11}00}$	$2f_{\underline{1}+\underline{1}00}$ $4f_{\underline{2}+\underline{0}00}$ $2f_{\underline{0}+\underline{0}11}$ $4f_{\underline{0}+\underline{0}20}$		$2f_{\underline{0}+\underline{011}}$
$1/R^{11}$	$4f_{4000}$ $4f_{3100}$ $2f^P_{2200}$ $2f^F_{2200}$ $4f_{2020}$ $4f_{1120}$ f_{1111}	$4f_{\underline{31}00}$ $2f_{\underline{22}00}$ $4f_{\underline{11}20}$ $2f_{\underline{11}11}$	$4f_{\underline{4}+\underline{0}00}$ $4f_{\underline{3}+\underline{1}00}$ $2f_{\underline{2}+\underline{2}00}$ $8f_{\underline{2}+\underline{0}20}$ $4f_{\underline{2}+\underline{0}11}$ $4f_{\underline{1}+\underline{1}20}$ $2f_{\underline{1}+\underline{1}11}$ $4f_{\underline{0}+\underline{0}40}$ $4f_{\underline{0}+\underline{0}31}$ $2f^P_{\underline{0}+\underline{0}22}$ $2f^F_{\underline{0}+\underline{0}22}$	$f_{\underline{1111}}$	$4f_{\underline{2}+\underline{011}}$ $2f_{\underline{1}+\underline{111}}$ $4f_{\underline{0}+\underline{031}}$ $2f_{\underline{0}+\underline{022}}$

interactions are of order α^4. Thus one may expect the e-e interaction terms to be dominant. The long-range coefficients K_7, K_9, and K_{11} may be written as

$$K_7 = K_7^{(0)} + \alpha^2 K_7^{(2)}, \tag{4.1}$$

$$K_9 = K_9^{(0)} + \alpha^2 K_9^{(2)} + \alpha^4 K_9^{(4)}, \tag{4.2}$$

$$K_{11} = K_{11}^{(0)} + \alpha^2 K_{11}^{(2)} + \alpha^4 K_{11}^{(4)}, \tag{4.3}$$

where $K_7^{(0)}$, $K_9^{(0)}$, and $K_{11}^{(0)}$ are given only by the e-e interaction terms, $K_7^{(2)}$, $K_9^{(2)}$, and $K_{11}^{(2)}$ are given by the e-m and d-e interaction terms, and $K_9^{(4)}$ and $K_{11}^{(4)}$ are given by the m-m and d-m interaction terms. We note that the terms which contribute to the same $K_n^{(m)}$ coefficient are of similar magnitude. In our model, there are no e-m, m-m, and d-m contributions to the K_7 long-range coefficient, since the electronic spins were not considered. However, by including the spin-spin interactions the dipole-dipole e-m, m-m, and d-m interactions are allowed, and can be explored further if needed. Also, all terms involving magnetic transitions will be corrected by the spin-spin interactions. We note that among all terms listed in Table I, only the expressions of f_{0000}, f_{1100}, f^P_{2200}, f^F_{2200}, f_{1111}, and $f_{\underline{0}+\underline{0}00}$ were mentioned previously in the literature.

It is customary to present the expressions of f in terms of the integrals over products of atomic multipole polarizabilities of imaginary frequencies. However, we prefer to use the $\mathcal{R}^l_{pq}$ matrix elements, defined by Eq. (2.11), rather than the atomic polarizabilities, since not all the f terms listed in Table I may be written in terms of the atomic polarizabilities. We mention that in our notation the atomic 2^l-polarizability may be written as

$$\alpha_l(\omega) = \frac{2}{2l+1} \mathcal{R}^l_{ll}(\omega). \tag{4.4}$$

The entire formalism developed in the previous sections was written for the case of two identical atoms. The extension to the case of two different interacting atoms is simple. In the final expressions for the f terms the atomic contributions are factored (actually the entire two center molecular problem was reduced to one center atomic problem). The expression for the d-e and d-m terms always contain a generic product as $\langle r^n \rangle \mathcal{R}^l_{p_1p_2}$, where the first factor $\langle r^n \rangle$ belongs to the first atom and the second factor $\mathcal{R}^l_{p_1p_2}$ belongs to the second atom. For the case of two different atoms, in the final expression of the f terms, one must replace this product by $\frac{1}{2}[\langle r^n \rangle_A \mathcal{R}^l_{p_1p_2;B} + \langle r^n \rangle_B \mathcal{R}^l_{p_1p_2;A}]$, where A designates quantities related to the first atom and B quantities related to the second atom. In the case of e-e, e-m, and m-m interactions, the generic product $\mathcal{R}^{l_1}_{p_1p_2} \mathcal{R}^{l_2}_{q_1q_2}$, which appears in the f term expressions, needs to be replaced by $\frac{1}{2}[\mathcal{R}^{l_1}_{p_1p_2;A} \mathcal{R}^{l_2}_{q_1q_2;B} + \mathcal{R}^{l_1}_{p_1p_2;B} \mathcal{R}^{l_2}_{q_1q_2;A}]$. In doing so, all the results obtained for the homonuclear case may be easily generalized to the heteronuclear case. A generalization to multielectron atoms case is also possible.

From the numerical point of view, the main quantities which have to be computed are the $\mathcal{R}^l_{pq}$ matrix elements [Eq. (2.11)], for both real and imaginary arguments. They are radial matrix elements containing Green's functions. Therefore, they may be efficiently computed using the Dalgarno-Lewis method [40]. A full description of the numerical approach adopted by us was presented in Refs. [34,41]. The final numerical results for the long-range interaction between alkali-metal atoms are presented in Sec. VI.

V. RANGE OF VALIDITY OF THE CASIMIR-POLDER FORM OF THE INTERACTION POTENTIAL

The multipolar CP interaction potential was obtained assuming the long-range approximation, in which the contact interaction term $\mathcal{V}$ [Eq. (1.8)], is neglected in the expression of the PZW Hamiltonian [Eq. (1.3)]. In order to establish the long-range domain where this approximation is valid, one must estimate the first-order correction to the energy given by $\mathcal{V}$. We mention that the functional

$$F[f] = \int\int d\vec{r}_1 d\vec{r}_2 \times \int_0^1 \int_0^1 d\xi_1 d\xi_2 \; \delta(\vec{R} + \xi_1 \vec{r}_1 - \xi_2 \vec{r}_2) f(\vec{r}_1, \vec{r}_2) \tag{5.1}$$

may by rewritten, after some transformations, as

$$F[f] = \int d\vec{u} \int_1^\infty \int_1^\infty d\rho_1 d\rho_2 \, \rho_1 \rho_2 \times f\left[\rho_1\left(\frac{\vec{R}}{2} - \vec{u}\right), \rho_2\left(\frac{\vec{R}}{2} + \vec{u}\right)\right]. \tag{5.2}$$

Thus, the expectation value of $\mathcal{V}$ from Eq. (1.8) is given by

$$\langle\mathcal{V}\rangle=4\pi\int d\vec{u}\int_1^\infty\int_1^\infty d\rho_1 d\rho_2\ \rho_1^2\rho_2^2\left(\frac{R^2}{4}-u^2\right)\times\left|\phi_0\left[\rho_1\left(\frac{\vec{R}}{2}-\vec{u}\right)\right]\right|^2\left|\phi_0\left[\rho_2\left(\frac{\vec{R}}{2}+\vec{u}\right)\right]\right|^2, \quad (5.3)$$

where ϕ_0 is the atomic ground-state wave function. Although exact numerical evaluation of the integrals in Eq. (5.3) is possible, we intend to obtain a simple analytical estimate of Eq. (5.3). The main contribution to the integrals comes from the overlapping region of the two atomic wave functions. We assume in our computation that the value of R is large enough, such that the overlapping occurs only in the asymptotic part of the atomic wave functions. Thus, for the atomic wave functions in Eq. (5.3), we use their asymptotic form,

$$\phi_0(\vec{r})=\frac{\mathcal{A}}{4\pi}r^{(1/\alpha)-1}e^{-\alpha r}, \quad (5.4)$$

where $\alpha=\sqrt{-2E_{n_g0}}$, and $\mathcal{A}$ is the asymptotic algebraic coefficient of the normalized atomic ground-state wave function. Numerical values of $\mathcal{A}$ for alkali-metal atoms were presented in Ref. [42]. Then the integrals over ρ_1 and ρ_2 may be carried out by using the identity

$$\int_1^\infty d\rho\,\rho^{2/\alpha}e^{-\beta\rho}=\beta^{-(2/\alpha)-1}\Gamma\left(\frac{2}{\alpha}+1,\beta\right), \quad (5.5)$$

where $\Gamma(a,\beta)$ is the incomplete gamma function. In our case β is proportional to R, and so, the right-hand side of Eq. (5.5), we use for its asymptotic expression $\beta^{-1}e^{-\beta}$, which leads to the approximation

$$\langle\mathcal{V}\rangle\approx\frac{\mathcal{A}^4}{16\pi\alpha^2}\int d\vec{u}\ \left(\frac{R^2}{4}-u^2\right)^{(2/\alpha)-2}\times\exp\left[-2\alpha\left|\frac{\vec{R}}{2}-\vec{u}\right|-2\alpha\left|\frac{\vec{R}}{2}+\vec{u}\right|\right]. \quad (5.6)$$

Further, neglecting the $\vec{u}$ dependency in the exponential and integrating over u from 0 to R we obtain the following simple estimate of the expectation value of $\langle\mathcal{V}\rangle$:

$$\langle\mathcal{V}\rangle\approx\frac{\sqrt{\pi}}{16\alpha^2}\frac{\Gamma\left(\frac{2}{\alpha}-1\right)}{\Gamma\left(\frac{2}{\alpha}+\frac{1}{2}\right)}\mathcal{A}^4R^{(4/\alpha)-1}e^{-2\alpha R}. \quad (5.7)$$

TABLE II. The contributions of the f terms from Table I to the K long-range coefficients (the multiplication factors are included) of the potassium dimer, in a.u. The numbers in square brackets indicate powers of ten.

	e-e	e-m	d-e	m-m	d-m
K_7	2.150[7]		5.535[0]		
K_9	2.119[9] 3.955[8]	4.757[2]	6.200[2] 2.943[2] 1.671[2] 1.050[2]		4.737[−5]
K_{11}	6.220[9] 3.976[10] 3.936[9] 1.594[11] 6.423[9] 2.505[10] 9.525[10]	1.043[4] 2.542[4] 5.795[3] 1.130[4]	9.022[3] 2.183[5] 7.443[4] 1.179[4] 1.331[4] 1.868[4] 3.457[4] 2.038[3] 7.537[3] 1.289[3] 9.110[3]	1.307[−3]	5.320[−3] 8.426[−3] 3.417[−3] 7.229[−3]

This result is similar to the expression of the exchange energy obtained by Smirnov and Chibisov [43], although it does not represent the exchange energy. In the evaluation of the exchange energy one also has to analyze the influence of the distortion of the wave functions as a result of the atomic interactions, by considering contributions from the higher orders of perturbation. However, Eq. (5.7) gives an upper limit to the exchange energy terms. We use Eq. (5.7) in order to define the long-range domain of R by requiring $\langle\mathcal{V}\rangle$ to be much smaller than the corresponding value of the CP potential. We denote by R_0 the smallest value of R for which the interactions between atoms may be described by the CP long-range potential form alone. The result of Eq. (5.7) may be generalized to the heteronuclear case by the expression

$$\langle\nu\rangle\approx\frac{\sqrt{\pi}}{16\alpha_A\alpha_B}\frac{\Gamma\left(\frac{1}{\alpha_A}+\frac{1}{\alpha_B}-1\right)}{\Gamma\left(\frac{1}{\alpha_A}+\frac{1}{\alpha_B}+\frac{1}{2}\right)}\times\mathcal{A}_A^2\mathcal{A}_B^2R^{(2/\alpha_A)+(2/\alpha_B)-1}e^{-(\alpha_A+\alpha_B)R}, \quad (5.8)$$

where A and B denoted the first and the second atoms, respectively. Numerical estimates for R_0 are presented in Sec. VI.

VI. NUMERICAL RESULTS AND DISCUSSION

Before presenting the final numerical results, we need to address two questions. First, what is the relative importance of the different processes which enter into the description of the CP long-range interaction potential (see Table I)? Second, how does the CP potential compare with the LvdW dispersion form of the potential? To clarify our discussion, we choose to study the case of two interacting potassium atoms, although the final conclusions are valid for any two interacting alkali-metal atoms.

Table II presents the contributions of the f terms from Table I to the K_7, K_9, and K_{11} long-range coefficients. They are computed using the asymptotic expressions of the f terms presented in Secs. II and III, omitting the $1/R^n$ dependences. By analyzing Table II, it is clear that in the asymptotic limit the e-e interaction is the dominant one. The e-m and d-e contributions are corrections of order α^2 relative to the e-e terms. Thus one may expect their contributions to

TABLE III. The value of the *f* terms from Table I (including the multiplication factors) of the potassium dimer, in a.u., at $R=30$ a.u. The numbers in square brackets indicate powers of ten.

e-e	e-m	d-e	m-m	d-m
−5.229[−6]		−2.729[−14]		
−6.241[−7]	−3.075[−21]	−1.886[−15]		−6.320[−23]
−5.987[−12]		−3.926[−16]		
		−1.878[−15]		
		−1.416[−16]		
−2.582[−16]	−4.912[−22]	−6.338[−18]	−6.110[−29]	−3.738[−24]
−9.713[−13]	−6.538[−19]	−4.981[−17]		−7.871[−24]
−3.101[−16]	−2.729[−22]	−1.614[−16]		−2.424[−24]
−5.145[−8]	−2.906[−19]	−8.366[−18]		−2.516[−23]
−3.048[−16]		−4.631[−17]		
−6.279[−13]		−1.763[−17]		
−3.736[−8]		−2.936[−16]		
		−5.845[−17]		
		−2.317[−17]		
		−1.543[−18]		
		−4.129[−18]		

be small. This is indeed the case. The numerical results from Table II show that the e-m and d-e contributions are seven orders of magnitude smaller than the e-e contributions. Similarly, the m-m and d-m contributions, which are corrections of order α^4 relative to the e-e terms, are eight orders of magnitude smaller than those of e-m and d-e terms. Therefore, e-m, d-e, m-m, and d-m contributions may be neglected. However, we note that the e-m and d-e contributions are of the same order of magnitude, as are the m-m and d-m contributions. Also, the different contributions to the same *K* long-range coefficients, from different multipole terms of the same type of process (e-e, etc.), are of the same order of magnitude. Thus, none of the e-e *f* terms may be neglected in the final expression of the *K* long-range coefficients.

In order to study the limit of small values of *R*, in Table III we present numerical evaluations of the *f* terms (including the multiplication factors) from Table I at $R=30$ a.u. Again the e-e interaction is the dominant one. Among the e-e multipole interactions we notice that the most important contribution comes from f_{0000}, f_{1100}, f_{2200}^F, and f_{1111} terms. In the limit of small values of *R*, we have [31]

$$f_{0000}=-\frac{C_6}{R^6}, \tag{6.1}$$

$$2f_{1100}=-\frac{C_8}{R^8}, \tag{6.2}$$

$$2f_{2200}^F+f_{1111}=-\frac{C_{10}}{R^{10}}, \tag{6.3}$$

where C_6, C_8, and C_{10} are the dispersion coefficients. Thus, for small values of *R* the LvdW dispersion form of the potential is expected to be a good approximation. In addition to these terms, the next important contribution is given by the f_{2000} term which, however, is almost six orders of magnitude smaller than f_{0000}. The rest of the e-e, e-m, d-e, the m-m, and d-m terms may be neglected in many practical applications. However, we note that the d-e contributions are larger than the e-m contributions, and the d-m interactions are larger than the m-m contributions.

To conclude, the main contribution to the CP long-range potential is given by the e-e multipolar interactions. For small values of *R* the main contributions are given by the f_{0000}, f_{1100}, f_{2200}^F, and f_{1111} terms, with a possible small correction from the f_{2000} term. In the asymptotic limit, all e-e multipolar processes contribute to the *K* long-range coefficients. However, in this limit one should realize that the relative importance of the K_9 and K_{11} coefficients is very small, since for $R>10^5$ a.u. the potential is essentially described only by the K_7 coefficient.

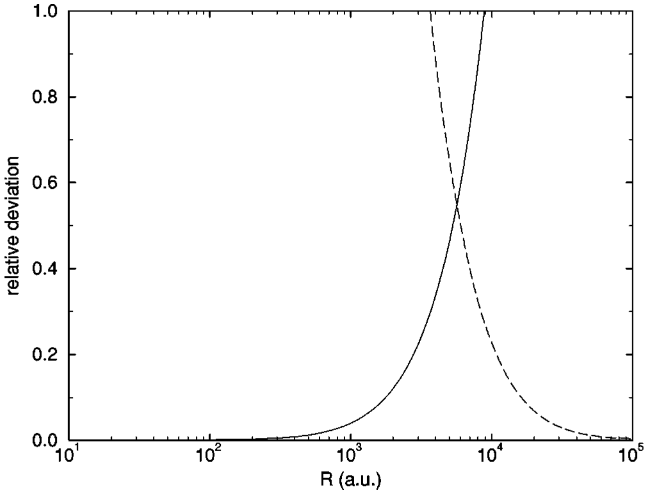

FIG. 3. Relative deviation of the dispersion form (solid line) [Eq. (1.2)], and asymptotic form (dashed line) [Eq. (1.1)], from the Casimir-Polder long-range potential, for a potassium dimer, as a function of *R*.

We have computed the CP long-range potential including all the contributions of the f terms presented in Table I. Then our numerical results were compared to numerical estimates based on the dispersion form of the potential [Eq. (1.2)], in order to gauge the importance of the retardation effects. Also, the numerical results of the CP long-range potential were compared to the numerical estimates obtained based on the asymptotic form of the potential [Eq. (1.1)], in order to estimate the convergence at large values of R. Figure 3 presents the relative deviation from the exact computation of the dispersion form of the potential as a function of R (solid line), and the relative deviation of the asymptotic expression as a function of R (dashed line), for two interacting potassium atoms. It is clear that for $R<200$ a.u. the LvdW dispersion form of the potential is a good approximation. For values of R larger than 200 a.u. the contribution of the retardation effects becomes essential. Also, we note that for $R>10^5$ a.u. the asymptotic expression [Eq. (1.1)], becomes a good approximation.

The numerical results of the CP interaction potential are presented in Table IV for homonuclear cases, and in Tables V and VI for heteronuclear cases. The numerical values of the R_0 radius are included at the top of each table. Also, in Table VII we present the numerical values of the K_7, K_9, and K_{11} long-range coefficients for all possible combinations of two alkali-metal atoms.

The CP long-range interaction potential between two different alkali-metal atoms has not yet been presented in literature. For the homonuclear cases, an alternative numerical estimate was presented in Ref. [31]. There, the numerical computations were based on the Au and Feinberg [20] approximation results, which considers (in our notation) only the contributions from f_{0000}, f_{1100}, f^F_{2200}, and f_{1111} terms. Moreover, the Au and Feinberg expressions [20] (see also Ref. [31]) for the f_{1100}, f^F_{2200}, and f_{1111} terms are given by

$$f_{1100}=\frac{2}{45\alpha\pi R^9}\int_0^\infty du\,\mathcal{R}^1_{11}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^2_{22}\left(i\frac{u}{\alpha R}\right)e^{-2u}(45+90u+84u^2+48u^3+19u^4+6u^5+2u^6), \tag{6.4}$$

TABLE IV. The Casimir-Polder long-range potential as a function of R, in a.u., for homonuclear alkali-metal dimers. The values of the R_0 radius are indicated in the second line. The numbers in square brackets indicate powers of ten.

	Li-Li	Na-Na	K-K	Rb-Rb	Cs-Cs
R	28	29	34	35	36
1.0[1]	−2.95702[−03]	−3.69685[−03]	−1.31511[−02]	−1.75884[−02]	−3.11436[−02]
1.5[1]	−1.67132[−04]	−1.92064[−04]	−5.85357[−04]	−7.36021[−04]	−1.19452[−03]
2.0[1]	−2.56633[−05]	−2.84505[−05]	−8.06745[−05]	−9.81119[−05]	−1.51306[−04]
3.0[1]	−2.04370[−06]	−2.20840[−06]	−5.94144[−06]	−7.03762[−06]	−1.04044[−05]
5.0[1]	−9.10442[−08]	−9.71683[−08]	−2.54939[−07]	−2.98005[−07]	−4.31146[−07]
7.0[1]	−1.19432[−08]	−1.27046[−08]	−3.31194[−08]	−3.85796[−08]	−5.54994[−08]
1.0[2]	−1.39562[−09]	−1.48197[−09]	−3.85109[−09]	−4.47793[−09]	−6.42306[−09]
1.5[2]	−1.21992[−10]	−1.29404[−10]	−3.35831[−10]	−3.90133[−10]	−5.58795[−10]
2.0[2]	−2.16581[−11]	−2.29619[−11]	−5.95905[−11]	−6.92057[−11]	−9.90873[−11]
3.0[2]	−1.89322[−12]	−2.00558[−12]	−5.21076[−12]	−6.05073[−12]	−8.66371[−12]
5.0[2]	−8.74376[−14]	−9.24649[−14]	−2.41195[−13]	−2.80121[−13]	−4.01488[−13]
7.0[2]	−1.14663[−14]	−1.20996[−14]	−3.17236[−14]	−3.68554[−14]	−5.28999[−14]
1.0[3]	−1.31875[−15]	−1.38638[−15]	−3.66693[−15]	−4.26269[−15]	−6.13425[−15]
1.5[3]	−1.10761[−16]	−1.15634[−16]	−3.10738[−16]	−3.61637[−16]	−5.22957[−16]
2.0[3]	−1.87712[−17]	−1.94565[−17]	−5.31309[−17]	−6.19082[−17]	−8.99834[−17]
3.0[3]	−1.48579[−18]	−1.51908[−18]	−4.27508[−18]	−4.99305[−18]	−7.33055[−18]
5.0[3]	−5.64430[−20]	−5.64488[−20]	−1.66714[−19]	−1.95494[−19]	−2.92016[−19]
7.0[3]	−6.21091[−21]	−6.11660[−21]	−1.86887[−20]	−2.19810[−20]	−3.32690[−20]
1.0[4]	−5.72222[−22]	−5.55290[−22]	−1.75354[−21]	−2.06885[−21]	−3.17480[−21]
1.5[4]	−3.62764[−23]	−3.47563[−23]	−1.13011[−22]	−1.33723[−22]	−2.07961[−22]
2.0[4]	−5.00891[−24]	−4.76950[−24]	−1.57336[−23]	−1.86457[−23]	−2.92036[−23]
3.0[4]	−3.01180[−25]	−2.85257[−25]	−9.53041[−25]	−1.13102[−24]	−1.78326[−24]
5.0[4]	−8.55854[−27]	−8.08053[−27]	−2.72040[−26]	−3.23127[−26]	−5.11619[−26]
7.0[4]	−8.15401[−28]	−7.69142[−28]	−2.59531[−27]	−3.08352[−27]	−4.88859[−27]
1.0[5]	−6.73076[−29]	−6.34568[−29]	−2.14389[−28]	−2.54756[−28]	−4.04178[−28]

TABLE V. The Casimir-Polder long-range potential as a function of R, in a.u., for heteronuclear alkali-metal dimers Li-Na, Li-K, Li-Rb, Li-Cs, and Na-K. The values of the R_0 radius are indicated in the second line. The numbers in square brackets indicate powers of ten.

	Li-Na	Li-K	Li-Rb	Li-Cs	Na-K
R	29	31	32	32	32
1.0[1]	−3.30529[−03]	−6.29110[−03]	−7.31521[−03]	−9.82177[−03]	−6.97766[−03]
1.5[1]	−1.78921[−04]	−3.12378[−04]	−3.50220[−04]	−4.44753[−04]	−3.33323[−04]
2.0[1]	−2.69806[−05]	−4.53742[−05]	−4.99858[−05]	−6.17220[−05]	−4.75449[−05]
3.0[1]	−2.12123[−06]	−3.47401[−06]	−3.77693[−06]	−4.56425[−06]	−3.59181[−06]
5.0[1]	−9.39127[−08]	−1.51881[−07]	−1.64047[−07]	−1.96120[−07]	−1.56012[−07]
7.0[1]	−1.22991[−08]	−1.98267[−08]	−2.13779[−08]	−2.54848[−08]	−2.03310[−08]
1.0[2]	−1.43594[−09]	−2.31111[−09]	−2.48968[−09]	−2.96366[−09]	−2.36773[−09]
1.5[2]	−1.25451[−10]	−2.01778[−10]	−2.17269[−10]	−2.58449[−10]	−2.06611[−10]
2.0[2]	−2.22664[−11]	−3.58141[−11]	−3.85581[−11]	−4.58587[−11]	−3.66628[−11]
3.0[2]	−1.94563[−12]	−3.13132[−12]	−3.37105[−12]	−4.00966[−12]	−3.20438[−12]
5.0[2]	−8.97817[−14]	−1.44798[−13]	−1.55901[−13]	−1.85556[−13]	−1.48065[−13]
7.0[2]	−1.17615[−14]	−1.90192[−14]	−2.04814[−14]	−2.43996[−14]	−1.94306[−14]
1.0[3]	−1.35025[−15]	−2.19334[−15]	−2.36280[−15]	−2.81930[−15]	−2.23722[−15]
1.5[3]	−1.13026[−16]	−1.85096[−16]	−1.99528[−16]	−2.38778[−16]	−1.88237[−16]
2.0[3]	−1.90886[−17]	−3.15170[−17]	−3.39975[−17]	−4.08088[−17]	−3.19524[−17]
3.0[3]	−1.50096[−18]	−2.51635[−18]	−2.71796[−18]	−3.28165[−18]	−2.53595[−18]
5.0[3]	−5.64137[−20]	−9.69114[−20]	−1.04906[−19]	−1.27919[−19]	−9.67179[−20]
7.0[3]	−6.16139[−21]	−1.07672[−20]	−1.16745[−20]	−1.43408[−20]	−1.06715[−20]
1.0[4]	−5.63591[−22]	−1.00139[−21]	−1.08756[−21]	−1.34611[−21]	−9.85811[−22]
1.5[4]	−3.55058[−23]	−6.40204[−23]	−6.96370[−23]	−8.68110[−23]	−6.26492[−23]
2.0[4]	−4.88760[−24]	−8.87689[−24]	−9.66332[−24]	−1.20916[−23]	−8.66121[−24]
3.0[4]	−2.93108[−25]	−5.35750[−25]	−5.83633[−25]	−7.32808[−25]	−5.21381[−25]
5.0[4]	−8.31609[−27]	−1.52586[−26]	−1.66297[−26]	−2.09251[−26]	−1.48263[−26]
7.0[4]	−7.91933[−28]	−1.45472[−27]	−1.58565[−27]	−1.99653[−27]	−1.41285[−27]
1.0[5]	−6.53538[−29]	−1.20125[−28]	−1.30946[−28]	−1.64937[−28]	−1.16638[−28]

$$f^{F}_{2200}=\frac{4}{11025\alpha\pi R^{11}}\int_0^\infty du\,\mathcal{R}^{1}_{11}\left(i\frac{u}{\alpha R}\right)\mathcal{R}^{1}_{31}\left(i\frac{u}{\alpha R}\right)e^{-2u}\times(630+1260u+1215u^2+750u^3+333u^4+114u^5+32u^6+8u^7+2u^8), \tag{6.5}$$

$$f_{1111}=\frac{1}{225\alpha\pi R^{11}}\int_0^\infty du\left[\mathcal{R}^{2}_{22}\left(i\frac{u}{\alpha R}\right)\right]^2 e^{-2u}\times(630+1260u+1215u^2+750u^3+333u^4+114u^5+32u^6+8u^7+2u^8), \tag{6.6}$$

and are different from those provided by the QED formalism, given in Eqs. (3.8), (3.15), and (3.18) respectively. In the limit of small values of R they obey the same relations from Eqs. (6.2) and (6.3). In the limit $R\to\infty$ the Au-Feinberg approximation obviously is failing to provide the correct expressions for the K_9 and K_{11} long-range coefficients. The analytical differences between the Au-Feinberg approximation and the QED results for the CP potential were also pointed out in Refs. [21,26]. However, as we indicate in Table II, the terms f_{0000}, f_{1100}, f^{F}_{2200}, f^{P}_{2200}, and f_{1111} provide an incomplete result for the K_9 and K_{11} long-range coefficients. It is interesting to note that despite the major analytical differences between Au-Feinberg approximation and the complete QED expression of the CP long-range potential, given by the sum of all the terms from Table I, the numerical differences between these two results are very small. The relative error given by the Au-Feinberg approximation is smaller than 10^{-5}. Thus, for many applications the numerical results from [31] are reliable. Recently Yan, Dalgarno, and Babb [32] computed the long-range interaction potential between two Li atoms using only the contributions of the f_{0000} and f_{1100} terms. Their numerical evaluation consists of a highly accurate computation of the atomic dynamic dipole and quadrupole polarizabilities, by employing Hyleraas-type base functions for the three electron problem. It is claimed that the results of Ref. [32] are the best *ab initio* estimations of the f_{0000} and f_{1100} terms for Li-Li long-range potential. However, by neglecting the contributions of the f^{F}_{2200} and

TABLE VI. The Casimir-Polder long-range potential as a function of R, in a.u., for heteronuclear alkali-metal dimers Na-Rb, Na-Cs, K-Rb, K-Cs, and Rb-Cs. The values of the R_0 radius are indicated in the second line. The numbers in the square brackets indicate powers of ten.

R	Na-Rb 32	Na-Cs 33	K-Rb 34	K-Cs 35	Rb-Cs 36
1.0[1]	−8.09731[−03]	−1.08210[−02]	−1.52187[−02]	−2.03015[−02]	−2.34204[−02]
1.5[1]	−3.73477[−04]	−4.72995[−04]	−6.56390[−04]	−8.35214[−04]	−9.36752[−04]
2.0[1]	−5.23513[−05]	−6.44742[−05]	−8.89587[−05]	−1.10252[−04]	−1.21674[−04]
3.0[1]	−3.90273[−06]	−4.70312[−06]	−6.46578[−06]	−7.84528[−06]	−8.54479[−06]
5.0[1]	−1.68402[−07]	−2.00744[−07]	−2.75612[−07]	−3.30839[−07]	−3.57943[−07]
7.0[1]	−2.19075[−08]	−2.60402[−08]	−3.57429[−08]	−4.27837[−08]	−4.62078[−08]
1.0[2]	−2.54903[−09]	−3.02546[−09]	−4.15241[−09]	−4.96316[−09]	−5.35554[−09]
1.5[2]	−2.22330[−10]	−2.63698[−10]	−3.61940[−10]	−4.32299[−10]	−4.66259[−10]
2.0[2]	−3.94464[−11]	−4.67787[−11]	−6.42139[−11]	−7.66828[−11]	−8.26945[−11]
3.0[2]	−3.44750[−12]	−4.08874[−12]	−5.61467[−12]	−6.70518[−12]	−7.23032[−12]
5.0[2]	−1.59319[−13]	−1.89087[−13]	−2.59913[−13]	−3.10562[−13]	−3.34907[−13]
7.0[2]	−2.09117[−14]	−2.48435[−14]	−3.41911[−14]	−4.08856[−14]	−4.40970[−14]
1.0[3]	−2.40867[−15]	−2.86646[−15]	−3.95336[−15]	−4.73393[−15]	−5.10716[−15]
1.5[3]	−2.02806[−16]	−2.42115[−16]	−3.35204[−16]	−4.02427[−16]	−4.34381[−16]
2.0[3]	−3.44505[−17]	−4.12624[−17]	−5.73489[−17]	−6.90363[−17]	−7.45592[−17]
3.0[3]	−2.73805[−18]	−3.30007[−18]	−4.61995[−18]	−5.59092[−18]	−6.04474[−18]
5.0[3]	−1.04671[−19]	−1.27487[−19]	−1.80527[−19]	−2.20453[−19]	−2.38792[−19]
7.0[3]	−1.15689[−20]	−1.42006[−20]	−2.02677[−20]	−2.49206[−20]	−2.70317[−20]
1.0[4]	−1.07056[−21]	−1.32453[−21]	−1.90466[−21]	−2.35870[−21]	−2.56228[−21]
1.5[4]	−6.81432[−23]	−8.49354[−23]	−1.22931[−22]	−1.53282[−22]	−1.66745[−22]
2.0[4]	−9.42840[−24]	−1.17968[−23]	−1.71278[−23]	−2.14340[−23]	−2.33339[−23]
3.0[4]	−5.67977[−25]	−7.13137[−25]	−1.03822[−24]	−1.30363[−24]	−1.42016[−24]
5.0[4]	−1.61586[−26]	−2.03322[−26]	−2.96485[−26]	−3.73068[−26]	−4.06592[−26]
7.0[4]	−1.54002[−27]	−1.93906[−27]	−2.82890[−27]	−3.56193[−27]	−3.88253[−27]
1.0[5]	−1.27145[−28]	−1.60149[−28]	−2.33702[−28]	−2.94366[−38]	−3.20884[−28]

f_{1111} terms an error of 1% is assumed in the final expression of the potential (as suggested by Table III), at least for small values of R. The relative error between our computation of the CP potential for Li-Li, and that based on the results of Ref. [32], ranges from 3% for small values of R, to 0.1% for large values of R. The main difference between these two computations is the numerical value of the C_6 dispersion coefficient generated in our case by a model potential formalism [34] and in Ref. [32] by an *ab initio* computation of the three electron problem. Kharchenko, Babb, and Dalgarno [33] presented an accurate estimation of the f_{0000} electric dipole term for two interacting Na atoms. The authors of Ref. [33] estimated the dynamic dipole polarizability of Na by an extended analysis of the available experimental data of the discrete oscillator strengths and photoionization cross sections. The final numerical results presented in Ref. [33] are probably the best empirical estimates for the f_{0000} term. We emphasize that the f_{0000} term may approximate the CP potential only at very large values of R ($\geqslant 10^4$ a.u.). The relative error between our computation of the CP potential of Na-Na and that based on the results of Ref. [33] is approximatively 4%.

TABLE VII. The values of the K_7, K_9, and K_{11} long-range coefficients for alkali-metal dimers, in a.u. The numbers in the square bracket indicate powers of ten.

	K_7	K_9	K_{11}
Li-Li	6.74591[6]	4.15815[8]	3.72305[10]
Li-Na	6.54847[6]	4.69326[8]	4.51786[10]
Li-K	1.20439[7]	1.07543[9]	1.19370[11]
Li-Rb	1.31298[7]	1.30945[9]	1.52114[11]
Li-Cs	1.65439[7]	1.94722[9]	2.40547[11]
Na-Na	6.35680[6]	5.19349[8]	5.37434[10]
Na-K	1.16914[7]	1.16122[9]	1.37645[11]
Na-Rb	1.27455[7]	1.39896[9]	1.73721[11]
Na-Cs	1.60597[7]	2.05131[9]	2.71393[11]
K-K	2.15028[7]	2.51463[9]	3.36065[11]
K-Rb	2.34415[7]	2.98606[9]	4.17377[11]
K-Cs	2.95369[7]	4.29328[9]	6.38710[11]
Rb-Rb	2.55551[7]	3.52206[9]	5.15484[11]
Rb-Cs	3.22001[7]	5.01650[9]	7.83057[11]
Cs-Cs	4.05729[7]	7.05000[9]	1.17785[12]

The R_0 radius (the minimum value of R for which the interaction between atoms is still well approximated by the CP form of the potential alone) was computed such that $\langle \mathcal{V} \rangle$, given by Eqs. (5.7) and (5.8), is approximatively four orders of magnitude smaller than the CP potential. In general, the numerical values of R_0, presented in Tables IV, V, and VI are 50% larger than the LeRoy radius [39],

$$R_{LR}=2[\langle r^2\rangle_A^{1/2}+\langle r^2\rangle_B^{1/2}]. \tag{6.7}$$

Thus the $R \geqslant R_0$ condition is more restrictive than the $R \geqslant R_{LR}$ condition, but it has a more rigorous mathematical support. However, R_0 should not be understood as a threshold value but rather as a point below which one have to consider the exchange energy contributions to the interaction potential.

VII. CONCLUSIONS

We have presented a complete analysis of the CP effect, including the e-e, e-m, m-m, d-e, and d-m multipole interactions between two alkali-metal atoms. Based on the PZW multipole form of the interaction Hamiltonian, general expressions for all two-photon processes were established. Explicit analytical forms were derived for all diagrams involved in the expression of K_7, K_9, and K_{11} long-range coefficients. Based on a quantitative analysis we have studied the importance of various two-photon processes which contribute to the final expression of the CP long-range potential. We found that the main contribution to the long-range coefficients K is given by the e-e multipole processes. For small values of R, we found that the CP potential is well described by the electric dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and dipole-octupole interactions which were previously mentioned in the literature. Based on a numerical comparison we found that the Au-Feinberg approximation [20] gives reliable results. We were also able to estimate that the dispersion form of the potential interaction is a good approximation for R up to several hundred a.u. Analyzing the contribution of the contact interaction term between the atomic charge distributions to the first-order correction to the energy, we were able to establish the range of validity of the CP long-range form of the interaction potential. Numerical evaluations of the CP potential were given for all alkali-metal dimers.

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