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Unified analysis of multipole and finite-mass corrections in long-range Coulombic interactions

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Simple expressions are derived for all multipole, nonadiabatic, and finite-nuclear-mass corrections to the long-range effective potential due to two–Coulomb-photon exchange at threshold energy and also first order in energy correction for the scattering between a spinless point charged particle and a spinless Coulombic complex and between two spinless Coulombic complexes. All these corrections are treated on equal footing and the results are expressed, respectively, in terms of single-center and London-analog two-center atomic multipole spectral sums. An isomorphism between the point-particle–complex interaction and the complex-complex interaction is derived. All Hughes-Eckert–type type mass-polarization terms are avoided by suitable choice of Jacobi coordinates.

I. INTRODUCTION

There has long been an interest in the study of long-range forces in Coulombic systems. These include, but are not limited to, interaction between a pair of atoms,[1-7] between a charged particle and an atom or an ion, and between the outer electron and the core ion in high Rydberg states.[8-18] This interest has recently intensified, especially in the high-l helium Rydberg state system where comparison between theory[19-21] and experiment[22,23] seems to verify the Casimir correction.[20,21]

Recently Drake[24] has developed a variational technique to calculate high-precision nonrelativistic eigenvalues for helium. In Drake's work, transverse-photon exchange between the electrons is incorporated through the Pauli form of the Breit interaction as given by Bethe and Salpeter[25] and the Araki-[26] Sucher[27] potential is used for two-electron correction of order α^3 Ry. Drake's calculation for the states he has considered is in good agreement with experiments.[28] However, as pointed out by Au,[29] the preceding method of including transverse-photon-exchange effects needs to be modified for high Rydberg states where the moderate to large-distance behavior of the Casimir correction becomes important. Au shows that this correction can be given in the form of a potential V'' that behaves as $\alpha^5 a/R^2$ at small distances and hence yields a finite-energy correction of order α^4 Rydberg even for low-l Rydberg states. The readers must be cautioned that for low-l Rydberg states, the correction potential V'' does not account for all the corrections at this level. Two-electron-contact–type and other short-ranged terms, spin-dependent terms, and exchange effects, which hitherto have not been included, may lead to corrections of similar magnitudes for the low-l Rydberg states and hence must be carefully examined in any precise calculations of this magnitude.

Following a suggestion of Feinberg, Au pointed out that $\langle V'' \rangle$ would be finite for the $\mu^- e^- \alpha^{+2}$ (muonic helium) system. This would provide another challenge to experimentalists if Drake could extend his calculation to lowest-lying states in the $\mu^- e^- \alpha^{+2}$ system. In the $\mu^- e^- \alpha^{+2}$ system, the muon mass is no longer negligible compared to the nuclear mass and the $\mu^- \alpha^{+2}$ core excitation energy becomes much larger compared to the electronic excitation energy. This has the interesting consequence of raising the importance of the mass-polarization effect and decreasing that of the nonadiabatic corrections.

The mass-polarization effect can be calculated either perturbatively or by including the mass-polarization operator in the Hamiltonian. An example of the latter is the variational-type calculation such as the one by Drake[24] where the mass-polarization operator is part of the Hamiltonian from which the variation wave function is obtained. In this case, the extent to which the mass-polarization effect is accounted for depends on the accuracy of the variational wave function. An example of the former where the mass-polarization effect is included perturbatively is the calculation by Drachman[19] where the mass-polarization (nuclear recoil) and nonadiabatic (outer electron recoil) corrections are added on piecewise. With suitable use of Jacobi coordinates, Drachman has shown that the nuclear recoil correction leads to a partial suppression of the multipole interactions and he displayed such effect on the adiabatic dipole and quadrupole polarization potentials in his calculation on helium Rydberg states.[19] The present paper examines the effects of mass polarization on all the nonadiabatic corrections.

In recent years, advances in modern experimental technique involving positronium atoms[30] have also brought much attention to the finite-mass corrections in the polarization forces in Coulombic systems involving positronium.[31-33] In the extreme case of two positronium atoms, the "atomic," "nuclear," and "electronic" masses are all of the same order. Thus "nuclear" recoil corrections and "atomic" recoil (nonadiabatic) corrections seem equally important. Earlier, Au has pointed out that in a self-conjugate system such as positronium, all electric even multipole interactions vanish.[34] We shall see that this is a case of maximal multipole suppression due to finite "nuclear" mass effects.

The present paper treats on equal footing and in a unified manner multipole, nonadiabatic, and mass-polarization (all finite-mass) corrections in the long-range interaction between Coulombic systems in the two-Coulomb-photon exchange channel. I first consider the case of three charged, spinless particles of masses m_1, m_2, and m_3 and charges Z_1e, Z_2e, and Z_3e. Particles 1 and 2 are assumed to form a bound system and, to simplify the discussion, in a state of zero angular momentum. This covers the case of the interaction between a charged particle and a neutral atom or an ion, with the latter applicable to the study of Rydberg states. Then I shall consider the case of four charged, spinless particles of masses m_1, m_2, m_3, and m_4 and charges Z_1e, Z_2e, Z_3e, and Z_4e such that particles 1 and 2 and particles 3 and 4 form bound complexes A and B, each in a state of zero angular momentum. When $Z_1+Z_2=0$ and $Z_3+Z_4=0$, this reduces to the case of the interaction between two neutral atoms (the van der Waals case). When either (Z_1+Z_2) or (Z_3+Z_4) or both are nonzero, regular Coulombic (Coulombic monopole) interactions must be included. This Coulombic interaction between bare charges can be included in the unperturbed Hamiltonian and hence has its effect iterated. Therefore I shall exclude from my consideration the graph corresponding to the exchange of two-monopole-Coulomb photons. Angular momentum conservation requires that the two photons interacting with the same atom be of the same multipolarity. However, this multipolarity does not have to be the same at complex A as it is at complex B. Thus complex A may exchange two-Coulomb photons of multipolarity L_A which turn into photons of multipolarity L_B at complex B. In particular L_B can be zero if complex B shows a net charge, i.e., when $Z_3+Z_4\neq 0$. However, this case is identical to that in the three-body situation and hence will not be considered. Therefore I only limit the discussion to $L_A\neq 0$ and $L_B\neq 0$.

As we shall see, finite "nuclear" mass within the Coulombic complex (atom) leads to the multipole suppression factor and finite reduced mass between the Coulombic systems leads to the nonadiabatic corrections. The results are expressed in terms of single-center atomic multipole spectral sums for the particle-complex case and two center atomic multipole spectral sums in the complex-complex case. Remarkably, there is an isomorphism between the L_A-L_B multipole interaction component in the complex-complex case and the $(L=L_A+L_B)$ multipole interaction component in the particle-complex case. The similarity between the dipole-dipole van der Waals interaction for a pair of atoms and the quadrupole interaction in electron-atom scattering has been noted earlier.[35] The present result generalizes this similarity. I use the Jacobi coordinates[36] and $\hbar$ is set equal to unity. Transverse-photon exchange effect (Casimir correction) is not considered.

II. CHARGED-PARTICLE–COULOMBIC-COMPLEX INTERACTION

Let $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ be the coordinate vectors of particles 1, 2 and 3 with masses m_1, m_2, and m_3 and charges Z_1e, Z_2e, and Z_3e. I define the following:

$$\alpha\equiv m_2/(m_1+m_2)\ , \tag{2.1}$$

$$m\equiv m_1+m_2+m_3\ , \tag{2.2}$$

$$\gamma_i\equiv\frac{m_i}{m},\quad i=1,2,3\ , \tag{2.3}$$

$$\mathbf{x}\equiv\mathbf{r}_1-\mathbf{r}_2\ , \tag{2.4}$$

$$\mathbf{X}=(1-\alpha)\mathbf{r}_1+\alpha\mathbf{r}_2\ , \tag{2.5}$$

$$\mathbf{R}\equiv\mathbf{r}_3-\mathbf{X}\ , \tag{2.6}$$

$$\mathbf{S}\equiv\gamma_1\mathbf{r}_1+\gamma_2\mathbf{r}_2+\gamma_3\mathbf{r}_3\ , \tag{2.7}$$

$$m'\equiv m_1+m_2\ , \tag{2.8}$$

$$\mu\equiv\gamma_3 m'=(\gamma_1+\gamma_2)m_3\ . \tag{2.9}$$

In terms of these coordinates and variables, the Hamiltonian of the three-body Coulombic system is

$$H_t=-\frac{\nabla_x^2}{2\alpha m_1}-\frac{\nabla_R^2}{2\mu}-\frac{\nabla_S^2}{2m}+e^2\left[\frac{Z_1Z_2}{|\mathbf{x}|}+\frac{Z_1Z_3}{|\mathbf{R}-\alpha\mathbf{x}|}+\frac{Z_2Z_3}{|\mathbf{R}+(1-\alpha)\mathbf{x}|}\right]. \tag{2.10}$$

We notice that in terms of the set of Jacobi coordinates ($\mathbf{x}$, $\mathbf{R}$, and $\mathbf{S}$), all Hughes-Eckert–type mass-polarization terms disappear.[19] Moreover, the total Hamiltonian is cyclic in $\mathbf{S}$ and so the center-of-mass energy term can drop out. Hence one can replace H_t by $H=H_0+H_1\equiv h_0+T+H_1$, where

$$h_0=-\frac{\nabla_x^2}{2\alpha m_1}+\frac{e^2Z_1Z_2}{|\mathbf{x}|}\ , \tag{2.11}$$

$$T=-\frac{\nabla_R^2}{2\mu}\ , \tag{2.12}$$

and

$$H_1=e^2\left[\frac{Z_1Z_3}{|\mathbf{R}-\alpha\mathbf{x}|}+\frac{Z_2Z_3}{|\mathbf{R}+(1-\alpha)\mathbf{x}|}\right]\ , \tag{2.13}$$

$$=\frac{e^2Z_3}{2\pi^2}\int\frac{d^3k}{k^2}e^{i\mathbf{k}\cdot\mathbf{R}}(Z_1e^{-i\alpha\mathbf{k}\cdot\mathbf{x}}+Z_2e^{i(1-\alpha)\mathbf{k}\cdot\mathbf{x}})\ , \tag{2.14}$$

$$=\frac{Z_3e^2}{2\pi^2}\int\frac{d^3k}{k^2}e^{i\mathbf{k}\cdot\mathbf{R}}\times\sum_{L=0}^{\infty}\frac{(-i\mathbf{k}\cdot\mathbf{x})^L}{L!}[Z_1\alpha^L+Z_2(\alpha-1)^L]\ , \tag{2.15}$$

$$\equiv\sum_{L=0}^{\infty}h_1^L\ . \tag{2.16}$$

At this point I would like to make the following observations. (i) The eigenvalues of h_0 are scaled to the hydrogenic eigenvalues by the factor $(-Z_1Z_2\alpha m_1/m_e)$, where m_e is the electron mass. (ii) For a neutral complex, $Z_1+Z_2=0$ and the $L=0$ term inside the square brackets in Eq. (2.15) vanishes, corresponding to the absence of Coulombic monopole interaction. (iii) For a neutral complex, the $L=1$ term in Eq. (2.15) is independent of α indicating that finite "nuclear" mass does not affect the Coulombic dipole interaction. This is not the case if the complex has a net charge. (iv) In the special case when $Z_1=-Z_2$ and $\alpha=\frac{1}{2}$ such as a self-conjugate system like positronium or true-muonium $(\mu^+\mu^-)$ or p-$\bar{p}$ systems, all terms with even L vanish. This corresponds to the total suppression of even electric multipole interactions in such self-conjugate systems. (v) For $\alpha=1$ corresponding to infinite nuclear mass, Eqs. (2.15) and (2.16) reduce to the regular multipole expansion. (vi) For a charged complex, the monopole term $(L=0)$ can be grouped with T to form a Coulombic-type Hamiltonian for particle 3 in the Coulomb field of the charged complex in the Jacobi coordinate **R**.

With the preceding observation in mind, one is ready to derive the effective multipole polarization potentials plus their nonadiabatic corrections. For simplicity, I assume a neutral complex, i.e., $Z_1+Z_2=0$. The modifications due to $Z_1+Z_2\neq 0$ will be discussed in Sec. IV. I shall follow a procedure I have used previously to obtain the multipole and nonadiabatic corrections to the two–Coulomb-photon exchange effective potential for electron-atom scattering.[37] Briefly stated, this method goes as follows. Let $|\mathbf{p}\rangle$ and $|\mathbf{p}'\rangle$ denote the incident and emergent momentum eigenstates of T in Eq. (2.12). Then one computes the second-order scattering T-matrix amplitude due to the interaction H_1 of the charged particle with the target complex. Let $\mathbf{Q}\equiv\mathbf{p}'-\mathbf{p}$ be the momentum transfer. Then the effective potential is obtained as the Fourier transform of the T-matrix amplitude in **Q** with respect to **R** with the energy-shell constraint $p^2=(p')^2$. For computational convenience, an exchange of the order of integration may result in a mathematical artifact, giving rise to a momentum-dependent effective potential. When the on-shell constraint is duly imposed, the pathology disappears resulting in an energy-dependent potential. In scattering processes, energy is conserved and so this is only a parametric dependence. The mathematical procedure of implementing this process has been given in detail elsewhere.[37]

Let $|0\rangle$ be the initial zero angular momentum state of the neutral complex and E_n be the energy eigenvalue of the state $|n\rangle$. I define

$$\Delta_n\equiv 2\mu(E_n-E_0)\ . \tag{2.17}$$

Then the effective potential in momentum-dependent form corresponding to the Fourier transform of the second-order T matrix due to the interaction H_1 is

$$\bar{V}(R,\mathbf{p}\cdot\mathbf{R},p^2)=\frac{2\mu Z_3^2e^4}{4\pi^4}\times\int\frac{d^3k}{k^2}e^{i\mathbf{k}\cdot\mathbf{R}}\int\frac{d^3q}{q^2}e^{i\mathbf{q}\cdot\mathbf{R}}K(\mathbf{p},\mathbf{k},\mathbf{q})\ , \tag{2.18}$$

where

$$K(\mathbf{p},\mathbf{k},\mathbf{q})=\sum_{L_1,L_2=1}^{\infty}\frac{[Z_1\alpha^{L_1}+Z_2(1-\alpha)^{L_1}][Z_1\alpha^{L_2}+Z_2(1-\alpha)^{L_2}]}{L_1!L_2!}\,\frac{\langle 0|(-i\mathbf{k}\cdot\mathbf{x})^{L_1}|n\rangle\langle n|(-i\mathbf{q}\cdot\mathbf{x})^{L_2}|0\rangle}{\Delta_n+k^2+2\mathbf{p}\cdot\mathbf{k}}\ . \tag{2.19}$$

I define the following single center Lth multipole atomic spectral sum:

$$A_{M+1}^{L}\equiv 2\mu e^2[Z_1\alpha^L+Z_2(1-\alpha)^L]^2\sum_n\frac{|\langle 0|x^LP_L|n\rangle|^2}{\Delta_n^{M+1}}\ . \tag{2.20}$$

Here P_L is the Legendre polynomial of order L. Then following a procedure I have developed recently,[37] Eq. (2.18) can be expressed in terms of these sum rules,

$$\bar{V}(R,\mathbf{p}\cdot\mathbf{R},p^2)=-Z_3^2e^2\sum_{N,L}A_{N+1}^{L}\frac{(2i)^N}{L!}\frac{(R_{i_1}\ldots R_{i_L})(p_{j_1}\ldots p_{j_N})}{R^{2L+1}}(\partial_{i_1}\ldots\partial_{i_L})(\partial_{j_1}\ldots\partial_{j_N})\left[\frac{1}{R}\right] \tag{2.21}$$

$$\equiv\sum_{L=1}^{\infty}\sum_{M=0}^{\infty}\sum_{J=0}^{\infty}\bar{V}_{MJ}^{L}(R)(-i\mathbf{p}\cdot\mathbf{R})M_p2J\ . \tag{2.22}$$

On directly comparing Eq. (2.22) with Eq. (2.21), I get

$$\bar{V}_{MJ}^{L}(R)=\frac{-Z_e^2e^2}{L!}A_{M+2J+1}^{L}R^{-2(L+M+J+1)}B(L,M,J)\ , \tag{2.23}$$

where

$$B(L,M,J)=2^{M+2J}C_{2J}^{M+2J}\frac{(2J)!}{2^JJ!}\times\sum_{k,j}k!C_k^MC_k^LC_{2j}^{L-k}\frac{(2j)!}{2^jj!}(-1)^{j+k}\times(2L+2M+2J-2j-2k-1)!!\ , \tag{2.24}$$

and $C_n^N \equiv N!/[n!(N-n)!]$ is the usual combinatoric factor and the double factorial $(2J+1)!$ is defined by the product $\prod_{i=0}^{j}(2i+1)$. I am able to carry out the sum in k and j in Eq. (2.24) for $L=1$ and 2 and for all values of M and J. Then by going back to Eq. (2.21) from which the coefficient $B(L,M,J)$ defined in Eq. (2.24) arises, I am able to prove by mathematical induction that

$$B(L,M,J)=\frac{(M+2J+L)!(2M+2J)!}{M!J!(M+J)!} . \tag{2.25}$$

For the particular case that $J=0$, this reduces to the combinatoric identity that I conjectured and subsequently verified on the computer before.[37] On substituting Eq. (2.25) into Eq. (2.23), I have

$$\bar{V}_{MJ}^{L}(R)=-Z_3^2e^2A_{M+2J+1}^{L}R^{-2(L+M+J+1)} \times\frac{(M+2J+L)!(2M+2J)!}{L!M!J!(M+J)!} . \tag{2.26}$$

Equation (2.26), when substituted into Eq. (2.22), provides a very convenient form to convert the momentum-dependent effective potential into a truly local form according to a prescription obtained previously.[37] Upon expanding the energy-dependent but otherwise local effective potential in powers of p^2, we have

$$V(R,p^2)\equiv\sum_{L=1}^{\infty}\sum_{M,J=0}^{\infty}V_{MJ}^{L}(R)p^{2J} . \tag{2.27}$$

Here M is the nonadiabatic index and J is the energy dependence index. The potentials V_{MJ}^L are related to $\bar{V}_{MJ}^L$ in Eq. (2.22) via

$$V_{MJ}^{L}=\left[\frac{\nabla^2}{2}\right]^{M}F_{MJ}^{L} , \tag{2.28}$$

$$F_{MJ}^{L}=I^{M}\bar{V}_{MJ}^{L} -\sum_{m=1}^{J}C_{2m}^{M+2m}(2m-1)!!(-i)^{2m}D^{m}F_{M+2m,J-M}^{L} , \tag{2.29}$$

where the operators D and I are defined by

$$D\equiv\frac{1}{R}\frac{d}{dR} , \tag{2.30}$$

and

$$I\equiv D^{-1} . \tag{2.31}$$

Using Eqs. (2.28) to (2.31), one can easily obtain the truly local effective potential at threshold energy and its lowest-order energy correction,

$$V_{M0}^{L}(R)=\left[\frac{\nabla^2}{2}\right]^{M}I^{M}\bar{V}_{M0}^{L}(R) , \tag{2.32}$$

and

$$V_{M1}^{L}(R)=\left[\frac{\nabla^2}{2}\right]^{M}[I^{M}\bar{V}_{M1}^{L}(R)+C_2^{M+2}I^{M+1}\bar{V}_{M+2,0}^{L}(R)] . \tag{2.33}$$

Then on using Eqs. (2.26) and (2.32), I find

$$V_{M0}^{L}(R)=\frac{(-1)^{M+1}Z_3^2e^2A_{M+1}^{L}}{R^{2(M+L+1)}}\frac{(2M)!(2M+2L)!}{2^{2M}(M!)^2(2L)!} \tag{2.34}$$

$$=\frac{(-1)^{M+1}Z_3^2e^2A_{M+1}^{L}}{R^{2(M+L+1)}} \times\frac{(2M+2L-1)!!(2M-1)!!(M+L)!}{(2L-1)!!L!M!} , \tag{2.35}$$

and on using Eqs. (2.26) and (2.33), I find

$$V_{M1}^{L}(R)=\frac{(-1)^{M+1}Z_3^2e^2A_{M+3}^{L}}{R^{2(M+L+2)}} \times\frac{(2M+2L+1)!!(2M+1)!!(M+L+1)!}{(2L-1)!!L!M!} \tag{2.36}$$

$$=\frac{(-1)^{M+1}Z_3^2e^2A_{M+3}^{L}}{R^{2(M+L+2)}}\frac{(2M+1)!}{2^{(2M+1)}} \times\frac{(2M+2L+2)!}{(M!)^2(2L))!} . \tag{2.37}$$

Equation (2.34) agrees with the results obtained earlier after noting the definition of A_M^L used in the present paper. In Eq. (2.35), $(2M-1)!!$ is taken to be 1 for $M=0$.

III. COMPLEX-COMPLEX LONG-RANGE COULOMBIC INTERACTION

Let $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$ be the coordinate vectors of particles 1, 2, 3 and 4, with masses m_1, m_2, m_3, and m_4, and charges Z_1e, Z_2e, Z_3e, and Z_4e, such that particles 1 and 2 form a spinless complex A and particles 3 and 4 form another spinless complex B. I define the following:

$$m_A\equiv m_1+m_2 , \tag{3.1}$$

$$m_B\equiv m_3+m_4 , \tag{3.2}$$

$$\alpha\equiv m_2/m_A , \tag{3.3}$$

$$\beta\equiv m_4/m_B , \tag{3.4}$$

$$m\equiv m_A+m_B , \tag{3.5}$$

$$\gamma_i\equiv m_i/m, \quad i=1,2,3,4 , \tag{3.6}$$

$$\mathbf{x}\equiv\mathbf{r}_1-\mathbf{r}_2 , \tag{3.7}$$

$$\mathbf{y}\equiv\mathbf{r}_3-\mathbf{r}_4 , \tag{3.8}$$

$$\mathbf{X}\equiv(1-\alpha)\mathbf{r}_1+\alpha\mathbf{r}_2 , \tag{3.9}$$

$$\mathbf{Y}\equiv(1-\beta)\mathbf{r}_3+\beta\mathbf{r}_4 , \tag{3.10}$$

$$\mathbf{R}\equiv\mathbf{Y}-\mathbf{X} , \tag{3.11}$$

$$\mathbf{S}\equiv\sum_i\gamma_i\mathbf{r}_i , \tag{3.12}$$

and

$$\mu\equiv m_Am_B/m . \tag{3.13}$$

Then, in terms of the Jacobi coordinates **x**, **y**, **R**, and **S**, the total Hamiltonian is cyclic in **S** and the kinetic energy of the center of mass of the entire system is a conserved quantity and can be dropped. The Hamiltonian can thus be expressed in the form

$$H = h_{0A} + h_{0B} + T + H_1 , \tag{3.14}$$

where

$$h_{0A} \equiv -\frac{\nabla_x^2}{2\alpha m_1} + \frac{Z_1 Z_2 e^2}{|\mathbf{x}|} , \tag{3.15}$$

$$h_{0B} \equiv -\frac{\nabla_y^2}{2\beta m_3} + \frac{Z_3 Z_4 e^2}{|\mathbf{y}|} , \tag{3.16}$$

$$T \equiv -\frac{\nabla_R^2}{2\mu} , \tag{3.17}$$

and

$$H_1 \equiv e^2 \left[\frac{Z_1 Z_3}{|\mathbf{R}+\beta\mathbf{y}-\alpha\mathbf{x}|} + \frac{Z_2 Z_4}{|\mathbf{R}+(1-\alpha)\mathbf{x}(1-\beta)\mathbf{y}|} + \frac{Z_2 Z_3}{|\mathbf{R}+(1-\alpha)\mathbf{x}+\beta\mathbf{y}|} + \frac{Z_1 Z_4}{|\mathbf{R}-\alpha\mathbf{x}-(1-\beta)\mathbf{y}|} \right] \tag{3.18}$$

$$= e^2 \int \frac{d^3k}{k^2} e^{i\mathbf{k}\cdot\mathbf{R}} [Z_1 e^{-i\alpha\mathbf{k}\cdot\mathbf{x}} + Z_2 e^{i(1-\alpha)\mathbf{k}\cdot\mathbf{x}}][Z_3 e^{i\beta\mathbf{k}\cdot\mathbf{y}} + Z_4 e^{-i(1-\beta)\mathbf{k}\cdot\mathbf{y}}] \tag{3.19}$$

$$= \sum_{L_A, L_B = 0}^{\infty} h_1^{L_A L_B} , \tag{3.20}$$

where

$$h_1^{L_A L_B} \equiv e^2 \int \frac{d^3k}{k^2} [Z_1(-\alpha)^{L_A} + Z_2(1-\alpha)^{L_A}] \frac{(i\mathbf{k}\cdot\mathbf{x})^{L_A}}{L_A!} [Z_3 \beta^{L_B} + Z_4(\beta-1)^{L_B}] \frac{(i\mathbf{k}\cdot\mathbf{y})^{L_B}}{L_B!} . \tag{3.21}$$

As observed in Sec. II, the quantities in the square brackets in Eq. (3.21) act as multipole suppression factors. Again, note that for a neutral complex, the monopole term disappears and also that for the dipole term, the finite "nuclear" mass has no effect for a neutral complex. In accordance with the discussion in the Introduction, I discard the monopole-multipole and the monopole-monopole interaction terms. The former reduces to the case of Sec. II and the latter corresponds to the Coulombic interaction between two charges. Let $|0_A\rangle$ and $|0_B\rangle$ be the initial zero angular momentum states of the complexes A and B and E_{n_A} and E_{n_B} be the energy eigenvalues of the states $|n_A\rangle$ and $|n_B\rangle$. I define

$$\Delta_{n_A n_B} \equiv 2\mu[E_{n_A} - E_{0_A} + E_{n_B} - E_{0_B}] , \tag{3.22}$$

and the two-center correlated multipole spectral sum

$$D_{M+1}^{L_A L_B} \equiv 2\mu e^2 [Z_1(-\alpha)^{L_A} + Z_2(1-\alpha)^{L_A}]^2 [Z_3\beta^{L_B} + Z_4(\beta-1)^{L_B}]^2 \sum_{n_A, n_B} \frac{|\langle 0_A | x^{L_A} P_{L_A} | n_A \rangle|^2 \, |\langle 0_B | y^{L_B} P_{L_B} | n_B \rangle|^2}{\Delta_{n_A n_B}^{M+1}} . \tag{3.23}$$

As before, the effective potential between the complexes is defined by the Fourier transform in the momentum transfer of the second-order T-matrix element due to the interaction H_1 in Eq. (3.20). Once again, I ignore all short-ranged terms and following the same procedure used in Sec. II. in terms of the two-center spectral sum defined in Eq. (3.23), I find the momentum-dependent effective potential to be

$$\bar{V}(R, \mathbf{p}\cdot\mathbf{R}, p^2) \equiv \sum_{L_A, L_B = 1}^{\infty} \sum_{M,J=0}^{\infty} \bar{V}_{MJ}^{L_A L_B}(R)(-i\mathbf{p}\cdot\mathbf{R})^M p^{2J} , \tag{3.24}$$

where

$$\bar{V}_{MJ}^{L_A L_B}(R) = -e^2 D_{M+2J+1}^{L_A L_B} R^{-2(L_A + L_B + M + J + 1)} \times \frac{B((L_A + L_B), M, J)}{(L_A + L_B)!} \frac{(2L_A + 2L_B)!}{(2L_A)!(2L_B)!} , \tag{3.25}$$

and

$$B((L_A + L_B), M, J) = \frac{(M + 2J + L_A + L_B)!(2M + 2J)!}{M!J!(M+J)!} \tag{3.26}$$

is the same function defined in Eq. (2.25) with $L_A + L_B$ replacing L. On comparing Eq. (3.25) with Eq. (2.26), the isomorphism between the $L_A - L_B$ multipole interaction in the complex-complex case and the $(L_A + L_B)$th multipole interaction in the charged-particle–complex case is obvious. One simply replaces the factor $-Z_3^2e^2A^L_{M+2J+1}$ by

$$-e^2D^{L_AL_B}_{M+2J+1}\frac{(2L_A+2L_B)!}{(2L_A)!(2L_B)!}$$

and then let L be replaced by (L_A+L_B) in the rest of the expression. The similarity in the dipole-dipole van der Waals interaction between a pair of atoms and the quadrupole interaction in the two–Coulomb-photon exchange effective potential in electron-atom interaction has been noted before.[35] The present analysis gives a generalization of this isomorphism.

The energy-dependent but otherwise local effective potential for the complex-complex long-range Coulombic interaction can be readily written down from Eqs. (2.34)–(2.37) and the isomorphism just identified. I write

$$V(R,p^2)\equiv\sum_{L_A,L_B=1}^{\infty}\sum_{M,J=0}^{\infty}V^{L_AL_B}_{MJ}(R)p^{2J}\ . \tag{3.27}$$

Then the Mth-order nonadiabatic correction to the L_AL_B multipole contribution to the effective potential at threshold energy is

$$V^{L_AL_B}_{M0}(R)=(-1)^{M+1}e^2D^{L_AL_B}_{M+1}R^{-2(M+L_A+L_B+1)}\times\frac{(2M)!(2M+2L_A+2L_B)!}{2^{2M}(M!)^2(2L_A)!(2L_B)!}\ . \tag{3.28}$$

For $M=0$, $\alpha=\beta=1$, $Z_1=-Z_2$, and $Z_3=-Z_4$, this reduces to the well-known L_A-L_B multipole analog of the London-van der Waals potential.[3–5,38,39] The Mth order nonadiabatic correction to the L_AL_B multipole contribution to the effective potential first order in energy correction is

$$V^{L_AL_B}_{M1}(R)=(-1)^{M+1}e^2D^{L_AL_B}_{M+3}R^{-2(M+L_A+L_B+2)}\times\frac{(2M+1)!}{2^{2M+1}}\frac{(2M+2L_A+2L_B+2)!}{(M!)^2(2L_A)!(2L_B)!}\ . \tag{3.29}$$

For $L_A=L_B=1$, $\alpha=\beta=1$, $Z_1=-Z_2=-1$, and $Z_3=-Z_4=-1$, this reduces to the result derived by the author recently.[35]

IV. FURTHER DISCUSSIONS AND SUMMARY

In this paper, corrections to the two-dipole–Coulomb-photon exchange effective potential due to multipole interactions, finite-mass effects between the interacting particles, and (nuclear) finite-mass effects within the complex have been considered in a unified manner. Finite nuclear mass leads to an effective damping of the multipole interaction. Finite projectile and/or target masses lead to the nonadiabatic corrections. There is also an isomorphism between the L_A-L_B multipole interaction involving two complexes and the (L_A+L_B)th order multipole interaction involving a point charge and a complex.

When both interacting particles have a net charge, there is a monopole interaction. This monopole interaction is the ordinary Coulomb interaction and can be included either in the unperturbed Hamiltonian or as part of the perturbation. In the former case, the relative motion between the interacting particles can no longer be described by plane waves as the unperturbed states. This has an effect on the calculation of the nonadiabatic corrections at second order and beyond. In the latter case, angular momentum conservation prevents the complex from participating in any two-photon process involving one-monopole and one-multipole photons. The two-monopole–Coulomb-photon exchange effective potential is divergent and in fact must be excluded because it duplicates the iteration of the one-monopole–Coulomb-photon exchange effective potential. For this case, the unperturbed states of the relative motion between the interacting particles are still plane waves. However, the three–Coulomb-photon exchange effective potential involving a monopole photon in between two multipole photon of the same multipolarity cannot be generated by iterating the Coulomb potential and the two-multipole–Coulomb-photon exchange potential and in fact this type of process generates part of the difference between the second nonadiabatic corrections calculated for the two cases. Therefore one must decide which case to follow depending on what best describes the initial conditions. Consistency is the key.

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