

## Multipole and Finite-Mass Corrections in Long-Range Coulombic Interactions†

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(Received November 25, 1988)

All multipole, nonadiabatic and finite nuclear-mass corrections to the long-range effective potential due to two-Coulomb-photon exchange between coulombic systems are considered on an equal footing and in a unified manner. Simple expressions are derived for these corrections to the effective potential at the threshold energy and also first-order in energy correction for the scattering between a spinless point-charged particle and a spinless coulombic complex (electron-atom scattering without spin) and between two spinless coulombic complexes (atom-atom scattering without spin). 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 mass-polarization terms are avoided by suitable choice of Jacobi coordinates.

† Presented at the First Asia-Pacific Conference on Atomic and Molecular Physics, 25-29 November, 1988, Taipei, Taiwan, Republic of China.

### 1. INTRODUCTION

Long-range coulombic interactions play an important role in the study of the properties of atoms and molecules. By long-range, I mean any effective potential that falls off according to some inverse power of  $R$ , the distance between the interacting systems. When one of the interacting systems is overall electrically neutral, the single-photon exchange effect is highly suppressed, leaving only short-range, exponentially decreasing potentials. However, multi-photon exchanges do lead to long-range potentials. The van der Waals interaction is a celebrated example.<sup>2-8</sup>

Another well known example for which multi-photon exchange leads to long-range forces is the scattering of a charged particle by a neutral atom.<sup>9-18</sup>

recognized that the classical polarization potential is inadequate to describe the effective interaction. The adjustment of the atomic electron cloud due to the motion of the scattering charged particle gives rise to the distortion or nonadiabatic potential. " - ' " If the target atom and a charged projectile are both infinitely massive, these nonadiabatic corrections vanish. In this case, the distance  $R$  between the target and the projectile is strictly a parameter, not a dynamic variable. The effective potential is then given by the energy shift, in the presence of each other, separated by the distance  $R$ .<sup>19</sup> This result was obtained long ago by Dalgarno and Lynn.<sup>20</sup>

Finite mass of the target also leads to the mass polarization effect, which is commonly known as the nuclear recoil effect.<sup>21,22</sup> Such classification into nonadiabatic and nuclear recoil corrections is quite arbitrary as they both arise from finite mass. In the case of scattering of a positronium atom by a heavy charged particle, such as a proton, the " nuclear" recoil or mass polarization, correction is maximal. One purpose of the present paper is to show that it is possible to treat all finite mass corrections in a unified manner.

Let  $W$  be a typical excitation energy of the coulombic composite system and  $\mu$  the reduced mass of the interacting systems. The nonadiabatic corrections go according to powers of  $(\mu W R^2)^{-1}$ . If  $\mu$  is of the order of the mass of the lighter particle in the coulombic composite, then  $(\mu W R^2)^{-1}$  is essentially  $(a/R)^2$  where  $a$  is the size of the coulombic composite. In this case, the nonadiabatic corrections are of the same order as the multipole corrections and they should be considered on equal footing. As we shall see, the nuclear recoil corrections lead to an effective modification of the multipole interactions. The degree of modification depends on the mass and charge ratios of the constituents of the coulombic composite. An important example is a system involving positronium.

The effective potential between the coulombic systems is defined as the Fourier transform of the scattering transition amplitude in the momentum transfer  $\vec{Q}$  with respect to  $\vec{R}$ , the distance vector between the systems. The transition amplitude is calculated according to time-ordered diagrammatic perturbation theory. In the present discussion, I concentrate on the Coulombic interaction and hence ignore all transverse photon exchange effects. Such transverse photon exchange contributions can be incorporated in a systematic manner and lead to the Casimir corrections in the long-range electromagnetic interaction. In the next section, we describe the procedure to obtain the effective potential from the scattering amplitude in a time-ordered calculation.

The present paper treats, on an equal footing and in a unified manner, the 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  $Z_1 e$ ,  $Z_2 e$  and  $Z_3 e$ . Particles 1 and 2 are assumed to form a bound system and to be, for the sake of a simplified discussion, in a state of zero angular momentum. of the interaction between a charged particle and either a neu case is applicable to the study of Rydberg states. Then I consider the case of four charged, spinless particles of masses  $m_1, m_2, m_3, m_4$  and charge  $eZ_1, Z_2 e, Z_3 e, Z_4 e$  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 exclude from consideration the graph corresponding to the exchange of two-monopole Coulomb photons. The conservation of angular momentum 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 in complex A as in 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 is not considered. Therefore, I limit the discussion to only the case  $L_A \neq 0$  and  $L_B \neq 0$ .

As stated earlier, a finite "nuclear" mass within the Coulombic complex (atom) leads to the multipole modification factor, and a 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. I use the Jacobi coordinates<sup>21</sup> and  $\mu$  is set equal to unity. The transverse-photon exchange effect (Casimir correction) is not considered. Much of the present discussion has recently appeared in print<sup>23,24</sup>

## 11. THE EFFECTIVE POTENTIAL FROM THE TIME-ORDERED SCATTERING AMPLITUDE

The transition amplitude for the state of relative motion from  $|\vec{p}\rangle$  to  $|\vec{p}'\rangle$  due to an interaction  $H_1$  is:

$$M(\vec{p}, \vec{p}') = -\sum_n \int \frac{d^3 l}{(2\pi)^3} \frac{\langle \vec{p}', 0 | H_1 | \vec{l}, n \rangle \langle \vec{l}, n | H_1 | \vec{p}, 0 \rangle}{\Delta_n + T}, \quad (2.1)$$

in which

$$\Delta_n \equiv E_n - E_0 \quad (2.2)$$

is the excitation energy for the internal degree of freedom and

$$T \equiv \frac{l^2 - p^2}{2\mu} \quad (2.3)$$

is the recoil energy of the relative motion. For the state denoted by  $|\vec{l}, n\rangle$ , the former variable describes the state of relative motion and the latter describes the state of internal motion of the interacting composite systems. Rotational invariance requires that  $M$  be a function of scalar quantities formed from  $\vec{p}$ ,  $\vec{p}'$ , or from  $\vec{Q} \equiv \vec{p}' - \vec{p}$  if the state  $|0\rangle$  is invariant under rotation. Off the energy shell,  $M$  is a function of  $p^2$ ,  $Q^2$  and  $\vec{p} \cdot \vec{Q}$ . I denote this by  $\bar{M}(p^2, Q^2, \vec{p} \cdot \vec{Q})$ . On the energy shell, because of overall energy conservation  $p^2 = p'^2$ ; thus  $\vec{p} \cdot \vec{Q} = -Q^2/2$ . According to this constraint,  $\bar{M}$  reduces to the on-shell amplitude  $M$ :

$$M(p^2, Q^2) = \bar{M}(p^2, Q^2, \vec{p} \cdot \vec{Q})|_{\vec{p} \cdot \vec{Q} = -Q^2/2} \quad (2.4)$$

In the physical region,  $Q^2 \leq 4p^2$ . However, it is possible to do an analytic continuation in  $Q$  for the function  $M$ ; in fact this is necessary before a Fourier transform of  $M$  in  $Q$  is carried out. Hence even at threshold energy when  $p^2 = 0$ , the transition amplitude is defined for all  $Q$ . The correct effective potential is given by the Fourier transform in  $\vec{Q}$  of the on-shell amplitude  $M$  and not of the off-shell  $\bar{M}$ . Thus the effective potential can only be a function of  $p^2$  and  $R$ , with the  $p^2$ -dependence signifying energy dependence,

$$V(p^2, R) = \int \frac{d^3Q}{(2\pi)^3} e^{i\vec{Q} \cdot \vec{R}} M(p^2, Q^2) \quad (2.5)$$

In some cases, it may be inconvenient to complete the calculation of the transition amplitude before the Fourier transform in  $Q$  is carried out. In this case, the opportunity to impose the energy shell condition, i.e.,  $\vec{p} \cdot \vec{Q} = -Q^2/2$  is missed, possibly as a result of a change in the order of integration. Consequently, instead of the correct effective potential  $V$  defined as the Fourier transform of the on-shell amplitude  $M$ , one obtains  $\bar{V}$ , the Fourier transform of the off-shell amplitude  $\bar{M}$ :

$$\bar{V}(p^2, R, i\vec{p} \cdot \vec{R}) = \int \frac{d^3Q}{(2\pi)^3} e^{i\vec{Q} \cdot \vec{R}} \bar{M}(p^2, Q^2, \vec{p} \cdot \vec{Q}). \quad (2.6)$$

However,  $\bar{V}$  would be the incorrect potential to use; it also suffers from the pathology of having nonhermitian terms. Thus, a procedure needs to be established to convert  $\bar{V}$  into  $V$ . The details of one such procedure have recently been given.<sup>23</sup> I give only the essence here and refer the readers to the original papers for the details. In fact, in the calculations reported later in this paper as well as in several other cases in which I try to obtain the effective potential from the time-ordered scattering amplitude, I find it more convenient to first calculate  $\bar{V}$  and then follow the procedure described below to obtain the correct effective potential  $V$ .

I begin with the assumption that  $\bar{V}$ , as given by Eq. (2.6) can be expanded in series:

$$\bar{V}(p^2, R, i\vec{p} \cdot \vec{R}) = \sum_{kj} \bar{V}_{kj}(R) (-i\vec{p} \cdot \vec{R})^k p^{2j}, \quad (2.7)$$

and that the off-shell amplitude  $\bar{M}$  is also expanded in series!

$$\bar{M}(p^2, Q^2, \vec{p} \cdot \vec{Q}) = \sum_{\mathbf{k}, j} M_{\mathbf{k}j}(Q^2) (\vec{p} \cdot \vec{Q})^k p^{2j}, \quad (2.8)$$

which on the energy shell reduces to:

$$M(p^2, Q^2) = \sum_{\mathbf{k}, j} M_{\mathbf{k}j}(Q^2) (-Q^2/2)^k p^{2j}. \quad (2.9)$$

The correct effective interaction potential is the Fourier transform of the on-shell scattering amplitude  $M$  in the variable  $\vec{Q}$  with respect to  $\vec{R}$ :

$$\begin{aligned} V(p^2, R) &\equiv \int \frac{d^3 Q}{(2\pi)^3} e^{i\vec{Q} \cdot \vec{R}} M(p^2, Q^2) \\ &= \sum_j p^{2j} \sum_k \left(\frac{\nabla^2}{2}\right)^k F_{\mathbf{k}j}(R) \\ &\equiv \sum_{\mathbf{j}, \mathbf{k}} p^{2j} V_{\mathbf{k}j}(R) \end{aligned} \quad (2.10)$$

in which

$$F_{\mathbf{k}j}(R) \equiv \int \frac{d^3 Q}{(2\pi)^3} e^{i\vec{Q} \cdot \vec{R}} M_{\mathbf{k}j}(Q^2). \quad (2.11)$$

In terms of the functions  $F_{\mathbf{k}j}$ , by direct use of Eqs. (2.7) and (2.10), one obtains

$$\bar{V} = \sum_{\mathbf{j}, \mathbf{k}, m} p^{2(j+m)} (-i\vec{p} \cdot \vec{R})^{k-2m} C_{2m}^k \frac{(2m+1)!!}{(2m+1)} (-i)^{2m} \left(\frac{1}{R} \frac{\partial}{\partial R}\right)^{k-m} F_{\mathbf{k}j}(R) \quad (2.12)$$

in which

$$C_{2m}^k = \frac{k!}{(2m)!(k-2m)!} \quad (2.13)$$

is the usual combinatorial factor. By direct comparison of Eq. (2.1) with Eq.(2.7), one obtains

$$V_{\mathbf{k}j}(R) = \sum_{m=0}^{\lfloor k/2 \rfloor} C_{2m}^{k+2m} \frac{(2m+1)!!}{(2m+1)} (-i)^{2m} D^{k+m} F_{\mathbf{k}+2\mathbf{m}, \mathbf{j}-\mathbf{m}}(R) \quad (2.14)$$

where for convenience, I define the differential operator:

$$D \equiv \frac{1}{R} \frac{d}{dR}, \quad (2.15)$$

and its inverse  $I \equiv D^{-1}$  such that for any function  $f(R)$

$$I f(R) \equiv \int_{-\infty}^R x f(x) dx. \quad (2.16)$$

In general, Eq. (2.16) can be inverted in sequence and a general solution can be written in recurrent form:

$$F_{kj} = I^k V_{kj} - \sum_{m=1}^j C_{2m}^{k+2m} \frac{(2m+1)!!}{(2m+1)} (-i)^{2m} D^m F_{k+2m, j-m} \quad (2.17)$$

in which we have suppressed the functional dependence on  $R$  of the  $F_{kj}$  and  $V_{kj}$  without fear of confusion. Once the  $F_{kj}$  are determined, the correct effective potential can be obtained by using Eq. (2.10). At threshold energy,  $p^2 = 0$  and only the terms with  $j = 0$  survive in the double sum. Higher terms in  $k$  give the nonadiabatic corrections.

### 111. THE CHARGED PARTICLE – COULOMBIC COMPLEX INTERACTION

Let  $\vec{r}_1, \vec{r}_2$  and  $\vec{r}_3$  be the coordinate vectors of particles 1, 2 and 3 with masses  $m_1, m_2$  and  $m_3$  and charges  $Z_1 e, Z_2 e$  and  $Z_3 e$ . I define the following:

$$\alpha \equiv \frac{m_2}{m_1 + m_2}, \quad (3.1)$$

$$m \equiv m_1 + m_2 + m_3, \quad (3.2)$$

$$\gamma_i \equiv \frac{m_i}{m}, \quad i = 1, 2, 3, \quad (3.3)$$

$$\vec{x} \equiv \vec{r}_1 - \vec{r}_2, \quad (3.4)$$

$$\vec{X} \equiv (1 - \alpha) \vec{r}_1 + \alpha \vec{r}_2, \quad (3.5)$$

$$\vec{R} \equiv \vec{r}_3 - \vec{X}, \quad (3.6)$$

$$\vec{S} \equiv \gamma_1 \vec{r}_1 + \gamma_2 \vec{r}_2 + \gamma_3 \vec{r}_3, \quad (3.7)$$

$$m' \equiv m_1 + m_2, \quad (3.8)$$

$$\mu \equiv \gamma_3 m' = (\gamma_1 + \gamma_2) m_3. \quad (3.9)$$

In terms of these coordinates and variables, the hamiltonian of the three-body coulombic system is:

$$H_t = -\frac{\nabla_x^2}{2\alpha m_1} - \frac{\nabla_R^2}{2\mu} - \frac{\nabla_S^2}{2m} + e^2 \left[ \frac{Z_1 Z_2}{|\vec{x}|} + \frac{Z_1 Z_3}{|\vec{R} - \alpha \vec{x}|} + \frac{Z_2 Z_3}{|\vec{R} + (1 - \alpha)\vec{x}|} \right], \quad (3.10)$$

We notice that in terms of the set of Jacobi coordinates ( $\vec{x}$ ,  $\vec{R}$  and  $\vec{S}$ ), all Hughes-Eckert type mass polarization terms disappear.<sup>21,25</sup> Moreover, because the total hamiltonian is cyclic in  $\vec{S}$ , the center-of-mass energy term drops out. Hence one can replace  $H_t$  by  $H = H_0 + H_1 \equiv h_0 + T + H_1$  in which

$$h_0 = -\frac{\nabla_x^2}{2\alpha m_1} + \frac{e^2 Z_1 Z_2}{|\vec{x}|} \quad (3.11)$$

$$T = -\frac{\nabla_R^2}{2\mu} \quad (3.12)$$

and

$$H_1 = e^2 \left[ \frac{Z_1 Z_3}{|\vec{R} - \alpha \vec{x}|} + \frac{Z_2 Z_3}{|\vec{R} + (1 - \alpha)\vec{x}|} \right], \quad (3.13)$$

$$= \frac{e^2 Z_3}{2\pi^2} \int \frac{d^3 k}{k^2} e^{i\vec{k} \cdot \vec{R}} [Z_1 e^{-i\alpha \vec{k} \cdot \vec{x}} + Z_2 e^{i(1-\alpha)\vec{k} \cdot \vec{x}}], \quad (3.14)$$

$$= \frac{Z_3 e^2}{2\pi^2} \int \frac{d^3 k}{k^2} e^{i\vec{k} \cdot \vec{R}} \sum_{L=0}^{\infty} \frac{(-i\vec{k} \cdot \vec{x})^L}{L!} [Z_1 \alpha^L + Z_2 (\alpha - 1)^L] \quad (3.15)$$

$$\equiv \sum_{L=0}^{\infty} h_1^L. \quad (3.16)$$

At this point, I make the following observations: i) the eigenvalues of  $h_0$  are scaled to the hydrogenic eigenvalues by the factor  $(-Z_1 Z_2 \alpha m_1 / m_e)$  with  $m_e$  the electron mass. ii) For a neutral complex,  $Z_1 + Z_2 = 0$ , and the  $L = 0$  term inside the square bracket in Eq. (3.15) vanishes, corresponding to the absence of the coulombic monopole interaction. iii) For a neutral complex, that the  $L = 1$  term in Eq. (3.15) is independent of  $\alpha$  indicates that a finite "nuclear" mass does not affect the coulombic dipole interaction. This case does not apply if the complex has a net charge. iv) In the special case that  $Z_1 = -Z_2$  and  $\alpha = 1/2$  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 condition corresponds to the total suppression of even electric multipole interactions in such self-conjugate systems.<sup>26</sup> v) For  $\alpha = 1$  corresponding to infinite nuclear mass, Eqs. (3.15) and (3.16) 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 Coulombic field of the charged complex in the Jacobi coordinate  $\vec{R}$ .

With the above observations 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  $Z_1 + Z_2 \neq 0$  are discussed in the last section. I follow the procedure described in Sec. II to obtain the multipole and non-adiabatic corrections to the two-coulomb-photon exchange effective potential. Let  $|0\rangle$  be the initial zero angular momentum state of the neutral complex and  $E_n$  be the energy eigenvalue for the state  $|n\rangle$ . I define:

$$\Delta_n \equiv 2\mu(E_n - E_0). \quad (3.17)$$

Then the effective potential in momentum-dependent form corresponding to the Fourier transform of the second-order transition amplitude due to the interaction  $H_1$  is:

$$\bar{V}(\mathbf{p}^2, \mathbf{R}, i\vec{p} \cdot \vec{R}) = \frac{2\mu Z_1^2 e^4}{4\pi^4} \int \frac{d^3 k}{k^2} e^{i\mathbf{k} \cdot \vec{R}} \int \frac{d^3 q}{q^2} e^{i\mathbf{q} \cdot \vec{R}} K(\vec{p}, \vec{k}, \vec{q}), \quad (3.18)$$

where

$$K(\vec{p}, \vec{k}, \vec{q}) = \sum_{L, L_2=1}^{\infty} \frac{[Z_1 \alpha^{L_1} + Z_2 (\alpha - 1)^{L_1}] [Z_1 \alpha^{L_2} + Z_2 (\alpha - 1)^{L_2}]}{L! L_2!} \frac{\langle 0 | (-i\vec{k} \cdot \vec{x})^{L_1} | n \rangle \langle n | (-i\vec{q} \cdot \vec{x})^{L_2} | 0 \rangle}{\Delta_n + k^2 + 2\vec{p} \cdot \vec{k}} \quad (3.19)$$

I define the following single-center  $L$ -th multipole atomic spectral sum:

$$A_{M+1}^L \equiv 2\mu e^2 [Z_1 \alpha^L + Z_2 (\alpha - 1)^L]^2 \sum_n \frac{|\langle 0 | x^L P_L | n \rangle|^2}{\Delta_n^{M+1}} \quad (3.20)$$

Here  $P_L$  is the Legendre polynomial of order  $L$ . For hydrogenic atoms, the sum rule in the right-hand side of Eq. (3.20) has recently been evaluated in closed form<sup>27,28</sup>. Its numerical evaluation is a straightforward computation. Then following the procedure described in Sec. II and taking advantage of the fact that factors of  $k_i$  and  $q_j$  inside the integral can be replaced by differentiation with respect to  $R_i$  and  $R_j$  outside the integral, one finds Eq. (3.18) can be expressed in terms of these sum rules:

$$\bar{V}(\mathbf{R}, \vec{p} \cdot \vec{R}, p^2) = -Z_1^2 e^2 \sum_{N,L} A_{N+1}^L \frac{(2i)^N (R_{i_1} \dots R_{i_L})(p_{j_1} \dots p_{j_N})}{L! R^{2L+1}} (\partial_{i_1} \dots \partial_{i_L})(\partial_{j_1} \dots \partial_{j_N}) \left(\frac{1}{R}\right) \quad (3.21)$$

$$\equiv \sum_{L=1}^{\infty} \sum_{M=0}^{\infty} \sum_{J=0}^{\infty} \bar{V}_{MJ}^L(\mathbf{R}) (-i\mathbf{f} \cdot \vec{R})^M p^{2J} \quad (3.22)$$



On directly, comparing Eq. (3.22) with Eq. (3.21) j. I find

$$\bar{V}_{MJ}^L(R) = \frac{-Z_3^2 e^2}{L!} A_{M+2J+1}^L R^{-2(L+M+J+1)} B(L, M, J) \quad (3.23)$$

in which

$$B(L, M, J) = 2^{M+2J} C_{2J}^{M+2J} \frac{(2J)!}{2J} \sum_{k,j} \frac{k!}{J!} C_k^M C_k^L C_{2j}^{L-k} \frac{(2j)!}{2^j j!} (-1)^{j+k} (2L + 2M + 2J - 2j - 2k - 1)!! \quad (3.24)$$

and  $C_n^N \equiv N!/[n!(N-n)!]$  is the usual combinational factor and the double factorial  $(2j+1)!!$  is defined by the product  $\prod_{i=0}^j (2i+1)$ . I carry out the sum in  $k$  and  $j$  in Eq. (3.24) for  $L=1$  and  $2$  and for all values of  $M$  and  $J$ . Then by reference to Eq. (3.21) from which the coefficient  $B(L, M, J)$  defined in Eq. (3.24) arises, I prove by mathematical induction that

$$B(L, M, J) = \frac{(M+2J+L)!(2M+2J)!}{M!J!(M+J)!}. \quad (3.25)$$

For the particular case that  $J=0$ , this reduces to the combinatorial identity that I conjectured and subsequently verified.<sup>29</sup> On substituting Eq. (3.25) into Eq. (3.23), I have

$$\bar{V}_{MJ}^L(R) = -Z_3^2 e^2 A_{M+2J+1}^L R^{-2(L+M+J+1)} \left[ \frac{(M+2J+L)!(2M+2J)!}{L!M!J!(M+J)!} \right] 1. \quad (3.26)$$

Equation (3.26), when substituted into Eq. (3.22), provides a convenient form to convert the momentum-dependent effective potential into a local form according to Eqs. (2.10) and (2.17). Upon expanding the energy-dependent but otherwise local effective potential in powers of  $p^2$  and in multipoles, one has:

$$V(p^2, R) \equiv \sum_{L=1}^{\infty} \sum_{M,J=0}^{\infty} V_{MJ}^L(R) p^{2J}. \quad (3.27)$$

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. (3.22) via the  $L$ -th multipole analog of Eqs. (2.10) and (2.17)

$$V_{MJ}^L = \left(\frac{\Delta^2}{2}\right)^M F_{MJ}^L, \quad (3.28)$$

$$F_{MJ}^L = I^M V_{MJ}^L - \sum_{m=1}^J C_{2m}^{M+2m} (2m-1)!! (-i)^{2m} D^m F_{M+2m, J-M}^L, \quad (3.29)$$

in which the operators  $D$  and  $I$  are defined in Eqs. (2.15) and (2.16). By a direct calculation, one can easily obtain the truly local effective potential at threshold energy and its lowest-order energy correction:

$$V_{M0}^L(R) = \left(\frac{\nabla^2}{2}\right)^M I^M \bar{V}_{M0}^L(R) , \quad (3.30)$$

and

$$V_{M1}^L(R) = \left(\frac{\nabla^2}{2}\right)^M [I^M \bar{V}_{M1}^L(R) + C_2^{M+2} I^{M+1} \bar{V}_{M+2,0}^L(R)] . \quad (3.31)$$

Then using Eqs. (3.26) and (3.30), I find

$$V_{M0}^L(R) = \frac{(-1)^{M+1} Z_3^2 e^2 A_{M+1}^L (2M)!(2M+2L)!}{R^{2(M+L+1)} 2^{2M} (M!)^2 (2L)!} \quad (3.32)$$

$$= \frac{(-1)^{M+1} Z_3^2 e^2 A_{M+1}^L (2M+2L-1)!!(2M-1)!!(M+L)!}{R^{2(M+L+1)} (2L-1)!! L! M!} , \quad (3.33)$$

and using Eqs. (3.26) and (3.31), I find:

$$V_{M1}^L(R) = \frac{(-1)^{M+1} Z_3^2 e^2 A_{M+3}^L (2M+2L+1)!!(2M+1)!!(M+L+1)!}{R^{2(M+L+2)} (2L-1)!! L! M!} \quad (3.34)$$

$$= \frac{(-1)^{M+1} Z_3^2 e^2 A_{M+3}^L (2M+1)! (2M+2L+2)!}{R^{2(M+L+2)} 2^{(2M+1)} (M!)^2 (2L)!} \quad (3.35)$$

In Eq. (3.33),  $(2M-1)!!$  is taken to be unity for  $M=0$ . In Eq. (3.32), the term corresponding to  $L=1$  (dipole),  $M=1$  (first nonadiabatic correction) agrees with earlier known results.<sup>9,11</sup> The present result is a generalization.

#### IV. THE COMPLEX-COMPLEX LONG-RANGE COULOMBIC INTERACTION

Let  $\vec{r}_1, \vec{r}_2, \vec{r}_3$  and  $\vec{r}_4$  be the coordinate vectors of particles 1, 2, 3 and 4, with masses  $m_1, m_2, m_3$  and  $m_4$ , and charges  $Z_1 e, Z_2 e, Z_3 e$  and  $Z_4 e$ , 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:

$$m_A \equiv m_1 + m_2 \quad (4.1)$$

$$m_B \equiv m_3 + m_4 \quad (4.2)$$

$$a \equiv m_2/m_A \quad (4.3)$$

$$\beta \equiv m_4/m_B \quad (4.4)$$

$$m \equiv m_A + m_B \quad (4.5)$$

$$\gamma_i \equiv m_i/m \quad , i = 1, 2, 3, 4, \quad (4.6)$$

$$\vec{x} \equiv \vec{r}_1 - \vec{r}_2 \quad (4.7)$$

$$\vec{y} \equiv \vec{r}_3 - \vec{r}_4 \quad (4.8)$$

$$\vec{X} \equiv (1 - \alpha)\vec{r}_1 + \alpha\vec{r}_2 \quad (4.9)$$

$$\vec{Y} \equiv (1 - \beta)\vec{r}_3 + \beta\vec{r}_4 \quad (4.10)$$

$$\vec{R} \equiv \vec{Y} - \vec{X} \quad (4.11)$$

$$\vec{S} \equiv \sum_i \gamma_i \vec{r}_i \quad (4.12)$$

and

$$\mu \equiv m_A m_B / m \quad (4.13)$$

Then, in terms of the Jacobi coordinates  $\vec{x}, \vec{y}, \vec{R}$  and  $\vec{S}$ , the total hamiltonian is cyclic in  $\vec{S}$  and the kinetic energy of the center of mass of the entire system is a conserved quantity and can be dropped. The hamiltonian is thus expressed in the form:

$$H = h_{0A} + h_{0B} + T + H, \quad (4.14)$$

in which

$$h_{0A} \equiv \frac{\nabla_x^2}{2\alpha m_1} + \frac{Z_1 Z_2 e^2}{|\vec{x}|} \quad (4.15)$$

$$h_{0B} \equiv -\frac{\nabla_y^2}{2\beta m_3} + \frac{Z_3 Z_4 e^2}{|\vec{y}|} \quad (4.16)$$

$$T \equiv \frac{\nabla_R^2}{2\mu}, \quad (4.17)$$

and

$$H_1 \equiv e^2 \left[ \frac{Z_1 Z_3}{|\vec{R} + \beta\vec{y} - \alpha\vec{x}|} + \frac{Z_2 Z_4}{|\vec{R} + (1-\alpha)\vec{x}(1-\beta)\vec{y}|} \right. \\ \left. + \frac{Z_2 Z_3}{|\vec{R} + (1-\alpha)\vec{x} + \beta\vec{y}|} + \frac{Z_1 Z_4}{|\vec{R} - \alpha\vec{x} - (1-\beta)\vec{y}|} \right] \quad (4.18)$$

$$= e^2 \int \frac{d^3 k}{k^2} e^{i\vec{k} \cdot \vec{R}} [Z_1 e^{-i\alpha\vec{k} \cdot \vec{x}} + Z_2 e^{i(1-\alpha)\vec{k} \cdot \vec{x}}] [Z_3 e^{i\beta\vec{k} \cdot \vec{y}} + Z_4 e^{-i(1-\beta)\vec{k} \cdot \vec{y}}] \quad (4.19)$$

$$= \sum_{L_A, L_B=0}^{\infty} h_1^{L_A L_B} \quad (4.20)$$

in which

$$h_1^{L_A L_B} \equiv e^2 \int \frac{d^3 k}{k^2} [Z_1 (-\alpha)^{L_A} + Z_2 (1-\alpha)^{L_A}] \frac{(i\vec{k} \cdot \vec{x})^{L_A}}{L_A!} \\ [Z_3 \beta^{L_B} + Z_4 (\beta-1)^{L_B}] \frac{(i\vec{k} \cdot \vec{y})^{L_B}}{L_B!} \quad (4.21)$$

As observed in Section III, the quantities in the square brackets in Eq. (4.21) act as multipole modification 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 Section III 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:

$$A_{n_A n_B} \equiv 2\mu [E_{n_A} - E_{0_A} + E_{n_B} - E_{0_B}] \quad (4.22)$$

and the two-center correlated multipole spectral sum:

$$D_{M+1}^{L_A L_B} \equiv 2\mu e^2 [Z_1 (-\alpha)^{L_A} + Z_2 (1-\alpha)^{L_A}]^2 [Z_3 \beta^{L_B} + Z_4 (\beta-1)^{L_B}]^2 \\ \sum_{n_A, n_B} \frac{|\langle 0_A | x^{L_A} P_{L_A} | n_A \rangle|^2 |\langle 0_B | y^{L_B} P_{L_B} | n_B \rangle|^2}{\Delta_{n_A n_B}^{M+1}} \quad (4.23)$$

For a pair of hydrogenic atoms, the two-center correlated multipole spectral sum can be calculated to very high precision using the pseudo-state method<sup>30</sup> and the relation between multipole and dipole spectral sums through  $O_4$  symmetry, as demonstrated in Ref. 28. As before, the effective potential between the complexes is defined by the Fourier transform in the momentum transfer of the second-order transition amplitude due to the interaction  $H_1$  in Eq. (4.20). Once again, I ignore all short-range terms; following the same procedure used in the last section, in terms of the two-center spectral sum defined in Eq. (4.23). I find the momentum-dependent effective potential to be:

$$\bar{V}(p^2, \mathbf{R}, i\vec{p} \cdot \vec{R}) \equiv \sum_{L_A, L_B=1}^{\infty} \sum_{M, J=0}^{\infty} \bar{V}_{MJ}^{L_A L_B}(\mathbf{R}) (-i\vec{p} \cdot \vec{R})^M p^{2J}, \quad (4.24)$$

in which

$$\bar{V}_{MJ}^{L_A L_B}(\mathbf{R}) = -e^2 D_{M+2J+1}^{L_A L_B} R^{-2(L_A+L_B+M+J+1)} \frac{B((L_A+L_B), M, J)}{(L_A+L_B)!} \left[ \frac{(2L_A+2L_B)!}{(2L_A)!(2L_B)!} \right], \quad (4.25)$$

and

$$B((L_A+L_B), M, J) = \frac{(M+2J+L_A+L_B)!(2M+2J)!}{M! J!(M+J)!} \quad (4.26)$$

is the same function defined in Eq. (3.25) with  $L_A+L_B$  replacing  $L$ . By comparison of Eq. (4.25) with Eq. (3.26), 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  $[-Z_3^2 e^2 A_{M+2J+1}^L]$  by  $[-e^2 D_{M+2J+1}^{L_A L_B} \frac{(2L_A+2L_B)!}{(2L_A)!(2L_B)!}]$  and then let  $L$  be replaced by  $(L_A+L_B)$  in the rest of the expression.

The energy-dependent but otherwise local effective potential for the complex-complex long-range Coulombic interaction can be written from Eqs. (3.32)–(3.35) and the isomorphism just identified. I write:

$$V(p^2, \mathbf{R}) \equiv \sum_{L_A, L_B=1}^{\infty} \sum_{M, J=0}^{\infty} V_{MJ}^{L_A L_B}(\mathbf{R}) p^{2J} \quad (4.27)$$

Then the  $M$ th order nonadiabatic correction to the  $L_A L_B$  multipole contribution to the effective potential at threshold energy is:

$$V_{M0}^{L_A L_B}(\mathbf{R}) = (-1)^{M+1} e^2 D_{M+1}^{L_A L_B} R^{-2(M+L_A+L_B+1)} \frac{(2M)!(2M+2L_A+2L_B)!}{2^{2M} (M!)^2 (2L_A)!(2L_B)!} \quad (4.28)$$

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.<sup>4,5,6,31,32</sup> For  $M=1$  (the first nonadiabatic correction) and  $L_A=L_B=1$  (the dipole-dipole interaction), Eq. (4.28) reduces to earlier known results.<sup>14</sup> The present result is a generalization. The  $M$ th order nonadiabatic

correction to the  $L_A L_B$  multipole contribution to the effective potential first-order in energy correction is:

$$V_{M1}^{L_A L_B}(\mathbf{R}) = (-1)^{M+1} e^2 D_{M+3}^{L_A L_B} \mathbf{R}^{-2(M+L_A+L_B+2)} \frac{(2M+1)!}{2^{2M+1}} \frac{(2M+2L_A+2L_B+2)!}{(M!)^2 (2L_A)!(2L_B)!} \quad (4.29)$$

## V. FURTHER DISCUSSION 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. The finite nuclear mass leads to an effective modification 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 condition has an effect on the calculation of the nonadiabatic corrections at second order and beyond. In the latter case, conservation of angular momentum 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 between two multipole photons of the same multipolarity cannot be generated by iterating the coulomb potential and the two-multipole-coulomb-photon exchange potential; 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.

The effective potentials in the form of Eq. (3.27) [via Eqs. (3.32)–(3.35)] for charged particle-neutral complex scattering and in the form of Eq. (4.27) [via Eqs. (4.28) and (4.29)] for neutral complex-complex scattering are expressed respectively through the

single-center atomic spectral sum  $A_{M+1}^L$  [Eq.(3.20)] and the two-center atomic spectral sum  $D_{M+1}^{LA LB}$  [Eq. (4.23)]. These spectral sums depend on the atoms involved. For hydrogenic atoms, the single-center multipole spectral sums can be given in closed form<sup>27,28</sup>; I refer the readers to these references for detail. For atoms other than hydrogen, the evaluation of these sums depends on the knowledge of the multipole transition oscillator strengths. Bounds on these sums for some atoms have previously been given.<sup>14</sup> Greater complications arise for the two-center spectral sums. For a pair of hydrogenic atoms, Au and Drachman<sup>30</sup> have demonstrated the efficient use of the pseudostate expansion in evaluating these two-center spectral sums. When the system involves atoms other than hydrogen, one may follow the method suggested in Ref. 14; in fact, some values have been suggested for the sum  $D_2^{1,1}$  (corresponding to the factor  $\gamma_1$  in Ref. 14) for certain systems.<sup>14</sup> The present paper is not concerned with the evaluation of these sums.

Note added in proof: Through the use of a dispersion theory approach, the author has recently obtained closed form expressions for energy corrections to all orders. In fact, the contribution to the effective potential from each atomic intermediate state can be expressed in closed form in terms of the Struve and Neuman functions.

#### ACKNOWLEDGEMENT

This work is supported by the National Science Foundation under Grant No. PHY82-17853, supplemented by funds from NASA at the Institute for Theoretical Physics at Santa Barbara and by the National Science Foundation under Grant No. PHY87-10118 at the University of South Carolina. I also thank the Institute for Atomic and Molecular Sciences, Academia Sinica for the kind hospitality during the conference.

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