Long-range forces between a charged and neutral system

G. Feinberg
Department of Physics, Columbia University, New York, New York 10027

J. Sucher
Center for Theoretical Physics, Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742
(Received 8 November 1982)

Dispersion-theory techniques, previously used to calculate the two-photon exchange potential $V_{2\gamma}(R)$ between two neutral systems, are used to study $V_{2\gamma}(R)$ acting between a neutral system A and a charged system B. For the case when A is an atom and B an electron, general results are given for all corrections of order $\lambda\!\!\!^{-}_e/R$ or of order $(a_0/R)^2$ relative to the leading R^{-4} term.

I. INTRODUCTION

Detailed calculations of the two-photon potential (van der Waals interaction) between two neutral atoms, at an arbitrary separation R greater than a few atomic radii, have been carried out by a variety of methods.[1,2] The most general of these calculations include magnetic effects as well as higher multipoles. The results can be expressed in terms of the frequency-dependent electric and magnetic polarizabilities of the atoms, in a variety of forms.[3,4]

Two-photon exchange also generates potentials between a neutral and a charged system. Some progress has been made in computing the potential in this case,[5–7] but, as far as we know, a result valid at all R has not been given. In this paper we calculate the two-photon exchange potential between a charge and a neutral spinless atom at all separations greater than a few atomic radii. The result can again be expressed in terms of electric and magnetic polarizabilities of the systems. In order to put these results into a form similar to that obtained for neutral systems, it is again necessary to use an expansion in inverse powers of the masses of the two systems. In the present case, if the charged system is an electron, this amounts to an expansion in the ratio of the electron Compton wavelength $\lambda\!\!\!^{-}_e$ to the separation R. This ratio is larger by a factor m_{atom}/m_e than the corresponding ratio in the neutral-neutral case but still small compared to unity, for R larger than a_0, the Bohr radius. Therefore, the first few terms of this expansion will provide an accurate representation of the potential. It is not necessary to expand in powers of kR, where k is a typical atomic excitation energy.

The potential we obtain could be applied, e.g., to the scattering of a low-energy electron from an atom, as long as the impact parameter is greater than several atomic radii. For an electron in a bound state with radius larger than the size of the ionic core, the determination of the two-photon exchange potential between the electron and the core is rather subtle because of the necessity of removing effects corresponding to iteration of the Coulomb interactions, which are normally included in the determination of the bound state wave function, from the overall two-photon exchange potential. This latter problem will not be discussed here.

Our method of calculation is the dispersion-theoretic approach that we have previously used to calculate the potential between neutral systems.[3,4] With a few minor changes, this method can be directly applied to the present case. It is only required to calculate the extra polarizability corresponding to a charged particle. We show in Sec. II that the main difference between this polarizability and that of a neutral system is that, for the charged system, there is a pole at zero energy in the electric polarizability considered as a function of photon energy. This pole contributes a characteristic term to the charge-atom potential whose variation with R is distinct from the neutral-neutral case, where poles occur only at complex photon energies. Nevertheless, as will be seen, this term can be written in various forms analogous to those describing the neutral-neutral potential. If the charge is a point charge, the zero-energy pole term generates the total potential. If the charge itself has a structure, as for an ion, there is an additional term identical to that between two neutral systems. The details of this analysis, as well as some comments on the results are given in Secs. II, III, and IV. Further comments and a comparison with previous work are given in the concluding Sec. V.

II. TWO-PHOTON EXCHANGE BETWEEN A NEUTRAL AND CHARGED PARTICLE

Although the dispersion theory approach to long-range forces has been used primarily to discuss the potentials arising from multiphoton exchange between neutral particles A and B, much of the formalism is applicable when one or both of the particles are charged. We first review the relevant definitions and formulas of Ref. 4 which allow one to express $V_{2\gamma}(R)$ as an integral involving electric and magnetic spectral functions ρ_E^A,ρ_M^A and ρ_E^B,ρ_M^B associated with A and B, respectively. We then consider the form of ρ_E^B and ρ_M^B when B is a charged spin-0 or spin-$\frac{1}{2}$ particle.

A. Notation and review of basic formulas

For the case of two spinless particles A and B, with masses m_A and m_B, respectively, the two-photon exchange potential $V_{2\gamma}(R)$ is given by[3]

$$V_{2\gamma}(R)=\frac{1}{16\pi^2 m_A m_B R}\times\int_0^\infty dt\,\rho_{2\gamma}(t)\exp(-t^{1/2}R)\ , \qquad (2.1)$$

where the spectral function $\rho_{2\gamma}(t)$ is proportional to the discontinuity of $F_{2\gamma}(s,t)$, the two-photon exchange contribution to the invariant amplitude $F(s,t)$ describing the scattering of A and B. Here

$$s=(p_A+p_B)^2\ ,\quad t=(p_A-p_A')^2$$

are the usual invariants, with p_A,p_B the initial momenta and p_A',p_B' the final momenta. Explicitly,

$$\rho_{2\gamma}(t)=\frac{-1}{16\pi^2}\int d\Phi(\Gamma^A_{\mu\nu}\Gamma^B_{\mu'\nu'})_{s=s_0}g^{\mu\mu'}g^{\nu\nu'}\ , \qquad (2.2)$$

where $d\Phi$ is the volume element in the two-photon phase space and $\Gamma^A_{\mu\nu}$ is the tensor amplitude for two-photon emission by A, with $\Gamma^B_{\mu\nu}$ a similarly defined absorption amplitude. The quantity s_0 is the value of s at the scattering threshold,

$$s_0=(m_A+m_B)^2\ .$$

The general form of $\Gamma^A_{\mu\nu}$, as determined by Lorentz covariance and current conservation [see Eq. (2.44) of Ref. 3] is

$$\Gamma^A_{\mu\nu}(k,k';P_A)=m_A[T^A_{E;\mu\nu}F^A_E(\sigma_A^-,t)+T^A_{M;\mu\nu}F^A_M(\sigma_A^-,t)]\ . \qquad (2.3)$$

Here k and k' denote the four-momenta of the emitted photons and

$$\sigma_A^{\pm}=(p_A\pm k)^2\ ,\quad P_A=p_A+p_A'\ .$$

The electric and magnetic tensors $T^A_{E;\mu\nu}$ and $T^A_{M;\mu\nu}$ are defined by

$$T^A_{E;\mu\nu}=\frac{-1}{2m^2}[k\cdot P_A k'\cdot P_A g_{\mu\nu}+k\cdot k' P_{A\mu}P_{A\nu}-k\cdot P_A k'_\mu P_{A\nu}-k'\cdot P_A k_\nu P_{A\mu}] \qquad (2.4a)$$

and

$$T^A_{M;\mu\nu}=T^A_{E;\mu\nu}+2(k\cdot k' g_{\mu\nu}-k_\nu k'_\mu)\ . \qquad (2.4b)$$

The invariant Compton amplitudes F_E^A and F_M^A admit spectral representations of the form

$$F_X^A(\sigma_A^-,t)=\frac{1}{\pi}\int_{m_A^2}^\infty d\sigma'_A\,\rho_X^A(\sigma'_A,t)\times\left[\frac{1}{\sigma'_A-\sigma_A^-}+\frac{1}{\sigma'_A-\bar\sigma_A^+}\right]\ , \qquad (2.5)$$

where

$$\bar\sigma_A^{\pm}=(p_A\mp k')^2$$

and ρ_X^A is a spectral density, determined by the discontinuity of the analytic function F_X^A across the cut on the real axis of the complex σ_A plane.

Although particle B is charged, the analysis given in Ref. 3 for the Compton amplitude still holds because B is on the mass shell. The tensor amplitude $\Gamma^B_{\mu\nu}(-k,-k';P_B)$ for two-photon absorption by B is therefore given in terms of tensors $T^B_{X;\mu\nu}$ and form factors $F_X^B(\sigma,t)$ by equations entirely analogous to (2.5)–(2.9) with the modification that σ_A^- and $\bar\sigma_A^+$ are replaced by σ_B^+ and $\bar\sigma_B^-$, respectively. Here

$$\sigma_B^{\pm}=(p_B\pm k)^2\ ,\quad \bar\sigma_B^{\pm}=(p_B\mp k')^2\ ,$$

$$P_B=p_B+p_B'\ .$$

Substitution of the spectral representations for the F_X's into (2.3) and reversal of the orders of integration yields

$$\rho_{2\gamma}(t)=\sum_{X,Y}\rho_{XY}(t)\ , \qquad (2.6)$$

where

$$\rho_{XY}(t)=\frac{-m_A m_B}{16\pi^2}\int\int d\sigma'_A d\sigma'_B \rho_X^A(\sigma'_A,t)\times\rho_Y^B(\sigma'_B,t)\times\Phi_{XY}(\sigma'_A,\sigma'_B;t) \quad (2.7)$$

with

$$\Phi_{XY}(\sigma'_A,\sigma'_B,t)=\int d\Phi\, T_X^A{:}T_Y^B\left[\frac{1}{\sigma'_A-\sigma_A^-}+\frac{1}{\sigma'_A-\bar{\sigma}_A^+}\right]\times\left[\frac{1}{\sigma'_B-\sigma_B^+}+\frac{1}{\sigma'_B-\bar{\sigma}_B^-}\right]. \quad (2.8)$$

Here

$$T_X^A{:}T_Y^B\equiv T_{X;\mu\nu}^A T_{Y;\mu',\nu'}^B g^{\mu\mu'}g^{\nu\nu'} .$$

The integration in (2.8) can be carried out exactly but the result is complicated and unilluminating. A substantial simplification is obtained by neglecting the ratios t/m_A^2, t/m_B^2, and $t/m_A m_B$ relative to unity. In our previous work[3] this was a marvelous approximation because the important values of t are of order $(\alpha m_e)^2$ or less; with m_A and m_B both atomic masses, all these ratios are of order 10^{-12}. In the present case, m_A is still an atomic mass, but B will be identified with the electron so that t/m_B^2 is at most of order $\alpha^2\sim 10^{-4}$. Thus, an approximation which neglects t/m_B^2 is still justifiable. An alternate way of looking at this comes from recognizing that each power of t in Φ_{XY} generates an additional factor of R^{-2} in $V_{2\gamma}(R)$. Therefore, compared with the leading term, the terms we are neglecting are down by two powers of $\lambda\!\!\!^-_B/R$, where $\lambda\!\!\!^-_B=m_B^{-1}$ is the Compton wavelength of particle B. However, we will keep terms which are down by only one power of $\lambda\!\!\!^-_B/R$.

With these approximations we get, using Eqs. (2.57) of Ref. 4 with ξ_A and ξ_B replaced by unity,

$$\Phi_{XY}\to\Phi_{XY}^{(1)}\equiv\frac{\pi t}{2m_A m_B}(2\tau_A\tau_B)\frac{g_{XY}(\tau_B)-g_{XY}(\tau_A)}{\tau_B^2-\tau_A^2}, \quad (2.9)$$

where

$$g_{EE}(\tau)=g_{MM}(\tau)=\tau^2-(2+2\tau^2+\tau^4)(\tan^{-1}\tau^{-1})\tau^{-1}, \quad (2.10a)$$

$$g_{EM}(\tau)=g_{ME}(\tau)=\tau^2-(2\tau^2+\tau^4)(\tan^{-1}\tau^{-1})\tau^{-1}, \quad (2.10b)$$

and

$$\tau_A=\frac{\sigma'_A-m_A^2+t/2}{m_A t^{1/2}},\quad \tau_B=\frac{\sigma'_B-m_B^2+t/2}{m_B t^{1/2}}. \quad (2.10c)$$

Corresponding to (2.9) we have

$$V_{2\gamma}(R)\to V_{2\gamma}^{(1)}(R)=\frac{-1}{(4\pi)^4 R}\sum_{X,Y}\int_0^\infty dt\exp(-t^{1/2}R)\int_{m_A^2}^\infty\int_{m_B^2}^\infty\frac{d\sigma'_A}{\pi}\frac{d\sigma'_B}{\pi}\rho_X^A(\sigma'_A,t)\rho_Y^B(\sigma'_B,t)\Phi_{XY}^{(1)}, \quad (2.11)$$

which exhibits the long-range part of $V_{2\gamma}(R)$ in terms of the various spectral functions $\rho_X(\sigma,t)$ associated with the $F_X(\sigma,t)$, and the structure-independent functions $\Phi_{XY}^{(1)}(\sigma'_A,\sigma'_B;t)$.

B. Spectral functions $\rho_X(\sigma,t)$ for charged particles (Ref. 8)

For a particle B with charge e, the spectral functions ρ_X^B needed in (2.11) may, to an accuracy sufficient for our purposes, be taken to be those given by the Born approximation to Compton scattering. The relevant Feynman diagrams, drawn to describe photon absorption by a spin-0 or spin-$\frac{1}{2}$ particle, are shown in Fig. 1. For the spin-0 case the relevant tensor amplitude $\Gamma_{\mu\nu}^B$ can be immediately written down as the sum of the contributions from the diagrams (a), (b), and (c) in Fig. 1:

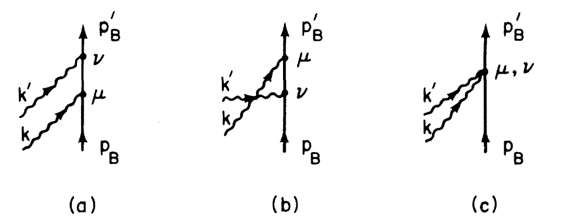

FIG. 1. Lowest-order Feynman graphs corresponding to the amplitude for two-photon absorption by a charged spinless particle. For a spin-$\frac{1}{2}$ particle, omit graph (c).

$$\Gamma^B_{\mu\nu}=e^2\left[\frac{(P_B+k)_\nu(P_B-k')_\mu}{D}+\frac{(P_B+k')_\mu(P_B-k)_\mu}{D'}-g_{\mu\nu}\right], \quad (2.12)$$

where

$$D=(p_B+k)^2-m_B^2=\sigma_B^+-m_B^2\,,$$
$$D'=(p_B+k')^2-m_B^2=\bar\sigma_B^- -m_B^2\,. \quad (2.13)$$

Using the relations $D=P_B\cdot k-k'\cdot k$, $D'=P_B\cdot k'-k'\cdot k$, and $t=(k+k')^2\to 2k\cdot k'$ on the photon mass shell, one finds that (2.12) may be rewritten in the form (2.3), with

$$F_E^B=\frac{e^2(8m_B^2+t)}{2m_BDD'}\,,\quad F_M^B=-\frac{e^2t}{2m_BDD'}\,. \quad (2.14)$$

Since $\sigma_B^+ +\bar\sigma_B^- +t=2m_B^2$ one may write

$$\frac{1}{DD'}=\frac{1}{t}\left[\frac{1}{m_B^2-\sigma_B^+}+\frac{1}{m_B^2-\bar\sigma_B^-}\right] \quad (2.15)$$

so that (2.14) takes the form

$$F_X^B=f_X^B(t)\left[\frac{1}{m_B^2-\sigma_B^+}+\frac{1}{m_B^2-\bar\sigma_B^-}\right], \quad (2.16)$$

where

$$f_E^B(t)=\frac{e^2(8m_B^2+t)}{2m_Bt}\,,\quad f_M^B(t)=\frac{-e^2}{2m_B}\,. \quad (2.17)$$

On comparison with the spectral representation for F_X^B it follows that

$$\rho_E^B=\pi f_E^B(t)\delta(\sigma'_B-m_B^2)\,,$$
$$\rho_M^B=\pi f_M^B(t)\delta(\sigma'_B-m_B^2)\,. \quad (2.18)$$

For the spin-$\frac{1}{2}$ case a little more work is required. The Feynman amplitude for photon absorption is given by the sum of Figs. 1(a) and 1(b) as

$$\Gamma_{\text{Born}}=\epsilon^{\mu}\epsilon'^{\nu}\bar u'(p',\tau')\Lambda_{\mu\nu}u(p,\tau)\,, \quad (2.19a)$$

where

$$\Lambda_{\mu\nu}=e^2\left[\gamma_\nu\frac{1}{\not p_B+\not k-m_B}\gamma_\mu+\gamma_\mu\frac{1}{\not p_B+\not k'-m_B}\gamma_\nu\right]. \quad (2.19b)$$

Here τ denotes the usual spin four-vector associated with the spinor u via the relation $i\gamma_5\not\tau u=u$. The problem of extracting an appropriately defined spin-independent part of (2.19) was discussed in Ref. 8. We first rationalize the denominators in $\Lambda_{\mu\nu}$ and use the relation $\not p\gamma_\nu=-\gamma_\nu\not p+2p_\nu$ together with the Dirac equation to eliminate the m_B terms in the numerators. We then use the identity

$$\gamma_\mu\gamma_\alpha\gamma_\nu=g_{\mu\alpha}\gamma_\nu+g_{\nu\alpha}\gamma_\mu-g_{\mu\nu}\gamma_\alpha-i\epsilon_{\mu\alpha\nu\beta}\gamma^\beta\gamma_5 \quad (2.20)$$

to eliminate the remaining products of three gamma matrices in the numerators. Finally, we evaluate the resulting expression, taken between $\bar u(p'_B,\tau')$ and $u(p_B,\tau)$, in the limit $\tau'=\tau$ (no spin flip). Using the relations

$$(\bar u'\gamma_\mu u)=(2mP^\mu/P^2)(\bar u'u)$$

and $(\bar u'\gamma^\mu\gamma_5u)=0$, valid for $\tau'=\tau$, one finds in this way that[8]

$$\bar u'\Lambda_{\mu\nu}u=L^B_{\mu\nu}(\bar u'u)\quad(\tau'=\tau) \quad (2.21a)$$

where

$$L^B_{\mu\nu}=e^2\frac{2m_B}{P_B^2}\frac{2}{DD'}(2m_B^2T^B_{E;\mu\nu})\,. \quad (2.21b)$$

Because our definition of the potential $V_{2\gamma}(R)$ is tailored for two spin-0 particles, and the conventional kinematical factors in the S matrix are $(m/E)^{1/2}$ for a spin-$\frac{1}{2}$ particle when $\bar uu$ is normalized to unity and $(2E)^{-1/2}$ for a spin-0 particle, we define the spin-$\frac{1}{2}$ analog of (2.12) by multiplying $L^B_{\mu\nu}$ by $2m_B$:

$$\Gamma^B_{\mu\nu}=2m_BL^B_{\mu\nu}\,. \quad (2.22)$$

On use of (2.3) with $A\to B$ and of Eq. (2.22) we see that, for a spin-$\frac{1}{2}$ particle,

$$F_E^B=\frac{16e^2m_B^3}{P_B^2DD'}\,,\quad F_M^B=0\,, \quad (2.23)$$

in Born approximation. It follows from (2.23) that in the spin-$\frac{1}{2}$ case F_X^B again has the form (2.16) where now

$$f_E^B(t)=\frac{16e^2m_B^3}{(4m_B^2-t)t}\,,\quad f_M^B(t)=0\,. \quad (2.24a)$$

Hence, we have

$$\rho_E^B(\sigma'_B,t)=\pi f_E^B(t)\delta(\sigma'_B-m_B^2)\,,$$
$$\rho_M^B(\sigma'_B,t)=0\,. \quad (2.24b)$$

Upon comparison of (2.24) and (2.17) we see that the difference between the $f_X^B(t)$ for the spin-$\frac{1}{2}$ and spin-0 cases is of order t/m_B^2. Since, as discussed in Sec. II A, we are neglecting terms of order $(\bar{\lambda}_B/R)^2$ relative to the leading term in $V_{2\gamma}(R)$, the results which we will obtain when B has spin $\frac{1}{2}$ will also be valid when B has spin 0. It should be noted that we have treated the spin-$\frac{1}{2}$ B particle as a purely Dirac particle, thereby ignoring effects coming from any anomalous magnetic moment which B may have. If B is an electron, the anomalous moment is of course very small.

III. $V_{2\gamma}(R)$ FOR THE CHARGED-NEUTRAL CASE

We now study the form of $V_{2\gamma}(R)$ for the case of a neutral spinless particle A and a charged spin-$\frac{1}{2}$ particle B. We shall often identify B with the electron and then set $m_B = m_e$.

A. Further approximations

Using Eqs. (2.11) and (2.24) one finds that

$$V_{2\gamma}^{(1)}(R) = V_{EE}^{(1)}(R) + V_{ME}^{(1)}(R) , \tag{3.1}$$

where

$$V_{XE}^{(1)}(R) = \frac{-1}{(4\pi)^4 R}\int_0^\infty dt \exp(-t^{1/2}R)\int_{m_A^2}^\infty \frac{d\sigma'_A}{\pi}\rho_X^A(\sigma'_A,t) f_E^B(t)\Phi_{XE}^{(1)} \tag{3.2}$$

and $\Phi_{XE}^{(1)}$ is evaluated at $\sigma'_B = m_B^2$. In keeping with the approximations already made in simplifying the form of Φ_{XY}, we will neglect t relative to m_B^2 in $f_E^B(t)$:

$$f_E^B(t) \to \frac{4m_B e^2}{t} . \tag{3.3}$$

We shall also temporarily make the replacement

$$\rho_X^A(\sigma',t) \to \rho_X^A(\sigma',0) . \tag{3.4a}$$

In the neutral-neutral case, this replacement isolates the dynamic dipole-polarizability contribution to $V_{2\gamma}(R)$. Inclusion of the t dependence of ρ, e.g., via a power-series expansion in t about $t=0$, generates the higher multipole contributions, which we discuss in Sec. IV. We follow a similar approximation scheme here. On introducing the variable

$$k = (\sigma'_A - m_A^2)/2m_A \tag{3.4b}$$

and the abbreviation

$$\rho_X^A(k) \equiv \rho_X^A(\sigma'_A, 0) , \tag{3.4c}$$

we get, on using (3.3) and (3.4) in (3.2),

$$V_{XE}^{(1)}(R) \approx \frac{-8m_B m_A e^2}{(4\pi)^4 R}\int_0^\infty dt \frac{\exp(-t^{1/2}R)}{t}\int_0^\infty \frac{dk}{\pi}\rho_X^A(k)\Phi_{XE}^{(1)} . \tag{3.5}$$

To proceed further, it is essential to simplify the expression (2.9) for $\Phi_{XE}^{(1)}$. Note that we can make the replacement

$$\tau_A \to \tau_A^{(1)} = \frac{2k_A}{t^{1/2}} , \tag{3.6a}$$

thereby neglecting terms of order t/km_A; since $k \gtrsim \alpha^2 m_e$ and the relevant region for t is $t \lesssim (\alpha m_e)^2$, this quantity is of order $m_e/m_A < 10^{-3}$. Alternatively stated, this approximation corresponds to the neglect of terms of order $(m_e/m_A)(a_0/R)^2$ relative to the leading term in $V_{XE}^{(1)}$. Furthermore, because $\sigma'_B = m_B^2$ in (3.5) we have

$$\tau_B \to \tau_B^{(1)} = \frac{t^{1/2}}{2m_B} . \tag{3.6b}$$

With these replacements, the denominator in $\Phi^{(1)}$ takes the form

$$\tau_B^2 - \tau_A^2 \to \frac{t}{4m_B^2} - \frac{4k^2}{t} = \frac{-4k^2}{t}\left[1 - \left[\frac{t}{4km_B}\right]^2\right] .$$

Finally, we shall neglect the quantity $(t/4km_B)^2$ relative to unity. Since each positive power of t in the integral (3.5) corresponds to an additional factor of R^{-2} in the potential and $k \gtrsim \alpha^2 m_e$, the terms we neglect in this way are of order $(a_0/R)^4$, when $m_B = m_e$, relative to the leading term in $V_{2\gamma}(R)$. Thus, they only contribute at the same level as those coming from the octupole polarizability of the atom. On making the replacements (3.6a), (3.6b), and

$$\tau_B^2 - \tau_A^2 \to -4k^2/t \tag{3.7}$$

in (2.9), we get

$$\Phi_{XE}^{(1)} \to \frac{-\pi t^2}{4m_A m_B^2 k}\left[g_{XE}\left[\frac{t^{1/2}}{2m_B}\right] - g_{XE}\left[\frac{2k}{t^{1/2}}\right]\right] . \tag{3.8}$$

On substituting (3.8) into (3.5)

$$V_{XE}^{(1)}(R)\to U_{XE}(R)+W_{XE}(R)\ , \tag{3.9}$$

where U_{XE} and W_{XE} denote the contribution of the first and second terms in the square brackets in (3.8), respectively. In the first term the integration over k may be carried out by use of the relation[3]

$$2\int \frac{dk}{\pi}\frac{\rho_X^A(k)}{k}=F_X^A(m_A^2,0)=4\pi\alpha_X^A\ , \tag{3.10}$$

where α_X^A is the dipole polarizability. It follows that

$$U_{XE}=\frac{e^2\alpha_X^A\pi}{(4\pi)^3R}\int_0^\infty dt\,\frac{t}{m_B}e^{-t^{1/2}R}g_{XE}\left[\frac{t^{1/2}}{2m_B}\right]. \tag{3.11}$$

In the second term we reverse the order of the k and t integrations so that

$$W_{XE}(R)=\frac{e^2}{(4\pi)^3Rm_B}\int_0^\infty \frac{dk}{\pi}\frac{\rho_X^A(k)}{k}L_X(k,R)\ , \tag{3.12}$$

where

$$L_X(k,R)=-\tfrac{1}{2}\int_0^\infty dt\,t\,e^{-t^{1/2}R}g_{XE}\left[\frac{2k}{t^{1/2}}\right]. \tag{3.13}$$

B. Study of U_{XE} and W_{XE}

Let us study the U_{XE} terms first. Since for large R only small values of t are important in the integral on the right-hand side of (3.11), we may use the Taylor expansion of the $g_{XE}(\tau)$ about $g=0$. This may be obtained from (2.10):

$$g_{EE}(\tau)=\frac{-\pi}{\tau}+2-\pi\tau+O(\tau^2)\ , \tag{3.14a}$$

$$g_{ME}(\tau)=-\pi\tau+O(\tau^2)\ . \tag{3.14b}$$

Using (3.14a) one finds that, with $m_B\to m_e$,

$$U_{EE}(R)=\frac{-1}{2}\frac{\alpha\alpha_E^A}{R^4}\left[1-\frac{3}{\pi}\frac{\lambda\!\!\!^-_e}{R}+O\left[\frac{\lambda\!\!\!^-_e{}^2}{R^2}\right]\right], \tag{3.15}$$

where

$$\alpha=\frac{e^2}{4\pi}\ ,\lambda\!\!\!^-_e=m_e^{-1}$$

are the fine-structure constant and electron Compton wavelength, respectively. The leading term in $U_{EE}(R)$ is just $-\alpha_E^A\vec{E}^2/2$, where $\vec{E}$ is the electric field produced by the electron, as expected on classical grounds. Similarly, using (3.14b), one gets

$$U_{ME}(R)=\frac{-3}{2}\frac{\alpha\alpha_M^A}{R^4}\frac{\lambda\!\!\!^-_e{}^2}{R^2}\left[1+O\left[\frac{\lambda\!\!\!^-_e}{R}\right]\right]. \tag{3.16}$$

Thus $U_{ME}(R)$ does not contribute in the order of interest.

Turning now to $W_{XE}(R)$, consider first the simpler function $W_{ME}(R)$. On putting $t=y^2$ in (3.13) and using (2.10b) for $g_{ME}(2k/t^{1/2})$ we get

$$L_M(k,R)=-4k\int_0^\infty dy\,e^{-yR}[ky-(y^2+2k^2)\tan^{-1}(y/2k)]\ . \tag{3.17}$$

On integrating by parts on the arctangent term, we may rewrite (3.17) in the form

$$L_M(k,R)=-4k\int_0^\infty dy\,e^{-yR}\left[ky-\frac{k}{R}-\frac{k}{4k^2+y^2}\left[\frac{y^2}{R}+\frac{4y}{R^2}+\frac{4}{R^3}\right]\right].$$

By writing $4k^2/(4k^2+y^2)=1-y^2/(4k^2+y^2)$ one may separate out the leading term in $L_M(k,R)$. On setting $y=2\zeta$ in the remaining integral we arrive at

$$L_M(k,R)=\frac{10}{R^4}+\frac{8}{R^5}\int_0^\infty d\zeta\frac{e^{-2\zeta R}P_M(\zeta R)}{k^2+\zeta^2}\ , \tag{3.18}$$

where the polynomial P_M is defined by

$$P_M(\eta)=-\eta^2(\eta+1)^2\ . \tag{3.19}$$

On substituting (3.18) into (3.12) and using (3.10) we find

$$W_{ME}(R)=\frac{5}{4\pi}\frac{(e^2/4\pi)\alpha_M^A}{m_BR^5}+\frac{(e^2/4\pi)}{16\pi^2m_BR^5}\int_0^\infty\frac{dk}{\pi}\frac{\rho_M^A(k)}{k}J_M(kR)\ , \tag{3.20}$$

where

$$J_M(kR)=\frac{8}{R}\int_0^\infty d\zeta\frac{e^{-2\zeta R}P_M(\zeta R)}{k^2+\zeta^2}\ . \tag{3.21}$$

Finally, we study $W_{EE}(R)$. From (2.10a) and (2.10b) we see that

$$g_{EE}(\tau)=g_{ME}(\tau)-2\tau^{-1}\tan^{-1}\tau^{-1} \tag{3.22}$$

so that

$$L_E(k,R)=L_M(k,R)+K\ , \tag{3.23a}$$

where

$$K=\frac{1}{2k}\int_0^\infty dt\, e^{-t^{1/2}R}t^{3/2}\tan^{-1}\left[\frac{t^{1/2}}{2k}\right]. \tag{3.23b}$$

Setting $t=4\zeta^2$ and integrating by parts one finds that

$$K=\frac{8}{R^5}\int_0^\infty d\zeta\frac{e^{-2\zeta R}Q(\zeta R)}{k^2+\zeta^2}\ , \tag{3.24}$$

where

$$Q(\eta)=2\eta^4+4\eta^3+6\eta^2+6\eta+3\ . \tag{3.25}$$

On using (3.18), (3.23a), and (3.24) we get

$$L_E(k,R)=\frac{10}{R^4}+\frac{8}{R^5}\int_0^\infty d\zeta\frac{e^{-2\zeta R}P_E(\zeta R)}{k^2+\zeta^2}\ , \tag{3.26}$$

where $P_E(\eta)$ is the sum of $P_M(\eta)$ and $Q(\eta)$:

$$P_E(\eta)=\eta^4+2\eta^3+5\eta^2+6\eta+3\ . \tag{3.27}$$

It follows from (3.12) and (3.26) that

$$W_{EE}(R)=\frac{5}{4\pi}\frac{\alpha\alpha_E^A}{m_BR^5}+\frac{\alpha}{16\pi^2m_BR^5}\int_0^\infty\frac{dk}{\pi}\frac{\rho_E^A(k)}{k}J_E(kR)\ , \tag{3.28}$$

where

$$J_E(kR)=\frac{8}{R}\int_0^\infty d\zeta\frac{e^{-2\zeta R}P_E(\zeta R)}{k^2+\zeta^2}\ . \tag{3.29}$$

We note, in passing, that the polynomials $P_E(\eta)$ and $P_M(\eta)$ coincide with the polynomials $P_{EE}(\eta)$ and $P_{ME}(\eta)$ defined in Ref. 3.

On combining Eqs. (2.11) and (3.9) with (3.15), (3.16), (3.20), and (3.28) we get, with $m_B=m_e$,

$$V_{2\gamma}(R)=\frac{-1}{2}\frac{\alpha\alpha_E^A}{R^4}+\frac{11}{4\pi}\frac{\alpha\alpha_E^A}{R^4}\frac{\lambda\!\!\!^{-}_e}{R}+\frac{5}{4\pi}\frac{\alpha\alpha_M^A}{R^4}\frac{\lambda\!\!\!^{-}_e}{R}+Y_{2\gamma}(R)+\cdots\ , \tag{3.30a}$$

where

$$Y_{2\gamma}(R)=\frac{\alpha}{16\pi^2}\frac{\lambda\!\!\!^{-}_e}{R^5}\int_0^\infty\frac{dk}{\pi}\left[\frac{\rho_E^A(k)}{k}J_E(kR)+\frac{\rho_M^A(k)}{k}J_M(kR)\right]. \tag{3.30b}$$

The dots in (3.30a) denote smaller terms, of order $(\lambda\!\!\!^{-}_e/R)^2$ or higher relative to the leading term in (3.30) or of order $(a_0/R)^4$ relative to this term. Equation (3.30) represents the van der Waals potential $V_{2\gamma}(R)$ for any separation R greater than atomic sizes. Alternative forms for $Y_{2\gamma}(R)$ involving the polarizability functions F_E^A and F_M^A at real or imaginary frequencies can easily be obtained from Eq. (3.30b) by following the methods of Ref. 3.

IV. HIGHER MULTIPOLE CONTRIBUTIONS TO $V_{2\gamma}$

In this section we describe the contribution to $V_{2\gamma}$ arising from the dependence of the spectral functions $\rho_X^A(k,t)$ on t, which we have thus far neglected [Eqs. (3.4a)–(3.4c)]. This dependence is related to the existence for the neutral system A of multipole moments higher than dipole.[9,10] We assume that $\rho_X^A(k,t)$ can be expanded in a power series in t,

$$\rho_X^A(k,t)=\sum_{n=0}^\infty\rho_{X,n}^A(k)t^n \tag{4.1}$$

and, correspondingly,

$$F_X^A(k,t)=\sum_{n=0}^\infty F_{X,n}^A(k)t^n\ . \tag{4.2}$$

It is shown in Refs. 9 and 10 that, to a good approximation (neglecting terms of relative order α^2), the coefficients $F_{X,n}^A$ are related to multipole polarizabilities by

$$F_X^A(k)=\frac{8\pi}{(2n+2)!}\alpha_{X,2^{n+1}}(k)\ , \tag{4.3}$$

where the $\alpha_{X,2^{n+1}}(k)$ are the frequency-dependent multipole polarizabilities of order 2^{n+1}.[11]

We substitute the expansion for ρ_X^A into Eq. (3.2) and proceed as in Sec. III A, for each term in the expansion. The result is a contribution to $V_{2\gamma}$ of the form

$$V_{2\gamma}=V_{2\gamma,E}+V_{2\gamma,M} \tag{4.4}$$

with

$$V_{2\gamma,X}=\sum_{n=0}^\infty V_{2\gamma,X,n}\ . \tag{4.5}$$

The terms $V_{2\gamma,X,n}$ arise from the $n+1$'st term in the expansion (4.3). We can see from (3.2) that each additional power of t can be written as d^2/dr^2 acting on the remaining integral defining $V_{2\gamma}$.

It follows that $V_{2\gamma,X,n}$ can be written in a form entirely similar to (3.30a) and (3.30b) with $\rho_{X,n}$ replacing what was there called ρ_X, and is here called $\rho_{X,0}$. There is also an additional factor of d^{2n}/dR^{2n} acting on the resultant integral. Therefore, we obtain

$$V_{2\gamma,E,n}=\frac{-1}{2}\frac{\alpha\alpha_{E,2^n+1}(0)}{R^{4+2n}}+\frac{11}{4\pi}\frac{\alpha\lambda\!\!\!^{-}_e}{R^{5+2n}}\alpha_{E,2^n+1}(0)\left[\frac{2n+3}{3}\right]+\frac{\alpha\alpha_{E,2^n+1}(0)}{16\pi^2}\frac{\lambda\!\!\!^{-}_e}{R}\frac{d^{2n}}{dR^{2n}}\int_0^\infty\frac{dk}{\pi}\frac{\rho^A_{E,n}(k)}{kR^4}J_E(kR)\ , \tag{4.6}$$

$$V_{2\gamma,M,n}=\frac{5}{4\pi}\frac{\alpha\lambda\!\!\!^{-}_e}{R^{5+2n}}\alpha_{M,2^n+1}(0)\left[\frac{2n+3}{3}\right]+\frac{\alpha}{16\pi^2}\frac{\lambda\!\!\!^{-}_e}{R}\frac{d^{2n}}{dR^{2n}}\int_0^\infty\frac{dk}{\pi}\frac{\rho^A_{M,n}(k)}{kR^4}J_M(kR)\ . \tag{4.7}$$

The magnitude of the multipole polarizability $\alpha_{X,2^n+1}(0)$ is expected to be given by

$$\alpha_{X,2^n+1}(0)\sim a_0^{2n}\alpha_{X,0}(0)\ . \tag{4.8}$$

It follows that the leading terms in $V_{2\gamma,X,n}$ are in the ratio $(a_0/R)^{2n}$ to the leading term in $V_{2\gamma,X,0}$. Note that for $n\geq 2$, these terms are similar in magnitude to the "kinematic" terms previously discussed in the paragraph following Eq. (3.5) and neglected.

The first term in $V_{2\gamma,X,n}$, which is proportional to the zero-frequency multipole polarizability, does not "retard," that is, it retains the same form at large and small R. The other terms behave like the familiar Casimir-Polder interaction, in that they develop an additional inverse power of R at large, as opposed to small, separations.

V. ANALYSIS OF $V_{2\gamma(R)}$

To conclude, we study the connection of the results obtained in Secs. III and IV with earlier work. With regard to the results for the dipole part of $V_{2\gamma}(R)$, given by Eqs. (3.30a) and (3.30b), the second and third terms in (3.30a) coincide with the results found by Kelsey and Spruch[6] and by Bernabeu and Tarrach.[12] The first term in the electric quadrupole term, defined by Eq. (4.6) with $n=1$, has previously been obtained by Kleinman, Hahn, and Spruch.[5] It should be noted that the leading term in (4.6) coincides with the result obtained from electrostatics for all values of n, not just $n=0$.

The function $Y_{2\gamma}(R)$ defined by (3.30b) represents an analogue of the generalized Casimir-Polder potential.[3,13] To find the behavior of $Y_{2\gamma}(R)$ for $R\gg a_0$, we put $\zeta=u/2R$ in (3.21) and (3.29) to get

$$J_X(kR)=16\int_0^\infty du\,\frac{e^{-u}P_X(u/2)}{4k^2R^2+u^2}\ . \tag{5.1}$$

For large R we can neglect u^2 in the denominator of (5.1). Doing this yields

$$J_E(kR)\sim 46/k^2R^2\ ,\quad J_M(kR)\sim -14/k^2R^2\ . \tag{5.2}$$

It follows that

$$Y_{2\gamma}(R)\sim CR^{-7}\ . \tag{5.3}$$

To estimate the magnitude of C we substitute (5.2) into (3.30b) and replace $(k^2)^{-1}$ by the inverse of a mean-square excitation momentum $\overline{k_X^2}$ in the integral involving $\rho_X(k)$. This yields

$$C=\frac{\alpha\lambda\!\!\!^{-}_e}{4\pi}\left[\frac{23\alpha_E^A}{\overline{k_E^2}}-\frac{7\alpha_M^A}{\overline{k_M^2}}\right]\ . \tag{5.4}$$

It is interesting to compare $Y_{2\gamma}(R)$ with $V_{2\gamma}^{AB}(R)$, the long-range potential between A and another neutral atom B: For large R, we have[3]

$$V_{2\gamma}^{AB}(R)\sim DR^{-7}\ , \tag{5.5a}$$

where

$$D\sim\frac{-1}{4\pi}[23(\alpha_E^A\alpha_E^B+\alpha_M^A\alpha_M^B)-7(\alpha_E^A\alpha_M^B+\alpha_M^A\alpha_E^B)]\ . \tag{5.5b}$$

For simplicity assume that $\alpha_M^A=\alpha_M^B=0$. Then

$$C\to\frac{\alpha\lambda\!\!\!^{-}_e}{\overline{k_E^2}}\frac{23}{4\pi}\alpha_E^A\ ,\quad D\to-\alpha_E^B\left[\frac{23}{4\pi}\alpha_E^A\right]\ , \tag{5.6}$$

so that the counterpart of α_E^B is $-\alpha\lambda\!\!\!^{-}_e/\overline{k_E^2}$. For $\overline{k}_E\gtrsim\alpha a_0^{-1}$ and $\alpha_E^B\sim a_0^3$, we then get

$$C/D\sim\alpha^{-1}\lambda\!\!\!^{-}_e/a_0=1\ . \tag{5.7}$$

Thus, when B is a unit point charge, for large R the part $Y_{2\gamma}(R)$ of the two-photon exchange potential $V_{2\gamma}$ between B and the neutral atom A is comparable in magnitude to the generalized Casimir-Polder (CP) potential between two neutral atoms. If B is an ion, not fully stripped of its electrons, there will actually be an additional term in $V_{2\gamma}$ arising jointly from the structure of A and B which has the same form and is similar in magnitude to this generalized CP potential.

The expressions (3.30a) and (3.30b) are valid for R of the order of a few times a_0 or larger. It is instructive to examine the behavior of these formulas for $R \gtrsim a_0$.

Proceeding as in Ref. 3, we write $J_X(kR)$ in the form

$$J_X(kR)=\frac{8}{R}P_X^{\rm op}\frac{f(2kR)}{k}\ , \qquad (5.8)$$

where the $P_X^{\rm op}$ are obtained from the polynomials $P_X(\eta)$, by replacing η^n by $(-R/2)^n\partial_R^n$:

$$P_E^{\rm op}=\tfrac{1}{16}R^4\partial_R^4-\tfrac{1}{4}R^3\partial_R^3+\tfrac{5}{4}R^2\partial_R^2-3R\partial_R+3\ , \qquad (5.9a)$$

$$P_M^{\rm op}=-\tfrac{1}{16}R^4\partial_R^4+\tfrac{1}{4}R^3\partial_R^3-\tfrac{1}{4}R^2\partial_R^2\ , \qquad (5.9b)$$

and the function $f(2kR)$ is defined by

$$\frac{f(2kR)}{k}=\int_0^\infty d\zeta\,\frac{e^{-2\zeta R}}{\zeta^2+k^2}\ . \qquad (5.10)$$

For small values of R, i.e., $kR \ll 1$, one finds

$$R^{-1}P_E^{\rm op}\frac{f(2kR)}{k}=-\frac{3\pi}{2kR}-\frac{11}{4}+\frac{\pi}{2}kR+O(k^2R^2)\ , \qquad (5.11a)$$

$$R^{-1}P_M^{\rm op}\frac{f(2kR)}{k}=-\frac{5}{4}+\frac{\pi}{2}kR+O(k^2R^2)\ . \qquad (5.11b)$$

It is easy to see that the constant terms in Eqs. (5.11a) and (5.11b) cancel the explicit R^{-5} terms in $V_{2\gamma}(R)$. Hence we find, for $R \gtrsim a_0$,

$$V_{2\gamma}(R)\to -\frac{1}{2}\frac{\alpha\alpha_E^A}{R^4}+\frac{3}{4\pi^2}\frac{\alpha\lambda\!\!\!^{-}_e}{R^6}\int_0^\infty dk\,\frac{\rho_E^A(k)}{k^2}+\frac{\alpha\lambda\!\!\!^{-}_e}{4\pi R^4}\int_0^\infty dk\,\rho_E^A(k)+\frac{\alpha\lambda\!\!\!^{-}_e}{4\pi R^4}\int_0^\infty dk\,\rho_M^A(k)+O(R^{-3})\ . \qquad (5.12)$$

The second term in (5.12) is smaller than the first by a factor of order $(a_0/R)^2$. This term has been known for a long time.[5] The third and fourth terms will normally be smaller by a factor α^2 and α^4, respectively, than the first term. These latter terms relate to the corresponding terms in Eq. (3.30), proportional to $\lambda\!\!\!^{-}_e$, in a way very similar to what happens in the neutral-neutral case. That is, the small R terms have one less power of R^{-1} than the large R terms.[3] However, the leading R^{-4} term does not change at all between large and small R. The same is true for its higher multipole equivalents in Eq. (4.6). These terms all arise from the classical interactions of the Coulomb field of the charge with a polarizable atom. Their dependence on distance would indeed change if we examined it for R of order $\lambda\!\!\!^{-}_e=\alpha a_0$, a distance scale characteristic of the electron rather than of the atom. It would be interesting to have a simple physical explanation for this difference in the retardation features of the interaction of a neutral and a charged system when compared to the interaction of two neutral systems.

ACKNOWLEDGMENTS

This work was supported in part by the U. S. Department of Energy and by the National Science Foundation. We thank L. Spruch for stimulating our interest in this problem and C. K. Au for a useful discussion. We thank the late Professor Henry M. Foley for pointing out to us the need to understand the fact that the R^{-4} term in $V_{2\gamma}(R)$ does not change its form from short to long distances. We also wish to record our indebtedness to him for sharing, over a period of many years, his exceptional physical intuition and his great knowledge of atomic and molecular physics.

[1]H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).

[2]For a review and further references, see D. Langebein, *Theory of van der Waals Attraction*, Springer Tracts in Modern Physics (Springer, Berlin, 1974), Vol. 72.

[3]G. Feinberg and J. Sucher, Phys. Rev. A 2, 2395 (1970).

[4]For a review with further references see J. Sucher, *Cargèse Lectures in Physics*, edited by M. Lévy (Gordon and Breach, New York, 1977), Vol. VII, pp. 43–110.

[5]C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev.

Lett. 65, 53 (1968).

[6]E. J. Kelsey and L. Spruch, Phys. Rev. A 18, 1055 (1978); 18, 845 (1970); 18, 15 (1978). See also R. J. Drachman, *ibid.* 26, 1228 (1982).

[7]J. Bernabeu and R. Tarrach, Ann. Phys. (N.Y.) 102, 323 (1976).

[8]G. Feinberg and J. Sucher, Phys. Rev. B 139, 1619 (1965).

[9]C. K. Au and G. Feinberg, Phys. Rev. A 6, 2433 (1977).

[10]G. Feinberg, Phys. Rev. B 9, 2490 (1974).

[11]These polarizabilities can be defined either as coefficients in the expansion for the energy of a system in an external field, as in Ref. 9, or as matrix elements of products of coordinates. The equivalence of these definitions has been shown by C. K. Au (private communication).

[12]See Ref. 7. These authors have also considered some other combinations of spin and charge than the ones studied here.

[13]We take the occasion, in an appropriately numbered footnote, to correct some errors in Ref. 3: In Eq. (2.43), for "m_A," read "$-m_A$." After Eq. (2.49) read "$p_{\bar{B}}=-p_B$," "$p_{\bar{B}}=\frac{1}{2}(t^{1/2},-\vec{p}\,')$" and for "real" read "complex." In Eq. (2.60), for "$\tan^{-1}\tau$" read "$\tan^{-1}\tau^{-1}$." After Eq. 2.105′, read "$f(x)=-\cos x\ \mathrm{si}x+\sin x\ \mathrm{Ci}x$" and immediately thereafter read "(here $\mathrm{si}x=\mathrm{Si}x-(\pi/2)$, and Si,Ci are the sine and cosine integral) we finally . . . ."