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Higher-Multipole Contributions to the Retarded van der Waals Potential*

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We calculate the two-photon exchange (retarded van der Waals) potential between neutral spinless systems, including the effects of higher partial waves in the atom-photon scattering amplitude. This is equivalent to including higher multipoles in the interaction of the charges in the atoms. We show that this potential can be expressed as an infinite series of terms, with coefficients that can, in principle, be measured in atom-photon scattering. The behavior of the various terms, at small separation and large separation of the system, is discussed. We show that the leading term in the contribution of each multipole has the property that it has one more power of R^{-1} in its large-R behavior than in its small-R behavior.

I. INTRODUCTION

A recent analysis[1] has shown that the two-photon exchange (retarded van der Waals) potential between spinless atoms can be expressed in terms of the scattering amplitudes for photon-atom scattering by the individual atoms. An exact expression for this potential has been given, involving an integral over these amplitudes, evaluated at positive photon energy, and at positive, and therefore unphysical, momentum transfers. In the previous analysis, it was shown that when the dependence of the scattering amplitude on momentum transfer was neglected, the potential could be expressed in terms of the atomic polarizability evaluated at real frequencies, a quantity directly measurable in photon-atom scattering. The approximation so made is equivalent to neglecting all partial waves other than s wave in the photon-atom scattering amplitude. The result obtained is an extension of the retarded van der Waals interaction of Casimir and Polder,[2] generalized to include magnetic effects and relativistic effects.

In the present work, we shall retain the dependence of the scattering amplitude on momentum transfer t and show that because of the analyticity of this dependence for small t, it is possible to express the van der Waals potential as an inverse series in R, with coefficients which are again quantities that are measurable in photon-atom scattering. The corrections to our previous result can be identified for small R as higher-multipole (e.g., dipole-quadrupole, quadrupole-quadrupole, etc.) contributions not included in the Casimir–Polder theory. At large R, these terms then give the retarded form of the higher-multipole corrections. We therefore arrive at a compact form, valid at all separations, and containing all the contributions to the van der Waals potential. This form can be expressed in several ways, as is the case when we neglect the dependence on momentum transfer. One form, analogous to Eq. (1.3) of FS is given by

$$V_{xy}=\frac{-1}{4\pi^5R}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}\left(R^{-5}\int_0^\infty dK_A\right.$$
$$\times\int_0^\infty dK_B\,K_A\rho^A_{x,n}(K_A)K_B\rho^B_{x,m}(K_B)$$
$$\left.\times\int_0^\infty\frac{d\zeta\,e^{-2\zeta R}P_{xy}(\zeta R)}{(\zeta^2+K_A^2)(\zeta^2+K_B^2)}\right)\,,\quad(1.1)$$

where the notation is as in FS with the addition that $\rho^A_{x,n}$ is defined by

$$\mathrm{Im}F^A_x(K_A,t)=\sum\rho^A_{x,n}(K_A)t^n\ .$$

Another form, analogous to (1.5) of FS is

$$V_{xy}=\frac{-1}{8\pi^4R}\sum_{n,m}\frac{d^{2(n+m)}}{dR^{2(n+m)}}\{R^{-5}P^{\phi\phi}_{xy}\int_0^\infty dK\,f(2KR)$$
$$\times[\mathrm{Re}F^A_{x,n}\,\mathrm{Im}F^B_{y,m}+\mathrm{Im}F^A_{x,n}\mathrm{Re}F^B_{y,n}]\}\ .\quad(1.2)$$

It follows from either of these formulas that as $R\to\infty$, the (n,m) term behaves as

$$V_{xy,nm}\sim\frac{1}{R}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-6})+\cdots$$
$$\sim R^{-(7+2n+2m)}+O(R^{-(9+2n+2m)})$$

while for K_0R small, where K_0 is a typical atomic wave number, they behave as

$$V_{xy,nm}\sim\frac{1}{R}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-5})+\cdots\sim R^{-(6+2n+2m)}\ .$$

This shows that for every multipole the effect of retardation is to introduce an extra power of R, in the long-range behavior compared to the short-range behavior, of the leading term.

In Sec. II, we derive the formulas above by the method of FS. In Sec. III, we consider the small-R and large-R limits of the formulas, and the interpretation of the coefficients appearing in them. In Sec. IV, we discuss the possibility of obtaining the $F_{x,n}$ from various measurements. Finally, in a series of Appendices, we consider in Appendix A the analytic properties of the atom-photon scattering amplitude, in Appendix B the relation between the $F_{x,n}$ and the multipole polarizabilities, and in Appendix C we present an explicit calculation of some of the $V_{xy,nm}$ for two hydrogen atoms.

II. DERIVATION OF THE GENERAL FORMULAS

To fix our notation, consider the scattering of a photon by an atom. If we neglect recoil of the atom, we can write the scattering amplitude as

$$M=K^2\epsilon_i\epsilon'_i[F_E\delta_{ij}+F_M(\delta_{ij}-\hat{K}'_i\hat{K}_j)](-1/8\pi)\ .$$

Here $\vec{\epsilon}$ and $\vec{\epsilon}'$ are the incoming and outgoing polarizations, $\vec{K}$ and $\vec{K}'$ the incoming and outgoing momenta ($K=|\vec{K}|=|\vec{K}'|=\vec{K}'$). F_E and F_M are the electric and magnetic form factors, which are functions of two scalar variables, which may be taken as K and $t\equiv2K^2(\cos\theta-1)$, with $\cos\theta=\hat{K}\cdot\hat{K}'$. Note that t, the momentum transfer, is negative in the physical scattering region, i.e., when K is real and $|\cos\theta|\leq1$.

The form factors F_E and F_M are complex functions, in general, and we can define $\rho_x(K,t)\equiv\mathrm{Im}F_x(K,t)$, where x is E or M.

In terms of these variables, we can write the van der Waals potential arising from two-photon exchange between the atoms A and B, according to Eq. (2.61) of FS as follows:

$$V_{2\gamma}(R)=\frac{-1}{(4\pi)^4R}\sum_{x,y}\int_0^\infty dt\exp(-Rt^{1/2})\int_0^\infty\left(\frac{dK_A}{\pi}\frac{dK_B}{\pi}\right.$$
$$\left.\times\rho^A_x(K_A,t)\rho^B_y(K_B,t)\,\Phi_{xy}(K_A,K_B,t)\right)\ .$$
$$(2.1)$$

In this equation, the subscripts x, y each take on the values E and M. We note that the integral over t is over positive, and therefore unphysical, values of this variable, so that the integral cannot be directly calculated in terms of measurable quantities. The quantity Φ_{xy} is a phase-space factor, given in FS as

$$\Phi_{xy}=2\pi t(2T_AT_B)\frac{g_{xy}(T_B)-g_{xy}(T_A)}{T_B^2-T_A^2}\ ,\qquad(2.2)$$

with $T=2K/t^{1/2}$ and

$$g_{EE}=T^2-T(2+2T^2+T^4)\tan^{-1}T^{-1}=g_{MM}\ ;$$
$$g_{EM}=T^2-T(2T^2+T^4)\tan^{-1}T^{-1}=g_{ME}\ .$$

In these expressions, following the discussion in FS, we have neglected terms of order m_e/M_A.

In order to proceed, we provisionally assume that the form factors F_x of each atom are analytic functions of t in some region including $t=0$, an assumption to be justified in Appendix A. We then have

$$F_x(K,t)=\sum_{n=0}^{\infty} F_{x,n}(K)t^n \quad \text{for } t<t_0\ , \tag{2.3}$$

and therefore

$$\rho_x(K,t)=\sum_{n=0}^{\infty} \rho_{x,n}(K)t^n \quad \text{for } t<t_0\ , \tag{2.4}$$

where, for real t,

$$\rho_{x,n}=\operatorname{Im}F_{x,n}=\frac{1}{n!}\operatorname{Im}\frac{d^nF_x(K,t=0)}{dt^n}\quad . \tag{2.5}$$

We note that the quantities $\rho_{x,n}$ and $F_{x,n}$ involve the scattering amplitude only for $t=0$ and therefore are related to quantities that occur in physical atom-photon scattering. The measurability of $F_{x,n}$ is discussed in detail in Sec. IV. The $F_{x,n}$ are also related to the coefficients $f_l(K)$ of the expansion of F_x in Legendre polynomials, through the equation $t=2K^2(\cos\theta-1)$. This relation is given by

$$F_{x,n}=\frac{1}{(2K)^{2n}(n!)^2}\sum_{l\geq n}(2l+1)f_{x,l}(K)\frac{(l+n)!}{(l-n)!}\ ,$$

where

$$F_x(K,\cos\theta)=\sum_l (2l+1)P_l(\cos\theta)f_{x,l}(K)\ .$$

We now write the t integral in Eq. (2.1) as a sum of terms, denoting all of the integrand other than the exponential by $I(t)$:

$$\int_0^\infty e^{-Rt^{1/2}}I(t)=\int_0^{t_0}e^{-Rt^{1/2}}I(t)\,dt+\int_{t_0}^\infty e^{-Rt^{1/2}}I(t)\,dt\ , \tag{2.6}$$

where we choose t_0 to be the smallest of the radii of convergence of the expansions (2.4), for the two atoms A, B, and for two form factors F_E and F_M. In the first term, we can then substitute the series expansion (2.4) for each form factor, which generates a corresponding expansion for $I(t)$. This can then be integrated term by term. The result of this is

$$\int_0^{t_0}e^{-Rt^{1/2}}I(t)\,dt=S_1(1/R)+e^{-Rt_0^{1/2}}S_2(1/R)\ , \tag{2.7}$$

where S_1, S_2 are power series. The first term arises from the lower limit of integration ($t=0$) and the second term from the upper limit ($t=t_0$). We shall see in Appendix A that $t_0^{1/2}$ is typically on the order of $1/a_0$, with a_0 the Bohr radius. The second term is therefore similar in structure to the short-range forces coming from electron exchange, or wave-function overlap, in that it decreases exponentially and is negligible outside a few atomic radii. We therefore do not include it in the van der Waals potential.

The second term in (2.6) can be bounded above as follows:

$$\int_{t_0}^\infty e^{-Rt_0^{1/2}}I(t)\,dt\leq e^{-Rt_0^{1/2}}\int_{t_0}^\infty |I(t)|\,dt \tag{2.8}$$

provided that the integral on the right-hand side exists. This will be demonstrated in Appendix A. It follows that this term also decreases exponentially with R, has the character of a short-range potential, and so can be omitted from the van der Waals potential. Therefore, the potential of interest is given by the term $S_1(1/R)$ alone. Formally, this term is obtained if we use the power series for $I(t)$ at all values of t, and carry out the t integral from zero to ∞ term by term. We shall follow this procedure, and write

$$V_{2\gamma}=\int_0^\infty e^{-Rt^{1/2}}I_s(t)\,dt+O(e^{-Rt_0^{1/2}})\ , \tag{2.9}$$

where $I_s(t)$ is obtained by substituting the expansions (2.4) into $I(t)$ for all values of t. The remainder of our work consists in a discussion of the integral in Eq. (2.9).

We note from (2.1), (2.4), and (2.5) that

$$I_s(t)=\frac{-1}{(4\pi)^4R}\sum_{x,y}\int\frac{dK_A}{\pi}\frac{dK_B}{\pi}\Phi_{xy}(K_A,K_B,t)\times\sum_{n,m}t^{n+m}\rho_{x,n}(K_A)\rho_{y,m}(K_B)\ . \tag{2.10}$$

The integral over t can now be carried out term by term, integrating by parts several times as described in FS. The result can be written

$$V_{2\gamma}=\sum_{x,y}V_{xy}\ ,$$

$$\begin{aligned}V_{xy}&\equiv\sum_{n,m}V_{xy,nm}\\&=\frac{-1}{4\pi^3R}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}\left(\frac{1}{R^5}\int_0^\infty\frac{dK_A}{\pi}\right.\\&\quad\times\int\frac{dK_B}{\pi}K_A\rho^A_{x,n}(K_A)K_B\rho^B_{y,m}(K_B)\\&\quad\left.\times\int_0^\infty\frac{d\zeta\, e^{-2\zeta R}P_{xy}(\zeta R)}{(\zeta^2+K_A^2)(\zeta^2+K_B^2)}\right)\end{aligned} \tag{2.11}$$

with $P_{xy}(\zeta R)$ a set of polynomials, given by

$$P_{EE}(x)=P_{MM}(x)=x^4+2x^3+5x^2+6x+3\ ,$$

$$P_{EM}(x)=P_{ME}(x)=-(x^4+2x^3+x^2)\ .$$

This is the equation given as (1.1).

To derive the other form given as (1.2) in the Introduction, we use the assumption that the quantities $F_{x,n}(K)$ satisfy unsubtracted dispersion relation, of the form

$$F_{x,n}(K)=\frac{2}{\pi}\int_0^\infty\frac{dK'K'\rho_{x,n}(K')}{K'^2-K^2}\quad . \tag{2.12}$$

It then follows, upon exchanging orders of integration, that V_{xy} can be written

$$V_{xy}=\frac{-1}{16\pi^3R}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}$$

$$\times\left[R^{-5}\int_0^\infty d\zeta\, e^{-2\zeta R}P_{xy}(\zeta R)F^A_{x,n}(i\zeta)F^B_{y,m}(i\zeta)\right] . \quad (2.13)$$

This form is a generalization of a well-known expression for the dipole contribution to the van der Waals potential, expressed as an integral over the polarizability at imaginary frequencies.

Finally, following FS, we define $D_{xy,nm}\equiv F_{x,n}(K)F_{y,m}(K)$, which also satisfies dispersion relations

$$D_{xy,nm}=\frac{2}{\pi}\int_0^\infty \frac{K'\,dK'}{K'^2-K^2}\,\mathrm{Im}D_{xy,nm}(K') ,$$

$$\mathrm{Im}D_{xy,nm}=\mathrm{Re}F_{x,n}\,\mathrm{Im}F_{y,m}+\mathrm{Re}F_{y,m}\,\mathrm{Im}F_{x,n} ; \quad (2.14)$$

and $D_{xy,nm}(i\zeta)=F_{x,n}(i\zeta)F_{y,m}(i\zeta)$ is real. It then follows that

$$V_{xy}=\frac{-1}{8\pi^4 R}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}\left(R^{-5}\int_0^\infty d\zeta\, e^{-2\zeta R}P_{xy}(\zeta R)\int_0^\infty \frac{K'\,dK'}{K'^2+\zeta^2}\left[\mathrm{Re}F^A_{x,n}(K')\,\mathrm{Im}F^B_{y,m}(K')+\mathrm{Re}F^B_{y,m}(K')\,\mathrm{Im}F^A_{x,n}(K')\right]\right) \quad (2.15)$$

$$=\frac{-1}{8\pi^4 R}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}\left\{R^{-5}P^{\mathrm{op}}_{xy}\int_0^\infty dK f(2KR)\left[\mathrm{Re}F^A_{x,n}(K)\,\mathrm{Im}F^B_{y,m}(K)+\mathrm{Re}F^B_{y,m}(K)\,\mathrm{Im}F^A_{x,n}(K)\right]\right\} , \quad (2.16)$$

which is Eq. (1.2). Here $f(x)$ is the function

$$-f(x)=\cos x\,\mathrm{si}\,x-\sin x\,\mathrm{Ci}\,x$$

and P^{op}_{xy} are given by

$$P^{\mathrm{op}}_{EE}=\tfrac{1}{16}R^4\frac{d^4}{dR^4}-\tfrac{1}{4}R^3\frac{d^3}{dR^3}+\tfrac{5}{4}R^2\frac{d^2}{dR^2}-3R\frac{d}{dR}+3$$

$$=P^{\mathrm{op}}_{MM} ,$$

$$P^{\mathrm{op}}_{EM}=\tfrac{-1}{16}R^4\frac{d^4}{dR^4}+\tfrac{1}{4}R^3\frac{d^3}{dR^3}-\tfrac{1}{4}R^2\frac{d^2}{dR^2}=P^{\mathrm{op}}_{ME} .$$

This completes the derivation of the formulas given in Sec. I. The detailed discussion of their implication is given in Sec. III.

III. POTENTIAL AT SHORT RANGE AND LONG RANGE

The formulas of Sec. II, e.g., (2.11) or (2.16), express the van der Waals potential over the whole range of interest, extending from a few atomic radii to infinity. The indicated sums over n, m are expected to converge rapidly in this region. This is because the quantities $F_{x,n}$ involve successive derivatives with respect to the momentum-transfer variable t, and such derivatives generally behave as $F_{x,n}(K, t=0)\simeq a^{2n}F_{x,0}(K, t=0)$, where a is the atomic radius.

Therefore, the sum over n, m generates an expansion in powers of $(a/R)^2$, which is small throughout the region of interest. We shall see that this is equivalent to saying that the higher-multipole corrections are usually small compared to the dipole terms everywhere.

It is possible to calculate, at each value of R, any term in (2.16) numerically, assuming that the corresponding $F_{x,n}F_{y,m}$ are known. In general, this is what would have to be done if R is somewhere in the middle of its range of interest. An example is given in Appendix C. It has however been customary, in previous treatments[3] of the $n=m=0$ term of our expansion, to consider the potential in two regions, corresponding to $K_0R\ll 1$ and $K_0R>1$, where K_0 is a typical atomic wave number. The potential is expressed as an ascending power series in R in the "small-R" region, and as a descending series in the large-R region. This is accomplished for example by using the small-argument or large-argument expansions of the function $f(2KR)$ that appears in (2.16).

A similar procedure can be carried through for each term with a given value of m and n in (2.11) or (2.16). To do this, it is convenient to calculate the quantity

$$R^{-5}P^{\mathrm{op}}_{xy}f(2KR)$$

which occurs in each of the terms, in the small-argument and large-argument limits.

A. Small-R Region

First take the case $KR\ll 1$, then

$$R^{-5}P^{\mathrm{op}}_{EE}f(2KR)\sim\tfrac{3}{2}\pi R^{-5}-\tfrac{11}{4}KR^{-4}+\tfrac{1}{2}\pi K^2R^{-3}-\tfrac{7}{6}K^3R^{-2}$$
$$+\tfrac{1}{2}\pi K^4R^{-1}+\tfrac{22}{15}K^5\ln(2KR)+O(\mathrm{const}) \quad (3.1)$$

and the same for $R^{-5}P^{\mathrm{op}}_{MM}f(2KR)$;

$$R^{-5}P^{\mathrm{op}}_{ME}f(2KR)\sim-\tfrac{5}{4}KR^{-4}+\tfrac{1}{2}\pi K^2R^{-3}-\tfrac{3}{2}K^3R^{-2}$$
$$+\tfrac{1}{2}\pi K^4R^{-1}+\tfrac{2}{3}K^5\ln(2KR)+O(\mathrm{const}) \quad (3.2)$$

and the same for $R^{-5}P^{\mathrm{op}}_{EM}f(2KR)$. These expressions can be substituted into (2.16) and the necessary derivatives carried out term by term. The result is a sum of explicit functions of R, with coefficients that are integrals over K of products of the form factors $F_{x,n}(K)$. We delay for the moment the discussion of the convergence of these integrals, and exhibit the first few terms[4]:

$$V^{AB}_{EE}=\frac{-1}{8\pi^4 R}\left\{\begin{array}{l} +\dfrac{3\pi}{2}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-5})\,I^{AB,0}_{EE,nm} \\[2ex] \dfrac{-11}{4}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-4})\,I^{AB,1}_{EE,nm} \\[2ex] +\dfrac{\pi}{2}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-3})\,I^{AB,2}_{EE,nm} \\[2ex] -\dfrac{7}{6}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-2})\,I^{AB,3}_{EE,nm} \\[2ex] +\dfrac{\pi}{2}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-1})\,I^{AB,4}_{EE,nm} \\[2ex] +\dfrac{22}{15}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(\ln R)\,I^{AB,5}_{EE,nm} \\[2ex] +\cdots\;, \end{array}\right. \qquad (3.3)$$

where

$$I^{AB,r}_{EE,nm}\equiv\int_0^\infty K^r\,\mathrm{Im}D^{AB}_{EE,nm}(K)\,dK \qquad (3.4)$$

$$=\int_0^\infty K^r[\mathrm{Re}F^A_{E,n}(K)\,\mathrm{Im}F^B_{E,m}(K)+\mathrm{Re}F^B_{E,m}(K)\,\mathrm{Im}F^A_{E,n}(K)]\,dK\,. \qquad (3.5)$$

A similar expression can be written for V^{AB}_{MM}, with $I^{AB,r}_{MM,nm}$ substituting for $I^{AB,r}_{EE,nm}$, where

$$I^{AB,r}_{MM,nm}=\int_0^\infty K^r\,\mathrm{Im}D^{AB}_{MM,nm}(K)\,dK \qquad (3.6)$$

$$=\int_0^\infty K^r[\mathrm{Re}F^A_{M,n}(K)\,\mathrm{Im}F^B_{M,m}(K)+\mathrm{Re}F^B_{M,m}(K)\,\mathrm{Im}F^A_{M,n}(K)]\,dK\,. \qquad (3.7)$$

Finally, we obtain for V^{AB}_{EM}:

$$V^{AB}_{EM}=\frac{-1}{8\pi^4 R}\left\{\begin{array}{l} -\dfrac{5}{4}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-4})\,I^{AB,1}_{EM,nm} \\[2ex] +\dfrac{\pi}{2}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-3})\,I^{AB,2}_{EM,nm} \\[2ex] -\dfrac{3}{2}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-2})\,I^{AB,3}_{EM,nm} \\[2ex] +\dfrac{\pi}{2}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-1})\,I^{AB,4}_{EM,nm} \\[2ex] +\dfrac{2}{3}\displaystyle\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(\ln R)\,I^{AB,5}_{EM,nm} \\[2ex] +\cdots\;, \end{array}\right. \qquad (3.8)$$

with

$$I^{AB,r}_{EM,nm}=\int_0^\infty K^r\,\mathrm{Im}D^{AB}_{EM,nm}(K)\,dK \qquad (3.9)$$

$$=\int_0^\infty K^r[\mathrm{Re}F^A_{E,n}(K)\,\mathrm{Im}F^B_{M,m}(K)+\mathrm{Im}F^A_{E,n}(K)\,\mathrm{Re}F^B_{M,m}(K)]\,dK \qquad (3.10)$$

and for V^{AB}_{ME} a similar expression obtained by the exchange $E \leftrightarrow M$ everywhere.

From the dispersion relation (2.14) for $D_{xy,nm}$, it follows that

$$I^{AB,1}_{xy,nm}=\int_0^\infty K\,\mathrm{Im}D^{AB}_{xy,nm}(K)\,dK$$

$$=-\tfrac{1}{2}\pi\lim_{K\to\infty}[K^2 D_{xy,nm}(K)]\,. \qquad (3.11)$$

However, according to the dispersion relations (2.12), and also by direct calculation for hydrogen atoms, we find that

$$\lim_{K\to\infty} D_{xy,nm}(K)=O(K^{-4})\,,$$

and hence

$$I^{AB,1}_{xy,nm}\equiv 0\,. \qquad (3.12)$$

Therefore the terms with R^{-4} in parentheses vanish in each of the V_{xy}.

We note further that the form factors F_n are expected to be significantly large over some region of K of the order of typical atomic wave numbers. It follows that successive values of r in $I^{AB,r}_{xy,nm}$ should be related approximately by

$$I^{AB,r+1}_{xy,nm}/I^{AB,r}_{xy,nm}\simeq K_0\,,$$

where K_0 is a typical atomic wave number for an atomic transition. It follows that the terms in $V^{AB}_{xy,nm}$ arising from successive I^r, will be of relative order K_0R, and therefore for a fixed value of n, m, the expansions (3.3) and (3.8) are expansions in K_0R, which is assumed small in the region we are now considering.

It is of interest to note the occurrence of terms proportional to $\ln R$, which show that the "small R expansion" is nonanalytic. This lack of analyticity for small R originates in the fact that the form factors $F_n(K)$ do not vanish exponentially at large K, but instead fall off as a finite power K^{-2}. As a result, if one tries for example to expand the integral in (2.13) in powers of R, one finds that the terms beyond R^2 have as coefficients integrals that diverge for large K. This occurrence signals a nonanalytic behavior of the integral at small R. From this argument, one might have expected terms of order $R^{-2}\ln R$ to occur in (3.3) or (3.8). These terms however cancel identically because of the form of the polynomials P_{xy} and the first logarithm appears in order $\ln R$. Because the successive terms in (3.3) or (3.8) are of relative order K_0R, the logarithmic singularities appear to be far too small to detect in practical experiments.

If we look at a term, say in V_{EE}, proportional to a given power R^p, we see that this term gets contributions from many different terms in the expansion (3.3). For example, the term going as R^{-6}

has as its coefficient

$$-\frac{1}{8\pi^4}\left[\tfrac{3}{2}\pi I^{AB,0}_{EE,00}+\tfrac{1}{2}\pi\,12(I^{AB,2}_{EE,10}+I^{AB,2}_{EE,01}) + \tfrac{1}{2}\pi\,24(I^{AB,4}_{EE,02}+I^{AB,4}_{EE,11}+I^{AB,4}_{EE,20})\right]+\cdots\,. \qquad (3.13)$$

It is easy to see that this coefficient, and that of all other inverse powers, involve those $I^{AB,r}_{EE,nm}$, in which $r-2(n+m)$ takes on some fixed value, as r, n, m vary. From the previous discussion, we have seen that increasing r by two units will approximately multiply I by K_0^2, while increasing n or m by 1 unit will approximately multiply I by a^2. Hence the leading term in a given coefficient will be that with r, n, m taking on the minimum values consistent with $r-2(n+m)$ taking on the required values. The other terms will in general be smaller than this leading term by some even power of (K_0a), which is a number of order $10^{-2}(=\alpha)$.

We write here for convenience these leading coefficients for the dominant powers of R:

$$V_{EE}\simeq\frac{-1}{8\pi^4}\left[\tfrac{3}{2}\pi R^{-6}I^{AB,0}_{EE,00}+\tfrac{1}{2}\pi R^{-4}I^{AB,2}_{EE,00}-\tfrac{7}{6}R^{-3}I^{AB,3}_{EE,00}+\cdots + \tfrac{3}{2}\pi\,20R^{-8}(I^{AB,0}_{EE,10}+I^{AB,0}_{EE,01}) + \tfrac{3}{2}\pi\,120R^{-10}(I^{AB,0}_{EE,20}+I^{AB,0}_{EE,11}+I^{AB,0}_{EE,02})\right]+\cdots\,. \qquad (3.14)$$

It may be seen from our estimates of the relative size of the $I^{AB,r}_{xy,nm}$, that the term $R^{-6}I^{AB,00}_{xy,00}$ will always be the largest within the region of interest. However, the relative size of the terms with powers of R greater or less than -6 will depend on where R lies in this region. It can be seen, for example, that the term in R^{-8} is greater than the term in R^{-4} when $R<a(K_0a)^{1/2}\sim 10a$, and is less when $R>10a$.

Consider next the convergence of the integrals over K that define the quantities $I^{AB,r}_{xy,nm}$. The critical place for the convergence of those integrals is obviously $K\to\infty$. The convergence will depend on the behavior at $K\to\infty$ of $\mathrm{Re}F_n(K)$ and $\mathrm{Im}F_n(K)$. From the dispersion relations, and from explicit calculation for hydrogen we find that[5]

$$\lim_{K\to\infty}\mathrm{Re}F_n(K)=O(K^{-2})\,.$$

For $\mathrm{Im}F_n(K)$, no simple theory is available. In the case of $\mathrm{Im}F_0(K)$, related by the optical theorem to the total cross section, we can get some information if we assume the nonrelativistic photoelectric effect to dominate the total cross section. This would then give $\mathrm{Im}F_0(K)\sim K^{-11/2}$ as $K\to\infty$, and then implies that the integrals $I^r_{AB,00}$ will converge for $r\leq 5$ and diverge for $r>5$. However, relativistic corrections might well change this estimate, as might the inclusion of other terms in the total cross section, such as the high-energy limit of the elastic scattering itself or the creation of pairs.

The explicit calculation for hydrogen (see Appendix C) gives an $\mathrm{Im}F_n(K)$ which decreases about as $K^{-(3n+11/2)}$. This suggests that for higher-multipole terms, it is likely that the convergence will be still better than for $I^{AB,r}_{xy,00}$. However, it would appear that in any case, only a finite number of the $I^{AB,r}_{xy,nm}$ will converge and that the expansion (3.8) is to be regarded as asymptotic rather than as exact.

We show in Appendix B that the $F_{x,n}(K)$ are related to the frequency dependent 2^{n+1} multipole polarizabilities $\alpha_{2n+1}(K)$. The relationship is of the form

$$F_{x,n}(K)=\frac{8\pi\alpha_{x,2^{n+1}}(K)}{(2n+2)!}+O(K^2a^2)\,\frac{\alpha_{x,2^{n+2}}(K)}{a^2} +O(K^4a^4)\,\frac{\alpha_{x,2^{n+3}}(K)}{a^4}+\cdots\,, \qquad (3.15)$$

where the powers of a are inserted for dimensional convenience. These formulas may be inserted into any of the formulas [(2.13) and (2.16)] to reexpress the potentials in terms of the perhaps more familar multipole polarizabilities. Upon doing this, we note that the values of K giving the major contributions to integrals are such that $Ka\sim\alpha$, whereas the quantities $\alpha_{x,2^{r+l}}/a^{2l}$ are all expected to be comparable in size. It follows that a good approximation to integrals over the form factors can be obtained by taking only the first term of Eq. (3.15):

$$F_{x,n}(K)\simeq\frac{8\pi}{(2n+2)!}\,\alpha_{x,2^{n+1}}(K)\,. \qquad (3.16)$$

If we substitute into Eq. (2.13), we get the retarded generalization of the van der Waals potential, expressed in terms of polarizabilities at imaginary frequencies:

$$V_{xy,nm}=\frac{-64\pi^2}{16\pi^3R}\,\frac{d^{2(n+m)}}{dR^{2(n+m)}}\left(R^{-5}\int_0^\infty d\zeta\,e^{-2\zeta R}P_{xy}(\zeta R) \times\frac{\alpha_{x,2^{n+1}}(i\zeta)\alpha_{y,2^{m+1}}(i\zeta)}{(2n+2)!\,(2m+2)!}\right)\,. \qquad (3.17)$$

The term involving $\alpha_{2^{n+1}}\alpha_{2^{m+1}}$ may be regarded as the retarded generalization of the 2^{n+1} pole-2^{m+1} pole force familiar from the Coulomb contribution to the small-R version of the van der Waals force.[6] However, the presence of terms beyond the first in Eq. (3.15) indicates that this formula is only approximate, and that the form factors F_n should replace the $\alpha_{2^{n+1}}$ in the exact formulas (2.13).

B. Large-R Region

Consider next the region of R in which $KR\gg 1$, for those K that contribute significantly to the integrals (2.16). This is the region in which "retardation" effects are important. In this region, we find

$$R^{-5}P^{op}_{EE}f(2KR)=\frac{23}{4KR^6}-\frac{129}{8K^3R^8}+\frac{5112}{32K^3R^{10}}+O(K^{-7}R^{-12}) \qquad (3.18)$$

and the same for $R^{-5}P^{op}_{MM}f(2KR)$;

$$R^{-5}P^{op}_{ME}f(2KR)=\frac{-7}{4KR^6}+\frac{81}{8K^3R^8}-\frac{3960}{32K^5R^{10}}+O(K^{-7}R^{-12}) \tag{3.19}$$

and the same for $R^{-5}P^{op}_{EM}f(2KR)$.

Upon substituting these into (2.16), we obtain a series of descending powers of R, with coefficients that are integrals over K of products of form factors[7]:

$$V_{EE}=\frac{-1}{8\pi^4R}\left\{\begin{aligned}&\frac{23}{4}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-6})J^{AB,1}_{EE,nm}\\&-\frac{129}{8}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-8})J^{AB,3}_{EE,nm}\\&+\frac{5112}{32}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-10})J^{AB,5}_{EE,nm}\\&+\cdots,\end{aligned}\right. \tag{3.20}$$

where

$$J^{AB,r}_{EE,nm}\equiv\int_0^\infty K^{-r}\,\mathrm{Im}D^{AB}_{EE,nm}(K)\,dK \tag{3.21}$$

$$\begin{aligned}&=\int_0^\infty K^{-r}[\mathrm{Re}F^A_{E,n}(K)\,\mathrm{Im}F^B_{E,m}(K)\\&\qquad+\mathrm{Im}F^A_{E,n}(K)\,\mathrm{Re}F^B_{E,m}(K)]\,dK\,.\end{aligned} \tag{3.22}$$

A similar expression may be written for V_{MM} in terms of $J^{AB,r}_{MM,nm}$, with $J^{AB,r}_{MM,nm}$ defined similarly in terms of magnetic form factors. Similarly, we obtain for V_{EM}:

$$V_{EM}=\frac{-1}{8\pi^4R}\left\{\begin{aligned}&-\frac{7}{4}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-6})J^{AB,1}_{EM,nm}\\&+\frac{81}{8}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-8})J^{AB,3}_{EM,nm}\\&-\frac{3960}{32}\sum_{n,m=0}^{\infty}\frac{d^{2(n+m)}}{dR^{2(n+m)}}(R^{-10})J^{AB,5}_{EM,nm}\,,\end{aligned}\right. \tag{3.23}$$

where

$$J^{AB,r}_{EM,nm}=\int_0^\infty K^{-r}\,\mathrm{Im}D^{AB}_{EM,nm}(K)\,dK \tag{3.24}$$

$$\begin{aligned}&=\int_0^\infty K^{-r}[\mathrm{Re}F^A_{E,n}(K)\,\mathrm{Im}F^B_{M,m}(K)\\&\qquad+\mathrm{Im}F^A_{E,n}(K)\,\mathrm{Re}F^B_{M,m}(K)]\,dK\,,\end{aligned} \tag{3.25}$$

and a similar expression for V_{ME}, with E and M interchanged everywhere.

One may regard a given term in these expansions with particular values of r, n, m, as the large distance limit of the term with the corresponding values of r, n, m, in the expansions (3.3), (3.8), etc. Hence we see that the leading term of all inverse powers of R, and not only the R^{-6} dipole-dipole interaction, falls off with one extra power of R at large R than at small R. Thus, for example, the dipole-quadrupole interaction behaves asymptotically as

$$\frac{-1}{8\pi^4}\,\frac{23}{4}\,42(J^{AB,1}_{EE,10}+J^{AB,1}_{EE,01})R^{-9}\,, \tag{3.26}$$

while the quadrupole-quadrupole term goes as

$$\frac{-1}{8\pi^4}\,\frac{23}{4}\,2964J^{AB,1}_{EE,21}R^{-11}\,. \tag{3.27}$$

Again in this limit, a given inverse power of R gets contributions from several terms in the series. However, here the coefficient of a given inverse power always gets its main contribution from the terms $J^{AB,r}_{xy,00}$. The higher-multipole terms now make contributions to a given term that are smaller by factors $(K_0a)^{2n+2m}$ than the dipole-dipole contributions.

If we assume, for the moment, that the integrals defining the J_{xy} are convergent, we can identify them with form factors and their derivatives, evaluated at $K=0$. To see this, we note from (2.14), for sufficiently small K,

$$D_{xy,nm}=\frac{2}{\pi}\int_0^\infty\sum_{r=0}^{\infty}\frac{K'\,dK'}{K'^2}\left(\frac{K^2}{K'^2}\right)^r\mathrm{Im}D_{xy,nm}(K')\,. \tag{3.28}$$

Hence

$$\left.\frac{d^{2p}D_{xy,nm}}{dK^{2p}}\right|_{K=0}=\frac{2(2p)!}{\pi}\int dK'\,(K')^{-1-2p}\,\mathrm{Im}D_{xy,nm}(K')\,, \tag{3.29}$$

and therefore, setting $2p+1=r$, which is always odd in Eq. (3.24), we find

$$J^{AB,r}_{xy,nm}=\frac{\pi}{2}\,\frac{1}{(r-1)!}\,\frac{d^{r-1}}{dK^{r-1}}\,D^{AB}_{xy,nm}\Big|_{K=0}\,. \tag{3.30}$$

Finally, from the definition of $D^{AB}_{xy,nm}$, we have

$$J^{AB,r}_{xy,nm}=\frac{\pi}{2}\,\frac{1}{(r-1)!}\,\frac{d^{r-1}}{dK^{r-1}}\,[F^A_{x,n}F^B_{y,m}]\Big|_{K=0}\,. \tag{3.31}$$

We have seen that the quantities $F_{x,n}(K=0)$ are proportional to the static 2^{n+1} multipole polarizabilities. It follows that the $J^1_{xy,nm}$, and hence the leading term in the large-R expansion of the van der Waals potential can always be expressed in terms of these polarizabilities. The correction terms, containing $J^r_{xy,nm}(r>1)$, involve derivatives with respect to K of $F_{x,n}$, evaluated at $K=0$. According to Appendix B, these can also be expressed in terms of derivatives of the static multipole polarizabilities. However, in this case several terms will occur in each derivative of F_n. It is not difficult to see that if the polarizabilities are regular at $K=0$, then an lth derivative of F_n can, in general, be expressed as a sum of polarizabilities and their derivatives from α_n to α_{n+l}. Of these terms, the important one is always

$$\left.\frac{d^l F_{x,n}}{dK^l}\right|_{K=0} \simeq \frac{8\pi}{(2n+2)!}\left.\frac{d^l \alpha_{2^{n+1}}}{dK^l}\right|_{K=0} . \qquad (3.32)$$

Consider next the convergence of the integrals defining the $J^{AB,r}_{xy,nm}$. Since $D_{xy,nm}$ decreases as $K \to \infty$, the integrals converge at ∞. Furthermore, it is not hard to see that the contribution from finite K, other than $K \simeq 0$, is finite, even in the "zero-width approximation," where the resonances are treated as real poles. The only question of convergence of the J comes from $K \simeq 0$. Here we must distinguish two treatments of the form factors.

(a) In the "zero-width approximation," we approximate the imaginary part of the form factors by a series of Dirac δ functions contributed by the various state resonances, and a continuum contribution, for $K > K_I$, the ionization energy of the atom. In this case, it is obvious that $\mathrm{Im} D^{AB}_{xy,nm} = 0$, when $K < K_1$, where K_1 is the lowest excited state energy of the atom. Therefore, the integrands in J vanish for $K < K_1$, and these integrals therefore converge at small K.

(b) If we want to improve upon the "zero-width approximation," then we must include the effects of the "tail" of the resonances, on $\mathrm{Im} F$, for small K. This can be done in a relatively model-independent way as follows: We know from the optical theorem, that $\mathrm{Im} F_{M,0}$ can be related to the total cross section for photon-atom scattering. This relation is given by

$$\mathrm{Im}(F_{E,0} + F_{M,0}) = \sigma_T(K)/K .$$

But for small K, we expect $\sigma_T(K) \simeq a^6 K^4$, from the usual analysis of Rayleigh scattering. This suggests, since usually $F_{E,0} \gg F_{M,0}$,

$$\lim_{K\to 0} (\mathrm{Im} F_{E,0}) \simeq a^6 K^3 .$$

On the other hand, $\mathrm{Re} F_{E,0}(K=0)$ is given through the dispersion relations, by contributions from $K > 0$ resonances, and behaves as

$$\lim_{K\to 0} (\mathrm{Re} F_{E,0}) \simeq a^3 .$$

These behaviors suggest the following conclusions: (i) The contributions of small K to $J^{AB,1}_{EE,00}$ and $J^{AB,3}_{EE,00}$ are finite, and are smaller than the resonance and continuum contribution by a factor $\sim (K_1 a)^3 \simeq 10^{-6}$. (ii) The integrals defining $J^{AB,r}_{EE,00}$ for $r > 3$ diverge at small K. Strictly speaking, this implies that in this case the expansion defined by Eq. (3.20) does not exist. Actually, the reason for this is apparent. If it is necessary to include contributions from very small K to the unexpanded integrals such as (2.16), then it is not possible to use the expansions Eq. (3.18) for $R^{-5} P^{op} f(2KR)$, since these are valid only when $KR \gg 1$. It would then be necessary to use the unexpanded form (2.16) even for $R \to \infty$, to pick out the correct contribution of small K. In the case of V_{EE}, this can be done explicitly, with the following result. In addition to the series of terms given in Eq. (3.20), the small values of K contribute a term proportional to $a^9 R^{-10}$. This term, of an analytic form intermediate to those in the series in Eq. (3.20), is small everywhere in the region of interest. It is therefore probably sufficient generally to follow the procedure described in (a) above, i.e., the zero-width approximation, and the expansion Eq. (3.20), which involves J's that are now all convergent.

IV. MEASURABILITY OF THE FORM FACTORS

In order to apply the formulas of Secs. II and III to specific atoms, it is necessary either to calculate, or to obtain from experiment, the form factors $F_{x,n}(K)$. In Appendix C, we present a calculation of these form factors for hydrogen atoms, and apply it to some calculations of the higher-multipole potentials. Such calculations are likely to be difficult for atoms other than hydrogen, since they involve substantial information about the wave function in the ground state and excited states.

We consider here instead how to obtain the $F_{x,n}(K)$ from measurements of the elastic scattering of light by atoms. This problem is rendered more difficult by the fact that, in general, the amplitudes are complex. This implies that in general, it is necessary to supplement measurements of the cross section by other information to determine the $F_{x,n}(K)$. We write the scattering amplitude as

$$M = \epsilon_i \epsilon'_j [K^2 F_E \delta_{ij} + K^2 F_M (\delta_{ij} - \hat{K}'_i \hat{K}_j)](-1/8\pi) .$$

The corresponding cross section without any sum over polarizations is given by

$$\frac{d\sigma(E,E')}{d\Omega} = \frac{1}{64\pi^2} \epsilon_i \epsilon^*_k \epsilon'_j \epsilon^{*\prime}_l [K^4 |F_E|^2 \delta_{ij}\delta_{kl} + K^4 |F_M|^2 (\delta_{ij} - \hat{K}'_i \hat{K}_j)(\delta_{jl} - \hat{K}'_k \hat{K}_l)$$
$$+ K^4 F_E F^*_M \delta_{ij} (\delta_{kl} - \hat{K}'_k \hat{K}_l) + K^4 F^*_E F_M \delta_{kl} (\delta_{ij} - \hat{K}'_i \hat{K}_j)] \qquad (4.1)$$

$$= \frac{K^4}{64\pi^2} [(\epsilon \cdot \epsilon')(\epsilon^* \cdot \epsilon^{*\prime}) |F_E|^2 + (\epsilon \cdot \epsilon' - \hat{K}' \cdot \epsilon \hat{K} \cdot \epsilon')(\epsilon^* \cdot \epsilon'^* - \hat{K}' \cdot \epsilon^* K \cdot \epsilon'^*) |F_M|^2$$
$$+ \epsilon \cdot \epsilon' (\epsilon^* \cdot \epsilon^{*\prime} - \hat{K}' \cdot \epsilon \hat{K} \cdot \epsilon'^*) F_E F^*_M + (\epsilon \cdot \epsilon' - \hat{K}' \cdot \epsilon \hat{K} \cdot \epsilon') \epsilon^* \cdot \epsilon'^* F^*_E F_M] . \qquad (4.2)$$

The use of complex polarization vectors is essential here if we are to allow (as we must) for the possibility of circular polarization of the incident or outgoing photons. By measuring the initial and final polarizations, we can determine from experiment the quantities $|F_E|^2$, $|F_M|^2$, and $F_E F_M^*$, which leaves undetermined the relative phase of F_E and F_M, which must be the case for any quantity bilinear in the matrix element.

An obvious candidate for the extra information we must supply is the unitarity relation, as this involves both linear and quadratic terms in F_E and F_M. In FS, it was mentioned that in the approximation where all terms other than $F_{E,0}$ are neglected, it is possible to determine $\mathrm{Im}F_{E,0}$ in terms of the total cross section by using the optical theorem

$$\mathrm{Im}F_{E,0}(K) = (1/K)\sigma_T(K) ,$$

and then to determine $\mathrm{Re}F_{E,0}(K)$ by measuring the elastic cross section. This procedure can still be used to fix $(\mathrm{Im}F_{E,0} + \mathrm{Im}F_{M,0})$, even when we do not neglect higher partial waves. However, the optical theorem alone does not give any information on the relative phase of $F_{E,n}$ and $F_{M,n}$ for $n > 0$.

Such information is given by the general unitarity relations for nonforward scattering. To clarify this question, we divide our discussion into two regions of K, i.e., those K below the threshold K_I for inelastic processes, and those above this threshold. When $K < K_I$ there are simple relations between $\mathrm{Re}F_{x,n}$ and $\mathrm{Im}F_{x,n}$ for each n. These relations follow from the fact that the $F_{x,n}$ are linearly related to amplitudes $M^J_{\lambda\lambda'}$ with definite angular momentum and helicity, and the latter amplitudes, in the region of purely elastic scattering, satisfy individual unitarity relations between real and imaginary parts, of the general form[8]

$$\mathrm{Im}M^J_{\lambda,\lambda'} = \sum_{\lambda''} M^J_{\lambda,\lambda''} M^{J*}_{\lambda',\lambda''} . \tag{4.3}$$

This is analogous to the scattering of spinless particles, where the partial-wave amplitudes f_l satisfy

$$\mathrm{Im}f_l = |f_l|^2 .$$

Hence, in the elastic region, measurements of the cross sections for polarized photons, together with the unitarity relations, are sufficient to determine $\mathrm{Re}F_{x,n}$ and $\mathrm{Im}F_{x,n}$, apart from ambiguities in sign, which can be settled by the dispersion relations. In the inelastic region however, the unitarity equations relate elastic to inelastic amplitudes, and, in general, a determination of the real and imaginary parts of all amplitudes must be done simultaneously through a measurement of elastic and inelastic cross sections in all coupled channels. In the present problem, this would mean the measurement of differential cross sections for the photoelectric effect and for the scattering of electrons by ions, as well as for the elastic scattering of photons by atoms. If all these quantities can be measured, there would be as many equations as unknown quantities, and the real and imaginary parts of all amplitudes can be determined.

Let us see how this would work in the case of two coupled channels consisting of atom-photon (channel 1), and of electron-ion (channel 2). We assume the ion to have spin $\frac{1}{2}$ for simplicity. The complications of polarization are most easily treated by using helicity amplitudes. The scattering amplitude may be written as a sum of amplitudes for a given total angular momentum, evaluated between definite helicity states[9]:

$$M_{i\lambda,k\lambda'} \sim \sum_J M^J_{i\lambda,k\lambda'} C^J_{\lambda\lambda'}(\hat{K},\hat{K}') , \tag{4.4}$$

where i, k are channel labels and λ, λ' helicity labels. The $C^J_{\lambda\lambda'}$ can be expressed in terms of the rotation matrices $D^J_{MM'}$. The helicity scattering amplitudes satisfy unitarity relations of the form

$$M^J_{i\lambda,k\lambda'} - M^{J*}_{i\lambda,k\lambda'} \sim \sum_{l,\lambda''} M^J_{i\lambda,l\lambda''} M^{J*}_{k\lambda',l\lambda''} \tag{4.5}$$

and are linear combinations of the form factors we have used previously.

In the present case, there are 12 such amplitudes for each value of J. The unitarity equations give 12 relations among these amplitudes. Another 12 relations can be obtained by measuring the differential cross sections

$$\frac{d\sigma_{i\lambda,k\lambda'}}{d\Omega} \propto |M_{i\lambda,k\lambda'}|^2 . \tag{4.6}$$

Again there are 12 differential cross sections that could be measured, and these equations together with the 12 unitarity equations determine (up to certain sign ambiguities) the 24 quantities $\mathrm{Re}M_{i\lambda,k\lambda'}$, $\mathrm{Im}M_{i\lambda,k\lambda'}$. If the number of coupled channels is greater, there will be more of each type of equation, but it is still possible, by measuring enough cross sections, to determine $\mathrm{Re}M_{ij}$ and $\mathrm{Im}M_{ij}$. However, if any of the channels involve states of three or more particles, these measurements are unlikely to be feasible.

In view of this, it may be of interest to see a different approach to the determination of the elastic amplitudes, which involves the measurement only of elastic scattering and of total cross sections for atom-photon scattering. The method makes use of dispersion relations to supplement the experimental data, and is analogous to one that has been used in high-energy physics.[10] We illustrate this method for the most common case, where $F_M \ll F_E$, and is neglected. The more general case can be found in the thesis of Au.[11]

We consider the amplitude with the factor of K^2 reinserted into the amplitude:

$$f(K,t)=(K^2/4\pi)F_E(K,t)\ . \tag{4.7}$$

We write down a series expansion in t for f instead of the common partial-wave expansion:

$$f=\sum_n A_n(K)t^n\ . \tag{4.8}$$

These A_n's are related to the partial-wave amplitude f_l defined by

$$f=\sum_l (2l+1)f_l(K)P_l(\cos\theta) \tag{4.9}$$

in the following way:

$$A_n(K)=\frac{1}{(2K)^{2n}(n!)^2}\sum_{l\geq n}(2l+1)f_l(K)\frac{(l+n)!}{(l-n)!} \tag{4.10}$$

and

$$f_l(K)=\frac{1}{2}\sum_{n\geq l}(-2)^n K^{2n}A_n(K)2^{n+1}D_{nl}\ , \tag{4.11}$$

where

$$D_{nl}=\sum_{m=0}^{l}\frac{(-1)^m}{(m!)^2}\frac{(l+m)!}{(l-m)!}\frac{1}{n+m+1}\ . \tag{4.12}$$

But, experimentally, we measure $|f(K,t)|^2$, and we write

$$|f(K,t)|^2=2\sum_n g_n(K)t^n\ . \tag{4.13}$$

From (4.8), we have

$$|f(K,t)|^2=\sum_{n,m}A_n(K)A_m^*(K)t^{n+m}\ . \tag{4.14}$$

Comparing coefficients we have

$$A_0(K)A_0^*(K)=2g_0\ , \tag{4.15}$$

$$A_0(K)A_1^*(K)+A_0^*(K)A_1(K)=2g_1(K)\ , \tag{4.16}$$

$$A_0(K)A_2^*(K)+A_2(K)A_0^*(K)+A_1^*(K)A_1(K)=2g_2(K)\ , \tag{4.17}$$

and so on. But

$$\operatorname{Im}f(K,t=0)=\operatorname{Im}A_0(K)\ ; \tag{4.18}$$

hence, by the optical theorem, $\operatorname{Im}A_0$ is measurable. By measuring the differential cross section in the forward direction, we can measure $\operatorname{Re}A_0$ at least up to a sign, which can be fixed by a dispersion relation. Hence A_0 is determined. We write A_0 and A_1 as

$$A_0=a+ib\ , \tag{4.19}$$

$$A_1=R+iL\ . \tag{4.20}$$

(The dependence on K is understood.) Then (4.16) gives

$$aR+bL=g_1\ , \tag{4.21}$$

where now a, b, g_1 are experimentally available. $F_{E,n}$ is related to A_n as $F_{E,n}=(4\pi/K^2)A_n$. As we have assumed the validity of a dispersion relation for $F_{X,n}$, a dispersion relation is assumed to be valid for A_n/K^2. Equation (4.21) can be rewritten

$$A_0R-ibA_1=g_1\ . \tag{4.22}$$

Dividing (4.22) by K^2 and writing down a dispersion relation for A_1/K^2 in terms of its real part, we have

$$A_0(K)\ \frac{R(K)}{K^2}=\frac{g_1(K)}{K^2}+\frac{2b(K)K}{\pi}\int_0^\infty\frac{R(K')\,dK'}{K'^2(K'^2-K^2-i\epsilon)} \tag{4.23}$$

or

$$\frac{R(K)}{K^2}=\frac{g_1(K)}{A_0(K)K^2}+\frac{2b(K)K}{A_0(K)\pi}\int_0^\infty\frac{R(K')\,dK}{K'^2(K'^2-K^2-i\epsilon)}\ . \tag{4.24}$$

Noting that the δ-function kind of singularities in the scattering amplitude at resonances are in fact symmetrical, highly peaked, but finite functions, we define the following two functions:

$$\phi(K)\cong R(K)/K^2\ , \tag{4.25}$$

$$\mathcal{T}(K)\cong g_1(K)/A_0(K)K^2\ . \tag{4.26}$$

We also note the following asymptotic behavior:

$$\lim_{K\to 0} g_1(K)\to K^4\ , \tag{4.27}$$

$$\lim_{K\to 0} A_0(K)\to K^2\ , \tag{4.28}$$

$$\lim_{K\to 0} b(K)\to K^5\ , \tag{4.29}$$

$$\lim_{K\to\infty} g(K)\to \text{const}\ , \tag{4.30}$$

$$\lim_{K\to\infty} A_0(K)\to \text{const}\ , \tag{4.31}$$

$$\lim_{K\to\infty} b(K)\to K^{-5/2} \tag{4.32}$$

$$\lim_{K\to\infty} R(K)\to \text{const}\ , \tag{4.33}$$

which follow from the usual nonrelativistic theory of atom-photon scattering. This shows that ϕ and $\mathcal{T}$ are regular function in the interval $(0,\infty)$. Equation (4.24) then becomes a singular integral equation of the Omnes type[12]:

$$\phi(K)=\mathcal{T}(K)+(1/\pi)\int_0^\infty\overline{K}(K,K')\,\phi(K')\,dK'\ , \tag{4.34}$$

where $\overline{K}(K,K')$ is the singular kernel

$$\overline{K}(K,K')=\frac{2K\,b(K)}{A_0(K)\,(K+K')\,(K'-K-i\epsilon)} \tag{4.35}$$

$$=\left[\frac{b(K')}{A_0(K')}+\left(\frac{2K\,b(K)}{A_0(K)\,(K+K')}-\frac{b(K')}{A_0(K')}\right)\right]\times\frac{1}{K'-K-i\epsilon}\ . \tag{4.36}$$

Writing

$$b(K)/A_0(K)=h^*(K)=e^{-i\delta(K)}\sin\delta(K)\ , \tag{4.37}$$

which is possible since $b = \mathrm{Im} A_0$, we find that

$$\delta(K) = \tan^{-1} b(K)/a(K) . \tag{4.38}$$

From the boundary conditions (4.27) to (4.33), we see that the function $\delta(K)$ is regular in the interval $(0, \infty)$ and falls off at infinity faster than $1/K$. Denoting the second part of $\bar{K}(K, K')$ by

$$\tilde{K}(K, K') = \left(\frac{2K\, b(K)}{A_0(K)\,(K + K')} - \frac{b(K')}{A_0(K')} \right) \Big/ (K' - K) \tag{4.39}$$

we see that $\tilde{K}(K, K')$ is a regular kernel with boundary conditions

$$\tilde{K}(K, K') \to 0 \quad \text{as } K \to \infty \quad \text{or } K' \to \infty . \tag{4.40}$$

This matches the boundary conditions of the kernel Omnes assumed.[12] Thus according to Omnes our singular integral equation in (4.24) is reducible to Fredholm's type (with regular kernel) and hence is soluble. Different techniques depending on the nature of the kernel are used to solve integral equations of Fredholm's type and are widely available in the literature.[13] Once $R(K)$ is known, $L(K)$ can be obtained from (4.21), and hence, A_1 is known. Equation (4.17) can be written as

$$A_0 A_2^* + A_2 A_0^* = 2 g_2(K) - |A_1|^2 . \tag{4.41}$$

Call

$$2 g_2(K) - |A_1|^2 \equiv 2 g_2'(K) , \tag{4.42}$$

and let

$$A_2 \equiv R'(K) + i L'(K) . \tag{4.43}$$

Equation (4.41) can be reduced to a type of singular integral equation like (4.24) with similar boundary conditions. The same technique that we have gone through for A_1 applies and we can find A_2. Having found A_2, we find that A_3 and, in general, A_n are of the form

$$A_0 A_n^* + A_n A_0^* = 2 g_n - \sum_{r=1}^{n-1} A_r A_{n-r}^* . \tag{4.44}$$

Hence all A_n's can be calculated provided A_0 to A_{n-1} are known, and so all the A_n's are calculable in sequence.

V. DISCUSSION

We have established a series of formulas expressing the two-photon exchange van der Waals force in terms of quantities referring to individual atoms, and in principle obtainable from experiments on the individual atoms. Earlier versions of these formulas have been used to do practical calculations[14] of forces between hydrogen and rare-gas atoms. If our present formulas are to be used similarly, detailed experimental data on elastic atom-photon scattering will be needed, which we leave as a challenge to the experimentalist.

It is of some interest to ask about what aspects of the van der Waals force are omitted from the present theory. One such aspect, alluded to in previous work, is that when electromagnetic radiative corrections to the photon-atom scattering amplitude are included, this amplitude is no longer an analytic function of K and t, near K or $t = 0$. As a result, expansions of the form (2.3) and (3.28) are impermissible, when such corrections are included. However, there is some indication[15] that the first few terms in an expansion such as (2.3) are correct, even including radiative corrections, and that the leading nonanalytic terms behave as $t^n \ln t$, with $n > 0$. This would imply that the first few terms of Eq. (2.15), for example, are correct but that the remaining terms would have to be modified. Detailed conclusions however will require a calculation of the radiatively corrected amplitudes, as a function of K and t, which does not seem to be available.

Another aspect omitted from our theory is the exchange of more than two photons, corresponding in other language to the use of higher orders of perturbation theory. These effects can, in principle, be treated in much the same way as Feinberg and Sucher have done the two-photon exchange, by first computing a general vertex for the process atom + antiatom → n photons, and then analytically continuing the form factors appearing in this vertex. While we have not carried through this procedure because of the immense labor involved, a simple estimate indicates that the leading term in the three-photon exchange would behave as R^{-13}, for $R \to \infty$. Again, we must leave this question to be investigated elsewhere.

Finally, our explicit calculation for H atoms uses the nonrelativistic atom-photon scattering amplitude, and it would be desirable to improve this by including relativistic effects. We emphasize that our general formulas for V_{xy} include relativistic corrections, and it is only a matter of putting these effects into the expression for the scattering amplitude.

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APPENDIX A: SOME ANALYTIC PROPERTIES OF THE FORM FACTORS

1. Anomalous Threshold in the Channel Atom + Antiatom → 2γ

The spectral functions appearing in Eq. (2.1) are given by the imaginary part of the form factors in the atom-photon amplitude in the s channel, i.e.,

$$\rho_x(s, t) = -\tfrac{1}{2} i \left[F_x(s + i\epsilon, t) - F_x(s - i\epsilon, t) \right] , \tag{A1}$$

where $s = m_A^2 + 2 m_A K$. The poles and cut on the s

plane correspond to the well-known resonances and the photoelectric threshold. It can be shown[11] that corresponding to each pole, the spectral function is expressable as a δ function in the variable s. $F(s, t)$ is analytic in t for $|t| < t_0$, where t_0 is the lowest anomalous threshold, or in the absence of such anomalous threshold, the square of the lightest masses that can be exchanged in the t channel. The problem of anomalous threshold has been extensively studied by Karplus, Sommerfield, and Wichmann.[16] These authors found that anomalous thresholds are very common in weakly bound systems, for example, the deuteron. We have followed the methods of KSW 1 and KSW 2 to study the possibility of an anomalous threshold in the crossed channel for atomic Compton scattering. We find that such an anomalous threshold does exist, and particularly for hydrogen, it occurs at $t_0 \simeq 4/a^2$ in the nonrelativistic case. This agrees with the region of validity for power series expansion in t for the hydrogenic Compton amplitude of Gavrila and Costescu.[5]

It was pointed out long ago in KSW 1 that for a triangular vertex (Fig. 1) which denotes the conversion of a particle of field ϕ_2 (mass M_2) to one of field ϕ_3 (mass M_3) by a virtual quantum of the field ϕ_1 with invariant momentum-transfer square q^2, if the masses of the intermediate fields ϕ_a, ϕ_b, and ϕ_c are m_a, m_b and m_c, an anomalous threshold exists if

$$(m_b M_2^2 + m_c M_3^2)/(m_b + m_c) > m_a^2 + m_b m_c \ . \qquad \text{(A2)}$$

In the case of the electromagnetic one-photon form factor, of an atom, we have (Fig. 2)

$M_2 = M_3 = M =$ mass of the atom (antiatom) ,

$m_b = m_c = m_0 = m_e$ (mass of the electron) ,

$m_a =$ mass of the singly ionized atom

$= M_p$ (mass of the proton in the case of hydrogen) ;

condition (A2) simplifies to

$$M^2 > m_a^2 + m_e^2 \qquad \text{(A3)}$$

and the branch point (the anomalous threshold) is

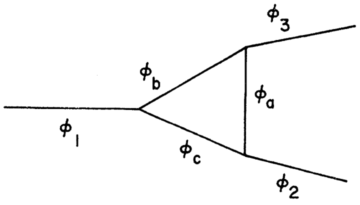

FIG. 1. General form of a triangular vertex graph.

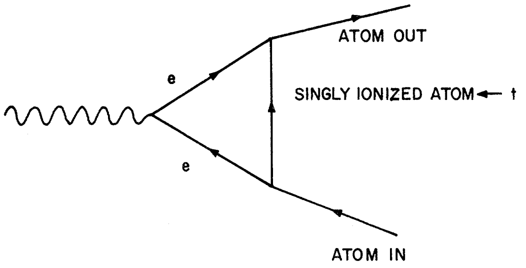

FIG. 2. Triangle graph generating an anomalous threshold in the electromagnetic one-photon form factor of an atom.

located at

$$t = t_0 = \frac{1}{m_0^2}\left[(m_0 + m_e)^2 - M^2\right]\left[M^2 - (m_0 - m_e)^2\right] \ . \qquad \text{(A4)}$$

Putting

$$M = m_a + m_e - E_B \ , \qquad \text{(A5)}$$

where $E_B \sim \alpha/a$ is the binding energy for the electron, or

$$E_B = \alpha/2a \quad \text{for hydrogen} \ , \qquad \text{(A6)}$$

we find that condition (A3) is satisfied for atoms and that it gives an anomalous threshold at $t_0 \sim 1/a^2$, which for hydrogen is at

$$t_0 = 4/a^2 \ . \qquad \text{(A7)}$$

For scattering of atoms by photons we really have to consider the graph in Fig. 3. In the discussion that follows, we shall abide by the notations of KSW 2. Consider a vertex in this graph with a photon as an external leg. In the notation of Fig. 3, and of Eq. (4) of KSW 2, we have

$$p_{kl}^2 = m_k^2 + m_l^2 - 2m_k m_l y_{kl} \ , \qquad \text{(A8)}$$

$p_{14}^2 = p_{34}^2 =$ (mass of photon)$^2 = 0$, $m_1 = m_3 = m_4 = m_e$

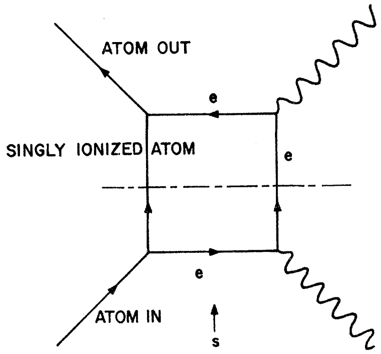

FIG. 3. Graph generating an anomalous threshold in the atom-photon scattering amplitude. Intermediate particles cut by the dotted line are put on the mass shell.

$$\Rightarrow y_{14} = 1 = y_{34} \ . \tag{A9}$$

Hence by the criterion given by the inequalities (22) of KSW 2, the domain of analyticity is determined by case (ii) of KSW 2. As shown in Appendix A of KSW 2, it is the same as the case of a triangular vertex. The above is equivalent to choosing one of the α's in the Feynman representation of the scattering amplitude to be zero where the α's are the Feynman parameters. We particularly choose here α_4 to be zero. Then

$$p_{13}^2 = t = -q^2 \ , \tag{A10}$$

and the denominator D_1 of Eq. (3) of KSW 2 reduces to the denominator of Eq. (A4) of KSW 1. Since the vanishing of this function determines the singularities of the Feynman amplitudes, the argument in KSW 1 follows, and we are led to the same conclusion on the anomalous threshold as for the triangular vertex.

2. Analytic Properties of the Spectral Functions

It is not difficult to see that the graph being studied in Fig. 3 gives the lowest possible t singularity in the atomic Compton amplitude, and so its imaginary part determines the spectral functions. To evaluate the imaginary part of the amplitude corresponding to Fig. 3, we employ Cutkosky's idea of generalized unitarity and put the intermediate particles in the s channel on the mass shell. Then the lower and upper parts of Fig. 3 are immediately recognized as photoelectric effects. Since the electron and the proton are both on shell, the graph (Fig. 4) is energetically possible only if the photon energy is above threshold. Hence the spectral function coming from the graph of Fig. 3 actually corresponds to the imaginary part of the Compton amplitude for photon energy greater than threshold evaluated as if the continuum states (the Coulomb scattering states) were the only intermediate states. However, the discrete states only give rise to δ-function-like terms and once the photon energy is above threshold, the argument of the δ functions can never vanish. Hence we conclude that the spectral function coming from the process in Fig. 3 is just the imaginary part of the Compton amplitude with all the atomic states as intermediate states. Moreover, since contribution to the van der Waals potential from the spectral function is important only for s close to the square of the mass of the atom, i.e., for photon energies of order α/a, the nonrelativistic form of the Compton amplitude can be used. The nonrelativistic hydrogenic Compton amplitude has been evaluated by Gavrila and Costescu.[5] The electric and magnetic form factors F_E and F_M are related to the scattering amplitude f in the following way:

$$f(K, \theta) = A(K, \theta)\,\vec{\epsilon}\cdot\vec{\epsilon}\,' + B(K, \theta)\,\vec{\epsilon}\cdot\vec{\mathrm{K}}'\,\vec{\epsilon}\,'\cdot\vec{\mathrm{K}} \ , \tag{A11}$$

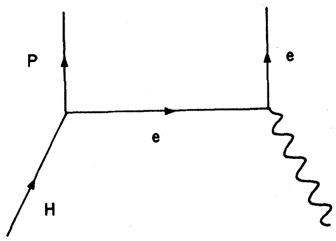

FIG. 4. Lower half of Fig. 3 for hydrogen, appearing as a graph for photoionization.

where $(K, \vec{\mathrm{K}}, \vec{\epsilon})$ and $(K', \vec{\mathrm{K}}', \vec{\epsilon}\,')$ are the energies, momenta, and polarization of the incident and outgoing photons, and θ is the scattering angle. Then

$$F_M = -4\pi B(K, \theta) \ , \tag{A12}$$

$$F_E = 4\pi A(K, \theta)/KK' + 4\pi B(K, \theta)\cos\theta \ . \tag{A13}$$

Since the only graph that gives an imaginary part is the direct graph, we have from (A12) and (A13) together with the results in Ref. 5

$$\rho_E = \frac{4\pi}{K^2}\left[\mathrm{Im}P^+(K, t) + \mathrm{Im}Q^+(K, t)\left(1 + \frac{t}{2K^2}\right)\right], \tag{A14}$$

$$\rho_M = (-4\pi/K^2)\,\mathrm{Im}Q^+(K, t) \ , \tag{A15}$$

where

$$P^+ = \frac{128\lambda^5 X^3}{[(X+\lambda)^2 + K^2]^4}\ \frac{F_1(2-\tau\,; 2, 2; 3-\tau; x_1, x_2)}{2-\tau} \ , \tag{A16}$$

$$Q^+ = \frac{2048\lambda^5 X^5 K^2}{[(X+\lambda)^2 + K^2]^6}\ \frac{F_1(3-\tau, 3, 3; 4-\tau; x_1, x_2)}{3-\tau} \ , \tag{A17}$$

$$\lambda = Z/a = 1/a \ \text{ for hydrogen} \ , \tag{A18}$$

$$X_+^2 = 2m(E_0 - K) \ , \quad E_0 = Z\alpha/2a \ , \tag{A19}$$

$$\tau = \lambda/X_+ \ , \tag{A20}$$

$$x_1, x_2 = \frac{(X^2 - \lambda^2 - K^2)^2 + 4X^2(\vec{\mathrm{K}}\cdot\vec{\mathrm{K}}\,')}{[(X+\lambda)^2 + K^2]^2} \pm \frac{\{-4X^2(\vec{\mathrm{K}} - \vec{\mathrm{K}}\,')^2[X^2(\vec{\mathrm{K}} + \vec{\mathrm{K}}\,')^2 + (X^2 - \lambda^2 - K^2)^2]\}^{1/2}}{[(X+\lambda)^2 + K^2]^2} \ . \tag{A21}$$

P^+ and Q^+ have integral representations in the forms

$$P^+ = 128\lambda^5 X^3 \left(\frac{ie^{i\pi\tau}}{2\sin\pi\tau}\right) \frac{1}{[(X+\lambda)^2 + K^2]^4} \times \int_C \rho^{1-\tau}(1 - s\rho + p\rho^2)^{-2}\, d\rho \ , \tag{A22}$$

$$Q^+ = \frac{2048\lambda^5 X^5}{[(X+\lambda)^2 + K^2]^6}\left(\frac{ie^{i\pi\tau}}{2\sin\pi\tau}\right) \times \int_C \rho^{2-\tau}(1 - s\rho + p\rho^2)^{-3}\, d\rho \ , \tag{A23}$$

where

$$s=x_1+x_2\,, \quad p=x_1x_2\,,$$

and C is a contour that runs from 1 on the real axis to the right of the origin, encircles it, and runs to 1 again. For $t<4/a^2$ in the H-Compton amplitude, Gavrila and Costescu showed that the following series expansions in t for P^+ and Q^+ are valid:

$$\begin{aligned}P^+ &= \sum P_n^+(K)\,t^n \\ &= \frac{2\lambda^2}{(X+\lambda)^2+K^2}\sum_p \frac{(2)_p}{p!}\left(\frac{t}{4\lambda^2}\right)^p \\ &\quad\times \frac{{}_2F_1(1,\,-1-p-\tau,\,3+p-\tau\,;u)}{2+p-\tau}\,, \qquad \text{(A24)}\end{aligned}$$

$$\begin{aligned}Q^+ &= \sum Q_n^+(K)\,t^n \\ &= \frac{2K^2}{(X+\lambda)^2+K^2}\sum_p \frac{(3)_p}{p!}\left(\frac{t}{4\lambda^2}\right)^p \\ &\quad\times \frac{{}_2F_1(1,\,-2-p-\tau,\,4+p-\tau\,;u)}{3+p-\tau}\,, \qquad \text{(A25)}\end{aligned}$$

where

$$u=[(X-\lambda)^2+K^2]/[(X+\lambda)^2+K^2]=(x_1x_2)^{1/2}\,.$$

Equations (A24) and (A25) were acnieved by employing the identity

$$(1-x_1\rho)(1-x_2\rho)=[1-(x_1x_2)^{1/2}\rho]^2 \times\left(1-\frac{[x_1+x_2-2(x_1x_2)^{1/2}]\rho}{[1-(x_1x_2)^{1/2}\rho]^2}\right) \qquad \text{(A26)}$$

and the binomial expansion

$$[(1-x_1\rho)(1-x_2\rho)]^{-b}=[1-(x_1x_2)^{1/2}\rho]^{-2b} \times\sum_{p=0}^{\infty}\frac{(b)_p}{p!}\left(\frac{[x_1+x_2-2(x_1x_2)^{1/2}]\rho}{[1-(x_1x_2)^{1/2}\rho]^2}\right)^p \qquad \text{(A27)}$$

which is valid only for $|t|<4/a^2$. For $t>4/a^2$, we write

$$(1-x_1\rho)(1-x_2\rho)=[1+(x_1x_2)^{1/2}\rho]^2 \times\left(1-\frac{[x_1+x_2+2(x_1x_2)^{1/2}]\rho}{[1+(x_1x_2)^{1/2}\rho]^2}\right) \qquad \text{(A28)}$$

and use the binomial expansion

$$[(1-x_1\rho)(1-x_2\rho)]^{-b}=[1+(x_1x_2)^{1/2}\rho]^{-2b} \times\sum_{p=0}^{\infty}\frac{(b)_p}{p!}\left(\frac{[x_1+x_2+2(x_1x_2)^{1/2}]\rho}{[1+(x_1x_2)^{1/2}\rho]^2}\right)^p \qquad \text{(A29)}$$

which is valid for

$$\frac{2(K^2-2K+2)}{K-1}>t>4\,, \qquad \text{(A30)}$$

and we have put $a=1$. We shall also neglect K compared to λ in the region of interest. We define $\kappa=K2a/\alpha$, and we divide the subregion in the $\kappa\otimes t$ plane ($\kappa>1$, $t>0$) into the following six regions (Fig. 5):

$$\mathrm{I}=\{|t|<4\}\,, \qquad \text{(A31)}$$

$$\mathrm{II}=\left\{t=\frac{\kappa^2}{\kappa-1}\right\}, \qquad \text{(A32)}$$

$$\mathrm{III}=\left\{4<t<\frac{\kappa^2}{\kappa-1}\right\}\,, \qquad \text{(A33)}$$

$$\mathrm{IV}=\left\{\frac{\kappa^2}{\kappa-1}<t<\frac{\kappa^2}{\kappa-1}+\frac{(\kappa-2)^2}{\kappa-1}\right\}, \qquad \text{(A34)}$$

$$\mathrm{V}=\left\{t>\frac{\kappa^2}{\kappa-1}+\frac{(\kappa-2)^2}{\kappa-1}\right\}, \qquad \text{(A35)}$$

$$\mathrm{VI}=\{t=4\,,\ \kappa=2\}\,. \qquad \text{(A36)}$$

Regions II ∪ III ∪ IV are covered by the inequality (A30). We then find

$$\mathrm{Im}P(\kappa,t)=\frac{64\pi}{3}\,\frac{\eta^6}{(1+\eta^2)^3}\,\frac{e^{-2\eta X}}{1-e^{-2\pi\eta}} \times{}_2F_1(2-i\eta,2+i\eta\,;\tfrac{5}{2},v) \quad \text{if} \quad (\kappa,t)\in I\,, \qquad \text{(A37)}$$

$$\mathrm{Im}Q(\kappa,t)=\alpha^2\kappa^2\,\frac{256\pi}{15}\,\frac{\eta^8(1+\frac{1}{4}\eta^2)}{(1+\eta^2)^5}\,\frac{e^{-2\eta X}}{1-e^{-2\pi\eta}} \times{}_2F_1(3-i\eta,3+i\eta\,;\tfrac{1}{2}\eta,v) \quad \text{if} \quad (\kappa,t)\in I\,, \qquad \text{(A38)}$$

$$\mathrm{Im}P(\kappa,t)=\frac{64\pi}{3}\,\frac{\eta^6}{(1+\eta^2)^3}\,\frac{e^{-2\eta X}}{1-e^{-2\pi\eta}} \times{}_2F_1(2-i\eta,2+i\eta;\tfrac{5}{2},1-v) \quad \text{if} \quad (\kappa,t)\in \mathrm{II}\cup\mathrm{III}\cup\mathrm{IV}\cup\mathrm{VI}\,, \qquad \text{(A39)}$$

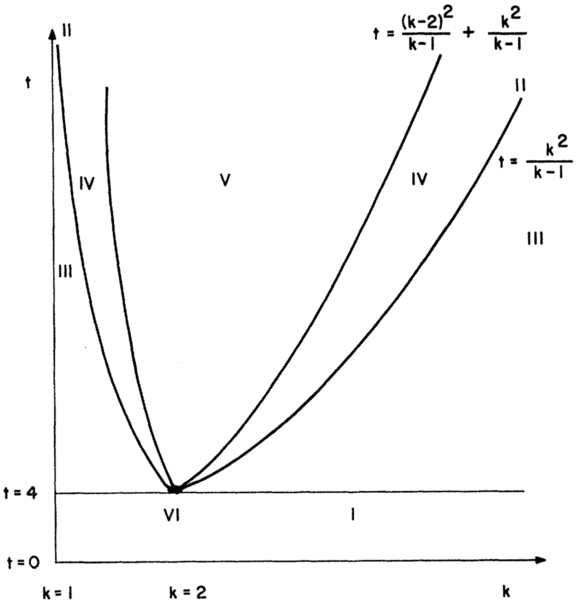

FIG. 5. Subregions in the {Ret ⊗ ReK, K >1, t >0} plane.

$$\operatorname{Im}Q(\kappa,t)=\alpha^2\kappa^2\,\frac{256\pi}{15}\,\frac{\eta^8(1+\frac{1}{4}\eta^2)}{(1+\eta^2)^5}\,\frac{e^{-2\eta X}}{1-e^{-2\pi\eta}}$$

$$\times\,{}_2F_1(3-i\eta,3+i\eta;\tfrac{1}{2}\eta,1-v)$$

$$\text{if}\quad(\kappa,t)\in \mathrm{II}\cup\mathrm{III}\cup\mathrm{IV}\cup\mathrm{VI}\,,\qquad\text{(A40)}$$

$$\eta=|\tau|=(\kappa-1)^{-1/2},$$

$$X=2\tan^{-1}(\kappa-1)^{1/2},\qquad v=[(\kappa-1)/\kappa^2]t\,.$$

For (κ, t) in $\mathrm{IV}\cup\mathrm{V}$, we notice that $|x_1 x_2|=1$, x_1, x_2 are both real. Thus either $|x_1|>1$ and $|x_2|<1$, or vice versa. We take, without loss of generality, $|x_1|>1$ and $|x_2|<1$. Then expanding the factor $(1-x_2\rho)$ by the binomial series in the integral representation of P and Q in (A22) and (A23), we find that P and Q are both convergent for (κ, t) in $\mathrm{IV}\cup\mathrm{V}$, and they have the same series representations. (The detail of this proof is given in Ref. 11.) Now analytic continuation of $\operatorname{Im}P$ and $\operatorname{Im}Q$ into V as given by the Gauss type of hypergeometric functions (A39) and (A40) exists and since IV is a nonempty region, we conclude by the uniqueness of analytic continuation that $\operatorname{Im}P$ and $\operatorname{Im}Q$ have the same form as (A39) and (A40) in region V. From (A37) to (A42) we see that ρ_x has a discontinuity at $t=t_0=4/a^2$. This comes as no surprise and in fact, conforms with the Mandlestam representation.

3. Convergence of the van der Waals Potential Integrals in the Case of Hydrogen

To demonstrate the assertion we make in (2.8) of Sec. II we have to examine the behavior of $I_{xy}(t)$ as $t\to\infty$. We note that in

$$I_{xy}(t)\sim\int_0^\infty\int_0^\infty\frac{dK_A\,dK_B}{\pi^2}\,\rho_x^A(K_A,t)\,\rho_y^B(K_B,t)$$

$$\times\Phi_{xy}(K_A,K_B,t)\qquad\text{(A41)}$$

the K integral is convergent from the explicit forms we have for $\operatorname{Im}P^+$ and $\operatorname{Im}Q^+$, and that the main contribution comes from $K\sim\alpha/a$. Hence to examine the asymptotic behavior of $I(t)$ as $t\to\infty$ it is sufficient to examine the behavior of $\rho_x(K_A,t)\times\rho_y(K_B,t)\,\Phi_{xy}(K_A,K_B,t)$ as $t\to\infty$ and for $K_A K_B\sim\alpha/a$. This results in the examination of

$${}_2F_1(2-i\eta,2+i\eta,\tfrac{5}{2},1-v)\,,$$

$${}_2F_1(3-i\eta,3+i\eta,\tfrac{7}{2},1-v)\,,$$

and $\Phi_{xy}(K_A,K_B,t)$ as $t\to\infty$, since the only t dependence of $\operatorname{Im}P^+$ and $\operatorname{Im}Q^+$ occurs in v. Using the explicit form of Φ_{xy} in Sec. II, we find

$$\Phi_{MM}=\Phi_{EE}\to(t)^{1/2}\,,\qquad\text{(A42)}$$

$$\Phi_{EM}=\Phi_{ME}\to\text{const}\,.\qquad\text{(A43)}$$

On the other hand we can use the formula

$$F(a,b,c,z)=\frac{\Gamma(c)\,\Gamma(b-a)}{\Gamma(c-a)\,\Gamma(b)}$$

$$\times(-z)^{-a}F(a,a+1-c;a+1-b,z^{-1})$$

$$+\frac{\Gamma(c)\,\Gamma(a-b)}{\Gamma(c-b)\,\Gamma(a)}(-z)^{-b}F(b+1-c,b;b+1-a,z^{-1})$$

and we obtain

$$\operatorname{Im}P^+(K,t)\to t^{-2}\quad\text{for }K\sim\alpha/a\,,\qquad\text{(A44)}$$

$$\operatorname{Im}Q^+(K,t)\to t^{-3}\quad\text{for }K\sim\alpha/a\,.\qquad\text{(A45)}$$

Thus we obtain

$$I_{EE}(t)\to t^{-7/2}\,,\qquad\text{(A46)}$$

$$I_{EM}(t)\to t^{-4}\,,\qquad\text{(A47)}$$

$$I_{MM}(t)\to t^{-11/2}\,,\qquad\text{(A48)}$$

which establishes the boundedness of

$$\int_{t_0}^\infty|I_{xy}(t)|\,dt\,.$$

APPENDIX B: S-MATRIX APPROACH TO MULTIPOLE-ELECTROMAGNETIC POLARIZABILITIES

It is shown in FS that the electromagnetic form factors at zero-energy and at zero-momentum transfer, denoted as $F_{E,0}(0)$ and $F_{M,0}(0)$ in this paper, are related to the dipole electromagnetic polarizabilities by

$$F_{E,0}(0)=4\pi\alpha_E\,,\qquad\text{(B1a)}$$

$$F_{M,0}(0)=4\pi\alpha_M\,.\qquad\text{(B1b)}$$

In this Appendix, we demonstrate similar relations between the derivatives of the electromagnetic form factors with respect to the momentum transfer evaluated at zero momentum transfer and the multipole-electromagnetic polarizabilities.[17] Such relations can be summarized as

$$F_{x,n}(0)=8\pi\alpha_{x,2^{n+1}}/(2n+2)!\,,\qquad\text{(B2)}$$

where $x=E$ or M, e.g., $\alpha_{E,2^2}$ would be the static electric quadrupole polarizability, and

$$F_{x,n}(0)=\frac{1}{n!}\,\frac{\partial^n F}{\partial t^n}(\omega,t)\bigg|_{\substack{t=0\\ \omega=0}}\,.$$

Note that in this Appendix we use ω instead of K, to avoid later confusion in taking derivatives. We also wish to point out that (B2) is true only in the static limit. In general

$$F_{x,n}(\omega)=\frac{8\pi\alpha_{2^{n+1}}(\omega)}{(2n+2)!}+O(\omega^2a^2)\,\frac{\alpha_{2^{n+2}}}{a^2}$$

$$+\,O(\omega^4a^4)\,\frac{\alpha_{2^{n+3}}}{a^4}+\cdots\,.\qquad\text{(B3)}$$

To prove (B2), we follow the arguments of Appendix A of FS and obtain the second-order S-matrix element corresponding to double scattering (Fig. 6)

$$S^{(2)}=\tfrac{1}{2}(iN)\int(F_1\hat{P}_\alpha\hat{P}_\beta+\tfrac{1}{2}F_2g_{\alpha\beta})$$

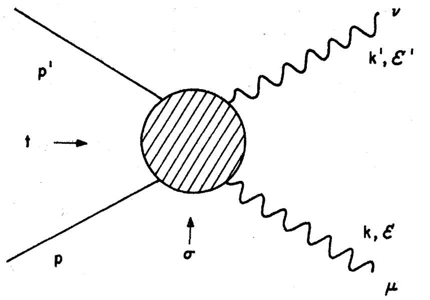

FIG. 6. Atom-photon scattering kinematics.

$$\times \tilde{F}_{\alpha\mu}(-K)\,\tilde{F}_{\beta\mu}(-K')\,dp'' , \qquad \text{(B4)}$$

where

$$P_\alpha = (p_\alpha + p'_\alpha) , \qquad \text{(B5a)}$$

$$p'' = p - K = p' + K' , \qquad \text{(B5b)}$$

$$\hat{P}_\alpha = P_\alpha/m \to 2mg_{\alpha 0} , \qquad \text{(B6)}$$

$$N = (4p'_0 p_0)^{-1/2} \to (2m)^{-1} , \qquad \text{(B7)}$$

as we go to the nonrelativistic limit, and $\tilde{F}_{\mu\nu}(K)$ is the Fourier transform of $F_{\mu\nu}(x)$, the electromagnetic field tensor. On expanding $F_{\mu\nu}(x)$ in a Taylor series about the spatial origin, we get

$$F_{\mu\nu}(x) = e^{i\omega t} \sum_{n=0}^{\infty} a_{\mu\nu i_1 \ldots i_n} x_{i_1} \ldots x_{i_n} , \quad i_s = 1, 2, 3 \qquad \text{(B8)}$$

where

$$a_{\mu\nu i_1 \ldots i_n} = \frac{1}{n!}\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, F_{\mu\nu}(x)\big|_{\vec{x}=0} \quad \text{for } n \geq 1 \qquad \text{(B9a)}$$

$$= F_{\mu\nu}(x)\big|_{\vec{x}=0} \quad \text{for } n = 0 . \qquad \text{(B9b)}$$

For a static field, we get

$$\tilde{F}_{\mu\nu}(-K) = (2\pi)^2\, \delta(K_0)$$
$$\times \left(\sum_{n=0}^{\infty} (i)^n a_{\mu\nu i_1 \ldots i_n} \partial_{i_1}(K) \cdots \partial_{i_n}(K)\, \delta(\vec{K}) \right) . \qquad \text{(B10)}$$

On substituting this into (B4) and going to the nonrelativistic limit in (B6) and (B7), we have

$$S^{(2)} = \frac{i(2\pi)^4}{4m} \int (4F_1 g_{\alpha 0} g_{\beta 0} + \tfrac{1}{2} F_2 g_{\alpha\beta})\, \delta(K_0)\, \delta(K'_0)$$
$$\times \sum (i)^{n+m} a_{\alpha\mu i_1 \ldots i_n} \partial_{i_1}(K) \ldots \partial_{i_n}(K)$$
$$\times a_{\beta\mu j_1 \ldots j_m} \partial_{j_1}(K') \ldots \partial_{j_m}(K')\, \delta(\vec{K})\, \delta(\vec{K}')\, d^4 p'' , \qquad \text{(B11)}$$

where

$$\partial_{i_1}(K) \equiv \frac{\partial}{\partial K_{i_1}} , \text{ etc., and } \partial_{j_1}(K') = \frac{\partial}{\partial K'_{j_1}} .$$

We can integrate this by parts using the relation in (B5) and obtain

$$S^{(2)} = \frac{i(2\pi)^4}{4m} \sum_{n,m} (i)^{n+m} (-1)^m a_{\alpha\mu i_1 \ldots i_n} a_{\beta\mu j_1 \ldots j_m}$$
$$\times \int \partial_{i_1}(K) \ldots \partial_{i_n}(K)\, \partial_{j_1}(K') \ldots \partial_{j_m}(K')$$
$$\times (4F_1 g_{\alpha 0}\, g_{\beta 0} + \tfrac{1}{2} F_2\, g_{\alpha\beta})\, \delta^4(K)\, \delta^4(K')\, d^4 p'' . \qquad \text{(B12)}$$

In the nonrelativistic limit, the form factors F_1 and F_2 are functions of K_0 and t, $[t = -(\vec{K} - \vec{K}')^2]$. Since the derivatives are taken only with respect to the spatial components of K, F_1 and F_2 can be regarded as functions of t only. To evaluate (B12) we note that

$$\partial_{i_1}(K) \ldots \partial_{i_n}(K)\, F(t)$$
$$= (-2)^n (K_{i_1} - K'_{i_1}) \ldots (K_{i_n} - K'_{i_n})\, F^n(t) + [(-2)^{n-2} F^{n-2}(t)$$
$$\times \delta_{i_1 i_2} (K_{i_3} - K'_{i_3}) \ldots (K_{i_n} - K'_{i_n}) + \text{permutations}]$$
$$+ \text{terms involving lower derivatives of } F(t) . \qquad \text{(B13)}$$

Because the external field satisfies the Laplace equation, we see that only the first term in (B13) will contribute. Also all the K'_{i_1} to K'_{i_n} must be differentiated when we take the derivatives $\partial_{j_1}(K') \ldots \partial_{j_m}(K')$ because of the adjoining δ function in (B12). This requires m to be equal to n. On differentiating, we obtain $n!$ ways of contracting the indices. Since the order of the indices are unimportant, we have

$$\int a_{\alpha\mu i_1 \ldots i_n} a_{\beta\mu j_1 \ldots j_m} \partial_{i_1}(K) \ldots \partial_{i_n}(K)$$
$$\times \partial_{j_1}(K') \ldots \partial_{j_m}(K')\, F(\omega, t)\, \delta(K)\, \delta(K')\, d^4 p''$$
$$= \delta_{mn} 2^n n!\, \frac{\partial^n}{\partial t^n} F(t)\Big|_{\substack{t=0\\ \omega=0}} a_{\alpha\mu i_1 \ldots i_n} a_{\beta\mu i_1 \ldots i_n} , \qquad \text{(B14)}$$

$$S^{(2)} \to \frac{i}{4m} \sum_n 2^n n! \left(4\, \frac{\partial^n}{\partial t^n} F_1\, g_{\alpha 0}\, g_{\beta 0} + \frac{1}{2} \frac{\partial^n}{\partial t^n} F_2\, g_{\alpha\beta} \right) K^n_{\alpha\beta} , \qquad \text{(B15)}$$

where

$$K^n_{\alpha\beta} = \int a_{\alpha\mu i_1 \ldots i_n} a_{\beta\mu i_1 \ldots i_n} (2\pi)^4\, \delta(K)\, \delta(K')\, d^4 p'' \qquad \text{(B16)}$$

$$= \frac{1}{(n!)^2} \int \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, F_{\alpha\mu}(0)\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)$$
$$\times F_{\beta\mu}(0)\, e^{i(p'-p)x}\, d^4 x \qquad \text{(B17)}$$

after going back to coordinate space. Here $\partial_{i_1}(x) \equiv \partial/(\partial x_{i_1})$, etc. Then using

$$g_{\alpha 0} g_{\beta 0}\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, F_{\alpha\mu}\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, F_{\beta\mu}$$
$$= -\partial_{i_1}(x) \ldots \partial_{i_n}(x)\, E_j\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, E_j , \qquad \text{(B18)}$$

$$g_{\alpha\beta}\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, F_{\alpha\mu}\, \partial_{i_1}(x) \ldots \partial_{i_n}(x)\, F_{\beta\mu}$$

$$= 2[-\partial_{i_1}(x)\ldots\partial_{i_n}(x)E_j\,\partial_{i_1}(x)\ldots\partial_{i_n}(x)E_j$$
$$+\partial_{i_1}(x)\ldots\partial_{i_n}(x)H_j\,\partial_{i_1}(x)\ldots\partial_{i_n}(x)H_j]\,, \quad \text{(B19)}$$

$$\frac{-1}{2m}\left[\frac{\partial^n}{\partial t^n}F_1(0)+\frac{\partial^n}{\partial t^n}F_2(0)\right]=\frac{\partial^n F_E(0)}{\partial t^n}=n!\,F_{E,n}(0)\,, \quad \text{(B20)}$$

$$\frac{1}{2m}\;\frac{\partial^n}{\partial t^n}F_2(0)=\frac{\partial^n}{\partial t^n}F_M(0)=n!\,F_{M,n}(0) \quad \text{(B21)}$$

and rewriting $K^n_{\alpha\beta}$ as

$$K^n_{\alpha\beta}=\frac{(2\pi)}{(n!)^2}\,\delta(p_0'-p_0)\langle\vec{p}'|\,\partial_{i_1}(x)\ldots\partial_{i_n}(x)F_{\alpha\mu}(0)$$
$$\times\partial_{i_1}(x)\ldots\partial_{i_n}(x)F_{\beta\mu}(0)\,|\vec{p}\rangle\,, \quad \text{(B22)}$$

where $|\vec{p}\rangle$ denotes the state with wave function $e^{i\vec{p}\cdot\vec{r}}$, we finally obtain

$$S^{(2)}=-2\pi i\,\delta(p_0'-p_0)\langle\vec{p}|H'|\vec{p}\rangle\,, \quad \text{(B23)}$$

where

$$H'=-\tfrac{1}{2}\sum_n 2^n[F_{E,n}(0)\,\partial_{i_1}(x)\ldots\partial_{i_n}(x)E_j$$
$$\times\partial_{i_1}(x)\ldots\partial_{i_n}(x)E_j+F_{M,n}(0)\,\partial_{i_1}(x)\ldots\partial_{i_n}(x)$$
$$\times H_j\,\partial_{i_1}(x)\ldots\partial_{i_n}(x)H_j]\,. \quad \text{(B24)}$$

The $n=0$ terms in (B24) reproduce the results in FS. We must now identify this Hamiltonian with the Hamiltonian describing the energy shift of an atom in external fields, in order to make the identification in (B2). Consider for example the case of an external electric field. The energy shift is then given by

$$\Delta E=-\frac{1}{2}\sum_{L=1}^{\infty}\left(\alpha_{2L}\,(\partial_{i_1}\ldots\partial_{i_L}V)^2\,\frac{2^L}{(2L)!}\right), \quad \text{(B25)}$$

where $\partial_{i_1}\ldots\partial_{i_L}V$ is the derivative of the perturbing potential evaluated at the origin, and the factor $2^L/(2L)!$ is inserted to properly normalize the potential. The quantities α_{2L} are the multipole polarizabilities.[17] Since $E_i=-\partial_i V$, comparison with (B24) shows that these two Hamiltonians are the same provided that (B2) is satisfied. Similar arguments can be given for an external magnetic field. The extra factor of 4π in (B2) comes from the change of the Heaviside unit to the Gaussian unit of charge.

For a nonstatic field, say a sinusoidal one, we have to replace the δ function in (B12) by

$$\delta^4(K)\to\delta(K_0-\omega)\,\delta(\vec{K})\,,$$
$$\delta^4(K')\to\delta(K_0'-\omega)\,\delta(\vec{K}')\,. \quad \text{(B26)}$$

Also, in this case, the field would satisfy the wave equation, and the terms that we throw away in (B13) will survive.

A contraction is now possible between any two indices among $i_1\ldots i_n$ and any two among $j_1\ldots j_m$. Such a contraction will decrease the order of the spatial derivative by 2 and will give a multiplicative factor of ω^2, e.g.,

$$a_{\mu\nu i_1 i_2 i_3\ldots i_n}\,\delta_{i_1 i_2}=-\omega^2\,a_{\mu\nu i_3\ldots i_n}\,. \quad \text{(B27)}$$

Consequently, in the expression analogous to Eq. (B4) for a sinusoidal field, we have terms like

$$H'=-\tfrac{1}{2}E^2[F_{E,0}(\omega)+O(\omega^2a^2)F_{E,1}(\omega)/a^2$$
$$+O(\omega^4a^4)F_{E,2}(\omega)/a^4+\cdots]-\tfrac{1}{2}\,\partial_iE_j\,\partial_iE_j\,[2F_{E,1}(\omega)$$
$$+O(\omega^2a^2)F_{E,2}(\omega)/a^2+\cdots]+\cdots\,. \quad \text{(B28)}$$

If we define α_2 as the coefficient of $\frac{1}{2}E^2$ in H' and α_4 as the coefficient of $\partial_iE_j\,\partial_iE_j$ and so on, we obtain

$$4\pi\alpha_2(\omega)=F_{E,0}(\omega)-4\omega^2F_{E,1}+O(\omega^4a^4)F_{E,2}/a^4+\cdots\,,$$
$$\frac{4\pi}{12}\,\alpha_4(\omega)=F_{E,1}(\omega)+O(\omega^2a^2)F_{E,2}/a^2 \quad \text{(B29)}$$
$$+O(\omega^4a^4)F_{E,3}/a^4+\cdots$$
$$\frac{4\pi 2}{(2L)!}\,\alpha_{2L}(\omega)=F_{E,L-1}(\omega)+O(\omega^2a^2)F_{E,L}/a^2+\cdots\,.$$

On inversion we obtain

$$F_{E,0}=4\pi\alpha_2+\tfrac{4}{3}\pi\omega^2\alpha_4+O(\omega^4)\,\alpha_8+\cdots,$$

etc.

APPENDIX C: APPLICATION TO POTENTIAL BETWEEN HYDROGEN ATOMS

As is clear from our discussion in Sec. II, the long-range forces corresponding to higher-multipole interactions can be computed if we know the form factors $F_{x,n}$ in the physical region. Because both the nonrelativistic Coulomb Green's function and the hydrogenic wave functions exist in exact analytic form, these $F_{x,n}$'s for hydrogen in the nonrelativistic approximation, can be calculated in closed form.[5] It is actually enough to know the imaginary part of $F_{x,n}$. The analytic expressions of these $F_{x,n}$ for hydrogen are essentially contained in Appendix B where we discuss the analytic properties of the spectral functions. However, because of the availability of the one-dimensional formula (2.16), it is also advantageous to know $\mathrm{Re}F_{x,n}$. Therefore in this Appendix, we present the analytic forms of $\mathrm{Re}F_{x,n}$ and $\mathrm{Im}F_{x,n}$ for hydrogen in the ground state and also some numerical results of our computation for the H-H system.

The two form factors A and B defined in Appendix A 2 have the general form

$$A=P^+(K,t)+P^-(K,t)-O\,, \quad \text{(C1)}$$

$$B=Q^+(K,t)+Q^-(K,t)\,, \quad \text{(C2)}$$

where +, − refer to the direct and crossed graph and O refers to the seagull term, and

$$P^-(K,t)=P^+(-K,t)\,, \tag{C3a}$$

$$Q^-(K,t)=Q^+(-K,t)\,. \tag{C3b}$$

$F_E(K,t)$ and $F_M(K,t)$ are given by

$$F_E=\frac{-4\pi}{K^2}[O-P^+-P^--(Q^++Q^-)(1+t/2K^2)]\,, \tag{C4a}$$

$$F_M=\frac{-4\pi}{K^2}(Q^++Q^-)\,. \tag{C4b}$$

Only the direct graph gives an imaginary part and we recover the result in the early part of Appendix A2.

O is a function of t only and is given by

$$O=\sum_p \frac{(2)_p}{p!}\left(\frac{t}{4\lambda^2}\right)^p, \tag{C5}$$

where

$$a_p\equiv\Gamma(a+p)/\Gamma(a)\,. \tag{C6}$$

Defining

$$X_\pm^2=2m(E_0\mp K)\,, \tag{C7}$$

$$\tau_\pm=\lambda/X_\pm\,, \tag{C8}$$

$$P^\pm(K,t)=\sum_p P_p^\pm(K)\,t^p\,, \tag{C9a}$$

$$Q^\pm(K,t)=\sum_p Q_p^\pm(K)\,t^p\,, \tag{C9b}$$

we have

$$P_p^\pm(K)=\frac{2\lambda^2}{(X+\lambda)^2+K^2}\,\frac{(2)_p}{p!}\left(\frac{1}{4\lambda^2}\right)^p \times\frac{{}_2F_1(1,-1-p-\tau_\pm,3+p-\tau_\pm,u)}{2+p-\tau_\pm}, \tag{C10}$$

$$Q_p^\pm(K)=\frac{2K^2}{(X+\lambda)^2+K^2}\,\frac{(3)_p}{p!}\left(\frac{1}{4\lambda^2}\right)^p \times\frac{{}_2F_1(1,-2-p-\tau_\pm,4+p-\tau_\pm,u)}{3+p-\tau_\pm}\,. \tag{C11}$$

On comparison we obtain

$$P_p^\pm(K)=Q_{p-1}^\pm/2p\,K^2\,. \tag{C12}$$

The above expressions are valid as long as $|t|$ is less than anomalous threshold. Above the photoionization threshold, $\mathrm{Im}P_p^+(K)$ has the analytic form

$$\mathrm{Im}P_p^+(K)=\frac{64\pi}{3i}\,\frac{|\tau_+|\,(1+|\tau_+|^2)\exp(-2|\tau_+|\chi)}{1-\exp(-2\pi|\tau_+|)} \times\frac{\lambda^5X_+^3}{[(X_+^2-\lambda^2-K^2)^2+4X_+^2K^2]^2}\,\frac{(2-\tau_+)_p(2+\tau_+)_p}{(\frac{5}{2})_p\,p!} \times\left(\frac{-X_+^2}{(X_+^2-\lambda^2-K^2)^2+4K^2X_+^2}\right)^p, \tag{C13}$$

where

$$\chi=\tan^{-1}\frac{2\lambda|X_+|}{\lambda^2+K^2+X_+^2}\quad\text{and}\quad 0<\chi<\pi\,. \tag{C14}$$

We remark that X_+ is purely imaginary above the photoelectric threshold. Then using (C13), we can verify the assertion we made on the asymptotic behavior of $F_n(K)$ in Sec. III.

$F_{x,p}(K)$ can be computed by computing $P_p^\pm(K)$ and $Q_p^\pm(K)$. But $P_p^+(K)$ and $Q_p^+(K)$ are singular as K approaches $(1-1/n^2)\,\alpha/2a$, corresponding to resonances. These singularities can be regulated by making the photon energy complex, and we can express the imaginary part of $P_p^+(K)$ and $Q_p^+(K)$ in terms of δ functions. Such techniques have been used by one of us previously.[11] We shall not go through the details here but simply give the result.

Singularities in $P_p^+(K)$ and $Q_p^+(K)$ occur in the hypergeometric function

$${}_2F_1(1,-1-p-\tau_+,3+p-\tau_+,u)/(2+p-\tau_+)$$

This becomes singular if τ_+ is equal to an integer $n\geq 2+p$. Now we find

$$\frac{{}_2F_1(1,-1-p-\tau_+,3+p-\tau_+,u)}{2+p-\tau_+}=\frac{1}{2+p-\tau_+}\sum_l\frac{(-1-\tau_+-p)_l}{(3+p-\tau_+)_l}\,u^l\,.$$

By making K complex $K\to K+i\epsilon$ and using the identification

$$\lim_{\epsilon\to 0}\frac{\epsilon}{(K-\omega_n)^2+\epsilon^2}=\pi\delta(K-\omega_n)\,,$$

where $\omega_n=(1-1/n^2)\,\alpha/2\alpha$, we obtain, on expansion in series of ϵ, and keeping only the leading terms,

TABLE I. The first correction term (E-E part) in the generalized formula of the van der Waals potential for H-H.[a]

R	$C^{\text{H-H}}_{E_1E_0}$	$C^{\text{H-H}}_{E_1E_0}R$	$C^{\text{H-H}}_{E_1E_0}/R^2$
0.100 (02)	0.1247 (03)	0.1247 (04)	0.1247 (01)
0.200 (02)	0.1247 (03)	0.2493 (04)	0.3116 (00)
0.300 (02)	0.1245 (03)	0.3736 (04)	0.1383 (−01)
0.400 (02)	0.1244 (03)	0.4975 (04)	0.7774 (−01)
0.500 (02)	0.1242 (03)	0.6210 (04)	0.4968 (−01)
0.750 (02)	0.1236 (03)	0.9269 (04)	0.2197 (−01)
0.100 (03)	0.1228 (03)	0.1228 (05)	0.1228 (−01)
0.250 (03)	0.1162 (03)	0.2904 (05)	0.1859 (−02)
0.500 (03)	0.1026 (03)	0.5132 (05)	0.4106 (−03)
0.750 (03)	0.8988 (02)	0.6741 (05)	0.1598 (−03)
0.100 (04)	0.7898 (02)	0.7898 (05)	0.7898 (−04)
0.125 (04)	0.6994 (02)	0.8742 (05)	0.4476 (−04)
0.150 (04)	0.6246 (02)	0.9368 (05)	0.2776 (−04)
0.200 (04)	0.5095 (02)	0.1019 (06)	0.1273 (−04)
0.400 (04)	0.2833 (02)	0.1133 (06)	0.1771 (−05)
0.100 (05)	0.1182 (02)	0.1182 (06)	0.1182 (−06)
0.100 (06)	0.1188 (01)	0.1188 (06)	0.1188 (−09)
0.100 (07)	0.1188 (00)	0.1188 (06)	0.1188 (−12)

[a] (n) indicates a multiplicative factor of 10^n. R is in units of the Bohr radius a; $C^{\text{HH}}_{E_1E_0}\equiv -V^{\text{HH}}_{EE,10}R^8$, in units of αa^7.

TABLE II. Asymptotic limit of $V^{\mathrm{HH}}_{EE,nm}$.

	$-V_{00}(R)$	$-V_{01}(R)$	$-V_{02}(R)$	$-V_{03}(R)$	$-V_{11}(R)$	$-V_{12}(R)$
$R\to 0$	$\frac{6.5\,\alpha a^5}{R^6}$	$\frac{62.35\,\alpha a^7}{R^8}$	$\frac{1077\,\alpha a^9}{R^{10}}$	$\frac{28960\,\alpha a^{11}}{R^{12}}$	$\frac{1140\,\alpha a^9}{R^{10}}$	$\frac{31930\,\alpha a^{11}}{R^{12}}$
$R\to\infty$	$\frac{5086\,\alpha a^6}{R^7}$	$\frac{5.94\times 10^4\,\alpha a^8}{R^9}$	$\frac{1.246\times 10^6\,\alpha a^{10}}{R^{11}}$	$\frac{3.246\times 10^7\,\alpha a^{12}}{R^{13}}$	$\frac{1.185\times 10^6\,\alpha a^{10}}{R^{11}}$	$\frac{3.120\times 10^7\,\alpha a^{12}}{R^{13}}$

$$\operatorname{Im}\frac{1}{2+p-\tau}\sum_{l}\frac{(-1-\tau_+-p)_l}{(3+p-\tau)_l}\,u^l$$

$$=\sum_{n}\frac{(n+p+1)!}{(n-p-2)!\,(2p+3)!}\,u^{n-2-p}(1-u)^{3+2p}$$

$$\times\frac{2\pi}{n^3}\,\delta\left[\kappa-\left(1-\frac{1}{n^2}\right)\right], \quad \text{(C15)}$$

where

$$\kappa=\frac{K}{\alpha/2\alpha}\ .$$

This is the zero-width approximation because ϵ can be interpreted as the width of the nth excited state. O, P_p^-, and Q_p^- are regular for all K; and P^+ and Q^+ are regular off the resonances. At resonances, $\operatorname{Re}P_p^+$ and $\operatorname{Re}Q_p^+$ are obtained from $\operatorname{Im}P_p^+(K)$ and $\operatorname{Im}Q_p^+(K)$ through dispersion relations. Then calculation of the higher-multipole forces with the one-dimensional integral can be proceeded with the method presented in an earlier paper.

We have constructed $\rho_{E,0}(K)$, $\rho_{E,1}(K)$, $\rho_{E,2}(K)$, and $\rho_{E,3}(K)$ for hydrogen by following the above procedure. The potential $V_{EE,00}(R)$ has been calculated in a previous paper.[11] According to (2.11) the potential $V^{AB}_{EE,10}$ can be written as

$$V^{AB}_{EE,10}(R)=\frac{-1}{4\pi^3R^8}\,Q^{\mathrm{op}}_{EE}\int_0^\infty\frac{dK_A}{\pi}$$

$$\times\int_0^\infty\frac{dK_B}{\pi}\,K_A\,\rho^A_{E,1}(K_A)\,K_B\,\rho^B_{E,0}(K_B)$$

$$\times\int_0^\infty\frac{d\zeta\,e^{-2\zeta R}}{(K_A^2+\zeta^2)(K_B^2+\zeta^2)}\ , \quad \text{(C16)}$$

where

$$Q^{\mathrm{op}}_{EE}=\frac{R^6}{16}\,\frac{d^6}{dR^6}-\frac{3R^5}{8}\,\frac{d^5}{dR^5}+\frac{19R^4}{8}\,\frac{d^4}{dR^4}-12R^3\,\frac{d^3}{dR^3}$$

$$+42R^2\,\frac{d^2}{dR^2}-90R\,\frac{d}{dR}+90\ . \quad \text{(C17)}$$

This potential has been computed for various distances for $A=B=\mathrm{H}$. The results are given in Table I. Also we have calculated the long- and short-distances limit for the potentials $V^{\mathrm{HH}}_{EE,02}$, $V^{\mathrm{HH}}_{EE,03}$, $V^{\mathrm{HH}}_{EE,12}$, $V^{\mathrm{HH}}_{EE,12}$. The results are given in Table II together with the corresponding values for $V^{\mathrm{HH}}_{EE,00}$ and $V^{\mathrm{HH}}_{EE,10}$. We also conjecture a simple interpolation formula $\tilde V_{EE,10}(R)$ similar to the one given by O'Carroll and Sucher[18] for $V_{EE,00}$. This conjectured formula works very well for hydrogen and we are encouraged to generalize it to all values of n and m. We define

$$C_{nm}\equiv\lim_{R\to 0}\,-R^{6+2(n+m)}\,V_{EE,nm}(R)\ ,$$

$$D_{nm}\equiv\lim_{R\to\infty}\,-R^{7+2(n+m)}\,V_{EE,nm}(R)\ .$$

We conjecture a possible interpolation formula $\tilde V_{EE,nm}(R)$ for $V_{EE,nm}(R)$ as the following:

$$\tilde V_{EE,nm}(R)=-\frac{-1}{R^{6+2(n+m)}}\,\frac{2}{\pi}\,C_{nm}\tan^{-1}\left(\frac{\pi D_{nm}}{2C_{nm}R}\right)\ .$$

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