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General Theory of the van der Waals Interaction: A Model-Independent Approach*

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We study the van der Waals interaction $V_{2\gamma}^{AB}(R)$ arising from two-photon exchange between neutral spinless systems A and B. By using the analytic properties of the two-photon contribution to the scattering amplitude for $A+B \to A+B$ and of the full amplitudes for $\gamma+A \to \gamma+A$ and $\gamma+B \to \gamma+B$, we show that it is possible to express $V_{2\gamma}^{AB}(R)$ entirely in terms of measurable quantities, the elastic scattering amplitudes for photons of various frequencies ω. This approach includes relativistic corrections, higher multipoles, and retardation effects from the outset and thus avoids any v/c expansion or any direct reference to the detailed structure of the systems involved. We obtain a generalized form of the Casimir-Polder potential, which includes both electric and magnetic effects, and, correspondingly, a generalized asympotic form $V_{2\gamma}^{AB}(r) \sim -D/R^7$, where $D=[23(\alpha_E^A\alpha_E^B+\alpha_M^A\alpha_M^B)-7(\alpha_E^A\alpha_M^B+\alpha_M^A\alpha_E^B)]/4\pi$ and the α's denote static polarizabilities. In addition, we show that the potential may be written as a single integral over ω, involving products of the dynamical polarizabilities $\alpha_X(\omega)$ evaluated at *real* frequencies, in contrast to the familiar integral over imaginary frequencies; for the case of interacting atoms, the domain of applicability of the various formulas is clarified, and the problem of evaluating $V_{2\gamma}^{AB}(R)$ from present experimental information is discussed. Some simple interpolation formulas are presented, which may accurately describe $V_{2\gamma}^{AB}(R)$ in terms of a few constants.

I. INTRODUCTION

In this paper we present a theoretical description of the van der Waals interaction between two neutral spinless systems. We show that this interaction may be expressed in terms of measurable quantities that describe the interaction of the individual systems with real photons, i.e., the elastic photon scattering amplitudes. We are thereby able to avoid any reference to the detailed structure of the system, such as is involved in the conventional atomic physics approach.[1] We also effectively avoid any expansion of the interparticle interaction in powers of velocity. Finally, we are able to treat electric and magnetic effects on an equal footing, which is essential for obtaining accurate expressions for the very long-range forces between systems such as hydrogen atoms, which have large magnetic polarizabilities.

The essence of our method lies in the recognition that the van der Waals force, which arises from the exchange of two virtual photons between the systems, can be calculated in terms of the amplitude for the emission or absorption of two real photons by each system; this approach, which is based on the dispersion theoretic techniques developed for elementary particle scattering problems, has been used by us previously[2,3] to discuss the asymptotic form for very large separations of the retarded van der Waals force. Here the same technique is used to discuss the force at any separation R large enough so that the two atoms do not overlap appreciably. Previous treatments of this problem[4] with the inclusion of magnetic and other relativistic effects have involved expanding the electron-electron interactions in powers of $1/R$ and v/c and extracting the presumably dominant terms. In that approach it appears difficult to decide whether one has really obtained the most important terms in some given region of R, and the fact that the answer can be expressed in terms of quantities referring to the isolated atoms is obscured.

The results we obtain are similar in some cases to those obtained by other authors[5] under substantially more restrictive assumptions than we have made. We believe that it is much clearer what the domain of applicability of our results is and what must be known about the systems of interest in order to calculate the van der Waals forces.

The main result of our work is an expression for the long-range part of two-photon exchange potential between any two systems A and B in terms of the amplitude for elastic photon scattering of each system. This amplitude is determined by two complex invariant form factors $F_E(\sigma, t)$ and $F_M(\sigma, t)$ which are functions of the square of the invariant energy $\sigma = (p+k)^2$ and of the squared four-momentum transfer $t = (k-k')^2$. Using the method of effective interactions, we show that

$$F_E(m^2, 0) = 4\pi\alpha_E, \quad F_M(m^2, 0) = 4\pi\alpha_M,$$

where α_E and α_M are the static electric and magnetic polarizability of the system. (An alternative derivation of this is given in Appendix A, using an S-matrix approach.) The expression for the potential can be written as

$$V_{2\gamma}(R) = V_{EE}(R) + V_{EM}(R) + V_{ME}(R) + V_{MM}(R)\ , \qquad (1.1)$$

where, for separations R large compared to the size of either system,

$$V_{XY}(R) \simeq -C_{XY}(R)/R^6 \quad (X, Y = E, M)\ , \qquad (1.2)$$

$$C_{XY}(R) = \frac{1}{4\pi^5}\int_0^\infty\int_0^\infty dk_A\, dk_B\, k_A k_B \rho_X^A(k_A)\rho_Y^B(k_B) \times \int_0^\infty \frac{d\zeta\, e^{-2\zeta R} P_{XY}(\zeta R)}{(\zeta^2+k_A^2)(\zeta^2+k_B^2)}\ . \qquad (1.3)$$

Here $k = (\sigma - m^2)/2m$ is essentially a photon energy, the ρ's are the spectral functions associated with the F's, i.e., $\rho_X = \mathrm{Im} F_X(\sigma, 0)$ and

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

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

In Sec. II, we derive Eqs. (1.1)–(1.3) above, and also show that they imply that for very large R the potential has the form given earlier,[3] i.e.,

$$V_{2\gamma}(R) \sim (1/4\pi R^7)(23\alpha_E^A\alpha_E^B + 23\,\alpha_M^A\alpha_M^B - 7\alpha_M^A\alpha_E^B - 7\alpha_E^A\alpha_M^B). \qquad (1.4)$$

A more direct derivation of this result is given in Appendix B.

It is well known that $C_{EE}(R)$ can be written as a single integral over the product of the dynamic polarizabilities $F_E^A(\omega)$ and $F_B^B(\omega)$ [$F_X(\omega) \equiv F_X(\sigma, 0)$, $\omega = (\sigma - m^2)/2m$] evaluated at *imaginary* values of ω. In Sec. II, we show that (1.3) can be written in the form

$$C_{XY}(R) = \frac{P_{XY}^{op}}{8\pi^4}\int_0^\infty d\omega\, f(2\omega R)[\mathrm{Re}F_X^A(\omega)\,\mathrm{Im}F_Y^B(\omega) + \mathrm{Im}F_X^A(\omega)\,\mathrm{Re}F_Y^B(\omega)]\ , \qquad (1.5)$$

where P_{XY}^{op} is obtained by replacing η^n by $R^n\partial^n/\partial R^n$ in $P_{XY}(\eta)$ and

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

Equation (1.5) involves the $F_X(\omega)$ only for *real* values of ω and exhibits the fact that $V_{2\gamma}(R)$ is determined by measurable quantities in a direct and simple way.

In Sec. III, we describe how experimental information about the scattering of light by atoms can be used with our formulas to obtain the interatomic potential. In Sec. IV, we generalize a simple but accurate interpolation formula previously given[6] for $C_{EE}(R)$ to the other $C_{XY}(R)$; these formulas may provide a few-parameter fit to the potential at all separations. Finally, in Sec. V, we consider some additional results and unsolved problems concerning our approach to the van der Waals force.

II. GENERAL FORM OF TWO-PHOTON EXCHANGE POTENTIAL

In this section we derive Eqs. (1.1)–(1.3) which give the general form of the long-range part of $V_{2\gamma}(R)$, the potential arising from two-photon exchange between a pair of neutral, spin-0 particles. In Sec. II A, we review the definition of the potential. In Sec. II B, we study the general form of the amplitude for the scattering of a real or virtual photon by either of the particles. In Sec. II C we first show that only the on-shell amplitudes are needed to determine $V_{2\gamma}(R)$ for separations R which are large compared to the size of either system. The use of the spectral representations for the invariant electric and magnetic "form factors" F_E and F_M associated with the particles then permits one to express $V_{2\gamma}$ in terms of the corresponding spectral functions ρ_E and ρ_M. In Sec. II D we show, using the method of effective interactions, that the threshold values of F_E and F_M may be interpreted as static electric and magnetic polarizabilities, respectively. (Appendix A describes an alternative approach based on an S-matrix definition of the polarizabilities which leads to the same conclusion.) The asymptotic form of $V_{2\gamma}$ now follows immediately from the results of Sec. II B together with this interpretation. A more direct computation of the asymptotic form is given in Appendix B. In Sec. II E we show that $V_{2\gamma}$ may be expressed as a single integral over directly measurable quantities.

A. Definition of Potential

Consider the elastic scattering of neutral spinless particles A and B,

$$A+B\rightarrow A'+B' , \qquad (2.1)$$

with initial four-momenta P_A, P_B and final four-momenta P'_A, P'_B, respectively. As usual, we define

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

with $s+t+u=2m_A^2+2m_B^2$; s is the square of the energy in the c.m. system and t is the negative of the square of the momentum transfer. We denote the invariant Feynman amplitude for the process (2.1) by $F(s,t)$. The normalization is such that the c.m. system scattering amplitude is given by $f=-F/8\pi s^{1/2}$.

Let $F_{2\gamma}(s,t)$ denote the contribution to F arising from the exchange of precisely two photons between A and B as symbolized by Fig. 1. For a fixed physical value of s, $F_{2\gamma}(s,t)$ is assumed to be an analytic function of t admitting, in terms of spectral functions $\rho_{2\gamma}$ and $\bar{\rho}_{2\gamma}$, a representation of the form

$$F_{2\gamma}(s,t)=\frac{1}{\pi}\int_{t_0}^{\infty}\frac{\rho_{2\gamma}(s,t')}{t'-t}\,dt'+\frac{1}{\pi}\int_{u_0}^{\infty}\frac{\bar{\rho}_{2\gamma}(s,u')}{u'-u}\,du'$$

$$=F_2^{(r)}(s,t)+F_2^{(l)}(s,t), \qquad (2.2)$$

where $t_0=0$ and $\bar{t}_0=2m_A^2+2m_B^2-s-u_0$ are the nearest right- and left-hand t singularities of $F_{2\gamma}(s,t)$. Since crossing symmetry implies that $u_0=s'_0$, where s'_0 is the nearest singularity in the s channel and $s'_0\sim s_0$ where

$$s_0\equiv(m_A+m_B)^2$$

(in the absence of anomalous thresholds in the s channel, $s'_0=s_0$), we have, for $s\sim s_0$, $\bar{t}_0\sim-4m_Am_B$. Thus, the second term in (2.2) arising from the left-hand cut, gives rise to only a very short-range force. The long-range two-photon potential $V_{2\gamma}(R)$ is therefore defined as essentially the Fourier transform of the first term in (2.2), evaluated at $s=s_0$,

$$V_{2\gamma}(R)=\frac{1}{4m_Am_B}\int\frac{d\vec{Q}}{(2\pi)^3}\,e^{i\vec{Q}\cdot\vec{R}}\int_0^{\infty}\frac{dt'}{\pi}\,\frac{\rho_{2\gamma}(s_0,t')}{t'-t} , \qquad (2.3)$$

with $t=-Q^2$; the factor $(4m_Am_B)^{-1}$ is such that for $s\simeq s_0$, $V_{2\gamma}(R)$ will, when used in a c.m. system nonrelativistic Schrödinger equation, reproduce $f_{2\gamma}^{(r)}=-F_{2\gamma}^{(r)}/8\pi s^{1/2}$ in first Born approximation. On reversing the order of integration in (2.3), we have

$$V_{2\gamma}(R)=\frac{1}{16\pi^2m_Am_BR}\int_0^{\infty}dt\,\rho_{2\gamma}(s_0,t)\exp(-t^{1/2}R). \qquad (2.4)$$

We already showed in Ref. 2 that $\rho_{2\gamma}(s_0,t)$ varies as t^2 near $t=0$ from which the universality of the asymptotic R^{-7} behavior of $V_{2\gamma}(R)$ follows immediately using (2.4). In the present paper we wish to derive the general form of the coefficient of R^{-7} and, more generally, to derive a transparent expression for $V_{2\gamma}(R)$ which is valid for all R much larger than the size of either system. We are thus faced, among other things, with the agony of keeping track of all factors of 2, π, i, and -1.

From Fig. 1 we see that $F_{2\gamma}(s,t)$ may be expressed as an integral involving a product of photon propagators and the amplitudes $\Gamma^A_{\mu\nu}$ and $\Gamma^B_{\mu\nu}$ for emission of a pair of virtual photons by A and B, respectively. It is convenient to express $\Gamma^A_{\mu\nu}$ and $\Gamma^B_{\mu\nu}$ in terms of the corresponding amplitudes $M^A_{\mu\nu}$ and $M^B_{\mu\nu}$ for photon scattering for each system. Thus, let

$$M=M_{\mu\nu}(p',k';p,k)\epsilon^{\mu}\epsilon'^{\nu} \qquad (2.5)$$

denote the Feynman amplitude for elastic scattering of a neutral particle by a photon, with the kine-

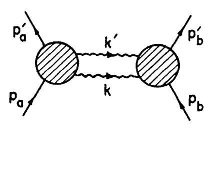

FIG. 1. Symbolic Feynman diagram defining $F_{2\gamma}(s,t)$, the amplitude arising from two-photon exchange.

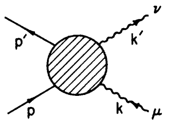

FIG. 2. Symbolic Feynman diagram defining the Compton amplitude $M_{\mu\nu}(p', k'; p, k)$.

matics indicated in Fig. 2; of course, $p+k=p'+k'$. We define $P\equiv p+p'$ and write

$$\Gamma_{\mu\nu}=\Gamma_{\mu\nu}(k, k'; P)\equiv M_{\mu\nu}(p', k'; p, -k) \qquad (2.6)$$

so that $\Gamma_{\mu\nu}$ is the amplitude for two-photon emission if both k_0' and k_0 are positive. $F_{2\gamma}(s, t)$ is then given by

$$-iF_{2\gamma}(s, t)=\frac{1}{2}\times(-i)^2\int\frac{d^4k\, d^4k'}{(2\pi)^4}\,\delta(Q-k-k')$$
$$\times\left(\frac{-i}{k^2}\right)\left(\frac{-i}{k'^2}\right)(\Gamma^A{:}\Gamma^B), \qquad (2.7)$$

where

$$\Gamma^A{:}\Gamma^B\equiv\Gamma^A_{\mu\nu}(k, k'; P_A)\Gamma^B_{\alpha\beta}(-k, -k'; P_B)g^{\mu\alpha}g^{\nu\beta} \qquad (2.8)$$

and

$$P_A=p_A'+p_A, \quad P_B=p_B'+p_B\ ,$$
$$Q=p_A-p_A'=-(p_B-p_B')\ . \qquad (2.9)$$

The factor $\frac{1}{2}$ in (2.7) is needed to avoid counting each diagram contributing to $F_{2\gamma}$ twice; the factor $(-i)^2$ arises from the fact that the Feynman rules applied to, for instance, the left-hand bubble in Fig. 1, give $-i\,M^A_{\mu\nu}\epsilon^\mu\epsilon'^\nu$, and we wish to be consistent with the normalization and phase conventions implied by (2.5). Before attempting to use (2.7) to compute the spectral function $\rho_{2\gamma}$, we consider form the general of $M_{\mu\nu}$.

B. Amplitude for Photon Scattering by Neutral Spinless Particles

The general form of $M_{\mu\nu}$, or equivalently of $\Gamma_{\mu\nu}$, form may be inferred the results of Ref. 2. We briefly review the argument. The identity of the photons requires that

$$\Gamma_{\mu\nu}(q, q'; P)=\Gamma_{\nu\mu}(q', q; P) \qquad (2.10)$$

or, in terms of $M_{\mu\nu}$,

$$M_{\mu\nu}(p', k'; p, k)=M_{\nu\mu}(p', -k; p, -k')\ , \qquad (2.10')$$

which is just the requirement of crossing symmetry. The neutrality of the particle together with the conservation of the electromagnetic current imply that

$$k^\mu M_{\mu\nu}=k_\nu' M^{\mu\nu}=0\ . \qquad (2.11)$$

On writing $M_{\mu\nu}$ as a linear combination of $g_{\mu\nu}$ and the nine second-rank tensors which may be formed from the three available independent four vectors k, k', and $P=p+p'$, the ten coefficients are subjected to six constraints, via Eqs. (2.8) and (2.9). On using these constraints to eliminate some of the coefficients, one may write $M_{\mu\nu}$ in the form

$$M_{\mu\nu}=-\sum_{a=1}^{5}T_{a;\mu\nu}F_a, \qquad (2.12)$$

where, with $\hat{P}=P/m$,

$$T_{1;\mu\nu}=k\cdot\hat{P}k'\cdot\hat{P}g_{\mu\nu}+k\cdot k'\hat{P}_\mu\hat{P}_\nu$$
$$-k\cdot\hat{P}k_\mu'\hat{P}_\nu-k'\cdot\hat{P}k_\nu\hat{P}_\mu\ , \qquad (2.13)$$

$$T_{2;\mu\nu}=k\cdot k'g_{\mu\nu}-k_\nu k_\mu'\ , \qquad (2.14)$$

and (less important for our purposes)

$$T_{3;\mu\nu}=k\cdot k'k_\mu k_\nu'+k^2k'^2g_{\mu\nu}-k^2k_\mu'k_\nu'-k'^2k_\mu k_\nu\ , \qquad (2.15)$$

$$T_{4;\mu\nu}=k'\cdot P(k^2g_{\mu\nu}-k_\mu k_\nu)+k\cdot k'k_\mu P_\nu-k^2k_\mu'P_\nu\ , \qquad (2.16)$$

$$T_{5;\mu\nu}=T_{4;\nu\mu}\big|_{k\leftrightarrow k'}\ . \qquad (2.16')$$

If all the particles are off the mass shell, the form factors F_a are functions of, for example, the six scalar products $k\cdot k'$, $k\cdot P$, $k'\cdot P$, P^2, k^2, and k'^2. F_1, F_2, and F_3 are symmetric under the interchange $k\leftrightarrow k'$. There are only *four* independent F_a', since, corresponding to (2.16) and (2.16′), one has

$$F_5=F_4\big|_{k\leftrightarrow k'}\ .$$

We note further that for real photons ($k^2=k'^2=0$, $\epsilon\cdot k=\epsilon'\cdot k'=0$) $M_{\mu\nu}$ may be replaced by

$$\tilde{M}_{\mu\nu}=-\sum_{a=1}^{2}T_{a;\mu\nu}F_a \qquad (2.17)$$

since, as is easily verified,

$$T_{a;\mu\nu}\epsilon^\mu\epsilon'^\nu=0 \quad (a=3, 4, 5) \qquad (2.18)$$

if the photons are on the mass shell. This fact has the important consequence that the long-range part of $V_{2\gamma}(R)$ is determined by the form factors F_1 and F_2 only. As we shall show in Sec. II C, the quantities

$$F_E\equiv-(4F_1+F_2)/2m \qquad (2.19)$$

and

$$F_M\equiv F_2/2m \qquad (2.20)$$

have a simple physical interpretation as generalized electric and magnetic polarizabilities. Correspondingly, it is useful to introduce "purely electric" and "purely magnetic" tensors T_E and T_M via

$$T_{E;\mu\nu}=-\tfrac{1}{2}T_{1;\mu\nu}\ , \qquad (2.21)$$

$$T_{M;\mu\nu}=-\tfrac{1}{2}T_{1;\mu\nu}+2T_{2;\mu\nu}\ , \qquad (2.22)$$

so that

$$\tilde{M}_{\mu\nu} = -m(T_{E;\mu\nu}F_E + T_{M;\mu\nu}F_M) . \qquad (2.23)$$

When all particles are on the mass shell ($p^2 = p'^2 = m^2$, $k^2 = k'^2 = 0$), the form factors F_E and F_M are conveniently regarded as functions of σ and t, the squares of the c.m. system energy and momentum transfer. Thus, we write

$$F_E = F_E(\sigma, t), \quad F_M = F_M(\sigma, t), \qquad (2.24)$$

with

$$\sigma = (p+k)^2 = (p'+k')^2, \quad t = (p-p')^2 = (k-k')^2 . \quad (2.24')$$

We note finally that, for fixed t, F_E and F_M are expected to be analytic functions of σ, admitting spectral representations analogous to (2.2), e.g., for F_E of the form

$$F_E(\sigma, t) = \frac{1}{\pi}\int_{\sigma_0}^{\infty} \frac{\rho_E^{(1)}(\sigma', t)}{\sigma' - \sigma}\, d\sigma' + \frac{1}{\pi}\int_{\bar{\sigma}_0}^{\infty} \frac{\rho_E^{(2)}(\bar{\sigma}', t)}{\bar{\sigma}' - \bar{\sigma}}\, d\bar{\sigma}', \qquad (2.25)$$

with $\bar{\sigma}$ analogous to u, i.e.,

$$\bar{\sigma} = (p-k')^2 = (p'-k)^2 . \qquad (2.26)$$

An important simplification now arises from the crossing relation (2.10′) which implies, since T_E and T_M are invariant under the transformation $k \leftrightarrow -k'$ while $\sigma \leftrightarrow \bar{\sigma}$ under the same transformation, that

$$F_E(\sigma, t) = F_E(\bar{\sigma}, t), \quad F_M(\sigma, t) = F_M(\bar{\sigma}, t) . \qquad (2.27)$$

It follows that $\rho_E^{(1)}(\zeta, t) = \rho_E^{(2)}(\zeta, t)$ and $\sigma_0 = \bar{\sigma}_0$ so that we may write F_E in terms of a single spectral function $\rho_E(\sigma, t)$, viz.,

$$F_E(\sigma, t) = \frac{1}{\pi}\int_{\sigma_0}^{\infty} d\sigma'\, \rho_E(\sigma', t)\left(\frac{1}{\sigma'-\sigma} + \frac{1}{\sigma'-\bar{\sigma}}\right) \qquad (2.28)$$

and, similarly,

$$F_M(\sigma, t) = \frac{1}{\pi}\int_{\sigma_0}^{\infty} d\sigma'\, \rho_M(\sigma', t)\left(\frac{1}{\sigma'-\sigma} + \frac{1}{\sigma'-\bar{\sigma}}\right) . \qquad (2.29)$$

In the absence of anomalous thresholds in the σ variable, $\sigma_0^{1/2} = m$, the threshold for elastic scattering in the c.m. system. Equation (2.23) for $\tilde{M}_{\mu\nu}$ together with the representations (2.28) and (2.29) are the results we shall need in Sec. II C.

C. Computation of $V_{2\gamma}(R)$

1. *Reduction to On-Shell Photon Amplitudes*

To compute $V_{2\gamma}(R)$ from (2.4) we need the spectral function $\rho_{2\gamma}(s_0, t)$, defined indirectly by the spectral representation (2.2). It follows from (2.2) that

$$\rho_{2\gamma}(s_0, t) = (1/2i)[F(s_0, t)] , \qquad (2.30)$$

where

$$[F(s_0, t)] = F(s_0, t+i\epsilon) - F(s_0, t-i\epsilon) \quad (t \geq 0) \qquad (2.31)$$

is the discontinuity of $F(s_0, t)$ across the cut starting at the branch point $t = 0$. This singularity may be thought of as arising from the two-photon intermediate state in the crossed-channel reaction

$$A + \bar{A} \to \bar{B} + B' , \qquad (2.32)$$

where a bar is used to denote the antiparticle. For tightly bound systems, the next singularity on the positive real t axis will be at a value t_1 such that $t_1^{1/2}$ is the rest mass of the next least massive system which can be exchanged by A and B. For example, if A and B are elementary particles, say π^0 mesons, $t_1^{1/2}$ will have the value $2m_e$ where m_e denotes the electron mass corresponding to the exchange-positron pair. However, for loosely bound systems such as atoms, the value of t_1 will be considerably smaller, $t_1^{1/2} \sim p_0$, where $p_0 = \alpha m_e$ is the Bohr momentum ($\alpha = e^2/4\pi\hbar c$); these smaller values of $t_1^{1/2}$ correspond to the presence of so-called anomalous thresholds whose values are not simply determined by the masses of intermediate states but are rather a measure of the *size* of the interacting systems.[7] Thus, if we define $a_1 \equiv t_1^{-1/2}$ we expect $a_1 \sim a_0$ = Bohr radius. Such thresholds already arise in the case of single-photon exchange where they give rise to terms which fall off exponentially with R.[8] Let us write

$$\rho_{2\gamma}(s_0, t) = \rho_{2\gamma}(t) + \Theta(t - t_1)\rho'_{2\gamma}(t), \qquad (2.33)$$

where $\rho_{2\gamma}(t)$ is the contribution to the discontinuity arising from real two-photon intermediate states in the crossed channel and $\rho'_{2\gamma}(t)$ is the remainder. It is easy to see from (2.4) that $\rho'_{2\gamma}(t)$ contributes a term which decreases for $R \gg a_1$ like

$$(\text{const})e^{-R/a_1}/R , \qquad (2.34)$$

or more rapidly if $\rho'_{2\gamma}(t_1) = 0$.

It follows from the above considerations that the *long-range* part of $V_{2\gamma}(R)$, i.e., the part which does not decrease exponentially, is determined by a knowledge of $\rho_{2\gamma}(t)$ alone. Thus, we may write

$$V_{2\gamma}(R) = (1/16\pi^2 m_a m_b R)\int_0^{\infty} dt\, \rho_{2\gamma}(t)\exp(-t^{1/2}R) + \cdots , \qquad (2.35)$$

where the dots indicate terms with which fall off exponentially for $R \gg a$, a denoting a measure of the size of the "larger" of the two interacting systems.

We can now see why knowledge of the photon scattering amplitudes is sufficient to determine the long-range part of the two-photon exchange force. According to the ideas of generalized unitarity, $\rho_{2\gamma}(t)$ may be obtained from (2.7) by putting the photons on the mass shell, i.e., by replacing the propagators $1/k^2$ and $1/k'^2$ by $-2\pi i\delta(k^2)\theta(k^0)$ and $-2\pi i\delta(k'^2)\theta(k'^0)$, respectively, in (2.10). Thus,

$$\rho_{2\gamma}(t) = -\tfrac{1}{4}[1/(2\pi)^2]\int d\Phi(\Gamma^A : \Gamma^B)\big|_{s=s_0} , \qquad (2.36)$$

where

$$d\Phi \equiv \delta(Q-k-k')\delta(k^2)\delta(k'^2)\theta(k^0)\theta(k'^0)d^4k\,d^4k' \quad (2.37)$$

is just the volume element in phase space for two photons. Furthermore, corresponding to the reduction of $M_{\mu\nu}$ to $\tilde{M}_{\mu\nu}$ [Eq. (2.17)] on the photon mass shell, we may, in (2.7), make the replacement

$$\Gamma^A:\Gamma^B \to \tilde{\Gamma}^A:\tilde{\Gamma}^B , \quad (2.38)$$

where

$$\tilde{\Gamma}_{\mu\nu}(k,k';P)=\tilde{M}_{\mu\nu}(p',k';p,-k) . \quad (2.39)$$

Lest there by any doubt about the replacement (2.38), we remark that it is easy to verify directly that if

$$T^A_{a;\mu\nu}=T_{a;\mu\nu}\big|_{P=P_A,\,m=m_A} \quad (2.40)$$

and T^B is similarly defined, then

$$T^A_a:T^B_b=0 \quad (a \text{ or } b\geq 3), \quad (2.41)$$

if $k^2=k'^2=0$. Thus,

$$\rho_{2\gamma}(t)=-(1/16\pi^2)\int d\Phi\,(\tilde{\Gamma}^A:\tilde{\Gamma}^B)_{s=s_0} \quad (2.42)$$

and only the on-shell amplitudes enter into the computation of $\rho_{2\gamma}(t)$, and hence into the determination of the van der Waals potential.

2. *Computation of* $\rho_{2\gamma}(t)$

To evaluate (2.42) we write for the on-shell photon scattering amplitudes, following the notation introduced in (2.22) and (2.10) but suppressing the polarization indices,

$$\tilde{M}^A(p'_A,k';p_A,k)=m_A[T^A_E F^A_E(\sigma_A,t)+T^A_M F^A_M(\sigma_A,t)] , \quad (2.43)$$

with $\sigma_A=(p_A+k)^2$, and a similar expression for $\tilde{M}^B_{\mu\nu}$. On noting that $T^{A,B}\to -T^{A,B}$ when $k\to -k$, we see that

$$\tilde{\Gamma}^A(k,k';P_A)=m_A[T^A_E F^A_E(\sigma^-_A,t)+T^A_M F^A_M(\sigma^-_A,t)],$$
$$\tilde{\Gamma}^B(-k,-k';P_B)=m_B[T^B_E F^B_E(\sigma^+_B,t)+T^B_M F^B_M(\sigma^+_B,t)] , \quad (2.44)$$

where, using (2.28),

$$F^A_E(\sigma^-_A,t)=\frac{1}{\pi}\int_{m_A^2}^{\infty} d\sigma'_A\,\rho^A_E(\sigma'_A,t)\left(\frac{1}{\sigma'_A-\sigma^-_A}+\frac{1}{\sigma'_A-\bar{\sigma}^+_A}\right) ,$$
$$F^B_E(\sigma^+_B,t)=\frac{1}{\pi}\int_{m_B^2} d\sigma'_B\,\rho^B_E(\sigma'_B,t)\left(\frac{1}{\sigma'_B-\sigma^+_B}+\frac{1}{\sigma'_B-\bar{\sigma}^-_B}\right) , \quad (2.45)$$

with

$$\sigma^\pm_A=(p_A\pm k)^2,\quad \bar{\sigma}^\pm_A=(p_A\mp k')^2,$$
$$\sigma^\pm_B=(p_B\pm k)^2,\quad \bar{\sigma}^\pm_B=(p_B\mp k')^2; \quad (2.46)$$

F^A_M and F^B_M are given by Eqs. (2.45), with ρ^A_E and ρ^B_E replaced by ρ^A_M and ρ^B_M, respectively.

On using (2.43) and (2.44) in (2.42) and reversing the orders of integration, we get

$$\rho_{2\gamma}(t)=\sum_{X,Y}\rho_{XY}(t) , \quad (2.47)$$

where

$$\rho_{XY}(t)=\frac{-m_Am_B}{16\pi^2}\iint d\sigma'_A\,d\sigma'_B\,\rho_X(\sigma'_A,t)\rho_Y(\sigma'_B,t)\times\Phi_{XY}(\sigma'_A,\sigma'_B;t) , \quad (2.48)$$

with

$$\Phi_{XY}(\sigma'_A,\sigma'_B;t)=\int d\Phi\,T^A_X:T^B_Y\left(\frac{1}{\sigma'_A-\sigma^-_A}+\frac{1}{\sigma'_A-\bar{\sigma}^+_A}\right)\times\left(\frac{1}{\sigma'_B-\sigma^+_B}+\frac{1}{\sigma'_B-\bar{\sigma}^-_B}\right)\bigg|_{s=s_0} , \quad (2.49)$$

and both X and Y assume the value E or M.

To evaluate (2.49), it is convenient to work in the c.m. system of the crossed reaction (2.32), thought of as a two-step process,

$$A+\bar{A}'\to\gamma+\gamma',\quad \gamma+\gamma'\to\bar{B}+B',$$

taking place at a total energy equal to $t^{1/2}$. Thus we write, with $p_{\bar{A}}\equiv -p'_A$ and $p_{\bar{B}}=p_B$,

$$p_A=(\tfrac{1}{2}t^{1/2},\vec{p}),\qquad p_{\bar{A}}=(\tfrac{1}{2}t^{1/2},-\vec{p}),$$
$$p'_B=(\tfrac{1}{2}t^{1/2},\vec{p}'),\quad p_{\bar{B}}=(\tfrac{1}{2}t^{1/2},\vec{p}'),$$
$$k=(\tfrac{1}{2}t^{1/2})(1,\hat{k}),\quad k'=(\tfrac{1}{2}t^{1/2})(1,-\hat{k}) ,$$

where $\hat{k}$ is a unit vector; since we are interested in $\rho_{2\gamma}(t)$ for values of t far below the thresholds $4m_A^2$ or $4m_B^2$ for the reactions $A+\bar{A}\leftrightarrow B+\bar{B}$, the mass-shell constraints $p_A^2=m_A^2$, $p_B^2=m_B^2$ imply that the three vectors $\vec{p}$ and $\vec{p}'$ are pure imaginary, so that we write

$$\vec{p}=im_A\xi_A\hat{p},\quad \vec{p}'=im_B\xi_B\hat{p}',$$

where $\hat{p}$ and $\hat{p}'$ are real unit vectors and

$$\xi_A=\left(1-\frac{t}{4m_A^2}\right)^{1/2},\quad \xi_B=\left(1-\frac{t}{4m_B^2}\right)^{1/2} .$$

In terms of these variables we readily find

$$\sigma'_A-\sigma^-_A=\sigma'_A-m_A^2+\tfrac{1}{2}t-it^{1/2}m_A\xi_Ax_A ,$$
$$\sigma'_A-\bar{\sigma}^+_A=\sigma'_A-m_A^2+\tfrac{1}{2}t+it^{1/2}m_A\xi_Ax_A ,$$
$$\sigma'_A-\sigma^+_B=\sigma'_B-m_B^2+\tfrac{1}{2}t+it^{1/2}m_B\xi_Bx_B ,$$
$$\sigma'_A-\bar{\sigma}^-_B=\sigma'_B-m_B^2+\tfrac{1}{2}t-it^{1/2}m_B\xi_Bx_B , \quad (2.50)$$

where

$$x_A=\hat{p}\cdot\hat{k},\quad x_B=\hat{p}'\cdot\hat{k} .$$

The two-photon phase space element $d\Phi$ assumes the form

$$d\Phi = \tfrac{1}{8}\, d\Omega \ ,$$

where $d\Omega$ is the element of solid angle for the integration over $\hat{k}$. A pleasant feature of the next step in the calculation is that on combining the denominators in (2.49), using (2.50), the square roots disappear and we get

$$\Phi_{XY} = \tfrac{1}{2}\int d\Omega\ \frac{\sigma_A' - m_A^2 + \frac{1}{2}t}{(\sigma_A' - m_A^2 + t/2)^2 + t m_A^2 \xi_A^2 x_A^2} \times \frac{\sigma_B' - m_B^2 + \frac{1}{2}t}{(\sigma_B' - m_B^2 + t/2)^2 + t m_B^2 \xi_B^2 x_B^2}\ (T_X^A : T_Y^B)\bigg|_{s=s_0} \ . \quad (2.51)$$

The contractions $T_X^A : T_Y^B$ are straightforward to evaluate. Using the definitions (2.13) and (2.14) we get

$$T_1^A : T_1^B = 2t^2 \xi_A^2 \xi_B^2 S \ ,$$

where

$$S = 2y^2 - 4y x_A x_B + x_A^2 + x_B^2 + x_A^2 x_B^2 \ ,$$

with

$$y = \hat{p}\cdot\hat{p}' \ ,$$

and, more simply,

$$T_1^A : T_2^B = t^2 \xi_A^2, \quad T_2^A : T_1^B = t^2 \xi_B^2 \ , \quad T_2^A : T_2^B = \tfrac{1}{2} t^2 \ .$$

From these equations we infer, using the definitions (2.21) and (2.22),

$$T_E^A : T_E^B = \tfrac{1}{2} t^2 \xi_A^2 \xi_B^2 S \ ,$$
$$T_M^A : T_M^B = \tfrac{1}{2} t^2 \xi_A^2 \xi_B^2 S + t^2 (t/4m_A^2 + t/4m_B^2) \ , \quad (2.52)$$

and

$$T_E^A : T_M^B = \tfrac{1}{2} t^2 \xi_A^2 (\xi_B^2 S - 2), \quad T_M^A : T_M^B = \tfrac{1}{2} t^2 \xi_B^2 (\xi_A^2 S - 2) \ . \quad (2.53)$$

It should be stressed that so far *no* approximations have been made in the evaluation of $\rho_{2\gamma}(t)$. However, to compute the long-range part of $V_{2\gamma}(R)$ in the case of interacting atoms or molecules, we only need accurate values of $\rho_{2\gamma}(t)$ for values of $t^{1/2}$ much less than a_0^{-1}, since for $t^{1/2} > a_0^{-1}$ we only get contributions to $V_{2\gamma}(R)$ which fall off as $\exp(-R/a_0)$. Thus, we shall make a number of approximations which will simplify the formulas without losing anything essential. (i) Since for $t < \alpha^2 m_e^2$ the quantities $t/4m_A^2$ and $t/4m_B^2$ are of order 10^{-12}, it is a marvelous approximation to neglect these terms relative to unity. (ii) In carrying out the angular integrations in (2.51) we may set $\hat{p}' = \hat{p}$. This is because from the relation $s = (p_A + p_B)^2 = (p_A - p_{\bar{B}})^2$ we infer, for $s = s_0 \equiv (m_A + m_B)^2$, that

$$y = \hat{p}\cdot\hat{p}' = \frac{1 + (t/4m_A m_B)}{\xi_A \xi_B} = 1 + O\left(\frac{t}{m^2}\right). \quad (2.54)$$

Hence, we may also set $y = 1$ and $x_A = x_B = x$, with $d\Omega = 2\pi dx$. Using approximations (i) and (ii), we have, to very high accuracy,

$$T_E^A : T_E^B \simeq T_M^A : T_M^B \simeq \tfrac{1}{2} t^2 (2 - 2x^2 + x^4),$$
$$T_E^A : T_M^B \simeq T_M^A : T_E^B \simeq \tfrac{1}{2} t^2 (-2x^2 + x^4) \ . \quad (2.55)$$

It follows that

$$\Phi_{XY} = \Phi_{XY}^0 [1 + O(t/m^2)] \ , \quad (2.56)$$

where

$$\Phi_{XY}^0 = \tfrac{1}{2}\pi \frac{t}{m_A m_B \xi_A \xi_B} \int_{-1}^{1} dx\ \frac{\tau_A}{\tau_A^2 + x^2}\ \frac{\tau_B}{\tau_B^2 + x^2}\ \Theta_{XY}(x) \ . \quad (2.57)$$

Here we have introduced the abbreviations

$$\tau_A = \frac{(\sigma_A' - m_A^2 + \frac{1}{2}t)}{m_A \xi_A t^{1/2}}, \qquad \tau_B = \frac{\sigma_B' - m_B^2 + \frac{1}{2}t}{m_B \xi_B t^{1/2}} \ ,$$

and

$$\Theta_{EE} = \Theta_{MM} = 2 - 2x^2 + x^4, \quad \Theta_{EM} = \Theta_{ME} = -2x^2 + x^4 \ . \quad (2.58)$$

The integration over x is now elementary and yields, without further approximation,

$$\Phi_{XY}^0 = \frac{\pi t}{2 m_A m_B \xi_A \xi_B}\,(2\tau_A \tau_B) \frac{[g_{XY}(\tau_B) - g_{XY}(\tau_A)]}{\tau_B^2 - \tau_A^2} \ , \quad (2.59)$$

where

$$g_{EE}(\tau) = g_{MM}(\tau) = \tau^2 - (2 + 2\tau^2 + \tau^4)(\tan^{-1}\tau)\tau^{-1} \ ,$$
$$g_{EM}(\tau) = g_{ME}(\tau) = \tau^2 - (2\tau^2 + \tau^4)(\tan^{-1}\tau)\tau^{-1} \ . \quad (2.60)$$

3. *Evaluation of the Long-Range Part of* $V_{2\gamma}(R)$

Corresponding to (2.56) we have, using (2.35) and (2.48) the "semifinal" result,

$$V_{2\gamma}(R) \simeq \sum_{X,Y} -\frac{1}{(4\pi)^4 R}\int_0^\infty dt \exp(-t^{1/2}R) \times \int_{m_A^2}^\infty \int_{m_B^2}^\infty \frac{d\sigma_A'}{\pi}\ \frac{d\sigma_B'}{\pi}\ \rho_X^A(\sigma_A', t)\rho_Y^B(\sigma_B', t)\Phi_{xy}^0 \ , \quad (2.61)$$

which exhibits the long-range part of $V_{2\gamma}(R)$ in terms of the spectral functions $\rho_X^A(\sigma_A, t)$ and $\rho_Y^B(\sigma_B, t)$ associated with $F_X^A(\sigma_A, t)$ and $F_Y^B(\sigma_B, t)$.

To proceed further, we note that for atoms, $\rho_X(\sigma, t)$ will be a slowly varying function of t for $t^{1/2} \ll a_0^{-1}$. To see why this is so, we observe that $\rho_X(\sigma, t)$ will in general be an analytic function of t, with a nearest singularity at $t = t_1 \sim a_0^{-2}$ corresponding to the presence of anomalous thresholds in the t channel referred to previously. On expanding the denominator $t'-t$ in a spectral representation of $\rho_X(\sigma, t)$, we infer that $\rho_X(\sigma, t) \simeq (1+tt_2^{-1}) \rho_X(\sigma, 0)$, where t_2^{-1} is a mean value of t^{-1} and hence of order t_1^{-1} or smaller. Thus, for $t \ll a_0^{-2}$ we may (iii) make the replacement

$$\rho_X(\sigma, t) \to \rho_X(\sigma, 0) \tag{2.62}$$

in (2.61). Using (2.62), we see that on introducing new variables

$$k_A = (\sigma_A' - m_A^2)/2m_A, \quad k_B = (\sigma_B' - m_B^2)/2m_B , \tag{2.63}$$

(2.61) assumes the form, on reversing orders of integration,

$$V_{2\gamma}(R) \simeq \sum_{X,Y} \int_0^\infty \int_0^\infty \frac{dk_A}{\pi} \frac{dk_B}{\pi} k_A \rho_X^A(k_A) k_B \rho_Y^B(k_B) U_{XY}^0 , \tag{2.64}$$

where

$$U_{XY}^0 = \frac{-(4m_A m_B)}{(4\pi)^4 k_A k_B R} \int_0^\infty dt \exp(-t^{1/2}R)\Phi_{XY}^0 \tag{2.65}$$

and

$$\rho_X^A(k_A) \equiv \rho_X^A(\sigma_A', 0), \quad \rho_X^B(k_B) \equiv \rho_X^B(\sigma_B', 0) . \tag{2.66}$$

We now make a last approximation: The major contributions to $V_{2\gamma}(R)$ will come from atomic excitation energies $\sigma^{1/2} - m \sim \alpha^2 m_e$ or larger. Hence,

$$t/(\sigma - m^2) < (\alpha m_e)^2/(\alpha^2 m_e)(2m) \sim m_e/m \sim 10^{-3}$$

and we may (iv) make the replacement, using (2.63) and $\xi_A \simeq \xi_B \simeq 1$,

$$\tau_A \to \tau_A^0 = 2k_A/t^{1/2}, \quad \tau_B \to \tau_B^0 = 2k_B/t^{1/2} \tag{2.67}$$

in Eq. (2.59) for Φ_{XY}. Replacing also ξ_A and ξ_B by unity once more we get

$$U_{XY}^0 \to U_{XY}(k_A, k_B; R) \equiv \frac{1}{16\pi^3 R} \int_0^\infty dt \exp(-t^{1/2}R) \times \frac{g_{XY}(\tau_A^0) - g_{XY}(\tau_B^0)}{\tau_B^{02} - \tau_A^{02}} \tag{2.68}$$

a *universal* function of R, k_A, and k_B.

We are finally in a position to make contact with previous work and to derive Eqs. (1.1)–(1.3) of the Introduction. For the case $X=Y=E$ (or $X=Y=M$) the integrand of (2.68) coincides essentially with that considered in Ref. 8, where it was shown that on setting

$$t = 4\zeta^2 \tag{2.69}$$

and carrying out repeated (fivefold) integration by parts, one has

$$U_{EE}(k_A, k_B; R) = U_{MM}(k_B, k_B; R) = \frac{1}{4\pi^3 R^6} \int_0^\infty d\zeta \frac{e^{-2\zeta R} P_{EE}(\zeta R)}{(k_A^2+\zeta^2)(k_B^2+\zeta^2)} , \tag{2.70}$$

where

$$P_{EE}(\eta) = P_{MM}(\eta) = \eta^4 + 2\eta^3 + 5\eta^2 + 6\eta + 3 . \tag{2.71}$$

For the case $X=E$, $Y=M$, or $X=M$, $Y=E$ a similar but much shorter calculation, given in Appendix C, shows that

$$U_{EM}(k_A, k_B; R) = U_{ME}(k_A, k_B; R) = \frac{1}{4\pi^3 R^6} \int_0^\infty d\zeta \frac{e^{-2\zeta R} P_{EM}(\zeta R)}{(k_A^2+\zeta^2)(k_B^2+\zeta^2)} , \tag{2.72}$$

where

$$P_{EM}(\eta) = P_{ME}(\eta) = -(\eta^4 + 2\eta^3 + \eta^2) . \tag{2.73}$$

On combining Eqs. (2.64), (2.68), and (2.70)–(2.73) we may write

$$V_{2\gamma}(R) = V_{EE}(R) + V_{MM}(R) + V_{EM}(R) + V_{ME}(R) , \tag{2.74}$$

where, for $R \gg a \sim a_0$,

$$V_{XY}(R) \simeq -C_{XY}(R)/R^6 , \tag{2.75}$$

with

$$C_{XY}(R) \equiv \frac{1}{4\pi^5} \int_0^\infty \int_0^\infty dk_A dk_B [k_A \rho_X^A(k_A)][k_B \rho_Y^B(k_B)] \times \int_0^\infty d\zeta \frac{e^{-2\zeta R} P_{XY}(\zeta R)}{(k_A^2+\zeta^2)(k_B^2+\zeta^2)} . \tag{2.76}$$

Equations (2.74)–(2.76) correspond to Eqs. (1.1)–(1.3) of Sec. I and are the principal results of this subsection.

D. Asymptotic Behavior of $V_{2\gamma}(R)$ and Interpretation of Form Factors

1. *Asymptotic Behavior of* $V_{2\gamma}(R)$

The asymptotic behavior of $V_{2\gamma}(R)$ for $R \to \infty$ follows readily from Eqs. (2.74)–(2.76). On setting $\zeta = \eta/R$ we get, from (2.76),

$$C_{XY}(R) \sim \frac{1}{4\pi^5 R} \int_0^\infty dk_A \frac{\rho_X(k_A)}{k_A} \int_0^\infty dk_B \frac{\rho_Y^B(k_B)}{k_B} \times \int_0^\infty d\eta \exp(-2n) P_{xy}(\eta). \tag{2.77}$$

From Eqs. (2.28), (2.29), and (2.63) we see that, since $t \to 0$, $\sigma = m^2$ implies $\bar{\sigma} = 2m^2 - \sigma - t \to m^2$,

$$F_X(m^2, 0) = \frac{2}{\pi} \int_{m^2}^\infty d\sigma' \frac{\rho_X(\sigma', 0)}{\sigma' - m^2} = \frac{2}{\pi} \int_0^\infty dk \frac{\rho_X(k)}{k} . \tag{2.78}$$

Furthermore, computation gives

$$\int_0^\infty d\eta\, e^{-2\eta} P_{EE}(\eta) = \tfrac{23}{4} , \quad \int_0^\infty d\eta\, e^{-2\eta} P_{EM}(\eta) = -\tfrac{7}{4} . \tag{2.79}$$

Using the fact that, as shown in Sec. IID 2,

$$F_X(m^2, 0) = 4\pi\,\alpha_X \quad (X = E, M), \tag{2.80}$$

where α_X is a polarizability, we get

$$C_{EE}(R) \sim \frac{23}{4\pi}\,\frac{\alpha_E^A\alpha_E^B}{R}, \quad C_{MM}(R) \sim \frac{23}{4\pi}\,\frac{\alpha_M^A\alpha_M^B}{R} \tag{2.81}$$

and

$$C_{EM}(R) \sim \frac{-7}{4\pi}\,\frac{\alpha_E^A\alpha_M^B}{R}, \quad C_{ME}(R) \sim \frac{-7}{4\pi}\,\frac{\alpha_M^A\alpha_E^B}{R}. \tag{2.82}$$

It follows from Eqs. (2.81), (2.82), and (2.75) that, as asserted in Ref. 3 for $R \to \infty$,

$$V_{2\gamma}(R) \sim -D/R^7, \tag{2.83}$$

where

$$D = \frac{23}{4\pi}(\alpha_E^A\alpha_E^B + \alpha_M^A\alpha_M^B) - \frac{7}{4\pi}(\alpha_E^A\alpha_M^B + \alpha_M^A\alpha_E^B). \tag{2.84}$$

It should be noted that Eq. (2.83) is an *exact* statement independent of any of the approximations made in Sec. IIIC above in the computation of $\rho_{2\gamma}(t)$ for $t > 0$. This is because the behavior of $V_{2\gamma}(R)$ at $R = \infty$ depends only on knowledge of $\rho_{2\gamma}(t)$ in the *immediate* neighborhood of $t = 0$. In particular, to obtain (2.83), it is only necessary to compute the first nonzero term in an expansion of $\rho_{2\gamma}(t)$ in powers of t, since higher powers of t will give higher inverse power of R. An alternative and more elegant derivation of (2.83) which is based on this feature, and which was in fact used by the authors in first obtaining (2.83), is described in Appendix B.[9]

2. *Interpretation of Form Factors*

We wish to justify the identification (2.80) of the threshold values of the form factors $F_E(\sigma, t)$ and $F_M(\sigma, t)$ with static susceptibilities. Perhaps the simplest way of seeing the validity of (2.80) is the following:

Let us note first that, according to Eq. (2.17), at low energies and momentum transfers ($\sigma \simeq m^2$, $t \simeq 0$), the particle-photon scattering amplitude is approximately given by $M' = M'_{\mu\nu}\epsilon^\mu\epsilon^\nu$, where

$$M'_{\mu\nu} = -[\,T_{1;\mu\nu}\,F_1(0) + T_{2;\mu\nu}F_2(0)] \tag{2.85}$$

and

$$F_j(0) \equiv F_j(m^2, 0) \quad (j = 1, 2). \tag{2.86}$$

We now find, for a spinless electrically neutral particle, the simplest effective Hamiltonian density $\mathcal{H}$ which leads, in lowest order, to an amplitude for two-photon emission given by (2.85). Guided by the form (2.13) and (2.14) of $T_{1;\mu\nu}$ and $T_{2;\mu\nu}$, and the requirement that $\mathcal{H}$ be bilinear in the particle and photon field operators ϕ and A_μ, as well as gauge invariant, we obtain

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2, \tag{2.87}$$

where

$$\mathcal{H}_1 = -\frac{F_1(0)}{2m^2}\,\{2[(\partial_\alpha\phi^\dagger)(\partial_\beta\phi) + (\partial_\beta\phi^\dagger)(\partial_\alpha\phi)]F^{\alpha\mu}F^{\beta\nu} - \phi^\dagger\phi\,\partial_\alpha\partial_\beta F^{\alpha\mu}F^{\beta\nu}\}g_{\mu\nu} \tag{2.88}$$

and

$$\mathcal{H}_2 = -\tfrac{1}{4}[F_2(0)]\,\phi^\dagger\phi F^{\mu\nu}F_{\mu\nu}, \tag{2.89}$$

with $F_{\mu\nu} = \partial_\nu A_\mu - \partial_\mu A_\nu$, the quantized electromagnetic field tensor.

If the particle is moving slowly in a region R where there are external (c number) electric and magnetic fields $\vec{E}$ and $\vec{H}$ whose sources are outside of R, the first line in Eq. (2.88) gets contributions only from $\alpha = \beta = 0$ so that, regarding $F^{\mu\lambda}$ as an external field in (2.88), we get

$$\mathcal{H}_1 \to F_1(0)\phi^\dagger\phi\vec{E}^2. \tag{2.90}$$

In arriving at (2.90), we have used $\partial_0\phi \sim im\phi$ and noted that the second line in (2.88) makes no contribution since $\partial_\alpha F^{\alpha\mu} \propto j^\mu$, which vanishes in R. Since $F^{\mu\nu}F_{\mu\nu} = -2(\vec{E}^2 - \vec{H}^2)$, (2.89) is equivalent to

$$\mathcal{H}_2 \to \tfrac{1}{2}[F_2(0)]\phi^\dagger\phi(\vec{E}^2 - \vec{H}^2). \tag{2.91}$$

Using (2.87), (2.90), and (2.91), we have

$$\mathcal{H} \to -\tfrac{1}{2}\alpha'_E(2m\phi^\dagger\phi)\vec{E}^2 - \tfrac{1}{2}\alpha'_M(2m\phi^\dagger\phi)\vec{H}^2, \tag{2.92}$$

with

$$\alpha'_E = -[4F_1(0) + F_2(0)]/2m \tag{2.93}$$

and

$$\alpha'_M = F_2(0)/2m. \tag{2.94}$$

Since $2m\phi^\dagger\phi \sim \sum(a_k^\dagger a_k + \cdots)$ in the nonrelativistic limit, we may infer from (2.92) that the corresponding addition to the Hamiltonian for the particle moving slowly in an external field is simply

$$H' = -\tfrac{1}{2}\alpha'_E\vec{E}^2 - \tfrac{1}{2}\alpha'_M\vec{H}^2. \tag{2.95}$$

It follows that α'_E and α'_M may be identified with the static electric susceptibility (polarizability) and static magnetic susceptibility, respectively. Since we are using the Heaviside unit of charge ($e^2/4\pi\hbar c = \frac{1}{137}$) we have

$$\alpha'_E = 4\pi\,\alpha_E, \quad \alpha'_M = 4\pi\,\alpha_M, \tag{2.96}$$

where α_E and α_M are in the usual Gaussian units. If we combine Eqs. (2.93), (2.94), and (2.96) with the definitions (2.19) and (2.20), we arrive at (2.80).

An alternative, perhaps more convincing approach to the interpretation of the form factors which also leads to (2.93) and (2.94) but which is based on the S matrix and gives some further physical insight into the significance of the F_a, is given in Appendix B.

E. Alternative Forms for $C_{XY}(R)$

Equation (2.76) exhibits $C_{XY}(R)$ as a double integral over the imaginary parts of the invariant functions $F_X(\sigma, 0)$, apart from an integral over the parameter. We now show that $C_{XY}(R)$ may be expressed as a *single* integral over measurable quantities, thereby arriving at a form which may be particularly useful for the determination of $C_{XY}(R)$ from experiment.

It is convenient to introduce the notation

$$F_X(\omega) \equiv F_X(\sigma, 0) \quad (\sigma = m^2 + 2m\omega)\ ;$$

the variable $\omega = (\sigma - m^2)/2m$ (which was denoted by k in Sec. II D) may be interpreted as the energy of a photon incident on a particle of mass m at rest in the laboratory system. It follows from the definitions (2.24′), (2.26), and from the dispersion integral (2.18) evaluated at $t=0$, that $F_X(\omega)$ may be written in the form

$$F_X(\omega) = \frac{1}{\pi}\int_0^\infty d\omega'\,\rho_X(\omega')\left(\frac{1}{\omega'-\omega} + \frac{1}{\omega'+\omega}\right) . \qquad (2.97)$$

From (2.97) we see that for $\omega = i\zeta$ we have

$$\int_0^\infty dk\,\frac{k\rho_X(k)}{k^2+\zeta^2} = \tfrac{1}{2}\pi F_x(i\zeta)\,. \qquad (2.98)$$

On reversing the integration over ζ in (2.76) and using (2.98) we get

$$C_{XY}^{(R)} = \frac{1}{16\pi^3}\int_0^\infty d\zeta\, e^{-2\zeta R} P_{XY}(\zeta R)\, F_X^A(i\zeta)\, F_Y^B(i\zeta). \qquad (2.99)$$

Equation (2.98) is well known for the case $X=Y=E$. However, although only a single integration is involved, the quantities $F_X(i\zeta)$ entering (2.98) correspond to dynamic polarizabilities at imaginary frequencies and are therefore not directly measurable, at least in scattering experiments.

To convert (2.99) to a form in which only directly measurable quantities enter we note first that, with ω regarded as a complex variable, the product function

$$D_{XY}(\omega) = F_X^A(\omega) F_Y^B(\omega) \qquad (2.100)$$

has analyticity and symmetry properties analogous to those of the individual factors; namely, $D_{XY}(\omega)$ is analytic in both the upper and lower halves of the complex ω plane with $D_{XY}(\omega) = D_{XY}(-\omega)$ and $D_{XY}^*(\omega) = D_{XY}(\omega)$. From these properties it follows that $D_{XY}(\omega)$ admits a spectral representation analogous to (2.97),

$$D_{XY}(\omega) = \frac{1}{\pi}\int_0^\infty d\omega'\,\mathrm{Im} D_{XY}(\omega')\left(\frac{1}{\omega'-\omega} + \frac{1}{\omega'+\omega}\right) . \qquad (2.101)$$

It follows from (2.100) and (2.101) that

$$F_X^A(i\zeta)\, F_Y^B(i\zeta) = \frac{2}{\pi}\int_0^\infty d\omega'\,\frac{\omega'}{\omega'^2+\omega^2}\,\mathrm{Im} D_{XY}(\omega') \qquad (2.102)$$

and

$$\mathrm{Im} D_{XY}(\omega') = \mathrm{Re} F_X^A(\omega')\mathrm{Im} F_Y^B(\omega') + \mathrm{Im} F_X^A(\omega')\mathrm{Re} F_Y^B(\omega') .$$

On substitution into (2.99) we obtain

$$C_{XY} = \frac{1}{8\pi^4}\int_0^\infty d\zeta\, P_{XY}(\zeta R) e^{-2\zeta R}\int_0^\infty d\omega'\,\frac{\omega'\mathrm{Im} D_{XY}^{AB}(\omega')}{\omega'^2+\zeta^2} .$$

We may remove $P_{XY}(\zeta R)$ from the integral by writing

$$P_{XY}(\zeta R) e^{-2\zeta R} = P_{XY}^{op} e^{-2\zeta R} ,$$

where

$$P_{EE}^{op} = P_{MM}^{op} = \tfrac{1}{16}R^4\partial_R^4 - \tfrac{1}{4}R^3\partial_R^3 + \tfrac{5}{4}R^2\partial_R^2 - 3R\partial_R + 3 ,$$
$$P_{EM}^{op} = P_{ME}^{op} = \tfrac{-1}{16}R^4\partial_R^4 + \tfrac{1}{4}R^3\partial_R^3 - \tfrac{1}{4}R^2\partial_R^2 , \qquad (2.103)$$

with $\partial_R \equiv d/dR$. We then obtain

$$C_{XY} = \frac{1}{8\pi^4} P_{XY}^{op}\int_0^\infty d\zeta\, e^{-2\zeta R}\int_0^\infty d\omega'\,\frac{\omega'\mathrm{Im} D_{XY}^{AB}(\omega')}{\omega'^2+\zeta^2} . \qquad (2.104)$$

Inverting the order of integration and using the identity

$$\int_0^\infty d\zeta\, e^{-2\zeta R}\,\frac{1}{\omega'^2+\zeta^2} = \frac{f(2\omega' R)}{\omega'} , \qquad (2.105)$$

where

$$f(x) = \cos x\,\mathrm{si}x - \sin x\,\mathrm{Ci}x. \qquad (2.105')$$

Here $\mathrm{si}x = \mathrm{si}x - \frac{1}{2}\pi$, and si, ci are the sine and cosine integrals, we finally obtain[10]

$$C_{XY} = \frac{1}{8\pi^4} P_{XY}^{op}\int_0^\infty d\omega' f(2\omega' R)(\mathrm{Re} F_X^A(\omega')\mathrm{Im} F_Y^B(\omega') + \mathrm{Im} F_X^A(\omega')\mathrm{Re} F_Y^B(\omega')) . \qquad (2.106)$$

In this form, the measurable form factors F_X^A, F_Y^B at real frequencies occur, and so the integral in (2.106) can in principle be calculated from experiment. We discuss the feasibility of this in Sec. III.

We can also derive the next terms in the asymptotic expansion of $V(R)$ from (2.99) or (2.104). We rewrite (2.99) as

$$C_{XY} = \frac{1}{16\pi^3} P_{XY}^{op}\int_0^\infty e^{-2\zeta R} F_X^A(i\zeta) F_Y^B(i\zeta)\, d\zeta . \qquad (2.107)$$

Changing variables from ζ to $\eta = 2\zeta R$ and expanding $F_{X,Y}$ in powers of η/R we get

$$C_{XY} = \frac{1}{16\pi^3} P_{XY}^{op}\left[\frac{1}{2R}\int_0^\infty e^{-\eta}\left(F_X^A(0)F_Y^B(0) - \frac{\eta^2}{8R^2}\times[F_X^A(0)F_Y^{B''}(0) + F_X^{A''}(0)F_X^B(0)]\right)\right] + \cdots , \qquad (2.108)$$

where F'' means the second derivative of F with respect to the frequency; we have used the fact that F is an even function. Thus

$$C_{XY}=\frac{1}{16\pi^3}\,P_{XY}^{op}\left(\frac{1}{2R}\;F_X^A(0)F_Y^B(0)-\frac{1}{8R^3}[F_X^A(0)F_Y^{B''}(0)+F_X^{A''}(0)F_Y^B(0)]\right)+\cdots . \qquad (2.109)$$

A simple calculation gives

$$P_{EE}^{op}\left(\frac{1}{2R}\right)=\frac{23}{4R},\quad P_{EM}^{op}\left(\frac{1}{2R}\right)=-\frac{7}{4R},$$
$$P_{EE}^{op}\left(-\frac{1}{8R^3}\right)=-\frac{129}{16R^3},\quad P_{EM}^{op}\left(-\frac{1}{8R^3}\right)=-\frac{81}{16R^3}. \qquad (2.110)$$

Hence, using (2.80), we get

$$C_{EE}(R)=\frac{23}{4\pi R}\;\alpha_E^A(0)\alpha_E^B(0)-\frac{129}{16\pi R^3}\;[\alpha_E^A(0)\alpha_E^{B''}(0)+\alpha_E^{A''}(0)\alpha_E^B(0)]+O\left(\frac{1}{R^5}\right),$$
$$C_{MM}(R)=\frac{23}{4\pi R}\;\alpha_M^A(0)\alpha_M^B(0)-\frac{129}{16\pi R^3}\;[\alpha_M^A(0)\alpha_M^{B''}(0)+\alpha_M^{A''}(0)\alpha_M^B(0)]+O\left(\frac{1}{R^5}\right),$$
$$C_{EM}(R)=-\frac{7}{4\pi R}\;\alpha_E^A(0)\alpha_M^B(0)+\frac{81}{16\pi R^3}\;[\alpha_E^A(0)\alpha_M^{B''}(0)+\alpha_E^{A''}(0)\alpha_M^B(0)]+O\left(\frac{1}{R^5}\right),$$
$$C_{ME}(R)=-\frac{7}{4\pi R}\;\alpha_M^A(0)\alpha_E^B(0)+\frac{81}{16\pi R^3}\;[\alpha_M^A(0)\alpha_E^{B''}(0)+\alpha_M^{A''}(0)\alpha_E^B(0)]+O\left(\frac{1}{R^5}\right). \qquad (2.111)$$

Further terms can also easily be calculated in this way.

III. DETERMINATION OF POTENTIAL FROM EXPERIMENTS ON ATOM-LIGHT SCATTERING

We have shown in Sec. II that the van der Waals potential is determined completely by the "polarizability form factors" $F_E(\omega)\equiv F_E(\sigma, t=0)$ and $F_M(\omega)\equiv F_M(\sigma, t=0)$. In Sec. III A, we discuss to what extent these quantities can be obtained from experiment. In Sec. III B we analyse the relative contribution to $C_{EE}(R)$ from various regions of ω, the photon energy in the lab system. In Sec. III C, we consider some simplified forms of $C_{XY}(R)$, suggested by examination of Eq. (2.106).

A. Information from Cross-Section Measurements

Let us see what can be determined by measuring the scattering of unpolarized light by the atom. The invariant on-shell transition amplitude is given, according to (2.5) and (2.23), by

$$M=\epsilon^\mu\epsilon'^\nu\tilde{M}_{\mu\nu}, \qquad (3.1)$$

where

$$\tilde{M}_{\mu\nu}=-m(T_{E;\mu\nu}F_E+T_{M;\mu\nu}F_M) \qquad (3.2)$$

and T_E and T_M are defined by (2.21) and (2.22). The scattering amplitude is, in the c.m. system, $f=-M/8\pi W$, with $W=\sigma^{1/2}$, the total energy in this system, so that the c.m. differential cross section averaged over the initial and summed on the final photon polarization is

$$\frac{d\sigma}{d\Omega}=\left(\frac{1}{8\pi W}\right)^2\times\frac{1}{2}\sum_{\text{pol}}|M|^2 . \qquad (3.3)$$

Since, for a gauge-invariant matrix element,

$$\sum_{\text{pol}}|M|^2=M_{\mu\nu}M^*_{\mu'\nu'}(-g^{\mu\mu'})(-g^{\nu\nu'}), \qquad (3.4)$$

we have, using (3.1)–(3.4),

$$\frac{d\sigma}{d\Omega}=\left(\frac{m}{3\pi W}\right)^2\tfrac{1}{2}[|F_E|^2\,T_E{:}T_E+|F_M|^2\,T_M{:}T_M+2\mathrm{Re}(F_EF_M^*)T_E{:}T_M], \qquad (3.5)$$

where

$$T_X{:}T_Y\equiv T_{X;\mu\nu}T_Y^{\mu\nu} . \qquad (3.6)$$

Using (2.21) and (2.22) we have

$$T_E{:}T_E=\tfrac{1}{4}T_1{:}T_1,\quad T_M{:}T_M=\tfrac{1}{4}T_1{:}T_1-2T_1{:}T_2+4T_2{:}T_2,$$
$$T_E{:}T_M=\tfrac{1}{4}T_1{:}T_1-T_1{:}T_2 . \qquad (3.7)$$

Computation, using (2.13) and (2.14), yields, with $\hat{P}=P/m$,

$$T_1{:}T_1=2(k\cdot\hat{P}k'\cdot\hat{P})^2+(k\cdot k'\hat{P}^2)^2-2k\cdot\hat{P}k'\cdot\hat{P}k\cdot k'\hat{P}^2,$$
$$T_2{:}T_2=2(k\cdot k')^2,\quad T_1{:}T_2=(k\cdot k')^2\hat{P}^2 . \qquad (3.8)$$

The amplitude for coherent forward scattering ($\epsilon'=\epsilon$, $k'=k$) is given by

$$f(0)\equiv-\frac{1}{8\pi W}\;\epsilon^\mu\epsilon^\nu\tilde{M}_{\mu\nu}|k'=k$$
$$=-\frac{1}{8\pi W}\;\frac{-2(k\cdot p)^2}{m}\;[F_E(\omega)+F_M(\omega)] \qquad (3.8')$$

or, since $k\cdot p=k_{\text{c.m.}}W=\omega m$ where $k_{\text{c.m.}}$ is the c.m. momentum of the photon,

$$f(0)=(k_{\text{c.m.}}\omega/4\pi)[F_E(\omega)+F_M(\omega)] . \qquad (3.9)$$

The total cross section is given by the optical theorem as

$$\sigma_T(\omega)=(4\pi/k_{\text{c.m.}})\mathrm{Im}f(0)=\omega\mathrm{Im}[F_E(\omega)+F_M(\omega)] . \qquad (3.10)$$

From (3.9) and (3.10) it is clear that measurement at or very near the forward direction can at best determine the combination $F_E(\omega)+F_M(\omega)$. However, if, as is normally the case, $|F_M|\ll|F_E|$, one may neglect F_M and use $\sigma_T(\omega)$ to determine $\mathrm{Im}F_E(\omega)$ [which is all that is needed in the computation of $V_{EE}(R)$ via Eq. (2.76)]; one may then use $d\sigma/d\Omega$ to find $|F_E|^2$ and hence $\mathrm{Re}F_E(\omega)$, at least up to a sign. The sign may be fixed by comparison with that predicted by the spectral representation (2.97).

It is interesting to ask what further information can be obtained by measuring $d\sigma/d\Omega$ for all values of θ. From (3.5) it would seem that, in principle, one could determine the three quantities $|F_E(\sigma,t)|^2$, $|F_M(\sigma,t)|^2$, and $\mathrm{Re}F_E(\sigma,t)F_M^*(\sigma,t)$, since they are the coefficients of functions $T_E\!:\!T_E$, $T_M\!:\!T_M$, and $T_E\!:\!T_M$ which have different dependences on θ. However, the values of ω which are important in determining $V_{2\gamma}(R)$ are of order 10 keV or less (see Sec. III B) and thus are small compared to $m \gtrsim 10^3$ meV. It is easy to verify that for

$$\omega \ll m \tag{3.11}$$

we may replace $P=(p+p')/m$ by (2, 0, 0, 0) in (3.7), the spatial components of p and p' being of order ω, by momentum conservation. Thus one finds

$$\begin{aligned} T_E\!:\!T_E &= 4\omega^4[1+\cos^2\theta+O(\omega/m)]\,,\\ T_M\!:\!T_M &= 4\omega^4[1+\cos^2\theta+O(\omega/m)],\\ T_E\!:\!T_M &= 4\omega^4[2\cos\theta+O(\omega/m)]\,, \end{aligned} \tag{3.12}$$

where θ is the scattering angle in the c.m. system ($\cos\theta = k\cdot k'$). Corresponding to (3.12) we have, on replacing also m/W by unity in (3.5),

$$\frac{d\sigma}{d\Omega}\approx\frac{2\omega^4}{(8\pi)^2}\,[(|F_E|^2+|F_M|^2)(1+\cos^2\theta) + 2\,\mathrm{Re}(F_EF_M^*)(2\cos\theta)]\,. \tag{3.13}$$

In arriving at (3.13) we have only neglected (purely kinematic) terms which are of order ω/m relative to unity.

It follows from (3.13) that for the interesting values of ω [satisfying (3.11)] one can at best hope to determine only two quantities, $|F_E|^2+|F_M|^2$ and $2\,\mathrm{Re}(F_EF_M^*)$, rather than three, by measurement of the differential cross section. We note also that, as discussed in Sec. II C 3, the quantities $F_E(\sigma,t)$ and $F_M(\sigma,t)$ are expected to be slowly varying functions of $t=2k^2_{\mathrm{c.m.}}(1-\cos\theta)$ for $|t|\gtrsim a_0^{-2}$. Hence, for

$$\omega \ll \alpha m\,, \tag{3.14}$$

we may also neglect the t dependence of $F_X(\sigma,t)$ and write

$$\frac{d\sigma}{d\Omega}\approx\frac{2\omega^4}{(8\pi)^2}\{[|F_E(\omega)|^2+|F_M(\omega)|^2](1+\cos^2\theta) + 2\,\mathrm{Re}\,(F_E(\omega)F_M^*(\omega))(2\cos\theta)\}\,. \tag{3.15}$$

The fact that $|F_E|^2$ and $|F_M|^2$ occur with the same angular factor in (3.13) and (3.15) is solely a result of the cancellation of the second and third terms in $T_M:T_M$ [Eq. (3.7)] in the limit $\hat{P}\to(2,0,0,0)$. As a consequence, even if the t dependence of $F_X(\sigma,t)$ is neglected, (3.5) and (3.10) could be used to determine both $F_E(\omega)$ and $F_M(\omega)$ in the domain $\omega\ll m$ only if $d\sigma/d\Omega$ were measured with fantastic accuracy. Of course, if experiments in which photon polarizations are measured were feasible, the separate determination of $F_E(\omega)$ and $F_M(\omega)$ would be possible, provided that $F_M(\omega)$ and $F_E(\omega)$ are not too different in magnitude.

B. Analysis of Frequency Range

From Eq. (2.106), we can determine over what region of frequency we need to know F_E, F_M in order to get the potential in the region $R >$ several atomic radii. For smaller values of R, other things than the two-photon exchange forces are important. Let us use the symbol a for $(\alpha m_e)^{-1}$, the Bohr radius.

We first show that frequencies $\omega \gtrsim a^{-1}$ are not important. Consider the contribution of frequencies $\gtrsim a^{-1}$ to the integral (2.106). This energy is generally well beyond the first ionization energy ω_I of the atom, and, for light atoms ($Z\lesssim 10$) is larger than the ionization energy for any of the electrons. In this case, it seems justified to use for ReF and ImF their high-energy expressions. Let us concentrate on $F_E(\omega)$, and use $\mathrm{Im}F_E(\omega)\sim(1/\omega)\sigma_T(\omega)$. It is known that for $\omega_I\ll\omega\ll m_e$, σ_T behaves as

$$\omega_I a^3(\omega_I/\omega)^{7/2}Z^5,$$

and hence,

$$\mathrm{Im}F_E(\omega)\sim a^3(\omega_I/\omega)^{9/2}Z^5.$$

On the other hand

$$\mathrm{Re}F_E(\omega)\sim -a^3(\omega_I/\omega)^2 Z$$

in this region.[11] As a result we have

$$I_{EE}(R)\equiv\int_{1/a}^{\infty}d\omega' f(2\omega' R)\;\mathrm{Re}F_E^A(\omega')\,\mathrm{Im}F_E^B(\omega') \sim -\alpha^6Z^6\int_{1/a}^{\infty}f(2\omega' R)\left(\frac{\omega_I}{\omega'}\right)^{13/2}d\omega'\,. \tag{3.16}$$

Since R is always $> a$, $2\omega' R>2$ in this region, and we can approximate $f(2\omega' R)\sim 1/2\omega' R$. Hence

$$I_{EE}(R)\sim-\frac{a^6Z^6}{2R}\int_{(\omega_I a)^{-1}}^{\infty}\frac{dx}{x^{15/2}}=-\frac{a^6}{2R}\,\frac{2Z^6}{13}\,(\omega_I a)^{13/2}\,. \tag{3.16$'$}$$

Since ωa is $\sim 10^{-2}$, the contribution of the region under consideration is generally very small compared to the contribution of smaller values of ω, which is of order a^6R^{-1}. (Similar results are probably true for the magnetic contributions, although we have not obtained any specific limits for these.)

We can therefore reasonably cut off the ω integrals at $\omega\sim a^{-1}$, or about 10 keV. We next consider the contribution of ω below the ionization limit of *either* atom A or B. In this region, $\mathrm{Im}F^A$ and $\mathrm{Im}F^B$ are appreciable only in the neighborhood of resonances, being smaller by a factor of $(\Gamma_R/\omega_R)^2 \sim 10^{-12}$ between resonances. We can in fact approximate $\mathrm{Im}F^A$ in this region by a sum of sharp resonances

$$\mathrm{Im}F^A \approx \sum_n \delta(\omega-\omega_n)\pi f_n, \tag{3.17}$$

where f_n is related to the oscillator strength for the excitation of the resonance. This approximation is certainly valid if A and B are different atoms; when A and B are identical, more care is needed because $\mathrm{Re}F^A$ will also be rapidly varying near $\omega=\omega_n$ in that case.

With approximation (3.17) for $\mathrm{Im}F^A$, the integral (2.106) over the region in question reduces to a sum of contributions from the resonances of each atom multiplied by the presumably smooth $\mathrm{Re}F$ from the other atom. It is regrettably the case that all resonances, whatever their angular momentum, contribute to the F, although the contribution of resonances with $J>1$ is smaller by a factor $(\omega a)^{J-1}$, and so it may be a good approximation to include only $J=1$ resonances.

When the energy ω is between the ionization limit of the two atoms, i.e., $\omega_I^A<\omega<\omega_I^B$, then $\mathrm{Im}F^A$ will be nonzero generally, and will be a relatively smooth function, perhaps with resonancelike peaks (auto-ionization states) superimposed on it. Similarly for $\mathrm{Re}F^A$. On the other hand $\mathrm{Im}F^B$ will continue to be approximated by a sum of sharp resonances and $\mathrm{Re}F^B$ by a smooth background with resonances superimposed. However, the resonance terms in $\mathrm{Re}F^B$ are unimportant since they change sign going through the resonance, and hence contribute essentially zero to the integrals in this approximation.

Finally, when ω_I^A, ω_I^B both $<\omega$, $\mathrm{Im}F^A$, $\mathrm{Im}F^B$, $\mathrm{Re}F^A$, and $\mathrm{Re}F^B$ all become comparable quantities, consisting of a smooth background with resonances superimposed.

An examination of the size of the contribution of these regions to the potential indicates that each region contributes comparable amounts, essentially independent of the value of R at which the potential is desired.

A cursory survey of available data on the elastic and inelastic scattering of light by atoms and molecules has convinced the authors that the necessary data to perform the integrals over frequency in (2.106) and (2.76) are simply unavailable at present. Whether such data could be obtained through presently available techniques is unclear to us, but we would hope that this question could be taken up by experimental physicists.

C. Simplified Forms of $C_{XY}(R)$

In order to simplify the expressions for C_{XY} as much as possible to use what experimental information does become available, we shall make some approximations on the function $f(x)$, defined by (2.105′). Note that

$$f(x)\approx \tfrac{1}{2}\pi \quad \text{for } x\ll 1, \qquad f(x)\approx 1/x \quad \text{for } x\gg 1. \tag{3.18}$$

We can then distinguish two regions of interest, in terms of whether R is large or small compared to ω_I^{-1}, or around 200 Å. (Here ω_I is the smaller of the ionization energies.)

(*a*) $\omega_I R>1$. To determine C_{XY}, we need the integral I_{XY}, defined by

$$I_{XY}\equiv \int_0^\infty d\omega\, f(2\omega R)\,[\mathrm{Im}D_{XY}(\omega)] \tag{3.19}$$

or

$$I_{XY}=\int_0^\infty d\omega \left(f(2\omega R)-\frac{1}{2\omega R}\right)\mathrm{Im}D_{XY}(\omega) + \tfrac{1}{4}\pi\,\frac{\mathrm{Re}D_{XY}(0)}{R}\ . \tag{3.19′}$$

In the first integral in (3.19′), we can approximate the bracket by zero when $\omega>R^{-1}$, and hence obtain

$$I_{XY}\approx \int_0^{1/R}\left[f(2\omega R)-\frac{1}{2\omega R}\right]\mathrm{Im}D_{XY}(\omega)\,d\omega + \frac{\pi}{4}\,\frac{\mathrm{Re}D_{XY}(0)}{R}\ . \tag{3.20}$$

In this expression, since $\omega_I>R^{-1}$, the first integral is over the region in which the $\mathrm{Im}D_{XY}(\omega)$ gets contributions only from the resonances. This formula gives explicitly the correction to the asymptotic formulas for the potential, i.e., to the last term. The correction involves an integral over the low-frequency, i.e., resonance region only.

(*b*) $\omega_I R<1$. Then we write

$$I_{XY}=\int_0^\infty d\omega\,[f(2\omega R)-\tfrac{1}{2}\pi]\,\mathrm{Im}D_{XY}(\omega) + \tfrac{1}{2}\pi\int_0^\infty \mathrm{Im}D_{XY}(\omega)\,d\omega\ . \tag{3.19″}$$

The term

$$(\pi/2)\int_0^\infty \mathrm{Im}D_{XY}(\omega)\,d\omega$$

is just the London constant $C_{XY}(0)$ determining the short-range behavior of the corresponding potential $C_{XY}(R)$. In the remaining integral, we approximate the bracket by zero when $\omega R<\frac{1}{4}$ and obtain

$$I_{XY}\approx C_{XY}(0)+\int_{1/4R}^\infty [f(2\omega R)-\tfrac{1}{2}\pi]\,\mathrm{Im}D_{XY}(\omega)\,d\omega \tag{3.21}$$

The integral now includes the continuum region for one or both atoms, but no very low-frequency contributions.

Finally, we note that if we approximate $f(x)$ by its asymptotic forms everywhere, i.e., if we make the replacement

$$f(x) \to \tfrac{1}{2}\pi \quad \text{for } x<1, \quad f(x)\to 1/x \quad \text{for } x>1,$$

we can obtain the unified expressions for I_{XY}

$$I_{XY} \sim \tfrac{1}{4}\pi \frac{\mathrm{Re} D_{XY}(0)}{R} + \int_0^{1/R} \left(\tfrac{1}{2}\pi - \frac{1}{2\omega R}\right) \mathrm{Im} D_{XY}(\omega)\, d\omega \tag{3.22}$$

or

$$I_{XY} \sim C_{XY}(0) + \int_{1/R}^{\infty} \left(\frac{1}{2\omega R} - \tfrac{1}{2}\pi\right) \mathrm{Im} D_{XY}(\omega)\, d\omega. \tag{3.23}$$

These two forms are expected to be good for relatively large and for relatively small values of R, respectively. Applications of these formulas to the calculation of the van der Waals potential for specific atoms will be given elsewhere.[12]

IV. INTERPOLATION FORMULAS FOR $V_{2\gamma}(R)$

It has been shown elsewhere[6] that there exists a simple interpolation formula $\tilde{C}_{EE}(R)$ to the function $C_{EE}(R)$ which agrees extremely well with the results of numerical calculations based on the definition (1.2), for the available cases $(A, B) = (\mathrm{H}, \mathrm{H})$, (H, He), and (He, He). This formula is

$$\tilde{C}_{EE}(R) = C_{EE} \times \frac{2}{\pi} \tan^{-1} \frac{d_{EE}}{R}, \tag{4.1}$$

where $C_{EE} = C_{EE}(0)$ and d_{EE} is a length defined by

$$d_{EE} = \tfrac{23}{8}\, \alpha_E^A \alpha_E^B / C_{EE}, \tag{4.2}$$

so that $\tilde{C}_{EE}(R)$ coincides with $C_{EE}(R)$ for both very small and very large R.

In this section we consider the extension of such formulas, first to $C_{MM}(R)$ and then to the more interesting case of the "interference" terms $C_{EM}(R)$ and $C_{ME}(R)$.

A. Interpolation for $C_{MM}(R)$

Since $P_{MM}(\eta) = P_{EE}(\eta)$, the suggested interpolation formula for $C_{MM}(R)$ is completely analogous to that for $C_{EE}(R)$, viz.,

$$\tilde{C}_{MM}(R) = C_{MM} \frac{2}{\pi} \tan^{-1}\left(\frac{d_{MM}}{R}\right), \tag{4.3}$$

where $C_{MM} = C_{MM}(0)$ is the magnetic analog of the van der Waals constant C_{EE}, i.e.,

$$C_{MM} = \frac{3}{8\pi^4} \int_0^\infty \int_0^\infty dk_A dk_B \frac{\rho_M^A(k_A)\rho_M^B(k_B)}{k_A + k_B} \tag{4.4}$$

and

$$d_{MM} = \tfrac{23}{8}\, \alpha_M^A \alpha_M^B / C_{MM}. \tag{4.5}$$

The motivation for (4.3) is the same as that given[6] for (4.1): Integration by parts of (1.3), followed by changing to $\eta = \zeta R$ as integration variable, leads to

$$C_{MM}(R) = \frac{-1}{8\pi^4} \int_0^\infty \int_0 dk_A dk_B \frac{\rho_M^A(k_A)\rho_M^B(k_B)}{k_A + k_B} \times \int_0 d\eta\, N_1 \frac{d}{d\eta}\left(P_{MM}(\eta) e^{-2\eta}\right), \tag{4.6}$$

where

$$N_1 = \frac{2}{\pi} \frac{k_B \tan^{-1}(\eta/k_A R) - k_A \tan^{-1}(\eta/k_B R)}{k_B - k_A}. \tag{4.7}$$

Since $N_1 \to 1$ for $R \to 0$, (4.6) has the form

$$C_{MM}(R) = C_{MM} \bar{N}_1(R), \tag{4.8}$$

where $\bar{N}_1(R)$ is a weighted average of $N_1 = N_1(k_A, k_B, \eta; R)$ over the three-dimensional space of the integration variables k_A, k_B, and η. Next one notes that (i) N_1 is a slowly varying function of these variables; (ii) the function

$$\tilde{N}_1 = (2/\pi) \tan^{-1}(\xi_1/R),$$

with $\xi_1 = \eta(k_A + k_B)/k_A k_B$, is, for fixed R, a very good approximation to N_1 for most values of k_A, k_B, and η; and (iii) N_1 has the same asymptotic form as N_1 for $R \to \infty$: $\tilde{N}_1 \sim N_1 \sim (2/\pi)(\xi_1/R)$. These facts suggest that if a mean value $\bar{\xi}_1 = \bar{\xi}_1(R)$ is defined by writing

$$\bar{N}_1(R) = (2/\pi) \tan^{-1}[\bar{\xi}_1(R)/R], \tag{4.9}$$

then $\bar{\xi}_1(R)$ will be a slowly varying function of R. On approximating $\bar{\xi}_1(R)$ by $\bar{\xi}_1(\infty)$, and noting that (2.81), (4.8), and (4.9) imply that $\bar{\xi}_1(\infty) = d_{MM}$, we arrive at Eq. (4.3).

B. Interpolation for $C_{ME}(R)$ and $C_{EM}(R)$

An interpolation formula for $C_{ME}(R)$ or $C_{EM}(R)$ is necessarily more complicated than that for $C_{EE}(R)$ or $C_{MM}(R)$. The reason is that although, like $C_{EE}(R)$, $C_{ME}(R)$ varies as R^{-1} for large R, its behavior for small R is quite different. Since

$$P_{ME}(\eta) = -\eta^2(1+\eta)^2 \sim -\eta^2$$

for small η,

$$\int_0^\infty d\zeta \frac{e^{-\zeta R} P_{ME}(\zeta R)}{(\zeta^2 + k_A^2)(\zeta^2 + k_B^2)} \; -R^2 \int_0^\infty d\zeta \frac{\zeta^2}{(\zeta^2 + k_A^2)(\zeta_B^2 + k_B)} = \tfrac{1}{2}\pi \frac{-R^2}{(k_A + k_B)}. \tag{4.10}$$

Hence, from (1.3) and (4.10), for $R \to 0$,

$$C_{ME}(R) \sim -R^2 C_{ME}, \quad C_{EM}(R) \sim -R^2 C_{EM}, \tag{4.11}$$

where

$$C_{ME}=\frac{1}{8\pi^4}\int_0^\infty\int_0^\infty dk_A dk_B\,\frac{[k_A\rho_M^A(k_A)]\,[k_B\rho_E^B(k_B)]}{k_A+k_B} \tag{4.12}$$

and C_{EM} is similarly defined.

Thus we shall require our interpolating function $\tilde{C}_{ME}(R)$ and $\tilde{C}_{EM}(R)$ to have the behavior (4.11) for $R\to 0$, and a behavior consistent with (2.82) for large R.

A possibility analogous to (4.3) is to take

$$\tilde{C}_{ME}(R)=-R^2\,C_{ME}\,\frac{2}{\pi}\left(\tan^{-1}\frac{d_{ME}}{R}-\frac{(d_{ME}/R)}{1+(d_{ME}/R^2)}\right), \tag{4.13}$$

which satisfies (4.11), and to pick d_{ME} so that $C_{ME}(R)$ has the correct asymptotic form for large R. Thus, since $\tan^{-1}z-z(1+z^2)\sim\frac{2}{3}z^3$ for $z\to 0$, we take

$$d_{ME}=(\tfrac{21}{16}\,\alpha_M^A\alpha_E^B/C_{ME})^{1/3}\,. \tag{4.14}$$

To motivate (4.13), we note first that integration by parts of (1.3) with respect to ζ, for $X=M$, $Y=E$, using $\zeta^2(\zeta^2+k_A^2)^{-1}(\zeta^2+k^2)^{-1}$ as one of the factors, yields, with $\eta=\zeta R$,

$$C_{ME}(R)=\frac{R^2}{8\pi^4}\int_0^\infty\int_0^\infty dk_A dk_B\frac{k_A\rho_M^A(k_A)k_B\rho_E^B(k_B)}{k_A+k_B}\times\int_0^\infty N_2\frac{d}{d\eta}\left[e^{-2\eta}(1+\eta)^2\right]d\eta\,, \tag{4.15}$$

where

$$N_2=\frac{2}{\pi}\left(\frac{k_B\tan^{-1}(\eta/k_BR)-k_A\tan^{-1}(\eta/k_AR)}{k_B-k_A}\right). \tag{4.16}$$

Since $N_2\to 1$ for $R\to 0$, (4.16) has the form

$$C_{ME}(R)=-R^2\,C_{ME}\,\bar{N}_2(R)\,, \tag{4.17}$$

where $\bar{N}_2(R)$ is a weighted average of N_2. We note further that (i) N_2 is a slowly varying function of the integration variables; (ii) the function

$$\tilde{N}_2=\frac{2}{\pi}\left(\tan^{-1}\frac{\xi_2}{R}-\frac{(\xi_2/R)}{1+(\xi_2/R)^2}\right)\,, \tag{4.18}$$

with

$$\xi_2=\eta\,[2k_A^2k_B^2/(k_A+k_B)]^{-1/3}\,,$$

is, for fixed R, a good approximation to N_2 in a large part of the integration volume; and (iii) $\tilde{N}_2$ has the same asymptotic form as N_2 for $R\to\infty$,

$$\tilde{N}_2\sim\tilde{N}_2\sim(4/3\pi)\,(\xi_2/R)^3.$$

In analogy to the considerations of Sec. IV A, these facts suggest that if we define a function $\bar{\xi}_2(R)$ by writing

$$\bar{N}_2(R)=\frac{2}{\pi}\left(\tan^{-1}\frac{\bar{\xi}_2(R)}{R}-\frac{\bar{\xi}_2(R)/R}{1+[\bar{\xi}_2(R)/R]^2}\right)\,, \tag{4.19}$$

we may expect $\bar{\xi}_2(R)$ to be a slowly varying function of R. For $R\to\infty$, (4.19) has the form

$$\bar{N}_2(R)\sim(4/3\pi)\,[\bar{\xi}_2(\infty)/R]^3\,,$$

so that, by comparison with (2.82) and (4.17),

$$\bar{\xi}_2(\infty)=d_{ME}\,,$$

defined by (4.14). If, in (4.19), we approximate $\bar{\xi}_2(R)$ by its value at $R=\infty$, we arrive at (4.13).

Of course, numerous other, almost equally simple interpolation formulas might be considered, e.g., $\tilde{C}_{ME}\propto R^2(\tan^{-1}d/R)^3$, but (4.13) seems closest in spirit to the very successful $\tilde{C}_{EE}(R)$, Eq. (4.1). Unfortunately, unlike the case of $C_{EE}(R)$, numerical calculations of $C_{EM}(R)$ or $C_{ME}(R)$, based on (1.3), are not available with which to make a comparison. This must await further work, perhaps by an interested reader.

V. SUMMARY AND DISCUSSION

We have seen, in Sec. II, that for separations R large compared to atomic dimensions the potential $V_{2\gamma}(R)$ arising from two-photon exchange between spinless atoms or molecules is given by Eqs. (2.74)–(2.76). These equations express $V_{2\gamma}(R)$ in terms of the absorptive parts $\rho_E(\omega)$ and $\rho_M(\omega)$ of the invariant amplitudes

$$F_E(\omega)=F_E(\sigma,t=0)\text{ and }F_M(\omega)=F_M(\sigma,t=0);$$

here $F_E(\sigma,t)$ and $F_M(\sigma,t)$ are defined by the general expression (2.31) for the photon-atom elastic scattering amplitude $\tilde{M}_{\mu\nu}(\sigma,t)$. Using an approach based on the method of effective interactions, it was shown that the threshold value $F_X(\sigma=m^2,t=0)$ could be identified with $4\pi\alpha_X$ where α_X is the static polarizability ($X=E,M$) (Sec. II C); the same result was obtained in Appendix A in an approach based directly on the S matrix. Using this identification, we also derived the asymptotic form (2.83) of $V_{2\gamma}(R)$, given in an earlier paper,[3] starting from the general form (2.74); an alternative and more direct derivation of (2.83), based on recognition of the fact that to determine $V_{2\gamma}(R)$ for large R only requires knowledge of the value of the second derivative of the spectral function at $t=0$, was given in Appendix B.

In Sec. II E it was shown how $V_{2\gamma}(R)$ could be written as a single integral involving products of the real and imaginary parts of the dynamic polarizabilities $F_X(\omega)$, evaluated for *real* values of ω_n [Eq. (2.106)]. This is to be contrasted with the familiar expression (2.99) in which the $F_X(\omega)$ must be evaluated at imaginary values of ω. In Sec. III A it was shown that if, as is normally the case, $|F_M|\ll|F_E|$, measurements of the differential and total photo-atom cross section would suffice to determine $F_E(\omega)$ and hence $V_{EE}(R)$; if F_M is comparable to F_E, measurements involving either initially polarized photons or detection of the final photon polarization appear to be necessary. In Sec. III B an analysis of the frequency regions important in the evaluation of $V_{EE}(R)$ was given and the inadequacy of the present experimental information in this regard was emphasized. In Sec. III C some simplified forms of $V_{XY}(R)$ based on approximations to (2.106) were considered. Finally, in Sec. IV, the interpolation formula for $V_{EE}(R)$ considered in Ref. 6 was generalized to the other $V_{XY}(R)$.

In connection with these results, there are a number of points which seem to merit further discussion.

A. Review of Approximations

Previous studies of the retarded van der Waals interaction invariably introduce the so-called dipole approximation at an early stage of the calculations. It is interesting to analyze to what extent and at what stage a corresponding approximation is introduced in our dispersion theoretic approach. We recall first the approximations made in arriving at our "semifinal" result (2.61), which was derived from the defining equation (2.4) for $V_{2\gamma}(R)$. The first approximation made was to replace $\rho_{2\gamma}(s_0, t)$ [Eq. (2.33)] by $\rho_{2\gamma}(t)$, i.e., to keep only the terms arising from real two-photon intermediate states in the crossed channel; it is this step which permits the computation of $V_{2\gamma}(R)$ to be reduced, in principle, to a knowledge of the photo-atom scattering amplitude (albeit, in unphysical regions of the σ, t plane). The neglect of $\rho'_{2\gamma}(t)$ corresponds to dropping a potential $V'_{2\gamma}(R)$ which falls off exponentially with R [Eq. (2.34)]. To estimate the relative importance of such terms we note that $V'_{2\gamma}(R)$ will certainly be smaller than $V_{1\gamma}(R)$, the potential arising from the exchange of a single photon, which also decreases exponentially with R. To get a numerical estimate, consider the interaction of two hydrogen atoms. Then[13]

$$V_{1\gamma}(R) \approx \frac{-e^2}{6a_0}\left(\frac{R}{a_0}\right)^2 e^{-2R/a_0}, \tag{5.1}$$

with a_0 the Bohr radius, while

$$V_{EE} \approx -6.5\,\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6. \tag{5.2}$$

$V_{1\gamma}$ and V_{EE} become equal for $(40)^{-1}\xi^8 e^{-2\xi}=1$ or $\xi \equiv R/a_0 \sim 5$. Thus, for say $R \gtrsim 10a_0$, $V_{1\gamma}$ and $V'_{2\gamma}$ will both be negligible compared to $V_{2\gamma}(R)$.

To arrive at the final form (2.74)–(2.76) for $V_{2\gamma}(R)$ we also neglected (a) the t dependence of the $\rho_X(\sigma, t)$—this leads to the intermediate Eq. (2.64)—and (b) terms of order $m_e/m \sim 10^{-3}$ in Θ_{XY}. Approximation (b) is essentially one of convenience and only serves to simplify the form of the function U^0_{XY} appearing in (2.64), permitting its replacement by $U_{XY}(k_A, k_B; R)$ [Eq. (2.68)]; both U^0_{XY} and U_{XY} are universal functions, independent of the details of atomic structure. It is approximation (a), i.e., the replacement

$$\rho_X(\sigma, t) \to \rho_X(\sigma, 0) \equiv \rho_X(k), \tag{5.3}$$

which is decisive for arriving at a formula which has essentially the same structure [(2.64)] as that obtained by Casimir and Polder.[1] The point which we wish to emphasize here is that (5.3) is a *weaker* approximation than the dipole approximation referred to above.

Let us consider this topic in more detail. We recall first that the contribution $M^{(n,l)}$ to the photoscattering amplitude M, arising from an intermediate (bound) state of energy E_n and angular momentum l, with the initial photon being absorbed first, has the form

$$M^{n,l} \sim N^{n,l}/(\omega_n - \omega),$$

where $\omega_n \equiv E_n - E_0$ and [for a one-electron atom with ground state $|0\rangle$]

$$N^{n,l}(\omega, t) = \sum_m \langle 0|\,\epsilon'\cdot\vec{p}\; e^{-i\vec{k}'\cdot\vec{r}}\,|n, l, m\rangle \times \langle n, l, m|\,\vec{\epsilon}\cdot\vec{p}\; e^{i\vec{k}\cdot\vec{r}}\,|0\rangle .$$

In the dipole approximation one makes the replacement

$$e^{i\vec{k}'\cdot\vec{r}} \to 1,\quad e^{i\vec{k}\cdot\vec{r}} \to 1. \tag{5.4}$$

This is equivalent to setting $\vec{k}'=\vec{k}=0$ and hence, to the replacement of $N^{n,l}(\omega, t)$ by $N^{n,l}(0, 0)$. In the dispersion theory approach one instead replaces $N^{n,l}(\omega, t)$ by $N^{n,l}(\omega_n, 0)$ to obtain the "pure" pole contribution to M corresponding to a term $\delta(\omega' - \omega_n) N^{n,l}(\omega_n, 0)$ in $\rho_E(\sigma', 0)$. However, the energy variation of the difference $[N^{n,l}(\omega, 0) - N^{n,l}(\omega_n, 0)]/(\omega_n - \omega)$ is not neglected; it is taken into account by the integration over the continuum in the spectral representation (2.97) for $F_E(\sigma, 0)$. The approximation (5.3) and (5.4) *are* related by virtue of the fact that the conditions for their validity are related; (5.3) is valid for $|t| \ll a_0^{-2}$, while (5.4) is valid for $a_0\omega \ll 1$. For a fixed physical scattering angle, the second condition implies the first, but the converse is not true.

B. Symmetry between F_E and F_M

We saw in Sec. III B that the separate determination of F_E and F_M from cross-section measurements is hindered by the fact that $|F_E|^2$ and $|F_M|^2$ enter the differential cross section in precisely the same way, for $\omega \ll m$. A simple way to see the source of this "degeneracy" is to make use of the effective Hamiltonian

$$H' = -\tfrac{1}{2}\,\alpha_E \vec{E}^2 - \tfrac{1}{2}\,\alpha_M \vec{H}^2$$

considered in Sec. IID, where $\vec{E}$ and $\vec{H}$ are now regarded as *quantized fields*; $\vec{E}=-\dot{\vec{A}}_T$, $\vec{H}=\vec{\nabla}\times\vec{A}_T$ with $\vec{A}_T$ the quantized transverse radiation field.

It follows that, in this approximation, the matrix element for phonon-atom scattering is proportional to

$$\alpha_E\, \vec{\epsilon}'\cdot\vec{\epsilon}\,\omega^2+\alpha_M\,(\vec{\epsilon}\times\vec{k})\cdot(\vec{\epsilon}'\times\vec{k}'). \qquad (5.5)$$

The equality of the coefficient of $|\alpha_E|^2$ and $|\alpha_M|^2$ in the differential cross section now follows immediately from (5.5) and the identity

$$\sum_{i,j=1}^{2}|\vec{\epsilon}_j'\cdot\vec{\epsilon}_i|^2=\sum_{i,j=1}^{2}|(\vec{\epsilon}_j'\times\hat{k}')\cdot(\vec{\epsilon}_i\times\hat{k})|^2 , \qquad (5.6)$$

where $(\vec{\epsilon}_1, \vec{\epsilon}_2, \hat{k})$ and $(\vec{\epsilon}_1', \vec{\epsilon}_2', \hat{k}')$ form right-handed systems. Since $\vec{\epsilon}_1\times\hat{k}=-\vec{\epsilon}_2$, $\vec{\epsilon}_2\times\hat{k}=\vec{\epsilon}_1$, etc., the right-hand side of (5.6) is just a reordered form of the left-hand side.

C. Sum Rule and Sign of α_E

On adding the spectral representations for $F_E(\omega)$ and $F_M(\omega)$ [Eq. (2.97)] and using the optical theorem (3.10) we see that, since $\rho_X(\omega)=\mathrm{Im}F_X(\omega)$, the coherent forward transition amplitude $F_E(\omega)+F_M(\omega)$ satisfies

$$F_E(\omega)+F_M(\omega)=\frac{1}{\pi}\int_0^\infty d\omega'\,\frac{\sigma_T(\omega')}{\omega'}\left(\frac{1}{\omega'-\omega}+\frac{1}{\omega'+\omega}\right). \qquad (5.6')$$

If we put $\omega=0$ and use the relations $F_X(0)=4\pi\alpha_X$, we arrive at the sum rule[14]

$$\alpha_E+\alpha_M=\frac{1}{2\pi^2}\int_0^\infty d\omega'\,\frac{\sigma_T(\omega')}{\omega'^2} , \qquad (5.7)$$

which shows that

$$\alpha_E+\alpha_M\geq 0 . \qquad (5.8)$$

The existence of paramagnetism and diamagnetism shows that α_M may be either positive or negative. However it appears that α_E is positive for all known substances. It would be interesting to know to what extent an inequality of the form $\alpha_E\geq 0$ is generally valid, i.e., derivable on the basis of general principles.

D. Extension to Include Spin

It is of some interest to ask to what extent the results of this paper can be generalized to neutral particles with nonzero spin. With regard to the asymptotic form of the two-photon potential, an analysis of this question has already been carried out,[15] with the following result. Let $\vec{S}_A$ and $\vec{S}_B$ denote the spin operators associated with neutral particles A and B. We define the *spin-independent part* $V_{2\gamma}^{\text{s.i.}}$ of $V_{2\gamma}$ as the part of $V_{2\gamma}$ which does not involve $\vec{S}_A$ or $\vec{S}_B$; more precisely,

$$V_{2\gamma}^{\text{s.i.}}(R)\equiv\frac{1}{(2S_A+1)}\,\frac{1}{(2S_B+1)}\sum\langle m_A, m_B|V_{2\gamma}|m_A, m_B\rangle , \qquad (5.9)$$

where the sum is over a complete set of product spin states $|m_A, m_B\rangle$, with eigenvalues m_A and m_B for the projection S_A^z and S_B^z on some arbitrary z axis. Furthermore, for a particle of spin S let us define the average polarizability by

$$\overline{\alpha}_E=\frac{1}{2S+1}\sum_{m=-S}^{S}\alpha_E^m , \qquad (5.10)$$

where α_E^m is the polarizability measured when the particle is a state with eigenvalue m for $\vec{S}\cdot\hat{z}$, and $\vec{E}=E_0\hat{z}$. Let α_M be similarly defined. The asymptotic form of $V_{2\gamma}^{\text{s.i.}}(R)$ is then given by[15]

$$V_{2\gamma}^{\text{s.i.}}(R)\sim -D/R^7, \qquad (5.11)$$

where

$$D=\frac{23}{4\pi}\left(\overline{\alpha}_E^A\,\overline{\alpha}_E^B+\overline{\alpha}_M^A\,\overline{\alpha}_M^B\right) -\frac{7}{4\pi}\left(\overline{\alpha}_E^A\,\overline{\alpha}_M^B+\overline{\alpha}_M^A\,\overline{\alpha}_E^B\right) . \qquad (5.11')$$

Equation (5.11) is indeed a very natural generalization of (2.83) and was originally guessed on intuitive grounds; its derivation turned out, however, to be of surprising complexity. In this connection, we mention here only one important way in which the case with spin differs from that treated in this paper and in Ref. 2. When the particles have spin, the one-photon exchange potential has a spin-dependent part which is *not* short range; it follows that the contributions to $M_{2\gamma}(s,t)$ arising from intermediate states in which the initial particles occur (or, equivalently, in which the atoms are in their ground states) must be *removed* from $M_{2\gamma}$ before a definition of $V_{2\gamma}$ is made as a Fourier transform of a thus modified $M_{2\gamma}$.

E. Higher-Order Electromagnetic Corrections

The asymptotic R^{-7} behavior of the two-photon exchange potential $V_{2\gamma}(R)$ depends on the behavior $\rho_{2\gamma}\sim t^2$ near $t=0$. This behavior is assured if the limit of $F_X(\sigma,t)$ as $\sigma\to m^2$ and $t\to 0$ exists which is in turn assured physically by the existence of a finite static polarizability α_X. From a purely theoretical point of view, one certainly expects that $F_X(m^2, 0)$ is finite in the lowest order of electromagnetic interactions. However, one should note when higher orders are included $F_X(\sigma, 0)$ will no longer be analytic near $\sigma=m^2$; as recent work shows,[16] near

$$\omega=(\sigma-m^2)/2m\sim 0,\ \ F_X\sim[1+O(\alpha)\omega\ln\omega].$$

Nonetheless this is still finite for $\omega\to 0$.

Similarly, as emphasized in Ref. 8, one may expect that $\rho_X(m^2,t)$ is no longer analytic for $t\sim 0$ when higher orders are included; if the singularities are no worse than those in ω, $F_X(m^2, 0)$ will continue to exist even when higher orders are included. (For atoms, the word "order" refers to the numbers of virtual transverse photons exchanged; the Coulomb interaction must be separated out, so as not to destroy the existence of bound states.) The problem of the precise behavior of $F_X(\sigma, t)$ near $\sigma = m^2$, $t=0$ seems to merit more detailed study.

F. R^{-7} Behavior from Photon-Pair Propagator

It is instructive to relate the asymptotic R^{-7} behavior of $V_{2\gamma}(R)$ to a simple model for an effective photon-pair propagator. We recall first that the single photon propagator is given by

$$:A_\mu(\underbrace{x_1)A_\nu(x_2}):= i\, g_{\mu\nu} D_F(X), \qquad (5.12)$$

where the horizontal bracket indicates the contraction operation encountered in the expansion of the S matrix, using Wick's theorem and

$$D_F(x) \propto 1/(x^2 - i\epsilon) \qquad (5.12')$$

with $x^2 = x_0^2 - |\vec{x}|^2$. For $|\vec{x}| \neq 0$ the time integral of $D_F(x)$ is (put $x_0 = \eta |\vec{x}|$)

$$\int_{-\infty}^{\infty} D_F(x)\, dx^0 \propto 1/|\vec{x}|, \qquad (5.13)$$

that is, proportional to the Coulomb potential arising from single-photon exchange.

Now let us consider the effective Hamiltonian (2.87), describing the interaction of a neutral spin-0 field with the electromagnetic field A_μ. For simplicity we restrict our attention to the second term $\mathcal{H}_2 \propto \phi^\dagger \phi F^{\mu\nu} F_{\mu\nu}$, with $F_{\mu\nu} = \partial_\nu A_\mu - \partial_\nu A_\mu$. The effective propagator $G(x_1 - x_2)$ for the exchange of a photon pair emitted at the world point x_1 by particle "1" and absorbed at the world point x_2 by particle "2" is then given by

$$G(x_1 - x_2) = D_{\mu\nu;\,\alpha\beta}(x_1 - x_2)\, D^{\mu\nu;\,\alpha\beta}(x_1 - x_2), \qquad (5.14)$$

where

$$D_{\mu\nu;\,\alpha\beta}(x_1 - x_2) = :F_{\mu\nu}(x_1) F_{\alpha\beta}(x_2):. \qquad (5.14')$$

Using (5.12′), (5.14), and

$$\partial_\rho\, \partial_\sigma\, (x^2)^{-1} = (x^2)^{-2}\,[(6x_\rho x_\sigma / x^2) - 2g_{\rho\sigma}],$$

one readily sees that

$$G(x) = \mathrm{const}/(x^2)^4. \qquad (5.14'')$$

In analogy to (5.12) and (5.13) one therefore expects a potential proportional to

$$\int G(x)\, dx_0 \propto \int \frac{dx_0}{(x_0^2 - \vec{x}^2 + i\epsilon)^4} \propto \frac{1}{|\vec{x}|^7}, \qquad (5.15)$$

as first found by Casimir and Polder.[1] (We remark that a similar argument can be used to predict the r^{-5} behavior of the potential arising from neutrino-pair exchange.)[17]

Furthermore, within the framework provided by an effective Hamiltonian, one can understand the R^{-7} behavior simply on dimensional grounds. For example, with $\mathcal{H} = g\, \phi^\dagger \phi\, F_{\mu\nu} F^{\mu\nu}$, we must have $\dim g = L^2$ in order to have, as required for an energy density, $\dim \mathcal{H} = L^{-4}$. On including a kinematical factor $M^{1/2}$ for each initial and final particle, one sees that the general form of a power-law potential will be $V \propto g^2 (M^{-1/2})^4 r^{-n}$. The requirement that $L^{-1} = \dim V = (L^4)(L^2) L^{-n}$ then leads to $-1 = 6 - n$ or $n = 7$.

G. Concluding Remarks

The question of the nature of the force between atoms is of fundamental interest for physical theory, especially for our understanding of the properties of matter. As we have seen, for spinless atoms, quantum electrodynamics makes clear predictions about the interatomic potential for $R \gg a_0$, independent of any atomic model. Although the retarded character of this potential has been indirectly verified in experiments involving the interaction between macroscopic bodies,[18] a more direct test of theory of the retarded van der Waals potential by means of atom-atom scattering experiments would seem highly desirable. We hope that this paper will help to stimulate the efforts of experimentalists in this direction. A calculation of the very low-energy atom-atom scattering cross section is currently in progress with the aim of determining the experimental accuracy which would be required to measure the retarded van der Waals potential at intermediate distances.[19]

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APPENDIX A: S MATRIX APPROACH TO ELECTROMAGNETIC SUSCEPTIBILITIES

In Sec. II D it was shown that the threshold values $F_E(m^2, 0)$ and $F_M(m', 0)$ of the form factors $F_E(\sigma, t)$ are proportional to the static electric and magnetic susceptibilities α_E and α_M, respectively, by a method based on the construction of an "equivalent" Hamiltonian. Since there might be some doubt about the uniqueness of this procedure, it seems worthwhile showing how the same conclusion can be reached directly, by study of the S matrix for scattering of a neutral spinless particle by an *external* electromagnetic field $A^\mu(x)$.

For a weak external field, we may assume that the S matrix can be expanded in powers of a parameter characterizing the strength of the field. The second-order term, corresponding to double scattering, is then given by [see Fig. (2)]

$$S^{(2)} = \frac{-i}{2!} N \int \Gamma_{\mu\nu}(k, k'; P)\, \tilde{A}^\mu(-k)\, \tilde{A}^\nu(-k')\, d^4p'', \qquad (A1)$$

where $\Gamma_{\mu\nu}$ is the amplitude for two-photon emission [see Eq. (2.6) and Fig. 1] and

$$A^\mu(k) = (2\pi)^{-2} \int A^\mu(x)\, e^{ik\cdot x}\, d^4x \;. \qquad \text{(A2)}$$

The integration variable in (A1) could be either k or k' but is more conveniently chosen as

$$p'' = p - k = p' + k' \;. \qquad \text{(A3)}$$

The quantity N is the kinematical factor appropriate for a spin-0 particle,

$$N = (4p'^0 p^0)^{-1/2} \;. \qquad \text{(A4)}$$

From Eqs. (2.13) and (2.14), we readily find that

$$T_{1;\mu\nu}\tilde{A}^\mu(-k)\tilde{A}^\nu(-k') = -\hat{P}_\alpha \hat{P}_\beta \tilde{F}^{\alpha\mu}(-k)\tilde{F}^\beta_\mu(-k'),$$
$$T_{2;\mu\nu}\tilde{A}^\mu(-k)\tilde{A}^\nu(-k') = -\tfrac{1}{2}\tilde{F}_{\alpha\beta}(-k)\tilde{F}^{\alpha\beta}(-k') \;, \qquad \text{(A5)}$$

where $\hat{P} = P/m$ and

$$\tilde{F}^{\mu\nu}(k) = -i[k^\nu \tilde{A}^\mu(k) - k^\mu \tilde{A}^\mu(k)].$$

is the Fourier transform, analogous to (A2), of the field tensor

$$F^{\mu\nu}(x) = \partial^\nu A^\mu(x) - \partial^\mu A^\nu(x) \;.$$

From (A1), (A5), and Eq. (2.5), we get

$$S^{(2)} = \tfrac{1}{2}(iN)\int (F_1 P_\alpha P_\beta + F_2 g_{\alpha\beta})\tilde{F}^{\alpha\mu}(-k) \times \tilde{F}^\beta_\mu(-k')\, d^4p'' + \ldots, \qquad \text{(A6)}$$

where the dots indicate the terms arising from F_3, F_4, and F_4'. These will, however, make no contribution to the limit we now consider.

For a *static* field $F^{\mu\nu}(x) = F^{\mu\nu}(\vec{x})$ we have $\tilde{F}^{\mu\nu}(k) \propto \delta(k^0)\tilde{F}^{\mu\nu}(\vec{k})$, so that in the arguments of the F_a in (A6) we may set $k^0 = k'^0 = 0$. For a field $F^{\mu\nu}(\vec{x})$ which is *slowly varying*, i.e., constant over a large region of space and falling smoothly to zero outside this region, we may also set $\vec{k} = \vec{k}' = 0$ in the F_a in (A6) since if $F^{\mu\nu}(\vec{x}) \to C^{\mu\nu}$, independent of x, $\tilde{F}^{\mu\nu}(\vec{k}) \to (2\pi)^{3/2} C^{\mu\nu}\delta(\vec{k})$. Under these circumstances the terms not written out in (A6) may also be dropped and (A6) assumes the form

$$S^{(2)} \to \tfrac{1}{2}(iN)[F_1(0)P_\alpha P_\beta + \tfrac{1}{2}F_2(0) g_{\alpha\beta}]K^{\alpha\beta} \;, \qquad \text{(A7)}$$

where

$$K^{\alpha\beta} = \int \tilde{F}^{\alpha\mu}(-k)\tilde{F}^\beta_\mu(-k')\, d^4p'' \;.$$

On going to coordinate space, we get, using (A3)

$$K^{\alpha\beta} = \int F^{\alpha\mu}(\vec{x}) F^\beta_\mu(\vec{x})\, e^{i(p'-p)\cdot x}\, d^4x$$

or

$$K^{\alpha\beta} = 2\pi\,\delta(p'^0 - p^0)\langle \vec{p}'\,|\,F^{\alpha\mu}(\vec{x})F^\beta_\mu(\vec{x})\,|\,\vec{p}\rangle, \qquad \text{(A8)}$$

where $|\vec{p}\rangle$ denotes the state with wave function $e^{i\vec{p}\cdot\vec{x}}$.

We now go to the nonrelativistic limit for the particle being scattered. Then $P_\alpha \to (2m, 0)$ so that $P_\alpha P_\beta \to 4m^2 g_{\alpha 0} g_{\beta 0}$, and $N \to (2m)^{-1}$. With these substitutions in (A7), we find, using (A8) and

$$F^{0\mu}F^0_\mu = -\vec{E}^2, \quad F^{\alpha\mu}F_{\alpha\mu} = 2(-\vec{E}^2 + \vec{H}^2),$$

that

$$S^{(2)} = -2\pi i\,\delta(p'^0 - p^0)\langle \vec{p}'\,|H'|\,\vec{p}\rangle \;, \qquad \text{(A9)}$$

where

$$H' = -\tfrac{1}{2}\alpha_E'\vec{E}^2 - \tfrac{1}{2}\alpha_M'\vec{H}^2, \qquad \text{(A10)}$$

with

$$\alpha_E' \equiv -[4F_1^{(0)} + F_2(0)]/2m = F_E(0), \qquad \text{(A11)}$$

$$\alpha_M' \equiv F_2(0)/2m = F_M(0) \;. \qquad \text{(A12)}$$

Since (A9) has the proper form to permit identification of H' as an effective interaction operator and since the quantities α_E', α_M', and H' defined by (A10)–(A12) coincide with α_E', α_M', and H' defined, respectively, by Eqs. (2.39)–(2.95), we have confirmed the interpretation of the $F_a(0)$ given in Sec. IID by an approach based directly on the S matrix.

It is interesting to consider the nature of the effects arising from the terms in $M_{\mu\nu}$ which did not contribute in the limit of static uniform fields. It is easy to verify that

$$T_{3;\mu\nu}A^\mu(-k)A^\nu(-k') = \tilde{J}_\alpha(-k)\tilde{J}_\alpha(-k'), \qquad \text{(A13)}$$

where

$$\tilde{J}_\alpha(k) \equiv -i\,k^\mu \tilde{F}_{\mu\alpha}(k) \;.$$

By Maxwell's equations, $\tilde{J}_\alpha(k)$ is just the Fourier transform of the electric current $J_\alpha(x)$ producing the external field. Similarly,

$$T_{4;\mu\nu}A^\mu(-k)A^\nu(-k') = i P_\alpha \tilde{J}_\beta(-k)\tilde{F}^{\alpha\beta}(-k'),$$
$$T_{5;\mu\nu}A^\mu(-k)A^\nu(-k') = i P_\alpha \tilde{J}_\beta(-k')\tilde{F}^{\alpha\beta}(-k) \;. \qquad \text{(A14)}$$

If we again consider a static source and neglect the variation of the F_a with momenta ($a = 3-5$), the contribution of (A13) to the effective Hamiltonian is proportional to

$$F_3(0) J_\alpha(\vec{x}) J^\alpha(\vec{x}) \qquad \text{(A15)}$$

and for (A14) [with $P_\alpha \to (2m, 0, 0, 0)$] to

$$m[F_4(0) + F_5(0)]\vec{J}(\vec{x})\cdot\vec{E}(\vec{x}) \;.$$

It follows that, in order to detect such terms, an experiment would have to be performed in which the wave packet of the neutral particle has appreciable overlap with the *source* of the external field, rather than just the field itself.

APPENDIX B: ALTERNATIVE DERIVATION OF THE ASYMPTOTIC FORM OF $V_{2\gamma}(R)$

We present here the original proof of the fact that, as stated in Ref. 3, for $R \to \infty$

$$V_{2\gamma}(R)=\frac{-D}{R^7}\left[1+O\left(\frac{1}{R^2}\right)\right] , \tag{B1}$$

where

$$D=\frac{23}{4\pi}(\alpha_E^A\,\alpha_E^B+\alpha_M^A\,\alpha_M^B)-\frac{7}{4\pi}(\alpha_E^A\,\alpha_M^B+\alpha_M^A\,\alpha_E^B) . \tag{B2}$$

Compared to the discussion given in Sec. II D, the approach to be described here is much more direct. It also has the advantage of making it clear that, as asserted in the text, the statement $V_{2\gamma}(R)\sim -D/R^7$ is an *exact consequence* of the definition (2.4) of $V_{2\gamma}(R)$, and of showing that the next term for large R is of order R^{-9}, as indicated in (B1).

We begin with the observation that, for $t\sim 0$, the spectral function $\rho_{2\gamma}(t)$ given by (2.42) will have the form

$$\rho_{2\gamma}(t)=C' t^2[1+O(t)] , \tag{B3}$$

where C' is a constant. On substituting (B3) into [see Eq. (2.35)]

$$V_{2\gamma}(R)=\frac{-1}{16\pi^2 m_1 m_2 R}\int_0^\infty \rho_{2\gamma}(t)\exp(-t^{1/2}R)+\cdots , \tag{B4}$$

where the omitted terms fall off exponentially with R, we see on using

$$\int_0^0 t^n\exp(-t^{1/2}R)\,dt=2\frac{(2n+1)!}{R^{2n+2}} , \tag{B5}$$

that $V_{2\gamma}(R)$ has the form (B1), with

$$D=-5!\,C'/8\pi^2 m_1 m_2 . \tag{B6}$$

We must therefore evaluate C' which, from (B3), is given by

$$C'=\lim \rho_{2\gamma}(t)/t^2 \quad \text{as } t\to 0 . \tag{B7}$$

From (2.42), (2.39), and (2.17) we see that (B7) reduces to

$$C'=\frac{-1}{16\pi^2}\sum_{a,b=1}^{2} F_a^A(0)F_b^B(0)K_{ab} , \tag{B8}$$

where

$$K_{ab}=\lim_{t\to 0,\,s\to s_0}\frac{1}{t^2}\int d\Phi\, T_a^A : T_b^B \tag{B9}$$

and

$$F_a(0)=F_a(\sigma=m^2, t=0) ; \tag{B10}$$

we have used the fact that for $s=s_0$, $t\to 0$ implies $\sigma\to m^2$. Using (2.13) and (2.14), we readily find that on the photon mass shell

$$T_1^A:T_2^B=t^2P_A^2/4m_A^2 ,\quad T_2^A:T_1^B=t^2P_B^2/4m_B^2 ,$$
$$T_2^A:T_2^B=\tfrac12 t^2$$

so that, since

$$P_A^2=4m_A^2-t,\ P_B^2=4m_B^2-t ,\ \text{ and } \int d\Phi=\tfrac12\pi ,$$

we get

$$K_{12}=K_{21}=\tfrac12\pi ,\quad K_{22}=\tfrac14\pi . \tag{B11}$$

The evaluation of K_{11} is rather more formidable, requiring some patience. Using (2.13), we first find

$$T_1^A:T_1^B=P_A^\sigma P_A^\rho P_B^\beta P_B^\alpha I_{\sigma\rho;\beta\alpha}/m_A^2 m_B^2 , \tag{B12}$$

where

$$I_{\sigma\rho;\beta\alpha}=(\tfrac12 t)^2 g_{\sigma\beta}g_{\rho\alpha}+\tfrac12 t\,[(k'_\sigma k_\rho g_{\beta\alpha}+k'_\beta k_\alpha g_{\sigma\rho}) - (k_\sigma k'_\beta+k_\beta k'_\sigma)g_{\rho\alpha}-(k_\rho k'_\alpha+k_\alpha k'_\rho)g_{\sigma\beta}] + k_\sigma k_\rho k'_\beta k'_\alpha + k_\beta k_\alpha k'_\sigma k'_\rho . \tag{B13}$$

From (B9) and (B13), we see that we need the integrals

$$J_{\rho;\alpha}\equiv\int k_\rho k'_\alpha\, d\Phi \tag{B14}$$

and

$$J_{\sigma\rho;\beta\alpha}\equiv\int k_\sigma k_\rho k'_\beta k'_\alpha\, d\Phi . \tag{B15}$$

To evaluate $J_{\rho;\alpha}$, we write, on grounds of covariance, $J_{\rho;\alpha}=ag_{\rho\alpha}+b\,Q_\rho Q_\alpha$, multiply (B14) in turn by $g^{\rho\alpha}$ and $Q^\rho Q^\alpha$, and sum on the indices to obtain

$$4a+bt=\int k\cdot k'\, d\Phi ,$$
$$at+bt^2=\int Q\cdot k\, Q\cdot k'\, d\Phi .$$

Since, on the mass shell,

$$k\cdot k'=Q\cdot k=Q\cdot k'=\tfrac12 t ,$$

the required integrals are immediately found and hence so are a and b. Thus we get

$$J_{\rho;\alpha}=(\pi/24)[tg_{\rho\alpha}+2Q_\rho Q_\alpha] . \tag{B14$'$}$$

Similarly, we write $J_{\sigma\rho;\beta\alpha}$ as a linear combination of the ten distinct fourth-rank tensors which can be formed from Q_ν and $g_{\lambda\mu}$, use obvious symmetry properties to reduce the number of coefficients to be found, and multiply by $g^{\rho\beta}$, $Q^\rho Q^\beta$, etc., to obtain a sufficient number of equations to determine the coefficients. This yields

$$J_{\sigma\rho;\beta\alpha}=(\pi/480)[t^2(g_{\sigma\rho}g_{\beta\alpha}+g_{\sigma\alpha}g_{\rho\beta}+g_{\sigma\beta}g_{\rho\alpha}) + 4t(g_{\sigma\beta}Q_\rho Q_\alpha+g_{\sigma\alpha}Q_\rho Q_\beta+g_{\rho\beta}Q_\sigma Q_\alpha+g_{\rho\alpha}Q_\sigma Q_\beta) - 6t(g_{\sigma\rho}Q_\beta Q_\alpha+g_{\beta\alpha}Q_\sigma Q_\rho)+8Q_\sigma Q_\rho Q_\beta Q_\alpha] . \tag{B15$'$}$$

From (B14′), (B15′), and (B13), it follows that

$$\int I_{\sigma\rho;\beta\alpha}\,d\Phi=(\pi/240)[t^2(11g_{\sigma\rho}g_{\beta\alpha}+11g_{\sigma\beta}g_{\rho\alpha}+g_{\sigma\alpha}g_{\rho\beta}) + 40t(g_{\sigma\rho}Q_\beta Q_\alpha+g_{\beta\alpha}Q_\sigma Q_\rho+g_{\sigma\alpha}Q_\rho Q_\beta+g_{\rho\beta}Q_\sigma Q_\alpha - 4g_{\sigma\beta}Q_\rho Q_\alpha-4g_{\rho\alpha}Q_\sigma Q_\beta)+80Q_\sigma Q_\rho Q_\beta Q_\alpha] . \tag{B16}$$

Thus, using (B12), we get

$$\int T_1^A:T_1^B\,d\Phi=\frac{\pi}{240}t^2 \times\frac{11P_A^2P_B^2+11(P_A\cdot P_B)^2+(P_A\cdot P_B)^2}{m_A^2 m_B^2} , \tag{B17}$$

where we have used the fact that the second and third lines in (B16) [or (B15)] make no contribution, since $P_j \cdot Q = 0$ on the mass shell. Since

$$P_A \cdot P_B = s - u = 2s - 2m_A^2 - 2m_B^2 + t ,$$

so that

$$\lim_{t\to 0,\, s\to s_0} P_A \cdot P_B = 4m_A m_B ,$$

and since $P_j^2 \to 4m_j^2$ as $t \to 0$, we get, finally, from (B9) and (B17)

$$K_{11} = (\pi/240)\times 4^2[11+11+1], \quad \text{or} \quad K_{11} = 23\pi/15 . \tag{B18}$$

Thus the famous factor of 23 makes its appearance.

Combining the results of Eqs. (B11) and (B18) for the K_{ab}, we get for C', defined by (B8),

$$C' = \frac{-1}{16\pi}\left[\frac{23}{15}F_1^A(0)F_1^B(0) + \tfrac{1}{4}F_2^A(0)F_2^B(0) + \tfrac{1}{2}F_1^A(0)F_2^B(0) + \tfrac{1}{2}F_2^A(0)F_1^B(0)\right] . \tag{B19}$$

Since, according to (2.19), (2.20), and (2.80) we have

$$F_1(0) = -2\pi m(\alpha_E + \alpha_M) , \; F_2(0) = 8\pi m \alpha_M , \tag{B20}$$

we get, on substitution into (B19),

$$C' = -(\pi m_A m_B/60)[23(\alpha_E^A \alpha_E^B + \alpha_M^A \alpha_M^B) - 7(\alpha_E^A \alpha_M^B + \alpha_M^A \alpha_E^B)] , \tag{B21}$$

so that D, given by (B6), assumes the form claimed in (B2).

APPENDIX C: TRANSFORMATION OF U_{EM}

The function $U_{EM} = U_{EM}(k_A, k_B; R)$ defined by Eq. (2.68) with $g_{EM}(7)$ defined by Eq. (2.60) may be transformed as follows: On setting $t = 4\zeta^2$, U_{EM} may be written in the form

$$U_{EM} = \frac{1}{2\pi^3 R}\frac{1}{k_B^2 - k_A^2}[L(k_B, R) - L(k_A, R)] , \tag{C1}$$

where

$$L(k,R) = \int_0^\infty (d\zeta\, e^{-2\zeta R})[k^2\zeta - k(2\zeta^2 + k^2)\tan^{-1}(\zeta/k)] . \tag{C2}$$

On integration by parts (C2) assumes the form

$$L(k,R) = \frac{-1}{2R}\int_0^\infty d\zeta\, e^{-2\zeta R}\left(\frac{k^2\zeta^2}{k^2+\zeta^2} + 4k\zeta\tan^{-1}\frac{\zeta}{k}\right) . \tag{C3}$$

Again, on integration by parts, we have

$$\int_0^\infty d\zeta\, e^{-2\zeta R}\zeta\tan^{-1}\left(\frac{\zeta}{k}\right) = \frac{1}{2R}\int_0^\infty d\zeta\, e^{-2\zeta R}\left(\frac{k\zeta}{k^2+\zeta^2} + \tan^{-1}\frac{\zeta}{k}\right) = \frac{1}{2R}\int_0^\infty d\zeta\, e^{-2\zeta R}\left(\frac{k\zeta}{k^2+\zeta^2} + \frac{1}{2R}\frac{k}{k^2+\zeta^2}\right) ,$$

so that (C3) becomes

$$L(k,R) = \frac{-k^2}{2R^3}\int_0^\infty d\zeta\, \frac{e^{-2\zeta R}}{k^2+\zeta^2}(R\zeta + 1)^2 . \tag{C4}$$

Using (C4), we see that (C1) may be written in the form

$$U = \frac{1}{4\pi^3 R^6}\int_0^\infty d\zeta\, \frac{e^{-2\zeta R}P_{EM}(\zeta R)}{(k_A^2+\zeta^2)(k_B^2+\zeta^2)} , \tag{C5}$$

with $P_{EM}(\eta) = -\eta^2(\eta+1)^2$, as claimed in Eq. (2.72).

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$$C_{XY}(0) = \frac{3}{8\pi^4}\times\tfrac{1}{2}\pi\int_0^\infty d\omega' \,[\mathrm{Re}F_X^A(\omega')\mathrm{Im}F_X^B(\omega') + (A \longleftrightarrow B)] .$$

This is the formula previously used, but arrived at in a somewhat different manner, in an exact evaluation of the van der Waals constant $C_{EE}(0)$ for two hydrogen atoms [M. O'Carroll and J. Sucher, Phys. Rev. Letters 21, 1143 (1968)].

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