The van der Waals interaction

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The interaction between two neutral but polarizable systems at separation R, usually called the van der Waals force, is discussed from different points of view. The change in character from $1/R^6$ to $1/R^7$ due to retardation is explained.
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I. INTRODUCTION

The interaction between charged particles via the Coulomb interaction is one of the most important features in physics and is familiar to any student of the subject. The way in which electrons and protons bind to form the hydrogen atom is also well known and is a staple of any quantum mechanics course.[1] However, less familiar is the interaction between such bound systems at separation R, which is the so-called van der Waals force and is of a completely different character from its Coulombic analog.[2] That this must be the case is clear from the fact that the hydrogen atom is neutral, so that to lowest order there is no interaction. On the other hand the system is polarizable, and thus can interact with the other polarizable system, leading to a short-ranged attraction which varies as $1/R^6$, and this feature is discussed by a number of quantum mechanical references.[3,4] Somewhat less well known is the fact that at larger distances the character of the interaction changes and varies as $1/R^7$—discussion of this feature can be found, e.g., in the quantum field theory book by Itzykson and Zuber.[5] It is clear that the origin of this change is retardation, i.e., the finite propagation time of signals connecting the two systems, but the precise way in which this modification comes about is not so easy to calculate and is not generally presented.

The nature of the van der Waals force is quite topical at present due to the possible importance of such effects for the interactions of small color dipoles such as charmonium or bottomonium,[6] so it is useful to examine the physics of this effect. In the next section, then, we review the usual textbook discussion leading to the London $\sim 1/R^6$ interaction.[7] Then in Sec. III, we show how retardation effects modify the character of the force and change its asymptotic dependence to the Casimir–Polder form $\sim 1/R^7$.[8] In a brief concluding section we summarize our findings and discuss the relevance to modern particle and nuclear physics.

II. STANDARD VAN DER WAALS INTERACTION

The basic physics of the van der Waals force can be understood from a simple one-dimensional model of the atom which consists of electrons bound by harmonic oscillator forces to heavy protons at fixed separation R in addition to Coulomb interactions between the four charges[9]

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1,$$

with (see Fig. 1)

$$\begin{aligned}\mathcal{H}_0&=\frac{1}{2m}p_1^2+\frac{1}{2}m\omega_0^2x_1^2+\frac{1}{2m}p_2^2+\frac{1}{2}m\omega_0^2x_2^2,\\ \mathcal{H}_1&=\frac{e^2}{4\pi}\left(\frac{1}{R}+\frac{1}{R+x_1-x_2}-\frac{1}{R+x_1}-\frac{1}{R-x_2}\right).\end{aligned}\tag{1}$$

Assuming that the atomic separation is large compared to the size of the atom $(R\gg x_1,x_2)$, we can approximate

$$\mathcal{H}_1\approx -2\frac{e^2x_1x_2}{4\pi R^3}\tag{2}$$

and the system can be diagonalized in terms of coordinates $x_\pm=(x_1\pm x_2)/\sqrt{2}$, yielding

$$\begin{aligned}\mathcal{H}=&\frac{p_+^2}{2m}+\frac{1}{2}\left(m\omega_0^2-\frac{2e^2}{4\pi R^3}\right)x_+^2+\frac{p_-^2}{2m}\\ &+\frac{1}{2}\left(m\omega_0^2+\frac{2e^2}{4\pi R^3}\right)x_-^2,\end{aligned}\tag{3}$$

i.e., in terms of independent harmonic oscillators with shifted frequencies

$$\begin{aligned}\omega_\pm&=\sqrt{\omega_0^2\mp\frac{2e^2}{4\pi mR^3}}\\ &\simeq\omega_0\mp\frac{e^2}{4\pi m\omega_0R^3}-\frac{e^4}{32\pi^2m^2\omega_0^3R^6}+\cdots.\end{aligned}\tag{4}$$

The van der Waals potential is simply the shift in the ground state (zero point) energy due to the Coulomb interaction and is found to be

$$V(R)=\frac{1}{2}\omega_++\frac{1}{2}\omega_--2\left(\frac{1}{2}\omega_0\right)\simeq-\frac{e^4}{32\pi^2m^2\omega_0^3R^6}.\tag{5}$$

We can write this result in a more familiar form by noting that when an external electric field is applied to this system, the leading order Hamiltonian becomes

$$\mathcal{H}=\mathcal{H}_0(x_1,x_2)+eE_0x_1+eE_0x_2=\mathcal{H}_0(z_1,z_2)-\frac{e^2E_0^2}{m\omega_0^2}\tag{6}$$

with $z_i=x_i+eE_0/m\omega_0^2$, and corresponds to an induced electric dipole moment

$$d=-\frac{\delta\mathcal{H}}{\delta E_0}=\frac{2e^2E_0}{m\omega_0^2}.\tag{7}$$

Defining the electric polarizability α_E in the conventional fashion, via $d=4\pi\alpha_EE_0$, we find $\alpha_E=2e^2/4\pi m\omega_0^2$ so that

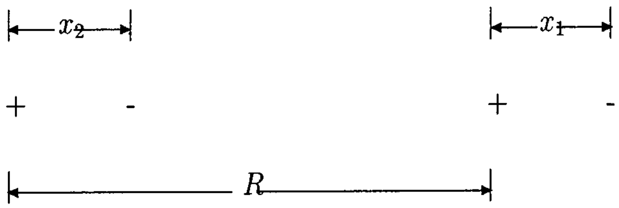

Fig. 1. Simple one-dimensional model of interacting hydrogen atoms.

the van der Waals interaction can be written in the ''London'' form[7]

$$V(R)=-\frac{\alpha_E^2\omega_0}{8R^6}. \tag{8}$$

One can also derive Eq. (8) via simple second-order perturbation theory

$$\Delta E_2=V(R)=\sum_{n\neq0}\frac{\langle0|\mathcal{H}_1|n\rangle\langle n|\mathcal{H}_1|0\rangle}{E_0-E_n}. \tag{9}$$

Since for a simple one-dimensional harmonic oscillator

$$\langle l|x|0\rangle=\delta_{l,1}\sqrt{\frac{1}{2m\omega_0}}, \tag{10}$$

Eq. (9) becomes

$$\begin{aligned}V(R)&=\left(\frac{2e^2}{4\pi R^3}\right)^2\sum_{n_1,n_2}\frac{\delta_{n_1,1}\delta_{n_2,1}|\langle1,1|x_1x_2|0,0\rangle|^2}{(n_1+n_2)\omega_0}\\&=\left(\frac{2e^2}{4\pi R^3}\right)^2\left(\sqrt{\frac{1}{2m\omega_0}}\right)^4\frac{-1}{2\omega_0}=-\frac{e^4}{32\pi^2m^2\omega_0^3R^6},\end{aligned} \tag{11}$$

in agreement with Eq. (5).

It is useful to spend a bit of time examining the ''physics'' of this result. The form of the interaction potential, Eq. (2), can be understood in terms of the energy of the dipole moment of ''atom'' #2 ($d_2=-ex_2$) in the electric field created by the dipole moment of ''atom'' #1,

$$\mathcal{H}_1\sim-d_2E_2(d_1)=ex_2\frac{-ex_1}{4\pi R^3}=-\frac{e^2x_1x_2}{4\pi R^3}. \tag{12}$$

Of course, $\langle x_1\rangle=\langle x_2\rangle=0$, i.e., there exists no average dipole moment, so this energy change vanishes in first-order perturbation theory

$$\Delta E_1=\langle\psi_0|\mathcal{H}_1|\psi_0\rangle=0.$$

However, there *is* a shift at second order since at any given instant of time there exists an instantaneous dipole moment in, say, atom #1. The corresponding electric field at the position of atom #2 generates a correlated electric dipole moment due to its electric polarizability,

$$d_2=4\pi\alpha_EE_1(R)=4\pi\alpha_E\frac{ex_1}{4\pi R^3}. \tag{13}$$

The electric field generated by *this* electric dipole moment then acts back on the original atom, yielding an energy

$$\Delta E_{\rm vdW}\sim-d_1E_2(R)=-\frac{e^2x_1^2\alpha_E}{4\pi R^6}, \tag{14}$$

which is the van der Waals interaction. What makes this work, then, is the point that one can use the instantaneous position of one atom to provide an action at a distance correlation with a second atom in the vicinity.

Finally, we note that the electric polarizability itself can be extracted by calculating the shift in energy of the atom in the presence of an external electric field E_0 in second-order perturbation theory[10]

$$\Delta E^{(2)}=\sum_{n\neq0}\frac{\langle0|eE_0x_1|n\rangle\langle n|eE_0x_1|0\rangle}{E_0-E_n}\equiv-\frac{1}{2}4\pi\alpha_EE_0^2. \tag{15}$$

We find then $\alpha_E\sim e^2\langle x_1^2\rangle/\omega_0$ and

$$\Delta E_{\rm vdW}\sim\frac{\alpha_E^2\omega_0}{4\pi R^6} \tag{16}$$

so that it is this *self-interaction energy* which is responsible for the London form—cf. Eq. (8).

With this background in hand it is straightforward to move to the physical (three-dimensional) situation.[11] In this case the dipole moment generated by atom #1 ($\mathbf{d}_1=e\mathbf{r}_1$) generates an electromagnetic potential

$$U(\mathbf{R})=\frac{\mathbf{d}_1\cdot\mathbf{R}}{4\pi R^3}, \tag{17}$$

which means that at location $\mathbf{R}$ one has the electric field

$$\mathbf{E}(\mathbf{R})=-\nabla_{\mathbf{R}}U=-\frac{e}{4\pi R^3}[\mathbf{r}_1-3\hat{R}\hat{R}\cdot\mathbf{r}_1]. \tag{18}$$

The corresponding dipole–dipole interaction energy is

$$U_{\rm vdW}=-\mathbf{d}_2\cdot\mathbf{E}(\mathbf{R})=\frac{e^2}{4\pi R^3}[\mathbf{r}_1\cdot\mathbf{r}_2-3\mathbf{r}_1\cdot\hat{R}\mathbf{r}_2\cdot\hat{R}]. \tag{19}$$

Choosing the z axis along the direction $\hat{R}$, we can write

$$U_{\rm vdW}=\frac{e^2}{4\pi R^3}[x_1x_2+y_1y_2-2z_1z_2]. \tag{20}$$

The lowest order energy shift involving a pair of hydrogen atoms is then

$$\Delta E_1=\langle\psi_{1,0,0}^{(1)}\psi_{1,0,0}^{(2)}|U_{\rm vdW}|\psi_{1,0,0}^{(1)}\psi_{1,0,0}^{(2)}\rangle=0 \tag{21}$$

and vanishes since $\langle\mathbf{r}_1\rangle=\langle\mathbf{r}_2\rangle=0$. However, to second order there exists a nonvanishing energy—this is the van der Waals interaction

$$V(R)=\Delta E_2=\left(\frac{e^2}{4\pi R^3}\right)^2\sum_{nlm;n'l',m'}\frac{|\langle\psi_{n,l,m}^{(1)}\psi_{n'l'm'}^{(2)}|x_1x_2+y_1y_2-2z_1z_2|\psi_{1,0,0}^{(1)}\psi_{1,0,0}^{(2)}\rangle|^2}{2E_{10}-E_{nl}-E_{n'l'}}. \tag{22}$$

Since the state $\psi_{1,0,0}$ is the ground state, the denominator is always negative and it is thus clear that this result is nonzero, although no exact evaluation is possible. Nevertheless, we can obtain an approximate form by noting that selection rules allow only electric dipole ($\Delta j=0,\pm 1$, parity change) excitation of both atoms so that, using closure, we can write

$$\begin{aligned} V(R) &\simeq \left(\frac{e^2}{4\pi R^3}\right)^2 \frac{1}{2E_{10}-2E_{21}} \\ &\quad\times \sum_{nlm;n'l'm'} |\langle \psi^{(1)}_{n,l,m}\psi^{(2)}_{n'l'm'}|x_1x_2 \\ &\quad + y_1y_2 - 2z_1z_2|\psi^{(1)}_{1,0,0}\psi^{(2)}_{1,0,0}\rangle|^2 \\ &= \left(\frac{e^2}{4\pi R^3}\right)^2 \frac{1}{2E_{10}-2E_{21}} \langle \psi^{(1)}_{1,0,0}\psi^{(2)}_{1,0,0}|x_1^2x_2^2 \\ &\quad + y_1^2y_2^2 + 4z_1^2z_2^2|\psi^{(1)}_{1,0,0}\psi^{(2)}_{1,0,0}\rangle. \end{aligned} \tag{23}$$

Using $\langle x_i^2\rangle = \langle \mathbf{r}^2\rangle/3 = a_0^2$, where $a_0=1/m\alpha$ is the Bohr radius, we find

$$V(R) \simeq -\frac{6\alpha a_0^5}{R^6}. \tag{24}$$

Expressing this result in terms of the electric polarizability via

$$\alpha_E = 2\alpha \sum_{nlm} \frac{|\langle \psi_{nlm}|z|\psi_{1,0,0}\rangle|^2}{E_{10}-E_{nl}} \simeq a_0^3, \tag{25}$$

we have

$$V(R) \sim \frac{\alpha}{a_0}\frac{a_0^6}{R^6} = \frac{\omega_0\alpha_E^2}{R^6}, \tag{26}$$

which is the London form.

III. RETARDATION

The discussion given in the previous section is standard, but it is clear that it must be altered at large distances since we have neglected the finite propagation time of electromagnetic interactions. Indeed, since the van der Waals force is due to the self-interaction of the dipole moment of an atom with the electric field generated by the correlated dipole moment of an atom at distance R, this simple nonrelativistic action at a distance analysis must begin to break down when the time required for a signal to travel from atom to atom ($\Delta T_1 \sim R$) becomes comparable to or greater than a characteristic time $[\Delta T_2 \sim 1/(E_{10}-E_{21})]$ associated with the evolution of the atom, i.e., when $\omega_0 R \geqslant 1$. For hydrogen this transition occurs at $R\sim \hbar c/10\,\mathrm{eV} \sim a_0/\alpha \sim 200\,\mathrm{A}$. For distances comparable to or greater than this value, we must take retardation into account. There are at least two ways in which this can be accomplished, and we shall consider each in turn.

A. Fourth-order perturbation theory

Perhaps the most straightforward way to understand the effects of retardation is through a simple perturbation theory evaluation. Of course, since the van der Waals interaction is $\mathcal{O}(e^4)$ this must be a fourth-order perturbative calculation. This is how the original calculation of Casimir and Polder was done.[8] However, use of the usual Coulomb gauge Hamiltonian for two neutral hydrogen atoms at distance R interacting with the electromagnetic field[12]

$$\begin{aligned} H &= \sum_{j=1,2} H_j^{(0)} + H^{\mathrm{rad}} + e^2 \frac{\mathbf{r}_1\cdot\mathbf{r}_2 - 3\mathbf{r}_1\cdot\hat{R}\mathbf{r}_2\cdot\hat{R}}{4\pi R^3} \\ &\quad + \sum_{j=1,2}\left[-\frac{e}{m}\mathbf{p}_i\cdot\mathbf{A}(\mathbf{r}_i) + \frac{e^2}{2m}\mathbf{A}^2(\mathbf{r}_i)\right] \end{aligned} \tag{27}$$

leads to a rather complicated analysis involving *thirteen* diagrams—including seagull terms [i.e., the diagrams arising from the term $\mathbf{A}^2(\mathbf{r}_i)$ in Eq. (27) involving a pair of photons emitted from the same point, which diagramatically look like a child's drawing of a flying seagull] and instantaneous Coulomb interactions [i.e., the term involving

$$e^2 \frac{\mathbf{r}_1\cdot\mathbf{r}_2 - 3\mathbf{r}_1\cdot\hat{R}\mathbf{r}_2\cdot\hat{R}}{4\pi R^3},$$

which arises from expansion of the instantaneous Coulomb interactions between the charged particles making up the system]. It is thus advantageous, as pointed out by Power and Zienau,[13] to isolate the important physics by working in the gauge $\phi=0$ and using the electric dipole approximation, wherein the variation of the vector potential over the atomic size is neglected. In this case the Hamiltonian becomes

$$H = \sum_{j=1,2} H_j^{(0)} + H^{\mathrm{rad}} - \sum_{j=1,2} e\mathbf{r}_i\cdot\mathbf{E}_t, \tag{28}$$

where $\mathbf{E}_t$ represents the *transverse* electric field so that only radiation photons are involved. The resulting fourth-order diagrams which contribute to the van der Waals interaction are now only six in number. They are shown in Fig. 2 and can be divided into three classes. One class is that where the interaction with the electric field by atom #1 occurs entirely previous to the interaction with the field by atom #2. For pedagogical simplicity, we suppose that the atom has only a single excited state ($|1\rangle$) connected to the ground state ($|0\rangle$) via the electric dipole operator $e\mathbf{r}$, and for didactic purposes we shall explicitly demonstrate how to evaluate one of the six diagrams—Fig. 2(a), which is shown in more detail in Fig. 3. We use

$$\Delta E_0^{(4)} = \sum_{n,l,k\neq 0} \frac{\langle 0|V|n\rangle\langle n|V|l\rangle\langle l|V|k\rangle\langle k|V|0\rangle}{(E_0-E_n)(E_0-E_l)(E_0-E_k)}, \tag{29}$$

where we have dropped self-energy terms, which do not contribute. In the gauge $\phi=0$ we can write the interaction as

$$V = e\sum_{j=1,2} \mathbf{r}_1\cdot\frac{\partial \mathbf{A}_t}{\partial t}, \tag{30}$$

where $\mathbf{A}$ is the quantized radiation field. For the diagram shown we identify $E_n-E_0=\omega_{10}+k_2$, $E_l-E_0=k_1+k_2$, and $E_k-E_0=\omega_{10}+k_1$, where $\omega_{10}=E_1-E_0$ is the excitation energy. Also,

$$\langle k|V|0\rangle = iek_1\hat{\boldsymbol{\epsilon}}_1\cdot\langle 1|r_1 e^{i\mathbf{k}_1\cdot(\mathbf{r}_1+\mathbf{X}_1)}|0\rangle,$$

where $\mathbf{X}_1$ is the location of the atom, with similar expressions for the remaining three transition amplitudes. Putting all these together we find

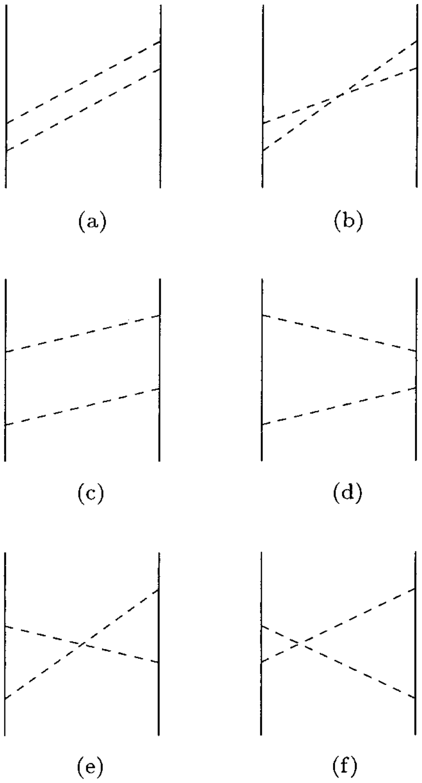

Fig. 2. Time-dependent perturbation theory diagrams contributing to the van der Waals interaction. Here the dashed line indicates a photon exchange.

$$\Delta E_{2a} = -e^4 \sum_{\mathbf{k}_1,\hat\epsilon_1}\sum_{\mathbf{k}_2,\hat\epsilon_2} k_1^2 k_2^2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times \frac{\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_2)(k_1+k_2)}, \tag{31}$$

where

$$\sum_{\mathbf{k}_2,\hat\epsilon_1} \equiv \int \frac{d^3k_1}{(2\pi)^3 2k_1}\sum_{\hat\epsilon_1}.$$

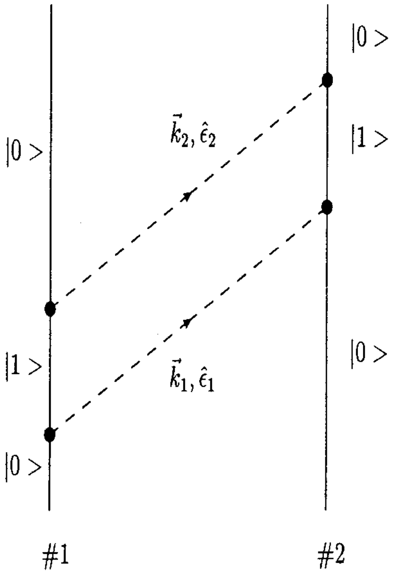

Fig. 3. One of the time-dependent perturbation theory diagrams contributing to the van der Waals interaction. Here the dashed line indicates a photon exchange.

Now combine this result with that obtained by interchanging atoms #1, #2 and include the corresponding contribution from Fig. 2(b). The result is

$$\Delta E_{a+b} = -e^4 \sum_{\mathbf{k}_1,\hat\epsilon_1}\sum_{\mathbf{k}_2,\hat\epsilon_2} k_1^2 k_2^2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times\Bigg[\frac{\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_2)(k_1+k_2)} + \frac{\hat\epsilon_1^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_2\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_1)(k_1+k_2)} + \#1\leftrightarrow\#2\Bigg]. \tag{32}$$

Similarly one finds contributions from Figs. 2(c) and 2(d),

$$\Delta E_{c+d} = -e^4 \sum_{\mathbf{k}_1,\hat\epsilon_1}\sum_{\mathbf{k}_2,\hat\epsilon_2} k_1^2 k_2^2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times\Bigg[\frac{\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_2)2\omega_{10}} + \frac{\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_2)2\omega_{10}} + \#1\leftrightarrow\#2\Bigg] \tag{33}$$

and from Figs. 2(e) and 2(f),

$$\Delta E_{e+f} = -e^4 \sum_{\mathbf{k}_1,\hat\epsilon_1}\sum_{\mathbf{k}_2,\hat\epsilon_2} k_1^2 k_2^2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times\Bigg[\frac{\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_1^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_2\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_1)(2\omega_{10}+k_1+k_2)} + \frac{\hat\epsilon_2^*\cdot\langle 0|\mathbf{r}_2|1\rangle\,\hat\epsilon_1\cdot\langle 1|\mathbf{r}_2|0\rangle\,\hat\epsilon_1^*\cdot\langle 0|\mathbf{r}_1|1\rangle\,\hat\epsilon_2\cdot\langle 1|\mathbf{r}_1|0\rangle}{(\omega_{10}+k_1)(\omega_{10}+k_2)(2\omega_{10}+k_1+k_2)} + \#1\leftrightarrow\#2\Bigg]. \tag{34}$$

Consider first the contribution from Figs. 2(a) and 2(b). Summing over polarization states, Figs. 2(a) and 2(b) become

$$\Delta E_{a+b} = -e^4 \int \frac{d^3k_1}{2k_1(2\pi)^3}\frac{d^3k_2}{2k_2(2\pi)^3} k_1^2 k_2^2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times \frac{|\langle 1|z_1|0\rangle|^2|\langle 1|z_2|0\rangle|^2(1+(\hat k_1\cdot\hat k_2)^2)}{(\omega_{10}+k_1)(k_1+k_2)} \times\left(\frac{1}{\omega_{10}+k_2}+\frac{1}{\omega_{10}+k_1}\right). \tag{35}$$

Consider first the long distance limit ($\omega_{10}R \gg 1$) wherein retardation effects are important. Then since, due to the exponential, the sum over photon momenta extends only to k_1, $k_2 \leqslant 1/R$, we can write

$$\Delta E_{a+b} \xrightarrow{\omega_{10}R\gg 1} -4\frac{e^4}{\omega_{10}^2}\int \frac{d^3k_1}{2k_1(2\pi)^3}\frac{d^3k_2}{2k_2(2\pi)^3} \times k_1^2k_2^2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times\frac{|\langle 1|z_1|0\rangle|^2|\langle 1|z_2|0\rangle|^2(1+(\hat{k}_1\cdot\hat{k}_2)^2)}{k_1+k_2}. \tag{36}$$

Using the definition of electric polarizability

$$\alpha_E=\frac{e^2}{2\pi}\sum_{n\neq 0}\frac{|\langle n|z|0\rangle|^2}{E_n-E_0}=\frac{e^2}{2\pi}\frac{|\langle 1|z|0\rangle|^2}{\omega_{10}}, \tag{37}$$

this becomes

$$\Delta E_{a+b} \xrightarrow{\omega_{10}R\gg 1} -\frac{\alpha_E^2}{(2\pi)^4} \times\int d^3k_1d^3k_2k_1k_2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}}\left(\frac{1+(\hat{k}_1\cdot\hat{k}_2)^2}{k_1+k_2}\right) \equiv -\frac{\alpha_E^2}{(2\pi)^4}J_1. \tag{38}$$

The integration can easily be performed, as shown in Appendix A, and the result is

$$\Delta E_{a+b}=-\frac{23\alpha_E^2}{4\pi R^7}, \tag{39}$$

which is the result given by Casimir and Polder.[8] Similarly, the contributions from the remaining diagrams become, in this limit,

$$\Delta E_{c+d}=\Delta E_{e+f} \xrightarrow{\omega_{10}R\gg 1} -\frac{\alpha_E^2}{(2\pi)^4 2\omega_{10}} \times\int d^3k_1d^3k_2k_1k_2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}}(1+(\hat{k}_1\cdot\hat{k}_2)^2). \tag{40}$$

By simple scaling arguments, it is easy to see that $\Delta E_{c+d}=\Delta E_{e+f}\sim\alpha_E^2/\omega_{10}R^8\sim\Delta E_{a+b}/\omega_{10}R\ll\Delta E_{a+b}$ and can be neglected in the long distance limit.

As an aside we note that it is also straightforward to include the effects of magnetic polarizability; since

$$\sum_{\hat{\epsilon}_1,\hat{\epsilon}_2}(\hat{\epsilon}_1\cdot\hat{\epsilon}_2)^2=1+(\hat{k}_1\cdot\hat{k}_2)^2=\sum_{\hat{\epsilon}_1,\hat{\epsilon}_2}(\hat{\epsilon}\times\hat{k}_1\cdot\hat{\epsilon}_2\times\hat{k}_2)^2 \tag{41}$$

the contribution to the van der Waals interaction from a pair of magnetic interactions is found simply by replacing $\alpha_E^2\to\beta_M^2$ in Eq. (39). Similarly, we can include interactions involving electric and magnetic polarizabilities via the identity

$$\sum_{\hat{\epsilon}_1,\hat{\epsilon}_2}(\hat{\epsilon}_1\times\hat{k}_1\cdot\hat{\epsilon}_2)^2=2\hat{k}_1\cdot\hat{k}_2=\sum_{\hat{\epsilon}_1,\hat{\epsilon}_2}(\hat{\epsilon}_1\cdot\hat{\epsilon}_2\times\hat{k}_2)^2. \tag{42}$$

Then the overall van der Waals interaction at long distance assumes the familiar form

$$V(R)=\frac{-23(\alpha_E^2+\beta_M^2)+7(\alpha_E\beta_M+\beta_M\alpha_E)}{4\pi R^7}, \tag{43}$$

where we have used the result

$$\int d^3k_1d^3k_2k_1k_2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}}\frac{2\hat{k}_1\cdot\hat{k}_2}{k_1+k_2}=-\frac{28\pi^3}{R^7}, \tag{44}$$

as shown in Appendix A.

Here the fact that the large distance–retardation corrected–van der Waals interaction varies as α_E^2/R^7 is easily understood from simple physical arguments, as cited by Kaplan.[14] In Figs. 2(a) and 2(b) the photon emission/absorption involving, say, atom #1 occur entirely before (or after) those involving atom #2, so this interaction may effectively be shrunk to a local two-photon vertex characterized by the electric/magnetic polarizability. Since polarizabilities have units of volume and since two such interactions are involved, the requirement that the potential energy have the proper units gives $V(R)\sim\alpha_E^2/R^7$, where we have used the feature that the separation R provides the only scale in the problem.

The above derivation breaks down, however, for short distances where the photon emission/absorption by the atoms is correlated so that the photon emitted from atom #2, say, is absorbed by atom #1 *before* any emission/absorption of the second photon. Indeed, if we assume that $\omega_{10}R\ll 1$, then it is easy to see that the dominant diagrams become Figs. 2(c) and 2(d) with

$$\Delta E_{c+d} \xrightarrow{\omega_{10}R\ll 1} -\frac{e^4}{2\omega_{10}}\int\frac{d^3k_1}{(2\pi)^3}\frac{d^3k_2}{(2\pi)^3}e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}} \times|\langle 1|z_1|0\rangle|^2|\langle 1|z_2|0\rangle|^2(1+(\hat{k}_1\cdot\hat{k}_2)^2). \tag{45}$$

The integration is performed in Appendix A, yielding

$$\Delta E_{c+d}=-\frac{3\omega_{10}\alpha_E^2}{4R^6}, \tag{46}$$

which is the London form. For this short distance situation the contribution of the remaining diagrams is found to be

$$\Delta E_{a+b}=\Delta E_{e+f} \xrightarrow{\omega_{10}R\ll 1} -\frac{\alpha_E^2\omega_{10}^2}{(2\pi)^4} \times\int d^3k_1d^3k_2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}}\frac{(1+(\hat{k}_1\cdot\hat{k}_2)^2)}{k_1+k_2}. \tag{47}$$

By simple scaling arguments we find that $\Delta E_{a+b}=\Delta E_{e+f}\sim\alpha_E^2\omega_{10}^2/R^5\sim\omega_{10}R\Delta E_{c+d}\ll\Delta E_{c+d}$ and can be neglected in the short distance limit.

The general form of the van der Waals interaction at arbitrary distance can, of course, be found by adding together *all* of the above diagrams,[13] which yields the Casimir–Polder integral

$$V(R)=-\frac{\alpha_E^2\omega_{10}^4}{\pi R^3}\int_0^\infty\frac{du\,\exp(-2u)}{(\omega_{10}^2R^2+u^2)^2} \times(u^4+2u^3+5u^2+6u+3). \tag{48}$$

However, the physics is more clearly identified by working in the separate long and short distance limits, as shown above. If intermediate distance results are needed, a good numerical match to the exact form is given by[15]

$$V(R) = -\frac{3\omega_{10}\alpha_E^2}{4R^6}\left(\frac{2}{\pi}\right)\tan^{-1}\frac{23}{6\omega_{10}R}. \tag{49}$$

It is also interesting to see why the Kaplan argument leading to $1/R^7$ behavior breaks down at short distance. The point is that since emission/absorption by atoms #1, #2 are correlated, it is not possible to shrink the interactions involving a single atom down to an effective point vertex involving the polarizability. Indeed, in this case one must deal with *both* the ground and excited states of both atoms, so that a new scale ω_{10} enters the problem and this is why simple Kaplan scaling fails.

B. Two-photon exchange

An alternative, but completely equivalent, way to derive the van der Waals interaction is to use the feature that the potential is the Fourier transform of the quantum mechanical scattering amplitude,[15]

$$V(\mathbf{R}) = \int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{R}}\,\mathrm{amp}(\mathbf{q}), \tag{50}$$

where $\mathbf{q} = \mathbf{p}_i - \mathbf{p}_f$ is the momentum transfer. Thus, for example, for the Coulomb scattering amplitude $\mathrm{amp}_{\mathrm{Coul}} = e^2/\mathbf{q}^2$ we find

$$V_{\mathrm{Coul}}(\mathbf{R}) = e^2\int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{R}}\frac{1}{\mathbf{q}^2} = \frac{e^2}{4\pi|\mathbf{R}|}, \tag{51}$$

as required. In our case, we wish to isolate the portion of the atom–atom scattering which is due to *two-photon exchange*. This is, in general, a nontrivial relativistic Feynman diagram calculation, but may be simplified by realizing that the scattering amplitude is causal (i.e., the scattered wave cannot be emitted before the incoming plane wave strikes the scattering center) and is an analytic function in momentum transfer-squared, meaning that it satisfies a dispersion relation in the variable $t = -\mathbf{q}^2$,

$$\mathrm{amp}_{2\gamma}(t) = \frac{1}{\pi}\int_0^\infty \frac{dt\,\mathrm{Im}\,\mathrm{amp}_{2\gamma}(t')}{t' - t - i\epsilon}. \tag{52}$$

The full discussion from this point onward is a bit technical and is outlined in Appendix B. However, it is possible to isolate the basic physics more simply and that is what we shall present here. Readers wishing a more complete discussion can refer to Appendix B or to Ref. 15.

The desired van der Waals potential is found by taking the Fourier transform of the two-photon-exchange amplitude. By reversing the order of integrations we see that the result can also be written in terms of a superposition of Yukawa potentials,

$$\begin{aligned} V(R) &= \frac{1}{\pi}\int_0^\infty dt'\,\mathrm{Im}\,\mathrm{amp}_{2\gamma}(t')\int \frac{d^3q}{(2\pi)^3}\frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{t' + \mathbf{q}^2 - i\epsilon} \\ &= \frac{1}{4\pi^2}\int_0^\infty dt\,\mathrm{Im}\,\mathrm{amp}_{2\gamma}(t')\frac{\exp(-\sqrt{t'}R)}{R}. \end{aligned} \tag{53}$$

The necessary input to Eq. (53) is provided by the unitarity stricture, which in the center-of-mass frame takes the form[16]

$$\begin{aligned} 2\,\mathrm{Im}\,\mathrm{amp}_{2\gamma}(t) = \frac{1}{2!}\sum_{\mathbf{k}_1,\hat{\epsilon}_1}\sum_{\mathbf{k}_2,\hat{\epsilon}_2}|M_{2\gamma}(t=(k_1+k_2)^2)|^2 \\ \times (2\pi)^4\delta^4(Q - k_1 - k_2), \end{aligned} \tag{54}$$

where the factor 2! is due to the identity of the two photons in the intermediate state and Q^μ represents the four-vector $(\sqrt{t},\mathbf{0})$. Note here that the unitarity relation gives the imaginary component of the amplitude $M_{2\gamma}$ at *positive* values of t, which can be related by crossing symmetry and analytic continuation to the Compton scattering amplitude at *negative t*. Defining $t = (2\omega)^2$, we can write

$$V(R) = \frac{1}{\pi^2}\int_0^\infty \omega'\,d\omega'\frac{\exp(-2\omega' R)}{R}\mathrm{Im}\,\mathrm{amp}_{2\gamma}(i\omega'). \tag{55}$$

The electric polarizability contribution to the Compton scattering amplitude from a neutral object can be written in the general form

$$M_{\mathrm{Comp}} \simeq 4\pi\alpha_E(\omega)\mathbf{E}^2(\omega) = 4\pi\alpha_E(\omega)\omega^2\hat{\epsilon}_1\cdot\hat{\epsilon}_2, \tag{56}$$

where $\alpha_E(\omega)$ is the dynamic polarizability. Thus the van der Waals potential assumes the form

$$V(R) \simeq -\frac{4}{3\pi}\int_0^\infty \omega'^5\,d\omega'\,\alpha_E^2(i\omega')\frac{\exp(-2\omega' R)}{R}. \tag{57}$$

Now suppose that the time taken by light to travel between the two systems $(\delta t_2 \sim R)$ is large compared to a typical excitation time $\delta t_1 \sim 1/\omega_{10}$. In this case $(\omega_{10}R \gg 1)$ the integration in Eq. (57) involves only values $\omega' \ll 1/R \ll \omega_{10}$. Then $\alpha_E(i\omega)$ may be approximated by its value at $\omega = 0$ and, after five integrations by parts, the van der Waals potential can be written in the form

$$\begin{aligned} V(R) &\overset{\omega_{10}R\gg 1}{\rightarrow} -\frac{5!\,\alpha_E^2(0)}{24\pi}\int_0^\infty d\omega'\frac{\exp(-2\omega' R)}{R^6} \\ &\simeq -\frac{20\alpha_E^2(0)}{4\pi R^7}. \end{aligned} \tag{58}$$

Here the coefficient sitting in front of the polarizability is not quite correct since we have not used the proper relativistic forms (cf. Appendix B), but the ‘‘physics’’ is properly included.

In the alternative limit where the light transition time is small compared to a typical excitation time $(\omega_{10}R \ll 1)$, the convergence of the integration in Eq. (57) is set now by $\omega' \ll \omega_{10} \ll 1/R$ and we must include the frequency dependence of the dynamic polarizability. The correct way to do this can be found in Appendix B, but one can understand the essential physics of this result by inserting $\alpha_E^2(i\omega')$ in Eq. (58),

$$\begin{aligned} V(R) &= -\frac{5!}{24\pi}\int_0^\infty d\omega'\frac{\alpha_E^2(i\omega')}{R^6}\exp(-2\omega' R) \\ &\overset{\omega_{10}R\ll 1}{\rightarrow} -\frac{5!}{24\pi R^6}\int_0^\infty d\omega'\,\alpha_E^2(i\omega'). \end{aligned} \tag{59}$$

Now the polarizability can itself be written in terms of a dispersion relation[17]

$$\alpha_E(\omega)=\frac{1}{\pi}\int_{\omega_0}^{\infty}\frac{d\omega'\,\omega'\sigma(\omega')}{\omega'^2-\omega^2}, \tag{60}$$

where the spectral density $\sigma(\omega')$ is nonzero only in the vicinity of excitations of the system in question. As a simple representation, we may write, then, for the case of a single such excitation [note that $\alpha_E(0)$ corresponds to α_E in the notation of the previous section]

$$\alpha_E(\omega)\simeq\alpha_E\frac{\omega_{10}^2}{\omega_{10}^2-\omega^2}. \tag{61}$$

Substituting into Eq. (59) we have

$$V(R)\overset{\omega_{10}R\ll 1}{\rightarrow}-\frac{5!\,\alpha_E^2(0)}{24\pi R^6}\int_0^{\infty}d\omega'\frac{\omega_{10}^4}{(\omega'^2+\omega_{10}^2)^2}$$
$$=-\frac{5!\,\pi\alpha_E^2(0)\omega_{10}}{96R^6}, \tag{62}$$

which is the expected London form.

IV. CONCLUSIONS

In this paper we have examined the origin of the van der Waals interaction, both in its traditional London—$1/R^6$—form, valid when the photon travel time between atoms is small compared to a typical quantum mechanical evolution time $\Delta T\sim 1/\omega_{10}$, and the retarded or Casimir–Polder—$1/R^7$—version, valid in the opposite limit when the quantum mechanical evolution time is small compared to the time required for interatomic photon travel so that finite propagation times must be considered. The calculation was performed in two very different but equivalent ways. The first was a direct evaluation of the atom–atom interaction in fourth-order perturbation theory, where the two limiting forms are seen to arise from the dominance of differing graphs depending on the interatomic separation. The second was based on dispersion relations wherein the difference between the two forms arises because of the requirement to utilize the static versus dynamic polarizability in the long versus short distance limits. Either discussion involves interesting pieces of physics and offers an attractive means by which to enhance discussion of this universal and familiar phenomenon.

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APPENDIX A

In order to perform the integrals

$$J_{[1;2]}(R)=\int d^3k_1d^3k_2k_1k_2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}}$$
$$\times\frac{[1+(\hat{k}_1\cdot\hat{k}_2)^2;2\hat{k}_1\cdot\hat{k}_2]}{k_1+k_2}, \tag{63}$$

we select the z axis to lie along the direction $\hat{R}$ and use the identities

$$\hat{k}_1\cdot\hat{k}_2=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2),$$
$$\frac{1}{k_1+k_2}=\int_0^{\infty}d\sigma\exp-\sigma(k_1+k_2), \tag{64}$$

where $\hat{k}_1,\hat{k}_2$ are chosen to lie along the directions θ, ϕ and θ', ϕ', respectively. Performing the ϕ, ϕ' integrations in Eq. (63) and defining $s_i=k_iR$, $\kappa=\sigma R$ we find

$$J_{[1;2]}=(2\pi)^2\int_0^{\infty}d\sigma\int_0^{\infty}dk_1\,k_1^3\int_0^{\infty}dk_2\,k_2^3\int_{-1}^{1}dz\int_{-1}^{1}dz'\exp(ik_1Rz+ik_2Rz')$$
$$\times\exp-\sigma(k_1+k_2)[\tfrac{3}{2}+\tfrac{3}{2}z^2z'^2-\tfrac{1}{2}(z^2+z'^2);2zz']$$
$$=\frac{(4\pi)^2}{R^7}\int_0^{\infty}d\kappa\int_0^{\infty}ds_1\,s_1^3\int_0^{\infty}ds_2\,s_2^3\left[\frac{3}{2}+\frac{3}{2}\frac{d^2}{ds_1^2}\frac{d^2}{ds_2^2}+\frac{1}{2}\left(\frac{d^2}{ds_1^2}+\frac{d^2}{ds_2^2}\right);-2\frac{d}{ds_1}\frac{d}{ds_2}\right]\frac{\sin s_1}{s_1}\frac{\sin s_2}{s_2}\exp-\kappa(s_1+s_2)$$
$$=\frac{(4\pi)^2}{R^7}\int_0^{\infty}d\kappa\int_0^{\infty}ds_1\,s_1^3\int_0^{\infty}ds_2\,s_2^3\left[\frac{3}{2}\frac{\sin s_1}{s_1}\frac{\sin s_2}{s_2}+\frac{3}{2}\left(\frac{\sin s_1}{s_1}-2\frac{\sin s_1}{s_1^3}+2\frac{\cos s_1}{s_1^2}\right)(\text{same with } s_1\rightarrow s_2)\right.$$
$$+\frac{1}{2}\left(\frac{\sin s_1}{s_1}-2\frac{\sin s_1}{s_1^3}+2\frac{\cos s_1}{s_1^2}\right)\sin\frac{s_2}{s_2}+(\text{same with } s_1\leftrightarrow s_2)$$
$$\left.-2\left(\frac{\cos s_1}{s_1}-\frac{\sin s_1}{s_1^2}\right)(\text{same with } s_1\rightarrow s_2)\right]\exp-\kappa(s_1+s_2). \tag{65}$$

Defining[13]

$$
\begin{aligned}
&M(x)=\sin x+N(x)=\sin x+\frac{\cos x}{x}-\frac{\sin x}{x^2},\\
&K(x)=\cos x-\frac{\sin x}{x},
\end{aligned}
\tag{66}
$$

we find

$$
\begin{aligned}
J_1=&\frac{2(4\pi)^2}{R^7}\int_0^\infty d\kappa\left[2\left(\int_0^\infty ds\, s^2N(s)e^{-\kappa s}\right)^2\right.\\
&\left.+\left(\int_0^\infty ds\, s^2M(s)e^{-\kappa s}\right)^2\right],\\
J_2=&\frac{2(4\pi)^2}{R^7}\int_0^\infty d\kappa\left(\int_0^\infty ds\, s^2K(s)e^{-\kappa s}\right)^2.
\end{aligned}
\tag{67}
$$

Using

$$
\begin{aligned}
&\int_0^\infty ds\, s^n\sin s\exp-\kappa s=(-)^n\frac{d^n}{d\kappa^n}\frac{1}{1+\kappa^2},\\
&\int_0^\infty ds\, s^n\cos s\exp-\kappa s=(-)^n\frac{d^n}{d\kappa^n}\frac{\kappa}{1+\kappa^2},
\end{aligned}
\tag{68}
$$

the remaining integrations over κ become trivial and we find

$$
J_{[1,2]}=\frac{[23,-7]4\pi^3}{R^7}.
\tag{69}
$$

Likewise the corresponding short distance integration

$$
L_1(R)=\int d^3k_1d^3k_2e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}}(1+(\hat{k}_1\cdot\hat{k}_2)^2)
\tag{70}
$$

may be performed. If we write

$$
k_i^2=k_i^3\int_0^\infty d\kappa_i\exp-\kappa_ik_i
\tag{71}
$$

then by very similar steps to those used in deriving Eq. (67) we find

$$
\begin{aligned}
L_1=&\frac{2(4\pi)^2}{R^6}\left[2\left(\int_0^\infty d\kappa\int_0^\infty ds\, s^2N(s)e^{-\kappa s}\right)^2\right.\\
&\left.+\left(\int_0^\infty d\kappa\int_0^\infty ds\, s^2M(s)e^{-\kappa s}\right)^2\right].
\end{aligned}
\tag{72}
$$

Using Eq. (68) the integrations are again straightforward, yielding

$$
L_1=\frac{24\pi^4}{R^6}.
\tag{73}
$$

APPENDIX B

The fully relativistic calculation of the van der Waals interaction via the Fourier transform method can be found in the work of Feinberg and Sucher.[15] We have tried in Sec. III B to identify the basic physics behind this result. However, a number of the steps are less than rigorous. Here we present a more detailed summary of how the calculation is performed.

We begin by decomposing the Compton scattering amplitude for the reaction $A(p)+\gamma(k)\rightarrow A(p')+\gamma(k')$ into electric and magnetic components. Defining

$$
\begin{aligned}
T^1_{\mu\nu}=&(k\cdot k'\cdot Pg_{\mu\nu}+k\cdot k'P_\mu P_\nu-k\cdot Pk'_\mu P_\nu\\
&-k'\cdot Pk_\nu P_\mu)/M_A^2,\\
T^2_{\mu\nu}=&k\cdot k'g_{\mu\nu}-k_\nu k_\mu,
\end{aligned}
\tag{74}
$$

where $P=p+p'$, it is easy to see that the corresponding electric and magnetic tensors can be written as

$$
T^E_{\mu\nu}=-\tfrac{1}{2}T^1_{\mu\nu},\quad T^M_{\mu\nu}=-\tfrac{1}{2}T^1_{\mu\nu}+2T^2_{\mu\nu}.
\tag{75}
$$

Then the general Compton scattering amplitude can be written as

$$
A^{\mathrm{Comp}}_{\mu\nu}=T^E_{\mu\nu}F_E(s_+,t)+T^M_{\mu\nu}F_M(s_+,t),
\tag{76}
$$

where we have defined $s_\pm=(p\pm k)^2$, $u_\pm=(p\mp k')^2$, and $t=(k-k')^2$. Using crossing symmetry, one now writes F_E,F_M in terms of a dispersion relation at fixed momentum transfer,

$$
\begin{aligned}
F_{E,M}(s_+,t)=&\frac{1}{\pi}\int_{M^2}^\infty ds'\,\rho_{E,M}(s',t)\\
&\times\left(\frac{1}{s'-s_+}+\frac{1}{s'-u_+}\right).
\end{aligned}
\tag{77}
$$

The amplitude $\mathrm{Im}\,\mathrm{amp}_{2\gamma}(t)$ needed for the Fourier transform in Eq. (53) is then given by unitarity as

$$
\begin{aligned}
\mathrm{Im}\,\mathrm{amp}_{2\gamma}=&-\sum_{X,Y=E,M}M^2\int ds\,ds'\,\rho_X(s,t)\rho_Y(s',t)\\
&\times\Phi_{XY}(s,s',t),
\end{aligned}
\tag{78}
$$

where

$$
\begin{aligned}
\Phi_{XY}(s,s',t)=&\int\frac{d^4k}{(2\pi)^42k_0}\frac{d^4k'}{(2\pi)^42k'_0}\\
&\times(2\pi)^4\delta^4(t-k-k')T_X:T_Y\\
&\times\left(\frac{1}{s-s_+}+\frac{1}{s-u_+}\right)\left(\frac{1}{s'-s_-}+\frac{1}{s'-u_-}\right).
\end{aligned}
\tag{79}
$$

In order that t be positive and small it is necessary to do an analytic continuation to consider the reactions $A+\bar{A}\rightarrow\bar{A}+A$ at a total center-of-mass energy $\sqrt{t}$. In order that particles A, $\bar{A}$ stay on their mass shells we must use

$$
\begin{aligned}
&P_{A,\bar{A}}=\left(\frac{\sqrt{t}}{2},\pm iM_A\hat{p}\right),\quad p'_{A,\bar{A}}=\left(\frac{\sqrt{t}}{2},\pm iM_A\hat{p}'\right),\\
&k,k'=\left(\frac{\sqrt{t}}{2},\pm\hat{k}\right).
\end{aligned}
\tag{80}
$$

Then

$$
\begin{aligned}
s-s_- &= s-M_A^2+\frac{t}{2}-i\sqrt{t}M_A z,\\
s-u_+ &= s-M_A^2+\frac{t}{2}+i\sqrt{t}M_A z,\\
s'-s_+ &= s'-M_A^2+\frac{t}{2}+i\sqrt{t}M_A z,\\
s'-u_- &= s'-M_A^2+\frac{t}{2}-i\sqrt{t}M_A z,
\end{aligned}
\tag{81}
$$

where $z=\hat{p}\cdot\hat{k}=-\hat{p}'\cdot\hat{k}$. We find then

$$
\begin{aligned}
\Phi_{XY} \simeq \frac{1}{2}\int d\Omega\, T_X : T_Y & \left(\frac{s-M_A^2}{(s-M_A^2)^2+tM_A^2 z^2}\right)\\
& \times\left(\frac{s'-M_A^2}{(s'-M_A^2)^2+tM_A^2 z'^2}\right).
\end{aligned}
\tag{82}
$$

Defining $\omega=(s-M_A^2)/M_A$, $\omega'=(s'-M_A^2)/M_A$, and $\tau=\omega/\sqrt{t}$, $\tau'=\omega'/\sqrt{t}$ the solid angle integration becomes

$$
\Phi \simeq \frac{\pi t}{2M_A^2}\int_{-1}^{1} dz\, \frac{\tau}{\tau^2+z^2}\,\frac{\tau'}{\tau'^2+z^2}\,\Theta_{XY}, \tag{83}
$$

where $\Theta_{EE}=\Theta_{MM}=2-2z^2+z^4$, $\Theta_{EM}=\Theta_{ME}=z^4-2z^2$, and may be performed directly, yielding

$$
\Phi_{XY}=\frac{\pi t\tau\tau'}{M_A^2}\,\frac{g_{XY}(\tau')-g_{XY}(\tau)}{\tau^2-\tau'^2} \tag{84}
$$

with

$$
\begin{aligned}
g_{EE}(\tau) &= g_{MM}(\tau)=\tau^2-\left(\frac{2+2\tau^2+\tau^4}{\tau}\right)\tan^{-1}\tau,\\
g_{EM}(\tau) &= g_{ME}(\tau)=\tau^2-\left(\frac{2\tau^2+\tau^4}{\tau}\right)\tan^{-1}\tau.
\end{aligned}
\tag{85}
$$

Using these results the integration in Eq. (53) can be performed by making the substitution $t=4\zeta^2$ followed by a fivefold integration by parts in order to remove the $\tan^{-1}\tau$ dependence. The result is

$$
V(R)=-\frac{C_{XY}(R)}{R^6}, \tag{86}
$$

where

$$
C_{XY}(R)=\frac{1}{\pi}\int_0^\infty d\zeta\, e^{-2\zeta R}P_{XY}(\zeta R)\,\alpha_E^2(i\zeta) \tag{87}
$$

with

$$
\begin{aligned}
P_{EE}(x) &= P_{MM}(x)=3+6x+5x^2+2x^3+x^4,\\
P_{EM}(x) &= P_{ME}(x)=-(x^2+2x^3+x^4).
\end{aligned}
\tag{88}
$$

The integration over ζ may now be done, yielding results identical to those found via perturbative methods.

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