Retardation effects on high Rydberg states: A retarded R^{-5} polarization potential

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The finiteness of the speed of light is known to change the long-range interaction of atomic systems. Stimulated by recent advances in precision measurements of high Rydberg states, we consider these "retardation effects," not on the interaction of two separate systems, but on the energy eigenvalues of the high Rydberg states of an isolated heliumlike ion, where the outer electron has quantum numbers $n > l \gg 1$, and where the core—the nucleus and the inner electron—is in its (spherically symmetric) ground state. We analyze the time-ordered Feynman-like graphs that contain one or two instantaneous or transverse photons, and find a retardation correction, $11e^2\hbar\alpha_d/(4\pi mcR^5)$ to the leading $(-e^2\alpha_d/2R^4)$ polarization potential; α_d is the static electric dipole polarizability of the ion core, and R is the nuclear–outer-electron separation. The correction is also applicable to scattering problems, to high Rydberg states of atoms and ions with more than two electrons, and, with $m \to m_\mu$, to a muon bound to a nucleus. Very recently, Bernabéu and Tarrach used dispersion theory to obtain an identical term as the retardation correction for the interaction of a charged particle with a *neutral* polarizable system; their procedure is not applicable, as it stands, to the present situation.

I. INTRODUCTION

The study of long-range electromagnetic interactions in atomic and molecular systems has had a long and noble history.[1,2] In addition to the Coulomb $1/R$ potential itself, there are other long-range potentials which have their origin in Coulomb and transverse photon interactions. In the nineteenth century, Van der Waals[3] asserted that the experimentally observed deviations from the ideal gas law indicate that there should be an attractive force at large distances between neutral atoms. In 1930, London[4] gave a quantum-mechanical basis to this interaction. Considering only the electrostatic interactions, he showed that the interaction between two hydrogen atoms, each in its ground state, behaved as $1/R^6$ for distances large compared to the Bohr radius a_0.

In a classic paper in 1948, Casimir and Polder[5] demonstrated that the inclusion in the formalism of retardation, that is, of the finiteness of the speed of light, changed the *very* large R dependence of the potential to R^{-7}. The theoretical work[6-8] which followed, using a variety of different approaches, extended and confirmed the R^{-7} dependence predicted by Casimir and Polder. This fascinating prediction has not yet been detected in experiments involving a pair of atoms, but there is experimental evidence indicating that similar retardation effects are present in bulk matter.[9] The Casimir-Polder result states that the interaction between two neutral hydrogen atoms each in its ground state behaves as[10]

$$V_{\mathrm{CP}}(R) \sim -(23\hbar c/4\pi)\alpha_d(1)\alpha_d(2)/R^7 \qquad (1.1)$$

as $R \sim \infty$, where $\alpha_d(i)$ is the static electric dipole polarizability of the ith atom. This is *not* an additive correction to the Van der Waals interaction, $V_{\mathrm{vdW}}(R)$, but a basic change in the interaction. Note that c appears in the numerator in V_{CP}.[11]

There are also well-known long-range potentials between a charged system and a neutral polarizable system, and between charged systems one or both of which are polarizable. If, for example, we have a point particle with a charge Q_1 and a system with charge Q_2 and static electric dipole and quadrupole polarizabilities $\alpha_d(2)$ and $\alpha_q(2)$, respectively, the asymptotic interaction, in the adiabatic approximation, includes not only the Coulomb potential Q_1Q_2/R but also

$$V_{\mathrm{adiab}}(R) \sim -\tfrac{1}{2}\alpha_d(2)Q_1^2/R^4 - \tfrac{1}{2}\alpha_q(2)Q_1^2/R^6. \qquad (1.2)$$

This result is obtained within the context of nonrelativistic theory. Still within the nonrelativistic context, we drop the adiabatic approximation, that is, we allow for the motion of the particle. The inability of the polarizable system to instantaneously adapt itself, for a given $\vec{R}$, to the state it would be in for that $\vec{R}$ if $\vec{R}$ were fixed leads to additional potentials, the dominant one of which is, asymptotically,[12-15] a nonadiabatic term

$$V_{\mathrm{nonad}}(R) \sim 3a_0\beta_{\mathrm{nonad}}Q_1^2/R^6, \qquad (1.3)$$

where β_{nonad} will be defined later.

In addition, there will be corrections originating in retardation effects if the motion of the point particle is taken into account. (There is no retardation effect if the point particle is at rest, even though the particles in the polarizable system are in motion; the relativistic interaction of two charged particles reduces to the Coulomb interaction if either particle is at rest.) For very large

R, though perhaps not for arbitrarily large R—we will comment on this point later—the leading correction will be shown to be

$$V_{\text{ret}}(R) \sim 11\hbar e^2 \alpha_d / 4\pi m c R^5 , \tag{1.4}$$

where m is the mass of the electron. Note that this correction contains c in the denominator and therefore vanishes in the nonrelativistic approximation. As opposed to the atom-atom problem, where the nonrelativistic potential is cancelled on introducing relativistic theory, the R^{-4} polarization potential persists as one introduces relativistic theory; the retardation correction of Eq. (1.4) is an addition.

In this paper we depart from the tradition of looking for evidence of retardation effects on long-range interactions by studying their effects on widely separated neutral atoms. Instead, we look for the effects of these same instantaneous and transverse photon interactions on the energy levels of an atom (or ion) which has one electron at a very great distance from the nucleus. This change of viewpoint is motivated by recent major advances[16-18] in the measurement of energy separations in high Rydberg states and the promise of further improvements. One may contrast the great accuracy attainable in these bound-state energy measurements with the immense difficulties in obtaining even moderately accurate scattering data, especially in the low-energy domain required for the validity of an approach which takes the adiabatic approximation as a starting point.

To obtain some idea of the size the orbit of the outer electron must have if the effects of the finite speed of light are to be significant, we offer the following heuristic argument. Consider a helium atom with an outer electron in essentially a circular orbit with a large radius $R = n^2 a_0$; the principal quantum number n and the orbital-angular-momentum quantum number l are both assumed to be large compared to 1. Let one of the electrons emit a photon to the other electron and receive a photon in return; at least one of the two photons is to be transverse, traveling with a speed c. The time for the round-trip process is of order $n^2 a_0/c \equiv \tau$. (Here and throughout this argument we ignore possible factors of order unity.) The periods of the inner and outer electrons are roughly $\tau_1 = a_0/(e^2/\hbar)$ and $\tau_2 = n^2 a_0/(e^2/\hbar)$. Retardation effects can be expected to be important if and only if $\tau \gtrsim \tau_1$ or τ_2, that is, if and only if

$$n^2 \alpha \gtrsim 1 , \tag{1.5}$$

where $\alpha = e^2/\hbar c$ is the fine structure constant. This result will be given a proper basis below. For the moment we simply remark that the imposition of (1.5) means that we have crossed the nonrelativistic Rubicon; we cannot return to the nonrelativistic domain by letting $c \sim \infty$ since (1.5) cannot then be satisfied.

We will argue later that the results are valid for a range of atoms and ions, but we will present the detailed analysis for the isoelectronic sequence of He; the core—a nucleus of arbitrary Z and the inner electron—is assumed to be in its (spherically symmetric) ground state, and the outer electron has $l \gg 1$. This has the advantage of simplifying the notation and the discussion. Furthermore, for $Z = 2$, and especially for ^{4}He which has zero nuclear spin and therefore no hyperfine structure, this is far and away the easiest multielectronic atomic system that can be studied from first principles.

Our theoretical framework[19] is akin to that used by Casimir and Polder. The electrons are assumed to be spinless and nonrelativistic, the electron–transverse-photon interaction is described by $\vec{p} \cdot \vec{A}_T$ and A_T^2 terms, where $\vec{A}_T$ is the second-quantized (transverse) photon field, and self-energy terms are ignored. Spin effects, certain relativistic effects, and radiative corrections in which a virtual photon is emitted and absorbed by the same electron are as large or larger than the retardation effects we calculate, and considerable theoretical work will be necessary to extract the retardation effects from the experimental energy-level data when they are available. (We have also neglected exchange effects. These can be expected to be small but ultimately should be included for completeness.) One should also consider three-photon exchange.[6]

Our analysis is necessarily more complicated than that of Casimir and Polder, for they can make the dipole approximation for a transverse photon emitted by either system, while we can make the dipole approximation only for a photon emitted by the inner electron. Thus, for two hydrogen atoms at a large separation R, the relevant range of values of the wave number k of either photon is from zero to of order $1/R$. For $\vec{r}_1$ and $\vec{r}_2$, the positions of the electrons with respect to their own nuclei, one can then approximate $\exp(i\vec{k} \cdot \vec{r}_1)$ by unity for $i = 1$ or 2, since the range of the $|\vec{r}_i|$ is roughly a_0. In the present helium-atom case, the range of k is determined by the radius R [where $R = n^2 a_0/(Z-1)$] of the orbit of the outer electron to be from zero to of order $1/R$, and $\exp(i\vec{k} \cdot \vec{r}_i)$ can therefore be approximated by unity only for the inner electron whose range is of order a_0/Z; the range of the outer electron is, of course, R.[20]

The other major difference between the present problem and that of Casimir and Polder is that the outer electron may be treated simply in the determination of the retardation terms; more precisely,

energy changes in the intermediate states of the outer electron may be neglected with respect to both characteristic photon energies and energy changes in the inner electron.

Our final result may be written as an effective potential

$$V(R)\sim\frac{-(Z-1)e^2}{R}-\frac{1}{2}\alpha_d(1)\frac{e^2}{R^4}\left(1-\frac{11}{2\pi}\frac{\hbar/mc}{R}\right)$$
$$-\frac{1}{2}\frac{\alpha_q(1)e^2}{R^6}+\frac{3a_0\beta_{\text{nonad}}(1)e^2}{R^6}+\cdots. \qquad (1.6)$$

The retardation correction term $11\hbar e^2\alpha_d(1)/4\pi mcR^5$ is the principal result of the present paper. It should be noted that it is likely that there are other terms in (1.6) proportional to R^{-6}, terms which we have not calculated; these terms are of the same size as those shown and come from the next to leading retardation correction. $V(R)$ should be applicable not only to the two-electron case, but to a range of problems involving a charged particle and a neutral or charged polarizable spherically symmetric system to which it is bound. (Further, it should be possible to extend the result so that it is applicable to a system which is not spherically symmetric and whose ground state therefore has multipole moments.) These include, for example, an electron bound to a spherically symmetric ion and a muon bound to a spherically symmetric nucleus. Still further, the results should be applicable to the scattering of a charged particle moving with small velocity relative to a neutral or charged polarizable spherically symmetric system. For the particular case of an electron bound to an atom or ion consisting of a nucleus of charge Z and an electron in its ground state, we have

$$\alpha_d(1)=\tfrac{9}{2}a_0^3/Z^4,\quad \alpha_q(1)=15a_0^5/Z^6,$$
$$\beta_{\text{nonad}}=\tfrac{43}{8}a_0^4/Z^6. \qquad (1.7)$$

Bernabéu and Tarrach[21] very recently obtained the same retardation term using a dispersion-relation analysis. Their analysis, however, is not applicable to the problem to which we have addressed ourselves, the high Rydberg states of He, for they assumed the polarizable system interacting with the charged particle to be neutral. Their work is therefore applicable to proton-neutron scattering, for example. (Of course, it may be possible to extend this dispersion relation analysis in some fashion to include charged polarizable systems.) On the other hand, their result is more general in that it includes a retardation term, $5e^2\hbar\beta_d/4\pi mcR^5$, associated with the static magnetic-dipole polarizability β_d of the system. (Note that there is no static term proportional to β_d/R^4.) This term would be difficult to extract by our approach since in our problem β_d is smaller than α_d by a factor of order α^2, and its effect could only appear in higher-order terms of the perturbation expansion.

II. METHOD OF CALCULATION

The Hamiltonian H for this calculation is taken to be

$$H=H_0+H_I'+H_T'\equiv H_0+H', \qquad (2.1)$$

with, respectively,

$$H_0=\frac{p_1^2}{2m}-\frac{Ze^2}{r_1}+\frac{p_2^2}{2m}-\frac{(Z-1)e^2}{r_2} \qquad (2.2)$$

and

$$H_I'=e^2/r_{12}-e^2/r_2. \qquad (2.3)$$

H_0 is the unperturbed Hamiltonian. The perturbation H' contains the screening correction H_I' to electron 2 (the outer electron) and the second-quantized transverse photon interaction H_T', given by

$$H_T'=\sum_{i=1}^{2}\left(\frac{e}{mc}\vec{p}_i\cdot\vec{A}(\vec{r}_i)+\frac{e^2}{2mc^2}\vec{A}(\vec{r}_i)\cdot\vec{A}(\vec{r}_I)\right), \qquad (2.4)$$

with

$$\vec{A}(\vec{r}_i)=\sum_{\vec{k},\vec{\epsilon}}cD_k\vec{\epsilon}\,[A^-_{\vec{k},\vec{\epsilon}}\exp(i\vec{k}\cdot\vec{r}_i)$$
$$+A^+_{\vec{k},\vec{\epsilon}}\exp(-i\vec{k}\cdot\vec{r}_i)]. \qquad (2.5)$$

The charge of the electron is $-e$. The sum over the polarization unit vector $\vec{\epsilon}$ is over two directions perpendicular to each other and $\hat{k}$. $A^-_{\vec{k},\vec{\epsilon}}$ and $A^+_{\vec{k},\vec{\epsilon}}$ are, respectively, the photon annihilation and creation operators of quantum electrodynamics, and the normalization factor D_k equals $(2\pi\hbar/ckV)^{1/2}$; we have normalized the modes of the radiation field in a box of volume V which we are to set equal to infinity eventually. We replace the summation over $\vec{k}$ by an integration in $\vec{k}$ space with the correspondence

$$\sum_{\vec{k}}\rightarrow\frac{V}{8\pi^3}\int d\vec{k}. \qquad (2.6)$$

The V is cancelled by two normalization factors; the necessity of taking the limit of infinite volume is avoided.

The wave function Ψ of the unperturbed system is the product of the wave function ψ_0 of electron 1 in its ground state, the wave function ψ_n of electron 2 in the state (n,l,m) and the wave function ψ_0^F of

the radiation field in its ground state, that is,

$$\Psi = \psi_0(1)\psi_n(2)\psi_0^F = \Psi_0\psi_0^F . \tag{2.7}$$

Note that ψ_0 and ψ_n are associated with nuclear charges Z and $Z-1$, respectively. The associated unperturbed energy is

$$E = E_0 + E_n = -\frac{e^2}{2a_0}\left(\frac{Z^2}{1^2} + \frac{(Z-1)^2}{n^2}\right). \tag{2.8}$$

H' produces a shift in energy which may be written as the perturbation series

$$\Delta E = \langle\Psi|H'|\Psi\rangle + \sum_I{}' \frac{\langle\Psi|H'|I\rangle\langle I|H'|\Psi\rangle}{E-E_I} + \sum_{I,II}{}' \frac{\langle\Psi|H'|II\rangle\langle II|H'|I\rangle\langle I|H'|\Psi\rangle}{(E-E_{II})(E-E_I)} - \langle\Psi|H'|\Psi\rangle \sum_I{}' \left|\frac{\langle I|H'|\Psi\rangle}{E-E_I}\right|^2$$
$$+ \sum_{I,II,III}{}' \frac{\langle\Psi|H'|III\rangle\langle III|H'|II\rangle\langle II|H'|I\rangle\langle I|H'|\Psi\rangle}{(E-E_{III})(E-E_{II})(E-E_I)} - \sum_I{}' \frac{\langle\Psi|H'|I\rangle\langle I|H'|\Psi\rangle}{E-E_I} \sum_I{}' \left|\frac{\langle\Psi|H'|I\rangle}{E-E_I}\right|^2 + \cdots . \tag{2.9}$$

The prime on the sum denotes the fact that an intermediate state identical to the initial state is to be excluded. The prime can therefore be omitted if the intermediate state involves one or more photons.

The perturbation expansion is reorganized in the form of graphs in Figs. 1 and 2. A dashed line denotes what we will refer to for simplicity as an instantaneous photon; in reality it generates an interaction H_I' which is the difference of two Coulomb interactions. A wavy line represents a transverse photon. A thick vertical line represents the nucleus and the inner electron, and the thin vertical line represents the outer electron. Figure 1 contains one-photon graphs, while Fig. 2 contains two-photon graphs; we ignore higher-order diagrams and, as noted above, graphs that contribute to Lamb shifts. [We will therefore not be concerned with the fourth and last terms of Eq. (2.9).] Subscripts I and T refer to instantaneous and transverse photons, respectively. All diagrams but the two involving only instantaneous photons, namely, 1(a) and 2(a), have reflections; the reflection diagram associated with a given diagram will be denoted by a prime. (We have not drawn the reflection diagrams in Fig. 2.) It is important to note that we must account carefully for the time-order of the graphs with one or two A^2 vertices. We count

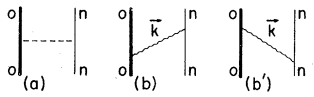

FIG. 1. One-photon graphs—a dashed line denotes what we will refer to as an instantaneous photon; it generates an interaction H_I' which is the difference of two Coulomb interactions. A wavy line represents a transverse photon. The thick vertical line denotes the nucleus and the inner electron, and the thin vertical line represents the outer electron. A prime on a figure citation denotes a graph in which the photon lines are reflected with respect to the corresponding unprimed graph.

both the "crossed" and "uncrossed" graphs.[22] This procedure doubles the contribution from Figs. 2(k)–2(n) and their reflections.

Our method of formulating approximations is nonrelativistic power counting.[23] We make power counting assignments for r_i, p_i, k, and k' which correspond to the regions of largest contribution in the various integrals which make up the matrix elements, namely,

$$p_1 \sim Z\alpha mc, \quad r_1 \sim a_0/Z ,$$
$$p_2 \sim (\tilde{Z}\alpha/n)mc, \quad r_2 \sim n^2 a_0/\tilde{Z} , \tag{2.10}$$
$$k, k' \sim \tilde{Z}/n^2 a_0 ,$$

where

$$\tilde{Z} \equiv Z - 1 . \tag{2.11}$$

The momentum and coordinate assignments are the Bohr values, while, as noted above, the k and k' assignments are the reciprocals of the radius of the outer electron.

These assignments are estimates and serve to determine which parts of the matrix elements we calculate exactly. To check these power counting estimates we examine other regions of the integrals in the matrix element. Because of cancellations

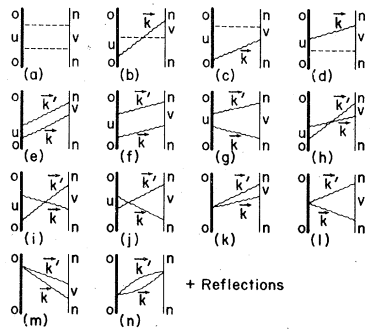

FIG. 2. Two-photon graphs—the notation is the same as in Fig. 1. The reflected graphs Fig. 2(b′)–2(n′) are not shown. Figure 2(a) does not have a reflection.

the nominal values obtained by power counting are often larger than the final answer. (See appendixes.)

III. CALCULATION

A. One instantaneous photon

The matrix element corresponding to Fig. 1(a), which involves just one instantaneous photon, is

$$M_I = \langle \Psi_0 | H_I' | \Psi_0 \rangle = e^2 \langle 1s, n | r_{12}^{-1} - r_2^{-1} | 1s, n \rangle . \quad (3.1)$$

We can replace $1/r_{12}$ by $1/r_>$, where $r_>$ is the greater of r_1 and r_2, because the initial and final states of electron 1 are both s states. M_I is nonvanishing only when the "outer" electron is inside the "inner" electron, that is, when $r_2 < r_1$. We will restrict our attention to states with $l \gg 1$ so that the outer particle is almost always far from the nucleus. Approximating $\psi_{nlm}(\vec{r}_2)$ by its form for $r_2 \lesssim a_0/Z$, the effective range of the inner electron, we find

$$M_I \approx -\frac{Ze^2}{a_0}\left(\frac{Z-1}{Z}\right)^{2l+3} \frac{l}{n^{2l+4}} \frac{(n+l)!}{(n-l-1)!(2l+1)!} . \quad (3.2)$$

For $l = n-1$, this reduces to[24]

$$M_I(l=n-1) \approx -\frac{Ze^2}{a_0}\left(\frac{Z-1}{Z}\frac{1}{n}\right)^{2n+1} , \quad (3.3)$$

a contribution which is negligible compared to the one-transverse–one-instantaneous contribution and the two-transverse-photon contribution calculated below.

B. One transverse photon

The matrix elements corresponding to Fig. 1(b) and its reflection 1(b′) each vanish, for in our formalism a system cannot go from an s state to an s state and emit a transverse photon, real or virtual.

C. Two instantaneous photons

The contribution M_{II} of the two instantaneous photon graph of Fig. 2(a) has been computed previously,[12-14] with results noted in the Introduction. We give a brief sketch of the analysis in Appendix A.

D. One instantaneous and one transverse photon

We are here concerned with the contribution M_{IT} of the graphs of Fig. 2(b)–2(d) and their reflections. We have

$$M_{IT} = \frac{\hbar e^2}{(2\pi)^2 m^2 c} \int \frac{d^3k}{k} \sum_{\vec{\epsilon}} \sum_{u,v} \langle \Psi_0 | \mathfrak{M}_{IT} | \Psi_0 \rangle , \quad (3.4)$$

in which

$$\mathfrak{M}_{IT} = \sum_\gamma \mathfrak{M}_\gamma , \quad (3.5)$$

where the $\mathfrak{M}_\gamma$'s are associated with the six different graphs. We often use the notation

$$X_j(\pm\vec{k}) \equiv \exp(\pm i \vec{k} \cdot \vec{r}_j), \quad j = 1 \text{ or } 2 . \quad (3.6)$$

u and v are states associated with electrons 1 and 2, respectively. We then have

$$\mathfrak{M}_{2b} = \vec{p}_2 \cdot \vec{\epsilon} X_2(\vec{k}) | 1s, v \rangle \langle 1s, v | H_I' | u, n \rangle \langle u, n | \vec{p}_1 \cdot \vec{\epsilon} X_1(-\vec{k}) \times [(E_{nv} - E_k)(E_{0u} - E_k)]^{-1} , \quad (3.7)$$

$$\mathfrak{M}_{2b'} = \vec{p}_1 \cdot \vec{\epsilon} X_1(\vec{k}) | u, n \rangle \langle u, n | H_I' | 1s, v \rangle \langle 1s, v | \vec{p}_2 \cdot \vec{\epsilon} X_2(-\vec{k}) \times [(E_{0u} - E_k)(E_{nv} - E_k)]^{-1} , \quad (3.8)$$

$$\mathfrak{M}_{2c} = H_I' | u, v \rangle \langle u, v | \vec{p}_2 \cdot \vec{\epsilon} X_2(\vec{k}) | u, n \rangle \langle u, n | \vec{p}_1 \cdot \vec{\epsilon} X_1(-\vec{k}) \times [(E_{0u} + E_{nv})(E_{0u} - E_k)]^{-1} , \quad (3.9)$$

$$\mathfrak{M}_{2c'} = H_I' | u, v \rangle \langle u, v | \vec{p}_1 \cdot \vec{\epsilon} X_1(\vec{k}) | 1s, v \rangle \langle 1s, v | \vec{p}_2 \cdot \vec{\epsilon} X_2(-\vec{k}) \times [(E_{0u} + E_{nv})(E_{nv} - E_k)]^{-1} , \quad (3.10)$$

$$\mathfrak{M}_{2d} = \vec{p}_2 \cdot \vec{\epsilon} X_2(\vec{k}) | 1s, v \rangle \langle 1s, v | \vec{p}_1 \cdot \vec{\epsilon} X_1(-\vec{k}) | u, v \rangle \langle u, v | H_I' \times [(E_{nv} - E_k)(E_{0u} + E_{nv})]^{-1} , \quad (3.11a)$$

$$\mathfrak{M}_{2d'} = \vec{p}_1 \cdot \vec{\epsilon} X_1(\vec{k}) | u, n \rangle \langle u, n | \vec{p}_2 \cdot \vec{\epsilon} X_2(-\vec{k}) | u, v \rangle \langle u, v | H_I' \times [(E_{0u} - E_k)(E_{0u} + E_{nv})]^{-1} , \quad (3.11b)$$

where

$$E_{0u} \equiv E_0 - E_u, \quad E_{nv} \equiv E_n - E_v, \quad E_k \equiv \hbar k c . \quad (3.12)$$

E_0 and E_n, the energies of the unperturbed states of electrons 1 and 2, respectively, are defined by Eq. (2.8).

With P_2 a Legendre polynomial and a caret denoting a unit vector, and making the approximations described in Sec. I, we obtain as the leading order term for M_{IT}

$$M_{IT} \approx -\frac{\hbar e^2 \alpha_d}{(2\pi^2) m c} \times \int \frac{d^3k}{k} \left\langle \psi_n(2) \left| e^{i\vec{k}\cdot\vec{r}_2} \frac{P_2(\hat{k}\cdot\hat{r}_2)}{r_2^3} \right| \psi_n(2) \right\rangle . \quad (3.13)$$

Some details are provided in Appendix B.

The power-counting estimate of M_{IT} is of order

$\tilde{Z}^5\alpha^3mc^2/Z^4n^{10}$. The leading corrections from making the dipole approximation for the inner electron are of order $\tilde{Z}^6\alpha^4mc^2/Z^4n^{11}$, those from neglecting $|E_{nv}/E_{0u}|$ and $|E_{nv}|/E_k$ are of order $\tilde{Z}^6\alpha^4mc^2/Z^4n^{10}$ and $\tilde{Z}^5\alpha^5mc^2/Z^2n^8$, respectively, and those from neglecting $E_k/|E_{0u}|$ are of order $\tilde{Z}^6\alpha^2mc^2/Z^6n^{12}$ (See Appendix D). Note that we are neglecting terms of order n^{-8}, while the dominant term goes as n^{-10}; this will be valid for n large but not too large, since the coefficient of the n^{-8} term is much smaller than the coefficient of the n^{-10} term. Clearly, however, the n^{-8} term must ultimately win (assuming it does not get cancelled) for n sufficiently large, or equivalently, for R sufficiently large.

E. Two transverse photons

In this section we consider the contribution M_{IT} of the graphs of Figs. 2(e)–2(n) and their reflections. We have

$$M_{TT}=\frac{\hbar^2e^4}{m^2c^2(2\pi)^4}\int\frac{d^3k}{k}\int\frac{d^3k'}{k'}\sum_{\vec{\epsilon},\vec{\epsilon}'}\sum_{u,v}\langle\Psi_0|\mathfrak{M}_{TT}|\Psi_0\rangle, \quad (3.14)$$

where

$$\mathfrak{M}_{TT}=\sum_\delta \mathfrak{M}_\delta\eta_\delta . \quad (3.15)$$

$\eta_\delta=1$ for Figs. 2(e)–2(j) and their reflections, but, in line with a remark above on counting certain figures twice, $\eta_\delta=2$ for Figs. 2(k)–2(n) and their reflections.

In arriving at Eqs. (3.16)–(3.20), we recognized that we can replace $\vec{k}$ by $-\vec{k}$ and/or $\vec{k}'$ by $-\vec{k}'$ since we ultimately integrate over $\vec{k}$ and $\vec{k}'$. In labeling reflected diagrams, the label $\vec{k}'$ is arbitrarily assigned to the second photon to interact with the outer electron. The $\mathfrak{M}_\delta$'s are given by

$$\begin{aligned}\mathfrak{M}_{2e}+\mathfrak{M}_{2e'}+\mathfrak{M}_{2f}+\mathfrak{M}_{2f'}+\mathfrak{M}_{2g}+\mathfrak{M}_{2g'}&=(1/m^2)\vec{p}_1\cdot\vec{\epsilon}'X_1(-\vec{k}')\vec{p}_2\cdot\vec{\epsilon}'X_2(\vec{k}')|u,v\rangle\langle u,v|\vec{p}_1\cdot\vec{\epsilon}X_1(-\vec{k})\vec{p}_2\cdot\vec{\epsilon}X_2(\vec{k})\\&\times\{[(E_{nv}-E_{k'})(-E_k-E_{k'})(E_{0u}-E_k)]^{-1}+[(E_{0u}-E_{k'})(-E_k-E_{k'})(E_{nv}-E_k)]^{-1}\\&+[(E_{nv}-E_{k'})(E_{0u}+E_{nv})(E_{0u}-E_k)]^{-1}+[(E_{nv}-E_k)(E_{0u}+E_{nv})(E_{0u}-E_{k'})]^{-1}\\&+[(E_{nv}-E_{k'})(E_{0u}+E_{nv})(E_{nv}-E_k)]^{-1}+[(E_{0u}-E_{k'})(E_{0u}+E_{nv})(E_{0u}-E_k)]^{-1}\},\end{aligned} \quad (3.16)$$

$$\begin{aligned}\mathfrak{M}_{2h}+\mathfrak{M}_{2h'}+\mathfrak{M}_{2i}+\mathfrak{M}_{2i'}+\mathfrak{M}_{2j}+\mathfrak{M}_{2j'}&=(1/m^2)\cdot\vec{p}_1\cdot\vec{\epsilon}X_1(-\vec{k})\vec{p}_2\cdot\vec{\epsilon}'X_2(\vec{k}')|u,v\rangle\langle u,v|\vec{p}_1\cdot\vec{\epsilon}'X_1(-\vec{k}')\vec{p}_2\cdot\vec{\epsilon}X_2(\vec{k})\\&\times\{[(E_{0u}-E_{k'})(-E_k-E_{k'})(E_{nv}-E_{k'})]^{-1}+[(E_{0u}-E_k)(-E_k-E_{k'})(E_{nv}-E_k)]^{-1}\\&+[(E_{0u}+E_{nv}-E_{k'}-E_k)(E_{0u}-E_{k'})(E_{nv}-E_{k'})]^{-1}\\&+[(E_{0u}-E_k)(E_{0u}+E_{nv}-E_k-E_{k'})(E_{nv}-E_k)]^{-1}\\&+[(E_{nv}-E_{k'})(E_{nv}-E_k)(E_{0u}+E_{nv}-E_k-E_{k'})]^{-1}\\&+[(E_{0u}-E_k)(E_{0u}+E_{nv}-E_k-E_{k'})(E_{0u}-E_{k'})]^{-1}\},\end{aligned} \quad (3.17)$$

$$\begin{aligned}\mathfrak{M}_{2k}+\mathfrak{M}_{2l}+\mathfrak{M}_{2m}&=\tfrac{1}{2}m^{-1}\vec{\epsilon}\cdot\vec{\epsilon}'X_1(-\vec{k}-\vec{k}')\vec{p}_2\cdot\vec{\epsilon}'X_2(\vec{k}')|u,v\rangle\langle u,v|\vec{p}_2\cdot\vec{\epsilon}X_2(\vec{k})\\&\times\{[(E_{nv}-E_{k'})(-E_k-E_{k'})]^{-1}+[(E_{nv}-E_k)(E_{nv}-E_{k'})]^{-1}+[(-E_k-E_{k'})(E_{nv}-E_k)]^{-1}\},\end{aligned} \quad (3.18)$$

$$\begin{aligned}\mathfrak{M}_{2k'}+\mathfrak{M}_{2l'}+\mathfrak{M}_{2m'}&=\tfrac{1}{2}m^{-1}\vec{p}_1\cdot\vec{\epsilon}'X_1(-\vec{k}')|u,v\rangle\langle u,v|\vec{p}_1\cdot\vec{\epsilon}X_1(-\vec{k})\vec{\epsilon}\cdot\vec{\epsilon}'X_2(\vec{k}+\vec{k}')\\&\times\{[(E_{0u}-E_{k'})(-E_k-E_{k'})]^{-1}+[(E_{0u}-E_{k'})(E_{0u}-E_k)]^{-1}+[(-E_k-E_{k'})(E_{0u}-E_k)]^{-1}\},\end{aligned} \quad (3.19)$$

$$\mathfrak{M}_{2n}+\mathfrak{M}_{2n'}=\tfrac{1}{4}\,2\vec{\epsilon}\cdot\vec{\epsilon}'X_1(-\vec{k}-\vec{k}')|u,v\rangle\langle u,v|\vec{\epsilon}\cdot\vec{\epsilon}'X_2(\vec{k}+\vec{k}')\times\{[(-E_k-E_{k'})]^{-1}\}, \quad (3.20)$$

where we have used the notation of (3.12). [The appearance of u in Eq. (3.18) is formal and only a matter of convenience; in substituting (3.18) into (3.15) one uses $\sum_u|u\rangle\langle u|=1$. Similarly, the appearance of v in Eq. (3.19) and of u and v in Eq. (3.20) is formal.]

Next we apply the approximations we explained in Sec. I to obtain the leading term for M_{TT}:

$$M_{TT}\approx-\frac{e^2\hbar\alpha_d}{mc(2\pi)^4}\int d^3k\int\frac{d^3k'}{(k+k')}[1+(\hat{k}\cdot\hat{k}')^2]\times\langle\psi_n(2)|\exp[i(\vec{k}+\vec{k}')\cdot\vec{r}_2]|\psi_n(2)\rangle . \quad (3.21)$$

The power-counting estimate of M_{TT} is of order $\tilde{Z}^5\alpha^3mc^2/Z^4n^{10}$. The leading corrections from making the dipole approximation for the inner electron are of order $\tilde{Z}^5\alpha^5mc^2/Z^2n^{10}$, those from neglecting $|E_{nv}|/E_k$ and $|E_{nv}|/E_{k'}$, and $|E_{nv}/E_{0u}|$ are of order $\tilde{Z}^5\alpha^7mc^2/n^7$ and $\tilde{Z}^6\alpha^6mc^2/Z^2n^9$, respectively, and those from neglecting $E_k/|E_{0u}|$ and $E_{k'}/|E_{0u}|$ are of order $\tilde{Z}^6\alpha^2mc^2/Z^6n^{12}$.

In Sec. III F we will evaluate M_{IT} (3.13) and M_{TT} (3.21) without further approximations. Their sum gives the leading two-photon retardation contribution to the high Rydberg states which, judging from

the estimates of the corrections, is the leading retardation term for l sufficiently large and n such that $(\bar{Z}/Z^2\alpha)^{1/2} \ll n \ll 1/Z\alpha$.

F. Evaluation

We turn now to the evaluation of the integrals in M_{IT} and M_{TT}. The integrals in M_{IT} and M_{TT} exist for the $l \gg 1$ case under consideration as they stand. We would, however, prefer to rewrite M_{IT} and M_{TT} as matrix elements of the form $\langle\psi_n(2)|\cdots|\psi_n(2)\rangle$, with the entity in the center then identifiable as a contribution to the effective potential. If we do so, however, nonconvergent integrals arise. We therefore introduce convergence factors $\exp(-\mu k)$ and $\exp(-\mu' k')$ which allow us to interchange the $\vec{k}$ and $\vec{r}_2$ and the $\vec{k}'$ and $\vec{r}_2$ integrations without introducing divergent integrals; at the appropriate point we set μ and μ' equal to zero. [The use of this cutoff is purely technical; we could perform the integration in the original order, and then seek an effective potential contribution operator whose diagonal matrix element with respect to $\psi_n(\vec{r}_2)$ gives the same numerical result. All integrals as originally defined are finite and independent of the order of integration; after making the various approximations, the integrals are finite only for a particular order.]

We rewrite Eq. (3.13) for M_{IT} as

$$M_{IT} \approx [\hbar e^2 \alpha_d/(2\pi)^2 mc]\langle\psi_n(2)|J(2)|\psi_n(2)\rangle, \quad (3.22)$$

where

$$J(2) = -\frac{2}{r_2^3} \lim_{\mu\to 0} \int \frac{d^3k}{k} \exp(i\vec{k}\cdot\vec{r}_2 - \mu k) P_2(\hat{k}\cdot\hat{r}_2). \quad (3.23)$$

Upon expansion of $\exp(i\vec{k}\cdot\vec{r}_2)$, retaining only its $l=2$ component, we arrive at

$$J(2) = \frac{8\pi}{r_2^3} \lim_{\mu\to 0} \int_0^\infty e^{-\mu k} j_2(kr_2) k\, dk. \quad (3.24)$$

The integral is a standard one,[25] and we obtain

$$M_{IT} \approx (4\hbar e^2 \alpha_d/\pi mc)\langle\psi_n(2)|r_2^{-5}|\psi_n(2)\rangle. \quad (3.25)$$

The two-transverse-photon term M_{TT} from (3.21) may be written as an expression where the integrals over $\vec{k}$ and $\vec{k}'$ are inside the matrix element. We write

$$M_{TT} \approx -\frac{\hbar e^2 \alpha_d}{(2\pi)^4 mc} \lim_{\mu'\to 0} \lim_{\mu\to 0} \langle\psi_n(2)|\left(\int d^3k \int \frac{d^3k'}{(k+k')} [1+(\hat{k}\cdot\hat{k}')^2] \exp[i(\vec{k}+\vec{k}')\cdot\vec{r}_2 - \mu k - \mu' k']\right)|\psi_n(2)\rangle. \quad (3.26)$$

After integrations over directions $\hat{k}$ and $\hat{k}'$, we find

$$\{\ \} = (4\pi)^2 \int_0^\infty k^2\, dk \int_0^\infty k'^2 \frac{dk'}{k+k'} \tfrac{4}{3}[j_0(kr_2) j_0(k'r_2) + \tfrac{2}{3} j_2(kr_2) j_2(k'r_2)] \exp(-\mu k - \mu' k'). \quad (3.27)$$

Employing the integral representation

$$(k+k')^{-1} = \int_0^\infty \exp[-(k+k')\eta]\, d\eta \quad (3.28)$$

to split the k and k' integrals, and the parametric representation[26]

$$j_2(qr) = (qr)^{-2}\left(\frac{1}{t}\frac{d}{dt}\right)^2 j_0(tqr)\Big|_{t=1}, \quad (3.29)$$

we can now perform the remaining integrations over k, k', and η.[27] Our answer for M_{TT} is

$$M_{TT} \approx \frac{-5}{4\pi} \frac{\hbar e^2 \alpha_d}{mc} \left\langle\psi_n(2)\left|\frac{1}{r_2^5}\right|\psi_n(2)\right\rangle. \quad (3.30)$$

Finally, the combined two-photon term ΔE_{ret}, where one or both of the photons is transverse, is given by the sum of (3.25) and (3.30). We have

$$\Delta E_{\text{ret}} = \frac{11}{4\pi} \frac{\hbar e^2 \alpha_d}{mc} \left\langle\psi_n(2)\left|\frac{1}{r_2^5}\right|\psi_n(2)\right\rangle. \quad (3.31)$$

IV. CONCLUSION

The presence of the $1/R^5$ term presents a new possibility for detecting retardation potentials in atomic and molecular systems. For Rydberg states of helium with sufficiently large l and n, it contributes an order $\alpha^3 mc^2/n^{10}$ energy correction. Previous discussions[28,29] of the energy levels of helium have indicated that the two-photon graphs we consider give an order $\alpha^5 mc^2$ contribution, where, however, powers of n are not counted. These discussions presume that most of the contribution of the outer electron comes from a region several Bohr radii from the nucleus. The perturbation expansions are based on this assumption. For states where the outer electron spends virtually no time around the nucleus, these expansions no longer are valid. We must use the alternate techniques employed in this paper and keep track of powers of n.

As was discussed previously, Bernabéu and Tarrach,[21] using dispersion relations, recently calculated the retardation correction to the $-\frac{1}{2}(Ze)^2(\alpha_d/R^4)$ leading term for the interaction potential between a charged (Ze) particle and a neutral polarizable system. Their answer, $[11(Ze)^2\alpha_d\hbar/4\pi mcR^5]$, while not applicable to Rydberg states of atoms, is formally the same

as ours, where α_d in our case is the dipole polarizability of the core ion of the Rydberg state. It is quite surprising that thirty diagrams and much analysis, or dispersion relations and much analysis, give such a simple answer depending only on the polarizability of the inner system, a few fundamental constants, and the distance R. Some insight into the reason for the simple answer has been given by a recent work[30] of ours in which, with no pretense of rigor, we are able to show with very little work that zero-point energy fluctuations of the electromagnetic field on the identical classical problem give rise to an energy change of the field which goes as $(Ze)^2\alpha_d\hbar/mcR^5$ for $R\sim\infty$. Further, a little more care gives the proper coefficient not only for the electric-polarizability term but also for the magnetic-polarizability term.

Since we are concerned with a very large value of l, the electron will therefore spend little time near the origin. With negligible error, we can assume Eq. (1.4) to be valid for all R, and tabulate the energy shift by using the known expectation value of $1/R^5$ for a hydrogenic state.

Note added in proof. As opposed to the various energy shifts discussed in the text, the possibility of transitions from the high Rydberg state causes the level to have a width. For a helium atom with the outer electron that has effective quantum numbers $n=15$ and $l=14$, the radiative width is approximately one hundred times the R^{-5} shift under consideration, making it more difficult to isolate the shift; an experimental check of this term will have to be performed with very good statistics. One might choose the value of l to be in the range where the ratio of the width to the shift is near its minimum value.

Using unitary transformations to simplify the Hamiltonian, E. A. Power, in an as yet unpublished work, has recently rederived the R^{-5} term. This effort, as that of Bernabéu and Tarrach,[21] does not treat the charged polarizable system-point charge case under consideration in this paper.

By examining the next terms in the various expansions considered above, we have obtained the R^{-6} contribution; the results will be submitted for publication shortly. Perhaps remarkably and perhaps not, the nonrelativistic nonadiabatic term is exactly cancelled!

It has been found that the vacuum fluctuation approach gives a rapid and exact result for various retardation effects, including the $1/R^3$ electron-electron interaction; in addition, we have found a new retardation effect, a $1/R^2$ correction to the image $1/R$ potential of a charge interacting with a perfectly conducting wall.

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APPENDIX A: APPROXIMATIONS IN EVALUATION OF M_{II}

In this appendix we consider the contribution of the two-instantaneous-photon graph M_{2a}. This term has been extensively discussed elsewhere so we merely outline our approach emphasizing an aspect of the power counting arguments which we found to be of use in other parts of the calculation.

The matrix element which corresponds to Fig. 2(a) is

$$M_{II}=\sum_{u,v}{}' \frac{|\langle 1s,n|H_I'|u,v\rangle|^2}{(E_0-E_u)+(E_n-E_v)}. \tag{A1}$$

We write

$$M_{II}=e^4\sum_{u,v}{}' \frac{|\langle 1s,n|K(1,2)|u,v\rangle|^2}{(E_0-E_u)+(E_n-E_v)}, \tag{A2}$$

with

$$K(1,2)=\sum_{m=0}^{\infty}\left(\frac{r_<}{r_>}\right)^m(1/r_>)P_m(r_>\cdot r_<)-1/r_2, \tag{A3}$$

where $r_>$ is the greater of r_1 and r_2, and $r_<$ the lesser. We neglect the contribution of the integrals in (A2) where $r_2<r_1$ since, as we showed in the evaluation of M_I, the matrix elements are negligible for n and l sufficiently large. Further, we rewrite the energy denominator in (A2) using the identity

$$\frac{1}{A+B}=\frac{1}{A}-\frac{1}{A}B\frac{1}{A+B}, \tag{A4}$$

with $A=E_0-E_u$ and $B=E_n-E_v$. The first term gives rise to the static dipole, quadrupole, etc., polarization potentials; the second term gives the nonadiabatic corrections.

A question which frequently arises in this calculation is the size of the nonadiabatic correction compared to the static term. We obtain as the dipole nonadiabatic correction for this case

$$V_{\text{nonad}}=-\beta_{\text{nonad}}\left\langle\psi_n(2)\left|\frac{\vec{r}_2}{r_2^3}\cdot(E_n-H_2)\frac{\vec{r}_2}{r_2^3}\right|\psi_n(2)\right\rangle, \tag{A5}$$

where

$$\beta_{\text{nonad}}=\frac{e^4}{3}\sum_u\frac{|\langle\psi_0(1)|\vec{r}_1|u\rangle|^2}{(E_0-E_u)^2}. \tag{A6}$$

We might expect that E_n-H_2 in (A5) is to be power counted as order $(\tilde{Z}\alpha)^2mc^2/n^2$ with both E_n and $H_2=p_2^2/2m-\tilde{Z}e^2/r_2$ being of that nominal order. How-

ever, we shall see that, in general, it can be counted as $(\tilde{Z}\alpha)^2 mc^2/n^3$ and in this example it is effectively of higher order. Since $(E_n - H_2)\psi_n(2) = 0$, we may rewrite (A5) in a form containing commutators as

$$V_{\text{nonad}} = -\tfrac{1}{2}\beta_{\text{nonad}}\left\langle \psi_n(2)\left|\left[\frac{\vec{r}_2}{r_2^3},(E_n - H_2)\right]\cdot\frac{\vec{r}_2}{r_2^3} + \frac{\vec{r}_2}{r_2^3}\cdot\left[(E_n - H_2),\frac{\vec{r}_2}{r_2^3}\right]\right|\psi_n(2)\right\rangle . \tag{A7}$$

The commutator of H_2 with $\vec{r}_2/r_2^3$ removes one p_2 and one r_2 from the matrix element and replaces them by $\hbar$. Since (2.10) would suggest that $p_2 r_2$ is of order n, the effect is to reduce the nominal order of V_{nonad} by $1/n$. This result is applicable in other matrix elements and throughout this calculation we power count $E_n - H_2$ as of order $(Z\alpha)^2 mc^2/n^3$. At this point the power count of V_{nonad} is of order $(\tilde{Z}/Z)^6\alpha^2 mc^2/n^{11}$. Further cancellations remove the leading term and simplify (A7) to the form given in (1.3). [Indeed, (A7) can be written as a *double* commutator.] There V_{nonad} is found to have the actual order of $(\tilde{Z}/Z)^6\alpha^2 mc^2/n^{12}$.

APPENDIX B: APPROXIMATIONS IN EVALUATION OF M_{IT}

We outline the derivation of the leading term of M_{IT} given in (3.13). We begin by observing that each primed term is the adjoint of some unprimed term. (For example, $\mathfrak{M}_{2c'}$ is the adjoint of $\mathfrak{M}_{2d}$.) We can therefore reexpress M_{IT} as twice the real part (Re) of the contributions of the unprimed terms.

M_{IT} is defined by Eqs. (3.4)–(3.11b). Several approximations are employed. The first is the dipole approximation for the inner electron in which we replace $X_1(\pm\vec{k})$ by unity. We then have, with t any normalized state of the second electron,

$$\langle 1s, t|\vec{p}_1\cdot\vec{\epsilon}|u,t\rangle = (imE_{0u}/\hbar)\langle 1s|\vec{r}_1\cdot\vec{\epsilon}|u\rangle . \tag{B1}$$

We will also use the complex conjugate of (B1). In the dipole approximation, the only excited states u are states with orbital angular momentum $l = 1$. We can, therefore without further approximation, replace H_I' by its dipole term. If, further, we neglect the possibility of the second electron lying inside the first, we can replace H_I' by $e^2\vec{r}_1\cdot\vec{r}_2/r_2^3$. Since we must ultimately sum over the orbital-angular-momentum projections +1, 0, and −1 of the u states, we can make the replacement

$$\langle 1s|\vec{r}_1\cdot\vec{\epsilon}|u\rangle\langle u|\vec{r}_1\cdot\vec{r}_2/r_2^3|1s\rangle \to -\tfrac{1}{3}|\langle 1s|\vec{r}_1|u\rangle|^2(\vec{\epsilon}\cdot\vec{r}_2)/r_2^3 . \tag{B2}$$

We now neglect $|E_{nv}|$ with respect to $|E_{0u}|$ and E_k. We can then use $\sum_v |v\rangle\langle v| = 1$, the unit operator, to sum over v. At this stage we find

$$M_{IT} = \mathrm{Re}\left(\frac{ie^2}{(2\pi)^2 mc}\right)\int\frac{d^3k}{k}\left(\sum_u \frac{2e^2}{3}\,\frac{|\langle 1s|\vec{r}_1|u\rangle|^2}{E_{0u} - E_k}\times\sum_{\vec{\epsilon}}\langle n|e^{i\vec{k}\cdot\vec{r}_2}T|n\rangle\right), \tag{B3}$$

where the commutator T is given by

$$T = [\vec{p}_2\cdot\vec{\epsilon},\vec{r}_2\cdot\vec{\epsilon}/r_2^3] = -i\hbar/r_2^3 + 3i\hbar(\vec{r}_2\cdot\vec{\epsilon})^2/r_2^5 . \tag{B4}$$

Summing over the polarization vector, we then have

$$\sum_{\vec{\epsilon}} T = -\frac{2i\hbar P_2(\hat{k}\cdot\hat{r}_2)}{r_2^3} . \tag{B5}$$

If, finally, we neglect E_k with respect to E_{0u}, the quantity in the curly brackets reduces to $-\alpha_d$, and, observing that only the P_2 component of $e^{i\vec{k}\cdot\vec{r}_2}$ survives and that the matrix element in (B3) is therefore pure imaginary, we obtain Eq. (3.13). Thus, the contributions associated with 2(b)–2(d) have effectively the same numerators and, neglecting E_{nv}, the denominators are $-E_k(E_{0u} - E_k)$, $E_{0u}(E_{0u} - E_k)$, and $-E_k E_{0u}$, respectively. Since E_k is smaller than E_{0u}, the 2(c) contribution is smaller than that associated with 2(b) or 2(d), but the leading terms of the latter cancel. This behavior is reflected in the power-counting estimates of the constituents of M_{IT}. All power-counting estimates use Eq. (2.10) and the further estimates $|E_{0u}| \sim Z^2 e^2/a_0$ and $|E_{nv}| \sim \tilde{Z}^2 e^2/n^3 a_0$. The energy estimates are obtained by assuming that the major contributions come from principal quantum numbers for the case of u from bound states and the near continuum, and for v from states near n. It should be clear that all of the power-counting estimates quoted could very likely be reduced by virtue of cancellation and commutation relations (see Appendix A) not accounted for.

APPENDIX C: APPROXIMATIONS IN EVALUATION OF M_{TT}

The power-counting estimates for the errors generated by making the dipole approximation for the inner electron, by neglecting $|E_{nv}/E_{0u}|$, $|E_{nv}/E_k|$, and $|E_{nv}/E_{k'}|$ and by neglecting terms of relative order $|E_k/E_{0u}|$ and $|E_{k'}/E_{0u}|$ are small; their values are given in Sec. III E. We convert the matrix elements of the first electron to the "length" form by using equations (B1) and (B2) of Appendix B. After this step the leading contribution to M_{TT} from Figs. 2(e)–2(j) and their reflections is

$$M_1 = -(2\hbar^2/m)S(\vec{\epsilon}\cdot\vec{\epsilon}')\times\langle n|\vec{p}_2\cdot\vec{\epsilon}X_2(\vec{k}+\vec{k}')\vec{p}_2\cdot\vec{\epsilon}'|n\rangle(E_k E_{k'})^{-1} , \tag{C1}$$

where

$$S \equiv \frac{e^4}{m^3c^2(2\pi)^4}\int\frac{d^3k}{k}\int\frac{d^3k'}{k'}\sum_{\vec{\epsilon},\vec{\epsilon}'}\,.$$

We have used the Thomas-Reiche-Kuhn sum rule

$$\sum_u E_{0u}|\langle 1s|\vec{r}_1|u\rangle|^2 = -\frac{3\hbar^2}{2m}\,. \tag{C2}$$

We note that because of cancellations the leading correction to M_1 is smaller than the terms which we are considering in this calculation.

The sum of the contributions from Figs. 2(k)–2(m) is denoted by M_2. Keeping terms through the requisite order, we immediately find

$$M_2 = -\tfrac{1}{2}M_1\,. \tag{C3}$$

Next, we use the same set of steps, used on the matrix elements from Fig. 2(e)–2(g) and their reflections, to evaluate the sum of the contributions, denoted by M_3, from Figs. 2(k′)–2(m′). We obtain through the requisite order

$$M_3 = \tfrac{1}{3}m^2S(\vec{\epsilon}\cdot\vec{\epsilon}')^2\langle n|X_2(\vec{k}+\vec{k}')|n\rangle \times\sum_u E_{0u}|\langle 1s|\vec{r}_1|u\rangle|^2 \times(E_k+E_{k'})^{-1}(-1+E_kE_{k'}/E_{0u}^2)\,. \tag{C4}$$

Similarly, through the necessary order, we find, the contribution M_4 from the remaining set of diagrams, Figs. 2(n) and 2(n′), namely, to be

$$M_4 = -\tfrac{1}{2}\hbar^2mS(\vec{\epsilon}\cdot\vec{\epsilon}')^2\langle n|X_2(\vec{k}+\vec{k}')|n\rangle(E_k+E_{k'})^{-1}\,. \tag{C5}$$

We can now write

$$M_{TT} = M_1 + 2(M_2+M_3+M_4) = 2(M_3+M_4)\,. \tag{C6}$$

Using (C2) we are left with twice the contribution of the second term in the integral of M_3. Employment of the definition of α_d, summation over the polarization vectors, and a slight rearrangement gives (3.21) as the leading part of M_{TT}.

APPENDIX D: ADDITIONAL DISCUSSION OF APPROXIMATIONS

Our first comment concerns the power counting of E_k and $E_{k'}$. As was noted earlier, the fact that the contribution to the integrals over $\vec{k}$ and $\vec{k}'$ from $k', k \gg 1/R$ is small, where R is the characterisitic size of r_2, is a consequence of the presence of the exponentials $\exp(\pm\vec{k}\cdot\vec{r}_2)$ and $\exp(\pm i\vec{k}'\cdot\vec{r}_2)$ in the matrix elements. Contributions to the integral from regions where k or k' are significantly less than $1/R$ are reduced by the reduction in the size of the phase space of $d\vec{k}$ or $d\vec{k}'$. (The argument can be made more explicit by actually estimating the integrals in non-nominal regions of contribution.) k and k' are therefore power counted as order $1/R$.

Another point that arises throughout the calculation is that the neglect of terms of relative order $E_k/|E_{0u}|$ and $E_{k'}/|E_{0u}|$ is performed at a later stage than the neglect of $E_{nv}/|E_{0u}|$, $|E_{nv}|/E_k$, and $|E_{nv}/|E_{k'}$. The latter three approximations are performed once the individual matrix elements are constructed. The relative errors introduced by their neglect are therefore with respect to rather large quantities. Nevertheless, as shown in their power-counting estimates, these omissions give only small absolute errors to the overall answer. The neglect of $E_k/|E_{0u}|$ and $E_{k'}/E_{0u}$, however, is performed after a considerable amount of cancellation between parts of the various matrix elements. In calculating M_{IT} (3.14) as in Appendix B, this procedure was shown explicitly. In constructing the leading part of M_{TT} (3.21), this process is far more elaborate. The individual matrix elements are expanded in a series of powers of $E_k/|E_{0u}|$ and $E_{k'}/|E_{0u}|$ and terms of relative order $E_k/|E_{0u}|$ and $E_{k'}|E_{0u}|$ are neglected in the leading nonvanishing term (3.21). The basis of this approximation ($E_k/|E_{0u}|$ and $E_{k'}/|E_{0u}| < 1$) is the counterpart in our calculation of the heuristic argument presented in Sec. I to suggest the conditions (1.5) under which the finiteness of the speed of light could play a role in the determination of the interaction of the outer electron with the core and therefore of the energy eigenvalues of high Rydberg states of atoms.

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[10]We note the coefficient of the R^{-7} term is modified if one allows the two atoms to have magnetic polarizabilities. Feinberg and Sucher (Ref. 6) have obtained a result analogous to (1.1) which includes these magnetic effects, and they note that for two hydrogen atoms and an asymptotic separation R the magnetic effects dominate.

[11]It may be interesting to note that the appearance of c in the numerator of V_{CP}, which falls off as R^{-7}, might suggest that the nonrelativistic limit of the full interaction V falls off less rapidly than R^{-7} (as indeed V_{VdW} does). We can write, presuming that the relativistic and nonrelativistic versions of the polarizabilities are essentially the same, that

$$\lim_{R\to\infty} R^7 V_{CP} = Ac,$$

where A is a constant, and therefore

$$\lim_{c\to\infty}\lim_{R\to\infty} R^7 V_{CP} = \infty .$$

If we can interchange the limiting processes, we then have, using

$$\lim_{c\to\infty} V_{CP} = V_{VdW},$$

that

$$\lim_{R\to\infty}\lim_{c\to\infty} R^7 V_{CP} = \lim_{R\to\infty} R^7 V_{VdW} = \infty,$$

which is in agreement with our assertion.

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