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Retardation effects and the vanishing as $R \sim \infty$ of the nonadiabatic R^{-6} interaction of the core and a high-Rydberg electron

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An electron in a high-Rydberg state will experience the Coulomb R^{-1} potential and the polarization R^{-4} potential. For R large compared to a_0/α, where α is the fine-structure constant—a_0/α is very large—it will also experience a retardation polarization R^{-5} potential. We here show that at very large R the nonrelativistic R^{-6} nonadiabatic potential which it experiences beyond a few Bohr radii is cancelled by retardation (or, better, vacuum fluctuation) effects.

I. INTRODUCTION

Recently the authors used standard time-ordered perturbation theory to calculate the leading retardation correction to the energy levels of a high-Rydberg state of an arbitrary neutral atom or positive ion[1]; the outer electron is effectively in a hydrogenlike state with high n and l quantum numbers. The energy shift can be expressed as the expectation value of an operator which is proportional to R^{-5}, where R is the separation of the outer electron and the nucleus. We are concerned only with n and l large, and therefore only with R large. The R^{-5} term arose from two-photon graphs. The contributions from the two instantaneous photon graphs, from the one instantaneous and one transverse photon graph, and from the two transverse graphs were labeled M_{II}, M_{IT}, and M_{TT}, respectively. Expressions for these contributions are given by Eqs. (I-A1), (I-3.4), and (I-3.14).[1] The expressions were evaluated only through terms of order R^{-5}.

It was pointed out that each of the three expressions also contained terms of order R^{-6}. The R^{-6} contributions from M_{II}, which involve only the static Coulomb interaction and are independent of the speed of light c, have been known for some time,[2] and represent the static quadrupole polarization potential and the leading (dipole) nonadiabatic potential. This term dominates at small R. At large R, however, it will be shown below that the contributions of M_{IT} and M_{TT} exactly cancel the nonadiabatic R^{-6} component of M_{II}. By large R, we mean,[1] for a neutral atom, a transit time comparable to a characteristic period, that is, $2R/c \gtrsim 2\pi a_0/(e^2/\hbar)$. We are thus in the region $R/a_0 \gtrsim \hbar c/e^2$, a region which has no meaning within the context of nonrelativistic physics, a domain defined by the limit $c \to \infty$.

II. CALCULATION

We use a prime on M to denote the component for which the operator behaves as r_2^{-6}, where we are now using r_2 rather than R for the separation of the outer electron and the nucleus. As noted above, M'_{II} is known and is written

$$M'_{II} = -\tfrac{1}{2}\alpha_q e^2\langle n|r_2^{-6}|n\rangle + M'_{II\beta}, \qquad (1)$$

where

$$M'_{II\beta} \equiv 3a_0\beta_{\text{nonad}}e^2\langle n|r_2^{-6}|n\rangle, \qquad (2)$$

and where, in turn,

$$\beta_{\text{nonad}} \equiv \frac{e^4}{3}\sum_u \frac{|\langle 1s|\vec{r}_1|u\rangle|^2}{E_{0u}^2}. \qquad (3)$$

α_q is the static electric quadrupole polarizability of the ionic core.

M_{IT} is given to sufficient accuracy by

$$M_{IT} = \frac{e^2\hbar}{2\pi^2 mc}\int\frac{d^3k}{k}\sum_u \frac{2e^2}{3}\,\frac{|\langle 1s|\vec{r}_1|u\rangle|^2}{E_{0u}-E_k}Q, \qquad (4)$$

where

$$Q \equiv \langle n|e^{i\vec{k}\cdot\vec{r}_2}P_2(\hat{k}\cdot\hat{r}_2)/r_2^3|n\rangle.$$

In our previous analysis we approximated the energy denominator by $1/E_{0u}$ and obtained an r_2^{-5} contribution. We now go one step further and write

$$(E_{0u}-E_k)^{-1} \approx E_{0u}^{-1} + E_k/E_{0u}^2. \qquad (5)$$

Using the second term, we have

$$M'_{IT} = \frac{\beta_{\text{nonad}}\hbar^2}{\pi^2 m}\int d^3k\,Q. \qquad (6)$$

The integral over $d\hat{k}$ is trivial. We then insert an exponential cutoff in k space in order to be able to interchange the order of integration over $\vec{r}_2$ and k without introducing a divergence. As discussed in I, this step is neither subtle nor dishonest, but a matter of convenience which enables us to write the contribution to the energy shift as the expectation value of a potential (The potential behaves as r_2^{-6}, and the expectation values of r_2^{-6} for hydrogenlike states are known.[3]) We find

$$M'_{IT} = (-4/\pi)\beta_{\text{nonad}} e^2 a_0 \langle n | I/r_2^3 | n \rangle , \quad (7)$$

where

$$I \equiv \lim_{\lambda \to 0} \int_0^\infty dk\, k^2 e^{-\lambda k} j_2(kr_2) . \quad (8)$$

The integral over k and the subsequent limit as λ goes to zero are straightforward to perform. We obtain the result

$$M'_{IT} = -2M'_{IIB} . \quad (9)$$

The extraction of the r_2^{-6} term from M_{TT}, given by Eq. (I-3.14), is relatively complicated. We follow the precedure used in I for obtaining the r_2^{-5} term. After we have integrated over $\hat{k}$ and $\hat{k}'$, we have

$$M_{TT} = \frac{4}{3\pi} \beta_{\text{nonad}} e^2 a_0 \int_0^\infty dk\, k^2 \times \int_0^\infty dk'\, k'^2 \langle n | [2j_0(kr_2) j_0(k'r_2) + j_2(kr_2) j_2(k'r_2)] | n \rangle . \quad (10)$$

Once again we employ exponential cutoffs on both k and k' in order to interchange the order of the integration of r_2 and k' or k. Subsequent integrals and limits are straightforward. We obtain

$$M'_{TT} = 3\beta_{\text{nonad}} e^2 a_0 \langle n | 1/r_2^6 | n \rangle , \quad (11)$$

which is identically equal to the nonadiabatic term in M'_{II}. Our final result is, therefore,

$$M'_{II} + M'_{IT} + M'_{TT} = \langle n | -\alpha_q e^2/2r_2^6 | n \rangle . \quad (12)$$

The terms in β_{nonad} vanish identically! Reverting to the notation R, the R^{-6} contribution to the interaction is

$$\tilde{V}(R) \equiv -\alpha_q e^2/2R^6 . \quad (13)$$

Since the nonadiabatic correction vanishes identically, it is natural to seek a simple explanation, but it may be difficult to do so in the present case since in some sense it is a higher-order term that vanishes, for the R^{-5} term does not vanish. A possible alternative attack might be a dispersion theoretic approach,[4] which has been used to obtain the R^{-5} term for the interaction of a charged particle and *neutral* polarizable system, *if* it could be extended to include a charged polarizable system.

A further comment on the distinction between small R, where a nonrelativistic theory can be meaningful, and R larger than a distance which is proportional to c, where nonrelativistic theory is meaningless, may be useful. We give a simple form of a potential, undoubtedly different from the physical potential, which also has this behavior. Consider the expression

$$v(R) = \frac{3e^2 a_0 \beta_{\text{nonad}}}{R^6} \left(\frac{1}{1 + (\alpha Z^2 R/a_0)} \right) .$$

$v(R)$ behaves as R^{-6} for $R/a_0 \ll 1/\alpha Z^2$, but vanishes to order R^{-7} for $R/a_0 \gg 1/\alpha Z^2$. Similarly, as was shown by Casimir and Polder,[5] at very large separations the Van der Waal–London R^{-6} interaction between neutral atoms does not exist when retardation is taken into account.[6]

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[1]E. J. Kelsey and L. Spruch, Phys. Rev. A (to be published). The various equations referred to in the present paper which have roman numeral I preceding them are in this particular work. The notation is taken from that paper. A derivation of the R^{-5} term and of a number of other long-range interactions, which is based on vacuum fluctuation on effects and is somewhat more physical, has been given by L. Spruch and E. J. Kelsey, Phys. Rev. A (to be published).

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