Retarded Long-Range Interaction in He Rydberg States

C. K. Au
Department of Physics, University of South Carolina, Columbia, South Carolina 29208

and

G. Feinberg
Department of Physics, Columbia University, New York, New York 10027

and

J. Sucher
Department of Physics, University of Maryland,
College Park, Maryland 20742

(Received 7 June 1984)

We calculate the energy shifts, in Rydberg states of helium, due to retardation corrections to the two-photon exchange potential. The correction to the level spacings is at the accuracy of existing measurements in the $n = 10$ states of neutral He. It may soon be possible for the first time to detect the effect of these corrections in atomic systems. Estimates of the energy shifts for high-Z He-like ions yield effects of several percent of the total spacing.

PACS numbers: 31.50.+w, 34.20.Fi

It is over 35 years since the first calculation of retarded van der Waals interactions was done by Casimir and Polder.[1] While there has been substantial theoretical progress[2] concerning these interactions, little has been done to observe them, except for macroscopic systems such as small mica plates.[3] The reason for the difficulty in observing retarded van der Waals interactions in atoms is that the retarded form of these interactions differs significantly from the nonretarded form only at large distances, typically many tens of atomic units, where the interaction energies are themselves very small.

Recent measurements of transitions in He Rydberg states[4] have reached the degree of accuracy at which the difference in retarded and nonretarded interactions between the Rydberg electron and the core might be observable.[5] For some such transitions, the accuracy of the measurements is a few kilohertz, and further improvements can be expected.[6] Theoretical calculations of the transition energies due to nonretarded interactions have been performed to a similar accuracy for some states.[7] It therefore seems timely to calculate the effect of retardation on Rydberg energy levels to an accuracy of 0.1 kHz. This can be done for hydrogenlike cores, with formalisms that have been previously developed.[8,9]

Since the total retarded van der Waals potential is complicated, it is useful to focus on those terms that can contribute to He Rydberg energy levels at the accuracy of 0.1 kHz. For the states of interest, the distance (R) of the Rydberg electron from the core is of the order of $100a$, where a is the Bohr radius. This means that the ratio a/R is of the same magnitude as the fine-structure constant α. Since 0.1 kHz is about 10^{-14} Ry, if a term in the interaction behaves as $\alpha^n(a/R)^m$ Ry in the region of interest, then in order to calculate the energy shifts to the required accuracy, we can drop terms for which $n+m>7$. This criterion allows the neglect of many of the terms in the general expression for the interaction, given in Ref. 8. However, it is not convenient to use an expansion in a/R for the actual calculations of the terms that we keep. To the required accuracy, it turns out that we need only keep terms involving the electric structure of the He$^+$ core. Furthermore, among these terms, multipoles beyond the octupole are again too small to keep.

Within these restrictions, it would be possible to carry out a complete calculation of the energy shifts, using our previous formalisms. However, we have not done quite that in this paper. Instead, we make use of the very precise calculations of the nonretarded energy shifts by Drachman.[7] The advantage of this is that we need not consider separately some terms calculated by Drachman that go beyond the two-photon–exchange interaction of our previous work. The price that we must pay is to understand which of the terms calculated by Drachman are included in our general formalism, so that we avoid double counting. This is straightforward within the accuracy of our calculation. A more general solution to the question of how to calculate energy shifts due to multiphonon exchange is more subtle, and will be described elsewhere. Here we present an outline of our calculation, and the results for the energy shifts in Rydberg helium and heliumlike atoms.

To the required accuracy, the energy shifts in the Rydberg states of heliumlike ions, arising from two-photon exchange between the inner hydrogenlike ionic core and the outer Rydberg electron, can be obtained from a previously derived formula for the potential for such an exchange.[8] The corrections to this formula, coming from the fact that the core is charged rather than neutral, are very small and can be neglected. This formula can be summarized as

$$V_{2\gamma}=\sum_{n=0}^{\infty} V_{2\gamma,E,n}, \tag{1}$$

with the potential in Hartrees given by

$$V_{2\gamma,E,n}=-\frac{1}{2}\frac{\alpha_{E,2^{n}+1}}{R^{4+2n}}+\frac{11}{4\pi}\frac{\alpha}{R^{5+2n}}\left(\frac{2n+3}{3}\right)\alpha_{E,2^{n}+1}+\frac{\alpha}{16\pi^2 R}\frac{d^{2n}}{dR^{2n}}\left(\int_0^\infty \frac{d\omega}{\pi}\frac{\rho_{E,n}(\omega)}{\omega R^4}J_E(\omega R)\right). \tag{2}$$

Here $\alpha_{E,2^{n}+1}$ is the static electric multipole polarizability for the core ion, and $\rho_{E,n}$ is the coefficient of t^n (t is the invariant momentum transfer) in a power-series expansion of the absorptive part $\rho_\epsilon(\omega,t)$ of the electric form factor for the scattering amplitude of a photon of energy ω by the ion, i.e.,

$$\rho_E(\omega,t)=\sum_{n=0}^{\infty}\rho_{E,n}(\omega)t^n. \tag{3}$$

The function $J_E(\omega R)$ is given by

$$J_E(z)=\frac{8}{z}[\tfrac{13}{4}z-\tfrac{1}{2}z^3+(3-5z^2+z^4)f(2z)+(6z-2z^3)g(2z)], \tag{4}$$

where the functions $f(z)$ and $g(z)$ are the auxiliary functions for the sine and cosine integrals, given by Gautschi and Cahill.[10]

The contribution of similar magnetic terms, discussed in Ref. 8, are too small to be of interest in neutral helium.

We can identify the first term in Eq. (2) as the classical electrostatic interaction between the Rydberg electron and the induced multipole moment of the ionic core. For the dipole and quadrupole, corresponding to $n=0$ and $n=1$, the effect of these terms has already been included in Drachman's calculation. For $n=0$, the second term in Eq. (2) coincides with the result found by Kelsey and Spruch[5] and by Bernabeu and Tarrach[11] for the asymptotic correction to the classical term. However, we will see that for the distances involved in existing measurements on Rydberg helium, this term by no means gives an accurate estimate of the correction to the potential.

To make contact with Drachman's calculation, we examine the expansion of J_E for small arguments:

$$J_E(\omega R)=8\left(\frac{3\pi}{2\omega R}-\frac{11}{4}+\frac{\pi}{2}\omega R+O(\omega^2R^2)\right). \tag{5}$$

If one substitutes the first term in this expansion into Eq. (2), one recovers, for $n=0$, Drachman's nonadiabatic β_1 term, and for $n=1$, his β_2 term. The terms generated by higher values of n in the sum[1] give higher multipole analogs of the nonadiabatic correction terms, all of which are too small for us to keep.

The second term in Eq. (5), upon substitution into Eq. (2), exactly cancels the generalized Kelsey-Spruch-Bernabeu-Tarrach (KSBT) term, for each value of n, when we use the relations

$$\alpha_{E,2^{n}+1}=\frac{1}{2\pi^2}\frac{(2n+2)!}{2}\int_0^\infty\frac{\rho_{E,n}(\omega)}{\omega}d\omega. \tag{6}$$

That is, there is no analog to the generalized KSBT term at small R.

In order to obtain the retardation correction to the terms calculated by Drachman, we define a correction potential, in Hartrees, by

$$V_n^{\mathrm{corr}}(R)=\frac{\alpha}{16\pi^2R}\frac{d^{2n}}{dR^{2n}}\left(\int_0^\infty\frac{d\omega}{\pi}\frac{\rho_{E,n}(\omega)}{\omega R^4}J_E^{\mathrm{corr}}(\omega R)\right), \tag{7}$$

where

$$J_E^{\mathrm{corr}}(\omega R)=J_E(\omega R)-\frac{12\pi}{\omega R}+22. \tag{8}$$

TABLE I. Expectation value (in kilohertz) of the retardation correction in $n = 10$ Rydberg states of neutral helium. The expectation values of the Kelsey-Spruch-Bernabeau-Tarrach term alone is given for comparison.

L	$\langle V^{\rm corr}\rangle$	$\langle V^{\rm KSBT}\rangle$ [a]
4	61.76	835.8
5	20.19	179.8
6	7.73	49.2
7	3.28	15.7
8	1.49	5.5
9	0.70	2.0

[a] $V^{\rm KSBT} = (99/128\pi)\alpha/R^5$.

TABLE II. Expectation values (in kilohertz) of the retardation correction in $n = 9-12$ Rydberg states of neutral helium.

	$\langle V^{\rm corr}\rangle$			
L	$n = 9$	$n = 10$	$n = 11$	$m = 12$
4	83.2	61.8	47.0	36.6
5	26.9	20.2	15.5	12.1
6	10.1	7.7	6.0	4.7
7	4.2	3.3	2.6	2.0
8	1.8	1.5	1.2	1.0
9		0.7	0.6	0.5
10			0.3	0.2
11				0.1

For $n > 0$, all contributions can be neglected to the accuracy with which we are working, at least in neutral helium, and so we make the further approximation of retaining only the $n = 0$ term in $\sum_n V_n^{\rm corr}$ and obtain

$$V^{\rm corr} \simeq \frac{\alpha}{16\pi^2 R^5}\int_0^\infty \frac{\rho_{E,0}(\omega)}{\pi\omega} J_E^{\rm corr}(\omega R)\, d\omega, \tag{9}$$

$$V^{\rm corr} \simeq \alpha^2/4R^4 + O(R^{-3}) + \dots\ . \tag{10}$$

Equations (9) and (10) imply that the leading term in $V^{\rm corr}$ at small distances behaves as R^{-4}, and is smaller than the classical term by a factor α^2 in neutral helium. Most of the correction that we calculate to the energies of Rydberg states in neutral He arises from this leading term. This correction has a similar magnitude to those arising from relativistic corrections to the polarizability and from mass polarization.[7]

The only quantity needed to calculate $V^{\rm corr}$ is the absorptive part of the electric form factor for the ion-photon Compton-scattering amplitude. To the required degree of accuracy, only the dipole approximation to this amplitude is needed, and recoil contributions to it can be neglected. This approximation to the amplitude has been shown previously[9] to be expressible in terms of the electric dipole oscillator strength $f_{J0} = 2m_e\omega_J|x_{J0}|^2$:

$$\rho_{E,0}(\omega) = \frac{2\pi^2\alpha}{m_e\omega^2}\sum_J{}' \omega_J f_{J0}\delta(\omega-\omega_J), \tag{11}$$

where the prime indicates that the continuum is included. For a hydrogenic ion core of charge Z, the oscillator strengths and excitation energies are known analytically. It is then straightforward to calculate the potential $V^{\rm corr}$ from Eq. (9), which we do by numerical summation and integration. To test the reliability of this procedure, we have computed the standard hydrogenic sum rules numerically, and compared with known analytic values. The results agree to within 0.03%.

The expectation values of this numerical potential in various Rydberg states of neutral helium were then computed; the results are given in Tables I and II. It can be seen that the KSBT term greatly overestimates the correction. For several of the

TABLE III. Expectation value (in megahertz) of the retardation correction in $n = 10$ Rydberg states of heliumlike ions of various charges.

L \ Z	10	20	30	40	50	60	70
4	13.8	57.8	122	199	285	379	479
5	4.3	16.9	34.2	54.3	76.4	100	124
6	1.5	5.8	11.3	17.5	24.2	31.1	38.2
7	0.61	2.2	4.1	6.3	8.5	10.8	13.2
8	0.26	0.88	1.6	2.4	3.2	4.0	4.9
9	0.11	0.36	0.65	0.95	1.3	1.6	1.9

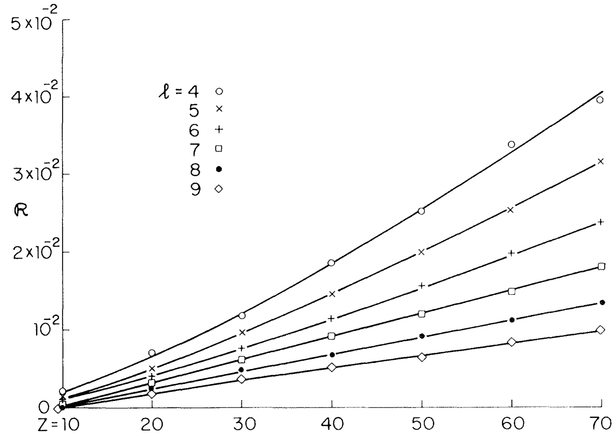

FIG. 1. The ratio $\mathscr{R}$ of the expectation value of the retardation correction potential to the expectation value of the classical potential for states of $n = 10$ and various L for heliumlike ions of several different charges.

$n = 10$ states, the retardation correction is similar in magnitude to reported experimental errors,[4] suggesting that some improvement in the experiment should make the observation of these corrections possible. The calculated corrections should be added to the results given by Drachman[7] to obtain the total level shifts in these states.

We have also calculated the expectation values of V^{corr} in the $n = 10$ Rydberg states of heliumlike ions of various Z from 10 to 70. The results, in megahertz, are given in Table III. To understand these results, we note that from simple scaling arguments, the classical term is proportional to $[(Z-1)/Z]^4$, whereas the retardation corrections increase roughly as Z^2.

This implies, as indicated in the table, that in high-Z heliumlike ions, the retardation correction becomes a larger fraction of the overall splitting. It can be seen from Fig. 1 that the ratio can be as large as several percent in some states of the ions of highest Z, suggesting that measurements on such ions, if they can be done, would be a good way to observe retardation corrections. In that connection, we must point out that at the highest Z values, some of the terms neglected in our calculation, such as magnetic and recoil terms, will become significant. Moreover, for large Z, a relativistic treatment of the inner electron becomes essential. There is no difficulty in principle in doing this if the experimental situation warrants it.

We thank Dr. R. Drachman, Dr. S. Lundeen, and Dr. L. Spruch for helpful conversations. This work was supported in part by the U.S. Department of Energy, by the National Science Foundation, and by the National Science Foundation EPSCoR program.

Note added.—The measurements of Palfrey and Lundeen[4] which show the need for this calculation are reported in the preceding Letter.

---

[1] H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).

[2] See D. Langbein, *Theory of van der Waals Attraction*, Springer Tracts in Modern Physics, Vol. 72 (Springer, Berlin, 1974); see also J. Sucher, in *Cargèse Lectures in Physics*, edited by M. Lévy (Gordon and Breach, New York, 1977), Vol. 7, pp. 43–110.

[3] J. N. Israelachvii and D. Tabor, Proc. Roy. Soc. London, Ser. A **331**, 19 (1972).

[4] S. L. Palfrey and S. R. Lundeen, preceding Letter [Phys. Rev. Lett. **53**, 1141 (1984)].

[5] This possibility for observing the effects of retardation was suggested by E. J. Kelsey and L. Spruch, Phys. Rev. A **18**, 15 (1978).

[6] S. Lundeen, private communication.

[7] R. J. Drachman, Phys. Rev. A **26**, 1228 (1982). For earlier work, see C. J. Kleinman *et al.*, Phys. Rev. **165**, 53 (1968); see also J. Callaway *et al.*, Phys. Rev. **168**, 12 (1968).

[8] G. Feinberg and J. Sucher, Phys. Rev. A **27**, 1958 (1983).

[9] C. K. Au, Phys. Rev. A **6**, 1232 (1972).

[10] W. Gautschi and W. F. Cahill, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1965), Chap. 5, p. 232.

[11] J. Bernabeu and R. Tarrach, Ann. Phys. (N.Y.) **102**, 323 (1976).