

## Evaluation of retardation energy shifts in a Rydberg helium atom

James F. Babb and Larry Spruch

*Department of Physics, New York University, New York, New York 10003*

(Received 15 October 1987; revised manuscript received 22 February 1988)

The microscopic system best suited to the high-precision confirmation of a retardation (or Casimir) effect—originating in the finiteness of the speed of light—would seem to be the Rydberg helium atom (a helium atom with one electron in its ground state and the other in a high- $n$  state, preferably with  $l \approx n$ ). For the helium atom, calculation of the retardation energy shift  $\Delta E_{\text{ret}}(n, l)$  that arises from the retardation effective potential  $V_{\text{ret}}(r)$  seen by the outer electron, where  $r$  is the separation of the nucleus and the outer electron, is not limited to the case of a Rydberg outer electron. We evaluate  $\Delta E_{\text{ret}}(n, l)$  numerically in the dipole approximation for a range of values of  $n$  and  $l$ . The dynamic electric dipole polarizability of the  $\text{He}^+$  core is approximated using pseudostates (a finite number of effective excitation energies and oscillator strengths for the core). We also show how the evaluation can be performed analytically, again using pseudostates. Finally, we give  $V_{\text{ret}}(r)$  as an expansion in powers of  $1/r$ ; this often provides an easy means of estimating  $\Delta E_{\text{ret}}(n, l)$  quickly and relatively accurately, and we present various results of use for the Rydberg helium atom, in tabular and graphical form. The effects of exchange, higher multipoles, and of the finite nuclear mass have not been included. As experimental capabilities improve, other systems, such as an ion composed of a nucleus with  $Z > 2$ , a single core electron, and a Rydberg electron, may someday prove as useful as helium. The formalism for helium can readily be adapted to this case.

### I. INTRODUCTION

The measurement best suited to the high-precision confirmation of a retardation (or Casimir) effect—an effect that originates in the finiteness of the speed of light—would seem to be the measurement of an energy shift of a microscopic system, and, in particular, of the Rydberg helium atom (a helium atom with one electron in its ground state and the other in a high- $n$  state, preferably with  $l \approx n$ ). The effect as first calculated<sup>1</sup> was valid only for  $n$  rather large compared to  $(137)^{1/2}$ . A fully relativistic quantum electrodynamic calculation extended inward the region of validity.<sup>2,3</sup> The essential results of this extension were reproduced by a nonrelativistic treatment of the electrons;<sup>4</sup> this latter approach is incapable of estimating corrections such as pair production effects (which are in any event small for the helium system<sup>5</sup>), but is much simpler than the full QED approach, and is the basis of the present analysis. Recent experimental work<sup>6</sup> finds no evidence for a retardation energy shift in the Rydberg helium atom, but there is no contradiction. Further improvements in the experimental accuracy are required if the shift is to be detected. In addition, there are many effects that do not originate in the finiteness of  $c$  and that are very much greater than the retardation effects; these effects must be evaluated with very high precision if retardation effects are to be extracted. Calculations for many nonrelativistic<sup>7-9</sup> and relativistic<sup>5,8-10</sup> contributions have been carried out.

Here we present several means of estimating and evaluating the retardation energy shift  $\Delta E_{\text{ret}}(n, l)$  for Rydberg helium atoms and heliumlike Rydberg ions. Some of the material given here is intended to allow the

nonspecialist in this subject, experimentalist or theorist, to rather quickly obtain a reasonably accurate estimate of  $\Delta E_{\text{ret}}(n, l)$  for the Rydberg systems just noted. A rough estimate follows immediately from Fig. 1. Should greater accuracy be desired, or should a system other than the ones noted above be under consideration—an  $\alpha$  particle or  $\text{Li}^{3+}$ , a muon, and an electron, for example—recourse can be had to the analytic and numerical approaches discussed below.

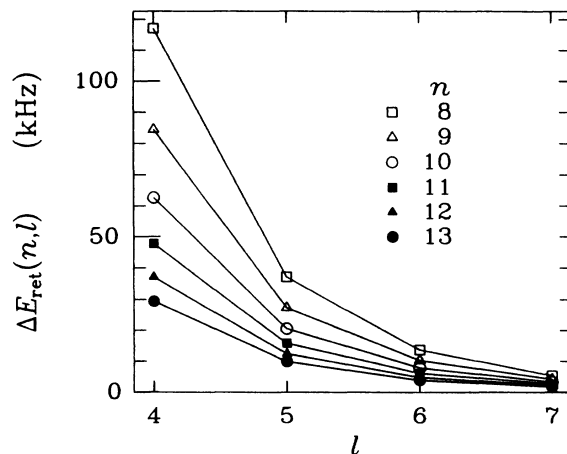


FIG. 1. The retardation energy shift  $\Delta E_{\text{ret}}(n, l)$  for helium (in kHz) plotted as a function of  $l$  for various values of  $n$ .

## II. RYDBERG SYSTEMS WITH HYDROGENIC OR NONHYDROGENIC CORES

Estimates of retardation effects for a Rydberg atom of He and estimates for the Rydberg ions  $\text{Li}^+$ ,  $\text{Be}^{2+}$ , . . . , all systems that have a hydrogenic core, follow from the material in Sec. III below. These estimates are accurate not only for  $l \approx n \gg 1$ , but also for much smaller  $n$ . We will return to the hydrogenic cores shortly, but the question of how to estimate retardation effects for systems with nonhydrogenic cores naturally arises. There may be some additional effects for such systems, but it is reasonable to believe that retardation effects for a multielectron core can be expressed in terms of the characteristics<sup>2,4,11,12</sup> of such a core—the dynamic electric dipole polarizability  $\alpha_d(k)$ , where  $k$  is the wave vector, and the frequency or wave-number-dependent nonadiabatic correction  $\beta(k)$ . (We follow very closely the notation of Refs. 1 and 4; references to equations<sup>13</sup> of Ref. 4 will be preceded by the symbol I.) However, for cores with more than one electron it often will be exceedingly difficult to obtain the characteristics of the core— $\alpha_d(k)$  and  $\beta(k)$ , or equivalently,  $F(k)$ —necessary to determine the retardation effect if the point particle is close to the core;  $F(k)$  is defined by

$$F(k) = \frac{2}{3} e^2 \sum_u \frac{|\langle 0 | \mathbf{r}_1 | u \rangle|^2}{E_{u0} + E_k}, \quad (2.1)$$

where  $\sum_u$  represents an infinite sum and continuum integration. It is for this reason that for many-electron cores the analysis is relatively simple only for the Rydberg electron at a great distance, for then the only relevant core characteristic required is the static electric dipole polarizability  $\alpha_d(0) = F(0)$ . While  $\alpha_d(0)$  for a many-electron core can itself be difficult to obtain with great accuracy, it is reasonably well known for a number of cases. Furthermore, since the energy shift  $\Delta E_{\text{ret}} \equiv \Delta E_{\text{ret}}(n, l)$  is a function of the quantum numbers  $n$  and  $l$  of the outer particle,  $\alpha_d(0)$  can be treated as an open parameter in a study of experimentally determined values of the energies  $E(n, l)$  for a set of values of  $n$  and  $l$ ; the  $E(n, l)$  contain as components  $\Delta E_{\text{ret}}(n, l)$ . [The extraction of  $\Delta E_{\text{ret}}(n, l)$  for a set of values of  $n$  and  $l$  for which the outer electron was nearby rather than in the distant regime would require the introduction of many open parameters to characterize  $F(k)$ . See below the discussion of approximations to  $F(k)$  in the one-electron core problem.]

## III. EVALUATION OF THE RETARDATION ENERGY SHIFT $\Delta E_{\text{ret}}(n, l)$ FOR A ONE-ELECTRON CORE

For a one-electron core and an outer electron, such as a Rydberg helium atom, the retardation effective potential  $V_{\text{ret}}(r)$ , with  $r$  the coordinate of the outer electron, will be identified<sup>14</sup> as Eq. I-(4.30); we make this identification on the basis of previous calculations and physical arguments.<sup>11,12</sup> The potential  $V_{\text{ret}}(r)$ , which arises from the exchange of two transverse photons or of

one transverse photon and one “instantaneous” photon—the latter is not quite the usual longitudinal photon since it generates the interaction  $(e^2/r) - e^2/|\mathbf{r}_2 - \mathbf{r}_1|$ , where  $r_2 = r$  and  $r_1$  is the coordinate of the inner electron, and involves quantities of electric dipole origin—is a subset of the two-photon interaction  $V(r)$  between the helium core and outer electron. For example, the usual polarization potential  $V_{\text{pol}} = -\frac{1}{2} \alpha_d(0) e^2 / r^4$ , with  $\alpha_d(0)$  the static electric dipole polarizability of the core, and other potentials, such as that given by Eq. I-(4.12), generated by the exchange of two instantaneous photons, which are independent of the value of  $c$ , are excluded from  $V_{\text{ret}}(r)$ . The complete two-photon interaction contains terms attributable to electric and magnetic multipoles of all orders,<sup>2,3</sup> spin,<sup>5</sup> and relativistic effects,<sup>5</sup> but for truly Rydberg-like systems, that is for all but very small values of  $n$ , the electric dipole terms strongly dominate, and those are the only contributions with which we will be concerned. In addition, we can understand most of the electric dipole contributions, especially those at large distances, through physical arguments that involve only the dynamic electric dipole polarizabilities  $\alpha_d(\omega)$  and vacuum fluctuations.<sup>11,12</sup>

The retardation effective potential, and the associated energy shift that it generates, are calculated with the nucleus considered to be of infinite mass; the effect on  $\Delta E_{\text{ret}}$  when the nuclear mass is taken to be finite has been analyzed,<sup>15</sup> but will not be discussed in the present paper. The retardation energy shift  $\Delta E_{\text{ret}}$  is the diagonal matrix element of  $V_{\text{ret}}(r)$  taken between shielded hydrogenic wave functions associated with the outer electron with quantum numbers  $n$  and  $l$ , with an effective nuclear charge  $Z_{\text{eff}}$ , which here reduces to  $\bar{Z} \equiv Z - 1$  for a nuclear charge  $Z$ .

Expressions for  $V_{\text{ret}}(r)$  in the form of an integral over virtual photon frequency,<sup>2-4</sup> or an integrated form<sup>2-4</sup> containing the auxiliary functions<sup>16</sup>  $f$  and  $g$ , have been given before; however, both forms contain the infinite sum and continuum integration over inner electron wave functions such as occurs in the definitions of  $\alpha_d(\omega)$  and related quantities. In particular, we showed in Eq. I-(4.27) that  $V_{\text{ret}}(r)$  could be written as an integral over the virtual photon wave vector  $k$  using  $F(k)$ , defined by Eq. (2.1). [Both  $\alpha_d(k)$  and the frequency-dependent nonadiabatic coefficient  $\beta(k)$ , the extension of  $\beta_{\text{nonad}} \equiv \beta(0)$ , can be expressed in terms of  $F(k)$ ; see Eq. I-(4.32).] Karplus and Kolker<sup>17</sup> evaluated the infinite sum and continuum integration  $\sum_u$  in  $F(k)$  and reexpressed  $F(k)$  in terms of an infinite but discrete summation. While their result for  $F(k)$  converges rapidly, its dependence on powers of  $(2E_k + 1)^{1/2}$  and other irrational forms makes the integral over  $k$  difficult to compute. On the other hand, if  $F(k)$  is left as in its definition Eq. (2.1) and the  $k$  integration is carried out, we obtain Eq. I-(4.30) for  $V_{\text{ret}}(r)$ . To calculate  $\Delta E_{\text{ret}}$  we must then at some point carry out the  $\sum_u$ , but now  $f$  and  $g$  appear in the sum-integrand—again difficult to compute. Fortunately, an alternative to the above procedures exists. We have previously outlined how the use of “pseudostates”—a set of  $P$  pairs of

effective oscillator strengths and effective excitation energies, with  $P$  usually small—enables one to replace the sum-integral by a finite sum; we now discuss in more detail the use of such a technique in the numerical evaluation of  $\Delta E_{\text{ret}}$ .

Using pseudostates for a hydrogen atom, but scaled for a hydrogenic ion of nuclear charge  $Z$  such as  $\text{He}^+$ , we can approximate  $F(k)$ , by

$$F(k) \approx e^4 a_0 \sum_{i=1}^P \frac{g_i}{E_i(E_i + E_k)}, \quad (3.1)$$

where  $E_k = \hbar kc$ ,  $E_i = \bar{\omega}_i Z^2 e^2 / a_0$  is an effective excitation energy,  $\bar{\omega}_i$  is dimensionless, and  $g_i$  is an effective oscillator strength. [Note the presence of  $Z$ , not  $\bar{Z}$ ;  $F(k)$  characterizes the inner (unshielded) electron.] We have found the pseudostates with  $P=4$  of Dalgarno and Victor<sup>18</sup> to be very useful, especially for preliminary investigations. They give  $\bar{\omega}_1 = 0.37646$ ,  $\bar{\omega}_2 = 0.51711$ ,

$\bar{\omega}_3 = 0.90146$ ,  $\bar{\omega}_4 = 2.60497$ ,  $g_1 = 0.44560$ ,  $g_2 = 0.29185$ ,  $g_3 = 0.20838$ , and  $g_4 = 0.05417$ . However, a more precise set consisting of ten pairs ( $P=10$ ), due to Johnson, Epstein, and Meath,<sup>19</sup> was used in our evaluations of  $\Delta E_{\text{ret}}$  reported here.

Using the pseudostate approximation for  $F(k)$ , Eq. I-(4.30), and screened (effective nuclear charge  $\bar{Z} \equiv Z - 1$ ) hydrogenic wave functions for the matrix element, we can express  $\Delta E_{\text{ret}}$  for the outer electron with quantum numbers  $n$  and  $l$  as<sup>2-4</sup>

$$\Delta E_{\text{ret}}(n, l, Z) = \langle nl | \bar{V}_{\infty}(r) | nl \rangle + \int_0^{\infty} ds e^{-s} \Phi(s; n, l, Z), \quad (3.2)$$

where, with the exponential from the squared outer electron wave function factored out,  $\Phi(s) \equiv \Phi(s; n, l, Z)$  is given by

$$\Phi(s) = A_{nl}^2 \frac{64}{\pi} \frac{e^2}{a_0} \left( \frac{\bar{Z}}{Zn} \right)^6 s^{2l-4} F_{nl}^2(s) \sum_{i=1}^P [f(2y)(y^4 - 5y^2 + 3) + g(2y)(6y - 2y^3) + \frac{13}{4}y - \frac{1}{2}y^3];$$

$A_{nl}$  and  $F_{nl}$  are the outer electron wave-function normalization constant and Laguerre polynomial, respectively,  $y = (Z^2/2\bar{Z})(e^2/\hbar c)\bar{\omega}_i ns$ , and  $\bar{V}_{\infty}(r)$  is given by Eq. I-(4.28). The first term of Eq. (3.2) can be evaluated readily using hydrogenic expectation values<sup>20</sup> for powers of  $1/r$ . The integral over  $s$  appearing in Eq. (3.2) for  $\Delta E_{\text{ret}}$  can be evaluated numerically or analytically. As the numerical approach is less tedious to apply, in general, and thus more practical, we discuss it first.

#### A. Numerical evaluation

The integral over  $s$  in Eq. (3.2) is of a form suited to numerical approximation using Laguerre polynomial quadrature.<sup>21</sup> Using a  $J$ -point quadrature we write

$$\Delta E_{\text{ret}} \approx \sum_{j=1}^J w_j \Phi(s_j), \quad (3.3)$$

where  $w_j$  is a weighting factor and  $s_j$  is a polynomial root;  $w_j$  and  $s_j$  have been tabulated for many values of  $J$ . In the present work we quote results for which  $J=20$  was used, but  $J=15$  yielded comparable precision. In the numerical computation we used the ten-pair approximation to  $F(k)$  and an additional approximation; the auxiliary functions  $f(x)$  and  $g(x)$  were approximated by series expansions for  $x < 1$  and rational approximations for  $x > 1$ . In this work we used the four-pair rational approximations for  $f$  and  $g$  of Ref. 16 for  $x > 1$ . We present results for  $\Delta E_{\text{ret}}$  in Table I for a somewhat wider range of values of  $n$  and  $l$  than do Au, Feinberg, and Sucher<sup>3</sup>; where their results are available, our values for  $\Delta E_{\text{ret}}$ , obtained using the above procedure, were typically about

1% greater than theirs. For example, for helium with  $n=10$  and  $l=4$  we find  $\Delta E_{\text{ret}} = 62.7$  kHz, while they find 61.8 kHz. Even a comparison of results for  $Z=70$  [although the expression Eq. (3.2) used for  $V_{\text{ret}}(r)$  is of questionable validity<sup>5</sup> for such a high  $Z$ ] shows the 1% difference. For example, for  $Z=70$ ,  $n=10$ ,  $l=4$  we find  $\Delta E_{\text{ret}} = 486$  MHz, while they find  $\Delta E_{\text{ret}} = 479$  MHz. Au and Feinberg<sup>22</sup> have informed us that, if the results of Ref. 3 are in fact too low, it may be due to the truncated spectral distribution used. We emphasize that the retardation energy shifts presented in this paper do not include the effects of exchange, higher multipoles, or the finite nuclear mass. Exchange effects may well be significant for low-lying levels.

#### B. Analytic evaluation

The shift  $\Delta E_{\text{ret}}$  can also be calculated analytically. We again use Eq. I-(4.26) and screened hydrogenic wave functions for the outer electron, but now evaluate the second term of Eq. (3.2), after some rearrangement, using the integrals<sup>23</sup>

$$\int_0^{\infty} dx e^{-\mu x} x^j g(x) = (-1)^j \frac{\partial^j}{\partial \mu^j} \left[ \frac{(\pi/2) + \mu \ln \mu}{1 + \mu^2} \right] \quad (3.4)$$

and

$$\int_0^{\infty} dx e^{-\mu x} x^j f(x) = (-1)^j \frac{\partial^j}{\partial \mu^j} \left[ \frac{(\pi\mu/2) - \ln \mu}{1 + \mu^2} \right]. \quad (3.5)$$

TABLE I. Retardation energy shift  $\Delta E_{\text{ret}}(n,l)$  for helium (in kHz) for various values of  $n$  and  $l$ . Numbers in brackets represent powers of ten.

$n$	$l$	$\Delta E_{\text{ret}}$	$n$	$l$	$\Delta E_{\text{ret}}$	$n$	$l$	$\Delta E_{\text{ret}}$
3	2	4.5969[4]	9	2	2.1537[3]	12	2	9.1899[2]
4	2	2.1924[4]		3	3.3668[2]		3	1.4548[2]
	3	2.9692[3]		4	8.4395[1]		4	3.7150[1]
5	2	1.1824[4]		5	2.7256[1]		5	1.2319[1]
	3	1.7194[3]		6	1.0258[1]		6	4.8118
	4	3.8205[2]		7	4.2466		7	2.0984
6	2	7.0312[3]		8	1.8556		8	9.8808[-1]
	3	1.0575[3]	10	2	1.5779[3]		9	4.9072[-1]
	4	2.4932[2]		3	2.4802[2]		10	2.5235[-1]
	5	7.3077[1]		4	6.2686[1]		11	1.3212[-1]
7	2	4.4993[3]		5	2.0486[1]	13	2	7.2436[2]
	3	6.8967[2]		6	7.8425		3	1.1493[2]
	4	1.6770[2]		7	3.3268		4	2.9451[1]
	5	5.1720[1]		8	1.5074		5	9.8118
	6	1.8132[1]		9	7.0875[-1]		6	3.8566
8	2	3.0452[3]	11	2	1.1898[3]		7	1.6960
	3	4.7232[2]		3	1.8778[2]		8	8.0754[-1]
	4	1.1699[2]		4	4.7742[1]		9	4.0709[-1]
	5	3.7118[1]		5	1.5734[1]		10	2.1364[-1]
	6	1.3609[1]		6	6.0940		11	1.1508[-1]
	7	5.4123		7	2.6274		12	6.2772[-2]
				8	1.2181			
				9	5.9206[-1]			
				10	2.9526[-1]			

The operations involved in computing Eq. (3.4) or (3.5) rapidly become unwieldy when  $n$  is large, the more so if  $l$  is small, for then many parametric differentiations are necessary in computing the necessary integrals. The process can be automated using a symbolic manipulation program such as MACSYMA.<sup>24</sup> We have used MACSYMA to carry out differentiation, simplification, and conversion to FORTRAN statements, which are then inserted into a program for evaluation. [Note that the pseudostate approximation to  $F(k)$  is used in both the numerical and analytical approaches; the analytic approach is analytic in the sense that the integral over the outer electron coordinate in the matrix element is carried out without the use of numerical integration. Note too that there are reasons for maintaining more significant figures for  $\Delta E_{\text{ret}}(n,l)$  than might seem to be warranted, see Table I, in that corrections such as the reduced mass effect have not been taken into account. For one thing, corrections can often be expressed as known factors multiplying the uncorrected result. Further, more accurate results for  $\Delta E_{\text{ret}}(n,l)$ , in a given approximation, allow us to better compare our analytic and numerical results and allow others to check their codes. Note finally that very accurate results for  $\Delta E_{\text{ret}}(n,l)$  are required, since experiments measure differences—normally for fixed  $n$  and different  $l$ —of the retardation energy shifts.]

### C. A more approximate, but simpler, evaluation

Finally, to conclude our discussion of the calculation of  $\Delta E_{\text{ret}}$ , we describe a method that allows one to readily determine  $\Delta E_{\text{ret}}$  approximately to a precision good enough for most practical cases and allows one to ascertain whether more precise calculations are warranted. Our main interest here is in the behavior of  $\Delta E_{\text{ret}}$  in the “distant regime,” defined by

$$\langle E_k \rangle / \langle E_{u_0} \rangle = [\tilde{Z} / (Z^2 n^2)] (\hbar c / e^2) \ll 1, \quad (3.6)$$

where  $\langle E_k \rangle$  is a characteristic energy of a transverse photon and  $\langle E_{u_0} \rangle$  is a characteristic excitation energy of the inner electron, and which is moderately well satisfied for helium by such cases as  $n=12$  and  $l=11$ . In this domain we use  $\hbar c / (r E_{u_0})$  as a small expansion parameter in Eq. I-(4.30) and find

$$V_{\text{ret}} \sim (11/4\pi) (\hbar/mc) [e^2 \alpha_d(0) / r^5],$$

and a  $r^{-7}$  correction term.<sup>2</sup> However, for most experimental studies one has  $\langle E_k \rangle / \langle E_{u_0} \rangle \gtrsim 1$ , for which  $r E_{u_0} / \hbar c$  is an appropriate small expansion parameter in Eq. I-(4.30).

The experiments on helium—no experiments have yet been performed on heliumlike ions—have been for  $n$  and  $l$  of the order of 10 and 4, respectively, for which<sup>25</sup>

$$V_{\text{ret}}(r) \approx \left[ \frac{(e^2/\hbar c)^2}{Z^2} \left( \frac{a_0}{r} \right)^4 - \frac{7(e^2/\hbar c)^3}{6\pi} \left( \frac{a_0}{r} \right)^3 + \frac{Z^2(e^2/\hbar c)^4}{3} \left( \frac{a_0}{r} \right)^2 \right] \frac{e^2}{a_0}. \quad (3.7)$$

Au<sup>10</sup> has pointed out that use of only the  $r^{-4}$  term of Eq. (3.7) for  $V_{\text{ret}}$  provides an approximation for  $\Delta E_{\text{ret}}$  good to within a factor of 2, but since the first three terms are available one can easily do better, especially when  $n$  and  $l$  are small. For example, for helium with  $n=3$  and  $l=2$  we find  $\Delta E_{\text{ret}}=46\,087$  kHz using Eq. (3.7) compared to 45 969 evaluating Eq. (3.2) analytically or numerically; the first term alone of Eq. (3.7) gives  $\Delta E_{\text{ret}}\approx 48\,063$  kHz. Also, since we have the first three terms available, we can delineate domains of  $n$ ,  $l$ , and  $Z$  for which the first term alone provides a reasonable approximation to  $\Delta E_{\text{ret}}$ . Using screened hydrogenic matrix elements for inverse powers<sup>20</sup> of  $r$  and denoting the matrix elements of the first and second terms of Eq. (3.7) by  $E_1$  and  $E_2$ , respectively, we find

$$\left| \frac{E_2}{E_1} \right| = \frac{7}{6\pi} \frac{e^2 Z^2 \langle r^{-3} \rangle}{\hbar c a_0 \langle r^{-4} \rangle} = \frac{28}{3\pi} \frac{e^2}{\hbar c} \frac{Z^2}{\bar{Z}} \frac{n^2(2l-1)(2l+3)}{[3n^2-l(l+1)]}. \quad (3.8)$$

For a helium atom, we thereby arrive at  $0.087n^2(2l-1)(2l+3)$  rather less than  $3n^2-l(l+1)$  as the condition for which the first term by itself is at least a rough approximation, and for  $l=(n-1)$ , this condition reduces to  $0.087n(2n-3)$  rather less than unity, which is true only for  $n \leq 3$ . However, a comparison of  $E_1$  with  $\Delta E_{\text{ret}}$  for various values of  $n$  and  $l$  indicates that requiring  $|E_2/E_1|$  to be rather less than one is too restrictive a condition for  $E_1$  to be a rough approximation.

#### IV. SOME ONE-ELECTRON CORE RETARDATION RESULTS IN TABULAR AND GRAPHICAL FORM

We have applied the numerical approach discussed in Sec. II using Eq. (3.2) to calculate  $\Delta E_{\text{ret}}$  for various values of  $Z$ ,  $n$ , and  $l$ .  $F(k)$  was approximated by 10 pairs of pseudostate parameters<sup>19</sup> as in Eq. (3.1) and the numerical integration was carried out by means of Laguerre

quadrature ( $J=20$ ). In Table I, we give a short tabulation of values of  $\Delta E_{\text{ret}}(n, l)$  in kHz for helium for some values of  $n$  and  $l$  that are or probably could be experimentally accessible. In Fig. 1, we present a plot of iso- $n$  curves of  $\Delta E_{\text{ret}}$  versus  $l$  for helium, which illustrates the rather smooth behavior of  $\Delta E_{\text{ret}}$  as a function of  $l$  for  $n$  and  $Z$  fixed. The smooth behavior can be attributed to the leading term of the expression Eq. (3.7) for  $V_{\text{ret}}$ . For fixed  $l$ , we denote the ratio of  $\Delta E_{\text{ret}}$  for  $n_1$ ,  $Z_1$ , and  $l$  to  $\Delta E_{\text{ret}}$  for  $n_2$ ,  $Z_2$ , and  $l$  by

$$R \equiv \frac{\Delta E_{\text{ret}}(n_1, Z_1, l)}{\Delta E_{\text{ret}}(n_2, Z_2, l)} = \left[ \frac{n_2}{n_1} \right]^5 \left[ \frac{Z_1}{Z_2} \right]^4 \left[ \frac{3n_1^2 - l(l+1)}{3n_2^2 - l(l+1)} \right]. \quad (4.1)$$

For  $l$  small compared to both  $n_1$  and  $n_2$ , we have the simple scaling law

$$R \approx (n_2/n_1)^3 (Z_1/Z_2)^4,$$

which reduces further, for  $Z_1=Z_2$ , to

$$R \approx (n_2/n_1)^3.$$

*Note added in proof.* E. A. Hessels, W. G. Sturru, and S. R. Lundeen have obtained (unpublished) results with much smaller error bars than those quoted in Ref. 6. They state that their result for the 10I-10K interval in helium "is in good agreement with theory, and while it is not very conclusive evidence for the presence of retardation effects, it appears to be the best evidence to date."

#### ACKNOWLEDGMENTS

We thank Dr. C.K. Au and Dr. G. Feinberg for a helpful discussion of the accuracy of the calculations in Ref. 3. This work was supported in part by the National Science Foundation under Grant No. PHY87-06114.

<sup>1</sup>E.J. Kelsey and L. Spruch, Phys. Rev. A **18**, 15 (1978); **18**, 1055 (1978).

<sup>2</sup>G. Feinberg and J. Sucher, Phys. Rev. A **27**, 1958 (1983).

<sup>3</sup>C.K. Au, G. Feinberg, and J. Sucher, Phys. Rev. Lett. **53**, 1145 (1984).

<sup>4</sup>J.F. Babb and L. Spruch, Phys. Rev. A **36**, 456 (1987).

<sup>5</sup>G. Feinberg, J. Sucher, and C.K. Au, Ann. Phys. (N.Y.) **173**, 355 (1987), and references therein.

<sup>6</sup>S.L. Palfrey and S.R. Lundeen, Phys. Rev. Lett. **53**, 1141 (1984); see also D.R. Cok and S.R. Lundeen, Phys. Rev. A **23**, 2488 (1981).

<sup>7</sup>See R.J. Drachman, Phys. Rev. A **31**, 1253 (1985); **33**, 2780 (1986), and references therein.

<sup>8</sup>R.J. Drachman, Phys. Rev. A **26**, 1228 (1982), and references therein.

<sup>9</sup>G.W.F. Drake, Phys. Rev. Lett. **59**, 1549 (1987).

<sup>10</sup>C.K. Au, Phys. Rev. A **31**, 1310 (1985).

<sup>11</sup>L. Spruch and E.J. Kelsey, Phys. Rev. A **18**, 845 (1978).

<sup>12</sup>L. Spruch, Phys. Today **39** (11), 37 (1986).

<sup>13</sup>We have found two minor typographical errors in Ref. 4. The line above Eq. I-(4.2) should read, "III A—and the second-order contribution is," and the line below Eq. I-(4.28) should read, "we have used the relationships  $\Psi(4)=\frac{11}{4}$  and  $\Psi(5)=3\pi/2$ ."

<sup>14</sup>Some comments on notation: In Ref. 4, we presented several forms for the retardation potential. Eqs. I-(2.8) and (2.10) are valid when  $r$  is large, as determined by the condition that either side of Eq. I-(4.15) be much less than one, or equivalently, by Eq. (3.6) of the present paper; Eqs. I-(4.30) and (4.34) are valid for  $r$  down to  $Ca_0/\bar{Z}$ , where  $C$  is of order 5 or 10. In Ref. 4, we used  $V_T(r)$  for Eqs. I-(4.30) and (4.34) in order not to confuse the domains of validity of these expressions. In the present work, we require only the more general result for the retardation potential, so we identify  $V_{\text{ret}}$  as  $V_T$  given by Eq. I-(4.30).

<sup>15</sup>J.F. Babb and L. Spruch (unpublished); a very preliminary re-

- port appears in Bull. Am. Phys. Soc. **33**, 953 (1988).
- <sup>16</sup>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.
- <sup>17</sup>M. Karplus and H.J. Kolker, J. Chem. Phys. **39**, 1493 (1963).
- <sup>18</sup>A. Dalgarno and G.A. Victor, Mol. Phys. **10**, 333 (1966), Table II.
- <sup>19</sup>R.E. Johnson, S.T. Epstein, and W.J. Meath, J. Chem. Phys. **47**, 1271 (1967), Table II.
- <sup>20</sup>K. Bockasten, Phys. Rev. **9**, 1087 (1974).
- <sup>21</sup>A.H. Stroud and D. Secrest, *Gaussian Quadrature Formulas* (Prentice-Hall, Englewood Cliffs, NJ, 1966), Table VI.
- <sup>22</sup>C.K. Au and G. Feinberg (private communication).
- <sup>23</sup>I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965), p. 647, Eqs. 6.263.1 and 6.263.2.
- <sup>24</sup>Copyright owned by the Massachusetts Institute of Technology and Symbolics, Inc. MACSYMA is a trademark of Symbolics, Inc.
- <sup>25</sup>The  $r^{-4}$  term was given in Ref. 2; the  $r^{-3}$  and  $r^{-2}$  terms follow from Eq. (4) of Ref. 3 or Eq. I-(4.30) using  $rE_{u0}/\hbar c$  as an expansion parameter.