PHYSICAL REVIEW A VOLUME 26, NUMBER 3 SEPTEMBER 1982

Rydberg states of helium: An optical-potential analysis

Richard J. Drachman
Atomic Physics Office, Laboratory for Astronomy and Solar Physics,
NASA, Goddard Space Flight Center, Greenbelt, Maryland 20771

(Received 22 March 1982)

The Feshbach projection-operator technique has been applied to the problem of electrostatic level shifts in 1*sNL* Rydberg states of helium. It is assumed at first that, for sufficiently high L, only long-range terms in the optical potential affect the energy of the outer electron. These terms up to x^{-8} are carefully derived, used in a first-order perturbation calculation, and compared with recent accurate experimental results. Second-order effects due to the leading x^{-4} potential and some short-range terms are also calculated in a few cases; these effects are generally not negligible for $L \leq 4$.

I. INTRODUCTION

A particularly simple type of excited state of a multielectron atom is the case in which a single electron moves in the field of a spherically symmetric core. If, in addition, the electron is far from the core, then the excited states will be approximately hydrogenic, and are known as Rydberg states. The high Rydberg states (NL) of helium are very tempting for theorist and experimentalist alike. Many calculations have treated this type of state in terms of perturbed hydrogen levels, with polarization of the core supplying the perturbing potential.[1-3] Recent very accurate measurements of the fine structure of high Rydberg levels of helium[4,5] have provided the motivation for a reexamination of the theory. Especially interesting is the possibility of detecting a new effect of retardation recently described by Spruch and Kelsey.[6]

If the state in question has "sufficiently large" values of N and L, its overlap with the core will be negligible. In such a case short-range shielding effects and exchange can be neglected. The remaining long-range perturbations can be evaluated analytically[2,7] and very simple analysis will give the electrostatic fine-structure splittings for comparison with experiment.[4,5] In this paper, I will use the Feshbach projection-operator method[8] to obtain these long-range terms up to the inverse eighth power and will give criteria for the applicability of the simple perturbation method.

In Sec. II, I review the formalism and apply it to the helium system. A sequence of formal expansions for the energy is then described; these include multipole expansions, perturbation series, and nonadiabatic corrections that are well defined in this formalism, although many of them have been derived previously. The detailed evaluation of the coefficient of each term is relegated to the Appendix, but the results are given here. In Sec. III, I give the results of the first-order theory, compared with experiment, and I estimate the error in the asymptotic series that results. In Sec. IV, short-range corrections and second-order effects are discussed for some cases. Finally, I give a critical discussion of the method.

II. FORMULATION

The goal of the Feshbach technique[8] for scattering is to reduce the many-body Schrödinger equation to an effective one-body equation describing the motion of the projectile. In the present problem, we wish instead to reduce the two-particle equation describing the helium atom to an effective equation for the outer Rydberg electron alone. I will assume from the outset that the core electron ($\vec{r}$) and the outer electron ($\vec{x}$) are distinguishable since their wave functions hardly ever overlap. Then the Hamiltonian of the system is

$$H = H_0(r) + H_0(x) + V(\vec{x},\vec{r}) \ , \qquad (1)$$

where

$$H_0(r) = -\nabla_r^2 - 4/r \ ,$$

$$H_0(x) = -\nabla_x^2 - 2/x \ ,$$

and

$$V(\vec{x},\vec{r}) = \frac{2}{|\vec{x}-\vec{r}|} - \frac{2}{x} - K\vec{\nabla}_x \cdot \vec{\nabla}_r \ .$$

Here energies are in reduced ^{4}He Rydberg units

$$R = 3.289\,391\,08(25) \times 10^9 \text{ MHz} \ ,$$

and

$$K=2m_e/(M_{\mathrm{He}}+m_e)=2.7415\times10^{-4}\ .$$

The unperturbed Hamiltonian

$$H_0=H_0(r)+H_0(x)$$

includes the effect of shielding, and leads to the unperturbed energies

$$E_0(1sNL)=-4-\frac{1}{N^2}\ , \tag{2}$$

where capital letters refer to the Rydberg electron $(\vec{x})$.

As usual, we will define projection operators P and Q referring to the core electron:

$$P=|\,1s\rangle\langle 1s\,|\ ,\quad Q=1-P\ , \tag{3}$$

where $P^2=P$ and $Q^2=Q$. Then the Schrödinger equation

$$(H-E_0-\Delta)\Psi(\vec{x},\vec{r})=0$$

is rewritten in the optical-potential form

$$\langle 1s\,|\,(H-E_0-\Delta)\,|\,1s\rangle X(\vec{x})+\left\langle 1s\left|VQ\frac{1}{Q(E_0-H+\Delta)Q}QV\right|1s\right\rangle X(\vec{x})=0\ . \tag{4}$$

This differs from the corresponding equation in the scattering case[8,9] only in the appearance of the energy shift Δ; in addition, the function $X(\vec{x})\equiv\langle 1s\,|\,\Psi\rangle$ is now normalizable. Equation (4) is seen to be a nonlinear eigenvalue equation, and Δ is the quantity of interest. Let us now carry out a sequence of formal expansions.

(i) First, expand the denominator of the optical potential in powers of $\Delta/Q(H-E_0)Q$. After evaluating the first term we obtain

$$\left[-\nabla^2-\frac{2}{x}+\bar{V}(x)+\frac{1}{N^2}-\Delta\right]X+\sum_{k=0}^{\infty}\Delta^kU_k(x)X=0\ , \tag{5}$$

where

$$\bar{V}(x)\equiv\langle 1s\,|\,V\,|\,1s\rangle=-2e^{-4x}\left[\frac{1}{x}+2\right]\ ,$$

and

$$U_k(x)\equiv-\left\langle 1s\left|VQ\frac{1}{[Q(H-E_0)Q]^{k+1}}QV\right|1s\right\rangle\ .$$

(ii) Next, let us carry out a conventional perturbation expansion, expanding X and Δ in some small parameter λ which is taken as representing the strength of the perturbing potential: $U_k\rightarrow\lambda U_k$ and $\bar{V}\rightarrow\lambda\bar{V}$. Then if

$$\Delta=\sum_{m=1}^{\infty}\lambda^m\Delta_m\ ,$$

$$X=\sum_{m=0}^{\infty}\lambda^mX_m\ ,$$

Eq. (5) becomes

$$[H_0(x)+1/N^2]X_0=0\ , \tag{6a}$$

$$[H_0(x)+1/N^2]X_1=(-U_0+\Delta_1-\bar{V})X_0\ , \tag{6b}$$

$$[H_0(x)+1/N^2]X_2=(-\Delta_1U_1+\Delta_2)X_0+(-U_0+\Delta_1-\bar{V})X_1\ , \tag{6c}$$

plus higher equations. Here $H_0(x)=-\nabla_x^2-2/x$, and Eq. (6a) verifies the consistency of the unperturbed hydrogenic description. Premultiplication by X_0^* and integration over $d\vec{x}$ gives expressions for the first two energy shifts:

$$\Delta_1=\int d\vec{x}\,X_0^*U_0X_0\ , \tag{7a}$$

$$\Delta_2=\int d\vec{x}\,X_0^*U_0X_1+\Delta_1\int d\vec{x}\,X_0^*U_1X_0\ , \tag{7b}$$

where the normalization of X_0 and its orthogonality to X_1 have been invoked. Since $\bar{V}$ is an exponentially decreasing, short-range function I have omitted it from Eq. (7); its effect will be examined in Sec. IV along with other short-range effects.

(iii) Let us now examine Eq. (7a), the first-order energy shift, and expand U_0 in powers of V as in Ref. 9. Defining

$$D\equiv Q(E_0-H_0)Q \tag{8}$$

one finds

$$\frac{1}{Q(E_0-H)Q}=\frac{1}{D}+\frac{1}{D}QVQ\frac{1}{D}+\frac{1}{D}QVQ\frac{1}{D}QVQ\frac{1}{D}+\cdots \tag{9}$$

and

$$U_0(x)=\left\langle VQ\frac{1}{D}QV\right\rangle+\left\langle VQ\frac{1}{D}QVQ\frac{1}{D}QV\right\rangle+\cdots\ . \tag{10}$$

(iv) Next, we make an expansion of $U_0(x)$ in terms of the quantities h and d, where

$$h = Q[H_0(x) + 1/N^2]Q \,,$$
$$d = -Q[H_0(r) + 4]Q \,. \tag{11}$$

Then

$$\frac{1}{D} = \frac{1}{d-h} = \sum_{j=1}^{\infty} \frac{h^{j-1}}{d^j} \,. \tag{12}$$

(v) Finally, the usual multipole expansion of V is made, where $r < x$:

$$V = \frac{2}{x} \sum_{q=1}^{\infty} \left[\frac{r}{x} \right]^q P_q(\hat{x} \cdot \hat{r}) \,. \tag{13}$$

(The mass-polarization term involving $\vec{\nabla}_x \cdot \vec{\nabla}_r$ will be dropped for the time being, since its coefficient is very small. It will be discussed later.)

I will not attempt in this paper to establish convergence properties for any of these expansions beyond observing the results obtained. There are, however, reasonably convincing plausibility arguments suggesting their usefulness for sufficiently highly excited states. These depend on the smallness of Δ and V relative to the core excitations and the smallness of nonadiabatic terms relative to adiabatic ones. As the controlling parameter I will take $1/x$; terms as small as $1/x^8$ will be retained. The optical potential has the form

$$U_0^{(x)} = \left\langle 1s \left| VQ \left[\sum_{j=1}^{\infty} \frac{h^{j-1}}{d^j} + \sum_{j,j'=1}^{\infty} \frac{h^{j-1}}{d^j} QVQ \frac{h^{j'-1}}{d^{j'}} + \sum_{j,j',j''=1}^{\infty} \frac{h^{j-1}}{d^j} QVQ \frac{h^{j'-1}}{d^{j'}} QVQ \frac{h^{j''-1}}{d^{j''}} + \cdots \right] QV \right| 1s \right\rangle . \tag{14}$$

It will turn out that to order x^{-8} one need retain only the following:

$$U_0(x) \approx \left\langle 1s \left| VQ \left[\sum_{j=1}^{3} \frac{h^{j-1}}{d^j} + \frac{1}{d} QVQ \frac{1}{d} + \frac{1}{d} QVQ \frac{1}{d} QVQ \frac{1}{d} \right] QV \right| 1s \right\rangle . \tag{15}$$

(Note that h commutes with Q and d but not with V.) Inserting the explicit form of Q, one obtains[9]

$$U_0(x) \approx \sum_{j=1}^{3} \langle 1s \,|\, V \,|\, \bar{n} \rangle \frac{h^{j-1}}{(d_n)^j} \langle \bar{n} \,|\, V \,|\, 1s \rangle + \frac{\langle 1s \,|\, V \,|\, \bar{n} \rangle \langle \bar{n} \,|\, V \,|\, \bar{m} \rangle \langle \bar{m} \,|\, V \,|\, 1s \rangle}{d_n d_m} + \frac{\langle 1s \,|\, V \,|\, \bar{n} \rangle \langle \bar{n} \,|\, V \,|\, \bar{m} \rangle \langle \bar{m} \,|\, V \,|\, \bar{p} \rangle \langle \bar{p} \,|\, V \,|\, 1s \rangle}{d_n d_m d_p} \,. \tag{16}$$

Here $d_n = 4(1/n^2 - 1)$ and

$$|\,\bar{n} \times \bar{n}\,| \equiv \sum_{\bar{n} \neq 1s} |\,\bar{n} \times \bar{n}\,| \,.$$

(The index $\bar{n}$ refers to the set of quantum numbers $\{n, l, m\}$.) Equation (16), for $j=1$, gives just the familiar adiabatic potential carried out to fourth order in V. A fourth-order term due to wave function normalization is missing; in this formalism it will reappear later when I consider Δ_2 [Eq. (7b)]. The adiabatic potential is

$$U_0^{\mathrm{AD}}(x) \approx -\frac{\alpha_1}{x^4} - \frac{\alpha_2}{x^6} + \frac{\delta}{x^7} - \frac{\alpha_3}{x^8} - \frac{\epsilon}{x^8} \,, \tag{17}$$

where α_q is the qth multipole polarizability, δ is the third-order term[9,10] involving dipole and quadrupole terms in V, and ϵ comes from the last term in (16) involving four dipole factors. (Numerical values will be given later.)

When $j \neq 1$ in some term of $U_0(x)$, "nonadiabatic" effects are produced,[10,11] necessarily involving a differential operator in x operating to the right. First derivatives appear when $j=2$ and more complicated tensorial forms occur for $j>2$. Since, however, we are interested here only in the expectation value (7a), where X_0 is a normalizable function, great simplifications are possible. It is important to note that the rigorous optical potential to be used in the asymptotic Schrödinger equation is (16) taken literally, not the form to be described below; the latter is for use in Eq. (7) only. Let us define

$$f_{\bar{n}}(x) \equiv \langle \bar{n} \,|\, V \,|\, 1s \rangle \tag{18}$$

and rewrite the first nonadiabatic term of the energy shift [from (7a) and (16) with $j=2$] as follows:

$$\Delta_{1,j=2} = \int d\vec{x}\, X_0^* f_{\bar{n}}^*(x) \frac{h}{(d_n)^2} f_{\bar{n}}(x) X_0 \,, \tag{19}$$

where summation over $\bar{n} \neq 1s$ is assumed. Commuting h to the right and using (6a), we obtain

$$\Delta_{1,j=2}=\int d\vec{\mathrm{x}}\, X_0^* f_{\bar{n}}^* \frac{1}{(d_n)^2}[h,f_{\bar{n}}]X_0 \,. \tag{20}$$

The commutator is

$$[h,f_{\bar{n}}]=-\nabla_x^2 f_{\bar{n}}-2\vec{\nabla}_x f_{\bar{n}}\cdot\vec{\nabla}_x \,, \tag{21}$$

and the term in ∇_x^2 vanishes since V satisfies Laplace's equation for large x. Then

$$\Delta_{1,j=2}=-\frac{2}{(d_n)^2}\int d\vec{\mathrm{x}}\, X_0 f_{\bar{n}}\vec{\nabla}_x f_{\bar{n}}\cdot\vec{\nabla}_x X_0 \,, \tag{22}$$

where we can take X_0 and $f_{\bar{n}}$ to be real without loss of generality. Then

$$\Delta_{1,j=2}=-\frac{1}{2(d_n)^2}\int d\vec{\mathrm{x}}\, \vec{\nabla}_x f_{\bar{n}}^2\cdot\vec{\nabla}_x X_0^2 \,. \tag{23}$$

For each multipole in V there is a corresponding smallest value of L for X_0 enabling one to integrate by parts without producing a nonvanishing term at $x\rightarrow 0$. Thus

$$\Delta_{1,j=2}=\frac{1}{2(d_n)^2}\int d\vec{\mathrm{x}}\, X_0^2\nabla_x^2 f_{\bar{n}}^2 \,, \tag{24}$$

and since

$$\sum_{\bar{n}\neq 1s}\left[\frac{f_{\bar{n}}}{d_n}\right]^2=\sum_{q\geq 1}\frac{\beta_q}{x^{2(q+1)}} \,,$$

$$\Delta_{1,j=2}=\sum_{q\geq 1}(2q+1)(q+1)\beta_q \times\int d\vec{\mathrm{x}}\, X_0\frac{1}{x^{2(q+2)}}X_0 \,. \tag{25}$$

Added to the potential in Eq. (17) then is the following:

$$U_0^{j=2}(x)\approx\frac{6\beta_1}{x^6}+\frac{15\beta_2}{x^8} \,. \tag{26}$$

At this point the mass polarization, dropped from Eq. (13), makes a contribution.[12] (It is possible to show that, for $j=1$ it gives negligible short-range effects only, and vanishes in first order unless $L=1$.) The leading mass-polarization term in Δ is

$$\Delta_{1,j=2}^{\mathrm{mp}}=-\frac{2K}{(d_n)^2}\int d\vec{\mathrm{x}}\, X_0^* f_{\bar{n}}^* h\langle \bar{n}\,|\,\vec{\nabla}_x\cdot\vec{\nabla}_r\,|\,1s\rangle X_0 \,. \tag{27}$$

Commutation of h to the right gives the expression

$$\Delta_{1,j=2}^{\mathrm{mp}}=-16K\frac{\langle 1s\,|\,\hat{x}\cdot\vec{\mathrm{r}}\,|\,\bar{n}\rangle\langle\bar{n}\,|\,\hat{x}\cdot\hat{r}\,|\,1s\rangle}{(d_n)^2} \times\int d\vec{\mathrm{x}}\, X_0\frac{1}{x^4}X_0 \,, \tag{28}$$

and only the dipole term in $f_{\bar{n}}$ contributes because $\vec{\nabla}_x\cdot\vec{\nabla}_r$ involves P_1 only. The sum over $\bar{n}$ is done easily, and the final result is a contribution to the optical potential proportional, like the dipole polarization potential, to x^{-4}:

$$U_0^{\mathrm{mp}}(x)=-\frac{K\mu}{x^4} \,. \tag{29}$$

(Further terms linear in K and falling like x^{-6}, x^{-7}, and x^{-8} also occur, and are small.)

The $j=3$ term in Eq. (16) gives the following contribution to the energy:

$$\Delta_{1,j=3}=\frac{4}{(d_n)^3}\int d\vec{\mathrm{x}}\,|\,\vec{\nabla}_x f_{\bar{n}}\cdot\vec{\nabla}_x X_0\,|^2 \,. \tag{30}$$

[Here I have used Eq. (21), and summation over $\bar{n}$ is understood.] The leading (dipole) term of $f_{\bar{n}}(x)$ is

$$f_{\bar{n}}(x)=\left\langle\bar{n}\left|\frac{2r}{x^2}\hat{x}\cdot\hat{r}\right|1s\right\rangle =\frac{4\pi}{3x^2}\sum_{m=-1}^{1}f_{\bar{n}m}Y_1^{m*}(\hat{x}) \,, \tag{31}$$

where

$$f_{\bar{n}m}\equiv\langle\bar{n}\,|\,2rY_1^m(\hat{r})\,|\,1s\rangle \,, \tag{32}$$

and the addition theorem for spherical harmonics has been used. In Eq. (32) the state $\bar{n}$ is restricted to $l=1$ and azimuthal quantum number m, so one can write Eq. (30) as

$$\Delta_{1,j=3}=\frac{4}{(d_n)^3}\left[\frac{4\pi}{3}\right]^2\sum_{m=-1}^{1}|f_{\bar{n}m}|^2\int d\vec{\mathrm{x}}\left|\vec{\nabla}_x\left[\frac{Y_1^{m*}}{x^2}\right]\cdot\vec{\nabla}_x X_0\right|^2 \,. \tag{33}$$

The orthonormality of spherical harmonics shows that $f_{\bar{n}m}$ is independent of m. The energy shift must be independent of the value of M in X_0, so the ϕ component of ∇_x can be omitted in Eq. (33):

$$\Delta_{1,j=3}=-\frac{16\pi\gamma}{3}\sum_{m=-1}^{1}\int d\vec{\mathrm{x}}\left|-\frac{2}{x^3}\frac{\partial X_0}{\partial x}Y_1^{m*}(\hat{x})+\frac{1}{x^4}\frac{\partial Y_1^{m*}(\hat{x})}{\partial\theta}\frac{\partial X_0}{\partial\theta}\right|^2 \,, \tag{34}$$

where

$$\gamma \equiv -\sum_{\bar{n}\neq 1s} \frac{|\langle \bar{n}\,|\,2\hat{x}\cdot\vec{r}\,|\,1s\rangle|^2}{(d_n)^3}\ . \tag{35}$$

Since

$$\sum_{m=-1}^{1} |Y_1^m|^2 = \sum_{m=-1}^{1} \left|\frac{\partial Y_1^m}{\partial\theta}\right|^2 = \frac{3}{4\pi}\ , \tag{36}$$

Eq. (34) can be rewritten as

$$\Delta_{1,j=3} = -4\gamma \int d\vec{x} \left[\frac{4}{x^6}\left[\frac{\partial X_0}{\partial x}\right]^2 + \frac{1}{x^8}\left[\frac{\partial X_0}{\partial\theta}\right]^2 \right]. \tag{37}$$

[The cross terms in Eq. (34) contain the factor

$$\sum_m Y_1^{m*}\frac{\partial Y_1^m}{\partial\theta} + \text{c.c.} = \frac{\partial}{\partial\theta}\sum_m |Y_1^m|^2\ ,$$

which vanishes due to Eq. (36).] The following steps then lead to a form that does not involve derivatives:

$$\Delta_{1,j=3} = -4\gamma\int d\vec{x}\left[\frac{4}{x^6}\vec{\nabla}X_0\cdot\vec{\nabla}X_0 - \frac{3}{x^8}\left[\frac{\partial X_0}{\partial\theta}\right]^2\right]$$

$$= 16\gamma\int d\vec{x}\left[X_0\frac{1}{x^6}\nabla^2 X_0 - \frac{3}{x^7}\frac{\partial}{\partial x}X_0^2 + \frac{3}{4x^8}\left[\frac{\partial x_0}{\partial\theta}\right]^2\right]. \tag{38}$$

The first term becomes energy-dependent when Eq. (6a) is applied. The second term is simplified using integration by parts in the radial variable. If we write

$$X_0 = \psi_{NL}(x)Y_L^0(\hat{x})\ , \tag{39}$$

then

$$\int d\Omega\left[\frac{\partial X_0}{\partial\theta}\right]^2 = L(L+1)\int d\Omega\, X_0^2\ .$$

Finally,

$$\Delta_{1,j=3} = -16\gamma \times \int d\vec{x}\,X_0\left[-\frac{1}{N^2x^6} + \frac{2}{x^7} + \frac{[15-\frac{3}{4}L(L+1)]}{x^8}\right]X_0\ . \tag{40}$$

Notice that the "potential" whose expectation value gives $\Delta_{1,j=3}$ is central but depends on energy $(-1/N^2)$ and angular momentum (L). It is worth noting that the coefficient of the energy-dependent term is not the same as the coefficient found by Seaton and Steenman-Clark[13] and Drachman[9] for scattering.[14] But recall that the present result is appropriate for energy calculations only, since Eq. (30) was obtained through an integration by parts.

In fact, the energy-dependent term can be completely eliminated from Eq. (40) by using the following identity[15]:

$$-\frac{1}{N^2}\left[\overline{\frac{1}{x^6}}\right] = -\frac{11}{5}\left[\overline{\frac{1}{x^7}}\right] + \tfrac{3}{10}\times[(2L+1)^2-36]\left[\overline{\frac{1}{x^8}}\right]\ , \tag{41}$$

where the bar indicates expectation value with respect to X_0. Using Eq. (41) one can write

$$\Delta_{1,j=3} = 16\gamma\int d\vec{x}\,X_0\left[\frac{1}{5x^7} - \tfrac{9}{2}\left[1+\frac{L(L+1)}{10}\right]\frac{1}{x^8}\right]X_0\ , \tag{42}$$

which is the final form of this energy term. The transformation from Eq. (40) to Eq. (42) is not just a convenience; rather, it shows that terms decreasing like Ex^{-6}, x^{-7}, and x^{-8} are, in some sense, of the same order. As long as $L\geq 3$ no singularities occur in Eq. (42), and it is not consistent to keep terms of order x^{-7} without also retaining terms of order x^{-8}. I will return to this point in Sec. III.

Next I will investigate the second-order energy shift, Δ_2, appearing in Eq. (7b). Using the expansion for U_0 in Eq. (16) (retaining terms up to $j=2$) and the analogous expansion for U_1 one obtains

$$U_1(x) = -\frac{\langle 1s\,|\,V\,|\,\bar{n}\rangle\langle\bar{n}\,|\,V\,|\,1s\rangle}{(d_n)^2} - 2\frac{\langle 1s\,|\,V\,|\,\bar{n}\rangle h\langle\bar{n}\,|\,V\,|\,1s\rangle}{(d_n)^3}\ . \tag{43}$$

Again commuting h to the right in U_0 and noting from Eq. (6b) that

$$hX_1=(-U_0+\Delta_1)X_0\ , \tag{6b'}$$

one can write

$$\Delta_2\approx\int d\vec{x}\,X_0^*U_{0,j=1}X_1 + \int d\vec{x}\,X_0^*\left[\frac{\beta_1}{x^4}(-U_0+\Delta_1)+\Delta_1U_1\right]X_0\ , \tag{44}$$

where the definition in Eq. (25) was used, the omitted terms are of shorter range than x^{-8}, and $U_{0,j=1}$ is the adiabatic potential of Eq. (17). From Eq. (43) the leading term of U_1 is $-\beta_1/x^4$ and from Eq. (17) the leading term of U_0 is $-\alpha_1/x^4$. The final form of Δ_2 is (to order x^{-8})

$$\Delta_2\approx\int d\vec{x}\,X_0^*U_0^{\mathrm{AD}}x_1 + \int d\vec{x}\,X_0^*\frac{\alpha_1\beta_1}{x^8}X_0\ . \tag{45}$$

The second term in Eq. (45) is recognized as the wave-function normalization part of the fourth-order adiabatic term, leading to an additional term in Eq. (17). The first term in Eq. (45) is the second-order energy shift due to the adiabatic potential; to order x^{-8} it depends only on the dipole polarizability, and will be treated in Sec. IV.

To summarize, the energy shift Δ and the effective potential U, including all significant terms up to order x^{-8} are the following:

$$\begin{aligned}\Delta&=\int d\vec{x}\,\Psi_{NLM}^*(x)\bar{U}(x)\Psi_{NLM}(x)\ ,\\ \bar{U}(x)&=-\frac{(\alpha_1+K\mu)}{x^4}+\frac{(-\alpha_2+6\beta_1)}{x^6}+\frac{\left[\delta+\frac{16\gamma}{5}\right]}{x^7}\\ &\quad+\left[-\alpha_3+15\beta_2-\epsilon+\alpha_1\beta_1-72\gamma\left[1+\frac{L(L+1)}{10}\right]\right]\Big/x^8\ .\end{aligned} \tag{46}$$

III. APPLICATION TO FINE STRUCTURE OF RYDBERG STATES

For helium, the constants appearing in Eq. (46) have, as shown in the Appendix, the following values:

$$\alpha_1=\tfrac{9}{32}=\mu,\ \ \alpha_2=\tfrac{15}{64},\ \ \alpha_3=\tfrac{525}{1024}\ ,$$

$$\beta_1=\tfrac{43}{512},\ \ \beta_2=\tfrac{107}{2048},\ \ \gamma=\tfrac{319}{12\,288}\ ,$$

$$\delta=\tfrac{213}{512},\ \ \epsilon=\tfrac{4329}{32\,768}\ .$$

This effective potential (Eq. 46) is then

$$\bar{U}(x)=-\frac{9(1+K)}{32x^4}+\frac{69}{256x^6}+\frac{3833}{7680x^7} -\left[\tfrac{55\,923}{32\,768}+\tfrac{957}{5120}L(L+1)\right]\frac{1}{x^8}\ . \tag{47}$$

Ultimately, the usefulness of this formalism depends on the existence of simple, analytical formulas for the expectation value of x^{-s} for hydrogenic atoms. The most complete reference seems to be that of Bockasten,[16] whose results extend to $s=8$. But the effectiveness of the method also requires reasonably rapid decrease of successive terms in $\bar{U}$ as well. In Table I I give values of the various contributions of Eq. (47) to the energy shifts of helium in the 1s NL state, for a number of values of N and L, using the analytical expressions of Bockasten.[16] I have taken the point of view that neither V_7 nor V_8 should be considered alone because of the identity (41). Instead, their sum should be treated as a single term, and V_7+V_8 is shown in Table I. (Here V_s is the expectation value of the term involving x^{-s} in $\bar{U}$.)

If the successive terms V_4, V_6, (V_7+V_8) actually represent the first three terms of an asymptotic series, then one should terminate the expansion at the smallest term, and the error should be of the order of that term. From Table I it appears that V_6 is the smallest term for $L=3$, while (V_7+V_8) is the smallest I have evaluated for $L>3$. A reasonable way to estimate the energy shifts might be to write

$$\begin{aligned}\Delta(L=3)&=(V_4+\tfrac{1}{2}V_6)\pm\tfrac{1}{2}V_6\ ,\\ \Delta(L>3)&=[V_4+V_6+\tfrac{1}{2}(V_7+V_8)]\\ &\quad\pm\tfrac{1}{2}(V_7+V_8)\ .\end{aligned} \tag{48}$$

This gives a conservative estimate of the accuracy

TABLE I. Shifts, in MHz, of various levels due to the successive terms in Eq. (47). In each case, V_s is the expectation value of the x^{-s} terms, obtained from the formulas of Ref. 16.

N	L	V_4	V_6	V_7	V_8	V_7+V_8
4	3	−34 426.893	687.154	318.099	−1258.660	−940.561
5		−19 741.757	504.373	253.499	−1055.841	−802.342
6		−12 089.553	341.849	177.902	−758.491	−580.589
7		−7865.727	234.679	124.459	−537.603	−413.144
8		−5379.202	165.769	88.938	−387.297	−298.359
9		−3830.846	120.581	65.192	−285.428	−220.236
10		−2820.251	90.084	48.965	−215.200	−166.235
5	4	−4700.418	24.018	4.447	−6.469	−2.022
6		−3022.388	20.109	4.137	−6.520	−2.383
7		−2018.075	15.121	3.260	−5.334	−2.074
8		−1401.852	11.225	2.485	−4.156	−1.671
9		−1008.593	8.419	1.896	−3.215	−1.319
10		−747.794	6.420	1.462	−2.504	−1.042
6	5	−961.669	1.828	0.188	−0.184	0.004
7		−667.395	1.657	0.192	−0.206	−0.014
8		−473.972	1.339	0.164	−0.185	−0.021
9		−345.824	1.053	0.133	−0.154	−0.021
10		−258.852	0.828	0.107	−0.126	−0.019
7	6	−256.690	0.223	0.015	−0.012	0.003
8		−188.084	0.213	0.016	−0.014	0.002
9		−139.860	0.181	0.014	−0.013	0.001
10		−106.006	0.149	0.0123	−0.0116	0.0007

of the expansion.

One further correction must be made before these results can be compared with experimental values. The first relativistic correction, due to the p^4 term in the kinetic energy of the outer electron, should be included; it has the following simple form[17]:

$$\Delta_{\rm rel}=\frac{R'}{N^3}\left[\frac{3}{4N}-\frac{1}{L+\frac{1}{2}}\right] . \tag{49}$$

Here $R'=\alpha^2 R_\infty(1-2K)=1.75092\times10^5$ MHz, and α is the fine-structure constant. In Table II the splitting between energy levels for $\Delta N=0$ and $\Delta L=1$ is presented. The theory is from Eqs. (48) and (49) while the experimental results are from Refs. 4 and 5 as presented in Ref. 5, where all magnetic and exchange effects have been removed.

IV. SHORT-RANGE AND SECOND-ORDER EFFECTS

(i) The first type of short-range correction is due to the penetration of the Rydberg electron into the core; it is obtained in first order by restoring $\bar{V}(x)$ in Eq. (7a). That is, an additional term in Δ_1 appears:

$$\Delta_{1p}=\int d\vec{x}\, X_0^* \bar{V}(x) X_0 \ , \tag{50}$$

where $\bar{V}(x)$ was defined in Eq. (5). This effect decreases approximately as N^{-3} and very rapidly with L. It is shown in Table III for $N=7$ and 8. It is insignificant for $L \gtrsim 4$.

(ii) A more subtle kind of short-range effect involves the true behavior of the x^{-s} terms I have derived above. Clearly, these must go over to less singular forms when $x\to0$. Let us first investigate the short-range behavior of the second-order adiabatic potential. An exact expression for this potential exists,[18] but it is more useful here to examine the various multipole contributions one at a time. The Callaway-Temkin (CT) form[7] is convenient for this purpose:

TABLE II. Comparison with experiment. Theoretical intervals are obtained from Table I, treated according to Eq. (48), and include the relativistic correction of Eq. (49). All results are in MHz.

Transition	Theory	Experiment (Refs. 4 and 5)	Theor.-Expt.
6*F*-*G*	8967 ±171	8904.22±0.05	63 ±171
7*F*-*G*	5777 ±117	5736.12±0.07	41 ±117
8*F*-*G*	3927 ±83	3898.52±0.04	28 ±83
9*F*-*G*	2785 ±60	2765.26±0.06	20 ±60
10*F*-*G*	2044 ±45	2030.41±0.14	14 ±45
11*F*-*G*	1544 ±34	1533.68±0.24	10 ±34
7*G*-*H*	1358.90 ±1.04	1359.16±0.11	−0.26±1.05
8*G*-*H*	932.66 ±0.84	931.34±0.44	1.32±0.95
9*G*-*H*	665.77 ±0.66		
10*G*-*H*	490.95 ±0.52		
11*G*-*H*	371.97 ±0.41		
7*H*-*I*	423.574±0.008	402.8 ±4.7	20.8 ±4.7
8*H*-*I*	294.351±0.011		
9*H*-*I*	211.830±0.011		
10*H*-*I*	157.082±0.010		
11*H*-*I*	119.496±0.008		

$$V_{\mathrm{CT}}(x)=-16\sum_{q=1}^{\infty}\frac{1}{(2q+1)x^{2(q+1)}}\int_0^x dy\,y^{2(q+1)}e^{-4y}\left[\frac{1}{q}+\frac{2y}{q+1}\right], \tag{51}$$

where the index q refers to the multipole order, and I have scaled the expression to apply to the He^+ core. As shown in Ref. 7, the sum in Eq. (51) can be carried out explicitly. In Table IV the results of the Callaway-Temkin potential are compared, for $N=8$ and $L=3,4$, with the ordinary inverse-power expressions and the total CT results. I conclude that, for the $L=3$ case at least, short-range effects are not negligible and multipoles with $q>3$ contribute significantly when compared with the experimental accuracy.

(iii) The first term in Eq. (45) gives an "effective" x^{-8} potential if only the leading term $(-\alpha_1/x^4)$ is retained in U_0^{AD} and X_1 satisfies Eq. (6b) approxi-

TABLE III. Energy shifts in MHz due to penetration of the core, obtained analytically from Eq. (50).

L	Δ_{1p} $(N=7)$	Δ_{1p} $(N=8)$
3	−18.970	−13.691
4	−0.054	−0.043
5	-7.1×10^{-5}	-7.1×10^{-5}

TABLE IV. Comparison of adiabatic potentials to illustrate the effect of short-range cutoffs and higher multipoles. Column 2 is the contribution of the first three long-range terms; column 3 is the Callaway-Temkin result, from Eq. (51). All entries are analytical and in MHz.

Multipole q	$N=8,\ L=3$ $\langle \alpha_q/x^{2q+2}\rangle$	$-\langle V_{q,\mathrm{CT}}\rangle$	Difference
1	5377.73	5354.92	22.81
2	144.15	128.27	15.88
3	50.27	14.61	35.66
4		(3.90)	
Sum 1+2+3	5572.15	5497.80	74.35
Total Callaway-Temkin value is 5505.78 MHz.			
	$N=8,\ L=4$		
1	1401.468	1401.395	0.073
2	9.761	9.720	0.041
3	0.391	0.351	0.040
Sum 1+2+3	1411.620	1411.466	0.154
Total Callaway-Temkin value is 1411.69 MHz.			

mately:

$$\left[-\nabla_x^2-\frac{2}{x}+\frac{1}{N^2}\right]X_1(x)=\left[\frac{\alpha_1}{x^4}-\left\langle\frac{\alpha_1}{x^4}\right\rangle\right]X_0(x)\ . \tag{52}$$

I have solved this equation numerically for $N=8$ for the resulting second-order energies are given in Table V. As a check on the numerical work, I also solved Eq. (52) analytically for the general nodeless case, where $L=N-1$. If one lets $X_1=FX_0$, then the function $F(x)$ satisfies the simple equation

$$F''+2\left[\frac{N}{x}-\frac{1}{N}\right]F'=\alpha_1\left[\frac{1}{x^4}-\left\langle\frac{1}{x^4}\right\rangle\right]\ . \tag{53}$$

TABLE V. Second-order energies due to x^{-4} potential in MHz. Asterisks indicate analytic results from Eq. (54); other entries are numerical.

L	Δ_2 $(N=7)$	Δ_2 $(N=8)$
3	-11.51	-8.01
4	-0.517	-0.373
5	-0.043	-0.033
6	-4.87×10^{-3}*	-4.14×10^{-3}
7		-6.38×10^{-4}*

This can be solved easily, since only F' and F'' appear explicitly, and using the first term of Eq. (45) one obtains

$$\Delta_2^{L=N-1}=-\frac{4\alpha_1^2}{N^8}\frac{(128N^4-560N^3+848N^2-518N+105)}{(2N-5)[(2N-1)(N-1)(2N-3)]^3}\ . \tag{54}$$

Again it is true that this higher-order effect is significant for $L=3$ at the 10-MHz level and for $L=4$ at about 5% of that level. For $L=5$ and 6 the effect is somewhat greater than the V_7+V_8 long-range part (Table I).

V. CONCLUSIONS

(i) The polarization potential[2] used to calculate Rydberg states of two-electron atoms and positive ions has been derived carefully by the Feshbach operator formalism[8] including all significant terms up to x^{-8}.

(ii) Using the expressions of Bockasten[16] for hydrogenic matrix elements of x^{-s} the energy shifts of various states of helium with $N\geq4$ and $L\geq3$ have been explicitly calculated. Mass-polarization and relativistic effects have been included, and estimates of the error due to the effect of short-range and higher-order terms have been made.

(iii) A comparison has been made between these results and the best measurements.[4,5] For $L=3$ the estimated errors of the polarization model preclude any kind of critical test, although it is just the $F-G$ intervals that are most thoroughly and accurately known.[19] For these cases, the discrepancy between theory and experiment is much smaller than the estimated error.

For the intervals $7G-H$ and $8G-H$ the accuracy of the theory is almost good enough to look for real discrepancies, such as the retardation effects derived by Kelsey and Spruch.[6] Indeed, the $H-I$ intervals seem to be known very well theoretically, but here the experiment has begun to lose accuracy seriously. These higher-L states should certainly be reexamined experimentally, after which it may be possible to confirm the existence of the Kelsey-Spruch effect.

ACKNOWLEDGMENTS

Many of the calculations reported here were performed using the remarkable symbolic manipulation program MACSYMA, which was developed by the Mathlab Group at MIT with partial support by the USERDA [Contract No. E(11-1)-3070] and by NASA [Grant No. NSG 1323]. I am grateful for discussions with W. H. Wing, D. R. Cok, and S. R. Lundeen on both theory and experiment. Some critical but very helpful correspondence with M. J. Seaton and M. H. Mittleman is also gratefully acknowledged.

APPENDIX: EVALUATION OF THE COEFFICIENTS

The various coefficients (α_q, β_q, δ, ϵ, γ, μ) appearing in Eq. (46) are easy to compute analytically, using the well-known Dalgarno-Lewis method.[20] In fact, most have been evaluated previously, usually for hydrogen rather than He$^+$. In this appendix I will indicate how to scale the results for any hydrogenic core, and will apply the method to some simple cases.

For the adiabatic terms $(j=1)$ the scaling is obtained as follows: A wave function for nuclear charge Z is related to the corresponding function for hydrogen by

$$\psi_Z(r)=Z^{3/2}\psi_H(Zr)\ . \tag{A1}$$

A matrix element of the potential of the $j=1$ type is

$$\begin{aligned}M_{nm}(x)&\equiv\left\langle n\left|\left[\frac{2}{|\vec{x}-\vec{r}|}-\frac{2}{x}\right]\right|m\right\rangle\\&=2Z^3\int d\vec{r}\,\psi_H^n(Zr)\left[\frac{1}{|\vec{x}-\vec{r}|}-\frac{1}{x}\right]\psi_H^m(Zr)_0\ .\end{aligned} \tag{A2}$$

Changing variables to $\vec{\rho}\equiv Z\vec{r}$ one obtains

$$\begin{aligned}M_{nm}(x)&=2\int d\vec{\rho}\,\psi_H^n(\rho)\left[\frac{Z}{|Z\vec{x}-\vec{\rho}|}-\frac{Z}{Zx}\right]\psi_H^m(\rho)\\&=Z[M_{nm}(Zx)]_H\ .\end{aligned} \tag{A3}$$

All $j=1$ terms involve k factors of M in the numerator and $k-1$ energy denominators, d_n, each proportional to Z^2; here k is the order of perturbation theory. It follows that the adiabatic potential of order k scales like

$$V_Z^k(x)=Z^{2-k}V_H^k(Zx)\ , \tag{A4}$$

in terms of the corresponding term in hydrogen.[10] It is only the second-order ($k=2$) potential which scales entirely by the substitution $x\rightarrow Zx$, although this seems to have been assumed for $k>2$ in some earlier work. It is clear, then, that the adiabatic coefficients scale as follows:

$$\begin{aligned}\alpha_{q,Z}&=\alpha_{q,H}/Z^{2(q+1)}\ ,\\ \delta_Z&=\delta_H/Z^8\ ,\\ \epsilon_Z&=\epsilon_H/Z^{10}\ .\end{aligned} \tag{A5}$$

The nonadiabatic terms ($j=2$) have an additional factor of h/d_n, which does not modify the results of Eq. (A4) as long as ∇_x^2 is the only part of h that survives the commutation operation of Eq. (21); in that case

$$\nabla_x^2/d_n\rightarrow\nabla_x^2/(Z^2d_n)=\nabla_{Zx}^2/d_n\ .$$

Thus we find that the nonadiabatic coefficients scale as follows:

$$\beta_{q,Z}=\beta_{q,H}/Z^{2(q+2)}\ . \tag{A6}$$

The energy-dependent ($j=3$) and mass-polarization ($j=2$) contributions also are of second order ($k=2$), but they involve the Coulomb part of h, which, in general, is $2(1-Z)/x$. The general form of the energy-dependent term [Eq. (42)] is

$$\Delta_{1,j=3}=16\gamma_H\int d\vec{x}\,X_0\left[\left[\frac{Z-1}{Z}\right]\frac{1}{5(Zx)^7}-\frac{9}{2(Zx)^8}\left[1+\frac{L(L+1)}{10}\right]\right]X_0\ , \tag{A7}$$

which scales like Zx except for the x^{-7} term. In the same way, Eq. (29) becomes

$$U_{0,Z}^{\mathrm{mp}}=-\frac{K\mu_H(Z-1)}{(Zx)^4} \tag{A8}$$

again deviating from the usual scaling for $k=2$.

If one defines a function $G(r)$ as the solution of the equation

$$\begin{aligned}&[H_0(r),G(r)]\,|\,1s\rangle\\&\qquad=(Q(r)-\langle 1s\,|\,Q(r)\,|\,1s\rangle)\,|\,1s\rangle\ ,\end{aligned} \tag{A9}$$

then the sort of matrix element that appears in all the coefficients in Eq. (46) becomes the following:

$$\langle\bar{n}\,|\,Q(r)\,|\,1s\rangle=-d_n\langle\bar{n}\,|\,G(r)\,|\,1s\rangle\ . \tag{A10}$$

Let me illustrate by first evaluating α_1 for $Z=1$:

$$\alpha_{1,H}\equiv\sum_{\bar{n}\neq 1s}\frac{\langle 1s\,|\,2\vec{r}\cdot\hat{x}\,|\,\bar{n}\rangle\langle\bar{n}\,|\,2\vec{r}\cdot\hat{x}\,|\,1s\rangle}{E_n-E_{1s}} \tag{A11}$$

and $G(r)$ satisfies the equation

$$-\nabla_r^2G+2\frac{\partial G}{\partial r}=2\vec{r}\cdot\hat{x}\ , \tag{A12}$$

whose solution is

$$G(\vec{r})=(r+\tfrac{1}{2}r^2)\hat{r}\cdot\hat{x}\ . \tag{A13}$$

Then the polarizability is

$$\begin{aligned}\alpha_{1,H}=&\sum_{\bar{n}\neq 1s}\langle 1s\,|\,2\vec{r}\cdot\hat{x}\,|\,\bar{n}\rangle\\&\qquad\times\langle\bar{n}\,|\,(r+\tfrac{1}{2}r^2)\hat{r}\cdot\hat{x}\,|\,1s\rangle\end{aligned} \tag{A14}$$

by virtue of Eq. (A10), and the sum over $\bar{n}$ can be carried out:

$$\alpha_{1,H}=\langle 1s\,|\,2r(r+\tfrac{1}{2}r^2)P_1^2\,|\,1s\rangle=\tfrac{9}{2}\ . \tag{A15}$$

In the mass-polarization term for $Z=1$

$$\mu_H\equiv\sum_{\bar{n}\neq 1s}\frac{8\langle 1s\,|\,\vec{r}\cdot\hat{x}\,|\,\bar{n}\rangle\langle\bar{n}\,|\,\hat{r}\cdot\hat{x}\,|\,1s\rangle}{(E_n-E_{1s})^2}\ , \tag{A16}$$

so $Q(r)=\hat{r}\cdot\hat{x}$ and the solution to Eq. (A9) is

$$G(r)=\frac{1}{2}\vec{r}\cdot\hat{x}\ . \qquad (A17)$$

Finally,

$$\mu_H=\sum_{\bar{n}\neq 1s}\frac{\langle 1s\,|\,2\vec{r}\cdot\hat{x}\,|\,\bar{n}\rangle\langle\bar{n}\,|\,2\vec{r}\cdot\hat{x}\,|\,1s\rangle}{(E_n-E_{1s})}\ , \qquad (A18)$$

identical to α_{1H} by inspection of Eq. (A11), and, from Eq. (A8) and (29),

$$\mu_Z=\frac{Z-1}{Z^4}\alpha_{1,H}=(Z-1)\alpha_{1,Z}\ . \qquad (A19)$$

The evaluation of δ_H appears in Ref. 9. The fourth-order coefficient, ϵ is evaluated by repeated application of (A9) and (A10), as follows:

$$\epsilon_H=\sum_{\bar{n},\bar{m},\bar{p}\neq 1s}\frac{\langle 1s\,|\,2\vec{r}\cdot\hat{x}\,|\,\bar{n}\rangle\langle\bar{n}\,|\,2\vec{r}\cdot\hat{x}\,|\,\bar{m}\rangle\langle\bar{m}\,|\,2\vec{r}\cdot\hat{x}\,|\,\bar{p}\rangle\langle\bar{p}\,|\,2\vec{r}\cdot\hat{x}\,|\,1s\rangle}{d_n d_m d_p}\ . \qquad (A20)$$

First solve Eq. (A12) and insert $G(r)$ from Eq. (A13) in the first and last matrix elements above, obtaining

$$\epsilon_H=-\sum_{\bar{m}\neq 1s}\frac{|\langle 1s\,|\,(2r^2+r^3)(\hat{x}\cdot\hat{r})^2\,|\,\bar{m}\rangle|^2}{E_m-E_{1s}}\ . \qquad (A21)$$

Then expand $(\hat{x}\cdot\hat{r})^2=\frac{1}{3}P_0+\frac{2}{3}P_2$ and solve two equations like (A9) for the P_0 and P_2 parts of $G(r)$. Then integrate to obtain the result $\epsilon_H=-4329/32$, which scales like $1/Z^{10}$. The coefficient γ_H was evaluated in Ref. 13; since d_n appears to the third power in Eq. (35) several repetitions of the method are needed.

---

[1] H. A. Bethe, *Handbuch der Physik* (Edward, Ann Arbor, 1943), Vol. 24, part 1, p. 339.

[2] C. Deutsch, Phys. Rev. A 13, 2311 (1976); 2, 43 (1970); 3, 1516(*E*) (1971).

[3] A. Temkin and A. Silver, Phys. Rev. A 10, 1439 (1974).

[4] J. W. Farley, K. B. MacAdam, and W. H. Wing, Phys. Rev. A 20, 174 (1979).

[5] D. R. Cok and S. R. Lundeen, Phys. Rev. A 23, 2488 (1981).

[6] E. J. Kelsey and L. Spruch, Phys. Rev. A 18, 1055 (1978); 18, 845 (1978); 18, 15 (1978).

[7] R. J. Drachman and A. Temkin, in *Case Studies in Atomic Collision Physics,* edited by E. W. McDaniel and M. R. C. McDowell (North-Holland, Amsterdam, 1972), Vol. 2, pp. 399-481. See references herein.

[8] H. Feshbach, Ann. Phys. (N.Y.) 19, 287 (1962).

[9] R. J. Drachman, J. Phys. B 12, L699 (1979).

[10] R. J. Drachman, Phys. Rev. 173, 190 (1968).

[11] C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. 165, 53 (1968); J. Callaway, R. W. LaBahn, R. T. Pu, and W. M. Duxler, *ibid.* 168, 12 (1968).

[12] D. R. Cok and S. R. Lundeen, Phys. Rev. A 24, 3283(E) (1981). The entries in Table V have an overall sign error.

[13] M. J. Seaton and L. Steenman-Clark, J. Phys. B 10, 2639 (1977).

[14] The coefficient is the same as that reported by S. Watanabe and C. H. Greene [Phys. Rev. A 22, 158 (1980)], but this agreement is evidently fortuitous.

[15] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1965), Vol. I, p. 484.

[16] K. Bockasten, Phys. Rev. A 9, 1087 (1974).

[17] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 120. A table containing a sample of relativistic shifts is in Ref. 12.

[18] A. Dalgarno and N. Lynn, Proc. Phys. Soc. London, Ser. A 70, 223 (1957).

[19] For these lower values of L the diagrammatic calculations of T. N. Chang and R. T. Poe [Phys. Rev. A 14, 11 (1976); 10, 1981 (1974)] should certainly be more reliable. See Ref. 5 for additional comparsions between theory and experiment.

[20] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London, Ser. A 233, 70 (1955); G. Lamm and A. Szabo, J. Phys. B 10, 995 (1977).