PHYSICAL REVIEW A VOLUME 50, NUMBER 4 OCTOBER 1994

Calculation of the Bethe logarithm for the Rydberg states of helium

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(Received 29 April 1994)

A very efficient technique for the finite-basis-set calculation of logarithmic sums is introduced. The basis sets contain sequences of nonlinear parameters determined by the zeros of Laguerre polynomials. It is shown that one can easily obtain convergence to 12 digits in fast calculations involving small basis sets. The method is then applied to calculations of the asymptotic expansion of the Bethe logarithm for the Rydberg states of helium. As pertubation calculations of the sums involved diverge, the present method is used to obtain accurate results for atoms in dipole and quadrupole fields from which the adiabatic contributions are extracted. A discussion of gauges in the multipole case and the suppression of roundoff errors by working in a mixed gauge is presented. A strategy for handling the nonadiabatic contributions to sums is presented and used to obtain preliminary bounds on these contributions.

PACS number(s): 31.30.Jv, 31.20.Di, 31.50.+w

I. THE BETHE LOGARITHM

In the past few years, experimental measurements [1] and theoretical predictions [2] of transition frequencies among the Rydberg states of helium have advanced substantially in accuracy to the point that they are sensitive to both QED contributions and Casimir-Polder retardation corrections. The largest uncertainty in the theoretical predictions was due to the uncertainty in the self-energy contribution to the energy, specifically the Bethe-logarithm contribution to the Lamb shift. Results for the variational calculation of the electric dipole polarizability contribution to the Bethe logarithm were published recently [3], eliminating the gap between the uncertaintainties in the theoretical predictions and experimental results and pointing to discrepancies between both that cannot be accounted for by residual Casimir-Polder retardation corrections [4]. It is still necessary to add to that calculation the electric quadrupole and (of the same order) the nonadiabatic dipole polarizability contributions to the Bethe logarithm in order to have an estimate of the uncertainty in the theoretical results. In this paper we present the details of the difficult calculations that yield the dipole corrections to the Bethe logarithm, as well as results for the quadrupole contribution and an estimate of the nonadiabatic dipole correction with a discussion of the difficulties one encounters in this last case.

Following Kabir and Salpeter [5], the lowest-order Lamb shift for a two-electron ion in an nLS state can be written as

$$\Delta E_{L,1} = \frac{2}{3\pi}\alpha^3 Z^4 D \left\{ \frac{19}{30} + \ln[(\alpha Z)^{-2}] + \ln[Z^2 R_M / k(nLS,Z)] + 2.296\pi\alpha Z + \frac{\mu}{M} C_M \right\} , \quad (1)$$

where

$$D = \frac{2\pi}{Z^3}\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle \quad (2)$$

is independent of Z in the hydrogenic limit and $(\mu/M)C_M$ involves finite-mass terms. There is in (1) a term that is difficult to calculate: the two-electron Bethe logarithm (BL from now on) defined for a state with energy E_0 by

$$\ln[Z^2/k(nLS,Z)] = A_1/B_1 , \quad (3)$$

where

$$A_k^{(p)} = \sum_n |\langle \Psi_0 | \mathbf{p}_1 + \mathbf{p}_2 | \Psi_n \rangle|^2 (E_n - E_0)^k \ln|E_n - E_0| , \quad (4)$$

$$B_k^{(p)} = \sum_n |\langle \Psi_0 | \mathbf{p}_1 + \mathbf{p}_2 | \Psi_n \rangle|^2 (E_n - E_0)^k . \quad (5)$$

The superscript (p) denotes that the expressions for the sums are written in the velocity gauge (velocity form of the dipole operator). The denominator B_1 can be easily calculated using commutator relations of the Hamiltonian with the operator $\mathbf{p}_1 + \mathbf{p}_2$:

$$B_1 = Z^4 D , \quad (6)$$

with D defined in (2). There is, however, no corresponding analog for the numerator in (3). Although the logarithmic sum A_1 is very similar to B_1, in which each term would be multiplied by a (slowly varying) logarithm of $|E_n - E_0|$, it is actually very hard to perform. To explain this difficulty, consider the nS states in two-electron systems (or analogously, the ns states in one-electron systems): the sum B_k is finite for $k \leq 1$ but diverges for $k > 1$. The sum A_1 is somewhere "in between" these two cases and is therefore described as an "almost divergent" sum. This sum involves large cancellations and, as will be seen later in the simpler one-electron case, requires an accurate representation of all Ψ_n close to the origin. Calculations of the BL for two-electron ions have been performed based on treating the electron-electron interaction as a perturbation [6] or in a simple screened hydrogenic approximation [7], and extremely accurate (correlated) calculations of the BL have been recently performed for the low lying states of helium [8]. In this paper, the BL of the Rydberg states of helium will be calculated in the framework of the asymptotic expansion [9–11] in terms of multipole polarizabilities of the inner electron induced by the outer one. This expansion, which becomes exact in the high-L limit, has been very successful in obtaining accurate energy levels and matrix elements for the Rydberg states of helium.

The asymptotic expansion is best exemplified by its expression of the energy levels [9]. The Hamiltonian for the Rydberg state is written as

$$H = H_0 + V_{12} = h_1 + h_2 + V_{12} \tag{7}$$

with

$$\begin{aligned} h_1 &= -\frac{1}{2}\nabla^2_{r_1} - \frac{Z}{r_1}\,, \\ h_2 &= -\frac{1}{2}\nabla^2_{r_2} - \frac{Z-1}{r_2}\,, \\ V_{12} &= \frac{1}{r_{12}} - \frac{1}{r_2}\,, \end{aligned} \tag{8}$$

where h_1 describes the inner electron, in the presence of a totally unscreened nucleus, h_2 describes the outer electron in the presence of a nucleus that is totally screened by the inner electron, and V_{12} describes the small correction to this last screened potential. Treating V_{12} as a perturbation leads to a multipole asymptotic expansion, which in the case of the energy, for example, yields a correction of the form [9]

$$\begin{aligned} \delta E \approx & -\frac{1}{2}\alpha_{1,a}\langle r_2^{-4}\rangle_{nL} \\ & -\frac{1}{2}\left(\alpha_{2,a} - 6\alpha_{1,na}\right)\langle r_2^{-6}\rangle_{nL} + \cdots \,, \end{aligned} \tag{9}$$

where the $\alpha_{l,a}$ and the $\alpha_{l,na}$ are the adiabatic and nonadiabatic l-pole polarizabilities, respectively, of the core electron. A similar expansion can be obtained for the expectation value of the δ function D in Eq. (2) and therefore for the sum B_1 in Eq. (6), with the coefficients of the asymptotic expansion (i.e., the coefficients of $\langle r_2^{-j}\rangle_{nL}$) obtained analytically as a result of a perturbation expansion of D [12]. A similar expansion does not exist however for the crucial quantity A_1 in (2) given that there is no closed form expression for that sum; therefore a direct calculation of the perturbation to the sum A_1 must be performed. A_1 can be written in terms of the leading hydrogenic contributions in (7) plus the (small) contribution of the polarization of the core electron due to the potential V_{12} in (8) as [3]

$$A_1 = 2Z^4\left[\beta_{1s} + \frac{(Z-1)^4}{Z^4 n^3}\beta_{nL}\right] + \Delta_{\rm pol}A_1\,, \tag{10}$$

where β_{nL} is the BL of an hydrogen atom in the state nL and $\Delta_{\rm pol}A_1$ is the correction to the BL of the core electron β_{1s} due to the polarization induced by the outer (Rydberg) electron. One could then try to apply standard perturbation techniques to A_1 in order to obtain the correction $\Delta_{\rm pol}A_1$. In the following sections, an outline describing the way in which to formulate such a calculation will be presented as well as the means to avoid the divergences that would occur in the standard formulation of perturbation theory.

II. ASYMPTOTIC EXPANSION OF THE BETHE LOGARITHM

As mentioned in the preceding section, one could attempt a simple second-order perturbation expansion of the sum A_1 for the inner-shell electron, with the perturbation given by the interaction with the outer (Rydberg) electron, formulated in terms of a multipole (asymptotic) expansion. In order to proceed this way, consider the dipole-adiabatic correction to the energy in Eq. (9), namely,

$$\delta E_{1,a} = -\frac{1}{2}\alpha_{1,a}\langle r_2^{-4}\rangle_{nL}\,. \tag{11}$$

Replacing in (11) the analytic expansion of the dipole-polarizability, we obtain

$$\delta E_{1,a} = \langle r_2^{-4}\rangle_{nL}\sum_i \frac{\langle 1s|z|i\rangle\langle i|z|1s\rangle}{E_{1s}-E_i}\,, \tag{12}$$

which can be rewritten as

$$\delta E_{1,a} = \sum_i \frac{\langle 1s|Fz|i\rangle\langle i|Fz|1s\rangle}{E_{1s}-E_i} \text{ with } F = \sqrt{\langle r_2^{-4}\rangle_{nL}}\,. \tag{13}$$

The last equation tells us that the perturbation to the energy can be interpreted as that produced by an external static, constant electric dipole field

$$\mathbf{F} = \sqrt{\langle r_2^{-4}\rangle_{nL}}\,\hat{\mathbf{z}}\,, \tag{14}$$

which is consistent with the concept of dipole polarizability and Eq. (11) written as

$$\delta E_{1,a} = -\frac{1}{2}\alpha_{1,a}F^2\,, \tag{15}$$

with $\mathbf{F}$ defined in (14). The problem of finding the asymptotic dipole contribution to matrix elements or sums is then reduced to finding the perturbation of the field (14) to the uncorrelated Hamiltonian $h_1 + h_2$ [Eq. (8)]. This applies in general to any static l-pole operator, so that in the adiabatic case we can write

$$\mathbf{F}_l^{\rm ad} = F_l^{\rm ad}C_{l,0}(\hat{\mathbf{r}}) = F_l^{\rm ad}\sqrt{\frac{4\pi}{2l+1}}Y_{l,0}(\hat{\mathbf{r}}) \tag{16}$$

with

$$F_l^{\rm ad} = \sqrt{\left\langle \frac{1}{r_2^{2l+2}} \right\rangle_{nL}} . \tag{17}$$

Then the calculation of sum rules such as the BL for the Rydberg states of helium can be formulated as an asymptotic expansion of the one-electron sum of the inner shell in the presence of l-pole fields obtained in terms of expectation values of inverse powers of the position of the Rydberg electron. This picture is based on the expansion of the perturbing potential

$$V_{12} = \frac{1}{r_{12}} - \frac{1}{r_2} = \sum_{\substack{l=1 \\ q}}^{\infty} u^{lq}(\mathbf{r_1})\, v^{lq}(\mathbf{r_2}) , \tag{18}$$

where

$$u^{lq}(\mathbf{r_1}) = r_1^l C_{l,q}(\hat{\mathbf{r_1}}), \tag{19}$$

$$v^{lq}(\mathbf{r_2}) = \frac{C^*_{l,q}(\hat{\mathbf{r_2}})}{r_2^{l+1}} , \tag{20}$$

with the perturbation to the energies and wave functions expressed as a sum of perturbations due to each term in (18). In this expansion, one starts with the uncorrelated (screened) one-electron states for which we introduce now the following notation:

$$\Psi_i = \psi_{n_i,l_i}(\mathbf{r}_1)\, \phi_{n_{i'},l_{i'}}(\mathbf{r}_2) \equiv |i\rangle|i'\rangle , \tag{21}$$

where a primed index will always refer to the Rydberg electron; in particular

$$\Psi_0 = |0\rangle|0'\rangle = \psi_{1,s}(\mathbf{r}_1)\, \phi_{n_{0'},l_{0'}}(\mathbf{r}_2) \tag{22}$$

describes the state for which the BL is considered. The one-electron functions are exact hydrogenic states:

$$\begin{aligned} &H_0\Psi_i = E_i\Psi_i = (e_i + e_{i'})|i\rangle|i'\rangle , \\ &h_1|i\rangle = e_i|i\rangle , \\ &h_2|i'\rangle = e_{i'}|i'\rangle , \end{aligned} \tag{23}$$

where $E_i = e_i + e_{i'}$. In what follows we call

$$\begin{aligned} &\Delta_{ij} = E_i - E_j = \epsilon_{ij} + \epsilon_{i'j'} , \\ &\epsilon_{ij} = e_i - e_j , \\ &\epsilon_{i'j'} = e_{i'} - e_{j'} . \end{aligned} \tag{24}$$

The jth-order perturbations to the energy and the wave function, respectively, $\delta_j E_n$ and $\delta_j \Psi_n$, are given for $j = 1, 2$ by

$$\delta_1 E_i = \langle \Psi_i | V_{12} | \Psi_i \rangle , \tag{25}$$

$$\delta_2 E_i = \sum_n \frac{\langle \Psi_i | V_{12} | \Psi_n \rangle \langle \Psi_n | V_{12} | \Psi_i \rangle}{\Delta_{in}} , \tag{26}$$

$$\delta_1 \Psi_i = \sum_n |\Psi_n\rangle \frac{\langle \Psi_n | V_{12} | \Psi_i \rangle}{\Delta_{in}} , \tag{27}$$

$$\begin{aligned} \delta_2 \Psi_i = &\sum_{nm} |\Psi_m\rangle \frac{\langle \Psi_m | V_{12} | \Psi_n \rangle \langle \Psi_n | V_{12} | \Psi_i \rangle}{\Delta_{im}\Delta_{in}} \\ &- \sum_n |\Psi_n\rangle \frac{\langle \Psi_n | V_{12} | \Psi_i \rangle \langle \Psi_i | V_{12} | \Psi_i \rangle}{\Delta_{in}^2} . \end{aligned} \tag{28}$$

These expressions simplify substantially in the adiabatic approximation, in which one assumes that $\epsilon_{i'j'} \ll \epsilon_{ij}$ for $j \neq i$. With this assumption, one can use in the expressions for $\delta_j E_i$ and $\delta_j \Psi_i$ the expansion

$$\frac{1}{\Delta_{nm}} = \frac{1}{\epsilon_{nm}} - \frac{\epsilon_{n'm'}}{\epsilon_{nm}^2} + \frac{\epsilon_{n'm'}^2}{\epsilon_{nm}^3} - \cdots . \tag{29}$$

The leading term yields the adiabatic correction while the others yield nonadiabatic corrections of different orders. The first adiabatic corrections of relevance to this paper are then

$$\delta_2^{(l)} E_i^{(\rm ad)} = \sum_{\substack{n \\ q,q'}} \frac{\langle i | u^{lq} | n \rangle \langle n | u^{lq'} | i \rangle}{\epsilon_{in}} \langle i' | v^{lq} v^{lq'} | i' \rangle , \tag{30}$$

$$\delta_1 \Psi_i^{(\rm ad)} = \sum_{\substack{n \\ l,q}} \frac{|n\rangle \langle n | u^{lq} | i \rangle}{\epsilon_{in}}\, v^{lq} | i' \rangle , \tag{31}$$

$$\begin{aligned} \delta_2 \Psi_i^{(\rm ad)} = &\sum_{\substack{nm \\ ll',qq'}} \frac{|m\rangle \langle m | u^{lq} | n \rangle \langle n | u^{l'q'} | i \rangle}{\epsilon_{im}\epsilon_{in}}\, v^{lq} v^{l'q'} | i' \rangle + \sum_{\substack{nn' \\ ll',qq'}} \frac{|i\rangle \langle i | u^{lq} | n \rangle \langle n | u^{l'q'} | i \rangle}{\epsilon_{in}}\, \frac{|n'\rangle \langle n' | v^{lq} v^{l'q'} | i' \rangle}{\epsilon_{i'n'}} \\ &- \sum_{\substack{n \\ ll',qq'}} \frac{|n\rangle \langle n | u^{lq} | i \rangle \langle i | u^{l'q'} | i \rangle}{\epsilon_{in}^2}\, v^{lq} | i' \rangle \langle i' | v^{l'q'} | i' \rangle . \end{aligned} \tag{32}$$

One could apply directly these perturbation techniques in the calculation of A_1 or B_1; however, perturbation theory yields diverging results given that the (excited) intermediate states in the summations in (4) and (5) are very strongly perturbed even for weak external fields. Notice that unlike the case $\mathbf{F} = \mathbf{0}$, no longer is there an infinite number of bound states, but a finite number of *resonances* describing an electron able to tunnel through the finite potential barrier that occurs when the electron is in the presence of both a Coulomb field and a constant

l-pole field.

Our strategy will then be to calculate *directly* A_1 and B_1 for a $1s$ electron in a Coulomb potential and a static, homogeneous external field $\mathbf{F}_l$ for different values of its magnitude F_l. Then, upon interpolation using a least-squares fit we will obtain for A_1, for example,

$$A_1 = \sum_{i=0}^{N} A_l^{(i)}\, F_l^i \ , \tag{33}$$

where $A_l^{(0)}$ is the field free result, $A_l^{(1)} = 0$, and $A_l^{(2)}$ is the adiabatic coefficient of F_l^2 being sought. This is a difficult task because it involves a very accurate calculation of the BL in order to extract a small perturbation out of the full value of the BL which consists in its first 5–6 digits of the purely hydrogenic value only.

III. THE HYDROGENIC BETHE LOGARITHM IN A DIPOLE FIELD

In order to find the static dipole perturbation directly from the BL values we need a variational procedure that will calculate the BL to about 9–10 digits accuracy. This will allow us to extract the sought second-order perturbation effects to about 3 digits accuracy. An efficient one-electron finite-basis-set variational BL calculation available makes use of a multiexponential basis set in which the exponential parameters are gradually optimized by an iterative process [6]. The accuracy obtained using this method for the ground state is only 6–7 digits in a direct calculation and 7–8 digits upon extrapolation of the results for different dimensions of the basis set. The direct use of a variational basis set to represent both the initial state and the intermediate states in the sums A_k and B_k is appealing because it can be implemented in a straightforward way to problems involving external fields. In this work, we will introduce an alternative method that improves the results obtained in [6] by providing faster computation times as well as (the necessary) higher accuracies with smaller basis sets.

We start, as customary for an external dipole field [13], by formulating the problem in the parabolic coordinates ξ, η, and φ. In terms of spherical coordinates, φ denotes the same angle in the x-y plane and

$$\xi = r + z \ , \quad \eta = r - z \ . \tag{34}$$

The advantage of parabolic coordinates is that the hydrogenic wave functions separate into the product of two independent functions, one of ξ and one of η, when a hydrogenic ion is in the presence of a constant dipole field in the z direction. If the dipole field has magnitude F, the Hamiltonian can be written as

$$\begin{gathered} H(Z,F)\Psi = E\Psi \ , \\ (\xi+\eta)H(Z,F) = \xi h_-(Z_1,F;\xi) + \eta h_+(Z_2,F;\eta) \ , \\ Z = Z_1 + Z_2 \ . \end{gathered} \tag{35}$$

The wave function can now be written as

$$\Psi(\xi,\eta,\varphi) = \psi_+(\xi)\psi_-(\eta)e^{im\varphi} \tag{36}$$

with the $\psi_\pm$ satisfying

$$h_\pm(Z_i,F;x)\psi_\pm(x) = E\psi_\pm(x) \ , \tag{37}$$

where

$$h_\pm(Z_i,F;x) = -\frac{2}{x}\frac{d}{dx}\left(x\frac{d}{dx}\right) - \frac{2Z_i}{x} + \frac{m^2}{2x^2} \pm \frac{1}{2}Fx \ . \tag{38}$$

With this choice of variables, one can then construct a variational basis set consisting of basis vectors that are *separable* products of functions of ξ, η, and φ, analogous to the exact hydrogenic functions but containing also a set of nonlinear variational parameters. Such a basis set will consist of functions of the form

$$\psi^{\text{var}} \propto e^{im\varphi} \underbrace{\xi^{|m|/2}e^{-\lambda\xi/2}L_j^{|m|}(\lambda\xi)}_{f_j(\xi)}\ \underbrace{\eta^{|m|/2}e^{-\lambda\eta/2}L_k^{|m|}(\lambda\eta)}_{f_k(\eta)} \ . \tag{39}$$

However, although this basis set will yield excellent results for the calculation of energy eigenvalues, the results obtained when it is applied to the calculation of sum rules are very bad. Even for the very simple sum rule (5) in the absence of an external field in its one-electron form

$$b_1 = \sum_n |\langle\psi_0|\mathbf{p}|\psi_n\rangle|^2(E_n - E_0) \ , \tag{40}$$

which can be checked against its exact value

$$b_1 = 2\pi Z\langle\psi_0|\delta(\mathbf{r})|\psi_0\rangle \ , \tag{41}$$

this basis set yields extremely poor convergence: only 2–3 digits even with very large basis sets. The reason for this can be seen if we rewrite (40) in the following way:

$$b_1 = \langle\psi_0|\mathbf{p}\cdot\left\{\left[\sum_n (E_n - E_0)|\psi_n\rangle\langle\psi_n|\right]\mathbf{p}|\psi_0\rangle\right\} \ . \tag{42}$$

In this expression, the sum $\sum_n c_n|\psi_n\rangle\langle\psi_n|$ can be seen as a probe into $\nabla\psi_0$. But if ψ_0 is in an s state, then $\nabla\psi_0 \sim r^0$ at the origin. In this case, however, the intermediate states are p states, i.e., $\psi_n \sim r^1$ at the origin. It is then very hard for a *finite* basis set of the form (39) to reproduce $\nabla\psi_0 \sim r^0$ and the convergence of the sum rule becomes very poor. This is a fact recognized a long time ago by Dalgarno and Epstein [14], who proved that in a sum rule of the type (40), if the intermediate variational basis set contains $\nabla\psi_0$, then the sum rule result will be exact. This has been used already in previous calculations of the BL in order to improve convergence by including the radial function for ψ_0 in the set of variational intermediate states [6], forcing the variational intermediate basis functions to behave (unphysically) as r^0 at the origin. We can attempt the same strategy here; however, if the *separable* basis set (39) is forced to behave as r^0 at the origin, the integrations involved in the calculation of matrix elements *diverge*. Both the divergence in the integrations and the convergence in the variational calculation of the sum rules can be overcome if a *nonseparable* basis set is used, namely, the basis set

$$\phi_k = e^{im_k\varphi}\,(\xi\eta)^{|m_k|/2}\,(\xi-\eta)^{i_k}\,(\xi+\eta)^{j_k}\,e^{-\lambda_k(\xi+\eta)}\,. \tag{43}$$

This set of functions separates into states of even parity and odd parity when the powers i_k of $\xi-\eta$ are even or odd, respectively, corresponding to states with even or odd values off l in spherical coordinates. In the case of a hydrogenic ion in an external dipole field, the following sets of vectors were used:

$$\begin{array}{lll} \text{if } m=0 & \text{then } \left\{\begin{array}{ll} j_k=0,1,2,\ldots & \text{if } i_k=0,2,4,\ldots \\ j_k=-1,0,1,2,\ldots & \text{if } i_k=1,3,5,\ldots \end{array}\right. \\ \text{if } |m|>0 & \text{then } j_k=-1,0,1,2,\ldots \text{ and } i_k=0,1,2,\ldots\,. \end{array} \tag{44}$$

With this basis set, the sum (40) is calculated to *machine accuracy*. Although the new basis set is composed by functions that are not separable, all the integrations involved in the calculations of matrix elements are easily performed. These can be expressed in terms of the general integral

$$I_{ij}^k(\alpha) \equiv \int_0^\infty \int_0^\infty (\xi+\eta)d\xi d\eta\, e^{-\alpha(\xi+\eta)} \times(\xi\eta)^k(\xi-\eta)^i(\xi+\eta)^j\,, \tag{45}$$

which, using the result

$$\sum_{n=0}^{k}\binom{k}{n}\frac{(-1)^{k-n}}{i+2k-2n+1}=\frac{(2k)!!(i-1)!!}{(i+2k+1)!!}\,, \tag{46}$$

can be written in closed form as

$$I_{ij}^k(\alpha)=\frac{(i+j+2k+2)!}{\alpha^{i+j+2k+3}}\,\frac{(2k)!!(i+1)!!}{4^k(i+1)(i+2k+1)!!}\,. \tag{47}$$

Notice that once the separability of the basis functions is lost, we lost also the main attraction for working in parabolic coordinates, as the symmetry of the problem is built into those functions of ξ and η. However, the basis set (43) and (44) is totally equivalent to a basis set in spherical coordinates, as $\xi+\eta=2r$ and $(\xi-\eta)/(\xi+\eta)=\cos\theta$. We can then use an equivalent Laguerre-type basis set [15] in spherical coordinates:

$$\Phi_k = N_k\, e^{-\lambda_k r}\, L_{n_k}^2(2\lambda_k r)\, Y_{l_k m_k}(\theta,\varphi)|, \quad k=1,2,\ldots,k^{\max}, \quad n_k=0,1,2,\ldots,n_k^{\max}, \quad l_k=0,1,2,\ldots,l_k^{\max}, \tag{48}$$

where the N_k are normalization constants, the L_n^α are generalized Laguerre polynomials, and the Y_{lm} are spherical harmonics. This basis set has the added advantages that the functions are orthogonal for the same value of the nonlinear parameter (same λ_k) and is therefore stable even for a very large number of powers [15] and that its application can be readily extended to the case of external multipole fields of higher order. Both parabolic and spherical representations were used in these calculations; however, from now on we will refer exclusively to basis set (48).

IV. CALCULATIONS

A. Hydrogenic Bethe logarithm with no external fields

We start by searching for a basis set that is very efficient in the calculation of the one-electron BL in the absence of external fields. It has been shown [6] that in order to achieve this, two conditions must be satisfied: the set of intermediate states should contain the radial functions used for the initial state and a set of exponential parameters must be chosen that represents adequately intermediate states with very high energy eigenvalues or equivalently regions of space very close to $r=0$.

Upon consideration of the distribution of values of the exponential parameters yielded by the iterational-variational method, we propose here a much more efficient distribution of exponential parameters given by

$$\begin{aligned} &\lambda_1 = Z\,, \\ &\lambda_k = Z\exp\left[(a\,x_{k-1})^b\right]\,,\ k=2,3,\ldots,N_{\text{par}}\,. \end{aligned} \tag{49}$$

In (49), the x_k are the zeros of a Laguerre polynomial of order N_{par}, and a and b are arbitrary nonlinear parameters. Notice that only two nonlinear parameters are varied in order to optimize the calculations, although many more (a number given by N_{par}) will actually be used in the calculations as exponential parameters in the basis set.

In order to perform the calculations, the overlap matrix of the basis vectors is first diagonalized in order to obtain an orthonormal basis set and then the Hamiltonian matrix constructed using these orthonormal basis set is diagonalized to obtain the variational eigenvalues and eigenfunctions. For the intermediate states in the summations (4) and (5), these variational eigenstates form a finite, discrete representation of the full energy spectrum that satisfies an important factor to consider in building a variational representation of the spectrum: to obtain the best convergence to exact values of the sum rules with the smallest possible size of a basis set.

In the present set of calculations, the results obtained for A_1 (and then the BL), were checked for convergence as the size of the basis sets involved was increased, numerical accuracy, and onset of numerical instabilities in two ways: (i) for each calculation, the value of B_1 was also calculated and its convergence compared with the analytical results available from perturbation theory; (ii) all the calculations were performed in two gauges, the velocity gauge of Eqs. (4) and (5) and the acceleration gauge. This gauge is obtained by using the identity

$$\langle i|\mathbf{p}|j\rangle = \frac{\langle i|[H,\mathbf{p}]|j\rangle}{E_i - E_j} . \tag{50}$$

The one-electron sums

$$b_k^{(p)} = \sum_n |\langle\psi_0|\mathbf{p}|\psi_n\rangle|^2 (E_n - E_0)^k , \tag{51}$$

$$a_k^{(p)} = \sum_n |\langle\psi_0|\mathbf{p}|\psi_n\rangle|^2 (E_n - E_0)^k \ln|E_n - E_0| \tag{52}$$

acquire then, in the acceleration gauge, the form

$$b_k^{(t)} = \sum_n |\langle\psi_0|\mathbf{t}|\psi_n\rangle|^2 (E_n - E_0)^{k-2} , \tag{53}$$

$$a_k^{(t)} = \sum_n |\langle\psi_0|\mathbf{t}\rangle\psi_n\rangle|^2 (E_n - E_0)^{k-2} \ln|E_n - E_0| , \tag{54}$$

with

$$\mathbf{t} = Z\,\hat{\mathbf{r}}/r^2 . \tag{55}$$

Although $a^{(t)} = a^{(p)}$ and $b^{(t)} = b^{(p)}$ for an infinite set of intermediate states, this equality is only approximate for finite basis sets and the degree to which it is satisfied is an indication of the completeness of the intermediate set of states and the accuracy of the results presented. All the calculations in this work have been carried out in both gauges. This check becomes very important because of the critical form of the basis sets used. Consider, for example, the BL calculation for hydrogen in the absence of external fields. For the field-free case we use for the 1s state $l = n = 0$ and $N_{\text{par}} = 1$ and for the intermediate p states $l = 1$ and $n^{\max} = 2$ while letting N_{par} vary in order to analyze the convergence of the results. The optimal values of a and b in (49) were found to be $2.75 \leq a \leq 3.25$ and $b = 0.6$. In Table I, we show the results obtained with this basis set as the number of exponential parameters N_{par} is increased; we also tabulate the largest exponential parameter in the basis set $\lambda_{n_{\text{par}}}$ to illustrate the importance of an accurate representation in regions that are very close to the origin. Because of the enormous spread in the values of the exponential parameters (from $\lambda = 1$ to $\lambda \approx 10^{12}$ for 28 exponential parameters) it is very important to keep track of the numerical results in order to avoid numerical dependences in the basis set, i.e., when the orthogonalization procedure is unable to differentiate between vectors to a significant number of digits. In the fourth column in Table I we tabulate $\delta b_1 = |b_1^{\text{variational}} - b_1^{\text{exact}}|$. One can see the deterioration in the ability of the diagonalization procedure to overcome numerical dependency as the number of exponential parameters increases substantially.

There is, however, a very interesting property of the variational sums: if the commutation relation (50) is used only once in b_1^p or b_1^t we obtain a sum rule without energies appearing explicitly:

$$b_1^{(pt)} = \sum_n \langle\psi_0|\mathbf{p}|\psi_n\rangle\langle\psi_n|\mathbf{t}|\psi_0\rangle . \tag{56}$$

The results for $|b_1^{(pt)} - b_1^{\text{exact}}|$ appear in the last column of Table I. Notice the much larger accuracy of these as compared with those of column four for the "pure gauge" calculations. These imply that the error in the calculations in the velocity or acceleration gauges stems from the variational *energy* eigenvalues rather than the matrix elements. This is confirmed by the following argument: call δE_n the *numerical* round-off error in the nth variational energy E_n; then the error introduced in the sum b_1 is

$$\delta b_1^{(p)} = \sum_n |\langle\psi_0|\mathbf{p}|\psi_n\rangle|^2 \delta(E_n - E_0) , \tag{57}$$

TABLE I. Field-free results for the hydrogenic Bethe logarithm in a.u., as a function of the number N_{par} of exponential parameters used for the intermediate variational states. N_{vect} is the actual number of intermediate states, β_{1s} is the variational BL, $\lambda_{\max}$ is the value of the largest exponential parameter used in the set, δb_1 is the error in b_1 in the p or t gauges, and δb_1^{pt} is the error in b_1 in the pt gauge. The digits in *italics* in the BL did not converge. The "exact" value obtained from Huff's method is $\beta_{1s} = 2.290\,981\,375\,205\,552\,301\,342\,544\,968\,59$.

N_{par}	N_{vect}	β_{1s}	$\lambda_{\max}$	δb_1	δb_1^{pt}
8	23	2.2909*663814606*	5.26×10^4	2.78×10^{-24}	5.42×10^{-29}
10	29	2.29097*97334402*	4.75×10^5	5.74×10^{-23}	9.90×10^{-29}
12	35	2.2909811*588670*	3.57×10^6	1.46×10^{-20}	4.81×10^{-28}
14	41	2.29098134*23689*	2.33×10^7	4.92×10^{-21}	7.34×10^{-28}
16	47	2.29098136*96272*	1.36×10^8	1.46×10^{-20}	5.68×10^{-28}
18	53	2.290981374*1659*	7.25×10^8	1.93×10^{-18}	2.89×10^{-27}
20	59	2.2909813749*961*	3.58×10^9	1.50×10^{-16}	5.80×10^{-27}
22	65	2.2909813751*604*	1.65×10^{10}	1.53×10^{-15}	3.76×10^{-26}
24	71	2.29098137519*52*	7.22×10^{10}	2.20×10^{-14}	6.38×10^{-27}
26	77	2.29098137520*31*	3.00×10^{11}	2.37×10^{-13}	1.35×10^{-26}
28	83	2.29098137520*48*	1.19×10^{12}	1.36×10^{-12}	1.00×10^{-25}
exact		2.2909813752056			

$$\delta b_1^{(t)} = -\sum_n |\langle\psi_0|\mathbf{t}|\psi_n\rangle|^2 \delta(E_n - E_0)/(E_n - E_0)^2$$
$$= -\sum_n |\langle\psi_0|\mathbf{p}|\psi_n\rangle|^2 \delta(E_n - E_0) \ , \qquad (58)$$

so that to lowest order

$$\delta b_1^{\text{average}} = \delta(b_1^{(p)} + b_1^{(t)})/2 \approx \delta b_1^{(pt)} \approx 0 \ . \qquad (59)$$

In other words, we can reduce the numerical round-off error by working in the "*pt*" gauge or by just taking the average of the results in the "*p*" and "*t*" gauges. Notice that the round-off error in E_n can also be avoided in the same way in the logarithmic sum a_1 if it is written as

$$a_1^{(pt)} = \sum_n \langle\psi_0|\mathbf{p}|\psi_n\rangle\langle\psi_n|\mathbf{t}|\psi_0\rangle \ln\left|\frac{\langle\psi_n|\mathbf{t}|\psi_0\rangle}{\langle\psi_n|\mathbf{p}|\psi_0\rangle}\right| \ . \qquad (60)$$

From Table I we obtain that the variational calculation of the BL using basis set (48) and (49) converges as $N_{\text{par}}^{-13.6}$ so that we can easily obtain a convergence of 12 digits in the BL with no extrapolations. This is more than we need for our calculations of the effects of external *l*-pole fields.

B. The adiabatic dipole contribution

As outlined earlier, we will in this section calculate $\beta_{1s}(F)$, the BL for a hydrogen atom in the 1*s* state, in the presence of an external dipole field $\mathbf{F} = F\hat{\mathbf{z}}$. We will then apply our results to the BL of the $n = 10$ states of helium, in which the dipole field acting on the core electron is of order $F^2 = \langle r_2^{-4}\rangle_{nL} \approx 10^{-5}$ a.u. The calculation will be performed for a range of values of the external field and then the lowest-order correction will be given by the coefficient of F^2 in the fit

$$\beta_{1s}(F) = c_0^\beta + c_2^\beta F^2 + c_4^\beta F^4 + \cdots \ , \qquad (61)$$

$$b_{1,1s}(F) = c_0^b + c_2^b F^2 + c_4^b F^4 + \cdots \ . \qquad (62)$$

TABLE II. Variational results of β_{1s}, $\langle\delta\rangle$, and b_1 obtained for a hydrogen atom in the ground state in an external dipole field with magnitudes $10^{-8} \leq F^2 \leq 10^{-4.5}$ in a.u.

$\log_{10} F^2$	$\beta_{1s}(F) - \beta_{1s}(0)$	$2\pi\langle\delta\rangle - 2$	$b_1^{(pt)} - 2$
-8.0	$3.087518437 \times 10^{-9}$	$-3.100001538 \times 10^{-7}$	$-3.100001551 \times 10^{-7}$
-7.9	$3.905533776 \times 10^{-9}$	$-3.902671214 \times 10^{-7}$	$-3.902671224 \times 10^{-7}$
-7.8	$4.941815754 \times 10^{-9}$	$-4.913172760 \times 10^{-7}$	$-4.913172771 \times 10^{-7}$
-7.7	$6.235248446 \times 10^{-9}$	$-6.185319299 \times 10^{-7}$	$-6.185319308 \times 10^{-7}$
-7.6	$7.865870653 \times 10^{-9}$	$-7.786857641 \times 10^{-7}$	$-7.786857648 \times 10^{-7}$
-7.5	$9.933821754 \times 10^{-9}$	$-9.803076125 \times 10^{-7}$	$-9.803076134 \times 10^{-7}$
-7.4	$1.251238372 \times 10^{-8}$	$-1.234134666 \times 10^{-6}$	$-1.234134667 \times 10^{-6}$
-7.3	$1.576874644 \times 10^{-8}$	$-1.553684287 \times 10^{-6}$	$-1.553684288 \times 10^{-6}$
-7.2	$1.987843991 \times 10^{-8}$	$-1.955973890 \times 10^{-6}$	$-1.955973891 \times 10^{-6}$
-7.1	$2.504411558 \times 10^{-8}$	$-2.462427231 \times 10^{-6}$	$-2.462427232 \times 10^{-6}$
-7.0	$3.154675241 \times 10^{-8}$	$-3.100015379 \times 10^{-6}$	$-3.100015380 \times 10^{-6}$
-6.9	$3.973423005 \times 10^{-8}$	$-3.902693151 \times 10^{-6}$	$-3.902693151 \times 10^{-6}$
-6.8	$5.004182975 \times 10^{-8}$	$-4.913207527 \times 10^{-6}$	$-4.913207528 \times 10^{-6}$
-6.7	$6.301477418 \times 10^{-8}$	$-6.185374402 \times 10^{-6}$	$-6.185374404 \times 10^{-6}$
-6.6	$7.934958231 \times 10^{-8}$	$-7.786944974 \times 10^{-6}$	$-7.786944975 \times 10^{-6}$
-6.5	$9.991350503 \times 10^{-8}$	$-9.803214541 \times 10^{-6}$	$-9.803214541 \times 10^{-6}$
-6.4	$1.258035360 \times 10^{-7}$	$-1.234156604 \times 10^{-5}$	$-1.234156604 \times 10^{-5}$
-6.3	$1.583993306 \times 10^{-7}$	$-1.553719056 \times 10^{-5}$	$-1.553719057 \times 10^{-5}$
-6.2	$1.994280149 \times 10^{-7}$	$-1.956028997 \times 10^{-5}$	$-1.956028997 \times 10^{-5}$
-6.1	$2.510809508 \times 10^{-7}$	$-2.462514571 \times 10^{-5}$	$-2.462514571 \times 10^{-5}$
-6.0	$3.161552105 \times 10^{-7}$	$-3.100153808 \times 10^{-5}$	$-3.100153808 \times 10^{-5}$
-5.9	$3.980374743 \times 10^{-7}$	$-3.902912554 \times 10^{-5}$	$-3.902912556 \times 10^{-5}$
-5.8	$5.011343140 \times 10^{-7}$	$-4.913555275 \times 10^{-5}$	$-4.913555275 \times 10^{-5}$
-5.7	$6.309287329 \times 10^{-7}$	$-6.185925578 \times 10^{-5}$	$-6.185925579 \times 10^{-5}$
-5.6	$7.943406251 \times 10^{-7}$	$-7.787818596 \times 10^{-5}$	$-7.787818598 \times 10^{-5}$
-5.5	$1.000086979 \times 10^{-6}$	$-9.804599270 \times 10^{-5}$	$-9.804599271 \times 10^{-5}$
-5.4	$1.259133345 \times 10^{-6}$	$-1.234376095 \times 10^{-4}$	$-1.234376095 \times 10^{-4}$
-5.3	$1.585301659 \times 10^{-6}$	$-1.554066979 \times 10^{-4}$	$-1.554066979 \times 10^{-4}$
-5.2	$1.995999414 \times 10^{-6}$	$-1.956580522 \times 10^{-4}$	$-1.956580522 \times 10^{-4}$
-5.1	$2.513157984 \times 10^{-6}$	$-2.463388890 \times 10^{-4}$	$-2.463388890 \times 10^{-4}$
-5.0	$3.164504293 \times 10^{-6}$	$-3.101539928 \times 10^{-4}$	$-3.101539927 \times 10^{-4}$
-4.9	$3.984785891 \times 10^{-6}$	$-3.905110242 \times 10^{-4}$	$-3.905110241 \times 10^{-4}$
-4.8	$5.017921490 \times 10^{-6}$	$-4.917040047 \times 10^{-4}$	$-4.917040045 \times 10^{-4}$
-4.7	$6.319315064 \times 10^{-6}$	$-6.191451908 \times 10^{-4}$	$-6.191451906 \times 10^{-4}$
-4.6	$7.958858651 \times 10^{-6}$	$-7.796583915 \times 10^{-4}$	$-7.796583912 \times 10^{-4}$
-4.5	$1.002480810 \times 10^{-5}$	$-9.818504718 \times 10^{-4}$	$-9.818504715 \times 10^{-4}$

TABLE III. Parameters defining the basis sets used in the calculations. The rows involving F^2 are for the dipole case and those involving Q^2 are for the quadrupole case. Notice that in the quadrupole case, l_k can assume only even or only odd values.

Field strength	ψ_{1s}			ψ_n		
$10^{-8} \leq F^2 < 10^{-6}$	$k = 1$	$0 \leq l_1 \leq 4$	$0 \leq n_1 \leq 11$	$k = 1$	$0 \leq l_1 \leq 4$	$0 \leq n_1 \leq 11$
				$2 \leq k \leq 20$	$l_k = 1$	$0 \leq n_k \leq 2$
$10^{-6} \leq F^2 < 10^{-5}$	$k = 1$	$0 \leq l_1 \leq 6$	$0 \leq n_1 \leq 15$	$k = 1$	$0 \leq l_1 \leq 5$	$0 \leq n_1 \leq 13$
				$2 \leq k \leq 20$	$l_k = 1$	$0 \leq n_k \leq 2$
$10^{-5} \leq F^2 \leq 10^{-4.5}$	$k = 1$	$0 \leq l_1 \leq 7$	$0 \leq n_1 \leq 21$	$k = 1$	$0 \leq l_1 \leq 5$	$0 \leq n_1 \leq 14$
				$2 \leq k \leq 18$	$0 \leq l_k \leq 1$	$0 \leq n_k \leq 2$
$10^{-9} \leq Q^2 < 10^{-8}$	$k = 1$	$0 \leq l_1 \leq 20$	$0 \leq n_1 \leq 18$	$k = 1$	$0 \leq l_1 \leq 14$	$0 \leq n_1 \leq 12$
				$2 \leq k \leq 18$	$l_k = 1$	$0 \leq n_k \leq 2$
$10^{-8} \leq Q^2 < 10^{-6}$	$k = 1$	$0 \leq l_1 \leq 24$	$0 \leq n_1 \leq 18$	$k = 1$	$0 \leq l_1 \leq 14$	$0 \leq n_1 \leq 12$
				$2 \leq k \leq 18$	$l_k = 1$	$0 \leq n_k \leq 2$

We need an accuracy of about ten digits in the value of $\beta_{1s}(F)$ in order to extract c_2 to less than 1% accuracy, which can be easily achieved with the basis set of Sec. IV A. The results of the calculations performed for a large range of field values are presented in Table II with the parameters defining the basis sets used appearing in Table III. In Table II, we present, in the second column, the deviations of the BL from the field-free results for each value of the dipole field; in column three we present the deviation of $\langle\delta\rangle$ from its field-free value of 2 and similarly in column four for the sum $b_1^{(pt)}$. The values of $\langle\delta\rangle$ control the accuracy of the variational representation of the 1s state, as well as serving as a check of the intermediate states via the sum rule $b_1^{(pt)}$. This sum rule is, on the other hand, used as a measuring stick for the reliability of the results by comparing the expansion coefficients in (61) with those obtained analytically in a perturbation expansion of $\langle\delta\rangle$. As shown in Table IV, the set of intermediate states includes a large number of powers and angular functions for those vectors that have the same exponential parameter as the ground state. For the other vectors it is only necessary to include angular functions with $l \leq 1$: only these contribute to the sums given the fact that their contribution comes mostly from regions very near the origin.

In Table IV we present results of least-squares fits of the values in Table II. Even with the enormous spread in exponential parameters used, the variational representation of b_1 is still able to produce excellent agreement with the variational-perturbational coefficients for $\langle\delta\rangle$. We obtain then for the adiabatic dipole correction to the BL:

$$\delta^{\mathrm{ad}}_{\mathrm{dipole}}\beta_{1s} = 0.316205(6)\,\langle r_2^{-4}\rangle_{nL}\ , \tag{63}$$

where r_2 is the radial coordinate of the Rydberg electron with quantum numbers n and L.

C. The adiabatic quadrupole contribution

Consider now the perturbation due to an external quadrupole field $\mathbf{Q}$:

$$\mathbf{Q} = \mathbf{F}_2^{\mathrm{ad}} = Q\,C_{2,0}(\hat{\mathbf{r}}) = Q\sqrt{\frac{4\pi}{5}}\,Y_{2,0}(\hat{\mathbf{r}})\ . \tag{64}$$

TABLE IV. Coefficients in the expansions in powers of F^2 of the variational calculations of β_{1s} [Eq. (61)], $\langle\delta\rangle$, and b_1 [Eq. (62)] for a hydrogen atom in an external dipole field $\mathbf{F}$ in a.u. The numbers in parentheses denote the error in the last digit.

Term	β_{1s}	$2\pi\langle\delta\rangle$	$b_1^{(pt)}$
F^0	2.2909813752(1)	2 ± 10^{-17}	2 ± 10^{-14}
F^2	0.316205(6)	−30.99999999999(1)	−31.00000001(2)
F^4	25.9(6)	−1537.875004(3)	−1537.87(4)
F^6		$-2.04841(3) \times 10^5$	$-2.049(1) \times 10^5$
F^8		$-4.405(1) \times 10^7$	$-4.3(2) \times 10^7$
F^{10}		$-1.36(2) \times 10^{10}$	

We repeat now the same procedure as the one used for the dipole case with the difference that now the perturbing potential due to (64) is

$$V_Q = Q\,r^2\sqrt{\frac{4\pi}{5}}\,Y_{2,0}(\hat{\mathbf{r}})\,. \tag{65}$$

The expansions corresponding to (61) and (62) are now

$$\beta_{1s}(Q) = d_0^\beta + d_2^\beta Q^2 + d_3^\beta Q^3 + d_4^\beta Q^4 + \cdots\,, \tag{66}$$

$$b_{1,1s}(Q) = d_0^b + d_2^b Q^2 + d_3^b Q^3 + d_4^b Q^4 + \cdots\,. \tag{67}$$

Care has to be taken, however, when switching from the velocity to the acceleration forms of the dipole operator **p** appearing in the sums. The form (55) of **t** is correct for the field-free case or for summations involving an external dipole field, but it is not in the general case of a perturbing l-pole field. In the general case, the commutator (50) will contain extra terms arising from the commutator $[\nabla, -Z/r + V_{\text{pert}}]$, where V_{pert} is the perturbing potential. Consider in general the gradient of a power times a spherical harmonic:

$$\begin{aligned}\nabla_\mu\left(r^b Y_{kq}\right) = {}& (-1)^{k+q+\mu+1}\sqrt{k+1}\begin{pmatrix} k+1 & k & 1 \\ q+\mu & -q & -\mu \end{pmatrix} \\ & \times Y_{k+1,q+\mu}(b-k)\,r^{b-1} + (-1)^{k+q+\mu}\sqrt{k} \\ & \times\begin{pmatrix} k-1 & k & 1 \\ q+\mu & -q & -\mu \end{pmatrix} \\ & \times Y_{k-1,q+\mu}(b+k+1)\,r^{b-1}\,. \end{aligned} \tag{68}$$

After some angular momentum algebra, we can obtain the matrix elements of $[\nabla_\mu, r^b C_{kq}]$ between the angular functions $Y_{l'm'}$ and Y_{lm}:

$$\begin{aligned}\langle l'm'|\nabla_\mu(r^b C_{kq})|lm\rangle = {}& (-1)^{k-m}\left[\frac{(2l+1)(2l'+1)}{(2k+1)}\right]^{1/2} r^{b-1} \\ & \times\Bigg\{-(b-k)\sqrt{(k+1)(2k+3)}\begin{pmatrix} k+1 & k & 1 \\ q+\mu & -q & -\mu \end{pmatrix}\begin{pmatrix} l' & k+1 & l \\ -m' & q+\mu & m \end{pmatrix}\begin{pmatrix} l' & k+1 & l \\ 0 & 0 & 0 \end{pmatrix} \\ & +(b+k+1)\sqrt{k(2k-1)}\begin{pmatrix} k-1 & k & 1 \\ q+\mu & -q & -\mu \end{pmatrix}\begin{pmatrix} l' & k-1 & l \\ -m' & q+\mu & m \end{pmatrix}\begin{pmatrix} l' & k-1 & l \\ 0 & 0 & 0 \end{pmatrix}\Bigg\}. \end{aligned} \tag{69}$$

From (68) we obtain, for the commutator on the Coulomb potential, the dipole operator in the acceleration gauge:

$$t_\mu = -Z\,[\nabla_\mu, r^{-1}] = Z\,C_{1\mu}(\hat{\mathbf{r}})/r^2\,. \tag{70}$$

For a dipole field $F\,r\,C_{10}$ we obtain, from (69),

$$\langle l'm'|[\nabla_\mu, (rC_{10})|lm\rangle = \delta_{\mu 0}\delta ll'. \tag{71}$$

This term does not contribute to the sums because of the fact that there is no function of r in the last result coupled with the fact that the matrix element forces $l = l'$: all states with $l' = l$ are orthogonal, except the one identical to the initial state in the sum, which does not contribute because of the coefficient $E_n - E_0$. For the quadrupole potential, $Q\,r^2\,C_{20}$ we obtain, however, nonzero contributions:

$$\begin{aligned}&\langle l'm'|[\nabla_\mu, (r^2 C_{20})|lm\rangle \\ &\quad = \frac{4}{3}\delta_{\mu 0}\delta ll'\,r + (-1)^m[10(2l+1)(2l'+1)/3]^{1/2} \\ &\qquad \times\begin{pmatrix} 2 & 1 & 1 \\ \mu & 0 & -\mu \end{pmatrix}\begin{pmatrix} l' & 2 & l \\ -m' & \mu & m \end{pmatrix}\begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix} r\,, \end{aligned} \tag{72}$$

which will connect the state nl to states with $l' = l-2$, l, and $l+2$. This contribution must be added to the matrix elements of t_μ in (70).

The parameters used for the basis sets in the quadrupole case are presented in the second portion of Table III. Notice that because of angular momentum addition rules, for a given set, l_k can be even or odd, so that the total num ber of values of l_k used is half of the maximum value $l_k^{\max}$ in the basis set. Again, only $l_k = 1$ is needed in the intermediate states with $k > 1$; the next possible value would be $l_k = 3$, which contributes insignificantly in the regions of space very close to $r = 0$ which are represented by these basis vectors. The values obtained for quadrupole fields in the range $10^{-9} \le Q^2 \le 10^{-6}$ are presented in Table V. The values in each column are the analogs of those for the dipole case in Table II. Care has to be taken while performing these calculations for large values of the fields as the "ground state" is now a resonance that may lay above other variational states that are now representing the continuum of negative solutions to the problem.

As in the dipole case, we perform now a least-square fit of the values obtained, in terms of powers of the external quadrupole field. These results are presented in Table VI. Again, we have very good agreement for the expansion coefficients of b_1 and $\langle\delta\rangle$ and enough digits in the calculation of β_{1s} to obtain a good estimate of the coefficient of Q^2 in its perturbation expansion. From here we obtain then the quadrupole term in the asymptotic expansion of β_{1s}:

$$\delta^{\text{ad}}_{\text{quadrupole}}\beta_{1s} = 5.81905(1)\,\langle r_2^{-6}\rangle_{nL}\,, \tag{73}$$

where r_2 is the radial coordinate of the Rydberg electron with quantum numbers n and L.

TABLE V. Variational results of β_{1s}, $\langle\delta\rangle$, and b_1 obtained for a hydrogen atom in the ground state in an external quadrupole field with magnitudes $10^{-9} \leq Q^2 \leq 10^{-6}$ in a.u.

$\log_{10} Q^2$	$\beta_{1s}(Q) - \beta_{1s}(0)$	$2\pi\langle\delta\rangle - 2$	$b_1^{(pt)} - 2$
-9.0	$5.435041433 \times 10^{-9}$	$-1.391813847 \times 10^{-7}$	$-1.391813849 \times 10^{-7}$
-8.9	$6.941096783 \times 10^{-9}$	$-1.752084886 \times 10^{-7}$	$-1.752084888 \times 10^{-7}$
-8.8	$8.835802412 \times 10^{-9}$	$-2.205596114 \times 10^{-7}$	$-2.205596117 \times 10^{-7}$
-8.7	$1.122308762 \times 10^{-8}$	$-2.776472080 \times 10^{-7}$	$-2.776472081 \times 10^{-7}$
-8.6	$1.422659672 \times 10^{-8}$	$-3.495076534 \times 10^{-7}$	$-3.495076536 \times 10^{-7}$
-8.5	$1.800768145 \times 10^{-8}$	$-4.399624962 \times 10^{-7}$	$-4.399624965 \times 10^{-7}$
-8.4	$2.276743435 \times 10^{-8}$	$-5.538213425 \times 10^{-7}$	$-5.538213427 \times 10^{-7}$
-8.3	$2.875839120 \times 10^{-8}$	$-6.971371037 \times 10^{-7}$	$-6.971371040 \times 10^{-7}$
-8.2	$3.630012481 \times 10^{-8}$	$-8.775270968 \times 10^{-7}$	$-8.775270970 \times 10^{-7}$
-8.1	$4.579292806 \times 10^{-8}$	$-1.104576953 \times 10^{-6}$	$-1.104576953 \times 10^{-6}$
-8.0	$5.774158129 \times 10^{-8}$	$-1.390348641 \times 10^{-6}$	$-1.390348642 \times 10^{-6}$
-7.9	$7.278132015 \times 10^{-8}$	$-1.750019386 \times 10^{-6}$	$-1.750019386 \times 10^{-6}$
-7.8	$9.171116220 \times 10^{-8}$	$-2.202685094 \times 10^{-6}$	$-2.202685094 \times 10^{-6}$
-7.7	$1.155362086 \times 10^{-7}$	$-2.772370555 \times 10^{-6}$	$-2.772370555 \times 10^{-6}$
-7.6	$1.455219925 \times 10^{-7}$	$-3.489299421 \times 10^{-6}$	$-3.489299421 \times 10^{-6}$
-7.5	$1.832607796 \times 10^{-7}$	$-4.391490565 \times 10^{-6}$	$-4.391490565 \times 10^{-6}$
-7.4	$2.307539847 \times 10^{-7}$	$-5.526764358 \times 10^{-6}$	$-5.526764358 \times 10^{-6}$
-7.3	$2.905232693 \times 10^{-7}$	$-6.955263684 \times 10^{-6}$	$-6.955263683 \times 10^{-6}$
-7.2	$3.657357864 \times 10^{-7}$	$-8.752621184 \times 10^{-6}$	$-8.752621182 \times 10^{-6}$
-7.1	$4.603786139 \times 10^{-7}$	$-1.101393758 \times 10^{-5}$	$-1.101393758 \times 10^{-5}$
-7.0	$5.794645576 \times 10^{-7}$	$-1.385877774 \times 10^{-5}$	$-1.385877774 \times 10^{-5}$
-6.9	$7.292978301 \times 10^{-7}$	$-1.743744355 \times 10^{-5}$	$-1.743744353 \times 10^{-5}$
-6.8	$9.178063455 \times 10^{-7}$	$-2.193884794 \times 10^{-5}$	$-2.193884791 \times 10^{-5}$
-6.7	$1.154956102 \times 10^{-6}$	$-2.760039694 \times 10^{-5}$	$-2.760039688 \times 10^{-5}$
-6.6	$1.453276365 \times 10^{-6}$	$-3.472038868 \times 10^{-5}$	$-3.472038856 \times 10^{-5}$
-6.5	$1.828514796 \times 10^{-6}$	$-4.367356764 \times 10^{-5}$	$-4.367356741 \times 10^{-5}$
-6.4	$2.300463654 \times 10^{-6}$	$-5.493063343 \times 10^{-5}$	$-5.493063299 \times 10^{-5}$
-6.3	$2.893994552 \times 10^{-6}$	$-6.908270647 \times 10^{-5}$	$-6.908270572 \times 10^{-5}$
-6.2	$3.640356166 \times 10^{-6}$	$-8.687200912 \times 10^{-5}$	$-8.687200844 \times 10^{-5}$
-6.1	$4.578761812 \times 10^{-6}$	$-1.092303514 \times 10^{-4}$	$-1.092303560 \times 10^{-4}$
-6.0	$5.762744307 \times 10^{-6}$	$-1.373275310 \times 10^{-4}$	$-1.373273871 \times 10^{-4}$

D. The nonadiabatic contribution

In this section we present a strategy for the calculation of the nonadiabatic contribution to the BL and preliminary bounds on the value of this contribution. Consider first the nonadiabatic contribution to the energy; we will use this, as in the adiabatic case, as a guide to develop a variationally viable approach to calculate this effect. Consider now the second term in the expansion (29) and use it in (26) to obtain the first nonadiabatic correction to the energy:

$$\delta_2^{(l)} E_i^{(\text{nonad})} = -\sum_{\substack{n,n'\\ q,q'}} \frac{\langle i|u^{lq}|n\rangle\langle n|u^{lq'}|i\rangle}{\epsilon_{in}^2} \times\langle i'|v^{lq}|n'\rangle\langle n'|v^{lq'}|i'\rangle\,\epsilon_{i'n'}\ . \tag{74}$$

The sumation over n' can be eliminated by eliminating $\epsilon_{i'n'}$ using a commutator

TABLE VI. Coefficients in the expansions in powers of Q of the variational calculations of β_{1s} [Eq. (61)], $\langle\delta\rangle$, and b_1 [Eq. (62)] for a hydrogen atom in an external quadrupole field $\mathbf{Q}$ in a.u. The numbers in parentheses denote the error in the last digit.

Term	β_{1s}	$2\pi\langle\delta\rangle$	$b_1^{(pt)}$
Q^0	2.2909813752(4)	2 ± 10^{-16}	$2 \pm 2 \times 10^{-16}$
Q^2	5.81905(1)	$-139.2499998(2)$	$-139.24999999(1)$
Q^3	$-67.47(6)$	2178.396(3)	2178.398(2)
Q^4	$7.50(7) \times 10^3$	$-2.7229(2) \times 10^5$	$-2.7230(2) \times 10^5$
Q^5		$1.929(5) \times 10^7$	$1.931(4) \times 10^7$
Q^6		$-2.82(8) \times 10^9$	$-2.85(5) \times 10^9$
Q^7		$1.6(5) \times 10^{11}$	$1.8(4) \times 10^{11}$

$$\delta_2^{(l)} E_i^{(\mathrm{nonad})} = -\sum_{\substack{n \\ q,q'}} \frac{\langle i|u^{lq}|n\rangle\langle n|u^{lq'}|i\rangle}{\epsilon_{in}^2} \times \langle i'|[h_2, v^{lq}]\, v^{lq'}|i'\rangle \qquad (75)$$

with which the l-pole nonadiabatic correction results in

$$\delta_2^{(l)} E_i^{(\mathrm{nonad})} = \sum_n \frac{\langle 1s|r_1^l\, C_{l0}|n\rangle\langle n|r_1^l\, C_{l0}|i\rangle}{\epsilon_{in}^2} \times \left[(k+1)(2k+1)\left\langle \frac{1}{r_2^{2l+4}} \right\rangle_{i'l}\right] , \qquad (76)$$

and in the dipole case for the ground state it becomes

$$\delta_{\mathrm{dipole}}^{\mathrm{nonad}} E_{1s} = 6 \left\langle \frac{1}{r_2^6} \right\rangle_{nL} \sum_n \frac{\langle 1s|z_1|n\rangle\langle n|z_1|1s\rangle}{\epsilon_{1s,n}^2} , \qquad (77)$$

where n and L are the quantum numbers describing the outer electron.

The sum involving the core electron in (77) cannot be interpreted any longer as pertaining to a second-order perturbation to the $1s$ energy because the quadratic power of $\epsilon_{1s,n}$ in the denominator and then the method used for the nonadiabatic operators are useless. A way can be worked out around this problem following a method introduced by Dalgarno and Lewis [16], based on the existance of a function $g = g(r,\theta)$ satisfying

$$[h_1, g]|1s\rangle = z|1s\rangle . \qquad (78)$$

In terms of g, $\delta_{\mathrm{dipole}}^{\mathrm{nonad}} E_{1s}$ can now be written as

$$\delta_{\mathrm{dipole}}^{\mathrm{nonad}} E_{1s} = -6 \left\langle \frac{1}{r_2^6} \right\rangle_{nL} \sum_n \frac{\langle 1s|z|n\rangle\langle n|g|1s\rangle}{\epsilon_{1s,n}} , \qquad (79)$$

where from now on we omit the subscript 1 in the operators acting on the core electron. In (79) we could replace the remaining matrix element of z again by a commutator and in such way obtain a closed form expression for the nonadiabatic perturbation. However, we propose to leave this equation as is and use the following argument. Consider the free Hamiltonian h_1 being perturbed by two potentials:

$$h = h_1 + w_1 + w_2 \ , w_1 = F\, z \ , w_2 = G\, g . \qquad (80)$$

Notice that h_1 is a scalar operator; then from (78) g, like z, is a tensor of rank one. The second-order perturbation to the energy due to these two perturbing potentials is

$$\begin{aligned} \delta^{(2)} E_{1s} &= \sum_n \frac{\langle 1s|w_1 + w_2|n\rangle\langle n|w_1 + w_2|1s\rangle}{\epsilon_{1s,n}} \\ &= F^2 \sum_n \frac{\langle s|z|n\rangle\langle n|z|1s\rangle}{\epsilon_{1s,n}} \\ &\quad + 2FG \sum_n \frac{\langle 1s|z|n\rangle\langle n|g|1s\rangle}{\epsilon_{1s,n}} \\ &\quad + G^2 \sum_n \frac{\langle 1s|g|n\rangle\langle n|g|1s\rangle}{\epsilon_{1s,n}} . \end{aligned} \qquad (81)$$

The term in F^2 yields the adiabatic dipole correction, the term in FG yields twice the sought nonadiabatic dipole correction, and the term in G^2 yields the second-order nonadiabatic dipole correction. Using the notation of (9) we can write

$$\delta^{(2)} E_{1s} = -\frac{1}{2} F^2\, \alpha_{1,a} - 2FG\, \alpha_{1,na} - \frac{1}{2} G^2\, \alpha_{1,na}^{(2)} . \qquad (82)$$

The value of $\alpha_{1,na}$ can be obtained by repeating the calculation of $\delta^{(2)} E$ for a range of values of F and G, and calculating the coefficient of FG by means of a least-squares fit. For the case of Rydberg states we would then use $F^2 = \langle r_2^{-4}\rangle_{nL}$ and $FG = -3\langle r_2^{-6}\rangle_{nL}$ to calculate the adiabatic and nonadiabatic dipole corrections, respectively.

The operator g satisfying (78) can be easily obtained:

$$g(r,\theta) = \left(\frac{Z}{2} r + 1\right) z = \left(\frac{Z}{2} r + 1\right) r\, C_{10} , \qquad (83)$$

where Z is the nuclear charge. Notice that this form of g is not unique; for example, it can be written in a form that explicitly states its validity, i.e., that of (78), for the $1s$ state only:

$$g(r,\theta) = |1s\rangle\langle 1s| \left(\frac{Z}{2} r + 1\right) r\, C_{10} + \left(\frac{Z}{2} r + 1\right) r\, C_{10}\, |1s\rangle\langle 1s| . \qquad (84)$$

Although any of these forms of g will yield the proper value for the nonadiabatic perturbation to the energy, the same is not true in the calculation of matrix elements, as the second-order perturbation to the wave function is different. For example, (83) contributes a spurious term to the second-order perturbation to the wave function that can be corrected by subtracting the first-order perturbation due to a potential $G^2 g^2$. Our calculations for the nonadiabatic corrections to B_1 are in excellent agreement with analytic perturbation expansion of the δ function. For the BL, we have, for the time being, obtained bounds on the possible values of the nonadiabatic dipole correction. Work is currently in progress in the pursuit of the nonadiabatic correction through a careful analysis of gauge transformations in the asymptotic-expansion framework, as well through a full calculation of the two-electron BL using a very efficient, configuration interaction technique. For the time being, we shall use our bounds on the nonadiabatic dipole correction as the error bound on the coefficient of $\langle r_2^{-6}\rangle_{nL}$. With this in mind, our value for the BL of the Rydberg states of two-electron atoms becomes

$$\beta = \beta_{1s} + \frac{(Z-1)^4}{Z^4 n^3} \beta_{nL} + \frac{0.316205(6)}{Z^6} \left\langle \frac{1}{r_2^4} \right\rangle_{nL} + \frac{5.8(2.5)}{Z^8} \left\langle \frac{1}{r_2^6} \right\rangle_{nL} . \qquad (85)$$

Interestingly, the $\langle r_2^{-6}\rangle_{nL}$ contributions cannot explain the discrepancy between the theoretical predictions and the experimental results for the $n = 10$ levels of helium.

ACKNOWLEDGMENTS

The author is thankful to Dr. Zonghua Chen and Dr. G.W.F. Drake for helpful discussions. Research support from the National Sciences and Engineering Council of Canada is gratefully acknowledged.

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