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High accuracy for atomic calculations involving logarithmic sums

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A method for the calculation of logarithmic sums that yields very high accuracy even for small basis-set dimensions is introduced. The best values achieved are accurate to 23 significant figures without extrapolation. The sums are performed directly on variational intermediate sets. The method automatically rejects any basis functions that could introduce linear dependence, therefore guaranteeing high numerical stability for a wide range of nonlinear parameters. Accurate values for the ordinary and a higher-order version of the Bethe logarithm are presented for a range of energy states and angular momenta. Given that the intermediate basis functions are increasingly confined to extremely small distances from the origin, a discussion of finite nuclear-size effects is given. The contribution to the sums from states with extremely high energies, orders of magnitude larger than the electron rest mass, is discussed.

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I. INTRODUCTION

The accuracy of the experimental and theoretical determination of transition frequencies in atoms with more than one electron is advancing substantially, increasingly being sensitive to higher-order effects. At the lowest- and higher-order QED corrections, one encounters quantities involving logarithmic sums that are very difficult to calculate. An example, appearing in the lowest-order QED correction, is the Bethe logarithm [atomic units (a.u.) will be used throughout the paper],

$$\beta_1=\frac{B_1}{C_1}, \tag{1}$$

where

$$B_1=\sum_n\!\!\!\!\!\!\int \; |\langle\Psi_0|\mathbf{p}|\Psi_n\rangle|^2(E_n-E_0)\ln|E_n-E_0|, \tag{2}$$

$$C_1=\begin{cases} S_1 & \text{for } s \text{ states}\\ 2Z^4/n^3 & \text{otherwise,}\end{cases} \tag{3}$$

and

$$S_1=\sum_n\!\!\!\!\!\!\int \; |\langle\Psi_0|\mathbf{p}|\Psi_n\rangle|^2(E_n-E_0) \tag{4}$$

$$=\frac{1}{2}\langle\Psi_0|\nabla^2V|\Psi_0\rangle \tag{5}$$

$$=2\pi Z\langle\Psi_0|\delta(\mathbf{r})|\Psi_0\rangle \tag{6}$$

In the case of more than one electron, $\mathbf{p}$ is replaced by $\mathbf{P}=\Sigma_i\mathbf{p}_i$, the momentum operator for all electrons, and $\delta(\mathbf{r})$ by $\Sigma_i\delta(\mathbf{r}_i)$. The summation integration over intermediate states includes the infinite set of discrete (bound) states as well as the (scattering) continuum.

A variety of nonvariational methods has been proposed for the particular case of a single electron in the Coulomb field of a point nucleus, for example, by direct application of the spectrum of eigenstates [1] or by direct application of group theoretical techniques [2]. In the last case an accuracy with an unlimited number of digits can be obtained without much difficulty using algebraic computation packages. These methods, however, need the complete set of *exact* solutions to the Schrödinger Hamiltonian and then cannot be used for calculations involving either an electron in a more complex potential or several interacting electrons. One is then left with approximation techniques. In this paper we demonstrate the enormous power of direct variational calculations for this family of calculations.

In a direct variational calculation of Eq. (1), the infinite set of intermediate states is replaced by a finite set of variational states. This set can be fine tuned by changing one or more variational parameters. As accuracies become higher, the need for a fast convergent and stable method for the calculation of sums of type (1) is necessary. Any method to be applied successfully to either correlated or multiconfiguration calculations must be such that in the one-electron case it is able to yield easily high accuracy with high numerical stability. Perhaps it is worth illustrating the difficulties involved in the calculation of logarithmic sums by performing the sum of Eq. (1) using a standard Slater basis set for the ground-state of hydrogen,

$$\psi_{nlm}(\mathbf{r})=\varphi^S_{nl_0}(r)Y_{lm}(\hat{\mathbf{r}}), \tag{7}$$

where the Slater radial functions are given by

$$\varphi^S_{nl_0}=e^{-\lambda r}r^{l_0+n}, \quad n=0,1,\ldots,N. \tag{8}$$

A variation of this set that allows one to use much larger basis dimensions without numerical dependency is a set of Slater-Laguerre radial functions:

TABLE I. Results for the ground-state Bethe logarithm (1) using for the intermediate states a basis set of the form (9). The exponential parameter used is $\lambda=1$. N is the number of basis functions.

N	E_{max}	β	$\delta_{beta}=\beta_{exact}-\beta$
20		2.15 800	1.33×10^{-1}
30		2.20 111	8.99×10^{-2}
40		2.22 311	6.79×10^{-2}
50		2.23 646	5.45×10^{-2}
60		2.24 542	4.56×10^{-2}
70		2.25 185	3.91×10^{-2}
80		2.25 669	3.43×10^{-2}
90		2.26 046	3.05×10^{-2}
100		2.26 349	2.75×10^{-2}
110		2.26 597	2.50×10^{-2}
120		2.26 804	2.29×10^{-2}
	exact	2.290981	
2692	extrapolated	2.289981	1.00×10^{-3}
26 918	extrapolated	2.290881	1.00×10^{-4}

$$\varphi_{nl_0}^{SL}=e^{-\lambda r}r^{l_0}L_n^{2l_0+2}(r),\quad n=0,1,\ldots,N,\tag{9}$$

where the L_n^{α} are generalized Laguerre polynomials. Notice that the basis sets for the intermediate states have an unphysical power at the origin r^{l_0} where l_0 is the angular momentum of the initial state Ψ_0. This simple artifice has the effect of substantially increasing convergence and stability. For example, the sum (1) for the ground state without the multiplicative logarithm converges with just one intermediate function if the exponential parameter coincides with that of the initial state $(\lambda=1)$.

The results with the basis set (9) for the ground state of hydrogen are shown in Table I, for successively increasing values of the size N of the intermediate basis set. The convergence is extremely slow: an extrapolation shows that one would need of the order of 27 000 basis functions to achieve a convergence only to the fourth decimal digit (the results follow very closely the linear fit $\delta\beta=2.6924/N$.) Such a demand on the size on the basis set is unrealistic. More importantly the application of this method to multielectron calculations would make it impossible to obtain any convergence at all.

II. A FAST CONVERGING METHOD

Alternatives to the basis sets (8) and (9) were proposed in the literature [3,4] in order to achieve a much better convergence for the sum in Eq. (1). The main thrust is to be able to perform these sums directly using these variational eigenstates instead of the exact eigenstates for the intermediate states. The best values obtained in quadruple precision for the hydrogenic ground-state Bethe logarithm had relative errors of 10^{-8} for a basis set used for a perturbation calculation [3] of the low states of He and 10^{-12} for an asymptotic calculation [4] for the Rydberg states of He. Although these convergences might seem excessive, in each case the hydrogenic accuracy was barely sufficient to obtain the sought two-electron contributions.

In this section we present a method that is able to yield 11 digits accuracy in double precision and 23 digits accuracy in quadruple precision calculations. Such accuracies might, again, look unnecessary but actually they emphasize the excellent convergence and stability of the method. As a result very good accuracies can be obtained in double precision calculations with relatively small basis sets, and therefore its application to calculations involving more electrons or screened or nonspherically symmetric potentials is now perfectly feasible. An application of this class of methods to accurate Bethelog calculations in two-electron systems can be found in Ref. [5]. We start by summarizing the main characteristics of the basis set used.

The radial basis set consists of a multiplet of basis sets of the form (9), each with a different exponential parameter. The basis set can be built in two totally equivalent ways,

$$\varphi_{i,l_0}=e^{-\lambda_i r}r^{l_0+n_i},\tag{10}$$

$$i=1,2,\ldots,N_{exp},\quad n_i=0,1,\ldots,N_i$$

or

$$\varphi_{i,l_0}=e^{-\lambda_i r}r^{l_0}L_{n_i}^{2l_0+2}(r),\tag{11}$$

$$i=1,2,\ldots,N_{exp},\quad n_i=0,1,\ldots,N_i,$$

where N_{exp} is the number of exponential parameters in the basis set and N_i is the number of different powers of r or Laguerre polynomials for each exponential parameter. When using explicitly in the calculations the orthogonality properties of the generalized Laguerre polynomials L_i^{α}, the second form of the basis set offers a much higher numerical stability as well as avoiding numerical roundoff. In this way this set is able to allow the use of a number of functions for a single exponential parameter much larger than the number one is able to use by using simple powers, before a breakdown in the calculations due to numerical dependency. For example, basis set (8) breaks down at about 14 functions in double precision calculations, while basis set (9) can easily accommodate hundreds of vectors [6] (the values of Table I were calculated in double precision.)

The two important issues to resolve are now (i) how to choose the sequence of nonlinear parameters λ_i and (ii) how to choose the number of functions for each of the nonlinear parameters in the series.

The first nonlinear parameter λ_1 is fixed at exactly the same value as that for the initial state λ_0 for reasons given earlier in the paper. The rest of the parameters need to increase very rapidly as an exponential or power series. Even though these sequences for λ_i already offer much better convergence, it was found that the series that most efficiently offered accurate results for either small or large numbers of exponential parameters was given by

$$\lambda_i=\lambda_0\exp[a(x_i^b-x_1^b)],\quad i=1,2,\ldots,N_{exp}\tag{12}$$

where the x_i are the zeros of a Laguerre polynomial of order N_{exp}. Notice that, as required, for $i=1$ we recover the parameter λ_0 of the initial state. *a* and *b* are arbitrary parameters that can be used to optimize the variational calculations. It was found that $b=0.5$ was an optimal value for *b* for the full set of calculations performed and was left fixed at that value. The value of *a* was optimized for different values of N_{exp}.

The maximum number of functions allowed per parameter was dependent on the values of the parameters themselves:

$$N_i^{max}=2\frac{\lambda_{i+1}}{\lambda_i}\frac{\epsilon}{\epsilon_{dp}}, \tag{13}$$

$$N_{N_{exp}}^{max}=\frac{1}{2}N_{N_{exp}-1}^{max}, \tag{14}$$

where ϵ is the smallest difference between two numbers for the precision and machine being used. ϵ_{dp} is a standard double precision value of 2.3×10^{-16}.

In order to avoid the onset of numerical dependency, in particular given the wide range of values of the exponential parameters, an additional condition was imposed on the basis set. Only the basis functions with a minimum overlap with the initial state were kept, i.e., those satisfying

$$\int \varphi_i\varphi_0 r^2 dr>\epsilon, \quad i=2,3,\ldots,N_{exp}. \tag{15}$$

Notice that, by construction, for $i=1$ the φ_i are orthogonal to the φ_0. By the use of Eqs. (13) and (15) the size of the basis set is dynamically allocated according to the properties of the basis sets as well as the precision (both machine dependent and program dependent) in which the calculations are performed. Condition (15) is actually very restrictive, placing a limit on the number of exponential parameters as well as the overall number of basis functions allowed in the calculation. For example, if $N_i=0$ then λ_i is not included. As a consequence, this constraint will not allow us to increase the dimension of the intermediate basis set after some tolerated maximum value. Notice that this value will change dynamically when the nonlinear parameters are changed.

Lastly, the calculations were performed also in two other gauges. One is the acceleration gauge in which the dipole operator is taken from the velocity form **p** to the acceleration form $\mathbf{a}=[H,\mathbf{p}]$ to obtain

$$S_1=\sum_n \int \left|\left\langle \Psi_0\left|\frac{Z\mathbf{r}}{r^3}\right|\Psi_n\right\rangle\right|^2 (E_n-E_0)^{-1}, \tag{16}$$

$$B_1=\sum_n \int \left|\left\langle \Psi_0\left|\frac{Z\mathbf{r}}{r^3}\right|\Psi_n\right\rangle\right|^2 \frac{\ln|E_n-E_0|}{(E_n-E_0)}. \tag{17}$$

The other gauge we call the pa-gauge which is a hybrid of the velocity and acceleration gauges that avoids the explicit inclusion of the energies of the intermediate states,

$$S_1=\sum_n \int \langle\Psi_0|Z\mathbf{r}/r^3|\Psi_n\rangle\langle\Psi_n|\mathbf{p}|\Psi_0\rangle, \tag{18}$$

$$B_1=\sum_n \int \langle\Psi_0|Z\mathbf{r}/r^3|\Psi_n\rangle\langle\Psi_n|\mathbf{p}|\Psi_0\rangle \ln\left|\frac{\langle\Psi_0|Z\mathbf{r}/r^3|\Psi_n\rangle}{\langle\Psi_n|\mathbf{p}|\Psi_0\rangle}\right|. \tag{19}$$

The different gauges were used to monitor the calculations. For very large basis sets, relative to the numerical machine precision, the best convergence is obtained in the acceleration gauge [3]. Otherwise the three gauges agree with the pa-gauge being the best at avoiding roundoff error (a rigorous discussion of this property is given in [4].)

A. The Bethe logarithm

The convergence of the results obtained for the ground state with the basis set (11) and (12) is presented in Table II for the full range of values of the number of exponential parameters: from $N_{exp}=1$ to $N_{exp}=20$. For each case we present the value of the largest exponential parameter used $\lambda_{max}=\lambda_{N_{exp}}$; the smallest is by construction λ_0. For the best convergence obtained, the largest exponential parameter has a remarkable value of 10^{22} a.u. We shall dwell on this in the following section. We present also the value of the energy for the intermediate state with the largest energy. For our best value this value is a remarkable 3.5×10^{46} a.u. This is 10^{42} times the rest mass of the electron ($m_e=1/\alpha_{fs}^2$ in a.u.) In other words an accurate calculation requires intermediate states with extremely high energy peaked extremely close to the origin. The values are compared to the group-theoretical result by Huff [2]. This comparison verifies the convergence in the table to 23 significant digits. For $N_{exp}>20$ the controls built in the program do not allow the calculations to collapse due to numerical dependence. The basis set is allowed to grow very marginally and the convergence remains at the same (best) value.

The negative contribution to the sum B_1 from the bound states and the continuum states with $E_n-E_0<1$ (a.u. are used throughout) is canceled by the lowest continuum states with $E_n-E_0>1$. The main contribution to B_1 will then come from the higher continuum states. What differentiates the sums B_1 and S_1 from other sum rules involving lower powers of E_n-E_0 is the very large contribution of states with very high energy, i.e., states with $E_n-E_0\gg mc^2$. This is presented in Fig. 1 for which the logarithmic sum B_1 is written in the form

$$B_1=\sum_n \int \delta B_n \tag{20}$$

with

$$\delta B_n=|\langle\Psi_0|\mathbf{p}|\Psi_n\rangle|^2(E_n-E_0)\ln|E_n-E_0|. \tag{21}$$

The plot in Fig. 1 was built with the data obtained for the largest set used in Table II. The relative contribution of the energy states appearing in the plot has converged already for smaller basis sets and does not vary much as the basis dimensions are increased. The oscillations are an artifact of the

TABLE II. Convergence of the results for the ground-state Bethe logarithm β_1 (1) using the intermediate states proposed in this paper. N_{exp} is the number of exponential parameters in the intermediate set; N is the number of basis functions; λ_{max} is the value of the largest exponential parameter in the set and E_{max} is the largest value in the energy spectrum of the set. β_{exact} is the group-theoretical value by Huff. The digits in *italics* did not converge. All values are given in a.u.

N_{exp}	N	λ_{max}	E_{max}	β_1	$\beta_{exact}-\beta$
1	25	1.00×10^{0}	5.34×10^{2}	2.18	1.07×10^{-1}
2	38	1.75×10^{2}	4.87×10^{6}	2.28*96*	1.37×10^{-3}
3	54	1.13×10^{4}	4.14×10^{9}	2.29 09*4 5*	3.61×10^{-5}
4	73	7.94×10^{5}	6.18×10^{13}	2.29 0980 *69*	6.81×10^{-7}
5	92	3.60×10^{7}	1.20×10^{17}	2.29 098 13*5 8*	1.72×10^{-8}
6	111	9.40×10^{8}	9.30×10^{19}	2.29 098 137 4*61*	5.91×10^{-10}
7	124	1.76×10^{10}	2.04×10^{22}	2.29 098 137 51*6 0*	4.57×10^{-11}
8	142	2.22×10^{11}	4.07×10^{24}	2.29 098 137 520 *28*	2.77×10^{-12}
9	160	2.80×10^{12}	7.74×10^{26}	2.29 098 137 520 5*35*	2.03×10^{-13}
10	178	3.22×10^{13}	1.02×10^{29}	2.29 098 137 520 55*3 5*	1.73×10^{-14}
11	196	3.07×10^{14}	9.32×10^{30}	2.29 098 137 520 555 *06*	1.68×10^{-15}
12	225	5.42×10^{15}	3.65×10^{33}	2.29 098 137 520 555 2*22*	8.05×10^{-17}
13	232	3.25×10^{16}	1.04×10^{35}	2.29 098 137 520 555 22*7 7*	2.40×10^{-17}
14	263	3.81×10^{17}	1.43×10^{37}	2.29 098 137 520 555 230 *02*	1.16×10^{-18}
15	282	2.96×10^{18}	8.64×10^{38}	2.29 098 137 520 555 230 1*19*	1.50×10^{-19}
16	301	1.67×10^{19}	2.76×10^{40}	2.29 098 137 520 555 230 13*2 1*	2.19×10^{-20}
17	320	1.82×10^{20}	3.28×10^{42}	2.29 098 137 520 555 230 133 *91*	3.48×10^{-21}
18	339	8.14×10^{20}	6.57×10^{43}	2.29 098 137 520 555 230 134 2*02*	5.30×10^{-22}
19	358	6.33×10^{21}	3.98×10^{45}	2.29 098 137 520 555 230 134 2*45*	9.83×10^{-23}
20	377	1.88×10^{22}	3.52×10^{46}	2.29 098 137 520 555 230 134 25*1 4*	3.15×10^{-23}
			exact	2.29 098 137 520 555 230 134 254 496 86	

finiteness of the basis set and decrease in amplitude with basis set size. The remarkable feature of this plot is the very large contribution of intermediate states with very large energy. We see that states with energies of the order of the rest mass of the electron ($mc^2 = 1/\alpha_{fs}^2 \approx 10^4$ a.u.) contribute at most to the second significant digit in B_1. On the other hand, a convergence to 1 ppm will involve states with energies of the order of 10^{14} a.u.($\approx 10^{10} mc^2$!). Given that the logarithm is a slow varying function of $E_n - E_0$, the same argument applies to S_1. A corroboration of the high contribution of highly energetic states is obtained by performing the sum S_1 fully relativistically, using the eigenstates of the Dirac Hamiltonian with positive energy eigenvalues, i.e., discarding the negative-energy (or positron) states. The value thus obtained for S_3 is 1.7608 rather than the nonrelativistic result of 2. This is consistent with the results in Fig. 1 that predict such a change for relativistic energies of order mc^2 or higher. Relativistic effects are treated separately in the nonrelativistic expansion of the QED calculation of the Lamb shift and the sum over intermediate states has to be seen as a sum over a complete set of intermediate sets. A delicate problem arises, however, when perturbations of the nuclear potential are introduced in a small region of space around the origin. This will be discussed later in the paper.

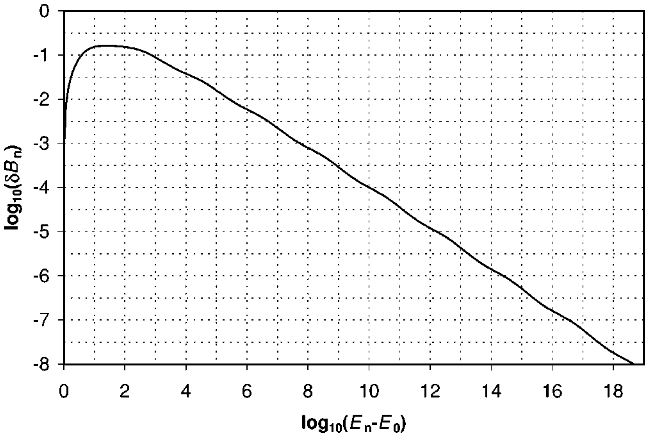

FIG. 1. Contribution δB_n of each intermediate state with energy E_n to the logarithmic sum B_1.

The very high convergence of the calculations is present for excited states as well. In Table III we present the results for several excited states with different angular momenta. To emphasize the number of digits for which convergence was achieved, in each case we present the values for the four best sets of exponential parameters, except for very high angular momenta for which only three exponential parameters are necessary for full convergence. The calculations were monitored also by checking the accuracy of the calculation of S_1 [Eq. (4)]. This was done by comparing the variational sum with the exact expression; their difference appears in the third column of Table III. The extremely high accuracy in

TABLE III. Convergence of the results for the Bethe logarithm (1) of excited states using the intermediate states proposed in this paper. N_{exp} is the number of exponential parameters; δS_1 is the numerical error in S_1 (4). The digits in *italics* did not converge.

	N_{exp}	$\log\lvert\delta S_1\rvert$	β
$2s$	17	-25.1	2.11 862 271 256 061 820 579 *57*
	18	-25.2	2.11 862 271 256 061 820 580 *14*
	19	-24.1	2.11 862 271 256 061 820 580 2*34*
	20	-25.3	2.11 862 271 256 061 820 580 23*3 8*
$3s$	17	-26.1	2.07 451 643 193 187 588 48*8 2*
	18	-26.0	2.07 451 643 193 187 588 489 *10*
	19	-26.1	2.07 451 643 193 187 588 489 2*42*
	20	-25.2	2.07 451 643 193 187 588 489 26*1 2*
$2p$	6	-27.2	−0.03 001 670 863 021 290 244 3*89*
	7	-26.4	−0.03 001 670 863 021 290 244 367 *68*
	8	-25.6	−0.03 001 670 863 021 290 244 367 6*05*
	9	-26.5	−0.03 001 670 863 021 290 244 367 60*0 2*
$3p$	6	-27.3	−0.03 819 022 938 531 244 770 *19*
	7	-27.6	−0.03 819 022 938 531 244 770 10*8 2*
	8	-26.5	−0.03 819 022 938 531 244 770 116 *00*
	9	-26.2	−0.03 819 022 938 531 244 770 116 2*06*
$4p$	6	-28.2	−0.04 195 489 459 808 554 867 *26*
	7	-25.8	−0.04 195 489 459 808 554 867 1*06*
	8	-25.5	−0.04 195 489 459 808 554 867 103 *74*
	9	-26.8	−0.04 195 489 459 808 554 867 103 9*21*
$3d$	2	-34.1	−0.00 523 214 814 09*2 0*
	3	-31.2	−0.00 523 214 814 088 300 *85*
	4	-29.7	−0.00 523 214 814 088 300 807 799 9*27*
	5	-27.3	−0.00 523 214 814 088 300 807 799 861 5*39*
$4d$	2	-34.2	−0.00 674 093 887 7*22*
	3	-30.4	−0.00 674 093 887 697 49*0 2*
	4	-28.8	−0.00 674 093 887 697 489 896 14*6 3*
	5	-27.1	−0.00 674 093 887 697 489 896 140 37*2 5*
$5d$	2	-34.9	−0.00 760 075 125 *90*
	3	-30.3	−0.00 760 075 125 794 65*7 6*
	4	-28.3	−0.00 760 075 125 794 656 517 3*74*
	5	-27.3	−0.00 760 075 125 794 656 517 349 33*1 0*
$4f$	1	-35.0	−0.00 173 366 1*59*
	2	-34.1	−0.00 173 366 148 212 57*8 4*
	3	-30.1	−0.00 173 366 148 212 577 599 49*1 2*
	4	-29.1	−0.00 173 366 148 212 577 599 490 62*4 1*
$5f$	1	-36.2	−0.00 220 216 *94*
	2	-34.3	−0.00 220 216 838 148 61*3 9*
	3	-29.2	−0.00 220 216 838 148 606 695 2*31*
	4	-28.3	−0.00 220 216 838 148 606 695 225 38*0 1*
$6f$	1	-35.7	−0.00 250 218 *50*
	2	-35.8	−0.00 250 217 976 027 8*91*
	3	-30.1	−0.00 250 217 976 027 851 336 *03*
	4	-28.1	−0.00 250 217 976 027 851 335 996 3*44*
$5g$	1	-34.9	−0.00 077 209 890 *24*
	2	-33.9	−0.00 077 209 890 153 656 48*3 3*
	3	-29.9	−0.00 077 209 890 153 656 482 663 284 *50*
$6g$	1	-35.6	−0.00 096 279 74*3 6*
	2	-32.9	−0.00 096 279 742 484 105 1*37*
	3	-29.4	−0.00 096 279 742 484 105 129 398 90*4 1*
$7g$	1	-35.1	−0.00 109 447 2*81*
	2	-27.1	−0.00 109 447 273 936 994 1*56*
	3	-25.7	−0.00 109 447 273 936 994 103 475 41*8 1*

the calculation of S_1 (sometimes full quadruple precision) is due to the inclusion of r^{l_0} in the intermediate basis set which makes this calculation exact, in principle independently of the size of the intermediate basis set. $\delta(S_1)$ is then a good check of the onset of numerical dependence in the basis set. The number of basis functions in the intermediate basis set can be obtained from Table II for the corresponding set N_{exp} of exponential parameters.

B. Higher-order logarithmic sums

Logarithmic sums of higher order in ΔE_n appear in higher-order QED corrections to the energy of states with $l > 0$ [7] (for states with $l=0$ these sums diverge.) In this section we calculate the logarithmic sum

$$B_2 = \sum_n \int \lvert\langle\Psi_0\lvert\mathbf{p}\rvert\Psi_n\rangle\rvert^2 (E_n - E_0)^2 \ln\lvert E_n - E_0\rvert \tag{22}$$

for several states with $l>0$. The basis set used is the same as the one used for the Bethe logarithm in Sec. II A. In this case, a subsidiary check on convergence and numerical errors is provided by the sum

$$S_2 = \sum_n \int \lvert\langle\Psi_0\lvert\mathbf{p}\rvert\Psi_n\rangle\rvert^2 (E_n - E_0)^2 \tag{23}$$

which, using commutator algebra, reduces to

$$S_2 = Z^2 \left\langle \Psi_0 \left\lvert \frac{1}{r^4} \right\rvert \Psi_0 \right\rangle . \tag{24}$$

In the case of hydrogenic functions (point nucleus) this results in

$$S_2 = Z^4 \frac{3n^2 - l(l+1)}{16n^5 l(l+1)(2l-1)(2l+1)(2l+3)} . \tag{25}$$

Numerical convergence and/or numerical roundoff can be checked by comparing S_2 of Eq. (23) with its exact value of Eq. (25).

The results obtained are presented in Table IV, where for a selection of states a few results for different sets of exponential parameters are shown to display the convergence of the results. $\delta\lvert S_2\rvert$ is the magnitude of the difference between the sum S_2 and its exact value from Eq. (25).

III. FINITE NUCELAR RADIUS EFFECTS

As we saw in the calculations of B_1, a very high accuracy is obtained when very large exponential parameters are included in the intermediate basis set. In fact, the digit affected by a certain basis set is roughly given by λ_{max}^{-1} for that basis set. Then for hydrogen, for example, any accuracy in B_1 better than 10^{-5} a.u. (10 ppm) requires intermediate wave functions that would peak inside the volume occupied by the proton if a finite nuclear radius was introduced. In fact for our best accuracies, intermediate basis functions that peak at 10^{-22} a.u. from the origin are used. This is 17 orders of magnitude smaller than the radius of the proton.

TABLE IV. Convergence of the results for the logarithmic sum of Eq. (22) for a variety of excited states using the intermediate states proposed in this paper. N_{exp} is the number of exponential parameters; δS_2 is the numerical error in S_2 [Eqs. (23) and (25)]. The digits in *italics* did not converge.

	N_{exp}	$\log\|\delta S_2\|$	B_2 (10^{-5} a.u)
$2p$	17	-22.5	5577.37 835 685 436 949 4*71*
	18	-23.1	5577.37 835 685 436 949 48*2 9*
	19	-24.1	5577.378 356 854 369 494 83*6 5*
	20	-24.6	5577.37 835 685 436 949 483 8*13*
$3p$	17	-22.7	2068.97 480 882 502 351 95*6 3*
	18	-23.4	2068.97 480 882 502 351 962 *06*
	19	-24.4	2068.97 480 882 502 351 962 *16*
	20	-24.4	2068.97 480 882 502 351 962 2*99*
$4p$	17	-22.7	933.02 752 794 440 696 93*5 1*
	18	-23.7	933.02 752 794 440 696 937 *87*
	19	-24.6	933.02 752 794 440 696 938 2*16*
	20	-25.0	933.02 752 794 440 696 938 22*1 5*
$3d$	5	-31.2	−102.19 687 960 985 532 60*4 7*
	6	-29.5	−102.19 687 960 985 532 607 53*9 8*
	7	-28.7	−102.19 687 960 985 532 607 547 1*72*
	8	-28.3	−102.19 687 960 985 532 607 547 19*1 0*
$4d$	5	-31.2	−42.75 477 133 686 967 84*9 7*
	6	-29.2	−42.75 477 133 686 967 854 6*47*
	7	-29.5	−42.75 477 133 686 967 854 661 *21*
	8	-27.4	−42.75 477 133 686 967 854 661 2*12*
$5d$	5	-31.3	−21.85 340 066 518 583 3*12*
	6	-29.1	−21.85 340 066 518 583 320 2*48*
	7	-29.2	−21.85 340 066 518 583 320 272 *04*
	8	-28.0	−21.85 340 066 518 583 320 272 11*5 2*
$4f$	2	-35.9	−12.00 662 565 01*9 8*
	3	-32.2	−12.00 662 565 020 193 8*91*
	4	-30.1	−12.00 662 565 020 193 895 021 *63*
	5	-29.3	−12.00 662 565 020 193 895 021 698 *80*
$5f$	2	-35.4	−6.40 070 950 052 *94*
	3	-32.5	−6.40 070 950 053 977 7*52*
	4	-30.0	−6.40 070 950 053 977 765 124 *63*
	5	-29.1	−6.40 070 950 053 977 765 124 86*3 6*
$6f$	2	-35.7	−3.78 858 598 90*8 7*
	3	-32.2	−3.78 858 598 910 766 *03*
	4	-30.4	−3.78 858 598 910 766 051 72*9 8*
	5	-29.1	−3.78 858 598 910 766 051 730 374 *38*

Should we then consider a finite nuclear radius for the proton? Although the finite nuclear radius correction for the energy is very small, roughly of the order of 1.8×10^{-10} a.u., we can expect the corrections to S_1 and to B_1 to be much larger. This is because while most of the contribution to $\langle H\rangle$ comes from the region of space in which the wave function is largest (around 1 a.u. for the ground state), as we saw earlier in the paper, for S_1 or B_1 it comes from regions very close to the origin, so that they will be very sensitive to the changes in the wave function in those regions.

Consider now the inclusion of a finite nuclear size in the calculations. The sum (4) no longer involves a Dirac δ function but has to be written as

$$S_1=\sum_n \int |\langle\Psi_0|\mathbf{p}|\Psi_n\rangle|^2(E_n-E_0) \tag{26}$$

$$=\frac{1}{2}\langle\Psi_0|\nabla^2V|\Psi_0\rangle. \tag{27}$$

For the purpose of these calculations we model the nucleus as a sphere with a homogeneous charge distribution and a radius $R=(5/3)^{1/2}\langle r^2\rangle^{1/2}$, where $\langle r^2\rangle^{1/2}$ is the root-mean square radius of the charge distribution. The results obtained are quite stunning. Consider the case of hydrogen with $\langle r^2\rangle^{1/2}=1.63\times10^{-5}$ a.u. The values obtained for the ground state are $S_1=1.999\,913\,415\,95$ and $\beta_1=2.290\,106\,937\,0$ while for the $2s$ state are $S_1=0.249\,989\,177\,05$ and $\beta_1=2.117\,740\,812\,5$. Further accuracy is not relevant given the uncertainty in the radius and shape of the nuclear charge distribution. These values involve a change of about 43 ppm for S_1 for both states, and for β_1 about 380 ppm for the $1s$ state and 416 ppm for the $2s$ state. The change in β would bring the theory more than an order of magnitude away from agreement with experiment. An estimate of the finite nuclear size correction to the Lamb shift due to the changes in S_1 and β_1 was first calculated by Borie [8]. That work, however, estimates incorrectly the change in the Lamb shift to be of the same order as agreement between theory and experiment. The reason is that in [8] it is assumed that the finite-size contribution comes mostly from the change in S_1 (the estimate of change in S_1 in that work is 38 ppm) while the change in β_1 is estimated to be negligible, while as we see from our results, the change is much larger than that in S_1. When the correct values for the finite nuclear size correction are taken into account the effect is, however, excessively large. An argument for the unphysical nature of this correction within the nonrelativistic expansion of the Lamb shift was given by Lepage, Erickson, and Yennie [9] on the basis that the small length scales of the order of the nuclear size imply very large momenta for the electron so that a nonrelativistic treatment of QED breaks down. The (previously unknown) large size of the correction to β_1 seems to further strengthen an argument for the inappropriateness of this correction.

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