

Nonrelativistic energy of the Li ground state

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Configuration-interaction calculations with energy-optimized basis sets and an empirical estimate of all sources of truncation-energy errors are used to evaluate the nonrelativistic electronic energy of the Li ground state. Our result $E_{\text{nr}} = -7.478\,062\,4(7)$ a.u. (Li) is $3 \mu\text{hartree}$ below an upper bound recently obtained by King using Hylleraas-type calculations, and $11 \mu\text{hartree}$ above an old estimate based on experimental data supplemented by relativistic, radiative, and mass-polarization corrections, thus suggesting a reassessment of several related issues.

I. INTRODUCTION

Recently,¹ very precise nonrelativistic ground-state energies for Li through Ne^{7+} were calculated by means of Hylleraas-type wave functions. Nevertheless, nonsystematic truncations of Hylleraas expansions, or of any other basis sets, fail to provide criteria for an internal quantitative assessment of energy eigenvalues, viz., it is not possible to obtain energy error bounds afforded by the calculation itself short of having to calculate a lower bound involving rather complicated integrals.

In his paper,¹ King quoted a nonrelativistic energy² lying $14 \mu\text{hartree}$ below his result, and he used that estimate to assess the convergence of his results although, as more Hylleraas terms are added, his successive energies settle down to within $1 \mu\text{hartree}$. Therefore, either King's results are *not* fully converged, as he seemed to believe contrary to our initial feelings, or the accepted nonrelativistic energy² is at fault.

In an effort to clarify this issue, we set out to calculate the nonrelativistic energy of the Li ground state to within less than $1 \mu\text{hartree}$ of uncertainty. We use configuration-interaction (CI), energy-optimized Slater-type orbitals (STO's), and empirical extrapolation formulas, as in previous work.³ Also, we employ a very general and efficient program⁴ for atoms and molecules and any number of electrons, all pointing to the possibility of carrying out similar work for larger systems.

In the Li ground state, beyond the Hartree-Fock configuration, there are $1s$ and $2s$ single excitations, $1s2s$ and $1s^2$ double excitations, and $1s^22s$ triple excitations. We have carried out extensive STO optimizations for the $1s2s$ pair (which we defined as including both $2s$ and $1s2s$ excitations), until the uncertainty δ in the corresponding truncation energy error Δ^{1s2s} becomes definitely below $1 \mu\text{hartree}$. This and the extent of the CI expansions employed guarantees that the remaining errors are in STO truncations for the $1s^2$ pair, which includes both $1s$ and $1s^2$ excitations. Thus the corresponding nonrelativistic energy E_{nr} may be expressed as the sum of the variationally calculated upper bound energy E_u plus the basis-set errors Δ^{1s2s} and Δ^{1s^2} in the corresponding $1s2s$ and $1s^2$ electron-pair calculations:

$$E_{\text{nr}} = E_u + \Delta_{\text{CI}} + \Delta^{1s2s} + \Delta^{1s^2} \pm \delta. \quad (1)$$

A small CI truncation-energy error Δ_{CI} will arise from neglecting certain triple excitations. The uncertainty δ is obtained from a sensitivity analysis.

Equations similar to (1) have been used for a long time;³ however, the present work seeks a substantially improved accuracy with respect to any previous three- or higher-electron calculations. Therefore, a detailed quantitative analysis is in order. In Sec. II we develop the one-electron basis set and carry out an analysis of the convergence of the $1s2s$ intershell CI expansion from which an estimate of Δ^{1s2s} is obtained. In Sec. III we consider the $1s^2$ electron-pair expansion and in Sec. IV we present the final results. Comparisons with previous work and conclusions are given in Sec. V.

II. INTERSHELL EXPANSIONS

In this section we consider ground-state $1s2s$ expansions of Li with the purpose of developing the basis set and characterizing patterns of convergence to extrapolate the energy for each l value in succession.

The energy increments ΔE_{il} follow patterns of the type

$$\Delta E_{il} = A(i+l+D)^{-p}, \quad (2)$$

where A , D , and p are parameters to be optimized and i is an index labeling successive radial functions.

Patterns of convergence based on invariants of the wave function,^{5,6} such as natural orbitals, yield very accurate extrapolation energies;⁶ however, their calculation might be extremely tedious. Here, instead, we recurred to a sequence of optimized STO's and their corresponding energies, feeling that this would be sufficient for our purposes.

The truncation-energy error Δ_l for a given l will be given by

$$\Delta_l = E_{\infty l} - E_{i_x l} = \sum_{i=i_x+1}^{\infty} \Delta E_{il}, \quad (3)$$

where i_x is the number of STO's in the basis set for a given l . Thus, we estimate the energy contribution of

TABLE I. STO basis set and intershall expansions for the Li ground state; energies in a.u. (Li) and energy increments in $\mu\text{hartree}$. The STO's of the extended basis are indicated by an asterisk.

Basis size	Energy	$-\Delta E_{II}$	$-\Delta_I$	$-\Delta E_I$
7s	-7.433 197 111			
8s	-7.433 198 761	1.650		
9s	-7.433 199 381	0.620		
10s	-7.433 199 667	0.286		
11s*	-7.433 199 802	0.141		
12s*	-7.433 199 871	0.063		
∞s	-7.433 199 951		0.284	474.259
First ten s-type STO's:	1s, 4.699; 1s, 2.478; 2s, 1.77; 2s, 0.81; 2s, 0.643; 3s, 4.85; 4s, 3.675; 5s, 9.184; 6s, 6.724; 7s, 9.50			
6p	-7.434 475 670			
7p	-7.434 477 192	1.876		
8p	-7.434 477 800	0.608		
9p	-7.434 478 072	0.272		
10p*	-7.434 478 219	0.147		
11p*	-7.434 478 296	0.077		
∞p	-7.434 478 410		0.338	1752.717
First nine p-type STO's:	2p, 2.531; 3p, 2.901; 3p, 4.97; 4p, 1.46; 4p, 9.50; 5p 3.668; 5p, 10.863; 6p, 1.863; 7p, 13.398			
5d	-7.432 898 293			
6d	-7.432 900 168	1.876		
7d	-7.432 901 007	0.839		
8d	-7.432 901 406	0.399		
9d*	-7.432 901 599	0.192		
10d*	-7.432 901 732	0.133		
∞d	-7.432 901 992		0.585	176.300
First eight d-type STO's:	3d, 3.78; 4d, 3.07; 4d, 12.60; 5d, 13.07; 6d, 3.69; 7d, 7.158, 8d, 17.34; 8d, 2.65			
4f	-7.432 761 916			
5f	-7.432 763 755	1.839		
6f	-7.432 764 570	0.815		
7f	-7.432 765 006	0.436		
8f*	-7.432 765 233	0.227		
9f*	-7.432 765 365	0.132		
∞f	-7.432 765 591		0.584	39.898
First seven f-type STO's:	4f, 2.28; 5f, 15.65; 6f, 6.06; 7f, 5.18; 8f, 21.32; 9f, 16.47, 9f, 5.79			
2g	-7.432 734 260			
3g	-7.432 736 384	2.124		
4g	-7.432 737 468	1.084		
5g	-7.432 738 178	0.710		
6g	-7.432 738 588	0.410		
7g*	-7.432 738 821	0.233		
8g*	-7.432 738 964	0.143		
9g*	-7.432 739 050	0.086		
10g*	-7.432 739 107	0.057		
∞g	-7.432 739 248		0.660	13.556
First six g-type STO's:	5g, 10.676; 6g, 3.51; 7g, 13.09; 8g, 6.23; 9g, 7.796; 10g, 16.658			
2h	-7.432 729 199			
3h	-7.432 730 036	0.838		

TABLE I. (Continued).

Basis size	Energy	$-\Delta E_{il}$	$-\Delta_l$	$-\Delta E_l$
4h	-7.432 730 515	0.495		
5h	-7.432 730 869	0.337		
6h*	-7.432 731 084	0.215		
7h*	-7.432 731 216	0.132		
8h*	-7.432 731 306	0.090		
∞h	-7.432 731 545		0.674	5.853
First five h-type STO's: 6h, 13.96; 7h, 4.42; 8h, 16.32; 9h, 6.56; 10h, 8.10				
1i	-7.432 726 744			
2i	-7.432 727 357	0.613		
3i	-7.432 727 757	0.400		
4i	-7.432 728 004	0.247		
5i	-7.432 728 176	0.172		
6i*	-7.432 728 300	0.124		
7i*	-7.432 728 381	0.080		
8i*	-7.432 728 442	0.061		
∞i	-7.432 728 677		0.500	2.985
First five i-type STO's: 7i, 16.72; 8i, 5.33; 9i, 6.36; 8i, 17.38; 10i 7.70				
1k	-7.432 726 247			
2k	-7.432 726 565	0.318		
3k	-7.432 726 771	0.206		
4k	-7.432 726 913	0.142		
5k	-7.432 727 026	0.112		
6k*	-7.432 727 099	0.074		
7k*	-7.432 727 146	0.046		
∞k	-7.432 727 261		0.234	1.569
First five k-type STO's: 8k, 18.18; 9k, 6.027; 10k, 7.032; 9k, 19.425; 11k, 8.157				
1l	-7.432 726 008			
2l	-7.432 726 191	0.183		
3l	-7.432 726 316	0.125		
4l	-7.432 726 403	0.087		
5l*	-7.432 726 466	0.063		
6l*	-7.432 726 512	0.046		
∞l	-7.432 726 700		0.296	1.008
First four l-type STO's: 9l, 20.521; 10l, 6.573; 10l, 21.841; 11l, 7.673				
2m*	-7.432 725 9859			
3m*	-7.432 726 0696	0.0837		
4m*	-7.432 726 1249	0.0553		
5m*	-7.432 726 1628	0.0379		
∞m	-7.432 726 2793		0.587	0.587
No m-type STO's included in final wave function				

STO's with $i > i_x$ by means of Eq. (3) with parameters obtained from i values up to i_x , and also using a few i values greater than i_x but which are not incorporated into the final basis set in order to keep the calculation within reasonable computer resources.

The $1s2s$ excitations contain terms of the type xy , where x and y are orthonormal orbitals with the same l quantum number. While studying the $l=1$ case, we no-

ticed that similar patterns were obtained if we removed the xy configurations with $l=0$, achieving corresponding truncation-energy errors coinciding to within 10^{-8} a.u. We also obtained similar results for $l=5$. Therefore, energy optimization of the STO basis and patterns of convergence were carried out separately for each l without including configurations with lower l values other than $1s^2s$.

In order to further simplify our analysis we lumped together $1s2s$ and $2s$ excitations. In Table I we present the STO basis set and intershell expansions for the Li ground state. The first five s -type STO's are taken from the work of Bagus *et al.*⁷ The energy increments ΔE_{il} correspond to the i th STO for a given l value. Because only a finite number of STO's are considered for each l , corresponding STO truncation-energy errors Δ_l will be associated to the $1s2s$ electron-pair expansion. For example, we use only 10 s -type STO's, resulting in $\Delta_0=0.284 \mu\text{hartree}$. From the values of Δ_l , collected again in Table II, we get the total intershell truncation-energy error for STO's up to $l=8$:

$$\Delta^{1s2s}(8) = \sum_{l=0}^8 \Delta_l = -4.155 \mu\text{hartree} . \quad (4)$$

We now add the values of Δ_l , $l \leq 8$, to the angular energy increments calculated with the given basis, to obtain *converged* angular energy increments ΔE_l shown in the last column of Table I, and given once again in Table III. These are subsequently fitted to an expression of the type

$$\Delta E_l = F(l + \gamma)^{-4} + G(l + \sigma)^{-6} , \quad (5)$$

based on theoretical arguments⁸ developed for the $1s^2$ electron pair in He. F , γ , G , and σ are parameters to be optimized. We found the -6 power to be the leading one, the -4 power affording a small correction. For the truncation-energy error in the $1s2s$ electron pair due to STO's with $l \geq 9$, we get

$$\Delta^{1s2s}(\infty) - \Delta^{1s2s}(8) = \sum_{l=9}^{\infty} \Delta E_l = -2.077 \mu\text{hartree} . \quad (6)$$

Thus, adding Eqs. (4) and (6), we get, for the total truncation-energy error Δ^{1s2s} ,

$$\Delta^{1s2s} = \Delta^{1s2s}(\infty) = -6.232 \mu\text{hartree} . \quad (7)$$

As can be seen in Table I, the last few STO's are not included in the final wave function. Thus we have two STO sets: the actual set used in the complete calculation, and an extended set used to further study the convergence patterns.

TABLE II. Estimated truncation energies for the $1s2s$ intershell electron-pair expansion, for $l \leq 8$; energies in $\mu\text{hartree}$.

l	Δ_l
0	-0.284
1	-0.338
2	-0.585
3	-0.584
4	-0.660
5	-0.674
6	-0.500
7	-0.234
8	-0.296
$\sum_{l=0}^8 \Delta_l$	-4.155

TABLE III. Breakdown of energy contributions to the $1s2s$ intershell electron-pair expansion; energies in $\mu\text{hartree}$.

l	ΔE_l
0	-474.259
1	-1752.717
2	-176.300
3	-39.898
4	-13.556
5	-5.853
6	-2.943
7	-1.553
8	-1.008
9	-0.587
$\sum_{l=9}^{\infty}$	-2.077
Δ^{1s2s}	-6.232

We assign to our empirical extrapolation an uncertainty equal to the sum of the three following terms.

(i) The sum over l of one-half the difference between the energies extrapolated by using the actual and the extended set, respectively, for each l value (uncertainty for each radial expansion).

(ii) The sum over l of the uncertainties obtained, for each l , as the sum of assigned absolute uncertainties in ΔE_{il} . The latter are equal to the difference between computed values of ΔE_{il} and those obtained from the fitting to a given pattern (an additional uncertainty for each radial expansion).

(iii) One-half the difference between two extrapolated energies corresponding to two different patterns for the l expansion, Eq. (5) (an uncertainty for the angular truncations for $l \geq 9$).

In this way, the uncertainty δ assigned to Δ^{1s2s} is

$$\delta = 0.72 \mu\text{hartree} . \quad (8)$$

III. K-SHELL EXPANSION

In principle, one could carry out calculations for the K -shell $1s^2$ excitations similar to those done for the intershell $1s2s$ excitations. However, the sought-after accuracy and the number of basis functions that would be required would exceed our presently available computational resources. Therefore, we have settled on a sensitivity analysis to estimate Δ^{1s^2} .

To this end we consider an electron-pair K -shell expansion for the Li ground state, involving $1s^2$ and $1s$ excitations truncated at increasingly large basis sizes, and compare the energy results with a two-electron Li^+ wave function computed with the same basis.⁹ The results, given in Table IV, show that as the basis set is increased from $7s6p5d4f3g2h2i2k1l$ to $10s9p8d7f6g5h5i5k4l$, the energy increments for the ground states of K -shell Li and Li^+ approach each other, coinciding in 10^{-8} a.u. in the last entry.

If this trend continues up to an arbitrarily large basis

TABLE IV. Comparison of energies for the Li ground-state $1s^2 K$ -shell expansion and the Li^+ ground-state expansion; energies in a.u. (Li). Energy increments, E_{incr} , in $\mu\text{hartree}$.

Basis size	Li (K shell)	$-E_{\text{incr}}$	Li^+	$-E_{\text{incr}}$
$7s6p5d4f3g2h2i2k1l$	-7.474 935 913		-7.279 283 945	
$8s7p6d5f4g3h3i3k2l$	-7.475 172 652	236.739	-7.279 520 928	236.983
$9s8p7d6f5g4h4i4k3l$	-7.475 354 305	181.653	-7.279 702 741	181.822
$10s9p8d7f6g5h5i5k4l$	-7.475 415 558	61.253	-7.279 764 013	61.262
∞ size			-7.279 913 386	149.373

size, the energy increments should coincide to the same accuracy, and the sum of them through infinite order will be equal to Δ^{1s^2} . Using the exact nonrelativistic energy result of Pekeris,¹⁰ we get

$$\begin{aligned} \Delta^{1s^2} &= E(\text{Li}^+, \text{Pekeris}) - E(\text{Li}^+, \text{current basis}) \\ &= -149.373 \mu\text{hartree}, \end{aligned} \quad (9)$$

as shown in the last entry of Table IV.

It might happen that the above-mentioned trend is interrupted before reaching a very large basis size. In that case our procedure would be unreliable and Δ^{1s^2} would likely be smaller (in absolute value) than that given by (9).

IV. FINAL RESULTS

A full list of configurations up to given l in the one-electron basis was computed by means of the program WONPSE.¹¹ The input to this program allows the missing of some configurations; thus we have been very careful to avoid this possibility. (Any errors in this step would cause the final energy to lie above the true eigenvalue E_{nr} .) To avoid human errors in constructing configuration lists for a larger number of electrons, a fully automatic program is being developed.

We first calculated the variational upper bound energy E_u with the final STO basis, including in the CI list all single and double excitations, as shown in the first entry of Table V.

We then add all triple excitations up to $l=3$, finding out that for a given type of configuration, say, excitations into pdf beyond certain orbital-index values (four p , two

d , and four f orbitals in this particular case), give very small energy contributions and may be removed from the final wave function at a cost of a CI truncation-energy error $\Delta_{\text{CI}}=0.15 \mu\text{hartree}$.

This reduction "trick" permits us to include triplet excitations until $l=5$, keeping computer times under 30 min on a microVAX 3900 computer. (We feel that short computer times are important in any tedious nonautomatic work, in order to carry out all computer runs within a single human concentration span, and to check whatever is deemed necessary.)

At this stage, $l=5$, we see that the energy contributions of triple excitations are $0.1 \mu\text{hartree}$; thus further harmonics in the triple-excitation expansion are not deemed necessary. In Table V we show the results of these calculations, the last entry being $E_u + \Delta_{\text{CI}}$.

In Table VI we collect the latter result with the data of Eqs. (7)–(9) and Eq. (1) to get $E_{\text{nr}}=7.478\,062\,41(72)$ a.u. (Li), and compare this result with previous ones.

V. CONCLUSIONS

In Tables I–V we presented basis sets, patterns of convergence for the energy, and truncation-energy errors. In Table VI we obtain a value of E_{nr} with an uncertainty $\delta=0.72 \mu\text{hartree}$ which differs from previous results: It is $3 \mu\text{hartree}$ below King's 600-term Hylleraas-type upper bound,¹ and $11 \mu\text{hartree}$ above a ponderated empirical estimate² based on experimental data supplemented by relativistic, radiative, and mass-polarization corrections.

TABLE V. Complete set of CI calculations with the final STO set.

Configurations included	Energy	CI length
Hartree-Fock $1s^2 2s$	-7.432 725 6920	1
Single and double excitations	-7.477 860 8867	804
Triplet excitations up to $l=1$	-7.477 890 2560	1620
Triple excitations up to $l=2$	-7.477 904 4	2948
Triple excitations up to $l=3$	-7.477 906 25	4740
Truncated triple excitations up to $l=3$	-7.477 906 10	2158
Δ_{CI}	-0.000 000 15	
Triple excitations up to $l=4$	-7.477 906 52	2778
Triple excitations up to $l=5$	-7.477 906 662	3653
$E_u + \Delta_{\text{CI}}$	-7.477 906 81	

TABLE VI. Nonrelativistic energy E_{nr} of the Li ground state, in a.u. (Li), and comparison with previous results.

Specification	Energy
$E_u + \Delta_{CI}$	$-7.477\,906\,81^a$
Δ^{1s2s}	$-0.000\,006\,23^b$
Δ^{1s^2}	$-0.000\,149\,37^c$
E_{nr}	$-7.478\,062\,41 \pm 0.000\,000\,72^d$
E_u (King)	$-7.478\,059^e$
E_{nr}	$-7.478\,073^f$

^aTable V.

^bEquation (7).

^cEquation (9).

^dEquation (8).

^eReference 1.

^fReference 2.

Our results indicate that King's upper bound recovers 99.993% of the correlation energy rather than the 99.97% originally reported.¹ This should encourage a more systematic Hylleraas-type calculation, done

“Pekeris-style” (keeping all terms up to a given sum of powers of r_1 , r_2 , and r_3) in an effort to obtain truly Hylleraas-type converged results.

On the other hand, the previously accepted estimate² of E_{nr} is definitely at fault, as any possible asymptotic irregularity in K -shell patterns of convergence will make $-\Delta^{1s^2}$ smaller than quoted in Eq. (9), causing an increase in the value of E_{nr} , which would increase the present discrepancy with the results of Ref. 2. Since the mass polarization used in Ref. 2 is essentially correct,¹ the causes of error must be looked in the relativistic and quantum-electrodynamic corrections.

Relativistic all-order many-body perturbation-theory calculations¹² yield very good agreement between calculated and experimental ionization potentials for Li and Be^+ ; however, corresponding nonrelativistic energies were not obtained. Recent developments in Dirac-Fock atomic calculations with finite basis sets¹³ indicate that it is feasible to carry out relativistic Ci calculations to the same accuracy as nonrelativistic ones, and this is surely the path to follow next.

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