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Hylleraas-Configuration Interaction study of the 1S ground state of the negative Li ion

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Abstract

In a previous work Sims and Hagstrom [J. Chem. Phys. 140, 224312 (2014)] reported Hylleraas-Configuration Interaction (Hy-CI) method variational calculations for the neutral atom and positive ion 1S ground states of the beryllium isoelectronic sequence. The Li^- ion, nominally the first member of this series, has a decidedly different electronic structure. This paper reports the results of a large, comparable calculation for the Li^- ground state to explore how well the Hy-CI method can represent the more diffuse L shell of Li^- which is representative of the $\text{Be}(2sns)$ excited states as well. The best non-relativistic energy obtained was $-7.500\,776\,596$ hartree, indicating that 10 – 20 nh accuracy is attainable in Hy-CI and that convergence of the $r_{12}r_{34}$ double cusp is fast and that this correlation type can be accurately represented within the Hy-CI model.

I. Introduction

Variational methods based on explicitly correlated wave functions are known to give the most accurate upper bounds to energy states, and hence the inclusion of terms containing the interelectronic distance r_{ij} in the wave function has become increasingly common, at least for few-electron atomic systems ($N \geq 4$) (so common in fact that a book dealing entirely with explicitly correlated wave functions has been produced [1]). Wave functions that are commonly referred to now as Hylleraas (Hy) follow the landmark calculation of Hylleraas [2] by employing powers of the interelectronic distance in the wave function. The Hylleraas-Configuration Interaction (Hy-CI) technique (developed by us [3] and also independently by Woźniak [4]) differs from the traditional Hy development by employing at most a single, linear r_{ij} factor with traditional Configuration Interaction orbital bases.

As a consequence of the formalism with an at most single r_{ij} factor per term, Hy-CI is unique (among the Hy methods) in that the mathematical problems for $N > 4$ can be reduced to problems with 4 electrons. While the work of Hylleraas demonstrated that two-electron atoms could be calculated accurately (for that time) with powers of r_{12} , it was Handy [5] who demonstrated that linear terms alone were sufficient for high accuracy for He. Hy-CI in its current incarnation utilizes only linear terms in r_{ij} , hence r_{12}/r_{12} [6, 1, 7] methods are related to Hy-CI but outside the scope of this study (but see Ruiz [8] for a discussion of CI- r_{12} and a comparison with Hy-CI in the two-electron He atom case). The other common explicitly correlated wave function, the explicitly correlated Gaussian (ECG) [1] wave function, in contrast to Hy and Hy-CI wave functions has the r_{ij} correlation appear as Gaussian exponentials.

Hy-CI calculations have recently been carried out on the 1S ground states of the Be isoelectronic series from $Z = 4$ through 113 [9]. Li^- (with $Z=3$), nominally the first member of this series, has a decidedly different electronic structure and was not included in those calculations and subsequent discussions. This paper corrects this "omission" and reports the results of a large, comparable calculation for the Li^- ground state.

A comprehensive review of the earlier non-relativistic, infinite nuclear mass calculations on this species can be found in the work of King [10]. More recently three ECG calculations have been reported [11, 12, 13], the last of which is the most extensive calculation and the best to date. A standard Hylleraas calculation of more limited scope than the present calculation is of note for its relatively compact basis sets and its study of how well the basis sets employed can describe the more diffuse region of configuration space for this species [14].

II. Variational Calculations

For N_e electrons, the total non-relativistic, stationary-point-nucleus energy E_{NR} is defined as the exact solution (eigenvalue) of the time-independent, nonrelativistic Schrödinger equation

$$H_{NR} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) = E_{NR} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}), \quad (1)$$

where the Hamiltonian H_{NR} is defined as (in atomic units)

$$H_{NR} = \sum_{i=1}^{N_e} \mathcal{H}_i + \sum_{i<j}^{N_e} r_{ij}^{-1}. \quad (2)$$

Here $\mathcal{H}_i = \mathcal{T}_i + \mathcal{V}_i$, $\mathcal{H}_i$ being a one electron operator (electron i) consisting of a kinetic energy part $\mathcal{T}_i = -\frac{1}{2} \nabla_i^2$ and a nuclear attraction part $\mathcal{V}_i = -Z/r_i$. N_e denotes the number of electrons and Z the corresponding nuclear charge.

The Hy-CI wave function for four electron atomic states is

$$\Psi = \sum_{K=1}^N C_K \Phi_K, \quad (3)$$

where

$$\Phi_K = \Lambda(r_{ij}^{\nu_K} \prod_{s=1}^4 \{\phi_{K_s}(\mathbf{r}_s)\} \Theta_K) = O_{as} O_{L, M_L} O_{S, M_S} (r_{ij}^{\nu_K} \prod_{s=1}^4 \{\phi_{K_s}(\mathbf{r}_s)\} \Theta_K) \quad (4)$$

denotes the K^{th} antisymmetrized spin and angular momentum projected Configuration State Function (CSF). O_{L,M_L} and O_{S,M_S} are idempotent orbital and spin angular momentum projection operators of the Löwdin type [15] for a state of total quantum numbers L, M_L, S, M_S (Russell–Saunders (LS) coupling is assumed). In practice it is sufficient to take ν_K equal to 0 or 1, with $\nu_K = 0$ the CI case. Θ_K is a primitive spin product function for term K and $\phi_{K_s}(\mathbf{r}_s)$ represents the s th basis orbital in the K^{th} term.

The basis orbitals are un-normalized Slater-type orbitals (STOs) $\phi(\mathbf{r})$ which are defined as

$$\phi_i(\mathbf{r}) = r^{n_i-1} e^{-\alpha_i r} Y_{l_i}^{m_i}(\theta, \phi), \quad (5)$$

where $Y_l^m(\theta, \phi)$ is a normalized spherical harmonic in the Condon and Shortley phase convention [16]. O_{as} is the idempotent antisymmetry projection operator. For four-electron singlet states there exist two linearly independent primitive spin functions $\Theta_1 = \alpha\beta\alpha\beta$ and $\Theta_2 = \alpha\alpha\beta\beta$. Cencek and Rychlewski [17] have given the general proof that only one primitive spin function is needed to ensure convergence of eigenvalues to the exact root of the Hamiltonian. Here it is the Θ_1 spin function which is used.

The coefficients C_K in Equation 3 are found in this work by solving the generalized eigenvalue problem

$$\mathbf{H}\mathbf{C} = E\mathbf{S}\mathbf{C}, \quad (6)$$

$$(\mathbf{H} - E_0\mathbf{S})\mathbf{C} = (E - E_0)\mathbf{S}\mathbf{C}, \quad (7)$$

$$\mathbf{C} = (E - E_0)(\mathbf{H} - E_0\mathbf{S})^{-1}\mathbf{S}\mathbf{C}, \quad (8)$$

where the matrix elements are given by $\mathcal{H}_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle$ and $\mathcal{S}_{KL} = \langle \Phi_K | \Phi_L \rangle$ with the Hamiltonian H given by Equation 2 and E_0 is some starting approximation for the eigenvalue E of interest.

(Shifted) inverse iteration [18] is the application of the power method [19] to $\mathbf{A}^{-1} = (\mathbf{H} - E_0\mathbf{S})^{-1}$ in the solution process used for solving for $\mathbf{C}$ in Equation 8 and leads to the iteration formula

$$\mathbf{v}_{k+1} = \mathbf{A}^{-1} \mathbf{S} \mathbf{v}_k, \quad k=0, 1, 2, \dots \quad (9)$$

with a convergence criterion for E , computed from

$$E_k = E_0 + \frac{\mathbf{v}_{k+1} \cdot \mathbf{S} \mathbf{v}_k}{\mathbf{v}_{k+1} \cdot \mathbf{S} \mathbf{v}_{k+1}}, \quad k=0, 1, 2, \dots \quad (10)$$

which converges rapidly to E provided that the trial E_0 is sufficiently close to the desired eigen-value, which turned out to be 5 digit accuracy in these calculations. In addition to a suitable E_0 , shifted inverse iteration requires a starting vector $\mathbf{v}_0$ (which was usually taken to be a vector of all 1s) and an efficient factorization for $\mathbf{A}^{-1}$ in Equation 9, which for us is

$$\mathbf{A}^{-1} = \mathbf{L}^T \mathbf{D}^{-1} \mathbf{L}, \quad (11)$$

where $\mathbf{D}$ is a diagonal matrix and $\mathbf{L}$ is the implicit representation of the lower triangular matrix $\mathbf{L}$ in terms of Gaussian transformations [20]. Quadruple precision was used in this work, and the Message Passing Interface (MPI) Standard [21] was used to parallelize the code.

III. Methodology

Atomic anions have a more diffuse electronic charge distribution than the neutral atom of the same nuclear charge. Hence the ground 1S state of Li^- is the same type of problem as the first excited state of Be; it is like Be(2s3s), not Be(2s2s). The basic expansion philosophy is what was used previously for Be and is one in which the bulk of the computing involved development of a base expansion (which we refer to as the CORE) whose purpose is to define both the STO basis and the CSF basis for the most important term types, and most importantly to calculate STO orbital exponents with a reasonable amount of effort. A goal of a few millihartrees was used to obtain the 24 block, 11665 CSF term expansion CORE which is described by the first 24 blocks in Table I utilizing two K-shell orbital types (one s orbital K and one p orbital K_p) and four L shell orbital types (L_1 and L_2 for the compact and diffuse s orbital types and L_3 and L_4 for the corresponding p orbital types). The level of difficulty in orbital exponent optimization is determined by the number of these orbital types which need to be optimized to self-consistency. After a CORE was established, the CORE was then augmented with post-CORE terms, adjustments to the CORE, refinements, etc., in approximately diminishing order of energy contributions.

In the table are listed energy results (column 5) for various expansion lengths N_{tot} shown in column 4. Column 2 lists the basis orbitals that are used to generate the CSFs for each block type in the order electron 1 (α spin), electron 2 (β spin), electron 3 (α spin), electron 4 (β spin). For example, in the first line $1:7s_K$ for the first electron means the basis orbitals are $1s_K$ through $7s_K$ orbitals (where K indicates an orbital exponent appropriate for a K shell electron). Products of four orbital types are built up by taking one pair of orbital types from the K-shell set and the other pair from the two L-shell sets. All the orbital promotions are within the shell, not between shells. This leaves out a substantial number of CSFs that turn out to be of no importance in this work. The number of CSFs in a block can be computed from the listed basis orbitals and the value of r-sum, the sum of the powers of r for each

Hartree orbital product of four basis orbitals [22, 23]. Each block in the CORE is listed separately in the table. Blocks after the CORE are combined where appropriate and displayed in the table as shown in the block specification (column 1) using the notation $R_1 = \{1, r_{12}, r_{34}\}$ to mean combine the blocks with 1, r_{12} , and r_{34} respectively and $R_2 = \{r_{13}, r_{14}\}$ to mean combine the blocks with r_{13} and r_{14} . Column 3 gives the number of CSFs added for the block or blocks shown in column 2. In Table I and elsewhere, E is the energy improvement for the blocks shown in column 1 and is shown in column 6.

In the table for *pppp* there are degenerate S states listed. One of these states is (10,10,10,10), where only the l and m orbital numbers are listed. For configurations with degeneracies, $m = 0$ unless otherwise noted. In this case, both the (10,10,10,10) and the (11,11,1-1,1-1) configurations contribute substantially ($\sim 1 \mu\text{h}$) and hence are included in the CORE. The term types are what one would expect from adding correlation to a typical closed K shell Be CI expansion using an s, p STO basis except that not included are the four *pppp* blocks which contribute $\sim 0.04 \mu\text{h}$. In addition *spps* blocks, which introduce pp correlation between the K shell and the compact L shell orbital, are included which contribute $\sim 0.6 \mu\text{h}$.

The Li^- CORE gives a reasonably good energy (approximately $5 \mu\text{h}$ accuracy) which can be thought of as a base ‘state’ of 5 decimal figure accuracy using a correlated s, p STO basis which is then augmented with enough correlated s, p, d basis blocks to achieve approximately 6 decimal place accuracy. Expanding the basis to include f orbital types, lowering the cutoff to 0.25 nh as less important blocks are considered, and previous experience, including the use of the Legendre expansion of possible Hy-CI term types to try [22], were all used to obtain a 132 block expansion of approximately $0.2 \mu\text{h}$ accuracy. Next come blocks 133–135 to provide additional correlation in the K-shell in the amount of $0.111 \mu\text{h}$, indicating a less than perfect description of the *ssss* part of the wave function.

The results in the table show that, not surprisingly, CI and intrashell correlations are more important than intershell correlations, as reflected by the E values for R_1 blocks vs. R_2 blocks (see Table I). R-sum adjustments to the CORE come next, starting with the first 5 blocks, which focuses attention on the largest energy contributors in seeking improvements to the energy description. Blocks 136 – 152 contain these adjustments where the added CSFs are obtained by taking the difference between the block listed and the block whose block number is the number following the trailing “-#”. Note that blocks 136–138 pick up an additional $0.013 \mu\text{h}$, further improving the description of the *ssss* R_1 part of the wave function. Doing this for all blocks in the CORE improves the result by $0.034 \mu\text{h}$.

The last step is to consider blocks previously neglected as well as blocks which didn’t pass a previous higher cutoff and to add in the remaining *sppd* and permutations contributing blocks as well as consider all possible *spdf* and permutations blocks. In arriving at the final wave function, all possible blocks of s, p, d type were tried, keeping all blocks which contributed $> 0.25 \text{ nh}$. For s, p, d, f types, most blocks were tried; the ones not tried were deemed unimportant at this level. In this way a 219 CSF block expansion was obtained. The order of CSFs in Table I is an attempt to put things in the order of diminishing energy contribution, but one has to be careful not to read too much into the present order because the energy lowering for a particular block depends to some extent on the order in which

blocks are added. For example, the energy contributions of the $s_{K1}s_{K1}ss$ blocks (blocks 133–135) would be much less if they were added at the end of the expansion. Table II compares the current result to the best previous variational Hylleraas (Hy), Configuration Interaction (CI), Multiconfiguration Hartree-Fock (MCHF), and Explicitly Correlated Gaussian (ECG) results. The current 219 CSF block expansion with an energy for $\text{Li}^{-1}S$ of $-7.5007\,7659\,6$ hartree, is within 17 nh of the best result of [13].

IV. Discussion

Table II shows the current best 38,931 expansion result is 15 nanohartrees below the Pachucki and Komasa [26] calculation, and is bettered only by the recent ECG results of Adamowicz, et al. [12, 13]. The Hy-CI restriction of one r_{ij} per CSF has been previously discussed [22, 9] and it has been pointed out [9] that the unlinked $r_{ij}r_{kl}$ (no indices in common) term types first occur in the four electron case, with $r_{12}r_{34}$ expected to be the most important. In the most recent Be work [9], it was pointed out that one can reason that the $r_{12}r_{34}$ double cusp leads to two convergence problems, $(ss)_K r_{12} \times [\text{L-shell cluster}]$ and $[\text{K-shell cluster}] \times (ss)_L r_{34}$, when the double cusp is represented by a superposition of normal Hy-CI term types. The $[\text{K-shell cluster}]$ and the $[\text{L-shell cluster}]$ are both basically a linear combination of pair functions $ss + pp + dd + ff + gg + \dots$.

How well the convergence of the $r_{12}r_{34}$ term type (“double cusp problem”) is treated in Hy-CI for Be was analyzed in Table III of the 2011 work [22] for Be. The results suggested that (for the four electron problem) compared to the slow, cusp-connected convergences in typical CI calculations, the convergence is fast and that this correlation type can be accurately, albeit slowly, represented within the Hy-CI model. In Table III are gathered together results from Table I which explore this point for Li^{-} . These results suggest that this is indeed the case for the more diffuse electronic distribution of Li^{-} . Interestingly the K-shell appears to be not a problem, while the L-shell is not converged in the r_{12} case. Addition of higher I STOs and blocks such as $(ss)_K r_{12} (gg)_L$, $(ss)_K r_{12} (hh)_L$, and $(ss)_K r_{12} (ii)_L$ could lead to perhaps an additional 10 nh to 20 nh and perhaps close in on the Bubin, et al. result [13] (although it should be pointed out that their energy has no accurate error bounds). Knowledge of the $(dd)_L$ and $(ff)_L$ entries in Column 2 of Table III can be used to predict the improvement one would get from higher $(ll)_L$ by using the I^{-4} behavior which was observed in He [27]. This is done in Table IV where the dd value is used to get the series started and the ff value as a sanity check. One can easily see where as much as 20 nanohartrees might be picked up in this way.

Ultimately slow convergence is built into Hy-CI for four or more electrons where one is trying to approximate the effect of the missing “double cusp” terms, as well as the $r_{ij}r_{ik}$ terms first encountered with three electrons. Previous experience with Li suggests that the linked product terms $r_{ij}r_{ik}$ shouldn’t be expected to give problems until the nh level, but in going beyond the nh level the slow double cusp convergence would become even more of a problem. This suggests further study of the double cusp problem using codes explicitly designed for this (our code is not). The results do appear to support the conclusion in previous work that while 10–20 nanohartree accuracy can be achieved without any difficulty, doing substantially better will require greater flexibility in the atomic orbital basis (including

adding $(ss)_K r_{12} \times [(gg)_L, (hh)_L$, and possibly $(ii)_L$ blocks) and extensive experimentation to find the best combination of CSFs and orbitals on which to base a much larger calculation.

A study of the Be(2sns) excited states, $n = 3, 7$ [28] is also being carried out. Li^- turns out to have a Be(2s3s) like structure as calculations have shown down to the block level. How much of the Li^- results can be carried over to Be(2s3s) remains to be seen. A significant decrease in the size (essentially cutting the size in half) of the expansion compared to recent Hy-CI calculations on the 1S ground states of the beryllium sequence [22, 9] is realized. The current 38,931 CSF expansion is 17 nh above the Bubin, et al. 2009 Li^- calculation [13], whereas the 41, 871 term 2011 Hy-CI Be calculation is 75 nh above the Stanke, et al. 2009 calculation [29], i.e. an approximately 5 times more accurate result with on the order of the same expansion length. The solver (shifted inverse iteration) used is one of the fastest methods for getting selected roots of the generalized eigenvalue problem. The only computational problem is the computation of the implicit representation of $\mathbf{L}$. To ensure stability in the use of inverse iteration the addition of partial and/or complete pivoting needs to be explored, which complicates the code as the matrices go from triangular to square and much of the speed advantage of inverse iteration is lost. Public domain codes are available for inverse iteration with partial and complete pivoting, but they do not meet our need for a parallel code which is fast, efficient, numerically stable, and of high enough precision (real*16) to enable calculations which go significantly beyond the current calculations. Recent advances in communication avoiding LU for overcoming communication bottlenecks in the usual methods for LU decomposition by Gaussian elimination with partial pivoting [30] should also be examined down to the block level.

V. Conclusion

Hy-CI has from its inception been an attempt to extend the success of the Hy method to systems with more than three electrons. Fundamental to the method is the restriction of one r_{ij} per CSF, which has achieved 10 – 20 nanohartree accuracy for the ground states of the Be isoelectronic series with $Z \leq 4$. For both extension of the method to $N > 4$ as well as for excited states of 4 electron systems, how well the method handles the “problem double cusp” when the L shell is more diffuse than in the ground state needs to be studied. Based on the calculations reported in Section III above as well as the analysis done in Table III in Section IV above, one can conclude that this correlation type can be accurately represented for the more diffuse distribution of Li^- . Combined with the previous Be isoelectronic series results, these calculations exemplify the level of accuracy that is now possible with Hy-CI in describing not only the ground state of Li^- , Be and Be-like ions, but also excited states as well.

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References

1. Rychlewski, J. Explicitly Correlated Wave Functions in Chemistry and Physics. Kluwar Academic Publishers; The Netherlands: 2003.
2. Hylleraas EA. Zeit Phys. 1929; 54:347–366.
3. Sims JS, Hagstrom SA. Combined configuration interaction - Hylleraas type wave function study of the ground state of the beryllium atom. Phys Rev A. 1971; 4(3):908–916.
4. Wo nicki, W. A Method of Construction of Variational Wave Functions for many-electron systems. In: Jucys, A., editor. Theory of Electronic Shells in Atoms and Molecules. Mintis; Vilnius: 1971. p. 103-109.
5. Handy NC. Towards an understanding of the form of correlated wavefunctions for atoms. J Chem Phys. 1973; 58:279–287.
6. Kutzelnigg W. r_{12} -Dependent terms in the wave function as closed sums of partial wave amplitudes for large l . Theor Chim Acta. 1985; 68:445–469.
7. Kong L, Bischoff F, Valeev EF. Explicitly Correlated R12/F12 Methods for Electronic Structure. Theor Chim Acta. 2011; 112:75–107.
8. Ruiz MB. Hylleraas-Configuration interaction calculations on the 1^1S ground state of the helium atom. J Coord Chem. 2015; 68(17–18):3340–3361.
9. Sims JS, Hagstrom SA. Hylleraas-configuration-interaction nonrelativistic energies for the 1^1S ground states of the beryllium isoelectronic sequence. J Chem Phys. 2014; 140:224312. [PubMed: 24929393]
10. King FW. Progress on high-precision calculations for the ground state of atomic lithium. J Mol Struct (Theochem). 1997; 400:7–56.
11. Pachucki K, Komasa J. Electron affinity of Li. J Chem Phys. 2006; 125:204304. [PubMed: 17144697]
12. Stanke M, Kedziera D, Bubin S, Adamowicz L. Electron affinity of ^7Li calculated with the inclusion of nuclear motion and relativistic corrections. J Chem Phys. 2007; 127:134107. [PubMed: 17919011]
13. Bubin S, Komasa J, Stanke M, Adamowicz L. Isotope shift in the electron affinity of lithium. J Chem Phys. 2009; 131:234112. [PubMed: 20025319]
14. King FW, Quicker D, Langer J. Compact wave functions for the beryllium isoelectronic series, Li^- to Ne^{+6} : A standard Hylleraas approach. J Chem Phys. 2011; 134:124114. [PubMed: 21456652]
15. Löwdin PO. Angular momentum wavefunctions constructed by projector operators. Rev Mod Phys. 1964; 36:966–976.
16. Condon, EU., Shortley, GH. The Theory of Atomic Spectra. Cambridge U. P; Cambridge, England: 1963.
17. Cencek W, Rychlewski J. Many-electron explicitly correlated Gaussian functions. I. General theory and test results. J Chem Phys. 1993; 98(2):1252–1261.
18. Golub, GH., Van Loan, CF. Matrix Computations. Johns Hopkins University Press; Baltimore: 2013.
19. Ralston, A., Rabinowitz, P. A First Course in Numerical Analysis. McGraw-Hill; New York: 1978.
20. Meyer, CD. Matrix Analysis and Applied Linear Algebra. SIAM; Philadelphia: 2000.
21. Message Passing Interface Forum. MPI: A message-passing interface standard. Int J Supercomput Appl. 1994; 8(3/4):159–416.
22. Sims JS, Hagstrom SA. Hylleraas-configuration interaction study of the 1^1S ground state of neutral beryllium. Phys Rev A. 2011; 83:032518.
23. Sims JS, Hagstrom SA. Hylleraas-configuration-interaction nonrelativistic energies for the 1^1S ground states of the beryllium isoelectronic sequence. J Chem Phys. 2014; 140:224312. Supplementary Material. [PubMed: 24929393]
24. Chung KT, Fullbright P. Electron Affinity of Lithium. Phys Scripta. 1992; 45:445.
25. Froese Fischer C. Convergence studies of MCHF calculations for Be and Li^- . J Phys B:At Mol Opt Phys. 1993; 26(5):855–862.
26. Pachucki K, Komasa J. Excitation energy of Be. Phys Rev A. 2006; 73:052502.

27. Sims JS, Hagstrom SA. High-precision Hy-CI variational calculations for the ground state of neutral helium and helium-like ions. *Int J Quant Chem.* 2002; 90(6):1600–1609.
28. Sims JS, Hagstrom SA. 2017 to be published.
29. Stanke M, Komasa J, Bubin S, Adamowicz L. Five lowest 1S states of the Be atom calculated with a finite-nuclear-mass approach and with relativistic and QED corrections. *Phys Rev A.* 2009; 80:022514.
30. Khabou A, Demmel JW, Grigori L, Gu M. LU Factorization with Panel Rank Revealing Pivoting and Its Communication Avoiding Version. *SIAM J Matrix Anal and Appl.* 2013; 34(3):1401–1429.

Table I

38,931 term $s, p, d, f r_{ij}$ Hy-CI expansion for the $\text{Li}^{-1}S$ ground state (in hartrees). In the table, $R_1 = \{1, r_{12}, r_{34}\}$, $R_2 = \{r_{13}, r_{14}\}$. N is the number of terms added and N_{tot} is the cumulative number of terms. All terms are r -sum (see text) filtered. Orbital exponents and energies are for the final wave function.

Block(s)	Terms added ^{1 2}	N	N_{tot}	$E(N_{tot})$ in hartrees	$-E$ in μh
1–24	CORE				
1	$1:7s_K 1:7s_K 1:6s_{L1} 1:7s_{L2}$ (r-sum=16)	1047	1047	−7.452 053 292 128	
2	$1:7s_K 1:7s_K 1:6s_{L1} 1:7s_{L2} r_{12}$ (r-sum=16)	1047	2094	−7.485 249 927 662	33196.635 534
3	$1:7s_K 1:7s_K 1:6s_{L1} 1:7s_{L2} r_{34}$ (r-sum=16)	1047	3141	−7.497 327 086 951	12077.159 289
4	$1:7s_K 1:7s_K 1:6s_{L1} 1:7s_{L2} r_{13}$ (r-sum=12)	700	3841	−7.497 351 056 784	23.969 833
5	$1:7s_K 1:7s_K 1:6s_{L1} 1:7s_{L2} r_{14}$ (r-sum=12)	700	4541	−7.497 360 599 748	9.542 964
6	$2:7p_{Kp} 2:7p_{Kp} 1:6s_{L1} 1:6s_{L2}$ (r-sum=16)	676	5217	−7.497 842 870 282	482.270 534
7	$2:7p_{Kp} 2:7p_{Kp} 1:6s_{L1} 1:6s_{L2} r_{12}$ (r-sum=12)	419	5636	−7.497 859 150 965	16.280 683
8	$2:7p_{Kp} 2:7p_{Kp} 1:6s_{L1} 1:6s_{L2} r_{34}$ (r-sum=16)	676	6312	−7.499 755 952 407	1896.801 442
9	$2:7p_{Kp} 2:7p_{Kp} 1:6s_{L1} 1:6s_{L2} r_{13}$ (r-sum=12)	419	6731	−7.499 808 979 421	53.027 014
10	$2:7p_{Kp} 2:7p_{Kp} 1:6s_{L1} 1:6s_{L2} r_{14}$ (r-sum=12)	419	7150	−7.499 878 759 157	69.779 736
11	$1:7s_K 1:7s_K 2:6p_{L3} 2:6p_{L4}$ (r-sum=16)	622	7772	−7.500 304 538 878	425.779 721
12	$1:7s_K 1:7s_K 2:6p_{L3} 2:6p_{L4} r_{12}$ (r-sum=16)	622	8394	−7.500 709 608 945	405.070 067
13	$1:6s_K 1:6s_K 2:6p_{L3} 2:6p_{L4} r_{34}$ (r-sum=12)	352	8746	−7.500 711 242 261	1.633 316
14	$1:6s_K 1:6s_K 2:6p_{L3} 2:6p_{L4} r_{13}$ (r-sum=12)	352	9098	−7.500 733 073 080	21.830 819
15	$1:6s_K 1:6s_K 2:6p_{L3} 2:6p_{L4} r_{14}$ (r-sum=12)	352	9450	−7.500 743 895 285	10.822 205
16	$2:6p_{Kp} 2:6p_{Kp} 2:6p_{L3} 2:6p_{L4}$ (r-sum=12)	212	9662	−7.500 749 009 182	5.113 897
17	$2:6p_{Kp} 2:6p_{Kp} 2:6p_{L3} 2:6p_{L4} r_{12}$ (r-sum=12)	212	9874	−7.500 753 797 012	4.787 830
18	$2:6p_{Kp} 2:6p_{Kp} 2:6p_{L3} 2:6p_{L4} r_{34}$ (r-sum=12)	212	10086	−7.500 758 486 568	4.689 556
19	$2:6p_{1Kp} 2:6p_{1Kp} 2:6p_{-1L3} 2:6p_{-1L4}$ (r-sum=12)	212	10298	−7.500 767 404 026	8.917 458
20	$2:5p_{1Kp} 2:5p_{1Kp} 2:5p_{-1L3} 2:5p_{-1L4} r_{12}$ (r-sum=12)	136	10434	−7.500 768 401 467	0.997 441
21	$2:5p_{1Kp} 2:5p_{1Kp} 2:5p_{-1L3} 2:5p_{-1L4} r_{34}$ (r-sum=12)	136	10570	−7.500 768 444 830	0.043 363
22	$1:5s_K 2:5p_{Kp} 2:5p_{L3} 1:5s_{L2}$ (r-sum=12)	365	10935	−7.500 769 063 401	0.618 571
23	$1:5s_K 2:5p_{Kp} 2:5p_{L3} 1:5s_{L2} r_{12}$ (r-sum=12)	365	11300	−7.500 770 585 622	1.522 220
24	$1:5s_K 2:5p_{Kp} 2:5p_{L3} 1:5s_{L2} r_{34}$ (r-sum=12)	365	11665	−7.500 771 710 875	1.125 253
25–132	Post-CORE				
25–26	$1:5s_K 2:5p_{Kp} 2:5p_{L3} 1:5s_{L2} R_2$ (r-sum=10)	572	12237	−7.500 771 924 870	0.213 995
27–29	$1:5s_K 2:5p_{Kp} 1:5s_{L1} 1:5p_{L4} R_1$ (r-sum=12)	1095	13332	−7.500 772 759 317	0.834 447
30–31	$1:5s_K 2:5p_{Kp} 1:5s_{L1} 1:5p_{L4} R_2$ (r-sum=10)	572	13904	−7.500 772 805 576	0.046 259
32	$3:6d_{Kd} 3:6d_{Kd} 1:5s_{L1} 1:5s_{L2}$ (r-sum=12)	177	14081	−7.500 773 141 939	0.336 363

Block(s)	Terms added ^{1 2}	N	N_{tot}	$E(N_{tot})$ in hartrees	$-E$ in μh
33	$3:6d_{Kd}3:6d_{Kd}1:5s_{L1}1:5s_{L2}r_{12}$ (r-sum=12)	177	14258	-7.500 773 172 416	0.030 477
34	$3:6d_{Kd}3:6d_{Kd}1:5s_{L1}1:5s_{L2}r_{34}$ (r-sum=12)	177	14435	-7.500 773 685 636	0.513 220
35–36	$3:6d_{Kd}3:6d_{Kd}1:5s_{L1}1:5s_{L2}R_2$ (r-sum=10)	214	14649	-7.500 774 280 124	0.594 488
37	$1:5s_K1:5s_K3:6d_{L5}3:6d_{L6}$ (r-sum=12)	169	14818	-7.500 774 288 953	0.008 829
38	$1:5s_K1:5s_K3:6d_{L5}3:6d_{L6}r_{12}$ (r-sum=12)	169	14987	-7.500 774 499 360	0.210 407
39	$1:5s_K1:5s_K3:6d_{L5}3:6d_{L6}r_{34}$ (r-sum=12)	169	15156	-7.500 774 503 226	0.003 866
40–41	$1:5s_K1:5s_K3:6d_{L5}3:6d_{L6}R_2$ (r-sum=10)	206	15362	-7.500 774 786 582	0.283 356
42–44	$1:5s_K3:6d_{Kd}3:6d_{L5}1:5s_{L2}R_1$ (r-sum=12)	858	16220	-7.500 775 085 209	0.298 627
45–46	$1:5s_K3:6d_{Kd}3:6d_{L5}1:5s_{L2}R_2$ (r-sum=8)	136	16356	-7.500 775 093 497	0.008 288
47–49	$1:5s_K3:6d_{Kd}1:5s_{L1}3:6d_{L6}R_1$ (r-sum=12)	858	17214	-7.500 775 182 631	0.089 134
50–51	$1:5s_K3:6d_{Kd}1:5s_{L1}3:6d_{L6}R_2$ (r-sum=8)	136	17350	-7.500 775 186 112	0.003 481
52–54	$1:5s_K2:5p_{Kp}2:5p_{L3}3:6d_{L6}R_1$ (r-sum=10)	480	17830	-7.500 775 803 275	0.617 163
55–56	$1:5s_K2:5p_{Kp}2:5p_{L3}3:6d_{L6}R_2$ (r-sum=8)	134	17964	-7.500 775 906 855	0.103 580
57–59	$1:5s_K3:6d_{Kd}2:5p_{L3}2:5p_{L4}R_1$ (r-sum=10)	480	18444	-7.500 775 951 783	0.044 928
60–61	$1:5s_K3:6d_{Kd}2:5p_{L3}2:5p_{L4}R_2$ (r-sum=8)	134	18578	-7.500 775 986 544	0.034 761
62–64	$2:5p_{Kp}1:5s_K2:5p_{L3}3:6d_{L6}R_1$ (r-sum=10)	480	19058	-7.500 776 034 133	0.047 589
65–66	$2:5p_{Kp}1:5s_K2:5p_{L3}3:6d_{L6}R_2$ (r-sum=8)	134	19192	-7.500 776 050 981	0.016 848
67–69	$3:6d_{Kd}2:5p_{Kp}1:5s_{L1}2:5p_{L4}R_1$ (r-sum=10)	480	19672	-7.500 776 122 988	0.072 007
70–71	$3:6d_{Kd}2:5p_{Kp}1:5s_{L1}2:5p_{L4}R_2$ (r-sum=8)	134	19806	-7.500 776 132 526	0.009 538
72	$2:5p_{Kp}2:5p_{Kp}1:5s_{L1}2:5d_{L6}$ (r-sum=10)	100	19906	-7.500 776 136 226	0.003 700
73	$4:7f_{Kf}4:7f_{Kf}1:5s_{L1}1:5s_{L2}$ (r-sum=12)	107	20013	-7.500 776 144 586	0.008 360
74	$4:7f_{Kf}4:7f_{Kf}1:5s_{L1}1:5s_{L2}r_{12}$ (r-sum=12)	107	20120	-7.500 776 154 583	0.009 997
75	$4:7f_{Kf}4:7f_{Kf}1:5s_{L1}1:5s_{L2}r_{34}$ (r-sum=12)	107	20227	-7.500 776 157 331	0.002 748
76–77	$4:7f_{Kf}4:7f_{Kf}1:5s_{L1}1:5s_{L2}R_2$ (r-sum=8)	22	20249	-7.500 776 158 556	0.001 225
78	$1:5s_K1:5s_K4:7f_{L7}4:7f_{L8}$ (r-sum=12)	103	20352	-7.500 776 160 118	0.001 562
79	$1:5s_K1:5s_K4:7f_{L7}4:7f_{L8}r_{12}$ (r-sum=12)	103	20455	-7.500 776 197 684	0.037 566
80	$1:5s_K1:5s_K4:7f_{L7}4:7f_{L8}r_{34}$ (r-sum=12)	103	20558	-7.500 776 199 081	0.001 397
81–82	$1:5s_K1:5s_K4:7f_{L7}4:7f_{L8}R_2$ (r-sum=8)	22	20580	-7.500 776 199 365	0.000 284
83–85	$1:5s_K4:7f_{Kf}4:7f_{L7}1:5s_{L2}R_1$ (r-sum=10)	204	20784	-7.500 776 209 305	0.009 940
86	$1:5s_K4:7f_{Kf}4:7f_{L7}1:5s_{L2}r_{13}$ (r-sum=8)	15	20799	-7.500 776 210 040	0.000 735
87	$1:5s_K4:7f_{Kf}1:5s_{L1}4:7f_{L8}$ (r-sum=10)	68	20867	-7.500 776 211 418	0.001 379
88	$1:5s_K4:7f_{Kf}1:5s_{L1}4:7f_{L8}r_{12}$ (r-sum=10)	68	20935	-7.500 776 212 639	0.001 221
89	$2:5p_{Kp}2:5p_{Kp}3:6d_{L5}3:6d_{L6}$ (r-sum=10)	43	20978	-7.500 776 214 532	0.001 893
90	$2:5p_{Kp}2:5p_{Kp}3:6d_{L5}3:6d_{L6}r_{12}$ (r-sum=10)	43	21021	-7.500 776 225 364	0.010 832

Block(s)	Terms added ^{1 2}	N	N_{tot}	$E(N_{tot})$ in hartrees	$-E$ in μh
91	$2:5p_{Kp} 2:5p_{Kp} 3:6d_{L5} 3:6d_{L6} r_{34}$ (r-sum=10)	43	21064	-7.500 776 230 254	0.004 890
92–93	$2:5p_{Kp} 2:5p_{Kp} 3:6d_{L5} 3:6d_{L6} R_2$ (r-sum=8)	22	21086	-7.500 776 231 627	0.001 373
94	$2:5p_{1Kp} 2:5p_{1Kp} 3:6d_{-1L5} 3:6d_{-1L6}$ (r-sum=10)	43	21129	-7.500 776 253 437	0.021 810
95	$2:5p_{1Kp} 2:5p_{1Kp} 3:6d_{-1L5} 3:6d_{-1L6} r_{12}$ (r-sum=10)	43	21172	-7.500 776 281 650	0.028 213
96	$2:5p_{1Kp} 2:5p_{1Kp} 3:6d_{-1L5} 3:6d_{-1L6} r_{34}$ (r-sum=10)	43	21215	-7.500 776 290 871	0.009 221
97–98	$2:5p_{1Kp} 2:5p_{1Kp} 3:6d_{-1L5} 3:6d_{-1L6} R_2$ (r-sum=8)	22	21237	-7.500 776 292 649	0.001 778
99	$3:6d_{Kd} 3:6d_{Kd} 2:5p_{L3} 2:5p_{L4}$ (r-sum=10)	43	21280	-7.500 776 296 067	0.003 418
100	$3:6d_{Kd} 3:6d_{Kd} 2:5p_{L3} 2:5p_{L4} r_{12}$ (r-sum=10)	43	21323	-7.500 776 297 504	0.001 437
101	$3:6d_{Kd} 3:6d_{Kd} 2:5p_{L3} 2:5p_{L4} r_{34}$ (r-sum=10)	43	21366	-7.500 776 298 546	0.001 042
102–103	$3:6d_{Kd} 3:6d_{Kd} 2:5p_{L3} 2:5p_{L4} R_2$ (r-sum=8)	22	21388	-7.500 776 298 978	0.000 432
104	$3:6d_{1Kd} 3:6d_{1Kd} 2:5p_{-1L3} 2:5p_{-1L4}$ (r-sum=10)	43	21431	-7.500 776 303 912	0.004 934
105	$3:6d_{1Kd} 3:6d_{1Kd} 2:5p_{-1L3} 2:5p_{-1L4} r_{12}$ (r-sum=10)	43	21474	-7.500 776 305 488	0.001 576
106	$3:6d_{1Kd} 3:6d_{1Kd} 2:5p_{-1L3} 2:5p_{-1L4} r_{34}$ (r-sum=10)	43	21517	-7.500 776 308 346	0.002 858
107–108	$3:6d_{1Kd} 3:6d_{1Kd} 2:5p_{-1L3} 2:5p_{-1L4} R_2$ (r-sum=8)	22	21539	-7.500 776 308 881	0.000 535
109–111	$2:5p_{Kp} 1:5s_K 1:5s_{L1} 2:5p_{L4} R_1$ (r-sum=12)	1095	22634	-7.500 776 325 103	0.016 222
112–113	$2:5p_{Kp} 1:5s_K 1:5s_{L1} 2:5p_{L4} R_2$ (r-sum=10)	572	23206	-7.500 776 340 714	0.015 611
114–118	$2:5p_{Kp} 1:5s_K 2:5p_{L3} 1:5s_{L2} R$ (r-sum=10)	1430	24636	-7.500 776 361 032	0.020 318
119–121	$3:6d_{Kd} 1:5s_K 1:5s_{L1} 3:6d_{L6} R_1$ (r-sum=12)	858	25494	-7.500 776 367 553	0.006 521
122–123	$3:6d_{Kd} 1:5s_K 1:5s_{L1} 3:6d_{L6} R_2$ (r-sum=10)	340	25834	-7.500 776 379 010	0.011 457
124–126	$3:6d_{Kd} 1:5s_K 3:6d_{L5} 1:5s_{L2} R_1$ (r-sum=12)	858	26692	-7.500 776 383 929	0.004 919
127–128	$3:6d_{Kd} 1:5s_K 3:6d_{L5} 1:5s_{L2} R_2$ (r-sum=10)	340	27032	-7.500 776 388 723	0.004 794
129–130	$2:6p_{Kp} 2:6p_{Kp} 2:6p_{L3} 2:6p_{L4} R_2$ (r-sum=10)	234	27266	-7.500 776 391 407	0.002 684
131–132	$2:5p_{1Kp} 2:5p_{1Kp} 2:5p_{-1L3} 2:5p_{-1L4} R_2$ (r-sum=10)	186	27452	-7.500 776 400 295	0.008 888
133–135	$1:6s_{K1} 1:6s_{K1} 1:6s_{L1} 1:6s_{L2} R_1$ (r-sum=10)	1257	28709	-7.500 776 511 946	0.111 651
136–152	CORE r-sum adjustments				
136	$1:9s_K 1:9s_K 1:9s_{L1} 1:9s_{L2}$ (r-sum=14) –#1	529	29238	-7.500 776 515 604	0.003 658
137	$1:9s_K 1:9s_K 1:9s_{L1} 1:9s_{L2} r_{12}$ (r-sum=12) –#2	253	29491	-7.500 776 522 700	0.007 096
138	$1:9s_K 1:9s_K 1:9s_{L1} 1:9s_{L2} r_{34}$ (r-sum=12) –#3	253	29744	-7.500 776 524 832	0.002 132
139	$2:9p_{Kp} 2:9p_{Kp} 1:9s_{L1} 1:9s_{L2}$ (r-sum=14) –#6	349	30093	-7.500 776 527 879	0.003 047
140	$2:9p_{Kp} 2:9p_{Kp} 1:9s_{L1} 1:9s_{L2} r_{34}$ (r-sum=12) –#8	139	30232	-7.500 776 529 413	0.001 534
141	$1:9s_K 1:9s_K 2:9p_{L3} 2:9p_{L4}$ (r-sum=12) –#11	167	30399	-7.500 776 531 451	0.002 038
142	$1:9s_K 1:9s_K 2:9p_{L3} 2:9p_{L4} r_{12}$ (r-sum=12) –#12	167	30566	-7.500 776 540 902	0.009 451
143	$1:8s_K 1:8s_K 1:9s_{L1} 1:9s_{L2} r_{13}$ (r-sum=12) –#4	218	30784	-7.500 776 541 679	0.000 777
144	$2:8p_{Kp} 2:8p_{Kp} 1:9s_{L1} 1:9s_{L2} r_{12}$ (r-sum=12) –#7	119	30903	-7.500 776 542 477	0.000 798

Block(s)	Terms added ^{1 2}	N	N _{tot}	$E(N_{tot})$ in hartrees	– E in μ h
145	$2:8p_{Kp} 2:8p_{Kp} 1:9s_{L1} 1:9s_{L2} r_{13}$ (r-sum=12) –#9	119	31022	–7.500 776 542 869	0.000 392
146	$1:8s_K 1:8s_K 2:9p_{L3} 2:9p_{L4} r_{13}$ (r-sum=12) –#14	192	31214	–7.500 776 543 507	0.000 638
147	$1:8s_K 1:8s_K 2:9p_{L3} 2:9p_{L4} r_{14}$ (r-sum=12) –#15	192	31406	–7.500 776 544 664	0.001 157
148	$1:9s_K 1:9s_K 1:9s_{L1} 1:9s_{L2} r_{14}$ (r-sum=12) –#5	253	31659	–7.500 776 545 328	0.000 664
149	$1:9s_K 1:9s_K 2:8p_{L3} 2:8p_{L4} r_{34}$ (r-sum=12) –#13	176	31835	–7.500 776 545 957	0.000 629
150	$2:6p_{0Kp} 2:6p_{0Kp} 2:8p_{0L3} 2:8p_{0L4} r_{12}$ (r-sum=12) –#17	40	31875	–7.500 776 546 212	0.000 255
151	$2:6p_{1Kp} 2:6p_{1Kp} 2:8p_{-1L3} 2:8p_{-1L4} r_{12}$ (r-sum=12) –#20	116	31991	–7.500 776 548 059	0.001 847
152	$2:6p_{1Kp} 2:6p_{1Kp} 2:8p_{-1L3} 2:8p_{-1L4} r_{34}$ (r-sum=12) –#21	116	32107	–7.500 776 549 293	0.001 234
153–219	Final adjustments				
153	$1:5s_K 4:7f_{Kf} 1:5s_{L1} 4:7f_{L8} r_{34}$ (r-sum=12)	170	32277	–7.500 776 550 078	0.000 785
154	$3:6d_{-1Kd} 3:6d_{1Kd} 2:5p_{-1L3} 2:5p_{1L4}$ (r-sum=10)	43	32320	–7.500 776 551 443	0.001 365
155	$3:6d_{-1Kd} 3:6d_{1Kd} 2:5p_{-1L3} 2:5p_{1L4} r_{12}$ (r-sum=10)	43	32363	–7.500 776 552 583	0.001 140
156–160	$3:6d_{0Kd} 2:5p_{0Kp} 3:6d_{0L5} 2:5p_{0L4} R$ (r-sum=10)	330	32693	–7.500 776 557 372	0.004 789
161	$3:6d_{1Kd} 2:5p_{1Kp} 3:6d_{-1L5} 2:5p_{-1L4}$ (r-sum=10)	66	32759	–7.500 776 558 558	0.001 186
162	$3:6d_{1Kd} 2:5p_{1Kp} 3:6d_{-1L5} 2:5p_{-1L4} r_{12}$ (r-sum=10)	66	32825	–7.500 776 558 934	0.000 376
163	$3:6d_{-1Kd} 2:5p_{1Kp} 3:6d_{-1L5} 2:5p_{1L4}$ (r-sum=10)	66	32891	–7.500 776 559 449	0.000 515
164	$3:6d_{-1Kd} 2:5p_{1Kp} 3:6d_{-1L5} 2:5p_{1L4} r_{12}$ (r-sum=10)	66	32957	–7.500 776 560 608	0.001 159
165	$3:6d_{0Kd} 2:5p_{0Kp} 2:5p_{0L3} 3:6d_{0L6}$ (r-sum=10)	66	33023	–7.500 776 561 664	0.001 056
166	$3:6d_{0Kd} 2:5p_{0Kp} 2:5p_{0L3} 3:6d_{0L6} r_{12}$ (r-sum=10)	66	33089	–7.500 776 561 867	0.000 203
167	$3:6d_{1Kd} 2:5p_{1Kp} 2:5p_{-1L3} 3:6d_{-1L6}$ (r-sum=10)	66	33155	–7.500 776 562 201	0.000 334
168	$3:6d_{1Kd} 2:5p_{1Kp} 2:5p_{-1L3} 3:6d_{-1L6} r_{12}$ (r-sum=10)	66	33221	–7.500 776 562 356	0.000 155
169	$3:6d_{-1Kd} 2:5p_{1Kp} 2:5p_{-1L3} 3:6d_{1L6}$ (r-sum=10)	66	33287	–7.500 776 562 670	0.000 314
170	$3:6d_{-1Kd} 2:5p_{1Kp} 2:5p_{-1L3} 3:6d_{1L6} r_{12}$ (r-sum=10)	66	33353	–7.500 776 563 298	0.000 628
171	$2:5p_{0Kp} 3:6d_{0Kd} 3:6d_{0L5} 2:5p_{0L4}$ (r-sum=10)	66	33419	–7.500 776 563 752	0.000 454
172	$2:5p_{0Kp} 3:6d_{0Kd} 3:6d_{0L5} 2:5p_{0L4} r_{12}$ (r-sum=10)	66	33485	–7.500 776 564 246	0.000 494
173	$2:5p_{0Kp} 3:6d_{0Kd} 3:6d_{0L5} 2:5p_{0L4} r_{13}$ (r-sum=10)	66	33551	–7.500 776 564 574	0.000 328
174	$2:5p_{Kp} 2:5p_{Kp} 1:5s_{L1} 3:6d_{L6} r_{12}$ (r-sum=10)	100	33651	–7.500 776 565 143	0.000 569
175	$2:5p_{Kp} 2:5p_{Kp} 1:5s_{L1} 3:6d_{L6} r_{34}$ (r-sum=10)	100	33751	–7.500 776 565 516	0.000 373
176–177	$2:5p_{Kp} 2:5p_{Kp} 1:5s_{L1} 3:6d_{L6} R_2$ (r-sum=10)	200	33951	–7.500 776 567 153	0.001 637
178	$2:5p_{Kp} 3:6d_{Kd} 1:5s_{L1} 2:5p_{L4}$ (r-sum=10)	160	34111	–7.500 776 567 725	0.000 572
179	$2:5p_{Kp} 3:6d_{Kd} 1:5s_{L1} 2:5p_{L4} r_{12}$ (r-sum=10)	160	34271	–7.500 776 569 178	0.001 453
180	$2:5p_{Kp} 1:5s_K 3:6d_{L5} 2:5p_{L4}$ (r-sum=10)	160	34431	–7.500 776 569 653	0.000 475
181	$2:5p_{Kp} 1:5s_K 3:6d_{L5} 2:5p_{L4} r_{12}$ (r-sum=10)	160	34591	–7.500 776 570 514	0.000 861

Block(s)	Terms added ^{1 2}	N	N _{tot}	E(N _{tot}) in hartrees	– E in μ h
182	3:6d _{Kd} 2:5p _{Kp} 2:5p _{L3} 1:5s _{L2} (r-sum=10)	160	34751	–7.500 776 570 586	0.000 072
183	3:6d _{Kd} 2:5p _{Kp} 2:5p _{L3} 1:5s _{L2} r ₁₂ (r-sum=10)	160	34911	–7.500 776 572 057	0.001 471
184	3:6d _{Kd} 2:5p _{Kp} 2:5p _{L3} 1:5s _{L2} r ₁₃ (r-sum=8)	67	34978	–7.500 776 572 497	0.000 440
185	3:6d _{Kd} 2:5p _{Kp} 2:5p _{L3} 1:5s _{L2} r ₁₄ (r-sum=8)	67	35045	–7.500 776 572 918	0.000 421
186	3:6d _{Kd} 1:5s _K 2:5p _{L3} 2:5p _{L4} (r-sum=10)	160	35205	–7.500 776 573 341	0.000 423
187	3:6d _{Kd} 1:5s _K 2:5p _{L3} 2:5p _{L4} r ₁₃ (r-sum=8)	67	35272	–7.500 776 573 858	0.000 515
188	3:6d _{Kd} 1:5s _K 2:5p _{L3} 2:5p _{L4} r ₁₄ (r-sum=8)	67	35339	–7.500 776 574 138	0.000 280
189	2:5p _{Kp} 3:6d _{Kd} 2:5p _{L3} 1:5s _{L2} (r-sum=10)	160	35499	–7.500 776 574 434	0.000 296
190	2:5p _{Kp} 3:6d _{Kd} 2:5p _{L3} 1:5s _{L2} r ₁₂ (r-sum=10)	160	35659	–7.500 776 574 727	0.000 293
191	1:5s _K 2:5p _{Kp} 3:6d _{L5} 2:5p _{L4} (r-sum=10)	160	35819	–7.500 776 575 021	0.000 294
192	3:6d _{Kd} 3:6d _{Kd} 3:6d _{L5} 3:6d _{L6} r ₁₂ (r-sum=12)	43	35862	–7.500 776 575 793	0.000 772
193	3:6d _{Kd} 3:6d _{Kd} 3:6d _{L5} 3:6d _{L6} r ₃₄ (r-sum=12)	43	35905	–7.500 776 576 815	0.001 022
194	3:6d _{1Kd} 3:6d _{1Kd} 3:6d _{1L5} 3:6d _{1L6} (r-sum=12)	43	35948	–7.500 776 578 251	0.001 436
195	3:6d _{1Kd} 3:6d _{1Kd} 3:6d _{1L5} 3:6d _{1L6} r ₁₂ (r-sum=12)	43	35991	–7.500 776 580 555	0.002 304
196	3:6d _{1Kd} 3:6d _{1Kd} 3:6d _{1L5} 3:6d _{1L6} r ₃₄ (r-sum=12)	43	36034	–7.500 776 583 209	0.002 654
197–199	3:6d _{Kd} 3:6d _{Kd} 1:5s _{L1} 3:6d _{L6} R ₁ (r-sum=12)	300	36334	–7.500 776 585 437	0.002 228
200	2:5p _{Kp} 2:5p _{Kp} 4:7f _{L7} 4:7f _{L8} (r-sum=14)	93	36427	–7.500 776 585 719	0.000 282
201	2:5p _{Kp} 2:5p _{Kp} 4:7f _{L7} 4:7f _{L8} r ₁₂ (r-sum=14)	93	36520	–7.500 776 586 639	0.000 920
202	2:5p _{Kp} 2:5p _{Kp} 4:7f _{L7} 4:7f _{L8} r ₃₄ (r-sum=14)	93	36613	–7.500 776 586 934	0.000 295
203	2:5p _{1Kp} 2:5p _{1Kp} 4:7f _{1L7} 4:7f _{1L8} (r-sum=14)	93	36706	–7.500 776 587 749	0.000 815
204	2:5p _{1Kp} 2:5p _{1Kp} 4:7f _{1L7} 4:7f _{1L8} r ₁₂ (r-sum=14)	93	36799	–7.500 776 590 740	0.002 991
205	4:7f _{Kr} 4:7f _{Kr} 2:5p _{L3} 2:5p _{L4} r ₁₂ (r-sum=14)	93	36892	–7.500 776 591 011	0.000 271
206	4:7f _{Kr} 4:7f _{Kr} 2:5p _{L3} 2:5p _{L4} r ₃₄ (r-sum=14)	93	36985	–7.500 776 591 288	0.000 277
207	4:7f _{1Kr} 4:7f _{1Kr} 2:5p _{1L3} 2:5p _{1L4} (r-sum=14)	93	37078	–7.500 776 591 689	0.000 401
208	4:7f _{1Kr} 4:7f _{1Kr} 2:5p _{1L3} 2:5p _{1L4} r ₃₄ (r-sum=14)	93	37171	–7.500 776 591 966	0.000 277
209	3:6d _{Kd} 1:5s _K 2:5p _{L3} 4:7f _{L8} (r-sum=12)	160	37331	–7.500 776 592 880	0.000 914
210	3:6d _{Kd} 1:5s _K 2:5p _{L3} 4:7f _{L8} r ₁₂ (r-sum=12)	160	37491	–7.500 776 593 372	0.000 492
211	3:6d _{Kd} 1:5s _K 2:5p _{L3} 4:7f _{L8} r ₁₄ (r-sum=12)	160	37651	–7.500 776 593 676	0.000 304
212	4:7f _{Kr} 3:6d _{Kd} 2:5p _{L3} 1:5s _{L2} r ₁₂ (r-sum=12)	160	37811	–7.500 776 593 886	0.000 210
213	4:7f _{Kr} 3:6d _{Kd} 2:5p _{L3} 1:5s _{L2} r ₁₃ (r-sum=12)	160	37971	–7.500 776 594 414	0.000 528
214	3:6d _{Kd} 4:7f _{Kr} 2:5p _{L3} 1:5s _{L2} r ₁₂ (r-sum=12)	160	38131	–7.500 776 594 808	0.000 394
215–216	4:7f _{Kr} 3:6d _{Kd} 1:5s _{L1} 2:5p _{L4} R ₂ (r-sum=12)	320	38451	–7.500 776 595 580	0.000 772
217–219	2:5p _{Kp} 4:7f _{Kr} 3:6d _{L5} 1:5s _{L2} R ₁ (r-sum=12)	480	38931	–7.500 776 596 297	0.000 717

¹K shell orbital exponents are $K = 2.739$, $K_1 = 7.50$, $K_p = 3.323$, $K_d = 3.690$, $K_f = 4.00$.

2L shell orbital exponents are $L_1 = 0.83$, $L_2 = 0.575$, $L_3 = 1.0175$, $L_4 = 0.786$, $L_5 = 1.383$, $L_6 = 1.152$, $L_7 = 1.580$, $L_8 = 1.350$.

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Table II

Comparison of theoretical Li^- ground state non-relativistic energies (in hartrees). All energies are variational.

Technique	Author	N	Energy(E) in hartrees
Hylleraas	King, Quicker, and Langer (2009) [14]	200	-7.500 40
CI	Chung and Fullbright (1992) [24]	729	-7.500 529 8
MCHF	Froese Fischer (1993) [25]	2997	-7.500 577 455
ECG	Pachucki and Komasa (2006) [26]	4200	-7.500 776 444
Hy-CI	This work s,p,d,f basis	38,931	-7.500 776 596 3
ECG	Stanke, et al. (2007) [12]	7,000	-7.500 776 601 2
ECG	Bubin, et al. (2009) [13]	10,000	-7.500 776 613 4

Table III

Convergence of the $r_{12} r_{34}$ double cusp with a superposition of normal Hy-CI term types.

Block	Energy(E) in nh	Block	Energy(E) in nh
$(ss)_K r_{12} (ss)_L$	33,196,642	$(ss)_K (ss)_L r_{34}$	12,078,592
$(ss)_K r_{12} (pp)_L$	405,077	$(pp)_K (ss)_L r_{34}$	1,896,803
$(ss)_K r_{12} (dd)_L$	210	$(dd)_K (ss)_L r_{34}$	513
$(ss)_K r_{12} (ff)_L$	38	$(ff)_K (ss)_L r_{34}$	3
$(pp)_K r_{12} (ss)_L$	16,281	$(ss)_K (pp)_L r_{34}$	1,634
$(pp)_K r_{12} (pp)_L$	5,787	$(pp)_K (pp)_L r_{34}$	4,735
$(pp)_K r_{12} (dd)_L$	39	$(dd)_K (pp)_L r_{34}$	4
$(pp)_K r_{12} (ff)_L$	4	$(ff)_K (pp)_L r_{34}$	1
$(dd)_K r_{12} (ss)_L$	30	$(ss)_K (dd)_L r_{34}$	4
$(dd)_K r_{12} (pp)_L$	3	$(pp)_K (dd)_L r_{34}$	14
$(dd)_K r_{12} (dd)_L$	3	$(dd)_K (dd)_L r_{34}$	4
$(dd)_K r_{12} (ff)_L$	0	$(ff)_K (dd)_L r_{34}$	0
$(ff)_K r_{12} (ss)_L$	10	$(ss)_K (ff)_L r_{34}$	1
$(ff)_K r_{12} (pp)_L$	0	$(pp)_K (ff)_L r_{34}$	0

Table IV

Energy improvements for $(ss)_K r_{12} (ll)_L$ blocks (nh).

Block	l	Predicted	Computed
$(ss)_K r_{12} (dd)_L$	2	210	210
$(ss)_K r_{12} (ff)_L$	3	42	38
$(ss)_K r_{12} (gg)_L$	4	13.3	
$(ss)_K r_{12} (hh)_L$	5	5.4	
$(ss)_K r_{12} (ii)_L$	6	2.6	
$(ss)_K r_{12} (kk)_L$	7	1.4	