Hylleraas-configuration-interaction study of the $2\,^2S$ ground state of neutral lithium and the first five excited $2\,^S$ states

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High-precision Hylleraas-configuration-interaction (Hy-CI) method variational calculations are reported for the $2\,^2S$ ground state of neutral lithium. The nonrelativistic energy is calculated to be $-7.478\,060\,323\,452$ hartree, demonstrating that the Hy-CI technique is capable of sub-nanohartree accuracy for three-electron systems. A Hylleraas expansion without linked products of odd powers of $r_{ij}$ gives $-7.478\,060\,323\,452$ hartree, showing the relative unimportance of such terms for lithium at the nanohartree level of accuracy. Hy-CI calculations are also reported for the $3\,^2S$, $4\,^2\Sigma$, $5\,^2\Sigma$, $6\,^2\Sigma$, and $7\,^2\Sigma$ lithium excited states.

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I. INTRODUCTION

Hylleraas-configuration-interaction (Hy-CI) [1] attempts to speed up the convergence of configuration interaction (CI) by directly introducing a correlation factor $r_{mn}^{-\nu}$ odd, into the wave function. In Hy-CI a wave function is constructed as a linear combination of so-called configuration state functions (CSFs),

$$\Psi = \sum_i c_i (\text{CSF})_i.$$  (1)

The CSFs are given by

$$(\text{CSF})_i = \sum_j d_{ij} A \left( r_{mn}^{ij} \prod_{k=1}^{N} \phi_{r_k}(k) \chi_{s_k}(k) \right),$$  (2)

where $A$ is the symmetry adaptation operator explained later [Eq. (4)], $N$ is the number of electrons, and $\phi_{r_k}(k)$ and $\chi_{s_k}(k)$ denote functions of the space and spin coordinates of the kth electron, respectively.

We have previously pointed out the close relationship between Hy-CI and Hylleraas (Hy) method calculations for two electrons [2]. For three electrons, the methods diverge and direct comparisons are not possible because products of $r_{mn}$ raised to odd powers (so-called odd-odd terms) may exist in Hy expansions but not in the corresponding Hy-CI expansions (Hy method even powers of $r_{mn}$ may be represented in Hy-CI by higher spherical harmonics in the basis set [2]). However, for three electrons there should still be a close relationship between the two methods provided the Hy expansion terms contain at most a single odd power of $r_{mn}$ in the $r_{mn}$ products [see Eq. (14)].

Therefore, one issue addressed here is whether linked terms [By linked products we mean $r_{mn}$ products with a common index, like $r_{iij}^{ij}$ or $r_{iij}^{ij}$. Unlinked terms (like $r_{iij}^{ij}$ or $r_{iij}^{ij}$ no common index) do not occur in Li.] like $r_{iij}^{ij}$ with odd-odd powers are necessary in Hy. This is an important point since it is the odd-odd $r_{mn}$ products that lead to some very difficult integrals and which are presumably the reason there have been no really accurate Hy calculations for atoms with more than three electrons. Pipin and Bishop [3] achieved microhartree accuracy in an Hy-CI calculation on lithium, showing that such terms are unimportant at the microhartree level of accuracy. Since odd-odd linked products are by definition excluded in Hy-CI, the accuracy obtainable in Hy-CI without them is also an issue. In this work we are able to achieve sub-nanohartree accuracy for the Li ground state using Hy-CI without such terms, and we further show that with the Hy method these factors are only important at the sub-nanohartree level of accuracy. We believe that in general, from an Hy perspective, the important linked products of $r_{ij}$ factors are those that have a single $r_{ij}$ factor to an odd power which can then easily be represented in the Hy-CI method by a single $r_{ij}$ factor times appropriate CI terms (CSFs). While we have demonstrated the unimportance of linked odd-odd products of $r_{ij}$, it remains to be seen how important unlinked products like $r_{i23}^{34}$ will turn out to be for systems with more than three electrons.

II. METHOD OF CALCULATION

For three electrons, the Hy-CI wave function we use is

$$\Psi_{Li} = \sum_K C_K \Phi_K,$$  (3)

where

$$\Phi_K = A \left[ r_{i1}^{ij} \prod_{s=1}^{3} \left\{ \phi_{r_s}(r_s) \right\} \Theta_K \right]$$
$$= O_{s} O_{LM_{Li}} O_{S,M_{S}} \left[ r_{i1}^{ij} \prod_{s=1}^{3} \left\{ \phi_{r_s}(r_s) \right\} \Theta_K \right]$$  (4)

denotes the $K_{sh}$ antisymmetrized spin and angular-momentum projected CSF. $O_{LM_{Li}}$ and $O_{S,M_{S}}$ are idempotent orbital and spin angular-momentum projection operators of the Löwdin type [4] for a state of total quantum numbers.
\( L, M_L, S, M_S \) [Russell-Saunders (LS) coupling is assumed]. \( \Theta_K \) is a primitive spin product function for term \( K \) and \( \phi_K(\mathbf{r}_s) \) represents the \( s \)th basis orbital in the \( K \)th term. The basis orbitals are taken to be un-normalized Slater-type orbitals. \( \mathcal{O}_{aa} \) is the idempotent antisymmetry projection operator. For three-electron doublet states there exist two linearly independent primitive spin functions \( \Theta_1 = \alpha \beta \alpha \) and \( \Theta_2 = \alpha \alpha \beta \). It is possible to converge on the exact wave function by employing only one primitive spin function, which for us is \( \Theta_1 = \alpha \beta \alpha \). Similar observations have been made by Larsen \( [5] \) for \( Li \). Cencek and Rychlewski \( [6] \) gave the general proof that only one primitive spin function is needed to ensure convergence of eigenvalues to the exact root of the Hamiltonian. As has been pointed out by King in his review article on \( Li \) \( [7] \), the second spin function can be important for computing precise values of properties other than the energy, such as hyperfine coupling constants \( [5,8-10] \) and spin-dependent expectation values like the Fermi contact term \( [5] \).

The wave function given by Eq. (3) is a linear combination of terms \( \Phi_K \), where the coefficients \( C_K \) are those which minimize the total energy, \( E \), given by

\[
E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \sum_{KL} C_K C_L H_{KL} + \sum_{KL} C_K C_L S_{KL},
\]

where

\[
H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle, \quad S_{KL} = \langle \Phi_K | \Phi_L \rangle.
\]

The nonrelativistic Hamiltonian \( \mathcal{H} \) is (in atomic units) \( [\text{the atomic unit of energy is chosen as } \mu e^4/\hbar^2 = 1 \text{ hartree, where } \mu = m_pm_n/(m_pm_n)] \)

\[
\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i + \sum_{i<j} r_{ij}^{-1}.
\]

\( \mathcal{H}_i = T_i + V_i \), where \( \mathcal{H}_i \) is a one-electron operator (electron \( i \)) consisting of a kinetic-energy part \( T_i = -1/2 \nabla_i^2 \) and a nuclear attraction part \( V_i = -Z/\mathbf{r}_i \). The condition for the energy to be an extremum, \( \delta E = 0 \), is the well-known matrix eigenvalue (secular) equation

\[
\sum_L H_{KL} C_L = \sum_L S_{KL} C_L.
\]

Solving this equation is equivalent to solving the \( N \)-dimensional generalized eigenvalue problem

\[
\mathbf{H} \mathbf{C} = \lambda \mathbf{S} \mathbf{C},
\]

where \( \mathbf{H} \) and \( \mathbf{S} \) have matrix elements \( H_{KL} \) and \( S_{KL} \) given by Eq. (6). Hence the coefficients \( C_K \) in Eq. (3) are found by solving the \( K_{max} \)-dimensional generalized eigenvalue problem using the familiar inverse iteration method. Quadruple precision and parallel processing were used throughout the calculation. We show in the appendix how we handle the antisymmetrization, spin, and angular-momentum projections involved in computing the Hamiltonian and overlap matrix elements.

III. RESULTS AND DISCUSSION

A. Hy-CI calculation of the \( 2^2S \) \( Li \) ground state

The CSFs given by Eq. (4) can be written as

\[
\Phi_K = \Lambda |F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\Theta_K|
\]

in terms of spatial and spin functions \( F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \) and \( \Theta_K \). In this work we use only the first spin function \( \Theta_K = \Theta_1 = \alpha \beta \alpha \) and the spatial part of the wave function \( F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \) is given by a particular choice of \( r_{ij} \) factor and Hartree orbital product

\[
F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_{ij}^\nu \prod_{s=1}^{3} (\phi_K(\mathbf{r}_s))
\]

where \( \nu_K \) is restricted, without loss of generality, to be either 0 or 1.

In Table I we list our best results for the lithium ground state at various levels of truncation, where we use different orbital exponents for \( s, p, d, \) and \( f \) orbitals, and we use different orbital exponents within each symmetry for \( K \) and \( L \) shell orbitals. In column five are shown the energy improvements for each CSF term type added. In column one are listed the basis orbitals that are used to generate the CSFs for each block type in the order electron 1 (\( \alpha \) spin), electron 2 (\( \beta \) spin), electron 3 (\( \alpha \) spin). For example, in the first line \( 1:9s_{K_1} \) means the basis orbitals are \( 1s_{K_1} \) through \( 9s_{K_1} \) orbitals \( (K_1 \) denotes an orbital exponent appropriate for a \( K \) shell electron). All of the listed basis orbitals are used to generate all of the CSFs that are unique for this basis set selection. The choice of terms is highly regular, there having been no attempt to cut down on the number of terms. The number of unique terms (CSFs) in a block can be easily computed from the listed basis orbitals. Since the orbital exponent for an \( L \) shell orbital is different from a \( K \) shell orbital and the \( K \) shell pair of electrons have different spins, the number of terms is just the product of the number of different orbitals for each electron times 4 (for \( 1, r_{12}, r_{13}, r_{23} \)). For example, for \( 1:9s_{K_1} 1:9s_{L_1} R \) there are nine \( s_{K_1} \) orbitals, nine \( s_{L_1} \) orbitals, and nine \( s_{L_1} \) orbitals, so the total number of CSF terms of type \( s_{K_1}, s_{K_1}, s_{L_1}, R \) becomes \( 9 \times 9 \times 9 \times 4 = 2916 \).

The wave function in Table I can be thought of in the following way. The first three term types are essentially an \( Li^+ \) core plus valence electron CI picture, with each orbital product multiplied by \( \{1, r_{12}, r_{13}, r_{23}\} \), what one might call an “explicitly correlated CI” picture. \( ffs \times R \) terms on the next to last line in the table completes this picture. The next four CSF blocks (after the first three) incorporate \( K-L \) shellshell CI correlation. Beyond this point CI is not much help in coming up with appropriate orbital products. For the remaining term types we use as our guide the expansion of likely important \( Hy \) \( r_{ij} \) products [see Eq. (14)] to see what types of Hy-CI terms arise. For example, consider the Hy term \( s_1 s_5 s_3 r_{12}^2 r_{13}^2 \) (only even power products need be considered). Since

\[
r_{ij}^2 = r_{ij}^2 + r_{ij}^2 - 2r_{ij} \cos \theta_{ij}
\]

and

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The expansion of $s_{12}s_{23} r_{12}^2 r_{13}^2$ gives rise to $sss$ terms, $psp$ terms, $pps$ terms, and $p(1)p(2)p^*(1)p^*(2)$ terms. Expanding this last term gives $ssp$ and $dpp$ terms. Similarly, $r_{12}^2 r_{23}^2$ gives rise to the new term $pdp$ and $ppd$ and $pdp$ products are obvious CI orbital promotions. Of course in the same way the earlier terms in Table I arise from suitable Hy terms, e.g., $r_{12}^4$ leads to $pps$, $r_{13}^4$ to $psp$, $r_{12}^2 r_{13}^2$ to $dds$, and so on. Indeed all orbital products have an Hy equivalent $r_{ij}$ product term. Of course all such orbital products are only candidate terms and must be tested individually for importance essentially by trial and error.

In our early calculations we did in fact overlook the $dppR$, $pdpR$, and $dppR$ terms, as did previous workers, yet were still able to get (surprisingly) within 10 nanohartree of nanohartree accuracy. After adding $ppdR$, $pdpR$, and $dppR$ terms we ran into another hard energy limit, preventing us from getting closer than 2 nanohartrees of nanohartree accuracy. The problem in this case turned out to be the absence of the $ddd$ and $(fpd, pfd, ...)$ term types shown in Table I. $ddd$ arises from the expansion of $r_{12}^4 r_{13}^2$ while $fpd$ comes from the expansion of $r_{12}^2 r_{13}^4$ and so on for the other permuted forms of $fpd$. As can be seen, maybe only two or three of the $fpdR$ term types are in fact needed. Finally, we added $fssR$ to acknowledge that $ff^*[1, r_{12}]$ is of importance in the description of the $Li^+$ ion at the nanohartree accuracy level. $fsfR$- and $sffR$-type terms were also tested and found not to be important. Also no instance of an orbital product including $g$ orbitals was found to be important, as for example, $ggSSR$. The last set of expansion terms in Table I introduces additional correlation into the $K$ shell in the amount of 0.836 nanohartree, indicating a less than perfect description of the $sssR$ part of the wave function. We attribute this to be a result of not having sufficient flexibility in the $s$-orbital basis sets, arising from the limit of just eight orbital exponents permitted for all orbitals, this limit imposed by a not easily remedied problem in the integral codes.

Orbital exponent optimization was rather carefully done at the $N=10$ 044 expansion level by hand (no analytical derivatives). The $sK$ orbital exponent splitting shown gained only 1 nanohartree. Due to limitations in the integral codes it was not possible to give every orbital type its own orbital exponent. Although with our sequential codes we could work around this problem, it was not practicable to implement similar changes in our parallel codes without major changes to the code itself. In a purely practical sense this was not a serious problem since the dependence of the final energy on the orbital exponents turned out to be very flat. As has been pointed out by Pulchalski and Pachucki [12] and Yan, Nörthershüser, and Drake [13], the number and choice of the nonlinear parameters is very important at the nanohartree level. This is true for both the Hy method and Hy-CI.

At this point we decided to call a halt to the $2\frac{1}{2}S$ calculations, having reached our goal of sub-nanohartree accuracy, because to do substantially better would involve substantial
TABLE II. Comparison of theoretical Li ground-state nonrelativistic energies (in hartrees).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Author</th>
<th>No. of terms</th>
<th>Energy (E) in hartrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF\textsuperscript{a}</td>
<td>Tong, Jönsson, and Fischer (1993) \cite{14}</td>
<td></td>
<td>−7.477 968 61</td>
</tr>
<tr>
<td>CI</td>
<td>Jitrik and Bunge (1997) \cite{15}</td>
<td>≤13</td>
<td>−7.478 025 4</td>
</tr>
<tr>
<td>Hy</td>
<td>King and Bergsbaken (1990) \cite{16}</td>
<td>296</td>
<td>−7.478 059 53</td>
</tr>
<tr>
<td>Hy-CI</td>
<td>This work, s,p r\text{ij} basis</td>
<td>8316</td>
<td>−7.478 059 573 327</td>
</tr>
<tr>
<td>Hy-CI</td>
<td>Pestka and Wożniicki (1996) \cite{17}</td>
<td>386</td>
<td>−7.478 060 1</td>
</tr>
<tr>
<td>Hy-CI</td>
<td>Pipin and Bishop (1992) \cite{3}</td>
<td>1618</td>
<td>−7.478 060 1</td>
</tr>
<tr>
<td>Hy</td>
<td>Lüchow and Kleindienst (1994) \cite{18}</td>
<td>1420</td>
<td>−7.478 060 320 8</td>
</tr>
<tr>
<td>Hy-CI</td>
<td>This work, s,p,d r\text{ij} basis</td>
<td>14364</td>
<td>−7.478 060 321 379</td>
</tr>
<tr>
<td>ECG\textsuperscript{b}</td>
<td>Pulchalski and Komasa (2006) \cite{19}</td>
<td>7000</td>
<td>−7.478 060 323 2</td>
</tr>
<tr>
<td>ECG-CI</td>
<td>This work, s,p,d,f r\text{ij} basis</td>
<td>16764</td>
<td>−7.478 060 323 451 9</td>
</tr>
<tr>
<td>Hy</td>
<td>Yan, Tambasco, and Drake (1998) \cite{20}</td>
<td>3502</td>
<td>−7.478 060 323 452</td>
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<tr>
<td>Hy</td>
<td>Pulchalski and Pachucki (2006) \cite{12}</td>
<td>9576</td>
<td>−7.478 060 323 899 7</td>
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<tr>
<td>Hy</td>
<td>Yan, Nörtershäuser, and Drake (2008) \cite{13}</td>
<td>9577</td>
<td>−7.478 060 323 892 4</td>
</tr>
<tr>
<td>Hy</td>
<td>Pulchalski, Kedziera, and Pachucki (2009) \cite{11}</td>
<td>13944</td>
<td>−7.478 060 323 909 560</td>
</tr>
<tr>
<td>Hy</td>
<td>Pulchalski, Kedziera, and Pachucki (2009) \cite{11} Exact(est.)</td>
<td>−7.478 060 323 910 10(32)</td>
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</tbody>
</table>

\textsuperscript{a}Multiconfigurational self-consistent field.
\textsuperscript{b}Explicitly correlated Gaussianians.

modifications to our codes to accommodate more orbital exponents, analytical derivatives, and mechanisms for shortening the expansion, like putting a limit on the sum of the powers of r\text{ij} as was done in the Hy method work [recall that inverse iteration is an O(N\textsuperscript{3}) process].

In Table II we compare our results with previous Li ground-state calculations. We have added two results to the table to facilitate this comparison. One is an s,p r\text{ij} energy of E(8316) = −7.478 059 573 327 hartree obtained using term types 1,2,4,5, and 19 in Table I. Notice that microhartree accuracy is achievable with just s and p orbitals. For comparison, Pestka and Wożniicki \cite{17} required a basis of s, p, d, and f and powers of r\text{ij} from 3 to get −7.478 060 1 hartree. Pipin and Bishop \cite{3} reported significant contributions from ffs and ggs, but we believe this just reflects an inadequate ss-, pp-, and dd-product basis.

The second result entered into Table II is an s,p,d r\text{ij} energy limit obtained terms 1–11 and 19 from Table I which gave an energy of E(14 364) = −7.478 060 321 379 hartree, no r\text{ij} powers higher than the first power. Adding f orbitals we obtained an s,p,d,f r\text{ij} energy of E(16 764) = −7.478 060 323 451 9 hartree. This is slightly better than the explicitly correlated Gaussian (ECG) result of Pulchucki and Komasa \cite{19} and better than all but the most accurate Hy calculations of Pulchalski and Pachucki \cite{12}, Yan, Nörtershäuser, and Drake \cite{13}, and Pulchalski, Kedziera, and Pachucki \cite{11}, coming to within 0.56 nanohartree of the estimated exact energy of Li.

B. Hy calculation of the 2\textsuperscript{3}S Li ground state

Next we used the code of Pulchalski and Pachucki \cite{12} to determine the importance of odd-odd and odd-odd-odd power r\text{ij}F\text{jk} and r\text{ij}F\text{jk}r\text{kl} terms as these are the only ones for which there is no correspondence with Hy-CI terms. The Pulchalski and Pachucki method of generating their wave functions is the multiple basis set method originally developed by Yan and Drake \cite{21}. The key idea is to start with a fully correlated Hy variational basis set of the form

\[ r_{23}^{n_1} r_{45}^{n_2} r_{12}^{n_3} r_{34}^{n_4} r_{56}^{n_6} e^{-a_1 r_{12} - b_{23} r_{23} - c_{34} r_{34}} \chi_1, \]

where \( \chi_1 \) is a spin function with spin angular momentum 1/2. The basis set is then replicated several times with different nonlinear scale parameters a, b, and c, with the scale parameters fully optimized for each sector. For the analysis given here, we used the 9576 term basis set of Pulchalski and Pachucki \cite{12}. The basis is divided up into five sectors as follows:

1. all \( n_3, n_1 = 0, n_2 = 0 \);
2. all \( n_3, n_1 = 0, n_2 \neq 0 \);
3. all \( n_3, n_1 \neq 0, n_2 = 0 \);
4. all \( n_3 = 0, n_1 \neq 0, n_2 \neq 0 \);
5. all \( n_3 \neq 0, n_1 \neq 0, n_2 \neq 0 \).

Table III gives the results of dropping odd-odd and odd-odd-odd terms where, in the table, \( N \) is the cumulative number of terms, and \( N' \) is the number of terms surviving after odd-odd and odd-odd-odd terms have been eliminated. Hence the \( N' \) column is the N-column wave function filtered to contain only at most a single odd r\text{ij} power.

The most striking observation [fifth line in the table, E(6170) vs E(9576)] is that products of odd powers of r\text{ij} contribute only at the sub-nanohartree level for accurate wave functions [E(6170) is E(9576) with odd-odd and odd-odd-odd r\text{ij} products removed].

We also did runs with only one odd r\text{ij} power and the maximum r\text{ij} power in any term restricted to 6 and then 5. The results are also tabulated in Table III.
Note that one does not need to go beyond $r_{ij}^3$ to achieve sub-nanohartree accuracy for lithium in Hy calculations, and since $r_{ij}^3$ in Hy-CI corresponds to $ddr_{ij}$, one doesn’t need $ffsr_{ij}$ in Hy-CI until one reaches the nanohartree level of accuracy. This agrees perfectly with what we showed in Sec. III A.

### C. Excited states

Following King [22], we calculate energies for the $^32S$, $^42S$, $^52S$, $^62S$, $^72S$ states of the lithium atom. The $^32S$ state provided another valuable test of the Hy-CI method as there exists an accurate Hy energy value [23] to compare with. As Table IV shows, selection of expansion terms for this state mirrors those for the ground $2^2S$ state except that we dropped the pdf term types (which contribute only at the sub-nanohartree level). We use more $L$-shell orbitals (the $K$-shell ionic core should be similar to the ground $2^2S$ state, but the $L$-shell orbitals should reflect the higher, more energetic state). The last two lines in Table IV suggest we have as many as are required for this state. $ffs*R$ and $s_{Ks}^3s_{Kd}s_{Ls}*R$ terms contribute like they do for the $2^2S$ state, indicating that these are truly $K$-shell core effects. As in the case of the $2^2S$ state, here and for the higher states we make no attempt to filter or otherwise weed out unimportant terms. Note that the $3^2S$ state is within 0.494 nanohartree of the Pulchalski, Kedziera, and Pachucki [23] calculation, demonstrating that Hy-CI can achieve sub-nanohartree accuracy for Li excited states as well as the ground state.

Table V shows energies for various truncations of the wave function for the remaining excited states. We have dropped $ddd*R$ (since it contributes only 0.5 nanohartree for the $3^2S$ state) and have changed the basis set description for the $L$ shell to hopefully be more flexible (we use two different $Ls$ orbital exponents) for these even more diffuse states. As one might expect, the importance of $7sLs$ and $5sLs$ increases as we go to higher excited states. The contributions of the various term types scale inversely roughly with the excited electron principle quantum number with some irregularities due probably to the less than perfect optimization of the orbital exponents in the $K$ shell. The improvement of our results over the previously best calculations of King [22] is consistent until one reaches the $6^2S$ state, where we are about 128 nanohartree better. For the $7s$ state it is evident from the contributions of the last two term types that the $sss*R$ part needs some further work, the wave function not being sufficiently flexible for this highly excited state (a change over to hydrogen-like orbitals is probably called for as the excited electron becomes more Rydberg-like). Despite

<table>
<thead>
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<th>Section</th>
<th>$N$</th>
<th>$E(N)$ in hartrees</th>
<th>$N'$</th>
<th>$E(N')$ in hartrees</th>
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<tr>
<td>1</td>
<td>1036</td>
<td>−7.476 983 290 850</td>
<td>1036</td>
<td>−7.476 983 290 850</td>
</tr>
<tr>
<td>1–2</td>
<td>3222</td>
<td>−7.478 060 320 124</td>
<td>2696</td>
<td>−7.478 060 305 902</td>
</tr>
<tr>
<td>1–3</td>
<td>5404</td>
<td>−7.478 060 323 278</td>
<td>4340</td>
<td>−7.478 060 321 990</td>
</tr>
<tr>
<td>1–4</td>
<td>6951</td>
<td>−7.478 063 233 29</td>
<td>5327</td>
<td>−7.478 060 322 893</td>
</tr>
<tr>
<td>1–5</td>
<td>9576</td>
<td>−7.478 060 323 889</td>
<td>6170</td>
<td>−7.478 060 323 452</td>
</tr>
<tr>
<td>1–6</td>
<td>5740</td>
<td>−7.478 060 323 438</td>
<td></td>
<td></td>
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<tr>
<td>1–5, $\nu_{max}=5$</td>
<td>5124</td>
<td>−7.478 060 322 122</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Yan, Nütershäuser, and Drake (2008) [13].

these deficiencies, Table VI (which gives a comparison of our excited-state results with previous theoretical work) shows that our 4 $^2S$, 5 $^2S$, 6 $^2S$, and 7 $^2S$ state results improve substantially upon previously published work. Included in the table are our best estimates of the exact energies of these states. These estimates are in line with the sensitivity analysis for the $ssss$ part of the wave function, which is probably where most of the error lines. The error in the 7 $^2S$ state is somewhat bigger due to the inadequate valence shell basis discussed above.

IV. CONCLUSION

In this work we have demonstrated the ability of Hy-CI calculations to achieve sub-nanohartree accuracy for lithium. We have also demonstrated that Hy calculations can achieve sub-nanohartree accuracy for three-electron systems using only a single odd $r_{ij}$ in any term in the wave function, showing the relative unimportance of linked products of odd $r_{ij}$ in the Hy method at the nanohartree level of accuracy. These calculations suggest that Hy-CI should also be capable of achieving sub-nanohartree accuracy for three-electron systems, and we have demonstrated that in these calculations. While we have shown the relative unimportance of linked products of $r_{ij}$ for on the order of less than nanohartree accuracy, it remains to be seen how important unlinked products like $r_{ij}^2s_{3s}$ will turn out to be for systems with more than three electrons. We intend to explore this point in a future publication. We have also shown how to pick expansion terms in an Hy-CI calculation both from CI considerations and by using the expansion of likely Hy $r_{ij}$ products as a guide. Finally, we point out that there still is room for a more systematic effort to determine a really accurate Hy-CI value for Li and its excited states (including $P$ and $D$) now that we understand the problem in the Hy-CI context.

ACKNOWLEDGMENTS

We are deeply indebted to Krzysztof Pachucki for making his Hylleraas code available to us, without which we would not have been able to do the Hy calculations reported in this paper. We also thank Arne Lüchow for kindly informing us of the activities of the late Professor H. Kleindienst’s group and Maria Belen Ruiz for filling us in on the work of Professor J. Rychlewski’s group and also of some of Jacek Komasa’s work.

APPENDIX: PROJECTION REDUCTION

Using Eq. (4), matrix element $H_{k\ell}$ becomes

$$H_{k\ell} = \langle \Phi_k^\prime | \mathcal{H} | \Phi_\ell \rangle = (\Delta \Phi_k^\prime | \mathcal{H} | \Delta \Phi_\ell^\prime),$$ (A1)

where $\Phi_k^\prime$ denotes the $k$th primitive (unprojected) function $r_{ij}^2\prod_{\alpha=1}^{6}(\phi_k(r_{\alpha}))\Theta_k$. $S_{k\ell}$ is similar, with $\mathcal{H}$ replaced by the unit operator $I$. Now notice that

TABLE V. Energies (in hartrees) for various truncations of the wave function of the 4–7 $^2S$ excited states of lithium. In the table $R=\{1, r_{12}, r_{13}, r_{23}\}$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>Terms added</th>
<th>$4 \ ^2S$ $^{a,b}$</th>
<th>$5 \ ^2S$ $^{c,d}$</th>
<th>$6 \ ^2S$ $^{e,f}$</th>
<th>$7 \ ^2S$ $^{g,h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>1:10$s_{Ks}$, 1:10$g_{Ks}$ ${1:6s_{Ls}, 1:4s_{Ls}}$ $R$</td>
<td>7.318 144 893 422</td>
<td>-7.303 167 312 632</td>
<td>-7.295 475 782 289</td>
<td>-7.291 010 447 021</td>
</tr>
<tr>
<td>7240</td>
<td>2:10$p_{Kp}$, 2:10$p_{Kp}$ ${1:6s_{Ls}, 1:4s_{Ls}}$ $R$</td>
<td>7.318 530 329 869</td>
<td>-7.303 550 963 613</td>
<td>-7.295 858 767 247</td>
<td>-7.291 393 343 377</td>
</tr>
<tr>
<td>9200</td>
<td>3:9$g_{Kg}$, 3:9$g_{Kg}$ ${1:6s_{Ls}, 1:4s_{Ls}}$ $R$</td>
<td>7.318 530 775 712</td>
<td>-7.303 551 347 519</td>
<td>-7.295 859 122 525</td>
<td>-7.291 391 712 630</td>
</tr>
<tr>
<td>11216</td>
<td>1:7$s_{Ks}$, 2:7$p_{Kp}$, 2:7$p_{Kp}$</td>
<td>7.318 530 835 014</td>
<td>-7.303 551 568 082</td>
<td>-7.295 859 494 639</td>
<td>-7.291 392 239 327</td>
</tr>
<tr>
<td>12080</td>
<td>3:8$d_{Kd}$, 1:6$s_{Ks}$, 3:8$d_{Kd}$</td>
<td>7.318 530 835 967</td>
<td>-7.303 551 569 884</td>
<td>-7.295 859 500 882</td>
<td>-7.291 392 257 397</td>
</tr>
<tr>
<td>12944</td>
<td>1:6$s_{Ks}$, 3:8$d_{Kd}$, 3:8$d_{Kd}$</td>
<td>7.318 530 856 739</td>
<td>-7.303 551 571 169</td>
<td>-7.295 859 503 301</td>
<td>-7.291 392 262 718</td>
</tr>
<tr>
<td>15408</td>
<td>4:8$s_{Ks}$, 4:8$s_{Ks}$</td>
<td>7.318 530 843 884</td>
<td>-7.303 551 576 190</td>
<td>-7.295 859 507 594</td>
<td>-7.291 392 266 942</td>
</tr>
<tr>
<td>16272</td>
<td>1:6$s_{Ks}$, 1:6$s_{Ks}$, 1:6$s_{Ks}$</td>
<td>7.318 530 845 168</td>
<td>-7.303 551 577 933</td>
<td>-7.295 859 509 441</td>
<td>-7.291 392 268 343</td>
</tr>
<tr>
<td>16672</td>
<td>1:10$s_{Ks}$, 1:10$s_{Ks}$, 7:7$s_{Ls}$</td>
<td>7.318 530 845 287</td>
<td>-7.303 551 578 188</td>
<td>-7.295 859 509 733</td>
<td>-7.291 392 272 268</td>
</tr>
<tr>
<td>17072</td>
<td>1:10$s_{Ks}$, 1:10$s_{Ks}$, 5:5$s_{Ls}$</td>
<td>7.318 530 845 331</td>
<td>-7.303 551 578 291</td>
<td>-7.295 859 509 943</td>
<td>-7.291 392 273 116</td>
</tr>
</tbody>
</table>

$^a$K-shell orbital exponents are $Ks=3.50$, $Kt=2.70$, $Kp=4.40$, $Kq=5.80$, and $Kd=4.65$.

$^b$L-shell orbital exponents are $Ls=0.33$, $La=0.75$, and $Lp=0.55$.

$^c$K-shell orbital exponents are $Ks=3.50$, $Kt=2.70$, $Kp=4.40$, $Kq=5.80$, and $Kd=4.65$.

$^d$L-shell orbital exponents are $Ls=0.25$, $La=0.37$, and $Lp=0.53$.

$^e$K-shell orbital exponents are $Ks=3.50$, $Kt=2.70$, $Kp=4.40$, $Kq=5.80$, and $Kd=4.65$.

$^f$L-shell orbital exponents are $Ls=0.18$, $La=0.30$, and $Lp=0.53$.

$^g$K-shell orbital exponents are $Ks=4.00$, $Kt=3.60$, $Kp=4.30$, $Kq=5.80$, and $Kd=4.65$.

$^h$L-shell orbital exponents are $Ls=0.14$, $La=0.28$, and $Lp=0.53$. 

052507-6
Using the quantum-mechanical "turnover rule" write
\[ \Lambda \Phi_K^P = O_{LM} O_{ai} O_{iM} g_k f_k \Theta_1, \]
where \( g_k = r_{ij}^k \) and \( f_k \) is the hartree product \( \Pi_i \phi_k (\mathbf{r}_i) \). Using the quantum-mechanical "turnover rule" [33], the

\( N^1 O_{ai} = \sum_p (-1)^p P = \left( \sum_a (-1)^a p^a \right) \left( \sum_v (-1)^v p^v \right) \)
\[ + \sum_{\gamma} (-1)^{p_{\gamma}} = A^a A^{\beta} + A^{\alpha \beta} \] (A2)

where \( N \) is the number of electrons, \( P^a \) refers to those permutations which permute only \( \alpha \) spins, \( P^\beta \) refers to those permutations which permute only \( \beta \) spins, and \( P^{\alpha \beta} \) refers to only those permutations which permute an \( \alpha \) spin and a \( \beta \) spin. If we rewrite the bra and ket functions in Eq. (A1) in terms of a single spin function, the \( H_{KL} \) matrix element will end up involving only \( A^a A^{\beta} \) since permutations between \( \alpha \) and \( \beta \) give zero results when integrating over spin.

In our case \( \Theta_K = \Theta_{LM} = \Theta_1 = \alpha(1) \beta(2) \alpha(3) = \alpha \beta \alpha \), so we can write

\( \\Lambda \Phi_K^P = O_{LM} O_{ai} O_{iM} g_k f_k \Theta_1, \)
commutivity of \( \Lambda \) and \( \mathcal{H} \), and the idempotency condition
\( \Lambda^3 \Lambda = \Lambda \), \( H_{KL} \) reduces to
\[
H_{KL} = \langle \Phi^p_{Kl} | \mathcal{H} | \Lambda \Phi^p_L \rangle. \tag{A4}
\]

Projecting on \( \Theta_1 \) with the Löwdin spin projection operator
\([4] \) \( O_{S,M_{S}}(S=1/2, M_{S}=1/2) \), we get
\[
O_{S,M_{S}} \Theta_1 = O_{S,M_{S}} \alpha \beta = \frac{2}{3} \alpha \beta - \frac{1}{3} \beta \alpha - \frac{1}{3} \alpha \beta \tag{A5}
\]
where the subscripts (not shown) on the \( \alpha \) and \( \beta \) are always
in the order 1,2,3.

This can be written
\[
O_{S,M_{S}} \Theta_1 = \left[ \frac{2}{3} - \frac{1}{3} P_{12} + \frac{1}{3} P_{23} \right] \Theta_1. \tag{A6}
\]

Using the identity
\[
O_{as} = (-1)^{P} O_{as} (P P_{as})^{-1}, \tag{A7}
\]
\( H_{KL} \) becomes
\[
H_{KL} = \langle g_{KfL} | \mathcal{H} | O_{L,M_L} O_{as} \left[ \frac{2}{3} + \frac{1}{3} P_{12} + \frac{1}{3} P_{23} \right] g_{LfL} \Theta_1 \rangle. \tag{A8}
\]

Now we can integrate over spin, effectively removing spin
from the matrix element:

\[
H_{KL} = \langle g_{KfL} | \mathcal{H} | A^a A^b O_{L,M_L} B(g_{LfL}) \rangle. \tag{A9}
\]

We have used the fact that \( O_{L,M_L} \) commutes with \( O_{as} \) in the
above equation. Here the “reduced” antisymmetrizer \( A^a A^b \)
\[
A^a A^b = (1 - P_{13}) \tag{A10}
\]
and
\[
B = \frac{2}{3} + \frac{1}{3} P_{12} + \frac{1}{3} P_{23} \tag{A11}
\]
operate on the spatial coordinates. \( r \) has been dropped from
the terms in \( B \) since only spatial coordinates remain.

Using Eq. \( (A10) \), we obtain for our final expression for \( H_{KL} \)
\[
H_{KL} = \langle g_{KfL} | \mathcal{H} | (1 - P_{13}) O_{L,M_L} B(g_{LfL}) \rangle. \tag{A12}
\]

In Eq. \( (A12) \) one can apply \( O_{L,M_L} \) either before or after
applying \( B \). We first apply the permutations \( B \) to \( g_{LfL} \), then we
project on the resulting terms with \( O_{L,M_L} \). In doing the \( O_{L,M_L} \)
projection, we use the fact that \( g_{L} = r_{as}^{P} \) commutes with \( O_{L,M_L} \)
\([1,3,4]\) and only apply \( O_{L,M_L} \) to the orbital products.

Depending on the structure of \( g_{LfL} \), \( (1 - P_{13}) B(g_{LfL}) \) may
further simplify, and this should be checked before application of
\( O_{L,M_L} \) (we in fact do this in working out the right-hand
side of \( H \)). In practice we routinely swap the bra and
kets if doing so will reduce the number of terms resulting from
Eq. \( (A12) \).

\[\text{[8] F. W. King and V. Shoup, Phys. Rev. A 33, 2940 (1986).}\]