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Hylleraas-configuration-interaction study of the 2 ^2S ground state of neutral lithium and the first five excited ^2S 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 −7.478 060 323 451 9 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 ^2S, 5 ^2S, 6 ^2S, and 7 ^2S 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}^{ν}, ν odd, into the wave function. In Hy-CI a wave function is constructed as a linear combination of so-called configuration state functions (CSFs),

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

The CSFs are given by

$$(\mathrm{CSF})_i = \sum_j d_{ij}\Lambda\left(r_{mn}^{\nu_i} \prod_{k=1}^{N} \phi_{j_k}(k)\chi_{j_k}(k) \right), \tag{2}$$

where Λ is the symmetry adaptation operator explained later [Eq. (4)], N is the number of electrons, and $\phi_{j_k}(k)$ and $\chi_{j_k}(k)$ 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 $r_{ij}^m r_{ik}^n$. Unlinked terms (like $r_{ij}^m r_{kl}^n$, no common index) do not occur in Li.] like $r_{12}^m r_{13}^n$ *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 $r_{12}r_{34}$ 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

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

where

$$\begin{aligned}\Phi_K &= \Lambda\left[r_{ij}^{\nu_K} \prod_{s=1}^{3} \{\phi_{K_s}(\mathbf{r_s})\}\Theta_K \right] \\ &= O_{as} O_{L,M_L} O_{S,M_S}\left[r_{ij}^{\nu_K} \prod_{s=1}^{3} \{\phi_{K_s}(\mathbf{r_s})\}\Theta_K \right]\end{aligned} \tag{4}$$

denotes the K_{th} antisymmetrized spin and angular-momentum projected CSF. O_{L,M_L} 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

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L, M_L, S, M_S [Russell-Saunders (LS) coupling is assumed]. Θ_K is a primitive spin product function for term K and $\phi_{K_s}(\mathbf{r_s})$ represents the sth basis orbital in the Kth term. The basis orbitals are taken to be un-normalized Slater-type orbitals. O_{as} 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 Larsson [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 Φ_K, where the coefficients C_K are those which minimize the total energy, E, given by

$$E = \frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\Sigma_{KL} C_K C_L H_{KL}}{\Sigma_{KL} C_K C_L S_{KL}}, \tag{5}$$

where

$$H_{KL} = \langle\Phi_K|\mathcal{H}|\Phi_L\rangle; S_{KL} = \langle\Phi_K|\Phi_L\rangle. \tag{6}$$

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

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i + \sum_{i<j} r_{ij}^{-1}. \tag{7}$$

$\mathcal{H}_i=T_i+V_i$, 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 $V_i=-Z/r_i$. The condition for the energy to be an extremum, $\delta E=0$, is the well-known matrix eigenvalue (secular) equation

$$\sum_L H_{KL} C_L = \sum_L S_{KL} C_L. \tag{8}$$

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

$$\mathbf{HC} = \lambda\mathbf{SC}, \tag{9}$$

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

$$\Phi_K = \Lambda[F_K(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3})\Theta_K] \tag{10}$$

in terms of spatial and spin functions $F_K(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ and Θ_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

$$F_K(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3}) = r_{ij}^{\nu_K}\prod_{s=1}^{3}\{\phi_{Ks}(\mathbf{r_s})\} \tag{11}$$

where ν_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 (α spin), electron 2 (β spin), electron 3 (α spin). For example, in the first line $1{:}9s_{Ks}$ means the basis orbitals are $1s_{Ks}$ through $9s_{Ks}$ orbitals (Ks 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 $1{:}9s_{Ks}$ $1{:}9s_{Kt}$ $1{:}9s_{Ls}$ R there are nine s_{Ks} orbitals, nine s_{Kt} orbitals, and nine s_{Ls} orbitals, so the total number of CSF terms of type s_{Ks} s_{Kt} s_{Ls} R becomes $9*9*9*4=2916$.

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. $ffs*R$ 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 intershell 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 $s_1 s_2 s_3$ r_{12}^2 r_{13}^2 (only even power products need be considered). Since

$$r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos\theta_{ij} \tag{12}$$

and

TABLE I. Hy-CI calculations of the Li ground-state energy (in hartrees). In the table $R=\{1,r_{12},r_{13},r_{23}\}$, N is the number of terms added, and N_{tot} is the cumulative number of terms.

Terms added	N	N_{tot}	$E(N_{tot})$ in hartrees[a,b]	$-\Delta E$ in nanohartrees
$1{:}9s_{Ks}\ 1{:}9s_{Kt}\ 1{:}9s_{Ls}\ R$	2916	2916	−7.477 634 670 861	
$2{:}9p_{Kp}\ 2{:}9p_{Kp}\ 1{:}7s_{Ls}\ R$	1792	4708	−7.478 059 148 015	424477.
$3{:}8d_{Kd}\ 3{:}8d_{Kd}\ 1{:}6s_{L}\ R$	864	5572	−7.478 059 958 638	810.623
$2{:}8p_{Kp}\ 1{:}7s_{Kt}\ 2{:}8p_{Lp}\ R$	1372	6944	−7.478 060 162 571	203.933
$1{:}7s_{Ks}\ 2{:}8p_{Kp}\ 2{:}8p_{Lp}\ R$	1372	8316	−7.478 060 224 321	61.750
$3{:}8d_{Kd}\ 1{:}6s_{Kt}\ 3{:}8d_{Lp}\ R$	864	9180	−7.478 060 245 033	20.712
$1{:}6s_{Ks}\ 3{:}8d_{Kd}\ 3{:}8d_{Lp}\ R$	864	10044	−7.478 060 252 297	7.264
$2{:}7p_{Kp}\ 2{:}7p_{Kp}\ 3{:}8d_{Lp}\ R$	864	10908	−7.478 060 314 870	62.573
$2{:}7p_{Kp}\ 3{:}8d_{Kd}\ 2{:}7p_{Lp}\ R$	864	11772	−7.478 060 317 298	2.428
$3{:}8d_{Kd}\ 2{:}7p_{Kp}\ 2{:}7p_{Lp}\ R$	864	12636	−7.478 060 318 157	0.859
$3{:}8d_{Kd}\ 3{:}8d_{Kd}\ 3{:}8d_{Lp}\ R$	864	13500	−7.478 060 320 454	2.297
$4{:}7f_{Kf}\ 2{:}5p_{Kp}\ 3{:}6d_{Lp}\ R$	256	13756	−7.478 060 321 720	1.266
$2{:}5p_{Kp}\ 4{:}7f_{Kf}\ 3{:}6d_{Lp}\ R$	256	14012	−7.478 060 321 979	0.259
$4{:}7f_{Kf}\ 3{:}6d_{Kd}\ 2{:}5p_{Lp}\ R$	256	14268	−7.478 060 322 140	0.161
$2{:}5p_{Kp}\ 3{:}6d_{Kd}\ 4{:}7f_{Lp}\ R$	256	14524	−7.478 060 322 183	0.043
$3{:}6d_{Kd}\ 4{:}7f_{Kf}\ 2{:}5p_{Lp}\ R$	256	14780	−7.478 060 322 236	0.053
$3{:}6d_{Kd}\ 2{:}5p_{Kp}\ 4{:}7f_{Lp}\ R$	256	15036	−7.478 060 322 245	0.009
$4{:}9f_{Kf}\ 4{:}9f_{Kf}\ 1{:}6s_{Ls}\ R$	864	15900	−7.478 060 322 637	0.392
$1{:}6s_{Ka}\ 1{:}6s_{Ka}\ 1{:}6s_{Ls}\ R$	864	16764	−7.478 060 323 451 9	0.815
Estimated exact [11]			−7.478 060 323 910 10(32)	

[a] K-shell orbital exponents are $Ks=4.40$, $Kt=3.60$, $Kp=4.65$, $Ka=7.65$, $Kd=5.30$, and $Kf=5.50$.

[b] L-shell orbital exponents are $Ls=1.05$ and $Lp=1.30$.

$$\cos\,\theta_{ij}=4\pi/3\sum_{m=-1}^{m=+1}Y_1^{m*}(\theta_i,\phi_i)Y_1^{m}(\theta_j,\phi_j), \tag{13}$$

expansion of $s_1s_2s_3\,r_{12}^2\,r_{13}^2$ gives rise to *sss* terms, *psp* terms, *pps* terms, and $p(1)p(2)p'(1)p'(3)$ terms. Expanding this last term gives *spp* and *dpp* terms. Similarly, $r_{12}^2r_{23}^2$ gives rise to the new term *pdp* and $r_{13}^2r_{23}^2$ to *ppd*. None of the *dpp*, *pdp*, or *ppd* 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}^2 leads to *pps*, r_{13}^2 to *psp*, r_{12}^4 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 $dpp*R$, $pdp*R$, and $dpp*R$ terms, as did previous workers, yet were still able to get (surprisingly) to within 10 nanohartree of nanohartree accuracy. After adding $ppd*R$, $pdp*R$, and $dpp*R$ terms we ran into another hard energy limit, preventing us from getting closer than 2 nanohartree 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 $r_{12}^4\,r_{13}^4$ 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 $fpd*R$ term types are in fact needed. Finally, we added $ffs*R$ to acknowledge that $ff*\{1,r_{12}\}$ is of importance in the description of the Li^+ ion at the nanohartree accuracy level. $fsf*R$- and $sff*R$-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, $ggs*R$. 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 $sss*R$ 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, Nörtershäuser, 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 $2\,^2S$ 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).

Technique	Author	No. of terms	Energy (E) in hartrees
MCSCF[a]	Tong, Jönsson, and Fischer (1993) [14]		−7.477 968 61
CI	Jitrik and Bunge (1997) [15]	$l<=13$	−7.478 025 4
Hy	King and Bergsbaken (1990) [16]	296	−7.478 059 53
Hy-CI	This work, s,p r_{ij} basis	8316	−7.478 059 573 327
Hy-CI	Pestka and Woźnicki (1996) [17]	386	−7.478 060 1
Hy-CI	Pipin and Bishop (1992) [3]	1618	−7.478 060 1
Hy	Lüchow and Kleindienst (1994) [18]	1420	−7.478 060 320 8
Hy-CI	This work, s,p,d r_{ij} basis	14364	−7.478 060 321 379
ECG[b]	Pachucki and Komasa (2006) [19]	7000	−7.478 060 323 2
Hy-CI	This work, s,p,d,f r_{ij} basis	16764	−7.478 060 323 451 9
Hy	This work, one odd r_{ij}	6170	−7.478 060 323 452
Hy	Yan, Tambasco, and Drake (1998) [20]	3502	−7.478 060 323 618 9
Hy	Pulchalski and Pachucki (2006) [12]	9576	−7.478 060 323 889 7
Hy	Yan, Nörtershäuser, and Drake (2008) [13]	9577	−7.478 060 323 892 4
Hy	Pulchalski, Kedziera, and Pachucki (2009) [11]	13944	−7.478 060 323 909 560
Hy	Pulchalski, Kedziera, and Pachucki (2009) [11]	Exact(est.)	−7.478 060 323 910 10(32)

[a] Multiconfigurational self-consistent field.

[b] Explicitly correlated Gaussians.

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_i as was done in the Hy method work [recall that inverse iteration is an $O(N^3)$ 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_{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 Woźnicki [17] required a basis of s, p, d, and f and powers of r_{ij} through 3 to get −7.478 060 1 hartree. Pipin and Bishop [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_{ij} energy limit obtained using terms 1–11 and 19 from Table I which gave an energy of $E(14\,364)=-7.478\,060\,321\,379$ hartree, no r_{ij} powers higher than the first power. Adding f orbitals we obtained an s,p,d,f r_{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 Pachucki and Komasa [19] and better than all but the most accurate Hy calculations of Pulchalski and Pachucki [12], Yan, Nörtershäuser, and Drake [13], and Pulchalski, Kedziera, and Pachucki [11], coming to within 0.56 nanohartree of the estimated exact energy of Li.

B. Hy calculation of the 2 ^2S Li ground state

Next we used the code of Pulchalski and Pachucki [12] to determine the importance of odd-odd and odd-odd-odd power $r_{ij}r_{ik}$ and $r_{ij}r_{ik}r_{kj}$ 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 [21]. The key idea is to start with a fully correlated Hy variational basis set of the form

$$r_{23}^{n_1}r_{31}^{n_2}r_{12}^{n_3}r_1^{n_4}r_2^{n_5}r_3^{n_6}e^{-\alpha_1 r_1-\beta_2 r_2-\gamma_3 r_3}\chi_1, \tag{14}$$

where χ_1 is a spin function with spin angular momentum 1/2. The basis set is then replicated several times with different nonlinear scale parameters α, β, and γ, 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 [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) $n_3=0$, $n_1\neq 0$, $n_2\neq 0$;
(5) $n_3\neq 0$, $n_1\neq 0$, $n_2\neq 0$.

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_{ij} power.

The most striking observation [fifth line in the table, $E(6170)$ vs $E(9576)$] is that products of odd powers of r_{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_{ij} products removed].

We also did runs with only one odd r_{ij} power and the maximum r_{ij} power in any term restricted to 6 and then 5. The results are also tabulated in Table III.

TABLE III. Hy calculations of the Li ground-state energy by section (in hartrees). ν_{max} is the maximum allowed r_{ij} power.

Section	N	$E(N)$ in hartrees	N'	$E(N')$ in hartrees
1	1036	−7.476 983 290 850	1036	−7.476 983 290 850
1–2	3222	−7.478 060 320 124	2696	−7.478 060 305 902
1–3	5404	−7.478 060 323 278	4340	−7.478 060 321 990
1–4	6951	−7.478 603 233 29	5327	−7.478 060 322 893
1–5	9576	−7.478 060 323 889	6170	−7.478 060 323 452
1–5, $\nu_{max}=6$			5740	−7.478 060 323 348
1–5, $\nu_{max}=5$			5124	−7.478 060 322 122
YND[a]	9577	−7.478 603 238 92		
PKP[b]	13944	−7.478 060 323 909 560		

[a] Yan, Nörtershäuser, and Drake (2008) [13].

[b] Pulchalski, Kedziera, and Pachucki (2009) [11].

Note that one does not need to go beyond r_{ij}^6 to achieve sub-nanohartree accuracy for lithium in Hy calculations, and since r_{ij}^5 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 3 ^2S, 4 ^2S, 5 ^2S, 6 ^2S, and 7 ^2S states of the lithium atom. The 3 ^2S 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 $s_{Ka}s_{Ka}s_{Ls}*R$ 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, Moro, 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 $5sLa$ 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 IV. Energies (in hartrees) for various truncations of the wave function of the 3 ^2S excited state of lithium. In the table $R=\{1,r_{12},r_{13},r_{23}\}$.

N	Terms added	3 ^2S [a,b]
4000	$1:10s_{Ks}$ $1:10s_{Kt}$ $1:10s_{Ls}$ R	−7.353 707 280 732
7240	$2:10p_{Kp}$ $2:10p_{Kq}$ $1:10s_{Ls}$ R	−7.354 097 937 123
8808	$3:9d_{Kd}$ $3:9d_{Kd}$ $1:8s_{Ls}$ R	−7.354 098 336 936
9816	$2:7p_{Kp}$ $1:7s_{Ks}$ $2:7p_{Lp}$ R	−7.354 098 375 949
10824	$1:7s_{Ks}$ $2:7p_{Kq}$ $2:7p_{Lp}$ R	−7.354 098 399 926
11688	$3:8d_{Kd}$ $1:6s_{Ks}$ $3:8d_{Lp}$ R	−7.354 098 401 484
12552	$1:6s_{Ks}$ $3:8d_{Kd}$ $3:8d_{Lp}$ R	−7.354 098 402 948
13416	$2:7p_{Kp}$ $2:7p_{Kq}$ $3:8d_{Lp}$ R	−7.354 098 416 384
13916	$2:6p_{Kp}$ $3:7d_{Kd}$ $2:6p_{Lp}$ R	−7.354 098 418 002
14416	$3:7d_{Kd}$ $2:6p_{Kq}$ $2:6p_{Lp}$ R	−7.354 098 418 592
14916	$3:7d_{Kd}$ $3:7d_{Kd}$ $3:7d_{Lp}$ R	−7.354 098 419 084
15516	$4:8f_{Kq}$ $4:8f_{Kq}$ $1:6s_{Ls}$ R	−7.354 098 419 557
16380	$1:6s_{Ka}$ $1:6s_{Ka}$ $1:6s_{Ls}$ R	−7.354 098 420 690
16780	$1:10s_{Ks}$ $1:10s_{Kt}$ $11:11s_{Ls}$ R	−7.354 098 420 909
17180	$1:10s_{Ks}$ $1:10s_{Kt}$ $12:12s_{Ls}$ R	−7.354 098 420 933
Exact (est.) [24]		−7.354 098 421 426(19)

[a] K-shell orbital exponents are $Ks=3.90$, $Kt=2.80$, $Kp=4.40$, $Kq=5.80$, $Kd=4.65$, and $Ka=8.0$.

[b] L-shell orbital exponents are $Ls=0.635$ and $Lp=0.86$.

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

N	Terms added	4 ^2S [a,b]	5 ^2S [c,d]	6 ^2S [e,f]	7 ^2S [g,h]
4000	$1{:}10s_{Ks}$ $1{:}10s_{Kt}$ $\{1{:}6s_{Ls}, 1{:}4s_{La}\}$ R	−7.318 144 893 422	−7.303 167 312 632	−7.295 475 782 289	−7.291 010 447 021
7240	$2{:}10p_{Kp}$ $2{:}10p_{Kq}$ $\{1{:}6s_{Ls}, 1{:}4s_{La}\}$ R	−7.318 530 329 869	−7.303 550 963 613	−7.295 858 767 247	−7.291 391 343 337
9200	$3{:}9d_{Kd}$ $3{:}9d_{Kd}$ $\{1{:}6s_{Ls}, 1{:}4s_{La}\}$ R	−7.318 530 775 712	−7.303 551 347 519	−7.295 859 122 525	−7.291 391 712 630
10208	$2{:}7p_{Kp}$ $1{:}7s_{Ks}$ $2{:}7p_{Lp}$ R	−7.318 530 802 894	−7.303 551 444 715	−7.295 859 339 642	−7.291 392 085 840
11216	$1{:}7s_{Ks}$ $2{:}7p_{Kp}$ $2{:}7p_{Lp}$ R	−7.318 530 835 014	−7.303 551 568 082	−7.295 859 494 639	−7.291 392 239 327
12080	$3{:}8d_{Kd}$ $1{:}6s_{Ks}$ $3{:}8d_{Lp}$ R	−7.318 530 835 967	−7.303 551 569 884	−7.295 859 500 882	−7.291 392 257 397
12944	$1{:}6s_{Ks}$ $3{:}8d_{Kd}$ $3{:}8d_{Lp}$ R	−7.318 530 836 739	−7.303 551 571 169	−7.295 859 503 301	−7.291 392 262 718
13808	$2{:}7p_{Kp}$ $2{:}7p_{Kq}$ $3{:}8d_{Lp}$ R	−7.318 530 841 199	−7.303 551 573 566	−7.295 859 505 242	−7.291 392 264 598
14308	$2{:}6p_{Kp}$ $3{:}7d_{Kd}$ $2{:}6p_{Lp}$ R	−7.318 530 842 944	−7.303 551 575 028	−7.295 859 506 393	−7.291 392 265 574
14808	$3{:}7d_{Kd}$ $2{:}6p_{Kq}$ $2{:}6p_{Lp}$ R	−7.318 530 843 272	−7.303 551 575 322	−7.295 859 506 709	−7.291 392 265 851
15408	$4{:}8f_{Kq}$ $4{:}8f_{Kq}$ $1{:}6s_{Ls}$ R	−7.318 530 843 884	−7.303 551 576 190	−7.295 859 507 594	−7.291 392 266 942
16272	$1{:}6s_{Kq}$ $1{:}6s_{Kq}$ $1{:}6s_{Ls}$ R	−7.318 530 845 168	−7.303 551 577 933	−7.295 859 509 441	−7.291 392 268 343
16672	$1{:}10s_{Ks}$ $1{:}10s_{Kt}$ $7{:}7s_{Ls}$ R	−7.318 530 845 287	−7.303 551 578 188	−7.295 859 509 733	−7.291 392 272 268
17072	$1{:}10s_{Ks}$ $1{:}10s_{Kt}$ $5{:}5s_{La}$ R	−7.318 530 845 331	−7.303 551 578 291	−7.295 859 509 943	−7.291 392 273 116

[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 $Ks=4.00$, $Kt=3.60$, $Kp=3.40$, $Kq=5.80$, and $Kd=4.65$.
[h] L-shell orbital exponents are $Ls=0.14$, $La=0.28$, and $Lp=0.53$.

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 $r_{12}r_{34}$ 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.

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APPENDIX: PROJECTION REDUCTION

Using Eq. (4), matrix element H_{KL} becomes

$$H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle = \langle \Lambda \Phi_K^P | \mathcal{H} | \; \Lambda \Phi_L^P \rangle \rangle, \tag{A1}$$

where Φ_K^P denotes the Kth primitive (unprojected) function $r_{ij}^{\nu_K} \prod_{s=1}^{3} \{ \phi_{K_s}(\mathbf{r_s}) \} \Theta_K$. S_{KL} is similar, with $\mathcal{H}$ replaced by the unit operator 1.

Now notice that

TABLE VI. Comparison of theoretical Li $n\ ^2S$ excited-state nonrelativistic energies (in hartrees).

State	Technique	Author	No. of terms	Energy (E) in hartrees
$3\ ^2S$	Hy	Perkins (1972) [25]	22	−7.353 5
	Hy	Larsson (1972) [26]	59	−7.353 917
	MCSCF	Jönsson, Fischer, and Bierón (1995) [27]	13306	−7.354 014
	Hy-CI	Pipin and Woźnicki (1983) [28]	170	−7.354 030
	Hy	King (1991) [29]	447	−7.354 076
	Hy	Lüchow and Kleindienst (1992) [30]	898	−7.354 097 8
		Wang, Zhu and Chung (1992) [31]		−7.354 098 0
	Hy-CI	Pestka and Woźnicki (1996) [17]	392	−7.354 098 04
	Hy	King (2007) [22]	1900	−7.354 098 355
	Hy	Lüchow and Kleindienst (1994) [18]	1398	−7.354 098 369
	Hy-CI	This work, s,p,d,f r_{ij} basis	17180	−7.354 098 420 933
	Hy	Yan and Drake (2000) [32]	3502	−7.354 098 421 082
	Hy	Pulchalski, Moro and Pachucki (2006) [23]	9576	−7.354 098 421 380
	Exact (est.)	Pulchalski and Pachucki (2008) [24]		−7.354 098 421 426(19)
$4\ ^2S$	Hy	Perkins (1972) [25]	18	−7.317 5
	Hy	Larsson (1972) [26]	59	−7.318 366
	MCSCF	Jönsson, Fischer, and Bierón (1995) [27]	13306	−7.318 451
	Hy	King (1991) [29]	501	−7.318 491
	Hy	Lüchow and Kleindienst (1992) [30]	898	−7.318 525
	Hy-CI	Pestka and Woźnicki (1996) [17]	241	−7.318 529 38
		Wang, Zhu and Chung (1992) [31]		−7.318 530 3
	Hy	Lüchow and Kleindienst (1994) [18]	1398	−7.318 530 665
	Hy	King (2007) [22]	1900	−7.318 530 816
	Hy-CI	This work, s,p,d,f r_{ij} basis	17072	−7.318 530 845 331
	Exact (est.)	This work, s,p,d,f r_{ij} basis		−7.318 530 846(1)
$5\ ^2S$	Hy	Larsson (1972) [26]	59	−7.303 392
	Hy	King (1991) [29]	450	−7.303 439
	Hy	Lüchow and Kleindienst (1992) [30]	898	−7.303 547
		Wang, Zhu and Chung (1992) [31]		−7.303 550 8
	Hy	King (2007) [22]	1900	−7.303 551 551
	Hy-CI	This work, s,p,d,f r_{ij} basis	17072	−7.303 551 578 291
	Exact (est.)	This work, s,p,d,f r_{ij} basis		−7.303 551 579(1)
$6\ ^2S$	Hy	Lüchow and Kleindienst (1992) [30]	898	−7.29 583
	Hy	King (2007) [22]	1900	−7.295 859 38
	Hy-CI)	This work, s,p,d,f r_{ij} basis	17072	−7.295 859 509 943
	Exact (est.)	This work, s,p,d,f r_{ij} basis		−7.295 859 511(2)
$7\ ^2S$	Hy-CI	This work, s,p,d,f r_{ij} basis	17072	−7.291 392 273 116
	Exact (est.)	This work, s,p,d,f r_{ij} basis		−7.291 392 276(3)

$$N!\,O_{as}=\sum_{p}(-1)^{p}P=\left(\sum_{u}(-1)^{u}P_{u}^{\alpha}\right)\left(\sum_{\nu}(-1)^{\nu}P_{\nu}^{\beta}\right)+\sum_{\gamma}(-1)^{\gamma}P_{\gamma}^{\alpha\beta}=\mathcal{A}^{\alpha}\mathcal{A}^{\beta}+\mathcal{A}^{\alpha\beta} \qquad \text{(A2)}$$

where N is the number of electrons, P^{α} refers to those permutations which permute only α spins, P^{β} refers to those permutations which permute only β spins, and $P^{\alpha\beta}$ refers to only those permutations which permute an α spin and a β 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 $\mathcal{A}^{\alpha}\mathcal{A}^{\beta}$ since permutations between α and β give zero results when integrating over spin.

In our case $\Theta_K=\Theta_L=\Theta_1=\alpha(1)\beta(2)\alpha(3)=\alpha\beta\alpha$, so we can write

$$\Lambda\Phi_{K}^{P}=O_{L,M_L}O_{as}O_{S,M_S}g_K f_K\Theta_1, \qquad \text{(A3)}$$

where $g_K=r_{ij}^{\nu_K}$ and f_K is the hartree product $\Pi_{s=1}^{3}\{\phi_{K_s}(\mathbf{r_s})\}$. Using the quantum-mechanical “turnover rule” [33], the commutivity of Λ and $\mathcal{H}$, and the idempotency condition $\Lambda^{\dagger}\Lambda=\Lambda$, H_{KL} reduces to

$$H_{KL}=\langle\Phi_K^P|\mathcal{H}|\Lambda\Phi_L^P\rangle. \tag{A4}$$

Projecting on Θ_1 with the Löwdin spin projection operator [4] $O_{S,M_S}(S=1/2,M_S=1/2)$, we get

$$O_{S,M_S}\Theta_1=O_{S,M_S}\alpha\beta\alpha=\frac{2}{3}\alpha\beta\alpha-\frac{1}{3}\beta\alpha\alpha-\frac{1}{3}\alpha\alpha\beta \tag{A5}$$

where the subscripts (not shown) on the α and β are always in the order 1,2,3.

This can be written

$$O_{S,M_S}\Theta_1=\left[\frac{2}{3}-\frac{1}{3}P_{12}^{\sigma}-\frac{1}{3}P_{23}^{\sigma}\right]\Theta_1. \tag{A6}$$

Using the identity

$$O_{as}=(-1)^pO_{as}(P^rP^{\sigma})^{-1}, \tag{A7}$$

H_{KL} becomes

$$H_{KL}=\left\langle g_Kf_K\Theta_1|\mathcal{H}\left|O_{L,M_L}O_{as}\left[\frac{2}{3}+\frac{1}{3}P_{12}^r+\frac{1}{3}P_{23}^r\right]g_Lf_L\Theta_1\right.\right\rangle. \tag{A8}$$

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

$$H_{KL}=\langle g_Kf_K|\mathcal{H}|\mathcal{A}^{\alpha}\mathcal{A}^{\beta}O_{L,M_L}B^r(g_Lf_L)\rangle. \tag{A9}$$

We have used the fact that O_{L,M_L} commutes with O_{as} in the above equation. Here the "reduced" antisymmetrizer $\mathcal{A}^{\alpha}\mathcal{A}^{\beta}$

$$\mathcal{A}^{\alpha}\mathcal{A}^{\beta}=(1-P_{13}) \tag{A10}$$

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}

$$H_{KL}=\langle g_Kf_K|\mathcal{H}|(1-P_{13})O_{L,M_L}B(g_Lf_L)\rangle. \tag{A12}$$

In Eq. (A12) one can apply O_{L,M_L} either before or after applying B. We first apply the permutations B to g_Lf_L, 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 $g_L=r_{ij}^{\nu_L}$ commutes with O_{L,M_L} [1,34] and only apply O_{L,M_L} to the orbital products.

Depending on the structure of g_Lf_L, $(1-P_{13})B(g_Lf_L)$ 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).

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