

# Hylleraas-configuration-interaction study of the $^1S$ ground state of neutral beryllium

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Hylleraas-configuration-interaction (Hy-CI) method variational calculations are reported for the  $^1S$  ground state of neutral beryllium. The best nonrelativistic energy obtained was  $-14.667\,356\,4$  hartree, which is estimated to be accurate to a tenth of a microhartree.

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## I. INTRODUCTION

Beryllium, with its four electrons and strong mixing of the  $1s^2 2s^2$  and  $1s^2 2p^2$  configurations, has long been the subject of investigation. The first reasonably accurate nonrelativistic calculations on the ground state were the configuration-interaction (CI) studies of Watson [1] and Weiss [2]. Szasz and Byrne [3] were the first to explicitly correlate the wave function by adding intrashell  $r_{ij}$  coordinates in a Hylleraas (Hy)-type wave function. Gentner and Burke [4] improved on Szasz and Byrne's work by including intershell  $r_{ij}$  coordinates. Sims and Hagstrom [5] combined the Hy and CI methods in a Hylleraas-configuration-interaction (Hy-CI) [5] calculation in 1971 with a considerable improvement in the energy. Bunge did his first Be calculation in 1968 [6] and his CI calculations for Be improved steadily over the years, culminating in a benchmark calculation of over 2.6 million terms in 2010 [7]. A multiconfiguration Hartree-Fock (MCHF) correlation study of Be was presented by Froese Fischer and Saxena in 1974 [8] and then was further refined by Froese Fischer in 1993 [9], leading finally to a calculation of over 650 000 terms in 2010 [10]. While significant progress was being made in Hy treatments of three-electron systems, integral problems with the conventional Hy expansions [11–13] brought calculations to a halt as far as four-electron systems were concerned until finally, in 1998, Büsse *et al.* [14] overcame serious integral problems and made major improvements through the use of Hy-type doubly linked terms in the wave-function expansions. This was the first major Hy-type calculation of near microhartree accuracy. In 1995 the exponentially correlated Gaussian (ECG) method was introduced by Komasa *et al.* [15]. The relative simplicity of the resultant integrals led to a sequence of impressively accurate calculations, culminating in the work of Adamowitz and co-workers [16,17] which stands as the best work to date (our work is second only to theirs). Table I summarizes Be ground-state variational results listed in order of increasing accuracy. In this paper, we present preliminary results from a very large Hy-CI calculation (over 40 000 symmetry adapted expansion functions) for the Be ground state.

## II. METHOD OF CALCULATION

For four electrons, the Hy-CI wave function used is

$$\Psi_{\text{Be}} = \sum_K C_K \Phi_K, \quad (1)$$

where

$$\begin{aligned} \Phi_K &= \Lambda \left( r_{ij}^{v_K} \prod_{s=1}^4 \{\phi_{K_s}(\mathbf{r}_s)\} \Theta_K \right) \\ &= O_{as} O_{L,M_L} O_{S,M_S} \left( r_{ij}^{v_K} \prod_{s=1}^4 \{\phi_{K_s}(\mathbf{r}_s)\} \Theta_K \right) \end{aligned} \quad (2)$$

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 [24] 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  $v_K$  equal to 0 or 1, with  $v_K = 0$  the CI case.  $\Theta_K$  is a primitive spin product function for the term  $K$  and  $\phi_{K_s}(\mathbf{r}_s)$  represents the  $s$ th basis orbital in the  $K$ th term. The basis orbitals are taken to be un-normalized Slater-type orbitals.  $O_{as}$  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  $\Theta_2 = \alpha\alpha\beta\beta$ . It is possible to converge on the exact wave function using only the  $\Theta_1$  product. Similar observations have been made by Larsson [25] and by Sims and Hagstrom [26] for Li, and by Sims and Hagstrom [5] for Be. Cencek and Rychlewski [27] 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. The Appendix contains a discussion of how to handle the antisymmetrization, spin, and angular momentum projections involved in computing the Hamiltonian and overlap matrix elements.

The  $C_K$  coefficients in Eq. (1) are found by solving the generalized eigenvalue problem  $\mathbf{HC} = \lambda\mathbf{SC}$ , where  $H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle$  and  $S_{KL} = \langle \Phi_K | \Phi_L \rangle$ , using the familiar inverse iteration method. Root  $\lambda$  will be an upper bound to the exact energy. The nonrelativistic Hamiltonian  $\mathcal{H}$  used in this work is

$$\mathcal{H} = \sum_{i=1}^4 \mathcal{H}_i + \sum_{i<j}^4 r_{ij}^{-1}, \quad (3)$$

where  $\mathcal{H}_i = T_i + V_i$  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  $V_i = -Z/r_i$ . Quadruple precision was used throughout the calculations. As in our recent work [26,28–30], MPI [31] was used to parallelize the code. The number of

TABLE I. Comparison of theoretical Be ground-state nonrelativistic energies (in hartree).  $N$  is the number of terms in the expansion. All energies are variational except those labeled “Estimated exact.”

Technique	Author(s)	$N$	Energy $E$ (hartree)
Hy	Szasz and Byrne (1967) [3]	28	-14.6565
CI	Watson (1960) [1]	37	-14.657 40
Hy	Gentner and Burke (1968) [4]	25	-14.6579
CI	Weiss (1961) [2]	55	-14.660 90
CI	Bunge (1968) [6]	180	-14.664 19
MCHF	Froese Fischer and Saxena (1974) [8]	52	-14.665 87
Hy-CI	Sims and Hagstrom (1971) [5]	107	-14.666 547
CI	Bunge (1976) [18]	650	-14.666 902
MCHF	Froese Fischer (1993) [9]	3381	-14.667 113
MCHF	Froese Fischer (2010) [10]	652 683	-14.667 114 52
CI	Jitrik and Bunge (1997) [19]	212 710	-14.667 275 57
CI	Bunge (2010) [7]	2 614 689	-14.667 347 30
Hy-CI	this work, $s, p, r_{ij}$ basis	20 330	-14.667 350 33
Hy	Büsse <i>et al.</i> (1998) [14]	5306	-14.667 354 7
ECG	Komasa <i>et al.</i> (1995) [15]	1200	-14.667 355 021
ECG	Komasa (2002) [20]	3700	-14.667 355 627
ECG	Pachucki and Komasa (2006) [21]	4600	-14.667 355 748
Hy-CI	this work, $s, p, d, r_{ij}$ basis	40 784	-14.667 356 359
Hy-CI	this work, $s, p, d, f, r_{ij}$ basis	41 871	-14.667 356 411
ECG	Stanke <i>et al.</i> (2007) [16]	4600	-14.667 356 458
ECG	Stanke <i>et al.</i> (2009) [17]	10 000	-14.667 356 486
Estimated exact	Bunge (2010) [7]		-14.667 355(1)
Estimated exact	Pachucki and Komasa (2004) [22]		-14.667 355 7(1)
Estimated exact	Davidson <i>et al.</i> (1991) [23]		-14.667 36
Estimated exact	Komasa <i>et al.</i> (1995) [15]		-14.667 360(2)

processes used varied from 12 to 48 with 32 being typical. This is not large by current standards and scaling to 128–256 processes with the existing code would be feasible on a routine basis provided one can be assured of adequate resources per process. The parallel environment for this work was the National Institute of Standards and Technology (NIST)’s 394 processor Linux cluster.

For Be the generation of the matrices  $\mathbf{H}$  and  $\mathbf{S}$  takes much longer than the solution of the secular equation due to the very large number of four-electron integrals. For large expansion lengths  $N$  the ratio of matrix element build to eigenvalue solve phases of the calculation was typically about 20 to 1 using an efficient solver (inverse iteration) but relatively inefficient integral and matrix element build packages. Inverse iteration scales as expected but matrix element build scales rather poorly (we do not really know why). Four-electron integrals totally dominate the integral calculation, 98 percent of the total integral time being typical. Improvements to the code will come in this area. Details of how we distribute the workload, allocate memory, manage mass storage, and deal with serial aspects of the algorithm will be described in a future publication.

### III. RESULTS

The CSFs given by Eq. (2) can be written

$$\Phi_K = \Lambda [F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \Theta_K] \quad (4)$$

in terms of spatial and spin functions  $F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$  and  $\Theta_K$ . Only one spin function  $\Theta_K = \Theta_1 = \alpha\beta\alpha\beta$  is used in this work

and the spatial part of a CSF is given by a particular choice of Hartree orbital product and  $r_{ij}$  factor:

$$F_K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = r_{ij}^{\nu_K} \prod_{s=1}^4 \{\phi_{Ks}(\mathbf{r}_s)\}, \quad (5)$$

where  $\nu_K$  is either 0 or 1.

Table II lists our best energy results (column 4) for various expansion lengths  $N_{\text{tot}}$  shown in column 3. Column 2 gives the number of CSFs added for the block shown in column 1. The energy improvements for each CSF block type are shown in column 5. Column 1 lists 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), electron 4 ( $\beta$  spin). For example, in the first line  $1:8s_K$  for the first electron means the basis orbitals are  $1s_K$  through  $8s_K$  orbitals (where  $K$  indicates an orbital exponent appropriate for a  $K$ -shell electron). Products of four orbitals are built up by taking one pair of orbitals from the  $K$ -shell set and the other pair from the  $L$ -shell set. 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 choice of terms is highly regular, there having been no serious attempt to eliminate energetically unimportant terms. The number of CSFs in a block can be computed from the listed basis orbitals and the condition that  $N_{r\text{sum}}$ , the sum of the powers of  $r$  for each Hartree product (HP), must be less than or equal to 16 (i.e.,  $N_{r\text{sum}} \leq 16$ ). For example, consider  $2:8p_{Kp} 2:8p_{Kp} 1:8s_L 1:8s_L r_{12}$ . There are  $(7 \times 8)/2 = 28$  unique pairs of orbitals for electrons 1 and 2, and  $(8 \times 9)/2 = 36$  unique pairs of

orbitals for electrons 3 and 4. Since the  $K$  and  $L$  shells have no orbital in common, there will be  $28 \times 36 = 1008$  different CSF terms for this block. Applying the condition that the sum of the powers of  $r$  for these orbitals has to be  $\leq 16$ , the number of terms is reduced to 630.

The leading CSF term types in Table II are what one would expect from adding explicit correlation to a typical Be CI expansion. For some of the remaining term types, the Legendre expansion of typical Hy  $r_{ij}$  product terms helped in determining possible Hy-CI term types to try [26]. For example, expansion of  $s_1 s_2 s_3 s_4 r_{23}^2 r_{34}^2$  (only even power products need to be considered) gives rise to a  $spdp$  term, in addition to  $ssss$ ,  $spsp$ ,  $sspp$ , and  $spps$  terms. Similarly,  $r_{12}^2 r_{23}^2$  gives rise to  $pdps$  and  $r_{13}^2 r_{23}^2$  to  $ppds$ . These are not exactly obvious important CI promotions. Of course, other orbital products arise from the appropriate Hy terms, e.g.,  $ppss$  from  $r_{12}^2$ ,  $spsp$  from  $r_{24}^2$ , and so on. From the possible  $r_{ij}^2 r_{kl}^2$  products, there are six linearly independent orbital products used in this work, namely,  $sppd$ ,  $ppsd$ ,  $sdpp$ ,  $pspd$ ,  $dpsp$ , and  $pdsp$ .

Column 6 in Table II lists  $\omega$ , the sum of the powers of the  $r_{ij}$  products for the Hy equivalent of the Hy-CI term. Except for the  $s_{K1}$  blocks toward the end of Table II, the blocks are ordered by increasing  $\omega$ . Except for  $ppdd$ ,  $ddpp$ , and  $pppp$ , all CSF types give rise to only one  $^1S$  state obtained from projecting the orbital product ( $l_1 0$ ,  $l_2 0$ ,  $l_3 0$ ,  $l_4 0$ ). For  $ppdd$ ,  $ddpp$ , and  $pppp$ , three  $^1S$  states are obtained by projection of  $(0, 0, 0, 0)$ ,  $(1, 1, -1, -1)$  and  $(1, -1, 1, -1)$ , where only the  $m$  quantum numbers are shown. For  $ddpp$  and  $pppp$ , all three projections were used. For  $ppdd$  only the first two cases proved to be energetically important. CSF blocks were tested individually for importance essentially by trial and error, keeping in mind that the contribution depends on the order in which blocks are added. All blocks which lowered the energy by more than 5 nanohartree were kept.

Final orbital exponent optimization was done at the  $N = 19076$  expansion level for  $s$  and  $p$  orbitals and at the  $N = 27468$  level for  $d$  orbitals.  $f$  orbital exponents were taken over from an earlier optimization. Due to limitations in the integral codes, it was not possible to give every orbital type its own orbital exponent. In a practical sense this was not a problem, since the dependence of the final energy surface on the orbital exponents turned out to be extremely flat for the 5-nanohartree cutoff used. Careful minimization of the  $\zeta$ s was not a particular problem for 0.1 microhartree accuracy.

#### IV. DISCUSSION

Table I summarizes earlier Be ground-state variational results listed in order of increasing accuracy and includes three important limiting energy values from the present work inserted to facilitate comparison with the earlier work. Note that 6-microhartree accuracy is obtained with just an  $s, p$   $r_{ij}$  basis, which is better than the best CI result of Bunge [7] using over 2.6 million CSFs with  $l$  up to 30. A 40784 term  $s, p, d$   $r_{ij}$  basis wave function (all the blocks in Table II except for the three blocks containing  $f$  orbitals) results in better than microhartree accuracy (0.2 microhartree). Finally adding  $f$  orbitals gives an  $s, p, d, f$   $r_{ij}$  energy of  $E(41871) = -14.667\,356\,411$  hartree. Use of an  $s, p, d, f$   $r_{ij}$  basis is

consistent with what we know from our earlier Li calculations [26]. However, it should be noted that the ECG result of Stanke *et al.* [17] is fully 75 nanohartree below our current best. From the various different estimates of the exact energy it should be clear that there is no doubt about the exact energy at the microhartree level, but beyond that it gets problematic.

In Table II are listed results for the Be wave function expansions at various levels of truncation. The most distinctive feature of the table is the obvious importance of CSF blocks with  $r_{12}$  and  $r_{34}$  reflecting the pronounced Be shell structure. There are a few important blocks incorporating intershell correlation (via  $r_{13}$ - and  $r_{14}$ -type terms), but there are also intershell blocks with anomalously small contributions, for which there is no ready explanation. There are 18 blocks that contribute at the microhartree level out of a total of 71 given in the table. Many more block types (approximately 78) were tested but not included in the final wave function due to the 5-nanohartree cutoff. The  $spdf\{1, r_{12}, r_{34}, r_{13}, r_{14}\}$  blocks are an example. Many blocks were not tried; many of the ones tried and dropped because of the 5-nanohartree cutoff could contribute at the 1-nanohartree level. Some blocks which lowered the energy by less than 5 nanohartree were kept because they function as “sanity” checks on the calculation. One example is the  $4:8f_{K_f} 4:8f_{K_f} 1:7s_L 1:7s_L r_{34}$  block which is involved in our attempt to include an  $r_{12}r_{34}$ -type correlation, as discussed below. Another example is that the last two blocks in the table are part of the  $s_{K1}$  set of expansion terms, which introduces additional correlation into the  $K$  shell. After we arrived at the 41871 term wave function, further tests were done to check the choice of blocks in the wave function. For example, blocks containing terms in which  $K$ - and  $L$ -shell orbitals are not both doubly occupied and containing either  $r_{23}$  or  $r_{24}$  were added to the 41871 term wave function, but none of these blocks added more than 2 nanohartree. As another example, our algorithm for building HPs omits HPs with  $\{ms_K, m's_K\}\{ns_L, n's_L\}$   $m \geq m', n \geq n'$ . These terms were also tested but not included in the final wave function because they led to only very small improvements; they were not important for Li [26] either.

The Hy calculation by Büsse *et al.* [14] in Table I is the calculation closest in spirit and results to the current calculation. A direct comparison is difficult, however, because of differences in choice of spin function as well as, of course, the presence of products of  $r_{ij}$  factors raised to odd powers (so-called odd-odd terms, e.g.,  $r_{ij}r_{ik}$  and  $r_{ij}r_{kl}$ ), which appear in Hy expansions but are not explicitly represented in the corresponding Hy-CI expansions. For Li [26] it has been shown that odd power linked product terms ( $r_{ij}$  products with one index in common) are unimportant at the nanohartree level, and by inference probably not a problem at the four-electron level, although there are more such terms in the Be case, and one might expect their contribution to be somewhat greater. The unlinked  $r_{ij}r_{kl}$  (no indices in common) term types, which first occur in the four-electron case, are expected to be of major importance, however. Support for this can be inferred from Büsse *et al.*'s [14]  $\omega = 2$  results. There is a big 2000-microhartree improvement due to odd power term types of which  $r_{12}r_{34}$  would be expected to be the most important. In Hy-CI this effect can hopefully be effectively represented using a superposition of normal Hy-CI term types. In particular we suggest that

TABLE II. Hy-CI results for the Be ground-state energy (in hartree). In the table,  $N$  is the number of CSF terms added with each CSF block,  $N_{\text{tot}}$  is the cumulative number of terms, and  $\omega$  is the sum of the  $r_{ij}$  powers in an equivalent Hy expansion. All terms are  $r$ -sum filtered;  $N_{r\text{sum}} = 16$ .

Terms added <sup>a,b</sup>	$N$	$N_{\text{tot}}$	$E(N_{\text{tot}})$ (hartree)	$-\Delta E$ (microhartree)	$\omega$
1:8s <sub>K</sub> 1:8s <sub>K</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub>	896	896	-14.591 724 231		0
1:8s <sub>K</sub> 1:8s <sub>K</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>12</sub>	896	1792	-14.659 886 529	68 162.298	0 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>34</sub>	896	2688	-14.662 973 074	3040.778	0 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>13</sub>	896	3584	-14.662 930 798	3.491	0 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>14</sub>	896	4480	-14.662 934 922	4.124	0 + 1
2:8p <sub>Kp</sub> 2:8p <sub>Kp</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub>	630	5110	-14.664 420 851	1485.930	2
2:8p <sub>Kp</sub> 2:8p <sub>Kp</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>12</sub>	630	5740	-14.664 504 277	83.426	2 + 1
2:8p <sub>Kp</sub> 2:8p <sub>Kp</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>34</sub>	630	6370	-14.666 606 396	2102.119	2 + 1
2:8p <sub>Kp</sub> 2:8p <sub>Kp</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>13</sub>	630	7000	-14.666 816 908	210.512	2 + 1
2:8p <sub>Kp</sub> 2:8p <sub>Kp</sub> 1:8s <sub>L</sub> 1:8s <sub>L</sub> r <sub>14</sub>	630	7630	-14.666 947 723	130.816	2 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 2:8p <sub>Lp</sub> 2:8p <sub>Lp</sub>	630	8260	-14.667 138 747	191.023	2
1:8s <sub>K</sub> 1:8s <sub>K</sub> 2:8p <sub>Lp</sub> 2:8p <sub>Lp</sub> r <sub>12</sub>	630	8890	-14.667 289 253	150.506	2 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 2:8p <sub>Lp</sub> 2:8p <sub>Lp</sub> r <sub>34</sub>	630	9520	-14.667 289 795	0.543	2 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 2:8p <sub>Lp</sub> 2:8p <sub>Lp</sub> r <sub>13</sub>	630	10 150	-14.667 306 512	16.717	2 + 1
1:8s <sub>K</sub> 1:8s <sub>K</sub> 2:8p <sub>Lp</sub> 2:8p <sub>Lp</sub> r <sub>14</sub>	630	10 780	-14.667 314 875	8.363	2 + 1
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 1:6s <sub>L</sub> 2:6p <sub>Lp</sub>	865	11 645	-14.667 314 971	0.096	2
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 1:6s <sub>L</sub> 2:6p <sub>Lp</sub> r <sub>12</sub>	865	12 510	-14.667 316 045	1.074	2 + 1
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 1:6s <sub>L</sub> 2:6p <sub>Lp</sub> r <sub>34</sub>	865	13 375	-14.667 316 303	0.258	2 + 1
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 1:6s <sub>L</sub> 2:6p <sub>Lp</sub> r <sub>13</sub>	865	14 240	-14.667 316 355	0.051	2 + 1
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 1:6s <sub>L</sub>	865	15 105	-14.667 316 402	0.048	2
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 1:6s <sub>L</sub> r <sub>12</sub>	865	15 970	-14.667 316 503	0.100	2 + 1
1:6s <sub>K</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 1:6s <sub>L</sub> r <sub>14</sub>	865	16 835	-14.667 316 618	0.115	2 + 1
2:7p <sub>Kp</sub> 2:7p <sub>Kp</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub>	987	17 822	-14.667 348 007	31.389	4
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 2:6p <sub>Lp</sub> r <sub>12</sub>	627	18 449	-14.667 350 243	2.236	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 2:6p <sub>Lp</sub> r <sub>34</sub>	627	19 076	-14.667 350 287	0.044	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 2:6p <sub>Lp</sub> r <sub>13</sub>	627	19 703	-14.667 350 326	0.040	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 2:6p <sub>Lp</sub> 2:6p <sub>Lp</sub> r <sub>14</sub>	627	20 330	-14.667 350 336	0.010	4 + 1
1:6s <sub>K</sub> 2:5p <sub>Kp</sub> 2:5p <sub>Lp</sub> 3:6d <sub>Ld</sub>	379	20 709	-14.667 352 968	2.632	4
1:6s <sub>K</sub> 2:5p <sub>Kp</sub> 2:5p <sub>Lp</sub> 3:6d <sub>Ld</sub> r <sub>12</sub>	465	21 174	-14.667 353 413	0.444	4 + 1
1:6s <sub>K</sub> 2:5p <sub>Kp</sub> 2:5p <sub>Lp</sub> 3:6d <sub>Ld</sub> r <sub>34</sub>	379	21 553	-14.667 353 496	0.084	4 + 1
1:6s <sub>K</sub> 2:5p <sub>Kp</sub> 2:5p <sub>Lp</sub> 3:6d <sub>Ld</sub> r <sub>13</sub>	379	21 932	-14.667 353 568	0.071	4 + 1
1:6s <sub>K</sub> 2:5p <sub>Kp</sub> 2:5p <sub>Lp</sub> 3:6d <sub>Ld</sub> r <sub>14</sub>	379	22 311	-14.667 353 644	0.076	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 1:7s <sub>L</sub> 3:6d <sub>Ld</sub>	375	22 686	-14.667 353 689	0.045	4
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 1:7s <sub>L</sub> 3:6d <sub>Ld</sub> r <sub>12</sub>	375	23 061	-14.667 353 803	0.114	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 1:7s <sub>L</sub> 3:6d <sub>Ld</sub> r <sub>14</sub>	375	23 436	-14.667 353 822	0.019	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 1:7s <sub>L</sub> 3:6d <sub>Ld</sub> r <sub>13</sub>	375	23 811	-14.667 353 832	0.010	4 + 1
2:6p <sub>Kp</sub> 2:6p <sub>Kp</sub> 1:7s <sub>L</sub> 3:6d <sub>Ld</sub> r <sub>34</sub>	375	24 186	-14.667 353 837	0.005	4 + 1
1:6s <sub>K</sub> 3:7d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub>	506	24 692	-14.667 353 992	0.155	4 + 1
1:6s <sub>K</sub> 3:7d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub> r <sub>12</sub>	506	25 198	-14.667 353 999	0.007	4 + 1
1:6s <sub>K</sub> 3:7d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub> r <sub>13</sub>	506	25 704	-14.667 354 005	0.006	4 + 1
1:6s <sub>K</sub> 3:7d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub> r <sub>34</sub>	506	26 210	-14.667 354 042	0.037	4 + 1
2:6p <sub>Kp</sub> 1:6s <sub>K</sub> 2:7p <sub>Lp</sub> 3:7d <sub>Kd</sub>	776	26 986	-14.667 354 049	0.007	4 + 1
2:6p <sub>Kp</sub> 1:6s <sub>K</sub> 2:7p <sub>Lp</sub> 3:7d <sub>Kd</sub> r <sub>14</sub>	776	27 762	-14.667 354 154	0.104	4 + 1
2:6p <sub>Kp</sub> 1:6s <sub>K</sub> 2:7p <sub>Lp</sub> 3:7d <sub>Kd</sub> r <sub>13</sub>	776	28 538	-14.667 354 169	0.015	4 + 1
3:7d <sub>Kd</sub> 2:6p <sub>Kp</sub> 2:7s <sub>L</sub> 2:7p <sub>Lp</sub>	702	29 240	-14.667 354 173	0.005	4 + 1
2:6p <sub>Kp</sub> 3:7d <sub>Kd</sub> 1:7s <sub>L</sub> 2:7p <sub>Lp</sub> r <sub>12</sub>	851	30 091	-14.667 354 180	0.007	4 + 1
2:6p <sub>Kp</sub> 3:7d <sub>Kd</sub> 1:7s <sub>L</sub> 2:7p <sub>Lp</sub> r <sub>14</sub>	851	30 942	-14.667 354 187	0.007	4 + 1
2:6p <sub>Kp</sub> 3:7d <sub>Kd</sub> 1:7s <sub>L</sub> 2:7p <sub>Lp</sub> r <sub>13</sub>	851	31 793	-14.667 354 194	0.007	4 + 1
1:6s <sub>K</sub> 1:6s <sub>K</sub> 3:7d <sub>Ld</sub> 3:7d <sub>Ld</sub>	266	32 059	-14.667 354 437	0.243	4 + 1
1:6s <sub>K</sub> 1:6s <sub>K</sub> 3:7d <sub>Ld</sub> 3:7d <sub>Ld</sub> r <sub>12</sub>	266	32 325	-14.667 355 886	1.449	4 + 1
1:6s <sub>K</sub> 1:6s <sub>K</sub> 3:7d <sub>Ld</sub> 3:7d <sub>Ld</sub> r <sub>34</sub>	266	32 591	-14.667 355 913	0.027	4 + 1
1:6s <sub>K</sub> 1:6s <sub>K</sub> 3:7d <sub>Ld</sub> 3:7d <sub>Ld</sub> r <sub>13</sub>	266	32 857	-14.667 355 941	0.028	4 + 1
1:6s <sub>K</sub> 1:6s <sub>K</sub> 3:7d <sub>Ld</sub> 3:7d <sub>Ld</sub> r <sub>14</sub>	266	33 123	-14.667 355 956	0.015	4 + 1
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 1:7s <sub>L</sub> 1:7s <sub>L</sub>	378	33 501	-14.667 356 065	0.110	4 + 1
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 1:7s <sub>L</sub> 1:7s <sub>L</sub> r <sub>34</sub>	378	33 879	-14.667 356 107	0.042	4 + 1
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 1:7s <sub>L</sub> 1:7s <sub>L</sub> r <sub>12</sub>	378	34 257	-14.667 356 122	0.015	4 + 1
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 1:7s <sub>L</sub> 1:7s <sub>L</sub> r <sub>13</sub>	378	34 635	-14.667 356 130	0.008	4 + 1



TABLE II. *Continued.*

Terms added <sup>a,b</sup>	$N$	$N_{\text{tot}}$	$E(N_{\text{tot}})$ (hartree)	$-\Delta E$ (microhartree)	$\omega$
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 1:7s <sub>L</sub> 1:7s <sub>L</sub> r <sub>14</sub>	378	35 013	-14.667 356 135	0.005	4 + 1
1:6s <sub>K</sub> 3:7d <sub>Kd</sub> 3:7d <sub>Ld</sub> 1:7s <sub>L</sub>	851	35 864	-14.667 356 140	0.005	4
1:6s <sub>K</sub> 3:7d <sub>Kd</sub> 3:7d <sub>Ld</sub> 1:7s <sub>L</sub> r <sub>14</sub>	851	36 715	-14.667 356 146	0.006	4 + 1
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub>	732	37 447	-14.667 356 179	0.034	6
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub> r <sub>34</sub>	732	38 179	-14.667 356 302	0.123	6 + 1
3:8d <sub>Kd</sub> 3:8d <sub>Kd</sub> 2:7p <sub>Lp</sub> 2:7p <sub>Lp</sub> r <sub>12</sub>	732	38 911	-14.667 356 308	0.006	6 + 1
2:7p <sub>Kp</sub> 2:7p <sub>Kp</sub> 3:8d <sub>Ld</sub> 3:8d <sub>Ld</sub>	488	39 399	-14.667 356 320	0.012	6
2:7p <sub>Kp</sub> 2:7p <sub>Kp</sub> 3:8d <sub>Ld</sub> 3:8d <sub>Ld</sub> r <sub>12</sub>	488	39 887	-14.667 356 324	0.004	6 + 1
1:6s <sub>K</sub> 1:6s <sub>K</sub> 4:8f <sub>Lf</sub> 4:8f <sub>Lf</sub> r <sub>12</sub>	210	40 097	-14.667 356 371	0.047	6 + 1
4:8f <sub>Kf</sub> 4:8f <sub>Kf</sub> 1:6s <sub>L</sub> 1:6s <sub>L</sub> r <sub>34</sub>	232	40 329	-14.667 356 374	0.003	6 + 1
1:6s <sub>K</sub> 4:8f <sub>Kf</sub> 4:8f <sub>Lf</sub> 1:6s <sub>L</sub> r <sub>34</sub>	645	40 974	-14.667 356 378	0.004	6
1:6s <sub>K1</sub> 1:6s <sub>K1</sub> 2:6s <sub>L</sub> 2:6s <sub>L</sub>	299	41 273	-14.667 356 404	0.026	0
1:6s <sub>K1</sub> 1:6s <sub>K1</sub> 2:6s <sub>L</sub> 2:6s <sub>L</sub> r <sub>12</sub>	299	41 572	-14.667 356 407	0.003	0 + 1
1:6s <sub>K1</sub> 1:6s <sub>K1</sub> 2:6s <sub>L</sub> 2:6s <sub>L</sub> r <sub>34</sub>	299	41 871	-14.667 356 411	0.004	0 + 1

<sup>a</sup> $K$ -shell orbital exponents are  $K = 3.3$ ,  $K1 = 10.0$ ,  $Kp = 4.65$ ,  $Kd = 4.65$ .  $Kf = 4.5$

<sup>b</sup> $L$ -shell orbital exponents are  $L = 1.6$ , and  $Lp = 2.0$ ,  $Ld = 2.6$ ,  $Lf = 3.0$ .

the forms  $(ss + pp + dd + \dots)_K(ss + pp + dd + \dots)_L$   $r_{34} + (ss + pp + dd + \dots)_{Kr_{12}}(ss + pp + dd + \dots)_L$  will accomplish this. In this representation one electron pair is being correlated primarily by the  $r_{ij}$  factor while the other pair is correlated by a CI pair expansion of the sort used for He [28], which is unfortunately slowly converging in the CI case, but may be better behaved in Be. In Table III are gathered together results from Table II, with additional test results using  $(ss)_{Kr_{12}}(gg)_L$  and  $(ff)_K(pp)_{Lr_{34}}$  term types added specifically to explore this point, suggesting that this is indeed the case. For example, the series  $(ss)_{Kr_{12}}(pp + dd + ff)_L$  converges nicely as does  $(pp + dd + ff)_K(ss)_{Lr_{34}}$ .  $(pp)_{Kr_{12}}(pp + dd + ff)_L$  and  $(pp + dd + ff)_K(pp)_{Lr_{34}}$  contribute similarly. There is one anomalous case for which we have no explanation. Note also that the numbers in Table III depend on the block order used in Table II, an ordering that was not explicitly designed to show the  $r_{12}r_{34}$  convergence effect. Compared to the slow, cusp-connected convergences in typical CI calculations, this is unusually fast convergence, suggesting that this correlation type can be accurately represented within the Hy-CI model.

However, further research into this point is warranted. In this connection, an Hy treatment of (hopefully) nanohartree

accuracy both with and without unlinked cluster terms, analogous to the way the effect of linked cluster terms like  $r_{12}r_{13}$  was examined in Li [26], would be most useful, especially since the issue of unlinked cluster terms is qualitatively different from the issue of linked cluster terms. Generalization of Hy-CI to include unlinked  $r_{ij}r_{kl}$  terms would certainly settle the issue, but at the cost of greatly complicating the calculation of matrix elements.

A 5-nanohartree threshold was used to determine which term types to include in the final wave function. Blocks which contribute less than this threshold value were dropped. Tests to date suggest that (20–25) nanohartree could probably be picked up using a 1-nanohartree cutoff leaving about 50 nanohartree to reach or surpass the Stanke *et al.* [17] value, but to do substantially better, assuming that  $r_{12}r_{34}$  is not a problem, will involve addressing issues of (i) greater flexibility in the atomic orbital basis (the number and choice of nonlinear parameters is very important at the nanohartree level for Li [26], and there is no reason to believe this will not be the case for Be as well); (ii) more careful optimization of the nonlinear parameters; (iii) focusing on the most important (core) CSF types involving  $s$  and  $p$  orbitals; and (iv) better CSF filtering to reduce the expansion lengths. Extensive experimentation

TABLE III. Convergence of  $r_{12}r_{34}$  as represented by Hy-CI.

Block	Energy $E$ (nanohartree)	Block	Energy $E$ (nanohartree)
$(ss)_{Kr_{12}}(ss)_L$	68 162 298	$(ss)_K(ss)_{Lr_{34}}$	3 040 778
$(ss)_{Kr_{12}}(pp)_L$	151 506	$(pp)_K(ss)_{Lr_{34}}$	2 102 114
$(ss)_{Kr_{12}}(dd)_L$	1449	$(dd)_K(ss)_{Lr_{34}}$	42
$(ss)_{Kr_{12}}(ff)_L$	47	$(ff)_K(ss)_{Lr_{34}}$	3
$(ss)_{Kr_{12}}(gg)_L$	0		
$(pp)_{Kr_{12}}(ss)_L$	83 426	$(ss)_K(pp)_{Lr_{34}}$	543
$(pp)_{Kr_{12}}(pp)_L$	2236	$(pp)_K(pp)_{Lr_{34}}$	44
$(pp)_{Kr_{12}}(dd)_L$	4	$(dd)_K(pp)_{Lr_{34}}$	123
		$(ff)_K(pp)_{Lr_{34}}$	3
$(dd)_{Kr_{12}}(ss)_L$	15	$(ss)_K(dd)_{Lr_{34}}$	27
$(dd)_{Kr_{12}}(pp)_L$	6	$(pp)_K(dd)_{Lr_{34}}$	4

will be needed to find the best combination of CSFs and orbital parameters upon which to base a much larger so-called “full, complete expansion.” It should be noted that the present calculations are very computationally expensive with the  $H$  and  $S$  matrix element build step taking an order of magnitude longer than the eigenvalue solve step. This is due to the complete dominance of the four-electron integral computation time (by a factor of 100 or more) over the time required for all other integrals. Fortunately, substantial improvements are possible in both the four-electron integral package and in the eigenvalue routines currently being used. Ideally these improved codes will lead to more efficient computational access to not only the ground state of Be, but to excited states (both  $S$  and non- $S$ , singlet and triplet) as well as Be-like ions.

## V. CONCLUSION

The ability of Hy-CI calculations to achieve 0.1-microhartree accuracy for beryllium is shown in this work. The convergence of  $r_{12}r_{34}$  term types has been investigated, and Hy-CI appears to accurately represent this term type, although more research is needed on this point. Given the close relationship between Hy-CI and Hy calculations when the Hy expansion terms contain at most a single odd power of  $r_{ij}$ , it should be possible using Hy expansions to achieve comparable accuracy for beryllium without using the odd-odd power products of  $r_{ij}$ , which leads to severe integral problems in Hy calculations for four or more electrons. Thus even though the present results are preliminary, they significantly advance prospects for accurate Hy-CI calculations on four or more electron atoms<sup>1</sup>. For Hy-CI calculations to go beyond the 0.1-microhartree accuracy achieved in this work, further research is needed on  $r_{12}r_{34}$  representation, more flexible atomic orbital basis sets, and better CSF filtering techniques to control expansion lengths.

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## APPENDIX: PROJECTION REDUCTION

In the generalized eigenvalue problem  $\mathbf{HC} = \lambda\mathbf{SC}$ , matrix element  $H_{KL}$  is

$$H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle = \langle \Lambda \Phi_K^P | \mathcal{H} | \Lambda \Phi_L^P \rangle, \quad (\text{A1})$$

<sup>1</sup>An extension of Hy-CI to the five-electron boron case is underway [32].

where  $\Phi_K^P$  denotes the  $K$ th primitive (unprojected) function  $r_{ij}^{v_K} \prod_{s=1}^4 \{\phi_{K_s}(\mathbf{r}_s)\} \Theta_K$ .  $S_{KL}$  is similar, with  $\mathcal{H}$  replaced by the unit operator 1.

Now notice that

$$\begin{aligned} N!O_{\text{as}} &= \sum_P (-1)^P P \\ &= \left( \sum_u (-1)^u P_u^\alpha \right) \left( \sum_v (-1)^v P_v^\beta \right) + \sum_\gamma (-1)^\gamma P_\gamma^{\alpha\beta} \\ &= \mathcal{A}^\alpha \mathcal{A}^\beta + \mathcal{A}^{\alpha\beta}, \end{aligned} \quad (\text{A2})$$

where  $N$  is the number of electrons,  $P^\alpha$  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  $\mathcal{A}^\alpha \mathcal{A}^\beta$  since permutations between  $\alpha$  and  $\beta$  give zero results when integrating over spin.

In our case  $\Theta_K = \Theta_L = \Theta_1 = \alpha(1)\beta(2)\alpha(3)\beta(4) = \alpha\beta\alpha\beta$ , so we can write

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

where  $g_K = r_{ij}^{v_K}$  and  $f_K$  is the Hartree product  $\prod_{s=1}^4 \phi_{K_s}(\mathbf{r}_s)$ . Using the quantum-mechanical “turnover rule” [33], the commutativity of  $\Lambda$  and  $\mathcal{H}$ , and the idempotency condition  $\Lambda^\dagger \Lambda = \Lambda$ ,  $H_{KL}$  reduces to

$$H_{KL} = \langle \Lambda \Phi_K^P | \mathcal{H} | \Lambda \Phi_L^P \rangle. \quad (\text{A4})$$

Projecting on  $\Theta_1$  with the Löwdin spin projection operator [24]  $O_{S,M_S}(S=0, M_S=0)$ , we get

$$\begin{aligned} O_{S,M_S} \Theta_1 &= O_{S,M_S} \alpha\beta\alpha\beta \\ &= \frac{1}{3} \alpha\beta\alpha\beta - \frac{1}{6} (\alpha\alpha\beta\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\beta\alpha\alpha) \\ &\quad + \frac{1}{3} \beta\alpha\beta\alpha, \end{aligned} \quad (\text{A5})$$

where the subscripts (not shown) on the  $\alpha$  and  $\beta$  are always in the order 1,2,3,4.

This can be written

$$O_{S,M_S} \Theta_1 = \left( \frac{1}{3} - \frac{1}{6} (P_{23}^\sigma + P_{34}^\sigma + P_{12}^\sigma + P_{14}^\sigma) + \frac{1}{3} P_{12}^\sigma P_{34}^\sigma \right) \Theta_1, \quad (\text{A6})$$

where  $P^\sigma$  is used to denote permutations over spin coordinates ( $P^r$  will be used later to denote permutations over spatial coordinates). Using the identity

$$O_{\text{as}} = (-1)^P O_{\text{as}} (P^r P^\sigma)^{-1}, \quad (\text{A7})$$

$H_{KL}$  becomes

$$\begin{aligned} H_{KL} &= \langle f_K g_K \Theta_1 | \mathcal{H} | O_{L,M_L} O_{\text{as}} \\ &\quad \times \left( \frac{1}{3} + \frac{1}{6} (P_{23}^r + P_{34}^r + P_{12}^r + P_{14}^r) + \frac{1}{3} P_{12}^r P_{34}^r \right)^r \\ &\quad \times g_L f_L \Theta_1 \rangle. \end{aligned} \quad (\text{A8})$$

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

$$H_{KL} = \langle g_K f_K | \mathcal{H} | \mathcal{A}^\alpha \mathcal{A}^\beta O_{L,M_L} B_r(g_L f_L) \rangle. \quad (\text{A9})$$

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

$$\mathcal{A}^\alpha \mathcal{A}^\beta = (1 - P_{13})(1 - P_{24}), \quad (\text{A10})$$

and

$$B = \frac{1}{3} + \frac{1}{6}(P_{23} + P_{34} + P_{12} + P_{14}) + \frac{1}{3}P_{12}P_{34} \quad (\text{A11})$$

operate on the spatial coordinates.  $r$  has been dropped from the terms in  $B$  since only spatial coordinates remain.

Using Eq. (A11), we obtain for our final expression for  $H_{KL}$

$$H_{KL} = \langle g_K f_K | \mathcal{H} | (1 - P_{13})(1 - P_{24}) O_{L,M_L} B(g_L f_L) \rangle. \quad (\text{A12})$$

In Eq. (A12) one can apply  $O_{L,M_L}$  either before or after applying  $B$ . We first apply the permutations  $B$  to  $g_L f_L$ , then we project on the resulting terms with  $O_{L,M_L}$ . The  $O_{L,M_L}$  projection is applied only on the orbital products since  $g_L = r_{ij}^{v_L}$  commutes with  $O_{L,M_L}$  [5,34].

Depending on the structure of  $g_L f_L$ ,  $(1 - P_{13})(1 - P_{24}) B(g_L f_L)$  may further simplify, and this should be checked before application of  $O_{L,M_L}$ . In practice we routinely swap the bras and kets if doing so will reduce the number of terms on the right-hand side in Eq. (A12) or otherwise simplify the process of assembling matrix elements.

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