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Hylleraas-configuration-interaction nonrelativistic energies for the ^1S ground states of the beryllium isoelectronic sequence

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In a previous work, Sims and Hagstrom ["Hylleraas-configuration-interaction study of the 1 ^1S ground state of neutral beryllium," Phys. Rev. A **83**, 032518 (2011)] reported Hylleraas-configuration-interaction (Hy-CI) method variational calculations for the ^1S ground state of neutral beryllium with an estimated accuracy of a tenth of a microhartree. In this work, the calculations have been extended to higher accuracy and, by simple scaling of the orbital exponents, to the entire Be 2 ^1S isoelectronic sequence. The best nonrelativistic energies for Be, B^+, and C^{++} obtained are −14.6673 5649 269, −24.3488 8446 36, and −36.5348 5236 25 hartree, respectively. Except for Be, all computed nonrelativistic energies are superior to the known reference energies for these states.
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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 and a test of theories. We recently contributed to this discussion by presenting results from a very large Hylleraas-Configuration Interaction (Hy-CI) calculation (over 40000 symmetry adapted expansion functions) of the beryllium ground ^1S state.[1] The purpose of this paper is to extend this calculation to the ground ^1S state of all beryllium-like ions, i.e., to the entire Be 2 ^1S isoelectronic sequence. Li^-, although a four electron system also, has a decidedly different electronic structure and is not included in the subsequent discussions.

The importance of the correlation of electronic motion for an accurate determination of atomic and molecular problems has long been recognized. From a computational point of view, the central problem is how to build electron-electron correlation into wave functions. A measure of the effectiveness of this correlation is the electron correlation energy, which has been most commonly defined as the difference between the exact nonrelativistic (NR) energy of the system and the Hartree-Fock energy.[2,3] Therefore accurate and dependable compilations of nonrelativistic atomic total energies are useful calibration points for the development of more sophisticated models used in electronic structure calculations.[4–8] For example, density functional theory uses correlation energies (McCarthy and Thakkar[9] compute closed-shell atom correlation energies from Z = 19 through Z = 86) for the evaluation and parameterization of nonrelativistic density functionals.[9,10] They are also useful as a starting point for more electron atoms by giving an accurate 4-electron core. In addition, the calculation of physical energies of interest, e.g., a transition energy or familiar chemical ionization potentials or electron affinities, involves these nonrelativistic energies. So the nonrelativistic energies need to be calculated accurately to guarantee the accuracy of the result, and hence can be regarded as fundamental atomic data (see, for example, the excellent recent reviews of their high accuracy work including corrections for relativistic and QED effects by Adamowicz and co-workers[11,12] or the recent high accuracy results for Be of Puchalski, Komasa, and Pachucki[13,14]).

The total nonrelativistic, stationary-point-nucleus energy, $E(N, Z)$, is defined as the exact solution (eigenvalue) of the nonrelativistic Hamiltonian H_{NR} defined as

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

in atomic units (the atomic unit of energy, the hartree (h), is chosen as $\frac{\mu e^4}{\hbar^2}$ with $\mu = m_e m_N/(m_e + m_N)$).

Here $\mathcal{H}_i = T_i + V_i$, $\mathcal{H}_i$ being a one electron operator (electron i) consisting of a kinetic energy part $T_i = -1/2\nabla_i^2$ and a nuclear attraction part $V_i = -Z/r_i$. N denotes the number of electrons ($N = 4$ for beryllium-like ions) and Z the corresponding nuclear charge.

For N electrons, the time-independent, nonrelativistic Schrödinger equation is then

$$H_{NR}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = E(N, Z)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N). \tag{2}$$

Partitioning the Hamiltonian in Eq. (1) into H_0 and H_1, where

$$H_0 = \sum_{i=1}^{N} \mathcal{H}_i \tag{3}$$

and

$$H_1 = \sum_{i<j}^{N} r_{ij}^{-1}, \tag{4}$$

one may show, by treating H_1 as a perturbation term and expanding the resulting total nonrelativistic energy, that $E(N, Z)/Z^2$ can be expanded in a formal Laurent sequence in Z^{-1}[13,5,15–17] from which one obtains the formal expression

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for $E(Z)$,

$$E(Z) = b_2 Z^2 + b_1 Z + a_0 + a_1 Z^{-1} + a_2 Z^{-2} + a_3 Z^{-3} + \ldots \tag{5}$$

where, since $N = 4$ for all of the ions in this study, the dependence of E on N is suppressed.

In earlier studies, Rayleigh-Schrödinger perturbation theory Z^{-1} expansions, which are a special case of the more general infinite series representation of $E(Z)$ given by Eq. (5), have been used to evaluate the energies of two-electron ions by Dalgarno and co-workers (for a review, see Ref. 18). Three-electron ions have been treated by Yan, Tambasco and Drake,[16] who discuss two different perturbation procedures for determining the energy coefficients in Eq. (5) and give nonrelativistic energy results for the Li ground ^{2}S state for Z = [15, 50] which have an estimated accuracy ranging from 6 decimal places (Z = 15) to 7 decimal places (for Z = 50). At the four-electron level, the studies of various members of the four-electron isoelectronic sequence include the work of Watson and ONeill,[19] who do a perturbative treatment to obtain energy expansion coefficients through order 10. However, the eigenvalues obtained with their equations understandably do not compete with the more refined calculations of Chung, Zhu, and Wang[20] and Clementi and co-workers.[21] The renormalization procedure of Kais, Sung, and Hershbach,[22] while not as accurate as the more refined calculations (see Table I), has proven useful in providing trial energies needed by our inverse iteration eigensolver, as will be discussed later.

Instead of perturbative expansion techniques which have not been particularly successful (certainly not in the 4 electron case), Frolov and Wardlaw[17,23] and Davidson and co-workers (who have done the most extensive work[4–7]) use least squares fits to obtain some or all of the coefficients of the powers of Z in Eq. (5). Frolov and Wardlaw's treatment is the most accurate previous treatment of a small part of the sequence (Z = [3, 12]) using explicitly correlated Gaussians (ECGs), but it is nowhere as extensive or accurate (their accuracy is 4-5 decimals) as the present treatment which covers the full range of Z from 4 to 113. The focus is on Z = [4, 48] with [49, 113] mostly of academic interest. In the case of Be, Chakravorty *et al.*[5] have pointed out that the leading coefficients of the complete-active-valence-space multiconfiguration Hartree-Fock (MCHF) expansion will give the correct b_2 and b_1 in the energy expansion Eq. (5). Using the Chakravorty *et al.* b_2 and b_1 values, we calculate a suitable number of $E(Z)$ values and predict/interpolate the rest using a suitable least squares derived fitting polynomial in 1/Z (see Eq. (5)) to obtain rather accurate nonrelativistic total energies for the entire Be 2 ^1S isoelectronic sequence.

TABLE I. Hy-CI results for the Be isoelectronic sequence ground state energies in hartrees (see Ref. 25 for the orbital exponents used). All energies in column 3 are variational using the 38,253 term CSF basis in Table I in Ref. 25.

Z	System	Energy	Reference	Reference 4	Reference 5
4	Be	− 14.6673 5640 7951	−14.6673 5649 49[13]		
5	B^+	− 24.3488 8438 1902	−24.3488 8444 6[41]		
6	C^{++}	− 36.5348 5228 5202	−36.5348 5233 8[42]		
7	N^{3+}	− 51.2227 1261 6143	−51.2227 083[44]	− 51.2228 2	− 51.2228 4
8	O^{4+}	− 68.4115 4165 7589	−68.4115 353[44]	− 68.4117 0	− 68.4117 1
9	F^{5+}	− 88.1009 2767 6354	−88.1009 188[44]	− 88.1011 4	− 88.1011 3
10	Ne^{6+}	− 110.2906 6107 0069	−110.2906 60[45]	− 110.2909 2	− 110.2908 9
11	Na^{7+}	− 134.9806 2460 4257	−134.9809[22]	− 134.9809 2	− 134.9808 8
12	Mg^{8+}	− 162.1707 4790 6692	−162.1711[22]	− 162.1710 8	− 162.1710 2
13	Al^{9+}	− 191.8609 8633 8262	−191.8613[22]	− 191.8613 5	− 191.8612 7
14	Si^{10+}	− 224.0513 1029 8012	−224.0517[22]	− 224.0517 0	− 224.0516 0
15	P^{11+}	− 258.7416 9942 7160	−258.7421[22]	− 258.7421 2	− 258.7420 0
16	S^{12+}	− 295.9321 3928 8646	−295.9326[22]	− 295.9325 8	− 295.9324 4
17	Cl^{13+}	− 335.6226 1937 5075	−335.6231[22]	− 335.6230 8	− 335.6229 3
18	Ar^{14+}	− 377.8131 3186 6050	−377.8130 93[45]	− 377.8136 1	− 377.8134 4
19	K^{15+}	− 422.5036 7082 6658	−422.5042[22]	− 422.5041 7	− 422.5039 8
20	Ca^{16+}	− 469.6942 3167 5265	−469.6947[22]	− 469.6947 4	− 469.6945 5
21	Sc^{17+}	− 519.3848 1082 1074			− 519.3851 3
22	Ti^{18+}	− 571.5754 0541 1671			− 571.5757 2
23	V^{19+}	− 626.2660 1315 3662			− 626.2663 3
24	Cr^{20+}	− 683.4566 3218 2920			− 683.4569 5
25	Mn^{21+}	− 743.1472 6096 9064			− 743.1475 8
26	Fe^{22+}	− 805.3378 9824 5040			− 805.3382 2
27	Co^{23+}	− 870.0285 4295 1686			− 870.0288 6
28	Ni^{24+}	− 937.2191 9419 9135			− 937.2195 1
30	Zn^{26+}	− 1079.1005 1340 7098	−1079.1001[21]		
36	Kr^{32+}	− 1564.7445 6819 8454	−1564.7441[21]		

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II. VARIATIONAL CALCULATIONS

The Hy-CI wave function for four electron states is

$$\Psi = \sum_{K=1}^{N} C_K \Phi_K, \tag{6}$$

where

$$\Phi_K = \Lambda\left(r_{ij}^{\nu_K} \prod_{s=1}^{4} \{\phi_{K_s}(\mathbf{r_s})\}\Theta_K\right)$$
$$= O_{as} O_{L,M_L} O_{S,M_S}\left(r_{ij}^{\nu_K} \prod_{s=1}^{4} \{\phi_{K_s}(\mathbf{r_s})\}\Theta_K\right) \tag{7}$$

denotes the Kth antisymmetrized spin and angular momentum projected configuration state function (CSF) (term in the wave function). 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 ν_K equal to 0 or 1, with $\nu_K = 0$ the CI case. Θ_K is a primitive spin product function for term K and $\phi_{K_s}(\mathbf{r_s})$ represents the sth basis orbital in the Kth term. The basis orbitals are taken to be un-normalized Slater-type orbitals (STOs) which are defined in the supplementary material.[25] 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 $\Theta_1 = \alpha\beta\alpha\beta$ product. Similar observations have been made by Larsson[26] and by Sims and Hagstrom[27] for Li, and by Sims and Hagstrom[28] for Be. Cencek and Rychlewski[29] 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. As has been pointed out by King,[30] the second spin function can be important for computing precise values of properties other than the energy, like hyperfine coupling constants[26,31–33] and spin-dependent expectation values like the Fermi contact term.[26,34,35] This issue has been extensively studied recently by Wang *et al.*[36]

The coefficients C_K in Eq. (6) 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. The nonrelativistic Hamiltonian $\mathbf{H}$ is given by Eq. (1). Quadruple precision is used in this work, and as in previous recent work,[1,27,37–39] the Message Passing Interface Standard (MPI)[40] is used to parallelize the code.

The configuration state functions (CSFs) given by Eq. (7) can be written as

$$\Phi_K = \Lambda(F_K(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4})\Theta_K) \tag{8}$$

in terms of spatial and spin functions $F_K(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4})$ and Θ_K. Only one spin function $\Theta_K = \Theta_1 = \alpha\beta\alpha\beta$ is used in this work and the spatial part of the wave function $F_K(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4})$ is given by a particular choice of r_{ij} factor and Hartree orbital product

$$F_K(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) = r_{ij}^{\nu_K} \prod_{s=1}^{4} \{\phi_{Ks}(\mathbf{r_s})\}, \tag{9}$$

where ν_K is either 0 or 1. Table I in Ref. 25 lists the CSF basis used in the initial calculations in this work. This CSF basis is based on previous work on the beryllium ground state;[1] the 38,253 $s, p, d, f r_{ij}$ CSF wave function used here was chosen to give the beryllium ground state energy to 7 decimal places (see Table I in Sec. III for reference energies). The STO orbital exponents used in this work for the Be ground state are given in Ref. 25. For the rest of the isoelectronic sequence orbital exponents were obtained by Z/4 scaling, a procedure which works quite well, as will be shown.

Parallel processing is an important aspect of these calculations, with the number of processors used varying from 128 to 256 with 192 being typical. This is not large by current standards and scaling to more processors with the current code would be feasible on a routine basis provided one can be assured of adequate resources per process. 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 existence of a very large number of four-electron integrals. For large expansion lengths N the ratio of matrix element build to eigenvalue solve times was typically about 20 to 1 using an efficient solver (inverse iteration) but relatively inefficient integral and matrix element packages. Inverse iteration scales as expected. In the previous work,[1] matrix element build scaled rather poorly due to the use of column partitioning of the H and S matrices rather than a more efficient block partitioning used in this work. In this work, the computation of all blocks is timed, and then in subsequent runs this information may be used to effect an optimal assignment of blocks to the various processors to equalize the load on each processor as much as possible (and hence to load-level). In this way, armed with knowledge of the computational cost of the different types of blocks, it is possible to efficiently distribute the load and achieve almost perfect theoretical scaling for the matrix element build part of the calculation (e.g., speedups of 127 on 128 processors were routinely predicted).

III. BERYLLIUM ISOELECTRONIC SEQUENCE

Table I shows the 38,253 term computed result for the ground state of Be and compares it with the recent high accuracy determination of Pulchalski, Komasa, and Pachucki[13] using ECGs, a result of nanohartree accuracy. From this comparison, it can be seen that the 38,253 term wave function has achieved 7 decimal place accuracy. The energies of the next two members of the Be isoelectronic sequence, B^+ and C^{++}, are computed simply by scaling all orbital exponents by Z/4 (the ratio of nuclear charges since Z = 4 for Be) and using the same 38,253 terms in the wave function. Comparing the results in column 3 to the high quality results of Adamowicz and co-workers[41,42] in column 4 shows that simply scaling all orbital exponents by Z/4 again results in an error of at most 1 in the seventh decimal place. Next the remaining members of the Be isoelectronic sequence listed in Table I were computed by the same procedure. Computed energies listed in column 3 are compared with reference values listed in columns 4–6, from which it is clear that the computed energies (except for the first three) are already superior to the known reference energies for these states.

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One complication is that using inverse iteration to solve the generalized eigenvalue problem requires an estimate of the desired eigenvalue. Reference values listed in columns 4–6 are of sufficient accuracy for this work. However, to continue on to higher Z, fairly accurate starting values are needed. These can be obtained by least squares fitting the known energy values over some specified Z-range, then extrapolating to estimate the energy E(Z) for some Z value outside the Z-range used to obtain the fitting polynomial. Calculate the new E(Z) and add it to the list of known energies and repeat the least squares fit, thus bootstrapping up to higher Z. This process is readily automated. E(38,253) values given in Table IV of Ref. 25 for $Z \geq 28$, $\Delta Z = 5$ were obtained in this way. Although not shown here, a total of 66 different NR energies were calculated to effectively cover the entire range of $Z = [4, 113]$ at the 38,53 expansion level, which were not particularly big calculations with the current code. Our least squares data fitting was done using QR factorization (subroutine DQRLS[43]). After least squares fitting, the predicted energies match the computed energies (data points) to much better than 7 decimal places, as expected.

To improve the results, the (Be) wave function was extended to 52,405 terms. This was accomplished by expanding the atomic orbitals (AOs) to both include higher powers, e.g., $9p_K$ and $9p_L$, and a different orbital exponent in the case of the p_{K2} AOs, and by changing the threshold used to determine which term types to include in the final wave function. In our earlier work,[1] the threshold was 5 nanohartrees. In this work, the threshold has been lowered to 0.25 nanohartrees, with many more smaller energy improvement blocks included in the 52,405 term expansion than in the 38,253 term case. An additional improvement introduced in this work was the treatment of degenerate states. In this work, all CSF types which give rise to only ^{1}S states are separately entered and projected, but only the ones greater than the 0.25 nh threshold were included in the final expansion, thereby keeping the overall size of the expansion down. The 52,405 term expansion given in Table II of Ref. 25, the net effect of all these changes, is a 57 nh improvement over the 38,253 term expansion and a 54 nh improvement over our best previous Be result.[1] The computed energy values for 26 values of Z are shown in Table IV of Ref. 25 and compared with the corresponding 38,253 term results.

In Table IV of Ref. 25, there are five 52,405 term energies which are labelled predicted energies. These entries are all ones for which energies have been computed for all expansion lengths but 52,405. One can form the energy difference for all systems for which both a 52,405 term expansion and a 38,253 term expansion exists, and then perform a least squares fit of the energy differences to come up with predicted energy differences for the Z values which are missing a 52,405 term calculated energy. Adding these differences to the 38,253 term energies gives "predicted" E(52,405,Z) values marked (P). The agreement between these "predicted" values and the least squares interpolated values is very good, sub-nanohartree accuracy being achieved.

Next the (Be) wave function was extended to 79,137 terms by lowering the cutoff to 0.025 nh (and in some cases raising r-sum to 20). The 79,137 term expansion is given in Table III of Ref. 25, and the computed energy values for 16 values of Z are shown in Table IV of Ref. 25 and compared with the corresponding 52,405 term results. Due to a basis set limitation which has forced us to add the *gg* terms in as a border at the end of the calculation, we ended up with separate 79,137 term and 80,073 term results. We are currently working on removing this restriction in our code.

To generate the final energies in Table IV of Ref. 25, calculated and predicted, the procedure used was the same one used for 52,405 energies, with one exception. The computed Ne6+ energy, −110.2906 6112 2441 nh, caused problems with the 79,137 − 52,405 expansion difference set. So we did not use it in predicting the extra 79,137 data points. We then interpolated from the resulting 79,137 data points (all of them) to obtain the interpolated Ne6+ data point in the table (the Ne6+ problem proved to be particularly vexing and remains under investigation). 80,073 − 79,137 expansion energy differences were then computed for all the data points in the table, including the interpolated data point, to give the "predicted" E(80,073,Z) values marked (P). Again these "predicted" values are very close to what one gets by interpolation of the 80,073 data points themselves.

Our previous 41,871 term result[1] was fully 75 nanohartrees above the best ECG result at the time, that of Stanke *et al.*[46] Our current best 80,073 expansion result is 15 nanohartrees below the Stanke *et al.*[46] calculation, and is bettered only by the recent ECG result of Puchalski, Komasa, and Pachucki[13] which is 2.3 nh better than our 80,073 expansion result (we compare with their computed variational upper bound to the NR energy, rather than their extrapolation based on convergence estimates given in the table in this reference as well as in their later publication[14]). We stopped at the 80,073 expansion level because of computer code basis set limitations and long computation times. Doing substantially better will require greater flexibility in the atomic orbital basis, including adding *hh* and possibly *ii* blocks, better CSF filtering to reduce the expansion lengths, and extensive experimentation to find the best combination of CSFs and orbitals on which to base a much larger so-called "full complete (benchmark) calculation."

Returning to Eq. (5),

$$E(Z) = -5/4Z^2 + 1.5592\,7420\,8401\,256Z + a_0 + a_1 Z^{-1} + a_2 Z^{-2} + a_3 Z^{-3} + \dots . \tag{10}$$

Our final result for the Be ^1S ground state isoelectronic sequence is given both as a single polynomial and as a three polynomial piece-wise fit in Table II where the powers Z^{-n} and the coefficients a_n are given for the polynomials making up both the single polynomial and the piece-wise fit (the data used for the fits is the 80,073 column in Table IV in Ref. 25). The coefficients in the table are given to the number of digits needed to reproduce the input data points to a few units in the 10th decimal place (Table VI in Ref. 25 gives the same table with all coefficients to full precision). The predictions obtained using these formulas are excellent (to a few tenths of a nanohartree when comparing with what one gets when a data point is dropped), unless the dropped point is for Z = 4, 5, or 6 where the differences are at the nanohartree level. A

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TABLE II. Coefficients for several piecewise Z^{-1} least square polynomial fits (see Eq. (10)) for the 80,073 CSF energy values in Table IV of Ref. 25. R_{max} is the maximum Residual.

	Z = [4, 113]	Z = [4, 18]	Z = [18, 48]	Z = [48, 113]
n	a_n	a_n	a_n	a_n
0	−0.8771 1915 78	−0.8771 1949 34	−0.8771 1919 353	−0.8771 1914 341
1	−0.0423 7633 89	−0.0423 4710 9	−0.0423 7082	−0.0423 8063 1
2	−0.1799 0117	−0.1809 9525 1	−0.1802 323	−0.1794 4031
3	−0.2069 4606	−0.1838 4291	−0.1972 96	−0.2279 2379
4	−0.3269 205	−0.6304 2234	−0.4645 8	
5	−0.8248 732	+1.7497 245		
6	+1.7840 76	−12.3336 573		
7	−16.9370 66	+31.3668 028		
8	+47.0175 21	−46.6461 677		
9	−78.4839 48			
R_{max}	0.88×10^{-10}	0.62×10^{-10}	0.74×10^{-10}	0.10×10^{-9}

detailed look at how things vary in this range is an avenue for future research to determine whether this is due to the shell structure, distribution of the correlation energies, or perhaps the "double cusp."

Table III gives both calculated nonrelativistic energies and predicted energies for Z ranges [4, 18] and [18, 48] (the whole Z range [4, 113] is given in Table VII in Ref. 25). By inspecting the table, one can see both the data points and the gaps for these two ranges. Using subroutine DQRLS, a best fit is obtained by varying the range and the order of the Z^{-1} expansion. The particular measure of the goodness of the fit used here is just the maximum Residual (maximum Difference in the table), which is better than 10^{-9} hartree for all the fits.

The 80,073 term results given in the last column of Table IV of Ref. 25 and by the piece-wise fit given by Eq. (10) with the coefficients tabulated in Table II are estimated to be good to 8 or probably 9 decimal places. The consistency of the fits is much better than 8 decimal places, but how accurate the energies are ultimately depends on how accurate the Be energy is. We are within 2.3 nh of the ECG best value of Pulchalski, Komasa, and Pachucki.[13] Those authors estimate that they are within 3 nh of the exact NR energy, but to really estimate this error will require a so-called "full, complete" expansion. However, it should be clear that the prescription that we have detailed has produced nonrelativistic energies for the whole isoelectronic sequence good to 10 nanohartrees or better.

Additional support for the 10 nanohartree accuracy claim comes from an additional final optimization of the Be AO orbital basis at the 79,137 term expansion level. We gained approximately −2.372 nh by an additional tedious optimization of the exponents of Be(79,137). Using these optimized orbital exponents and a slightly larger expansion (83,598), our best result for the Be ground state is −14.6673 5649 269 h, which is within 2.3 nh of the best ECG value. Using these new exponents, we scale to get a C++ energy. This then was optimized further to pick up an additional −1.488 nh of energy, giving an improved C++ ground state energy of −36.5348 5236 25 hartree. The new orbital exponents corresponding to the best Be and C++ results are given in Ref. 25. So simple scaling of the orbital exponents of the optimized Be calculation is not sufficient for all Z, but the error is small (on the order of 1–2 nh).

We have previously discussed the Hy-CI restriction of one r_{ij} per CSF. For Li,[27] 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 in the four electron case either. The unlinked $r_{ij}r_{kl}$ (no indices in common) term types, which first occur in the four electron case, are expected to be more important, however, with $r_{12}r_{34}$ 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. One can reason that the $r_{12}r_{34}$ double cusp leads to two convergence problems, $s_K s_K \times r_{12} \times$ [L-shell cluster] and [K-shell cluster] $\times\ s_L s_L \times r_{34}$. In both cases, the cluster is basically a linear combination of pair functions $ss + pp + dd + ff + gg + \ldots$. Reasoning from our experience with He[37] the convergence of each cluster can be very slow as it goes like $1/l^2$. And is very likely the reason for the relatively long expansions and slow convergences in the present calculations. In this connection, generalization of Hy-CI to include odd power unlinked $r_{ij}r_{kl}$ products (no indices in common, a "double-unlinked Hy-CI") would settle the issue, but at the cost of greatly complicating the calculation of matrix elements. Note that Be is the perfect test case for this since there is only one double-unlinked pair product of likely importance, $r_{12}r_{34}$.

To test how well the convergence of the $r_{12}r_{34}$ term type ("double cusp problem") is treated in Hy-CI, the calculations presented in Table V in Ref. 25 were done.

Compared to the slow, cusp-connected convergences in typical CI calculations, this is fast convergence, suggesting that this correlation type can be accurately, albeit slowly, represented within the Hy-CI model. Modifying the Hy-CI model to include unlinked $r_{ij}r_{kl}$ products (no indices in common, a "double-unlinked Hy-CI") is an avenue for future research. In addition there is another problem. Just because the energy contributions get small does not mean one can get by with fewer terms in the pair expansions. This was a surprise in He where the CI calculation was done out to l=20 terms. Five and six orbitals of each l-type were needed

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TABLE III. Calculated 80,073 CSF nonrelativistic energy values and predicted energy values obtained from least squares fits for the piecewise expansions of the Z ranges [4, 18] and [18, 48]. Energies are in hartrees, energy differences are in nanohartrees. Maximum residual for [4, 18] is 0.62×10^{-10} and for [18, 48] is 0.74×10^{-10}.

Z	System	Data E(Z)	Predicted E(Z)	Difference
4	Be	− 14.6673 5649 0770	− 14.6673 5649 0756	− 0.014
5	B^{+}	− 24.3488 8446 3615	− 24.3488 8446 3613	− 0.002
6	C^{++}	− 36.5348 5236 1036	− 36.5348 5236 1034	− 0.002
7	N^{3+}	− 51.2227 1268 5352	− 51.2227 1268 5362	− 0.010
8	O^{4+}	− 68.4115 4172 0832	− 68.4115 4172 0808	−0024
9	F^{5+}	− 88.1009 2773 4599	− 88.1009 2773 4609	− 0.010
10	Ne^{6+}	− 110.2906 6112 4111	− 110.2906 6112 4158	− 0.047
11	Na^{7+}	− 134.9806 2465 4977	− 134.9806 2465 4915	− 0.062
12	Mg^{8+}		− 162.1707 4795 4568	
13	Al^{9+}	− 191.8609 8638 3868	− 191.8609 8638 3877	− 0.009
14	Si^{10+}	− 224.0513 1034 1733	− 224.0513 1034 1763	− 0.030
15	P^{11+}		− 258.7416 9946 9346	
16	S^{12+}	− 295.9321 3932 9531	− 295.9321 3932 9504	− 0.027
17	Cl^{13+}		− 335.6226 1941 4807	
18	Ar^{14+}	− 377.8131 3190 4835	− 377.8131 3190 4842	− 0.007
18	Ar^{14+}	− 377.8131 3190 4835	− 377.8131 3190 4834	− 0.001
19	K^{15+}		− 422.5036 7086 5000	
20	Ca^{16+}		− 469.6942 3171 2927	
21	Sc^{17+}		− 519.3848 1085 8044	
22	Ti^{18+}		− 571.5754 0544 8027	
23	V^{19+}	− 626.2660 1318 9454	− 626.2660 1318 9500	− 0.046
24	Cr^{20+}	− 683.4566 3221 8406	− 683.4566 3221 8332	− 0.074
25	Mn^{21+}	− 743.1472 6100 4233	− 743.1472 6100 4272	− 0.039
26	Fe^{22+}		− 805.3378 9827 9818	
27	Co^{23+}		− 870.0285 4298 6446	
28	Ni^{24+}	− 937.2191 9423 3518	− 937.2191 9423 3468	− 0.050
29	Cu^{25+}		− 1006.9098 5126 6204	
30	Zn^{26+}		− 1079.1005 1344 1099	
31	Ga^{27+}		− 1153.7911 8020 6092	
32	Ge^{28+}	− 1230.9818 5108 4933	− 1230.9818 5108 4986	− 0.053
33	As^{29+}	− 1310.6725 2566 4884	− 1310.6725 2566 4911	− 0.027
34	Se^{30+}		− 1392.8632 0358 6175	
35	Br^{31+}		− 1477.5538 8453 4008	
36	Kr^{32+}		− 1564.7445 6823 1785	
37	Rb^{33+}		− 1654.4352 5443 5447	
38	Sr^{34+}	− 1746.6259 4292 8910	− 1746.6259 4292 8854	− 0.056
39	Y^{35+}		− 1841.3166 3351 9929	
40	Zr^{36+}		− 1938.5073 2603 7400	
41	Nb^{37+}		− 2038.1980 2032 8079	
42	Mo^{38+}		− 2140.3887 1625 4533	
43	Tc^{39+}	− 2245.0794 1369 3116	− 2245.0794 1369 3125	− 0.009
44	Ru^{40+}		− 2352.2701 1253 2325	
45	Rh^{41+}		− 2461.9608 1267 1270	
46	Pd^{42+}		− 2574.1515 1401 8523	
47	Ag^{43+}		− 2688.8422 1649 0998	
48	Cd^{44+}	− 2806.0329 2001 3026	− 2806.0329 2001 3032	− 0.006

to pick up the contribution for a given l. Another g orbital as well as 4 h orbitals and perhaps i orbitals may be needed to get nanohartree accuracy. Thus it appears that while 10 nanohartree accuracy can be achieved without any difficulty, the remaining difficulty with Be can be explained as poor convergence of the $r_{12}r_{34}$ double cusp which can only be explored further rigorously with hh and ii terms, etc.

IV. CONCLUSION

The ability of Hy-CI calculations to achieve 10 nanohartree accuracy for the beryllium ground state isoelectronic sequence 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. Rather ambitious variational calculations are combined with a fitting polynomial of the sort given by Eq. (5) to achieve 10 nanohartree or better accuracy for the entire beryllium ground state isoelectronic sequence. The calculations exemplify the level of accuracy that is now possible with Hy-CI in describing not only the ground state of Be, but also excited states (S and non-S, singlet and triplet) as well as Be-like ions. Such calculations are currently in progress.

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