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REGULAR ARTICLE

Configuration interaction benchmark for Be ground state

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Abstract A set of 432 energy-optimized Slater-type radial orbitals together with spherical harmonics up to $\ell = 30$ is used to approximate the corresponding full configuration interaction (CI) expansion for Be ground state. An analysis of radial and angular patterns of convergence for the energy yields a basis set incompleteness error of 8.7 μhartree of which 85% comes from radial basis truncations for $\ell \le 30$. Select-divide-and-conquer CI (Bunge in J Chem Phys 125:014107, 2006; Bunge and Carbó-Dorca in J Chem Phys 125:014108, 2006) produces an energy upper bound 0.02(1) μhartree above the full CI limit. The energy upper bound $E = -14.6673473$ corrected with these two truncation energy errors yields $E = -14.6673560$ a.u. (Be) in fair agreement with the latest explicitly correlated Gaussian results of $E = -14.66735646$ a.u. (Be). The new methods employed are discussed. It is acknowledged that at this level of accuracy traditional atomic CI has reached a point of diminishing returns. Modifications of conventional (orbital) CI to seek for significantly higher accuracy without altering a strict one-electron orbital formalism are proposed.

Keywords Brown's formula · Configuration interaction · Coupled cluster · Electron correlation · Full CI · Highly correlated wave functions · Be ground state · Schrödinger's equation · Truncation energy error · Variational calculations

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Dedicated to the memory of Professor Jean-Pierre Daudey and published as part of the Daudey Memorial Issue.

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1 Introduction

It is difficult for me to say good-bye to a friend like Jean-Pierre Daudey. As the terrible circumstances surrounding his last years come to mind, strong emotions fill my body. He had to confront a cascade of serious and painful facts in the first years of the present decade. I received his last email on March 2008, showing a radiant Jean-Pierre full of scientific projects. But he was not fully recovered, and science alone proved to be insufficient motivation to carry on.

The present paper deals with nonrelativistic Be ground state: how far can one go in accuracy with present configuration interaction (CI) and computer equipment, a detailed account of the reasons preventing higher accuracy and possible improvements within CI but beyond spherical harmonics.

Three main obstacles limit the accuracy of atomic CI: (i) slow convergence of the radial expansion [1, 2] for a given angular momentum ℓ of the orbital basis, thought to be caused by an indefiniteness of derivatives with respect to r_1 or r_2 in the Legendre series for r_{12}^{-1} when $r_1 = r_2$ [3, 4], (ii) slow convergence of the angular expansions [3, 5] for a given order of excitations relative to a reference configuration due, as we shall see later, to the use of angular orbitals expressed *only* in terms of spherical harmonics, and (iii) slow convergence of the full CI expansion within each excitation level as well as with successive excitation levels, the first one as a consequence of (i) and (ii), and the latter well understood after the connection between CI and coupled cluster expansions was exhibited [6–8]. While not exhausting these issues, particularly the last one, Be ground state provides a higher and desirable bench point (higher than He ground state) to appreciate the landscape of electron correlation [9–11].

An outline of selected CI theory is given in Sect. 2. Section 3 is devoted to strategies to construct radial orbital bases, energy-optimization of very large bases, the calculation of the basis set incompleteness error, and possible improvements.

There remains how to approximate full CI. Following the recent selected CI (SCI) method [8] and its partner, the select-divide-and-conquer (SDC) CI method [12], the full CI list can be truncated a priori before and after evaluation of symmetry eigenfunctions, while corresponding truncation energy errors can be calculated in both instances. The SDC-CI method is reviewed in Sect. 4.

Results and comparisons with previous work are presented in Sect. 5. Conclusions are given in Sect. 6 together with a discussion about promising paths towards greater accuracy.

2 Selected CI theory

Schrödinger's equation

$$H\Psi = E\Psi, \tag{1}$$

can be approximated by a matrix-eigenvalue equation:

$$\mathbf{H}C = E^{\mathrm{FCI}}C, \tag{2}$$

where $\mathbf{H}$ is the representation of H in terms of Slater determinants or N-electron symmetry-eigenfunctions constructed from a given orbital basis. Equation 2 defines the full configuration interaction (CI) method [9] and E^{FCI} is the full CI(FCI) energy. In terms of FCI quantities, the exact eigenvalues E of Eq. 1 can be expressed as:

$$E = E^{\mathrm{FCI}} + \Delta E^{\mathrm{OBI}}, \tag{3}$$

where ΔE^{OBI} is the error due to orbital basis incompleteness [1]. Interest in estimates of ΔE^{OBI} has been revived [13–16]. In atoms, accurate ab initio estimates of ΔE^{OBI} can be obtained [17–19]. ΔE^{OBI} shall be further discussed in Sect. 3. B in connection with the present calculation.

2.1 CI expansion

A general CI wave function can be written as [20, 21]:

$$\Psi = \sum_{K=1}^{K_x}\sum_{g=1}^{g_K} F_{gK}C_{gK}. \tag{4}$$

where K and g label configurations and degenerate elements, respectively, and C_{gK} denotes a CI coefficient. Triply and higher excited configurations can be classified into disconnected and connected ones. Disconnected configurations are those made up of excitations that can be obtained as products of lower-order excitations, whereas connected configurations are all others, viz., $2p^2 3p^2$ is a disconnected configuration while $1s2p3d4f$ is a connected one. F_{gK} is an N-electron symmetry-eigenfunction or configuration-state-function (CSF) expressed as a linear combination of n_K Slater determinants D_{iK},

$$F_{gK} = O(\Gamma,\gamma)\sum_{i=1}^{g} D_{iK}b_i^g = \sum_{i=1}^{n_K} D_{iK}c_i^g, \qquad g = 1,\ldots,g_K, \tag{5}$$

where $O(\Gamma,\gamma)$ is a symmetric projection operator [22, 23] for all pertinent symmetry operators Γ and a given (N-electron) irreducible representation γ [24–27]. Subsequent focus on configurations K rather than CSFs should not distract from the fact that all reported calculations herein use the full range of g_K degenerate elements.

2.2 Selected CI

Full CI work shows that most of the determinantal or configurational space can be dispensed with [28–30], suggesting the consideration of a configuration selection strategy. In fact, FCI methodology developed the other way around: CI perturbing a multiconfigurational wave function selected iteratively, known as CIPSI [31, 32], was the first systematic and efficient approach to selected CI, eventually giving way to a method to approximate FCI itself [33].

(It is pertinent to remark that Jean-Pierre Daudey and Michel Pelissier were the main program developers behind the original CIPSI method. Moreover, Jean Pierre, with his unique dedication and the kind acquiescence of his collaborators at Toulouse, used CIPSI for the first ab initio molecular work beyond Hartree-Fock in Latin America, particularly in applications to catalysis pioneered by Octavio Novaro worldwide [34, 35].)

Systematicity and reliability call for three things:

(i) an a priori selection of configurations [11, 31, 36, 37],
(ii) an a priori estimate of truncation energy errors,
(iii) an a posteriori assessment of all other errors not calculated in (ii).

The recently developed selected CI method [8] together with SDC-CI [12] is the only method available meeting these three requirements.

2.3 Brown's formula for truncation energy errors

Let $\Psi(-F_{gK})$ denote $\mathcal{N}(\Psi - F_{gK}C_{gK})$ where $\mathcal{N}$ is a normalization factor, viz., let us assume that upon deletion of F_{gK} from Ψ, the new wave function $\Psi(-F_{gK})$ has the same remaining expansion coefficients except for renormalization. The energy contribution ΔE_{gK} of F_{gK} can be approximated by:

$$\Delta E_{gK} = \langle\Psi|H|\Psi\rangle - \langle\Psi(-F_{gK})|H|\Psi(-F_{gK})\rangle, \tag{6}$$

which readily yields the Brown formula [40]:

$$\Delta E_{gK} = (E - H_{gK,gK})C_{gK}^2/(1 - C_{gK}^2). \tag{7}$$

In Eq. 7, $E = \langle\Psi|H|\Psi\rangle$. Approximation (7) is particularly good for small values of ΔE_{gK}, viz., for expansion terms F_{gK} eventually to be discarded, for example, for triply and higher excited configurations without limitation in excitation order.

Equation 7 requires previous knowledge of C_{gK} coefficients which can only be obtained *after* making a calculation [41]. Quick prediction of C_{gK}s for each g of a given K is probably hopeless. Fortunately, as recently shown [8], it is possible to approximate configurational B_K coefficients defined below.

First, Eq. 4 is rewritten as:

$$\Psi = \sum_{K=1}^{K_x} G_K B_K, \tag{8}$$

in terms of normalized symmetry-configurations G_K:

$$G_K = N_K \sum_{g=1}^{g_K} F_{gK} C_{gK}, \tag{9}$$

therefore,

$$B_K = \frac{1}{N_K}, \tag{10}$$

$$N_K = \sqrt{1 \Big/ \sum_{g=1}^{g_K} C_{gK}^2}. \tag{11}$$

Similarly as ΔE_{gK} in Eq. 7, ΔE_K for expansion (8) is given by:

$$\Delta E_K = (E - H_{KK})B_K^2/(1 - B_K^2), \tag{12}$$

to be used just for estimating an approximate truncation energy error. The variational calculations are still carried out via Eq. 4 but the selection process targets configurations G_K instead of F_{gK}s whereby the need to predict C_{gK} coefficients is eliminated. Accurate formulas for B_K coefficients of triply and higher excited disconnected configurations have been reported [8].

In sum, the energy contributions of all disconnected configurations K can be assessed a priori before incorporating these K both into the configuration list, and into the wave function after a configuration list is obtained explicitly. Connected configurations are selected differently through a sensitivity analysis. In general, even after a selection process, the CI size may turn out to be too large for a straight treatment of the corresponding matrix eigenvalue equation therefore warranting a CI-by-parts method as described in Sect. 4.

Unlike other orbital correlated methods which show an inexorable M^q cost-dependence with the number of orbitals M, with q usually between 6 and 10, both SCI and CIPSI elude this trap: their only M^q rate-dependence is an M_0^5 step involving the four-index transformation of the two-electron integrals [42–44], where M_0 is the largest among the numbers of symmetry orbitals.

The present SCI method, however, differs from CIPSI and its descendants in the use of the Brown formula [40] (applicable to any N-electron basis function), of variational rather than perturbational origin, thus providing for more accurate truncation energy errors. Also the present selection scheme [8] targets configurations (all degenerate CSFs of a given configuration at once) at any level of excitation, their number being several orders of magnitude smaller than the number of determinants.

3 Orbital bases

The most accurate CI for Be ground state previous to this work used 106 energy-optimized Slater-type (radial) orbitals (STOs) and harmonics up to $\ell = 13$ [18]. The present calculation is considerably larger: 432 energy-optimized STOs, exceeding the number of distinct two-electron integrals by a factor of 276. A total of 7 billion two-electron integrals (calculated in quadruple precision arithmetic but stored in double precision) were needed requiring 55 GB of random access memory (RAM) for quick retrieval during Hamiltonian matrix-element evaluation. In spite of such large number of radial functions the truncations in the radial basis turned out to be the major source of the final energy error.

Orbitals up to $\ell = 30$ were incorporated, exceeding by a factor of 2.3 the $\ell = 13$ limit in previous work; however, since the number of Condon–Shortley coupling coefficients increases as ℓ^5 the number of the latter increased by a factor of 65. As shall be seen later, the truncation of the orbital basis at $\ell = 30$ constitutes the second most important cause of error of the present work.

3.1 Strategies for constructing large radial orbital sets

Let an orthonormal set of radial orbitals $\{R_{i\ell}, i = 1, i_x;\ \ell = 0, \ell_x\}$ be expanded into a normalized primitive set $\{P_{j\ell}, j = 1, j_x;\ \ell = 0, \ell_x\}$:

$$R_{i\ell} = \sum_{j=1}^{j_x} P_{j\ell} a_{ji\ell}. \tag{13}$$

For energy-optimized STOs $j_x = i_x$. Moreover, for double precision arithmetic the magnitude of the coefficients $a_{ji\ell}$ must not exceed 1,000 in order to guarantee sufficient precision in radial two-electron integrals. Likewise, under quadruple precision these magnitudes must not exceed 1 million. In practice, the above imposes limits of 13–16 energy-optimized STOs per ℓ value in double precision and 26–32 STOs in quadruple precision. Larger non-optimized STO bases may be used for sufficiently delocalized bases, however, in such cases, numerical precision collapses upon energy optimization for highly localized states like Be $1s^2 2s^2$.

When using other radial functions like B-splines [45, 46] considerably larger bases are possible, however, energy-optimization for not too large basis size (suitable for full CI purposes) has not been attempted.

In analogy with numerical integration grids of the logarithmic kind [47], a starting basis set for energy optimization may be chosen so that primitive functions are localized having their maximum values on the "integration points".

Let $P_{j\ell}$(R) be a normalized STO,

$$P_{j\ell}(R) = N_{j\ell} R^{n_{j\ell}-1} \exp(-Z_{j\ell} R) \tag{14}$$

where R is given in atomic units. The maximum of $RP_{j\ell}(R)$ occurs at $R = n_{j\ell}/Z_{j\ell}$. The basis set will be localized between R_{in} and R_{out}; $R_{\text{in}} = 0.1$ and $R_{\text{out}} = 2.0$ are suitable starting values for Be ground state and a basis set size with $j_x = 20$; these starting values may be further optimized for each ℓ value. The interval R_{in},R_{out} is subdivided into $j_x{-}1$ subintervals and the j_x points on the logarithmic grid are given by:

$$\begin{gathered} R_j = \exp^{(a+bj)}; \quad j = 1, 2, \ldots, j_x, \\ b = (\log(R_{\text{out}}) - \log(R_{\text{in}}))/(j_x - 1); \quad a = \log(R_{\text{in}}) - b, \end{gathered} \tag{15}$$

yielding the orbital exponents $Z_{j\ell}$,

$$Z_{j\ell} = n_{j\ell}/R_j = n_{j\ell} \exp^{(-(a+bj))}, \tag{16}$$

to be used as a starting point for energy-optimization. Since Be ground state has only a K and an L shell, the quantum numbers $n_{j\ell}$ in (14) may be chosen as

$$n_{j0} = j_x,\ j_x - 2, \ldots, 1,\ j_x - 1,\ j_x - 3, \ldots, 2 \quad (\text{for odd } j_x), \tag{17}$$

$$n_{j0} = j_x - 1,\ j_x - 3, \ldots, 1,\ j_x, j_x - 2, \ldots, 2 \quad (\text{for even } j_x), \tag{18}$$

assuring acceptable numerical stability and 1s and 2s orbitals as inner and outer orbitals, respectively. For $\ell > 0$,

$$\begin{aligned} n_{j\ell} = {} & j_x + \ell - 1,\ j_x + \ell - 3, \ldots, \ell + 2,\ j_x + \ell,\ j_x + \ell \\ & - 2, \ldots, \ell + 1 \quad (\text{for odd } j_x), \end{aligned} \tag{19}$$

$$\begin{aligned} n_{j\ell} = {} & j_x + \ell,\ j_x + \ell - 2, \ldots, \ell + 2,\ j_x + \ell - 1,\ j_x + \ell \\ & - 3, \ldots, \ell + 1 \quad (\text{for even } j_x), \end{aligned} \tag{20}$$

guaranteeing $n_{j_x l}$, which appears to be a suitable choice.

Equation 16 is a generalization of the concept of even-tempered basis functions [48] for arbitary sequences of principal quantum numbers $n_{j\ell}$. Therefore, the STOs given by Eqs. 14–20 will be called generalized even-tempered STOs (GET-STOs).

Once GET-STOs are decided upon, the orbital exponents $Z_{j\ell}$ may be subjected to free variations by a variety of methods and strategies (after which the original basis ceases to be GET-STO). Only one thing should be avoided: energy-optimization of the parameter b of Eq. 16. By doing so, the interval [R_{in}, R_{out}] starts shrinking and the basis set quickly becomes numerically unstable.

3.2 Energy optimization and basis set incompletness error

It was found out that s-type and p-type orbitals need to be optimized together; this is probably due to the near degeneracy between $2s$ and $2p$. A $13s12p$ basis was carefully optimized with full CI (19,904 CSFs and 202,680 Slater determinants). A final $23s24p$ basis was developed by adding all singles and doubles of the HF configuration to the $13s12p$ full CI space. Approximate truncation energy errors were estimated from several calculations including $30s30p$ STOs optimized in various ways.

These $13s12p$ STOs at the singles and doubles level of approximation were used for the optimization of higher harmonic orbitals. The truncation energy error for each harmonic was guessed by calculations with up to 30 STOs for the given harmonic. L shell, intershell ($1s2s$ excitations or I shell) and K shell truncation energy errors were computed separately.

The ℓ composition of the final STO basis is as follows: 23 s-type orbitals, 24 radial functions for $\ell = 1$, 23 for $\ell = 2$ and 3, 22 for $\ell = 4$ and 5, 21 ($\ell = 6,7$), 20 ($\ell = 8,9$), 19 ($\ell = 10$), 18 ($\ell = 11,12$), 17 and successively diminishing by one from $\ell = 13$ through $\ell = 25$, and 5, 4, 3, 2, 1 for $\ell = 26$, 27, 28, 29, and 30, respectively. This composition (or one very similar to it) leads to the lowest possible energy for a maximum allowance of 55 GB of computer RAM; the calculation run on 63.9 GB of RAM, close to the limit of the available node. After exhausting the 26 letters of the alphabet, the last 5 symmetry orbitals ($\ell = 26$–30) are denoted by symbols /, >,),], and }, respectively. The complete set of orbital exponents and principal quantum numbers is available [49].

Basis set truncation energy errors are presented in Table 1. Moving through successive harmonics, a few abrupt changes in corresponding values of truncation energy errors reflect poor energy-optimization.

Table 1 Harmonic contributions to ΔE^{OBI}, in μhartree, for K, I and L shells

ℓ	$-\Delta E$(K)	$-\Delta E$(I)	$-\Delta E$(L)
0	0.08	0.005	0.010
1	0.08	0.010	0.035
2	0.09	0.010	0.065
3	0.09	0.015	0.030
4	0.14	0.015	0.070
5	0.13	0.015	0.060
6	0.17	0.020	0.070
7	0.16	0.025	0.050
8	0.20	0.020	0.060
9	0.18	0.020	0.070
10	0.19	0.020	0.070
11	0.22	0.020	0.060
12	0.19	0.020	0.055
13	0.20	0.025	0.060
14	0.20	0.030	0.060
15	0.21	0.035	0.070
16	0.21	0.035	0.060
17	0.21	0.040	0.080
18	0.21	0.040	0.060
19	0.20	0.035	0.055
20	0.19	0.030	0.060
21	0.18	0.030	0.050
22	0.18	0.025	0.060
23	0.17	0.020	0.050
24	0.17	0.020	0.060
25–26	0.33	0.025	0.080
27–28	0.29	0.025	0.120
29–30	0.19	0.010	0.040
Sum	5.05	0.640	1.670

For the K shell expansion, it is assumed that the truncation energy error for $\ell > 30$ is equal to the corresponding energy error in Be^{2+}. The main difference between Be^{2+} and K-shell Be correlation energies is due to Pauli Principle [50], viz., the absence of orbital 2s in the latter. Thus it is fair to assume that after large ℓ values the corresponding truncation energy errors will coincide.

In Table 2, the angular energy convergence of Be^{2+} is exhibited as a function of the harmonic functions included in the basis set. An $(\ell + 1/2)^{-4}$ angular energy convergence is well established [2, 3]. Using the present basis and fitting angular energy limits to the $(\ell + 1/2)^{-4}$ law, an extrapolated energy $E = -13.6555662973$ a.u.(Be) is obtained, slightly below the exact value $E = -13.6555662384$ [51]. In order not to confuse the reader I have adjusted some angular energy limits to converge towards the exact result, however, the sought result $E(30){-}E(\infty) = 1.34$ μhartree remains unaltered. Adding this result to the 5.05 μhartree from Table 1, a total K-shell energy error of -6.39 μhartree is obtained.

Table 2 Angular convergence for Be^{2+}, energies in a.u.

ℓ	E
5	−13.6553840605
10	−13.6555363593
15	−13.6555565033
20	−13.6555619279
25	−13.6555639659
30	−13.6555648972
35	−13.6555653819
40	−13.6555656585
45	−13.6555658278
50	−13.6555659372
60	−13.6555660624
70	−13.6555661269
80	−13.6555661634
90	−13.6555661856
100	−13.6555661998
120	−13.6555662161
140	−13.6555662244
160	−13.6555662291
180	−13.6555662319
200	−13.6555662337
250	−13.6555662361
300	−13.6555662372
350	−13.6555662377
400	−13.6555662380
450	−13.6555662382
500	−13.6555662383

Over the years, I have heard people questioning the use of the Be^{2+} truncation energy error to estimate the one for Be K-shell, thus permit me to disgress about it, as I now have something concrete to say. The corresponding truncation energy error for Be^{2+} for the current basis set is only -5.40 μhartree instead of the -6.39 μhartree for Be K-shell, suggesting that after correction for Pauli Principle, K-shell truncation energy errors can be predicted from Be^{2+} results with an accuracy not larger than 1 μhartree resulting from subtle differences occurring presumably for not too large values of ℓ.

In Table 3, the results in Tables 1 and 2 are added up to yield a total basis set incompleteness error $\Delta E^{\mathrm{OBI}} = 8.7$ μhartree (neglecting truncation errors for I and L shell expansions beyond $\ell = 30$).

By assuming the same percentual error as for $\ell \leq 30$ a conveniently larger total truncation energy error by 0.4 μhartree is obtained yielding an extrapolated energy in very good agreement with the latest value for the nonrelativistic energy of Be ground state [71]. However, there are strong indications for supposing that I and L shell

Table 3 Estimated basis set incompleteness error ΔE^{OBI}, in μhartree

Characterization	$-\Delta E^{\mathrm{OBI}}$
K shell ($\ell \leq 30$)	5.05
I shell ($\ell \leq 30$)	0.64
L shell ($\ell \leq 30$)	1.67
K shell ($\ell > 30$)	1.34
Total	8.70

expansions for $\ell > 30$ are significantly smaller than 0.4 μhartree; therefore, failure of the present calculation to reproduce the exact eigenvalue to within 0.1 μhartree must be attributed to an intrinsic limitation of the method employed to obtain truncation energy errors.

3.3 Other radial orbitals

Recall that utmost accuracy requires compact orbital bases in order to simplify approximations to the full CI and also to fit two-electron integrals into RAM. Little known is the fact that energy-optimized STOs do as well [18] as natural orbitals [52]. The problem with energy-optimized STOs is that they can be obtained only after difficult and tedious work. Multiconfiguration SCF orbitals show a significantly better radial convergence [53] but they have the inconvenience of being hard to obtain and that their intrinsic precision prevents their use in large basis sets for which quadruple precision is necessary.

Primitive bases are needed with accompanying two-electron integrals that can be evaluated comparatively fast in quadruple precision, and that after straightforward energy-optimization yield better convergence than STOs. This is an open problem and work in this direction is in progress.

4 Select-divide-and-conquer CI

Suppose a target space S is too large for a straight solution of a corresponding matrix eigenproblem. A subdivision into subspaces S_j, ($j = 0, 1, 2, ..., R$) of dimensions $d_0, d_1, ..., d_R$ is carried out. One then proceeds to evaluate a smaller eigenproblem in $S_0 + S_1$ after which the vector coefficients in S_1 are frozen and their contributions to the corresponding matrix are added up as an extra column and row. The resulting matrix, of dimension $d_0 + 1$ is now extended into subspace S_2, and the process is repeated up to the last subspace S_R. Thus formulated, there is no guarantee that the final solutions will exhibit any resemblance with the eigenvalues of the original eigenproblem in S. As recently shown [12], a proper selection of subspaces does allow to keep a close relationship between both eigenproblems.

4.1 Energy threshold $\mathrm{T}^{\mathrm{egy}}$

The Brown formula provides a useful criterion to select disconnected configurations K based on energy thresholds $\mathrm{T}^{\mathrm{egy}}$. The subspaces S_j, ($j = 0,1,2, ..., R$) are partially characterized by:

$$|\Delta E_K| > \mathrm{T}_j^{\mathrm{egy}}, \tag{21}$$

$$\mathrm{T}_0^{\mathrm{egy}} \geq \mathrm{T}_1^{\mathrm{egy}} \geq \mathrm{T}_2^{\mathrm{egy}} \geq \cdots \geq \mathrm{T}_R^{\mathrm{egy}}. \tag{22}$$

4.2 Occupation number threshold T^{on}

Connected configurations are selected according to occupation number thresholds T^{on} based on density matrix concepts. The SDC-CI method requires the correlation orbitals $a,b,c..$ to be approximate natural orbitals [52, 54], viz., eigenfunctions χ_a of the reduced first-order density matrix $\gamma(1,1')$:

$$\gamma(1,1') = \sum n_a \chi_a^*(1)\chi_a(1'), \tag{23}$$

where the n_as are the eigenvalues or occupation numbers.

For each q-excited configuration K the product $P(\mathrm{q}, K)$ of corresponding occupation numbers is given by:

$$P(\mathrm{q},K) = \prod_{i=1}^{\mathrm{q}} n_{K_i}, \tag{24}$$

where K_i represents a correlation natural orbital. The characterization of the subspaces S_j, ($j = 0, 1, 2, ..., R$) is enriched by enforcing:

$$P(\mathrm{q},K) > \mathrm{T}_j^{\mathrm{on}}, \tag{25}$$

$$\mathrm{T}_0^{\mathrm{on}} \geq \mathrm{T}_1^{\mathrm{on}} \geq \mathrm{T}_2^{\mathrm{on}} \geq \cdots \geq \mathrm{T}_R^{\mathrm{on}}. \tag{26}$$

In (25, 26), $\mathrm{T}_j^{\mathrm{on}}$ may be a number or, more generally, a suitable function of some parameters:

$$\mathrm{T}^{\mathrm{on}}() = F_{\mathrm{dh}} F_{\mathrm{con}} 10^{-m\mathrm{q}}, \tag{27}$$

where $F_{\mathrm{dh}} \geq 1$ is a deep-hole factor [8] associated to holes involving inner electrons, and $F_{\mathrm{con}} \geq 1$ is a factor for connected configurations [8]. F_{dh} and F_{con} are introduced to recognize well-characterized families of configurations that are comparatively less important for a given value of $P(\mathrm{q},K)$ [8]. The parameter m is shown explicitly on the LHS of (27) for later purposes. $10^{-m}(F_{\mathrm{dh}}F_{\mathrm{con}})^{\frac{1}{\mathrm{q}}}$ may be interpreted as an average occupation number below which configurations involving that natural orbital are deleted from an original target space S.

4.3 Pseudoenergy threshold $\mathrm{T}^{\mathrm{psegy}}$

Analogous to $\mathrm{T}^{\mathrm{egy}}$, it differs from it in that pseudoenergy contributions ΔpsE_K are calculated as:

$$\Delta psE_K = (E - H_{KK})P(\mathrm{q},K). \tag{28}$$

Pseudoenergies are useful quantities to carry out a selection process particularly for connected configurations but their relationship with actual energies can only be done a posteriori through a sensitivity analysis. These thresholds were introduced specifically for the present calculation and they have become an important ingredient of selected CI [8].

4.4 Harmonic truncation threshold $\mathrm{T}^{\mathrm{har}}$

The subspaces S_j, ($j = 0, 1, 2, \ldots, R$) are also specified by a harmonic truncation threshold $\mathrm{T}_j^{\mathrm{har}}$ indicating that subspace S_j is truncated in the orbital basis after a given harmonic ℓ_j:

$$\mathrm{T}_j^{\mathrm{har}} = \frac{1}{\ell_j}. \tag{29}$$

Resort to a fraction in Eq. 28 is dictated by the rule that first occurring subspaces have larger thresholds than subspaces further down the sequence:

$$\mathrm{T}_0^{\mathrm{har}} \geq \mathrm{T}_1^{\mathrm{har}} \geq \mathrm{T}_2^{\mathrm{har}} \geq \cdots \geq \mathrm{T}_R^{\mathrm{har}}. \tag{30}$$

4.5 Selection strategy

A subspace S_j consists of the following configurations:

(i) All (connected and disconnected) triples with $\mathrm{T}_{j-1}^{\mathrm{on}} \geq P(3,K) \geq \mathrm{T}_j^{\mathrm{on}}$. Here, the occurrence of disconnected triples is due to their carrying connected contributions in the many-body perturbation theory sense [8].
(ii) Of the remaining (disconnected) triples, those with $\mathrm{T}_{j-1}^{\mathrm{egy}} \geq |\Delta E_K| > \mathrm{T}_j^{\mathrm{egy}}$.
(iii) Connected quadruples with $\mathrm{T}_{j-1}^{\mathrm{on}} \geq P(4,K) > \mathrm{T}_j^{\mathrm{on}}$.
(iv) Disconnected quadruples with $\mathrm{T}_{j-1}^{\mathrm{egy}} \geq |\Delta E_K| > \mathrm{T}_j^{\mathrm{egy}}$. Here it is assumed that disconnected quadruples have negligible connected contributions; otherwise, they must also enter in (iii).
(v) Finally, S_j contains configurations with harmonics up to $1/\mathrm{T}_j^{\mathrm{har}}$.

4.6 Comparison with other methods

The concept of CI by parts is not a new one. In an effort to lower the size of multireference (MR) CI expansions, internally contracted MRCI was proposed [38]. Meyer's and similar approaches [11] using perturbation theory estimates of various CI coefficients are the nearest relatives of SDC-CI. These methods achieve large simplifications [39] at the expense of losing control over accuracy.

In SDC-CI, on the other hand, the thresholds and the selection stratetgy defined above allow to control CI by parts in a way that the obtained upper bounds remain sufficiently close to the exact eigenvalues for the corresponding selected space S [12].

5 Results for Be ground state

5.1 Truncations before evaluation of symmetry eigenfunctions

In principle one might be tempted to generate a complete list of CSFs for any given basis set. For very large basis sets, however, this is not a reasonable proposition both in terms of needed CPU time and also due to loss of accuracy for configurations involving many orbitals with very high angular momentum. Thus before evaluation of symmetry eigenfunctions the configuration list was subjected to a pruning controlled by various thresholds and guaranteeing a total truncation energy error less than 10^{-9} a.u. for disconnected configurations and an equivalent truncation error for the set of neglected connected configurations.

5.2 Select-divide-and-conquer CI results

Having an explicit configuration list defining the target space S one proceeds with SDC-CI. Applying SDC-CI demands familiarity with many of thresholds which reminds one of the console of a large automatic industrial device. There are separate thresholds for the free-varying S_0 subspace, for the S_1 subspace that may be treated outside RAM with disk auxiliary memory, and for the S_R subspaces ($R \geq 2$) that take up the vast majority of terms and are processed in RAM. Only the CI coefficients in S_0 are allowed to vary freely in each iteration, while in the other spaces the CI coefficients are frozen after their first variational occurrence. There are thresholds for energy contributions of disconnected configurations and for pseudoenergy contributions of connected ones, and there are also occupation number thresholds for configurations higher than doubly-excited ones, and harmonic thresholds to keep S_0 and S_1 within reasonable size.

Table 4 shows the progress of a SDC-CI calculation through all 39 iterations corresponding to the fourth entry in Table 5. For simplification, iterations with energy lowerings smaller than 2×10^{-9} a.u. have been deleted. With a CI size of 1,919,572, correponding to about 800,000 configurations given in terms of more than 300 million determinants, slightly more than 200 billion matrix elements between CSFs were required. Wall time for running on a single processor of a workstation with AMD Opteron 850 processors and 333 MHz RAM was of 7,577 s. Hamiltonian matrix elements with magnitudes smaller than 2×10^{-9} a.u. were zeroed whence those with magnitudes smaller than 2×10^{-2} were kept in single precision. After

Table 4 Selected-divide-and-conquer CI for Be ground state: iteration number, accumulated CI size, CPU time (s) for Hamiltonian matrix evaluation, and variational energy upper bound

Iteration	Total CI size	CPU time	*E*
1	97,515	51	−14.66734672299
2	148,446	39	−14.66734679016
3	196,828	58	−14.66734680031
4	245,288	75	−14.66734701434
10	541,277	154	−14.66734701889
11	590,360	46	−14.66734704106
12	641,154	87	−14.66734706109
13	691,876	93	−14.66734710282
14	739,097	116	−14.66734710778
15	789,504	131	−14.66734711014
19	988,046	138	−14.66734715029
21	1,083,816	135	−14.66734715529
22	1,133,073	122	−14.66734715948
24	1,232,721	110	−14.66734718050
25	1,279,251	125	−14.66734719056
26	1,328,219	139	−14.66734720870
27	1,378,609	122	−14.66734722610
28	1,424,621	75	−14.66734723409
29	1,472,411	124	−14.66734723649
30	1,521,515	100	−14.66734724497
31	1,570,489	167	−14.66734724882
32	1,621,032	103	−14.66734725132
35	1,766,457	73	−14.66734725904
36	1,811,356	63	−14.66734726706
37	1,861,305	49	−14.66734727858
38	1,912,181	38	−14.66734729451
39	1,919,572	2	−14.66734729668

Table 5 Selected-divide-and-conquer CI for Be ground state for various combinations of selection thresholds A, B, C, D, and E, described in the text; CI size, total CPU time (min), and variational energy upper bound

Thresholds	Total CI size	Total CPU time	*E*
A	727,281	28	−14.66734703669
B	715,574	26	−14.66734721897
C	798,846	30	−14.66734726047
D	1,919,572	126	−14.66734729668
E	18,452,381	5,693	−14.66734734312

the first iteration all CI matrices were of dimension ≤65,536 thus allowing indices of matrix elements to be kept in a two-byte representation (INTEGER*2).

The thresholds A, B, and C used in the first three entries are omitted. A comparison between the thresholds D and E is in order. Always in a.u., both D and E have $T_0^{egy} = 10^{-6}$, $T_1^{egy} = 10^{-10}$, $T_R^{egy} = 10^{-13}$, $T_0^{on} = 10^{-9}$, $T_1^{on} = 10^{-11}$, $T_R^{on} = 10^{-13}$. The thresholds with subindices 0 and 1 guarantee better than μhartree agreement between the exact eigenvalues in *S* and the SDC-CI eigenvalues.

The difference between D and E thresholds lie in the pseudoenergy thresholds, which are $T_0^{psegy} = 10^{-6}$, $T_1^{psegy} = 10^{-8}$, $T_R^{psegy} = 10^{-11}$ in D, while the last two of them are 100-fold smaller in *E*. The energy difference between both calculations is less than 5×10^{-8} a.u. but the difference in calculation effort is staggering: from 2 to 18 million CSFs (from 315 to 5,400 million determinants) and from 2 to 96 h of CPU time. (Compare with 86 million CSFs and 41 billion determinants used in a Ne calculation [8].) In sum, the pseudoenergy thresholds, even if lacking an a priori interpretation, are extremely effective for selecting connected configurations.

5.3 Comparison with previous work

Only CI and CI $- r_{ij}$ variational results will be discussed. Other calculations have been reviewed elsewhere [18, 55].

CI work for Be ground state improved steadily over the years. The CI energies reported in Table 6 are believed to be the best ones at the time within the last fifty years. Watson's wave function [56] inspired a whole generation during the sixties. The decisive improvement of Weiss [57] over Watson [56] came as a result of using optimized

Table 6 Comparison with previous CI energies and also with best variational results using explicit r_{12} factors in the wave functions

Wave function	ℓ_x	Year	*E*
37-term CI [56]	4	1960	−14.65740000
55-term CI [57]	3	1961	−14.66090000
180-term CI [20]	2	1968	−14.66419000
52-term CI [58]	4	1974	−14.66587000
650-term CI [41]	6	1976	−14.66690200
CI [60]	6	1991	−14.66695980
3,381-term CI [62]	9	1993	−14.66711300
212,710-term CI [18]	13	1997	−14.66727500
97,515-term CI (Table 4)	30	2009	−14.66734672
Table 5, result E	30	2009	−14.66734734
28-term r_{ij} [64]	∞	1967	−14.65250000
25-term r_{ij} [65]	∞	1968	−14.65770000
107-term r_{ij} [67]	∞	1971	−14.66654700
913-term r_{ij} [66]	∞	1993	−14.66704341
1,200-term r_{ij} [68]	∞	1995	−14.66735502
1,600-term r_{ij} [69]	∞	2002	−14.66735555
1,600-term r_{ij} [70]	∞	2006	−14.66735575
6,500-term r_{ij} [71]	∞	2007	−14.66735646

The column labeled ℓ_x holds maximum ℓ values used in the wave functions orbital exponents. My own 1968 work [20] was devoid of both orbital exponent optimization and harmonics beyond $\ell = 2$ (the computer program for the general application of projection operators was just beginning to be used for harmonics higher than two, and my energy-optimization codes were in their infancy). Improvements were achieved, however, by using approximate natural orbitals and through a systematic introduction of all CSFs of degenerate configurations by means of projection operators.

Froese-Fischer and Saxena [58] did a wonderful job at optimizing multiconfiguration Hartree-Fock orbitals in 1974, while my 1976 work [41, 59] profited from a general program for large-scale CI and an a posteriori selection scheme based on the Brown formula.

After 15 years, the 1991 work of Clementi et al. [60] used the Sasaki program [61], a large basis of Gaussian orbitals, and featured a comparatively more powerful computer. The crafty 1993 calculation of Froese Fischer [62] went as far as could be done for a code that had yet to be uplifted for large-scale CI. The 1997 work of Jitrik and myself [18] used a program essentially identical to the 1976 program (same subroutine names) except for orders of magnitude more efficient algorithms, particularly the development of formulas [63] for efficient wholesale matrix element evaluation.

In 2001, motivated by the announcement that very cheap and large RAM memories would soon be available, and by the fact that nobody seemed to care for large-scale atomic CI, I developed SCI [8] and SDC-CI [12], the latter together with Ramon Carbó-Dorca. The present calculation resulted as a consequence of applying these improved methods and using the promised very large RAM.

This work on Be ground state was carried out in February–March 2007 motivated by correspondence with Jim Sims and Stanley Hagstrom. Unable to overcome poor radial convergence I became frustrated and left the calculations unpublished. Recently, I repeated the calculations with new basis sets and improved energy-optimization methods but obtained exactly the same results, which stimulated my interest in unconventional CI as discussed in Sect. 6.

In contrast, for four-electron systems, the evolution of methods with r_{ij} terms in the wave function [64, 65] progressed slowly [66] after the classical work of Sims and Hagstrom [67]. Then, in 1995, a landmark publication by Komasa et al. [68] precipitated a sequence of impressively accurate calculations [69–71].

Quantum Monte Carlo (QMC) methods have been progressing quite fast [72] thus it is of interest to find out where in the CI chronology of Table 6 stand QMC Be ground state results. The lowest QMC energy result for Be ground state appears to be that of Brown et al. [73] yielding $E = -14.667328(6)$. Notice that the error bars are meaningless in an absolute sense, viz., an accurate upper bound to the energy [71] is 28 μhartree below the QMC result, well outside the reported bound of 6 μhartree. Nevertheless, in 2007, QMC Be ground state wave functions were superior to CI ones and were only surpassed by the 1995 r_{ij} wave functions of Komasa et al. [68]. Only after the present work does CI perform better than QMC. For Ne ground state, on the other hand, QMC [73] was far behind 1997 CI results [8, 18].

In conclusion, unless modified CI methods are introduced, conventional CI cannot compete in accuracy with r_{ij} methods for four-electron states with two occupied $1s$ orbitals. Beyond four electrons, however, r_{ij} methods have yet to prove their potential. The method by Chung [66], on the other hand, should be amenable of implementation for larger systems, however, large-scale CI capabilities must be incorporated before becoming competitive with present day conventional CI.

6 Conclusions and general discussion

A reliable strategy to energy optimize large basis sets was used. Thanks to SDC-CI [8, 12] the full CI energy could be approximated to within 0.02 μhartree. A set of 432 energy-optimized radial functions with spherical harmonics up to $\ell = 30$ yields a Be ground state full CI energy only 8.7 μhartree above the expected exact energy [71]. These 8.7 μhartree are accounted for by both radial and angular basis set incompleteness, of which only 1.3 μhartree come from the truncation after $\ell = 30$, thus radial orbital truncations constitute by far the largest source of error for a CI on a small and highly localized state like Be $1s^22s^2$. In order to obtain a competitive estimate of the exact Be ground state energy after the impressive work of Stanke et al. [71], a significant reduction of the radial truncation energy error is necessary and I am presently unable to do that.

While increased computer RAM requirements have been met here using a larger computer than in 1997 [18] (of comparable cost, however), it is clear that a point of diminishing returns has been reached even foreseeing vast computer improvements over the next decade. It is true that poor radial convergence might be improved by the use of radial functions better than STOs but then the well-known poor angular convergence [5] will prevent μhartree accuracy. Consequently, increased accuracy through still larger calculations does not appear to be a reasonable approach, particularly having in mind larger atoms.

The reason of this slow convergence with ℓ values was suggested by studies [74, 75] where the Legendre expansion for the Coulomb repulsion was replaced by Taylor series for the cosine of the interparticle angle θ_{12}. A simple numerical exercise shows that this Legendre series itself converges very slowly with ℓ for $\cos\theta_{12}$ values around 1 and -1 and also for r_1 values near those of r_2 [74]. Using spherical harmonics in atomic orbitals up to ℓ_x, the selection rules for the Condon and Shortley coefficients imply that the Legendre series for the electron repulsion is effective up to order $2\ell_x$. Because of the mathematical uniqueness of the integrals involved, this will continue to be true irrespective of whatever series to express r_{12}^{-1} is used. In other words, the Clebsch–Gordan selection rules heralded to simplify the trivial two-electron integral problem ultimately constitute the real cause for slow convergence of atomic CI when spherical harmonics are used to construct basis orbitals.

Of course, spherical harmonics are important to obtain symmetry eigenfunctions and thus are necessary to classify and identify energy states through their various symmetries. However, after enough harmonics are introduced to assure proper state identification, one is not obliged to continue using spherical harmonics for the angular parts. One may use, for example, in addition to spherical harmonics, various powers of the latitudinal angle θ or functions of θ such as $\exp^{(\alpha\ \theta)}$ or $\exp^{\alpha\ \cos\theta}$ with α being a variational parameter. Orthonormalization of the angular basis can be achieved in various ways. N-electron symmetry will be lost to some extent, the more harmonics are retained the less symmetry will be lost, while the newly introduced functions of θ will not interrupt the Legendre series, therefore allowing the wave function “to see” the entire Legendre series without explicit introduction of r_{12} factors.

At this point two options are possible: either the Legendre expansion for r_{12}^{-1} is used up to, say, $\ell = 500$ or even $\ell = 1{,}000$, or a better convergent expansion for r_{12}^{-1} is used. There are two good reasons to replace the Legendre expansion by an expansion in terms of $\cos\theta_{12}$: one is that the latter being more rapidly convergent, the number of necessary powers of cosines is deemed to be inferior than the number of harmonics in the Legendre series for a given prescribed accuracy (the corresponding integrals appear to be equally complicated). The other reason is that the latter expansion is more rapidly convergent in r_1 and r_2 which now participate in a symmetric way. Moreover, the indefiniteness of the derivative with respect to r_1 or r_2 in the Legendre series when $r_1 = r_2$ has disappeared suggesting a more rapid radial convergence mathematically protected from interference by selection rules.

An ingenious modified CI method has been proposed [76] to overcome slow angular convergence. Unfortunately, the method uses correlated angular bases depending on θ_{12} rather than θ_1 and θ_2 thus preventing its straightforward extension to N-electron systems and therefore it should not be called CI.

SDC-CI has been shown here to be a powerful tool to approximate very large full CI expansions involving billions of Slater determinants to within a fraction of one μhartree. For truly many-electron systems, both single-reference and multireference CI are limited to a given number of excitations. At the present stage of the development of SDC-CI theory [8], the introduction of orbital excitations higher than six poses unsolved computational problems. (Because of their greater symmetry, up to eightfold excitations are tractable in atomic calculations).

With increased nuclear charge and number of electrons the error sources reverse in importance, the full CI approximation becoming critical after the middle of the first transition metal period. This is due mainly to the occurrence of very high angular momentum degeneracies for quadruple excitations like $3d^4 \rightarrow 4d^2 4f 5f$ excitations in atomic Ga. (Very high degeneracies in LS symmetry are drastically diminished by resorting to jj-JM symmetry at the expense of a hundredfold increase in CI size.)

Atomic calculations with very large conventional orbital bases require quadruple precision only for the two-electron integrals consuming a relatively small part of total computer resources. Since two-electron integrals for relativistic calculations do require numerical integration and thus significantly more computer time, high accuracy for straight conventional calculations within the relativistic regime may have to await general availability of quadruple precision hardware. Further developments in SDC-CI combined with the foregoing are expected to extend the scope of accurate atomic CI calculations well beyond Ne [8], possibly up to the first few transition metals.

In sum, due to the high degree of accuracy attained by SDC-CI, current pressing needs have moved to search for faster convergent radial atomic orbitals once again, not from the old perspective of using just a few terms but for ambitious accurate basis sets that must inevitably be large ones. On the other hand, angular orbital bases beyond spherical harmonics will be necessary to achieve μhartree and perhaps even subμhartree accuracy. The price to be paid for shortening the CI expansion is having to deal with more complicated two-electron integrals of which the angular parts need to be computed only once for all future atomic calculations. Most of the computer work, therefore, will be in the calculation of an increased number of radial integrals. Work in this direction together with Eugenio Ley-Koo is in progress.

One more thought about Jean-Pierre: we have lost a great human being and a unique quantum chemist. In particular, he is credited with starting in Mexico (and Latin America) the development of quantum chemistry beyond Hartree-Fock. He was also the first one to introduce atomic pseudopotentials into a molecular Hartree-Fock program (HONDO) giving rise to PSHONDO. After he merged PSHONDO with CIPSI, routine use of atomic pseudopotentials in ab initio work taking into account electron correlation was established. I have also lost a close friend, and like so many others who came to love him, we all will keep his many and most affectionate images very much alive in our brains for the rest of our lives.

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