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Reduced First Order Density Matrix for the Be Ground State

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Abstracts

A reduced first order density matrix for the Be ground state is computed from an extensive configuration interaction (CI) wave function. A sequence of increasingly accurate CI wave functions Φ_q converging towards the exact Ψ is used to assess the quality of the results which include approximate bounds for the overlaps $\langle\Phi_q|\Psi\rangle$, electron–nuclear coalescence cusp data, Weinhold's overlap between density matrices, virial ratios, occupation number spectra, and some expectation values. The nuclear magnetic shielding constant and the molar diamagnetic susceptibility are determined with 2.0 and 1.5% of uncertainty, respectively.

Une matrice densité réduite du premier ordre pour l'état fondamental de Be a été calculée d'une fonction d'onde obtenue par une interaction de configurations (CI) élaborée. Une séquence de fonctions d'onde de type CI, Φ_q, qui convergent vers la fonction exacte Ψ, est utilisée pour décrire la qualité des résultats, y inclu des bornes approchées du recouvrement $\langle\Phi_q|\Psi\rangle$, des données pour les "cusps" électron–noyau, le recouvrement de Weinhold entre des matrices densité, des rapports viriels, des spectres de nombres d'occupation et quelques valeurs moyennes. La constante d'écran magnétique nucléaire et la susceptibilité diamagnétique molaire sont déterminées avec des incertitudes de 2.0 et 1.5 pour cent, respectivement.

Eine reduzierte Dichtematrix erster Ordnung für den Grundzustand des Be-Atoms ist von einer umfassenden Konfigurationswechselwirkungsfunktion (CI) berechnet worden. Eine Reihenfolge von zunehmend genauen CI-Funktionen Φ_q, die gegen die exakte Funktion Ψ konvergieren, sind angewandt worden um die Qualität der Ergebnisse zu beschreiben. Die folgenden Eigenschaften sind untersucht worden: angenäherte Schranken für die Überlappungen $\langle\Phi_q|\Psi\rangle$, Kern-Elektron-"Cusps", Weinhold'sche Überlappungen zwischen Dichtematrizen, Virialverhältnisse, Spektren für Besetzungszahlen und einige Erwartungswerte. Die kernmagnetische Abschirmungskonstante und die molare diamagnetische Suszeptibilität sind mit 2.0 und 1.5 v.H. Unsicherheit, bzw. bestimmt worden.

1. Introduction

A reduced first order density matrix for the Be ground state is computed from the most accurate [1] configuration interaction (CI) wave function presently available. Details of the method for the construction of the wave function have been given [2] and the extrapolated energy eigenvalue together with relativistic, radiative, mass polarization, and finite nuclear size effects have been compared with experiment [3].

Because rigorous error bounds to expectation values [4] are usually too large, approximate error bounds are also considered. This requires an assessment of the

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quality of the wave function which is undertaken in Section 2. The eigenvalues of the 1-matrix and some expectation values are presented in Section 3.

The 1-matrix for the Be ground state has been studied with CI wave functions [5]. A direct determination of the 1-matrix via a many-body Green's function has also been reported [6]. The present calculation differs from previous ones in (1) the emphasis that is given to the discussion of the stability of the results, and (2) the use of a much larger orbital basis. The wave function employed accounts for 99.55% of the theoretical correlation energy [2] and the general characteristics of the missing configurations are fairly well understood [1, 2].

One-electron expectation values for the Be ground state have been recently discussed by Banyard and Taylor [7] from the point of view of the nearly additive contributions of K shell, L shell, and intershell pair correlation functions. Their numerical results concerning correlation effects are significantly different from the ones in the present work.

Although both rigorous and reasonable margins of stability for the computed quantities have not been established, the results of this work are believed to be stable for the given orbital basis (i.e., the limited CI results are believed to be stable with respect to the full CI treatment), and as such they may serve as an excellent guide to test recent methods [6, 8] for the direct determination of the 1-matrix.

2. Quality of the Wave Function

The approximate wave function Φ is a 650-term CI series [1]:

$$\Phi = \sum_{m=1}^{650} \varphi_m a_m, \qquad |a_m| > |a_{m+1}| \tag{1}$$

The configuration state functions (CSFS) φ_m are LS eigenfunctions which are classified according to inner electron couplings [1, 9] when degeneracies occur. The orthonormal $10s9p8d7f5g3h1i$ orbital basis consists of approximate natural orbitals (NOS) [10] computed as described in Ref. [2], and expressed as linear combinations of Slater-type orbitals (STOS). The search for the final 650 CSFS is made as follows: (1) all singles and doubles, leading four-excited unlinked CSFS, and major three-excited linked CSFS are included in a primitive trial wave function, (2) CSFS are deleted according to Brown's energy criterion [11] if $|a_m| < 0.0003$ and new CSFS are variationally tried. (The important quadruple excitations turn out to be unlinked clusters and so it is easy to classify them according to predicted partial energy contributions and eigenvector components. The linked three-excited CSFS are arranged in a hierarchy based on occupation numbers of the participating NOS; such an ordering turns out to be approximately correct with regard to partial energy contributions and eigenvector components. Since the basis orbitals are very close to Brueckner orbitals, unlinked triple excitations are for the most part negligible.) The leading terms not included in Φ are CSFS with high harmonic functions not included in the orbital basis such as $1s^2(i_L)^2$ with $a_m^2 \approx 0.00001$. These CSFS interact largely with the reference configuration $1s^22s^2$ and so they affect the other a_m's essentially through renormalization. The energy eigenvalue of Φ, $E = -14.666902$ a.u. (Be), differs from the estimated [2] exact nonrelativistic energy $E_{nr} = -14.667328(25)$ by 30 parts per million.

Information about the quality of Φ can be divided into "field" information obtained in the process of wave function construction (truncation of CSFS, extrapolations, stability of a_m's) and "face value" information, which can be obtained from a knowledge of Φ alone.

By construction, Φ is a very close approximation to the full CI wave function Φ_{FCI} for the given orbital basis, as supported by the following field information: (1) among all possible CSFS, those with $|a_m| > 0.0003$ are believed to be included without exceptions, (2) $\langle\Phi|\Phi_{FCI}\rangle$ is estimated to be greater than 0.999999, see Section 2A, and (3) $E - E_{FCI} = -0.000019(2)$ a.u. [2]. The above considerations constitute the basis of my belief that the results are stable with respect to the full CI treatment.

Face value indicators of wave function quality are considered next. A useful one is the overlap between Φ and the exact Ψ because it can be used directly in the computation of rigorous error bounds to expectation values [4]. Weinhold's overlap between approximate and exact density matrices [4] is also useful. Other quality indicators such as electron–nuclear coalescence cusp data and virial ratios are valuable for diagnosis of specific wave function deficiencies.

A. *Overlap between Φ and Ψ*

A rigorous bound to $S = \langle\Phi|\Psi\rangle$ can be obtained by means of Eckart's criterion [12], which yields $S > 0.99915$. Tighter rigorous bounds require an increased amount of information and the improvement over Eckart's criterion is not significant enough to warrant their calculation [13].

Improved but nonrigorous bounds to S can be obtained by considering a sequence of variational wave functions $\Phi_1, \Phi_2, \Phi_3, \ldots$, converging towards the exact Ψ. Let Φ_{q_r} be the normalized projection of Φ_r on the space spanned by the CFSS of Φ_q. In particular, let $\Phi \equiv \Phi_3$, and for later purposes let us write:

$$\Psi = \alpha_{3\infty}\Phi_{3\infty} + \beta_{3\infty}R_{3\infty} \tag{2}$$

$$\Phi_3 = \alpha_{23}\Phi_{23} + \beta_{23}R_{23} = \alpha_{13}\Phi_{13} + \beta_{13}R_{13} \tag{3}$$

The wave functions Φ_{23} and Φ_{13} are ordered truncations of $\Phi_3 \equiv \Phi$, Eq. (1), with $\beta_{23}^2 = 0.000004$ and $\beta_{13}^2 = 0.000008$; Φ_2 and Φ_1 are the variational counterparts.

The main properties of the approximate wave functions are summarized in Table I: (1) the energy eigenvalues are accurate to all figures reported, (2) the lower bounds to $S_q = \langle\Phi_q|\Psi\rangle$ are found by Eckart's criterion using an extrapolated energy eigenvalue $E = -14.667328(25)$ a.u. (Be) [2] and the experimental energy difference [14] between the ground state and the first excited state of the same symmetry (the difference between corresponding relativistic and radiative corrections is negligible in the present context).

The lower bounds $S_2^<$ and $S_1^<$ shown in Table I can be rigorously improved by using the Gram determinantal inequality [4, 15] for a linearly independent set of

TABLE I. Salient properties of the sequence of approximate wave functions.

Property	Φ_1	Φ_2	Φ_3	Ψ
Energy eigenvalue[a]	-14.666 333	-14.666 594	-14.666 902	-14.667 328(25)[b]
$S_q' < S_q \equiv \langle \Phi_q \vert \Psi \rangle$	0.998 000[c]	0.998.550[c]	0.999 150[c]	1.
$S_{q3} \equiv \langle \Phi_q \vert \Phi_3 \rangle$	0.999 993	0.999 997	1.	
β_{q3}^2, Eq. (3)	0.000 008	0.000 004		
$\alpha_{q3} = (1-\beta_{q3}^2)^{1/2}$	0.999 996	0.999 998		
S_q', Eqs. (9-10)	0.999 961	0.999 972	0.999 987	
Size STO basis	10s9p8d7f5g3hli	same	same	
Size orbital basis	8s7p6d6f4g2hli	9s8p7d6f4g3hli	10s9p8d7f5g3hli	
Number of CSF's	253	310	650	

[a] In a.u. (Be); 1 a.u. (Be) = 219,461.275(17) cm^{-1}.
[b] From Ref. [2].
[c] Rigorous lower bound obtained by Eckart's criterion.

functions $\{f_i\}$:

$$D \equiv \det |\langle f_i | f_j \rangle| > 0 \tag{4}$$

using $f_1 = \Psi$, $f_2 = \Phi_3$, and $f_3 = \Phi_2$ or Φ_1. For example, if one sets $f_3 = \Phi_1$ and considers the value computed for $S_{13} = \langle \Phi_1 | \Phi_3 \rangle$ (see Table I), one finds, using Eq. (4),

$$S_1 > S_3 S_{13} - \sqrt{(1-S_3^2)(1-S_{13}^2)} = 0.999133 \tag{5}$$

which is very close to $S_3 > 0.999150$ reported in Table I. If one could establish independently a lower bound for S_3/S_1, one could then use the result in Eq. (5) to get an improved value for S_3, and the cycle could be repeated until convergence. Unfortunately this possibility is not presently available.

There is an approximate way, however, to improve S_3. From studies of patterns of convergence of K shell, L shell, and intershell wave functions with large basis sets, [2] I estimate (conservatively) that in Eq. (2) $\beta_{3\infty}$ satisfies $\beta_{3\infty}^2 < 0.000020$. Thus $\alpha_{3\infty} = (1-\beta_{3\infty}^2)^{1/2} > 0.999990$ and

$$S_3 = \alpha_{3\infty} \langle \Phi_3 | \Phi_{3\infty} \rangle > 0.999990 \langle \Phi_3 | \Phi_{3\infty} \rangle \tag{6}$$

where the value of $\langle \Phi_3 | \Phi_{3\infty} \rangle$ still needs to be estimated. For that I assume

$$\langle \Phi_3 | \Phi_{3\infty} \rangle \geq \langle \Phi_1 | \Phi_{13} \rangle \tag{7}$$

since the leading terms not included in Φ_3 are configurations with high harmonic functions such as $1s^2(i_L)^2$ which, as discussed earlier, affect the other a_m's essentially through renormalization. Multiplying Eq. (3) by Φ_1^* and integrating one finds

$$\langle \Phi_1 | \Phi_3 \rangle \equiv S_{13} = \alpha_{13} \langle \Phi_1 | \Phi_{13} \rangle \tag{8}$$

because $\langle \Phi_1 | R_{13} \rangle = 0$. Using the values of α_{13} and S_{13} given in Table I, one gets $\langle \Phi_1 | \Phi_{13} \rangle = 0.999997$. Using Eq. (7) and replacing into Eq. (6) one finally gets

$$S_3 > 0.999987 \tag{9}$$

as a realistic lower bound for S_3. Improved lower bounds for S_1 and S_2 can now be obtained by replacing the value obtained in Eq. (9) into Eq. (5):

$$S_1 > 0.999961, \qquad S_2 > 0.999972 \tag{10}$$

B. *Overlaps between Density Matrices*

The 1-matrices $\gamma_q(1/1')$ are defined in the usual way [10]:

$$\gamma_1(1/1') = N \int \Phi_q^*(1', 2, \ldots, N) \Phi_q(1, 2, \ldots, N) d(2, 3, \ldots, N) \tag{11}$$

and the corresponding occupation numbers $n_j^{(q)}$ and natural spin-orbitals $\chi_j^{(q)}$ are given by

$$\gamma_q(1/1') \chi_j^{(q)} = n_j^{(q)} \chi_j^{(q)} \tag{12}$$

Weinhold [4] has introduced a new scalar product $[\xi, \eta]$ between vectors ξ and η whose components are spin-orbitals:

$$\xi = \begin{pmatrix} \xi_1(1) \\ \xi_2(1) \\ \cdots \end{pmatrix} \qquad \eta = \begin{pmatrix} \eta_1(1) \\ \eta_2(1) \\ \cdots \end{pmatrix} \tag{13}$$

by definition

$$[\xi, \eta] = \sum_k \int \xi_k^*(1) \eta_k(1) d(1) \tag{14}$$

In particular, he considers vectors like γ_Ψ

$$\gamma_\Psi = \begin{pmatrix} (n_1)^{1/2} \chi_1 \\ (n_2)^{1/2} \chi_2 \\ \cdots \end{pmatrix} \tag{15}$$

and similar vectors γ_Φ (the n_i's are in Coleman's [16] normalization convention). He then derives error bounds to one-electron expectation values where the quantity σ

$$\sigma = [\gamma_\Psi, \gamma_\Phi] \tag{16}$$

replaces the usual overlap $S = \langle \Phi | \Psi \rangle$. The point is that σ is usually smaller than S. Unfortunately, numerical bounds for σ are not presently available. However, one can compute overlaps σ_{qr} between approximate density matrices

$$\sigma_{qr} = [\gamma_{\Phi_q}, \gamma_{\Phi_r}] \tag{17}$$

and compare them with the S_{qr}'s in Table I. One finds $\sigma_{23} = 0.9999994$, $\sigma_{12} = 0.9999996$, and $\sigma_{13} = 0.9999989$, suggesting that σ is indeed much closer to 1 than S.

C. Cusp Data and Virial Ratios

A necessary and sufficient condition for Φ to satisfy the electron–nuclear coalescence cusp condition [17],

$$(4\pi)^{-1}\frac{\partial}{\partial r_i}\left[\int d\Omega_i\,\Psi(1,2,\ldots,N)\right]_{r_i=0}=-Z\Psi(r_i=0) \tag{18}$$

is given by the "l-wave cusp" [18]

$$-(l+1)\frac{\partial}{\partial r}[\ln(r^{-l}\chi_{il}(r))]_{r=0}=Z \tag{19}$$

for the radial part $\chi_{il}(r)$ of each natural orbital [19]. Selected results for the NOs of Φ_3 are given in Table II. Except for the first four s-type NOs the results are

TABLE II. Electron–nuclear coalescence cusp data for selected natural orbitals of Φ_3.

i	$-(\ell+1)[\partial \ln(r^{-\ell}\chi_{i\ell}(r))/\partial r]_{r=0}$
1 0	4.003[a]
2 0	3.982
3 0	3.920
4 0	3.653
5 0	0.955
1 1	-9.204
2 1	2.562
1 2	105.
2 2	51.

[a] For the exact wave function all entries must be equal to $Z=4$.

completely erratic. For χ_{11} the cusp actually becomes negative due to the presence of a $3p$ STO with orbital exponent 14.9 corresponding to the innermost K shell STO, see Ref. [2]. A $4p$ STO localized in the same region would have been equally effective for the energy while having little influence on the cusp. A reasonable rule to get acceptable cusps might be to have no nl STO's $n=l+1$, and $n=l+2$ localized near the nucleus or, at least, have the $n=l+2$ STOs localized farther away than the $n=l+1$ ones. The cusp condition for the total electronic density

$\rho(r)$ reads [20]:

$$-(1/2)\frac{\partial}{\partial r}[\ln\rho(r)]_{r=0}=Z \tag{20}$$

while the result obtained with Φ_3 is 4.0020. The electronic density at the nucleus, however, does not come out as badly as might be expected (see Section 3).

Kinetic energy results and virial ratios are given in Table III. Virial ratios are just close enough to 1 to guarantee a good total energy (to more than eight

TABLE III. Kinetic energy results and virial ratios, in a.u. (Be).

	Φ_1	Φ_2	Φ_3	Ψ
Total energy	-14.666 333	-14.666 598	-14.666 902	-14.667 328
Kinetic energy	14.664 975	14.666 240	14.667 526	14.667 328
$z\sum r_i^{-1}$	-33.705 281	-33.706 541	-33.708 134	
$\sum r_{ij}^{-1}$	4.373 973	4.373 707	4.373 706	
-V/2T	1.000 046	1.000 012	0.999 979	1.

significant figures in the present case); the truncations to the full CI, although quite stable with respect to the total energy, might be responsible for the poor virial ratios.

3. Results and Discussion

A. Occupation Numbers

For a ^1S state the natural spin-orbitals are symmetry adapted with equivalence restrictions [21]:

$$\chi_{ilmm_s}=\chi_{il}(r)Y_{lm}(\theta,\phi)\sigma_{m_s} \tag{21}$$

and the occupation numbers are $(4l+2)$-fold degenerate:

$$n_{ilmm_s}=n_{il} \tag{22}$$

The occupation numbers obtained from the best approximate wave function considered, Φ_3, are given in Table IV. Most n_{il}'s converge from below; n_{10}, n_{20}, and n_{15} converge from above, while n_{40}, n_{41}, n_{12}, and n_{14} show oscillatory convergence. Also shown in Table IV are quantities Δ_{il}

$$\Delta_{il}=2\max|(n_i^{(q)}-n_i^{(3)})|\approx n_{il}-n_{il}^{(3)} \tag{23}$$

where $q=1$ or 2. The Δ_{il}'s are tentatively interpreted as margins of instability. Except for Δ_{20} and Δ_{11} the Δ_{il}'s are smaller than 0.0001. Those Δ_{il}'s which exceed

TABLE IV. Occupation numbers $n_{il}^{(3)}$ and tentative margins of instability Δ_{il}, Eq. (23).

i	n_{i0}	Δ_{i0}	n_{i1}	Δ_{i1}	n_{i2}	Δ_{i2}
1	0.998 087	20(-6)	0.029 103	200(-6)	0.5978(-4)	120(-8)
2	0.910 531	700(-6)	0.3560(-3)	8(-7)	0.1217(-4)	20(-8)
3	0.1846(-2)	30(-6)	0.4346(-4)	8(-7)	0.4803(-5)	15(-8)
4	0.4829(-3)	2(-6)	0.1406(-4)	5(-7)	0.1772(-5)	60(-8)
5	0.2026(-4)	2(-6)	0.3511(-5)	5(-7)	0.5241(-6)	20(-8)
6	0.5957(-5)	1(-6)	0.8935(-6)	?	0.1059(-6)	?
7	0.8284(-6)	?	0.1882(-6)	?	0.1960(-7)	?
8	0.2196(-6)	?	0.3156(-7)	?	0.1528(-8)	?
9	0.6468(-7)	?	0.5839(-8)	?		
10	0.7675(-8)	?				

i	n_{i3}	Δ_{i3}	n_{i4}	Δ_{i4}	n_{i5} [b]	Δ_{i5}
1	0.5439(-5)	50(-8)	0.9148(-6)	9(-9)	0.2196(-6)	100(-8)
2	0.1064(-5)	12(-8) [a]	0.1658(-6)	30(-9)	0.3468(-7)	60(-8)
3	0.6640(-6)	?	0.1520(-6)	20(-9)	0.7282(-8)	16(-8)
4	0.2674(-6)	?	0.3060(-7)	6(-9)		
5	0.9869(-7)	?	0.5878(-8)	?		
6	0.2481(-7)	?				
7	0.5244(-8)	?				

[a] The apparent instability of the n_{i3}'s for $i \geq 3$ is due to a circumstantial truncation of many configurations including f-type orbitals when going from Φ_2 to Φ_1.
[b] Only up to h-type occupation numbers are tabulated. $n_{16} = 0.8190(-8)$ but it is a K shell NO; the leading L shell NO of i-type has a considerably larger occupation number.

their corresponding n_{il}'s in 50% appear as "?" and are considered to be meaningless.

It is of interest to examine the relationship between the Δ_{il}'s and the estimate for S_3 given in Eq. (9). Ando [22] showed that if Ψ and Φ have p-matrices with eigenvalues λ_i and μ_i, respectively, then it holds that

$$\sum_j |\lambda_j - \mu_j| \leq 2\left\{\int |\Psi - \Phi|^2 \, d\tau\right\}^{1/2} \tag{24}$$

when the p-matrices are normalized in Coleman's [16] convention. One therefore must have

$$\sum_j |n_j - n_j^{(3)}| \leq 8(2 - 2S_3)^{1/2} = 0.040 \tag{25}$$

Because of the limited amount of information required by Eq. (24), the corresponding inequality is probably a weak result. Using Eq. (23) and the results of Table IV, one finds

$$\sum_j |n_j - n_j^{(3)}| \leq \sum_{il} (4l+2)\Delta_{il} = 0.004 \tag{26}$$

where only Δ_{10}, Δ_{20}, Δ_{30}, and Δ_{11} make effective contributions. Thus, Eq. (26) allows for Δ_{il}'s ten times greater (in average) than those reported in Table IV, but not any greater.

The eigenvalue spectra obtained by Olympia and Smith [5] follow the present ones very closely (to within a few percent or better) up to n_{40}, n_{51}, and n_{22}, after which the discrepancies reach over 50%. In the present set of calculations the margins of instability are less than 50% up to n_{60}, n_{51}, n_{52}, n_{23}, n_{44}, and n_{35}.

B. *Some Expectation Values and the Density at the Nucleus*

Consider one-electron expectation values of symmetric operators f

$$f = \sum_{i=1}^{N} f(i) \tag{27}$$

$$\langle f \rangle = \sum_j n_j \langle \chi_j | f(1) | \chi_j \rangle \tag{28}$$

Some expectation values are given in Table V, together with error bounds Δ based on the Jennings–Wilson formula [23]:

$$\Delta \leq 2N\varepsilon \left(\langle \Phi | f^2(1) | \Phi \rangle - \langle \Phi | f(1) | \Phi \rangle^2\right)^{1/2} \tag{29}$$

$$\varepsilon = (2 - 2S)^{1/2} = 0.005 \tag{30}$$

where S is the approximate lower bound to the overlap given by Eq. (9).

TABLE V. Some expectation values for the Be ground state, in a.u. (Be).

Wave function	r^{-2}	r^{-1}	r	r^2	r^4
Φ_1	57.5901	8.426 320	5.977 09	16.279 5	233.08
Φ_2	57.5954	8.426 635	5.976 44	16.275 1	232.91
Φ_3	57.5966	8.427 033	5.974 82	16.263 8	232.43
Jennings-Wilsons's bounded result		8.43(15)	5.97(5)	16.26(25)	

For the nuclear magnetic shielding constant σ [24] one finds

$$\sigma = -(1/3)\alpha^2 \langle r^{-1} \rangle = 0.0001496(30) \text{ a.u.} \tag{31}$$

with an uncertainty of 2.0%. The Hartree–Fock result [25], $\sigma = 0.0001493$, is quite similar but its Jennings–Wilson's uncertainty is 120%. The molar diamagnetic susceptibility χ_d [26] is

$$\chi_d = -(1/6)N_{av}\alpha^2 a_0^3 \langle r^2 \rangle = -12.88(20) \quad (\text{in } 10^{-6} \text{ cm}^3 \text{ mole}^{-1}) \tag{32}$$

with an uncertainty of 1.5%. The Hartree–Fock result [27], $\chi_d = -13.724$, is 6% above the present prediction but its Jennings–Wilson's uncertainty is 90%.

The results for the density at the nucleus $\rho(0)$ are given in Table VI. For Be^{2+} the present result agrees with the "exact" result of Pekeris [28] to within 30 parts per million, confirming that CI is an appropriate method [29] for the density at the nucleus. In going from Be^{2+} to Be there is a 3% increase in $\rho(0)$ due to the valence electrons. Since these are better described [2] than the K shell electrons, it is assumed (conservatively) that $\rho(0)$ for Be is given with 100 parts per million of uncertainty, as reported in Table VI.

TABLE VI. Density at the nucleus $\rho(0)$ for the Be ground state, in a.u. (Be).

Wave function	$\rho(0)$
Be^{2+}, present work	34.3974
Be^{2+}, "exact"	34.3962[a]
Φ_1	35.3660
Φ_2	35.3713
Φ_3	35.3698
Empirical extrapolation	35.370(3)

[a] From Ref. [28].

C. *Recent Results of Banyard and Taylor*

Banyard and Taylor [7] have recently reported some expectation values for Be-like ions which are significantly different from the ones reported in Tables V and VI. One possible reason for the discrepancies is that they neglected single excitations which for Be in a Hartree–Fock basis of reference orbitals come out with large (about 0.04) CI coefficients [30]. Their poor virial ratio $-V/2T = 1.0019$, however, is not inconsistent with four decimal precision in the energy, i.e., scaling will not improve their total energy.

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