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Accurate determination of the total electronic energy of the Be ground state

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New configuration-interaction (CI) ideas are tested and utilized to yield the most accurate determination to date of the Be nonrelativistic energy $E_{\mathrm{nr}} = -14.667\,358(28)$ a.u. Be, including a mass-polarization correction of $-0.000\,030(3)$ estimated from literature data. A 650-term CI series gives a rigorous upper bound $E_u = -14.666\,902$. The truncation error of the $10s9p8d7f5g3h1i$ carefully optimized Slater-type orbital set is estimated largely from studies of apparent energy limits for each harmonic; it amounts to $-0.000\,407(22)$. An additional $-0.000\,019(2)$ energy error arises from truncating the full CI expansion. A relativistic energy correction $E_{\mathrm{expt}} - E_{\mathrm{nr}} = -0.001\,987(30)$ is predicted, which agrees well with an *ab initio* estimate of $-0.001\,986$ obtained by combining the Hartree-Fock quality results of Hartmann and Clementi with Pekeris's exact result for Be^{2+}, thus including K-shell correlation effects in the relativistic correction. The correlation energy is determined with 0.03% of uncertainty, $E_c = -2.566\,04 \pm 0.000\,68$ eV. Particular attention is given to construction of basis sets, energy extrapolation procedures, and compact approximations to the full CI expansion. Comparisons with previous calculations are made, and it is pointed out how the present results may be improved.

I. INTRODUCTION

This paper is concerned with (i) an accurate means of estimating the eigenvalues E_{nr} of the atomic nonrelativistic Schrödinger equation, and (ii) a determination of the total electronic energy of the ground state of Be. We aim at a small uncertainty in the extrapolated E_{nr}, sufficiently narrow to permit a prediction of the relativistic energy correction E_r to within 1%, in order to possibilitate very accurate numerical tests of the many-electron relativistic Hamiltonian. For Be, 1% of E_r is about 0.000 020 a.u. = 4.4 cm^{-1}, amounting to 1.4 ppm of the total energy, which is just about the uncertainty in the present calculation.

We use standard configuration-interaction (CI) techniques. By standard we mean the use of (i) a Slater-type orbital (STO) basis, (ii) orthogonal one-electron symmetry-adapted spin orbitals, with equivalence of partner orbitals in degenerate representations, and (iii) an N-electron basis with L-S symmetry.

Four *ab initio* estimates of E_{nr} have been reported previously. The many-body perturbation theory (MBPT) estimates[1,2] have an uncertainty of 0.004 and 0.002 a.u., respectively. Since Kelly's and Kaldor's calculations were aimed at demonstrating a method and not at highly accurate results, it should not be concluded that the large uncertainty of their results is intrinsic to their particular implementation of MBPT. My own earlier estimate,[3] obtained from a standard CI calculation, has a reported uncertainty of 0.000 150 a.u., more than ten times smaller than the MBPT results, and here, again, the purposes were primarily directed at describing a strategy for atomic CI calculations. In recent work,[4] Sims and Hagstrom have used a CI-Hylleraas approach to compute the lowest upper bound to E_{nr} previous to the present work. Also, they have estimated for Be $E_{\mathrm{nr}} = -14.6667 \pm 0.0001$ a.u. which is compatible with our previous CI result[3] of $-14.666\,540 \pm 0.000\,150$. We have discovered, however, that the true energy E_{nr} lies outside and well below the reported margin of error of both previous variational calculations.

The crucial aspect that permitted the calculation of these *ab initio* estimates was the recognition of patterns of convergence for the energy. Other extensive calculations[5-8] on the ground state of Be have omitted any reference to the uncertainty of their results and are therefore inconclusive regarding the actual value of E_{nr}. Their authors have interpreted their calculations as probes of computational methods for well-known quantities, and so they have relied on empirical estimates which make use of experimental energies and an approximate relativistic energy correction.

A recent calculation[9] by Froese Fischer and Saxena has distinguishing features that deserve special mention: they used a numerical multiconfiguration Hartree-Fock (MCHF) technique and obtained the lowest CI upper bound to E_{nr} previous to the present work. Unfortunately, the possible existence of patterns of convergence was not considered and no estimate of E_{nr} was given.

In Sec. II we discuss the salient features of an accurate CI calculation for closed-shell atomic states. Open-shell states shall be discussed in a companion paper.[10] In Sec. III we present the results of the nonrelativistic calculation for the ground state of Be and compute an *ab initio* relativistic correction using literature data. We also discuss correlation energy, convergence of the CI series and a description of it, and pair energies and how to improve standard CI upper bounds. The discussion in Sec. IV is devoted to comparisons with previous calculations and to point out the way towards improved results.

II. SALIENT FEATURES OF CI

The starting point of any CI calculation is the selection of a reference configuration.

For optimization purposes it is more convenient (see Sec. II C) to use a Hartree-Fock reference configuration, rather than one formed with major natural orbitals[11] (NO's). This is probably because canonical Hartree-Fock (HF) orbitals are localized in shells, while major NO's are less localized, and efficient optimization strategies[12] are based on shell-localized model wave functions.

For CI purposes anything that provides for a short-range fluctuation potential[13] might seem[14] adequate. Unfortunately, it has not yet been clarified how an optimum short range fluctuation potential should be constructed such that the importance of three and higher excited *linked* clusters is minimized.

We intended to use an HF reference configuration expressed in canonical HF orbitals, following earlier CI calculations,[3,15] and in order to allow detailed comparisons with previous work. The HF orbitals had to be abandoned, however, and replaced by major NO's, as discussed in Sec. II D.

A. Outline of procedure

The distinctive feature of our method is that the truncation error of the orbital basis is largely determined at the very outset of the calculation. The main steps in our method are (i) construction of a prototype set, (ii) study of patterns of convergence, (iii) optimization of STO parameters, and (iv) checking the stability of the patterns of convergence by increasing the size of the prototype set with a few optimized STO's. At this stage we have an optimized STO basis together with the largest portion of its truncation energy error. We then proceed to (v) obtain a particular NO basis, and finally (vi) approximate the full CI in the given orbital basis. The only difficult decisions arise in steps (ii) and (iii) in trying to get maximum accuracy at a reasonable cost in both human and computer time.

B. Patterns of convergence

In this subsection we discuss a set of calculations which are primarily directed at obtaining intermediate results useful to compute the truncation error of a primitive basis set (to be determined in Sec. II C). As a bonus, these intermediate results will provide us with a guide to the energy optimization of the primitive set.

Let us define L-, K-, and I-shell wave functions as

$$\Psi(L\ \text{shell}) = (1s)^2(2s)^2 + A\left((1s)^2 \sum_{a\le b}(x_a x_b) l_{ab}\right), \tag{1}$$

$$\Psi(K\ \text{shell}) = (1s)^2(2s)^2 + A\left((2s)^2 \sum_{a\le b}(x_a x_b) k_{ab}\right), \tag{2}$$

$$\Psi(I\ \text{shell}) = (1s)^2(2s)^2 + A\left({}^1S(1s2s)\sum_{a\le b}{}^1S(x_a x_b)\, i_{abs}\right) + A\left[{}^1S\left({}^3S(1s2s)\sum_{a<b}{}^3S(x_a x_b)\, i_{abt}\right)\right], \tag{3}$$

where $1s$ and $2s$ may be canonical SCF orbitals of double ζ quality and the sums run over a set of predetermined orbitals.

Let us now consider a given set of functions. We define its L-shell truncation error as the difference between the energies of the $\Psi(L$ shell) with a complete set and with the given set, respectively. The only obstacle to the computation of the L-shell truncation error of a given set is an estimate of the energy of $\Psi(L$ shell) with the complete set. This we are unable to approach directly because of the large number of integrals involved if energy convergence to within a few microhartrees is sought. Instead we consider apparent angular energy limits for each successive harmonic function.

The apparent angular energy limits are obtained with a small prototype set containing harmonic functions up to $l-1$ and a large set of even-tempered[16,17] STO's,

$$S_{kl} = e^{-Z_k r} r^l Y_{lm}(\theta,\phi), \tag{4}$$

$$Z_k = ab^k, \quad k = 1, 2, \ldots, \tag{5}$$

for the given harmonic investigation.

The prototype set is given at the top of Table I; it consists of Huzinaga and Arnau's[18] double ζ basis and L-shell STO's energy optimized in the order $2p$, $4p$, $3p$, $3d$, $4f$, $5g$, and $6h$, except that for the p orbitals we only use the first L-shell p-type NO. Hereafter small energies are reported in microhartrees, 1 μhartree $= 10^{-6}$ a.u.

Our results for the L shell are given in Table I in the first two rows following the identifier for each angular limit. The convergence of the calculated energy (top entry) towards the extrapolated limit is ascertained by testing the stability of the energy contribution of each NO upon many vari-

TABLE I. Radial patterns of convergence in the L shell. The characterization of the prototype set is as follows: For STO's,[a] $1s=3.347\,64$, $1s'=5.543\,03$, $2s=0.588\,61$, $2s'=1.008\,96$, $3s=1.03$; $2p=1.036$ ($2p=0.978$ only in s limits), $4p=4.18$, $3p=2.20$; $3d=1.18$, $4f=1.56$, $5g=1.9$, $6h=2.4$. For orbitals, s_1, s_2 (canonical self-consistent field with $1s$, $1s'$, $2s$, $2s'$), s_3, s_4, s_5; $p_1=(2p)1.101\,26-(4p)0.017\,591-(3p)0.105\,419$; d_1, f_1, g_1, h_1. **All energies are given in a.u. Be.**

	s	p	d	f	g	h	i
E_{nr}	−14.617 575 73	−14.617 196 87	−14.617 544 34	−14.617 568 46	−14.617 581 80	−14.617 588 33	−14.617 591 96
(Constants)[b]	($a=0.3$, $b=1.15$, $M=10$)[c]	($a=0.5$, $b=1.3$, $M=10$)	($a=0.7$, $b=1.3$, $M=8$)	($a=0.9$, $b=1.2$, $M=7$)	($a=0.8$, $b=1.3$, $M=6$)	($a=0.8$, $b=1.3$, $M=6$)	($a=0.6$, $b=1.3$, $k=4, 5, 6, 7$)
(Extended prototype set)[d]			(−14.617 613 88)				
Extrapolated limit	−14.617 577 0(10)	−14.617 198 0(10)	−14.617 545 5(10)	−14.617 569 5(10)	−14.617 583 0(10)	−14.617 589 5(10)	−14.617 593 0(10)
Energy prototype set						−14.617 566 36	−14.617 581 14
L-shell optimized STO's	−14.617 573 86	−14.617 181 49	−14.617 530 79	−14.617 551 13			
(Extended prototype set)[d]			(−14.617 600 92)				
All optimized STO's	−14.617 576 03	−14.617 191 32	−14.617 537 61	−14.617 561 30	−14.617 576 02	−14.617 581 18	
Truncation error (μhartree)	$\Delta_s(L)=1(1)$	$\Delta_p(L)=7(1)$	$\Delta_d(L)=8(1)$	$\Delta_f(L)=8(1)$	$\Delta_g(L)=7(1)$	$\Delta_h(L)=8(1)$	$\Delta_i(L)=12(1)$
Energy contribution (μhartree)						$\epsilon_h(L)=13(1)$	$\epsilon_i(L)=12(1)$

[a] STO's $1s$, $1s'$, $2s$, and $2s'$ are taken from S. Huzinaga and C. Arnau, J. Chem. Phys. 53, 451 (1970).

[b] The orbital exponents Z_k of the even-tempered set are $Z_k=ab^k$, $k=1, 2, \ldots, M$.

[c] For the s limit, the s-type prototype set is from Bagus and Gilbert, Ref. 23. The functions $k=4$ and $k=7$ are deleted to avoid approximate linear dependence with the prototype set.

[d] Result obtained by using the full p-orbital basis for the given prototype set of STO's.

TABLE II. Energy contributions of L-shell p-type NO's, in μhartree.

NO	Energy	L-shell energy
2	76.74 [a]	−14.617 157 41
3	19.46 [b]	−14.617 176 87
4	11.86 [b]	−14.617 188 73
5	4.21 [c]	−14.617 192 94
6	2.80 [c]	−14.617 195 74
7	0.61 [c]	−14.617 196 35
8	0.34 [c]	−14.617 196 69
9	0.18 [c]	−14.617 196 87
10	0.00 [c]	−14.617 196 87

[a] Stable to all figures.

[b] Last figure may not be stable upon improvement of basis set.

[c] Last two figures may not be stable.

ations in the values of a, b, and k, as illustrated in Table II. Unfortunately, the separate energy contributions of each NO are not upper bounds to their corresponding limiting values; neither do they satisfy handy empirical laws, as found in the heliumlike systems.[19] The uncertainty of the extrapolated limit is computed by adding up conservative margins of instability for each NO contribution. The extrapolated limit is obtained by adding the uncertainty computed above (with minus sign) to the lowest calculated energy.

An extended prototype set including all three possible p-type orbitals was used to test the stability of the apparent L-shell truncation error for $l = 2$, as shown in Table I under "d limit."

For the I shell, results analogous to those of Table I are obtained in a similar fashion (these results are later condensed in Table VI).

Our CI calculations of apparent angular energy limits stop at $l = 6$. The L-shell harmonic contributions for $l > 6$ are estimated in Table III on the basis of a conspicuous $(l+\frac{1}{2})^{-4}$ asymptotic empirical law, similar to the one discovered by Schwartz (on theoretical grounds) for the ground state of He.[20] The harmonic contributions to the I shell appear to follow instead a 3^{-l} exponential law, as illustrated also in Table III.

Finally, for the K shell we have relied on previous studies.[3,19] The important results are synthesized in the three equations below:

$$\epsilon_K = E(\text{Be, } K \text{ shell, exact}) - E(\text{Be, K shell, approx.}) \tag{6}$$

$$\cong E(\text{Be}^{2+}\text{, exact, without } 2s) - E(\text{Be}^{2+}\text{, approx., without } 2s) \tag{7}$$

$$\cong E(\text{Be}^{2+}\text{, exact}) - E(\text{Be}^{2+}\text{, approx.}), \tag{8}$$

where ϵ_K is the K-shell error. With a basis considerably inferior to the present one, these equations were found valid[3] to an accuracy better than 1 μhartree. The results for the K shell are given in Table IV.

In Sec. IV D we point out to another possible method for computation of truncation errors.

C. Basis optimization

Eight years ago, when my previous Be paper[3] came out, there was immediate concern with what are now considered coarse descriptions of electronic correlation, and so the details of basis-set optimization were of secondary interest. Today, atomic CI techniques have developed[21] to the point where it is feasible to consider very large calculations. I claim that these[21] and other currently available techniques can be used to yield expectation values of near-spectroscopic accuracy. In this context basis-set optimization of some sort becomes inevitable.

Many hypotheses about interdependence of STO parameters might be advanced at the outset. We do not need any of these hypotheses, however, because the uncertainties in each step of the op-

TABLE III. Extrapolation of energy contributions for $l > 6$, in μhartree.

	L shell		I shell	
l	Energy contributions	$A(l+\frac{1}{2})^{-4}$	Energy contributions	$B(3^{-l})$
3			80 ± 1	
4	60 ± 1		27 ± 3	28
5	23 ± 1	23	9 ± 1	9.3
6	12 ± 1	12	3.5 ± 0.5	3.1
7		6.7		1.0
8		4.1		0.3
9		2.6		0.1
Sum ($l = 7, \ldots, \infty$)		21 ± 2		2 ± 1

TABLE IV. *K*-shell STO truncation error.

Limit \ Energy Be^{2+}	Present work[a]	Exact	$\Delta_l(K)$ (μhartree)
s	−13.626 841	−13.626 859[b]	18
p	−13.651 076	−13.651 118[b]	24
d	−13.654 113	−13.654 172[b]	27
f	−13.654 893		
g	−13.655 159		
h	−13.655 261		
i	−13.655 295		
∞		−13.655 566[c]	
Truncation error, Eqs. (6)–(8)			271 ± 1

[a] Upper bound with present $10s9p8d7f5g3h1i$ basis.
[b] Reference 19.
[c] Reference 38.

timization are ascertained from NO analyses of apparent angular energy-limit wave functions which are studied before doing the optimization (Sec. II B).

The optimization is carried out in two steps. In the first one we optimize *L*-shell wave functions. In the second and final step we optimize *K*-shell wave functions, including all orbitals from the previous step. Intershell optimizations are made only exceptionally (as explained later), but the concomitant truncation error is duly estimated. By carrying out *L*-shell optimizations first, the *K*-shell optimizations which follow are quite simple, the energetically important STO's being very much localized.[22]

We start with the nominal canonical HF orbitals of Bagus *et al.*[23] plus the virtual orbitals, totaling four *s*-type functions. An *L*-shell 2*p* STO is optimized first. Then (keeping the 2*p* fixed) we optimize, successively, 3*s*, 4*s*, and 5*s* STO's in the *L*-shell. We stop adding *s* orbitals at this stage, because the results of patterns of convergence indicate that we have reached convergence to within 3 μhartree. A cyclic reoptimization has little effect. Similar calculations with NO's instead of canonical HF orbitals yield results which are definitely poorer.

Next we optimize 2*s*, 3*s*, and 4*s* STO's in the *K* shell. The end result is the same one from a similar optimization based on the ground state of Be^{2+}. At this stage we are 18 μhartree away from either the *s* limit of Be^{2+} or the *s* limit of a *K*-shell CI, and the result is stable upon further isolated variations in any of the ten *s*-type STO's.

The optimization of *p* STO's in the *L* shell presented some surprises. The order is somewhat altered: 2*p*, 4*p*, 3*p*, and 6*p*. After successive optimizations of these four STO's the truncation error is 112 μhartree. Many cyclic optimizations are required to bring down the truncation error to 17 μhartree. At this stage it is noted that the first four *L*-shell *p*-type accurate NO's (see Table II) give an energy 7 μhartree below the energy obtained with the four *L*-shell optimized STO's (reported in Table I under "*p* limit"), which shows how well we have done with the optimization. The accurate NO results of Table II also suggest that further energy improvements do require the introduction of additional STO's, which are not included in order to keep the computational cost within budget limitations. After addition of the *K*-shell optimized STO's we are only 7 μhartree above (Table I under "*p* limit") the apparent *p* energy limit (Table I under "*p* limit"). We see that the *L*-shell truncation error of our full *p*-type basis is 7±1 μhartree.

Fortunately, the optimization of higher harmonics becomes simple again. After successive optimization of 3*d*, 4*d*, and 5*d*, the energy is 22 μhartree away from the apparent *L*-shell *d* limit. Two further cyclic reoptimizations place the energy within 15 μhartree. For higher harmonics cyclic reoptimizations are unnecessary. An analogous behavior is observed in *K*-shell optimizations.

Many methods for parameter optimization are currently used in atomic and molecular quantum mechanics. To our surprise, we have found that the simple-minded cyclic optimization (originally advocated by Roothaan and Bagus[24]) works out satisfactorily. For the optimization of a single orbital exponent we have resorted to an admixture of brute force and common sense, the later consisting in recognizing that multiple minima are accompanied by multiple maxima which occur, approximately, when the overlap integral between any two STO's approaches its highest possible value (for a large basis one of these maxima is usually very close to the absolute minimum). If our common sense fails us (for example, if we are too lazy to search around all minima), the information given by the NO analyses of apparent angular energy-limit wave functions will alert us.

In Table V we give the STO basis together with corresponding average radii. Notice the distribution of average radii of CI optimized STO's relative to the nominal set of Bagus *et al.* What is amazing is that this distribution was not imposed *a priori*, i.e., we did not look for local minima consistent with a preestablished localization of the STO's, except for the use of L- and K-shell wave functions.

TABLE V. Characterization and localization of STO set.

STO	Orbital exponent	$\langle r \rangle$ (bohr)	Shell
$1s$	6.225	0.241	K (HF)
$4s$	16.0	0.281	K
$2s$	7.45	0.335	K
$3s$	8.80	0.398	K
$1s$	3.437	0.437	K (HF)
$4s$	2.7	1.67	L
$3s$	1.776	1.97	L (HF)
$5s$	2.2	2.50	L
$2s$	0.869	2.87	L (HF)
$3s$	1.08	3.24	L
$3p$	14.9	0.235	K
$4p$	14.0	0.321	K
$5p$	14.0[a]	0.407	K
$6p$	14.0[a]	0.479	K
$2p$	2.9[b]	0.86	K
$4p$	5.00	0.90	L
$3p$	2.10	1.68	L
$6p$	2.80	2.32	L
$2p$	1.036	2.41	L
$3d$	16.0[a]	0.219	K
$4d$	16.0	0.281	K
$5d$	16.0	0.344	K
$6d$	16.0[a]	0.406	K
$3d$	7.1	0.493	K
$5d$	2.55	2.15	L
$3d$	1.60	2.19	L
$4d$	1.74	2.59	L
$5f$	17.0	0.323	K
$6f$	18.0	0.361	K
$7f$	18.5[a]	0.405	K
$4f$	10.0	0.450	K
$4f$	3.6	1.25	I,L
$5f$	2.40	2.29	L
$4f$	1.56	2.88	L
$6g$	20.0	0.325	K
$7g$	20.0[a]	0.375	K
$5g$	13.0	0.423	K
$6g$	2.8	2.32	L
$5g$	1.9	2.89	L
$7h$	22.0	0.341	K
$6h$	15.5	0.419	K
$6h$	2.4	2.71	L
$7i$	18.0	0.417	K

[a] Orbital exponent has been estimated.

[b] Upon one cyclic reoptimization it changed from 4.9 to 2.9.

TABLE VI. Summary of truncation-energy estimates for I and L shells, in μhartree.

l	$\Delta_l(I)$	$\Delta_l(L)$
0	1 ± 0.5	1 ± 1
1	3 ± 1	7 ± 1
2	10 ± 2	8 ± 1
3	3 ± 1	8 ± 1
4	15 ± 3	7 ± 1
5	4.5 ± 1	8 ± 1
6	2.5 ± 0.5	12 ± 1
Sum	39 ± 9	51 ± 7

By now we are in a position to compute L- and I-shell apparent angular energy limits using the prototype set and the final basis for the higher harmonic under investigation; the L-shell results are given in Table I. The truncation errors in the L shell, $\Delta_l(L)$, for $l \leqslant 6$, can now be computed from the data in Table I, and they are collected in Table VI together with the I-shell truncation errors computed in the same way.

After computing the I-shell energy with our originally optimized STO basis for $l = 3$, and upon verifying that the truncation error was 32 μhartree, we decided to optimize an f-type I-shell STO which turned out to be $4f = 3.6$. This STO contributes 29 μhartree to the I shell and 8 μhartree to the L shell, and was incorporated into our final STO basis.

Finally, we assume that for small truncation errors, such as those in this work, the total truncation error is the sum of L-, I-, and K-shell truncation errors. In Table VII we summarize the STO truncation-error results. The truncation error of our STO basis is estimated in 384±20

TABLE VII. Summary of STO truncation results, in μhartree.

Shell \ Wave function	$l \leq 6$	$l > 6$	Total
L	51 ± 7	21 ± 2	72 ± 9
I	39 ± 9	2 ± 1	41 ± 10
K			271 ± 1
Subtotal ($L + I + K$)			384 ± 20
$^1S(xy)\,^1S(p_1)^2$			23 ± 3[a]
Total			407 ± 23

[a] See discussion in Sec. II G.

μhartree, except for minor corrections due to unlinked terms of the type $^1S(xy)\,^1S(p_1)^2$ which we discuss in Sec. II G. Any further truncation errors shall be attributed to truncations in the full CI expansion.

D. Selection of orbital basis

The *spd* orbitals are NO's of a wave function which includes the HF configuration and all single and double excitations. This wave function is not invariant upon the NO transformation, and so one might be tempted to carry out NO iterations, which we consider superfluous in the present case. The *fghi* orbitals are NO's of an analogous wave function with a small $4s2p2d$ STO basis.

At this stage it is convenient to repeat both CI calculations with their respective NO's, in order to identify the leading unlinked clusters for later use in the approximation to the full CI (Sec. II G).

The HF space was abandoned because (i) the relatively large matrix elements between single and double L-shell excitations demanded several hundred iterations for the evaluation of eigenvectors of large matrices, and (ii) the large CI coefficients of the L-shell single excitations were responsible for the presence of too many three-excited-unlinked clusters.

The question of whether there exists a kind of NO or other orthogonal orbital with definite interpretative and computational advantages remains open. The present NO's, however, are definitely superior to NO's which include HF orbitals,[3] for the reasons stated above.

E. N-electron functions

We use L-S eigenfunctions obtained as successively orthogonalized symmetric projections[25] of Slater determinants. When degeneracies exist the different L-S functions may be characterized by internal couplings of electron groups.[26] An extensive theoretical discussion[27] and computational details[28] are given in the literature. All possible types of L-S functions for a given orbital basis are stored on magnetic tape (master tape). Input to the CI program, other than options and, possibly, basis functions, consists of a string of numbers in a one-to-one correspondence with the L-S functions of the master tape.

F. Eigenvectors of large matrices

The computation of eigenvectors of large real symmetric matrices can be done very efficiently with Shavitt's algorithm,[29] based on a method by Nesbet.[30] Quick convergence depends upon matrix characteristics which are not easy or even desirable to control,[31] so that one must be ready to abandon a seemingly suitable orbital basis if eigenvector convergence becomes problematic. The accuracy of the eigenvalues can be rigorously tested by Wilkinson's formula,[32] $\tilde{E} = E \pm |r|$, where r is the residual vector, $r = (H - \tilde{E}I)\,\tilde{c}$, and $\tilde{C}$ is normalized. The computation of eigenvectors consumes a small fraction of the total computational time. Our final upper bound had a precision of 0.01 μhartree and required 66 iterations.

G. Approximation of the full CI

Although our energy uncertainty due to the truncation of the STO set is about 23 μhartree, it seems possible (see Sec. IV D), in principle, to reduce this uncertainty to 2 μhartree or less, so that a comparable uncertainty in the approximation to the full CI energy is desirable.

The full CI is approximated by a sequence of CI calculations, as described in Table VIII. We start with a 659-term CI which includes all singles and doubles plus 15 leading linked and unlinked terms. This is in order to get as close as possible to the final result so as to minimize the uncertainties in further CI truncations. The first truncation was obtained by deleting 253 terms selected by Brown's criterion,[33] which says that the energy contribution of the mth configuration, ΔE_m, is given by

$$\Delta E_m = E(\Psi) - E(\Psi - \Psi_m) = c_m^2(E - H_{mm})/(1 - c_m^2)\,. \tag{9}$$

Equation (9) is derived assuming that upon deletion of Ψ_m from Ψ the resulting function is well approximated by the same linear coefficients c_m, except for renormalization. In each step the truncation error is computed as a difference between two variational energies which, in the present set of calculations, agrees with the sum of the deleted ΔE_m's to better than 99%.

Next we include the 149 unlinked terms with predicted energy contributions greater than 0.1 μhartree. These predictions are based on Eq. (9), with

$$H_{mm} \equiv D_{ijkl}^{abcd} \cong D_{ij}^{ab} + D_{kl}^{cd} - D_0\,, \tag{10}$$

$$c_m \cong \sum_{(abcd)} c_{ij}^{ab}\, c_{kl}^{cd}\,. \tag{11}$$

In Eq. (10), D_0 is the average energy of the reference configuration, D_{ij}^{ab} is the average energy of the $ij \rightarrow ab$ excitation,[34] and so on. In Eq. (11) we understand the sum to be over all possible products permitted by the *unlinked* cluster expansion.[13]

After another truncation we include 233 terms believed to represent the remaining important

TABLE VIII. Sequence of calculations to approximate the full CI.

Order	Wave function[a]	CI size	Energy	Truncation[b] energy (μhartree)
1	All $S+D$ plus 15 leading $T+Q$	659	−14.666 040 00	
2	Same as 1, truncated	406	−14.666 034 01	5.99
3	Same as 2 plus 149 unlinked	555	−14.666 468 97	
4	Same as 3, truncated	523	−14.666 467 95	1.02
5	Same as 4 plus 233 linked	756	−14.666 732 97	
6	Same as 5, truncated	589	−14.666 730 56	2.41
7	Same as 6 plus 160 U and L	749	−14.666 765 33	
8	Same as 7, truncated	604	−14.666 762 67	2.66
9	Same as 8 plus 194 terms, mostly linked ones	798	−14.666 895 06	
10	Same as 9, truncated	637	−14.666 892 41	2.65
11	Same as 10 plus 60 U and L	697	−14.666 902 85	
12	Same as 11, truncated	650	−14.666 901 84	1.01
	Remaining unlinked clusters, Eqs. (9)–(11).			3.0 ± 1.0
	Total CI truncation error			19 ± 2
	Extrapolated full CI energy		−14.666 921(2)	

[a] See text for more precise explanations.

[b] Difference between two variational energies.

linked clusters, mainly single and double excitations of leading double excitations such as $(1s)^2(p_1)^2$, $(p_2)^2(2s)^2$, and $(1s)^2(d_1)^2$, and three-body "collisions."[13] In identifying these terms it is convenient to use a hierarchy of configurations based on occupation numbers (eigenvalues of the 1 matrix).

The energy effect of other linked and unlinked clusters is computed through new secular equations, and the energy contributions of the still remaining unlinked clusters are estimated via Eqs. (9)–(11). The energy effect of the remaining linked terms is believed to be less than 1 μhartree. The final upper bound, $E_u = 14.666\,902$, is 19 μhartree above the full CI energy, which has been estimated with an uncertainty of 2 μhartree. The nonrelativistic energy is estimated in Sec. III.

An analysis of energy contributions of ${}^1S(xy)\,{}^1S(p_1)^2$ terms indicates that the present STO basis is significantly incomplete in this respect. The energy contribution of these terms can be estimated very accurately by means of Eq. (9), even without explicit knowledge of the c_m's and H_{mm}'s. Introducing (10) in (9), with $D_0 \cong E$, we get

$$\Delta E_m \cong c_m^2 [(E - D_{ij}^{ab}) + (E - D_{kl}^{cd})] . \tag{12}$$

For the types of terms we are considering, Eq. (11) can be well approximated by

$$c_m \cong c_{2s\,2s}^{p_1 p_1} c_{1s\,1s}^{xy} . \tag{13}$$

Placing (13) into (12) we get

$$\Delta E_{1s\,1s\,2s\,2s}^{xy\,p_1 p_1} \cong (c_{2s\,2s}^{p_1 p_1})^2 \Delta E_{1s\,1s}^{xy} + (c_{1s\,1s}^{xy})^2 \Delta E_{2s\,2s}^{p_1 p_1} , \tag{14}$$

where the last term on the right-hand side of (14) is relatively small. Using $c_{2s\,2s}^{p_1 p_1} = -0.29$, we have

$$\Delta E_{1s\,1s\,2s\,2s}^{xy\,p_1 p_1} \cong 0.084\, \Delta E_{1s\,1s}^{xy} . \tag{15}$$

We have found that the energy correction given by (15) is accurate to 85% or better, for terms of magnitude comparable to the ones we wish to approximate. Summing both members of (15) over all xy not included in our orbital basis, we get, on the left-hand side, the total STO truncation error due to the ${}^1S(xy)\,{}^1S(p_1)^2$ excitations. On the right-hand side, we get, from Table IV,

$$\sum_{x,y} \Delta E_{1s\,1s}^{xy} = -271\ \mu\text{hartree} , \tag{16}$$

to about 95% accuracy, so that from (15) and (16) we get a STO truncation error of 23±3 μhartree, which we report in Table VII.

III. RESULTS

The experimental electronic energy for the Be ground state is given in Table IX, where use is made of the latest recommended values of the physical constants.[35] A summary of the relevant energies involved in our *ab initio* estimate of the total electronic energy is given in Table X. A Burroughs 6700 computer and double-precision arithmetic (22 significant figures) have been used throughout.

The mass polarization term has not been computed, but Prasad and Stewart[36] have done so very accurately for Be^+ and Be^{2+} using Weiss's wave functions.[37] For Be^{2+} they get $E_{mp} = -5.63$ cm^{-1}

TABLE IX. Experimental electronic energy in cm^{-1} of the Be ground state.

Ionization potential	Energy [a]
First	75 192.07 ± 0.1 [b]
Second	146 882.87 ± 0.1 [b]
Third	1 241 259.5 ± 0.1 [c]
Fourth	1 756 018.82 ± 0.1 [d]
Electronic energy, Be	3 219 353.26 ± 0.4 [e]
In a.u.	−14.668 452(2)
In a.u.(Be)	−14.669 345(2)

[a] $R_\infty = 109\,737.3177(83)$ cm^{-1}; $R(^9Be) = 109\,730.6377(83)$ cm^{-1} (Ref. 35).

[b] L. Johansson, Ark. Fys. 20, 489 (1961); 23, 119 (1962); J. E. Holmstrom and L. Johansson, *ibid.* 40, 133 (1969).

[c] Ref. 38, corrected for present R_∞. The most recent experimental value [M. Eidelsberg, J. Phys. B 5, 1031 (1972)] has an uncertainty of 10 cm^{-1}.

[d] J. D. Garcia and J. F. Mack, J. Opt. Soc. Am. 55, 654 (1965), corrected for present R_∞.

[e] The uncertainty in the value of R_∞ is not taken into account because we finally use a.u.(Be).

= − 0.000 025 a.u., in excellent agreement with Pekeris's "exact" result[38] of −5.62 cm^{-1}. For Be^+ they get $E_{mp} = -0.000\,027$, and the result should be as reliable for Be^{2+}. Since E_{mp} receives contributions largely from regions with high kinetic energy contributions, i.e., the *K* shell, we conclude that for the additional 2*s* electron in going from Be^+ to Be, E_{mp} must not change by more than −0.000 003(3) a.u., giving a total value of $E_{mp} = -0.000\,030(3)$, which we report in Table X. Therefore we predict a nonrelativistic energy $E_{nr} = -14.667\,358(28)$ a.u. for Be and a relativistic and radiative energy correction $E_r = E - E_{nr} = -0.001\,987(30)$ a.u.

Hartmann and Clementi[39] have computed the relativistic energy correction by perturbation theory,[40] using self-consistent-field wave functions of near-Hartree-Fock quality. They use an extended form of the Breit equation for *N*-electron systems, expand the Hamiltonian in powers of $Z\alpha$ up to and including the order α^2, and get an expectation value of −0.002 198 a.u. They have also calculated[39] a low-order Lamb-shift correction for Be^{3+} but not for Be, arguing that the effect of the outer electrons is expected to be relatively small. Their value for the Lamb shift of Be^{3+} is + 0.000 323 a.u. In this way they get a total relativistic and radiative energy correction $\tilde{E}_r = -0.001\,875$ a.u.

The result of Hartmann and Clementi can be improved[39] by adding the full relativistic electron correlation in the *K* shell. In the same spirit that we used for the estimation of *K*-shell STO truncation errors, we assume with Hartmann and Clementi that this effect is approximately equal to the difference between Pekeris's relativistic correction for Be^{2+}, which is − 0.001 878 a.u. and the Hartree-Fock quality relativistic energy of

TABLE X. *Ab-initio* prediction of the electronic energy of the Be ground state.

	Energy correction	Total energy
650-term CI, E_u		−14.666 902 [a]
Truncation error, full CI	−0.000 019(2) [a]	
Full CI, extrapolated		−14.666 921(2)
Truncation error, STO basis	−0.000 407(23) [b]	
Nonrelativistic energy, $E_{nr} - E_{mp}$		−14.667 328(25)
Mass polarization, estimate	−0.000 030(3) [c]	
E_{nr}, final estimate		−14.667 358(28)
E, experimental		−14.669 345(2) [d]
$E_r = E - E_{nr}$, our prediction		− 0.001 987(30)
Breit interaction	−0.002 198 [e]	
Lamb shift	+ 0.000 323 [e,f]	
K-shell relativistic correlation	−0.000 111 [e,g]	
$\tilde{E}_r$, total relativistic and radiative correction	−0.001 986	

[a] See Table VIII.

[b] See Table VII.

[c] See discussion in text.

[d] See Table IX.

[e] Reference 39.

[f] Computed in Ref. 39 using the formula of P. K. Kabir and E. E. Salpeter, Phys. Rev. 108, 1256 (1957).

[g] Reference 38.

Hartmann and Clementi,[39] which is − 0.001 767 a.u. When taking into account this effect, Hartmann and Clementi's value of − 0.001 875 must be corrected by − 0.000 111 a.u., giving $\tilde{E}_r = -0.001\,986$, which agrees well with our predicted $E_r = -0.001\,987(30)$. The full significance of this result is discussed elsewhere.[41]

Correlation energy remains the theme which unifies, if tenuously, the various outputs of diverse *ab initio* methods. In Table XI is shown our correlation energy result in perspective against previous estimates (the HF energy is taken from Reffenetti[17]). (In accord with common usage, the Hamiltonian used to define correlation energy does not include the mass polarization term.) We notice that the present correlation energy estimate is outside and well below the error bounds of three previous estimates. The probable reasons for previous failures are common ones, (i) underestimation of STO truncation errors and (ii) complete negligence of other effects. (In our previous calculation[3] we erred by underestimating the L- and I-shell STO truncation errors, and by neglecting $1sp_1pd$ three-excited configurations; in other works[2,4] the treatment of error bounds is not sufficiently documented to reach conclusions in this respect.) In the present work we believe that the only possible source of error is a possible omission of some configuration; such type of error (human errors) are probably unavoidable unless the calculation is fully automatized from beginning (nuclear charge, number of electrons, charge) to end.

In Table XII are given the energies of several variational wave functions for comparison with recent work by Sims and Hagstrom,[42] where convergence is discussed in terms of energy versus number of expansion functions in the CI series. The results in Table XII reflect well on the rate of convergence of the standard CI series up to the first 200 terms or so. From this point the convergence is spoiled by basis-set incompleteness. Even so, it is clear that CI converges much more rapidly than anyone expected.[43] It now remains to be seen if the work of Sims and Hagstrom[4] and that of Froese Fischer and Saxena[9] can practically be extended towards increased accuracy.[44]

TABLE XI. Comparison of *ab initio* determinations of the correlation energy of the Be ground state.

Author	Correlation energy (μhartree)	Percentage deviation
Kelly	92 000 ± 4000 [a]	−2.44
Bunge	93 520 ± 150 [b]	−0.83
Sims and Hagstrom	93 700 ± 100 [c]	−0.64
Kaldor	92 200 ± 1900 [d]	−2.23
This work	94 305 ± 25	±0.03

[a] Reference 1.
[b] Reference 3.
[c] Reference 4.
[d] Reference 2.

TABLE XII. Comparison of energies of truncated wave functions with other variational calculations.

Authors	Number of terms	Energy
This work	2	−14.616 770
FS [a]	2	−14.616 837
This work	15	−14.655 526
FS	15	−14.661 587
SH [b]	15	−14.661 73
This work	20	−14.658 319
SH	20	−14.663 09
FS	20	−14.663 494
This work	32	−14.660 735
FS	32	−14.665 146
SH	31	−14.665 31
This work	52	−14.663 458
FS	52	−14.665 870
SH	44	−14.666 06
SH	57	−14.666 32
This work	236	−14.666 322 [c]
SH	107	−14.666 547 [d]
This work	300	−14.666 549
This work	650	−14.666 902
All $S+D$, this work	644	−14.662 857
		−14.663 241(20) [e]
spd limit, this work	510	−14.665 445
		−14.665 567(11) [e]
spdfg limit, this work	639	−14.666 750
		−14.666 970(30) [e]

[a] Froese Fischer and Saxena, Ref. 9.
[b] Sims and Hagstrom, Ref. 42.
[c] At this stage our results reflect basis-set incompleteness.
[d] At this stage Sims and Hagstrom's results reflect basis-set incompleteness.
[e] Extrapolated value.

In Table XIII are given the overlaps between our final wave function and several invariant portions of it. These overlaps will probably not be very much affected by increased accuracy in the wave function. From the relationship between the overlap and error bounds to expectation values[45] one can appreciate how these error bounds are affected by systematic truncations such as are found in simplified models for atomic calculations. A detailed description of the wave function is given elsewhere.[46]

A. Pair energies

Pair energies in general are of interest inasmuch as they are invariant quantities for given refer-

TABLE XIII. Overlap between 650-term wave function and several invariant portions of it.

Invariant	Number of terms	Overlap ($\times 10^6$)
Reference configuration	1	908 750
$(1s)^2(2p)^2$	1	86 979 [a]
Other two-excitations (L shell)	90	2063
I shell, $^1S(1s2s)$	112	237
I shell, $^3S(1s2s)$	71	206
Two-excitations (K shell)	103	1510
One-excitations	8	47
Three-excitations	147	59
Four-excitations	117	147

[a] Certainly not an invariant, but it is singled out here because of its importance.

ence orbitals. Symmetry-adapted pair energies[47] seem to be of even more interest because they add up to the correlation energy very closely, to within 1% in the present case, as shown in Table XIV. Froese Fischer and Saxena[9] have defined symmetry-adapted pair energies, taking into account near-degeneracy effects. Their pair energies add up to *their* computed correlation energy to within[9] 0.001% for a wave function which accounts for almost 99% of the correlation energy. If this notable result is maintained for more accurate wave functions [certainly by introducing additional "pair energies," such as $\epsilon(2s, p_2)$, etc.] Froese Fischer and Saxena's pair energies might well constitute the much sought answer about how to do quantitative CI "by parts."

In Table XIV we also give absolute pair energies,[3] which are of special interest because they add up exactly to the variational upper-bound energy.

TABLE XIV. Symmetry-adapted and absolute pair energies from 650-term CI expansion.

Energy	Symmetry	Absolute
$\epsilon(1s,1s)$	$-$ 0.042 564	$-$ 0.042 537
$\epsilon(2s,2s)$	$-$ 0.046 731	$-$ 0.046 560
$\epsilon(1s,2s)$	$-$ 0.006 016	$-$ 0.005 416
$\epsilon(1s)$	... [a]	0
$\epsilon(2s)$	... [b]	+ 0.000 092 [c]
E (reference configuration)	$-14.572\,481$ [d]	$-14.572\,481$
Sum	$-14.667\,792$	$-14.666\,902$

[a] Included in $\epsilon(1s,1s)$.

[b] Included in $\epsilon(2s,2s)$.

[c] With HF orbitals at *spd* level of approximation, $\epsilon(1s)+\epsilon(2s)=0.0001$ μhartree.

[d] Our $10s$ STO basis gives a self-consistent-field energy $E_{\text{SCF}}=-14.573\,020\,48$, which is 2.7 μhartree above the HF energy (Ref. 17).

B. How to improve standard CI upper bounds

One possibility is to use considerably larger STO sets and to attempt to reduce the size of the orbital basis and of the CI expansion by means of energy-optimized spin orbitals.[48] Another possibility is to use radial functions other than STO's[49]; in this context what is of interest is improved asymptotic convergence. One might also consider CI-Hylleraas[4] wave functions with orthogonal orbitals. The important issue, however, is how to improve CI results; this is discussed in Sec. IV D.

DISCUSSIONS

The increased tempo and evolving structure of modern CI methods as a powerful technique for atomic and molecular calculations is nowhere better reflected than in Schaefer's monograph.[50] Other uses of accurate CI wave functions are discussed by Bonham and Fink.[51] Shavitt[52] has recently reviewed the status of general CI methods. We shall consider comparisons with previous works and perspectives for more accurate results.

A. CI and MBPT

In Table XII we give an extrapolated *spd* energy limit believed to be accurate to within 11 μhartree. Kelly[1] estimated the *spd* energy at -14.6650 a.u. for Be, in remarkable agreement with our more precise estimate. Our earlier estimate,[3] $E_{spd}=-14.664\,53$, was too high, because of the reasons given in Sec. III. One simple and strong test of CI and MBPT would be to check the CI *spd* energy-limit results (both finite-basis upper bound and extrapolated energy) by carrying out a discrete-basis[2] MBPT calculation with our present basis set.

B. CI and numerical MCHF

Froese Fischer and Saxena[9] optimize *different* bases for L, I, and K shells. These authors end up with a *13s16p12d4f3g* basis of *nonorthogonal* numerical orbitals. As far as the number of basis functions is concerned, standard CI converges definitely faster than MCHF, and it is clear that this is a shortcoming of MCHF, since a nonorthogonal basis cannot be increased much further without compromising numerical accuracy. On the other hand, MCHF converges much faster than standard CI with regard to the number of configurations (see Table XII). This does not constitute a severe handicap for standard CI, however, since considerably larger Hamiltonian matrices are currently being handled[29] with standard methods.

The MCHF energy is 880 μhartree above our computed $10s9p8d7f5g3h1i$ standard CI upper bound and 1100 μhartree above our estimated *spdfg* energy limit (see Table XII). Nevertheless, Froese Fischer and Saxena[9] state that in CI "the effect of a finite basis is difficult to analyze," whereas their numerical method "has an accuracy which, to a large extent, is independent of the nature of the solution." A general assessment of the potential accuracy of MCHF seems to be premature at this time.

C. CI and CI-Hylleraas

It is likely that for Be, CI-Hylleraas expansions[4,42] converge much faster than standard CI expansions (see Table XIII). On the other hand, patterns of energy convergence in CI-Hylleraas calculations have not yet been recognized, and, as a consequence, it is difficult to assess convergence and uncertainties. It is not clear whether CI-Hylleraas is more economical than CI for Be, for present or higher levels of accuracy. An approach that exploits the advantages of both standard CI and CI-Hylleraas methods should give better results than either method. It might consist of a CI-Hylleraas expansion based on *orthogonal* one-electron functions including the HF configuration. Even so, the feasibility of this program for $N>10$ seems questionable.[53] If CI-Hylleraas can be pushed towards convergence, it will provide the best wave functions for expectation and transition values, while CI will provide accurate nonrelativistic energies to be used in concomitant error-bound calculations based on bounds for the overlap.[53]

D. Perspectives for more accurate results

For closed-shell atomic states it might be possible to reduce the uncertainty in the energy by another order of magnitude, well below 1 cm^{-1}, with methods that are presently available.

Our main source of uncertainty is in the estimate of the STO truncation error by means of costly studies of patterns of convergence.[54] The $(L+I+K)$-shell part of these can be largely simplified[55] if one solves the exact two-electron pair equations,[56,57] which should be achievable with an accuracy of better than 0.1 cm^{-1},[58] using variational[57,59] r_{ij} expansions and recent integral evaluation procedures[60] of Sims and Hagstrom. It should be stressed that such calculations have not been attempted yet. Note also that we are thinking in terms of borrowing pair-equation results to improve CI results, inverting one of the proposals[13] made by Sinanoǧlu 14 years ago.[61] The estimate of the energy difference between the truncated and full CI can be improved by doing larger CI calculations and using Shavitt's methods.[52]

E. Conclusions

We have determined the nonrelativistic energy of the Be ground state with an uncertainty of 2 ppm. The relativistic and radiative energy correction is predicted to within 1.5%, and it agrees remarkably well with an *ab initio* estimate which makes explicit use of the relativistic Hamiltonian. It is clear that meaningful numerical tests of the relativistic many-electron Hamiltonian for small atoms are at hand as Musher hoped for.[62]

Purists may not like the empirical nature of our calculations. The error bounds to our results, however, are based on empirical extrapolations, much in the same spirit used by experimentalists in determining the uncertainties of their ionization potentials.[63]

As new computational methods make their entries in electronic-structure calculations, it is inevitable that there will continue to be interest in "recovering" x percent of the empirical correlation energy. Physically, however, that is of no interest. Here we have *determined* the correlation energy to less than 0.03% error.

Never before has CI been regarded as a powerful technique for atomic calculations of near-spectroscopic accuracy. The present results may constitute a turning point in this respect. One must realize, however, that the conceptual simplicity of CI is effective only with the help of efficient and versatile computer codes which need constant updating to keep abreast of new theoretical ideas.

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