Beryllium atom reinvestigated: A comparison between theory and experiment

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(Received 27 December 1989; revised manuscript received 12 December 1990)

We compare the theoretical and experimental energies for the ground state of the beryllium atom and investigate possible sources for the small discrepancy of about 60 μhartrees found by Bunge [Phys. Rev. A **14**, 1965 (1976); **17**, 486(E) (1978)]. Indications that the correlation energy may be underestimated in Bunge's work have been confirmed by a recent, very extensive multiconfigurational Hartree-Fock (MCHF) calculation. We emphasize that the critical part of the comparison between theory and experiment is the sum of the first and second ionization energies—the third and fourth are known more accurately from theory—and present the theoretical results accordingly. Before a comparison with experimental results can be performed, corrections must be added to account for mass polarization, for the effect of relativity including the Breit interaction and for radiative effects. The previously unknown mass-polarization contribution to the first ionization energy has recently been determined experimentally. Relativity is most important for the 1s electrons and this effect was included in Bunge's work, whereas the relativistic effect on the correlation involving the 2s electrons was neglected. Here, these contributions have been calculated to leading order. A crude estimate of the contribution to the Lamb shift from the 2s electrons is also given. When the revised relativistic corrections are combined with recent results from a very extensive MCHF calculation, the discrepancy in the beryllium ground-state energy is reduced to $(10\pm50)\mu$ hartrees.

I. INTRODUCTION

By using the algorithms available today, one can determine the electronic structure of systems with many electrons only by invoking a number of approximations. For systems like beryllium with only a few electrons essentially "complete" nonrelativistic calculations are within reach, and these benchmark calculations have become important sources of information concerning the accuracy of the various algorithms, approximations, and basis sets. Before a comparison between a nonrelativistic calculation and experiment can be attempted, however, a num-

ber of other effects must be included, e.g., the motion of the nucleus with its finite mass and relativistic and radiative contributions. Many of these effects have been accurately calculated only for systems with one or two electrons. For this reason more precise calculations of both relativistic and nonrelativistic few-electron systems are needed.

A good example of a complete nonrelativistic calculation is Bunge's study of the ground-state energy of the beryllium atom.[1-3] Using large basis sets and a complete configuration-interaction (CI) calculation, Bunge reported that the theoretical and experimental values for this

system differ only by one μhartree.[1] It seems not to be generally known, however, that the theoretical value that Bunge uses for this comparison is not his variational result but is based on a carefully performed extrapolation. In an erratum Bunge later pointed out that the mass polarization energy was included with the wrong sign. The difference between theory and experiment then widens to almost 60 μhartrees. In view of new developments and results we have taken a review of a number of theoretical and experimental studies of the beryllium atom and examine four possible reasons for this discrepancy: an error in the computed nonrelativistic energy, an error in the computed mass polarization energy, an error in the computed relativistic energy, and the neglect of radiative corrections for the 2s electrons. In Sec. II we compare a number of computational approximations which have been applied to Be and discuss what conclusions may be extracted from these comparisons. In Sec. III we analyze the corrections which must be added to the result of a nonrelativistic calculation before a comparison with experiment can be performed.

II. APPROXIMATE CALCULATIONS AND THE IMPORTANCE OF DIFFERENT EFFECTS

The most accurate calculations for two-electron systems follow the tradition of Hylleraas[4] and use a wave function which contains interelectronic coordinates. The classic work of Pekeris and co-workers[5] has long been used as a source of "exact" nonrelativistic results. Recent studies have been able to improve the convergence of these calculations by imposing the correct cusp conditions and asymptotic form on the wave function.[6,7] For systems with more than two electrons, several Hylleraas-type wave functions have been examined[8,9] but most calculations today are based instead on expansions in one-electron orbitals. Such expansions, however, converge relatively slowly ($\approx l^{-4}$) when orbitals with higher angular momenta are included.[10] Kutzelnigg[11] has suggested a way of dealing with the cusp at $r_i = r_j$, which would improve the convergence to l^{-8}, for second-order energies, but this method has not yet been applied to beryllium. The problem of slow convergence can also be avoided by expressing each pair function in terms of explicitly correlated Gaussian geminals.[12]

The ground state of beryllium has been computed using analytical, discrete basis sets in several large CI studies,[1-3,13] in a number of applications of many-body perturbation theory (MBPT), e.g., Refs. 14 and 15 and recently also in relativistic second-order calculations.[16] Several calculations using numerical basis sets have also been performed. Kelly used a numeric description of both bound and continuum orbitals in his pioneering application of MBPT to atoms.[17] In 1974 Froese-Fisher and Saxena[18] solved numerically the multiconfigurational Hartree-Fock[19] (MCHF) equations for this system. By allowing the potential to vary between each orbital the MCHF approach often gives surprisingly accurate results with only a small number of configurations. Another method which has been used to examine this system is the direct numerical solution of the "pair equation."[20-23]

In these calculations the summation over excited orbitals was performed implicitly by invoking the closure relation for each angular momentum value. More efficient methods have since been developed that produce a complete discretized numerical basis set, complete on the grid chosen.[24,25] These have been applied to relativistic as well as to nonrelativistic MBPT calculations. The most accurate nonrelativistic ground-state energy for beryllium is that from the recent very extensive MCHF calculation by Olsen and Sundholm[26] who performed full CI in completely energy optimized orbitals obtained by the finite-element method.

A. Approximation schemes

For a many-electron system, a complete CI calculation using an adequate basis set becomes computationally impractical and the complexity of MBPT grows rapidly with order. Clearly, some truncation scheme must be used in either approach. In MBPT calculation, a truncation after a given order is one possibility, but it is also possible to truncate with respect to the complexity of the terms or number of particles involved and sum certain diagrams to all orders. In contrast, when CI is truncated to a limited number of excitations it suffers from lack of size consistency—in terms of MBPT a truncated CI can be "simulated" by including a number of "unlinked diagrams" to all orders. Various methods have been devised to treat each electron pair separately. These methods are closely related to a "coupled-cluster" approach including only double excitations. In the coupled-cluster approach the corrections to the unperturbed wave function are expressed in terms of an exponential of excitation clusters. A numerical implementation of the coupled-cluster approach has been developed by Lindgren and Salomonson,[23] initially including only double excitations (CC-D), but recently extended[27] to include also a complete treatment of single excitations (CC-SD). Without single excitations this method is equivalent to the coupled-pair many-electron theory (CP-MET) applied to Be by Adams, Jankowski, and Paldus[28] using an analytical basis set. It is also quite similar to the CCD calculation in Ref. 12 which used explicitly correlated Gaussian geminals to circumvent the partial-wave expansion. Recently, the coupled-cluster approach has been extended to include three-particle excitations.[29] For Be, a calculation with single, double, and triple excitations can be expected to yield almost all of the correlation energy provided a sufficiently large basis set is used to describe the excitations. Below we discuss the accuracy of the various approximate approaches. With the development of modern computers and algorithms it has recently become possible to perform a complete MCHF calculation for beryllium[26] and this calculation constitutes a new benchmark for the comparisons.

B. Single, double, triple, and quadruple excitations

Table I compares the results for various approximations obtained in the d limit as well as results extrapolated to include all higher l values. The d-limit results may

also be compared with results from order-by-order MBPT. Silver, Wilson, and Bunge[14] performed both CI and MBPT calculations using the same basis set and their second- and third-order MBPT correlation energies, -71.95 and -83.80 mhartrees, respectively, can be compared directly with their CI results given in Table I. (The more complete calculation in Ref. 27 gave instead the results -72.14 and -83.89 mhartrees for the d limit in second and third order.) The difference between the third-order value and the results of both CI and CC when truncated after double excitations is due to diagrams appearing in fourth and higher orders. The effects of single and triple excitations also enter in fourth order—but the comparison in Table I indicates that these give consider-

ably smaller contributions for Be than the diagrams included in CI-D and CC-D. The correlation energy in CI-D gives rise to unlinked terms in the wave function which are products of a pair energy and a double excitation. The part involving the pair energy of the same electron pair can be rewritten in terms of linked diagrams, whereas terms involving different pair excitations cannot and thus destroy the size consistency. In complete CI— or in CC-D—four-particle excitations that are products of two pair excitations are present and cancel exactly the unlinked terms arising in CI-D but lead also to linked diagrams, which have to be evaluated. The difference between CC-D and CI-D (-3.46 mhartrees in the d limit), can thus be attributed to these "factorizable" four-

TABLE I. Comparison between correlation energies to be added to the HF energy, $-14.573\,023$ a.u. for the ground state of beryllium (in mhartree $= 10^{-3}$ a.u.).

Excitation	d limit			Extrapolated to the limit $l = \infty$		
	CI	CC-CI	CC	CI	CC-CI	CC
Double (D) excitations	-87.79[a]		-91.247[b,c] -91.218[b,d]			-92.989[b,c] -92.961[b,d] -92.983[e,c] -92.952[e,d]
Factorizable quadruple excitations (CC-D–CI-D)		-3.46				
Single+double (SD) excitations	-88.37[a]		-91.94[b,c] -91.911[b,d]	$-90.218(20)$[f]		-93.667[b,d]
(SD-D) Factorizable triple or quadruple excitations (CC-SD–CI-SD)	$(-0.58$[g]$)$	-3.57	$(-0.693$[g]$)$		-3.45	$(-0.706$[g]$)$
Total CI	-92.39[a] -92.422[h]			$-94.305(25)$[a]		
(Extrapolated)	-92.43[a] -92.544[h]					
MCHF (Nonfactorizable triple or quadruple excitations	-92.547[i] $(-0.633$[j,a]$)$ $(-0.636$[j,i]$)$			-94.35[i] $-(0.638$[j,a]$)$ $(-0.68$[j,i]$)$		

[a]Configuration interaction [d-limit results from Ref. 14, Table II, the l-extrapolated results from Table II, (Ref. 1)].
[b]Coupled-cluster diagrams, Salomonson and Öster, Ref. 27.
[c]Including only the "factorizable" coupled-cluster diagrams, which can be obtained as an integral of one pair function times another pair function.
[d]Including all coupled-cluster diagrams.
[e]Alexander, Monkhorst, and Szalewicz, Ref. 12.
[f]Bunge, Ref. 1, Table XII.
[g]The contribution from single excitations obtained as the difference between the results with and without single excitations.
[h]Results from Ref. 1. Differs from a by the inclusion of one additional $3d$ basis function (see Ref. 14, p. 1376).
[i]Olsen and Sundholm, Ref. 26. Full CI, thus including all single, double, triple, and quadruple excitations.
[j]The difference between the final coupled-cluster results (CC-SD) and the total CI results.

particle excitations.

The most accurate single- and double-excitation calculation in Table I is the -93.667-mhartrees result from Ref. 27. This value was calculated using a numerical basis set complete on the grid used and includes an extrapolation to account for all angular-momentum terms. The numerical accuracy of this calculation has been estimated to be about 1 μhartree with the uncertainty dominated by the l extrapolation. To include more of the correlation energy excitation clusters involving more than two particles must be taken into account.

The terms neglected in CC-SD are the nonfactorizable triple and quadruple excitations which enter in fourth and sixth order of perturbation theory, respectively.[30] If a reliable triple-excitation calculation were available, this value could be added directly to the final CC-SD result and should give a very accurate estimate of the total correlation energy.

Previous estimates of the triple-excitation contributions to the energy of Be have varied widely. Silver, Wilson, and Bunge[14] found that in the d limit the sum of *all* triple and quadruple excitations was -4.02 mhartrees. Combination of this result with our value of -3.57 mhartrees (Table I) for the factorizable triple and quadruple excitations leads to an estimate of -0.45 mhartree for the nonfactorizable ones. From the work of Bauschlicher, Langhoff, and Taylor[31] the value -0.267 mhartree for this effect can be obtained by comparing the d-limit "full" CI values and the results obtained using the modified coupled-pair functional[32] (MCPF) approach. The latter is closely related to CC-SD. This estimate of the nonfactorizable triple and quadruple excitations is considerably smaller than the one obtained in Table I. The discrepancy is probably caused by basis-set deficiencies, since an error of 0.480 mhartree exists already at the Hartree-Fock level. Similarly the "full" CI correlation energy is -84.080 mhartrees (calculated using the HF value in this basis) but a CI with only single and double excitations gives -80.675. Not only are these values about 5% smaller than the results by Silver, Wilson, and Bunge[14] but the difference between them, -3.405 mhartrees, is very different from the value in Ref. 14, i.e., 4.02 mhartrees.

Another estimate of triple excitations can be obtained from the work of Froese-Fischer and Saxena.[18] They found that excitations from the pair $1s2p$ account for -0.416 mhartree in the g limit. The interference of this pair with the $1s2s$ excitations gives an additional -0.025 mhartree and the total interference effect on the other pair excitations is -0.074 mhartree, which might indicate a total contribution from the $1s2p$ excitation of about ≈ -0.51 mhartree, the pair excitations from the $1s^22p^2$ configuration are responsible for a large part of the triple excitations. The near degeneracy between $2s^2$ and $2p^2$ in Be enhances the importance of triple excitations and emphasizes the usefulness of combining multiconfiguration and MBPT methods. Unfortunately, the approaches so far using multiconfiguration reference functions[22,33,34] have not yet reached the accuracy of the CC-SD calculations presented here.

Although no direct estimate of nonfactorizable triple

and quadruple excitations can be obtained from the CI calculation by Bunge[1-3] the total energy from the single- and triple-excitation contributions was found to be -0.33 and -1.01 mhartrees, respectively.[12] These two numbers, however, contain a certain amount of overlap because two-particle interactions have matrix elements between singly and triply excited configurations. We note also that none of these results can be compared directly with the value obtained by the difference between the CC-D and CC-SD numbers in Table I, -0.706 mhartree. This difference includes not only the single excitations in the CI calculation but also the effect of factorizable triple excitations. In a later work[35] Bunge has given the value -0.631 mhartree from the triple excitations $1snln'l'n''l''$ but excluding the parts $1snsn'ln''l$. Since none of these excitations are including in the CC-SD (for a closed-shell system the single excitations always conserve the orbital angular momentum) this calue can be added directly to the final CC-SD result, giving -94.298 mhartrees for the total nonrelativistic correlation energy, which is close to Bunge's value -94.305 mhartrees. This procedure, however, neglects the contributions from triple excitations where at least one of the electrons is excited into an s state. It seems likely that these excitations would contribute more than -0.007 mhartree or 1% of the contribution from the other triple excitations. This is thus an indication that Bunge's correlation energy may be too small.

To help clarify the size of the triple excitations we have performed a CC calculation that includes certain triple excitations together with single and double excitations (CC-SDT-1). A detailed description of the terms included is given in Ref. 29. The calculation was performed using a basis set consisting of $29s$, $19p$, $12d$, and $9f$ orbitals obtained numerically as described in Ref. 36. In Table II we compare the results of this calculation with the f-limit result obtained from the numerical solution of the two-particle equations. The difference between the total CC-SDT-1 correlation energy and the CC-SD result indicates that the triple excitations contribute -0.576 mhartree. To estimate the uncertainty in this value, we note that the *single-excitations* contribution, which is of about the same size, differs by about -0.02 mhartree from the final

TABLE II. Coupled-cluster results (in mhartrees) for the correlation energy in the f limit and extrapolated to account for higher l values. An estimate of -94.244 mhartrees for the total nonrelativistic correlation energy is obtained from these results by adding the value for the triple excitations in the f limit to the final CC-SD result.

	Numerical orbitals f	Pair equation (Ref. 27) f	extrap.
CC-D	-92.049	-92.217	-92.961
CC-SD	-92.736	-92.917	-93.667
(single excitations)	(-0.687)	(-0.700)	(-0.706)
CC-SDT-1	-93.312		
(triple excitations)	(-0.576)		

result for the single excitations obtained in Ref. 27. Since triple excitations are also believed to be more sensitive to incompleteness in the basis set,[37] the true error may be larger.

Our triple excitations' value, −0.576 mhartree, is in essential agreement with our earlier estimates of the triple-excitation contributions from the works by Froese-Fischer and Saxena[18] and by Bunge.[1−3] From the comparison in Table II with the pair-equation calculation of Ref. 27, we see that most of the error in the correlation energy is due to the slow convergence of the double excitations.

The discussions above point to the difficulty of obtain-

ing μhartree accuracy. To improve this result requires both a large orbital set and inclusion of at least triple excitations. The inclusion of triple as well as quadruple excitations using a large basis set has become possible with the recently developed MCHF program by Olsen and Sundholm[26] which employs the finite-element method to expand each radial function in terms of a set of local polynomials. Compared with the more commonly used finite difference approach, the finite-element method has the advantage of a well-defined energy function, enabling the use of modern optimization algorithms for the energy minimization, leading to fast convergence also for large MCHF expansions. The program uses efficient vectoriz-

TABLE III. The separation of the beryllium energy into the contributions for heliumlike beryllium and for the changes due to the addition of two additional 2s electrons. (In hartree atomic units for ^{9}Be.) Numbers in square brackets are for reference only.

	Be^{2+}	Be-Be$^+$
	Experiment	
Binding energies		
First	−8.001 497 47[a]	−0.342 621 1[b]
Second	−5.655 925 55[c]	−0.669 228 3[b]
Total, experiment:	−13.657 423 02	−1.011 909 4
	Theory	
Coulomb energy		
Hartree-Fock correlation	−13.611 299	−0.961 724
CC-SD	−0.044 267[d]	[−0.049 400[e]]
CI	[−0.043 996[f]]	[−0.050 038(28)[f]]
MCHF		−0.050 08(3)[g]
Total, nonrelativistic:	−13.655 566 19[a]	−1.011 80(3)[g]
Corrections		
Mass polarization	0.000 025 60[a]	+0.000 003[h]
Relativistic correction		
(DFB-HF)	−0.002 035[i]	−0.000 132[i]
Correlation	−0.000 191[j]	+0.000 022(10)[k]
Lamb shift	0.000 344 04[a,c]	+0.000 008(15)[l]
Total, corrections	−0.001 856 83	−0.000 099(25)
Total, theory	−13.657 423 02	−1.011 90(5)

[a]Theoretical value, Drake, Ref. 41.
[b]Experimental value, Johansson, and Holmström and Johansson, Ref. 39.
[c]Theoretical value, Johnson and Soff, Ref. 50.
[d]The CC-SD is "exact" for a two-electron system and this value is taken from the work of Pekeris.[5]
[e]Salomonson and Öster, Ref. 27.
[f]Bunge (Refs. 1-3) brought the value for Be^{2+} in agreement with the value given in Ref. 5 by adding a correction, −271 μhartrees, to account for the basis-set truncation error.
[g]Olsen and Sundholm, Ref. 26.
[h]The mass polarization in the first and second ionization limits are taken from the recent experiment by Wen et al. (Ref. 43) and from the calculation in Refs. 9 and 50, respectively. Bunge used the estimate 5(5) mhartrees between Be and Be^{2+} for this effect.
[i]Obtained by subtracting the nonrelativistic Hartree-Fock values from the results of a Dirac-Fock-Breit calculation, which includes the Breit interaction together with the Coulomb interaction, following the procedures described by Quiney, Grant, and Wilson, Ref. 46.
[j]Obtained by subtracting the one-electron contribution (DFB-HF) from the value −2.226 46 mhartrees for the relativistic contribution for Be^{2+} (Drake, Ref. 41, Johnson and Soff, Ref. 50).
[k]Second-order correlation contribution, as presented in Table IV.
[l]See the discussion in Sec. III C.

able routines based on CI algorithms from Ref. 38, making it possible to treat very large CI expansions. To obtain the results for Be shown in Tables I and III, Olsen and Sundholm performed a sequence of MCHF calculations using full CI in each set of shells, where the radial functions defining the shells were optimized. Each calculation thus represents the best possible energy that can be obtained with a given number of shells. Calculations with an increasing number of radial functions were carried out for each value of the maximum angular momentum, thereby making it possible to monitor the angular convergence of the correlation energy. Simple extrapolations were then used to get estimates for the total correlation energy. Up to about 80 fully optimized orbitals and more than half a million Slater determinants were included. As seen from Table I the d-limit result is about 3 μhartrees below the CI result by Bunge. For the g limit, Olsen and Sundholm obtain $-14.666\,98$ hartrees, about 0.01 mhartree lower than that given by Bunge and it appears that the contribution from higher l values for the correlation involving the $2s$ electrons was underestimated in Bunge's work. The final MCHF value is $-14.667\,37$ hartrees, corresponding to a correlation energy of -94.35 mhartrees, which is 0.04 mhartree below Bunge's extrapolated value.

III. CORRECTIONS TO THE NONRELATIVISTIC ENERGY

In a nonrelativistic calculation with only Coulomb interactions a number of effects are neglected which must be included before a comparison with experiment can be performed. For a light atom, the motion of the nucleus can give significant energy contributions. This topic is discussed in Sec. III A. For highly accurate results relativistic effects must also be taken into account, even for light atoms, such as Be. These effects enter in many ways, as discussed in Secs. III B and III C. The treatment of relativistic effects in many-electron systems has received considerable attention in recent years and significant progress has been made, making possible a direct calculation of the relativistic effects on the correlation.

In Bunge's paper the total "experimental" ground-state energy of beryllium atom $-14.669\,345(2)$ a.u. was obtained by adding the experimental first and second ionization potentials[39] to the calculated third and fourth ionization potentials of Pekeris[5] and of Garcia and Mack,[40] respectively. Drake has recently obtained an improved value, $124\,125\,6.601$ cm^{-1} for the third ionization potential by using higher-order radiative two-electron corrections.[41] Although this calculation changes the best estimate of the total "experimental ground-state energy" it will not affect the comparison between theory and experiment since experimental results are used only for the first and second ionization potentials and the same correction must be added to the theoretical relativistic result.

A. Mass polarization

For light atoms like Be, the kinetic energy associated with the nuclear motion $P^2/2M = \sum_i p_i^2/2M$

$+ \sum_{i(<j)} p_i p_j/2M$ is significant. The first term leads to the *normal mass shift* and is obtained by replacing the free-electron mass m_e by the reduced mass $\mu_e = m_e/(1+m_e/M)$. This is the origin of the mass-dependent conversion factor between atomic units and wave numbers: $R\,(^9\mathrm{Be}) = 109\,730.634\,7$ cm^{-1}. This gives a positive energy contribution, thus reducing the binding energy. The second term, the mass polarization, arises from a correlation between the electronic momenta through the motion of the nucleus. Since only exchange contributions enter in first order (the direct terms are excluded in lowest order by the odd parity of the $\mathbf{p}$ operator for each electron), this effect usually gives a negative energy contribution for each level. Because the ground states of He, Li, and Be contain only s electrons the lowest-order contribution is zero. The first contribution to appear is caused by admixtures of $2p^2$ (and higher $npn'p$ states) and is positive. In his accurate studies of two-electron systems, Pekeris[5] obtained the total contribution 25 μhartrees for the mass polarization of Be^{2+}. Since the value is due largely to admixtures of p states, we do not expect it to change significantly when two $2s$ electrons are added. Although the $2s$ electrons may give rise to additional contributions these are much smaller—for one-valence systems, the mass polarization due to the valence electron scales as n^{-3}, just as, e.g., the hyperfine structure, and, indeed, Prasad and Stewart[42] find a contribution of 2 μhartrees when one $2s$ electron is added. This result was confirmed in the recent, very accurate calculation of King.[9] However, the contribution from the second $2s$ electron has recently been determined experimentally. Wen *et al.*[43] used resonance ionization mass spectroscopy to study the isotope shift between ^{10}Be and ^{9}Be. By examining two-photon transitions from the ground state to a series of $2sns$ and $2snd$ states they extracted a shift of 270 MHz between the two isotopes for the ground state in Be relative to that of Be$^+$. This result corresponds to an energy contribution from the mass polarization of 0.4 μhartree for ^{9}Be and can be compared with Bunge's estimate of 3(3) μhartrees.

B. Relativistic and radiative corrections

Relativistic effects are comparable to the higher-order correlation contributions and must be considered with some care. The dominating relativistic contribution is accounted for by using the Dirac rather than the Schrödinger equation to describe the electron orbitals. In addition, we have to account for the effect of the exchange of transverse photons in the electron-electron interaction: to lowest order, i.e., $O(\alpha^2)$, this exchange is accounted for by inclusion of the Breit interaction, but in higher orders of α [$O(\alpha^3)$ and higher], the transverse photons lead also, e.g., to the Lamb shift.

As mentioned, the comparison between theory and experiment is affected only by the difference between the corrections for Be and Be^{2+}. Whereas the leading relativistic effects [i.e., to $O(\alpha^2)$] are calculated accurately by Pekeris[5] for the heliumlike doubly ionized beryllium, no calculation including both correlation and relativistic effects has been published for neutral Be. To estimate the

effect of relativity due to the two $2s$ electrons Bunge used the Hartree-Fock expectation values for the relativistic energy corrections from the work of Hartmann and Clementi.[44] The corrections were found to be relatively insensitive to the degree of ionization: The correction -2.198 mhartrees for neutral beryllium is changed to -2.090 mhartrees by removing the two outer electrons, giving a Hartree-Fock contribution of -0.108 mhartree for the difference between Be and Be^{2+}. A fully relativistic calculation leads to a Dirac-Fock (DF) energy value of $-14.575\,891$ hartrees, giving a correction of -2.869 mhartrees to the nonrelativistic Hartree-Fock value $-14.573\,023$ hartrees. The DF expectation value of the Breit interaction is 0.702 mhartree (in agreement with the older, somewhat less accurate, result by Mann and Johnson[45]), and the effect is changed by only 0.04 μhartree by using the Dirac-Fock-Breit (DFB) procedure,[46] where the Breit interaction is treated self-consistently together with the Coulomb interaction. The total one-electron relativistic and Breit contribution is thus -2.167 mhartrees which differs by 0.031 mhartree from the nonrelativistic HF expectation value.[44] It is possible that the discrepancy can be ascribed to $O(\alpha^4)$ effects due to relativistic changes in the orbitals which modifies the electron-electron interaction, but it seems more likely that it is a result of incompleteness in the old nonrelativistic calculation. [The $O(\alpha^4)$ contribution to the hydrogenic $1s$ energy is less than 1 μhartree.] For the comparison with experiment the important relativistic correction is that involving the $2s$ electrons and their effect on the $1s$ electrons, which is found to be only -0.132 mhartree. (If the Breit interaction were neglected, the correction from the $2s$ electrons would instead be -0.167 mhartree.) Table III shows the results separated into contributions the energy of Be^{2+} and to the difference in energy between Be and Be^{2+}.

In order to estimate the change in the correlation energy of Be^{2+} due to relativistic effects, Hartmann and Clementi[44] computed the expectation value of these effects using a Hartree-Fock wave function. To this result, -2.090 mhartrees, they then added a value for the

Lamb shift, $+0.323$ mhartree, which they obtained using their Hartree-Fock wave function and the formula by Kabir and Salpeter.[47] The sum, -1.767 mhartrees, was then compared with the value, -1.878 mhartrees, for the total corrections obtained by Pekeris using his "exact" nonrelativistic wave function.[5] The difference in these two numbers, 0.111 mhartree, is taken by Hartmann and Clementi (and later by Bunge) to be the change in correlation energy due to relativistic effects. A closer examination of this procedure, however, reveals two disturbing problems. First, Pekeris's value of -1.878 mhartrees includes a contribution of 0.0256 mhartree due to mass polarization. Thus Bunge includes the mass polarization energy of Be^{2+} twice (once directly and then again when he adjusts for the change in correlation energy due to relativistic effects). Second, the difference between Hartmann and Clementi's value for the Lamb shift, 0.323 mhartree, and Pekeris's value, 0.331 mhartree, was never corrected for. The total relativistic correction from Pekeris' work, -2.226 mhartrees (including the Breit interaction and the hydrogenic contribution, -1.704 mhartrees, but excluding the Lamb shift), should instead have been compared directly with Hartmann and Clementi's Hartree-Fock expectation value, -2.090 mhartrees, for these effects.[5] However, as discussed above, Hartmann and Clementi's expectation value of the correction may be somewhat inaccurate. From a comparison of a Dirac-Fock-Breit and a Hartree-Fock calculation for Be^{2+} we obtained the value -2.035 mhartrees. The difference, -0.191 mhartree, between this result and the total correction from Pekeris, can be attributed to correlation contributions to the Breit interaction and to changes in the Coulomb correlation energy induced by the relativistic changes in the one-electron orbitals and their energies.

Up to this point, relativistic effects on the correlation involving the $2s$ electrons have been neglected. To remedy this situation a fully relativistic calculation of the second-order correlation contribution was performed using the procedure described by Quiney[48] for Be as well as for Be^{2+} and the results are shown in Table IV. Although, as seen above, the relativistic corrections in the

TABLE IV. Relativistic effects on the second-order correlation contributions obtained by performing a relativistic Dirac-Fock-Breit calculation (using the Dirac one-electron Hamiltonian together with the electron-electron interaction given by the sum of the Coulomb interaction and the Breit interaction) and subtracting the results of a nonrelativistic calculation, (μhartrees).

Excitation	Be^{2+} $1s^2$	$1s^2$	Be $1s2s$	$2s^2$	$(Be-Be^{2+})$ Total
s^2	-52.244	-38.476	-3.971	13.042	22.839
p^2	-90.438	-89.942	-5.175	3.500	-1.179
d^2	-19.895	-19.913	-1.094	2.390	1.278
f^2	-8.853	-8.836	-0.400	0.311	-0.073
g^2	-4.947	-4.927	-0.256	-0.051	-0.286
h^2	-3.066	-3.058	-0.158	-0.032	-0.182
i^2	-2.055	-2.049	-0.104	-0.026	-0.124
Sum	-181.495	-167.200	-11.160	19.138	22.27
Extrapolated	-193				21.6

Dirac-Fock-Breit energies are dominated by the effect of using the Dirac rather than the Schrödinger one-electron Hamiltonian, the dominating relativistic effect on the *correlation* energy involves the Breit interaction as noted earlier for He-like systems.[24,49] The relativistic correlation contributions converge very slowly with angular momentum; like l^{-2} compared with l^{-4} for the nonrelativistic Coulomb interaction, although the $2s^2$ contributions in Table IV show some deviation from this behavior at the higher l values. The l^{-2} dependence has been used to estimate the contributions from l values larger than 6, which were not calculated explicitly. The slow convergence in the energy seems to be caused by the $\delta(r_{12})$ function, which is present in the nonrelativistic limit both of the Breit interaction and of the relativistic correction to the Coulomb interaction.

As expected, the relativistic effects are largest for the $1s^2$ electron pair, which is relatively insensitive to the presence of two additional $2s$ electrons. The higher partial waves give nearly identical contributions for these two systems and the large change for the $1s^2 \rightarrow s^2$ excitation is dominated by the exclusion of the $1s^2 \rightarrow 2sns$ excitations for neutral beryllium. We note that the relativistic corrections to the second-order energy for heliumlike beryllium is quite close to the all-order result obtained from Pekeris's work.[5] There is a certain amount of cancellation between the contributions from the $1s^2$ pair and the $1s2s$ pair energies, leaving the total correction close to that from the $2s^2$ pair. The nonrelativistic second-order energy for this pair is changed by nearly 50% when higher-order terms are included and we assign an uncertainty of this size to the relativistic corrections obtained in second order. The sum of the relativistic corrections for the first two ionization energies, -0.110 mhartree, coincides with the value used by Bunge based on a HF calculation, and it appears that the error caused by the incompleteness in the older HF calculation to a large extent compensates the omission of the correlation contribution.

C. The Lamb shift

Using a Hartree-Fock wave function Hartmann and Clementi[44] obtained a Lamb shift contribution of 323 μhartrees for Be^{2+}. This value was added by Bunge[1–3] to his nonrelativistic results. The hydrogenic contribution obtained in the recent work of Johnson and Soff[50] is 45.507 cm^{-1}=207.3 μhartrees which is in agreement with the older value by Garcia and Mack[40] used by Bunge for the "experimental" fourth ionization energy. For the second $1s$ electron, Pekeris, using his "exact" nonrelativistic wave function, obtained a Lamb shift contribution of 27.1 cm^{-1}=123.5 μhartrees, which was included in the experimental third ionization energy used in Bunge's comparison. Together with the hydrogenic contribution, this gives 331 μhartrees. Adding this contribution, rather than the smaller HF value, removes an inconsistency in Bunge's comparison with experiment and increases the discrepancy by 8 μhartrees. Drake[6,41] has obtained an improved value, 29.996 cm^{-1}=136.7 μhartrees of the Lamb shift for the third ionization ener-

gy by including higher-order radiative corrections. However, as discussed above, this improvement does not affect the comparison between theory and experiment, which involves only the first and second ionization energies.

To get a very rough estimate of the contributions involving $2s$, we can use the values given by Drake,[41] for the addition of a $2s$ electron to a $1s$ electron into a singlet and triplet state. These numbers, 13.3 and 16.3 μhartrees, respectively, include both the contributions from the $2s$ electron and the modification of the $1s$ contribution and should be compared with the hydrogenic $2s$ contribution[41] of 26.8 μhartrees. The presence of *one* $1s$ electron thus results in an average shielding of -11.3 μhartrees for the $2s$ electron. If we assume that the interaction with the second $1s$ electron is of the same order, we get a net contribution of 4.2 μhartrees from each of the two $2s$ electrons. Since the two $1s$ electrons screen each other they are located somewhat further out than in the $1s2s$ states, and their interaction with the $2s$ electrons may thus give even larger contributions. Neglecting this effect as well as the $2s$-$2s$ interaction gives us an estimate of 8 μhartrees for the difference in Lamb shift between Be and Be^{2+}. We have included a relatively large error, ±15 μhartrees, in view of the large cancellations involved in the hand-waving argument. The correct theoretical treatment of radiative corrections for many-electron systems is still an open question, but clearly more reliable estimates would be worthwhile.

IV. DISCUSSION

Obtaining an accuracy of 1 μhartree or even 10 μhartrees for a few-electron system is a nontrivial problem. At this level many effects which are often neglected give contributions which are many times larger than the desired accuracy. For the Be atom Bunge found a discrepancy of about 60 μhartrees (or, rather, 40 μhartrees if the estimates of relativistic corrections had been used in a consistent way). Correction terms such as the effect of relativity on the correlation involving the $2s$ electrons and the radiative corrections from these electrons are close to this size but were neglected in Bunge's study. In comparisons such as these, it is essential that calculations be performed on those quantities which are known most accurately from experiment. In general, the experimental uncertainty is smallest for the binding energy of the outer electrons, which are least tightly bound. For heliumlike systems like Be^{2+}, on the other hand, the accuracy of the most complete theoretical calculations surpasses the experimental accuracy. In the present work we have examined in detail the energy differences between Be and Be^{2+}. Our best theoretical estimate for this difference is $-1.011\,90(5)$ hartrees, to be compared with the experimental value[38] $-1.011\,909\,4$ hartrees. Several of the individual energy components in the final result have undergone substantial revision since Bunge's paper. In particular, the extensive MCHF calculation of Olsen and Sundholm,[26] which gave a final ground-state energy of $-14.667\,37$ hartrees, has shown that the nonrelativistic energy of Be was previously underestimated by almost 45 μhartrees. Many of the components to the energy difference which we have examined could be further im-

proved by more extensive calculations. It is our hope that this paper will stimulate further work in this area.

ACKNOWLEDGMENTS

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