Corrections to the beryllium ground-state energy

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A relativistic coupled-cluster calculation including single and double excitations has been performed for the ground-state energy of beryllium. Comparison with corresponding nonrelativistic calculations shows the effect of relativity on the pair correlation which, together with the relativistic corrections to the Hartree-Fock energy, can be combined with the most accurate nonrelativistic ground-state energy available. Many-body radiative corrections were estimated by multiplying accurate results for hydrogenlike Be with the ratio between the Dirac-Hartree-Fock and hydrogenic electron densities at the nucleus. The energy associated with the motion of the nucleus with its finite mass can be deduced with sufficient accuracy from experiment. Subtraction of all these corrections from the experimental result leads to an "experimental nonrelativistic energy" of −14.667 353(2) hartrees.

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I. GROUND-STATE ENERGY OF BERYLLIUM

With its four electrons, Be has been the subject of several *ab initio* investigations using a nonrelativistic formalism, which usually gives a good description for light atoms such as Be. The classic configuration interaction (CI) calculation by Bunge [1] gave a nonrelativistic ground-state energy of −14.667 328 hartrees for Be. This value has been improved only recently through a very extensive multiconfiguration Hartree-Fock (MCHF) calculation by Olsen and Sundholm [2,3], who obtained the result −14.667 37(3) hartrees.

However, before a calculated nonrelativistic value can be compared to the experimental result, several additional effects must be taken into account: the motion of the nucleus with its finite mass, as well as relativistic and radiative corrections and possibly also the effect of nuclear charge distribution. For the heliumlike system Be^{2+}, the ground-state energy including all corrections is, in fact, known more accurately from theory [4,5] than the corresponding experimental result which is a sum of the third and fourth ionization energies. The crucial comparison is thus the energy difference between Be and Be^{2+}, which can be obtained experimentally as the sum of the first and second ionization energies [6]. The motion of the nucleus leads to a "reduced" electron mass, but also to the so-called "mass polarization." This correction to the first ionization energy has recently been determined experimentally [7] from studies of isotope shifts between ^{9}Be and ^{10}Be and the mass polarization for the second ionization energy is known from calculations [8]. In their recent compilation and analysis of Be results, Mårtensson-Pendrill *et al.* [3] thus find that the major uncertainty in the extraction of a "nonrelativistic experimental" energy arises from two sources: from the relativistic effects on the electron correlation and from the Lamb shift and other radiative corrections. In this work we study these two contributions in more detail, with the results summarized in Table I.

II. RELATIVISTIC CORRECTIONS

A relativistic treatment affects the wave function and energy in several ways. First and most important is the use of a Dirac rather than a Schrödinger one-electron Hamiltonian. The Hartree-Fock (HF) wave function is then replaced by a Dirac-Hartree-Fock (DHF) wave function, with the resulting energy-expectation value changed from its nonrelativistic value −14.573 023 0 to −14.575 891 7 hartrees. This changes also the correlation between the electrons, as seen from Table II. In addition to the modification of the kinetic-energy term in the Hamiltonian due to relativity, also the exchange of transverse virtual photons must be accounted for. To leading order in α^2, this is described by the original (energy-independent) Breit interaction. The Dirac-Hartree-Fock expectation value of this electron-electron interaction is 0.702 mhartrees as determined already by Mann and Johnson [9]. Including higher orders of the Breit interaction by using a self-consistent treatment, the "Dirac-Fock-Breit" (DFB) procedure, was found to give negligible contributions (0.04 μhartrees) for Be (Ref. [9]).

In Ref. [3] the relativistic contributions, including the effect of the Breit interaction, to the HF energy were treated self-consistently, but the correlation effects were obtained only to lowest order (two Coulomb interactions or one Coulomb and one Breit interaction). Quite a large uncertainty had to be assigned to the unknown higher-order pair-correlation effects. Here the "pair equation" has been solved to all orders also in the relativistic case by using the computer program developed by Salomonson and Öster [10]. The "pair functions" are expanded into terms with different angular momentum l of the excited orbitals and the effect of angular momenta not included is accounted for by extrapolation. Whereas the nonrelativistic energy contributions decrease with l^{-4}, the relativistic and Breit corrections have a slower angular convergence due to the presence of a $\delta(r_{12})$ function in the nonrelativistic expansion of these operators. This

slower convergence leads to larger contributions from higher l values and may reduce the accuracy of the final results. Attempts to fit the results from different angular momenta to an l^{-x} dependence gives x slightly larger than 2. As alternatives, a fit to an expansion $al^{-2}+bl^{-n}$ with $n=3$ or 4 could be performed. Although the parameters are uncertain due to the lack of significant digits in the small corrections, the extrapolated result is relatively insensitive to the method used.

The pair program has recently been extended, as described in more detail elsewhere [11], to include all terms with one Coulomb interaction replaced by a Breit interaction (although this led to an order-of-magnitude longer computing time). As mentioned above, terms with two or more Breit interactions were found to give negligible contributions for Be already in the one-particle case and were neglected here. Table II compares the effects of relativity on the pair-correlation energies in second order and all orders. The second-order result is somewhat different from the values obtained by Quiney and coworkers [3,12] mainly for the $2s^2$ pair. As seen from Table II the Breit interaction, although giving a smaller part of the total energy, has a much larger effect on the *correlation* energy than the use of a Dirac one-electron Hamiltonian. The total energy contribution is somewhat uncertain, due to the large contributions from higher l values. However, most of the Breit-correlation energy is due to the more relativistic $1s^2$ pair and changes very little—only about 3.3 μhartrees—when the two $2s$ electrons of Be are added. Higher angular momenta are found to have negligible effect on the *change* in the $1s^2$ pair energy, and essentially also for the $1s2s$ and the $2s^2$ pairs.

The relativistic corrections in Tables I and II can be used to establish a direct comparison between nonrelativistic and relativistic calculations. Recently a relativis-

TABLE I. 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 hartrees for ^{9}Be, $\mathcal{R}(^9\text{Be})=109\,730.6347\ \text{cm}^{-1}$.]

	Be^{2+}	$Be-Be^{2+}$	Be
Theory			
Nonrelativistic			
HF	−13.611 299	−0.961 724	−14.573 023
Correlation	−0.044 267	−0.050 08(3)	−0.094 35(3)
Total	−13.655 566 19[a]	−1.011 80(3)	−14.667 37(3)[b]
Mass polarization	+0.000 025 60[a]	+0.000 003[c]	+0.000 028
Rel. corrections			
DF−HF	−0.002 701[d]	−0.000 167[d]	−0.002 868
DFB−DF	+0.000 666[d]	+0.000 036[d]	+0.000 702
Correlation, Coul.	+0.000 012[e]	+0.000 005[f]	+0.000 017
Correlation, Breit	−0.000 203[e]	−0.000 009[f]	−0.000 212
Lamb shift	0.000 344 04[a,g]	+0.000 010(1)[f]	+0.000 354(1)
Total Theory	−13.657 423 02[a,g]	−1.011 93(3)	−14.669 35(3)
Experiment		−1.011 909 4[h]	−14.669 332 4[h]

[a]Theoretical value, Drake, Ref. [5].
[b]Olsen and Sundholm, Ref. [2].
[c]The mass polarization in the first and second ionization limits are taken from the recent experiment by Wen *et al.* [7] and from the calculation in Ref. [8], respectively.
[d]Obtained as the difference between the Dirac-Fock (DF) and the nonrelativistic Hartree-Fock (HF) value and between the Dirac-Fock-Breit (DFB) and the DF results, respectively. The DFB calculation includes the Breit interaction together with the Coulomb interaction, following the procedures described by Quiney, Grant, and Wilson, Ref. [12]. The relativistic calculations are performed with an extended nucleus which result in an upward shift compared to the point nucleus of 0.6 μhartrees for Be^{2+} as well as for Be.
[e]The sum of the correlation contributions is obtained by subtracting the one-electron contribution (DFB−HF) from the value −2.226 46 *m*hartrees for the relativistic contribution for Be^{2+} (Drake, Ref. [5], Johnson and Soff, Ref. [4]). The separation into Coulomb and Breit correlation is obtained from Pekeris, Ref. [13], as described in Sec. II.
[f]This work.
[g]Theoretical value, Johnson and Soff, Ref. [4].
[h]The experimental values for the first and second ionization energies are taken from Johansson, and Holmström and Johansson, Ref. [6]. The total "experimental" Be ground-state energy is obtained by adding the theoretical value for Be^{2+}.

tic calculation was performed by Liu and Kelly [13], who used a multiconfiguration Dirac-Fock wave function as a starting point for a coupled-cluster calculation including single and double excitations (CCSD) (although the excitations from the $2p^2$ pair were treated only to second order), giving a correlation energy of -0.0951. Since no Breit interaction was included, only the relativistic corrections to the Coulomb part of the pair energy enters, which, according to our calculations is only 0.017 mhartrees. Their result thus corresponds to the same nonrelativistic correlation energy for all figures quoted and we see that the correlation energy is overestimated by about 0.8 mhartrees compared to the value $-0.094\,35(3)$ from Olsen and Sundholm [2]. This error is comparable to that in the pair-correlation energy, $-0.093\,667$, obtained by Salomonson and Öster [10] in a CCSD calculation starting from a single configuration.

A. Relativistic corrections for Be^{2+}

After extrapolation to account for the higher angular momenta, our all-order result for the relativistic corrections to the pair correlation for heliumlike beryllium becomes (-189 ± 2) μhartrees, with (12 ± 1) μhartrees due to relativistic effects on the Coulomb interaction and (-201 ± 1) μhartrees due to the Breit interaction. These results can be compared to the values given by Pekeris [14] or to the more recent results by Drake [5], who used "exact" nonrelativistic wave functions to calculate the expectation value of the corrections. Subtraction of the Dirac-Fock-Breit correction leaves a relativistic correction to the correlation energy of -191.2 μhartrees. The contribution due to the Breit interaction alone can be deduced from Pekeris's work by adding all terms contributing to the expression

$$H_B = 2\pi\alpha^2\langle\delta(r_{12})\rangle - \frac{\alpha^2}{2r_{12}}\left[\mathbf{p}_1\cdot\mathbf{p}_2 + \frac{\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2}{r_{12}^2}\right]$$

for the nonrelativistic reduction of the Breit interaction [15] which gives 462.8 μhartrees, 666.2 μhartrees of which are due to one-electron effects, leaving -203.4 μhartrees from the correlation contribution. The results are not completely equivalent, since the fully relativistic treatment automatically includes certain terms of order α^3 and higher.

TABLE II. Comparison between the relativistic corrections to the pair-correlation energy treated in second order and to all orders caused by the use of a Dirac one-electron Hamiltonian and by the Breit interaction. The values are given in μhartrees and were obtained with a maximum angular momentum of 7. For the all-order calculation also the l-extrapolated results are given.

	Be^{2+}	$Be-Be^{2+}$			
Pair	$1s^2$	$1s^2$	$1s2s$	$2s^2$	Total
Coulomb					
Second order	14.5	1.1	−0.6	0.3	0.7
All orders	8.9	1.4	−1.3	5.1	5.2
l-extrapolated	12±1[a]	1.4	−1.3	5.1	5.2
Breit					
Second order	−201.4	3.7	−11.1	−3.3	−10.7
All orders	−190.4	3.3	−10.9	−1.4	−9.0
l-extrapolated	−201±1[a]	3.3	−11.4	−1.4	−9.5
Total					
Second order	−183.2	4.8	−11.7	−3.0	−10.0
All orders	−181.5	4.7	−12.2	3.7	−3.8
l-extrapolated	−189±2[a]	4.7	−12.7	3.7	−4±1

[a]The fully relativistic results for Be^{2+} can be compared to the very accurate results by Pekeris [14] or Drake [5], who use "exact" nonrelativistic wave functions to calculate the relativistic shifts. As described in Sec. II A the total relativistic correction to the correlation can be obtained from Ref. [13] or [5] and amounts to -191.2 μhartrees. The shift due to the Breit correlation alone may be deduced from [14] to be -203.4 μhartrees leaving 12.2 μhartrees from the relativistic shift in the Coulomb correlation.

B. Corrections to the energy difference between Be and Be^{2+}

The relativistic corrections to the correlation for both the $1s^2$ and the $1s2s$ pairs are essentially unchanged by the higher-order terms. For the $2s^2$ contribution, on the other hand, the correction even changes sign. This pair is known to have a large admixture of $2p^2$ which lead to large higher-order terms if described by perturbation theory. The total relativistic correction to the correlation energy difference between Be and Be^{2+} is in fact quite small, around -4 μhartrees, and we estimate an uncertainty of around 1 μhartree which should cover the uncertainty in the contributions from the higher l values as well as neglected relativistic corrections to three- and four-particle effects.

III. RADIATIVE CORRECTIONS

The Lamb shift has been calculated accurately only for one- and two-electron systems. The study of the screening of the Lamb shift in the presence of other electrons constitutes a major task in QED studies. Here we employ a method used by Indelicato, Gorceix, and Desclaux [16] to account approximately for this screening. The Lamb shift for an s electron is described by an effective contact-type interaction in the nonrelativistic limit, which should be adequate for a light atom. The presence of one electron screens the nuclear charge felt by the other electrons in the atom. However, since the electrons have a very small probability of being close to the nucleus, this screening leads to a change in wave-function *normalization* without changing the shape of the orbitals close to the nucleus. Indelicato, Gorceix, and Desclaux [16] use this observation to account approximately for the screening by multiplying the hydrogenic Lamb-shift value by the ratio between the probability density within

the nucleus for Dirac-Hartree-Fock orbitals and hydrogenic orbitals. The procedure neglects effects where the Coulomb interaction occurs during the time between the emission and the reabsorption of the virtual photon.

For heliumlike beryllium, Drake's calculations [5] show that the second $1s$ electron adds 136.68 μhartrees to the hydrogenic Lamb shift of 207.358 μhartrees for the first $1s$ electron [4], giving a total of 344.04 μhartrees. Using instead the ratio between the DHF and hydrogenic $1s$ solution gives a total of 348.4 μhartrees for the two $1s$ electrons of Be^{2+}, which is only 1.3% larger than Drake's value. The ratio is found to be very insensitive to details in the evaluation of the contact interaction.

The number of interest for the comparison with experiment is the difference in energies between Be and Be^{2+}. The presence of the two additional $2s$ electrons leads to a small reduction of the probability density for the $1s$ electrons in the nucleus, changing the estimate of their contribution by -0.8 μhartrees. More important is the Lamb shift of the two $2s$ electrons, themselves. The hydrogenic value, 26.77 μhartrees for *one* $2s$ electron, is significantly reduced by the presence of the $1s$ electrons. In Ref. [3], the screening of the radiative corrections was estimated from comparison between the calculated values for the $1s2s$ states in heliumlike beryllium and for the $2s$ state in hydrogenic beryllium, giving a total of 8 μhartrees for the energy difference between neutral and doubly ionized beryllium, with an estimated uncertainty of 3 μhartrees. The comparison, expected to give only a very coarse estimate of the Lamb shift, in fact, exaggerates the importance of the screening. In the present work the DHF $2s$ electrons were found to contribute around 6.0 μhartrees each. Adding their contribution to the change in the $1s^2$ value gives a Lamb shift in the energy difference between Be and Be^{2+} of 11 μhartrees. The most important correlation effect for the $2s^2$ pair is the admixture of $2p^2$. It is known that around 10% [13,17,18] of the normalization integral comes from this admixture. Since the $2p$ electrons have a smaller Lamb shift this leads to a decrease of the Lamb shift to about 10 μhartrees. The correlation effects are more important for the outer electrons and thus the relative error in this value may be somewhat larger than for the $1s^2$ pair and we estimate the uncertainty to be around 1 μhartree.

IV. DISCUSSION

Table I shows the various contributions to the ground-state energy in beryllium. The uncertainty in the relativistic and radiative corrections to the energy difference between Be and Be^{2+} has been reduced significantly through the calculations described here. The final theoretical value is $-14.669\,35(3)$ hartrees which can be compared to the "experimental" result $-14.669\,332\,4$ hartrees (given by the sum of the best theoretical value [4,5] for Be^{2+} and the experimental first and second ionization energies [6]. Alternatively, the sum, $-0.001\,979(2)$ hartrees, of all corrections (including the mass polarization) can be subtracted from the experimental value, giving a "nonrelativistic experimental energy" of $-14.667\,353(2)$ hartrees, which can be compared directly to the best calculated nonrelativistic value of $-14.667\,37(3)$ hartrees. An accurate calculation of a nonrelativistic energy for Be thus remains a challenge to be pursued.

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