Relativistic corrections to atomic energies from quantum Monte Carlo calculations

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Relativistic corrections to the ground-state energies of the He, Be^{2+}, Ne^{8+}, Be, and Ne atoms are calculated using first-order perturbation theory, yielding results accurate to order $1/c^2$, where c is the velocity of light. Accurate nonrelativistic wave functions and variational and diffusion quantum Monte Carlo techniques are used to calculate the required expectation values. Our results agree with previous work for the two-electron cases, and in all cases we obtain excellent agreement with the experimental total energies. Our values for the expectation values of the relativistic correction to the Coulomb interaction (the Breit interaction) are considerably smaller than those calculated within Dirac-Fock theory, and therefore our calculations give a quantitative estimate of the importance of correlation effects in determining this contribution.

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I. INTRODUCTION

Relativistic corrections to the energies of atoms may be calculated using first-order perturbation theory, giving results accurate to order $1/c^2$, where c is the velocity of light [1,2]. For atoms of low atomic number the $1/c^2$ correction gives an accurate estimate of the total relativistic correction. In this paper we report the results of first-order relativistic perturbation calculations for He, Be^{2+}, Ne^{8+}, Be, and Ne atoms using accurate wave functions and both variational and diffusion quantum Monte Carlo techniques.

A large number of previous calculations of relativistic corrections to atomic energies have been performed using first-order perturbation theory. The early calculations of Kinoshita [3] for the He atom and Pekeris [4] for two-electron atoms with nuclear charges up to $Z=10$ yielded accurate results using wave functions with many parameters. For large numbers of electrons the only practical method for performing the required integrations with accurate many-body wave functions is to use Monte Carlo techniques [5,6]. Variational Monte Carlo (VMC) calculations of this type have been performed by Vrbik, De Pasquale, and Rothstein [7] for the four-electron molecule LiH. In our work we have considered five cases, including the ten-electron atom Ne, which is the heaviest atom to which diffusion Monte Carlo (DMC) techniques have been applied, without the use of approximations to treat the core electrons [8]. The method that we have used is similar to that of Vrbik, De Pasquale, and Rothstein in many respects, although there are important differences as well, which will be described below.

First-order relativistic perturbation theory works well for atoms of low nuclear charge Z, but is not satisfactory when Z is large. The next correction beyond $1/c^2$ is the Lamb shift, whose magnitude has been estimated for a number of cases [9,10] and is much smaller than the $1/c^2$ correction in the cases we consider. Relativistic theories are not limited to the use of first-order perturbation theory and the Dirac-Fock method [11,12] has been applied to atoms with considerable success. This method offers the advantage that the most important relativistic corrections are included without the use of perturbation theory and therefore quite accurate results may be obtained even when the $1/c^2$ perturbation theory is inadequate. The $1/c^2$ correction to the electron-electron interaction (the Breit interaction) and the Lamb shift may also be calculated within the Dirac-Fock formalism. However, this method does not include electron correlation effects, whereas quantum Monte Carlo methods can give a very accurate description of electron correlation. The importance of correlation effects for the relativistic energy shifts has already been demonstrated by calculations on two-electron atoms [13], but has not until now been investigated for atoms such as Ne. Although our method is limited to cases where the relativistic corrections are small, so that the perturbation theory is accurate, in the near future it should be possible to apply it to systems containing many atoms, such as molecules and solids.

II. RELATIVISTIC AND MASS-POLARIZATION CORRECTIONS

The effective Hamiltonian, correct to order $1/c^2$, for a system of electrons in a static electric field was derived by Bethe and Salpeter [1], while a more satisfactory derivation was given by Itoh [2]. If the static electric field arises from a nucleus of charge Z, then the resulting perturbation to the nonrelativistic Schrödinger equation is, in hartree atomic units,

$$\Delta_r = -\sum_i \frac{\nabla_i^4}{8c^2} + \sum_i \frac{Z\pi}{2c^2}\delta(\mathbf{r}_i) - \sum_{i<j} \frac{\pi}{c^2}\delta(\mathbf{r}_i-\mathbf{r}_j) - \sum_{i<j} \frac{1}{2c^2}\overleftarrow{\nabla}_i \cdot \left[\frac{(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)}{r_{ij}^3} + \frac{1}{r_{ij}} \right] \cdot \vec{\nabla}_j$$
$$- \sum_{i<j} \frac{8\pi}{3c^2}\delta(\mathbf{r}_i-\mathbf{r}_j)\mathbf{s}_i\cdot\mathbf{s}_j - \sum_{i<j} \frac{1}{c^2}\mathbf{s}_i \cdot \left[\frac{3(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)-r_{ij}^2}{r_{ij}^5} \right] \cdot \mathbf{s}_j - \sum_i \frac{Z}{2c^2}\frac{1}{r_i^3}\mathbf{s}_i\cdot[\mathbf{r}_i \times i\vec{\nabla}_i]$$
$$+ \sum_{i\neq j} \frac{1}{c^2}\frac{1}{r_{ij}^3}\mathbf{s}_i\cdot[(\mathbf{r}_j-\mathbf{r}_i)\times i\vec{\nabla}_j] + \sum_{i\neq j} \frac{1}{2c^2}\frac{1}{r_{ij}^3}\mathbf{s}_j\cdot[(\mathbf{r}_j-\mathbf{r}_i)\times i\vec{\nabla}_j] \,, \tag{1}$$

where $\mathbf{r}_i$ is the position vector of the ith electron, whose spin operator is $\mathbf{s}_i$, and r_{ij} is the distance between the ith and jth electrons. The arrows above the ∇_i symbols indicate the directions in which the gradient operators act. The first term in Eq. (1) arises from the relativistic variation of mass with velocity. The second and third terms may be interpreted as arising from the spread of the electronic charge and we refer to these as the electron-nucleus and electron-electron Darwin terms, respectively. The fourth term arises from the retardation of the electromagnetic field produced by an electron. The fifth term arises from the interaction between spin magnetic moments which are mutually penetrating, while the sixth term arises from the same interaction, but between spin magnetic moments which are not mutually penetrating. The seventh, eighth, and ninth terms give rise to the spin-orbit interaction. The expectation value of the operators in Eq. (1), evaluated with the nonrelativistic wave function, gives the relativistic correction to the energy to order $1/c^2$. We neglect other correction terms of order $1/(Mc^2)$, where M is the nuclear mass in units of the electron mass, which are very small in the cases considered here.

In addition to the relativistic corrections we calculate the expection value of the "mass-polarization" term

$$\frac{1}{M}\sum_{i<j}\overleftarrow{\nabla}_i\cdot\vec{\nabla}_j \,. \tag{2}$$

The combination of this term and the standard renormalization of the Rydberg energy unit accounts for the correction due to the finite mass of the nucleus to order $1/M$.

III. ACCURATE NONRELATIVISTIC WAVE FUNCTIONS

It is important to use reasonably accurate approximations to the nonrelativistic wave functions for evaluating the various expectation values. For the He, Be^{2+}, and Ne^{8+} cases we used wave functions of the form

$$\Phi(\mathbf{r}_1,\mathbf{r}_2) = \exp\left[-Zr_1\left(\frac{1+ar_1}{1+br_1}\right) - Zr_2\left(\frac{1+ar_2}{1+br_2}\right) + \frac{1}{2}\frac{r_{12}e^{-cr_{12}}}{1+dr_{12}} \right] , \tag{3}$$

where r_1 and r_2 are the distances of the two electrons from the nucleus and r_{12} is the interelectronic distance. These wave functions obey the "cusp conditions" [14] when the two electrons, or one electron and the nucleus, are coincident. The values of the parameters a, b, c, and d that we have used are given in Table I, and were obtained by minimizing the variance of the local energy, which has been shown to be an effective method for optimizing multiparameter wave functions [15,16]. For the Be and Ne atoms we used the "simple" wave functions due to Umrigar, Nightingale, and Runge [8], which consist of a single Slater determinant multiplied by a Jastrow factor which correlates the motion of pairs of electrons. The Be and Ne wave functions very nearly obey the cusp conditions.

Umrigar, Nightingale, and Runge have also produced a more accurate four-determinant wave function for Be [8], but we have not used this function. In addition, it is straightforward to produce more accurate wave functions for the two-electron atoms, and in this case essentially exact calculations of the expectation values of the terms in Eqs. (1) and (2) have been performed by Kinoshita [3] and Pekeris [4]. However, our purpose in performing the two-electron calculations was to test the sensitivity of the expectation values to the quality of the wave functions used and to test the extrapolated estimator procedure [17] (see the end of Sec. IV), and for this purpose we require wave functions which differ appreciably from the exact forms. The case of most interest to us is Ne, which provides the greatest challenge to our computational techniques and for which there is greatest uncertainty about the size of the relativistic corrections. For Ne we have used the most accurate, reasonably compact, wave function that we could locate [8].

IV. EVALUATION OF EXPECTATION VALUES USING VMC AND DMC METHODS

For closed-shell atomic configurations the expectation values of the sixth, seventh, eighth, and ninth terms in Eq. (1) vanish [1]. A further simplification can be made by combining the third and fifth terms in Eq. (1). The ex-

TABLE I. Optimized values of the parameters a, b, c, and d for the wave function of Eq. (3) for He, Be^{2+}, and Ne^{8+}. Each parameter has the units of an inverse length and is given in atomic units.

Atom	a	b	c	d
He	0.0316	0.455	0.0620	0.003 83
Be^{2+}	0.063	0.92	0.10	0.041
Ne^{8+}	0.175	2.26	0.20	0.138

pectation value of the Dirac δ function is zero for electrons with parallel spins, while the expectation value of $\mathbf{s}_i \cdot \mathbf{s}_j$ is $-\frac{3}{4}$ for antiparallel spins, and therefore the third and fifth terms can be combined into a single δ-function term with a prefactor of $+\pi/c^2$. With these simplifications the relativistic perturbation reduces to

$$\Delta_r = -\sum_i \frac{\nabla_i^4}{8c^2} + \sum_i \frac{Z\pi}{2c^2}\delta(\mathbf{r}_i) + \sum_{i<j} \frac{\pi}{c^2}\delta(\mathbf{r}_i - \mathbf{r}_j) - \sum_{i<j} \frac{1}{2c^2} \overleftarrow{\nabla}_i \cdot \left[\frac{(\mathbf{r}_i - \mathbf{r}_j)(\mathbf{r}_i - \mathbf{r}_j)}{r_{ij}^3} + \frac{1}{r_{ij}} \right] \cdot \vec{\nabla}_j \ . \quad (4)$$

We have used variational and diffusion quantum Monte Carlo techniques to evaluate the expectation values of the operators in Eqs. (2) and (4) for the ground states of the He, Be^{2+}, Ne^{8+}, Be, and Ne atoms. The VMC level of approximation was used by Vrbik, De Pasquale, and Rothstein [7] to calculate the $1/c^2$ relativistic correction for LiH, although they did not include all of the terms in Eq. (1) which have nonvanishing expectation values. In our calculations for closed-shell atoms we have included all the terms [Eqs. (2) and (4)] which have nonvanishing expectation values.

In the VMC method the expectation value of an operator $\hat{A}$ is written as

$$A_V = \frac{\int \Phi^2 \Phi^{-1} \hat{A} \Phi}{\int \Phi^2} \ , \quad (5)$$

where Φ is an approximate nonrelativistic wave function (assumed to be real) and Φ^2 is a probability distribution which is everywhere real and positive. In a VMC calculation the probability distribution is generated pointwise using a random walk procedure [5,6]. After an initial equilibration step the required averages are accumulated by summing $\Phi^{-1}\hat{A}\Phi$ along the random walk.

The various expectation values are conveniently written in terms of the quantity $\mathbf{F}_i(\mathbf{R})$, where $\mathbf{R}$ is the $3N$-dimensional vector of the electron coordinates and

$$\mathbf{F}_i(\mathbf{R}) = \Phi(\mathbf{R})^{-1} \nabla_i \Phi(\mathbf{R}) \ . \quad (6)$$

For the mass-polarization term [Eq. (2)] we have

$$\varepsilon_1 = \frac{1}{M} \sum_{i<j} \mathbf{F}_i \cdot \mathbf{F}_j \ , \quad (7)$$

as given by Vrbik, De Pasquale, and Rothstein [7]. For the mass-velocity term [first term of Eq. (4)] Vrbik, De Pasquale, and Rothstein give

$$\varepsilon_2 = -\frac{1}{8c^2} \sum_i (\nabla_i \cdot \mathbf{F}_i + \mathbf{F}_i^2)^2 \ , \quad (8)$$

which is proportional to the square of the nonrelativistic kinetic energy. We deal with the expectation values of the second and third terms of Eq. (4) in the way suggested by Vrbik, De Pasquale, and Rothstein. We replace the δ functions using the relations

$$\sum_i \delta(\mathbf{r}_i) = -\frac{1}{4\pi} \left[\sum_i \nabla_i^2 \right] \left[\sum_j \frac{1}{r_j} \right] \quad (9)$$

and

$$\sum_{i<j} \delta(\mathbf{r}_i - \mathbf{r}_j) = -\frac{1}{4\pi} \left[\sum_i \nabla_i^2 \right] \left[\frac{1}{2} \sum_{j<k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \right] \quad (10)$$

and integrate the expectation values by parts twice, giving

$$\varepsilon_3 + \varepsilon_4 = \frac{1}{4c^2} \left[\sum_i (\nabla_i \cdot \mathbf{F}_i + 2\mathbf{F}_i^2) \right] \times \left[-\sum_j \frac{Z}{r_j} - \sum_{j<k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \right] \ . \quad (11)$$

We have also calculated the expectation values of the δ-function terms by a direct method in which the δ functions are replaced by Gaussians with a number of different widths and the required integrals are estimated by extrapolating to zero Gaussian width. This method works reasonably well, but the variance is significantly greater than that obtained using Eq. (11). Finally, for the retardation term [fourth term of Eq. (4)] Vrbik, De Pasquale, and Rothstein give

$$\varepsilon_5 = -\frac{1}{2c^2} \sum_{i<j} \left[\frac{(\mathbf{r}_{ij} \cdot \mathbf{F}_i)(\mathbf{r}_{ij} \cdot \mathbf{F}_j)}{r_{ij}^3} + \frac{\mathbf{F}_i \cdot \mathbf{F}_j}{r_{ij}} \right] \ , \quad (12)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

In contrast to the work of Vrbik, De Pasquale, and Rothstein [7] we have not found it necessary to limit the size of the largest and smallest values obtained from Eqs. (7), (8), (11), and (12) at points along the random walk. This may be because we use wave functions Φ that obey, or very nearly obey, the cusp conditions. We have found that the above expressions give stable estimates of the various integrals and that the variance of each estimate can be made small with reasonable sampling so that the calculations are not computationally too expensive. The terms ε_2 and ε_3 have the largest magnitudes but are of opposite sign. The expressions that we use to evaluate these terms [Eqs. (8) and (11)] have a strong statistical correlation, which means that the statistical error in $\varepsilon_2 + \varepsilon_3$ is considerably smaller than in the individual terms. For the VMC calculations for He, Be^{2+}, and Ne^{8+} the averages were accumulated over 10^8 configurations, while for Be and Ne we used 4×10^7 configurations.

In the DMC method, within the fixed-node approximation, the joint distribution $\Phi\Psi$ is generated, where Ψ is the best (lowest-energy) wave function consistent with the nodal surface of Φ. For the ground states of the two-electron atoms the wave function is nodeless, but for the Be and Ne atoms the fixed-node approximation leads to a small error. We refer the reader to Refs. [6,17,18] for more details of the DMC method. For both the VMC and DMC calculations we employ a method in which the electrons are moved one at a time. We used the short-time approximation and have tested a variety of time steps for our calculations. For our final results we use time steps of 0.012 a.u. (He), 0.005 a.u. (Be^{2+} and Be), and 0.0001 a.u. (Ne^{8+} and Ne), which our tests indicate give negligible time-step errors. In all these runs the average number of configurations in the ensemble was

500. In each case the number of attempted moves of all the electrons in all the members of the ensemble was 400 000, apart from He where we used 600 000 moves.

From the averages over the variational distribution Φ^2 and the diffusion or mixed distribution $\Phi\Psi$ we can use the method of extrapolated estimation [17] to approximate the average over the distribution Ψ^2. The extrapolated estimation of the expectation value of the operator $\hat{A}$ is given by

$$A_{\rm ex}=2\frac{\int \Phi\Psi\Phi^{-1}\hat{A}\Phi}{\int \Phi\Psi}-\frac{\int \Phi^2\Phi^{-1}\hat{A}\Phi}{\int \Phi^2}\ , \qquad (13)$$

which reproduces the average over Ψ^2 with an error only at order $(\Psi-\Phi)^2$ [17], which is small if Φ is a high-quality wave function. The size of the extrapolation tests the accuracy of the VMC and DMC results, as a large extrapolation indicates that the distributions Φ^2 and $\Phi\Psi$ differ significantly from one another and hence must differ significantly from the exact distribution Ψ^2. In addition the extrapolated estimation may be more accurate than the VMC and DMC results, although in this application we have found that it does not result in any significant improvement in accuracy over the DMC results (see the following section).

V. RESULTS AND COMPARISON WITH OTHER CALCULATIONS AND EXPERIMENT

The calculated values of the nonrelativistic energies E_0, the mass-polarization corrections ε_1, and the various relativistic terms ε_2 to ε_5 are given in Table II, together with the essentially exact results of Pekeris [4] for He, Be^{2+}, and Ne^{8+} and the best nonrelativistic total energies for Be and Ne reported in Ref. [19]. The most accurate Monte Carlo results for the nonrelativistic total energies are the DMC values. The DMC total energies for He, Be^{2+}, and Ne^{8+} are very close to the exact values, which is clear evidence that the time-step errors are small. Our DMC total energies for Be and Ne are, respectively, 0.0102 and 0.015 hartree higher than the best nonrelativistic ground-state energies quoted in Ref. [19]. We use the same time steps for Be and Be^{2+} and for Ne and Ne^{8+}, which is expected to result in similar time-step errors, and therefore we conclude that the major source of error in our Be and Ne calculations is the use of the fixed-node approximation. Indeed, Umrigar, Nightingale, and Runge [8] have performed a DMC calculation for Be using a highly accurate guiding wave function and obtained an energy which was 0.010 hartree lower than ours.

The two-electron results for the various expectation values ε_1 to ε_5 can be used to test the accuracy of the

TABLE II. The nonrelativistic energies E_0, the mass-polarization correction ε_1, the mass-velocity correction ε_2, the electron-nucleus Darwin term ε_3, the sum of the electron-electron Darwin and mutually penetrating spin magnetic moment terms ε_4, the retardation term ε_5, and the sum $\varepsilon_{\rm total}$ of ε_1 to ε_5 for He, Be^{2+}, Ne^{8+}, Be, and Ne. For He, Be^{2+}, and Ne^{8+} the essentially exact results of Pekeris [4] are also given, and for Be and Ne the best nonrelativistic ground-state energies from Davidson *et al.* [19] are given. The notation 2DMC-VMC means twice the DMC result minus the VMC result. All entries are in hartee atomic units and the numbers in parentheses are the standard deviation in the last figure.

Atom	Method	E_0	ε_1	ε_2	ε_3	ε_4	ε_5	$\varepsilon_{\rm total}$
He	VMC	−2.899 33(1)	0.000 022 11(2)	−0.000 712(4)	0.000 603(4)	0.000 019 2(1)	−0.000 008 188(7)	−0.000 076 3(2)
He	DMC	−2.903 66(5)	0.000 021 4(1)	−0.000 708(2)	0.000 593(2)	0.000 018 26(6)	−0.000 008 07(3)	−0.000 083 8(2)
He	2DMC-VMC		0.000 020 7(1)	−0.000 705(5)	0.000 583(5)	0.000 017 4(1)	−0.000 007 94(4)	−0.000 091 3(3)
He	Exact[a]	−2.903 724	0.000 021 80	−0.000 720 1	0.000 605 8	0.000 017 8	−0.000 007 407	−0.000 082 1
Be^{2+}	VMC	−13.651 63(3)	0.000 025 02(5)	−0.013 89(4)	0.011 47(4)	0.000 263 3(3)	−0.000 048 8(1)	−0.002 184(2)
Be^{2+}	DMC	−13.655 4(1)	0.000 024 5(2)	−0.014 01(8)	0.011 53(8)	0.000 257(1)	−0.000 048 8(4)	−0.002 248(5)
Be^{2+}	2DMC-VMC		0.000 024 0(3)	−0.014 1(1)	0.011 6(1)	0.000 251(1)	−0.000 048 7(6)	−0.002 313(7)
Be^{2+}	Exact[a]	−13.655 57	0.000 025 60	−0.013 94	0.011 51	0.000 254 8	−0.000 046 79	−0.002 234
Ne^{8+}	VMC	−93.902 85(6)	0.000 031 7(1)	−0.613(2)	0.497(2)	0.005 513(5)	−0.000 378(1)	−0.110 28(6)
Ne^{8+}	DMC	−93.905 8(2)	0.000 031 2(4)	−0.615(3)	0.499(3)	0.005 48(1)	−0.000 380(4)	−0.111 2(1)
Ne^{8+}	2DMC-VMC		0.000 030 8(6)	−0.618(5)	0.500(5)	0.005 44(1)	−0.000 382(5)	−0.112 0(2)
Ne^{8+}	Exact[a]	−93.906 806	0.000 033 40	−0.6137	0.4979	0.005 457	−0.000 372 7	−0.110 4
Be	VMC	−14.627 28(7)	0.000 029 25(6)	−0.014 5(1)	0.011 9(1)	0.000 280 4(8)	−0.000 051 8(1)	−0.002 313(4)
Be	DMC	−14.657 2(3)	0.000 027 3(2)	−0.014 49(6)	0.011 85(6)	0.000 272(1)	−0.000 051 8(3)	−0.002 39(1)
Be	2DMC-VMC		0.000 025 4(2)	−0.014 5(2)	0.011 8(2)	0.000 263(2)	−0.000 051 7(4)	−0.002 48(1)
Be	Exact[b]	−14.667 36						
Ne	VMC	−128.713 2(4)	0.000 343 1(3)	−0.655(6)	0.516(6)	0.006 45(5)	−0.001 969(3)	−0.131 1(4)
Ne	DMC	−128.924(2)	0.000 353(4)	−0.655(2)	0.514(2)	0.006 2(1)	−0.001 88(1)	−0.133(1)
Ne	2DMC-VMC		0.000 364(6)	−0.655(6)	0.512(7)	0.006 0(2)	−0.001 79(2)	−0.135(2)
Ne	Exact[b]	−128.939						

[a]From Ref. [4].
[b]From Ref. [19].

Monte Carlo calculations. The agreement between the VMC and DMC results (and hence the extrapolated estimation, which is equal to twice the DMC result minus the VMC result) is quite good in all cases. A comparison of the Monte Carlo and exact results in Table II for the two-electron atoms shows that the DMC results are consistently better than the VMC results, but the extrapolated estimation is generally no better than the DMC result and therefore we will use the DMC results in the rest of the discussion.

In Table III we give the DMC nonrelativistic energies E_{DMC}, the multiplicative factors from the finite-nuclear mass renormalization of the energy unit R, the sum of the relativistic and mass-polarization corrections $\varepsilon_{\mathrm{total}}$ (the DMC results from Table II), the Lamb shift corrections $\varepsilon_{\mathrm{Lamb}}$, taken from Ref. [10], the resulting calculated total energies E_{calc}, and the experimental total energies E_{expt}. The calculated total energies were obtained by taking the calculated nonrelativistic energy, multiplying by the mass-renormalization factor, then adding the relativistic and mass-polarization correction, and finally the Lamb shift correction, i.e., $E_{\mathrm{calc}}=E_{\mathrm{DMC}}R+\varepsilon_{\mathrm{total}}+\varepsilon_{\mathrm{Lamb}}$. The experimental energies quoted in Table III were obtained by summing the ionization energies given in Ref. [20]. We emphasize that all the calculated energies except the Lamb shift were obtained within the framework of quantum Monte Carlo calculations. In fact, the expectation values of the δ-function terms (ε_3 and ε_4) are very important constituents of approximations to the Lamb shift, so that the quantum Monte Carlo results will be of use in obtaining more accurate estimates of Lamb shifts. The Lamb shift is essentially a $1/c^3$ correction, and the largest contribution to the relativistic corrections of order $1/c^4$ and higher may be estimated from the difference between the exact solution of the Dirac equation with a Z/r potential [1] and the $1/c^2$ perturbation result. Taking twice this difference for an electron in the lowest-energy level yields corrections to the nonrelativistic energies of -2.3×10^{-8}, -1.5×10^{-6}, and -3.6×10^{-4} hartree for He, Be, and Ne, respectively, which are negligible compared with the $1/c^2$ corrections and the Lamb shifts.

The agreement between the calculated and experimental total energies in Table III is excellent in all cases. The major source of inaccuracy in the calculated Be and Ne energies is believed to be from the nonrelativistic energy. For Be the best value for the nonrelativistic energy is 0.0102 hartree lower than our DMC value, which accounts for the difference between the calculated and experimental energies. For Ne the best value of the nonrelativistic energy is 0.015 hartree lower than our DMC value, but applying this correction to our calculations does not produce such good agreement with the experimental energy. However, we note that the uncertainty in the experimental energy for Ne is larger; the error bar quoted in [20] for the experimental value of the sixth ionization energy of Ne amounts to an uncertainty in the total energy of 0.005 hartree.

We can also compare our results with those of Dirac-Fock calculations. The first accurate Dirac-Fock calculations for atoms were performed by Mann and Johnson [11]. However, for comparison we use the very precise Dirac-Fock energies of $-2.861\,813$ [21,22], $-14.575\,892$ [22], and $-128.691\,97$ hartree [21] for He, Be, and Ne, respectively, and for Be^{2+} and Ne^{8+} we use the values $-13.614\,001$ and $-93.982\,79$ hartree from our own Dirac-Fock calculations (all results calculated with the nuclear mass taken to be infinite). The corresponding nonrelativistic Hartree-Fock energies for He, Be, and Ne are $-2.861\,680$ [19], $-14.573\,023$ [19], and $-128.547\,10$ hartree [19], and from our own calculations for Be^{2+} and Ne^{8+}, $-13.611\,299$ and $-93.861\,11$ hartree. These Dirac-Fock energy shifts may be compared with the values of $\varepsilon_2+\varepsilon_3$, as the corrections of order $1/c^4$ and higher are negligible. In Table IV we give the DMC and exact values of $\varepsilon_2+\varepsilon_3$ and the Dirac-Fock energy shifts. The agreement between the DMC and exact values for the two-electron atoms is excellent and the agreement between the DMC results and the Dirac-Fock corrections is good.

It is also possible to calculate the relativistic modification of the Coulomb interaction or Breit interaction in Dirac-Fock theory either perturbatively or by including the Breit interaction in the self-consistent field. Mann and Johnson [11] performed a set of perturbative calculations, while Quiney, Grant, and Wilson [22] give more accurate values for He and Be. These Dirac-Fock results are compared with the DMC and exact values of $\varepsilon_4+\varepsilon_5$ in Table IV. From Table IV it appears that the Dirac-Fock values for the Breit interaction are far too large and electron correlation must play an important

TABLE III. The DMC nonrelativistic energies E_{DMC}, the factors from the finite-nuclear mass renormalization of the energy unit R, the total relativistic and mass-polarization corrections calculated using DMC $\varepsilon_{\mathrm{total}}$, the Lamb shift corrections $\varepsilon_{\mathrm{Lamb}}$ from Ref. [10], the calculated total energies E_{calc}, and the experimental total energies E_{expt}. All entries are given in hartree atomic units and the numbers in parentheses are the standard deviations in the last figure.

Atom	E_{DMC}	R	$\varepsilon_{\mathrm{total}}$	$\varepsilon_{\mathrm{Lamb}}$	E_{calc}	E_{expt}
He	−2.903 66(5)	0.999 863[a]	−0.000 083 8(2)	0.000 022 6[b]	−2.903 33(5)	−2.903 386[c]
Be^{2+}	−13.655 4(1)	0.999 939[a]	−0.002 248(5)	0.000 344[b]	−13.656 6(1)	−13.656 60[c]
Ne^{8+}	−93.905 8(2)	0.999 972[a]	−0.111 2(1)	0.009 34[b]	−94.006 0(3)	−94.005 76[c]
Be	−14.657 2(3)	0.999 939[a]	−0.002 39(1)	0.000 344[b]	−14.658 5(3)	−14.668 45[c]
Ne	−128.924(2)	0.999 972[a]	−0.133(1)	0.009 34[b]	−129.045(3)	−129.051[c]

[a]From Ref. [4].
[b]From Ref. [10].
[c]Deduced from Ref. [20].

TABLE IV. The DMC values of $\varepsilon_2+\varepsilon_3$, exact values of $\varepsilon_2+\varepsilon_3$ from Pekeris [4], the Dirac-Fock relativistic correction (from Refs. [21,22]), the DMC values of the Breit interactions ($\varepsilon_4+\varepsilon_5$), exact values of the Breit interaction from Pekeris [4], and values of the Breit interaction calculated perturbatively using the Dirac-Fock wave function (from Refs. [11,21,22]). All entries are given in hartree atomic units.

Atom	$\varepsilon_2+\varepsilon_3$ DMC	$\varepsilon_2+\varepsilon_3$ exact	Dirac-Fock	$\varepsilon_4+\varepsilon_5$ DMC	$\varepsilon_4+\varepsilon_5$ exact	$\varepsilon_4+\varepsilon_5$ Dirac-Fock
He	−0.000 115	−0.000 114 3[a]	−0.000 133[b,c]	0.000 010 19	0.000 010 393[a]	0.000 063 8[c]
Be^{2+}	−0.002 48	−0.002 43[a]	−0.002 70[d]	0.000 208 2	0.000 208 01[a]	
Ne^{8+}	−0.116	−0.1158[a]	−0.1217[d]	0.0051	0.005 058[a]	
Be	−0.002 64		−0.002 869[c]	0.000 220 2		0.000 702 5[c]
Ne	−0.141		−0.144 87[b]	0.004 32		0.016 6[e]

[a]From Ref. [4].
[b]From Ref. [21].
[c]From Ref. [22].
[d]This work.
[e]From Ref. [11].

role in determining the size of this contribution.

Finally, the difference between the total relativistic shift for Be^{2+} and Be of −0.000 142 hartree is somewhat larger in magnitude than the estimates of Davidson *et al.* [19] and Mårtensson-Pendrill *et al.* [23] of −0.000 116 and −0.000 102 hartree, respectively. (Note that these authors include a contribution from the difference in the Lamb shift between Be^{2+} and Be in their values, while our calculation does not, but this is not expected to make a significant difference.)

VI. SUMMARY

We have used accurate nonrelativistic wave functions and variational and diffusion quantum Monte Carlo techniques to perform first-order relativistic perturbation calculations for the ground states of the He, Be^{2+}, Ne^{8+}, Be, and Ne atoms. The DMC results for He, Be^{2+}, and Ne^{8+} are very close to those of Pekeris [4], who used essentially exact nonrelativistic wave functions and performed the required integrations by standard quadrature techniques. When both relativistic and finite-nuclear-mass corrections are included we obtain excellent agreement with the experimental energies for all five cases considered. Our Monte Carlo results for the expectation values of the relativistic correction to the Coulomb interaction (the Breit interaction) are considerably smaller than those calculated within Dirac-Fock theory. We conclude that quantum Monte Carlo techniques offer a simple and accurate means of evaluating perturbative relativistic energy corrections for atoms of low atomic number.

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