Quantum Monte Carlo study of the first-row atoms and ions

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Quantum Monte Carlo calculations of the first-row atoms Li–Ne and their singly-positively-charged ions are reported. Multi-determinant-Jastrow-backflow trial wave functions are used which recover more than 98% of the correlation energy at the Variational Monte Carlo (VMC) level and more than 99% of the correlation energy at the Diffusion Monte Carlo (DMC) level for both the atoms and ions. We obtain the first ionization potentials to chemical accuracy. We also report scalar relativistic corrections to the energies, mass-polarization terms, and one- and two-electron expectation values.

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I. INTRODUCTION

Quantum Monte Carlo (QMC) methods can yield highly accurate energies for correlated quantum systems. QMC calculations based on many-body wave functions are considerably more accurate than density functional theory (DFT) methods, and their accuracy rivals that of the most sophisticated quantum chemistry methods. The intrinsically parallel nature of QMC algorithms makes them well-suited for taking advantage of the computing power offered by modern massively-parallel machines. The first-row atoms are a natural set of systems to use in learning how to achieve chemical accuracy, which is reached when an error of less than 1 kcal/mol ≃ 1.6 mEₜ per atom ≃ 43 meV per atom is achieved. Accurate benchmark data are available for light atoms, as are results from many different electronic structure techniques. The cost of all-electron QMC calculations scales with the atomic number roughly as \( Z^{5.5} \), so that pseudopotentials must be used for heavy atoms, but it is perfectly possible to perform highly-accurate all-electron calculations for atoms up to at least the ten-electron neon atom.

Here we apply the variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) methods to calculating the ground-state energies and other properties of the atoms Li–Ne and their singly-positively-charged ions. VMC expectation values of operators such as the Hamiltonian are calculated with an approximate many-body trial wave function, \( \Psi \), and the integrals are evaluated using a Monte Carlo technique. The functional form of \( \Psi \) is chosen to contain a number of parameters whose values are obtained by stochastic optimization. Higher accuracy is achieved in the DMC method by evolving the wave function in imaginary time so that it decays towards the ground-state, while the fixed-node approximation is used to maintain the fermionic symmetry. Both the VMC and DMC methods are variational, which is helpful in monitoring the accuracy of the calculations and in promoting cancellation of errors in energy differences. The DMC energy is bounded from above by the VMC energy and from below by the exact energy. These methods are discussed extensively in the literature and we direct the reader to Refs. 1, 3 and 4 for a detailed description.

Our trial wave functions consist of a multi-determinant expansion which describes near-degeneracy or static correlation, a Jastrow factor which captures dynamic correlation, and a backflow transformation which allows further variations in the nodal surface. We recover over 98% of the correlation energy for all the atoms and ions studied at the VMC level and
over 99% at the DMC level. Chemically-accurate values of the first ionization potentials are obtained. Total energies, scalar relativistic corrections to the energies, mass-polarization terms, and one- and two-electron expectation values are evaluated. All of our QMC calculations were performed using the CASINO package.  

II. TRIAL WAVE FUNCTIONS

The all-electron multi-determinant-Jastrow-backflow wave functions take the form:

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R}; \mathbf{a})} \sum_{j=1}^{N_{\text{CSF}}} \sum_{k=1}^{N_{\text{det}}^j} c_j d_{k,j}^\dagger \langle \mathbf{x}_1, \ldots, \mathbf{x}_{N^+} \rangle D_{k,j}^\dagger \langle \mathbf{x}_{N^++1}, \ldots, \mathbf{x}_N \rangle,$$

(1)

where \(\mathbf{R}\) is the vector of electron positions, \(J(\mathbf{R}; \mathbf{a})\) is the Jastrow factor, and \(D_{k,j}^\sigma(\mathbf{X})\) are the Slater determinants whose orbitals are evaluated at the backflow-transformed coordinates \(\mathbf{x}_i = \mathbf{r}_i + \xi_i(\mathbf{R}; \mathbf{b})\). \(N_{\text{CSF}}\) denotes the total number of configuration state functions (CSFs) and \(N_{\text{det}}^j\) is the number of determinants in the \(j\)th CSF. The vector \(\mathbf{a}\) denotes the parameters in the Jastrow factor, \(\mathbf{b}\) those in the backflow transformation, and \(\mathbf{c} = (c_1, \ldots, c_{N_{\text{CSF}}})\) the coefficients of the CSFs. The coefficients of the determinants \(\mathbf{d} = (d_{1,1}, \ldots, d_{N_{\text{det}}N_{\text{CSF}}})\) are held fixed to maintain the proper symmetry of the CSFs.

The Slater determinants and CSFs were generated using the atomic multi-configuration Hartree-Fock (MCHF) package ATSP2K. We allowed single- and double-excitations from the HF ground-state configuration defined by the Aufbau principle up to configurations with principal quantum number \(n \leq 7\) and orbital angular momentum quantum number \(l \leq 4\). Terms representing excitations from the 1s\(^2\) core were used for Li, Li\(^+\) and Be\(^+\) to ensure that double-excitations were included. The CSFs with the largest weights were included in \(\Psi\). Core excitations significantly lowered the MCHF energy of the Be atom, but they did not improve the VMC energy and were therefore not included in the QMC calculations. Excitations from the core become less important for larger \(Z\), and we did not include them for systems with more than three electrons. The high-energy excited-state configurations in the MCHF expansion mostly describe electron-electron cusps, which are captured by the Jastrow factor in QMC calculations. The high-energy MCHF excitations are therefore expected to be much less important in the QMC calculations than in the MCHF ones. Indeed, including very-high-energy excitations serves only to hinder the optimization procedure (see below) and worsen \(\Psi\). We tested wave functions containing 1, 20 and 50
CSFs for all the atoms, and finally used 50 CSFs for all atoms and ions except O, O\(^+\), F and F\(^+\), for which we used 100 CSFs. The number of determinants ranged from 171 (Li\(^+\)) to 4613 (F\(^+\)).

We used a modified form\(^6\) of the polynomial Jastrow factor proposed by Drummond \textit{et al.}\(^7\), consisting of an expansion in powers of \(r/(r^\beta + \alpha)\), where \(r\) is the inter-particle separation and \(\alpha\) and \(\beta\) are optimizable parameters, with \(\beta\) constrained to be greater than unity. The optimal values of \(\alpha\) were found to lie within the range 0.5–17.1 and those of \(\beta\) within the range 1.05–4.67 for the atoms and ions studied. This modification removes the need for cut-offs at large inter-particle separations, as the basis functions decay to zero at large \(r\). Based on our tests, we chose expansion orders of 8 for the electron-electron and electron-nucleus parts of the Jastrow factor and an expansion order of 4 for the terms in the electron-electron-nucleus Jastrow factor, which gave a total of 118 optimizable parameters.

The backflow transformation of López Ríos \textit{et al.}\(^8\) was used, with electron-electron and electron-nucleus functions of expansion order 8 and an electron-electron-nucleus function of expansion order 3, resulting in a further 142 optimizable parameters. When using a backflow transformation, each orbital must be evaluated at each electron configuration, which significantly increases the computational cost. We have found it to be much more efficient to move the electrons individually in QMC calculations, even with backflow wave functions\(^8,9\), because the correlation length is shorter.

We used identical parameter values for pairs of up-spin electrons and pairs of down-spin electrons in both the Jastrow and backflow functions. This significantly reduced the number of variable parameters without any noticeable loss in wave function quality. The parameter values for the anti-parallel-spin channel were allowed to differ from those of the parallel-spin channel. The parallel and anti-parallel-spin cusp conditions were imposed in the Jastrow factor, and the backflow transformation does not introduce cusps\(^8\).

III. OPTIMIZATION

Various stochastic methods have been developed for optimizing many-body wave functions in QMC calculations\(^10–14\). Methods based on minimizing the variance of the local energies obtained from a VMC calculation can be robust and effective\(^10–12\), as is the related technique of minimizing the mean absolute deviation of the local energies from the median.
local energy (MAD minimization)\textsuperscript{3}. Simple implementations of variance minimization are very poor at optimizing nodal surfaces. The reason for this is that the particle configurations are fixed within an optimization cycle, but changing parameters which alter the nodal surface may move it through the fixed configurations. The local energy diverges when the nodal surface coincides with configurations, leading to a poor optimization. Variance-based optimization schemes can be effective in optimizing nodal surfaces if the values of the local energies and/or the weights of configurations near the nodal surface are limited\textsuperscript{12}. However, lower total energies can be achieved by minimizing the VMC energy itself\textsuperscript{13,14}. The energy minimization scheme of Umrigar and coworkers\textsuperscript{13,14} is quite robust and is also extremely effective in optimizing linear parameters in $\Psi$ such as CSF coefficients. We found MAD minimization to be superior to energy minimization for optimizing the cut-off functions, and superior to variance minimization methods for optimizing parameters which alter the nodal surface. We have therefore used MAD minimization in the early stages of the optimizations, but the final optimizations are performed with energy minimization.

We tested optimization of the single-particle orbitals for N, O and F, but found this to have a negligible effect, in agreement with previous atomic studies\textsuperscript{15,16}.

We tested several optimization schemes that could potentially reduce the computational effort of wave function optimization. The Jastrow factor and backflow transformation were optimized for a single determinant and then applied to the multi-determinant expansion of a B wave function containing 50 CSFs. Optimizing the CSF coefficients while holding the Jastrow factor and backflow parameters fixed improved the wave function but the final results remained unsatisfactory. This may be expected as the Jastrow and backflow functions attempt to compensate for some of the dynamical correlation which is then included via the CSFs. The CSF coefficients in the B wave function were optimized for one final cycle, as energy minimization of linear coefficients is in general very robust. No improvement was observed, confirming that energy minimization is able to optimize the linear and non-linear parameters simultaneously.

As the optimization process is currently the most costly step in human time and consumes a substantial fraction of the computer time, it is desirable to establish an optimization strategy which is reliable for all of the atoms and ions and may be useful in other systems. Of the several optimization strategies tried, the following consistently gave the best results and was used for all of the final results reported here:
1. Set the CSF coefficients to their MCHF values and the Jastrow parameters \( a \) to zero. Note that the Jastrow factor is non-zero as the term enforcing the cusp condition is still present.

2. Generate a set of VMC configurations\(^\text{17}\) and optimize the Jastrow parameters \( a \) including the Jastrow basis function parameters \( \alpha \) and \( \beta \), and the CSF coefficients \( c \), using MAD minimization. We refer to this step as an ‘optimization cycle’.

3. Run two more optimization cycles using the parameters obtained in the previous cycle as initial parameters.

4. Optimize the wave function parameters \( a \) and \( c \) using VMC energy minimization until converged (usually about 5–8 cycles). The Jastrow basis function parameters \( \alpha \) and \( \beta \) are not re-optimized at this stage.

5. Introduce backflow functions with the parameters \( b \) initially set to zero, and optimize all wave function parameters \( (a, b, c) \), including \( \alpha \) and \( \beta \), and the backflow cut-off parameters, using MAD minimization until converged (usually about 3 cycles).

6. Use VMC energy minimization to optimize wave function parameters \( (a, b, c) \) until converged (usually about 5–8 cycles). The Jastrow basis function parameters and backflow cut-off parameters are not re-optimized.

The improvements in the VMC energies of the atoms at different levels of optimization are shown in Fig. 1. The figure clearly shows that the VMC energy minimization scheme yields significantly larger percentages of the correlation energy than MAD minimization. While this strategy has not been tested for any other systems, we expect it to work well in many cases.

### IV. RESULTS AND DISCUSSION

#### A. Atomic and ionic energies

The VMC optimizations were performed using \( 5 \times 10^4 \) statistically-independent particle configurations. One measure of wave function quality is its variance, and Table I reports the variances of optimized Slater-Jastrow and Slater-Jastrow-backflow wave functions for
FIG. 1. Percentages of the correlation energy (% CE) retrieved for single-determinant Slater-Jastrow (SJ) and Slater-Jastrow-backflow (SJBF) wave functions using mean absolute deviation minimization (MADmin) and energy minimization (Emin).

both single-determinant and multi-determinant Slater forms. The variance is reduced by approximately a factor of 2 or more when a multi-determinant expansion is introduced to a Slater-Jastrow-backflow wave function. The improvement is particularly large for Be, B and C, where the variance drops by factors of approximately 10, 8 and 4, respectively. This reflects the strong 2s–2p near-degeneracy effects exhibited in these systems and determinants beyond the HF ground-state configuration must be included to capture the static correlation. With a few exceptions, the variance decreases as the variational energy decreases for a given system. The variance of a wave function after MAD minimization also approaches that after energy minimization as the variational energy decreases.

The DMC calculations were performed with a target population of 2048 DMC configurations and a minimum of $10^5$ steps and a time-step corresponding to the smaller of the two
TABLE I. VMC variances for single-determinant (SD) and multi-determinant (MD) Slater-Jastrow (SJ) and Slater-Jastrow-backflow (SJBF) wave functions. All variances are in atomic units and the numbers in parentheses indicate the statistical uncertainty in the last digit shown.

|       | SD-SJ   | SD-SJBF | MD-SJ   | MD-SJBF |
|-------|---------|---------|---------|---------|
| Li    | 0.00274 | 0.00130 | 0.00193 | 0.00067 |
| Be    | 0.0443  | 0.0524  | 0.01066 | 0.00526 |
| B     | 0.0915  | 0.1434  | 0.0326  | 0.01867 |
| C     | 0.1941  | 0.1784  | 0.0819  | 0.0473  |
| N     | 0.340   | 0.263   | 0.2198  | 0.1126  |
| O     | 0.548   | 0.4763  | 0.442   | 0.353   |
| F     | 0.846   | 0.619   | 0.644   | 0.493   |
| Ne    | 1.233   | 0.797   | 0.623   | 0.361   |

used in Ref. 15, ranging from 0.00375 a.u. for Li to 0.00070 a.u. for Ne. These calculations already showed that the errors from this choice of time steps is negligible, and the corresponding errors in the current calculations should be even smaller as the trial wave functions are superior.

Table II gives the VMC and DMC energies and percentages of the correlation energy retrieved for each of the atoms and ions studied. The reference non-relativistic energies, assuming a clamped point nucleus, are taken from Refs. 18 and 19. Percentages of the correlation energy retrieved at the VMC and DMC levels for the neutral atoms in the present work and those of Ref. 15 are compared in Fig. 2 and for singly-charged ions are shown in Fig. 3. In both figures, the percentage of the correlation energy required to achieve chemical accuracy is indicated.

There are several differences between the wave functions used in the present study and Ref. 15. While both calculations relied on the energy minimization scheme of Refs. 13 and 14, our current implementation is more effective and robust. For example, Brown et al. 15 were unable to lower the VMC energy of Ne using a multi-determinant expansion, which was easily achieved in the present study. The present optimization strategy is significantly different as we use MAD minimization to first optimize the non-linear parameters at each stage. Brown et al. 15 used a Jastrow factor based on an expansion in $r$, while we have used
TABLE II. VMC and DMC energies of the first-row atoms and ions. Also included are Hartree-Fock energies $E_{HF}$ calculated using ATSP2k, the reference energies $E_{ref}$, the correlation energies $E_{HF} - E_{ref}$, and the percentage of the correlation energy recovered at the VMC level (VMC-corr%) and DMC level (DMC-corr%). All energies are in atomic units and the numbers in parentheses indicate the statistical uncertainty in the last digit shown.

|       | Li (2S) | Be (1S) | B (2P) | C (3P) | N (4S) | O (3P) | F (2P) | Ne (1S) |
|-------|---------|---------|--------|--------|--------|--------|--------|---------|
| VMC   | -7.478034(8) | -14.66719(1) | -24.65337(4) | -37.84377(7) | -54.5873(1) | -75.0632(2) | -99.7287(2) | -128.9347(2) |
| DMC   | -7.478067(5) | -14.667306(7) | -24.65379(3) | -37.84446(6) | -54.58867(8) | -75.0654(1) | -99.7318(1) | -128.9366(1) |
| $E_{HF}$ | -7.432727  | -14.573023  | -24.529061  | -37.688619  | -54.400934  | -74.809398  | -99.409349  | -128.547098  |
| $E_{ref}$ | -7.47806032 | -14.66736   | -24.65391   | -37.8450    | -54.5892    | -75.0673    | -99.7339    | -128.9376    |
| $E_{HF} - E_{ref}$ | 0.0453333 | 0.094337   | 0.124849   | 0.156381    | 0.188266    | 0.257902    | 0.324551    | 0.390502    |
| VMC-corr% | 99.94(2)%    | 99.82(1)%   | 99.57(3)%   | 99.21(4)%   | 98.99(5)%   | 98.41(8)%   | 98.40(6)%   | 99.26(5)%   |
| DMC-corr% | 100.01(1)%   | 99.943(7)%  | 99.90(2)%   | 99.65(4)%   | 99.72(4)%   | 99.26(4)%   | 99.35(3)%   | 99.74(3)%   |

|       | Li+ (1S) | Be+ (2S) | B+ (1S) | C+ (2P) | N+ (3P) | O+ (4S) | F+ (3P) | Ne+ (2P) |
|-------|---------|---------|--------|--------|--------|--------|--------|---------|
| VMC   | -7.279844(9) | -14.324721(9) | -24.34836(4) | -37.43034(6) | -54.0530(1) | -74.5655(1) | -99.0880(2) | -128.1377(2) |
| DMC   | -7.279914(3) | -14.324761(3) | -24.34887(2) | -37.43073(4) | -54.05383(7) | -74.56662(7) | -99.0911(2) | -128.1412(2) |
| $E_{HF}$ | -7.236415  | -14.277395  | -24.237575  | -37.292224  | -53.888005  | -74.372606  | -99.831720  | -127.817814  |
| $E_{ref}$ | -7.27991  | -14.32476  | -24.34892  | -37.43103  | -54.0546  | -74.5668  | -99.0928  | -128.1431  |
| $E_{HF} - E_{ref}$ | 0.043495 | 0.047365 | 0.111345 | 0.138806 | 0.166595 | 0.194194 | 0.26108 | 0.325286 |
| VMC-corr% | 99.85(2)% | 99.92(2)% | 99.50(4)% | 99.50(4)% | 99.44(6)% | 99.33(5)% | 98.16(8)% | 98.34(6)% |
| DMC-corr% | 100.009(7)% | 100.002(6)% | 99.96(2)% | 99.78(3)% | 99.54(4)% | 99.91(4)% | 99.35(8)% | 99.42(6)% |

an expansion in powers of $r/(r^\beta + \alpha)$. We have also employed a larger number of CSFs.

We have obtained more than 99% of the correlation energy at the DMC level for all of the atoms and ions, and at the VMC level for all atoms except O and F and all ions except F+ and Ne+. This is a substantially higher accuracy than has been achieved in the all-electron QMC calculations reported in the literature. We have calculated the virial ratios for the atoms and ions in both VMC and DMC, finding them to be within one standard error of the exact value of 2 in each case, with the standard errors lying within the range 0.001–0.02.
FIG. 2. Percentages of the correlation energy (% CE) retrieved for each atom within VMC and DMC. Chemical accuracy is achieved for Li–N and Ne at the DMC level.

B. Ionization potentials

Although the total atomic energies can be measured as the sum of the ionization energies, they are not quantities of significant chemical interest. In quantum chemistry one is normally interested in energy differences for which the cancellation of errors between calculations is important. We have therefore calculated the first ionization potentials (IPs) of the atoms Li–Ne as energy differences between the neutral and singly-ionized states. The errors in the calculated IPs from those computed using values from Ref. 19 are shown in Fig. 4. Data from the stochastic full configuration interaction method (FCI-QMC) with an aug-cc-pVQZ basis set for Li, Be and Ne and an aug-cc-pV5Z basis for B–F are shown, together with coupled cluster single and double excitation (CCSD) data with a d-aug-cc-pwCV5Z basis and CCSD-F12-HLC data. Each CCSD-F12-HLC energy is the sum of the CCSD energy, an F12 energy which corrects for the finite basis set, and a higher-level correction (HLC) which accounts for the treatment of excitations beyond the doubles in CCSD. It is
FIG. 3. Percentages of the correlation energy (% CE) retrieved for each ion within VMC and DMC. Chemical accuracy is achieved for Li$^+$–O$^+$ at the DMC level. The values for F$^+$ and Ne$^+$ are within statistical uncertainty of chemical accuracy.

likely that the CCSD-F12-HLC results\textsuperscript{24} are even more accurate than the data of Ref. \textsuperscript{19} that we have used as a reference, as they obtain results in closer agreement with experiment when corrections for relativistic effects and the finite nuclear mass are included. However, Klopper \textit{et al.}\textsuperscript{24} did not give values for the total energies of the atoms, and therefore we have used the data of Ref. \textsuperscript{19} to avoid using different reference data for the total energies and IPs. The differences from using the IP data of Klopper \textit{et al.}\textsuperscript{24} are small, as can be seen in Fig. \textsuperscript{4}. Using this data as the reference would not significantly affect the comparisons for Li and Be, but it would slightly worsen the agreement with our results for B, C and Ne and slightly improve it for N, O and F.

The IPs from DMC are within statistical error of chemical accuracy of the reference data for all atoms. Our errors are smaller than or equal to those in the CCSD results with a d-aug-cc-pwCV5Z basis\textsuperscript{24} for all atoms, and smaller than those of the FCI-QMC calculations.
FIG. 4. Errors in the ionization potentials ($\Delta = IP_{\text{calc}} - IP_{\text{ref}}$) for the first-row atoms obtained at the VMC and DMC levels compared to those from FCI-QMC, CCSD and CCSD-F12-HLC. The reference values are taken from Ref. 19. The shaded region represents chemical accuracy of Booth and Alavi for all atoms except C. The mean deviation, mean absolute deviation and maximum deviation of the IPs from the reference values for these methods and those obtained in DFT using the B3LYP, LSDA and PBE-GGA density functionals are presented in Table III. The mean absolute deviations of the DFT IPs are between 24 and 30 times larger than for our DMC calculations.

The FCI-QMC approach is exact up to a basis set convergence error and a small statistical error. They consistently underestimate IPs, perhaps because there are fewer electron-electron and electron-nucleus cusps in an ion than in the corresponding neutral atom. As is clear from Fig. 4, we similarly underestimate the IPs in all cases except Ne, but for a different reason, as explained below.

The critical approximation made in DMC is the fixed-node approximation, which is necessary to evade the fermion sign problem. In general, the nodal structure of an ion is easier to describe than that of the corresponding neutral atom. However, for closed-shell atoms such as Ne, the initial restricted HF atomic nodal surface is superior to that of the open-shell ion.
The energy of the neutral atom is more accurate and consequently the IP is overestimated.

To summarize, the additional complexity that arises for larger system sizes manifests itself differently in FCI and DMC. In the former, describing the electron-electron cusps becomes more challenging and requires a larger expansion in determinants, whereas the nodal structure of the larger system is more difficult to describe in DMC.

**TABLE III.** Comparison of the mean deviation ($\overline{\Delta}$), mean absolute deviation ($|\overline{\Delta}|$) and maximum deviation ($\Delta_{\text{max}}$) of the ionization potentials obtained from several electronic structure methods. Deviations are from the reference non-relativistic, clamped point nucleus values of Ref. 19. Averages were taken over Li–Ne, unless otherwise indicated. All values are in electron volts and the numbers in parentheses indicate the statistical uncertainty, if present, in the last digit shown.

|         | $\overline{\Delta}$ | $|\overline{\Delta}|$ | $\Delta_{\text{max}}$ |
|---------|----------------------|------------------------|------------------------|
| VMC     | $-0.005(2)$          | $0.023(2)$             | $0.076(5)$             |
| DMC     | $-0.005(1)$          | $0.012(1)$             | $0.046(2)$             |
| FCI-QMC a | $-0.0250(7)$        | $0.0250(7)$           | $0.054(3)$             |
| CCSD b  | $0.0586$             | $0.0585$               | $0.1140$               |
| CCSD-F12-HLC c | $-0.0001$     | $0.0021$               | $0.0054$               |
| B3LYP c  | $0.2925$             | $0.2924$               | $0.5206$               |
| LSDA d   | $0.2657$             | $0.3521$               | $0.5447$               |
| PBE d    | $0.1971$             | $0.2892$               | $0.4507$               |

a Ref. 23.
b Ref. 24.
c Averages taken over B–Ne values. Ref. 24.
d Averages taken over Li–F values. Ref. 26.

**C. Other expectation values**

Scalar relativistic and mass-polarization corrections to the energies of the atoms and ions were computed using first-order perturbation theory within VMC and DMC. The mass-velocity, one-electron Darwin, two-electron Darwin, retardation and mass-polarization terms are given in Table IV. We did not calculate the spin-orbit terms, although we note that a paper reporting VMC results for spin-orbit energies of electronic states of the He atom...
has recently appeared. As the VMC and DMC values agree to within one standard error in most cases, we have decided not to give the extrapolated estimates (2×DMC-VMC) in Table IV and instead we quote only the DMC values. Our results for Li, Li+, Be and Be+ are close to those given in Refs. 29, 30 and 31, obtained from Hylleraas calculations, and in Ref. 32, from exponentially-correlated Gaussian calculations.

TABLE IV. Scalar relativistic terms: mass-velocity (MV), electron-nucleus Darwin (D1), two-electron Darwin (D2), spin-spin contact interaction (SSC), retardation (Ret), and mass-polarization (MP) energies calculated at the DMC level. Values from the literature are given for Li, Li+, Be and Be+. All values are in atomic units and the numbers in parentheses give the statistical uncertainty in the last digit shown.

|       | MV       | D1        | D2+SSC    | Ret       | MP        |
|-------|----------|-----------|-----------|-----------|-----------|
| Li    | −0.00417(1) | 0.00346(1) | 0.0000914(3) | −0.00000232(1) | 0.0000239(1) |
| Be    | −0.01439(2) | 0.01181(2)  | 0.0002690(5) | −0.0000478(1) | 0.0002815(9) |
| B     | −0.0368(1) | 0.0300(1)  | 0.000598(2) | −0.0000585(7) | 0.0000137(3) |
| C     | −0.0790(2) | 0.0639(2)  | 0.001115(8) | −0.0000117(2) | −0.0000178(5) |
| N     | −0.1504(6) | 0.1207(7)  | 0.00185(4) | 0.000147(5) | −0.000069(2) |
| O     | −0.2610(7) | 0.2086(7)  | 0.00299(3) | 0.000415(4) | −0.0001278(8) |
| F     | −0.424(1)  | 0.337(1)   | 0.00451(5) | 0.000935(7) | −0.000195(1) |
| Ne    | −0.655(2)  | 0.518(2)   | 0.00646(8) | 0.00186(1)  | −0.000303(1) |
| Li+   | −0.00411(1) | 0.00341(1)  | 0.0000895(2) | −0.00002291(9) | 0.00002298(8) |
| Be+   | −0.01426(2) | 0.01171(2)  | 0.0002649(3) | −0.0000485(1) | 0.0002756(7) |
| B+    | −0.0377(3) | 0.0307(3)  | 0.000597(2) | −0.0000802(6) | 0.000305(3) |
| C+    | −0.0796(3) | 0.0643(3)  | 0.001115(5) | −0.0000561(7) | −0.0000003(4) |
| N+    | −0.1506(5) | 0.1208(5)  | 0.00190(1)  | 0.000071(2)  | −0.0000494(6) |
| O+    | −0.263(2)  | 0.210(2)   | 0.00299(2)  | 0.0000388(4) | −0.0001143(8) |
| F+    | −0.425(2)  | 0.337(2)   | 0.00441(1)  | 0.000911(5)  | −0.000183(3) |
| Ne+   | −0.658(2)  | 0.519(2)   | 0.00636(8)  | 0.001719(9)  | −0.000287(1) |
| Li    | −0.00418368 | 0.00347366 | 0.0000911359 | −0.0000232018 | 0.0000236819 |
| Li+   | −0.00413427 | 0.00344389 | 0.0000589292 | −0.0000227911 | 0.0000235916 |
| Be    | −0.01444539d | 0.011834014  | 0.0002685577d | −0.0000474909d | 0.0000278121d |
| Be+   | −0.0142882124d  | 0.0117455724d  | 0.0002644146d | −0.0000043576d | 0.0000237304d |

In Table V we report some one-electron expectation values for the atoms and ions, while two-electron expectation values are reported in Table VI. Variational calculations using Hylleraas-type wave functions have given very accurate results for three systems included.
in our study: the Li atom, the Li\(^+\) ion, and the Be\(^+\) ion. Our results for these systems are in good agreement with the Hylleraas data. The data available in the literature for systems with more than three electrons are of much lower accuracy. Cohen et al. have reported values of \(\langle r_i^2 \rangle\) for some atoms, including Be, B and C, calculated within unrestricted HF theory and correlated theories such as FCI. Electron correlation is expected to reduce the size of atoms as measured by \(\langle r_i^2 \rangle\). Our value of \(\langle r_i^2 \rangle\) for Be reported in Table V is slightly larger than the FCI values of 16.27, while our values for B and C are slightly smaller than the FCI values of 15.54 (B) and 13.84 (C). In almost all cases the values of the one-electron expectation values (summed over the electrons) are larger for the neutral atoms than for the corresponding ions, as one would expect. However, the expectation values of \(\langle \delta(r_i) \rangle\) and \(\langle r_i^{-2} \rangle\), which are the most strongly weighted towards the region close to the nucleus, are larger for the ion than for the neutral atom for B/B\(^+\), and very similar for C/C\(^+\)–Ne/Ne\(^+\). The larger error bars and lower quality of the wave functions make it more difficult to draw firm conclusions for C/C\(^+\)–Ne/Ne\(^+\).

TABLE V. One-electron expectation values: electron moments \(\langle r_i^n \rangle\) for \(-2 \leq n \leq 3\) and electron density at the coalescence point \(\langle \delta(r_i) \rangle\), summed over all electrons \(i\). All values are in atomic units and the numbers in parentheses indicate the statistical uncertainty in the last digit shown.

|         | \(\langle \delta(r_i) \rangle\) | \(\langle r_i^{-2} \rangle\) | \(\langle r_i^{-1} \rangle\) | \(\langle r_i \rangle\) | \(\langle r_i^2 \rangle\) | \(\langle r_i^3 \rangle\) |
|---------|------------------|------------------|------------------|------------------|------------------|------------------|
| Li\(^+\) | 13.79(5)         | 30.25(4)         | 5.7193(4)        | 4.9842(3)        | 18.300(2)        | 92.10(1)         |
| Be\(^+\) | 35.30(6)         | 57.59(3)         | 8.4275(2)        | 5.9794(1)        | 16.2986(4)       | 57.078(2)        |
| B\(^+\)  | 71.7(3)          | 93.51(9)         | 11.3993(7)       | 6.7446(3)        | 15.5322(9)       | 46.011(4)        |
| C\(^+\)  | 127.2(4)         | 138.8(1)         | 14.7065(8)       | 7.1230(3)        | 13.7401(7)       | 33.940(3)        |
| N\(^+\)  | 206(1)           | 193.0(1)         | 18.3491(9)       | 7.3612(2)        | 12.1750(5)       | 25.740(2)        |
| O\(^+\)  | 312(1)           | 257.1(2)         | 22.271(1)        | 7.6364(2)        | 11.3283(5)       | 21.756(2)        |
| F\(^+\)  | 448(2)           | 330.8(2)         | 26.537(1)        | 7.8166(2)        | 10.4132(4)       | 18.003(1)        |
| Ne\(^+\) | 619(2)           | 414.3(3)         | 31.134(1)        | 7.9298(2)        | 9.5220(4)        | 14.8372(9)       |
| Li\(^+\) | 13.60(4)         | 29.81(4)         | 5.3770(4)        | 1.14539(7)       | 0.89252(7)       | 0.8880(1)        |
| Be\(^+\) | 35.01(5)         | 56.97(2)         | 7.9760(2)        | 3.10220(6)       | 6.5122(2)        | 18.7046(8)       |
| B\(^+\)  | 73.5(8)          | 93.94(9)         | 10.9332(7)       | 4.1791(2)        | 7.6318(5)        | 17.736(2)        |
| C\(^+\)  | 128.1(6)         | 138.9(1)         | 14.1589(8)       | 4.9235(2)        | 7.9284(4)        | 16.672(1)        |
| N\(^+\)  | 206.3(9)         | 193.2(2)         | 17.727(1)        | 5.4338(2)        | 7.7161(4)        | 13.742(1)        |
| O\(^+\)  | 314(3)           | 257.1(2)         | 21.618(1)        | 5.8097(2)        | 7.3423(3)        | 11.6156(8)       |
| F\(^+\)  | 447(3)           | 331.3(2)         | 25.811(1)        | 6.1624(2)        | 7.1305(3)        | 10.3950(7)       |
| Ne\(^+\) | 621(2)           | 414.9(3)         | 30.323(1)        | 6.4236(2)        | 6.7976(3)        | 9.0808(5)        |
TABLE VI. Two-electron expectation values: inter-electronic moments $\langle r_{ij}^n \rangle$ for $-2 \leq n \leq 3$, the electron-pair density at the coalescence point $\langle \delta(r_{ij}) \rangle$ and the mass-polarization term $-\langle \nabla_i \cdot \nabla_j \rangle$, summed over all electron-pairs $ij$. All values are in atomic units and the numbers in parentheses indicate the statistical uncertainty in the last digit shown.

| Element | $\langle \delta(r_{ij}) \rangle$ | $\langle r_{ij}^{-2} \rangle$ | $\langle r_{ij}^{-1} \rangle$ | $\langle r_{ij}^1 \rangle$ | $\langle r_{ij}^2 \rangle$ | $\langle r_{ij}^3 \rangle$ | $-\langle \nabla_i \cdot \nabla_j \rangle$ |
|---------|---------------------------------|-------------------------------|---------------------------------|-----------------------------|-----------------------------|-----------------------------|---------------------------------|
| Li      | 0.546(2)                        | 4.386(6)                      | 2.1993(1)                       | 8.6574(4)                   | 36.731(2)                   | 191.000(2)                  | 0.304(2)                        |
| Be      | 1.608(3)                        | 9.532(4)                      | 4.37330(9)                      | 15.2895(2)                  | 52.9958(9)                  | 223.436(6)                  | 0.466(1)                        |
| B       | 3.57(1)                         | 17.45(1)                      | 7.6657(3)                       | 22.4696(6)                  | 67.189(2)                   | 244.63(1)                   | 0.272(6)                        |
| C       | 6.66(5)                         | 29.15(2)                      | 12.5191(4)                      | 29.0654(6)                  | 73.574(2)                   | 225.629(9)                  | -0.39(1)                        |
| N       | 11.1(2)                         | 45.74(2)                      | 19.2241(5)                      | 35.5092(6)                  | 77.550(2)                   | 204.547(6)                  | -1.78(5)                        |
| O       | 17.9(2)                         | 68.85(3)                      | 27.9913(6)                      | 42.5224(6)                  | 83.693(2)                   | 200.810(6)                  | -3.76(2)                        |
| F       | 27.0(3)                         | 99.76(4)                      | 39.2235(7)                      | 49.3275(7)                  | 87.469(2)                   | 189.260(5)                  | -6.82(4)                        |
| Ne      | 38.6(5)                         | 140.37(5)                     | 53.2639(8)                      | 55.8986(6)                  | 89.587(1)                   | 175.092(4)                  | -11.23(5)                       |
| Li$^+$  | 0.535(1)                        | 4.088(6)                      | 1.5684(1)                       | 0.86210(7)                  | 0.92684(9)                  | 1.1888(2)                   | 0.293(1)                        |
| Be$^+$  | 1.584(2)                        | 8.901(3)                      | 3.24613(7)                      | 5.26857(9)                  | 13.0819(3)                  | 39.457(1)                   | 0.456(1)                        |
| B$^+$   | 3.57(1)                         | 16.47(1)                      | 5.9706(3)                       | 10.5411(3)                  | 24.698(1)                   | 69.807(4)                   | 0.606(5)                        |
| C$^+$   | 6.67(3)                         | 27.57(2)                      | 10.0797(4)                      | 16.2100(4)                  | 34.253(1)                   | 86.994(4)                   | -0.007(9)                       |
| N$^+$   | 11.33(7)                        | 43.38(3)                      | 15.9096(5)                      | 21.9744(4)                  | 41.344(1)                   | 93.139(3)                   | 1.27(2)                         |
| O$^+$   | 17.8(1)                         | 65.03(3)                      | 23.7541(6)                      | 27.8183(5)                  | 46.843(1)                   | 94.164(3)                   | 3.36(2)                         |
| F$^+$   | 26.3(9)                         | 94.80(4)                      | 33.9176(7)                      | 34.0801(5)                  | 52.794(1)                   | 98.132(3)                   | -6.39(9)                        |
| Ne$^+$  | 38.0(5)                         | 133.80(5)                     | 46.7451(8)                      | 40.2711(5)                  | 57.231(1)                   | 97.664(2)                   | -10.62(5)                       |

V. CONCLUSIONS

We have calculated energies for the first-row atoms with significantly more accuracy than previous DMC studies. Our DMC energies for the atoms heavier than Li and ions heavier than Be$^+$ are the lowest so far reported from a variational method. Our DMC IPs are also superior to very recent FCI-QMC results\textsuperscript{23}. Our IPs are, however, substantially less accurate than the CCSD-F12-HLC data of Klopper et al.\textsuperscript{24}. Our DMC IPs are considerably better than the CCSD values, but the addition of the F12 and HLC corrections leads to errors which are roughly an order of magnitude smaller than in our DMC calculations. The DMC calculations have the feature that the results are obtained from a single calculation, and the cost of calculating the F12 and HLC corrections in the CCSD scheme will increase very rapidly with the number of electrons.

It would be extremely useful if post hoc corrections could be developed for QMC methods. One method which has shown some success in VMC is to plot the total energy versus the variance of the local energy using a set of trial wave functions of different qualities\textsuperscript{38}. Such
a plot normally shows an approximately linear variation so that an extrapolation to zero variance can be performed. The linear variation can be derived by assuming that the set of wave functions differ by a term of the form $\epsilon \Phi(R)$, where $\epsilon$ is a parameter and $\Phi(R)$ is an (unknown) wave function, but there is no guarantee that this assumption is valid. Perhaps a post hoc correction scheme can be developed for DMC calculations.

For the most difficult case of the O atom we obtained an error in the energy of 2.17(8)% in our 2007 study\textsuperscript{15} compared with 0.74(4)% in the present study. There is every prospect of making substantial further improvements to the VMC and DMC results. The stochastic optimization techniques used to obtain the optimal values of the wave function parameters have improved greatly in recent years, mainly due to the work of Umrigar and collaborators\textsuperscript{13,14}. The development of VMC sampling strategies which allow more reliable and efficient optimization of wave functions is extremely promising\textsuperscript{39}. There have been major improvements in the available wave function forms\textsuperscript{8,40–42}, and many more such developments can be expected in the coming years. The cost of the QMC calculations reported here increases rapidly with system size because of the use of a multi-determinant expansion. However, we expect that the computational cost could be substantially reduced by using a more efficient representation such as geminal\textsuperscript{42} or Pfaffian wave functions\textsuperscript{40,41}.

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