# Diffusion Monte Carlo Study of Atomic Systems from Li to Ne

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A systematic diffusion Monte Carlo (DMC) study of both neutral and charged atomic systems from Li to Ne in the ground state is performed to evaluate the correlation energy ($E_c$), the ionization energy (IE), and the electron affinity (EA) of these systems. The present study is based on the fixed-node approximation in which the nodal surfaces of the DMC wavefunction is assumed to be the same as those of the Hartree-Fock wavefunction. The present calculations reproduce $90 \pm 7\%$ of the exact value of correlation energy for the cations, $91 \pm 3\%$ for the neutral atoms, and $92 \pm 2\%$ for the anions, respectively. The theoretical values of IE and EA in the present study are in good agreement with experimental values within an accuracy of 0.3 eV for IE and 0.1 eV for EA. The variation of $E_c$ and IE with respect to the atomic number $Z$ is interpreted.   [doi:10.2320/matertrans.47.2612]

## 1. Introduction

Owing to its self-consistency, Hartee-Fock (HF) theory[1–3] describes the true ground state of all atoms in complete agreement with Hund's first and second rules and reproduces 99.5% of the exact ground-state energy. On the other hand, an accurate evaluation of the ionization energy (IE) and the electron affinity (EA) for atoms, *i.e.*, information about one-electron excitations, requires a sophisticated theoretical treatment involving correlation beyond the scope of HF theory.

We shall start with the evaluation of IE and EA in the framework of HF theory. According to Koopmans' theorem,[4] the negative sign of the highest occupied orbital energy and the lowest unoccupied orbital energy can respectively be interpreted as IE and EA, if correlation and orbital relaxation are both neglected. The Koopmans' interpretation generally gives a good evaluation of IE for atoms within an accuracy of $\pm 8\%$. This is because a considerable amount of cancellation favorably occurs between the two errors arising from lack of correlation and orbital relaxation. On the other hand, the same interpretation gives a quite poor evaluation of EA for atoms since the two errors are accumulated instead of being cancelled; according to the Koopmans' interpretation, the $(N + 1)$ state (anion) cannot be stabilized for most cases.

If one takes full account of only orbital relaxation in the evaluation of IE, *i.e.*, if one evaluates both the $(N - 1)$ and the $N$ state energies by the HF variational theory, the resulting IE for atoms is necessarily underestimated in magnitude by about 10% since no cancellation occurs between the two errors. The same evaluation of EA still remains underestimated in magnitude by an amount of about 1 eV.

Diffusion Monte Carlo (DMC) method[5] can provide accurate numerical results involving correlation, which is comparable to the conventional quantum chemistry method such as configuration interaction (CI) method. There are a number of DMC studies about light atoms and molecules. For example, Langfelder *et al.* have already evaluated the correlation energy for neutral atoms from Li to Ne,[6] based on the fixed-node approximation[7,8] in which the nodal surfaces of the DMC wavefunction is assumed to be the same as those of the HF wavefunction. Their calculations have reproduced $93 \pm 4\%$ of the exact value of the correlation energy for the atoms. However, no one has ever tried to evaluate by DMC method IE and EA of atoms as well as the correlation energy for the positively and negatively ionized states of atoms.

In the present study, we have performed a systematic DMC study of both neutral and charged atomic systems from Li to Ne in order to evaluate the ionization energy and the electron affinity as well as the correlation energy. Section II deals with the computational methods. Section III provides numerical results and some discussions.

## 2. Computational Methods

DMC is a powerful technique in which the exact wavefunction component is extracted from a starting trial wavefunction to develop into its complete form. The time-dependent Schrödinger equation has an exponential factor with an imaginary argument $\exp(-i\hat{H}t/\hbar)$, where $\hat{H}$ is the many-electron Hamiltonian. By introducing the imaginary-time $\tau = it$, the equation is transformed into a diffusion-type Fokker-Planck equation. Its imaginary-time evolution, owing to the presence of a damping factor $\exp(-\hat{H}\tau/\hbar)$, can in principle lead to the exact wavefunction after a long enough interval $\tau$, unless the starting trial wavefunction happens to be orthogonal to the exact one.

The practice of DMC method depends strongly on a starting trial wavefunction chosen: (1) DMC usually resorts to the fixed-node approximation.[7,8] If the nodal surfaces of the trial wavefunction is accurate enough, this approximation is expected to give a very accurate energy. Generally, the fixed-node DMC energy is variational in the sense that it is less than or equal to the energy calculated with the starting trial wavefunction that is called the variational Monte Carlo (VMC) energy and greater than or equal to the exact energy. (2) Owing to the singular behavior of the Coulomb interaction at short distances, the many-electron wavefunction exhibits spatial singularities called cusps.[9] It forms a cusp-like shape whenever an electron approaches any nucleus or any two electrons approach each other with

Table 1　The correlation energy $E_c$ for both neutral and charged atomic systems from Li to Ne in the ground state. Statistical errors in the present DMC study are indicated in the parenthesis. All energies are in hartree units. The recovering percentage of the exact correlation energy ($\%E_c$) is also given.

| Atom | Method | neutral ($N = Z$) | | cation ($N = Z - 1$) | | anion ($N = Z + 1$) | |
|------|--------|-------|--------|-------|--------|-------|--------|
| | | $E_c$ | $\%E_c$ | $E_c$ | $\%E_c$ | $E_c$ | $\%E_c$ |
| Li | DMC | −0.0445(4) | 98.18(4) | −0.0434(2) | 99.80(2) | −0.0689(3) | 95.02(3) |
| ($Z = 3$) | Exact | −0.0454 | 100 | −0.0435 | 100 | −0.0725 | 100 |
| Be | DMC | −0.0843(4) | 89.43(4) | −0.0471(4) | 99.50(4) | | |
| ($Z = 4$) | Exact | −0.0943 | 100 | −0.0473 | 100 | | |
| B | DMC | −0.1079(5) | 86.47(5) | −0.0901(5) | 80.95(5) | −0.1295(6) | 89.40(6) |
| ($Z = 5$) | Exact | −0.1248 | 100 | −0.1113 | 100 | −0.1449 | 100 |
| C | DMC | −0.1380(4) | 88.21(4) | −0.1133(4) | 81.62(4) | −0.1659(7) | 90.82(7) |
| ($Z = 6$) | Exact | −0.1565 | 100 | −0.1388 | 100 | −0.1827 | 100 |
| N | DMC | −0.1696(9) | 89.96(9) | −0.1416(9) | 84.91(9) | | |
| ($Z = 7$) | Exact | −0.1886 | 100 | −0.1668 | 100 | | |
| O | DMC | −0.2346(11) | 90.98(11) | −0.1744(11) | 89.82(11) | −0.3047(13) | 91.98(13) |
| ($Z = 8$) | Exact | −0.2579 | 100 | −0.1942 | 100 | −0.3313 | 100 |
| F | DMC | −0.2963(11) | 92.03(11) | −0.2343(11) | 90.56(11) | −0.3715(13) | 93.65(13) |
| ($Z = 9$) | Exact | −0.3220 | 100 | −0.2587 | 100 | −0.3967 | 100 |
| Ne | DMC | −0.3576(15) | 91.71(15) | −0.2924(15) | 90.06(15) | | |
| ($Z = 10$) | Exact | −0.3899 | 100 | −0.3247 | 100 | | |

parallel or antiparallel spin configuration and hence its first-order derivative has a discontinuity at $r_{iI} = 0$ or $r_{ij} = 0$, where $r_{iI}$ denotes the distance between an electron and a nucleus and $r_{ij}$ the interelectronic distance. Unless such cusp discontinuities are properly taken into account in a starting trial wavefunction, no reasonably convergent result can be obtained for the DMC energy.

A single-determinant Slater-Jastrow type function is adopted as a starting trial wavefunction in the present study. We have calculated the HF orbitals entering the Slater determinant with the GAUSSIAN98 code[10] and a 6-311++G(3df) basis set. The resulting HF orbitals are by construction unable to reproduce the nucleus-electron cusp. In order to recover the nucleus-electron cusp we have adopted an extrapolation method in which the main-body behavior of these HF orbitals is smoothly connected to an appropriate analytic form near the nucleus.[11] The Jastrow factor is usually constructed from homogeneous isotropic electron-electron terms and isotropic nucleus-electron terms centered on the nucleus.[12,13] The first terms are responsible for the description of both the spin-antiparallel and spin-parallel electron-electron cusps.

The Jastrow factor we have adopted here includes 12 parameters which are optimized by minimizing the variance of the VMC energy.[14,15] In order to arrive at high accuracy we have accumulated the numerical results over $3 \times 10^6$ steps. A time step of $0.002 \sim 0.003$ a.u. is used to make the time-step error negligibly small. We have used the CASINO code.[16]

## 3. Results and Discussions

### 3.1 Correlation energy

Table 1 gives a list of an estimated exact correlation energy and the present DMC correlation energy for the neutral atoms from Li to Ne and their cations and anions. The exact correlation energy is defined as the difference between the exact energy $E^{\mathrm{exact}}$ and the HF energy $E^{\mathrm{HF}}$. We have calculated $E^{\mathrm{HF}}$ from the HF code due to Fischer et al.[17] $E^{\mathrm{exact}}$ is the value that Chakravorty et al. have estimated from a systematic investigation of various isoelectronic systems.[18] The recovering percentage of the estimated exact correlation energy for the present DMC calculations is also given in Table 1.

The present DMC study gives the recovering percentage of $91 \pm 3\%$ for neutral atoms, which is comparable to the previously reported value $93 \pm 4\%$.[6] For the cations and anions, the recovering percentage amounts to $90 \pm 7\%$ and $92 \pm 2\%$, respectively. The recovering percentage tends to be somewhat improved as the electron number of the system is increased.

Figure 1 shows the dependence of the correlation energy $E_c$ on the atomic number $Z$ for neutral atoms and their cations in the present DMC calculations. As is obvious from Fig. 1, the correlation energy $E_c$ for both neutral atoms and their cations is reduced nearly linearly with increasing $Z$. The difference in $E_c$ between neutral atoms and their cations, if averaged, amounts to about 1 eV. This is ascribed to the presence of an extra electron in neutral atoms. For neutral atoms, one can observe a discontinuity in the linear coefficient of $E_c$ versus $Z$ at $Z = 7$ (N). For their cations, the same kind of discontinuity is shifted to $Z = 8$ (O$^+$). The negative slope of $E_c$ with respect to $Z$ becomes steeper abruptly at $Z = 7$ for neutral atoms and $Z = 8$ for their cations where the spherically symmetric distribution of the electron density is realized owing to completion of all the possible spin-parallel pair arrangements. Thus, the variation in the magnitude of correlation energy with respect to $Z$ reflects the electronic structure in neutral atoms and their cations. The presence of the spin-antiparallel pair arrangements in the valence electron density is responsible for such an abrupt increase in the negative slope of $E_c$, which
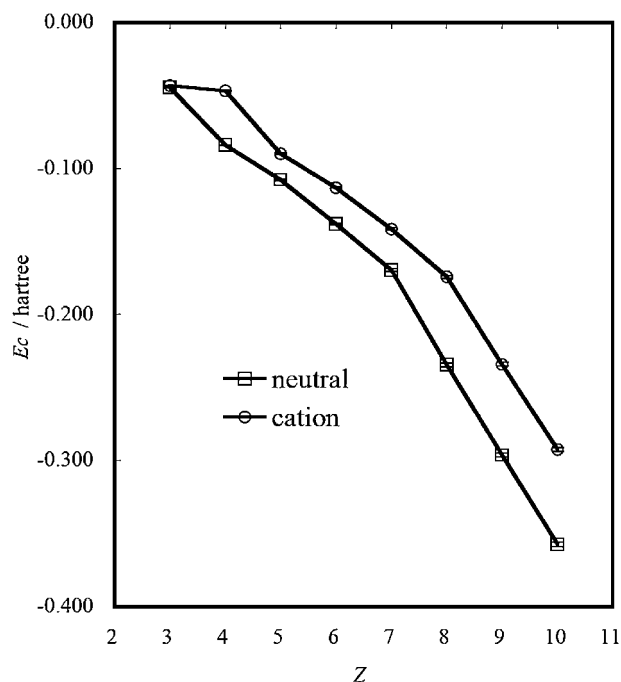
Fig. 1   The variation of $E_c$ with respect to $Z$ for neutral atoms and their cations in the present DMC study. Statistical errors in the figure are too small to discern.

continues until all the possible spin-antiparallel pair arrangements are completed. The contribution to $E_c$ from a spin-antiparallel pair is about three times larger in magnitude than that from a spin-parallel pair, *i.e.*, the spin-antiparallel contribution to $E_c$ from the Coulomb hole due to the Coulomb repulsive interaction is by a factor of about 3 larger than the spin-parallel contribution to $E_c$ from the deepening Fermi hole due to the Coulomb repulsive interaction. To conclude, an abrupt change in the nearly linear coefficient of $E_c$ observed at $Z = 7$ or 8 comes from the fact that the number of spin-parallel pairs is increased for $Z < 7(8)$ following the Hund's first and second rules and thereafter the number of spin-antiparallel pairs is increased for $Z > 7(8)$. In a word, an abrupt change observed in the variation of $E_c$ with respect to $Z$ reflects the Hund's first and second rules.

### 3.2   Ionization energy

Table 2 shows a list of various theoretical values and experimental values[19] for IE of the eight atoms. The DMC calculations evaluate IE as the difference in the total energy between a cation and a neutral atom. By $\Delta$HF we mean the method for evaluating IE from the difference between the two HF variational calculations. The $\Delta$HF method necessarily underestimates IE since it takes full account of orbital relaxation alone. The averaged magnitude of the underestimate amounts to about 1 eV, which is equivalent to an increase in the correlation energy due to the presence of an extra electron. The Koopmans' interpretation underestimates IE for metallic elements (Li and Be) by about 0.5 eV and overestimates IE for non-metallic elements (B, C, N, O, F, and Ne) by about 1.5 eV. All values of IE in the present DMC study are in good agreement with experimental values within an accuracy of 0.3 eV.

Table 2   The ionization energies for the neutral atoms. Statistical errors in the present DMC study are indicated in the parenthesis. By $\Delta$HF we mean the method for evaluating IE from the difference between the two HF variational calculations. All energies are in eV units.

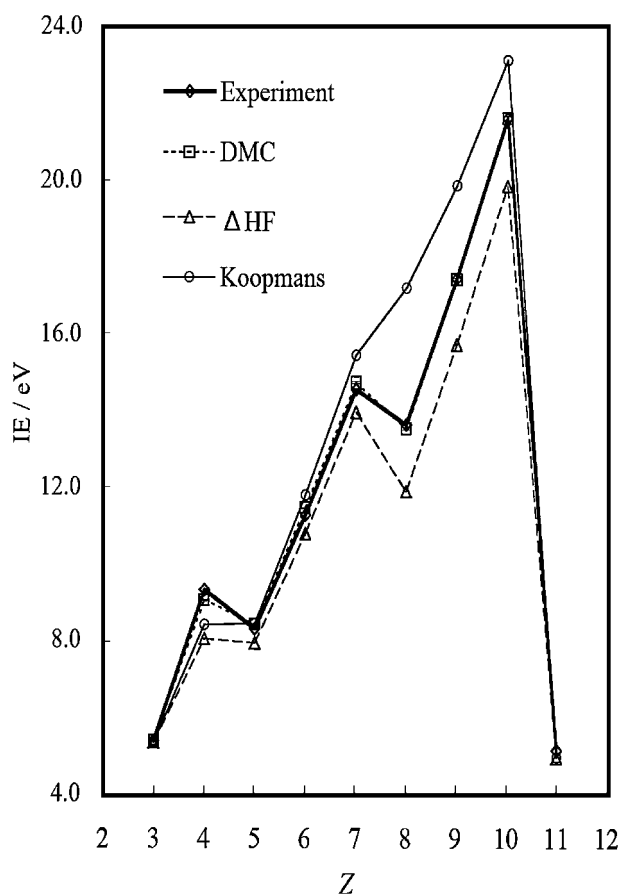| Atom | Koopmans | $\Delta$HF | DMC | Experiment |
|---|---|---|---|---|
| Li ($Z = 3$) | 5.34 | 5.34 | 5.35(2) | 5.39 |
| Be ($Z = 4$) | 8.42 | 8.04 | 9.06(1) | 9.32 |
| B ($Z = 5$) | 8.43 | 7.93 | 8.41(2) | 8.30 |
| C ($Z = 6$) | 11.79 | 10.79 | 11.46(2) | 11.27 |
| N ($Z = 7$) | 15.44 | 13.96 | 14.71(3) | 14.55 |
| O ($Z = 8$) | 17.19 | 11.89 | 13.52(4) | 13.62 |
| F ($Z = 9$) | 19.86 | 15.72 | 17.40(4) | 17.43 |
| Ne ($Z = 10$) | 23.14 | 19.84 | 21.61(6) | 21.62 |



Fig. 2   A comparison of three different theoretical values for IE with experimental values. Statistical errors in the figure are too small to discern. The DMC value of IE for $Z = 11$ is missing.

Figure 2 gives a comparison of three different theoretical values of IE with experimental values. As is seen from the figure, IE takes its local maximum values at $Z = 4$, 7, and 10 where the spherically symmetric distribution of the electron density is realized. This is because the spherically symmetric distribution causes a remarkable contraction of the electron density around the nucleus to lower effectively the nucleus-electron attractive Coulomb interaction energy. Both DMC and $\Delta$HF give an appropriate description of all the local maximum values of IE (except $Z = 11$ for DMC), while the Koopmans' interpretation fails to reproduce two local maximum values at $Z = 4$, 7.
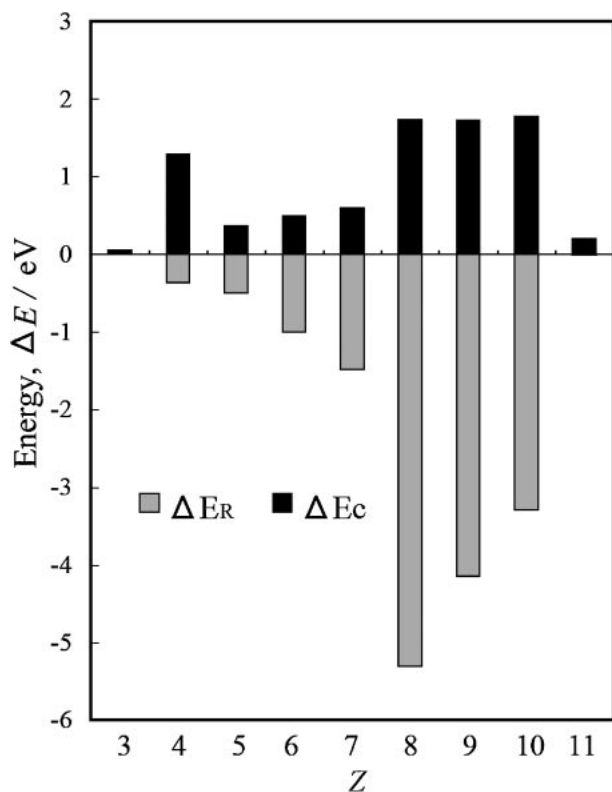
Fig. 3 A plot of both the orbital relaxation energy ($\Delta E_R$) and the correlation energy difference between a cation and a neutral atom ($\Delta E_c$) as a function of $Z$.

Here we give an explanation of why the Koopmans' interpretation fails to reproduce the two local maximum values of IE at $Z = 4, 7$ and succeeds to reproduce the third local maximum at $Z = 10$. The exact, or experimental value of IE ($\mathrm{IE}^{\mathrm{exp}}$) and the value of IE evaluated from Koopmans' theorem ($\mathrm{IE}^{\mathrm{KT}}$) are related as follows:

$$\mathrm{IE}^{\mathrm{exp}} = \mathrm{IE}^{\mathrm{KT}} + \Delta E_R + \Delta E_c,$$
$$\Delta E_R \equiv \mathrm{IE}^{\Delta\mathrm{HF}} - \mathrm{IE}^{\mathrm{KT}}, \qquad (1)$$
$$\Delta E_c \equiv \mathrm{IE}^{\mathrm{exp}} - \mathrm{IE}^{\Delta\mathrm{HF}},$$

where $\mathrm{IE}^{\Delta\mathrm{HF}}$ is the value of IE evaluated from the $\Delta$HF method, $\Delta E_R (< 0)$ is the orbital relaxation energy, and $\Delta E_c (> 0)$ is the difference in the correlation energy between a cation and a neutral atom. Figure 3 gives a plot of both $\Delta E_R$ and $\Delta E_c$. As is obvious from Fig. 3, the correlation contribution to IE for metallic elements (Li and Be) is greater than that for non-metallic elements (B, C, N, O, F, and Ne). On the other hand, the orbital relaxation contribution to IE for the non-metallic elements is greater than that for the metallic elements. The reason why the Koopmans' interpretation fails to give the local maximum at $Z = 4$ is that the correlation contribution to IE for the Be atom ($Z = 4$) is particularly important among all the atoms for $Z \leq 7$ since the presence of occupied $2s$ levels and near-degenerate unoccupied $2p$ levels gives rise to a local increase in the magnitude of $E_c$. On the other hand, the reason why the Koopmans' interpretation fails to give the local maximum at $Z = 7$ is different from the case of $Z = 4$. As is obvious from Fig. 2, it is because the Koopmans' interpretation overestimates $\mathrm{IE}^{\mathrm{KT}}$ of the neigh-

Table 3 The electron affinities for the neutral atoms. Statistical errors in the present DMC study are indicated in the parenthesis. By $\Delta$HF we mean the method for evaluating EA from the difference between the two HF variational calculations. All energies are in eV units.

| Atom | $\Delta$HF | DMC | Experiment |
|---|---|---|---|
| Li ($Z = 3$) | $-0.12$ | 0.54(1) | 0.62 |
| B ($Z = 5$) | $-0.31$ | 0.32(2) | 0.28 |
| C ($Z = 6$) | 0.46 | 1.31(2) | 1.26 |
| O ($Z = 8$) | $-0.58$ | 1.37(5) | 1.46 |
| F ($Z = 9$) | 1.20 | 3.41(5) | 3.40 |

boring O atom ($Z = 8$) by more than 3 eV for lack of orbital relaxation; the overestimate is too large for $\mathrm{IE}^{\mathrm{KT}}$ of the N atom ($Z = 7$) to be prominent. The third local maximum at $Z = 10$ is successfully described by the Koopmans' interpretation since no remarkable behavior appears in the magnitude of $E_c$ at $Z = 10$ and in the magnitude of orbital relaxation at the neighboring atom ($Z = 11$).

### 3.3 Electron affinity

Table 3 gives a list of various theoretical values and experimental values[20] for EA of Li, B, C, O, and F atoms. The DMC method evaluates EA as the difference in the total energy between a neutral atom and an anion. Note that each of Be, N, and Ne atoms is unable to form a stable negative ion. This is because remarkable contraction of the electron density around the nucleus due to its spherically symmetric distribution occurring in each of these atoms screens its nuclear attractive Coulomb interaction so perfectly that an additional electron can no more be bounded to the nucleus. This interpretation is based on the assumption that in the formation of a negative iron the original electron config-uration for a neutral atom is not changed by adding an extra electron to it.

For lack of correlation, the $\Delta$HF method fails to stabilize a negative ion for each of Li, B, and O atoms. All values of EA in the present DMC study are in good agreement with experimental values within an accuracy of 0.1 eV. The agreement in the evaluation of EA is better than in the evaluation of IE. This probably reflects that the recovering percentage of the correlation energy tends to be somewhat improved as the electron number of the system is increased.

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