Interpretation of Hund's multiplicity rule for the $2p$ and $3p$ atoms by quantum Monte Carlo methods

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(Dated: March 3, 2006)

A systematic quantum Monte Carlo study of $2p$ atoms (C, N, O) and $3p$ atoms (Si, P, S) is performed in order to investigate the origin of Hund's multiplicity rule. This is based on a detailed examination of the correlation contribution to individual energy components of the total energy. In contradiction with the traditional explanation due to exchange energy, the stability of the highest spin-multiplicity state of all the atoms is ascribed to a lowering in the nucleus-electron attractive interaction that is gained at the cost of increasing the electron-electron repulsive interaction as well as the kinetic energy. The accuracy of the present calculations is by an order of the magnitude improved compared with our previous study. The virial ratio $-V/T$ in the present study is accurate to the significant figure 2.000.

I. INTRODUCTION

The traditional explanation of Hund's multiplicity rule[1,2] due to exchange energy was first criticized in the 1960's.[3] The energy difference between the ground state with the highest multiplicity and the lowest excited state with lower multiplicity is traditionally explained as due to a difference in the electron-electron repulsive interaction $V_{\rm ee}$, i.e., exchange energy. This is based on the assumption that the two states could have quite the same set of orbitals. This assumption gives the same expectation value of one-electron operators, the same kinetic energy T and the same nucleus-electron attractive interaction $V_{\rm ne}$ for the two states, thereby ascribing the energy difference to the expectation value of the two-electron operator, $V_{\rm ee}$.

In fact, this traditional explanation is incorrect even in the stage of the Hartree-Fock (HF) approximation, because by the virial theorem a set of self-consistent HF orbitals cannot be identical for different states with different values of spin-multiplicity $2S+1$. In actual fact the traditional explanation resorts to first-order perturbation theory with respect to the electron-electron repulsive interaction and hence violates the virial theorem.

According to the virial theorem, the kinetic energy T and the total potential energy $V(=V_{\rm ne}+V_{\rm ee}+V_{\rm nn})$ are not independent of each other; $V_{\rm nn}$ denotes the nucleus-nucleus repulsive interaction for molecules and solids. The virial theorem[4]

$$2T+V=0 \quad \Leftrightarrow \quad E=T+V=-T=V/2 \ < \ 0 \quad (1)$$

holds for any stationary state. The highest and the next highest multiplicity states of atoms both fulfill the virial theorem independently, giving different values of T and V. Hence the virial relation follows, $2\Delta T+\Delta V=0$. The ground state can be stabilized compared with the lowest excited state if and only if the total potential energy is lowered by an amount of $2\Delta T$ at the cost of increasing the kinetic energy ($\Delta T>0$).

The HF approximation, because of its self-consistent character from variational theory, fulfills the virial theorem to give the correct interpretation of Hund's rule.[3,5–7] The stability of the highest multiplicity state is ascribed to a lowering in the nucleus-electron attractive interaction, which is realized at the cost of increasing the electron-electron repulsive interaction as well as the kinetic energy. This is because the exchange potential in the HF equations has the effect to reduce the Hartree screening of the nucleus. Hence the electron density distribution associated with valence electrons contracts around the nucleus to give a lowering in $V_{\rm ne}$. A number of authors have already reported that the inclusion of correlation does not change the above HF interpretation of Hund's multiplicity rule for the ground state and the low-lying excited states of small systems.[8–13]

In this paper, we report for the first time a systematic quantum Monte Carlo (QMC) study of $2p$ atoms (C, N, O) and $3p$ atoms (Si, P, S) in order to confirm the origin of Hund's multiplicity rule. We have made a detailed examination of the correlation contribution to individual components of the total energy for these atoms. The accuracy of the present calculations is by an order of the magnitude improved, compared with our previous study.[15] The virial ratio $-V/T$ in the present study is accurate to the significant figure 2.000.

The assertion that the more stable stationary state has the more negative $V_{\rm ne}$ appears to be widely accepted from experience. We examine this assertion in some detail. Consider all energy components of the stationary state:

$$E \ = \ T+V_{\rm ne}+V_{\rm ee}+V_{\rm nn} \ < \ 0, \quad (2)$$

the negative value of E means the predominance of the nucleus-electron attractive interaction $V_{\rm ne}$. The interaction $V_{\rm ee}$ and $V_{\rm nn}$ play a rather minor role in fulfilling $2T+V=0$. The stationary state is realized as a consequence of balancing the decreasing rate of V with the increasing rate of T. The attractive interaction $V_{\rm ne}$ is larger than the total repulsive interaction $V_{\rm ee}+V_{\rm nn}$ in magnitude and furthermore is responsible for the decreasing rate of V.

The property above may be termed *the predominance of $V_{\rm ne}$ in the stationary state* to stress its importance

in the theoretical study of the electronic structure. Actually, for the specific case where a single-determinant wavefunction is applied to atoms, the predominance of $V_{\rm ne}$ has already been demonstrated using the virial theorem.[14] The energy difference in $V_{\rm ne}$ between any two stationary states is always larger in magnitude than that in $V_{\rm ee}$ between the same two. In the present study we have confirmed the predominance of $V_{\rm ne}$ in the stationary state for all the atoms calculated.

Generally, the inclusion of correlation does not change the HF interpretation of Hund's rule for atoms, molecules and ions. So far as the HF theory gives a qualitatively correct description of atoms and molecules, correlation merely lowers both of the highest and the next highest multiplicity states without reversing the order of the two. The predominance of $V_{\rm ne}$ in the stationary state is not influenced by the inclusion of correlation.

The present paper is organized as follows: In section II, we improve the Slater-Jastrow trial wavefunction in order to obtain rapid convergence and high accuracy in the numerical study of diffusion Monte Carlo method. In section III, we give a detailed analysis of present numerical results. The last section IV summarizes our conclusions.

II. IMPROVEMENT OF TRIAL WAVEFUNCTION

Diffusion Monte Carlo method (DMC) is a powerful technique for numerically solving the many-electron Schrödinger equation for any stationary state.[16] The Schrödinger equation in its time-dependent form involves an exponential factor with an imaginary argument $\exp(-i\hat{H}t/\hbar)$. The equation can be transformed into a diffusion-like equation by introducing the imaginary time $\tau = it$. Its imaginary-time evolution, owing to the presence of a damping factor $\exp(-\hat{H}\tau/\hbar)$, can in principle lead to the exact solution after a long enough τ, provided the initial trial wavefunction has a nonzero overlap with the exact wavefunction.

The practice of DMC depends critically on the trial wavefunction: (1) Usually, DMC assumes the fixed-node approximation[17,18] in which the nodal surfaces of the many-electron wavefunction are assumed to be the same as those of the HF wavefunction. (2) The lower the initial value of the total energy calculated from the initial trial wavefunction the more rapid convergence of the DMC total energy. Usually, the total energy evaluated from variational Monte Carlo method (VMC) is adopted as the initial value in DMC. (3) Under the requisite conditions DMC can in principle give the correct expectation value of the Hamiltonian $\hat{H}$ and any other operator that commutes with $\hat{H}$. However, it cannot be used to evaluate the expectation value of any operator that does not commute with $\hat{H}$. This is because DMC relies on the importance-sampling technique. A combination of VMC and DMC however makes it possible to evaluate individual components of the total energy.[19] From an analysis of the difference between the DMC and VMC wavefunctions, it has been proven that

$$\begin{aligned} \langle\hat{O}\rangle_{\rm pure} &= 2\langle\hat{O}\rangle_{\rm mixed} - \langle\hat{O}\rangle_{\rm VMC} + O(\Delta^2), \\ \langle\hat{O}\rangle_{\rm linear} &\equiv 2\langle\hat{O}\rangle_{\rm mixed} - \langle\hat{O}\rangle_{\rm VMC}. \end{aligned} \tag{3}$$

The expectation value of any operator $\hat{O}$ with respect to the DMC wavefunction $\langle\hat{O}\rangle_{\rm pure}$ differs from twice the mixed expectation value $\langle\hat{O}\rangle_{\rm mixed}$ (the expectation value of $\hat{O}$ inserted between the VMC and DMC wavefunctions) minus the expectation value of $\hat{O}$ with respect to the VMC wavefunction $\langle\hat{O}\rangle_{\rm VMC}$ by the order of the squared difference between the two wavefunctions. The expectation value of $\langle\hat{O}\rangle_{\rm linear}$ thus defined is termed a linear extrapolated estimator. In the limit $\Delta^2 \to 0$, $\langle\hat{O}\rangle_{\rm linear}$ tends to $\langle\hat{O}\rangle_{\rm pure}$.

The DMC calculations are classified into two types depending on how the expectation value is evaluated: One is the DMC due to the mixed estimator (mixed DMC) and the other is the DMC due to the linear extrapolated estimator (extrapolated DMC).

In order to interpret Hund's rule correctly and investigate the role of correlation, it is necessary to evaluate each of energy components to high accuracy in DMC. For instance, the present DMC total energy of the carbon atom gives almost the same value as the previous one, but the present ratio $-V/T$ deviates from 2 only by 0.01% and $-V^{\rm corr}/T^{\rm corr}$ by 5%, whereas the previous ratio $-V/T$ deviates from 2 by 0.1% and $-V^{\rm corr}/T^{\rm corr}$ by 30%. We have also attained the same level of accuracy for N, O, Si, P, and S atoms. The accuracy in the present study has been achieved by improving the initial trial wavefunction. This key aspect on how to improve the initial trial wavefunction will be described in the following.

The initial trial wavefunction we have adopted is of the Slater-Jastrow type.[20]

$$\Psi(\{\boldsymbol{r}_i\},\{\boldsymbol{r}_I\}) = D(\{\boldsymbol{r}_i\})\,\exp[J(\{\boldsymbol{r}_i\},\{\boldsymbol{r}_I\})], \tag{4}$$

where $\{\boldsymbol{r}_i\}$ and $\{\boldsymbol{r}_I\}$ denote the electron and ion coordinates, respectively; D denotes a single Slater-determinant and $\exp[J]$ the Jastrow factor. The Slater-determinant is constructed from the HF orbitals calculated with GAUSSIAN98 code[21] and 6-311++G(3df) basis set. The Jastrow function J we have adopted consists of three sums: The first sum runs over homogeneous isotropic electron-electron terms u, the second over isotropic electron-nucleus terms χ_I centered on the nuclei, and the third over isotropic electron-electron-nucleus terms f_I centered on the nuclei.

$$\begin{aligned} J(\boldsymbol{r}_i,\boldsymbol{r}_I) = &\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u(r_{ij}) + \sum_{I=1}^{N_{\rm nuclei}}\sum_{i=1}^{N}\chi_I(r_{iI}) \\ &+ \sum_{I=1}^{N_{\rm nuclei}}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} f_I(r_{iI},r_{jI},r_{ij}), \end{aligned} \tag{5}$$

where N is the number of electrons and $N_{\rm nuclei}$ the number of nuclei; $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and $r_{iI} = |\boldsymbol{r}_i - \boldsymbol{r}_I|$; we have preserved the ion coordinates $\{\boldsymbol{r}_I\}$ for the sake of generality. The explicit form of u, χ_I, and f_I terms are seen in Ref.22.

The homogeneous, isotropic electron-electron terms u in the Jastrow function is responsible for the appropriate description of the electron-electron cusp for both spin-antiparallel and -parallel configurations. On the other hand, the Slater-determinant D is responsible for the description of the nucleus-electron cusp.

Owing to the singular behavior of the Coulomb interaction at short distances, the many-electron wavefunction exhibits a spatial singularity called a cusp condition.[23] It forms a cusp-like shape whenever an electron approaches any nucleus and any two electrons approach each other for both spin configurations and hence its first-order derivative becomes discontinuous at the points $r_{ij} = 0$ and $r_{iI} = 0$. The appropriate description of such a singularity in the wavefunction guarantees that the divergence arising from the operation of the kinetic energy operator on the wavefunction is completely canceled by the corresponding divergence from the operation of the Coulomb potential operator. Unless the cusp condition is properly described in the initial trial wavefunction, both VMC and DMC are not convergent because of incomplete cancellation between the two divergences.

In the previous study[15] we only used the first and second sums in eq.(5), which is then usually called the two-body Jastrow factor.[24] In the present study we have included the third sum, i.e., the sum over isotropic electron-electron-nucleus terms f_I centered on the nuclei, which is called the three-body Jastrow factor. We give a detailed explanation of how the inclusion of the third sum in eq.(5) changes the VMC total energy. Fig. 1 shows a comparison of the two-body and three-body Jastrow factor calculations for the triplet and singlet states of the carbon atom. As is obvious from the figure, the DMC total energy remains almost unchanged, whereas the VMC total energy is drastically lowered in the three-body Jastrow factor calculation for the two states. Thus, the difference between the two total energies is significantly reduced compared with the same difference in the two-body Jastrow factor calculation. The reduction in the energy difference indicates that an overlap between the DMC and VMC wavefunctions is increased. In other words, the reliability in DMC is enhanced, thereby giving a more precise evaluation of individual energy components of the total energy. The following ratio is a good measure of the reliability in DMC.

$$\eta = \frac{E^{\rm HF} - E^{\rm VMC}}{E^{\rm HF} - E^{\rm DMC}} \times 100\%, \tag{6}$$

where $E^{\rm HF}$ is the energy evaluated only with the Slater determinant and $E^{\rm VMC}$ the energy evaluated with the Slater-Jastrow wavefunction; $E^{\rm DMC}$ is the DMC energy. The present study gives $\eta_{J_{\rm 3body}} = 83\%$, whereas the previous study gives $\eta_{J_{\rm 2body}} = 60\%$, where by $J_{\rm 3body}$ and $J_{\rm 2body}$ we imply three-body and two-body Jastrow factor calculations, respectively. The higher value of η means the higher reliability in the evaluation of individual energy components from a linear extrapolated estimator. We have thus attained the present numerical results that are by an order of the magnitude more accurate than the previous ones. All the numerical results in the next section are obtained using the three-body Jastrow factor calculations.

The number of parameters in the Jastrow factor is 24 for u terms, 8 for χ terms, and 57 for f_I terms. In total, we use 89 adjustable parameters in the Jastrow factor for all $2p$ and $3p$ atoms which are optimized by minimizing the variance of the VMC energy.[24–26] The VMC wavefunction thus obtained is used as the initial trial wavefunction for DMC. The present DMC uses a time step $0.0003 \sim 0.001$ a.u., which is small enough to neglect the time-step error. The numerical calculations for the $3p$ atoms require about 10 times longer Monte Carlo runs than those for the $2p$ atoms to attain the same level of accuracy. The main reason for this is that the statistical error in QMC increases as the absolute magnitude of energy in the system becomes larger. In addition, the energy splitting between the different multiplet states for the $3p$ atoms is by a factor of about 1.5 smaller than that for the $2p$ atoms. All the QMC calculations in the present study are performed using CASINO code.[27]

III. NUMERICAL RESULTS

A. The ground-state energy

Table I shows a list of various numerical results for the ground-state energy of the $2p$ atoms (C, N, O) and the $3p$ atoms (Si, P, S). $E^{\rm HF}$ is the Hartree-Fock ground-state energy calculated from the celebrated HF code due to C. F. Fischer *et al.*.[28] $E^{\rm exact}$ is the exact non-relativistic ground-state energy estimated by S. J. Chakravorty *et al.*.[29] $E^{\rm VMC}$ and $E^{\rm DMC}$ are the VMC and the DMC ground-state energies, respectively. For comparison we also list the SDCI ground-state energy $E^{\rm SDCI}$ which we have performed by GAUSSIAN98 code[21] and the same basis set 6-311++G($3df$) as used in the present VMC and DMC calculations.

The correlation energy is defined by

$$E^{\rm corr} \equiv E^{\rm exact} - E^{\rm HF} < 0. \tag{7}$$

By the "exact" correlation energy (100%) we imply the most reliable value of correlation eneregy that can be estimated from a systematic consideration of various iso-electronic systems. The value of $E^{\rm corr}$ is seen on the right hand side of each column in Table I. The recovering percentage of the exact value of $E^{\rm corr}$ for each calculation is given in the parenthesis.

The recovering percentage for SDCI is $68 \sim 69\%$ for the $2p$ atoms and $44 \sim 47\%$ for the $3p$ atoms. An abrupt

drop in the percentage for the $3p$ atoms is due to the serious error of truncated CI methods that increasingly underestimate the magnitude of correlation energy as the number of electrons is increased. On the other hand, the recovering percentage is $70 \sim 81\%$ for VMC and $90 \sim 94\%$ for DMC for both of the $2p$ and $3p$ atoms. Thus DMC is a powerful method to evaluate the correlation energy, as long as the fixed-node problem does not become serious with increasing number of electrons.[31]

B. Individual energy components

An analysis of the total energy of the system into the individual energy components is needed for the complete understanding of Hund's rule. This is because a comparison has to be made between the ground-state energy and the lowest excited state energy under the condition that both of the two states fulfill the virial theorem independently.

In the following, by the *high-spin state* (high-S) we imply the ground-state and by the *low-spin state* (low-S) the lowest excited state. For the carbon, oxygen, silicon, and sulfur atoms, high-S and low-S correspond to the triplet (S=1) and the singlet (S=0) states, respectively. For the nitrogen and phosphorus atoms, high-S and low-S correspond to the quartet ($S=3/2$) and the doublet ($S=1/2$) states, respectively. The value of S for each state is written in the parenthesis.

Table II gives a list of individual energy components $V_{\rm ee}, V_{\rm ne}$, and T of the total energy E for the $2p$ atoms (C,N,O). The virial ratio $-V/T$ is listed on the last column in Table II. Table III gives the same list for the $3p$ atoms (Si,P,S).

All the VMC, mixed DMC, and extrapolated DMC calculations in the present study reproduce the virial ratio to the significant figure 2.000, which is by an order of the magnitude improved compared with the previous study. The deviation from 2 is $\pm 0.01\%$ in this paper and $\pm 0.1\%$ in the previous study. This accuracy is sufficient to investigate the origin of Hund's rule.

From a systematic comparison between high-S and low-S based on the VMC, mixed DMC, and extrapolated DMC calculations we have arrived at the following relation for all $2p$ and $3p$ atoms.

$$\begin{aligned} V_{\rm ne}^{\text{high-}S} &< V_{\rm ne}^{\text{low-}S}, \\ T^{\text{high-}S} &> T^{\text{low-}S}, \\ V_{\rm ee}^{\text{high-}S} &> V_{\rm ee}^{\text{low-}S}. \end{aligned} \tag{8}$$

Thus we can conclude as follows: The stability of the highest multiplicity state of these atoms is ascribed to a lowering in the nucleus-electron attractive interaction $V_{\rm ne}$ that is gained at the cost of increasing the electron-electron repulsive interaction $V_{\rm ee}$ as well as the kinetic energy T. The lowering in $V_{\rm ne}$ for high-S is caused by an increase in the electron density distribution of valence electrons around the nucleus. This increase in the valence electron density is ascribed to the fact that exchange and correlation both reduce the Hartree screening of the nucleus at short interelectronic distances. The remarkable change in the valence electron density that is induced by exchange and correlation in high-S increases the electron-electron repulsive interaction $V_{\rm ee}$ as well as the kinetic energy T.

It is important to recognize that the above-mentioned change in the valence electron density involves a change in the core electron density distribution. A slight expansion of the core electron density distribution occurs as a counterpart effect of the contraction of the valence electron distribution. A combination of the expansion in the core region and the contraction in the valence region leads to an increase in the electron-electron repulsive interaction $V_{\rm ee}$.

C. Correlation energy and its components

As is evident from subsection **B**, the HF interpretation of Hund's rule for atoms is not changed qualitatively by the inclusion of correlation, i.e., correlation lowers both high-S and low-S without reversing the order of the two states. Generally, correlation gives rise to a quantitative change in each of the energy components as well as in the total energy under the condition that $2T + V = 0$.

The virial theorem is satisfied for both of the HF and exact wavefunctions:

$$2T^{\rm exact} + V^{\rm exact} = 0, \tag{9}$$

$$2T^{\rm HF} + V^{\rm HF} = 0. \tag{10}$$

Hence we obtain the correlational virial relation:

$$2T^{\rm corr} + V^{\rm corr} = 0, \tag{11}$$

where $V^{\rm corr} = V^{\rm exact} - V^{\rm HF}$ and $T^{\rm corr} = T^{\rm exact} - T^{\rm HF}$. We have thus arrived at the following identity for the correlation energy $E^{\rm corr}$,

$$E^{\rm corr} = -T^{\rm corr} = V^{\rm corr}/2 < 0. \tag{12}$$

The correlation energy $E^{\rm corr}$ consists of an inevitable increase in the kinetic energy $T^{\rm corr}$ and a simultaneous lowering in the total potential energy $V^{\rm corr}$ whose magnitude equals $2T^{\rm corr}$.

From the correlational virial relation and the physical considerations, the following inequalities result:

$$\begin{aligned} V_{\rm ee}^{\rm exact} &< V_{\rm ee}^{\rm HF}, \\ V_{\rm ne}^{\rm exact} &< V_{\rm ne}^{\rm HF}, \\ T^{\rm exact} &> T^{\rm HF}. \end{aligned} \tag{13}$$

Correlation lowers the electron-electron repulsive interaction $V_{\rm ee}$ by forming the so-called Coulomb hole and deepening the Fermi hole. It also reduces the Hartree-Fock

screening of the nucleus at short interelectronic distances and increases the electron density distribution around the nucleus as a result. Correlation increases the kinetic energy in two distinct ways. One is ascribed to an increase in the curvature of the many-electron wavefunction and the other to a correlation-induced increase in the electron density distribution around the nucleus.

Table IV gives a list of various correlation contributions evaluated from the extrapolated DMC calculation. Accuracy in the treatment of correlation can be checked by the ratio $-V^{\rm corr}/T^{\rm corr}$. In the present study, the deviation of the ratio $-V^{\rm corr}/T^{\rm corr}$ from 2 is about $\pm 10\%$ and that of the total ratio $-V/T$ from 2 about $\pm 0.01\%$. The accuracy in the evaluation of $-V/T$ does not guarantee a satisfactory description of correlation unless it attains the HF level; the ratio in HF equals 2 within an accuracy of $\pm 10^{-8}\%$.

As can be seen in Table IV, the present study fulfills all the relations in eq.(13), though the deviation of the correlational virial ratio amounts to about $\pm 10\%$. The magnitude of $V_{\rm ee}^{\rm corr}(= V_{\rm ee}^{\rm exact} - V_{\rm ee}^{\rm HF})$ is larger than that of $V_{\rm ne}^{\rm corr}(= V_{\rm ne}^{\rm exact} - V_{\rm ne}^{\rm HF})$ by a factor of $2 \sim 7$ for the $2p$ atoms and by a factor of about 2 for the $3p$ atoms. Because of its small magnitude, it is quite difficult to evaluate $V_{\rm ne}^{\rm corr}$. Frequently, less accurate calculations gives the wrong sign of $V_{\rm ne}^{\rm corr}$. This is because the correlation-induced change in the electron density distribution is very difficult to evaluate to high accuracy. In other words, the electron density distribution is very sensitive to the initial trial wavefunction adopted. From the present numerical results and the physical considerations above, we are confident that $V_{\rm ne}^{\rm corr} < 0$.

D. Predominance of $V_{\rm ne}$

Fig. 2 shows the energy differences $\Delta E, \Delta V_{\rm ne}, \Delta T$, and $\Delta V_{\rm ee}$ between high-S and low-S for the $2p$ and $3p$ atoms, calculated from HF, VMC, mixed DMC and extrapolated DMC. The following relations hold for any atom calculated.

$$\begin{aligned} \Delta E &\equiv E^{\text{high-}S} - E^{\text{low-}S} < 0, \\ \Delta V_{\rm ne} &\equiv V_{\rm ne}^{\text{high-}S} - V_{\rm ne}^{\text{low-}S} < 0, \\ \Delta T &\equiv T^{\text{high-}S} - T^{\text{low-}S} > 0, \\ \Delta V_{\rm ee} &\equiv V_{\rm ee}^{\text{high-}S} - V_{\rm ee}^{\text{low-}S} > 0. \end{aligned} \tag{14}$$

Obviously, the stability of high-S, or equivalently the negative value of ΔE is ascribed to that $\Delta V_{\rm ne} < 0$. Note that this stability of high-S is realized at the cost of increasing $V_{\rm ee}$ as well as T. The energy difference $\Delta V_{\rm ne}$ is largest among all the energy differences in magnitude. The lower value of the total energy E is a direct consequence of the lower value of $V_{\rm ne}$. We have already termed this property *the predominance of $V_{\rm ne}$ in the stationary state* in Sec. I.

The energy differences between high-S and low-S, $|\Delta E|$ for the $3p$ atoms are smaller than those for the $2p$ atoms by a factor of about 1.5. This trend is consistent with experiment. Both $\Delta V_{\rm ne}$ and $\Delta V_{\rm ee}$ are increased in magnitude as one transfers from the $2p$ atoms to the $3p$ atoms. More cancellation occurs between $\Delta V_{\rm ne}$ and $\Delta V_{\rm ee}$ in the $3p$ atoms than in the $2p$ atoms.

From a comparison of HF theory and experiment, it may be concluded that correlation tends to reduce the energy difference between high-S and low-S. In other words, the highly accurate self-consistent HF calculations show a systematic overestimate in the energy difference between high-S and low-S for the $2p$ atoms (C, N, O) and the $3p$ atoms (Si, P, S).

The correlation-induced reduction in the energy difference may be interpreted as follows: The number of electron pairs with parallel spin in high-S is larger than that in low-S, or equivalently the number of electron pairs with antiparallel spin in low-S is larger than that in high-S. Correlation produces the Coulomb hole between two electrons with antiparallel spins and makes the Fermi hole deeper between two electrons with parallel spins. Note that both of the two effects play a significant role in reducing the HF expectation value of $V_{\rm ee}$. The former is more effective than the latter by about three times. Hence we may conclude that the correlation-induced reduction in $V_{\rm ee}$ in low-S is larger than that in high-S.

Using the virial relation $\Delta E = -\Delta T = \Delta V/2$, we may obtain the following relation between HF theory and experiment:

$$|\Delta E^{\rm HF}| > |\Delta E^{\rm exact}| \;\Leftrightarrow\; |\Delta V^{\rm HF}| > |\Delta V^{\rm exact}|. \tag{15}$$

Therefore, we get a relation,

$$(\Delta V_{\rm ne} + \Delta V_{\rm ee})^{\rm HF} < (\Delta V_{\rm ne} + \Delta V_{\rm ee})^{\rm exact} < 0. \tag{16}$$

From the discussion in the preceding paragraph we have found that

$$\Delta V_{\rm ee}^{\rm exact} > \Delta V_{\rm ee}^{\rm HF} > 0 \;\Leftrightarrow\; (\Delta V_{\rm ee})^{\rm corr} > 0. \tag{17}$$

This means that correlation increases the energy difference in $V_{\rm ee}$ between high-S and low-S since in HF theory the magnitude of $V_{\rm ee}$ in low-S is smaller than that in high-S. Such behavior of $(\Delta V_{\rm ee})^{\rm corr}$ is favorable for explaining the experimental fact. In order to be consistent with experiment, it is then required that

$$\Delta V_{\rm ne}^{\rm HF} < \Delta V_{\rm ne}^{\rm exact} < 0 \;\Leftrightarrow\; (\Delta V_{\rm ne})^{\rm corr} > 0, \tag{18}$$

or

$$(\Delta V_{\rm ee} + \Delta V_{\rm ne})^{\rm corr} > 0 \quad \text{if} \quad (\Delta V_{\rm ne})^{\rm corr} < 0. \tag{18'}$$

Regrettably, the present study fails to reduce the energy difference between high-S and low-S, $|\Delta E|$, i.e., it succeeds to describe that $(\Delta V_{\rm ee})^{\rm corr} > 0$, but $(\Delta V_{\rm ee} + \Delta V_{\rm ne})^{\rm corr} < 0$. The present study gives the wrong sign of $(\Delta V_{\rm ne})^{\rm corr}$. This failure may be ascribed to that the initial HF wavefunction adopted in the present study is not appropriate for low-S since it fails to discriminate between different angular momentum states specified with

L. The initial HF energy adopted is too high for QMC to arrive at a reasonably lowered level of low-S. In other words, the initial electron density distribution is too diffuse for lack of the discrimination between different angular momentum states. The correlation-induced lowering in $V_{\rm ne}$ in low-S should be more effective than that in high-S in parallel with the correlation-induced lowering in $V_{\rm ee}$.

It is concluded that the correct description of $(\Delta V_{\rm ne})^{\rm corr}$ requires a more accurate description of initial HF wavefunction depending both on S and L, so far as we rely on DMC and VMC. A more accurate HF wavefunction could lead to a correlation-induced reduction in the energy difference between high-S and low-S.

Very recently, Gálvez *et al.* have performed a VMC calculation for the ^3P ground-state, ^1D and ^1S low-lying excited states of the carbon isoelectronic series.[32] The total energy difference between the three terms in their calculation gives quite a good agreement with experiment. On the other hand, accuracy of the present calculation seems somewhat better than theirs in the fulfillment of the virial theorem, since the ratio $-V^{\rm corr}/T^{\rm corr}$ in their calculation stays around $1.62(9) \sim 1.80(11)$ for the carbon atom.

IV. CONCLUDING REMARKS

The stability of the highest spin-multiplicity state in atoms that has long been known as Hund's first rule is ascribed to the predominance of the nucleus-electron attractive Coulomb interaction $V_{\rm ne}$. It is very likely that Hund's second rule is also ascribed to the predominance of $V_{\rm ne}$. In order to demonstrate the above statement for $3d$ transition metal atoms by DMC, we have to start with the Russell-Saunders representation of HF wavefunction specified with S and L. Both of the first and second rules may be interpreted in a unified way in terms of the predominance of $V_{\rm ne}$.

ACKNOWLEDGMENTS

The computation in this work has been performed using the facilities of the Center for Computational Materials Science (IMR; Institute for Materials Research, Tohoku University) and the Supercomputer Center (ISSP; Institute for Solid State Physics, University of Tokyo). The authors would like to thank Dr. Ryo Maezono for his generous help and support, and Prof. Michael Philpott for his fruitful comments.

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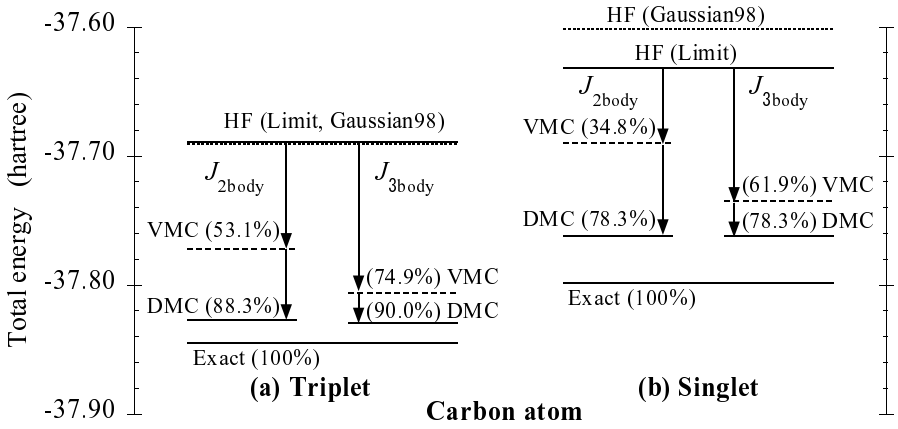

FIG. 1: Comparison of the two-body and three-body Jastrow factor calculations for the triplet and singlet states of the carbon atom. J_{2body} and J_{3body} refer to two-body and three-body Jastrow factor calculations, respectively. HF(Gaussian98) is a HF energy calculated by GAUSSIAN98 code,[21] and HF(Limit) is the HF limit energy.[28] "Exact" non-relativistic energy are taken from Ref.29 and 30. The recovering percentage (%) of the exact correlation energy is also given in each parenthesis. All energies are in hartree units.

TABLE I: The ground-state energy and the correlation energy for the $2p$ atoms (C,N,O) and the $3p$ atoms (Si,P,S). Statistical errors in the QMC results are indicated in the parentheses. The recovering percentage (%) of the exact correlation energy is also given in each parenthesis. All energies are in hartree units.

$2p$ atom	Carbon atom ($Z=6$)		Nitrogen atom ($Z=7$)		Oxygen atom ($Z=8$)	
Energy	Total	Correlation	Total	Correlation	Total	Correlation
E^{HF}	-37.68862		-54.40093		-74.80940	
E^{SDCI}	-37.79553	-0.1069 (68.4%)	-54.52985	-0.1289 (68.5%)	-74.98738	-0.1780 (69.0%)
E^{VMC}	-37.80576(2)	-0.1171 (74.9%)	-54.55003(5)	-0.1491 (79.2%)	-75.01847(4)	-0.2091 (81.1%)
E^{DMC}	-37.82937(15)	-0.1408 (90.0%)	-54.57545(20)	-0.1745 (92.7%)	-75.05032(22)	-0.2409 (93.4%)
E^{exact}	-37.8450	-0.1564 (100%)	-54.5892	-0.1883 (100%)	-75.0673	-0.2579 (100%)

$3p$ atom	Silicon atom ($Z=14$)		Phosphorus atom ($Z=15$)		Sulfur atom ($Z=16$)	
Energy	Total	Correlation	Total	Correlation	Total	Correlation
E^{HF}	-288.85436		-340.71878		-397.50490	
E^{SDCI}	-289.07858	-0.2242 (44.4%)	-340.96336	-0.2446 (45.3%)	-397.78927	-0.2844 (47.0%)
E^{VMC}	-289.23042(6)	-0.3761 (74.5%)	-341.13186(6)	-0.4131 (76.5%)	-397.92552(6)	-0.4206 (69.5%)
E^{DMC}	-289.32852(36)	-0.4741 (94.0%)	-341.22005(88)	-0.5013 (92.8%)	-398.06186(23)	-0.5570 (92.0%)
E^{exact}	-289.359	-0.5046 (100%)	-341.259	-0.5402 (100%)	-398.110	-0.6051 (100%)

TABLE II: Energies for the *high-spin* and *low-spin* states of the $2p$ (Carbon, Nitrogen, and Oxygen) atoms. Statistical errors in the QMC results are indicated in the parentheses. All energies are in hartree units.

Atom	Method	State	E	V_{ee}	V_{ne}	T	Virial ratio
C ($Z=6$)	HF	Triplet	-37.68862	12.7596	-88.1369	37.6886	2.0000
		Singlet	-37.63133	12.7283	-87.9910	37.6313	2.0000
[He]$2s^2 2p^2$	VMC	Triplet	-37.80576(2)	12.5300(2)	-88.141(6)	37.806(6)	2.0000(4)
		Singlet	-37.73481(2)	12.4758(2)	-87.953(5)	37.742(5)	1.9998(3)
	mixed DMC	Triplet	-37.82937(15)	12.5269(19)	-88.177(8)	37.821(7)	2.0002(4)
		Singlet	-37.76219(20)	12.4611(28)	-87.978(10)	37.754(8)	2.0002(5)
	extrapolated DMC	Triplet		12.5238(38)	-88.213(17)	37.836(15)	2.0005(9)
		Singlet		12.4464(56)	-88.002(21)	37.766(17)	2.0006(11)
N ($Z=7$)	HF	Quartet	-54.40093	19.5494	-128.3513	54.4009	2.0000
		Doublet	-54.29617	19.5101	-128.1024	54.2962	2.0000
[He]$2s^2 2p^3$	VMC	Quartet	-54.55003(5)	19.2587(4)	-128.384(12)	54.575(12)	1.9995(5)
		Doublet	-54.42984(7)	19.1576(6)	-128.020(16)	54.433(16)	1.9999(7)
	mixed DMC	Quartet	-54.57545(20)	19.2556(27)	-128.419(10)	54.588(9)	1.9998(4)
		Doublet	-54.45990(17)	19.1488(22)	-128.074(8)	54.465(7)	1.9999(3)
	extrapolated DMC	Quartet		19.2525(54)	-128.455(24)	54.601(21)	2.0000(9)
		Doublet		19.1401(44)	-128.128(23)	54.498(21)	1.9998(9)
O ($Z=8$)	HF	Triplet	-74.80940	28.4558	-178.0746	74.8094	2.0000
		Singlet	-74.72926	28.4272	-177.8858	74.7293	2.0000
[He]$2s^2 2p^4$	VMC	Triplet	-75.01847(4)	27.9725(4)	-178.029(10)	75.038(10)	1.9997(3)
		Singlet	-74.91112(5)	27.9283(4)	-177.775(13)	74.935(13)	1.9997(4)
	mixed DMC	Triplet	-75.05032(22)	27.9854(36)	-178.085(13)	75.049(11)	2.0000(3)
		Singlet	-74.94507(28)	27.9345(44)	-177.833(19)	74.954(16)	1.9999(5)
	extrapolated DMC	Triplet		27.9984(72)	-178.141(28)	75.060(24)	2.0003(7)
		Singlet		27.9406(89)	-177.892(39)	74.972(34)	2.0001(11)

TABLE III: Energies for the *high-spin* and *low-spin* states of the $3p$ (Silicon, Phosphorus, and Sulfur) atoms. Statistical errors in the QMC results are indicated in the parentheses. All energies are in hartree units.

Atom	Method	State	E	V_{ee}	V_{ne}	T	Virial ratio
Si ($Z=14$)	HF	Triplet	-288.85436	111.7061	-689.4149	288.8544	2.0000
		Singlet	-288.81521	111.5926	-689.2230	288.8152	2.0000
[Ne]$3s^2 3p^2$	VMC	Triplet	-289.23042(6)	110.6168(3)	-689.064(13)	289.216(13)	2.0000(1)
		Singlet	-289.16679(6)	110.4191(3)	-688.738(14)	289.152(13)	2.0000(1)
	mixed DMC	Triplet	-289.32852(36)	110.812(6)	-689.435(10)	289.294(9)	2.0001(1)
		Singlet	-289.28689(29)	110.626(5)	-689.136(13)	289.224(10)	2.0002(1)
	extrapolated DMC	Triplet		111.007(11)	-689.806(23)	289.372(22)	2.0002(2)
		Singlet		110.833(11)	-689.535(30)	289.295(24)	2.0004(2)
P ($Z=15$)	HF	Quartet	-340.71878	130.7835	-812.2210	340.7188	2.0000
		Doublet	-340.64887	130.6381	-811.9358	340.6489	2.0000
[Ne]$3s^2 3p^3$	VMC	Quartet	-341.13186(6)	129.4905(4)	-811.758(19)	341.136(18)	2.0000(1)
		Doublet	-341.05377(7)	129.4283(5)	-811.526(21)	341.044(21)	2.0000(1)
	mixed DMC	Quartet	-341.22005(88)	129.770(14)	-812.236(31)	341.247(19)	1.9999(2)
		Doublet	-341.15358(64)	129.638(17)	-811.935(25)	341.144(15)	2.0001(1)
	extrapolated DMC	Quartet		130.049(28)	-812.714(64)	341.357(43)	1.9999(3)
		Doublet		129.848(35)	-812.345(54)	341.244(37)	2.0000(3)
S ($Z=16$)	HF	Triplet	-397.50490	151.8838	-946.8936	397.5049	2.0000
		Singlet	-397.45235	151.7920	-946.6967	397.4524	2.0000
[Ne]$3s^2 3p^4$	VMC	Triplet	-397.92552(6)	150.8549(4)	-946.710(19)	397.930(19)	2.0000(1)
		Singlet	-397.84234(6)	150.7458(4)	-946.455(18)	397.867(18)	1.9999(1)
	mixed DMC	Triplet	-398.06186(23)	150.963(5)	-947.037(15)	398.012(12)	2.0001(1)
		Singlet	-397.99838(30)	150.838(6)	-946.775(23)	397.939(20)	2.0001(1)
	extrapolated DMC	Triplet		151.072(10)	-947.364(36)	398.094(31)	2.0003(2)
		Singlet		150.930(11)	-947.095(50)	398.011(43)	2.0004(3)

TABLE IV: Extrapolated DMC correlation energies for the $2p$ atoms (C,N,O) and the $3p$ atoms (Si,P,S). Statistical errors in the QMC results are indicated in the parentheses. All energies are in hartree units.

Atom	State	$E^{\rm corr}$	$V_{\rm ee}^{\rm corr}$	$V_{\rm ne}^{\rm corr}$	$T^{\rm corr}$	$-V^{\rm corr}/T^{\rm corr}$
C ($Z=6$)	Triplet	−0.1408(2)	−0.236(4)	−0.076(17)	+0.147(15)	2.12(24)
	Singlet	−0.1309(2)	−0.282(6)	−0.011(21)	+0.135(17)	2.17(32)
N ($Z=7$)	Quartet	−0.1745(2)	−0.297(5)	−0.103(24)	+0.200(21)	2.00(24)
	Doublet	−0.1637(2)	−0.370(4)	−0.026(23)	+0.202(21)	1.96(24)
O ($Z=8$)	Triplet	−0.2409(2)	−0.457(7)	−0.066(28)	+0.251(24)	2.09(23)
	Singlet	−0.2158(3)	−0.487(9)	−0.006(39)	+0.243(34)	2.03(33)
Si ($Z=14$)	Triplet	−0.4742(4)	−0.699(11)	−0.391(23)	+0.518(22)	2.10(10)
	Singlet	−0.4717(3)	−0.760(11)	−0.312(30)	+0.480(24)	2.23(13)
P ($Z=15$)	Quartet	−0.5013(9)	−0.735(28)	−0.493(64)	+0.639(43)	1.92(17)
	Doublet	−0.5047(6)	−0.790(35)	−0.409(54)	+0.595(37)	2.02(17)
S ($Z=16$)	Triplet	−0.5570(2)	−0.812(10)	−0.470(36)	+0.589(31)	2.18(13)
	Singlet	−0.5460(3)	−0.862(11)	−0.398(50)	+0.559(43)	2.26(20)

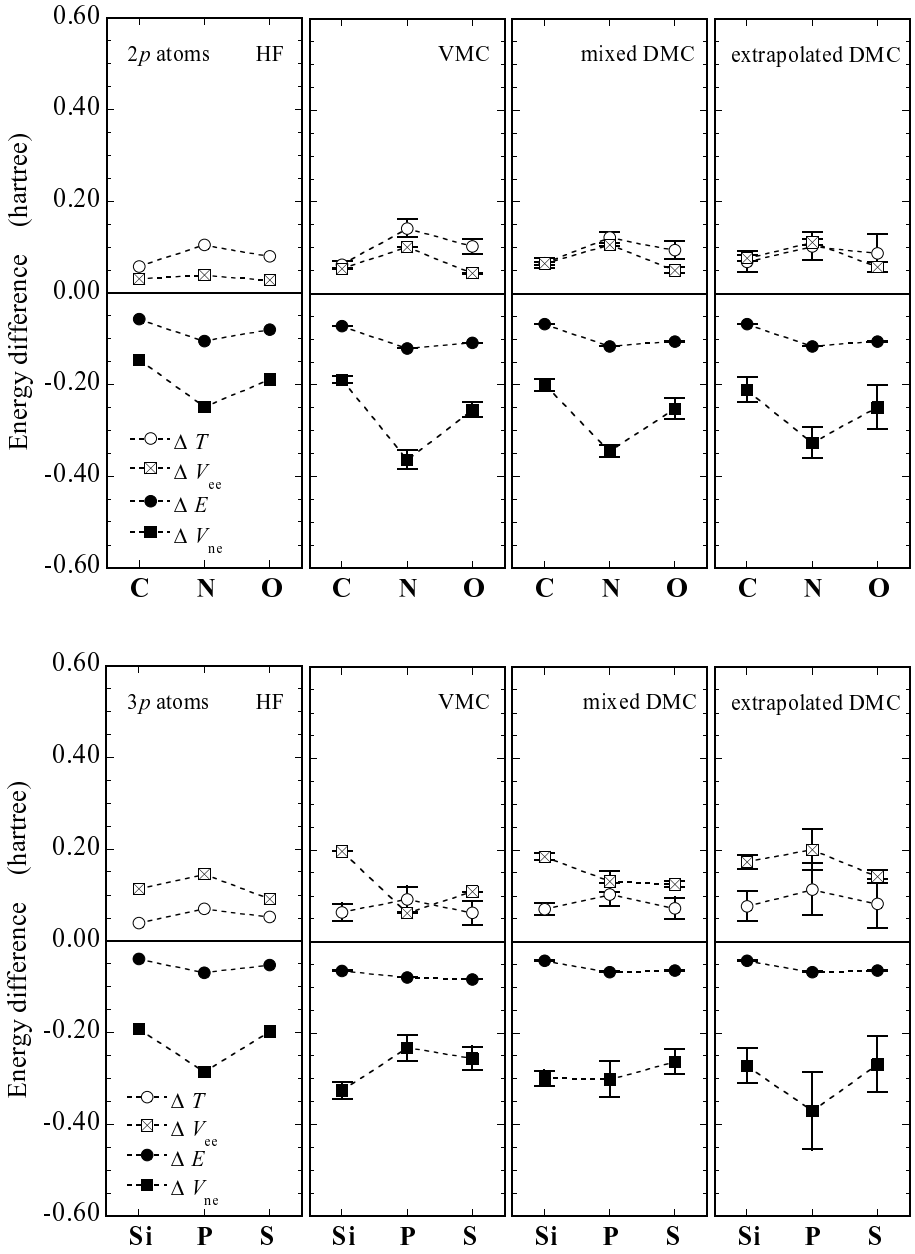

FIG. 2: Energy difference between *high-spin* and *low-spin* states. Each symbol indicates each energy difference; black-circle : the total energy $\Delta E \equiv E^{\text{high-}S} - E^{\text{low-}S}$, black-square : the nucleus-electron energy $\Delta V_{\text{ne}} \equiv V_{\text{ne}}^{\text{high-}S} - V_{\text{ne}}^{\text{low-}S}$, white-circle : the kinetic energy $\Delta T \equiv T^{\text{high-}S} - T^{\text{low-}S}$, and crossed-square : the electron-electron repulsion energy $\Delta V_{\text{ee}} \equiv V_{\text{ee}}^{\text{high-}S} - V_{\text{ee}}^{\text{low-}S}$. All energies are in hartree units.