電子の波動方程式に基づくものであるが、数値解析を用いての解の近似を検討している。検討結果から、電子の波動方程式に基づくものであるが、数値解析を用いての解の近似を検討している。検討結果から、
Correct Interpretation of Hund’s Rule and Chemical Bonding
Based on the Virial Theorem

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We have investigated Hund’s spin-multiplicity rule for the second and third row atoms (C, N, O, Si, P, and S) and the methylene molecule (CH2) by means of diffusion Monte Carlo method and complete active space self-consistent field method, respectively. It is found that Hund’s rule is interpreted to be ascribed to a lowering in the electron-nucleus attractive Coulomb interaction energy as well as the kinetic energy. We have also studied correlation in the hydrogen molecule H2. Correlation in H2 gives an increase of the electron density distribution n(r) in the left and right anti-binding regions, a reduction of n(r) in the binding region, and an increase in the equilibrium internuclear separation. The importance of the virial theorem is stressed in the evaluation of correlation effects on both Hund’s rule and chemical bonding in H2.

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1. Introduction

The virial theorem 2T + V = 0 holds for any stationary state of many-electron systems,1–3) where T is the kinetic energy and V (= V_en + V_ee + V_in) the total Coulomb potential energy; V_en, V_ee, and V_in are the electron-nucleus, the electron-electron, and the nucleus-nucleus Coulomb potential energies, respectively. Hence the theorem is a necessary condition for an accurate evaluation of the stationary state energies of atoms, molecules and solids as well as their various electronic properties. In accordance with the virial theorem we have given for the first time the correct interpretation of Hund’s spin-multiplicity rule for six atoms and a molecule by diffusion Monte Carlo (DMC) method and complete active space self-consistent field (CASSCF) method, respectively. We have also studied how correlation changes the electron density distribution n(r) in the hydrogen molecule H2.

Hund’s rule states that the highest spin-multiplicity state is the most stable among all the possible states arising from a single electronic configuration.4,5) This empirical rule is applied to the ground state of atoms, ions, and molecules and even their low-lying excited states in most cases. In almost all textbooks excluding Levine’s,3) Hund’s rule has long been interpreted to be ascribed to a reduction in V_en in the ground state with the highest spin-multiplicity, i.e., the largest possible amount of exchange energy.6,7) This traditional interpretation assumes that the ground and the lowest excited states could have the same set of orbitals. It gives the same T and V_en for the two states and ascribes the energy difference to V_ee. In spite of giving the correct ordering of the two states, the traditional interpretation is invalid since it violates the virial theorem. Correctly, the two states independently fulfill the virial theorem and hence ∆T + ∆V = 0, i.e., the stabilization of the ground state is realized by lowering V by an amount of 2∆T at the cost of increasing T by ∆T (∆T > 0).

A number of authors have studied Hund’s rule for atoms8–19) and light molecules20–28) by Hartree-Fock (HF) and other variational calculations. They have found that the stabilization of the highest multiplicity state relative to the lower multiplicity states is ascribed to a lowering in V_en that is gained at the cost of increasing V_ee as well as T. Davidson8,9) has first pointed out that V_ee is larger for the triplet than for the singlet by HF calculations for low-lying excited states of the helium atom. Boyd17) has first introduced the concept of less screening to explain how V_en is lowered. In the higher multiplicity state there are more parallel spin pairs and hence a larger Fermi hole around each electron. Owing to the presence of a larger Fermi hole the Hartree screening of the nuclear charge is reduced more effectively at short interelectronic distances in the higher multiplicity state. Thus, each electron experiences the nuclear charge more effectively in the higher multiplicity state and hence the electron density distribution contracts around the nucleus to give a lowering in V_en and an increase in both T and V_ee.

The Heitler-London (HL) model29,30) has long been appreciated as the pioneering study of chemical bonding in H2, but in fact fails to describe the essence of chemical bonding since it violates the virial theorem.31–33) The linear combination of 1s atomic orbitals (LCAO) also violates the theorem. The minimal basis full configuration interaction (CI), i.e., an interpolation of HL and LCAO is the best approach to H2 so far as one uses 1s atomic orbitals alone. A number of solid-state physicists still believe that the truth of chemical bonding in H2 lies in between HL and LCAO34–37) since such an interpolation compensates for individual shortcomings. However, the minimal basis full CI is far from describing the essence of chemical bonding since it violates the virial theorem. The truth does not lie in between.

The virial theorem holds for both a molecule and its constituent atoms. Hence the binding energy of a molecule ∆E(∆E < 0) is given as ∆E = −∆T = ∆V/2, where ∆T is an increase in T and ∆V a lowering in V involved in chemical bonding. The essence of chemical bonding is an inevitable increase in T, ∆T and a concomitant lowering in V, ∆V whose magnitude equals 2∆T.
2. Hund’s Rule for the Second and Third Row Atoms

Figure 1 shows the energy differences $\Delta E$, $\Delta T$, $\Delta V_{en}$, and $\Delta V_{ee}$ between the highest (high-$S$) and the next highest (low-$S$) multiplicity states for the $2p$ and $3p$ atoms, evaluated from HF$^{28}$ and DMC.$^{39}$ We have ascertained that the following relations hold for any atom calculated: $\Delta E = E^{\text{high-$S$}} - E^{\text{low-$S$}} < 0$, $\Delta V_{en} = V_{en}^{\text{high-$S$}} - V_{en}^{\text{low-$S$}} < 0$, $\Delta T = T^{\text{high-$S$}} - T^{\text{low-$S$}} > 0$, and $\Delta V_{ee} = V_{ee}^{\text{high-$S$}} - V_{ee}^{\text{low-$S$}} > 0$. The stabilization of high-$S$ state relative to low-$S$ state, or equivalently the negative value of $\Delta E$ is ascribed to that $\Delta V_{en} < 0$. The energy difference $\Delta V_{en}$ is largest in magnitude among all the energy differences. The lower value of $E$ in the ground state is a direct consequence of the lower value of $V_{en}$ therein. This property may be termed the predominance of $V_{en}$ in the ground state.

Correlation gives a rather small change in the energy difference $\Delta E$ between the two states for all the atoms, though it lowers the energy level for both high-$S$ and low-$S$ states by about 1 eV per electron. On the other hand, correlation increases both $\Delta V_{ee}$ and $\Delta V_{en}$ in magnitude by a factor of $1.3 \sim 2.9$, i.e., it produces a greater amount of cancellation between $\Delta V_{ee}$ and $\Delta V_{en}$. The inclusion of correlation does not change the HF interpretation of Hund’s rule.

It is summarized as follows: The stabilization of the highest multiplicity state of all the atoms calculated is ascribed to the greatest $|V_{en}|$ that is gained at the cost of increasing $V_{ee}$ to its highest possible extent. Exchange in the highest multiplicity state reduces most effectively the Hartree screening of the nuclear charge at short interelectronic distances. The resulting contraction of the electron density distribution around the nucleus gives rise to the greatest $|V_{en}|$. Hund’s rule is not ascribed to the exchange energy gain, but to exchange-induced less screening.

By means of CASSCF we have also ascertained that the same conclusion holds for CH$_2$: $^{28} \Delta E = -0.0618$, $\Delta T = 0.0618$, $\Delta V = -0.1235$, $\Delta V_{en} = -0.1230$, $\Delta V_{ee} = 0.0161$, $\Delta V_{en} = -0.0166$, and $-\Delta V/\Delta T = 2.00$; all energies are in hartree units. It is to be noted that spin-polarization in the ground state of CH$_2$ lowers $V_{en}$ through concomitant changes in the molecular geometries, i.e., the equilibrium internuclear separations and the equilibrium bond angles. Variational optimization of the molecular geometries can be allowed for through the fulfillment of the virial theorem in the present CASSCF.

3. Chemical Bonding in H$_2$

A list of the binding energy, its components, the virial ratio, and the equilibrium internuclear separation evaluated from various methods is given for H$_2$ in Table 1. Both the binding energy and the equilibrium internuclear separation in DMC$^{40}$ are in good agreement with those by Kols and Wolniewicz$^{41}$ or experimental values.$^{32,43}$ HF underestimates the binding energy by about 23% and the equilibrium internuclear separation by 1% for lack of correlation.$^{40}$ The virial ratio $-\Delta V/\Delta T$ is accurate to the significant figure 2.0 for DMC and 2.00 for HF.$^{40}$

An increase in $T$, $\Delta T (\Delta T > 0)$ comes from an increase in the curvature of the two-electron wavefunction induced by a spatial variation of the combined attractive Coulomb field of the two nuclei separated by $R_{ee}$ and by the correlated motion of two electrons. A lowering in $V$, $\Delta V (\Delta V < 0)$ is ascribed to a lowering in $V_{en} (\Delta V_{en} < 0)$ that overwhelms an increase in $V_{ee}$ and $V_{en}$ ($\Delta V_{ee} > 0$ and $\Delta V_{en} > 0$).

As can be seen from Table 1, violation of the virial theorem in HL, LCAO, and minimal basis full CI gives the wrong sign of $\Delta T$ and $\Delta V$.

The application of the so-called scaling method enables one to give each improved version of HL, LCAO, and minimal basis full CI that obeys the virial theorem. A list of various quantities for these improved versions with their optimized scaling factors is given at the bottom of Table 1. The scaling method above changes both the sign of $\Delta T$ and that of $\Delta V$ involving a reduction in $R_{eq}$.

A comparison of the electron density distribution $n(r)$ is made between HL, LCAO, minimal basis full CI, HF, and DMC along the molecular axis $z$ of H$_2$ in Fig. 2 (a), (b), (c), and (d). HF gives a good description of $n(r)$ as a whole. The difference in $n(r)$ between HF and DMC is rather small.

Each of HL, LCAO, and minimal basis full CI underestimates $n(r)$ around the two nuclei and overestimates $n(r)$ in the remote region far away from the two nuclei. This is because any approximation using 1s atomic orbitals alone is unable to give an appropriate description of such an essential reconstruction of $n(r)$ as is caused by the combined attractive Coulomb field of the two nuclei separated by $R_{eq}$. The scaling method could give a description of $n(r)$ resembling the HF value.

Correlation in H$_2$ gives a couple of significant changes in $n(r)$ involving an increase in the equilibrium internuclear separation $R_{eq}$. Firstly, correlation enhances $n(r)$ in the left and right anti-binding regions; $^{34}$ the value of $n(r)$ at the position of each nucleus is 0.466 bohr$^{-3}$ for DMC and 0.460 bohr$^{-3}$ for HF. Secondly, correlation reduces $n(r)$ in the binding region$^{43}$ intervening between the nuclei; the value of $n(r)$ at the middle point between the nuclei is
4. Concluding Remarks

The virial theorem and the Pauli exclusion principle are the most fundamental requirements for the study of many-electron systems. In accordance with the two requirements we have interpreted Hund’s empirical rule for the six atoms in the second and third rows in the periodic table and for the methylene molecule, taking full account of correlation. The traditional interpretation of Hund’s rule allows only for the Pauli exclusion principle, completely neglecting the virial theorem. Both of the two are indispensable for the correct interpretation. We have analyzed the influence of correlation on chemical bonding in the hydrogen molecule, with emphasis on the fact that the truth of chemical bonding does not lie in between the two naive models that resort to 1s atomic orbitals alone.

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