Correct Interpretation of Hund's Rule and Chemical Bonding Based on the Virial Theorem

Correct Interpretation of Hund's Rule and Chemical Bonding Based on the Virial Theorem

Kenta Hongo, Takayuki Oyamada, Youhei Maruyama,
Yoshiyuki Kawazoe and Hiroshi Yasuhara

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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 (CH_2) 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 which is realized at the cost of increasing the electron-electron repulsive Coulomb interaction energy as well as the kinetic energy. We have also studied correlation in the hydrogen molecule H_2. Correlation in H_2 gives an increase of the electron density distribution $n(\mathbf{r})$ in the left and right anti-binding regions, a reduction of $n(\mathbf{r})$ 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 H_2.　[doi:10.2320/matertrans.48.662]

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 $V(= V_{en} + V_{ee} + V_{nn})$ the total Coulomb potential energy; V_{en}, V_{ee}, and V_{nn} 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 $n(\mathbf{r})$ in the hydrogen molecule H_2.

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_{ee} 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 $2\Delta T + \Delta V = 0$, *i.e.*, the stabilization of the ground state is realized by lowering V by an amount of $2\Delta T$ at the cost of increasing T by $\Delta T (\Delta T > 0)$.

A number of authors have studied Hund's rule for atoms[8–19] and light molecules[20–28] 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. Davidson[8,9] 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. Boyd[17] 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) model[29,30] has long been appreciated as the pioneering study of chemical bonding in H_2, 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 H_2 so far as one uses $1s$ atomic orbitals alone. A number of solid-state physicists still believe that the truth of chemical bonding in H_2 lies in between HL and LCAO[34–37] 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 $\Delta E (\Delta E < 0)$ is given as $\Delta E = -\Delta T = \Delta V/2$, where ΔT is an increase in T and ΔV a lowering in V involved in chemical bonding. The essence of chemical bonding is an inevitable increase in T, ΔT and a concomitant lowering in V, ΔV whose magnitude equals $2\Delta T$.
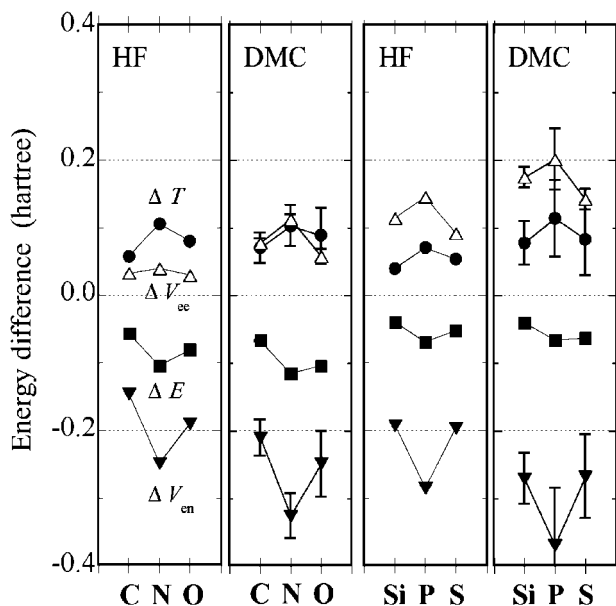
Fig. 1 Energy differences between high-S and low-S states for the $2p$ and $3p$ atoms evaluated from HF and DMC.

2. Hund's Rule for the Second and Third Row Atoms

Figure 1 shows the energy differences ΔE, ΔT, ΔV_{en}, and ΔV_{ee} between the highest (high-S) and the next highest (low-S) multiplicity states for the $2p$ and $3p$ atoms, evaluated from HF[38] and DMC.[39] We have ascertained that the following relations hold for any atom calculated: $\Delta E \equiv E^{high\text{-}S} - E^{low\text{-}S} < 0$, $\quad \Delta V_{en} \equiv V_{en}^{high\text{-}S} - V_{en}^{low\text{-}S} < 0$, $\quad \Delta T \equiv T^{high\text{-}S} - T^{low\text{-}S} > 0$, and $\Delta V_{ee} \equiv V_{ee}^{high\text{-}S} - V_{ee}^{low\text{-}S} > 0$. The stabilization of high-S state relative to low-S state, or equivalently the negative value of ΔE is ascribed to that $\Delta V_{en} < 0$. The energy difference ΔV_{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 ΔE 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 ΔV_{ee} and ΔV_{en} in magnitude by a factor of $1.3 \sim 2.9$, *i.e.*, it produces a greater amount of cancellation between ΔV_{ee} and ΔV_{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 has also ascertained that the same conclusion holds for CH$_2$;[28] $\Delta E = -0.0618$, $\Delta T = 0.0618$, $\Delta V = -0.1235$, $\Delta V_{en} = -0.1230$, $\Delta V_{ee} = 0.0161$,

$\Delta V_{nn} = -0.0166$, and $-\Delta V/\Delta T = 2.000$; all energies are in hartree units. It is to be noted that spin-polarization in the ground state of CH$_2$ lowers V_{nn} 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 Kolos and Wolniewicz[41] or experimental values.[42,43] 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, ΔT ($\Delta T > 0$) 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_{eq} and by the correlated motion of two electrons. A lowering in V, ΔV ($\Delta V < 0$) is ascribed to a lowering in V_{en} ($\Delta V_{en} < 0$) that overwhelms an increase in V_{ee} and V_{nn} ($\Delta V_{ee} > 0$ and $\Delta V_{nn} > 0$).

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 ΔT and ΔV.

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 ΔT and that of ΔV involving a reduction in R_{eq}.

A comparison of the electron density distribution $n(\mathbf{r})$ 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 $n(\mathbf{r})$ as a whole. The difference in $n(\mathbf{r})$ between HF and DMC is rather small.

Each of HL, LCAO, and minimal basis full CI underestimates $n(\mathbf{r})$ around the two nuclei and overestimates $n(\mathbf{r})$ 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 $n(\mathbf{r})$ 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 $n(\mathbf{r})$ resembling the HF value.

Correlation in H$_2$ gives a couple of significant changes in $n(\mathbf{r})$ involving an increase in the equilibrium internuclear separation R_{eq}.[40] Firstly, correlation enhances $n(\mathbf{r})$ in the left and right anti-binding regions;[44] the value of $n(\mathbf{r})$ at the position of each nucleus is 0.466 bohr^{-3} for DMC and 0.460 bohr^{-3} for HF. Secondly, correlation reduces $n(\mathbf{r})$ in the binding region[44] intervening between the nuclei; the value of $n(\mathbf{r})$ at the middle point between the nuclei is

Table 1 The binding energy, its components, the virial ratio, and the equilibrium internuclear separation evaluated from various methods. The exact values by Kolos and Wolniewicz[41] and experimental values[42,43] are also given. Energies are measured in units of hartree. The equilibrium internuclear separation is measured in units of bohr. The figure in each parenthesis indicates the statistical error in the last digit.

	ΔE	ΔT	ΔV	ΔV_{en}	ΔV_{ee}	ΔV_{nn}	$-\Delta V/\Delta T$	R_{eq}
HL	−0.11597	−0.1623	0.0463	−1.0611	0.4986	0.6088	0.285	1.643
LCAO	−0.09908	−0.2033	0.1042	−1.0723	0.5527	0.6238	0.513	1.603
minimal basis full CI	−0.11865	−0.1838	0.0652	−1.0435	0.5092	0.5995	0.355	1.668
HF[a]	−0.13365(2)	0.1333(1)	−0.2669(1)	−1.6494(1)	0.66113(2)	0.7214	2.003(1)	1.386
DMC[b]	−0.17447(4)	0.1749(14)	−0.3518(19)	−1.6535(17)	0.5880(4)	0.7137	2.011(19)	1.401
Exact[c]	−0.17447	0.1745	−0.3489				2.000	1.401
Experiment[d]	−0.17447							1.401
HL($\alpha = 1.193$)	−0.13908	0.1391	−0.2782	−1.5659	0.5805	0.7072	2.000	1.414
LCAO($\alpha = 1.166$)	−0.12823	0.1282	−0.2565	−1.6338	0.6555	0.7218	2.000	1.385
minimal basis full CI($\alpha = 1.194$)	−0.14794	0.1479	−0.2959	−1.6070	0.6120	0.6991	2.000	1.430

a) Ref. 40)
b) Ref. 40)
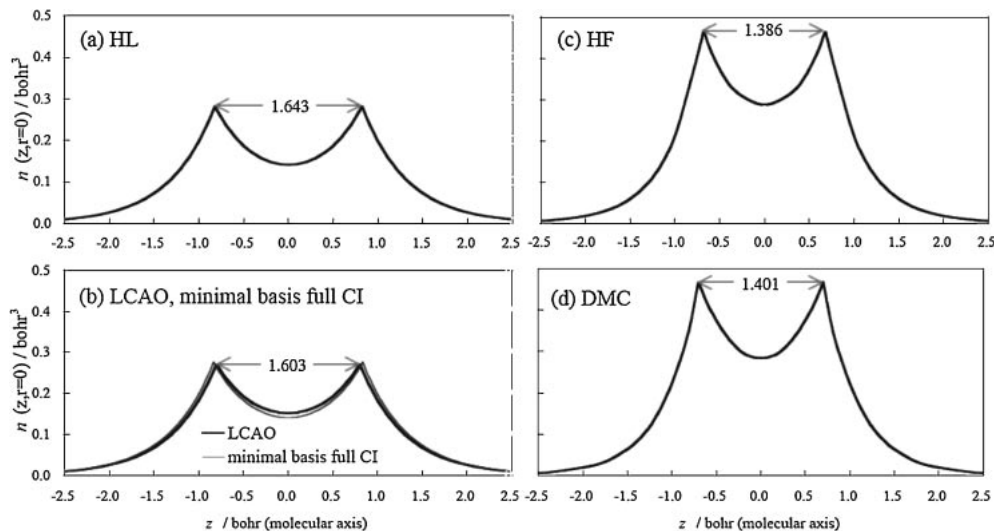c) Ref. 41)
d) Ref. 42, 43)

Fig. 2 The electron density distribution $n(\mathbf{r})$ evaluated from (a) HL, (b) LCAO, minimal basis full CI, (c) HF, and (d) DMC along the molecular axis z of H_2.

0.284 bohr^{-3} for DMC and 0.288 bohr^{-3} for HF. Corresponding to these changes in $n(\mathbf{r})$, the equilibrium internuclear separation is increased by an amount of about 1%, *i.e.*, $R_{eq}^{DMC} = 1.401$ bohr and $R_{eq}^{HF} = 1.386$ bohr.

These correlation-induced features can be interpreted as follows: The presence of the Coulomb hole around each electron reduces the Hartree screening of the nuclear charge at short interelectronic distances. This may be termed correlation-induced less screening. Owing to less screening, $n(\mathbf{r})$ is enhanced in the left and right anti-binding regions. On the other hand, the same less screening in the binding region is overwhelmed by an increase in R_{eq} to give a reduction of $n(\mathbf{r})$ therein. A set of interconnected correlation effects above are reasonable in the light of the electrostatic theorem[45] which is closely related to the virial theorem.

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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