Theor Chem Acc (2003) 110: 338–344
DOI 10.1007/s00214-003-0487-6

Theoretical
Chemistry Accounts

Regular article

Hund's multiplicity rule: a unified interpretation

Shubin Liu[1,2], **Wilfried Langenaeker**[3]

[1] Department of Academic Technology & Networks, University of North Carolina, Chapel Hill, NC 27599-3455, USA
[2] College of Chemistry and Chemical Engineering, Hunan Normal University, Hunan China 410081
[3] Eenheid Algemene Chemie, Faculteit Wetenschappen, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

Received: 25 April 2003 / Accepted: 9 June 2003 / Published online: 7 October 2003

Abstract. Hund's multiplicity rule, stating that a higher spin state has a lower energy within the same electron configuration, is empirical but has shown to be valid for both atoms and molecules. Several theoretical interpretations for its validity, including explanations in terms of the lower interelectron repulsion and the greater electron–nuclear attraction in the higher spin state, are available. None of them, however, are satisfactory. Here we show that Hund's rule can be explained by the Janak theorem in density functional theory, extended to excited states and multiplets. In the exact density functional theory theory, it leads to $\Delta E_{\mathrm{ST}} = E_{\mathrm{S}} - E_{\mathrm{T}} = \Delta\varepsilon_{\mathrm{HOMO}}$, with E_{S} and E_{T} the singlet and triplet state energies and $\varepsilon_{\mathrm{HOMO}}$ the highest occupied molecular orbital energies of the spin states. This relationship was previously obtained by M. Levy [(1995) *Physical Review A* 52:R4313]. In this paper, numerical results within the Hartree–Fock framework for both atoms and molecules confirm the previously mentioned justification. Good results of the Hartree–Fock method come from the accurate description of the exchange effect from where Hund's multiplicity rule originated.

Keywords: Hund's rule – Density functional theory – Highest occupied molecular orbital – Janak theorem

Introduction

Hund's multiplicity rule, stating that if two states arise from the same electronic configuration, the state having the higher spin multiplicity possesses the lower energy, although proven to be generally valid, came into quantum structure theory of atoms and molecules merely as an empirical regulation. A general theoretical rationalization of its origin is still lacking. For atoms, a pretty strong case has been established in providing a general description for the interpretation [1, 2, 3, 4, 5, 6, 7], but for molecules, the situation is quite complicated because many factors, such as the vertical-adiabatic separation, the molecular virial relation, the electron correlation, and molecular geometry, have to be taken into account [8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. No unified explanation for both atoms and molecules is available yet.

Consider an electronic configuration of two electrons with antiparallel spins in two different orbitals and change the spin state of one electron from the antiparallel state to the parallel state, i.e., transit from the singlet state to the triplet state. Intuition suggests that this change leads to the lower exchange energy (negative sign), and higher correlation energy (negative sign), because the number of pairs of electrons with parallel spins increases and that of pairs with antiparallel spins decreases. Since Fermi correlation is stronger than Coulomb correlation, one expects a net decrease in the total energy. This is the original interpretation by Slater [1] based on the interelectronic repulsion energy. He claimed that the higher spin state has the lower electron–electron repulsion energy. This interpretation proved to be incorrect as numerical results were accumulated at various levels showing that the higher spin state, on the contrary, often has the higher electron–electron repulsion [2, 3, 4, 5, 6, 7]. Furthermore, ab initio calculations for atomic systems indicated that the increase of the electron–nuclear attraction energy in the higher spin state is responsible for the lower total energy (vide infra). Although Slater's explanation is partly true, it does not take other effects, of the transition from one state to another, taking place simultaneously into account. These effects, including molecular orbital contraction and expansion [8, 9], anisotropic screening [7], nuclear relaxation through the virial theorem [10, 11, 12, 13, 14], etc., can be seen as the result of electron redistribution, i.e., the change in electron distribution, affecting all

---

Correspondence to: S. Liu
e-mail: shubin@email.unc.edu

energy components of the system considered. They provide explanation frameworks for the validity of Hund's rule, but none of them are generally applicable to molecular systems, as shown by Darvesh and coworkers [10, 11, 12] and Liu and coworkers [13, 14]. In some ranges of nuclear separation, the kinetic energy component becomes a dominant contributor to the rule [10, 11, 12, 13]. In an extreme case, an example has been disclosed where the kinetic energy is the single dominant component contributing to the rule in the whole range of nuclear separation [14].

Inspired by the new theoretical development in the density functional theory (DFT) [18, 19, 20] on excited states [21, 22, 23] and multiplets [24, 25, 26], the present work proposes a new theoretical interpretation for Hund's rule. Our theory is based on the extension of the Janak theorem [27] in excited-state DFT for multiplets, which shows that the singlet–triplet energy difference is equal to the highest occupied molecular orbital (HOMO) energy difference [24]. Numerical data for both atoms and molecules confirm, as shown later, the previously mentioned theoretical justification.

Theory

The energy difference between the singlet and triplet states of an atomic or molecular system with the same electron configuration, which was first thoroughly investigated by the pioneering theoretical work of Borden and Davidson [28], can be analyzed in a few ways. The first and relatively simple way is to decompose the total energy difference, ΔE_{ST}, into various components according to their nature, i.e.,

$$\Delta E = \Delta T + \Delta V_{\mathrm{ne}} + \Delta V_{\mathrm{ee}} + \Delta V_{\mathrm{nn}}, \tag{1}$$

where E_{S} and E_{T} are total energies of the singlet and triplet spin states, and T, V_{ne}, V_{ee}, and V_{nn} stand for the kinetic energy, electron–nuclear attraction, electron–electron repulsion, and nuclear–nuclear repulsion energies, respectively. These quantities can be calculated in either Hartree–Fock (HF) or post-HF, for example, configuration interaction and multiconfigurational self-consistent-field (SCF) frameworks. The validity of Hund's rule can be rationalized by finding the dominant contributor among these energy components. For example, Slater claimed that ΔV_{ee} was the dominant contributor in Eq. (1), whereas later numerical results from ab initio calculations show that the dominant term for atoms is ΔV_{ne}.

The second option is to employ virial relations [1, 19, 20]. For each spin state of an atomic system, one has

$$E = -T = \frac{1}{2}(V_{\mathrm{ne}} + V_{\mathrm{ee}}). \tag{2}$$

Thus, the energy difference between two spin states is

$$\Delta E = -\Delta T = \frac{1}{2}(\Delta V_{\mathrm{ne}} + \Delta V_{\mathrm{ee}}). \tag{3}$$

A thorough study in which good linear relations between E and T are observed has recently been carried out by Koga and coworkers [15, 16, 17] for neutral atoms up to Fm ($Z = 100$). For molecular systems, Eq. (3) turns out to be more complicated,

$$\begin{aligned}\Delta E &= -\Delta T - \sum_{A} \sum_{B(>A)} R_{AB}\left(\frac{\partial \Delta E}{\partial R_{AB}}\right) \\ &= \frac{1}{2}\left[\Delta V_{\mathrm{ne}} + \Delta V_{\mathrm{ee}} + \sum_{A} \sum_{B(>A)} R_{AB}\left(\frac{\partial \Delta E}{\partial R_{AB}}\right)\right].\end{aligned} \tag{4}$$

and shows that the influence of the geometry of the system has to be considered. This formula was employed both by Darvesh and coworkers [10, 11, 12] and by Liu and coworkers [13, 14] to analyze their results.

The third approach to interpret the total energy difference is via the orbital picture in the HF framework [13, 14],

$$\Delta E = \sum_i \Delta \varepsilon_i - \Delta V_{\mathrm{ee}} + \Delta V_{\mathrm{nn}}, \tag{5}$$

where ε_i are the molecular orbital energies. All components in Eq. (5) are first computed, and the dominant term rationalizing the validity of the rule is then extracted. In two-electron molecular systems with a fixed geometry, Eq. (5) becomes [13]

$$\Delta E = \Delta \varepsilon_i + \Delta \varepsilon_{\mathrm{HOMO}} - \Delta V_{\mathrm{ee}}, \tag{6}$$

where $\varepsilon_{\mathrm{HOMO}}$ and ε_i stand for the frontier and inner molecular orbitals, respectively. Liu and Yu [13] showed that the following equality is valid to good accuracy,

$$\Delta E = \Delta \varepsilon_{\mathrm{HOMO}}. \tag{7}$$

Equation (7) provides an alternative interpretation for Hund's rule, as it shows that the energy decrease in the triplet state can be attributed solely to the energy change of the frontier orbital owing to the orbital contraction and does not explicitly depend on ΔV_{ee}. Equation (5), however, is valid only within HF theory, where the dynamic correlation effect among the electrons with antiparallel spins (Coulomb correlation) is excluded. This formalism fortunately has an analogue in the ground-state DFT [19], in a slightly different form,

$$\Delta E = \sum_i \Delta \varepsilon_i - \Delta J - \Delta E_{\mathrm{xc}} + \Delta\langle \rho(r)[\rho]\frac{\delta E_{\mathrm{xc}}}{\delta \rho(r)}\rangle + \Delta V_{\mathrm{nn}}, \tag{8}$$

where J stands for the classical electron–electron Coulomb repulsion energy and E_{xc} denotes the exchange–correlation energy, both of which are unique and universal functionals of the density, $\rho(\mathbf{r})$, of the system, according to the Hohenberg–Kohn theorems [18]. $\delta E_{\mathrm{xc}}/\delta \rho(r)$ in Eq. (8) is the functional derivative of the exchange–correlation energy density functional with respect to the density, called the exchange–correlation potential. One anticipates that in Eq. (8) the orbital contributing most to the energy difference is the frontier orbital. Indeed, Levy [24] has shown that the excitation energy, ΔE, between the ground-state and the first-excited-state electronic energies can be expressed as

$$\Delta E \equiv E_A - E_B = \varepsilon_{N+1}^{w} - \varepsilon_N^0 = \Delta\varepsilon_{\mathrm{HOMO}}, \tag{9}$$

where E_A is the ground-state energy of the N-electron Hamiltonian, E_B is its first-excited-state energy, and w is the scalar factor, with $0 \le w \le 1/2$. Supporting evidence to justify this formalism is the following formula in the DFT framework [19]:

$$\Delta E \equiv E_N - E_{N-1} \equiv -I = \varepsilon_{\mathrm{HOMO}}, \tag{10}$$

where E_N and E_{N-1} denote total energies of the N and N–1 electron systems, respectively, I is the ionization potential of the N-electron system, and $\varepsilon_{\mathrm{HOMO}}$ is its HOMO orbital energy. These formulas stem from the well-known Janak theorem [27], showing that

$$\frac{\partial E}{\partial n_i} = \varepsilon_i, \tag{11}$$

where n_i and ε_i are orbital occupation numbers and orbital energies.

We are aware that Eqs. (8) and (9) were originally formulated for systems in the ground state only and that excited states with different symmetries (multiplets) are considered in this study. However, extension of DFT to excited states [21, 22, 23] and to different multiplets [24, 25, 26] of the same electron configuration has recently been established and applied to obtain, for instance, excitation energies of different symmetries of atoms [24, 29]. The modified version of Eq. (9) in the exact DFT for the singlet and triplet excited states then reads [24]

$$\Delta E_{\mathrm{ST}} \equiv E_S - E_T = \Delta\varepsilon_{\mathrm{HOMO}}^{\mathrm{S-T}} > 0, \tag{12}$$

where $\Delta\varepsilon_{\mathrm{HOMO}}^{\mathrm{S-T}}$ stands for the HOMO energy difference between the singlet and triplet states. Equation (12) is exact in the context of excited-state DFT. The reason for its validity is that the asymptotic decay of any atomic or molecular state is given by $\rho(\mathbf{r}) \sim \exp[-2(2(E_0{}^{(N-1)} - E_k{}^N)]$, where $E_k{}^N$ is the energy of the kth excited state of the N-electron system. This forces the HOMO energy to be related to the difference in energy between the N-electron system energy and that of the ground state of the cation [29]. Equation (12) demonstrates that the sole contribution in the energy rationalizing the validity of Hund's multiplicity rule originates from the HOMO energy difference resulting from contraction of the HOMO of the triplet state or expansion of the HOMO of the singlet state.

To verify Eq. (12), SCF DFT calculations of the Kohn–Sham type are required for different symmetries and states. Examples of the exchange-only DFT method for different symmetries and excited states are available in the literature for atomic systems [26]. At the present time, there has been no practical scheme to perform Kohn–Sham-type SCF calculations including both exchange and correlation effects for different symmetries and excited states. Since Hund's rule results from a change in the number of parallel electron pairs, an exchange-only approach will be sufficient to do the job. In addition, evidence [30] shows that an exchange-only approach of DFT gives almost the same result as the HF method. For these reasons, we performed numerical evaluations of Eq. (13) at the unrestricted HF (UHF) level in this study. At this level, as a good approximation, we anticipate that

$$\Delta E_{\mathrm{ST}} \approx \Delta\varepsilon_{\mathrm{HOMO}}^{\mathrm{S-T}}, \tag{13}$$

because the HF method gives the accurate E_x and, more importantly, the correct asymptotic behavior for the exchange potential that has been shown to be important in reproducing acceptable HOMO energies [19].

Computational method

Both atomic and molecular systems have been investigated. To have a broad range of representative systems, the singlet and triplet states of neutral, cation, and anion species were included in the atomic systems studied. The electron configurations investigated are $1s^1 2p^1$ for Li^+, $1s^2 2s^1 2p^1$ for Be, $1s^2 2s^2 2p^5 3s^1$ for F^-, Ne, and Na^+, and $1s^2 2s^2 2p^6 3s^2 3p^5 4s^1$ for both Cl^- and Ar. For molecules, five species, H_2, BH, CH^+, CH_2, and HCHO, were chosen, some of which have been investigated before by others [10, 11, 12] and thus provide examples for comparison. The electron configurations from which the singlet and triplet states are produced are $1\sigma_g^1 1\pi_g^1$ for H_2, $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$ for BH, $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$ for CH^+, $1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$ for CH_2, and $1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 5a_1^1 1b_1^1 2b_2^1 2b_1^1$ for HCHO.

To simplify the situation, we neglect the dynamic correlation effect among electrons with antiparallel spins, which was shown to have no significant impact on the validity of the rule [2, 8, 9, 11]. Also, since DFT exchange-only calculations give practically the same results as the HF method [29], UHF calculations were used throughout this work.

The UHF calculations were performed with the GAUSSIAN94 program [31] using Dunning's augmented correlation-consistent polarized-valence triple zeta basis set [32] for H_2 and Pople's 6-311++G (3df,2p) basis set [33] for other systems. The former constitutes a [4s3p2d1f/3s2p1d] contraction of a (10s5p2d1f/5s2p1d) primitive set, plus an added diffuse function of each angular momentum to the original set [34]. To obtain a desired multiplet for each species, Guess = Alter was employed in combination with the quadratically convergent SCF procedure. Since the UHF calculation for singlet states causes spin contamination, spin projection was carried out. The value of $<S^2>$ was checked for all the systems studied and no severe spin contamination was observed.

For molecules, two energy differences are considered separately, i.e., adiabatic and vertical. An adiabatic energy difference is the energy difference when each state is in its optimized geometrical structure. A vertical difference is taken when both states are at a given fixed geometry. Hund's multiplicity rule applies to both cases in principle. Molecular geometries were all optimized at the UHF/6-311++G(3df,2p) level for adiabatic comparison. When the vertical difference was considered, different bond lengths were used. For example, in CH_2 case, we fixed the HCH angle at the optimized 132.06° and changed the C–H bond length from 1.0 to 3.0 Å.

Results

Atomic results are shown in Table 1. It is found that for all the systems investigated, the conventional ΔV_{ne} picture persists but that Slater's explanation in terms of ΔV_{ee} fails. That is, ΔV_{ne} contributes most to the total energy difference $\Delta E_{\mathrm{ST}} > 0$ in Eq. (1). For Be and Cl^-, ΔV_{ee} is less than zero, contributing negatively to the stability of the triplet state. These results validate the early conclusion by Boyd [7] and others. However, we notice that there is only one species, Be, where ΔV_{ne} is the only term having a positive contribution while ΔT and ΔV_{ee} are both negative. In all other cases, either ΔT or ΔV_{ee} or both have a positive contribution to ΔE. For instance, in the cases of Na^+ and Ne, the ΔV_{ne} component is 0.0150 and 0.0063, respectively, while the ΔV_{ee} component contributes 0.0090 and 0.0043, respectively. It is incorrect to say that ΔV_{ee} is negligibly small for these two systems. Indeed, it plays in these cases a significant role in the interpretation of Hund's rule. It seems, however, that there exists no apparent regularity to assess contributions from ΔV_{ee} and ΔT and thus no single physical interpretation based on the decomposition of the total energy difference into these components can be given for all circumstances. In terms of Eq. (13), however, a unique picture is available. One sees from Table 1 that to very good accuracy, ΔE_{ST} is equal to the highest occupied atomic orbital energy difference $\Delta\varepsilon_{\mathrm{HOMO}}$.

For molecules, we first consider the adiabatic case when differences are calculated at the optimized geometry of each state. The results for a series of molecules are shown in Table 2. Within the traditional framework of Eq. (1), ΔV_{ne} dominance prevails in all cases except H_2. ΔV_{ee} and ΔT both contribute negatively. For H_2, all three terms contribute positively, with the biggest contribution coming from ΔT, but not ΔV_{ne}. These results invalidate the original explanations in terms of ΔV_{ee} and ΔV_{ne} for molecules. More counterexamples will readily be seen in the comparison of vertical differences. The HOMO picture, nevertheless, still survives. The accuracy of the equality $\Delta E_{\mathrm{ST}} = \Delta\varepsilon_{\mathrm{HOMO}}$ is as good as in the atomic case.

A more severe test is the vertical difference for molecules. It is known [10, 11, 12, 13, 14] that the situation is much more complicated in this case. At some ranges of nuclear separation of a molecule, ΔT may become dominant, while at other places ΔV_{ne} governs the validity of Hund's rule. No particular rules describing this phenomenon have been found either. An extreme example [13] has been disclosed that ΔT dominates all ranges of a bond separation and that ΔV_{ne} does not play any positive role at all. To rationalize numerical data, various analysis tools have been applied, such as the molecular virial theorem [10, 11, 12, 14], electron density redistribution difference [10, 11, 12], yet no unitary picture emerges. The systems reported in the literature include H_2 [8, 9], $X\mathrm{H}^{n+}$ (X=Li–F, n=2–8) [13, 14], XH (X=B, C, N,O, F) [12], CH_2 [10], and HCHO [11]. To show that the new interpretation applies to all these systems, four representative species, H_2, LiH^{+2}, BH, and CH_2, were chosen for vertical evaluation. They represent both diatomic and polyatomic two-electron and many-electron systems. The results are plotted in Figs. 1, 2, 3, and 4, respectively.

Table 1. Energy differences of singlet and triplet states for a few atomic systems, Li^+, Be, F^-,Ne, Na^+, Cl^-, and Ar. Electronic configurations: Li^+ $1s^1 2p^1$; Be $1s^2 2s^1 2p^1$; $\mathrm{F}^- 1s^2 2s^2 2p^5 3s^1$; Ne $1s^2 2s^2 2p^5 3s^1$; Na^+ $1s^2 2s^2 2p^5 3s^1$; $\mathrm{Cl}^- 1s^2 2s^2 2p^5 3s^2 3p^5 4s^1$; Ar $1s^2 2s^2 2p^5 3s^2 3p^5 4s^1$. Atomic units

	ΔT	ΔV_{ee}	ΔV_{ne}	$\Delta\varepsilon_{\mathrm{HOMO}}$	ΔE_{ST}
Li^+	0.0063	0.0013	0.0095	0.0173	0.0171
Be	−0.0693	−0.0427	0.1816	0.0679	0.0696
F^-	−0.0203	0.0064	0.0224	0.0085	0.0085
Ne	−0.0149	0.0090	0.0150	0.0092	0.0091
Na^+	−0.0046	0.0043	0.0063	0.0061	0.0060
Cl^-	0.0121	−0.0341	0.0272	0.0055	0.0052
Ar	−0.0082	0.0036	0.0103	0.0060	0.0057

Table 2. Adiabatic energy differences of singlet and triplet states for a few molecules, H_2, CH^+, BH, CH_2, and HCHO. Electronic-configurations: H_2 $\sigma_g^1 1\pi_g^1$;BH $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$;$\mathrm{CH}^+$ $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$; CH_2 $1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$;HCHO $1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 5a_1^1 1b_1^1 2b_2^1 2b_1^1$. Atomic units

	ΔT	ΔV_{ee}	ΔV_{nn}	ΔV_{ne}	$\Delta\varepsilon_{\mathrm{HOMO}}$	ΔE_{ST}
H_2	0.0110	0.0014	0.0084	−0.0172	0.0037	0.0035
BH	−0.0386	−0.0583	−0.0396	0.1780	0.0412	0.0415
CH^+	−0.0428	−0.0936	−0.1487	0.3288	0.0458	0.0438
CH_2	−0.0299	−0.0055	−0.0063	0.0644	0.0366	0.0354
HCHO	−0.0055	−0.0703	−0.0920	0.1730	0.0051	0.0052

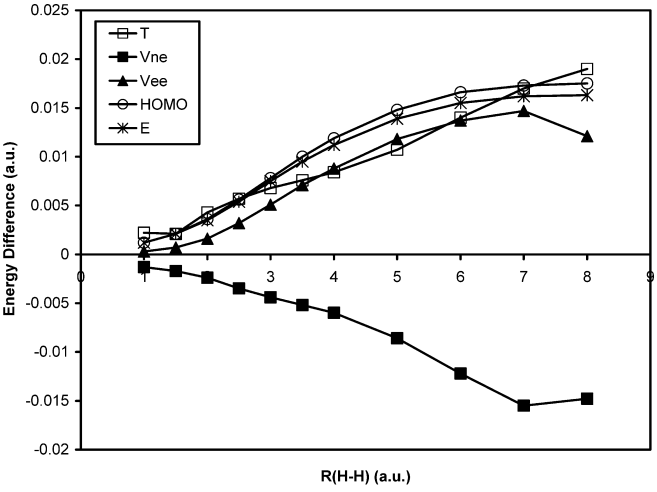

Fig. 1. Vertical energy differences (S–T) of various energy components for the triplet and singlet states of the $1\sigma_g^1 1\pi_g^1$ electron configuration of the hydrogen molecule at different H–H bond lengths (atomic units). Calculations were performed the unrestricted Hartree–Fock (*UHF*)/aug-cc-pVTZ level. See text

ΔE_{ST} and its components of H_2 is shown in Fig. 1 versus different H–H bond lengths, $R_{\mathrm{H–H}}$. The energy components include ΔT, ΔV_{ne}, ΔV_{ee}, and $\Delta\varepsilon_{\mathrm{HOMO}}$. These curves provide two different pictures for the rationalization of Hund's rule. In terms of Eq. (1), we find that at all ranges $\Delta V_{\mathrm{ne}} < 0$ and that $\Delta T > 0$ and $\Delta V_{\mathrm{ee}} > 0$, both contribute positively. ΔV_{ee} is the largest in the range 4.0–6.0 Å and ΔT dominates at other distances. This example apparently provides another counterexample that the ΔV_{ne} scenario of the interpretation of Hund's rule is invalid. Turning to the HOMO picture, one finds that $\Delta\varepsilon_{\mathrm{HOMO}}$ follows ΔE_{ST} at all distances, with $\Delta\varepsilon_{\mathrm{HOMO}}$ slightly larger than ΔE_{ST}. It is safe to say that $\Delta\varepsilon_{\mathrm{HOMO}}$ plays a major role in determining ΔE_{ST} for all $R_{\mathrm{H–H}}$ investigated here in this case, indicating the soundness of the present interpretation.

Another example of the two-electron system is given in Fig. 2. LiH^{+2} has been studied previously [13, 14], but here we are concerned with a different configuration, $1\sigma^1 1\pi^1$. In the framework of Eq. (1), ΔT is dominant when $R_{\mathrm{Li–H}} < 4.0$ Å and ΔV_{ne} is dominant otherwise. ΔV_{ee} is positive all the way down with significant contributions at small $R_{\mathrm{Li–H}}$. At large $R_{\mathrm{Li–H}}$, even though ΔV_{ne} is the largest, we still see significant positive contributions from ΔT. With the HOMO picture, no matter how complicatedly the previously mentioned components behave, only one conclusion can be drawn: $\Delta\varepsilon_{\mathrm{HOMO}}$ corresponds to ΔE and to a very good approximation $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E$ is valid.

Now, let us consider many-electron systems. The BH molecule has previously been investigated by Darvesh et al. [12].The behavior of its energy components can be seen in Fig. 3. One observes that when $R_{\mathrm{B–H}} < 2.5$ Å, ΔV_{ne} is the only term contributing positively to ΔE_{ST}, while both ΔV_{ee} and ΔT are negative. When $R_{\mathrm{B–H}} > 2.5$ Å, the only positive term changes to ΔT, with both $\Delta V_{\mathrm{ne}} < 0$ and $\Delta V_{\mathrm{ee}} < 0$. Comparing it with Figs. 1 and 2, we find no similarity of behavior among these energy components. In terms of the HOMO picture, however, another case is shown that a unique explanation exists for Hund's rule using $\Delta\varepsilon_{\mathrm{HOMO}}$. Again, to satisfactory accuracy, $\Delta\varepsilon_{\mathrm{HOMO}}$ follows ΔE_{ST} as $R_{\mathrm{B–H}}$ changes and the equality $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E$ is a good approximation.

Our final vertical example for molecules is $\mathrm{CH_2}$ ($\mathrm{B_1}$), a many-electron polyatomic species, which has also been previously investigated [10]. The H–C–H angle was kept at the optimized value of 132.06°. Various energies are plotted versus the C–H bond length in Fig. 4. Though

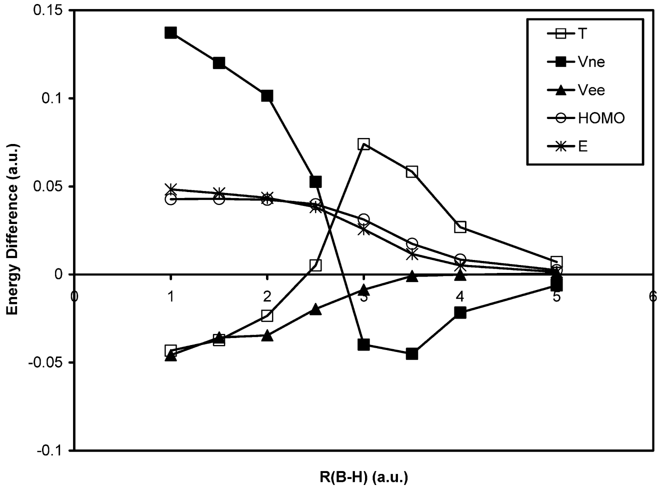

Fig. 3. Vertical energy differences (S–T) of various energy components for the triplet and singlet states of the $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^1$ electron configuration of the BH molecule at the UHF/6-311++G(3df,2p) level (atomic units)

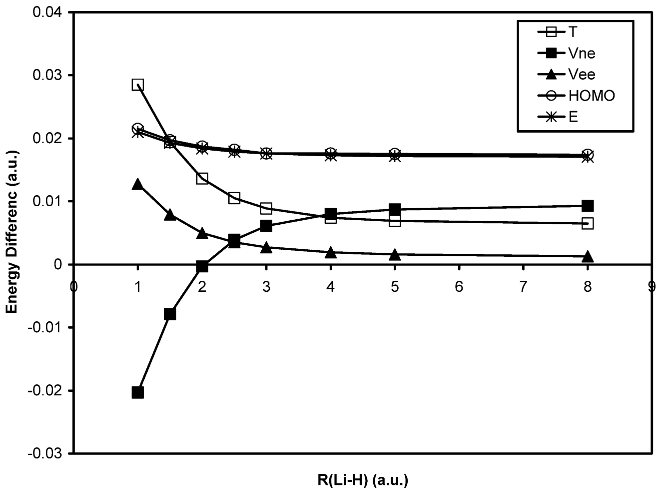

Fig. 2. Vertical energy differences (S–T) of various energy components for the triplet and singlet states of the $1\sigma^1 1\pi^1$ electron configuration of the LiH^{2+} ion at the UHF/6-311++G(3df,2p) level (atomic units)

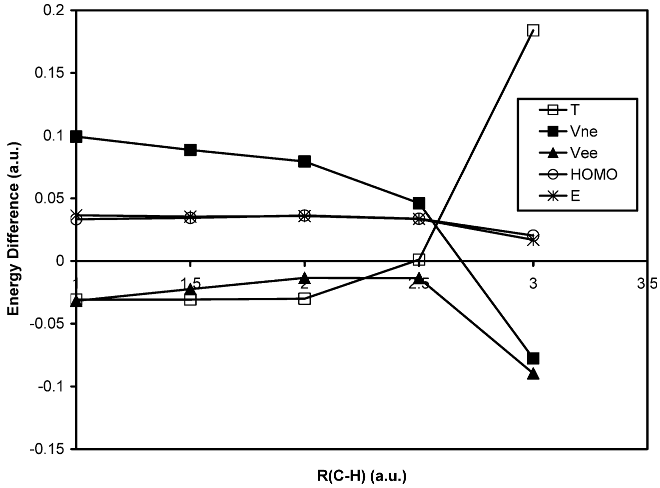

Fig. 4. Vertical energy differences (S–T) of various energy components for the triplet $^3\mathrm{B}_1$ and singlet $^1\mathrm{B}_1$ states of the $1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$ electron configuration of the $\mathrm{CH_2}$ molecule at the UHF/6-311++G(3df,2p) level (atomic units). <HCH = 132.059°

numerical values are quite different, general tendencies of the energy differences are almost the same as those of Fig. 3. ΔT exchanges its role with ΔV_{ne} at about 2.5 Å and ΔV_{ee} is always less than zero. Also, we find that $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E_{\mathrm{ST}}$ is still valid for all distances of $R_{\mathrm{C-H}}$ investigated.

Discussion

Our results show collectively that a new theoretical interpretation for Hund's multiplicity rule is in place. The theory is based on Eq. (12) [24], indicating that the single contribution to ΔE_{ST} originates from the energy difference of the highest occupied atomic or molecular orbitals of the singlet and triplet. To very good accuracy, within the HF framework, we found that $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E_{\mathrm{ST}}$. This is because the HF method gives the correct exchange energy and, more importantly, the correct asymptotic behavior for the exchange potential that plays a major role in determining the HOMO energy. This has been confirmed by tests from atomic and adiabatic and vertical molecular results reported here. In contrast, using the conventional scheme of Eq. (1), one observes that quite complicated situations are encountered for molecules and that no single component has been found responsible for the behavior of ΔE_{ST} in all circumstances.

This picture has previously been applied to a few two-electron diatomics by one of the present authors [13]. Thanks to the recent development of DFT on excited states and multiplets, its extension to systems of general interest is now possible. The validity of the equation $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E_{\mathrm{ST}}$ may be thought of as a consequence of the Janak theorem applied to excited multiplets in DFT. One may also think of the equality as a consequence of the extended Koopman theorem [35]. Though our numerical tests were simply based on the UHF approach, the previously mentioned theoretical rationale is the basis of the present development.

What is the physical meaning of the present interpretation? The first option is the orbital contraction picture. The concept of orbital contraction has previously been applied to explain this rule [8, 9]. It came along with another concept, orbital expansion. It is hard to imagine that while all orbitals are either contracted or expanded, only the contracted HOMO is responsible for the validity of Hund's rule. There may exist cancellations of contributions from inner orbitals. The other option has to do with the HOMO–lowest unoccupied molecular orbital (LUMO) gap, or more generally, the maximum hardness principle (MHP) [36, 37, 38]. As stated by Pearson, nature tends to have species as hard as possible, or have the HOMO–LUMO gap as large as possible for atoms and molecules. Stabler means harder. MHP has been used to explain aromaticity [38], the stability of C_{60} and other cluster molecules [36], etc. Hund's rule provides another example for the MHP. When a system transits from a lower spin state to a higher spin state, stability is produced by the lower HOMO, and thus by the larger HOMO–LUMO gap. Of course, redefinitions for orbitals and hardness have to be made in the framework of excited multiplets in DFT.

Generally speaking, when transiting from a lower spin state to a higher spin state, a system experiences many changes simultaneously. These can be summarized by electron redistribution, leading to changes in energy components, orbital movement, nuclear relaxation, and electron correlation. All these changes are, however, due to one variation: the variation in the number of pairs of electrons with parallel spins. The previous interpretation via ΔV_{ne} attributes its physics to the anisotropic screening effect [7] among electrons. Our present theory attributes the stability of a higher spin state to the MHP. It is out of question that the present interpretation is more general than the previous one, as the earlier examples showed. However, questions remain to be answered as to how a change in the number of pairs of electrons with the same spin leads to so many changes in properties, and why changes in the HOMOs are solely responsible for all others.

Finally, we mention that our presentation is based on some approximations. First, the dynamic electron correlation was neglected. This neglect could prove too much for some systems. We justified our approximation, on the one hand, by the fact that Hund's rule resulted from the change in the number of pairs of electrons with parallel spins and thus Fermi correlation is more important. On the other hand, Darvesh and coworkers [10, 11, 12] demonstrated that the dynamical effect is not qualitatively essential though numerically significant. Also, our numerical data of vertical molecular differences for BH and CH_2 reproduce well what Darvesh and coworkers [11, 12] obtained when the dynamic correlation effect was included. More study is needed from the DFT viewpoint by explicitly taking into account the electron correlation. Secondly, the UHF method was employed to replace the exchange-only Kohn–Sham approach [29]. In addition, all systems we investigated are nondegenerate where a single Slater determinant is adequate for the description. More work is needed for degenerate states where one has to resort to such methods as multiconfigurational SCF and multireference configuration interaction. The idea of explaining Hund's rule for those systems in terms of the HOMO–LUMO gap or hardness needs to be further developed.

Conclusions

A theoretical basis has been proposed in this paper to explain the general validity of Hund's multiplicity rule, which states that a higher spin state has a lower energy than a lower spin state if they arise from the same electron configuration. The theory is based on the extension of modern DFT on excited states and multiplets. It stems from the Janak theorem and the extended Koopman theorem. It was shown that the energy difference comes from the highest occupied atomic or molecular orbitals [24] and to quite satisfactory accuracy the equality $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E_{\mathrm{ST}}$ holds even at the HF level. The underlying physics of this interpretation was attributed to the MHP of Pearson [36, 37], dictating in this case that the stabler a species is, the harder it is. Numerical tests for a number of atoms and molecules confirmed this formalism. The most critical evaluation is the vertical comparison for a few molecules, as shown in Figs. 1, 2, 3, and 4. No matter how complicated the energy components in Eq. (1) behave, we have the same scenario in Eq. (12), $\Delta\varepsilon_{\mathrm{HOMO}} = \Delta E_{\mathrm{ST}}$.

Acknowledgements. Support from the Petroleum Research Fund of the American Chemical Society and the North Carolina Supercomputing Center is gratefully acknowledged. We thank Robert G. Parr, Mel Levy, Weitao Yang, and Paul Ayers for stimulating discussion. S.B.L. is grateful to R.J. Boyd of Dalhousie University, Canada, for stimulating interest in the present research, to Ágnes Nagy of Kossuth Lajos University, Hungary, for providing preprints and results of her papers in advance of publication on excited-state DFT, and to Jan Hermans for partial support from a Research Resource project in computational structural biology (NIH grant RR08102). W.L. is a postdoctoral fellow of the Fund for Scientific Research, Flanders, Belgium, (F.W.O.) and is additionally supported by Fulbright and NATO travel grants enabling a stay at the University of North Carolina at Chapel Hill.

References

1. Slater JC (1960) Quantum theory of atomic structure, vol 1. McGraw-Hill, New York
2. Katrile J, Pauncz R (1977) Advances in quantum chemistry, vol 10. Academic, New York, pp 143–185
3. Davidson ER (1965) J Chem Phys 42:4199
4. Messer RP, Birss FW (1969) J Phys Chem 73:2085
5. Katriel J (1972) Theor Chim Acta 23:309
6. Shim I, Dahl JP (1978) Theor Chim Acta 48:165
7. Boyd RJ (1984) Nature 310:480
8. Colpa JP, Brown RE (1978) J Chem Phys 68:4248
9. Brown RE, Colpa JP (1983) Int J Quantum Chem 24:593
10. Darvesh KV, Boyd RJ (1987) J Chem Phys 87:5329
11. Darvesh KV, Boyd RJ (1989) J Chem Phys 90:5643
12. Darvesh KV, Fricker PD, Boyd RJ (1990) J Phys Chem 94:3480
13. Liu S, Yu Y (1991) J Mol Struct (THEOCHEM) 235:115
14. Liu S, Liu X, Yang Q, Yu Y (1991) J Mol Struct (THEOCHEM) 251:271
15. Koga T, Aoki H, Thakkar AJ (1996) Can J Chem 74:775
16. Koga T, Thakkar AJ (1996) Int J Quantum Chem 57:89
17. Koga T, Takagi T, Thakkar AJ (1996) Theor Chim Acta 93:157
18. Hohenberg P, Kohn W (1964) Phys Rev B 136:864
19. Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, Oxford
20. March NH (1992) Electron density theory of atoms and molecules. Academic, London.
21. Theophilou AK (1978) J Phys C 12:5419
22. Gross EKU, Oliveira LN, Kohn W (1988) Phys Rev A 37:2821
23. Nagy Á (1997) Adv Quantum Chem 29:159
24. Levy M (1995) Phys Rev A 52:R4313.
25. Görling A (1996) Phys Rev A 54:3912
26. Nagy Á (1996) Phys Rev A 57:1672
27. Janak JF (1978) Phys Rev B 18:7165
28. Borden WT, Davidson ER (1977) J Am Chem Soc 99:4587
29. Levy M, Nagy A (1999) Phys Rev A 59:1687
30. (a) Görling A, Ernzerhof M (1995) Phys Rev A 51:4501; (b) Gritsenko OV, Schipper PRT, Baerends EJ (1997) J Chem Phys 107:6693
31. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) Gaussian 94, revision E.3. Gaussian, Pittsburgh, PA
32. Dunning TH Jr (1989) J Chem Phys 90:1007
33. Gill PMW, Johnson BG, Pople JA, Frisch MJ (1992) Chem Phys Lett 197:499
34. Kendall RA, Dunning TH Jr, Harrison RJ (1992) J Chem Phys 96:6796
35. Morrison RC (1994) Int J Quantum Chem 49:649
36. Pearson RG (1987) J Chem Ed 64:561
37. Pearson RG (1993) Acc Chem Res 26:250
38. Parr RG, Zhou Z (1993) Acc Chem Res 26:256