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# The inequality formulation of Hund's rule and a reinterpretation of singlet-triplet energy differences, generalized for molecules at equilibrium geometry

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An inequality formulation in the open-shell Hartree-Fock approximation for Hund's multiplicity rule for atoms has been generalized for the energy differences between a singlet and a triplet state of a molecule with different geometries for the two states. A numerical example is given for the lowest  ${}^1\Pi_u$  and  ${}^3\Pi_u$  states of  $H_2$ . As in neutral atoms the energy difference is dominated by the difference in electron nuclear attraction and the interelectronic repulsion is higher for the triplet state than for the singlet state. The  $\pi$  orbital is more contracted in the triplet state than in the singlet state; the  $\sigma$  orbital gives a minor expansion in going from the  ${}^1\Pi_u$  state to the  ${}^3\Pi_u$  state.

## INTRODUCTION

The traditional textbook explanation for Hund's rules for atomic states has some serious deficiencies, as was noticed first by Davidson for the excited states of He.<sup>1</sup> Excited states of many atoms were later considered by other authors by a variety of methods. The main conclusion of this work is that the state of lower energy in a multiplet always has the most negative value for  $\langle V_{en} \rangle$ , the expectation value of the electron nuclear attraction. One finds furthermore for all neutral atoms and usually for the first few positive ions of an isoelectronic series, that a state of lower energy in a multiplet has a higher value for  $\langle V_{ee} \rangle$ , the expectation value for the interelectronic repulsion energy.<sup>2-8</sup> The traditional treatment predicted a lower value for  $\langle V_{ee} \rangle$  for a state of lower energy. It was also noticed that the outer singly occupied orbital contracts considerably in going from a singlet state to the corresponding triplet state, whereas the singly occupied inner orbital usually shows a minor expansion.<sup>2, 4, 5, 8, 9, 10</sup> This explains the behavior for  $\langle V_{en} \rangle$  and  $\langle V_{ee} \rangle$  mentioned above.

Katriel studied the  ${}^1, {}^3P$  terms of He and their electron pair distribution<sup>10a, b</sup> and proved for Hund's multiplicity rule the validity in the Hartree-Fock approximation.<sup>10b</sup> One of the present authors (J. P. C.) reformulated the theory for Hund's multiplicity and angular momentum rule in the form of coupled inequalities also valid within the HF approximation.<sup>9</sup> For a detailed discussion of the interpretation of Hund's first rule for atoms, the reader is referred to a recent review by Katriel and Pauncz.<sup>11</sup>

The understanding of the origin of singlet triplet differences is less complete for molecules (in particular, the large ones) than for atoms. The only molecular

case for which an accurate component analysis is available is, to the best of our knowledge, the lowest  ${}^1\Pi_u - {}^3\Pi_u$  energy difference for  $H_2$ .<sup>7, 12</sup> The results of these accurate configuration interaction calculations are similar to those for atoms. There are, however, some unexpected correlation effects in the  ${}^1, {}^3\Pi_u$  states when one changes the internuclear distance.<sup>13</sup> Orbital expansion and contraction effects<sup>14</sup> have been predicted for diatomic molecules.

Several authors did accurate calculations on the singlet and triplet excited states of ethylene,<sup>15</sup> *trans* butadiene,<sup>16</sup> carbon dioxide and acetylene,<sup>17</sup> and benzene.<sup>18</sup> In these papers no component analysis or pair correlation is given, but the second moments  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ , and  $\langle z^2 \rangle$  are tabulated in many of them and a contraction for the triplet states and a certain diffuseness for the singlet states are noticed for many molecules. This suggests that for some large molecules  $\langle V_{en} \rangle$  is also the dominating component in the energy difference.

The inequality formulation for Hund's rules mentioned above can be applied to molecules, but in its derivation it is assumed that both states have the same geometry, which is usually not the case for equilibrium positions. We show in the present paper that the formalism can be generalized for molecules in the equilibrium geometry for each of the respective states. Furthermore, we give a component analysis of the  ${}^1\Pi_u - {}^3\Pi_u$  states of  $H_2$  at the HF level together with exchange integrals and discuss the second moments for the orbitals in the two states.

## The inequality formulation for singlet-triplet energy differences (Hund's first rule) for molecules in equilibrium positions

The following inequality has been shown to be valid for an atom or for a molecule with the same geometry for the excited states involved, when the atom or molecule has two singly occupied orbitals  $A$  and  $B$ ,<sup>9</sup>

$$2K_{AB}^T \geq E^S - E^T \geq 2K_{AB}^S. \quad (1)$$

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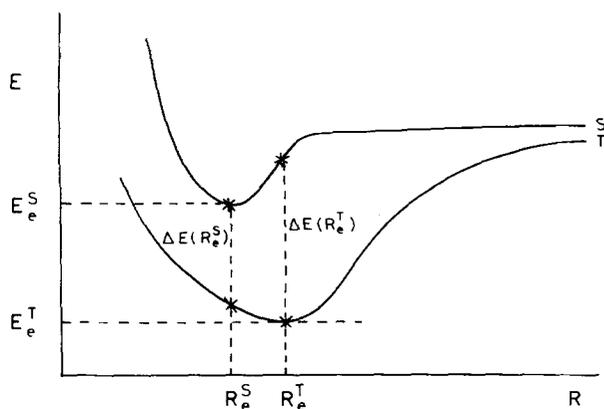


FIG. 1. Potential energy curves for an excited singlet state  $S$  and a triplet state  $T$  as a function of the internuclear distance  $R$ . For further explanation, see text.

$K_{AB}^S$  and  $K_{AB}^T$  are the exchange integrals for the best orbitals  $A$  and  $B$  as obtained from the restricted open-shell Hartree-Fock equations for the singlet and triplet state, respectively. (Hence, we use different orbitals for different states.)  $E^S$  and  $E^T$  are the corresponding HF energies for the two states under consideration. We generalize here the original inequality formulation to one for diatomic molecules with singlet and triplet states in their respective equilibrium positions; a further generalization to a polyatomic system is straightforward. We consider only the case in which both states are bound. The situation is then as shown in Fig. 1.

The symbols  $R_e^S$  and  $R_e^T$  indicate the Hartree-Fock equilibrium distances for the singlet and triplet state, respectively;  $E_e^S$  and  $E_e^T$  indicate that each Hartree-Fock energy is given for the equilibrium geometry that corresponds to its state. Note that we have a nonequilibrium situation when we take the molecule in its triplet state at a bond distance  $R_e^S$ .

We apply inequality (1) (which is valid for any frozen geometry) first for the bond distance  $R_e^S$  for both the singlet and the triplet states. It follows from (1) that

$$2K_{AB}^T(R_e^S) \geq E^S(R_e^S) - E^T(R_e^S) \geq 2K_{AB}^S(R_e^S). \quad (2)$$

The symbol  $(R_e^S)$  indicates that each quantity is evaluated for the bond distance  $R_e^S$ . With an obvious notation we can rewrite (2) as

$$2K_{AB}^T(R_e^S) \geq \Delta E(R_e^S) \geq 2K_{AB}^S(R_e^S). \quad (3)$$

When we apply (1) at the frozen geometry  $R_e^T$  we get the following analog of (3):

$$2K_{AB}^T(R_e^T) \geq \Delta E(R_e^T) \geq 2K_{AB}^S(R_e^T). \quad (4)$$

An inspection of the figure gives another inequality:

$$\Delta E(R_e^T) > E_e^S - E_e^T > \Delta E(R_e^S) \quad (5)$$

[note that  $E_e^S = E^S(R_e^S)$  and  $E_e^T = E^T(R_e^T)$ ]. In the figure we arbitrarily took  $R_e^T > R_e^S$ . Expression (5) is also correct, however, when  $R_e^T < R_e^S$ . Only when  $R_e^T = R_e^S$  (which in reality is never the case) is it necessary to replace the "larger than" symbols by equality signs.

From (3), (4), and (5) it follows that

$$2K_{AB}^T(R_e^T) \geq \Delta E(R_e^T) > E_e^S - E_e^T > \Delta E(R_e^S) \geq 2K_{AB}^S(R_e^S),$$

and consequently

$$2K_{AB}^T(R_e^T) > E_e^S - E_e^T > 2K_{AB}^S(R_e^S), \quad (6)$$

with

$$K_{AB}^T(R_e^T) > K_{AB}^S(R_e^S) \quad (7)$$

as a special case.

### A numerical example for the lowest $^1\Pi_u$ and $^3\Pi_u$ states of $H_2$

We calculated the energies and their components of the lowest  $^3\Pi_u$  and  $^1\Pi_u$  states of the  $H_2$  molecule in the open-shell restricted Hartree-Fock approximation. The two orbitals in this system, a bonding  $\sigma$  and a bonding  $\pi$  orbital, were expanded as a linear combination of six elliptical orbitals. For each distance the orbital exponents were optimized independently. We found from our calculations that  $R_e^S = 1.9336$  a. u. and  $R_e^T = 1.9470$  a. u.

In Table I we summarize the results for the  $^1\Pi_u$  and the  $^3\Pi_u$  states both taken at their respective equilibrium distances as given above. The table gives the Hartree-Fock energies  $E_{HF}$ , the orbital energies  $\epsilon_\sigma$  and  $\epsilon_\pi$ , the expectation values for the kinetic energy  $\langle T \rangle$ , for the interelectron repulsion  $\langle V_{ee} \rangle$ , for the electron nuclear attraction  $\langle V_{en} \rangle$ , and for the nuclear repulsion  $\langle V_{nn} \rangle$ , and further the Coulomb and exchange integrals  $J$  and  $K$ , and finally the second moments for the  $\sigma$  and the

TABLE I. Hartree-Fock energies, energy differences, and their components and orbital second moments for the  $^1\Pi_u$  and  $^3\Pi_u$  states of  $H_2$  at their respective HF equilibrium distances ( $R_e^S = 1.9336$  a. u.,  $R_e^T = 1.9470$  a. u.). All quantities are in atomic units. The  $z$  axis is in the internuclear direction with the molecular midpoint at  $z = 0$ ; the  $x$  and  $y$  axes are perpendicular to this direction. With our choice of orbitals we have  $\langle x^2 \rangle = \langle y^2 \rangle$ .

	$^1\Pi_u(R_e^S)$	$^3\Pi_u(R_e^T)$	Singlet-triplet differences at equilibrium geometries
$E_{HF}$	-0.71395	-0.73290	+0.01895
$\epsilon_\sigma$	-0.90411	-0.86921	
$\epsilon_\pi$	-0.11171	-0.13134	
$\langle T \rangle$	0.71393	0.73286	-0.01893
$\langle V_{ee} \rangle$	0.21500	0.24595	-0.03095
$\langle V_{en} \rangle$	-2.16005	-2.22532	+0.06527
$\langle V_{nn} \rangle$	0.51717	0.51361	+0.00356
$J_{0r}$	0.20939	0.26147	
$K_{0r}$	0.00561	0.01551	
$\langle x^2 + y^2 \rangle$ , $\sigma$ orb.	1.22363	1.36662	
$\langle z^2 \rangle$ , $\sigma$ orb.	1.06947	1.12184	
$\langle x^2 + y^2 \rangle$ , $\pi$ orb.	30.66895	20.79728	
$\langle z^2 \rangle$ , $\pi$ orb.	7.96243	5.48628	

TABLE II. Exchange integrals for singlet and triplet orbitals, energy differences, and their components for Hartree-Fock and CI wavefunctions for the  $^1\Pi_u$  and  $^3\Pi_u$  states of  $H_2$  at various internuclear distances  $R$ . (All quantities in atomic units.)

$R$	Open-shell Hartree-Fock results						CI results				
	$2K_{0\sigma}^S$	$\Delta E_{HF}$	$2K_{0\sigma}^T$	$\Delta\langle V_{en}\rangle$	$\Delta\langle V_{ee}\rangle$	$\Delta\langle T\rangle$	$\Delta E_{CI}$	$\Delta\langle V_{en}\rangle$	$\Delta\langle V_{ee}\rangle$	$\Delta\langle T\rangle$	
0	0.00624	0.00897	0.01284	0.04043	-0.02249	-0.00897	0.00934	0.04031	-0.02163	-0.00934	
1	0.00962	0.01540	0.02430	0.06728	-0.03115	-0.02073	0.0161	0.0654	-0.0283	-0.0211	
2	0.01126	0.01904	0.03118	0.07182	-0.03098	-0.02179	0.0193	0.0640	-0.0249	-0.0202	
3	0.01140	0.01870	0.02970	0.05188	-0.02314	-0.01004	0.0181	0.0392	-0.0156	-0.0055	
4	0.01040	0.01646	0.02532	0.03543	-0.01744	-0.00154	0.0145	0.0155	-0.0086	+0.0077	

$\pi$  orbitals. In the last column the singlet-triplet differences for most of the quantities are given. From the data in Table I it follows that the inequality (6) has for our example its numerical counterpart

$$0.03102 > 0.01895 > 0.01122.$$

In Table II we summarize the energy differences and their components from the present open-shell Hartree-Fock calculation for a variety of internuclear distances, together with twice the value for the exchange integrals,  $2K_{\sigma\sigma}^S$  and  $2K_{\sigma\sigma}^T$ . We also include for the purpose of comparison the results for the energy differences and their components according to a previously published configuration interaction calculation by the present authors.<sup>7</sup> Near the equilibrium distances ( $R \approx 2$  a.u.) the energy differences calculated with the Hartree-Fock method and the exact values differ by at most a few percent.

## DISCUSSION

As already mentioned above, the inequality (6) is obeyed by the relevant data in Table I. It follows also from the data in the tables that the energy difference and the exchange integrals for  $H_2$  at equilibrium are considerably larger than those for the  $^1P$  and  $^3P$  states of He, which are the united atom situations for our  $H_2$  states. Moreover,  $K^T/K^S = 2.058$  for He and  $K^T(R_e^T)/K^S(R_e^S) = 2.765$  for  $H_2$ ; hence the inequality becomes more outspoken for  $H_2$  than for He.

From the component analysis for  $E_e^S - E_e^T$  as given in the last column of Table I, we see that also in comparing equilibrium situations the  $\Delta\langle V_{en}\rangle$  is the major component with the same sign as  $\Delta E$ ; there is in addition a small positive contribution from  $\Delta\langle V_{nn}\rangle$  (one should not generalize this last statement, however<sup>19</sup>). We have in the equilibrium situation

$$\Delta\langle V_{ee}\rangle = J_{\sigma\sigma}^S(R_e^S) - J_{\sigma\sigma}^T(R_e^T) + K_{\sigma\sigma}^S(R_e^S) + K_{\sigma\sigma}^T(R_e^T),$$

a generalization of formula 77 in Ref. 11. When  $\Delta\langle V_{ee}\rangle < 0$ , as is correct in our example, it follows that  $J_{\sigma\sigma}^T(R_e^T) > J_{\sigma\sigma}^S(R_e^S)$ , which is again illustrated in Table I.

In going from the  $^1\Pi_u$  state to the  $^3\Pi_u$  state one sees from the second moments a large contraction from the outer  $\pi$  orbital and a minor expansion of the inner  $\sigma$  orbital. This is analogous to the behavior found for orbitals in atoms and for the second moments of the  $\pi$  orbitals in large molecules.<sup>15-18</sup> It suggests also for large systems a more negative  $\langle V_{en}\rangle$  for their triplet states than for the corresponding singlet states.

The difference in spatial extension of singlet and triplet wavefunctions has as one of its observable consequences a difference in bond lengths.<sup>19</sup> There may be other effects, however. Recent experimental work done onphanes with two aromatic ring systems at short distance shows a remarkable difference between the fluorescence spectra which are broad and structureless with large red shifts and the phosphorescence spectra of the largerphanes with clear vibrational structures and small red shifts compared with the monomeric substances. It has been suggested that this difference is related to the diffuse  $\pi$  orbitals in the singlet states, which give a much stronger interaction between the subunits of thephanes than the rather contracted  $\pi$  orbitals in a triplet state.<sup>20</sup>

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