Ferromagnetic State of a Model Chain System

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Ferromagnetic states of two linear chains are determined. The comparison with the solution of the restricted Hartree-Fock method shows that such states are energetically very unlikely.

The existence of organic ferromagnetics has been suggested [1, 2], but actual calculations on the proposed systems have not been done yet.

In this note we describe calculations done on ferromagnetic states of linear chains. The ab-initio crystal orbital approach used in this work is too cumbersome to be applied to molecular systems proposed in Ref. [1] or [2]. Therefore we did calculations on two model systems: chain of H atoms and chain of H_2 molecules. These model systems are completely different from the organic molecules proposed as candidates for ferromagnetics, but we think that our results have some relevance to the question of the existence of organic ferromagnetics.

The methods used were fully described in our previous publications [3, 4]. The restricted Hartree-Fock (RHF) approach was used to determine the energies of the metallic state of H chains and H_2 chains. The energies of the ferromagnetic and the antiferromagnetic states have been deduced with the unrestricted Hartree-Fock (UHF) method.

We used a STO-3G [5] basis set, and the number of neighbours included into the calculations was nine. An enlargement of the basis set, as we have already noticed [4] in an other context, does not change the main conclusion of our work. The results are given in Table 1 and also in Fig. 1 for the H chain.

Both the ferromagnetic and the antiferromagnetic state have the correct limiting behaviour. With growing distance between the H atoms both energies approach the energy of the isolated H atom. This seems to be of special importance since the ferromagnetic state is the metallic state resulting from the fact that there is only one H atom in the unit cell. The antiferromagnetic solution of the UHF method corresponds to the insulator state of the system. Formally we have two H atoms per unit cell, with antiparallel spins, and the resulting state is insulating. As is well known, the metallic state determined from RHF approach has the wrong limiting behaviour (Figure 1).

Table 1. The energies (a.u.) of various states.

H chain[a] Interatomic distance (a.u.)	Metallic	Antiferro-magnetic	Ferro-magnetic
1.5	0	− 0.0177	+ 4.2088
1.88	0	− 0.0380	+ 1.9469
4	0	− 0.7004	− 0.6318
6	0	− 1.1861	− 1.1847
H_2 chain[a, b]	insulator		
$R_1 = 1.45$ $R_2 = 1.9$	0		+ 4.3088
$R_3 = 1.45$ $R_4 = 2.9$	0		+ 4.4632

[a] Relative to the energy of the RHF solution.
[b] R_1 and R_2 are the distances within and between the H_2 molecules, respectively.

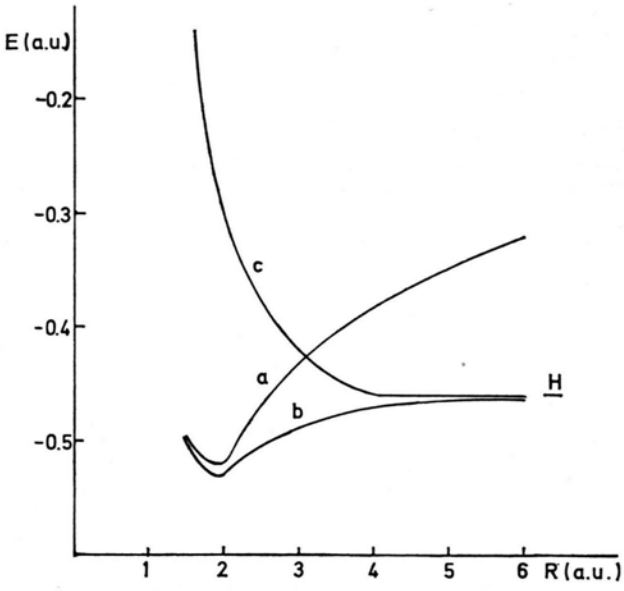

Fig. 1. Energy per atom: metallic (a), antiferromagnetic (b) and ferromagnetic (c) states. H indicates the energy of H atom.

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Energetically both the metallic and antiferromagnetic state have much lower energies around the equilibrium distance than the ferromagnetic state.

The same conclusion resulted also from calculations done on the H_2 chain. As we noted elsewhere [6], we were unable to find an antiferromagnetic solution of the UHF approach. In Table 1 we quote only the energies of the RHF and the ferromagnetic solution of UHF. The energy of RHF is much lower than the energy of UHF. Both approaches have the correct dissociation limit. With increasing distances between the H_2 molecules the energies of the two solution approach the energy of isolated H_2 molecules.

Are these results relevant to the question of the existence of organic ferromagnetics? What seems to be relevant is the extremely large energy difference between the energies of the RHF approach and energies of the ferromagnetic state at the interatomic distances of interest. This will not change even if the correlation energy is included. The correlation energy is certainly larger for the solution from the RHF approach than for the ferromagnetic solution of the UHF. The inclusion of the correlation energy will favour the first solution (RHF) even more.

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