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Magnetic properties of Hubbard clusters: non-collinear spins in 3-atom clusters

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ABSTRACT. The ground-state magnetic properties of clusters with $N = 3$ atoms are studied by solving the single band Hubbard Hamiltonian in the unrestricted Hartree-Fock approximation. Three-dimensional arrangements of spins are considered in the solution. Results for the total energy and magnetic order, as a function of the Coulomb interaction strength U/t and number of electrons ν, are presented. For half-band filling an antiferromagnetic non-collinear spin arrangement is the most stable for the triangle structure. For $\nu = 2$ and $U/t \geq 16.2$, $\nu = 4$ and $U/t \leq 2.3$ the linear chain is the most stable structure. In particular, it is found that the inclusion of non-collinear spins improves in the Hartree-Fock ground-state energy as compared with collinear spins. Our results are compared and discussed with exact calculations.

RESUMEN. Las propiedades magnéticas del estado base de cúmulos con $N = 3$ átomos son estudiadas resolviendo el hamiltoniano de Hubbard para una banda en la aproximación no restringida de Hartree-Fock. Se consideran soluciones magnéticas con arreglos de espines no colineales. Se presentan los resultados de la energía total y el orden magnético en función de la intensidad de la interacción de Coulomb y el número de electrones. Para la banda semillena la solución más estable para la estructura triangular, corresponde a un arreglo antiferromagnético no colineal de espines. Para $\nu = 2$ y $U/t \geq 16.2$, $\nu = 4$ y $U/t \leq 2.3$ la cadena lineal es la estructura más estable. En particular, se encuentra que considerar espines no colineales mejora la energía del estado base de Hartree-Fock comparada con espines colineales. Se discuten y comparan nuestros resultados con soluciones exactas.

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1. INTRODUCTION

In recent years, the study of the magnetic properties of complex systems has been a subject of considerable research effort. Most of the theoretical and experimental studies on magnetism have been dedicated to the $3d$-transitions metals (TM) due to their fundamental relevance in both basic and applied science [1, 2]. In particular, the magnetic behavior of the itinerant electrons in the $3d$-TM is very sensitive to the geometric structure and to the local atomic environment. For instance, α-Fe (bcc) is ferromagnetic while γ-Fe (fcc) is weak antiferromagnetic. Therefore, a detailed study of the interplay between magnetism and geometrical structure and the stability of magnetism *versus* structural changes is of fundamental importance for the understanding of the magnetic phenomena.

Clusters offer the unique opportunity to study how the magnetic properties of a system consisting of an isolated atom change when more atoms are added with different geometries and, when as cluster size increases, bulk behavior is achieved. Nonetheless, *ab initio* results for the magnetic properties of clusters are a very difficult task due to the lack of symmetry. Therefore, one have to consider a model which is simple enough to allow at least an accurate solution and at the same time contains enough complexity to be able to shed light on the physics of real systems (*e.g.*, 3*d*-TM). In the past a considerable amount of results on clusters of 3*d*-TM have been found by using a tight-binding Hubbard Hamiltonian within the unrestricted Hartree-Fock approximation [3, 4].

Generally, theoretical results for clusters have been found by assuming collinear spins, *i.e.*, all the atomic spins pointing along a common direction. It is well known that when the band is half-filled the magnetic solution is antiferromagnetic, *i.e.*, each spin has its nearest neighbors pointing in the opposite direction to it. Nonetheless, when the geometrical arrangement of the atoms is such, that does not allow an array of spins as described above (*e.g.*, atoms positioned in the vertices of an equilateral triangle), then the structure is said to be antiferromagnetic frustrated. Thus, from physical grounds, one can expect that the cluster, if it is allowed by the current approximation, develops a non collinear arrangement of spins in order to reduce its energy [5, 6].

In the present work, we investigate the role of non-collinear spins on the magnetic properties of clusters of atoms by considering the Hubbard model within the unrestricted Hartree-Fock approximation. For the sake of simplicity we only consider into our calculations 3-atom clusters, since in this way, the number of possible cluster geometries is small and a systematic study of all of them can be done at the same time. Nonetheless our formalism is not limited by the cluster size.

2. THEORETICAL FRAMEWORK

2.1. MODEL HAMILTONIAN

The magnetic properties of the clusters are obtained by considering a single-band Hubbard Hamiltonian [7]

$$H = -t \sum_{\langle i,j\rangle,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}. \tag{1}$$

In Eq. (1), i and j stand for the atomic sites of the cluster, $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) refers to the one-particle creation (annihilation) operator in the local $|i\sigma\rangle$ basis and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ to the particle-number operator in the i-site with spin σ. For a given number of electrons ν, the only parameter of the Hubbard Hamiltonian is the Coulomb-interaction strength U/t.

Notice that the first term in Eq. (1), takes into account the kinetic energy due to the electronic motion throughout the cluster. The second term, gives the Coulomb energy contribution due to the double occupations of the electrons in the atomic sites. As it is evident, there is a competition between these two terms. On the one hand, the electrons tend to delocalize in order to gain kinetic energy, on the other hand, and opposite to this mechanism, is the increase in the Coulomb energy due to local charge fluctuations which occur when the electrons delocalize. Therefore, the many-body state is a delicate balance between these terms in which, electronic correlations play an important role by reducing the double occupations in a mutually avoided motion.

2.2. THE UNRESTRICTED HARTREE-FOCK APPROXIMATION

Although that an exact treatment of electrons correlations is necessary for a correct description of the many-body solution of N-atoms clusters, most of the physics involved in the problem, in particular the magnetic properties, may be captured with the use of the unrestricted Hartree-Fock (UHFA) approximation. The main assumption on any type of Hartree-Fock approximation, is that the ground state of the Hamiltonian can be approximated by a single Slater determinant in a basis of one electron states, which minimizes the total energy

$$|\Psi_{\mathrm{HF}}\rangle = \prod_{k=1}^{\nu} a_k^{\dagger}|0\rangle. \tag{2}$$

$|\Psi_{\mathrm{HF}}\rangle$ denotes the occupied Hartree-Fock ground state, $a_k^{\dagger}$ is the creation operator for an electron in the k-level of the cluster, ν is the total number of electrons ($1 \leq \nu \leq 2N$), and $|0\rangle$ is the vacuum state. In order to allow three-dimensional arrangements of the local spins, the creation operator is written as

$$a_k^{\dagger} = \sum_{i\sigma} A_{i\sigma}^{k} c_{i\sigma}^{\dagger}. \tag{3}$$

The single-particle density matrix is determined in terms of the complex coefficients $A_{i\sigma}^{k}$

$$\rho_{i\sigma,j\sigma'} = \langle c_{i\sigma}^{\dagger} c_{j\sigma'}\rangle = \sum_{k=1}^{\nu} \bar{A}_{i\sigma}^{k} A_{j\sigma'}^{k}, \tag{4}$$

where $\langle c_{i\sigma}^{\dagger} c_{j\sigma'}\rangle$ refers to the average value of the operator $c_{i\sigma}^{\dagger} c_{j\sigma'}$ in the HF ground state, which is obtained by minimizing the total energy $\langle H\rangle$, with respect to variations on the set $\{A_{i\sigma}^{k}\}$. Taking into account all these considerations, the self-consistent Hartree-Fock equations (SHFE) can be read as

$$-t{\sum_{j}}' A_{j\sigma}^{k} + U\left(\rho_{i\bar{\sigma},i\bar{\sigma}}\, A_{i\sigma}^{k} - \rho_{i\bar{\sigma},i\sigma}\, A_{i\bar{\sigma}}^{k}\right) = \varepsilon_k A_{i\sigma}^{k}. \tag{5}$$

In equation (5) ε_k corresponds to the single-particle level, the prime in the summation denotes that it is restricted to the nearest-neighbor sites of the site i. For a given self-consistent solution of Eq. (5), all the physical quantities of interest can be determined in terms of the density matrix, for example the Cartesian components of the local spin vector at site i:

$$\begin{aligned}\langle S_i^x\rangle &= \mathrm{Re}\left(\rho_{i\uparrow,i\downarrow}\right),\\ \langle S_i^y\rangle &= \mathrm{Im}\left(\rho_{i\uparrow,i\downarrow}\right),\\ \langle S_i^z\rangle &= \tfrac{1}{2}\left(\rho_{i\uparrow,i\uparrow} - \rho_{i\downarrow,i\downarrow}\right).\end{aligned} \tag{6}$$

Note that, if $\rho_{i\uparrow,i\downarrow} = 0$ for all i, the spins are collinear. In the present approximation, the HF state is not an eigenstate of the total spin operator S^2, due to this fact, the spin quantum number S is calculated through out the average

$$\langle\Psi_{\rm HF}|S^2|\Psi_{\rm HF}\rangle = S(S+1). \tag{7}$$

However, we will discuss later that this symmetry breaking solution improves in the total energy as compared with the restricted Hartree-Fock method.

3. RESULTS

From the point of view of the Hubbard Hamiltonian, there are only two structures with three sites to be considered, they are the equilateral triangle and the linear chain. Notice that the triangle is more compact than the linear chain with an average coordination number $\bar{z} = 2$, and $\bar{z} = \frac{4}{3}$ for the linear chain. For a 3-sites cluster, in the context of the Hubbard Hamiltonian, the representative values of the band filling are $\nu = 2$, 3, 4. Moreover, for these values of ν we can calculate the exact ground-state vector of the Hamiltonian. Therefore, these simple systems offer a good opportunity to learn—by comparing the Hartree-Fock ground state with the exact one—what is the main role of the electronic correlations on the magnetic solution, and furthermore, to what extent the Hartree-Fock state can be considered as a good approximation to the exact ground state.

3.1. BAND-FILLING $\nu = 2$

This is a two-electron problem, indeed the simplest one in the many-body problem. However, this simple system when it is solved exactly within the Hubbard model, it exhibits the behavior characteristic of a strongly correlated system [8]. Concerning the Hartree-Fock solution although it gives good insight into the problem for instance, the kind of spin-spin correlations, local magnetic moments, etc., it fails to yield the correct stability between the structures as the electron correlations increase in importance.

Figures 1a, 1b, and 1c show the Hartree-Fock energies for the considered two structures as a function of U/t. For $U/t \geq 16.2$ the linear chain is the most stable structure. This is in contrast to the exact results, in which the triangle has the lowest ground state energy in the whole range of U/t with total spin quantum number $S = 0$. At small values of U/t ($U/t \leq 4.5$ for the triangle and $U/t \leq 2.2$ for the linear chain), both structures have total spin quantum number $S = 0$, having zero values of the local magnetic moments. In the triangle, the charge distribution is quite uniform (all the sites are equivalent), and in the linear chain there is a tendency to allocate charge in the central site due to its large local bandwidth relative to its neighbor sites. In this regime (paramagnetic phase), the ground state is dominated by the kinetic energy part of the Hamiltonian, as it can be inferred from Fig. 1b; the average value of the kinetic-energy operator in the Hartree-Fock state is approximately equal to the value at $U = 0$ and the average value of the Coulomb-energy operator varies linearly with U/t (see Fig. 1c). Therefore, the stability of the triangle over the linear chain in this regime is mainly determined by its highest average coordination number, which allows the electrons to be more delocalized

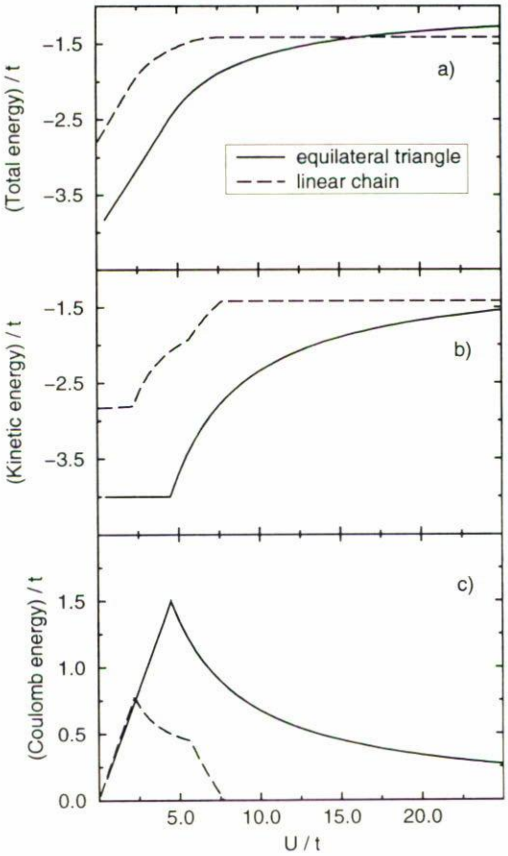

FIGURE 1. Hartree-Fock energies as a function of U/t for the triangle and the linear chain with $\nu = 2$.

than in the linear chain. Nevertheless, the approximated Hartree Fock solution with local magnetic moments equal to zero may yield to wrong conclusions concerning the main features of the ground state in this regime [9]. This can be seen in Fig. 2, where the average value of the kinetic-energy operator for the triangle of the exact solution and the present approximation is given. Notice the abrupt change of the kinetic energy by using the Hartree Fock approximation at about $U/t \approx 4.5$. Beyond this value of U/t, a new solution emerges. In contrast, by solving the Hamiltonian exactly, the variation of the kinetic energy is rather smooth in the whole range of U/t. In both structures, the main features of this new solution are a strong reduction of the Coulomb energy (see Fig. 1c), and the development of local magnetic moments (local spins); although the charge distribution through out the cluster remains the same. Nonetheless, this changes result in a decreasing (localization) in the absolute value of the kinetic energy being this effect stronger in the Hartree-Fock solution than in the exact one (see Fig. 2 for $U/t > 5.4$). Notice that as a typical mean field calculation, the repulsive Coulomb energy is overestimated and the effect becomes critical as U/t is further increased.

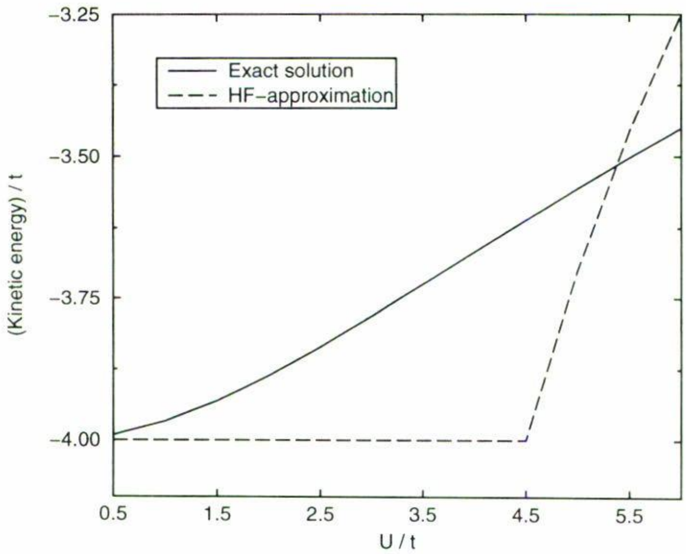

FIGURE 2. Average value of the kinetic-energy operator for the triangle in the exact ground state (solid line) and in the Hartree-Fock approximation (dashed line) as a function of U/t with $\nu = 2$.

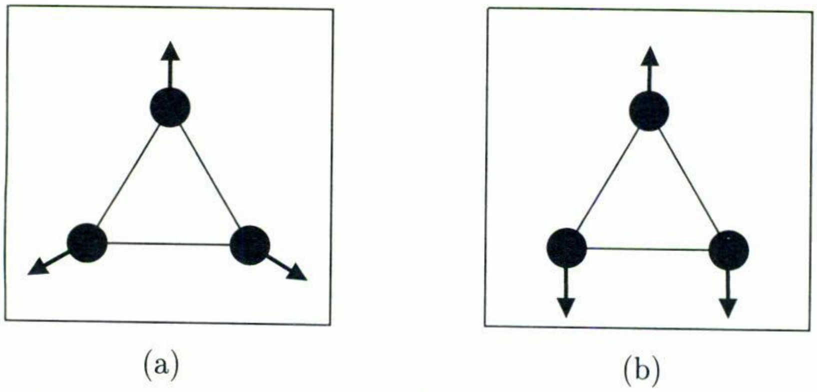

FIGURE 3. Local spin vectors for the triangle. In (a) the spins are non-collinear, which corresponds to the Hartree-Fock solution with $\nu = 2$ for $U/t > 4.5$ and to the lowest energy solution with $\nu = 3$ for all values of U/t. In (b) the lowest energy solution having collinear spins with $\nu = 3$.

The magnetic solution for the triangle yields a non integral value for the spin quantum number and a non-collinear arrangement of the local spins. This arrangement of the spins lie on a plane as shown in Fig. 3a, and the total spin vector $\vec{S} = (\langle S^x \rangle, \langle S^y \rangle, \langle S^z \rangle) = \sum_i (\langle S_i^x \rangle, \langle S_i^y \rangle, \langle S_i^z \rangle)$ is equal to zero. The fact that the total spin vector is equal to zero, and that the charge distribution remains the same as in the previous paramagnetic solution is indicative that the system is still trying to be in the lowest spin state $S = 0$ but the Hartree-Fock solution breaks rotational symmetry. The arrangement of the local spins clearly shows a trend toward antiferromagnetic spin-spin correlations. This is the

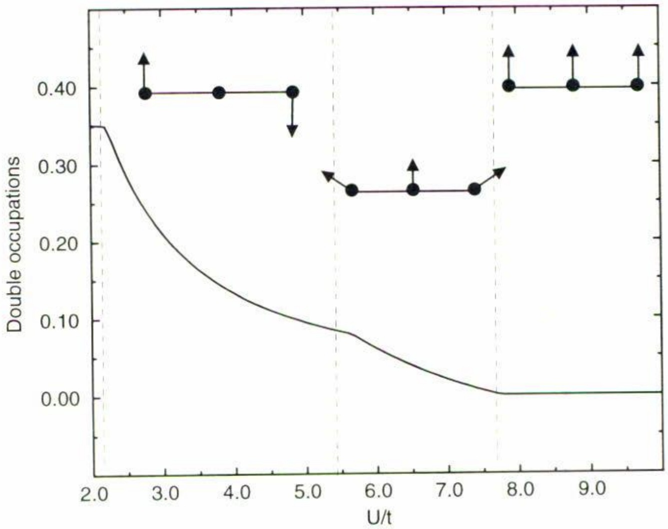

FIGURE 4. Double occupations of the linear chain with $\nu = 2$ as a function of U/t, the different kind of solutions are separated in regions by a vertical dashed line; the insets represent the spin arrangements.

actual behavior of the exact solution, but the correlations are less stronger in the Hartree-Fock solution.

The behavior of the linear chain is more diverse. For intermediate values of U/t ($2.2 \leq U/t \leq 7.7$), we found two different solutions (see Fig. 4); one with collinear arrangement of the spins ($2.2 \leq U/t \leq 5.4$) and other with non-collinear spins ($5.4 \leq U/t \leq 7.7$). The collinear solution starts as U/t is further increased from 2.2, its features are similar to those of the triangle, *i.e.*, $\langle \vec{S} \rangle = 0$, and the charge distribution is the same as in the paramagnetic phase. Moreover the central site has no local moment, the outer and less coordinated atomic sites have antiparallel moments. Again the arrangement of the local spins resemble the sort of spin-spin correlations found in the exact solution. The second and non-collinear solution appears almost at the middle of the interval ($U/t \approx 5.4$). Its principal features are a sudden increase from a small value of S towards $S = 1$, partially inclusion of ferromagnetic spin-spin correlations ($\langle S_i \cdot S_j \rangle > 0$ for $i \neq j$), and $\langle \vec{S} \rangle \neq 0$ with only one component. Moreover, the charge distribution is the same as in the ferromagnetic phase. For $U/t \geq 7.8$ the solution turns on the ferromagnetic solution $S = 1$ (ferromagnetic phase).

Concerning the stability of the solutions, there are two main deviations of the present approximation from the exact ground state. One is the stabilization of the linear chain over the triangle for $U/t \geq 16.2$. The other is that the solution for the linear chain is ferromagnetic ($S = 1$) for $U/t \geq 7.8$ while the exact ground state shows that ferromagnetism is stabilized only in the $U = \infty$ limit (Nagaoka's theorem [10]). The onset of ferromagnetism at a finite value of U/t is well understood. Due to symmetry requirements in the $S = 1$ state there can be no double occupied sites resulting in a Coulomb energy equal zero. Thus, the Hartree-Fock energy in the ferromagnetic solution is exact and is a constant for all U/t. Furthermore, me may notice that this state for finite U/t

corresponds to the first excited state of the exact solution. Hence the onset of ferromagnetism is a level crossing in the spectrum of the Hartree-Fock energy. Due to the neglection of electronic correlations, the non-ferromagnetic solution lies above the ferromagnetic one. This is the reason why the Hartree-Fock energy for the triangle is greater than for the linear chain for $U/t \geq 16.2$.

3.2. BAND-FILLING $\nu = 3$

It is well known that at half band filling the Hubbard Hamiltonian leads to the Antiferromagnetic Heisenberg Hamiltonian for $U/t \to \infty$. In transition metals, antiferromagnetism is found for low values of the effective exchange interaction parameter J/W at the middle of the d band (here, J refers to the Coulomb exchange integral and W to the band width). From a local moment picture of magnetism, a solution is said to be antiferromagnetic, if the nearest neighbors moments of one atomic site in the lattice are pointing on the opposite direction. This requires the lattice to be formed by two interpenetrating sublattices, one for each moment direction. If this is not the case, the structure is said to be frustrated. Clearly the linear chain being bipartite corresponds to the first case. Its lowest energy HF solution is antiferromagnetic and nothing new can be learn from it. The triangle, in agreement with the exact calculation, is the more stable between the two considered structures at this band filling ($\nu = 3$), and also shows a more interesting behavior. It is not hard to see that the magnetic characteristics of the spins correspond to a frustrated structure. This structure offers a good example to see the physics behind the non-collinear spins. In order to see the role of non-collinearity of the spins, two kinds of solutions for the triangle are studied in the present work, one with collinear spins (CS) and the other with non-collinear (NCS). The solution with collinear arrangement has two spins pointing in a given direction and one in the opposite (see Fig. 3b), the charge distribution is not uniform and favors slightly more charge in the sites with the same spins. The arrangement of the spins in the CS, clearly indicate a tendency toward antiferromagnetism but with a frustrated structure. If the restriction of collinear spins is relaxed, a non-collinear spin solution with lower energy is obtained. The spin directions are the same as in Fig. 3a and the charge distribution is uniform. Furthermore, the spins have the full symmetry operations of the triangle. One can argue from this solution that the frustration is partially removed, all the spins have an antiferromagnetic component with respect to both neighbors. This can be better appreciated in the spin-spin correlations which are clearly antiferromagnetic. Concerning the trends on the stability Fig. 5 shows the total energy differences between the CS and NCS calculations. The difference in the energy components are also shown for comparison. Positive values in the total energy, means that the NCS solution has a lower energy, and in the kinetic energy means a larger delocalization for the electrons in the NCS relative to the CS. A positive difference for the Coulomb energy corresponds to a reduction of the double occupations of the NCS relative to the CS. With this in mind, Fig. 5 shows that for small values of U/t the NCS has smaller double occupations. This is mainly due to the fact that the charge spreads uniformly in the NCS. Although the electrons in the NCS solution are more localized (smaller kinetic energy) than the CS solution, the gain in the kinetic energy is not enough for the CS to be the lowest energy solution. For large

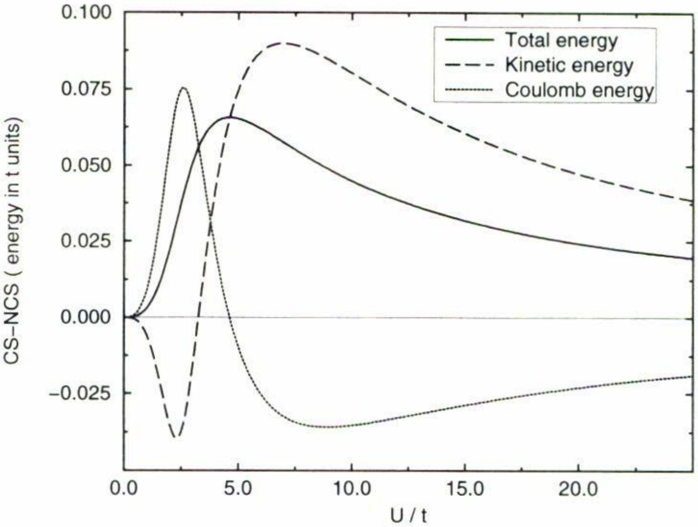

FIGURE 5. Energy difference for the triangle between collinear spin (CS) and non-collinear spin (NCS) solutions as a function of U/t.

values of U/t which is the regime for saturation of the spins, the electrons in the NCS are much more delocalized than the those of the CS solution. This is due to the symmetry of the NCS solution which allows a smaller kinetic energy lost upon magnetization. In contrast, the bond formed in the CS between the two sites with the same spins is now almost broken due to the saturation of the spins.

3.3. BAND-FILLING $\nu = 4$

Since the linear chain is bipartite, the results for this structure at this band filling remain the same as for $\nu = 2$. For $U = 0$ the triangle is degenerate in its last two paramagnetic levels. This result causes the triangle to be ferromagnetic ($S = 1$), for all $U > 0$. It may be argued that the stability between these structures is determined by this fact. The ferromagnetic state in the triangle always has lower energy than the ferromagnetic state in the linear chain. This is due to the large average coordination number of the triangle. On the other hand, for small values of U/t ($0 \leq U/t \leq 5.3$) the linear chain in the paramagnetic state yields the lowest energy.

4. SUMMARY

In this work the magnetic properties of clusters of $N = 3$ atoms have been studied by solving the Hubbard Hamiltonian within the unrestricted Hartree-Fock approximation, which allows three dimensional arrangements of spins. It has been found that close to half band, antiferromagnetic frustrated structures may develop a non-collinear spin solution having the lowest HF-energy. Moreover, for non-frustrated clusters (as is the case of the linear chain), a non-collinear spins solution may be found. Therefore, at least for frustrated clusters at half-band filling, one has to take into account the possibility of non-collinear solutions when using the Hartree Fock approximation. In comparison with exact calculations we found that our results for the spin-spin correlations with non-collinear spins are in very good agreement with exact calculations. Concerning the magnetic moments and total energy, the Hartree-Fock calculations overestimates the local moments and total energy. Calculations for larger clusters are currently in progress.

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