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Electron correlation effects on the electronic properties of clusters

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Abstract. The Hubbard model is applied to icosahedral, face-centered cubic (FCC), hexagonal close-packed (HCP), and body-centered cubic (BCC) clusters having $N = 13$ atoms. Exact ground-state results are given as a function of the Coulomb repulsion strength U/t, number of electrons ν, and total spin S. Electron correlation effects on magnetic behavior and structural changes are discussed.

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1 Introduction

Electron correlations in finite systems, and the many-body effects which result from them, are subjects of main interest in current cluster research. As in the solid state, magnetism is one of the most fascinating and challenging related problems. Consequently, a large body of experimental and theoretical work has been focused on this subject [1, 2]. Most theoretical studies of cluster magnetism have been performed using a mean-field treatment of the electron–electron interactions such as the unrestricted Hartree–Fock or local spin density approximations [2]. Still, a detailed understanding of the electronic correlations responsible for the magnetic behavior of clusters is important, not only from a fundamental standpoint, but also in view of the description of more delicate properties, such as excitation spectra and temperature dependences. Full many-body calculations of magnetic properties have been achieved only by the application of simple models, mainly the Hubbard model [3], to systems with a small number N of atoms [4, 5]. While rigorous results have been obtained for $N \leq 8$, the properties of larger systems remain largely unexplored. It would therefore be interesting to extend the size range covered by these investigations.

Our purpose in the present contribution is to discuss several ground-state and excited-state properties of clusters having $N = 13$ atoms in the framework of the Hubbard model. Electron correlations are treated exactly within Lanczos' numerical diagonalization method. The structural dependence of the magnetic properties is studied by the consideration of four different geometries: icosahedral clusters, which maximize the average coordination number, face-centered cubic (FCC) and hexagonal close-packed (HCP) clusters, which are examples of compact structures found in the solid state, and body-centered cubic (BCC) clusters, as an example of a rather open bipartite structure [6]. These clusters, which are formed by a central atom and its nearest neighbors (NN) in the corresponding lattices, are representative of the various types of geometries found in rigorous optimizations for $N \leq 8$ [5]. At $N = 13$ in particular, the compact structures (FCC, HCP, and icosahedral) have a complete NN shell. In the following section, the model Hamiltonian and the method of calculation are briefly recalled. A summary of results on the ground-state magnetic behavior and on the relative stability of the different structures is discussed in Sect. 3.

2 Theory

The magnetic properties of clusters are determined by the consideration of the Hubbard Hamiltonian [3], which in the usual notation is given by

$$H = -t \sum_{\langle i,j \rangle,\sigma} \hat{c}^{\dagger}_{i\sigma}\, \hat{c}_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow}\, \hat{n}_{i\downarrow}\,. \qquad (1)$$

The first term is the kinetic-energy operator, which describes the electronic hopping between NN sites i and j that lead to electron delocalization and bond formation ($t > 0$). The second term takes into account the intra-atomic Coulomb repulsion, which is the dominant contribution from the electron–electron interaction ($U \geq 0$) [3]. The model is characterized by the number of electrons ν (or band filling ν/N) and by the dimensionless parameter U/t, which measures the importance of correlations. $U/t = 0$ corresponds to the uncorrelated tight-binding or Hückel

model, while for $U/t = \infty$ (strongly correlated limit), double electron occupations are forbidden on every site. The electronic behavior results from the interplay between kinetic and Coulomb energies, which depends on U/t and on the total spin S.

The properties of the Hubbard Hamiltonian are determined by expanding its eigenfunctions $|\Psi_l\rangle$ ($|\Psi_0\rangle$ = ground state) in a complete set of basis states which have definite electron-occupation numbers on all orbitals $i\sigma$ [7]. $|\Psi_l\rangle$ is written as

$$|\Psi_l\rangle = \sum_m \alpha_{lm} |\Phi_m\rangle \,, \tag{2}$$

where the $|\Phi_m\rangle$ describe all possible electronic configurations in real space ($\hat{n}_{i\sigma}|\Phi_m\rangle = n^m_{i\sigma}|\Phi_m\rangle$, with $n^m_{i\sigma} = 0$ or 1). In practice, taking into account all configurations may involve an important numerical effort, which limits considerably the size of the clusters under study. For instance, the dimension of the $S_z = 1/2$ ($S_z = 0$) subspace is of the order of 10^6 (10^7) for $N = \nu = 13$ ($N = \nu = 14$).

In the present work, we use a Lanczos iterative method which allows us to determine the lowest-energy eigenstate for each value of S [8,9]. If the ground state is sought, we usually work in the subspace of minimal S_z ($S_z = 0$ or $1/2$), i.e., no restrictions are imposed on S. The actual ground-state spin is determined, once convergence is achieved, by the application the total spin operator $\hat{S}^2$. For other values of S, we use higher values of S_z, and projection operations of the form

$$|0\rangle = \left[\hat{S}^2 - S'(S'+1)\right] |\tilde{0}\rangle \tag{3}$$

in order to remove unwanted components of spin S' from the Lanczos starting vector $|0\rangle$. This restricts the spin of the Krylov series and of the computed eigenstate $|\Psi_l\rangle$. The convergence of the energy eigenvalue E_l is monitored as a function of the number of Lanczos iterations M, and the sequence is interrupted once $|E(M) - E(M-5)| < \varepsilon$. In this way, the ground state and low-lying excited states are obtained exactly within a controlled accuracy ε. In the present calculations $\varepsilon \simeq 10^{-10}$ t.

3 Results and discussion

In Table 1 the ground-state spin of icosahedral, FCC, HCP, and BCC clusters having $N = 13$ atoms is given. The results correspond to the Hubbard model in the limit of very strong Coulomb repulsion (i.e., $U/t \to +\infty$). This is a particularly interesting limit from the point of view of correlations, and it provides the most favorable conditions for magnetism. For low electron or hole [10] concentrations, the ground-state spin S can be understood by applying Hund's first rule to the single-particle (SP) spectrum of the cluster as if it were a single structured atom. Thus, magnetic states ($S \geq 1$) are obtained when orbital degeneracies are present, or sometimes when the SP excitation energies are small. This is the case, for example, in the FCC, HCP, and icosahedral structures for $\nu = 4$–6, where a 3-fold degenerate SP level is partially filled at $U = 0$. A similar situation is found for a small number of holes $\nu_{\rm h} = 2N - \nu$. For instance, a saturated spin $S = 3$ ($S = 3/2$) is obtained in the FCC (icosahedral) cluster, with $\nu_{\rm h} = 6$ ($\nu_{\rm h} = 3$), since a 6-fold (3-fold) degenerate SP level is half filled. A particular effect is observed in the 13-atom FCC cluster for $\nu_h = 2$ and 3. Here we find that two different S are degenerate for all $U/t \geq 0$, which implies that a singlet (doublet) ground state can be formed that has no empty-site configurations – no double hole occupation on the same site – just as in the fully polarized triplet (quartet). Otherwise, the degeneracy would not hold for all U/t, since $\partial E/\partial U = \sum_i \langle n_{i\uparrow} n_{i\downarrow}\rangle$. The exceptionally large 6-fold degeneracy of the highest antibonding state seems to be at the origin of this effect, which was not observed in the other cases. In the absence of degeneracies, the ground state has usually the minimum spin multiplicity (small ν or $\nu_{\rm h}$). For example, in the BCC structure, there are no degeneracies at the extremes of the SP spectrum, and thus S is minimal for $\nu \leq 9$ and $\nu \geq 17$ (see Table 1) [11].

The previous Hund-rule-like magnetic behavior is of course expected for small or moderate U/t. However, it is remarkable that it holds even in the limit of very large Coulomb repulsion. Two main reasons contribute to the validity of this simple interpretation: the presence of well-defined groups of levels having the same or almost the same energy, and the fact that the carrier concentration is low. Moreover, these results reflect

Table 1. Ground-state spin S in the limit of $U/t = \infty$ of icosahedral, FCC, HCP, and BCC clusters having $N = 13$ atoms and ν electrons. For $\nu = N$, S corresponds to $U/t = 256$. The FCC structure with $\nu = 23$ and 24 shows ground-state spin degeneracy.

ν	Icos.	FCC	HCP	BCC
2	0	0	0	0
3	1/2	1/2	1/2	1/2
4	1	1	1	1
5	3/2	3/2	3/2	1/2
6	1	1	1	0
7	1/2	1/2	1/2	1/2
8	0	0	0	0
9	1/2	1/2	1/2	1/2
10	1	0	0	5
11	1/2	1/2	1/2	7/2
12	0	0	0	6
13	1/2	1/2	1/2	3/2
14	6	6	6	6
15	7/2	9/2	9/2	7/2
16	4	4	4	5
17	9/2	9/2	9/2	1/2
18	3	3	4	0
19	1/2	5/2	1/2	1/2
20	1	3	1	0
21	3/2	5/2	1/2	1/2
22	2	2	2	1
23	3/2	1/2, 3/2	3/2	1/2
24	1	0, 1	1	0

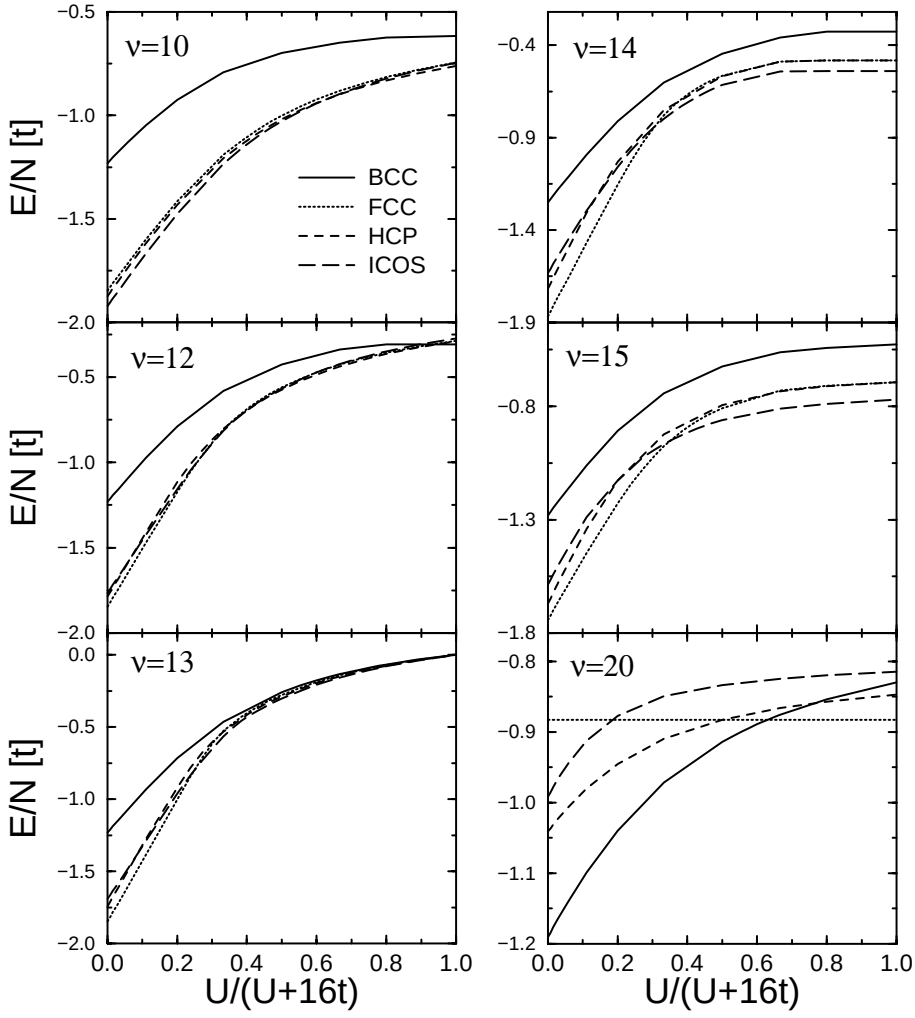

Fig. 1. Ground-state energy per atom of 13-atom clusters as a function of $U/(U+16t)$. The cluster structures and the number of electrons ν are indicated.

the importance of electron correlations for determining the relative stability of states having different magnetic behaviors. In fact, in the Hartree–Fock approximation, the energy of low-spin states is so overestimated that for large U/t, a ferromagnetic-like ground state is always favored.

An interpretation of the magnetic properties in terms of the SP spectrum is no longer possible close to half-band filling ($0.5 < \nu/N < 1.5$) where a more complex competition between low-spin and high-spin states is observed. For $0.5 < \nu/N \leq 1$ the compact structures show low-spin states, in most cases with the minimum spin multiplicity ($S = 0$ or $1/2$) [12]; see the results for the FCC, HCP, and icosahedral clusters for $\nu = 10$–13. In contrast, the BCC structure develops large magnetic moments for $\nu =$ 10–12 and 14–16 [11]. In some cases, S is saturated for $U/t = \infty$. At half-band filling, the 13-atom BCC cluster has $S = 3/2$ for all U/t [12], in agreement with a theorem demonstrated by Lieb for the case of an even number of sites N [13]. The theorem states that for all $U > 0$, the ground-state spin S of the half-filled Hubbard Hamiltonian on a bipartite lattice is $S = |N_A - N_B|/2$, where N_A and N_B are the number of sites belonging to the two sublattices A and B ($N = N_A + N_B$ even) [13]. Physically, the result may be visualized as the spin of a perfect antiferromagnetic Néel state with sublattice magnetizations $N_A/2$ and $-N_B/2$, which need not cancel each other. For $\nu > N$, the compact structures, which are also the most stable geometries at these band fillings, develop large magnetic moments. For $\nu = N + 1 = 14$, all structures show saturated ferromagnetism, as predicted by Nagaoka's theorem ($U/t = +\infty$) [14]. A strong tendency to ferromagnetism is also observed for $\nu/N = 1.2$–1.4. In particular, for $\nu = 17$, all compact structures show the same maximal $S = 9/2$.

In Fig. 1, the ground-state energy of 13-atom clusters are given as a function of U/t, for the different considered structures and for representative numbers of electrons in the range $10 \leq \nu \leq 20$. For smaller or larger ν, the most stable geometries (among the considered ones) are the icosahedron for $\nu \leq 9$ and the BCC structure for $\nu \geq 21$. This holds for all values of U/t, i.e., the geometry which yields the lowest kinetic energy (uncorrelated limit) remains the most stable one, irrespective of the strength of the intra-atomic Coulomb interaction. In these cases, the corresponding ground state S is small, though not always minimal. $S \geq 1$ is also observed, even for small U/t, as a result of the polarization

of degenerate or quasi-degenerate SP levels. One concludes that for low carrier concentrations (electrons or holes), the effects of Coulomb interactions are considerably reduced by correlations, so that the magnetic and geometric structures of the clusters are dominated by the kinetic term. As already observed in smaller clusters ($N \leq 8$ [5]) for small ν, the most compact structures (e.g., icosahedra) yield the lowest energy, while for small $\nu_{\rm h}$, rather open bipartite structures (e.g., BCC) are the most stable. This can be qualitatively understood in terms of the SP spectrum. In the first case (small ν), the largest stability corresponds to the largest bandwidth for bonding states, which is achieved by the most compact structure ($\varepsilon_b \leq -\bar{z}t$). In the second case (small $\nu_{\rm h}$) the largest stability is obtained for the largest bandwidth for antibonding (positive-energy) states which corresponds to bipartite structures.

Close to half-band filling ($10 \leq \nu \leq 20$), the effects of correlation on structure and magnetism are more important. Several structural changes are observed as a function of U/t. For $\nu = 10$–13, the compact structures have very similar energies, particularly for large U/t. For $\nu = 10$, the most stable geometry is the icosahedron if $U/t < 27.19$ and the HCP cluster otherwise. For $\nu = 12$, a more complex sequence of structures is obtained: FCC for $U/t < 5.79$, icosahedral for $5.79 < U/t < 10.94$, HCP for $10.94 < U/t < 260.9$, and finally, BCC for $U/t > 260.9$. In the last case (BCC structure), the ground state shows saturated ferromagnetism ($S = 6$), while in all other cases, $S = 0$. It is in fact the onset of ferromagnetism that stabilizes the BCC structure with respect to the compact structures as the Coulomb repulsion increases. For $\nu = 13$, the spin of the lowest-energy geometry is always $S = 1/2$, corresponding to frustrated antiferromagnetism. In contrast, for $\nu = 14$ and 15, the change from FCC to icosahedral structure is accompanied by an important increase of the total magnetic moment. For example, for $\nu = 15$, $S = 1/2$ in the FCC structure ($U/t < 24$), and $S = 5/2$ or $7/2$ in the icosahedron ($U/t > 6.5$). One concludes that these structural changes are driven by ferromagnetism. Notice that the high-spin states have a nearly completely filled majority band ($\nu > N$), and therefore the structural stability is dominated by the minority electrons. Since the minority band contains a small number of electrons, the most compact structures (icosahedral or FCC) are favored when ferromagnetism dominates at large U/t. A similar situation is found for $\nu = 20$. In the FCC structure, the spin is saturated ($S = 3$) already for very small U/t, and consequently, the ground-state energy is independent of U/t. In contrast, the BCC structure, which yields the lowest kinetic energy and is therefore the most stable for small U/t, has $S = 0$ for all U/t, and the HCP and icosahedral clusters have $S \leq 1$. Since the low-spin structures are destabilized by an increase in the Coulomb repulsion U/t, the FCC geometry yields the lowest energy in the strongly correlated limit.

To conclude, it is important to recall that the limited set of structures considered in this paper does not necessarily include the most stable one. In fact, previous geometry optimization studies of small clusters ($N \leq 8$) have already shown that the symmetry of the optimal structures is often reduced by distortions or rearrangements of bonds [5]. This could also affect the magnetic behavior, since lower-symmetry structures may be found that are stabilized by the removal of SP degeneracies (the Jahn–Teller effect), and which then often show minimal S. In order to explore the problem, we have considered a few additional structures for $N = 13$, which are derived from the perfect FCC and icosahedral clusters by the distortion of the cluster surface (e.g., by the removal of one or two surface bonds). As in smaller clusters, one observes that distortions may result in an energy lowering at intermediate values of U/t, thereby improving the ground-state geometry. In any case, the calculated energy differences are very small (see Fig. 1 for $\nu = 13$), which suggests that similar structures may easily coexist at finite temperatures (small surface melting temperatures). For definitive conclusions on the interdependence of correlations, magnetism and cluster structure in this size range, geometry optimization studies would be useful.

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