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Electronic correlation effects on the properties of an half-filled octahedron cluster in a magnetic field

R.J. Tarento[a], P. Joyes, and J. van de Walle

Laboratoire de Physique des Solides, bâtiment 510, Université Paris-Sud, 91405 Orsay, France

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Abstract. The present study focuses on electronic correlation effects on magnetic energy, the spin-spin correlation function of an octahedron cluster in the (3↑, 3↓) electronic configuration threaded by a magnetic field. Some other spin configurations are also discussed and various field directions are considered. An accurate diagonalisation technique has been used to solve the Hubbard Hamiltonian. A result is analysed on a linear energy stabilisation at low magnetic flux. Moreover, two types of antiferromagnetic transition *versus* the flux occurring for a correlation term larger than a critical one have been observed, *i.e.* the likelihood of a charge excitation before the antiferromagnetic transition. Finally, a comparison between the results obtained from the exact diagonalisation and the Gutzwiller method has been carried out, leading to a suggested modification of the Gutzwiller approach in order to improve it.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Cg Electronic and magnetic properties of clusters – 36.20.Kd Electronic structure and spectra

1 Introduction

In the last few years, the electronic response of small aggregates threaded by a magnetic flux has received much attention. Interest in the subject has been stimulated by the prediction of giant diamagnetism [1] or giant paramagnetism [2] and by the observation of mesoscopic currents in pure metallic nanostructures [3]. It is also worth mentioning the experimental study of the magnetoresistance of a mesoscopic semi-conducting ring which exhibits oscillations *versus* the flux with a period ϕ_0 [4], where ϕ_0 stands for the flux quantum

$$\phi_0 = \frac{hc}{e} \cdot$$

The difficulty in modelling the relatively large mesoscopic media has led many authors to consider smaller systems [5–9] with a limited number of electrons, the role of the various physical quantities being then more easily followed and grasped. In the present study, a 6-electron octahedron with one s orbital on each site has been observed and an accurate Hubbard Hamiltonian diagonalisation performed. The magnetic flux and the electron-electron interaction have been taken into account simultaneously. Such calculations have two applications, the first one being straightforward and giving the octahedron cluster behaviour *versus* the magnetic field (discussion of the ϕ-value can be seen below). A further purpose of our exact diagonalisation is to examine the effect of electronic correlation on permanent current. Such calculations have been made on small rings where the introduction of electronic interaction induces an antiferromagnetic instability [5]. Similar results on the electron configuration in aggregates threaded by a magnetic flux have been recently obtained. For example, the stability of charge density wave in a ring is studied in reference [6] by a spinless fermion model. One of the interests of the geometric structure (octahedron) studied here lies in the fact that it can be considered as a method shift from a 2 dimension mesoscopic system to a 3D one.

Most of the studies mentioned above have been calculated here for the non magnetic (3↑, 3↓) configuration. Roughly speaking, as will be seen below by the study of (4↑, 2↓) and (5↑, 1↓) configurations, the (3↑, 3↓) configuration is the most stable in the range of ϕ values available experimentally ($\phi < 10^{-4}$) (larger ϕ might be achieved nearby a vortex in a superconductor).

For larger ϕ values, the magnetic configurations become more stable due to the Zeeman effect. In this large field region only (3↑, 3↓) configuration has been focussed upon because this kind of study gives sheds some light on the effects of electronic correlation on permanent current in mesoscopic system, where ϕ/ϕ_0 could be 1. Hence our study of such a system for large ϕ values deals with the evolution of such physical quantities, and, as is traditionally the case, only the (3↑, 3↓) configuration [7] have been analysed here.

In our calculations three different directions (see Fig. 1) of the magnetic field have also been considered. One of our main results is the occurrence of an

[a] e-mail: tarento@lps.u-psud.fr

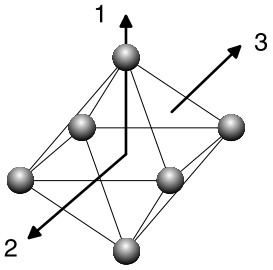

Fig. 1. The geometry of the cluster and the 3 studied magnetic field direction called 1, 2 and 3.

antiferromagnetic order in the atoms of the square perpendicular to the field, for an interatomic repulsion energy $U > U_c(\phi)$ where ϕ stands for the magnetic flux across the square. Surprisingly enough, the $U_c(\phi)$ function exhibits ϕ-region where U_c is large ($\cong$ 8 eV) as well as other ϕ-regions where U_c is smaller ($\cong$ 3.4 eV). As will be seen, these results are connected with two different types of antiferromagnetic transition.

2 The model

Matter magnetism has been intensively studied with the Hubbard Hamiltonian, chiefly for transition metal and cluster. The one band Hubbard Hamiltonian reads as:

$$H = -\sum_{\substack{\langle ij\rangle \\ \sigma}} t c^+_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \qquad (1)$$

The first term is the contribution due to electron hopping between nearest neighbour lattice sites. $c^+_{i\sigma}(c_{j\sigma})$ are the creation(annihilation) electron operators on site i with spin σ. The on-site interaction between electrons is described by the second term. For small clusters, an accurate solution can be reached through a numerical approach (*i.e.* exact diagonalisation (ED)) [8–10]. Such a procedure has been used by Pastor, Hirsch and Muschlegel [8] to investigate the effect of electron correlation on magnetism and the structure of small cluster as well as to supply information on the ground state and thermodynamic properties (specific heat...).

The presence of a magnetic field is taken into account within the London approximation [11], *i.e.* the molecular orbitals are a linear combination of gauge invariant atomic orbitals φ_j

$$\varphi_j = \exp\left(-\frac{\mathrm{i}e}{\hbar c}\mathbf{A}\cdot\mathbf{r}\right)\phi_j \qquad (2)$$

where ϕ_j stands for the orbital centred on the atom j, $\mathbf{A}$, the vector potential at point $\mathbf{r}$. The Hamiltonian is then accurately diagonalised in the complete 6-electron determinant basis. In the $(3\uparrow, 3\downarrow)$ case, the basis dimension is 400, while in the $(4\uparrow, 2\downarrow)$ and $(5\uparrow, 1\downarrow)$ configurations, it is 225 and 36 respectively.

Besides the various states energies, current J is investigated in each bond:

$$J_{ij} = -\frac{e}{2m}\int \mathrm{d}r(\varphi_i P\varphi_j + (P\varphi_i)^*\varphi_j)$$

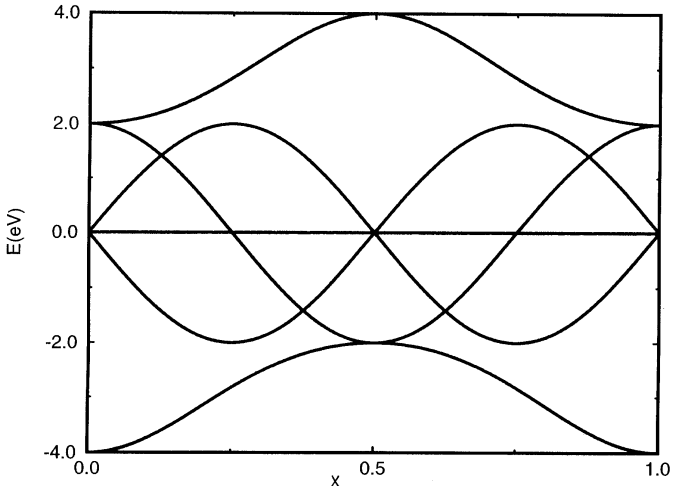

Fig. 2. One-electron energies E_{1-6}(eV) of an octahedron in a magnetic field perpendicular to the basis *versus* the flux ($x = \phi/8\phi_0$).

where $P = -\mathrm{i}\hbar\nabla + eA/C$.

The spin distribution in the molecule is obtained by calculating the spin-spin correlation function:

$$C_{\mu\nu}(j) = \frac{1}{4}\langle j|(n_{\mu\uparrow} - n_{\mu\downarrow})(n_{\nu\uparrow} - n_{\nu\downarrow}|\rangle \qquad (3)$$

where μ and ν denote sites, $|j\rangle$, an eigenstate.

In the various figures we let $|t| = 1$ eV. It is to be noticed that as our basis consists of s functions, the Zeeman contribution due to L_z is also zero.

Section 3 is not yet devoted to the results. Indeed, it has been deemed necessary, for a better understanding of the paper to study the effect of the magnetic flux and the electron-electron interaction separately. In the subsequent sections, the results are given and some conclusions drawn.

3 Separate study of the flux and of the electron repulsion effects

In this section, only the $(3\uparrow, 3\downarrow)$ configuration and field direction 1 (see Fig. 2) are focussed upon.

Let us first consider what happens when ϕ varies at $U = 0$. The one-electron energy levels are plotted *versus* the flux (in fact, *versus* $x = \phi/8\phi_0$), in the case when the magnetic field is along direction 1 which is perpendicular to the base built up with four atoms (Fig. 2). At $x = 0$, there are only 3 different levels (one non degenerate level at $-4|t|$, a 3-degenerate level at $E = 0$ and a 2-degenerate level at $E = 2|t|$). The magnetic field removing the level degeneracy, let us label the six one-electron levels E_1 to E_6, from the most stable to the less (for $x \cong 0$). Level E_1 is always the fundamental level; as for the other levels, crossings occur. Let us pay attention to the wave function. Levels E_1 and E_6 have contributions from all the cluster atoms; levels E_2, E_4, E_5 have only from the 4 atoms of octahedron square, as for level E_3 ($E_3 = 0$ for any x), only the off square atoms contribute.

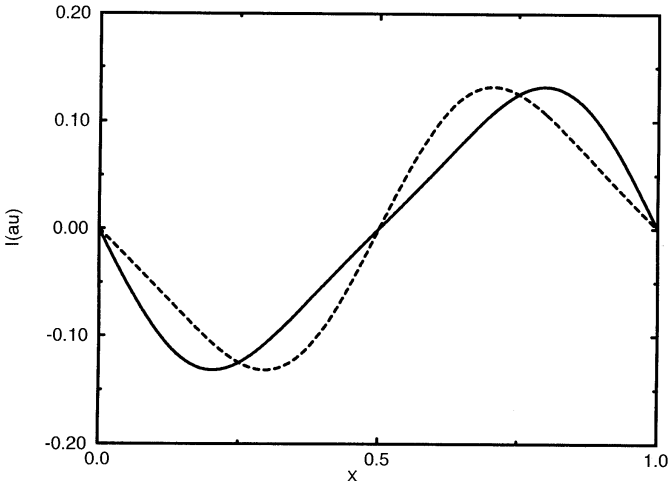

Fig. 3. The current in the bond between two atoms of the square *versus* the flux ($x = \phi/8\phi_0$) associated to one-energy levels: the lowest one E_1 (—), the highest one E_6 (- - -).

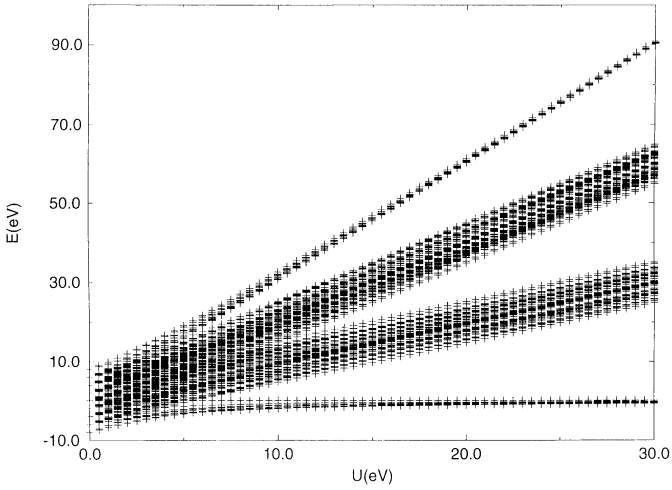

Fig. 4. Energy level distribution of the (3↑, 3↓) configuration *versus* the electronic correlation term U for $x = \phi/8\phi_0 = 0$.

The calculations show the occurrence of 2 cases (i) for levels E_1, E_2, E_4, E_5, E_6 the presence of a current only between two atoms of the square, (ii) for level E_3, the absence of current (this is the reason why the level is flux independent). The currents in states E_1 and E_6 are reported in Figure 3 for a magnetic field perpendicular to the base.

The level energy distribution *versus* U in the $\phi = 0$ case is given in Figure 4. As U increases: 4 bands appear, corresponding to states with 0, 1, 2, 3 doubly-occupied sites. The band separation with 0 and 1 doubly-occupied sites occurs at $U \cong 6$ eV, that between 1 and 2 doubly occupied sites at $U = 11$ eV and between 2 and 3 doubly occupied sites, at $U = 6$ eV. For the states with 0 and 3 doubly occupied sites, the bands are narrow, this being due to the fact that there is no direct hopping between configurations. As soon as the band with no doubly occupied sites is clearly separated from the others, *i.e.* for about $U > 6$ eV, the levels in the band can be described by the Heisenberg Hamiltonian, with an exchange energy $J = 4t^2/U$. This accounts for the fact that its width decreases as U increases. On the contrary, the energy levels in the second and third bands (with 1 or 2 doubly occupied sites) are mainly governed by the hopping term t. As a consequence their width ($\sim 10t = 10$ eV) is almost U independent.

4 Comparison of the (3↑, 3↓) and (4↑, 2↓) configurations for the three magnetic field directions

The ground state energy of the (3↑, 3↓) configuration *versus* ϕ is given in Figure 5a for various U values and also for different magnetic field directions (see Fig. 5b). Two interesting features will be discussed: the energy linear stabilisation for small ϕ values, and the presence of cusps for some particular ϕ values.

However, before dealing with these aspects, let us first examine the behaviour *versus* ϕ of another electronic configuration (4↑, 2↓), which has a Zeeman contribution. In Figure 5c, the energies of the (3↑, 3↓) and (4↑, 2↓) states are reported for $U = 0$, 1, 2, 3 eV at low ϕ ($\phi < 0.005$, ϕ-range including the experimentally available B values). For $U = 0$ with a magnetic field perpendicular to the octahedron base, state (4↑, 2↓) is slightly more stable, whereas for B inferior to 10 T, the energy difference is only less than a few 10^{-3} eV. For $U \neq 0$ eV, $U = 1$, 2, 3 eV respectively, configuration (3↑, 3↓) is the most stable, up to a critical field

$$B_c(U) = 16\ \text{T}, 63\ \text{T}, 141\ \text{T} \quad \text{for field direction 1}$$
$$B_c(U) = 21\ \text{T}, 93\ \text{T}, 201\ \text{T} \quad \text{for field direction 2}$$
$$B_c(U) = 53\ \text{T}, 200\ \text{T}, 405\ \text{T} \quad \text{for field direction 3}$$

(the various directions are reported in Fig. 1). These results show that for the experimentally available ϕ range, and $U \neq 0$ the (3↑, 3↓) configuration is the ground state.

For the (5↑, 1↓) configuration, the starting energy for $\phi = 0$ is much larger than the (4↑, 2↓) one. Though the Zeeman stabilisation is more rapid, it is assumed that the $B_c(U)$ values where the crossing with the (3↑, 3↓) states occurs, are much larger. By calculation for direction 1 we obtain $B_c(U) = 1008$ T, 2410 T, 3411 T, 3890 T for $U = 0$, 1, 2, 3 eV, respectively.

Let us now analyse the energy linear stabilisation for the (3↑, 3↓) configuration. There seems to be a positive magnetic dipole (paramagnetism) independent of ϕ. This result sounds somewhat surprising since, for benzene, which is a 6-site 3↑3↓ system too, the magnetic dipole is opposite to the field (diamagnetism) and linearly depend on ϕ. Our results can be accounted for by the fact that two of the occupied levels (E_2 and E_3) come from a triply degenerate level at $\phi = 0$; as can be seen in Figure 2, the E_2 level is linearly stabilised with ϕ. As the two other levels vary less rapidly with ϕ (E_3 being constant and E_1 quadratically destabilised), the E_2 behaviour is

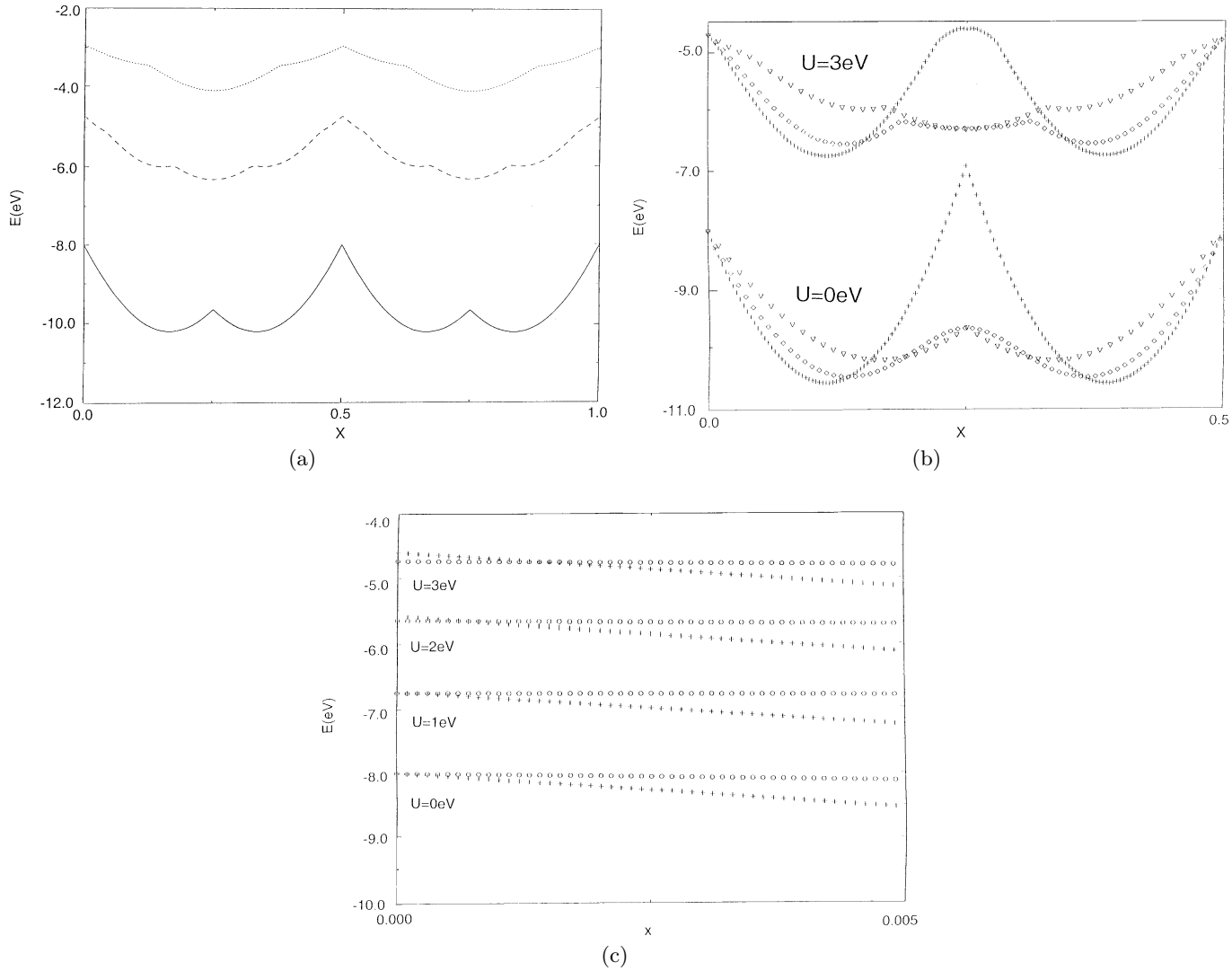

Fig. 5. (a) Magnetic energy *versus* the flux ($x = \phi/8\phi_0$) of an octahedron cluster in the ($3\uparrow$, $3\downarrow$) electronic configuration for different electronic correlation term U (the magnetic field direction is 1). $U = 0$ eV(—), $U = 3$ eV (- - -), $U = 6$ eV ($\cdots$). (b) Magnetic energy *versus* the flux ($x = \phi/8\phi_0$) of an octahedron cluster in the ($3\uparrow$, $3\downarrow$) electronic configuration for different magnetic field directions (direction 1: $\diamondsuit$, direction 2: $\triangledown$, direction 3: $+$) for the lower set of curves $U = 0$ eV and for the upper one $U = 3$ eV (see Fig. 1 for the field direction). (c) Magnetic energy *versus* the flux ($x = \phi/8\phi_0$) of an octahedron cluster in the electronic configurations (($3\uparrow$, $3\downarrow$): $\circ$ and ($4\uparrow$, $2\downarrow$): $+$) for different electronic correlations term U (the magnetic field direction is 1).

dominant and gives the global stabilisation observed. Such a behaviour has also been noticed in other works, when highly degenerate levels appear for $\phi = 0$. This is the case when the aggregate is modelled by a sphere with infinite walls [12] or when rings are considered [4]. We also observe that, as U increases, the magnetic dipole decreases. This fact can be grasped by a self-consistent Hartree-Fock calculation (see Fig. 6), which gives the evolution with U of the $E_i(\phi)$ curves given in Figure 2 for $U = 0$. This calculation shows that the E_2 level stabilisation for small ϕ values is less rapid when U increases, which leads to a smaller magnetic dipole.

5 The presence of cusps in the ($3\uparrow$, $3\downarrow$) configuration in the large ϕ range

For $U = 0$, the presence of cusps at $x = 0.25$; 0.5; 0.75 can be noticed in Figure 5a. A look at Figure 2 reveals that they arise from level crossings which cause changes in the occupation of the one-electron levels. For example, for $x < 0.25$, the E_3 level is occupied, while for $x > 0.25$ it is empty and level E_5 is occupied. Similar changes also occur at $x = 0.5$ and 0.75. As can be seen in Figure 5a, the cusp structure is different at $U = 3$ eV and 6 eV. To grasp this fact, reference can again be made to the self-consistent

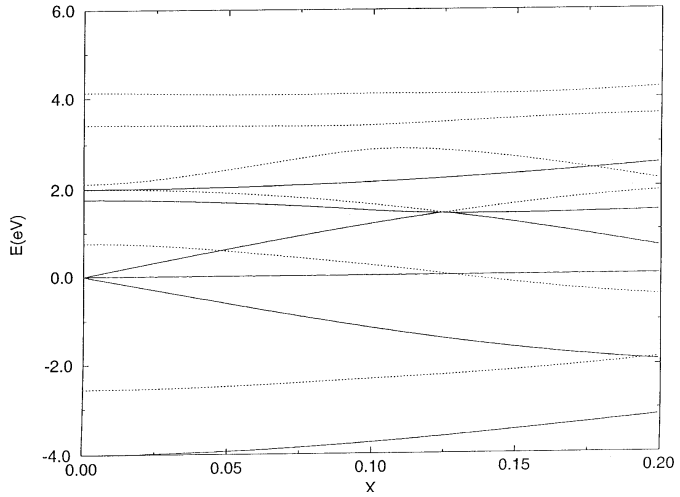

Fig. 6. One electron Hartree-Fock energies E_1 to E_6(eV) of an octahedron with the (3↑, 3↓) electronic configuration *versus* the flux ($x = \phi/8\phi_0$) for different electronic correlation terms U. (—) $U = 0$ eV, $(\cdots)$ $U = 3$ eV (the magnetic field direction is 1).

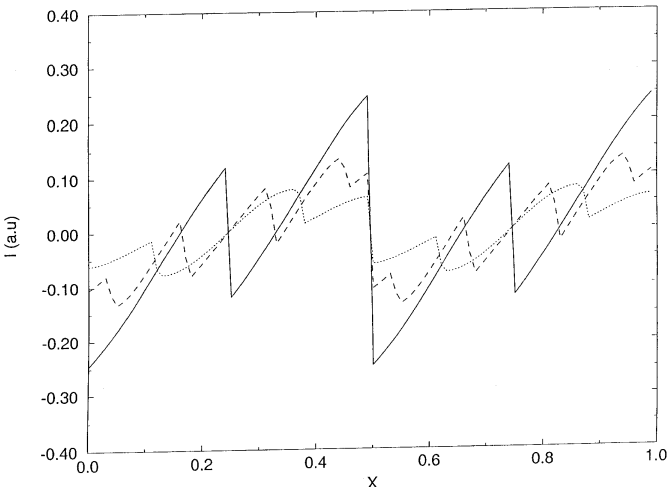

Fig. 7. Permanent current I (a.u.) *versus* the flux ($x = \phi/8\phi_0$) of an octahedron cluster in the (3↑, 3↓) electronic configuration for different electronic correlation term U. (—) $U = 0$ eV, (- - -) $U = 3$ eV, $(\cdots)$ $U = 6$ eV (the magnetic field direction is 1).

Hartree-Fock calculation (Fig. 6). When U increases, the slopes of all the E_i curves decrease in absolute value. This accounts for the fact that the cusps position may be displaced and the difference between the slopes on the two sides of the cusp is less significant.

Some physical quantities can be derived from the energy calculation. Thus, one challenge of mesoscopic physics consists in measuring and calculating the persistent current ($I = -(1/2\pi)(\partial E/\partial\phi)$) in mesoscopic device. The discrepancy between measured and experimental persistent current has been interpreted due to the electronic correlation. Our previous calculations have enabled us to derive the persistent current in the octahedron cluster without disorder *versus* the flux and the correlation has the expected tendency of decreasing the permanent current and of smoothing the curve (Fig. 7).

6 The antiferromagnetic transition in the (3↑, 3↓) configuration

Let us turn our attention to some properties of the (3↑, 3↓) state. If we dilate the ϕ-axis scale and examine the $E(\phi)$ curves for $U > 6$ eV, we observe an interesting behaviour reported in Figure 8. For $U > U_c \sim 6.01$ eV, the $E(\phi)$ curve begins by a plateau, *i.e.* it presents a zero slope at the origin. It is to be noticed that the ϕ extension of the zero slope region increases with U. Similarly, one may introduce the $U_c(\phi)$ critical energy, reported in Figure 9, which gives the lowest U value so that the $E(\phi)$ curve has a zero slope at point ϕ. We can then see that the $U_c(\phi)$ function is a two-valued function with ϕ-regions at $U_c \sim 8$ eV and others at $U_c \sim 3.4$ eV.

In order to account for our results, we have calculated the charge densities on the sites and the spin-spin correlation coefficients given by formula (3). Such calculations show that, in the ϕ-regions where U_c is large and

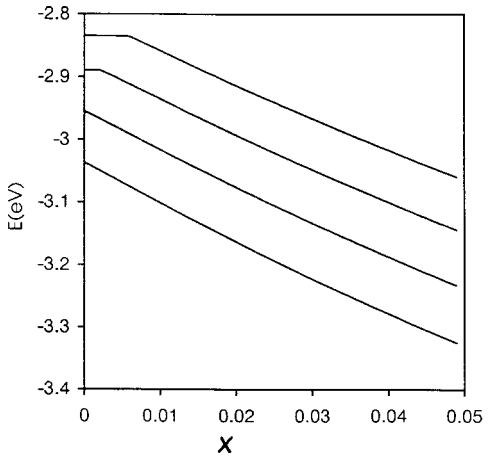

Fig. 8. Evolution of E(eV) and of the slope $\mathrm{d}E/\mathrm{d}x$ ($x = \phi/8\phi_0 = 0$) of an octahedron cluster in the (3↑, 3↓) electronic configuration *versus* the flux ($x = \phi/8\phi_0$) for different electronic correlation term U (from $U = 5.8$ to 6.4 eV with an increase of 0.2 eV) (the magnetic field direction is 1).

for $U < U_c(\phi)$, there is a charge excitation in the system with a density larger than 1 on the off square atoms (the average population on the square atoms being less than one) and there is no magnetic order for the electrons on the square atoms. However, when $U > U_c(\phi)$, the charge excitation disappears and an antiferromagnetic order appears on the square atoms. Thus, the occurrence of the zero slope $E(\phi)$ zone is linked to the presence of an antiferromagnetic order.

In the ϕ-range where U_c is small ($U_c \cong 3.4$ eV), the system behaves differently with U. No charge excitation occurs for U smaller than U_c. The lack of charge excitation is certainly due to the fact that the one-electron energy levels are closer (Fig. 2), leading to a larger electron delocalisation through the molecule. As a consequence,

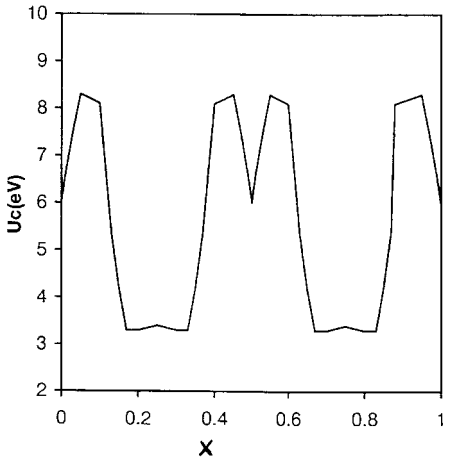

Fig. 9. The critical electronic correlation term U_c(eV) (associated to the non magnetic/antiferromagnetic transition) *versus* the flux ($x = \phi/8\phi_0$) of an octahedron cluster in the (3↑, 3↓) electronic configuration (the magnetic field direction is 1).

the charge excitation is less stable in this ϕ region in comparison with the $\phi \sim 0$ region and the antiferromagnetic order appears more easily.

7 The Gutzwiller method

An accurate calculation method based on an accurate diagonalisation is possible only for small clusters. For large clusters or bulks, variational or perturbation methods are available. One of these methods is the variational Gutzwiller method [13], which has been applied intensively for high T_c superconductor material and clusters like fullerene [14]. From the Kotliar and Ruckenstein work, the Gutzwiller framework is equivalent to the saddle point of the slave boson approach. The Gutzwiller method provides accurate results on the ground state. In the classical variational Gutzwiller method, a trial variational wavefunction Ψ is obtained from the groundstate wave function Ψ_0 of the unperturbed system (*i.e.* $U = 0$) by applying the Gutzwiller operator (thus Ψ is guessed in order to decrease the contribution of the doubly occupied states):

$$\Psi = \prod_i [1 - (1-g) n_{i\uparrow} n_{i\downarrow}] \Psi_0 \qquad (4)$$

here g is a variational parameter that has to be determined so as to minimise the energy.

Let us investigate the diamagnetic energy of the (3↑, 3↓) configuration as a function of the flux to compare the Gutzwiller results to the exact calculation ones for $U = 3$ eV (Fig. 10). The agreement is quite good except if $x \cong 0.25$ or $x \cong 0.75$, where we have noticed curvature change. This discrepancy is linked with the level crossing occurring at $U = 0$ eV but which disappears for larger U. In fact to better adapt the Gutzwiller method to our case, it is more appropriate to apply the Gutzwiller operator, not on Ψ_0 (the ground state) but on the state $\beta_1\Psi_0 + \beta_2\Psi_1$ where Ψ_1 is the first excited state. β_1 and β_2 are obtained by minimising the Gutzwiller energy. The calculation is

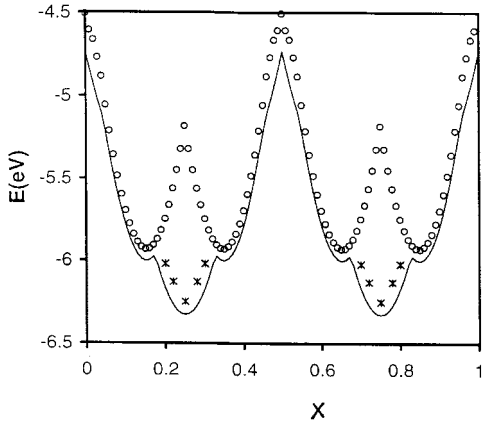

Fig. 10. Energy *versus* the flux ($x = \phi/8\phi_0$) of an octahedron cluster in the (3↑, 3↓) electronic configuration with an electronic correlation term $U = 3$ eV. Exact diagonalisation (—), Classical Gutzwiller (○), modified Gutzwiller (∗).

longer. Verification has been made for some points (in the $x \cong 0.25$ range (or $x \cong 0.75$ range) that the agreement turns out to be very satisfactory (Fig. 10).

8 Conclusion

The exact diagonalisation applied to the octahedron molecule has allowed the investigation of the electronic energy dependence *versus* the flux and shows surprising magnetic transition evolution with the flux, which cannot be obtained through other techniques. We have noticed a linear stabilisation of the energy at low magnetic field for various magnetic field directions, which would be interesting to further investigate. Moreover, particularly for small ϕ value, the transition from antiferromagnetism to paramagnetism, in elements where $U > U_c$, could be experimentally observed.

References

1. A.I. Buzdin, O.V. Dolzov, Yu.E. Lozovick, Phys. Lett. A **100**, 261 (1984).
2. D.C. Johnson, R.E. Benfield, P.P. Edwards, W.J.H. Nelson, M.D. Vargas, Nature **314**, 231 (1985).
3. L.P. Levy, G. Dolan, J. Dunsmuir, H. Bouchiat, Phys. Rev. Lett. **64**, 2074 (1990).
4. B. Reulet, Ann. Phys. Fr. **20**, 233 (1995).
5. R. Berkovits, Y. Avishai, Europhys. Lett. **29**, 475 (1995).
6. G. Montambaux, Eur. Phys. J. B **1**, 377 (1998).
7. G. Bouzerar, D. Poilblanc, in *Correlated Fermions and Transport in Mesoscopic Systems*, edited by T. Martin, G. Montambaux, J. trân Thanh Vân (Éditions Frontières, 1996), p. 149.
8. G.M. Pastor, R. Hirsch, B. Mühlschlegel, Phys. Rev. Lett. **72**, 3819 (1994).
9. J. Callaway, D.P. Chen, R. Tang, Phys. Rev. B **36**, 2084 (1987).
10. J. Callaway, Phys. Rev. B **35**, 8723 (1987).
11. F. London, J. Phys. Rad. **8**, 397 (1937).
12. J.M. van Ruitenbeek, D.A. van Leeuven, Phys. Rev. Lett. **67**, 640 (1991).
13. M.C. Gutzwiller, Phys. Rev. A **134**, 923 (1964).
14. P. Joyes, R.J. Tarento, Phys. Rev. B **45**, 12077 (1992).