

On the graphical analysis of the electronic structure of ferromagnetic clusters of medium size

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Abstract

In a previous work, a theoretical approach, suitable to describe systems having a large number of fermions, was proposed, and results for ferromagnetic surface clusters of medium size (100–1000 atoms) were presented. The aim of the present contribution is to complete this previous work. Several significant theoretical and technical details, omitted previously, are provided here. The obtained spin orbitals are analyzed, by studying their symmetry, energy, and d contribution properties.

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1. Introduction

Knowledge of the surface of ferromagnetic metals formed by particles of medium size (between 100 and 1000 atoms) is an important topic in the chemical industry [1]. However, works about this subject, using the cluster model, are scarce and incomplete [2,3]. A theoretical method, allowing the calculation of the electronic structure of these large systems of high spin multiplicity, has been presented recently [4]. The basis of the approach is to minimize the electronic energy with respect to the occupation number of a suitable set of spin orbitals (SO). The method is general and computationally efficient. Using this method we have been able to explain, simultaneously, the experimental magnetization of small clusters [5] and surface films [6].

The aim of the present contribution is to complete this previous work [4], because several significant theoretical and technical aspects were omitted and the analysis of the obtained SO was very poor, since only the atomic spin densities were given. In Section 2, the theory is reviewed and completed. In Section 3, the obtained SO are analyzed in

several ways. Symmetry and energy properties of some selected SO are discussed. The SO symmetry is analyzed by representing its spatial part, the molecular orbital (MO), graphically. The relative contributions of the atomic basis s, p, d to the occupied SO, as function of the number of valence electrons, is also studied. The Co₉₀₄ cluster has been used, mainly, for performing the present analysis.

2. Methodology

Any system having N fermions can be described by using the general approach [4]:

- For any fermion i a basis representation, C_i , of its one-body i wave-function can be obtained by expanding it in a suitable set of basis functions. These functions are built up as a direct product of a set of spatial functions χ by another set of spin functions ρ . The optimal expansion coefficients C_i (C) are the eigenvectors of a proper secular matrix eigen-value equation:

$$FC = SCA \quad (1)$$

- A two-body algebraic expression of the energy, $E^n(C_i, n_i)$, is minimized with respect to the occupation number

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n_i of each i wave-function. The set of numbers n_i , \mathbf{n} , is constrained to satisfy the conditions $0 \leq n_i \leq 1$, and $\sum_i n_i = N$. The expression E^n (not linear with respect to \mathbf{n}) can be built-up by using first principles ('ab initio'), or (semi)-empirical arguments.

The usefulness of the method has been established by calculating the electronic structure of ferromagnetic clusters of medium size, having n_a atoms in the range $n_a = 100$ –1000. This is a difficult problem [7], due to the un-localized nature of the metal bond, and to the large number of unpaired electrons. Results for 90 surface clusters (Co, Ni, Cu) were presented. Further details will be given now.

A hexagonal nuclear bulk geometry was used, since this packing is compact in both the surface and in the inside of the cluster. For this geometry, cyclic conditions were difficult to be implemented and translational symmetry [8] was not considered. So, only the D_{3h} point symmetry was used.

Two orthonormal spin functions, α and β , were used to represent the ρ set. The χ one was built-up by using M ZINDO (Zerner's Intermediate Neglect of Differential Overlap) [9] atomic basis functions. An M by M ZINDO Hückel (tight binding) \mathbf{h}^3 matrix was formed and diagonalized by a \mathbf{c} one. The calculations were made to a restricted level. So, from any eigenvector \mathbf{c}_i of \mathbf{h}^3 , one MO ($\mathbf{c}_i \chi$), and two SO ($\mathbf{c}_i \chi \cdot \alpha$; $\mathbf{c}_i \chi \cdot \beta$) were formed. The non-orthogonality effect of the basis was not considered, and a single diagonalization was performed. These two approximations are justified only for large systems.

A non-parallel (rotary) atomic basis, adapted to the global ternary symmetry, was used. The upper index of \mathbf{h}^3 indicates that the nuclear structure is three-dimensional. Proper [10] diagonalization of the \mathbf{h}^3 matrix was made by performing symmetry-adapted diagonalizations of lower dimensionality according to the scheme:

$$(\mathbf{p}^d)^t \mathbf{h}^d \mathbf{p}^d = \mathbf{b}^d; \quad (\mathbf{r}^d)^t \mathbf{b}^d \mathbf{r}^d = \varepsilon^d; \quad \mathbf{c}^d = \mathbf{p}^d \mathbf{r}^d; \quad (2)$$

$$d = 1, 2, 3$$

The blocked diagonal \mathbf{b}^d matrix is led to diagonal form, ε^d , by using Jacobi's rotations (\mathbf{r}^d). The symmetry projector \mathbf{p}^d is obtained from the \mathbf{c}^{d-1} coefficients. The operations were performed in sparse form by avoiding multiplication between small components, and using dynamic memory allocation.

The non-linear optimization of E^n , with respect to \mathbf{n} , was performed in an iterative way, by using a two-point gradient procedure. At each point the components of the gradient (changed sign) are given by the chemical potentials, $\mu_i(\mathbf{n})$, $\mu_i(\mathbf{n}) = (\partial E^n / \partial n_i)_n$. Once the \mathbf{n} set has converged the potentials $\mu_i(\mathbf{n})$ can also be seen as the self consistent field (with respect to \mathbf{n}) mono-electronic energies. It can be proven easily that if the non linear dependence of E^n , with respect to \mathbf{n} , is quadratic and positive, then the optimal occupation numbers n_i have to take integer values. The used

algebraic expression of E^n basically fulfills this condition, so fractional n_i values appear very rarely. Repulsive Coulomb and attractive exchange (atomic and global) effects were considered to build-up this quadratic part of E^n . Convergence of n_i to integer values is equivalent to obtaining the best restricted one-determinant wave-function possible.

The starting occupation numbers were obtained by filling first the α SO, and then the β ones. The stabilizing exchange term favours the population of the α SO over the β ones. So, the occupation optimization process leads to a determinant formed only by MO doubly occupied, and α SO. Such a determinant is automatically an eigen-function of the S^2 , S_z spin operators, and has the largest multiplicity (for a given number of unpaired electrons), which, usually, is related with the lowest Energy. Although it is true that several methods have been proposed for studying open-shell molecular systems [9,11,12], the present approach is, probably, the only one able to obtain an SO representation for systems having a large number (more than 1000) of unpaired electrons.

3. Analysis of results

The Co_{904} system has been selected for this analysis, since only for this surface cluster has charge neutrality of the innermost atoms been achieved, and occupation numbers converged to integer values. Much worse size cluster convergence was observed for Cu and Ni metals. This Co_{904} cluster has the structure BABABABAB, where the layers B, A are formed by 108 and 91 atoms. The layer A has a perfect hexagonal shape, with an outer line formed by six equal sides, each one with 5 atoms (4 + 2 corner ones). The surface layer B has lower, ternary, symmetry, and its six sides have 6, 5, 6, 5, 6, and 5 atoms. Considering that the atomic ZINDO Slater basis set has nine functions (1s, 5d, 3p), and the Co has also nine valence electrons, the number of generated MO, and total electrons, is 8136. Since each MO generates two (α and β) SO the total number of SO is 16272.

The behavior of the spatial part of some SO (their MO), with respect to the D_{3h} symmetry operations, will be analysed now. The C_3 axis is taken normal to the surface layer B. In the standard notation, the irreducible representations (IR) that are (not) invariant with respect to the C_3 operations are represented by the letters A (E). Symbols with (double) prime refer to IR that (do) do not change their sign when a reflection, with respect to the central plane of the cluster, is performed. The non standard (c) s suffix is used here to represent the symmetries (not IR) that do not change their sign when a reflection, with respect to a symmetry plane normal to the surface layer B, is performed.

The MO have been classified, in a standard way, according to their occupancy. The number of closed (C), open (O) and virtual (V) MO has been found to be 3333, 1470 and 3333. For any MO the chemical potential of the generated α SO is lower than the one of the β SO, because of

Table 1

Chemical potentials (μ), in a.u., and spatial symmetries (A) of the lowest (L) and highest (H) SO. The two generated SO (α , β) from a given MO have the same spatial symmetry

	μ_{LC}	μ_{HC}	μ_{LO}	μ_{HO}	μ_{LV}	μ_{HV}
α	−0.24914	−0.08696	−0.08607	−0.04340	−0.04327	0.09516
β	−0.24533	−0.04339	−0.04336	−0.01882	−0.01852	0.10510
Symmetry	A'_c	A''_c	A'_s	E'_c	E'_s	A'_s

The doubly occupied (closed), singly occupied (open) and empty (valence) MO have represented by the C, O, V symbols. For the O case only the α SO is filled.

the previously mentioned stabilization exchange effect. For the closed MO set their SO having the lowest (α) and the highest (β) μ values were localized. A similar procedure was applied to the virtual set. For the open set a different, more convenient, criteria was adopted. The highest SO open (whose MO is singly occupied) was defined as the α (full) one that has the highest μ value. On the other hand, the lowest open SO was defined as the β (empty) one with lowest μ . The chemical potentials μ and spatial symmetries of these three lowest (L) and three highest (H) SO are collected in Table 1. From each one of these six SO, another SO can be obtained by changing its spin function. Results for these new SO are also given.

Several proper energy orderings can be observed in this table. Probably the most interesting is the chemical potential of the highest full SO (−0.04339 a.u.), which is lower than the one of the lowest empty SO (−0.04336 a.u.). This confirms that a transfer of electronic occupation between any two SO cannot produce a decrease of the total electronic energy.

The spatial part (the MO) of the highest closed (A'_c) and lowest open (A'_s) SO are represented, respectively, in Figs. 1 and 2. A free version of the code Gopenmol, developed by Laaksonen et al. [13], has been used to make

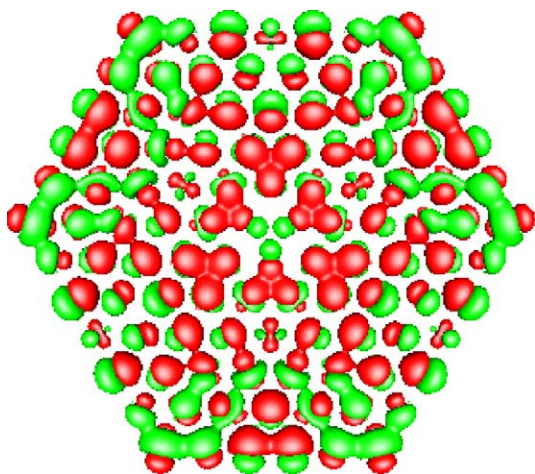


Fig. 1. Above sight of the doubly occupied MO (A'_c), whose SO has the highest μ value. The two drawn surfaces represent the points where the MO takes the values +0.001 and −0.001. Sign assignment is arbitrary since the sign (phase) of any MO is always undetermined.

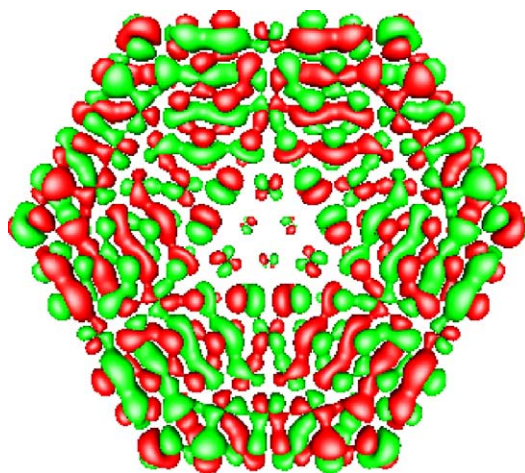


Fig. 2. Above sight of the singly occupied MO (A'_s), whose β SO has the lowest μ value. The two drawn surfaces represent the points where the MO takes the values ± 0.001 .

these graphical representations. Only the MO section above the crystal surface (nuclear uppermost B layer) has been considered. It can be seen that these MO have a deformed hexagonal shape, since the upper (lower) side of the B layer has 6 (5) atoms. Both MO are invariant under the C_3 operation, and present three symmetry planes normal to the surface of the crystal. The (c) s MO (does not change) changes its sign when it is reflected by any of these planes. Fulfillment of the symmetry requirements has been checked algebraically and graphically for all the symmetries and operations, for several clusters. The number of nodes is larger, in general, for the MO having a higher value of the chemical potential.

The relative contribution of the s, p and d atomic basis functions to the MO of the SO is analysed in Figs. 3 and 4. In Fig. 3, the sum of s, s + p, and s + p + d, atomic squared coefficients of the spatial part of each 904 SO, corresponding to the addition of one valence electron by atom, is obtained, and represented. The SO have been sorted according to their chemical potential. So, the lowest 904 SO are considered for the first valence electron, the next 904 SO for the second valence electron, and so on. Of course, the total sum (s + p + d) gives about 904 for any valence electron. It can be observed that the occupied SO are mainly formed by d atomic functions and the highest (empty) SO by p ones.

Atomic basis spin asymmetry (polarization) is analyzed in Fig. 4. In this case, for the valence electron n_v the lowest n_v by 904 SO are considered. The sum of the s, p, and d squared atomic coefficients is formed for the α , and β SO. The differences between these α , and β sums, for the s, p, d atomic basis sets, are represented. Of course, these three differences become zero when $n_v = 18$. The observed strong d spin asymmetry supports the well-known explanation of ferromagnetism provided by the solid-state physicists. A large number of unpaired, parallel electrons exist in the α d band, since it is energetically

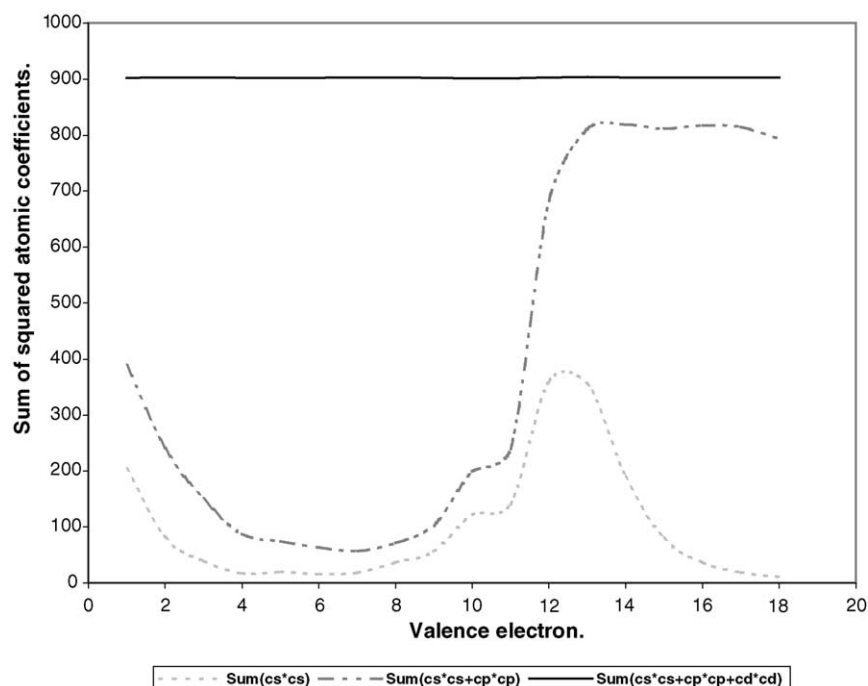


Fig. 3. Relative contribution of the atomic basis functions to the spatial part of the SO. Sum of the squared s, s + p, s + p + d atomic coefficients of the MO, for each 904 SO, vs. the number of added valence electron. The uppermost horizontal line represents the total (s + p + d) contribution, and the lowest line the s one.

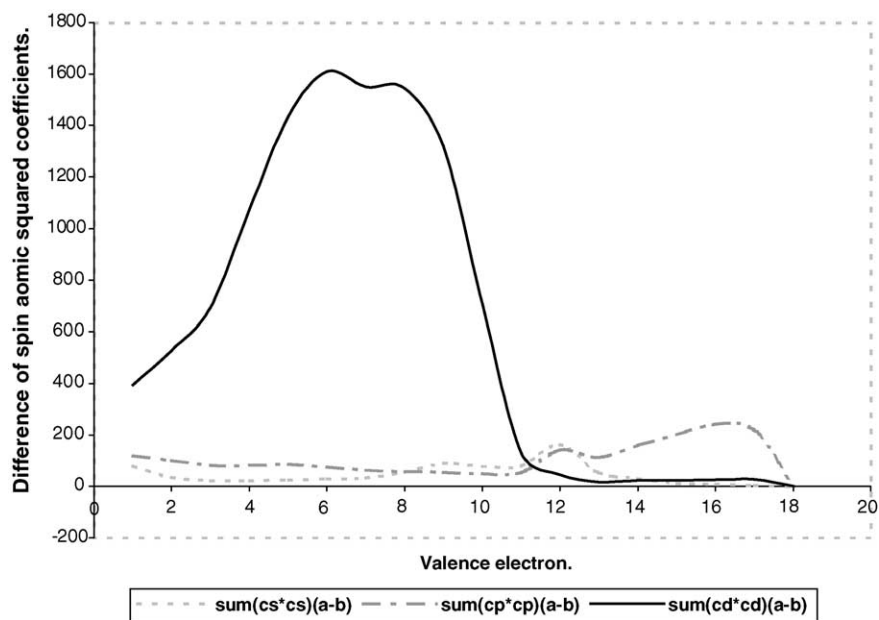


Fig. 4. Difference between the contributions of the s, p, and d atomic functions to the α (a) and β (b) SO, vs. the number of existing valence electrons. In the left part of the figure, the lowest (highest) line corresponds to s (d) contributions.

favorable over the β one. However, when this α band is filled, electrons are forced to occupy the β one, and ferromagnetism is reduced. Finally, for the Cu, $n_v = 11$, both d bands are full, as is the bonding s one, so the number of unpaired electrons is very small (see Fig. 4) and consequently the metal is diamagnetic.

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