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Magnetic properties of Ni and Fe clusters: a tight binding molecular dynamics study

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Abstract

We introduce an efficient approach which incorporates structural and magnetic ordering in transition metal clusters of sizes well beyond the range of ab initio techniques. The method combines the Hubbard model approximation with the tight binding molecular dynamics technique. Applications of the present scheme to Ni_n ($n \leqslant 7$), and Fe_n ($n \leqslant 5$) clusters show that while magnetic ordering does not affect the geometric ordering of Ni clusters, inclusion of magnetic effects strongly influences the structure of Fe clusters, forcing them to attain geometric configurations of higher symmetry than paramagnetic states.

The tight binding molecular dynamics (TBMD) scheme has been shown to be an effective tool for studying clusters of both semiconductor and transition metal atoms [1–3]. Following successful applications of this method on semiconductor systems [1] we recently reported applications of the TBMD method to paramagnetic Ni_n clusters with $n \leqslant 55$ [2,3]. Our results dealing with the structural ordering of paramagnetic Ni clusters, even without the inclusion of magnetic effects, were found to be in very good agreement with both ab initio theory and experimental results [4–8], especially in the range $10 < n \leqslant 55$. This is most probably due to the fact that while the cluster stability results from an interplay between structural and magnetic ordering, the overall effects of the mutual interaction between the two do not appear to significantly impact results for Ni clusters. However, the effect of the structural ordering may play a crucial role in the type of the magnetic state which depends on both the local coordination number of the atoms and the bond lengths. It has been found, for example, that for Ni_4 and Ni_5 clusters, a significant decrease in the coordination number increases the splitting between spin-up and spin-down electrons, thereby enhancing the value of the local magnetic moments [4,9]. On the other hand, a contraction in the Ni–Ni bond in Ni_4 may result in a reduction of the local magnetic moments due to an increase in the d-band width. Thus, the interplay between geometric and magnetic ordering

seems to be more pronounced for small clusters. The investigation of the effects of this interplay, therefore, remains a challenging problem for both small and large clusters, especially when one considers, that the determination of the outcome of this interplay is very sensitive to the model approximations used. A characteristic example is Ni_{13} for which different approximations result in different ground state geometries [10–12].

The complexity of the calculations involving transition metal atoms allows ab initio methods to lend themselves only for very small clusters. Furthermore, a full symmetry unconstrained geometry optimization of clusters, required for a realistic structural determination, poses additional complications on account of the prohibitive computational demands when ab initio methods are employed. As a result, ab initio calculations on transition metal atom clusters which include magnetic ordering are very rare and are restricted to clusters of 3–5 atoms [4,13]. In this Letter we introduce an efficient semi-empirical approach based on the TBMD method applicable to both semiconductors and metals. The method allows one to incorporate magnetic ordering and has the necessary computational efficiency for applications to large size clusters while allowing for full symmetry unrestricted geometry optimizations.

The TBMD scheme for transition metal atoms [2,3] is based on the calculation of the total energy, E_{tot}, which includes a "band structure term", $E_{el}(\{R\})$, and a repulsion term, $E_{rep}(\{R\})$, both of which depend explicitly on the geometric configuration $\{R\}$ of the cluster. An additional term, $E_{bond}(n_b)$, is also included in the total energy expression to bring cohesive energies in exact agreement with ab initio results for paramagnetic clusters of arbitrary sizes [14]. The repulsive term is taken to be a sum of pair potentials of the form, $\phi_{ij}(r_{ij}) = \phi_0 \exp[-\beta(r_{ij} - d_0)]$, [2,3] where $\beta = 8/d_0$ and d_0 is the interatomic distance at equilibrium in the bulk and ϕ_{ij} describes the interaction between the pair of atoms i and j located at positions r_i and r_j, respectively, and $r_{ij} = |r_i - r_j|$. The parameter ϕ_0 is determined by a fitting procedure that requires that the correct experimental (or theoretical) dimer bond length be reproduced.

The success of the present method in describing small clusters as well as the bulk, is a consequence

of an accurate fitting of ϕ_0 and $E_{bond}(n_b)$ parameters. As a result, the proposed scheme can be reliably used to make quantitative estimates of the system properties that rely explicitly on both the electronic and the repulsive energy terms. Such properties include the geometric ordering of small clusters, their vibrational frequencies and the dependence of their average bond length and binding energy on the cluster size [15].

In this Letter we show that our TBMD calculational approach can also be used to describe the magnetic properties of small clusters, by the incorporation of the electron spin dependence in the electronic TB Hamiltonian in an efficient way. The generalization of the method, proposed here, is based on two salient features: (i) the fitting parameter ϕ_0 contains the correction to the double counting of the electron–electron interactions in $E_{el}(\{R\})$, and (ii) the electron spin-dependent terms of the Hamiltonian can be simulated by a Hubbard-U term which creates an energy difference between spin-up and spin-down electrons.

Based on our experience with Hubbard systems [16,17], we recall that a Hubbard-U term introduces an average magnetic moment, $\mu^{(i)}$, per atom which results in an energy shift $s^{(i)} = \pm \mu^{(i)} U/2$ in the site-diagonal matrix elements of the TB Hamiltonian for the spin-up and spin-down electrons (the "plus" is for electrons with spin-up and the "minus" is for electrons with spin down) relative to the paramagnetic case. This shift is expected to be orbital dependent as both $\mu^{(i)}$ and U depend on the wavefunctions of the electrons. In terms of the numbers, $n_+^{(i)}$ and $n_-^{(i)}$, of the spin-up and spin-down electrons, respectively, the magnetic moment, $\mu^{(i)}$, is given by, $\mu^{(i)} = n_+^{(i)} - n_-^{(i)}$. It is clear that an exact solution must involve a self-consistent treatment of $n_\pm^{(i)}$ [16,17].

In developing the present model, however, we make the simplest possible approximation: We assume that the energy shifts $s^{(i)}$ are site and orbital independent, i.e. $s^{(i)} = s_0 \, \forall \, i$, s_0 being one additional adjustable parameter in our original model. We then utilize the fact that, ϕ_0, contains the correction to the double counting of electron–electron interaction terms in $E_{el}(\{R\})$, including those originating from the Hubbard terms, and therefore, the same expression for $E_{tot}(\{R\})$ can be retained with the only requirement being that the adjustable parameters ϕ_0

and s_0 of the model be simultaneously fitted to ab initio (or experimental) results. In practice this is achieved by fitting the parameters ϕ_0 and s_0 so as to reproduce the correct bond length of the dimer and a known energy difference between two or more mag-

netic states, preferably of the dimer and a few other small clusters.

We next apply this theory to study small nickel and iron clusters, for which necessary data exist for comparison. In determining our parameters for nickel,

Table 1

Results for the binding energy per atom of Fe_n clusters. Energies are expressed relative to the ground state (lowest found on optimization) energy for each cluster size

Cluster	Symmetry	μ	E_{tot}/atom (eV)			r_e (Å)	
			present work		Ref. [18]	present work	Ref. [18]
			$s_0 = 0.95$	$s_0 = 1.05$			
Fe_2		0	2.251 [a]	2.551 [a]	1.350	1.95	1.83
		6	0.000	0.000	0.000	2.02	1.98
Fe_3	C_{2v}	0	1.804 [a]	2.071 [a]	0.991	1.96, 2.09, 2.09	1.97
	C_{3v}	2	1.190	1.390	–	2.04	
	C_{3v}	4	0.668	0.801		2.05	
		4			–		
	C_{2v}	6	0.217	0.284	0.193	2.06, 2.07, 2.07	2.12, 2.12, 2.07
	C_{3v}	6			0.206		2.04
	C_{3v}	8	0.000	0.000	0.00	2.10	2.04
	C_{2v}	8			0.003		2.15, 2.11
	C_{2v}	10	0.108	0.042		2.10, 2.22 × 2	
Fe_4	T_d	0	1.628 [a]	1.903 [a]	0.791	2.11	2.12
	square		–	2.230	0.548	2.01	1.96
	distorted T_d	2	1.176	1.401		2.04, 2.13 × 5	
	distorted T_d	4	0.732	0.907		2.09 × 3, 2.14 × 3	
	distorted T_d	6	0.451	0.326		2.07 × 2, 2.16 × 4	
	distorted T_d	8	0.194	0.269		2.07 × 4, 2.30, 2.38	
	square			0.502 [b]	0.293 [b]	2.03	2.05
	distorted T_d	10	0.000	0.025		2.13 × 4, 2.23 × 2	
	rhombus			0.414		2.07 × 4, 2.81, 3.03	
	distorted T_d	12	0.025	0.000		2.16 × 3, 2.24 × 3	
	T_d				0.000		2.25
	planar			0.400 [b]		2.07 × 2, 2.16 × 2, 2.94, 3.04	
Fe_5	distorted octahedral	0		1.172			
	distorted octahedral	12		0.030			
	distorted octahedral	14		0.000			
	square pyramid	16		0.059		2.11 × 4, 2.29 × 4	
	planar	0		2.864			
	planar	14		1.591			
	planar	16		1.019 [b]			

[a] Relative to the energy of the optimum state (otherwise the $\mu = 0$ state has the same energy for different s_0 values.)
[b] Optimum magnetic state for the specific geometric configuration.

we use the experimental value for the bond length of the dimer (2.20 Å [4]) and the ab initio results of Mlynarski and Salahub [4] for Ni_4. For the iron clusters we also use the experimental bond length of the dimer (2.02 Å [18]) and the ab initio results of Chen et al. [18] for Fe_2 and Fe_4. For the ground state of the dimers, by requiring that the experimental bond length be reproduced, we found the following ϕ_0 and s_0 values:

For Ni($\mu = 2$): $\phi_0 = 0.367$ eV,

$$s_0 = 0.35{-}0.60 \text{ eV}.$$

For Fe($\mu = 6$): $\phi_0 = 0.350$ eV,

$$s_0 = 0.30{-}1.05 \text{ eV}.$$

Interestingly, the ϕ_0 value for Ni, when used for paramagnetic state ($\mu = 0$) of Ni_2, resulted in the same bond length as that for the $\mu = 2$ (ground state). For the Fe_2 dimer, on the other hand, we find the magnetic ground state ($\mu = 6$) to have a larger bond length than the paramagnetic state ($\mu = 0$) (see Table 1). From the range of the s_0 values available for the dimer, either for Ni or for Fe, we have the freedom to select those values that reproduce the magnetic state(s) of the corresponding trimer (and/or the tetramer). As will be shown later, no appreciable changes are obtained in our results for an uncertainty of up to ± 0.1 eV in s_0. A value of $s_0 = 0.45$ eV

was found to be appropriate for Ni, while for Fe we find a value of $s_0 = 1.05$ eV to be most suitable. These values were obtained by fitting to ab initio results for Ni_4 of Ref. [4] and those for Fe_4 of Ref. [18], respectively.

It is worth noticing that the deduced values of s_0 for both materials are surprisingly very close to the values of s_0 that one can deduce from the exchange splitting reported by Papaconstantopoulos and found to be in the range 0.35–0.39 eV for Ni and 0.86–0.93 eV for Fe [19]. In our case, however, one has to take into account the fact that the s-state energy is taken to be the same as the d-states energy and that the p-states do not participate in the bonding of the cluster atoms [2,3,20].

Using the set of (ϕ_0, s_0) values found for Ni, we studied Ni_n clusters with $n \leqslant 7$. Our results, in agreement with the reported values of Mlynarski and Salahub [4], indicate that for these clusters no appreciable geometric changes are induced by switching on the magnetic interactions. On the other hand, our application on Fe clusters indicated that magnetic effects do in fact significantly affect the geometric ordering. In Table 1 we include two sets of results for Fe clusters obtained with two different values of s_0 in order to demonstrate the sensitivity of the results to the fitted values. From Table 1 it can also be seen that for Fe_3 clusters the high-μ magnetic states are better described with $s_0 = 0.95{-}1.05$ eV

Table 2
Calculated values (in Bohr magnetons) of the average magnetic moment per atom, $\bar{\mu}_n$, with the cluster size for fully relaxed Ni and Fe clusters

Cluster	Ref. [4]	Ref. [13]	Ref. [11]	Present work	Experiment
Ni_2	1.0	1.0	1.0	1.0	
Ni_3	–	0.67	0.33	0.67	
Ni_4	1.0	1.5	0.5	1.0	
Ni_5	1.2	1.6	–	1.6	1.66 [28]
Ni_6		1.0		1.33–2.0 [a]	1.35 [28]
Ni_7				1.14	1.40 [28]
bulk					0.606 [27]

	Ref. [18]	Ref. [26]	Ref. [11]	Present work	Experiment
Fe_2	3.0	3.0	3.0	3.00	
Fe_3	2.67	3.0	2.33	2.67	
Fe_4	3.0	2.5	3.0	3.0	
Fe_5	–	–	3.0	2.80	
bulk					2.2 [27]

[a] Ni_6 has three high-spin levels in the range 1.33–2.0 that are isoenergetic.

when compared to the ab initio results. However, the high-μ magnetic states of Fe_4 are better described with $s_0 = 1.05$ eV which is the s_0 value chosen. (While making these comparisons, it should be kept in mind, however, that the geometries being compared can be different on account of the full symmetry unrestricted geometry optimization possible within our molecular dynamics scheme. More importantly, the geometry optimization can result in different bond lengths than the starting configuration. As discussed before, a change in geometry and bond length can affect the magnetic configuration of the ground state.) We then use these values in the study of larger clusters of Ni and Fe. The results of Fe are summarized in Table 1. The results obtained can be used as an applicability test for the present method when data are available for comparison. In cases where no such data exist, our results may be considered as predictions for future work.

A careful study of these results points to some interesting trends. In particular, the average value, $\bar{\mu}_n$, of the magnetic moment per atom in a cluster of n atoms, defined by $\bar{\mu}_n = \mu/n$ where μ is the magnetic moment of the ground state of the cluster, was found to be larger in clusters than in the bulk. As the size of cluster increases, $\bar{\mu}_n$ decreases tending gradually to its bulk value. In Table 2 we present our results for $\bar{\mu}_n$ for both Fe and Ni clusters along with other reported results for comparison. From this one can clearly observe the sensitivity of the results on the approximations made in each calculation. For example, Pastor et al. [11,12], ignoring s–d interactions, find smaller magnetic moments for Ni for which such an approximation seems more drastic. On the other hand, Reuse and Khanna [13], using smaller bond lengths, seem to underestimate the magnetic moment of Ni_6 clusters. Furthermore, from the results of Table 1, one can clearly observe that as μ increases the average bond length between two nearest neighbors also increases. The same was found for Ni clusters as well. This qualitative result is in agreement with the ab initio calculations [4,18]. Finally, the present results allow us to answer the interesting question about whether magnetic ordering affects geometric structures and vice versa. Our work has conclusively shown that magnetic effects do, in fact, affect the interatomic distances. A comparison of the geometric configuration of the magnetic ground

state to that of the paramagnetic state, however, shows that for Ni clusters in the range $n = 3$–7 there is hardly any change in the geometric configuration resulting from a change in magnetic ordering. The symmetries also remain largely unaffected by the magnetic ordering. This explains why our calculations on Ni clusters were found to be so successful despite a neglect of magnetic effects [2,3,15]. An exception appears to be Ni_{13} for which we find that magnetic effects drive the cluster from its singlet icosahedral structure to a high-spin state of capped anti-prism geometry [21]. On the other hand, for the Fe clusters, appreciable changes are observed in the equilibrium geometry of the cluster as the magnetic state is changed. For example, in Fe_3, its C_{2v} symmetry for $\mu = 0$ undergoes a change in the angle and bond length resulting in a C_{3v} symmetry for $\mu = 8$. In Fe_4 the ground state ($\mu = 12$) geometry is found to be a trigonal pyramid (elongated T_d) which has a higher symmetry than the distorted T_d structure of the paramagnetic state ($\mu = 0$). Our results for the paramagnetic state of Fe are in disagreement with the results of Chen et al. [18], who found the planar geometry to be optimal for $\mu = 0$ state. (However, we agree with Ref. [18] that the ground state has an approximate T_d geometry for $\mu = 12$.) Finally, for Fe_5 we find that by including magnetic effects, the ground state ($\mu = 14$) evolves into a perfect square pyramid which is of much higher symmetry than the trigonal bipyramid geometry of the $\mu = 0$ state (see Fig. 1). We also find a distorted trigonal bipyramid with $\mu = 12$ to be slightly more stable (by 0.02 eV per atom). Thus, with a possible exception for Fe_5, we see that inclusion of magnetic effects in Fe
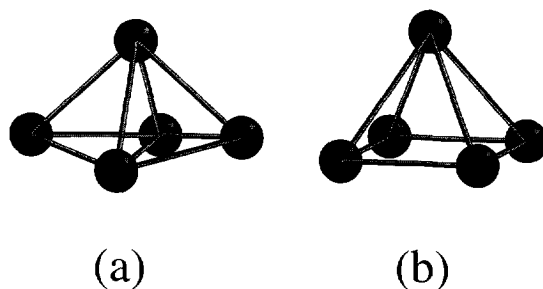

(a)   (b)

Fig. 1. The relaxed configuration of Fe_5 cluster (a) in the paramagnetic state ($\mu = 0$) and (b) in the magnetic (ground) state ($\mu = 14$).

clusters drives the cluster to stabilize in geometries of higher symmetries than those of paramagnetic state, strongly demonstrating the effect of magnetic ordering on the geometric configuration of a cluster. These results are in agreement with Dunlap's statement [22,23] although its validity has been debated recently [10]. At the completion of this work we became aware of the work by Ballone and Jones [24] on Fe_n clusters with $n \leq 7$. Interestingly, our conclusions on Fe_3 and Fe_4 are in excellent agreement with theirs as both predict the same ground states (C_{3v} ($\mu = 8$) and distorted T_d ($\mu = 12$) states respectively). The only difference being that our calculated bond lengths are systematically smaller than theirs and that for Fe_5, we find that the structures of the distorted trigonal bipyramid is almost isoenergetic with the square pyramid, the former being slightly more stable.

In conclusion, we have presented a TBMD calculational scheme which can satisfactorily incorporate magnetic ordering effects and be applicable to both covalent and metallic systems, while allowing for full geometry optimization with no symmetry constraints. Our method being semi-empirical in nature, is simple and computationally very efficient for studying clusters (free or embedded [1]) of transition metal atoms of intermediate sizes beyond the range of ab initio methods. This proposed new approach can be subjected to further levels of improvement depending on the level of accuracy and efficiency desired. For instance, the Hubbard-U term may be allowed to be orbital and site dependent and self-consistent in μ while a more realistic scaling scheme for the SK-TB parameters may be employed [25]. Nevertheless, as shown in this work, the proposed calculational scheme, in its present form, can give realistic quantitative results, providing a very promising method for the treatment of technologically significant complex systems such as magnetic materials.

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