

## Quantum size effect on the magnetism of finite systems

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The magnetic moments of the ferromagnetic transition metals Fe, Co, and Ni confined to one-dimensional chains are found to fluctuate with increasing chain length before converging to the infinite limit. This quantum size effect is derived from a simple first-principles theory that we have developed to study the evolution of the electronic structure of systems as a function of size and dimensionality. The quantitative accuracy of the predictions of this simple formulation is confirmed by carrying out *ab initio* self-consistent calculations using the molecular-orbital approach. The convergence of moments to the respective infinite limit is found to depend on the dimensionality of the system.

Recent advances in experimental techniques such as molecular-beam epitaxy, metallo-organic chemical vapor deposition, and supersonic jet expansion have made it possible to produce small particles ranging from a few angstroms (quantum wells and clusters) to a few thousand angstroms (nanostructures) in size. Studies of these finite systems are unraveling some novel features hitherto unknown to man. In very small systems (a few Å in size), the electronic length scales (e.g., mean free path) are comparable to the physical dimension of the sample whereas it becomes insignificant in nanoscale materials. Thus, one expects to see quantum size effects in ultrasmall particles. These effects are expected to diminish as the particles grow and ultimately disappear when the particles reach a certain critical size. Unfortunately, one does not know *a priori* when this limit is reached nor how the criticality depends on the electronic property under study.

In this Brief Report we report the observation of the quantum size effect on the magnetism of ferromagnetic transition metals. The magnetic moments per atom of Fe, Co, and Ni confined to one-dimensional chains are found to fluctuate with the chain lengths and approach the limiting values when the chains contain about 20 atoms. In Ni, the moments for odd-numbered atoms in the chain are larger than those for even-numbered atoms. Our results are based on a first-principles calculation<sup>1</sup> that utilizes the features of the tight-binding as well as the linear combination of atomic orbitals (LCAO) theory. The method enables us to calculate the electron-spin density of states and magnetic moments for clusters consisting of two to a few thousand atoms with remarkable ease, accuracy, and computational speed.

The method has also enabled us to address an important question that has plagued theorists modeling clusters of atoms as fragments of bulk systems. How big does a cluster have to be before its properties can converge to the bulk value? Traditionally, one attempts to answer this question by repeating the calculations in larger and larger clusters. The largest size, of course, depends on the method of the calculation and the computer time available. The more sophisticated the method is, the smaller the size of the cluster it can handle. In semiempirical techniques, such as the intermediate neglect of differential overlap and the complete neglect of differential overlap,

typically clusters of 100 atoms can be easily studied, whereas those based on self-consistent field techniques can treat clusters of 2–50 atoms depending on the level of approximation in the exchange and correlation potentials. No theory based on first principles is yet available, to our knowledge, that can realistically treat clusters containing thousands of atoms. The only attempt we are aware of that successfully treated the cluster convergence problem to the infinite limit is that due to Hintermann and Maninen.<sup>2</sup> These authors approximated a cluster by a jellium sphere and calculated the electron-density distribution as a function of cluster radius. They concluded that the Friedel oscillations are not correctly reproduced until the cluster contains about 100 atoms. Interesting as this result may be, it is clear that real clusters are not jellium spheres and the results clearly are not applicable to transition-metal systems.

We describe here a method that enables us to calculate the magnetic moment per atom of transition-metal systems containing any number of atoms. Our procedure exploits the simplicity of the tight-binding and LCAO theories. The method, hereafter referred to as the *ab initio* tight-binding (ATB) theory, contains no adjustable parameters, requires no symmetry in the problem, and therefore is versatile in its application. We shall first apply the theory to the studies of the electronic structure of one-dimensional chains of Fe, Co, and Ni and discuss the quantum size effect and the underlying physical mechanism. We shall then model surfaces and bulks using clusters of varying sizes until convergence is reached.

We start our theoretical procedure by carrying out *ab initio* self-consistent electronic-structure calculations on a dimer. Within a variational LCAO approach, the dimer wave function  $\Phi_2$  can be expressed as

$$\Phi_2 = \sum_{i=1}^2 \sum_{\lambda} C_{i\lambda} |i, \lambda\rangle. \quad (1)$$

$|i, \lambda\rangle$  is an atomic orbital located at size  $i$  and  $\lambda$  is the spin-orbital index. The coefficients of linear combinations  $C_{i\lambda}$  are determined variationally by solving the secular equation,<sup>3</sup>

$$(\underline{H} - E\underline{S})\underline{C} = 0, \quad (2)$$

where  $\underline{H}$  and  $\underline{S}$  are Hamiltonian and overlap-matrix ele-

ments given by  $\langle j, \mu | H | i, \lambda \rangle$  and  $\langle j, \mu | i, \lambda \rangle$ . The Hamiltonian  $H$  is given in atomic units by

$$H = -\frac{\nabla^2}{2} + V_{es}(r) + V_{xc}(r). \quad (3)$$

$V_{es}$  is the electrostatic potential and  $V_{xc}$  is the spin-dependent exchange-correlation potential evaluated in the local-density approximation. We solve Eqs. (1)–(3) self-consistently for the dimer as a function of dimer-bond distance  $R$ . It has been found<sup>1</sup> that the Hamiltonian and overlap-matrix elements decrease exponentially with  $R$ . We also find that the overlap matrix  $\langle j, \mu | i, \lambda \rangle$  is nearly diagonal, i.e., our basis functions  $|i, \lambda\rangle$  are nearly orthogonal.

We now use the Hamiltonian matrix elements obtained above to determine the electronic structure of a cluster of  $N$  atoms. For the cluster of  $N$  atoms the wave function  $\Phi_N$  is written as

$$\Phi_N = \sum_{i=1}^N \sum_{\lambda} C_{i\lambda} |i, \lambda\rangle. \quad (4)$$

For the  $N$ -atom cluster, the calculation of  $C_{i\lambda}$  and the eigenvalues require self-consistent solutions of Eqs. (2)–(4). Here we adopt an approximate procedure. We replace the Hamiltonian matrix elements  $\langle i, \lambda | H | j, \mu \rangle$  in the real cluster by the corresponding self-consistent matrix elements obtained for the dimer. The electronic states for the cluster are then obtained by diagonalizing the  $N$ -atom Hamiltonian in Eq. (2). The Hamiltonian  $H$  in this procedure, however, is not obtained self-consistently.

As the cluster size becomes large, the diagonalization of the Hamiltonian in Eq. (2) becomes more and more difficult (e.g., with nine orbitals per atom, a cluster of say 50 atoms requires diagonalization of a  $450 \times 450$  matrix). For a cluster having more than  $\sim 50$  atoms we adopt a different procedure to determine the eigenstates. Instead of diagonalizing the Hamiltonian equation, we determine the electronic spectrum via a moment and the recursion scheme.<sup>4</sup> This method which constructs the electronic density of states from its moments is numerically efficient when the density of states is free from gaps and singularities. This is clearly the case for bigger clusters. For smaller clusters, the electronic spectrum consists of  $\delta$  functions and the moment approach becomes inefficient since it takes a large number of moments to reproduce a singular spectrum.

The Hamiltonian and overlap-matrix elements and the spin density of states for Fe, Co, and Ni were calculated by considering both  $3d$  and  $4s$  valence orbitals. This enables us to take into account  $s$ - $d$  hybridization. The method has been applied to a large class of systems including linear chains of Fe, Co, and Ni in which the interatomic distances are set equal to the nearest-neighbor spacing in the corresponding bulk, monolayers of Fe(100), Co(001), and Ni(111), and clusters corresponding to fragments of the respective bulk having bcc, hcp, and fcc structures. The number of atoms range from 2 to 19 in the chains; from 3 to 21 in the monolayers, and from 3 to 43 in the clusters. In addition, we also present results on infinite systems for comparison. These were obtained by using the recursion technique.

In Fig. 1, the average magnetic moments per atom cal-

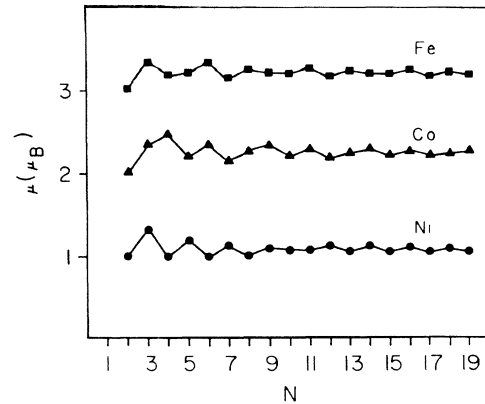


FIG. 1. Magnetic moment  $\mu$  in Fe, Co, and Ni chains as a function of the number of atoms in the chain.

culated by summing over  $s$  and  $d$  states are plotted as a function of the number of atoms forming linear chains of Fe, Co, and Ni. It is interesting to note that the moments, instead of varying monotonically, fluctuate with the increasing number of atoms before converging to their asymptotic values. In particular, the moment in the odd-atom chains of Ni containing less than 9 atoms are always higher than those in the even-atom chains.

To understand the origin of the odd-even alternation of moments in Ni, we plot in Fig. 2 the density of states for majority and minority spins for Ni chains containing 2, 3, and 4 atoms. These were obtained by broadening each eigenvalue with a Gaussian of half-width 0.2 eV. Note that

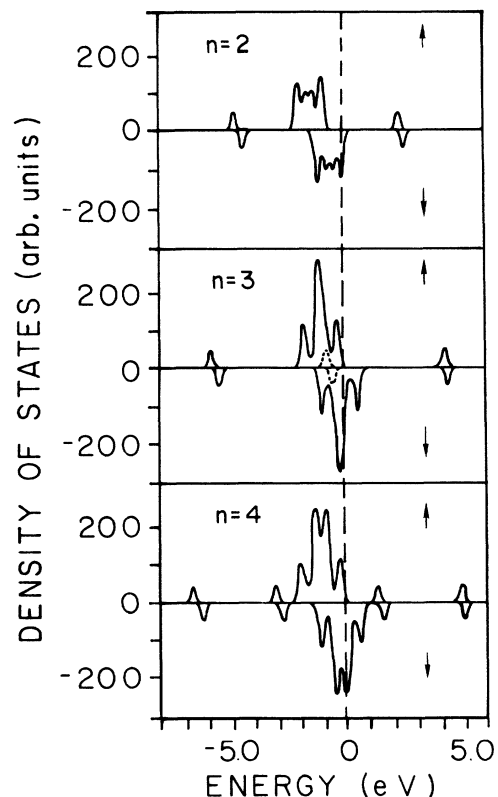


FIG. 2. Density of electronic states in Ni chains having 2–4 atoms.

TABLE I. Average moment per atom, and the  $d$  contribution to moment  $\mu_d$  in Fe, Co, and Ni chains using DVM and the ATB methods.

No. of atoms		Fe		Co		Ni	
		DVM	ATB	DVM	ATB	DVM	ATB
2	$\mu_{\text{tot}}$	3.62	3.0	2.0	2.0	1.0	1.0
	$\mu_d$	3.31		2.0		1.0	
3	$\mu_{\text{tot}}$	3.33	3.33	2.33	2.33	1.31	1.32
	$\mu_d$	3.30		2.05		1.0	
4	$\mu_{\text{tot}}$	3.50	3.19	2.06	2.45	1.0	1.0
	$\mu_d$	3.27		2.02		0.98	
5	$\mu_{\text{tot}}$	3.56	3.20	2.20	2.20	1.17	1.19
	$\mu_d$	3.33		2.04		1.0	
6	$\mu_{\text{tot}}$	3.34	3.33	2.24	2.33	1.0	1.0
	$\mu_d$	3.29		2.04		0.97	
7	$\mu_{\text{tot}}$	3.42	3.14	2.14	2.14	1.13	1.12
	$\mu_d$	3.26		2.03		1.0	

for even-atom chains there are bonding and antibonding  $s$  states that are well separated from the  $d$  manifold. However, for the odd-atom chains, a nonbonding  $s$  state occurs in the center of the  $d$  density of states. The  $d$  band in linear chains is fairly narrow due to the low coordination number and the majority  $d$  band is always full. If the total number of  $d$  electrons were fixed, then the number of minority spin electrons and, consequently, the magnetic moment would be independent of the location of the Fermi energy. Therefore, the origin of the moment fluctuation would have to incorporate the  $s$  band contribution to the moment.

The behavior of the  $s$  band is similar to that of the  $d$  band. For an odd-atom chain an extra peak due to the nonbonding orbital appears in the middle of the  $d$  band just below the Fermi energy and has to be filled up. To occupy this extra band some electrons are transferred from the minority  $d$  band to the  $s$  band causing the magnetic moment to increase. This situation does not arise in the even-atom chains. Thus, the moment fluctuation in the linear chains originates from the electron charge fluctuation in the  $d$  band caused by  $s$ - $d$  mixing. The nature of fluctuation of moments would, in general, depend on the relative spacings of  $s$  and  $d$  levels and the total number of electrons. Thus the variation in the moments with chain size is different in Fe and Co from that in Ni, as seen in Fig. 1.

The features in the density of states in Fig. 2 can also be understood using a simple Hückel-type model.<sup>5</sup> In this model, there is an on-site energy term  $\alpha$  (the diagonal matrix element) and the hopping term  $\beta$  (the off diagonal term). For  $N=2$ , the diagonalization of a  $2 \times 2$  matrix yields the energy eigenvalues  $\alpha \pm \beta$  corresponding to antibonding and bonding states. For  $N=3$ , the diagonalization yields three roots at  $\epsilon = \alpha + \sqrt{2}\beta$ ,  $\alpha$ , and  $\alpha - \sqrt{2}\beta$ . These correspond respectively to antibonding, nonbonding, and bonding states. The nonbonding states are situated at exactly the same position as the original atomic level. It is easy to show that when  $N$  is odd, there is always a nonbonding state which is absent when  $N$  is even. It is the appearance of this nonbonding state that is responsible for

the fluctuation in the moment. When  $N$  is large, the broadening in the density of states wipes out this special feature and the quantum size effect ceases to exist.

The first-principles approach, used above to show the quantum size effect, is non-self-consistent. Since the existence of quantum size effect involves electron transfer between  $s$  and  $d$  states, it is only fair to ask if the findings of the ATB are reliable under such charge-transfer situations. To investigate this, we carried out *ab initio* self-consistent molecular-orbital electronic-structure calculations on Fe, Co, and Ni chains containing 2-7 atoms. The particular scheme we have employed is the discrete variational method (DVM) and the local-density functional theory. The reader is referred to earlier papers<sup>3</sup> for details. In Table I we compare the results of the DVM calculations with those based on the ATB method. For the DVM calculations we also give the net spin moment from the  $d$  orbitals. The magnetic moment per atom obtained from DVM again fluctuates with chain length as predicted by the ATB theory. Whereas the DVM and ATB results are nearly identical for Ni, there are minor differences for Co and Fe. A comparison between the average total moment and the  $d$  component of the moment from the DVM calculations reconfirms our earlier conclusion that the oscillations in the moment are due to the  $s$  component.

Now we turn our attention to the convergence of magnetic moments as the number of atoms increase. The re-

TABLE II. Average moment per atom in Fe clusters.

No. of atoms	Chain	Plane	Bulk
4	3.19	3.50	2.5( $T_d$ )
6	3.33		3.0( $O_h$ )
9	3.20	3.33	2.89
13	3.23	3.38	
15	3.20		2.80
21		3.24	
27			2.96
Infinite	3.21	3.15	2.53

TABLE III. Average moment per atom in Co clusters.

No. of atom	Chain	Plane	Bulk
3	2.33	1.67	
4	2.45	2.00	1.50( $T_d$ )
6	2.33		2.33( $O_h$ )
7	2.14	1.86	1.57
13	2.23	2.07	1.79
19	2.26	1.87	2.05
Infinite	2.23	1.85	1.69

sults for Fe, Co, and Ni for linear chains, as well as for surfaces and bulk, are given in Tables II–IV, respectively. First, we discuss the results in the chains. The moments per atom of the 15-atom chain of Fe, and 19-atom chains of Co, and Ni are, respectively 3.20, 2.26, and  $1.05\mu_B$ . These agree very well with the “infinite” limit result (obtained from the recursion technique) of 3.21, 2.23, and  $1.02\mu_B$ . It is worth pointing out that our calculated “infinite” chain results of  $3.21\mu_B$  for Fe and  $1.02\mu_B$  for Ni agree very well with the full-potential linear augmented plane-wave (FLAPW) results<sup>6</sup> of 3.30 and  $1.10\mu_B$ .

Next we discuss the magnetic moments of monolayers and bulk given in Tables II–IV. We start with the results of Ni.

Reading row by row, we see that the moment in the chain is higher than that in the plane, while the moment in the plane is higher than that in the bulk. It turns out generally that the lower the dimension, the more open the structure is and, consequently, the higher the magnetic moment. The reason is that in the case of low dimension or open structure, the overlap between adjacent atomic orbitals is smaller. Consequently, the band is narrower. Magnetic moment is proportional to the effective exchange splitting  $J$  and inversely proportional to the bandwidth  $W$  so that narrowing of the band leads to an increase of the moment.

A column-wise examination of the results in Table IV reveals that the moment per atom in chains, planes, and bulk containing 19 atoms have converged to their respective infinite limit. We should, however, note that 19 atoms correspond to nine shells in chains, three shells in (111) monolayer, and two shells in bulk fcc Ni. Thus it takes a larger number of shells in linear structure than in monolayer and a larger number of shells in monolayer than in bulk to converge to the corresponding infinite limit.

The results in Table II for Fe and in Table III for Co are similar to those discussed above with one exception.

TABLE IV. Average moment per atom in Ni clusters.

No. of atoms	Chain	Plane	Bulk
3	1.33	0.67	
4	1.00	0.89	0.5( $T_d$ )
6	1.00		0.94( $O_h$ )
7	1.12	0.85	
13	1.06	0.73	0.71
19	1.05	0.66	0.63
43			0.61
Infinite	1.02	0.65	0.59

The moment in the Fe chain is lower than that in the Fe (100) monolayer containing the identical number of atoms. This anomaly arises due to the competition between two factors: the coordination number in the monolayer is larger than that in the linear chain, thereby causing the moment in the plane to be less than that in the chain. On the other hand, the interatomic spacing in the Fe(100) plane is larger than that in the Fe chain causing the moment in the plane to be more than that in the chain. Clearly, the interatomic separation dominates over the coordination number in determining the size of the moment. Several calculations on small clusters using self-consistent-field LCAO and on monolayers of Fe using FLAPW have been carried out. It is instructive to compare our results with these to gain additional confidence in the predictions of the ATB theory. The moment of  $3.15\mu_B$  for Fe(001) monolayer agrees well with the FLAPW result<sup>6</sup> of  $3.20\mu_B$ . For 9-atom Fe cluster our calculated value of  $2.89\mu_B$  agrees well with the SCF-LCAO result<sup>7</sup> of  $2.89\mu_B$ . For 15-atom Fe cluster the multiple scattering  $x\alpha$  (Ref. 8) and the local spin-density methods<sup>9</sup> yield the moment to be  $2.67\mu_B$ .

In conclusion, we have developed a theory that is capable of predicting accurately the magnetic moments of atoms from clusters to crystals. We have also demonstrated that the fluctuation in the magnetic moment of linear chains of Fe, Co, and Ni is a manifestation of the quantum size effect. This originates from the nature of non-bonding orbitals. It is hoped that with sophisticated experimental techniques such as molecular-beam epitaxy, it will be possible to make Fe, Co, and Ni chains of finite size. Experimental investigation of the magnetic moments may confirm the novel quantum size effect predicted here.

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