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Simple theory of electronic structure: Clusters to crystals

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A simple scheme based upon a cross between the molecular clusters and the tight-binding theory has been developed to calculate the electronic structure of a large class of systems ranging from molecules to solids. The method is applied to study the variations in the magnetic moments of Fe and Ni forming clusters, bulk, surfaces, thin films, and voids. The results are in good agreement with state-of-the-art theoretical techniques and available experimental data. The present method has the additional advantage that it can be applied to imperfect systems with equal ease.

In this Rapid Communication, we report the development of a new first-principles approach based upon a combination of molecular cluster[1,2] and tight-binding formulation that is capable of describing accurately the electronic structure of a vast class of systems ranging from molecules and clusters to solids, surfaces, interfaces, and thin films. The method does not make use of the Bloch's theorem. Consequently, it can be applied to systems containing point defects or defects with complex composition and morphology just as easily as it can be applied to systems with long-range order. The results of the magnetic moments of Fe and Ni in clusters, bulk solids, surfaces, and thin films obtained using this method agree very well with the systematics derived from the state-of-the-art theoretical techniques.[3,4]

The last decade has witnessed a remarkable development of theoretical methods for describing the electronic structure of complex systems. This has been possible because of the advent of high-speed computers and the formulation of the density-functional theory. Of all the important advances in theoretical methods, two stand out as being quantitative and versatile. These are the full-potential linearized augmented plane-wave method (FLAPW)[3-5] and the molecular cluster approach based upon the self-consistent-field linear-combination-of-atomic-orbitals molecular-orbital (SCF LCAO MO) theory.[6] The former exploits the Bloch's theorem and is suitable for systems with long-range periodic order. Although it is, in principle, possible to treat point defects in this method by creating an artificial superlattice containing periodic arrays of supercells of defect and host atoms, computational limitations only permit the use of small supercells. As a result, one introduces a large defect concentration—a clearly undesirable feature. The cluster technique, on the other hand, is based upon the real space analysis. While it does not share the aforementioned difficulty with the FLAPW method, it also has serious limitations. Only about 30 atoms per cluster can be treated satisfactorily in the SCF method and it often takes hundreds of atoms for certain properties to converge to bulk values.[7] For example, the magnetic moments at the central atoms are quite different from those in the outer shells and do not converge to the bulk value until the cluster is large.[6]

Semiempirical and approximate methods based upon the tight-binding[1] and effective-medium theories,[8] respectively, have been developed to circumvent the difficulties alluded to previously. These methods, by their very nature, are not quantitative and can only be used for qualitative analyses. They also have some inherent limitations. For example, in the tight-binding model, the matrix elements of the tight-binding Hamiltonian are *fitted* to some known band-structure data. With these parameters, one then explores the electronic density of states and properties of the system. A serious question concerns the transferability of these parameters to different systems. For example, can the tight-binding parameters obtained from bulk-band structure be applicable for systems with reduced dimensionality such as surfaces and linear chains? Common experience[3] points to the contrary.

Here we describe a method that overcomes this difficulty. We *calculate* the various overlap matrix elements appearing in the tight-binding method from SCF-LCAO-MO studies of diatomic molecules. We then use these matrix elements in a wide class of systems such as bulk solids, surfaces of varying crystallographic orientations, slabs of varying thickness, linear chains, and defects in Fe and Ni. The density of states for majority and minority spins and the magnetic moments per atom have been calculated. The agreement we have achieved with the state-of-the-art theories bears testimony to the fact that our tight-binding parameters are *transferable* to systems with different environments. In this regard, our method resembles the pseudopotential procedure, where pseudopotentials obtained from atomic calculations are used in systems with different environments. It is also similar to the approach taken by Chadi and Robertson[9] in treating semiconductor systems. In the following, we provide details of our procedure and results.

Consider a system of N particles described by a one-electron Hamiltonian H in atomic units

$$H=-\tfrac{1}{2}\nabla^2+\int\frac{\rho(\mathbf{r}')d^3r'}{|\mathbf{r}-\mathbf{r}'|}+\sum_j Z_j/|\mathbf{r}-\mathbf{R}_j|+V_{xc}^{\sigma}(\mathbf{r})\,. \tag{1}$$

Here j is the atomic site index. The second and the third terms represent, respectively, the electronic and nuclear contribution to the electrostatic energy. The last term is the exchange correlation contribution to the potential for spin σ and is approximated by the von Barth–Hedin approximation[10] to the local-spin-density (LSD) functional. The wave function ψ for the system is expressed in terms of a linear combination of atomic orbitals (LCAO) $|j,\alpha\rangle$ localized at the site j. α represents the spin-orbital index.

$$\psi=\sum_{j\alpha}C_{j\alpha}\phi_{j\alpha}\,. \tag{2}$$

We assume that $\phi_{j\alpha}\equiv|j,\alpha\rangle$ forms a complete orthonormal set (the orthogonality condition can be easily relaxed). $C_{j\alpha}$ are variational parameters to be determined from a solution of the Rayleigh-Ritz equation

$$(\underline{H}-E\underline{S})\underline{C}=0\,. \tag{3}$$

Here $\underline{H}$ and $\underline{S}$ are the Hamiltonian and overlap matrices and E is the eigenvalue. The Hamiltonian and overlap matrix elements are evaluated as weighted sums over a set of points $\mathbf{r}_k$ with weight functions $\omega(\mathbf{r}_k)$, namely[6]

$$\begin{aligned} H_{ij}&=\sum_{\mathbf{r}_k}\omega(\mathbf{r}_k)\phi_{i\alpha}^{*}(\mathbf{r}_k)H\phi_{j\alpha}(\mathbf{r}_k)\,,\\ S_{ij}&=\sum_{\mathbf{r}_k}\omega(\mathbf{r}_k)\phi_{i\alpha}^{*}(\mathbf{r}_k)\phi_{j\alpha}(\mathbf{r}_k)\,. \end{aligned} \tag{4}$$

The matrix equations are solved self-consistently to determine $C_{j\alpha}$.

The electronic structure of the system is described in terms of local density of states $n_j^{\lambda}(E)$ with j as the site and λ as the orbital index. We express $n_j^{\lambda}(E)$ using the moment and continued fraction approach[2]

$$n_j^{\lambda}(E)=-\frac{1}{\pi}\mathrm{Im}G_j^{\lambda}(E+i0^{+})\,, \tag{5a}$$

where $G(E)$ is the Green's function. It is related to the moments μ_n of the density of states by

$$\begin{aligned} G_j^{\lambda}(E)&=\sum_{p=0}^{\infty}\frac{\mu_p^{j,\lambda}}{E^{p+1}}\\ &=\cfrac{1}{E-a_1^j-\cfrac{b_1^j}{E-a_2^j-\cfrac{b_2^j}{\cdots}}}\,. \end{aligned} \tag{5b}$$

Here a^j and b^j are continued fraction coefficients. The moments $\mu_p^{i,\lambda}$ are given by the relation[2]

$$\begin{aligned} \mu_p^{i,\lambda}=\frac{1}{N}\sum_{\substack{j,k,\ldots\\ \mu,\nu,\ldots}}&\langle i,\lambda|H|j,\mu\rangle\\ &\times\langle j,\mu|H|k,\nu\rangle\langle k,\nu|H\cdots H|i,\lambda\rangle\,. \end{aligned} \tag{6}$$

Given a set of orbitals $|i,\lambda\rangle$, a calculation of μ_n requires a knowledge of the matrix elements $\langle i,\lambda|H|j,\mu\rangle$. In the conventional applications of the moment method, the diagonal elements are usually chosen as zero while the off-diagonal elements are regarded as adjustable parameters (Slater-Koster parameters) to be fitted to some known band structure. Depending on the band structure chosen, one obtains differing sets of parameters with no knowledge of sites to which orbitals $|i,\lambda\rangle$ belong.

In our present work, we put the moment approach on an *ab initio* basis. We *calculate* the matrix elements $\langle i,\lambda|H|j,\mu\rangle$ *explicitly* from the SCF-LCAO-MO method described in Eqs. (1)-(4). Thus, there are *no* adjustable parameters. We have used the discrete variational method (DVM)[6] to calculate the matrix elements from a self-consistent study of the dimer with bond length set equal to the interatomic distance in the bulk. The DVM is particularly suited for this grafting, since both the DVM and the moment approach require an orthonormal set $|i,\lambda\rangle$ of orbitals. We demonstrate that the parameters calculated from the spin-polarized study of $\mathrm{Fe_2}$ and $\mathrm{Ni_2}$ dimers are transferable to a wide range of systems with varying environments.

For the moment calculation, 4*s* and 3*d* orbitals of Fe and Ni were used, and the continued fraction was constructed from 22 moments. The density of states for each spin was obtained by averaging over the partial densities of states [Eq. (5a)] for each orbital, namely

$$n_j(E)=\frac{1}{M}\sum_{\lambda=1}^{M}n_j^{\lambda}(E)\,, \tag{7}$$

where M is the number of orbitals. The density of states for electrons of both spins was constructed in a number of systems: linear chain, ⟨100⟩ and ⟨111⟩ surfaces, slabs containing 5, 7, and 9 layers of atoms, bulk, and vacancy complexes in Fe and Ni. The magnetic moment, μ per atom is constructed by integrating over the density of states. The reason for choosing such a wide variety of systems is because accurate FLAPW (Refs. 3 and 4) results of magnetic moments are available for comparison. In addition, these systems represent rather diverse environments where the coordination numbers (number of atoms in the nearest-neighbor shell) vary from 2 in the linear chain to as many as 12 in the bulk.

The change in the magnetic moments from their calculated bulk value (μ_0)

$$\Delta\mu=\mu-\mu_0$$

is plotted as a function of the coordination number in Fe and Ni in Figs. 1(a) and 1(b), respectively. The decrease

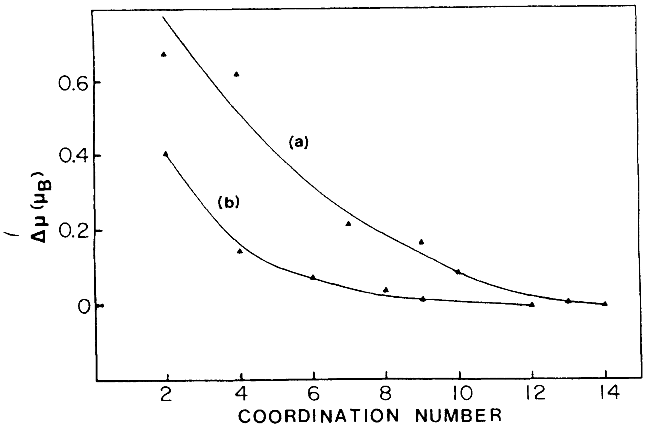

FIG. 1. Deviation from the bulk magnetic moment μ in Fe and Ni as a function of nearest coordination number (in various structures). (a) and (b) correspond to Fe and Ni, respectively. The triangles are actual calculated points. The smooth lines are drawn simply to guide the eye. ($\mu_{\mathrm{bulk}}^{\mathrm{Ni}}=0.59\mu_B$; $\mu_{\mathrm{bulk}}^{\mathrm{Fe}}=2.53\mu_B$.)

in the moment with increasing coordination is apparent. To understand the latter trend, we plot in Fig. 2 the density of states for majority and minority spin bands for Ni in linear chain, ⟨111⟩ surface plane, and bulk. These have coordination numbers of 2, 6, and 12, respectively. The Fermi energies are at $E=0$. Note that the bands are narrow in smaller coordination systems due to poor overlap between electronic states at adjoining sites. As this number increases, the overlap continues to rise and the bands broaden. There is a concomitant promotion of electrons from majority spin band to minority spins. Consequently, it results in a systematic decrease of the magnetic moment as one goes from linear chain to bulk as shown in Fig. 1. It is instructive to compare the results in Fig. 1 with the experimental bulk value and the FLAPW calculations of Freeman and his group.[3,4] Our calculated moments for bulk Fe and Ni are $2.53\mu_B$ and $0.59\mu_B$, respectively. These agree well with the experimental values of $2.2\mu_B$ and $0.6\mu_B$, respectively. We obtain $1.0\mu_B$ for linear chain in Ni and $3.2\mu_B$ for linear chain in Fe, in good agreement with the corresponding FLAPW values[3] of $1.1\mu_B$ and $3.3\mu_B$. The surface layer of a five-layer slab of Ni(100) has a magnetic moment that is enhanced by 4.3% over the central layer. This agrees well with FLAPW results of 5.2% by Jepsen, Madsen, and Anderson and 5.8% of Krakauer, Freeman, and Wimmer.[4]

A similar trend is also visible in magnetic moments at various layers in thin slabs. We plot in Figs. 3(a) and 3(b) the change in the magnetic moments as one goes from the surface layer to the middle layer in nine-layer slabs of Ni ⟨111⟩ and ⟨100⟩ planes. Note that the surface layer is more magnetic than the inner layers. The middle layer of the nine-layer slab has a magnetic moment that is identical to its bulk value. This trend is also consistent with the variation in the coordination numbers. An additional feature is also noticed in Fig. 3(b)—that of an oscillatory dependence of the magnetic moment as one approaches the surface from within the bulk. Such a trend is less prominent for the more compact ⟨111⟩ slab. These subtle features are also in agreement with FLAPW results.[3,7,8]

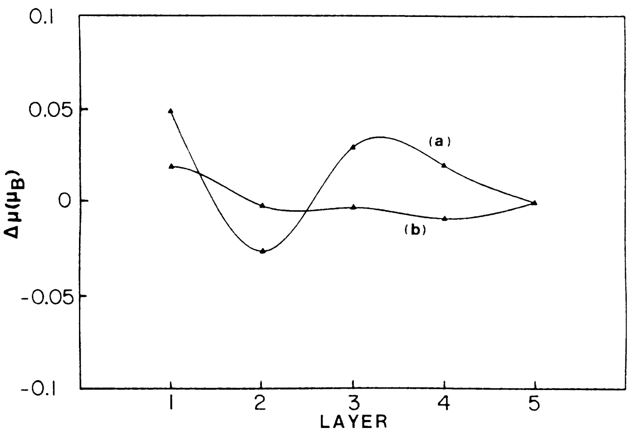

FIG. 3. Variation in the magnetic moments μ of sites in various layers of nine-layer slabs of Ni. (a) and (b) correspond to ⟨100⟩ and ⟨111⟩ planes, respectively. Here, μ is measured with respect to the central layer. ($\mu_{\rm center}^{\langle 111\rangle}=0.59\mu_B$; $\mu_{\rm center}^{\langle 100\rangle}=0.57\mu_B$.)

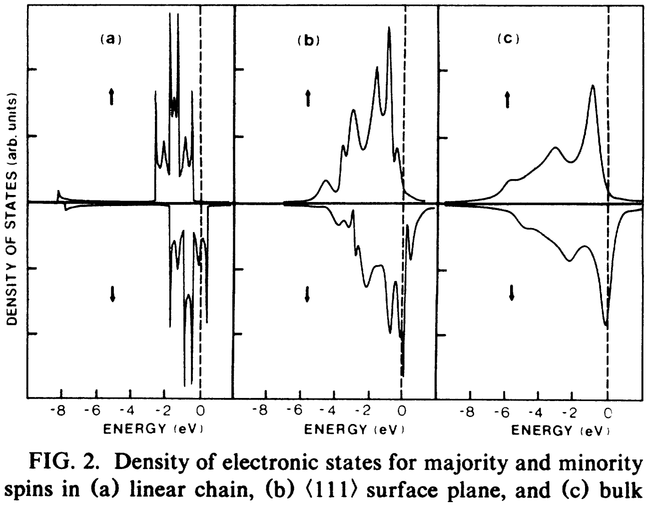

FIG. 2. Density of electronic states for majority and minority spins in (a) linear chain, (b) ⟨111⟩ surface plane, and (c) bulk Ni. The Fermi energy is at $E=0$. Scale for the density of states in (a) is double of that in (b) and (c).

To demonstrate the versatility of the method, we have applied it to the study of the magnetic moments of atoms surrounding voids of varying sizes successively from the bulk, since a void of infinite radius mimics a planar surface. To understand how big a void has to be for the moment at its innermost shell to converge, we have calculated magnetic moments of atoms around a monovacancy, and voids of 9, 15, 27, and 51 atoms in Fe. The voids correspond, respectively, to the removal of first, second, third, and fourth shells of atoms. The magnetic moments at the inner layer of atoms surrounding the void center is given as a function of void size in Table I.

It is interesting to note that these moments also oscilate with void size. In order to understand the source of such an oscillatory behavior, we have given in Table I the number of nearest and next-nearest neighbors of the atoms on the inner shell for various voids. In the case of Fe, the distances of the nearest and next nearest-neighbor atoms are close to each other. So we identify the coordination number in Fe as the sum of these two numbers. It is clearly seen that the change in moment is related to the changes in the local environment. Sites having greater coordination number show lower moments. Note that for a 51-atoms void, the magnetic moment has approached its asymptotic value. No other theoretical studies are available to compare with our results in Table I.

Thus, we have demonstrated that the continued fraction method with parameters *calculated* from *ab initio* SCF-LCAO-MO theory of dimers can explain, systematically, the variation in the electronic and magnetic structure of Fe and Ni in a wide variety of systems. Our method demonstrates that the tight-binding parameters obtained in the above manner are transferable much in the same spirit as pseudopotentials The strength of our method lies not only in the simplicity of its construction and transparency, but its wide applicability to imperfect systems and modest demand on computer time. For example, the calculation of a 25 000-atom cluster using the IBM 3081D computer requires only twenty minutes of central processing unit time. It is an order of magnitude faster than

TABLE I. Magnetic moments at the inner layer of atoms surrounding the void center in Fe.

Size of void	Nearest neighbor	Next-nearest neighbor	Coordination number	Moment (μ_B)
Monovacancy	7	6	13	2.55
9	4	5	9	2.70
15	6	4	10	2.61
27	5	5	10	2.64
51	4	3	7	2.75

competing first-principles methods. We are presently trying to extend the calculations for systems involving heteroatomic atoms. This will enable us to treat overlayers and modulated structures. Unlike the FLAPW method, we can here introduce the surface defects in the calculation of our electronic structure. Results will be published in due course.

In spite of the optimism expressed here, the reader should be cautioned that our starting point is a diatomic molecule. Consequently, the method does not account for three-body terms such as effects associated with crystal fields. These problems may be of a lesser significance for transition metals due to the localized nature of d electrons.

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