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Universal tight-binding model for transition metals: from bulk to cluster

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Abstract

A universal orthogonal tight-binding (TB) model is developed for transition metals, with special emphasis on spin-polarized self-consistent calculations. The parameters of the TB model are directly obtained from the *ab initio* bulk calculations within the linear muffin-tin orbital atomic sphere approximation method, without any fitting. With the environmental dependence of the Hamiltonian included in the localized structure constants, the TB model can be reliably applied to various situations, from periodic bulk structures to small clusters, for both pure metals and alloys. We have tested the model in spin-polarized calculations against *ab initio* results for small computational cell systems, and applied the model to study the spin and orbital magnetism of some large clusters.

1. Introduction

The magnetic properties of low-dimensional systems have attracted considerable attention from both theorists and experimentalists in the last two decades [1]. Due to the lack of full periodicity in these systems, theoretical studies usually involve a computational cell with a large number of atoms, which prohibits first-principles calculations in the local-density approximation (LDA) or generalized gradient approximation (GGA) of density-functional theory (DFT) [2, 3], methods which are recognized as being quite reliable for the prediction of the properties of both periodic systems and small clusters. For complicated systems, tight-binding (TB) models provide an attractive alternative to the resource demanding *ab initio* calculations. The major challenge, however, for the TB-based microscopic description of materials is the development of transferable potentials that can be reliably used from bulk through to surfaces and clusters.

Considerable progress has been made in improving the transferability of TB potentials. Environment dependent two-centre TB schemes [4–10] are quite successful in describing the bulk properties of metals. However, highly accurate TB calculations on metal clusters

are relatively rare [19]. There is a body of theoretical work on the magnetic properties of transition metal clusters, which employs largely bulk determined TB parameters and Hubbard-type on-site terms [11–18]. The environmental dependence of the Hamiltonian of a cluster was considered via local charge neutrality [11], electron spillover at the cluster surface [15, 16], and local coordination dependent energy levels [17]. The exchange interactions among the d orbitals J_{dd} are usually determined by reproducing the *ab initio*/experimental bulk magnetic moments, which are sometimes quite different in different contexts (e.g., $J_{dd} = 0.71$ eV for Fe in [17] and 1.05 eV for Fe in [15]).

As pointed out by us earlier [19], there is a problem in applying the bulk TB model directly to clusters. Certain terms that are present generally in the TB Hamiltonian cancel for symmetry reasons in bulk materials. This was first recognized by Mercer and Chou [9]. These terms arise from two-centre integrals, which contribute to the on-site elements of the TB Hamiltonian. If bulk data are used solely in the fitting, the evaluation of these terms is precluded, and this poses inherent limitations on transferability. Recently, we have applied the TB model determined from fitting to both bulk and cluster data to study the magnetism of transition metal clusters [20]. The main difficulty with this approach is that huge effort is needed in determining the TB parameters for a specific system, which impedes the scope of the research. In this paper, we propose a simple TB scheme based on the tight-binding linear muffin-tin orbital method in the atomic sphere approximation (TB-LMTO-ASA) [21–23].

It is well known that the LMTO-ASA method is quite successful in describing the properties of close-packed bulk materials. In this work we show that the second-order orthogonal TB Hamiltonian in the ASA [23] with the potential parameters of the corresponding bulk materials can produce excellent results for small clusters and thin films. The environmental dependence of the TB model can be fully contained in the localized structure constants. For all transition metals and alloys, the TB models are universal with the material dependence included solely in the standard potential parameters [21, 22].

Our TB model is directly derived from the orthogonal representation of the TB-LMTO-ASA method [22]. In the following section we describe the TB method and present some discussions on it. In section 3 results are presented on the spin and orbital moments of some small clusters and thin films, and a comparison is made with available *ab initio* results. Some results on large clusters are also presented.

2. Tight-binding model

In the LMTO-ASA method, the transformation between the conventional MTOs and the tight-binding ones is realized through the transformation between the bare structure constants S^0 and the 'screened' structure constants (SSCs) S^α via the 'Dyson equation' [22]

$$S^\alpha = S^0 + (S^0\alpha S^\alpha + S^\alpha\alpha S^0)/2 \tag{1}$$

or, equivalently,

$$S^\alpha = \alpha^{-1}[(\alpha^{-1} - S^0)^{-1} - \alpha]\alpha^{-1}, \tag{2}$$

where α are the site-independent screening constants [21]. In equation (1) we have used the symmetric form to ensure that the on-site S^α are Hermitian when some approximate forms of the off-site S^α are used (see below). The SSCs are quite localized, which enables them to be calculated for each site by inverting the Hermitian positive-definite matrix $\alpha^{-1} - S^0$ in equation (2) for the cluster containing a few neighbour shells of that site. Due to the finite size effect, S^α obtained from inversion is not strictly Hermitian, $S^\alpha_{Ri,R'i'} \approx S^\alpha_{R'i',Ri}$, where $S^\alpha_{Ri,R'i'}$ is obtained from inverting the matrix for the cluster containing the site $\mathbf{R}$. We take the arithmetic

average to ensure the Hermiticity and the symmetry of S^α. The strict Hermiticity of S^α is important in the calculation of orbital moments.

Under certain conditions, the off-site elements of S^α follow the universal interpolation formula [22, 23]

$$S^\alpha_{ll'm} = A^\alpha_{ll'm} \exp(-\lambda^\alpha_{ll'm} d/w), \tag{3}$$

where l denotes the angular momentum, m denotes σ, π and δ, and d the interatomic distance $|\mathbf{R} - \mathbf{R}'|$. The values of $A^\alpha_{ll'm}$ and $\lambda^\alpha_{ll'm}$ [22, 23] are independent of structures and materials. A length w is introduced to make the structure constants dimensionless, and it is normally chosen to be the average Wigner–Seitz radius [23]. In our construction of the TB Hamiltonian, w is chosen as the Wigner–Seitz radius of the bulk material from which the self-consistent potential parameters are taken. Since S^0 has no on-site elements, a simple approximation for the on-site elements of S^α can be obtained through equation (1).

In terms of the SSCs, the second-order Hamiltonian H in the ASA can be broken down into one-, two-and three-centre terms,

$$\begin{aligned} H &= h^1 + \sqrt{d^\alpha}(S^\alpha - S^\alpha h^2 - h^2 S^\alpha - S^\alpha h^3 S^\alpha)\sqrt{d^\alpha}, \\ h^1 &= c^\alpha - (c^\alpha - \varepsilon_v)o^\alpha(c^\alpha - \varepsilon_v), \\ h^2 &= (c^\alpha - \varepsilon_v)o^\alpha, \\ h^3 &= d^\alpha o^\alpha. \end{aligned} \tag{4}$$

Unless explicitly stated, our symbols hereafter follow the definitions of [23]. Note that H is block diagonal in the spin index σ along the magnetization direction. The potential parameters c^α, d^α and o^α are directly related to the standard self-consistent potential parameters C, Δ and γ.

According to our experience, the difference of γ for $\sigma = \pm 1$ is quite small. In implementing our TB scheme, we have chosen the arithmetic average value of γ for both spin-indices. By slightly adjusting the values of ε_v of the minority spin bands, we can make h^2 and h^3 in equation (4) spin-independent. Thus the spin dependence of the Hamiltonian involving two and three centres is entirely included in the spin dependence of the on-site diagonal terms $\sqrt{d^\alpha}$, which, as shown below, can be easily obtained from linear interpolation. Because we are going to treat the spin splittings self-consistently, the on-site diagonal matrix elements of the one-centre terms are replaced with $h^1 = (h^{1\uparrow} + h^{1\downarrow})/2$.

To include the spin polarization self-consistently, the on-site spin dependent energy levels are given as

$$H^C_{l\sigma} = h^1_l + \sum_{l'} \left[U_{ll'}(n_{l'} - n^0_{l'}) - \sigma \frac{J_{ll'}}{2} \mu_{l'} \right], \tag{5}$$

where $U_{ll'}$ and $J_{ll'}$ respectively denote the intra-atomic direct and exchange Coulomb integrals. $\mu_l = n^\uparrow_l - n^\downarrow_l$ is the spin polarization of angular momentum l. n^0_l is the orbital occupation of the bulk which is directly taken from the bulk spin-polarized TB-LMTO-ASA calculations. We have expressed the direct Coulomb interactions in terms of $n_l - n^0_l$ in (5) to exclude the double counting terms contained in the bulk LDA-LMTO calculation. In conventional TB schemes, J_{dd} are usually chosen to yield the proper magnetic moment of bulk while other $J_{ll'}$ are set to be zero. Ignoring the exchange interactions between s and p orbitals, we directly obtain $J_{\mathrm{d}l}$ from the *ab initio* calculations,

$$J_{\mathrm{d}l} = \frac{(C^\downarrow_l - C^\uparrow_l)}{\mu_{\mathrm{d}}}. \tag{6}$$

The magnetic moments are mainly determined by J_{dd} for transition metal systems. It was found that J_{dd} obtained from LMTO-ASA calculations are almost independent of the local environment of atoms, i.e., both the surface and the bulk atoms have almost the same J_{dd} [24].

Although it was well established that the relative change of the majority and minority spin band widths can play an important role in ferromagnetism [25], most TB models so far do not consider the spin dependence of the hopping terms because it is too complicated. Within our TB model, the spin dependence of the hopping terms is introduced through the on-site diagonal potential parameter $\sqrt{d^\alpha}$, which is linearly interpolated as

$$\sqrt{d_l^\alpha}(\sigma) = \frac{\sqrt{d_l^{\alpha\uparrow}} + \sqrt{d_l^{\alpha\downarrow}}}{2} - \sigma \frac{\sqrt{d_l^{\alpha\uparrow}} - \sqrt{d_l^{\alpha\downarrow}}}{C_l^\uparrow - C_l^\downarrow} \sum_{l'} \frac{J_{ll'}}{2} \mu_{l'}, \tag{7}$$

where $\sqrt{d_l^{\alpha\uparrow}}$ and $\sqrt{d_l^{\alpha\downarrow}}$ are the LMTO-ASA calculated bulk potential parameters of $\sigma = \pm 1$.

Within our TB model, the calculated magnetic properties are not sensitive to the chosen values of $U_{ll'}$ in equation (5). The $U_{ll'}$ are introduced to ensure reasonable local charge neutrality because the TB Hamiltonian is blind with respect to the charge of the system. For simplicity, we have chosen $U_{\mathrm{ss}} = U_{\mathrm{pp}} = U_{\mathrm{sp}} = 0.3U_{\mathrm{dd}}$ and $U_{\mathrm{sd}} = U_{\mathrm{pd}} = 0.4U_{\mathrm{dd}}$ and arbitrary chosen $U_{\mathrm{dd}} = 3$–5 eV. The charge neutrality of atoms at the cluster boundary is normally better than $0.3e$, within the range of the DFT calculations.

Our TB Hamiltonian is constructed from (4) with h^1 replaced by $H_{l\sigma}^C$ in (5). All the parameters except $U_{ll'}$ are directly taken from the *ab initio* TB-LMTO-ASA calculations. Thus our TB model can be regarded as an *ab initio* one. In the so-called LDA + U method [26], a similar '*ab initio*' tight-binding model was constructed from the LMTO-ASA in the context of periodic bulk systems. We focus on the transferability of the TB model from bulk to cluster in the present work. We have shown before [19] that the intra-atomic Hamiltonian elements can greatly improve the TB transferability within a two-centre scheme. From (1) it can be seen very clearly, due to the local symmetry breaking at the cluster surface, that both the diagonal and off-diagonal on-site elements of S^α are not zero. In first-order approximation, $h^2 \equiv 0$ and $h^3 \equiv 0$ in equation (4), the off-diagonal on-site elements arise from S^α. Thus the environmental dependence of the TB Hamiltonian is included in the localized structure constants S^α. Actually, our TB model also *automatically* includes the environment dependence of the tight-binding hopping integrals [7, 8] through the change of S^α and the three-centre contributions.

3. Results and discussion

3.1. Thin films and small clusters

In the *ab initio* LMTO-ASA calculations of thin films and other open structures, the empty space is normally filled with empty spheres. However, in the study of low-dimensional systems, it suffers from the uncertainty of where to put the empty spheres, particularly when the atoms depart from their corresponding bulk sites. In our TB model, we have not introduced any empty spheres. As a test of transferability of the proposed TB model, we first use it to calculate the magnetic properties of thin films and compare the results obtained with those from the full potential linear augmented-plane-wave (FLAPW) method [27]. We have calculated the magnetic moments for seven-layer slabs of bcc Fe(001), fcc Ni(001) and hcp Co(0001) and present the results in figure 1.

Our TB results are in very good agreement with those from FLAPW, which implies that the surface spillover [15] is not necessary if the local symmetry breaking at the surface is taken into account properly through the TB structure constants S^α. We have chosen the atomic spacing as in the bulk and used the experimental lattice constants. The standard potential parameters C, Δ and γ are taken from the corresponding bulk calculations. Our TB results reproduce the moment enhancement of the surface, and the discrepancies between our data

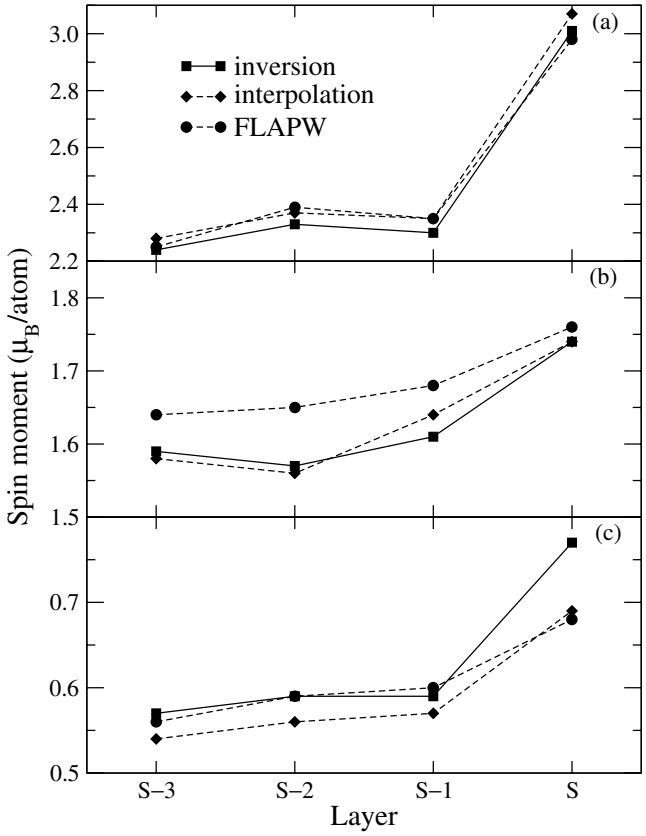

Figure 1. Local magnetic moments obtained for the seven-layer (a) Fe(001), (b) Co(0001), and (c) Ni(001) thin films. We have used matrix inversion and interpolation to construct the TB Hamiltonian. $S-n$ represents the different underlayers below the surface (S) and $S-3$ corresponds to the centre of the slab.

and those of FLAPW are within the difference between different *ab initio* calculations [28]. In all the calculations reported in this paper, we have simply chosen $U_{\mathrm{dd}} = 3$ eV.

Another interesting feature revealed from the plots is that the tight-binding Hamiltonian constructed from matrix inversion and that from off-site interpolation give very close results. It has been pointed out that [23], for reasonably homogeneous structures, the off-site structure constants follow the universal interpolation formula of equation (3). From the calculated magnetic moments, it seems that equation (3) is a reasonable approximation even for the extremely inhomogeneous structures consisting of a surface of a semi-infinite solid when w is taken to be the Wigner–Seitz radius of the bulk. Even for Co(0001) and Ni(001) monolayers, the interpolation scheme can give relative reasonable results. It seems that introducing empty spheres in the TB-LMTO-ASA *ab initio* calculations is of computational convenience rather than of physical requirement. However, the interpolation scheme fails to give reasonable results for Fe(001) monolayer because in this extreme case there is no nearest neighbour of the bcc bulk structure. Nevertheless, the TB Hamiltonian constructed from S^{α} obtained from matrix inversion gives a spin moment of 3.18 μ_{B}/atom, in excellent agreement with the FLAPW result of 3.20 μ_{B}/atom [27].

We now consider the magnetism of small clusters. The TB calculated magnetic spin moments are compared with those of the DFT calculations in table 1. All the clusters listed

Table 1. Comparison of the TB calculated spin magnetic moments of clusters with from Dmol calculations. Column TB-I corresponds to the TB Hamiltonian with S^{α} calculated from inversion, and column TB-II to that with S^{α} calculated from interpolation.

	TB-I	TB-II	Dmol		TB-I	TB-II	Dmol
Fe_9	26	34	28	Co_{55}	101	105	101
Fe_{15}	44	44	48	Ni_{13}	8	8	8
Fe_{27}	80	80	80	Ni_{19}	14	12	12
Fe_{51}	142	142	148	Ni_{43}	34	28	34
Co_{13}	27	27	27	Ni_{55}	40	34	40
Co_{19}	39	31	39	Rh_{13}	19	19	19
Co_{43}	83	83	83	$Fe_{15}Co_{12}$	68	68	68

in the table are constructed as an O_h symmetrical portion of a bcc or fcc lattice with the experimental lattice spacing. The DFT calculations for clusters were carried out using the linear combination of atomic orbitals (LCAO) method in the local spin density approximation. The atomic orbitals are obtained via a radial solution of the atomic Schrödinger equation. Double numerical basis s and d orbitals in addition to p polarization functions are included in the valence basis set. The core orbitals are allowed to hybridize with the valence orbitals. The computations were performed using the Dmol [29][1] software package. In constructing the TB parameters of Rh, we have performed the TB-LMTO-ASA calculations in a fixed-spin-moment procedure [30]. It is not possible to get the values of $J_{ll'}$ from equation (6) in a standard self-consistent procedure because the bulk Rh is nonmagnetic. We have fixed the spin moment per site to be 1 μ_B in the LMTO calculation. Actually, J_{dd} is not sensitive to the chosen fixed moment value, which validates the Stoner concept. In the case of the binary cluster $Fe_{15}Co_{12}$, which is a portion of the bcc lattice with the experimental lattice constant of bcc Fe, the TB parameters are constructed from the pure Fe and Co TB-LMTO-ASA calculations. A constant shift to the on-site energy levels is used to make the Fermi energy of different pure metals the same. We have also tested the TB parameters directly taken from a hypothetical ordered alloy calculation. Both give the same spin moment.

Two features can be seen very clearly in the table. First, the TB results from the matrix inversion always produce excellent agreement with the DFT results. Second, in most cases the two TB schemes give very close or exactly the same results. There are large difference between the two TB schemes for Fe_9 and Co_{19}, where the coordinations of the surface atoms are drastically different from those of the bulks, i.e. 8 for Fe and 12 for Co. The nearest neighbour coordination is only 1 for the surface atoms of Fe_9, while for Co_{19} the nearest neighbour coordination of the outmost atoms is only 4. We conclude that for reasonably close packed clusters, the interpolated SSCs can construct a reasonable tight-binding Hamiltonian. Obtaining S^{α} from interpolation is much more efficient than matrix inversion. In order to construct the full S^{α} matrix from inversion, we have to invert a cluster for each geometrically inequivalent site and then use symmetry operation to build the whole S^{α} matrix. Moreover, the exponential variation relation of equation (3) makes it very easy to implement into molecular dynamic simulations if some fitted repulsive pair potentials were introduced. We focused on the magnetic properties in this paper and avoided any fitting in the construction of the TB model. Except for some extreme cases, it seems that the universal interpolation of equation (3) is quite reasonable.

Taking the potential parameter from the experimental lattice spacing bulk calculations, we can apply the TB model to study the magnetism of different cluster structures and atomic

[1] DMol^3, Molecular Simulations Inc., San Diego, CA.

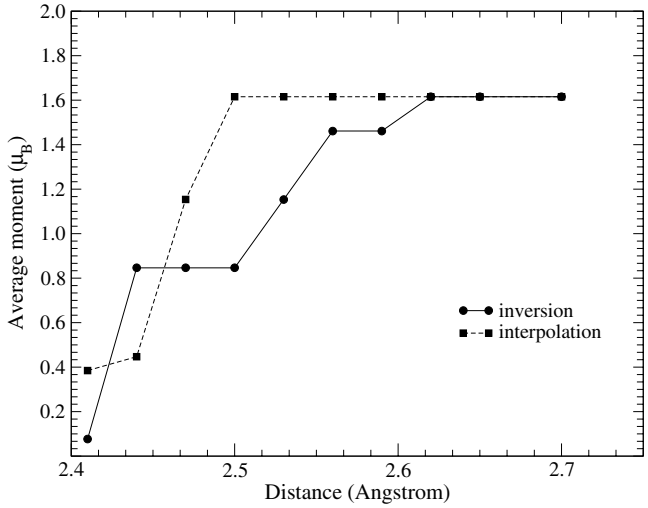

Figure 2. Variation of the magnetic moment versus interatomic distance between the central atom and a surface atom in the Rh_{13} icosahedron cluster. As in figure 1, two types of TB Hamiltonian have been considered.

spacing. For example, the magnetism of Rh clusters is very sensitive to the cluster structure and atomic spacing. The nonmagnetic material Rh can become magnetic when the size is reduced from bulk to clusters [31]. We have calculated the magnetic moment as a function of the interatomic distance in an Rh_{13} icosahedron cluster. The distance dependence of the Hamiltonian is fully contained in S^{α} while the potential parameters are taken from the bulk fcc LMTO-ASA calculation. As shown in figure 2, our TB results are in good agreement with the DFT Dmol calculations [32]. The magnetic moment at large distance is 21 μ_B (1.62 μ_B/atom). As the interatomic distance is reduced, the moment changes to 15 μ_B (1.15 μ_B/atom) at a distance 0.254 nm, which is close to the equilibrium distance of the Dmol LDA calculation. The results of the matrix inversion are better than those of the interpolation scheme, which overestimates the moment at reduced distances.

In applying TB methods to alloy systems, the heteronuclear hoppings are usually obtained as the geometric average of the corresponding homonuclear hoppings [33]. As shown in equation (4), this approximation is correct to first order without any environmental dependence. Our TB model can be applied to alloy systems straightforwardly. In the case of the binary cluster $Fe_{15}Co_{12}$, our TB model exactly reproduces the Dmol calculated magnetic moment. Actually, the local moment profiles are also quite similar to those of the Dmol calculations. In the next subsection, we will study the spin and orbital magnetism of free and embedded Co clusters.

3.2. Free and Cu-coated Co clusters

There are a few reports in the literature of *ab initio* calculations of the local moments of cobalt grains embedded in a copper host, and the results obtained are contradictory. In particular, Gómez and Guenzburger [34] obtain a moment increasing toward the interface while Nogueira and Petrilli [35] find the opposite behaviour.

The main problem facing theoretical calculations on embedded clusters is how to treat the embedding matrix. As noted, different approaches can give very different results [34, 35]. To

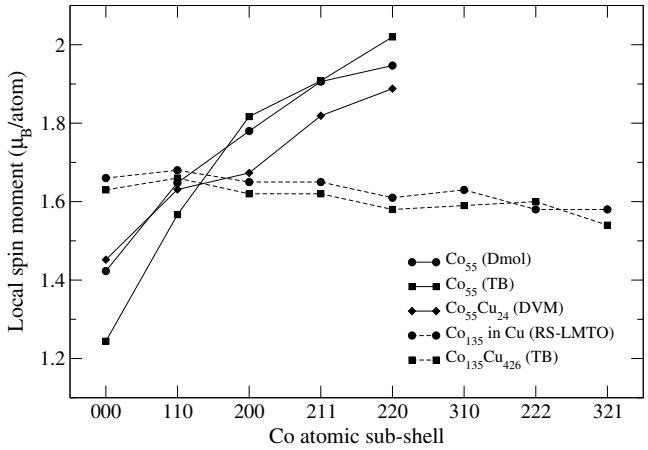

Figure 3. Local spin moment of small free and embedded Co clusters.

resolve the issue, we have treated the embedding copper matrix as shells surrounding the cobalt core. The TB results together with the different *ab initio* results for the local moments within a cluster are shown in figure 3 for a few clusters. The experimental bulk Cu lattice spacing is used hereafter in all calculations, and we only consider the TB Hamiltonian constructed from matrix inversion. The geometries of the clusters studied are chosen to be fcc cubo-octahedral structures.

In a different context, recently we have shown that [20], the inclusion of at least one layer of matrix material is essential to get reasonably reliable results for embedded clusters, and that the large discrepancy between different *ab initio* calculations [34, 35] depends on whether the electron hopping between the cluster core and the embedded matrix is included or not. Our TB local spin moments for Co_{55} are in good agreement with those of Dmol. The largest embedded size in *ab initio* calculations is Co_{135} embedded in Cu [35]. As seen in figure 3, our TB results and the *ab initio* ones are almost indistinguishable. Both show that the spin moment of Co remains fairly constant and decreases slightly towards the interface. In their real space (RS) LMTO-ASA calculations [35], Nogueira and Petrilli had properly considered the hopping between the cluster core and the embedded matrix using a very large cluster in the recursion method.

Although the calculated spin moments of embedded Co clusters are reduced compared with free clusters and bulk materials, a recent experiment has shown a highly enhanced orbital magnetism [36]. It is straightforward to include spin–orbital interaction in our TB model. The spin–orbital coupling term is treated in the single-site approximation, and the coupling constants are taken from the last iteration of the self-consistent TB-LMTO-ASA calculations [37]. The one-electron problem is solved by exact numerical diagonalization without resort to any kind of approximation. In the calculation of the orbital moments, we have fixed the spin magnetization to the [001] direction. Because all the considered clusters have an O_h symmetry, the orbital moment anisotropy is expected to be small. The symmetry-adapted basis sets of the double point group D_{4h} are used in the calculations.

The results for 147 and 309 Co atom clusters are shown in figure 4, both for bare Co and for Cu-coated cores. Because of the reduced symmetry in the presence of the spin–orbit interactions, atoms in the same subshell that were previously equivalent display different orbital moments. The local orbital moments are averaged over all atoms in a subshell. As can be seen, there are some small fluctuations about $\sim 0.8\ \mu_B$ for core Co atoms, and enhancements for the

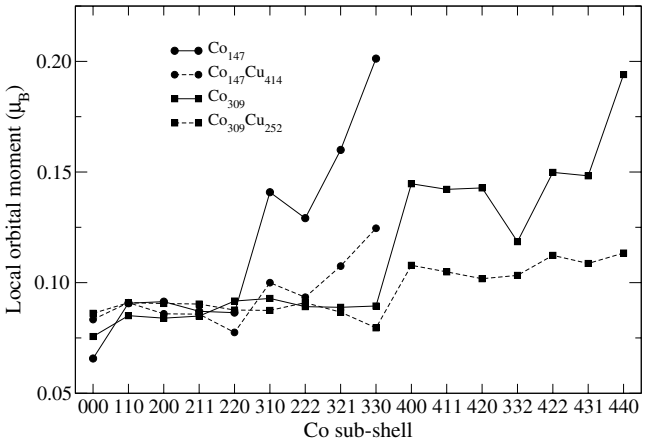

Figure 4. Local orbital moments of Co_{147}, $Co_{147}Cu_{414}$, Co_{309}, and $Co_{309}Cu_{252}$. The moments are averaged over the atoms in a subshell. The subshell sites are labelled as lattice positions in units of one-half the lattice constants.

interface atoms to 0.15–0.20 μ_B if there is no Cu coating. The Cu coating considerably reduces the orbital moment of the interface atoms. However, in contrast to the spin moment, the orbital moment always increases towards the interface. The spin moment is mainly determined by the local density of states at the Fermi energy. Due to the presence of the noble metal coating, the transition metal d-band width is slightly broadened and causes a slight reduction in the spin moments. On the other hand, the local orbital moments are mainly determined by the local geometrical symmetry. For the inner part of the Co clusters, the orbital moments are quenched to around the bulk value, while the local orbital moments are increased due to symmetry breaking at the interface. This trend is in agreement with the recent experiment [36].

Because our TB model is directly derived from the DFT calculations, it is not surprising that, like the LDA, the current TB model underestimates the orbital moment. Very recently, we have studied the orbital polarization in the ferromagnetic transition metals [37]. We have implemented the orbital polarization scheme into the current TB model for clusters. Some preliminary results show that the orbital magnetic moments on the cluster surface is highly enhanced. We have focused on presenting the TB model in this paper. The detailed results of the orbital moments of clusters will be presented elsewhere.

4. Conclusions

Based on the TB-LMTO-ASA method, we have proposed a simple universal tight-binding model. If one accepts the accuracy of the orthogonal TB-LMTO-ASA method, our scheme presents a natural tight-binding model for the periodic bulk materials including all three-centre terms. We have further shown that the TB model can be applied to a wide range of structures if the environmental dependence is properly accounted for. In addition to the self-consistent terms to the on-site energy levels, a very simple spin dependence of the hoppings is introduced via linear interpolation of the on-site potential parameters.

With the environmental effect largely accounted for by the localized structure constants, we have used the TB model to study the magnetic properties of thin films and clusters. The excellent agreement between the TB results and available *ab initio* results proves that the TB model can be a very useful alternative to the extremely resource-demanding *ab initio* calculations in calculating the magnetic properties of large systems.

We have presented an account of the magnetic properties of cobalt clusters embedded in copper. We find that the local spin moments on Co decrease slightly toward the interface. Unlike the local spin moment, the local orbital moment increases towards the interface with the Cu, although to a lesser extant than that obtained for the free clusters.

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