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Parametrization of modified embedded-atom-method potentials for Rh, Pd, Ir, and Pt based on density functional theory calculations, with applications to surface properties

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A scheme to obtain modified embedded-atom-method (MEAM) potentials from density functional theory calculations for fcc metals has been developed. This scheme is applied to the platinum-group metals Rh, Pd, Ir, and Pt. Bulk and surface properties, including surface reconstructions and self-diffusion barriers, are calculated with these MEAM potentials and are compared with available experimental data. The potentials are able to predict the (100)-(1 × 5) hexagonal and (110)-(1 × 2) missing row surface reconstructions of Ir and Pt as well as their absence on Rh and Pd. Also, the physical interpretation of the MEAM and related models is addressed, linking it to the bond-order conservation principle. With the help of the latter, it is shown that the MEAM has a solid theoretical base and is able to give straightforward relations between such properties as the vacancy formation energy and the occurrence of the (1 × 5) surface reconstruction on the (100) surface.

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I. INTRODUCTION

The platinum-group metals are among the most important in heterogeneous catalysis, which makes the study and prediction of their surface properties of great interest. Examples include the oscillatory behavior of, e.g., NO reactions on surfaces1–3 and the CO-induced lifting of the quasihexagonal, clean surface reconstruction of Pt(100) during catalytic oxidation.4 Much research on these metals has been performed both experimentally and theoretically. Here we will focus on the (pure) fcc metals Rh, Pd, Ir, and Pt and their surface properties in particular. The modified embedded-atom method (MEAM) as developed by Baskes and co-workers5–7 is employed to describe bulk and surface phenomena. The MEAM parametrization of Baskes is able to describe many fcc, bcc, and hcp bulk properties of various metals,7–9 as well as the (110)-(1 × 2) missing row (MR) surface reconstruction of Pt (Ref. 10) and several surface properties of the Si (100) and (111) surfaces.11,12 However, considerable and inherent arbitrariness still is contained in the potential parametrization, mainly due to the lack of experimental data to which the parameters were fitted. The aim of the present work is twofold. First, we present a scheme to derive parameters for the MEAM potentials from density functional theory (DFT) calculations and, and secondly, the physical picture of the MEAM is put in a slightly different perspective to enhance the physical interpretation of the results of our simulations.

One of the surface properties of interest is the (quasi)hexagonal surface reconstruction of the clean (100) surface of the late 5d elements Ir, Pt, and Au. It plays an important role in, e.g., the CO oxidation on Pt mentioned above and has been the subject of many experimental and theoretical studies. Theoretically this phenomenon has proved to be a challenging feature: of the applied methods—DFT in the local density approximation,13 effective-medium theory (EMT),14 and glue Hamiltonian15–17—only the last is able to actually predict the hexagonal surface reconstruction. Drawbacks of the glue Hamiltonian, however, are the large parameter set (44 in total), the restriction to systems with a higher coordination number than seven only, and the ill-defined physical meaning of its interaction functions when considered separately.

We developed potentials for Rh, Pd, Ir, and Pt based on metal properties calculated with DFT. The advantage of using theoretical data is that the input data set can be enlarged at will and may include information on systems which cannot be investigated experimentally (such as hcp Pt). This is all the more relevant for modeling of heteroatomic interactions such as adsorbate/surface interactions. Our MEAM parametrization is based on a fit to selected DFT data; it is subsequently tested on a different set of data, relating in particular to surface properties. The physical interpretation of the MEAM we use to interpret our results is based on the bond-order conservation principle (BOCP).18

The organization of this paper is as follows. In Sec. II the basic equations of the MEAM are addressed and the scheme used to determine the parameter sets is described. Section III describes the computational techniques regarding our DFT and MEAM calculations. In Sec. IV the results of the MEAM simulations using our potentials are presented and compared to simulations with previously developed potentials and to experiment, if available. Finally, in Sec. V a physical interpretation of some of the simulation results is given, using the bond-order picture of the MEAM. Some general features of the MEAM and subtleties of its application in simulations are also discussed.

II. THEORY

A. The MEAM

In this section the modified embedded-atom method due to Baskes7 for a system of single type particles is recaptured and also its physical interpretation is discussed.

The original embedded-atom method (EAM) is a semi-empirical, many-atom potential for computing the total energy of a metallic system. The EAM has been extensively applied to various systems of interest and has proved to give good results in a wide range of applications. For a review of the EAM, see Ref. 19. The modified embedded-atom method

-
is an empirical extension of the EAM, initially introduced to
describe covalent bonding in Si and Ge.\textsuperscript{5} The extension lies
in the fact that angular forces and therefore the effects of
directional bonding are included. The total energy $E$ of a
system of single type atoms in both the EAM and the
MEAM can be written as

$$E = \sum_i E_i = \sum_i \left[ \frac{1}{2} \Phi_i + F(n_i) \right],$$

(1a)

with

$$\Phi_i = \sum_{j(\neq i)} \phi(r_{ij}).$$

(1b)

Here, $E_i$ denotes the energy of atom $i$, which depends on its
environment by means of the total pair potential $\Phi_i$ and a
many-body correction term $F$. The distance between atoms $i$ and $j$ is denoted $r_{ij}$, and $\phi$ describes the actual pair interaction. Within the EAM one has

$$n_i = \sum_{j(\neq i)} \rho(r_{ij}).$$

(2)

Baskes and co-workers introduce $\rho(r_{ij})$ as the spherically
averaged atomic electron density of atom $j$ and $n_i$ is the
background electron density at site $i$.

In the original interpretation, every atom is considered to
be embedded in the electron sea (background density) consti-
tuted by all other atoms of the system. Therefore, $F$ is
conventionally termed the embedding function. While not
discarding this general view, a slightly different interpreta-
tion, namely, the BOCP, can be employed to understand the
physical meaning of $F$ and the general success of both the
EAM and the MEAM.

The essential difference between the EAM and the
MEAM is in the way $n_i$ is computed. In the MEAM it is
written as

$$n_i = n_i^{(0)} \sqrt{1 + \Gamma_i},$$

(3a)

$$\Gamma_i = 3 \sum_{k=1}^3 w^{(k)} \left( \frac{n_i^{(k)}}{n_i^{(0)}} \right)^2,$$

(3b)

where the $n_i^{(k)}$ are corrections to $n_i$ that include angular de-
dependence and the $w^{(k)}$ are weighting factors. Although other forms for $n_i$ are used,\textsuperscript{20–23} we found the form of Eq. (3a) to
be most adequate for our applications, especially for systems
involving low coordination.

The $n_i^{(k)}$ are written as

$$n_i^{(0)} = \sum_{j(\neq i)} \rho^{(0)}(r_{ij}),$$

(4a)

$$(n_i^{(1)})^2 = \sum_{\mu} \left[ \sum_{j(\neq i)} \rho^{(1)}(r_{ij}) \frac{r_{ij}}{n_i^{(0)}} \right]^2,$$

(4b)

$$(n_i^{(2)})^2 = \sum_{\mu, \nu, \tau} \left[ \sum_{j(\neq i)} \rho^{(2)}(r_{ij}) \frac{r_{ij}}{n_i^{(0)}} \right]^2 - \frac{1}{3} \sum_{j(\neq i)} \rho^{(2)}(r_{ij})^2,$$

(4c)

$$(n_i^{(3)})^2 = \sum_{\mu, \nu, \tau} \left[ \sum_{j(\neq i)} \rho^{(3)}(r_{ij}) \frac{r_{ij}}{n_i^{(0)}} \right]^2,$$

(4d)

where $\mu, \nu,$ and $\tau$ denote the components of the distance
vector between atoms $i$ and $j$. The $n_i^{(0)}$ has spherical sym-
metry and setting $\Gamma_i$ equal to 0 would retrieve the EAM expre-
sion for $n_i$, with $\rho^{(0)}$ being the spherically averaged atomic
electron density of Eq. (2). This form of $n$ ensures that in a
nearest-neighbor model the energy of a hcp lattice is differ-
ent from that of a fcc lattice, which is not the case in the
EAM or in the glue Hamiltonian.

The partial atomic electron densities are assumed to be
given by a simple exponential form:

$$\rho^{(k)}(r) = \exp \left[ - \beta^{(k)} \frac{r}{r_0} - 1 \right],$$

(5)

where $\beta^{(k)}, k = 0–3,$ are parameters to be determined and
where $r_0$ denotes the equilibrium nearest-neighbor distance
in the bulk of the perfect fcc crystal.

Thus, whereas in the EAM $n$ can be thought of as an
electron density, in the MEAM $n$ cannot be associated any
longer with the physical electron density. This is due to the
fact that the specific forms of Eqs. (4b)–(4d) imply that $n$
is no longer conserved whereas the atomic densities $\rho^{(k)}$ of the
individual atoms do not change for different systems. For
instance, the value for $n$ experienced by an atom in a fcc
lattice is different from that in a hcp lattice with the same
atom-atom distances, despite the fact that the number of
nearest neighbors and the atomic densities are equal. The
difference in $n$ is therefore clearly an angular dependent ef-
fect and not a particle density effect. Instead, one can con-
sider $n$ to be an effective coordination number,\textsuperscript{15} which for
the MEAM incorporates both the atomic electron density and
the angular effects. Consequently, $F$ can be considered a
bond-order correction term to the total pair potential $\Phi$, which
accounts for the fact that the effective coordination number
$n$—and therefore the BO—changes according to the
number of atoms and the symmetry of the system.

Note that from Eqs. (3) and (4) for a symmetric cubic
 crystal $n_i = n_i^{(0)}$, which reduces to $N_0^{(0)}$ when considering
nearest neighbors only; as will be done from now on. As
pointed out by Baskes, some justification for ignoring all but
nearest neighbors lies in the surprising result that the equi-
librium spacing between layers is governed by highly
screened local interactions.\textsuperscript{24} Also, Baskes and co-
workers recently found that the forces in Al may be well described by
a short-range many-body potential.\textsuperscript{25}

The bond-order function (BOF) $F$ is given by

$$F(n) = A E_0 n \ln \frac{n}{N_0},$$

(6)

where $A$ is a scaling parameter to be determined, $E_0$ is the
sublimation energy (the negative of the cohesive energy
accounts for this phenomenon [see, e.g., Eq. (9)] and therefore we choose to refer to $F$ as the bond-order function.

In its original formulation, where an atom is considered to be embedded in the electron density constituted by the other atoms of the system, $F$ has no clear physical meaning. Here this picture is extended to a BO-corrected interaction, both theoretically and physically well understood, which depends on the effective coordination number. Note that the BO picture is inherent to the current forms for $\phi$ and $F$, whereas the original view is more general since the nonuniqueness between $\phi$ and $F$ allows more general forms for $\phi$ and $F$. This is, e.g., the case for the initial formulation of the EAM, where $\phi$ was assumed to be entirely repulsive.\cite{Finnis1984} This resembles the mathematically equivalent formulation by Finnis and Sinclair,\cite{Finnis1984} who use a tight-binding interpretation in which $\phi$ represents a core-core repulsion and $F$ a band energy. In the case of Ercolessi and co-workers’ glue Hamiltonian, the physical interpretation of their forms for both $\phi$ and $F$ is not well defined, when considered separately.\cite{Ercolessi1991}

In order to theoretically support the BO picture and its functional form in the MEAM, DFT is used to calculate the energy of a Rh atom $E_i$ in several systems with varying numbers of nearest neighbors. These systems are fcc ($N_{\text{fcc}} = 12$), bcc ($N_{\text{bcc}} = 8$), simple cubic ($N_{\text{sc}} = 6$), diamond cubic ($N_{\text{dc}} = 4$), and a single atom ($N = 0$), which is set as a reference of 0 eV. For simplicity, $r$ is set equal to the equilibrium nearest-neighbor distance of bulk fcc $r_0$ and we neglected higher than $k = 0$ contributions to $n_i$, which appear only in the case of the four-coordinated system. By neglecting $k > 0$, the MEAM is reduced to the EAM, but, again, the EAM and the MEAM differ here only for the four-coordinated system (i.e., the $k = 3$ contribution is nonzero in the MEAM). The energy per atom $E_i$ is then given by Eq. (9) with $n_i = N$. By substituting the DFT value for $E_0$ [which is obtained by the procedure described below in Sec. II C 1] and using Eq. (9), $F$ as it is determined by DFT is found. Fitting to it the functional form of Eq. (6) results in the function as depicted in Fig. 1. Obviously, the functional form for $F$ of Eq. (6) accurately fits the calculated atomic energies. This confirms the BOCP and the interpretation of $F$ as a BO function.

C. Determination of the MEAM parameters

In general, parameters can be obtained by relating them to physical quantities. In the original derivation of (M)EAM parameters, experimental data for bulk properties were used.\cite{Haas2002} However, due to the lack of data, some parameters were set arbitrarily.

Apart from filling up these "experimental gaps," theory can provide detailed information on the physical behavior of atoms in systems that are not observed experimentally, such as the surface energy as a function of surface relaxation, or the cohesive energy in a hcp lattice. The overall results of the DFT calculations used to determine the MEAM parameters and (where available) the experimental values are listed in Tables I and II. All DFT values are reproduced by the MEAM within a few percent. The resultant parameters are given in Table III.

The exponential decay factor $\alpha$ is related to the bulk modulus and the atomic volume: $\alpha = \sqrt{9B11/E_0}$.

Now we can write for the energy per atom for any configuration of single type atoms at $r = r_0$,

$$E_i = -\frac{N}{N_0} E_0 + F(n_i(r_0)),$$

(9)

where $N$ denotes the number of nearest neighbors for a specific configuration. The physical picture is that, in a certain system, the interaction energy per atom is proportionally equal to the interaction energy in a fcc lattice corrected by a bond-order energy in terms of the bond-order function $F$. For systems with atomic distances other than $r_0$, Eq. (9) becomes slightly more complicated, but the general view of the energy per atom being approximately proportional to the number of nearest neighbors with a correction for the BO still remains valid.

B. Bond-order function

In this section the bond-order conservation principle\cite{Rice1989} and its relation to the current formulation of the MEAM will be addressed. The concept of bond order will be shown to follow naturally from DFT calculations performed on several Rh systems and it will prove to be useful in explaining relations between properties of the fcc metals studied here.

The BOCP states that a certain amount of bonding strength is shared among all bonds of an atom. This rationalizes the well-known fact that, when the number of bonds of an atom is reduced, the strength of each of the remaining bonds increases. The dependence of bond strength on coordination illustrates the inadequacy of simple two-body interactions to describe metallic systems: when using a two-body interaction potential only (where each bond has the same strength, regardless of the number of bonds) one needs to correct for this BOCP. Within the (M)EAM, $F$ obviously
and a function of Eq. of state is obtained from DFT calculations. By fitting the lowed, but in reverse order. The reference structure equation treated here, the procedure used by Baskes is closely fol-

In all systems the atoms are equally spaced at \( r_0 \), the equilibrium nearest-neighbor distance of Rh in a fcc lattice. The solid line depicts the fit to the calculated values according to Eq. 6, resulting in \( AE_0 = 5.48 \text{ eV} \).

1. Reference structure equation of state

For the equilibrium lattice structure of the Pt-group metals treated here, the procedure used by Baskes is closely followed, but in reverse order. The reference structure equation of state is obtained from DFT calculations. By fitting the function of Eq. (8) to the calculated energy per atom as a function of the nearest-neighbor distance, values for \( E_0, r_0, \) and \( \alpha \) are readily obtained.

![FIG. 1. Bond-order function \( F \) and bond-order correction energy per bond \( F/n \) for Rh. Values indicated by the circular symbols are obtained using Eq. (9) and calculating with DFT the atomic energies of fcc, bcc, simple cubic (sc), and diamond cubic (dc) systems. In all systems the atoms are equally spaced at \( r_0 \), the equilibrium nearest-neighbor distance of Rh in a fcc lattice. The solid line depicts the fit to the calculated values according to Eq. 6, resulting in \( AE_0 = 5.48 \text{ eV} \).](image)

2. Partial weights and scaling parameter

In systems where all nearest-neighbor distances are equal to \( r_0 \), the atomic densities all equal 1 [see Eq. (5)]. This indicates that the energy of such a system is, apart from \( A, E_0, r_0, \) and \( \alpha \), entirely determined by the weighting factors \( w_i^{(k)} \). The scaling parameter \( A \) should be close to unity in order to avoid anomalies such as negative values for the unrelaxed vacancy formation energy in the EAM limit. Further, we chose not to use a value for \( A \) derived from the procedure sketched in Fig. 1, since there \( k > 0 \) contributions are neglected and all computed systems are fixed with atom-atom spacings of \( r_0 \) (i.e., nonequilibrium configurations for the dc, sc, and bcc systems). For these reasons and for simplicity, \( A \) is chosen to equal 1 in all parameter sets. Alternatively, one could follow the procedure sketched in Fig. 1 to determine \( A \) (in this case, it would result in \( A = 0.96 \) for Rh). Such a procedure would probably be most suitable for parametrizing potentials that are used to describe a wide range of different bulk systems.

For the three weighting factors, the unrelaxed surface energies of the low index planes, the fcc/hcp crystal structure energy difference (which represents a fitting quantity rather than a physical quantity), and the unrelaxed vacancy formation energy are used. In general, DFT in the generalized gradient approximation (GGA) tends to underestimate for the late \( 5d \) elements the values for quantities such as the surface energy and the unrelaxed vacancy formation energy, as compared to experimental measurements. A similar feature has been discussed by Schmid et al. concerning the sublimation energy of Pt. They suggest that this underestimation is rather due to the GGA than to relativistic effects. Although we consider the discrepancies for the sublimation and surface energies obtained from GGA-DFT to be acceptable (at most

| TABLE I. Results of the DFT calculations used for fitting MEAM parameters compared with experimental data. The values listed are sublimation energy \( E_0 \) (eV/atom) (Ref. 46), equilibrium nearest-neighbor distance in bulk fcc \( r_0 \) (Å) (Ref. 47) exponential decay factor \( \alpha \) (related to the bulk modulus) (Ref. 48), unrelaxed vacancy formation energy \( E_v^{(k)} \) (eV) (Ref. 52), and unrelaxed surface energies of the low index surfaces \( \sigma_{hkl} \) (eV/Å\(^2\)) (Ref. 52). For \( E_v^{(k)} \) of Rh, Pd, and Ir we used the LDA-DFT values of Refs. 30–32, since our GGA-DFT values differ by over 0.5 eV from the experimental values. The experimental values for \( \Delta E \) were derived from stacking fault or phase diagram information. The experimental surface energies are polycrystalline average values, which have been crudely extrapolated from the melt to 0 K and are accurate at least to 10%. |
|-----------------|-----------------|-----------------|-----------------|
|                | Rh              | Pd              | Ir              | Pt              |
|                | DFT            | Expt.           | DFT            | Expt.           | DFT            | Expt.           | DFT            | Expt.           |
| \( E_0 \)       | 5.72           | 5.75            | 3.68           | 3.91            | 7.44           | 6.93            | 5.47           | 5.77            |
| \( r_0 \)       | 2.72           | 2.69            | 2.80           | 2.75            | 2.75           | 2.72            | 2.82           | 2.77            |
| \( \alpha \)     | 5.89           | 6.00            | 6.34           | 6.43            | 6.37           | 6.52            | 6.23           | 6.44            |
| \( E_v^{(k)} \) | 2.26\(^a\)      | 1.9–2.5         | 1.65\(^b\)     | 1.7–1.85        | 2.27\(^c\)     | 1.07            | 1.2–1.6        |
| \( \Delta E \)  | 0.04           | 0.19            | 0.03           | 0.10            | 0.07           | 0.32            | 0.08           | 0.15            |
| \( \sigma_{100} \) | 0.147         | (0.162)         | 0.094          | (0.125)         | 0.180          | (0.187)         | 0.114          | (0.156)         |
| \( \sigma_{110} \) | 0.306         | (0.162)         | 0.200          | (0.125)         | 0.374          | (0.187)         | 0.243          | (0.156)         |
| \( \sigma_{111} \) | 0.122         | (0.162)         | 0.082          | (0.125)         | 0.142          | (0.187)         | 0.092          | (0.156)         |

\(^a\)See Ref. 31.
\(^b\)See Ref. 32.
\(^c\)See Ref. 30.

165106-4
TABLE II. Results of the DFT calculations for the (100) and (111) surface layer relaxations, used for fitting MEAM parameters \( \beta^{(1)} \) and \( \beta^{(3)} \) (see also Fig. 2). All layers except the surface layer are kept fixed. The optimized change in first-layer–second-layer spacing \( \Delta d_{12} \) obtained in this way is given as a percentage of the ideal bulk spacing (a negative value indicates inward relaxation). The calculated relaxations for (100) are in good agreement with the DFT results presented in Ref. 13. Note that our DFT calculations predict the relaxation of the (111) surfaces to be in opposite directions for elements in different rows of the periodic table of elements. Also shown are experimental results, mostly obtained by low energy electron diffraction, reported in Ref. 53. Note that, in general, the experimental errors are too large to be conclusive about the actual direction of the relaxations.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta d_{12}(100) )</th>
<th>( \Delta d_{12}(111) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>DFT</td>
<td>Expt.</td>
</tr>
<tr>
<td>Pd</td>
<td>-4.1</td>
<td>0.5 ± 1.1, 0.5 ± 1.0</td>
</tr>
<tr>
<td>Ir</td>
<td>-4.8</td>
<td>-3.6 ± 0.5</td>
</tr>
<tr>
<td>Pt</td>
<td>-2.6</td>
<td>0.0 ± 0.2</td>
</tr>
</tbody>
</table>

\(^a\)Multilayer relaxation.

around 0.3 eV per atom), the discrepancies for the unrelaxed vacancy formation energies of Rh, Pd, and Ir are too large (around 0.5–1.0 eV per atom) for obtaining reliable parameter sets. Therefore, for these three metals the unrelaxed vacancy formation energies as calculated previously in the local density approximation by others are used.\(^30–32\)

3. Atomic electron densities

As shown in Eq. (5), the atomic densities are assumed to depend only on one additional parameter \( \beta \) at distances other than \( r_0 \). In order to include bulk as well as surface properties, systems are used from which information about the elastic constants and surface relaxations can be extracted.

Information about the elastic constants is obtained by systematically calculating, using DFT, the energy of a fcc unit cell in which the layer spacing in the [100] direction is varied. Due to symmetry, the effective coordination number \( n \) of this system depends only on \( k = 0.2 \). Using the previously determined value for \( \omega^{(2)} \), the parameters \( \beta^{(0)} \) and \( \beta^{(2)} \) can then be determined by fitting the analytical MEAM expression for the energy of this system to the DFT calculations. It turns out, as already indicated by Baskes, that the \( k = 2 \) contribution to the energy of a system close the bulk fcc is rather unimportant. In the case of Pt, the value for \( \beta^{(2)} \) even tends to unphysical values (i.e., negative values), and it is therefore fixed to unity, considering that this hardly affects the energy. This implies that most of the elastic properties are contained in \( \beta^{(0)} \) and that \( \beta^{(2)} \) is the least important parameter in our fits. It should be noted that the weighting parameters influence the energy most, whereas the exponential decay parameters rather determine relaxation effects.

For the surface energy as a function of the relaxation of the top layer, all parameters contribute to the total effective coordination number \( n \). Thus, from the previously determined values of \( \omega^{(k)}, k = 1,2,3 \), and \( \beta^{(k)}, k = 0,2 \), values for \( \beta^{(k)}, k = 1,3 \), can be obtained by similarly fitting the corresponding MEAM energy expression to the DFT calculations of the relaxation of the (100) and (111) surfaces (see Table II and Fig. 2).

4. Differences from existing parameter sets

To recapitulate, parameters \( \omega^{(k)} \) include both bulk and surface properties (unrelaxed vacancy formation energy, unrelaxed surface energies, hcp-phase energy). Parameters \( \beta^{(k)}, k = 0,2 \), are determined by nonequilibrium bulk properties, whereas parameters \( \beta^{(k)}, k = 1,3 \), are determined by surface relaxations. Of course, all parameters \( \beta^{(k)} \) implicitly bear the features contained in \( \omega^{(k)} \). In this way we combined several important bulk and surface properties in our parameter sets, which should imply that a wide range of bulk and surface properties—in addition to of the ones used for the fit—are reproduced.

The parameter sets as originally determined by Baskes for several fcc metals include, as already noted, considerable

TABLE III. MEAM parameters for Rh, Pd, Ir, and Pt. Values listed are sublimation energy \( E_0 \) (eV/atom), equilibrium nearest-neighbor distance in bulk fcc \( r_0 \) (Å), exponential decay factor of the \( E_{fcc}(r) \) function \( \alpha \), scaling parameter \( A \) for the bond-order function, exponential decay factors for the atomic densities \( \beta^{(k)} \), and weights for the corrections to the effective coordination number \( \omega^{(k)} \).

<table>
<thead>
<tr>
<th></th>
<th>( E_0 )</th>
<th>( r_0 )</th>
<th>( \alpha )</th>
<th>( A )</th>
<th>( \beta^{(0)} )</th>
<th>( \beta^{(1)} )</th>
<th>( \beta^{(2)} )</th>
<th>( \beta^{(3)} )</th>
<th>( \omega^{(0)} )</th>
<th>( \omega^{(1)} )</th>
<th>( \omega^{(2)} )</th>
<th>( \omega^{(3)} )</th>
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<td>2.06</td>
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<td>1</td>
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<td>0.40</td>
<td>1</td>
<td>0.45</td>
<td>-1.30</td>
<td>6.84</td>
</tr>
<tr>
<td>Pt</td>
<td>5.47</td>
<td>2.82</td>
<td>6.23</td>
<td>1</td>
<td>4.39</td>
<td>2.74</td>
<td>1.00</td>
<td>2.08</td>
<td>1</td>
<td>1.76</td>
<td>-3.90</td>
<td>4.55</td>
</tr>
</tbody>
</table>
Baskes already pointed out, this selection of more definitive evaluation of the optimized and theoretical calculations are recommended for unobserved systems. The drawback, however, is the absence of data and information obtained from phase diagrams. The small offset is due to the fact that the MEAM energy expression of this system to the DFT calculations reported previously; see Sec. II C 2, the method described in Ref. 30 was followed, where \( E_v^f \) is determined according to
\[
E_v^f = E(1) - \frac{N-1}{N} E(0) .
\]
Here \( E(i) \) denotes a cell with \( i \) vacancies and \( N \) denotes the number of atoms in the cell without vacancies. It was found that \( N = 32 \) was sufficient. 30

The surface energy per \((1 \times 1)\) surface unit \( \sigma \) was calculated according to
\[
\sigma = (E - NE_{\text{coh}})/N_{1 \times 1} ,
\]
where \( E \) is the total energy of the periodic slab (generally 10–13 layers), \( N \) is the number of atoms in the slab, and \( N_{1 \times 1} \) is the total number of \((1 \times 1)\) surface units. The results of the DFT calculations are shown in Tables I and II.

B. MEAM calculations

For the MEAM energy minimization calculations, the DYNAMO code as developed by Baskes and co-workers was used.

Since we focus mainly on the general features of our potentials and the scheme for obtaining them, not all simulated properties, such as relaxations of atoms and layers, have been investigated extensively.

As mentioned in Sec. II A, we restrict ourselves to nearest-neighbor interactions only. By choosing to consider only nearest-neighbor interactions, it is necessary to provide a cutoff or screening procedure that defines what a nearest neighbor is. This procedure must be continuous in the energy and its first two derivatives to ensure that, e.g., no force discontinuities appear in molecular dynamics (MD) calculations.

Initially Baskes opted for a method that imposes only screening between an atom and its neighbors, whereas in more recent work he included a radial cutoff as well. 9 There are several arguments for choosing a cutoff besides (or instead of) screening. First, in our work the MEAM parameters are explicitly fitted to nearest neighbors only, which means that by taking into account contributions from atoms other than nearest neighbors (as is done in a screening-only method), artifacts can be introduced in the interaction. Sec-

III. COMPUTATIONAL ASPECTS

Here, the computational details of both the DFT and the MEAM simulation calculations are addressed. Also, the expressions for the physical quantities used throughout the manuscript are specified.

A. DFT calculations

The DFT calculations were performed using the VASP package, 33 which uses periodic cells, a plane wave basis set, and ultrasoft pseudopotentials with scalar relativistic corrections. For the GGA the PW91 functional is used. In all the calculations on the different systems the total energy was converged to approximately 1 meV with respect to the \( \mathbf{k} \) point sampling, energy cutoff, and cell size. In calculating the unrelaxed vacancy formation energy (calculated only for Pt, since the values for Rh, Pd, and Ir were obtained from calculations reported previously; see Sec. II C 2), the method described in Ref. 30 was followed, where \( E_v^f \) is determined according to
\[
E_v^f = E(1) - \frac{N-1}{N} E(0) .
\]
ond, the parameters are fitted to systems that are all at or near equilibrium. Therefore, the specific choice of the parameters may be expected to fail in describing properly systems far from equilibrium. Even when this is not the case, the energy differences between a cutoff and screened interaction can be expected to be rather unimportant in these off-equilibrium and hence high energy systems. A third argument, which applies when using no screening at all, but only a cutoff, is from the computational point of view: since, in contrast to screening, a cutoff does not depend on the actual spatial configuration of the atoms under consideration, it can be evaluated faster and more straightforwardly than angular screening (i.e., screening cannot be cast in the computationally efficient two-particle form). Finally, we should remark here that it appears from our simulations (discussed below in Sec. V B) that screening introduces its own specific behavior. Since, to our knowledge, this behavior has not been verified very thoroughly and since it makes the MEAM altogether less transparent, we chose not to apply screening in our MEAM simulations. Instead, only a smooth cutoff as described in Ref. 9 is applied at distances greater than \(1.13 r_0\) \((\approx r_0 + 0.4 \ \text{Å})\) from the atom. The cutoff region is taken to be 0.1 Å in all cases.

Typically the slabs used here consisted of 50–600 atoms, which appeared to be sufficient to converge the total energy to within 1 meV. In order to model bulk effects, the central layer in the slab was fixed in the simulations for the surface energies and the bottom layer was fixed in all other simulations. For calculating the hexagonal reconstruction energies on \(\{100\}\), a \(\{1 \times 5\}\) hexagonal surface reconstruction is used, which is equal to the hexagonal reconstruction observed on Ir(100), but slightly different from the two hexagonal phases observed for Pt\(^{36,37}\).

The heat of reconstruction of a surface \(H_r\) is defined according to Ref. 13 as

\[
H_r = (E_u + \Delta NE_{\text{coh}} - E_r)/N_{1 \times 1}.
\]

where \(E_u\) is the total energy of the unreconstructed slab, \(E_r\) is the total energy of the reconstructed slab, and \(\Delta N\) is the difference in number of atoms between the two slabs [i.e., \(\Delta N = 2\) for each slab unit of \(\{100\}\)-(1 \times 5) versus its \(\{100\}\)-(1 \times 1) counterpart and \(\Delta N = 0\) for \((110)-(1 \times 2)\) versus \((110)-(1 \times 1)\)]. \(N_{1 \times 1}\) is the total number of \((1 \times 1)\) surface units in the unreconstructed slab. This refers the energy to the area of the \((1 \times 1)\) slab. A positive value for \(H_r\) thus indicates that reconstruction is favored.

The self-diffusion barrier was obtained by taking the difference of the energies of a fully relaxed slab with an adatom on a bridging site and of a fully relaxed slab with an adatom on a hollow site. On the \(\{111\}\) surface two three-coordinated hollow sites exist: a fcc and a hcp site. The hollow site, which is found from our MEAM simulations to be preferred, is used in determining the self-diffusion barrier.

### IV. APPLICATION TO SURFACE PROPERTIES

Since in the present work we are mainly interested in surface properties, the potentials and the MEAM itself are put to the test in calculating, e.g., diffusion barriers of single adatoms on \(\{100\}\) and \(\{111\}\), and surface reconstructions of the \(\{100\}\) surface \([(1 \times 5)\text{-hex}]\) and the \(\{110\}\) surface \([(1 \times 2)\text{-MR}]\). Of course, one should expect the results to be at best as good as DFT itself.

The simulation results are compared with experiment (where available) and the results obtained using the potentials determined by Baskes. All results are shown in Table

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work (DFT input)</th>
<th>Baskes (experimental input)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_0)</td>
<td>equation of state Eq. (8)</td>
<td>direct</td>
</tr>
<tr>
<td>(r_0)</td>
<td>equation of state Eq. (8)</td>
<td>direct</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>equation of state Eq. (8)</td>
<td>bulk modulus Eq. (8b)</td>
</tr>
<tr>
<td>(A)</td>
<td>fixed</td>
<td>fcc/bcc energy difference</td>
</tr>
<tr>
<td>(\beta^{(0)})</td>
<td>elastic properties</td>
<td>shear elastic constants</td>
</tr>
<tr>
<td>(\beta^{(1)})</td>
<td>(100) and (111) surface relaxations</td>
<td>relaxation behavior near vacancy and surface, fixed</td>
</tr>
<tr>
<td>(\beta^{(2)})</td>
<td>elastic properties</td>
<td>shear elastic constants</td>
</tr>
<tr>
<td>(\beta^{(3)})</td>
<td>(100) and (111) surface relaxations</td>
<td>fixed to (\beta^{(1)})</td>
</tr>
<tr>
<td>(w^{(1)})</td>
<td>vacancy formation energy, surface energies, and fcc/hcp energy difference</td>
<td>vacancy formation energy</td>
</tr>
<tr>
<td>(w^{(2)})</td>
<td>vacancy formation energy, surface energies, and fcc/hcp energy difference</td>
<td>shear elastic constants, fixed</td>
</tr>
<tr>
<td>(w^{(3)})</td>
<td>vacancy formation energy, surface energies, and fcc/hcp energy difference</td>
<td>fcc/hcp energy difference</td>
</tr>
</tbody>
</table>
V. Apart from the prediction of the preferred site on Ir
(Ref. 38,39), which is according to experiment the hcp site,
we can see from Table V that there is good agreement of our
MEAM calculations with experiment. Also the results based
on the potentials determined by Baskes agree quite well.

The surface reconstructions especially agree very well
with experiment. In order to compare with other theoretical
studies, we mention the DFT calculations in the local density
approximation (LDA) approach by Fiorentini et al. who
predict that the Pd(100) surface does not reconstruct, but find

\begin{table}
\centering
\begin{tabular}{lccc}
\hline
 & \text{expt.} & \text{This work} & \text{Baskes} \\
\hline
\text{Rh} & & & \\
$H_{\text{hex}}(100)$ & $<0.0$ & $-0.17$ & $-0.08$ \\
$H_{\text{MR}}(110)$ & $<0.0$ & $-0.08$ & $-0.08$ \\
$E_{\text{ads}}(100)$ & $-5.06$ & $1.01$ & $0.96$ \\
$E_{\text{diff}}(100)$ & $0.88\pm0.02$ & $-4.50$ & $-4.56$ \\
$E_{\text{ads}}(111)$ & $0.16\pm0.02$ & $0.23$ & $0.35$ \\
$\Delta E_{\text{ads}}(111)$ & & $-0.02$ & $-0.03$ \\
\text{Pd} & & & \\
$H_{\text{hex}}(100)$ & $<0.0$ & $-0.09$ & $0.06$ \\
$H_{\text{MR}}(110)$ & $<0.0$ & $-0.07$ & $-0.02$ \\
$E_{\text{ads}}(100)$ & $-3.27$ & $0.57$ & $0.70$ \\
$E_{\text{diff}}(100)$ & $-2.94$ & $3.22$ & $0.06$ \\
$E_{\text{ads}}(111)$ & $0.16\pm0.02$ & $0.14$ & $-0.03$ \\
$\Delta E_{\text{ads}}(111)$ & & $-0.02$ & $-0.03$ \\
\text{Ir} & & & \\
$H_{\text{hex}}(100)$ & $>0.0$ & $0.08$ & $-0.31$ \\
$H_{\text{MR}}(110)$ & $>0.0$ & $0.05$ & $-0.13$ \\
$E_{\text{ads}}(100)$ & $-6.88$ & $1.67$ & $1.07$ \\
$E_{\text{diff}}(100)$ & $1.39\pm0.04$ & $-5.87$ & $-5.43$ \\
$E_{\text{ads}}(111)$ & $0.22\pm0.02$ & $0.26\pm0.03$ & $0.02\pm0.001$ \\
$E_{\text{diff}}(111)$ & $0.02\pm0.001$ & $0.016\pm0.001$ & $-0.06$ \\
$\Delta E_{\text{ads}}(111)$ & $0.25\pm0.02$ & $0.16$ & $0.12$ \\
\text{Pt} & & & \\
$H_{\text{hex}}(100)$ & $0.21\pm0.03$ & $0.26\pm0.03$ & $0.28$ \\
$H_{\text{MR}}(110)$ & $>0.0$ & $0.06$ & $0.03$ \\
$E_{\text{ads}}(100)$ & $-5.34$ & $1.21$ & $1.15$ \\
$E_{\text{diff}}(100)$ & $1.0\sim1.2$ & $-4.50$ & $5.00$ \\
$E_{\text{ads}}(111)$ & $0.25\pm0.02$ & $0.16$ & $0.12$ \\
$\Delta E_{\text{ads}}(111)$ & $<0.06$ & $-0.04$ & $-0.05$ \\
\hline
\end{tabular}
\caption{Results of the MEAM simulations with the potentials of Table III and the potentials by Baskes (Ref. 7). Where available, experimental data are listed. Values listed are heat of reconstruction of the (100)-hex phase $H_{\text{hex}}(100)$ and (110)-MR phase $H_{\text{MR}}(110)$, adatom adsorption energies $E_{\text{ads}}(hkl)$, self-diffusion barriers $E_{\text{diff}}(hkl)$, and adatom adsorption energy difference between fcc and hcp sites on (111) $\Delta E_{\text{ads}}(111) = E_{\text{ads}}(111) - E_{\text{ads}}(hkl)$. All values are listed in units of eV. The experimental self-diffusion barriers on Pd are estimated, based on the experimental data from the other metals. For Ir and Pt there probably exists an atomic exchange mechanism for the self-diffusion process on (100) (Ref. 54). Therefore, the “experimental” value reported here for Pt is an estimate based on the values for the diffusion barriers of Pt/Rh(100) (Ref. 55), Rh/Rh(100) and Pt/Rh(111) (Ref. 56), and Pt/Pt(111) (Ref. 42). For Ir the DFT value by Boisvert et al. (Ref. 57) is used.}
\end{table}

\footnotesize
\textsuperscript{a}See Ref. 56.
\textsuperscript{b}Estimated value.
\textsuperscript{c}Theoretical value, see Ref. 57.
\textsuperscript{d}See Ref. 38.
\textsuperscript{e}See Ref. 39.
\textsuperscript{f}See Ref. 60.
\textsuperscript{g}See Ref. 58.
for Pt(100) a slightly negative heat of reconstruction, which is not in agreement with experiment. The EMT calculations performed by Ritz et al. predict the unreconstructed Pt(100) surface to be more stable and the EAM potentials by Foiles and Voter are reported to suffer from the same problem. To our knowledge, only the glue Hamiltonian for Au by Ercolessi et al. is able to predict a hexagonal reconstruction on the Au(100) surface. As mentioned before, this method has a lower limit to the coordination number as high as 8 and requires four times as many parameters as the current formulation of the MEAM, making its extension beyond Au and certainly to binary systems problematic.

The self-diffusion energy barriers calculated with our potentials as well as with Baskes’ potentials are generally in qualitative agreement and in most cases in quantitative agreement with experiment. Even more, they appear to be on qualitative agreement and in most cases in quantitative agreement as well as with Baskes’ potentials are generally in potentials by Baskes still perform remarkably well, regarding the considerable amount of arbitrariness involved in determining the potentials from the scarce experimental data.

In conclusion, in addition to the fit values of Tables I and II, the MEAM and our potentials are able to describe surface properties such as surface reconstructions and self-diffusion barriers, indicating that our potentials as well as the MEAM are suitable for application to bulk and surfaces.

V. DISCUSSION

In this section it will be shown that the MEAM is based on the well-defined theoretical concept of the BOCP, apart from the more empirical view of embedding atoms in a background electron sea. Also, a straightforward relation between the vacancy formation energy and the (100) surface reconstruction will be established. Further, the general features of the MEAM and the computational aspects of applying a cutoff are addressed.

A. Physical evaluation

As a demonstration of the BO picture and the descriptive power of the MEAM, the relation between the vacancy formation energy and the occurrence of the hexagonal reconstruction on (100) will be discussed. The latter phenomenon will serve as a typical example in the forthcoming sections.

1. Bond-order correction

It can be seen from Table I that relatively high values for $E_v^f$ with respect to $E_0$ are found for the 4$d$ elements Rh and Pd, which do not reconstruct to a hexagonal phase on the (100) surface. For the 5$d$ metals Ir and Pt, on the other hand, $E_v^f$ is relatively low with respect to $E_0$. A similar observation can be found in Ref. 31. Within the MEAM it can be understood qualitatively that there is a relation between these two phenomena.

Recalling Fig. 1 one sees that, for $n > 4.41$ (i.e., $12/e$), large BO corrections (i.e., high values of $n^{(k)}$) to $n$ result in less BO correction energy (higher values of $F$). This implies less stabilization of the bonds of the atom under consideration. Equivalently, the metal-metal bonds are less stabilized. Higher values for $n^{(k)}$ thus result in a higher value for, e.g., the vacancy formation energy where the atoms neighboring the vacancy each have 11 less stabilized bonds.
In the first instance, one might expect the hexagonal reconstruction on \(100\) surfaces, where the real coordination (i.e., the local atomic density) of a surface atom is increased, to always be favored, since the total pair potential \(F\) is then lowered. However, two effects play an important role here. First, in the case of relatively high \(n(k)\) described above, the bonds in the hexagonally reconstructed surface are less stabilized. This is the result of a higher effective coordination, since \(n\) will be higher. A second effect is the appearance of repulsion in the second layer, which increases with higher \(n(k)\) values, since then the effective coordination is considerably higher than 12. This results in a positive value for the BO correction energy, as seen from Fig. 1.

Reinspection of Table III indicates that the sum of \(w(k)\) parameters, being an indication of the correction to \(n\), is higher for the 4\(d\) elements Rh and Pd than for the 5\(d\) elements Ir and Pt, mainly due to the negative value of \(w(2)\) for the latter two elements. This is also illustrated by the fact that Baskes’ potential for Ir does not predict \((100)-(1\times5)\), since in this parameter set the value for \(w(2)\) is as high as 8.10. Further, Baskes’s potential for Pd does predict \((100)\)-hex to occur, since \(w(2)=1.38\) in this case, which is considerably smaller than the \(w(2)\) for Pd and Rh found here. To illustrate the foregoing, Fig. 3 depicts the \(w(2)\) dependence of \(E_v\), \(\sigma_{100}(1\times1)\), and \(\sigma_{100}(1\times5)\).

2. Effective coordination

In Fig. 4 the average values for \(n_i\), \(\Phi_i\), and \(E_i\) per layer are shown. The repulsion in the layer below the hexagonally reconstructed surface layer due to \(\langle n\rangle >12\) causes an outward relaxation (approximately 0.3 Å, not shown). This causes \(\langle n\rangle\) for this layer to drop from approximately 11.3 (not shown) to a value even below \(\langle n\rangle\) of the \((1\times1)\) surface layer. For Pt, \(\langle n\rangle\) is reduced to a lower value than for Rh due to the smaller average contribution of \(n(k)\) to \(n\) for Pt. Inspec-
tion of the $\langle \Phi \rangle$ plot, which can be considered as a measure of the real coordination, shows that the second layer has a higher value for $\langle \Phi \rangle$ for (1×5) than for (1×1) (i.e., lower real coordination). This is to be expected, since due to the outward relaxation of the reconstructed surface layer the real coordination is reduced in the second layer. Further, the $\langle \Phi \rangle$ values for the two surface phases are nearly equal in the first and third layers. This indicates that the difference in $\langle n \rangle$ for Pt and Rh in the (1×5) surface layer is entirely determined by angular dependent effects.

This gives a simple explanation within the MEAM model of the relation between the relative size of the vacancy formation energy and the occurrence of (100)-hex surface reconstruction. Additional support is found from the case of Ag versus Au: Au undergoes (100)-hex surface reconstruction and has a lower $E_{\text{f}}/E_{\text{o}}$ ratio (0.23) than Ag (0.39), which indeed does not reconstruct.

Considering the features addressed in Sec. V A 1, it might seem natural for the EAM, which has no $n^{(k)}$ contributions at all, to predict (100)-(1×5) surface reconstruction for any fcc metal. Indeed, in the case of the EAM limit, the unreconstructed vacancy formation energy is extremely low (around 10% of the actual value, not shown here). However, as explained above, the crucial factor in determining whether reconstruction is favored or not is the angular dependence. Since this is absent in the EAM, hexagonal reconstruction cannot be predicted by the EAM in its current form. We should note, however, that Ercolessi and co-workers are able to predict (100)-(1×5) surface reconstruction for Au without use of any symmetry. This indicates that the derivation of $\phi$, $F$, and $n^{(k)}$ in the current form of the MEAM is part of a proper description of surface reconstructions.

The fact that the effective coordination number $n$ in the surface layer is determined by symmetry rather than actual coordination can be understood as follows. Due to the outward relaxation of the (1×5) top layer, as mentioned before, the contribution of the second-layer atoms to $\langle n \rangle$ of the top layer atoms is reduced. The real coordination remains more or less unchanged, such that $\Phi$ (and in the EAM $F$ as well) remains more or less the same on average. However, from Eqs. (4) it can be derived that atoms within a plane tend to cancel each other’s contribution to $n^{(k)},k \geq 1$. Then, due to the reduced contribution from atoms below the surface plane and the increased contribution from the additional atoms within the (1×5) surface plane, the $n^{(k)}$ are canceled more in the (1×5) than in the (1×1) surface plane. This causes $\langle n \rangle$ for the (1×5) surface to decrease, even below $\langle n \rangle$ of the unreconstructed (100) surface. Since the $n^{(k)}$ contributions to $n$ in total are larger for Rh than for Pt, the remaining contributions in the (1×5) surface layer are also larger for Rh than for Pt. This can be seen in Fig. 4. Again we emphasize that this is a pure symmetry related effect and therefore an implicit property of the MEAM.

**B. Interaction cutoff**

In the few papers on the MEAM that have appeared so far, screening is generally applied to limit the interactions to nearest neighbors. Screening, however, introduces even more angular dependence and its own physics [e.g., the diffusion barrier for an adatom on Pt(100) is 1.21 eV without screening and with screening 1.43 eV]. Therefore, when used, screening should be considered a fundamental part of the MEAM.

Since, apart from the arguments put forward before, screening has not proved to give better results, we have chosen not to apply screening in our simulations.

A cutoff, as applied here, has its own drawbacks. For instance, when simulating bcc systems, where the ratio of second- to first-neighbor distances is 1.15, one should apply a smaller cutoff distance than the one we used in the present work (1.13$r_0$), or extend the model to include next nearest neighbors as well. Also, somewhat rugged interactions may result when the number of nearest neighbors changes during a simulation. In our case this is probably best shown by the energy barrier of an adatom passing a bridged site when diffusing from one hollow site on the (100) surface to another (Fig. 5). Similar artifacts in other systems may be expected from a screening procedure as well, since screening is similar to a cutoff in the sense that it can be considered as an angular dependent cutoff: a cutoff is applied only for certain spatial configurations.

However, since this anomaly is rather small (on the order of meV), we do not believe severe problems or artifacts will appear in molecular mechanics or molecular dynamics simulations: in MD simulations a diffusion process such as shown in Fig. 5 will most probably hardly be affected.
C. Limitations of the MEAM

Like every classical effective potential method, the MEAM has its limitations. For instance, the preference between fcc and hcp sites on the (111) surface of the fcc metals studied here always appears to be for the fcc site in contrast with experimental results. Also, not shown here, the alternating preference for small groups of adatoms to form either an island or a chain, as studied experimentally by Schwoebel and co-workers and modeled using the EAM by Schwoebel and co-workers, is not found for any of the MEAM potentials presented in this work or in the work by Baskes.

We believe that further improvements of the MEAM should be focused mainly on the way in which the above mentioned island shape alternation is correctly predicted in the EAM limit of the current MEAM. However, the current form for in may serve as a good basis, since it appears to be essential in predicting several surface properties in combination with the current forms of ϕ and F. Also, the current forms of ϕ and F are responsible for supporting the BOCP, which makes adjusting them undesirable.

Although we cannot give better suggestions at this stage for improving the way symmetry should be incorporated in the MEAM, we do believe further justification of the empirical forms of n(κ) should not be looked for in terms of the real electron density, such the s, p, and d bands. This argument is based on the BO picture introduced here and the essential role of symmetry as well.

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