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Interpretation of *ab initio* total energy results in a chemical language: I. Formalism and implementation into a mixed-basis pseudopotential code

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Abstract

A new variant of the recently developed energy-partitioning scheme is introduced, which allows us to give an interpretation of *ab initio* total energy results in a chemical language. In this scheme the energy of the bonds between atom-localized orbitals is represented by the covalent bond energy, which is invariant with respect to a constant shift of the effective crystal potential. This feature is a precondition for a comparison of the bond energies for various crystal structures within the framework of a band structure calculation. The implementation in a mixed-basis pseudopotential code is described, which requires the projection of the crystal pseudowavefunctions onto a minimal set of atom-localized non-orthogonal basis functions.

1. Introduction

Electronic structure calculations are an extremely powerful tool to predict many important properties of materials, and they are applied routinely in fields ranging from biochemistry to catalysis. However, although they yield the total energy very accurately the chemical understanding of bonding as a localized phenomenon is sometimes lacking. Most of the density functional theory programs are designed to yield the total energy but do not provide the tools to analyse the local interactions between the constituent atoms, and, hence, do not help us to *understand* the results.

Many attempts have been undertaken to track these local interactions beginning with Mulliken's [1] analysis, where the electron charge on a particular atom within a molecule is written as a sum of charge which is localized on this particular atom and a charge which is equally shared with all surrounding atoms. This concept of shared electronic charge has been further developed and adapted to describe periodic structures by Hoffmann [2–4] (the so-called crystal orbital overlap population, COOP) and has been applied to many different systems including surface interactions in the framework of extended Hückel calculations. The

major weakness of these approaches resides in the fact that the charge is partitioned and not the energy. The bonding charge does not yield information about the bond strength since the concept of strength is related to energy. The COOPs of Hoffmann have been modified by Dronskowski and Blöchl [5] to partition the energy and not the charge, defining a true bond strength (called crystal orbital Hamilton population, COHP) that can be applied when an orthogonal basis is used. This concept has been successfully applied to extended Hückel calculations recently [6, 7].

For non-orthogonal basis sets the COHPs cannot be used to characterize the bond strength because they are not invariant against arbitrary shifts of the potential, which are routinely performed in band structure calculations when comparing different crystal structures [8, 9]. Therefore, Börnsen *et al* [8, 9] have introduced a new measure for bond strength, the covalent bond energy E_{cov}, which is invariant and which allows us to compare quantitatively the bonding properties of different crystal structures when using orthogonal or non-orthogonal basis sets. In section 2.1 of the paper we adopt a slightly different definition of the covalent bond energy, which has a simpler physical interpretation while still being invariant against constant potential shifts. Our procedure was inspired by the work of Sutton *et al* [10–12], where the bonding properties of a solid are discussed within the framework of the tight-binding bond model. In some sense, our energy-partitioning scheme is an extension of their scheme to the case of a non-orthogonal basis set. The relation between the present energy-partitioning scheme and the tight-binding bond model is discussed in section 2.2. In section 3 the implementation of the scheme into a mixed-basis pseudopotential code is described.

2. A new energy-partitioning scheme

2.1. Definition of an invariant covalent bond energy

The starting point of our analysis is the expression for the total energy in density-functional theory [13, 14]

$$E_{\text{total}} = E_{\text{band}} + D + E_{\text{ii}}. \tag{1}$$

Here

$$E_{\text{band}} = \sum_n f_n \langle \Psi_n | \hat{H} | \Psi_n \rangle \tag{2}$$

is the band structure term, where the sum runs over all one-electron eigenstates Ψ_n, f_n are the occupation numbers and $\hat{H}$ denotes the self-consistent Kohn–Sham Hamiltonian. The second term is the so-called double-counting term,

$$D = -\int n(r) \, V_{\text{eff}}(r) \, \mathrm{d}^3 r + E_{\text{H}} + E_{\text{xc}} + \int n(r) V_{\text{ext}}(r) \, \mathrm{d}^3 r \tag{3}$$

where $n(r)$ is the electron density, and E_{H}, E_{xc}, V_{eff} and V_{ext} denote the Hartree energy, the exchange–correlation energy, the effective potential and the external potential. In an all-electron calculation $n(r)$ is the density of the valence and the core electrons, V_{ext} describes potential of the nuclei and E_{ii} denotes the interaction energy of the nuclei. In a pseudopotential calculation $n(r)$ is the density of the valence electrons, and then V_{ext} describes the potential of the ionic cores and E_{ii} is the interaction energy of the ionic cores. We will refer to this latter case in the following.

We want to analyse E_{total} in the intuitive chemical language developed for molecules, i.e. in terms of bonding and antibonding hybrid states between atom-localized orbitals. To do this, we represent the crystal wavefunction $\Psi_n(r)$ by a set of normalized atomic localized orbitals

$\varphi_{i\alpha}(\mathbf{r})$ which are assigned to the atoms i located at the positions $\mathbf{R}_i$ and which have the orbital character α characterized by the quantum numbers (l, m) for atom-like states (in the following we consider only orbitals with the same principal quantum number for each l),

$$\Psi_n(\mathbf{r}) = \sum_{i\alpha} C_{i\alpha}^n \varphi_{i\alpha}(\mathbf{r} - \mathbf{R}_i). \tag{4}$$

An analysis of this type is self-suggesting if a localized basis set is used from the very beginning for the solution of the Kohn–Sham equations. If the original basis set includes plane waves, then the crystal wavefunctions Ψ_n must be projected (section 3) on a set of suitably defined atomic-like orbitals $\varphi_{i\alpha}(\mathbf{r})$ for the succeeding chemical analysis of the total energy.

We first rewrite the band structure energy by inserting (4) into (1) and by adding and subtracting the terms

$$\sum_n \sum_{i\alpha, j\beta} \left[f_n c_{i\alpha}^n \left(c_{j\beta}^n \right)^* O_{j\beta i\alpha} - N_{i\alpha}^{\text{free atom}} \delta_{j\beta, i\alpha} \right] H_{i\alpha i\alpha}^{\text{free atom}} \tag{5}$$

and

$$\sum_n \sum_{i\alpha, j\beta} f_n c_{i\alpha}^n \left(c_{j\beta}^n \right)^* O_{j\beta i\alpha} H_{i\alpha i\alpha}. \tag{6}$$

Here $O_{j\beta i\alpha}$ and $H_{i\alpha i\alpha}$ denote the elements of the overlap and the (self-consistent) Hamiltonian matrix, $N_{i\alpha}^{\text{free atom}}$ is the number of electrons in the state α of the atom i when it is isolated as a free atom and $H_{i\alpha i\alpha}^{\text{free atom}}$ denotes the eigenvalues of these states.

Second, the remaining terms in (1) are calculated by approximating $n(\mathbf{r})$ by a superposition of the densities $n_i^{\text{free atom}}(\mathbf{r} - \mathbf{R}_i)$ of the corresponding free atoms, i.e.

$$n(\mathbf{r}) = \sum_i n_i^{\text{free atom}}(\mathbf{r} - \mathbf{R}_i). \tag{7}$$

It has been shown [15] that in this case the double-counting term D is given by a sum of atomic contributions, $\sum_i D[n_i^{\text{free atom}}(\mathbf{r})]$, a pair-potential contribution and a small remainder E_{mb} with many-body interactions. Finally, the energy of the free atoms before they are condensed to the crystal is

$$E^{\text{free atom}} = \sum_{i\alpha} N_{i\alpha}^{\text{free atom}} H_{i\alpha i\alpha}^{\text{free atom}} + \sum_i D[n_i^{\text{free atom}}(\mathbf{r})]. \tag{8}$$

With all these manipulations we can write the cohesive energy $E_c = E_{\text{total}} - E^{\text{free atom}}$ as

$$E_c = E_{\text{prom}} + E_{\text{cf}} + E_{\text{polar}} + E_{\text{cov}} + E_{\text{pair}} + E_{\text{mb}} \tag{9}$$

where E_{pair} is the sum of the pair-potential contribution to the double-counting term and the term E_{ii} of (1).

To elucidate the physical meaning of the various terms, we subdivide the physical process of bonding of free atoms to a crystal into various steps. First, we redistribute the electrons among the various orbitals from the occupation numbers $N_{i\alpha}^{\text{free atom}}$ to the occupation numbers which will be found in the crystal and which we characterize by the gross charge $q_{i\alpha}$ of orbital α corresponding to Mulliken's analysis of the total charge,

$$q_{i\alpha} = \sum_{j\beta} \sum_n f_n c_{i\alpha}^n \left(c_{j\beta}^n \right)^* O_{j\beta i\alpha}. \tag{10}$$

The cost in energy for this redistribution is described by the promotion energy

$$E_{\text{prom}} = \sum_{i\alpha} \left(q_{i\alpha} - N_{i\alpha}^{\text{free atom}} \right) H_{i\alpha i\alpha}^{\text{free atom}}. \tag{11}$$

For instance, the atom configuration of the free carbon atom is $2s^2 2p^2$ and changes in diamond to $2s^1 2p^3$ forming the well known sp^3 hybrid orbitals.

In a second step, we bring the atoms to their crystal positions but do not allow for a hybridization between the orbitals. Then the on-site energies change because the potential acting on an electron at atom i is not just the atomic potential of this atom but the environment-dependent crystal potential, and the resulting change of the total energy is given by the crystal-field term

$$E_{\text{cf}} = \sum_{i\alpha} q_{i\alpha} \left(H_{i\alpha i\alpha} - H_{i\alpha i\alpha}^{\text{free atom}} \right). \tag{12}$$

In a third step, we allow for a hybridization of the orbitals localized at one atom, yielding the polarization energy

$$E_{\text{polar}} = \sum_{ni\alpha\beta} f_n \, c_{i\alpha}^n \left(c_{i\beta}^n \right)^* \left[H_{i\beta i\alpha} - \delta_{i\alpha}^{i\beta} H_{i\alpha i\alpha} \right]. \tag{13}$$

Finally we allow for a hybridization of orbitals localized at different atoms, gaining the covalent bond energy

$$E_{\text{cov}} = \sum_{\substack{i\alpha, j\beta \\ j \neq i}} E_{\text{cov},i\alpha j\beta} \tag{14}$$

with

$$E_{\text{cov},i\alpha j\beta} = \sum_n f_n \, c_{i\alpha}^n \left(c_{j\beta}^n \right)^* \left[H_{j\beta i\alpha} - O_{j\beta i\alpha} \, \overline{\varepsilon_{j\beta i\alpha}} \right] \tag{15}$$

$$\overline{\varepsilon_{j\beta i\alpha}} = \tfrac{1}{2} \left(H_{i\alpha i\alpha} + H_{j\beta j\beta} \right). \tag{16}$$

$E_{\text{cov},i\alpha j\beta}$ can be subdivided further into energy-resolved contributions,

$$E_{\text{cov},i\alpha j\beta}(E) = \sum_n \delta(E - \varepsilon_n) \, f_n \, c_{i\alpha}^n \left(c_{j\beta}^n \right)^* \left[H_{j\beta i\alpha} - O_{j\beta i\alpha} \, \overline{\varepsilon_{j\beta i\alpha}} \right] \tag{17}$$

where the ε_n denote the eigenvalues for the eigenstates Ψ_n. $E_{\text{cov},i\alpha j\beta}(E)$ is negative (positive) for bonding (antibonding) states. The respective quantity integrated up to a certain energy E will be referred to as

$$I E_{\text{cov},i\alpha j\beta}(E) = \int_{-\infty}^{E} E_{\text{cov},i\alpha j\beta}(E') \, \mathrm{d}E'. \tag{18}$$

The energy partitioning scheme introduced in the present section has the following benefit: in a band structure calculation which deals with an infinitely extended periodic system the average effective potential $\overline{V_{\text{eff}}(\boldsymbol{r})}$ has no physical meaning, and it is usually set to an arbitrary value for all the various crystal structures. Therefore, it is physically meaningful to analyse only those energy contributions which are invariant against a constant shift of the effective potential. This is fulfilled for E_{total}, because a shift of the effective potential results in opposite shifts of E_{band} and of the first term on the right-hand side of (3), which therefore compensate each other. Furthermore, the terms E_{prom}, E_{polar} and E_{cov} of (9) as well as their atom- and orbital-resolved contributions (and in addition the respective energy-resolved contributions to E_{cov}) are all invariant. Because E_{c} is also invariant, this must hold also for the sum $E_{\text{pair}} + E_{\text{mb}} + E_{\text{cf}}$. However, it is not possible to calculate separately the crystal-field term E_{cf} in a band-structure calculation, because $H_{i\alpha i\alpha}$ is shifted by a constant shift of the effective crystal potential whereas $H_{i\alpha i\alpha}^{\text{free atom}}$ is not. (For the calculation of $H_{i\alpha i\alpha}^{\text{free atom}}$ the effective potential is normalized to zero for infinitely large distances from the nucleus.) It is therefore only meaningful to analyse the terms E_{total}, E_{c}, E_{prom}, E_{polar}, E_{cov} and $E_{\text{pair}} + E_{\text{mb}} + E_{\text{cf}}$. The covalent bond energy E_{cov} is the only term with matrix elements involving orbitals on different atoms, and it therefore clearly represents the contribution of the interatomic bonding. It will be the objective of part II of this

paper to figure out whether the difference in the energetics of pure and doped $TiAl_3$ and of $ScAl_3$ may be traced back to this term E_{cov}.

For systems with delocalized electronic states the Ψ_n are better represented by a set of plane waves rather than by atom-localized functions. Alternatively, the Ψ_n can again be represented by a set of atom-localized functions in this case also, but then often orbitals have to be included which are not occupied in the free atom in order to make the basis set more complete. Then formally a covalent bond energy E_{cov} can be calculated even for a nearly-free-electron system. Whereas the term metallic conductivity is well defined, it is indeed a problem to discriminate between metallic and covalent bonding (see, e.g., [16]). It is common practice to associate metallic bonding with a situation with a more or less homogeneous charge density. However, this simple classification overlooks the fact that a quasi-homogeneous charge density may arise for situations which are electronically completely different. For instance, consider on the one hand graphite. The bonding in this material may be well described by a tight-binding basis which involves only orbitals (2s, 2p) which are already occupied in the free C atom. Thereby the bonding between carbon atoms in the planes is mediated by sp^2 hybrid orbitals, whereas the p–π orbitals produce a more or less homogeneous charge distribution between the planes. This situation is totally different from that in Li. If we want to describe the nearly homogeneous charge distribution in this material by atomic orbitals we have to include very many orbitals which are not occupied in the free Li atom. As a working hypothesis we define a covalent bonding as a bonding which is dominated by the hybridization of those orbitals on the various atoms which are already occupied in the respective free atoms. Note that this does not necessarily mean that the corresponding charge-density difference plot exhibits directionality; for example, it can be imagined that the p_z orbitals of graphite do not necessarily create a charge density with considerable directionality. Because our definition of E_{cov} is a generalization of the covalent bond energy introduced by Sutton *et al* [10–12] to the case of non-orthogonal basis sets we retain the historically founded nomenclature 'covalent bond energy', although this quantity may also contain metallic bonding contributions in the above-defined sense.

In addition to the analysis with the above-discussed energy-partitioning scheme we shall perform in part II an analysis with the well known charge partitioning scheme, i.e. in terms of the bond order [3]

$$\Theta_{i\alpha j\beta} = \sum_n f_n c_{i\alpha}^n \left(c_{j\beta}^n\right)^* O_{j\beta i\alpha} \tag{19}$$

and in terms of the energy-resolved bond order [17], which is called COOP,

$$\text{COOP}_{i\alpha j\beta}(E) = \sum_n \delta(E - \varepsilon_n) f_n c_{i\alpha}^n \left(c_{j\beta}^n\right)^* O_{j\beta i\alpha}. \tag{20}$$

These quantities are in general positive (negative) for bonding (antibonding) states; i.e., they are able to describe the character of a bond but do not give quantitative numbers for the contribution of the bonds to the total energy.

2.2. Comparison with former definitions

In our former version of the energy-partitioning scheme [8, 9] the various terms have been arranged in a slightly different manner, arriving at the equivalent expression

$$E_c = \tilde{E}_{prom} + \tilde{E}_{cf} + \tilde{E}_{cov} + E_{pair} + E_{mb} \tag{21}$$

with

$$\tilde{E}_{prom} = \sum_{i\alpha} \left(q_{i\alpha} - N_{i\alpha}^{\text{free atom}}\right) H_{i\alpha i\alpha} \tag{22}$$

i.e. $H_{i\alpha i\alpha}^{\text{free atom}}$ of E_{prom} has been replaced by $H_{i\alpha i\alpha}$,

$$\tilde{E}_{\text{cf}} = \sum_{i\alpha} N_{i\alpha}^{\text{free atom}} \left(H_{i\alpha i\alpha} - H_{i\alpha i\alpha}^{\text{free atom}} \right) \tag{23}$$

i.e. the $q_{i\alpha}$ of E_{cf} have been replaced by $N_{i\alpha}^{\text{free atom}}$ and

$$\tilde{E}_{\text{cov}} = \sum_{i\alpha, j\beta} E_{\text{cov},i\alpha j\beta} \tag{24}$$

i.e. the on-site contributions $i\alpha i\beta$ have not been excluded from the covalent bond energy. When comparing the definitions E_{prom} and E_{cf}, with the definitions $\tilde{E}_{\text{prom}}$ and $\tilde{E}_{\text{cf}}$, it becomes obvious that they correspond to a different succession of processes in a gedanken experiment for the condensation of free atoms into the crystal. In the first case we promote the electrons by redistributing them among the various orbitals of the free atoms and then we bring the free atoms into the crystal positions (without allowing for a redistribution of the charge densities) and experience a change in energy described by E_{cf} due to a shift of the on-site energies in the crystal potential. In the second case we freeze the occupation numbers $N_{i\alpha}^{\text{free atom}}$ when bringing the free atoms into the crystal positions and calculate the crystal-field shift $\tilde{E}_{\text{cf}}$ for these circumstances, and then we allow for a redistribution of the electrons among the on-site energy levels in the crystal potential. We think that the first case is closer to the commonly used definitions of the promotion and the crystal-field energy, and we therefore prefer the new variant of the energy partitioning scheme. Finally, we think that it is reasonable to exclude the on-site hybridization contributions $E_{\text{cov},i\alpha i\beta}$ from the covalent bond energy because they do not describe interatomic interactions. In the new variant these terms enter the polarization energy, which also has a well defined physical meaning.

Sutton *et al* [10–12] have defined a covalent bond energy and a promotion energy within the framework of the tight-binding bond model. The starting point for their discussion was not the total energy of the density-functional theory evaluated for the self-consistent electron density $n(r)$, but the Harris–Foulkes functional [15, 18], where the band structure energy is evaluated for a Hamiltonian $\hat{H}^0$ constructed from an input charge density, for example from the superposition of free-atom charge densities, whereas the double-counting term D is calculated from the output charge density obtained for the eigenfunctions of the Kohn–Sham equations for $\hat{H}^0$. They arrived at the definitions

$$\tilde{E}'_{\text{prom}} = \sum_{i\alpha} \left(\tilde{q}'_{i\alpha} - N_{i\alpha}^{\text{free atom}} \right) H_{i\alpha i\alpha}^0 \tag{25}$$

with

$$\tilde{q}'_{i\alpha} = \sum_{n} f_n c_{i\alpha}^n \left(c_{i\alpha}^n \right)^* . \tag{26}$$

Refrained from the difference between $\hat{H}$ and $\hat{H}^0$, (25) coincides with (11) for an orthonormal basis set, but it differs drastically for a non-orthogonal basis set because it totally neglects the overlap population occurring in Mulliken's gross charge, so that charge is lost in the promotion process. The covalent bond energy was defined as

$$\tilde{E}'_{\text{cov}} = \sum_{\substack{i\alpha, j\beta \\ j \neq i}} \tilde{E}'_{\text{cov},i\alpha j\beta} \tag{27}$$

with

$$\tilde{E}'_{\text{cov},i\alpha j\beta} = \sum_{n} f_n c_{i\alpha}^n \left(c_{j\beta}^n \right)^* H_{j\beta i\alpha}^0 \tag{28}$$

which—refrained from the difference between $\hat{H}$ and $\hat{H}^0$—coincides with equations (14) and (15) for an orthonormal basis set but which is different and not invariant against a potential shift for a non-orthogonal basis set.

3. Implementation for plane-wave band structure methods

When using a band structure method which represents the crystal wavefunctions $\Psi_n = \Psi_{kj}$ (k = wavevector, j = band index) from the very beginning by a set of atom-localized functions then the analysis described in section 2 is straightforward. For instance, Börnsen *et al* [8,9] used the tight-binding linear muffin-tin orbitals [19]. In our present calculations we used the mixed-basis pseudopotential code [20–23], where the crystal wavefunctions Ψ_{kj} are represented by plane waves and additional atom-localized orbitals, i.e.

$$\psi_{kj}(r) = \sum_G \alpha_G^{kj} \frac{1}{\sqrt{\Omega}} \exp\left(i(k+G)r\right) + \sum_{vlm} \beta_{vlm}^{kj} \phi_{vlm}^k(r) \tag{29}$$

$$\phi_{vlm}^k(r) = \sum_T \exp\left(ik(T+R_v)\right) \phi_{vlm}(r-T-R_v). \tag{30}$$

Here G denotes reciprocal lattice vectors, Ω is the volume of the unit cell and the ϕ_{vlm}^k are Bloch functions constructed from *non-overlapping* orbitals localized at the atoms at $T+R_v$, where T and R_v denote the translation vectors and the positions of the atoms v in the respective unit cells. For the systems under consideration we have chosen five 3d orbitals (distinguished by m) per transition-metal atom. For a chemical analysis we project the crystal wavefunctions onto a minimal basis of Bloch functions $\tilde{\phi}_{vlm}^k$ constructed from *overlapping* atom-localized non-orthogonal orbitals $\tilde{\phi}_{vlm}(r-T-R_v)$. The crystal wavefunctions can be expressed as

$$\psi_{kj}(r) \simeq \sum_{vlm} c_{vlm}^{kj} \tilde{\phi}_{vlm}^k \tag{31}$$

with

$$c_{vlm}^{kj} = \langle \tilde{\phi}_{vlm}^{k+} | \psi_{kj} \rangle. \tag{32}$$

Here the $\tilde{\phi}_{vlm}^{k+}$ are the Bloch functions of the conjugate basis, which are represented as

$$\tilde{\phi}_{vlm}^{k+} = \sum_{v'l'm'} \tilde{\phi}_{v'l'm'}^k \tilde{O}_{v'l'm',\,vlm}^{-1}(k) \tag{33}$$

where $\tilde{O}^{-1}$ is the inverse of the overlap matrix $\langle \tilde{\phi}_{v'l'm'}^k | \tilde{\phi}_{vlm}^k \rangle$. In principle we can define E_{cov}, E_{prom}, E_{cf} and E_{polar} in Bloch space by using the coefficients c_{vlm}^{kj} obtained by the projection according to (32). However, these quantities then would characterize the individual bonds between the atom-localized orbitals $\tilde{\phi}_{vlm}(r-T-R_v)$ only if large non-primitive unit cells were used, because otherwise the bonding characteristics between two atoms in the unit cell would intrinsically carry information about the bonds between the atoms located in the original unit cell ($T=0$) and all the equivalent atoms located at $T+R_v$, where T can be any translation vector of the lattice. To obtain information about the bonding between two individual atoms we have to start from a representation of the crystal wavefunctions by the individual atom-localized orbitals $\tilde{\phi}_{vlm}(r-T-R_v)$ as we did in section 2 (see (4) and the definition of E_{cov}, E_{prom}, E_{cf} and E_{polar} derived from this representation), i.e.

$$\Psi_{kj}(r) \simeq \sum_{Tvlm} c_{Tvlm}^{kj} \tilde{\phi}_{vlm}(r-T-R_v) \tag{34}$$

with the index i of (4) corresponding to (Tv), and with

$$c_{Tvlm}^{kj} = c_{vlm}^{kj} \exp\left(ik(T+R_v)\right). \tag{35}$$

In terms of the coefficients c_{vlm}^{kj} (15) may be written as

$$E_{cov\ Tvlm\ ov'l'm'} = \mathrm{Re}\left\{ \sum_{kj} f_{kj} c_{vlm}^{kj} \left(c_{v'l'm'}^{kj}\right)^* \exp\left(ik(T+R_v-R_v')\right) \right.$$

$$\left. \times \left[\tilde{H}_{ov'l'm'\ Tvlm} - \tilde{O}_{ov'l'm'\ Tvlm}\left(\frac{H_{ov'l'm'\ ov'l'm'} + H_{ovlm\ ovlm}}{2} \right) \right] \right\}. \tag{36}$$
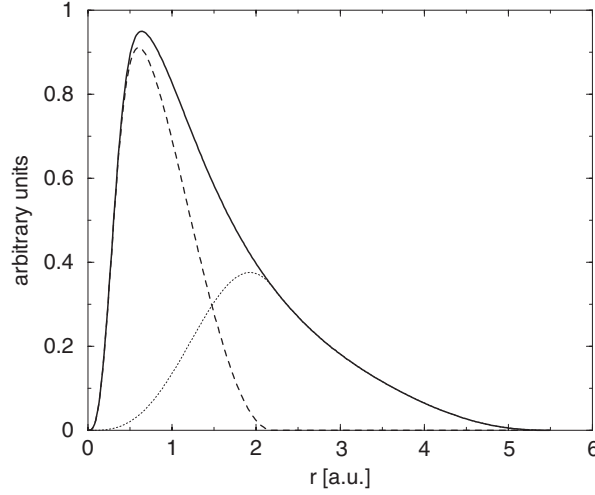
Figure 1. Radial part of the atom-localized orbitals (solid curve) split into a modified Bessel function (dotted curve) and a remainder (dashed curve).

Similarly, the Mulliken charges are calculated in terms of the c_{vlm}^{kj} via

$$q_{\mathbf{o}vlm} = \mathrm{Re}\left\{ \sum_{kj} \sum_{\mathbf{T}v'l'm'} f_{kj} c_{vlm}^{kj} \left(c_{v'l'm'}^{kj}\right)^* \exp\left(\mathrm{i}\mathbf{k}(\mathbf{T} + \mathbf{R}_v - \mathbf{R}_v')\right) \tilde{O}_{\mathbf{T}v'l'm'\,\mathbf{o}vlm} \right\}. \tag{37}$$

Instead of calculating the matrix elements $\tilde{H}_{\mathbf{o}v'l'm'\,\mathbf{T}vlm}$ and $\tilde{O}_{\mathbf{o}v'l'm'\,\mathbf{T}vlm}$ directly in real space, we first calculate the matrix elements $\tilde{H}_{v'l'm'\,vlm}(\mathbf{k})$ and $\tilde{O}_{v'l'm'\,vlm}(\mathbf{k})$ for the Bloch-transformed orbitals $\tilde{\phi}_{vlm}^k$ and then transform back by the inverse Bloch transformation

$$\tilde{H}_{\mathbf{o}v'l'm'\,\mathbf{T}vlm} = \frac{1}{N} \sum_{\mathbf{k}} \exp\left(-\mathrm{i}\mathbf{k}(\mathbf{T} - \mathbf{R}_v' + \mathbf{R}_v)\right) \tilde{H}_{v'l'm'\,vlm}(\mathbf{k}) \tag{38}$$

where N is the number of k-points in the first Brillouin zone used in the calculation. In the mixed-basis pseudopotential code [20–23] a technique has been developed to calculate the matrix elements for the Bloch-transformed orbitals ϕ_{vlm}^k constructed from non-overlapping atom-localized orbitals $\phi_{vlm}(\mathbf{r} - \mathbf{T} - \mathbf{R}_v)$ in a computationally efficient way. We want to use a similar procedure for the Bloch-transformed matrix elements involving the overlapping atom-localized orbitals $\tilde{\phi}_{vlm}(\mathbf{r} - \mathbf{T} - \mathbf{R}_v)$. To do this we decompose these orbitals into long-range parts represented by modified Bessel functions and short-range and practically non-overlapping remainders (figure 1), and the matrix elements are calculated partly in Fourier space, in real space or in a mixed space.

For the atom-localized orbitals we chose

$$\tilde{\phi}_{vlm}(\mathbf{r} - \mathbf{T} - \mathbf{R}_v) = R_{vl}(|\mathbf{r} - \mathbf{T} - \mathbf{R}_v|)\, \mathrm{i}^l\, K_{lm}(\mathbf{r} - \hat{\mathbf{T}} - \mathbf{R}_v) \tag{39}$$

with

$$R_{vl}(r) = C_{vl}\, \phi_{vl}^{\mathrm{PS}}(\lambda_{vl}\, r) \begin{cases} \left(1 - \exp\left(-\gamma_{vl}(r_{vl}^{\mathrm{cut}} - r)^2\right)\right) & \text{for} \quad r \leqslant r_{vl}^{\mathrm{cut}} \\ 0 & \text{for} \quad r \geqslant r_{vl}^{\mathrm{cut}} \end{cases} \tag{40}$$

where C_{vl} is a normalization constant, ϕ_{vl}^{PS} is the radial pseudo-atomic wavefunction constructed according to Vanderbilt [24], λ_{vl} denotes a contraction factor and r_{vl}^{cut} represents a cut-off length. In part II we confine ourselves to a minimal basis set of 3d, 4s and 4p orbitals for the transition metals and 3s, 3p and 3d orbitals for the Al atom.

In principle, the parameters λ_{vl}, γ_{vl} and r_{vl}^{cut} should be obtained according to Ritz's variational principle by minimizing for each considered atomic configuration the total energy. Alternatively, one could fix the values of the parameters to those obtained from Ritz's variational principle for one special reference configuration. Both procedures would require us to calculate the total energy and hence the Hamiltonian matrix elements with the overlapping atom-localized orbitals from many combinations of parameter values. It has therefore become customary [22, 25–27] to choose the parameter values in such a way that the spillage is minimal, which characterizes the loss of the norm of the wavefunctions due to the incompleteness of the pseudo-atomic-orbital projection. It has been shown for several materials [26] that the spillage correlates with the mean-square error in the energy bands obtained from the projected Hamiltonian matrix, and therefore it is reasonable to assume that the minimization is often close to a total-energy variational optimization. According to our experience, problems occur for the case of Al when including the d orbitals in the minimal basis set. In this case the minimization of the spillage yields d orbitals with very large spatial spread, which seems to be unphysical and which renders the chemical analysis more difficult. However, it turns out that the spillage increases only slightly and the quality of the band structure obtained from the projected Hamiltonian matrix remains the same when contracting these d orbitals, at least up to some limit where the spillage and the band structure deteriorate drastically upon further compression. Indeed, the band structure would be considerably modified if the d orbitals were completely omitted. To combine a good quality of the band structure with a good localization of the d orbital of Al we therefore contracted the orbital up to that limit.

Acknowledgments

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