Ab-initio investigation of the covalent bond energies in the metallic covalent superconductor MgB\textsubscript{2} and in AlB\textsubscript{2}

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The contributions of the covalent bond energies of various atom pairs to the cohesive energy of MgB\textsubscript{2} and AlB\textsubscript{2} are analysed with a variant of our recently developed energy-partitioning scheme for the density-functional total energy. The covalent bond energies are strongest for the intralayer B-B pairs. In contrast to the general belief, there is also a considerable covalent bonding between the layers, mediated by the metal atom. The bond energies between the various atom pairs are analysed in terms of orbital- and energy-resolved contributions.

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I. INTRODUCTION

The ceramic compound magnesium diboride, MgB\textsubscript{2}, has the highest superconducting critical temperature \(T_c = 39\) K ever reported for a binary system. The structure is graphite-like, i.e., it consists of honeycomb layers of B separated by triangular metal planes. Its discovery has triggered a tremendous activity to investigate the electronic and phononic properties as well as the electron–phonon coupling and is responsible for the high \(T_c\) value.

The Mg atoms are responsible for a downward shift of the B \(\pi\)-bands relative to the \(\sigma\)-bands, as compared to the corresponding C bands in graphite. As a result, there is a partial ionic character, but these electrons are not well localized at the B sites, they are rather distributed over the whole crystal.

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The compound is hold together by dominant intralayer B-B covalent bonds, dominant interlayer metallic bonds and by a substantial ionic character. There are indications for an additional interlayer B-Mg contribution to the bonding, e.g., the slight increase in the \(k_z\) dispersion of the B \(\sigma\)-bands as compared to a hypothetical structure where the Mg atoms are removed. When going from MgB\textsubscript{2} to AlB\textsubscript{2}, the valence charge-difference plots show a stronger directional M-B bond (M=metal atom), and our own calculations show a slightly stronger \(k_z\) dispersion of the \(\sigma\)-bands.

It is the objective of the present paper to analyse and compare the covalent bonding properties of MgB\textsubscript{2} and AlB\textsubscript{2} quantitatively within a variant of our recently developed energy-partitioning scheme\textsuperscript{6}. A first attempt in this direction was made by Ravindran et al.\textsuperscript{7} by means of the crystal-orbital-Hamilton population analysis\textsuperscript{8} (COHP). It will be shown below, however, that for the use of non-orthogonal basis functions the COHP do not have a well-defined physical meaning and cannot be used to compare quantitatively the covalent bonding properties between various structures.

II. THE ENERGY-PARTITIONING SCHEME

Starting point of the discussion is the expression for the total energy \(E_{\text{tot}}\) from the density functional theory in local density approximation,

\[
E_{\text{tot}} = \sum_n f_n \varepsilon_n - \int n(r)v_{\text{eff}}(r)d^3r + E_{\text{H}} + E_{\text{xc}} + \int n(r)v_{\text{ext}}(r)d^3r + E_{\text{ii}},
\]

with the occupation numbers \(f_n\) and the eigenvalues \(\varepsilon_n\) of the Kohn-Sham single-particle wave functions \(\Psi_n\), the electron density \(n(r)\), the effective potential \(v_{\text{eff}}(r)\), the Hartree energy \(E_{\text{H}}\), the exchange-correlation energy \(E_{\text{xc}}\), the potential \(v_{\text{ext}}(r)\) of the nuclei (or of the ionic cores in the case of a pseudopotential calculation) and the interaction energy \(E_{\text{ii}}\) between the nuclei (or between the ionic cores). The hope is that the trends for the total energies are already well described by the first term (band-structure energy \(E_{\text{band}}\)) when comparing various
systems. This assumption is made implicitly in the common practice to discuss the energetics via the electronic density of states. An energy-partitioning scheme is a tool to analyse $E_{\text{band}}$ further.

For systems with covalent bonding the crystal wavefunctions $\Psi_n$ are best represented by a minimal set of well-localized orbitals $\varphi_{i\alpha}$ (with character $\alpha$ described by the angular and magnetic atom quantum numbers $l$ and $m$) attached to the various atoms $i$ (tight-binding representation),

$$
\Psi_n = \sum_{i\alpha} c_{i\alpha}^{n} \varphi_{i\alpha} \ .
$$

The band-structure energy is calculated by inserting (2) into

$$
\sum_n f_n \varepsilon_n = \sum_n f_n \langle \Psi_n | \hat{H} | \Psi_n \rangle
$$

with the Kohn-Sham Hamiltonian $\hat{H}$. The remaining terms on the right-hand side of eq. (1) which we abbreviated by $D$ in Refs. [3-4] are calculated by approximating $n(r)$ by a superposition of atomic charge densities, yielding\[4\]

$$
D = E_{\text{pair}} + E_{\text{mb}} + E_{\text{free atom}}^{\text{free}} - \sum_{i\alpha} N_{i\alpha}^{\text{free atom}} H_{i\alpha}^{\text{free atom}} \ .
$$

Here $E_{\text{pair}}$ is a pair potential term, $E_{\text{mb}}$ a many-body potential term which is small for nearly charge neutral systems, $E_{\text{free atom}}^{\text{free}}$ denotes the total energy of the free atoms before being condensed to the crystal, and the $N_{i\alpha}^{\text{free atom}}$ are the occupation numbers for the energy levels $H_{i\alpha}^{\text{free atom}}$. We now add to and subtract from $E_{\text{tot}}$ the terms

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

and

$$
\sum_n \sum_{i\alpha,j\beta} c_{i\alpha}^{n} (c_{j\beta}^{n})^{*} O_{j\beta,i\alpha} H_{i\alpha}^{\text{free atom}} \ .
$$

where $O_{j\beta,i\alpha}$ and $H_{i\alpha}^{\text{free atom}}$ denote the elements of the overlap and Hamiltonian matrix.

Rearranging the terms in an appropriate manner yields the cohesive energy

$$
E_c = E_{\text{tot}} - E_{\text{free atom}}^{\text{free}}
$$

$$
= E_{\text{prom}} + E_{\text{cf}} + E_{\text{polar}} + E_{\text{cov}} + E_{\text{pair}} + E_{\text{mb}} \ .
$$

The first term is the promotion energy

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

with Mulliken’s gross charge.[2]

$$
q_{i\alpha} = \sum_{j\beta} \sum_{n} f_n c_{i\alpha}^{n} (c_{j\beta}^{n})^{*} O_{j\beta,i\alpha} \ .
$$

This term describes the cost in energy when starting the condensation process from free atoms and then redistributing the electrons among the various orbitals from the occupation numbers $N_{i\alpha}^{\text{free atom}}$ to the occupation number $q_{i\alpha}$ found in the crystal and characterized by $q_{i\alpha}$. The second term is the crystal-field term

$$
E_{\text{cf}} = \sum_{i\alpha} q_{i\alpha} (H_{i\alpha,i\alpha} - H_{i\alpha}^{\text{free atom}}) \ ,
$$

which describes the change in energy due to a shift of the on-site energies when the atoms are condensed to form the crystal so that the potential acting on an electron at atom $i$ is not just the atomic potential of this atom but the environment-dependent crystal potential. The polarization energy

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

describes the change in energy due to the hybridization of orbitals localized at one atom when the atom is embedded in the crystal. Finally, the covalent bond energy $E_{\text{cov}}$ is the change in energy arising from the hybridization of orbitals localized at different atoms,

$$
E_{\text{cov}} = \sum_{i\alpha,j\beta} E_{\text{cov},i\alpha,j\beta}
$$

with

$$
E_{\text{cov},i\alpha,j\beta} = \sum_{n} f_n c_{i\alpha}^{n} (c_{j\beta}^{n})^{*} \left[H_{j\beta,i\alpha} - O_{j\beta,i\alpha} \varphi_{i\alpha} \varphi_{j\beta}\right]
$$

$$
\varphi_{i\alpha} \varphi_{j\beta} = \frac{1}{2} (H_{i\alpha,i\beta} + H_{j\beta,j\alpha}) \ .
$$

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

$$
E_{\text{cov},i\alpha,j\beta}(E) = \sum_{n} \delta(E - \varepsilon_n) f_n c_{i\alpha}^{n} (c_{j\beta}^{n})^{*} \times \left[H_{j\beta,i\alpha} - O_{j\beta,i\alpha} \varphi_{i\alpha} \varphi_{j\beta}\right] \ .
$$

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

$$
IE_{\text{cov},i\alpha,j\beta}(E) = \int_{-\infty}^{E} E_{\text{cov},i\alpha,j\beta}(E') \, dE' \ .
$$

The energy-partitioning scheme discussed above has the following very attractive property: In a bandstructure calculation which deals with an infinitely extended periodic system the average effective potential does not have a physical meaning, and it is therefore
set to an arbitrary value which is the same for different crystal structures. In order to be physically meaningful the total energy \( E_{\text{tot}} \) and the considered terms of an energy-partitioning scheme for a band-structure calculation therefore must be invariant against a constant shift of the effective potential of the band-structure calculation. This is fulfilled for \( E_{\text{tot}} \) (and hence also for \( E_c \)) which becomes obvious from eq. (14): Shifting \( v_{\text{eff}} \) by \( \Phi_0 \) yields opposite shifts for the first two terms which therefore compensate each other (the remaining terms can be calculated without ambiguity, see for instance, Ref. [19]. Furthermore the terms \( E_{\text{prom}} \), \( E_{\text{polar}} \) and \( E_{\text{cov}} \) of eq. (15) as well as their atom- and orbital-resolved contributions (and in addition the respective energy-resolved contributions to \( E_{\text{cov}} \)) are all invariant. For instance, if the potential is shifted by a constant \( \Phi_0 \), then the matrix elements \( H_{j\beta i\alpha} \) are transformed into \( H_{j\beta i\alpha} + \Phi_0 O_{j\beta i\alpha} \) and \( H_{i\alpha i\alpha} \), \( \varepsilon_{j\beta i\alpha} \) into \( H_{i\alpha i\alpha} + \Phi_0 \), \( \varepsilon_{j\beta i\alpha} + \Phi_0 \) because \( O_{i\alpha i\alpha} = 1 \), so that \( \Phi_0 \) drops out of the covalent bond energy. Because \( E_c \) is also invariant, this must hold for the sum of the terms \( E_{\text{pair}} + E_{\text{mb}} + E_{\text{cf}} \), too. However, we cannot calculate separately, for instance, the crystal-field term \( E_{\text{cf}} \) in a band-structure calculation, because the matrix element \( H_{i\alpha i\alpha} \) is shifted by the shift of the effective potential of the crystal whereas \( H_{\text{free atom}} \) is not (because for the calculation of the latter quantity the effective potential is always normalized to zero for distances far from the atom). It is therefore physically meaningful only to discuss the terms \( E_{\text{prom}}, E_{\text{polar}}, E_{\text{cov}} \) and \( E_{\text{pair}} + E_{\text{mb}} + E_{\text{cf}} \). The covalent bond energy thereby is the only term which involves matrix elements for orbitals on different atoms, and therefore it clearly represents the contribution of the interatomic bonding to the band-structure energy. In the following we will confine ourselves to the discussion of this term.

It should be noted that in our former version of the energy-partitioning scheme the various terms have been arranged in a slightly different manner, arriving at the equivalent expression

\[
E_c = \tilde{E}_{\text{prom}} + \tilde{E}_{\text{cf}} + \tilde{E}_{\text{cov}} + E_{\text{pair}} + E_{\text{mb}}
\]  

(16)

with

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

(17)

i.e., \( H_{i\alpha i\alpha} \) of \( E_{\text{prom}} \) has been replaced by \( H_{i\alpha i\alpha} \).

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

(18)

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

\[
\tilde{E}_{\text{cov}} = \sum_{i\alpha,j\beta} E_{\text{cov},i\alpha j\beta}
\]  

(19)

i.e., the on-site contributions \( i\alpha j\beta \) have not been excluded from the covalent bond energy. When comparing the definitions \( E_{\text{prom}}, E_{\text{cf}} \), with the definitions \( \tilde{E}_{\text{prom}}, \tilde{E}_{\text{cf}} \), it becomes obvious that they correspond to a different succession of processes in a gedanken experiment for the condensation of free atoms to 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 in the crystal positions (without allowing for a redistribution of the charge densities) and experience a change in energy described by \( E_{\text{cf}} \) 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 to 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 \( E_{\text{cov},i\alpha j\beta} \) 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.

It should be noted that \( \tilde{E}_{\text{prom}}, \tilde{E}_{\text{cov}} \) and \( \tilde{E}_{\text{cf}} + E_{\text{pair}} + E_{\text{mb}} \) are also invariant against a constant shift of the effective potential of a band-structure calculation, as well as the atom-, orbital- and energy-resolved contributions of \( E_{\text{cov}} \). Again, \( \tilde{E}_{\text{cf}} \) alone is not invariant and cannot be calculated separately in a band-structure calculation.

In former papers the crystal-orbital-Hamilton population

\[
COHP_{i\alpha j\beta}(E) = \sum_n \delta(E - \varepsilon_n) f_n c_n^{i\alpha} (c_n^{j\beta})^\dagger H_{j\beta i\alpha}
\]  

(20)

has been used to characterize the bonding properties. If orthonormal basis functions are used, this quantity is identical to \( E_{\text{cov}, i\alpha j\beta}(E) \). However, in the chemical analysis very often non-orthogonal basis sets are used. Then \( COHP_{i\alpha j\beta}(E) \) is not invariant against a constant shift of the effective potential and therefore does not have a well-defined physical meaning in the context of a band-structure calculation.

For systems with metallic bonding the \( \Psi_n \) are better represented by a set of plane waves rather than by atom-localized functions. Alternatively, the \( \Psi_n \) again can be represented by a set of atom-localized functions also in this case, 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 \( E_{\text{cov}} \) 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. As a working hypothesis we define a covalent bonding as a bonding which is dominated by the hybridization of those orbitals
on 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, e.g., it can be imagined that the \( p_z \)-orbitals do not necessarily create a charge density with considerable directionality. Because our definition of \( E_{\text{cov}} \) is a generalization of the covalent bond energy introduced by Sutton et al.\(^\text{[22]} \) to the case of non-orthogonal basis sets we keep this historical founded nomenclature “covalent bond energy” although this quantity may also contain metallic bonding contributions in the above defined sense.

III. DETAILS OF THE CALCULATIONS

The calculations were performed with the ab-initio pseudopotential method.\(^\text{[23,24]} \) Band structure and charge density difference plots were practically identical to those of previous calculations.\(^\text{[23,24]} \) For the energy-partitioning analysis the \( \Psi_n \) were projected onto a set of overlapping atom-localized non-orthogonal orbitals. For these orbitals we chose

\[
\psi_{i\alpha}(r) = f_{i\alpha}(r) \phi_{i\alpha} \quad ,
\]

\[
f_{i\alpha}(r) = C_{il} \phi_{i\alpha}^{\text{PS}}(\lambda_{il} r) \left\{ \begin{array}{ll}
1 - e^{-\gamma_{il}(r_{\text{cut}} - r)^2} & \text{for } r \leq r_{\text{cut}} \\
0 & \text{for } r \geq r_{\text{cut}}
\end{array} \right.,
\]

where \( C_{il} \) is a normalization constant, \( \phi_{i\alpha}^{\text{PS}} \) is the radial pseudo-atomic wavefunction constructed according to Vanderbilt\(^\text{[25]} \), \( \lambda_{il} \) denotes a contraction factor and \( r_{\text{cut}} \) represents a cut-off length. The parameters \( \lambda_{il}, \gamma_{il} \) and \( r_{\text{cut}} \) were selected in such a way that the spillage was minimized, where the spillage characterizes the loss of the norm of the wavefunctions due to the incompleteness of the pseudo-atomic-orbital projection. We confined ourselves to a minimal set of \( s,p \) and \( d \) orbitals for Mg and B. The band-structure calculated with the projected wavefunctions was nearly identical to the original band structure from the pseudopotential calculation for energies below and not too far above the Fermi level.

IV. RESULTS AND DISCUSSION

Table III represents the covalent bond energies for various atom pairs in MgB\(_2\) and AlB\(_2\). It should be recalled that the covalent bonding properties of the two materials may be compared only by the measure \( E_{\text{cov}} \) and not by COHP because the latter quantity is not invariant against a constant shift of the potential when nonorthogonal basis functions are used, which is the usual case for a chemical analysis in terms of atom-like functions. The total covalent bond energy is larger in absolute value for AlB\(_2\) than for MgB\(_2\). As expected, the B-B intralayer covalent bond energy is largest. Interestingly enough, it is larger in absolute value for the Mg compound although the B-B distance is larger. Contrary to the general belief, there is also a considerable covalent bond energy between the layers (the B-M energy is only a factor of about 2-2.5 smaller) and even in the M layers (the intralayer M-M energy is a factor of about two smaller than the B-M energy). The B-M covalent bond energy increases when going from M=Mg to M=Al, and this is consistent with the smaller c/a ratio of the Al compound. The B-M distance is in fact smaller for M=Al than for M=Mg. The interlayer B-B (M-M) bonds are two orders of magnitude (one order of magnitude) smaller than the respective intralayer bonds, i.e., their contributions to the cohesion between the layers is much smaller than the B-M contribution. Our calculations show that the covalent bond energies between all further-distant atoms are considerably smaller than the nearest-neighbor intralayer bonds and the nearest-neighbor B-M bonds. This means that a nearest-neighbor bond model suffices to describe the two materials. This is not at all trivial, because in intermetallic compounds, e.g., FeAl, CoAl and NiAl the further distant bonds are essential.

In Table IV the covalent bond energies for the most important atom pairs are further analysed by considering the dominant angular-resolved contributions. In all cases, the p-p contributions are strongest and the s-s contributions weakest. It becomes obvious from Table IV that the \( d \)-orbitals make a non-negligible contribution to the bonding between the B and the M layer. Because the \( d \)-orbitals are not occupied in the respective free atoms we would denote this as a “metallic contribution” according to our working hypothesis of section II. This metallic contribution is stronger for AlB\(_2\) than for MgB\(_2\). Nevertheless, the “covalent contribution” is dominant also for the bonding between the layers, mediated by the metal atom.

The energy-resolved covalent bond energies for the \( p-p \) and \( s-s \) contributions of the B-B intra, B-M and M-M intra atom pairs are shown in Fig. I for MgB\(_2\) and AlB\(_2\). The benefit of the energy-resolved representation is that we can clearly discriminate between bonding and antibonding states. The \( s-s \) bonds are weakened because both bonding and antibonding states are occupied. Without the energy-resolved analysis we could erroneously assume that the \( s-s \) covalent bond energy is low because the corresponding matrix elements are small. For the other orbital pairs of Table III dominantly bonding states are occupied, but there are slight differences between MgB\(_2\) and AlB\(_2\). For instance, the stronger B-B intra bond energy of MgB\(_2\) (Table II) results mainly from a stronger \( p-p \) contribution (Table IV), and the reason for this is that for the trivalent Al part of the antibonding \( p-p \) states are occupied (Fig. II). Furthermore, the stronger B-M bond for M=Al (Table III) again results mainly from a stronger \( p-p \) contribution, and the reason for this is that the bonding \( p-p \) states are more filled for Al than for Mg.
V. CONCLUSION

We have represented a new variant of an energy-partitioning scheme for the density-functional total energy which allows to define a covalent bond energy which is invariant against a constant potential shift. This property is a precondition for the comparison of the bonding properties in different systems within the framework of band-structure calculations.

The atom-, orbital- and energy resolved contributions to the covalent bond energy have been calculated for MgB$_2$ and AlB$_2$. One central result of the calculations is that a nearest-neighbor bond model is sufficient to describe the bonding properties of these materials. A working hypothesis has been introduced to discriminate between a covalent and a metallic bonding character. It has been shown that both in MgB$_2$ and AlB$_2$ there is a metallic contribution to the bonding between the layers which is stronger for Al than for Mg. The benefits of the energy-resolved representation are demonstrated by discussing the differences between the trivalent Al and the divalent Mg.

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FIG. 1. Energy resolved covalent bond energies for the p-p (full line) and s-s (dashed line) contributions of various atom pairs in MgB$_2$ (upper panels) and AlB$_2$ (lower panels).