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LETTER TO THE EDITOR

 E_{cov} — a new tool for the analysis of electronic structure data in a chemical language

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Abstract. It is shown that a generalization of the covalent bond energy of the tight-binding bond model to the case of a non-orthogonal basis set is an appropriate tool to describe the bonding properties of solids in a chemical language. It does not suffer from problems related to the ill-defined average electrostatic potential in periodic systems, in contrast to the formerly proposed crystal orbital Hamilton population (COHP). The new tool is applied to discuss the stability of the bcc, fcc and hcp structures of Nb, Mo, Ru and Rh.

In the last three decades, electronic density functional calculations (Hohenberg and Kohn 1964, Kohn and Sham 1965) have become a very powerful method to determine the most stable structures of molecules or solids by computing total energies. However, a physical insight may only be gained when analysing the results by methods based on simple models, for instance, the nearly-free-electron model for sp-valent materials or the tight-binding model for transition metals or semiconductors (see, e.g., Pettifor 1995). In the latter method the one-electron wave function $\psi_n(\mathbf{r})$, which is the solution of the one-electron Schrödinger equation in the effective potential of the density functional theory, is expanded in a basis set of normalized atomic-like localized orbitals $|\varphi_\beta\rangle$ assigned to the atoms at the various sites,

$$\psi_n(\mathbf{r}) = \sum_{\beta} c_n^{\beta} \varphi_{\beta}(\mathbf{r}). \quad (1)$$

Here the index β denotes both the site i of the atom and the type of the orbital given by the quantum numbers for atomic-like states. The appealing feature of such an expansion is that it allows the analysis of *ab initio* results in the intuitive chemical language developed for molecules, i.e., in terms of bonding and anti-bonding hybrid orbitals. An analysis of this type is self-suggesting if a localized basis set is used from the very beginning for the solution of the effective one-electron Schrödinger equation, as in the linear combination of atomic orbitals method (Mott and Jones 1936) or in the tight-binding linear muffin-tin orbital method (Andersen and Jepsen 1984). When the original basis set includes plane waves, then the resulting wave function afterwards can be projected (Sanchez-Portal *et al* 1995, 1996, Meyer 1998, Elsässer *et al* 1999) on a set of suitably defined atomic-like orbitals for a succeeding tight-binding analysis of the data.

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In density functional theory the total electronic density $\rho(\mathbf{r})$ and the total energy E_{total} of the system (including the interaction energy of the nuclei) may be written in the form (Kohn and Sham 1965)

$$\rho(\mathbf{r}) = \sum_n f_n |\psi_n(\mathbf{r})|^2 \quad (2)$$

$$E_{total} = \sum_n f_n E_n + D[\rho(\mathbf{r}), \{\mathbf{R}_i\}]. \quad (3)$$

Here the f_n are the occupation numbers for the one-electron wave functions ψ_n with energy $E_n = \langle \psi_n | \hat{H} | \psi_n \rangle$, and D is a functional of $\rho(\mathbf{r})$ depending on the positions \mathbf{R}_i of the nuclei. The first term of equation (3) denotes the so-called band energy E_{band}

$$E_{band} = \sum_n f_n E_n. \quad (4)$$

The tight-binding analysis of the charge density is straightforward by inserting equation (1) into equation (2), yielding (for real basis functions φ_α)

$$\rho(\mathbf{r}) = \sum_{\alpha\beta} \sum_n f_n c_n^\alpha (c_n^\beta)^* \varphi_\alpha(\mathbf{r}) \varphi_\beta(\mathbf{r}). \quad (5)$$

Integrating over the whole volume gives

$$N = \sum_{\alpha\beta} \theta_{\alpha\beta} \quad (6)$$

where N is the number of electrons and $\theta_{\alpha\beta}$ denotes the orbital-resolved bond order defined as

$$\theta_{\alpha\beta} = \sum_n f_n c_n^\alpha (c_n^\beta)^* O_{\beta\alpha}. \quad (7)$$

Inclusion of the overlap matrix $O_{\beta\alpha} = \langle \varphi_\beta | \varphi_\alpha \rangle$ is indispensable for the case of a non-orthogonal basis set. The quantity $\theta_{\beta\alpha}$ is an appropriate tool (Hoffmann 1987) to characterize the bonding character of the hybrid orbitals between states φ_α and φ_β . It changes sign when going from a bonding state to an anti-bonding state. Summing $\theta_{\alpha\beta}$ over all orbitals at the atoms i and j yields the bond order θ_{ij} between the two atoms which has a simple physical meaning (see, e.g., Pettifor 1995, Horsfield *et al* 1996). It is one half the difference between the number of electrons in bonding states and anti-bonding states between atoms i and j . For an analysis of the bonding character in a solid where there is a continuum of eigenvalues and corresponding eigenfunctions, Hughbanks and Hoffmann (1983) have introduced an energy-resolved bond order which is called crystal orbital overlap population,

$$COOP_{\alpha\beta}(E) = \sum_n \delta(E - E_n) f_n c_n^\alpha (c_n^\beta)^* O_{\beta\alpha}. \quad (8)$$

Whereas $COOP_{\alpha\beta}(E)$ is able to describe the bonding character, it cannot analyse quantitatively the contribution of the bonds to the total energy. Therefore Dronskowski and Blöchl (1993) have introduced the crystal orbital Hamilton population $COHP_{\alpha\beta}(E)$ by writing the band energy in the form

$$E_{band} = \sum_{\alpha\beta} \int_{-\infty}^{E_F} COHP_{\alpha\beta}(E) dE \quad (9)$$

with

$$COHP_{\alpha\beta}(E) = \sum_n \delta(E - E_n) f_n c_n^\alpha (c_n^\beta)^* H_{\beta\alpha} \quad (10)$$

with the Hamiltonian matrix element $H_{\beta\alpha} = \langle \varphi_\beta | \hat{H} | \varphi_\alpha \rangle$ and the Fermi energy E_F . This quantity changes sign at the same energy as $COOP_{\alpha\beta}(E)$, i.e., it also yields the bonding character of the hybrid orbitals: it is negative (positive) for bonding (anti-bonding) states. Furthermore, it is designed to characterize quantitatively the contribution of a given bond to the total energy.

Unfortunately, the band energy is not invariant against a shift of the potential by a constant value, ϕ_0 , whereas the total energy is independent when the system as a whole is charge neutral. Therefore, just by shifting the potential, the contributions of the two terms in equation (3) to the total energy may be drastically modified whereas the sum of the two terms remains constant. This does not constitute a problem when comparing the energies of various molecules, as long as we consider the same shift of the potential for all molecules relative to the potential at infinity. However, many density functional calculations are performed for periodic, i.e., infinitely extended systems. For these systems the average electrostatic potential has no physical meaning. The average electrostatic potential of a finite system characterizes the average change in energy which arises when a charge is put from far outside the system to all possible sites of the system. This prescription is meaningless for an infinitely extended system, and therefore the average electrostatic potential is not defined. Because a constant potential shift does not affect the total energy, in most density functional calculations the average electrostatic potential is just set to zero for all periodic systems. On the other hand, the average electrostatic potential in a real finite system does have a well-defined physical meaning, which depends on the termination of the system at the surface and on the charge distribution in the bulk (Keefe and Spence 1994). If we generate an infinite system by infinitely increasing the size of the finite system while keeping the shape and type of termination constant we arrive at this value for the average potential. Therefore, setting the average potential to zero for all periodic systems does not necessarily have the same meaning for each system, i.e., it does not represent a unique constant shift of the potential for all the systems. As a result, it does not make sense to compare the contributions of the band energies to the total energies of various periodic systems, and therefore the use of $COHP_{\alpha\beta}(E)$ is not well justified from a theoretical point of view. This problem was already mentioned in the paper of Dronskowski and Blöchl (1993), but no solution was given.

It will be shown in the following that the above discussed problem does not appear when an analysis is performed in the spirit of the tight-binding bond model (Sutton *et al* 1988), i.e., when generalizations of the promotion energy and the covalent bond energy of this model to the case of a non-orthogonal basis set are used. To do this, we write equation (3) in the form

$$E_{total} = \sum_n f_n E_n - \sum_\alpha N_\alpha^{freeatom} H_{\alpha\alpha} + D + \sum_\alpha N_\alpha^{freeatom} H_{\alpha\alpha} \quad (11)$$

where $N_\alpha^{freeatom}$ denotes the number of electrons in state α of the respective free atom. Inserting equation (1) yields

$$E_{total} = \sum_{\alpha,\beta} \sum_n f_n c_n^\alpha (c_n^\beta)^* H_{\beta\alpha} - \sum_\alpha N_\alpha^{freeatom} H_{\alpha\alpha} + D' \quad (12)$$

where D' represents the sum of the last two terms in equation (11).

We now define the promotion energy E_{prom} as

$$E_{prom} = \sum_\alpha (q_\alpha - N_\alpha^{freeatom}) H_{\alpha\alpha} \quad (13)$$

where

$$q_\alpha = \sum_\beta \sum_n f_n c_n^\alpha (c_n^\beta)^* O_{\beta\alpha} \quad (14)$$

is the gross charge of orbital α corresponding to Mulliken's analysis (Mulliken 1955) of the total charge. The promotion energy is about the energy associated with the change of occupancy of the atomic orbitals when forming the solid from free atoms. Equation (13) is a generalization of the expression given in Sutton *et al* (1988) to the case of a non-orthogonal basis set. In this case the inclusion of $O_{\beta\alpha}$ in the definition of q_α is indispensable to guarantee that all electrons are considered for the promotion, i.e., $\sum_\alpha q_\alpha = N = \sum_\alpha N_\alpha^{freeatom}$. Finally, we define the covalent bond energy as

$$E_{cov} = \sum_{\alpha,\beta} \sum_n f_n c_n^\alpha (c_n^\beta)^* H_{\beta\alpha} - \sum_\alpha N_\alpha^{freeatom} H_{\alpha\alpha} - E_{prom} = \sum_{\alpha,\beta} E_{cov,\alpha\beta} \quad (15)$$

with

$$E_{cov,\alpha\beta} = \sum_n f_n c_n^\alpha (c_n^\beta)^* [H_{\beta\alpha} - O_{\beta\alpha} \bar{\varepsilon}_{\beta\alpha}] \quad (16)$$

and

$$\bar{\varepsilon}_{\beta\alpha} = \frac{1}{2}(H_{\alpha\alpha} + H_{\beta\beta}). \quad (17)$$

$E_{cov,\alpha\beta}$ may be envisaged as the covalent bond strength of the pair of orbitals α and β . (For the limitation of this assertion a similar discussion holds as given at the end of section 2 in the paper of Dronskowski and Blöchl (1993).) Again, it is the generalization of the covalent bond energy of the tight-binding bond model (Sutton *et al* 1988) to the case of a non-orthogonal basis set. The corresponding energy-resolved covalent bond energy is given by

$$E_{cov,\alpha\beta}(E) = \sum_n \delta(E - E_n) f_n c_n^\alpha (c_n^\beta)^* [H_{\beta\alpha} - O_{\beta\alpha} \bar{\varepsilon}_{\beta\alpha}] \quad (18)$$

$$= COHP_{\alpha\beta}(E) - \bar{\varepsilon}_{\beta\alpha} COOP_{\alpha\beta}(E). \quad (19)$$

Because $COHP_{\alpha\beta}(E)$ and $COOP_{\alpha\beta}(E)$ change sign at the same energy when going from bonding to anti-bonding states (or vice versa) the sign of $E_{cov,\alpha\beta}(E)$ can equally well be used to describe the bonding character.

The quantities $E_{cov,\alpha\beta}(E)$, $E_{cov,\alpha\beta}$ and E_{cov} are the counterparts to $COHP_{\alpha\beta}(E)$, $COHP_{\alpha\beta}$ and E_{bond} , but they have the advantage that they do not depend on a shift of the potential by a constant ϕ_0 . Shifting by ϕ_0 transforms $H_{\beta\alpha}$ into $H_{\beta\alpha} + \phi_0 O_{\beta\alpha}$ and $H_{\alpha\alpha}$, $\bar{\varepsilon}_{\beta\alpha}$ into $H_{\alpha\alpha} + \phi_0$, $\bar{\varepsilon}_{\beta\alpha} + \phi_0$ because $O_{\alpha\alpha} = 1$, so that ϕ_0 drops out of equation (16). Furthermore, the total promotion energy E_{prom} is independent of ϕ_0 because of $\sum_\alpha (q_\alpha - N_\alpha^{freeatom}) = 0$ (whereas the contributions of the single orbitals α to E_{prom} do depend on ϕ_0). Because E_{total} , E_{cov} and E_{prom} are independent of ϕ_0 , this holds also for D' , and we thus have subdivided the total energy into three contributions, E_{prom} , E_{cov} and D' which are all independent of ϕ_0 , in contrast to the subdivision given in equation (3). It is therefore physically meaningful to compare these contributions as well as the orbital- and energy-resolved quantities $E_{cov,\alpha\beta}(E)$ for different structures in order to figure out which term is most important for the stability of a given structure.

It should be noted that the quantitative values of $E_{cov,\alpha\beta}(E)$ depend to some extent on the form of the orbitals used in the atomic-like basis set. A discussion of the same problem for the $COHP_{\alpha\beta}(E)$ is given in the paper of Dronskowski and Blöchl (1993). If possible, the analysis therefore should be performed with different choices for the basis set in order to figure out the features which are invariant with respect to the change of the basis orbitals.

For an illustration, we consider the stability of the bcc, fcc and hcp structure of Nb, Mo, Ru and Rh as obtained by the tight-binding linear muffin-tin orbital method in atomic-sphere approximation (Andersen and Jepsen 1984) and a minimal basis set of s, p and d states for the valence electrons. Table 1 represents the cohesive energy E_{coh} (which is the total energy minus

Table 1. Cohesive energy E_{coh} , covalent bond energy E_{cov} , promotion energy E_{prom} , and the sum $E_1 = E_{cov} + E_{prom}$ for Nb, Mo, Ru and Rh in the bcc, fcc and hcp structures (in Ryd) and the respective contributions to the structural energy differences (in mRyd). Ω_{at} denotes the atomic volume for which the calculation has been performed.

	E_{coh}	E_{cov}	E_{prom}	E_1
Nb, $\Omega_{at} = 120.3$ a.u.				
bcc	-0.8018	-1.5787	0.2757	-1.3030
fcc	-0.7720	-1.5689	0.2863	-1.2826
hcp	-0.7710	-1.5496	0.2668	-1.2827
bcc-fcc	-29.80	-9.84	-10.60	-20.44
hcp-fcc	0.35	12.15	-13.05	-0.89
Mo, $\Omega_{at} = 105.5$ a.u.				
bcc	-0.8584	-1.8067	0.3836	-1.4230
fcc	-0.8268	-1.7370	0.3328	-1.4042
hcp	-0.8238	-1.7169	0.3148	-1.4021
bcc-fcc	-31.59	-69.66	50.82	-18.84
hcp-fcc	3.05	14.90	-13.28	1.61
Ru, $\Omega_{at} = 91.8$ a.u.				
bcc	-0.6958	-1.6587	0.3627	-1.2960
fcc	-0.7389	-1.7092	0.3827	-1.3265
hcp	-0.7446	-1.7186	0.3894	-1.3292
bcc-fcc	43.11	50.49	-20.02	30.47
hcp-fcc	-5.66	-7.91	4.92	-2.99
Rh, $\Omega_{at} = 97.3$ a.u.				
bcc	-0.5843	-1.3135	0.2731	-1.0404
fcc	-0.6072	-1.3733	0.3184	-1.0549
hcp	-0.6029	-1.3694	0.3184	-1.0511
bcc-fcc	22.88	59.80	-45.25	14.55
hcp-fcc	4.36	6.47	-2.75	3.72

the energy of the free atoms forming the crystal), the covalent bond energy E_{cov} , the promotion energy E_{prom} and the sum $E_1 = E_{cov} + E_{prom}$. It becomes obvious that the differences E (bcc-fcc) and E (hcp-fcc) are of the same order of magnitude for $E = E_{coh}$, E_{cov} , E_{prom} and E_1 , and that therefore in principle all three parts (E_{cov} , E_{prom} , D') to the total energy may be relevant for the structural stability. Nevertheless, if we consider just E_{cov} it exhibits the same energetic succession for the different structures as E_{coh} , and it is therefore tempting to analyse the structural stability in terms of the various contributions to the covalent bond energy. It thereby turns out that the contributions of the bonds between two atoms decrease rather rapidly with increasing separation of the atoms, and we therefore confine ourselves, in the following discussion, to contributions from nearest-neighbour pairs. Figure 1 exhibits, for the bcc structures of Mo and Ru, the energy- and orbital-resolved contributions of a nearest-neighbour pair, where we have summed the $E_{cov,\alpha\beta}(E)$ over the magnetic quantum numbers of the orbitals, yielding the energy-resolved s-s, s-p, s-d, p-p, p-d and d-d contributions. The figure exhibits in addition the respective quantities integrated over all energies up to the considered energy, i.e.,

$$I E_{cov,\alpha\beta}(E) = \int_{-\infty}^E E_{cov,\alpha\beta}(E') dE'. \quad (20)$$

Obviously, the d-d contributions are most relevant. For Mo they have bonding character almost

up to the Fermi energy E_F , whereas for Ru they change from bonding to anti-bonding character in the middle of the d band, thus destabilizing the bcc structure. The weakening of the d–d bond due to anti-bonding contributions at higher energies appears also for the hcp structure of Ru, but the weakening is less strong than for the bcc structure, and this is compatible with the fact that the hcp structure is the ground-state structure of Ru.

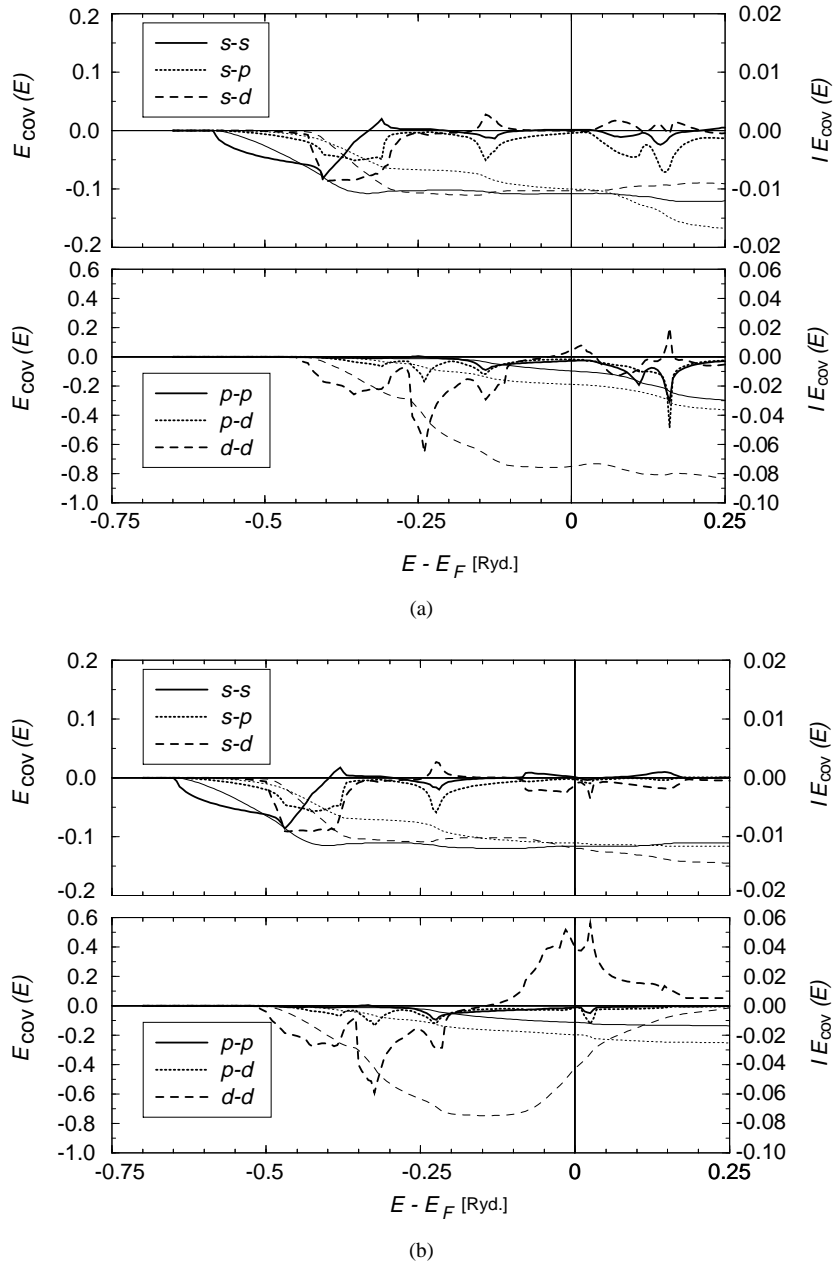


Figure 1. Energy-resolved covalent bond energy $E_{cov}(E)$ (strong curves) for s–s, s–p, s–d, p–p, p–d and d–d bonds between nearest-neighbour atoms of bcc Mo (a) and bcc Ru (b), and the corresponding energy-integrated quantities $IE_{cov}(E)$ (weak curves, units in Ryd).

To conclude we have shown that a generalization of the covalent bond energy of the tight-binding bond model to the case of a non-orthogonal basis set is an appropriate tool to describe the bonding properties of periodic systems without suffering from the problems related to the ill-defined average electrostatic potential in these systems. In addition to the analysis of the electronic structure in a chemical language by means of this tool we plan to use it for the development of semi-empirical tight-binding models for intermetallic compounds. In order to obtain transferable tight-binding models it is necessary to find appropriate analytical parametrizations of the Hamiltonian matrix and the overlap matrix (see, e.g., Haas *et al* 1997) and to fit the parameters to a data base which is a representative signature of the binding properties of the material. We think that *ab initio* results for $E_{cov,\alpha\beta}(E)$ of properly chosen reference configurations should be included in the data base in order to account for the complicated electronic structure of intermetallic compounds (Schultz and Davenport 1993).

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