J. Phys. Chem. A **2007,** *111,* 5609−5613

Tight-Binding Density Functional Theory: An Approximate Kohn−Sham DFT Scheme[†]

G. Seifert*

Physical Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

Received: December 31, 2006; In Final Form: February 21, 2007

The DFTB method is an approximate KS-DFT scheme with an LCAO representation of the KS orbitals, which can be derived within a variational treatment of an approximate KS energy functional. But it may also be related to cellular Wigner−Seitz methods and to the Harris functional. It is an approximate method, but it avoids any empirical parametrization by calculating the Hamiltonian and overlap matrices out of DFT-derived local orbitals (atomic orbitals, AO's). The method includes ab initio concepts in relating the Kohn−Sham orbitals of the atomic configuration to a minimal basis of the localized atomic valence orbitals of the atoms. Consistent with this approximation, the Hamiltonian matrix elements can strictly be restricted to a two-center representation. Taking advantage of the compensation of the so-called "double counting terms" and the nuclear repulsion energy in the DFT total energy expression, the energy may be approximated as a sum of the occupied KS single-particle energies and a repulsive energy, which can be obtained from DFT calculations in properly chosen reference systems. This relates the method to common standard "tight-binding" (TB) schemes, as they are well-known in solid-state physics. This approach defines the density-functional tight-binding (DFTB) method in its original (non-self-consistent) version.

1. Introduction

The DFTB method is an approximate Kohn−Sham density functional theory (KS-DFT) scheme with an LCAO representation of the KS orbitals. On the basis of earlier work,[1] the DFTB method[2,3] was developed as a KS-LCAO method, which avoids any empirical parametrization by calculating the Hamiltonian and overlap matrices out of DFT-derived local orbitals (atomic orbitals, AO's) and corresponding atomic potentials. The method includes ab initio DFT concepts, but keeps efficiency and flexibility by using also - ideas of the semiempirical "tight-binding" (TB) method. It may also be related to the cellular Wigner−Seitz method[4] and to the Harris functional.[5] A theoretical justification of DFT-based "tight-binding" (TB) schemes was also given by Foulkes and Haydock,[6] who generalized the ideas of Harris.[5] There are also relations to the Harris functional-based method proposed by Sankey and Niklewsky.[7] For an overview and comparison to the manifold of TB methods, see e.g., refs 8,9

The DFTB method has been applied for a large variety of problems in chemistry, physics, materials science, and biochemistry; for an overview, see e.g., ref 10. During the past decade it has been continually further developed to improve its accuracy and the applicability. After the development of a non-self-consistent ("zeroth-order") approach,[2] a self-consistent charge (SCC) extension[11] was formulated with an extension to the consideration of spin polarization.[12] Furthermore, the method was adapted for the calculation of optical properties within a time-dependent DFT approach[13] and in combination with the nonequilibrium Green's function technique for the calculation of electron transport properties on the molecular scale.[14] This development is still in progress with the extension of the spin-polarized DFTB to the consideration of noncollinear spin configurations,[15] the extension to higher-order terms in the expansion of density fluctuations in the SCC-DFTB scheme, the development of an LDA+U version of DFTB,[16] or the realization of a Car−Parrinello treatment within DFTB,[17] to mention some of the recent developments.

The aim of the present paper is to show the relation of the DFTB method to the density functional theory (DFT) in general. Furthermore, the justification of the DFTB approximations for the solution of the Kohn−Sham equations will be sketched and the calculation of the total energy will be outlined. Especially, the total energy has not been described clearly before within the DFT context. Some practical computational aspects related to the DFTB approximations will be demonstrated. Finally, the calculated orbital energies of molecules, band structures of solids, and binding energies are discussed in a few examples.

2. Theory

Within density functional theory (DFT), the total energy of a system of M electrons in the field of N nuclei can be expressed as a functional of a charge density

$$E_{\text{tot}}(n(x)) = T(n(x)) + \int\int \mathrm{d}x\,\mathrm{d}x'\,\frac{n_{\text{N}}(x)n(x')}{|x-x'|} + \frac{1}{2}\int\int \mathrm{d}x\,\mathrm{d}x'\,\frac{n(x)n(x')}{|x-x'|} + \frac{1}{2}\int\int \mathrm{d}x\,\mathrm{d}x'\,\frac{n_{\text{N}}(x)n_{\text{N}}(x')}{|x-x'|} + E_{\text{XC}}[n(x)] \quad (1)$$

$T(n)$ is the functional of the kinetic energy, $n(x)$ and $n_{\text{N}}(x)$ are the electronic and the nuclear charge density distributions, respectively. $E_{\text{XC}}(n)$ stands for the functional of the exchange and correlation energy. The symbol x is used as a shorthand for the coordinates. The electron density distribution can be obtained as solutions of the Kohn−Sham

---

[†] Part of the "DFTB Special Section".

* Gotthard.Seifert@chemie.tu-dresden.de.

10.1021/jp069056r CCC: $37.00

equations

$$n(x) = \sum_i^{\text{occ}} \psi_i^*(x)\psi_i(x) \quad \left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(x)\right]\psi_i(x) = \epsilon_i\psi_i(x)$$

$$V_{\text{eff}} = V_{\text{H}} + V_{\text{XC}}$$

$$V_{\text{H}} = \int \mathrm{d}x' \frac{n(x') + n_{\text{N}}(x')}{|x - x'|} \quad V_{\text{XC}} = \delta E_{\text{XC}}/\delta n \tag{2}$$

Using the Kohn−Sham eq 2, the total energy can be rewritten as

$$E_{\text{tot}} = \frac{1}{2}\{T + \sum_i^{\text{occ}} \epsilon_i + \int \mathrm{d}x V_{\text{H}}(x)n_{\text{N}}(x)\} + E_{\text{XC}}[n(x)] - \frac{1}{2}\int \mathrm{d}x V_{\text{XC}}(x)n(x) \tag{3}$$

Because E_{tot} is variational with respect to density variations, the total energy may be calculated from an approximated density

$$E_{\text{tot}} = \min_n E(n) \approx E(\tilde{n}) \qquad \tilde{n} \approx n \tag{4}$$

The density $\tilde{n}$ shall be connected with approximate solutions of the KS equations

$$\left[-\frac{1}{2}\nabla^2 + w(x)\right]\tilde{\psi}_i(x) = \tilde{\epsilon}_i\tilde{\psi}_i(x)$$

$$\tilde{n}(x) = \sum_i^{\text{occ}} \tilde{\psi}_i^*(x)\tilde{\psi}_i(x) \tag{5}$$

The approximate effective potential w in eq 5 is determined by $\tilde{n}$. The total energy may then be written as

$$E_{\text{tot}}(\tilde{n}) = T(\tilde{n}) + \int \mathrm{d}x\tilde{V}_{\text{H}}(\tilde{n} + n_{\text{N}}) + E_{\text{XC}}[\tilde{n}] \tag{6}$$

Writing $E_{\text{tot}}(\tilde{n})$ in the form of eq 3, one obtains

$$E_{\text{tot}}(\tilde{n}) = \frac{1}{2}\{T(\tilde{n}) + \sum_i^{\text{occ}} \tilde{\epsilon}_i + \int \mathrm{d}x(\tilde{V}_{\text{H}} + \tilde{V}_{\text{XC}} - w)\tilde{n} + \int \mathrm{d}x\tilde{V}_{\text{H}}n_{\text{N}}\} + E_{\text{XC}}[\tilde{n}] - \frac{1}{2}\int \mathrm{d}x\tilde{V}_{\text{XC}}\tilde{n} \tag{7}$$

Note that $\tilde{V}_{\text{H}} + \tilde{V}_{\text{XC}}$ is different from w through the approximate character of the solutions of eq 5. Therefore, there is no cancellation of $\int \mathrm{d}x(\tilde{V}_{\text{H}} + \tilde{V}_{\text{XC}} - w)\tilde{n}$ as is the case if the exact n is used, eq 7.

The LCAO treatment allows to write an ansatz for the solutions of eq 5 as

$$\psi(\vec{r}) = \sum_\mu C_\mu\phi_\mu \tag{8}$$

The expansion coefficients are obtained in the usual way as variatonal solutions of eq 5. Using as basis functions atomic orbitals ($|\phi_\mu)$) only of the valence shell of the atoms, constituting the molecule, cluster, or solid, the orthogonality of the basis functions to the core functions of the atoms has to be satisfied. This orthogonality can be achieved by

$$|\varphi_\mu\rangle = |\varphi_\mu) - \sum_{l \neq j}\sum_{c_l} |\varphi_{c_l})(\varphi_{c_l}|\varphi_\mu) \qquad \mu \in \{\text{j}\} \tag{9}$$

The orthogonalized basis functions are $|\varphi_\mu\rangle$, and the core orbitals at atom l are $|\varphi_{c_l})$. Equation 9 presumes the orthogonality of the valence orbital to the core orbitals at the same center. Inserting eqs 8 and 9 into eq 5 gives

$$\tilde{\epsilon}_i = \sum_\mu\sum_\nu C_\mu^i\left[\left(\varphi_\mu\middle| -\frac{1}{2}\nabla^2 + w\middle|\varphi_\nu\right) - \sum_l\sum_{c_l}(\varphi_\nu|\varphi_{c_l})\epsilon_{c_l}(\varphi_{c_l}|\varphi_\mu)\right]C_\nu^i \qquad \mu,\nu \notin \{l\} \tag{10}$$

ϵ_{c_l} is the energy of a core state at center l. The potential w together with the core correction term in eq 10 can be interpreted as a pseudopotential (w_{PP})

$$\tilde{\epsilon}_i = \sum_\mu\sum_\nu C_\mu^i\left[\left(\varphi_\mu\middle| -\frac{1}{2}\nabla^2 + w_{\text{PP}}\middle|\varphi_\nu\right)\right]C_\nu^i \tag{11}$$

Writing w as a superposition of atom-centered potentials

$$w = \sum_j w_j(\vec{r}_j) \tag{12}$$

and inserting it into eq 10, one can see that the potential becomes a pseudopotential for all atoms in the system, but not for the atoms where φ_μ and φ_ν are centered. This means that the pseudopotential appears in the three-center terms and in the crystal-field-like terms of eq 8, whereas the "full" potential stands in all the other terms. The orbital energies obtained neglecting the pseudopotential terms are

$$\tilde{\epsilon}_i = \sum_\mu\sum_\nu C_\mu^i\left[\left(\varphi_\mu\middle| -\frac{1}{2}\nabla^2 + w_j + w_{j'}(1 - \delta_{jj'})\middle|\varphi_\nu\right)\right]C_\nu^i \qquad \mu \in \{j\},\ \nu \in \{j'\} \tag{13}$$

For the sum of the orbital energies, this leads to

$$\sum_i \tilde{\epsilon}_i = \tilde{T} + \int \mathrm{d}x\tilde{w}\tilde{n} \tag{14}$$

$\tilde{T}$ is the expectation value of the kinetic energy, and $\int \mathrm{d}x\tilde{w}\tilde{n}$ means that the three-center and crystal-field terms have been omitted, according to eq 13. Consideration of eq 14 gives a modified expression for the total energy (eq 7)

$$E_{\text{tot}}(\tilde{n}) = \{T(\tilde{n}) - \tilde{T}(\tilde{n})\} + \frac{1}{2}\{\int \mathrm{d}x(\tilde{V}_{\text{H}} + \tilde{V}_{\text{XC}} - \tilde{w})\} + \frac{1}{2}\{\tilde{T}(\tilde{n}) + \sum_i^{\text{occ}} \tilde{\epsilon}_i + \int \mathrm{d}x\tilde{V}_{\text{H}}n_{\text{N}}\} + E_{\text{XC}}[\tilde{n}] - \frac{1}{2}\int \mathrm{d}x\tilde{V}_{\text{XC}}\tilde{n} \tag{15}$$

In all terms of eq 15, only one- and two-center contributions are considered. Assuming also

$$T(\tilde{n}) \approx \tilde{T}(\tilde{n}), \qquad \tilde{V}_{\text{H}} + \tilde{V}_{\text{XC}} \approx w \tag{16}$$

eq 15 simplifies to

$$E_{\text{tot}}(\tilde{n}) \approx \frac{1}{2}\{\tilde{T}(\tilde{n}) + \sum_i^{\text{occ}} \tilde{\epsilon}_i + \int \mathrm{d}x\tilde{V}_{\text{H}}n_{\text{N}}\} + E_{\text{XC}}[\tilde{n}] - \frac{1}{2}\int \mathrm{d}x\tilde{V}_{\text{XC}}\tilde{n} \tag{17}$$

Using eq 14, eq 17 can be written as

$$E_{\mathrm{tot}}(\tilde{n}) \approx \sum_i^{\mathrm{occ}} \tilde{\epsilon}_i - \frac{1}{2}\{\int \mathrm{d}x\tilde{w}\tilde{n} - \int \mathrm{d}x\tilde{V}_{\mathrm{H}}n_{\mathrm{N}}\} + E_{\mathrm{XC}}[\tilde{n}] - \frac{1}{2}\int \mathrm{d}x\tilde{V}_{\mathrm{XC}}\tilde{n} \quad (18)$$

Writing $\tilde{n}$,$\tilde{w}$ and $\tilde{V}_{\mathrm{XC}}$ as superpositions of atomic contributions (see eq 12), the separation of $\tilde{V}_{\mathrm{H}}$ and considering the relation

$$E_{\mathrm{XC}} - \frac{1}{2}\int \mathrm{d}x\tilde{V}_{\mathrm{XC}}\tilde{n} = \frac{1}{2}\int \mathrm{d}x\tilde{V}_{\mathrm{XC}}\tilde{n} - \int \mathrm{d}x\tilde{n}^2\frac{\delta\epsilon_{\mathrm{XC}}}{\delta n} = \frac{1}{2}\sum_j\sum_l\left[\int \mathrm{d}x\tilde{V}_{\mathrm{XC}_j}\tilde{n}_l - 2\int \mathrm{d}x\tilde{n}_j\tilde{n}_l\frac{\delta\epsilon_{\mathrm{XC}}}{\delta n}\right] \quad (19)$$

leads to

$$E_{\mathrm{tot}}(\tilde{n}) \approx \sum_i^{\mathrm{occ}} \tilde{\epsilon}_i - \frac{1}{2}\sum_j\sum_l\int \mathrm{d}x\tilde{w}_j\tilde{n}_l - \frac{1}{2}\sum_j\sum_l\int \mathrm{d}x\frac{Z_j}{r_j}\tilde{n}_l + \frac{1}{2}\sum_j\sum_{l\neq j}\frac{Z_jZ_l}{R_{lj}} + \frac{1}{2}\sum_j\sum_l\left[\int \mathrm{d}x\tilde{V}_{\mathrm{XC}_j}\tilde{n}_l - 2\int \mathrm{d}x\tilde{n}_j\tilde{n}_l\frac{\delta\epsilon_{\mathrm{XC}}}{\delta n}\right] \quad (20)$$

For large interatomic distances, the integral for the electron−nucleus interaction can be approximated by a point charge approximation $\int \mathrm{d}x(Z_j)/(r_j)\tilde{n}_l \approx (Z_jQ_l)/(R_{jl})\ Q_l = \int \mathrm{d}x\tilde{n}_l$. For the large distance limit $Q_l \rightarrow Z_l$. This holds for homonuclear as well as for heteronuclear systems, as already pointed out by Slater a long time ago.[18] Therefore, for large distances, the energy terms from nuclear−nuclear repulsion and electron−nuclear energy in eq 20 compensate each other. In the large distance range, the two-center terms with the potential vanish. The potential around each center is completely screened (Wigner−Seitz limit[4]): $\sum_j\sum_l \int \mathrm{d}x\tilde{w}_j\tilde{n}_l = 0(l \neq j)$. Approximating also $\int \mathrm{d}x\tilde{V}_{\mathrm{XC}_j}\tilde{n}_l = 0 \wedge \int \mathrm{d}x\tilde{n}_j\tilde{n}_l(\delta\epsilon_{\mathrm{XC}})/(\delta n) = 0(l \neq j)$, then the total energy is just the sum of the KS single-particle energies ($\sum_{\boldsymbol{i}}^{\mathbf{occ}} \tilde{\epsilon}_{\boldsymbol{i}}$) plus the one-center terms of eq 20. Considering the corresponding expressions for the total energies of the isolated atoms, then the binding energy (E_{B}) is approximately given by the simple relation

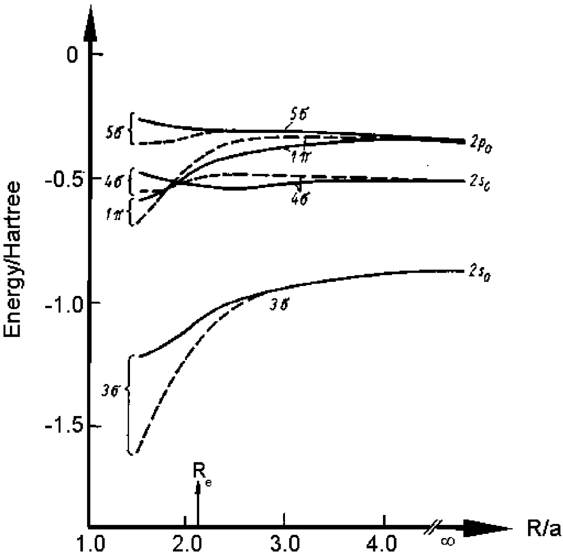

Figure 1. Kohn−Sham orbital energies of CO as a function of the C−O distance (*R*). (— DFTB, --- DFT).

$$E_{\mathrm{B}} = E_{\mathrm{tot}} - \sum_j E_{\boldsymbol{j}} \approx \sum_i \tilde{\epsilon}_i - \sum_j\sum_{n_j}\epsilon_{\boldsymbol{n}_j} \quad (21)$$

where ϵ_{n_j} are the orbital energies of the atoms. This is just the result as obtained by Inglesfield[4] for the binding energies in the Wigner−Seitz limit in a quasiparticle approach and, of course, the result which Wigner and Seitz used in their calculations of the binding energy of alkaline metals.[19]

3. Practical Aspects

The orbitals in the Kohn−Sham equations (eq 5) are represented in a minimal basis of optimized pseudoatomic orbitals φ_μ, eq 8, see below. Considering the core-orthogonalization (eq 9) and assuming the "weakness" of the corresponding pseudopotentials (eqs 10,11) leads to the two-center approximation for the Hamilton matrix elements (see eq 13)

$$\begin{aligned} h_{\mu\nu} &= \langle\varphi_\mu|\hat{t} + w_j^0 + w_k^0|\varphi_\nu\rangle & \mu \in \{j\}, \nu \in \{k\} \\ h_{\mu\nu} &= \langle\varphi_\mu|\hat{t} + w_j^0|\varphi_\nu\rangle & \mu \cap \nu \in \{j\} \end{aligned} \quad (22)$$

It is important to notice that the potentials $w_{\boldsymbol{j}}^0$ in eq 22 correspond to potentials of neutral atoms ($Z_l = Q_l = \int \mathrm{d}x\tilde{n}_l$). With the overlap matrix $\mathbf{S}_{\mu\nu} \equiv \langle\varphi_\mu|\varphi_\nu\rangle$, the orbital energies $\tilde{\epsilon}_i$ are obtained as the solution of the general eigenvalue problem

$$\sum_\mu C_\mu(h_{\mu\nu} - \tilde{\epsilon}S_{\mu\nu}) = 0 \quad (23)$$

The $h_{\mu\nu}$ can be tabulated together with the overlap matrix elements $\mathbf{S}_{\mu\nu}$ with respect to the interatomic distance R_{jk}.

The approximations formulated in eq 22 lead to the same structure of the secular equations as in (nonorthogonal) tight-binding (TB) or the extended Hückel method (EHT), but there is the important advantage that all matrix elements are calculated within the density functional theory. The neglect of the pseudopotential terms, which related to the two-center approximation in eq 22, also has a resemblance to the cellular Wigner−Seitz method.[4,19] As in the cellular method, the neglect of integrals $\langle\varphi_\mu|w_j^0|\varphi_\nu\rangle\mu \cap \nu\notin\{j\}$ means the density around j screens the nucleus j completely. This approximation is improving with better screening, i.e., depending from the atomtype with increasing the internuclear distance.

The pseudoatomic basis functions φ_μ are obtained by solving the Kohn−Sham equation for a spherical symmetric spin-unpolarized neutral atom self-consistently

$$\left[\hat{T} + w_j^0(r) + \left(\frac{r}{r_0}\right)^{n_0}\right]\varphi_\mu(r) = \epsilon_\mu\varphi_\mu(r) \quad (24)$$

Here a contraction potential $(r/r_0)^{n_0}$ has been added as introduced by Eschrig[20,21] to form a more efficient basis set for molecular and solid-state systems. The parameter r_0 is chosen to be about 1.85 times the atomic covalent radius.[22] However, this parameter can also be determined using a variational principle for the total energy. The atomic orbitals can be represented by linear combinations of Slater-type orbitals (STO)

$$\varphi_\mu(\vec{r}) = \sum_\zeta\sum_i (a_\zeta r^{l+i})e^{-\zeta r}Y_{lm}\left(\frac{\vec{r}}{r}\right) \quad (25)$$

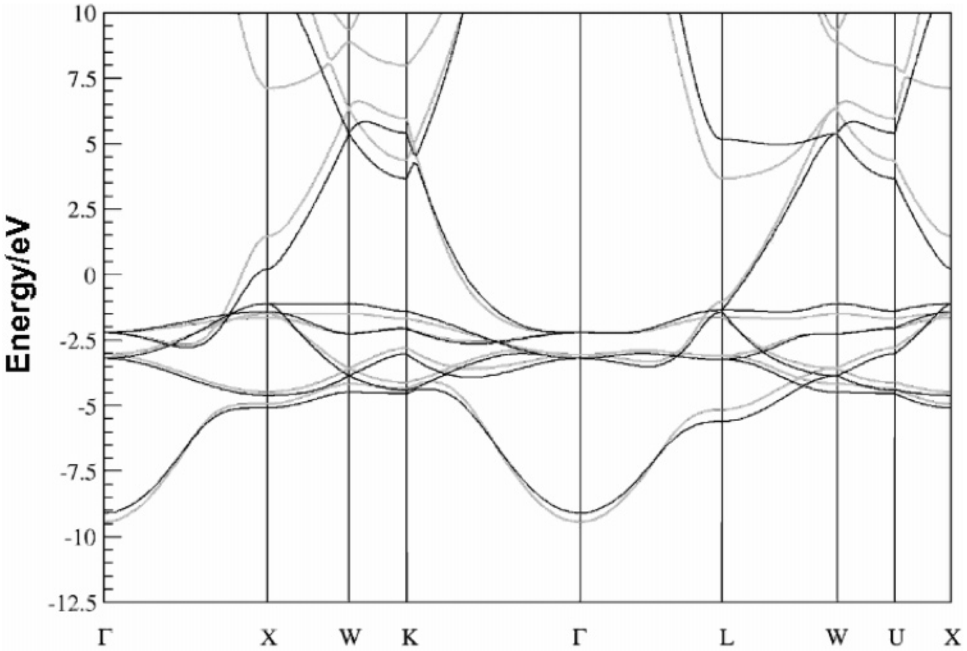

Figure 2. Band structure of Cu in fcc structure (black lines: DFTB; gray lines: DFT).

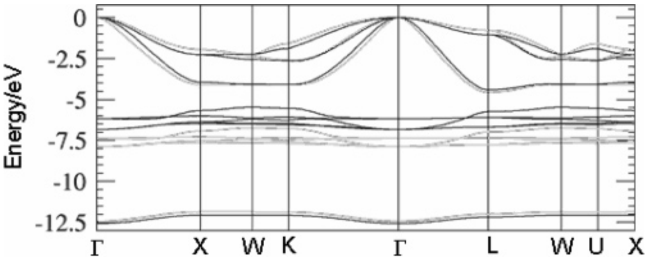

Figure 3. Band structure of CdS (zinc blend structure) (black lines: DFTB; gray lines: DFT).

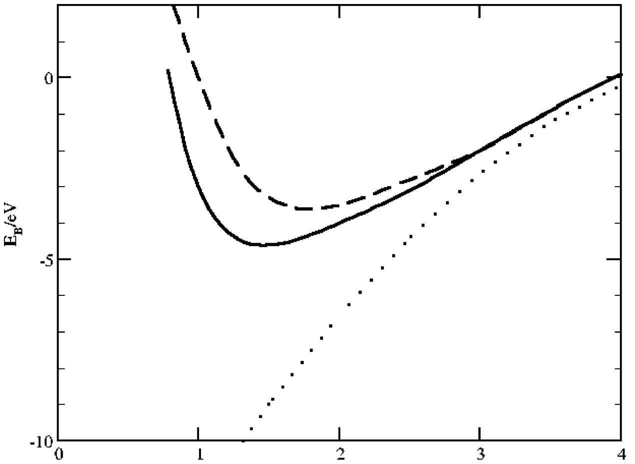

Figure 4. Binding energy curve of the H_2 molecule (--- DFTB, — DFT, ··· $\sum\epsilon_i$). (The energy is given with respect to the "spin-polarized" atoms).

where *l* and *m* are the angular momentum and the magnetic quantum numbers associated with the orbital μ, respectively. Extensive tests have shown that 5 different values of ζ and $i = 0,1,2,3$ form a sufficiently accurate basis set.[20] Instead of STO, Gauss-type orbitals can also be used.[23] From this procedure, we obtain for each atom-type optimized atomic basis sets $\{\varphi_\mu\}$ and atomic potentials w_j^0.

As discussed above, the total energy expression (eq 20) contains compensating terms. Therefore, for large interatomic distances, the total energy approaches the expression of eq 21. Hence, instead of calculating the total energy from eq 20, one could approximate the compensating terms in eq 20, which are only two-center terms, by a pairwise repulsive energy $E_{\text{rep}} = \sum_{l\neq j} U[R_{lj}]$. The binding energy (eq 21) can then simply be written as:

$$E_{\text{B}} \approx \sum_i \tilde{\epsilon}_i - \sum_j \sum_{n_j} \epsilon_{n_j} + \frac{1}{2}\sum_j \sum_l \sum\nolimits_{l\neq j} U[R_{lj}] \qquad (26)$$

The atom-type specific pair potentials $U[R_{lj}]$ can be obtained as the difference between the total energy versus distance calculated from eq 20 and the corresponding electronic energy (eq 21) calculated within the DFTB approach for properly chosen reference systems, in the most simple case, a dimer.

3. Discussion

For illustration of the usability of the DFTB approximations (see eq 22) concerning the Kohn−Sham energies, the orbital energies of the CO molecule from a DFTB calculation and DFT calculation, using the same basis and the same XC functional, are drawn in Figure 1 as a function of the C−O distance. As expected, the error is decreasing with increasing interatomic distance. Near the equilibrium distance (R_e), the deviation is <10%. The performance of the approximations for a densily packed bulk system is shown in Figure 2. In this figure, the band structure of copper in the fcc lattice is shown for DFTB in comparison to the band structure self-consistently calculated with the same basis set and XC potential but without the DFTB approximations. As an example for a heteronuclear system, the band structure calculated in the DFTB approximation of CdS in the zinc-blende structure is shown together with that from an SCF-DFT calculation in Figure 3. From Figures 2 and 3, one can clearly see that the DFTB approximations work quantitatively correctly for these bulk structures. It is important to note that, in both cases, the potentials of neutral free atoms were used in the DFTB KS equations (eq 22).

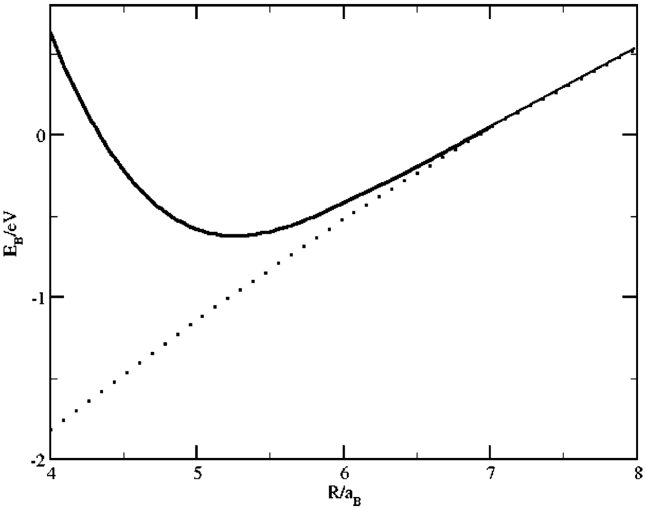

Figure 5. Binding energy curve of the Li$_2$ molecule (— DFTB, ⋯ $\sum\epsilon_i$). (The energy is given with respect to the “spin-polarized” atoms).

The validity of the DFTB approximations for the total energy calculation can be seen from Figure 4 for the H$_2$ molecule. From this figure, one can also see the long-range behavior of the binding energy, i.e., the transition to the Wigner−Seitz limit (eqs 20 → 21), which justifies the introduction of $U(R_{lj})$ (eq 26) as the difference between the energies obtained using eqs 20 and 21. In the case of the Li-dimer, the WS limit is reached already for a distance only slightly larger than the equilibrium distance (see Figure 5). The determination of $U(R_{lj})$ in practice was shown for the first time for carbon in ref 2.

4. Conclusions

The DFTB method can be understood as an approximate DFT scheme, keeping essential features of DFT, having the computational speed of traditional semiempirical quantum chemical methods but without having a large number of empirical parameters. In principle, there are no empirical parameters in the method. All quantities are either calculated within DFT (integral tables) or they are determined in reference structures by DFT(B) calculations (E_{rep}). Because the KS orbitals are well defined, one can derive expressions within the DFTB method for properties in the same way as within a “full” DFT scheme.

In this paper, we have concentrated on the non-self-consistent (“zeroth-order”) approach of the DFTB method, i.e., we have considered in the representation of the potential (w) in eq 12 the potentials of neutral free atoms. The discussions concerning the DFTB-like approximations, eq 22 (“two-center approach”) for solution of the KS equations, and eq 20 for the calculation of the total energy, hold in principle also for further developments of the DFTB method, e.g., the self-consistent charge (SCC) extension.

Acknowledgment. I thank Thomas Frauenheim, Dirk Porezag, Markus Elstner, Gerd Jungnickel, Christof Köhler, Ben Houraine, and Thomas Heine for many discussions and contributions concerning the DFTB method.

References and Notes

(1) Seifert, G.; Eschrig, H.; Bieger, W. *Z. Phys. Chem. (Leipzig)* **1986,** *267*, 529.

(2) Porezag, D.; Frauenheim, T.; Köhler, T.; Seifert, G.; Kaschner, R. *Phys. Rev. B* **1995**, *51*, 12947.

(3) Seifert, G.; Porezag, D.; Frauenheim, Th. *Int. J. Quantum Chem.* **1996**, *58*, 185.

(4) Inglesfield, J. E. *Mol. Phys.* **1979**, *37*, 873.

(5) Harris, J. *Phys. Rev. B* **1985**, *11*, 1770.

(6) Foulkes, W.; Haydock, R. *Phys. Rev. B* **1989**, *40*, 12520.

(7) Sankey, O. F.; Niklewski, D. J. *Phys. Rev. B* **1989**, *40*, 3979.

(8) Goringe, C. M.; Bowler, D. R.; Hernandez, E. *Rep. Prog. Phys.* **1997**, *60*, 1447.

(9) Turchi, P. E. A., Gonis, A., Colombo, L., Eds. *Tight-Binding Approach to Computational Materials Science*; Pittsburgh: Materials Research Society Symposium Proceedings: Pittsburgh, 1998, Vol. 491.

(10) Frauenheim, Th.; Seifert, G.; Elstner, M.; Niehaus, T. A.; Köhler, C.; Amkreutz, M.; Sternberg, M.; Hajnal, Z.; di Carlo, A.; Suhai, S. *J. Phys. C* **2002**, *14*, 3015.

(11) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Suhai, S.; Seifert, G.; Frauenheim, T. *Phys. Rev. B* **1998**, *58*, 7260.

(12) Köhler, C.; Seifert, G.; Gerstmann, U.; Elstner, M.; Overhof, H.; Frauenheim, Th. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5109.

(13) Niehaus, T.; Suhai, S.; Della Sala, F.; Lugli, P.; Elstner, M.; Seifert, G.; Frauenheim, T. *Phys. Rev. B* **2001**, *63*, 085108.

(14) di Carlo, A.; Gheorghe, M.; Lugli, P.; Sternberg, M.; Seifert, G.; Frauenheim, Th. *Physica B* **2002**, *314*, 86.

(15) Köhler, C.; Hourahine, B.; Seifert, G.; Frauenheim, Th. *J. Phys. Chem.*, in press.

(16) Hourahine, B. to be published.

(17) Rapacioli, M.; Heine, Th.; Seifert, G. *J. Chem. Phys.* **2007**, in press.

(18) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.

(19) Wigner, E.; Seitz, F. *Phys. Rev.* **1933**, *43*, 804; *Phys. Rev.* **1934**, 509.

(20) Eschrig, H. *Optimized LCAO Method and the Electronic Structure of Extended Systems*; Akademie-Verlag: Berlin, 1988.

(21) Eschrig, H.; Bergert, I. *Phys. Status Solidi B* **1978**, *90*, 621.

(22) Frauenheim, T.; Seifert, G.; Elstner, M.; Hajnal, Z.; Jungnickel, G.; Porezag, D.; Suhai, S.; Scholz, R. *Phys. Status Solidi B* **2000**, *217*, 41.

(23) Heine, T.; Seifert, G.; Fowler, P.; Zerbetto, F. *J. Phys. Chem. A* **1999**, *103*, 8738.