

The scaling of the tight-binding Hamiltonian

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 L61

(<http://iopscience.iop.org/0953-8984/7/6/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 11:51

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

The scaling of the tight-binding Hamiltonian

A N Andriotis

Institute of Electronic Structure and Lasers, Foundation for Research and Technology—Hellas,
PO Box 1527, 71110 Heraklion, Crete, Greece

Received 2 December 1994

Abstract. We re-examine the variation of the Slater–Koster tight-binding (SKTB) parameters with the interatomic distance and the lattice structure. It is shown that when volume effects are separated from lattice (field) effects, the scaling with the volume can be described in terms of the electron density (or equivalently the parameter r_s) while the scaling with the lattice structure can be described in terms of the number of nearest neighbours. The proposed scaling form appears to fit very accurately the SKTB parameters of Si obtained by the TB-LMTO method.

The tight-binding (TB) method as proposed by Slater and Koster [1] (SK) has been implemented as a key approach in the solution of many problems of condensed matter physics due mainly to its simplicity and its low demands in computer usage. The method requires the knowledge of the appropriate parameters, known as the SK parameters, which are usually determined by fitting to *ab initio* calculated band structures. In such applications the SKTB method takes firm *ab initio* character. On the other hand, in other applications of the method, such as in those that investigate the pressure dependence of various electronic properties [2, 3], phase transformations and more recently in problems that utilize the SKTB method in molecular dynamics simulations [4], the *ab initio* character of the TB molecular dynamics method is suppressed because necessarily simple semiempirical scaling schemes are introduced in order to describe the variation of the SKTB parameters with the interatomic distance. In the latter cases however one can retain both the simplicity of the scaling scheme (so as to be applicable with computer time demanding simulations), and much of the *ab initio* character of the method if suitably chosen scaling schemes are used, which are determined by *ab initio* methods. It is the purpose of the present work to propose such a simple scaling scheme that retains its *ab initio* character.

The most commonly used scaling scheme has the form

$$V_{ijm}(d) = V_{ijm}^{(0)}(d_0/d)^\nu \quad (1)$$

where $V_{ijm}^{(0)}$, $i, j = s, p, d, \dots$ and $m = \sigma, \pi, \delta, \dots$ are the SKTB parameters calculated at the equilibrium interatomic distance d_0 and $V_{ijm}(d)$ their corresponding values at the interatomic distance d . For $\nu = 2$, (1) represents the scaling scheme of Harrison [6], which, although appropriate over a small range around the equilibrium distance d_0 , is often used for even larger ranges of interatomic distances. Simple arguments that have their origin in the exponential variation of the wave functions far from atomic nucleus imply that for large $(d - d_0)$ values an exponential form of the scaling should be more appropriate [7]. This was in fact found in our earlier calculations [8] where we employed the restricted Hartree–Fock (RHF) approximation in cluster calculations, namely the clusters Si_2H_6 and

Si_8H_{18} . On the other hand a fitting of the SKTB parameters onto the free electron bands [7] reveals the d^{-2} scaling of (1). Due to the fact that the energy bands of the real solids are poorly approximated by the free electron bands, one can argue that deviations of the d^{-2} scaling can be expected if the fitting of the SKTB parameters is performed onto the correct band structure of the material. Series of such calculations have indicated that the exponent ν in (1) differs substantially from Harrison's $\nu = 2$ value and additionally it was found that the exponent is orbital dependent or more generally it appears different for each SKTB parameter [2, 3, 8–10].

Harrison's scaling form described by (1) with $\nu = 2$ refers to intersite interactions between first-nearest neighbours. For more distant neighbours it was found that the SKTB parameters vary much faster than the d^{-2} variation. However, it appears common practice to avoid the scaling of more distant interactions than those between first-nearest neighbours. The scaling laws are also not used in practice for intrasite matrix elements although some calculations have indicated a weak dependence on the lattice constant [9–11]. There appear some cases, however, where the scaling of the intrasite parameters is taken on an equal footing with the scaling of the intersite parameters, as for example in the case of strained lattices for which the scaling aims to reproduce experimentally or theoretically determined deformation potentials [3]. Such a procedure allows part of the crystal field effect to be incorporated in the scaling of the intrasite SKTB parameters. On the other hand the total energy parametrization of Sigalas and Papaconstantopoulos [5] indicated that an appropriate incorporation of crystal field effects is necessary in order for the scaling procedure to be satisfactorily transferable. An improved scaling procedure, proposed recently by Cohen and coworkers [12], assigns a firm *ab initio* character to transferable SKTB parameters. In that scheme both intersite and intrasite SKTB parameters are scaled simultaneously and the crystal field effect on the SKTB parameters, in other words their variation with changes in the lattice structure, is taken into account by fitting additionally to total energies.

In the present letter a simpler scaling scheme will be proposed, which allows one to separate scaling effects due to the changes in the interatomic distance from changes due to the variation of the local lattice structure (i.e. the variation of the number of nearest neighbours (NNS)). No fitting to total energies appears necessary within the proposed scheme, which has the additional advantages of being very simple and computationally efficient. The proposed scaling of the SKTB parameters with the number of NNS is tested for the case of Si, using results obtained by the TB-LMTO method.

In order to separate the crystal structure effect on the SKTB matrix elements from the effect that is due to the variation of the interatomic distance, we initially expressed Harrison's universal SKTB matrix elements (derived by fitting to free electron energy bands) [7] in terms of the electron density parameter $r_s = (3\omega_0/4\pi)^{1/3}$ where ω_0 is the volume of the crystal unit cell. This is a necessary procedure, since a change in the crystal structure under the same r_s implies a change in the interatomic distances, which is accounted for by (1). It was found that when the energy difference ($E_p - E_s$) (where E_s , E_p are the intrasite parameters) is expressed in terms of the parameter r_s , it does not depend on the crystal structure if this is diamond, simple cubic or FCC type. For BCC structure ($E_p \sim E_s$) was found to be 20% larger than for the other structures. On the other hand, the universal intersite parameters, η_{ijm} , for the first-nearest neighbours, when expressed in terms of r_s , showed a strong dependence on the crystal structure. Approximately this dependence can be expressed in terms of the number of the first-nearest neighbours n with an expression analogous to (1), i.e.

$$\eta_{ijm}(n) = \eta_{ijm}^{\text{diam}} (n_{\text{diam}}/n)^{\lambda_{ijm}} \quad (2)$$

where n_{diam} and η_{ijm}^{diam} refer to the number of first NNS and the universal parameters for a diamond lattice respectively, while n and $\eta_{ijm}(n)$ to the corresponding parameters in a

lattice with number of NNS equal to n . Using the results of [7] we find $\lambda_{ss\sigma} \cong 1$ and $\lambda_{sp\sigma} \cong \lambda_{pp\sigma} \cong \lambda_{pp\pi} \cong \frac{2}{3}$.

(2) is obtained by assuming that for the different lattice structures (diamond, FCC, BCC, SC) the parameter r_s is constant. In this way we eliminate possible changes in the interatomic distance due to small variations in the volume per single atom as the crystal structure changes and thus we can isolate the effects of the lattice structure.

A combination of (1) and (2) yields the following form of scaling for the intersite SKTB parameters:

$$V_{ijm}(r_s, n) = \tilde{V}_{ijm}^{(0)} \left(r_s^{(0)} / r_s \right)^{v_{ijm}} \left(n^{(0)} / n \right)^{\lambda_{ijm}} \left[\mu(n_0) / \mu(n) \right]^{v_{ijm}} \quad (3)$$

where $\mu(n) = 1, \sqrt{3}/2^{2/3}, 2^{1/6}$ and $\sqrt{3}/2$ for SC, BCC, FCC and diamond structures respectively and $\tilde{V}_{ijm}^{(0)}$ and $n^{(0)}$ correspond to the SKTB parameters and number of first NNS respectively for a reference lattice, which here is taken to be the diamond lattice with electron density specified by the parameter $r_s^{(0)}$ at the equilibrium volume.

(3) is the proposed generalization of (1). It is apparent that (3) reduces to (1) if it refers to a system that does not undergo any change in its lattice structure as it is expanded or contracted. In the following we make some further approximations of (3) and bring it into a simpler form, much suitable for numerical simulations. In particular, our previous findings on λ_{ijm} values allow us to assume that the exponents λ_{ijm} are the same and equal to one for every orbital. Furthermore, we take the exponent of $[\mu(n_0)/\mu(n)]$ equal to one as we observed that values of this exponent in the range between one and two do not change appreciably the resulting form of (3). Under these approximations the n dependence of (3) is found to fit approximately to a power law and (3) takes the simple form

$$V_{ijm}(r_s, n) = 5.657 \tilde{V}_{ijm}^{(0)} \left(r_s^{(0)} / r_s \right)^{v_{ijm}} n^{-1.25} \quad (4)$$

with respect to the diamond lattice as the reference lattice.

More accurate determination of the SKTB parameters than that obtained by fitting to the free electron bands can be achieved by fitting to an *ab initio* calculated band structure of the element under consideration. Equation (4) indicates that the exponents v_{ijm} can be found by fitting only to the *ab initio* calculated band structure of the element in one reference lattice, and in particular the diamond lattice, at various lattice constants. Then, the SKTB parameters suitable for other types of lattice can be obtained from (4) by replacing the correct value of the number of NNS and lattice parameter r_s .

The approximations made in deriving (4) do not affect the variation of $V_{ss\sigma}$ and $V_{pp\pi}$ (derived by fitting to the free electron bands) as the lattice structure changes. They appear however less satisfactory for the description of $V_{sp\sigma}$ and $V_{pp\sigma}$. On the other hand, we have checked the predictions of (4) with results for Si in various lattice structures that have been obtained by Bratkovsky [13], who used the orthogonal TB-LMTO method. The comparison, shown in figure 1, is very satisfactory.

The above results indicate that scaling forms of the type of (4) are realistic and can ensure a satisfactory transferability. On the other hand, (4) may be not universal: most probably its n dependence may not be satisfactorily described as in the case of Si and, therefore, it has to be determined by fitting to *ab initio* calculations when applied to other systems. It is evident, however, that by separating the contributions that affect the variation of the SKTB parameters to those due to volume changes and to those due to lattice changes one can achieve

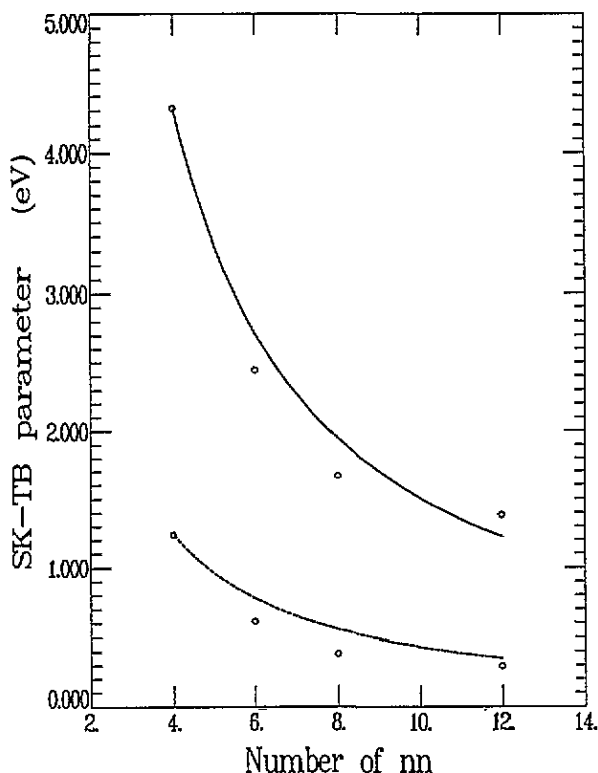


Figure 1. The variation of V_{pps} (solid curve) and V_{ppr} (dashed curve) according to (4) of the text. The results of Bratkovsky [13], shown with open circles, are equated to those of (4) for $n = 4$.

(i) reduction of the computational effort for fitting the variation of the SKTB with both the lattice structure and the volume because volume effects can be now fitted only for one reference lattice structure (i.e. the diamond one) and the lattice effects require knowledge of the SKTB parameters for two or three structures at the equilibrium volume only,

(ii) avoidance of both the scaling of the intrasite SKTB matrix elements with volume and the fitting to total energies and

(iii) use of a simple scaling scheme that ensures transferability, is computationally efficient and is easily incorporated in TB-molecular dynamics simulations.

In concluding, it is worth mentioning that the idea of describing interatomic interactions in terms of number of nearest neighbours appears as a key factor in the determination of the classical interatomic potential of Tersoff [14], who discusses the physical reasoning for such an approach. The so obtained classical interatomic potential exhibits the required simplicity we are looking for in the present work, which allows it to be extensively used in both Monte Carlo and molecular dynamics simulations.

We thank Dr Alexis Bratkovsky for providing us with his TB-LMTO results. The present work was partly supported by the grant ECUS-007-9825 of the European Communities.

References

- [1] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
- [2] Ren S Y, Dow J D and Wolford D J 1982 *Phys. Rev. B* **22** 7661
- [3] Priester C, Allan G and Lannoo M 1988 *Phys. Rev. B* **37** 8519
- [4] Menon M and Allen R E 1988 *Phys. Rev. B* **38** 6196; 1991 *Phys. Rev. B* **44** 11293
- [5] Sigalas M M and Papaconstantopoulos D A 1994 *Phys. Rev. B* **49** 1574
- [6] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco: Freeman)
- [7] Froyen S and Harrison W A 1979 *Phys. Rev. B* **20** 2420
- [8] Lathiotakis N and Andriotis A N 1993 *Solid State Commun.* **87** 871
- [9] Brey L, Tejedor C and Verges J A 1984 *Phys. Rev. B* **29** 6840
- [10] Brey L and Tejedor C 1987 *Phys. Rev. Lett.* **59** 1022
- [11] Tserbak C, Polatoglou H M and Theodorou G 1993 *Phys. Rev. B* **47**
- [12] Cohen R E, Mehl M J and Papaconstantopoulos D A 1994 *Phys. Rev.* at press
- [13] Bratkovsky A M private communication
- [14] Tersoff J 1988 *Phys. Rev. B* **37** 6991