

A fast real-space method for determining tight-binding linear muffin-tin orbital two-centre integrals

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

1992 J. Phys.: Condens. Matter 4 5391

(<http://iopscience.iop.org/0953-8984/4/24/008>)

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

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:07

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

A fast real-space method for determining tight-binding linear muffin-tin orbital two-centre integrals

J Kollár and B Ujfalussy

Central Research Institute for Physics, H-1525 Budapest, PO Box 49, Hungary

Received 21 October 1991, in final form 9 February 1992

Abstract. We derive an equation for the direct real space determination of approximate two-centre integrals in the tight-binding LMTO method. The method allows us to define explicitly the most localized screened structure constants for different crystal structures. Examples are given for SC, FCC, BCC and diamond structures and for silicon.

In the last decade the linear methods of band theory, especially the LMTO method [1], has become one of the most frequently used techniques in electronic structure calculations. One of the most important steps in the evolution of the method was the development of the so called tight-binding (TB LMTO) theory [2]. It has been successfully applied to several problems such as the calculation of the electronic states in substitutionally random alloys [3].

An important and one of the most time-consuming steps in such a band-structure calculation is the determination of the structure constant matrix. Recently this has usually been made using standard real-space techniques to generate the screened structure constant matrix (\bar{S}) by inverting the positive definite matrix $\alpha - \bar{S}$ (α stands for the screening matrix, and, in this paper, for technical reasons, we use a 'bar' to denote the unscreened structure constants), or by iterating the Dyson equation. The main purpose of this paper is to provide a simple and efficient way to calculate real-space tight-binding LMTO structure constants within the framework of the two-centre approximation, and to carry out fine tuning of the screening parameters. While in the traditional methods the sizes of the matrices to be inverted are determined by the number of atoms considered (and, of course, by the number of orbitals), in our case the matrix dimensions are determined by the number of shells used in the calculation.

In the TB LMTO method the bare (\bar{S}) and screened (S) structure constants are connected by the Dyson equation [4]

$$S(\mathbf{R}) = \bar{S}(\mathbf{R}) + \sum_{\mathbf{R}'} \bar{S}(\mathbf{R} - \mathbf{R}') \alpha S(\mathbf{R}'). \quad (1)$$

The bare structure constants and the corresponding two-centre integrals are defined, for example, in [5] or [4]. The quantities appearing in the above equation are matrices in the (L, L') indices, where L denotes the (l, i) angular momentum quantum numbers. We have assumed that the screening matrix α is site independent and diagonal in (L, L') :

$$\alpha_{L, L'} = \alpha_L \delta_{L, L'}.$$

Table 1. Two-centre integrals for the SC, FCC and BCC lattices. Results are obtained by solving equation (12) for six shells for the optimized localization parameters.

<i>I</i>	SC			BCC			FCC		
	Shell 1	Shell 2	Shell 3	Shell 1	Shell 2	Shell 3	Shell 1	Shell 2	Shell 3
	$\alpha_s = 0.372\ 117$			$\alpha_s = 0.336\ 008$			$\alpha_s = 0.296\ 067$		
	$\alpha_p = 0.075\ 298$			$\alpha_p = 0.047\ 311$			$\alpha_p = 0.030\ 007$		
	$\alpha_d = 0.019\ 453$			$\alpha_d = 0.008\ 179$			$\alpha_d = 0.003\ 169$		
<i>ss</i>	-1.131	-0.064	-0.008	-0.568	-0.208	0.000	-0.446	-0.038	0.000
<i>sp</i>	2.226	0.081	0.011	1.143	0.447	0.000	0.924	0.091	-0.001
<i>pp</i>	4.417	0.125	0.030	2.320	0.965	-0.001	1.952	0.204	0.000
<i>pp</i>	-0.864	-0.091	-0.023	-0.373	-0.064	-0.001	-0.342	0.002	-0.001
<i>sd</i>	-2.512	-0.024	-0.014	-1.364	-0.609	0.000	-1.083	-0.140	0.002
<i>pd</i>	-5.248	-0.092	-0.057	-2.855	-1.309	0.000	-2.388	-0.298	0.001
<i>pd</i>	1.720	0.121	0.028	0.842	0.163	0.001	0.744	-0.001	0.002
<i>dd</i>	-7.061	-0.207	-0.115	-3.788	-1.762	-0.001	-3.203	-0.387	-0.002
<i>dd</i>	3.572	0.125	0.027	1.900	0.422	0.001	1.642	0.015	0.003
<i>dd</i>	-0.547	-0.054	-0.016	-0.205	-0.028	0.000	-0.205	-0.003	0.000

Since the on-site elements of the bare structure constant matrix vanish, the on-site elements of the screened structure constants are determined by the equation

$$S(0) = \sum_{R' \neq 0} \bar{S}(-R') \alpha S(R'). \quad (2)$$

Now let us write the Slater-Koster [6] relations which connect the structure constant matrix to the two-centre integrals in the form

$$S_{l',i}^{i',i}(\mathbf{R}) = \sum_{\mu=0}^{\min(l',l)} \bar{z}_{l',l,\mu}^{i',i}(\hat{\mathbf{R}}) I_{l',l,\mu}(|\mathbf{R}|). \quad (3)$$

Here $I_{ss\sigma}, I_{sp\sigma}, \dots$ are the two-centre overlap integrals, while the values of the matrix \bar{z} can be easily derived from table 1 of the paper by Slater and Koster [6]. Using the relation

$$\sum_{i',i} \bar{z}_{l',l,\mu}^{i',i} \bar{z}_{l',l,\mu'}^{i',i} = \beta(\mu)^{-1} \delta_{\mu,\mu'} \quad (4)$$

equation (3) can be inverted in the following way:

$$I_{l',l,\mu}(|\mathbf{R}|) = \beta(\mu) \sum_{i'=1}^{2l'+1} \sum_{i=1}^{2l+1} \bar{z}_{l',l,\mu}^{i',i}(\hat{\mathbf{R}}) S_{l',i}^{i',i}(\mathbf{R}). \quad (5)$$

Here $\beta(\mu)^{-1} = 1$ for $\mu = \sigma$ and 2 for $\mu = \pi, \delta$. We call attention to the fact that the above equation can also serve as a definition of the effective two-centre integrals for the general case without using the two-centre approximation. This relation allows us to derive a system of inhomogeneous linear equations directly for the two-centre integrals from the Dyson equation (1). For a system having some kind of point-group symmetry, where the different sites are arranged in shells around the origin, this

reformulation of the Dyson equation allows us to reduce the number of variables drastically and serves as a very effective tool for the real-space determination of the TB LMTO structure constants within the framework of the two-centre approximation. Let us denote the atomic positions in the n th shell by R_n and their distance from the origin by R_n . Using the relations for the on-site elements (2) after some manipulation we get

$$I_{l',l,\mu}(n) = \bar{I}_{l',l,\mu}(R_n) + \beta(\mu) \sum_{n' \neq 0} \sum_{l''}^{\min(l',l)} \sum_{\mu''=0} \alpha_{l''} \bar{Z}_{l',l,\mu}^{l'',\mu''}(n, n') I_{l'',l,\mu''}(n') \quad (6)$$

where

$$\bar{Z}_{l',l,\mu}^{l'',\mu''}(n, n') = \sum_{R_n} \sum_{i, i', i''} \bar{z}_{l',l,\mu}^{i',i}(R_n) \bar{S}_{l',l,\mu}^{i',i''}(R_n, R_{n'}) \bar{z}_{l'',l,\mu''}^{i'',i}(R_{n'}). \quad (7)$$

In equation (7) the matrix $\bar{S}(R_n, R_{n'})$ is defined in terms of the bare structure constant matrix by the expression

$$\bar{S}(R_n, R_{n'}) = \bar{S}(R_n - R_{n'}) + \bar{S}(R_n) \alpha \bar{S}(-R_{n'}). \quad (8)$$

In order to show that the right-hand side of equation (7) does not depend on the position vector R_n but does depend on the shell index n , let us define

$$U_{l',l,l'',\mu,\mu''}^{i,i'}(R_n) \delta_{\mu',\mu''} = \sum_{i''} \bar{z}_{l',l,\mu}^{i',i''}(-R_n) \bar{z}_{l'',l,\mu''}^{i'',i}(R_n) \quad (9)$$

and

$$V_{l',l',l'',\mu,\mu''}^{\mu',\mu''}(R_n, R_{n'}) = \sum_{i, i', i''} \bar{z}_{l',l,\mu}^{i',i}(R_n) \bar{z}_{l',l'',\mu'}^{i',i''}(R_n - R_{n'}) \bar{z}_{l'',l,\mu''}^{i'',i}(R_{n'}) \quad (10)$$

$$W_{l',l',l'',l''',\mu,\mu''}^{\mu',\mu''}(R_n, R_{n'}) = (-1)^{l+l'} \sum_{i, i''} U_{l',l''',l',\mu}^{i,i''}(R_n) U_{l''',l',l'',\mu''}^{i'',i}(R_{n'}).$$

In terms of these quantities the matrix \bar{Z} can be written as

$$\bar{Z}_{l',l,\mu}^{l'',\mu''}(n, n') = \sum_{R_n} \sum_{\mu'} \bar{I}_{l',l'',\mu'}(|R_n - R_{n'}|) V_{l',l',l'',\mu,\mu''}^{\mu',\mu''}(R_n, R_{n'}) + \sum_{R_n} \sum_{l'''} \bar{I}_{l',l''',\mu}(R_n) \alpha_{l'''} \bar{I}_{l''',l'',\mu''}(R_{n'}) W_{l',l',l'',l''',\mu,\mu''}^{\mu',\mu''}(R_n, R_{n'}). \quad (11)$$

It is easy to show that the matrices V and W have the following symmetry properties:

$$V(\tau R_n, \tau R_{n'}) = V(R_n, R_{n'})$$

and

$$W(\tau R_n, \tau R_{n'}) = W(R_n, R_{n'})$$

where \mathbf{T} is some symmetry operation of the lattice. Now the lattice vectors in the n th shell can be written as $\mathbf{R}_n = \mathbf{T}\mathbf{R}_n^0$, while in the n' th shell $\mathbf{R}_{n'} = \mathbf{T}'\mathbf{R}_{n'}^0$. Using this notation the summation over $\mathbf{R}_{n'}$ (or \mathbf{T}') in equation (11) can be rewritten as a summation over $\mathbf{T}'' = \mathbf{T}^{-1}\mathbf{T}'$ using the relation

$$\mathbf{V}(\mathbf{R}_n, \mathbf{R}_{n'}) = \mathbf{V}(\mathbf{T}\mathbf{R}_n^0, \mathbf{T}'\mathbf{R}_{n'}^0) = \mathbf{V}(\mathbf{R}_n^0, \mathbf{T}''\mathbf{R}_{n'}^0).$$

Furthermore, if we notice that $|\mathbf{T}\mathbf{R}_n^0 - \mathbf{T}'\mathbf{R}_{n'}^0| = |\mathbf{R}_n^0 - \mathbf{T}''\mathbf{R}_{n'}^0|$, we can really see that the right-hand side of equation (11) does not depend on \mathbf{T} and takes the same values for all the lattice sites belonging to the n th shell.

By using the above argument we can now give a more precise definition for the shells used in our method, namely that the position vectors of lattice sites belonging to the same shell are connected by the local symmetry transformations of the lattice. For simple lattices this definition coincides with the conventional definition of shells (i.e. sites with equal distances from the origin), but generally it is not true. For example, for diamond structure in the sixth shell (in the conventional sense) there are 24 atoms, but only 12 of them are connected by the tetrahedral symmetry operations \mathbf{T}_d of the diamond lattice and therefore they have to be separated into two different shells.

Finally we can rewrite equation (6) by introducing the abbreviation Λ for the (l', l, μ) indices in the following way:

$$I_\Lambda(n) = \bar{I}_\Lambda(n) + \sum_{n' \neq 0} \sum_{\Lambda'} Z_{\Lambda, \Lambda'}(n, n') I_{\Lambda'}(n'). \quad (12)$$

Here the elements of the matrix \mathbf{Z} can be easily expressed in terms of the elements of the matrix $\bar{\mathbf{Z}}$ by comparing equations (6) and (12). Equation (12) is the main result of our paper. For example, for s, p and d states ($\Lambda = 1, \dots, 10$) the solution of equation (12) means the inversion of a $10N \times 10N$ matrix, where N is the number of shells considered (usually three to five shells are sufficient to ensure the required accuracy). From the derivation of our main equation it is obvious that our method is the most efficient for such α -values where the screened structure constant is localized for a few shells. Based on equation (12) it is possible to define the most localized structure constants explicitly in the following way. Let us define the quantity

$$\Gamma_{n_0}(\alpha_s, \alpha_p, \alpha_d) = \sum_{n=n_0}^{\infty} \sum_{\Lambda} I_\Lambda^2(n). \quad (13)$$

(One could, of course, modify this definition, e.g. by introducing some weighting factors in the n, Λ -summation, which would lead to slightly different results.) In the localized region the n -summation can be truncated after a few shells beyond n_0 . The most localized screening constants can be defined now from the minimum of Γ . This is illustrated in figure 1 where the quantity Γ is plotted around its minimum as a function of α_s, α_p and α_d for the FCC structure. The values of the most localized screening constants obtained in this way and the corresponding two-centre integrals are tabulated in table 1 for cubic, and in table 2 for the diamond structure. We calculated the two-centre integrals with the α -values given in [2] and compared them with those tabulated in table 1 of [2]. We found that even for such a loosely packed structure as SC the deviations are not higher than a few per cent.

One possible field of application of the method is the following. The structure constants of two-centre form obtained by solving (12) may serve as an input for an

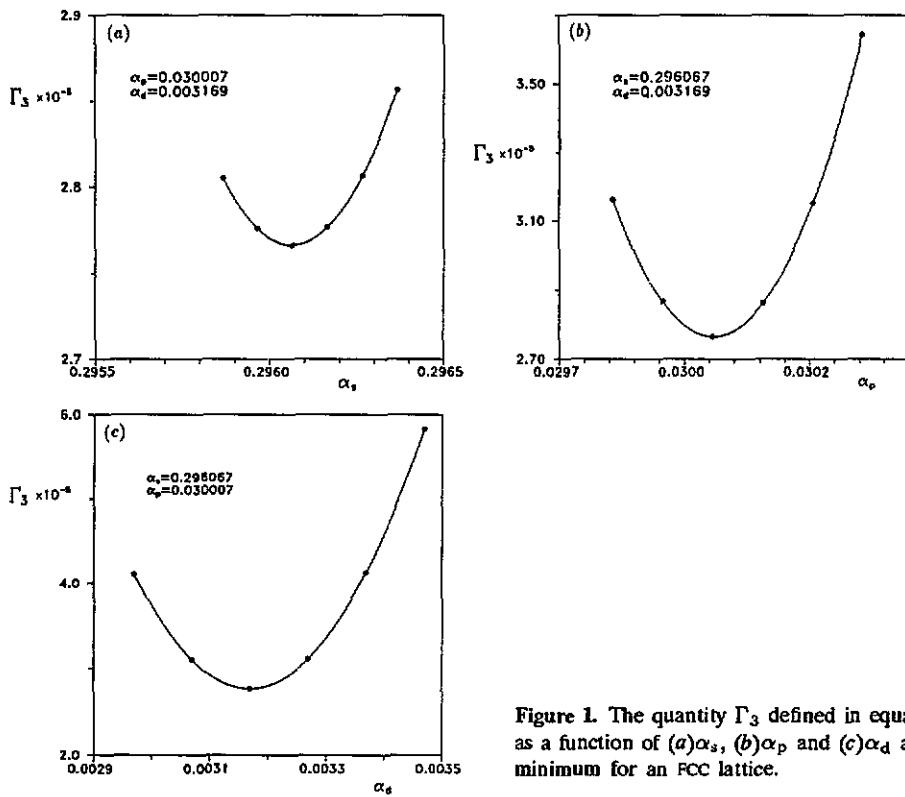


Figure 1. The quantity Γ_3 defined in equation (13) as a function of (a) α_s , (b) α_p and (c) α_d around its minimum for an FCC lattice.

Table 2. Two-centre integrals for the diamond lattice. The results are obtained by solving equation (12) for ten shells for the optimized localization parameters.

Diamond				
	$\alpha_s = 0.346\ 546$			
	$\alpha_p = 0.056\ 125$			
	$\alpha_d = 0.014\ 006$			
<i>I</i>	Shell 1	Shell 2	Shell 3	Shell 4
<i>ssσ</i>	-1.848	-0.120	-0.027	-0.006
<i>spσ</i>	3.904	0.199	0.044	0.009
<i>ppσ</i>	8.554	0.341	0.095	0.016
<i>ppπ</i>	-1.663	-0.085	-0.014	-0.005
<i>sdσ</i>	-4.659	-0.191	-0.052	0.009
<i>pdσ</i>	-11.275	-0.275	-0.116	0.008
<i>pdπ</i>	3.472	0.202	0.014	0.011
<i>ddσ</i>	-17.351	-0.065	-0.178	-0.003
<i>ddπ</i>	7.989	0.482	0.028	0.012
<i>ddδ</i>	-1.601	-0.013	-0.005	-0.001

iterative procedure to solve the original Dyson equation (1) without using the two-centre approximation. Another possibility is to apply a similar procedure for the κ^2 -dependent structure constants using energy-dependent two-centre integrals. This would allow us to investigate the problem of the energy dependence of the most localized screening parameters [7].

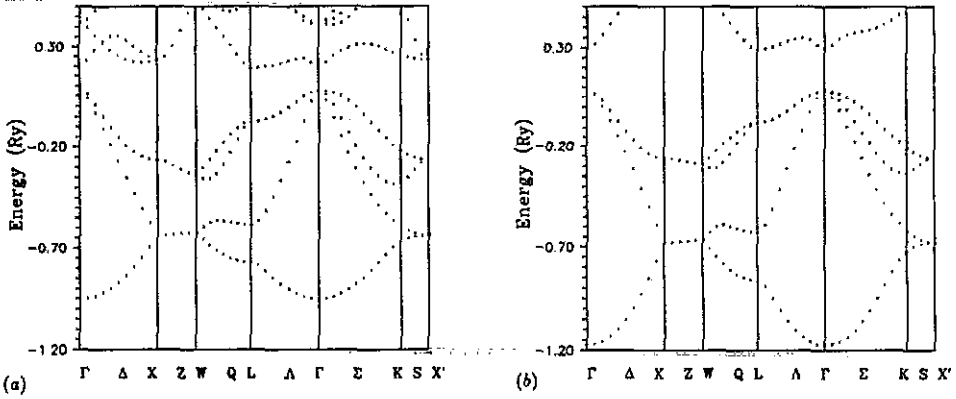


Figure 2. Band structure of silicon using sp screening (a) with two silicon atoms and two empty spheres per unit cell with optimized BCC screening ($\alpha_s = 0.298454$ and $\alpha_p = 0.027172$) and (b) with two silicon atoms per unit cell with optimized diamond screening ($\alpha_s = 0.316251$ and $\alpha_p = 0.036422$).

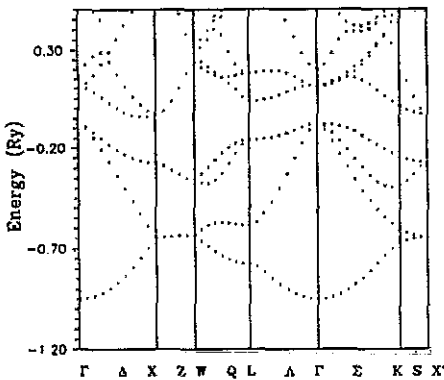


Figure 3. Band structure of silicon with two silicon atoms and two empty spheres per unit cell using the optimized BCC two-centre integrals given in table 1 for spd screening.

Finally, we have tested our method by calculating the band structure of silicon, first using the sp screening shown in figure 2 optimized for the BCC structure (two Si atoms and two empty sites per unit cell in figure 2(a)), and then for optimized diamond screening (two Si atoms per unit cell in figure 2(b)). A comparison of the figures reflects the accuracy of the two-centre approximation for an open structure such as diamond using a minimal basis set. In figure 3 we have plotted the silicon band structure using spd screening optimized for the BCC structure (the screening parameters are given in table 1). The results are in reasonable agreement with those obtained by Christensen [8]. In the calculations we used the potential parameters given by Andersen *et al* [4].

Acknowledgment

This work was supported by the research project OTKA 2950 of the Hungarian National Scientific Research Foundation.

References

- [1] Andersen O K 1975 *Phys. Rev. B* **12** 3060
- [2] Andersen O K and Jepsen O 1984 *Phys. Rev. Lett.* **54** 2571
- [3] Kudrnovský J, Drchal V and Mašek J 1986 *Phys. Rev. B* **35** 2487
- [4] Andersen O K, Jepsen O and Sob M 1987 *Electronic Band Structure and its Applications* ed M Yussouff (Berlin: Springer)
- [5] Andersen O K, Klose W and Nohl H 1978 *Phys. Rev. B* **17** 1209
- [6] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
- [7] Andersen O K, Postnikov A V and Savrasov S Yu 1992 *The Muffin-Tin-Orbital Point of View* preprint
- [8] Christensen N E 1985 *Phys. Rev. B* **32** 6490