

Parametrisation of the LCAO Bandstructure of BCC Transition Metals

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Abstract

In this paper we present a direct parameter fitting scheme appropriate to a linear combination of atomic orbitals (LCAO) model Hamiltonian representation of the BCC transition metals incorporating first and second neighbour interactions. Explicit expressions are given for the one-electron eigenvalues at all of the important symmetry points of the BCC Brillouin zone. This direct parameter fitting scheme is shown to produce an excellent representation of the bandstructure of paramagnetic iron, and yields parameter values little different from those obtained from a full least-squares optimisation of the LCAO model Hamiltonian bandstructure. The extension of this scheme to include more distant interactions, and relativistic and spin-orbit effects, is also discussed.

1. Introduction

The electronic structure of transition metals can now be determined very accurately by a variety of first-principles techniques (Koelling 1981). Such methods, however, are not really suitable for evaluating quantities such as Compton profiles or dielectric constants, which involve integration over the entire Brillouin zone. For such purposes one needs a fast and accurate interpolation scheme. For transition metals this is provided by a purely tight-binding (LCAO) model Hamiltonian (Cornwell *et al.* 1968; Dempsey *et al.* 1978; Boyer *et al.* 1977; Anderson *et al.* 1981; Smith 1985), or by a hybrid LCAO-orthogonalised plane wave (OPW) representation (Hodges *et al.* 1966; Mueller 1967; Smith and Mattheiss 1974; Baker and Smith 1977). The essence of these model Hamiltonian interpolation schemes is to represent the various interactions by parameters. These are then determined by fitting to an accurate first-principles bandstructure calculation at selected symmetry points within the irreducible symmetry element of the appropriate Brillouin zone (BZ). Given that the model Hamiltonian contains a sufficient basis it should then reliably interpolate between these chosen wavevectors, and yield accurate eigenvalues for any general k point within the BZ.

Explicit energy level expressions for determining the parameter values within the combined LCAO-OPW model Hamiltonian interpolation scheme have been given for both FCC (Smith and Mattheiss 1974) and BCC (Baker and Smith 1977) transition metals. To the authors' knowledge, however, a sufficiently general direct parameter fitting scheme has only been provided within the LCAO interpolation approach for

the FCC transition metals (Smith 1985). The purpose of the present paper, therefore, is to present such a procedure for the BCC metals. As in the FCC case, these directly fitted parameter values can then be employed as suitable starting values in a least-squares optimisation of the LCAO model Hamiltonian parameter set. Moreover, one can determine the dependence of each of the energy levels upon the individual parameters from the corresponding energy level expressions.

In the following section, we define our tight-binding model Hamiltonian and derive explicit expressions for the various symmetry point energy levels within the irreducible symmetry element of the BCC BZ. Our proposed direct parameter fitting scheme is also outlined in this section. The application of this scheme to the case of paramagnetic BCC iron is then presented in Section 3. The final section summarises the main conclusions to be drawn from this work, and discusses possible generalisations of the overall approach.

2. Basic Method

The minimum basis set that will adequately represent the electronic structure of the BCC transition metals to order 5–10 eV above the Fermi energy consists of one s-orbital, three p-orbitals and five d-orbitals on each atomic site. Since there is only one atom per primitive unit cell, this results in a 9×9 , k -dependent, LCAO model Hamiltonian matrix of the form

$$\begin{bmatrix} H_{ss}(k) & H_{sp}(k) & H_{sd}(k) \\ H_{ps}(k) & H_{pp}(k) & H_{pd}(k) \\ H_{ds}(k) & H_{dp}(k) & H_{dd}(k) \end{bmatrix}$$

Explicit expressions for the Hamiltonian matrix elements $H_{\alpha\alpha}(k)$ in terms of the appropriate energy integrals $E_{ij}(l, m, n)$ were given by Slater and Koster (1954).

In the case of the FCC transition metals it was found necessary to include only the nearest neighbour interactions in order to obtain an accurate representation of the overall electronic structure (Smith 1985). This is not the case, however, for the BCC transition metals, because of their different crystal structure, and one must incorporate second neighbour interactions to produce reliable results. This gives rise to a model Hamiltonian characterised by 27 independent parameters; the four self-energies E_s , E_p , E_d^{ig} and E_d^{cg} , twelve first neighbour interactions $E_{ij}(111)$, and eleven second neighbour interactions of the form $E_{ij}(100)$, $E_{ij}(010)$ and $E_{ij}(001)$. For simplicity of expression these parameters are henceforth referred to as $E_i(1 < i < 4)$, $A_i(1 < i < 12)$ and $B_i(1 < i < 11)$ respectively, and are identified specifically in Table 1 below.

In order to obtain values for these parameters we need to derive explicit expressions for the various energy levels at selected symmetry points of the irreducible symmetry element of the BCC BZ. Since our LCAO basis functions are assumed to be comprised of Löwdin (orthogonalised) atomic orbitals, this simply requires the diagonalisation of the LCAO model Hamiltonian matrix at each chosen wavevector k . The resultant expressions for the energy levels at the Γ , N , P , H , Δ , Σ , G and D symmetry points are as follows:

Γ point, $k = 2\pi/a (0, 0, 0)$:

$$\begin{aligned} E(\Gamma_1) &= E_1 + 8A_1 + 6B_5, \\ E(\Gamma_{25'}) &= E_3 + 8A_9 + 4B_1 + 2B_2, \\ E(\Gamma_{12}) &= E_4 + 8A_{12} + 3B_3 + 3B_4, \\ E(\Gamma_{15}) &= E_2 + 8A_4 + 2B_8 + 4B_9. \end{aligned}$$

N point, $k = 2\pi/a (\frac{1}{2}, \frac{1}{2}, 0)$:

$$\begin{aligned} E(N_2) &= E_3 + 8A_{10} - 2B_2, \\ E(N_1') &= E_2 - 8A_5 - 2B_8, \\ E(N_4) &= E_4 - 3B_3 + A_4, \\ E(N_3) &= E_3 - 8A_{10} - 2B_2, \\ E(N_4') &= E_2 + 2B_8 - 4B_9. \end{aligned}$$

P point, $k = 2\pi/a (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$:

$$\begin{aligned} E(P_3) &= E_4 - 3B_3 - 3B_4, \\ E(P_4) &= \frac{1}{2}[E_2 + E_3 - 4B_1 - 2B_2 - 2B_8 - 4B_9 \\ &\quad \pm \{(E_2 - E_3 + 4B_1 + 2B_2 - 2B_8 - 4B_9)^2 + 256A_7^2\}^{\frac{1}{2}}], \\ E(P_1) &= E_1 - 6B_5. \end{aligned}$$

H point, $k = 2\pi/a (1, 0, 0)$:

$$\begin{aligned} E(H_{12}) &= E_4 - 8A_{12} + 3B_3 + 3B_4, \\ E(H_{25'}) &= E_3 - 8A_9 + 4B_1 + 2B_2, \\ E(H_{15}) &= E_2 - 8A_4 + 2B_8 + 4B_9, \\ E(H_1) &= E_1 - 8A_1 + 6B_5. \end{aligned}$$

Δ point, $k = 2\pi/a (\frac{1}{2}, 0, 0)$:

$$\begin{aligned} E(\Delta_2) &= E_4 + 3B_3 - B_4, \\ E(\Delta_5) &= \frac{1}{2}[E_2 + E_3 + 2B_2 + 2B_8 \\ &\quad \pm \{(E_2 - E_3 - 2B_2 + 2B_8)^2 + 256A_6^2\}^{\frac{1}{2}}], \\ E(\Delta_2) &= E_3 + 4B_1 - 2B_2. \end{aligned}$$

Σ point, $k = 2\pi/a (\frac{1}{4}, \frac{1}{4}, 0)$:

$$\begin{aligned} E(\Sigma_2) &= E_3 + 4A_9 + 4A_{10} + 2B_1, \\ E(\Sigma_3) &= \frac{1}{2}[E_2 + E_3 + 4A_9 - 4A_{10} + 2B_1 + 2B_8 \\ &\quad \pm \{(E_2 - E_3 + 4A_4 - 4A_9 + 4A_{10} - 2B_1 + 2B_8)^2 + 128(A_6 + \frac{1}{2}B_{10})^2\}^{\frac{1}{2}}], \\ E(\Sigma_4) &= \frac{1}{2}[E_2 + E_4 + 4A_4 + 4A_5 + 4A_{12} + 2B_4 + 2B_9 \\ &\quad \pm \{(E_2 - E_4 + 4A_4 + 4A_5 - 4A_{12} - 2B_4 + 2B_9)^2 + 128(A_8 + \frac{1}{4}\sqrt{3}B_{11})^2\}^{\frac{1}{2}}]. \end{aligned}$$

G point, $k = 2\pi/a (\frac{3}{4}, \frac{1}{4}, 0)$:

$$E(G_4) = \frac{1}{2}[E_2 + E_4 - 4A_4 - 4A_5 - 4A_{12} + 2B_4 + 2B_9 \\ \pm \{(E_2 - E_4 - 4A_4 - 4A_5 + 4A_{12} - 2B_4 + 2B_9)^2 + 128(A_8 - \frac{1}{4}\sqrt{3} B_{11})^2\}^{\frac{1}{2}}],$$

$$E(G_3) = \frac{1}{2}[E_2 + E_3 - 4A_4 - 4A_9 + 4A_{10} + 2B_1 + 2B_8 \\ \pm \{(E_2 - E_3 - 4A_4 + 4A_9 - 4A_{10} - 2B_1 + 2B_8)^2 + 128(A_6 - \frac{1}{2} B_{10})^2\}^{\frac{1}{2}}],$$

$$E(G_2) = E_3 - 4A_9 - 4A_{10} + 2B_1.$$

D point, $k = 2\pi/a (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$:

$$E(D_2) = E_4 - 3B_3 - B_4,$$

$$E(D_3) = \frac{1}{2}[E_2 + E_3 - 4\sqrt{2} A_5 - 4\sqrt{2} A_{10} - 2B_1 - 2B_2 - 2B_8 - 2B_9 \\ \pm \{(E_2 - E_3 - 4\sqrt{2} A_5 + 4\sqrt{2} A_{10} + 2B_1 + 2B_2 - 2B_8 - 2B_9)^2 \\ + 128(A_7 - B_{10}/2\sqrt{2})^2\}^{\frac{1}{2}}],$$

$$E(D_4) = \frac{1}{2}[E_2 + E_3 + 4\sqrt{2} A_5 + 4\sqrt{2} A_{10} - 2B_1 - 2B_2 - 2B_8 - 2B_9 \\ \pm \{(E_2 - E_3 + 4\sqrt{2} A_5 - 4\sqrt{2} A_{10} + 2B_1 + 2B_2 - 2B_8 - 2B_9)^2 \\ + 128(A_7 + B_{10}/2\sqrt{2})^2\}^{\frac{1}{2}}].$$

By fitting these expressions to the corresponding eigen-energies of an accurate first-principles bandstructure calculation we can now determine specific values for the LCAO model Hamiltonian parameters. Whilst there is some arbitrariness in the choice of energy levels to employ in this direct parameter fitting scheme, the resulting parameter values are nonetheless fairly well prescribed. In order to determine the d self-energies, and the d-d energy integrals, for example, we have chosen to fit to the $\Gamma_{25'}$, Γ_{12} , $H_{25'}$, H_{12} , N_2 , N_3 , N_4 , Δ_2 and Δ_2' energy levels, although the Σ_2 , G_2 , P_3 and D_2 levels would serve equally well. The resulting parameter values are, in fact, little different. Similarly, to determine the x - xy parameters, A_6 and B_{10} , we have elected to use the $\Sigma_3^{(1)}$ and $G_3^{(1)}$ energy level expressions, rather than the $\Delta_5^{(1)}$ level, as this choice seems to give a better overall fit to all three levels. Determining values for the parameters via the remaining energy level expressions, however, is more or less unique. Values for the s self-energy and the s-s energy integrals, A_1 and B_5 , are derived from the Γ_1 , H_1 and P_1 energy level expressions. The p self-energy and the p-p interaction parameters A_4 , A_5 , B_8 and B_9 are determined from the Γ_{15} , H_{15} , N_1 , and N_4' levels, and the sum of the $P_4^{(1)}$ and $P_4^{(2)}$ energy levels. Finally, the p-d parameters A_7 , A_8 and B_{11} are calculated from $P_4^{(1)}$, $\Sigma_4^{(1)}$ and $G_4^{(1)}$.

This leaves just the five parameters A_2 , A_3 , A_{11} , B_6 and B_7 to be determined. None of these particular parameters appears explicitly in any of the above energy level expressions, and hence must be determined independently. The parameter A_{11} can be calculated from the derived values for the other d-d energy integrals using the two-centre approximation:

$$A_{11} = 2\sqrt{\frac{1}{3}}(A_9 - A_{10} - A_{12}).$$

The s-d parameters A_3 and B_7 can be determined most readily by fitting to the $N_1^{(1)}$

and $N_1^{(2)}$ energy levels. These are defined by the 3×3 determinantal equation

$$\det \begin{vmatrix} E_1 - 2B_5 - \lambda & -8A_3 & 4B_7 \\ -8A_3 & E_3 - 4B_1 + 2B_2 - \lambda & -8A_{11} \\ 4B_7 & -8A_{11} & E_4 + B_3 - 3B_4 - \lambda \end{vmatrix} = 0.$$

For the two remaining parameters, the s-p Hamiltonian matrix elements A_2 and B_6 , we fit the $\Delta_1^{(1)}$ and $A_1^{(1)}$ energy levels. These are given by the smallest roots of the determinantal equations

$$\det \begin{vmatrix} E_1 + 2B_5 - \lambda & -8A_2 & -4B_7 \\ -8A_2 & E_2 - 2B_8 + 4B_9 - \lambda & 16A_8/\sqrt{3} \\ -4B_7 & 16A_8/\sqrt{3} & E_4 - B_3 + 3B_4 - \lambda \end{vmatrix} = 0,$$

$$\det \begin{vmatrix} E_1 + 2\sqrt{2}A_1 - \lambda & -2\sqrt{3}(\sqrt{2}C_2 + A_6) & -2\sqrt{6}C_3 \\ -2\sqrt{3}(\sqrt{2}C_2 + A_6) & E_2 + 2\sqrt{2}(A_4 - 2A_5) - \lambda & 2\sqrt{2}(2C_6 + \sqrt{2}A_{10} - C_7) \\ -2\sqrt{6}C_3 & 2\sqrt{2}(2C_6 + \sqrt{2}A_{10} - C_7) & E_3 + 2\sqrt{2}(C_9 - 2C_{10}) - \lambda \end{vmatrix} = 0.$$

It should be noted that, in each case, we have elected to fit to the lowest energy levels, as our primary objective is to obtain a good representation of the occupied (valence) bandstructure.

3. Application to Paramagnetic BCC Iron

We now turn to consider the application of this direct parameter fitting scheme to the case of paramagnetic BCC iron. For our first-principles bandstructure we have chosen the augmented plane wave (APW) calculation of Wood (1962). This well-established bandstructure is known to be in good agreement with other determinations of the electronic structure of paramagnetic iron. Moreover, Wood's paper contains a very comprehensive list of one-electron eigenvalues for incorporation into either a direct parameter fitting or least-squares optimisation routine.

Applying the direct parameter fitting scheme outlined in the previous section to this APW bandstructure of Wood yields the parameter set given in Table 1. The ability of this direct parameter fitting scheme to reproduce Wood's APW bandstructure for paramagnetic iron is shown in Fig. 1. With the exception of the one energy band from N_1 to $\Gamma_{25'}$ via $\Sigma_1^{(2)}$, the reproduction of Wood's valence bandstructure by our LCAO model Hamiltonian with directly fitted parameters is clearly excellent. Levels well above the Fermi energy are not so well reproduced, however, as one would expect.

The accuracy with which our LCAO model Hamiltonian can reproduce the overall electronic structure can, of course, be improved by optimising the parameters using a least-squares fitting routine. In fact, one of the main advantages of our direct parameter fitting scheme is that it provides an excellent set of starting parameters from which to begin such an optimisation procedure. In order to obtain optimum values for our 27 parameters we have performed a least-squares fit to 131 levels at the Γ , A , P , F , H , G , N and Δ symmetry points, and their intermediate k points. The resulting set of optimised parameters is also given in Table 1. Comparison

Table 1. Values (in Ryd) for the 27 parameters defining our LCAO model Hamiltonian obtained from both direct parameter fitting, and least-squares optimisation, of Wood's bandstructure for paramagnetic iron

Symbol	Energy integral	Directly fitted parameters	Optimised parameters
E_1	E_s	1.35450	1.31320
E_2	E_p	1.75775	1.77397
E_3	E_s^{fg}	0.71300	0.68123
E_4	E_d^{fg}	0.68400	0.68327
A_1	$E_{s;s}(111)$	-0.13388	-0.13438
A_2	$E_{s;x}(111)$	0.10151	0.11296
A_3	$E_{s;xy}(111)$	-0.04712	-0.01577
A_4	$E_{x;x}(111)$	0.10344	0.09991
A_5	$E_{x;y}(111)$	0.08141	0.09072
A_6	$E_{x;xy}(111)$	-0.02538	-0.00008
A_7	$E_{x;yz}(111)$	-0.03947	-0.02927
A_8	$E_{x;x^2-y^2}(111)$	0.02520	0.02241
A_9	$E_{xy;xy}(111)$	-0.01313	-0.01235
A_{10}	$E_{xy;xz}(111)$	-0.02075	-0.02149
A_{11}	$E_{xy;3z^2-r^2}(111)$	-0.01638	-0.02010
A_{12}	$E_{3z^2-r^2;3z^2-r^2}(111)$	0.02181	0.02223
B_1	$E_{xy;xy}(100)$	0.00750	0.02033
B_2	$E_{xy;xy}(001)$	0.00100	-0.00813
B_3	$E_{3z^2-r^2;3z^2-r^2}(001)$	-0.03379	-0.03488
B_4	$E_{x^2-y^2;x^2-y^2}(001)$	0.00163	0.00287
B_5	$E_{s;s}(100)$	-0.02925	-0.02476
B_6	$E_{s;x}(100)$	0.08383	0.05143
B_7	$E_{s;3z^2-r^2}(001)$	-0.03440	-0.02299
B_8	$E_{x;x}(100)$	0.17925	0.15845
B_9	$E_{y;y}(100)$	0.03656	0.03297
B_{10}	$E_{x;xy}(010)$	0.00992	0.03248
B_{11}	$E_{z;3z^2-r^2}(001)$	-0.03699	-0.03455

with the parameter values obtained from the direct parameter fitting scheme shows excellent correlation. With the exception of the nearest-neighbour s-d parameter A_3 , the two p-d Hamiltonian matrix elements A_6 and B_{10} , and the second neighbour xy - xy parameters B_1 and B_2 , the optimised parameter values are little different from the directly fitted parameters.

The bandstructure which results from employing these optimised parameter values in our second-neighbour LCAO model Hamiltonian is shown in Fig. 2. The overall agreement with Wood's APW bandstructure is seen to be extremely good, even for energies 10 eV above the Fermi energy. Whilst the most poorly reproduced energy level is A_2 , with an error of 0.037 Ryd, the largest deviation within the valence band is 0.023 Ryd at $N_1^{(1)}$. The average r.m.s. deviation over all of the least-squares fitted levels is only 0.0124 Ryd. This compares well with the accuracy obtained by other LCAO-OPW (Baker and Smith 1977) and LCAO (Cornwell *et al.* 1968) model Hamiltonian calculations on paramagnetic BCC iron.

The curve for the density of spin states obtained from our second neighbour LCAO model Hamiltonian with optimised parameters is shown in Fig. 3. This has been obtained by sampling at 10^6 random k -points within the irreducible symmetry

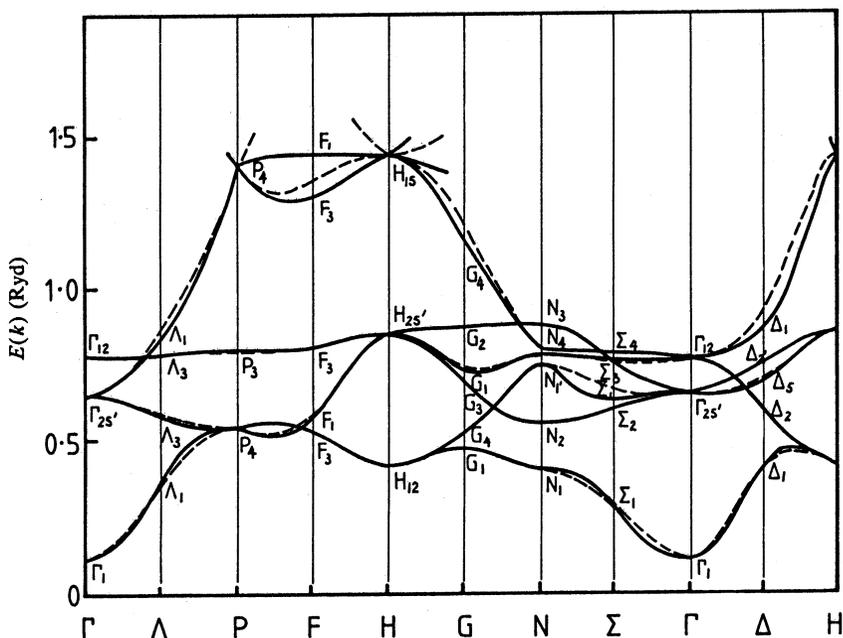


Fig. 1. Comparison between Wood's APW bandstructure for paramagnetic iron (full curve) and that derived from the LCAO model Hamiltonian with directly fitted parameters (dashed curve). It should be noted that the latter has only been plotted when it deviates from the first-principles bandstructure by more than 0.005 Ryd. (1 Ryd = 13.606 eV.)

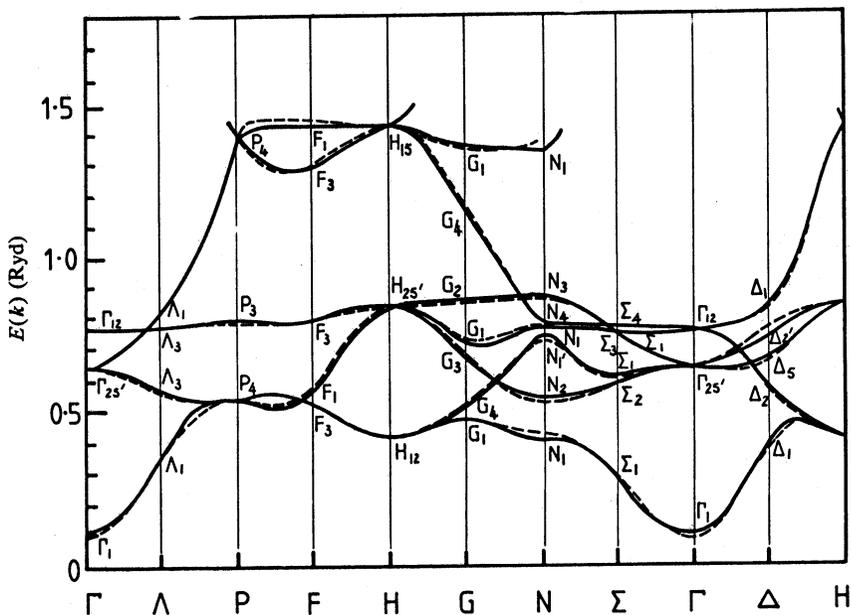


Fig. 2. Comparison of the paramagnetic iron bandstructure of Wood (full curve) with that obtained from the LCAO model Hamiltonian employing least-squares optimised parameters (dashed curve).

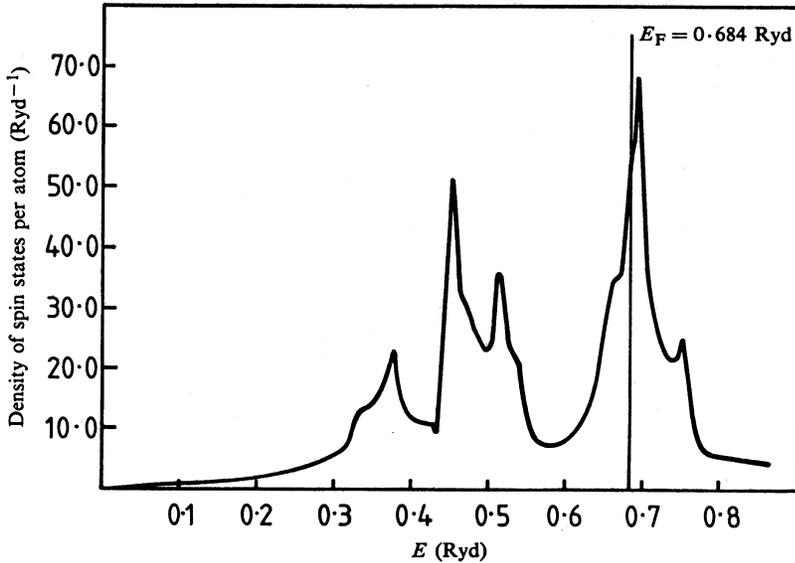


Fig. 3. Density of spin states curve resulting from our second neighbour LCAO model Hamiltonian with optimised parameters.

element of the BCC BZ. Whilst the overall curve is in good agreement with that obtained by Cornwell *et al.* (1968) for paramagnetic BCC iron, our calculated Fermi energy of 0.684 Ryd is more than 0.02 Ryd higher than the values of 0.662 and 0.660 Ryd determined by Wood (1962) and Cornwell *et al.* (1968) respectively. This discrepancy, however, arises almost entirely from the lowering of the Γ_1 energy level by our optimisation procedure and could thus be easily remedied by either assigning this level greater weight, or simply keeping it invariant.

It should be pointed out that in this paper we have optimised the parameters in our LCAO model Hamiltonian so as to give a good representation of Wood's bandstructure up to 10 eV above the Fermi energy. An even more accurate description of the valence band electronic structure could have been achieved by least-squares fitting to just the occupied energy levels. We would expect the parameter values derived from such an optimisation procedure to demonstrate an even closer correlation with the parameters derived from our direct parameter fitting scheme.

4. Discussion and Conclusions

In this paper we have presented a direct parameter fitting scheme appropriate to a LCAO model Hamiltonian representation of the BCC transition metals, incorporating all first and second neighbour interactions. When applied to the case of paramagnetic BCC iron, this direct parameter fitting scheme has been shown to yield an excellent description of the overall electronic structure. Moreover, the parameter values obtained via this direct parameter fitting scheme have been shown to be little different from those derived by least-squares optimisation of the LCAO model Hamiltonian bandstructure. The bandstructures of other BCC metals such as tungsten, tantalum and molybdenum may also be represented by the scheme. The APW calculation of

Petroff and Viswanthan (1971) provides detailed lists of the appropriate energy levels for these metals. It thus follows that the parameter sets obtained from our direct-fitting LCAO model Hamiltonian scheme can provide both an accurate representation of the BCC transition metal bandstructures in their own right, and provide a reliable starting point for further refinement of those bandstructures via a suitable optimisation routine. As stated earlier, a further advantage of such a direct parameter fitting scheme is that it enables one to determine the actual dependence of any particular energy level upon the various LCAO parameters from the explicit energy expressions.

The scheme that we have presented here could presumably be extended to incorporate more distant interactions if greater accuracy were required. Cornwell *et al.* (1968) and Boyer *et al.* (1977), for example, have both included four additional parameters in their LCAO model Hamiltonian descriptions of the BCC transition metals in order to represent the third neighbour s-s, s-p and s-d interactions. In more recent work, Papaconstantopoulos and his co-workers (Anderson *et al.* 1981; Johnson *et al.* 1984) have incorporated all 17 third neighbour interactions into their least-squares optimisation procedure in order to obtain extremely accurate bandstructure fits for some of the BCC transition metals. The extension of our direct-parameter fitting scheme to progressively larger parameter sets, however, will always be bounded by the number of linearly independent energy level expressions that can be obtained from diagonalisation of the LCAO model Hamiltonian.

Finally, it is worth noting that our direct-fitting LCAO model Hamiltonian scheme can also be used to describe relativistic and spin-dependent features in the bandstructures of the BCC transition metals. Neglect of the spin-orbit interactions, as assumed in recent calculations of the bandstructure of ferromagnetic iron (Tawil and Callaway 1973; Johnson *et al.* 1984), leads to two separate sets of spin-up and spin-down energy bands. These two completely independent sets of bands can then each be described, as in the paramagnetic case, by a 9×9 LCAO model Hamiltonian, and the parameters defining these tight-binding representations determined by our direct parameter fitting set. The extension of this scheme to take into account the spin-orbit interactions, however, would be much more difficult. In order to satisfactorily describe the role of the spin-orbit interactions in the BCC transition metals we would now need to diagonalise an 18×18 complex Hermitian LCAO model Hamiltonian (Abate and Asdente 1965). While this is still feasible with the introduction of suitable group theoretical techniques (Friedel *et al.* 1964), the resulting energy level expressions would be considerably more complicated than we have obtained above for the paramagnetic case, as a result of the coupling of the electron spins.

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