

Band Structure Calculations for the Heavy Transition Metals: Parametrisation Methods, Band Structures and Problems with Iteration Techniques*

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Abstract

This paper discusses a parametrisation method developed by the author as a technique for the determination of band structures for the 4d transition metals and their compounds. It is suggested that some of the earlier work that has been published may not have found all the roots. Re-examination of the earlier work of the author reveals systematic discrepancies from benchmark band structure calculations. It is suggested that these results are an example of the unreliability of the earlier parametric band structure calculations, in which iteration techniques were used to determine the roots. Examples presented exhibit well known repeller behaviour, and so provide an early example where variation of initial conditions could have led to the discovery of bifurcation behaviour associated with the onset of chaos. The paper concludes with an application of the method to the calculation of electron-phonon interaction elements in the nonrelativistic limit.

1. Introduction

This paper is dedicated to Geoff Fletcher, who with Rod Millar helped me to test a generalisation of John Hubbard's parametric approach for calculating the band structures of the 3d transition metals (Hubbard and Dalton 1968; Hubbard 1969) to include relativistic effects, so that the 4d and 4f metals and their alloys could be studied. The theoretical derivation is to be found in Osborne (1970). Geoff was calculating the band structure of Au, using the augmented plane wave (APW) method, and the method of Osborne (1970) was applied to Au as a check of the method. Geoff was fortunate to have as his assistant Rod Millar, who programmed my method. The work was not published because we seemed to miss some of the eigenvalues. This paper addresses the probable reason for the discrepancies. Geoff has always been interested in interacting with the experimentalists in the Physics Department, and he performed a number of band structure calculations for them. Such interactions now are rare in the department.

The calculation of the band structures of the transition metals and the rare earths goes back to the early 1940s. One of the more popular approaches is the APW method, first introduced by Slater (1937). Ziman (1965) discussed how this method could be expressed as a generalised pseudo-potential, and found that

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by exploiting this scattering potential it was possible to partition the scattering matrix to show physically, for the transition metals, how the s and d electrons interact. Lloyd (1965) extended this work, showing clearly the physical basis for the orthogonal plane wave (OPW), Kohn–Korringa–Rostaker (KKR) and APW methods. The method involves the folding of the KKR determinant into a structure which shows s–s, s–d and d–d electron interactions.

In the relativistic limit [i.e. the generalisation of Hubbard and Dalton (1968) and Hubbard (1969)] the folding yields the following determinant:

$$\begin{vmatrix} (\mathbf{K}_P + \mathbf{V}_P)(\epsilon_c) - E\mathbf{I} & \mathbf{h}_{P\kappa_1} & \mathbf{h}_{P\kappa_2} \\ \mathbf{h}_{P\kappa_1}^* & \mathbf{A}_{\kappa_1\kappa_1}^{(\epsilon_1)} - E\mathbf{I} & \mathbf{A}_{\kappa_1\kappa_2}^{(\epsilon_1)} \\ \mathbf{h}_{P\kappa_2}^* & \mathbf{A}_{\kappa_2\kappa_1}^{(\epsilon_1)} & \mathbf{A}_{\kappa_2\kappa_2}^{(\epsilon_1)} - E\mathbf{I} \end{vmatrix} = 0. \quad (1)$$

The conduction band terms are given by

$$\begin{aligned} (\mathbf{K}_P + \mathbf{V}_P)_{gg'}^{ss'}(\epsilon_c) &= (\mathbf{k} + \mathbf{g})^2 \delta_{gg'} \delta_{ss'} \\ &\quad - \frac{(4\pi)^2}{\tau} \sum_{\kappa\mu} \{ C(l\frac{1}{2}j, \mu - s, s) C(l\frac{1}{2}j, \mu - s', s') \\ &\quad \times Y_{l,\mu-s}^*(\mathbf{g} + \mathbf{k}) Y_{l,\mu-s'}(\mathbf{g}' + \mathbf{k}) \\ &\quad \times j_l(|\mathbf{g} + \mathbf{k}|R_l) j_l(|\mathbf{g}' + \mathbf{k}|R_l) \gamma_{\kappa'} \}. \end{aligned} \quad (2)$$

The part of the determinant $\mathbf{K} + \mathbf{V}$ that refers to the s–p states is evaluated at the energy $(\mathbf{K} + \mathbf{V})_{00}^{ss'} = \epsilon_c$, which is a mean conduction-band energy. In (2), \mathbf{g} refers to a lattice vector, $\kappa = l$ if $\kappa > 0$ and $\kappa = -l - 1$, if $\kappa < 0$. Further, μ refers to the z component of the angular momentum of the electron, $C(lj, \mu - s, s)$ is a Clebsch–Gordan coefficient, $Y_{lm}(\mathbf{g})$ a spherical Bessel function, p the relativistic momentum of the electron, τ the volume of the lattice's atomic cell, and s is the spin of an individual electron. The hybridisation matrix elements are

$$\begin{aligned} [h_{P\kappa_n^s}]_{g\mu} &= -4\pi(\Gamma_{\kappa_n}/\tau)^{\frac{1}{2}} j_{l_n}(|\mathbf{g} + \mathbf{k}|R_{l_n}) C(l_n\frac{1}{2}j_n, -\mu - s, s) \\ &\quad \times Y_{l_n,\mu-s}(\mathbf{g} + \mathbf{k}). \end{aligned} \quad (3)$$

Here it has been assumed that there is a discrete set of κ values which have a resonance in γ_κ at p values $p_{0\kappa_n}^2$ and that the resonances have widths Γ_{κ_n} . The parameters Γ and $p_{0\kappa}$ are obtainable from the generalised phase shift, which is defined as

$$\gamma_\kappa = R_S^2 p [\mathcal{L}_\kappa(R_S) - (\kappa + 1)/R_S - j'_l(pR_S)/j_l(pR_S)]. \quad (4)$$

Here $\mathcal{L}_\kappa(R_S)$ is the ratio of the large and small component of the Dirac equation with a muffin-tin potential radius R_S . For the d and f states, the γ_κ have the resonant contribution subtracted according to

$$\gamma_\kappa = \gamma_{\kappa'} - \delta_{\kappa\kappa_n} \Gamma_{\kappa_n} / (p_{0\kappa_n}^2 - p^2). \quad (5)$$

The $p_{0\kappa}$ denotes the momentum value for which the γ_κ exhibits a resonance. The d-d (f-f) interaction matrix elements are:

$$\begin{aligned} (A_{\kappa_i\kappa_j})_{\mu\mu'}(p^2) &= p_{0\kappa_n}^2 \delta_{\mu\mu'} \delta_{\kappa_i\kappa_j} - \sum_{sg} \frac{(4\pi)^2}{\tau} \sqrt{\Gamma_{\kappa_i} \Gamma_{\kappa_j}} \\ &\times \{j_{l_n}^2(|\mathbf{g} + \mathbf{k}|R_{l_n}) [(\mathbf{k} + \mathbf{g})^2 - p^2]^{-1} C(l_n \tfrac{1}{2}j_n, \mu - s, s) \\ &\times C(l_n \tfrac{1}{2}j_n, \mu' - s, s) Y_{l_n, \mu-s}^*(\mathbf{g} + \mathbf{k}) Y_{l_n, \mu+s}(\mathbf{g} + \mathbf{k})\}. \end{aligned} \quad (6)$$

In the next section we discuss the performance of the formal equations for 3d and 4d transition metals.

2. Results for Cu, Au and Pd, and Comments

Rod Millar programmed the equations in the period 1972–3. While preparing for this talk, I found the old print-outs, in his unique handwriting. In the table below, I present some of the results. We chose six preferential vectors (000,111,111,020,111,111) and summed the angular momentum terms up to $L = 6$. This was done scientifically, of course, i.e. it gave us the closest results to the reported energy levels for metals. These included Burdick's (1963) Cu data, and Shaiwatna's (1960) and Christensen's (1970) Au results. Tables 1 to 3 show the agreement between the two methods for determining the energy levels. Table 1 gives some results for some of the Cu levels: of the 36 levels calculated, the differences show an r.m.s. error of 0.0068 Ry, with three levels having an error >0.01 Ry, and one with error >0.015 Ry, the maximum error being 0.016 Ry. This compares favourably with the original Hubbard calculations. Tables 2 and 3 show the results for Au, as calculated by Geoff's ex-student Shaiwatna and by Christiansen, and the calculations using the parametrisation method. Table 2 presents the results of Shaiwatna. Of the 36 levels calculated, the differences show an r.m.s. error of 0.0115 Ry, with eight errors lying between 0.01 and 0.015 Ry, four errors >0.015 Ry, and a maximum error of 0.033 Ry. Table 3 presents a comparison of the results for Au, as calculated by Christensen, and the calculations using the parametrisation method. Of the 36 levels calculated, the differences yield an r.m.s. error of 0.020 Ry, with three errors lying between 0.01 and 0.015 Ry, 25 errors >0.015 Ry, and a maximum error of 0.045 Ry.

The results summarised here show that the program produces results in reasonable agreement with other calculations. In determining these roots, Millar had implemented matrix diagonalisation routines which we felt at the time would be more suitable for calculating the roots of the determinant (1). This was done because we had not had much success with the routines for root-finding of determinants that were then available from the Monash Computer Centre. We had in turn varied the method for finding the mean 'conduction-band energy', $p_{0\kappa}$, and the resonant energies. We found that while we were using the iteration

Table 1. Lowest six calculated levels for four reciprocal lattice directions in Cu
Reference is to Burdick (1963)

	Level	1	2	3	4	5	6
(000)	Burdick	-0.100	0.209	0.299	0.299	0.357	0.357
	Osborne	-0.099	0.296	0.297	0.297	0.358	0.358
	Error	-0.001	0.003	0.002	0.002	-0.001	-0.001
(080)	Burdick	0.163	0.200	0.399	0.412	0.412	0.704
	Osborne	0.1655	0.196	0.405	0.423	0.423	0.710
	Error	-0.0025	0.004	-0.006	-0.011	-0.011	-0.006
(444)	Burdick	0.164	0.297	0.297	0.401	0.401	0.510
	Osborne	0.168	0.296	0.297	0.410	0.410	0.515
	Error	-0.004	0.001	0.000	-0.009	-0.009	-0.005
(660)	Burdick	0.205	0.228	0.327	0.367	0.396	0.906
	Osborne	0.208	0.233	0.333	0.377	0.404	0.912
	Error	-0.003	-0.005	-0.006	-0.010	-0.008	-0.006

Table 2. Lowest six calculated levels for four reciprocal lattice directions in Au I
Reference is to Shaiwatna (1970)

	Level	1	2	3	4	5	6
(000)	Shaiwatna	-0.157	0.101	0.101	0.203	0.275	0.275
	Osborne	-0.147	0.089	0.089	0.181	0.265	0.265
	Error	-0.010	0.012	0.012	0.022	0.010	-0.010
(080)	Shaiwatna	-0.014	0.012	0.308	0.322	0.402	0.638
	Osborne	-0.027	-0.021	0.310	0.329	0.407	0.643
	Error	0.013	0.033	-0.002	-0.007	-0.005	-0.005
(444)	Shaiwatna	-0.008	0.092	0.188	0.308	0.362	0.477
	Osborne	0.017	0.082	0.172	0.313	0.366	0.479
	Error	-0.025	0.010	0.016	-0.005	-0.004	-0.002
(660)	Shaiwatna	0.020	0.060	0.220	0.275	0.350	0.928
	Osborne	0.017	0.055	0.220	0.272	0.345	0.843
	Error	0.003	0.005	0.000	0.003	0.005	-0.015

Table 3. Lowest six calculated levels for four reciprocal lattice directions in Au II
Reference is to Christensen (1969)

	Level	1	2	3	4	5	6
(000)	Christensen	-0.164	0.155	0.115	0.211	0.288	0.288
	Osborne	-0.147	0.079	0.079	0.166	0.258	0.258
	Error	-0.017	0.076	0.036	0.045	0.030	0.030
(080)	Christensen	-0.013	0.015	0.327	0.339	0.418	0.638
	Osborne	-0.034	-0.029	0.321	0.347	0.423	0.647
	Error	0.021	0.044	0.006	-0.008	-0.005	-0.009
(444)	Christensen	-0.010	0.103	0.196	0.324	0.376	0.477
	Osborne	-0.025	0.077	0.163	0.325	0.377	0.482
	Error	0.015	0.026	0.033	-0.001	-0.001	-0.005
(660)	Christensen	0.029	0.071	0.277	0.282	0.358	0.828
	Osborne	0.008	0.055	0.225	0.278	0.345	0.847
	Error	0.021	-0.016	0.050	0.004	0.013	-0.019

methods we could get wild disagreements. These disagreements vanished when we used the diagonalisation techniques. As an example, Table 4 shows the results obtained for Pd, using a potential that was generated following a method described by Loucks (1967); these results are compared with those of Kaga (1971).

Table 4. Lowest six calculated levels for four reciprocal lattice directions in Pd
Reference is to Kaga (1971)

	Level	1	2	3	4	5	6
(000)	Kaga	0.105	0.339	0.339	0.339	0.445	0.445
	Osborne	0.082	0.438	0.438	0.459	0.587	0.589
	Error	0.023	-0.099	-0.099	-0.120	-0.142	-0.144
(080)	Kaga	0.149	0.332	0.525	0.554	0.554	
	Osborne	0.132	0.283	0.535	0.567	0.587	
	Error	0.017	0.049	-0.010	-0.013	-0.033	
(444)	Kaga	0.186	0.332	0.332	<i>0.530</i>	<i>0.530</i>	0.666
	Osborne	0.188	0.368	0.368	0.671	0.690	0.704
	Error	-0.002	-0.036	-0.036	-0.141	-0.160	-0.038
(660)	Kaga	0.202	0.248	<i>0.411</i>	0.466	0.525	
	Osborne	0.2125	0.266	0.454	0.556	0.613	
	Error	-0.010	-0.018	-0.043	-0.090	-0.088	

What is immediately obvious is that for (000) the triply degenerate energy level at 0.339 Ry has been missed. In modern terminology this root was a repeller. Other examples are shown in italics. This results had been seen in the earlier work of Hubbard and Dalton (1968). Dalton and I spent many hours discussing our work whilst we were at Harwell in the late sixties, and Norris spent a large amount of time playing with the adjustable parameters of the theory in his earlier experimentation. Hubbard was keen to use the library routines at Harwell, and a well tried polynomial root-finding routine was the basis of the energy-finding routine. In later work they abandoned this method and introduced a matrix diagonalisation routine to find the eigenvalues. This method was highly successful and the iteration method was no longer used.

Other printouts from our calculations in the early 70s show that when we changed the value of ϵ_c and ϵ_1 were varied by small amounts, the values of the energy levels varied in an irregular manner. This possibly suggests that the iterative procedure was extremely sensitive to initial inputs, and so represented another example where potential chaotic behaviour could have been detected. The net result of this experimentation was that the technique was not pursued and the interest of the author moved to other fields.

3. Electron-Phonon Matrix Elements

With the current interest in high-temperature superconductivity, it is timely to return to the problem of how to calculate electron-phonon matrix elements. Surprisingly, there appears to have been little advance in this area since the early 1970s, although there has been some resurgence with the introduction of vector processors. In this section I report some work which, while developed in 1970, has not been published. My interest was to see if I could calculate this interaction for chromium. The first-principles calculations, which were analysed by Golibersuch

(1967) amongst others, were computationally expensive, and consequently were largely ignored by workers in the field. The use of the parametrised approach to the band structure appeared to offer some hope for the development of a manageable program.

To first order in the electron-phonon interaction, the matrix element describing the scattering of an electron with wavevector \mathbf{k} and band index n , into a state with wavevector \mathbf{k}' , is given by

$$M_{\mathbf{k}'n',kn} = \int dV \Psi_{\mathbf{k}'n'}^*(\mathbf{r}) \sum_j \delta \mathbf{R}_j \cdot \frac{\partial U}{\partial \mathbf{R}_j} \bigg|_{\mathbf{R}_j=\mathbf{R}_{j_0}} \Psi_{kn}(\mathbf{r}). \quad (7)$$

Here \mathbf{R}_{j_0} is the position vector of the j th ion in its equilibrium position, and $\delta \mathbf{R}_j$ is the displacement of the ion from its equilibrium position. The muffin-tin potential $U(\mathbf{R}_j)$ is that for the case where the ions are at the undisplaced positions and the wavefunctions are evaluated at the Fermi level.

On writing the wavefunction in the KKR form, i.e.

$$\Psi_{kn}(\mathbf{r}) = \sum_L C_L(\mathbf{k}) \Psi_{kLn}(\mathbf{r}), \quad (8)$$

we can simplify the matrix element to the form

$$\begin{aligned} M_{\mathbf{k}'n',kn} &= \sum_{jLL'\mu} C_{L'}^*(\mathbf{k}') C_L(\mathbf{k}) (-1)^\mu \delta \mathbf{R}_{j\mu} \\ &\times \int_{\text{sphere}} R_{L'}^*(r) Y_{L'}^*(\mathbf{r}) \nabla_{-\mu} U(r) R_L(r) Y_L(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (9)$$

The wavefunctions have the form

$$\Psi_{kLn}(\mathbf{r}) = R_L(r) Y_L(\mathbf{r}). \quad (10)$$

Here $Y_L(\mathbf{r})$ is a spherical Bessel function, with the radial function $R_L(r)$ satisfying the equation

$$-\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_L}{dr} \right) + \left[\frac{\hbar^2 l(l+1)}{8\pi^2 m r^2} + U(r) \right] R_L(r) = E_F R_L(r). \quad (11)$$

In writing (9) we have expressed a vector general \mathbf{V} in the form

$$\begin{aligned} \mathbf{V} &= v_x \mathbf{i} + v_y \mathbf{j} + v_z \mathbf{k} \\ &= \mathbf{V}_+ + \mathbf{V}_- + v_z \mathbf{k}. \end{aligned} \quad (12)$$

Here $\mathbf{V}_\mu = -(\mu/\sqrt{2})(v_x \mathbf{i} + \mu v_y \mathbf{j})$, with $\mu = \pm 1$.

After some tedious algebra, described in considerable detail in Golibersuch (1967), the integral in equation (11) can be reduced to

$$\begin{aligned}
 \int d\Omega R_L^*(r) Y_{l+1,m}(\Omega) \nabla_\mu R_L(r) Y_{lm}(\Omega) &= \frac{h^2 R_S^2 (-1)^{l+m} A_\mu^+}{8\pi^2 m \sqrt{2(2l+3)(2l+1)}} \\
 &\times \left\{ \frac{8\pi^2 m}{h^2} [U(R_S) - E_F] \right. \\
 &+ \frac{l(l+2)}{R_S^2} - \frac{(l+1)\mathcal{L}_l}{R_S} + \frac{1\mathcal{L}_{l+1}^*}{R_S} \\
 &\left. - \mathcal{L}_{l+1}^* \mathcal{L}_l \right\} R_{L+1}^*(R_S) R_L(R_S), \quad (13)
 \end{aligned}$$

$$\begin{aligned}
 \int d\Omega R_{L-1}^*(r) Y_{l-1,m+\mu}^*(\Omega) \nabla_\mu R_L(r) Y_{lm}(\Omega) &= \frac{h^2 R_S^2 (-1)^{l+m} A_\mu^-}{8\pi^2 m \sqrt{2(2l+1)(2l-1)}} \\
 &\times \left\{ \frac{8\pi^2 m}{h^2} [U(R_S) - E_F] \right. \\
 &+ \frac{(l+1)(l-1)}{R_S^2} - \frac{(l+1)\mathcal{L}_{l-1}^*}{R_S} \\
 &+ \frac{(l-1)\mathcal{L}_l}{R_S} - \mathcal{L}_{l-1}^* \mathcal{L}_l \left. \right\} \\
 &\times R_{L-1}^*(R_S) R_L(R_S). \quad (14)
 \end{aligned}$$

The constants A are given by

$$\begin{aligned}
 A_0^+ &= \sqrt{2(l+m+1)(l-m+1)}, & A_0^- &= \sqrt{2(l-m)(l+m)}, \\
 A_1^+ &= \sqrt{(l+m+1)(l+m+2)}, & A_1^- &= \sqrt{(l-m)(l-m-1)}, \\
 A_{-1}^+ &= \sqrt{(l-m+1)(l-m+2)}, & A_{-1}^- &= \sqrt{(l+m-1)(l+m)}. \quad (15)
 \end{aligned}$$

The coefficients C_L can be calculated using a method described in Hubbard (1969). These coefficients are given by

$$C_L = (4\pi/\sqrt{\tau})i^l \sum_n B_n j_l(k_n r_l) Y_L^*(\mathbf{k}_n). \quad (16)$$

Here the B_n are calculated from the matrix equation

$$\begin{bmatrix} \mathbf{K}_R - E\mathbf{I} & 0 & \mathbf{h}_R \\ 0 & \mathbf{K}_P + \mathbf{V}_P - E\mathbf{I} & \mathbf{h}_P \\ 0 & \mathbf{h}_P^* & (\epsilon_0 - E)\mathbf{I} - \mathbf{h}_R^*(\mathbf{K}_R - E\mathbf{I})^{-1}\mathbf{h}_P \end{bmatrix} \begin{bmatrix} \mathbf{B}_R \\ \mathbf{B}_P \\ \mathbf{a} \end{bmatrix} = \mathbf{0}. \tag{17}$$

The matrix elements are defined as

$$\begin{aligned} K_{nn'} &= k_n^2 \delta_{nn'} , \\ V_{nn'} &= (4\pi/\tau) \sum_l (2l + 1) R_S^2 \gamma_{ll'} j_l(k_n R_S) j_{l'}(k_{n'} R_S) P_l(\cos \theta_{nn'}) , \\ h_{mn} &= -4\pi R_S \sqrt{(\Gamma/\tau)} j_\lambda(k_n R_S) Y_{\lambda m}(k_n) . \end{aligned} \tag{18}$$

The subscripts P and R in (17) refer to the preferred vectors and the rest. By means of an interpolation scheme it is possible to reduce the equation for the B_n to the form

$$\mathbf{M}_1 = \begin{bmatrix} \mathbf{K}_P + \mathbf{V}(\epsilon_0) \frac{\epsilon_0}{\epsilon_0 - \epsilon_1} + \mathbf{V}(\epsilon_1) \frac{\epsilon_1}{\epsilon_0 - \epsilon_1} & \mathbf{h}_P \\ \mathbf{h}_P^* & \mathbf{A}(\epsilon_1) + \epsilon_1 \mathbf{A}'(\epsilon_1) \end{bmatrix}, \tag{19}$$

$$\mathbf{M}_2 = \begin{bmatrix} \mathbf{I} + \frac{\mathbf{V}(\epsilon_0) - \mathbf{V}(\epsilon_1)}{\epsilon_0 - \epsilon_1} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} + \mathbf{A}'(\epsilon_1) \end{bmatrix}. \tag{20}$$

The equations for the B_n are then given by

$$[\mathbf{M}_2^{-\frac{1}{2}} \mathbf{M}_1 \mathbf{M}_2^{\frac{1}{2}} - E\mathbf{I}] \mathbf{M}_2^{\frac{1}{2}} \begin{bmatrix} \mathbf{B}_P \\ \mathbf{a} \end{bmatrix} = \mathbf{0}. \tag{21}$$

$$\mathbf{B}_R = -(\mathbf{K}_R - E\mathbf{I})^{-1} \mathbf{h}_R \mathbf{a}. \tag{22}$$

Equations (13)–(15), (19) and (22) then define the expressions for the evaluation of the matrix elements. These expressions are currently being programmed and results of the work will be reported in a future publication.

4. Conclusion

In this paper I have re-introduced a parametrisation method for the evaluation of the band structure of heavy transition metals, and have shown that it reproduces the energy levels of known band structure calculations to a reasonable accuracy. Further, I have indicated that the use of iteration methods for the determination of these energy levels gave indications of repeller and chaotic behaviour in the system. Finally, I have presented a formal expression for the electron-phonon matrix element.

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