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Real-Space Methods for Interpreting Electron Micrographs in Cross-Grating Orientations. II. Analysis and Semiclassical Approximations

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The two-dimensional version of the KKR eigenvalue equation is analysed in different limiting situations. and reduction due to symmetry is discussed. With the aid of the semiclassical approximation to the Bloch functions, it is shown that simple expressions are obtained for the complex eigenvalues responsible for absorption. A qualitative understanding of some of the basic features of pole patterns results from a consideration of the approximations to both wave functions and dispersion surface.

1. Introduction

The main objective of the following discussion is to bring out the physical content of the formulae for the dispersion surface and the diffracted amplitudes contained in part I (Ozorio de Almeida, 1975). To begin with we analyse limiting regions of the two-dimensional dispersion surface, obtaining results which should remain approximately valid over wider domains, though this has yet to be computationally verified. Subsequently the results of §4 of Berry (1971) are generalized, leading to the semiclassical approximation of the Bloch functions. This in its turn permits one to deduce simple formulae for the imaginary components of the eigenvalues, which hold for all orientations. Finally, in §6, we begin to see how the preceding considerations can be directly applied to the understanding of pole patterns [see *e.g.* Berry, Buxton & Ozorio de Almeida (1973), again referred to as BBOA].

Symbols occurring in part I are not redefined here.

2. Approximations to the KKR eigenvalue equation

(i) *Born approximation*

In the weak scattering limit the assumption is made that the wave function in equation (4.5) of part I can be approximated by a plane wave:

$$\exp(i\mathbf{K}_0 \cdot \mathbf{R}) = \frac{1}{\alpha} \sum_{\mathbf{G}}{}^{-} \frac{\exp(i\mathbf{K}_\mathbf{G} \cdot \mathbf{R})}{S - K_\mathbf{G}^2} \times \int_{\text{mesh}} \mathrm{d}^2R' \bar{U}(R') \exp(-i\mathbf{G} \cdot \mathbf{R}') . \quad (2\text{–}1)$$

The Born approximation demands that all but the $\mathbf{G}=0$ term be neglected, leading to the eigenvalue condition

$$S^{\text{Born}} - K_0^2 = \langle \bar{U}(\mathbf{R}) \rangle . \quad (2.2)$$

This result, which also follows simply from perturbation theory (see Ziman, 1964), is not valid even for weak potentials at a zone boundary. A proof of condition (2.2) directly from the KKR eigenvalue equation is too involved to be included here, but it is worth pointing out that it involves summations to infinite order in angular momentum, thus indicating that use of the full KKR determinant to calculate the dispersion surface is not advisable when $S \gg \langle \bar{U}(\mathbf{R}) \rangle$.

The empty-lattice limit, $\langle \bar{U} \rangle \to 0$ in (2.2), is also satisfied by the APW equation, since a whole row ($\mathbf{G}=0$) of the determinant vanishes.

(ii) *Small-energy limit*

Analysis of the behaviour of phase shifts and structure constants shows that for $|S| \to 0$ the KKR determinant tends to a diagonal form. Except for anomalous cases referred to as *partial wave resonances*, when given phase shifts may tend to infinity, it is also

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found that the zeroth phase shift is dominant, so that

$$1+\mathscr{G}_0'(\mathbf{K}_0,S)\exp(i\eta_l)\sin\eta_l \underset{s\to 0}{\rightarrow} 0\,. \qquad (2.3)$$

To resolve the indeterminacy hidden in (2.3) one makes use of the reciprocal-lattice expansion of the structure constant, (B.8) of part I, which leads to

$$\sum_{\mathbf{G}}\frac{J_0(K_G R_M)}{S-K_G^2}=\frac{\alpha}{2\pi R_M L_0(S)}\,. \qquad (2.4)$$

Finally, if $\mathbf{K}_0$ is not near a Brillouin zone boundary, we have

$$S-K_0^2=\frac{1}{\alpha}2\pi R_M L_0(S)\,, \qquad (2.5)$$

which can be observed to take the same form as (2.2) in the limit of weak potentials.

(iii) *Negative energies*

This is the region where the KKR method is most transparent. The structure constants decrease exponentially as the energy is lowered, which follows from (B.5) in part I, it being again possible, therefore, to use a diagonal expansion of the determinant. This leads to the eigenvalue condition

$$1+\mathscr{G}_0'(\mathbf{K}_0,S)\sum_l(\cot\eta_l-i)=0\,. \qquad (2.6)$$

Deep in the core of the potential we expect very flat bands, near to the level of bound states of a single 'muffin-tin', since there will be very little tunnelling between the wells. This picture is exactly reflected in the form taken by (2.6): the bound state of angular momentum l will match almost exactly to an exponentially decreasing wave outside the well, causing one of the terms of the sum over l to blow up. In the limit when $s\to-\infty$, the eigenvalue equation becomes simply the single-well bound-state condition

$$L_l(S)=\frac{1}{K_l[(-S)^{1/2}R_M]}\frac{\partial}{\partial R}K_l[(-S)^{1/2}R_M]\,, \qquad (2.7)$$

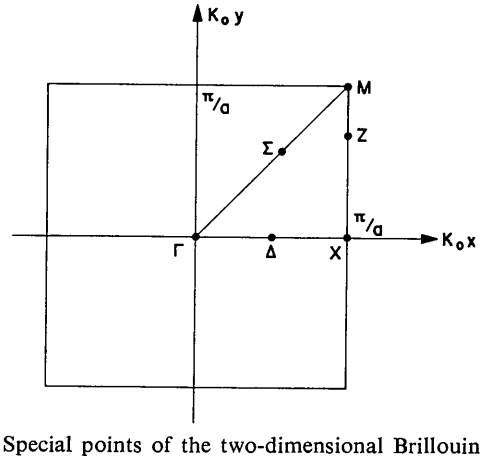

Fig. 1. Special points of the two-dimensional Brillouin zone.

where $K_l(x)$ is a modified Hankel function (see Berry & Ozorio de Almeida, 1973).

At high energies, the off-diagonal terms of the KKR determinant are not small, and yet one can show that the Born approximation is included in the weaker approximation (2.6). Thus, the same diagonal approximation is valid for very high energies, negative energies and small energies, and computations are planned to assess its validity over the rest of the range.

3. Effect of symmetry

Further simplifications arise when the wave vector $\mathbf{K}_0$ is in one of the symmetry directions or boundaries of the Brillouin zone labelled in Fig. 1.

There exist excellent accounts of group-theoretical aspects of band structure [Heine (1960) deals specifically with two-dimensional examples], so that one can limit the discussion to the formulae derived in part I.

Firstly we notice from (4.7) in part I that, if $\mathbf{A}$ is a symmetry operation belonging to the *little group* of the wave vector $\mathbf{K}_0$, $\mathscr{G}(\mathbf{AR})=\mathscr{G}(\mathbf{R})$. It follows that, if $\mathbf{A}$ is a rotation by an angle $\Delta\theta$, $\mathscr{G}_l=0$, unless $l=n(2\pi/\Delta\theta)$, where n is any integer. For $\mathbf{K}_0$ lying on the lines Δ and Σ, the little group is restricted to mirror symmetry, and we find that the only restriction is that $\mathscr{G}_l$ must be real if l is even, or pure imaginary if l is odd.

To this must be added the knowledge that only Bloch functions belonging to an irreducible representation of the little group can be intrinsically degenerate. Thus, for positions Σ and Δ, $\psi_{\mathbf{K}}$ must be even or odd with respect to the mirror symmetry across the $\theta=0$ axis which implies that $a_{-l}=(-1)^l a_l$ or $-a_{-l}=(-1)^l a_l$ respectively. The effect of rotational symmetries is the same as in the preceding paragragh, *i.e.* $a_l=0$ unless $l=n(2\pi/\Delta\theta)$.

Taken together the simplifications of both the wave functions and the matrix elements lead to reductions in the size of the KKR matrix if $\mathbf{K}_0$ lies in a symmetry direction. In the APW method one constructs Bloch functions of the appropriate symmetry by matching angular momentum functions to symmetrized plane waves of the same irreducible representation of the wave vector.

It is evident that the diagonal approximations put forward in the preceding section will be most accurate near the points of highest symmetry. The qualitative feeling gained for the nature of the negative energy states can now be refined. In the limit where $S\to-\infty$ the potential seen by the wave function has complete circular symmetry. The eigenvalues are then doubly degenerate with the exception of the $l=0$ states. As one approaches $S=0$, these bands start to split in the general regions of the Brillouin zone, the split spreading later to the points of high symmetry. The approximate eigenvalue condition (2.6) cannot give this fine splitting though it does give a departure from complete flatness for the bound bands.

4. Semiclassical wave functions

The semiclassical approximation for the wave function is obtained by extending the form of the eigenvector solutions of the KKR matrix equation, valid in the limit $S \to \pm\infty$ to the whole of the energy range. The justification is that in the semiclassical regime only a small proportion of the contributing states have small values of $|S|$. For negative energies the wave functions are taken to have a unique value of l, whereas for positive energies the limiting solutions have coefficients which are the same as for plane waves.

It is necessary to recall some of the formulae concerning the nature of partial waves in two dimensions, derived by Berry & Ozorio de Almeida (1973), before proceeding to the form of the Bloch functions. There it was shown that in the *classically allowed region, i.e.* where $S > \bar{U}(\mathbf{R}) - l^2/R^2$, the semi-classical approximation to the lth partial wave is

$$\tau_l(R) \simeq \cos\left(\Phi_l(R_1, R) - \pi/4\right)/[RQ_l(R)]^{1/2}, \quad (4.1)$$

where $R_1 = 0$ for $l = 0$, or else it is the smallest *turning point* (for which $S - \bar{U}(R) - l^2/R^2 = 0$); also $Q_l^2 \equiv S - \bar{U}(R) - l^2/R^2$ and

$$\Phi_l(R_1, R) = \int_{R_1}^{R} Q_l(R)\mathrm{d}R\,. \quad (4.2)$$

In the classically forbidden region ($Q_l^2 < 0$) the partial waves are exponentially small and can be neglected in a first approximation. In this way for negative energies the degenerate pairs of Bloch functions become

$$\tau_j(\mathbf{R}) = \begin{cases} \dfrac{\cos\left(\Phi_l(R_1, R) - \pi/4\right)\begin{cases}\cos l\theta \\ \sin l\theta\end{cases}}{[RQ_l^j(R)]^{1/2}\left[\dfrac{\pi}{2}\displaystyle\int_{R_1}^{R_2} \mathrm{d}R/Q_l^j(R)\right]^{1/2}} \\ \qquad \text{(classically allowed region)} \\ 0 \quad \text{(classically forbidden region)} \end{cases} \quad (4.3)$$

where the exponentially small wave function has been neglected, and in the normalization integral, taken between the two turning points, $\cos^2$ has been set equal to $\frac{1}{2}$, thus neglecting an oscillatory integral. For positive energies the angular momentum expansion of a plane wave together with the partial wave solutions (4.1) lead to

where, beside the approximations used previously, the unit cell has been assumed circular. The presence of the upper limit to the angular momentum summation,

$$l_{\max}(S_j) = S_j^{1/2} R_{\mathrm{W-S}}\,, \quad (4.5)$$

is consistent with the assumption that the wave function can be neglected in the classically forbidden region. Near $S = 0$ these expressions for the wave function break down, but in the semiclassical limit the contribution from this range is negligible.

The semiclassical approximations given by (4.3) and (4.4) are considerably cruder than the diagonal formulae for the eigenvalues. This is a similar situation to that found in perturbation theory where one always knows the energy to an order better than the eigenfunction.

5. Complex eigenvalues

The way to take absorption into account is indicated in §6 of BBOA. It should be noted that the formula for the imaginary part of the eigenvalue S_j^i:

$$S_j^i \simeq \int_{\text{mesh}} \mathrm{d}^2R |\tau_j(\mathbf{R})|^2 \bar{U}^i(\mathbf{R})\,, \quad (5\text{–}1)$$

where $\bar{U}^i(\mathbf{R})$ is the imaginary component of the potential, does not in principle necessitate the use of the semiclassical approximations which are here generalized to two dimensions. What is generally valid and useful is to circularize the unit mesh in (5.1), since the greatest contributions to the imaginary potential arise from near the atomic strings.

It is important to understand just how S_j^i varies among the Bloch waves j for varying $\mathbf{K}_0$ and E, the incident beam energy. Use of the semiclassical Bloch functions, given in §4, in (5.1) gives

$$S_j^i(S_j) = \frac{\mathrm{Re}\displaystyle\int_0^{R_{\mathrm{W-S}}} \mathrm{d}R\bar{U}^i(R)/Q_l^j(R)}{\mathrm{Re}\displaystyle\int_0^{R_{\mathrm{W-S}}} \mathrm{d}R/Q_l^j(R)} \quad (S<0) \quad (5.2)$$

and

$$S_j^i(S_j) = \frac{\mathrm{Re}\displaystyle\int_0^{R_{\mathrm{W-S}}} \mathrm{d}R\bar{U}^i(R)\sum_{l=0}^{l_{\max}} \varepsilon_l/Q_l^j(R)}{\mathrm{Re}\displaystyle\int_0^{R_{\mathrm{W-S}}} \mathrm{d}R\sum_{l=0}^{l_{\max}} \varepsilon_l/Q_l^j(R)} \quad (S>0). \quad (5.3)$$

The 'real part' notation ensures that only classically accessible regions contribute to the integrals.

$$\tau_j(\mathbf{R}) = \begin{cases} \dfrac{\displaystyle\sum_{l=0}^{l_{\max}} \varepsilon_l \cos\left[\Phi_l(R_1, R) - \dfrac{\pi}{4}\right]\cos l\left(\theta + \dfrac{\pi}{2}\right)/[RQ_l^j(R)]^{1/2}}{\left[\dfrac{\pi}{2}\displaystyle\sum_l \varepsilon_l \int_{R_1}^{R_2} \mathrm{d}R/Q_l^j(R)\right]^{1/2}} \\ \qquad \text{(classically allowed region)} \\ 0 \qquad \text{(classically forbidden region)} \end{cases} \quad (4.4)$$

Under fully semiclassical conditions one can replace the sum over l in equation (5.3) by an integral, leading to the simple result

$$S_j^i(S_j)=\frac{\int_0^{R_{w-s}} dR\bar{U}^i(R)/(S_j-\bar{U}(R))^{1/2}}{\int_0^{R_{w-s}} dR/[S-\bar{U}(R)]^{1/2}} \quad (S>0)\,. \quad (5.4)$$

It is important to note that the variation of S_j^i with $\mathbf{K}_0$ is only of the form $S_j^i[S_j(K_0)]$, *i.e.* universal curves S_j^i of S_j are predicted for all orientations.

Examination of (5.4) shows that absorption will decrease with 'energy' when $S>0$. Absorption will be strongest for $S<0$, the dominant contribution coming from the region near the smallest turning point. Thus, for $l\neq 0$ the absorption will diminish as the angular momentum is increased, whereas the variation of S_j^i among partial waves of the same angular momentum will be small. For $l=0$ the situation is different, since there is only one turning point. In this case we find that the absorption will decrease sharply as the energy increases towards zero.

6. Qualitative considerations about pole patterns

We are now in a position to analyse directly some features of the diffracted amplitudes. Inserting the semiclassical wave functions into formula (2.12) of part I we find for the bright-field beam

$$A_0(\mathbf{K}_0,z)=\alpha\sum_{j<0}\left[\mathrm{Re}\int_0^{R_{w-s}} R\,dR \times\frac{\cos\{\Phi_l^j(R_1,R)-\pi/4\}}{c_j^2\{RQ_l^j(R)\}^{1/2}}J_l(K_0R)\right]^2\exp(-iS_jz/2k_0)$$
$$+\alpha\sum_{j>0}\left[\mathrm{Re}\int_0^{R_{w-s}}\frac{R\,dR}{c_j^2}\sum_{l=0}^{l_{max}}\varepsilon_l \times\frac{\cos\{\Phi_l^j(R_1,R)-\pi/4\}}{\{RQ_l^j(R)\}^{1/2}}J_l(K_0R)\right]^2\exp(-iS_jz/2k_0)\,, \quad (6.1)$$

where the $c_j'S$ are normalization factors. If, in the same way as Berry (1971), we use the criterion that only integrals having stationary points will give a large contribution to the diffracted amplitude it is seen that bound states of angular momentum l will only contribute if $K_0^2<[Q_l^2(R)]_{max}$. Correspondingly, by approximating the angular momentum sum by an integral and applying stationary-phase arguments a second time, one finds that the contribution of the nearly-free states is negligible as $\mathbf{K}_0\to 0$.

Ideal pole patterns as described in BBOA effectively provide a map of $A_G(\mathbf{K}_0)$ for a constant thickness Z. The arguments presented above are thus tantamount to saying that the centre of the figure will be dominated by interference among the bound states, whereas the outer regions will only be sensitive to the nearly free states. A further investigation of equation (6.1) shows that only the modulus of the wave vector $\mathbf{K}_0$ appears explicitly. Since it was shown before that we must expect bound bands to be flat and to have approximately uniform excitation, it follows that those features of pole patterns that depend exclusively on the bound states will have near-circular symmetry. The nearly free bands will be strongly dependent on $\mathbf{K}_0$.

As well as this, one must take into account that if $S>0$ the circularization of the unit mesh was seen to be a relatively crude approximation. Thus it is to be expected that the pattern due to the nearly free states will not show circular symmetry.

So far the effect of absorption of the diffracted amplitudes has been left out. As was shown in §5, it will be heaviest for the bound states. The complete picture is thus that in the outer regions of pole patterns there will be features that depend mostly on nearly-free states and exhibit the symmetry of the Brillouin zone. Near the centre of the pole one may find a set of concentric rings connected with the bound bands, but this pattern will tend to disappear as the thickness of the specimen is increased.

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