A Comparison between Electron Crystal Scattering Potentials derived from X-ray Electron Densities and from Atom Muffin Tin Potentials*

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Abstract

Two different forms of electron crystal potential are compared for the particular cases of aluminium and niobium diselenide. One of these is the solid-state muffin tin potential frequently used for band structure and low energy electron diffraction problems, and with its natural representation in real space. The other potential, derived from X-ray structure factors, is that most commonly used in electron microscopy structure determinations. It is expressed in terms of its Fourier coefficients and is accordingly a reciprocal space representation. Comparisons are carried out in both spaces. It is concluded that differences between the potentials are only minor and are mainly due to details in truncation and superposition.

1. Introduction

The results of electron diffraction experiments can often be used to determine a scattering potential for a given crystal. At high electron energies, that is, greater than 50 keV, this measured potential refers to the bulk structure of the material, whereas at low energies, less than 1 keV, surface structure plays an increasing part. The scattering potential can be interpreted as that arising from the superposition of potential distributions of the individual atoms in the structure. Furthermore, each of these atomic potential distributions is unique to that particular atomic species. It is by no means obvious that the scattering potential that is valid for a given atom at 200 keV is also valid at 100 eV.

It has been found that for high energy experiments a good first estimate of the scattering potential can be readily derived by firstly superposing neutral atom electron charge densities obtained from standard tabulations (see e.g. Doyle and Turner 1968; Cromer and Waber 1965). This is followed by solving for the resulting charge distribution (including nuclear charges) the Poisson equation (or Mott formula) to determine the potential (see e.g. Dawson *et al.* 1974). Such a structure factor potential is usually within 5% of the actual measurements for the inner Fourier coefficients and in much better agreement with the outer coefficients (e.g. Goodman and Lehmpful 1967).

Recent work by us (Lynch and Smith 1983; Smith and Lynch 1984, 1985*a*) has shown that for some non-metallic compounds (e.g. BaO, MgO, MoS_2, $NbSe_2$) the

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use of these same potentials can give a reasonable fit to data obtained in certain very low energy electron scattering experiments. In addition, in recent work (Smith and Lynch 1985 b), we have successfully employed such a potential in comparisons between calculated and measured very low energy current images for the Al (111) and (100) surfaces (Bargeron et al. 1983). Hence it is of some interest to see to what extent such potentials can be related to the muffin tin potentials, which are the most convenient starting point for various solid-state band structure calculations, and which are frequently used in conventional low energy electron diffraction (LEED) calculations (see e.g. Pendry 1974). In the present communication we compare, for the particular cases of the elemental metal aluminium and the layered compound material niobium diselenide, the potential distributions calculated by means of structure factors with muffin tin potentials [for $NbSe_2$ see Mattheiss (1973) and Mrstik et al. (1977), for Al see Moruzzi et al. (1978), Van Hove and Tong (1979) and Kawamura (1983)].

2. Method of Comparison

We carry out the comparisons in both real and reciprocal space. The potential construction using the X-ray structure factors determines directly the Fourier coefficients of the crystal potential, i.e. it is a reciprocal space representation. On the other hand, the muffin tin potential is essentially a real space representation. Accordingly, for comparisons in both spaces, it is only necessary to carry out a single Fourier transformation for one of the potential types from its natural representational space to the dual space.

(a) Reciprocal Space Comparison

In previous LEED work using a multislice method (see e.g. Lynch and Smith 1983), the Fourier transform of slices of the potential $\phi(x, y, z)$ was calculated for an orientation perpendicular to the surface normal of the crystal. The Fourier transform of the potential slice projection from $z_m - \frac{1}{2}\Delta z$ to $z_m + \frac{1}{2}\Delta z$ then takes the form

$$\mathscr{F}\{\phi^P(x, y)\} = \mathscr{F}\left(\int_{z_m - \frac{1}{2}\Delta z}^{z_m + \frac{1}{2}\Delta z} \phi(x, y, z)\, \mathrm{d}z\right)\Big/ \Delta z, \qquad (1)$$

where x, y and z are the real space axes with z parallel to the surface normal. The slice thickness Δz is equal to a/n, where a is the unit cell length parallel to the z axis and n is the number of slices.

In reciprocal space the zeroth order Fourier coefficient for a given slice is the average value of the potential in that slice, and the low order coefficients are a measure of the potential distribution between atoms. The high order coefficients (which are those most strongly affected by thermal effects established by, for example, a Debye–Waller treatment) are a measure of atomic position as well as the exact strength of the potential at the centres of the atoms.

In the case of X-ray form factors there is a well-known procedure for the calculation of the Fourier coefficients for each slice. The coefficients for a complete unit cell are calculated by (see e.g. Dawson et al. 1974)

$$V_{hkl} = \Omega^{-1} \sum_p f_p \exp\{2\pi\, \mathrm{i}(hx + ky + lz)\}, \qquad (2)$$

where (h, k, l) is the reciprocal lattice position, Ω is the unit cell volume in real space

and f_p is the atomic scattering factor at the site labelled p. Using the Mott formula one has

$$f_p(s_{hkl}) = \frac{f_x(s_{hkl}) - Z}{(s_{hkl})^2} \, 1 \cdot 1456, \tag{3}$$

where f_p is in units of eV $\overset{\circ}{A}{}^3$. The factor $1 \cdot 1456$ is necessary because of the choice of units (Dawson $et\ al.$ 1974), and s is of the form

$$s_{hkl} = \sin\theta/\lambda = 1/2d_{hkl}, \tag{4}$$

with d_{hkl} the planar distance corresponding to the (h, k, l) reflection. The Mott formula, of course, exhibits a singularity at s equal to zero in the case of the unit cell with net charge or dipole moment, a situation which does not often occur.

In a consistent convention, the standard summation for the real space potential may be written as (Dawson $et\ al.$ 1974)

$$\phi(x, y, z) = \sum_{hkl} V_{hkl} \exp\left[-\{2\pi\,\mathrm{i}(hx + ky + lz)\}\right] \tag{5}$$

and the Fourier transform of the potential slice projection easily shown to be

$$V_{hk}^{\mathrm{p}} = \mathscr{F}\{\phi^{\mathrm{p}}(x, y)\}$$

$$= \sum_l V_{hkl} \frac{\sin(\pi l \Delta z)}{\pi l \Delta z} \exp\{-(2\pi\,\mathrm{i}\,l z_{\mathrm{m}})\} \exp\left[-\{2\pi\,\mathrm{i}(hx + ky)\}\right]. \tag{6}$$

It should perhaps be pointed out that this particular formula is restricted to slices normal to the z direction (associated with the l coefficients), i.e. there is an assumption that the unit cell angles α and β are 90°. However, this particular case which pertains to most surfaces of interest in common materials can be easily generalized. It is adequate to demonstrate the arguments here but not, it must be emphasized, necessarily true for a projection into slices of arbitrary orientation.

The structure factor calculation allows overlap of the spherically symmetric charge distributions and hence gives some approximation to the effect of bonding. However, the model does not permit the redistribution of charge due to bonding and may thus be in error, although of course ionic scattering factors could be used. This is normally realized and in consequence such a model is treated as a first approximation to be improved by refinement. Accordingly, the inner V_{hkl} coefficients are expected to be modified as a result of measurement. For example, in the case of the MgO (200) coefficient, Goodman and Lehmpfuhl (1967) have found that the coefficient required a modification of 5% from the neutral (not ionic!) atom value.

In contrast the use of muffin tin potentials involves positioning the spherically symmetric potential distributions on the atom centres in the structure. These distributions, conventionally, are not allowed to overlap and the truncation length, called the muffin tin radius, is a parameter for the derived unit cell distribution. For low energy electron scattering calculations, correction procedures are sometimes carried out to allow for some effects of overlap, exchange and correlation (see e.g. Pendry 1974; Van Hove and Tong 1979). The space between atoms is filled by a constant potential (the absolute value of which is often adjusted $a\ posteriori$ to match experimental results).

In the present work a three-dimensional potential map was determined. The potential in a given slice was found and then Fourier transformed using a fast Fourier transform, due to Higgins (1976), in order to obtain the appropriate coefficients. The mean potential slice from the muffin tin potential was calculated by

$$\phi^P(x, y) = \tfrac{1}{5} \sum_{n=1}^{5} \phi(x, y, z_n), \qquad (7)$$

where the sum is taken over five sandwiches within the slice and then averaged in order to allow for the strong troughs at the atom sites, whilst minimizing the computational size of the Fourier transformation.

For the muffin tin potentials, the atom centres were not convoluted by a realistic gaussian function in order to simulate the effect of thermal motion (Debye–Waller treatment) and, accordingly, the outer coefficients may be too large. In addition, it is expected that the inner coefficients (those most affected by the regions between the atoms, known as the bonding volume) might be severely in error. The truncation of the muffin tin potentials can give rise to very high spatial frequency artefacts due to the 'sharp edges' on the atoms. This is relatively easily dealt with in Fourier space by using a suitable aperture, that is without using or calculating the very large order (or large hkl) terms.

(b) Real Space Comparison

One possible form of real space comparison is between the (inverse) Fourier transform of the quantity calculated in equation (6) and the appropriate muffin tin potential. In the present work, we employ the Higgins (1976) algorithm for a two-dimensional fast Fourier transform of a thin slice centred on a single atom of the appropriate type. Appealing to spherical symmetry we are then able to plot appropriate potential radial distribution curves.

An alternative and more precise comparison, which is also possible, is to calculate the potential in equation (5), but with y and z set to zero:

$$\phi(x, 0, 0) = \sum_{hkl} V_{hkl} \exp(-2\pi i\, hx). \qquad (8)$$

For simplicity, this quantity can be computed for a synthetic cubic unit cell with one atom at the origin. The tabulation of $\phi(x, 0, 0)$ is then directly comparable with the muffin tin potential radial distribution. This approximation enables a more structurally simple computational program to be utilized for comparison purposes. It also avoids some of the averaging processes involved in the 'slice' approach, which of course is the potential used in our previous work (Lynch and Smith 1983; Smith and Lynch 1984, 1985 a, 1985 b). The actual Fourier transform in radial coordinates may be written in the form (see e.g. Kasper and Lonsdale 1959; Doyle and Turner 1968)

$$\phi(r) = \int_0^\infty 4\pi s^2 \mathscr{F}\{\phi(r)\}\, \frac{\sin(4\pi r s)}{4\pi r s}\, \mathrm{d}s. \qquad (9)$$

3. Results

(a) Reciprocal Space

The basis of the structure factor approach is the use of the atomic scattering factor f. A comparison of electron scattering factors for the case of aluminium in reciprocal space is given in Fig. 1. Shown is the electron form factor (dashed curve) as a function of s (equation 4) as determined by Doyle and Turner (1968). This series of tabulations has often been used in electron microscopy calculations. In comparison, the solid curve was obtained by applying the inverse of equation (9) to the appropriate muffin tin potential from the tabulations by Moruzzi *et al.* (1978). This series of potentials has been employed in LEED studies (Van Hove and Tong 1979; Kawamura 1983). The difference for small values of s can be attributed to the truncation of the muffin tin potential for large real space distances (the potential is not defined for a Bohr radius greater than $2 \cdot 687$).
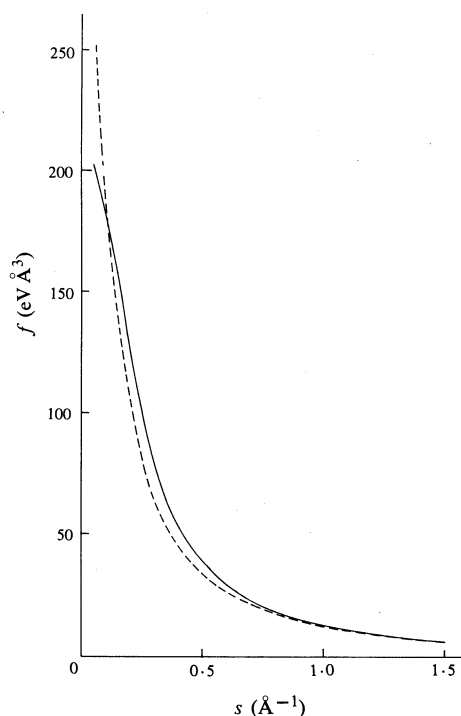

Fig. 1.   Comparison of electron scattering factors as functions of s (equation 4) for aluminium. The dashed curve was obtained directly from Doyle and Turner (1968), while the solid curve was found by Fourier transforming the muffin tin potential by Moruzzi *et al.* (1978).

A comparison of the zeroth order Fourier coefficient, i.e. the mean inner potential, is displayed as a function of slice number through a unit cell in Fig. 2 for (*a*) aluminium and (*b*) niobium diselenide. The form factor calculations (dashed curves), based on the use of equations (2) and (6), employ atomic form factors for Al and Se from Doyle and Turner (1968), and for Nb from Cromer and Waber (1965). The muffin tin potentials (solid curves) are from Moruzzi *et al.* (1978) for Al, and from Mattheiss (1973) for $NbSe_2$. This latter potential has been used in a LEED calculation (Mrstik
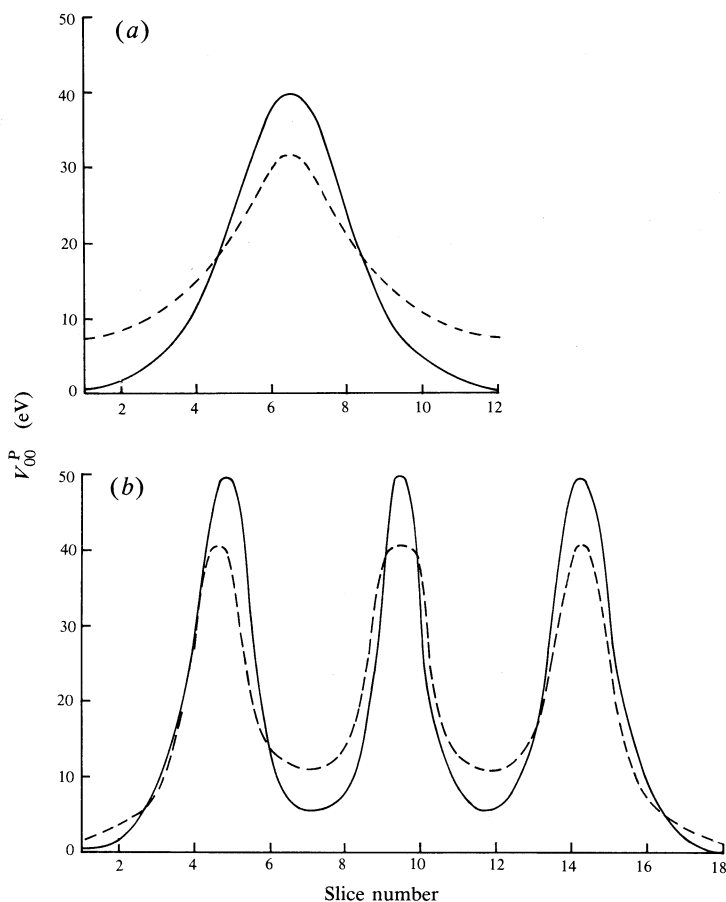
Fig. 2. Comparison of the zeroth order Fourier component of the projected potentials V_{00}^p as functions of the slice number through a unit cell for (a) the Al (111) face and (b) the $NbSe_2$ (001) face. Solid curves correspond to results obtained from a fast Fourier transform of the Moruzzi *et al.* (1978) muffin tin potential in (a), and the Mattheiss (1973) muffin tin potential in (b). Dashed curves correspond to results obtained by means of the Doyle and Turner (1968) tabulation together with equations (2) and (6).

et al. 1977).* For the muffin tin potential, V_{00}^p has also been determined by the use of the Higgins (1976) fast Fourier transform. In both Figs 2a and 2b the curve calculated from the muffin tin potential is sharper than that derived from the X-ray form factor and closer to a value of zero between the atoms. This is a result of not allowing the muffin tin potentials to overlap at all in the calculation, whereas the structure factor calculation permits charge overlap in the usual manner of X-ray crystal structure analysis.

* The potential is tabulated on computer tape available from Van Hove and Tong (1979) which contains their program listings and data files.
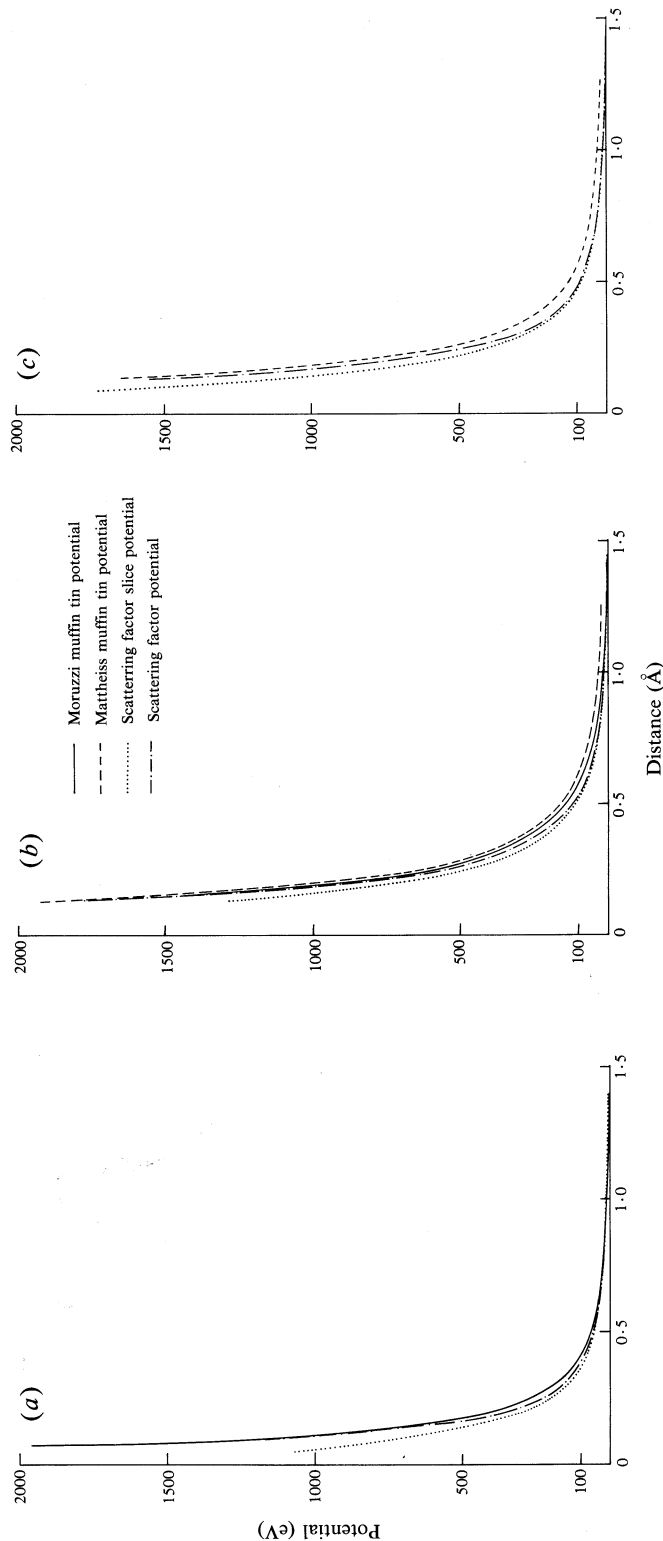
Fig. 3. Real space comparison of potentials as functions of distance for (*a*) Al, (*b*) Nb and (*c*) Se. Solid curves correspond to results obtained directly from the Moruzzi *et al.* (1978) muffin tin potential, and dashed curves from the Mattheiss (1973) muffin tin potential. Dotted curves were obtained from the Doyle and Turner (1968) scattering factors and by use of equations (2) and (6) and a fast Fourier transform, whereas the dot-dash curves were obtained from the Doyle and Turner (1968) scattering factors and by use of equations (2) and (8).

(b) Real Space

Fig. 3*a* shows, for the case of Al, a comparison between real space potentials for single (isolated) atoms obtained from the X-ray structure factors by the two methods outlined in Section 2*b* and those obtained directly from the Moruzzi *et al.* (1978) muffin tin potential tabulations. Clearly there is close agreement between the Moruzzi tabulation (solid curve) and the dot–dash curve derived from equation (8). The projection of the potential obtained through the use of equation (6) (dotted curve) is of lesser magnitude and consequently there is worse agreement.

The dotted curve obtained using the projected potential on a thin slice was calculated on a net of 64×64 points. The outer coefficients were reduced by multiplication with a factor of $\exp(-0.03 s^2)$, which removes oscillatory effects due to series truncation and is formally identical to an isotropic Debye–Waller factor of magnitude 0·03. This truncation principally modifies the peak height near the atomic origin and thus the largest difference between this curve and the other two is in this region. For comparison, even a rigid lattice such as silicon exhibits a measured Debye–Waller factor of the order of 0·467 at room temperature (Price *et al.* 1978).

Fig. 3*b* shows the same comparison for niobium. It also shows (dashed curve) a second muffin tin calculation from the $NbSe_2$ potential by Mattheiss (1973). The differences between the curves calculated from the X-ray form factor data and the muffin tin potentials exhibit the same properties as seen for aluminium. It is of interest to note a difference between the two muffin tin curves which is at least as great as that between the curve from equation (8) and the tabulation of Moruzzi *et al.* (1978).

Fig. 3*c* shows the same comparison but this time for selenium. In this case, there is no relevant data from Moruzzi *et al.* (1978) and, by comparison with Fig. 3*b*, we conclude that the apparent larger differences between the curves derived from structure factors and that from the muffin tin treatment (dashed curve) might be lessened by further muffin tin calculations.

4. Conclusions

Calculated X-ray form factors are derived from wavefunctions determined by using Hartree, Fock, Slater, Dirac etc. self-consistent field schemes. On the other hand, muffin tin potentials are themselves also arrived at as the potential resulting from self-consistent calculations in the same spirit. Thus, it is not really surprising that these potentials are nearly identical. Accordingly, the differences that have been exhibited in the present work can principally be ascribed to details of superposition and truncation.

It is well known that the 'isolated' atom 'muffin tin' potential can be adjusted in LEED calculations for effects such as charge overlap, exchange and correlation (see e.g. Pendry 1974, p. 345; Van Hove and Tong 1979, p. 26). In simple form factor calculations the only overlap considered is direct superposition of charge density giving rise to the appropriate potential distribution. More elaborate schemes involving postulated or measured redistribution of charge density in interatomic bonds have been used in X-ray and high energy electron diffraction structure refinement.

Our results appealingly indicate the relative straightforwardness of the task to relate, for instance, atomic form factors measured by X-ray experiments to the potential required for a one electron, self-consistent field band structure calculation, and also to the details of a precise convergent beam, fast electron diffraction pattern.

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