PSEUDOPOTENTIAL CALCULATIONS OF COMPTON PROFILES

The theoretical methods for evaluation of $\rho(p), \rho^{2\gamma}(p), J(q)$ and $N(q)$ are discussed. We formulated the required formula for the above quantities. In order to calculate all these quantities, we need to know both $\Psi_n(r)$ and $\Psi_p(r)$ by a standard band structure method. Usually the computation of band structure is time consuming. We took empirical pseudopotential method (EPM) to evaluate the required energies and pseudowavefunctions which are used to calculate the above mentioned quantities. In this chapter we will discuss about the EPM method and a simplified computational method to get the convergent pseudowavefunctions and use them to calculate $H(r)$ and $J(q)$ in different crystallographic directions.

(4.1) Pseudo-Potential Method

Before starting the computational methods for the pseudopotential band structure, we will discuss the meaning of pseudo-potential in brief. A useful starting point for pseudopotential theory is orthogonalised plane wave (OPW) method [4.1]. The Hamiltonian for this method is

$$ H = \frac{p^2}{2m} + V_c(r) $$

(4.1)

where $V_c(r)$ is the attractive core potential. The wavefunctions for this Hamiltonian will be

$$ \Psi(r) = \Phi(r) + \sum_c b_c \phi_c(r) $$

(4.2)

where $\Phi(r)$ is the smooth interstitial part of the $\Psi(r)$ and the second term is the sum of all core orbitals. Since $\Psi(r)$ is orthogonalised to the core orbital $\phi_c(r)$, we can take $\langle \Psi(r) | \phi_c(r) \rangle = 0$ and get the value of $\delta_c = -\langle \Psi(r) | \phi_c(r) \rangle$ so that (4.2) becomes

$$ \Psi(r) = \Phi(r) - \sum_c \langle \phi_c(r) | \Phi(r) \rangle \phi_c(r) $$

(4.3)

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When $H$ operates on $\Psi(r)$, it gives the energy eigen value $E$.

$$H\Psi(r) = E\Psi(r) \quad (4.4)$$

Taking $H\phi_c(r) = E_c\phi_c(r)$, we can simplify the above equation as

$$H\Phi(r) - \sum_c \langle \phi_c(r) | \Phi(r) \rangle E_c\phi_c(r) = E\Phi(r) - E \sum_c \langle \phi_c(r) | \Phi(r) \rangle \phi_c(r) \quad (4.5)$$

which can be written as

$$H\Phi(r) + \sum_c (E - E_c)\phi_c(r)\langle \phi_c(r) | \Phi(r) \rangle = E\Phi(r) \quad (4.6)$$

Taking

$$V_R(r)\Phi(r) = \sum_c (E - E_c)\phi_c(r)\langle \phi(r) | \Phi(r) \rangle \quad (4.7)$$

eqn(4.5) takes the form

$$(H + V_R(r))\Phi(r) = E\Phi(r) \quad (4.8)$$

The potential $V_R$ behaves like a short-ranged non-Hermitian repulsive potential because its effect is to keep valence electrons out of the core region. The (4.8) solves the energy eigen values $E$ with the same accuracy as in OPW. The potential in the Schrödinger equation can be factored to write it

$$\left[ \frac{p^2}{2m} + V_c(r) + V_R(r) \right] \Phi(r) = E\Phi(r) \quad (4.9)$$

In this equation we can find that the attractive long range potential $V_c(r)$ and the short range repulsive potential $V_R(r)$ cancel each other to make the total potential weak near the core region. This is called **Phillips Kleinman cancellation theorem** [4.2]. Since the potential is weak, a nearly free electron model (NFEM) can be used to solve (4.9) to get the pseudowavefunctions and energy eigen values.
The validity of this method rests upon two arguments: (i) \( E_k \gg E_c \) so that \((E_k - E_c)\) can be replaced by a mean energy in (4.8) such as \( E_F \) (proving one is interested in only a limited energy range), and (ii) the cancellation is equal for all \( l \) (or at least \( l \) components of the valence wave functions which are significant). These assumptions have been found to be valid in pseudopotential theory.

There are three pseudopotential methods available in recent few years: (1) empirical pseudopotential method, (2) self consistent pseudopotential method and (3) \textit{ab initio} pseudopotential method [4.3,4.4]. The last two methods work with Kohn-Sham local density approximation [4.5]. The difficulty is that the band gap is not reproduced well in both the methods. However, the empirical pseudopotential method does not have this problem. The pseudowavefunctions and the energies are well reproduced because the potentials are based on the experimental based structure data. Moreover, the calculation is fast in comparison to other methods.

4.2 The Empirical Pseudopotential Method

The atomic pseudopotentials were obtained by fitting directly to the experiments connected with band structures like photoemission and reflectivity [4.6]. The crystal potential can be obtained from the atomic potentials \( V^a(r) \). The crystal potential are assumed to be a linear combination of atomic potentials.

\[
V(r) = \sum_{\mathbf{R},\tau} V^a(r - \mathbf{R} - \tau) \tag{4.10}
\]

where \( \mathbf{R} \) and \( \tau \) are the lattice and basis vectors respectively. If the potential is expanded in the reciprocal lattice vector, then

\[
V(r) = \sum_{\mathbf{G}} V^a(\mathbf{G})S(\mathbf{G})e^{i\mathbf{G} \cdot \mathbf{r}} \tag{4.11}
\]
where the structure factor is

$$S(G) = \frac{1}{N_a} \sum_{\tau} e^{-iG \cdot \tau} \quad (4.12)$$

where $N_a$ is the number of basis atoms. The pseudo wavefunctions $\Psi_{\nu k}(r)$ and the band eigen value $E_{\nu k}$ are the solution of the Schrödinger equation

$$\left[ \frac{p^2}{2m} + V(r) \right] \Psi_{\nu k}(r) = E_{\nu k} \Psi_{\nu k}(r) \quad (4.13)$$

In the reciprocal lattice vector space the Schrödinger equation takes the form

$$[|k + G|^2 - E_{\nu k}] C_{\nu k}(G) + \sum_{G'} V(G - G') C_{\nu k}(G') = 0 \quad (4.14)$$

The eigen values are obtained by solving the secular determinant

$$\text{det} \left( |k + G|^2 - E_{\nu k} + \sum_G V(G - G') \right) = 0 \quad (4.15)$$

For diamond structure $\tau = \frac{2\pi}{8} (a, a, a)$ where $a$ is a lattice constant, the structure factor can be solved as

$$S(G) = \frac{1}{N_a} \sum_{\tau} e^{-iG \cdot \tau} = \cos(G \cdot \tau)$$

so that the crystal potential in momentum space takes the form,

$$V(G) = \cos(G \cdot \tau) V^a(G) \quad (4.16)$$

For zinc blende structures the inversion symmetry breaks down. The crystal potential becomes

$$V(G) = V^s(G) \cos(G \cdot \tau) + i V^a(G) \sin(G \cdot \tau) \quad (4.17)$$

where $V^s(G)$ and $V^a(G)$ are the symmetric and antisymmetric potentials given by the expressions,

$$V^s(G) = [V^C(G) + V^A(G)]/2$$

$$V^a(G) = [V^C(G) - V^A(G)]/2$$

$$P_2 m + V(r)$$
\[ V^a(G) = \frac{[V^C(G) - V^A(G)]}{2} \]  

(4.18b)

where \( V^C(G) \) and \( V^A(G) \) are the atomic form factors for cation and anion respectively. For spherically symmetric potentials \( V(G) = V(|G|) \). The potentials are retained only up to a few numbers \( G^2 = 3, 4, 8, \) and \( 11 \) in units of \( \left( \frac{2\pi}{a} \right)^2 \).

So far we have discussed the use of local pseudopotential to get the band structure. But the local pseudopotential method was found to be inadequate to explain the X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) data. The measured charge densities have a different bond shape than the charge densities calculated by local pseudopotential method. Sometimes the ionicity is also overestimated by the local pseudopotential method as seen in InSb. Owing to these reasons an energy dependent non-local pseudopotential has to be considered to make the empirical pseudopotential method free from the discrepancies. As in the local pseudopotential approach, we can construct the non-local potential from atomic structure calculations or parameterise the potential using EPM. The non-local pseudopotentials are used to account for variations in the pseudopotential for electrons with different angular momentum \( l \). To describe this \( l \)-dependence, the atomic pseudopotential can be expanded in angular momentum components \( V_l(r) \) together with projection operator \( \mathcal{P}_l \) which project out the \( l \)th angular momentum component of the wavefunction.

\[ V_{NL}(r, E) = \sum_{l=0}^{\infty} A_l^a(E)V_l^a(r)\mathcal{P}_l \]  

(4.19)

where \( A_l^a(E) \) is an energy dependent well depth. Only \( l=0, 1, \) or \( 2 \) components are significant for the case at hand, therefore, we may write (symbolically)

\[ s + p + d = 1 \]
Because of the non-local nature of the potential, the form factors $V_{NL}(|G|)$ are no longer simple functions of $G$, but depend on the wavevector $K = k + G$. This can be illustrated by using plane wave basis set by investigating the matrix element of the non-local potential $V_{NL}(r, E)$ taken between plane waves $\langle K |$ and $| K' \rangle$. First the plane wave is decomposed into a sum of standard functions in the usual way

$$e^{iK \cdot r} = 4\pi \sum_{l=0}^{\infty} (2l + 1)i^l P_l(\cos \gamma) j_l(|K| r)$$  \hspace{1cm} (4.20)

where $P_l(x)$ is a legendre polynomial, $j_l(x)$ is a spherical Bessel functions and $\gamma$ is the angle between $r$ and $K$. The matrix elements for a radially symmetric potential may then be written as

$$V_{NL}(K, K') = \frac{4\pi}{\Omega_0} (2l + 1) P_l(\theta_{K,K'}) \int_0^\infty dr r^2 V_{NL}^a(r, E) j_l(K r) j_l(K' r)$$  \hspace{1cm} (4.21)

Two simple, yet accurate forms of the model potential $V^a_l(r)$ are used, these are the square well and Gaussian model potential. In both the cases, radial symmetry is assumed. Apart from the parameter $A^a_l(E)$ which is already defined, the spatial range($R$) of the potential is also taken as a parameter. It is fixed by model potential calculation and by physical considerations. In particular, the $s$ radius is taken from Heine-Animalu-model calculations, and the $d$-well radius is taken from Phillips and Pandey data [4.7, 4.8]. The form of the Gaussian potential is

$$V_l(r) = e^{-(\frac{r}{\delta})^2}$$  \hspace{1cm} (4.22)

Similarly, the form of square well potential is

$$V_l(r) = \begin{cases} 1 & r < R \\ 0 & r \geq R \end{cases}$$  \hspace{1cm} (4.23)
Taking this potential, (4.21) can be evaluated as

\[ V_{NL}(K, K') = \frac{4\pi}{\Omega_0} \sum_{l, \alpha} A_0^\alpha(E)(2l + 1)P_l(\cos(\theta_{K, K'}))S^\alpha(K - K')F_l^\alpha(K, K') \]  

(4.24)

where

\[ F_l(K, K') = \begin{cases} 
\left(\frac{1}{2R^3}\right)[ j_l(KR)^2 - j_{l-1}(KR)j_{l+1}(KR)] & K = K' \\
\frac{R^2}{K_l + K_{l-1}}[Kj_{l+1}(KR)j_l(K'R) - K'j_{l+1}(K'R)j_l(KR)] & K \neq K' 
\end{cases} \]  

(4.25)

To simulate energy dependence for the s states, we make the approximation for the matrix elements between K and K' as follows:

\[ A_0(E) = \alpha_0 + \beta_0 \left[ (E^0(K)E^0(K'))^2 - E^0(K_F) \right] \]  

(4.26)

where \( E^0(K) = \frac{K^2}{2m} \). \( \alpha_0 \) and \( \beta_0 \) are two parameters fixed by detailed comparisons with experimental reflectivity and photoemission data.

Taking pseudopotential form factors the energy band spectrum can be solved. The eigenvalues and eigenvectors are found by solving the secular equation.

\[ \det | H_{G, G'}(k) - E_{nk}\delta_{G, G'} | = 0 \]  

(4.27)

For the local approximation, we have

\[ H_{G, G'}^L = (k + G)^2\delta_{G, G'} + V(| G - G' |) \]  

(4.28)

For non-local corrections we may take

\[ H_{G, G'}^{NL} = H_{G, G'}^L + V^{NL}(K, K') \]  

(4.29)

To achieve satisfactory convergence in energies and wavefunctions we did not take the conventional Löwdin method of perturbation, rather worked with the exact
Table 1
Local Pseudopotential Parameters in Ry

<table>
<thead>
<tr>
<th>compound</th>
<th>$V^S(\sqrt{3})$</th>
<th>$V^S(\sqrt{8})$</th>
<th>$V^S(\sqrt{11})$</th>
<th>$V^A(\sqrt{3})$</th>
<th>$V^A(\sqrt{4})$</th>
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Table 2
Non-Local Pseudopotential Parameters in Ry

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<th>$V^S(\sqrt{11})$</th>
<th>$V^A(\sqrt{3})$</th>
<th>$V^A(\sqrt{4})$</th>
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Table 3
Non-Local Parameters

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<th>compound</th>
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<th>$A_2^C$</th>
<th>$\alpha_0^A$</th>
<th>$\beta_0^A$</th>
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method by taking 90 plane waves [4.9]. Since there is no inversion symmetry the crystal potential is complex in compound semiconductors. The secular matrix is solved in the complex matrix method as given by Bergstresser which takes a 180×180 matrix to get sufficient convergence on both energies and wavefunctions. The form factors used for the local and non-local pseudopotential band structures are given in the Table 4.1, Table 4.2 and Table 4.3.

(4.3) Compton Profile Calculation

There are two methods available to calculate the $J(q)$. One can calculate $\rho(p)$ and then use it to evaluate the $J(q)$ in different crystallographic directions. $B(z)$ which is an important quantity as mentioned earlier, can be calculated from the $J(q)$ data by Fourier transforming them. The other method is to calculate $B(z)$ first in different crystallographic directions and then Fourier transform them to calculate the $J(q)$. We have taken the second approach to calculate CPs in different directions of compound semiconductors [4.9]. As derived earlier we can take the autocorrelation function for pseudowavefunctions as:

$$B(r) = \frac{1}{N\Omega_0} \sum_{k=1}^{10} \omega_k \sum_{\nu=1}^{4} \sum_{G=1}^{90} S_{max} C_{\nu k}(G) |^2 e^{i(k+G).sr}$$

where $s$ is a star operation which select a subgroup of of $O_h$ group. $\omega_k$ is a weight factor corresponding to each $k$. The summation over the wave vectors in the Brillouin zone was performed by means of the special point method [4.10]. Nara et al pointed out that the two point scheme could not be used because the calculation contained spurious oscillations. The ten point scheme was used in our calculation. The star summation is performed in (100), (110), and (111) directions with $S_{max}$ taken as 6, 12 and 8 respectively [4.11]. The four valence bands are taken into considerations. In order to preserve the normalisation, the area of the valence profile
was taken to be the number of valence electrons and then the value of $B(0)$ was taken to be

$$B(0) = \int_{-\infty}^{\infty} J(p_x) dp_x = 8$$  \hspace{1cm} (4.31)

For comparing the calculated profiles with the experimental ones, profiles for core orbitals are added to the valence orbitals and then convoluted with the RIF functions.
References


