CHAPTER II

APPROXIMATIONS IN THE THEORY OF LATTICE DYNAMICS
AND SECULAR DETERMINANT

2.1 Introduction

The theory of lattice dynamics of metals has been an active area of research in solid state physics. A good deal of progress in understanding phonon in metals has been achieved through experimental and theoretical studies during the past seventy years following the publication of Debye\(^7\) and Born & Von Karman\(^8\) which lead the foundation of modern theory of lattice dynamics.

In metals there are several electrons interacting with ions that constitute the periodic lattice. It is therefore, imperative to resort to various approximations in our attempt to solve the problem.

2.2 The Adiabatic Approximation

A metal is regarded as an assembly of positively charged ions forming the periodic lattice and valence electrons moving through it. The core electrons are assumed to move rigidly with nuclei. The valence electrons respond to the motion of ions in such a way as to screen out the local charge fluctuations. The adiabatic approximation assumes that the electrons adjust themselves instantaneously corresponding to the positions of the nuclei in the perturbed crystal and the electronic state is deformed
progressively by nuclear displacements. The adiabatic approximation allows us to decouple the motion of conduction electrons from that of ions.

The total Hamiltonian of the system can be written as

$$H = H_\text{e} + H_\text{i}$$  \hspace{1cm} (2.1)

where $H_\text{e}$ is called electronic Hamiltonian and $H_\text{i}$ is the Hamiltonian for the system of bare ions. Further

$$H_\text{e} = - \sum_{i} \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r_i^2} + \sum_{l} V_i(r_i - \vec{R}_1) + \sum_{i \neq j} \frac{e^2}{r_i - r_j} \right)$$

and

$$H_\text{i} = - \sum_{l} \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial R_l^2} + \sum_{i \neq 1} U_i(\vec{R}_1 - \vec{R}_l) \right)$$

Thus Hamiltonian operator for whole system consisting of ions and electrons can be written as

$$H = - \sum_{i} \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r_i^2} + \sum_{l} V_i(r_i - \vec{R}_1) + \sum_{i \neq j} \frac{e^2}{r_i - r_j} \right)$$

$$- \sum_{l} \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial R_l^2} + \sum_{i \neq 1} U_i(\vec{R}_1 - \vec{R}_l) \right)$$  \hspace{1cm} (2.2)

Here $m$ is the mass of electron and $M$ is the mass of ion. $\vec{r}_i$ represents the position of $i$th electron and $\vec{R}_1$ denotes the displaced position of $1$th ion. The indices $i$ and $j$ run over all the valence electrons whereas $l$ and $l'$ extend overall ions. The first term in equation (2.2) is the kinetic energy operator for the electrons, the second term
for the electron ion potential and the third term represents potential due to electron electron interaction. The fourth term is the K.E. operator of ions and the last term is the potential energy of direct interaction between ions.

\[ V_I(r_i - R_1) \] includes exchange interaction between conduction and core electrons. Core electrons are regarded as tightly bound with the nuclei. \[ U_I(R_i - R_1) \] includes Coulomb repulsion between ions and core-exchange interaction.

The problem of determining the eigenvalues of Hamiltonian (2.2) is a difficult task, however the adiabatic approximation or the Born Openheimer approximation introduces tremendous simplification in the problem by separating the dynamical aspects of electron and ion motion in equation (2.2).

Let the eigenfunction for Hamiltonian \( H \) is given by

\[ \Psi_q = \psi(r, R) \varphi(R) \] (2.3)

where \( \psi(r, R) \) satisfies the Schrödinger equation for the electrons in a static lattice frozen with the 1th ion at \( R_1 \), as given below

\[ H \psi(r, R) = E_e(R) \psi(r, R) \] (2.4)

The eigenfunction \( \psi(r, R) \) and eigenvalue \( E_e(R) \) depend on the position of ions.

Applying operator \( H \) to the crystal wave function \( \Psi_q \) and using equations (2.1) and (2.4) one gets

\[ H \Psi_q = H_I \Psi_q + H_e \Psi_q \]
\[ H \Psi_q = \Psi(\vec{r}, \vec{R}) \left[ -\sum_{i=1}^{M} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial r_i^2} + \sum_{l \neq 1'} U_I(\vec{R}_1 - \vec{R}_1') \right. \]

\[ \left. + E_{e}(\vec{R}) \right] \varphi(\vec{R}) - \sum_{i=1}^{M} \frac{\hbar^2}{2M} \left[ 2 \frac{\partial \Psi}{\partial \vec{R}_1} \frac{\partial \varphi}{\partial \vec{R}_1} + \frac{\partial^2 \Psi}{\partial \vec{R}_1^2} \varphi(\vec{R}) \right] \]

(2.5)

If the last summation in equation (2.5) deleted we can solve our complete eigen value problem \( H \Psi_q = E_q \Psi_q \), by making \( \varphi(\vec{R}) \) satisfy a Schrodinger type equation

\[ \left[ \sum_{i=1}^{M} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial r_i^2} + \sum_{l \neq 1'} U_I(\vec{R}_1 - \vec{R}_1') + E_{e}(\vec{R}) \right] \varphi(\vec{R}) = E_q \varphi(\vec{R}) \]

(2.6)

Equation (2.6) represents the Schrodinger equation for ions alone. It shows that the motion of an ion is governed by the effective potential \( \left[ \sum_{l \neq 1'} U_I(\vec{R}_1 - \vec{R}_1') + E_{e}(\vec{R}) \right] \).

Obviously electrons contribute adiabatically to the lattice energy.

The justification of this approximation can be understood by knowing the magnitudes of different terms neglected in equation (2.5). The last term of equation (2.5) contains two factors. We can easily prove that they contribute almost nothing to the expectation value of energy of the system in the state \( \Psi_q \). The first factor of last term vanishes as it produces integral like

\[ \int \Psi^* \frac{\partial \Psi}{\partial \vec{R}_1} d\tau = \frac{1}{2} \frac{\partial \Psi^* \Psi}{\partial \vec{R}_1} d\tau \]

\[ = \frac{1}{2} \frac{\partial n_e}{\partial \vec{R}_1} \]
where \( n_e \) is the total number of electrons. In the same way the second factor of last term is small in view of the fact that the electrons are tightly bound to their ions

\[
\psi(r_i, R_1) = \psi(r_i - R_1)
\]

It gives a contribution like

\[
- \int \psi^* \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial r_i^2} \, dt = - \frac{m}{M} \int \psi^* \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial r_i^2} \, dt
\]

so it is kinetic energy of electrons multiplied by \( \frac{m}{M} \), but \( \frac{m}{M} \) is \( 10^{-5} \) so entire contribution can be neglected in comparison to ordinary thermal energies.

In this approximation the electrons respond so quickly to the motion of the ions that their state is always a function of ionic coordinates. The adiabatic approximation allows us to separate ionic motion from the electronic motion leaving only a residual interaction between electrons and phonons. So we can treat the electrons and lattice waves as nearly independent entities and can assign for electrons and ions the same coordinates.

2.3 Harmonic Approximation

In the harmonic approximation the potential energy of crystalline solid is expanded in powers of the amplitude of atomic vibrations and the terms higher than the quadratic are neglected. The crystal lattice with a basis is assumed to have no vacancies, dislocations and impurities.
The equilibrium position of Kth ion in the 1th cell is given by
\[
\vec{R}^O(1, k) = \vec{R}^O(1) + \vec{R}^O(k)
\] (2.7)
where \(\vec{R}^O(k)\) denotes the equilibrium position of kth ion with respect to the cell while \(\vec{R}^O(1)\) is the position of origin of 1th cell. The ions execute small oscillations about their equilibrium positions at finite temperature because of thermal agitation. If the displacement of the (1, k)th ion from the equilibrium position be \(\vec{u}(1, k)\), so the displaced position of ion is given by
\[
\vec{R}(1, k) = \vec{R}^O(1, k) + \vec{u}(1, k)
\] (2.8)
Distance between the kth ion in the 1th cell and k'th ion in 1'th cell at any moment is given by
\[
\vec{R}(1, k) - \vec{R}(1', k') = \vec{R}(1, 1')
\] (2.9)

The potential \(V\) of the whole lattice will be function of \(R(k, k')\) as two ions vibrate about their equilibrium positions. The total energy of the lattice
\[
T = \frac{1}{2} \sum_{1, k, \alpha} M_k \vec{u}_{\alpha=x,y,z}(1, k) \] (2.10)
If the displacement \(\vec{u}(1, k)\) is smaller than the interatomic spacing the potential energy may be expanded in powers of \(\vec{u}(1, k)\) in Taylor's series. Because of rapid convergence series, higher terms than second order of \(\vec{u}(1, k)\) are neglected.
If $V$ is the total potential energy due to nuclear displacement, then under this approximation

$$V(R) = V_0 + V_1 + V_2$$  \hspace{1cm} (2.11)

where $V_0$ = equilibrium potential energy of the crystal

$$V_1 = \sum_{l,k,\alpha} V_{\alpha}(l, k) \ddot{u}_{\alpha}(l, k)$$

where

$$V_{\alpha}(l, k) = \left. \frac{\partial^2 V}{\partial u_{\alpha}(l, k)} \right|_0$$  \hspace{1cm} (2.12)

also

$$V_2 = \frac{1}{2} \sum_{l,k,\alpha,\beta} V_{\alpha\beta}(l k, l'k') \ddot{u}_{\alpha}(l, k) \ddot{u}_{\beta}(l', k')$$

where

$$V_{\alpha\beta} = \left. \frac{\partial^2 V}{\partial u_{\alpha}(l,k) \partial u_{\beta}(l'k')} \right|_0$$  \hspace{1cm} (2.13)

The subscript zero shows that derivation is to be evaluated for equilibrium. $\alpha$ and $\beta$ are the Cartesian components.

$V_{\alpha}(l, k)$ is the negative of the force on the ion in the direction at $R^0(l, k)$ which is clearly zero. $V_{\alpha\beta}(l k, l'k')$ is the force constant acting on the ion at $R(l, k)$ in the $\alpha$-direction when the ion at $R(l', k')$ is displaced a unit distance along $\beta$ direction. The equation of motion is

$$M_k \ddot{u}(l, k) = \frac{V(R)}{\ddot{u}_{\alpha}(l, k)}$$

$$= - \sum_{l',k',\beta} \frac{\partial^2 V}{\partial u_{\alpha}(l,k) \partial u_{\beta}(l'k')} \ddot{u}_{\beta}(l'k')$$

$$= - \sum_{l',k',\beta} V_{\alpha\beta}(l, k, l'k') u_{\beta}(l'k')$$  \hspace{1cm} (2.14)
where

\[ V_{\alpha\beta}(l, k, l', k') = \left. \frac{\partial^2 V}{\partial u_\alpha(l, k) \partial u_\beta(l', k')} \right|_0 \]

The solution of equation (2.14) can be obtained by running wave of the form as given below as there exists the periodicity of the lattice. The wave is

\[ \tilde{u}_\alpha(l, k) = \frac{u_\alpha(k)}{\sqrt{M_k}} \exp \left[ -i \left\{ \omega(q) t - \vec{q} \cdot \vec{R}(l, k) \right\} \right] \]

(2.15)

where \( \omega \) is the frequency and \( q \) is propagation vector with magnitude \( 2\pi/\lambda \), \( \lambda \) being the wavelength. We assume here that all ions of type \( k \) vibrate with the vector amplitude \( \tilde{u}(k) \) which is independent of \( l \).

Substituting the value of \( u(k) \) and its second time derivative in equation (2.14) we get

\[ M_k \omega^2 \frac{1}{\sqrt{M_k}} u_\alpha(k) = \Sigma_{l', k', \beta} V_{\alpha\beta} u_\beta(k') \exp \left[ -i \vec{q} \cdot \left\{ \vec{R}(l', k') - \vec{R}(l, k) \right\} \right] \]

or

\[ \omega^2(q) u_\alpha(k) = \frac{1}{\sqrt{M_k} M_{k'}} \Sigma_{l', k', \beta} V_{\alpha\beta} u_\beta(k') \exp \left[ -i \vec{q} \cdot \left\{ \vec{R}(l', k') - \vec{R}(l, k) \right\} \right] \]

(2.16)

Let us define

\[ D_{\alpha\beta}(q, k k') = \frac{1}{\sqrt{M_k M_{k'}}} \Sigma_{l' k'} V_{\alpha\beta} \exp \left[ -i \vec{q} \cdot \left\{ \vec{R}(l, k) - \vec{R}(l', k') \right\} \right] \]

(2.17)

so that
$\Sigma_{\kappa' \beta'} D_{\alpha \beta}(\vec{q}, \kappa' \kappa') u_{\beta}(\kappa') - \omega^2 u_{\alpha}(\kappa) = 0$

$\Sigma_{\kappa' \beta'} D_{\alpha \beta}(\vec{q}, \kappa' \kappa') - \omega^2 \delta_{\alpha \beta} \delta_{\kappa' \kappa'}) u_{\beta}(\kappa') = 0 \quad (2.18)$

where $\delta_{\alpha \beta}$ and $\delta_{\kappa' \kappa'}$ are Kronecker deltas. In the matrix notation (2.18) can be written in the form

$[D_{\alpha}(\vec{q}) - \omega^2 I] u_{\beta}(\kappa) = 0 \quad (2.19)$

The matrix $D_{\alpha}(\vec{q})$ is called Dynamical matrix and $D_{\alpha \beta}(\vec{q}, \kappa' \kappa')$ are its elements. This matrix is Hermitian in nature. $I$ is a unit matrix and $u_{\beta}(\kappa)$ a column matrix. The condition that the set of equations represented by equation (2.19) have a nontrivial solution is that the determinant of the coefficients must vanish. Hence

$|D_{\alpha}(\vec{q}) - \omega^2 I| = 0 \quad (2.20)$

This is called secular determinant. The matrix $D_{\alpha}(\vec{q})$ is of order $(6 \times 6)$ in hcp structure.

2.4 The Self Consistent Field Approximation

In the pseudopotential theory the most crucial approximation to be made is the self consistent field approximation. The electrons in a metal form a kind of gas which is different from the perfect gas because of strong interactions of electrons among themselves and also with the positive ions. Due to large interaction, a gas of this kind must be too complicated for simple calculations. However in quantum mechanics the effect of one electron on
all others to a large extent can be averaged and so each electron is thought as moving in the field of other electrons. The average potential depends on the distribution of electrons and upon the states which are occupied by them. These states in turn depend upon the potential as so we must compute the potential self consistently. Lastly the only important interaction between the electrons is the Coulomb repulsion, but this is further divided into three distinct contributions.

(a) Hartree potential\(^{12}\) obtained by computing the time average of electron distribution and then using Poissons equation to determine the corresponding potential.

(b) The correction for the potential seen by an electron with spin is at a position \(\mathbf{r}\), no other electron of the same spin can lie at that point simply because of antisymmetry of the wavefunction. This effectively gives a hole in the electron distribution and gives rise to exchange interactions.

(c) The contribution arising from the correlated motion of the electron, which is known as correlation energy. These corrections fall under the well known Hartree Fock approximation. In Hartree Fock approximation the effect of correlation has not been properly considered. On account of the use of determinantial wavefunction the correlation of parallel spins only is taken into account while the correlation due to antiparallel spin is not being
considered. Such type of correlation has been considered by Seitz and Bohm and Pins.\textsuperscript{13}

2.5 Formulation of the Pseudopotential

Sophisticated attempts have been made in recent years to treat many electron effects which has been ignored in the Hartree Fock approximation. The proper use of this approximation, its flexibility and usefulness of the technique has been discussed in 'Modern many body theory' by Anderson.\textsuperscript{14} The study of simple metals traditionally begins with the Hartree equation which is widely simplified form of true Schrodinger equation for a metal. In practice exchange and correlation effects are included in one or self consistent approximations.

The basic aim in the lattice dynamic studies is to find techniques for obtaining wavefunctions and energy dispersion relations for electron in metals. If these relations are, one can in principle calculate any property of the metal.

If wavefunction $|\Psi_k>$ describes the electron with crystal momentum $\mathbf{k}$ moving in a periodic lattice with potential $V_I$, the self consistent potential due to all other electrons in the lattice is given by $V_e$ and $E_k$, the energy eigenvalue we seek, then one tries to solve equation

$$(T + V_I + V_e) |\Psi_k> = E_k |\Psi_k>$$

(2.21)

The equation (2.21) is most simplified form of the true problem but the solution of above equation is very difficult. In approximate method for solution one can expand the
wavefunction $|\Psi_k\rangle$ in some orthogonal basis such as plane waves,

$$<\vec{r} | \vec{k}> = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}}$$  \hspace{1cm} (2.22)

where $\Omega$ is the volume of the system. The energy $E_k$ is then determined by diagonalizing a Hamiltonian matrix. One hopes that the wavefunction expansion converges rather rapidly so that the resulting matrices are not too unwieldy.

Rather elegant and sophisticated techniques have been developed for solving equation (2.21). The two methods most frequently used are augmented-plane-wave (APW) method and orthogonalized-plane-wave (OPW) method. Both methods yield the energy dispersion relation known in solid state theory as band structure. In practice it is difficult to use the band structure to calculate all the important properties about solids of our interest.

The perturbation theory can also be useful method for the solution of equation (2.21), but this suffers from a serious drawback. The deep core potential $V_I(r)$ is strong and attractive and wavefunction $\Psi_k$ has several nodes in the core region. The oscillatory behaviour of true wavefunction shows that the electron has large $k.E$ as it traverses the core region and so it would require many plane wave to expand such oscillatory wavefunction. However, this difficulty has been largely overcome in APW and OPW methods. The problem in application of perturbation theory, is the depth of core potential at the ion site. It is not tenable to regard this potential as perturbation in the free electron frame.
To overcome this difficulty the model potential theories have been developed.

The motivation behind all the theories is to replace the deep ion core potential by a shallow potential well $W(\mathbf{r})$. Since the potential in the core region is shallow the electron can move across the core. It means that the model wavefunction $\varphi_k(r) = \langle \mathbf{r} | \varphi_k \rangle$ is smooth. The model wavefunction is constructed in such a way as to preserve the true eigenvalue of the system and is generally a function of this eigenvalue. The equation (2.21) can be written as

\[
(T + W(E_k) + V) |\varphi_k\rangle = E_k |\varphi_k\rangle
\]  
(2.23)

Equation (2.21) as well as equation (2.23) has same value of $E_k$. In the equation (2.23) although the dispersion relation is not changed but the metal wavefunction does not describe electron in a metal exactly and so the pseudo wavefunction $|\varphi_k\rangle$ is to be related with true wavefunction $|\Psi_k\rangle$. The difference between various model potential methods is the technique used to construct $W(\mathbf{r})$. In the equation (2.23) the potential can be regarded as a perturbation in the free electron system. The problem now remains that of algebra to obtain perturbation expansion for both $E_k$ and $\varphi_k(\mathbf{r})$.

From these results several metallic properties can be studied directly. The importance of the model theories is this that using perturbation theory the calculation of properties of metals can be done from the first principles.
2.6 The Orthogonalised Plane Wave Method

Pseudopotential theory as developed by Harrison\textsuperscript{15,16} and others\textsuperscript{17,18} has been extensively used in studying various properties of metals. The phenomenological or model pseudopotential theory differs from the first principle theory by the fact that the later does not require any explicit parameter which is borrowed from experimental data.

In self consistent field approximation the electronic behaviour is obtained from a one electron Schrodinger equation of the type,

\[ H \psi_i = \{T + V_I(r)\} \psi_i = E_i \psi_i \]  

(2.24)

Here $E_i$ is the energy of $i$th state while $T$ is the kinetic energy operator ($-\frac{\hbar^2}{2m} \nabla^2$). $V_I(r)$ is the self consistent potential seen by each electron. The core state $\psi_\alpha$ with energies $E_\alpha$ are different from the conduction band state $\psi_\kappa$ with energies $E_\kappa$. The suffix $\alpha$ denotes the position of the ion as well as energy and angular momentum quantum number of the state.

As the positive kinetic energy of the valence electron inside the atomic core is almost completely cancelled by the negative potential, the free electron like character of the electronic energy bands of simple metals allows the effect of periodic potential on the electrons to be treated as perturbation. In the small core approximation the core states are the same as in the isolated ion but their energies $E_\alpha$ are different. These core states are
computed in Hartree-Fock approximation. Now it remains the problem of obtaining the conduction band states, by solving the eigenvalue equation

$$H |\Psi_k\rangle = \{T + V_I(\vec{r})\} |\Psi_k\rangle = E_k |\Psi_k\rangle \quad (2.25)$$

If the wavefunction is expanded by choosing the plane waves then large number of plane waves are needed to get reasonably correct wavefunction. According to Herring an expression in terms of orthogonalised plane waves would require much fewer terms and to produce less inconvenience in the calculation.

An OPW of wavenumber $K$ may be written as

$$\text{OPW}_K = e^{iK \cdot \vec{r}} - \sum_\alpha \Psi_\alpha(\vec{r}) \Psi_\alpha^*(\vec{r}') e^{iK \cdot \vec{r}'} d\tau' \quad (2.26)$$

This is in fact orthogonal to any core state.

The normalization of plane waves is done in volume of the metal $\Omega$ such that plane waves and normalized core functions are written as kets:

$$|\vec{K}\rangle = \Omega^{-1/2} e^{i\vec{K} \cdot \vec{r}} \quad (2.27)$$

$$|\alpha\rangle = \Psi_\alpha(\vec{r}) \quad (2.28)$$

In which $|\vec{K}\rangle$ denotes the plane waves and $|\alpha\rangle$ is the core wavefunctions. The normalized plane waves in this notation become as

$$\text{OPW}_K = |\vec{K}\rangle - \sum_\alpha |\alpha\rangle \langle\alpha| K\rangle \quad (2.28)$$

where a bra $\langle \alpha | = |\alpha\rangle^*$ and a ket facing each other represent an integral:
\[ <\alpha | \mathbf{K} > = \Omega^{-1/2} \int \psi^{*}_\alpha(r) e^{i\mathbf{K} \cdot \mathbf{r}} d\tau \]  

(2.29)

Sometimes it is very useful to write OPW in terms a projection operator \( P \) which projects any wavefunction on to the core state so we write

\[ P = \sum_\alpha |\alpha> <\alpha| \]  

(2.30)

So OPW takes the form

\[ \text{OPW}_K = (1 - P) |K> \]  

(2.31)

Now conduction band state can be expanded in terms of a general linear combination of OPW's

\[ \psi_K = \sum_q C_q(K) (1 - P) |K + q> \]  

(2.32)

When this function for \( \psi_K \) is substituted into the Schrödinger equation (2.25) we get

\[ \sum_q C_q(K) H(1 - P) |K + q> = E_K \sum_q C_q(K) (1 - P) |K + q> \]  

(2.33)

multiplying on left by \( <K + q| \) keeping in view that

\[ HP = \sum_\alpha E\alpha |\alpha> <\alpha|, \] we get

\[ C_q'(K) \frac{\hbar^2}{2m} |K + q|^2 + \sum_q C_q(K) \left[ <K + q'| V |K + q> \right] \]

\[ - \sum_\alpha E\alpha <K + q'| \alpha> <\alpha| K + q> \]

\[ = [C_q'(K) - \sum_q C_q(K) <K + q'| P |K + q>] E_K \]  

(2.34)

This is called orthogonalized plane wave (OPW) calculation.
2.7 The Pseudopotential and Cancellation Theorem

It was noted by Phillips and Kleinman that all the terms in the projection operator in equation (2.33) could be taken to the left side to obtain a form

$$T\phi_k + W\phi_k = E\phi_k$$  \hspace{1cm} (2.35)

where $W$ is called the pseudopotential and is defined by

$$W = V(\hat{r}) + \sum \langle \phi | (E_k - E)|\alpha \rangle \langle \alpha | = V(\hat{r}) + (E_k - H)\phi$$  \hspace{1cm} (2.36)

$\phi_k$ is called the pseudowave function and is defined by

$$\phi_k = \sum_q C_q(\hat{K}) |\hat{K} + q\rangle$$  \hspace{1cm} (2.37)

where $C_0(\hat{K}) = 1$

The equation (2.35) is called the pseudopotential equation since $\phi_k$ is expected to be smooth, $W$ is expected to be small in some sense. Thus it may form the basis for the free electron like description of the state. An interesting point to be noted is that due to presence of the projection operator the pseudopotential is not a simple potential. The pseudopotential is nonlocal in contrast to $V(\hat{r})$, a local potential that depends only on position ($\hat{r}$). A nonlocal potential means, that the potential depends not only on the scattering momentum but also on initial state number and on the scattering angle between them. This complicates the calculation based upon the pseudopotential; but the simplicity arising from the weakness of the pseudopotential far outweighs this complication for many purposes. Further
it will be reasonable to approximate $W$ by local pseudo-potential.

One of the important features is the value of $W$ is small in comparison to the true potential. The potential $V_I(\mathbf{r})$ is attractive. The second term in the pseudopotential equation (2.36) contains the difference $(E_K - E_\alpha)$ which will always be positive since the core energies $E_\alpha$ lie below $E_K$. The projection operator $P$ is essentially positive and therefore, this positive term will cancel to some extent the attractive potential $V_I(\mathbf{r})$. This cancellation is known as "the cancellation theorem". The net effective potential arising from the cancellation theorem is very weak and is known as the pseudopotential.