

Electronic Structure in the condensed state

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L11: Part III Chemistry

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Lectures 1-6

Books

There are a large number of excellent books which cover the material of this course, of which the following is a small selection:

D. Pettifor, ‘Structure and Bonding in Molecules and Solids’ (OUP)

R.M. Martin, ‘Electronic Structure’ (CUP)

S.R. Elliott, ‘Physics and Chemistry of Solids’

A. Szabo and N.S. Ostlund, ‘Modern quantum chemistry’, Dover.

I. INTRODUCTION

The first part of this course will be concerned with *band theory of crystals*, i.e. electronic structure as studied in the context of non-interacting electrons immersed in periodic potentials.

Crystals can be idealized as consisting of a *large* (i.e. macroscopic) number of *unit-cells*, assembled together in a pattern which repeats itself indefinitely. The simplest example that we can think about is simply a one-dimensional (1D) row of identical atoms, with *lattice constant* a , i.e. whose atoms are located at sites $R_n = n.a$ along the x -axis. In 2D and 3D, more complex lattices arise. In these cases we need to specify *lattice vectors* ($\mathbf{a}_1, \mathbf{a}_2$ and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ respectively). We will leave these more complex situations until later. Our purpose initially is to understand the implications that an underlying periodic potential has on the electronic structure. Let us consider our 1D crystal. The potential due to the nuclei $V(x)$ must also be periodic:

$$V(x + a) = V(x) \tag{1}$$

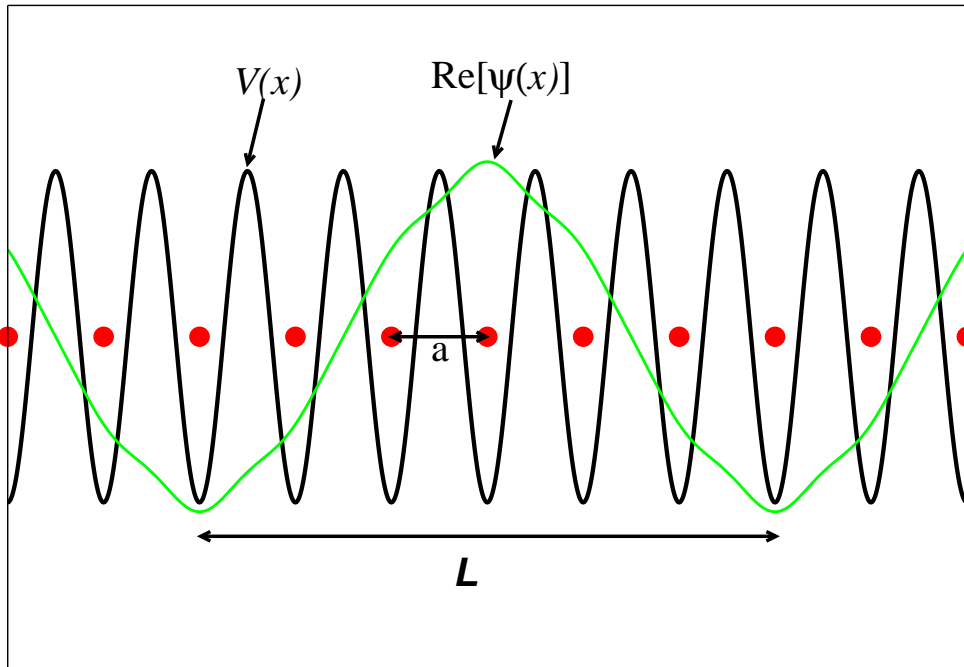


FIG. 1: Born-Kármán boundary conditions: $V(x)$ is periodic over a ; $\psi(x)$ is periodic over L .

But is this true? It would be true if the crystal extended to infinity, but obviously won't be true for a finite crystal which terminates at a surface (in this case two terminal atoms). This introduces complicating surface effects which we would like to avoid. To do so, we introduce a computational trick called the *Born-Kármán* boundary conditions: We 'tie' the end atoms together to form a ring. Formally stated, we say that there are N atoms in our 1D chain, so that the length of the chain is

$$L = Na. \quad (2)$$

Then the Born-Kármán boundary condition amounts to stating that all distances x are modulo L , so that

$$x + nL \rightarrow x, \quad \text{for any integer } n, \quad (3)$$

making

$$V(x + L) = V(x), \quad \text{for all } x. \quad (4)$$

A crucial implication is that the one-particle wavefunctions have the periodicity of the length L of the crystal:

$$\psi(x + L) = \psi(x) \tag{5}$$

Note the distinction between the periodicity of the potential and that of the wavefunction. The potential is periodic over a (a microscopic distance), while the wavefunction is periodic over L (a potentially macroscopic distance).

These two different periodicities are a constant source of confusion, so you will need to be totally clear about them. The first, over a , expresses the fundamental translational symmetry of the lattice. It is a property of the lattice. In 2D and 3D, the corresponding quantities are the lattice vectors. The second, periodicity over L , is purely a convenient theoretical device. It has no deep consequence of its own, being introduced only to remove complicating surface effects. In fact, in many cases we will be interested in what happens when we let N (and therefore L) tend to ∞ .

II. PLANE WAVES AND RECIPROCAL SPACE

How are we going to describe the one-electron wavefunctions in our crystal? One way to do so (and a very popular way) is to use *plane-wave* functions. Consider first of all the following situation. Let us remove (i.e. ‘switch off’) the underlying crystal potential, and at the same time maintain the Born-Kármán B.C. What are the solutions to the Schrödinger equation there? Answer:

$$\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx} \tag{6}$$

Satisfy yourselves that this function has the following properties:

- (1) It is normalised over L .
- (2) It is a periodic function with periodicity $2\pi/k$.
- (3) It carries a definite momentum $\hbar k$.
- (4) A particle of mass m in such a state has a definite amount of kinetic energy $\hbar^2 k^2 / 2m$ associated with it. For finite L , the values which k can assume are *discrete*:

$$k_n = \frac{2\pi \cdot n}{L}, \tag{7}$$

where n is any integer $n = 0, \pm 1, \pm 2, \dots$. The spacing between two adjacent k_n is obviously

$$k_{n+1} - k_n = \frac{2\pi}{L} \quad (8)$$

which for a given L is a constant, and in addition, diminishes linearly as $L \rightarrow \infty$. Since N (and therefore L) is rather arbitrary (it simply defines the number of unit cells in our crystal), you can see that the spacing between the k_n can be made arbitrarily small by making the crystal larger. In this sense k_n is said to be *quasi-continuous*. The energy levels ϵ_k associated with $\psi_k(x)$ are simply:

$$\epsilon_k = \frac{\hbar^2}{2m} k^2 \quad (9)$$

[We will frequently use Hartree atomic units in which:

$$\hbar = m_e = e^2 = 1 \quad (10)$$

in which case $\epsilon_k = k^2/2$].

If we sketch eqn.(9) as a function of k we simply get a parabola extending off to infinity as $k \rightarrow \pm\infty$. Note there is no restriction as to how large k can get; a very large k corresponds to a very short wavelength (and therefore high-energy) plane-wave, but it is a perfectly good solution to the free-electron Schrödinger equation. Suppose we now recall that there is supposed to be an underlying crystal periodicity of length a . As soon as we introduce this second (shorter length) periodicity we introduce a subtle structure on the k (actually k_n), which amounts to a new way of classifying the k_n . How so? Let us take an example. Suppose $N = 10$ (i.e. $L = 10a$). Consider a specific but otherwise arbitrary k_n , e.g. k_{91} . We could write this as follows:

$$k_{91} = \frac{2\pi}{10a} .91 \quad (11)$$

$$= \frac{2\pi}{a} .9 + \frac{2\pi}{10a} .1 \quad (12)$$

$$= G_9 + k_1 \quad (13)$$

where

$$G_n = \frac{2\pi}{a} .n, \quad n = 0, \pm 1, \pm 2, \dots \quad (14)$$

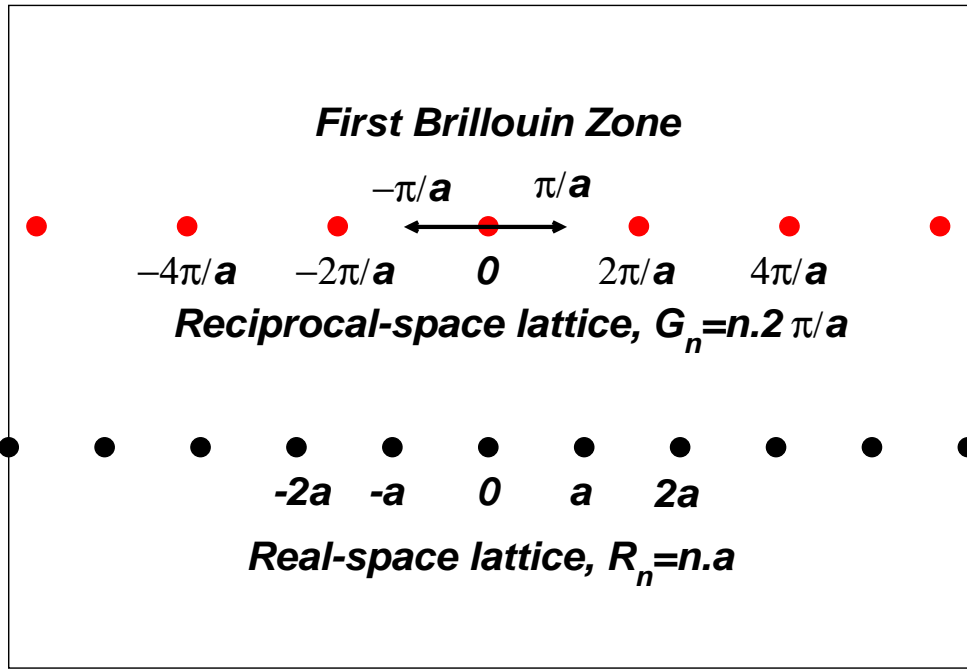


FIG. 2: Real-space and reciprocal-space lattices in 1D.

is a *reciprocal lattice number*.

Note that G_m is defined purely by the underlying lattice (i.e. lattice constant a): it's unrelated to N or L . What we have done is to write k_{g1} as a sum of a reciprocal lattice number (in this case G_9) and a wavenumber k_1 *which is smaller than the smallest reciprocal lattice number i.e. G_1* . Obviously, this result is quite general: any k_n can be written in this way:

$$k_n = G_{\text{nint}(n/N)} + k_{\text{frac}(n/N)} \quad (15)$$

where

$$\text{nint}(n/N) = \text{the nearest integer to } n/N \quad (16)$$

and

$$\text{frac}(n/N) = n - N.\text{nint}(n/N) \quad (17)$$

(i.e., roughly speaking, 'the remainder'). For example

$$\text{nint}(96/10) = \text{nint}(9.6) = 10, \quad (18)$$

$$\text{frac}(96/10) = 96 - 10 \times 10 = -4. \quad (19)$$

Eqn.(15) has the following implication. Consider the set of all k_n with $n = 0, \pm 1, \pm 2, \dots$. This set can be divided into two, those fall within:

$$-\frac{\pi}{a} \leq k_n \leq \frac{\pi}{a} \quad (20)$$

with

$$n = 0, \pm 1, \pm 2, \dots, \pm N/2 \quad (21)$$

and those which are outside this zone, i.e.

$$|n| > N/2.$$

For those which fall outside this zone, can be written as a sum of a wavenumber k_n which falls *inside* the zone and a specific G_m . The zone:

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a} \quad (22)$$

is the *First Brillouin Zone* (FBZ) of the 1D crystal. We shall see that it plays a fundamental role in the theory of solids.

Any wavenumber k_m outside the FBZ can be labeled (or mapped on to) a wavevector inside the FBZ by a simple translation by an integer multiple of G_1 . This leads to the idea of a *reduced* zone representation of the free-electron expression:

$$\epsilon_k = \frac{\hbar^2}{2m} k^2$$

Rather than drawing the free-electron parabola, extending to $k \rightarrow \pm\infty$, we draw it as follows: (1) k from 0 to $\pm\pi/a$ i.e. up to the FBZ, we draw the free-electron parabola as usual.

(2) For all k between π/a and $2\pi/a$, we translate them back by $G_1 = 2\pi/a$ (i.e. $k \rightarrow k - G_1$). This brings them (or folds them) back in to the FBZ. However, the energy of these states is still $\hbar^2 k^2 / 2m$.

(3) Generalizing this procedure, any k between $m\pi/a$ and $(m+1)\pi/a$ is mapped back

Free electron bands in reduced- and full-zone scheme

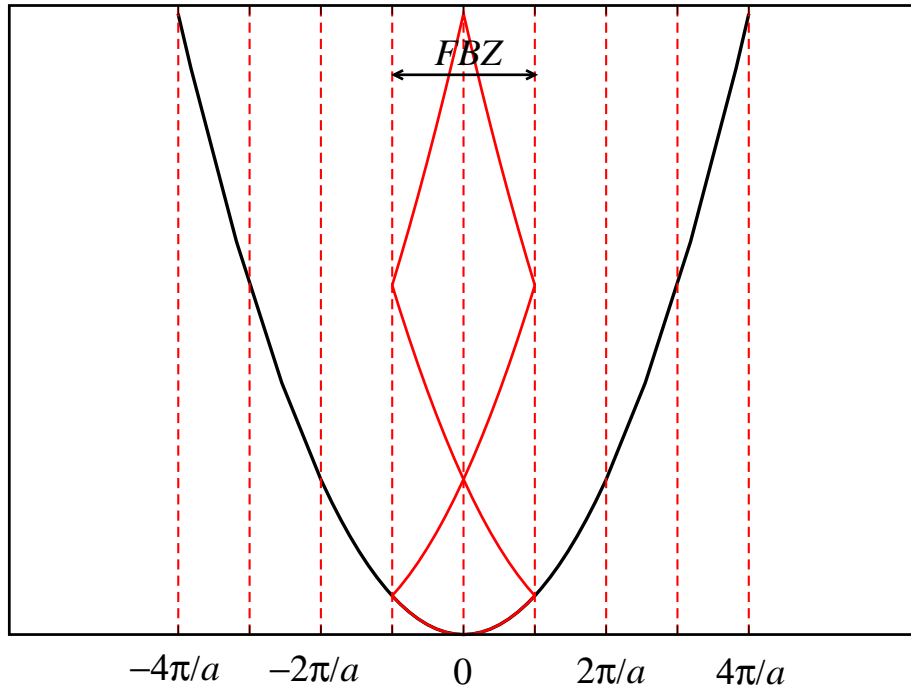


FIG. 3: Free electron bands in reduced and full-zone scheme

into the FBZ by $k \rightarrow k - G_m$.

Therefore, in this reduced zone scheme, each wavenumber k inside the FBZ is a *multiple-valued* function for the energy

$$\epsilon_k^{(m)} = \frac{\hbar^2}{2m}(k + G_m)^2, \quad m = 0, \pm 1, \pm 2 \dots$$

where the label $m \neq 0$ refers to a particular k outside the FBZ.

III. BLOCH'S THEOREM

We are now in a position to state a crucial theorem. We have noted for our 1D crystal obeying the Born-Kármán boundary conditions that:

(1) the potential is periodic with the lattice constant a :

$$V(x) = V(x + a);$$

(2) the one-particle wavefunctions are periodic with crystal length $L = Na$:

$$\psi(x) = \psi(x + L).$$

If the potential $V(x)$ is periodic with a , then the number density (or *density* for short) of electrons $n(x)$ must also be periodic with a . But for any one-particle state $\psi(x)$, its associated density is:

$$n(x) = \psi^*(x)\psi(x) = |\psi(x)|^2 \quad (23)$$

Therefore $\psi(x + a)$ must be related to $\psi(x)$ via

$$\psi(x + a) = e^{ika}\psi(x) \quad (24)$$

where k is (for the moment) any arbitrary wavenumber independent of x , since then:

$$|\psi(x + a)|^2 = |\psi(x)|^2 \quad (25)$$

as required by the density $n(x)$.

Eqn.(24) is a statement of Bloch's theorem. It says that the wavefunction $\psi(x)$ can only change by a *constant* phase factor e^{ika} when the particle is shifted by one lattice constant. Of course k will depend on $\psi(x)$. In other words, different ψ 's will change by different phase factors for a displacement of $x \rightarrow x + a$. i.e. k can be used to label the ψ :

$$\boxed{\psi_k(x + a) = e^{ika}\psi_k(x)} \quad (26)$$

Let us examine the implications of Bloch's theorem. The most important is that $\psi_k(x)$ can be written as:

$$\boxed{\psi_k(x) = e^{ikx}u_k(x)} \quad (27)$$

where $u_k(x)$ is a periodic function with periodicity a :

$$u_k(x + a) = u_k(x) \quad (28)$$

This can be easily verified:

$$\begin{aligned}
 \psi_k(x+a) &= e^{ik(x+a)}u_k(x+a) \\
 &= e^{ika}.e^{ikx}u_k(x+a) \\
 &= e^{ika}.e^{ikx}u_k(x) \\
 &= e^{ika}\psi_k(x)
 \end{aligned}$$

as, is required by Eqn(26). $u_k(x)$ is called a *Bloch function*. It is *not* the wavefunction, but the latter can be obtained from it easily using eqn.(27). In fact $u_k(x)$ obeys a differential equation that can be derived from the Schrödinger equation by applying \hat{H} to $\psi_k(x)$:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x) \right] e^{ikx}u_k(x) = \epsilon_k\psi_k(x) \quad (29)$$

It is left as a exercise to show that this implies:

$$\left[\frac{\hbar^2}{2m} (-i\nabla + k)^2 + V(x) \right] u_k(x) = \epsilon_k u_k(x) \quad (30)$$

[Hint: show

$$\nabla\psi_k(x) = ik\psi_k(x) + e^{ikx}\nabla u_k \quad (31)$$

and:

$$\nabla^2\psi_k(x) = -e^{ikx}[-i\nabla + k]^2 u_k \quad (32)$$

It is important you that should be able to derive these equations.]

Therefore, given a periodic potential $V(x)$, we need to solve Eqn.(30) for *each value of k* to obtain $u_k(x)$, from which we can obtain $\psi_k(x)$ using Eqn.(26). Let us now investigate the properties of $u_k(x)$, and the corresponding energy eigenvalues ϵ_k . In the simplest case, in which the potential $V(x) = V$ is a constant, (this is a special case of a periodic function), then it immediately follows that $u_k(x) = \text{constant}$. Why? If the potential is constant, then from a direct solution to the Schrödinger equation, we know that:

$$\epsilon_k = \frac{\hbar^2}{2m}k^2 + V \quad (33)$$

and therefore that the RHS of Eqn.(30) is:

$$\epsilon_k u_k = \left[\frac{\hbar^2}{2m} k^2 + V \right] u_k \quad (34)$$

But if $u_k(x) = \text{constant}$, then the LHS of Eqn.(30) is:

$$\frac{\hbar^2}{2m} (-i\nabla + k)^2 u_k + V u_k = \left[\frac{\hbar^2}{2m} k^2 + V \right] u_k \quad (35)$$

since the gradient terms on u_k vanish, and therefore Eqn.(35) and Eqn.(34) agree. In other words, we have:

$$\psi_k(x) = e^{ikx} \times \text{constant} \quad (36)$$

which is our old friend, the plane-wave.

Thus we can expect that, in the case of a nearly constant potential, (as for example would be found in metals), the Bloch functions $u_k(x)$ should also be nearly constant. Since k varies quasi-continuously, the energy ϵ_k also varies quasi-continuously with k . If ϵ_k varies significantly with k , it is said to show *dispersion*.

The opposite extreme occurs when $u_k(x)$ is highly localised to each atom. Examples of highly localised functions are *core* electrons, which are very tightly bound to the nuclei. The portion of $u_k(x)$ near an atomic nucleus is then identical with that of an atomic core state of the free atom. In this case, it can be shown that ϵ_k depends very little on k (i.e. it shows very little dispersion), and has a different value for each type of core state. In the intermediate case, where $u_k(x)$ is neither completely constant, nor completely localised the atomic nuclei, the energy ϵ_k is not completely quasi-continuous, as it is in the free-electron case. Instead ϵ_k shows the property of *banding*: i.e. it is quasi-continuous for large ranges of k , but is discontinuous for certain values of k . We shall see shortly that these discontinuities in ϵ_k occur at our old friend, the *Brillouin zone boundaries*.

IV. BLOCH'S THEOREM: AN APPLICATION

To see Bloch's theorem in action, we next consider the simple periodic potential:

$$V(x) = -V \cos(2\pi x) \quad (37)$$

This potential has a periodicity of 1, (i.e. we have let the lattice parameter be unity), with successive minima at $0, \pm 1, \pm 2, \dots$, and maxima at $\pm 1/2, \pm 3/2, \dots$

The Bloch equation for a given $u_k(x)$ becomes:

$$-\frac{1}{2} \frac{d^2 u_k}{dx^2} - ik \frac{du_k}{dx} + \frac{k^2}{2} u_k - V \cos(2\pi x) u_k = \epsilon_k u_k \quad (38)$$

We can solve this with the aid of a Fourier transform. Writing

$$V(x) = \sum_g \tilde{v}_g e^{i2\pi g x} \quad (39)$$

where the sum over g runs over all integers (positive and negative), note that [show]:

$$\tilde{v}_g = \begin{cases} -V/2 & \text{for } g = \pm 1 \\ 0 & \text{otherwise} \end{cases} \quad (40)$$

Now expanding $u_k(x)$ in a Fourier series:

$$u_k(x) = \sum_g \tilde{u}_g^{(k)} e^{i2\pi g x} \quad (41)$$

and substituting into the Bloch equation we obtain [show]:

$$\begin{aligned} & \sum_g e^{i2\pi g x} [2\pi^2 g^2 + 2\pi g k + k^2/2] \tilde{u}_g^{(k)} \\ & - \sum_g \frac{V}{2} [e^{i2\pi(g+1)x} + e^{i2\pi(g-1)x}] \tilde{u}_g^{(k)} \\ = & \sum_g \epsilon_k \tilde{u}_g^{(k)} e^{i2\pi g x} \end{aligned}$$

The potential term can be re-organized with the help of:

$$\sum_g [e^{i2\pi(g+1)x} + e^{i2\pi(g-1)x}] \tilde{u}_g^{(k)} = \sum_g [\tilde{u}_{g-1}^{(k)} + \tilde{u}_{g+1}^{(k)}] e^{i2\pi g x}$$

Gathering terms in $e^{i2\pi g x}$, we arrive at the banded (tridiagonal) eigenvalue equation:

$$(2g^2 \pi^2 + 2gk\pi + \frac{k^2}{2}) \tilde{u}_g^{(k)} - \frac{V}{2} (\tilde{u}_{g+1}^{(k)} + \tilde{u}_{g-1}^{(k)}) = \epsilon_k \tilde{u}_g^{(k)} \quad (42)$$

which can be solved numerically for a given value of k . To do so, we need to introduce a cut-off on the highest value g_{max} of g we consider in the Fourier expansion [41]. The matrix problem yields g_{max} distinct eigenstates, which be label according to the band index, $\tilde{u}_g^{(k,n)}, n = 1, \dots, g_{max}$. We can form the eigenstates in real-space by performing the Fourier sum [41]. In the plots below, we look at ϵ_k as a function of k and the band-index n , and several of the Bloch functions. We have set $V = 1$. Note the behaviour of ϵ_k for the lowest band $n = 1$, as k increases from 0 to π . The energy increases approximately quadratically initially, but tails off to a maximum at $k = \pi$. The second band decreases from $k = 0$, reaching a minimum at $k = \pi$: a **band-gap** of 1 ($= 2|V_1|$) has opened at $k = \pi$. We will later see this is a quite general property of periodic potentials. The gap between bands is of the order of $2|V_G|$, where $G/2$ is the g-vector of the Brillouin zone boundary.

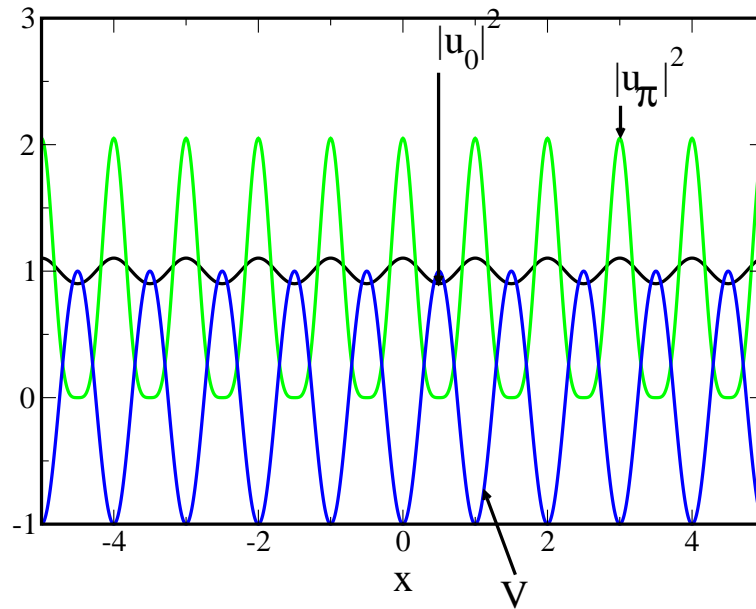
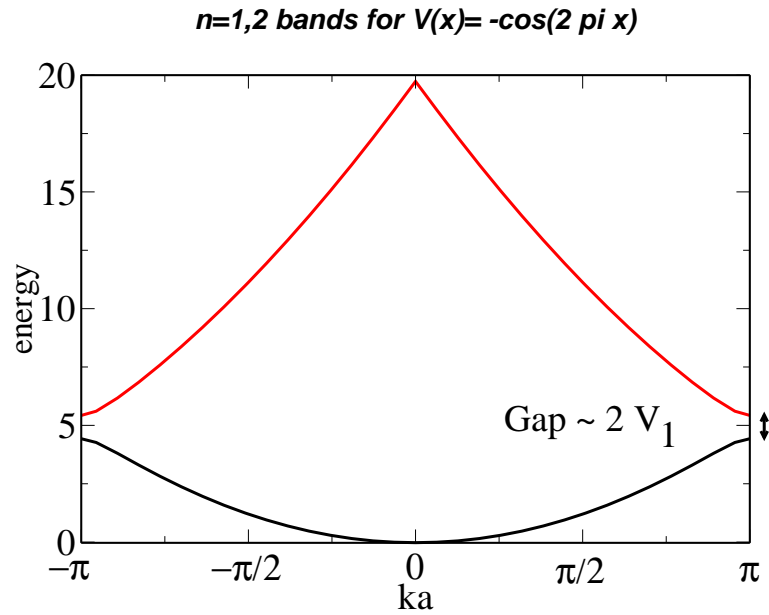


FIG. 4: Bands and Bloch functions for $V = -\cos(2\pi x)$.

V. ENERGY BANDS: THE KRONIG-PENNEY MODEL

Another instructive example which shows clearly the banding behaviour of ϵ_k is the model of Kronig-Penney, which is exactly solvable. It can be thought of as the

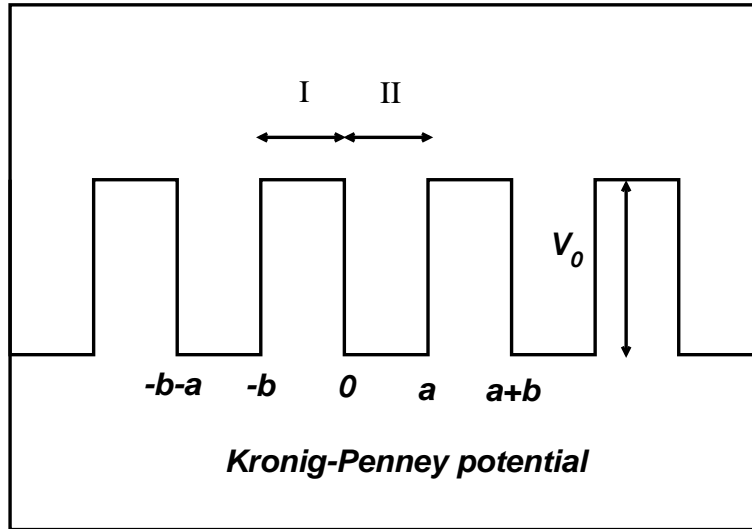


FIG. 5: Kronig-Penney potential

‘particle-in-a-box’ of solid-state theory.

In the KP model, assume the potential:

$$V(x) = \begin{cases} V_0 & -b < x < 0 \\ 0 & 0 \leq x \leq a \end{cases} \quad (43)$$

with:

$$V(x + a + b) = V(x) \quad (44)$$

The Schrödinger equation for this problem is:

$$\frac{d^2\psi}{dx^2} + \kappa^2[E - V(x)]\psi = 0, \quad \kappa^2 = \frac{2m}{\hbar^2} \quad (45)$$

Using Bloch’s theorem, in conjunction with the Born-Kármán boundary conditions, we have:

$$\psi(x) = e^{ikx}u(x), \quad k = 2\pi.n/L \quad (46)$$

where $L = N(a + b)$ is the length of the crystal, with N being large, and $u(x + a + b) = u(x)$ being periodic over $a + b$.

To find $u(x)$, we limit ourselves to one period of the lattice, say from $x = -b$ to $x = a$, and moreover, we will assume that $E < V_0$, since we shall later take the limit $V_0 \rightarrow \infty$.

Substituting $\psi(x)$ into Eqn.(45) imposes on u_k the following condition in the range $-b \leq x \leq 0$:

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 + \gamma^2)u = 0 \quad (47)$$

with solution:

$$u_I = Ae^{(-ik+\gamma)x} + Be^{(-ik-\gamma)x} \quad (48)$$

while in the region $0 \leq x \leq a$ we have:

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (k^2 - \beta^2)u = 0 \quad (49)$$

with solution:

$$u_{II} = Ce^{i(-k+\beta)x} + De^{i(-k-\beta)x} \quad (50)$$

[Verify these solutions!] Here

$$\beta = \kappa\sqrt{E}, \quad \gamma = \kappa\sqrt{V - E} \quad (51)$$

In particular, β and γ are real quantities, and will be assumed to be positive without loss of generality.

The constants A, B, C, D are going to be chosen so that $u(x)$ in the two regions have the same value and the same first derivative at $x = 0$, i.e.

$$u_I(0) = u_{II}(0) \quad (52)$$

$$u'_I(0) = u'_{II}(0) \quad (53)$$

In addition, from the periodic nature of $u(x)$, it follows that

$$u_I(-b) = u_{II}(a) \quad (54)$$

$$u'_I(-b) = u'_{II}(a) \quad (55)$$

These four conditions result in the following linear equations for

$$A + B = C + D$$

$$\begin{aligned}
(-ik + \gamma)A + (-ik - \gamma)B &= i(-k + \beta)C + i(-k - \beta)D \\
Ae^{(ik-\gamma)b} + Be^{(ik+\gamma)b} &= Ce^{i(-k+\beta)a} + De^{i(-k-\beta)a} \\
(-ik + \gamma)Ae^{(ik-\gamma)b} + (-ik - \gamma)Be^{(ik+\gamma)b} &= \\
i(-k + \beta)Ce^{i(-k+\beta)a} + i(-k - \beta)De^{i(-k-\beta)a} &
\end{aligned}$$

These four equations lead to a horrendous 4x4 determinantal problem, which after non-trivial manipulation simplifies to the following equation relating β and γ (and hence E) to the wavevector k :

$$\begin{aligned}
\frac{\gamma^2 - \beta^2}{2\beta\gamma} \sinh(\gamma b) \sin(\beta a) + \cosh(\gamma b) \cos(\beta a) \\
= \cos[k(a + b)]
\end{aligned} \tag{56}$$

Passing now to the limit $b = 0$ and $V_0 = \infty$ in such a way that that $\gamma^2 b$ stays finite (i.e. the area under the potential stays finite), and calling

$$\lim_{b \rightarrow 0, \gamma \rightarrow \infty} \frac{\gamma^2 ab}{2} = P \tag{57}$$

this relation becomes:

$$P \frac{\sin(\beta a)}{\beta a} + \cos(\beta a) = \cos(ka) \tag{58}$$

which is a transcendental equation for βa . To understand what this equation implies for βa (and hence E) we plot (Fig. 6.) the LHS of Eqn.(58) as a function of $x \equiv \beta a$.

The values of βa satisfying Eqn.(58) are obtained as projections on the βa axis of the intersections of the curve with a straight line drawn at the distance $\cos(ka)$ parallel to this axis. Since $\cos(ka)$ lies between -1 and 1, and since ordinates of the maxima of the curve have an absolute magnitude greater than 1, then upon varying k , there exist portions between the parallels ± 1 on which there lie intersections, and portions outside these parallels which there are no intersections. By projection, therefore, the βa axis is also divided into portions containing permissible values of βa , and portions not containing such values. In other words, *the energy values $E(k)$ which an electron moving through the lattice may have, form a spectrum consisting of continuous pieces separated by finite intervals.* This is shown on the following figure:

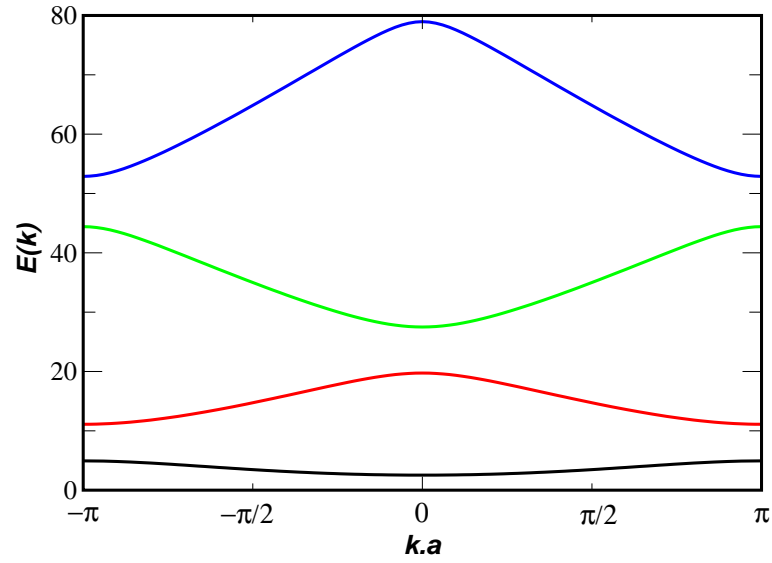
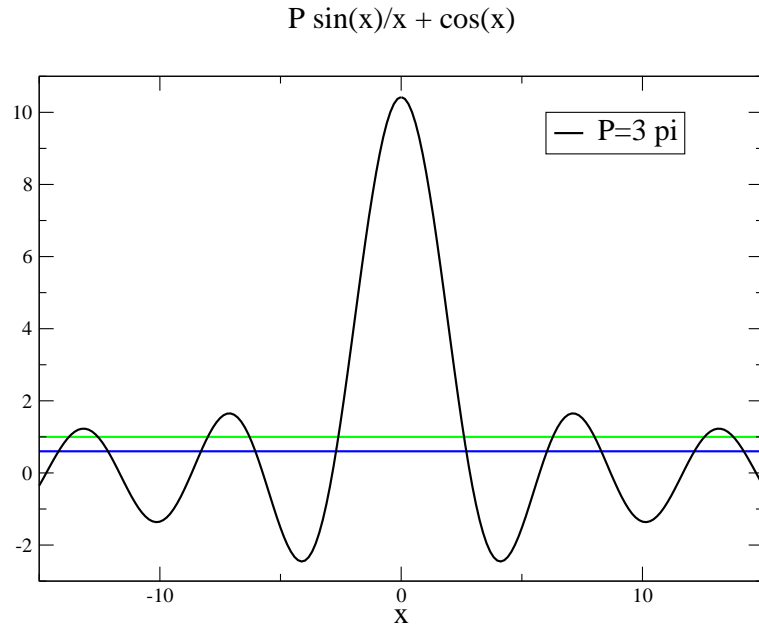


FIG. 7: The lowest four energy bands of the Kronig-Penney model, with $P = 3\pi/2$.

The effect of changing P is the following. If P vanishes, then the first term of the LHS of Eqn.(58) vanishes, and we are left with

$$\cos(\beta a) = \cos(ka) \quad (59)$$

This has solutions $\beta = k$, i.e. $E = k^2/2$ in atomic units, precisely the free-electron limit. In this case, $E(k)$ is quasi-continuous for all values of k .

When $P \rightarrow \infty$, (i.e. the potential wells become infinitely deep), we approach the opposite limit that

$$E = \frac{n^2\pi^2}{2a^2}, \quad n = 1, 2, \dots \quad (60)$$

which is the limit of the electron-in-a-box problem. Here the electrons are *bound* to each box, and the energy curve shows no dispersion. As a function of increasing P , we successively span all the regimes which are encountered on the solid-state:

- (1) $P = 0$: Free electrons.
- (2) $P < 1$: Nearly free electrons.
- (3) $P > 1$: Tight-binding regime.
- (4) $P = \infty$: Free atom.

VI. KRONIG-PENNEY MODEL: A FOURIER APPROACH

It is quite instructive to examine the Kronig-Penney model using a different approach based on Fourier transforms. This will introduce the idea of a plane-wave expansion of the Bloch functions, and some basic calculational ideas which are routinely used in condensed-matter theory.

Consider first the Fourier transform of the potential. Let $T = a + b$, and write:

$$V(x) = \sum_{g=-\infty}^{\infty} \tilde{v}_g e^{i2\pi gx/T} \quad (61)$$

The Fourier coefficients are given by [show!]:

$$\tilde{v}_g = \frac{1}{T} \int_{-b}^a V(x) e^{-i2\pi gx/T} dx \quad (62)$$

$$= \frac{V_0}{\pi g} \sin[\pi gb/T] e^{-i\pi gb/T} \quad (63)$$

Notice that

$$\tilde{v}_{-g} = \tilde{v}_g^* \quad (64)$$

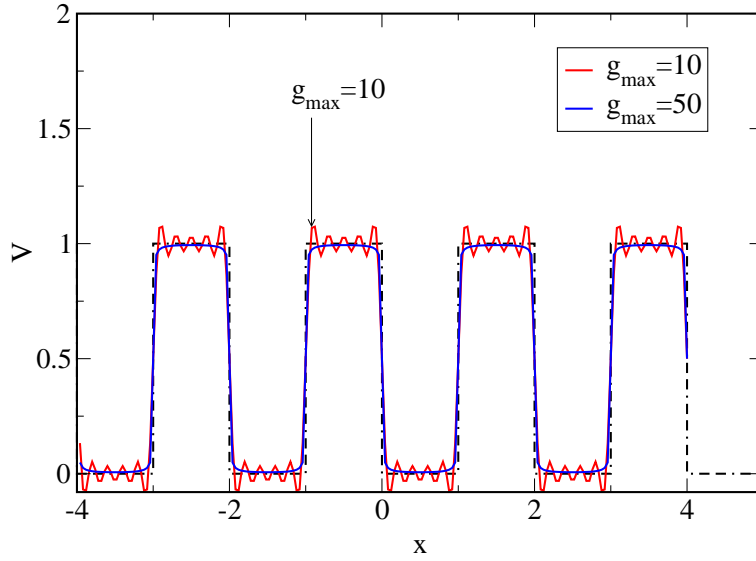


FIG. 8: Fourier representations of the Kroing-Penney potential

This symmetry is a property of all Fourier expansions of real functions, since then $V(x)^* = V(x)$.

In practice, the Fourier expansion [61] needs to be truncated at some value g_{max} . We show below representations of the potential for increasing g_{max} . The potential here is challenging, since it is discontinuous, and the Fourier expansion converges most slowly around the discontinuities. Nevertheless, by increasing g_{max} , an increasingly better representation of the potential is obtained.

Note the enhanced oscillation close to the discontinuity (Gibb's phenomenon), which results in the slow decay ($1/g$) of the Fourier coefficients. Similarly, write the Bloch function in terms of a Fourier series:

$$u_k(x) = \sum_g \tilde{u}_g^{(k)} e^{i2\pi g x/T} \quad (65)$$

[To normalize, include a factor of $1/\sqrt{T}$.] Substituting into the Bloch equation:

$$\begin{aligned} & \sum_g e^{i2\pi g x} [2\pi^2 g^2/T^2 + 2\pi g k/T + k^2/2] \tilde{u}_g^{(k)} + \\ & \sum_g \tilde{v}_g e^{i2\pi g x/T} \sum_{g'} \tilde{u}_{g'}^{(k)} e^{i2\pi g' x/T} \\ = & \sum_g \epsilon_k \tilde{u}_g^{(k)} e^{i2\pi g x/T} \end{aligned}$$

Lets look at the potential term:

$$\begin{aligned} \sum_g \tilde{v}_g e^{i2\pi g x/T} \sum_{g'} \tilde{u}_{g'}^{(k)} e^{i2\pi g' x/T} = \\ \sum_g \sum_{g'} \tilde{v}_g \tilde{u}_{g'}^{(k)} e^{i2\pi(g+g')x/T} \end{aligned} \quad (66)$$

Now let $l = g + g'$, therefore $g = l - g'$, we obtain:

$$\sum_l \sum_{g'} \tilde{v}_{l-g'} \tilde{u}_{g'}^{(k)} e^{i2\pi l x/T} \quad (67)$$

Now, relabelling g' as g we obtain:

$$\sum_l \sum_g \tilde{v}_{l-g} \tilde{u}_g^{(k)} e^{i2\pi l x/T} \quad (68)$$

and then interchanging the labels of g and l , we obtain

$$\sum_g \sum_l \tilde{v}_{g-l} \tilde{u}_l^{(k)} e^{i2\pi g x/T} \quad (69)$$

Hence substituting into the Bloch equation we obtain:

$$\begin{aligned} [2\pi^2 g^2/T^2 + 2\pi g k/T + k^2/2] \tilde{u}_g^{(k)} + \sum_l \tilde{v}_{g-l} \tilde{u}_l^{(k)} \\ = \epsilon_k \tilde{u}_g^{(k)} \end{aligned} \quad (70)$$

There is a subtlety to which you need to pay attention: The cutoff of the Bloch function needs to be $g_{max}/2$, half that used for the potential. This is because we need to access the elements: \tilde{v}_{g-l} , where the maximum allowed value of $g - l$ is g_{max} :

$$|g - l| \leq g_{max} \quad (71)$$

Therefore the maximum value of g and l in the expansions of the Bloch function must be $g_{max}/2$. This is a general property of plane-wave expansions: the cutoff wavenumber of the wavefunction must be half that of the potential.

The eigenvalue equation [70] can be solved numerically, for a given choice of parameters V, a, b, k and g_{max} . This yields the Fourier coefficients $\tilde{u}_g^{(k)}$, from which the Bloch functions can be constructed in real space [65]. Several remarks:

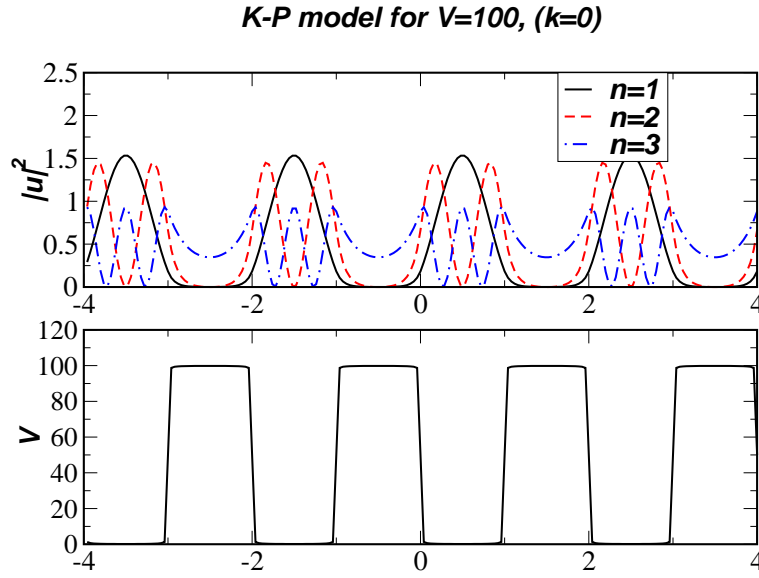


FIG. 9: The K-P Bloch functions for a strong potential ($P = 50$): the behaviour is particle-in-a-box-like.

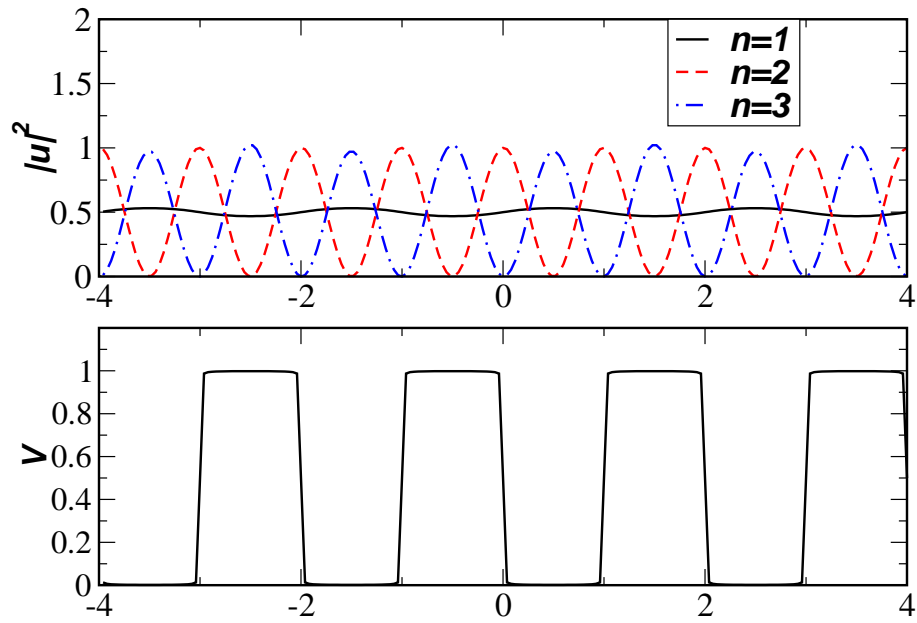
- (i) The use of a plane-wave basis amounts to a change of representation.
- (ii) Plane-waves form a complete orthogonal set.
- (iii) The size of basis is determined by the cutoff parameter g_{max} .

This determines the length-scale of the fast oscillation in the wavefunction.

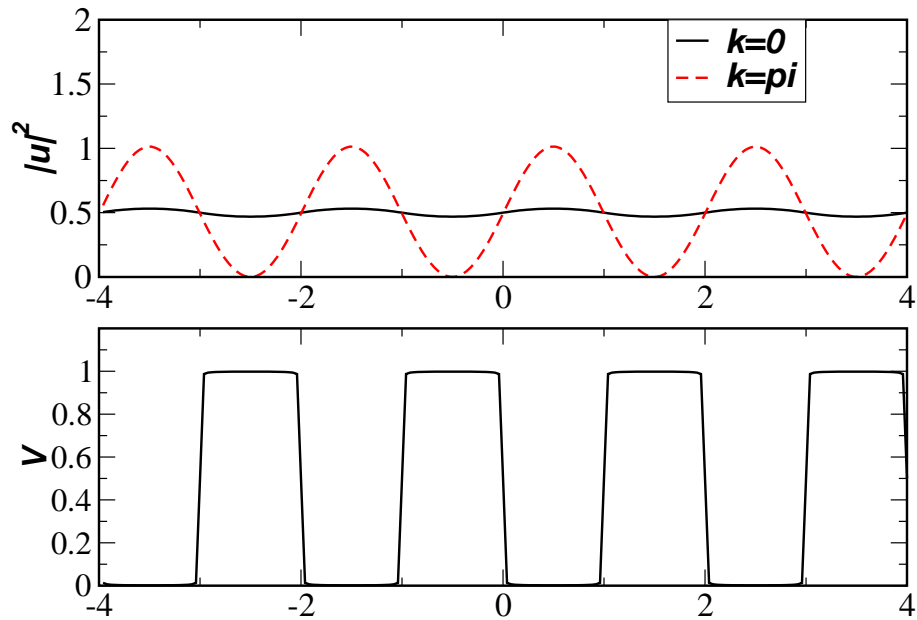
- (iv) The Fast-Fourier transform algorithm can be employed in actual machine calculations: this is highly efficient.

The K-P Bloch functions for a weak potential ($P = 0.5$): the bands are nearly-free-electron like. Note the lowest band is only weakly perturbed by the potential.

K-P model for $V=1, (k=0)$



K-P model for $V=1, (n=1)$



The K-P Bloch functions for a weak potential ($P = 0.5$) showing dispersion. Note that the $k = \pi$ state is more concentrated towards the low-potential regions.

VII. OTHER APPLICATION OF FOURIER METHODS IN SOLID-STATE PROBLEMS: COMPUTING THE ELECTRON-ION INTERACTION, AND THE EWALD METHOD

Fourier transform methods abound in solid-state problems, and we make a brief digression to mention some important applications. The most important of these is the calculation of the Coulomb interaction - which is long-ranged - between an electron density inside a unit cell with an infinite periodic lattice of nuclei, and secondly, the interaction of a lattice of point charges (the Ewald method), of which the Madelung sum is an example. In both cases, one faces the difficulty of summing an infinite number of (distant) interactions.

A. Electron-ion interactions

Let us suppose we have a periodic electron density, $n(\mathbf{r}) = n(\mathbf{r} + \mathbf{T})$, (where \mathbf{T} is a lattice-vector which can be expressed as $\mathbf{T} = \sum_i n_i \mathbf{a}_i$), and we wish to compute the Coulomb interaction of this density with *all* nuclei (i.e. those located inside the unit-cell at \mathbf{R}_I , and all periodic images outside the cell located at $\mathbf{R}_I + \mathbf{T}$), i.e.:

$$E_{ext} = \int_{\Omega} d\mathbf{r} n(\mathbf{r}) \underbrace{\sum_{\mathbf{T}} \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I - \mathbf{T}|}}_{V_{ext}} \quad (72)$$

In the above, Ω is the volume of the unit cell, and the sum over \mathbf{T} is an infinite sum over all lattice vectors. Evidently, the external potential V_{ext} is periodic in \mathbf{T} :

$$V_{ext}(\mathbf{r}) = \sum_{\mathbf{T}} \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I - \mathbf{T}|} \quad (73)$$

$$= V_{ext}(\mathbf{r} + \mathbf{T}) \quad (74)$$

Let us therefore expand it in a Fourier series:

$$V_{ext}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{v}_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (75)$$

where \mathbf{G} is a reciprocal lattice vector (i.e. $\mathbf{G} \cdot \mathbf{T} = 2\pi \times \text{integer}$). Now:

$$\tilde{v}_{\mathbf{G}} = \frac{1}{\Omega} \int_{\Omega} \exp(-i\mathbf{G} \cdot \mathbf{r}) \sum_{\mathbf{T}} \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I - \mathbf{T}|} d\mathbf{r} \quad (76)$$

Let $\mathbf{s} = \mathbf{r} - \mathbf{R}_I$, and therefore $d\mathbf{s} = d\mathbf{r}$.

$$\tilde{v}_{\mathbf{G}} = \frac{1}{\Omega} \sum_I Z_I \int_{\Omega} \exp(-i\mathbf{G}\cdot\mathbf{s}) \exp(-i\mathbf{G}\cdot\mathbf{R}_I) \sum_{\mathbf{T}} \frac{1}{|\mathbf{s} - \mathbf{T}|} d\mathbf{s} \quad (77)$$

$$= \frac{1}{\Omega} \sum_I Z_I \exp(-i\mathbf{G}\cdot\mathbf{R}_I) \times \int_{\Omega} \exp(-i\mathbf{G}\cdot\mathbf{s}) \sum_{\mathbf{T}} \frac{1}{|\mathbf{s} - \mathbf{T}|} d\mathbf{s} \quad (78)$$

$$= \frac{1}{\Omega} \sum_I Z_I \exp(-i\mathbf{G}\cdot\mathbf{R}_I) \times \int_{\Omega} \sum_{\mathbf{T}} \exp(-i\mathbf{G}\cdot(\mathbf{s} - \mathbf{T})) \frac{1}{|\mathbf{s} - \mathbf{T}|} d\mathbf{s} \quad (79)$$

$$= \frac{1}{\Omega} \underbrace{\sum_I Z_I \exp(-i\mathbf{G}\cdot\mathbf{R}_I)}_{S_{\mathbf{G}}} \times \int_{all\ space} \exp(-i\mathbf{G}\cdot\mathbf{s}) \frac{1}{|\mathbf{s}|} d\mathbf{s} \quad (80)$$

$$= \frac{1}{\Omega} S_{\mathbf{G}} \times \frac{4\pi}{G^2} \quad (81)$$

where we have used the fact that the Fourier transform of $1/r$ is $4\pi/G^2$ (to be later derived). Note that, in going from Eq.(79) to Eq.(80) we have used the fact that for each \mathbf{s} inside the cell, $\mathbf{s} - \mathbf{T}$ maps us to a unique point outside the cell. As a result, as we integrate over \mathbf{s} inside the cell, the sum over \mathbf{T} integrates over *all space*. Since $\mathbf{T}\cdot\mathbf{G} = 2\pi \times integer$, this has no effect inside the complex exponential, and it means that we can replace $\int_{\Omega} \sum_{\mathbf{T}}$ with $\int_{all\ space}$. $S_{\mathbf{G}} = \sum_I Z_I \exp(-i\mathbf{G}\cdot\mathbf{R}_I)$ is called the (nuclear) *structure factor*, and can be computed (for each \mathbf{G}) from the nuclear coordinates inside the unit cell.

This enables one to compute the external energy through:

$$E_{ext} = \int_{\Omega} n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \quad (82)$$

$$= \int_{\Omega} \sum_{\mathbf{G}} \tilde{n}_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) \times \sum_{\mathbf{G}'} \tilde{v}_{\mathbf{G}'} \exp(i\mathbf{G}'\cdot\mathbf{r}) d\mathbf{r} \quad (83)$$

$$= \sum_{\mathbf{G}} \sum_{\mathbf{G}'} \tilde{n}_{\mathbf{G}} \tilde{v}_{\mathbf{G}'} \underbrace{\int_{\Omega} d\mathbf{r} \exp(i(\mathbf{G} + \mathbf{G}')\cdot\mathbf{r})}_{\Omega \times \delta_{\mathbf{G}-\mathbf{G}'}} \quad (84)$$

$$= \sum_{\mathbf{G}} \tilde{n}_{\mathbf{G}} \tilde{v}_{-\mathbf{G}} \Omega \quad (85)$$

$$= \sum_{\mathbf{G}} \tilde{n}_{\mathbf{G}} S_{-\mathbf{G}} \frac{4\pi}{G^2} \quad (86)$$

which is three-dimensional sum over reciprocal lattice vectors of the fourier transform of the electron density, the structure factor, and the Coulomb potential.

B. The Ewald sum

Evaluating the electrostatic energy of a lattice of positive and negative point charges is a frequently encountered problem (e.g. the Madelung energy). Let us suppose the point charges inside the unit cell are located at \mathbf{R}_I (carrying charges Z_I), and we wish to evaluate the total electrostatic energy of the nuclei in the cell:

$$E_{NN} = \frac{1}{2} \sum_{\mathbf{T}}' \sum_I \sum_J \frac{Z_I Z_J}{|\mathbf{R}_{IJ} - \mathbf{T}|} \quad (87)$$

where $\mathbf{R}_{IJ} = \mathbf{R}_I - \mathbf{R}_J$ and the prime indicates that if $\mathbf{T} = 0$, then the $I = J$ terms (the “self” terms) should be omitted. The above sum is conditionally convergent, i.e. the answer you get depends on the order of summation of the interactions. It seems reasonable to perform the sum in such a way that the nearby interactions are summed first, and the distant ones summed later. One way to achieve this is to sum the unit cells in spherical shells, i.e. with increasing $|\mathbf{T}|$.

The Coulomb interaction actually presents two difficulties. On the one hand it is long-ranged ($1/r$ in 3D), so that all the interactions, even from very distant ions, must be taken into account. It also has a singularity at $r = 0$, and it proves convenient to separate out the two “bits” of the interaction. Let us consider the following decomposition of the Coulomb interaction, into a long-range part and a short-range part:

$$\frac{1}{r} = \underbrace{\frac{\text{erf}(r/\alpha)}{r}}_{\text{long-range part}} + \underbrace{\frac{\text{erfc}(r/\alpha)}{r}}_{\text{short-range part}} \quad (88)$$

where $\text{erf}(x)$ and $\text{erfc}(x)$ is the *error function* and complementary error function respectively:

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (89)$$

$$\text{erfc}(x) = 1 - \text{erf}(x) \quad (90)$$

A plot of the error function is shown in Fig. 10.

The error function acts as a kind of “switch” function. α is a range parameter whose significance can be discovered as follows: $\text{erf}(r/\alpha)$ is linear for $r \ll \alpha$, and therefore

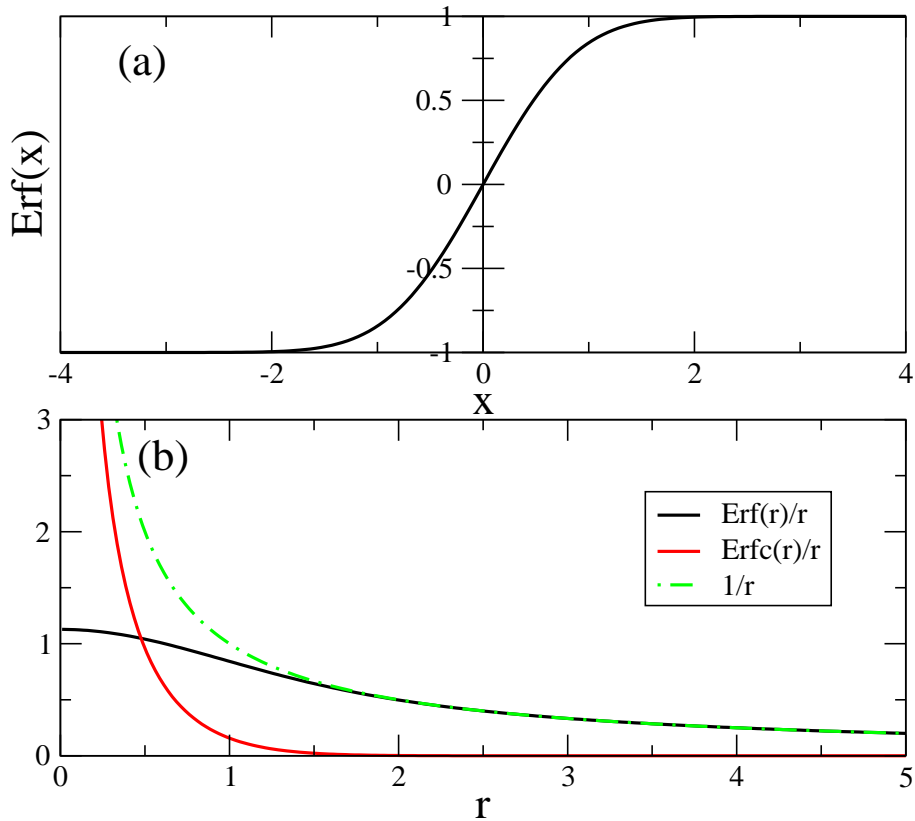


FIG. 10: (a) error function $\text{erf}(x)$, (b) $1/r$ decomposed into short and long-ranged parts

$\text{erf}(r/\alpha)/r$ does not diverge in the small r limit. Instead, it has the following limiting behaviour:

$$\lim_{r \rightarrow 0} \frac{\text{erf}(r/\alpha)}{r} = \frac{2}{\alpha\sqrt{\pi}} \quad (91)$$

On the other hand, for $r > 2\alpha$, $\text{erf}(r/\alpha) \approx 1$, and therefore $\text{erf}(r/\alpha)/r$ rapidly approaches $1/r$ at sufficiently large distance.

The complementary error function part, $\text{erfc}(r/\alpha)/r$, captures the short-range singularity, but decays very rapidly for $r \gg 2\alpha$, implying that this term can be truncated for interactions between distant particles. For a unit cell of length L , if one chooses $\alpha < L/2$, then the interaction between particles outside the unit cell (plus possibly a small shell of neighbouring cells) can be explicitly neglected.

One can write:

$$E_{NN} = \frac{1}{2} \sum_{\mathbf{T}} \sum'_{I,J} Z_I Z_J \frac{\operatorname{erfc}(|\mathbf{R}_{IJ} - \mathbf{T}|/\alpha)}{|\mathbf{R}_{IJ} - \mathbf{T}|} + \frac{1}{2} \sum'_{\mathbf{T}} \sum_{I,J} Z_I Z_J \frac{\operatorname{erf}(|\mathbf{R}_{IJ} - \mathbf{T}|/\alpha)}{|\mathbf{R}_{IJ} - \mathbf{T}|} \quad (92)$$

Since one can truncate the first sum over a finite number of shells (with $|\mathbf{T}| \leq T_{max}$), we have:

$$E_{NN} = \frac{1}{2} \sum_{\mathbf{T}}^{T_{max},'} \sum_{I,J} Z_I Z_J \frac{\operatorname{erfc}(|\mathbf{R}_{IJ} - \mathbf{T}|/\alpha)}{|\mathbf{R}_{IJ} - \mathbf{T}|} + \frac{1}{2} \sum'_{\mathbf{T}} \sum_{I,J} Z_I Z_J \frac{\operatorname{erf}(|\mathbf{R}_{IJ} - \mathbf{T}|/\alpha)}{|\mathbf{R}_{IJ} - \mathbf{T}|} \quad (93)$$

The second set of terms can be written as:

$$\frac{1}{2} \sum_{I,J} Z_I Z_J \sum_{\mathbf{T}} \frac{\operatorname{erf}(|\mathbf{R}_{IJ} - \mathbf{T}|/\alpha)}{|\mathbf{R}_{IJ} - \mathbf{T}|} - \sum_I Z_I^2 \frac{1}{\alpha\sqrt{\pi}} \quad (94)$$

(i.e. we have dropped the $'$ and explicitly removed the $I = J$ “self” terms using the limiting formula). Consider now the following function defined for any \mathbf{r} (which will eventually set to \mathbf{R}_{IJ}):

$$V(\mathbf{r}) = \sum_{\mathbf{T}} \frac{\operatorname{erf}(|\mathbf{r} - \mathbf{T}|/\alpha)}{|\mathbf{r} - \mathbf{T}|} \quad (95)$$

which is evidently periodic in \mathbf{T} , and in terms of which Eq.(96) can be written:

$$\frac{1}{2} \sum_{I,J} Z_I Z_J V(\mathbf{R}_{IJ}) - \sum_I Z_I^2 \frac{1}{\alpha\sqrt{\pi}} \quad (96)$$

Since $V(\mathbf{r})$ is a periodic function, it can be written as a Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{V}_{\mathbf{G}} \exp(-i\mathbf{G} \cdot \mathbf{r}) \quad (97)$$

where

$$\tilde{V}_{\mathbf{G}} = \frac{1}{\Omega} \int_{\Omega} \exp(i\mathbf{G} \cdot \mathbf{r}) V(\mathbf{r}) d\mathbf{r} \quad (98)$$

$$= \frac{1}{\Omega} \int_{\Omega} \exp(i\mathbf{G} \cdot \mathbf{r}) \sum_{\mathbf{T}} \frac{\operatorname{erf}(|\mathbf{r} - \mathbf{T}|/\alpha)}{|\mathbf{r} - \mathbf{T}|} d\mathbf{r} \quad (99)$$

$$= \frac{1}{\Omega} \sum_{\mathbf{T}} \int_{\Omega} \exp(i\mathbf{G} \cdot (\mathbf{r} - \mathbf{T})) \frac{\operatorname{erf}(|\mathbf{r} - \mathbf{T}|/\alpha)}{|\mathbf{r} - \mathbf{T}|} d\mathbf{r} \quad (100)$$

$$= \frac{1}{\Omega} \int_{allspace} \exp(i\mathbf{G} \cdot \mathbf{r}) \frac{\operatorname{erf}(|\mathbf{r}|/\alpha)}{|\mathbf{r}|} d\mathbf{r} \quad (101)$$

$$= \frac{1}{\Omega} \frac{4\pi e^{-G^2\alpha^2}}{G^2} \quad (102)$$

[Show this last step! Hint: note that $r = |\mathbf{r}|$, and $\mathbf{g} \cdot \mathbf{r} = gr \cos \theta$, then use spherical polars. You may find it useful also to apply a damping factor $\exp(-r/\lambda)$ to the integrand and then take the $\lambda \rightarrow \infty$ limit].

Inserting this into the first term of Eq.(96) we find:

$$\frac{1}{2} \sum_{I,J} Z_I Z_J V(\mathbf{R}_{IJ}) = \frac{1}{2} \sum_{I,J} Z_I Z_J \sum_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{R}_{IJ}) \tilde{V}_{\mathbf{G}} \quad (103)$$

$$= \frac{1}{2} \sum_{I,J} Z_I Z_J \sum_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{R}_I) \exp(-i\mathbf{G} \cdot \mathbf{R}_J) \tilde{V}_{\mathbf{G}} \quad (104)$$

$$= \frac{1}{2} \sum_{\mathbf{G}} \left[\sum_I Z_I \exp(i\mathbf{G} \cdot \mathbf{R}_I) \right] \left[\sum_J Z_J \exp(-i\mathbf{G} \cdot \mathbf{R}_J) \right] \times \tilde{V}_{\mathbf{G}} \quad (105)$$

$$= \frac{4\pi}{2\Omega} \sum_{\mathbf{G}} |S_{\mathbf{G}}|^2 \frac{e^{-G^2\alpha^2}}{G^2} \quad (106)$$

This sum is rapidly convergent over \mathbf{G} , since the Gaussian ensures that whenever $|\mathbf{G}| \gg 1/\alpha$ the summand is very small. The sum over \mathbf{G} can therefore be truncated at a suitable cutoff, G_{max} , taking into account all \mathbf{G} with $|\mathbf{G}| \leq G_{max}$.

Therefore the complete lattice sum becomes:

$$E_{NN} = \frac{1}{2} \sum_{\mathbf{T}} \sum_{I,J}^{T_{max}'} Z_I Z_J \frac{\text{erfc}(|\mathbf{R}_{IJ} - \mathbf{T}|/\alpha)}{|\mathbf{R}_{IJ} - \mathbf{T}|} + \frac{4\pi}{2\Omega} \sum_{\mathbf{G}}^{G_{max}} |S_{\mathbf{G}}|^2 \frac{e^{-G^2\alpha^2}}{G^2} - \frac{1}{\alpha\sqrt{\pi}} \sum_I Z_I^2 \quad (107)$$

It can be seen that the α parameter is crucial. If it is chosen to be too small, the first terms (in erfc) are rapidly convergent, but instead one has to sum over many \mathbf{G} vectors. On the other hand, if α is chosen to be too large, the direct sum over the lattice vectors must be extended afar (i.e. over many shells of unit cells), although the Fourier sum is then rapidly convergent. In practice, one wants to choose α in such a way that the computational effort of the two sums is roughly equivalent.

VIII. RELATIONSHIP WITH HÜCKEL THEORY

There is a close link of the discussion in section VI with Hückel theory (*aka* tight-binding method). There we expand the molecular orbitals ψ_n in a *localised* basis, (e.g.

s-orbitals, or p-orbitals centred on atomic sites ϕ_j):

$$\psi_n = \sum_j c_j^{(n)} \phi_j \quad (108)$$

We can often make a lot of progress without ever specifying the nature of ϕ_j , referring instead to the *on-site* integrals (α_j) and *hopping* integrals (β_{ij}):

$$\alpha_j = \langle \phi_j | \hat{H} | \phi_j \rangle \quad (109)$$

$$\beta_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \quad (110)$$

$$(111)$$

In the simplest model, (a ring of N identical sites with nearest-neighbour hopping only) we set:

$$\alpha_j = \alpha \quad (112)$$

$$\beta_{ij} = \begin{cases} \beta & \text{for } i = j \pm 1 \\ 0 & \text{otherwise} \end{cases} \quad (113)$$

we obtain the Hückel equations:

$$\beta c_{j-1}^{(n)} + (\alpha - \epsilon_n) c_j^{(n)} + \beta c_{j+1}^{(n)} = 0 \quad (114)$$

with boundary conditions $c_j^{(n)} = c_{j+N}^{(n)}$. The solutions are:

$$\begin{aligned} c_j^{(n)} &= \frac{1}{\sqrt{N}} e^{i2\pi n j / N}, \quad n = -N/2, \dots, 0, \dots, N/2 - 1 \\ \epsilon_n &= \alpha + 2\beta \cos(2\pi n / N) \end{aligned} \quad (115)$$

Letting $k_n \equiv 2\pi n / N$, we recover forms very similar to the previous discussion, (setting the lattice constant to unity). Several remarks:

(1) The small k_n part of the band is parabolic:

$$\epsilon_{k_n} \approx \alpha + 2\beta - 2\beta \cdot \frac{k_n^2}{2} \quad (116)$$

(2) The *band-width* is $4|\beta|$.

(3) β can be either negative (s or p^π interactions) or positive (p^σ interactions). In the latter case, the energy of the ϵ_n *drops* with increasing n from $n = 0$ to $n = N/2$.

IX. BAND ENERGY AND DENSITY OF STATES

For a crystal consisting of N atoms, there will be N distinct k-points in the Brillouin zone, corresponding to

$$k_n = 2\pi.n/(Na), \quad n = -N/2, \dots, 0, \dots, N/2 - 1$$

At each k-point, there will be bands labelled by the band-index m , which in principle runs from $m = 1$ to ∞ , though in practice the number of bands is determined by the number of basis functions (e.g. plane waves, atomic-orbitals etc) used in the expansion. Let $\epsilon_n^{(m)} \equiv \epsilon^{(m)}(k_n)$ denote our energy levels.

If the crystal contains N_{el} electrons, the lowest $N_{el}/2$ states out the $\epsilon_n^{(m)}$ will be occupied. (Note the role of the Pauli principle: no state can be more than doubly occupied by electrons - spin-1/2 Fermions). Let ϵ_F denote the Fermi energy. Then the occupation numbers are defined as:

$$f_n^{(m)} = \begin{cases} 2 & \text{for } \epsilon_n^{(m)} < \epsilon_F \\ 0 & \epsilon_n^{(m)} > \epsilon_F \end{cases} \quad (117)$$

with the sum-rule:

$$\sum_{n,m} f_n^{(m)} = N_{el}. \quad (118)$$

The band energy is defined as the sum over the occupied energy levels:

$$E = \sum_{n,m} f_n^{(m)} \epsilon_n^{(m)} \quad (119)$$

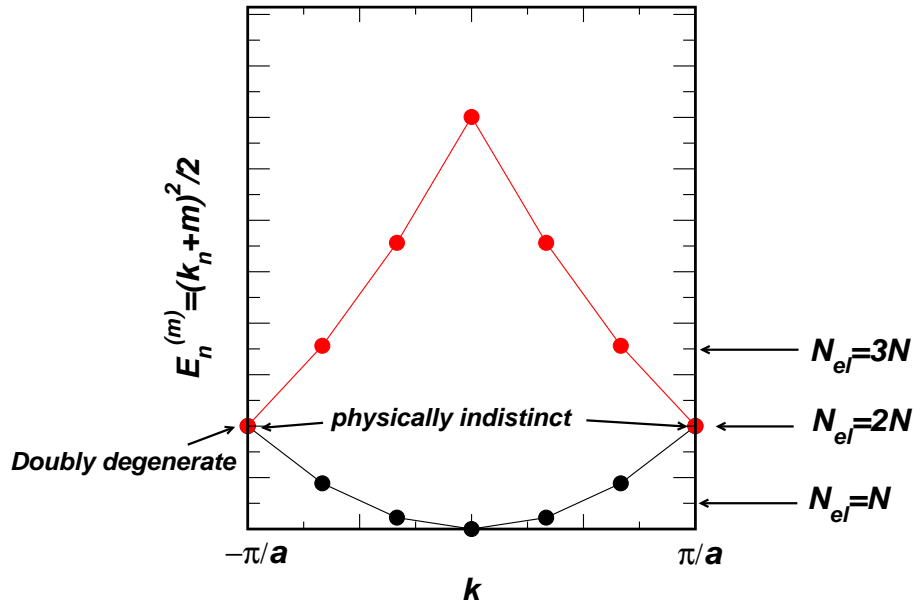
The *density of states* $g(\epsilon)$ is defined as the number of states S in the energy interval between ϵ and $\epsilon + d\epsilon$, i.e.:

$$g(\epsilon) = \frac{dS}{d\epsilon} \quad (120)$$

This is best thought of as the being the product of number of kpoints in an interval dk (this is a constant proportional to the number of atoms in the crstyal, N , divided by the length of the FBZ e.g. $2\pi/a$), and $dk/d\epsilon$:

$$g(\epsilon) = \frac{dS/dk}{|d\epsilon/dk|} \quad (121)$$

Occupation of free-electron bands with $N=6$



For example, for the 1D free-particle system we have:

$$g(\epsilon) = 2 \cdot \frac{Na}{2\pi} \cdot \frac{1}{\sqrt{2\epsilon}} \quad (122)$$

In this case, this is expressing the fact that as we move to higher energies, the more widely the energy levels are distributed (their energy is going as k_n^2).

The band energy can be written as an integral over ϵ as

$$E = \int^{\epsilon_F} \epsilon g(\epsilon) d\epsilon \quad (123)$$

If a band is partially filled, the system will be metallic, electronic conductors at zero K.

As N increases, a more dense, uniformly distributed (quasi-continuous) set of k-points appears. Note that the states at $k = +\pi/a$ and at $k = -\pi/a$ are physically indistinct (only count for one). For the free-particle case (above) those states are also (accidentally) doubly degenerate.

X. PEIERL'S DISTORTION

We have seen that a periodic potential induces the appearance of a gap in energy spectrum at wavenumbers corresponding to the Brillouin zone boundary. If the number of electrons in the system is not sufficient to fill entirely the band, the system remains a metal. For example, in a monovalent crystal, where one electron is donated per atom, the band is only half filled (i.e. upto wavenumber $|k| \leq \pm\pi/2a$).

However, if the lattice is distorted, resulting in a periodicity larger than a , then additional gaps will appear in the spectrum, at wavenumbers commensurate with the effectively smaller Brillouin zone of the distorted lattice. This effect is known as the Peierl's distortion.

As an example, we show the effect on the Kronig-Penney bands of doubling the periodicity by introducing pairing up wells, as shown in the figure below. The Brillouin zone boundary is reduced from π/L to $\pi/2L$ (where $L = a + b$ in the original K-P model). The effect of this pairing is to induce a gap at the new Brillouin zone boundary $k = \pi/2L$, leaving largely unaffected the energy of the bands close to $k = 0$.

This has two effects. First, because the energies of the bands close to the gap are lowered, the overall energy may be lowered (the overall energy is determined by other factors such as nuclear-nuclear repulsion, elastic strain etc). Second, by inducing as a gap, a metal can be converted into an insulator. In the example above, a monovalent metal would become an insulator, since a gap would have been created at the Fermi energy. As a result, 1D metals tend to be unstable with respect to such Peierl's distortions. In 3D, where the *wavevector* of the distortion lies on a Fermi Surface, only the states in its vicinity will be affected, the remaining states being unaffected. As a result, the Peierl's distortion tends not to as an overwhelming effect in 3D.

Peierl's distortion (Double periodicity)

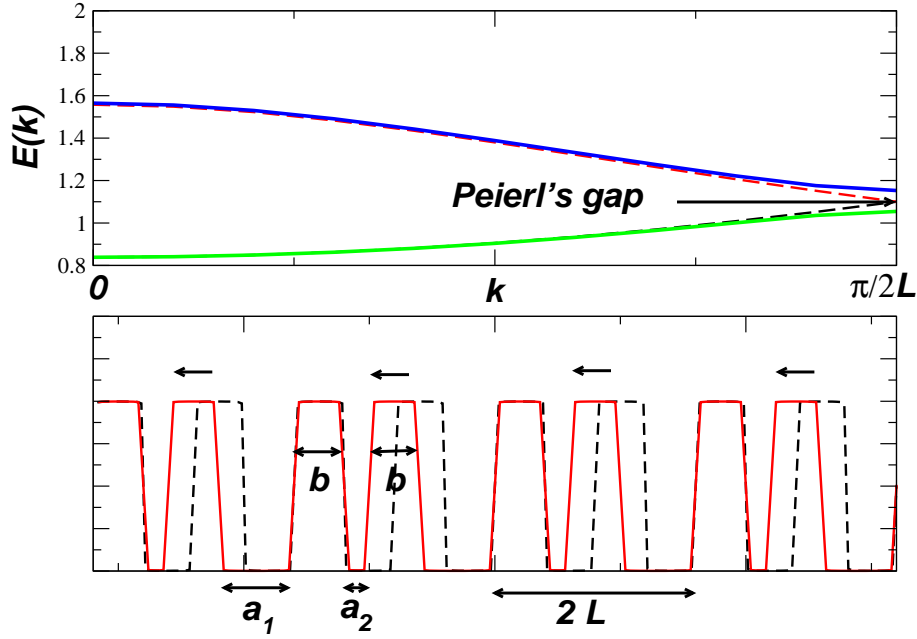


FIG. 11: K-P model exhibiting a Peierl's distortion.

The potential is:

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a_1 \\ V_0 & a_1 < x < a_1 + b \\ 0 & a_1 + b < x < a_1 + b + a_2 \\ V_0 & a_1 + b + a_2 < x < a_1 + 2b + a_2 \end{cases} \quad (124)$$

The original K-P model is recovered when $a_1 = a_2$.

XI. TWO AND THREE DIMENSIONS

All that we have said thus far can be generalised to 2D and 3D. In practice, you will need to get out a pencil and paper to draw out the lattices, because very complex situations arise out of even the simplest of 2D or 3D lattices.

Let us consider the 2D rectangular lattice of lattice constants a and b , with Born-Kármán boundary conditions applied in the x and y directions. Thus for example if

there are N unit-cells in each of the two directions, then

$$\psi(x + Na, y + Nb) = \psi(x, y). \quad (125)$$

The plane-wave functions now have the form:

$$e^{i(k_x x + k_y y)} \equiv e^{i\mathbf{k} \cdot \mathbf{r}} \quad (126)$$

with k_x and k_y restricted to

$$k_x = \frac{2\pi}{Na} n_x, \quad k_y = \frac{2\pi}{Nb} n_y, \quad (127)$$

The two primitive lattice vectors of the rectangular lattice are:

$$\mathbf{a}_1 = \begin{pmatrix} a \\ 0 \end{pmatrix}, \quad \mathbf{a}_2 = \begin{pmatrix} 0 \\ b \end{pmatrix} \quad (128)$$

The primitive reciprocal lattice vectors \mathbf{b}_j of the rectangular lattice satisfy the condition

$$e^{i\mathbf{b}_j \cdot (\mathbf{r} + n\mathbf{a}_1 + m\mathbf{a}_2)} = e^{i\mathbf{b}_j \cdot \mathbf{r}} \quad (129)$$

where m and n are arbitrary integers. Therefore:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (130)$$

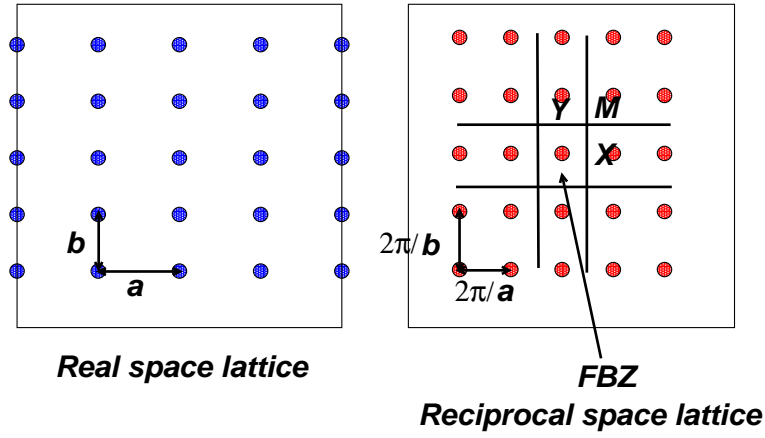
which gives:

$$\mathbf{b}_1 = \frac{2\pi}{a} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \mathbf{b}_2 = \frac{2\pi}{b} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (131)$$

Any reciprocal lattice vector \mathbf{G} can be expressed as

$$\mathbf{G} = n \cdot \mathbf{b}_1 + m \cdot \mathbf{b}_2, \quad n, m \text{ are integers} \quad (132)$$

In the present example, the reciprocal lattice vectors form a rectangular lattice in their own right, with lattice constants $2\pi/a$ and $2\pi/b$. Note that the *shorter* lattice constant in real-space gives rise to a *longer* reciprocal lattice constant.



A wavevector $\mathbf{k} = (k_x, k_y)$ falls inside the FBZ of the rectangular lattice if:

$$-\pi/a \leq k_x \leq \pi/a, \quad -\pi/b \leq k_y \leq \pi/b \quad (133)$$

In precise analogy with the reduced-zone scheme in 1D, the wavevectors \mathbf{k} inside the FBZ can be used to label those outside the FBZ. Thus, an arbitrary wavevector can always be written as:

$$\mathbf{k} = \mathbf{k}_{FBZ} + \mathbf{G} \quad (134)$$

where \mathbf{k}_{FBZ} refers to a wavevector in the FBZ. The corresponding *multiple-valued* free-electron energies are given by:

$$\epsilon_{\mathbf{k}}^{\mathbf{G}} = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 \quad (135)$$

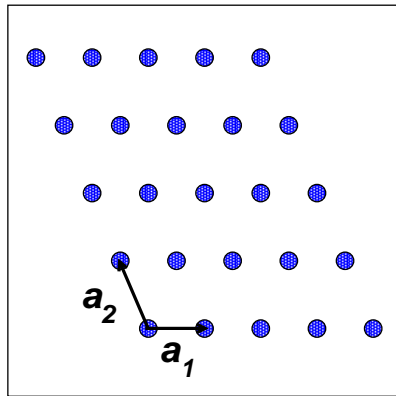
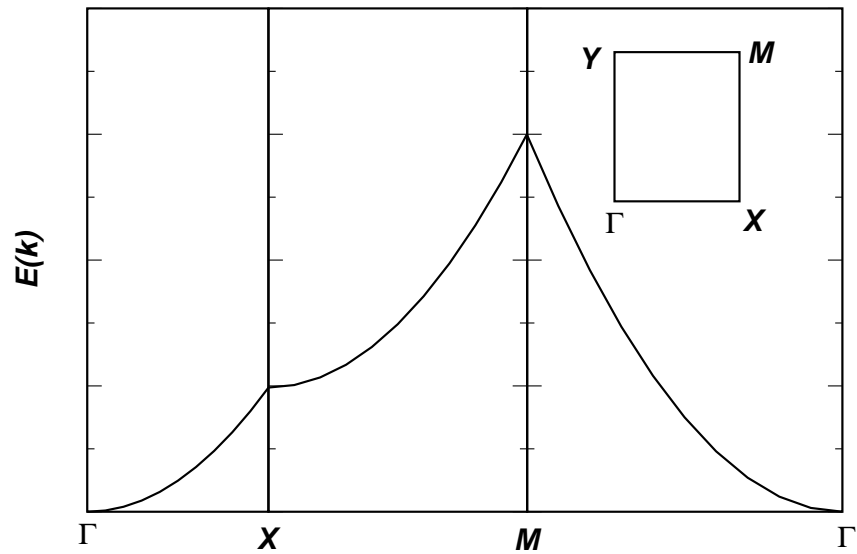
The band-structure is often drawn along high-symmetry directions of the reciprocal lattice. Another important example of a 2D lattice is the triangular lattice. Here the lattice vectors are:

$$\mathbf{a}_1 = \begin{pmatrix} a \\ 0 \end{pmatrix}, \quad \mathbf{a}_2 = \begin{pmatrix} -a/2 \\ \sqrt{3}a/2 \end{pmatrix} \quad (136)$$

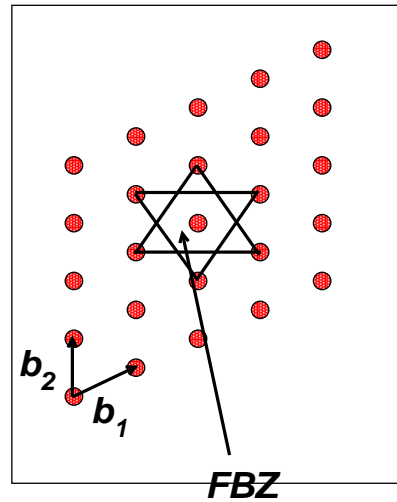
with corresponding reciprocal lattice vectors:

$$\mathbf{b}_1 = \frac{2\pi}{a} \begin{pmatrix} 1 \\ 1/\sqrt{3} \end{pmatrix}, \quad \mathbf{b}_2 = \frac{2\pi}{a} \begin{pmatrix} 0 \\ 2/\sqrt{3} \end{pmatrix} \quad (137)$$

Free electron band structure for a rectangular lattice



Triangular lattice



Reciprocal space lattice

Note that the reciprocal lattice vector \mathbf{b}_1 is perpendicular to \mathbf{a}_2 , and has a length determined by \mathbf{a}_1 . The reciprocal space lattice is also a triangular lattice, rotated by 30 degrees, and the FBZ is a hexagon surrounding a given reciprocal lattice site. If we

write Eqn.(135) in an alternative form, we notice the following

$$\epsilon_{\mathbf{k}}^{\mathbf{G}} = \frac{\hbar^2}{2m}(k^2 + 2\mathbf{k}\cdot\mathbf{G} + G^2) \quad (138)$$

What happens if we are at a particular \mathbf{k} such that:

$$2\mathbf{k}\cdot\mathbf{G} + G^2 = 0, \quad \text{for some } \mathbf{G}. \quad (139)$$

Evidently, if this happens, then:

$$\epsilon_{\mathbf{k}}^{\mathbf{G}} = \frac{\hbar^2}{2m}(k^2) = \epsilon_{\mathbf{k}}^0 \quad (140)$$

i.e. for those special \mathbf{k} for which Eqn.(139) is true, the energy of those states is degenerate with that for \mathbf{k} inside the FBZ.

Where do these special \mathbf{k} lie in relation to the Brillouin zone? Let us express Eqn.(139) in a different way:

$$-\mathbf{k}\cdot\frac{\mathbf{G}}{|\mathbf{G}|} = \frac{|\mathbf{G}|}{2}, \quad (141)$$

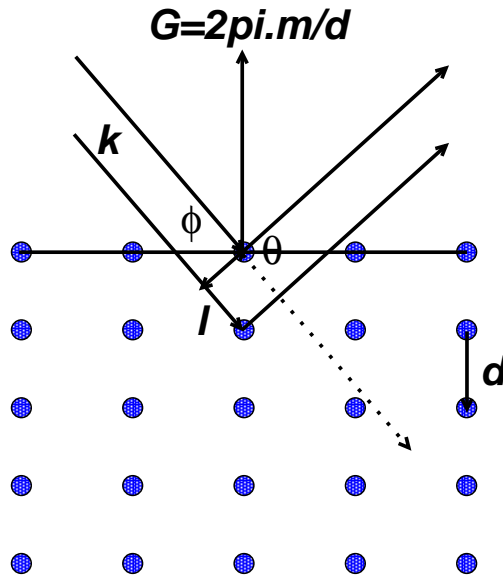
Geometrically this occurs when *the projection of \mathbf{k} on a reciprocal lattice vector $-\mathbf{G}$ is equals to half of magnitude of the reciprocal lattice vector \mathbf{G}* . In other words for a given \mathbf{G} , you take the plane that bisects the vector \mathbf{G} . But this is precisely the definition of the Brillouin zones! You need to satisfy yourselves of this, because it is a crucial point: The free-electron energy levels are degenerate at Brillouin zone edges (or in 3D, the BZ surfaces). The implications of this are profound, as we shall later see.

Before we leave this point, you may have noticed a familiarity with Eqn.(141) in the context of diffraction experiments. In fact, this Bragg's Law in disguise. If θ is angle the incident wavevector \mathbf{k} makes to the *normal* of the Bragg planes (i.e. with \mathbf{G}), then expanding the dot product we have:

$$-\frac{2\pi}{\lambda} \cos \theta = \frac{2\pi m}{2d} \quad (142)$$

where d is the spacing between the Bragg planes. Now let ϕ be the angle the incident wavevector makes with the Bragg planes, then

$$\theta = \pi/2 + \phi$$



$$\theta = \phi + \pi/2$$

$$l = d \sin \phi$$

$$\text{Bragg's criterion: } 2d \sin \phi = m \lambda$$

$$\text{von Laue: } -\mathbf{k} \cdot \mathbf{G} = |\mathbf{G}|^2 / 2$$

Substituting,

$$\begin{aligned} \frac{2\pi}{\lambda} \sin(\phi) &= \frac{2\pi m}{2d}, \quad \text{i.e.} \\ 2d \sin(\phi) &= m \lambda \end{aligned} \quad (143)$$

which is Bragg's law. In other words, the condition Eqn.[141] is the condition needed for constructive interference of the wavevectors \mathbf{k} given a lattice with reciprocal lattice vectors \mathbf{G} . The wavevectors whose tips lie on the Brillouin zone boundaries satisfy this condition for constructive interference. Everything that we have said about 2D can be generalised to 3D. Let the three lattice vectors be denoted by $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Then the three basic reciprocal lattice vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ satisfy:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (144)$$

which can be satisfied if:

$$\mathbf{b}_1 = \frac{2\pi}{\Omega} (\mathbf{a}_2 \times \mathbf{a}_3) \quad (145)$$

$$\mathbf{b}_2 = \frac{2\pi}{\Omega}(\mathbf{a}_3 \times \mathbf{a}_1) \quad (146)$$

$$\mathbf{b}_3 = \frac{2\pi}{\Omega}(\mathbf{a}_1 \times \mathbf{a}_2) \quad (147)$$

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (148)$$

and a general reciprocal lattice vector \mathbf{G} is given by:

$$\mathbf{G} = n\mathbf{b}_1 + m\mathbf{b}_2 + l\mathbf{b}_3$$

for integer n, m, l .

A. The FCC lattice

Two important 3D lattices (which a large number of metallic elements exist in) are the face-centred cubic (FCC) and body-centred cubic (BCC) structures. Primitive lattice vectors of the FCC lattice are:

$$\mathbf{a}_1 = \begin{pmatrix} 0 \\ a/2 \\ a/2 \end{pmatrix}, \quad \mathbf{a}_2 = \begin{pmatrix} a/2 \\ 0 \\ a/2 \end{pmatrix}, \quad \mathbf{a}_3 = \begin{pmatrix} a/2 \\ a/2 \\ 0 \end{pmatrix}$$

where a is the edge-length of the conventional cubic unit-cell that contains four atoms per cell. You should verify [See problems] the following features of the FCC cell:

- (1) $\Omega = a^3/4$.
- (2) The coordination number N_c : 12.
- (3) The WS cell is a rhombic dodecahedron.
- (4) The reciprocal lattice vectors of the FCC cell form a BCC lattice, with the length of the cubic cell being $4\pi/a$.

i.e.

$$\mathbf{b}_1 = \frac{4\pi}{a} \begin{pmatrix} -1/2 \\ 1/2 \\ 1/2 \end{pmatrix}, \quad \mathbf{b}_2 = \frac{4\pi}{a} \begin{pmatrix} 1/2 \\ -1/2 \\ 1/2 \end{pmatrix}$$

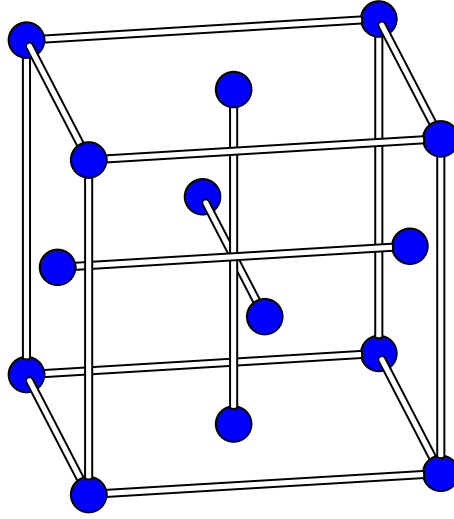


FIG. 13: Conventional unit cell of the FCC lattice

$$\mathbf{b}_3 = \frac{4\pi}{a} \begin{pmatrix} 1/2 \\ 1/2 \\ -1/2 \end{pmatrix}$$

(5) The packing fraction is $\sqrt{2}\pi/6 = 0.74$.

B. The BCC lattice

The following can be chosen to be primitive lattice vectors of the BCC cell:

$$\mathbf{a}_1 = \begin{pmatrix} -a/2 \\ a/2 \\ a/2 \end{pmatrix}, \quad \mathbf{a}_2 = \begin{pmatrix} a/2 \\ -a/2 \\ a/2 \end{pmatrix}, \quad \mathbf{a}_3 = \begin{pmatrix} a/2 \\ a/2 \\ -a/2 \end{pmatrix}$$

(1) $\Omega = a^3/2$.

(2) First shell $N_c = 8$, and second-shell $N_c = 6$. (3) The WS cell: truncated octahedron.

(4) The reciprocal lattice vectors of the BCC lattice is an FCC lattice, with the length of the cubic cell being $4\pi/a$.

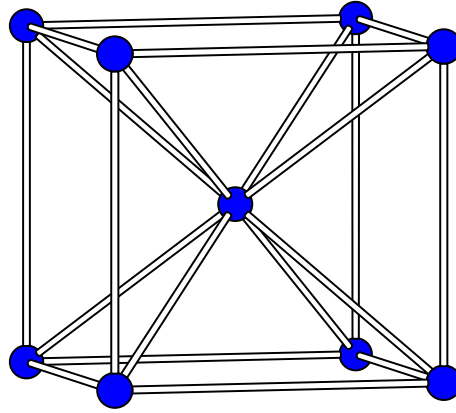


FIG. 14: Conventional unit cell of the BCC lattice

$$\mathbf{b}_1 = \frac{4\pi}{a} \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \end{pmatrix}, \quad \mathbf{b}_2 = \frac{4\pi}{a} \begin{pmatrix} 1/2 \\ 0 \\ 1/2 \end{pmatrix}$$

$$\mathbf{b}_3 = \frac{4\pi}{a} \begin{pmatrix} 1/2 \\ 1/2 \\ 0 \end{pmatrix}$$

(5) The packing fraction is $\sqrt{3}\pi/8 = 0.68$.

For completeness, we mention that Bloch's theorem generalised to 2D and 3D reads as:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{a}_i) = e^{i\mathbf{k}\cdot\mathbf{a}_i} \psi_{\mathbf{k}}(\mathbf{r}) \quad (149)$$

from which it follows that:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{a}_i) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad (150)$$

where $u_{\mathbf{k}}(\mathbf{r} + \mathbf{a}_i) = u_{\mathbf{k}}(\mathbf{r})$. Note that the Wigner-Seitz cell is that of the BCC lattice in real space.

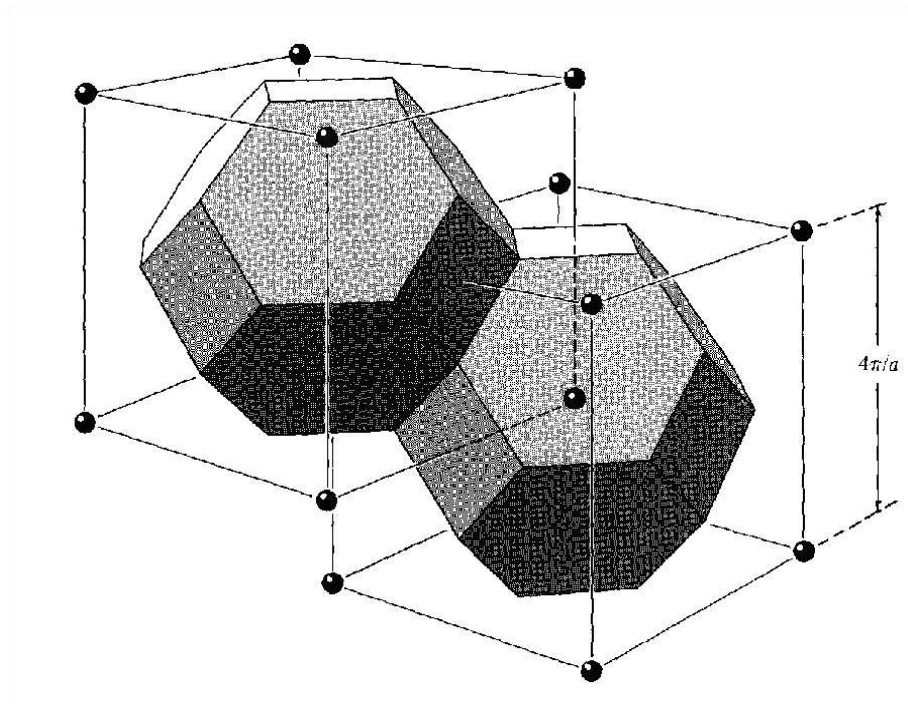


FIG. 15: FBZ of the FCC lattice: it is the Wigner-Seitz cell of a BCC lattice with lattice constant $4\pi/a$.

XII. THE FREE ELECTRON GAS

The free-electron gas (or Jellium) is a simple model system. Imagine taking N electrons in a cubic volume $L^3 = \Omega$ with a uniform positive compensating background (so that the system is charge neutral). The electron density will be uniform, and characterized by the single parameter

$$r_s = (3/4\pi n)^{1/3} \quad (151)$$

where $n = N/\Omega$ is the density. r_s is the radius a sphere that contains one electron.

If we assume that the electrons move independently of each other, then each feels the *average* repulsive field from all the other electrons. This is exactly cancelled by the attractive electrostatic potential of the compensating uniform background. Therefore, the energy of such a electron gas will be purely kinetic. The wavevector of the highest occupied state (the Fermi wavevector k_F) can obtain from the volume of the sphere of

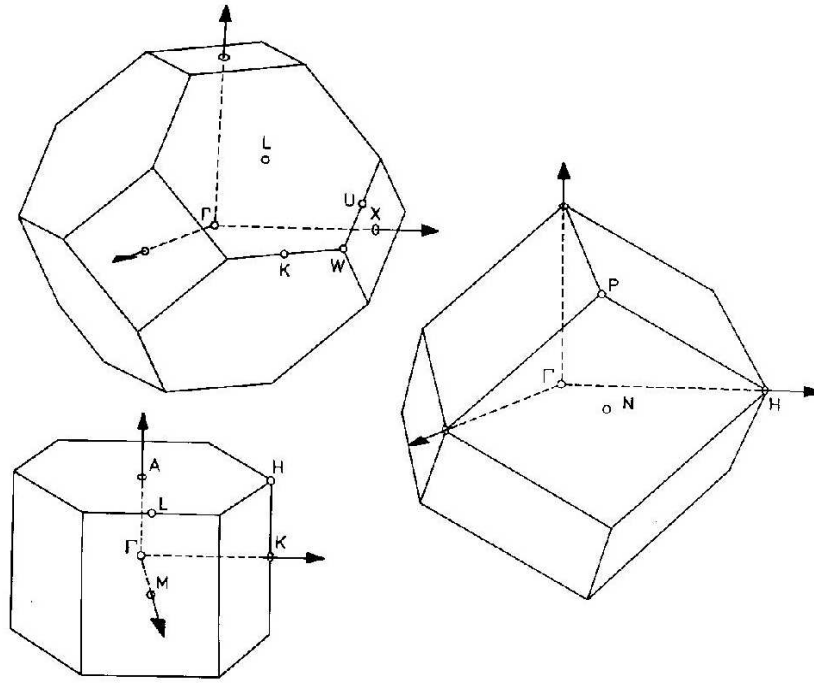


FIG. 16: FBZ of the FCC, BCC and Hexagonal lattices showing high symmetry points. Surfaces enclosing the Brillouin zones are planes that bisect the shortest reciprocal lattice vectors.

radius k_F times the density of states in k -space should equal N :

$$\frac{4\pi k_F^3}{3} \cdot 2 \cdot \left(\frac{L}{2\pi}\right)^3 = N \quad (152)$$

i.e.

$$k_F = (3\pi^2 n)^{1/3} = \frac{(9\pi/4)^{1/3}}{r_s} \quad (153)$$

The Fermi energy E_F is

$$E_F = \frac{\hbar^2 k_F^2}{2m}. \quad (154)$$

The density of states $g(\epsilon)$ is [See problem sheet]:

$$g(\epsilon) = \frac{\sqrt{2}}{\pi^2} \Omega \sqrt{\epsilon} \quad (155)$$

from which we can deduce the kinetic energy per electron using:

$$U_{ke} = \int_0^{E_F} \epsilon g(\epsilon) d\epsilon / N = \frac{3}{5} E_F \quad (156)$$

which in terms of r_s can be written as:

$$U_{ke} = \frac{1.105}{r_s^2} \text{ a.u.} \quad (157)$$

Of course, the motion of the electrons is, in reality, *correlated*. There are two sources of correlation: electrons with parallel spin keep apart from each other because of the Pauli exclusion principle. Anti-parallel electrons keep apart from each other because of their Coulomb repulsion. For interacting electrons, the former leads to a lowering of the energy by an amount called the *exchange energy*, and the latter by an amount called the *correlation energy*. For a homogeneous electron gas, the exchange-correlation energy is (in a.u.):

$$U_{xc} = \frac{-0.458}{r_s} - (0.0575 - 0.01565 \log r_s) \quad (158)$$

To understand the lowering of the energy, imagine each electron is accompanied by its own mutual exclusion zone, or *exchange-correlation hole*. The hole has a radius of r_s , which corresponds to exactly one electron being excluded. Each electron sees, therefore an additional attractive potential proportional to $1/r_s$ from the positive background which is not screened by the electrons. This is the leading term in the XC energy above. The remaining contributions come from using the correct XC hole (which is not a sharply defined sphere, but one with diffuse boundaries).

As a result, the energy of the electron gas is:

$$U_{eg} = U_{ke} + U_{xc} \quad (159)$$

which now is attractive, and possesses a minimum at a value of 0.08 a.u. (2.2eV), at an $r_s = 4.23$.

This is not a bad description of the simple metal Na which has a exptl. cohesive energy of 1.1eV, and an effective electronic radius of 4.0 a.u.

XIII. THE NEARLY FREE ELECTRON APPROXIMATION

In this section we will try to develop a perturbation expansion for the one-electron wavefunction $\psi_{\mathbf{k}}$ in the presence of weak periodic potential $V(\mathbf{r})$. Since the potential is assumed to be weak, we think that we will be able to write

$$\psi_{\mathbf{k}} \sim e^{i\mathbf{k}\cdot\mathbf{r}} + \text{small admixtures of } e^{i\mathbf{g}\cdot\mathbf{r}} \quad (160)$$

where $\mathbf{g} \neq \mathbf{k}$.

First of all note that the only \mathbf{g} which are mixed in are those for which $\mathbf{g} = \mathbf{k} + \mathbf{G}$. This is because the matrix element of the potential between any two plane-waves vanishes unless the two plane waves are related by a reciprocal-lattice vector:

$$\langle \mathbf{g} | V | \mathbf{k} \rangle = 0, \text{ unless } \mathbf{g} = \mathbf{k} + \mathbf{G} \quad (161)$$

[This is crucial. Show!]. As a result, a first-order perturbation expansion would read as follows:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{N\Omega}} + \sum_{\mathbf{G} \neq 0} \frac{\langle \mathbf{k} + \mathbf{G} | V | \mathbf{k} \rangle}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{G}}} \frac{e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}}{\sqrt{N\Omega}} \quad (162)$$

Note that this expansion can be cast in the form of Bloch function, multiplied by $e^{i\mathbf{k}\cdot\mathbf{r}}$:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \left[1 + \sum_{\mathbf{G} \neq 0} \frac{\hat{V}_{\mathbf{G}}}{\epsilon_{\mathbf{k}+\mathbf{G}} - \epsilon_{\mathbf{k}}} e^{i\mathbf{G}\cdot\mathbf{r}} \right] \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{N\Omega}} \quad (163)$$

where

$$\hat{V}_{\mathbf{G}} = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) d\mathbf{r} \quad (164)$$

[Derive this result!] In this expression Ω is the volume of the unit-cell, and N , as usual, is the number of unit cells in the crystal.

The question is: is the perturbation expansion Eqn.[163] valid for *all* \mathbf{k} , even for a very weak potential?

The problem that arises is when the denominator goes to zero. When is that going to occur? When:

$$\epsilon_{\mathbf{k}+\mathbf{G}} = \epsilon_{\mathbf{k}} \quad (165)$$

In that case, for those special \mathbf{k} , we need to use *degenerate* perturbation theory. Of course, as we discussed earlier, this occurs for plane-waves when the \mathbf{k} satisfies the Bragg criterion:

$$(\mathbf{k} + \mathbf{G})^2 = k^2 \quad (166)$$

$$2\mathbf{k} \cdot \mathbf{G} + G^2 = 0 \quad (167)$$

i.e. for those \mathbf{k} which lie on the Brillouin zone boundaries.

To deal with this case, we have to solve the Secular equations of degenerate perturbation theory. Let us assume (for simplicity) that there are only two states, $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}+\mathbf{G}}$, which are degenerate. In that case, the zeroth order approximation to $\psi_{\mathbf{k}}$ will consist of a certain admixture

$$\psi_{\mathbf{k}} = c_1 e^{i\mathbf{k} \cdot \mathbf{r}} + c_2 e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \quad (168)$$

The Schrödinger equation in this basis of two plane-waves becomes [show!]

$$\begin{bmatrix} k^2/2 - E & \hat{V}_{\mathbf{G}} \\ \hat{V}_{\mathbf{G}}^* & (\mathbf{k} + \mathbf{G})^2/2 - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad (169)$$

whose non-trivial solutions are obtained by setting the determinant of the matrix to zero and solving it. Note that in deriving this equation, the energy E is chosen relative to the average value of the potential in the unit-cell [Why?].

The resulting quadratic equation is

$$\left[k^2/2 - E \right] \left[(\mathbf{k} + \mathbf{G})^2/2 - E \right] = |\hat{V}_{\mathbf{G}}|^2 \quad (170)$$

whose two solutions are:

$$E_{\pm} = \frac{1}{2} [k^2/2 + (\mathbf{k} + \mathbf{G})^2/2] \pm \quad (171)$$

$$\frac{1}{2} \sqrt{[(\mathbf{k} + \mathbf{G})^2/2 - k^2/2]^2 + 4|\hat{V}_{\mathbf{G}}|^2} \quad (172)$$

Therefore, at a zone boundary where $k^2 = (\mathbf{k} + \mathbf{G})^2$ we have:

$$E_{\pm} = k^2/2 \pm |\hat{V}_{\mathbf{G}}| \quad (173)$$

i.e. a gap has opened up with band-gap $2|\hat{V}_{\mathbf{G}}|$. An instructive example of this occurs in the case of aluminium. If we consider the band-structure along ΓX , where

$$\mathbf{k}_{\Gamma} = (0, 0, 0), \quad \mathbf{k}_X = (2\pi/a)(1, 0, 0) \quad (174)$$

(a is the edge-length of the fcc unit cell. Note that for the fcc cell, X occurs at $2\pi/a$ and not π/a). The reciprocal lattice vector \mathbf{G} which maps \mathbf{k}_X onto a vector of the same magnitude is:

$$\mathbf{G} = \frac{2\pi}{a}(\bar{2}, 0, 0) \quad (175)$$

(note the convention that $\bar{2} \equiv -2$). In that case:

$$\mathbf{k}_X + \mathbf{G} = \frac{2\pi}{a}(\bar{1}, 0, 0)$$

which obviously has the magnitude as \mathbf{k}_X . Therefore the relevant Fourier component of V which will induce a band-gap to appear at X is:

$$\hat{V}(\bar{2}00)$$

which for the fcc lattice is the same as $\hat{V}(200)$, since the symmetry of the lattice implies that $\hat{V}_{-\mathbf{G}} = \hat{V}_{\mathbf{G}}$ (i.e. $\hat{V}_{\mathbf{G}}$ is real). The measured band-gap of Al at X is $\sim 1\text{eV}$, implying that $\hat{V}(200) \sim 0.5\text{eV}$. This is small compared to the Fermi-energy of about 10eV for Al, confirming that the NFE approximation should be valid in this case.

The wavefunctions we obtain for $\psi_{\pm}(x)$ along the ΓX direction are:

$$\psi_{\pm} = \sqrt{\frac{2}{L^3}} \begin{cases} \cos(2\pi x/a) \\ \sin(2\pi x/a) \end{cases} \quad (176)$$

Thus ψ_+ (the higher energy state) has a density *maximum* at the origin, and ψ_- , has a density *minimum*.

Is this reasonable? A density minimum for E_- at the origin must imply a *repulsive* potential there. Therefore, from our previous discussion for Al, we should conclude that:

$$\hat{V}(200) = +0.5\text{eV}$$

On the other hand, the crystal potential due to the Al cores is strongly negative (and divergent) at the origin. In fact an ab initio calculation shows $\hat{V}(200)$ to be:

$$\hat{V}(200) \approx -5\text{eV}$$

i.e., rather than getting a small positive term, the actual potential is actually large and negative, contradicting the NFE picture!

What has gone wrong? To answer this question we have to probe a little deeper.

XIV. PSEUDOPOTENTIALS

The basic problem arises because the NFE states we are treating are the 3s and 3p *valence* states, of Al. But these must be orthogonal to the tightly bound s and p core states. The valence states must have nodes in the core region, and this implies that these valence states can only be properly described by plane-waves of high momentum, not just the two that we considered before. i.e. retaining the two lowest energy plane waves provides an extremely poor approximation to the the valence wavefunctions. One way to circumvent this problem is to use the *Orthogonalised Plane-Wave* method [C. Herring, 1940], by using plane-waves which are from the outset orthogonalised to the core states:

$$\psi_{\mathbf{k}} = c_1 u_{\mathbf{k}}^{(1)} + c_2 u_{\mathbf{k}}^{(2)} \quad (177)$$

where $u_{\mathbf{k}}^{(1)}$ and $u_{\mathbf{k}}^{(2)}$ are orthogonalised plane-waves:

$$u_{\mathbf{k}}^{(1)} = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{N\cdot\Omega}} - \sum_c \beta_c^{(1)} \psi_c \quad (178)$$

$$u_{\mathbf{k}}^{(2)} = \frac{e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}}{\sqrt{N\cdot\Omega}} - \sum_c \beta_c^{(2)} \psi_c \quad (179)$$

where the sum over c runs over core states. The coefficients $\beta_c^{(i)}$ are chosen so that $u_{\mathbf{k}}^{(i)}$ are orthogonal to the ψ_c :

$$\langle \psi_c | u_{\mathbf{k}}^{(i)} \rangle = 0 \quad (180)$$

from which we get:

$$\beta_c^{(1)} = \langle \psi_c | e^{i\mathbf{k}\cdot\mathbf{r}} \rangle \quad (181)$$

$$\beta_c^{(2)} = \langle \psi_c | e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \rangle \quad (182)$$

If we now construct the Secular matrix element

$$\langle u_{\mathbf{k}}^{(1)} | \hat{H} - E | u_{\mathbf{k}}^{(2)} \rangle \quad (183)$$

we obtain [Show!]

$$\langle u_{\mathbf{k}}^{(1)} | \hat{H} - E | u_{\mathbf{k}}^{(2)} \rangle = \hat{V}_{\mathbf{G}} + \sum_c (E - E_c) \beta_c^{(1)*} \beta_c^{(2)} \quad (184)$$

where E_c is the energy of the core state c satisfying:

$$\hat{H}\psi_c = E_c\psi_c \quad (185)$$

The energy gap at X will be twice the modulus of this matrix element with $\mathbf{k} = \mathbf{k}_X$, i.e.

$$E_{gap} = 2 \left| \hat{V}_G + \sum_c (E_X - E_c) |\beta_c^{(1)}|^2 \right| \quad (186)$$

where we have substituted E_X , the energy of at the centre of the gap for E , which is an excellent approximation for small-gap systems.

Since $E_X - E_c \gg 0$ (because the valence states are much higher in energy than the core states) the core-orthogonality terms above are repulsive, the individual contributions being proportional to the $|\beta_c^{(1)}|^2$. This resolves the paradox we encountered earlier. The energy gap at X is small and positive because the large negative crystal potential, due to the nuclei, is counter-acted by an even larger positive core-orthogonality contribution. Thus we can hope to maintain an NFE picture of bonding in the sp-metals as long as we replace the true crystal potential with a *pseudopotential* which includes in it (effectively) the repulsive core-orthogonality terms.

The simplest such pseudo-potential is the Ashcroft empty-core PP:

$$V_{ps}(r) = \begin{cases} 0, & \text{for } R < R_c \\ -\frac{Z}{r}, & \text{for } R > R_c \end{cases} \quad (187)$$

where R_c is a parameter that characterises the size of the core.

Let us take the Fourier transform of this:

$$\hat{V}_{ps}(\mathbf{G}) = -\frac{4\pi Z}{\Omega.G^2} \cos(GR_c) \quad (188)$$

In the absence of a core ($R_c = 0$), this has the expected form of $-4\pi Z/G^2$, but in the presence of R_c , it oscillates in sign, going first from negative to positive when:

$$G_0 = \frac{\pi}{2R_c} \quad (189)$$

Heine and Abarenkov [1964] showed that the PP for aluminium behaves such that the first node occurs at a G slightly smaller than $G = (200)$, and that indeed $\hat{V}(200)$ is small and positive, as required to explain the smallness of the observed gap at X . The $R_c = 1.2\text{a.u.}$, implying that the core occupies a small fraction of the bulk atomic volume (about 6%). It nevertheless has a marked repulsive effect that determines not only the bond-length but also its crystal structure.

XV. THE WIGNER-SEITZ MODEL OF THE METALLIC BOND

Wigner and Seitz [1933] were the first to apply quantum-mechanics to understand the metallic bond (in sodium). They proposed a very simple argument.

The crystal structure of Na is BCC: each Na atom is surrounded by 14 first and second-nearest neighbour atoms. The ‘Wigner-Seitz’ cell is a truncated octahedron. Rather than considering the valence wavefunction of each Na atom in this complicated geometry, they replaced the WS cell *by a sphere of the same volume*. They further argued that the 3s valence bonding state in each sphere will satisfy the boundary condition that across the WS sphere, the gradient of the wavefunction should vanish

$$\left. \frac{dR_{3s}}{dr} \right|_{r=R_{WS}} = 0 \quad (190)$$

where R_{WS} is the radius of the WS sphere, and R_{3s} is the solution to the radial Schrödinger equation inside the WS cell.

In the free atom, R_{3s} satisfies the same S.E., but with different boundary conditions:

$$R_{3s} \rightarrow 0, \text{ as } r \rightarrow \infty$$

They solved the S.E. for the 3s function, as a function of R_{WS} , and found that its shows a minimum at about 2.9 a.u. They then added to this energy the k.e. per electron of a free-electron gas of the appropriate density, in order to obtain the total binding energy. As a result they found that the binding energy had a minimum at an R_{WS} from which the following could be obtained

$$\begin{aligned} a &= 4.2\text{\AA} && [4.30 \text{ expt}] \\ U &= 25.6 \text{ kcal/mole} && [26.00] \\ B &= 1.6 \times 10^{-12} \text{ J/m}^3 && [1.67 \times 10^{-12}] \end{aligned}$$

where U is the cohesive energy and $B = Vd^2U/dV^2$ is the bulk modulus, which is related to the second derivative of the energy-volume curve.

Remarkable agreement indeed!

Why are the Wigner-Seitz results so good (for Na)?

To understand the binding energy curves of the simple metals, we can consider the metallic bond as arising from the immersion of a lattice of empty-core pseudo-potentials into a free-electron gas. Since the PP will perturb the free-electron gas weakly, we can assume, to a first approximation, that the free-electron gas remains uniformly distributed. In this approximation, the total binding energy per atom is:

$$U = ZU_{eg} + U_{es} \quad (191)$$

where Z is the valence. U_{eg} is the sum of the exchange-correlation and kinetic energies per electron, defined earlier in Eqn.[159],

$$U_{eg} = \frac{1.105}{r_s^2} - \frac{0.458}{r_s} - (0.0575 - 0.01565 \log r_s) \quad (192)$$

U_{es} is the electrostatic energy of the interaction between the electrons and the ions. This is evaluated by neglecting the electrostatic interaction between different WS cells (they are electrically neutral), and by approximating the electrostatic energy of a single WS cell by that of a sphere:

$$U_{es} = - \int n(\mathbf{r})V_{ps}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (193)$$

Using the Ashcroft empty core PP with core radius R_c , and $n = Z/\Omega = Z/(4\pi R_{WS}^3/3)$, we obtain:

$$U_{es} = -\frac{3Z^2}{2R_{WS}} \left[1 - \left(\frac{R_c}{R_{WS}} \right)^2 \right] + \frac{0.6Z^2}{R_{WS}} \quad (194)$$

For the monovalent metals $Z = 1$ and $r_s = R_{WS}$. We find a good cancellation between the second term $[0.6Z^2/R_{WS}]$ and the XC energy

$$U_{eg} = -\frac{0.458}{r_s} - (0.0575 - 0.01565 \log r_s)$$

and thus:

$$U \approx -\frac{3Z^2}{2R_{WS}} \left[1 - \left(\frac{R_c}{R_{WS}} \right)^2 \right] + \frac{1.105}{r_s^2} \quad (195)$$

This expression mirrors what Wigner and Seitz found. The first term models the variation of the 3s orbital energy with R_{WS} : as the atoms are brought together, the bonding state is first reduced in energy, until the atoms are brought to such a distance that the cores begin to overlap, in which case its energy starts to increase rapidly. The distance at which the minimum in the first term occurs when is

$$R_{WS} = \sqrt{3}R_c \quad (196)$$

which for an $R_c \approx 1.7$ a.u. gives $R_{WS} = 2.9$ a.u., in good agreement with the result of Wigner and Seitz for the solutions to the radial S.E..

We can invert the process, and say, given values of R_{WS} (taken from experiment), what value of R_c to minimize the U - and what values of B arise as a result?

The table below shows the results: R_c increases down a period, and decreases across the period, as expected. The bulk moduli of the SP metals is reasonably well reproduced, whereas the bulk moduli of the sd-valent noble metals are very poor.

XVI. SCREENING: THE THOMAS-FERMI APPROXIMATION

The approach we have adopted thus far was to compute energy of the uniform electron gas immersed into a lattice of empty-core pseudopotentials, while assuming that *the system of electrons remain uniformly distributed*.

	R_{WS}	R_c	B/B_{ke}	Expt
Li	3.27	1.32	0.63	0.50
Na	3.99	1.75	0.83	0.80
K	4.86	2.22	1.03	1.10
Rb	5.31	2.47	1.14	1.55
Cs	5.70	2.76	1.29	1.43
Be	2.36	0.76	0.45	0.27
Mg	3.35	1.31	0.73	0.54
Ca	4.12	1.73	0.95	0.66
Sr	4.49	1.93	1.05	0.78
Ba	4.67	2.03	1.11	0.84
Al	2.99	1.11	0.69	0.32
Ga	3.16	1.20	0.74	0.33
In	3.48	1.37	0.83	0.39
Tl	3.58	1.43	0.87	0.39
Cu	2.67	0.91	0.45	2.16
Ag	3.02	1.37	0.71	2.94
Au	3.01	1.35	0.69	4.96

Code I: Table of effective R_c and bulk-moduli.

In reality, of course, the electron density will change in response to the lattice of ions, leading to a *screening* of the ionic cores. The modulated electron density may, in turn, lead to forces on the ions and cause the ions to move. This leads to a *structure dependent* term in the energy. In the next few sections we will develop methods to treat these aspects. Consider a point ion of charge Z at the origin, immersed in a free-electron gas of charge density $-n_0$. The presence of the ion will modify the electron

density from n_0 to $n_0 + \delta n(\mathbf{r})$ which can be related to the new potential $\phi(\mathbf{r})$ through Poissons's equations:

$$\nabla^2 \phi(\mathbf{r}) = -4\pi[Z\delta(\mathbf{r}) - \delta n(\mathbf{r})] \quad (197)$$

The first term on the RHS refers to the charge density of the ion at the origin, and the second refers to the change in the electron density.

We will solve Eqn.[197] in the Thomas-Fermi approximation, by linking the change in density $\delta n(\mathbf{r})$ to the *local* potential $\phi(\mathbf{r})$. At equilibrium, the chemical potential of the electrons must be everywhere the same. At zero Kelvin, the chemical potential is equal on the one hand equal to the Fermi Energy E_F , and on the other hand is equal to the sum of the kinetic and potential energies:

$$T(\mathbf{r}) + (-e).\phi(\mathbf{r}) = E_F \quad (198)$$

[Note that the potential *energy* $V(\mathbf{r})$ of an electron is the potential $\phi(\mathbf{r})$ times $(-e)$

$$V(\mathbf{r}) = -\phi(\mathbf{r}) \text{ in a.u.}$$

In this section, you need to keep a clear head as to meanings of the potential and the potential energy!].

E_F is the Fermi energy of the free electron gas of density n :

$$E_F = \frac{1}{2}(3\pi^2 n)^{2/3} \quad (199)$$

In the TF approximation, we assume that the spatial variation in the density to be sufficiently slow so that local kinetic energy $T(\mathbf{r})$ is equal to that of the free-electron of the same local density. We therefore write

$$T(\mathbf{r}) = \frac{1}{2}[3\pi^2 n(\mathbf{r})]^{2/3} \quad (200)$$

[Note this is saying that the relevant local kinetic energy is that of the *highest* occupied state, rather than the average value of the K.E per electron, namely $3.E_F/5$]. Next, noting that $n(\mathbf{r}) = n_0 + \delta n(\mathbf{r})$, we obtain:

$$\begin{aligned} T(\mathbf{r}) &= \left[1 + \frac{\delta n(\mathbf{r})}{n_0} \right]^{2/3} E_F \\ &\approx \left[1 + \frac{2}{3} \frac{\delta n(\mathbf{r})}{n_0} \right] E_F \end{aligned} \quad (201)$$

Substituting in Eqn.[198] we obtain:

$$\left[1 + \frac{2}{3} \frac{\delta n(\mathbf{r})}{n_0}\right] E_F - \phi(\mathbf{r}) = E_F \quad (202)$$

and therefore we can relate the induced density to $\phi(\mathbf{r})$:

$$\delta n(\mathbf{r}) = \frac{3n_0}{2E_F} \phi(\mathbf{r}) \quad (203)$$

Substituting into the Poisson Eqn. gives:

$$\nabla^2 \phi(\mathbf{r}) = -4\pi Z \delta(\mathbf{r}) + \kappa_{TF}^2 \phi(\mathbf{r}) \quad (204)$$

where

$$\kappa_{TF} = \left(\frac{12\pi n_0}{2E_F}\right)^{1/2} = 2 \left[\frac{3n_0}{\pi}\right]^{1/6} \quad (205)$$

The solution of the TF Poisson equation is well known, and can be obtained through Fourier transformation. Let

$$\hat{\phi}(\mathbf{g}) = \int e^{-i\mathbf{g}\cdot\mathbf{r}} \phi(\mathbf{r}) d\mathbf{r} \quad (206)$$

The inverse transform is:

$$\phi(\mathbf{r}) = \frac{1}{(2\pi)^3} \int e^{i\mathbf{g}\cdot\mathbf{r}} \hat{\phi}(\mathbf{g}) d\mathbf{g} \quad (207)$$

Taking Fourier transforms of both sides of Eqn.[204] we obtain [Show!]:

$$-g^2 \hat{\phi}(\mathbf{g}) = -4\pi Z + \kappa_{TF}^2 \hat{\phi}(\mathbf{g}) \quad (208)$$

which can be solved for $\hat{\phi}(\mathbf{g})$:

$$\hat{\phi}(\mathbf{g}) = \frac{4\pi Z}{g^2 + \kappa_{TF}^2} \quad (209)$$

Taking its Inverse Fourier Transform, we obtain the potential:

$$\phi(\mathbf{r}) = \frac{Z}{r} e^{-\kappa_{TF} r} \quad (210)$$

Thus the potential energy of the electrons away from nucleus go as:

$$V(\mathbf{r}) = -\frac{Z}{r} e^{-\kappa_{TF} r} \quad (211)$$

which is a screened Coulomb potential. $\lambda = 1/\kappa_{TF}$ is the Thomas-Fermi screening length. The Thomas-Fermi dielectric constant ϵ can be obtained from the relation

$$\hat{V}(\mathbf{g}) = \hat{V}_{ext}(\mathbf{g})/\epsilon(\mathbf{g}) \quad (212)$$

(i.e. the actual screened potential should be given by the external potential divided by the dielectric constant). Since V_{ext} is the bare potential due to the nucleus, we have:

$$\hat{V}_{ext}(\mathbf{g}) = -4\pi Z/g^2 \quad (213)$$

we have that:

$$\epsilon_{TF}(\mathbf{g}) = 1 + \frac{\kappa_{TF}^2}{g^2} \quad (214)$$

Thus in the long-wavelength limit $\mathbf{g} \rightarrow 0$, the dielectric constant diverges.

XVII. LINEAR RESPONSE THEORY

It turns out that the Thomas Fermi theory is not a good model of the sp metals. The basic assumption, namely that the local potential should vary on a sufficiently long length scale so that the local approximation to the kinetic energy is valid, is not met. The potential in practice varies on length scales of R_c , which is comparable to, not longer than, the Thomas-Fermi screening length.

In fact TF theory totally fails to distinguish between the various competing metallic structures such as FCC, BCC and HCP.

In Linear Response Theory, we start off by saying that a potential with a definite wavevector, $\hat{V}(\mathbf{g})$, (i.e. definite periodicity), induces a density $\delta\hat{n}(\mathbf{g})$ which is linearly proportional:

$$\delta\hat{n}(\mathbf{g}) = \chi(\mathbf{g})\hat{V}(\mathbf{g}) \quad (215)$$

$\chi(\mathbf{g})$, the *response function*, is a function of \mathbf{g} , i.e. different periodicities \mathbf{g} of the potential will in general give rise to different amounts of the induced density. Our goal in this section is to work out an expression for $\chi(\mathbf{g})$. Before we begin, let us note a

relationship between χ and the dielectric constant ϵ . The potential $\hat{V}(\mathbf{g})$ can be written as the external potential $\hat{V}_{ext}(\mathbf{g})$ plus the induced potential due to the electrons $\delta\hat{V}$:

$$\hat{V}(\mathbf{g}) = \hat{V}_{ext}(\mathbf{g}) + \delta\hat{V}(\mathbf{g}) \quad (216)$$

[This is the definition of δV].

Since from Poisson's equation:

$$\delta\hat{V} = (4\pi/g^2)\delta\hat{n},$$

we have:

$$\hat{V} = \hat{V}_{ext} + (4\pi/g^2).\delta\hat{n} \quad (217)$$

$$\hat{V} = \hat{V}_{ext} + (4\pi/g^2).\chi\hat{V} \quad (218)$$

i.e.

$$\begin{aligned} \hat{V} \cdot (1 - 4\pi\chi/g^2) &= \hat{V}_{ext} \\ \hat{V} &= \frac{\hat{V}_{ext}}{1 - \frac{4\pi\chi}{g^2}} \end{aligned}$$

But we also write:

$$\hat{V} = \hat{V}_{ext}/\epsilon(\mathbf{g}) \quad (219)$$

and therefore

$$\epsilon(\mathbf{g}) = 1 - \frac{4\pi}{g^2}\chi(\mathbf{g}) \quad (220)$$

So it can be seen that in the Thomas-Fermi approximation,

$$\chi = -\kappa_{TF}^2/4\pi \quad (221)$$

which is independent of the wavevector g . i.e. in the TF theory, the response of the system does not depend on the wavelength of the potential - which, as we shall see, is unphysical.

How can we evaluate χ ? We shall use perturbation theory. We consider a potential which has only a single periodicity \mathbf{g} . i.e. in real space, this will be:

$$V(\mathbf{r}) = V_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{r}} + \text{complex conjugate} \quad (222)$$

where the c.c. is added to make the potential real.

From first order perturbation theory, we know that (to first-order) the wavefunctions of the system under a potential is given by:

$$\psi_{\mathbf{k}}^{(1)}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r}) + \sum_{\mathbf{q} \neq \mathbf{k}} \frac{\langle \mathbf{k} | V | \mathbf{q} \rangle}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{q}}} \psi_{\mathbf{q}} \quad (223)$$

where $\psi_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}}$ are the unperturbed wavefunctions and energy levels. In the present case, since the potential only contains only one periodicity, the sum over \mathbf{q} will contain only two terms, corresponding to $\mathbf{q} = \pm\mathbf{g}$. In addition, $\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{\Omega}$. Thus:

$$\psi_{\mathbf{k}}^{(1)}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \left[e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{V_{\mathbf{g}}}{k^2/2 - (\mathbf{k}+\mathbf{g})^2/2} e^{i(\mathbf{k}+\mathbf{g})\cdot\mathbf{r}} + \frac{V_{-\mathbf{g}}}{k^2/2 - (\mathbf{k}-\mathbf{g})^2/2} e^{i(\mathbf{k}-\mathbf{g})\cdot\mathbf{r}} \right] \quad (224)$$

The change in the electron density is:

$$\delta n(\mathbf{r}) = \sum_{\mathbf{k}} \left[|\psi_{\mathbf{k}}^{(1)}|^2 - |\psi_{\mathbf{k}}|^2 \right] f_{\mathbf{k}} \quad (225)$$

where $f_{\mathbf{k}}$ are the occupation number of state \mathbf{k} . We find, substituting Eqn.[224], that:

$$\delta n(\mathbf{r}) = 2 \left[\frac{1}{\Omega} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}}}{k^2 - (\mathbf{k}+\mathbf{g})^2} + \frac{f_{\mathbf{k}}}{k^2 - (\mathbf{k}-\mathbf{g})^2} \right] \times [V_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{r}} + \text{c.c}] \quad (226)$$

so that:

$$\chi(\mathbf{g}) = \frac{2}{\Omega} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}}}{k^2 - (\mathbf{k} + \mathbf{g})^2} + \frac{f_{\mathbf{k}}}{k^2 - (\mathbf{k} - \mathbf{g})^2} \quad (227)$$

Since the sum over \mathbf{k} runs over all \mathbf{k} , we can make the substitution $\mathbf{k}' = \mathbf{k} - \mathbf{g}$ in the second summation, and sum over \mathbf{k}' instead. We finally arrive at:

$$\chi(\mathbf{g}) = \frac{2}{\Omega} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{g}}}{k^2 - (\mathbf{k} + \mathbf{g})^2} \quad (228)$$

This summation can actually be performed by replacing by an integration. Before we do that, however, notice that the only terms which contribute to it are those for which one of the states, say \mathbf{k} , is occupied state, and the other, $\mathbf{k} + \mathbf{g}$, is unoccupied. This is because if they are both occupied, or both unoccupied, the numerator, which is the difference in the occupation numbers, will vanish. We should expect, therefore, that only electrons close to the Fermi energy will be able to respond to the potential. The integral can be done as follows:

$$\frac{2}{\Omega} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}}}{k^2 - (\mathbf{k} + \mathbf{g})^2} = \frac{2.2}{(2\pi)^3} \int_0^{k_F} 2\pi k^2 dk \int_0^\pi \frac{\sin \theta}{-g^2 - 2gk \cos \theta} d\theta$$

The integral over θ can be done, yielding:

$$\frac{1}{(2\pi)^2 g} \int_0^{k_F} k \log \left| \frac{g + 2k}{g - 2k} \right| dk$$

which can also be integrated to give:

$$\frac{2}{\Omega} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}}}{k^2 - (\mathbf{k} + \mathbf{g})^2} = -2 \cdot \frac{k_F}{4\pi^2} \left[\frac{1}{2} + \frac{1 - \eta^2}{4\eta} \log \left| \frac{1 + \eta}{1 - \eta} \right| \right] \quad (229)$$

where $\eta = g/(2k_F)$. Changing $\mathbf{g} \rightarrow -\mathbf{g}$ in the initial sum leaves the final sum the same. Thus we end up doubling the result, which can be expressed as follows:

$$\chi(\eta) = \left[\frac{1}{2} + \frac{1 - \eta^2}{4\eta} \log \left| \frac{1 + \eta}{1 - \eta} \right| \right] \chi_{TF} \quad (230)$$

where we have used

$$-4 \cdot k_F / (4\pi^2) = -(\kappa_{TF}^2 / 4\pi) = \chi_{TF} \quad (231)$$

Eqn.[230] is known as the Lindhard response function.

It has the following properties: (1) As $\eta \rightarrow 0$ (i.e. as $\mathbf{g} \rightarrow 0$, tends to χ_{TF} . i.e. the long wavelength limit of the Lindhard function is the same as the Thomas-Fermi response. This is expected, since in that limit $2\pi/g \gg \lambda_{TF}$, which is the expected

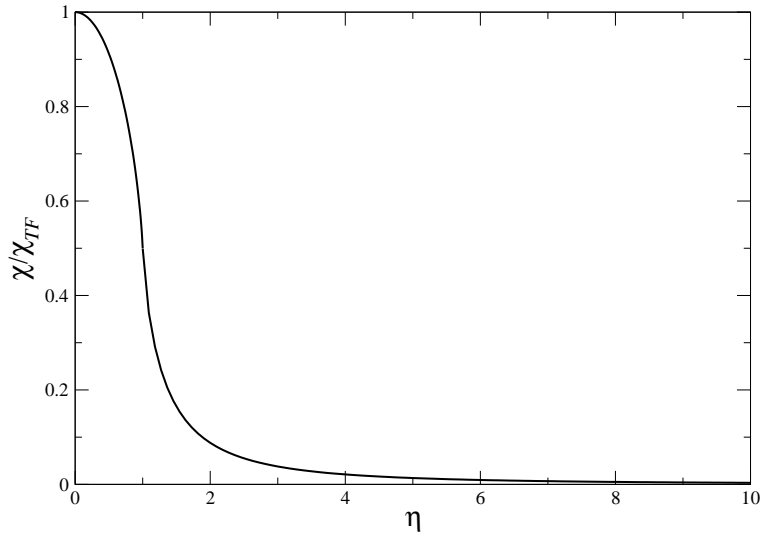


FIG. 17: The Lindhard function.

domain of applicability of TF theory.

(2) As $g \rightarrow \infty$, $\chi \rightarrow 0$. i.e. as the wavelength of the potential gets shorter, the response of the system to it becomes smaller: the electrons are not able to screen out very short wavelength potentials. Note that the shortest wavelength free-electron plane-wave has wavelength $2\pi/k_F$, and we would not expect the electrons to respond to shorter wavelength perturbations.

(3) The Lindhard function has a logarithmic singularity at $g = 2k_F$. This is a very weak singularity, but gives rise to very long wavelength oscillations in the electron density of wavelength $2k_F$. Its consequence is that the screening cloud around an ionic core also oscillates:

$$\delta n(\mathbf{r}) \sim \frac{\cos(2k_F r)}{r^3} \quad (232)$$

These oscillations are known as *Friedel* oscillations. The Coulomb interaction between these oscillatory screening clouds give rise to oscillatory interatomic potentials.

The physical origin of the weak singularity at $g = 2k_F$ can be traced back to the fact that for that there are many more states which can scatter from an occupied state close to (but below) the Fermi surface into states just above the Fermi surface by scattering across the Fermi sphere (whose diameter is $2k_F$).

XVIII. STRUCTURE DEPENDENT TERMS IN THE ENERGY

We want to evaluate the total binding energy of an NFE metal within second-order perturbation theory. In the presence of a perturbation V , the 2nd order correction to the energy of the state \mathbf{k} is:

$$E_{\mathbf{k}}^{(2)} = \sum_{\mathbf{g} \neq 0} \frac{|\langle \mathbf{k} | V | \mathbf{k} + \mathbf{g} \rangle|^2}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k} + \mathbf{g}}} \quad (233)$$

$$= \sum_{\mathbf{g} \neq 0} \frac{|V(\mathbf{g})|^2}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k} + \mathbf{g}}} \quad (234)$$

where V is the potential due to the ions (i.e. the external potential) *and* the electrons. This V can be related to the ionic potential via:

$$\hat{V}(\mathbf{g}) = \hat{V}_{ext}(\mathbf{g})/\epsilon(\mathbf{g}) \quad (235)$$

i.e. by dividing the ionic potential by the dielectric constant. Now, in real space, the potential due to the ions is simply:

$$V_{ext}(\mathbf{r}) = \sum_I V_{ps}(\mathbf{r} - \mathbf{R}_I) \quad (236)$$

where $V_{ps}(\mathbf{r} - \mathbf{R}_I)$ is the pseudo-potential due to ion I at \mathbf{r} , and the sum over I is over all nuclei in the crystal. Taking its Fourier transform gives $\hat{V}_{ext}(\mathbf{g})$:

$$\hat{V}_{ext}(\mathbf{g}) = \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{g}\cdot\mathbf{r}} V_{ext}(\mathbf{r}) d\mathbf{r} \quad (237)$$

$$= \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{g}\cdot\mathbf{r}} \sum_I V_{ps}(\mathbf{r} - \mathbf{R}_I) d\mathbf{r} \quad (238)$$

$$= \sum_I e^{-i\mathbf{g}\cdot\mathbf{R}_I} \cdot \frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{g}\cdot\mathbf{r}} V_{ps}(\mathbf{r}) d\mathbf{r} \quad (239)$$

$$= S(\mathbf{g}) \hat{V}_{ps}(\mathbf{g}) \quad (240)$$

where

$$S(\mathbf{g}) = \sum_I e^{-i\mathbf{g}\cdot\mathbf{R}_I}. \quad (241)$$

As a result, we have:

$$\hat{V}(\mathbf{g}) = S(\mathbf{g})\hat{V}_{ps}(\mathbf{g})/\epsilon(\mathbf{g}) \quad (242)$$

Substituting into Eqn.[234], and summing over all occupied states, we have the total 2nd-order change in the energy due to the perturbation:

$$U^{(2)} = \sum_{\mathbf{k}} f_{\mathbf{k}} \sum_{\mathbf{g} \neq 0} \frac{|S(\mathbf{g})|^2 |\hat{V}_{ps}(\mathbf{g})|^2}{[k^2/2 - (\mathbf{k} + \mathbf{g})^2/2]} \frac{1}{\epsilon(\mathbf{g})^2} \quad (243)$$

The sum over \mathbf{k} can be performed, the result being expressed in terms of the Lindhard function over 2, $\chi(\mathbf{g})/2$, times the volume of the crystal, Ω :

$$U^{(2)} = \frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} \frac{|S(\mathbf{g})|^2 |\hat{V}_{ps}(\mathbf{g})|^2 \chi(\mathbf{g})}{\epsilon(\mathbf{g})^2} \quad (244)$$

In fact, this expression contains a double-counting of the Hartree energy. This arises because what we have calculated are the changes in the energy eigenvalues, where we have assumed that the total potential $V(\mathbf{r})$ arises from the sum of the external potential and the Hartree potential. When we sum over the eigenvalues, we double count the Hartree energy, since what we compute is, effectively

$$\begin{aligned} & \sum_{\mathbf{k}} f_{\mathbf{k}} [\langle \psi_{\mathbf{k}}^{(1)} | \phi_H | \psi_{\mathbf{k}}^{(1)} \rangle - \langle \psi_{\mathbf{k}} | \phi_H | \psi_{\mathbf{k}} \rangle] \\ &= \int d\mathbf{r} \delta n(\mathbf{r}) \phi_H(\mathbf{r}) \end{aligned} \quad (245)$$

where $\psi^{(1)}$ are the perturbed wavefunctions, ψ_k the unperturbed ones, and ϕ_H is the Hartree potential. This is twice the change in the Hartree energy, and thus we need to subtract out half of it, i.e.:

$$U^{(2)} \rightarrow U^{(2)} - \frac{1}{2} \int d\mathbf{r} \delta n(\mathbf{r}) \phi_H(\mathbf{r}) \quad (246)$$

Now in Fourier space, the Hartree integral can be written as:

$$\frac{1}{2} \int d\mathbf{r} \delta n(\mathbf{r}) \phi_H(\mathbf{r}) = \frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} |\delta \hat{n}(\mathbf{g})|^2 \frac{4\pi}{g^2} \quad (247)$$

The expression simplifies considerably. Using, :

$$\delta\hat{n}(\mathbf{g}) = \chi(\mathbf{g})\hat{V}(\mathbf{g}) \quad (248)$$

$$= \chi(\mathbf{g})\frac{\hat{V}_{ext}(\mathbf{g})}{\epsilon(\mathbf{g})} \quad (249)$$

$$= \chi(\mathbf{g})S(\mathbf{g})\frac{\hat{V}_{ps}(\mathbf{g})}{\epsilon(\mathbf{g})} \quad (250)$$

and therefore we obtain:

$$\frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} \frac{|S(\mathbf{g})|^2 |\hat{V}_{ps}(\mathbf{g})|^2 \chi(\mathbf{g})}{\epsilon(\mathbf{g})^2} - \quad (251)$$

$$\frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} |S(\mathbf{g})\hat{V}_{ps}(\mathbf{g})|^2 \chi(\mathbf{g})^2 \cdot \frac{1}{\epsilon(\mathbf{g})^2} \frac{4\pi}{g^2} \quad (252)$$

$$= \frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} |S(\mathbf{g})\hat{V}_{ps}(\mathbf{g})|^2 \frac{\chi(\mathbf{g})}{\epsilon(\mathbf{g})^2} \left[1 - \frac{4\pi\chi(\mathbf{g})}{g^2}\right] \quad (253)$$

$$= \frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} |S(\mathbf{g})\hat{V}_{ps}(\mathbf{g})|^2 \frac{\chi(\mathbf{g})}{\epsilon(\mathbf{g})} \quad (254)$$

where we have used the fact that:

$$\epsilon(\mathbf{g}) = 1 - \frac{4\pi\chi(\mathbf{g})}{g^2} \quad (255)$$

Thus we end up with a remarkably simple expression for the second-order change in the energy of an NFE metal:

$$U^{(2)} = \frac{\Omega}{2} \sum_{\mathbf{g} \neq 0} |S(\mathbf{g})\hat{V}_{ps}(\mathbf{g})|^2 \frac{\chi(\mathbf{g})}{\epsilon(\mathbf{g})} \quad (256)$$

Looking at this expression, we see that $U^{(2)}$ can be written as a structure dependent factor through $S(\mathbf{g})$, and a part $\Phi(\mathbf{g})$ that depends on the properties of the free electron gas, and the pseudopotential:

$$U^{(2)} = \sum_{\mathbf{g} \neq 0} |S(\mathbf{g})|^2 \Phi_{bs}(\mathbf{g}) \quad (257)$$

$$\Phi_{bs}(\mathbf{g}) = \frac{\Omega}{2} |\hat{V}_{ps}(\mathbf{g})|^2 \frac{\chi(\mathbf{g})}{\epsilon(\mathbf{g})} \quad (258)$$

Of course, if the atoms are in perfect lattice positions, then the sum over \mathbf{g} contains only reciprocal lattice vectors \mathbf{G} , and the energy reduces to

$$U^{(2)} = \sum_{\mathbf{G} \neq 0} |S(\mathbf{G})|^2 \Phi_{bs}(\mathbf{G}) \quad (259)$$

$$(260)$$

$\Phi_{bs}(\mathbf{g})$ (called the energy-wavenumber characteristic) has the following properties:

(1) It is less than or equal to zero for all \mathbf{g} , and therefore $U^{(2)}(\mathbf{g})$ is always negative.

(2) $\Phi_{bs}(\mathbf{g})$ is zero at \mathbf{g}_0 at which $\hat{V}_{ps}(\mathbf{g})$ vanishes.

(3) The band-structure energy can be used to predict if a particular lattice is stable against lattice distortions. In fcc Ga and In, for example, \mathbf{g}_0 lies close to the reciprocal lattice vectors (200) and (111), and therefore only a modest gain in energy is obtained in these structures from the band-structure energy. However, it can be seen that if the structure distorts its lattice, *so as to go to larger unit cells*, then the reciprocal lattice vectors shrink, and as a result there is an enhanced gain in energy due to the band-structure. i.e. the band-structure energy favours distorted lattices of lower symmetry. Of course this distortion may be offset by other effects, such as the increase in Madelung energy that accompanies such distortions. In practice, therefore there is a balance to be achieved between these two effects. Detailed calculations show that the distorted fcc structure adopted by Ga is precisely due to such an effect.