PROPERTIES OF WANNIER FUNCTIONS

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ABSTRACT

«Wannier functions provide us with a means for the development of rigorous theorems which are analogous to the crude theorems we might derive with a tight binding approximation. However, a good and accurate Wannier function would be extremely difficult to calculate and its structure would be quite complicated.»[1]

Excluding calculations obtained using the O.A.O. approximation few works exist on the mathematical properties of Wannier functions and only very few have been explicitly determined.

The present study attempts to provide a partial solution for this situation and seeks to extend the use and knowledge of these functions. First, a theoretical investigation is made of the mathematical properties of Wannier functions and then some calculations are carried out to obtain some of these functions for various forms of potential fields.

The original results obtained concern;

I) Free electron Wannier functions for many of the familiar crystal types.

II) A method for obtaining Wannier functions from relatively simple functions (unperturbed Wannier functions). The method has been applied to several particular cases (potential field with inversional symmetry etc.) and has been modified for other applications.

III) Nearly free electron Wannier functions calculated both using analytical methods and the method outlined in section II .

IV) The extension of Kohn's one dimensional treatment to three dimensions using a new approach.

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[1] Harrison, W.A.,Solid State Theory, McGraw-Hill,inc.,1970.

V) The relation, that for weakly bound electrons the rate of exponential fall-off of the Wannier functions is given by the Fourier coefficients of the perturbing field.

VI) An analytic method to find the arbitrary phases of the Bloch functions which yield the most localized Wannier functions.

VII) Exact three dimensional Wannier functions for an intermediate potential field. The expressions for these functions have been given in analytic forms and can be applied by adjustment of parameters to similiar problems.

VIII) Finally, the Wannier functions for tightly bound electrons for a B.C.C. lattice. The atomic analogy of these functions has been discussed including some miscellaneous cases involving the presence of different atomic species in a unit cell etc..

CHAPTER I

1. INTRODUCTION

In 1928 Bloch[1] made the suggestion of approximating the wave function of an electron in a given energy band by linear combinations of atomic orbitals (abbreviated L.C.A.O) which has greatly influenced subsequent development of the methods of calculating electronic energy levels of solids.

He was also the first to realize that solutions of Schrödinger's equation for solids (Bloch functions) may be expressed in terms of a plane wave modulated by a function $U_n(\underline{k},\underline{r})$ which has the period of the lattice (Bloch's theorem), though Floquet in a purely mathematical sense had derived such a result much earlier (for a discussion of Floquet's theorem and other related topics see for instance Wilson[2] Whittaker and Watson[3]). Both the approximation and the periodicity condition for crystal orbitals , through which his name perpetrated are a result of the translation symmetry in crystals.

Bloch's method received immediate applications because there were few other methods available at the time and also because of its conceptual clarity. However, there was a serious drawback connected with the method since the free atomic functions used in the usual Bloch summation, though normalized, were not orhogonal; for in real crystals the atomic orbitals extended considerable further than the interatomic distance hence giving rise to non-zero overlap integrals.

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[1] Bloch, F. Z. physik 52, 555 (1928).

[2] Wilson, A.H.,The Theory of Metals, 1st ed. Camb.Univ. Press, New York(19

[3] Whittaker, E.T. and Watson, G.N., Modern Analysis, Camb. Univ. Press , Newyork (1943).

Furthermore the wave functions constructed from these non-orthogonal basis functions were not exact solutions of Schrödinger's equation for the one electron problem.

The existence of this difficulty was pointed out, soon after the appearance of Bloch's suggestion, by Slater[4](1930), Vleck and Sherman[5](1935), and Inglis[6](1934).

At first, in the development of the tight binding method all such overlap integrals were ignored, however, in later years attempts were made to overcome this difficulty either by taking account of nonorthogonality (i.e. see Mulliken[7]et al, Hoffman[8] et al, Wohlfarth[9] et al, Coulson[10]et al, etc.).or by the construction of Bloch sums from orthogonalized atomic orbitals. We shall consider here only the latter method.

In 1936 Landshoff[11]worked out an expression for the orthogonalized atomic orbitals (O.A.O.) using a linear combination of free atomic functions, where the coefficients of the expansion were expressed in terms of overlap integrals. This treatment was later on reformulated and developed by Löwdin[12](1950) who utilised a matrix notation for the cases involving larger overlap integrals. In 1951

4) Slater, J.C. Phys.Rev. 35,509(1930)
5) Van Vleck, J.H. and Sherman, A. Rev. Mod. Phys. 7,167(1935)
6) Inglis, D.R. Phys. Rev. 46, 135(1934)
7) Mulliken,R.S.,Rieke,C.A.,Orloff,D.,and Orloff,H.,J.Chem.Phys.17,1248 (1949)
8) Hoffmann,T.A. and Kónya,A. J.Chem.Phys.16,1172(1948)
9) Wohlfarth, E.P. Proc. Phys. Soc. 66A,889(1953)
10) Coulson, C.A. and Taylor, R. Proc. Phys. Soc. A65,815(1952)
11) Landshoff,R. Z.Phys. 102,201(1936);Phys. Rev. 52,246(1937)
12) Löwdin, P.O.; Thesis, Almquist and Wicksell, Uppsala,Sweden,1948.
ii) Arkiv Mat. Astron. Fis. vol.A35,no.9(1947);no.30(1948).
iii) J.Chem. Phys. 18,365(1950).

Löwdin[13] used his extended scheme to calculate the energy bands for sodium. This treatment was later criticised by Raimes[14] (1954). In a rigorous study where the crystal wave function was approximated by several Bloch sums of orthogonalized atomic orbitals, Slater and Koster[15] (1954) suggested that this scheme would be used as an interpolation procedure to obtain additional information about energy bands once certain minimum information had been obtained by other means.

Thus to recap;

The first approach has the disadvantage of using a nonorthogonal and non-complete set of functions (and hence yields crystal wave functions which are not exact solutions of the one electron Schrödinger equation) and the second method, though orthogonalized, is only an approximation to the wave function, since in an expansion in Landshoff's sense one only considers a finite number of terms (in the general case one also approximates the crystal wave function by a finite number of Bloch sums of O.A.O.).

A set of basis functions which have the orthogonality (and completeness) lacking in the atomic orbitals of the tight binding scheme was first introduced by Wannier[16] in 1937 which in subsequent literature has come to bear his name. The wave functions constructed by linear combinations of Wannier functions are exact solutions

[13] Löwdin, P.O., J. Chem. Phys. 19, 1570-79 (1951)

[14] Raimes, S., Proc. Phys. Soc. A67, 52 (1954)

[15] Slater, J.C. and Koster, G.F. Phys. Rev. 94. 1498 (1954)

[16] Wannier, G.H., Phys. Rev. 52, 191(1937)

of the one-electron Schrödinger equation. We will briefly delineate the properties of this latter representation.

i) Wannier functions are associated with unit cells rather than atomic centers (and for each unit cell there is only one such function).

ii) For each band there is one and only one Wannier function (under certain assumptions). Therefore, in expanding an exact wave function associated with a certain band, only a single sort of Wannier function is to be used.

These functions which may be approximated by orthogonalized atomic orbitals in the tight binding scheme are not, in fact, generally O.A.O.s as often quoted in the literature. They represent a more general class of functions and, as we have shown in the text, even in the case of quasi-bound electrons only in special circumstances are they identical with an O.A.O. . However, the analogy is useful for a discussion of the behaviour of Wannier functions.

Wannier functions are localized; the exact nature of this localization is however quite complicated and as we have shown in the text the degree of localization will vary with the (arbitrary) choice made for the phases of the Bloch functions. However in order to obtain a picture of the behaviour of Wannier functions one has to consider them for the limiting cases of bound and free electrons where in the first case they behave like free atomic functions and therefore are strongly localized around lattice points and decrease outwards exponentially, while in the second case they behave like sinx/x in each basic direction and therefore oscillate and decrease rather slowly (extending over many unit cells). Returning to the historical outline, in his 1937 paper Wannier[16] also set up an important theorem (known as Wannier's theorem) with the intention of using it in the problem of excitons which eventually led to the setting up of the roots of the Wannier representation (see appendices 1 and 2). Slater[17] some twelve years later was the first to realize this. This development was soon followed with works by Adams[18,19,20,21] (1952-1957) who generalized Wannier's theorem to take into account transitions between energy bands. Koster[22] (1954), Koster and Slater[23,24,25] (1954), James[26] (1954), Friedel[27,28] (1954), Clogston[29,30] (1962), des Cloizeaux[31] (1963) and others[31A] subsequently

[17] Slater, J.C., Phys. Rev. 76, 1592 (1949)
[18] Adams, E.N., Phys. Rev. 85, 41 (1952)
[19] Adams, E.N., J. Chem. Phys. 21, 2013 (1953)
[20] Adams, E.N., Phys. Rev. 102, 605 (1956)
[21] Adams, E,N., Phys. Rev. 107, 698 (1957)
[22] Koster, G.F., Phys. Rev. 95, 1436 (1954)
[23] Koster, G.F. and Slater, J.C. 94, 1392 (1954)
[24] Koster, G.F. and Slater, J.C. 95, 1167 (1954)
[25] Koster, G.F. and Slater, J.C. 96, 1208 (1954)
[26] James, H.M., Phys. Rev. 76, 1602 (1954)
[27] Friedel, J., Adv. Phys. 3, 446 (1954)
[28] Friedel, J., Can. J. Phys. 34, 1190 (1956)
[29] Clogston, A.M. Phys. Rev. 125, 439 (1962)
[30] Clogston, A.M. Phys. Rev. 136, A1643 (1964)
[31] des Cloizeaux, J. Phys. Rev. 129, 554 (1963); 135, A698 (1964)
[31A] Also see Wolff, P.A. Phys. Rev. 124, 1030 (1961), Lax, M. Phys. Rev. 94, 1391 (1954) , and the references given in appendix 3.

enlarged the scope of the Wannier representation.

In 1952 Slater[32] proved that crystal momentum eigenfunctions and Wannier functions are Fourier transforms of each other; obtained explicitly the one dimensional Wannier functions for a cosine potential with the use of the momentum eigenfunctions and also indicated how his calculations may be extended to a larger number of dimensions.

This was one of the first calculations involving Wannier functions in the presence of a potential field (excluding the approximate approach of the tight binding scheme). His approach however is different to that used in the present work.

In 1953 Parzen[33] and Koster[34] derived independently a differential equation (equivalent to Schrödinger's equation) as well as a variational method appropriate to these functions.

Wainwright and Parzen[35] later in the same year used the variational method to calculate Wannier functions (in one dimension) for a square potential and also for the energy bands of lithium (with a preference towards the use of momentum eigenfunctions). This work has been criticised. The variational principle has received little application since that time.

In 1959 Kohn[36] studied the properties of Schrödinger's equation in one dimension in a periodic field with inversion symmetry under the assumption of nondegenaracy with emphasis on the nature

[32] Slater, J.C., Phys. Rev. 87, 807 (1952)

[33] Parzen, G., Phys. Rev. 89, 237 (1953)

[34] Koster, G.F., Phys. Rev. 89, 67 (1953)

[35] Wainwright, T., and Parzen, G., Phys. Rev. 92, 1129 (1953)

[36] Kohn, W., Phys. Rev. 115, 809 (1959)

of the associated Bloch waves and Wannier functions. This was the first thorough investigation of the analytic properties of Wannier functions. It was shown that under the conditions imposed, there is one and only one Wannier function which is real and symmetric (or antisymmetric) through an appropriate site which falls off exponentially with distance (see chapter 7 , where we have proved that in the presence of a weak field the rate of exponential fall off is given by the Fourier coefficients of the applied field).

Inspite of its leading contribution in specifying the nature of these functions the approach in this paper was such that, an extension to a larger number of dimensions would hardly be possible. Also this work did not provide a practical means of choosing the most concentrated Wannier functions in more general circumstances.

The criteria for such a choice came from Weinreich[37](1965) who by means of a variational procedure derived a differential equation solutions of which provided the particular phase functions which yield the most localized Wannier functions. This method, however contains an approximation (see chapter 8 , where we have given an analytic method to determine the phase functions under discussion. The method is also particularly useful for understanding the behaviour in some particular cases.).

A recent work on the properties of Wannier functions is that of Ferreira and Parada[38](1970)who showed that the Wannier functions

37) Weinreich, G., Solids, Elementary Theory for Advanced Students, pp. 134., Wiley, New York, 1965.

38) Ferreira, L. . and Parada, N.J., Phys. Rev.B, Vol.2, 1614(1970).

calculated by summing Bloch waves obtained point by point by a k.p perturbation are the most localized.

For an account of some related topics we refer the reader to an extensive review by Blount[39](1962)

Further references to be found in the book.

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39) Blount, E.I., Solid State Physics 13, 305(1962)

CHAPTER 2

DEFINITION AND BASIC PROPERTIES OF WANNIER FUNCTIONS

2.1 DEFINITION

Let $\psi_s(\underline{k},\underline{r})$ be exact solutions of the one,electron Schrödinger equation of the crystal potential,then these functions are orthogonal (and may be normalised by multiplying by a suitable constant) in the following sense,

$$\int_{\text{Whole crystal}} \psi s(\underline{k}',\underline{r})\, \psi t(\underline{k},\underline{r})\, d^3 r = \delta_{st}\, \delta(\underline{k} - \underline{k}') \qquad 2.1$$

Then from those wave (Bloch) functions the Wannier function (i.e the one for the s^{th} band and centered at lattice site $\underline{R}_n$) is defined as follows

$$\begin{aligned} a s(\underline{r}-\underline{R}_n) &= (\Omega_B)^{-1/2} \int_{\text{B.Z.}} \exp(-i\cdot\underline{k}\cdot\underline{R}_n)\ \psi_s\ (\underline{k},\underline{r})\ d^3\underline{k} \\ &= \frac{\Omega^{1/2}}{\cdot(2\pi)^{3/2}} \int_{\text{B.Z.}} \exp(-i\underline{k}\cdot\underline{R}_n)\ \psi_s\ (\underline{k},\underline{r})\ d^3\underline{k} \qquad 2.2 \end{aligned}$$

Where,

Ω is the volume of the unit cell

and $$d^3 k = d k_x\, d k_y\, d k_z \qquad 2.3$$

and the integral is carried out over one particular B.Z only (i.e for the above case it is carried out over s^{th} B.Z only)

The above equation can be put into a more convenient form simply by replacing the wave function with the Bloch wave form.

i.e $$\psi_s(k,r) = \exp(i\ \underline{k}\cdot\underline{r})\ u_s(\underline{k},\underline{r}) \qquad 2.4$$

Then,

$$a_s(\underline{r} - \underline{R}_n) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int_{s^{th}\ B.Z.} \exp(i\ \underline{k}\cdot(\underline{r} - \underline{R}_n)\ u_s(\underline{k},\underline{r})\ d^3k \qquad 2.5$$

However, if the crystal considered is not sufficiently large*

then the wave vectors $\underline{k}$ constitute a discrete set of vectors in reciprocal space in the following sense

$$\underline{k} = (l/L)\ \underline{k}_x + (m/M)\ \underline{k}_y + (n/N)\ \underline{k}_z \qquad 2.6$$

Where $\underline{k}_x$, $\underline{k}_y$, $\underline{k}_z$ are the reciprocal base vectors

L , M , N are no of unit cells in x , y , and z directions

and l , m , n are integers ($0 \leq l \leq L$ etc) chosen such that the vector $\underline{k}$ always lies in the B.Z. concerned .

Then the Wannier function is given not by integration but by the following summation;

$$a_s(\underline{r} - \underline{R}_n) = (V)^{-1/2} \sum_{s^{th}\ B.Z.} \exp(-i\ \underline{k}.\underline{R}_n)\ \Psi_s(\underline{k},\underline{r}) \qquad 2.7$$

Where V= N·L·M and the summation is over all possible $\underline{k}$ vectors which lie in the B.Z. concerned.

More generally if there are N of these vectors , one can write

$$a_s(\underline{r} - \underline{R}_n) = (N)^{-1/2} \sum_{\underline{k} = \underline{k}_1}^{\underline{k}_n} \exp(-i\underline{k}\cdot\underline{R}_n)\ \Psi_s(\underline{k},\underline{r}) \qquad 2.8$$

and the Wannier function centered at origin (i.e $R_n = 0$) is given by

$$a_s(\underline{r}) = (N)^{-1/2} \sum_{B.Z} \Psi_s(\underline{k},\underline{r}) \qquad 2.9$$

where in both cases the sum is over N vectors in the B.Z. concerned.

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* Note ; If L,M,N are large then $\underline{k}$ may be considered as a continuous function of k_x, k_y, k_z (i.e case of a large crystal)

2.2 WANNIER FUNCTIONS ARE LOCALIZED FUNCTIONS

A formal proof will not be attempted considering the brief introductory nature of this chapter. A long and rigorous discussion of this matter can be found in a few articles (i.e see Blount[1]). for the present purposes this property might be demonstrated qualitatively as follows. Let $a_s(\underline{r} - \underline{R}_n)$ be the Wannier function for the s^{th} band centered at lattice point $\underline{R}_n$, then

$$a_s(\underline{r}-\underline{R}_n)= \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int_{B.Z.} \exp(\, i\, \underline{k}\cdot(\underline{r}-\underline{R}_n))\, u_s(\underline{k},\underline{r})\, d^3k \qquad 2.10$$

Now consider the amplitude of this Wannier function at a particular point, say at $\underline{r}=\underline{R}_i$, then

$$a_s(\underline{R}_i-\underline{R}_n)= \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int_{B.Z} \exp(\, i\, \underline{k}(\underline{R}_i-\underline{R}_n))\, u_s(\underline{k},\underline{R}\}\, d^3k \qquad 2.11$$

Now , if $|\underline{R}_i - \underline{R}_n|$ is large then the exponential term varies rapidly in $\underline{k}$ space (so does the total integrand) and the integral value becomes small. However if $|\underline{R}_i-\underline{R}_n|$ is small then the integrand varies less rapidly in $\underline{k}$ space and the integral may attain a larger value.

Hence to conclude this qualitative discussion , Wannier functions have their peak at their lattice locations[2] and vanish rapidly

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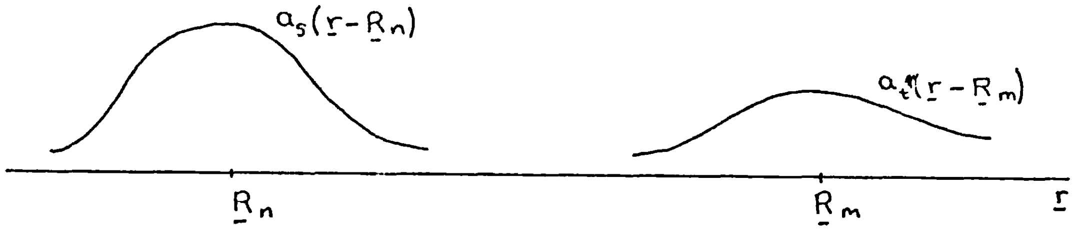
1) Blount, E.I., Solid State Physics 13, 305(1962)

2)As will be shown in the later chapters this is not always the case.

when one moves away from these points. We shall see that a Wannier function $a_s(\underline{r})$ decays exponentially if the momentum eigenfunction and its derivatives (for the same band) are continuous.

2.3 WANNIER FUNCTIONS CONSTITUTE A COMPLETE ORTHOGONAL SET OF FUNCTIONS

Let us consider two Wannier functions belonging to bands, say s and t and centered respectively at $\underline{R}_n$ and $\underline{R}_m$



then we have.

$$a_s^*(\underline{r}-\underline{R}_n)= \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int_{B.Z} \exp(i\ \underline{k}'\cdot\underline{R}_n)\ \psi_s^*(\underline{k}',\underline{r})\ d^3k' \qquad 2.12$$

$$a_t(\underline{r}-\underline{R}_m)= \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int_{B.Z} \exp(-i.\underline{k}\cdot\underline{R}_m)\ \psi_t(\underline{k},\underline{r})\ d^3k \qquad 2.13$$

Now let us work out the following integral

$$\int_{\text{Whole crystal}} a_s^*(\underline{r}-\underline{R}_n)\ \ a_t(\underline{r}-\underline{R}_m)\ d^3r \qquad 2.14$$

Substituting equations (2.12) and (2.13) into equation (2.14)

$$\int_{\text{whole crystal}} a_s^*(\underline{r}-\underline{R}_n)\ a_t(\underline{r}-\underline{R}_m)\ d^3r= \frac{\Omega}{(2\pi)^3}\iiint e^{-i(\underline{k}\cdot\underline{R}_m-\underline{k}'\cdot\underline{R}_n)}\ \psi_s^*(\underline{k}',\underline{r})\ \psi_t(\underline{k},\underline{r})\ d^3k\ d^3k'\ d^3r \qquad 2.15$$

Since

$$\int \psi_s^*(\underline{k}',\underline{r})\ \psi_t(\underline{k},\underline{r})\ d^3r = \delta_{st}\,\delta(\underline{k}-\underline{k}') \tag{2.16}$$

$$\int a_s^*(\underline{r}-\underline{R}_n)\, a_t(\underline{r}-\underline{R}_m)\ d^3r = \frac{\Omega}{(2\pi)^3}\,\delta_{st}\iint e^{-i(\underline{k}\cdot\underline{R}_m-\underline{k}'\cdot\underline{R}_n)}\ \delta(\underline{k}-\underline{k}')\ d^3k\ d^3k' \tag{2.17}$$

$$= \frac{\Omega}{(2\pi)^3}\,\delta_{st}\int e^{-i\,\underline{k}\cdot(\underline{R}_m-\underline{R}_n)}\ d^3k$$

$$\int_{\text{Whole crystal}} a_s^*(\underline{r}-\underline{R}_n)\, a_t(\underline{r}-\underline{R}_m)\ d^3r = \delta_{st}\,\delta_{mn} \tag{2.18}$$

Hence Wannier functions belonging to different bands and different locations are orthogonal. For completeness see sections 2.4 and 2.8.

2.4 THE ONE ELECTRON BLOCH FUNCTIONS CAN BE OBTAINED FROM THE WANNIER FUNCTIONS , AND VICE VERSA

A Wannier function is obtained from the one electron wave function by the following expression (see section 2.1) ,

$$a_s(\underline{r}-\underline{R}_n) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}}\int_{s^{th}\ \text{B.Z.}} e^{-i\,\underline{k}\cdot\underline{R}_n}\ \psi_s(\underline{k},\underline{r})\ d^3k \tag{2.19}$$

Multiplying both sides of equation (2.19) by $\exp(i\,\underline{k}'\cdot\underline{R}_n)$ and summing over all lattice vectors $\underline{R}_n$ one gets,

$$\sum_n e^{i\,\underline{k}'\cdot\underline{R}_n}\, a_s(\underline{r}-\underline{R}_n) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}}\int_{s^{th}\ \text{B.Z}} \sum_n e^{i\,\underline{R}_n\cdot(\underline{k}'-\underline{k})}\ \psi_s(\underline{k},\underline{r})\ d^3k \tag{2.20}$$

$$\sum_n e^{i(\underline{k}-\underline{k}')\cdot\underline{R}_n} = \frac{(2\pi)^3}{\Omega}\sum_m \delta(\underline{k}-\underline{k}'-\underline{K}_m) \tag{2.21}$$

In the last equation the sum is over reciprocal lattice vectors $\underline{K}_m$.

However if we constrain $\underline{k}'$ to lie in the same band as $\underline{k}$ (i.e in the s^{th} band for this case), then the only contribution to the sum comes from the zero reciprocal lattice vector. (i.e $\underline{K}_m=0$)

Therefore,

$$\sum_{n} e^{i\,\underline{R}_n\cdot(\underline{k}-\underline{k}')} = \frac{(2\pi)^3}{\Omega}\,\delta(\underline{k}-\underline{k}') \qquad 2.22$$

$$\sum_{n} e^{i\,\underline{k}'\cdot\underline{R}_n}\, a_s(r-R_n) = \frac{(2\pi)^{3/2}}{\Omega^{1/2}}\int \delta(\underline{k}-\underline{k}')\,\psi_s(\underline{k},\underline{r})\, d^3k \qquad 2.23$$

$$= \frac{(2\pi)^{3/2}}{\Omega^{1/2}}\,\psi_s(\underline{k}',\underline{r}) \qquad 2.24$$

$$\therefore \quad \psi_s(\underline{k}',\underline{r}) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}}\sum_{n} e^{i\,\underline{k}'\cdot\underline{R}_n}\, a_s(\underline{r}-\underline{R}_n) \qquad 2.25$$

Hence Wannier functions and one electron wave functions can be obtained from each other by certain operations. Indeed they are connected to each other by means of a linear transformation (unitary).

$$\text{i.e} \qquad \psi = U\, a \qquad 2.26$$

where the transformation matrix is given by,

$$U = \{ u_{sn} \} = N^{-1/2}\{ e^{i\underline{k}_s\cdot\underline{R}_n} \} \qquad 2.27$$

It can easily be shown that U is a unitary matrix and making use of a fundamental property of unitary matrices (i.e $(U^{*})' = U^{-1}$).

Therefore the inverse transformation is given by ,

$$a = (U^*)' \Psi \qquad 2.28$$

where $(U^*)'$ stands for the complex conjugate transpose of matrix U.

Finally we would like to point out that a unitary transformation preserves lenghts (Inner products).

$$\text{i.e} \quad \int_{\Omega} \left| \psi s(\underline{k},\underline{r}) \right|^2 d^3r = \int_{\text{all } r} \left| a_s(\underline{r} - \underline{R}n) \right|^2 d^3r \qquad 2.29$$

Therefore if $\psi s(\underline{k},\underline{r})$ is normalized in the elementary cell the corresponding Wannier function is normalised in the whole of space.

2.5 WANNIER FUNCTIONS AND MOMENTUM EIGENFUNCTIONS ARE FOURIER TRANSFORMS OF EACH OTHER [3]

Consider the following Wannier function,

$$a_n(\underline{r} - \underline{R}_i) = \Omega_B^{-1/2} \int_{n^{th}\ \text{Band}} \exp(-i\ \underline{k}\cdot\underline{R}_i)\ \psi n(\underline{k},\underline{r})\ d^3k \qquad 2.30$$

Now expanding the wave function in terms of momentum eigenfunctions

$$\psi n(\underline{k},\underline{r}) = \sum_{\underline{K}n} \nu_n(\underline{k} + \underline{K}n)\ \exp(\ i(\ \underline{k} + \underline{K}n)\cdot\underline{r}) \qquad 2.31$$

Substituting equation (2.31) into equation (2.30)

$$a_n(\underline{r} - \underline{R}_i) = (\ \Omega_B)^{-1/2} \int \exp(\ -i\ \underline{k}\cdot\underline{R}_i) \sum_{\underline{K}n} \nu n(\underline{k} + \underline{K}_n)\ \exp(i(\underline{k} + \underline{K}_n)\cdot\underline{r})\ d^3k \qquad 2.32$$

$$= (\ \Omega_B)^{-1/2} \int \sum_{\underline{K}n} \nu n(\underline{k} + \underline{K}n)\ \exp\ (i(\underline{k} + \underline{K}n)\cdot\underline{r}\ - i\ \underline{k}\ \underline{R}i)\ d^3k \qquad 2.33$$

Since

$$\exp\ (-i\ \underline{K}n\cdot\underline{R}i) = 1 \qquad 2.34$$

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[3] This has been first shown by Slater, see; Slater, J.C.,Phys. Rev. 87, 807(1952).

We can rewrite the exponential term in the integrand as follows,

$$\exp(i\ (\underline{k}+\underline{K}n)\cdot\underline{r}\ -i\ \underline{k}\cdot\underline{R}i\ ) = \exp(\ i\ (\underline{k}+\underline{K}_n)\cdot(\underline{r}-\underline{R}_i)\ ) \qquad 2.35$$

Therefore,

$$a_n(\underline{r}-\underline{R}_i) = (\Omega_B)^{-1/2}\sum_{\underline{K}n}\int_{n^{th}\ Band}\mathcal{V}n(\underline{k}+\underline{K}_n)\ \exp\ (i\ (\underline{k}+\underline{K}_n)\cdot(\underline{r}-\underline{R}i))d^3k \qquad 2.36$$

Integration over one band and sum over all $\underline{K}n$ is equivalent to integration over all $\underline{k}$ space. Therefore,

$$a_n(\underline{r}-\underline{R}i) = (\Omega_B)^{-1/2}\int_{all\ \underline{k}}\mathcal{V}n(\underline{k})\ \exp(i\ \underline{k}\cdot(\underline{r}-\underline{R}i))\ d^3k \qquad 2.37$$

To bring the last expression into a more familiar form consider the Wannier function centered at origin.

i.e $\underline{R}_i = 0$

Therefore,

$$a_n(\ \underline{r}\ ) = (\Omega_B)^{-1/2}\int_{all\ \underline{k}}\mathcal{V}n(\ \underline{k})\ \exp\ (i\ \underline{k}\cdot\underline{r}\ )\ d^3k \qquad 2.38$$

Hence Wannier functions are fourier transforms of momentum eigenfunctions and vice versa.

2.6 WANNIER FUNCTIONS ARE FUNCTIONS OF DIFFERENCE $\underline{r}-\underline{R}_i$

This property of Wannier functions can easily be proved as follows.

Say,

$$a_n(\ \underline{r}-\underline{R}i) = (\Omega_B)^{-1/2}\int_{n^{th}\ Band}\psi_n(\underline{k},\underline{r})\ e^{-i\ \underline{k}\cdot\underline{R}i}\ \ d^3k \qquad 2.39$$

Adding any lattice vector $\underline{R}_m$ to both $\underline{r}$ and $\underline{R}_i$,

$$a_n(\underline{r}+\underline{R}_m-(\underline{R}_i+\underline{R}_m)) = (\Omega_B)^{-1/2}\int \psi_n(\underline{k},\underline{r}+\underline{R}_m)\, e^{-i\,\underline{k}\cdot(\underline{R}_i+\underline{R}_m)}\, d^3k \qquad 2.40$$

$$= (\Omega_B)^{-1/2}\int \psi_n(\underline{k},\underline{r})\, e^{i\,\underline{k}\cdot\underline{R}_m}\; e^{-i\,\underline{k}\cdot(\underline{R}_i+\underline{R}_m)}\, d^3k \qquad 2.41$$

$$= (\Omega_B)^{-1/2}\int \psi_n(\underline{k},\underline{r})\, e^{-i\,\underline{k}\cdot\underline{R}_i}\, d^3k \qquad 2.42$$

$$= a_n(\underline{r}-\underline{R}_i) \qquad 2.43$$

2.7 WANNIER FUNCTIONS OF SAME BAND BUT OF DIFFERENT LOCATIONS ARE IDENTICAL

This property of Wannier functions is a direct result of the proof given in section 2.6 (See equation 2.43)

2.8 SUMMARY

Wannier functions and one electron wave functions are connected by a unitary transformation . Wannier functions are fourier transforms of momentum eigenfunctions. W.F. s being localized functions attain their largest amplitudes in the unit cells where they are centered and vanish rapidly as one goes off these centres.

If one considers a crystal with N lattice points then for each band there are N identical Wannier functions each localised at a lattice site. Wannier functions of different bands are not identical in principle.

Wannier functions constitute a complete orthogonal set of functions.(To complete the set it is esential to include all the Wannier functions from different bands and from different locations). They are functions of difference $\underline{r}-\underline{R}i$ that is why it is costumary to write them as, i.e. $a_n(\underline{r}-\underline{R}_i)$.

In general, they have a resemblance to momentum eigenfunctions. (See also comparision with atomic orbitals given in the introduction part) Wannier functions being localized at lattice points are functions of position vector only, while momentum eigenfunctions being localised at reciprocal lattice points are functions of crystal momentum vector only.

CHAPTER 3

THE DIFFERENTIAL EQUATION AND THE VARIATIONAL PRINCIPLE FOR THE WANNIER FUNCTIONS

3 .1 A DIFFERENTIAL EQUATION FOR THE WANNIER FUNCTION

The Wannier functions in crystals may be defined in terms of a differential equation (see G.F. Koster[1] and G. Parzen[2]) which is in principle an alternative form of Schrödinger's equation.

This differential equation may easily be obtained as follows; Consider the following one electron Schrödinger equation

$$H\Psi_n(\underline{k},\underline{r}) = E_n(\underline{k})\,\Psi_n(\underline{k},\underline{r}) \qquad 3.1$$

where $E_n(\underline{k}+\underline{K}_m) = E_n(\underline{k})$. Now expressing $E_n(\underline{k})$ as a Fourier series and $\Psi_n(\underline{k},\underline{r})$ in terms of Wannier functions

$$E_n(\underline{k}) = \sum_m \varepsilon_n(\underline{R}_m)\exp(-i\underline{k}.\underline{R}_m) \qquad 3.2$$

$$\Psi_n(\underline{k},\underline{r}) = \sum_p a_n(\underline{r}-\underline{R}_p)\exp(i\underline{k}.\underline{R}_p) \qquad 3.3$$

and substituting 3.2 and 3.3 into 3.1 we get

$$H\sum_p a_n(\underline{r}-\underline{R}_p)\exp(i\underline{k}.\underline{R}_p) = \sum_j\sum_m \varepsilon_n(\underline{R}_m)\,a_n(\underline{r}-\underline{R}_j)\exp(i\underline{k}.(\underline{R}_j-\underline{R}_m)) \qquad 3.4$$

Now making a fundamental condition that H operates on the position vector $\underline{r}$ only (i.e $H = -\nabla^2 + V(\underline{r})$) then multiplying both sides of the last equation by $\exp(-i\cdot\underline{k}\cdot\underline{R}_n)$ and integrating over a B.Z. ,

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1) Koster, G.F., Phys. Rev. 89, 67(1953)

2) Parzen, G., Phys. Rev. 89, 237(1953)

$$H\sum_{p} a_n(\underline{r}-\underline{R}_p)\int_{B.Z.} \exp(i\underline{k}.(\underline{R}_p-\underline{R}_n))d^3k = \sum_{j}\sum_{m} \varepsilon_n(\underline{R}_m)\, a_n(\underline{r}-\underline{R}_j)\int_{B.Z.} \exp(i\underline{k}.(\underline{R}_j-\underline{R}_m-\underline{R}_n))d^3k \tag{3.5}$$

since

$$\int_{B.Z.} \exp(i\underline{k}.(\underline{R}_p-\underline{R}_n))d^3k = \Omega_B\,\delta_{pn} \tag{3.6}$$

we have

$$H\, a_n(\underline{r}-\underline{R}_n) = \sum_{m} \varepsilon_n(\underline{R}_m)\, a_n(\underline{r}-\underline{R}_n-\underline{R}_m) \tag{3.7}$$

which may be written more simply (by letting $\underline{R}_n = 0$) as follows,

$$H a_n(\underline{r}) = \sum_{m} \varepsilon_n(\underline{R}_m)\, a_n(\underline{r}-\underline{R}_m) \tag{3.8}$$

where as pointed out before $\mathcal{E}_n(\underline{R}_m)$ is the m^{th} Fourier coefficient in the Fourier series of $E_n(\underline{k})$ and the summation on the right is over all lattice vectors .

$\mathcal{E}_n(\underline{R}_m)$ can be expressed in terms of Wannier functions simply by multiplying both sides of the last equation by $a_p^*(\underline{r}-\underline{R}_m)$ and integrating over all $\underline{r}$

$$\delta_{pn}\, \varepsilon_n(\underline{R}_m) = \int a_p^*(\underline{r}-\underline{R}_m)\, H\, a_n(\underline{r})\, d^3r \tag{3.9}$$

or

$$\varepsilon_n(\underline{R}_m) = \int a_n^*(\underline{r}-\underline{R}_m)\, H\, a_n(\underline{r})\, d^3r \tag{3.10}$$

Note that there are no matrix elements of the Hamiltonian between Wannier functions of different bands.[3]

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[3] This applies when the bands in concern are nondegenerate.

It can be shown that if atoms are well seperated or the Wannier functions are strongly localized then they overlap very little, hence in the limiting case

$$\varepsilon_n(\underline{R}_m) = \int a_n^*(\underline{r} - \underline{R}_m)\, H\, a_n(\underline{r})\, d\, r \neq 0 \quad \text{if} \quad \underline{R}_m = 0 \qquad 3.11$$

$$= 0 \quad \text{if} \quad \underline{R}_m \neq 0$$

Therefore for these isolated atoms the flattened energy levels become equal to their first fourier coefficients , i.e $E_n(\underline{k}) = \varepsilon n(0)$ and the Wannier functions become practically identical with the atomic functions centred at the corresponding lattice sites .

Now instead 3.7 we have ,

$$H\, a_n(\underline{r} - \underline{R}_m) = \varepsilon_n(0)\, a_n(\underline{r} - \underline{R}_m) \qquad 3.12$$

where ε_n (0) is the n^{th} free atomic level.

In general equation 3.7 is not of much practical use due to the multiplicity of the terms on the right hand side. However for mathematical purposes it is still a fundamental equation .

The few applications which have been made so far concern the variational principle .

3.2 A VARIATIONAL PROCEDURE

In the previous section we pointed out that equation 3.7 was not of much practical use due to multiplicity of the terms on the right hand side of the equation. Hence in order to work out this equation G.F. Koster[1] and G. Parzen[2] independently suggested a variational procedure . Below we give a description of this procedure.

To start with we will consider the following integral and try to make it have an extremum.

$$J = \int_{\text{all } r} a(\underline{r})\, H\, a(\underline{r})\, d\tau \qquad 3.13$$

subject to the constraints

$$\int_{\text{all } r} a(\underline{r})a(\underline{r})d\tau = 1 \qquad 3.14$$

$$\int_{\text{all } r} a(\underline{r})\, a(\underline{r} - \underline{R}_n)d\tau = 0 \qquad \underline{R}_n \neq 0 \qquad 3.15$$

which is clearly a calculus of variation problem subject to a set of constraints which appear to be in the forms of integrals

Now to generalize the problem let the Hamiltonian H be invariant under some group of translational operations and let T(n) be such a translational operator which changes the coordinates $\underline{r}$ to $\underline{r} - \underline{R}_n$, then , the constraints 3.14 and 3.15 may be given by

$$I(n) = \int_{\text{all } r} a(\underline{r})T(n)\, a(\underline{r})\, d\tau = 1 \quad \text{if} \quad n = 0 \qquad 3.16$$

$$= 0 \quad \text{if} \quad n \neq 0$$

where I(n) represents the overlap of two Wannier functions displaced by $\underline{R}_n$.

From the fundamental properties of Wannier functions one can easily show that

$$\int a(\underline{r})T(n)a(\underline{r})d\tau = \int a(\underline{r})T(-n)a(\underline{r})d\tau \qquad 3.17$$

therefore we have

$$I(n) = I(-n) \qquad 3.18$$

Now appliying the method of Lagrangian multipliers to the variational problem given by equation 3.13 subject to the modified constraints 3.16 and 3.18 the extremum of the integral J is found by taking the variation of the following integral

$$\int \left[a(\underline{r})Ha(\underline{r}) - \sum_{n=-\infty}^{+\infty} \lambda(n)a(\underline{r})T(n)a(\underline{r}) \right] d\tau \qquad 3.19$$

Since $\lambda(n)$ and $\lambda(-n)$ correspond to the same constraints (see equations 3.17 and 3.18) we have

$$\int a(\underline{r}) \left[H - 2\sum_{n=0}^{+\infty} \lambda(n)T(n) \right] a(\underline{r})d\tau \qquad 3.20$$

Now taking the variation and equating it to zero

$$\delta \int a(\underline{r}) \left[H - 2\sum_{n} \lambda(n)T(n) \right] a(\underline{r})d\tau = 0 \qquad 3.21$$

where the integrand has to satisfy the usual Euler equation , which is

$$\frac{\partial F}{\partial y_i} - \sum \frac{\partial}{\partial x_j} \frac{\partial F}{\partial(\partial y_i/\partial x_j)} = 0 \qquad 3.22$$

In the last equation y_i and x_j are the dependent and independent variables respectively . f is the total integrand given by

$$f(\underline{r}) = a(\underline{r})\Big[H - 2\sum_n \lambda(n)T(n)\Big]a(\underline{r}) \qquad 3.23$$

However if one considers the usual Hamiltonian operator

$$H = -\nabla^2 + V(\underline{r}) \qquad 3.24$$

the integrand $f(\underline{r})$ may have an alternative form. This may be shown as follows, consider the following

$$-\int a \frac{\partial^2}{\partial x} a \, dx = a \frac{\partial a}{\partial x}\Big| + \int \frac{\partial a}{\partial x}\frac{\partial a}{\partial x}\, dx \qquad 3.25$$

then the first term on the right hand side vanishes due to large integration limits . The integrations for the remaining y and z components give similiar contributions , therefore the variational integral and it's integrand may be rewritten

$$\int\Big[\nabla u(\underline{r})\,\nabla a(\underline{r}) + V(\underline{r})a^2(\underline{r}) - 2\sum_n \lambda(n)a(\underline{r})T(n)a(\underline{r})\Big]d\tau \qquad 3.26$$

$$f(\underline{r}) = \nabla a(\underline{r})\,\nabla a(\underline{r}) + V(\underline{r})a^2(\underline{r}) - 2\sum_n \lambda(n)a(r)T(n)a(\underline{r} \qquad 3.27$$

and the Euler equation

$$\frac{\partial F}{\partial a} - \frac{\partial}{\partial x}\frac{\partial F}{\partial(\partial a/\partial x)} - \frac{\partial}{\partial y}\frac{\partial F}{\partial(\partial a/\partial y)} - \frac{\partial}{\partial z}\frac{\partial F}{\partial(\partial a/\partial z)} = 0$$

3.28

yields

$$\partial F/_{\partial a(\underline{r})} = 2V(\underline{r})a(\underline{r}) - 2\sum \lambda(n)T(n)a(\underline{r}) \qquad 3.29$$

$$-\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial\left(\frac{\partial a(\underline{r})}{\partial x}\right)}\right) = -\frac{\partial}{\partial x}\left(2\,\frac{\partial a(\underline{r})}{\partial x}\right) = -2\,\frac{\partial^2 a(\underline{r})}{\partial x^2} \qquad 3.30$$

$$-\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial\left(\frac{\partial a(\underline{r})}{\partial y}\right)}\right) = -2\,\frac{\partial^2 a(\underline{r})}{\partial^2 y} \qquad 3.31$$

$$-\frac{\partial}{\partial z}\left(\frac{\partial F}{\partial\left(\frac{\partial a(\underline{r})}{\partial z}\right)}\right) = -2\,\frac{\partial^2 a(\underline{r})}{\partial z^2} \qquad 3.32$$

Now substituting 3.29 , 3.30 , 3.31 , and 3.32 into 3.28 we obtain

$$-2\nabla^2 a(\underline{r}) + 2V(\underline{r}) - 2\sum \lambda(n)T(n)a(\underline{r}) = 0 \qquad 3.33$$

$$\left[-\nabla^2 + V(\underline{r})\right]a(\underline{r}) = \sum \lambda(n)T(n)a(\underline{r}) \qquad 3.34$$

The last equation may be written more simply by substituting $H = -\nabla^2 + V(\underline{r})$ and $T(n)\ a(\underline{r}) = a(\underline{r}-\underline{R}_n)$, giving ;

$$H\,a(\underline{r}) = \sum \lambda(n)\,a(\underline{r}-\underline{R}_n) \qquad 3.35$$

Now comparing this with equation 3.8 we see that

$$\lambda(n) = \varepsilon(R_n) = \Omega_B^{-1}\int E(\underline{k})\exp(i\underline{k}\cdot R_n)\,d^3k \qquad 3.36$$

Equation 3.35 can be rewritten in a more general form by applying to either side of the equation another translational operator which commutes with the Hamiltonian .

$$T(m)Ha(\underline{r}) = HT(m)a(\underline{r})$$

$$= \sum_{n} \lambda(n)T(m)T(n)a(\underline{r}) \qquad 3.37$$

However

$$T(m)T(n)a(\underline{r}) = a(\underline{r}-\underline{R}_m-\underline{R}_n) \qquad 3.38$$

hence

$$H a(\underline{r}-\underline{R}_m) = \sum \lambda(n)a(\underline{r}-\underline{R}_m-\underline{R}_n) \qquad 3.39$$

3.3 SOME REMARKS ON THE APPLICATION OF THE VARIATIONAL PRINCIPLE

So far we have dealt with the extrema properties of equation 3.13 . However it can be shown that (See G. Parzen[2]) this extrema corresponds to a minimum.

Therefore to summarize, the desired solutions of equation 3.7 are the ones which minimize the integral 3.13 subject to constraints 3.14 and 3.15 . Hence the differential equation given in section 3.1 and the variational procedure outlined in section 3.2 are equivalent in principle .

Although , in principle one can use either method for calculations the variational procedure is more convenient for practical applications .

The constraints 3.14 and 3.15 do not involve the orthogonality of the Wannier functions of different bands , therefore the variational procedure that we illustrated in section 2 is good for calculating the energy levels of the lowest band only.

If one goes to higher bands then the constraints have to be modified in such a way that the new trial function must be orthogonal to the Wannier functions of lower bands.

Hence the variational procedure for the higher bands (say for the mth one) may be outlined as minimization of the following integral

$$\mathcal{E}_m(0) = J = \int a_m(\underline{r})\, H\, a_m(\underline{r})\, d\tau \qquad 3.40$$

subject to the following (modified)constraints

$$\int a_m(\underline{r})\, T(n)\, a_s(\underline{r})\, d\tau = 0 \quad \text{for all } n \text{ and } s \quad \text{where} \quad s < m \qquad 3.41$$

$$\int a_m(\underline{r})\, T(n)\, a_m(\underline{r})\, d\tau = 1 \quad \text{if} \quad n=0 \qquad 3.42$$
$$= 0 \quad \text{if} \quad n \neq 0$$

where we assume that one knows the Wannier functions of the lower (s th band) band .

The general routine may be outlined as follows;

i) One starts by choosing the Wannier functions for the lowest band which minimize the integral 3.13 subject to constraints 3.14 and 3.15 .

ii) For the next band one sets up a series of trial functions all orthogonal to the Wannier functions of the lowest band (also orthogonal to the Wannier functions of the same band but of different locations) and among them one chooses the one which minimizes the usual variational integral .

iii) For the higher bands one follows a similiar routine.

Some applications (one dimensional) using variational procedures have been given by G. Parzen[2] and G. Parzen and T. Wainwright.[4] The method has been used by G. Parzen[2] for calculating the energy levels of a one dimensional periodic square potential where the Wannier functions for the lowest band are approximated by free atomic wave functions and the trial function for the next band is constructed from the linear combinations of free atomic wave functions and free electron Wannier functions in such a way that it is orthogonal to the Wannier functions of the lower band.

In a later paper by G. Parzen and T. Wainwright[4] the variational principle has been used for determining the energy bands of a one dimensional cosine potential and and the valence band of Lithium. The choice of the trial functions follows a similiar routine to that already described .

We refer to the papers mentioned above for a detailed discussion of the calculations .

In chapters 5 and 6 (where we will suggest a different method for obtaining the Wannier functions) we will also show how the coeefficients associated with the simpler (Wannier) functions used in constructing a Wannier function can be determined.

4) Wainwright, T., and Parzen, G., Phys. Rev. 92, 1129(1953)

CHAPTER 4

FREE ELECTRON WANNIER FUNCTIONS CALCULATED FOR SEVERAL CRYSTAL TYPES

4.1 GENERAL

As pointed out in chapter 2 the Wannier functions are obtained from the one electron wave (Bloch)functions by integrating them over the relevant Brillouin zones.

Hence, the Wannier function for a particular band say for the n^{th} band is given by,

$$a_n(x,y,z,X,Y,Z) = C \iiint\limits_{n^{th}B.Z.} \Psi n(k_x,k_y,k_z,x,y,z)\exp(-i(k_xX+k_yY+k_zZ))dk_xdk_ydk_z \qquad 4.1$$

where X,Y,Z are the coordinates of the lattice point, where the Wannier function is centered.

In practice to work out the above integral one needs to know the shape of the Brillouin zone concerned (the region of the integration) and the expression for the wave function.

In the case of free electrons the wave functions have simple forms therefore the integral for the Wannier function becomes comparatively easy to deal with. [However the considerations about the choice of the (arbitrary) phases for the wave functions (which we will discuss in detail in the presence of a crystal potential in chapters 8 , 9 and appendix 1) still have to be taken into account.]

If we now consider the Wannier function centered at the origin, then we need to work out the following integral

$$a_n(x,y,z) = C \iiint\limits_{n^{th}\ \mathrm{B.Z.}} \exp(i\varphi_n(k_x,k_y,k_z))\exp(i(k_xX+k_yY+k_zZ))dk_xdk_ydk_z \qquad 4.2$$

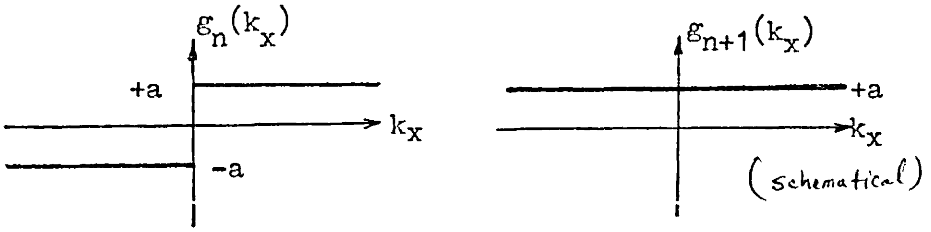
where $\exp(i\varphi_n(k_x,k_y,k_z))$ is the arbitrary phase.

i) But, the problem is separable and the arbitrary phase can be written as (see chapter 9)

$$\exp(i\varphi n(k_x,k_y,k_z)) = g_n(k_x)g_n(k_y)g_n(k_z) \qquad 4.3$$

where $g_n(k_x)$, $g_n(k_y)$, and $g_n(k_z)$ are to be chosen as either even or odd functions of the variables k_x,k_y, and k_z depending upon the particulars of the Brillouin zone (see chapter 9). Though in all of the functions, $g_n(k_x)$,...etc. we have used a common band index n they may indeed be derived from completely different bands (i.e. see chapter 9).

ii) Also, as it is proved in chapter 8 , if we now let the functions $g_n(k_x)$, etc. have constant amplitudes (i.e. like a step function) but still remaining odd or even in character,



then the resulting Wannier function is the best that one can obtain (the most localised). The fundamental difficulties in obtaining the expressions for the Wannier functions have been mainly due to;

i) Complicated integration limits arising from the shapes of the relevant Brillouin zones.

ii) A very large number of terms , mostly complex, arising from the partial integrations.

In general, the calculations are quite long and time consuming due to the multiplicity of terms involved. This is particularly true for the multidimensional cases. Therefore in the calculations the general task has been to minimize the labour and the number of terms involved. To ensure this the coordinate systems were chosen such that maximum use could be made of symmetry considerations.

The first integrations have usually been carried out only in a convenient part of the relevant Brillouin zone , then the integrations for the remaining zones have been obtained by appropriate coordinate transformations through symmetry considerations.

It is not possible to give all the details of the calculations. As an example we give the details of the calculations only for the first band of a body-centered cubic lattice , whereas for the remaining cases we give the results only.

We extended the case of the square lattice to a rectangular one with a variable side ratio in order to generalize the formulations for the Wannier functions as much as possible.

The Wannier functions that are calculated have inversion~~al~~ symmetry (symmetric or antisymmetric) for the position coordinates x,y, and z.

4.2 ONE DIMENSIONAL LATTICE

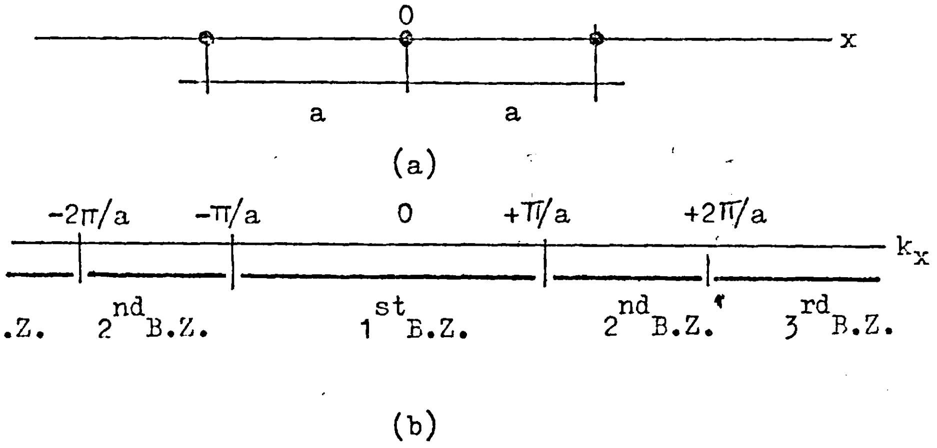


Fig. 4.1 (a) Linear chain of atoms with spacing a

(b) The corresponding reciprocal lattice and the B.Z.'s

The normalised free electron Wannier functions for the above one dimensional lattice are given by;

i) For the first(ground band) and the subsequent odd numbered bands,

$$\boxed{a_q(x - X_m) = \frac{\sqrt{a}}{\pi} \; \frac{\sin\frac{q\pi}{a}(x - X_m) - \sin\frac{(q-1)\pi}{a}(x - X_m)}{(x - X_m)}}$$

where q (q=1,3,5,7,.....) is the band index 4.4

ii) For the second and the subsequent even numbered bands,

$$\boxed{a_q(x - X_m) = -i\,\frac{\sqrt{a}}{\pi} \; \frac{\cos\frac{q\pi}{a}(x - X_m) - \cos\frac{(q-1)\pi}{a}(x - X_m)}{(x - X_m)}}$$

4.5

where q (q=2,4,6,8,......) is the band index

In both equations X_m (X_m=ma , m= ±1, ±2, ±3,....) is the lattice translation vector pointing the site where the Wannier function is localised.

4.3 TWO DIMENSIONAL LATTICES

4.3.1 RECTANGULAR LATTICE WITH $a_2/a_1 = n$

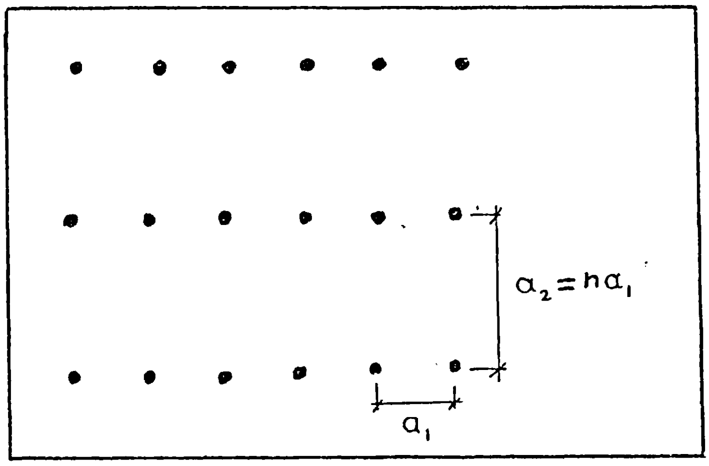


Fig. 4.2 Rectangular lattice with $a_2/a_1 = n$

Below, we give the corresponding reciprocal lattice and some of the B.Z. 's .

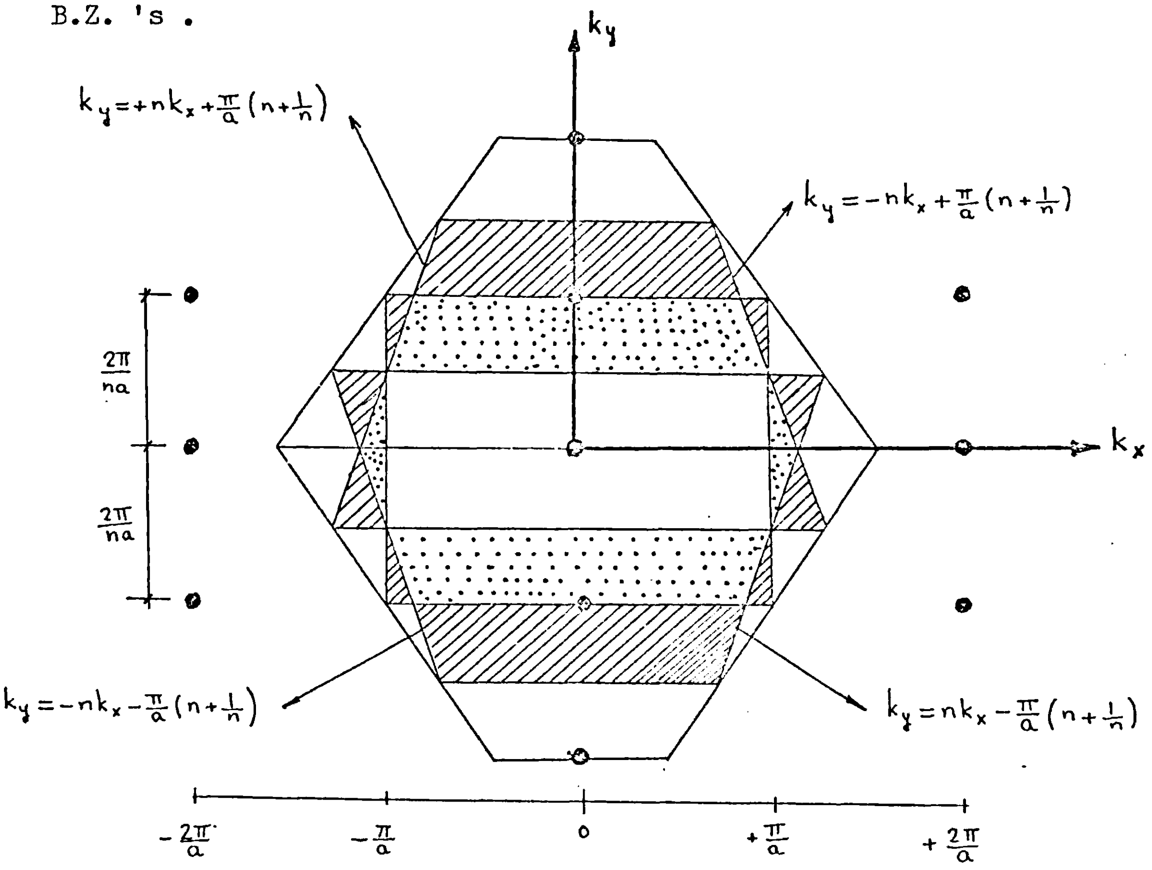


Fig. 4.3 The first four B.Z's of a rectangular lattice with $a_2/a_1 = n$

☐ 1st B.Z. ░ 2nd B.Z. ▨ 3rd B.Z. ☐ 4th B.Z.

For simplicity , below we give the expressions for the central (those which are localised at the origin) Wannier functions only.

If desired, any displaced Wannier function say the one localised at lattice site $\underline{R}_W$ can easily be obtained by replacing the varable $\underline{r}$ by $\underline{r} - \underline{R}_W$.

To do so , in the following expressions one has to replace x and y by $x - X_W$ and $y - Y_W$ etc.

The normalised free electron Wannier functions for the first three bands are given below.

The expressions are valid for all* rectangular lattices provided that one inserts the correct ratio n corresponding to that particular lattice.

For the first band,

$$a_1(n,x,y) = \frac{a\sqrt{n}}{\pi^2} \; \frac{\sin k_o x \, \sin\frac{k_o}{n}y}{x \, y} \qquad 4.6$$

where n is any positive number

For the second band,

$$a_2(n,x,y) = i\,\frac{a\sqrt{n}}{\pi^2}\left[\frac{\frac{x}{n}\,(-\cos k_o x \sin k_o\frac{y}{n}) + \frac{y}{n}(\sin k_o(1+1/n^2)x - \sin k_o x \cos k_o\frac{y}{n})}{y(y^2-x^2/n^2)} + \right.$$
$$\left.\frac{y(\cos\frac{2k_o}{n}y \sin k_o(1/n^2-1)x + \cos k_o\frac{y}{n}\sin k_o x) + \frac{x}{n}(\sin\frac{k_o}{n}y \cos k_o x - \sin\frac{2k_o}{n}y \cos k_o(1/n^2-1)x)}{x(y^2-x^2/n^2)}\right]$$

where n is any positive number

4.7

---

* The expression for the third band is valid for $n \geq 1.5$

For the third band,

$$a_3(n,x,y) = \frac{a\sqrt{n}}{\pi^2}\left[\frac{y\left[\sin k_o\left(x-\frac{2x}{n^2}\right)\sin\frac{3k_o}{n}y - 2\sin k_o\left(x-\frac{x}{n^2}\right)\sin\frac{2k_o}{n}y + \sin k_o\left(x+\frac{2x}{n^2}\right)\sin\frac{k_o}{n}y\right]}{x\left(y^2 - x^2/n^2\right)}\right.$$

$$- \frac{\frac{x}{n}\left[\cos k_o\left(x-\frac{2x}{n^2}\right)\cos\frac{3k_o}{n}y - 2\cos k_o\left(x-\frac{x}{n^2}\right)\cos\frac{2k_o}{n}y - \cos k_o\left(x+\frac{2x}{n^2}\right)\cos\frac{k_o}{n}y + 2\cos k_o\left(x+\frac{x}{n^2}\right)\right]}{x\left(y^2 - x^2/n^2\right)}$$

$$\left. + \frac{\sin k_o x\left(\sin\frac{2k_o}{n}y - \sin\frac{k_o}{n}y\right)}{xy}\right] \qquad 4.8$$

where $n \geq 1.5$ and $k_o = \pi / a$

4.3.2 PARTICULAR CASE (n = 1) , SQUARE LATTICE

Substituting n= 1 in expressions 4.6 and 4.7 one obtains the expressions for the Wannier functions of a square lattice.

This is not permissible in case of expression 4.8 since it is valid only for $n \geq 1.5$. Therefore we had to work out seperately an expression for the Wannier function of the third band of a square lattice .

The normalised free electron Wannier functions for the first three bands are given below .

For the first band,

$$\boxed{a_1 (x,y) = \frac{a}{\pi^2} \left[\frac{\sin k_o x \sin k_o y}{xy} \right]} \qquad 4.9$$

where $k_o = \pi/a$

For the second band,

$$\boxed{a_2(x,y) = i \frac{a}{\pi^2} \left[\frac{x \cos k_o x \sin k_o y + y (\sin k_o x \cos k_o y - \sin 2k_o x)}{y(x^2 - y^2)} + \frac{y \cos k_o y \sin k_o x + x(\sin k_o y \cos k_o x - \sin 2k_o y)}{x(y^2 - x^2)} \right]} \qquad 4.10$$

where $k_o = \pi/a$

For the third band,

$$\boxed{a_3(x,y) = \frac{a}{\pi^2} \left[\frac{\sin 2k_o y \sin k_o x + \sin k_o y \sin 2k_o x - \sin k_o y \sin k_o x}{x\,y} - \frac{\cos 2k_o y - \cos 2k_o x}{x^2 - y^2} \right]} \qquad 4.11$$

4.4 THREE DIMENSIONAL LATTICES

4.4.1 THE SIMPLE HEXAGONAL LATTICE

Below we give some details of the lattice itself and its first Brillouin zone .

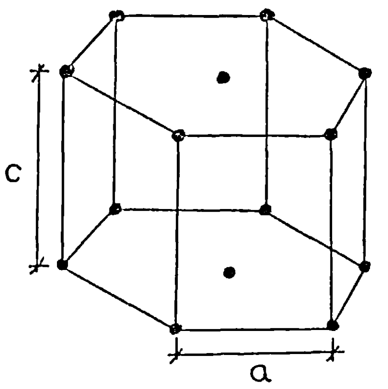
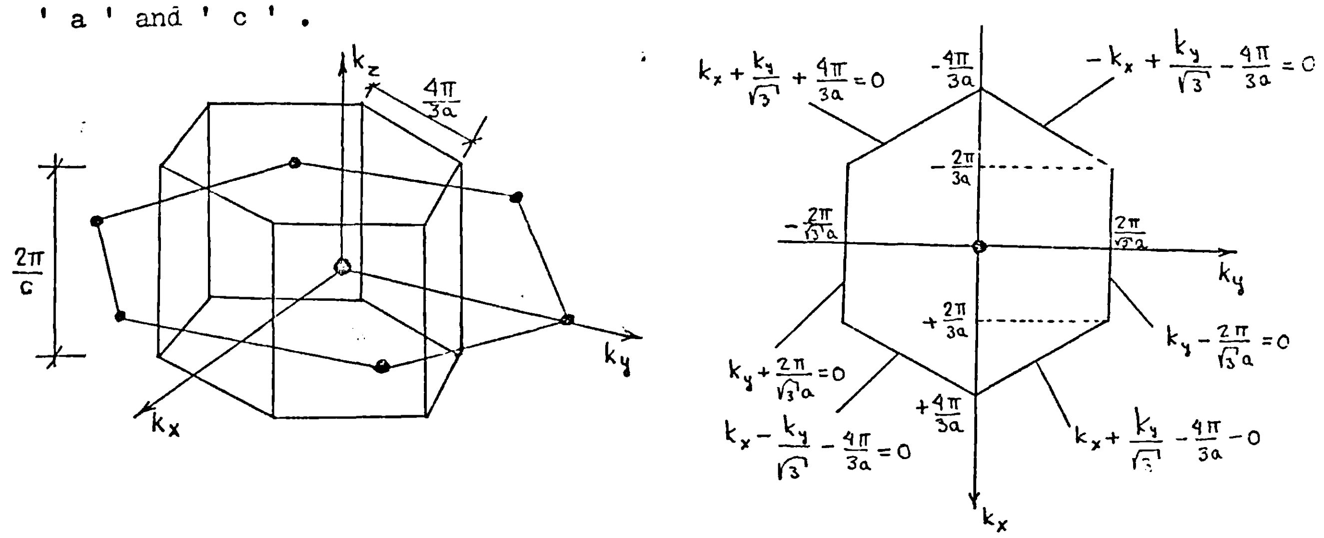


Fig. 4.4 The simple hexagonal lattice in three dimensions

The lattice points are shown , marked ● . The lattice constants are ' a ' and ' c ' .



(a) (b)

Fig. 4.5 a) First Brillouin zone for the simple hexagonal lattice. Some points of the reciprocal lattice are shown , marked ⊗ . The coordinate system (k_x , k_y , k_z axes) is chosen as shown .
The zone has as its faces the planes

$$k_z \mp \frac{\pi}{c} = 0 \quad , \quad k_y \mp \frac{2\pi}{\sqrt{3}\,a} = 0 \quad , \quad \mp k_x \mp \frac{k_y}{\sqrt{3}} = \frac{4\pi}{3a}$$

b) $k_z = 0$ ~~k_x , k_y~~ plane of the zone.

The free electron Wannier function for the first band of a simple hexagonal lattice is given below .

$$\boxed{a_1(x,y,z) = C\,\frac{\sin\frac{\pi}{c}z}{xz\left(y^2-\frac{x^2}{3}\right)}\left[y\,\sin\frac{2\pi}{\sqrt{3}a}y\cdot\sin\frac{2\pi}{3a}x-\frac{x}{\sqrt{3}}\left[\cos\frac{2\pi}{\sqrt{3}a}y\,\cos\frac{2\pi}{3a}x-\cos\frac{4\pi}{3a}x\right]\right]} \qquad 4.12$$

where C is a constant .

4.4.2 THE CLOSED-PACKED HEXAGONAL LATTICE

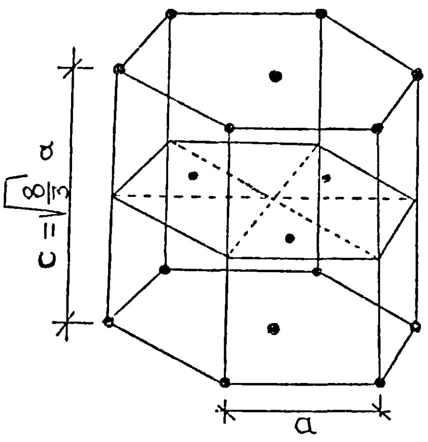


Fig. 4.6 The closed-packed hexagonal lattice

This closed-packed structure having hexagonal symmetry is one of the two ways of arranging equivalent spheres in a regular array to minimize the interstitial volume. (The other one is face-centered cubic with cubic symmetry).

In the basal plane each sphere is in contact with six others. Now being different from the simple hexagonal lattice a second similiar layer is packed on top of this by placing each sphere in contact with three spheres of the bottom plane (see the figure above).

The closed packed hexagonal lattice has the same reciprocal lattice and Brillouin zones as a simple hexagonal lattice, except that this time the ratio c/a (c and a being the lattice constants) must have a particular value which is ,

$$\frac{c}{a}=\sqrt{\frac{8}{3}}=1.6330 \quad \text{or} \quad c=\sqrt{\frac{8}{3}}\,a \qquad 4.13$$

If we substitute 4.13 into 4.12 we obtain the equation 4.14

$$a_1(x,y,z)=C\,\frac{\sin\sqrt{\frac{3}{8}}\frac{\pi}{a}z}{xz(y^2-x^2/3)}\left[y\sin\frac{2\pi}{\sqrt{3}a}y\,\sin\frac{2\pi}{3a}x-\frac{x}{\sqrt{3}}\left[\cos\frac{2\pi}{\sqrt{3}a}y\,\cos\frac{2\pi}{3a}x-\cos\frac{4\pi}{a}x\right]\right]$$

which is the free electron Wannier function for the first band of a closed-packed hexagonal lattice . (Where C is a constant .)

4.4.3 THE SIMPLE CUBIC LATTICE

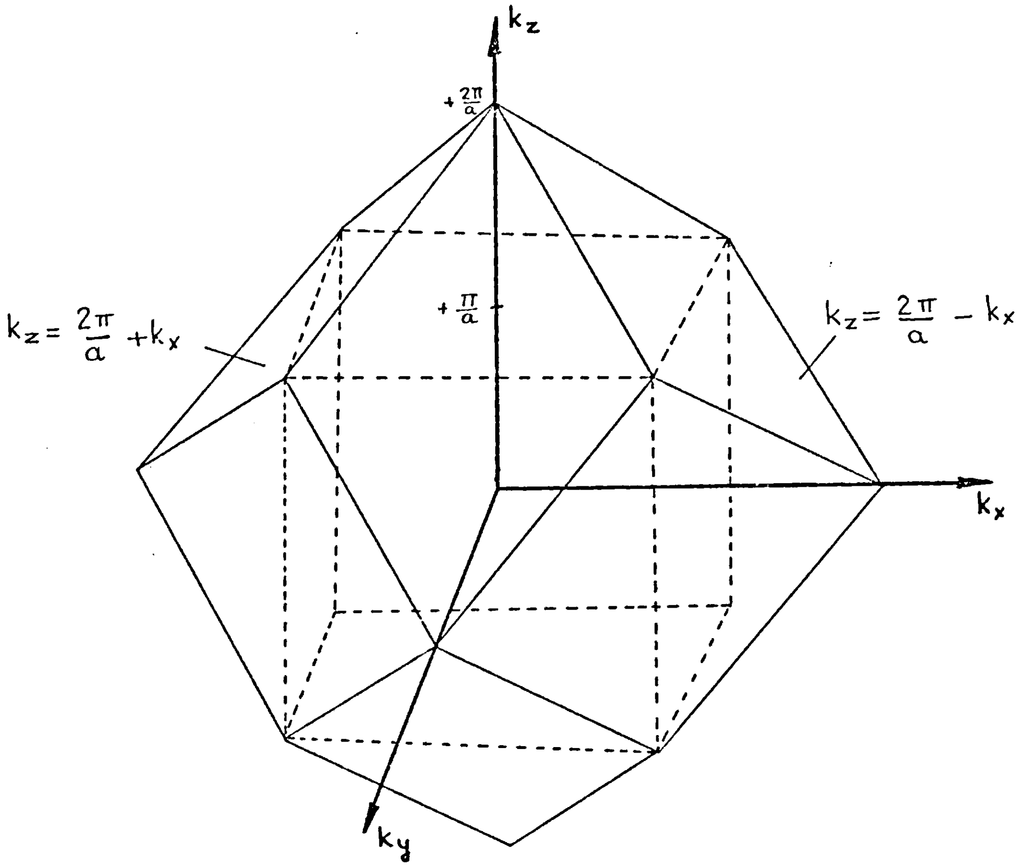


Fig. 4.7 First and second Brillouin zones of a simple cubic lattice. The second zone is between the cube and the dodecaedron.

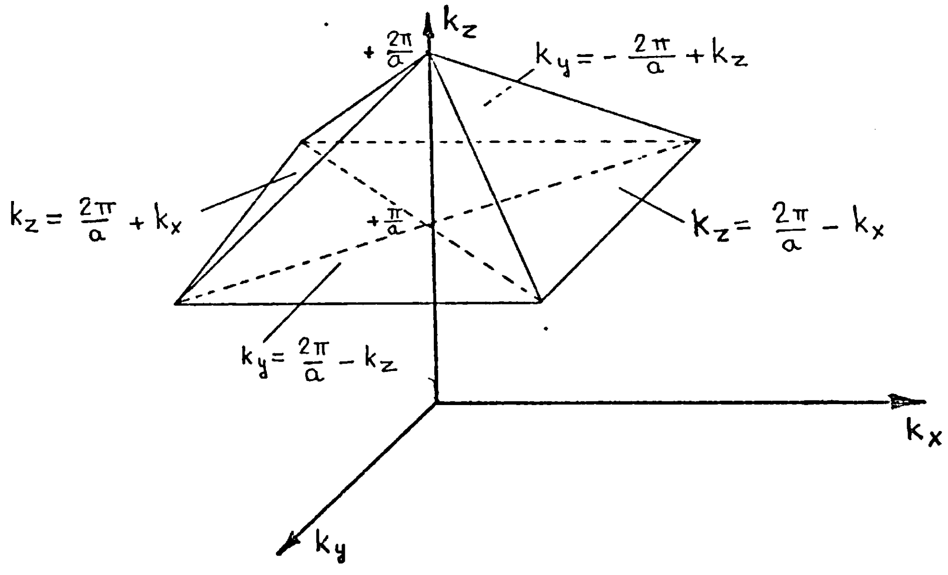


Fig. 4.8 The usual integration can be carried out at once over the partial zone shown above . The free electron Wannier function for the second band is constructed by considering five similiar contributions

The normalized free electron Wannier functions for the first two bands are given below,

i) For the first band,

$$\boxed{a_1(\underline{r}-\underline{R}) = \frac{a^{3/2}}{\pi^3}\,\frac{\sin k_0(x-X_m)\,\sin k_0(y-Y_m)\,\sin k_0(z-Z_m)}{(x-X_m)\,(y-Y_m)\,(z-Z_m)}} \qquad 4.15$$

where $k_0 = \pi/a$

ii) For the second band (for simplicity we let $\underline{R} = 0$),

4.16

$$\boxed{\begin{aligned}
a_2(x,y,z) = i\,\frac{C}{xy}\Bigg[&\frac{(z-x)(\sin k_0(z+x)\sin k_0 y)+y(\cos 2k_0 z-\cos k_0(z+x)\cos k_0 y)}{(z-x)^2-y^2}\\
&-\frac{(z+x)(\sin k_0(z-x)\sin k_0 y)+y(\cos 2k_0 z-\cos k_0(z-x)\cos k_0 y)}{(z+x)^2-y^2}\Bigg]\\
+i\,\frac{C}{yz}\Bigg[&\frac{(x-y)(\sin k_0(x+y)\sin k_0 z)+z(\cos 2k_0 x-\cos k_0(x+y)\cos k_0 z)}{(x-y)^2-z^2}\\
&-\frac{(x+y)(\sin k_0(x-y)\sin k_0 z)+z(\cos 2k_0 x-\cos k_0(x-y)\cos k_0 z)}{(x+y)^2-z^2}\Bigg]\\
+i\,\frac{C}{zx}\Bigg[&\frac{(y-z)(\sin k_0(y+z)\sin k_0 x)+x(\cos 2k_0 y-\cos k_0(y+z)\cos k_0 x)}{(y-z)^2-x^2}\\
&-\frac{(y+z)(\sin k_0(y-z)\sin k_0 x)+x(\cos 2k_0 y-\cos k_0(y-z)\cos k_0 x)}{(y+z)^2-x^2}\Bigg]
\end{aligned}}$$

where $k_0 = \pi/a$, $C = a^{3/2}/\pi^3$

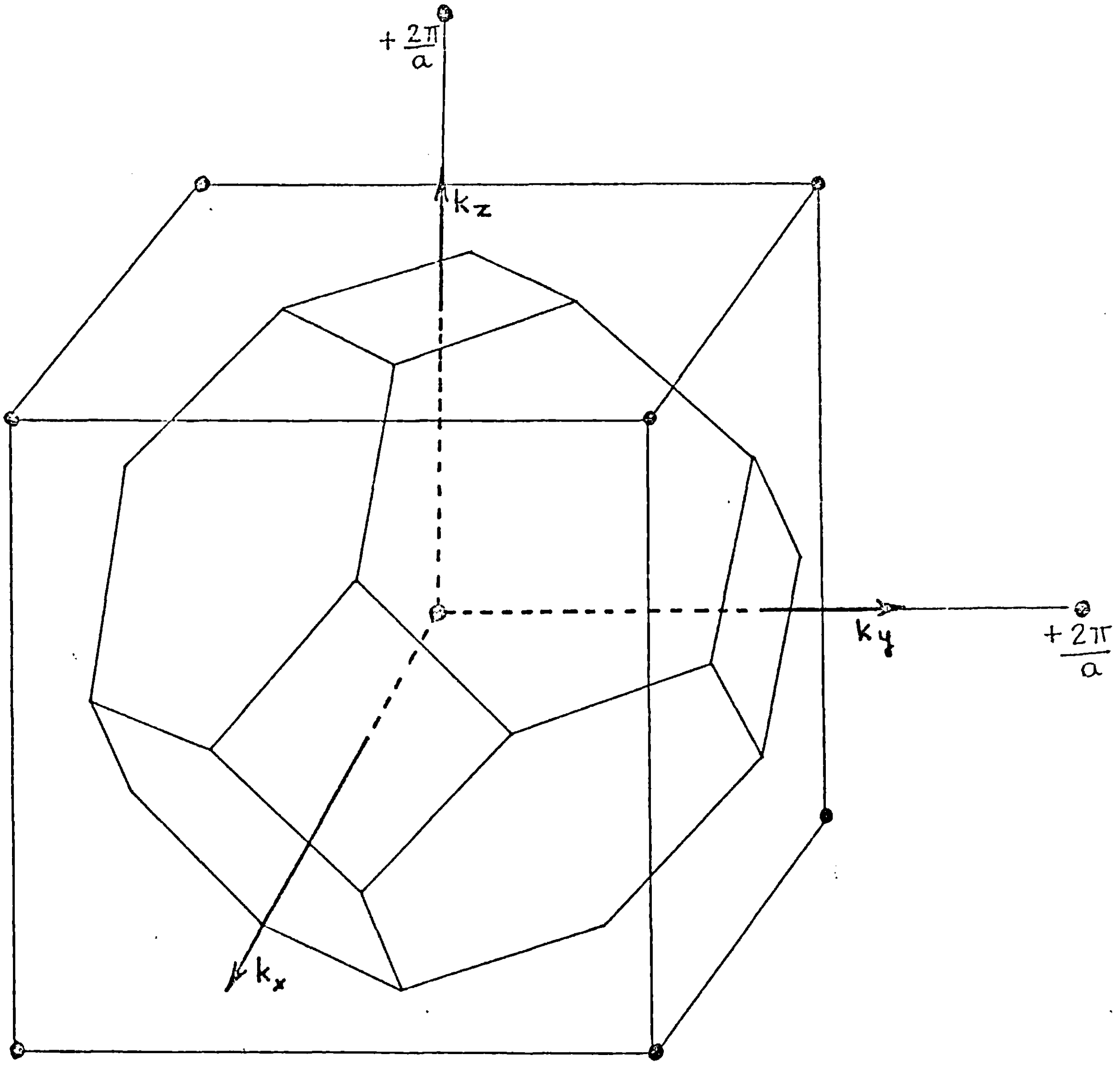


Fig. 4.9 First Brillouin zone for the face-centered cubic lattice . Some points of the reciprocal lattice are shown, marked ● . The zone is a truncated octahedron. The six square faces have the equations

$$k_x = \mp\pi/a \quad , \quad k_y = \mp\pi/a \quad , \quad k_z = \mp\pi/a \ .$$

The eight hexagonal faces have the equations

$$\mp k \mp k \mp k = 3\pi/2a \ .$$

The free electron Wannier function for the first band of a face-centered cubic lattice is given by[1]

$$\boxed{\begin{aligned} a_1(x,y,z) = {} & \frac{C}{(x^2-y^2)(x^2-z^2)}\left[\cos\frac{k_0}{2}x\,(y\sin k_0y+z\sin k_0z)+x\sin\frac{k_0}{2}x(\cos k_0y+\cos k_0z)\right] \\ & \frac{C}{(y^2-z^2)(y^2-x^2)}\left[\cos\frac{k_0}{2}y\,(z\sin k_0z+x\sin k_0x)+y\sin\frac{k_0}{2}y\,(\cos k_0z+\cos k_0x)\right] \\ & \frac{C}{(z^2-x^2)(z^2-x^2)}\left[\cos\frac{k_0}{2}z\,(x\sin k_0x+y\sin k_0y)+z\sin\frac{k_0}{2}z\,(\cos k_0+\cos k_0y)\right] \end{aligned}}$$

4.17

Where $k_0 = \pi/a$

and C is a constant

---

1) See Pincherle, L. ,Electronic Energy Bands in Solids, p. 65, London, Macdonald (1971)

4.4.5 THE BODY-CENTERED CUBIC LATTICE

In this section as an example we will give briefly the details of the calculations . Similiar arguments were used in the remaining sections (Also see section 4.1 for the choice of the arbitrary phases)

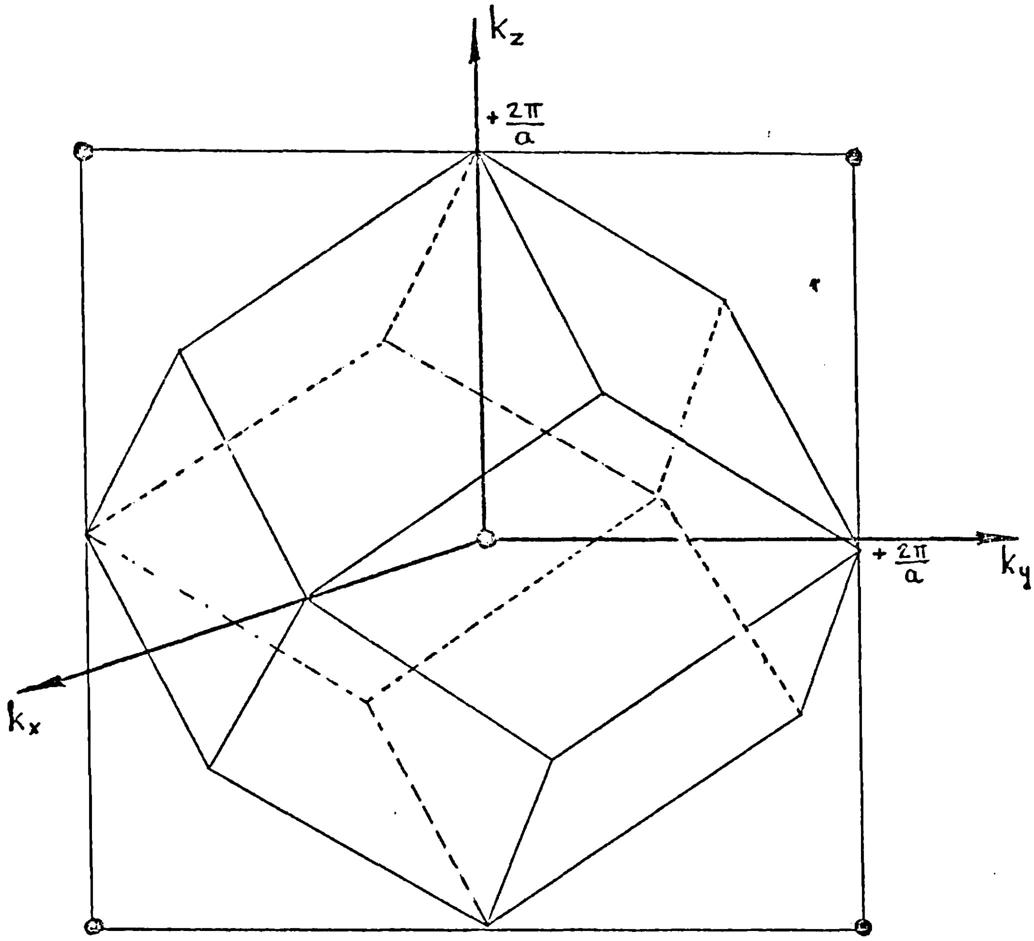


Fig. 4.10 The first Brillouin zone for the B.C.C lattice

The following knowledge is relevant to the future calculations

i) The zone has 12 equal faces in forms of rhombus with acute angles $2\times\mathrm{Tan}^{-1}\frac{1}{\sqrt{2}} = 70.5^{\circ}$

ii) Four faces intersect at $\frac{2\pi}{a}(\mp 1,0,0)$, $\frac{2\pi}{a}(0,\mp 1,0)$, $\frac{2\pi}{a}(0,0,\mp 1)$

iii) Three faces intersect at $\frac{2\pi\sqrt{3}}{2a}(\mp1,\mp1,\mp1)$

iv) The equations of the faces are given in detail on the next page

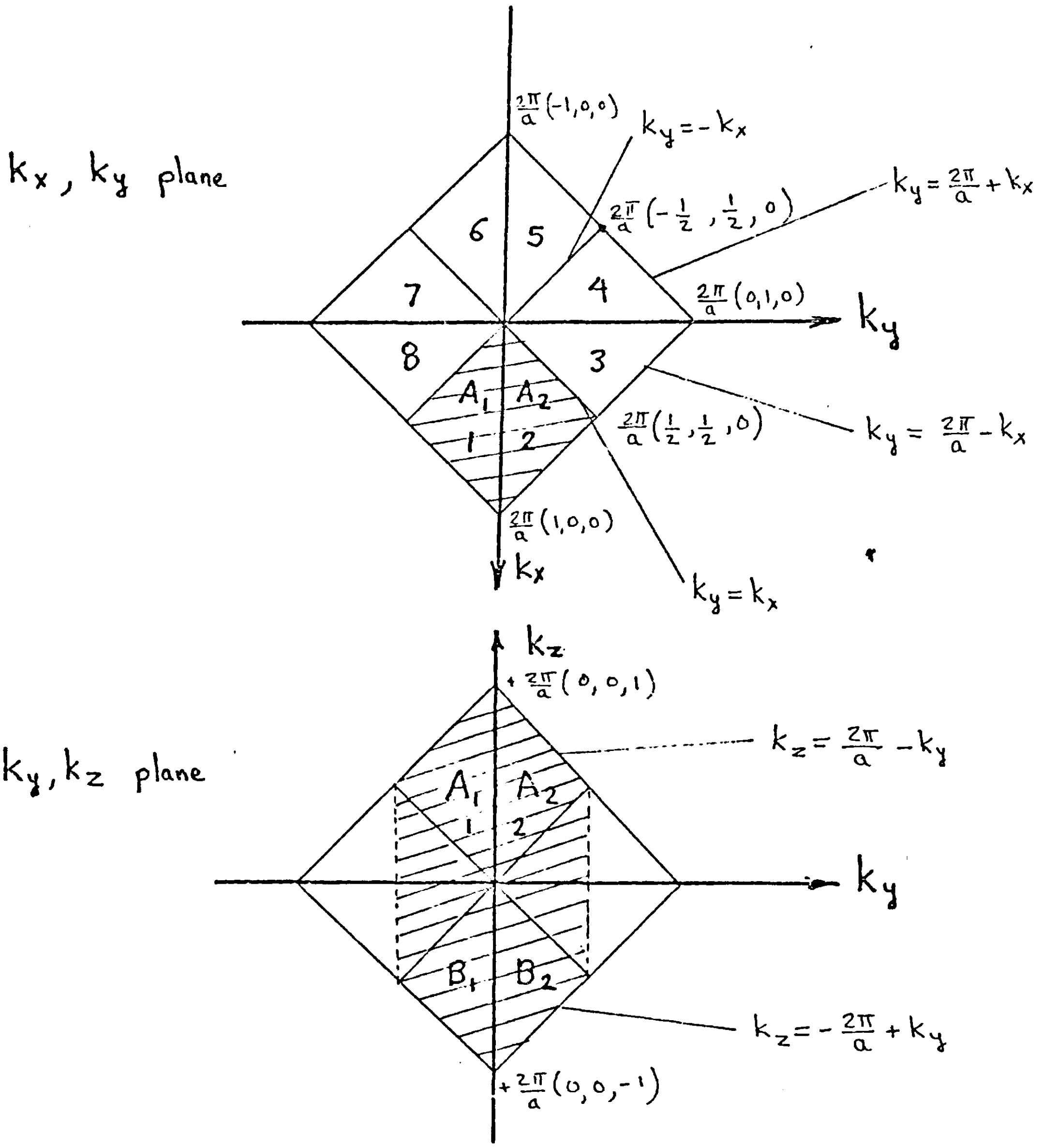


Fig. 4.11 The k_x , k_y and the k_y, k_z planes of the zone (The shaded part shown above makes 1/4 of the total zone)

The coordinate system is chosen as shown above to make most out of the symmetry considerations .

The usual integration will be first carried over the partial zone (shaded) shown above . The contributions of the remaining regions can be obtained by appropriate coordinate transformations due to symmetry considerations.

The equation of the planes A_1 and A_2 is $k_z = \frac{2\pi}{a} - k_x$

The equations of the planes B_1 and B_2 is $k_z = -\frac{2\pi}{a} + k_x$

The contribution of the first partial zone (the prism bounded by plane A1 at top and by plane B_1 at bottom , see fig. 4.11) is

$$I_1 = \int_{k_y = -\pi/a}^{k_y = 0} \int_{k_x = -k_y}^{k_x = k_y + 2\pi/a} \int_{k_z = -\frac{2\pi}{a} + k_x}^{k_z = \frac{2\pi}{a} - k_x} e^{ik_x x + ik_y y + ik_z z} \, dk_x \, dk_y \, dk_z \tag{4.18}$$

The contribution of the second partial zone (the prism bounded by planes A_2 and B_2 , see Fig. 4.11) is ,

$$I_2 = \int_{k_y = 0}^{k_y = +\pi/a} \int_{k_x = k_y}^{k_x = \frac{2\pi}{a} - k_y} \int_{k_z = -\frac{2\pi}{a} + k_x}^{k_z = \frac{2\pi}{a} - k_x} e^{ik_x x + ik_y y + ik_z z} \, dk_x \, dk_y \, dk_z \tag{4.19}$$

Carrying out the relevant integrations in equations 4.18 and 4.19 and then summing up and simplifying the results we obtain

$$I_1 + I_2 = \frac{2\left[\exp(ik_0(-x-y+z)) + \exp(ik_0(-x+y+z)) - (\exp(-i2k_0x) + \exp(i2k_0z))\right]}{iz\left[(x+z)^2 - y^2\right]}$$

$$\frac{2\left[\exp(i2k_0x) + \exp(-i2k_0z) - (\exp(ik_0(x+y-z)) + \exp(ik_0(x-y-z)))\right]}{iz\left[(x+z)^2 - y^2\right]} \tag{4.20}$$

Contribution of the fifth and sixth partial zones can be obtained from equation 4.20 by the following transformation

$$x \longleftrightarrow -x$$

Hence, we have

$$\frac{2\left[\exp(ik_o(-x-y+z)) + \exp(ik_o(-x+y+z)) - (\exp(-i2k_o x) + \exp(i2k_o z))\right]}{iz\left[(x+z)^2 - y^2\right]}$$

$$\frac{2\left[\exp(-i2k_o x) + \exp(-i2k_o z) - (\exp(ik_o(-x+y-z)) + \exp(-ik_o(x+y+z))\right]}{iz\left[(x-z)^2 - y^2\right]}$$

4.21

Summing up the equations 4.20 and 4.21 we find the following

$$\frac{16}{z\left[(x^2-y^2+z^2)^2 - 4x^2z^2\right]}\Big[2xz\sin k_o x\,(\cos k_o y\cos k_o z - \cos k_o x) + (x^2+z^2-y^2)\sin k_o z\,(\cos k_o x\cos k_o y - \cos k_o z)\Big]$$

4.22

which is the total contribution of the partial zones 1,2,5, and 6 (see the figure below)

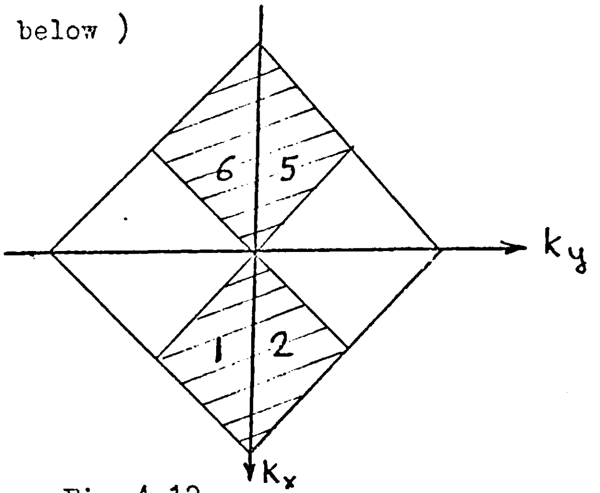


Fig. 4.12

Now it is clear that the contribution of the remaining partial zones (the partial zones 3,4,7, and 8) can be obtained from equation by the following transformation

$$x \longleftrightarrow y$$

Hence we have

$$+\frac{16}{z\left[(-x^2+y^2+z^2)^2-4y^2z^2\right]}\Bigg[2yz\sin k_0y\left(\cos k_0x\cos k_0z-\cos k_0y\right)$$

$$+(-x^2+y^2+z^2)\sin k_0z\left(\cos k_0y\cos k_0x-\cos k_0z\right)\Bigg]$$

4.23

Sum of the equations 4.22 and 4.23 yields us the total Wannier function which is

$$a_1(x,y,z)=\frac{C}{z\left[\left(x^2-y^2+z^2\right)^2-4x^2z^2\right]}\Bigg[2xz\sin k_0x\left(\cos k_0y\cos k_0z-\cos k_0x\right)$$

$$+\left(x^2+z^2-y^2\right)\sin k_0z\left(\cos k_0x\cos k_0y-\cos k_0z\right)\Bigg]$$

$$+\frac{C}{z\left[(-x^2+y^2+z^2)-4y^2z^2\right]}\Bigg[2yz\sin k_0y\left(\cos k_0x\cos k_0z-\cos k_0y\right)$$

$$+\left(-x^2+y^2+z^2\right)\sin k_0z\left(\cos k_0y\cos k_0x-\cos k_0z\right)\Bigg]$$

4.24

where $k_0=\pi/a$ and C is a constant .

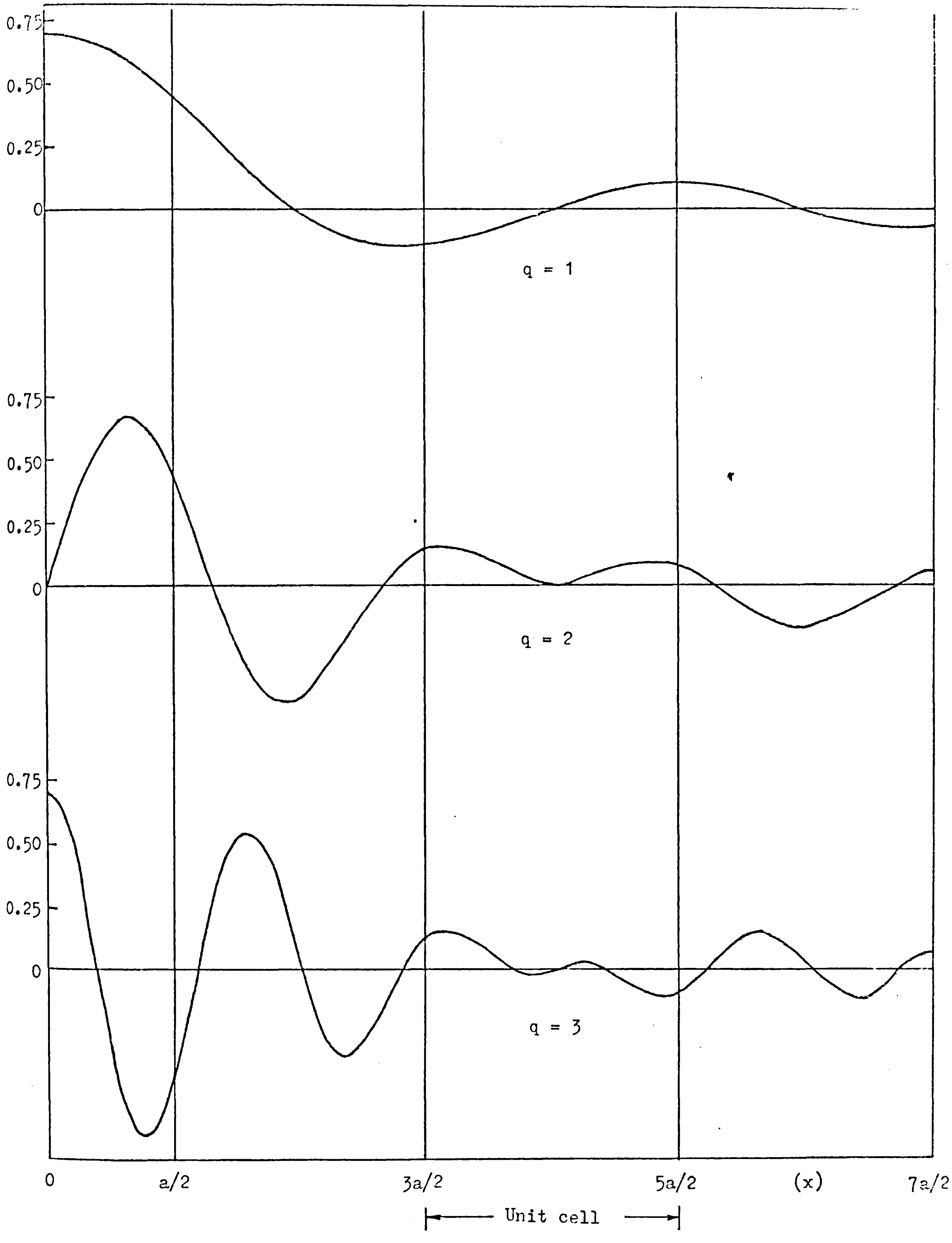


Fig.4.12 Wannier functions (normalised) for three lowest energy bands. Even function, lowest band; odd function, second band, etc.

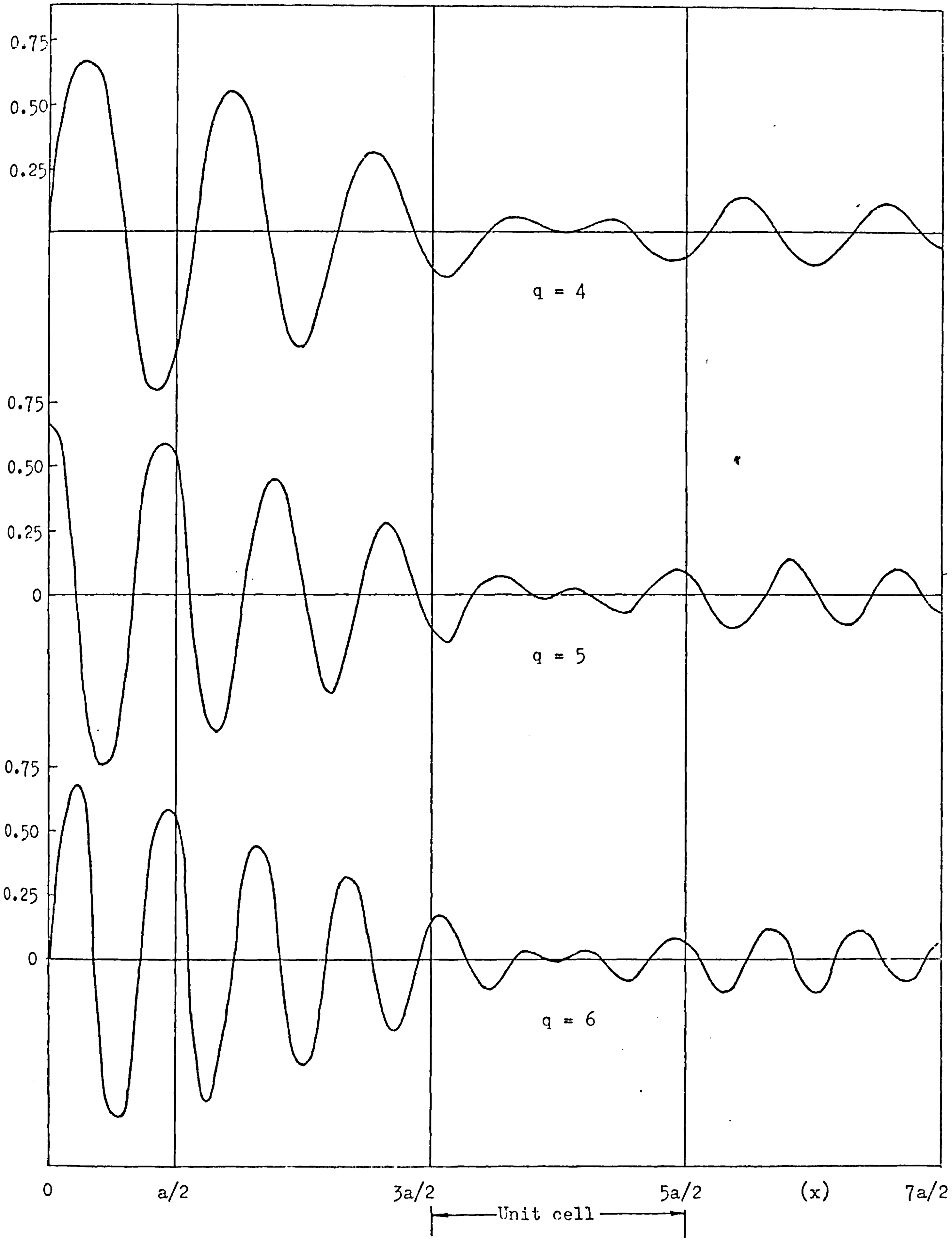


Fig. 4.13 Wannier functions (normalised) for fourth to sixth energy bands.

CHAPTER 5

A PERTURBATION METHOD FOR WANNIER FUNCTIONS

Below we suggest a perturbation method appropriate to Wannier functions.

5.1. THE PERTURBATION METHOD IN THE GENERAL CASE

Suppose that an unperturbed system in the Wannier representation is given by,

$$H^{\circ} a^{\circ}_{t}(\underline{r}-\underline{R}_{m}) = \sum_{\underline{R}_n} \varepsilon^{\circ}_{t}(\underline{R}_{n})\, a^{\circ}_{t}(\underline{r}-\underline{R}_{m}-\underline{R}_{n}) \qquad 5.1$$

where 't' and '$\underline{R}$'$_m$ are the band and the localization indices of the Wannier functions.

Now let us assume that a small perturbation H' has been applied to the system (a general discussion of time - dependent (independent) perturbation theory may be found in a number of places in modern literature, see for instance Dalgarno, A.[1] and Morse, P.M. and Feshbach, H.[2])

Hence,

$$(H^{\circ}+H')\, a^{p}_{t}(\underline{r}-\underline{R}_{m}) = \sum_{\underline{R}_n} \varepsilon^{p}_{t}(\underline{R}_{n})\, a^{p}_{t}(\underline{r}-\underline{R}_{m}-\underline{R}_{n}) \qquad 5.2$$

where $a^{p}_{t}(\underline{r}-\underline{R}_{m})$ and $\varepsilon^{p}_{t}(\underline{R}_{n})$ are the slightly perturbed Wannier functions and the energy fourier coefficients.

Now let us expand the perturbed Wannier function in terms of a complete set of orthonormal functions made up of unperturbed Wannier functions from different bands and locations.

---

1) Dalgarno, A. Quantum Theory, vol. 1 , chap.5- 8, Academic press New York and London, (edited by D.R. Bates) 1961 .

2) Morse, P.M. and Feshbach, H. , Methods of Theoretical Physics, Mcgraw-hill, New York, 1953.

$$a_t^p(\underline{r}-\underline{R}_m) = \sum_s \sum_{\underline{R}_p} C_s(\underline{R}_p)\, a_s^o(\underline{r}-\underline{R}_m-\underline{R}_p) \qquad 5.3$$

At this stage one can make the following points about the last expression,

i) If H' is small, then the perturbed Wannier function is only slightly different from the corresponding unperturbed Wannier function.

$$a_t^p(\underline{r}-\underline{R}_m) \cong a_t^o(\underline{r}-\underline{R}_m) \qquad 5.4$$

Hence equation 5.3 may be rewritten as follows by letting the coefficient $C_t(0) = 1$.

$$a_t^p(\underline{r}-\underline{R}_m) = a_t^o(\underline{r}-\underline{R}_m) + \sum_s{}' \sum_{\underline{R}_p} C_s(\underline{R}_p)\, a_s^o(\underline{r}-\underline{R}_m-\underline{R}_p) \qquad 5.5$$

where the prime on the summation notation denotes that the simultaneous values of $s = t$ and $\underline{R}_p = 0$ is not included in the summation.

ii) The perturbed Wannier function must be normalized.

Consider;

$$\int_{\text{All } \underline{r}} |a_t^p(\underline{r}-\underline{R}_m)|^2 d^3r = \int_{\text{All } \underline{r}} |a_t^o(\underline{r}-\underline{R}_m)|^2 d^3r + \sum_s{}' \sum_{\underline{R}_p} |C_s(\underline{R}_p)|^2 \int_{\text{All } \underline{r}} |a_s^o(\underline{r}-\underline{R}_m-\underline{R}_p)|^2 d^3r$$

$$= 1 + \sum_s{}' \sum_{\underline{R}_p} |C_s(\underline{R}_p)|^2 \qquad 5.6$$

$$= 1 + \varepsilon \cong 1$$

In general when H' is small, then we have $C_s(\underline{R}_p) \ll 1$, therefore $|C_s(\underline{R}_p)|^2$ is negligible compared with unity.

The last steps in equation 5.6 is valid if,

i) the series $1 + \sum_s{}' \sum_{\underline{R}_p} |C_s(\underline{R}_p)|^2$ is convergent. To ensure this we must have,

$$\lim_{s,\,\underline{R}_p \to \infty} \frac{|C_{s+1}(\underline{R}_{p+1})|^2}{|C_s(\underline{R}_p)|^2} < 1 \qquad 5.7$$

ii) However ,remembering that all of the terms in the series are positive and that the sum converges to a positive number we see that $C_s(\underline{R}_p)$ must converge to zero for large s and $\underline{R}_p$.

$$\lim_{s,\,\underline{R}_p \to large} C_s(\underline{R}_p) \to 0 \qquad 5.8$$

Now let us assume that the perturbed energy Fourier coefficient with the correction to the first order is given by,

$$\varepsilon_t^{p}(\underline{R}_n) = \varepsilon_t^{0}(\underline{R}_n) + \varepsilon_t^{\prime}(\underline{R}_n) \qquad 5.9$$

Substituting equations 5.5 and 5.9 into equation 5.2 and letting $\underline{R}_m = 0$ for simplicity (This is permissible as $\underline{R}_m$ is an arbitrary lattice vector) we get ,

$$(H^0 + H')\Big[a_t^0(\underline{r}) + \sum_s{}' \sum_{\underline{R}_p} C_s(\underline{R}_p)\, a_s^0(r - \underline{R}_p)\Big] =$$

$$\sum_{\underline{R}_n} \Big[\varepsilon_t^0(\underline{R}_n) + \varepsilon_t^{\prime}(\underline{R}_n)\Big]\Big[a_t^0(r - \underline{R}_n) + \sum_s{}' \sum_{\underline{R}_p} C_s(\underline{R}_p)\, a_s^0(\underline{r} - \underline{R}_n - \underline{R}_p)\Big] \qquad 5.10$$

Neglecting second order terms we get,

$$H^0 a_t^0(\underline{r}) + H^0 {\sum_s \sum_{\underline{R}_p}}' C_s(\underline{R}_p)\, a_s^0(\underline{r}-\underline{R}_p) + H' a_t^0(\underline{r}) = \sum_{\underline{R}_n} \varepsilon_t^0(\underline{R}_n)\, a_t^0(\underline{r}-\underline{R}_n)$$

$$+ \sum_{\underline{R}_n} \varepsilon_t^0(\underline{R}_n) {\sum_s \sum_{\underline{R}_p}}' C_s(\underline{R}_p)\, a_s^0(\underline{r}-\underline{R}_n-\underline{R}_p) + \sum_{\underline{R}_n} \varepsilon'_t(\underline{R}_n)\, a_t^0(\underline{r}-\underline{R}_n) \qquad 5.11$$

The first terms on the right and left hand sides cancel since they are equal to each other by equation 5.1 , therefore we have

$$H' a_t^0(\underline{r}) + H^0 {\sum_s \sum_{\underline{R}_p}}' C_s(\underline{R}_p)\, a_s^0(\underline{r}-\underline{R}_p) =$$

$$\sum_{\underline{R}_n} \varepsilon_t^0(\underline{R}_n) {\sum_s \sum_{\underline{R}_p}}' C_s(\underline{R}_p)\, a_s^0(\underline{r}-\underline{R}_n-\underline{R}_p) + \sum_{\underline{R}_n} \varepsilon'_t(\underline{R}_n)\, a_t^0(\underline{r}-\underline{R}_n) \qquad 5.12$$

Now multiplying both sides of equation 5.12 by $\left(a_q^0(\underline{r}-\underline{R}_w)\right)^*$ and integrating over all $\underline{r}$ space

$$\int_{\text{all } \underline{r}} a_q^0(\underline{r}-\underline{R}_w)^* H' a_t^0(\underline{r})\, d^3r + {\sum_s \sum_{\underline{R}_p}}' C_s(\underline{R}_p) \int_{\text{all } \underline{r}} a_q^0(\underline{r}-\underline{R}_w)^* H^0 a_s^0(\underline{r}-\underline{R}_p)\, d^3r$$

$$= \sum_{\underline{R}_n} \varepsilon_t^0(\underline{R}_n) {\sum_s \sum_{\underline{R}_p}}' C_s(\underline{R}_p) \int_{\text{all } \underline{r}} a_q^0(\underline{r}-\underline{R}_w)^* a_s^0(\underline{r}-\underline{R}_n-\underline{R}_p)\, d^3r$$

$$+ \sum_{\underline{R}_n} \varepsilon'_t(\underline{R}_n) \int_{\text{all } \underline{r}} a_q^0(\underline{r}-\underline{R}_w)^* a_t^0(\underline{r}-\underline{R}_n)\, d^3r \qquad 5.13$$

It can easily be shown that the unperturbed Hamiltonian does not have matrix elements between the Wannier functions of different bands[2A] (nondegenerate) therefore,

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[2A] See section 3.1

$$\int_{\text{all } \underline{r}} a^{0}_{q}(\underline{r}-\underline{R}_{w})^{*}\, H^{0}\, a^{0}_{s}(\underline{r}-\underline{R}_{p})\, d^{3}r = \delta_{qs}\, \mathcal{E}^{0}_{qs}(\underline{R}_{w}-\underline{R}_{p}) \qquad 5.14$$

and from the orthogonality of Wannier functions we have

$$\int_{\text{all } \underline{r}} a^{0}_{q}(\underline{r}-\underline{R}_{w})^{*}\, a^{0}_{s}(\underline{r}-\underline{R}_{n}-\underline{R}_{p})\, d^{3}r = \delta_{qs}\, \delta_{\underline{R}_{w},\, \underline{R}_{n}+\underline{R}_{p}} \qquad 5.15$$

Hence equation 5.13 can be written as

$$\int_{\text{all } \underline{r}} a^{0}_{q}(\underline{r}-\underline{R}_{w})^{*}\, H'\, a^{0}_{t}(\underline{r})\, d^{3}r + \sum_{s}{}' \sum_{\underline{R}_{p}} C_{s}(\underline{R}_{p})\, \delta_{qs}\, \mathcal{E}^{0}_{qs}(\underline{R}_{w}-\underline{R}_{p})$$

$$= \sum_{\underline{R}_{n}} \mathcal{E}^{0}_{t}(\underline{R}_{n}) \sum_{s}{}' \sum_{\underline{R}_{p}} C_{s}(\underline{R}_{p})\, \delta_{qs}\, \delta_{\underline{R}_{w},\, \underline{R}_{n}+\underline{R}_{p}} + \sum_{\underline{R}_{n}} \mathcal{E}'_{t}(\underline{R}_{n})\, \delta_{qt}\, \delta_{\underline{R}_{w},\, \underline{R}_{n}} \qquad 5.16$$

Note that the matrix elements of H', (the perturbing potential), between the unperturbed Wannier functions of different bands generally do not vanish.

Now considering the effects of the Kronecker's deltas in the summations equation 5.16 can be simplified to the following form.

$$\int_{\text{all } \underline{r}} a^{0}_{q}(\underline{r}-\underline{R}_{w})^{*}\, H'\, a^{0}_{t}(\underline{r})\, d^{3}r + \sum_{\underline{R}_{p}}{}' C_{q}(\underline{R}_{p})\, \mathcal{E}^{0}_{qq}(\underline{R}_{w}-\underline{R}_{p})$$

$$= \sum_{\underline{R}_{p}}{}' \mathcal{E}^{0}_{t}(\underline{R}_{w}-\underline{R}_{p})\, C_{q}(\underline{R}_{p}) + \mathcal{E}'_{t}(\underline{R}_{w})\, \delta_{qt} \qquad 5.17$$

where as before q is the index of an arbitrary band. When q is compared with the index of a particular band say t , we have two possibilities, i) q = t ii) q ≠ t

i) Consider the first case $q = t$,

equation 5.17 becomes;

$$\int_{\text{all } \underline{r}} a_t^0(\underline{r}-\underline{R}_w)^* H' a_t^0(\underline{r})\, d^3r + \sum_{\underline{R}_p}^{\prime} C_t(\underline{R}_p) \cancel{\mathcal{E}_{tt}^0(\underline{R}_w-\underline{R}_p)}$$

$$= \sum_{\underline{R}_p}^{\prime} C_t(\underline{R}_p) \cancel{\mathcal{E}_{tt}^0(\underline{R}_w-\underline{R}_p)} + \mathcal{E}_t'(\underline{R}_w) \qquad 5.18$$

therefore

$$\mathcal{E}_{tt}'(\underline{R}_w) = \int_{\text{all } \underline{r}} a_t^0(\underline{r}-\underline{R}_w)^* H' a_t^0(\underline{r})\, d^3r \qquad 5.19$$

which is the first order correction to the energy Fourier coefficient.

Therefore the perturbed energy Fourier coefficient is given by

$$\mathcal{E}_{tt}^{p}(\underline{R}_w) = \mathcal{E}_{tt}^0(\underline{R}_w) + \mathcal{E}_{tt}'(\underline{R}_w)$$

$$= \mathcal{E}_{tt}^0(\underline{R}_w) + \int_{\text{all } \underline{r}} a_t^0(\underline{r}-\underline{R}_w)^* H' a_t^0(\underline{r})\, d^3r \qquad 5.20$$

ii) Consider now the second case $q \neq t$,

we have (Using equation 5.19)

$$\mathcal{E}_{qt}'(\underline{R}_w) + \sum_{\underline{R}_p}^{\prime} C_q(\underline{R}_p)\, \mathcal{E}_{qq}^0(\underline{R}_w-\underline{R}_p)$$

$$= \sum_{\underline{R}_p}^{\prime} C_q(\underline{R}_p)\, \mathcal{E}_{tt}^0(\underline{R}_w-\underline{R}_p) \qquad 5.21$$

or,

$$\sum_{\underline{R}_p}^{\prime} C_q(\underline{R}_p) \left[\mathcal{E}_{tt}^0(\underline{R}_w-\underline{R}_p) - \mathcal{E}_{qq}^0(\underline{R}_w-\underline{R}_p) \right] = \mathcal{E}_{qt}'(\underline{R}_w) \qquad 5.22$$

through which we can obtain the coefficients of the expansion for the perturbed Wannier function (See equation 5.5).

Equation 5.22 can be worked out as follows;
For any particular band under consideration say the q^{th} band the summation over N values of lattice vector $\underline{R}_p$ yields only one inhomogenous linear equation in N unknowns which are $C_q(\underline{R}_i)$, $i = 1, 2, \ldots N$
Now assigning N different values to the arbitrary lattice vector $\underline{R}_\omega$, one gets a set of N inhomogenous equations in N unknowns.

REMARKS: The equations when written out for one dimension have the following form,

$$C_q(0)\left[\varepsilon_t^0(0) - \varepsilon_q^0(0)\right] + C_q(a)\left[\varepsilon_t^0(-a) - \varepsilon_q^0(-a)\right] + \cdots + C_q(na)\left[\varepsilon_t^0(-na) - \varepsilon_q^0(-na)\right] = \varepsilon'_{qt}(0)$$

$$C_q(0)\left[\varepsilon_t^0(a) - \varepsilon_q^0(a)\right] + C_q(a)\left[\varepsilon_t^0(0) - \varepsilon_q^0(0)\right] + \cdots + C_q(na)\left[\varepsilon_t^0(-na+a) - \varepsilon_q^0(-na+a)\right] = \varepsilon'_{qt}(a$$

$$- -$$

$$- -$$

$$C_q(0)\left[\varepsilon_t^0(na) - \varepsilon_q^0(na)\right] + C_q(a)\left[\varepsilon_t^0(na-a) - \varepsilon_q^0(na-a)\right] + \cdots + C_q(na)\left[\varepsilon_t^0(0) - \varepsilon_q^0(0)\right] = \varepsilon'_{qt}(n$$

5.23

Now we can write this system of linear equations in terms of of matrices,

$$E\,C = H \qquad 5.24$$

where

$$E = \begin{bmatrix} \varepsilon_t^0(0) - \varepsilon_q^0(0) & \varepsilon_t^0(-a) - \varepsilon_q^0(-a) & \cdots & \varepsilon_t^0(-na) - \varepsilon_q^0(-na) \\ \varepsilon_t^0(a) - \varepsilon_q^0(a) & \varepsilon_t^0(0) - \varepsilon_q^0(0) & \cdots & \varepsilon_t^0(-na+a) - \varepsilon_q^0(-na+a) \\ \vdots & \vdots & \ddots & \\ \varepsilon_t^0(na) - \varepsilon_q^0(na) & \varepsilon_t^0(na-a) - \varepsilon_q^0(na-a) & \cdots & \varepsilon_t^0(0) - \varepsilon_q^0(0) \end{bmatrix}$$

5.25

and

$$C = \begin{bmatrix} C_q(0) \\ C_q(a) \\ C_q(2a) \\ \vdots \\ C_q(na) \end{bmatrix} \qquad H = \begin{bmatrix} \mathcal{E}'_{qt}(0) \\ \mathcal{E}'_{qt}(a) \\ \vdots \\ \mathcal{E}_{qt}(na) \end{bmatrix} \tag{5.26}$$

The general solution of equation 5.24 for the $C_q(R)$'s[3] is well known and can be written in terms of determinants (if E is a nonsingular matrix)

$$C_q(ma) = \frac{|E^{(m)}|}{|E|} \qquad m=0,1,\ldots,n \tag{5.27}$$

The numerators in this expression are the determinants of $(n+1)\times(n+1)$ matrices formed from E by replacing the m^{th} column with column of H's .

NOTE; Further remarks on the matrix structures are possible . i.e. Let us recall equation

$$\mathcal{E}^0_t(X_m) = \sum_k E_k\, e^{ik\cdot X_m} \tag{5.28}$$

$$\mathcal{E}^0_t(-X_m) = \sum_k E_k\, e^{-ik\cdot X_m} \tag{5.29}$$

where the summation is over the t^{th} B.Z only.

Now let us assume that the B.Z under consideration has inversion symmetry for ' k ' , then equation 5.29 can be rewritten as,

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[3] In sec.5.3 we have shown that for a 3 dim. crystal with inversional symmetry, these coefficients are related to each other by

$$C_q(\underline{R}_m) = \mu \cdot C^*_q(-\underline{R}_m)$$

where μ is either +1 or -1 (also see chap. 6)

$$\mathcal{E}_t^0(-X_m) = \sum_k E_{-k}\, e^{i k . X_m} \qquad 5.30$$

But from time reversal we have

$$E_k = E_{-k} \qquad 5.31$$

Therefore

$$\mathcal{E}_t^0(-X_m) = \sum_k E_k\, e^{i k . X_m} = \mathcal{E}_t^0(X_m) \qquad 5.32$$

As a consequence of equation 5.32 the coefficient matrix $E = \left[e_{ij} \right]$ becomes a symmetric matrix ($e_{ij} = e_{ji}$ for all i and j) and is given by

$$E = \begin{bmatrix} \mathcal{E}_t^0(0) - \mathcal{E}_q^0(0) & \mathcal{E}_t^0(a) - \mathcal{E}_q^0(a) & \cdots & \mathcal{E}_t^0(na) - \mathcal{E}_q^0(na) \\ \mathcal{E}_t^0(a) - \mathcal{E}_q^0(a) & \mathcal{E}_t^0(0) - \mathcal{E}_q^0(0) & \cdots & \mathcal{E}_t^0(na-a) - \mathcal{E}_q^0(na-a) \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \mathcal{E}_t^0(na) - \mathcal{E}_q^0(na) & \mathcal{E}_t^0(na-a) - \mathcal{E}_q^0(na-a) & \cdots & \mathcal{E}_t^0(0) - \mathcal{E}_q^0(0) \end{bmatrix}$$

5.33

5.2 THE PERTURBATION METHOD IN THE CASE WHERE THE WANNIER FUNCTIONS HAVE SMALL OVERLAP

If the Wannier functions are strongly localized or if the atoms in the lattice are well seperated then the Wannier functions concerned may not overlap appreciably.

The general perturbation equations developed in section 5.1.~~do~~ then simplify.

Consider the general expression given by equation 5.22

$$\sum_{\underline{R}_p} C_q(\underline{R}_p)\left[\varepsilon_t^{\circ}(\underline{R}_w-\underline{R}_p)-\varepsilon_q^{\circ}(\underline{R}_w-\underline{R}_p)\right]=\varepsilon'_{qt}(\underline{R}_w) \qquad 5.34$$

where $\underline{R}_w$ is an arbitrary lattice vector. Let us also recall the system of linear equations in terms of matrices which are obtained from equation 5.34

$$E\,C = H \qquad 5.35$$

Now following the above assumptions (i.e , the atoms are well seperated etc.) the energy bands under consideration will become so narrow (Very close to a free atomic energy level) that in the following equation

$$E_q^{\circ}(\underline{k})=\sum_{\underline{R}_n}\varepsilon_q^{\circ}(\underline{R}_n)\,e^{i\underline{k}\cdot\underline{R}_n} \qquad 5.36$$

only the first Fourier coefficient will be appreciably different from zero, in other terms

$$\begin{aligned}\varepsilon_q^{\circ}(\underline{R}_n) &\neq 0 \qquad \text{if} \quad \underline{R}_n = 0\\ \varepsilon_q^{\circ}(\underline{R}_n) &\simeq 0 \qquad \text{if} \quad \underline{R}_n \neq 0\end{aligned} \qquad 5.37$$

also,

~~also~~,

$$\mathcal{E}^0_q(\underline{R}_\omega - \underline{R}_p) \neq 0 \qquad \text{if} \quad \underline{R}_p = \underline{R}_\omega$$
$$\cong 0 \qquad \text{if} \quad \underline{R}_p \neq \underline{R}_\omega \tag{5.38}$$

Now let us consider the terms on the right hand side of equation 5.34 which are given by,

$$\mathcal{E}'_{qt}(\underline{R}_\omega) = \int_{\text{all } \underline{r}} a^0_q(\underline{r} - \underline{R}_\omega)^* H' a^0_t(\underline{r})\, d^3r \tag{5.39}$$

Since the Wannier functions do not overlap appreciably we have

$$\mathcal{E}'_{qt}(\underline{R}_\omega) \neq 0 \qquad \text{if} \quad \underline{R}_\omega = 0$$
$$\cong 0 \qquad \text{if} \quad \underline{R}_\omega \neq 0 \tag{5.40}$$

Considering equations 5.36 , 5.37 , 5.38 , and 5.39 the matrices E and H (see equations 5.25 and 5.26) will now have the following forms

$$E = \begin{bmatrix} \mathcal{E}^0_t(0) - \mathcal{E}^0_q(0) & & & \bigcirc \\ & \mathcal{E}^0_t(0) - \mathcal{E}^0_q(0) & & \\ & & \ddots & \\ \bigcirc & & & \mathcal{E}^0_t(0) - \mathcal{E}^0_q(0) \end{bmatrix} \tag{5.41}$$

$$H = \begin{bmatrix} \mathcal{E}'_{qt}(0) \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \tag{5.42}$$

Hence we see that for this particular case the coefficient matrix E becomes diagonalized and in the matrix H all elements except the first have vanished.

We can now write the coefficient matrix E as follows

$$E = \left[\varepsilon_t^o(0) - \varepsilon_q^o(0) \right] \cdot I = \alpha \cdot I \qquad 5.43$$

where I is an $n \times n$ unitary matrix . Substituting 5.43 into 5.34 we obtain

$$\left[\varepsilon_t^o(0) - \varepsilon_q^o(0) \right] \cdot IC = H \qquad 5.44$$

but

$$IC = C \qquad 5.45$$

$$\therefore \quad \left[\varepsilon_t^o(0) - \varepsilon_q^o(0) \right] \cdot C = H \qquad 5.46$$

Now writing out the last expression,

$$\left[\varepsilon_t^o(0) - \varepsilon_q^o(0) \right] \cdot \begin{bmatrix} C_q(0) \\ C_q(\underline{R}_1) \\ C_q(\underline{R}_2) \\ \vdots \\ C_q(\underline{R}_n) \end{bmatrix} = \begin{bmatrix} \varepsilon_{qt}'(0) \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} . \qquad 5.47$$

we find

$$C_q(0) = \frac{\varepsilon_{qt}'(0)}{\varepsilon_t^o(0) - \varepsilon_q^o(0)} \; , \qquad C_q(\underline{R}_n) = 0 \qquad n = 1, 2, \ldots n \qquad 5.48$$

and recalling that the perturbed Wannier function was given by the following expansion (See equation 5.5) .

$$a_t^p(\underline{r} - \underline{R}_m) = a_t^o(\underline{r} - R_m) + \sum_q \sum_{\underline{R}_n}{}' C_q(\underline{R}_n)\, a_q^o(\underline{r} - \underline{R}_m - \underline{R}_n) \qquad 5.49$$

Substituting the equations (5.48) into equation 5.49 we find the following final expression for the perturbed Wannier function.

$$a^{p}_{t}(\underline{r}-\underline{R}_m) = a^{o}_{t}(\underline{r}-\underline{R}_m) + \sum_{\substack{q \\ (q \neq t)}} \frac{\mathcal{E}^{1}_{qt}(0)}{\mathcal{E}^{o}_{t}(0) - \mathcal{E}^{o}_{q}(0)} \, a^{o}_{q}(\underline{r}-\underline{R}_m) \qquad 5.50$$

Hence , for this particular case in the expansion of the perturbed Wannier functions one has to include unperturbed Wannier functions from different bands only.

REMARK ; For a qualitative verification of the results given by 5.50 consider the case of tightly bound electrons for which the Wannier functions are given by atomic orbitals. Any small perturbation applied to the system would favour a perturbed function(which resembles the original unperturbed function)which does not oscillate at distant cells. Hence , an expansion for the perturbed function which avoids using Wannier functions from different locations ensures the above condition .

5.3 THE PERTURBATION METHOD IN THE CASE WHERE THE PERTURBING POTENTIAL HAS INVERSION SYMMETRY

If we now assume that both the crystal and the perturbing potential has a center of symmetry (say at $\underline{r}=0$), then the associated (perturbed) Wannier functions will also have inversion symmetry about the same point (see chapter 7). Therefore if we consider the first (ground) and the subsequent odd numbered bands the associated Wannier functions (perturbed or unperturbed) are symmetric in the sense,

$$a^{o}_{t}(-\underline{r}) = a^{o}_{t}(+\underline{r}) \;,\quad a^{P}_{t}(-\underline{r}) = a^{P}_{t}(+\underline{r}) \qquad t = 1,3,5,\ldots \tag{5.51}$$

If we impose these conditions on the expression (which we have written in a form convenient for the present discussion) given for the above perturbed Wannier function,

$$a^{o}_{t}(-\underline{r}) + \sum C_s(0)\, a^{o}_{s}(-\underline{r}) + \sum_{s}\sum_{p} C_s(\underline{R}_p)\, a^{o}_{s}(-\underline{r}-\underline{R}_p) + \sum_{s}\sum_{-p} C_s(-\underline{R}_p)\, a^{o}_{s}(-\underline{r}+\underline{R}_p) + \ldots \tag{5.52}$$

$$= a^{o}_{t}(\underline{r}) + \sum_{s} C_s(0)\, a^{o}_{s}(\underline{r}) + \sum_{s}\sum_{p} C_s(\underline{R}_p)\, a^{o}_{s}(\underline{r}-\underline{R}_p) + \sum_{s}\sum_{-p} C_s(-\underline{R}_p)\, a^{o}_{s}(\underline{r}+\underline{R}_p) + \ldots$$

The first terms (on both sides) cancel, the second terms however are equal in the sense,

$$C_s(0)\, a^{o}_{s}(-\underline{r}) = C_s(0)\, a^{o}_{s}(\underline{r}) \tag{5.53}$$

and yield $C_s(0) = 0$ for s = even (since, $a^{o}_{s}(\underline{r})$ for this choice is antisymmetric and not zero for all $\underline{r}$) and $C_s(0) \neq 0$ for s = odd.

Finally for the remaining terms of equation 5.52 we can write the following (since the unperturbed Wannier functions ~~in concern~~ are functions of difference only, see chapter 2)

$$C_s(+\underline{R}_p)\, a^{o}_{s}(-\underline{r}-\underline{R}_p) = C_s(-\underline{R}_p)\, a^{o}_{s}(\underline{r}+\underline{R}_p)$$
$$\text{or} \tag{5.54}$$
$$C_s(+\underline{R}_p)\, a^{o}_{s}(-\underline{r}+\underline{R}_p) = C_s(-\underline{R}_p)\, a^{o}_{s}(\underline{r}-\underline{R}_p)$$

which through similiar arguments yield

$$C_s(+\underline{R}_p) = -\,C_s(-\underline{R}_p) \quad \text{for } s = \text{even}$$

$$C_s(+\underline{R}_p) = C_s(-\underline{R}_p) \quad \text{for } s = \text{odd} \qquad 5.55$$

In chapter 7 we have also shown that as a result of time reversal symmetry the Wannier functions can be chosen as either real or pure imaginary. In the present discussion we have started with a symmetric (and real) perturbed Wannier function, therefore in expanding this function the coefficients $C_s(\underline{R}_p)$'s associated with the unperturbed Wannier functions of even numbered bands (pure imaginary) are to be chosen pure imaginary (in order to end up with a real function). Therefore condition 5.55 could also be written as

$$C_s(+\underline{R}_p) = C_s^*(-\underline{R}_p) \quad \text{for } s = \text{even} \qquad 5.56$$

Hence to summarize; symmetry in the applied potential (provided that the crystal has a center of inversion) has the following implications on the choice of the coefficients $C_s(\underline{R}_p)$'s for;

a) The perturbed Wannier function of ~~any~~ odd numbered band

$$\left.\begin{aligned} &C_s(0) \neq 0 \\ &C_s(+\underline{R}_p) = C_s(-\underline{R}_p) \end{aligned}\right| \text{ for s=odd (C is real)}$$

$$5.57$$

$$\left.\begin{aligned} &C_s(0) = 0 \\ &C_s(+\underline{R}_p) = C_s^*(-\underline{R}_p) \end{aligned}\right| \text{ for s=even (C is imaginary)}$$

b) The perturbed Wannier function of an even numbered band

$$\left.\begin{aligned} &C_s(o) = 0 \\ &C_s(+\underline{R}_p) = C_s^*(-\underline{R}_p) \end{aligned}\right| \text{ for s=odd (C is imaginary)}$$

$$5.58$$

$$\left.\begin{aligned} &C_s(0) \neq 0 \\ &C_s(+\underline{R}_p) = C_s(-\underline{R}_p) \end{aligned}\right| \text{ for s=even (C is real)}$$

Similar proofs follow for coefficients associated with the second (or higher) order corrections.

5.4 SECOND ORDER CORRECTIONS

In the previous sections the effect of the perturbative potential $H'(\underline{r})$ in the Hamiltonian operator for crystals on both the Wannier functions and eigenenergy Fourier coefficients has been obtained to the first order, which are

$$\varepsilon^{p}_{t}(\underline{R}_m) = \varepsilon^{0}_{t}(\underline{R}_m) + \langle t, \underline{R}_m | H' | t, 0 \rangle \qquad 5.59$$

$$a^{p}_{t}(\underline{r}-\underline{R}_m) = a^{0}_{t}(\underline{r}-\underline{R}_m) + \sum_{s}{\sum_{p}}' C_s(\underline{R}_p)\, a^{0}_{s}(\underline{r}-\underline{R}_m-\underline{R}_p) \qquad 5.60$$

where the coefficients $C_s(\underline{R}_p)$'s are to be obtained through the following set of linear simultaneous equations (see equation 5.22)

$$\sum_{p} C_s(\underline{R}_p)\left[\varepsilon^{0}_{tt}(\underline{R}_w-\underline{R}_p) - \varepsilon^{0}_{ss}(R_w-R_p)\right] = \varepsilon'_{st}(\underline{R}_w) \qquad 5.61$$

where $\varepsilon^{0}tt(\underline{R}_w-\underline{R}_p)$ and $\varepsilon^{0}ss(\underline{R}_w-\underline{R}_p)$ as usual stand for the unperturbed eigenenergy Fourier coefficients

$$\text{i.e.} \quad \varepsilon^{0}_{tt}(\underline{R}_w-\underline{R}_p) = \langle t, \underline{R}_w | H^{0} | t, \underline{R}_p \rangle \quad , \text{etc.} \qquad 5.62$$

and $\varepsilon'st(\underline{R}_w)$ is an (interband) matrix element of the perturbative potential which is given as

$$\varepsilon'_{st}(\underline{R}_w) = \langle s, \underline{R}_w | H' | t, 0 \rangle \qquad 5.63$$

The second order corrections to the Wannier functions and the fourier coefficients of the energy can be obtained in a way similiar to that followed in the previous sections (by using the first order solutions). If we now denote these second order terms as follows

$$\varepsilon^{p}_{t}(\underline{R}_m) = \varepsilon^{0}_{t}(\underline{R}_m) + \varepsilon'_{t}(\underline{R}_m) + \varepsilon''_{t}(\underline{R}_m) \qquad 5.64$$

$$a^{p}_{t}(\underline{r}-\underline{R}_m) = a^{0}_{t}(\underline{r}-\underline{R}_m) + \sum_{s}\sum_{p} C_s(\underline{R}_p)\, a^{0}_{s}(\underline{r}-\underline{R}_p-\underline{R}_m) + \sum_{s}\sum_{p} B_s(\underline{R}_p)\, a^{0}_{s}(\underline{r}-\underline{R}_p-\underline{R}_m) \qquad 5.65$$

then substitute equations 5.64 and 5.65 into equation 5.2 and let $\underline{R}_m = 0$ (for simplicity) we get

$$(H^{0}+H')\Big(a^{0}_{t}(\underline{r})+\sum_{s}\sum_{p}C_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{p})+\sum_{s}\sum_{p}B_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{p})\Big)$$

$$=\sum_{m}\left[\varepsilon^{0}_{t}(\underline{R}_{m})+\varepsilon^{1}_{t}(\underline{R}_{m})+\varepsilon^{11}_{t}(\underline{R}_{m})\right]\Big[a^{0}_{t}(\underline{r}-\underline{R}_{m})+\sum_{s}\sum_{p}C_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{m}-\underline{R}_{p}) \qquad 5.66$$

$$+\sum_{s}\sum_{p}B_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{m}-\underline{R}_{p})\Big)$$

or (by neglecting third and higher order terms)

$$H^{0}a^{0}_{t}(\underline{r})+H^{0}\sum_{s}\sum_{p}C_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{p})+H^{0}\sum_{s}\sum_{p}B_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{p})$$

$$+H'a^{0}_{t}(\underline{r})+H'\sum_{s}\sum_{p}C_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{p}) \qquad 5.67$$

$$=\sum_{m}\varepsilon^{0}_{t}(\underline{R}_{m})a^{0}_{t}(\underline{r}-\underline{R}_{m})+\sum_{m}\sum_{s}\sum_{p}\varepsilon^{0}_{t}(\underline{R}_{m})C_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{m}-\underline{R}_{p})$$

$$+\sum_{m}\sum_{s}\sum_{p}\varepsilon^{0}_{t}(\underline{R}_{m})B_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{m}-\underline{R}_{p})+\sum_{m}\varepsilon'_{t}(\underline{R}_{m})a^{0}_{t}(r-R_{m})$$

$$+\sum_{m}\sum_{s}\sum_{p}\varepsilon'_{t}(\underline{R}_{m})C_{s}(\underline{R}_{p})a^{0}_{s}(\underline{r}-\underline{R}_{m}-\underline{R}_{p})+\sum_{m}\varepsilon''_{t}(\underline{R}_{m})a^{0}_{t}(\underline{r}-\underline{R}_{m})$$

The first terms on the right and left hand sides cancel since they are equal to each other by equation 5.1 . Now, multiplying both sides of the last equation by $\left[a^{0}_{q}(\underline{r}-\underline{R}_{n})\right]^{*}$ and integrating over all $\underline{r}$ space (and also using the orthogonality of the Wannier functions) we get

$$\sum_{s}\sum_{p}C_{s}(\underline{R}_{p})\delta_{qs}\varepsilon^{0}_{s}(\underline{R}_{n}-\underline{R}_{p})+\sum_{s}\sum_{p}B_{s}(\underline{R}_{p})\delta_{qs}\varepsilon^{0}_{s}(\underline{R}_{n}-\underline{R}_{p})+\varepsilon'_{qt}(\underline{R}_{n})+\sum_{s}\sum_{p}C_{s}(\underline{R}_{p})\varepsilon'_{qs}(\underline{R}_{n}-\underline{R}_{p})=$$

$$\sum_{m}\sum_{s}\sum_{p}\varepsilon^{0}_{t}(\underline{R}_{m})C_{s}(\underline{R}_{p})\delta_{qs}\delta_{n,m+p}+\sum_{m}\sum_{s}\sum_{p}\varepsilon^{0}_{t}(\underline{R}_{m})B_{s}(\underline{R}_{p})\delta_{q,s}\delta_{n,m+p}+\sum_{m}\varepsilon'_{t}(R_{m})\delta_{qt}\delta_{mn}$$

$$+\sum_{m}\sum_{s}\sum_{p}\varepsilon'_{t}(\underline{R}_{m})C_{s}(\underline{R}_{p})\delta_{qs}\delta_{n,m+p}+\sum_{m}\varepsilon''_{t}(R_{m})\delta_{qt}\delta_{mn} \qquad 5.68$$

which yields; i) for q=t

$$\sum_{p}C_{t}(\underline{R}_{p})\varepsilon^{0}_{t}(\underline{R}_{n}-\underline{R}_{p})+\sum_{p}B_{t}(\underline{R}_{p})\varepsilon^{0}_{t}(\underline{R}_{n}-\underline{R}_{p})+\varepsilon'_{tt}(\underline{R}_{n})+\sum_{s}\sum_{p}C_{s}(R_{p})\varepsilon'_{ts}(\underline{R}_{n}-\underline{R}_{p})=$$

$$\sum_{p}C_{t}(\underline{R}_{p})\varepsilon^{0}_{t}(\underline{R}_{n}-\underline{R}_{p})+\sum_{p}B_{t}(R_{p})\varepsilon^{0}_{t}(R_{n}-R_{p})+\varepsilon'_{tt}(\underline{R}_{n})+\sum_{p}C_{t}(R_{p})\varepsilon'_{t}(R_{n}-R_{p})+\varepsilon''_{t}(\underline{R}_{n})$$

5.69

or

$$\varepsilon''_t(\underline{R}_n) = \sum_s \sum_p C_s(\underline{R}_p)\,\varepsilon'_{st}(\underline{R}_n - \underline{R}_p) - \sum_p C_t(\underline{R}_p)\,\varepsilon'_t(\underline{R}_n - \underline{R}_p) \qquad 5.70$$

Note that the coefficients $C_t(\underline{R}_p)$'s for $\underline{R}_p \neq 0$ (we have $C_t(0)=1$) which were not determined in section 5.1 do not appear in the last expression

$$\varepsilon''_t(\underline{R}_n) = \sum_s \sum_p{}' C_s(\underline{R}_p)\,\varepsilon'_{st}(\underline{R}_n - \underline{R}_p) \qquad 5.71$$

Hence, the perturbed eigenenergy Fourier coefficients to the second order are thoroughly determined and given by, 5.72

$$\varepsilon^p_t(\underline{R}_n) = \langle t, \underline{R}_n | H^\circ | t, 0 \rangle + \langle t, R_n | H' | t, 0 \rangle + \sum_s \sum_p{}' C_s(\underline{R}_p) \langle t, \underline{R}_n | H' | t, R_p \rangle$$

where $C_s(\underline{R}_p)$'s are to be obtained from the usual set of linear eqs.

ii) for $q \neq t$ 5.73

$$\sum_p C_q(\underline{R}_p)\,\varepsilon^\circ_q(\underline{R}_n - \underline{R}_p) + \sum_p B_q(\underline{R}_p)\,\varepsilon^\circ_q(\underline{R}_n - \underline{R}_p) + \varepsilon'_{qt}(\underline{R}_n) + \sum_s \sum_p C_s(\underline{R}_p)\,\varepsilon'_{qs}(R_n - R_p)$$

$$= \sum_p \varepsilon^\circ_t(\underline{R}_n - \underline{R}_p) C_q(\underline{R}_p) + \sum_p \varepsilon^\circ_t(\underline{R}_n - \underline{R}_p) B_q(\underline{R}_p) + 0 + \sum_p \varepsilon'_t(\underline{R}_n - \underline{R}_p) C_q(R_p) + 0$$

or

$$\sum_p B_q(\underline{R}_p)[\varepsilon^\circ_t(\underline{R}_n - \underline{R}_p) - \varepsilon^\circ_q(\underline{R}_n - \underline{R}_p) = -\sum_p C_q(\underline{R}_p)[\varepsilon^\circ_t(\underline{R}_n - \underline{R}_p) - \varepsilon^\circ_q(\underline{R}_n - \underline{R}_p)] + \varepsilon'_{qt}(\underline{R}_n)$$
$$+ \sum_s \sum_p C_s(\underline{R}_p)\,\varepsilon'_{qs}(\underline{R}_n - \underline{R}_p) - \sum_p C_q(\underline{R}_p)\,\varepsilon'_t(\underline{R}_n - \underline{R}_p)$$

The first two terms on the r.h.s. of the last equation cancel by equation 5.61 , therefore we have

$$\sum_p B_q(\underline{R}_p)[\varepsilon^\circ_t(\underline{R}_n - \underline{R}_p) - \varepsilon^\circ_q(\underline{R}_n - \underline{R}_p)] = \sum_s \sum_p C_s(R_p)\,\varepsilon'_{qs}(\underline{R}_n - \underline{R}_p) - \sum_p C_q(R_p)\,\varepsilon'_t(\underline{R}_n - \underline{R}_p) \qquad 5.74$$

The right hand side of the last equation involve only the first order corrections[4] which are readily obtained (in the previous sections) Therefore, if we now assume that $\beta(H', \underline{R}_n, q, t)$ is obtained from the first order corrections mentioned above as follows[5]

$$\beta(H', \underline{R}_n, q, t) = \sum_s \sum_p C_s(\underline{R}_p)\,\varepsilon'_{qs}(\underline{R}_n - \underline{R}_p) - \sum_p C_q(\underline{R}_p)\,\varepsilon'_t(\underline{R}_n - \underline{R}_p) \qquad 5.75$$

---

[4]) In the part of the equation mentioned we have multiplication of two such first order terms, therefore the magnitude of the expression is second order.

[5]) Using equation 5.71 the expression for $\beta(H', \underline{R}_n, q, t)$ can alternatively be given as

$$\beta(H', \underline{R}_n, q, t) = \varepsilon''_q(\underline{R}_n) + \sum_p C_q(\underline{R}_p)[\varepsilon'_q(\underline{R}_n - \underline{R}_p) - \varepsilon'_t(\underline{R}_n - \underline{R}_p)] \qquad 5.76$$

where $\varepsilon'_t(\underline{R}_n - \underline{R}_p)$ and $\varepsilon''_t(\underline{R}_n)$ are the first and second order corrections to the eigenenergy Fourier coefficients.

then, to find the second order corrections to the Wannier function one has to solve the following set of linear simultaneous equations

$$\sum_{p} B_q(\underline{R}_p)\left[\varepsilon_t^{\circ}(\underline{R}_n-\underline{R}_p)-\varepsilon_q^{\circ}(\underline{R}_n-\underline{R}_p)\right]=\beta(H',\underline{R}_n,q,t) \qquad 5.77$$

in a way similiar to that followed in the previous sections.

The perturbed Wannier function to the second order is now given by

$$a_t^{p}(\underline{r}-\underline{R}_m)=a_t^{\circ}(\underline{r}-\underline{R}_m)+\sum_{s}\sum_{p}C_s(\underline{R}_p)a_s^{\circ}(\underline{r}-\underline{R}_p-\underline{R}_m)+\sum_{s}\sum_{p}B_s(\underline{R}_p)a_s^{\circ}(\underline{r}-\underline{R}_p-\underline{R}_m) \qquad 5.78$$

The higher order corrections to the eigenenergy Fourier coefficients and the Wannier functions can be found in a similiar way.

CHAPTER 6

NEARLY FREE ELECTRON WANNIER FUNCTIONS BY THE PERTURBATION METHOD THAT WE HAVE SUGGESTED

6.1 INTRODUCTION

In chapter 5 we have suggested a perturbation method appropriate to Wannier functions. Now we will use the method to calculate the lowest Wannier function of the one dimensional crystal given in chapter nine. (The deviation of the higher band Wannier functions from those of free electrons looks insignificant.)

The purpose of the present calculations is, first, to give an application of the method and secondly to deduce certain remarks about its feasibilty and the accuracy by comparing the Wannier function hence obtained with the exact Wannierfunction obtained by direct calculations.

The crystal model (one dimensional) is similiar to that assumed in section 9.4 (see fig.9.) . Hence , the perturbing potential is a periodic square potential with a small magnitude ($V_0 = 0.10$ a.u.) and the atoms are separated from each other by a distance $a = 2.0$ a.u. Therefore the unperturbed system is represented by the Wannier functions corresponding to zero potential $V(x)= 0$, (free electron Wannier functions). It can easily be observed that these (free electron) Wannier functions overlap appreciably, therefore referring to what we have said in chapter 5 (section 5.1) we have to use the following set of linear equations in order to obtain the coefficients of the expansion ($C_q(X_p)$'s) for the perturbed Wannier function.

$$\sum_{p} C_q(X_p)\left[\mathcal{E}^{\circ}_{t}(X_w - X_p) - \mathcal{E}^{\circ}_{q}(X_w - X_p)\right] = \mathcal{E}^{'}_{qt}(X_w) \qquad 1$$

The perturbed Wannier function will then be given by the following expression (See chapter 5),

$$a_t^p\,(x - X_m) = a_t^o(x - X_m) + \sum_{r,p}{\sum}' C_r(X_p)\, a_r^o(x - X_m - X_p) \qquad 2$$

In this particular problem we are interested in finding the Wannier function of the ground band only , therefore we have $t = 1$, and also , for simplicity we will let $X_m = 0$ (this means that we will be calculating the Wannier function centered at the origin) .

Hence, we will solve the following set of linear equations for $C_q(X_p)$'s

$$\sum_p C_q(X_p) \left[\mathcal{E}_1^o(X_w - X_p) - \mathcal{E}_q^0(X_w - X_p) \right] = \mathcal{E}'_{q1}(X_w) \qquad 3$$

and then using these coefficients we will set up the following linear combination of the unperturbed Wannier functions (belonging to different bands and locations)

$$a_1^p(x) = a_1^o(x) + \sum_{r,p}{\sum}' C_r(X_p)\, a_r^o(x - X_p) \qquad 4$$

to obtain an expression for the perturbed Wannier function.

In order to solve the set of equations given by equation we need to know

i) unperturbed (free electron) energy Fourier coefficients, $\mathcal{E}_q^o(X_w - X_p)$'s

ii) the matrix elements of the perturbing potential between the Wannier functions of the unperturbed system .

The perturbative potential that we consider has inversion symmetry through the origin which implies that (see chapter 7) the perturbed Wannier function will also have inversion symmetry through the same point. In section 6.3 , in calculating the coefficients $C_r(X_p)$'s these restrictions will be taken into account.

In the following sections we will first calculate the unperturbed energy Fourier coefficients and also obtain several matrix elements of the perturbative potential between the Wannier functions of different locations and bands.

In the next tables we give the results only.

6.2 UNPERTURBED (FREE ELECTRON) ENERGY FOURIER COEFFICIENTS AND WANNIER FUNCTIONS(NORMALIZED)

Below in tables 6.1 and 6.2 we quote the results only;

UNPERTURBED (FREE ELECTRON) ENERGY FOURIER COEFFICIENTS

$$\mathcal{E}_q^o(X_p) = \frac{1}{\pi}\int_{q^{th}\ \text{band}} k^2 \cos(k\cdot X_p)\, dk$$

	$X_p = 0$	$X_p = \mp 2$	$X_p = \mp 4$	$X_p = \mp 6$	$X_p = \mp 8$	$X_p = \mp 2n$
$q = 1$	$\pi^2/12$	$-1/2$	$+1/8$	$-1/18$	$+1/32$	$\frac{(-1)^n}{2n^2}$
$q = 2$	$+7\pi^2/12$	$+3/2$	$+1/8$	$+1/6$	$+1/32$	$\frac{2-(-1)^n}{2n^2}$
$q = 3$	$+19\pi^2/12$	$-5/2$	$+1/8$	$-10/36$	$+1/32$	$\frac{3(-1)^n-2}{2n^2}$
$q = 4$	$+37\pi^2/12$	$+7/2$	$+1/8$	$+7/18$	$+1/32$	$\frac{4-3(-1)^n}{2n^2}$
$q = 5$	$+61\pi^2/12$	etc.				

Table 6.1 (above) Table 6.2 (below)

NORMALIZED, UNPERTURBED (FREE ELECTRON) WANNIER FUNCTIONS

$$a_q^o(x - X_W) = (1/\sqrt{2})\, \frac{\sin((q\pi/2)(x - X_W)) - \sin(((q-1)\pi/2)(x - X_W))}{\pi(x - X_W)/2}$$

where $q = 1,3,5,7,\ldots\ldots$ is the band index

$$a_q^o(x - X_W) = -i(1/\sqrt{2})\, \frac{\cos((q\pi/2)(x - X_W)) - \cos(((q-1)\pi/2)(x - X_W))}{\pi(x - X_W)/2}$$

where $q = 2,4,6,8,\ldots\ldots$ is the band index

In both equations X_W ($X_W = 0, \mp 2, \mp 4, \mp 6, \ldots$) is the localization site

6.3 MATRIX ELEMENTS OF THE PERTURBATIVE POTENTIAL

Below, in tables 6.3 , 6.4 , and 6.5 we have tabulated the matrix elements of the perturbative potential within each unit cell. We give only the results of the calculation. q again is the band index.

$$\mathcal{E}'_{q1}(0)=C\int_{all\,x} a_q^0(x)V(x)a_1^0(x)\,dx$$

	$\mathcal{E}'_{12}(0)$	$\mathcal{E}'_{13}(0)$	$\mathcal{E}'_{14}(0)$	$\mathcal{E}'_{15}(0)$
1st Unit Cell	......	-5.840	......	+0.290
2nd Unit Cell	......	-0.179	......	-0.193
3rd Unit Cell	......	-0.126	.....	-0.018
4th Unit Cell	......	-0.045	......	-0.025
5th Unit Cell	......	-0.034	....	-0.0065
Total **	0.0000	-6.224	0.00000	+0.047
Total considering constant of integration	0.00000	-0.03112	0.00000	+0.00023

Table 6.3 Matrix elements of the perturbing potential between the Wannier functions centered at the same lattice point ($X_w = 0$) . The matrix elements in the cells marked (.....) are non-zero. However, we have not bothered to write them since their total effect is identically zero.

** Approximate contributions of the remaining cells are also included.

$$\mathcal{E}'_{1q}(\mp 2) = C \int_{\text{all } x} a_q^{\circ}(x \mp 2)\, V(x)\, a_1^{\circ}(x)\, dx$$

	LEFT $(X \leq 0)$					$(X \geq 0)$ RIGHT							
	5th Unit Cell	4th Unit Cell	3rd Unit Cell	2nd Unit Cell	1st Unit Cell	1st Unit Cell	2nd Unit Cell	3rd Unit Cell	4th Unit Cell	5th Unit Cell	Contributions of the remaining cells	Total	Total considering the constant of integration
$\mathcal{E}'_{12}(\mp 2)$	----	+0,010i	-0.035i	+0.087i	-0.330i	-1.237i	-0.550i	+0.072i	-0.039i	+0.016i	+0.005i	-2.001i	$-20.01\times10^{-3}i$
$\mathcal{E}'_{13}(\mp 2)$	+0.005	+0.011	+0.013	+0.053	+0.022	-0.612	+0.378	+0.025	+0.021	+0.0075	+0.024	-0.103	-1.03×10^{-3}
$\mathcal{E}'_{14}(\mp 2)$	----	------	+0.002i	-0.020i	-0.174i	0.0000	-0.210i	+0.007i	+0.005i	+0.001i	nil	-0.389i	$-3.89\times10^{-3}i$
$\mathcal{E}'_{15}(\mp 2)$	+0,003	+0.003	+0.0105	+0.0085	+0.2785	-0.3993	+0.012	+0.0295	+0.0005	+0.006	nil	-0.0478	-0.478×10^{-3}

Table 6.5 Matrix elements of the perturbing potential between the Wannier functions centered at one lattice distance apart ($X_W = \mp 2$)

	$\mathcal{E}'_{1q}(\mp 4)=C\int_{all\,x} a_q^0(x \mp 4)\ V(x)\ a_1^0(x)\,dx$												
	LEFT $(x \leq 0)$					$(x \geq 0)$ RIGHT							
	5th Unit Cell	4th Unit Cell	3rd Unit Cell	2nd Unit Cell	1st Unit Cell	1st Unit Cell	2nd Unit Cell	3rd Unit Cell	4th Unit Cell	5th UUnit Cell	Contributions of the remaining cells	Total	Total considering the constant of integration
$\mathcal{E}'_{12}(\mp 4)$	-----	+0.010i	-0.037i	+0.075i	-0.533i	-1.293i	-0.310i	+0.087i	-0.033i	+0.021i	nil	-2.013i	-20.13×10^{-3}i
$\mathcal{E}'_{13}(\mp 4)$	-0.0055	-0.0065	-0.016	-0.019	-0.217	+0.297	+0.296	-0.217	-0.018	-0.016	-0.029	+0.050	$+0.50\times 10^{-3}$
$\mathcal{E}'_{14}(\mp 4)$	-----	-----	+0.006i	+0.005i	+0.179i	+0.050i	-0.211i	-0.022i	-0.002i	-0.001i	nil	+0.004i	$+0.04\times 10^{-1}$i
$\mathcal{E}'_{15}(\mp 4)$	-0.002	-0.0035	-0.004	-0.020	-0.011	+0.053	+0.053	-0.011	-0.014	-0.004			

Table 6.4 Matrix elements of the perturbing potential between the Wannier functions centered at two lattice distance apart ($X_W = \mp 4$)

6.4 CALCULATION OF THE COEFFICIENTS $C_q(X_p)$'s

In the previous pages we have obtained the necessary information (the matrix elements of the perturbing potential, etc.) for calculating the coefficients $C_q(X_p)$'s.

Now using equation 1 and the arguments given in section 5.3 we can write at once;

I) for q = 2,4,6,8,....etc.

5

$$C_q(0)[\varepsilon_1^0(0)-\varepsilon_q^0(0)]+C_q(+2)[\varepsilon_1^0(-2)-\varepsilon_q^0(-2)-(\varepsilon_1^0(+2)-\varepsilon_q^0(+2))]$$
$$+C_q(+4)[\varepsilon_1^0(-4)-\varepsilon_q^0(-4)-(\varepsilon_1^0(+4)-\varepsilon_q^0(+4))|+\ldots=\varepsilon'_{1q}(0)$$

$$C_q(0)[\varepsilon_1^0(+2)-\varepsilon_q^0(+2)]+C_q(+2)[\varepsilon_1^0(0)-\varepsilon_q^0(0)-(\varepsilon_1^0(+4)-\varepsilon_q^0(+4))]$$
$$+C_q(+4)[\varepsilon_1^0(-2)-\varepsilon_q^0(-2)-(\varepsilon_1^0(+6)-\varepsilon_q^0(+6))]+\ldots\ldots\ldots=\varepsilon'_{1q}(+2$$

$$C_q(0)[\varepsilon_1^0(+4)-\varepsilon_q^0(+4)]+C_q(+2)[\varepsilon_1^0(+2)-\varepsilon_q^0(+2)-(\varepsilon_1^0(+6)-\varepsilon_q^0(+6))]$$
$$+C_q(+4)[\varepsilon_1^0(0)-\varepsilon_q^0(0)-(\varepsilon_1^0(+8)-\varepsilon_q^0(+8))]+\ldots\ldots\ldots\ldots\ldots=\varepsilon'_{1q}(+$$

2) for q = 3,5,7,....etc.

6

$$C_q(0)[\varepsilon_1^0(0)-\varepsilon_q^0(0)]+C_q(+2)[\varepsilon_1^0(-2)-\varepsilon_q^0(-2)+\varepsilon_1^0(+2)-\varepsilon_q^0(+2)]$$
$$+C_q(+4)[\varepsilon_1^0(-4)-\varepsilon_q^0(-4)+\varepsilon_1^0(+4)-\varepsilon_q^0(+4)]+\ldots\ldots=\varepsilon'_{1q}(0)$$

$$C_q(0)[\varepsilon_1^0(+2)-\varepsilon_q^0(+2)]+C_q(+2)[\varepsilon_1^0(0)-\varepsilon_q^0(0)+\varepsilon_1^0(+4)-\varepsilon_q^0(+4)]$$
$$+C_q(+4)[\varepsilon_1^0(-2)-\varepsilon_q^0(-2)+\varepsilon_1^0(+6)-\varepsilon_q^0(+6)]+\ldots\ldots\ldots=\varepsilon'_{1q}(+2)$$

$$C_q(0)[\varepsilon_1^0(+4)-\varepsilon_q^0(+4)]+C\ (+2)[\varepsilon_1^0(+2)-\varepsilon_q^0(+2)+\varepsilon_1^0(+6)-\varepsilon_q^0(+6)]$$
$$+C_q(+4)[\varepsilon_1^0(0)-\varepsilon_q^0(0)+\varepsilon_1^0(+8)-\varepsilon_q^0(+8)]+\ldots\ldots\ldots=\varepsilon'_{1q}(+4$$

Now we will start by determining these coefficients. The precision of the solutions for $C_q(X_p)$'s will normally depend on the number of the terms (on the dimensions of the coefficient matrices) that one considers in equations 5 and 6

For the present purposes we found it sufficient enough to deal with 3X3 matrices . Actually it has been observed that (i.e. see tables 6.3 , 6.4 , and 6.5) the coefficients $C_q(X_p)$'s converges rapidly to zero for only few higher values of q or X_p as claimed in chapter 5 , therefore to consider even larger matrices than what we intend to use does not alter the present results by any appreciable amount.

Now using the above arguments and the tables given in the previous pages the sets of equations 5 and 6 can be written in the following matrix forms.

i) for q =2

$$\begin{vmatrix} -0.5\pi^2 & 0 & 0 \\ -2.0 & -0.5\pi^2 & -16/9 \\ 0 & -16/9 & -0.5\pi^2 \end{vmatrix} \begin{vmatrix} C_2(0) \\ C_2(+2) \\ C_2(+4) \end{vmatrix} = \begin{vmatrix} 0 \\ -20.1\times 10^{-3}i \\ -20.13\times 10^{-3}i \end{vmatrix} \tag{7}$$

ii) for q =3

$$\begin{vmatrix} -1.5\pi^2 & +4.00 & 0 \\ +2.0 & -1.5\pi^2 & +20/9 \\ 0 & +20/9 & -1.5\pi^2 \end{vmatrix} \begin{vmatrix} C_3(0) \\ C_3(+2) \\ C_3(+4) \end{vmatrix} = \begin{vmatrix} -31.12\times 10^{-3} \\ -1.03\times 10^{-3} \\ +0.50\times 10^{-3} \end{vmatrix} \tag{8}$$

iii) for q =4

$$\begin{vmatrix} -3.0\pi^2 & 0 & 0 \\ -4.00 & -3.0\pi^2 & -32/9 \\ 0 & -32/9 & -3.0\pi^2 \end{vmatrix} \begin{vmatrix} C_4(0) \\ C\ (+2) \\ C\ (+4) \end{vmatrix} = \begin{vmatrix} 0 \\ -3.89\times 10^{-3}i \\ +0.04\times 10^{-3}i \end{vmatrix} \tag{9}$$

Solving the last three equations for the (nine) unknown coefficients and obtaining the remaining ones (those associated with negative lattice vectors) through the arguments given in section 5.3 we have set up the following table.

The coefficients (weights) to be associated with each unperturbed Wannier function (from which the perturbed Wannier function is constructed) are shown.

X_p q	-4.0	-2.0	0	+2.0	+4.0
1	-	-	1.0	-	-
2	$+3.0\times10^{-3}i$	$-3.0\times10^{-3}i$	0	$+3.0\times10^{-3}i$	$-3.0\times10^{-3}i$
3	$+0.022\times10^{-3}$	$+0.372\times10^{-3}$	$+2.2\times10^{-3}$	$+0.372\times10^{-3}$	$+0.022\times10^{-3}$
4	$+0.018\times10^{-3}i$	$-0.134\times10^{-3}i$	0	$+0.134\times10^{-3}i$	$-0.018\times10^{-3}i$

Table 6.6 The calculated values of $C_q(X_p)$'s .

6.5 THE PERTURBED WANNIER FUNCTION

Using the coefficients in table 6.6 the perturbed Wannier function for the lowest band is now given by,

$$\begin{aligned} a_1^p(x) = {} & a_1(x) + 3.0\times10^{-3}i(a_2^o(x+2) - a_2^o(x-2)) + 3.0\times10^{-3}i(a_2^o(x-4) - a_2^o(x+4)) \\ & + 2.2\times10^{-3}a_3(x) + 0.372\times10^{-3}(a_3(x-2) + a_3(x+2)) + 0.022\times10^{-3}(a_3(x-4) + a_3(x+4)) \\ & + 0.134\times10^{-3}i(a_4(x+2) - a_4(x-2)) + 0.018\times10^{-3}(a_4(x-4) - a_4(x+4)) \end{aligned} \tag{10}$$

In the last equation the calculated values of $C_q(X_p)$'s provided us with the combinations $a_q^o(x-X_p) - a_q^o(x+X_p)$ for the bands

(q = 2,4,6,8,.... etc.) with antisymmetric Wannier functions and $a_q^o(x-X_p) + a_q^o(x+X_p)$'s for the bands (q = 1,3,5,7,..etc.) with symmetric Wannier functions which are all even functions of x. This final point fulfils the requirement that the perturbed ground band Wannier function for this problem should be symmetric about x=0 .

Some of the expansion coefficients that we have used on the right hand side of equation 10 are pure imaginary ,how ever this creates no problem since the unperturbed Wannier functions associated with these coefficients are also pure imaginary(see Tables 6.4 and 6.5). Hence the perturbed Wannier function obtained through equation 10 is real, as it should be expected to be so for the lowest band.

Also, due to the signs of the calculated $C_q(X_p)$'s ,the combinations of the Wannier functions, used in expanding the perturbed Wannier function (see equation 10),are such as to reduce the spread of the (original) free electron Wannier function.[1] The situation has been illustrated in figure 6.1.

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1) This point is in agreement with the fact that the N.F.E. Wannier function is (in general) more localized (in other terms has less mean square spread) than the free electron Wannier function (see, chapters 7 and 8)

6.6 COMPARISON WITH THE EXACT WANNIER FUNCTION

Below we compare the Wannier function that we have calculated with the exact Wannier function.[2]

x	F.E. Wan. Func.	Wan.Func.for a weakly bound elec. (EXACT W.F.)	(BY PERTURBATION)
0.00	0.70710	0.71299	0.71209
0.10	0.70410	0.70987	0.70831
0.20	0.69542	0.70075	0.69912
0.30	0.68112	0.68440	0.68402
0.40	0.66138	0.66187	0.66332
0.50	0.63651	0.63354	0.63743
0.60	0.60686	0.60680	0.60682
0.80	0.53504	0.53227	0.53357
1.00	0.45003	0.44208	0.44799
1.20	0.35664	0.34770	0.35466
1.40	0.26001	0.25110	0.25830
1.60	0.16525	0.15498	0.16369
2.00	0.00000	-0.01903	-0.00380

Table 6.7 Free and nearly free electron Wannier functions (both functions are normalized).

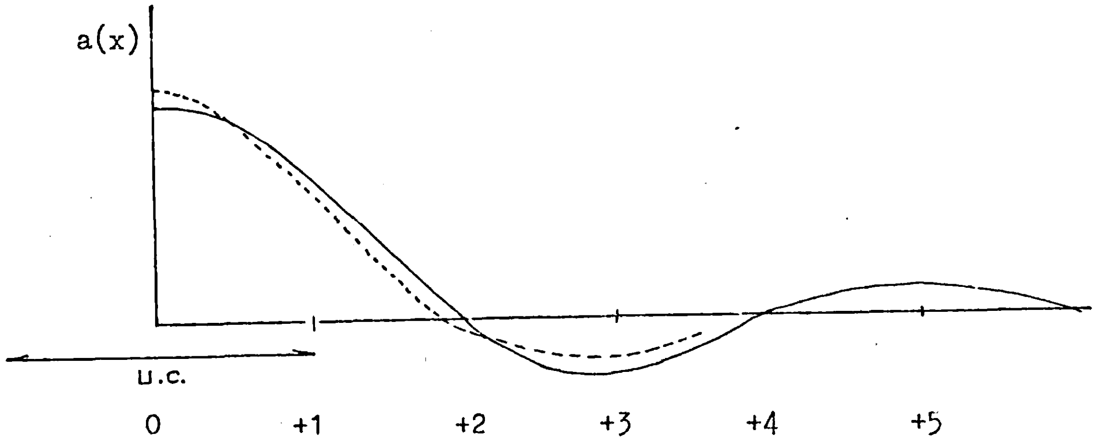

Fig.6.1 [——] Free electron Wannier function

[......] Nearly free electron Wannier function (not to the scale).

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2) The considerations for obtaining the exact (N.F.E.) Wannier (cont.)

6.7 DISCUSSION OF THE RESULTS

The N.F.E. Wannier functions that we have calculated (using two different methods being exact and approximate) deviate from the free electron ones in a similar way. The agreement is particularly good within the central unit cell where the Wannier function is localized. This is due to the fact that the terms $C_1(X_p)a_1^o(x-X_p)$'s associated with the(only) undetermined coefficients $C_1(X_p)$, $X_p \neq 0$ in the series 4 have zero effect in the vicinity of the origin (in central cell) since $a_1(x-X_p)=0$ for $x=0$. The agreement is comparatively not so good, i.e. within the second cell for the reasons outlined above. However, in a problem where the Wannier functions do not spread out so far (unlike the present case of free electrons) this would not be the case (see section 5.2). The latter case would also simplify the present calculations.

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cont.2) function are similiar to those given in chapter 9. However, the present case is comparatively more complicated for; in obtaining the ground band Wannier function the total integration (of the wave functions over the B.Z. concerned) had to be carried out as two partial integrations, one over the states with corresponding eigenvalues less than the applied potential and one over the states with corresponding eigenvalues larger than the applied potential. Also we had to carry out the calculations and the computational works with a much higher precision than the previous cases, since both the applied potential and the deviation of the perturbed Wannier function from that of the free electron were very small.

It has also been observed that the second order corrections would considerably improve the present results (especially those at points outside the central unit cell)

CHAPTER 7

MISCELLANEOUS PROPERTIES OF WANNIER FUNCTIONS

In the first chapter we have given the basic properties of Wannier functions such as orthogonality, localizations, etc. Most of these properties arise from the basic definition of the functions themselves and hold true regardless of any restrictive condition, i.e. type of crystal symmetry etc.

However, bringing in some restrictive conditions such as assuming that the crystal under consideration has inversional symmetry etc, forces Wannier functions to have some particular shapes and properties. In the following sections we will be particularly interested in the shapes and properties of Wannier functions for a crystal field with inversional symmetry. In handling each problem the particular conditions assumed will be mentioned in detail.

Most of these properties were studied in detail by Kohn[1] in a remarkable article. However the proofs given by Kohn[1] are based upon one dimensional arguments and can not be so easily generalized to three dimensions. (also see Weinreich[2] and des Cloizeaux[2A] and Blount[2B])

Most of the proofs that are given in this chapter are rewritten and sometimes use completely different approaches and methods (i.e case of exponential fall-off of Wannier functions in three dimensions). Further all proofs that are given are generalized to three dimensions.

In the last section a small contribution has been made to Kohn's one dimensional argument and it has been shown that for weakly bound electrons the exponential decay of the Wannier functions can be expressed through the Fourier coeffcients of the perturbing potential.

1) Kohn, W., Phys. Rev. 115, 809 (1959)

2) Weinreich, G., Solids, Elementary Theory for Advanced Students, pp. 127., Wiley, New York, 1965.

7.1 REALITY OF WANNIER FUNCTIONS

Consider the following one electron (time independent) Schrödinger equation which is a second order, linear ,

$$H(\underline{r})\,\Psi_{n\underline{k}}(\underline{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})\right]\Psi_{n\underline{k}}(\underline{r}) = E_n(\underline{k})\,\Psi_{n\underline{k}}(\underline{r}) \qquad 7.1.$$

homogenous, differential equation with a real operator and real parameters (eigenvalues). Now , by writing its solutions in Bloch wave forms, substituting them into the equation, taking it's complex conjugate, and comparing the outcoming form with that of equation 7.1.1 where wave vector $\underline{k}$ is replaced by $-\underline{k}$, one can easily verify that*

$$E(-\underline{k}) = E(\underline{k}) \qquad 7.1.2\ *$$

$$U_{-\underline{k}}(\underline{r}) = C\,U^{*}_{\underline{k}}(\underline{r}) \qquad 7.1.3$$

where $U_{\underline{k}}(\underline{r})$ is the periodic part of the Bloch wave and C is a constant with modulus one .

Equation 7.1.3 may alternatively be written (by multiplying both sides of equation by exp($-i\underline{k}\cdot\underline{r}$)) as follows

$$\Psi_{-\underline{k}}(\underline{r}) = C\,\Psi^{*}_{\underline{k}}(\underline{r}) \qquad 7.1.4$$

Now assume that the constant C in expressions 7.1.3 and 7.1.4 is adjusted to be unity then instead these expressions we will have

$$U_{-\underline{k}}(\underline{r}) = U^{*}_{\underline{k}}(\underline{r}) \qquad 7.1.5$$

$$\Psi_{-\underline{k}}(\underline{r}) = \Psi^{*}_{\underline{k}}(\underline{r}) \qquad 7.1.6$$

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*)This condition is known as time reversal symmetry and it follows whether the point group contains inversion or not , in other terms it holds true immaterial of the crystal symmetry.

The Wannier function for the n^{th} band which is centered at the origin ($\underline{R}$=0) is defined as follows

$$a_n(\underline{r}) = \sum_{\underline{k}} \psi_{n\underline{k}}(\underline{r}) \qquad 7.1.7$$

where the sum is over all possible $\underline{k}$ vectors in the n^{th} B.Z.

Now let us divide the B.Z. concerned into two subregions where one contains vectors of the sort $+\underline{k}$ only and the other contains vectors of the sort $-\underline{k}$ only then equation 7.1.7 may be rewritten as

$$a_n(\underline{r}) = \underset{\substack{(\text{over } +\underline{k} \text{ vectors} \\ \text{of } n^{th} \text{ zone only})}}{\sum_{+\underline{k}} \psi_{n\underline{k}}(\underline{r})} + \underset{\substack{(\text{over } -\underline{k} \text{ vectors} \\ \text{of } n^{th} \text{ zone only})}}{\sum_{-\underline{k}} \psi_{n\underline{k}}(\underline{r})} \qquad 7.1.8$$

Now we will impose one more condition; that the B.Z. under consideration has inversional symetry for $\underline{k}$. Therefore to every vector $+\underline{k}$ there corresponds a vector with opposite sign (i.e. $-\underline{k}$) .

Hence , the equation 7.1.8 can be rewritten as

$$a_n(\underline{r}) = \sum_{+\underline{k}} \left(\psi_{n\underline{k}}(\underline{r}) + \psi_{n\,-\underline{k}}(\underline{r}) \right) \qquad 7.1.9$$

Now considering expression 7.1.6 which states that

$$\psi_{-\underline{k},n}(\underline{r}) = \psi^{*}_{n\underline{k}}(\underline{r}) \qquad 7.1.10$$

and substituting it into equation 7.1.9 , we have

2A) des Cloizeaux, J. Phys. Rev. 135 , A698(1964)

2B) Blount, E. I., Solid state physics 13 , 305 (1962)

$$a_n(\underline{r}) = \sum_{+\underline{k}} \left(\psi_{n\underline{k}}(\underline{r}) + \psi^*_{n\underline{k}}(\underline{r})\right) = 2\sum_{+\underline{k}} \mathrm{Re}\,\psi_{n\underline{k}}(\underline{r}) \qquad 7.1.11$$

where the right hand side of equation is a real function of $\underline{r}$.

In general the Bloch wave being a complex function can be seperated into its real and imaginary parts .

i.e.

$$\psi_{n\underline{k}}(\underline{r}) = g_n(\underline{k},\underline{r}) + i f_n(\underline{k},\underline{r}) \qquad 7.1.12$$

then, the Wannier function related is given by the following expression

$$a_n(\underline{r}) = \sum_{+\underline{k}} 2\, g_n(\underline{k},\underline{r}) = \text{real}$$

Note that if the constant C in expressions 7.1.3 and 7.1.4 is adjusted to be -1 then the outcoming Wannier function is pure imaginary.

7.2 SYMMETRY AND ANTISYMMETRY OF WANNIER FUNCTIONS

In addition to the above considerations if the crystal has an inversional symetry,

i.e.

$$V(\underline{r}) = V(-\underline{r}) \qquad 7.2.1$$

then similarly one can verify the following

$$U^*_{\underline{k}}(-\underline{r}) = C'\, U_{\underline{k}}(+\underline{r}) \qquad 7.2.2$$

$$\psi^*_{\underline{k}}(-\underline{r}) = C'\, \psi_{\underline{k}}(+\underline{r}) \qquad 7.2.3$$

Again assuming that C' is adjusted to be unity, then we have

$$U^*_{\underline{k}}(-\underline{r}) = U_{\underline{k}}(+\underline{r}) \qquad 7.2.4$$

and

$$\psi^*_{\underline{k}}(-\underline{r}) = \psi_{\underline{k}}(+\underline{r}) \qquad 7.2.5$$

Now referring to the previous arguments and satisfying the condition that the B.Z. under consideration has inversional symetry , then

$$a_n(-\underline{r}) = \sum_{+\underline{k}} \left(\psi_{n\underline{k}}(-\underline{r}) + \psi_{-\underline{k},n}(-\underline{r})\right) \qquad 7.2.6$$

$$= \sum_{+\underline{k}} \left(\psi_{n\underline{k}}(-\underline{r}) + \psi^*_{n\underline{k}}(-\underline{r})\right) \qquad 7.2.7$$

By taking complex conjugates of both sides equation 7.2.5 can be written as follows

$$\psi_{n\underline{k}}(-\underline{r}) = \psi^*_{n\underline{k}}(+\underline{r}) \qquad 7.2.8$$

Substituting equations 7.2.5 and 7.2.8 into equation 7.2.7, we get

$$a_n(-\underline{r}) = \sum_{+\underline{k}} \left(\psi^*_{n\underline{k}}(+\underline{r}) + \psi_{n\underline{k}}(+\underline{r})\right) \qquad 7.2.9$$

$$= \sum 2\,\mathrm{Re}\,\psi_{n\underline{k}}(+\underline{r}) = a_n(+\underline{r}) \qquad 7.2.10$$

or simply

$$a_n(-\underline{r}) = a_n(+\underline{r}) \qquad 7.2.11$$

which means that the resulting Wannier function is symmetric (and real).

However if C is taken to be -1 in equations 7.1.3 and 7.1.4 then instead of equation 7.1.6 we have

$$\psi_{-\underline{k}}(\underline{r}) = -\psi_{\underline{k}}^{*}(\underline{r}) \qquad 7.2.12$$

also

$$\psi_{\underline{k}}(-r) = \psi_{\underline{k}}^{*}(r) \qquad 7.2.13$$

using the last two identities, equation 7.2.6 is then given by,

$$\begin{aligned} a(-r) &= \sum_{+\underline{k}} \left(\psi_{\underline{k}}(-\underline{r}) + \psi_{-\underline{k}}(-\underline{r})\right) \\ &= \sum_{+\underline{k}} \left(\psi_{\underline{k}}(-\underline{r}) - \psi_{\underline{k}}^{*}(-\underline{r})\right) \qquad 7.2.14 \\ &= \sum_{+\underline{k}} \left(\psi_{\underline{k}}^{*}(\underline{r}) - \psi_{\underline{k}}(\underline{r})\right) \\ &= -2\sum_{+\underline{k}} \operatorname{Im} \psi_{\underline{k}}(\underline{r}) \end{aligned}$$

or simply

$$a(-\underline{r}) = -a(\underline{r}) \qquad 7.2.15$$

Therefore, the resulting Wannier function is antisymmetric (and pure imaginary).

7.3 EXPONENTIAL FALL OFF OF WANNIER FUNCTIONS IN THREE DIMENSIONS

Below we will give an original approach to the problem by employing momentum eigenfunctions. The usefulness of this treatment is that , first it generalizes the problem into three dimensions and secondly it allows qualitative discussion of the behaviour of the Wannier functions at large distances from the point at which they are centered.

The Wannier function for an arbitrary band is given by[3]

$$a(\underline{r}) = \Omega_B^{-1/2} \int_{\text{all } \underline{k}} \nu(\underline{k})\, e^{i\underline{k}\cdot\underline{r}}\, d^3k \qquad 7.3.1$$

Multiplying both sides of equation 7.3.1 by an arbitrary power of $\underline{r}$ say $\underline{r}^n$ we get

$$\underline{r}^n a(\underline{r}) = \Omega_B^{-1/2} \int_{\text{all } \underline{k}} \nu(\underline{k})\, r^n\, e^{i\underline{k}\cdot\underline{r}}\, d^3k \qquad 7.3.2$$

$$= (i)^{-n}\, \Omega_B^{-1/2} \int \nu(\underline{k})\, \nabla_k^n\, e^{i\underline{k}\cdot\underline{r}}\, d^3k \qquad 7.3.3$$

In general we can write the following;

$$\nabla_k^n\left(\nu(\underline{k})e^{i\underline{k}\cdot\underline{r}}\right) = \nu(\underline{k})\,\nabla_k^n e^{i\underline{k}\cdot\underline{r}} + \binom{n}{1}\nabla_k\nu(\underline{k})\,\nabla_k^{n-1}e^{i\underline{k}\cdot\underline{r}} + \binom{n}{2}\nabla_k^2\nu(\underline{k})\nabla_k^{n-2}e^{i\underline{k}\cdot} \qquad 7.3.4$$

$$\cdots + \binom{n}{p}\nabla_k^p\,\nu(\underline{k})\,\nabla_k^{n-p}e^{i\underline{k}\cdot\underline{r}} + \cdot\ \cdot\ \cdot\ \cdot\ \cdot + e^{i\underline{k}\cdot\underline{r}}\,\nabla_k^n\,\nu(\underline{k})$$

Intermediate terms on the right hand side of equation 7.3.4 (those with binomial coefficients $\binom{n}{1}$ $\binom{n}{2}$, etc.) may be written as

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3) See, chapter 2.

$$\nabla_k \nu(\underline{k}) \nabla_k^{n-1} e^{i\underline{k}\cdot\underline{r}} = \nabla_k \left(\nu(\underline{k}) \nabla_k^{n-1} e^{i\underline{k}\cdot\underline{r}}\right) - \nu(\underline{k}) \nabla_k^{n} e^{i\underline{k}\cdot\underline{r}}$$

$$\nabla_k^{2} \nu(\underline{k}) \nabla_k^{n-2} e^{i\underline{k}\cdot\underline{r}} = \nabla_k \left(\nabla_k \nu(\underline{k}) \nabla_k^{n-2} e^{i\underline{k}\cdot\underline{r}}\right) - \nabla_k \left(\nu(\underline{k}) \nabla_k^{n-1} e^{i\underline{k}\cdot\underline{r}}\right)$$

$$\nabla_k^{3} \nu(\underline{k}) \nabla_k^{n-3} e^{i\underline{k}\cdot\underline{r}} = \ldots \text{ etc.} \qquad + \nu(\underline{k}) \nabla_k^{n} e^{i\underline{k}\cdot\underline{r}}$$

$$\text{etc} \ldots\ldots\ldots \qquad 7.3.5$$

Now using equations 7.3.4 and 7.3.5 we can write the following[4]

$$\nu(\underline{k}) \nabla_k^{n} e^{i\underline{k}\cdot\underline{r}} = - e^{i\underline{k}\cdot\underline{r}} \nabla_k^{n} \nu(\underline{k}) + \nabla_k^{n}\left(\nu(\underline{k}) e^{i\underline{k}\cdot\underline{r}}\right)$$

$$- a_1 \nabla_k \left(\nu(\underline{k}) \nabla_k^{n-1} e^{i\underline{k}\cdot\underline{r}}\right) - a_2 \nabla_k \left(\nabla_k \nu(\underline{k}) \nabla_k^{n-2} e^{i\underline{k}\cdot\underline{r}}\right) - a_3 \nabla_k (\ldots)$$

$$\ldots\ldots\ldots \text{ etc.} \qquad 7.3.6$$

Converting the volume integral given by 7.3.3 to a surface integral with radius $\underline{k} = \infty$ and assuming that

$$\lim_{\underline{k} \to \infty} \nu(\underline{k}) = 0 \qquad 7.3.7$$

integrals of all the terms on the right hand side of equation 7.3.6 vanish except the first one. Therefore we have

$$\underline{r}^{n} a(\underline{r}) = -(i)^{n} \Omega_B^{-1/2} \int_{\text{all } \underline{k}} e^{i\underline{k}\cdot\underline{r}} \nabla_k^{n} \nu(\underline{k}) d^3k \qquad 7.3.8$$

Now let us define a function $g(\underline{r})$ as follows

$$g(\underline{r}) = \underline{r}^{n} a(\underline{r}) = -(i)^{n} \Omega_B^{-1/2} \int e^{i\underline{k}\cdot\underline{r}} \nabla_k^{n} \nu(\underline{k}) d^3k \qquad 7.3.9$$

then,

$$g^{*}(\underline{r}) = -(-i)^{n} \Omega_B^{-1/2} \int_{\text{all } \underline{k}} e^{-i\underline{k}\cdot\underline{r}} \nabla_k^{n} \nu^{*}(\underline{k}) d^3k \qquad 7.3.10$$

4) In equation 7.3.6 we have not bothered to write down the magnitudes of the outcoming coefficients a_1, a_2, a_3, etc. since volume integrals of all these terms will vanish, as explained in the later paragraphs.

therefore

$$\int g(\underline{r})\, g^*(\underline{r})\, d^3r = (-1)^{2n}\, \Omega_B^{-1} \iiint e^{i\underline{r}.(\underline{k}-\underline{k}')} \nabla_k^n \nu(\underline{k})\, \nabla_k^n \nu^*(\underline{k}')\, d^3k\, d^3k'\, d^3 \qquad 7.3.11$$

$$= \Omega_B^{-1}\, \Omega_B \iiint \delta(\underline{k}-\underline{k}')\, \nabla_k^n \nu(\underline{k})\, \nabla_k^n \nu^*(\underline{k}')\, d^3k'\, d^3k\, d^3r$$

or

$$\int_{\text{all } \underline{r}} |g(\underline{r})|^2 d^3r = \int_{\text{all } \underline{r}} \underline{r}^{2n}\, |a(\underline{r})|^2 d^3r = \int_{\text{all } \underline{k}} |\nabla_k^n\, \nu(\underline{k})|^2\, d^3k \qquad 7.3.12$$

Provided that the function $\nabla_k^n\, \nu(\underline{k})$ may be normalized (this means that the right hand side of the equation 7.3.12 is finite) so may the function $g(\underline{r})$.

That means

$$\lim_{\underline{r} \dashrightarrow \infty} g(\underline{r}) = 0 \qquad 7.3.13$$

or recalling

$$g(\underline{r}) = \underline{r}^n\, a(\underline{r}) \qquad 7.3.14$$

therefore

$$\lim_{\underline{r} \dashrightarrow \infty} \underline{r}^n\, a(\underline{r}) = 0 \qquad 7.3.15$$

which means that the Wannier functions fall off faster than any finite power of position vector $\underline{r}$, hence they fall off exponentially at large $\underline{r}$.

7.4 DISCUSSION OF THE ASYMPTOTIC BEHAVIOR

For free electrons momentum eigenfunctions are stepwise functions and are not differentiable everywhere and the integral on the right hand side of equation 7.3.12can easily shown to be divergent.

Hence,

$$\lim_{\underline{r} \to \infty} (\underline{r}^n \, a(\underline{r})) = \infty \qquad 7.4.1$$

therefore the free electron Wannier functions do not fall off exponentially.

However if any small perturbing potential is applied to these free electrons (and provided that the band in concern is non-degenerate) then the momentum eigenfunctions become differentiable(i.e. n times) everywhere and the integral given by equation becomes a proper integral and attains a finite value , therefore

$$\lim_{\underline{r} \to \infty} (\underline{r}^n \, a(\underline{r})) = 0 \qquad 7.4.2$$

which implies that , any small field applied to the free electron Wannier functions (which fall off as r^{-1}) make them fall off exponentially. The above argument is valid for a potential of any magnitude (non zero).

The case of a Wannier function for a degenerate band is however more complicated[5] since degeneracy generally implies discontinuity in $\nu n(\underline{k})$ as a function of $\underline{k}$,and each particular case has to be treated separately.

In the following sections we shall try to say something about the rate of exponential decay.

5) Lix, B. Phys. Status Solidi (Germany) Vol. 44, No 1, p.411-24 (1971)

7.5 RATE OF EXPONENTIAL DECAY OF WANNIER FUNCTIONS IN THREE DIMENSIONS

Below we suggest an approach to this problem in 3 dim.[6] To determine the rate of exponential decay of Wannier functions in three dimensions consider the average value of exp($\underline{h}_n\cdot\underline{r}$) (where h_n is a constant vector in $\underline{k}$ space related to the n^{th} band in a particular way) with respect to the Wannier function of the n^{th} band .

Then ,

$$\langle e^{\underline{h}_n\cdot\underline{r}} \rangle = \int_{\text{all } \underline{r}} a_n^*(\underline{r})\, e^{\underline{h}_n\cdot\underline{r}}\, a_n(\underline{r})\, d^3r \qquad 7.5.1$$

where

$$a_n(\underline{r}) = \int_{\text{all } \underline{k}} \nu_n(\underline{k})\, e^{i\underline{k}\cdot\underline{r}}\, d^3k \qquad 7.5.2$$

therefore

$$\langle e^{\underline{h}_n\cdot\underline{r}} \rangle = \iiint \nu_n^*(\underline{k})\, e^{-i\underline{k}\cdot\underline{r}}\, e^{\underline{h}_n\cdot\underline{r}}\, \nu_n(k')\, e^{i\underline{k}'\cdot\underline{r}}\, d^3k\, d^3k'\, d^3r$$

$$= \iiint \nu_n^*(\underline{k})\, \nu_n(\underline{k}')\, e^{i\underline{r}\cdot(\underline{k}'-\underline{k}-i\underline{h}_n)}\, d^3k\, d^3k'\, d^3r \qquad 7.5.3$$

$$\int e^{i\underline{r}\cdot(\underline{k}'-\underline{k}-i\underline{h}_n)}\, d^3r = \delta(\underline{k}'-\underline{k}-i\underline{h}_n) \qquad 7.5.4$$

$$\langle e^{\underline{h}_n\cdot\underline{r}} \rangle = \iint \nu_n^*(\underline{k})\, \nu_n(\underline{k}')\, \delta(\underline{k}'-\underline{k}-i\underline{h}_n)\, d^3k\, d^3k' \qquad 7.5.5$$

$$\therefore \quad \langle e^{\underline{h}_n\cdot\underline{r}} \rangle = \int_{\text{all } \underline{k}} \nu_n^*(\underline{k})\, \nu_n(\underline{k}+i\underline{h}_n)\, d^3k \qquad 7.5.6$$

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[6] It is not necessary to consider the constants of integrations for the proof given in this section, therefore all numerical constants of the integrations have been ignored.

This shows that

$$\int_{\text{all } \underline{r}} |a_n(\underline{r})|^2 e^{\underline{h}_n\cdot\underline{r}}\, d^3r = \int_{\text{all } \underline{k}} \nu_n^*(\underline{k})\, \nu_n(\underline{k}+i\underline{h}_n)\, d^3k \qquad 7.5.7$$

Now if we assume that $\nu_n(k)$ (the momentum eigenfunction for the n^{th} band) treated as a function of the complex variable k can be extended into the complex space as far as $i\underline{\sigma}_n$, then the integral

$$\int_{\text{all } \underline{k}} \nu_n^*(\underline{k})\, \nu_n(\underline{k}+i\underline{h}_n)\, d^3k \qquad 7.5.8$$

is convergent if $\underline{h}_n$ is less than the radius of convergence of the power series expansion of $\nu_n(k)$ in the complex $\underline{k}$ space .

Hence

$$\int_{\text{all } \underline{r}} |a_n(\underline{r})|^2 e^{h_n\cdot\underline{r}}\, d^3\underline{r} \longrightarrow \text{Finite} \qquad 7.5.9$$

which means that Wannier functions fall off exponentially at least as $e^{-\frac{\underline{h}_n}{2}\cdot\underline{r}}$ From the arguments above we can come to the following important conclusions;

1) Any small potential applied to free electrons by producing forbidden energy gaps extends the wave functions or momentum eigenfunctions (also see sections 7.6 and7.7)into the complex $\underline{k}$ space as far as $i\underline{\sigma}_n$ where n refers to the index of the particular band under consideration. Therefore as proved above the Wannier functions fall off exponentially at least as $e^{-\frac{\underline{h}_n}{2}\cdot\underline{r}}$ where we have, $\frac{\underline{h}_n}{2} \leq \frac{\sigma_n}{2}$

2) The maximum possible rate of fall off of Wannier functions is therefore given by $e^{-\frac{\sigma_n}{2}\underline{r}}$ where this time we have, $\frac{\underline{h}_n}{2} = \frac{\sigma_n}{2}$.

Note that Wannier functions cannot fall off faster than this limiting value for if $\frac{h_n}{2} > \frac{\sigma_n}{2}$ the integral given by equation 7.5.7 is no longer convergent,

In section 7.7 we shall prove that for weakly bound electrons in the one dimensional case h_n can be expressed through the Fourier coefficients of the perturbing potential .

In general however for multi-dimensional crystals extensions into the complex $\underline{k}$ space are quite complicated and difficult to deal with , so in "chapter eight" a method will be suggested to obtain directly the Wannier functions with maximum possible rates of exponential fall off (the most localized Wannier functions) .

7.6 RATE OF EXPONENTIAL DECAY OF WANNIER FUNCTIONS IN ONE DIMENSION

Kohn[1] in a paper mentioned previously suggests that, for a one dimensional crystal under the assumptions that the bands in question are nondegenerate and the potential has a centre of inversion, the rate of exponential decay of the Wannier function of a particular band (say the n th one) can be obtained from the Kramers plot as follows;

Let

$$f(k) = \cos ka \tag{7.6.1}$$

where k is not neccessarily real, and consider some particular points in the complex k plane

i.e.

$$k_n = n\frac{\pi}{a} + i h_n \tag{7.6.2}$$

then the amplitudes of the Kramer's function at these particular points are given by

$$f(k_n) = f_n = \pm \cosh(h_n a) \qquad 7.6.3$$

therefore the h_n 's which Kohn shows to be the coefficients of the exponential decay can be obtained from the Kramer's function by the following relation

$$h_n = \frac{1}{a} \cosh^{-1}(f_n) \qquad 7.6.4$$

From the last expression it is apparent that h_n's are largest (i.e. corresponding to highest possible rate of exponential decay) at the points where f_n 's corresponds to the peaks of the function. We may also add that in order to know the h_n's we need to know the Kramer's function explicitly.

As it is apparent from expression 7.6.4 ,the higher the value of the potential , the larger will be the coefficients of exponential decay.

We have also

$$\lim_{n \to \text{Large}} h_n \longrightarrow 0 \qquad 7.6.5$$

which means that the Wannier functions for higher bands fall off more slowly than those of the lower bands and for sufficiently large values of n the Wannier functions of these higher bands resemble those for free electrons. As a particular example consider the case of free electrons, for which we have $-1 \leq f(k) \leq +1$, then it can easily be shown that , we have $h_n = 0$ for all n , which implies that no Wannier function falls off exponentially.

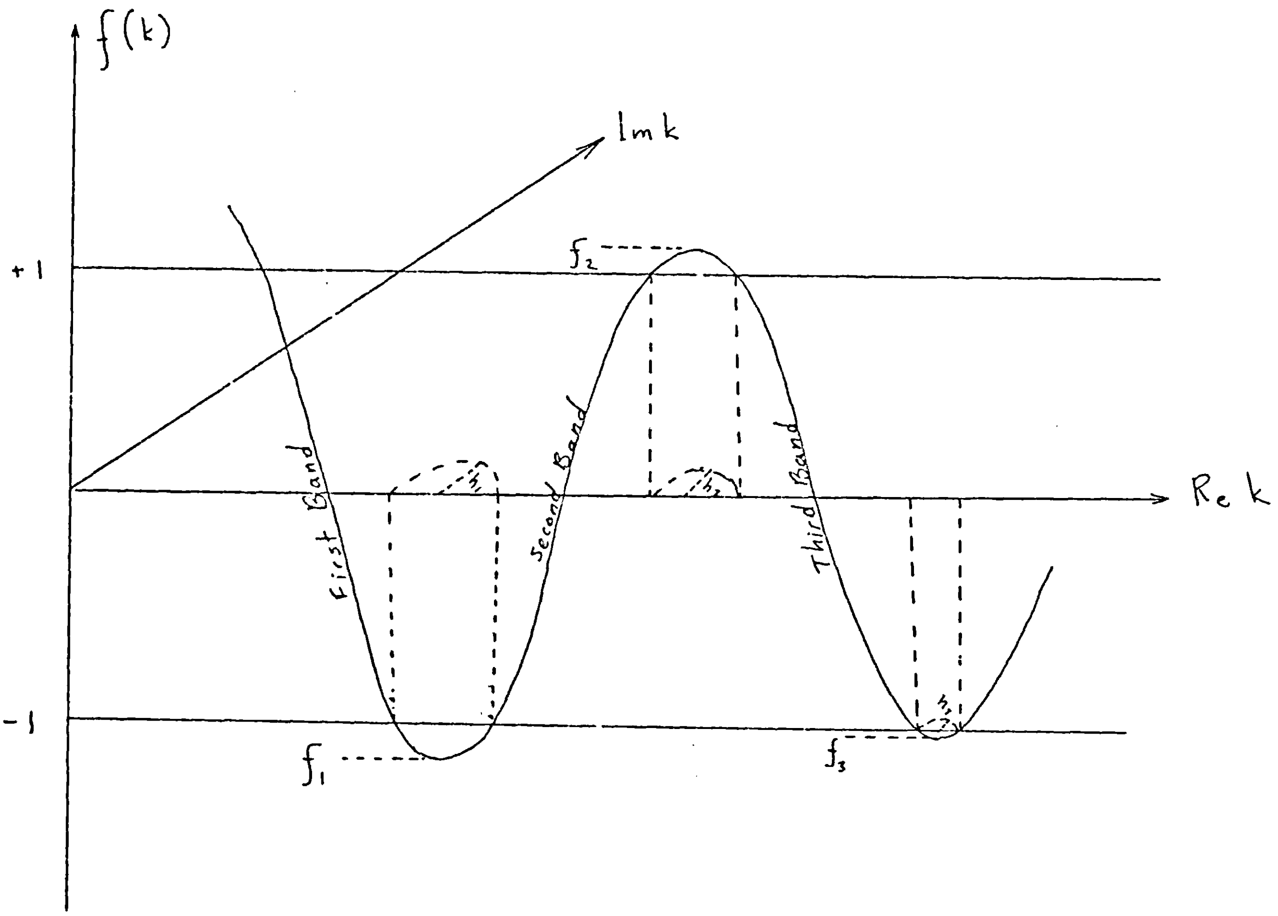


Fig. 7.6.1 $f(k)$ represented as a function of complex variable k . Note that the peaks of the function corresponds to $k = n\frac{\pi}{a} + ih_n$ and the function tends to be tangent to $f(k) = \mp 1$ axises for large n.

The allowed and forbidden regions are shown in the figure.

7.7 FOR WEAKLY BOUND ELECTRONS EXPONENTIAL DECAY IS GIVEN BY THE FOURIER COEFFICIENTS OF THE PERTURBING POTENTIAL

In this section we will prove by extending Kohn's one dimensional argument that for weakly bound electrons the exponential decay of Wannier functions is given by the fourier coefficients of the perturbing potential.

Consider the following Kramer's plot where the regions $|f(E)|>1$ correspond to forbidden values of E which are the usual energy gaps. Now;

1) As it is well known, for weakly bound electrons these gaps can be proved to be equal to twice the fourier coefficients of the perturbing potential (n^{th} gap being given by the n^{th} Fourier coefficient)

2) Further for weakly bound electrons the function f slightly exceeds $f = \mp 1$ hence has it s extrima $|f_n| = 1 + \xi_n$ where ξ_n is a small positive quantity.

3) As far as the behaviour of the function $f(E)$ is considered we have two limiting conditions, i.e.

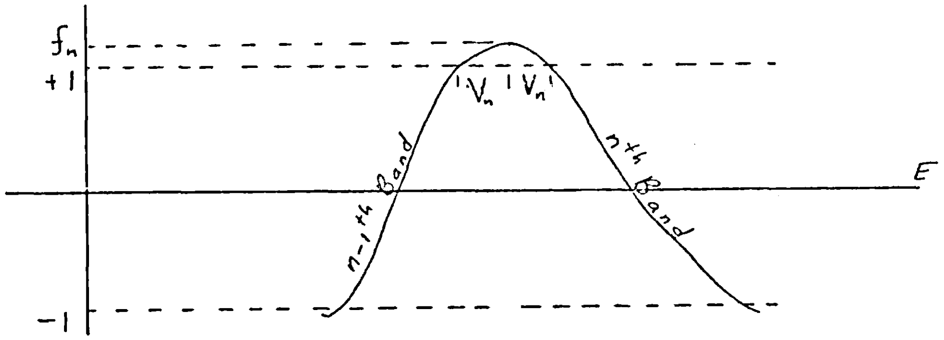
$$\lim_{E \to \text{Large}} f(E) \to \cos\sqrt{E}\, a \tag{7.7.1}$$

or

$$\lim_{V \to 0} f(E) \to \cos\sqrt{E}\, a \tag{7.7.2}$$

where V is the applied potential.

Hence, the forbidden region of energy between the $(n-1)^{th}$ and n^{th} bands is given by $2V_n$ where V_n is the n^{th} Fourier coefficient of the perturbing potential and the behaviour of the function $f(E)$ is as shown below.



Now, we can write by approximating the part of the function(see the fig. above) above $f(E) = \pm 1$ axis by that of $\cos\sqrt{E}\,a$ (This is a very admissible approximation as explained in the previous page).

$$f_n - 1 = 1 - \cos\sqrt{|V_n|}\,a \tag{7.7.3}$$

$$f_n = 2 - \cos\sqrt{|V_n|}\,a \tag{7.7.4}$$

$$= 2 - 1 + \frac{|V_n|\,a^2}{2} = 1 + \frac{|V_n|\,a^2}{2} \tag{7.7.5}$$

However by equation 7.6.3 f_n is given by

$$f_n = \cosh(a h_n) \tag{7.7.6}$$

$$\cong 1 + \frac{(a h_n)^2}{2} \tag{7.7.7}$$

Therefore from equations 7.7.5 and 7.7.7 ,

$$1 + \frac{|V_n|\,a^2}{2} = 1 + \frac{a^2 h_n^2}{2} \tag{7.7.8}$$

Hence

$$(a h_n)^2 = |V_n| \, a^2 \qquad 7.7.9$$

$$h_n = |V_n|^{1/2} \qquad 7.7.10$$

Hence, we conclude that for weakly bound electrons the coefficients of exponential decay are given by fourier coefficients of the perturbing potential, that is to say the n^{th} Wannier function for weakly bound electrons falls off as $\exp\left(-|V_n|^{1/2} \cdot x \right)$.

Note that if $V=0$ then all $V_n = 0$ (which also means $h_n=0$) which means that none of the Wannier functions fall off exponentially.

Also, since, in general for an applied potential $\lim_{n \to \infty} V_n \dashrightarrow 0$, the exponential fall off is strongest for the lower bands (n=small) and decreases (or in other terms is effective only at larger distances than the origin) as one goes to higher bands (n=large).

CHAPTER 8

ON THE CHOICE OF THE ARBITRARY PHASES

8.1 A METHOD FOR OBTAINING THE MOST LOCALIZED WANNIER FUNCTIONS IN THREE DIMENSIONS

Bloch functions which are solutions of Schrödinger equation are defined up to an arbitrary phase, that is to say if the Bloch functions $\psi_n(\underline{k}, \underline{r})$ satisfy the given Schoredinger equation then so do the functions $e^{i\phi_n(\underline{k})}\psi_n(\underline{k}, \underline{r})$.

One can get more information about the arbitrary phase $e^{i\phi_n(\underline{k})}$ by considering that this new set of functions must possess the fundamental properties of Bloch functions.

i.e. 1) The new set of functions must satisfy the usual one electron Schröedinger equation, this only tells us that the function ϕ_n must be a function of wave vector $\underline{k}$ only.

2) Bloch functions are periodic in k space, therefore, we must have

$$e^{i\phi_n(\underline{k}+\underline{K}_n)}\psi_n((\underline{k}+\underline{K}_n),r) = e^{i\phi_n(\underline{k})}\psi_n(\underline{k}, \underline{r}) \qquad 8.1$$

from which by a simple argument we can show that

$$\phi_n(\underline{k} + \underline{K}_n) = \phi_n(\underline{k}) \qquad 8.2$$

Hence $\phi_n(\underline{k})$ must also be a periodic function in the given $\underline{k}$ space

3) Bloch functions may be normalized in the $\underline{r}$ space,

i.e. $$\int_{\text{all } \underline{r}} \psi^*_n(\underline{k}\,.\,\underline{r})\,\psi_n(\underline{k}\,.\,\underline{r})\,d^3r = 1 \qquad 8.3$$

Then, in order that the new set of functions may be normalized $\phi n(\underline{k},\underline{r})$ must be a real function of $\underline{k}$.

Therefore the sets of functions $\psi n(\underline{k}, \underline{r})$ and $e^{i\phi n(\underline{k})}\psi_{n(\underline{k},\underline{r})}$ where $\phi n(\underline{k})$ is a real and periodic function of $\underline{k}$ are equally admissable sets of functions .

Hence the choice of Wannier functions which are given by the following expression

$$a_n(\underline{r} - \underline{R}_m) = \int_{B.Z} \psi n(\underline{k}, \underline{r})\, e^{-i\, \underline{k}\cdot\underline{R}_m}\, d^3k \qquad 8.4$$

is not unique but infinite because of the arbitrary phases which may be assigned to the Bloch functions . In general the shapes of the outcoming Wannier functions largely depend on the choice of these phases.

Hence the present task is to find the phases which yield the most localized Wannier functions.

Below we will suggest an exact method for finding these particular phases , using the fundamental criteria that the mean square extent of the corresponding Wannier functions must be a minumum.

Weinreich[1] suggests a method using a similiar criteria , however the method is based upon an approximation (The nature of this approximation will be mentioned in connection with equation 8.12).

Parada[2], as a special case considers some particular forms of Bloch functions (those obtained point by point by $\underline{k}\underline{p}$ approximation) and states that for this particular case the mean spread integral of

1) Weinreich, G., Solids , Elementary Theory for Advanced Students pp. 134., Wiley, New York, 1965.

2) Parada, N.J.,and Ferreira, L., Phys. Rev. B, Vol.2, 1614(1970)

Wannier functions is stationary.

In order to find a general solution to this problem, we will start by expanding the relevant Bloch functions in the reciprocal vector space.

$$\psi_n(\underline{k}\,,\,\underline{r}) = \sum_{\underline{K}_n} \nu_n(\underline{k} + \underline{K}_n)\, e^{i(\underline{k} + \underline{K}_n)\cdot\underline{r}} \qquad 8.5$$

Assigning an arbitrary phase to the Bloch function

$$e^{i\phi_n(\underline{k})}\, \psi_n(\underline{k}\,,\,\underline{r}) = \sum_{\underline{K}_n} \nu_n(\underline{k} + \underline{K}_n)\, e^{i(\underline{k} + \underline{K}_n)\underline{r}}\, e^{i\phi_n(\underline{k})} \qquad 8.6$$

As mentioned before $\phi_n(k)$ is periodic in k space therefore,

$$e^{i\phi_n(\underline{k})} = e^{i\phi_n(\underline{k} \pm \underline{K}_n)} = \;.\;\;.\;\; = e^{i\phi_n(\underline{k} \pm \underline{K}_m)} \text{ etc.} \qquad 8.7$$

Hence we can rewrite equation 8.6 as follows

$$e^{i\phi_n(\underline{k})}\, \psi_n(\underline{k}\,,\,\underline{r}) = \sum_{\underline{K}_n} \nu_n(\underline{k} + \underline{K}_n)\, e^{i(\underline{k} + \underline{K}_n)\cdot\underline{r}}\, e^{i\phi_n(\underline{k} + \underline{K}_n)} \qquad 8.8$$

and the corresponding Wannier function (i.e. The one centered at origin , $\underline{R}=0$) is given by

$$a_n(\underline{r}) = \int_{B.Z} \psi_n(\underline{k}\,,\,\underline{r})\, e^{i\phi_n(\underline{k})}\, d^3k \qquad 8.9$$

$$= \sum_{\underline{K}_n} \int_{B.Z} \nu_n(\underline{k} + \underline{K}_n)\, e^{i(\underline{k} + \underline{K}_n)\underline{r}}\, e^{i\phi_n(\underline{k} + \underline{K}_n)}\, d^3k \qquad 8.10$$

which leads to

$$a_n(\underline{r}) = \int_{\text{all } \underline{k}} \nu_n(\underline{k})\, e^{i\underline{k}\cdot\underline{r}}\, e^{i\phi_n(\underline{k})}\, d^3k \qquad 8.11$$

The mean square extent of Wannier functions is defined as[3]

$$\langle r_n^2 \rangle = \int_{\text{all } \underline{r}} a_n^*(\underline{r})\, r^2\, a_n(\underline{r})\, d^3r \qquad 8.12$$

Substituting equation 8.10 into equation 8.12 we get

$$\langle r_n^2 \rangle = \iiint_{\text{all } \underline{k},\underline{k}',\underline{r}} \nu_n^*(\underline{k})\, e^{-i\underline{k}\cdot\underline{r}}\, e^{-i\phi_n(\underline{k})}\, r^2\, \nu_n(\underline{k}')\, e^{i\underline{k}'\cdot\underline{r}}\, e^{i\phi_n(\underline{k}')}\, d^3k\, d^3k'\, d^3r \qquad 8.13$$

which may alternatively be written as

$$\langle r_n^2 \rangle = \iiint \nu_n^*(\underline{k})\, \nu_n(\underline{k}')\, e^{-i\phi_n(\underline{k})}\, e^{i\phi_n(\underline{k}')}\, \nabla_k\, e^{-i\underline{k}\cdot\underline{r}}\, \nabla_{k'}\, e^{i\underline{k}'\cdot\underline{r}}\, d^3k\, d^3k'\, d^3r \qquad 8.14$$

where one can rewrite the integrand as follows

$$\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\, \nu_n(\underline{k}')\, e^{i\phi_n(k')}\, \nabla_k\, e^{-i\underline{k}\cdot\underline{r}}\, \nabla_{k'}\, e^{i\underline{k}'\cdot\underline{r}} =$$

$$\nabla_k \cdot \nabla_{k'} \cdot \left(e^{-i\underline{k}\cdot\underline{r}}\, e^{i\underline{k}'\cdot\underline{r}}\, \nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\, \nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')} \right) - e^{i\underline{k}'\cdot\underline{r}}\, e^{-i\underline{k}\cdot\underline{r}} \Big[\nabla_k \left(\nu_n^*(\underline{k})\, e^{i\phi_n(\underline{k})} \right) \cdot$$

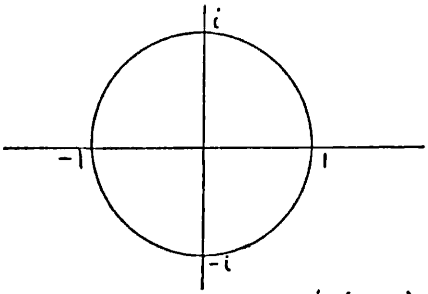
$$\cdot \nabla_{k'} \left(\nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')} \right) \Big] - \nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\, e^{i\underline{k}'\cdot\underline{r}}\, \nabla_k\, e^{-i\underline{k}\cdot\underline{r}}\, \nabla_{k'} \left(\nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')} \right)$$

$$- e^{-i\underline{k}\cdot\underline{r}}\, \nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')}\, \nabla_k \left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})} \right) \nabla_{k'}\, e^{i\underline{k}'\cdot\underline{r}} \qquad 8.15$$

---

3) The approximation in Weinreich's treatment starts here. In order to be able to work out this integral he considers the mean square extent of the discrete lattice vectors $\underline{R}$ (i.e. $\langle \underline{R}^2 \rangle$) instead of the mean square extent of the continous variable $\underline{r}$.

Now let us consider the integration of the first term on the right hand side of eqution 8.15 . One can use Gauss's (Divergence) theorem to transform this volume integral into a surface integral, over a surface with a very large radius (i.e. $\underline{k},\underline{k}' \longrightarrow \infty$) . The exponential terms in the integrand are bounded into a finite region for all $\underline{k}$ and $\underline{r}$, i.e . into a unit circle in the complex plane



Hence provided that the functions $\nu_n(\underline{k})$ ' s vanish at infinity (that means over the large spherical surface considered)

i.e.

$$\lim_{k,k' \to \infty} \nu_n(\underline{k}) , \nu_n(\underline{k}') = 0 \qquad 8.16$$

the surface integral yields zero.

Now consider the second and the third terms on the right hand side of equation 8.15 . Their sum can be rewritten as follows,

$$-e^{i\underline{k}'\underline{r}} \left[\nabla_{k'} \left(\nu_n(\underline{k}') e^{i\phi_n(\underline{k}')} \right) \right] \left[e^{-i\underline{k}\underline{r}} \nabla_k \nu_n^*(\underline{k}) e^{-i\phi_n(\underline{k})} + \nu_n^*(\underline{k}) e^{-i\phi_n(\underline{k})} \nabla_k e^{-i\underline{k}\underline{r}} \right]$$

$$= -e^{i\underline{k}'\underline{r}} \nabla_{k'} \cdot \left(\nu_n(\underline{k}') e^{i\phi_n(\underline{k}')} \right) \nabla_k \cdot \left(\nu_n^*(\underline{k}) e^{-i\phi_n(\underline{k})} e^{-i\underline{k}\underline{r}} \right) \qquad 8.17$$

and again from similiar arguments and the fact that

$$\lim_{k \to \infty} \nu^*(\underline{k}) \rightarrow 0 \qquad 8.18$$

one can show that the surface integrals due to these terms also vanish.

The only nonvanishing term (The fourth term on the right hand side of equation 8.15) may be written as follows

$$-\left[\nabla_k\left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\right)\right] e^{-i\underline{k}\cdot\underline{r}}\left[\nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')}\;\nabla_{k'}\left(e^{i\underline{k}'\cdot\underline{r}}\right)\right] \tag{8.19}$$

$$=-\left[\nabla_k\left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\right)\right]\left[\left(\nabla_{k'} e^{i\underline{k}'\cdot\underline{r}}\,\nu_n(\underline{k}')\,e^{i\phi_n(\underline{k}')}\right)+e^{i\underline{k}'\cdot\underline{r}}\left(\nabla_{k'}\nu_n(\underline{k}')\,e^{i\phi_n(\underline{k}')}\right)\right] e^{-i\underline{k}\cdot\underline{r}}$$

Through similiar arguments the only nonvanishing part can be shown to be

$$e^{-i\underline{k}\cdot\underline{r}}\, e^{i\underline{k}'\cdot\underline{r}}\;\nabla_k\left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\right)\nabla_{k'}\left(\nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')}\right) \tag{8.20}$$

Therefore we are left with the following integral to be minimized

$$\langle r_n^2\rangle = \iiint\limits_{\text{all }\underline{k},\,\underline{k}',\,\underline{r}} \nabla_k\left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\right)\;\nabla_{k'}\left(\nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')}\right) e^{i\underline{r}\cdot(\underline{k}'-\underline{k})}\, d^3k\, d^3k'\, d^3r \tag{8.21}$$

but,

$$\int\limits_{\text{all }\underline{r}} e^{i\underline{r}\cdot(\underline{k}'-\underline{k})}\, d^3r \;=\; \delta\left(\underline{k}-\underline{k}'\right) \tag{8.22}$$

(The constants are not shown)

therefore,

$$\langle r_n^2\rangle = \iint\limits_{\text{all }\underline{k},\,\underline{k}'} \nabla_k\left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\right)\nabla_{k'}\left(\nu_n(\underline{k}')\, e^{i\phi_n(\underline{k}')}\right)\delta\left(\underline{k}-\underline{k}'\right) d^3k\, d^3k' \tag{8.23}$$

$$= \int\limits_{\text{all }\underline{k}} \nabla_k\left(\nu_n^*(\underline{k})\, e^{-i\phi_n(\underline{k})}\right)\nabla_k\left(\nu_n(\underline{k})\, e^{i\phi_n(\underline{k})}\right) d^3k \tag{8.24}$$

or

$$\langle r_n^2 \rangle = \int_{\text{all } \underline{k}} \left| \nabla_k \left(\nu_n(\underline{k})\, e^{i\phi_n(\underline{k})} \right) \right|^2 d^3k \qquad 8.25$$

In the last expression, it is apparent that the integrand is a real function of $\underline{k}$ and the task is to choose the real function $\phi_n(\underline{k})$ such that the integral under consideration will attain its minimum.

Rewriting the integrand as

$$\langle r_n^2 \rangle = \int_{\text{all } \underline{k}} \Big[\left|\nabla_k \phi_n(\underline{k})\right|^2 \left|\nu_n(\underline{k})\right|^2 + 2\,\mathrm{IM}\left[\nu_n^*(\underline{k}) \nabla_k \nu_n(\underline{k})\right] . \nabla_k \phi_n(\underline{k}) + \left|\nabla_k \nu_n(\underline{k})\right|^2 \Big] d^3k \qquad 8.26$$

where $\mathrm{IM}\left[\nu_n^*(\underline{k}) \nabla_k \nu_n(\underline{k})\right]$ is the imaginary part of the expression $\nu_n^*(\underline{k}) \nabla_{\underline{k}} \nu_n(\underline{k})$ and using Euler's expression for the integral, we get

$$\nabla_k \left[\left(2 \nabla_k \phi_n(\underline{k})\right) \left|\nu_n(\underline{k})\right|^2 + 2\,\mathrm{IM}\left[\nu_n^*(\underline{k}) \nabla_k \nu_n(\underline{k})\right] \right] = 0 \qquad 8.27$$

Simplifying the last expression we get

$$\nabla_k^2 \phi_n(\underline{k}) + \nabla_k \cdot \phi_n(\underline{k}) . \left(\frac{\nabla_k \cdot \left|\nu_n(\underline{k})\right|^2}{\left|\nu_n(\underline{k})\right|^2} \right) + \frac{\nabla_k \cdot \left[\mathrm{IM}\, \nu_n^*(\underline{k}) \nabla_k \nu_n(\underline{k})\right]}{\left|\nu_n(\underline{k})\right|^2} = 0 \qquad 8.28$$

Now, defining

$$f_n(\underline{k}) = \frac{\nabla_k \cdot \left|\nu_n(\underline{k})\right|^2}{\left|\nu_n(\underline{k})\right|^2} \qquad g_n(\underline{k}) = \frac{\nabla_k \cdot \left[\mathrm{IM}\, \nu_n^*(\underline{k}) \nabla_k \nu_n(\underline{k})\right]}{\left|\nu_n(\underline{k})\right|^2} \qquad 8.29$$

we finally get

$$\nabla_k^2 \cdot \phi_n(\underline{k}) + f_n(\underline{k}) \cdot \nabla_k \cdot \phi_n(\underline{k}) + g_n(\underline{k}) = 0 \qquad 8.30$$

which is a real, second order, differential equation, solutions of which gives the desired phase function $\phi_n(\underline{k})$

Hence knowing $f_n(k)$ and $g_n(k)$ (That means knowing the Bloch functions or the momentum eigenfunctions $\nu_n(\underline{k})$'s explicitly) one can work out the phases through equation 8.30, which yields the most localized Wannier functions for the particular problem.

SOME REMARKS; For free electrons the momentum eigenfunctions are stepwise functions, thus the mean square extent of the corresponding Wannier functions (see equation 8.25) is infinite. However, when a periodic potential is introduced, the momentum eigenfunctions become differentiable everywhere, so that, providing the condition 8.16 is satisfied, the integral in equation 8.25 attains a finite value. Then, depending upon the choice of the $\phi_n(\underline{k})$, we have ~~in~~finite values for $\left\langle \underline{r}_n^2 \right\rangle$. The smallest is obtained when the phases of the Bloch functions satisfy equation 8.30.

8.2 THE MOST LOCALIZED WANNIER FUNCTIONS FOR A CRYSTAL (THREE DIMENSIONAL) WITH INVERSION SYMMETRY

Above we have suggested a method to obtain the most localized Wannier functions for a general three dimensional crystal.

** However, as a special case, if the crystal in concern has inversion symmetry, then the momentum eigenfunctions ($\nu_n(\underline{k})$'s) that we deal with can be taken as real. Therefore the second term (imaginary) in the integrand in the equation given below (see equation 8.26)

$$\langle r_n^2\rangle = \int_{\text{all } \underline{k}} \Big[|\nabla_k \phi_n(\underline{k})|^2 |\nu_n(\underline{k})|^2 + 2\,\mathrm{IM}\left[\nu_n^*(\underline{k})\nabla_k \nu_n(\underline{k})\right] \nabla\, \phi_n(\underline{k}) + |\nabla_k \nu_n(\underline{k})|^2 \Big]\, d^3k \tag{8.31}$$

vanishes, to yield

$$\langle r_n^2\rangle = \int_{\text{all } \underline{k}} \Big[|\nabla_k \phi_n(\underline{k})|^2 |\nu_n(\underline{k})|^2 + |\nabla_k \nu_n(\underline{k})|^2 \Big]\, d^3k \tag{8.32}$$

where the integrand is made up of positive valued functions only and the integral attains a minimum when

$$\nabla_k \phi_n(\underline{k}) = 0 \qquad \text{or} \qquad \phi_n(\underline{k}) = \text{Constant} \tag{8.33}$$

Through above arguments we arrive at the following important conclusion, that for a crystal with inversion symmetry it is enough to assign constant phases to the wave functions in concern to end up with the most localized Wannier functions.

Hence, the Wannier functions that we have calculated in the previous chapters (where we have chosen the phases $e^{i\phi_n(\underline{k})} = \pm 1$, which means $\phi_n(\underline{k}) = \pi, 2\pi$, etc.) represent the best one could do in getting concentrated functions.

** I am indebted to Prof. L. Pincherle for bringing this result to my attention.

CHAPTER 9

EXACT WANNIER FUNCTIONS IN THREE DIMENSIONS (FOR AN INTERMEDIATE POTENTIAL)

9.1 GENERAL

Excluding the cases of free and tightly bound electrons, which we have studied in detail in chapters 4 and 10, the Wannier functions in general (for all intermediate cases of bindings) are extremely difficult to compute, since to do so one needs a complete knowledge of Bloch functions (corresponding to all values of wave vector $\underline{k}$) in a given band. This difficulty has also been admitted by a number of authors like Parzen[1], Wainwright[2], Slater[3], Smith[4], and Harrison[5] etc., where the former three have actually dealt with the problem.

The few reported calculations on the Wannier functions (excluding the case of tightly bound electrons) have been mainly on the one and two dimensional problems and include;

i) that of Parzen's using a one dimensional square potential (which we believe involves some serious mistakes) .

ii) and also that of Slater's employing a cosine potential. The first of these works employs the variational approach (suggested by the author[1] himself and Koster[6]) which we have described in detail in chapter 3.

In a second paper the authors[2] calculate the energy bands of a one dimensional cosine potential and that of lithium using

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1 Parzen, G. Phys. Rev. 89, 237 (1953)

2 Parzen, G. and Wainwright, T. Phys. Rev. 92, 1129 (1953)

3 Slater, J.C. Phys. Rev. 87, 807 (1952)

the same method. However, they employ momentum eigenfunctions instead of the Wannier functions stating that they found it easier to deal with the former.

In the second of the works referred above, Slater[3] proves that the Wannier functions are the Fourier transforms of the momentum eigenfunctions, which he readily calculated for the one and two dimensional problems. Possibility of an extension to three dimensions has also been mentioned.

In this chapter we intend to calculate exact (analytical) Wannier functions in three dimensions. The model that we have chosen is a cubic lattice with square potential wells. This particular choice for the model has enabled us to obtain the Bloch waves in analytical forms for all points in each band which we have used to calculate the Wannier functions. We have first started with the one dimensional case and extended the argument at once to three dimensions for a seperable problem. As is shown later, the problem in the three dimensional case is much more involved compared with the one dimensional problem.

We start with a general discussion on the separability of the Wannier functions.

9.2 ON THE SEPARABILITY OF THE WANNIER FUNCTIONS

In the present literature we haven't come ac~~c~~ross a general study on the separability of the Wannier functions. However, as we shall prove below, the conditions for which these functions are seperable can be set up easily.

[4] Smith, R.A. Wave Mechanics of Crystalline Solids, Chapman and Hall(1961)

[5] Harrison, W.A. Solid State Theory, McGAW-HILL (1970)

[6] Koster, G.F. Phys. Rev. 89, 67 (1953)

It is well known that the solutions of the following one electron Schrödinger's equation

$$-\hbar^2/2m\,\nabla^2\psi_{n\underline{k}}(\underline{r}) + V(\underline{r})\,\psi_{n\underline{k}}(\underline{r}) = E_n(k)\,\psi_{n\underline{k}}(\underline{r}) \qquad 1$$

is separable (in the cartesian coordinates) in the sense,

$$\psi_{n\underline{k}}(\underline{r}) = X_n(k_x,x)\,Y_n(k_y,y)\,Z_n(k_z,z) \qquad 2$$

if the potential V($\underline{r}$) is a sum of the terms each depending on one coordinate only

$$V(\underline{r}) = V_1(x) + V_2(y) + V_3(z) \qquad 3$$

The Wannier function is now given by

$$a_n(\underline{r}-\underline{R}) = \int_{n^{th}\,B.Z.} \psi_{n\underline{k}}(\underline{r})\,\exp(-i\underline{k}.\underline{R})\,d^3k \qquad 4$$

or

$$a_n(x-X,\,y-Y,\,z-Z) = \iiint X_n(k_x,x)\,Y_n(k_y,y)\,Z_n(k_z,z)\,\exp i(-k_xX - k_yY - k_zZ)\,dk_x\,dk_y\,dk_z \qquad 5$$

Now, provided that the B.Z. in concern has such line (in case of a two dimensional B.Z.) or plane (in case of a three dimensional B.Z.) boundaries that each of which can be defined by a single wave vector only (to this assumption the equations of these boundaries would read; $k_x \mp C_1 = 0$, $k_y \mp c_2 = 0$, and $k_z \mp c_3 = 0$), then the above triple integral is given by the product of three integrals each carried out separately over the one dimensional functions $X_n(k_x,x)$, $Y_n(k_y,y)$, and $Z_n(k_z,z)$. In other words, the Wannier function in concern is separable

$$a_n(x-X,\,y-Y,\,z-Z) = a_n(x-X)\,a_n(y-Y)\,a_n(z-Z) \qquad 6$$

This is possible only if the B.Z. in concern is a simple one such as a square or a rectangular one for two dimensional problems or a simple cube for the three dimensional cases, etc. In either case the B.Z. corresponds to the lowest band.

However, for most of the familiar crystal types and particularly for the higher energy bands the Wannier functions would not be separable. In sections 9.6 and 9.7 we have shown how to obtain the three dimensional Wannier functions also for a non-separable case.

9.3 THE POTENTIAL FIELD

The three dimensional crystal that we shall consider consists of a cubic array of square potential wells as shown in figure 9.1

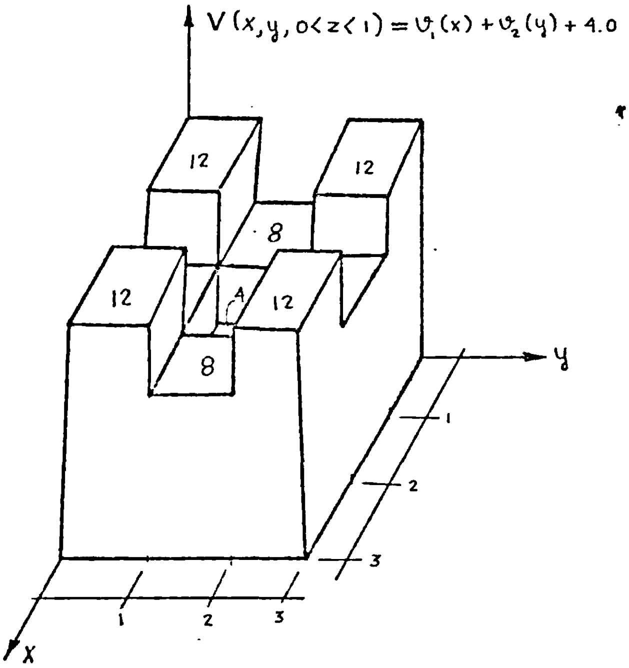

Fig. 9.1 The potential field (a part only) for $0 < z < +1$.

The potential function $V(\underline{r})$ is a sum of three functions,

$$V(\underline{r}) = V_1(x) + V_2(y) + V_3(z) \qquad 7$$

each being stepwise and defined along one of the principal directions, as follows

$$n.a \leq x,y, \text{ or } z \leq (n+1).a \qquad 8$$

$$V_1(x), V_2(y), \text{ or } V_3(z) = 0 \quad \text{for } n=1,3,5,7,\dots \qquad 9$$

$$V_1(x), V_2(y), \text{ or } V_3(z) = 4.0 \text{ a.u. for } n=0,2,4,6,\dots \qquad 10$$

We have found this crystal model very useful for obtaining analytic expressions for the associated Bloch functions and hence for the Wannier functions themselves.

9.4 EXACT WANNIER FUNCTIONS FOR THE ONE DIMENSIONAL PROBLEM

We first intend to obtain the (exact) Wannier functions for some energy bands of the one dimensional crystal. The results of the one dimensional calculations (though not a prerequsite for extensions to higher dimensions in the method that we use) are particularly useful in understanding the approach and the nature of the higher dimensional (three dimensional) Wannier functions.

The one dimensional calculations may be given in any one of the principal axes, say x. The one dimensional potential energy of the crystal is then simply made up of square wells (see equations 7 - 10) with the following parameters;

The internuclear distance $a = 2$ a.u.

The potential barriers $V_o = 4$ a.u.

9.4.1 FORMULATIONS FOR OBTAINING THE COEFFICIENTS OF THE WAVE FUNCTIONS

The solutions of the Schrodinger's equation for the two subsequent regions (see equations 8,9,and 10) are respectively

$$\psi_1(k_1, x) = A\cos k_1(x+0.5) + iB\sin k_1(x+0.5) \tag{11}$$

$$\psi_2(k_2, x) = C\cos k_2x + D\sin k_2x \tag{12}$$

where

A and B are real numbers

C and D are complex numbers

$$k_1 = \sqrt{E} \tag{13}$$

$$k_2 = \sqrt{E - V_0} = \sqrt{k_1^2 - V_0} \tag{14}$$

The boundary conditions are choosen as follows

B.C.1 $$\psi_1(k_1,0) = \psi_2(k_2,0) \;,\; \left(\frac{d\psi_1(k_1,x)}{dx}\right)_{x=0} = \left(\frac{d\psi_2(k_2,x)}{dx}\right)_{x=0} \tag{15}$$

B.C.2 $$\psi_2(k_2,+1) = e^{i2k}\psi_1(k_1,-1) \;,\; \left(\frac{d\psi_2(k_2,x)}{dx}\right)_{x=+1} = e^{i2k}\left(\frac{d\psi_1(k_1,x)}{dx}\right)_{x=-1} \tag{16}$$

B.C.3 $$\int_{-1}^{0}\left|\psi_1(k_1,x)\right|^2 dx + \int_{0}^{+1}\left|\psi_2(k_2,x)\right|^2 dx = 1 \tag{17}$$

From now on we will give only the results of the formulations. Substituting the expressions 11 and 12 into the equations 15 and 16 , we get the following relations.

$$A\cos 0.5\,k_1 + iB\sin 0.5\,k_1 = C \tag{18}$$

$$-Ak_1\sin 0.5\,k_1 + ik_1B\cos 0.5\,k_1 = k_2D \tag{19}$$

$$C\cos k_2 + D\sin k_2 = \exp(i\,2\,k)\,(A\cos 0.5\,k_1 - i\,B\sin 0.5\,k_1) \tag{20}$$

$$-C\,k_2\sin k_2 + D\,k_2\cos k_2 = \exp(i\,2\,k)\,(k_1 A\sin 0.5k_1 + i\,k_1 B\cos 0.5\,k_1) \tag{21}$$

In order that we may have non trivial solutions for A , B , C and D we must have

$$\begin{vmatrix} \cos 0.5\,k_1 & i\sin 0.5\,k_1 & -1 & 0 \\ -k_1\sin 0.5\,k_1 & i\,k_1\cos 0.5\,k_1 & 0 & -k_2 \\ \exp(i2k)\cos 0.5k_1 & -i\exp(i2k)\sin 0.5k_1 & -\cos k_2 & -\sin k_2 \\ k_1\exp(i2k)\sin 0.5k_1 & ik_1\exp(i2k)\cos 0.5k_1 & +k_2\sin k_2 & -k_2\cos k_2 \end{vmatrix} = 0 \tag{22}$$

Working out the above determinant , we get

$$\cos(2k) = \cos k_1\cos k_2 - ((k_1^2 + k_2^2)/\ 2k_1k_2)\sin k_1\sin k_2 \tag{23}$$

Actually this is the Kramer's function for the problem(the dispersion relation in an implicit form)

Now let us consider the equation 17 . Working out the integrals and after a number of algebraic simplifications , we get

$$\frac{A^2+B^2}{2} + \frac{A^2-B^2}{2k_1}\sin k_1 + (|C|^2+|D|^2)\,\frac{\sin k_2\cos k_2}{2\,k_2} \tag{24}$$

$$\frac{|C|^2+|D|^2}{2} + (\mathrm{Re}C\,\mathrm{Re}D + \mathrm{Im}C\,\mathrm{Im}D)\,\frac{\sin^2 k_2}{k_2} = +1$$

where the notations Re and Im stand respectively for the real and the imaginary parts of the coefficients.

In equations 18 , 19 , 20 , 21 , and 24 we have 8 unknowns , which are A , B , ReC , ImC, ReD , ImD , k_1 , and k (we have not counted k_2 since it can be obtained from k_1).

Now eliminating k and solving the remaining equations for A , B , ReC , ImC , ReD , and ImD (in terms of k_1 and k_2) and simplifying the outcoming equations as much as possible we get the following analytical expressions for the above named coefficients (we give the results only)

$$A = (\beta)^{-\frac{1}{2}} \qquad 26$$

$$B = (\alpha)^{\frac{1}{2}}(\beta)^{-\frac{1}{2}} \qquad 27$$

$$ReC = \cos 0.5k_1 (\beta)^{-\frac{1}{2}} \qquad 28$$

$$ImC = \sin 0.5k_1 (\alpha)^{\frac{1}{2}}(\beta)^{-\frac{1}{2}} \qquad 29$$

$$ReD = -\frac{k_1}{k_2} \sin 0.5k_1 (\beta)^{-\frac{1}{2}} \qquad 30$$

$$ImD = \frac{k_1}{k_2} \cos 0.5k_1 (\alpha)^{\frac{1}{2}}(\beta)^{-\frac{1}{2}} \qquad 31$$

where α and β are functions of k_1 and k_2 and are given by the following equations

$$\alpha(k_1,k_2)=\frac{-\left(\frac{k_1}{k_2}\right)^2(\sin 0.5k_1)\sin k_2+\left(\frac{k_1}{k_2}\right)\sin k_1\cos k_2+(\cos 0.5k_1)\sin k_2}{\left(\frac{k_1}{k_2}\right)^2(\cos 0.5k_1)\sin k_2+\left(\frac{k_1}{k_2}\right)\sin k_1\cos k_2-(\sin 0.5k_1)\sin k_2} \qquad 32$$

and

$$\begin{aligned}\beta(k_1,k_2) &= 0.5(1+\alpha)+(1-\alpha)\left(\frac{\sin k_1}{2k_1}-\frac{k_1\sin^2 k_2\,\sin k_1}{2k_2}\right)\\ &+\sin^2 0.5k_1\left[\frac{\sin 2k_2}{4k_2}\left(\alpha-\left(\frac{k_1}{k_2}\right)^2\right)+0.5\left(\alpha+\left(\frac{k_1}{k_2}\right)^2\right)\right]\\ &+\cos^2 0.5k_1\left[\frac{\sin 2k_2}{4k_2}\left(1-\alpha\left(\frac{k_1}{k_2}\right)^2\right)+0.5\left(1+\alpha\left(\frac{k_1}{k_2}\right)^2\right)\right]\end{aligned} \qquad 33$$

So far we have obtained expressions (explicit) for the coefficients A , B , ReC , ImC , ReD , and , ImD in terms of k_1 and k_2 Now , it is very easy to compute these coefficients (that means the wave functions themselves) for all bands and at as many points (eigenvalues) as required simply by using these direct expressions.

The present task is to calculate the wave functions corresponding only to those permissible values of k_1 and k_2 (the bands). Below , we give the allowed regions of the energy eigenvalues (the bands), over which we intend to carry out the present calculations.

9.4.2 ALLOWED RANGE OF THE PARAMETERS k_1 AND k_2 (THE BANDS)

We have worked out the dispersion relation given by equation 23 both for imaginary ($V > E$) and real ($V < E$) values of the parameter k_2 . The bands correspond to the real values of the wave vector k .

We need this information about the bands for obtaining the Wannier functions.

k_1	k_2	cos2k	k	
1.280	1.538	1.08784	imaginary	
1.290	1.525	1.02853	imaginary	
1,295	1.520	1.000	0	First band
.	.	.	.	
1.765	0.940	-1.000	$\mp \pi/2$	
1.770	0.930	-1.0125	imaginary	
2.360	1.250	-1.02971	imaginary	
2.375	1.280	-1.000	$\mp \pi/2$	Second band
.	.	.	.	
3.430	2.790	+1.000	$\mp \pi$	
3.440	2.800	+1.00113	imaginary	
3.490	2.860	+1.000	$\mp \pi$	Third band
.	.	. .	.	
4.880	4.450	-1.000	$\mp 3\pi/2$	
4.890	.		imaginary	
4.970		-1.000	$\mp 3\pi/2$	Fourth band
. .	.	.	.	
6.430		+1.000	$\mp 2\pi$	

Table 1

9.4.3 FORMULATIONS FOR OBTAINING THE WANNIER FUNCTIONS

The wave function for the m band and for $-1 \leq x \leq 0$ is given by the following equation (see equation 11)

$$\psi_m = A_m(k_1, k_2)\cos k_1(x + 0.5) + i\, B_m(k_1, k_2)\sin k_1(x + 0.5) \qquad 34$$

Then the Wannier function for the m^{th} band (which is centered at origin , $X_n = 0$) is given by

$$a_m(x) = \sum_k A_m(k_1, k_2)\cos k_1(x+0.5) + i\, B_m(k_1,k_2)\sin k_1(x + 0.5) \qquad 35$$

where the sum is over the allowed k values of the m^{th} Brillouin zone. Also note that this equation is valid only for $-1 \leq x \leq 0$, since the wave function in the sum is defined in this domain only.

If we investigate the nature of equations that we have developed in the previous sections, we observe the following

1) k_1 and k are related to each other by equation 23 therefore summation over k in equation 35 can be replaced by a summation over k_1 .

2) changing sign of k (i.e $+k$ to $-k$) changes the sign of k_1 also (i.e. $+k_1$ to $-k_1$)

3) The expressions for α , β , A , B , ReC , etc. (see equations 32,, 33 , 26 , 27 , 28 , etc.) are invariant of the change of sign of k . However, these coefficients are obtained from α and β by square root operations , therefore they may be taken either positive or negative (and the wave functions can be constructed by any combinations of these coefficients)

Above we have said that the summation over the k values of the m^{th} band (equation 35) could be replaced by a summation over the k_1 values of the same band. Therefore we have

$$a_m(x) = \sum_{\substack{k_1 \\ m^{th}\ \mathrm{B.Z.}}} A_m\ (k_1,k_2)\cos k_1(x+0.5) + i\ B_m \sin k_1(x+0.5) \qquad 36$$

Before we proceed any further , we have to have the following arguments .

9.4.4 WANNIER FUNCTIONS FOR THE ODD NUMBERED BANDS

If we assume that $A_m(k_1, k_2)$ and $B_m(k_1, k_2)$ do not change their signs along the whole of the m^{th} Brillouin zone (both either positive or negative all along the zone) then we can easily show that

$$\psi_m(-k\ ,\ x) = \psi_m^{*}(+k\ ,\ x) \qquad 37$$

and

$$\psi_m(k_1,\ -x) = \psi_m^{*}(+k_1,\ x) \qquad 38$$

Now referring to what we have said in chapter 7 we then conclude that the outcoming Wannier functions are real and symmetric . This last point can easily be verified, if we write the right hand side of equation 35 as two seperate summations over the positive and the negative values of k_1

$$a_m(x) = \sum_{\substack{+k_1 \\ (\text{positive values of } k_1 \text{ only})}} \psi_m(k\ ,\ k\ ,\ x) + \sum_{\substack{-k_1 \\ (\text{negative values of } k_1 \text{ only})}} \psi_m(k\ ,\ k\ ,\ x) \qquad 39$$

The imaginary terms in the last expression cancel each other, therefore we have

$$a_m(x) = 2 \sum_{+k_1} A_m(k_1, k_2) \cos k_1(x + 0.5) \qquad -1 \leq x \leq 0 \qquad 40$$

which is real and symmetric about $x = -0.5$. Actually for a crystal with inversion~~al~~ symetry , one can show that the outcoming wave functions satisfy either one of the symmetry requirements given by equations 7.2.11 and 7.2.15 . Then as we have shown in chapter 7 ,the associated Wannier functions are either symmetric or antisymmetric (the ground band and the subsequent odd numbered bands Wannier functions being always symmetrical) .

Therefore the present considerations correspond to the Wannier functions of the ground and the subsequent odd numbered bands (i.e. $m = 1, 3, 5, 7$, etc.)

So far we have considered some formulations for the amplitude of a Wannier function in a limited domain (i.e. $-1 \leq x \leq 0$, the first well) . However, we would like to calculate these functions for all x .

Now , using Bloch's theorem the wave function at subsequent wells , say at n^{th} one is given by

$$\psi_m(k, x') = \exp(i\, 2\, n\, k)\, \psi_m(k, x) \qquad 41$$

where

$$-1 \leq x \leq 0$$

$$-1 + 2n \leq x' \leq 2n$$

and $x' = x + 2n$, $n = 1, 2, 3,$ etc.

Now , through arguments similiar to the previous ones , we can show that the Wannier functions at the subsequent wells say at the n^{th} well is given by

$$a_m(x') = 2 \sum_{\substack{+k_1 \\ (m^{th}\ \text{B.Z.})}} A_m(k_1,k_2)\cos 2nk\ \cos k_1(x+0.5) - B_m(k_1,k_2)\sin 2nk\ \sin k_1(x+0.5) \qquad 42$$

Where again , we have

$$\begin{aligned} -1 \leq x \leq 0 \\ -1 + 2n \leq x' \leq 2n \end{aligned} \qquad \text{and} \qquad x' = x + 2n \quad , n = 1,2,3, \text{ etc .}$$

Wannier functions at the first and the subsequent hills;

The general considerations in obtaining the expressions (43 and 44)below,are similiar to those given in the previous sections , therefore we give the results of the formulations only.

The amplitude of the Wannier functions (for the odd numbered bands) within the first hill is given by **

$$a_m(x) = 2 \sum_{+k_2} \operatorname{Re}C(k_1,k_2) \cos k_2x + \operatorname{Re}D(k_1, k_2) \sin k_2x \qquad 43$$

$$\text{where} \quad 0 \leq x \leq +1$$

The amplitude of the Wannier functions for the subsequent hills (say for the n^{th} one) is given by

$$\begin{aligned} a_m(x') = 2 \sum_{+k_2} & \cos(2nk) \Big(\operatorname{Re}C(k_1,k_2)\cos k_2x + \operatorname{Re}D(k_1,k_2)\sin k_2x\Big) \\ & -\sin(2nk) \Big(\operatorname{Im}C(k_1,k_2)\cos k_2x + \operatorname{Im}D(k_1,k_2)\sin k_2x\Big) \end{aligned} \qquad 44$$

where

$$\begin{aligned} 0 \leq x \leq +1 \\ 2n \leq x' \leq 2n + 1 \end{aligned} \qquad \text{and} \qquad x' = x + 2n \quad , \ n = 1,2,3,4,\text{etc.}$$

** When k_2 is imaginary simply replace $\sin k_2x$ and $\cos k_2x$ by sinh and cosh

9.4.5 WANNIER FUNCTIONS FOR THE EVEN NUMBERED BANDS ($m = 2, 4, 6$, etc.)

Even numbered bands are represented by the antisymmetrical Wannier functions (see also the previous arguments) .

In chapter 7 we have said that if the phases of the wave functions are such choosen that

$$\psi_{-k}(x) = -\psi_k^*(x) \qquad 45$$

then the outcoming Wannier functions are antisymmetric .

Now, if we take both coefficients ,$A_m(k_1 ,k_2)$ and $B_m(k_1 ,k_2)$ in equation 11 , as positive valued over the half Brillouin zone containing $+ k_1$ vectors and as negative valued over the other half Brillouin zone containing $-k_1$ vectors , then the wave functions constructed from these coefficients according to the combination 1 satisfy the requirement 45 . Consequently, the antisymmetric property of the outcoming Wannier functions can be seen more clearly, if we write down the full expression for them , and work them out under the above assumptions , as we have done it below

$$\begin{aligned} a_m (x) = \sum_{+k_1} & A_m(k_1,k_2)\cos k_1(x + 0.5) + i\, B_m(k_1,k_2)\sin k_1(x + 0.5) \\ (\, m^{th} B.Z) \quad & A_m(k_1,k_2)\cos(-k_1(x+0.5)) +i\, B_m(-k_1,k_2)\sin(-k_1(x+0.5)) \end{aligned} \qquad 46$$

Now using the conditions imposed on the functions $A_{m+1}(k\ ,k\ )$ and $B_{m+1}(k_1,k_2)$, the last equation simply yields

$$a_m (x) = 2\, i \sum_{+k_1} B_m (k_1,k_2) \sin k_1(x + 0.5) \qquad 47$$

where $-1 \leq x \leq 0$

which is antisymmetrical with respect to x and around the origin $x = -0.5$

As it is apparent from equation 47 the Wannier functions for the even numbered bands are all pure imaginary , though those for odd numbered bands were all real. However, this creates no problem ; we can either divide $a_{m+1}(x)$ by i in plotting or take the wave function in concern such that it will be related to the previous one as follows

$$\Psi'(k,x) = +i\,\Psi(k,x) \qquad 48$$

Through arguments , similiar to those given previously , the Wannier functions at several other regions of the crystal are given as follows ;

At subsequent wells. say at the n^{th} one , we have

$$a_m(x') = 2i \sum_{\substack{+k_1 \\ (m^{th}\ \text{zone})}} A_m(k\ ,k\ )\sin 2nk\cos k_1(x+0.5)+B_m(k_1,k_2)\cos 2nk\sin k_1(x+0.5) \qquad 49$$

where

$$-1 \leq x \leq 0 \qquad \text{and} \qquad x' = x + 2n \ , \ n = 1,2,3,\text{etc.}$$
$$-1+2n \leq x' \leq 2n$$
$$m = 2,4,6,\ldots.$$

At hills (including the first one) , say at the n^{th} one we have

$$a_m(x') = 2i \sum_{+k_2} \cos 2nk\Big(\mathrm{Im}C_m(k_1,k_2)\cos k_2x + \mathrm{Im}D_m(k_1,k_2)\sin k_2x\Big) + \sin 2nk\Big(\mathrm{Re}C_m(k_1,k_2)\cos k_2x + \mathrm{Re}D_m(k_1,k_2)\sin k_2x\Big) \qquad 50$$

where

$$0 \leq x \leq +1 \qquad \text{and} \qquad x' = x + 2n \ , \ n = 0,1,2,3,\ldots$$
$$2n \leq x' \leq 2n+1$$
$$m = 2,4,6,8,\ldots.$$

9.4.6 THE CALCULATED WANNIER FUNCTIONS FOR THE ONE DIMENSIONAL PROBLEM

Below, as an illustration we give the calculated Wannier functions related to the first and and the second bands of the one- dimensional problem.

x	Ground band Wan. Func.	x	Ground band Wan. Func.
-1.0	0.67242	3.2	0.00117
-0.9	0.76506	3.4	0.01132
-0.8	0.83611	3.6	0.01939
-0.7	0.88810	3.8	0.02409
-0.6	0.91981	4.0	0.02042
-0.5	0.93046	4.2	0.01916
-0.4	0.91981	4.4	0.01792
-0.3	0.88810	4.6	0.01693
-0.2	0.83611	4.8	0.01641
-0.1	0.76506	5.0	0.01662
0.0	0.67242	5.2	0.03196
0.2	0.50144	5.4	0.03134
0.4	0.36701	5.6	0.02831
0.6	0.26115	5.8	0.02334
0.8	0.17821	6.0	0.02216
1.0	0.11454	6.2	0.01622
1.2	0.07004	6.4	0.01195
1.4	0.02048	6.6	0.00902
1.6	-0.01827	6.8	0.00721
1.8	-0.04265	7.0	0.00639
2.0	-0.04 32	7.2	-0.00249
2.2	-0.04535	7.4	-0.00281
2.4	-0.04063	7.6	-0.00212
2.6	-0.03390	7.8	-0.00058
2.8	-0.02639	8.0	-0.00250
3.0	-0.01904	8.2	0.00008

Table 2

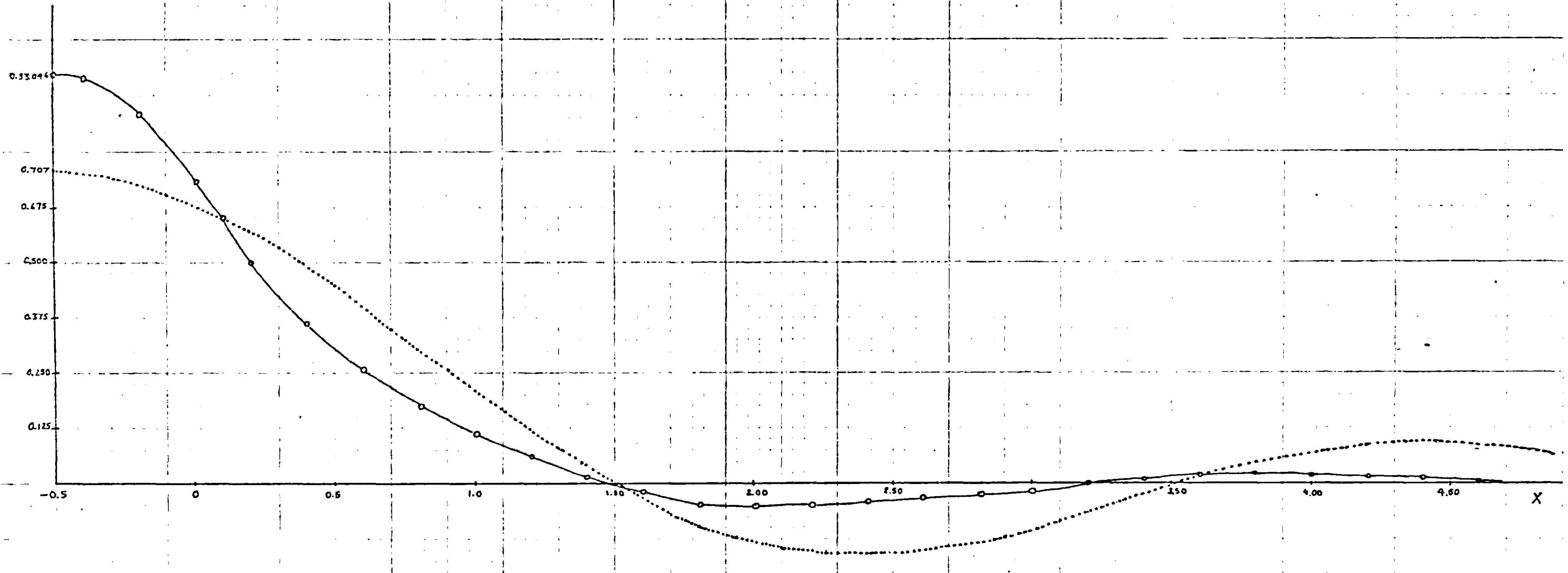

Fig. 3 The ground band Wannier function (one dimensional) in the first three unit cells ($-0.5 \leq x \leq 4.50$). The maximum of the function occurs at $x=-0.5$ and is 0.93046. The oscillations outside the cells considered are rather small and vanish rapidly as one moves away. The function is symmetrical about $x=-0.5$. For comparison purposes we have also plotted the free electron Wannier function (dashed lines). The former function is deviated from the free electron one in such a way that it is more localized (or in other words it has less mean square spread, as discussed in chapters 7 and 8) and vanish more rapidly by distance. Both functions are normalized.

x	Second band Wan. Func.
-1.0	-1.12329
-0.9	-1.03986
-0.8	-0.86888
-0.7	-0.62411
-0.6	-0.32602
-0.5	0.00000
-0.4	0.32602
-0.3	0.62411
-0.2	0.86888
-0.1	1.03986
0.0	1.12330
0.1	1.13583
0.2	1.10062
0.3	1.02144
0.4	0.90436
0.5	0.75731
0.6	0.58957
0.7	0.41106
0.8	0.23180
0.9	0.06120
1.0	-0.09246
1.1	-0.21987
1.2	-0.31102
1.3	-0.37112
1.4	-0.34500
1.5	-0.29116
1.6	-0.29116
1.7	-0.22006
1.8	-0.14306
1.9	-0.07093
2.0	-0.01260
2.1	0.02591
2.2	0.04248
2.3	0.03757
2.4	0.01343
2.5	-0.02011
2.6	-0.04602
2.7	-0.08052
2.8	-0.10552
2.9	-0.12514
3.0	-0.12217
3.1	-0.11317
3.2	-0.09430
3.3	-0.07623
3.4	-0.05304
3.5	-0.03184
3.6	-0.00808
3.7	0.02627
3.8	0.04931
3.9	0.06258
4.0	0.07337
4.1	0.07507
4.2	0.07448
4.3	0.06501
4.4	0.05452

Table 3

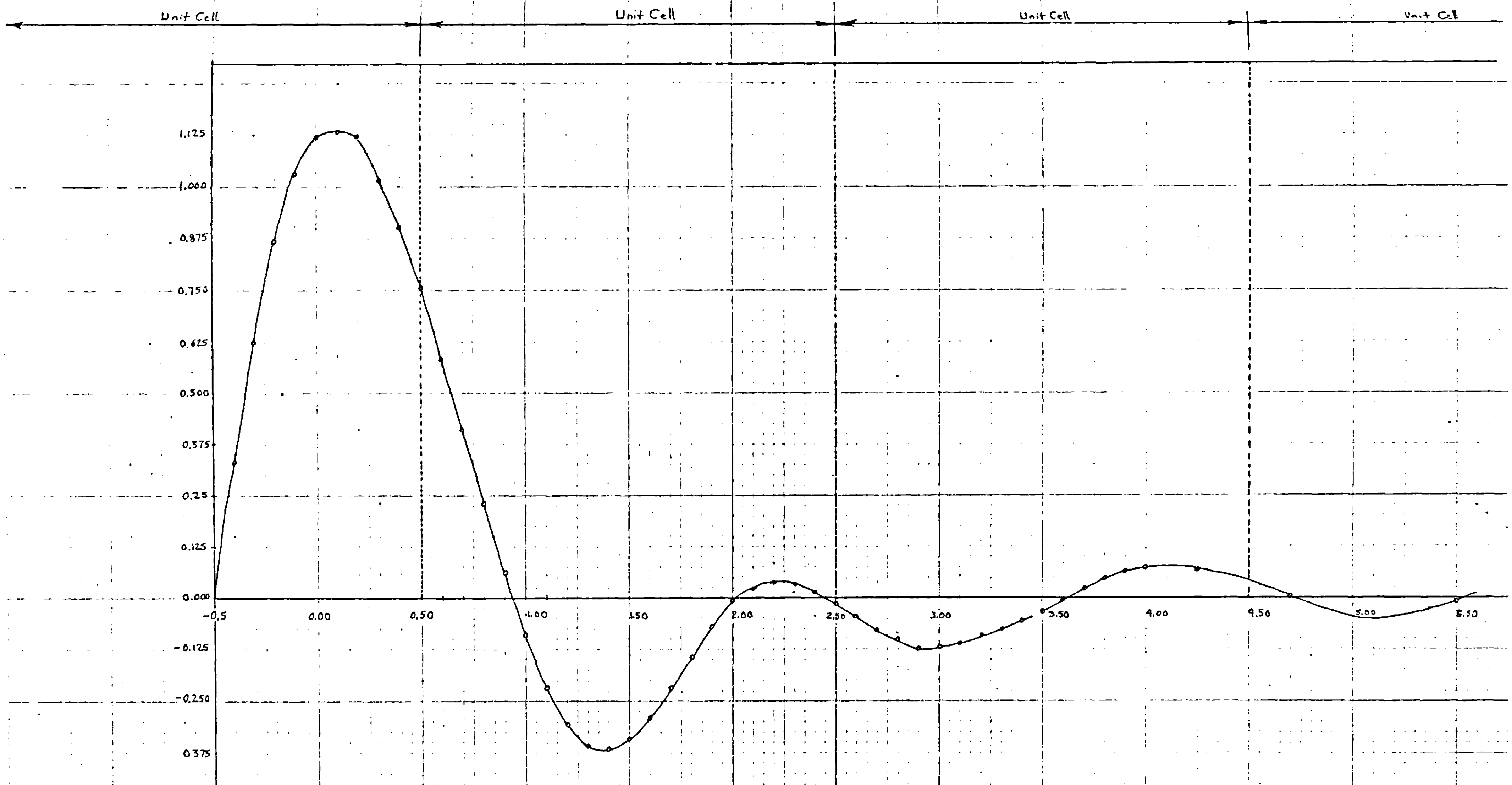

Fig. 4 The second band Wannier function (one dimensional) for $-0.5 \leq x \leq +5.50$. The maximum of the function occurs at $x = 0.10$ and is 1.13583. The Wannier function extend out into other unit cells with larger amplitudes compared with the previous (ground band) Wannier function. This is due to the fact that the latter corresponds to less strongly bound electrons. The function is antisymmetrical about $x = -0.5$. The unit cells are shown by dashed lines.

9.5 EXACT GROUND BAND WANNIER FUNCTION IN THREE DIMENSIONS

The B.Z. associated with the lowest band is a simple cube therefore, following the arguments given in section 10.2 it will be understood that the Wannier function for this band is separable. That is to say the three dimensional Wannier function is a product of the three one dimensional Wannier functions a_x , a_y , and a_z ,all equal to the one we have calculated in the previous sections.

The situation is illustrated in table 4 where we give the calculated values of the Wannier function (for 1/4 th of the configuration space). Entries are given only to three figures though they were computed to greater accuracy. We have cut off the tables, for the sake of brevity before we have gone to very large values of $\underline{r}$. The tables repeat symmetrically in the remaining four quadrants of the configuration space.

It is apparent that this function has Γ_1 type of symmetry, that is to say it is unchanged under the following cubic group of operations which leave a cube invariant.

Class	Operation	Class	Operation	Class	Operation
E	x y z	C_3	z x y	JC_2	-z -y x
C_4^2	-x -y z		y z x		z -y -x
	x -y -z		z -x -y		-y -x z
	-x y -z		-y -z x		-z y -x
C_4	-y x z		-z -x y		x -z -y
	y -x z		-y z -x		y x z
	x -z y		-z x -y		z y x
	x z -y		y -z -x		x z y
	z y -x	J	-x -y -z	JC_3	-z -x -y
	-z y x	JC_4^2	x y -z		-y -z -x
C_2	y x -z		-x y z		-z x y
	z -y x		x -y z		y z -x
	-x z y	JC_4	y -x -z		z x -y
	-y -x -z		-y x -z		y -z x
	-z -y -x		-x z -y		z -x y
	-x -z -y		-x -z y		-y z x

y x	-0.5	-0.4	-0.2	0.0	0.2	0.4	0.6	0.8	1.0	1.20	1.40	1.60	1.80
-0.5	0.805	0.795	0.722	0.580	0.435	0.316	0.221	0.154	0.100	0.061	0.017	-0.015	-0.037
-0.4	0.795	0.785	0.715	0.575	0.432	0.313	0.220	0.152	0.098	0.060	0.017	-0.015	-0.036
-0.2	0.772	0.715	0.650	0.523	0.393	0.284	0.200	0.138	0.089	0.054	0.016	-0.014	-0.033
0.0	0.580	0.575	0.523	0.420	0.314	0.228	0.160	0.112	0.072	0.044	0.013	-0.011	-0.027
0.2	0.435	0.432	0.393	0.314	0.236	0.173	0.120	0.083	0.054	0.033	0.009	-0.008	-0.020
0.4	0.316	0.313	0.284	0.228	0.173	0.125	0.089	0.062	0.041	0.025	0.007	-0.005	-0.015
0.6	0.220	0.220	0.200	0.160	0.120	0.089	0.063	0.042	0.026	0.018	0.005	-0.004	-0.010
0.8	0.154	0.152	0.138	0.112	0.083	0.062	0.042	0.028	0.018	0.012	0.003	-0.003	-0.007
1.0	0.100	0.098	0.089	0.072	0.054	0.041	0.026	0.019	0.012	0.008	0.002	-0.002	-0.005
1.2	0.061	0.060	0.054	0.044	0.033	0.025	0.018	0.012	0.008	0.005	0.001	-0.001	-0.003
1.4	0.017	0.017	0.015	0.013	0.009	0.0 7	0.005	0.003	0.002	0.001	0.0004	-0.0003	-0.0008
1.6	-0.015	-0.015	-0.014	-0.011	-0.008	-0.005	-0.004	-0.003	-0.002	-0.001	-0.0003	0.0003	0.0007
1.8	-0.037	-0.036	-0.033	-0.027	-0.020	-0.001	-0.010	-0.007	-0.005	-0.003	-0.0008	0.0007	0.002
2.0	-0.040	-0.039	-0.036	-0.029	-0.022	-0.002	-0.011	-0.008	-0.005	-0.003	-0.0009	0.0008	0.002

Table 4 The ground band Wannier function (three dimensional) over z=-0.5 plane. There are three such equivalent planes (x=-0.5, y=-0.5, and z=-0.5) Over which the function reads similiar values. The function over planes other than z=-0.5 can be obtained from the above entries by multiplying them by a certain constant. The oscillations outside the region considered are rather small and vanish rapidly as one moves away. This is due to the fact that the band in concern corresponds to rather well bound electrons.

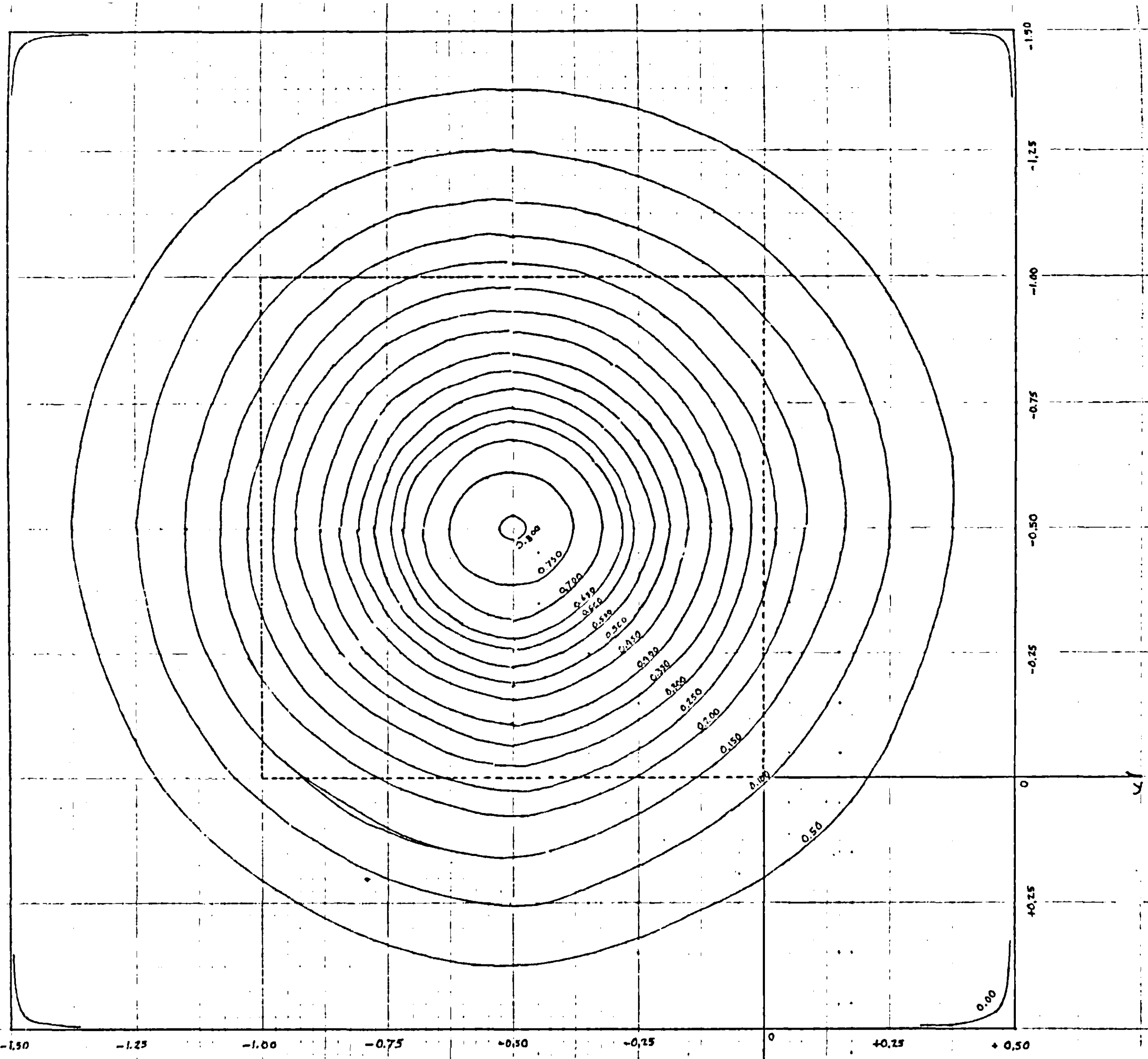

Fig: 5 The ground band Wannier function (Three dimensional) over z = -0.5 plane. We have similiar contours (multiplied by a constant) for planes other than z = -0.5. The maximum of the function occurs at (-0.5, -0.5, -0.5) and is 0.805255. The central unit cell is shown by dashed lines.

9.6 EXACT THREE DIMENSIONAL WANNIER FUNCTIONS FOR HIGHER BANDS

In this particular problem when one goes to second and higher energy bands the situation becomes much more complex since the Wannier functions associated with these bands are no longer seperable. In other terms they may not be constructed from the one dimensional Wannier functions as done before.

In this case as will be shown, one has to construct a composite wave function from several different bands and integrate them over(rather peculiar) B.Z.'s while paying a great deal of attention to certain zone boundaries and the choices of phases in order to end up with a Wannier function with the required characteristics. The calculation could be carried out because we had available the one dimensional wave functions in analytical forms.

Consider then the second band. We start with the construction of the composite wave function in three dimensions. However, since the constituent wave functions 11 and 12 of the one dimensional problem are defined within certain regions only, each time different combinations of them have to be considered in different regions of space. These regions as a consequence of the one dimensional analysis will be cubes of size $a/2 \times a/2 \times a/2$ where a is the lattice spacing in one of the principal directions.

Let us now start with the three dimensional wave function defined within the central cube, $-1 \leq x, y,$ or $z \leq 0$

$$
\begin{aligned}
\Psi(k_1^x, k_1^y, k_1^z, x, y, z) = {} \\
& A(k_1^x)A(k_1^y)A(k_1^z)\,\mathrm{Cos}\,k_1^x(x+0.5)\,\mathrm{Cos}\,k_1^y(y+0.5)\,\mathrm{Cos}\,k_1^z(z+0.5) \\
& +iA(k_1^x)B(k_1^y)A(k_1^z)\,\mathrm{Cos}\,k_1^x(x+0.5)\,\mathrm{Sin}\,k_1^y(y+0.5)\,\mathrm{Cos}\,k_1^z(z+0.5) \\
& +iB(k_1^x)A(k_1^y)A(k_1^z)\,\mathrm{Sin}\,k_1^x(x+0.5)\,\mathrm{Cos}\,k_1^y(y+0.5)\,\mathrm{Cos}\,k_1^z(z+0.5) \\
& -B(k_1^x)B(k_1^y)A(k_1^z)\,\mathrm{Sin}\,k_1^x(x+0.5)\,\mathrm{Sin}\,k_1^y(y+0.5)\,\mathrm{Cos}\,k_1^z(z+0.5) \\
& +iA(k_1^x)A(k_1^y)B(k_1^z)\,\mathrm{Cos}\,k_1^x(x+0.5)\,\mathrm{Cos}\,k_1^y(y+0.5)\,\mathrm{Sin}\,k_1^z(z+0.5) \\
& -A(k_1^x)B(k_1^y)B(k_1^z)\,\mathrm{Cos}\,k_1^x(x+0.5)\,\mathrm{Sin}\,k_1^y(y+0.5)\,\mathrm{Sin}\,k_1^z(z+0.5) \\
& -B(k_1^x)A(k_1^y)B(k_1^z)\,\mathrm{Sin}\,k_1^x(x+0.5)\,\mathrm{Cos}\,k_1^y(y+0.5)\,\mathrm{Sin}\,k_1^z(z+0.5) \\
& -iB(k_1^x)B(k_1^y)B(k_1^z)\,\mathrm{Sin}\,k_1^x(x+0.5)\,\mathrm{Sin}\,k_1^y(y+0.5)\,\mathrm{Sin}\,k_1^z(z+0.5)
\end{aligned}
\tag{51}
$$

Where k_1^x, k_1^y, and k_1^z stand for the square roots of the energy eigenvalues along the k_x, k_y, and k_z directions respectively. In the previous sections we have obtained (explicit) expressions for the functions $A(k_1^x)$, $A(k_1^y)$, $A(k_1^z)$, $B(k_1^x)$, $B(k_1^y)$, and $B(k_1^z)$.

As will be made clear later on, the functional entries given in equation 51 are not necessarily confined to the same energy band.

The space dependence of the wave function is given only by sinusoidal functions where even and odd characters of these functions will be of considerable use in discussions of symmetries both in the configuration and the momentum spaces.

The equation 51 now has to be integrated (subject to certain conditions) over the whole of the second B.Z. shown in figure 6. We have already discussed the possibility of carrying such an integration over k_1^x, k_1^y, and k_1^z instead k_x, k_y, and k_z (the wave vectors) corresponding values of which are readily obtained through the dispersion relations.

A numerical integration of a lengthy function like this(though the function that we consider for the central cube is the simplest of all) over a peculiar zone like the one given below would be rather complicated and tiresome. To minimize the effort one has to make full use of the symmetry in the reciprocal space. Below, we will show how this could be done; The B.Z. in concern has been subdivided into regions 1,2,3,......24 as shown in figure 6 in each of which the function 51 has different character.

Though the volume of a minimal subdivision could reach half of the present one, we have made the present choice for computational reasons.

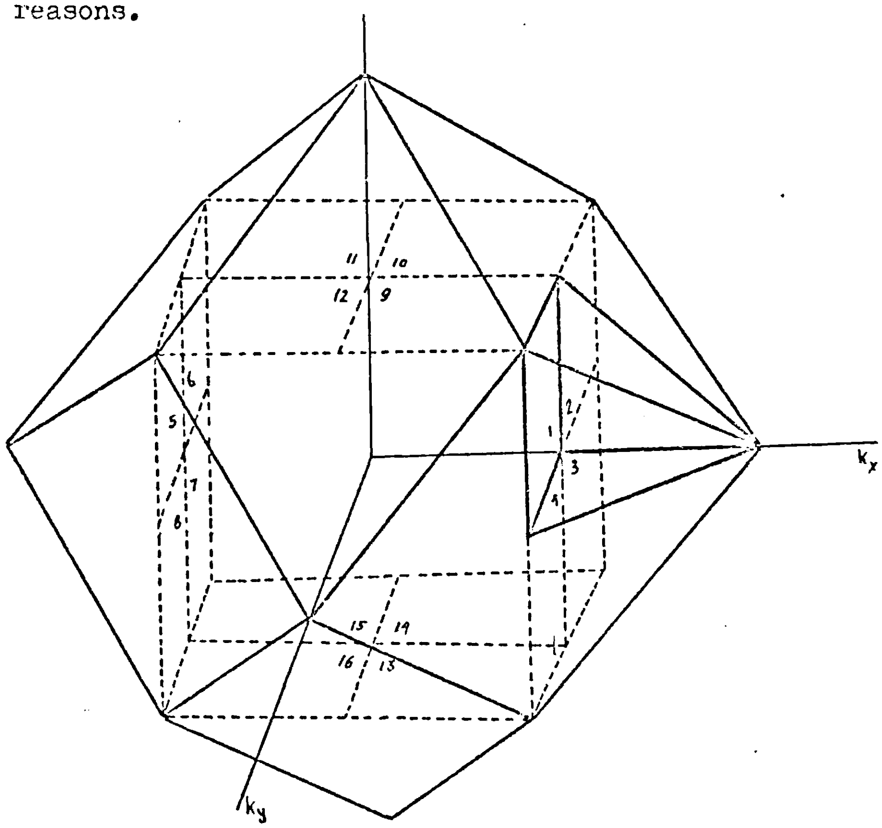

Fig. 6 The second B.Z. subdivided into regions 1,2,...24 The pyramide with number 1 is shown. There are similiar pyramids (though not in the same orientations) at places numbered 2 to 24. Those with numbers 16 to 24 are omitted in order not to complicate the figure.

An important point to be made here is the choice of the arbitrary phases for the wave function in concern. In our approach we will think them as implicit in the coefficient functions $A(k_1^x)$, $A(k_1^y)$, $A(k_1^z)$, $B(k_1^x)$, $B(k_1^y)$, and $B(k_1^z)$. Therefore, the type of Wannier function that is going to be obtained will depend on the symmetry properties of these coefficient functions. However, if we now stuck to the choice of the phases that we have made in the previous sections we end up with a particular Wannier function which in the one dimensional case we have found to be symmetric (and real) for the first and the consequent odd numbered bands and antisymmetric (and pure imaginary) for the second and the subsequent even numbered bands, then to this choice the coefficient functions in different regions of the reciprocal space transform as shown in table 5 The transformation of the total wave function is given by a combination of these individual transformations.

zone	1	2	3	4	5	6	7	8
operation	$k_x \; k_y \; k_z$	$k_x \, -k_y \; k_z$	$k_x \, -k_y \, -k_z$	$k_x \; k_y \, -k_z$	$-k_x \; k_y \; k_z$	$-k_x \, -k_y \; k_z$	$-k_x \, -k_y \, -k_z$	$-k_x \; k_y \, -k_z$
$A(k_1^x)$	+1	+1	+1	+1	−1	−1	−1	−1
$A(k_1^y)$	+1	+1	+1	+1	+1	+1	+1	+1
$A(k_1^z)$	+1	+1	+1	+1	+1	+1	+1	+1
$B(k_1^x)$	+1	+1	+1	+1	−1	−1	−1	−1
$B(k_1^y)$	+1	+1	+1	+1	+1	+1	+1	+1
$B(k_1^z)$	+1	+1	+1	+1	+1	+1	+1	+1

Table 5 The transformation of the coefficient functions in the first eight regions of the reciprocal space. A negative number denotes that the function in concern changes sign in the particular region. The reason for considering only eight of the regions will soon be clear.

We will now employ a short notation in order to avoid lenghty writings, i.e. the sinusoidal functions which represent the space dependence of the total wave function $\Psi(k_1^x, k_1^y, k_1^z, x, y, z)$ will be written as $S(k_1^x, x)$, $C(k_1^x, x)$ etc. where the letters S or C refer to sine or cosine like functions respectively. To this notation the first term of equation 51 will now read

$$A(k_1^x)\,A(k_1^y)\,A(k_1^z)\,C(k_1^x, x)\,C(k_1^y, y)\,C(k_1^z, z) \qquad 52$$

The sinusoidal functions of equation 51 which multiply the coefficient functions already described are even or odd functions of the wave vectors k_x, k_y and k_z . One could therefore include them in the tables similiar to 5 , however, the next thing we would like to work out is not the transformation properties of the total wave function but those of the integral expressions arising from the integrations of it s constitituent parts over a part of the zone.

If we now consider the integral values of all eight terms of equation 51 in the first region only, we get i.e. for the first term

$$+\sum_{k_x}\sum_{k_y}\sum_{k_z} A(k_1^x)A(k_1^y)A(k_1^z)\,C(k_1^x, x)\,C(k_1^y, y)\,C(k_1^z, z) \qquad 52$$

where the triple sum runs over the values of the wave vectors confined to the volume of the square pyramid denoted as region one

$$+\pi/a \le k_x \le 2\pi/a\ ,\quad 0 \le k_y \le +\pi/a\ ,\quad 0 \le k_z \le +\pi/a \qquad 53$$

The integral expressions arising from similiar triple sums (which are functions of x,y, and z only) of each of the eight terms in equation 51 now transform as follows

function \ Zone	1	2	3	4
Operation	$k_x\ k_y\ k_z$	$k_x\ -k_y\ k_z$	$k_x\ -k_y\ -k_z$	$k_x\ k_y\ -k_z$
$A(k_1^x)A(k_1^y)A(k_1^z)C(k_1^x,x)C(k_1^y,y)C(k_1^z,z)$	+1	+1	+1	+1
$A(k_1^x)B(k_1^y)A(k_1^z)C(k_1^x,x)S(k_1^y,y)C(k_1^z,z)$	+1	-1	-1	+1
$B(k_1^x)A(k_1^y)A(k_1^z)S(k_1^x,x)C(k_1^y,y)C(k_1^z,z)$	+1	+1	+1	+1
$B(k_1^x)B(k_1^y)A(k_1^z)S(k_1^x,x)S(k_1^y,y)C(k_1^z,z)$	+1	-1	-1	+1
$A(k_1^x)A(k_1^y)B(k_1^z)C(k_1^x,x)C(k_1^y,y)S(k_1^z,z)$	+1	+1	-1	-1
$A(k_1^x)B(k_1^y)B(k_1^z)C(k_1^x,x)S(k_1^y,y)S(k_1^z,z)$	+1	-1	+1	-1
$B(k_1^x)A(k_1^y)B(k_1^z)S(k_1^x,x)C(k_1^y,y)S(k_1^z,z)$	+1	+1	-1	-1
$B\ k_1^x)B(k_1^y)B(k_1^z)S(k_1^x,x)S(k_1^y,y)S(k_1^z,z)$	+1	-1	+1	-1

Table 6

function \ Zone	5	6	7	8
Operation	$-k_x\ k_y\ k_z$	$-k_x\ -k_y\ k_z$	$-k_x\ -k_y\ -k_z$	$-k_x\ k_y\ -k_z$
$A(k_1^x)A(k_1^y)A(k_1^z)C(k_1^x,x)C(k_1^y,y)C(k_1^z,z)$	-1	-1	-1	-1
$A(k_1^x)B(k_1^y)A(k_1^z)C(k_1^x,x)S(k_1^y,y)C(k_1^z,z)$	-1	+1	+1	-1
$B(k_1^x)A(k_1^y)A(k_1^z)S(k_1^x,x)C(k_1^y,y)C(k_1^z,z)$	+1	+1	+1	+1
$B(k_1^x)B(k_1^y)A(k_1^z)S(k_1^x,x)S(k_1^y,y)C(k_1^z,z)$	+1	-1	-1	+1
$A(k_1^x)A(k_1^y)B(k_1^z)C(k_1^x,x)C(k_1^y,y)S(k_1^z,z)$	-1	-1	+1	+1
$A(k_1^x)B(k_1^y)B(k_1^z)C(k_1^x,x)S(k_1^y,y)S(k_1^z,z)$	-1	+1	-1	+1
$B(k_1^x)A(k_1^y)B(k_1^z)S(k_1^x,x)C(k_1^y,y)S(k_1^z,z)$	+1	+1	-1	-1
$B(k_1^x)B(k_1^y)B(k_1^z)S(k_1^x,x)S(k_1^y,y)S(k_1^z,z)$	+1	-1	+1	-1

Table 7

As a result of the tables 6 and 7, the only nonvanishing function (resulting from the terms in the third row of tables 6 and 7) of space coordinates x,y, and z is

$$\alpha_1(x,y,z) = 8i \sum_{k_x} \sum_{k_y} \sum_{k_z \, (1^{st} \text{ Subzone})} B(k_1^x) A(k_1^y) A(k_1^z) \, \text{Sin}\, k_1^x(x+0.5) \, \text{Cos}\, k_1^y(y+0.5) \, \text{Cos}\, k_1^z(z+0.5) \tag{54}$$

So far we have integrated equation 51 only over the first eight subzones. To find the results of integrations over the sixteen remaining subzones one has to follow a way similiar to what we have just done. However, here we will quote the results only.

For ninth to sixteenth subzones (resulting from the functions in the fifth row of the previous tables).

$$\alpha_2(x,y,z) = 8i \sum_{k_z} \sum_{k_x} \sum_{k_y \, (9^{th} \text{ Subzone})} A(k_1^x) A(k_1^y) B(k_1^z) \, \text{Cos}\, k_1^x(x+0.5) \, \text{Cos}\, k_1^y(y+0.5) \, \text{Sin}\, k_1^z(z+0.5) \tag{55}$$

For seventeenth to twentyfourth subzones (resulting from the functions in the second row of the same tables)

$$\alpha_3(x,y,z) = 8i \sum_{k_y} \sum_{k_z} \sum_{k_x \, (17^{th} \text{ Subzone})} A(k_1^x) B(k_1^y) A(k_1^z) \, \text{Cos}\, k_1^x(x+0.5) \, \text{Sin}\, k_1^y(y+0.5) \, \text{Cos}\, k_1^z(z+0.5) \tag{56}$$

The three dimensional Wannier function for the second band is now given by

$$a_2(x,y,z) = \alpha_1(x,y,z) + \alpha_2(x,y,z) + \alpha_3(x,y,z) \tag{57}$$

The first of these functions (on the right hand side) has the same symmetry properties as a p_x like atomic orbital, the second that of a p_y like atomic orbital and finally the third that of a p_z like atomic orbital under the point group.

Therefore the resulting Wannier function is an antisymmetric function of the space coordinates (about the origin x,y,z =-0.5)

The present problem is the calculation of the constituent functions $\alpha_1(x,y,z)$, $\alpha_2(x,y,z)$, and $\alpha_3(x,y,z)$ where to obtain each one has to run a seperate triple sum over the values of the wave vectors confined to a different region.This is not desirable for computational reasons. However certain symmetry considerations simplify the calculation and the final Wannier function may be obtained by a single triple summation over the values of the wave vectors k_x,k_y,and k_z which are all confined to the first region only (the latter considerations involve transformations on the space coordinates which follow a permutational order). The final Wannier function is now given by

$$a_z(x,y,z) = 8i \sum_{\substack{k_x\ k_y\ k_z \\ 1^{st}\ \text{Subzone}}} \sum \sum B(k_1^x)A(k_1^y)A(k_1^z)\Big\{ \text{Sin}\,k_1^x(x+0.5)\ \text{Cos}\,k_1^y(y+0.5)\ \text{Cos}\,k_1^z(z+0.5) + \text{Sin}\,k_1^x(y+0.5)\ \text{Cos}\,k_1^y(z+0.5)\ \text{Cos}\,k_1^z(x+0.5) + \text{Sin}\,k_1^x(z+0.5)\ \text{Cos}\,k_1^y(x+0.5)\ \text{Cos}\,k_1^z(y+0.5) \Big\} \qquad 58$$

In the above equation the variation of space coordinates x,y, and z is restricted to a single cube only, $-1 \leq x,y,\text{or } z \leq 0$.

It took us around two minutes on a modern computer to obtain several hundred values for the function within the cube defined (including all preliminary computations) . In the following tables (i.e. see table 10) we quote the results only.

Let us now calculate the Wannier function in the next cube ($0 \leqq x,y,$ or $z \leqq +1$) along a diagonal direction.

The total wave function is now given by (in the following equation we do not write the real and imaginary parts of the coefficient functions $C(k_2)$'s and $D(k_2)$'s seperately as we usually did in the one dimensional calculations since that would mean handling an expression eight times larger than the one given below)

$$\begin{aligned}\psi_2(k_2^x, k_2^y, k_2^z, x,y,z) = {} & C(k_2^x)\,C(k_2^y)\,C(k_2^z)\,\mathrm{Cos}\,k_2^x x\ \mathrm{Cosk}\ k_2^y y\ \mathrm{Cos}\,k_2^z z \\ & C(k_2^x)\,D(k_2^y)\,C(k_2^z)\,\mathrm{Cos}\,k_2^x x\ \mathrm{Sinh}\,k_2^y y\ \mathrm{Cosh}\,k_2^z z \\ & D(k_2^x)\,C(k_2^y)\,C(k_2^z)\,\mathrm{Sin}\,k_2^x x\ \mathrm{Cosh}\,k_2^y y\ \mathrm{Cosh}\,k_2^z z \\ & D(k_2^x)\,D(k_2^y)\,C(k_2^z)\,\mathrm{Sin}\,k_2^x x\ \mathrm{Sinh}\,k_2^y y\ \mathrm{Cosh}\,k_2^z z \\ & C(k_2^x)\,C(k_2^y)\,D(k_2^z)\,\mathrm{Cos}\,k_2^x x\ \mathrm{Sinh}\,k_2^y y\,\mathrm{Sinh}\,k_2^z z \\ & C(k_2^x)\,D(k_2^y)\,D(k_2^z)\,\mathrm{Cos}\,k_2^x x\ \mathrm{Sinh}\,k_2^y y\ \mathrm{Sinh}\,k_2^z z \\ & D(k_2^x)\,C(k_2^y)\,D(k_2^z)\,\mathrm{Sin}\,k_2^x x\ \mathrm{Cosh}\,k_2^y y\ \mathrm{Sinh}\,k_2^z z \\ & D(k_2^x)\,D(k_2^y)\,D(k_2^z)\,\mathrm{Sin}\,k_2^x x\ \mathrm{Sinh}\,k_2^y y\ \mathrm{Sinh}\,k_2^z z\end{aligned} \qquad 59$$

where k_2^x, k_2^y, and k_2^z stand for the square root of kinetic energy along the principal directions x,y, and z.

In the present case the situation is more involved since the coefficient functions $C(k_2^x)$, $C(k_2^y)$, $C(k_2^z)$, $D(k_2^x)$ $D(k_2^y)$, and $D(k_2^z)$ are complex quantities.

As usual, we start by working out the transformation properties of the coefficient functions mentioned above (which are basically different than those given earlier). In the following table we quote the results

Zone	1	2	3	4	5	6	7	8
Operation	$k_x\ k_y\ k_z$	$k_x\ -k_y\ k_z$	$k_x\ -k_y\ -k_z$	$k_x\ k_y\ -k_z$	$-k_x\ k_y\ k_z$	$-k_x\ -k_y\ k_z$	$-k_x\ -k_y\ -k_z$	$-k_x\ k_y\ -k_z$
$C(k_z^x)$	$+1$	$+1$	$+1$	$+1$	-1^*	-1^*	-1^*	-1^*
$C(k_z^y)$	$+1$	$+1^*$	$+1^*$	$+1$	$+1$	$+1^*$	$+1^*$	$+1$
$C(k_z^z)$	$+1$	$+1$	$+1^*$	$+1^*$	$+1$	$+1$	$+1^*$	$+1^*$
$D(k_z^x)$	$+1$	$+1$	$+1$	$+1$	$+1^*$	$+1^*$	$+1^*$	$+1^*$
$D(k_z^y)$	$+1$	-1^*	-1^*	$+1$	$+1$	-1^*	-1^*	$+1$
$D(k_z^z)$	$+1$	$+1$	-1^*	-1^*	$+1$	$+1$	-1^*	-1^*

Table 8 The transformations of the coefficient functions (complex) in the first eight regions of the reciprocal space. A positive number means that the function remains unchanged under the operation in concern. A negative or a positive number with a star means a complex conjugate operation accompanied with or without a change in the sign of the function respectively.

The functions arising from integrations of each of the eight terms of equation 59 in the first region of reciprocal space, now transform as shown in the tables given below (In the present case C and D are complex quantities and the transformations do also involve complex conjugate operations on different parts of a constitutent term. Further, we will employ a different representation than we did before, the indices 1,2, and 3 associated with the functions given below refer to the principal directions x,y, and z respectively, also for shorter notation the total sinusoidal parts of each of the eight constitutent functions (space dependent) in equation 59 will now be represented by $\gamma_1, \gamma_2, \cdots \gamma_8$).

Zone	1	2	3	4
Operation	$k_x \quad k_y \quad k_z$	$k_x \quad -k_y \quad k_z$	$k_x - k_y - k_z$	$k_x \quad k_y - k_z$
First term	$C_1 C_2 C_3 \gamma_1$	$C_1 C_2^* C_3 \gamma_1$	$C_1 C_2^* C_3^* \gamma_1$	$C_1 C_2 C_3^* \gamma_1$
2nd	$C_1 D_2 C_3 \gamma_2$	$C_1 D_2^* C_3 \gamma_2$	$C_1 D_2^* C_3^* \gamma_2$	$C_1 D_2 C_3^* \gamma_2$
3rd	$D_1 C_2 C_3 \gamma_3$	$D_1 C_2^* C_3 \gamma_3$	$D_1 C_2^* C_3^* \gamma_3$	$D_1 C_2 C_3^* \gamma_3$
4th	$D_1 D_2 C_3 \gamma_4$	$D_1 D_2^* C_3 \gamma_4$	$D_1 D_2^* C_3^* \gamma_4$	$D_1 D_2 C_3^* \gamma_4$
5th	$C_1 C_2 D_3 \gamma_5$	$C_1 C_2^* D_3 \gamma_5$	$C_1 C_2^* D_3^* \gamma_5$	$C_1 C_2 D_3^* \gamma_5$
6th	$C_1 D_2 D_3 \gamma_6$	$C_1 D_2^* D_3 \gamma_6$	$C_1 D_2^* D_3^* \gamma_6$	$C_1 D_2 D_3^* \gamma_6$
7th	$D_1 C_2 D_3 \gamma_7$	$D_1 C_2^* D_3 \gamma_7$	$D_1 C_2^* D_3^* \gamma_7$	$D_1 C_2 D_3^* \gamma_7$
8th	$D_1 D_2 D_3 \gamma_8$	$D_1 D_2^* D_3 \gamma_8$	$D_1 D_2^* D_3^* \gamma_8$	$D_1 D_2 D_3^* \gamma_8$

(a)

Zone	5	6	7	8
Operation	$-k_x \quad k_y \quad k_z$	$-k_x - k_y \quad k_z$	$-k_x - k_y - k_z$	$-k_x \quad k_y - k_z$
First term	$-C_1^* C_2 C_3 \gamma_1$	$-C_1^* C_2^* C_3 \gamma_1$	$-C_1^* C_2^* C_3^* \gamma_1$	$-C_1^* C_2 C_3^* \gamma_1$
2nd	$-C_1^* D_2 C_3 \gamma_2$	$-C_1^* D_2^* C_3 \gamma_2$	$-C_1^* D_2^* C_3^* \gamma_2$	$-C_1^* D_2 C_3^* \gamma_2$
3rd	$-D_1^* C_2 C_3 \gamma_3$	$-D_1^* C_2^* C_3 \gamma_3$	$-D_1^* C_2^* C_3^* \gamma_3$	$-D_1^* C_2 C_3^* \gamma_3$
4th	$-D_1^* D_2 C_3 \gamma_4$	$-D_1^* D_2^* C_3 \gamma_4$	$-D_1^* D_2^* C_3^* \gamma_4$	$-D_1^* D_2 C_3^* \gamma_4$
5th	$-C_1^* C_2 D_3 \gamma_5$	$-C_1^* C_2^* D_3 \gamma_5$	$-C_1^* C_2^* D_3^* \gamma_5$	$-C_1^* C_2 D_3^* \gamma_5$
6th	$-C_1^* D_2 D_3 \gamma_6$	$-C_1^* D_2^* D_3 \gamma_6$	$-C_1^* D_2^* D_3^* \gamma_6$	$-C_1^* D_2 D_3^* \gamma_6$
7th	$-D_1^* C_2 D_3 \gamma_7$	$-D_1^* C_2^* D_3 \gamma_7$	$-D_1^* C_2^* D_3^* \gamma_7$	$-D_1^* C_2 D_3^* \gamma_7$
8th	$-D_1^* D_2 D_3 \gamma_8$	$-D_1^* D_2^* D_3 \gamma_8$	$-D_1^* D_2^* D_3^* \gamma_8$	$-D_1^* D_2 D_3^* \gamma_8$

(b)

Table 9 Transformation of the functions arising from the integrations in the first region of the reciprocal space; a) in the first four zones b) fifth to eighth zones.

In the table given above we have 64 integral expressions in each of which there is an unknown function (of space coordinates x,y, and z) appearing always under the same integral sign. Now further seperating the coefficient functions $C(k_i^x)$, $C(k_i^y)$, $C(k_i^z)$, $D(k_i^x)$, $D(k_i^y)$ and $D(k_i^z)$

into their real and imaginary parts as we did in the one dimensional calculations and denoting them as $REC_1, REC_2, REC_3, IMC_1, IMC_2$, and IMC_3 $RED_1, \ldots$, etc. where as usual the subscripts 1,2, and 3 refer to the choice of these functions along the principal directions x,y, and z, and summing up the integral expressions (seperately for each of the eight rows) of tables 9a and b, we find the following

$$\begin{aligned}
&8i\, IMC_1 REC_2 REC_3 \gamma_1\\
&8i\, IMC_1 RED_2 REC_3 \gamma_2\\
&8i\, IMD_1 REC_2 REC_3 \gamma_3\\
&8i\, IMD_1 RED_2 REC_3 \gamma_4\\
&8i\, IMC_1 REC_2 RED_3 \gamma_5\\
&8i\, IMC_1 RED_2 RED_3 \gamma_6\\
&8i\, IMD_1 REC_2 RED_3 \gamma_7\\
&8i\, IMD_1 RED_2 RED_3 \gamma_8
\end{aligned} \tag{60}$$

Substituting the expressions for $\gamma_1, \gamma_2 \cdots \gamma_8$ and after a number of operations the last equation can be given as the following product, which as before we will call $\alpha_1(x,y,z)$

$$\begin{aligned}
\alpha_1(x,y,z) = 8i \sum_{k_x} \sum_{k_y} \sum_{k_z} \Big[& \Big\{ IMC(k_2^x) Cos(k_2^x)x + IMD(k_2^x) Sin(k_2^x)x \Big\} \Big\{ REC(k_2^y) Cosh(k_2^y)y \\
& + RED(k_2^y) Sink(k_2^y)y \Big\} \Big\{ REC(k_2^z) Cosh(k_2^z)z + RED(k_2^z) Sinh(k_2^z)z \Big\} \Big]
\end{aligned} \tag{61}$$

The results (α_2 and α_3) arising from the sums of the integral equations for the sixteen remaining subzones can be found through arguments similiar to those given in the previous section. To save space, below we quote the results only, the final Wannier function is now given by

$$\begin{aligned} a_2(x,y,z) = 8i \sum\sum\sum & \Big\{ IMC(k_1^x)\,Cos(k_1^x)x + IMD(k_2^x)\,Sin(k_2^x)x \Big\} \Big\{ REC(k_2^y)\,Cosh(k_2^y)y \\ & + RED(k_2^y)\,Sinh(k_2^y)y \Big] \Big\{ REC(k_2^z)\,Cosh(k_2^z)z + RED(k_2^z)\,Sinh(k_2^z)z \Big\} \\ & + \Big\{ IMC(k_2^x)\,Cos(k_2^x)z + IMD(k_2^x)\,Sin(k_2^x)z \quad REC(k_2^y)\,Cosh(k_2^y)x \\ & + RED(k_2^y)\,Sinh(k_2^y)x \Big] \Big\{ REC(k_2^z)\,Cosh(k_2^z)y + RED(k_2^z)\,Sinh(k_2^z)y \Big\} \\ & + \Big\{ IMC(k_2^x)\,Cos(k_2^x)y + IMD(k_2^x)\,Sin(k_2^x)y \Big\} \Big\{ REC(k_2^y)\,Cosh(k_2^y)z \\ & + RED(k_2^y)\,Sinh(k_2^y)z \Big] \Big\{ REC(k_2^z)\,Cosh(k_2^z)x + RED(k_2^z)\,Sinh(k_2^z)x \Big\} \end{aligned} \tag{62}$$

The variation of space coordinates x,y, and z in the above equation is restricted to the region $0 \leq x, y, \text{or } z \leq +1$. The integral (or the triple sum) is as usual over the first subzone only. It took us around three to four minutes on a modern computer to obtain several hundred values for the function within the region defined.

In the following table (11) we quote these results.

9.13 THE WANNIER FUNCTION AT LARGE DISTANCES FROM THE ORIGIN

As mentioned earlier, to find Wannier functions for any cubic region (of interest) in coordinate space one first has to construct the three dimensional wave function appropriate to the region chosen. Then the wave function at a region displaced from the previous one by $\underline{R}_n = n_x \underline{a}_x + n_y \underline{a}_y + n_z \underline{a}_z$ is given by

$$\exp(i k_x n_x a_x + i k_y n_y a_y + i k_z n_z a_z)\, \psi(k_i^x, k_i^y, k_i^z, x, y, z) \qquad 63$$

where $i = 1, 2$. In this case the formulations as should be expected are more complicated than the previous cases, since in considering transformation properties of the total wave function in the reciprocal space one must also take into account that of the exponential functions. However once this has been done then the values for the Wannier function can be computed at as many cells as required by setting a variation (in the main program) on the integers n_x , n_y , and n_z .

As an illustration we give an analytical expression for the Wannier function at a cell displaced from the central one by

$$n_x \underline{a}_x + n_y \underline{a}_y + n_z \underline{a}_z \qquad 64$$

The formulations and the tables that have been used in obtaining this expression are rather lengthy to represent (and involves use of the previous tables associated with the tables representing the transformation properties of the exponential functions) therefore below we quote the results only.

$$
\begin{aligned}
&a_2(x,y,z,2n_x,2n_y,2n_z)\\
&=8i\sum_{k_x}\sum_{k_y}\sum_{k_z} +A(k_1^x)A(k_1^y)A(k_1^z)C(k_1^x,x)C(k_1^y,y)C(k_1^z,z)\,\mathrm{Sin}\,2n_xk_x\,\mathrm{Cos}\,2n_yk_y\,\mathrm{Cos}\,2n_zk_z\\
&\qquad -A(k_1^x)B(k_1^y)A(k_1^z)C(k_1^x,x)S(k_1^y,y)C(k_1^z,z)\,\mathrm{Sin}\,2n_xk_x\,\mathrm{Sin}\,2n_yk_y\,\mathrm{Cos}\,2n_zk_z\\
&\qquad +B(k_1^x)A(k_1^y)A(k_1^z)S(k_1^x,x)C(k_1^y,y)C(k_1^z,z)\,\mathrm{Cos}\,2n_xk_x\,\mathrm{Cos}\,2n_yk_y\,\mathrm{Cos}\,2n_zk_z \quad +\cdots\cdots+\cdots\cdots\\
&\qquad -B(k_1^x)B(k_1^y)A(k_1^z)S(k_1^x,x)S(k_1^y,y)C(k_1^z,z)\,\mathrm{Cos}\,2n_xk_x\,\mathrm{Sin}\,2n_yk_y\,\mathrm{Cos}\,2n_zk_z\\
&\qquad -B(k_1^x)A(k_1^y)B(k_1^z)S(k_1^x,x)C(k_1^y,y)S(k_1^z,z)\,\mathrm{Sin}\,2n_xk_x\,\mathrm{Cos}\,2n_yk_y\,\mathrm{Sin}\,2n_zk_z\\
&\qquad +A(k_1^x)B(k_1^y)B(k_1^z)C(k_1^x,x)\quad(k_1^y,y)S(k_1^z,z)\,\mathrm{Sin}\,2n_xk_x\,\mathrm{Sin}\,2n_yk_y\,\mathrm{Sin}\,2n_zk_z\\
&\qquad -B(k_1^x)A(k_1^y)B(k_1^z)S(k_1^x,x)C(k_1^y,y)S(k_1^z,z)\,\mathrm{Cos}\,2n_xk_x\,\mathrm{Cos}\,2n_yk_y\,\mathrm{Sin}\,2n_zk_z\\
&\qquad -B(k_1^x)B(k_1^y)B(k_1^z)S(k_1^x,x)S(k_1^y,y)S(k_1^z,z)\,\mathrm{Cos}\,2n_xk_x\,\mathrm{Sin}\,2n_yk_y\,\mathrm{Sin}\,2n_zk_z
\end{aligned}
\tag{65}
$$

where $2n_x-1 \leq x \leq 2n_x$, $2n_y-1 \leq y \leq 2n_y$, and $2n_z-1 \leq z \leq 2n_z$, and the lattice parameters along three principal directions are $a_x, a_y, a_z = 2$. The other two terms (that we haven't shown in the equation) are to be obtained through permutations over x , y , and z . The equation looks rather lengthy due to the reason that we have derived it for the most general case. However in calculations associated with the cells along the principal directions (i.e for $n_x \neq 0$, $n_y, n_z = 0$ or $n_y \neq 0$, $n_x, n_z = 0$ etc.) the number of terms that one has to deal with reduces at once from 24 to 6 . Further in calculating the Wannier function within the cells lying on xy, xz , and yz planes ($n_x, n_y \neq 0$, $n_z = 0$ etc) one has to consider 12 terms only. In the final case of calculations along any of the body diagonals ($n_x, n_y, n_z \neq 0$) one has to consider all of the terms of the expression given above. For checking purposes only if one sets simultaneously n_x , n_y , and $n_z = 0$, the expression given above becomes identical with equation 58 which is the expression for the Wannier function within the central cell.

Neverthless, once the values of the coefficient functions have been supplied as an input in the main program (as we have done) then the Wannier function within any subsequent distant cell and for as many points as required can be obtained by means of a single program only.

However, in preparation of such a program extreme care should be spent since one (provided that the dispersion relations and the coefficient fuctions are provided explicitly as inputs) has to set simultaneous variations on a large number of parameters (9 altogether)

	y x	-0.500	-0.375	-0.250	-0.125	0.000
z=-0.500	-0.500	0.0000	0.3280	0.6236	0.8578	1.0078
	-0.375	0.3280	0.6450	0.9195	1.1234	1.2352
	-0.250	0.6236	0.9195	1.1647	1.3332	1.4054
	-0.125	0.8578	1.1234	1.3332	1.4639	1.4983
	0.000	1.0078	1.2352	1.4054	1.4983	1.4997
z=-0.375	-0.500	0.3280	0.6450	0.9195	1.1234	1.2352
	-0.375	0.6450	0.9514	1.2053	1.3799	1.4548
	-0.250	0.9195	1.2053	1.4314	1.5725	1.6 01
	-0.125	1.1234	1.3799	1.5725	1.6785	1.6819
	0.000	1.2352	1.4548	1.6101	1.6819	1.6567
z=-0.250	-0.500	0.6236	0.9195	1.1647	1.3332	1.4054
	-0.375	0.9195	1.2053	1.4314	1.5725	1.6101
	-0.250	1.1647	1.4314	1.6317	1.7422	1.7462
	-0.125	1.3332	1.5725	1.7422	1.8214	1.7956
	0.000	1.4054	1.6101	1.7462	1.7956	1.7465
z=-0.125	-0.500	0.8578	1.1234	1.3332	1.4639	1.4983
	-0.375	1.1234	1.3749	1.5725	1.6785	1.6819
	-0.250	1.3332	1.5725	1.7422	1.8214	1.7956
	-0.125	1.4639	1.6785	1.8214	1.8740	1.8236
	0.000	1.4983	1.6819	1.7956	1.8236	1.7554
z= 0.000	-0.500	1.0078	1.2352	1.4054	1.4983	1.4997
	-0.375	1.2352	1.4548	1.6101	1.6819	1.6567
	-0.250	1.4054	1.6101	1.7462	1.7956	1.7465
	-0.125	1.4983	1.6819	1.7956	1.8236	1.7554
	0.000	1.4997	1.6567	1.7465	1.7554	1.6724

Table 10 The second band Wannier function (in three dimensions)

		x				
	y	0.000	0.250	0.500	0.750	1.000
	0.000	1.6724	1.4341	1.2094	0.9834	0.7655
	0.250	1.4341	1.1994	0.9916	0.7979	0.6239
z=0.000	0.500	1.2094	0.9916	0.8043	0.6363	0.4916
	0.750	0.9834	0.7979	0.6363	0.4905	0.3650
	1.000	0.7655	0.6239	0.4916	0.3650	0.2512
	0.000	1.4341	1.1994	0.9916	0.7979	0.6239
	0.250	1.1994	0.9844	0.8022	0.6409	0.5039
z=0.250	0.500	0.9916	0.8022	0.6441	0.5076	0.3952
	0.750	0.7979	0.6409	0.5076	0.3911	0.2946
	1.000	0.6239	0.5039	0.3952	0.2946	0.2076
	0.000	1.2094	0.9916	0.8043	0.6363	0.4916
	0.250	0.9916	0.8022	0.6441	0.5076	0.3952
z=0.500	0.500	0.8043	0.6441	0.5113	0.3981	0.3067
	0.750	0.6363	0.5076	0.3981	0.3026	0.2242
	1.000	0.4916	0.3952	0.3067	0.2242	0.1525
	.000	0.9834	0.7979	0.6363	0.4905	0.3650
	0.250	0.7979	0.6409	0.5076	0.3911	0.2946
z=0.750	0.500	0.6363	0.5076	0.3981	0.3026	0.2242
	0.750	0.4905	0.3911	0.3026	0.2222	0.1537
	1.000	0.3650	0.2946	0.2242	0.1537	0.0888
	0.000	0.7655	0.6239	0.4916	0.3650	0.2512
	0.250	0.6239	0.5039	0.3952	0.2946	0.2076
z=1.000	0.500	0.4916	0.3952	0.3067	0.2242	0.1525
	0.750	0.3650	0.2946	0.2242	0.1537	0.0888
	1.000	0.2512	0.2076	0.1525	0.0888	0.0236

Table 11 The second band Wannier function (in three dimensions)

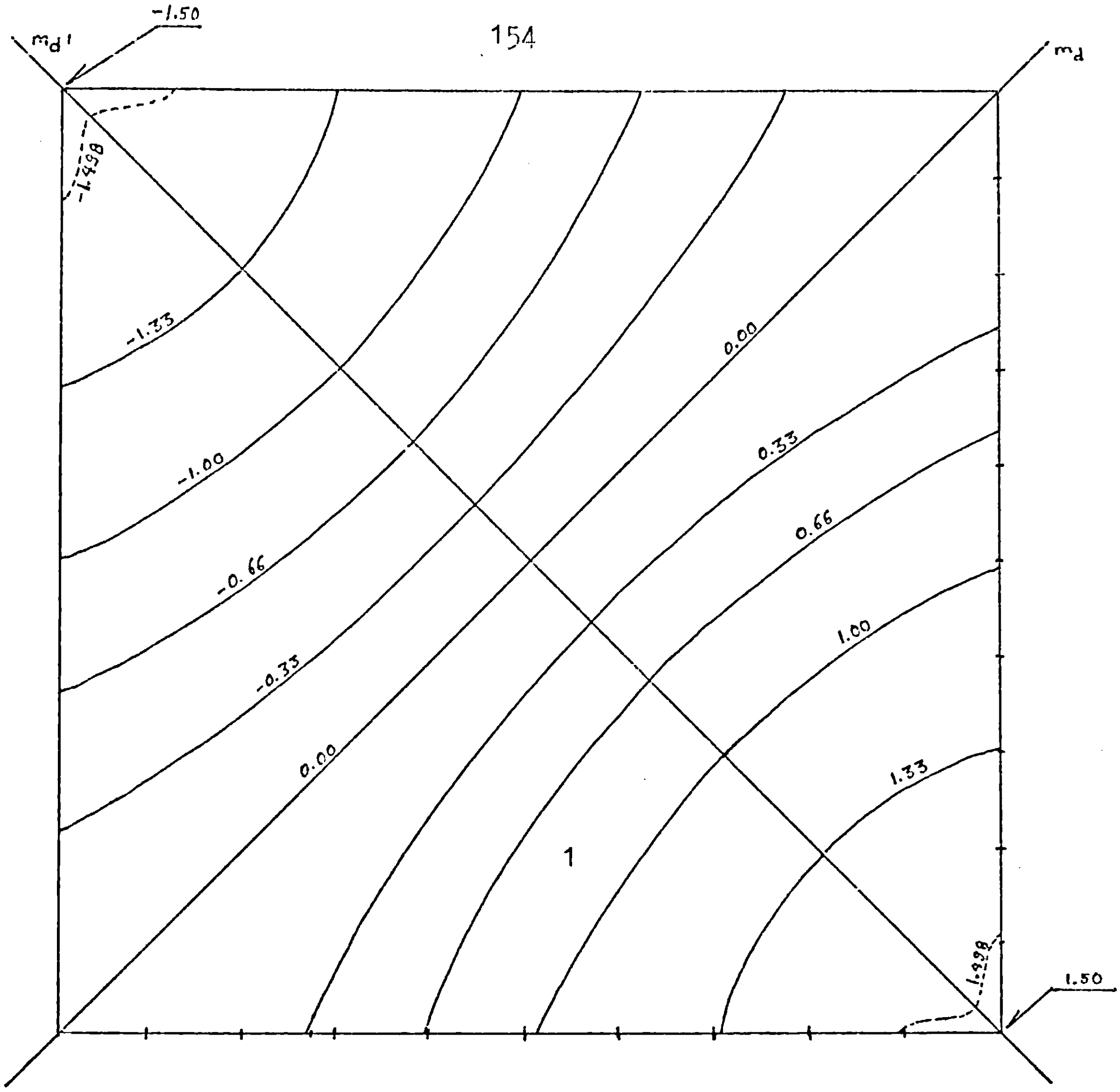

Fig. 7 Wannier function for second band, three dimensional case, for z =-0.5 (the plane through the origin)

The function in region 1 (see the fig. above) transforms as follows,

	E	$m_{d'}$	m_d	C_2
$a_2(x,y,z=-0.5)$	+1	+1	-1	-1

Therefore if only one-fourth of the elementary cell (i.e. region 1 of fig. 7) is filled then the function[1] can be extended by using (successively) it's symmetry or antisymmetry on reflection in the 45° lines m_d and $m_{d'}$.

The function is identically zero on the line m_d.

---

[1] The combination of the symmetry operations m_d and $m_{d'}$ results in the operation C_2 (or J, inversion with respect to the point (-0.5,-0.5,-0.5)), therefore, for this particular case the outcoming function has inversion symmetry about the center of the plane considered.

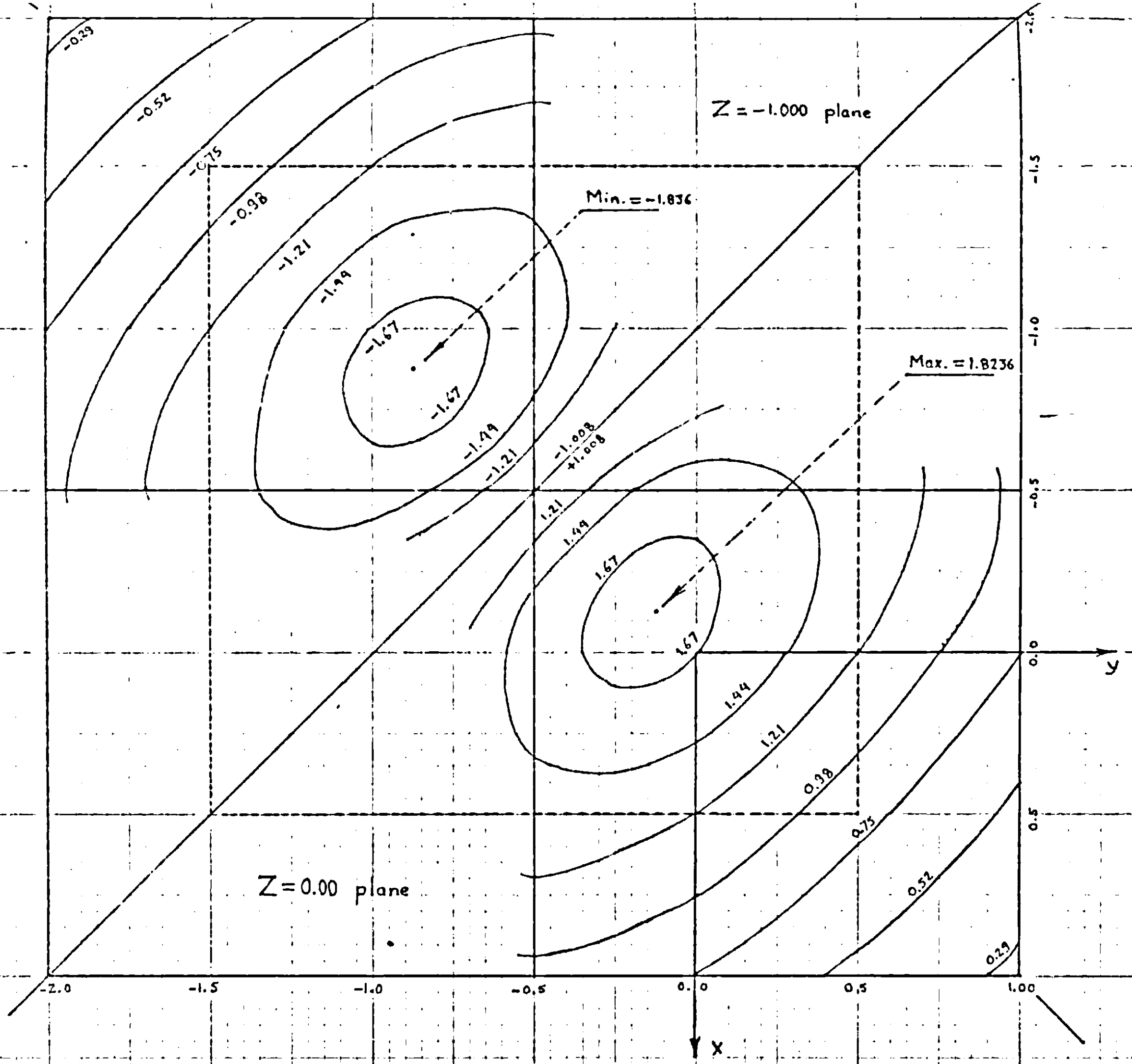

Fig. 8 The second band Wannier function (three dimensional) for $z=0.000$ and $z=-1.000$ (two different planes are shown in the same picture). The central unit cell where the function is localized is shown by dotted lines. The function (on both planes) is symmetrical on reflection in in the 45° ($x=y$, $z=0.000$ or $x=y$, $z=-1.000$) lines, and has inversion symmetry with respect to the origin $(-0.5, -0.5, -0.5)$.

The maximum of the function occurs at $x=-0.125$, $y=-0.125$, $z=0.000$, and is 1.8236. The minimum (-1.8236) is at $x=-0.875$, $y=-0.875$, $z=-1$. The function reads similiar values over the planes $x=0.000$, $x=-1.000$ and $y=0.000$, $y=-1.000$, and there are three such (equivalent) maxima and minima (The point of inversion is at $x, y, z = -0.5$)

CHAPTER 10

THE APPROXIMATE WANNIER FUNCTIONS FOR TIGHTLY BOUND ELECTRONS

10.1 GENERAL

In chapter 4 we have calculated the free electron Wannier functions for several crystal types. In this chapter we shall study the Wannier functions for tightly bound electrons, as opposed to those for free electrons. As we shall see later on, the title " Approximate " for the Wannier functions comes from the fact that the tight binding method is only an approximation to the crystal problem, and further in an infinite series expansion for the Wannier function (i.e. in practical calculations) one deals with a finite number of terms only. However , in this chapter while studying certain properties of the Wannier functions (for mathematical purposes only) we have considered the whole of these infinite series.

In some text-books the Wannier functions are said to be identical with the O.A.O. However , this is true in a particular case only, and unfortunately this restriction has often not been made clear to the reader. We have also noticed that nothing much is said about the real nature of these functions in the more general case of tight bindings.

We have studied this problem in the sections 10.5,10.9,10.10, and 10.11 and have shown that these Wannier functions are in general more complicated functions than the O.A.O.'s, for example they have lower symmetries etc.. Also, using certain fundamentals of the tight binding approach we were able to extend the study of the Wannier functions to more general problems, such as degenerate levels, crystals containing different atomic species , presence of several atoms within a unit cell, etc..

In section 10.7 we have calculated (explicitly)the ground band Wannier function for a B.C.C. crystal, where we have taken into account the effects of the 26 nearest neighbours.

10.2 A REVIEW OF THE TIGHT BINDING APPROXIMATION

In this section we will review only certain principles and the aspects of the tight binding method which are related to our main concern that is to say to the Wannier functions themselves.

The tight binding method (or L.C.A.O. or Bloch[1]'s method) is one of the earliest methods in the history of the band theory and since then both the original method and its extensions have been studied and used extensively. The fundamental idea of this method has somehow been used in other methods which were developed later years.

The technique consists of constructing a crystal wave function from a linear combination of atomic functions each of which is centered on one of the constituent atoms of the solid. To keep the argument simpler , let us consider a monatomic crystal where only a single level say the ' n^{th}' one contributes to the crystal wave function. Then, one has to start with the solutions to the atomic problem

$$((-h^2/2m)\nabla^2 + v(\underline{r}-\underline{R}_i))\,\phi_n(\underline{r}-\underline{R}_i) = E_n^o\,\phi_n(\underline{r}-\underline{R}_i) \qquad 10.1$$

where $v(\underline{r}-\underline{R}_i)$ is an atomic potential.

Then, as Bloch[1] pointed out in 1928 the crystal wave function with the required translational symmetry can be constructed from a linear combinations of these atomic functions

[1] F. Bloch, Z. Physik 52, 555 (1928)

$$\psi n(\underline{k},\underline{r}) = (N)^{-1/2}\sum_{i} Cn(\underline{k},\underline{R}_i)\,\phi n\,(\underline{r}-\underline{R}_i) \qquad 10.2$$

where the coefficients $C_n(\underline{k}\ ,\ \underline{R}_i)$'s are not arbitrary. In order to satisfy the Bloch's periodicity requirement one has to set $C_n(\underline{k},\underline{R}_i) = \exp(i.\underline{k}.\underline{R}_i)$, then

$$\begin{aligned}\psi_n(\underline{k},\underline{r}+\underline{R}_m) &= (N)^{-1/2}\sum_{i}\exp(i.\underline{k}.\underline{R}_i)\,\phi n(\underline{r}-\underline{R}_i+\underline{R}_m)\\ &= (N)^{-1/2}\exp(\underline{i}.\underline{k}.\underline{R}_m)\sum_{i}\exp(\underline{i}.\underline{k}.(\underline{R}_i-\underline{R}_m)\,\phi n(\underline{r}-(\underline{R}_i-\underline{R}_m))\\ &= \exp(\underline{i}.\underline{k}.\underline{R}_m)\,\psi n(\underline{k},\underline{r}) \qquad 10.3\end{aligned}$$

For the present let us further assume that the overlap integrals between the $\phi n(\underline{r}-\underline{R}_i)$'s are small enough to be neglected (that is what Bloch[1] has assumed) , hence provided that the A.O.'s are normalized

$$\int_{\text{all } \underline{r}}\phi n(\underline{r}-\underline{R}_i)\,\phi n(\underline{r}-\underline{R}_j)\,d^3r = \delta_{ij} \qquad 10.4$$

In this case the orthogonality of the crystal wave function can also be easily verified, i.e.

$$\int\psi n(\underline{k}',\underline{r})\,\psi n(\underline{k},\underline{r})\,d^3r = \delta(\underline{k}-\underline{k}') \qquad 10.5$$

The next thing is to substitute this crystal wave function into the Schrödinger equation for the crystal and solve for the energy level by a procedure similiar to that used in perturbation theory.

Hence,

$$\left(-(\hbar^2/2m)\nabla^2 + V(\underline{r})\right)\sum_{i}\exp(i.\underline{k}.\underline{R}_i)\,\phi n(\underline{r}-\underline{R}_i) = E_n(\underline{k})\sum_{i}\exp(i.\underline{k}.\underline{R}_i)\,\phi n(\underline{r}-\underline{R}_i)$$

10.6

where $V(\underline{r})$ is the crystal potential obtained by the superposition of the atomic potentials, i.e.

$$V(\underline{r}) = \sum_i v(\underline{r} - \underline{R}_i) \qquad 10.7$$

Now, multiplying the equation 10.6 by $\phi_n^*(\underline{r} - \underline{R}_j)$, and integrating over the space coordinates

$$\sum_i \exp(i.\underline{k}.\underline{R}_i) \int \phi_n^*(\underline{r}-\underline{R}_j)\left(-(\hbar^2/2m)\nabla^2 + V(\underline{r}) \right) \phi_n(\underline{r}-\underline{R}_i)\, d^3r$$

$$= E_n(\underline{k}) \sum_i \exp(i.\underline{k}.\underline{R}_i)\, \delta_{ij}$$

$$= E_n(\underline{k})\, \exp(i.\underline{k}.\underline{R}_j) \qquad 10.8$$

Now, using equation 10.1

$$-(\hbar^2/2m)\nabla^2\phi_n(\underline{r} - \underline{R}_i) = \left(E_n^0(\underline{k}) - v(\underline{r} - \underline{R}_i) \right) \phi_n(\underline{r} - \underline{R}_i) \qquad 10.9$$

Substituting this into the equation 10.8 and rearranging the terms one simply gets

$$E_n(\underline{k}) - E_n^0(\underline{k}) = \sum_i \exp(i.\underline{k}(\underline{R}_i - \underline{R}_j)) \int \phi_n(\underline{r}-\underline{R}_j)(V(\underline{r}) - v(\underline{r}-\underline{R}_i))\phi_n(\underline{r}-\underline{R}_i)\, d^3r \qquad 10.10$$

and using the following definitions

$$E_n'(\underline{k}) = E_n(\underline{k}) - E_n^0(\underline{k}) \quad , \quad V'(\underline{r}) = V(\underline{r}) - v(\underline{r} - \underline{R}_i) \qquad 10.11$$

$$\text{and} \quad \alpha_n(\underline{R}_i - \underline{R}_j) = \int \phi_n(\underline{r} - \underline{R}_j)\, V'(\underline{r})\, \phi_n(\underline{r} - \underline{R}_i)\, d^3r \qquad 10.12$$

this simplifies to ,

$$E_n'(\underline{k}) = \sum_i \alpha_n(\underline{R}_i - \underline{R}_j) \exp(i.\underline{k}(\underline{R}_i - \underline{R}_j))$$

$$= \alpha_n(0) + \sum_{i \neq j} \alpha_n(\underline{R}_i - \underline{R}_j) \exp(i.\underline{k}(\underline{R}_i - \underline{R}_j)) \qquad 10.13$$

In the last equation $E_n'(\underline{k})$ plays the role of the perturbed energy (the shift from the original atomic level) and $V'(\underline{r})$ that of the perturbing potential. If the atomic functions overlap only slightly, then $\alpha_n(\underline{R}_i - \underline{R}_j)$ is appreciable only when $\underline{R}_i \cong \underline{R}_j$. Hence the equation 5.13 reduces to

$$E_n'(\underline{k}) = \alpha_n(0) \qquad 10.14$$

10.3 EXTENSIONS OF THE TIGHT BINDING METHOD

The original tight binding method (section 10.2) is applicable only to a limited number of problems , where the atomic functions overlap only slightly. However, in the usual crystal problem the atomic functions indeed extend considerably further than the interatomic separations. To remedy this situation the modifications on the tight binding method have proceeded in two ways;

i) Inclusion of the overlap and the interaction integrals between more distant neighbours,

ii) or equivalently to employ a different set of functions, which are like the atomic functions centered about the lattice sites but, constructed in such a way that the function centered about one lattice site is rigorously orthogonal to all those centered at the other sites.

For the present we shall start with the first of the above categories. Now, defining the overlap integral (between the two atomic functions) by

$$S_{nn}(\underline{R}_i - \underline{R}_j) = \int \phi_n(\underline{r} - \underline{R}_i)\, \phi_n(\underline{r} - \underline{R}_j)\, d^3r \qquad 10.15$$

the equation 10.13 is then simply given by

$$E'_n(\underline{k}) = E_n(\underline{k}) - E^0_n(\underline{k}) = \frac{\sum_i \alpha_n(\underline{R}_i-\underline{R}_j)\exp(i.\underline{k}(\underline{R}_i-\underline{R}_j))}{\int \psi^*_n(\underline{k},\underline{r})\,\psi_n(\underline{k},\underline{r})\,d^3r} \qquad 10.16$$

$$= \frac{\sum_i \alpha_n(\underline{R}_i-\underline{R}_j)\exp(i.\underline{k}(\underline{R}_i-\underline{R}_j))}{\sum_i S_{nn}(\underline{R}_i-\underline{R}_j)\exp(i.\underline{k}(\underline{R}_i-\underline{R}_j))} \qquad 10.17$$

or

$$E'_n(k) = E^0_n(k) + \frac{\alpha_n(0) + \sum_{i\neq j} \alpha_n(\underline{R}_i-\underline{R}_j)\exp(i.\underline{k}(\underline{R}_i-\underline{R}_j))}{1 + \sum_{i\neq j} S_{nn}(\underline{R}_i-\underline{R}_j)\exp(i.\underline{k}(\underline{R}_i-\underline{R}_j))} \qquad 10.18$$

The last equation is true regardless the normalization of the crystal wave function. In general one has to extend the above series over a few nearest neighbours. Sometimes by adjusting the lattice parameters calculations carried out for a crystal may be used for a completely different type of crystal. So far there have been numerous applications involving equation 10.18. For instance, J.C.Slater and G.F. Koster[2], T.A. Hoffman and A. Konya[3], C. A. Coulson and R.Taylor[4], and E.P. Wohlfarth[5], etc.

The ~~overlap~~ interaction integrals given in the equation 10.18 are generally three center integrals, as one can not in practise so easily write $V'(\underline{r})$ as a single analytical function of $\underline{r}$ but puts it in a form such as a sum of identical functions, one in each unit cell, i.e. $V'(\underline{r})=\sum_l v(\underline{r}-\underline{R}_l)$.

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[2] J.C.Slater and G.F.Koster , Phys. Rev. 94, 1498, (1954)

[3] T.A.Hoffmann and A.Konya , J. Chem. Phys. 16, 1172 (1948)

[4] C.A.Coulson and R.Taylor , Proc. Phys. Soc. A65, 815, (1952)

[5] E.P.Wohlfarth , Proc. Phys. Soc. 66A, 889 , (1953)

In principle these can be reduced to two centre integrals; however this is a difficult and a lengthy process. In many of the applications three centre integrals have been neglected. However as Wohlfarth[5] (1953) has shown, the neglect of the three centre integrals is not always justifiable.

Many of the two centre integrals can be obtained from the tables of Mulliken[6] et al (1949). Also a table for the two centre interaction integrals (for cubic lattices) has been given by Slater and Koster [2]. An extension of these calculations to hexagonal structures has been given by Miasek [7](1957).

10.4 ABOUT THE OVERLAP INTEGRALS

The quantities that we have defined as (two centre) overlap integrals will be of considerable importance to us both in the definition of the Wannier functions and in the explicit calculations that we have given in section 10.7.

In general the overlap integral S for a pair of overlapping atomic functions ϕa and ϕb (where they refer to the atoms a and b) with an internuclear separation R is defined by

$$S(\phi a, \phi b; R) = \int \phi_a^* \phi_b \, d\tau \qquad 10.19$$

There are great advantages of using spherical polar coordinates in the problem. In this case every central field atomic wave function is of the form

$$\phi_a^{n,l,m}(r_a; \theta_a; \phi_a) = R_{nl}(r_a) \, Y_{l,m}(\theta_a, \phi_a) \qquad 10.20$$

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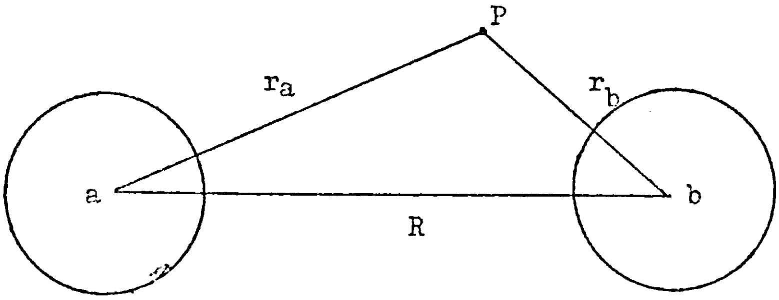
[6] R.S.Mulliken, C.A.Rieke, D.Orloff and H.Orloff, J. Chem. Physics 17, 1248 (1949)

[7] M.Miasek, Phys. Rev. 107, 92 (1957)

Now, using the polar coordinates for both atomic wave functions the position of a point P common to both atoms can be represented as follows



If both atoms are chosen along the z direction then the plane in which r_a and r_b lies is given by $\Phi = \Phi a = \Phi b$.

In the central field problem the normalized angular wave functions (of s,p,and d types , etc.) are simply given by

$$s ; \quad l = 0 , m = 0, \quad Y_{oo}(\theta a, \Phi a) = (1/ 4\pi)^{1/2} \qquad 10.21$$

$$p ; \quad l = 1 , m = 0 , \quad Y_{1,o}(\theta a, \Phi a) = (3/ 4\pi)^{1/2} \cos \theta a \qquad 10.22$$

$$m = \pm 1 , \quad Y_{1,\pm 1}(\theta a, \Phi a) = (3/ 4\pi)^{1/2} \sin \theta a (\sin \Phi a \text{ or } \cos \Phi a)$$

$$d ; \quad l = 2, \quad m = o , \quad \text{etc. ...} \qquad 10.23$$

The radial wave functions however in the presence of a single electron only take the form

$$R_{nl}(r_a) = \sum_{k=1}^{n-1} C_{nlk}\, r_a^k \exp(-z\, r_a / n\, a_h) \qquad 10.24$$

In general for more electrons Rnl 's must be of self consistent type (i.e. see Hartree-Fock method) however they can not be so easily given in analytical forms since the results are often expressed in the form of numerical tables. Slater[8] has approximated these self consistent field type radial equations by a finite series

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[8] J.C. Slater , Phys. Rev. 42 , 33 (1932)

$$R_{nl}(r_a) = \sum_{k=1}^{n-1} d_k \, r^k \exp(-\mu_k \cdot r_a/a_h) \qquad 10.25$$

where d_k and μ_k depend on n,l, and the atomic and the electronic particulars of the system. A better representation is obtained if a particular term (the one with k=n-1) is replaced by a sum of two or three exponential terms as shown below

$$R_{nl}(r_a) = \sum_{k=1}^{n-2} d_k \, r^k \exp(-\mu_k \, r_a/a_h) + r^{n-1} \sum_{i} d_i \exp(-\mu_i \, r_a/a_h) \qquad 10.26$$

For 1s, 2s, and 2p electrons Morse[9] et al and Duncanson and Coulson[10] have also given improved equations to approximate the functions $R_{nl}(r_a)$'s . However , being the simplest case the well known Slater[11] A.O.'s are obtained by approximating these series by a single term

$$R_{nl}(r_a) = N_{nl} \, r^{n-1-\delta} \exp(-\mu r / a_h) \qquad 10.27$$

where

$$\mu_{ns} = \mu_{np} = Z_{a,n} / n-\delta \qquad 10.28$$

and

$$1/N_{nl}^2 = \int_0^\infty r^{2n-2\delta} \exp(-2\mu_{nl} \, r_a / a_h) \, d\tau \qquad 10.29$$

where the values for δ has to be chosen as follows

$$\begin{aligned} \delta &= 0 && \text{for } n = 1,2,3 \\ \delta &= 0.3 && \text{for 4s, 4p electrons} \qquad 10.30 \\ \delta &= 1 && \text{for 5s, 5p electrons} \end{aligned}$$

Since the Slater A.O.'s have no nodes the A.O.'s with different 'n' s are not orthogonal. However it is possible to orthogo-

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[9] Morse, Young, and Haurwitz, Phys. Rev. 48, 948 (1935)

[10] W.E. Duncanson and C.A. Coulson, Proc. Roy. Soc. Edingburgh 62A,37(1944)

[11] J.C. Slater, Phys. Rev. 36, 57 (1930)

nalize them (this also means the introduction of the missing nodes) where this time the single term approximation becomes converted into a similiar series given by the equation 10.25. However in quite a number of cases it has been observed that the orthogonalization has little effect on the calculated values of the overlap integrals.

When we come next to the evaluation of the overlap integrals , the computations are often carried out by transforming from the polar coordinates to the spheroidal ones.

i.e. $$\xi = (r_a + r_b)/ R \qquad \eta = (r_a - r_b)/ R \qquad \phi = \phi a = \phi b \qquad 10.31$$

Extensive tables and explicit expressions for the overlap integral S between the two atomic orbitals of either sort , i.e. Slater or Non-Slater (usually the latter can be obtained from a linear combination of the first) have been given by R.S. Mulliken[6] et al.

Below,as an illustration we give one such explicit expression (taken from these tables) for the overlap integral of $\phi 1s$ atomic orbitals ,which we will also use in section 10.7

$$S_{nn}(\phi 1s, \phi 1s, R) = (6)^{-1} p^3 (3A_2 - A_0) \qquad 10.32$$

where $p = (1/2)(\mu a + \mu b) R/ a_h$ and,

$$A_k (p) = \int_1^{\infty} \xi^k \exp(-p\xi)\, d\xi = \exp(-p) \sum_{\mu=1}^{k+1} (k!/(p (k-\mu+1)!))$$

and μ's are to be obtained from the Slater's equations (i.e. eqn. 10.28) .

10.5 THE WANNIER FUNCTION FOR A MONATOMIC CRYSTAL

At the very beginning of this chapter we had assumed that the atomic functions had zero overlap integrals . This assumption is true when the interatomic spacings are large. However when the atoms are brought closer the atomic orbitals start to overlap and the crystal wave function given by equation 10.2 is no longer normalized but,

$$\int \Psi_n^*(\underline{k},\underline{r})\ \Psi_n(\underline{k},\underline{r})\ d^3r = \sum_{\underline{R}_1} Snn(\underline{R}_1)\ \exp(-i.\underline{k}.\underline{R}_1) \qquad 10.33$$

$$= 1 + \sum_{\underline{R}_1 \neq 0} Snn(\underline{R}_1)\exp(-i.\underline{k}.\underline{R}_1) \qquad 10.33$$

Hence in order to normalize the wave function in concern one has to multiply it by

$$\left(1 + \sum_{\underline{R}_1 \neq 0} Snn(\underline{R}_1)\ \exp(-i.\underline{k}.\underline{R}_1)\right)^{-1/2} \qquad 10.34$$

The normalized wave function is then given by

$$\Psi_n(\underline{k},\underline{r}) = (N)^{-1/2}\ \frac{\sum_j \exp(i.\underline{k}.\underline{R}_j)\ \phi_n(\underline{r}-\underline{R}_j)}{\left(1 + \sum_{1\neq 0} \exp(\ -i.\underline{k}.\underline{R}_1)\ S_{nn}(\underline{R}_1)\right)^{1/2}} \qquad 10.35$$

As we have seen in Chapter 2 the Wannier function can be obtained from this crystal wave function by the following transformation,

$$a_n(r\ -R\ ) = (N)^{-1} \sum_{\substack{\underline{k} \\ n^{th}.\,B.Z.}} \frac{\sum_j \exp(i.\underline{k}.(\underline{R}_j-\underline{R}_i))\ \phi_n(\underline{r}\ -\underline{R}_j)}{\left(1 + \sum_{1\neq 0} \exp(-i.\underline{k}.\underline{R}_1)\ S_{nn}(\underline{R}_1)\right)^{1/2}} \qquad 10.36$$

However, making use of the following binomial expansion with remainder

$$(1+a)^{\alpha} = 1 + \alpha a + \frac{\alpha(\alpha-1)}{2!}a^{2} + \ldots\ldots \frac{\alpha(\alpha-1)\ldots.(\alpha-(r-1))}{r!}a^{r} + A.r \qquad 10.37$$

we can write the following

$$\Big(1 + \sum_{l\neq 0} \exp(-i.\underline{k}.\underline{R}_l)\mathrm{Snn}(\underline{R}_l)\Big)^{-1/2} = 1 - 1/2\sum_{l}\exp(-i.\underline{k}.\underline{R}_l)\mathrm{Snn}(\underline{R}_l)$$

$$+3/8\sum_{l,n}\exp(-i.\underline{k}.(\underline{R}_l-\underline{R}_n))\mathrm{Snn}(\underline{R}_l)\mathrm{Snn}(\underline{R}_n)$$

$$-15/48\ldots\ldots\ldots\ldots\ldots\ldots + R \qquad 10.38$$

where one considers a sufficient number of terms for the accuracy required. Also, if

$$\Big|\sum_{l}\exp(-i.\underline{k}.\underline{R}_l)\mathrm{Snn}(\underline{R}_l)\Big| < 1 \qquad 10.39$$

then this series is absolutely convergent, and the expression 10.36 can be written as

$$a_n(\underline{r})/(N)^{-1} = \sum_{k,j}\exp(i.\underline{k}.\underline{R}_j)\phi n(\underline{r}-\underline{R}_j) - \tfrac{1}{2}\sum_{k,j,l}\exp(i.\underline{k}.(\underline{R}_j-\underline{R}_l))\phi n(\underline{r}-\underline{R}_j)\mathrm{Snn}(\underline{R}_l)$$

$$+3/8\sum_{k,j,l,n}\exp(i.\underline{k}.(\underline{R}_j-\underline{R}_l+\underline{R}_n))\phi n(\underline{r}-\underline{R}_j)\mathrm{Snn}(\underline{R}_l)\mathrm{Snn}(\underline{R}_n)$$

$$-15/48\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots + \ldots\ldots\ldots + G(\underline{r}) \qquad 10.40$$

where for simplicity we have set $\underline{R}_i = 0$.

Working out the terms on the right hand side of the last equation one by one one obtains the following expression

$$a_n(\underline{r})) = \phi n(\underline{r}) - 1/2\sum_{j}\phi n(\underline{r}-\underline{R}_j)\mathrm{Snn}(\underline{R}_j) + 3/8\sum_{j,n}\phi n(\underline{r}-\underline{R}_j)\mathrm{Snn}(\underline{R}_j+\underline{R}_n)\mathrm{Snn}(\underline{R}_n)$$

$$-15/48\ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots + G(\underline{r}) \qquad 10.41$$

which expresses the Wannier function in terms of the atomic orbitals. The expression on the right is identical with that of a Landshoff[12]-Löwdin[13] function (or an O.A.O.) in principle (in other words for a monatomic crystal where the atomic levels don't interact, the Wannier function[14] can be approximated by an O.A.O.) however, Löwdin[13] for example uses a different representation by employing matrices

$$\varphi_i = \sum_i \phi_i \left(S^{-1/2} \right)_{ij}$$

$$= \phi i \; - 1/2 \sum_j \phi j \; S_{ij} \; + 3/8 \sum_{j,m} \phi j \; S_{jm} \, S_{mi} \; - \cdots\cdots \qquad 10.42$$

Altough these two equations are exactly the same the difference comes in their handling, i.e. in equation 5.52 the second summation on the right will be obtained by the matrix multiplication

$$\sum_{j\,m} \phi_j \, S_{jm} S_{mi} \qquad 10.43$$

while in the alternative form that we have used (where for simplicity we have also set $\underline{R}_i = 0$)

$$\sum_{j,n} \phi_n(\underline{r}-\underline{R}_j) Snn(\underline{R}_j+\underline{R}_n) Snn(\underline{R}_n) \qquad 10.44$$

the same sum will be obtained by a simple permutation over the vectors $\underline{R}_j$, and $\underline{R}_n$. This alternative approach (if the overlap integrals are small) will enable us to pick up the most significant terms in the whole of the series without ever bothering with the construction of the matrices, etc..

Our next concern will be the symmetry properties of these Wannier functions. Symmetry properties of the O.A.O.'s have been worked out by Slater and Koster[2]. In the next section we will outline their approach.

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12 R. Landshoff , Z. Physik 102, 201 (1936)

13 P.O. Lowdin , J. Chem. Phys. 18, 365 (1950)

14 In case of large interatomic separations Snn(R)'s are all zero and the Wannier function is given by a single atomic orbital(see eqn.10.41).

10.6 THE SYMMETRY PROPERTIES OF THE WANNIER FUNCTION

Assume that under some operation 0 of the group of the crystal the atomic orbitals are transformed as follows

$$0\phi_n = \sum_m \phi_m \Gamma(0)_{mn} \qquad 10.45$$

where $\Gamma(0)_{mn}$ is a unitary matrix , i.e. $\Gamma(0)^{-1}_{mn} = \Gamma(0)^{*}_{nm}$.

The present task is to show that the Wannier functions obtained in the previous section do also transform in the same way, or in other terms we must show that the equation given below is true

$$0\varphi_n = \sum_m \varphi_m \Gamma(0)_{mn} \qquad 10.46$$

But φ_n is given by (see equation 5.52)

$$\varphi_n = \sum_m \phi_m (S^{-\frac{1}{2}})_{mn} \qquad 10.47$$

where the overlap matrix S is defined by the elements

$$S_{mn} = \int \phi_m \phi_n \, d\tau \qquad 10.48$$

Now , applying the same operator 0 to equation 10.47

$$0\varphi_n = \sum_m 0\phi_m (S^{-\frac{1}{2}})_{mn} = \sum_l \sum_m \phi_l \Gamma(0)_{lm} (S^{-\frac{1}{2}})_{mn} \qquad 10.49$$

Now , using equations 10.46 and 10.49,

$$\sum_l \sum_m \phi_l \Gamma(0)_{lm} (S^{-\frac{1}{2}})_{mn} = \sum_m \varphi_m \Gamma(0)_{mn} \qquad 10.50$$

Substituting equation 10.47 to the right hand side of the last equation

$$\sum_l \sum_m \phi_l \Gamma(0)_{lm} (S^{-\frac{1}{2}})_{mn} = \sum_l \sum_m \phi_l (S^{-\frac{1}{2}})_{lm} \quad (0)_{mn} \qquad 10.51$$

This last equation reduces to the following form(where l is arbitrary)

$$\sum_{m} \Gamma(0)_{lm}(S^{-\frac{1}{2}})_{mn} = \sum_{m} (S^{-\frac{1}{2}})_{lm}\, \Gamma(0)_{mn} \qquad 10.52$$

Now, multiplying both sides of the last equation by $(\Gamma(0)^{-1})_{ql}$ and summing over the arbitrary values of l

$$\sum_{l}\sum_{m} (\Gamma(0)^{-1})_{ql}\, \Gamma(0)_{lm}(S^{-\frac{1}{2}})_{mn} = \sum_{l}\sum_{m} (\Gamma(0)^{-1})_{ql}(S^{-\frac{1}{2}})_{lm}\Gamma(0)_{mn} \qquad 10.53$$

or

$$\sum_{m} \delta_{qm}(S^{-\frac{1}{2}})_{mn} = \sum_{l}\sum_{m} (\Gamma(0)^{-1})_{ql}(S^{-\frac{1}{2}})_{lm}(\Gamma(0))_{mn} \qquad 10.54$$

$$(S^{-\frac{1}{2}})_{qn} = \sum_{l}\sum_{m} (\Gamma(0)^{-1})_{ql}(S^{-\frac{1}{2}})(\Gamma(0))_{mn} \qquad 10.55$$

In general the overlap matrix S is invariant with respect to the unitary transformation $\Gamma(0)$

i.e.

$$S_{mn} = \int \phi_m \phi_n \, d\tau = \int 0\phi_{m0}\phi_n \, d\tau \qquad 10.56$$

$$= \sum_{q}\sum_{l} \Gamma(0)^{*}_{qm}\, \Gamma(0)_{ln} \int \phi_q \phi_l \, d\tau \qquad 10.57$$

$$= \sum_{q}\sum_{l} (\Gamma(0)^{-1})_{mq}\, S_{ql}\, (\Gamma(0))_{ln} \qquad 10.58$$

Hence, under some general conditions (that the matrix $S^{-\frac{1}{2}}$ is also invariant with respect to the unitary transformation $\Gamma(0)$) the equation 10.46 becomes verified. Therefore , the symmetry properties of the Wannier functions given in section 10.5 are derived from the symmetry properties of their constitutent atomic orbitals.

10.7 THE CALCULATED WANNIER FUNCTION

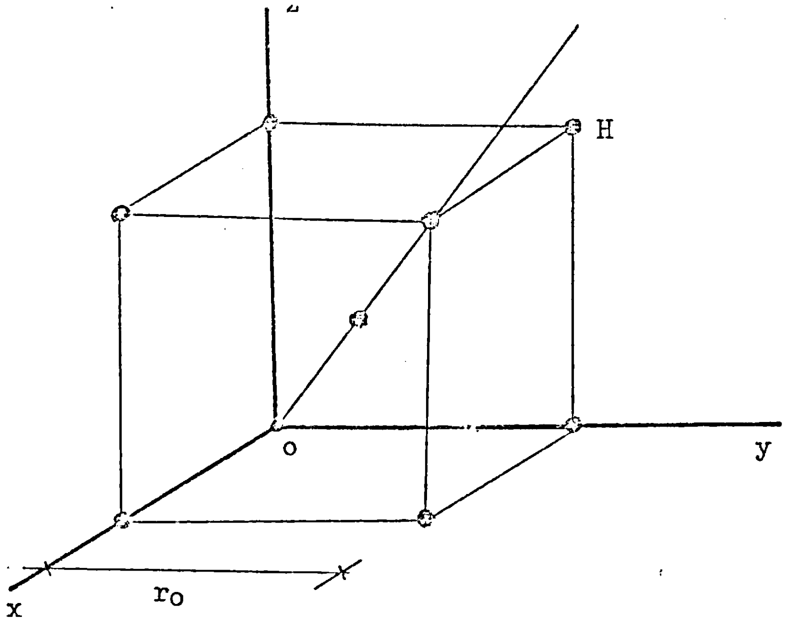
The model that we have used is a B.C.C. lattice where the lattice points are occupied by hydrogen (or hydrogen- like) atoms. For convenience we have assumed that the crystal is built up of the unit cubes(cells) as shown in figure 1 , also the basis vectors have been chosen in the directions of the principal cartesian coordinates so that they retain the symmetry of the unit cube (cell)

The atomic separations along the principal $\{1,0,0\}$, $\{0,1,0\}$ and $\{0,0,1\}$ directions have been taken as $r_0 = 6\ a_h$ (the separations of the remaining atoms can easily be worked out).

The Wannier function in concern has been calculated in the principal $\{1,0,0\}$, $\{1,1,0\}$ and $\{1,1,1\}$ directions, which characterize the variation of the function in the '$\underline{r}$ ' space.

Finally in the calculations effects of up to the third nearest neighbours (26 neighbours all together) have been considered.

Fig. 1



i) The eight nearest neighbours are located at $\underline{R}_1 = r_o(+\frac{1}{2} , +\frac{1}{2} , +\frac{1}{2})$ and at a distance $R_1 = 3/2\ r_0$

ii) The six second nearest neighbours are at $\underline{R}_2 = r_o(+1, 0, 0)$ and at a distance $R_2 = r_o$

iii) The twelve third nearest neighbours are at $R = r$ (+1, +1, 0) and at a distance $R_3 = 2\ r_0$

For the location of these neighbours , see the figure below

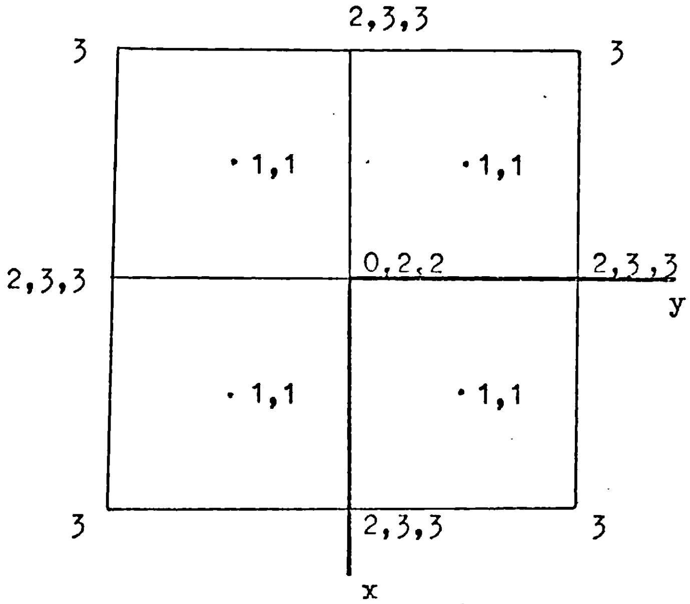


Fig. 2 The projection of the figure 1 (including the seven neighbouring unit cells which are not shown in the figure) on to the xy plane , where the numbers 1,2 and 3 denote respectively the first , second and the third nearest neighbours. If a number is repeated twice (i.e. 3,3) this means that at that orientation there are two such equivalent neighbours. O is the origin where the Wannier function in concern is localized.

Through the tables given by R.S. Mulliken et al (i.e. see equation 10.32) we have found the following values for the overlap integrals;

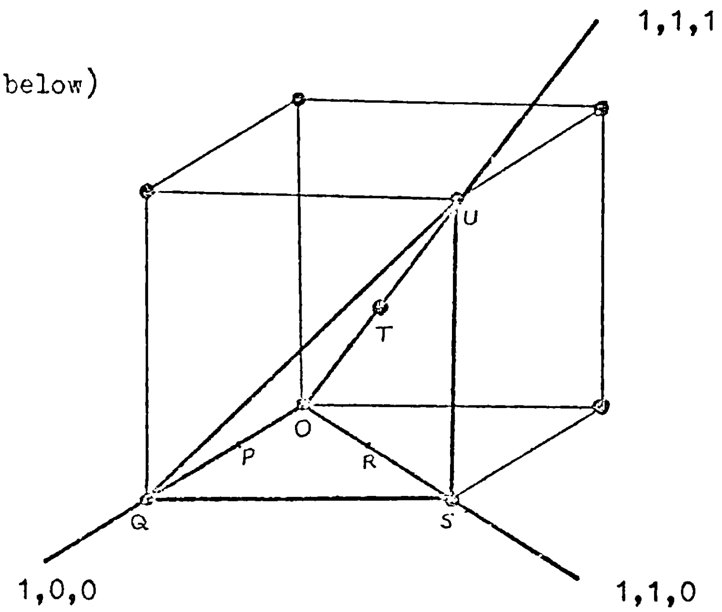
i)For the 8 nearest neighbours $Snn(\phi 1s,\phi 1s,R_1)=8.35\times10^{-2}$

ii)For the 6 second nearest neighbours $Snn(\phi 1s,\phi 1s,R_2)=4.27\times10^{-2}$

iii)For the 12 third nearest neighbours $Snn(\phi 1s,\phi 1s,R_3)=0.67\times10^{-2}$

At each point where the Wannier function has been calculated the full effects of all of the 26 neighbours have been considered by using several symmetry considerations. Below, we quote the results only. The effects of the third (and the higher order) terms on the right hand side of equation 10.41 have been found to be insignificant.

Table 1 (below)



Point	$-0.5\sum_i S(\phi 1s,\phi 1s,\underline{R}_i)\phi 1s(\underline{r}-\underline{R}_i)$			$\phi 1s$	The Wannier function
P	8 nearest neighbours	6 second nearest neighbours	12 third nearest neighbours		
(0,0,0)	-1.84×10^{-3}	-0.316×10^{-3}	-0.0079×10^{-3}	1.000	0.99784
$(\frac{1}{2},0,0)$	-0.0244×10^{-3}	-1.17×10^{-3}	-0.018×10^{-3}	0.04979	0.04858
(1,0,0)	-0.935×10	-22×10^{-3}	-0.033×10^{-3}	0.002479	-0.02049

Point	$-0.5\sum_i S(\phi_{1s},\phi_{1s},\underline{R}_i)\,\phi_{1s}(\underline{r}-\underline{R}_i)$			ϕ_{1s}	The Wannier function
T	8 nearest neighbours	6 second nearest neighbours	12 third nearest neighbours		
(o,o,o)	-1.84×10^{-3}	-0.316×10^{-3}	-0.0079×10^{-3}	1.000	0.99784
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	-42.0×10^{-3}	-0.355×10^{-3}	-0.0555×10^{-3}	0.0056	-0.03681
(1,1,1)	-0.246×10^{-3}	-0.0128×10^{-3}	-0.0245×10^{-3}	0.0000167	-0.00027

Table 2

Point	$-0.5\sum_i S(\phi_{1s},\phi_{1s},\underline{R}_i)\,\phi_{1s}(\underline{r}-\underline{R}_i)$			ϕ_{1s}	The Wannier function
R	8 nearest neighbours	6 second nearest neighbours	12 third nearest neighbours		
(o,o,o)	-1.84×10^{-3}	-0.316×10^{-3}	-0.0079×10^{-3}	1.000	0.99784
$(\frac{1}{2},\frac{1}{2},0)$	-4.355×10^{-3}	-0.628×10^{-3}	-0.0555×10^{-3}	+0.01425	0.00921
(1,1,0)	-0.468×10^{-3}	-0.054×10^{-3}	-3.3×10^{-3}	+0.0002	-0.00362

Table 3

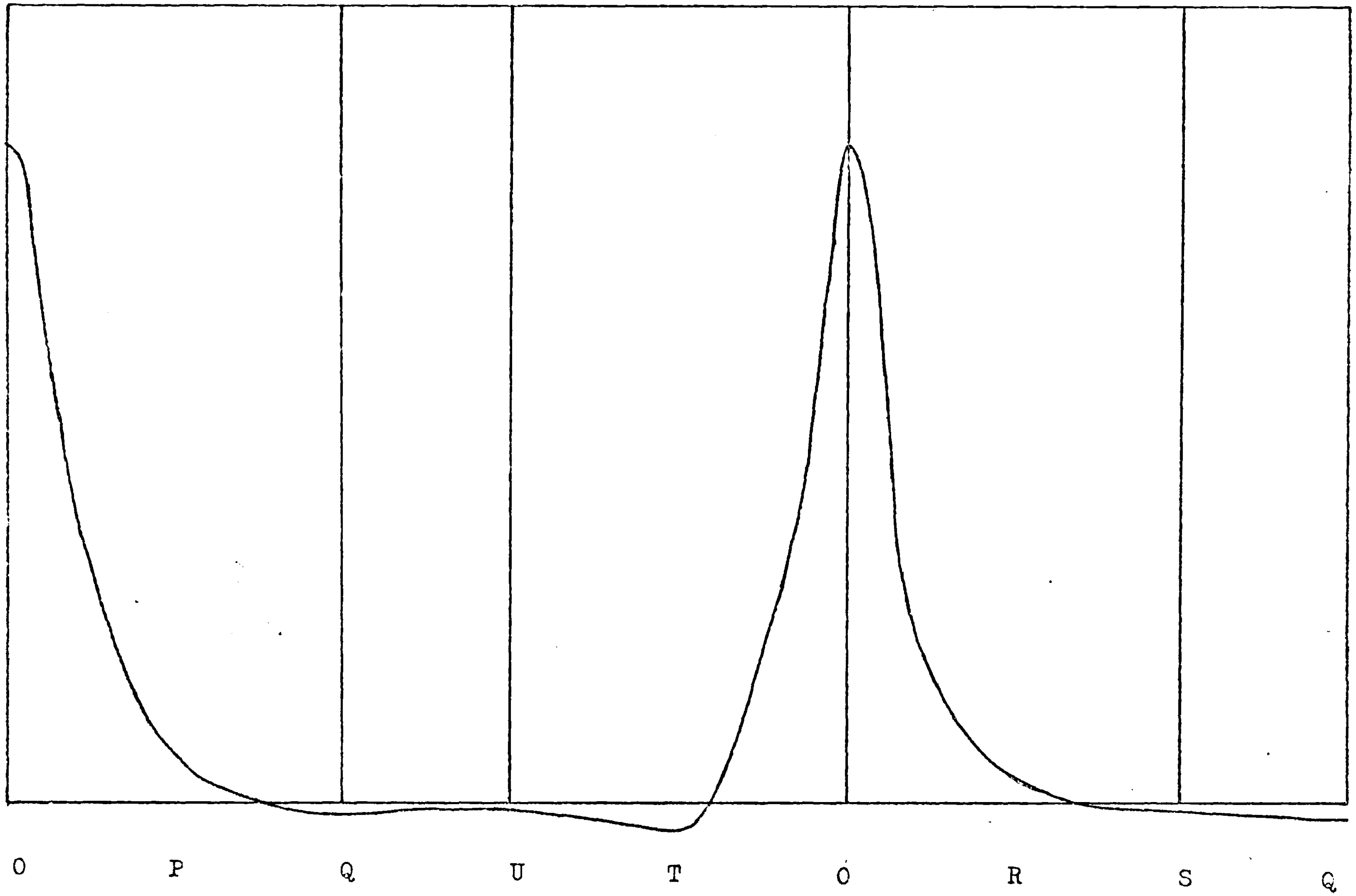


Fig . 3 The Wannier function along the symmetry directions (the ordinary atomic orbitals for this particular problem, do not cut the horizantal axis)

10.8 THE WANNIER FUNCTIONS FOR TIGHTLY BOUND ELECTRONS , THE GENERAL CASE

In the section 10.1 we have said that the Wannier functions are identical with the O.A.O. 's only in a particular case (where the crystal wave function is given by a single gle Bloch sum). However, in most of the problems it may be essential to use several Bloch sums in constructing the crystal wave functions.

In general, the more Bloch sums one uses the better is the approximation to the real crystal wave function.

Hence, to get precise results;

i) One should set up a separate Bloch sum for each atomic level which might in some way contribute to the energy band in concern .

ii) A separate Bloch sum to be used for each of the degenerate atomic functions. I.e. in case of the 2p atomic functions, a separate Bloch sum to be constructed from each of the degenerate $2p_x$, $2p_y$ and $2p_z$ atomic functions.

iii) If there is more than one atom in the unit cell(may be same or different atomic species) then a separate Bloch sum for each of the atomic sites has to be included.

Hence the crystal wave function in its most general form is a linear combination of n such separate Bloch sums.

$$\psi(\underline{k},\underline{r}) = C_1\psi_1(\underline{k},\underline{r}) + C_2\psi_2(\underline{k},\underline{r}) + \dots\dots\dots\dots + C_n\psi_n(\underline{k},\underline{r}) \qquad 10.59$$

Now , expressing each separate Bloch sum in terms of the O.A.O. 's from which they are derived, then substitute it into the Schrödinger equation for the crystal one ends up with the following

$$\begin{array}{llll} c_1(\gamma_{11}-E(\underline{k})) & c_2\gamma_{12} & c_3\gamma_{13} & \ldots\ldots\ldots\ldots c_n\gamma_{1n}=0 \\ c_1\gamma_{21} & c_2(\gamma_{22}-E(\underline{k})) & & \ldots\ldots\ldots c_n\gamma_{2n}=0 \\ & & & \\ c_1\gamma_{n1} & c_2\gamma_{n2} & & c_n(\gamma_{nn}-E(\underline{k}))=0 \end{array} \qquad 10.60$$

where

$$\gamma_{nm}(\underline{R}_j) = -\sum_i \exp(i.\underline{k}.(\underline{R}_i-\underline{R}_j))\,\alpha_{nm}(\underline{R}_i-\underline{R}_j) \qquad 10.61$$

and

$$\alpha_{nm}(\underline{R}_i-\underline{R}_j) = -\int \phi^*_n(\underline{r}-\underline{R}_i)\,V'\phi_m(\underline{r}-\underline{R}_j)\,d^3r \qquad 10.62$$

From the above set of linear equations a secular determinant is formed which has to be solved for the energy $E(\underline{k})$. On the assumption that all the coefficients C_i 's have been obtained for any energy, one can write the crystal wave function in terms of the O.A.O. 's (that have been employed in the sum) as follows

$$\psi(\underline{k},\underline{r}',\underline{r}'',..\underline{r}^n) = \sum_{\underline{R}_1}\exp(i.\underline{k}.\underline{R}_1)C_1\varphi_1(\underline{r}'-\underline{R}_1) + \sum_{\underline{R}_2}\exp(i.\underline{k}.\underline{R}_2)C_2\varphi_2(\underline{r}''-\underline{R}_2)$$

$$+\ldots\ldots\ldots\ldots\ldots\ldots + \sum_{\underline{R}_n}\exp(i.\underline{k}.\underline{R}_n)C_n\varphi_n(\underline{r}^n-\underline{R}_n) \qquad 10.63$$

where $\underline{R}_1$, $\underline{R}_2$, ... $\underline{R}_n$, are the position vectors pointing out to the atomic sites that contribute to the crystal wave function (though some of these vectors may be identical).

Now let us construct a unit cell (containing several atoms of the same or different sort) for the crystal.

Also let a set of translation vectors $\underline{R}$'s be such defined that translation through any of the vectors $\underline{R}$ is a symmetry operation of the crystal ($\underline{R}$ carries any point in the unit cell that we have just defined to an equivalent point in another unit cell)

Now, if the separate sums over $\underline{R}_1$, $\underline{R}_2$, ...$\underline{R}_n$'s are replaced by a common summation over the vector $\underline{R}$, the equation 10.59 takes the following general form,

$$\Psi(\underline{k},\underline{r}) = \sum_{\underline{R}} \exp(i.\underline{k}.\underline{R}) \; (C_1(\underline{k})\Upsilon_1\varphi_1(\underline{r}-\underline{R}) + C_2(\underline{k})\Upsilon_2\varphi_2(\underline{r}-\underline{R}) + \ldots\ldots + C_n(\underline{k})\Upsilon_n\varphi_n(\underline{r}-\underline{R})) \qquad 10.64$$

Where Υ_1, Υ_2,...., Υ_n represent the necessary operations to be carried out over the space coordinates of the φ's (O.A.O.'s) when a common origin has to be used (in the unit cell).

Hence , provided that the above procedure is followed a single Wannier function associated with each unit cell (and which also allows the representation of the crystal wave function as follows where $\underline{R}_o$ is an arbitrary lattice vector)

$$a(\underline{r} - \underline{R}_o) = \sum_{\underline{k}} \Psi(\underline{k},\underline{r}) \exp(-i.\underline{k}.\underline{R}_o) \qquad 10.65$$

(the constant Of normalization is not shown)

is then given by(through equation 10.64)

$$a(\underline{r} - \underline{R}_o) = \sum_{\underline{R}} C_1(\underline{R}-\underline{R}_o)\Upsilon_1\varphi_1(\underline{r}-\underline{R}) + C_2(\underline{R}-\underline{R}_o)\Upsilon_2\varphi_2(\underline{r}-\underline{R}) + \ldots\ldots\ldots + C_n(\underline{R}-\underline{R}_o)\Upsilon_n\varphi_n(\underline{r}-\underline{R}) \qquad 10.66$$

where the coefficients of the superpositions to be obtained through the solutions of the secular equations as follows

$$C_i(\underline{R} - \underline{R}_o) = \sum_{\underline{k}} \exp(\, i\, \phi_i(\underline{k}) + i.\underline{k}.(R-R_o))\; C_i(\underline{k}) \qquad 10.67$$

$\phi_i(\underline{k})$ is the arbitrary phase mentioned previously.

As is apparent from the equation 10.66 , the Wannier functions have in general lower symmetries than the O.A.O.'s . Their symmetry is no longer derived from a particular sort of atomic function as we have shown in section 10.6 .

10.9 THE WANNIER FUNCTION FOR A DEGENERATE LEVEL

Now , let us consider a monatomic crystal where the atomic level that contributes to the crystal wave function is a p state, and let φ_1 , φ_2 and φ_3 be three such O.A.O.'s constructed from the degenerate atomic p functions as we have shown in the previous sections. On the assumption that the atomic levels are well seperated and no additional levels need be considered in the wave function for the solid, the crystal wave function is then set up as

$$\Psi(\underline{k},\underline{r}) = C_1 \sum_1 \exp(i.\underline{k}.\underline{R}_1)\,\varphi_{px}(\underline{r}-\underline{R}_1) + C_2 \sum_2 \exp(i.\underline{k}.\underline{R}_2)\,\varphi_{py}(\underline{r}'-\underline{R}_2) + C_3 \sum_3 \exp(i.\underline{k}.\underline{R}_3)\,\varphi_{pz}(\underline{r}''-\underline{R}_3) \quad 10.68$$

But, the crystal is monatomic , and the degenerate functions (O.A.O.'s) φ px, φpy, and φpz are all centered on the same atomic sites , therefore , a common space coordinate system can be used for all of the three functions (such that $\underline{r} = \underline{r}' = \underline{r}''$ and the origin is at $\underline{r} = 0$). The common translational vector $\underline{R}$ is then given by,

$$\underline{R} = \underline{R}_1 = \underline{R}_2 = \underline{R}_3 \quad 10.69$$

The equation 10.68 now becomes

$$\Psi(\underline{k},\underline{r}) = \sum_{\underline{R}} \exp(i.\underline{k}.\underline{R})\left(c_1(\underline{k})\varphi px(\underline{r}-\underline{R}) + c_2(\underline{k})\varphi py(\underline{r}-\underline{R}) + c_3(\underline{k})\varphi pz(\underline{r}-\underline{R}) \right) \quad 10.70$$

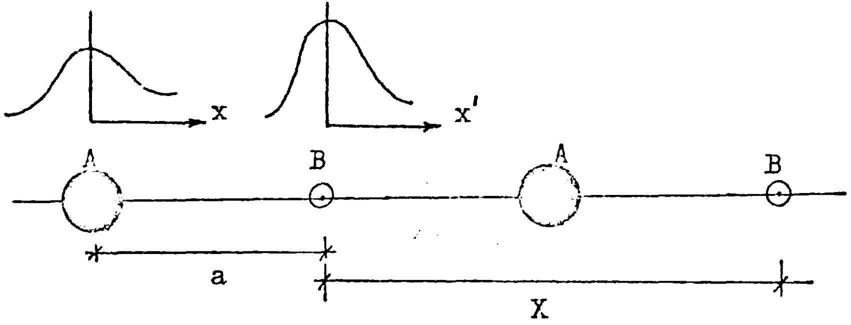
Therefore, the Wannier function (one for each of the degenerate bands) is given by

$$a_p(\underline{r}-\underline{R}_o) = \sum_{\underline{R}} C_1(\underline{R}-\underline{R}_o)\,\varphi_{px}(\underline{r}-\underline{R}) + C_2(\underline{R}-\underline{R}_o)\varphi_{py}(\underline{r}-\underline{R}) + C_3(\underline{R}-\underline{R}_o)\varphi_{pz}(r-R) \qquad 10.71$$

Hence, for this particular problem, each of the Wannier functions (centered at a particular site $\underline{R}$) is given by a linear combination of the degenerate O.A.O.'s centered at the same atomic site. The coefficients of the superpositions to be obtained as described in the previous sections.

10.10 THE WANNIER FUNCTION FOR A CRYSTAL WITH DIFFERENT ATOMIC SPECIES IN THE UNIT CELL

To keep the argument simpler let us assume that there are two such atomic specimens(say, atoms A and B) in the unit cell of a linear crystal. Also let only a single level from each atom contributes to the crystal wave function(though, the following argument is true for more general cases).



The crystal wave function is then given by

10.72

$$\psi(k,x) = c_A(\underline{k})\sum_X \exp(i.k.X)\ \varphi_A(x-X) + c_B(\underline{k})\sum_X \exp(i.k.X)\ \varphi_B(x'-X)$$

If a common space coordinate system will be used for all of the atomic specimens ($x' = x - a$, where a is the inter atomic seperation between the atoms A and B) then equation 10.72 becomes

$$\Psi(k,x)m = \sum_X \exp(i.k.X)(C_A(\underline{k})\,\varphi A(x-X) + C_B(\underline{k})\varphi B(x-a-X)) \qquad 10.73$$

The Wannier function associated with a unit cell is then given by (assuming that the effects of the arbitrary phases are implicitly given by the equation 10.67)

$$a(x-X_o) = \sum_X C_A(X-X_o)\,\varphi A(x-X) + C_B(X-X_o)\,\varphi B(x-X) \qquad 10.74$$

where $C_A(X-X_o)$ and $C_B(X-X_o)$ to be determined as usual.

Hence, instead of two O.A.O.'s centered around each atom we have now a Wannier function for each unit cell containing these atoms. Also under some general conditions the Wannier function $a(x-X_o)$ will not attain its peak at $x=X_o$, since (loosely speaking) at this point $\varphi A(x-X)$ and $\varphi B(x-X)$ do not simultaneously attain their maximums.

APPENDIX 1

AN OUTLINE OF THE BASIC PRINCIPLES OF WANNIER REPRESENTATION

A1.1 INTRODUCTION

In general the term "Representation" both in classical and quantum mechanics has been used as a homonym. For example in quantum mechanics one mentions Schrödinger, Heisenberg, and the interaction representations and also coordinate, momentum, and the energy representations , though the former ones are sometimes referred as pictures (reference can be made to any text-book in quantum mechanics) . In this chapter we will frequently refer (to the latter) to two fundamental representations , which are the momentum and the coordinate representations of ordinary quantum mechanics. In the first case the momentum operator is the generator of infinitesmal translations and provided that the Hamiltonian commute with all translations the true momentum is a constant of the motion . However, in general in crystals the usual Hamiltonian do not commute with all of the translations and the true momentum is no longer a constant of the motion. In this case a new quantity (in some sense being a modification of the true momentum) has been defined what is known as crystal momentum(in the particular case of the free electrons where the lattice potential is constant , the crystal momentum is the true momentum). In some way being appropriate to the realism of the crystals this new quantity generates the finite lattice translations and the Hamiltonian commutes with these finite translations . The former claim can be verified as follows; Assume that an explicit function $F(\underline{p})$ (which may be written as a plynamial in $\underline{p}$ or as a Fourier series) of the crystal momentum operator has been given. This when acted upon a Bloch state yields

$$F(\underline{p})\,\psi n(\underline{k},\underline{r}) = F(h\,\underline{k})\,\psi n(\underline{k},\underline{r}) \qquad \text{A1.1}$$

then it s action on an arbitrary wave function $\Psi(\underline{r})$ (in the C.M.R.)

$$\exp(i.\underline{p}.\underline{R}/h)\Psi(\underline{r}) = \sum_{n}\int_{B.Z} f n(\underline{k})\exp(i.\underline{p}.\underline{R}/h)\,\psi n(\underline{k},\underline{r})\; d^3k \qquad \text{A1.2}$$

$$= \sum_{n}\int_{B.Z} f n(\underline{k})\exp(i.\underline{k}.\underline{R})\;\psi\, n(\underline{k},\underline{r})\; d^3k \qquad \text{A1.3}$$

then,from Bloch's periodicity condition(i.e. $\exp(i.\underline{k}.\underline{R})\psi n(\underline{k},\underline{r})=\psi n(\underline{k},\underline{r}+\underline{R})$)

$$\exp(i.\underline{P}.\underline{R}/h)\Psi(\underline{r}) = \sum_{n}\int_{B.Z} f n(\underline{k})\psi n(\underline{k},\underline{r}+\underline{R})\; d^3k = \Psi(\underline{r}+\underline{R}) \qquad \text{A1.4}$$

Hence, the crystal momentum operator $\underline{p}$ does indeed generate finite lattice translations (this point will later on be redisscussed in greater detail).

The C.M.R. where one uses the energy eigenfunctions (i.e. Bloch waves) as the basis function is analogous to the true momentum representation of continuum mechanics. In general , in this representation as an Hamiltonian one can use either one of the Schrödinger, Pauli and the Dirac Hamiltonians. In appendix 2 we will give briefly the fundamentals of the C.M.R. and that of M.C.M.R. (or what is known as Kohn- Luttinger's modified C.M.R.). Also a short reference will be made to some of the mixed representations .

In analogy with the existence of the momentum and the conjugate coordinate representations in continuum mechanics one might also look for a sort of coordinate representation (in crystals) conjugate to the C.M.R. . One starts by looking for an operator $\underline{R}$ canonically conjugate to $\underline{p}$.

As pointed out above , the eigenvalues of the coordinates $\underline{q}$ and the conjugate momento $\underline{p}$'s of ordinary quantum mechanics represent a continuum from $-\infty$ to $+\infty$ (where the transition from one representation to the other is characterized by the

Fourier transforms with the limits of the integrations on the $\underline{p}$'s and the $\underline{q}$'s extending to infinity. In crystals however because of the existence of the bands the continuity of the eigenvalues of $\underline{p}$ are restricted to some finite regions only . This intuitively suggests that the eigenvalues of the conjugate operator must also be discrete. The eigenfunctions of the continous variable $\underline{r}$ (in continuum mechanics) are the δ functions.. Then eigenfunctions of the discrete variables $\underline{R}$'s would also be expected to be localized, in some sense (even though not as localized as the δ functions themselves). If conjugate operator $\underline{R}$ is chosen such that it also commutes with the band index, then the transformations from one basis to the other will be characterized by either integral transforms evaluated over single B.Z.'s or by the summations over the discrete eigenvalues $\underline{R}_i$'s .

The roots of this new crystal coordinate representation from now on which we will call simply Wannier representation(after Wannier) was first set up by Wannier[1] in 1937. There has been a considerable delay in realising the importance of the Wannier's [1] theorem and in the development of the representation itself. This may partly be due to Wannier's trying his method initially on a problem (the excitons) which is a too complicated problem even in todays standarts.

It was Slater[2] who first realized the importance of Wannier's theorem and he who also initiated the development of the representation. This development was followed by Adams[3,4,5,6] who generalized Wannier's theorem to take into account transitions between energy bands

1 G.H. Wannier, Phys. Rev. 52, 191 (1937)

2 J.C. Slater, Phys. Rev. 76, 1592(1949)

3 N.E. Adams, Phys. Rev. 85, 41(1952)

4 N.E. Adams, J. Chem. Phys. 21, 2013 (1953)

and the others(see the references in Ch.1). The following steps taken in later years will be given in appendix two under the heading of ' The Wannier representation in the presence of non-periodic perturbations'.

A1.2 AN OUTLINE OF THE BASIC PRINCIPLES OF WANNIER REPRESENTATION

As mentioned earlier the Wannier representation is analogous to the coordinate representation of the continuum mechanics. basis functions are the Wannier functions[1] defined in the coordinate space. These functions are obtained from the basis functions of the C.M.R. (i.e. Bloch waves) by the unitary transformation exp(i.$\underline{k}$.$\underline{R}$)

$$a_n(\underline{r}-\underline{R}) = \int_{n^{th}\ \mathrm{B.Z.}} \Psi_n(\underline{k},\underline{r})\exp(-i.\underline{k}.\underline{R})\, d^3k \qquad \text{A1.5}$$

and the basis functions of the C.M.R. are obtained from the last equation by a reverse transformation

$$\Psi_n(\underline{k},\underline{r}) = \sum_{\underline{R}} a_n(\underline{r}-\underline{R})\exp(i.\underline{k}.\underline{R}) \qquad \text{A1.6}$$

One useful character of the Wannier representation is that one deals with the basis functions which do not spread to the whole of the coordinate space(localized functions [7]) as basis functions of the C.M.R. generally do.

B) Now, the wave function $g_n(\underline{k})$ of C.M.R. which is given by the following expansion

$$\Psi(\underline{r}) = \sum_n \int_{\mathrm{B.Z.}} g_n(\underline{k})\Psi_n(\underline{k},\underline{r})\, d^3k \qquad \text{A1.7}$$

in Wannier representation is transformed to

$$f_n(\underline{r}) = \int_{\mathrm{B.Z.}} \exp(i.\underline{k}.\underline{R})\, g_n(\underline{k})\, d^3k \qquad \text{A1.8}$$

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5 E.N. Adams, and P.N. Argyres, Phys. Rev. 102, 605(1956)

6 E.N. Adams, Phys. Rev. 107, 698(1957)

7 For the real nature of this localization see, i.e. chapters 1,2,7,and 8

B) then, $\Psi(\underline{r})$ in the Wannier representation is given by(using the equations A1.6 ,A1.7 , and A1.8)

$$\Psi(\underline{r}) = \sum_{n} \int_{B.Z.} g_n(\underline{k}) \Psi_n(\underline{k},\underline{r})\, d^3k = \sum_{n} \sum_{\underline{R}} \int a_n(\underline{r}-\underline{R})\; g_n(\underline{k}) \exp(i.\underline{k}.\underline{R})$$

$$= \sum_{n} \sum_{\underline{R}} f_n(\underline{R})\; a_n(\underline{r}-\underline{R}) \qquad \text{A1.9}$$

hence

$$\Psi(\underline{r}) = \sum_{n} \sum_{\underline{R}} f_n(\underline{R}) a_n(\underline{r}-\underline{R}) \qquad \text{A1.10}$$

C) The following can immediately be verified about the expansion coefficients $f_n(\underline{R})$'s ;

C1) If $\Psi(\underline{r})$ is normalized then (omitting all normalization constants for simplification)

$$\langle \underline{r} \mid \underline{r} \rangle = \sum_{m} \sum_{j} \sum_{m'} \sum_{j'} f^{*}_{m}(\underline{R}_j)\; f_{m'}(\underline{R}_{j'}) \quad \langle m,\underline{R}_j \mid m',\underline{R}_{j'} \rangle \qquad \text{A1.11}$$

$$= \sum_{m} \sum_{j} \sum_{m'} \sum_{j'} f_{m}(\underline{R}_j)\; f_{m'}(\underline{R}_{j'})\; \delta^{j,j'}_{m,m'} \qquad \text{A1.12}$$

$$= \sum_{m} \sum_{j} \left| f_m(\underline{R}_j) \right|^{2} = 1 \qquad \text{A1.13}$$

C2) Also, using the property that the Wannier functions have their largest amplitudes in the cells that they are localized and the assumption that $f_m(\underline{R}_j)$ is a slowly varying function of $\underline{R}_j$ (also see sections A2.4 - 7) , the probability of finding an electron within the volume δV (where δV is small compared with the size of the crystal but still containing several unit cells) is given by;

$$\delta P = \int_{\delta V} |\Psi(\underline{r})|^2 \, d^3r = C^{-1} \sum_{m} \sum_{m'} \sum_{j} \sum_{j'} \int_{\delta V} f_m(\underline{R}_j) \, f_{m'}(\underline{R}_{j'}) a_m(\underline{r}-\underline{R}_j) a_{m'}(\underline{r}-\underline{R}_{j'}) d^3r \qquad \text{A1.14}$$

but, due to the above assumption (that $f_m(\underline{R}_j)$ is almost constant over the region δV) we have

$$\delta P \doteq C^{-1} \, |f_m(\underline{R}_j)|^2 \sum_{m} \sum_{j} \sum_{m'} \sum_{j'} \int a_m(\underline{r}-\underline{R}_j) \, a_{m'}(\underline{r}-\underline{R}_{j'}) \, d^3r \qquad \text{A1.15}$$

however,

$$\sum_{m} \sum_{j} \sum_{m'} \sum_{j'} \int_{\delta V} a_m(\underline{r}-\underline{R}_j) \, a_{m'}(\underline{r}-\underline{R}_{j'}) \, d^3r = C \, \delta V \qquad \text{A1.16}$$

Where C is a constant introduced for purposes of normalization (for example if one uses an expansion over a single band in equation A1.10, then $C = N/V$ (where N is the number of the unit cells in the crystal and V is the volume of the crystal) , so that $C.\delta V$ gives the number of the unit cells in the volume δV. Therefore,

$$\delta P = \sum_{m} |f_m(\underline{R}_j)|^2 \, \delta V \qquad \text{A1.17}$$

Hence, $f_m(\underline{R}_j)$'s have a similiar behaviour to that of a wave function. Later on we will see in detail (in appendices 1 and 2) that under certain conditions they may be replaced by the functions of a continous variable $\underline{r}$, then the probability mentioned above will be given by

$$\delta P = \sum_{m} \int_{\delta V} f_m(\underline{r})^{2} d^3r \qquad \text{A1.18}$$

9 leading to the normalization of these functions (i.e. if the expansion A1.10 is over a single band, dropping the band index)

$$\int_{\delta V} | f(\underline{r}) |^2 d^3r = 1 \qquad \text{A1.19}$$

D) An operator $Hnn'(\underline{k},\underline{k}')$ of the C.M.R. becomes

$$Hnn'(\underline{R},\underline{R}') = \int_{B.Z} \exp(-i.\underline{k}'.\underline{R}')\, Hnn(\underline{k},\underline{k}')\, \exp(i.\underline{k}.\underline{R})\, d^3k\, d^3k' \qquad A1.20$$

E) Now consider as a particular case the matrix elements of the crystal momentum operator $\underline{P}_c = h\underline{k}$ between the basis functions of the C.M.R. which is given by

$$\underline{P}_{c,n,m}(\underline{k} - \underline{k}') = h\,\underline{k}\; \delta(\underline{k} - \underline{k}')\, \delta_{m,n} \qquad A1.21$$

then, in the Wannier representation the simple crystal momentum operator will be given by

$$\underline{P}_c = \int_{B.Z} \exp(-i.\underline{k}.\underline{R}')\; h\underline{k}\; \exp(i.\underline{k}.\underline{R})d^3k = \int h\underline{k}(\cos\underline{k}(\underline{R}-\underline{R}') + i\sin\underline{k}(\underline{R}-\underline{R}'))d^3k \qquad A1.22$$

where the integration is over a symmetric region of $\underline{k}$, therefore the non-zero part is given by

$$\underline{P}_c = ih \int_{B.Z} \underline{k}\, \sin\underline{k}(\underline{R} - \underline{R}')d^3k \qquad A1.23$$

In one dimension this yields

$$P_c = ih \left[\frac{\sin k_0(X-X')}{(X-X')^2} - \frac{k_0 \cos k_0(X-X')}{(X-X')} \right] \qquad A1.24$$

$$= -ih \frac{\partial}{\partial X} \frac{\sin k_0(X-X')}{(X-X')} \qquad A1.25$$

The proof can easily be generalized to three dimensions, now calling [8]

$$\delta(\underline{R} - \underline{R}') = \frac{\sin k_{0x}(X-X')\sin k_{0y}(Y-Y')\sin k_{0z}(Z-Z')}{(X-X')\;(Y-Y')\;(Z-Z')} \qquad A1.26$$

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8) Note that, $\delta(\underline{R}-\underline{R}')$ is unity when $\underline{R}=\underline{R}'$ and is zero when $\underline{R}-\underline{R}' \neq 0$ [where $\underline{R}$ and $\underline{R}'$ are proper lattice vectors]. Hence, $\delta(\underline{R}-\underline{R}')f(\underline{R}') = f(\underline{R})$.

In the later sections we have discussed the approximation of replacing the crystal coordinate operator $\underline{R}$ by the ordinary $\underline{r}$. To this assumption

(cont.)

$$\underline{P}_c = -ih \frac{\partial}{\partial \underline{R}} \delta(\underline{R}-\underline{R}') \qquad \text{A1.27}$$

If $\underline{P}_c$ operates on a function of $\underline{R}'$ say $f(\underline{R}')$ (see the foot note[8] and also the appendix 2)

$$\underline{P}_c f(\underline{R}') = -ih \frac{\partial f(\underline{R})}{\partial \underline{R}} \qquad \text{A1.28}$$

Successive applications of the operator $\underline{P}_c$ yields

$$\underline{P}_c^n f(\underline{R}) = (-ih \frac{\partial}{\partial R})^n f(\underline{R}) \qquad \text{A1.29}$$

Therefore,using equations A1.28 and A1.29 any function of $\underline{P}_c$ say $F(\underline{P}_c)$ which may be expanded as a polynamial in $\underline{P}_c$ may be replaced by the following operational form

$$F(\underline{P}_c) f(\underline{R}) = F(-i \frac{\partial}{\partial R}) f(\underline{R}) . \qquad \text{A1.30}$$

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8)(cont.)... $\delta(\underline{r} - \underline{r}')$ is a Dirac delta function ,

$\delta(\underline{r} - \underline{r}') = \lim_{k_0 \to \infty} \frac{\sin k_0(\underline{r} - \underline{r}')}{(\underline{r} - \underline{r}')}$. However in the present case k_0 is finite . Therefore this function is not a proper Dirac delta function [though localized, it oscillates and decreases only as $1/\underline{r}$].

However if $f(\underline{r})$ is a slowly varying function $\underline{r}$ (such that it varies very little over a lenght of several unit cells) then we may regard it as a constant over a part of the crystal of particular interest (say, over the cells that $\delta(\underline{r} - \underline{r}')$ is localized)) then

$$\underset{(\text{all } \underline{r})}{\int_V} \delta(\underline{r} - \underline{r}') f(\underline{r}) d^3r = (f(\underline{r}))_{\underline{r}=\underline{r}'} \int_V \delta(\underline{r} - \underline{r}') d^3r$$

but,

$$\int \delta(\underline{r} - \underline{r}') d^3r = 1$$

$$\int \delta(\underline{r} - \underline{r}') f(\underline{r}) d^3r = f(\underline{r}')$$

Therefore to this assumption (that $f(r)$ varies slowly) $\delta(\underline{r} - \underline{r}')$ may be treated as a Dirac delta function

Also consider the following exponential function of $\underline{P}_c$, $\exp(i\,\underline{P}_c.\underline{R}/h)$. This exponential function may be expanded in terms of a power series , therefore, using equations A1.28 and A1.29 this will have the following operational form on the function $f(\underline{R})$

$$\exp(i\,\underline{P}\cdot\underline{R}/h)\, f(\underline{R}) = \exp(\underline{R}\cdot\frac{\partial}{\partial R})\, f(\underline{R}) \qquad \text{A1.31}$$

So far we have shown that a function of $\underline{k}$ which may be expanded as either a polynomial or as a Fourier series in $\underline{k}$, may be replaced by an operational form where $\underline{k}$ is replaced by $\partial/\partial R$ (the approximation of replacing the crystal coordinate operator $\underline{R}$ by the ordinary $\underline{r}$ will be discussed in the later sections)

When the energy $E(\underline{k})$ is given as an explicit function in $\underline{k}$ (usually a quadratic) it will be a common practise to replace $\underline{k}$'s by the operational forms given above (i.e. see appendix 2)

F) In the Wannier representation an arbitrary function of $\underline{k}$, say $G(\underline{k})$ (in the C.M.R.) becomes,

$$G'(\underline{R} - \underline{R}) = \int \exp(-i.\underline{k}.\underline{R}')\, G(\underline{k}) \exp(i.\underline{k}.\underline{R})\, d^3k \qquad \text{A1.32}$$

Two familiar examples of these transformations are the transformations of the energy $E_n(\underline{k})$ and the wave function $g_n(\underline{k})$ of the C.M.R. to the $\mathcal{E}_n(\underline{R})$ (the Fourier coefficient of the energy) and the $f_n(\underline{R})$ the wave function of the Wannier representation.

i.e.

$$f_n(\underline{R} - \underline{R}') = \int g_n(\underline{k}) \exp(i.\underline{k}.(\underline{R} - \underline{R}'))\, d^3k \qquad \text{A1.33}$$

$$\mathcal{E}_n(\underline{R} - \underline{R}') = \int \mathcal{E}_n(\underline{k}) \exp(i.\underline{k}.(\underline{R} - \underline{R}'))\, d^3k \qquad \text{A1.34}$$

G) In appendix 2 we will see in detail that the approximate one band Hamiltonian of the Wannier representation will have either one of the following forms

$$H'_m(\underline{R}_i-\underline{R}_j) = \sum_j H_m(\underline{R}_i-\underline{R}_j) + V_m(\underline{R}_j)\,\delta(\underline{R}_i-\underline{R}_j) \qquad \text{A1.35}$$

or

$$H'_m(\underline{R}) = H_m(\partial/i\,\partial\underline{R}) + V_m(\underline{R}) \qquad \text{A1.36}$$

and the more general Hamiltonians (which takes into account transitions between energy bands) will be given by

$$H'(\underline{R}_i-\underline{R}_j) = \sum_j H_m(\underline{R}_i-\underline{R}_j) + V_m(\underline{R}_j)\ (\underline{R}_i-\underline{R}_j) + \sum_n V_{mn}(0) \qquad \text{A1.37}$$

or

$$H'(R) = H_m(\partial/i\,\partial R) + V_m(\underline{R}) + \sum_n V_{mn}(0) \qquad \text{A1.38}$$

where $V_{mn}(0) = \langle n,0\,|\,V\,|\,m,0\rangle$ and V is a non-periodic perturbation.

The difference equations and the differential equations which employ the above Hamiltonians are equivalent in sense , and are also to the same order of approximation. However in most applications the differential equations have been found to be more convenient. But, even though, the differential equations are simple enough to be handled only if $H(\partial/i\,\partial\underline{R})$ is a simple polynomial of $\partial/i\,\partial\underline{R}$ and probably is upto second order (i.e. case of spherical or elliptical energy surfaces). The straightforward derivations for the above Hamiltonians have been given in appendix 2 .

II) In appendix 2 we have studied in detail the problem of treating $H'(\underline{R})$ as a continous function. The present discussion will be restricted to the justification of some of the principles involved.

For the moment if we define a continuum Hamiltonian (as we have done in equation A1.20) simply by replacing $\underline{R}$ and $\underline{R}'$ by $\underline{r}$ and $\underline{r}'$

$$H(\underline{r},\underline{r}') = \int \exp(i.\underline{k}.\underline{r})\ H(\underline{k},\underline{k}')\exp(-i.\underline{k}'.\underline{r}')d^3k\ d^3k' \qquad \text{A1.39}$$

where we can think as $H(\underline{r},\underline{r}')$ at some well defined points (i.e. at $\underline{r}=\underline{R}$ and $\underline{r}=\underline{R}'$) is equal in value to $H(\underline{R},\underline{R}')$ which is the Hamiltonian in the difference equations. Also, let $f(\underline{r})$ be an eigenfunction of the continuum Hamiltonian $H(\underline{r},\underline{r}')$ such that

$$\int H(\underline{r},\underline{r}')\, f(\underline{r}')\, d^3r' = E\, f(\underline{r}) \qquad \text{A1.40}$$

Now, multiplying the last equation by $\exp(-i.\underline{k}^*.\underline{r})$ and $\exp(i.\underline{k}^{*'}.\underline{r}')$ (where $\underline{k}^*$ and $\underline{k}^{*'}$ are some particular points in the $\underline{k}$ space, and not necessarily in the B.Z. shown) then integrating over $\underline{r}$ and $\underline{r}'$ (they span the same space)

$$\int \exp(-i.\underline{k}^*.\underline{r})H(\underline{r},\underline{r}')\exp(i.\underline{k}^{*'}.\underline{r}')d^3r\,d^3r' = \int \delta(\underline{k}-\underline{k}^*)H(\underline{k},\underline{k}')\;\delta(\underline{k}-\underline{k}^{*'})d^3k\; d^3k$$

$$= H(\underline{k}^*,\underline{k}^{*'}) \qquad \text{A1.41}$$

If $\underline{k}^*$ or $\underline{k}^{*'}$ are not in the B.Z. concerned then,

$$H(\underline{k}^*,\underline{k}^{*'}) = \int \delta(\underline{k}-\underline{k}^*)\; H(\underline{k},\underline{k}')\;\delta(\underline{k}-\underline{k}^{*'})d^3k\; d^3k' = 0$$

$$\text{A1.42}$$

The equation A1.41 is the inverse transformation of the equation A1.39 . Now, multiplying equation A1.40 by $\exp(-i.\underline{k}^*.\underline{r})$ and integrating over $\underline{r}$, one gets

$$\int \exp(-i.\underline{k}^*.\underline{r})\; H(\underline{r},\underline{r}')\; f(\underline{r}')\; d^3r\; d^3r' = E\int \psi(\underline{r})\exp(-i.\underline{k}^*.\underline{r})d^3r$$

$$\text{A1.43}$$

If one now defines

$$\mathfrak{g}n(\underline{k}^*) = \int f(\underline{r})\exp(-i.\underline{k}^*.\underline{r})d^3r \qquad \text{A1.44}$$

and

$$\mathfrak{g}n(\underline{k}^{*'}) = \int f(\underline{r}')\exp(-i.\underline{k}^{*'}.\underline{r}')d^3r' \qquad \text{A1.45}$$

then, equation A1.43 may be replaced by

$$\int \exp(-i.\underline{k}^*.\underline{r})H(\underline{r},\underline{r}')\exp(i.\underline{k}^{*'}.\underline{r}')\; g(\underline{k}^{*'})\; d^3r\; d^3r'\, d^3k^{*'} = E\int f(\underline{r})\exp(-i.\underline{k}^*.\underline{r})d^3r \qquad \text{A1.46}$$

Now, using equation A1.41 this reduces to

$$\int H(\underline{k}^*,\underline{k}^{*'})\; g(\underline{k}^{*'})\; d^3k^{*'} = E\, g(\underline{k}^*) \qquad \text{A1.47}$$

Hence on the assumption that $g(\underline{k})$ satisfies the eigenvalue equation A1.47 in C.M.R. , then a continous function of $\underline{r}$ obtained from this by the following transformation (similiar to what we did in finding the wave function in the Wannier representation)

$$f(\underline{r}) = \int g(\underline{k})\exp(i.\underline{k}.\underline{r}\ )\; d^3k \qquad \text{A1.48}$$

satisfies the Wannier representation equation , replaced with a continuum Hamiltonian as given by the equation A1.40 .

Thus,we have shown in the principle that it is possible to define a continuum Hamiltonian and a continous wave function for the Wannier representation still fullfilling the requirements of the transformations with the C.M.R..

However,the basic conditions that still must be satisfied in passing from the difference equations (with discrete solutions) to the differential ones (where the solutions are continous functions) are

$$\left(f_n(\underline{r}')\ \right)_{\underline{r}'=\underline{R}} = F_n(\underline{R}) \qquad \text{A1.49}$$

and

$$\left(H'(\underline{r},\underline{r}')\right)_{\substack{\underline{r}=\underline{R}\\ \underline{r}'=\underline{R}'}} = H(\underline{R} - \underline{R}') \qquad \text{A1.50}$$

These final points will be discussed in appendix 2 in greater detail.

I) Finally comes the justification of an expansion which uses a single band only. Under some particular conditions this can easily be prooved to be the case. See for example Blount [9] (also see appendix 2). Roughly speaking , when the energy of the states in concern are small compared with the seperation of the levels then usage of a single band Hamiltonian (see equation A1.35) is justifiable.

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[9] E.I. Blount , Solid State Phys. 13, 305(1962)

A1.3 THE PROBLEM OF THE PHASES

In general the basis functions of the C.M.R. are defined upto an arbitrary phase i.e. $\exp(i\varphi n(\underline{k}))$. In chapters 7 and 8 we study in detail the properties of the phase fuction i.e. its reality , periodicity, its dependence only on the vector $\underline{k}$ and a differential equation which chooses its particular forms, etc.

Though the arbitrary phases must not effect any experimentally verifiable results , certain equations and variables are phase dependent (phase sensitive).

One of the worst and the simplest example to this is the non uniqueness of the Wannier functions which are obtained through the following transformation,

$$a_n(\underline{r} - \underline{R}_j) = \int_{B.Z.} \exp(i\varphi n(\underline{k}) - i.\underline{k}.\underline{R}_j)\, \psi n(\underline{k},\underline{r}) d^3k \qquad \text{A1.51}$$

where $\varphi n(\underline{k})$ is an arbitrary phase function defined in the n^{th} band. In this case dependence of the Wannier function on the phase function $\varphi n(\underline{k})$ is apparent, and among the infinite choice of the phases (that satisfies the requirements given in chapter 8) one tries to choose the best according to certain criteria(see chapters 8 and 9 , i.e. in chapter 8 we have given an original analytical method to determine the particular phases which yield the most localized Wannier functions)

Now to generalize the problem we will work out some of the most familiar equations and variables and show which are phase dependent (phase sensitive) and which are not;

To start with let us check the phase dependence of the matrix elements of an operator Q between the basis functions of Wannier representation.

We can write at once,

$$\int a^{*}_{n'}(\underline{r})\; Q\; a_{n}(\underline{r})\; d^{3}r = \iint \left[\exp(\, i\varphi_{n}(\underline{k}) - i\varphi_{n'}(\underline{k}')) \right] Q_{nn'}(\underline{k},\underline{k}')\, d^{3}k\, d^{3}k'$$

where A1.52

$$Q_{nn'}(\underline{k},\underline{k}') = \int \psi_{n}(\underline{k},\underline{r})\; Q\; \psi_{n}(\underline{k},\underline{r})\; d^{3}r \qquad \text{A1,53}$$

If $Q = 1$

$$Q_{nn}(\underline{k},\underline{k}) = \delta_{nn'}\, \delta(\underline{k} - \underline{k}') \qquad \text{A1.54}$$

then to this choice equation A1.52 is phase independent(it is either a constant number or zero)

However if we now choose $Q = F(\underline{r})$ (where F is a function of $\underline{r}$) then $Q_{nn'}(\underline{k},\underline{k}')$ is no longer diagonal in $\underline{k}$ and n , therefore to this choice equation A1.52 is phase dependent (including the case $n = n'$)

As a final illustration if we choose $Q = F(\nabla_{\underline{k}})$ (where F is a function of $\text{grad}_{\underline{k}}$) in the following matrix element A1.55

$$\int \psi_{n'}(\underline{k}',\underline{r})\; Q\; \psi_{n}(\underline{k},\underline{r})\, d^{3}r = \int \exp(-i\varphi_{n'}(\underline{k}'))\, \psi_{n'}(\underline{k}',\underline{r})\, F(\nabla_{\underline{k}}) \exp(i\varphi_{n}(\underline{k}))\, \psi_{n}(\underline{k},\underline{r})\, d^{3}r \;.$$

then it is phase dependent (including the case $n = n'$, $k = k'$)

i.e. if one sets $Q = -i\nabla_{\underline{k}}$, then equation A1.55 becomes

$$\exp(i\varphi_{n}(\underline{k}) - i\varphi_{n'}(\underline{k}')) \cdot \left[\delta_{nn'}\, \delta(\underline{k}-\underline{k}')\, \nabla_{k} \varphi_{n}(\underline{k}) + S_{nn'}(\underline{k},\underline{k}') \right]$$

A1.56

where

$$S_{nn'}(\underline{k},\underline{k}') = -i\int \psi_{n'}(\underline{k}',\underline{r})\, \nabla_{\underline{k}}\, \psi_n(\underline{k},\underline{r})\; d^3r \qquad \text{A1.57}$$

which yields; for $n \neq n'$, $\underline{k} \neq \underline{k}'$

$$\exp(i\varphi_n(\underline{k}) - i\varphi_{n'}(\underline{k}')) \cdot S_{nn'}(\underline{k},\underline{k}') \qquad \text{A1.58}$$

and for $n = n'$, $\underline{k} = \underline{k}'$

$$\frac{\partial}{\partial \underline{k}}\varphi_n(\underline{k}) + S_{nn}(\underline{k},\underline{k}) \qquad \text{A1.59}$$

where both expressions are phase dependent.

We have worked out the phase dependence of several familiar equations and variables in both Wannier and crystal momentum representations. Below in table A1.1 we quote the results only. Blount[9] further gives explicit expressions for some of the quantities given in this table , which however will not concern us.

PHASE DEPENDENT

IN W.R	IN C.M.R
The basis function $a_n(\underline{r}-\underline{R}_j)$	The basis function $\psi n(\underline{k},\underline{r})$
The wave function $\sum_n\sum_j f n(\underline{R}_j)a_n(\underline{r}-\underline{R}_j)$	The wave function $\sum_n \int g n(\underline{k})\psi n(\underline{k},\underline{r})$
The position matrix of $\underline{r}^m$ * $\langle n,\underline{R}_i\lvert\underline{r}^m\rvert n',\underline{R}_j\rangle$ $\langle n,\underline{R}_i\lvert\underline{r}^m\rvert n,\underline{R}_i\rangle$	$\langle n',\underline{k}'\lvert\underline{r}^m\rvert n,\underline{k}\rangle$ (including $n=n'$ or $\underline{k}=\underline{k}'$, but not both at once)
	The matrix element of the true momentum $\langle n',\underline{k}\lvert p\rvert n,\underline{k}\rangle$ $(n \neq n')$
*Note that if m = 0 the phase dependence vanishes in both representations (see also the table given below)	

PHASE INDEPENDENT

IN W.R.	IN C.M.R.
The integrals $\langle n,\underline{R}_i\mid n,\underline{R}_j\rangle$ $\langle n,\underline{\underline{R}}_i\mid n,\underline{R}_i\rangle$	The probabibility distributions $\psi^*_n(\underline{k},\underline{r})\ n'(\underline{k}',\underline{r})$ $\psi^*_n(\underline{k},\underline{r})\,\psi n(\underline{k},\underline{r})$ and their sums $\langle n,\underline{k}\mid n,\underline{k}\rangle$, $\langle n,\underline{k}\mid n',\underline{k}\rangle$
The energy Fourier coefficient $\langle n,\underline{R}_i\lvert H^\circ\rvert n,\underline{R}_j\rangle$ (including i=j)	The energy eigenvalue of the cryst. Hamilt. $\langle n,\underline{k}\lvert H^\circ\rvert n,\underline{k}\rangle$
	The matrix elements of the crystal momentum. $\langle n',\underline{k}'\lvert h\underline{k}\rvert n,\underline{k}\rangle$ (inc. $n=n'$, $\underline{k}=\underline{k}'$)
	The position matrix of $\underline{r}^m$ $\langle n,\underline{k}\lvert\underline{r}^m\rvert n,\underline{k}\rangle$
	The matrix elements of the true momentum $\langle n,\underline{k}'\lvert\underline{p}\rvert n,\underline{k}\rangle$ $\langle n,\underline{k}\lvert\underline{p}\rvert n,\underline{k}\rangle$

Table A3.1 Phase dependence of some familiar equations and variables in both Wannier and Crystal momentum representations. n,n', $\underline{k},\underline{k}'$ and $\underline{R}_i,\underline{R}_j$ are not equal unless otherwise stated.

APPENDIX 2

WANNIER REPRESENTATION EQUATIONS AND THE PROBLEMS CONNECTED WITH POINT IMPURITIES AND EXTERNAL FIELDS (NON-PERIODIC PERTURBATIONS)

A2.1 GENERAL

In chapter 5 we have suggested a method to find out the perturbed Wannier functions in the presence of a periodic perturbation. In general , these Wannier functions which are the solutions to the periodic problem(and being a complete set of functions in the coordinate space) can be used as a basis in expanding the wave function of the non-periodic (defect) structures. This actually is the basis of the Wannier representation.

The non-periodic perturbations in solids may be due to;

i) Internal imperfections as impurities , dislocations, and surfaces , etc.

ii) External effects as electric fields, magnetic fields, etc.

We will first start with the perturbations associated with the time dependent Schrödinger equation. Therefore we are concerned with the solutions of the following time dependent equation

$$\left[H + V \right] \Psi = i h \frac{\partial \Psi}{\partial t} \qquad \text{A2.1}$$

where H is the Hamiltonian of the periodic structure and V is a (non-periodic) perturbation. The perturbing field V in general may be uniform or non-uniform (i.e. interaction of electrons with electromagnetic radiation) and also the system itself may be conservative or non-conservative depending on whether the perturbing field is also a function of time or not.

Some aspects of the problem has been handled by several authors[1], (like Wannier , Slater , Adams , Kohn , Luttinger , Blount , Roth , Gibson , Zener , Houston , Koster , Cloizeaux , etc.)

References to some of the fundamental work will be made during the treatment of each topic.

The main classifications in the approaches depend on the choice of the basis functions for expanding the perturbed wave function Ψ .

There are only few fundamental choices(though infinite in principle) for the basis functions , each leading to a different representation like Crystal momentum representation (C.M.R.) or Wannier representation.

Modified forms of these basis functions (i.e. Kohn-Luttinger functions) which lead to some alternative forms of the fundamental representations (like, Kohn-Luttinger modified crystal momentum representation , M.C.M.R.),have also been suggested.

We can finally mention a mixed representation which employs the principles of both representations (i.e. Blount[2], Zak[3], etc.)

In the following sections though we will give a brief out line of the fundamental representations, the primary emphasis will be on the Wannier representation.

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1) See the references given in chapter 1 and appendix 1

*2) Blount, E.I.,Solid State Physics 13, 305(1962)

3) See for instance,J.Zak, Comments Solid State Phys. 2,209(1970)

A2.2 CRYSTAL MOMENTUM REPRESENTATION (C.M.R.)

This is the one used fundamentally by Adams [4] and may be outlined as follows;

The eigenfunctions of the periodic system (unperturbed) are the Bloch functions satisfying

$$H\,\psi_n(\underline{k},\underline{r}) = E_n(\underline{k})\,\psi_n(\underline{k},\underline{r}) \qquad \text{A2.2}$$

These Bloch functions are orthonormal in the following sense

$$\int \psi_n^*(\underline{k},\underline{r})\,\psi_m(\underline{k},\underline{r})\,d^3r = \delta_{nm}\;\delta(\underline{k}-\underline{k}) \qquad \text{A2.3}$$

and they constitute a complete orthonormal set which may be used as basis functions in expansion of the wave function of the perturbed system A2.1.

$$\Psi(\underline{r}) = \sum_n \int_{B.Z.} g_n(\underline{k})\,\psi_n(\underline{k},\underline{r})\,d^3k \qquad \text{A2.4}$$

Substituting equation A2.4 into the equation A2.1 and using the equation A2.2 one simply gets

$$\sum_n \int_{B.Z.} g_n(\underline{k})E_n(\underline{k})\,\psi_n(\underline{k},\underline{r})\,d^3k + V\sum_n \int g_n(\underline{k})\,\psi_n(\underline{k},\underline{r})\,d^3k$$

$$= i\,h\,\frac{\partial}{\partial t}\sum \int g_n(\underline{k})\,\psi_n(\underline{k},\underline{r})\,d^3k$$

$$\text{A2.5}$$

Multiplying both sides of this equation by $\psi_m^*(\underline{k}',\underline{r})$ and integrating over the entire crystal (or over the unit cell depending on where the Bloch waves are normalized) one gets

$$\left[E_n(\underline{k}') - i\,h\,\frac{\partial}{\partial t}\right] g_n(\underline{k}') + \sum_n \int \langle n,\underline{k} \mid V \mid m,\underline{k}' \rangle\, g_n(\underline{k})\,d^3k = 0$$

$$\text{A2.6}$$

This is the crystal momentum representation (C.M.R.) by Adams [4].

4) See the references in chapter 1 and appendix 1

A2.3 KOHN-LUTTINGER MODIFIED CRYSTAL MOMENTUM REPRESENTATION(M.C.M.R.)

A variation of crystal momentum representation has been given by Kohn and Luttinger[5] in 1955 . They choose a set of basis functions related to the Bloch functions at a particular $\underline{k}$ point in the band. This point is usually taken to be a minumum or a maximum. If we call such a point $\underline{k}_o$ then the basis functions of the Kohn-Luttinger scheme are obtained by,

$$\chi n(\underline{k},\underline{r}) = \exp(i.(\underline{k} - \underline{k}_o).r)\, \psi n(\underline{k}_o,\underline{r}) \qquad \text{A2.7}$$

$$= \exp(i.\underline{k}.\underline{r})\, U_n(\underline{k}_o,\underline{r}) \qquad \text{A2.8}$$

Apparently they have the form of Bloch functions with the exception that $U_n(\underline{k}_o,\underline{r})$ is the periodic part of the Bloch function of a particular crystal momentum vector $\underline{k}_o$, and the dependence of $\chi n(\underline{k},\underline{r})$ upon $\underline{k}$ lies entirely in the plane wave function.

In order that these functions can be used as an alternative basis their completeness (and for convenience their orthonormality) has to be verified . In other terms the following has to be proved;

i) An arbitrary function of $\underline{r}$, that can be expanded in terms of Bloch functions can also be expanded in $\chi n(\underline{k},\underline{r})$'s

ii) $\chi n(\underline{k},\underline{r})$'s and $\chi\ (\underline{k}',\underline{r})$'s must be orthogonal for $n \neq m$ and $k \neq k'$ and each must be square integrable.

Here, we will avoid the lenghty formulations, however,these can easily be proved to be the case (i.e. see Callaway[6]) .

Now, expanding the solution of equation A2.1 in the Kohn Luttinger functions $\chi n(\underline{k},\underline{r})$

$$\Psi(\underline{r}) = \sum_n \int_{B.Z.} C_n(\underline{k})\, \chi n(\underline{k},\underline{r})\, d^3k \qquad \text{A2.9}$$

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5) J.M.Lutting and W.Kohn , Phys. Rev. 97, 869(1955)

6) J. Callaway , Energy Band Theory ,pp.217, Academic Press(1963)

Substituting this into equation A2.1 , then multiplying both sides of the equation by $\Psi^*(r)$, integrating over all crystal and working out the outcoming terms in a similiar way that we have done in the previous sections , one finds the following equation to be solved for the coefficients $Cm(\underline{k})$'s .

$$\left[Em + h^2\underline{k}^2/2m - ih\frac{\partial}{\partial t} \right] Cm(\underline{k}) + h.\underline{k}/m \sum_n PmnCn(\underline{k}) \qquad A2.10$$

$$+\sum_n \int \langle m,k|V|n,k'\rangle Cn(k')\, d^3k' = 0 \qquad A2.11$$

where

$$Pmn = 2\pi^3/\Omega \int u_m^*(\underline{r}) P\, u_n(\underline{r})\, d^3r \;, \quad P = h\nabla/i \qquad A2.12$$

and

$$\langle m,\underline{k}\,|\,V\,|\,n,\underline{k}'\rangle = 2\pi^3/\Omega \int \chi m(\underline{k},\underline{r})\, V\, \chi n(\underline{k}',\underline{r})\, d^3r \qquad A2.13$$

A2.4 WANNIER REPRESENTATION

In appendix 1 we have mentioned about the possibility of expanding the wave function $\Psi(\underline{r})$ in terms of Wannier functions. In chapter 2 we have also verified the completeness , orthogonality etc. of these functions. Hence, expanding $\Psi(\underline{r})$ in the Wannier functions

$$\Psi(\underline{r}) = \sum_m \sum_j f m(\underline{R}_j)\, a_m(\underline{r} - \underline{R}_j) \qquad A2.14$$

where we assume that $a_m(\underline{r} - \underline{R}_j)$'s have been obtained by solving the periodic (unperturbed) system. Hence, they satisfy

$$H\, a_m(\underline{r} - \underline{R}_j) = \sum_s \overset{\circ}{\varepsilon} m(\underline{R}_s)\, a_m(\underline{r} - \underline{R}_j - \underline{R}_s) \qquad A2.15$$

and

$$\overset{\circ}{\varepsilon} m(\underline{R}_s) = \sum_{\underline{k}\ B.Z} \overset{\circ}{Em}(\underline{k}) \exp(i.\underline{k}.\underline{R}_s) \qquad A2.16$$

where $\overset{\circ}{\varepsilon} m(\underline{R}_s)$'s and $\overset{\circ}{Em}(\underline{k})$'s represent the unperturbed energy fourier coefficients and the energy itself.

A2.5 WANNIER REPRESENTATION EQUATIONS

The present task is to solve the following equation

$$(H + V)\,\Psi(\underline{r}) = E\,\Psi(\underline{r}) \qquad \text{A2.17}$$

where H is the Hamiltonian of a perfect crystal and V is a perturbation caused by one or another disturbance of the periodic potential (impurities, dislocations, external fields , etc.) .

Now, substituting equation A2.14 into equation A2.17 one gets

$$H\sum_{n}\sum_{j} f_n(\underline{R}_j)\,a_n(\underline{r}-\underline{R}_j) + V\sum\sum f_n(\underline{R}_j)\,a_n(\underline{r}-\underline{R}_j) = E\sum\sum f_n(\underline{R}_j)\,a\,(\underline{r}-\underline{R}_j) \qquad \text{A2.18}$$

multiplying both sides of this equation by $a^{*}_{m}(\underline{r}-\underline{R}_k)$, again integrating over the entire crystal , and using equation A2.15 one finds

$$\sum_{n}\sum_{j} \varepsilon^{o}_{nm}(\underline{R}_k-\underline{R}_j)\, f_n(\underline{R}_j)\,\delta_{nm} + \sum_{n}\sum_{j} f_n(\underline{R}_j) V_{nm}(\underline{R}_k-\underline{R}_j) = E\, f_m(\underline{R}_k) \qquad \text{A2.19}$$

or

$$\sum_{j} \varepsilon^{o}_{mm}(\underline{R}_k-\underline{R}_j)\, f_m(\underline{R}_j) + \sum_{n}\sum_{j} f_n(\underline{R}_j) V_{nm}(\underline{R}_k-\underline{R}_j) = E\, f_m(\underline{R}_k) \qquad \text{A2.20}$$

The final equation can alternatively be written as

$$\sum_{j} \left[\, \varepsilon^{o}_{mm}(\underline{R}_k-\underline{R}_j) + V_{mm}(\underline{R}_k-\underline{R}_j) \,\right] f_m(\underline{R}_j) + \sum_{j}\sum_{n} V_{nm}(\underline{R}_k-\underline{R}_j)\, f_n(\underline{R}_j) = E\, f_m(\underline{R}_k) \qquad \text{A2.21}$$

where

$$\varepsilon^{o}_{mm}(\underline{R}_k-\underline{R}_j) = \langle m,\underline{R}_k|\,H\,|m,\underline{R}_j\rangle \qquad \text{A2.22}$$

$$V_{nm}(\underline{R}_k-\underline{R}_j) \qquad \langle m,\underline{R}_k|\,V\,|\,n,\underline{R}_j\rangle \qquad \text{A2.23}$$

If instead equation A2.17 a time dependent Schrodinger eqn. is used, i.e.

$$(\,H + V\,)\,\Psi(\underline{r}) = i\,h\,\partial\Psi/\partial t \qquad \text{A2.24}$$

one ends up with the following equation to be solved for the coefficients $f_m(\underline{R}_j)$'s .

$$\sum_{j} \left(\, \varepsilon^{o}_{mm}(\underline{R}_k-\underline{R}_j) - ih\,\partial/\partial t\;\delta_{k,j}\,\right) f_m(\underline{R}_j) + \sum_{\substack{n \\ n\neq m}}\sum_{j} V_{mn}(\underline{R}_k-\underline{R}_j)\, f_n(\underline{R}_j) = 0 \qquad \text{A2.25}$$

These are the general difference equations for $f_n(\underline{R}_j)$'s which we have obtained without any approximation . Now, the perturbed energy E on the right and the coefficients $f_n(\underline{R}_j)$'s remain to be determined (we assume that the periodic problem has already been solved and the perturbation V has been given explicitly such that $V_{mm}(\underline{R}_k-\underline{R}_j)$'s can be determined by equation A2.23)

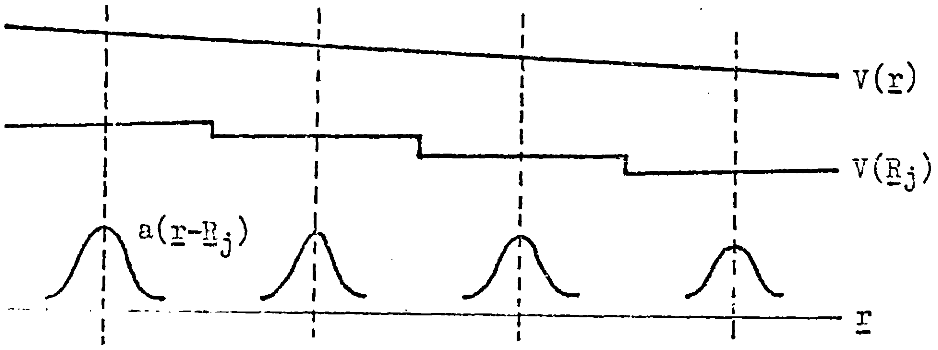
In general the solution of these difference equations is quite difficult and the applications are limited to a number of relatively simpler problems.

In the next sections we will show how these equations can be put into more practical forms using certain assumptions and approximations.

A2.6 SLOWLY VARYING PERTURBING FIELDS(THE FIRST APPROXIMATION)

When the perturbing field V varies very slowly compared with the distance of atomic seperations (or in other words it varies very little over a lenght of several unit cells) , then we may regard it as a constant over a part of the crystal (say over a unit cell) of particular interest.

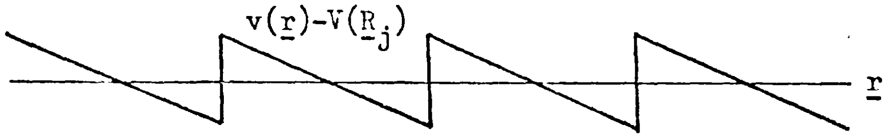
This point may schematically be illustrated as follows,



The slowly varying function $V(\underline{r})$ is approximated in terms of a stepwise function $V(\underline{R}_j)$ where $V(\underline{R}_j)$ is obtained by setting succesively $\underline{r} = \underline{R}_j$ in the function $V(\underline{r})$

$$V(\underline{R}_j) = \left(V(\underline{r}) \right)_{\underline{r} = \underline{R}_j} \qquad \text{A2.26}$$

The difference in taking the stepwise function $V(\underline{R}_j)$ instead the real perturbing field $V(\underline{r})$ can be illustrated as follows (on the assumption that $V(\underline{r})$ varies linearly)



Clearly the slower the $V(\underline{r})$ varies the smaller is the amplitude of the saw-tooth function and the more justifiable is the approximation.

Then on this assumption(that $V(\underline{r})$ varies slowly)

$$\begin{aligned} Vmm(\underline{R}_k - \underline{R}_j) &= \langle m, \underline{R}_k \mid V \mid m, \underline{R}_j \rangle \cong 0 \quad \text{if } \underline{R}_j \neq \underline{R}_k \qquad \text{A2.27} \\ &= \left(V(\underline{r}) \right)_{\underline{r}=\underline{R}_k} \langle m, \underline{R}_k \mid m, \underline{R}_k \rangle \quad \text{if } \underline{R}_j = \underline{R}_k \\ &= \left(V(\underline{r}) \right)_{\underline{r}=\underline{R}_k} \quad \text{if } \langle m, \underline{R}_k \mid m, \underline{R}_k \rangle = 1 \\ &= V(\underline{R}_k) \end{aligned}$$

and

$$\begin{aligned} Vmn(\underline{R}_k - \underline{R}_j) &= \langle m, \underline{R}_k \mid V \mid n, \underline{R}_j \rangle \cong 0 \quad \text{if } \underline{R}_j \neq \underline{R}_k \qquad \text{A2.28} \\ &= \langle m, \underline{R}_k \mid V \mid n, \underline{R}_k \rangle \quad \text{if } \underline{R}_j = \underline{R}_k \\ &= V'mn(0) \end{aligned}$$

Note that, in this case it is not possible to take V out of the integral since that would mean setting this second order term automatically to zero, i.e. $V \langle m, \underline{R}_k \mid n, \underline{R}_k \rangle = 0$

Using equations A2.27 and A2.28 equation A2.21can now be written as

$$\sum_{j} \varepsilon^{0}_{mm}(\underline{R}_k-\underline{R}_j)\, f_m(\underline{R}_j) + V(\underline{R}_k) f_m(\underline{R}_k) + \sum_{j}\sum_{\substack{n \\ n\neq m}} V'_{mn}(0)\, f_n(\underline{R}_k) = E\, f_m(\underline{R}_k) \qquad \text{A2.29}$$

which is a (modified) difference equation for $f(\underline{R}_j)$'s .

A2. 7 REPLACEMENT BY DIFFERENTIAL FORMS

Now, we will show how this set of difference equations can be reduced to differential forms. The possibility of such a conversion has fundamentally been shown by Wannier[7] (1937) and also has been rediscussed by Slater[7] (1949) for a particular case where the expansion A2.14 has been restricted to a single band only.The development has been followed by others (see the references in appendix 1)

Here,we will keep the argument more general and give the differential forms for a multiband Hamiltonian first. The first term on the left hand side of equation A2.29 may be rearranged (by defining $\underline{R}_s = \underline{R}_k - \underline{R}_j$) as follows

$$\sum_{j} \varepsilon^{0}_{mm}(\underline{R}_k - \underline{R}_j)\, f_m(\underline{R}_j) = \sum_{s} \varepsilon^{0}_{mm}(\underline{R}_s)\, f_m(\underline{R}_k - \underline{R}_s) \qquad \text{A2.30}$$

Equation A2.29 , can now be written as follows

$$\sum_{s} \varepsilon^{0}_{mm}(\underline{R}_s)\, f_m(\underline{R}_k - \underline{R}_s) + V(\underline{R}_k) f_m(\underline{R}_k) + \sum_{\substack{n \\ n\neq m}} V'_{mn}(0)\, f_n(\underline{R}_k) = E\, f_m(\underline{R}_k) \qquad \text{A2.31}$$

Let us now examine the effect of an exponential operator $\exp(-\underline{R}_s . \nabla)$ on an arbitrary function of $\underline{r}$, say $f(\underline{r})$

$$\exp(-\underline{R}_s . \nabla)\, f(\underline{r}) = f(\underline{r}) - \underline{R}_s . \nabla f(\underline{r}) + (\underline{R}_s . \nabla)(\underline{R}_s . \nabla f(\underline{r}))/2 - \ldots\ldots \qquad \text{A2.32}$$

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[7] see the references in chapter 1 and appendix 1 .

which is simply the Taylor expansion of the function $f(r)$, hence

$$\exp(-\underline{R}_s . \nabla)\, f(\underline{r}) = f(\underline{r} - \underline{R}_s) \qquad \text{A2.33}$$

In chapter 2, we have also shown that $\varepsilon^{\circ}_{mm}(\underline{R}_s)$'s are the Fourier coefficients of the unperturbed energy function $Em(\underline{k})$, hence

$$Em(\underline{k}) = \sum_{S} \varepsilon^{\circ}_{m}(\underline{R}_s)\exp(-i.\underline{k}.\underline{R}_s) \qquad \text{A2.34}$$

Now let us define a fundamental operator from $Em(\underline{k})$ by replacing $\underline{k}$ by ∇/i,

$$Em(\nabla/i) = \sum_{S} \varepsilon^{\circ}_{m}(\underline{R}_s)\exp(-\underline{R}_s . \nabla) \qquad \text{A2.35}$$

when this operates on an arbitrary function $f m(r)$

$$Em(\nabla/i)\, f m(\underline{r}) = \sum_{S} \varepsilon^{\circ}_{m}(\underline{R}_s)\exp(-\underline{R}_s . \nabla)\, f m(\underline{r}) = \sum_{S} \varepsilon^{\circ}_{m}(\underline{R}_s)\, f m(\underline{r} - \underline{R}_s)$$

Now, comparing the following equation A2.36

$$Em(\nabla/i)\, f m(\underline{r}) + V(\underline{r})\, f m(\underline{r}) + \sum_{\substack{n \\ n \neq m}}{}' V_{mn}(0)\, f m(\underline{r}) = E\, f m(\underline{r}) \qquad \text{A2.37}$$

with the equation given below (see equation A2.31)

$$\sum_{S} \varepsilon m(\underline{R}_s)\, f m(\underline{R}_k - \underline{R}_s) + V(\underline{R}_k)\, f m(\underline{R}_k) + \sum_{\substack{n \\ n \neq m}}{}' V_{mn}(0)\, f m(\underline{R}_k) = E\, f m(\underline{R}_k) \qquad \text{A2.38}$$

where the first terms on the left hand side of the equations A2.37 and A2.38 are identical by equation A2.36 provided that the arbitrary vector $\underline{R}_k$ which generates the crystal is replaced by $\underline{r} = \underline{R}_k$.

Actually what this implies has been discussed in detail in the previous sections.

When one also sets $\underline{r} = R_k$ in the remaining terms of the equation A2.37 the two equations A2.37 and A2.38 become identical, which proves that the last equation may be replaced by an (equivalent) differential equation of the form A2.37.

To solve this differential equation one has to know the function $Em(\underline{k})$ explicitly. Expansions employing quadratic forms have found some useful applications in practice (where the differential operator $Em(\nabla/i)$ has been obtained simply by replacing k_x, k_y, etc. by $-i\partial/\partial x$ $-i\partial/\partial y$, etc.).

A2.8 THE SECOND APPROXIMATION, EXPANSIONS USING WANNIER FUNCTIONS OF A SINGLE BAND ONLY

When one deals with states where energy is small compared with the seperation of the bands such that

$$E/\delta E \ll 1 \qquad \text{A2.39}$$

where E is the energy of the state and δE is the seperation of the bands then it can be proved (i.e. see Blount) that it is not necessary to include in A2.14 Wannier functions of bands other than the one under consideration. Hence, when an expansion using Wannier functions of a single band only is justified, i.e.

$$\Psi(\underline{r}) = \sum_{j} f m(\underline{R}_j) a_m(\underline{r} - \underline{R}_j) \qquad \text{A2.40}$$

then the terms (in equations A2.37 and A2.38) containing the inter-band interactions vanish, i.e.

$$\sum_{\substack{n \\ n \neq m}} V'mn(0) f m(\underline{r}) = 0 \; , \quad \sum_{\substack{n \\ n \neq m}} V'mn(0) f m(\underline{R}_k) = 0 \qquad \text{A2.41}$$

to yield the following simpler set of difference and differential equations

$$\sum_{s} \mathcal{E}\overset{\circ}{m}(\underline{R}_s)\ Cm(\underline{R}_k-\underline{R}_s) + V(\underline{R}_k) \int m(\underline{R}_k) = E \int m(\underline{R}_k) \qquad \text{A2.42}$$

and

$$Em(\nabla/i) \int m(\underline{r}) + V(\underline{r}) \int m(\underline{r}) = E \int m(\underline{r}) \qquad \text{A2.43}$$

These are the forms fundamentally suggested by Wannier[7] (1937) and used by Slater[7] (1949).

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