CHAPTER III

METAL SURFACE.

In this chapter we will discuss the finite bounded metallic crystal, in which there are no intrinsic localized states. There are three important approaches to the surface problem, the crystal orbital (CO) method,[60] the crystal potential method[61] and the density functional formalism.[41-45] The first two methods have been reviewed by Davison and Levine (1970)[6] with the aim of studying the surface states, especially the intrinsic surface states.[62,63] Of these two methods the crystal potential method has more advantag . The Mathieu crystal potential method[64] can display a smooth conceptual transition between NFE and LCAO limit ; this method can be worked out relativistically[6] thus generalizing Tamm's classic work (1932).[62] The third approach has been reviewed by Lang (1973),[7] using the density functional formalism to calculate spatial charge density directly.[65,66] This approach has the advantage of being able to take into account correlation effect. Its disadvantage is that the wave function can not be directly calculated. This formalism can only be work well, self-consistently for small varying or nearly constant charge density.[42]

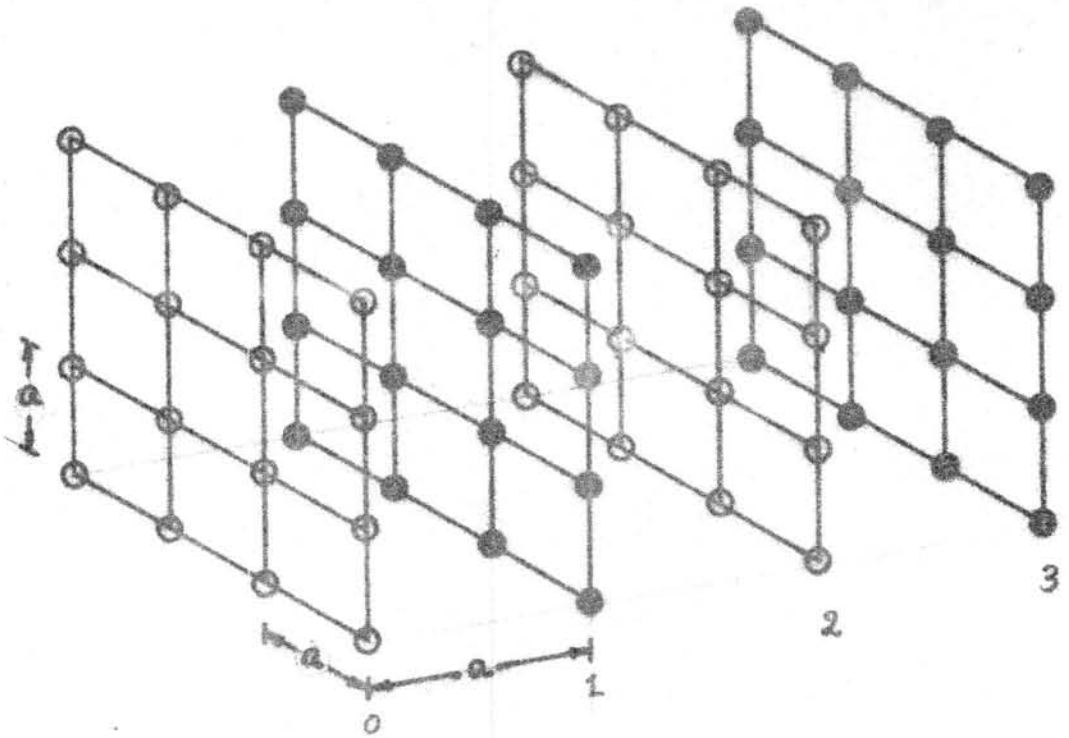
All of the methods at present time have been applied to a model metal surface. Nearly all of the models used is the

semi-infinite crystal (SIC) model. Usually, the one - dimensional (1-D) model is studied. This model is believed to be a good representation of crystal surface. However, no one has proved that it is a really good model. Like others we will use SIC as our model.

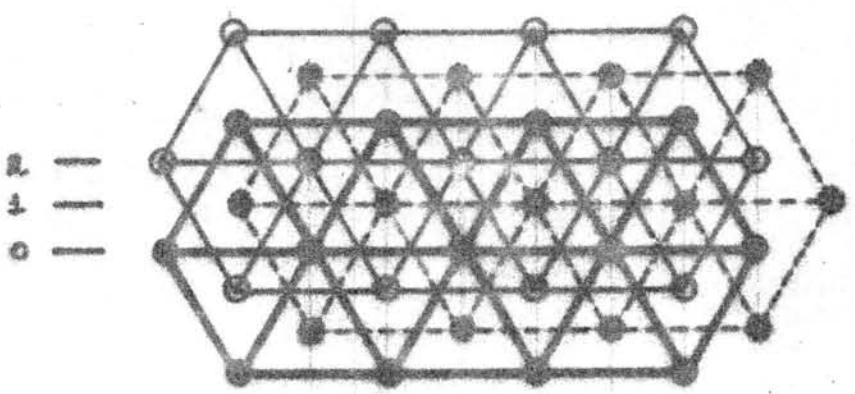
3.1 Semi-infinite crystal (SIC) model.

The best known crystal model, that has been used to discuss the chemisorption phenomenon, is SIC model. In this model, there is a single surface plane which divides the space into two half, the crystal and vacuum. Any SIC can be built from various suitable 2-D infinite planar crystal sheet. We can label the first layer, the surface, by 0 and the next by 1,2,3,..., j, ..., M-1, where M is large number. Then the combined sheet system is SIC. One simple example is simple cubic crystal (SCC) with (001) plane as crystal surface. All 2-D crystal layers to be chosen to have the same 2-D lattice structure as (001) surface plane (see Fig. 3.I.1a). Another example is face center cubic crystal (FCC) with (111) as surface plane. Since we know that FCC can be built from ABC-closest pack, all layers parallel to (111) plane has the same 2-D lattice structure. There are three different configurations correspond to A, B and C packing layers(see Fig. 3.1.1.b).

Clearly, the crystal have 2-D translation symmetry parallel to the surface plane. This means that Bloch's theorem is satisfied for every layers. We now define z to be normal to the surface plane and



(a)



(b)

Fig.3.1.1 : The semi-infinite crystal of (a) the simple cubic lattice with (001) surface plane, (b) the face center cubic lattice with (111) surface plane.

$$\bar{R}_{\ell_j} = \ell \cdot \hat{a}_j + \ell' \cdot \hat{b}_j \quad , \tag{3.1.1}$$

where $\hat{a}_j$ and $\hat{b}_j$ are translation vectors for j-layer in xy-direction, ℓ and ℓ' are arbitrary integers. Then the wave function $X_k^j(\bar{r})$ for j layer have boundary conditions

$$\hat{T}_{\ell_j} \cdot X_k^j(\bar{r}) = X_k^j(\bar{r}-\bar{R}_{\ell_j}) = \exp(i\bar{k}\cdot\bar{R}_{\ell_j})\, X_k^j(\bar{r}) \quad , \tag{3.1.2}$$

and

$$\lim_{z \to \infty} \cdot X_k^j(\bar{r}\pm\bar{z}) = 0 \quad , \tag{3.1.3.a}$$

$$\lim_{z \to \infty} \frac{d}{dz} X_k^j(\bar{r}\pm\bar{z}) = 0 \quad . \tag{3.1.3.b}$$

If $X_k^j(\bar{r})$ is known for all layers, the crystal wave function, $\Psi_k(\bar{r})$, can be expanded by linear combination of layer orbitals similar to LCAO.

$$\Psi_k(\bar{r}) = \sum_j \cdot C_j(\bar{k}) \cdot X_k^j(\bar{r}-\bar{Z}_j) \cdot \tag{3.1.4}$$

We now let H_m be the one-electron Hamiltonian of the crystal. Then we have

$$H_m \cdot \Psi_k(\bar{r}) = E_k \cdot \psi_k(\bar{r}) \quad . \tag{3.1.5}$$

Multiplying 3.1.5 by $X_k^{i*}(\bar{r}-\bar{Z}_i)$, integrating over all space and substituting $\psi_k(\bar{r})$ by 3.1.4, we get

$$(H - E_k \cdot S)_{ij} \cdot C_j(\bar{k}) = 0 \quad , \tag{3.1.6}$$

which is the secular equation. The repeated indices imply summation. The explicit expressions of the matrix elements are

$$H_{ij} = \int d^3r . X_k^{i*}(\bar{r}-\bar{Z}_i) . H_m . X_k^j(\bar{r}-\bar{Z}_j) \ , \qquad (3.1.7)$$

$$S_{ij} = \int d^3r . X_k^{i*}(\bar{r}-\bar{Z}_i) . X_k^j(\bar{r}-\bar{Z}_j) . \qquad (3.1.8)$$

Since H_m can be separated out into two part, j-layer's Hamiltonian H_j^o and $\bar{V}_j = V - V_j$, where V is total one-electron potential and V_j is j-layer's one-electron potential. So that

$$H_m = H_j^o + \bar{V}_j \ , \qquad (3.1.9.a)$$

where

$$H_j^o = \frac{-h^2}{2m} . \nabla^2 + V_j \ . \qquad (3.1.9.b)$$

Then we have

$$H_j^o . X_k^j(\bar{r}) = E_j^o(\bar{k}) . X_k^j(\bar{r}) \ . \qquad (3.1.10)$$

Note that, this separation has no effect on the total Hamiltonian H_m.

Equation 3.1.8 becomes

$$S_{ij} = \int d^3r . X_k^{i*}(\bar{r}-(\bar{Z}_i-\bar{Z}_j)) . X_k^j(\bar{r}) \ . \qquad (3.1.11)$$

Similarly, 3.1.9 becomes

$$H_{ij} = \int d^3r . X_k^{i*}(\bar{r}-(\bar{Z}_i-\bar{Z}_j)) . (H_j^o + \bar{V}_j) . X_k^j(\bar{r})$$

$$= E_j^o . S_{ij} + J_{ij} \ , \qquad (3.1.12)$$

where $$J_{ij} = \int d^3r . X_k^{i*}(\bar{r}-(\bar{Z}_i-\bar{Z}_j)) . \bar{V}_j . X_k^j(\bar{r}) \ . \qquad (3.1.13)$$

If i = j, J_{ij} becomes

$$J_{ii} = \int d^3r . X_k^{i*}(\bar{r}) . \bar{V}_j . X_k^j(\bar{r}) \ ,$$

the crystal field integral. If $i \neq j$, then J_{ij} is the interaction integral, which is alway negative. For the bulk layers, where the indices i and j are large, we have $J_{ij} = J_{ji}$.

All of these parameters can not be calculated unless the one-electron Hamiltonian and wave function of the layer j are known. We now let v(r) be the atomic potential acting on an electron, where the atomic core is at(0,0,0) position in space. We have

$$H_m = \frac{-h^2}{2m} . \nabla^2 + \sum_{\ell_j j} . v(\bar{r}-\bar{R}_{\ell_j} - \bar{Z}_j)$$

or $$= \frac{-h^2}{2m} . \nabla^2 + \sum_j \sum_{\ell_j} . v(\bar{r}-\bar{R}_{\ell_j} - \bar{Z}_j) \ .$$

This equivalent to

$$H_m = \frac{-h^2}{2m} . \nabla^2 + \sum_j . V_j(\bar{r}-\bar{Z}_j) \ ,$$

which can be rewritten as

$$H_m = \left[\frac{-h^2}{2m} . \nabla^2 + V_j(\bar{r}-\bar{Z}_j)\right] + \sum_{j' \neq j} . V_{j'}(\bar{r}-\bar{Z}_{j'}) . \qquad (3.1.14)$$

This expression is the detail description of 3.1.9.a and b. The wave function $X_k^i(\bar{r})$ of j-layer can be expanded by LCAO with the boundary conditions 3.1.2 and 3.1.3, i.e.

$$X_k^i(\bar{r}) = A.\Sigma_j.\exp(-i\bar{k}.\bar{R}_j) \cdot \phi_d(\bar{r}-\bar{R}_{\sim j}). \qquad (3.1.15)$$

In principle, all parameters can then be calculated since we know $v(\bar{r})$ and $\phi_d(\bar{r})$. Practically, it is very difficult to do so since we would have to do this on great number of different layers. The layers may differ in 2-D lattice structureitself or the same 2-D lattice structure but different in xy-position. For example

$$0'.1^*.2\#.\ 3^*.4\#.5^*.6\# \ldots\ldots\ldots\ldots j^*.(j+1)\#\ldots\ldots\ldots\ldots$$

The simplest example is SCC with (001) plane as surface, which will be discussed in detail in the next section.

3.2 SIC model of SCC.

In this section, we will study in detail the SIC with SCC lattice. The primitive translation are given by

$$\bar{R}_{pqr} = p.R\hat{i} + q.R\hat{j} + r.R\hat{k}. \qquad (3.2.1)$$

Here R is the lattice spacing and $\hat{i}$, $\hat{j}$, $\hat{k}$ are unit vectors in x, y, z direction respectively. The surface plane is chosen to be perpendicular to $\hat{k}$, indicated by miller indice (001), and which cuts z-axis at 0. All of the layers are defined by $\bar{Z}_j = j.R\hat{k}$.

We shall assume that only the 0^{th} layer is perturbed by surface potential[6]. The tight-binding (TB)calculation of nearest-neighbor (NN) will be now performed. For simple calculation, we neglect overlap contribution and assume that

$$S_{ij} = \delta_{ij} .$$

We now define

$$x = (E_k - H_{ii})/H_{ii+1} , \qquad (3.2.2.a)$$

$$z = (H_{oo} - H_{ii})/H_{ii+1} \qquad (3.2.2.b)$$

and $$\eta = H_{o1}/H_{ii+1} = H_{1o}/H_{ii+1} \qquad (3.2.2.c)$$

for all i=2. Equation 3.1.6 now becomes

$$\begin{bmatrix} z-x & \eta & 0 & 0 & 0 & . & . & . & . \\ \eta & -x & 1 & 0 & 0 & . & . & . & . \\ 0 & 1 & -x & 1 & 0 & . & . & . & . \\ 0 & 0 & 1 & -x & 1 & . & . & . & . \\ . & . & . & . & . & & & & \\ . & . & . & . & . & . & 1 & -x & 1 \\ . & . & . & . & . & . & . & 1 & -x \end{bmatrix} \begin{Bmatrix} C_o \\ C_1 \\ C_2 \\ C_3 \\ . \\ C_{M-2} \\ C_{M-1} \end{Bmatrix} = 0. \qquad (3.2.3)$$

There are many ways to solve this equation.[67] The simplest way is to guess that

$$C_j = B.\sin(M-j)\theta , \qquad (3.2.4)$$

which satisfies the boundary condition that $C_M = 0$ since there is no M-layer in the SIC. The C must also satisfy the surface perturbed difference equation, i = 0 and 1,

$$(z-x) \cdot C_o + \eta \cdot C_1 = 0 \qquad (3.2.5.a)$$

and

$$\eta \cdot C_o - x \cdot C_1 + C_2 = 0. \qquad (3.2.5.b)$$

We can now find that the bulk difference equation for i = 2,

$$C_{i-1} - x \cdot C_i + C_{i+1} = 0 \qquad (3.2.6)$$

or $$x = (C_{i+1} + C_{i-1})/C_i \ .$$

Applying 3.2.4, we get

$$x = (\sin(M-i-1)\theta + \sin(M-i+1)\theta)/\sin(M-i)\theta$$

$$= 2\cos\theta \qquad (3.2.7)$$

Putting x in 3.2.7 into 3.2.5, we have

$$(z-2\cos\theta) \cdot C_o + \eta \cdot C_1 = 0 \qquad (3.2.8.a)$$

and $$\eta \cdot C_o - 2\cos\theta \cdot C_1 + C_2 = 0 \ . \qquad (3.2.8.b)$$

Multiplying 3.2.8.a and b by η and $z-2\cos\theta$ respectively, subtracting the first from the later, we obtain

$$\eta^2 . C_1 + (z-2\cos\theta).(2\cos\theta . C_1 - C_2) = 0 .$$

Then
$$\eta^2 = (2\cos\theta - z).(2\cos\theta - C_2/C_1)$$

$$= (2\cos\theta - z).(2\cos\theta - \sin(M-2)\theta/\sin(M-1)\theta)$$

$$= (2\cos\theta - z).(\cos\theta + \cot(M-1)\theta . \sin\theta) . \quad (3.2.9)$$

The θ solution has M+1 roots and has at least M-1 real roots.[6] The remaining two roots may be either both real or complex number. The metals have been modeled in such a way that there are no localized surface states. Therefore only M+1 real roots exist. Limitting 3.2.9 to the case of an ideal unperturbed SIC, i.e. $\eta = 1$ and $z = 0$, we have

$$1 = 2\cos\bar{\theta} . (\cos\bar{\theta} + \cot(M-1)\bar{\theta} . \sin\bar{\theta})$$

$$= 2\cos\bar{\theta} . \sin M\bar{\theta}/\sin(M-1)\bar{\theta} .$$

This implies that

$$\sin(M+1)\bar{\theta} = 0 , \quad (3.2.10)$$

which gives
$$\bar{\theta} = n\pi/(M+1) , \quad 1 \leq n \leq M . \quad (3.2.11)$$

Since for metals $\eta \simeq 1$ and $z \simeq 0$, we have from 3.2.9

$$\eta^2 = (2\cos\theta - z) . \sin M\theta/\sin(M-1)\theta .$$

Multiplying by $\sin(M-1)\theta$, we obtain

$$\eta^2 . \sin(M-1)\theta = (2\cos\theta - z) . \sin M\theta .$$

The trigonometric function can be expanded to give

$$\eta^2.(\sin(M+1)\theta.\cos2\theta - \cos(M+1)\theta.\sin2\theta)$$

$$= (2\cos\theta - z).(\sin(M+1)\theta.\cos\theta - \cos(M+1).\sin\theta),$$

which can be rearranged to

$$((\eta^2-1).\cos2\theta - z.\cos\theta - 1).\sin(M+1)\theta - ((\eta^2-1).\sin2\theta + z.\sin\theta) .$$

$$.\cos(M+1)\theta = 0 .$$

This can be rewritten as

$$A(\theta,\eta,z).\sin(M+1)\theta - B(\theta,\eta,z).\cos(M+1)\theta = 0 . \qquad (3.2.12)$$

The equation 3.2.12 can be solved by iteration process. Defining

$$A_i(\theta_{i-1},\eta,z) = (\eta^2-1).\cos2\theta_{i-1} + z.\cos\theta_{i-1} - 1 \qquad (3.2.13.a)$$

$$B_i(\theta_{i-1},\eta,z) = (\eta^2-1).\sin2\theta_{i-1} + z.\sin\theta_{i-1}. \qquad (3.2.13.b)$$

Replacing A and B in 3.2.12 by A_i and B_i, we have

$$A_i.\sin(M+1)\theta_i - B_i.\cos(M+1)\theta_i = 0 \qquad (3.2.14)$$

or

$$\sin((M+1)\theta_i - \delta_i) = 0 , \qquad (3.2.15)$$

where

$$\delta_i = \tan^{-1}(B_i/A_i) . \qquad (3.2.16)$$

In the limit $i \longrightarrow \infty$, these equations should converge to give the solution. However, we can work with a small i if η and z are sufficiently close to the ideal unpertubed crystal value. Working with $i = 1$ or $\theta = \theta_1$, we could find that

$$\delta_1 = \tan^{-1}\left[\frac{(\eta^2-1).\sin 2\bar{\theta} + z.\sin\bar{\theta}}{(\eta^2-1).\cos 2\bar{\theta} + z.\cos\bar{\theta} - 1}\right]$$

where $\lim_{\substack{\eta\to 1 \\ z\to 0}} \delta_1 = \tan^{-1}\left[-\theta(\eta^2-1,\ z)\right] = 0.$

This imply that we should be able to find a small number, $m<<1$, to bound δ, as small as (η,z) close to $(1,0)$ (see Fig. 3.2.1). However, the results show that our choice has only small effect on the density of states since only small shift of θ occurs. The number of solution is however the same. Thus the density of states of slightly perturbed SIC can be approximated by the ideal unperturbed SIC's density of states.

Let us now go back to 3.2.2.a, where we have

$$x_o = (E_k^o - H_{ii})/H_{ii\pm 1} ,$$

as the unperturbed reduced energy. The following calculation will show how our layer view point can be related to the conventional atomic view point. From 3.1.7 and 3.1.13, and assuming that $S_{ij} = \delta_{ij}$, we get

$$H_{ii} = E_i^o + J_{ii} \qquad (3.2.17.a)$$

and $$H_{ii\pm 1} = J_{ii\pm 1} , \qquad (3.2.17.b)$$

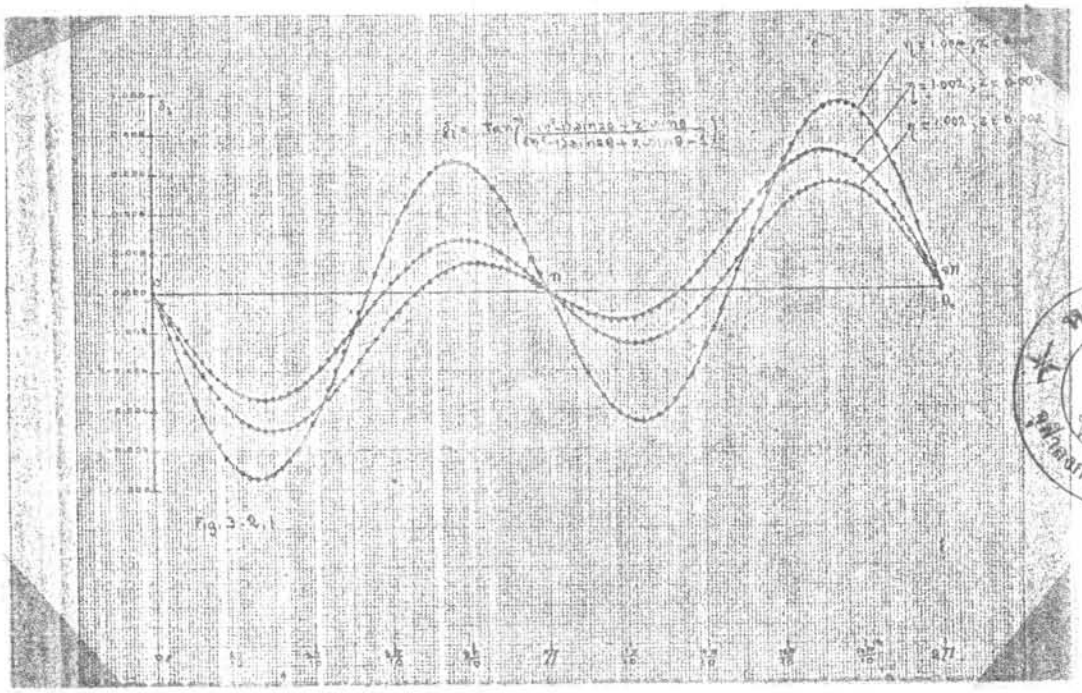


Fig.3.2.1 : The numerical plot of δ_1.

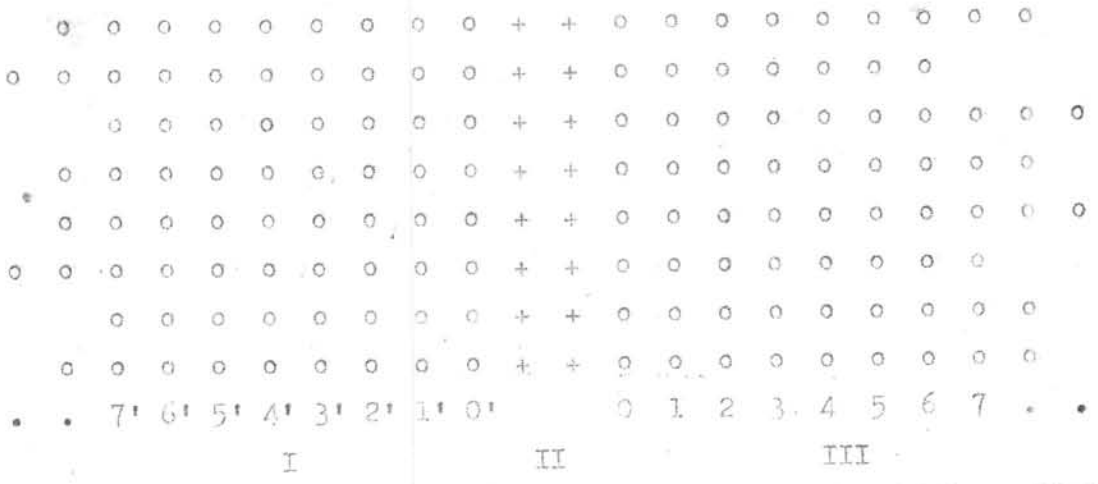


Fig.3.2.2 : Creation of SIC from infinite crystal by taking off the layers in the II region then the I and III region are two SIC.

where $$E_i^o = \int d^3r . X_k^{i*}(\bar{r}) . H_i^o . X_k^i(\bar{r}) \ , \qquad (3.2.18.a)$$

$$J_{ii} = \int d^3r . X_k^{i*}(\bar{r}) . \bar{V}_i . X_k^i(\bar{r}) \qquad (3.2.18.b)$$

and $$J_{ii\pm1} = \int d^3r . X_k^{i*}(\bar{r}\pm\bar{R}k) . \bar{V}_i . X_k^i(\bar{r}) \ . \qquad (3.2.18.c)$$

The i-layer wave function $X_k^i(\bar{r})$ is the same for all layers and is obtained from

$$H_i^o . X_k^i(\bar{r}) = E_i^o . X_k^i(\bar{r}) \qquad (3.2.19)$$

with the boundary conditions 3.1.2 and 3.1.3. The solution can be written in Wannier representation as

$$X_k^i(\bar{r}) = p^{-1} . \sum_{\ell_i} . \exp(-i\bar{k} . \bar{R}_{\ell_i}) . a(\bar{r}-\bar{R}_{\ell_i}) \ , \qquad (3.2.20)$$

where P^2 is total number of unit cell (atom) in the i-layer. In LCAO limit $a(\bar{r})$ is the atomic orbital $\phi(\bar{r})$, which is taken to be non-degenerated orbital. For large i

$$H_{ii} = \int d^3r . X_k^{i*}(\bar{r}) . (H_i^o + \sum_{j\neq i} . \sum_j . v(\bar{r}-\bar{R}_{\ell_j}-\bar{Z}_j+\bar{Z}_i)) . X_k^i(\bar{r}) \ .$$

This can be rewritten as

$$H_{ii} = \int d^3r . X_k^{i*}(\bar{r}) . (H_\Lambda^o + \sum_{i\neq 0} . v(\bar{r}-\bar{R}_i) + \sum_{j\neq i} . \sum_j . v(\bar{r}-\bar{R}_{\ell_j}-\bar{Z}_j+\bar{Z}_i)) . X_k^i(\bar{r}) \ ,$$

where H_Λ^o is atomic Hamiltonian. The potential term can be sum to

$$\bar{v}_A = \sum_{(\ell_j, j) \neq (O_i, i)} \cdot v(\bar{r} - \bar{R}_{\ell_j} - \bar{Z}_j + \bar{Z}_i) \cdot$$

Applying 3.2.2.20 and this summation, we get

$$H_{ii} = P^{-2} \cdot \sum_{\ell_i, \ell_i'} \cdot \exp\left[-i\bar{k} \cdot (\bar{R}_{\ell_i} - \bar{R}_{\ell_i'})\right] \cdot \int d^3\mathbf{r} \cdot \phi^*(\bar{r} - \bar{R}_{\ell_i'}) \cdot H_A^o + \bar{v}_A) \cdot \phi(\bar{r} - \bar{R}_{\ell_i})$$

$$H_{ii} = E_A^o + \alpha_i + \sum_{p_i \neq 0} \cdot \exp(-i\bar{k} \cdot \bar{R}_{p_i}) \cdot \beta^i_{p_i} \cdot \qquad (3.2.21)$$

For nearest neighbor approximation, we have

$$H_{ii\pm1} = E_A^o + \alpha_i + 2 \cdot \sum_{p_i(1)} \cdot \beta^i_{p_i} \cdot \cos(\bar{k} \cdot \bar{R}_{p_i}) \cdot \qquad (3.2.22)$$

Similarly

$$H_{ii\pm1} = P^{-2} \cdot \sum_{\ell_i, \ell'_{i\pm1}} \cdot \exp\left[-i\bar{k} \cdot (\bar{R}_{\ell_i} - \bar{R}_{\ell'_{i\pm1}})\right] \cdot \int d^3\mathbf{r} \cdot \phi^* (\bar{r} - \bar{R}_{\ell'_{i\pm1}} - \bar{Z}_{i\pm1} + \bar{Z}_i) \cdot$$

$$\cdot (H_A^o + \bar{v}_A) \cdot \phi(\bar{r} - \bar{R}_{\ell_i}) \cdot$$

Since the shortest interatomic distance in SCC is xyz-direction, we find that

$$H_{ii\pm1} = b_{(O_i, i), (O_{i\pm1}, i\pm1)} = b^o_{ii\pm1}$$

(see Fig. 3.1.1.a). If i is large, we could find

$$b^o_{ii\pm1} = \beta^i_{p_i(1)} = \beta \qquad (3.2.23.a)$$

and $$\alpha_i = \alpha \,. \qquad (3.2.23.b)$$

Then 3.2.2 becomes

$$x_o = (E_k^o - E_A^o - \alpha - 2\beta . \sum_{p(1)} .\cos(\bar{k}.\bar{R}_p))/\beta$$

From 3.2.7, we have $x_o = 2\cos\bar{\theta}$. So that the above expression can be rearranged to give

$$E_k^o = E_A^o + \alpha + 2\beta.(\cos\bar{\theta} + \sum_{p(1)} .\cos(\bar{k}.\bar{R}_p)). \qquad (3.2.24)$$

Since β is always negative, we can write

$$\varepsilon_k = -(\cos(k_x.R) + \cos(k_y.R) + \cos\bar{\theta}), \qquad (3.2.25)$$

where $$\varepsilon_k = (E_k^o - E_A^o - \alpha)/2\|\beta\| \,.$$

As be shown previously for unperturbed metals, we have

$$\bar{\theta} = n\pi/(M+1) = 2nR\pi/(2(M+1)R) \,. \qquad (3.2.26.a)$$

From this relation, we obtain some relationships between infinite crystal and SIC.

Shockley has pointed out that any surface must created in pair[63] and not as the single surface as proposed by Tamm.[62] It is well known that the infinite crystal must satisfying the Born-von Karman cyclic boundary condition in xyz-direction. To produce surface, we must take off some atoms from those cyclic chain. In our layer view point we just have to remove

some layers, perpendicular to z-axis, then two SIC would be produced (see Fig. 3.2.2).

We shall assume that the lattice space under consideration is of a cubic form with the length L in x, y and z direction. Number of atom in any j-layer is

$$P^2 = (L/R)^2 \quad .$$

In this simple model the number of layer in z direction is also P. If we take off K layers, the number of layer for SIC is

$$M = (P-K)/2 \quad .$$

Substituting this into 3.2.26.a, we obtain

$$\bar{\theta} = 2nR\pi/((P-K+2).R) \quad .$$

Since $P >> K$ and 2, that is no difference between K = 2 or small number greater than 2, i.e. K = 5. So that

$$\bar{\theta} = 2nR\pi/L \quad ,$$

which gives $= k_z.R$ (3.2.26.b)

For ideal unperturbed SIC, we have

$$\varepsilon_k = -(\cos(k_x.R) + \cos(k_y.R) + \cos(k_z.R)) \quad , \quad (3.2.27)$$

which is the same as that of the infinite crystal.[68] Since we know that it is impossible to produce real surfaces without some

perturbation, the closest we can get to the ideal case is to take the perturbation as being small. From 3.2.15 and 3.2.26.b, we have

$$\Theta = k_z.R + 2R.\delta/L \ .$$

This implies that 3.2.27 can be developed to be

$$\varepsilon_k = -(\cos(k_x.R) + \cos(k_y.R) + \cos(k_z.R) + 2R.\delta/L)) \ . \quad (3.2.28)$$

This slightly perturbed SIC model may not be very good for metals since the crystal is assumed to be perturbed only in the O-layer. A more reasonable model for metals would be a small varying perturbation SIC model. This model would have a large number of perturbed layers so that it would be difficult to solve the secular equation or boundary difference equation. Since TB approximation gives a good result only when the perturbed potential tends to zero in a short distance from the perturbation source, we would not be able to apply this approximation to the small varying perturbation SIC model.

However, our slightly perturbed SIC model is the only model which would possibly be studied mathematically at present.[6]

From 3.1.4, 3.1.15 and 3.2.4, $\Psi_k(\bar{r})$ can be expanded by LCAO of $\phi(\bar{r})$ as

$$\Psi_k(\bar{r}) = \sum_j B.\sin(M-j)\Theta.A.\sum_{\ell_j} .\exp(-i\bar{k}.\bar{R}_{\ell j}).\phi(\bar{r}-\bar{R}_{\ell_j}-\bar{Z}_j)$$

$$= AB.\sum_j\sum_{\ell_j} .\sin(M-j)\Theta.\exp(-i\bar{k}.\bar{R}_{\ell_j}).\phi(\bar{r}-\bar{R}_{\ell_j}-\bar{Z}_j). \quad (3.2.29)$$

The normalization is

$$1 = \int d^3r.\Psi_k^*(\bar{r}).\Psi_k(\bar{r}) \ .$$

Substituting 3.2.29 into this expression, we get

$$1 = (AB)^2 \cdot \sum_{jj'} \cdot \sum_{\ell_j \ell'_{j'}} \cdot \sin(M-j)\theta \cdot \sin(M-j')\theta \cdot \exp -i\bar{k} \cdot (\bar{R}_{\ell_j} - \bar{R}_{\ell'_{j'}}) \cdot$$

$$\cdot \int d^3r \cdot \psi^*(\bar{r}-\bar{R}_{\ell'_{j'}}-\bar{Z}_{j'}) \cdot \psi(\bar{r}-\bar{R}_{\ell_j}-\bar{Z}_j) \cdot$$

Since the atomic orbital itself is normalized, the expression becomes

$$1 = (AB)^2 \cdot \sum_j \cdot \sum_{\ell_j} \cdot \sin^2(M-j)\theta$$

$$= (AB)^2 \cdot P^2 \cdot \sum_j \cdot \sin^2(M-j)\theta \ ,$$

where P^2 is number of atom in the j-layer. Since M is very large, we can change the summation over j to be integral of

$$\zeta_j = j\pi/(M+1) \ .$$

Thus we get

$$1 = (ABP)^2 \cdot (M+1)/\pi \cdot \int_o^\pi d\zeta_j \cdot \sin(M - \zeta_j \cdot (M+1)/\pi \cdot \theta) \ ,$$

This can easily be integrated to give

$$1 = (ABP)^2 \cdot (M+1)/\pi \cdot \frac{1}{2} \cdot \left[\frac{\sin 2(M - \zeta_j \cdot (M+1)/\pi \cdot \theta)}{2(M+1)/\pi \cdot \theta} - \delta_j \right]_o^\pi$$

$$= (ABP)^2 \cdot \frac{1}{2}(M+1) \cdot \left[\frac{\sin 2\theta + \sin 2M\theta}{2(M+1)\theta} - 1 \right] \cdot$$

This can be simplified to

$$1 = (ABP)^2 \cdot \frac{1}{2}(M+1) \cdot \left[\frac{\sin(M+1)\theta \cdot \cos(M-1)\theta}{(M+1)\theta} - 1 \right] . \quad (3.2.30)$$

Since $(M+1)\theta = n\pi$,

(see 3.2.11), the first term in the bracket of 3.2.30 is zero. Now 3.2.30 is

$$1 = (ABP)^2 \cdot -\frac{1}{2}(M+1) .$$

Then $$AB = \frac{i}{P} \cdot \sqrt{\frac{2}{M+1}} . \quad (3.2.31)$$

Substituting this result into 3.2.29, we obtain the normalized wave function

$$\Psi_k(\bar{r}) = \frac{i}{P} \cdot \sqrt{\frac{2}{M+1}} \cdot \sum_{j \ell_j} \cdot \sin(M-j)\theta \cdot \exp(-i\bar{k} \cdot \bar{R}_{\ell_j}) \cdot \phi(\bar{r} - \bar{R}_{\ell_j} - \bar{Z}_j) . \quad (3.2.32)$$

To see the 1-D limit, we reduce P = 1 and sum ℓ_j contains $\ell_j = 0$ only. The result agrees exactly with the direct 1-D calculation (i.e. see Newns(1969)[37], and also appendix F).

3.3 Density of states.

A quantities of fundamental interest in band theory is the number of electron states in an interval of energy.

This quantity is refered to as the density of states function D(E). The density of states is defined[68] as

$$D(E) = \frac{\Omega}{(2\pi)^3} \cdot \frac{d}{dE} \cdot \int d^3k \qquad (3.3.1.a)$$

or

$$= \frac{\Omega}{(2\pi)^3} \cdot \frac{d}{dE} \cdot \int_E \frac{dS}{\nabla_k \cdot E_k} , \qquad (3.3.1.b)$$

where $\int_E dS$ is an integration over constant energy surface in k-space. For infinite crystal, we work with Wigner-Seitz cell. However, this can not be done for SIC. Thus the usual band calculation are not appropriate for SIC. We have to attack the problem indirectly. As mention proviously, this can be done by using bulk density of states for unperturbed SIC (see 3.2.27).

The transition metals are of the most interest for chemisorption phenomena. We will limit our discussion to d-band. Many authors have studied the band structure of transition metals, especially the iron series[69-72]. The density of states is related to Green function [73-75] by

$$D(E) = \pi^{-1} \cdot \mathrm{Im}\left[\mathrm{Tr}(G)\right] , \qquad (3.3.2)$$

where G is the matrix representation of Green operator. Here G is defined by

$$G = (E.I - H)^{-1}, \qquad (3.3.3)$$

which is the resovent operator. H is diagonalized so that

$$\langle k|G|k'\rangle = (E-E_k)^{-1} \cdot \delta_{kk'} . \qquad (3.3.4)$$

Applying the identity to this expression.

$$\langle m|G|m'\rangle = \sum_{kk'} \cdot \langle m|k\rangle \cdot \langle k|G|k'\rangle \cdot \langle k'|m'\rangle \quad ,$$

we get

$$\langle m|G|m'\rangle = \sum_{k} \cdot \langle m|k\rangle \cdot (E-E_k)^{-1} \cdot \langle k|m'\rangle \quad .$$

In the above expressions $|m\rangle$ and $|m'\rangle$ are wave vectors in site representation. Thus

$$\mathrm{Tr}(G_{mm'}) = \sum_{m} \cdot \sum_{k} \cdot |\langle m|k\rangle|^2 \cdot (E-E_k)^{-1}$$

$$= \sum_{k} \cdot \left(\sum_{m} \cdot |\langle m|k\rangle|^2 \right) \cdot (E-E_k)^{-1} \quad .$$

Since $\sum_{m} |\langle m|k\rangle|^2$ is unity for normalized wave function $\Psi_k(\bar{r})$, we have

$$\mathrm{Tr}(G) = \sum_{k} \cdot (E-E_k)^{-1} \quad .$$

This can be rewritten as

$$\mathrm{Tr}(G) = \sum_{k} \cdot i \int_{o}^{\infty} dt \cdot \exp\left[-i(E-E_k) \cdot t\right] \cdot \qquad (3.3.5)$$

Substituting F_k from 3.2.27 into this, we get

$$\mathrm{Tr}(G) = \int_{o}^{\infty} dt \cdot i \cdot \exp(-iEt) \cdot N \cdot (R/2\pi)^3 \cdot$$

$$\cdot \int d^3k \cdot \exp\left[-it(\cos(k_x \cdot R) + \cos(k_y \cdot R) + \cos(k_z \cdot R))\right] \cdot$$

This can be simplified to

$$Tr(G) = \int_0^{\infty} dt.i.\exp(-iEt).N/\pi^3 . \left[\int_0^{\pi} dk.\exp(-itcos(k)) \right]^3 .$$

Since we know that the k integral term in this expression is the zeroth order Bessel function of first kind $J_o(t)$, we get

$$Tr(G) = \int_0^{\infty} dt.i.(cosEt - i.sinEt).N.J_o^3(t). \qquad (3.3.6)$$

We then have $$Re\left[Tr(G)\right] = N. \int_0^{\infty} dt.sinEt.J_o^3(t) \qquad (3.3.7.a)$$

and $$Im\left[Tr(G)\right] = N. \int_0^{\infty} dt.cosEt.J_o^3(t) \qquad (3.3.7.b)$$

Here N is number of site or atom in the crystal. The density states per atom can then easily be evaluated, i.e.

$$\bar{D}(E) = D(E)/N = \pi^{-1}.Im\left[Tr(G)/N\right] = \pi^{-1}. \int_0^{\infty} dt.cosEt.J_o^3(t). \qquad (3.3.8)$$

The density of states per atom is normalized so that

$$\int_{-3}^{3} dE.\bar{D}(E) = n , \qquad (3.3.9)$$

where n is number of electron per atom (i.e. for d-electron n = 10).

For slightly perturbed SIC, we can use the expression for E_k from 3.2.28 in 3.3.5. Similarly we have

$$Tr(G) = \int_0^{\infty} dt.i.(\cos Et - i.\sin Et).N.J_o^2(t).$$

$$. \int_0^{\pi} dk.\exp\left\{-it\cos(k + 2R\,\delta/L)\right\}. \qquad (3.3.10)$$

In analogy to the previous calculation for unperturbed SIC, the density of states for slightly perturbed SIC can be obtained.