Application of projection operator method to define basis functions for use in photoemission calculations

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Abstract : We have applied projection operator method of group theory in deriving the symmetry adapted wavefunctions defined by ψ_i which represents the surface electronic states in the case of a strong periodic potential. The method involves the defining of basis function pertaining to a particular symmetry point of Cu(110), from which ψ_i is formulated by the LCAO method This has been applied to calculate photocurrent from Cu (110) surface state. We have also used this method of calculation for a metal like Al

1. Introduction

For the use of Projection Operator for the case of strongly bonded metals, we define the crystal potential by a Kronig-Penney δ -potential which is periodic with the periodicity of
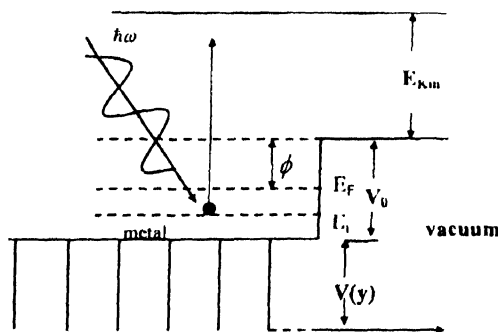

Figure 1. Schematic representation of Kronig-Penney δ -potential model.

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the lattice as shown in Figure 1. In our calculation, the Schrodinger equation will then be solved to obtain the solution in terms of Green function [1].

The method involves the projection operator operating on linear combination of atomic orbitals (LCAO) representation of the surface states giving the basis function and this basis function has been incorporated in defining ψ_i. This had been applied to calculate photocurrent from the Cu (110) surface state. The calculation has been carried out in one-dimension and it was found that the basis function derived in one dimensional form can be extended to a metal like Al.

2. Formalism

2.1. Derivation of basis function by projection operator method :

For Cu (110), surface state occurs [2] in $L_{2'} - L_1$ band gap. The LCAO representation for $L_{2'}$ point is $\frac{1}{\sqrt{3}}(x + y + z)$. The projection operator formula [3] is given by

$$\mathcal{P}_{mn}^p = \frac{l_p}{g} \sum_T \Gamma^p(T)_{mn}^* P(T).$$ (1)

Here l_p is the dimension of the unitary irreducible representation of the group $\mathcal{G}$, g is order of $\mathcal{G}$ and $\sum_T$ extends over all the transformation T of $\mathcal{G}$.

Eq.(1) operating on the LCAO representation for $L_{2'}$ gives a set of basis functions $\frac{1}{\sqrt{3}}(x + y + z)$. This basis function in one dimensional form is incorporated in the derivation of initial state wave functions.

2.2. Derivation of initial state wavefunction:

The solution of Schrodinger equation in terms of Green function, in one dimensional form may be written by the integral equation

$$\psi(z) = \int_{-\infty}^{+\infty} V(y)\psi(y)G(z,y)\,dy.$$ (2)

Let the Kronig-Penney potential be represented by a linear Dirac δ-function i.e

$$V(y) = \left(\frac{2p}{a}\right) \sum_{-\infty}^{\infty} \delta(y - na)$$ (3)

where $p = \lim_{\substack{b \to 0 \\ V_1 \to \infty}} \frac{1}{2}\chi_0^2\, ab$ with $\chi_0^2 = 2(V_1 - E_i)$. Here, b is the width of Kronig-Penny potential moad and V_1 is the height of the potential, p is the strength of the δ-function barrier

and it is assumed to be positive. The final electronic wavefunction after substitution of the above value (eq.3) in eq. (2) gives

$$\psi(z) = \frac{\tau(0)}{\sin k_l a}\left[e^{ika}\sin k_l z - \sin k_l(z-a)\right] \quad (4)$$

where

$$\tau(0) = \frac{2Cipsin^2 k_l a}{k_l a(e^{ika} - e^{-ik_l a})(\cos ka - \cos k_l a)}. \quad (5)$$

Introducing the atomic orbital $\phi(z)$ which includes the basis function derived by P.O method as discussed above the initial state wavefunction can be represented by

$$\psi_l(z) = \begin{cases} \psi_l(0)\phi(z)e^{\mu z}(k_l \cos k_l z - \chi \sin k_l z), & z \leq 0 \;(bulk\,\&\,surface) \\ \psi_l(0)k_l e^{-\chi z}, & z \geq 0 \;(vacuum) \end{cases} \quad (6)$$

where

$$\psi_l(0) = \frac{2i \sin ka\,\tau(0)}{k_l \cos k_l a - k_l e^{-ika} - \chi \sin k_l a}. \quad (7)$$

2.3. Photocurrent calculations :

The photocurrent density formula from golden rule approximation can be written as

$$\frac{dj(E)}{d\Omega} = \frac{2\pi}{\hbar}\sum |< \psi_f \mid H' \mid \psi_l >|^2\,\delta(E-E_f)\delta(E_f - E_l - \hbar\omega)f_0(E-\hbar\omega)[1-f_0(E)] \quad (8)$$

where $\Psi_l(\Psi_f)$ refer to the initial (final) state wavefunctions and perturbation H' can be written as

$$H' = \frac{e}{mc}\left[\tilde{A}_\omega(z)\frac{d}{dz} + \frac{1}{2}\frac{d}{dz}\tilde{A}_\omega(z)\right] \quad (9)$$

where $\tilde{A}_\omega(z) = \frac{A_\omega^z(z)}{A_o}$, $A_\omega^z(z)$ is the component of vector potential along z-axis. The final state wavefunction $|\Psi_f\rangle$ used is the scattering state of the step potential[4] which is encountered by the electron. The matrix element $I = \langle \psi_l \mid H' \mid \psi_l \rangle$ in eq. (8) can be written in one dimensional form as :

$$I = \int_{-\infty}^{-d}\psi_f^*\,\tilde{A}_\omega(z)\frac{d\psi_l}{dz}\,dz + \int_{-d}^{0}\psi_f^*\,\tilde{A}_\omega(z)\frac{d\psi_l}{dz}\,dz + \frac{1}{2}\int_{-d}^{0}\psi_f^*\,\frac{d\tilde{A}_\omega}{dz}\psi_l\,dz + \int_{0}^{\infty}\psi_f^*\,\tilde{A}_\omega(z)\frac{d\psi_l}{dz}\,dz. \quad (10)$$

The integrals in Eq. (10) are evaluated numerically by writing FORTRAN programmes.

3. Results and discussions

3 1 Copper

The plot of photocurrent against the photon energy $\hbar\omega$ for Cu is shown in Figure 2 For the same value of surface state [5] energy (2.72 eV below Fermi level) and potential barrier height (11.4 eV) , photocurrent was calculated for two values of surface widths We find that for d = 10 a.u., a maximum in the value of photocurrent occurs at $\hbar\omega$ = 14 eV. With further increase of photon energy, photocurrent decreases to a minimum value at $\hbar\omega$ = 19 eV and the next hump occurs again at $\hbar\omega$ = 23 eV But for a narrow surface width (d = 0), the behaviour of photocurrent is quite different as shown in Figure 2. We do not find any peak for values of photon energy below and above 19 eV The behaviour of photocurrent shows a qualitative agreement with those shown by other metalslike W, Si, *etc.* in which Kronig-Penney potential model was also used [5]
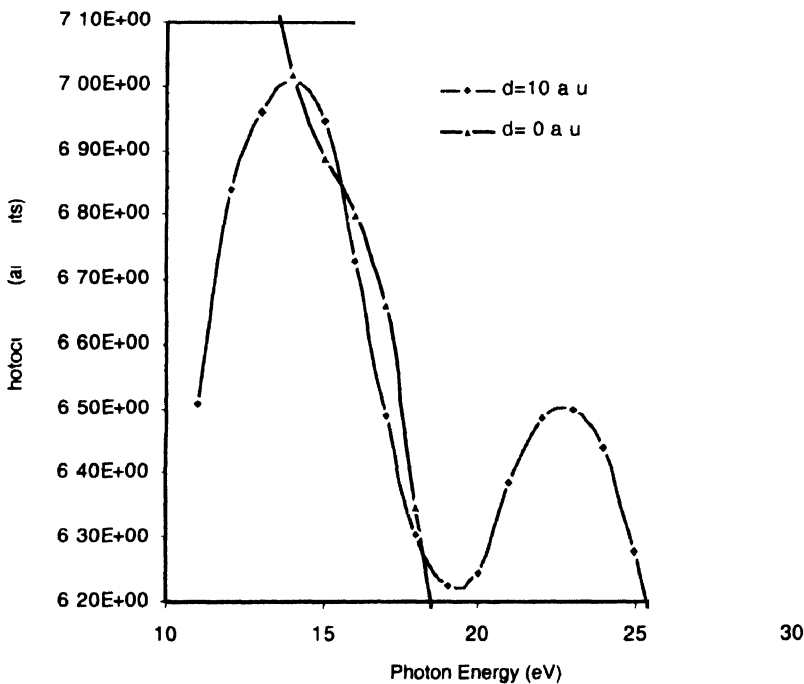

Figure 2. Plot of variation of photocurrent with photon energy for surface widths d = 10 a u and d = 0 in copper using Kronig-Penney δ -potential where ψ_i is derived by projection operator method of Group Theory

3.2. Aluminium:

Figure 3 shows the plot of photocurrent *versus* photon energy ($\hbar\omega$) for the surface width d = 10 a.u and narrow surface width d = 0 a.u. We have chosen the initial state energy E_i for a high lying surface state occurring at 0.41 eV below Fermi level, the location of the Fermi level and the work function ϕ for Al are taken as 11.7 eV and 4.25 eV,

respectively. The photocurrent profile for d = 10 a.u. showed a strong photoemission at photon energy $\hbar\omega$ = 9 eV, which was followed by a decrease in photocurrent and the minimum occurring at $\hbar\omega$ = 15 eV (the plasmon energy of Al is $\hbar\omega_p$ = 15.3 eV). There is another hump in the photocurrent data at $\hbar\omega$ = 20 eV. The behaviour of photocurrent in the case of narrow surface width is quite different. For example, almost a flat peak in a photon energy range 10 eV-14 eV was obtained. Although the minima in photocurrent was seen at $\hbar\omega$ ≈ 15 eV, contribution to photoemission was far less important. However the photoemission results for d = 10 a.u. seems to be in qualitative agreement with the experimental results of Levison *et al* [7] (see Figure 3 (inset)). For example, the experimental data of Levinson *et.al* [7] showed a maxima in photocurrent at $\hbar\omega$ = 13 eV with occurrence of a minima at the plasmon energy (≈ 15.3 eV). Also, it showed similar behaviour with the calculated results of Thapa *et al* [8,9].
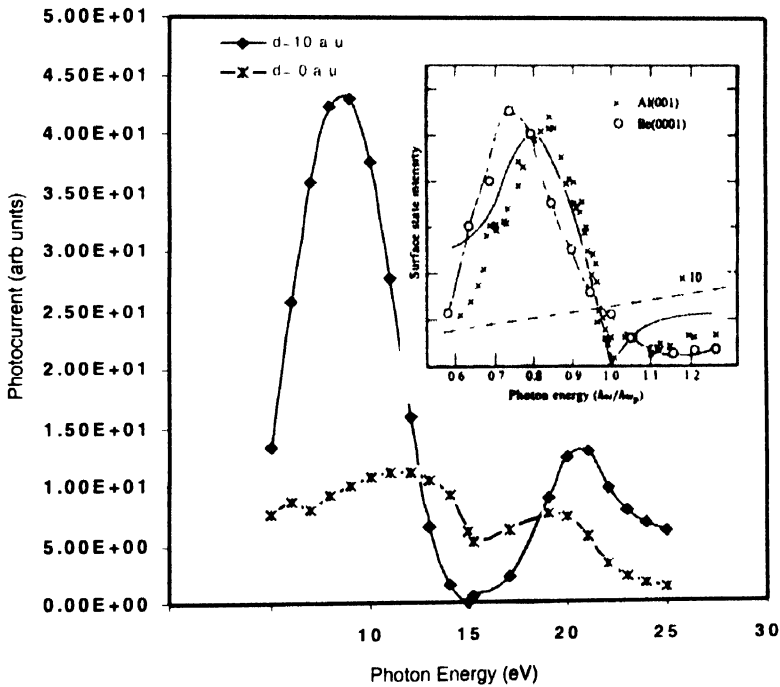

Figure 3. Plot of photocurrent variation against photon energy in the case of aluminium, for surface width d = 10 a.u. and d = 0 by employing Kronig-Penney δ -potential where ψ_l is derived by projection operator method of Group Theory.

Inset · Experimental results for aluminium and beryllium as obtained by Levinson *et al* [7].

4. Conclusion

In our calculations of photocurrent, we have seen that photoemission was considered to take place in metal, for location of surface state below the Fermi level. Symmetry state or direction to the existence of surface state in a particular band gap was ignored. Therefore, to include band structure effect, we have applied projection operator method of

group theory to derive initial state wavefunction ψ_i pertaining to a particular band gap When compared to experimental data and other previous theoretical results like Kronig-Penney potential model of Thapa *et al* [6], we find that calculated data with this approach of calculations seemed to agree in a better way. This is quite evident from the photoemission result from Al especially for which also experimental result is available. However, there are still certain drawbacks remaining for further corrections. For example, we have not considered the nature and type of potentials which defines the bulk and surface regions This plays equally important role in the definition of dielectric response function too. From all the above facts, the model employed in our calculations seems to be highly simplified However, as evidenced from the comparison with other approach of calculations, as well as with experimental results [7], our method seems to be quite appropriate.

Acknowledgment

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