CHAPTER - 2

*Calculations of electromagnetic field*
In angle-resolved photoemission, electromagnetic field in a solid when electromagnetic radiation is incident on it plays an important role. Hence, in this chapter we shall discuss the calculation of the electromagnetic field which is an extremely complex problem. Ab initio calculations of the electromagnetic field have been done only for jellium model in the presence of a surface and these calculations have not been extended to other metals where jellium model is not applicable. For calculations of electromagnetic fields on d-bands metals and semiconductors, one requires to start with simpler model. Such a model was proposed by Bagchi and Kar and they showed that consideration of variation of field near the surface gave a reasonable qualitative agreement with experimental results for the photocurrent from the tungsten surface as a function of photon energy. In their model they used experimentally measured optical data as input and hence can be extended to the case of semiconductors as well. Thapa et al. have also used this model and applied it successfully to aluminium and other metals and semiconductors. We have also used this model in our photoemission calculations and therefore we shall give a brief description of the modified form of dielectric model as used by Bagchi and Kar to derive the electromagnetic field. In Bagchi and Kar model, the surface width was defined by \(- \frac{a}{2} \leq z \leq \frac{a}{2}\), and \(z = 0\) was the nominal surface plane. But in our calculations, we consider \(- a \leq z \leq 0\) as the realistic surface region with \(z = 0\) as the true surface plane as shown in Fig. (2.1). We shall then discuss the application of the derived electromagnetic field to metals and semiconductor.
Figure (2.1): Dielectric model used for the calculation of vector potential. Here $a$ is the width of the surface, $\hbar\omega$ is the incident photon energy and $\theta_i$ is the angle of incidence.
2.1 Dielectric model and electromagnetic fields calculation:

For calculation of electromagnetic field the dielectric model is shown in Fig. (2.1). In this model, the metal is assumed to occupy the space to the left of the \( z = 0 \) plane. The response of the electromagnetic field is bulk like everywhere except in the surface region defined by \(-a \leq z \leq 0\) and in this region, the model dielectric function is chosen to be a local function interpolating between the bulk value inside the metal and the vacuum value (unity) outside. The frequency-dependent dielectric model is given by:

\[
\varepsilon(z) = \begin{cases} 
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), & \text{for } z \leq -a \quad \text{(bulk)}, \\
1 + \left[1 - \varepsilon(\omega)\right] \frac{z}{a}, & \text{for } -a \leq z \leq 0 \quad \text{(surface)}, \\
1, & \text{for } a \geq 0 \quad \text{(vacuum)}. 
\end{cases}
\]  

(2.1)

where \( a \) is the width of the surface, and \( \varepsilon(\omega) \) is a complex dielectric function.

The incident radiation is taken to be a \( p \)-polarized light incident on the surface plane at an angle \( \theta \), with the \( z \)-axis. A gauge was chosen so that the scalar potential is set equal to zero and the electromagnetic field \( \vec{E}(\vec{K}, \omega; z) \) is expressed in terms of the vector potential \( \vec{A}(\vec{K}, \omega; z) \) as

\[
\vec{E}(\vec{K}, \omega; z) = \frac{i \omega}{c} \vec{A}(\vec{K}, \omega; z) 
\]  

(2.2)

For \( p \)-polarized light, the magnetic field \( B(z) = B(\vec{K}, \omega, z) \) is in the \( y \)-direction and it obeys the Landau and Lifshitz equation which is given by

\[
\frac{\partial}{\partial z} \left( \frac{1}{\varepsilon} \frac{\partial B}{\partial z} \right) + \left( \frac{\omega^2}{c^2} - \frac{K^2}{\varepsilon} \right) B = 0 
\]  

(2.3)
This equation may be obtained from Maxwell’s equations and can be solved under the boundary condition that both \( B \) and \( \frac{\partial B}{\partial z} \) are continuous. Once \( B \) is known, the electric field components can be found by using the relations

\[
E_z(K, \omega, z) = \frac{c}{i\omega} \frac{dB}{dz} \quad (2.4a)
\]

\[
E_i(K, \omega, z) = -\frac{\sin \theta_i B}{\varepsilon} \quad (2.4b)
\]

The solution of the above equations lead to the normal component of the electric field in the long wavelength limit (\( \frac{\omega a}{c} \rightarrow 0 \)) as:

\[
\tilde{A}_\omega(z) = \frac{E_i(z)}{E_o} \quad (2.5)
\]

\[
= \begin{cases} 
\frac{\varepsilon \sin 2\theta_i}{\left[\varepsilon - \sin^2 \theta_i\right]^\frac{1}{2} + \varepsilon \cos \theta_i}, & z \geq 0 \\
\frac{\sin 2\theta_i}{\left[\varepsilon - \sin^2 \theta_i\right]^\frac{1}{2} + \varepsilon \cos \theta_i} \cdot \frac{\varepsilon a}{a + (1 - \varepsilon)z}, & -a \leq z \leq 0 \\
\frac{\sin 2\theta_i}{\left[\varepsilon - \sin^2 \theta_i\right]^\frac{1}{2} + \varepsilon \cos \theta_i}, & z \leq -a
\end{cases}
\]

2.2 Evaluation of electromagnetic fields:

By using Eq. (2.5) electromagnetic fields as a function of incident photon energy are calculated for different metals and semiconductors. We have also calculated the electromagnetic field as a function of the distance \( z \) from the surface of solids. The value of the dielectric constant \( \varepsilon(\omega) \) is unity for vacuum region. For the
bulk and the surface region, we have used the experimental data for $\varepsilon(\omega)$ \cite{48,49}. In all our calculations, we have taken the width of the surface to be $a = 10$ a.u. In this section we present the results of electromagnetic field calculations for metals $W$, $Mo$ and semiconductors $PbS$ and $PbSe$.

(i) Tungsten:

In Fig (2.2), a graph of $|\tilde{A}_\omega(z)|^2$ against the incident photon energy ($h\omega$) is plotted for the surface plane located at $z = 0$ (vacuum), $z = -0.5a$ (surface) and $z = -a$ (bulk) for $W$ where $a$ is the width of the surface. We find that for the surface region $z = -0.5a$, $|\tilde{A}_\omega(z)|^2$ increases with the increase in the incident photon energy and a peak occurs at photon energy $h\omega = 21$ eV after which it starts decreasing with further increase in the photon energy and becomes minimum at $h\omega = 26$ eV. The experimental plasmon energy ($h\omega_p$) of $W$\cite{50} is 25.3 eV. For the location of the surface plane at $z = 0$, which is the vacuum region, we find that with the increase in the photon energy, $|\tilde{A}_\omega(z)|^2$ decreases slightly and we do not observe a proper peak below the plasmon energy but a minimum is observed near the plasmon energy. For the other locations of the surface plane at $z = -a$, which is the bulk region, $|\tilde{A}_\omega(z)|^2$ increases slightly with the increase in the photon energy and a hump is observed at around $h\omega = 21$ eV. Behaviour of $|\tilde{A}_\omega(z)|^2$ in the surface region agrees qualitatively with the experimental results as shown by Weng et al\cite{51}. This result also agrees with the theoretical calculation of Bagchi and Kar\cite{27} in which they have obtained a
Figure (2.2): Plot of variation of $|\vec{A}_\omega(z)|^2$ against photon energy for location of surface planes at $z = -a$, $-0.5a$ and $0$ for $W$. Plasmon energy of $W^{50}$ is 25.3 eV.
Figure (2.3): Plot of $\frac{dA_{\omega}}{dz}$ against distance $z$ from the surface for photon energies ($\hbar\omega$) 16 eV, 21 eV and 25 eV respectively for $W$. The distance $z$ is measured in atomic unit.
maximum in the electromagnetic field at $\hbar\omega = 20$ eV and a suppression at photon energy $\hbar\omega = 25$ eV.

For further investigation of the origin of the peak at $\hbar\omega = 21$ eV, we have also plotted $\frac{dA_\omega(z)}{dz}$ as a function of distance (z) from the surface defined by $z = 0$ plane, for values of photon energy at $\hbar\omega = 16$ eV, 21 eV and 25 eV as shown in Fig. (2.3). We see that there is a strong peak in the middle of the surface region for $\hbar\omega = 21$ eV. On the other hand, for $\hbar\omega = 16$ eV and 25 eV, the plot of $\frac{dA_\omega(z)}{dz}$ does not show peak in the surface region. Hence this shows that the origin of the peak at $\hbar\omega = 21$ eV is a surface feature.

(ii) Molybdenum:

In Fig (2.4), a graph of $|\tilde{A}_\omega(z)|^2$ against the incident photon energy $\hbar\omega$ is plotted for the surface planes located at $z = 0$ (vacuum), $z = -0.5 \ a$ (surface) and $z = -a$ (bulk) for Mo. At the surface region, that is $z = -0.5 \ a$, as photon energy increases $|\tilde{A}_\omega(z)|^2$ increases and reaches maximum value at photon energy $\hbar\omega = 20$ eV and then starts decreasing and attains minimum value at $\hbar\omega = 25$ eV. The plasmon energy ($\hbar\omega_p$) of Mo is 24.4 eV \cite{52}. For $z = 0$, which is the vacuum region, we also observe a suppression in $|\tilde{A}_\omega(z)|^2$ at $\hbar\omega = 25$ eV but we do not have a prominent peak value below the plasmon energy. For $z = -a$, which is the bulk region, $|\tilde{A}_\omega(z)|^2$ also increases with the increase in photon energy but the peak value occurs at $\hbar\omega = 25$ eV.
Figure (2.4): Plot of variation of $|\bar{A}_\omega(z)|^2$ against photon energy for location of surface planes at $z = -a$, $-0.5a$ and $0$
for the case of Mo. The plasmon energy of Mo is 24.4 eV
Figure (2.5): Plot of $\frac{d\tilde{A}}{dz}$ against distance $z$ from the surface for photon energies 12 eV, 20 eV and 26 eV in Mo. The distance $z$ is measured in atomic unit.
which is near the plasmon energy and a clear minimum is not observed. The
behaviour of the electromagnetic field for the surface plane located at \( z = - 0.5a \)
agrees well with the results of Thapa et al.\textsuperscript{53,54} where they have also obtained a
maximum in the electromagnetic field at \( h\omega = 20 \text{ eV} \) and a minimum at \( h\omega = 25 \text{ eV} \).

In Fig. (2.5), we have a plot of the spatial variation of electromagnetic field \( \frac{dA_y}{dz} \)
with respect to the location of the surface plane \( z \) at \( z = 0 \) for different values
of incident photon energy \( h\omega = 12 \text{ eV}, 20 \text{ eV} \) and \( 26 \text{ eV} \). For photon energy \( h\omega = 20 \text{ eV} \), we see a strong peak in the middle of the surface region. But for photon energy
\( h\omega = 12 \text{ eV} \) and \( 26 \text{ eV} \), the plot of \( \frac{dA_y}{dz} \) does not show peak in this region. Hence
we can say that the origin of the peak at \( h\omega = 20 \text{ eV} \) is a surface feature.

(iii) Lead Sulphide:

Semiconductors, like metals, also have surface states which had been shown
by angle integrated photoemission technique\textsuperscript{55,56,57}. In Fig (2.6), we have a graph of
\(|\vec{A}_y(z)|^2\) against the incident photon energy \( h\omega \) for the surface planes located at \( z = 0 \)
(vacuum), \( z = - 0.5 \text{ a} \) (surface) and \( z = - \text{ a} \) (bulk) for PbS. For the location of the
surface plane in the surface region, i.e at \( z = - 0.5 \text{ a} \), we find that as photon energy
increases \(|\vec{A}_y(z)|^2\) also increases showing maximum value at photon energy \( h\omega = 13 \text{ eV} \). As the photon energy is further increased, \(|\vec{A}_y(z)|^2\) decreases and a suppression is
observed at \( h\omega = 15 \text{ eV} \). By defining the plasmon frequency as the frequency at
which the real value of \( \varepsilon_1(\omega) \) disappear, the plasmon energy \( (h\omega_p)_i \) of PbS is found to
Figure (2.6): Plot of variation of $|\Delta_{\alpha}(z)|^2$ against photon energy for location of surface planes at $z = -\alpha$, $-0.5\alpha$ and $0$ for PbS.
be $\hbar \omega = 14.4$ eV. For other locations of the surface plane, we have a different plot. For the location of the surface plane at $z = 0$, which is the vacuum region, $|\tilde{A}_\omega(z)|^2$ decreases with the increase in photon energy and we do not observe a peak below the plasmon energy though a slight suppression is observed near the plasmon energy. For the location of the surface plane at $z = -a$, which is the bulk region, $|\tilde{A}_\omega(z)|^2$ also increase with the increase in photon energy but the maximum and minimum values of $|\tilde{A}_\omega(z)|^2$ are both observed above the plasmon energy at $\hbar \omega = 17$ eV and $\hbar \omega = 29$ eV respectively.

(iv) Lead Selenide:

In Fig. (2.7) we have a graph showing the variation of $|\tilde{A}_\omega(z)|^2$ with respect to the incident photon energy $\hbar \omega$ for the surface planes located at $z = 0$ (vacuum), $z = -0.5a$ (surface) and $z = -a$ (bulk) for PbSe. In this graph, for the location of the surface plane at the surface region which is at $z = -0.5a$, we observed that as the incident photon energy increases, $|\tilde{A}_\omega(z)|^2$ increases sharply showing a sharp peak at $\hbar \omega = 5$ eV followed by a minimum value at $\hbar \omega = 7.5$ eV. Here also, the plasmon frequency is defined to be the frequency at which the real value of $\varepsilon_i(\omega)$ disappear. Hence, the plasmon energy ($\hbar \omega_p$) of PbSe is found to be $\hbar \omega = 7.6$ eV. For the location of the surface plane at the vacuum region which is at $z = 0$, we find that as the photon energy increases, $|\tilde{A}_\omega(z)|^2$ initially decreases sharply and becomes almost
Figure (2.7): Plot of variation of $|A_{\omega}(z)|^2$ against photon energy for location of surface planes at $z = -a$, $-0.5a$ and $0$ for $PbSe$. 
constant without showing a maximum or a minimum value below and near the plasmon energy. For the other location of the surface plane at \( z = -a \), which is the bulk region, we have a completely different plot. In this case, \( |\widetilde{A}_m(z)|^2 \) increases slowly with the increase in the photon energy and keeps on increasing without showing a maximum or a minimum value. Features such as peak below the plasmon energy and a suppression in the neighbourhood of the plasmon energy are expected and its occurrence only for the surface plane located at \( z = -0.5a \) indicates the importance of the surface.

In all the plots shown above showing the variation of the electromagnetic field as a function of the incident photon energy \( (\hbar \omega) \), for the location of the surface plane at the surface region, we observed a maximum in the electromagnetic field below the plasmon energy and a suppression near the plasmon energy. The plasmon energy is chosen to be defined as the energy at which the real value of \( \varepsilon_i(\omega) \) disappears. The peak value in \( |\widetilde{A}_m(z)|^2 \) at incident photon energy below the plasmon energy is due to the excitations of the surface plasmon. The suppression of the electromagnetic field in the neighbourhood of the plasmon energy for the surface region indicates that the behaviour of the electromagnetic field in the surface region is very similar to its behaviour outside the surface. For other locations of the surface plane, that is, at the vacuum and at the bulk region, peak in electromagnetic field below the plasmon energy and minimum near the plasmon energy were not observed. This shows the importance of the surface region in metals as well as semiconductors.
For further investigation on the origin of the peak below the plasmon energies, we have plotted $\frac{dA_u}{dz}$ as a function of the distance of the surface plane defined by $z = 0$. For $W$, at photon energy $\hbar \omega = 21$ eV, we see that there is a strong peak in the middle of the surface region whereas peaks in this region are not observed at photon energies $\hbar \omega = 16$ eV and 25 eV. Similarly, for $Mo$, at photon energy $\hbar \omega = 20$ eV, a strong peak is found in the middle of the surface region while such peaks in this region are not seen at photon energies $\hbar \omega = 12$ eV and 26 eV. Hence we can conclude that the origin of a peak in the field calculation is a surface feature. From the results shown above, we can also conclude that the electromagnetic field we have used which is deduced using simple dielectric model is applicable for photoemission calculations for metals and semiconductors.