CHAPTER 5

CONCLUSION
In chapter 2 of this thesis, we have presented the calculations of electromagnetic fields in the bulk, surface and vacuum regions of metals W and Mo and semiconductor PbS and PbSe. The electromagnetic fields in these systems were calculated using the modified form of dielectric model developed by Bagchi and Kar. In all these systems, both in metals and semiconductors, we have found that in the surface region, for incident photon energies below the plasmon energy, there is a peak in the field. With the increase in photon energy, the field decreases and attains a minimum at incident photon energy equal to the bulk plasmon energies. With the further increase of incident photon energies, beyond the plasmon energy, field values increases and attain a small hump, and decreases towards minimum. Our calculated results showed agreement with the experimental values especially in the case of W and Mo. For example, peak in intensity occurs at $\hbar\omega = 22$ eV in the experimental data for the case of W, whereas our calculated data showed peak at $\hbar\omega = 21$ eV. It therefore appears that there is a close agreement between the calculated and experimental results. For the other two regions, that is the vacuum and bulk regions; we found that with the increase in incident photon energy, we do not observe a peak in the fields below the plasmon energies and minimum at the plasmon energies are also not observed. For the semiconductors PbS and PbSe, as we do not have experimental results to compare, we define the plasma frequency as the frequency at which the real part $\epsilon_1(\omega)$ of the dielectric response function $\epsilon(\omega)$ tends to zero. In that case the plasmon energy of PbS is 14.4 eV and that of PbSe is 7.6 eV. Our calculations also show the expected features for these semiconductors. That is, we observed a peak in the electromagnetic field below the plasmon energy ($\hbar\omega_p$) and a
minimum near the plasmon energy \( (h\omega_p) \). To further investigate the origin of the peaks below the plasmon energies, we have also plotted a graph of \( \frac{dA_\omega}{dz} \) against distance from the surface plane defined by \( z = 0 \) for different values of the incident photon field \( h\omega \) in the case of \( W \) and \( Mo \). In these plots, we have seen that for \( W \), at photon energy \( h\omega = 21 \text{ eV} \), there is a strong peak in the middle of the surface region. But for other photon energies \( h\omega = 16 \text{ eV} \) and \( 25 \text{ eV} \), peaks in the middle of the surface regions are not observed. For \( Mo \), at photon energy \( h\omega = 21 \text{ eV} \), a strong peak is also seen in the middle of the surface region while such peaks are not seen for photon energies \( h\omega = 12 \text{ eV} \) and \( 26 \text{ eV} \) in that region. Hence, from these evidences, we can conclude that the origin of the peak in the field calculation is a surface feature.

From our results, we can also conclude that the vector potential \( \tilde{A}_\omega(z) \) deduced in Chapter 2 by using the modified form of dielectric model of Bagchi and Kar for the surface region of solid can be employed in the calculation of the photoemission for metals as well as semiconductors.

In Chapter 3, we have presented photoemission calculations by developing the formulation for the initial state wavefunction by using two approaches. Firstly, we used Green function’s method to deduce the initial state wavefunction by solving the one-dimensional Schrödinger’s equation where we have considered the bulk potential to be a Kronig-Penny \( \delta \)-potential. This wavefunction was used for the calculation of the photocurrent from the bulk region. For the surface region, the initial state wavefunction was defined by a Gaussian type of wavefunction. Photocurrents were calculated from systems \( W \), \( Be \), \( PbS \) and \( SiC \). In our calculations, the vector potential used in the evaluation of the matrix element involved is the one given in chapter 2. In
all the cases, for the location of the initial state wavefunction at the surface region, photocurrents showed maximum value below plasmon energy and suppression at the plasmon energy. The results of \( W \) and \( Be \) were compared with experimental results as well as theoretical results and seems to agree qualitatively well.

In the photoemission calculations by Green function’s method, the initial state wavefunction was developed for the bulk region only and for the surface we assumed a Gaussian type wavefunction. Therefore, a proper initial state wavefunction for the surface region needs to be considered and formulated. Moreover, band structure effects of solids were neglected in our calculations. Hence, to include band effect, we deduced the basis functions by using projection operator method of group theory which is to be employed in the formulation of the initial state wavefunction. The basis functions were developed for \( Cu \) which is an fcc crystal and also for \( W \) which is a bcc crystal. These basis functions developed are employed separately as a model for fcc and bcc crystal structures for the formulation of the initial state wavefunction. Hence we obtain two different initial state wavefunctions, one for solids having fcc crystal structure and the other for those having bcc crystal structures. The initial state wavefunction developed for fcc crystal is used to find the photocurrents of fcc crystals like \( Cu, Al, Ni \) and \( PbS \), and that for bcc crystal is used for \( W, Mo \) and \( Fe \) which are all bcc. Whenever applicable, the results we have obtained are compared with the experimental results as well as other theoretical results. We found that they agree reasonably well. Hence, the formulation presented in Chapter 3 works reasonably well and is applicable for photocurrent calculations of metals and semiconductors.

Although the photocurrent calculations by Green function’s method and the projection operation method of group theory seem to work well when compared to
experimental and other theoretical results, there are still some drawbacks. First of all, in Green function's method, the initial state wavefunction was deduced for the bulk region only. Hence a proper initial state wavefunction for the surface region needs to be developed. This in part was achieved by developing the basis function for the surface by using projection operator method of group theory. This basis function was used for the development of initial state wavefunction for the surface region and we have extended it to the bulk also. In fact, it would be more appropriate if we can develop a proper initial state wavefunction for the bulk and surface region separately by considering the nature and type of potentials which define these regions. Also, in our calculation we have ignored the development of the final state wavefunction. Another drawback is that the basis functions we have developed are for Cu and W and we have used it for calculations from other solids as well.

In Chapter 4, we have presented the calculation of band structure by using FP-LAPW method. We applied it to the case of lead salts namely PbS, PbSe and PbTe, and metal W. The band structures are plotted at various symmetry points in the Brillouin zone. Volume optimization was performed by plotting Murnaghan's plot in which total energy was plotted against volume. By using the volume corresponding to the lowest energy in the Murnaghan's plot, lattice constants were evaluated. These theoretical values of lattice constants are used in the band structure calculations. Our results were compared with the experimental results and found to agree well. The band gaps at L symmetry point we have obtained for all the lead salts also agrees well with the experimental results as well as theoretical results of others using different methods. The band gap of PbTe was found to be larger than that of PbSe which is also observed experimentally. But the band gap of PbTe we have obtained is also larger
than that of PbS which is unexpected. This may be due to the value of lattice constant $a$ we have calculated and used for band structure calculation of PbTe. The experimental value of $a$ is 6.4603 Å whereas our calculated value is 6.50 Å. For PbS, the experimental value of $a$ is 5.9362 Å and the calculated value is extremely close to this which is 5.973 Å. The band structure of W we have calculated also showed features which are in qualitative agreement with experimental results. Overall, we can conclude that FP-LAPW method is very appropriate for the calculation of band structure of solids and the computer code WIEN2k code we have employed in our calculation also works well.

Further work is now carried on FP-LAPW method not only for band structure calculations but also for calculation of other properties like density of state, electron charge density, optical properties etc. of metals and semiconductors. We are also working on band structure calculations from perovskite compounds like perovskite oxide barium aluminium niobate $BaAl_{1/2}Nb_{1/2}O_3$ which has a variety of technological applications such as capacitors, sensors, actuators and integrated electromechanical systems.