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# Multiharmonic generation and photoemission from solid surfaces


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City University of New York, 1991



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# MULTI-HARMONIC GENERATION AND PHOTOEMISSION FROM SOLID SURFACES

by

*Aparajita Mishra*

A dissertation submitted to Graduate Faculty in Physics in partial fulfilment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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# ABSTRACT

## MULTI-HARMONIC GENERATION AND MULTIPHOTON ELECTRON EMISSION FROM SOLID SURFACES

by

Aparajita Mishra

Advisor : Joel I. Gersten

The purpose of the dissertation is to study the interaction of intense laser fields with the surfaces of metals. The goals are to elucidate the nature of the elementary processes involved, to calculate the size of various properties associated with the interactions and to determine what information concerning the surface of a metal can be obtained from such experiments. The primary attention of the dissertation is directed towards the study of the generation of optical harmonics and the electronic photoemission produced when the metal is made to interact with the strong laser field. The research involves formulating models, developing the theory for such interactions, and doing detailed calculations to determine the expected magnitudes of the effects.

The thesis begins with a study of classical collisions of electrons with the surface of a metal. The electronic excitation process in the presence of an electromagnetic wave is studied. It is found that multiple wall collisions are responsible for nonlinear effects in the classical case. Also a study is made of the classical theory for the scattering of electromagnetic radiation and the influence that multiple collisions have on the spectrum.

A perturbation theory is developed for multi-harmonic generation and multi- photon electron emission from the surface of the solid. The perturbation theory is developed for

arbitrary number of photons but in the 'undressed' limit. Thus only the lowest order diagrams that contribute to a given process are included. Detailed formulas are derived and calculations performed for both a hard wall model and a finite step Sommerfeld model. Explicit formulas are obtained in the high frequency limit.

The problem of arbitrary numbers of photons and arbitrary orders are then considered in a non-perturbative theory. Thus a study is made of the interaction of electromagnetic waves with solids in a fully dressed approach. The theory is applied first to the hard wall potential, then to the finite sharp step potential and finally to the smooth step potential.

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I would also like to thank my colleagues Ms. Asima Pradhan and Mr. B.B. Das of Physics department, and Dr. Sanjukta Das of Chemistry department of Stevens Institute of Technology, Hoboken, NJ for their assistance and the many stimulating discussions during the course of this research.

*To my husband*

**and**

*parents*

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# I.INTRODUCTION

Ever since intense sources of electromagnetic radiation have become available, interest in the nonlinear optical properties of matter has persisted. One of the most elementary manifestations of such a nonlinear property is multi-photon photoemission (MPE). In this process some number of photons are absorbed and the energy is used to promote an electron from some state below the Fermi surface to a state which is above the vacuum level and which leaves the metal.

## I.1 MULTI-PHOTON PHOTOEMISSION

Experimental studies of multiphoton photoemission from a variety of solids have been made by a number of research groups. These solids include metals, semiconductors and insulators. Korshunov et. al. [1] studied the multiphoton photoemission from metals into a solution. They looked at mercury droplets in HClO(4) solution irradiated by ruby and Nd laser radiation and found that the photocurrent depended on the second or third power of the laser intensity. Fujimoto et. al. [2] used high intensity femtosecond laser pulses to study the multiphoton photoelectron emission from tungsten and found evidence for thermal nonequilibrium between the electrons and the lattice. Vodopyanov et. al. [3] probed the laser- induced emission of electrons from the surface of gold using picosecond 2.8 micron radiation. They briefly discussed the effect of surface heating and concluded that multi-quantum photoemission stimulated by heating was observed in their experiment.

Studies of semiconductor surfaces include the following: Massey et. al. [4] reported nonlinear photoemission images of GaAs and LiNbO(3) using a novel imaging technique. Photoelectron generated by multiphoton absorption were used to form images of evanescent waves in optical waveguide surface structures.

Bensoussan et. al. [5] observed nonlinear photoemission from Silicon 111 surfaces. Two well-defined photoemission regions were detected. At low laser fluence and at photon energies greater than half the work function two and three photon processes were identified as the dominant ones. It was found that the density of states of the initial and intermediate states influenced the resulting photoelectron spectrum. At high fluences the emitted electron spectrum resembled a thermal Maxwellian spectrum. Weiner et. al. [6] used picosecond pulses and a transmission line geometry to study the temporal resolution of multiphoton processes on GaAs.

Studies of insulators were conducted primarily by Nielsen et. al. [7] who observed two and five photon induced emission of electron and ions from the 111 surface of BaF(2). In the case of ion yield they found the intensity of the ion yield varied as the tenth power of the laser intensity, indicating that two holes in the valence band were needed for ion emission to occur. Resonance enhancement due to the existence of surface states was observed. This conclusion was supported by elementary cluster calculations.

Multiphoton photoemission was also observed from several organic cathodes by Massey et. al. [8] . Xue et. al. [9] observed multiphoton photoelectron emission from ultrafine metal particles and semiconductor thin films. Particular attention was paid to the photocathode Ag-Cs(2)O.

Several theoretical studies of multiphoton photoemission have been reported. Farkas et. al. [10] studied the multiphoton photoemission from the solid state with special regards to metals. Friedkin et. al. [11] studied the external multiphoton photoeffect from impure semiconductors and dielectrics using the method of kinetic equations. They studied the role played by localized states and the interaction with phonons in determining the distribution of the emitted electrons. Arutyunyan et. al. [12] studied the multiphoton emission of electrons from metal surfaces with the assumption that electrons move in the field of a Sommerfeld barrier. Giessen et. al. [13] studied the image potential states seen via two photon photoemission and second harmonic generation.

## 1.2 MULTIHARMONIC GENERATION

Another elementary nonlinear process that can occur when intense electromagnetic radiation strikes a solid is the process of multiharmonic generation (MHG). In this process, some number of photons are absorbed from the incident laser beam and an outgoing photon is produced instead. The energy of the outgoing photon is a multiple of the incident photon energy.

Experimental studies of multiharmonic generation have been reported in the literature. These studies include a variety of metals, semiconductors and insulators as well as adsorbate covered solids. Kexiang He [14] reported studying the anisotropic second harmonic generation at single crystal metal surfaces. Murphy et. al. [15] studied the second harmonic generation from the 111 and 110 surfaces of Aluminum as well as from polycrystaline samples. It was found that at low frequencies the second harmonic response is sensitive to the charge density profile near the surface region. It was also argued that band structure effects played a visible role in determining the anisotropy of the response. This was used to determine information regarding the surface states. Akhmanov et. al. [16] presented experimental data on second harmonic generation from aluminum and tungsten. They also reported detecting second and third harmonics from irradiated films and single crystals of high temperature superconducting materials. Stern et. al. [17] studied the electron structure of disordered alloys such as AgCd and AgMg.

Studies of semiconductors include those of Aktsipetrov et. al. [18] who looked at the contribution of the surface to the generation of reflected second harmonics for centrally symmetric semiconductors. They presented data for germanium. Aktsipetrov et. al. [19] also studied silicon and came up with a nonlinear optical method for the study and control of the microheterogeneity of metal and semiconductor surfaces. They measured the intensity of the polarized second harmonic generated by laser heating at phase boundaries. Govorkov et. al. [20] studied the silicon 111 surface and found interference effects in the third harmonic and sum frequency generation in reflection. They related their measurements to the symmetry of the reflecting surface. In a paper entitled "Nonlinear optical methods in the nondestructive testing of metal surfaces", Pedersen et. al. [21] reached similar conclusions. They were also able to see the effect of residual strains. Second harmonic generation from semiconductor-metal waveguiding structures were made by Azarenkov et. al. [22] The semiconductors studied included n-type PbTe and GaAs.

Studies of insulators included the in situ probing of electronic surface structure in ionic crystals by resonant second harmonic generation by Reif et. al. [23] Results were reported for $BaF(2)$, NaCl and KCl. For the divalent crystals the signal was ascribed to the surface dipole interaction whereas for the monovalent crystal the role of long range interactions was stressed. Strong asymmetry effects were found. Optical second harmonic generation was also studied by Wijekoon [24] on metal oxide surfaces.

In addition, multiharmonic generation has been used to study adsorbed layers on solids. Brown [25] looked at the effect of an adsorbed gas layer on silver and concluded that adsorption effects could strongly modify the degree of second harmonic generation. P. Qiu et. al. [26] studied second and third harmonic generation of laser dye molecules adsorbed on an optical surfaces fused quartz and K9 glass. G. Berkovic et. al. [27] concluded that the molecular orientation and conformational dynamics of an adsorbed molecule could be obtained by studying third harmonic generation from a monolayer film of polydiacetylene, poly-4-BCMU. Belyi et. al. [28] studied the second harmonic generation enhancement by a pyridine layer adsorbed on copper and aluminum substrates. They concluded that the second harmonic signal intensity could serve as a source of information on the thickness and structure of the absorbed layer.

Theoretical studies of multiharmonic generation has focused primarily on metals. First-principles calculations of the effect in bulk matter have been carried out by numerous researchers. Adler [29] discussed the general symmetry properties of nonlinear media and outlined a formalism to compute nonlinear polarization currents. Early theoretical studies of the nonlinear optical behavior were conducted by Jha [30] Jha and Warke [31] Bloembergen et. al. [32], Rudnick and Stern [33], Sipe and Stegeman [34] Corvi and Schaich [35] and Agarwal and Jha [36] Experiments on media with inversion symmetry by Bloembergen et. al. [32] confirmed, to within an order of magnitude, these theoretical models. Additional support came from the experiment of Quail and Simon [37]. Sonnenberg [38] presented a theory of optical second harmonic generation in metals which is in agreement with the hydrodynamic model of Jha [30]. Chen et. al. [39] presented a theory based on a free electron model and calculations were made for alkali covered surface of germanium, copper and silver. They found that the shifting of the surface electronic states relative to the Fermi surface could profoundly affect the results. The free electron model was also employed by Akhmediev [40] to study the role of the boundary layer in second harmonic generation during reflection from various alkali metals. Sipe et. al. [41] formulated a hydrodynamic model second harmonic generation of a metal surface. The role of the surface plasmon in second harmonic generation was studied extensively. Simon et. al. [42] looked at the alkali metals and found that when the angle was such that surface plasmons could be excited the SHG signal was enhanced. Mills [43] studied the role of surface polaritons on metals and their influence on second harmonic generation in the infrared frequency range. Chen [44] studied second and third harmonic generation at metal dielectric interfaces. Agarwal et. al. [30] presented a theory of second harmonic generation at a metal surface with surface plasmon excitation in which a resonant enhancement of the SHG signal was predicted. Moshrefzadeh et. al. [45] examined the second harmonic generation by monolayers using long-range surface plasmon excitation and also concluded that there should be large enhancement effects. Weber [46] analyzed copper films and found that second harmonic generation could be enhanced by a factor of 3000 over that found in surfaces of semi- infinite metals if certain phase matching conditions were satisfied for the surface polariton. Tzeng et. al. [47] used the hydrodynamic model to make predictions concerning the surface plasmon enhancement of SHG for silver films.

Second harmonic generation from grating structures were studied by Kovalev et. al. [48] who concluded that enhancement occurs on such structures. This comes about both because of the excitation of the surface electromagnetic wave and because of the ability to satisfy phase matching conditions. The boundary conditions associated with this problem were further studied by Kondratenko

[49] . Calculations for second harmonic generation from grating structures for the semiconductors GaAs, CdTe and GeP on aluminum metalized surfaces were made by Cui et. al. [50] .

In recent years, attention has turned to rough surfaces, mainly because of the observation of surface enhanced Raman scattering. Agarwal and Jha [51] have studied the surface enhancement of SHG at a metal grating using a perturbation expansion in terms of the surface roughness parameter. Chen et. al. [52] have studied the interconnection between SHG and Raman scattering. Arya [53] has developed a Green's function formalism for treating SHG from a rough metal surface. Boyd et. al. [54] made a detailed study of the local field enhancement of various solids using SHG as a probe. Recently Keller [55] emphasized the need for including nonlocal electronic transport effects in describing SHG. Additional studies by Shen [56] , Tom et. al. [57] , Heinz et. al. [58] , and Heskett et. al. [59] have shown SHG to have general utility in probing surface chemistry and structure. Hamilton and Anderson [60] used SHG as a probe for structural and compositional information. They described experiments relating SH intensity and azimuthal orientation and hydrogen coverage of a Na(111) surface in UHV.

Bower [61] studied the effects of electron band structure on optical SHG at metal surfaces. His results indicate that this method can give detailed resolution of the energy band structure of electrons in the surface layer of atoms. Rako et. al.[62] reported an extensive study of optical SHG with the simultaneous excitation of surface plasmon mode at the interface between a metal and a nonlinear piezoelectric crystal. Wokaun et. al.[63] studied SHG from metal island films. They explicitly demonstrated the dependence of the SHG enhancement on the resonant excitation of a localized surface plasmon. Persson et. al.[64] considered the electronic properties of alkali metals adsorbed on a metal surface. They observed a strong increase in SHG at low alkali metal concentration. Hua and Gersten [65] have discussed the theory of second- harmonic generation by small metal spheres. They utilized the hydrodynamical model for the electron gas and a Green's function formalism to solve for the cross-section for producing SHG. More recently, Liebsch [66] has studied the frequency dependence of SHG at simple metal surfaces using the time-dependent density functional formalism. This work has been followed by experimental studies of Song et. al. [67] on the dynamical screening at a metal surface probed by SHG. The system studied by them consisted of a thin film of Rb on Ag substrates.

Very little is known about the effects of higher order multiple harmonic generation. I shall use the acronym MHG to denote multi-harmonic generation . Naturally, SHG is special case of MHG. In the limit of low laser intensities SHG is the only significant form of MHG. However, as the intensities grow stronger, the higher harmonic generations become important. I want to develop a theory which will help me consider MHG for arbitrary order.

Most work dealing with MPE has been done in atomic physics. There also has been some work on MHG in atomic physics. For example G. Banderedge et. al. [68] have studied harmonic generation by a classical hydrogen atom in the presence of an intense radiation field and found that a large number of harmonics may be produced for a sufficiently intense laser.

A lot of work has been done on MPE for Hydrogen atom. Gontier and Trahin [69] studied multiphoton processes for hydrogen atom. They used a novel procedure to sum over intermediate states. Gao and Starace [70] used a variational principle calculation for high order multiphoton processes for atomic hydrogen. Eberly and Su [71] did calculations for hydrogen for very high intensities (of the order of $10^{13}-10^{16} W / cm^2$. They observed that perturbation theory is not valid for such high intensity. They did the calculation nonperturbatively. They discussed harmonics of the order of 33 for this high intensity and connected this with above threshold ionization.

## 1.3 GOALS.

I start by considering the simplest form of a metal described by the Sommerfeld model. The goal is to derive expressions for the MHG yield and the MPE spectrum to arbitrary order in the incident electromagnetic field and to carry out the numerical computations involved. Once the results of this model are obtained one may proceed to other more sophisticated models of the solid.

In the Sommerfeld model the metal is taken to be a free electron gas terminated by an abrupt step in the potential. The electronic states are filled up to the Fermi level and the electromagnetic field appears as a perturbation to the Hamiltonian describing the system. I will approach the problem with three levels of approximation. At the crudest level I will simply terminate the solid by a hard wall. At the next level of approximation I will terminate the solid with a sharp step instead of a hard wall. In the third level the sharp step will be replaced by a graded step. In relaxing each approximation I will learn something about the importance of the physical parameters involved. For example, in going from the hard wall to the sharp step I will see how important the work function of the metal is. In going from the sharp step to the smooth step, I will see how important the range of the potential step is in determining the strength of the nonlinear processes. The goals of the thesis are the following:

(a) To calculate, within the confines of the approximations, the photon yield for the various orders of MHG. That is, to determine what the probability distribution is for producing an $n^{th}$ order harmonic photon as a function of incident laser intensity.

(b) To calculate the angular radiation pattern produced in MHG. I would like to study it as a function of primary intensity, orientation, polarization and frequency.

(c) To analyze the polarization properties of the outgoing radiation. Again these would be made as a function of the same parameters above.

(d) To study the MPE process in which a high energy electron is emitted from the solid. Again I want to study the yield and angular distribution.

(e) To study the effect of using approximation methods rather than the exact $n^{th}$ order calculation. In particular I would like to study the effect of using 'dressed' versus 'undressed' treatments of the nonlinear problem.

(f) To study the effect of allowing the abrupt surface step to be replaced by a smooth transition in potential from bulk to vacuum.

## 1.4 THESIS ORGANIZATION:

The thesis is organized as follows. I start in chapter 2 by studying classical collisions of a charged particle with the surface of a solid. The solid is modeled by the simplest of all models - the hard wall potential. The processes of electron excitation and of photon emission during the collision are studied. Particular interest centers on the role played by multiple collisions with the wall in strong electromagnetic fields.

In chapter 3 I develop the quantum mechanical perturbation theory for the interaction of electromagnetic radiation with a solid. Both multiharmonic generation(MHG) and multiphoton electron emission(MPEE) are considered and applied to the case of hard wall potential.

Chapter 4 concerns itself with perturbation theory as applied to the sharp step potential. Numerical estimates are obtained for MHG and MPEE yields.

In chapter 5 a study is made of the high frequency limit of perturbation theory. Rather general analytical formulas are obtained in this case.

The theory is extended to nonperturbative (strong field) situations in chapter 6. Results are obtained for the low frequency limit and are compared with the perturbation theory case. Attention is restricted here to the wall potential problem.

Chapter 7 generalizes the results of chapter 6 to sharp step potential case. The nonperturbative nature of the solutions are studied in detail.

Finally in chapter 8 the theory is generalized to the case of a graded step surface potential.

From the studies of the thesis I am able to obtain insights into the behavior of nonlinear optical processes at the surface of solids with particular emphasis on multiphoton harmonic generation and multiphoton electron emission.

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# 2. CLASSICAL WALL COLLISIONS

## 2.1 ELECTRON EXCITATION IN CLASSICAL WALL COLLISIONS

### 2.1.a Theory

In this chapter I will study the classical collision of an electron with the surface of a solid. My goal will be to elucidate the physics of the interaction of the electron inside the solid with an electromagnetic field. I make the simplest possible assumption about the solid - that it only confines the electron to a half-space. The solid will be modeled by the wall potential

$$V(z) = \infty \qquad \text{if } z < 0$$

$$= 0 \qquad \text{if } z > 0 \tag{2.1}$$

The electromagnetic field will be treated in the electric dipole approximation so it will be described in terms of a time-dependent vector potential $\vec{A}(t)$. This potential will be taken to be of the form

$$\vec{A}(t) = A_0 \hat{e} \cos(\omega t + \phi) \tag{2.2}$$

where $A_0$ is the amplitude, $\hat{e}$ is the polarization vector, $\omega$ is the radian frequency and $\phi$ is the phase. It will be assumed that collisions of the electrons with the walls are both specular and elastic.

Newton's second law determines the rate of change of the momentum vector

$$\frac{d\vec{p}}{dt} = -e\vec{E}(t) \tag{2.3}$$

where $e$ is the magnitude of the electron's charge and the electric field is given by

$$\vec{E}(t) = -\frac{1}{c}\frac{\partial \vec{A}(t)}{\partial t} \qquad (.2.4)$$

and $c$ is the speed of light. Let $t_0$ denote the time when the electron strikes the wall. For times $t < t_0$ the momentum is

$$\vec{p}(t) = \vec{p}_0 + \frac{e}{c}\vec{A}(t) \qquad (.2.5)$$

or

$$\vec{p}(t) = \vec{p}_- + \frac{e}{c}\left[\vec{A}(t) - \vec{A}(t_0)\right] \qquad (.2.6)$$

where $\vec{p}_0$ is the electron's momentum in the absence of the field. Just prior to the wall collision the momentum is

$$\vec{p}_- = \vec{p}(t_0^-) = \vec{p}_0 + \frac{e}{c}\vec{A}(t_0) \qquad (.2.7)$$

Immediately after the collision the momentum is

$$\vec{p}_+ = \vec{p}_- - 2\hat{k}\hat{k}\cdot\vec{p}_- \qquad (.2.8)$$

corresponding to the fact that the collision is both elastic and specular. I will assume for now that only one collision occurs with the wall. For times $t > t_0$ the momentum is given by

$$\vec{p}(t) = \vec{p}_+ + \frac{e}{c}\left[\vec{A}(t) - \vec{A}(t_0)\right] \qquad (.2.9)$$

In the course of the collision the electron, on the average, gains energy. To see this let us compare the average kinetic energy prior to the collision with the average kinetic energy after the collision. Prior to the collision

$$\bar{E} = \frac{1}{2m} < \left\{ \vec{p}_- + \frac{e}{c} \left[ \vec{A}(t) - \vec{A}(t_0) \right] \right\}^2 > \quad (2.10)$$

where $m$ is the electronic mass. After the collision

$$\bar{E}' = \frac{1}{2m} < \left\{ \vec{p}_+ + \frac{e}{c} \left[ \vec{A}(t) - \vec{A}(t_0) \right] \right\}^2 > \quad (2.11)$$

Noting that $p_+^2 = p_-^2$ I form the difference

$$\Delta E = \bar{E}' - \bar{E} \quad (2.12)$$

and find that

$$\Delta E = \frac{e}{mc} < (\vec{p}_+ - \vec{p}_-) \cdot \left[ \vec{A}(t) - \vec{A}(t_0) \right] > \quad (2.13)$$

Averaging over time $t$ and using the fact that

$$< \vec{A}(t) > = 0 \quad (2.14)$$

reduces this to

$$\Delta E = \frac{2e}{mc} < \hat{k} \cdot \vec{p}_- \hat{k} \cdot \vec{A}(t_0) >$$

$$= \frac{2e}{mc} < \left[ \hat{k} \cdot \vec{p}_0 + \frac{e}{c} \hat{k} \cdot \vec{A}(t_0) \right] \hat{k} \cdot \vec{A}(t_0) > \quad (2.15)$$

In general, the collisions will occur at random times, so

$$< \vec{A}(t_0) > = 0 \quad (2.16)$$

and

$$< \hat{k} \cdot \vec{A}(t_0) \hat{k} \cdot \vec{A}(t_0) > = \frac{1}{2} (\hat{k} \cdot \hat{e} A_0)^2 \quad (2.17)$$

Hence the net average gain in energy per collision is given by

$$\Delta E = \frac{e^2}{mc^2}(\hat{k}\cdot\hat{e})^2 A_0^2 \tag{2.18}$$

This result is independent of the original momentum of the electron.

It is interesting to note, however, that the mean particle momentum change upon colliding with the wall does not depend on the applied field. Thus, the mean momentum change for the one-collision case is

$$<\Delta\vec{p}> = <\left|\vec{p}_+ - \frac{e}{c}\vec{A}(t_0)\right| - \left|p_- - \frac{e}{c}\vec{A}(t_0)\right|>$$

$$= <2\hat{k}\hat{k}\cdot\vec{p}_0 + \frac{2e}{c}\hat{k}\hat{k}\cdot\vec{A}(t_0)>$$

$$= 2\hat{k}\hat{k}\cdot\vec{p}_0 \tag{2.19}$$

In the Sommerfeld model of a solid, however, the energy states are filled only up to the Fermi energy, $E_F$ (at absolute zero temperature). Furthermore only those electrons near the Fermi surface are able to find unoccupied states to which to make transitions. I will consider these effects later when I discuss the quantum mechanical description of wall collisions.

In a semiclassical description, where I treat the radiation field in terms of photons, I know that the electron can only absorb or emit an integer number of photons. Therefore I must interpret the energy gain quantity $\Delta E$. In increasing the energy of the electron by amount $\Delta E$ the mean number of photons absorbed is

$$\bar{n} = \frac{\Delta E}{\hbar\omega} \tag{2.20}$$

or

$$\bar{n} = \frac{e^2 A_0^2}{\hbar\omega m c^2}(\hat{k} \cdot \hat{e})^2 \tag{2.21}$$

The actual distribution is more difficult to get by the classical model.

In this analysis I have made the assumption that there is only a single collision with the wall. This assumption is good provided $A_0$ is sufficiently small. For larger $A_0$ I must worry about the possibility of multiple collisions. In order to detect the possibility of such multiple collsions let us study the coordinate $z(t)$ for times $t > t_0$. Then

$$z(t) = \left[v_+ - \omega x \cos(\omega t_0 + \phi)\right](t - t_0) +$$

$$x\left[\sin(\omega t + \phi) - \sin(\omega t_0 + \phi)\right] \tag{2.22}$$

If a collision were to occur at time $t_1$ then

$$z(t_1) = 0 \tag{2.23}$$

and the velocity prior to that collision would be

$$v_-' = v(t_1^-) = v_+ + \omega x\left[\cos(\omega t_1 + \phi) - \cos(\omega t_0 + \phi)\right] \tag{2.24}$$

Again, the velocity just after the second collision would be given by

$$v_+' = v(t_1^+) = -v(t_1^-) \tag{2.25}$$

If no second collsion were to occur then as time progressed $z(t)$ would get larger and larger. When $z(t) > 2x$ I would be certain that no further wall collisions would occur, since $x$ is the amplitude of the classical excursion of the electron. Of course I may also have three collision events, four collision events, etc.

### 2.1.b Results

The computer program CLASSIC.FOR is a FORTRAN program to study the gain of electron energy in collisions with the wall of the solid when the solid is exposed to an electromagnetic field. The input data consists of the excursion parameter $x = eA_0/(mc\,\omega)$, the photon frequency, $\omega$, the electron energy, $E_z$ , an initial value for the time step, $\Delta t$ , and an integer, $n$ giving the number of phases, $\phi$, to be included in the average. The output data consists of $\Delta E$ , the average change in energy, $<N>$, the mean number of collisions that an electron makes with the wall, and an estimate of the energy gain, $\Delta E$, based on the single wall-collision assumption derived previously.

Results are presented in Fig. 2.1 for the case $\omega$=0.2, $E_z$ =0.1, $\Delta t$ =0.1 and $n$ =100 ( $\omega$, $E_z$ , $\Delta t$ are in atomic units). The mean energy gain, $\Delta E$ is plotted as a function of the excursion parameter $x$ and compared with the estimated energy gain. I see that for $x<1$ the estimated and exact results coincide. For $x>1$ the two results are different. This is due to the presence of multiple collisions as is illustrated in Fig. 2.2, where the mean number of collision, $<N>$, is plotted as a function of $x$ . For $x<1$ there are no multiple collisions. For $x>1$ multiple collisions appear. There is first a threshold for two collisions, then for three collisions, etc. I see evidence for this threshold behavior in both Figs. 2.1 and 2.2.

## 2.2 PHOTON EMISSION DURING CLASSICAL WALL COLLISIONS

2.2.a Theory

When an electron undergoes a wall collision it experiences a rapid deceleration as it reverses its velocity component normal to the surface. On the basis of classical electrodynamic theory I should expect radiation to occur. Here I analyze the power spectrum associated with the collision.

The Larmor formula gives the power radiated by an accelerating charge in the nonrelativistic dipole limit as

$$P(t) = \frac{2e^2a^2(t)}{3c^3} \tag{2.26}$$

The total energy emitted over all times for the electron is

$$W = \int_{-\infty}^{\infty} dt P(t) \tag{2.27}$$

Fourier expanding the acceleration

$$\vec{a}(t) = \int_{-\infty}^{\infty} \vec{a}(\omega)\exp(-i\omega t)d\omega \tag{2.28}$$

leads to the expression

$$W = \frac{8\pi e^2}{3c^3}\int_0^{\infty} |\vec{a}(\omega)|^2 d\omega \tag{2.29}$$

Use has been made of the reality condition $\vec{a}(-\omega) = \vec{a}^*(\omega)$.

Let us begin by looking at the case where the external electromagnetic field is not present. Then, in the case where there is only a single wall collision,

$$\vec{a}(t) = -2\hat{k}\hat{k}\cdot\vec{v}_0\delta(t-t_0) \tag{.2.30}$$

so the Fourier transform is

$$\vec{a}(\omega) = -\frac{\hat{k}\hat{k}\cdot\vec{v}_0}{\pi}\exp(i\,\omega t_0) \tag{.2.31}$$

The spectral energy emission is given by

$$\frac{dW}{d\,\omega}=\frac{8e^2}{3\pi c^3}(\vec{v}_0\cdot\hat{k})^2 \tag{.2.32}$$

If I am dealing with a solid at $T=0^0K$, then the Fermi sea is filled and the emission process is supressed. However, for a hot electron this Brehmsstrahlung radiation is permitted.

Let us next see what happens when the external electromagnetic radiation is turned on. The net acceleration is given by

$$\vec{a} = \Delta\vec{v}\,\delta(t-t_0)+\frac{e}{mc}\frac{d\vec{A}}{dt} \tag{2.33}$$

where the change in velocity is

$$\Delta\vec{v} = -2\hat{k}\hat{k}\cdot\left|\vec{v}_0+\frac{e}{mc}\vec{A}(t_0)\right| \tag{2.34}$$

Now,

$$\vec{a}(\omega) = -\frac{\hat{k}\hat{k}}{\pi}\cdot\left|\vec{v}_0+\frac{e}{mc}\vec{A}(t_0)\right|\exp(i\,\omega t_0)+\frac{ie\,\omega}{mc}\vec{A}(\omega) \tag{2.35}$$

If I square this and realize that the cross term will average to zero due to the randomness of the collision time, I get

$$|\vec{a}(\omega)|^2 = \frac{1}{\pi^2}\left[\hat{k}\cdot\left[\vec{v}_0+\frac{e}{mc}\vec{A}(t_0)\right]\right]^2 + \left[\frac{e\,\omega}{mc}\right]^2 A^2(\omega) \qquad (.2.36)$$

If I average over the phase of the vector potential I obtain for the energy spectrum

$$\frac{dW}{d\,\omega} = \frac{8e^2}{3\pi c^3}\left\{\left[(\hat{k}\cdot\vec{v}_0)^2+\frac{e^2(\hat{e}\cdot\hat{k})^2}{2m^2c^2}A_0^2\right] + \left[\frac{e\,\omega}{mc}\right]^2 A^2(\omega)\right\} \qquad (.2.37)$$

The first term is the same collisional Brehmsstrahlung as before. The second term is field dependent emission. The third term is Thomson scattering.

The question that may be asked is whether or not the field dependent emission will be emitted by the solid even at $T=0^0K$. Since the solid is bathed in electromagnetic radiation it is no longer a system in thermodynamic equilibrium. It is possible for some of the incident radiation to be converted into emitted radiation. However, one must recognize that the system is being exposed to harmonic radiation and therefore the energy of the electromagnetic field may only be changed by integer numbers of photons. It is possible that the field dependent emission will appear at multiples of the frequency of the driving laser. One of the main tasks of the thesis will be to study this process.

The above formulas can only be expected to be valid for small field strengths. I have seen that multiple wall collisions introduce a non-quadratic behavior in the photoexcitation energy gain. A similar effect is to be expected in multiharmonic generation. For example, for a two collision event, the Fourier transform is

$$\vec{p}\,(\omega) = \frac{e}{c}\vec{A}\,(\omega) + \int_{-\infty}^{t_0} \frac{dt}{2\pi} \left[ \vec{p}_- - \frac{e}{c}\vec{A}\,(t_0) \right] \exp(i\,\omega t\,)$$

$$+ \int_{t_0}^{t_1} \frac{dt}{2\pi} \left[ \vec{p}_+ - \frac{e}{c}\vec{A}\,(t_0) \right] \exp(i\,\omega t\,)$$

$$+ \int_{t_1}^{\infty} \frac{dt}{2\pi} \left[ \vec{p}_+' - \frac{e}{c}\vec{A}\,(t_1) \right] \exp(i\,\omega t\,) \qquad (.2.38)$$

where $t_0$ and $t_1$ are the collision times. Thus

$$\vec{p}\,(\omega) = \frac{e}{c}\vec{A}\,(\omega) + \frac{1}{2\pi i\,\omega} \left[ \vec{p}_- - \frac{e}{c}\vec{A}\,(t_0) \right] \exp(i\,\omega t_0)$$

$$+ \frac{1}{2\pi i\,\omega} \left[ \exp(i\,\omega t_1) - \exp(i\,\omega t_0) \right] \left[ \vec{p}_+ - \frac{e}{c}\vec{A}\,(t_0) \right]$$

$$- \frac{1}{2\pi i\,\omega} \exp(i\,\omega t_1) \left[ p_+' - \frac{e}{c}\vec{A}\,(t_1) \right] \qquad (.2.39)$$

This leads to a power spectrum, when averaged over $t_0$, which is

$$|\,\vec{p}\,(\omega)\,|^2 = \frac{e^2}{c^2}\,|\,\vec{A}\,(\omega)\,|^2 +$$

$$\frac{1}{4\pi^2\omega^2}\,|\,\vec{p}_- - \frac{e}{c}\vec{A}\,(t_0) + \left[ \exp(i\,\omega(t_1 - t_0)) - 1 \right] \left[ \vec{p}_+ - \frac{e}{c}\vec{A}\,(t_0) \right] -$$

$$\left[ \vec{p}_+' - \frac{e}{c}\vec{A}\,(t_1) \right] \exp(i\,\omega(t_1 - t_0))\,|^2 \qquad (.2.40)$$

This formula may readily be extended to higher order multiple collisions.

## 2.2.b Results

The program POWER.FOR calculates the power spectrum $<|\vec{p}(\omega)|^2>$ averaged over a series of collisions with different initial phases , $\phi$ . It is an adaptation of the previously developed program CLASSIC.FOR and uses it to calculate the collision times and the values of the momenta before and after the collisions.

Results are presented in Fig. 2.3 for the case in which $\omega$=0.2, $E_z$ =0.1, $\Delta t$ =.1 and $n$ =100. The graph shows the power spectrum $<|\vec{p}(\omega')|^2>$ plotted as a function of $\omega'$ for several values of $x = eA_0 / (mc\,\omega)$. I see that for $x$ =0.5, where I am still in the one collision regime, the power spectrum falls off monotonically with increasing frequency, $\omega'$. As $x$ is increased the power spectrum increases in magnitude and a shoulder appears at larger values of $\omega'$. Thus more intensity is thrown into the higher frequency radiation. This may be seen more clearly in Fig. 2.4 where the power spectrum of the acceleration is plotted for three values of $x$ .

In Fig. 2.5 I display an example of a multiple wall collision. The parameters are $x$ =5, $\omega$=.2,$E_z$ =.1 and $\Delta t$ =0.1. The trajectory was started at $z = 1^-$ and allowed to propagate sufficiently far from the surface so no further collisions could occur.

# 3. PERTURBATION THEORY

## 3.1 GENERAL THEORY

In this chapter I will develop the perturbation theory for the interaction of electromagnetic radiation with a solid. Particular attention will be directed towards metals and these will be treated within the framework of the Sommerfeld model. The dipole approximation for the electromagnetic wave will be made since the wave length of light is long compared to other relevant length scales of the problem, such as the inverse Fermi wave vector or the distance over which the bulk potential relaxes to the vacuum level near the surface.

The one electron Hamiltonian in the solid in the presence of the electromagnetic field is

$$H = \frac{1}{2m}\left[\vec{p} + \frac{e}{c}\vec{A}(t)\right]^2 + V(z) \tag{3.1}$$

My goal is to solve the time dependent Schrodinger equation

$$H\,\psi(\vec{r},t) = i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} \tag{3.2}$$

Henceforth I will use atomic units( $\hbar = e = m = 1$ ). I will be interested in the case where the electromagnetic field consists of two parts: a strong driving field $\vec{A}_1(t)$ maintained, for example, by an incident laser, and a radiation field $\vec{A}_2$. The latter is responsible for reradiating electromagnetic energy. Thus,

$$\vec{A} = \vec{A}_1 + \vec{A}_2 \tag{3.3}$$

If I separate out the transverse coordinates $\vec{r}_{\parallel}$ I may write the wave function as

$$\psi(\vec{r},t) = \exp\left[ i\,(\vec{k}_{\parallel}\cdot\vec{r}_{\parallel} - \chi(t)) \right] \phi(z,t) \tag{3.4}$$

Here $\chi(t)$ is chosen to simplify the form of the resulting Schrodinger equation.

$$\chi(t) = \int dt \left[ \frac{1}{2}(\vec{k}_{\parallel} + \frac{\vec{A}_{1\parallel}}{c} + \frac{\vec{A}_{2\parallel}}{c})^2 + \frac{1}{2c^2}(A_{1z}^2 + A_{2z}^2) \right] \tag{3.5}$$

So I find

$$\left\{ \frac{1}{2} p_z^{\,2} + \frac{1}{c} A_{1z}\, p_z + \frac{1}{c} A_{2z}\,(p_z + \frac{A_{1z}}{c}) + V(z) - i\frac{\partial}{\partial t} \right\} \phi(z,t) = 0 \tag{3.6}$$

In this equation I see that the z - component of the radiation field is coupled to the velocity of the electron.

Another useful representation is obtained by letting

$$\psi(\vec{r},t) = \exp\left[ i\,(\vec{k}_{\parallel}\cdot\vec{r}_{\parallel} - \chi(t) - \frac{1}{c} z A_{2z}) \right] \phi'(z,t) \tag{3.7}$$

where

$$\chi(t) = \int dt \left[ \frac{1}{2}(\vec{k}_{\parallel} + \frac{\vec{A}_{1\parallel}}{c} + \frac{\vec{A}_{2\parallel}}{c})^2 + \frac{A_{1z}^2}{2c^2} \right] \tag{3.8}$$

in which case

$$\left\{ \frac{1}{2} p_z^{\,2} + \frac{1}{c} A_{1z}\, p_z + z E_{2z} + V(z) - i\frac{\partial}{\partial t} \right\} \phi'(z,t) = 0 \tag{3.9}$$

Here the dipole moment of the electron is coupled to the electric field of the radiation.

$$\vec{E}_2 = -\frac{1}{c}\frac{\partial \vec{A}_2}{\partial t} \tag{3.10}$$

Let me expand the radiation field in terms of creation and annihilation operators

$$\vec{A}_2(\vec{r}) = \sum_{\vec{k},\lambda} \left[\frac{2\pi c}{k}\right]^{1/2} \hat{e}_{\vec{k},\lambda} \left[a_{\vec{k},\lambda}\exp(i\vec{k}\cdot\vec{r})+a^{+}_{\vec{k},\lambda}\exp(-i\vec{k}\cdot\vec{r})\right] \quad (3.11)$$

where $\lambda$ is a polarization index taking on two possible values, $\hat{e}_{\vec{k},\lambda}$ is the polarization vector, obeying the condition

$$\hat{e}_{\vec{k},\lambda}\cdot\vec{k} = 0 \quad (3.12)$$

and $a_{\vec{k},\lambda}$ is the annihilation operator for mode $\vec{k},\lambda$ and $a^{+}_{\vec{k},\lambda}$ is the corresponding creation operator. In the dipole approximation the exponentials are replaced by 1. If I select a particular mode, then

$$A_{2z} = \left[\frac{2\pi c^2}{\omega'}\right]^{1/2} \hat{z}\cdot\hat{e}'\left[a'+a'^{+}\right] \quad (3.13)$$

Similarly the electric field is given by

$$E_{2z} = i\,(2\pi\omega')^{1/2}\hat{z}\cdot\hat{e}'\left[a'-a'^{+}\right] \quad (3.14)$$

## 3.2 MULTIHARMONIC GENERATION

### 3.2.1 Theory

In developing a perturbation expansion for multiharmonic generation (MHG) I note that for n-harmonic generation, I am dealing with a closed Feynman loop with $n$ absorption vertices and one emission vertex. The intermediate states involve, in general, both electrons and holes. It is possible, however, to write the matrix elements so that all intermediate states are included without the need for Fermi factors. This is illustrated explicitly for the case of second-harmonic generation in appendix A. Since there are $n+1$ possible time orderings for the emission and absorption I have $n+1$ independent graphs. I illustrate the case $n=4$ in order to elucidate the general structure of the matrix element. The Feynman diagrams are illustrated in Fig. 3.1. The matrix element is

$$M^{(4)} = \sum_q \left[\frac{A_0\hat{e}_z}{2c}\right]^4 \left[\frac{2\pi}{\omega'}\right]^{1/2} \hat{e}_z \cdot \left[M_1+M_2+M_3+M_4+M_5\right] f_q^{(-)} \tag{3.15}$$

where

$$M_1 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(4\omega+\epsilon_q-\epsilon_p)(3\omega+\epsilon_q-\epsilon_n)(2\omega+\epsilon_q-\epsilon_m)(\omega+\epsilon_q-\epsilon_l)} \tag{3.16}$$

$$M_2 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\epsilon_q-\epsilon_p)(3\omega+\epsilon_q-\epsilon_n)(2\omega+\epsilon_q-\epsilon_m)(\omega+\epsilon_q-\epsilon_l)} \tag{3.17}$$

$$M_3 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\epsilon_q-\epsilon_p)(-2\omega+\epsilon_q-\epsilon_n)(2\omega+\epsilon_q-\epsilon_m)(\omega+\epsilon_q-\epsilon_l)} \tag{3.18}$$

$$M_4 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\epsilon_q-\epsilon_p)(-2\omega+\epsilon_q-\epsilon_n)(-3\omega+\epsilon_q-\epsilon_m)(\omega+\epsilon_q-\epsilon_l)} \tag{3.19}$$

$$M_5 = \sum_{l,m,n,p} \frac{\langle q|p_z|p\rangle\langle p|p_z|n\rangle\langle n|p_z|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(-\omega+\epsilon_q-\epsilon_p)(-2\omega+\epsilon_q-\epsilon_n)(-3\omega+\epsilon_q-\epsilon_m)(-4\omega+\epsilon_q-\epsilon_l)} \tag{3.19}$$

I introduce a set of perturbed states defined as follows

$$|u_+^{(1)}\rangle \equiv \sum_l \frac{|l\rangle\langle l|p_z|q\rangle}{\omega+\epsilon_q-\epsilon_l} \tag{3.20}$$

$$|u_+^{(2)}\rangle \equiv \sum_{l,m} \frac{|m\rangle\langle m|p_z|l\rangle\langle l|p_z|q\rangle}{(2\omega+\epsilon_q-\epsilon_m)(\omega+\epsilon_q-\epsilon_l)} =$$

$$\sum_l \frac{|l\rangle\langle l|p_z|u_+^{(1)}\rangle}{2\omega+\epsilon_q-\epsilon_l} \tag{3.21}$$

$$|u_+^{(n)}> \equiv \sum_l \frac{|l><l|p_z|u_+^{(n-1)}>}{n\,\omega+\epsilon_q-\epsilon_l} \tag{.3.22}$$

Similarly

$$|u_-^{(1)}> \equiv \sum_l \frac{|l><l|p_z|q>}{-\omega+\epsilon_q-\epsilon_l} \tag{3.23}$$

$$|u_-^{(n)}> \equiv \sum_l \frac{|l><l|p_z|u_-^{(n-1)}>}{-n\,\omega+\epsilon_q-\epsilon_l} \tag{3.24}$$

It is convenient to define

$$|u_+^0> = |u_-^0> = |q> \tag{.3.25}$$

so that for $n \geqslant 1$

$$|u_\pm^{(n)}> = \sum_m \frac{|m><m|p_z|u_\pm^{(n-1)}>}{\pm n\,\omega+\epsilon_q-\epsilon_m} \tag{.3.26}$$

In terms of the perturbed states I may write the individual matrix elements as

$$M_1 = <u_-^{(0)}|p_z|u_+^{(4)}> \tag{.3.27}$$

$$M_2 = <u_-^{(1)}|p_z|u_+^{(3)}> \tag{3.28}$$

$$M_3 = <u_-^{(2)}|p_z|u_+^{(2)}> \tag{.3.29}$$

$$M_4 = <u_-^{(3)}|p_z|u_+^{(1)}> \tag{.3.30}$$

$$M_5 = <u_-^{(4)}|p_z|u_+^{(0)}> \tag{3.31}$$

The unperturbed states satisfy the inhomogeneous differential equations

$$\left[\pm j\,\omega+\epsilon_q-H_o\right]|u_{\pm}^{(j)}>=p_z\;|u_{\pm}^{(j-1)}> \tag{3.32}$$

where j=1,2,3 etc. From the above example it is clear that for $n^{th}$ order multi-harmonic generation

$$M^{(n)}=\left[\frac{A_o}{2c}\hat{e}_z\right]^n\left[\frac{2\pi}{\omega'}\right]^{1/2}\hat{e}_z\,{}'\sum_{q,s}f_q^{(-)}\sum_{j=0}^{n}<u_{-}^{(j)}\;|p_z\;|u_{+}^{(n-j)}> \tag{3.33}$$

where $\omega'=n\,\omega$ . The notation has been expanded to include spin states.

### 3.2.2 Application to the hard wall potential

Having obtained a general formula for multiharmonic generation based on the lowest order perturbation theory, let me now apply it to the case of a simple problem. I consider the case of the hard wall potential. Let the solid be represented by a potential

$$V(z)=\infty \qquad \text{if } z<0$$

$$V(z)=0 \qquad \text{if } z>0 \tag{3.34}$$

The solution to the unperturbed Schrodinger equation

$$\left[H_o-\epsilon\right]|q>=0,$$

where $H_o=p_z^2/2$, is given by

$$<z\;|q>=N\left[exp(-iqz)-exp(iqz)\right]$$

$$=-2iN\,\sin qz \tag{3.35}$$

where N is a normalization factor $N=1/(2L)^{1/2}$, L being the thickness of the solid, and $q=(2\epsilon)^{1/2}$

In solving the perturbed wave equation I will have both a homogeneous solution and an inhomogeneous solution. I choose the homogeneous solution to correspond to an outgoing wave or an evanescent wave, depending on whether its energy is positive or negative. The amplitude of the wave is chosen so that the boundary condition

$$u_{\pm}^{(j)} = 0 \tag{3.36}$$

is obeyed. Let me define

$$q_j = (2(\epsilon + j\omega))^{1/2} \quad \text{if } \epsilon + j\omega > 0$$

$$= i(-2(\epsilon + j\omega))^{1/2} \quad \text{if } \epsilon + j\omega < 0 \tag{3.37}$$

Then I find

$$u_{+}^{(1)} = -\frac{2qN}{\omega}\left[\cos qz - \exp(iq_1 z)\right] \tag{3.38}$$

$$u_{-}^{(1)} = -\frac{2qN}{\omega}\left[\cos qz - \exp(iq_{-1} z)\right] \tag{3.39}$$

$$u_{+}^{(2)} = -\frac{iNq^2}{\omega^2}\sin qz + 2q\frac{q_1}{\omega^2}\left[\exp(iq_1 z) - \exp(iq_2 z)\right]N \tag{3.40}$$

$$u_{-}^{(2)} = -\frac{iNq^2}{\omega^2}\sin qz + \frac{2qq_{-1}}{\omega^2}\left[\exp(iq_{-1} z) - \exp(iq_{-2} z)\right]N \tag{3.41}$$

The individual matrix elements are

$$\langle u_{-}^{(0)} | p_z | u_{+}^{(2)} \rangle = -\frac{iq^2}{2\omega^2}\left[1 + \frac{4q_1^2}{\omega} - \frac{2q_1 q_2}{\omega}\right]N^2 \tag{3.42}$$

$$\langle u_-^{(1)} | p_z | u_+^{(1)} \rangle = -\frac{iq^2}{\omega^2}\left[1-\frac{q_1^2}{\omega}+\frac{q_1q_{-1}}{\omega}-\frac{2q^2}{\omega}\right]N^2 \qquad (.3.43)$$

$$\langle u_-^{(2)} | p_z | u_+^{(0)} \rangle = -\frac{iq^2}{2\omega^2}\left[1+\frac{4q_{-1}^2}{\omega}-\frac{2q_{-1}q_{-2}}{\omega}\right]N^2 \qquad (.3.44)$$

Thus the matrix element for second harmonic generation is

$$M^{(2)} = \left[\frac{A_o}{2c}\hat{e}_z\right]^2\left[\frac{2\pi}{2\omega}\right]^{1/2}\hat{e}_z{}'\sum_q\frac{iq^2}{\omega^3}\left[q_1q_2+q_{-1}q_{-2}-q^2-q_1q_{-1}\right]f_q^{(-)}N^2 \qquad (.3.45)$$

It is also useful to have the matrix element for first harmonic generation. The individual matrix elements are

$$\langle u_-^{(0)} | p_z | u_+^{(1)} \rangle = \left[-2\frac{q^2}{\omega}L+\frac{2iq_{-1}q^2}{\omega^2}\right]N^2 \qquad (.3.46)$$

$$\langle u_-^{(1)} | p_z | u_+^{(0)} \rangle = \left[\frac{2q^2}{\omega}L-\frac{2iq_{+1}q^2}{\omega^2}\right]N^2 \qquad (.3.47)$$

where L is a cutoff length. It cancels out of the final result. Thus the matrix element is

$$M^{(1)} = \left[\frac{A_o}{2c}\hat{e}_z\right]\left[\frac{2\pi}{\omega}\right]^{1/2}\hat{e}_z{}'\sum_q\frac{2iq^2}{\omega^2}\left[q_{-1}-q_{+1}\right]f_q^{(-)}N^2 \qquad (.3.48)$$

Let me now derive the general expression for the matrix element. Let

$$u^{(n)} = N\left\{\sum_{j=1}^{n^*}B_j^n\exp(iq_j z)+d_n\left[\exp(-iqz)-(-1)^n\exp(iqz)\right]\right\}N \qquad (.3.49)$$

Here I suppress the index + or - . When the + index is to be used I use + $\omega$ , when the negative index is to be used I use - $\omega$ . The coefficients $B_j^n$ and $d_n$ are determined by inserting this into the inhomogeneous differential equation

$$(n\omega+\epsilon-H_o)u^{(n)} = p_z u^{(n-1)} \tag{3.50}$$

Thus

$$\sum_{j=1}^{n}\left(n\omega+\frac{q^2}{2}-\frac{q_j^2}{2}\right)B_j^n\exp(iq_j z)+n\omega d_n\left[\exp(-iqz)-(-1)^n exp(iqz)\right]$$

$$=\sum_{j=1}^{n-1}B_j^{n-1}q_j\, exp(iq_j z)+d_{n-1}\left[-qexp(-iqz)+(-1)^n q\exp(iqz)\right] \tag{3.51}$$

I obtain the following recursion relations

$$B_j^n = B_j^{n-1}\frac{q_j}{\omega}\frac{1}{n-j} \tag{3.52}$$

where $1 \leqslant j \leqslant n$ and

$$d_n = -\frac{q}{n\omega}d_{n-1} \tag{3.53}$$

In order for $u^{(0)}$ to be equal to the unperturbed state,

$$d_0=1 \tag{3.54}$$

Note that if $n = j+1$

$$B_j^{j+1} = B_j^j\frac{q_j}{\omega} \tag{3.55}$$

By iterating the recurrence formula I obtain

$$B_n^j = B_j\left(\frac{q_j}{\omega}\right)^{n-j}\frac{1}{(n-j)!} \qquad \text{for } j \leqslant n \tag{3.56}$$

where I have defined

$$B_j = B_j^j \tag{3.57}$$

Similarly

$$d_n = \frac{(-1)^n}{n!}(\frac{q}{\omega})^n \quad (3.58)$$

The unknown constants $B_j$ are determined by the boundary condition

$$u^{(j)}(0)=0 \quad (3.59)$$

which leads to

$$\sum_{j=1}^{n} B_j^n + d_n [1-(-1)^n] = 0 \quad (3.60)$$

Let me rewrite this as a matrix equation. I define a triangular matrix

$$S_{nj} = (\frac{q_j}{\omega})^{n-j} \frac{1}{(n-j)!} \quad \text{if } 1 \leqslant j \leqslant n$$

$$= 0 \qquad \textit{otherwise} \quad (3.61)$$

and a column vector

$$T_n = [(-1)^n - 1]\frac{1}{n!}(\frac{q}{\omega})^n \quad (3.62)$$

Then the equation for $B_j$ becomes

$$S \cdot B = -T \quad (3.63)$$

The solution to this may be obtained by using a theorem proved in appendix C.

$$B_j = \frac{\det N_j}{\prod_{l=1}^{j} S_{ll}} \quad (3.64)$$

where

$$N_j = \begin{vmatrix} S_{11} & 0 & 0 & .. & -T_1 \\ S_{21} & S_{22} & 0 & .. & -T_2 \\ .. & .. & .. & .. & .. \\ S_{j1} & S_{j2} & S_{j3} & .. & -T_j \end{vmatrix} \tag{3.65}$$

The wave functions are

$$u_+^{(n)} = N\left\{\sum_{j=1}^{n} B_{j(+)}^{n} \exp(iq_j z) + d_{n(+)}\left[\exp(-iqz) - (-1)^n \exp(iqz)\right]\right\} \tag{3.66}$$

$$u_-^{(n)} = N\left\{\sum_{j=1}^{n} B_{j(-)}^{n} \exp(iq_{-j} z) + d_{n(-)}\left[\exp(-iqz) - (-1)^n \exp(iqz)\right]\right\} \tag{3.67}$$

The matrix element contribution is

$$\langle u_-^{(l)} \mid p_z \mid u_+^{(n-l)} \rangle = N^2 \sum_{k=1}^{l} \sum_{j=1}^{n-l} \frac{B_{j(+)}^{n-l} q_j B_{k(-)}^{l*}}{i(q_{-k}^{*} - q_j)}$$

$$+ iN^2 \sum_{j=1}^{n-l} B_{j(+)}^{n-l} q_j d_{l(-)}^{*} \left[\frac{1}{q+q_j} - \frac{(-1)^l}{q_j - q}\right]$$

$$+ iqN^2 \sum_{k=1}^{l} B_{k(-)}^{l*} d_{n-l}(+) \left[\frac{1}{q+q_{-k}^{*}} + \frac{(-1)^{n-l}}{q_{-k}^{*} - q}\right]$$

$$+ N^2 \frac{1}{2i}(-1)^l \left[1+(-1)^n\right] d_{l(-)}^{*} d_{n-l(+)} - qL\left[1-(-1)^n\right] d_{l(-)}^{*} d_{n-l(+)} \tag{3.68}$$

where L is a cutoff distance. When summed over $l$, it gives zero since

$$\sum_{l=0}^{n} d_{l(-)}^{*} d_{n-l(+)} = \frac{(-1)^n}{n!} \sum_{l=0}^{n} \binom{n}{l} \left(\frac{q}{\omega}\right)^{n-l} \left(\frac{-q}{\omega}\right)^{l} = 0 \tag{3.69}$$

Similarly

$$\sum_{l=0}^{n} d_{l(-)}^{*} d_{n-l(+)} (-1)^l = \frac{(-1)^n}{n!} \left(\frac{2q}{\omega}\right)^n \tag{3.70}$$

Thus the general expression for matrix element is

$$M^{(n)} = \left(\frac{A_o}{2c}\hat{e}_z\right)^n \left[\frac{2\pi}{n\,\omega}\right]^{1/2} \hat{e}_z{}' \sum_q f_q{}^{(-)} N\, 2[$$

$$+i \sum_{l=0}^{n} \sum_{k=1}^{l} \sum_{j=1}^{n-l} \frac{q_j\, B_{j(+)}^{n-l} B_{k(-)}^{l}}{q_j - q_{-k}}$$

$$+i \sum_{l=0}^{n} \sum_{j=1}^{n-l} q_j\, d_{l(-)}^{\,'} B_{j(+)}^{n-l} \left[\frac{1}{q+q_j} + \frac{(-1)^l}{q-q_j}\right]$$

$$+iq \sum_{l=0}^{n} \sum_{k=1}^{n} B_{k(-)}^{l} d_{n-l(+)} \left[\frac{1}{q+q_{-k}} - \frac{(-1)^{n-l}}{q-q_{-k}}\right]$$

$$+\frac{1}{2i}[1+(-1)^n]\frac{(-1)^n}{n!}\left(\frac{2q}{\omega}\right)^n ] \qquad (.3.71)$$

The evaluation of the general matrix element has been reduced to elementary algebraic calculations.

## 3.3 MULTIPHOTON EXCITATION

### 3.3.1 Theory

Multiphoton photoexcitation of a solid is the process in which n photons are absorbed and the electronic energy is elevated by $n\hbar\omega$. If the electronic energy is high enough to overcome the work function then photoemission can occur. I will refer to this latter process as multiphoton electron emission. The process results in a hole being created in some state $|q>$ and the electron transferring to some excited state $|f>$. Diagrams for the first,second and third order processes are shown in Figs 3.2,3.3 and 3.4. These diagrams show electrons and/or holes in the intermediate states.

The matrix element for the first order process is

$$M^{(1)} = \frac{A_o \hat{e}_z}{2c} < f \mid p_z \mid q >$$

$$= \frac{A_o \hat{e}_z}{2c} < f \mid p_z \mid u_+^{(0)} > \qquad (.3.72)$$

For the second order process it is

$$M^{(2)} = \left(\frac{A_o \hat{e}_z}{2c}\right)^2 \sum_m \frac{< f \mid p_z \mid m >< m \mid p_z \mid q >}{\omega + \epsilon_q - \epsilon_m}$$

$$= \left(\frac{A_o \hat{e}_z}{2c}\right)^2 < f \mid p_z \mid u_+^{(1)} > \qquad (3.72)$$

For the third order process it is

$$M^{(3)} = \left(\frac{A_o \hat{e}_z}{2c}\right)^3 \sum_{mn} \frac{<f \mid p_z \mid m><m \mid p_z \mid n><n \mid p_z \mid q>}{(2\omega+\epsilon_q-\epsilon_m)(\omega+\epsilon_q-\epsilon_n)}$$

$$= \left(\frac{A_o \hat{e}_z}{2c}\right)^3 <f \mid p_z \mid u_+^{(2)}> \qquad (3.73)$$

In deriving these concise formulas I have shown that the diagrams involving intermediate electrons and holes may be replaced by a single diagram in which all intermediate states are included. Details are given in Appendix B.

The $n^{th}$ order process results in the matrix element.

$$\overline{M}^{(n)} = \left(\frac{A_o \hat{e}_z}{2c}\right)^n <f \mid p_z \mid u_+^{(n-1)}> (2\pi)^2 \delta(\vec{q}_{\parallel}' - \vec{q}_{\parallel}) \qquad (3.74)$$

Here I have included the integration over transverse momentum states. The transition rate is obtained from the Fermi Golden Rule.

$$\Gamma^{(n)} = 2\pi \sum_s \sum_{f\,q} \mid \overline{M}^{(n)} \mid^2 \delta(\epsilon_q + n\,\omega - \epsilon_f)\, f_q^{(-)} f_f^{(+)} \qquad (3.75)$$

Here $s$ denotes the electron spin projection. Since multiphoton excitation preserves spin projection there is only a single spin common to both the initial and final state. In the delta function $\epsilon_q$ and $\epsilon_f$ should actually refer to the total energy including the kinetic energy associated with motion parallel to the surface, $q_{\parallel}^2/2$ and $q_{\parallel}'^2/2$. However, since $\vec{q}_{\parallel} = \vec{q}_{\parallel}'$ this transverse kinetic energy cancels out and I may take $\epsilon_q$ and $\epsilon_f$ as the kinetic energy associated with z-motion.

### 3.3.2 Application to the wall collision model

In the wall collision model the $n-1^{st}$ order perturbed state is

$$u_+^{(n-1)} = N\left\{\sum_{j=1}^{n-1} B_j^{n-1} exp\,(iq_j z) + d_{n-1}\left[exp\,(-iqz) + (-)^n\, exp\,(iqz)\right]\right\} \tag{3.76}$$

where

$$N = \frac{1}{(2L)^{1/2}} \tag{3.77}$$

The final state is

$$< z \mid f > = -2iN \sin q_n z \tag{3.78}$$

The matrix element is evaluated to be

$$M^{(n)} = (\frac{A_o \hat{e}_z}{2c})^n \frac{iN^2}{\omega}\left\{\sum_{j=1}^{n-1} B_j^{n-1}\frac{q_j q_n}{n-j} - q\frac{q_n}{n} d_{n-1}\left[1-(-)^n\right]\right\} \tag{3.79}$$

For the lowest two orders these are

$$M^{(1)} = -2iN^2 \frac{qq_1}{\omega} A_o \frac{\hat{e}_z}{2c} \tag{3.80}$$

and

$$M^{(2)} = 2iN^2 qq_1 \frac{q_2}{\omega^2}(\frac{A_o \hat{e}_z}{2c})^2 \tag{3.81}$$

The sum over final states may be computed as follows. First, the integral over transverse final momenta cancels the $(2\pi)^2\delta(\vec{q}_{\parallel}-\vec{q}_{\parallel}')^2$ factor. So

$$\Gamma^{(n)} = \sum_s \sum_q \int_0^\infty \frac{dq_z'}{2\pi} \mid M^{(n)} \mid^2 \delta(\frac{q_z^2}{2} + n\,\omega - \frac{q_z'^2}{2})$$

$$\Theta(\epsilon_f - \frac{q_z^2}{2} - \frac{q_{\parallel}^2}{2})\Theta(-\epsilon_f + \frac{q_z^2}{2} + \frac{q_{\parallel}^2}{2} + n\,\omega) \tag{3.82}$$

Performing the integration over $q_z'$ gives

$$\Gamma^{(n)} = \sum_s \sum_{\vec{q}} \frac{|M^{(n)}|^2}{q_n} \Theta(\epsilon_f - \frac{q_z^2}{2} - \frac{q_\parallel^2}{2}) \Theta(-\epsilon_f + \frac{q_n^2}{2} + \frac{q_\parallel^2}{2}) \tag{3.83}$$

The sum over transverse momenta leads to

$$\sum_{\vec{q}_\parallel} \Theta(\epsilon_f - \frac{q_z^2}{2} - \frac{q_\parallel^2}{2}) \Theta(-\epsilon_f + \frac{q_n^2}{2} + \frac{q_\parallel^2}{2}) =$$

$$\frac{1}{4\pi} \Theta(q_f - q_z) \left[ 2n\,\omega \Theta(q_f - q_n) + (q_f^2 - q_z^2) \Theta(q_n - q_f) \right] \tag{3.84}$$

so

$$\Gamma^{(n)} = \frac{1}{4\pi^2} \int_0^{q_f} d\frac{q_z}{q_n} |M^{(n)}|^2 \left[ 2n\,\omega \Theta(q_f - q_n) + (q_f^2 - q_z^2) \Theta(q_n - q_f) \right] \tag{3.85}$$

# 4. THE SHARP STEP POTENTIAL

## 4.1 PERTURBATION THEORY

Let me consider the case of a sharp step potential. The form of the potential energy is

$$V(z) = -V_0 \qquad \text{if } z < 0$$

$$V(z) = 0 \qquad \text{if } z > 0 \tag{.4.1}$$

Here $V_0$ is the depth of the inner core potential. It is related to the work function $\phi$ ,and the Fermi energy, $\epsilon_f$ by

$$V_0 = \epsilon_f + \phi \tag{.4.2}$$

The solution to the unperturbed Schrodinger equation

$$\left[\frac{p_z^{\,2}}{2} + V(z) - \epsilon\right] | q \rangle = 0 \tag{.4.3}$$

is given by

$$u^{(0)} = \exp(ik_z z) + r \exp(-ik_z z) \qquad \text{for } z < 0$$

$$u^{(0)} = (1+r)\exp(-q_z z) \qquad \text{for } z > 0 \tag{.4.4}$$

where $k_z$ is the z component of the wave vector in the solid.

$$k = [2(\epsilon + V_0)]^{1/2} \tag{.4.5}$$

$$\gamma = (-2\epsilon)^{1/2} \tag{.4.6}$$

The reflection coefficient is determined by matching the derivative of the wave function at $z=0$

$$r = \frac{ik_z + q_z}{ik_z - q_z} \tag{4.7}$$

I have let $\epsilon$ represent the net energy associated with the z-motion ( $\epsilon = \epsilon_q - \frac{k_{\parallel}^2}{2}$).

The perturbed wave function satisfies the differential equation

$$\left[\pm n\,\omega + \epsilon + \frac{1}{2}\frac{d^2}{dz^2} - V(z)\right] u_{\pm}^{(n)}(z) = p_z\, u_{\pm}^{(n-1)}(z) \tag{4.8}$$

As before, the solution will consist of a homogeneous and inhomogeneous part. The homogeneous solution is chosen to correspond to either a wave propagating away from the surface or an evanescent wave decaying away from the surface. This applies both to the vacuum region ( $z > 0$ ) as well as the solid itself ($z < 0$ ). For example, let me look at the $n=1$ case:

$$\left[\omega + \epsilon + \frac{1}{2}\frac{d^2}{dz^2} - V(z)\right] u^{(1)} = p_z\, u^{(0)} \tag{4.9}$$

so

$$(\omega + \epsilon + \frac{1}{2}\frac{d^2}{dz^2} + V_0) u^{(1)} = k \exp(ikz) - rk\exp(-ikz) \qquad \text{for } z < 0 \tag{4.10}$$

$$(\omega + \epsilon + \frac{1}{2}\frac{d^2}{dz^2}) u^{(1)} = i\,\gamma(1+r)\exp(-\gamma z) \qquad \text{for } z > 0 \tag{4.11}$$

Let me define $k_j$ and $\gamma_j$ as;

$$k_j = \left[2(j\,\omega + \epsilon + V_0)\right]^{1/2} \tag{4.12}$$

$$\gamma_j = \left[-2(j\,\omega+\epsilon)\right]^{1/2} \tag{4.13}$$

If $\epsilon + j\,\omega < 0$ then $\gamma_j$ is the useful real parameter representing the attenuation constant for an electron that has absorbed $j$ photons but still decays into the vacuum. However, if $\epsilon + j\,\omega > 0$ then I let

$$\gamma_j = -iq_j \tag{4.14}$$

where

$$q_j = \left[2(\epsilon + j\,\omega)\right]^{1/2} \tag{4.15}$$

This is the propagation vector in vacuum. Thus, for $z > 0$

$$u^{(1)} = A_1 \exp iq_1 z + \frac{i\gamma(1+r)}{\omega} \exp(-\gamma z) \tag{4.16}$$

and for $z < 0$

$$u^{(1)} = B_1 \exp(-\text{[illegible]}) \frac{k}{\omega} \left[\exp(ikz) - r\exp(-ikz)\right] \tag{4.17}$$

These expressions are written as if $\epsilon+\omega > 0$. The constants $A_1$ and $B_1$ are determined by matching the wave function and its derivative at $z = 0$. I obtain

$$A_1 = -\frac{2ik}{\omega}\left[\frac{\gamma+ik}{q+k_1}\right] \tag{4.18}$$

and

$$B_1 = -\frac{2ik}{\omega}\left[\frac{\gamma+ik}{q+k_1}\right] \tag{4.19}$$

For $n = 2$, the inhomogeneous differential equations are

$$\left[2\omega+\epsilon+\frac{1}{2}\frac{d^2}{dz^2}\right]u^{(2)} = -i\frac{du^{(1)}}{dz} \quad \text{for } z>0 \tag{4.20}$$

$$\left[2\omega+\epsilon+V_0+\frac{1}{2}\frac{d^2}{dz^2}\right]u^{(2)} = -i\frac{du^{(1)}}{dz} \quad \text{for } z<0 \tag{4.21}$$

Inserting the values of $u^{(1)}$ found before I get

$$u^{(2)} = A_2 exp\,(iq_2 z)+\frac{q_1}{\omega}A_1 exp\,(iq_1 z)-\frac{\gamma^2}{2\omega^2}(1+r)exp\,(-\gamma z) \quad \text{for } z>0 \tag{4.22}$$

$$u^{(2)} = B_2 exp\,(-ik_2 z)-\frac{k_1}{\omega}B_1 exp\,(-ik_1 z)+\frac{k^2}{2\omega^2}\left[exp\,(ik_z z)+r exp\,(-ik_z z)\right] \quad \text{for } z<0 \tag{4.23}$$

The constants $A_2$ and $B_2$ are again obtained by matching the wave function and its derivative at $z=0$.

From an examination of the n=1 and n=2 cases I can conjecture the form of the perturbed wave function for arbitrary n. I then verify that it indeed is the solution by inserting it into the inhomogeneous differential equation. Thus

$$u^{(n)} = \sum_{j=1}^{n} A_j^{(n)} \exp(iq_j z)+c_n \exp(-\gamma z) \quad \text{for } z>0 \tag{4.24}$$

and

$$u^{(n)} = \sum_{j=1}^{n} B_j^{(n)} exp\,(-ik_j z)+d_n \left[exp\,(ikz)+(-)^n r \exp(-ikz)\right] \quad \text{for } z<0 \tag{4.25}$$

For $z>0$ the inhomogeneous differential equation becomes

$$n\,\omega c_n\, exp\,(-\gamma z)+\sum_{j=1}^{n} A_j^{(n)}\left[\frac{q_n^2}{2}-\frac{q_j^2}{2}\right]\exp(iq_j z)$$

$$=i\gamma c_{n-1}exp(-\gamma z)+\sum_{j=1}^{n-1}A_j^{(n-1)}q_j\,exp(iq_j z) \tag{4.26}$$

From which it follows that

$$c_n=i\frac{\gamma}{n\,\omega}c_{n-1} \tag{4.27}$$

and

$$A_j^{(n)}\omega(n-j)=q_j A_j^{(n-1)} \tag{4.28}$$

The value of $c_0$ is fixed by the condition that $u^{(0)}$ should equal the unperturbed wave function

$$c_0=1+r \tag{4.29}$$

Similarly, for $z<0$

$$n\,\omega d_n\left[exp(ikz)+(-)^n r\,exp(-ikz)\right]+\sum_{j=1}^{n}B_j^{(n)}\left[\frac{k_n^2}{2}-\frac{k_j^2}{2}\right]exp(-ik_j z)$$

$$=kd_{n-1}\left[exp(ikz)+(-)^n\exp(-ikz)\right]-\sum_{j=1}^{n-1}k_j B_j^{(n-1)}exp(-ik_j z) \tag{4.30}$$

From which it follows that

$$d_n=\frac{k}{n\,\omega}d_{n-1} \tag{4.31}$$

$$B_j^{(n)}=-\frac{k_j B_j^{(n-1)}}{\omega(n-j)} \tag{4.32}$$

The value of $d_0$ is again set by the condition that $u^{(0)}$ should equal the unperturbed wave function

$$d_0=1 \tag{4.33}$$

Iterating the above recurrence formulas leads to the following solutions

$$A_j^{(n)} = \left(\frac{q_j}{\omega}\right)^{n-j} \frac{1}{(n-j)!} A_j \tag{4.34}$$

where $A_j$ denotes $A_j^{(j)}$

$$c_n = \left(i\frac{\gamma}{\omega}\right)^n \frac{1}{n!}(1+r) \tag{4.35}$$

$$B_j(n) = \left[-\frac{k_j}{\omega}\right]^{n-j} \frac{1}{(n-j)!} B_j \tag{4.36}$$

where $B_j$ denotes $B_j^{(j)}$ and

$$d_n = \left(\frac{k}{\omega}\right)^n \frac{1}{n!} \tag{4.37}$$

The constants $A_j$ and $B_j$ are determined from matching the wave function and its derivative at $z = 0$

$$u^{(n)}{}_{z=0^+} = u^{(n)}{}_{z=0^-} \tag{4.38}$$

$$\frac{du^{(n)}}{dz}\bigg|_{z=0^+} = \frac{du^{(n)}}{dz}\bigg|_{z=0^-} \tag{4.39}$$

These two boundary conditions simplify to:

$$\sum_{j=1}^{n} \left[A_j^{(n)} - B_j^{(n)}\right] = d_n \left[1+(-)^n r\right] - c_n \tag{4.40}$$

$$\sum_{j=1}^{n} \left[q_j A_j^{(n)} + k_j B_j^{(n)}\right] = d_n k_z \left[1-(-)^n r\right] - i\gamma c_n \tag{4.41}$$

Let me define the following triangular matrices for j $\leqslant$ n

$$\rho_{nj} = \left[\frac{q_j}{\omega}\right]^{n-j} \frac{q_j}{(n-j)!} \tag{4.42}$$

$$\sigma_{nj} = \left[-\frac{k_j}{\omega}\right]^{n-j} \frac{k_j}{(n-j)!} \tag{4.43}$$

$$R_{nj} = \left[\frac{q_j}{\omega}\right]^{n-j} \frac{1}{(n-j)!} \tag{4.44}$$

$$S_{nj} = \left[-\frac{k_j}{\omega}\right]^{n-j} \frac{1}{(n-j)!} \tag{4.45}$$

For $n < j$ these are taken to vanish. I also define the vectors

$$T_n = d_n \left[1+(-)^n r\right] - c_n \tag{4.46}$$

$$F_n = d_n k \left[1-(-)^n r\right] - i \gamma c_n \tag{4.47}$$

There are now four triangular matrices ($R$, $S$, $\rho$ and $\sigma$) and four column vectors ($A$, $B$, $F$ and $T$) in the problem. In order to completely determine the perturbed wave functions I must solve the matrix equations

$$\rho A + \sigma B = F \tag{4.48}$$

and

$$RA - SB = T \tag{4.49}$$

The solution to these equations are

$$A = K^{-1} U \tag{4.50}$$

and

$$B = L^{-1}V \tag{4.51}$$

where

$$K = \rho+\sigma S^{-1}R \tag{4.52}$$

$$L = \sigma+\rho R^{-1}S \tag{4.53}$$

$$V = F-\rho R^{-1}T \tag{4.54}$$

$$U = F+\sigma S^{-1}T \tag{4.55}$$

Since the $K$ and $L$ matrices are triangular matrices with vanishing upper components I may solve the equations

$$KA = U \tag{4.56}$$

and

$$LB = V \tag{4.57}$$

directly through the use of a theorem. The theorem is proved in Appendix C. The result is

$$A_j = \frac{detM_j}{\prod_{l=1}^{j} K_{ll}} \tag{4.58}$$

where

$$M_j = \begin{vmatrix} K_{11} & 0 & .. & 0 & U_1 \\ K_{21} & K_{22} & .. & 0 & U_2 \\ K_{31} & K_{32} & .. & 0 & U_3 \\ .. & .. & .. & 0 & .. \\ K_{j-1,1} & K_{j-1,2} & .. & K_{j-1,j-1} & U_{j-1} \\ K_{j1} & K_{j2} & .. & K_{j,j-1} & U_j \end{vmatrix} \tag{4.59}$$

similarly

$$B_j = \frac{detN_j}{\prod_{l=1}^{j} L_{ll}} \tag{4.60}$$

where

$$N_j = \begin{vmatrix} L_{11} & 0 & - & 0 & V_1 \\ L_{21} & L_{22} & - & 0 & V_2 \\ L_{31} & L_{32} & - & 0 & V_3 \\ - & - & - & 0 & - \\ L_{j-1,1} & L_{j-1,2} & - & L_{j-1,j-1} & V_{j-1} \\ L_{j1} & L_{j2} & - & L_{j,j-1} & V_j \end{vmatrix} \tag{4.61}$$

## 4.2 MULTIHARMONIC GENERATION

In chapter 3 , I have developed the formula for the MHG matrix element. Here I have to evaluate it for the case of sharp step. The previous equations were developed for the case in which I was interested in $u_+^{(n)}$. For $u_-^{(n)}$ I would simply replace $\omega$ by $-\omega$ and repeat the calculation. Thus I could write, for $z > 0$ ;

$$u_-^{(n)} = \sum_{j=1}^{n} A_j^{(-n)} \exp(iq_{-j} z) + c_n^{(-)} \exp(-\gamma z) \tag{4.62}$$

For $z < 0$;

$$u_-^{(n)} = \sum_{j=1}^{n} B_j^{(-n)} exp(-ik_{-j} z) + d_n^{(-)} \left[ exp(ikz) + (-)^n r \exp(-ikz) \right] \tag{4.63}$$

where $C_n^{(-)}$, $A_j^{(-n)}$, $q_{-j}$, $d_n^{(-)}$, $B_j^{(-n)}$ and $k_{-j}$ are calculated just like the corresponding quantities $C_n, \ldots, k_j$ except that $\omega$ is replaced by $-\omega$. The matrix element is

$$<u_-^{(j)} | p_z | u_+^{(n-j)} > =$$

$$\int_{-\infty}^{0} dz \left[ d_j^{(-)*} \left[ \exp(-ikz) + (-)^j r^* \exp(ikz) \right] + \sum_{l=1}^{j} B_l^{(-j)*} \exp(ik_{-l}^* z) \right]$$

$$\left[ kd_{n-j} \left[ \exp(ikz) - (-)^{n-j} r \exp(-ikz) \right] - \sum_{l=1}^{n-j} B_l^{(n-j)} k_l \exp(-ik_l z) \right] +$$

$$\int_{0}^{\infty} \left[ c_j^{(-)*} \exp(-\gamma z) + \sum_{l=1}^{j} A_l^{(-j)*} \exp(-iq_{-l}^* z) \right]$$

$$\left[ i\gamma c_{n-j} \exp(-\gamma z) + \sum_{l=1}^{n-j} A_l^{(n-j)} q_l \exp(iq_l z) \right] \quad (4.64)$$

The individual integrals are readily computed. Thus

$$\langle u_-^{(j)} | p_z | u_+^{(n-j)} \rangle = \sum_{m=1}^{8} I_m \quad (4.65)$$

where

$$I_1 = \frac{1}{2i} d_j^{(-)*} d_{n-j} \left\{ (-1)^{n-j} r + (-1)^j r^* \right\} \quad (4.66)$$

$$I_2 = -id_j^{(-)*} \sum_{l=1}^{n-j} B_l^{(n-j)} k_l \left[ \frac{1}{k+k_l} - (-1)^j \frac{r^*}{k-k_l} \right] \quad (4.67)$$

$$I_3 = -i \sum_{l=1}^{j} B_l^{(-j)*} k d_{n-j} \left[ \frac{1}{k+k_{-l}^*} + \frac{(-1)^{n-j} r}{k-k_{-l}^*} \right] \quad (4.68)$$

$$I_4 = i \sum_{l=1}^{j} \sum_{l'=1}^{n-j} k_{l'} B_l^{(-j)*} B_{l'}^{(n-j)} \frac{1}{k_{-l}^* - k_{l'}} \quad (4.69)$$

$$I_5 = \frac{i}{2} C_j^{(-)*} C_{n-j} \quad (4.70)$$

$$I_6 = C_j^{(-)'} \sum_{l=1}^{n-j} q_l A_l^{(n-j)} \frac{1}{\gamma - iq_l} \tag{4.71}$$

$$I_7 = i\gamma \sum_{l=1}^{j} A_l^{(-j)'} C_{n-j} \frac{1}{\gamma + iq_{-l}} \tag{4.72}$$

$$I_8 = -i \sum_{l=1}^{j} \sum_{l'=1}^{n-j} q_{l'} A_l^{(-j)'} A_{l'}^{(n-j)} \frac{1}{q_{-l} - q_{l'}} \tag{4.73}$$

There is also an L-dependent term

$$I' = kd_j^{(-)'} d_{n-j} L [1-(-1)^n \, |r|^2] \tag{4.74}$$

but this term sums to zero when summed over j

In evaluating the matrix element the sum over spins gives a factor 2. Let S denote the term $\langle u_-^{(j)} | p_z | u_+^{(n-j)} \rangle$. Then

$$\sum_{sq} f_q^{(-)} \sum_{j=0}^{n} S = 2\int \frac{d^3k}{(2\pi)^3} \theta(k_f^2 - k_{\parallel}^2 - k_z^2) S \tag{4.75}$$

The three dimensional integral can be reduced to a one dimensional integral by integrating out the parallel component. So the matrix element becomes

$$M^{(n)} = \left(\frac{A_0 \hat{e}_z}{2c}\right)^n \left(\frac{2\pi}{\omega'}\right)^{1/2} \hat{e}'_z \frac{1}{4\pi^2} \int_0^{k_f} dk_z (k_f^2 - k_z^2) \sum_{j=0}^{n} \langle u_-^{(j)} | p_z | u_+^{(n-j)} \rangle \tag{4.76}$$

The scattering rate is

$$d\Gamma_n = 2\pi \sum_{k',\lambda} |M^{(n)}|^2 \delta(\omega' - n\omega) \tag{4.77}$$

Either the incident or outgoing photon may be polarized parallel to or perpendicular to the scattering plane. The four possibilties are depicted in Fig 4.1. Since M is proportional to a power of $\hat{e}_z$ it is clear that those states in which the incident polarization vector is perpendicular to the scattering plane will not contribute to the MHG signal. This rules out situations 1 and 2 in Fig. 4.1. Likewise, situation 3 will also not contribute because the matrix element also is proportional to $\hat{e}_z'$. Only situation 4 will contribute and I may replace $\hat{e}_z$ by $-\sin\theta$ and $\hat{e}_z'$ by $-\sin\theta'$ giving me

$$d\,\Gamma_n = 2\pi \int \frac{d\vec{k}'}{(2\pi)^3} \frac{1}{16\pi^4} \left(\frac{A_o}{2c}\right)^{2n} \sin^{2n}\theta \, \frac{2\pi}{n\,\omega} \sin^2\theta' \delta(\omega' - n\,\omega)$$

$$\left| \int_0^{q_f} dq_z \, (q_f^2 - q_z^2) \sum_{j=0}^{n} \langle u_-^{(j)} \mid p_z \mid u_+^{(n-j)} \rangle \right|^2 \quad (.4.78)$$

If the initial light beam is unpolarized then I must divide this expression by 2. If I introduce an element of solid angle, $d\,\Omega'$, and use the dispersion relation $\omega' = k'c$ I obtain

$$\frac{d^2\Gamma}{d\,\omega' d\,\Omega'} = \frac{1}{64\pi^5} \left|\frac{E_o}{2\omega}\right|^{2n} \frac{\omega'}{c^3} \sin^2\theta' \sin^{2n}\theta \, \delta(\omega' - n\,\omega)$$

$$\left| \int_0^{q_f} dq_z \, (q_f^2 - q_z^2) \sum_{j=0}^{n} \langle u_-^{(j)} \mid p_z \mid u_+^{(n-j)} \rangle \right|^2 \quad (.4.79)$$

where I have replaced the amplitude of the vector potential by the amplitude of the electric field using the relationship $E_o = i\,\omega A_o / c$

From the above expression it is clear that emission in directions nearly parallel to the surface are favored. The differential scattering cross section is

$$\frac{d^2\Gamma}{d\,\omega' d\,\Omega'} = \frac{\omega'}{c^3} \frac{1}{64\pi^5} \left|\frac{E_0}{2\omega}\right|^{2n} \sin^{2n}\theta \sin^2\theta' \delta(\omega' - n\,\omega)$$

$$| \int_0^{k_f} dk_z (k_f^2 - k_z^2) \sum_{j=0}^{n} < u_-^{(j)} | p_z | u_+^{(j)} > |^2 \qquad (4.80)$$

where $k_f = (2\epsilon_f)^{1/2}$ and $E_z = k_z^2/2 - V_0$ and $\phi + k_f^2/2 = V_0$

The total radiation emitted into the half space $0 \leqslant \theta' \leqslant \frac{\pi}{2}$ is obtained by integrating over solid angles . The integration over $\omega'$ can be used to eliminate the delta function. Finally, dividing the rate by the incident flux provides me with a formula for the total scattering yield for MHG.

$$Y = \frac{n}{24\pi^3} \left[\frac{e^2}{\hbar c}\right]^4 \left[\frac{eE_0\hbar}{2m\,\omega e^2}\right]^{2n-2} \sin^{2n}\theta\, T \qquad (4.81)$$

where

$$T = | \int_0^{k_f} dk_z (k_f^2 - k_z^2) \sum_{j=0}^{n} < u_-^{(j)} | p_z | u_+^{(j)} > |^2 \qquad (4.82)$$

Note that the units have been restored.

## 4.3 MULTIPHOTON ELECTRON EMISSION

In the previous chapter I have written out the form for a general matrix element for any potential. Now I have to calculate the matrix elements for a sharp step potential case. The $n^{th}$ order process results in the matrix element.

$$\overline{M}^{(n)} = (\frac{A_0 \hat{e}_z}{2c})^n < f \;| p_z | u_+^{(n-1)} > (2\pi)^2 \delta(\vec{q}_{\parallel}' - \vec{q}_{\parallel}) \qquad (4.83)$$

Here I have included the integration over transverse momentum states. The transition rate is obtained from the Fermi Golden Rule.

$$\Gamma^{(n)} = 2\pi \sum_{s} \sum_{f\,q} | \overline{M}^{(n)} |^2 \delta(\epsilon_q + n\,\omega - \epsilon_f) f_q^{(-)} f_f^{(+)} \qquad (4.84)$$

Here $s$ denotes the electron spin projection. Since multiphoton excitation preserves spin projection there is only a single spin common to both the initial and final state. In the delta function $\epsilon_q$ and $\epsilon_f$ should actually refer to the total energy including the kinetic energy associated with motion parallel to the surface, $q_{\parallel}^2/2$ and $q_{\parallel}'^2/2$ . However, since $\vec{q}_{\parallel} = \vec{q}_{\parallel}'$ this transverse kinetic energy cancels out and I may take $\epsilon_q$ and $\epsilon_f$ as the kinetic energy associated with z-motion.

I now need to calculate the matrix element for the sharp step potential case. The matrix element for multiphoton emission is

$$M^{(n)} = \left[\frac{A_0\hat{e}_z}{2c}\right]^n \langle f \mid p_z \mid u_+^{(n-1)} \rangle (2\pi)^2 \delta(\vec{q}_{\parallel}' - \vec{q}_{\parallel}) \tag{4.85}$$

where

$$\langle z \mid f \rangle = \begin{cases} (1+\rho)exp\,(-ik_n z) & \text{if } z < 0 \\ exp\,(iq_n z) + \rho \exp(-iq_n z) & \text{if } z > 0 \end{cases} \tag{4.86}$$

The final state is chosen to be an "out state", i.e. a state which has a unit amplitude wave emerging from the solid into vacuum. The reflection amplitude for the time reversed state is

$$\rho = \frac{q_n + k_n}{q_n - k_n} \tag{4.87}$$

Substituting the formula for $\mid u_+^{(n-1)} \rangle$ and evaluating the integral gives

$$\langle f \mid p_z \mid u_+^{(n-1)} \rangle = -i\,(1+\rho^*)kd_{n-1}\left[\frac{1}{k+k_n^*} - \frac{(-1)^n r}{k-k_n^*}\right]$$

$$+ i\,(1+\rho^*)\sum_{j=1}^{n-1} B_j^{(n-1)} \frac{k_j}{k_n^* - k_j} + \frac{i\,\gamma c_{n-1}}{\gamma + iq_n^*}$$

$$+i\sum_{j=1}^{n-1} A_j^{n-1}\frac{q_j}{q_j-q_n^*}+\frac{i\gamma\rho^* c_{n-1}}{\gamma-iq_n^*}$$

$$+i\rho^*\sum_{j=1}^{n-1} A_j^{n-1}\frac{q_j}{q_j+q_n^*} \tag{4.88}$$

According to Fermi's Golden rule, the rate per unit area for the process in which n photons are absorbed and an electron in state |q> and a hole in state |k> are created is given by

$$\Gamma=2\pi\sum_{\vec{k},\vec{q},s} |M|^2[(2\pi)^2\delta(\vec{k}_{\parallel}-\vec{q}_{\parallel})]\delta(\epsilon_k+n\,\omega-\epsilon_q)f_k^{(-)}$$

$$f_q^{(+)}\Theta(q_z) \tag{4.89}$$

Since I am interested in those states producing electrons which leave the solid, I have included the factor $\Theta(q_z)$. I have also factored out $(2\pi)^2\ \delta(\vec{k}_{\parallel}-\vec{q}_{\parallel})$ from the square of the matrix element corresponding to the conservation of transverse momentum. If I average over the polarization of the incident photon then only half the states contribute so I will include an additional factor of ½. A factor of 2 comes from the summation over spins. Note that the factor $\Theta(q_z)$ forces $f_q^{(+)}$ to be 1. I may carry out the integral over transverse momenta and find

$$\int d^2k_{\parallel} f_k^{(-)} f_q^{(+)}\Theta(q_z)=\Theta(q_z)\pi(k_f^2-k_z^2)\Theta(k_f^2-k_z^2) \tag{4.90}$$

Using the relations $\epsilon_z=k_z^2/2-V_0$ and $\epsilon_z'=q_z^2/2=\epsilon_z+n\,\omega$, I get

$$\langle\Gamma\rangle_{pol}=\frac{1}{8\pi^2}\int_{-\infty}^{\infty} dk_z\int_0^{\infty} dq_z\,\delta(\frac{k_z^2}{2}-V_0+n\,\omega-\frac{q_z^2}{2})|M|^2$$

$$(2\epsilon_f - k_z^2)\Theta(2\epsilon_f - k_z^2) \quad (4.91)$$

This can be rewritten as

$$\Gamma = \frac{1}{8\pi^2} \int_0^{k_f} dk_z \frac{|M|^2}{(k_z^2 - 2V_0 + 2n\omega)^{1/2}} (k_f^2 - k_z^2) \quad (4.92)$$

It has been assumed that the incident radiation is unpolarized so that only the part that is perpendicular to the surface contributes. Here I take for M the expression obtained previously.

$$M = \left[ \frac{A_0}{2c} \sin\theta \right]^n <f \mid p_z \mid u_+^{(n-1)}> \quad (4.93)$$

Dividing the rate per unit area by the incident photon flux gives the yield. Restoring the units results in the final formula

$$Y = \frac{me^6}{4\hbar^4 \pi \omega c} \left[ \frac{eE_0 \hbar}{2m\,\omega e^2} \right]^{2n-2} \sin^{2n}\theta \int_0^{k_f} dk_z \frac{|<f \mid p_z \mid u_+^{(n-1)}>|^2}{(k_z^2 - 2V_0 + 2n\omega)^{1/2}} (k_f^2 - k_z^2) \quad (4.94)$$

## 4.4.RESULTS AND DISCUSSION

In this chapter I considered two nonlinear processes that occur at the surface of an idealized metal. One process is multiharmonic generation and the other is multiphoton electron emission. Expressions were derived for the yields of these processes when the metal is illuminated by an intense laser field. In this section I present the results of the calculation.

In Fig. 4.2 and 4.3 I show the yield, Y defined in the previous section, for first, second, third and fourth harmonic generation as a function of laser frequency for the free electron metals Na and K. I start with frequency $\omega$ = .05 a.u. and go upto $\omega$ =0.5 a.u. Note that as the laser frequency is increased the yield decreases rapidly and monotonically. In these calculations I took the work functions for Na and K to be 2.35 and 2.22 eV, respectively, and the corresponding Fermi energies to be 3.24 and 2.12 eV, respectively. The magnitude of the yield is sensitive to the size of both of these parameters. Also in Fig. 4.2 and Fig. 4.3 I show the yield vs frequency for two different laser intensities. These intensities are related to a nonlinear parameter $x$ which is defined by $x = eE_0\hbar/(2m\omega e^2)$ I see that when the nonlinear parameter $x$ is smaller perturbation theory works well.

Let me estimate the numerical size of the expected MHG yield for the case in which the parameter $x$ =1.0 For a $1.17eV$ photon (YAG laser, $1.06\mu$ ) which corresponds to an intensity of $2.62\times10^{14} W/cm^2$ this gives $8.868\times10^{-12}$ for the second harmonic generation for Na. The third harmonic and fourth harmonic yields are found to be $1.247\times10^{-11}$ and $6.316\times10^{-10}$ respectively. At these field strengths perturbation theory has probably already broken down, because the third harmonic yield is larger than the second harmonic yield and the fourth harmonic yield is larger than the third harmonic yield. At weaker field strengths, however, the third harmonic signal will, of course fall more rapidly than the second harmonic. I can see this for $x$ =.1 (which corresponds to an intensity of $2.62\times10^{12} W/cm^2$) where the second harmonic yield is $8.868\times10^{-14}$ and the third harmonic yield is $1.247\times10^{-15}$ for Na.

In Fig. 4.4 and 4.5 I plot the nonlinear photoelectric yield versus photon frequency for Na and K for two different fields. Data is presented for several orders of MPEE. The curves plotted have an extra factor of $4\pi$ for the yield. One notes that the yield decreases with increasing frequency . I start with frequency

$\omega$=0.25$a.u.$ and go up to 2.5$a.u.$. Estimated yield for K for the two photon case is $6.816\times10^{-4}$ when the electric field is $1.63\times10^{15} Watts / cm^2$ ( corresponding to $x$ =0.5 ) and the incident frequency is .215 a. u. which is 5.848 eV. frequency is in the ultraviolet region. When the intensity is $1.63\times10^{13} W / cm^2$ (corresponding to $x$ =.05 ) the yield is $6.816\times10^{-6}$.

In all these calculations I have taken the angle of incidence to be $\pi/2$. I notice that the MPEE yield is much greater (of the order of $10^9$ ) than the MHG yield. This may be attributed to the greater availability of states for MPEE than that available for MHG.

I have also studied the dependence of the MHG yield and the MPEE yield as a function of the Fermi energy and the work function parameters. I notice that the MHG yield is essentially a function of the Fermi energy and not the work function and it decreases as the Fermi energy decreases. The reasons for this behavior is simple. As the Fermi energy is increased, the number of electrons that contribute to the nonlinear response of the system increases and so the yield also increases. Since it is not necessary for the electron to leave the solid in the case of MHG the work function plays only a minor role in determining the size of the yield.

In the MPEE case I have found that the yield is a function of both the Fermi energy and the work function. It decreases when the Fermi energy decreases and increases when the work function decreases. This is reasonable because in the case of MPEE, the electron gets excited before leaving the surface. Again a decrease in the Fermi energy implies a reduced number of active electrons and hence a decreased yield. On the other hand, a decreased work function means both that more electrons from the Fermi sea may be photoionized as well as a weakening of the binding to the solid.

The frequency of the laser beam also plays a major role in determining the magnitude of the yield. Notice that for lower frequencies there is no MPEE yield because the frequency is simply not large enough for the electron to cross the photoemission threshold. At high frequencies, the matrix elements become small due to the presence of the energy denominators.

In principle it should be possible to get multiphoton electron emission from a thermal process as well as from the direct quantum process considered here. For example, in the theory of thermionic emission it is the tail of the Fermi distribution that extends above the vacuum level that is responsible for the emitted electrons. The energy distribution is approximately Maxwellian since it is the high energy tail of a Fermi distribution. If an intense radiation field impinges on a solid the temperature of the surface could become very high and this could broaden the tail of the distribution considerably. One would expect the temperature to be related to the energy fluence of the pulse. One may distinguish the thermal process from the quantum processes discussed here by shortening the duration of the pulse while maintaining the same fluence. This will drive the peak strength of the electric field up and thereby accentuate the higher order nonlinear processes. Electrons would be emitted after having absorbed two, three or more photons. Thus I should find that the electrons would start to be emitted with a nonthermal distribution.

In this analysis I have completely disregarded the effect of surface roughness in determining the yields. For rough surfaces enhancement of the local fields can have an extraordinarily large effect on higher order multiphoton processes. However , my results for the smooth step derived in this chapter, may be combined with a knowledge of surface field enhancement factors to allow one to extend the present theory to such problems.

# 5. THE HIGH FREQUENCY LIMIT

In the limit where the laser photon energy is high compared with the electronic energy and the depth of the potential one might obtain simple analytic formulas for the low order multi-harmonic generation matrix elements. I illustrate this for the cases $n=1$ and $n=2$. Starting with the expression

$$M^{(1)}=\sum_q \left(\frac{A_0\hat{e}_z}{2c}\right)\left(\frac{2\pi}{\omega'}\right)^{1/2}\hat{e}_z\cdot\left[M_1+M_2\right]f_q^{(-)} \tag{5.1}$$

where

$$M_1=\sum_l \frac{<q\mid p_z\mid l><l\mid p_z\mid q>}{\omega+\epsilon_q-\epsilon_l} \tag{5.2}$$

and

$$M_2=\sum_l \frac{<q\mid p_z\mid l><l\mid p_z\mid q>}{-\omega+\epsilon_q-\epsilon_l} \tag{5.3}$$

I develop the denominator in a power series in powers of $1/\omega$.

$$M_1+M_2\approx\frac{1}{\omega}\sum_l<q\mid p_z\mid l><l\mid p_z\mid q>\left[1-\frac{\epsilon_q-\epsilon_l}{\omega}+\cdots\right]$$

$$-\frac{1}{\omega}\sum_l<q\mid p_z\mid l><l\mid p_z\mid q>\left[1+\frac{\epsilon_q-\epsilon_l}{\omega}+\cdots\right] \tag{5.4}$$

The terms going as $1/\omega$ cancel. The terms going as $1/\omega^2$ may be rewritten as commutators using the closure relation.

$$M_1+M_2\approx-\frac{1}{\omega^2}<q\mid[[H,p_z],p_z]\mid q>$$

$$=\frac{1}{\omega^2}<q\ |V''(z)|\,q> \tag{.5.5}$$

so

$$M^{(1)}=\frac{1}{\omega^2}\left(\frac{A_0\hat{e}_z}{2c}\right)\left(\frac{2\pi}{\omega'}\right)^{1/2}\hat{e}_z\cdot\sum_q<q\ |V''(z)|\,q>f_q^{(-)} \tag{.5.6}$$

Similarly, for n=2 :

$$M^{(2)}=\sum_q\left(\frac{A_0\hat{e}_z}{2c}\right)^2\left(\frac{2\pi}{\omega'}\right)^{1/2}\hat{e}_z\cdot\left[M_1+M_2+M_3\right]f_q^{(-)} \tag{.5.7}$$

where

$$M_1=\sum_{lp}\frac{<q\ |p_z|\ p><p\ |p_z|\ l><l\ |p_z|\ q>}{(2\omega+\epsilon_q-\epsilon_p)(\omega+\epsilon_q-\epsilon_l)} \tag{5.8}$$

$$M_2=\sum_{lp}\frac{<q\ |p_z|\ p><p\ |p_z|\ l><l\ |p_z|\ q>}{(-\omega+\epsilon_q-\epsilon_p)(\omega+\epsilon_q-\epsilon_l)} \tag{.5.9}$$

$$M_3=\sum_{lp}\frac{<q\ |p_z|\ p><p\ |p_z|\ l><l\ |p_z|\ q>}{(-\omega+\epsilon_q-\epsilon_p)(-2\omega+\epsilon_q-\epsilon_l)} \tag{5.10}$$

As $\omega\to\infty$ the leading order terms going as $1/\omega^2$ cancel. The next leading order terms combine to give

$$-\sum_{j=0}^{2}\frac{(-1)^j}{2\omega^{2+1}j!(2-j)!}<q\ |p_z^j[H,p_z]p_z^{2-j}|\,q> \tag{.5.11}$$

$$=\frac{i}{4\omega^3}<q\ |V^{(3)}(z)|\,q> \tag{.5.12}$$

Let me apply these formulas to a sharp step potential. Here

$$V(z)=V_0\Theta(z) \tag{.5.13}$$

so

$$V'(z) = V_0\delta(z) \tag{5.14}$$

$$V''(z) = V_0\delta'(z) \tag{5.15}$$

Then

$$<q \mid V''(z) \mid q> = \int dz\, \phi^*(z) V_0 \delta'(z)\phi(z)$$

$$= -V_0 \int dz\, \delta(z)(\mid \phi \mid^2)'$$

$$= -2V_0 \mathrm{Re}\phi^* \phi' \mid_{z=0} \tag{5.16}$$

Note that both $\phi$ and $\phi'$ are continuous at $z=0$ so the integral is well defined. Inserting my expressions for the wave function of the step potential leads to

$$M^{(1)} = \left(\frac{A_0\hat{e}_z}{2c\,\omega}\right)\left(\frac{2\pi}{\omega'}\right)^{1/2}\hat{e}_z \cdot \sum_q \frac{4\gamma k^2}{\omega} f_q^{(-)} \tag{5.17}$$

It is interesting to note that for the wall potential, neither $M^{(1)}$ nor $M^{(2)}$ have simple inverse power law behavior as a function of $\omega$. The reason is because I am never able to go to the limit in which $\omega$ is high compared with $V_0$ for the hard wall case, because $V_0$ is infinite.

Let me now look at the general order $n$ in the high frequency limit. The matrix element is

$$M^{(n)} = \left(\frac{A_0\hat{e}_z}{2c}\right)^n \left(\frac{2\pi}{\omega'}\right)^{1/2} \hat{e}_z \cdot \sum_q f_q^{(-)} \left[M_0 + M_1 + \dots + M_n\right] \tag{5.18}$$

where

$$M_i = \sum_{l_1 \ldots l_n} \frac{N_n}{\Delta_i} \tag{.5.19}$$

and

$$N_n = <q \mid P_z \mid l_1><l_1 \mid p_z \mid l_2><l_2 \mid p_z \mid l_3> \ldots <l_n \mid p_z \mid q> \tag{.5.20}$$

and

$$\Delta_0 = (n\,\omega + \epsilon_q - \epsilon_{l_1})((n-1)\omega + \epsilon_q - \epsilon_{l_2}) \ldots (\omega + \epsilon_q - \epsilon_{l_n}) \tag{.5.21}$$

$$\Delta_1 = (-\omega + \epsilon_q - \epsilon_{l_1})((n-1)\omega + \epsilon_q - \epsilon_{l_2}) \ldots (\omega + \epsilon_q - \epsilon_{l_n}) \tag{.5.22}$$

$$\Delta_2 = (-\omega + \epsilon_q - \epsilon_{l_1})(-2\omega + \epsilon_q - \epsilon_{l_2}) \ldots (\omega + \epsilon_q - \epsilon_{l_n}) \tag{5.23}$$

$$\Delta_n = (-\omega + \epsilon_q - \epsilon_{l_1})(-2\omega + \epsilon_q - \epsilon_{l_2}) \ldots (-n\,\omega + \epsilon_q - \epsilon_{l_n}) \tag{.5.24}$$

I expand the denominators to first order in $\omega$

$$\frac{1}{\Delta_0} = \frac{1}{n!\omega^n}\left[1 - \frac{\epsilon_q - \epsilon_{l_1}}{n\,\omega} - \frac{\epsilon_q - \epsilon_{l_2}}{(n-1)\omega} - \cdots \frac{\epsilon_q - \epsilon_{l_n}}{\omega}\right] \tag{.5.25}$$

$$\frac{1}{\Delta_1} = \frac{-1}{(n-1)!1!\omega^n}\left[1 + \frac{\epsilon_q - \epsilon_{l_1}}{\omega} - \frac{\epsilon_q - \epsilon_{l_2}}{(n-1)\omega} - \cdots \frac{\epsilon_q - \epsilon_{l_n}}{\omega}\right] \tag{.5.26}$$

$$\frac{1}{\Delta_2} = \frac{1}{(n-2)!2!\omega^n}\left[1 + \frac{\epsilon_q - \epsilon_{l_1}}{\omega} + \frac{\epsilon_q - \epsilon_{l_2}}{2\omega} - \cdots \frac{\epsilon_q - \epsilon_{l_n}}{\omega}\right] \tag{5.27}$$

$$\frac{1}{\Delta_n} = (-)^n \frac{1}{0!n!\omega^n}\left[1 + \frac{\epsilon_q - \epsilon_{l_1}}{\omega} + \frac{\epsilon_q - \epsilon_{l_2}}{2\omega} + \cdots \frac{\epsilon_q - \epsilon_{l_1}}{n\,\omega}\right] \tag{.5.28}$$

The $\omega$ independent coefficients sum to zero since

$$\sum_{j=0}^{n} \frac{(-1)^j}{(n-j)!\,j!} = 0 \tag{5.29}$$

The coefficients of $\epsilon_q - \epsilon_{l_j}$ may be readily be shown to be given by a simple sum so

$$\sum_{l=0}^{n} \frac{1}{\Delta_l} = -\frac{n+1}{\omega^{n+1}} \sum_{j=1}^{n} (\epsilon_q - \epsilon_{l_j}) \frac{1}{j(n+1-j)} \sum_{m=0}^{j-1} \frac{(-1)^m}{(n-m)!\,m!} \tag{5.30}$$

Let me write this in the form

$$c_0(\epsilon_q - \epsilon_{l_1}) + c_1(\epsilon_{l_1} - \epsilon_{l_2}) + \cdots + c_{n-1}(\epsilon_{l_{n-1}} - \epsilon_{l_n}) + c_n(\epsilon_{l_n} - \epsilon_q) \tag{5.31}$$

By comparing with the previous expression, I find that

$$c_j - c_{j-1} = \frac{n+1}{\omega^{n+1}} \frac{1}{j(n+1-j)} \sum_{m=0}^{j-1} \frac{(-1)^m}{(n-m)!\,m!} \tag{5.32}$$

The solution is

$$c_j = -\frac{(-1)^j}{n\,\omega^{n+1} j!\,(n-j)!} \tag{5.33}$$

so

$$\sum_i \sum_{l_1 \cdots l_n} \frac{N_n}{\Delta_i} = -\sum_{j=0}^{n} \frac{(-1)^j}{n\,\omega^{n+1} j!\,(n-j)!} < q \mid p_z^j [H, p_z] p_z^{n-j} \mid q > \tag{5.34}$$

where I have made use of the eigenvalue equation and the closure condition. The commutator is proportional to the derivative of the potential. The sum may be reexpressed as a multiple commutator.

$$\sum_i \sum_{l_1 \cdots l_n} \frac{N_n}{\Delta_i} = -\frac{i}{n\,\omega^{n+1} n!} < q \mid [[V', p_z] \ldots p_z] \mid q >_n \tag{5.35}$$

$$= -\frac{i^{n+1}}{n\,\omega^{n+1} n!} < q \mid V^{(n+1)} \mid q > \tag{5.36}$$

So finally

$$M^{(n)} = -\left(\frac{A_0 \hat{e}_z}{2c}\right)^n \left(\frac{2\pi}{\omega'}\right)^{1/2} \hat{e}_z \,{}' \sum_q f_q^{(-)} \frac{i^{n+1}}{n\,\omega^{n+1} n!} < q \mid V^{(n+1)} \mid q > \qquad (.5.37)$$

The matrix element is proportional to the expectation $n+1^{st}$ derivative of the potential summed over the Fermi sea. Note that the sum over spins is included in the q sum.

While the above formula has been derived for the purpose of studying surface nonlinear effects, one notes that it is also applicable to the case of a one dimensional solid. All one must do is to take $V(z)$ as a periodic potential.

# 6. THE WALL POTENTIAL

## 6.1 GENERAL THEORY

Perhaps the simplest model for a solid is a half-space bounded by an impenetrable wall. The solid is completely described in terms of one parameter - the Fermi wave vector of the electrons. The depth of the inner ion core potential, the shape of the surface potential and the presence of the ions are completely neglected in this model. In this section I study the solution to the time- dependent Schrodinger equation for the wall potential.

The Schrodinger equation is

$$\left[\frac{1}{2}p_z{}^2+\frac{1}{c}A_z(t)p_z+V(z)-i\frac{\partial}{\partial t}\right]\psi(z,t)=0 \qquad (6.1)$$

where

$$V(z)=\infty \text{ if } z<0$$

$$=0 \text{ if } z>0 \qquad (6.2)$$

I search for a solution which will evolve from a left-travelling wave that was initially unperturbed at an early time $-T$. For times $t>-T$ the effect of the interaction is felt and the wave evolves into a time-dependent solution. The general solution consists of this wave plus time-dependent reflected waves. The reflected waves may either propagate away from the surface towards positive $z$ or be attenuated in the positive $z$ direction.

The left-travelling wave is of the form

$$\psi_0(z,t) = \exp[-ik_0 z - if(t)] \tag{6.3}$$

where $k_0$ is the electron's wave-vector in the z-direction

$$k_0 = (2E_z)^{\frac{1}{2}} \tag{6.4}$$

and $E_z$ is the kinetic energy associated with z-motion. Then the Schrodinger equation gives

$$\frac{k_0^2}{2} - \frac{1}{c}k_0 A_z(t) - \frac{df}{dt} = 0 \tag{6.5}$$

so

$$f(t) = \frac{k_0^2}{2}(t+T) - \frac{k_0}{c}\int_{-T}^{t} dt' A_z(t') \tag{6.7}$$

and

$$\psi_0(z,t) = \exp\left|-ik_0 z - iE_z(t+T) + ik_0/c\int_{-T}^{t} dt' A_z(t')\right| \tag{6.8}$$

This function satisfies the Schrodinger equation for $z > 0$ but not the boundary condition at the wall

$$\psi(0,t) = 0 \tag{6.9}$$

In order to satisfy this boundary condition I must mix in reflected waves. I will be concerned with harmonic interactions which are switched on at early times and are adiabatically increased in strength as time goes on. Thus let

$$A_z(t) = A_z \exp(\alpha t)\cos(\omega t)\Theta(t+T) \tag{6.10}$$

where $A_z = A_0\hat{\epsilon}_z$ is the amplitude of the vector potential's z- component, $\omega$ is the radian frequency of the radiation and $\alpha$ is assumed to be a small adiabatic rate satisfying the conditions

$$\alpha T \gg 1 \tag{6.11}$$

and

$$\alpha \ll \omega \tag{6.12}$$

Then

$$\int_{-T}^{t} dt' A_z(t') = \int_{-T}^{t} dt' A_z \exp(\alpha t') \cos(\omega t')$$

$$\rightarrow \frac{A_z}{\omega} \sin(\omega t) \tag{6.13}$$

Since I am concerned with a harmonic field, the energy may only be changed by multiples of the laser frequency, $\omega$. Thus the reflected wave vectors for the problem are given by

$$k_n = [2(E_z + n\,\omega)]^{\frac{1}{2}} \tag{6.14}$$

The general solution is

$$\psi(z,t) = \psi_0(z,t) + \sum_n D_n \exp\left[ ik_n z - i\frac{k_n^2}{2}(t+T) - i\frac{k_n}{c}\int_{-T}^{t} dt' A_z(t') \right] \tag{6.15}$$

In this solution I must include contributions from all values of $n$, positive or negative. If $E_z + n\,\omega > 0$ then I will have an admixture of reflected right-travelling waves. For $E_z + n\,\omega < 0$ I let

$$k_n = i\,\gamma_n \tag{6.16}$$

where

$$\gamma_n = [-2(E_z + n\,\omega)]^{\frac{1}{2}} \tag{6.17}$$

These values of $n$ correspond to the attenuated waves. They may be thought of as radiation-induced surface states!

The solution may be written as

$$\psi(z,t) = \exp[-ik_0 z - iE_z(t+T) + \frac{ik_0 A_z}{\omega c}\sin(\omega t)] +$$

$$\sum_{-\infty}^{\infty} D_n \exp[ik_n z - iE_z(t+T) - in\,\omega(t+T) - \frac{ik_n A_z}{\omega c}\sin(\omega t)] \tag{6.18}$$

Let me make a harmonic expansion of $\psi(z,t)$ using the formula

$$\exp[a\sin(\omega t)] = \sum_{\mu=-\infty}^{\infty} (-i)^{\mu} I_{\mu}(a)\exp(i\mu\omega t) \tag{6.19}$$

where $I_{\mu}(a)$ is the modified Bessel function of the first kind. Then

$$\psi(z,t) = \sum_{\mu} (-i)^{\mu} \exp[i\mu\omega t - iE_z(t+T)] \times$$

$$\left[\exp(-ik_0 z) I_{\mu}\left[\frac{ik_0 A_z}{\omega c}\right] + \sum_n B_n \exp(ik_n z)(-i)^n I_{\mu+n}\left[\frac{-ik_n A_z}{\omega c}\right]\right] \tag{6.20}$$

where I have let

$$B_n = D_n \exp(-in\,\omega T) \tag{6.21}$$

The boundary condition leads to the formula

$$I_{\mu}\left[\frac{ik_0 A_z}{\omega c}\right] + \sum_{n=-\infty}^{\infty} B_n (-i)^n I_{\mu+n}\left[\frac{-ik_n A_z}{\omega c}\right] = 0 \tag{6.22}$$

If I utilize the sum rule

$$\sum_{\mu=-\infty}^{\infty} (-)^{\mu} I_{\mu+\sigma}(a) I_{\mu+\sigma'}(b) = (-)^{\sigma'} I_{\sigma-\sigma'}(a-b) \tag{.6.23}$$

and

$$I_{\mu}(0) = \delta_{\mu,0} \tag{.6.24}$$

I obtain

$$\sum_{n=-\infty}^{\infty} B_n\, i^n\, I_{\sigma-n} \left[\frac{i\,(k_0+k_n)A_z}{\omega c}\right] + \delta_{\sigma,0} = 0 \tag{.6.25}$$

6.2 THE LOW FREQUENCY LIMIT

In the case where the laser frequency is small compared with $E_z$ I may take

$$k_n \approx k_0 \tag{.6.26}$$

so

$$\sum_n B_n\, i^n\, I_{\sigma-n} \left[\frac{2ik_0A_z}{\omega c}\right] + \delta_{\sigma,0} \approx 0 \tag{.6.27}$$

Multiplying through by the appropriate modified Bessel function and carrying out the sum leads to

$$\sum_{\sigma} (-)^{\sigma} I_{\sigma-n'} \left[\frac{2ik_0A_z}{\omega c}\right] \sum_n B_n\, i^n\, I_{\sigma-n} \left[\frac{2ik_0A_z}{\omega c}\right] + I_{-n'} \left[\frac{2ik_0A_z}{\omega c}\right] \approx 0 \tag{.6.28}$$

so

$$B_n \approx -\, i^n\, I_n \left[\frac{2ik_0A_z}{\omega c}\right] \tag{.6.29}$$

where I have used the formula ( valid for integer $n$ )

$$I_{-n}(a) = I_n(a) \qquad (6.30)$$

This formula may be improved somewhat by making corrections of order $\omega / k_0^2$. After a lengthy calculation I have found

$$B_n \approx -i^n \left[\frac{k_0}{k_n}\right]^{1/2} I_n\left(2ix\,(k_0 k_n)^{1/2}\right) \qquad (6.31)$$

If I make use of the expansion

$$I_n(a) \approx \frac{1}{|n|!}\left[\frac{a}{2}\right]^{|n|} \qquad (6.32)$$

valid for small $a$, I see that for weak fields ( $k_0 |A_z| / (c\,\omega) \ll 1$ ) the coefficients $B_n$ fall off rapidly with increasing $n$. Then the admixture of excited ( or de-excited ) states is not important. However, for stronger fields these states play a more important role.

## 6.3 MULTI-HARMONIC GENERATION

In evaluating the multi-harmonic generation one needs the expectation value of the z-component of the momentum operator in the perturbed state $\psi$. I begin by assuming the solid extends from $z=0$ to $z=L$ and then I let $L$ approach infinity. The expectation value is

$$<\psi | p_z | \psi> = \int_0^L dz$$

$$\left[\exp\left[ik_0 z - i\frac{k_0 A_z}{\omega c}\sin(\omega t)\right] + \sum_{n'} B_{n'}^{*} \exp\left[-ik_{n'}^{*} z + in'\omega t + i\frac{k_{n'}^{*} A_z}{\omega c}\sin(\omega t)\right]\right]$$

$$\left[ -k_0 \exp\left[ -ik_0 z + i\frac{k_0 A_z}{\omega c}\sin(\omega t) \right] + \sum_n k_n B_n \exp\left[ ik_n z - in\omega t - i\frac{k_n A_z}{\omega c}\sin(\omega t) \right] \right] \quad (6.34)$$

Write this as the sum of four terms:

$$\langle\psi | p_z | \psi\rangle = p^{(1)} + p^{(2)} + p^{(3)} + p^{(4)} \quad (6.35)$$

where

$$p^{(1)} = -k_0 L \quad (6.36)$$

$$p^{(2)} = i\sum_n \frac{k_n B_n}{k_0 + k_n}\exp\left[ -in\omega t - \frac{i(k_n + k_0)A_z}{c\omega}\sin(\omega t) \right] \quad (6.37)$$

$$p^{(3)} = i\sum_n \frac{k_0 B_n^*}{k_0 + k_n^*}\exp\left[ in\omega t + \frac{i(k_0 + k_n^*)A_z}{c\omega}\sin(\omega t) \right] \quad (6.38)$$

$$p^{(4)} = i\sum_{\substack{nn' \\ n \neq n'}} \frac{k_n B_n B_{n'}^*}{k_n - k_{n'}^*}\exp\left[ i(n' - n)\omega t + i\frac{(k_{n'}^* - k_n)A_z}{c\omega}\sin(\omega t) \right] +$$

$$i\sum_n \frac{k_n |B_n|^2}{k_n - k_n^*}\Theta(-E_z - n\omega)\exp\left[ i\frac{(k_n^* - k_n)A_z}{c\omega}\sin(\omega t) \right] +$$

$$L\sum_n k_n |B_n|^2 \Theta(E_z + n\omega) \quad (6.40)$$

Note that the incident flux and reflected fluxes must match, so that the terms in $p^{(1)}$ and $p^{(4)}$ proportional to $L$ cancel

$$-k_0 + \sum_n k_n |B_n|^2 \Theta(E_z + n\omega) = 0 \quad (6.41)$$

I interpret this by saying that $|B_n|^2$ represents the relative probability of making a transition to a state in which n photons have been absorbed ( or |n|

photons emitted if $n < 0$). Only the open channels corresponding to positive kinetic energy contribute to the reflected flux. In the above expressions I have dropped the exponentials evaluated at $z = L$. They either oscillate wildly for large $L$ or are exponentially attenuated.

I next make a harmonic expansion of the expectation value of the momentum operator:

$$<\psi \mid p_z \mid \psi> = \sum_{\mu} P_{\mu} \exp(i\,\mu\omega t\,) \tag{.6.42}$$

where

$$P_{\mu} = i\sum_{n} \frac{k_n\, B_n}{k_0 + k_n}(-i\,)^{n+\mu} J_{n+\mu}\left[-i\frac{(k_0 + k_n\,)A_0}{c\,\omega}\right] +$$

$$i\sum_{n} \frac{k_0 B_n^*}{k_0 + k_n^*}(-i\,)^{\mu-n}\, J_{\mu-n}\left[i\frac{(k_0 + k_n^*)A_0}{c\,\omega}\right] +$$

$$i\sum_{n} \frac{k_n \mid B_n \mid^2}{k_n - k_n^*}\Theta(-E_z - n\,\omega)(-i\,)^{\mu} J_{\mu}\left[i\frac{(k_n^* - k_n\,)A_0}{c\,\omega}\right] +$$

$$i\sum_{\substack{nn' \\ n \neq n'}} \frac{k_n\, B_n\, B_{n'}^*}{k_n - k_{n'}^*}(-i\,)^{\mu+n-n'}\, J_{\mu+n-n'}\left[i\frac{(k_{n'}^* - k_n\,)A_0}{c\,\omega}\right] \tag{.6.43}$$

The current carried by the electron is determined by the mechanical momentum and not the canonical momentum. Thus the velocity is given by

$$v_z = \frac{<\psi \mid (p_z + \frac{1}{c}A_z\,) \mid \psi>}{<\psi \mid \psi>}$$

$$= \frac{<\psi \mid p_z \mid \psi>}{<\psi \mid \psi>} + \frac{1}{c} A_z (t) \tag{6.44}$$

In writing this expression I recognize that I have chosen $\mid \psi>$ so that it had a given incident wave vector $k_0$. It was not normalized to unit probability. In order to calculate the true expectation value I must divide by the normalization integral. I may expand $v_z$ in a harmonic expansion.

$$v_z = \sum_\mu v_\mu \exp(i \mu\omega t) + \frac{A_0}{2c}\hat{e}_z \left[\exp(i \omega t) + \exp(-i \omega t)\right] \tag{6.45}$$

The overlap integral is evaluated as follows:

$$<\psi \mid \psi> = \int_0^\infty dz\, (A + B)(A^* + B^*) \tag{6.46}$$

where

$$A = \exp(ik_0 z + iE (t + T) - \frac{ik_0 A_0}{c\,\omega} \sin\omega t) \tag{6.47}$$

and

$$B = \sum_n D_n^* \exp(-ik_n^* z + iE (t + T) + in\,\omega(t + T) + \frac{ik_n^* A_0}{c\,\omega} \sin\omega t) \tag{6.48}$$

$$A^* = \exp(-ik_0 z - iE (t + T) + \frac{ik_0 A_0}{c\,\omega} \sin\omega t) \tag{6.49}$$

and

$$B^* = \sum_n D_n \exp(+ik_n z - iE (t + T) - in\,\omega(t + T) - \frac{ik_n A_0}{c\,\omega} \sin\omega t) \tag{6.50}$$

The four integrals contributing the overlap integrals are

$$\langle\psi|\psi\rangle = N^{(1)}+N^{(2)}+N^{(3)}+N^{(4)} \tag{.6.51}$$

where

$$N^{(1)} = L \tag{.6.52}$$

$$N^{(2)} = \sum_n \frac{iB_n}{k_0+k_n}\exp[-in\,\omega t - i\frac{(k_n+k_0)}{c\,\omega}A_0\sin\omega t\,] \tag{.6.53}$$

$$N^{(3)} = -\sum_n \frac{iB_n^*}{k_0+k_n^*}\exp[+in\,\omega t + i\frac{(k_n^*+k_0)}{c\,\omega}A_0\sin\omega t\,] \tag{6.54}$$

$$N^{(4)} = \sum_{nn'n'\neq n} \frac{iB_n\,B_{n'}^*}{k_n-k_{n'}^*}\exp[i\,(n'-n\,)\omega t + i\,(k_{n'}^*-k_n\,)\frac{A_0}{c\,\omega}\sin\omega t\,]$$

$$+\sum_n i\frac{|B_n|^2}{k_n-k_n^*}\Theta(-E_z-n\,\omega)\exp[i\,(k_n^*-k_n\,)\frac{A_0}{c\,\omega}\sin\omega t\,]$$

$$+L\sum_n |B_n|^2\Theta(E_z+n\,\omega) \tag{6.55}$$

This may be broken into terms proportional to L ( which are time independent ) and terms of order unity ( containing the various harmonics)

$$\langle\psi|\psi\rangle = L\left[1+\sum_n |B_n|^2\Theta(E_z+n\,\omega)\right]+\sum_\mu N_\mu\exp(i\,\mu\omega t\,) \tag{.6.56}$$

where

$$N_\mu = i\sum_n \frac{B_n}{k_0+k_n}(-i\,)^{n+\mu}I_{n+\mu}\left[-i\frac{(k_0+k_n\,)A_0}{c\,\omega}\right]-$$

$$i\sum_n \frac{B_n^*}{k_0+k_n^*}(-i\,)^{\mu-n}\,I_{\mu-n}\left[i\frac{(k_0+k_n^*)A_0}{c\,\omega}\right]+$$

$$i\sum_n \frac{|B_n|^2}{k_n - k_n^*}\Theta(-E_z - n\omega)(-i)^{\mu} I_{\mu}\left[i\frac{(k_n^* - k_n)A_0}{c\,\omega}\right] +$$

$$i\sum_{\substack{nn' \\ n\neq n'}} \frac{B_n B_{n'}^*}{k_n - k_{n'}^*}(-i)^{\mu+n-n'} I_{\mu+n-n'}\left[i\frac{(k_{n'}^* - k_n)A_0}{c\,\omega}\right] \qquad (6.57)$$

It is to be noted that the leading order corrections to $v_z$ only involve the L-dependent term so

$$v_{\mu} = \frac{p_{\mu}}{L(1+\sum_n |B_n|^2\Theta(E_z + n\omega))} \qquad (6.58)$$

The normalization is affected by the $B_n$ coefficients associated with open outgoing channels.

The term $A_z(t)/c$ apppearing in the expression for $v_z$ is due to the Thomson scattering of free electrons and is not associated with the wall collision.

The transition amplitude for emitting the photon $\omega'=\sigma\omega$ is given by

$$c_{\sigma} = -i\left[\frac{2\pi}{\omega'}\right]^{\frac{1}{2}}\int_{-\infty}^{\infty} dt\, \exp[i\,\omega' t\,]\epsilon_z{}' \langle\psi\,|\,p_z\,|\,\psi\rangle$$

$$= 2\pi\sum_{\sigma} T_{\sigma}\epsilon_z{}'\delta(\omega' - \sigma\omega) \qquad (6.59)$$

Inserting the Fourier decomposition of $p$ gives

$$c_{\sigma} = -i\left[\frac{2\pi}{\omega'}\right]^{\frac{1}{2}}\int_{-\infty}^{\infty} dt\, \exp[i\,\omega' t\,]\epsilon_z{}'\sum_{\mu} P_{\mu}\exp(i\,\mu\omega t\,)$$

$$= -i\left[\frac{2\pi}{\omega'}\right]^{\frac{1}{2}}\epsilon_z{}'\sum_{\mu}P_{\mu}2\pi\delta(\omega'+\mu\omega) \tag{.6.60}$$

so

$$T_{\sigma} = -i\left[\frac{2\pi}{\sigma\omega}\right]^{\frac{1}{2}}P_{-\sigma} \tag{.6.61}$$

Therefore the differential cross section is given by

$$\frac{d\sigma}{d\omega' d\Omega} = \frac{2\sin^2\theta'}{\pi^2 c^2 A_0^2\,\omega}\sum_{\sigma}\sigma\delta(\omega'-\sigma\omega)\int_0^{E_F}\frac{dE_z}{(2E_z)^{\frac{1}{2}}}(E_F - E_z)\,|P_{-\sigma}|^2 \tag{,6.62}$$

## 6.4 CHANGE IN KINETIC ENERGY IN WALL COLLISIONS

Previously I encountered the equation

$$\sum_n k_n \,|B_n|^2 \Theta(E_z + n\,\omega) = k_0 \qquad (6.63)$$

This is interpreted as the equation describing the conservation of flux. If the electron is spread out in a volume V then $k_0/V$ is the number of electrons per unit area per unit time incident on the wall. The quantity $k_n \,|B_n|^2/V$ is the flux scattered into the $n^{th}$ channel. Only open channels carry flux away from the wall so that the $\Theta$ function ensures that only they contribute to the sum. Let us now calculate the incident kinetic energy flux

$$J_E = \left(\frac{k_0^2}{2} + \frac{k_\|^2}{2}\right)\frac{k'_0}{V} \qquad (.6.64)$$

and the reflected kinetic energy flux

$$J_E' = \sum_n \frac{k_n \,|B_n|^2}{V}\left(\frac{k_n^2}{2} + \frac{k_\|'^2}{2}\right)\Theta\left(E_z + n\,\omega\right) \qquad (6.65)$$

The mean change in kinetic energy flux is the difference in the above two equations.

$$\Delta J_E = \frac{1}{V}\sum_n k_n \,|B_n|^2\left(\frac{k_n^2}{2} - \frac{k_0^2}{2}\right)\Theta\left(E_z + n\,\omega\right)$$

$$= \frac{1}{V}\sum_n k_n \,|B_n|^2 n\,\omega\Theta\left(E_z + n\,\omega\right) \qquad (6.66)$$

where I have made use of the fact that collision is specular, so $\vec{k}_\| = \vec{k}_\|'$ and have made use of the conservation of flux equation.

Let us examine the equation in perturbation theory.

$$\Delta J_E = \frac{1}{V}\left[k_1 |B_1|^2 \left(\frac{k_1^2}{2}-\frac{k_0^2}{2}\right)+k_{-1} |B_{-1}|^2 \left(\frac{k_{-1}^2}{2}-\frac{k_0^2}{2}\right)\Theta\left(E_z-\omega\right)\right]$$

$$= \frac{\omega}{V}\left[k_1 B_1^2 - k_{-1} B_{-1}^2\, \Theta\left(E_z-\omega\right)\right]$$

$$= \frac{x^2 k_0^2\, \omega}{V}\left[k_1 - k_{-1}\Theta\left(E_z-\omega\right)\right] \qquad (.6.67)$$

If I assume that $2\omega/ k_0^2 \ll 1$ so that I am in the low frequency domain, then $\Theta(E_z-\omega)=1$ and the n = -1 channel is open. I may expand $k_1-k_{-1}$ in powers of $2\omega/ k_0^2$ and find

$$k_1-k_{-1} = \frac{2\omega}{k_0}+\cdots \qquad (.6.68)$$

So

$$\Delta J_E = \frac{2k_0\omega^2 x^2}{V} \qquad (.6.69)$$

Dividing this by the incident flux gives an expression for the mean energy change

$$\Delta E = \frac{\Delta J_E}{\frac{k_0}{V}} = 2\omega^2 x^2 = 2\left(\frac{eA_0}{mc}\right)^2 \qquad (.6.70)$$

where I have restored e and m. This is twice the classical result.

It is perhaps disturbing at first sight that the quantum mechanical result is twice the classical answer. However, it must be realized that there is no scale length with which to compare the wavelength of the electron. The abruptness of the onset of the wall is always sharp compared with the wave length, no matter how high its energy is. Thus the classical limit is unattainable.

I see from the general formula

$$\Delta E = \sum_n \frac{k_n}{k_0} | B_n |^2 n \, \omega \Theta(E_z + n \, \omega) \qquad (.6.71)$$

that there are thresold breaks in the $\Delta E$ versus $\omega$ curve whenever $E_z / \omega$ passes through a negative integer value.

6.5 ALTERNATE METHOD

An alternate method for computing the $B_n$ coefficients follows from the real time expression for the boundary condition

$$\psi(0,t) = 0 = \exp(-iE_z t + \frac{ik_0 A_z}{c \, \omega} \sin\omega t)$$

$$+ \sum_n B_n \exp(-iE_z t - in \, \omega t - \frac{ik_n A_z}{c \, \omega} \sin\omega t)$$

which may be rewritten as

$$0 = 1 + \sum_n B_n \exp(-in \, \omega t - \frac{i(k_n + k_0)A_z}{c \, \omega} \sin\omega t) \qquad (.6.72)$$

I may discretize this by breaking up the period $2\pi / \omega$ into 2J+1 parts by letting

$$t_j = \frac{2\pi}{\omega} \frac{j}{2J+1} \qquad j = -J, \ldots, J \qquad (.6.73)$$

So

$$\sum_{n=-J}^{J} M_{jn} B_n = -1 \qquad (.6.74)$$

where I define a 2J+1 dimensional matrix

$$M_{jn} = \exp(-in\,\theta_j - i\,(k_0+k_n)x\,\sin\theta_j) \qquad (.6.75)$$

Here $x = A_0/c\,\omega$ and the phase angles are defined by

$$\theta_j = \omega t_j \qquad (.6.76)$$

The program DALTBVTST.F implements this alternate method. Results are shown in Fig.6.1 for the case where $E_z = .1$ and $\omega = .2$ . The logarithm of $|B_n|^2$ is plotted as a function of n for a number of x values. For x=0, $B_n = -\delta_{n\,0}$. As x increases the $B_n$ distribution widens including a significant contribution from more and more n. This is expected as nonlinear effects become more important. In this range I have let n range from -20 to 20 but only display the range from -10 to 10.

In Fig 6.2 I plot $|B_n|^2$ as a function of $\log_{10}x$ for several values of n. Here I took $E_z = .2$ and $\omega = 0.05$. In Fig 6.3 I plot $\log_{10}(|B_n|^2)$ vs $\log_{10}x$ for $n = 0$ to 5. I see that at small $x$ there is a power law behavior, as would be expected on the basis of perturbation theory. For larger values of x dressing becomes important and the magnitude of $B_n$ saturates and actually goes through zero.

## 6.6 POWER SERIES DEVELOPMENT

Let us make a power series expansion for the $B_n$ coefficients. I start with the equation

$$0 = 1 + \sum_n B_n \exp(-in\,\theta - i\,(k_0+k_n)x\,\sin\theta) \qquad (.6.77)$$

Let

$$W_n \equiv \frac{k_0+k_n}{2} \tag{.6.78}$$

So

$$0 = 1+\sum_n B_n \exp(-in\theta - xW_n(\exp(i\theta)-\exp(-i\theta))) \tag{.6.79}$$

Let us expand this to third order in x

$$0 = 1+\sum_n B_n \exp(-in\theta)\Big[1-xW_n(\exp(i\theta)-\exp(-i\theta))$$

$$+\frac{x^2}{2}W_n^2(\exp(2i\theta)+\exp(-2i\theta)-2)$$

$$-\frac{x^3}{6}W_n^3(\exp(3i\theta)-3\exp(i\theta)+3\exp(-i\theta)-\exp(-3i\theta)+\cdots \tag{.6.80}$$

I assume that $B_n \approx |x|^{|n|}$ ( and show that it satisfies this equation). If I group terms with similar powers of $\exp(i\theta)$ together I find

$$0 = \exp(-3i\theta)\left[B_3+xB_2W_2+\frac{x^2}{2}B_1W_1^2+\frac{x^3}{6}B_0W_0^3\right]$$

$$+\exp(-2i\theta)\left[B_2+xB_1W_1+\frac{B_0x^2}{2}W_0^2\right]$$

$$+\exp(-i\theta)\left[-xB_2W_2+B_1-B_1x^2W_1^2+B_0xW_0-\frac{x^3}{2}W_0^3B_0+\frac{x^2}{2}B_{-1}W_{-1}^2\right]$$

$$+\left[-xB_1W_1+B_0-B_0x^2W_0^2+xB_{-1}W_{-1}+1\right]$$

$$+\exp(+i\theta)\left[+xB_{-2}W_{-2}+B_{-1}-B_{-1}x^2W_{-1}^2-B_0xW_0+\frac{x^3}{2}W_0^3B_0+\frac{x^2}{2}B_1W_1^2\right]$$

$$+\exp(+2i\,\theta)\left[B_{-2}-xB_{-1}W_{-1}+\frac{B_0x^2}{2}W_0^2\right]$$

$$+\exp(+3i\,\theta)\left[B_{-3}-xB_{-2}W_{-2}+\frac{x^2}{2}B_{-1}W_{-1}^2-\frac{x^3}{6}B_0W_0^3\right] \quad (.6.81)$$

Let

$$B_0 = b_0+d_0x^2+.. \quad (.6.82)$$

$$B_1 = c_1x+e_1x^3+.. \quad (.6.83)$$

$$B_2 = d_2x^2+.. \quad (.6.84)$$

$$B_3 = e_3x^3+.. \quad (.6.85)$$

$$B_{-1} = c_{-1}x+e_{-1}x^3+.. \quad (6.86)$$

$$B_{-2} = d_{-2}x^2+.. \quad (6.87)$$

$$B_{-3} = e_{-3}x^3+.. \quad (6.90)$$

I proceed to solve for the 10 unknowns $b_0, d_0, c_1, e_1, d_2, e_3, c_{-1}, e_{-1}, d_{-3}, e_{-3}$.

Equating like powers of x and like powers of $exp\,(i\,\theta)$ leads to 10 equations for the 10 unknowns

$$\frac{W_0^3}{6}b_0+\frac{W_1^2}{2}c_1+W_2d_2+e_3 = 0 \quad (.6.91)$$

$$\frac{W_0^2}{2}b_0+W_1c_1+d_2 = 0 \quad (.6.92)$$

$$\frac{W_{-1}^2}{2}c_{-1}+W_0d_0-\frac{W_0^3}{2}b_0+e_1-W_1^2c_1-W_2d_2=0 \quad (6.93)$$

$$W_0b_0+c_1=0 \quad (6.94)$$

$$W_{-1}c_{-1}+d_0-W_0^2b_0-W_1c_1=0 \quad (6.95)$$

$$b_0=-1 \quad (6.96)$$

$$W_{-2}d_{-2}+e_{-1}-c_{-1}w_{-1}^2-W_0d_0+\frac{W_0^3}{2}b_0+\frac{W_1^2}{2}c_1=0 \quad (6.97)$$

$$c_{-1}-W_0b_0=0 \quad (6.98)$$

$$d_{-2}-W_{-1}c_{-1}+\frac{W_0^2}{2}b_0=0 \quad (6.99)$$

$$e_{-3}-W_{-2}d_{-2}+\frac{W_{-1}^2}{2}c_{-1}-\frac{W_0^3}{6}b_0=0 \quad (6.100)$$

Solving for the unknowns I get

$$b_0=-1 \quad (6.101)$$

$$d_0=W_0(W_1+W_{-1}-W_0) \quad (6.102)$$

$$c_1=W_0 \quad (6.103)$$

$$e_1=\frac{W_0^3}{2}-\frac{W_0^2}{2}(2W_1+2W_{-1}-W_2)+W_0(\frac{W_{-1}^2}{2}+W_1^2-W_1W_2) \quad (6.104)$$

$$d_2=\frac{W_0^2}{2}-W_0W_1 \quad (6.105)$$

$$e_3 = \frac{W_0^3}{6} - \frac{W_0}{2} W_1^2 - \frac{W_0^2}{2} W_2 + W_0 W_1 W_2 \tag{6.106}$$

$$c_{-1} = -W_0 \tag{6.107}$$

$$e_{-1} = -\frac{W_0^3}{2} + \frac{W_0^2}{2}(2W_1 + 2W_{-1} - W_{-2}) - W_0\left(\frac{W_1^2}{2} + W_{-1}^2 - W_{-1}W_{-2}\right) \tag{6.108}$$

$$d_{-2} = \frac{W_0^2}{2} - W_0 W_{-1} \tag{6.109}$$

$$e_{-3} = -\frac{W_0^3}{6} + \frac{W_0}{2} W_{-1}^2 + \frac{W_0^2}{2} W_{-2} - W_0 W_1 W_2 \tag{6.110}$$

The $B_n$ coefficients have some elementary symmetry properties. First note that the functional dependence of $B_n$ is

$$B_n = B_n\left(\frac{\omega}{k_0^2}, k_0 x\right) \tag{6.111}$$

In the equation

$$0 = 1 + \sum_n B_n\left(\frac{\omega}{k_0^2}, k_0 x\right) \exp(-in\,\theta - i\,(k_0 + k_n)\,x \sin\theta) \tag{6.112}$$

replace $\theta$ by $-\theta$ , x by -x , $\omega$ by $-\omega$ and n by -n. I then find the equation restored and

$$B_{-n}\left(-\frac{\omega}{k_0^2}, -k_0 x\right) = B_n\left(\frac{\omega}{k_0^2}, k_0 x\right) \tag{6.113}$$

Similarly, if I replace $\theta$ by $\pi-\theta$ , then change $\theta$ to $-\theta$ and replace x by -x I find

$$B_n\left(\frac{\omega}{k_0^2}, -k_0 x\right) = (-1)^n\, B_n\left(\frac{\omega}{k_0^2}, k_0 x\right) \tag{6.114}$$

For this formula it follows that $B_n$ is an even function of x for even n and an odd function of x for odd n.

## 6.7 RESULTS

I begin by solving the set of linear algebraic equations given by 6.25. Use is made of the PORT library subroutine CLINQ to do the linear algebra and the NUMERICAL RECIPES program BESSI to evaluate the modified Bessel function. The program BVECTST.FOR was written to evaluate the $B_n$ coefficients appearing in 6.25. These coefficients depend on two parameters: $y = k_0 A_0 / \omega c$ and $z = \omega / E_z$

In the first run I truncate the linear equations to a set of 15 coupled equations. The program was run for the parameters (y,z) = (0.1,0.1). The real and imaginary parts of the $B_n$ matrix ( -7 <= n <= 7 ) are printed out. Below them appear the results from the approximate low frequency formula Eq. 6.29. The results are in good agreement since z<<1. Note that the largest $B_n$ coefficients occur for n=0. This is expected, since y<<1.

I repeat the calculation for the 31 coupled equations and find that the values of $B_n$ coefficients are mainly unaltered, showing that convergence has been attained. It is also noted that as z and y are increased to (.89,.5) the values of the $B_n$ coefficients get to be larger for larger n. For large z I also see that the approximate formula becomes unreliable. I also see significant departures from the perturbation results appearing in this run.

For comparison I also display the results based on the perturbation theory expressions beneath them for the cases n = -2,-1,0,1 and 2. Only the leading power in the perturbation expression is included. For the case of small y I see that the perturbation formula is quite good.

The program DALTBV4.F computes the average change in energy for an electron striking a wall in the presence of an electromagnetic field. Results are presented in Fig. 6.4 for the case in which $E_z = 0.1$ and $\omega$=0.05 (atomic units ). In order to get convergence for large x, it was found to be necessary to calculate with large matrices (e.g. 81) and to use double precision arithmetic. The plot of $\Delta E$ vs x is similar to that found classically except that there are no sharp discontinuities due to multiple wall collisions. The curve departs somewhat from the perturbation formula $\Delta E = 2(\omega x)^2$ for $x \geqslant 4$ in this case . Classically this departure was attributed to multiple wall collisions. Also shown in Fig 6.5 are results for $E_z$ = 0.1 and $\omega$ = 0.2. Here I see the approximate solution slightly above the exact solution as opposed to the previous figure in which it was reversed.

## 6.8 AVERAGE ENERGY ABSORBED PER COLLISION BY THE FERMI SEA

Let us now study the process of energy absorption of a bounded Fermi sea of electrons. Particular interest will center on the average energy change an electron experiences when it collides with a wall in the presence of an intense electromagnetic wave. The change of energy flux is given by the previous formula but now summed over the Fermi sea with appropriate Fermi factors included to ensure that the Pauli principle is obeyed.

$$\Delta J_E = \sum_s \sum_{\vec{k}} \sum_n f_k^{(-)} f_f^{(+)} k_n \, |B_n|^2 \left[ \frac{k_n^2}{2} - \frac{k_0^2}{2} \right] \Theta(E_z + n\omega) \tag{6.115}$$

where the final energy is

$$E_F = E_z + \frac{k_{\parallel}^2}{2} + n\,\omega$$

$$= \frac{k_0^2}{2} + \frac{k_{\parallel}^2}{2} + n\,\omega \tag{6.116}$$

Because of the Fermi factors, only positive n will contribute. I may rewrite the change in energy flux as

$$\Delta J_E = \sum_n 2\int \frac{d^2k_{\parallel}}{(2\pi)^3}\int_0^{\infty} dk_0\,\Theta\left(\frac{k_{\parallel}^2}{2}+E_z+n\,\omega-E_F\right)\Theta\left(E_F-\frac{k_{\parallel}^2}{2}-E_z\right)$$

$$k_n\,|B_n|^2 n\,\omega\Theta(E_z+n\,\omega) \tag{6.117}$$

The integral over transverse momenta is readily performed

$$\int \frac{d^2k_{\parallel}}{(2\pi)^2}\Theta\left(E_F-\frac{k_{\parallel}^2}{2}-E_z\right)\Theta\left(\frac{k_{\parallel}^2}{2}+E_z+n\,\omega-E_F\right)$$

$$= \frac{1}{2\pi}\min\left(n\,\omega, E_F-E_z\right)\Theta\left(E_F-E_z\right) \tag{6.118}$$

So

$$\Delta J_E = \sum_{n=1}^{\infty}\frac{1}{2\pi^2}\int_0^{E_F} dE_z\,\min(n\,\omega, E_F-E_z)\frac{k_n}{k_0}\,|B_n|^2 n\,\omega \tag{6.119}$$

The total flux of incident electrons is

$$J_e = \sum_s\sum_{\vec{k}} k_0 f_k^{(-)}$$

$$= 2\int_0^{\infty}\frac{dk_0}{2\pi}k_0\int\frac{d^2k_{\parallel}}{(2\pi)^2}\Theta(E_F-\frac{k_{\parallel}^2}{2}-E_z)$$

$$= \frac{1}{2\pi^2}\int_0^{E_F} dE_z\,(E_F - E_z)$$

$$= \frac{1}{4\pi^2}E_F^2 \tag{.6.120}$$

Hence the average energy change is

$$\Delta E = \frac{\Delta J_E}{\Delta J}$$

$$= \frac{2}{E_F^2}\sum_{n=1}^{\infty}\int_0^{E_F} dE_z \min(n\,\omega, E_F - E_z)\frac{k_n}{k_0}\,|B_n|^2 n\,\omega \tag{.6.121}$$

## 6.9 CALCULATION OF VELOCITY FOURIER COEFFICIENTS

The procedure for calculating the Fourier coefficients $p_\mu$ involves making a Fourier expansion of $P_z(t)$ at a series of times in the interval 0 to $2\pi/\omega$. Thus I let

$$P(t_j) = \sum_\mu P_\mu exp\,(i\,\mu\omega t_j) \tag{.6.122}$$

where

$$\theta_j = \frac{2\pi j}{2J+1} = \omega t_j \qquad j = 0,1,\ldots 2J \tag{.6.123}$$

Then from the Fourier expression for the coefficients.

$$P_\mu = \frac{1}{2J+1}\sum_j P(t_j) exp\,(-i\frac{2\pi j\,\mu}{2J+1})$$

The real time behavior of P(t) is given by

$$P(t) = \sum_n \frac{ik_n B_n}{k_0+k_n} \exp(-in\,\omega t - i(k_n + k_0)x \sin\omega t)$$

$$+\sum_n \frac{ik_0 B_n^*}{k_0+k_n} \exp(in\,\omega t + i(k_n^* + k_0)x \sin\omega t)$$

$$+\sum_n \frac{ik_n |B_n|^2}{k_n - k_n^*} \exp(+i(-k_n + k_n^*)x \sin\omega t)\Theta(-E_z - n\,\omega)$$

$$+ \sum_{n,n',n\neq n'} \frac{ik_n B_n B_{n'}^*}{k_n - k_{n'}^*} \exp(i(n'-n)\omega t + i(-k_n + k_{n'}^*)x \sin\omega t) \qquad (6.124)$$

where $x = \frac{A_0}{c\,\omega}$

The Fourier coefficients $v_\mu$ are computed using the program MOMENTUM.FOR . In this program I renormalize $p(t)$ by dividing by $<\psi|\psi>$ so

$$v_\mu = \frac{P_\mu}{1+\sum_n |B_n|^2\Theta(E_z + n\,\omega)} \qquad (6.125)$$

Typical results are given in Fig. 6.6 for the case $E_z = 0.1$ and $\omega = 0.05$ . I plot $|P_\mu|$ vs $x$ on a log-log plot in order to illustrate the power law behavior expected from perturbation theory. Results are presented for $\mu$=1,2,3 and 4.

# 7. THE SHARP-STEP POTENTIAL

## 7.1 GENERAL THEORY

In my previous study of the sharp step potential I looked at processes in which $n$ photons of frequency $\omega$ were absorbed and an electron photoemitted or in which a single photon $\omega'=n\,\omega$ was emitted. These processes, however, corresponded to 'undressed' nonlinear effects. If I were to consider 'dressed' processes then many more than n photons could be involved in an apparent $n^{th}$ order process. I could, for example, have $N$ photons involved (where $N>n$ ). In the photoemission process $N$ photons are absorbed, $N-n$ are reemitted into the driving mode and the remaining energy $n\,\omega$ goes into exciting the electron. Similarly in the dressed multiharmonic generation process I could have $N$ photons absorbed, $N-n$ reemitted into the driving mode and $n\,\omega=\omega'$ emitted into a single radiated photon. The study in the present chapter is undertaken, in part, to study the effect of dressing on nonlinear processes.

The potential energy is of the form

$$V(z)=\begin{cases} V_0/2 & \text{if} \quad z>0 \\ -V_0/2 & \text{if} \quad z<0 \end{cases} \tag{7.1}$$

I expand the wave function in the domain $z<0$ in terms of a perturbed plane wave incident on the surface and a sum of reflected waves

$$\psi(z,t)=exp\left(ik_0z-iE_z(t+T)-\frac{ik_0A_0}{c\,\omega}\text{fiin}\omega t\right)$$

$$+\sum_n \overline{D_n}\, exp\left(-ik_n z - i(E_z + n\omega)(t+T) + \frac{ik_n A_0}{c\,\omega}\sin\omega t\right) \quad (7.2)$$

where

$$k_n = \left[2(E_z + n\omega) + V_0\right]^{1/2} \quad (7.3)$$

and

$$\gamma_n = \left[V_0 - 2(E_z + n\omega)\right]^{1/2} \quad (7.4)$$

The $\overline{D_n}$ coefficients correspond to 'reflection' coefficients for the various inelastic channels. For $z > 0$ I likewise have an expansion

$$\psi(z,t) = \sum_n \overline{F_n}\, exp\left(-\gamma_n z - i(E_z + n\omega)(t+T) + \frac{\gamma_n A_0}{c\,\omega}\sin\omega t\right) \quad (7.5)$$

where $\overline{F_n}$ are a set of 'transmission' coefficients. It should be noted that $D_n$ and $F_n$ describe the coupling to both open (reflecting or transmitting ) and closed (attenuating ) channels.

Matching boundary conditions at $z=0$ lead to the coupled set

$$\sum_n D_n \exp(-in\,\theta_j + ik_n x \sin\theta_j) - \sum_n F_n \exp(-in\,\theta_j + \gamma_n x \sin\theta_j) = -exp(-ik_0 x \sin\theta_j)$$

(7.6)

$$\sum_n ik_n D_n \exp(-in\,\theta_j + ik_n x \sin\theta_j) - \sum_n \gamma_n F_n \exp(-in\,\theta_j + \gamma_n x \sin\theta_j) = ik_0 \exp(-ik_0 x \sin\theta_j)$$

(7.7)

where $D_n = \overline{D_n}\exp(-in\,\omega T)$ and $F_n = \overline{F_n}\exp(-in\,\omega T)$ . These equations are similar in form to those found previously in the case of the wall potential. I may, in fact , create a super-vector from the 2J+1 $D_n$ coefficients and 2J+1 $F_n$ coefficients.

$$G_n = \begin{pmatrix} D_n \\ F_n \end{pmatrix} \tag{7.8}$$

and write these equations as the matrix equation.

$$\sum_{n'=1}^{4J+2} M_{jn} G_n = R_j \tag{7.9}$$

where $j = 1,...,4J+2$ and

$$R_j = -exp(-ik_{0x} \sin\theta_j) \qquad j \leq 2J+1$$

$$= ik_{0}\exp(-ik_{0x} \sin\theta_{j-2J-1}) \qquad j > 2J+1 \tag{7.10}$$

The M matrix elements are defined in the linear equations written before. By solving these linear equations I determine $G_n$, and hence $D_n$ and $F_n$. The program DFVALTST.FOR was written to calculate the set of $D_n$ and $F_n$ coefficients.

Explicit formulas for the lowest order $D_n$ and $F_n$ coefficients in the undressed limit may be obtained by truncating the linear equations and solving the algebra explicitly. I find

$$D_0 = \frac{ik_0 + \gamma_0}{ik_0 - \gamma_0} \tag{7.11}$$

$$F_0 = 2\frac{ik_0}{ik_0 - \gamma_0} \tag{7.12}$$

$$D_1 = -\frac{k_{0x}}{2\gamma_0}(\gamma_0 + ik_0)(\gamma_1 + ik_1) \tag{7.13}$$

$$F_1 = -\frac{k_{0x}}{2\gamma_0}(\gamma_0 + ik_0)(\gamma_1 + ik_1) \tag{7.14}$$

These formulas are useful in checking computer program.

## 7.2 MULTIHARMONIC GENERATION

Using the form of the time dependent wave function I may calculate the expectation value of the momentum operator.

$$<p_z> = \int_{-L}^{0} dz \left\{ \exp(-ik_0 z) + \sum_n D_n^* \exp(ik_n^* z + in\,\omega t - i(k_0 + k_n^*) \frac{A_0}{c\,\omega} \sin\omega t) \right\}$$

$$\left\{ k_0 \exp(ik_0 z) - \sum_m k_m D_m \exp(-ik_m z - im\,\omega t + i(k_0 + k_m) \frac{A_0}{c\,\omega} \sin\omega t) \right\}$$

$$+ \int_0^L dz \left\{ \sum_n F_n^* \exp(-\gamma_n^* z + in\,\omega t + (\frac{\gamma_n^* A_0}{c\,\omega} \sin\omega t)) \right\}$$

$$\left\{ \sum_m i\,\gamma_m F_m \exp(-\gamma_m z - im\,\omega t + \frac{\gamma_m A_0}{c\,\omega} \sin\omega t \right\} \qquad (7.15)$$

Here the solid occupies the space $z = -L$ to 0 and the vacuum occupies the space $z = 0$ to $L$ .The integral may be written as the sum of two types of terms. The $L$ - dependent terms are

$$<p_z>_L = L \sum_n q_n \mid F_n \mid^2 \Theta(2(E_z + n\,\omega) - V_0) + L \left[ k_0 - \sum_n k_n \mid D_n \mid^2 \Theta(2(E_z + n\,\omega) + V_0) \right] \qquad (7.16)$$

These coefficients are, in fact, equal. $p_z / (2L)$ is proportional to the net photo-current emerging from the solid. Thus $\sum_n q_n \mid F_n \mid^2$ is the relative probability of exciting the n-photon photoemission channel. The L-independent terms are

$$<p_z> = -i \sum_m \frac{k_m}{k_0 + k_m} D_m \, exp\,(-im\,\omega t + i(k_m + k_0)x \sin\omega t)$$

$$-i\sum_n \frac{k_0}{k_0+k_n^*} D_n^* exp\,(+in\,\omega t\,-i\,(k_n^*+k_0)x\,\sin\omega t\,)$$

$$+i\sum_{n,m\;n\neq m} \frac{k_m}{k_n^*-k_m} D_n^* D_m\,exp\,(i\,(n-m\,)\omega t\,+i\,(k_m-k_n^*)x\,\sin\omega t\,)$$

$$+i\sum_n k_n\,\frac{|D_n|^2}{k_n^*-k_n}\exp(i\,(k_n-k_n^*)x\,\sin\omega t\,)\Theta(-2E_z-2n\,\omega-V_0)$$

$$+i\sum_{n,m\;n\neq m} \frac{q_m}{\gamma_n^*+\gamma_m} F_n^* F_m\,exp\,(i\,(n-m\,)\omega t\,+i\,(\gamma_m+\gamma_n^*)x\,\sin\omega t\,)$$

$$+i\sum_n \gamma_n\,\frac{|F_n|^2}{\gamma_n^*+\gamma_n}\exp((\gamma_n+\gamma_n^*)x\,\sin\omega t\,)\Theta(-2E_z-2n\,\omega+V_0) \qquad (7.17)$$

where I have let

$$q_n = (2(E_z+n\,\omega)-V_0)^{1/2} \qquad (7.18)$$

and set

$$-\gamma_n = iq_n \qquad (7.19)$$

Recalling that the velocity expectation value is

$$v_z = \frac{\langle\psi\,|\,p_z\,|\,\psi\rangle}{\langle\psi\,|\,\psi\rangle}+\frac{1}{c}A_z \qquad (7.20)$$

I evaluate the normalization integral

$$\langle\psi\,|\,\psi\rangle = \int_{-L}^{0} dz \left[\exp(-ik_0 z\,)+\sum_n D_n^* \exp(ik_n^* z\,+in\,\omega t\,-i\frac{(k_n^*+k_0)}{c\,\omega}A_0\sin\omega t\,)\right]$$

$$\left[\exp(ik_0 z\,)+\sum_n D_n \exp(-ik_n\,z\,-in\,\omega t\,+i\frac{(k_n+k_0)}{c\,\omega}A_0\sin\omega t\,)\right]$$

$$+\int_0^L \sum_n F_n^* \exp(-\gamma_n^* z + in\,\omega t + \frac{\gamma_n^* A_0}{c\,\omega}\sin\omega t\,)$$

$$\sum_m F_m \exp(-\gamma_m z - im\,\omega t + \frac{\gamma_m A_0}{c\,\omega}\sin\omega t\,) \tag{7.21}$$

This may be expressed as a sum of L dependent terms:

$$<\psi \mid \psi>_L \;= L\left[1+\sum_n [\,\mid D_n \mid^2 \Theta(E_z + n\,\omega + \frac{V_0}{2}) + \mid F_n \mid^2 \Theta(E_z + n\,\omega - \frac{V_0}{2})]\right] \tag{.7.22}$$

The L-independent terms are

$$<\psi \mid \psi>' = i\sum_m \frac{D_m}{k_0+k_m} exp\,(-im\,\omega t + i\,(k_m + k_0)x\,\sin\omega t\,)$$

$$-i\sum_m \frac{D_m^*}{k_0+k_m^*} exp\,(+im\,\omega t - i\,(k_m^* + k_0)x\,\sin\omega t\,)$$

$$-i\sum_{n,m\;n\neq m} \frac{D_n^* D_m}{k_n^* - k_m} exp\,(i\,(n-m\,)\omega t + i\,(k_m - k_n^*)x\,\sin\omega t\,)$$

$$-i\sum_n \frac{\mid D_n \mid^2}{k_n^* - k_n} \exp(i\,(k_n - k_n^*)x\,\sin\omega t\,)\Theta(-2E_z - 2n\,\omega - V_0)$$

$$+\sum_{n,m\;n\neq m} \frac{F_n^* F_m}{\gamma_n^* + \gamma_m} exp\,(i\,(n-m\,)\omega t + (\gamma_m + \gamma_n^*)x\,\sin\omega t\,)$$

$$+\sum_n \frac{\mid F_n \mid^2}{\gamma_n^* + \gamma_n} \exp((\gamma_n + \gamma_n^*)x\,\sin\omega t\,)\Theta(-2E_z - 2n\,\omega + V_0)$$

$$= \sum_\mu N_\mu \exp(i\,\mu\omega t\,) \tag{7.23}$$

If I evaluate the velocity expectation value then in addition to the DC term

$$\langle v_z \rangle_{DC} = \frac{k_0 - \sum_n k_n \mid D_n \mid^2 \Theta(E_z + n\,\omega + \frac{V_0}{2}) + \sum_n q_n \mid F_n \mid^2 \Theta(E_z + n\,\omega - \frac{V_0}{2})}{1 + \sum_n \mid D_n \mid^2 \Theta(E_z + n\,\omega + \frac{V_0}{2}) + \sum_n \mid F_n \mid^2 \Theta(E_z + n\,\omega - \frac{V_0}{2})} \qquad (7.24)$$

I have the $L$ -independent term

$$\langle v_z \rangle' = \frac{\sum_\mu (p_\mu - \langle v \rangle_{DC} N_\mu) \exp(i\,\mu\omega t)}{1 + \sum_n \mid D_n \mid^2 \Theta(E_z + n\,\omega + \frac{V_0}{2}) + \sum_n \mid F_n \mid^2 \Theta(E_z + n\,\omega - \frac{V_0}{2})}$$

$$= \sum_\mu v_\mu \exp(i\,\mu\omega t) \qquad (7.25)$$

It is interesting to note that there is now a contribution stemming from the DC current which is time-dependent. The correction did not exist previously for the hard wall problem because there was no DC current.

The program DVEL1.F evaluates the velocity Fourier coefficients. In Fig 7.1 I show the average DC velocity of the photoemitted electrons as a function of $x$ for the case $E_z$ =0.1, $\omega$=0.049 and $V_0$=0.25. I included values of $x$ ranging from -10 to +10 in the calculation. For small $x$ I notice that the photocurrent is proportional to $x^2$. This is expected because a single photon is able to promote an electron to a state in which it is able to leave the solid. For large values of $x$ , nonlinearities begin to appear.

In Fig. 7.2 I show the velocity Fourier coefficients $v_\mu$ plotted as a function of $x$ for several values of $n$ . Again I see power law behavior of these coefficients at small $x$ (with evidence of nonlinearity setting in at larger $x$ ). The corresponding $F_n$ and $D_n$ coefficients are present in Figs 7.3 and 7.4. Note that the symmetry between $n$ =1 and $n$ =−1 is fairly well maintained whereas the n=2 and n=-2 symmetry is broken.

In Figs 7.5 and 7.6 I show the variation of $|D_n|^2$ and $|F_n|^2$ with $n$, respectively. Graphs are presented for several values of $x$. I note that as the order $n$ decreases in magnitude the values of the coefficients falls off, as would be expected.

# 8. SMOOTH STEP POTENTIAL

## 8.1 INTRODUCTION

In the previous chapters I studied oversimplified models of the solid surface in order to elucidate the underlying physics. I started with the hard wall case in which there were no characteristic parameters describing the surface. There was only the depth of the Fermi sea. I then studied the sharp potential step case. Here the solid was characterized by the size of the potential step. Alternatively , the solid was described by a work function as well as a Fermi energy. In this section I go on to consider the effect of a rounded potential step. A new parameter will be introduced - the distance over which the solid's potential relaxes to the vacuum.

I can expect this new parameter to have some influence on the physics of nonlinear processes. If I recall, a free electron does not absorb energy at all. The reason that energy absorption is possible is that momentum is provided by the presence of the spatial variation of the potential. In my discussion, this has been provided by the surface of the solid. The range over which the surface potential varies governs the strength of the Fourier components of the momentum. In the limit where the smooth step varies over a large distance I could expect the non-linear effects to be very weak. In the other limit the sharp step results should be approached.

## 8.2 THE UNPERTURBED SOLID

The Schrodinger equation describing the unperturbed solid is

$$\left[\frac{p^2}{2}+V(z)-E\right]\phi(\vec{r}) = 0 \tag{8.1}$$

where

$$\phi(\vec{r}) = \phi(z)\exp(i\vec{k}_{//}\cdot\vec{r}_{//}) \tag{8.2}$$

so

$$\left[-\frac{1}{2}\frac{d^2}{dz^2}+V(z)-E_z\right]\phi(z) = 0 \tag{8.3}$$

where I have defined the kinetic energy associated with the z- motion

$$E_z = E - \frac{k_{//}^2}{2} \tag{8.4}$$

In my theory use will be made of a particular form for the potential energy function

$$V(z) = \frac{V_0}{2}\tanh\left(\frac{sz}{2}\right) \tag{8.5}$$

where $V_0$ is the depth of the inner potential of the solid and $1/s$ is the length over which the potential relaxes from its inner value to the vacuum level. This potential defines a generalized Sommerfeld model. In the limit $s \to \infty$ I regain the sharp step behavior of the conventional Sommerfeld model. The solution to this Schrodinger equation is known and appears in Landau and Lifschitz's book "Quantum Mechanics". However, the coordinate transformation used by them will not lend itself to generalization later, so I start by solving the equation in a different manner. In my solution to the Schrodinger equation I discuss separately the regions $z < 0$ and $z > 0$.

### Case 1. Positive $z$

The potential function may be expanded in powers of $\exp(-sz)$ and this expansion will be convergent for $z > 0$

$$V(z) = \frac{V_0}{2} + V_0 \sum_{n=1}^{\infty} (-1)^n \exp(-nsz) \tag{8.6}$$

The Schrodinger equation possesses two different types of solutions, depending on whether the energy $E_z$ lies above or below the top of the potential barrier. If the energy is below the top of the barrier the electron is bound to the solid. The spectrum is a nondegenerate continuum as far as z-motion is concerned. If the energy lies above the barrier then left- traveling and right-traveling waves constitute independent solutions with the same energy. I will refer to these states as the degenerate continuum. In the case of photoemission to be studied later, for example, the electromagnetic wave causes a transition to occur between a nondegenerate continuum state and a degenerate continuum state.

### Case 1a. The nondegenerate continuum

$$|E_z| < V_0 / 2$$

Let me look for a solution to the Schrodinger equation of the form

$$\phi(z) = \sum_{n=0}^{\infty} u_n \exp[-(\gamma+n)sz] \tag{8.7}$$

Inserting this into the Schrodinger equation gives

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} + \frac{V_0}{2} + V_0 \sum_{m=1}^{\infty} (-1)^m \exp(-msz) - E_z\right] \sum_{n=0}^{\infty} u_n \exp[-(\gamma+n)sz] = 0 \tag{8.8}$$

Rearranging some terms in the sum and making use of the matrix relation

$$\sum_{m=1}^{\infty}\sum_{j=m}^{\infty} A_{mj} = \sum_{j=1}^{\infty}\sum_{m=1}^{j} A_{mj} \tag{8.9}$$

leads to the formula

$$\sum_{n=0}^{\infty} u_n \exp[-(\gamma+n)sz]\left[-\frac{1}{2}s^2(\gamma+n)^2 + \frac{V_0}{2} - E_z\right]$$

$$+ V_0 \sum_{j=1}^{\infty}\sum_{m=1}^{j}(-1)^m u_{j-m} \exp[-(\gamma+j)sz] = 0 \tag{8.10}$$

Since this is effectively a power series in the variable $\exp(-sz)$ and the series equals zero, each coefficient in the series must vanish

$$\left[-\frac{s^2}{2}(\gamma+n)^2+\frac{V_0}{2}-E_z\right]u_n + V_0\left[1-\delta_{n0}\right]\sum_{m=1}^{n}(-1)^m u_{n-m} = 0 \tag{8.11}$$

These define a set of algebraic equations which may be solved recursively.

For $n=0$ the equation is

$$\left[-\frac{(s\gamma)^2}{2} + \frac{V_0}{2} - E_z\right]u_0 = 0 \tag{8.12}$$

so

$$\gamma = \frac{1}{s}(V_0-2E_z)^{\frac{1}{2}} \tag{8.13}$$

I choose the positive square root so that the state will decay into the vacuum region. As $z \to \infty$

$$\phi(z) \to u_0 \exp[-z(V_0-2E_z)^{\frac{1}{2}}] \tag{8.14}$$

as would be expected for the step potential.

For $n>0$ I solve the algebraic equations as follows

$$u_n = \frac{V_0 \sum_{m=1}^{n} (-1)^m u_{n-m}}{\frac{s^2}{2}(\gamma+n)^2+E_z-\frac{V_0}{2}}$$

$$= \frac{2V_0 \sum_{m=1}^{n} (-1)^m u_{n-m}}{s^2 n(n+2\gamma)} \tag{8.15}$$

which reduces to

$$u_{n+1} = -\frac{2V_0}{s^2}\frac{1+\frac{s^2}{2V_0}n(n+2\gamma)}{(n+1)(n+1+2\gamma)}u_n \tag{8.16}$$

Iteratating this expression gives

$$u_n = \left[-\frac{2V_0}{s^2}\right]^n \frac{u_0\Gamma(2\gamma+1)}{n!\Gamma(n+2\gamma+1)} \prod_{m=1}^{n} \left[1+\frac{s^2}{2V_0}(n-m)(n-m+2\gamma)\right] \tag{8.17}$$

I can verify that the solution is convergent for $z>0$ by examining the large $n$ behavior. For large $n$

$$u_n \rightarrow -u_{n-1} \tag{8.18}$$

which is solved by

$$u_n = C(-1)^n \tag{8.19}$$

Then

$$\sum_{n=0}^{\infty} u_n \exp[-(\gamma+n)sz] \rightarrow \frac{C\exp(-\gamma sz)}{1+\exp(-sz)} \tag{8.20}$$

A further simplification follows by noting that the product

$$P = \prod_{m=1}^{n} \left[ 1 + \frac{s^2}{2V_0}(n-m)(n-m+2\gamma) \right] =$$

$$\left[ \frac{s^2}{2V_0} \right]^n \prod_{l=0}^{n-1} (l+\gamma+ik)(l+\gamma-ik) =$$

$$\left[ \frac{s^2}{2V_0} \right]^n \frac{\Gamma(\gamma+ik+n)\Gamma(\gamma-ik+n)}{\Gamma(\gamma+ik)\Gamma(\gamma-ik)} \tag{8.21}$$

where

$$k = \frac{1}{s}(2E_z + V_0)^{\frac{1}{2}} \tag{8.22}$$

so finally

$$u_n = (-1)^n u_0 \frac{\Gamma(2\gamma+1)\Gamma(\gamma+ik+n)\Gamma(\gamma-ik+n)}{n!\Gamma(n+2\gamma+1)\Gamma(\gamma+ik)\Gamma(\gamma-ik)} \tag{8.23}$$

**Case 1b. The degenerate continuum $E_z > V_0/2$**

In general I have two degenerate continuum states to examine, the out-state and the in-state. The out-state has a wave of unit amplitude leaving the solid in the vacuum region and an incoming wave in that region as well. In the interior of the solid it has a wave directed towards the surface. If I were to create a wave packet by superimposing such waves, then at early times the out-wave would have amplitude both in the vacuum region as well as the solid region, but at later times only the wave travelling away from the solid in the vacuum region will be present. It is the out-state that is of primary concern to me in the photoemission problem.

The solution to the Schrodinger equation may be expanded in the form (for $z > 0$)

$$\phi(z) = \sum_{n=0}^{\infty} g_n \exp[i(q+in)sz)] + \sum_{n=0}^{\infty} h_n \exp[-i(q-in)sz)] \quad (8.24)$$

The quantity $q$ denotes the propagation vector of the wave in the vacuum region. To get the out-state I choose

$$g_0 = 1 \quad (8.25)$$

The Schrodinger equation becomes

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} + \frac{V_0}{2} + V_0 \sum_{m=1}^{\infty} (-1)^m \exp(-msz) - E_z\right] \sum_{n=0}^{\infty} g_n \exp[i(q+in)sz] +$$

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} + \frac{V_0}{2} + V_0 \sum_{m=1}^{\infty} (-1)^m \exp(-msz) - E_z\right] \sum_{n=0}^{\infty} h_n \exp[-i(q-in)sz] = 0 \quad (8.26)$$

Comparing this to the previous case studied, I see that the first term is the same except for the replacement

$$u_n \rightarrow g_n \quad (8.27)$$

and

$$\gamma \rightarrow -iq \quad (8.28)$$

The second term is the same except for the replacement

$$u_n \rightarrow h_n \quad (8.29)$$

and

$$\gamma \rightarrow iq \quad (8.30)$$

Hence I can take over the previous solutions and obtain

$$g_n = (-1)^n \frac{\Gamma(1-2iq)\Gamma(n+ik-iq)\Gamma(n-ik-iq)}{n!\Gamma(n+1-2iq)\Gamma(ik-iq)\Gamma(-ik-iq)} \tag{8.31}$$

$$h_n = (-1)^n h_0 \frac{\Gamma(1+2iq)\Gamma(n+ik+iq)\Gamma(n-ik+iq)}{n!\Gamma(n+1+2iq)\Gamma(ik+iq)\Gamma(-ik+iq)} \tag{8.32}$$

where

$$q = \frac{1}{s}(2E_z - V_0)^{\frac{1}{2}} \tag{8.33}$$

**Case 2. Negative $z$**

The potential function may be expanded in powers of $\exp(sz)$ and this expansion will be convergent for $z<0$

$$V(z) = -\frac{V_0}{2} - V_0 \sum_{n=1}^{\infty} (-1)^n \exp(nsz) \tag{3.34}$$

This could simply be obtained from my result for $z>0$ by using $V(-z)=-V(z)$.

**Case 2a. The nondegenerate continuum $|E_z|<V_0/2$**

I expand the solution in the form

$$\phi(z) = \sum_{n=0}^{\infty} v_n \exp[(n+ik)sz] + \sum_{n=0}^{\infty} v_n' \exp[(n-ik)sz] \tag{8.35}$$

The Schrodinger equation becomes

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} - \frac{V_0}{2} - V_0 \sum_{m=1}^{\infty} (-1)^m \exp(msz) - E_z\right] \sum_{n=0}^{\infty} v_n \exp[(n+ik)sz] +$$

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} - \frac{V_0}{2} - V_0 \sum_{m=1}^{\infty} (-1)^m \exp(msz) - E_z\right] \sum_{n=0}^{\infty} v_n' \exp[(n-ik)sz] = 0 \tag{8.36}$$

Comparing this to case 1a I see that in the first term the equations are the same except for the substititions $V_0 \to -V_0, s \to -s, u_n \to v_n$ and $\gamma \to ik$ while in the second term I must make the substitutions $V_0 \to -V_0, s \to -s, u_n \to v_n'$ and

$\gamma \to -ik$ The quantity

$$k = \frac{1}{s}(2E_z + V_0)^{\frac{1}{2}} \tag{8.37}$$

is the propagation vector deep inside the crystal. Note that as $z \to -\infty$ the wave function approaches

$$\phi(z) \to 2|v_0|\cos(ksz + \delta) \tag{8.38}$$

If I choose the normalization

$$\int_{-L}^{+L} |\phi(z)|^2 dz = 1 \tag{8.39}$$

where $L$ is a big number I determine the normalization constant

$$|v_0| = (2L)^{-\frac{1}{2}} \tag{8.40}$$

The solution for the coefficients $v_n$ are given by

$$v_n = (-1)^n v_0 \frac{\Gamma(1+2ik)\Gamma(ik-\gamma+n)\Gamma(ik+\gamma+n)}{n!\Gamma(n+1+2ik)\Gamma(ik-\gamma)\Gamma(ik+\gamma)} \tag{8.41}$$

**Case 2b. The degenerate continuum $E_z > V_0/2$**

In the region $z < 0$ I expand the wave function for the out-wave so as to include only waves travelling towards the surface. Thus

$$\phi(z) = \sum_{n=0}^{\infty} f_n \exp[i(k - in)sz] \tag{8.42}$$

The Schrodinger equation becomes

$$\left| -\frac{1}{2}\frac{d^2}{dz^2} - \frac{V_0}{2} - V_0 \sum_{m=1}^{\infty}(-1)^m \exp(msz) - E_z \right| \sum_{n=0}^{\infty} f_n \exp[i(k-in)sz] = 0 \tag{8.43}$$

This equation is of the same form as previously found for $v_n$ so

$$f_n = (-1)^n f_0 \frac{\Gamma(1+2ik)\Gamma(ik-\gamma+n)\Gamma(ik+\gamma+n)}{n!\Gamma(n+1+2ik)\Gamma(ik-\gamma)\Gamma(ik+\gamma)} \tag{8.44}$$

It is important to note that the two power series expansions I have used for the potential function $V(z)$

$$V(z) = \frac{V_0}{2} + V_0 \sum_{n=1}^{\infty} (-1)^n \exp(-nsz), \quad z > 0 \tag{8.45}$$

and

$$V(z) = -\frac{V_0}{2} - V_0 \sum_{n=1}^{\infty} (-1)^n \exp(nsz), \quad z < 0 \tag{8.46}$$

are not convergent at $z=0$. Indeed the first expression becomes

$$V(z) = \frac{V_0}{2} - V_0 + V_0 - V_0 + \cdots \tag{8.47}$$

which is not defined. Likewise the second expression becomes

$$V(z) = -\frac{V_0}{2} + V_0 - V_0 + V_0 - \cdots \tag{8.48}$$

which is also not defined. Effectively, the form for the potential I have chosen is discontinuous at z=0. In solving the Schrodinger equation, I must treat the equation as if it had a discontinuous potential. Hence I can only match the wave function and its derivative at z=0, but no higher derivatives.

I have written a computer program entitled TESTAMPL.FOR whcih will calculate the coefficients $f$, $g$ and $h$ or $u$, $v$ and $\delta$. The input data consists of the parameters $E_z$, $V_0$ and $s$ and the output data are the complex amplitudes $f$, $g$, $h$, $u$ and $v$ or the phase angle $\delta$. Typical results are presented in Fig. 8.1.

The Landau-Lifschitz solution

In order to join the solutions inside the solid to those outside the solid it is useful to digress and examine the Landau-Lifschitz solution to the same problem. I start with the Schrodinger equation

$$\left[ -\frac{1}{2}\frac{d^2}{dz^2} + \frac{V_0}{2}\tanh\left(\frac{sz}{2}\right) - E_z \right]\phi(z) = 0 \tag{8.49}$$

and examine the same cases as before.

**Case a. The nondegenerate continuum $|E_z| < V_0/2$**

Let me make the change of variables

$$y = \exp(sz) \tag{8.50}$$

Then the point $z = \infty$ is mapped into $y = \infty$ and the point $z = -\infty$ is mapped into $y = 0$. I look for a solution of the form

$$\phi(z) = (2L)^{-\frac{1}{2}} F(y) y^{ik} \exp(i\delta) + (2L)^{-\frac{1}{2}} F^*(y) y^{-ik} \exp(-i\delta) \tag{8.51}$$

Here $\delta$ is chosen so that the wave will be exponentially attenuated as $z \to \infty$. First try the first term

$$\phi_1(z) = (2L)^{-\frac{1}{2}} F(y) y^{ik} \exp(i\delta) \tag{8.52}$$

Carrying out the differentiation leads to the equation

$$y(y+1)F'' + (1+2ik)(y+1)F' - \frac{2V_0}{s^2}F = 0 \tag{8.53}$$

Letting $y = -\xi$ brings this to the form of the standard hypergeometric differential equation

$$\xi(1-\xi)\frac{d^2w}{d\xi^2} + [c - (a+b+1)\xi]\frac{dw}{d\xi} - abw = 0 \tag{8.54}$$

where

$$c = 1+2ik \tag{8.55}$$

$$a = ik+\gamma \tag{8.56}$$

and

$$b = ik-\gamma \tag{8.57}$$

Hence

$$\phi_1(z) = (2L)^{-\frac{1}{2}} y^{ik} \exp(i\delta) F(ik+\gamma, ik-\gamma; 1+2ik; -y) \tag{8.58}$$

If I add to this the complex conjugate solution I get the general solution

$$\phi(z) = (2L)^{-\frac{1}{2}} y^{ik} \exp(i\delta) F(ik+\gamma, ik-\gamma; 1+2ik; -y) + \tag{8.59}$$

$$(2L)^{-\frac{1}{2}} y^{-ik} \exp(-i\delta) F(-ik+\gamma, -ik-\gamma; 1-2ik; -y) \tag{8.60}$$

As $z \to -\infty$, $y \to 0$ and $F \to 1$. Then

$$\phi(z) \to (2/L)^{\frac{1}{2}} \cos(ksz+\delta) \tag{8.61}$$

and so

$$v_0 = (2L)^{-\frac{1}{2}} \exp(i\delta) \tag{8.62}$$

From Abramowitz and Stegun's "Handbook of Mathematical Functions" I find the following relation

$$F(a, b; c; x) = (1-x)^{-a} \frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)} F(a, c-b; a-b+1; \frac{1}{1-x}) +$$

$$(1-x)^{-b}\frac{\Gamma(c)\Gamma(a-b)}{\Gamma(a)\Gamma(c-b)}F\left(b, c-a; b-a+1; \frac{1}{1-x}\right) \tag{8.63}$$

provided $|\arg(1-x)| < \pi$. Since $x$ will get replaced by $-y$ this condition is obeyed. Then, as $z \to \infty$, $y \to \infty$ and $x \to -\infty$ and

$$F(a, b; c; -y) \to y^{-a}\frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)} + y^{-b}\frac{\Gamma(c)\Gamma(a-b)}{\Gamma(a)\Gamma(c-b)} \tag{8.64}$$

Hence the asymptotic behavior of $\phi(z)$ is

$$\phi(z) \to$$

$$(2L)^{-\frac{1}{2}}\exp[i(ksz+\delta)]\left[\exp[-(ik+\gamma)sz]\frac{\Gamma(1+2ik)\Gamma(-2\gamma)}{\Gamma(ik-\gamma)\Gamma(1+ik-\gamma)}+\exp[-(ik-\gamma)sz]\frac{\Gamma(1+2ik)\Gamma(2\gamma)}{\Gamma(ik+\gamma)\Gamma(1+ik+\gamma)}\right]+$$

$$(2L)^{-\frac{1}{2}}\exp[-i(ksz+\delta)]\left[\exp[-(-ik+\gamma)sz]\frac{\Gamma(1-2ik)\Gamma(-2\gamma)}{\Gamma(-ik-\gamma)\Gamma(1-ik-\gamma)}+\exp[(ik+\gamma)sz]\frac{\Gamma(1-2ik)\Gamma(2\gamma)}{\Gamma(-ik+\gamma)\Gamma(1-ik+\gamma)}\right] \tag{8.65}$$

The part which varies as $\exp(\gamma sz)$ should vanish in the vacuum, so

$$\phi(z) \to u_0\exp(-\gamma sz) \tag{8.66}$$

Hence

$$\exp(2i\delta) = -\frac{\Gamma(1-2ik)\Gamma(ik+\gamma)\Gamma(1+ik+\gamma)}{\Gamma(1+2ik)\Gamma(-ik+\gamma)\Gamma(1-ik+\gamma)} \tag{8.67}$$

and

$$u_0 = (2L)^{-\frac{1}{2}}\exp(-i\delta)\frac{\Gamma(1-2ik)\Gamma(-2\gamma)}{\Gamma(ik-\gamma)\Gamma(1+ik-\gamma)}\times$$

$$\left| \frac{\Gamma(ik-\gamma)\Gamma(1-\gamma+ik)}{\Gamma(-ik-\gamma)\Gamma(1-\gamma-ik)} - \frac{\Gamma(ik+\gamma)\Gamma(1+\gamma+ik)}{\Gamma(-ik+\gamma)\Gamma(1+\gamma-ik)} \right| \tag{8.68}$$

**Case b. The degenerate continuum $E_z > V_0/2$**

Let me now make the transformation

$$x = \exp(-sz)$$

Then the point $z=\infty$ is mapped into $x=0$ and the point $z=-\infty$ is mapped into $x=\infty$. I look for a solution of the form

$$\phi(z) = F(x)x^{-iq} + h_0 G(x)x^{iq} \tag{8.69}$$

corresponding to the out-wave. Here the constant $h_0$ is determined so as to keep the wave travelling solely towards the surface as $z \to -\infty$. The Schrodinger equation applied to the first term becomes

$$x(1+x)F'' + (1-iq)(1+x)F' + \frac{2V_0}{s^2}F = 0 \tag{8.70}$$

Letting $x=-\xi$ gives a solution in the standard hypergeometric equation form again

$$\xi(1-\xi)\frac{d^2w}{d\xi^2} + [c-(a+b+1)\xi]\frac{dw}{d\xi} - abw = 0 \tag{8.71}$$

where

$$a = i(k-q) \tag{8.71a}$$

$$b = -i(k+q) \tag{8.71b}$$

$$c = 1-2iq \tag{8.71c}$$

Again,

$$w = F(a, b; c; \xi) \tag{8.72}$$

I next apply the Schrodinger equation to the second term

$$\phi_2 = h_0 G(x) x^{iq} \tag{8.73}$$

The equation is the same as before except $F \to h_0 G$ and $q \to -q$. As $z \to \infty$ I have $G \to 1$ so

$$\phi(z) \to h_0 \exp(-iqsz) \tag{8.74}$$

Superimposing the two solutions leads to the general solution for the out-wave

$$\phi(z) = x^{-iq} F(-iq+ik, -iq-ik; 1-2iq; -x) +$$

$$h_0 x^{iq} F(iq+ik, iq-ik; 1+2iq; -x) \tag{8.75}$$

Making use of the asymptotic formula

$$F(a, b, c; -x) \to x^{-a} \frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)} + x^{-b} \frac{\Gamma(c)\Gamma(a-b)}{\Gamma(a)\Gamma(c-b)} \tag{8.76}$$

Hence

$$\phi(z) \to \exp(iksz) \left[ \frac{\Gamma(1-2iq)\Gamma(-2ik)}{\Gamma(-iq-ik)\Gamma(1-iq-ik)} + h_0 \frac{\Gamma(1+2iq)\Gamma(-2ik)}{\Gamma(iq-ik)\Gamma(1+iq-ik)} \right] +$$

$$\exp(-iksz) \left[ \frac{\Gamma(1-2iq)\Gamma(2ik)}{\Gamma(-iq+ik)\Gamma(1-iq+ik)} + h_0 \frac{\Gamma(1+2iq)\Gamma(2ik)}{\Gamma(iq+ik)\Gamma(1+iq+ik)} \right] \tag{8.77}$$

In order to make the wave travelling purely towards the surface, the second line must vanish, so

$$h_0 = -\frac{\Gamma(1-2iq)\Gamma(iq+ik)\Gamma(1+iq+ik)}{\Gamma(1+2iq)\Gamma(-iq+ik)\Gamma(1-iq+ik)} \tag{8.78}$$

Then

$$\phi(z) \to f_0 \exp(iksz) \tag{8.79}$$

and

$$f_0 = \frac{\Gamma(1-2iq)\Gamma(-2ik)}{\Gamma(iq-ik)\Gamma(1+iq-ik)} \times$$

$$\left[ \frac{\Gamma(iq-ik)\Gamma(1+iq-ik)}{\Gamma(-iq-ik)\Gamma(1-iq-ik)} - \frac{\Gamma(iq+ik)\Gamma(1+iq+ik)}{\Gamma(-iq+ik)\Gamma(1-iq+ik)} \right] \tag{8.80}$$

### The sharp step limit

As a simple check on the above equations I can quickly look at what is expected in the sharp step limit $s \to \infty$ Then in the nondegenerate continuum $|E_z| < \frac{V_0}{2}$ I have for $z < 0$

$$\phi(z) = (2/L)^{\frac{1}{2}} \cos(ksz + \delta) \tag{8.81}$$

and for $z > 0$

$$\phi(z) = u_0 \exp(-\gamma s z) \tag{8.82}$$

From the continuity of $\phi$ and its derivative at $z = 0$ I find

$$c\alpha\ \delta = \frac{k}{\gamma} \tag{8.83}$$

and

$$u_0 = (2/L)^{\frac{1}{2}} \frac{k}{(k^2+\gamma^2)^{\frac{1}{2}}} \tag{8.84}$$

In the limit of large $z$

$$\Gamma(z) \to \frac{1}{z} \tag{8.85}$$

so

$$\exp(2i\,\delta) = -\frac{\Gamma(1-2ik\,)\Gamma(ik\,+\gamma)\Gamma(1+ik\,+\gamma)}{\Gamma(1+2ik\,)\Gamma(-ik\,+\gamma)\Gamma(1-ik\,+\gamma)} \rightarrow$$

$$-\frac{\gamma-ik}{\gamma+ik} =$$

$$\exp(-2i\,\theta+i\,\pi) \tag{8.86}$$

where

$$\theta = \tan^{-1}\frac{k}{\gamma} \tag{8.87}$$

so

$$\cot\,\delta = \tan\theta$$

which agrees with the previous formula for the infinitely sharp step. Similarly I find that $u_0$ approaches the appropriate limiting value

$$u_0 \rightarrow \frac{\exp(-i\,\delta)\Gamma(1)(-2\gamma)^{-1}}{(2L\,)^{\frac{1}{2}}(ik\,-\gamma)^{-1}\Gamma(1)}\left[\frac{-ik\,-\gamma}{ik\,-\gamma} - \frac{\gamma-ik}{\gamma+ik}\right] = \tag{8.88}$$

$$\frac{\exp(-i\,\delta)2ik}{(2L\,)^{\frac{1}{2}}(\gamma+ik\,)} \tag{8.89}$$

Since

$$\exp(i\,\delta) = i\left[\frac{\gamma-ik}{\gamma+ik}\right]^{\frac{1}{2}} \tag{8.90}$$

I find

$$u_0 \rightarrow (2/L)^{\frac{1}{2}} \frac{k}{(k^2+\gamma^2)^{\frac{1}{2}}} \tag{8.91}$$

as obtained before.

In the degenerate continuum limit $E_z > V_0/2$ I have for $z > 0$

$$\phi(z) = \exp(iqsz) + h_0 \exp(-iqsz) \tag{8.92}$$

and for $z < 0$

$$\phi(z) = f_0 \exp(iksz) \tag{8.93}$$

Continuity of $\phi$ at $z = 0$ gives

$$1 + h_0 = f_0 \tag{8.94}$$

and continuity of $\phi'$ gives

$$q(1-h_0) = kf_0 \tag{8.95}$$

Hence

$$f_0 = \frac{2q}{q+k} \tag{8.96}$$

and

$$h_0 = \frac{q-k}{q+k} \tag{8.97}$$

If I look at the $s \rightarrow \infty$ limits of the analytic formulas I find

$$h_0 = -\frac{\Gamma(1-2iq)\Gamma(iq+ik)\Gamma(1+iq+ik)}{\Gamma(1+2iq)\Gamma(-iq+ik)\Gamma(1-iq+ik)} \rightarrow$$

$$\frac{q-k}{q+k} \tag{8.98}$$

Similarly,

$$f_0 = \frac{\Gamma(1-2iq)\Gamma(-2ik)}{\Gamma(iq-ik)\Gamma(1+iq-ik)} \times$$

$$\left[\frac{\Gamma(iq-ik)\Gamma(1+iq-ik)}{\Gamma(-iq-ik)\Gamma(1-iq-ik)} - \frac{\Gamma(iq+ik)\Gamma(1+iq+ik)}{\Gamma(-iq+ik)\Gamma(1-iq+ik)}\right] \rightarrow$$

$$\frac{k-q}{2k}\left[\frac{k+q}{k-q} + \frac{q-k}{q+k}\right] \rightarrow$$

$$\frac{2q}{k+q} \tag{8.99}$$

as before.

## 8.3 THE PERTURBED SOLID

Having solved the unperturbed problem, I now turn my attention to the perturbed problem. The time-dependent Schrodinger equation becomes

$$\left[\frac{1}{2}[\vec{p}+\frac{1}{c}\vec{A}(t)]^2+V(z)-i\frac{\partial}{\partial t}\right]\psi(\vec{r},t)=0 \qquad (8.100)$$

where $\vec{A}(t)$ is the vector potential defining the incident electromagnetic wave. In the electric dipole approximation it is independent of the spatial coordinates. I decouple the transverse coordinates by letting

$$\psi(\vec{r},t)=\exp[i\vec{k}_{//}\cdot\vec{r}_{//}-i\,\beta(t)]\psi(z,t) \qquad (8.101)$$

where $\beta(t)$ is chosen to be

$$\beta(t)=\int_{-T}^{t}dt'\left[\frac{1}{2}[\vec{k}_{//}+\frac{1}{c}\vec{A}_{//}(t')]^2+\frac{1}{2c^2}A_z^2(t')\right] \qquad (8.102)$$

so

$$\left[\frac{p_z^2}{2}+\frac{A_z(t)p_z}{c}+V(z)-i\frac{\partial}{\partial t}\right]\psi(z,t)=0 \qquad (8.103)$$

It will be assumed that the vector potential is gradually turned on at an early time $-T$ and slowly builds up at negative times to its ambient value with some time constant $\alpha$. Likewise I assume that for positive times it slowly decays with the same time constant and is turned off at time $T$. Thus, for $-T<t<0$

$$A_z(t)=A_0\cos\omega t\left[\frac{\exp[\alpha(t+T)]-1}{\exp[\alpha T]-1}\right] \qquad (8.104)$$

and for $0<t<T$

$$A_z(t) = A_0\cos\omega t \left[\frac{\exp[\alpha(T-t)]-1}{\exp[\alpha T]-1}\right] \tag{8.105}$$

For a large range of times near $t=0$ I have

$$A_z(t) = A_0\cos\omega t \tag{8.106}$$

Following the previous outline I begin by looking at the solutions in the positive z region. I can classify the solutions of the time-dependent wave equation as being either 'nondegenerate continuum' or 'degenerate continuum' depending on how their behavior was for times $t<-T$. Of course, since the vector potential mixes states throughout the spectrum, neither label is an accurate description for any state for times $-T<t<T$.

**Case 1a The nondegenerate continuum**

**($|E_z|<V_0/2$) for positive $z$**

I wish to solve the time-dependent Schrodinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dz^2}-\frac{i}{c}A_z(t)\frac{d}{dz}+\frac{V_0}{2}\tanh\frac{sz}{2}-i\frac{\partial}{\partial t}\right]\psi^{(+)}(z,t)=0 \tag{8.107}$$

I look for a solution that was a nondegenerate continuum state at $t=-T$ and evolves forward in time. Thus

$$\psi^{(+)}(z,t) = \sum_{n=0}^{\infty}\phi_n(t)\exp[-(\gamma+n)sz] \tag{8.108}$$

Substituting the series expansion for the potential, the Schrodinger equation becomes

$$\sum_{n=0}^{\infty}\exp[-(\gamma+n)sz]\left[-\frac{s^2}{2}(\gamma+n)^2\phi_n(t)+\frac{is}{c}A_z(t)(\gamma+n)\phi_n(t)\right.$$

$$+\frac{V_0}{2}\phi_n(t)+V_0\phi_n(t)\sum_{m=1}^{\infty}(-1)^m\exp(-msz)-i\frac{d\,\phi_n(t)}{dt} \qquad (8.109)$$

Rearranging the sum leads to the expression

$$\sum_{j=0}^{\infty}\exp[-(\gamma+j)sz]\left[-\frac{s^2}{2}(\gamma+j)^2\phi_j(t)+\frac{is}{c}A_z(t)(\gamma+j)\phi_j(t)+\frac{V_0}{2}\phi_j(t)\right]+$$

$$V_0\sum_{j=1}^{\infty}\sum_{m=1}^{j}(-1)^m\exp[-jz-\gamma z]\phi_{j-m}(t)-i\sum_{j=0}^{\infty}\frac{d\,\phi_j(t)}{dt}\exp[-(\gamma+j)sz]=0 \qquad (8.110)$$

For $j=0$ this becomes

$$\left[-\frac{s^2\gamma^2}{2}+\frac{is}{c}\gamma A_z(t)+\frac{V_0}{2}\right]\phi_0(t)-i\frac{d\,\phi_0(t)}{dt}=0 \qquad (8.111)$$

For $j>0$ I obtain

$$\left[-\frac{s^2}{2}(\gamma+j)^2+\frac{is}{c}(\gamma+j)A_z(t)+\frac{V_0}{2}\right]\phi_j(t)+V_0\sum_{m=1}^{j}(-1)^m\phi_{j-m}(t)-i\frac{d\,\phi_j(t)}{dt}=0$$

$$(8.112)$$

For $t<-T$ the potential is zero and

$$\left[-\frac{s^2\gamma^2}{2}+\frac{V_0}{2}\right]\phi_0(t)-i\frac{d\,\phi_0(t)}{dt}=0 \qquad (8.113)$$

The solution is

$$\phi_0(t)=constant\ \exp(-iE_z t) \qquad (8.114)$$

Hence

$$\gamma=\frac{1}{s}[V_0-2E_z]^{\frac{1}{2}} \qquad (8.115)$$

Integrating the $j=0$ equation gives

$$\phi_0(t) = B_0 \exp -i\int_{-T}^{t} \left[ -\frac{s^2\gamma^2}{2} + \frac{is}{c}\gamma A_z(t') + \frac{V_0}{2} \right] dt' =$$

$$B_0 \exp -i\int_{-T}^{t} \left[ E_z + \frac{is}{c}\gamma A_z(t') \right] dt' \tag{8.116}$$

Note that the integral of the vector potential is

$$\int_{-T}^{t} dt' A_z(t') =$$

$$\mathrm{Re}\frac{A_0 \exp(-i\omega T)}{\exp(\alpha T)-1} \left[ \frac{\exp[(\alpha+i\omega)(t+T)]-1}{\alpha+i\omega} - \frac{\exp[i\omega(t+T)]-1}{i\omega} \right] \tag{8.117}$$

Assuming that $\alpha \ll \omega$ and $\alpha T \ll 1$ I get

$$\int_{-T}^{t} dt' A_z(t') \rightarrow \frac{A_0 \sin\omega t}{\omega} \tag{8.118}$$

Hence

$$\phi_0(t) = B_0 \exp \left[ -iE_z(t+T) + \frac{s\gamma A_0}{c\omega}\sin\omega t \right] \tag{8.119}$$

In order for the above solution to reduce to the unperturbed solution at $t=-T$ I further require that $B_0 = u_0$. Thus

$$\phi_0(t) = u_0 \exp \left[ -iE_z(t+T) + \frac{s\gamma A_0}{c\omega}\sin\omega t \right] \tag{8.120}$$

For $j > 0$ the differential equations are

$$i\frac{d\phi_j(t)}{dt} - \left[ -\frac{s^2}{2}(\gamma+j)^2 + \frac{is}{c}(\gamma+j)A_z(t) + \frac{V_0}{2} \right] \phi_j(t) = V_0 \sum_{m=1}^{j} (-1)^m \phi_{j-m}(t)$$

(8.121)

Let

$$\phi_j(t) = \chi_j(t)\exp -i\int_{-T}^{t} dt' \left[ -\frac{s^2}{2}(\gamma + j)^2 + \frac{is}{c}(\gamma + j)A_z(t') + \frac{V_0}{2} \right] \tag{8.122}$$

This leads to a differential equation for $\chi_j(t)$ which, when integrated, gives

$$\chi_j(t) = -iV_0 \int_{-T}^{t} dt' \sum_{m=1}^{j} (-1)^m \phi_{j-m}(t') \exp i\int_{-T}^{t'} dt'' \left[ -\frac{s^2}{2}(\gamma + j)^2 + \frac{is}{c}(\gamma + j)A_z(t'') + \frac{V_0}{2} \right] \tag{8.123}$$

so

$$\phi_j(t) = -iV_0 \int_{-T}^{t} dt' \sum_{m=1}^{j} (-1)^m \phi_{j-m}(t') \exp i\int_{t}^{t'} dt'' \left[ -\frac{s^2}{2}(\gamma + j)^2 + \frac{is}{c}(\gamma + j)A_z(t'') + \frac{V_0}{2} \right] \tag{8.124}$$

The general solution is

$$\phi_j(t) = \delta_{j0} u_0 \exp\left[ -iE_z(t + T) + \frac{s\gamma A_0}{c\omega}\sin\omega t \right] -$$

$$-i(1-\delta_{j0})V_0 \int_{-T}^{t} dt' \sum_{m=1}^{j} (-1)^m \phi_{j-m}(t') \times$$

$$\exp i\int_{t}^{t'} dt'' \left[ -\frac{s^2}{2} j(j + 2\gamma) + \frac{is}{c}(\gamma + j)A_z(t'') + \frac{V_0}{2} \right] \tag{8.125}$$

Let me now make a harmonic expansion of this equation. I will use the expansion formula

$$\exp[z\sin\theta] = \sum_{k=-\infty}^{\infty} (-i)^k \exp(ik\theta) I_k(z) \tag{8.126}$$

where $I_k(z)$ are the modified Bessel functions of the first kind of order $k$ and argument $z$. I expand

$$\phi_j(t) = \sum_{\mu=-\infty}^{\infty} u_{j,\mu} \exp[-iE_z(t+T)+i\mu\omega t] \tag{8.127}$$

After considerable algebra I obtain

$$u_{j,\mu} = \delta_{j0} u_0 (-i)^\mu I_\mu \left( \frac{s\gamma A_0}{c\omega} \right) -$$

$$V_0(1-\delta_{j0}) \sum_{m=1}^{j} (-1)^m \sum_{\lambda\nu} (-i)^{\nu+\lambda} u_{j-m,\mu+\lambda-\nu} \times$$

$$\frac{I_\nu \left( \frac{s(\gamma+j)A_0}{c\omega} \right) I_\lambda \left( \frac{s(\gamma+j)A_0}{c\omega} \right)}{\omega(\mu-\nu)-\frac{s^2}{2}j(j+2\gamma)} \tag{8.128}$$

I note that this has the correct behavior for $A_0 \to 0$. In that case,

$$I_\lambda(0) = \delta_{\lambda 0} \tag{8.129}$$

and

$$u_{j,\mu} \to \delta_{j,0}\delta_{\mu,0} u_0 - V_0(1-\delta_{j,0}) \sum_{m=1}^{j} (-1)^m \frac{u_{j-m,\mu}}{\omega\mu - \frac{s^2}{2} j(j+2\gamma)} \tag{8.130}$$

This is satisfied by

$$u_{j-m,\mu} = 0 \tag{8.131}$$

for $\mu \neq 0$ and

$$\phi_{j,0} = \delta_{j,0} u_0 + V_0(1-\delta_{j,0}) \sum_{m=1}^{j} (-1)^m \frac{u_{j-m,0}}{\frac{s^2}{2} j(j+2\gamma)} \tag{8.132}$$

which is satisfied by

$$u_{j,0} = u_j \tag{8.133}$$

**Case 2a The nondegenerate continuum**

**($|E_z| < V_0/2$) for negative $z$**

The Schrodinger equation is

$$\left[-\frac{1}{2}\frac{d^2}{dz^2}-\frac{i}{c}A_z(t)\frac{d}{dz}-\frac{V_0}{2}-V_0\sum_{n=1}^{\infty}(-1)^n\exp(nsz)-i\frac{\partial}{\partial t}\right]\psi(z,t)=0 \tag{8.134}$$

I look for a solution of the form

$$\psi^{(+)}(z,t)=\sum_{n=0}^{\infty}\left[v_n(t)\exp[(n+ik)sz]+w_n(t)\exp[(n-ik)sz]\right] \tag{8.135}$$

By comparing this differential equation to that previously obtained, I see that the first term would be equivalent if

$V_0 \rightarrow -V_0$

$s \rightarrow -s$

$\phi_n(t) \rightarrow v_n(t)$

$\gamma \rightarrow ik$

and

$u_0 \rightarrow v_0$

The second term would be equivalent if

$V_0 \rightarrow -V_0$

$$s \rightarrow -s$$

$$\phi_n(t) \rightarrow w_n(t)$$

$$\gamma \rightarrow -ik$$

and

$$u_0 \rightarrow v_0^{\cdot}$$

Thus the coefficients $v_{j,\mu}$ obey the relations

$$v_{j,\mu} = \delta_{j,0} v_0 (-i)^{\mu} I_{\mu}\left(\frac{-sikA_0}{c\,\omega}\right) +$$

$$V_0(1-\delta_{j,0}) \sum_{m=1}^{j} (-1)^m \sum_{\lambda\nu} (-i)^{\nu+\lambda} v_{j-m,\mu+\lambda-\nu} \times$$

$$\frac{I_{\nu}\left(\frac{-s(ik+j)A_0}{c\,\omega}\right) I_{\lambda}\left(\frac{-s(ik+j)A_0}{c\,\omega}\right)}{\omega(\mu-\nu)-\frac{s^2}{2} j(j+2ik)} \qquad (8.136)$$

and

$$w_{j,\mu} = \delta_{j,0} v_0^{\cdot} (-i)^{\mu} I_{\mu}\left(\frac{sikA_0}{c\,\omega}\right) +$$

$$V_0(1-\delta_{j,0}) \sum_{m=1}^{j} (-1)^m \sum_{\lambda\nu} (-i)^{\nu+\lambda} w_{j-m,\mu+\lambda-\nu} \times$$

$$\frac{I_{\nu}\left(\frac{-s(j-ik)A_0}{c\,\omega}\right) I_{\lambda}\left(\frac{-s(j-ik)A_0}{c\,\omega}\right)}{\omega(\mu-\nu)-\frac{s^2}{2} j(j-2ik)} \qquad (8.137)$$

## Case 1b The degenerate continuum ($E_z > V_0/2$) for positive $z$

I consider a state at a different energy $E'_z$. In the case of multiharmonic excitation of the state with energy $E_z$,

$$E'_z = E_z + \sigma\omega$$

where $\sigma$ is an integer. I am looking for a state which will evolve into a particular unperturbed state at the time $t = T$. Such a state will be called an out-state. The differential equation is

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} - \frac{i}{c}A_z(t)\frac{d}{dz} + \frac{V_0}{2} + V_0\sum_{m=1}^{\infty}(-1)^m \exp(-msz) - i\frac{\partial}{\partial t}\right]\psi^{(-)}(z,t) = 0 \tag{8.138}$$

Let me expand the solution as

$$\psi^{(-)}(z,t) = \sum_{n=0}^{\infty}\left[g_n(t)\exp[(-n+iq')sz] + h_n(t)\exp[(-n-iq')sz]\right] \tag{8.139}$$

Comparing this to the previous differential equation shows that in the first term I make the replacements

$$\phi_n \rightarrow g_n$$

$$\gamma \rightarrow -iq'$$

while in the second term

$$\phi_n \rightarrow h_n$$

$$\gamma \rightarrow iq'$$

Expanding the time-dependent solutions in a harmonic series gives

$$g_j(t) = \sum_{\mu=-\infty}^{\infty} g_{j,\mu} \exp[-iE'_z(t-T)+i\mu\omega t] \qquad (.8.140)$$

$$h_j(t) = \sum_{\mu=-\infty}^{\infty} h_{j,\mu} \exp[-iE'_z(t-T)+i\mu\omega t] \qquad (.8.141)$$

The Fourier coefficients satisfy the relations

$$g_{j,\mu} = \delta_{j,0} g_0 (-i)^{\mu} I_{\mu}\left(\frac{-iq'sA_0}{c\,\omega}\right) -$$

$$V_0(1-\delta_{j,0}) \sum_{m=1}^{j} (-1)^m \sum_{\lambda\nu} (-i)^{\nu+\lambda} g_{j-m,\mu+\lambda-\nu} \times$$

$$\frac{I_{\nu}\left(\frac{s(j-iq')A_0}{c\,\omega}\right) I_{\lambda}\left(\frac{s(j-iq')A_0}{c\,\omega}\right)}{\omega(\mu-\nu)-\frac{s^2}{2}j(j-2iq')} \qquad (.8.142)$$

where $g_0=1$. Similarly,

$$h_{j,\mu} = \delta_{j,0} h_0 (-i)^{\mu} I_{\mu}\left(\frac{iq'sA_0}{c\,\omega}\right) -$$

$$V_0(1-\delta_{j,0}) \sum_{m=1}^{j} (-1)^m \sum_{\lambda\nu} (-i)^{\nu+\lambda} h_{j-m,\mu+\lambda-\nu} \times$$

$$\frac{I_{\nu}\left(\frac{s(j+iq')A_0}{c\,\omega}\right) I_{\lambda}\left(\frac{s(j+iq')A_0}{c\,\omega}\right)}{\omega(\mu-\nu)-\frac{s^2}{2}j(j+2iq')} \qquad (.8.143)$$

**Case 2b The degenerate continuum ($E_z > V_0/2$) for negative $z$**

The state is now expanded as

$$\psi^{(-)}(z,t) = \sum_{n=0}^{\infty} f_n(t)\exp[(n+ik')sz] \quad (8.144)$$

where

$$k' = \frac{1}{s}(2E'_z + V_0)^{\frac{1}{2}}$$

These satisfy the same equation as the $v_n$ coefficients except

$$v_n \rightarrow f_n$$

$$k \rightarrow k'$$

The Fourier expansion is

$$f_j(t) = \sum_{\mu=-\infty}^{\infty} f_{j,\mu}\exp[-iE'_z(t-T)+i\mu\omega t] \quad (8.145)$$

The coefficients satisfy

$$f_{j,\mu} = \delta_{j,0} f_0(-i)^{\mu} I_{\mu}\left(\frac{-ik'sA_0}{c\omega}\right) +$$

$$V_0(1-\delta_{j,0})\sum_{m=1}^{j}(-1)^m \sum_{\lambda\nu}(-i)^{\nu+\lambda} f_{j-m,\mu+\lambda-\nu} \times$$

$$\frac{I_{\nu}\left(\frac{-s(j+ik')A_0}{c\omega}\right) I_{\lambda}\left(\frac{-s(j+ik')A_0}{c\omega}\right)}{\omega(\mu-\nu)-\frac{s^2}{2}j(j+2ik')} \quad (8.146)$$

Following the procedure employed earlier for the hard wall and sharp step potentials I may now solve the full time Schrodinger equation for the smooth step potential. The incident wave for $z<0$ is

$$\psi(z,t) = \sum_{m=0}^{\infty} v_m^{(0)}(t)\exp\left[(m+ik_0)sz\right] \tag{8.147}$$

where $v_m^{(0)}(t)$ has been obtained explicitly in the preceding analysis. The incident wave gives rise to a shower of left travelling reflecting waves in the region $z<0$

$$\psi_L = \sum_{n=-\infty}^{\infty} D_n \sum_{m=0}^{\infty} W_m^{(n)}(t)exp\left[(m-ik_n)sz\right] \tag{8.148}$$

where $D_n$ are a set of reflection coefficients and

$$k_n = \frac{1}{s}\sqrt{[2(E_z+n\omega)+V_0]} \qquad \text{if } 2(E_z+n\omega)+V_0>0$$

$$k_n = \frac{i}{s}\sqrt{[-2(E_z+n\omega)-V_0]} \qquad \text{if } 2(E_z+n\omega)+V_0<0 \tag{8.149}$$

and a shower of right travelling transmitted waves.

$$\psi_R = \sum_{n=-\infty}^{\infty} F_n \sum_{m=0}^{\infty} u_m^{(n)}(t)\exp\left[-(m+\gamma_n)sz\right]$$

$$\gamma_n = \frac{1}{s}\sqrt{[-2(E_z+n\omega)+V_0]} \qquad \text{if } -2(E_z+n\omega)+V_0>0$$

$$\gamma_n \equiv -iq_n = \frac{-i}{s}\sqrt{[+2(E_z+n\omega)-V_0]} \qquad \text{if } -2(E_z+n\omega)+V_0<0 \tag{8.150}$$

Let me match $\psi(z)$ at z = 0

$$\sum_{m=0}^{\infty} v_m^{(0)}(t) + \sum_{n=-\infty}^{\infty} D_n \sum_{m=0}^{\infty} W_m^{(n)}(t) = \sum_{n=-\infty}^{\infty} F_n \sum_{m=0}^{\infty} u_m^{(n)}(t) \tag{8.151}$$

and $\psi'(z)$ at z =0

$$\sum_{m=0}^{\infty}(m+ik_0)v_m^{(0)}(t) + \sum_{n=-\infty}^{\infty} D_n \sum_{m=0}^{\infty}(m-ik_n)w_m^{(n)}(t) =$$

$$-\sum_{n=-\infty}^{\infty} F_n \sum_{m=0}^{\infty} (m+\gamma_n) u_m^{(n)}(t) \tag{8.152}$$

The coefficients $u_m^{(n)}(t)$, $v_m^{(n)}(t)$ and $w_m^{(n)}(t)$ are evaluated at energy $E_n = E_z + n\,\omega$. The harmonic expansions are

$$v_m^{(0)}(t) = \sum_\mu v_{m\,\mu}^{(0)} \exp[-iE_z t + i\,\mu\omega t]$$

$$u_m^{(n)}(t) = \sum_\mu u_{m\,\mu}^{(n)} \exp[-i(E_z + n\,\omega)t + i\,\mu\omega t]$$

$$w_m^{(n)}(t) = \sum_\mu w_{m\,\mu}^{(n)} \exp[-i(E_z + n\,\omega)t + i\,\mu\omega t] \tag{8.153}$$

So

$$\sum_{n=-\infty}^{\infty} [\sum_{m=0}^{\infty} w_{m,\mu+n}^{(n)}] D_n + \sum_{n=-\infty}^{\infty} [-\sum_{m=0}^{\infty} u_{m,\mu+n}^{(n)}] F_n = [-\sum_{m=0}^{\infty} v_{m\,\mu}^{(0)}]$$

$$\sum_{n=-\infty}^{\infty} [\sum_{m=0}^{\infty} (m - ik_n) w_{m,\mu+n}^{(n)}] D_n + \sum_{n=-\infty}^{\infty} [\sum_{m=0}^{\infty} (m+\gamma_n) u_{m,\mu+n}^{(n)}] F_n$$

$$= [-\sum_{m=0}^{\infty} (m + ik_0) v_{m\,\mu}^{(0)}] \tag{8.154}$$

These equations are of the same form encountered previously for the sharp step potential:

$$\sum_n M_{jn} G_n = R_j \tag{8.155}$$

I may therefore adapt the previously developed program for the present case. The program DFSMTST2.FOR calculates the $D_n$ and $F_n$ amplitudes for the case of the perturbed smooth step potential. In solving for these coefficients I am able to set the constants $u_0$, $v_0$, $w_0$ all equal to 1, since their magnitudes can be absorbed into the definitions of $D_n$ and $F_n$.

In the following section I go on to consider the problem of multiharmonic generation. In that state use will be made of the perturbed non-degenerate continuum states. These states will also enable one to study multiphoton excitation. the perturbed degenerate continuum states would find applicability in studying the inverse photoemission process, but I don't consider this problem in my thesis.

## 8.4 MULTIHARMONIC GENERATION

In order to compute the multiharmonic generated signal I need to know the expectation value of the velocity operator and to develop it in a Fourier series. Thus

$$v_z = \frac{<\psi \mid [p_z + \frac{1}{c}A_z] \mid \psi>}{<\psi \mid \psi>}$$

$$= \frac{<\psi \mid p_z \mid \psi>}{<\psi \mid \psi>} + \frac{1}{c}A_z \tag{8.156}$$

Let me start by computing the expectation value of the momentum operator.

$$<p_z> = \int_{-L}^{0} dz \, [\sum_{m=0}^{\infty} v_m^{(0)}(t)^* \exp[(m - ik_0)sz] +$$

$$\sum_{n=-\infty}^{\infty} D_n^* \sum_{m=0}^{\infty} w_m^{(n)}(t)^* \exp[(m + ik_n^*)sz]]$$

$$\sum_{m=0}^{\infty} v_m^{(0)}(t)(-is)(m + ik_0)exp(sz(m + ik_0)) +$$

$$\sum_{n=-\infty}^{\infty} D_n \sum_{m=0}^{\infty} w_m^{(n)}(t)(-is)(m-ik_n)\exp((m-ik_n)sz)+$$

$$\int_0^L dz \left[ \sum_{n=-\infty}^{\infty} F_n^* \sum_{m=0}^{\infty} u_m^{(n)}(t)^* \exp(-(m+\gamma_n^*)sz) \right]$$

$$\left[ \sum_{n=-\infty}^{\infty} F_n \sum_{m=0}^{\infty} u_m^{(n)}(t)(is)(m+\gamma_n)\exp(-(m+\gamma)sz) \right] \tag{8.157}$$

Carrying out the integrals, as before, I can separate the terms into L-dependent and L-independent parts. The L-dependent part is

$$<p_z>_L = Ls\left\{k_0|v_0^{(0)}(t)|^2-\sum_n k_n\ |D_n|^2|w_0^{(n)}(t)|^2\Theta(V_0+2(E_z+n\omega))\right\}$$

$$+Ls\left\{\sum_n |F_n|^2 q_n\ |u_0^{(n)}(t)|^2\Theta(2(E_z+n\omega)-V_0)\right\} \tag{8.158}$$

This may be interpreted as being proportional to the DC particle flux, and hence to the photocurrent. This may be shown to be time independent as folows:

$$|u_0^{(n)}(t)|^2 = \sum_{\mu\mu'} u_{o\mu'}^{(n)*} u_{o\mu+\mu'}^{(n)} \exp(i\mu\omega t)$$

$$= \sum_\mu \exp(i\mu\omega t)|u_0|^2\sum_{\mu'}(-i)^\mu I_\mu(\frac{sA_0}{c\omega}\gamma_n^*)I_{\mu+\mu}(\frac{sA_0}{c\omega}\gamma_n) \tag{8.159}$$

Since $\gamma_n$ is pure imaginary ( because $V_0-2(E_z+n\omega)<0$) it follows that

$$|u_0^{(n)}(t)|^2 = \sum_\mu(-i)^\mu\exp(i\mu\omega t)|u_0|^2\sum_{\mu'}I_\mu(\frac{-sA_0}{c\omega}\gamma_n)I_{\mu+\mu}(\frac{sA_0}{c\omega}\gamma_n)$$

$$= \sum_\mu(-i)^\mu\exp(i\mu\omega t)|u_0|^2\sum_{\mu'}(-)^{\mu'}I_\mu(\frac{sA_0}{c\omega}\gamma_n)I_{\mu+\mu}(\frac{sA_0}{c\omega}\gamma_n)$$

$$= |u_0|^2 \tag{8.160}$$

Similarly

$$|v_0^{(0)}(t)|^2 = |v_0|^2 \tag{8.161}$$

and

$$|w_0^{(0)}(t)|^2 = |w_0|^2 \tag{8.162}$$

So

$$<p_z>_L = Lsk_0|v_0|^2 - |w_0|^2\sum_n k_n\ |D_n\ |^2\Theta(V_0+2(E_z+n\ \omega))$$

$$+ |u_0|^2\sum_n q_n\ |F_n\ |^2\Theta(2(E_z+n\ \omega)-V_0) \tag{8.163}$$

As stated earlier, we will take $|v_0| = |w_0| = |u_0| = 1$.

I normalize this by dividing through by the normalization so

$$<\psi|\psi> = Ls\left[|v_0|^2 + |w_0|^2\sum_n |D_n\ |^2\Theta(V_0+2(E_z+n\ \omega))\right]$$

$$+Ls\left[|u_0|^2\sum_n |F_n\ |^2\Theta(2(E_z+n\ \omega)-V_0)\right] \tag{8.164}$$

Hence the DC component of the velocity is

$$<v_z>_{DC} = \frac{k_0 - \sum_n k_n\ |D_n\ |^2\Theta(V_0+2(E_z+n\ \omega)) + \sum_n q_n\ |F_n\ |^2\Theta(2(E_z+n\ \omega)-V_0))}{1-\sum_n |D_n\ |^2\Theta(V_0+2(E_z+n\ \omega)) + \sum_n F_n\ |^2\Theta(2(E_z+n\ \omega)-V_0))} \tag{8.165}$$

The L-independent parts of $<p_z>$ may be written as

$$\langle p_z \rangle = \sum_{\mu} P_{\mu} \exp(i\,\mu\omega t) \tag{8.166}$$

where

$$
\begin{aligned}
P_{\mu} = -i & \sum_{m,m';\,m,m'\neq 0} \frac{m+ik_0}{m+m'} \sum_{\mu'} v_{m',\mu'}^{(0)*} v_{m,\mu+\mu'}^{(0)} + \\
& \sum_{m,m'} \sum_{n} \frac{D_n (m-ik_n)}{m+m'-i(k_0+k_n)} \sum_{\mu'} v_{m',\mu'}^{(0)*} w_{m,\mu+\mu'+n}^{(n)} + \\
& \sum_{m,m'} \sum_{n}{}' \frac{D_n^*(m+ik_0)}{m+m'+i(k_0+k_n^*)} \sum_{\mu'} v_{m,\mu'}^{(0)} w_{m',\mu'+n'-\mu}^{(n)*} + \\
& \sum_{mm';\,mm'\neq 0} \sum_{nn'} D_{n'}^* D_n \frac{(m-ik_n)}{m+m'+i(k_{n'}^*-k_n)} \sum_{\mu'} w_{m',\mu'}^{(n')*} w_{m,\mu+\mu'-n'+n}^{(n)} + \\
& \sum_{nn';\,n\neq n'} D_{n'}^* D_n \frac{-k_n}{k_{n'}^*-k_n} \sum_{\mu'} w_{o,\mu'}^{(n')*} w_{o,\mu+\mu'-n'+n}^{(n)} + \\
& \sum_{n} |D_n|^2 \frac{-k_n}{k_n^*-k_n} \Theta\left(-\frac{V_0}{2}-E_z-n\omega\right) \sum_{\mu'} w_{o,\mu'}^{(n)*} w_{o,\mu+\mu'}^{(n)} + \\
& \sum_{mm';\,mm'\neq 0} \sum_{nn'} F_{n'}^* F_n \frac{(-m-\gamma_n)}{m+m'+\gamma_{n'}^*+\gamma_n} \sum_{\mu'} u_{m',\mu'}^{(n')*} u_{m,\mu+\mu'-n'+n}^{(n)} + \\
& \sum_{nn';\,n\neq n'} F_{n'}^* F_n \frac{-\gamma_n}{\gamma_{n'}^*-\gamma_n} \sum_{\mu'} u_{o,\mu'}^{(n')*} u_{o,\mu+\mu'-n'+n}^{(n)} + \\
& \sum_{n} |F_n|^2 \frac{-\gamma_n}{\gamma_n^*-\gamma_n} \Theta\left(\frac{V_0}{2}-E_z-n\omega\right) \sum_{\mu'} u_{o,\mu'}^{(n)*} u_{o,\mu+\mu'}^{(n)}
\end{aligned}
\tag{8.167}
$$

The overlap integral $\langle\psi|\psi\rangle$ may be written as a sum of the L- dependent term (given before) and an L-independent term

$$\langle\psi\mid\psi\rangle' = \sum_{\mu} N_{\mu}\exp(i\,\mu\omega t) \tag{8.168}$$

where

$$N_{\mu} = \frac{-i}{s}\sum_{m,m',m,m'\neq 0}\frac{1}{m+m'}\sum_{\mu'} v_{m'\mu'}^{(0)*} v_{m,\mu+\mu'}^{(0)} +$$

$$\sum_{m,m'}\sum_{n} D_n\,\frac{i}{s}\,\frac{1}{m+m'-i\,(k_0+k_n)}\sum_{\mu'} v_{m'\mu'}^{(0)*} w_{m\,\mu+\mu'+n}^{(n)} +$$

$$\sum_{m,m'}\sum_{n}{}' D_n{}^{*}\frac{i}{s}\,\frac{1}{m+m'+i\,(k_0+k_n{}^{*})}\sum_{\mu'} v_{m\,\mu'}^{(0)} w_{m'\mu'+n'-mu}^{(n)} +$$

$$\sum_{nn'} D_{n'}^{*} D_n\,\frac{i}{s}\,\frac{1}{m+m'+i\,(k_{n'}^{*}-k_n)}\sum_{\mu'} w_{m'\mu'}^{(n')*} w_{m\,\mu+\mu'-n'+n}^{(n)} +$$

$$\sum_{nn',n\neq n'} D_{n'}^{*} D_n\,\frac{1}{s}\,\frac{1}{k_{n'}^{*}-k_n}\sum_{\mu'} w_{o\,\mu'}^{(n')*} w_{o\,\mu+\mu'-n'+n}^{(n)} +$$

$$\sum_{n}\mid D_n\mid^2\frac{1}{s}\,\frac{1}{k_n^{*}-k_n}\Theta(-\frac{V_0}{2}-E_z-n\,\omega)\sum_{\mu'} w_{o\,\mu'}^{(n)*} w_{o\,\mu+\mu'}^{(n)} +$$

$$\sum_{nn'} F_{n'}^{*} F_n\,\frac{i}{s}\,\frac{1}{m+m'+\gamma_{n'}^{*}+\gamma_n}\sum_{\mu'} u_{m'\mu'}^{(n')*} u_{m\,\mu+\mu'-n'+n}^{(n)} +$$

$$\sum_{nn',n\neq n'} F_{n'}^{*} F_n\,\frac{i}{s}\,\frac{1}{\gamma_{n'}^{*}-\gamma_n}\sum_{\mu'} u_{o\,\mu'}^{(n')*} u_{o\,\mu+\mu'-n'+n}^{(n)} +$$

$$\sum_{n}\mid F_n\mid^2\frac{i}{s}\,\frac{1}{\gamma_n^{*}-\gamma_n}\Theta(\frac{V_0}{2}-E_z-n\,\omega)\sum_{\mu'} u_{o\,\mu'}^{(n)*} u_{o\,\mu+\mu'}^{(n)} \tag{8.169}$$

As before, I write the time dependent expectation value as

$$v_z = \sum_{\mu} v_{\mu} \exp(i\,\mu\omega t) \tag{8.170}$$

where

$$v_{\mu} = \frac{p_{\mu} - \langle v_{DC} \rangle N_{\mu}}{1 + \sum_{n} [\,|D_n|^2 \Theta(\frac{V_0}{2} + E_z + n\,\omega) + |F_n|^2 \Theta(E_z + n\,\omega - \frac{V_0}{2})]} \tag{8.171}$$

The program DSMVEL1.F evaluates the velocity Fourier coefficients.

# APPENDIX A REDUCTION OF SUMMATION OVER INTERMEDIATE STATES FOR MHG

In this appendix I show explicitly that the six Feynman diagrams describing second harmonic generation with electrons and holes in the intermediate states can be reduced to three diagrams involving sums over all states. The six diagrams are illustrated in Fig. 3.5 . Associated with each downward pointing line is a hole and an associated Fermi factor $f^{(-)}$ representing the Fermi distribution for filled electrons. At $T = 0^\circ$ K

$$f^{(-)} = \Theta(E_F - E) \tag{A1}$$

where $E_F$ is the Fermi energy. At finite temperatures,

$$f^{(-)} = \frac{1}{\exp[\beta(E-\mu)]+1} \tag{A2}$$

where $\mu$ is the chemical potential. Similarly, associated with with each upward pointing line is an electron and an associated Fermi factor $f^{(+)}$. At $T = 0^\circ$ K

$$f^{(+)} = \Theta(E - E_F) \tag{A3}$$

while at finite temperatures,

$$f^{(+)} = 1 - f^{(-)} \tag{A4}$$

Associated with each diagram is a sign $(-)^N$ , where N is the number of holes plus the number of closed loops. Each vertex for an absorption introduces a matrix element of $\frac{A_o}{2c}\hat{e}_z\, p_z$ while the emission introduces the matrix element $\left[\frac{2\pi}{\omega'}\right]^{1/2} \hat{e}_z{}' p_z$ .

The contribution from the diagrams is thus

$$M^{(2)} = (\frac{A_0}{2c}\hat{e}_z)^2 \left[\frac{2\pi}{\omega'}\right]^{1/2} \hat{e}_z \cdot \left[M_1+M_2+M_3+M_4+M_5+M_6\right] \tag{A5}$$

Let me list all possible diagrams for a second harmonic generation where two photons of frequency $\omega$ are absorbed and one photon of frequency $2\omega$ is emitted. Six diagrams are possible. Here diagrams 1,3 and 5 have a relative minus sign because I have one loop and two holes for them . My aim is to show that these six diagrams reduce to three distinct diagrams. Let me write

$$M_{mnl} = \langle m \mid p_z \mid n \rangle \langle n \mid p_z \mid l \rangle \langle l \mid p_z \mid m \rangle \tag{A6}$$

Then

$$M_1 = -\sum_{mnl} f_n^- f_m^- f_l^+ \frac{M_{mnl}}{(\omega+\epsilon_n-\epsilon_l)(2\omega+\epsilon_m-\epsilon_l)} \tag{A7}$$

$$M_2 = \sum_{mnl} f_n^+ f_m^+ f_l^- \frac{M_{mnl}}{(\omega+\epsilon_l-\epsilon_n)(2\omega+\epsilon_l-\epsilon_m)} \tag{A8}$$

$$M_3 = -\sum_{mnl} f_n^- f_m^- f_l^+ \frac{M_{mnl}}{(\omega+\epsilon_n-\epsilon_l)(\omega-\omega'+\epsilon_m-\epsilon_l)} \tag{A9}$$

$$M_4 = \sum_{mnl} f_n^+ f_m^+ f_l^- \frac{M_{mnl}}{(\omega+\epsilon_l-\epsilon_n)(\omega-\omega'+\epsilon_l-\epsilon_m)} \tag{A10}$$

$$M_5 = -\sum_{mnl} f_n^- f_m^- f_l^+ \frac{M_{mnl}}{(-\omega'+\epsilon_n-\epsilon_l)(\omega-\omega'+\epsilon_m-\epsilon_l)} \tag{A11}$$

$$M_6 = \sum_{mnl} f_n^+ f_m^+ f_l^- \frac{M_{mnl}}{(-\omega'+\epsilon_l-\epsilon_n)(\omega-\omega'+\epsilon_l-\epsilon_m)} \tag{A12}$$

For second harmonic generation

$$\omega' = 2\omega \tag{A13}$$

Let me introduce a shorthand notation

$$A = \omega+\epsilon_n - \epsilon_l \tag{A14}$$

$$B = 2\omega+\epsilon_m - \epsilon_l \tag{A15}$$

$$C = \omega+\epsilon_m - \epsilon_n \tag{A16}$$

where

$$C + A - B = 0 \tag{A17}$$

Also let me note that $M_{mnl}$ remains unchanged under permutation of indices. Using the fact that $f_l^{(+)} = 1 - f_l^{(-)}$ I may rewrite $M_1$ as

$$M_1 = -\sum_{lmn} \left[ f_m^{(-)} f_n^{(-)} - f_m^{(-)} f_n^{(-)} f_l^{(-)} \right] \frac{M_{mnl}}{AB} \tag{A18}$$

In the $M_2$ expression interchange $l$ and $m$ and again express the $f^{(+)}$ factors in terms of the $f^{(-)}$ factors so

$$M_2 = \sum_{lmn} \left[ f_m^{(-)} - f_m^{(-)} f_l^{(-)} - f_n^{(-)} f_m^{(-)} + f_n^{(-)} f_m^{(-)} f_l^{(-)} \right] \frac{M_{mnl}}{BC} \tag{A19}$$

In $M_3$ I make the cyclic interchange $l \to n \to m \to l$ and get

$$M_3 = \sum_{lmn} \left[ f_l^{(-)} f_m^{(-)} - f_l^{(-)} f_m^{(-)} f_n^{(-)} \right] \frac{M_{mnl}}{AC} \tag{A20}$$

In $M_4$ I interchange $l$ and $n$ to find

$$M_4 = -\sum_{lmn} \left[ f_n^{(-)} - f_n^{(-)} f_l^{(-)} - f_n^{(-)} f_m^{(-)} + f_n^{(-)} f_l^{(-)} f_m^{(-)} \right] \frac{M_{mnl}}{AC} \tag{A21}$$

In $M_5$ the cyclic interchange $n \to l \to m \to n$ results in

$$M_5 = -\sum_{lmn} \left[ f_n^{(-)} f_l^{(-)} - f_n^{(-)} f_l^{(-)} f_m^{(-)} \right] \frac{M_{mnl}}{BC} \qquad \text{(A22)}$$

Finally, in $M_6$ the interchange of $n$ and $m$ gives

$$M_6 = \sum_{lmn} \left[ f_l^{(-)} - f_l^{(-)} f_m^{(-)} - f_l^{(-)} f_n^{(-)} + f_m^{(-)} f_n^{(-)} f_l^{(-)} \right] \frac{M_{mnl}}{AB} \qquad \text{(A23)}$$

If I group together all terms with the prefactor $f_l^{(-)}\ f_m^{(-)} f_n^{(-)}$ I find that they sum to

$$\sum_{lmn} M_{mnl}\ f_l^{(-)} f_m^{(-)} f_n^{(-)} 2 \left[ \frac{1}{AB} + \frac{1}{BC} - \frac{1}{CA} \right] = 0 \qquad \text{(A24)}$$

Similarly the sums involving $f_l^{(-)} f_m^{(-)}$ are

$$\sum_{lmn} M_{mnl}\ f_l^{(-)} f_m^{(-)} \left[ -\frac{1}{BC} + \frac{1}{AC} - \frac{1}{AB} \right] = 0 \qquad \text{(A25)}$$

Likewise

$$\sum_{lmn} M_{mnl}\ f_l^{(-)} f_n^{(-)} \left[ \frac{1}{AC} - \frac{1}{BC} - \frac{1}{AB} \right] = 0 \qquad \text{(A26)}$$

and

$$\sum_{lmn} M_{mnl}\ f_m^{(-)} f_n^{(-)} \left[ -\frac{1}{AB} - \frac{1}{BC} + \frac{1}{AC} \right] = 0 \qquad \text{(A27)}$$

I am left with

$$\sum_i M_i = \sum_{lmn} M_{lmn} \left[ \frac{f_m^{(-)}}{BC} - \frac{f_n^{(-)}}{AC} + \frac{f_l^{(-)}}{AB} \right] \qquad \text{(A28)}$$

Interchanging $m$ with $l$ in the first term and $n$ with $l$ in the second term results in

$$M^{(n)} = \left[\frac{A_o}{2c}\hat{e}_z\right]^2 \left[\frac{2\pi}{\omega'}\right]^{1/2} \hat{e}_z{}' \sum_{mnl} f_l{}^{-} M_{mnl} \tag{A29}$$

$$\left[\frac{1}{(\omega+\epsilon_l-\epsilon_n)(2\omega+\epsilon_l-\epsilon_m)} + \frac{1}{(2\omega+\epsilon_n-\epsilon_l)(\omega+\epsilon_m-\epsilon_l)} - \frac{1}{(\omega+\epsilon_n-\epsilon_l)(\omega+\epsilon_l-\epsilon_m)}\right] \tag{A30}$$

In the last two terms I have also interchanged indices $m$ and $n$ . This expression corresponds to the three Feynman diagrams displayed in Fig. 3.6 . Thus I have three distinct diagrams for second harmonic generation. In general I can say that for $n^{th}$ harmonic generation I have $n+1$ distinct diagrams.

## APPENDIX B REDUCTION OF SUMMATION OVER INTERMEDIATE STATES FOR MPEE

The matrix elements corresponding to the two second order processes in Fig 3.3 are

$$M^{(2)} = \left(\frac{A_o \hat{e}_z}{2c}\right)^2 \left[M_1 + M_2\right] \tag{B1}$$

where

$$M_1 = -\sum_m \frac{<f\ |p_z|\ m><m\ |p_z|\ q>f_m^{(-)}}{\omega+\epsilon_m-\epsilon_f} \tag{B2}$$

$$M_2 = \sum_m \frac{<f\ |p_z|\ m><m\ |p_z|\ q>f_m^{(+)}}{\omega+\epsilon_q-\epsilon_m} \tag{B3}$$

Using energy conservation

$$2\omega+\epsilon_q = \epsilon_f \tag{B4}$$

and the relation

$$f_m^{(+)}+f_m^{(-)}=1 \tag{B5}$$

I may sum these to give

$$M^{(2)} = \left(\frac{A_o\,\hat{e}_z}{2c}\right)^2 \sum_m \frac{<f \mid p_z \mid m><m \mid p_z \mid q>}{\omega+\epsilon_q-\epsilon_m} \tag{B6}$$

For the third order multiphoton excitation process (see Fig. 3.4) I have

$$M^{(3)} = \left(\frac{A_o\,\hat{e}_z}{2c}\right)^3 \left[M_1+M_2+M_3+M_4+M_5+M_6\right] \tag{B7}$$

where, letting

$$M_{fnmq} = <f \mid p_z \mid n><n \mid p_z \mid m><m \mid p_z \mid q> \tag{B8}$$

$$M_1 = \sum_{mn} \frac{M_{fnmq}\, f_m^{(-)} f_n^{(-)}}{(2\omega+\epsilon_m-\epsilon_f)(\omega+\epsilon_n-\epsilon_f)} \tag{B9}$$

$$M_2 = -\sum_{mn} \frac{M_{fnmq}\, f_m^{(-)} f_n^{(+)}}{(2\omega+\epsilon_q-\epsilon_n)(\omega+\epsilon_m-\epsilon_n)} \tag{B10}$$

$$M_3 = \sum_{mn} \frac{M_{fnmq}\, f_m^{(+)} f_n^{(+)}}{(2\omega+\epsilon_q-\epsilon_n)(\omega+\epsilon_q-\epsilon_m)} \tag{B11}$$

$$M_4 = -\sum_{mn} \frac{M_{fnmq}\, f_m^{(+)} f_n^{(-)}}{(2\omega+\epsilon_q+\epsilon_n-\epsilon_m-\epsilon_f)(\omega+\epsilon_n-\epsilon_f)} \tag{B12}$$

$$M_5 = -\sum_{mn} \frac{M_{fnmq}\, f_m^{(-)} f_n^{(+)}}{(2\omega+\epsilon_m-\epsilon_f)(\omega+\epsilon_m-\epsilon_n)} \tag{B13}$$

$$M_6 = -\sum_{mn} \frac{M_{fnmq}\, f_m^{(+)} f_n^{(-)}}{(2\omega+\epsilon_q+\epsilon_n-\epsilon_m-\epsilon_f)(\omega+\epsilon_q-\epsilon_m)} \tag{B14}$$

Using energy conservation

$$3\omega+\epsilon_q = \epsilon_f \tag{B15}$$

and expressing the $f_m^{(+)}$ and $f_n^{(+)}$ factors in terms of $f_m^{(-)}$ and $f_n^{(-)}$ I may readily show that, when the $M_i$ are added together, the coefficients of $f_m(-)$, $f_n^{(-)}$ and $f_m^{(-)} f_n^{(-)}$ are all zero. What remains is a single expression

$$M^{(3)} = \left(\frac{A_o \hat{e}_z}{2c}\right)^3 \sum_{mn} \frac{\langle f \mid p_z \mid n \rangle \langle n \mid p_z \mid m \rangle \langle m \mid p_z \mid q \rangle}{(2\omega+\epsilon_q-\epsilon_n)(\omega+\epsilon_q-\epsilon_m)} \tag{B16}$$

Here all intermediate states are included in the sum.

## APPENDIX C A THEOREM

Theorem: If $RT = F$ where $R$ is a lower triangular matrix of dimension $n \times n$ and $T$ and $F$ are column matrices of dimension $n$ then;

$$T_j = \frac{\det N_j}{\det R_j} \tag{C1}$$

where $N_j$ is given by

$$N_j = \begin{vmatrix} R_{11} & 0 & \cdot & 0 & F_1 \\ R_{21} & R_{22} & \cdot & 0 & F_2 \\ R_{31} & R_{32} & \cdot & 0 & F_3 \\ \cdot & \cdot & \cdot & 0 & \cdot \\ R_{j-1,1} & R_{j-1,2} & \cdot & R_{j-1,j-1} & F_{j-1} \\ R_{j1} & R_{j2} & \cdot & R_{j,j-1} & F_j \end{vmatrix} \tag{C2}$$

and $R_j$ is a matrix of dimension $j \times j$ constructed from the upper left $j \times j$ elements of the $R$ matrix.

Lemma: The inverse of a lower triangular matrix is also lower triangular.

Proof of lemma: Consider the set of linear equations.

$$\sum_{j=1}^{n} R_{ij} T_j = F_i \tag{C3}$$

Since R is lower triangular, $R_{ij} = 0$ if $j > i$. Then

$$\sum_{j=1}^{i} R_{ij} T_j = F_i \tag{C4}$$

or

$$R_{ii} T_i = F_i - \sum_{j=1}^{i-1} R_{ij} T_j \tag{C5}$$

or

$$T_i = \frac{F_i}{R_{ii}} - \sum_{j=1}^{i-1} \frac{R_{ij}}{R_{ii}} T_j \tag{C6}$$

From this I see that a given $T_i$ depends linearly on $F_i$ and values of $T_j$ for j ≤ i. Hence when I write

$$T_i = \sum_{j=1}^{n} M_{ij} F_j \tag{C7}$$

I must have

$$M_{ij} = 0 \qquad \text{if } j > i \tag{C8}$$

Q.E.D.

Proof of the theorem:

From the above lemma

$$\begin{bmatrix} M_{11} & 0 & .. & 0 \\ M_{21} & M_{22} & .. & 0 \\ .. & .. & .. & 0 \\ M_{j-1,1} & M_{j-1,2} & .. & M_{j-1,j} \\ M_{j1} & M_{j2} & .. & M_{j,j} \end{bmatrix} \times \begin{bmatrix} R_{11} & 0 & .. & 0 \\ R_{21} & R_{22} & .. & 0 \\ .. & .. & .. & 0 \\ R_{j-1,1} & R_{j-1,2} & .. & R_{j-1,j} \\ R_{j1} & R_{j2} & .. & R_{j,j} \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & .. & 0 \\ 0 & 1 & .. & 0 \\ 0 & 0 & .. & 0 \\ .. & .. & .. & 0 \\ 0 & 0 & .. & 0 \\ 0 & 0 & .. & 1 \end{bmatrix} \tag{C9}$$

From the derivation of the above lemma it follows that

$$M_{jj} = \frac{1}{R_{jj}} \tag{C10}$$

This equation can be rewritten as a set of linear equations for the 'unknowns' $M_{j1}, M_{j2}, \ldots, M_{j-1,j-1}$

$$\begin{bmatrix} R_{11} & R_{21} & R_{31} & .. & R_{j-1,1} \\ 0 & R_{22} & R_{32} & .. & R_{j-1,2} \\ 0 & 0 & R_{33} & .. & R_{j-1,3} \\ .. & .. & .. & .. & .. \\ 0 & 0 & 0 & .. & R_{j-1,j-1} \end{bmatrix} \times \begin{bmatrix} M_{j,1} \\ M_{j,2} \\ M_{j,3} \\ .. \\ M_{j,j-1} \end{bmatrix} = -\frac{1}{R_{j,j}} \begin{bmatrix} R_{j,1} \\ R_{j,2} \\ R_{j,3} \\ .. \\ R_{j,j-1} \end{bmatrix} \tag{C11}$$

Let me refer to the matrix on the left hand side as D. The solution for the $M_{ji}$ coefficients is given by Cramer's rule.

$$M_{j,1} = \frac{\det D_{j,1}}{\det D} \tag{C12}$$

$$M_{j,2} = -\frac{\det D_{j,2}}{\det D} \tag{C13}$$

$$\ldots \tag{C14}$$

$$M_{j,j-1} = (-)^{j-2}\frac{\det D_{j,j-1}}{\det D} \tag{C15}$$

where

$$D_{j1} = -\frac{1}{R_{jj}}\begin{vmatrix} R_{j1} & R_{21} & .. & R_{j-1,1} \\ R_{j2} & R_{22} & .. & R_{j-1,2} \\ .. & 0 & .. & .. \\ R_{j,j-1} & 0 & .. & R_{j-1,j-1} \end{vmatrix} \tag{C16}$$

$$D_{j2} = -\frac{1}{R_{jj}}\begin{vmatrix} R_{j1} & R_{11} & R_{31} & .. & R_{j-1,1} \\ .. & 0 & R_{32} & .. & R_{j-1,2} \\ .. & 0 & R_{33} & .. & .. \\ R_{j,j-1} & 0 & 0 & .. & R_{j-1,j-1} \end{vmatrix} \tag{C17}$$

etc. In the higher order $D_{jl}$ the $l^{th}$ row is replaced by the right hand side of the previous equation. Note that

$$T_j = M_{j1}F_1 + M_{j2}F_2 + M_{j3}F_3 + ... + M_{j,j-1}F_{j-1} + M_{jj}F_j \tag{C18}$$

and

$$R_{jj}\det D = \det R_j \tag{C19}$$

hence

$$T_j = \frac{F_1\det D_{j1} - F_2\det D_{j2} + .....}{\det D} \tag{C20}$$

However the numerator is just the expansion of a determinant, so

$$T_j = \frac{detS_j}{detR_j} \tag{C21}$$

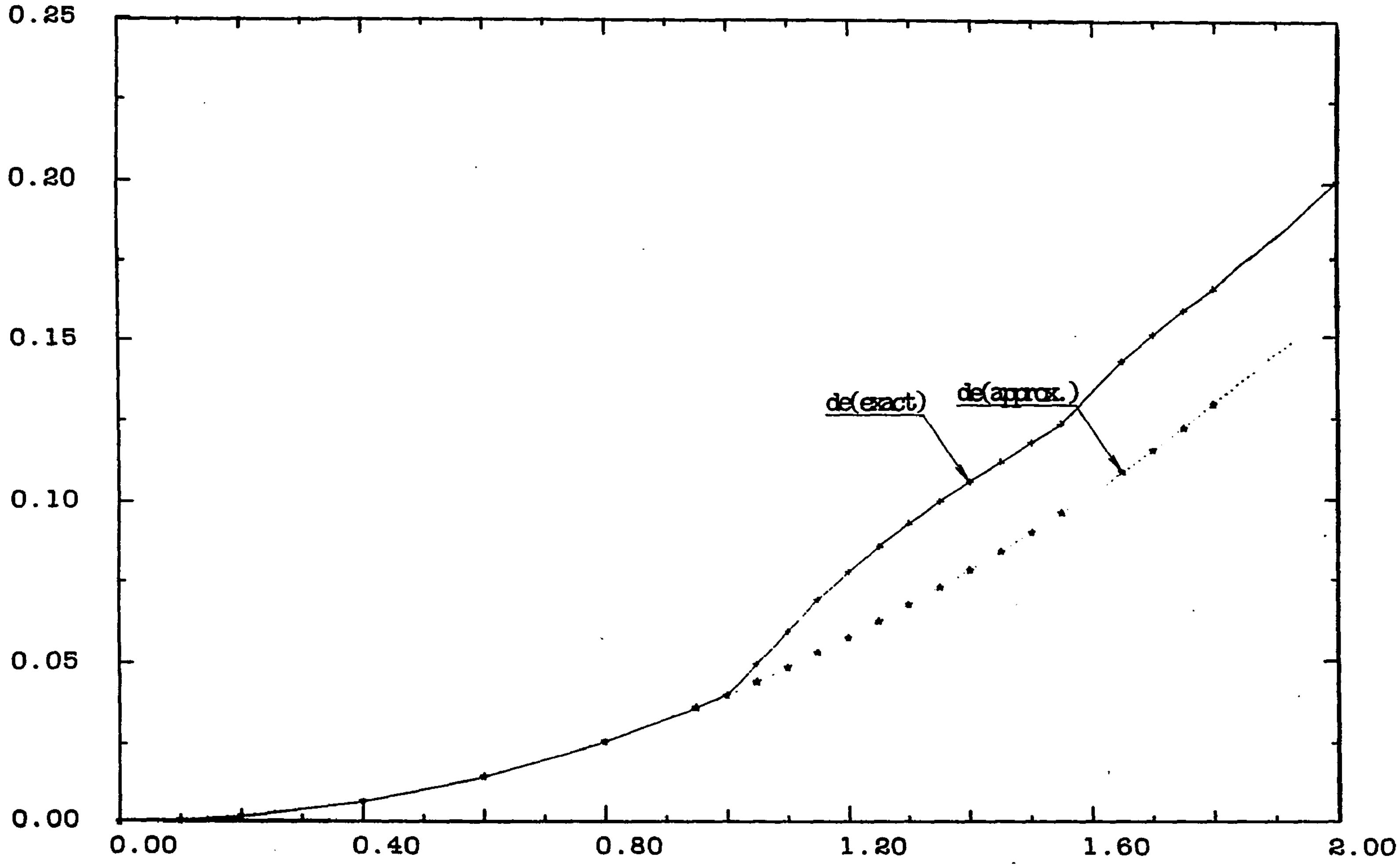
where

$$S_j = (-)^{j-1} \begin{vmatrix} F_1 & F_2 & F_3 & .. & F_j \\ R_{11} & R_{21} & R_{31} & .. & R_{j1} \\ 0 & R_{22} & R_{32} & .. & R_{j2} \\ 0 & 0 & .. & .. & .. \\ 0 & 0 & .. & .. & R_{j,j-1} \end{vmatrix} \quad \text{(C22)}$$

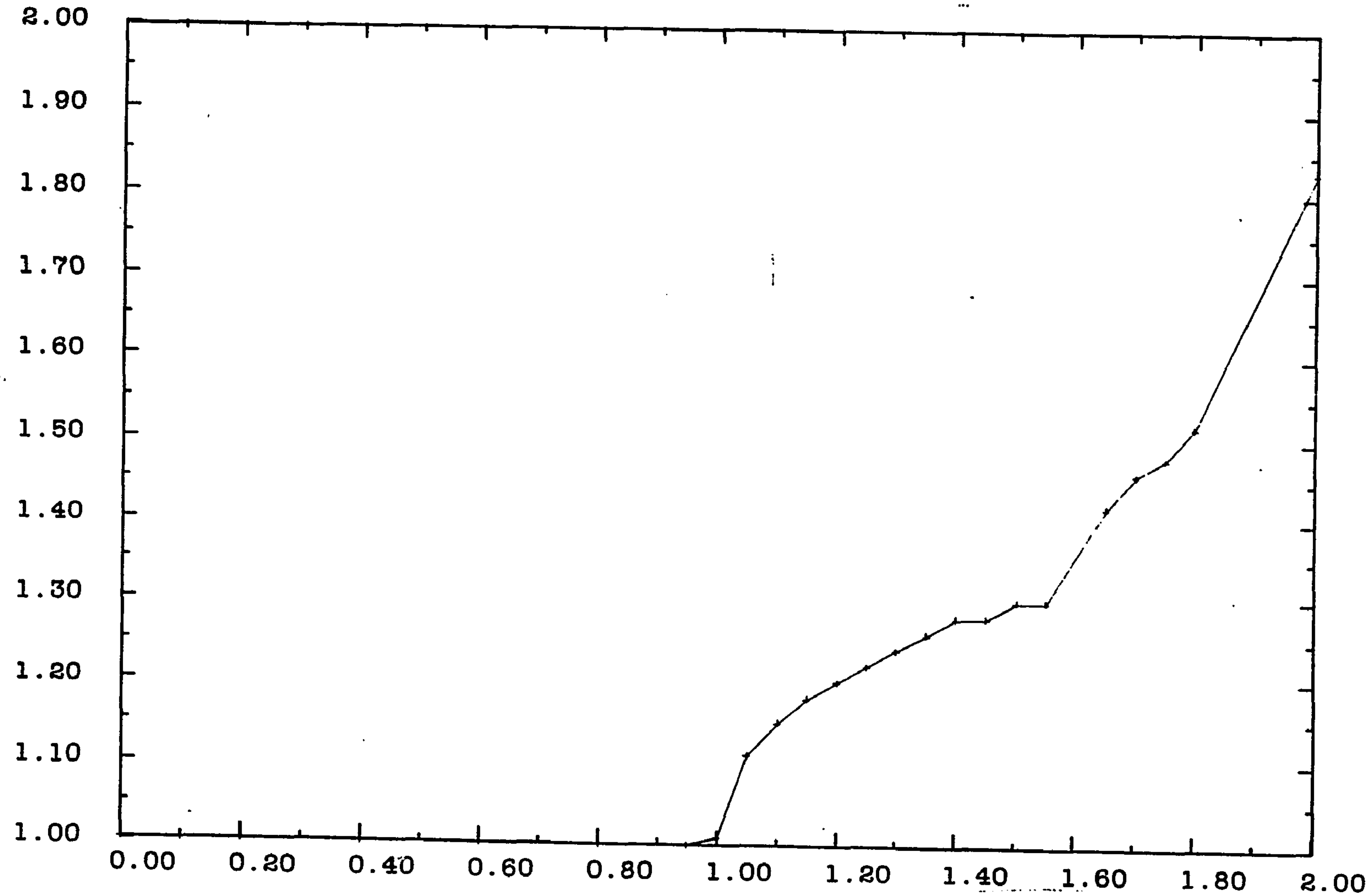
Upon permuting the rows one step up and interchanging rows and columns.

$$detS_j = \det \begin{vmatrix} R_{11} & 0 & .. & 0 & F_1 \\ R_{21} & R_{22} & .. & 0 & F_2 \\ R_{31} & R_{32} & .. & 0 & F_3 \\ .. & .. & .. & R_{j-1,j-1} & .. \\ R_{j1} & R_{j2} & .. & R_{j,j-1} & F_j \end{vmatrix} \quad \text{(C23)}$$

Q. E. D.




2.1 The mean energy gain , $\Delta E$ and the estimated energy gain, $\Delta E$ approx versus the excursion parameter x. $\dot{w}=.2, cz=.1, \Delta t=.1$ n=100.




2.2 The mean number of collisions <N> versus x. w=.2,e7=.1,Δt =.1 n=100.

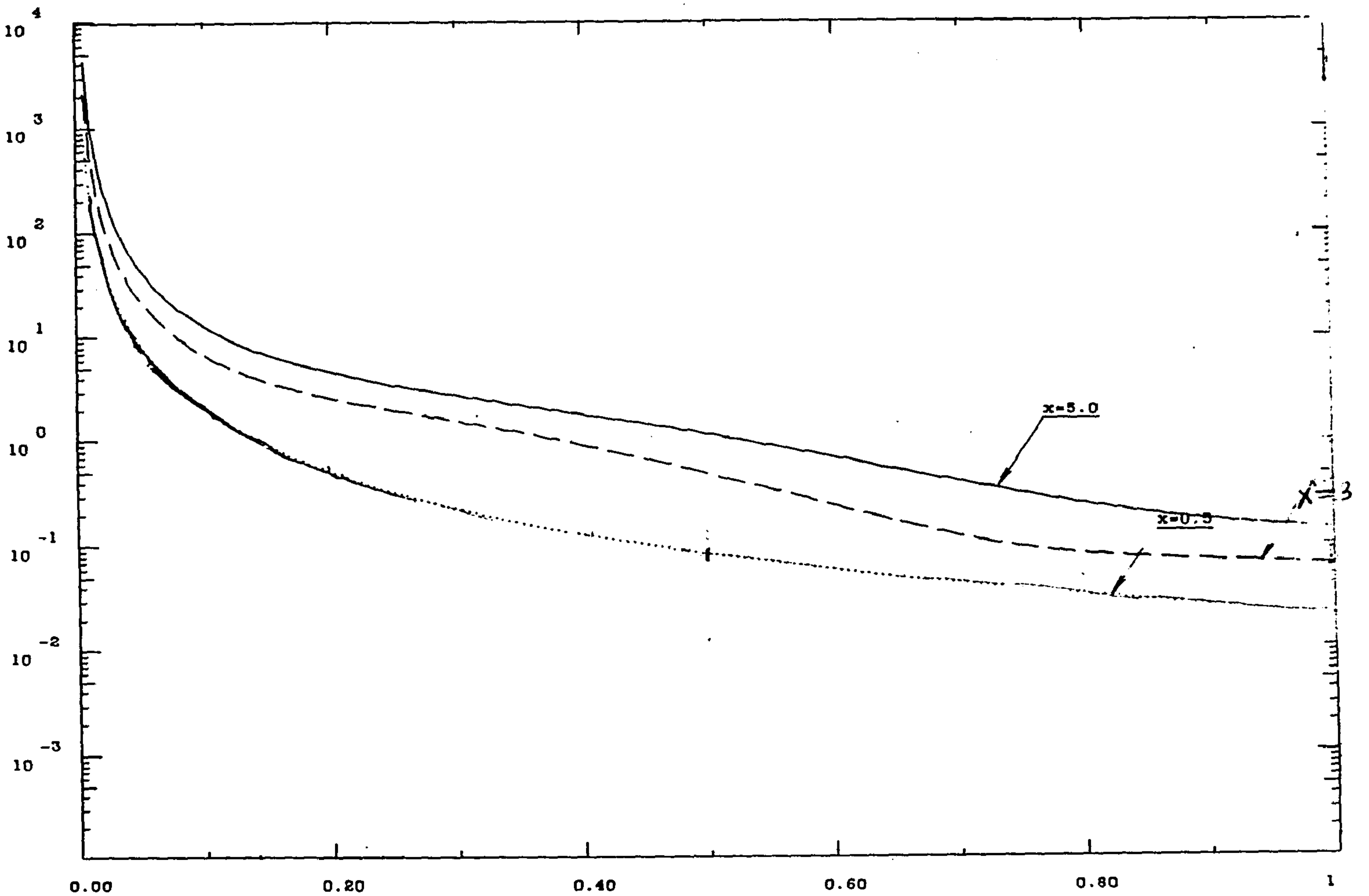



Fig. 2.3 Power spectrum of momentum, ln| P(ω')|**2. vs ω'

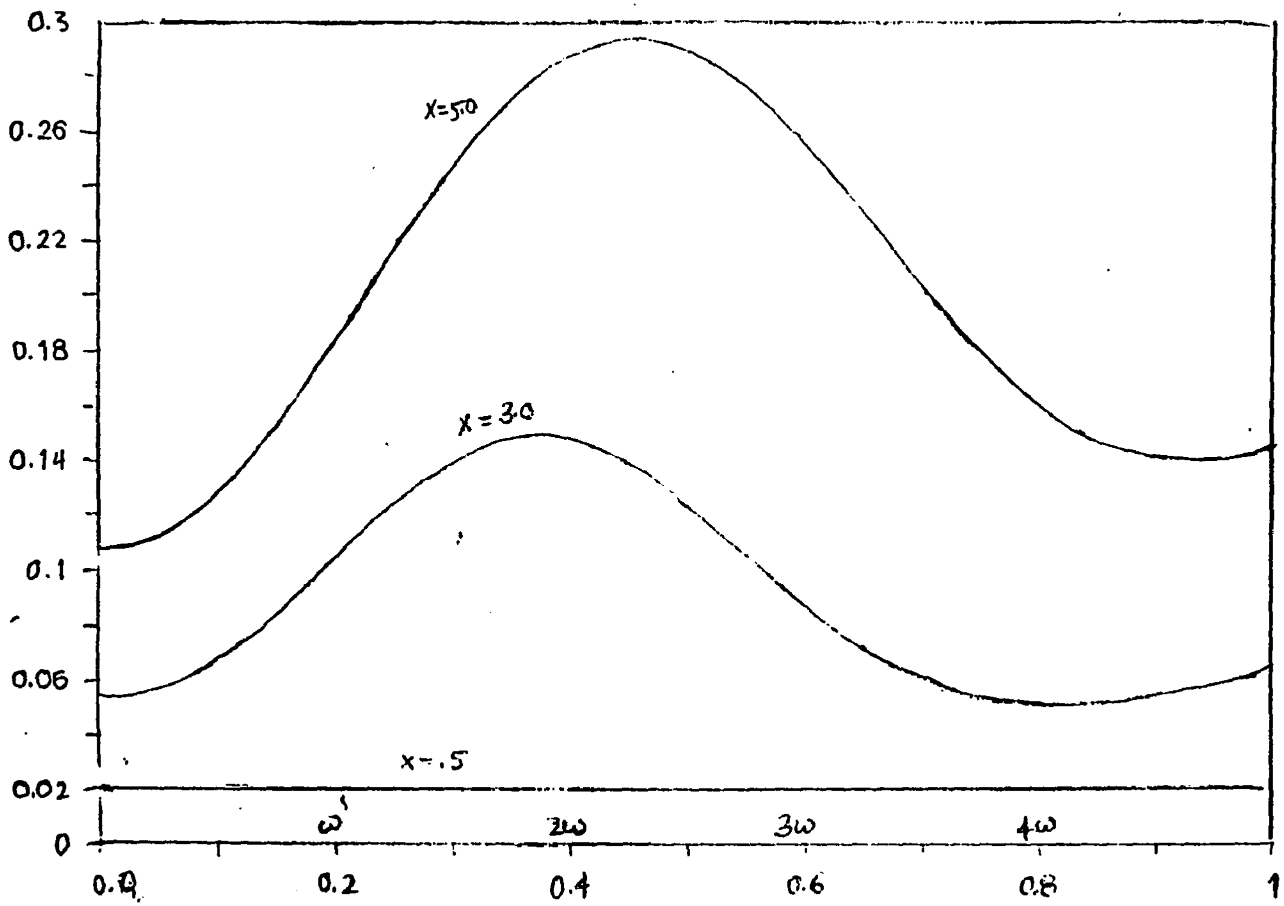
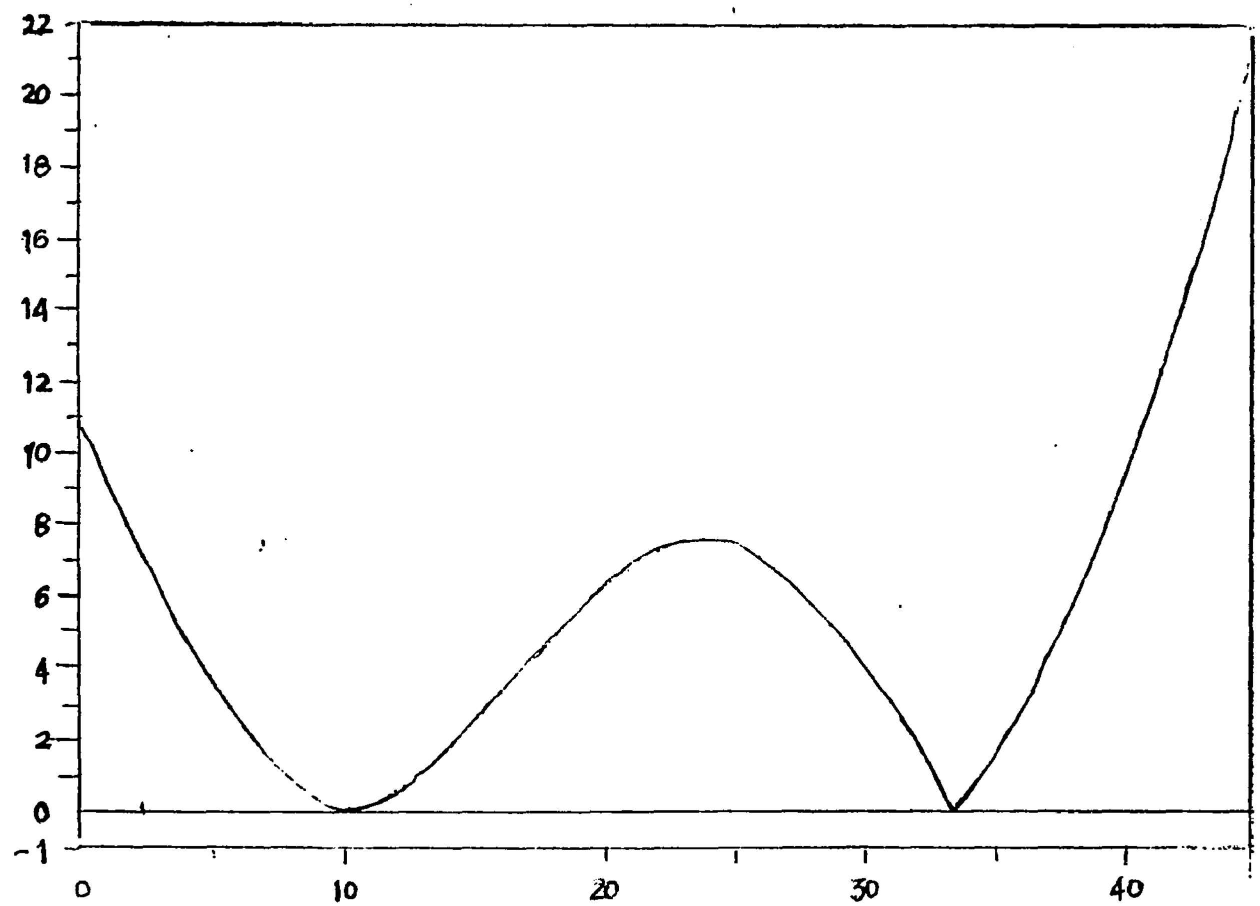



Fig. 2.4 Power spectrum of acceleration, |ma(ω')|**2 vs ω'




2.5 Trajectory for a classical wall collision. Here x =5,w=.2 ez=.1 $\Delta t$ =.1 .

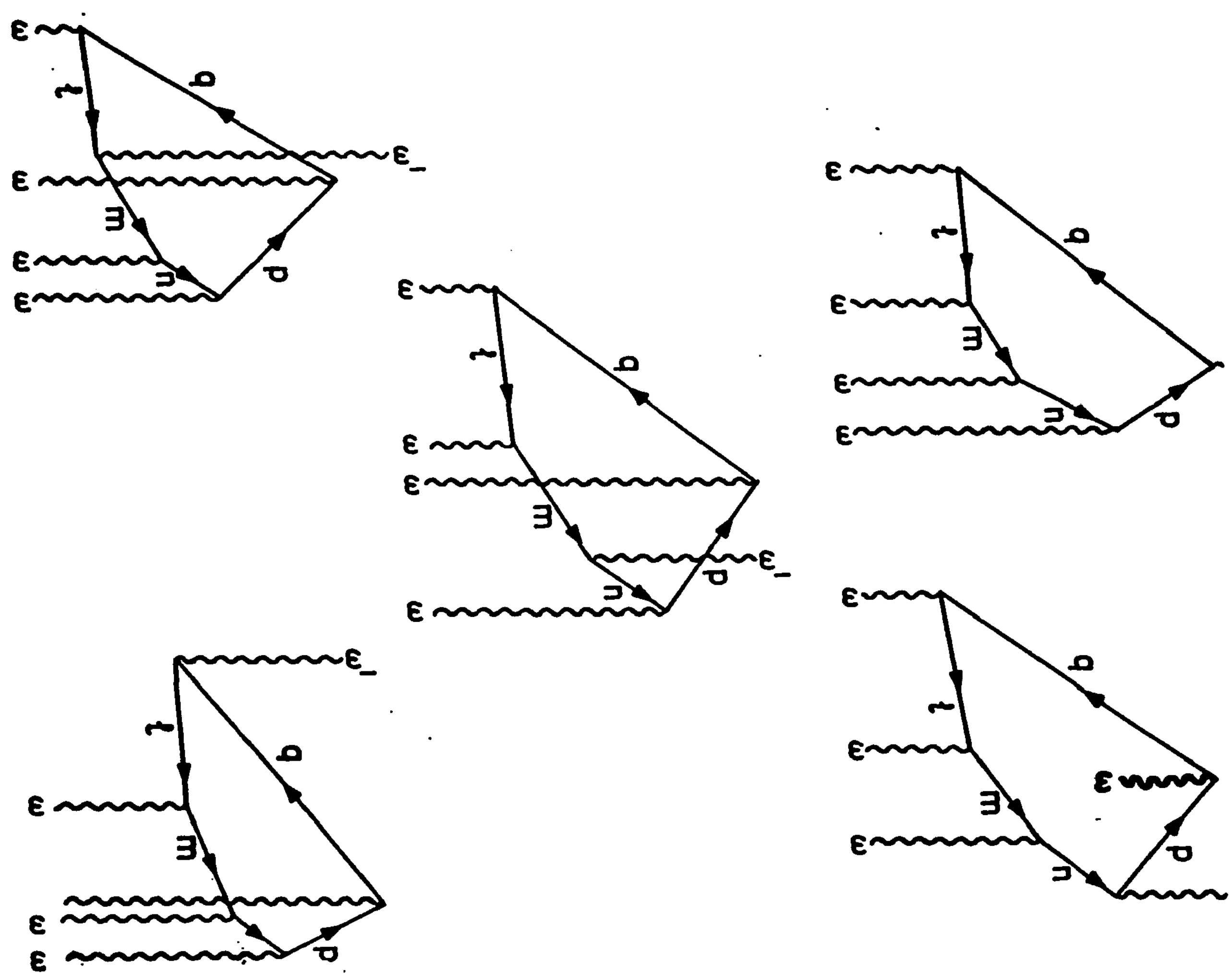


Fig.3.1 Feynman diagrams for multiharmonic generation for the case n=4. Four photons of frequency ω combine to create one photon of frequency 4ω.

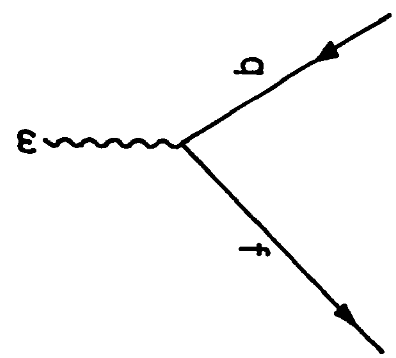


Fig. 3.2 First order photoemission.

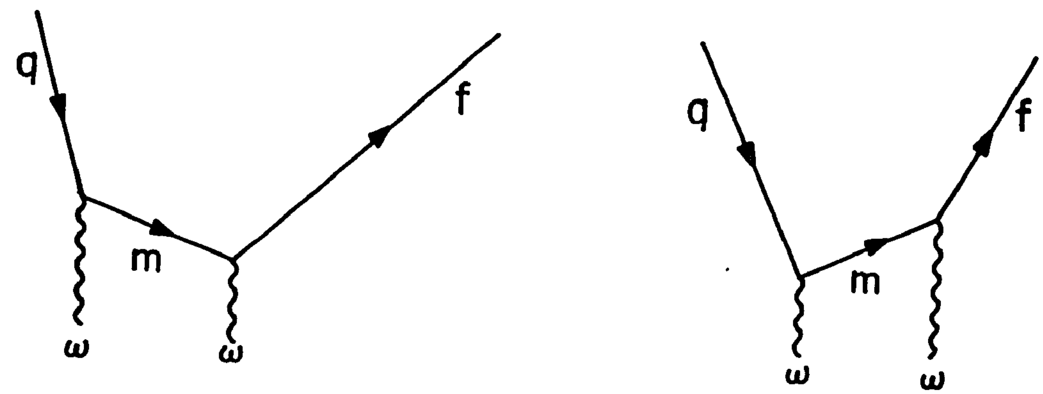



Fig. 3.3 Second order photoemission.

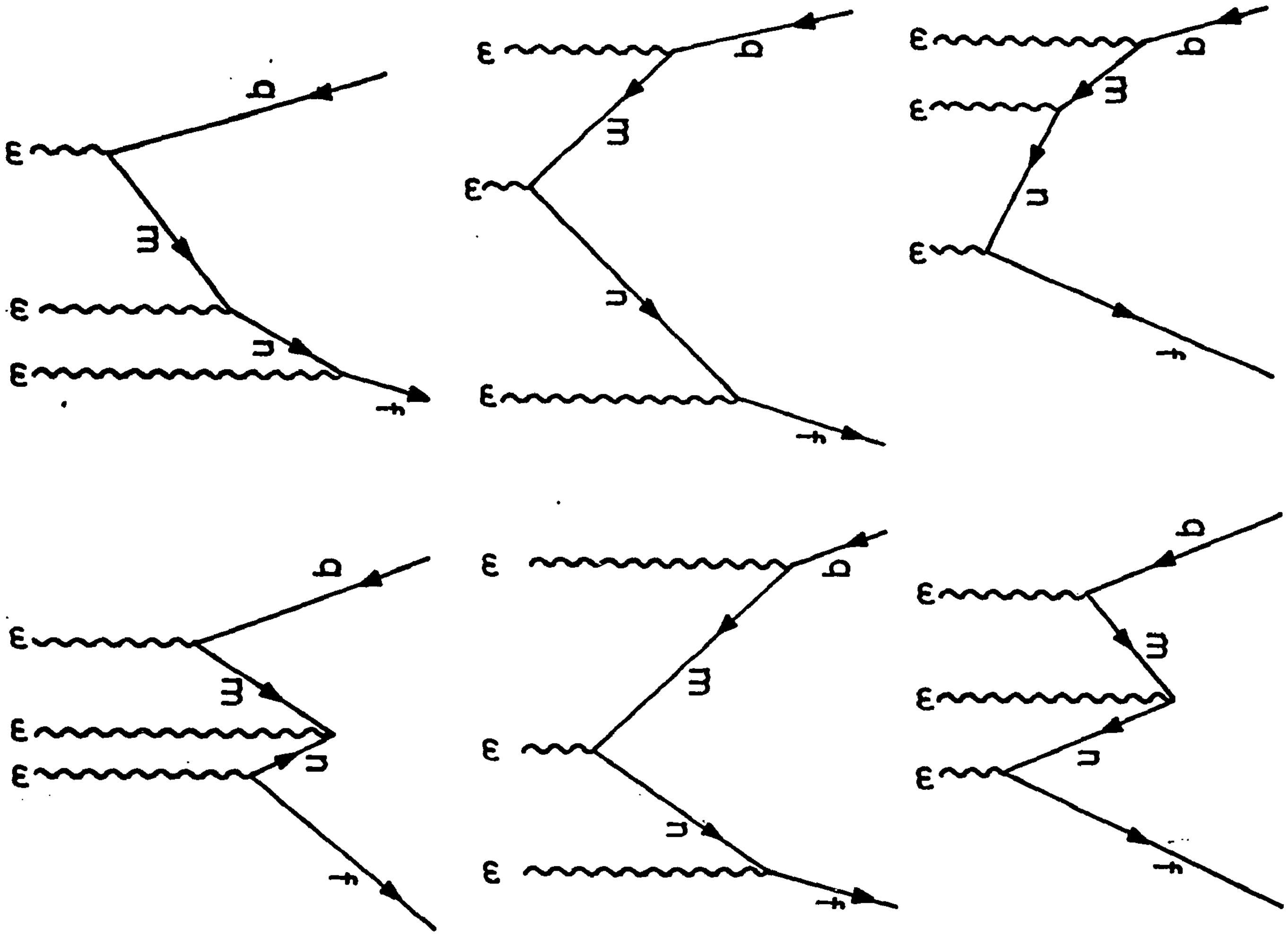


Fig. 3.4 Third order photoemission.

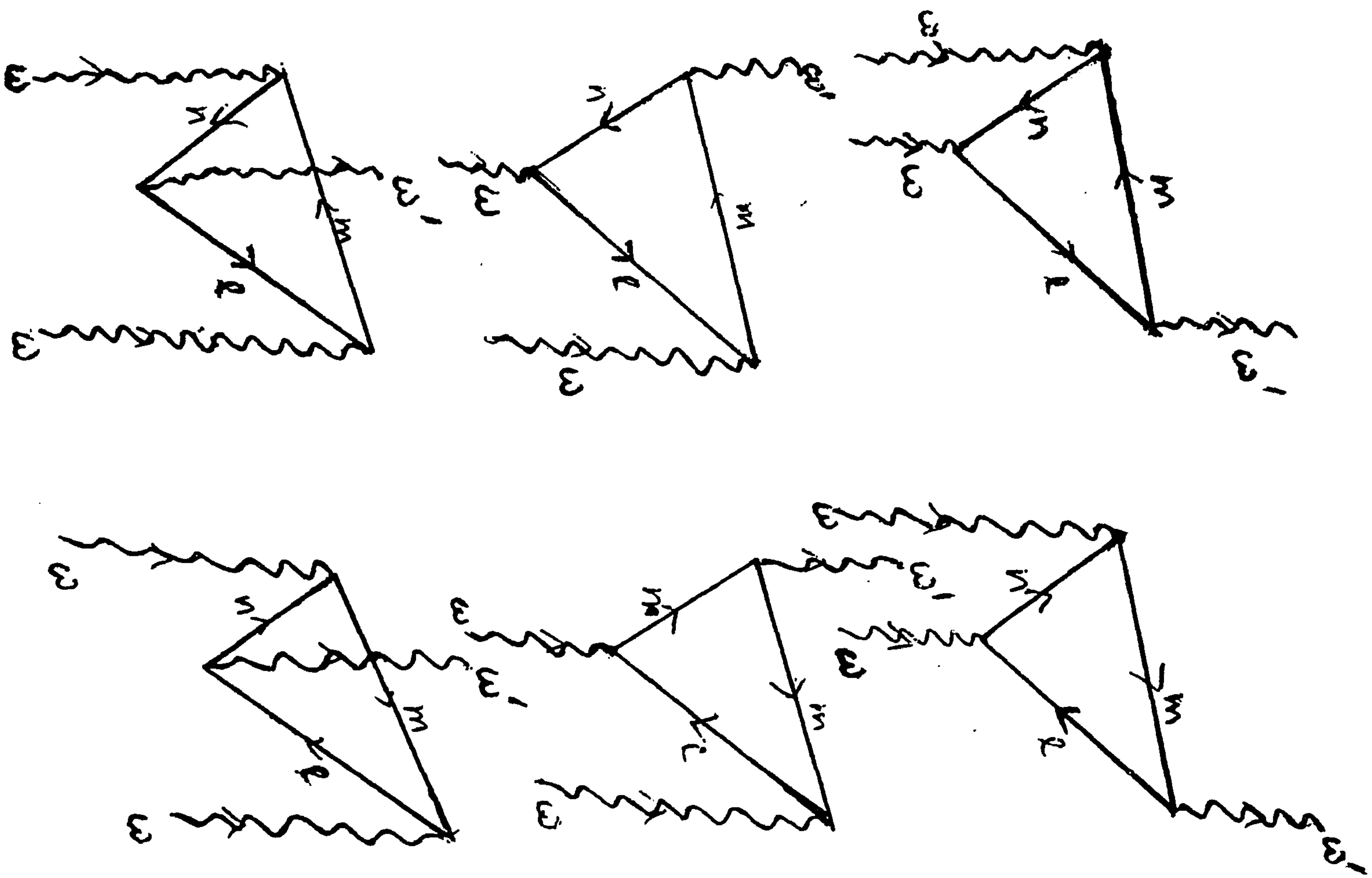


Fig. 3.5 All six diagrams of SHG including the intermediate states.

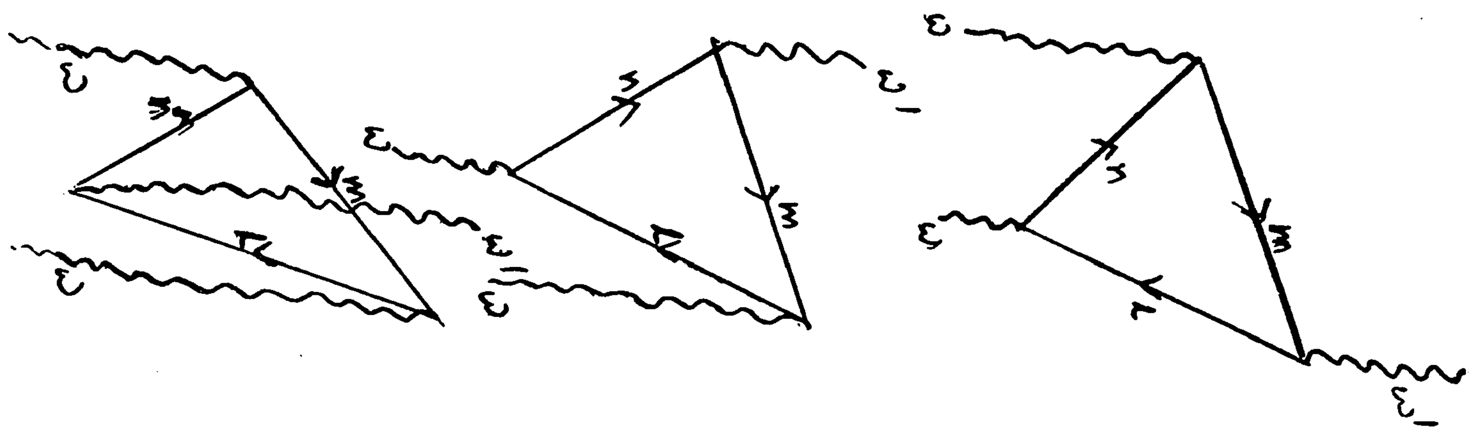


**Fig. 3.6 Three diagrams of SHG after summing over intermediate states.**

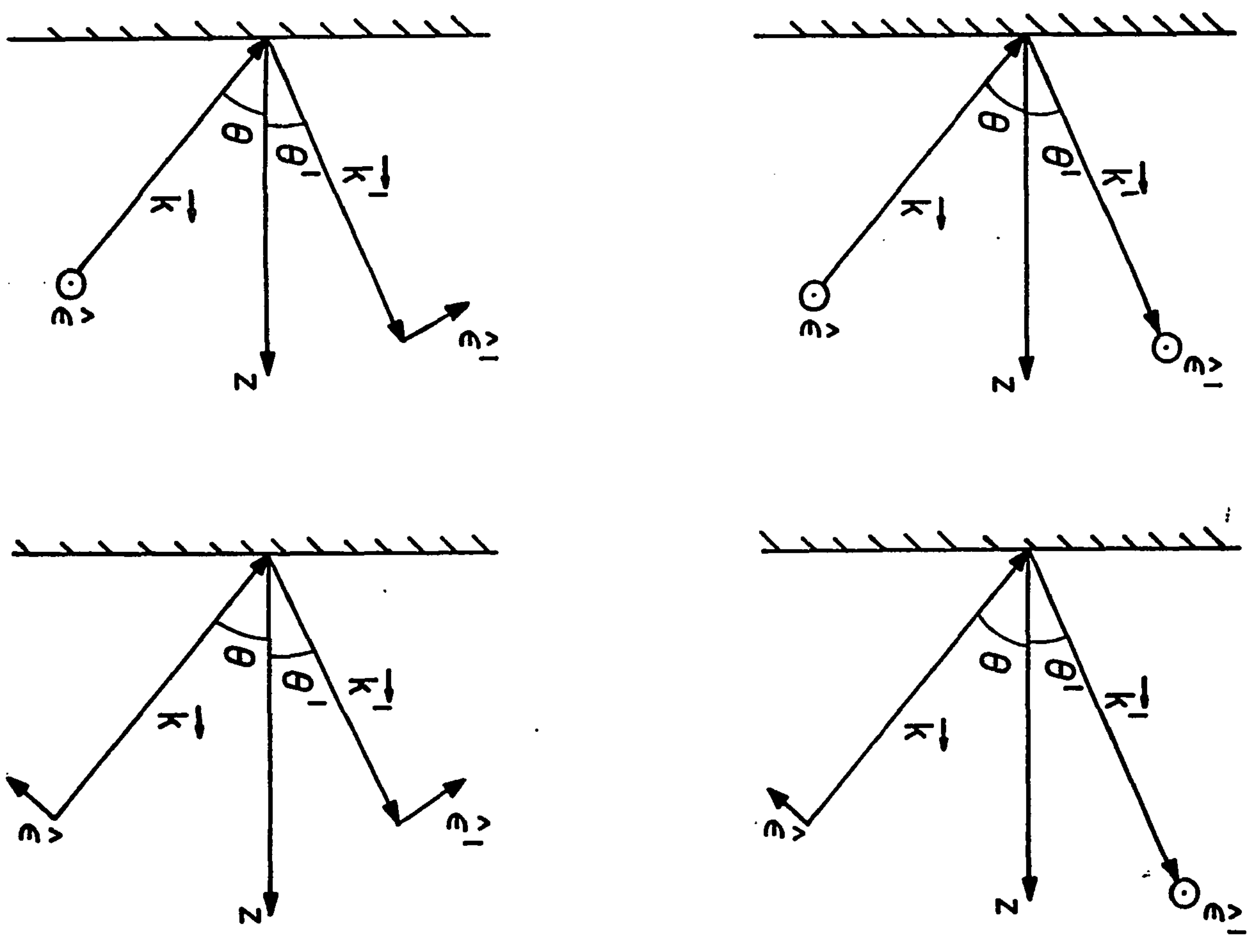


Fig. 4.1 The four states of polarization. The propagation vectors are denoted by $\vec{k}$ and $\vec{k}\,'$ and their respective polarization vectors by $\hat{e}$ and $\hat{e}\,'$.

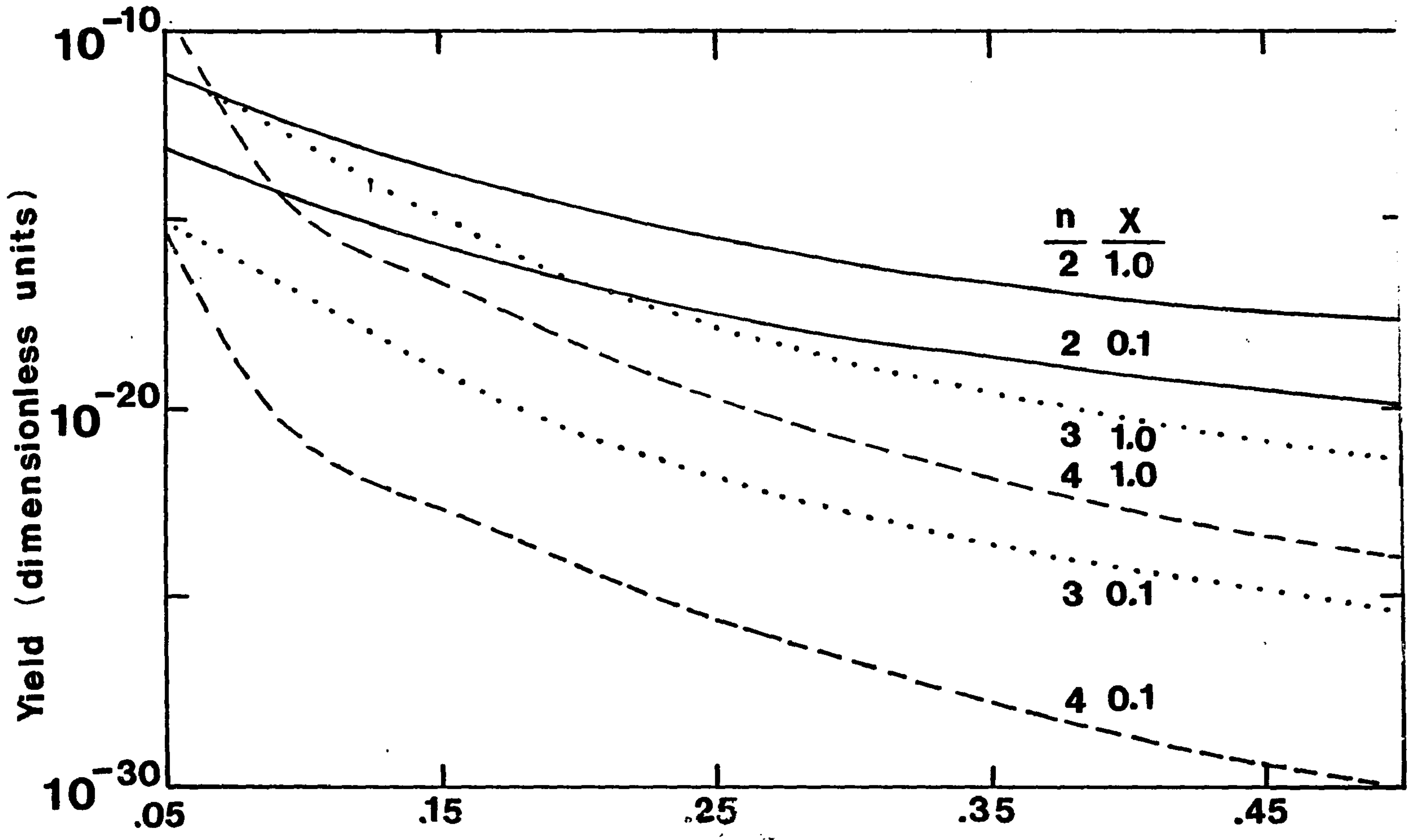



Fig. 4.2 Multi-harmonic yield versus photon frequency from Na surface. Results are for two different laser intensities labeled by x=.1andx=1 (see text) and for the cases n=2,3 and 4.

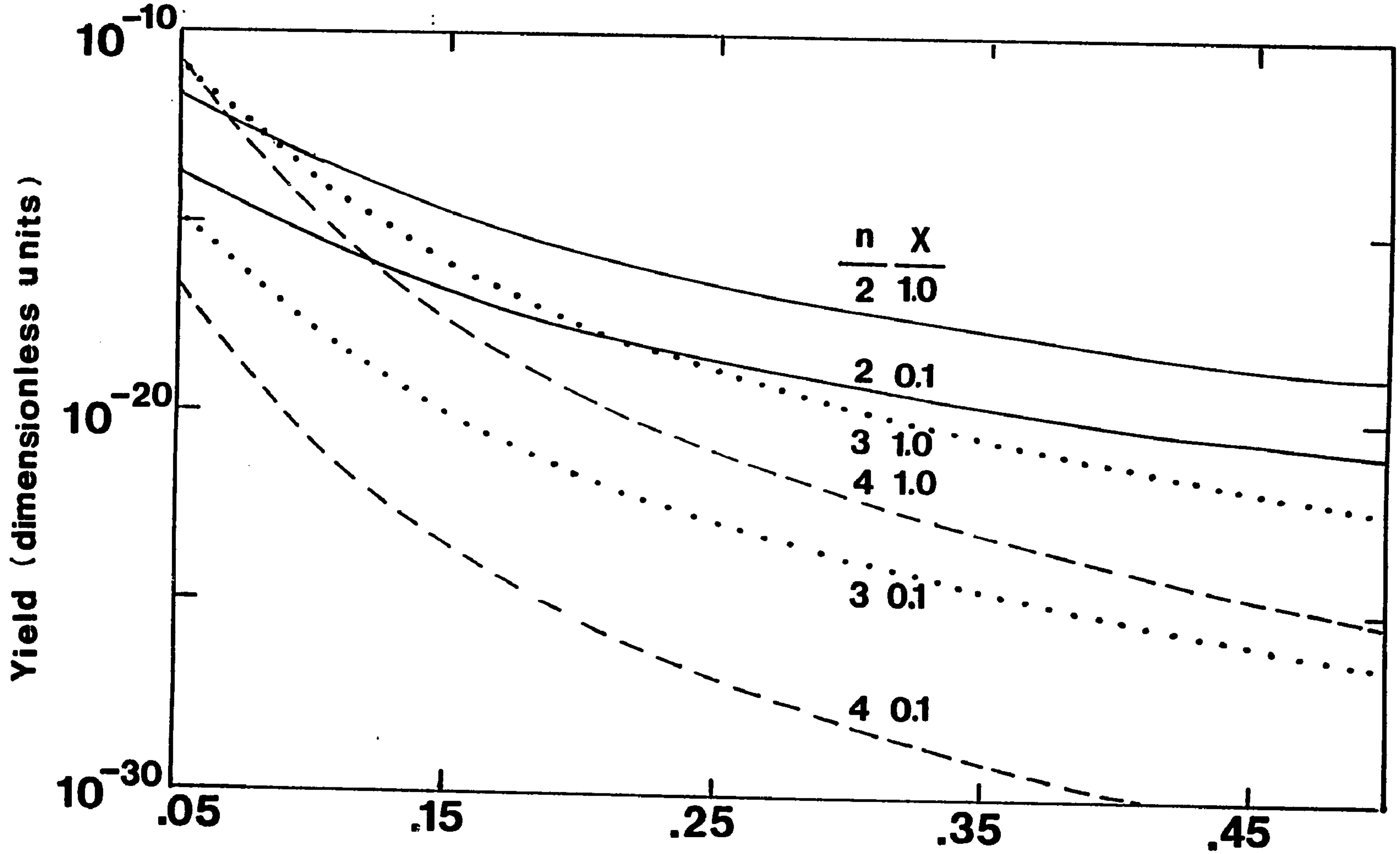



Fig. 4.3 Same as Fig. 4.2 but for K instead of Na.

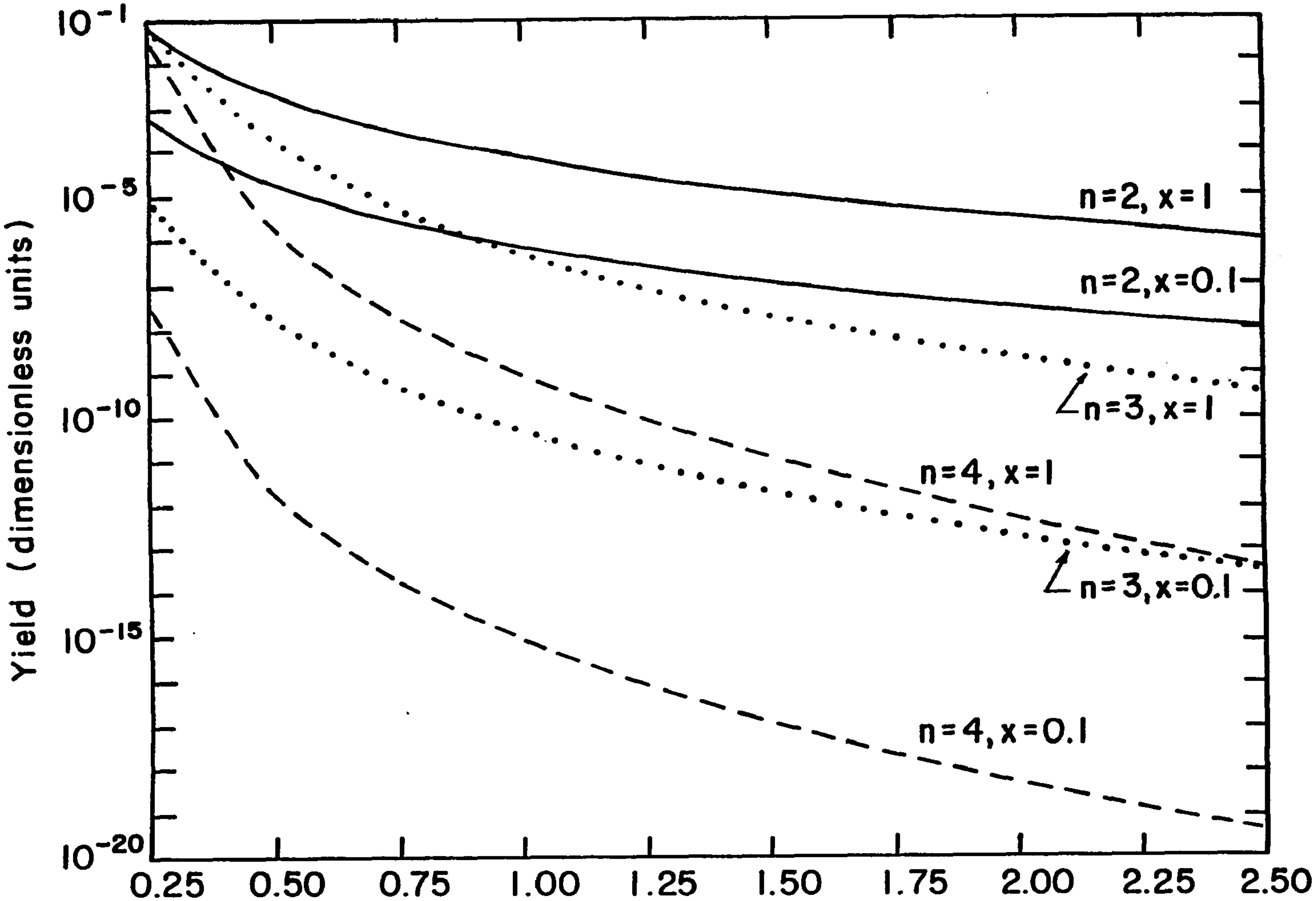



Fig. 4.4 Multiphoton electron emission yield versus photon frequency from a Na surface for two different laser intensities (see text). Results are presented for the cases n=2,3 and 4.

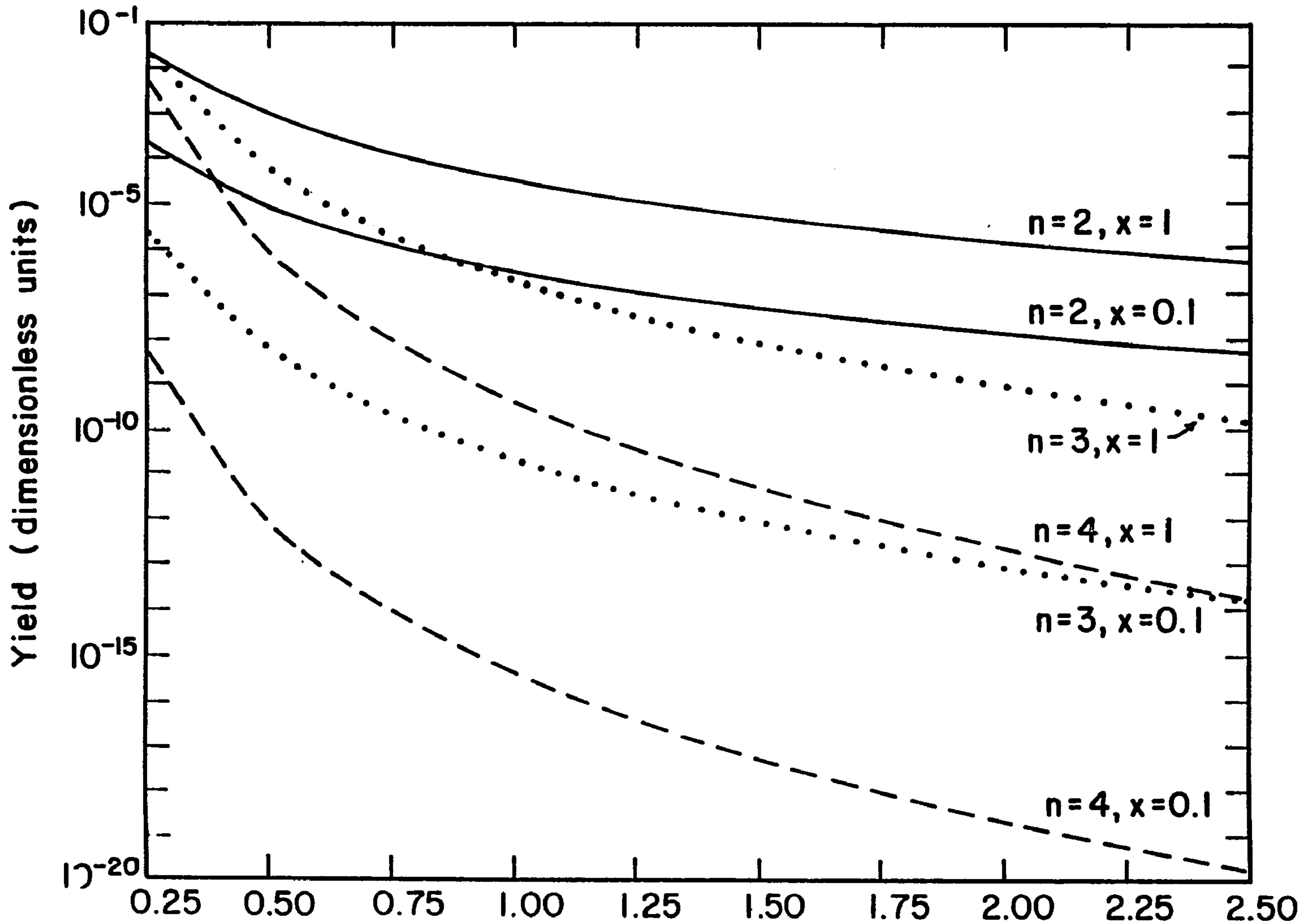



Fig. 4.5 Same as Fig. 4.4 but for K instead of Na.

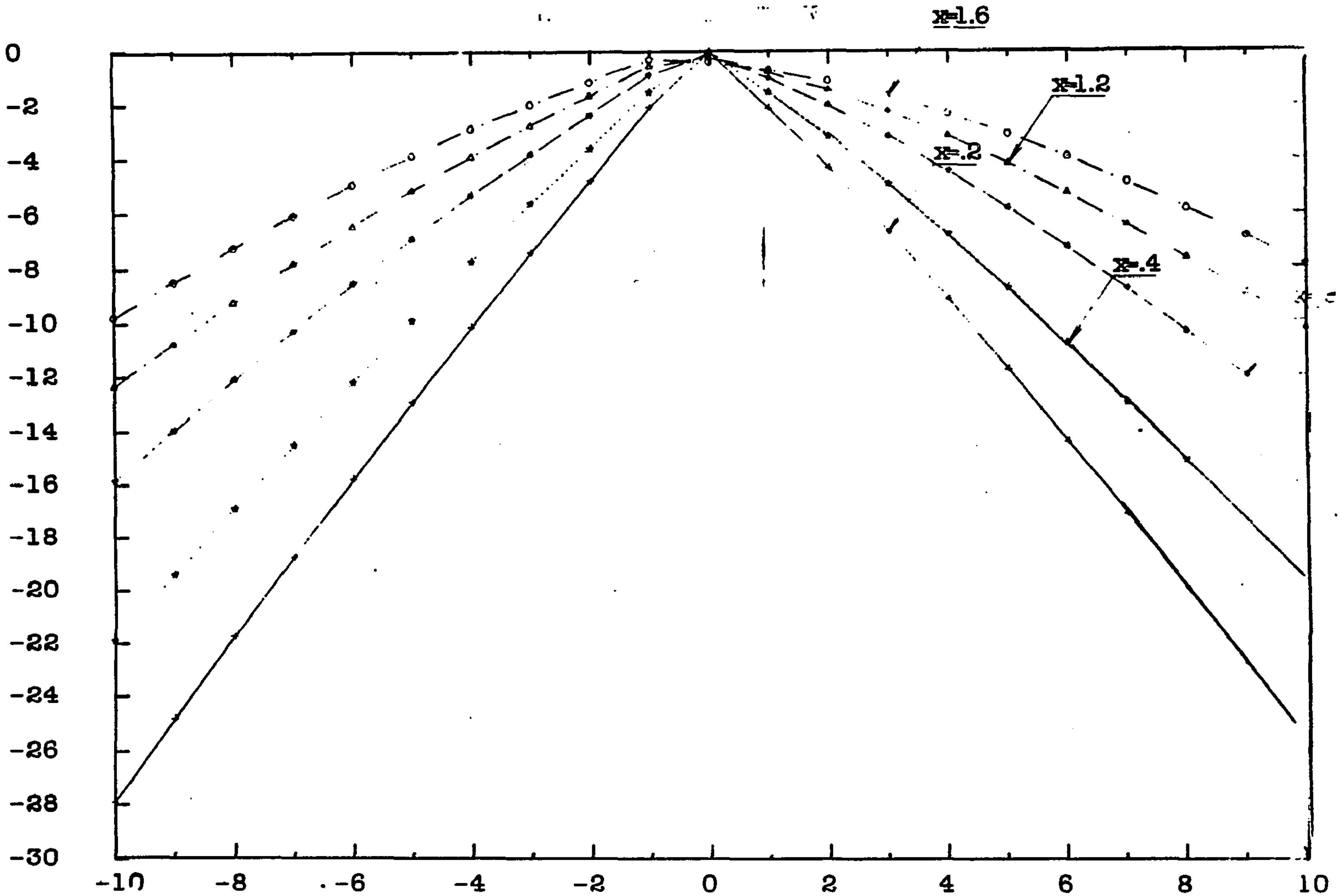



Fig. 6.1 log(|Bn|**2) as a function of n for a number of x values. Here ez=.1 and w=.2.

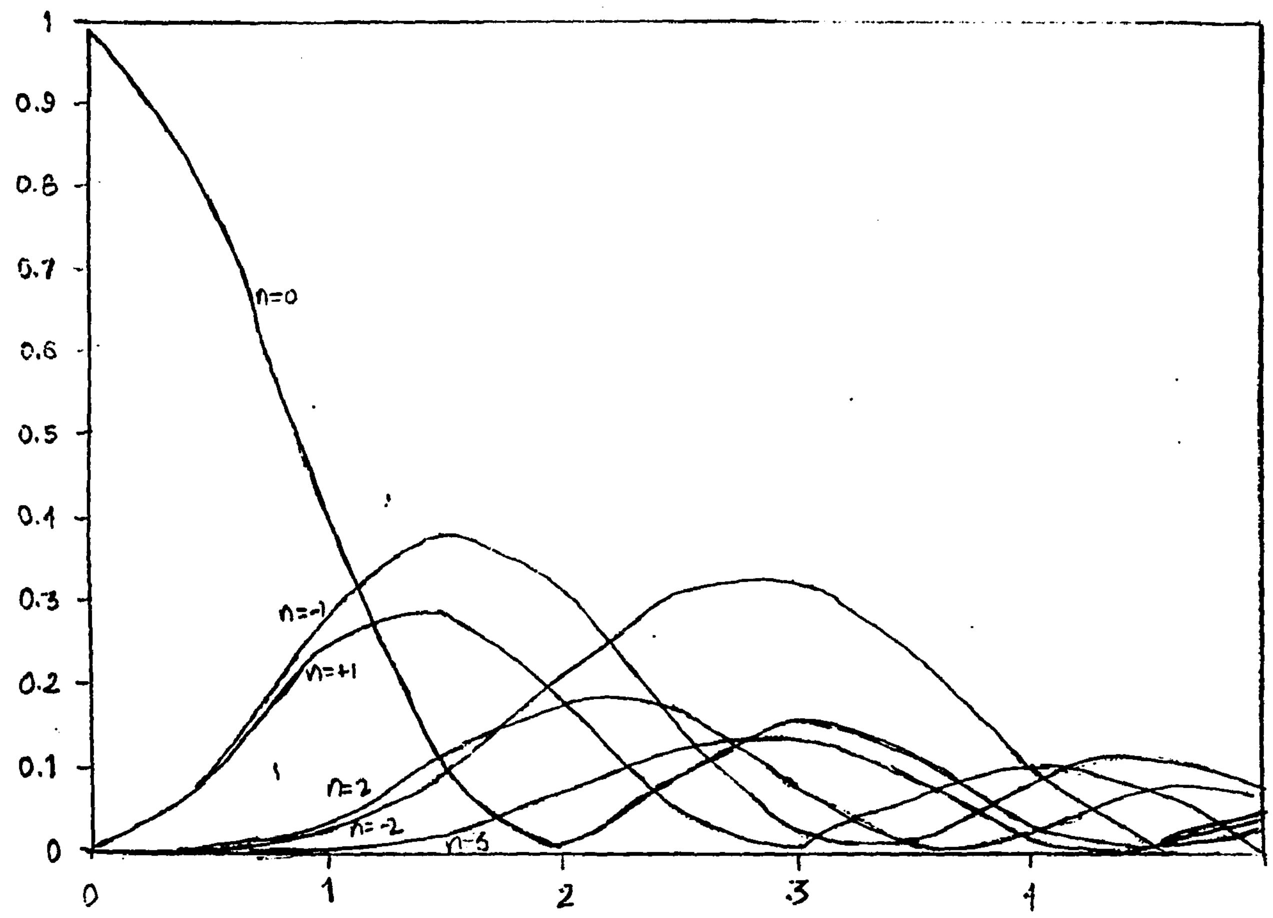



Fig. 6.2 |Bn|**2 vs x for a number of n values. n=-2 to 3, cz=0.2,w=0.05.

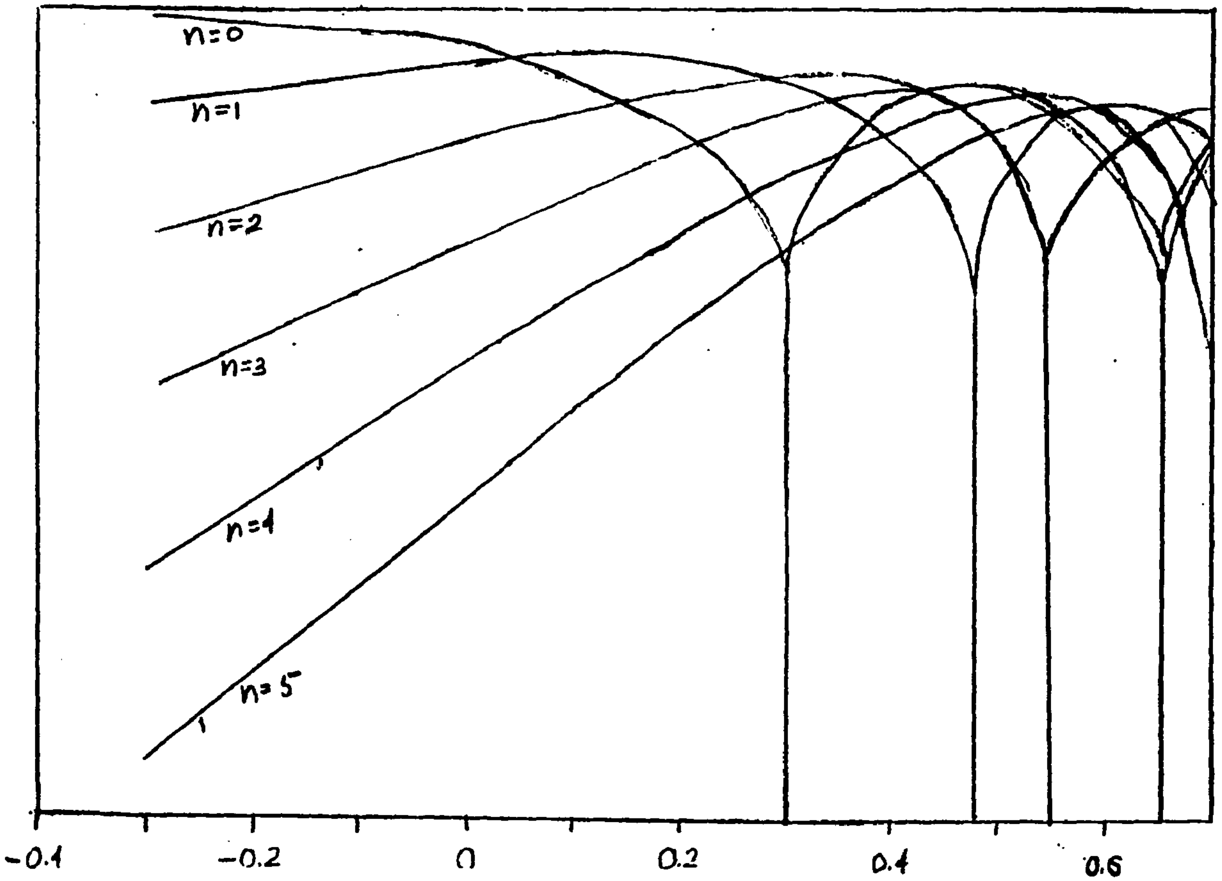



Fig. 6.3 log(|Bn|**2) vs log(x) for a number of n values. n=0 to 5, ez=0.2,w=0.05.

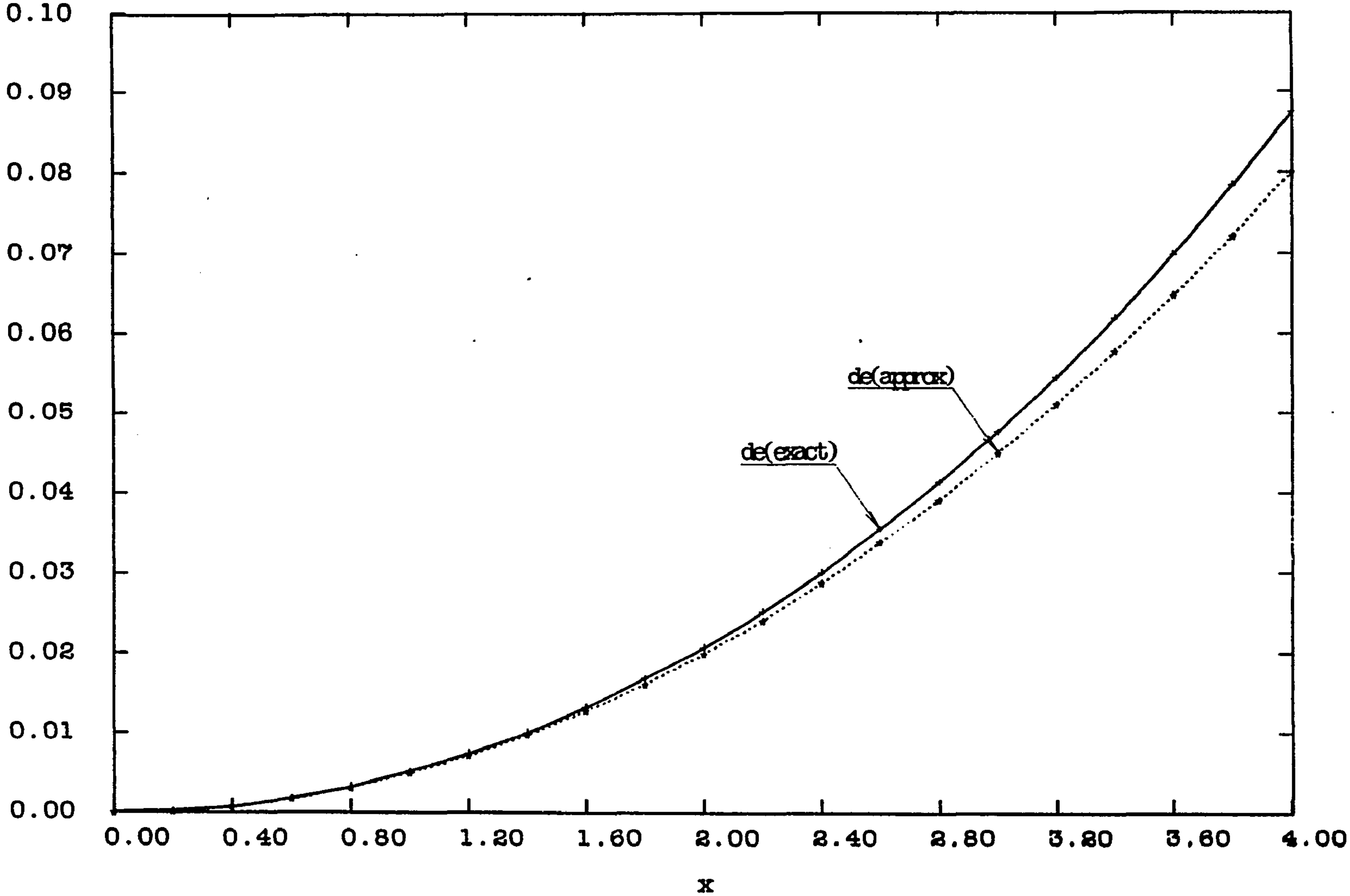



Fig. 6.4 Exact and approximate change in energy plotted as a function of x for ez=0.1,w=0.05 .

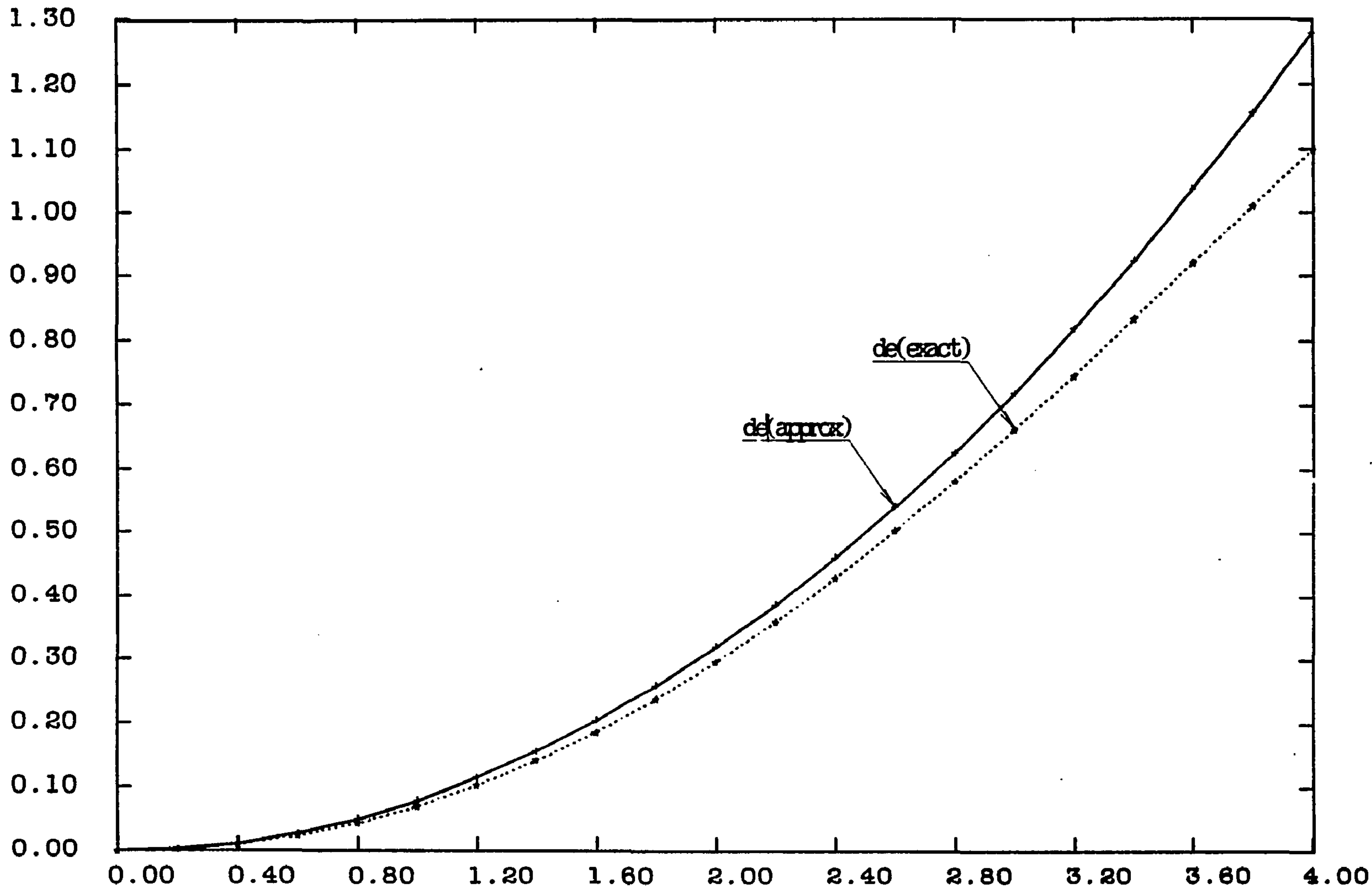



Fig. 6.5 Exact and approximate change in energy plotted as a function of x for ez=0.1 and w=0.2.

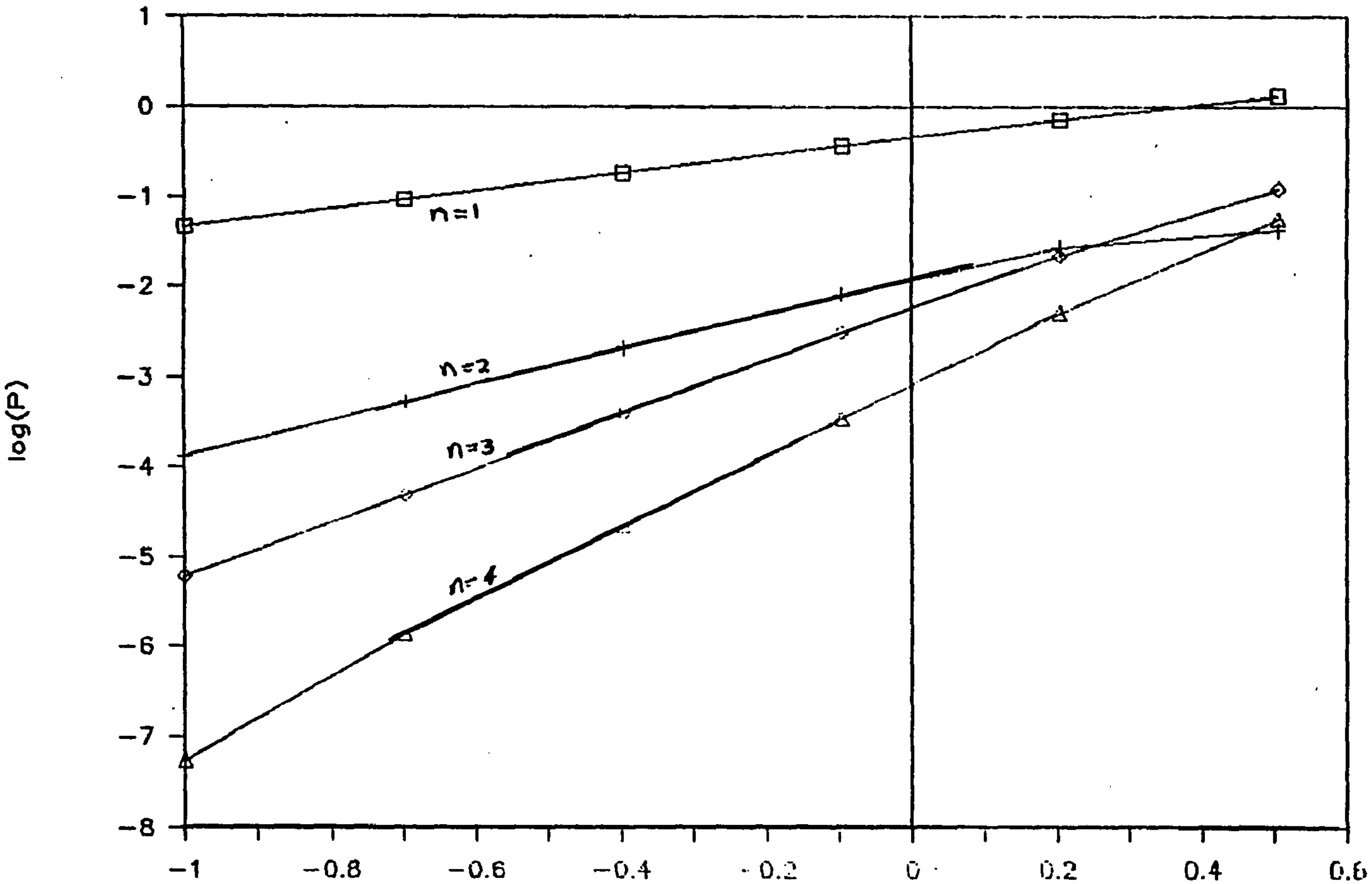



Fig. 6.6 Magnitude of velocity fourier coefficients, log(P) vs log(x) for various n values and cz=.1, w=0.05.

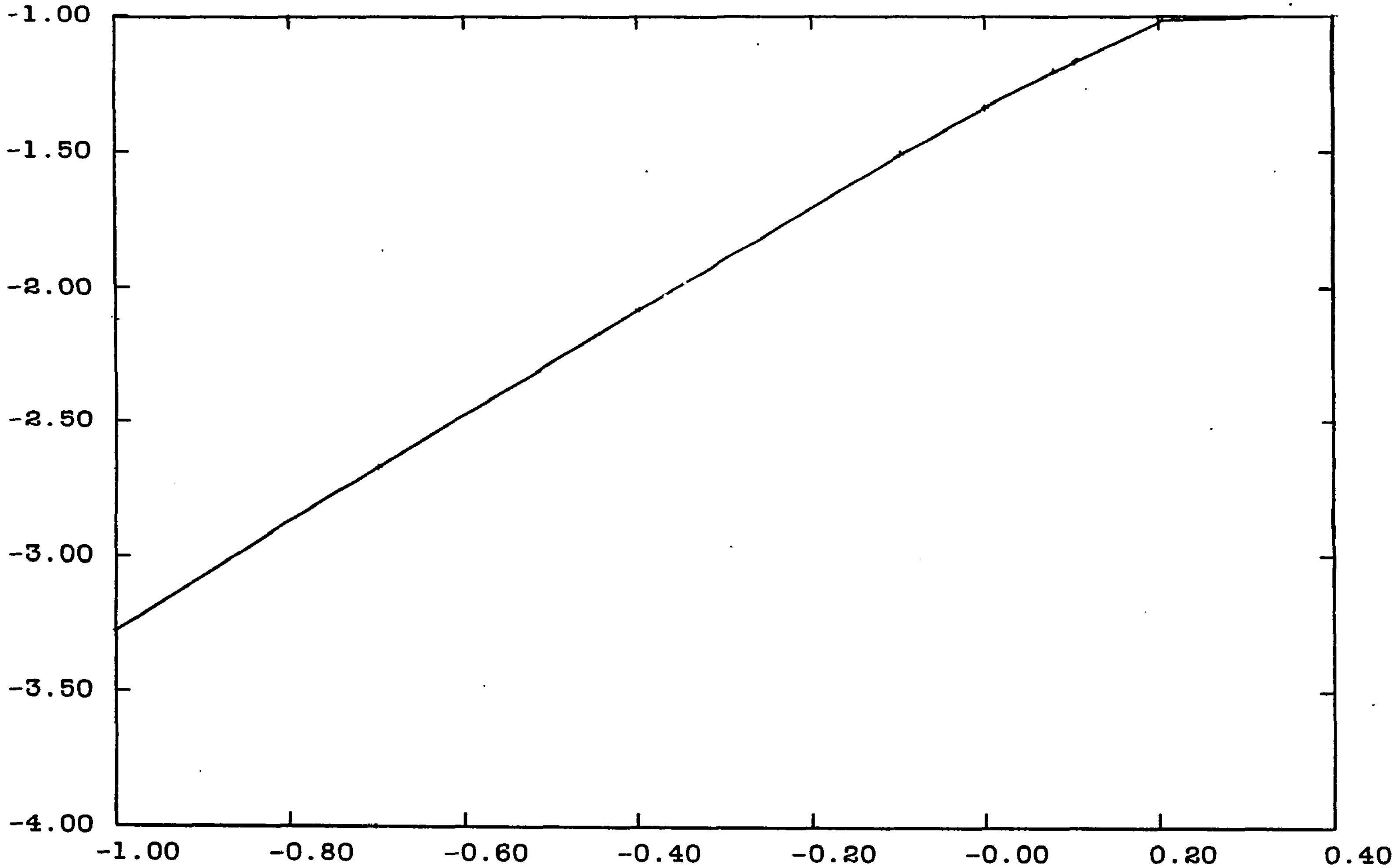



Fig. 7.1 log(vdc) vs log(x) for ez=.1,w=0.049,vz=.25.

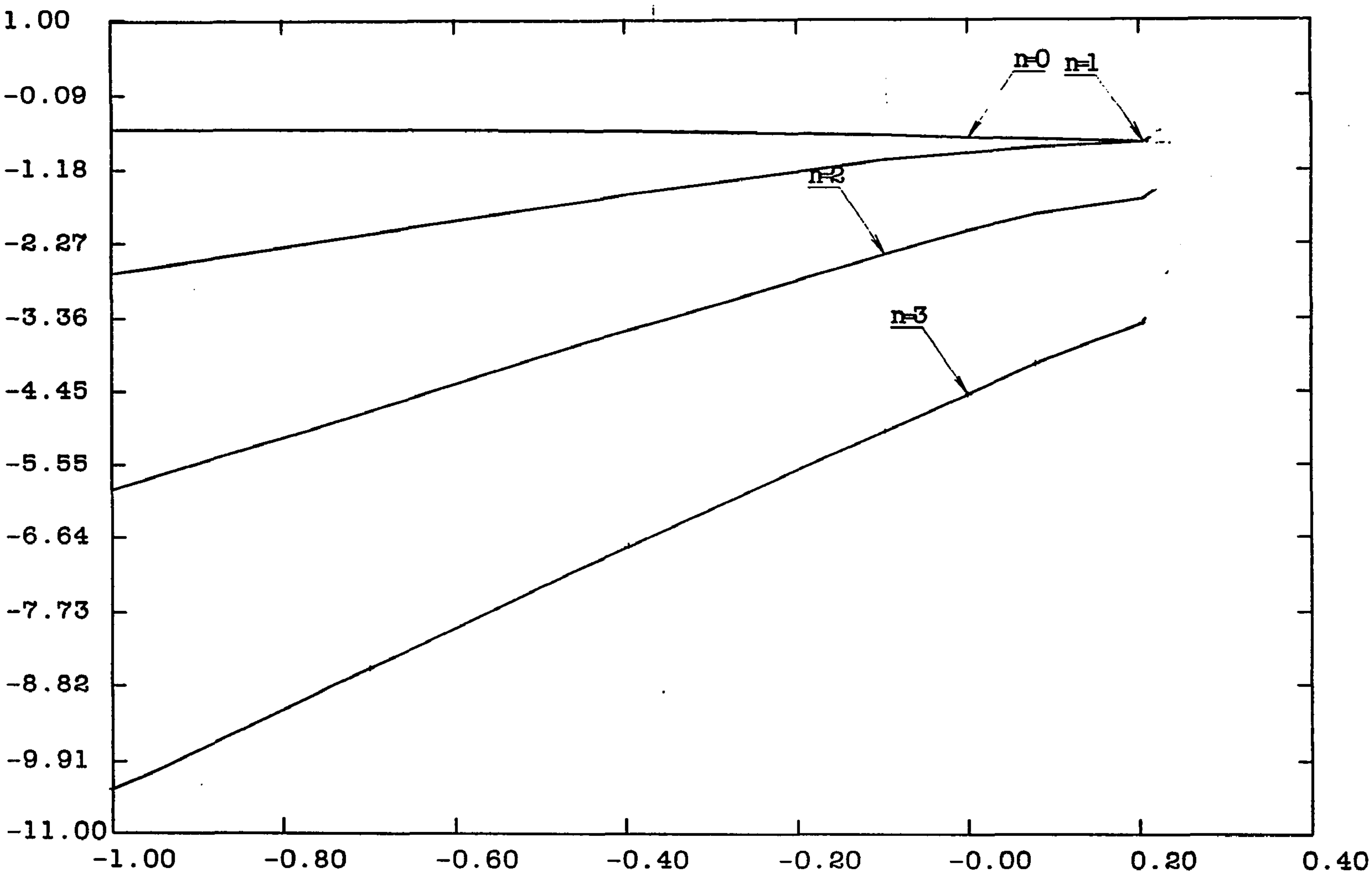



Fig. 7.2 log(vn**2) vs log(x) for various n values and cz=.1,w=0.049,vz=.25.

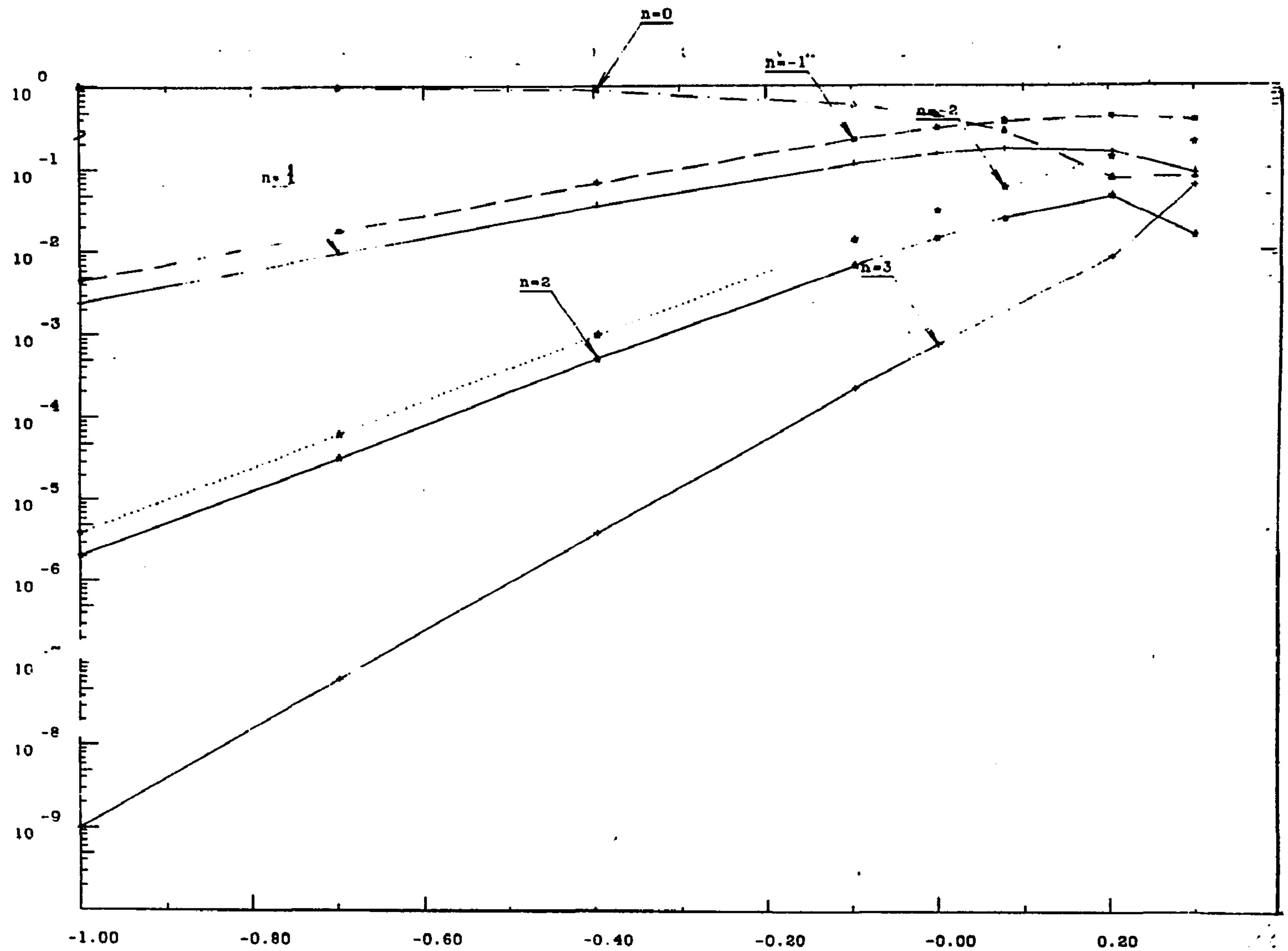



Fig. 7.3 Dn**2 vs log(x) for various n and ez=.1,w=.049,vz=.25.

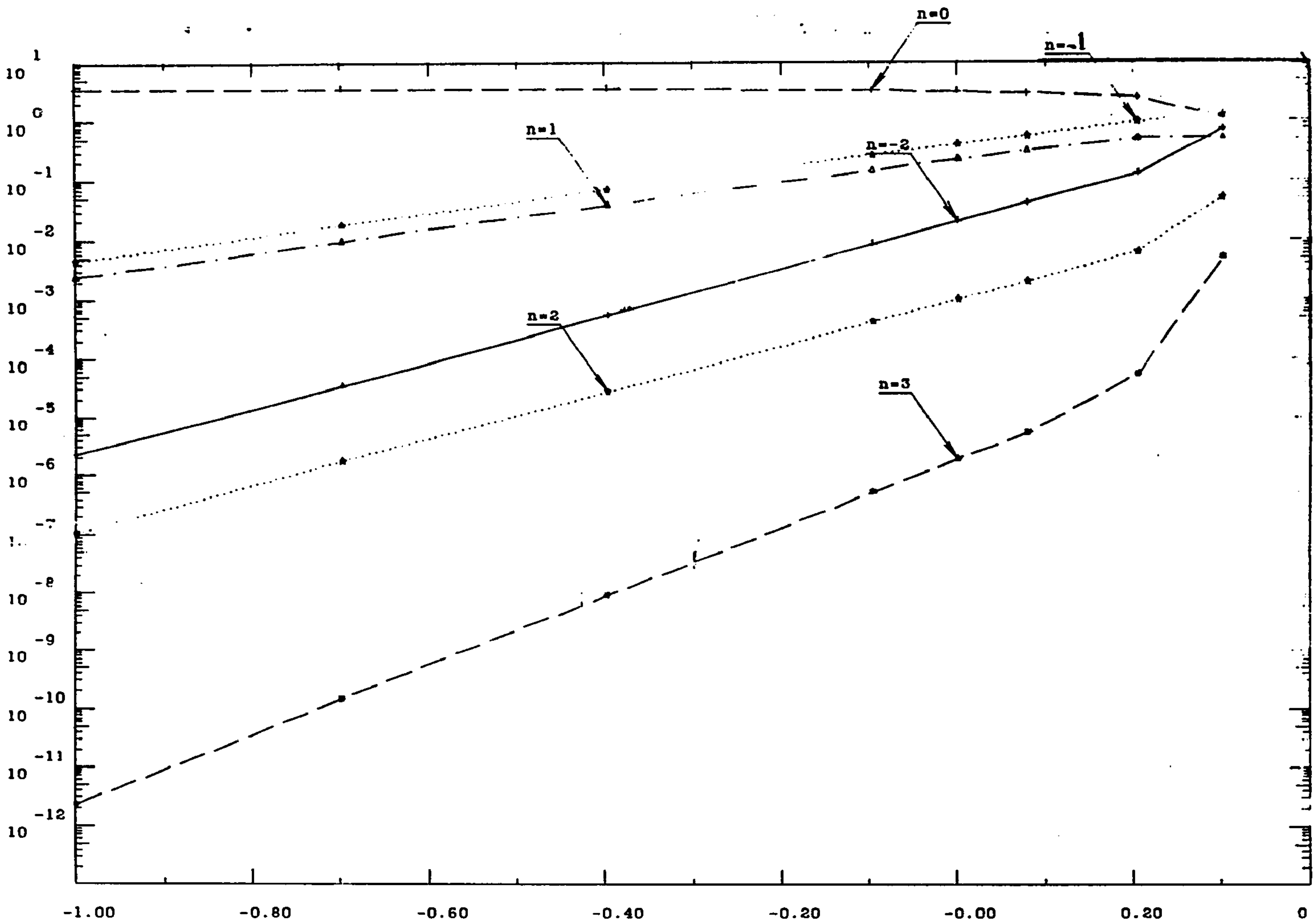



Fig. 7.4 Fn**2 vs log(x) for various n and ez =.1,w=.049,vz=.25.

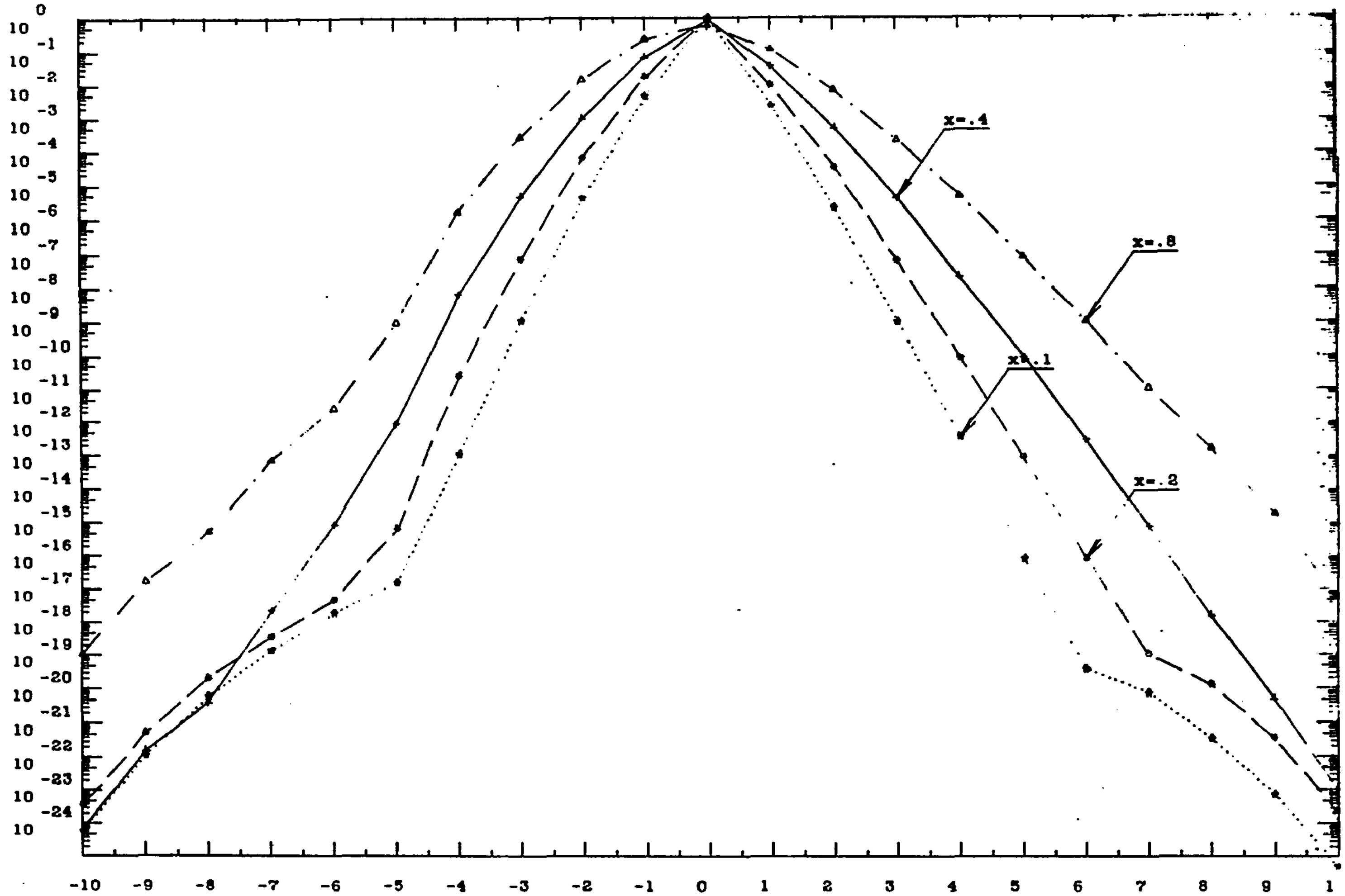



Fig. 7.5 Dn**2 vs n (on a semilog plot) for various x and ez=.1,w=.049, vz=.25.

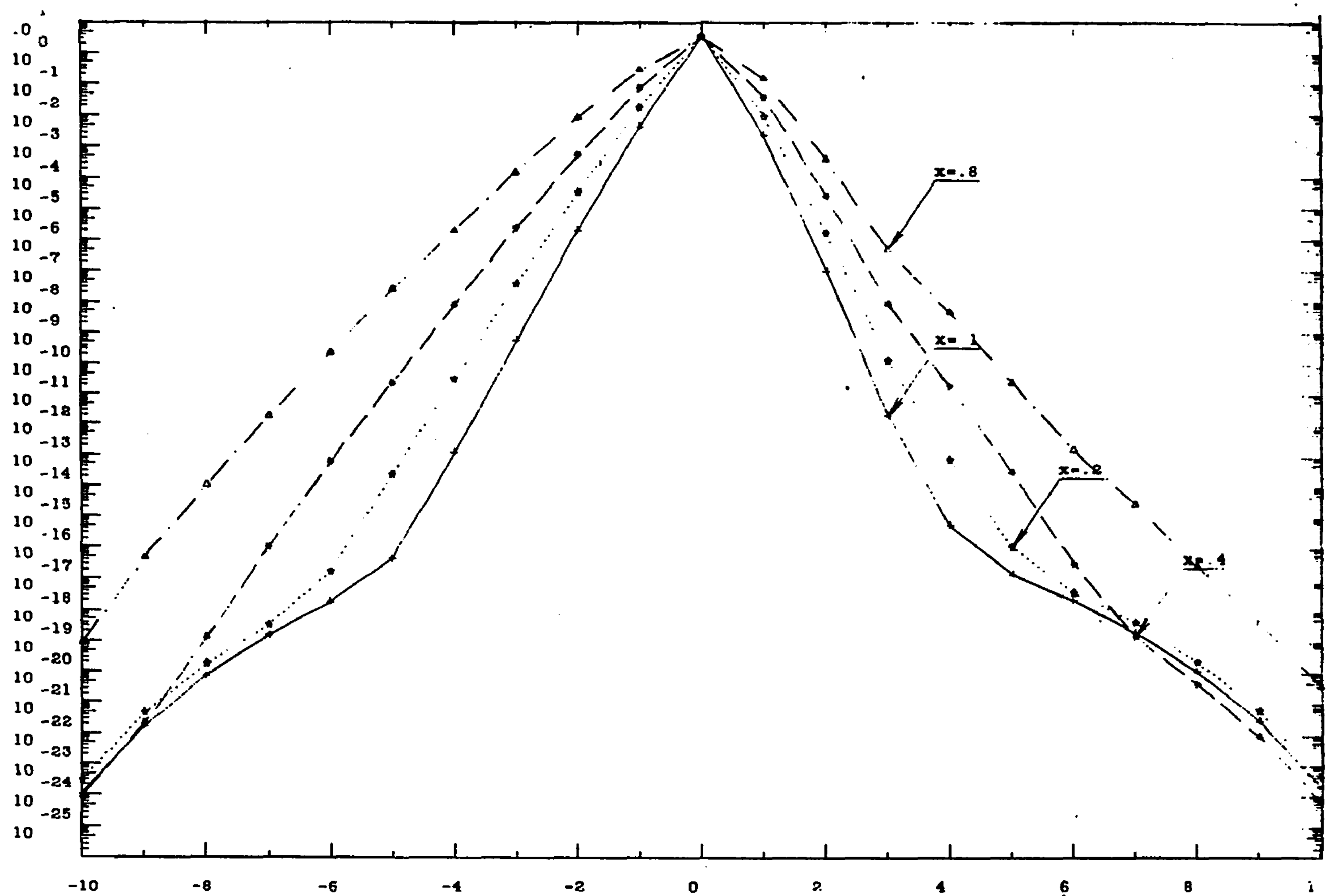



Fig. 7.6 Fn**2 vs n (on a semilog plot) for various x and ez=.1,w=.049, vz=.25.

| | | |
|---|---|---|
| | **Exact Results** | |
| -7 | ( -4.59712953e-12, | -1.40663469e-18) |
| -6 | ( -5.24890631e-10, | -1.37662349e-16) |
| -5 | (-4.52440609e-08, | -9.88842187e-15) |
| -4 | (-2.94168376e-06, | -5.14339764e-13) |
| -3 | (-1.41001670e-04, | -1.84901382e-11) |
| -2 | (-4.72926907e-03, | -4.13445861e-10) |
| -1 | (-9.95267481e-02, | -4.35045200e-09) |
| 0 | (-0.99003744, | -1.00685873e-16) |
| 1 | (9.94768068e-02, | -4.34827108e-09) |
| 2 | (-5.22490218e-03, | 4.56775395e-10) |
| 3 | (1.90848092e-04, | -2.50267029e-11) |
| 4 | (-5.43567603e-06, | 9.50403818e-13) |
| 5 | (1.28376229e-07, | -2.80575581e-14) |
| 6 | (-2.61190913e-09, | 6.85023602e-16) |
| 7 | (4.70688315e-11, | -1.44022104e-17) |
| | **Low frequency results** | |
| -7 | ( -1.98164818e-11, | 6.06344193e-18) |
| -6 | ( -1.38690581e-09, | 3.63741491e-16) |
| -5 | ( -8.31945428e-08, | 1.81827464e-14) |
| -4 | ( -4.15834029e-06, | 7.27067332e-13) |
| -3 | ( -1.66250407e-04, | 2.18011095e-11) |
| -2 | ( -4.98335436e-03, | 4.35658704e-10) |
| -1 | ( -9.95008349e-02, | 4.34932002e-09) |
| 0 | (-0.99003744, | 0.00000000e-01) |
| 1 | ( 9.95008349e-02, | 4.34932002e-09) |
| 2 | ( -4.98335436e-03, | -4.35658704e-10) |
| 3 | ( 1.66250407e-04, | 2.18011095e-11) |
| 4 | ( -4.15834029e-06, | -7.27067332e-13) |
| 5 | ( 8.31945428e-08, | 1.81827464e-14) |
| 6 | ( -1.38690581e-09, | -3.63741491e-16) |
| 7 | ( 1.98164818e-11, | 6.06344193e-18) |
| | **Perturbation theory results** | |
| -2 | (-4.74341679e-03, | 0.00000000e-01) |
| -1 | ( -0.10000000, | 0.00000000e-01) |
| 0 | ( -0.99001253, | 0.00000000e-01) |
| 1 | ( 0.10000000, | 0.00000000e-01) |
| 2 | (-5.24404412e-03, | 0.00000000e-01) |
| -2 | (-4.74341679e-03, | 0.00000000e-01) |
| -2 | (-4.74341679e-03, | 0.00000000e-01) |

**Table 1 Compared values of exact, low frequency and perturbation formula.**

# CONCLUSION:

In this thesis I have studied nonlinear opto-electronic processes that occur on the surface of a metal. Particular attention has been devoted to the multiharmonic generation and multiphoton electron emission processes. The problem has been studied using a variety of theoretical techniques. These included a classical analysis, a quantum mechanical perturbation theory study ( the "undressed " problem) and a nonperturbative study (the "dressed" problem). The theory was applied to simple models, such as the hard wall model, the finite step (Sommerfeld) model and the smooth step model.

It was found that nonlinearity in classical problem is due to multiple collisions with the surface induced by a strong electromagnetic field. In the quantum mechanical problem I have found that perturbation theory may be used for low intensities. However, as the intensity is increased nonlinear dressing effects become important. The formalism presented permits me, in principle, to calculate the nonlinear opto-electronic properties of the surface for arbitrary strengths of the incident laser fields. The techniques presented here may be extended to more realistic models of the solid. The purpose of this thesis was , however, was to give an insight into the basic nonlinear mechanism of laser-solid coupling and not so much to make detailed predictions for a broad class of solids. Attention was limited to the alkali metals as these are approximately represented by the Sommerfeld model.

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