NON-LINEAR OPTICAL PROPERTIES OF TWO DIMENSIONAL QUANTUM WELL STRUCTURES

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ABSTRACT

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In this work optical properties of two dimensional quantum well structures are studied. Variational calculation of the eigenstates in an isolated quantum well structure with and without the external electrical field is presented. At weak fields a quadratic Stark shift is found whose magnitude depends strongly on the finite well depth. It is observed that under external electrical field, the asymmetries due to lack of inversion symmetry leads to higher order nonlinear optical effects such as second order optical polarization and second order optical susceptibility.

Keywords: quantum wells, semiconductor heterostructures, Stark effect, electronic states, optical properties

ÖZ

İKİ BOYUTLU KUANTUM KUYUSU YAPILARININ LİNEER OLMAYAN OPTİK ÖZELLİKLERİ

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Bu çalışmada iki boyutlu kuantum kuyularının optik özellikleri incelendi. İzole kuantum kuyusuna elektriksel alan uygulandığı ve uygulanmadığı durumlarda öz durumları bulmak için varyasyonel hesaplama metodu kullanıldı. Zayıf alanlarda büyüklüğü sonlu kuyunun derinliğine bağlı kuadratik Stark kayması gözlendi. Dışarıdan elektriksel alan uygulandığında inversiyon simetrisinin kaybolmasına bağlı olarak ortaya çıkan asimetrilerin, ikinci dereceden optik polarizasyon ve ikinci dereceden optik alınganlık gibi yüksek dereceden lineer olmayan optik etkilere yol açtığı saptandı.

Anahtar Kelimeler: kuantum kuyuları,yarıiletken karma yapılar, Stark etkisi, elektronik durumlar, optik özellikler

To my mother Münire Küçükçalık.

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CHAPTER 1

INTRODUCTION

Recent advances in fabrication of thin semiconductor layers i.e. Molecular Beam Epitaxy and lithography techniques started the studies on nanometer scale. Technology developed on this scale usually called nanotechnology and spans an interdisciplinary area of research such as physics, material sciences, chemistry and quantum electronics. Fabrication of quantum well (QW) heterostructures and superlattices allowed precise engineering of optical and electronic responses of the semiconductor materials. The technology has resulted in a considerable increase in research activity directed towards the novel electronic and optoelectronic devices [1, 2, 3, 4].

The fabrication techniques allow many different composition of the QW profiles and thereby implementation of a potential V in the growth direction z. Along with first principle calculations a variety of simple potential models such as the infinite square well, finite square well, parabolic well, asymmetric step QW etc. are studied [5, 6, 7]. It is well known that exact analytical solutions are only available to such simple potential structures. In the presence of perturbations like electric field, the problem becomes more complicated.

The calculation of eigenstates of an infinite QW under a constant electric field bias is an exactly solvable problem whose solutions are linear combinations of two independent Airy functions [8]. Variety of numerical techniques and related approximations for individual QWs are also employed [7, 9, 10, 11, 6]. These solutions are approximations to manage the behavior of the resulting eigenfuncitons.

Main parameters to control eigenstates of a finite QW are the potential height and the well thickness. In the presence of perturbation due to the electric field, polarization of carriers and shift of energy levels are observed. If the field is not excessively large, the energy states will have long life time and can therefore be considered as quasibound [12, 13, 14, 15].

Resulting asymmetries by adding perturbations such as electric field modify the optical properties of the QWs. The response of the QW is nonlinear in the sense of nonlinear dependence of applied field strength. Discovery of second harmonic generation by Franken and co-workers in 1961 followed by increased theoretical and experimental study on nonlinear optics area. Optical nonlinear responses such as sum and difference frequency generation, the Kerr effect, the Raman effect, Brillouin scattering are also studied [16, 17, 18, 19, 20, 21, 22].

In this thesis the aim is calculating the electronic structure of one electron in a QW problem and introducing its some nonlinear optical properties. Second order perturbation calculation and variational calculation are employed to find the energies and wave functions. Using variational method as one of the simplest methods for electronic structure calculations allowed easier manipulation of nonlinear properties.

Calculated weak field approximation results of energy shifts by these methods are consistent with results of Bastard's and Miller's. For large fields and sufficiently thick wells, it is observed that perturbation calculation is not adequate to describe the energy shift because of the concentrated charge distribution near the well barrier. This physical situation is better described by employing variational wave functions because it compensates the resulting deviations from quadratic form of energy shift.

Different variational wave function forms are taken into account for the finite potential well structure and field induced energy shifts calculated analytically. At large fields variational wave function turns to a Fang - Howard wave function form.

In the calculation of the nonlinear polarizability for second harmonic generation in an infinite QW under electric field bias, variational wave functions of first, second and third electronic states are employed. Results are found consistent with the literature [23, 24, 22].

This thesis is organized as follows: In Chapter 2 a literature survey on perturbed QW structures done. Comparison between analytical and some numerical models for mostly semiconductor heterostructures reviewed. Terms of second harmonic generation are explained. In Chapter 3 the employed variational calculation for shifted energy

states and formulations for polarization is given. In Chapter 4 calculated results is discussed. In Chapter 5 a brief conclusion is given. Finally in References section scientific studies used in this thesis is cited.

CHAPTER 2

LITERATURE SURVEY

2.1 Experimental

The progress in material sciences has led to the development of new materials whose performance is superior to those of only a few years ago. New techniques for materials synthesis draw on knowledge from physics, chemistry, and other disciplines to create entirely new materials. Recent innovations in nanotechnology allowed growth of low dimensional heterostructures in nano scale such as quantum wells(1D), quantum wires(2D) and quantum dots(3D). In addition, better theoretical understanding of established processes allows material scientists to control material properties in a previously unachievable degree [25, 7, 26, 9, 27, 28].

Various properties can be achieved by changing material type, layer thickness, and doping over a wide range. Liquid-phase and gas-transport epitaxies are generally unsuitable for growing such heterostructures. Molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) are widely used for growing QWs with different potential profiles [29, 30, 31, 32].

2.1.1 Molecular Beam Epitaxy (MBE)

MBE process can be explained simply as follows: A beam of atoms or molecules is directed towards a crystalline substrate under ultra-high vacuum conditions, such that they stick at the surface forming a new layer of deposited material [1, 33, 34, 35, 36, 4].

2.1.2 Metal-organic Chemical Vapour Deposition (MOCVD)

Metal-organic chemical vapour deposition (MOCVD) is a method of epitaxial growth of materials, especially semiconductors from the pyrolysis of organic compounds containing the required chemical elements. For example, $GaAs$ could be grown in a MOCVD

system on a substrate by introducing trimethyl gallium ((CH3)3Ga) and triphenyl arsenic (C6H5)3As). In contrast to MBE the growth of crystals is not achieved in a vacuum, but from the gas phase at moderate pressures (2 to 100 kPa). One can find extended theoretical and experimental studies in literature [37, 38, 39].

The field of heterostructures is an important new field of research. Potential well that confines carrirs (i.e. an electron) in one dimension and force them to occupy a planar region is called a *quantum well*. The combination of the thin layers and possible lattice strain allow flexibility in engineering the properties of QW. The properties that may be controlled include the energy bandgap, effective masses and lattice constants. The energy bandgap of a QW can be controlled by changing either the type of material or the thickness of the layers or both [40, 41, 42, 43, 44, 38, 39]. The electronic properties are related to the behavior of the particle-in-box solutions of the Schrödinger wave equation.

2.2 Theory

The confined particles in narrow potential wells do not behave classically [45]. If the QW width is comparable with the de Broglie wavelength of the carriers, then a completely new phenomena, *quantum size effects* is observed. This new phenomena drastically effects electronic properties of the structure and results in a variety of new device applications.

Quantum mechanically, carriers in the potential well can only have size quantized discrete energy states E_n where $n = 1, 2, 3, ...$

The potential well can be considered infinitely deep if the well depth exceeds the thermal energy of the carriers k_BT by at least an order of magnitude. Here k_B is the Boltzman's constant and at room temperature k_BT is around $0.026eV$. Although other types of confining potential profiles with finite depth and non-rectangular shapes have different energy states, the quantization concept is valid for them.

Two important criteria to observe quantum size effects are:

1. Energy level separation between quantized levels $E_{N+1} - E_N$ must be sufficiently

large compared to the thermal energy of carriers k_BT. Otherwise frequent carrier transitions and equivalent occupation of states prevent observing quantum size effects.

2. In a QW, there always exist probability of carrier scattering by impurities, phonons etc. that effects momentum change. This probability can be characterized by a relaxation time τ which is proportional to carrier mobility μ. Relaxation time represents the mean life time of the carriers in a quantum state. Desired condition to observe quantum size effects due to relaxation time can be given as

$$E_{N+1} - E_N \gg \frac{\hbar}{\tau} = \frac{\hbar e}{m\mu} \tag{2.1}$$

where e and m are electronic charge and mass, respectively.

In summary, observing quantum size effects in a QW can be possible under small layer thickness, low temperature, high carrier mobility and low carrier concentration conditions [29, 46].

Schrieffer theoretically predicted that scattering effects would prevent observing quantization. Opposed to this prediction, first experimental observations done by Fang, Howard, Fowler, Stiles and Dorda [47, 48, 49]. Experimental observations followed by various optoelectronic device applications and theoretical studies on this new concept [6, 14, 50, 51, 52].

2.2.1 Effective Mass Approximation and Electronic Structure for One Electron

One can consider one-dimensional motion of a particle of mass m^* which is subjected to a potential $V_b(z)$ such as

$$V_b(z) = \begin{cases} 0 & |z| > \frac{L}{2} \\ V_b & |z| < \frac{L}{2}, \end{cases} \tag{2.2}$$

where L is the potential well thickness.

For energies ε such that $-V_b \leq \varepsilon < 0$, *the classical analysis* gives bound particle motion with the constant velocity $v_z = \pm\sqrt{\frac{2}{m^*}(\varepsilon + V_b)}$ in the interval $\frac{-L}{2} < z < \frac{L}{2}$ and the particle never penetrates the barrier [13].

When the wavelength of the particle is comparable to the dimensions of the confining structure, quantization of the motion along the growth direction is expected.

Quantum mechanical analysis depicts the motion by a wave function $\psi(z,t)$ as a solution of time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial z} = H\psi$$

where H is the Hamiltonian

$$H = (-\frac{\hbar^2\nabla^2}{2m^*} + V_b(\vec{r})) \tag{2.3}$$

m^* is the effective mass that includes the crystal potential effect. At the interface of a semiconductor heterostructure (interface of a semiconductor with another material) the motion of carriers (i.e. electrons) can be treated in the *effective mass approximation* (EMA). One can calculate electron energies and the wave functions with an effective potential consisting of the attractive potential on the side of the semiconductor and on slowly varying abrupt potential barrier at the interface [53, 54, 45].

The electron wave function can be expanded in terms of Bloch waves of the semiconductor crystal. The coefficients of this expansion form an envelope wave function that obeys the Schrödinger equation with an effective potential. This effective potential includes any potential over and above the periodic potential of the lattice [55, 56, 14]. Solution for 2.2 in the case of $V_b \to \infty$ can be written as

$$\psi(r) = \frac{1}{L}\chi(z)e^{i(k_x x + k_y y)}u_c(\vec{k} \simeq 0, \vec{r}) \tag{2.4}$$

where $\chi(z)$ is the slowly varying envelope wave function, u_c is the Bloch function, k_x and k_y are the wave vectors for the x and y planes respectively.

If the effective potential V_b is only a function of z, $\chi(z)$ satisfies the Schrödinger equation [57, 13]

$$[-\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial z^2} + V_b(z)]\chi(z) = E\chi(z). \tag{2.5}$$

2.2.2 Many-Body Effects

Calculations described thus far are for Schrödinger equation of a single charge carrier in a known potential profile. In a variety of device applications there are a large number of carriers which require an electrostatic description of the system [58, 59, 60, 61].

Existence of a charge distribution ρ gives rise to an additional potential term V_H which can be calculated using the Poisson's equation

$$\nabla^2 V_\rho = -\frac{\rho}{\epsilon}, \tag{2.6}$$

where ϵ is the permittivity of the material.

Solutions which satisfy both Schrödinger and Poisson's equation simultaneously are desired. For self-consistent solution, the Hartree potential term is added to the Schrödinger equation. This term describes the interaction of the electron with the charge distribution ρ [6, 62].

An exchange potential arises as a direct consequence of including the Pauli exclusion principle for electrons. The remaining interaction in a many carrier system is the correlation term. These two terms are included into the Schrödinger equation as a single term V_{XC} [6, 62, 63, 64].

The Schrödinger equation can be written as in the following form:

$$[-\frac{\partial^2}{\partial z^2} + V_b(z) + V_H(z) + V_{XC}]\chi(z) = E\chi(z). \tag{2.7}$$

The many-body effects are studied extensively including optical and transport properties [65, 66, 67, 68, 69, 14, 70, 71, 72, 73, 74].

2.2.3 Potential Profiles

Deposition of symmetric and asymmetric potential profiles can be realized in an infinite or a finite confinement of electrons in QWs. Electronic and optical properties of those structures can be derived by different doping pattern and external effects [75, 29].

2.2.4 Infinite Well

If a semiconductor material is sandwiched with an insulator (or another semiconductor material) sufficiently thick, the conduction electrons can be confined in an infinite potential barrier and cannot penetrate through the barriers [29, 14, 7, 13].

Well known eigenfunctions for the one dimensional Schrödinger equation given in 2.5 for $V_0 \to \infty$ which corresponds to infinite barrier case is given as

$$\chi(z) = A\sin(k_z z) + B\cos(k_z z) \tag{2.8}$$

where A and B are coefficients to be determined and

$$k_z^2 = 2m^* \frac{E^2}{\hbar^2} \tag{2.9}$$

Confinement potential has an inversion symmetry around $z = 0$ and boundary condition

$$\chi(L/2) = \chi(-L/2) = 0 \tag{2.10}$$

is satisfied. Thus, envelope wave functions in 2.8 is classified into even and odd states with A or B equal to zero, respectively.

$$\chi(z)_{even} = \sqrt{\frac{2}{L}}\cos(k_z z) \tag{2.11}$$

$$\chi(z)_{odd} = \sqrt{\frac{2}{L}}\sin(k_z z) \tag{2.12}$$

The boundary condition 2.10 yields

$$k_{z,even} = \frac{\pi}{L}(2n-1) \tag{2.13}$$

$$k_{z,odd} = \frac{\pi}{L}(2n) \tag{2.14}$$

Corresponding energy values

$$E_{z,even} = \frac{\pi^2\hbar^2}{2m^*L^2}(2n-1)^2 \tag{2.15}$$

$$E_{z,odd} = \frac{\pi^2\hbar^2}{2m^*L^2}(2n)^2 \tag{2.16}$$

for $n = 1, 2, 3, ...$

Equations 2.13-2.16 leads to inhibited motion in z-direction. Only discrete k_z values are allowed and lead to a series of quantized states. The total energy of electrons is given by the equation:

$$E_n = \frac{\hbar^2}{2m^*}(\frac{n^2\pi^2}{L^2} + k_\perp^2) \tag{2.17}$$

where $k_\perp^2 = k_x^2 + k_y^2$ is the amplitude squared of the wave vector on the transverse plane.

Separation of energy parabola $\hbar^2k_\perp^2/2m^*$ by $\frac{\hbar^2n^2\pi^2}{2m^*L^2}$ indicates the creation of energy *subbands*.

Carrier population and behavior of subbands are the fundamental guide of electronic and optical properties of these structures.

2.2.5 Finite Well

By controlling the deposition parameters, potential barriers can be constructed in different shapes and finite height. For a single finite QW case the Schrödinger equation is as given in 2.5. The theory and related calculation for finite potential well is given in *Chapter*3.

Finiteness of the barrier can let the carriers be transmitted through the boundaries. This transmission phenomena is called *tunneling* and has been studied by theoretically and experimentally [9]. Many electronic and optical quantum device applications proposed by using tunneling phenomena.

Besides finiteness, the case of multiple QW structures where identical QWs follow each other and the carriers see a periodic potential is called *superlattice*. This potential structures resembles the infinite bulk crystal structure where the wave functions are no longer localized but have infinite extent. These states are called *Bloch states*. These structures are studied as a high power source of mid-infrared radiation by many scientists [76, 77, 7].

2.2.6 Effect of External Field

Influence of external electrical and magnetic fields to the heterostructures have been studied by researchers from various disciplines. The resultant asymmetries by the field effects leads to change of optoelectronic behavior of carriers in heterostructures [6, 9, 78, 24, 79].

Field induced polarizability and shifts of energy bands are calculated analytically [80, 81] and numerically [82, 7] in the literature.

Applications like photodetectors, transistors and light emitters are based on the quantum theory of heterostructures under influence of external field [83, 84, 78]. In this thesis, the external field induced energy shifts and optical second order susceptibility calculations are done.

2.2.7 Methods of Calculation

Approximate Calculations

Solutions to Schrödinger equation for infinite and finite well profiles are straight forward and can be achieved by well known differential methods.

Addition of an external field to the QW, tilts the potential barriers. The solutions to Schrödinger equation is given in terms of Airy functions.

Perturbation Calculations

Perturbation potential of a conduction electron with the charge e in the minus sign under an applied constant field F, is given as $-eFz$. First order correction of perturbing potential to the ground state is as follows

$$\Delta E^{(1)} = \langle \psi_1 | (-eFz) | \psi_1 \rangle \tag{2.18}$$

Above first order perturbation calculation results zero for low fields. In the other hand, for larger fields the second order correction

$$\Delta E^{(2)} = \sum_{m=2}^{\infty} \frac{|\langle \psi_1 | (-eFz) | \psi_1 \rangle|^2}{E_m - E_1} \tag{2.19}$$

gives an energy difference proportional to F^2. Confined energy levels suppressed by the electrical field proportional to F^2 and that is known as *quantum confined Stark effect* [7, 14, 13].

Although calculated energy difference is consistent at low fields for a single QW heterostructure, the observed shift is not quadratic for higher fields and multiple QWs [13, 12, 29]. One can find a comparison of corrections in $Chapter3$.

Variational Calculations

Complication of analytical solution in the presence of an electrical field, using approximate solutions is more convenient. First approximate wave function to the ground state by Fang and Howard [85] is gives as

$$\xi_0(z) = (\frac{b^3}{2})^{1/2} z e^{-(1/2)bz} \tag{2.20}$$

where b is the variational parameter would be obtained by minimizing the total energy.

Another form of variational wave function for a single QW proposed by Bastard is given as

$$\chi_1(z) = \chi_1^0(z) e^{-bz} \tag{2.21}$$

which has the same shape of Fang and Howard variational wave function near the interface $|z| = L/2$ [13, 12].

First Principles Calculations

In a first principles calculation, no approximation to the total potential is done. It is calculated usually in a self consistent manner using the Density Functional Theory(DFT) [86, 87].

To obtain self-consistent solutions which satisfies both Schrödinger and Poisson's equations simultaneously, variety of computer algorithm implementations can be done. Usual numerical methods for self-consistent calculations such as shooting and finite elements methods, begins with initial conditions and repeats a loop of equation statements until desired energy is converged [7, 88].

2.3 Optical Properties

Quantization of energy levels depending on the relative band offsets allows the possibility of optical transitions in conduction or valence subbands(*intersubband transition*) as well as optical transitions between valence and conduction subbands(*interband transition*). First observations are done on heterostructures with a thin semiconductor layer of the order $100\mathring{A}$ embedded in a larger-gap semiconductor [5, 6]. Device applications using intersubband transitions (such as IR photo-detection and imaging, high frequency detectors) has become popular [89, 79].

The optical properties of QWs can be classified as *linear* and *non-linear*. Similar to optical properties of bulk materials, QWs show a dependence to field induced perturbations. When an electric field is applied, a polarization of energy levels is induced. This polarization can be written as:

$$\tilde{P}(t) = \chi^{(1)}\tilde{E}(t), \tag{2.22}$$

where $\tilde{P}(t)$ is the induced time dependent polarization, $\tilde{E}(t)$ is the electric field strength of the incident light beam and $\chi^{(1)}$ is the linear susceptibility as a proportionality constant [16, 90, 78]. Polarization $\tilde{P}$ is linearly dependent on the strength of the applied field and oscillates at the same frequency. $\chi^{(1)}$ describes linear reflection, transmission and absorbtion of the material. For high fields, equation 2.22 can be generalized by a power series expansion as follows:

$$\tilde{P}(t) = \chi^{(1)}\tilde{E}(t) + \chi^{(2)}\tilde{E}^2(t) + \chi^{(3)}\tilde{E}^3(t) + ... \tag{2.23}$$

The vector nature of the field sets $\chi^{(1)}$ as a second rank tensor. $\chi^{(2)}(\chi^{(3)})$ is the second(third) order non-linear optical susceptibility and a tensor of the third(fourth) rank [16, 90, 14].

Theoretical understanding of the optical properties involves computation of subband structure (i.e. determination of energy states and wave functions) and formulation of light - QW interaction in terms of subband structure. The interaction of the QW with the electric field is taken into account by letting the quantum properties of the structure

(i.e. the subband energies, envelope wave functions) depend on it [13, 24, 14]. *Linear* optical susceptibility can be written as [24]:

$$\chi^{(1)}(\omega, F) = \sum_{i,j} \chi_{ij}^{(1)}(\omega, F)$$
$$= \frac{e^2}{\varepsilon_0 \hbar} \sum_{i,j} \frac{z_{ij}(F) z_{ji}(F)}{[\omega - \omega_{ij}(F) - i\Gamma_{ij}]} (N_j(F) - N_i(F)), \quad (2.24)$$

where i and j are the subband indices, $z_{ij} = \langle \psi_i | z | \psi_j \rangle$ is the electric dipole matrix element between the subbands, ψ is the envelope wave function, ω_{ij} is the transition frequency, N is the density of the carriers in the subband and Γ is the dephasing time of the carriers and related to their tendency to rate in a band [24, 46].

Historically, nonlinear optics originated with the experimental work of P. A. Franken, who in 1961 noticed that a weak optical signal at 3471 Å could be generated in a quartz crystal when the material was illuminated with a high-power ruby laser at 6942 Å [91, 92]. Coherent mixing of electric field in the quartz produced a *second harmonic* response in the bulk region of the material. The several theoretical and experimental studies showed that second harmonic generation (SHG) is related to the second order polarizability of the material [93, 16, 94, 95]. Characterizing SHG can be made by deriving second order polarization terms and thus second order nonlinear susceptibility of the material [96, 16, 90, 97].

Using equation 2.23 the nonlinear polarization term of the second order can be written as,

$$\tilde{P}^{(2)}(\omega) = \chi^{(2)}(\omega) \tilde{E}(\omega_1) \tilde{E}(\omega_2). \quad (2.25)$$

As in the linear polarization process, the frequency ω of the second-order-polarization depends on the frequencies of the sources ω_1 and ω_2 and the frequency $\omega = \omega_1 + \omega_2$. Equation 2.25 is valid when the nonlinear terms are small enough to be considered as perturbations to the linear terms. Usually the magnitude of the $\chi^{(2)}$ is about five orders of magnitude weaker than $\chi^{(1)}$ [16, 90]. Application of very high optical or DC fields (i.e. a laser) to a QW can make higher order nonlinear processes more efficient.

SHG with a large second order non-linear optical susceptibility can have many potential applications. The fast response time of intersubband transition based systems can be used as electro-optic modulator of infrared light [24] and optical switching processes which requires certain wavelength [98].

CHAPTER 3

THEORY

3.1 Finite Well Calculations without External Electrical Field Effect

For the finite QW case introduced in the equation 2.2 of the previous chapter, $\chi(z)$ fulfills the following boundary conditions [13, 57]:

I $\chi(z)$ is continuous everywhere,

II Around any z_0, and for the specific potential of the square QW, $\frac{d\chi}{dz}$ is continuous everywhere,

III $\lim_{z\to\pm\infty} |\chi(z)|$ is finite.

Since $V_b(z)$ is constant exact solutions can be obtained and $\chi(z)$ is the sum of two opposite plane waves within the well. Characteristic wave vectors are defined by

$$k_w = \sqrt{\frac{2m^*}{\hbar^2}(\varepsilon + V_b)}. \tag{3.1}$$

The wave vectors of the evanescent waves outside the well are

$$\kappa_b = \sqrt{-\frac{2m_*\varepsilon}{\hbar^2}}. \tag{3.2}$$

For an even $V_b(z)$ in terms of z, $\chi(z)$ can be chosen either even or odd.

Inside the well:

$$\chi(z) = \begin{cases} A\cos(k_w z) & \varepsilon = -V_b + \frac{\hbar^2 k_w{}^2}{2m^*} \quad \text{for even states} \\ A\sin(k_w z) & \varepsilon = -V_b + \frac{\hbar^2 k_w{}^2}{2m^*} \quad \text{for odd states} \end{cases} \tag{3.3}$$

Outside the well:

$$\chi(z) = \begin{cases} B\exp[-\kappa_b(z - \frac{L}{2})] + C\exp[\kappa_b(z - \frac{L}{2})] & z \geq \frac{L}{2} \\ D\exp[-\kappa_b(z + \frac{L}{2})] + E\exp[\kappa_b(z + \frac{L}{2})] & z \leq \frac{L}{2} \end{cases} \tag{3.4}$$

Concerning boundary condition III one can see that $C = D = 0$ and $B = E$ for even states, $B = -E$ for odd states.

From the boundary conditions at $z = \pm\frac{L}{2}$ wave vectors satisfies the transcendental equations

$k_w \tan(k_w \frac{L}{2}) = \kappa_b$ for even states and $k_w \cot(k_w \frac{L}{2}) = -\kappa_b$ for odd states.

Those equations can be satisfied only for discrete values of ε. This discreteness is the main reason of quasi two-dimensional motion of the carriers in $III-V$ heterostructures. When the motion is quasi two-dimensional in the (x, y) plane, the motion in z direction is quantized in one of the bound states defined by $\chi(z)$.

3.2 Finite Well Calculations with External Electrical Field Effect

In the presence of an external uniform electric field F, motion of carriers can still be assumed as plane waves in the plane of the layer. Those waves form into isotropic, parabolic and non-degenerate bands. When the electric field is parallel to the growth direction $\hat{z}$, Schrödinger equation inside the finite well is described in the effective mass approximation as [13, 99]

$$(-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} \pm eFz)\chi(z) = \varepsilon\chi(z) \tag{3.5}$$

where $+$ and $-$ signs refer to electrons and holes, respectively. At the barrier,

$$(-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} \pm eFz + V_0)\chi(z) = \varepsilon\chi(z) \tag{3.6}$$

where V_0 is the potential well depth. Using atomic units where $\hbar = c = e = 1$, equation 3.5 and equation 3.6 are simplified as

$$\frac{d^2\chi_n}{dz^2} + 2m^*(\varepsilon_n + Fz)\chi_n = 0, \tag{3.7}$$

$$\frac{d^2\chi_n}{dz^2} + 2m^*(\varepsilon_n + Fz - V_0)\chi_n = 0, \tag{3.8}$$

respectively where n refers to the corresponding states.

One can define new variables as

$$r = -(2m^*/F)^{1/3}(Fz + \varepsilon_n), \tag{3.9}$$

$$s = -(2m^*/F)^{1/3}(Fz + \varepsilon_n - V_0), \tag{3.10}$$

and differential equations turn into Airy equations whose solutions are in the form

$$\chi = C_1 Ai(r) + C_2 Bi(r), |z| < L/2, \tag{3.11}$$

$$\chi = C_3 Ai(s) + C_4 Bi(s), |z| > L/2, \tag{3.12}$$

where L is centered at the $z = 0$.

One can obtain recursion relation between $C1, C2, C3$ and $C4$ by applying boundary conditions [100, 13]. After some calculations the difference between ground state energy and the total energy in the limit of continuous spectrum ($L \to \infty$) is found as in [100],

$$\triangle\varepsilon \sim \frac{F^{\frac{1}{2}}\pi}{\sqrt{2m^*}}. \tag{3.13}$$

The applied field causes a shift of the energy levels with respect to their zero field values, accompanied by a broadening and this phenomena is called Stark effect. Since the potential barrier tends to minus infinity, no bound states exists. Since applied electric field is nonzero, the particle may lower its potential energy by tunneling out of the well and the zero field bound states are converted into resonances [101].

For the finite well cases, ionization energy is a restriction as

$$F_c L = -\varepsilon_0, \tag{3.14}$$

where ε_0 is the zero field binding energy and F_c is the field for which the tunneling barrier to ionization disappears completely. F_c corresponds to the value of the applied field for which the top of the well is pulled down by the field to the level of the zero field bound state [101].

The particle will be pushed against or along the direction of the field due to its charge and the charge distribution will be concentrated near the well barrier. In semiconductor QWs (e.g. $GaAs - Ga_{1-x}Al_xAs$) the band discontinuities are of the order of a few

hundred meVs. For thin QWs where $L \leq 50\mathring{A}$ the energy spectrum at $F = 0$ consists of a single bound level and a continuum, instead of the increasingly spaced levels.

Bastard and co-workers described this physical situation for the infinite well problem by using a variational wave function given by [12],

$$\psi(z) = \quad N(\beta)\cos(\tfrac{\pi z}{L})\exp(-\beta(\tfrac{z}{L}+\tfrac{1}{2})) \quad , \tfrac{|z|}{L} < \tfrac{1}{2}, \tag{3.15}$$

where β is the variational parameter and $N(\beta)$ is a normalization constant.

One can see that in the equation 3.15, wave function becomes zero field wave function for $\beta = 0$.

Using variational wave functions in the Hamiltonian and by applying the standard variational procedure (minimizing the energy respect to β) yields β in terms of electric field and ground state energy. Substituting β into the energy equation one can see that energy difference is proportional to square of the external field as

$$\Delta E_1 \sim \frac{m^* F^2 L^4}{\hbar^2}, \tag{3.16}$$

which is in good agreement with the quadratic Stark shift results at low field for an infinite QW. Since the external field is not excessively large, the states will have longer life time and therefore they can be considered as *"quasibound"* [13, 12] under the condition of

$$\frac{|e|FL}{q_0} \ll \frac{\hbar^2 q_0^2}{2m^* L^2}, \tag{3.17}$$

where

$$q_0^2 = \frac{2m^* L^2}{\hbar^2}(V_0 - E_1), \tag{3.18}$$

q_0 is the characteristic dimensionless wave vector and E_1 is the zero field ground state energy. Under the above condition, larger fields causes deviation in the shift from quadratic dependence of electric field. To describe the physical situation better, variational wave function is described in the following form:

$$\psi(z) = \begin{cases} \mathcal{A}\exp((q_0-\beta)(\tfrac{z}{L}+\tfrac{1}{2})) & , z \leq -L/2 \\ \mathcal{B}\sin(k_0\tfrac{z}{L}+\delta)\exp(-\beta(\tfrac{z}{L}) & , |z| \leq L/2 \\ \mathcal{C}\exp(-(q_0+\beta)(\tfrac{z}{L}-\tfrac{1}{2})) & , z \geq L/2 \end{cases} \tag{3.19}$$

where $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$ are normalization constant to be determined from the continuity equation. Relations between k_0, q_0 and δ is found by applying the boundary conditions as follows

$$k_0^2 - q_0^2 = 2q_0k_0\cot(k_0), \tag{3.20}$$

$$\delta = \frac{k^0}{2} + \arctan(\frac{k_0}{q_0}). \tag{3.21}$$

To obtain the higher energy levels under envelope wave function approach where the eigenfunctions form an orthogonal set, Gram-Schmidt orthogonalization method is used [102].

To calculate the nonlinear optical susceptibilities, one needs these energy eigenvalues and eigenfunctions.

3.3 Perturbation Calculations for Infinite Well

A second order perturbation correction to the energy eigenstates is given as

$$\Delta E_1^{(2)} = \sum_{n>1} \frac{|\langle\psi_n|H|\psi_1\rangle|^2}{E_0^1 - E_0^n}. \tag{3.22}$$

Using wave function $\psi_n = \sqrt{\frac{2}{L}\sin(\frac{n\pi z}{L})}$ equation 3.22 becomes

$$\Delta E_1^{(2)} = \sum_{n>1} \frac{4e^2F^2L^2\frac{[(2n+2n\cos(n\pi)+(n^2-1)\pi\sin(n\pi))]^2}{(n-1)^4(n+1)^4\pi^4}}{\frac{\hbar^2\pi^2}{2m^*L^2}(1-n^2)}, \tag{3.23}$$

$$= -C_{pert}\frac{m*e^2F^2L^4}{\hbar^2}$$

where

$$C_{pert} = \frac{1}{24\pi^2}(\frac{15}{\pi^2} - 1). \tag{3.24}$$

3.4 Variational Calculations for Infinite Well

In the presence of higher electric fields, charged particles tend to pile up near the barriers. To describe this physical situation, a variational wave function is given as in the equation 3.15. Using the normalization condition

$$\int_{-L/2}^{L/2} \psi(z)\psi^*(z)dz = 1, \tag{3.25}$$

the normalization constant $N(\beta)$ is found as

$$N(\beta) = \frac{1}{\pi}\sqrt{\frac{Exp(\beta)(2\beta^3 + 2\beta\pi^2)cosech(\beta)}{L}}. \tag{3.26}$$

Substituting $N(\beta)$ into the wave function the energy equation as a function of β can be found,

$$E(\beta) = \int_{-L/2}^{L/2} \psi^*[\frac{d^2\psi}{dz^2} + eFz\psi]dz \tag{3.27}$$

$$= -\frac{\beta^2}{4L^2} + \frac{eFL}{\beta} - \frac{\pi^2}{L^2} + \frac{\frac{\beta}{2}eFL}{\frac{\beta^2}{4} + \pi^2} - \frac{1}{2}eFL\coth(\frac{\beta}{2}). \tag{3.28}$$

Zero-field ground state energy is,

$$E_1^{(0)}(\beta) = \int_{-L/2}^{L/2} \psi^*[\frac{d^2\psi}{dz^2}]dz \tag{3.29}$$

$$= -\frac{\beta^2 + 4\pi^2}{4L^2}. \tag{3.30}$$

In terms of ground state energy,

$$E(\beta) = E_1^{(0)}(\beta)[1 + \frac{eFL}{E_1^{(0)}(\beta)}(\frac{1}{\beta} + \frac{2\beta}{\beta^2 + 4\pi^2} - \frac{1}{2}\coth(\frac{\beta}{2}))]. \tag{3.31}$$

Setting a dimensionless electrostatic energy $\phi = \frac{|e|FL}{E_1^{(0)}(\beta)}$, and minimizing the energy with respect to β in the low external field limit $\phi \ll 1$ yields,

$$\beta_{min-low} = \phi(\frac{\pi^2}{6} - 1), \tag{3.32}$$

where a series expansion up to second order terms with respect to β is used.

Under stronger external field which makes $\phi \gg 1$ and β larger, energy minimizing term becomes

$$\beta_{min-high} = (6^{1/3}\pi^{2/3})\phi^{1/3}. \tag{3.33}$$

3.5 Variational Calculations for Finite Well

Space dependent Hamiltonian for a two dimensional finite potential barrier V_0 is given as

$$H = \begin{cases} -\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} + |e|Fz & , -L/2 < z < L/2 \\ -\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} + (V_0 + |e|Fz) & , -L/2 < z < L/2, \end{cases} \tag{3.34}$$

and Schrödinger equation for the ground state is

$$H\psi(z) = E_1\psi(z). \tag{3.35}$$

To solve the equation one can set L/q_0 as the characteristic decay length of the ground state wave function where

$$q_0^2 = \frac{2m^*L^2}{\hbar^2}(V_0 - E_1). \tag{3.36}$$

The criteria for quasi-bound states is

$$\frac{|e|FL}{q_0} \ll \frac{\hbar^2 q_0^2}{2m^*L^2}, \tag{3.37}$$

which yields the fast decay of the wave function inside the barrier. Thus one can assume that the amplitude of the wave function is negligible where the potential barrier is lowered by the external field.

3.5.1 Weak Field Approximation

For the finite QW structure, the variational wave function is given as an admixture of even ground state wave function and odd extended states as follows [12]

$$\psi(z) = N(\beta)(1 + \beta z/L)\psi_0(z), \tag{3.38}$$

where $\psi_0(z) = \sqrt{\frac{2}{L}}\cos(\frac{\pi z}{L})$ is the zero field ground state wave function. Normalization function $N(\beta)$ can be found from the continuity relation 3.25 under the condition 3.37,

$$N(\beta) = \frac{\pm 2\sqrt{3}\sqrt{L}\pi}{(-6\beta^2 + 12L\pi^2 + \beta^2 L\pi^2)^{1/2}}. \tag{3.39}$$

Zero field ground state energy is

$$E_1^{(0)}(\beta) = -\frac{\pi^2}{L^2}. \tag{3.40}$$

The expectation value of z^2 is

$$< z^2 >_0 = \frac{2}{L}(\frac{L^3}{24} - \frac{L^3}{4\pi^2}). \tag{3.41}$$

Substituting $< z^2 >_0$ into the energy term $E(\beta)$ gives,

$$E(\beta) = E_1^{(0)} + \frac{L^2}{L^2 + \beta^2 < z^2 >_0 (\frac{2e\beta F < z^2 >_0}{L} - \frac{\beta^2}{L^2})}. \tag{3.42}$$

Minimizing 3.42 under weak field condition $\beta^2 < z^2 >_0 / L^2 \ll 1$ yields,

$$\beta_{min-weak} = 2eF(\frac{L^3}{24} - \frac{L^3}{4\pi^2}). \tag{3.43}$$

Substituting equation 3.41 and 3.40 into equation 3.43 gives minimum variational parameter

$$\beta_{min-weak} = eFL < z^2 >_0 . \tag{3.44}$$

To find the field induced energy shift, one has to take into account the extended wave functions (tails) out of the potential barrier. Solution of 3.34 gives to wave functions of the ground state as:

$$\psi_1 = N_1(\beta) \cos(\frac{k_0 z}{L}); -L/2 < z < L/2, \tag{3.45}$$

$$\psi_2 = N_2(\beta) \exp(-\frac{q_0 z}{L}); L/2 < z < \infty, \tag{3.46}$$

$$\psi_3 = N_3(\beta) \exp(\frac{q_0 z}{L}); -\infty < z < -L/2. \tag{3.47}$$

$$\tag{3.48}$$

Using normalization relation once again, one can find the following normalization constants:

$$N_1(\beta) = \frac{\sqrt{2}}{\sqrt{L + \frac{L \sin(k_0)}{k_0}}}, \tag{3.49}$$

$$N_2(\beta) = \frac{1}{\sqrt{\frac{\exp(-q_0 L)}{q_0}}}, \tag{3.50}$$

$$N_3(\beta) = \frac{1}{\sqrt{\frac{\exp(-q_0 L)}{q_0}}}. \tag{3.51}$$

Integration of the corresponding wave functions in the regions $-L/2 < z < L/2$, $L/2 < z < \infty$ and $-\infty < z < -L/2$, the field-induced energy shift is found as in the next chapter section 4.2.

3.6 Second Order Optical Susceptibility Formulation

In the presence of an electric field, instead of the discrete bound states, quasi-discrete states in the form of narrow resonances appear. The carriers are subject to the given [103] actual total macroscopic potential of

$$V(z) = -eFz + U_h(z) + U_{exc}(z) + U_{im}(z) + \frac{\hbar^2 k_t^2}{2m(z)} \tag{3.52}$$

where $U_h(z)$ is the well confining potential, $U_{exc}(z)$ is the local exchange-correlation potential, $U_{im}(z)$ is the image charge potential that arises from different dielectric permittivity of different materials and $\frac{\hbar^2 k_t^2}{2m(z)}$ term counts for the transverse motion of the electrons in well. $U_{im}(z)$ can be neglected for close dielectric permittivity materials and $U_{exc}(z)$ can be neglected for low electron concentration. The obtained potential is already used to solve **??** variationally. The structure will give a response, namely optical polarization $\tilde{P}$ that linearly dependent to the applied external field.

$$\tilde{P} = \chi \tilde{E} \tag{3.53}$$

One can expand $\tilde{P}$ into a power series to search nonlinear contributions.

$$\tilde{P} = \chi^{(1)}\tilde{E} + \chi^{(2)}\tilde{E}^{(2)} + \chi^{(3)}\tilde{E}^{(3)} + ... \tag{3.54}$$

$\chi^{(2)}$ and $\chi^{(3)}$ are second and third order nonlinear optical susceptibilities, respectively [16]. The process of second harmonic generation can be described as the conversion of incident photon radiation at frequency ω to the outgoing radiation of second harmonic frequency at 2ω. Polarization for the second harmonic generation can be written in the form [90]

$$\begin{pmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{pmatrix} \tag{3.55}$$

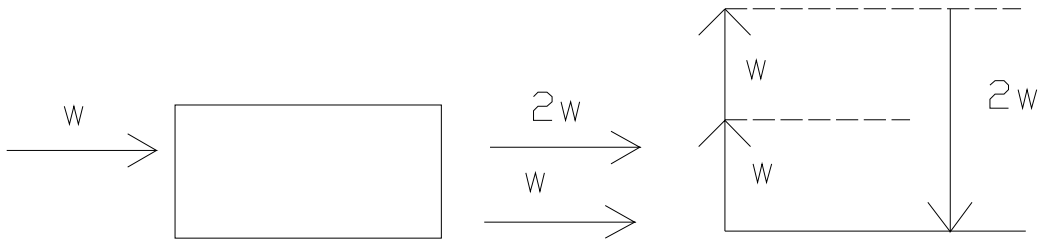

Figure 3.1: Illustration of second harmonic generation for a three level system

First term of the 3.55 is the 3×6 nonlinear susceptibility tensor. Elements of the tensor carries Kleinman indices that represent the symmetry condition of the structure. From equation 3.54 second order polarization can be given as

$$\tilde{P}^2 = \chi^{(2)} \tilde{E}^{(2)} \tag{3.56}$$

For the centro-symmetric structures, change of the electric field sign, must change the sign of the induced polarization $\tilde{P}^2$.

$$-\tilde{P}^2 = \chi^{(2)} (-\tilde{E})^{(2)} \tag{3.57}$$

$$-\tilde{P}^2 = \chi^{(2)} \tilde{E}^{(2)} \tag{3.58}$$

3.56 and 3.58 can be satisfied together only under condition of $\chi^{(2)} = 0$. Thus symmetry condition to observe second harmonic terms for the materials is having non-centro-symmetry. Taking into account of non-centro-symmetry properties, direction of the applied electric field for a 2-dimensional structure, one can find the desired term for nonlinear polarizability of second harmonic generation [23].

$$\begin{aligned} \alpha_{33}^3 = \frac{2e^3}{\epsilon_0 \hbar^2} \sum_{mn} & < z_{1n} >< z_{nm} >< z_{m1} > [(\omega - \Omega_{n1} - i\gamma_{n1})(2\omega - \Omega_{m1} - i\gamma_{m1})]^{-1} \\ & + [(\omega + \Omega_{n1} - i\gamma_{n1})(2\omega + \Omega_{m1} - i\gamma_{m1})]^{-1} - (2\omega - \Omega_{mn} - i\gamma_{mn})^{-1} \\ & [(\omega - \Omega_{m1} - i\gamma_{m1})^{-1} + (\omega + \Omega_{n1} - i\gamma_{n1})^{-1}] \end{aligned} \tag{3.59}$$

where $< z_{ij} >=< \psi_i | z | \psi_j >$, $\Omega_{ij} = (E_i - E_j)/\hbar$, $1/\gamma_{ij}$ is the de-phasing time and ω is the transition frequency. Nonlinear susceptibility for a three level structure $n = 2$ and $m = 3$ as sketched in the figure is taken into account.

CHAPTER 4

RESULTS AND DISCUSSION

Under applied electric field, bound states tends to be quasi-bound states as explained in previous chapters. Variational and perturbational methods are employed to obtain wave functions and energy shifts of the states in an infinite quantum well QW structure. Field dependence of variational parameters are sketched. Finite well structure is also studied using variational method.

Polarization terms of nonlinear susceptibility for infinite well are calculated. Variational wave functions are employed for the calculation. Qualitative agreement with previous studies [12, 23] is reached.

Mathematica 5.0 program is used for calculations and graphics.

4.1 Perturbation Calculations vs. Variational Calculations for Infinite Well

One can calculate the energy shift of the ground state due to applied electric field

$$\Delta E_1 = E_1 - E_1^0. \tag{4.1}$$

Substituting in the low field limit variational energy calculation 4.1 gives

$$\begin{aligned}\Delta E_1(\beta_{min}) = E_1^0[&\frac{(-6+\pi^2)^2}{144\pi^2}\phi^2 + \frac{6}{-6+\pi^2} + \\ &\frac{-6+\pi^2}{3(4\pi^2+\frac{1}{36}(-6\phi+\pi^2\phi)^2)} - \frac{1}{2}\coth(\frac{1}{12}(-6\phi+\pi^2\phi))].\end{aligned} \tag{4.2}$$

From 3.23 energy shift is

$$\Delta E_1^2 = [\frac{1}{24\pi^2}(\frac{15}{\pi^2}-1)]\frac{e^2F^2L^4}{2}. \tag{4.3}$$

From figure 4.1 one can see that, increasing the dimensionless field intensity ϕ, leads deviation from the quadratic behavior of the shift. In this thesis, the same procedure

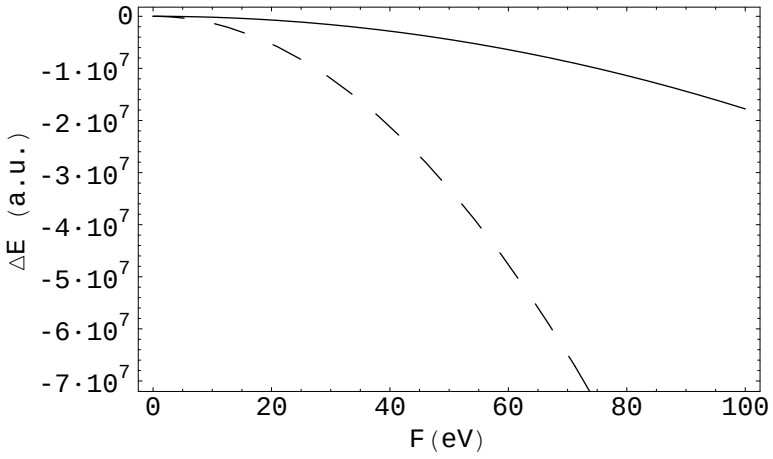

Figure 4.1: Scaled energy shift for the ground state vs. field intensity F for a well of thickness $L = 30\mathring{A}$. Solid and dashed lines are perturbation and variational calculations, respectively.

is employed to calculate variational parameters and energies of subbands. The second quasi-state trial wave function that taken into account as

$$\psi_2(z) = N_2(\beta_2)\sin(\frac{2\pi z}{L})\exp(\beta_2(\frac{z}{L}+\frac{1}{2})). \tag{4.4}$$

From normalization condition, normalization factor $N_2(\beta 2)$ for the second state is found as,

$$N_2(\beta_2) = \frac{\sqrt{\exp(\beta_2)(\beta_2^3+4\beta_2\pi^2)cosec(\beta_2)/L}}{\sqrt{2}\pi}. \tag{4.5}$$

The energies under external field and zero field for the second quasi-state are found as follows

$$E_2 = -\frac{\beta_2^2}{4L^2} - \frac{eFL}{\beta_2^2} - \frac{4\pi^2}{L^2} - \frac{\beta_2^2 eFL}{2(\frac{\beta_2^2}{4}+4\pi^2)} + \frac{1}{2}eFL\coth(\frac{\beta_2}{2}), \tag{4.6}$$

$$E_2^0 = -\frac{(\frac{\beta_2^2}{4}+4\pi^2)}{L^2}, \tag{4.7}$$

respectively. Equation 4.6 can be rewritten in terms of 4.7 and dimensionless field intensity ϕ,

$$E_2 = E_2^0\left[1+\phi(-\frac{1}{\beta_2}+\frac{\beta_2}{2E_2^0}+\frac{1}{2}\coth(\frac{\beta_2}{2}))\right]. \tag{4.8}$$

Minimizing equation 4.8 with respect to variational parameter β_2 gives,

$$\beta 2 = \frac{2\sqrt{5}\sqrt{6+E_2^0}}{\sqrt{E_0^2}}. \tag{4.9}$$

Substituting $\beta 2$ into wave function, electric field effect can be seen. Energy shift of second state is found as,

$$\Delta E_2 = E_2^0\left(\frac{\coth[\beta_2/2]}{2} - \frac{1}{\beta_2 + \frac{\beta_2}{2E_2^0}}\right). \tag{4.10}$$

Corresponding trial function for the third quasi state is

$$\psi_3(z) = N_3(\beta_3)\cos\left(\frac{3\pi z}{L}\right)\exp\left(-\beta_3\left(\frac{z}{L}+\frac{1}{2}\right)\right). \tag{4.11}$$

Normalization condition gives,

$$N_3(\beta_3) = \frac{2\sqrt{\frac{\beta_3^3+9\beta\pi^2}{-1+\exp(2\beta_3)}}}{3\pi}. \tag{4.12}$$

Zero field energy of the third state is

$$E_3^0 = -\left(\frac{\beta_3^2}{4} + 9\pi^2\right) \tag{4.13}$$

Energy of the third quasi-state under applied field is

$$E_3^0 = -\frac{\beta_3^2}{4} + \frac{eF}{\beta_3} - 9\pi^2 + \frac{\beta_3 eF}{2(\frac{\beta_3^2}{4}+9\pi^2)} - \frac{1}{2}eF\coth\left(\frac{\beta_3}{2}\right). \tag{4.14}$$

In the low field limit, energy and variational parameter rewritten in terms of ϕ and zero field energy are

$$E_3 = E_3^0\left[1+\phi\left(\frac{1}{\beta_3 L} - \frac{\beta_3}{2L(\frac{\beta_3^2}{4}+9\pi^2)} - \frac{1}{2L}\coth\left(\frac{\beta_3}{2}\right)\right)\right], \tag{4.15}$$

$$\beta_3 = \frac{3\sqrt{2}\sqrt{4L\pi^2-\pi^2\phi}}{\sqrt{6L\pi^2+\phi}}, \tag{4.16}$$

respectively. Energy shift of the third state is found as follows,

$$\Delta E_3 = E_3^0\phi\left(\frac{1}{\beta_3 L} - \frac{\beta_3}{2L(\frac{\beta_3^2}{4}+9\pi^2)}\right) - \frac{1}{2L}\coth\left(\frac{\beta_3}{2}\right). \tag{4.17}$$

The change of variational parameters β_1, β_2, β_3 due to dimensionless field intensity is sketched in the figures 4.1, 4.3 and 4.4, respectively. Wave functions of first, second and third states given by the equations 3.15, 4.4 and 4.11 are sketched in the figures 4.5, 4.6 and 4.7, respectively.

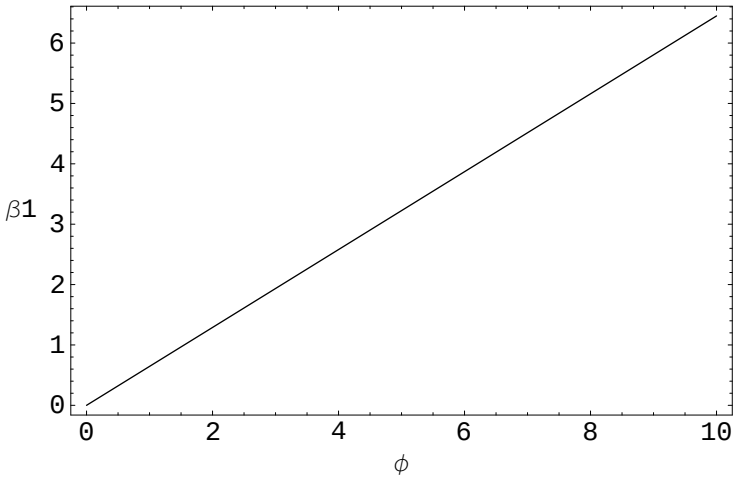

Figure 4.2: Variational parameter β_1 vs. dimensionless field intensity ϕ.

4.2 Variational Calculations for Finite Well

Using calculated variational parameter in 3.44 and wave functions 3.45, same procedure is used to obtain ground state energy shift.

$$\Delta E = e^2 F^2 (\Delta\Omega)^2, \tag{4.18}$$

where

$$\begin{aligned}\Delta\Omega = \frac{L^2}{4}[1 + \frac{\sin(k_0)}{k_0} + \frac{2}{q_0}\cos(\frac{k_0}{2})^2]^{-1} \\ [\frac{1}{3} + \frac{\sin(k_0)}{k_0} + 2\frac{\cos(k_0)}{k_0^2} - 2\frac{\sin(k_0)}{k_0^3} \\ + \frac{2}{q_0}(1 + \frac{2}{q_0} + \frac{2}{q_0^2})\cos(\frac{k_0}{2})^2].\end{aligned} \tag{4.19}$$

For an infinite barrier height $q_0 \rightarrow\rightarrow \infty$ and $k_0 \rightarrow \pi$,

$$\Delta\Omega \rightarrow \Delta\Omega_\infty = \frac{1}{3} - \frac{2}{\pi^2}. \tag{4.20}$$

In the equation 4.19 k_0 is the dimensionless wave vector is given by

$$k_0^2 = \frac{2m^* L^2 E_1}{\hbar^2}.$$

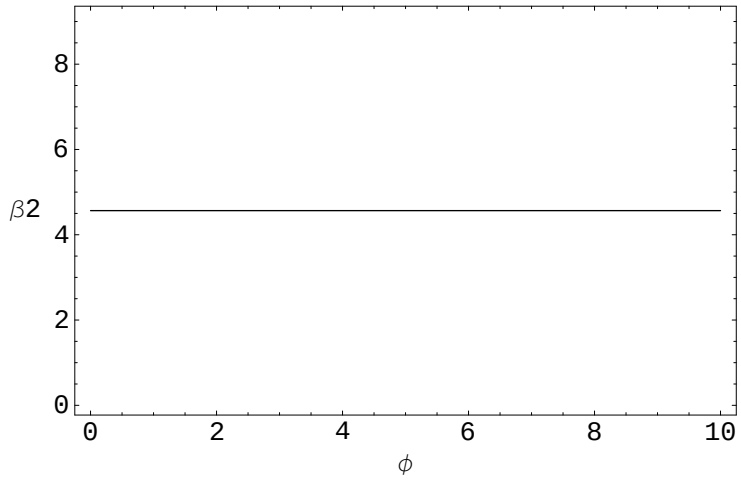

Figure 4.3: Variational parameter β_2 vs. dimensionless field intensity ϕ.

Table 4.1: Dimensionless field dependence of second order polarization terms. Columns are the polarization terms.

ϕ	$< z_{1,1} >$	$< z_{1,2} >$	$< z_{1,3} >$	$< z_{2,2} >$	$< z_{2,3} >$	$< z_{3,3} >$
1	0.0108	5.0029	17.2856	-0.01103	-20.4988	-91.7998
10	-0.0006	4.0049	47.4156	-0.01103	-20.7513	-91.561
20	-0.0352	3.1784	54.2224	-0.0110	0.01085	-91.2986
30	-0.0930	2.3487	48.1813	-0.01103	-21.4142	-91.0391
40	-0.1739	1.7560	40.0381	-0.01103	-21.8124	-90.7824
50	-0.2779	1.3553	32.7468	-0.01103	-22.2683	-90.5285

4.3 Nonlinear Polarizability for Second Harmonic Generation of Infinite Well

Contributions of individual states to nonlinear polarizability for second harmonic generation are calculated. Variational wave functions given by 3.15, 4.4, 4.11 and calculated energies 4.8 and 4.15 are employed. Frequency of emission is $\omega = (E_3 - E_1)/\hbar$. The terms of nonlinear polarizability as explained in Chapter 3 are found as given in the table 4.3.

Findings for $< z >$ are in agreement with [23]. Magnitude and sign of nonlinear

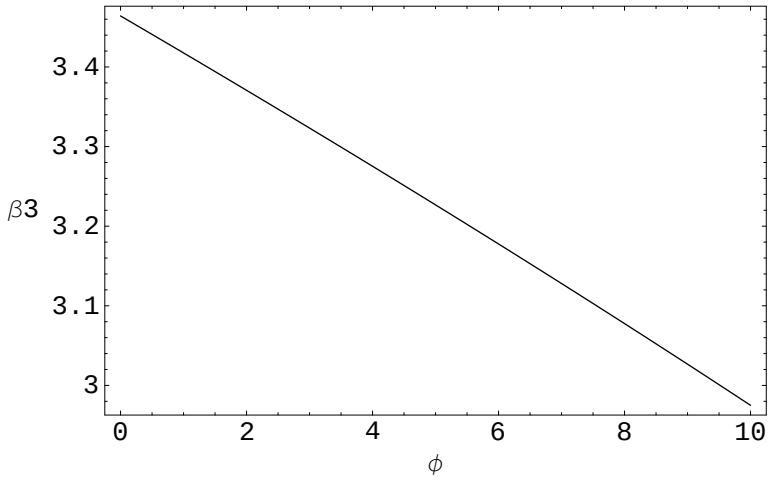

Figure 4.4: Variational parameter β_3 vs. dimensionless field intensity ϕ.

susceptibility depends on the magnitude of the applied dimensionless electric field intensity ϕ. In the figure 4.8, the near resonance and low electron density conditions are assumed. Dephasing time γ of order 10^{-12} *sec.* and electron concentration N of order 10^{15} cm^3 are taken into account.

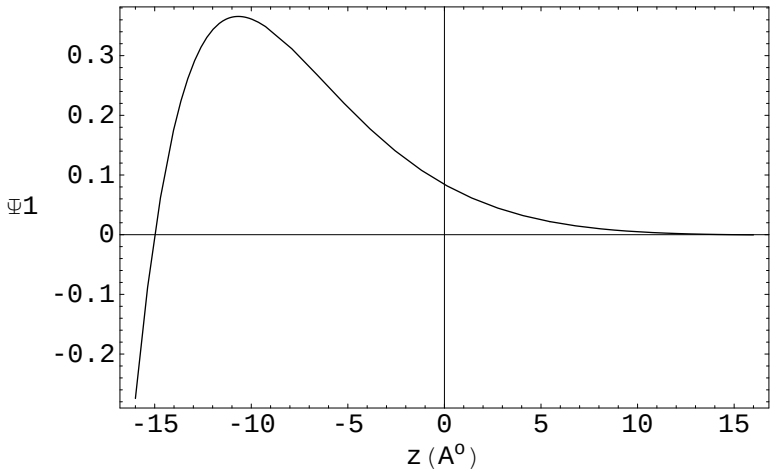

Figure 4.5: Variational wave function ψ_1 for the ground state vs. z for $\phi = 10$ in a well of thickness $30\mathring{A}$ and energy of $E_1^0 = 142meV$.

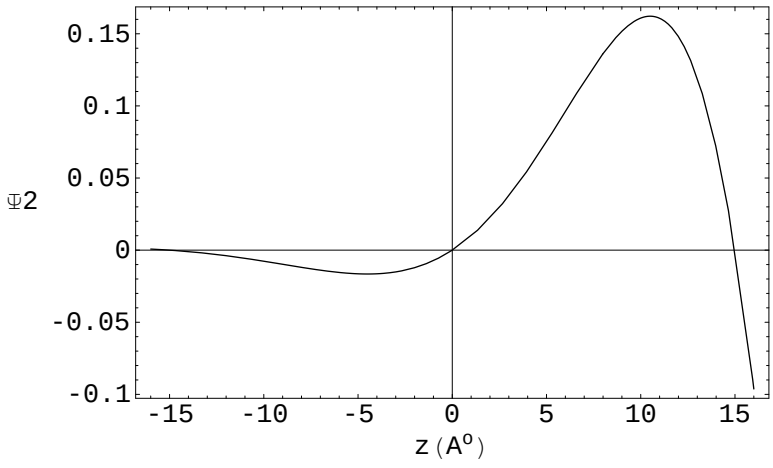

Figure 4.6: Variational wave function ψ_2 for the second state vs. z for $\phi = 10$ in a well of thickness $30\mathring{A}$.

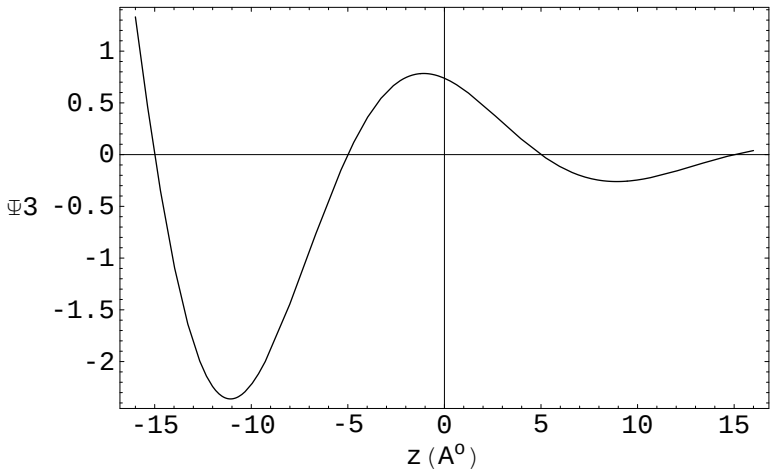

Figure 4.7: Variational wave function ψ_3 for the third state vs. z for $\phi = 10$ in a well of thickness $30\mathring{A}$.

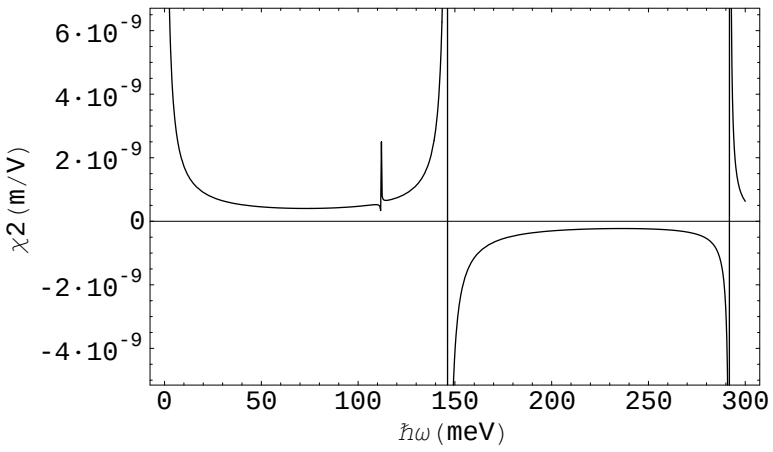

Figure 4.8: Second order non-linear optical susceptibility $\chi^{(2)}$ calculated for SHG. $\phi = 100$, $E1 = 40eV$, $E2 = 152eV$, $E3 = 332eV$ in a well of thickness $100\mathring{A}$.

CHAPTER 5

CONCLUSION

In this thesis, electronic and optical properties of a QW under external electric field is studied. Calculated wavefunctions and eigenenergies are used to study the second order optical non-linear susceptibility $\chi^{(2)}$ of the QW.

First the variational method is employed to obtain the electronic structure of the subbands. Using the variational wavefunctions, the energy equation of the QW under external electric field is solved. Minimising the energy terms with respect to variational parameters, the wavefunctions and energy states are obtained in terms of the zero-field ground state energies and applied electrical field. This procedure is applied to both finite and infinite QW structures. The results are consistent with those available in the literature [12, 99, 13].

The wavefunctions and the energy eigenstates are also found by the perturbation method. The results are consistent with the results obtained from the variational method at low fields up to 100 keV for a QW with a thickness of 30 $\mathring{A}$. It is observed that at larger fields for thinner QWs the perturbation method is not adequate.

Variational wavefunctions are used in the calculation of $\chi^{(2)}$ for SHG. First the polarization terms of an infinite QW under external bias are calculated. It is seen that the magnitude and the sign depend on the applied electric field. This result is also consistent with the work of Fejer [23].

At low electron concentration of the order 10^{15} cm^3 and near resonance which yields a dephasing time of the order 10^{-12} $sec.$, $\chi^{(2)}$ is calculated. $\chi^{(2)}$ versus incident photon beam frequency has given sharper peaks in comparison with Fejer's results [23].

While the envelope wavefunction approximation is used and results obtained in agreement with previous works [23, 12], piling of electrons towards the barrier for high electron concentration and exchange-correlation contributions are not taken into

account. The simplicity of the variational method used, allowed to manipulate non-linear calculations easily. The correlation effects of carriers can be included in to the density matrix formalism for future studies.

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