

STUDIES ON
NON-RESONANT MULTIPHOTON PROCESSES
IN ATOMIC HYDROGEN

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for the award of the degree of

DOCTOR OF PHILOSOPHY

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CERTIFICATE

Certified that the work presented in this thesis is a bonafide work done by Mr. R. Radhakrishnan, under my guidance in the Department of Physics, Cochin University of Science and Technology and that this work has not been included in any other thesis submitted previously for the award of any degree.

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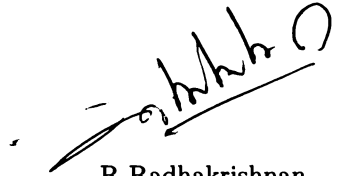
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Dr. Ramesh Babu T
(Supervising Guide)

DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of Dr. Ramesh Babu T, Professor, Department of Physics, Cochin University of Science and Technology and has not been included in any other thesis submitted previously for the award of any degree.

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R Radhakrishnan

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Preface

Studies on multiphoton process has gained momentum after the advent of lasers in 1960, but the history traces back to 1930's when Göppert-Mayer developed the theory on spontaneous and stimulated two-photon process based on second order perturbation theory. It is well known that even 'Rayleigh and Raman scattering' are bona fide two-photon process. Invention of laser led to the observation of various higher order process like stimulated Raman scattering, higher harmonic generation, multiphoton ionization (MPI) and selective excitation of atoms, which became topics of immense interest to both theoreticians as well as experimentalists. Unlike the single-photon transitions, multiphoton processes depends on intensity and polarization of the incident radiation. This intensity dependence makes this process a nonlinear one. Area of multiphoton ionization is rich with many interesting phenomena. Multiple ionization of atomic system was observed in 1975 and then follows the experimental observations of electrons with large kinetic energies which can not be accounted by the single photon absorption. The area became more interesting with the experimental observation of ac-Stark shifts, tunneling ionization and recently the atomic stabilization in the presence of intense laser fields.

The availability of lasers with intense-short pulses, leads to the possibility of using multiphoton spectroscopy for probing the fundamental physics

of atom-field interaction. The availability of increasingly intense lasers has also made possible the observation of a wide variety of multiphoton processes, including multiphoton ionization, harmonic generation and laser-assisted electron atom scattering. Since the laser pulses are so short the electric field can oscillate only a few times during the pulse width time interval, the tunneled electron wave packet moves under the influence of the strong field, when the electric field switches it can re-collide with its parent ion. This electron can interfere or diffract with the bound state wave function and can even scatter from its parent ion elastically or inelastically and excite it.

Multiphoton process corresponds to higher order terms in the perturbation theory of matter-field interaction. Perturbation theory proves to be valid for intensity of light up to $I = 10^{13} \text{ Wcm}^{-2}$. It was found that at moderate intensities, direct multiphoton ionization as well as above threshold ionization (ATI) are satisfactorily explained by perturbation theory. The process of ATI is the absorption of more number of photon than the minimum number required for the ionization, thus leading to transitions among the continuum states. ATI can be studied using high resolution photo-electron spectroscopy.

In the present thesis, we concentrate on various multiphoton process in hydrogen atom. This study on hydrogen atom provide, a basis for the studies on a large number of atomic systems like alkali atoms, negative ions etc. We restrict our work on multiphoton process which can be treated in the framework of perturbation theory. Under the framework of perturbation theory, we also studied above threshold ionization (ATI) for the case of two- and three-photon ionization.

The introductory chapter (Chapter 1) is a review on various multiphoton processes, starting from the description of simple one-photon ionization. We reviewed the main topics in atom-field interaction covering both theoretical and experimental investigation of the subject over a broad range.

We tried our best to discuss various experimental observations and its theoretical explanations, making the review a complete one.

This includes the effect of intensity on ionization processes, polarization dependence of MPI, angular distribution of the ejected electron, multiple ionization and resonance enhanced MPI. A separate section is added for the discussion on tunneling ionization, which is entirely independent of multiphoton ionization physics. We dedicate separate sections for describing the observed nature of ionization spectrum in different atomic systems other than hydrogen atom, which includes theoretical models for describing alkali atoms and atoms with many valence electrons. We conclude the chapter by discussing the recent developments in the superintense laser physics. In each sections we tried to describe the experimental observation using the available theoretical explanation on the subject.

In **Chapter 2** we mainly concentrate on the theoretical methods available for the description of multiphoton ionization. The range of intensity considered is such that the perturbative treatment is feasible. In the first part we highlight the problems arising in the formulation of multiphoton ionization using perturbation theory, especially problem of infinite summation appearing in the perturbative expansion. These infinite sum of intermediate states includes discrete as well as continuum states. Then few methods are described where the infinite sum is approximated using various methods and we also reviewed two methods which avoid the explicit summing of the contribution from intermediate states.

First the expression for two-photon transition probability is derived using perturbation theory in the dipole approximation. Then the available methods are reviewed. The approximate methods used in perturbation theory are technique by *Bebb* and *Gold*, truncated summation, variational treatment, Green's function method and Dalagarno-Lewis method. Non-perturbative treatment includes WKB method and R-Matrix Floquet method. Among these Green's function method is extensively used for per-

turbative and for high intense fields R-Matrix Floquet method is widely used.

Chapter 3 consists of mainly a discussion on second order processes, where we have grouped together a few processes which can be explained using second order perturbation theory. Starting from the second order matrix element we illustrated the application of the Dalgarno-Lewis procedure. The analytical expressions obtained can be used for various two-photon processes involving the hydrogen atom.

Various two-photon processes includes bound-bound transitions, two-photon ionization, acStark effect and elastic scattering of photon from the hydrogen atom. In the section where two-photon bound bound transition is discussed, we have calculated the transition probability for a two-photon transition to occur from the ground state to any excited state, with the quantum numbers n and l . The section for two-photon ionization deals with the evaluation of the scattering cross section for two-photon processes. This includes both 'direct' and 'above threshold ionization'. We have formulated the method, derived the relevant amplitude expressions and also described the origin of two-photon selection rules. We have extended the range of applicability of the relevant expression for all values of incident photon energy, by the process of analytical continuation.

In presence of intense laser fields, the atomic levels are shifted or broadened and these stimulated radiative corrections are known as the ac-Stark shift. This is one of the interesting subject in the intense laser field science. We have done a perturbative treatment for the ac-Stark effect experienced by a non relativistic hydrogen atom irradiated by a mono mode laser field. Here we obtained an alternate expression for dipolar polarizability and it was found that at the limit where the frequency of the incident photon goes to zero corresponds to the static polarizability of the hydrogen atom. Then the dispersion relation of *Kramers* and *Heisenberg* is evaluated in our formalism. Since both are two-photon processes, we used a unified treatment

to obtain the alternate analytical expressions and the results are compared with values reported in the literature.

In **Chapter 4** we discuss three-photon processes. The first one which we discuss is the three-photon transition probability from ground state of atomic hydrogen to any excited bound state allowed by three-photon selection rules. Secondly we obtained scattering cross section for three-photon ionization of atomic hydrogen. Three-photon ionization includes three separate cases depending on the energy of the incident photon. They are direct ionization, above one-photon and two-photon ionization threshold. Finally we have discussed analytic continuation, which is mainly used to describe above threshold ionizations.

From the analytical expressions for three-photon radiative transition matrix elements the cross section for three-photon ionization of atomic hydrogen is calculated for both linearly and circularly polarized light with a wide range of photon energy spectrum including the near resonance and numerical comparison is made with the values obtained by different methods. We dedicate a separate section for the description of above threshold calculation which is obtained by the analytical continuation of the relevant expressions previously obtained. Taking the expression for two-photon processes we also demonstrate the process of analytical continuation in detail.

Chapter 5 contains concluding remarks which summarize our work. The future perspectives are also discussed.

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Chapter 1

Introduction

The study of ionization of atomic system is one of the important ways to investigate the characteristic property of the interaction of atomic system with electromagnetic field. Starting from the absorption of a single photon with necessary energy for the ionization, the studies have now been extended to the processes of ionization by absorbing more than one photon which ranges from the minimal number of photons necessary for ionization to that of hundreds of extra photons [1, 2, 3].

The study of the interaction of intense laser fields with atoms, ions and molecules has attracted considerable attention in recent years. The availability of increasingly intense lasers has made possible the observation of a wide variety of multiphoton processes, including multiphoton ionization, harmonic generation and laser-assisted electron atom scattering [4, 5]. Since the laser pulses are so short, the electric field oscillates only a few times during the pulse duration. The tunnelled electron wave packet moves under the influence of the strong field and when the electric field switches can re-collide with its parent ion. This electron can interfere or diffract with the bound state wave function and even these electron can scatter

from its parent ion elastically or inelastically and excite it.

Numerical as well as analytical studies have been done for hydrogen, alkali and noble gas atoms and even atoms with two active electrons and with many electron atoms where the electron correlations play a crucial role. Lowest order perturbation theory (LOPT) has been used to study various properties in the low intensity regime and has well explained most of the available experimental results. For an N photon ionization the theory predicts that the ionization rate Γ_N has a power dependence on intensity as $\Gamma_N \sim I^{N-1}$. In principle it is possible to extend the LOPT for high intensity electromagnetic field by including the higher order contributions, but its implementation is impractical. It was also noted that the observed ionization rate decreases as the intensity increases and it does not agree with the predictions of LOPT. The phenomenon of this decrease in the ionization rate is termed as ‘stabilization effect’, which is of current interest to the atomic, molecular and optical physicists. This indicate the breakdown of perturbation theory and the need for the solution of the Schrödinger equation directly.

This chapter begins with Bohr condition for one photon absorption and we extend it to multiphoton processes, then a small discussion on the behavior of atomic system in presence of intense field is done. This is followed by a simple schematic description of experimental setup for multiphoton ionization.

1.1 Emission and absorption of radiation by atoms

A photon with necessary energy interact with an atom and as a result the electrons undergo transitions between different states. This is according to

the Bohr's quantum condition,

$$E_f - E_i = \hbar\omega \quad (1.1)$$

where E_i and E_f are the initial and final state energies respectively and ω is the frequency of the incident photon. But in general, all transitions which satisfies the above equation are not allowed. The radiative transition can take place only between the states allowed by certain selection rules. Apart from the energy conservation given in Eq. (1.1), angular momentum also has to be conserved and this leads to selection rules and the dependence of the transition probability on the polarization of the incident radiation. For a multiphoton excitation of atoms the above condition given in Eq. (1.1) can be generalized as

$$E_f - E_i = N\omega\hbar.$$

where N is the number of photons absorbed.

Perturbation theory is valid provided the radiation field strength F is much less than atomic field strength F_a i.e., $F \ll F_a$ or $\gamma^2 \gg 1$, where γ is the adiabaticity parameter. Then the ionization can takes place as a result of multiphoton absorption and we assume that the kinetic energy of the ejected electrons is not perturbed by the electromagnetic field.

1.2 Multiphoton processes

The broad area of interaction of atoms by 'intense laser pulses' can be divided into two regimes: the first regime involves relatively weak laser fields of long duration ($> 1\text{ns}$) and the second involves strong fields of short duration ($< 1\text{ps}$).

In the first case, the intensity is high enough for multiphoton transitions to occur and it does not obey single-photon selection rules.

For the second case the fields are too strong that the perturbative anal-

ysis is not valid and the ionization of many electrons may occur. Since the radiation field intensity is high in this case its classical description is enough, but we have to solve the time dependent Schrödinger equation directly to study the atom field interaction.

For weak pulses, the electronic states are only weakly perturbed by the electromagnetic field. Then the rate of an N -photon transition can be calculated using N th order perturbation theory result for the atom-field interaction. Following the perturbation theory the N th-order transition amplitude $\mathcal{M}_{fi}^{(N)}$ corresponding to a transition from the initial state $|i\rangle$ to a final state $|f\rangle$ in atomic unit (Appendix A) reads,

$$\mathcal{M}_{fi}^{(N)} = \sum_{i_{N-1} \dots i_1} \frac{\langle f | H' | i_{N-1} \rangle \dots \langle i_2 | H' | i_1 \rangle \langle i_1 | H' | i \rangle}{(E_{i_{N-1}} - E_g - (N-1)\omega) \dots (E_{i_1} - E_g - \omega)} \quad (1.2)$$

where H' is the interaction part of the Hamiltonian, and the energies E_g , E_i and ω are in units of (e^2/a_0) where a_0 is the Bohr radius. The $N-1$ intermediate state sum is over the complete set of states including the continuum states.

Since the laser frequency can be varied, the energy of m -photons can match with one of the intermediate state in the infinite sum and the remaining $N-m$ photons can cause the electron to reach the continuum states. This can lead to the resonance enhancement of ionization cross section and it is called ' N, m resonance enhanced multiphoton ionization (REMPI)'. It is useful to note that in this case, the corresponding energy denominator vanishes in Eq. (1.2), causing the breakdown of perturbation theory.

Recently developed laser systems can produce very short pulses, some as short as a few to tens of femtoseconds, and can have peak intensity of 10^{19}W/cm^2 . At these high intensities, the field can shift the energies of atomic levels, which is termed as 'dynamic or ac-Stark effect'. The

electrons in the highly excited state responds to the oscillating field, in the same manner as the free electrons. Their energy shift by an amount U_p , called ponderomotive energy, which is the cycle-averaged kinetic energy of a free electron in the field. It can be viewed as the minimum kinetic energy a free electron possesses as a result of its oscillations in a laser field or as the potential energy of a free electron due to its interaction with the field. 'Ponderomotive potential' is given by the expression

$$U_p = \frac{e^2}{2m\omega^2} \langle F \rangle,$$

where $\langle F \rangle$ is the time average over a period of the applied laser field.

The change in the energy may be larger than the incident photon energy. The electrons in the continuum will have the ponderomotive energy and oscillate with the field. Suppose the initial velocity of an electron is small after ionization, it can be accelerated by the field back into the ion core. This rescattering changes the photoelectron energy and angular distributions and it may also lead to the emission of high energy photons.

A strongly bound electron can respond to the instantaneous laser field. If the amplitude of the laser field is large enough, the Coulomb attraction of the ion core combines with the laser electric field to form an oscillating barrier through which the electron can escape by tunneling. This phenomenon is called 'tunneling ionization'. The ratio of the incident laser frequency to the tunneling rate is called the 'Keldysh parameter' γ , which determines whether the ionization is due to multiphoton absorption or by tunneling. When it is less than unity tunneling dominates and when it is larger than unity multiphoton ionization dominates. With these parameters, a necessary (but not sufficient) condition for perturbation theory to be valid is $\gamma > 1$.

Atoms can lose several electrons and can be released sequentially due to a high intense single radiation pulse. The probability for simultaneous

ejection of two or more electrons is very less, though a finite possibility still exist. This simultaneous ejection of more than one electron is called ‘multiple ionization of atoms’.

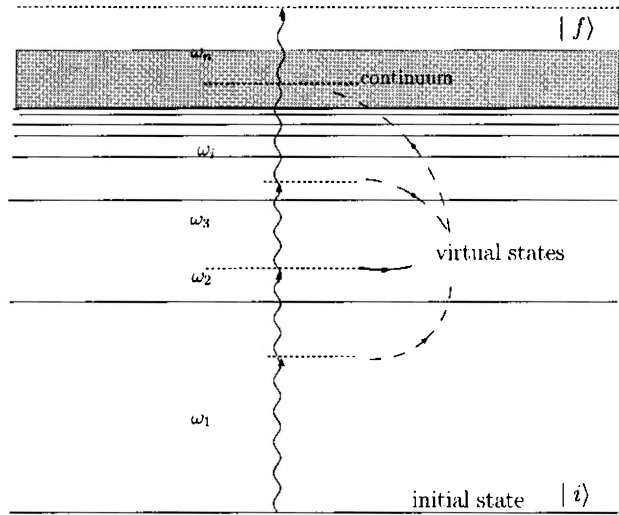


Figure 1.1: Schematic diagram for multiphoton ionization: the transition is from an initial state $|i\rangle$ to a final continuum state $|f\rangle$ through succession of intermediate virtual states (represented with dotted lines). If the virtual states matches with one of the eigenstates, the situation is called resonance enhanced multiphoton ionization

It is also possible that electrons can gain more than the minimum amount of energy required for ionization. Thus instead of forming a single peak, the emitted electron energy spectrum contains a series of peaks separated by the incident photon energy. This is called ‘above threshold ionization (ATI)’. The peaks will appear at the electron energies

$$E_e = (k + s)\hbar\omega - I_p$$

where I_p is the ionization energy, k is the minimum number of photons required for ionization and $k + s = N$ is the total number of photon absorbed.

It was found recently that at higher intensities atoms undergo dynamic stabilization and that means as intensity increases the ionization rate saturates. This leads to the new interesting area of ‘stabilization of atoms in intense laser pulses’. It was found that stabilization indeed occurs for laser field strengths and frequencies of the order of one atomic unit.

Among the different interesting phenomena occurring in various types of multiphoton processes, we mainly concentrate on multiphoton ionization (MPI) of atomic systems. Multiphoton ionization (MPI) is described as the ionization of an atomic system by simultaneous absorption of several photons. In this case photons with energy too low to ionize the atom by single photon absorption are piled up to reach the ionization threshold. For the description of the problem we use perturbation theory. MPI is schematically described in the Fig. 1.1.

Most of the available experimental results on MPI can be successfully explained using the semiclassical and full quantum treatment. There are various methods available for the determination cross section of multiphoton ionization. Using numerical estimate *Lambopoulos* and *Tang* [33] has introduced a generalized cross section for N -photon ionization which is given by

$$\hat{\sigma}(N) = (\hbar\omega)^N w^{(N)} / I^{(N)} [\text{cm}^{2N} \text{s}^{N-1}]$$

and used it to estimate the multiphoton cross section of complex atoms.

1.3 Experimental setup for multiphoton Ionization

The schematic diagram of the experimental setup is given in Fig. 1.2. The basic setup consists of vacuum vessel for preparing target gaseous atoms.

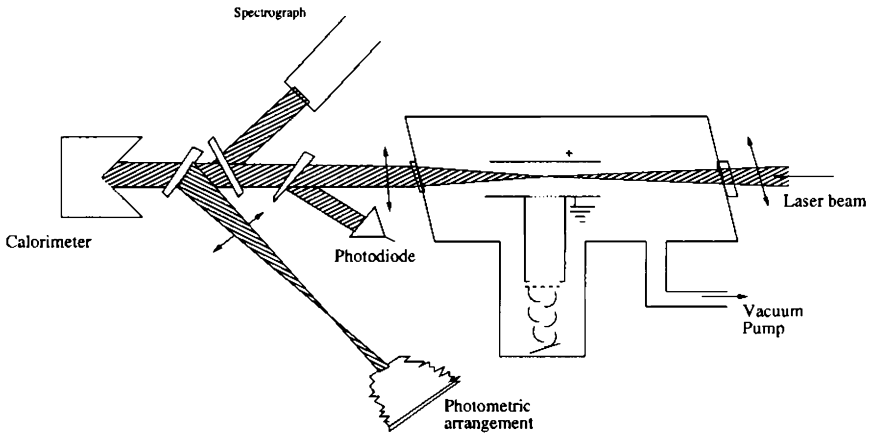


Figure 1.2: Schematic diagram for multiphoton ionization experiments [2]

The vacuum pump reduce the pressure of residual gases to 10^{-6} to 10^{-8} Torr. Then the target gas is induced with a pressure whose upper limit is 10^{-3} Torr ($\sim 4 \times 10^{13}$ atoms/cm³). When it is alkali atoms, the density is limited to $10^9 - 10^{10}$ atoms/cm³. An interelectrode system is used to ionize the atom. Lenses are placed on either inside or outside the vacuum cell depending on the focal length, the choice depends on intensity required at the focus. Electric charges are separated by applying a transversal electric field and the ions are repelled towards a time of flight mass analyser. The obtained ion signal is amplified by using an electron multiplier.

Photodiode and calorimeter measures respectively the time duration and the laser pulse energy. The photometric arrangement makes the determination of spatial distributions of laser intensity.

1.4 Above threshold ionization of atoms

The emission of electrons with large kinetic energies in multiphoton experiments were first observed in mid seventies. The total 'Direct ionization' probability W , at frequency ω has a power dependence to the radiation intensity I as $W \sim I^N$. In practice accuracy of multiphoton cross section is much worse than the single photon cross section. Important theoretical methods available for the calculation of these multiphoton ionizations are Greens function method, Dalgano-Lewis method, variational method, Floquet method and WKB method. A detailed discussion on these methods are done in the next chapter.

Agostini et al. [34] first investigated the 6-photon ionization of Xe atom and observed the electrons with kinetic energies $E_e = 6\hbar\omega - E_i$ and above threshold electrons with kinetic energy $E_e^1 = 7\hbar\omega - E_i$. Many experiments on above threshold ionization are then reported.

From the WKB results the ratio of $N + 1$ above threshold and N threshold ionization rates is found to be

$$w^{N+1}/w^N = 0.14F^2/\omega^{10/3}$$

where w^k is the k -photon transition rate and F is the field strength.

In the case of hydrogen atom, two-photon above threshold ionization, the energy of the first photon exceeds the ionization energy of the hydrogen atom. There are many literatures available for hydrogen atom, *Karule* [21],[23] *Aymar-Crance* [26], *Gao-Starace* [39] *Berson* [38] and *Ramesh* [19, 14, 17, 106] are few of them. A detailed discussion and derivation of the analytical formula is obtained in section 4.4. The experimental investigation of above threshold ionization are reported by *Petite et al.* for 5-photon ionization of Cs atom [35], the first above threshold maximum appears at the intensity 5×10^{10} W/cm² and a 7-photon ionization of Xe

atom for a radiation intensity 10^{11} W/cm² [36, 37]. *Petite* et al. also measured the ratio of the rates of $N + 1$ photon and N -photon processes for the Cs atom with threshold maximum of $N = 4$ and the ratio was found to be 0.03 for a radiation intensity $I = 10 \times 10^{11}$ W/cm². With a model potential *Aymar* was able reproduce the results exactly. In 1979 *Agostini* et al. measured the 6-photon ionization of Xe and found both the threshold and above threshold ionization (with one more photon i. e. , with $6 + 1$ photons).

From the experimental data it was clear that the perturbation theory was sufficient to describe the above threshold ionization at moderate intensities. The main difficulty in the theoretical investigation was to obtain the dipole matrix element of free-free transitions which are taken between the continuum states which are not normalized. In general, for an atomic system the requirement of having normalized wavefunctions, leads to the condition that the wavefunctions be regular at the origin. It was achieved by considering the wavefunctions to be a standing wave insted of traveling wave. In this case we have to add standing waves with different energies to vanish the convergent spherical part, thus we can construct wave functions which are regular at origin and divergent at infinity. 'In the case of hydrogen atom this problem can be avoided by analytically continuing the wave function'.

1.5 Polarization effects in multiphoton ionization

First theoretical explanation on the polarization dependence of MPI was in the letters by *Lambropoulos* [58]. He reported two- three- and four-photon ionization differential cross section and its dependance on the polarization using a one-electron model of atom, which was used for hydrogen, Cs and

other alkali atoms. The ratio of linear to circular cross section can even vary upto a factor of 2 and this ratio depends strongly on the frequency of the incident radiation.

Polarization dependence are best understood by the relation connecting the cross sections of linear and circular polarization. For this purpose the ratio of N -photon ionization cross section by fields of linear and circular polarization with the same intensity and frequency is used.

It is important to note that " N -photon matrix element of absorption of circularly and linearly polarized radiation differ from each other, only by the Clebsh-Gordan algebra". Thus the ratio of cross section for N -photon ionization in a circularly and linearly polarized fields can be derived in general for any atomic structure. The famous factorial formula derived by *Klarsfeld* and *Maquett* is given by

$$w_c/w_l = R = (2N - I)!!/N! \quad (1.3)$$

where w_c and w_l are ionization rates for circular and linear polarization respectively. In the case of hydrogen atom, this factorial formula is correct for $N \leq 3$. but there is no experimental data on polarization dependence of multiphoton ionization cross section for hydrogen atom. The factorial formula hold for any atoms with arbitrary number of valence electrons in the single particle approximation. *Alimov* [40] reviewed the experimental investigation of polarization dependence in alkaline earth atoms, there they found that the observed values are slightly lesser than the predicted value $R = 2.5$ and are always found to be greater than unity. The reason may be due to the fact that single particle approximation is not completely correct for the standard classification of excited states of alkali atom.

1.6 Photoelectron angular distributions

Differential cross section for multiphoton ionization of hydrogen atom by circularly polarized radiation depends on the angle θ by

$$\frac{d}{d\Omega}\sigma^N \sim \sin^{2N} \theta$$

where N is the number of absorbed photon and θ is the angle between the direction of propagation of the emitted electron and the direction of propagation of the electromagnetic radiation.

But in the case of linearly polarized light the dependence is proportional to $P_l^2(\cos \theta)$, where P_l is the usual Legendre polynomials corresponding to the value of the orbital quantum number l of the final continuum state. Here θ corresponds to the angle between direction vector of electric field strength and the direction of the ejected electron. The property Legendre polynomials are oscillatory functions with maximum at $\theta = 0$ and $\theta = \pi$, thus leading to the property that the angular distributions have 2 maxima's at these end points and an oscillatory behavior in between.

In general the angular distribution of the form [41]

$$\frac{d}{d\Omega}\sigma^N = A_0 + A_1 \cos^2(\theta) + A_2 \cos^4(\theta) + \dots + A_N \cos^{2N}(\theta)$$

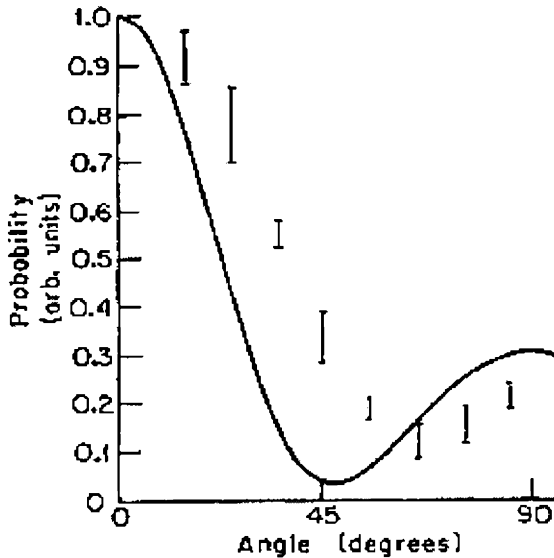
Since these are even powers of $\cos \theta$ we can express this in term of Legendre Polynomial of even orders as

$$\frac{d}{d\Omega}\sigma^N = B_0 + B_1 P_2(\cos \theta) + B_2 P_4(\cos \theta) + \dots + B_N P_{2N}(\cos \theta) \quad (1.4)$$

and the coefficients A_i 's can determined using N -photon transition matrix elements. Since these coefficients depend on the radiation frequency, the cross section for linear polarization depends on the frequency.

Experimental differential rates of multiphoton ionization of the hydro-

Figure 1.3: Four photo electron angular distribution of Cs with $N_0=4$



gen atom from ground state were measured by *Feldmann et al.* and *Wolff et al.* [42, 43]. They used linearly polarized radiation of 355 and 532 nm wavelengths. Electron angular distributions of threshold number of '4-photons' have been theoretically verified by *Gontier* [44] and the results are in good agreement with the experiments.

In the case of photoelectron angular distribution of 'alkali atoms' also, the Eq. (1.4) is applicable. The experimental values of *Dodhy et al.* [46] agree well with the theoretical values for Cs and Rb atom for two-photon ionization. The coefficients are evaluated from the two-photon radial matrix elements. *Petite et al.* [35] experimentally determined the intensity dependence of these coefficients. At low intensities the coefficients are completely independent of intensities, and they had shown that the shape is changing as intensity is increased. There are a few discrepancies in the

compared results of experimental and theoretical values and it is assumed that this disagreement may be due to the change of energies of atomic states because of ac-Stark effect.

1.7 Alkali atoms

In the present section we summarize two of the theoretical methods used for studying multiphoton processes in alkali atoms, they are Quantum defect method and model potential method. Alkali atoms contain only one electron in the outer shell. The binding energy of the valence electron is approximately one order of magnitude less than the binding energy of the electrons in the next highest filled shell. Thus it might be expected that the one electron approximation can be used to describe the interaction of an electromagnetic field with alkali atoms, as in the case with hydrogen atom. However, the multi electron core produces a potential for the external electron which differs strongly from a coulomb potential at small distances between this electron and atomic core. Therefore approximate wavefunction for the valence electron must be constructed.

For the perturbative treatment of MPI in alkali atom, we must construct an approximate expression for the potential of the atomic core and the wavefunction of the valence electron. One of the approximate method of solving this is the so called 'quantum defect method (QDM)' this was first used by *Bates* and *Damgaard* [48] in calculations of matrix elements of one-photon bound-bound transition. *Burger* modified it for bound-free transitions [49]. QDM is based on Coulomb interaction between the valence electron and atomic core. The wavefunction of the valence electron at large distances from the atomic core is approximated by a hydrogen like wavefunctions with an effective principal quantum no, $n^* = n - \delta_l$ where δ_l is called the 'quantum defect'. The value of n^* 's determined from experimental data of the energies E_{nl} of excited atomic state using the relation

for hydrogen like atoms $E_{nl} = -Z^2/2(n^*)^2$ (in a.u.), where Z is the ionic charge. In order to determine the continuum wavefunction at large distances, the relationships of the scattering phase μ_l to the quantum defect δ_l is used such that $\mu_l = \pi\delta_l$. The QDM Greens function description for alkali atoms was discussed by *Zone et al.* [50]

In ‘Model potential method’, the core potential is approximated by a model potential [51]

$$U(r) = -Z/r + \sum_{l=0}^{\infty} \hat{P}_l B_l / r^2$$

where P_l is the l projection operator and B_l is determined from the spectrum of excited atomic states with fixed value of orbital quantum number l . Single particle MPM Greens function expressions can be found in Ref. [52]

WKB approximations [53] are also available for treating MPI on alkali atoms and they give a close agreement with the experimental results [70, 63].

1.8 Atoms with many valence electron and noble gases

In this section we briefly summarize the experimental details and the theoretical analysis needed for understanding MPI on atoms with many valence electron. The electrons in the valence shell of a many electron atom interact with the external electromagnetic field as well as with each other. In the simplest approximation we assume that the electrons independently interact with the electromagnetic field. Many things can happen during the interaction, like, several electrons can be simultaneously ejected from the atom, the filled electron shell can shield the field of an electromagnetic

field, the first ejected electron can interact with the remaining electrons in the valence shell and so on.

If we neglect the residual interaction between valence electrons, the electron angular distribution for direct multiphoton ionization of ‘many electron’ atoms must be qualitatively same as of hydrogen and alkali atoms.

Experimental data on multiphoton ionization cross section for alkaline earth atoms are reviewed by *Ammosov et al.* [63] For Noble gases, the large ionization potential leads to a high threshold intensity (intensity at which ionization processes are observed). Because of the large intensity, perturbation of atomic spectrum due to ac-Stark shift is very important. It was also found that except for $N = 2$ and $N = 3$ the cross section for MPI of noble gases are less than that for the alkali and alkaline earth atoms.

Using wavefunctions for single particle states, and using Greens function method (discussed in section 2.2.3) a few theoretical attempts were made [54, 55], and was found to be in good agreement with the experimental results. *Gangopadhyay* [55] truncated the sum after 10 terms, and used multi-channel quantum defect method for single particle wave functions, the continuum wavefunctions are expressed via scattering phases, which are calculated in WKB approximation.

Two and three-photon ionization for noble gases are also studied by *McGuire* [54] for both polarization. He had used self-consistent ‘Herrma-Skillman potential’ as the single particle atomic potential. This includes the effective potential of the atomic core as well as the self-consistent potential between a given electron and all other electrons in the valence shell, finally local exchange potential (central) given by $U_{XC}(r) = a[3\rho(r)/8\pi]$ is added, where $\rho(r)$ is the density of electron in valence shell. They calculated atomic Green’s function using the above potential and applied perturbation theory to find the cross section. The ratio of cross sections of circular and linear polarization agrees with the factorial formula. *Kulender* [56] used the Herrma-Skillman potential and calculated the wavefunctions of the valence

electron numerically. Residual interaction between valence electron was investigated in detail by *L'Hullier et al.* [57]. It was done by considering effective laser atom interaction term as

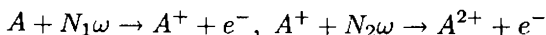
$$V_{eff}(\mathbf{r}, t) = \mathbf{r}(\omega)F \cos \omega t$$

where $\mathbf{r}(\omega)$ is the effective dipole operator Using this effective dipole operator $\mathbf{r}(\omega)$ instead of \mathbf{r} the multiphoton transition matrix elements are evaluated.

1.9 Multiple ionization of atoms

It is known that binding energy is high for an electron in a singly charged ion. It is approximately double the ionization energy for alkaline-earth and noble gases and > 5 times for alkali atoms. Therefore it was believed that in order to observe ionization of multiple electrons we need very intense and high frequency radiation[45]. Now multiple ionization is a typical process observed in a wide range of experimental conditions i. e. , for laser intensities ranging from subatomic to superatomic ranges [64, 65]. Let us consider few cases where the production of doubly charged ions is possible. In order to make the theoretical description simple let us consider double ionization.

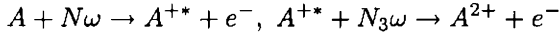
For the case where the field intensity is much lower than atomic field strength, i. e. , $F \ll F_a$ we expect the ionization to be of the character of multiphoton process. It is described as a 'step wise process' i. e. , initially one electron is detached, then subsequently the second one. Both the electrons are detached by the same laser pulse. It can be described as



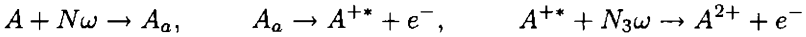
for this case the probability of the above process is equal to the product of the probability of each individual transition. This stepwise processes can

be resonant or non resonant.

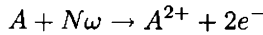
The second case is the formation of doubly charged ion through an intermediate excited state of singly charged ion A^{+*} . This excited state ion can be obtained by absorbing an energy which is higher than the ionization potential of the atom and the excess energy is not transformed into kinetic energy of the electron, instead is transferred to the ion. It can be described by the process



Suppose the system possesses an autoionizing state A_a , it is possible that the state can decay via autoionization, resulting in the formation of the ion in the excited state. this can be described by



it is interesting to note that the first process is a real processes(not virtual as in the previous case). In the final case simultaneous detachment of two electrons are also possible and is described by



Experimental results were reported by *Agostini* and *Petite* for the formation of Sr^+ and Sr^{2+} [86], ionization observed at the laser intensities $10^{10} - 10^{12} \text{W/cm}^2$. Subsequently there were many experiments reported on multiple ionization of various atomic systems [85, 87, 88, 90, 84]. UV ionization of noble gas atoms were reported by *Johan* et al. [89], they found the ionization for intensities ranging from $10^{13} - 10^{15} \text{W/cm}^2$.

Theoretical description of the step wise process is done by considering the rate equations and a brief idea can be obtained from the Ref. [45]p. 213.

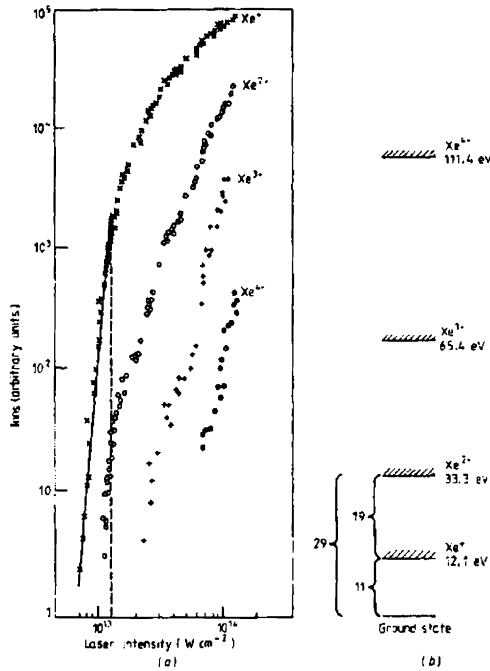


Figure 1.4: Log-log plot of the variation in the number of xenon ions formed as a function of the laser intensity I . The vertical broken line indicates the saturation intensity I_s , which indicates a marked change in the intensity dependence of Xe^+ and Xe^{2+} . Schematic representation of the 29-photon one-step process, and the (11+ 19)-photon two-step process leading to Xe^{2+} ions. Source: [84]

1.10 Tunneling ionization of atoms

The qualitative difference between multiphoton and tunneling ionization lies in the frequency dependence of the rates for these processes. According to *Keldysh*, nonlinear ionization is determined by the so called adiabatic

parameter

$$\gamma = \omega(2E_{bind})^{1/2}/F$$

The $\gamma^2 \ll 1$ condition, implies the tunneling ionization. Here the rate of ionization depends on the field strength exponentially

$$w \sim \exp \left[-2(2E_{bind})^{3/2}/3F \right]$$

Here the ionization rate is frequency independent, whereas multiphoton ionization rates are frequency dependent. For example the ionization rate for the ground state of hydrogen atom perturbed by a constant electric field is given by [66]

$$w = \frac{4}{F} \exp(-2/3F)$$

It can be seen that for different polarization the above expression for rate has the same form, which depends only on the amplitude part and not on the exponent. The above formulation is simple and many areas can not be exploited.

Landau-Dykhne adiabatic approximation : In the case where the frequency ω of the incident photon is less than the ionization potential of the atomic system, a simple analytical expression is obtained from the adiabatic approximation of quantum mechanics and is given by the Landau-Dykhne formula

$$w_{fi} = \exp \left\{ -2Im \int_0^{t_0} (E_f(t) - E_i(t))dt \right\}.$$

where w_{fi} is the transition probability between the initial state $|i\rangle$ to the final state $|f\rangle$, t_0 is the complex turning point in the plane of complex time which is found from the condition $E_i(t_0) = E_f(t_0)$. The rate of tunneling ionization in a monochromatic, linearly polarized field from excited states of hydrogen atom with principle quantum number n , orbital quantum number

l and magnetic quantum number m is given by [67]

$$w = \left(\frac{3}{\pi}\right)^{1/2} 2^{4n-2|m|-2} (2l+1)(l+|m|)! \\ n^{-6n+3|m|+3/2} \frac{F^{-2n+|m|+3/2} \exp(-2/3n^3 F)}{(n+l)!(n-l-1)!|m|!(l-|m|)!}$$

This is valid when $F \ll F_a$ where $F_a = 1/16n^4$ is the atomic field strength for an excited state of hydrogen atom with principal quantum number n . We can use the same expression for complex atoms by replacing $n \rightarrow n^*$ where the n^* is determined from quantum defect method. The expression for circular polarization can be obtained by multiplying an appropriate constant to the above equation. The energy spectrum of electrons for both circular and linear polarization are reported in Ref.[68] using adiabatic approximation.

1.11 Resonance enhanced multiphoton ionization

In this section we consider ionization of atomic systems through intermediate resonant transitions. When sum of the ground state energy and energies of few number of photons matches with the energy of some excited bound state, resonances occurs and it is reflected by an increases in the probability of ionization rate of the atom. Non-resonant multiphoton ionization can be described by perturbation theory but resonant multiphoton ionization has a profiles whose shapes change according to the length and intensity of the laser pulse and can be quite different from that predicted by LOPT. Suppose the N' photons ($N' < N$) have an energy equal to the transition energy from an initial state $|i\rangle$ to some excited bound state $|n\rangle$, and ionization are possible with N photon absorption, the situation termed as

resonance enhanced ionization. Condition for resonant enhanced ionization is

$$\Delta_{ni}(F) = |E_n(F) - E_i(F) - N'\omega| \lesssim \Gamma_{ni}(F)$$

where $\Delta_{ni}(F)$ is the resonance detuning and $E_i(F)$ and $E_n(F)$ are the energies of the initial and resonant states, $\Gamma_{ni}(F)$ is the reduced width of the resonant transition. It is useful to note that all the quantities take into account the perturbation due to radiation field strength F . For enhanced ionization in a weak field ($\Gamma_n \ll \gamma_n$), the rate of ionization W can be written as

$$W = \frac{\Gamma_n(F) |F^{N'} M_{ni}^{(N')}|^2}{(E_n - E_i - N'\omega)^2 + \gamma_n^2/4}$$

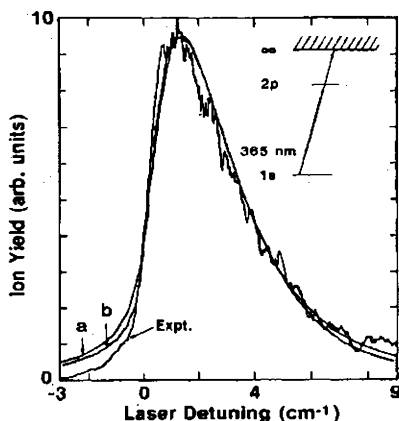
where Γ_n is the ionization width of the resonance level γ_n is the natural line width of this level $M_{ni}^{(N')}$ is the N' th order transition matrix element. For intense fields the ionization width will be larger and we have to consider ac-Stark shifts. When resonance widths exceeds the natural width of the resonance level, multiple resonances can occur.

Resonance enhanced Multiphoton Ionization (REMPI) is used to study energies of excited atomic states, Stark shift, to measure the multiphoton bound-bound transition matrix elements and also to look for exotic transitions (quadrupole, forbidden, 2-electron transitions etc.). Since the angular momentum of the continuum states are now different the electron angular distributions are interesting. *Dodhy et al.* [47] measured angular distributions of photo electrons in the 2-photon ionization of Rb atom with one photon resonance between the ground $4s$ state and a quadrupole coupled $4d$ state.

In the experiments, REMPI was observed as a multiphoton transitions from an initial state to a resonant state followed by a single photon transition from the resonant state to the continuum.

Armstrong and Feneuille [80] used a model of 2-level and 4-level system

Figure 1.5: Dependence of the rate of resonance enhanced 4-photon ionization of ground state of hydrogen atom. Experimental data from Ref.[69]



to analyse the behavior of resonant multiphoton ionization to describe the REMPI.

REMPI on Hydrogen atom: In the experiment reported by *Kelleher* [69] they measured the rate of 4-photon ionization of ground state of atomic hydrogen in the presence of 3-photon resonance between 1s and 2p levels. The resonant width is determined by the single-photon ionization of the resonant 2p level and its ac-Stark shift. Thus the ionization rate is given by

$$w = |z_{ni}^{(3)} F^3|^2 \frac{\Gamma_n(F)}{(\Delta_{ni}(F) + \delta E_{ni})^2 + \Gamma_n^2(F)/4}$$

Here $\Gamma_n^2(F)$ is the single photon ionization width of 2p level, $z_{ni}^{(3)}$ is the matrix element of the dipole operator between the states $|i\rangle = |1s\rangle$ and $|n\rangle = |2p\rangle$, and F is the amplitude of the electric field strength, Δ_{ni} is the 3-photon detuning and δE_{ni} is the difference of the ac-Stark shift of the 2p and 1s levels. The dependence $w \sim I^2 \sim F^4$ is confirmed by the experimental data for hydrogen atom.

REMPI for alkali atoms was reported by *Mollerec et al.* [70] and they

observed a 4-photon ionization Cs with the condition of a 3-photon resonance between the states $6s$ and $6f$. For noble gas atoms *Landen et al.* [71] observed 4-photon ionization Kr atom by laser field under the condition for a 3-photon resonance.

1.12 Atoms in super intense fields

The usual description of MPI is valid under the condition that the ac-Stark shift of atomic levels is less than other spreading of levels present in the system. In this case we can distinguish the direct multiphoton ionization from resonance multiphoton ionization. In the later case multiphoton resonance occurs with some excited atomic state. Opposite limit of a large ac-Stark shift, results in mixing of resonance and direct multiphoton process. In weak fields we can separate direct and resonance ionization, but in the case of strong field this is impossible.

Numerical simulation of ground state hydrogen atom in a super intense pulse was considered by *Kulander et al.* [72] and it was found that the ionization rate decreases with increase in intensity of the incident radiation (above 10^{16} W/cm²). This decrease is termed the 'stabilization effect'. Atomic stabilization is seemed to occur as long as the pulse is within an intensity window bound by 5×10^{13} W/cm² and 2×10^{14} W/cm². *Volkova and Popov* [73] consider one dimensional square well potential of finite radius and depth carrying a single bound state. It was found that the stabilization effects can be explained by the production of an electronic wave packet which oscillates with a large amplitude and consequently, has a weak coupling with atomic core. *Dorr et al.* [74] has solved the time dependent Schrödinger equation for a hydrogen atom, initially in its ground state, subject to superintense, ultrashot laser pulse of high frequency $\omega = 2$ a.u) the peak field strength $F = 16$ au. The total ionization probability is $W(\infty) \sim 0.6 - 0.7$. The value of $W(\infty) = 1$ is not achieved due to a short

duration of the laser pulse. They compared and interpreted their results in terms of the time independent Floquet eigenvalues. The Floquet approximation is very successful to describe overall features of the time dependant case.

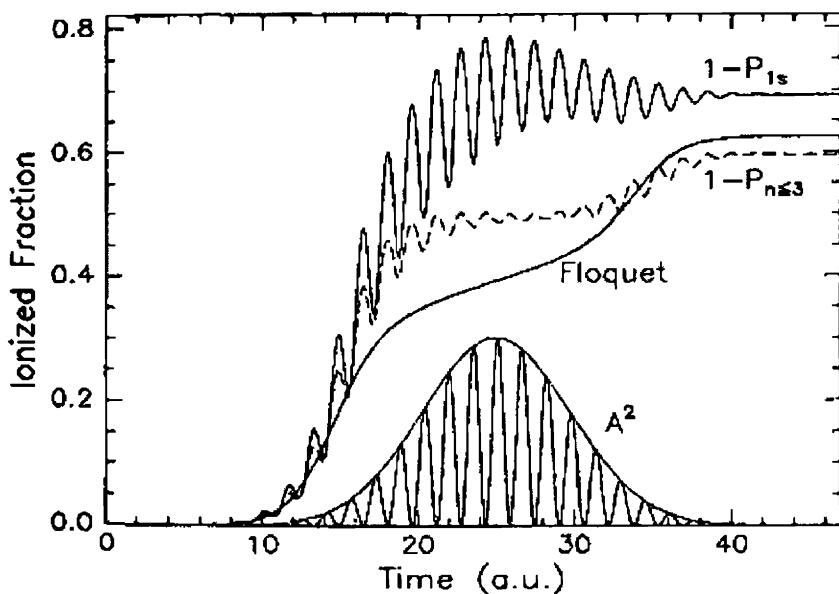


Figure 1.6: Total ionization probability for hydrogen atom, subject to ultrashort laser pulse. Numerical calculation of *Dorr et al.* [74]

The most successful approach for studying quantum systems in super intense field is by Kramers-Henneberger (KH) method. This is done by analysing the problem in a noninertial frame of reference, in which the electron in an electromagnetic wave field is at rest. It implies changing to a so called Kramers frame co-oscillating with electron. The transition to

this system can be achieved by a unitary transformation of the form

$$\Psi_{KH}(\mathbf{r}', t) = \exp \left[i \int_{-\infty}^t V(\mathbf{r}, t') dt' \right] \Psi(\mathbf{r}, t)$$

where the Schrödinger equation satisfied by Ψ is

$$i\hbar \frac{\partial}{\partial t} \Psi = \left[-\frac{1}{2} \nabla^2 + U(\mathbf{r}) + V(\mathbf{r}, t) \right] \Psi$$

and $V(\mathbf{r}) = \mathbf{r} \cdot \mathbf{F} \cos \omega t$ and $U(\mathbf{r})$ is the electron core potential. This can be written as the Schrödinger equation for KH potential as

$$i\hbar \frac{\partial}{\partial t} \Psi_{KH} = \left[-\frac{1}{2} \nabla'^2 + U_0(\mathbf{r}') \right] \Psi_{KH}$$

and the KH potential is given by

$$U_0(\mathbf{r}') = \frac{1}{2\pi} \int_0^{2\pi} U \left(\mathbf{r}' + \frac{\mathbf{F}}{\omega^2} \cos \omega t \right) d(\omega t)$$

Volkova et al. [75] carried out a direct numerical integration of the time dependant SE to investigate the dynamics of a one dimensional quantum system with a short range potential and proved the validity of KH approximation.

Chapter 2

Theoretical analysis of multiphoton ionization

2.1 Interaction of radiation with matter and dipole approximation

In this section, we consider semiclassical treatment of interaction of radiation field with atomic system using perturbation theory. In the presence of electromagnetic field the Hamiltonian of an electron in the atom can be written as

$$H(\mathbf{r}, t) = \frac{1}{2m} (\mathbf{p} + e\mathbf{A}(\mathbf{r}, t))^2 - e\Phi(\mathbf{r}, t) + V(r) \quad (2.1)$$

where \mathbf{p} is the electron momentum, $-e$ is the electronic charge, V is the static electric potential, \mathbf{A} and Φ are the vector and scalar potential for the electromagnetic field respectively.

The time dependant Schrödinger equation satisfied by the electron in

the presence of external field is

$$H(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) \quad (2.2)$$

We have \mathbf{A} and Φ , invariant under the following gauge transformations

$$\begin{aligned} \Phi'(\mathbf{r}, t) &= \Phi(\mathbf{r}, t) - \frac{\partial}{\partial t} \chi(\mathbf{r}, t) \\ \mathbf{A}'(\mathbf{r}, t) &= \mathbf{A}(\mathbf{r}, t) + \nabla \chi(\mathbf{r}, t). \end{aligned}$$

In order to simplify the discussion we introduce a unitary transformation such that $\Psi'(\mathbf{r}, t) = R\Psi(\mathbf{r}, t)$, then we have the Schrödinger equation transformed as

$$H_g \Psi'(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi'(\mathbf{r}, t)$$

where the gauge transformed Hamiltonian H_g is defined as [61]

$$H_g = RHR^\dagger + i\hbar \frac{\partial}{\partial t} RR^\dagger$$

We can choose the operator as $R = \exp[-ie\chi(\mathbf{r}, t)/\hbar]$. Then the gauge transformed Hamiltonian has the form

$$H_g = \frac{1}{2m} [\mathbf{p} + e\mathbf{A} + \nabla\chi]^2 + e\frac{\partial}{\partial t}\chi + V(r). \quad (2.3)$$

Now we choose the Coulomb gauge where $\nabla \cdot \mathbf{A} = 0$ and $\phi = 0$. In this gauge the field is completely described by the vector potential \mathbf{A} and it satisfies the wave equation

$$\nabla^2 \mathbf{A} - \frac{\partial^2}{\partial t^2} \mathbf{A} = 0. \quad (2.4)$$

The solution of the wave equation has the form

$$\mathbf{A} = \mathbf{A}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \mathbf{A}_0^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)},$$

where \mathbf{k} is the wave vector of the field.

If the size of the atomic system is small compared to the wavelength of the radiation field, variation of the field over the extend of the atom can be neglected and we can take $e^{-i\mathbf{k}\cdot\mathbf{r}} \sim 1$. This is called dipole approximation. Now by choosing the gauge function $\chi(r, t) = -\mathbf{A} \cdot \mathbf{r}$ we get

$$\nabla\chi(r, t) = -\mathbf{A}(t) \quad (2.5)$$

$$\frac{\partial}{\partial t}\chi(r, t) = -\mathbf{r} \cdot \frac{\partial}{\partial t}\mathbf{A} = -\mathbf{r} \cdot \mathbf{F} \quad (2.6)$$

where \mathbf{F} is the electric field strength. With these, the transformed Hamiltonian will take the form

$$H_g = \frac{\mathbf{p}^2}{2m} + V(r) + e\mathbf{r} \cdot \mathbf{F} \quad (2.7)$$

From now on we denote the transformed Hamiltonian as H and this form of interaction is in the so called 'length' gauge. The operator $-e\mathbf{r}$ is called dipole operator \mathbf{d} . Further terms in the expansion of $\exp(-i\mathbf{k} \cdot \mathbf{r})$ in powers of $\mathbf{k} \cdot \mathbf{r}$ gives higher order electric and magnetic moments.

Now we discuss the perturbative treatment of multiphoton ionization in the dipole approximation using interaction picture. Expressions for transition amplitude can be obtained by a Dyson expansion of the transition operator. Once the transition amplitude is obtained the rates and cross sections can be obtained by squaring the amplitude and averaging it over a transition cycle. Now consider the total Hamiltonian of the form

$$H = H_0 + H'$$

where H_0 is the unperturbed part and H' is the interaction part of the total Hamiltonian.

The quantum mechanical treatment of this problem is done by expressing the wavefunction in the 'interaction picture' i.e. ,

$$\phi(t) = e^{iH_0 t/\hbar} \Psi(t)$$

where $\Psi(t)$ is the state vector in the Schroedinger picture. Substituting this in the Schrödinger equation, $\phi(t)$ should satisfy

$$i\hbar \frac{\partial}{\partial t} \phi(t) = e^{iH_0 t/\hbar} H' e^{-iH_0 t/\hbar} \phi(t) = H'_I \phi(t). \quad (2.8)$$

where H'_I is the interaction picture representation of H' . The integral solution to Eq. (2.8) can be written as

$$|\phi(t)\rangle = |\phi(t_0)\rangle + \left(-\frac{i}{\hbar}\right) \int_{t_0}^t dt_1 H'_I(t_1) |\phi(t_1)\rangle \quad (2.9)$$

Now we define the unitary operator $T(t, t_1)$, which takes a state from time $t = t_1$ to a state at time t i.e. , $|\phi(t)\rangle = T(t, t_1) |\phi(t_1)\rangle$. From Eq. (2.9)

$$T(t, t_1) = 1 - \frac{i}{\hbar} \int_{t_1}^t dt'_1 H'_I(t'_1) T(t'_1, t_1)$$

This leads to the final Dyson expansion

$$T(t, t_1) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_1}^t dt_1 \int_{t_1}^{t'_1} dt_2 \dots \int_{t_1}^{t'_{n-1}} dt_n H'_I(t'_1) \dots H'_I(t'_n)$$

The n th order term has the form

$$T^{(n)}(t, t_1) = \left(-\frac{i}{\hbar}\right)^n \int_{t_1}^t dt_1 \int_{t_1}^{t'_1} dt_2 \dots \int_{t_1}^{t'_{n-1}} dt_n H'_I(t'_1) \dots H'_I(t'_n) \quad (2.10)$$

Considering the system to be in initial state $|i\rangle$ at time $t = -\infty$. The probability of finding the state in the final state $|f\rangle$ at a time $t = \infty$ can be obtained by

$$\mathcal{T}_{fi}(t, -t) = \langle f | T(t, -t) | i \rangle. \quad (2.11)$$

by taking the limit $t \rightarrow +\infty$. $|i\rangle$ and $|f\rangle$ are the eigenstates of the unperturbed part of the Hamiltonian. We have the interaction Hamiltonian in the length form as

$$H'_I = e^{iH_0 t/\hbar} [\mathbf{d} \cdot \mathbf{F}] e^{-iH_0 t/\hbar}$$

and \mathbf{F} , the electric field strength can be written in the form

$$\mathbf{F} = \frac{1}{2} (\mathbf{F}^* e^{i\omega t} + \mathbf{F} e^{-i\omega t})$$

With this, H'_I will take the new form

$$H'_I = e^{iH_0 t/\hbar} \frac{1}{2} (\mathbf{d} \cdot \mathbf{F}^* e^{i\omega t} + \mathbf{d} \cdot \mathbf{F} e^{-i\omega t}) e^{-iH_0 t/\hbar}$$

Therefore from Eq. (2.10) one-photon transition amplitude is

$$\mathcal{T}_{fi}^{(1)}(t, t_1) = \left(-\frac{i}{\hbar}\right) \int_{t_1}^t dt'_1 \frac{1}{2} \left[e^{i(\omega_0 + \omega)t'_1} (\mathbf{d} \cdot \mathbf{F})_{fi} + e^{i(\omega_0 - \omega)t'_1} (\mathbf{d} \cdot \mathbf{F})_{fi} \right]$$

where $\omega_{fi} = (E_f - E_i)/\hbar$ and $(\mathbf{d} \cdot \mathbf{F})_{fi} = \langle f | \mathbf{d} \cdot \mathbf{F} | i \rangle$.

In order to perform the integration we assume that the interaction will take place only over the length of the pulse, which is in fact longer than the dimension of the atomic system. This will make the integration limits $t_1 \rightarrow -\infty$ and $t \rightarrow \infty$ and finally using the definition of delta function, the

transition amplitude becomes

$$T_{fi}^{(1)}(\infty, -\infty) = -\frac{2\pi i}{\hbar} \left[\frac{(\mathbf{d} \cdot \mathbf{F}^*)_{fi}}{2} \delta(\omega_0 + \omega) + \frac{(\mathbf{d} \cdot \mathbf{F})_{fi}}{2} \delta(\omega_0 - \omega) \right]. \quad (2.12)$$

Transition rate is thus proportional to modulus square of transition amplitude. Here the first term corresponds to emission and second corresponds to absorption.

For a two-photon (second order) process $T_{fi}^{(2)}$ have the form

$$\begin{aligned} T_{fi}^{(2)}(t, t_1) &= \left(-\frac{i}{\hbar}\right)^2 \sum_j \int_{t_1}^t dt'_1 e^{i(\omega_{fj}-\omega)t'_1} \left(\frac{(\mathbf{d} \cdot \mathbf{F}^*)_{fj}}{2} + \frac{(\mathbf{d} \cdot \mathbf{F})_{fj}}{2} \right) \\ &\times \int_{t_1}^{t'_1} dt'_2 e^{i(\omega_{ji}-\omega)t'_2} \left(\frac{(\mathbf{d} \cdot \mathbf{F}^*)_{ji}}{2} + \frac{(\mathbf{d} \cdot \mathbf{F})_{ji}}{2} \right) \end{aligned} \quad (2.13)$$

where $\omega_{ji} = \omega_j - \omega_i$ and $\omega_{fj} = \omega_f - \omega_j$. After the integrals are done, the second order transition amplitude becomes

$$\begin{aligned} T_{fi}^{(2)}(-\infty, \infty) &= -\frac{\pi i}{2\hbar^2} \sum_j \left[\delta(\omega_0 + 2\omega) \frac{(\mathbf{d} \cdot \mathbf{F})_{fj}(\mathbf{d} \cdot \mathbf{F})_{ji}}{\omega_{ji} + \omega} \right. \\ &+ \delta(\omega_0 - 2\omega) \frac{(\mathbf{d} \cdot \mathbf{F})_{fj}(\mathbf{d} \cdot \mathbf{F})_{ji}}{\omega_{ji} - \omega} \\ &\left. + \delta(\omega_0) |F^2| \left(\frac{(\mathbf{d} \cdot \mathbf{F})_{fj}(\mathbf{d} \cdot \mathbf{F})_{ji}}{\omega_{ji} + \omega} + \frac{(\mathbf{d} \cdot \mathbf{F})_{fj}(\mathbf{d} \cdot \mathbf{F})_{ji}}{\omega_{ji} - \omega} \right) \right] \end{aligned} \quad (2.14)$$

The first two terms corresponds to two-photon absorption and emission respectively and the last term corresponds to ac-Stark shifts.

Thus, in order to find the second order transition amplitude we have to evaluate the expression inside the bracket of the Eq. (2.14) which is in general difficult. The main problems arises due to the infinite summation coming in the expression and also due to the resonance cases where the denominator become zero. In the coming sections, we discuss various

methods for the evaluation of these kind of matrix elements. From Eq. 2.13 it is clear that the matrix element corresponding to two-photon absorption can be expressed in atomic unit (Appendix A) by

$$\mathcal{M}_{fi}^{(2)} = \sum_n \frac{\langle f | \epsilon \cdot \mathbf{r} | n \rangle \langle n | \epsilon \cdot \mathbf{r} | i \rangle}{E_n - E_i - \omega} \quad (2.15)$$

where ϵ is the unit polarization vector. Here the interaction is considered in the dipole approximation, and the infinite summation \sum_n runs over the complete set of states. Under the framework of perturbation theory, evaluation of n -photon transition requires the evaluation of n th order transition matrix element of the form of Eq.2.15.

It should be kept in mind that the probability for emission of two photons with frequency ω , is very small as compared to the probability of emission of a single-photon with the frequency $\omega + \omega$. However, if the selection rules prohibit the single-photon transition, then only the two-photon processes are allowed.

2.2 Theory of multiphoton ionization

In the following sections, we summarize few of the available and widely used methods for analyzing various multiphoton processes. This includes both perturbative as well as nonperturbative treatments. Non-perturbative methods includes WKB and R-Matrix Floquet methods. In the perturbative treatments the transition amplitude can be evaluated in various order of perturbation. From now onwards we use the atomic unit (Appendix A) for the discussion unless otherwise specified.

Proceeding in the similar manner as in the previous section in the dipole approximation a general N th order matrix element which corresponds to

N -photon process has the form

$$\mathcal{M}_{fi}^{(N)} = \sum_{i_{N-1} \cdots i_1} \frac{\langle f | \epsilon \cdot \mathbf{r} | i_{N-1} \rangle \cdots \langle i_2 | \epsilon \cdot \mathbf{r} | i_1 \rangle \langle i_1 | \epsilon \cdot \mathbf{r} | i \rangle}{(E_{i_{N-1}} - E_i - (N-1)\omega) \cdots (E_{i_1} - E_i - \omega)} \quad (2.16)$$

Various standard procedures are there to evaluate this matrix element, which includes explicit summation technique as well as indirect methods for summation and variational methods.

2.2.1 Method of *Bebb* and *Gold*

This is one of the simplest method for the evaluation of higher order matrix element as given in Eq. (2.16). The evaluation of the matrix element of N -photon transition matrix involves $N - 1$ infinite summation over the intermediate states. Since the presence of the energy dependent term in the denominator is the main reason for the difficulty in performing this sum, *Bebb* and *Gold* [7] suggested to replace the varying frequency with an average constant frequency so that the sum can be performed with a simple procedure and the matrix elements can be evaluated very easily.

Among the $N - 1$ intermediate summations, let us take the n th term ($|i_n\rangle\langle i_n| / (\omega_{i_n} - \omega_i - n\omega)$) which involves the summation over the index i_n . If we replace the atomic frequency difference $\omega_{i_n} - \omega_i$ by a constant average $\bar{\omega}(n)$, the energy dependence in the denominator corresponding to the state $|i_n\rangle$ will be removed. Now we can use closure relation $|i_n\rangle\langle i_n| = I$ and the complex N th order matrix element takes the simple form

$$M_{fi}^N = \frac{\langle f | (\epsilon \cdot \mathbf{r})^N | i \rangle}{\prod_{n=1}^{N-1} (\bar{\omega}(n) - n\omega)}$$

Further simplification can be done by replacing all the $\bar{\omega}(n)$ with an average frequency $\bar{\omega}$ independent of n . This average frequencies can be found by 'trial and error method'. *Bebb* and *Gold* applied this method for the case

of hydrogen and rare gas atoms. An alternate method by replacing the numerator with an average matrix element is proposed by *Morton* [8].

2.2.2 Method of truncated summation

In this method, instead of considering the complete set of states a limited number of intermediate states are included in the summation. From the infinite summation, the expansion is truncated and explicit summation is performed to get the transition matrix element. The virtue of this method is its generality. By doing so the error accumulated due to the truncation can also be calculated. However, the convergence of the method often depends sensitively on the representation chosen as well as on the size of the truncated basis. Many authors have used this method [77, 78, 79]

2.2.3 Green's function method

Green's function method is one of the widely used method where the explicit summation of the intermediate contribution is not done. For the illustration of this method, let us consider two-photon ionization of atomic hydrogen. The associated transition matrix element is given by

$$\mathcal{M}^{(2)} = \sum_n \frac{\langle f | \epsilon \cdot \mathbf{r} | n \rangle \langle n | \epsilon \cdot \mathbf{r} | i \rangle}{E_n - E_i - \omega}$$

Here E_i and E_n are the unperturbed energies of the initial and intermediate states respectively and ω is the frequency of the external electromagnetic field. Since it is an ionization process the final state $|f\rangle$ is a continuum state. It is very important to note that in the above equation the summation is over the discrete states as well as integration over the continuum

states. Since the Green's function is defined as

$$G(\mathbf{r}, \mathbf{r}', \Omega) = \sum_n \frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{E_n - \Omega}.$$

we can rewrite the matrix element as follows

$$\mathcal{M}^{(2)} = \int \psi_f^*(\mathbf{r})\epsilon \cdot \mathbf{r}G(\mathbf{r}, \mathbf{r}', E_i + \omega)\epsilon \cdot \mathbf{r}'\psi_i(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

It is useful to have the radial Green's function $G_l(r, r', \Omega)$ related to the full Green's function as

$$G(\mathbf{r}, \mathbf{r}', \Omega) = \sum_n G_l(r, r', \Omega)Y_{lm}^*(\mathbf{r}/r)Y_{lm}(\mathbf{r}'/r').$$

The radial Green's function can be expanded in a series of complete basis of radial atomic wave functions and we have

$$G_l(\mathbf{r}, \mathbf{r}', \Omega) = \sum_{n=l+1}^{\infty} R_{nl}(r)R_{nl}(r')(E_n - \Omega)^{-1} + \int_0^{\infty} R_{El}(r)R_{El}(r')(E - \Omega)^{-1}dE$$

where $R_{nl}(r)$ and $R_{El}(r)$ corresponds to bound and continuum spectrum respectively of hydrogen atom. The integral representation of these Green's function was first developed by *Hostler* and *Prat* [82]. Later *Hostler* [81] obtained a closed expression for Green's function of hydrogen atom in terms of regular and irregular Whittaker functions. *Mizuno* also obtained a series expansion of these Green's function for hydrogen atom in terms of Sturmian functions which is of the form [83]

$$S_{nl}(r) = 2[p(2l+1)!]^{-1}[(n+1)!]^{1/2}[(n-l-1)!]^{-1/2} \times (2r/p)^l \exp(-r/p)F(-n+l+1, 2l+2; 2r/p)$$

where $p = (-2\Omega)^{-1/2}$. Apart from the scaling factors in the argument these functions coincide with the radial wavefunction of hydrogen atom within a constant multiplication factor. And the representation of Green's function in terms of Sturmian functions are most suitable for the evaluation of various matrix elements involving multiphoton processes. All the multiple integrals can be finally reduced to a one dimensional integral. The disadvantage of this method is that for above threshold calculations (i.e., when $\Omega > 0$) this series diverges. For two-photon processes from the ground state of hydrogen atom the results can be easily obtained as by *Karule* [3]. Similarly we can extend the method to processes involving higher number of photons. *Karule* has extensively used this method in many places [3]. A detailed discussion can be found in the extensive review by *Maquet* [15] where different representation of Coloumb Green's function are used for various multiphoton process.

2.2.4 Variational method

In 1988, *Gao* and *Starace* presented a variational procedure for calculating the N th-order perturbative matrix elements and have applied it for the calculation of high-order multiphoton processes in atomic hydrogen [9]. Variational method consists of defining two unknown functions such that

$$|\psi\rangle = \frac{H'}{E_{N-1} - H} \frac{H'}{E_{N-2} - H} \frac{H'}{E_2 - H} \frac{H'}{E_1 - H} |i\rangle \quad (2.17)$$

$$\langle\psi'| = \frac{H'}{E_{N-1} - H} \frac{H'}{E_{N-2} - H} \frac{H'}{E_2 - H} \frac{H'}{E_1 - H}. \quad (2.18)$$

the functional $M_{fi}^N(\psi, \psi')$ given below

$$M_{fi}^N(\psi, \psi') = \langle f | H' | \psi \rangle + \langle \psi' | H' | i \rangle - \langle \psi' | (E_1 - H) \frac{E_2 - H}{H'} \dots \frac{E_{N-1} - H}{H'} | \psi \rangle \quad (2.19)$$

is stationary with respect to the variation of ψ and ψ' . Here the completeness of the $(N - 2)$ -fold summation is automatically guaranteed. As a result, a smaller basis set can be used. For a second order process the above equation will take the form

$$M_{fi}^N(\psi, \psi') = \langle f | H' | \psi \rangle + \langle \psi' | H' | i \rangle + \langle \psi' | (E_1 - H) | \psi \rangle$$

They claimed that the the results are variationally stable with respect to any errors in the determination of two unknown functions $|\psi\rangle$ and $\langle\psi'|$.

2.2.5 WKB approximation

Apart from the usual perturbation methods, it is also possible to apply semiclassical treatment like WKB methods to deal with the multiphoton processes. This method was developed for hydrogen atom by Berson [38]. WKB treatment for MPI is valid only for highly excited states of atomic electrons. A summary of the formulation of WKB approximation for MPI is described in the Ref. [45]. When $l \sim n$, the electron moves on a circular trajectory and in this case the ionization probability is quasiclassically small. For states with small orbital momentum $l \ll n$ the electron moves on an elliptic curve with a large eccentricity, so that the ionization take place only near the perihelion when the electron is inside the atomic core. At other points of space the electron is nearly free, hence the ionization probability is negligible due to the absence of the third body. If we consider the energy of the highly excited states as very small, we can take the elliptic orbit as parabolic. In this case we assume the situation be of *bremstrahlung* kind, where the absorption or emission of photons by a low energy electron scattered by a coulomb field. Thus the probability of absorbing N -photons can be calculated by semiclassical treatment. Let $a(t)$ be the amplitude of the electron being near perihelion, then the Schrödinger equation for $a(t)$

is of the form

$$i \frac{d}{dt} a(t) = r_{if} F a(t) \cos \omega t.$$

Here F is the field strength amplitude and ω is the field frequency, r_{if} is the dipole matrix element between the states i and f , and $\omega_{if} = \omega$ is the transition energy.

These matrix elements are the Fourier components r_ω of the classical coordinate $r(t)$ as the function of time t on the frequency ω . The above Schrödinger equation has a simple solution

$$a(t) = \exp[(-ir_\omega)(F/\omega) \sin \omega t]$$

If we expand in fourier series of monochromatic states, we obtain

$$a(t) = \sum_N J_N(r_\omega F/\omega) \exp[iN\omega t]$$

Thus the probability for N -photon processes is equal to the square of the modulus of the above equation, i. e. ,

$$W^{(N)} = | J_N(r_\omega F/\omega) |^2$$

This is the probability for a N -photon process during one orbit and if we divide it by the period $2\pi n^3$ of this orbit we obtain the rate of n -photon ionization [38]

$$w^{(N)} = (2\pi n^3)^{-1} | J_N(r_\omega F/\omega) |^2$$

For weak electromagnetic field we can expand the Bessel function in a series of weak electromagnetic field we can obtain the rate of N -photon ionization in perturbation theory as

$$w^{(N)} = (r_\omega F/2\omega)^{2N} / (2\pi n^3 N!^2)$$

The N -photon cross section can be obtained by averaging the above expression over all angles and then dividing by photon flux $cF^2/8\pi\omega$.

Two-photon cross section of the ground state of hydrogen atom is calculated using the above expression in Ref. [38].

2.2.6 R-Matrix Floquet theory

R-Matrix Floquet (RMF) method was introduced by *Burke et al.* [76] for the analysis of interaction of laser field with atoms or ions with the applications to multiple ionization, laser- assisted electron-atom scattering etc. A detailed review on the topic is available in Ref. [31]. In RMF theory, the laser field is treated classically and the interacting radiation is assumed to be monochromatic, monomode and spatially homogeneous. In applications of RMF theory considered so far, the laser field is also assumed to be linearly polarized. The fundamental idea is from R-Matrix method where we divide our configuration space into two or more regions where the process in each of these regions has distinctly different physical properties. Fig. 2.1 schematically represent the partitioning of the configuration space in R-Matrix theory. In each regions, we use the most appropriate form of the laser-atom interaction. Different representation of the wave function and Hamiltonian describing the process is adopted in the respective region. Then finally, these wave functions are connected through R-matrix defined on their common boundaries.

We describe the method by considering multiphoton ionization of atom. Neglecting relativistic effects, the atom which has $(K + 1)$ electrons is described by the time-dependent Schrödinger equation given by

$$\left(H_{K+1} + \mathbf{A}(t) \cdot \mathbf{p}_{K+1} + \frac{K+1}{2} \mathbf{A}^2 \right) \Psi(X_{K+1}, t) = i \frac{\partial}{\partial t} \Psi(X_{K+1}, t) \quad (2.20)$$

where $\mathbf{p}_{K+1} = \sum_1^{K+1} p_i$ is the total electron momentum operator and \mathbf{A}

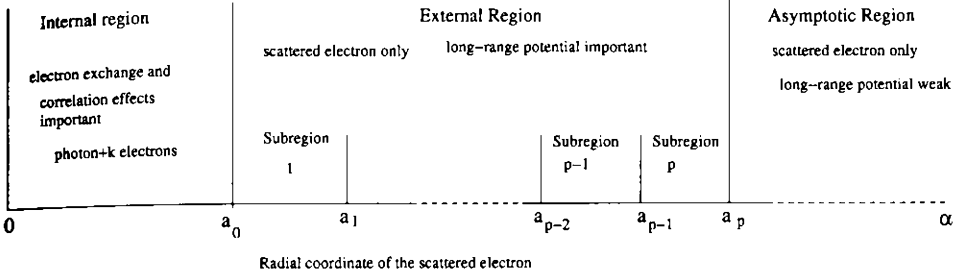


Figure 2.1: Schematic diagram for the partitioning of the configuration space in R-Matrix theory [31]

is the vector potential describing the laser field. We have \mathbf{A} is defined by $\mathbf{A} = \epsilon A_0 \sin \omega t$, here ϵ is a unit vector along the laser polarization direction and ω is the angular frequency. We separate the configuration space into three regions as illustrated in the Fig. 2.1. A Floquet-Fourier expansion is done for the wavefunction in these regions by writing

$$\Psi(X_{K+1}, t) = e^{-iEt} \sum_{n=-\infty}^{\infty} e^{-in\omega t} \psi_n(X_{K+1}) \quad (2.21)$$

Substituting this in Eq. (2.20) we obtain a set of coupled time independent equations for the functions ψ_n .

In the internal region we transform the wave function to the length gauge as

$$\Psi(X_{K+1}, t) = \exp(-i\mathbf{A} \cdot \mathbf{R}_{K+1}) \Psi_L(X_{K+1}, t)$$

where $\mathbf{R}_{K+1} = \sum_{i=1}^{K+1} \mathbf{r}_i$. Substituting this in Eq. (2.20) we get infinite set of coupled time-independent equations of the form

$$(H_{K+1} - E - n\omega) \psi_n^L + D_{K+1} (\psi_{n-1}^L \psi_{n+1}^L) = 0$$

where $D_{K+1} = \frac{1}{2} \mathbf{F}_0 \hat{\mathbf{e}} \cdot \mathbf{R}_{K+1}$. Then truncate the ψ_n^L to a finite number and expand them in configuration interaction basis, followed by determination of the R-matrix in the length gauge.

In the external region the transformation is of mixed kind, where the ejected electron is in velocity gauge and the remaining K electrons are considered in length gauge. The transformation is given by

$$\Psi(X_{K+1}, t) = \exp \left(-i \mathbf{A} \cdot \mathbf{R}_K - \int^t \mathbf{A}^2(t') dt' \right) \Psi_V(X_{K+1}, t)$$

where

$$r_i \leq a_0, i = 1, \dots, K \quad \text{and} \quad r_{K+1} \geq a_0$$

Substituting this in Eq. (2.20) we get infinite set of coupled time-independent equations of the form

$$(H_{K+1} - E_V - n\omega) \psi_n^V + D_{K+1} (\psi_{n-1}^V \psi_{n+1}^V) + P_{K+1} (\psi_{n-1}^V \psi_{n+1}^V) = 0$$

where $P_{K+1} = A_0 \hat{\mathbf{e}} \cdot \mathbf{p}_{K+1}/2$. Again truncate the series and expand the floquet components in terms of the channel functions and substituting it in the above equation we get a set of coupled second-order differential equations satisfied by the corresponding reduced radial wave functions. The solution in the internal region yields the R-matrix which is then used to match the internal and external region wavefunctions.

The R-matrix obtained from the internal region is transformed to velocity gauge and propagate through the p subregions(as shown in Fig. 2.1) outward and then it is fitted to an asymptotic expansion. In the case of multiphoton ionization the radial functions are fitted to outgoing boundary conditions defined by

$$F_i(r) = K_i \exp(ik_i r)$$

where k_i are complex wave numbers of the ejected electron in the i th

channel and K_i are the normalization factors. Finally, a quasi-energy, $E = E_R - i\Gamma/2$ is obtained where E_R is the energy and Γ is the multiphoton ionization rate.

2.2.7 Dalgarno-Lewis method

Dalgarno-Lewis method was originally introduced for the evaluation of long range forces between atoms [10] and later on it was modified by Schwartz for various simple higher order processes [60]. A clear demonstration of the method is available in Ref. [91], where it is used to calculate second order Stark effect in hydrogen atom. The analytical expressions are derived without explicitly summing over the intermediate states and the final dipolar polarizability is presented. Here, in this section we will outline the method using the N th order transition matrix element given in Eq. (2.16)

A detailed discussion on the subject is given in Section 3.2. The idea is to include the contributions from the infinite summation over the intermediate state coming in the higher order perturbation matrix elements given in Eq. (2.16) exactly. This can be done by defining a set of $N - 1$ operators M_n with $n = 1, 2, \dots, N - 1$ such that

$$\epsilon \cdot \mathbf{r} M_{n-1} |g\rangle = (M_n H_0 - H_0 M_n + n\omega M_n) |g\rangle \quad (2.22)$$

where H_0 is the unperturbed Hamiltonian for the system under consideration. Using Eq. (2.22) and the closure relation $\sum_i |i\rangle\langle i| = I$ the transition matrix element in Eq.(2.16) is reduced to

$$\mathcal{M}_{fg}^{(N)} = \langle f | \epsilon \cdot \mathbf{r} M_{N-1} | g \rangle \quad (2.23)$$

It is also clear from the Eq. (2.22) that the appearance of $(N - 1)$ -th order transition amplitude as inhomogeneous term for the determination of the N th order transition amplitude is a general feature of this method. Thus

instead of finding the contribution from summing over all the intermediate states it is enough to find an analytical expression for M_n . In the coming chapters we describe this method to find a closed form expression for the operator M_{fg}^N up to third order in different physical situations by taking hydrogen atom as the model system.

2.3 Conclusion

In the present chapter, we followed the perturbation theory to obtain expressions corresponding to higher order matrix element. A general text book description is presented for the derivation of second order transition amplitude. We described the general problems associated with the theoretical formulation for multiphoton process and briefly reviewed a few available methods used for the treatment of multiphoton ionization. This includes both perturbative and nonperturbative methods. In the coming chapters we consider two- and three-photon processes in atomic hydrogen, where we have used a variation of Dalgarno-Lewis method and obtained the closed form expression for second and third order matrix element.

Chapter 3

Two-photon processes

3.1 Introduction

We devote our attention to the details of some of the processes which involve interaction of radiation with atomic system. This includes transitions of atomic electrons between available states, shift in the energy levels due to this interaction and cross section for scattering of the electromagnetic field from the atom. We treat the interaction due to radiation as a perturbation to the atomic system and used perturbation theory for the formulation of the problem. As the intensity of the radiation field increases, the transition which are forbidden by single photon transitions can occur through multiphoton transitions. In this chapter we investigated various two-photon processes like two-photon absorption, elastic scattering of photon and ac-Stark shift, which are second order processes in the perturbative analysis of the problem.

3.2 Dalgarno-Lewis method

In the present section we discuss the implementation of Dalgarno-Lewis method for a second order process. Consider an atomic system interacting with a monomode radiation field of frequency ω and assume that the atom makes a transition from the initial state $|i\rangle$ to a final state $|f\rangle$ by absorbing two photons. As we have seen in the Section 2.1 this two-photon processes can be studied using the results of second order perturbation theory. The corresponding second order transition amplitude in the non relativistic case is given by

$$\mathcal{M}_{fi}^{(2)} = \sum_n \frac{\langle f | \epsilon^* \cdot \mathbf{r} | n \rangle \langle n | \epsilon \cdot \mathbf{r} | i \rangle}{(E_i - E_n + \omega)} \quad (3.1)$$

where $\epsilon \cdot \mathbf{r}$ is the interaction part of the Hamiltonian in the dipole approximation.

The main difficulty in evaluating the above matrix element is the presence of infinite sum over the complete set of states which includes both discrete as well as continuum states. This infinite summation over the complete set of states can be done by Dalgarno Lewis method [10], which is a very simple and elegant procedure. We can also see from Eq. (3.1) that the matrix element is not defined when $\omega = E_n - E_i$, i.e. when the incident photon energy correspond to an excitation of the atomic state allowed by one photon transitions. We call these situation as intermediate resonances. The results of the standard perturbation theory is not valid for these particular values of photon energy.

For a bound to bound transitions with frequencies of the two photons being the same, it is a most unlikely chance that there is an intermediate resonance. But it is possible to have resonance enhanced two-photon ionization in these cases. One has to rely on modification of perturbative methods to deal with these kind of resonance enhanced multiphoton processes.

For the case of second order matrix element like the one given Eq. (3.1) the method of Dalgarno-Lewis can be implemented by defining one auxiliary dimensionless operator D_1 such as

$$\epsilon \cdot \mathbf{r} |i\rangle = (D_1 H_0 - H_0 D_1 + \omega D_1) |i\rangle \quad (3.2)$$

where H_0 is the unperturbed part of the Hamiltonian for the system under consideration. The eigenstates of the unperturbed system satisfy the time independent Schrödinger equation

$$H_0 |j\rangle = E_j |j\rangle$$

where E_j is the energy eigenvalue corresponding to the stationary state $|j\rangle$.

After taking the scalar product of the Eq. (3.2) with $|n\rangle$ we get

$$\begin{aligned} \langle n | \epsilon \cdot \mathbf{r} |i\rangle &= \langle n | D_1 H_0 - H_0 D_1 + \omega D_1 |i\rangle \\ &= (E_n - E_i + \omega) \langle n | D_1 |i\rangle \end{aligned} \quad (3.3)$$

using Eq. (3.3) in Eq. (3.1) and after canceling the denominator the Eq. (3.1) becomes

$$\mathcal{M}_{fi}^{(2)} = \sum_n \langle f | \epsilon \cdot \mathbf{r} |n\rangle \langle n | D_1 |i\rangle,$$

now using the closure relation $\sum_n |n\rangle \langle n| = I$ the Eq. (3.1) will reduce to

$$\mathcal{M}_{fi}^{(2)} = \langle f | \epsilon \cdot \mathbf{r} D_1 |i\rangle. \quad (3.4)$$

Now the difficulties associated with the infinite summation is reduced to the problem of finding an appropriate expression for the operator D_1 . Since $\mathcal{M}_{fi}^{(2)}$ is a function of ω , we have to keep in our mind the important

fact that any analytical expression for the unknown operator D_1 should display all the analytical properties present in the definition of the second order matrix element given in Eq. (3.1).

In order to find the analytical form of D_1 we have to start from its defining equation (3.2). Also from Eq. (3.2) it is clear that the form of D_1 depends on the initial state $|i\rangle$. Since we are considering transitions from the ground state of atomic hydrogen we have $|i\rangle = e^{-r}/\sqrt{\pi}$. For simplicity we consider radiation to be linearly polarized along the z -axis. With these assumptions the defining equation (3.2) for D_1 becomes

$$z|i\rangle = (D_1 H_0 - H_0 D_1 + \omega D_1)|i\rangle$$

where

$$H_0 = -\frac{\nabla^2}{2} - \frac{1}{r}.$$

By taking $\varphi = e^{-r}/\sqrt{\pi}$ we have

$$\begin{aligned} (D_1 H_0 - H_0 D_1 + 2\omega D_1)\varphi = & \left[D_1 \left(-\frac{\nabla^2}{2} - \frac{1}{r} \right) \right. \\ & \left. - \left(-\frac{\nabla^2}{2} - \frac{1}{r} D_1 \right) + \omega D_1 \right] \varphi \end{aligned}$$

Using this and after some rearrangement Eq. (3.2) becomes

$$z\varphi = \frac{\nabla^2 D_1}{2}\varphi + \nabla D_1 \cdot \nabla \varphi + \omega D_1 \varphi \quad (3.5)$$

By inspection we can see that the operator D_1 have an angular dependence given by $P_l(\cos\theta)$, where $P_l(\cos\theta)$ is Legendre polynomials of order l and we can assume

$$D_1 = f_1(r)P_l(\cos\theta)$$

The relations given below are useful for further algebra

$$\nabla^2 P_l = -\frac{l(l+1)}{r^2} P_l \quad (3.6)$$

$$\begin{aligned} \nabla(f_1(r)P_1) &= \hat{r}f_1'P_1 + \frac{\hat{\theta}}{r}f_1\frac{d}{d\theta}P_1 \\ \nabla^2 D_1(\mathbf{r}) &= \left[\nabla^2 f_1 - \frac{2}{r^2}f_1 \right] P_1 \end{aligned} \quad (3.7)$$

Writing $z = r \cos \theta$, from Eq. (3.5) we get

$$rP_1 = \frac{1}{2} \left[\nabla^2 f_1 - \frac{2}{r^2}f_1 \right] P_1 - \left[\hat{r} \cdot (\hat{r}f_1'P_1 - \frac{\hat{\theta}}{r} \sin \theta P_1) \right] + \omega f_1 P_1 \quad (3.8)$$

After simplification we will get the differential equation satisfied by $f_1(r)$ as

$$\frac{\nabla^2}{2} f_1 - f_1 + \left(\omega - \frac{1}{r^2} \right) f_1 = r$$

Now it is convenient to take $f_1(r) = r\psi(r)$ and rewrite operator D_1 as

$$D_1(\mathbf{r}) = r\psi_1(r)P_1(\cos \theta), \quad (3.9)$$

and we can obtain the following differential equation for the unknown radial function $\psi_1(r)$

$$r \frac{d^2}{dr^2} \psi_1(r) + (4 - 2r) \frac{d}{dr} \psi_1(r) + (2\omega r - 2) \psi_1(r) = 2r, \quad (3.10)$$

If we define the following differential operator

$$\mathcal{D}_{1\lambda_1} = r \frac{d^2}{dr^2} + (4 - 2r) \frac{d}{dr} + 2\omega r - 2.$$

where $\lambda_1 = \sqrt{1 - 2\omega}$, then we can write Eq. (3.10) as

$$\mathcal{D}_{1\lambda_1} \psi_1 = 2r$$

This short notation is very useful for further discussions on the differential equation and for the determination of the solution.

Here we have used the method of Laplace transform [16] for the solution of the differential equation. For this we try a solution of the form

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)} K(p, q, \lambda, s) \quad (3.11)$$

where

$$K(p, q, \lambda, s) = \left(\frac{1 - \lambda}{1 + \lambda} \right)^{\frac{1}{\lambda}} (s + \lambda)^{p + \frac{1}{\lambda}} (s - \lambda)^{q - \frac{1}{\lambda}} \quad (3.12)$$

It is very important to note that the integrals in Eq. (3.11) is defined only if the real part of $(q - 1/\lambda + 1)$ is greater than zero. A detailed discussion of the analytic continuation of this function when this condition is not satisfied is given in Section 4.5.

Now we have the following relations satisfied by the differential operator $\mathcal{D}_{1\lambda_1}$

$$\mathcal{D}_{1\lambda_1}(1) = 2\omega r - 2. \quad (3.13)$$

We also have the following relations satisfied by $K(\cdot)$ and $\Phi(\cdot)$

$$\frac{\partial}{\partial s} K(p, q, \lambda, s) = K \left[\frac{\left(p + \frac{1}{\lambda}\right)}{(s + \lambda)} + \frac{\left(q - \frac{1}{\lambda}\right)}{(s - \lambda)} \right] \quad (3.14)$$

$$\frac{d}{dr}\Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)} K(p, q, \lambda, s)(1-s) \quad (3.15)$$

$$r\Phi(p, q, \lambda, t, r) = -\int_{\lambda}^t ds \frac{\partial}{\partial s} \{e^{-r(s-1)}\} K(p, q, \lambda, s) \quad (3.16)$$

Operating $\mathcal{D}_{1\lambda_1}$ on Eq. (3.11) and perform a partial integration and use the properties given in Eqs. (3.14)-(3.15) rearranging the expressions we get

$$\begin{aligned} \mathcal{D}_{1\lambda_1}\Phi(p, q, \lambda, t, r) &= -(1-\lambda^2) \quad (3.17) \\ &+ \int_{\lambda}^1 e^{-r(s-1)} K(p, q, \lambda, s) \{s(p+q-2l) + \lambda(q-p)\} \end{aligned}$$

Now with appropriate values of the p , q and λ we can find the solution. When $p = q = l$ we have

$$\mathcal{D}_{l\lambda_1}\Phi(l, l, \lambda_1, t, r) = -e^{-r(t-1)} K(l+1, l+1, \lambda_1, t). \quad (3.18)$$

we also have

$$K(l, l, \lambda, 1) = (1-\lambda^2)^l$$

and

$$\mathcal{D}_1\Phi(1, 1, \lambda, 1, r) = -K(2, 2, \lambda, 1)$$

With the relation given in Eq. (3.18) and using the above equation we can obtain the solutions to the differential equation Eq. (3.10) as

$$\psi_1(r) = \frac{1}{\omega} - \frac{1}{2\omega^3}\Phi(1, 1, \lambda_1, 1, r) \quad (3.19)$$

and $\lambda_1 = \sqrt{1-2\omega}$.

Hence for a second order matrix element with ground state of hydrogen

atom as the initial state, the final form of $D_1(r)$ is

$$D_1(\mathbf{r}) = r \left(\frac{1}{\omega} - \frac{1}{2\omega^3} \Phi(1, 1, \lambda_1, 1, r) \right) P_1(\cos \theta) \quad (3.20)$$

Once D_1 is known, using Eq. (3.4) we can determine the transition matrix element corresponding to various second order processes.

Two-photon selection rule

Selection rules for a two-photon processes can be seen directly from the expression for the second order matrix element given in Eq. (3.1). Since

$$|f\rangle = R_{nl}(\mathbf{r}) Y_{l0}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} R_{nl}(r) P_l(\cos \theta)$$

$$|g\rangle = e^{-r/\sqrt{\pi}}$$

$$z = r P_1(\cos \theta)$$

the Eq. (3.1) become

$$\begin{aligned} \mathcal{M}_{fi}^{(2)} &= \frac{\sqrt{2l+1}}{2\pi} \int_0^\infty e^{-r} r^4 R_{nl}(r) \left(\frac{1}{\omega} - \frac{1}{2\omega^3} \Phi(1, 1, \lambda_1, 1, r) \right) dr \\ &\times \int_0^\pi P_l(\cos \theta) P_1^2(\cos \theta) \sin(\theta) d\theta \int_0^{2\pi} d\phi \end{aligned} \quad (3.21)$$

Now the angular part of the integration in Eq. (3.21) can be done exactly using the orthogonality property of the Legendre polynomials and the recursion relation below

$$x P_l(x) = \frac{l+1}{2l+1} P_{l+1}(x) + \frac{l}{2l+1} P_{l-1}(x) \quad (3.22)$$

and integrals in Eq. (3.21) will be nonzero only for $l = 0$ and $l = 2$. Thus the only final states accessible by two-photon transitions from an initial s state are s and d states, which are the well known selection rules for two photon transitions.

3.3 Two-photon bound - bound transition

Here we consider transitions from ground state $|1s\rangle$ to an excited state $|nl\rangle$ of hydrogen atom, due to the absorption of two photons. We have the expression for the energy in atomic unit for ground state and excited state with principal quantum number n as

$$E_g = -\frac{1}{2} \quad \text{and} \quad E_n = -\frac{1}{2n^2}$$

Since it is a two-photon process the radiation frequency required for the transition is

$$2\omega = (1 - 1/n^2) / 2.$$

For a specific value of principal quantum number n , transitions are possible only to the states with particular angular momentum, which are allowed by the selection rules. For example, when principal quantum number $n = 2$, transition is possible to $2s$ state only, which is a forbidden transition with single photon absorption.

For simplicity first we consider linearly polarized light along the z -axis so that $\epsilon \cdot \mathbf{r} = z$. Since two-photons are absorbed from the same beam of laser, there will not be any intermediate resonant transitions in two-photon bound-bound transitions of hydrogen atom. In general if the two beams have different frequencies, intermediate resonant transitions are possible. In the later sections we will see that, in case of two-photon as well as the multiphoton ionization cases, intermediate resonances can occur.

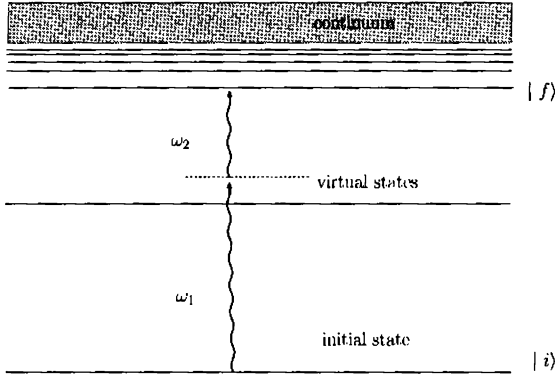


Figure 3.1: Schematic diagram for two-photon bound to bound transitions: the transition is from an initial state $|i\rangle$ to a final state $|f\rangle$ through virtual states

We have schematically depicted the two-photon bound to bound transitions in the Fig. (3.1), here two-photons with different energies are simultaneously absorbed and the system is excited to a final state. From the discussions of the previous section we have all the relevant expressions needed for evaluating the two-photon transition rate. With D_1 known, we can calculate various transition amplitudes from ground state. We take the final state wavefunctions of the hydrogen atom to be[19]

$$|f\rangle = \sqrt{\frac{2l+1}{4\pi}} R_{nl}(r) P_l(\cos\theta) \quad (3.23)$$

where

$$R_{nl} = \frac{2}{n^{l+2}(2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}} (2r)^l \exp\left(-\frac{r}{n}\right) F\left(l+1-n, 2l+2, \frac{2r}{n}\right)$$

and $F(\cdot)$ is the confluent hypergeometric function.

In order to perform the numerical analysis it is useful to define the following quantities

$$I_{nl}(s, k) = \int_0^{\infty} dr R_{nl}(r) e^{-rs} r^k \quad (3.24)$$

$$\mathcal{I}_{nl}(p, q, \lambda, t, k) = \int_0^{\infty} dr R_{nl}(r) e^{-r} r^k \Phi(p, q, \lambda, t, r) \quad (3.25)$$

Radial integration can be performed in Eq. (3.24) [18] and we obtain

$$I_{nl}(s, l+1) = \frac{2^{l+1}}{n^{l+2}} \sqrt{\frac{(n+l)!}{(n-l-1)!}} \frac{(s - \frac{1}{n})^{n-l-1}}{(s + \frac{1}{n})^{n+l+1}} \quad (3.26)$$

and it obeys the following property

$$I_{nl}(s, k+1) = -\frac{\partial}{\partial s} I_{nl}(s, k) \quad (3.27)$$

Using the expression for $\Phi(p, q, \lambda, t, r)$ given in Eq. (3.11) we can write

$$\mathcal{I}_{nl}(p, q, \lambda, t, k) = \int_{\lambda}^t ds K(p, q, \lambda, s) I_{nl}(s, k). \quad (3.28)$$

These expressions are used for the numerical evaluation of the transition amplitudes.

Second order transition amplitude

We have the compact form of second order transition amplitude as

$$\mathcal{M}^{(2)} = \langle f | z D_1 | i \rangle$$

where D_1 and $|f\rangle$ is given by Eq. (3.20) and Eq. (3.23) respectively and $|i\rangle = \exp(-r)/\sqrt{\pi}$ is the ground state of hydrogen atom.

We now introduce a new notation $\mathcal{M}_{nl}^{(2)}$ to denote the transition amplitude $\mathcal{M}_{fi}^{(2)}$ for the transition from ground state of hydrogen atom to a final state with principal quantum number n and orbital angular momentum quantum number l . Using Eqs. (3.24)-(3.25) the amplitudes for $l = 0$ and $l = 2$ respectively can be written in a compact form as

$$\mathcal{M}_{n0}^{(2)} = \frac{2}{3} \mathcal{I}_{n0}(1, 1, \lambda_1, 1, 4) \quad (3.29)$$

and

$$\mathcal{M}_{n2}^{(2)} = \frac{4}{3\sqrt{5}} \mathcal{I}_{n2}(1, 1, \lambda_1, 1, 2). \quad (3.30)$$

The amplitudes for various transitions corresponding to different n values, can be obtained from the above expressions. After the radial integration is done, the transition amplitudes for $l = 0$ becomes [19]

$$\mathcal{M}_{n0}^{(2)} = \frac{2}{3} \int_{\lambda_1}^1 ds K(1, 1, \lambda_1, s) I_{n0}(s, 4) \quad (3.31)$$

$$= \frac{2^5}{3n^5} \sqrt{\frac{(n+3)!}{(n-4)!}} \int_{\lambda_1}^1 ds \frac{(s - \frac{1}{n})^{n-4}}{(s + \frac{1}{n})^{n+4}} K(1, 1, \lambda_1, s) \quad (3.32)$$

and the transition amplitude corresponding to $l = 2$ is

$$\mathcal{M}_{n2}^{(2)} = \frac{2^4}{3\sqrt{5}n^3} \sqrt{\frac{(n+1)!}{(n-2)!}} \int_{\lambda_1}^1 ds \frac{(s - \frac{1}{n})^{n-2}}{(s + \frac{1}{n})^{n+2}} K(1, 1, \lambda_1, s) \quad (3.33)$$

where $\lambda_1 = \sqrt{1 - 2\omega}$.

As mentioned earlier following the Eq. (3.12), integrals in Eq. (3.31) and Eq. (3.33) are defined only if $1 - 1/\lambda_1 > -1$. But we need to evaluate

these transition amplitudes for a range of values of radiation frequency ω such that $1 - 1/\lambda_1 < -1$ also. The details this analytic continuation procedure is discussed in Section .4.5

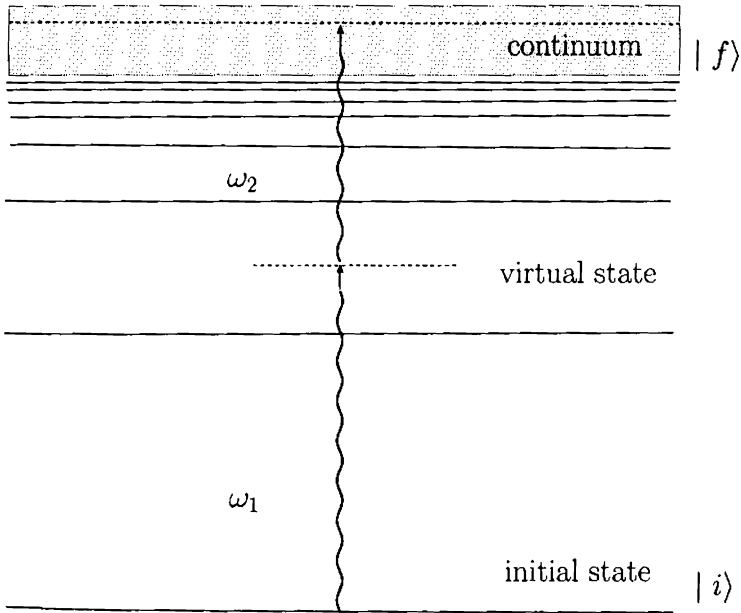


Figure 3.2: Schematic diagram for two-photon direct ionization, the transition is from an initial state $|i\rangle$ to final continuum state $|f\rangle$ through virtual states

3.4 Two-photon ionization of atomic hydrogen

In this section we have studied nonresonant two-photon ionization of atomic hydrogen, which includes 'threshold' as well as 'above threshold ionization (ATI)'.

Schematic diagram for the two-photon ionization is depicted in the Fig. (3.2). This figure corresponds to the 'threshold or direct ionization' where the minimum number of photons are involved in the process of ionization.

In the dipole approximation, the differential cross section for two-photon ionization in atomic units can be written as [15, 9, 30, 11]

$$\frac{d\sigma^{(2)}}{d\Omega} = \frac{\alpha}{4\pi} \left(\frac{I}{I_0} \right) |\mathcal{M}_{fi}^{(2)}|^2 a_0^2 \omega k, \quad (3.34)$$

where α is the fine structure constant, $a_0 = 5.2917 \times 10^{-9}$ cm, is the Bohr radius, I is the field strength intensity of the radiation field, $I_0 = 7.019 \times 10^{16}$ W/cm² is the atomic unit of field strength intensity and k is the momentum of the photo-electron ejected in the direction of the unit vector \hat{k} and $\mathcal{M}_{fi}^{(2)}$ is the second order transition amplitude given in Eq. (3.1). Here the final states are the continuum states. For transitions from ground state of atomic hydrogen involving two-photons, by conservation of energy

$$2\omega - 1/2 = \frac{k^2}{2}$$

thus the momentum of the ejected electron k is given as

$$k = \sqrt{4\omega - 1} \quad (3.35)$$

The amplitude for continuum transitions can be calculated by taking

Table 3.1: Two-photon scattering cross section per unit intensity $\sigma_L^{(2)}/I$ for linear polarization when two-photon ionization is energetically possible.

$\lambda(\text{\AA})$	Present	Karule ^a	Gao-Starace ^b	Chan-Tan ^c
1100	4.001(-34)	4.00(-33)	4.024(-34)	4.013(-34)
1200	6.422(-32)	6.42(-32)	6.441(-32)	6.303(-32)
1300	1.274(-32)	1.27(-32)	1.276(-32)	1.276(-32)
1400	8.446(-32)	8.45(-32)	8.451(-32)	8.450(-32)
1500	8.337(-33)	–	–	–
1600	9.151(-33)	9.15(-33)	9.153(-33)	9.154(-33)
1700	1.024(-33)	1.03(-33)	1.025(-33)	1.025(-33)
1800	1.143(-32)	–	–	–
1900	–	–	4.74(-54)	4.74(-54)

^a Karule [21]

^b Gao and Starace [9]

^c Chan and Tang[28]

the final state wave function as

$$|f\rangle = 4\pi \sum_{lm} i^l R_{kl}(r) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{k}) \quad (3.36)$$

where $Y_{lm}(\cdot)$ are the well known spherical harmonics. Here the radial part of hydrogen atom wave function for an attractive Coulomb potential can be taken as

$$R_{kl}(r) = e^{\frac{\pi\gamma}{2}} \frac{\Gamma(l+1-i\gamma)}{\Gamma(2l+2)} (2rk)^l e^{ikr} F(l+1-i\gamma, 2l+2, -2ikr)$$

Now substituting Eq. (3.36) and Eq. (3.19) in Eq. (3.1) and after performing

the angular integration we obtain the second order transition amplitude as

$$\mathcal{M}^{(2)} = \mathcal{D}_0^{(2)} Y_{00}(\hat{k}) + \mathcal{D}_2^{(2)} Y_{20}(\hat{k}) \quad (3.37)$$

where

$$\mathcal{D}_0^{(2)} = \frac{8\pi}{3} \int dr R_{k0}^*(r) r^4 \psi_1 e^{-r} \quad (3.38)$$

$$\mathcal{D}_2^{(2)} = \frac{16\pi}{3\sqrt{5}} \int dr R_{k2}^*(r) r^4 \psi_1 e^{-r} \quad (3.39)$$

It is useful to note that the form of the amplitudes are consistent with the selection rules for two-photon transitions. Substituting the above expressions in Eq. (3.34) and integrating over the emitted electron direction we obtain total two-photon ionization cross section for linear polarization $\sigma_L^{(2)}$ as [14, 106]

$$\frac{\sigma_L^{(2)}}{I} = \frac{\alpha}{4\pi I_0} a_0^2 \left\{ |\mathcal{D}_0^{(2)}|^2 + |\mathcal{D}_2^{(2)}|^2 \right\} \omega k \quad (3.40)$$

These integrals can be put in a neat form using the notations we have defined in the previous section.

Circularly polarized light : Using the Clebsch-Gordan algebra, we can similarly write the cross sections for circular polarization as [14, 106]

$$\frac{\sigma_C^{(2)}}{I} = \frac{\alpha}{4\pi I_0} a_0^2 \frac{3}{2} |\mathcal{D}_2^{(2)}|^2 \omega k \quad (3.41)$$

Here we can see that the contribution is only from the $l = 2$ states.

Now for a given wavelength of the radiation, we can compute the complex amplitudes $\mathcal{D}_0^{(2)}$ and $\mathcal{D}_2^{(2)}$ by performing a numerical integration in Eqs. (3.38) and (3.39). Numerical discussion will depend on the value of the laser frequency. In particular, for the case of below threshold photon energies ($0 \leq \omega < 1/2$) λ_1 is real and we have to rely on analytic continua-

tion discussed in Section 4.5 if $(1 - 1/\lambda_1) < -1$, for the evaluation of these cross sections.

Above threshold ionization

Two-photon above threshold ionization occurs when energy of one of the photon exceeds the ionization energy of the hydrogen atom [6, 27]. For these photon energies both two-photon and one-photon ionization occur simultaneously. For the case of Green's function method where the Sturmian expansion is used, the transition rates diverges and *Karule* used Appel function in order to make it a converging one for the relevant photon energies [21]. Other authors have even used WKB approximation for the evaluation of the scattering crosssection [38], and is found to be valid for multiphoton ionization of highly excited atoms.

Schematic diagram for the two-photon above one-photon ionization is depicted in the Fig. (3.3). This figure corresponds to the 'above threshold ionization', where with single photon itself the ionization occur. This simultaneous one-photon as well as two-photon ionization can be measured by investigating the ejected electrons energy distribution. The probability of such a processes is less compared to the one-photon ionization probability and but the ejected electrons have more kinetic energy than the electrons ejected by single photon ionization.

Since $\omega > 1/2$ in this case, $\lambda_1 = \sqrt{1 - 2\omega}$ is purely imaginary. Thus the analytic continuation for this case is very simple because the condition $\Re[1 - 1/\lambda_1] > 0$ is always satisfied and the expression given in Eq. (3.38)-(3.39) are all well defined for all values of $\omega > 1/2$. The peculiarity of our method is that, the analytical continuation can be done in a straight forward and very easy way.

The values obtained are presented in Table. 3.1 for linear polarization and in Table. 3.2 for circular polarization. The values inside the brackets

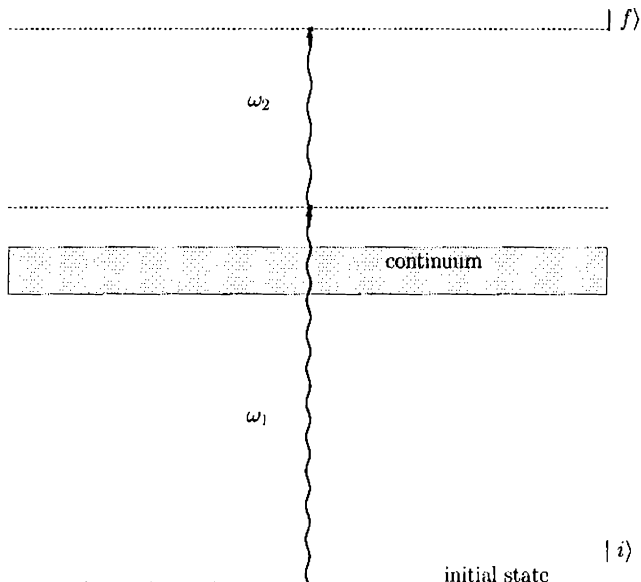


Figure 3.3: Schematic diagram for two-photon above threshold ionization: the transition is from an initial state $|i\rangle$ to final continuum state $|f\rangle$ -both two-photon and one-photon ionization occur simultaneously. The virtual state lies in the continuum.

are exponents.

3.5 ac-Stark effect

In presence of intense laser field, the atomic levels are displaced (shifted or broadened), these stimulated radiative corrections are known alternatively as the ac-Stark shift, the light shift, and sometimes as the Lamp shift. In the present section we briefly summarize the application of Dalgarno Lewis method for the evaluation of these energy shifts.

Our aim is to get an analytical expression for dipole dynamical polar-

Table 3.2: Two-photon scattering cross section per unit intensity $\sigma_C^{(2)}/I$ for circular polarization when two-photon ionization is energetically possible. The values given in brackets are exponents

$\lambda(\text{\AA})$	Laplace ^a	Present
1100	4.284(-34)	4.241(-34)
1200	7.725(-32)	7.731(-32)
1300	1.879(-32)	1.874(-32)
1400	1.270(-32)	1.266(-32)
1500	–	1.252(-32)
1600	1.358(-32)	1.353(-32)
1700	1.498(-32)	1.493(-32)
1800	–	1.636(-32)
1900	–	6.63(-54)

^a Laplanche et al. [25]

izability from which we can calculate the level shift and level width. The second-order level shift for atomic hydrogen was previously calculated in both perturbative and nonperturbative methods [93, 94, 95, 96, 97, 98, 99, 100] and experimentally studied in some atomic systems[101, 102].

An analytical expression for the second-order ac-Stark shift of the ground state of atomic hydrogen can also be derived within the framework of perturbation theory. The level shift depends on the intensity and the frequency of the radiation. The complex second order shift $\Delta^{(2)}$ is given by [93, 95, 97, 98]

$$\Delta^{(2)} = \delta E^{(2)} - i\Gamma^{(2)} = -\frac{I}{I_0}\tau^{(2)}(\omega) \quad (3.42)$$

Its real part $\delta E^{(2)}$ is the energy shift and its imaginary part $\Gamma^{(2)}$ gives the level width, I and $I_0 = 7.016 \times 10^{16}$ W/cm² are the laser intensity and characteristic atomic field strength intensity respectively. Here $\tau^{(2)}(\omega)$ is the dipole dynamic polarizability given by the expression

$$\tau^{(2)} = \sum_j \left\{ \frac{\langle g | \epsilon^* \cdot \mathbf{r} | j \rangle \langle j | \epsilon \cdot \mathbf{r} | g \rangle}{(E_g - E_j + \omega)} + \frac{\langle g | \epsilon \cdot \mathbf{r} | j \rangle \langle j | \epsilon^* \cdot \mathbf{r} | g \rangle}{(E_g - E_j - \omega)} \right\} \quad (3.43)$$

where E_j are the intermediate state energy and E_g is the ground state energy. First term in the bracket is the absorption-emission term and the second is the emission-absorption term.

Dalgarno Lewis method

Proceeding as in the previous section the infinite summation over the complete set of states in Eq. (3.43) can be performed exactly by defining a set of operators F and \tilde{F} , such that

$$\epsilon \cdot \mathbf{r} |g\rangle = (FH_0 - H_0F + \omega F) |g\rangle \quad (3.44)$$

$$\epsilon^* \cdot \mathbf{r} |g\rangle = (\tilde{F}H_0 - H_0\tilde{F} - \omega\tilde{F}) |g\rangle \quad (3.45)$$

where $H_0 = -\nabla^2/2 - 1/r$, is the unperturbed Hamiltonian for the hydrogen atom and $|g\rangle = e^{-r}/\sqrt{\pi}$ is the ground state wave function in atomic units. With the use of above definitions and the closure relation $\sum_i |i\rangle\langle i| = I$ the expression in Eq. (3.43) for dipole dynamical polarizability will be reduced to

$$\tau^{(2)} = \langle g | \epsilon^* \cdot \mathbf{r} F | g \rangle + \langle g | \epsilon \cdot \mathbf{r} \tilde{F} | g \rangle \quad (3.46)$$

so the infinite summation over the intermediate states are reduced to the determination of the operator F and \tilde{F} . Using $F = \epsilon \cdot \mathbf{r} f(r)$ and $\tilde{F} = \epsilon^* \cdot \mathbf{r} \tilde{f}(r)$ the differential equations satisfied by $f(r)$ and $\tilde{f}(r)$ are found to

Table 3.3: Comparison of the values of dipole dynamical polarizability in atomic units for below one photon ionization threshold $\omega < 0.5$. In the limit $\omega \rightarrow 0$; $\tau^{(2)}(\omega)$ approaches the dc polarizability which is -4.5 .

ω (a.u)	This work	ABM ^a
0.001	4.50003	–
0.002	4.50011	–
0.02	4.51066	-4.51
0.04	4.5429	-4.5431
0.08	4.6775	-4.6776
0.10	4.7843	-4.7843
0.20	5.9416	-5.9416
0.43	0.2971	–
0.46	3.9273	–
0.465	3.0867	–
0.477	1.2644	–
0.478	1.9330	–
0.489	0.6465	–

^a Values obtained using Coulomb Green function by *Arnous et al.* [93] with an additional ω^{-2} factor as explained in Section 3.6.

be

$$r \frac{d^2}{dr^2} f(r) + (4 - 2r) \frac{d}{dr} f(r) + (2\omega r - 2)f(r) = 2r \quad (3.47)$$

$$r \frac{d^2}{dr^2} \tilde{f}(r) + (4 - 2r) \frac{d}{dr} \tilde{f}(r) - (2\omega r + 2)\tilde{f}(r) = 2r$$

Solutions

Again using the method of Laplace transform [115] for the solution of differential equation we can obtain the solutions to the above differential equa-

tions as

$$f(r) = \frac{1}{\omega} - \frac{1}{2\omega^3} \Phi(1, 1, \lambda, 1, r) \quad (3.48)$$

and

$$\tilde{f}(r) = \frac{1}{\omega} + \frac{1}{2\omega^3} \tilde{\Phi}(1, 1, \tilde{\lambda}, 1, r) \quad (3.49)$$

where

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)} K(p, q, \lambda, s) \quad (3.50)$$

$$\tilde{\Phi}(p, q, \lambda, t, r) = \int_t^{\lambda} ds e^{-r(s-1)} \tilde{K}(p, q, \lambda, s) \quad (3.51)$$

with

$$K(p, q, \lambda, s) = \left(\frac{1-\lambda}{1+\lambda} \right)^{\frac{1}{\lambda}} (s+\lambda)^{p+\frac{1}{\lambda}} (s-\lambda)^{q-\frac{1}{\lambda}} \quad (3.52)$$

and

$$\tilde{K}(p, q, \lambda, s) = \left(\frac{\lambda-1}{\lambda+1} \right)^{\frac{1}{\lambda}} (\lambda+s)^{p+\frac{1}{\lambda}} (\lambda-s)^{q-\frac{1}{\lambda}} \quad (3.53)$$

where $\lambda = \sqrt{1-2\omega}$ and $\tilde{\lambda} = \sqrt{1+2\omega}$. As in the previous case these expressions clearly displays all the analytics properties present in the perturbation theory result. Using Eqs. (3.48)-(3.49) in Eq. (3.46) we get

$$\tau^{(2)}(\omega) = \frac{2}{3\omega^3} \int_0^{\infty} dr e^{-2r} r^4 \{ \tilde{\Phi}(1, 1, \tilde{\lambda}, r) - \Phi(1, 1, \lambda, r) \} \quad (3.54)$$

With the use of $\mathcal{I}(\cdot)$ defined in Eq. (3.25) the final form of the dipolar polarizability becomes

$$\tau^{(2)} = \frac{2}{3\omega^3} \left\{ \tilde{\mathcal{I}}(1, 1, \tilde{\lambda}, 1, 4) - \mathcal{I}(1, 1, \lambda, 1, 4) \right\} \quad (3.55)$$

where

$$\begin{aligned} \tilde{I}(p, q, \lambda, 1, n) &= \int_0^{\infty} dr e^{-2r} r^n \tilde{\Phi}(p, q, \lambda, 1, r) \\ &= n! \left(\frac{\lambda - 1}{\lambda + 1} \right)^{\frac{1}{2}} \int_1^{\lambda} ds \frac{(\lambda + s)^{p+\frac{1}{2}} (\lambda - s)^{q-\frac{1}{2}}}{(1 + s)^{n+1}} \end{aligned} \quad (3.56)$$

$$\begin{aligned} \mathcal{I}(p, q, \lambda, 1, n) &= \int_0^{\infty} dr e^{-2r} r^n \Phi(p, q, \lambda, 1, r) \\ &= n! \left(\frac{1 - \lambda}{1 + \lambda} \right)^{\frac{1}{2}} \int_{\lambda}^1 ds \frac{(s + \lambda)^{p+\frac{1}{2}} (s - \lambda)^{q-\frac{1}{2}}}{(1 + s)^{n+1}} \end{aligned} \quad (3.57)$$

In the limit $\omega \rightarrow 0$, the expression for Δ should approach to the corresponding dc-stark shift corrections (i. e., dc-stark effect) and the dynamical polarizability tends toward the static dipolar polarizability which is $9/2$. Our numerical results are consistent with this observation. In Table. 3.3 these values are listed for ω below one photon ionization threshold i.e., $\omega < 0.5$, and we can see that even when $\omega = 0.001$, this value approaches the value of dc polarizability (i. e., 4.5).

The discrepancies arise with the values obtained by CGF method [93] within a factor of $1/\omega^2$, but we have checked our calculation by looking at the result when $\omega \rightarrow 0$ i. e., the dc limiting case. With this inspection we found that we get exact values for the polarizability with values of *Maquet et al.* [93], if we use ω instead of ω^3 in the denominator of the expression for polarizability.

Dipole dynamical polarizability in atomic units for above one photon ionization threshold is also presented in Table. 3.4.

Table 3.4: Comparison of the values of dipole dynamical polarizability in atomic units for above one photon ionization threshold

$\omega(\text{a.u.})$	$\text{Re } \tau^{(2)}(\omega)$		$\text{Im } \tau^{(2)}(\omega)$	
	This work	ABM ^a	This work	ABM ^a
0.6	3.297	–	2.505	–
0.7	2.493	–	1.408	–
0.8	1.915	1.915	0.850	0.8506
1.0	1.205	1.205	0.362	0.3627
2.0	0.275	0.275	0.023	0.0239
3.0	0.117	–	0.004	--
4.0	0.064	–	0.001	–
5.0	0.041	0.041	0.0005	0.00057
6.0	0.028	–	0.00027	–
9.0	0.012	–	0.000049	–
10	0.010081	0.01008	0.0000319	0.00003

^a Arnous et al.

3.6 Elastic scattering of photons

Kramers-Heisenberg formula alternatively called as dispersion relation plays an important role in the scattering theory. Most of the scattering cross-section is essentially given by the Kramers-Heisenberg equation [108]. Considering its existence for very long period, very few attempts were made to evaluate it analytically [109, 110].

Similar to the ac stark shift this is also a second order process and includes the evaluation of the second order matrix element. Evaluation of the perturbative matrix element containing infinite sum running over the whole hydrogenic spectrum (discrete and continuous) is performed by using

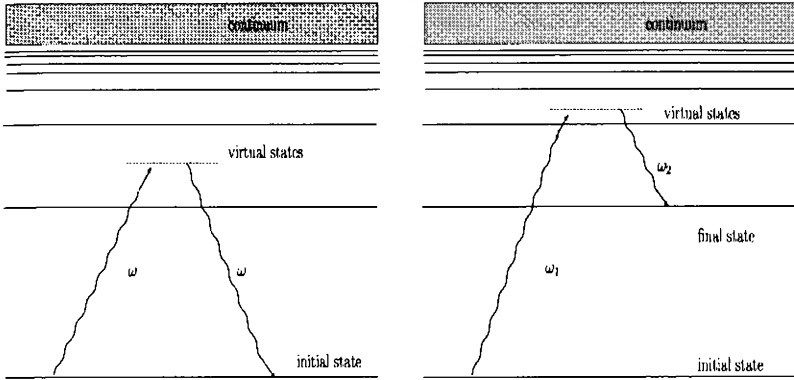


Figure 3.4: Schematic diagrams of elastic scattering of photons and of Raman scattering. In the stimulated Raman scattering initial and final states are different.

implicit summation techniques discussed in the section 3.2

The differential scattering cross section for the low energy elastic scattering of photons of frequency ω from atoms is given by the dispersion relation [108, 109, 110]

$$\frac{d\sigma}{d\Omega} = a_0^2 (\epsilon \cdot \epsilon')^2 |M|^2 = a_0^2 (\epsilon \cdot \epsilon')^2 |1 - P(\omega) - P(-\omega)|^2, \quad (3.58)$$

where a_0 , is the Bohr radius, M is the Kramers-Heisenberg matrix element, ϵ and ϵ' respectively are the initial and final polarization of photons. For an atomic system in the ground state $|g\rangle$, $P(\omega)$ in atomic units is given as [110]

$$P(\omega) = -\frac{2}{3} \sum_n \frac{\langle g | \mathbf{p} | n \rangle \cdot \langle n | \mathbf{p} | g \rangle}{(E_g - E_n + \omega)}. \quad (3.59)$$

Here \mathbf{p} is the momentum operator, E_g is the atomic ground state energy and the summation is over the complete set of states including continuum states.

It is useful to note from Eq. (3.58) that the differential cross section for coherent scattering of photons is just the Thompson cross section modified by the dynamic polarizability. In a similar fashion we can consider Raman effect where initial and final states are different, thus the matrix element will be from the ground state to a final state through intermediate states. The analytical expressions for $P(\omega)$ is derived earlier using Coulomb Greens Function formalism (CGF) [110] and *Schwartz and Teinman* [109] method.

A slight variation of the formalism we had used in the earlier sections is used here. The infinite summation over the intermediate state in Eq. (3.59) is performed here by defining a set of operators \vec{U} and \vec{U} such that,

$$\begin{aligned} \mathbf{p} |g\rangle &= \left(\vec{U} H_0 - H_0 \vec{U} + \omega \vec{U} \right) |g\rangle \\ \mathbf{p} |g\rangle &= \left(\vec{U} H_0 - H_0 \vec{U} - \omega \vec{U} \right) |g\rangle \end{aligned} \quad (3.60)$$

Proceeding as in the previous sections now the expression for M will become

$$M = 1 + \frac{2}{3} \left(\langle g | \mathbf{p} \cdot \vec{U} | g \rangle + \langle g | \mathbf{p} \cdot \vec{U} | g \rangle \right) \quad (3.61)$$

Thus the evaluation of the infinite summation again reduced to finding the appropriate operators \vec{U} and \vec{U} satisfying the Eq. (3.60). To obtain the explicit expression for these operators, we use the coordinate space representation by taking $\mathbf{p} = -i\vec{\nabla}$, $H_0 = -\nabla^2/2 - 1/r$, $\vec{U} = ru(r)$ and $\vec{U} = r\tilde{u}(r)$, then the Eqs. (3.60) becomes

$$\begin{aligned} r \frac{d^2}{dr^2} u(r) + (4 - 2r) \frac{d}{dr} u(r) + (2\omega r - 2)u(r) &= 2i \\ r \frac{d^2}{dr^2} \tilde{u}(r) + (4 - 2r) \frac{d}{dr} \tilde{u}(r) - (2\omega r + 2)\tilde{u}(r) &= 2i \end{aligned} \quad (3.62)$$

These differential equation has the same form which we considered in the earlier sections. By using the same method the solutions to the above

Table 3.5: Kramers-Heisenberg matrix element M in atomic units for ω below one photon ionization threshold. Comparison is made with values in Ref. [110].

ω (a.u.)	This		This		This	
	Work	Ref.	ω (a.u.)	Work	Ref.	ω (a.u.)
0.002	0.000018	-	0.376	77.8416	-	-
0.02	0.0018	0.0018	0.38	15.3829	15.3828	0.481
0.04	0.0072	0.0072	0.4	2.6916	2.6916	0.484
0.06	0.0165	0.0165	0.429	0.0611	-	0.485
0.08	0.0299	0.0299	0.43	0.0549	0.0549	0.486
0.10	0.0478	0.0478	0.44	3.1503	3.1503	-
0.12	0.0708	0.0708	0.444	38.8927	-	0.488
0.14	0.0999	0.0999	-	-	-	0.489
0.16	0.1361	0.1361	0.445	32.2604	32.2603	0.49
0.18	0.1812	0.1812	0.453	2.3124	2.3124	0.491
0.20	0.2376	0.2376	0.464	0.2004	-	0.492
0.22	0.3091	0.3091	0.465	0.6674	0.6674	0.493
0.24	0.4016	0.4016	0.468	8.1693	8.1693	0.494
0.26	0.5246	0.5246	-	-	-	0.496
0.30	0.9507	0.9507	0.469	27.9814	27.9814	0.497
0.32	1.3752	1.3752	0.473	1.97857	1.9785	0.497
0.36	5.3036	5.3036	0.477	0.2876	-	0.498
0.37	15.763	15.763	0.478	0.4416	0.4416	-

differential equations are

$$u(r) = -\frac{i}{2\omega^2} \Phi(1, 1, \lambda, 1, r) \quad (3.63)$$

and

$$\tilde{u}(r) = \frac{i}{2\omega^2} \tilde{\Phi}(1, 1, \tilde{\lambda}, 1, r) \quad (3.64)$$

where $\lambda = \sqrt{1 - 2\omega}$ and $\tilde{\lambda} = \sqrt{1 + 2\omega}$. Substituting the values of $u(r)$ and $\tilde{u}(r)$ in Eq. (3.61) we get a closed form expression for the Kramers-Heisenberg matrix element and it will take the form

$$M = 1 - \frac{8}{3\omega^2} \int_0^\infty dr e^{-2r} r^3 \left\{ \Phi(1, 1, \lambda, 1, r) - \tilde{\Phi}(1, 1, \tilde{\lambda}, 1, r) \right\} \quad (3.65)$$

With the definitions given in Eqs. (3.25)-(3.56), the Kramers-Heisenberg matrix element will take the form

$$M = 1 - \frac{8}{3\omega^2} \left\{ \tilde{I}(1, 1, \lambda, 1, 3) - \mathcal{I}(1, 1, \tilde{\lambda}, 1, 3) \right\} \quad (3.66)$$

If the incident photons are unpolarized and the polarization of the scattered photons are not observed, the differential scattering crosssection has the standard form

$$d\sigma = r_0^2 \frac{1}{2} (1 + \cos^2\theta) |M|^2 d\Omega \quad (3.67)$$

Numerical discussion

Evaluation of all the integrals coming in the final expressions of various sections has to be evaluated numerically. For numerical evaluation the more convenient form given in Eqs. (3.26) and (3.56) has to be used. The radial integrals are done using the standard integrals, and all the final

Table 3.6: Real and Imaginary part of Kramers-Heisenberg matrix element for photons of energies above one-photon ionization threshold ($\omega > 0.5$) and comparison is made with values in Ref. [110].

ω (a.u)	Re M		Im M	
	This work	Ref. [110]	This work	Ref. [110]
0.6	1.1872	1.1872	0.9018	0.9018
0.7	1.22161	1.2216	0.6900	0.6900
0.8	1.22612	1.2261	0.5444	0.5444
0.9	1.21842	1.2184	0.4400	0.4400
1.0	1.20598	1.2059	0.3627	0.3627
2.0	1.10007	1.10007	0.0958	0.0958
3.0	1.05696	1.0569	0.0421	0.0421
4.0	1.03685	1.0368	0.0231	0.0231
5.0	1.02589	1.0258	0.0144	0.0144
6.0	1.01924	1.0192	0.00977	0.00977
7.0	1.01489	1.0148	0.00699	0.00699
8.0	1.01188	1.0118	0.00522	0.00522
9.0	1.00971	1.0097	0.00403	0.00403
10	1.0081	1.0081	0.00319	0.00319
20	1.00236	1.0023	0.00066	0.00066
30	1.00112	–	0.000262	–
40	1.00066	–	0.000133	–
50	1.00042	–	0.000075	–
90	1.00014	–	0.0000196	–

expressions involve only one dimensional integrals, these has to be evaluated numerically for various values of incident frequency.

If the photon energy is below the one-photon ionization threshold ($0 \leq \omega < 1/2$) λ_1 and $\tilde{\lambda}$ are real. The integrals can be evaluated by proper analytical continuation (given in Section 4.5) without additional difficulty.

3.7 Conclusion

In this chapter we have presented the application of Dalgarno Lewis method for the evaluation of various amplitudes related to two-photon processes. All these processes are treated in an unified manner. These two-photon processes includes, two-photon bound bound transition probabilities, two-photon ionization cross section which includes both above and below threshold ionization, ac-Stark correction and finally the Kramers-Heisenberg matrix element which is relevant for the study of elastic scattering of photons.

In the Section 3.2 we have described the method which implicitly carry out the summation over the complete states. Then we have obtained an alternate expression for two-photon bound-bound transition probability amplitude using Dalgarno-Lewis method. In the Section 3.4 we have obtained the relevant expression for two-photon ionization cross section for both linear and circular polarizations. Then we have obtained an analytical expression for the shift in the energy level of hydrogen atom due to the interaction with the external field and is presented in Section 3.5. Finally we have obtained the closed form expression for elastic scattering of photons from ground state of atomic hydrogen, we have presented the results and compared the obtained values with available results in the literatures.

Chapter 4

Three-photon processes

In the present chapter we consider three-photon processes especially, transitions from the ground state to an excited bound state and ionization in hydrogen atom due to three-photon absorption. We obtained closed form analytical expressions for bound to bound transition probabilities as well as the cross sections for three-photon ionization for both linearly and circularly polarized light, for a wide range of photon energy including the near resonances.

This chapter is a continuation of the analytical method considered for two-photon processes in the previous chapter. Here we have extended Dalgarno-Lewis procedure for the evaluation of transition matrix elements for three-photon processes also. As in the case of two-photon processes, here also we have to find solutions to a set of inhomogeneous second order differential equations. The integral representation of the solutions to these equations are obtained and its analytical properties are studied. A discussion on the analytical continuation of the solution, which is essential for the calculation of above threshold and near resonant transitions, are also presented. Finally the calculated numerical values for three-photon cross

sections are compared with a wide range of available numerical results obtained by different methods.

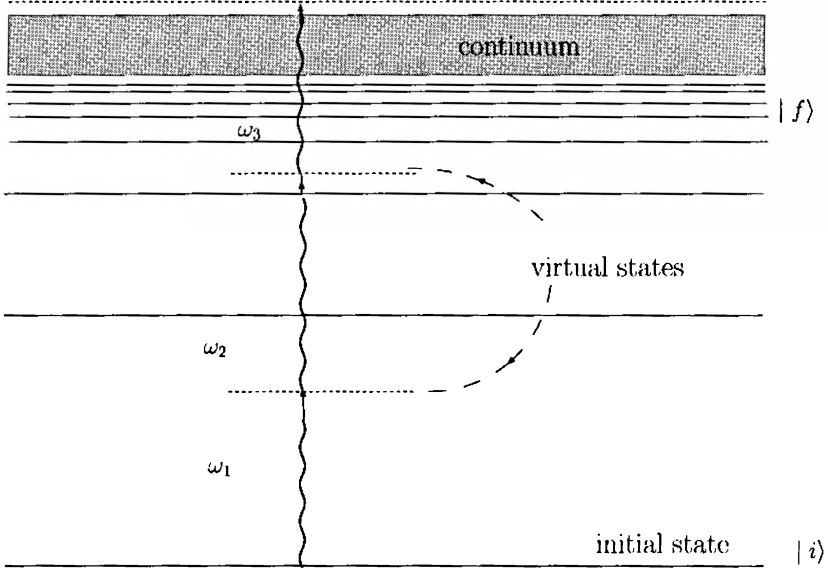


Figure 4.1: Schematic diagram of a typical three-photon ionization by successive absorption of 3-photons. The intermediate virtual states denoted by dotted lines are complete set of states. When these states matches with the bound states resonances occur.

4.1 Three-photon transition amplitude

In the present section we consider the atomic hydrogen absorbing three photons simultaneously with frequency ω , and make a transition from an initial state $|i\rangle$ to an excited state $|f\rangle$ allowed by the three-photon transition selection rules. We have used perturbation theory for studying these effects and this is an extension of the discussion in the previous chapter.

In the dipole approximation the three-photon transition rate for a general transition from an initial state $|i\rangle$ to a final state $|f\rangle$ can be calculated using the third order transition matrix element

$$M_{fi}^{(3)} = \sum_{n,n'} \frac{\langle f | \epsilon \cdot \mathbf{r} | n \rangle \langle n | \epsilon \cdot \mathbf{r} | n' \rangle \langle n' | \epsilon \cdot \mathbf{r} | i \rangle}{(E_n - E_i - 2\omega)(E_{n'} - E_i - \omega)} \quad (4.1)$$

Our main objective is to obtain a compact expression for the matrix element given in Eq. (4.1) exhibiting all analytic properties of it as a function of the incident photon energy ω . The problems associated with the two photon processes are also present here and the presence of an additional infinite summation makes it more complicated.

4.2 Dalgarno-Lewis method

In order to perform the infinite double summation over the complete set of states including contribution from continuum states, we have made suitable modification of the Dalgarno-Lewis procedure discussed in the preceding chapter. For this we have to define one more auxiliary operator D_2 in addition to D_1 (given in Eq. (3.2) of the Section 3.2) and these operators are defined using the relations

$$\epsilon \cdot \mathbf{r} | i \rangle = (D_1 H_0 - H_0 D_1 + \omega D_1) | i \rangle \quad (4.2)$$

$$\epsilon \cdot \mathbf{r} D_1 | i \rangle = (D_2 H_0 - H_0 D_2 + 2\omega D_2) | i \rangle \quad (4.3)$$

where H_0 is the field free Hamiltonian of the system which obey the following eigenvalue equation

$$H_0 | n \rangle = E_n | n \rangle.$$

Now proceeding in a similar manner as in the previous chapter, the operator D_1 can be used to remove one of the energy denominator. Then with the use of closure relation $\sum_{n'} |n'\rangle\langle n'| = \hat{I}$ one of infinite summation can be eliminated. This is done by taking the scalar product of Eq. (4.2) with $|n'\rangle$ to obtain

$$\begin{aligned}\langle n' | \epsilon \cdot \mathbf{r} | i \rangle &= \langle n' | (D_1 H_0 - H_0 D_1 + \omega D_1) | i \rangle \\ &= (E_i - E_{n'} + \omega) \langle n' | D_1 | i \rangle\end{aligned}\quad (4.4)$$

substituting the above relation in Eq. (4.1) we can write

$$M_{fi}^{(3)} = \sum_{n, n'} \frac{(E_i - E_{n'} + \omega) \langle f | \epsilon \cdot \mathbf{r} | n \rangle \langle n | \epsilon \cdot \mathbf{r} | n' \rangle \langle n' | \epsilon \cdot \mathbf{r} | i \rangle}{(E_n - E_i - 2\omega)(E_{n'} - E_i - \omega)}. \quad (4.5)$$

Canceling out one of the energy denominator and using the closure relation $|n'\rangle\langle n'| = I$ the expression in Eq. (4.1) becomes

$$M_{fi}^{(3)} = - \sum_n \frac{\langle f | \epsilon \cdot \mathbf{r} | n \rangle \langle n | \epsilon \cdot \mathbf{r} D_1 | g \rangle}{(E_n - E_g - 2\omega)}. \quad (4.6)$$

Similarly by taking the scalar product of Eq. (4.3) with $\langle n |$ on both sides we will get

$$\begin{aligned}\langle n | \epsilon \cdot \mathbf{r} D_1 | i \rangle &= \langle n | (D_2 H_0 - H_0 D_2 + \omega D_2) | i \rangle \\ &= (E_i - E_n + \omega) \langle n | D_2 | i \rangle\end{aligned}\quad (4.7)$$

Now using the above relation in Eq. (4.6) we can cancel the remaining energy denominator, finally using closure relation $\sum_n |n\rangle\langle n| = \hat{I}$, we can write the third order matrix element as

$$M_{fi}^{(3)} = \langle f | \epsilon \cdot \mathbf{r} D_2 | i \rangle. \quad (4.8)$$

Thus the problem of finding an analytic expressions for the transition matrix element is reduced to a problem of finding operator D_2 . We have already seen that the operator D_1 is used to calculate matrix element for various two-photon process and it appears as the inhomogeneous term for the determination of D_2 in the Eq. (4.3). As in the previous case of two-photon process our goal is to find an analytical expression for D_2 .

Again we are considering the case of atomic hydrogen which is described by the Hamiltonian

$$H_0 = \frac{-\nabla^2}{2} - \frac{1}{r}$$

and for simplicity, first we consider linearly polarized light along the z -axis so that $\epsilon \cdot \mathbf{r} = z$. By taking $|i\rangle = e^{-r}/\sqrt{\pi} = \varphi$ we can write

$$(D_2 H_0 - H_0 D_2 + 2\omega D_2) \varphi = \left[D_2 \left(-\frac{\nabla^2}{2} - \frac{1}{r} \right) - \left(-\frac{\nabla^2}{2} - \frac{1}{r} D_2 \right) + 2\omega D_2 \right] \varphi. \quad (4.9)$$

After some simplification this becomes

$$z D_1 \varphi = \frac{\nabla^2 D_2}{2} \varphi + \nabla D_2 \cdot \nabla \varphi + 2\omega D_2 \varphi \quad (4.10)$$

The separation of the radial and angular part of the unknown operator D_2 can be done by writing

$$D_2 = \sum_l f_l(r) P_l(\cos \theta). \quad (4.11)$$

Using the following properties of $P_l(\cos \theta)$

$$\begin{aligned}\nabla^2 P_l &= -\frac{l(l+1)}{r^2} P_l \\ \cos^2(\theta) &= \frac{2P_2(\cos \theta) + 1}{3}\end{aligned}\quad (4.12)$$

we have

$$\begin{aligned}\nabla D_2 &= \sum_l \hat{r} f'_l(r) P_l + \sum_l \frac{\hat{\theta}}{r} f_l(r) \frac{d}{d\theta} P_l \\ \nabla^2 D_2 &= \sum_l \left\{ \nabla^2 f_l(r) - \frac{l(l+1)}{r^2} f_l(r) \right\} P_l(\cos \theta).\end{aligned}$$

With the above mentioned identities and using the expression for $D_1(r)$ as

$$D_1(\mathbf{r}) = r\psi_1(r)P_1(\cos \theta). \quad (4.13)$$

we can see that, Eq. (4.10) will take the new form in $f_l(r)$ as

$$r \cos^2 \theta g(r) = \sum_l \frac{1}{2} \left[\nabla^2 f_l - \frac{l(l+1)}{r^2} f_l \right] P_l - f'_l P_l + 2\omega f_l P_l \quad (4.14)$$

Using the recurrence relation of P_l given in Eq. (3.22), in the left hand side of the above equation, we can see that, from the partial wave expansion on the right hand side, the contribution is only from $l = 0$ and $l = 2$.

Comparing the coefficients of $P_l(\cos \theta)$ on both sides of the Eq. (4.14) for $l = 0$ and $l = 2$ we get, the differential equation satisfied by $f_2(r)$ and

$f_0(r)$ as

$$\begin{aligned}\frac{1}{3}rg(r) &= \frac{1}{2}\nabla^2 f_0 - f'_0 + 2\omega f_0 \\ \frac{2}{3}rg(r) &= \frac{1}{2}\left[\nabla^2 f_2 - \frac{6}{r^2}f_2\right] - f'_2 + 2\omega f_2.\end{aligned}\quad (4.15)$$

Using the polar form of ∇^2 we can write

$$\nabla^2 f_l(r) = \frac{d^2}{dr^2}f_l(r) + \frac{2}{r}\frac{d}{dr}f_l(r).$$

Then the differential equation satisfied by $f_0(r)$ and $f_2(r)$ can be rewritten as

$$\begin{aligned}f''_0 + \left(\frac{1}{r} - 1\right)2f'_0 + 4\omega f_0 &= \frac{2}{3}rg \\ f''_2 + 2\left(\frac{1}{r} - 1\right)f'_2 - 2\left(\frac{6}{r^2} - 2\omega\right)f_2 &= \frac{4}{3}rg\end{aligned}\quad (4.16)$$

Now we define new radial functions $\psi_l(r)$ such that

$$f_l(r) = r^l\psi_l(r),$$

this gives the final form of D_2 as

$$D_2(\mathbf{r}) = \psi_0(r) + r^2\psi_2(r)P_2(\cos\theta).\quad (4.17)$$

From the Eq. (4.16) the differential equations satisfied by the unknown radial functions $\psi_0(r)$ and $\psi_2(r)$ are

$$r\frac{d^2}{dr^2}\psi_0(r) + (2 - 2r)\frac{d}{dr}\psi_0(r) + 4\omega r\psi_0(r) = \frac{2}{3}r^3\psi_1(r)\quad (4.18)$$

$$r\frac{d^2}{dr^2}\psi_2(r) + (6 - 2r)\frac{d}{dr}\psi_2(r) + (4\omega r - 4)\psi_2(r) = \frac{4}{3}r\psi_1(r)\quad (4.19)$$

In connection with the two photon processes, we already have the differential equation satisfied by $\psi_1(r)$ derived in the Section 3.2 of the previous chapter as

$$r \frac{d^2}{dr^2} \psi_1(r) + (4 - 2r) \frac{d}{dr} \psi_1(r) + (2\omega r - 2) \psi_1(r) = 2r, \quad (4.20)$$

low $\psi_1(r)$ appear as the inhomogeneous term in the differential equations for ψ_0 and ψ_2 associated with three-photon processes. In general as one goes to higher and higher orders in perturbation ψ 's corresponding to the lower order process will appear as a inhomogeneous term in the differential equations for the determination of ψ 's corresponding to higher process.

It is straightforward to see from Eq. (4.8) that the infinite summation over the intermediate states are now reduced to the determination of the solutions of the inhomogeneous differential equations in Eqs. (4.18)-(4.19). It is also clear that the evaluation of three-photon transition amplitude requires the knowledge of the the two-photon transition amplitude.

Now our aim is to find an appropriate solution to these differential equations, which eventually give the transition matrix element corresponding to three-photon transition from the ground state of hydrogen atom, without explicitly summing over the complete set of states. The above Eqs. (4.18)-4.20) can be written in a more general form by defining the differential operator $\mathcal{D}_{l\lambda_l}$ as

$$\mathcal{D}_{l\lambda_l} = r \frac{d^2}{dr^2} + (2l + 2 - 2r) \frac{d}{dr} + (1 - \lambda_l^2)r - 2l. \quad (4.21)$$

where λ_l in $\mathcal{D}_{l\lambda_l}$ corresponding to the three values of l are

$$\lambda_1 = \sqrt{1 - 2\omega} \quad (4.22)$$

$$\lambda_0 = \lambda_2 = \sqrt{1 - 4\omega} \quad (4.23)$$

The Eqs. (4.18)-(4.20) can be written as a single equation

$$\mathcal{D}_{l\lambda_l}\psi_l(r) = h_l(r) \quad (4.24)$$

where $h_1(r) = 2r$, $h_0(r) = (2/3)r^3\psi_1(r)$ and $h_2(r) = (4/3)r\psi_1(r)$. The equations (4.18)-(4.20) can be obtained from Eq. (4.24) by taking $l = 0, 2$ and 1 respectively.

The general properties of the above differential operator $\mathcal{D}_{l\lambda_l}$ can be established by operating it on an arbitrary function $\varphi(r)$ and this leads to

$$\mathcal{D}_{l\lambda}(r\varphi) = r\mathcal{D}_{l\lambda}\varphi + 2r\frac{d}{dr}\varphi + (2l + 2 - 2r)\varphi \quad (4.25)$$

We can again try to find a solution to the differential equation given in Eqs. (4.18) and (4.19). In order to solve for $\psi_0(r)$ and $\psi_2(r)$, ψ_1 should be specified. The closed integral form of ψ_1 is given in Eq. (3.19) of the Section 3.2 is

$$\psi_1(r) = \frac{1}{\omega} - \frac{1}{2\omega^3}\Phi(1, 1, \lambda_1, 1, r) \quad (4.26)$$

where

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)}K(p, q, \lambda, s) \quad (4.27)$$

and

$$K(p, q, \lambda, s) = \left(\frac{1-\lambda}{1+\lambda}\right)^{\frac{1}{\lambda}} (s+\lambda)^{p+\frac{1}{\lambda}} (s-\lambda)^{q-\frac{1}{\lambda}} \quad (4.28)$$

Here p, q are real numbers and λ 's are in general complex.

In order to solve the differential equations satisfied by ψ_0 and ψ_2 , we have to find solutions to the equation of the form

$$\mathcal{D}_{l\lambda_l}\Psi_l(r) = \mathcal{B} \int_{\lambda_l}^1 e^{-r(t-1)}k(t)dt$$

where \mathcal{B} is a constant and $k(t)$ is given. Let us take $\Psi_l(r)$ of the form

$$\begin{aligned}\Psi_l(r) &= \int_a^1 dt \frac{k(t)}{K(l+1, l+1, \lambda, t)} \Phi(l, l, \lambda, t, r) \\ &= \int_a^1 dt \frac{k(t)}{K(l+1, l+1, \lambda, t)} \int_\lambda^t ds e^{-r(s-1)} K(l, l, \lambda, s)\end{aligned}\quad (4.29)$$

Direct substitution of Eq. (4.29) in $\mathcal{D}_{l\lambda_l} \Psi_l(r)$ gives us

$$\begin{aligned}\mathcal{D}_{l\lambda_l} \Psi_l(r) &= \int_a^1 dt \frac{k(t)}{K(l+1, l+1, \lambda, t)} \mathcal{D}_{l\lambda_l} \Phi(l, l, \lambda, t, r) \\ &= \int_a^1 dt \frac{k(t)}{K(l+1, l+1, \lambda, t)} (-) e^{-r(t-1)} K(l+1, l+1, \lambda, t) \\ &= - \int_a^1 dt e^{-r(t-1)} k(t)\end{aligned}\quad (4.30)$$

Solution for $\psi_0(r)$:

We have the differential equation satisfied by $\psi_0(r)$ as

$$\mathcal{D}_{0\lambda_0} \psi_0(r) = \frac{2}{3} r^3 \psi_1(r)$$

In order to facilitate the process of finding the solutions, the following properties of the operators $\mathcal{D}_{0\lambda_0}$ are very useful

$$\begin{aligned}\mathcal{D}_{0\lambda_0} \Phi(1, 1, \lambda_1, 1, r) &= -K(2, 2, \lambda_1, 1) + \\ &\quad (2\omega r + 2\lambda_1) \Phi(1, 1, \lambda_1, 1, r) + 2\Phi(1, 1, \lambda_1, 1, r)\end{aligned}\quad (4.31)$$

$$\mathcal{D}_{0\lambda_0} [r \Phi(1, 1, \lambda_1, 1, r)] = -r K(2, 2, \lambda_1, 1) + (2\omega r^2 + 2) \Phi(1, 1, \lambda_1, 1, r)\quad (4.32)$$

we also have

$$\mathcal{D}_{0\lambda_0}\Phi(0, 0, \lambda_0, 1, r) = -K(1, 1, \lambda_0, 1) \quad (4.33)$$

$$\mathcal{D}_{0\lambda_0}(1) = 4\omega r \quad (4.34)$$

$$\mathcal{D}_{0\lambda_0}(r) = (2 - 2r) + 4\omega r^2 \quad (4.35)$$

$$\mathcal{D}_{0\lambda_0}(r^2) = 6r + 2r^2 + 4\omega r^3 \quad (4.36)$$

and

$$\mathcal{D}_{0\lambda_0}\frac{1}{4\omega}\left\{r^2 + \frac{r}{\omega} + \frac{1}{2\omega}\left(\frac{r}{\omega} - 3\right) - \frac{2}{\omega}\frac{\Phi(0, 0, \lambda_0, 1, r)}{K(1, 1, \lambda_0, 1)}\right\} = r^3 \quad (4.37)$$

With the above properties and using the Eq. (4.30) we have obtained the form of $\psi_0(r)$ as

$$\begin{aligned} \psi_0(r) = & \frac{2}{3\omega^2}\left\{\frac{r^2}{4} + \frac{1}{4\omega^2}(1 - 2\lambda_1) - \frac{3}{8\omega}\right\} - \frac{1}{3\lambda_1\omega^4}\Phi(0, 0, \lambda_2, 1, r) \\ & - \frac{1}{6\omega^4}\left\{r^2 + \frac{\lambda_1}{\omega}r - \frac{1}{\omega}\left(1 + \frac{1}{\lambda_1}\right)\right\}\Phi(1, 1, \lambda_1, 1, r) \\ & - \frac{1}{3\omega^4}\left(1 + \frac{1}{\lambda_1}\right)\int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)}{K(1, 1, \lambda_2, t)} \\ & \times \left\{\frac{1 - 2\omega}{\omega(1 + \lambda_1)} - \frac{t}{\omega} - \frac{2}{t + \lambda_1} + \frac{2}{(t + \lambda_1)^2}\right\}\Phi(0, 0, \lambda_2, t, r) \quad (4.38) \end{aligned}$$

Solution for $\psi_2(r)$:

We have the differential equation satisfied by $\psi_2(r)$ as

$$\mathcal{D}_{2\lambda_2}\psi_2(r) = \frac{4}{3}r\psi_1(r)$$

Proceeding in a similar manner as in the previous case, we use the

Following properties of the differential operator $\mathcal{D}_{2\lambda_2}$

$$\mathcal{D}_{2\lambda_2}\Phi(2, 2, \lambda_2, 1, r) = -K(3, 3, \lambda_2, 1) \quad (4.39)$$

$$\mathcal{D}_{2\lambda_2}(1) = 4\omega r - 4 \quad (4.40)$$

$$\mathcal{D}_{2\lambda_2} \left\{ \frac{1}{4\omega} - \frac{1}{\omega} \frac{\Phi(2, 2, \lambda_2, 1, r)}{K(3, 3, \lambda_2, 1)} \right\} = r \quad (4.41)$$

$$\mathcal{D}_{2\lambda_2} \left\{ \frac{\Phi(2, 2, \lambda_2, 1, r)}{K(3, 3, \lambda_2, 1)} \right\} = 1 \quad (4.42)$$

$$\begin{aligned} & \mathcal{D}_{2\lambda_2} \left\{ \frac{1}{3\omega^2} - \frac{1}{3\omega^4} \Phi(1, 1, \lambda_1, 1, r) \right\} = \\ & \frac{4}{3\omega} r - \frac{1}{3\omega^3} r \Phi(1, 1, \lambda_1, 1, r) + \frac{1}{3\omega^3} \int_{\lambda_1}^1 ds e^{-r(s-1)} K(1, 1, 1, \lambda_1, s) s \end{aligned} \quad (4.43)$$

we can obtain the final form of $\psi_2(r)$ as

$$\psi_2(r) = \frac{1}{3\omega^2} - \frac{1}{3\omega^4} \Phi(1, 1, \lambda_1, 1, r) + \frac{2}{3\omega^4} \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)} \Phi(2, 2, \lambda_2, t, r) \quad (4.44)$$

Substituting the above expressions in Eqs. (4.13) and (4.17), we can obtain the analytic expressions for the operators D_1 and D_2 . From this we can obtain a compact form of third order transition amplitude as

$$M_{fg}^{(3)} = \langle f | zD_2 | g \rangle. \quad (4.45)$$

In this discussion we have considered the initial state $|i\rangle$ to be the ground state $|g\rangle$ of hydrogen atom. With this we can obtain amplitudes for three-photon process corresponding to bound state transitions as well as ioniza-

tion cross sections from the ground state.

4.3 Ground to bound state transitions

In the present section we are going to consider three-photon transition from ground state to an excited bound state of atomic hydrogen. In order to obtain the three-photon transition probability, we have to evaluate the corresponding transition matrix element given in Eq. (4.1). With $D_2(\mathbf{r})$, defined in Eq. (4.17) of the last section, we can calculate various transition amplitudes from ground state to excited states allowed by the three-photon selection rules.

The schematic diagram for three-photon bound to bound transitions are depicted in Fig. (4.2). In order to have a three-photon transition from ground state, system has to absorb three photons simultaneously. Here we are considering the three frequencies to be same $\omega_1 = \omega_2 = \omega_3 = \omega$ i.e., all the photons having the same energy and by energy conservation law $E_f - E_i = 3\omega$. The dotted lines in the Fig. (4.2) represent the intermediate virtual states, which are in general, not the eigenstates of the system. Depending on the energy of the incident photon, it is possible that one or both the intermediate state can coincide with the eigenstate of the system, which leads to the 'resonance enhanced transitions'. We can see that the perturbation theory break down for these particular values of photon energy. This is reflected as the singularities of the matrix element given in Eq. (4.1), Because when $E_n - E_i$ become 2ω or ω one of the the denominator in this equation vanishes.

Since the analytical expression for the bound states of atomic hydrogen are known we can evaluate the matrix element in the Eq. (4.8). For a three-photon transition from the ground state to an excited state of principle

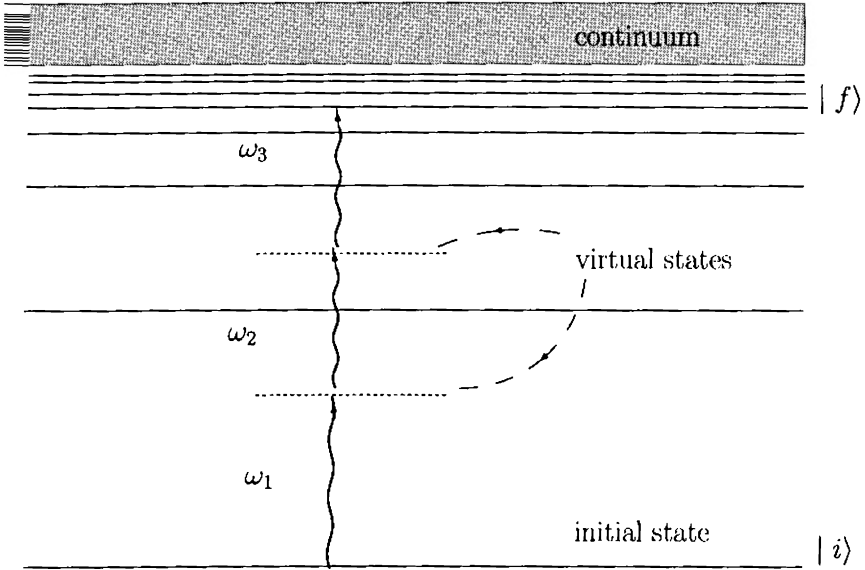


Figure 4.2: Schematic diagram for three-photon transition: the system absorbs three photon simultaneously and get excited to a final bound state $|f\rangle$.

quantum number n , the energy needed for the incoming photon is

$$\omega = \frac{1}{6} \left(1 - \frac{1}{n^2} \right)$$

Now the transition matrix element from the ground state to a final state $|f\rangle$ with principle quantum number n and orbital angular momentum l can be calculated by taking the form of the final state wavefunction as

$$|f\rangle = |nl\rangle = \sqrt{\frac{2l+1}{4\pi}} R_{nl}(r) P_l(\cos\theta) \quad (4.46)$$

where

$$R_{nl}(r) = \frac{2}{n^{l+2}(2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}} (2r)^l \exp\left(-\frac{r}{n}\right) \times F\left(l+1-n, 2l+2, \frac{2r}{n}\right) \quad (4.47)$$

and $F(\cdot)$ is the confluent hypergeometric function. Substituting (4.38), (4.44) and (4.46) in (4.17) and using the orthogonality relation for Legendre polynomials we can see that the transitions are possible only for $l = 1$ and $l = 3$ states. To demonstrate this, let us consider third order matrix element $M_{fg}^{(3)}$ given in Eq. (4.45) and D_2 given in Eq. (4.17)

$$D_2 = \psi_0(r)P_0(u) + r^2\psi_2(r)P_2(u).$$

where $u = \cos\theta$. Now using the recurrence relation

$$uP_2(u) = \frac{3}{5}P_3(u) + \frac{2}{5}P_1(u)$$

we can write

$$zD_2 = r\psi_0(s)P_1(u) + r^3 \left\{ \frac{3}{5}P_3(u) + \frac{2}{5}P_1(u) \right\} \psi_2(r)$$

We have the ground state of hydrogen $|g\rangle = \exp(-r)/\sqrt{\pi}$ as the initial state and the excited bound state given by Eq. (4.46) as the final state. With these expressions the matrix element given in Eq. (4.8) can be written as

$$M_{fi}^3 = \sqrt{\frac{2l+1}{4\pi^2}} \int_0^{2\pi} d\varphi \int_0^\infty r^2 dr R_{nl}(r) e^{-r} \times \int_{-1}^{+1} du P_l(u) \left\{ r\psi_0(s)P_1(u) + r^3 \left(\frac{3}{5}P_3(u) + \frac{2}{5}P_1(u) \right) \right\} \quad (4.48)$$

The angular part of the integration Eq. (4.48) can be done exactly using the orthogonality property of Legendre Polynomial, with the result that from the various possible angular momentum quantum number of the final states, the transition matrix element will have nonzero only when $l = 1$ and $l = 3$. Thus the only final states accessible by three-photon transitions from an initial s state are p and f states, which are the well known selection rules for three-photon transitions.

Now we denote $M_{fg}^{(3)}$ by $M_{nl}^{(3)}$ i. e. , a transition from $|g\rangle$ to final bound state $|nl\rangle$ with principle quantum number n and angular momentum quantum number l . Now the matrix element for a transition to a final state with $l = 1$ and principle quantum number n can be written as

$$M_{n1}^{(3)} = \frac{2}{\sqrt{3}} \int_0^\infty dr R_{n1}(r) e^{-r} \left\{ r^3 \psi_0(r) + \frac{2}{5} r^5 \psi_2(r) \right\} \quad (4.49)$$

and similarly the matrix element for the $l = 3$ transition is

$$M_{n3}^{(3)} = \frac{6}{5\sqrt{7}} \int_0^\infty dr R_{n3}(r) r^5 e^{-r} \psi_2(r) \quad (4.50)$$

The r integration in Eqs. (4.49) and (4.50) can be performed exactly by the use of the standard integrals.

In order to express these integrals in more ordered and compact form, we make use of the functions $I_{nl}(s, k)$ and $\mathcal{I}_{nl}(p, q, \lambda, t, k)$ defined in Eqs. (3.24)

and (3.25) of the previous chapter. Thus

$$\int_0^{\infty} dr R_{nl}(r) e^{-r} r^5 \psi_2(r) = \frac{1}{3\omega^2} I_{nl}(1, 5) - \frac{1}{3\omega^4} \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 5) \quad (4.51)$$

$$+ \frac{2}{3\omega^4} \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)} \mathcal{I}_{nl}(2, 2, \lambda_2, t, 5)$$

$$\int_0^{\infty} dr R_{nl}(r) e^{-r} r^3 \psi_0(r) = \frac{1}{6\omega^2} I_{nl}(1, 5) + \frac{2}{3\omega^2} \left\{ \frac{1}{4\omega^2} (1 - 2\lambda_1) - \frac{3}{8\omega} \right\} I_{nl}(1, 3)$$

$$- \frac{1}{3\lambda_1\omega^4} \mathcal{I}_{nl}(0, 0, \lambda_2, 1, 3) - \frac{1}{6\omega^4} \left\{ \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 5) + \frac{\lambda_1}{\omega} \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 4) \right.$$

$$\left. - \frac{1}{\omega} \left(1 + \frac{1}{\lambda_1} \right) \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 3) \right\} - \frac{1}{3\omega^4} \left(1 + \frac{1}{\lambda_1} \right) \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)}{K(1, 1, \lambda_2, t)}$$

$$\times \left\{ \frac{1 - 2\omega}{\omega(1 + \lambda_1)} - \frac{t}{\omega} - \frac{2}{t + \lambda_1} + \frac{2}{(t + \lambda_1)^2} \right\} \mathcal{I}_{nl}(0, 0, \lambda_2, t, 3) \quad (4.52)$$

By choosing proper values for l in (4.51) and (4.52) the transition matrix elements $M_{n1}^{(3)}$ and $M_{n3}^{(3)}$ in Eqs. (4.49) and (4.50) can be calculated. The integrals given in the above equations can be numerically evaluated for various values for principle quantum number n . Numerical values of $M_{n1}^{(3)}$ and $M_{n3}^{(3)}$ given in Eqs. (4.49) and (4.50) are presented in Table. 4.1 in atomic units for various values of n .

4.4 Three-photon ionization cross sections

In this section we describe the process of three-photon ionization depending on the incident photon energy we can have direct ionization, above one-

n	2	3	4	5	6
$M_{n1}^{(3)}$	182.0	-107.5	-85.23	-65.35	-51.58
$M_{n3}^{(3)}$	-	-	45.32	36.66	29.08
n	7	8	9	10	
$M_{n1}^{(3)}$	-41.87	-34.80	-29.47	-25.36	
$M_{n3}^{(3)}$	23.53	19.47	16.43	14.09	

Table 4.1: Three-photon transition matrix element $M_{n1}^{(3)}$ and $M_{n3}^{(3)}$ for atomic hydrogen in atomic units for various values of principle quantum number n

photon threshold ionization and above two-photon threshold ionization. In order to evaluate the above threshold as well as near resonant processes we need to analytically continue the expressions obtained for direct three-photon ionization.

The differential scattering cross section for three-photon ionization is given by [106]

$$\frac{d\sigma^{(3)}}{d\Omega} = \frac{\alpha}{2\pi} \left(\frac{I}{2I_0} \right)^2 |\mathcal{M}_{fg}^{(3)}|^2 a_0^2 \omega k,$$

where $\mathcal{M}_{fg}^{(3)}$ is the third order transitions matrix element.

In order to evaluate the three-photon scattering cross section, we need to know the expression for the matrix element $\mathcal{M}_{fg}^{(3)}$. The reduced form of the third order matrix element corresponding to the ionization of an electron from the ground state $|g\rangle$ is given by

$$\mathcal{M}_{fg}^{(3)} = \langle f | zD_2 | g \rangle \quad (4.53)$$

The amplitude for continuum transitions can be calculated by taking the

final state wave function to be [107]

$$|f\rangle = 4\pi \sum_{lm} i^l R_{kl}(r) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{k}) \quad (4.54)$$

where $Y_{lm}(\theta, \phi)$ are the well known spherical harmonics and

$$\hat{r} = (\theta, \phi), \hat{k} = (\theta_k, \phi_k)$$

The radial part of the continuum wave function of hydrogen atom for an attractive Coulomb potential can be taken as [107]

$$R_{kl}(r) = e^{\frac{\pi\gamma}{2}} \frac{\Gamma(l+1-i\gamma)}{\Gamma(2l+2)} (2rk)^l e^{ikr} F(l+1-i\gamma, 2l+2, -2ikr) \quad (4.55)$$

Substituting the values of D_2 from Eq. (4.3) and using $z = r \cos(\theta)$ we have

$$\mathcal{M}_{fg}^{(3)} = \langle f | r \cos \theta \{ \psi_0 + r^2 \psi_2 P_2(\cos \theta) \} | g \rangle \quad (4.56)$$

Using the following relations

$$\begin{aligned} P_l(\cos \theta) &= \sqrt{\frac{4\pi}{2l+1}} Y_{l0} \\ \cos \theta P_2(\cos \theta) &= \frac{3}{5} \sqrt{\frac{4\pi}{7}} Y_{30} + \frac{2}{5} \sqrt{\frac{4\pi}{3}} Y_{10} \end{aligned} \quad (4.57)$$

in Eq. (4.56) we get

$$\begin{aligned} \mathcal{M}_{fg}^{(3)} &= \sqrt{\frac{4\pi}{3}} \langle f | r \left\{ \psi_0 + \frac{2}{5} r^2 \psi_2 \right\} Y_{10} | g \rangle \\ &\quad + \sqrt{\frac{4\pi}{7}} \frac{3}{5} \langle f | r^3 \psi_2 Y_{30} | g \rangle \end{aligned} \quad (4.58)$$

Table 4.2: Three-photon scattering cross section per unit squared intensity $\sigma^{(3)}/I^2(\text{cm}^6/W^2)$ for linear polarization when three-photon ionization is energetically possible.

$\lambda(\text{\AA})$	Present	Gao-Starace ^a	Laplanche ^b	Karule ^c
1900	1.17(-46)	1.172(-46)	1.186(-46)	–
2000	5.423(-48)	5.429(-48)	5.581(-48)	5.58(-48)
2100	2.539(-47)	2.541(-47)	2.542(-47)	2.58(-47)
2200	1.588(-47)	1.589(-47)	1.593(-47)	1.59(-47)
2300	2.640(-47)	2.641(-47)	2.650(-47)	2.60(-47)
2400	7.056(-46)	7.057(-46)	7.125(-46)	6.42(-46)
2500	2.948(-46)	2.948(-46)	2.980(-46)	3.03(-46)
2600	1.002(-46)	1.002(-46)	1.008(-46)	1.01(-46)
2700	6.705(-47)	–	–	6.74(-47)

^a Gao and Starace[9] : Using variational method

^b Laplanche et al. [25]

^c Karule.[24] : Using Greens function method

This can be rewritten as

$$\begin{aligned} \mathcal{M}_{fg}^{(3)} = & -i\frac{8\pi}{\sqrt{3}}Y_{10}(\hat{k}) \int dr R_{k1}^*(r) \left\{ r^3\psi_0 + \frac{2}{5}r^5\psi_2 \right\} e^{-r} \\ & + i\frac{24\pi}{5\sqrt{7}}Y_{30}(\hat{k}) \int dr R_{k3}^*(r)r^5\psi_2 e^{-r} \end{aligned} \quad (4.59)$$

Defining $\mathcal{D}_3^{(3)}$ and $\mathcal{D}_1^{(3)}$ as

$$\mathcal{D}_3^{(3)} = i\frac{24\pi}{5\sqrt{7}} \int dr R_{k3}^*(r)r^5\psi_2 e^{-r} \quad (4.60)$$

$$\mathcal{D}_1^{(3)} = -i\frac{8\pi}{\sqrt{3}} \int dr R_{k1}^*(r) \left\{ r^3\psi_0 + \frac{2}{5}r^5\psi_2 \right\} e^{-r} \quad (4.61)$$

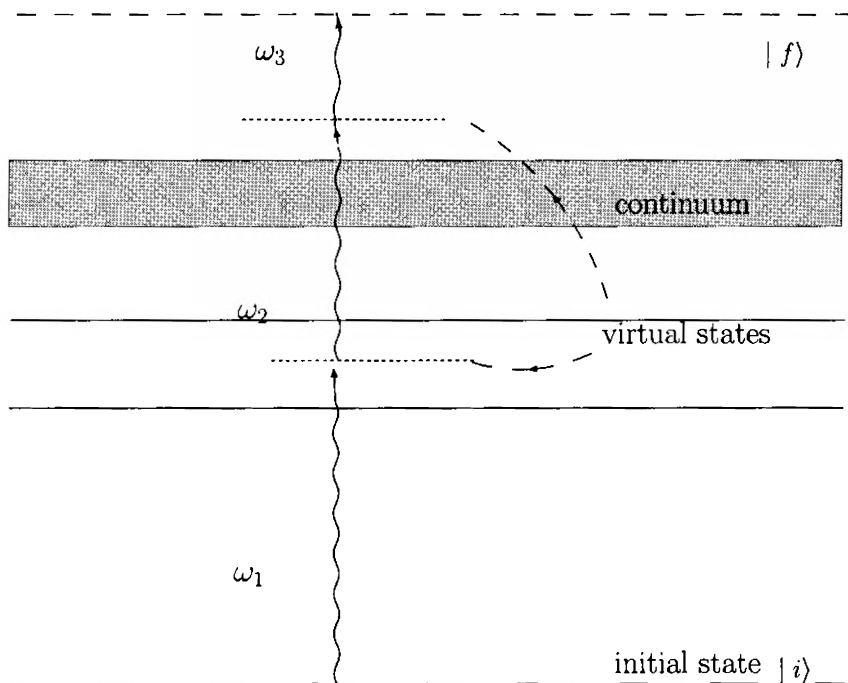


Figure 4.3: Schematic diagram for three-photon ionization: when two-photon ionization is energetically possible

we can write the transition amplitude in a more compact form as

$$\mathcal{M}^{(3)} = \mathcal{D}_3^{(3)} Y_{30}(\hat{k}) + \mathcal{D}_1^{(3)} Y_{10}(\hat{k}) \quad (4.62)$$

It is useful to note that the form of the amplitudes are consistent with the well known selection rules for three-photon transition.

Thus the differential cross section for three-photon ionization for a linear

polarized light in atomic units will take the form

$$\frac{d\sigma^{(3)}}{d\Omega} = \frac{\alpha}{2\pi} \left(\frac{I}{2I_0} \right)^2 | \mathcal{D}_3^{(3)} Y_{30}(\hat{k}) + \mathcal{D}_1^{(3)} Y_{10}(\hat{k}) |^2 a_0^2 \omega k, \quad (4.63)$$

Again these integrals can be put in a neat form using the notations used in the Eqs. (3.24)-(3.25) the integrals in Eqs. (4.60)-(4.61) can be written as

$$\int_0^\infty dr R_{kl}(r) e^{-r} r^5 \psi_2(r) = \frac{1}{3\omega^2} I_{kl}(1, 5) - \frac{1}{3\omega^4} \mathcal{I}_{kl}(1, 1, \lambda_1, 1, 5) \quad (4.64)$$

$$+ \frac{2}{3\omega^4} \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)} \mathcal{I}_{kl}(2, 2, \lambda_2, t, 5)$$

$$\int_0^\infty dr R_{kl}(r) e^{-r} r^3 \psi_0(r) = \frac{1}{6\omega^2} I_{kl}(1, 5) + \frac{2}{3\omega^2} \left\{ \frac{1}{4\omega^2} (1 - 2\lambda_1) - \frac{3}{8\omega} \right\} I_{kl}(1, 3)$$

$$- \frac{1}{3\lambda_1\omega^4} \mathcal{I}_{kl}(0, 0, \lambda_2, 1, 3) - \frac{1}{6\omega^4} \{ \mathcal{I}_{kl}(1, 1, \lambda_1, 1, 5)$$

$$+ \frac{\lambda_1}{\omega} \mathcal{I}_{kl}(1, 1, \lambda_1, 1, 4) - \frac{1}{\omega} (1 + \frac{1}{\lambda_1}) \mathcal{I}_{kl}(1, 1, \lambda_1, 1, 3) \}$$

$$- \frac{1}{3\omega^4} \left(1 + \frac{1}{\lambda_1} \right) \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)}{K(1, 1, \lambda_2, t)}$$

$$\times \left\{ \frac{1 - 2\omega}{\omega(1 + \lambda_1)} - \frac{t}{\omega} - \frac{2}{t + \lambda_1} + \frac{2}{(t + \lambda_1)^2} \right\} \mathcal{I}_{kl}(0, 0, \lambda_2, t, 3) \quad (4.65)$$

Substituting Eq. (4.62) in Eq. (4.63) and integrating over the emitted elec-

tron direction we obtain the total cross section

$$\frac{\sigma_L^{(3)}}{I^2} = \frac{\alpha}{8\pi} \left(\frac{a_0}{I_0} \right)^2 \left\{ |D_3^{(3)}|^2 + |D_1^{(3)}|^2 \right\} \omega k \quad (4.66)$$

where $\sigma_L^{(3)}$ is three-photon cross section for linear polarization. Using the Clebsh-Gordan algebra we can similarly write the cross sections for circular polarization as

$$\frac{\sigma_C^{(3)}}{I^2} = \frac{\alpha}{8\pi} \left(\frac{a_0}{I_0} \right)^2 \frac{5}{2} |D_3^{(3)}|^2 \omega k \quad (4.67)$$

These closed form expressions Eqs. (4.66)-(4.67) for scattering cross section are more elegant than the expressions obtained by other methods.

We have calculated the three-photon cross section for values of photon energy both below and above threshold ionization. This is achieved by performing the integrals in Eqs.(4.65)-(4.65) numerically and substituting it in Eqs.(4.60)-(4.61) and finally using the Eqs.(4.66)-(4.67). The numerical values of these scattering cross sections are presented in different Tables. The tables are organized in such a manner that the incident photon energy falls under various regions, according to which the three-photon ionizations are characterized. Depending on the photon frequency we have to make sure that the expressions obtained for cross sections are defined for the corresponding frequency, if not we have to analytically continue the expressions to suit the numerical evaluation. The manipulation of these expressions are given in the coming section.

4.5 Analytical continuation

As we have mentioned in the earlier sections, the expressions for two-photon and three-photon transition amplitudes are not defined for certain values

Table 4.3: Three-photon scattering cross section per unit squared intensity $\sigma^{(3)}/I^2(cm^6/W^2)$ for circular polarization when three-photon ionization is energetically possible.

$\lambda(\text{\AA})$	Karule ^a	Laplanche ^b	Gao-Starace ^c	Present]
1900	1.65(-45)	2.479(-46)	2.459(-46)	2.454(-46)
2000	1.37(-47)	1.365(-47)	1.326(-47)	1.324(-47)
2100	5.85(-47)	5.771(-47)	5.776(-47)	5.772(-47)
2200	3.95(-47)	3.957(-47)	3.945(-47)	3.943(-47)
2300	3.84(-47)	3.853(-47)	3.840(-47)	3.839(-47)
2400	3.92(-47)	3.935(-47)	3.917(-47)	3.917(-47)
2500	3.97(-47)	3.998(-47)	3.972(-47)	3.972(-47)
2600	3.91(-47)	3.947(-47)	3.906(-47)	3.906(-47)
2700	3.65(-47)	-	-	3.641(-47)

^a Karule.[24]

^b Laplanche et al. [25]

^c Gao and Starace[9]

of energy and it is very interesting to note that those values of energies are coming as the simple poles of the function $\Phi(p, q, \lambda, t, s)$. This requires analytical continuation of the function to expand its region of analyticity so that the function will be 'defined' in extended regions of the complex λ plane. In general, it is complicated method but in our formalism it is very easy to implement this procedure. In order to make the discussion simple, in this section we present the details of analytical continuation of the amplitudes for two-photon process. Generalization to three-photon matrix elements can be easily done.

The solutions of our three differential equations given in Eqs. (4.18)-

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4.5 Analytical continuation

Table 4.4: Three-photon scattering cross section per unit squared intensity $\sigma^{(3)}/I^2 (cm^6/W^2)$ for both linear and circular polarization versus wavelength above one-photon ionization threshold $\omega > 1/2$.

λ (Å)	$\sigma_L^{(3)}/I^2$		$\sigma_C^{(3)}/I^2$	
	Present	Klar-Maq ^a	Present	Klar-Maq ^a
20	5.596(-66)	-	2.470(-66)	-
100	1.959(-59)	-	9.254(-60)	-
200	1.169(-56)	1.16(-56)	6.417(-57)	6.38(-57)
300	4.799(-55)	-	3.023(-55)	-
400	6.632(-54)	6.60(-54)	4.744(-54)	4.72(-54)
500	5.065(-53)	-	4.078(-53)	-
600	2.667(-52)	2.65(52)	2.398(-52)	2.39(-52)
700	1.089(-51)	-	1.085(-51)	-
800	3.702(-51)	3.68(-51)	4.065(-51)	4.04(-51)
900	1.972(-50)	-	1.317(-50)	-

^a Klarsfeld and Maquet[27]

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(4.20) is related to

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)} K(p, q, \lambda, s) \tag{4.68}$$

where

$$K(p, q, \lambda, s) = \left(\frac{1-\lambda}{1+\lambda}\right)^{\frac{1}{2}} (s+\lambda)^{p+\frac{1}{2}} (s-\lambda)^{q-\frac{1}{2}} \tag{4.69}$$

and it is important to note that the integral given in Eq. (4.68) is only defined for $\Re(q - 1/\lambda) > -1$, where \Re denote the real part of. Since λ

is related to ω , for example $\lambda_1 = \sqrt{(1-2\omega)}$, we cannot use the above expression for all values of incident photon energy.

Table 4.5: Three-photon scattering cross section per unit squared intensity $\sigma^{(3)}/I^2(\text{cm}^6/W^2)$ for both linear and circular polarization when two-photon ionization is energetically allowed ($1/4 < \omega < 1/2$).

$\lambda(\text{\AA})$	$\sigma_L^{(3)}/I^2$			$\sigma_C^{(3)}/I^2$	
	Present	Karule ^a	Klar-Maq ^b	Klar-Maq ^b	Present
1000	1.484(-48)	-	-	-	-
1100	3.430(-50)	-	-	-	5.472(-50)
1200	6.121(-48)	5.55(-48)	5.55(-48)	4.67(-48)	5.234(-48)
1300	1.168(-48)	-	-	-	2.379(-48)
1400	1.007(-48)	1.01(-48)	1.00(-48)	2.39(-48)	2.404(-48)
1500	1.355(-48)	1.35(-48)	-	-	3.370(-48)
1600	2.024(-48)	2.02(-48)	2.03(-48)	5.07(-48)	5.056(-48)
1700	3.104(-48)	3.09(-48)	-	-	7.663(-48)
1800	4.761(-48)	4.74(-48)	4.67(-48)	1.13(-47)	1.151(-47)

^a E Karule[20]

^b Klarsfeld and Maquet[27]

But for numerical analysis we need this solution ψ_1 for values of λ such that $\Re(q - 1/\lambda) < -1$. This is done by analytical continuation which is described below.

Since

$$(s - \lambda)^{q - \frac{1}{\lambda}} = \frac{1}{(q + 1 - \frac{1}{\lambda})} \frac{\partial}{\partial s} \{(s - \lambda)^{q + 1 - \frac{1}{\lambda}}\}, \quad (4.70)$$

then substituting in Eq. (4.69) and using it in Eq. (4.68) and performing

an integration by parts we get

$$\begin{aligned} \Phi(p, q, \lambda, t, r) = & \frac{1}{q+1-\frac{1}{\lambda}} \left\{ e^{-r(t-1)} K(p, q+1, \lambda, t) \right. \\ & \left. + r\Phi(p, q+1, \lambda, t, r) - \left(p + \frac{1}{\lambda}\right) \Phi(p-1, q+1, \lambda, t, r) \right\} \end{aligned} \quad (4.71)$$

The appearance of $q+1$ in the right hand side of Eq. 4.71 makes this an important **recurrence relation**. Now it can be used to analytically continue the function $\Phi(p, q, \lambda, t, r)$ for $q - 1/\lambda > -2$, since the right hand side of the equation is well defined for $q - 1/\lambda > -2$. By repeated application of this formula we can analytically continue the function $\Phi(\cdot)$ for $q - 1/\lambda > -3, -4, \dots$ and this is used for calculation of various matrix elements.

The recurrence relation also clearly displays the singularities of $\Phi(\cdot)$ as a function of λ , due the appearance of the simple pole at $q+1 = 1/\lambda$. By repeating this procedure we can see that the function $\Phi(\cdot)$ has simple poles for those values of λ such that $q+n = 1/\lambda$ where $n = 1, 2, 3, \dots$

The transition matrix element can be expressed in terms of the function given in Eq. (4.68) with q as a positive integer. Since λ is related to the photon frequency ω (for example $\lambda_1 = \sqrt{1-2\omega}$), these values of λ corresponds to one- and two-photon intermediate resonance singularities present in Eq. (4.1).

Since

$$\mathcal{D}_{l\lambda}\Phi(l, l, \lambda, 1, r) = -K(l+1, l+1, \lambda, 1) \quad (4.72)$$

this is only true for $l - \frac{1}{\lambda} > -1$. If $l - \frac{1}{\lambda} > -2$. By operating \mathcal{D}_l on the

right hand side the equation 4.71 we get

$$\begin{aligned} \mathcal{D}_l & \left(\frac{1}{l+1-\frac{1}{\lambda}} \left\{ e^{-r(t-1)} K(l, l+1, \lambda, t) r \Phi(l, l+1, \lambda, t, r) \right. \right. \\ & \left. \left. - \left(l + \frac{1}{\lambda} \right) \Phi(l-1, l+1, \lambda, t, r) \right\} \right) \\ & = -e^{-r(t-1)} K(l+1, l+1, \lambda, t) \end{aligned} \quad (4.73)$$

From this result we can see that the analytical continuation indeed results in a solution to the differential equation 4.72 for $l - \frac{1}{\lambda} > -2$ also.

The simple poles of the function $\Phi(l, l, \lambda, t)$ at $l + k - 1/\lambda = 0$ (where l and k are positive integers), are due to intermediate state resonances. For example, if $\lambda = \lambda_1 = \sqrt{1 - 2\omega}$ these poles correspond to one-photon intermediate state resonance. Similarly if $\lambda = \lambda_2 = \sqrt{1 - 2\omega}$, the photon energy corresponds to two-photon intermediate state resonance. This is a very important property of the solution we obtained because any analytic expression equivalent to the Eq. (4.1) should exhibit this property.

And these simple poles as a function of ω present in the original expression given in Eq. (4.1) is clearly manifested in our solution by repeated application of the recurrence relation given in Eq. (4.71).

We have expressed the various amplitudes in terms of $\mathcal{I}_{nl}(l, l, \lambda, t, k)$ and $I_{nl}(s, k)$ given in Eqs. (3.25)-(3.24), which is convenient for numerical evaluation. Since these functions are related to $\Phi(\cdot)$, repeated use of the recurrence relation given in Eq. (4.71) also has to be appropriately used for the evaluation of $\mathcal{I}_{nl}(l, l, \lambda, t, k)$. For example if $l - 1/\lambda < -1$ for $\mathcal{I}_{nl}(\cdot)$ given in Eqs. (4.65)-(4.65) we have to use the recursion relation once. If integrable singularities are present standard method like subtraction procedure has to be employed for the numerical evaluation of the integrals in Eqs. (4.51) and (4.52).

Intermediate resonance will occur when $\omega = (1/2)(1 - 1/n^2) =$, for

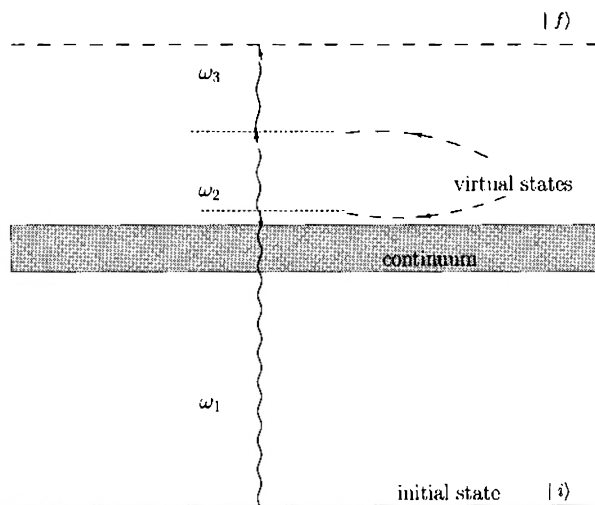


Figure 4.4: Schematic diagram for above one-photon ionization threshold. Transitions are also possible between the continuum states. Here photon energy is sufficient for one-photon ionization to occur and the additional energy is added to the kinetic energy of the emitted electron

$n = 2, 3, 4, 5, \dots$, with corresponding values of $\omega = 0.375, 0.4444, 0.4687, 0.48, \dots$

When $\omega > 1/2$ both λ_1 and λ_2 are purely imaginary, in that case the analytical continuation is very simple and is done by considering the expressions for purely imaginary λ_1 .

Above threshold ionization

Many authors have dealt the problem of above threshold ionization (ATI) in the case of three-photon ionization and there are no single formulation applicable for a wide range of incident photon energy. But we are able to perform a detailed numerical calculation for a wide range of incident wave-

lengths of physical interest using this method. Depending upon the photon energy, we have extensively used the relation given in Eq. (4.71) for analytical continuation for the evaluation of amplitude for various multiphoton processes. The closed integral form of the solution in Eqs. (4.26), (4.38) and (4.44) is very convenient for numerical computation. This form is also useful to see the resonance singularities present in the original perturbation theory result given by Eq. (4.1). By repeatedly using the recurrence relation given by Eq. (4.71), all the singularities will be appear as simple poles in the expression for the transition amplitude[17]. In the case of above one-photon ionization threshold ($\omega > 1/2$) both λ_1 and λ_2 are purely imaginary and above two photon threshold (i. e. , $\omega > 1/4$) only λ_2 is purely imaginary. But even in these cases, we take the analytic expression in Eqs. (4.26), (4.38) and (4.44) as solution to the Eqs. (4.18)-(4.20).

Most of the available data are for the range of wavelengths varying from 1824.472 Å to 2736.708 Å. This range corresponds to the frequency range where three-photon ionization is energetically possible i. e. , threshold or direct ionization. In this range we find that $q - 1/\lambda$ is positive for all values of λ , and hence there so no problem of numerical instability. It may be seen that our data agree quite well with those obtained by Klarsfeld and Maquet [27], where they have used Pade-Sturmian method for the determination of the matrix element but near the vicinity of threshold their method fails. For this range of frequencies cross sections for linear and circular polarization are given in Tables. 4.2-4.3. The available data are compared with results obtained by various other methods for both linear and circular polarization[9, 12, 24, 25].

When two-photon ionization is energetically possible, i. e. , for range of wavelengths between 912.236Å to 1824.472 Å ($1/4 < \omega < 1/2$), only λ_2 is purely imaginary and λ_1 is real, depending on the photon energy we repeatedly use the recursion relation in Eq. (4.71). At $\lambda = 1200$ Å we get the same result (6.42×10^{-32}) published by *Chang* and *Poe* [29], where they

have used the same implicit summation technique. Numerical values for selected wavelengths are compared with results available in the literature and are given in Table 4.5.

Thus for a wide range of incident energy spectrum, the three-photon ionization cross sections from ground state of hydrogen atom are obtained by analytically continuing the solutions wherever needed.

4.6 Conclusion

In the present chapter we have formulated the Dalgarno-Lewis method for three-photon transitions from the ground state of hydrogen atom. We took the third order transition matrix element and obtained an alternate expression, which is elegant and very convenient for numerical evaluation. We have seen from the last chapter that Dalgarno-Lewis procedure recast the problem of infinite summation to the problem of solving second order differential equations. Unlike the second order case, here we have to solve two more differential equations. We obtained the integral representation of solutions to these differential equations by method of laplace transform.

In the section for bound-bound transitions we obtained the transition probabilities for all allowed three-photon transition from the ground state. We found that the expressions are consistent with three-photon selection rules. The radial integrals are done using standard integral and final amplitudes are obtained by numerically integrating the final analytical expressions.

In the section for three-photon ionization, we have calculated the three-photon scattering cross section for both linear and circular polarization. In our formalism the analytical continuation of the expressions are very easy, thus we were able to obtain the values of cross section for incident radiation for almost all values of the frequency. Our results are in excellent agreement with those previously obtained by other authors through different methods.

Chapter 5

Results and Conclusion

Since perturbation theory is valid for intensity of light up to $I = 10^{13}$ Wcm^{-2} , for the treatment of multiphoton processes, the evaluation of higher order perturbative matrix elements become important and among different methods for its evaluation Dalgarno-Lewis treatment has its own merits. The basic idea is to recast the problem of summing over the intermediate states to a problem of solving a system of inhomogeneous differential equations. By doing this we can overcome the problem of infinite summation coming in the perturbative treatment for higher order processes.

In the present thesis we have formulated the Dalgarno-Lewis procedure for two- and three-photon processes and an elegant alternate expressions are derived. Starting from a brief review on various multiphoton processes we have discussed the difficulties coming in the perturbative treatment of multiphoton processes. A small discussion on various available methods for studying multiphoton processes are presented in chapter 2. These theoretical treatments mainly concentrate on the evaluation of the higher order matrix elements coming in the perturbation theory. In chapter 3 we have described the use of Dalgarno-Lewis procedure and its implimenta-

tion on second order matrix elements. The analytical expressions for two-photon transition amplitude, two-photon ionization cross section, dipole dynamic polarizability and Kramers-Heiseberg are obtained in a unified manner. Fourth chapter is an extension of the implicit summation technique presented in chapter 3. We have clearly mentioned the advantage of our method, especially the analytical continuation of the relevant expressions suited for various values of radiation frequency which is also used for efficient numerical analysis.

A possible extension of the work is to study various multiphoton processes from the stark shifted first excited states of hydrogen atom. We can also extend this procedure for studying multiphoton processes in alkali atoms as well as Rydberg atoms. Also, instead of going for analytical expressions, one can try a complete numerical evaluation of the higher order matrix elements using this procedure.

Appendix A

Atomic unit

'Atomic units' (au) is widely used system of units in atomic physics[92]. In 'atomic system of units' we use electron mass and charge as the unit of mass and charge. Bohr radius is taken as unity. Units of length and time are chosen such that $4\pi\epsilon_0 = 1$ and $\hbar = 1$. We have the atomic unit of energy, the 'Hartree energy' E_h as

$$E_h = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_e}{\hbar^2} = \alpha\hbar c/a_0 = 4.35974381(34) \times 10^{-18} \text{ J}$$

which is twice the ionization energy of the hydrogen atom. Here α is the fine-structure constant, where $\alpha^{-1} = 137.035999710(96)$. Hartree energy is related to the SI unit of energy as

$$\begin{aligned} 1 \text{ a.u.} &= 1 \text{ Hartree} = 27.2113834(11) \text{ eV} \text{ and} \\ (1/2) \text{ a.u.} &= 1 \text{ Rydberg} = 13.60569172(53) \text{ eV} \end{aligned}$$

1 atomic unit of energy is equivalent to Hartree = 2 Rydberg = 27.2113834(11)eV

Table A.1: atomic units

Length	Bohr radius a_0
Mass	Electron rest mass m_e
Charge	Elementary charge e
Angular momentum	Planck's constant \hbar
Energy	Hartree energy E_h
Electrostatic force constant	Coulomb's constant $1/(4\pi\epsilon_0)$

Table A.2: derived units

Time	\hbar/E_h	Current	eE_h/\hbar
Velocity	a_0E_h/\hbar	Temperature	E_h/k_B
Force	E_h/a_0	Pressure	E_h/a_0^3

Various quantities in atomic units are presented as tables A1 and A2. Atomic unit of Dipole Moment $ea_0 = 8.47835267(33) \times 10^{-28}$ C cm. In atomic unit the, time scale is set by the electrons period in the Bohr orbit, $\tau_{a_0} = a_0/(\alpha c) = 2.418884326500(18) \times 10^{-17}$ s, where αc is the atomic velocity

One of the widely used definition is the 'Characteristic Atomic Field Strength'. It is the electric field strength associated with the field produced by the proton at the Bohr distance,

$$F_{a_0} = \frac{e}{4\pi\epsilon_0 a_0^2} = 5.14220624(20) \times 10^9 \text{ V/cm.}$$

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