Fractional Revivals in Quantum Systems and their Applications

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for the degree of Doctor of Philosophy in PHYSICS

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CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any University or Institution.

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to

the memory of my brother Sumit

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Abstract

In chapter 1.1, the basic theory of revival and fractional revival phenomena of a wave packet and the autocorrelation function are described. In 1.2, Rydberg atomic system and the diatomic molecular systems are introduced. Next, we have discussed the coherent state in section 1.3. In chapter 1.4, explanation of phase space Wigner distribution, Schrödinger cat states and the definition of sub-Planck scale structure are given. The basic idea of two time scale revival and fractional revival phenomena are described in section 1.5. We end the chapter with definitions of Fourier transform, short-time Fourier transform and the wavelet transform.

In chapter 2, we demonstrate the possibility of realizing sub-Planck scale structures in the mesoscopic superposition of molecular wave packets involving vibrational levels. The time evolution of the wave packet, taken here as the SU(2) coherent state of the Morse potential describing hydrogen iodide molecule, produces cat-like states. Interference of these cat-like states produces sub-Planck structures in phase space. We investigate the phase space dynamics of the coherent state through the Wigner function approach and identify the interference phenomena behind the sub-Planck scale structures. The optimal parameter ranges are specified for observing these features.

In chapter 3, we study the revival and fractional revivals of a diatomic molecular wave packet of circular states whose weighting coefficients are peaked about a vibrational quantum number $\overline{\nu}$ and a rotational quantum number \overline{j} . Furthermore, we show that the interplay between the rotational and vibrational motion is determined by a parameter $\gamma = \sqrt{D/C}$ where D is the dissociation energy and C is inversely proportional to the reduced mass of the two nuclei. Using I_2 and H_2 as examples, we show, both analytically and visually, that for $\gamma \gg \overline{\nu}$, \overline{j} , the rotational and vibrational time scales are so far apart that the ro-vibrational motion gets decoupled and the revival dynamics depends essentially on one time scale. For $\gamma \sim \overline{\nu}$, \overline{j} , on the other hand, the evolution of the wave packet depends crucially on both the rotational and vibrational time scales of revival. In the latter case, an interesting rotational vibrational fractional revival is predicted and explained.

In chapter 4, we show that the time frequency analysis of the autocorrelation function is, in many ways, a more appropriate tool to resolve fractional revivals of a wave packet than the usual time domain analysis. This advantage is crucial in reconstructing the initial state of the wave packet when its coherent structure is short-lived and decays before it is fully revived. Our calculations are based on the model example of fractional revivals in a Rydberg wave packet of circular states. We end by providing an analytical investigation which fully agrees with our numerical observations on the utility of timefrequency analysis in the study of wave packet fractional revivals.

Chapter 1

Introduction

1.1 Introduction

In 1926, Schrödinger proposed a new kind of mechanics known as wave mechanics. In his approach, motion of a particle is described by an equation known as the Scrödinger equation.

A wave function or a quantum state $\Psi(x,t)$, is a solution of wave equation, plays the role of probability amplitude. The quantity $\Psi^*(x,t)\Psi(x,t) dx$ gives the probability of finding the particle in the region dx of configuration space at time t. A wave packet of a quantum system is a superposition of some of its eigenstates. In certain nonlinear quantum systems, a suitably prepared wave packet will, in the course of its evolution, regain its initial form periodically. This is known as the revival of the wave packet [1]. At some intermediate times, the evolving wave packet will break up into a set of replicas of its original form. This is known as the fractional revivals of the wave packet [2]. The phenomena of revival and fractional revivals have been predicted and observed in the wave packet dynamics of various atomic, molecular and optical systems [3, 4]. Rich structures have emerged in the space-time behavior of the probability density for a particle in some exactly solvable potentials [5, 6, 7]. The advent of short-pulsed laser has made it possible to produce and detect coherent superpositions of quantum mechanical states for a variety of physical systems.

In this thesis, we will study fractional revivals in quantum systems that have not been explored yet. Various applications of fractional revivals will also be found.

1.1.1 Revival and fractional revivals

Revivals and fractional revivals [1, 2, 3, 4] occur in the time evolution of a suitably prepared wave packet. Revival closely follows the phrase 'history repeats itself'. If a system, evolving in time, comes back to its initial state at some time, then we will say that the system has undergone a 'revival'. Classical systems such as a pendulum or a planet in Kepler orbit revive after their classical time periods. Quantum mechanically, if the system is described by a wave function $|\Psi(t)\rangle$ at an instant t, then the system will have revived if the absolute square of the overlap between $|\Psi(t)\rangle$ and $|\Psi(0)\rangle$ is unity. This overlap is known as the auto-correlation function of the system and, in Dirac's bra-ket notation, is written as $\langle \Psi(t)|\Psi(0)\rangle$.

Consider a quantum system whose eigenvalues and eigenfunctions are $\{E_n\}$ and $\{\psi_n\}$ respectively (we use $\hbar = 1$). Let the system at t = 0 be described by a wave packet

$$|\Psi(0)\rangle = \sum_{n} c_{n} |\psi_{n}\rangle.$$
(1.1)

Then the time dependent wave packet,

$$|\Psi(t)\rangle = \sum_{n} c_n e^{-iE_n t} |\psi_n\rangle.$$
(1.2)

If E_n is equi-spaced, i.e., of the form $E_n = \alpha n$, as in the case of a simple harmonic oscillator, then revival takes place at the classical period $T_{cl} = 2\pi/\alpha$ since $exp(-iE_nT_{cl}) = exp(-2\pi in) = 1$ for all vales of n.

If E_n is quadratic in n, $E_n = \alpha n + \beta n^2$, then around $T_{rev} = 2\pi/\beta$, the excess phases caused by the quadratic term will be exact multiples of 2π and the system will again behave 'classically'.

Let us then consider a fictitious wave packet which evolves 'classically' in the sense that the corresponding energy spectrum is linear:

$$|\Psi_{\rm cl}(t)\rangle = \sum_{n} c_n |\psi_n\rangle \exp[-2\pi i n t/T_{\rm cl}].$$
(1.3)

This wave packet is identically equal to the initial wave packet at t = 0, i.e., $|\Psi_{cl}(0)\rangle = |\Psi(0)\rangle$. Fractional revivals occur for the original wave packet $|\Psi(t)\rangle$ at $t = \frac{r}{s}T_{rev}$ where

r and s are mutually prime integers. At such times, the phase factor due to the quadratic term $exp(-i\beta n^2 t)$ will have the value $exp(-2\pi i r n^2/s)$. We expand this nonlinear phase in terms of linear phases by means of a discrete Fourier transform:

$$exp(-2\pi i rn^2/s) = \sum_{p=0}^{l-1} a_p \ exp(-2\pi i pn/l)$$
 (1.4)

where l = s/2 when s is an integer multiple of 4 and l = s in all other cases. Substituting in Eq. (1.2) and simplifying, we obtain

$$|\Psi(rT_{\rm rev}/s)\rangle = \sum_{p=0}^{l-1} a_p |\Psi_{\rm cl}(rT_{\rm rev}/s + pT_{\rm cl}/l)\rangle.$$
(1.5)

where,

$$a_p = \frac{1}{l} \sum_{m=0}^{l-1} exp\left[-2\pi i (m^2 \frac{r}{s} - m \frac{p}{l})\right].$$
 (1.6)

Thus, the initial wave packet splits into a set of classical wave packets evaluated at a shifted time. This is known as fractional revivals.

In general, the energy eigenvalues do not have a quadratic form. However, if the weighting probabilities $|c_n|^2$ are strongly centered around a mean value \bar{n} with the condition $\Delta n = |\bar{n} - n| \ll \bar{n}$, then it is appropriate to expand the energy in a Taylor series in n around the value \bar{n} ,

$$E_n \simeq E_{\bar{n}} + E'_{\bar{n}}(n-\bar{n}) + \frac{1}{2}E''_{\bar{n}}(n-\bar{n})^2 + \dots$$
(1.7)

Neglecting the overall time dependent phase and considering up to second order term, we may write Eq. (1.2) as

$$|\Psi(t)\rangle = \sum_{n} c_{n} |\psi_{n}\rangle \exp\left[-2\pi i \left(\frac{(n-\bar{n})}{T_{\rm cl}} + \frac{(n-\bar{n})^{2}}{T_{\rm rev}}\right)t\right]$$
(1.8)

where each term in the expansion defines an important characteristic time scale that depends on \bar{n} :

$$T_{\rm cl} = \frac{2\pi}{E'_{\bar{n}}}, \quad T_{\rm rev} = \frac{4\pi}{E''_{\bar{n}}}.$$
 (1.9)

A classical analogy or picture of the time dependence of the quantum state or the features of the revival and fractional revivals can be given by an ensemble of runners on a circular track. At the beginning of the race, the runners are bunched together, i.e.; they form a well localized initial wave packet. After a few circuits, the runners begin to spread around the track. It is simply that the wave packet consists of a collection of waves of varying frequencies–a group of runners moving at different speeds. The quantum features begin to appear when the racers start to clump–i.e., when the fastest runner catches up to the slowest runner or the quicker runners overtake the slower runners. After many more circuits, they clump back into a single group, corresponding to a full revival or can return, including smaller 'packs' of racers, clumped together, which model fractional revival.

1.1.2 Specific cases of fractional revivals

(i) Consider the wave packet at time $T_{rev}/2$, i. e, r = 1, s = 2, l = s = 2. Eq. (1.5) yields

$$\Psi(t = \frac{1}{2}T_{\rm rev}) = \sum_{p=0}^{1} a_p \Psi_{\rm cl}(\frac{1}{2}T_{\rm rev} + \frac{1}{2}T_{\rm cl})$$

= $a_0\Psi_{\rm cl}(\frac{1}{2}T_{\rm rev}) + a_1\Psi_{\rm cl}(\frac{1}{2}T_{\rm rev} + \frac{1}{2}T_{\rm cl}).$ (1.10)

Using Eq. (1.6), one gets $a_0 = 0$ and $a_1 = 1$, i.e., at $t = \frac{1}{2}T_{rev}$,

$$\Psi(t) = \Psi_{cl}(t + \frac{1}{2}T_{cl}).$$
(1.11)

It is the initial wave packet shifted by half a classical period.

(ii) When $t = \frac{1}{4}T_{rev}$, r = 1, s = 4, l = s/2 = 2, Eq. (1.5) and Eq. (1.6) give

$$\Psi(t = \frac{1}{4}T_{\rm rev}) = \frac{1}{\sqrt{2}} \left[e^{-i\pi/4}\Psi_{cl}(t) + e^{i\pi/4}\Psi_{cl}(t + \frac{1}{2}T_{cl}) \right].$$
 (1.12)

So the initial wave packet will split up into two macroscopically distinct wave packets. This splitting is essentially a non-classical behavior.

(iii) Similarly, at $t = \frac{1}{8}T_{rev}$ (r = 1, s = 8, l = s/2 = 4), one can find

$$\Psi(t = \frac{1}{8}T_{\rm rev}) = \frac{1}{\sqrt{2}}e^{-i\pi/4} \left[\left(\Psi_{cl}(t) - \Psi_{cl}(t + \frac{1}{2}T_{cl}) \right) + e^{i\pi/4} \left(\Psi_{cl}(t + \frac{1}{4}T_{cl}) + \Psi_{cl}(t + \frac{3}{4}T_{cl}) \right) \right].$$
(1.13)

Thus, at $t = \frac{1}{8}T_{rev}$, there will be four-way break up of the initial wavepacket. For other cases at $t = \frac{r}{s}T_{rev}$ (where r, s are mutually prime), the initial wave packet breaks up accordingly and shows the signature of fractional revivals.

1.1.3 Autocorrelation function

The revival dynamics of wave packets has mostly been studied through the autocorrelation function as it relates directly to the observable signal in the pump-probe type experiments for studying the wave packet dynamics [8, 9, 10, 11]. Furthermore, the ionization signal in a pump-probe type experiment should show the same periodicity in the autocorrelation function. This function for an evolving wave packet $\Psi(\mathbf{r}, t)$ is given by the overlap integral $A(t) = \langle \Psi(\mathbf{r}, t) | \Psi(\mathbf{r}, 0) \rangle$. It is, by now, well understood how the prominent features of revival and fractional revivals can be gauged from a plot of $|A(t)|^2$ as a function of time. System will revive if the absolute square of the overlap between $\langle \Psi(\mathbf{r}, t) |$ and $|\Psi(\mathbf{r}, 0) \rangle$ is unity. Fractional revivals appear as periodic peaks in the autocorrelation function. The absolute square of the autocorrelation function can be written as

$$|A(t)|^{2} = \left|\sum_{n} |c_{n}|^{2} e^{-iE_{n}t}\right|^{2}$$
(1.14)

where $|c_n|^2$ gives the weighting probabilities. The above expression can well describe, in detail, the time dependence of a generic wave packet, even in the absence of any other information of the system. The general structure of $|A(t)|^2$ is given by

$$|A(t)|^{2} = \left|\sum_{n} |c_{n}|^{2} e^{-iE_{n}t}\right|^{2} = \sum_{n} |c_{n}|^{4} + 2\sum_{n \neq m} |c_{n}|^{2} |c_{m}|^{2} \cos\left(\frac{(E_{n} - E_{m})t}{\hbar}\right). \quad (1.15)$$

The second (oscillatory) term in Eq. (1.15) remains highly correlated and reproduces the approximate periodicity for smaller time scales. For larger time scales, this oscillatory term becomes gradually out of phase. Thus, it can lead to high frequency oscillation around the constant value given by the first term in Eq. (1.15).

In our work, we have chosen atomic and molecular systems to see the specific applications of fractional revivals in (i) Rydberg atom and (ii) diatomic molecular system.

1.2 Atomic and molecular systems

1.2.1 Rydberg atom

A Rydberg atom is an excited atom whose outer electron has been excited to very high energy states, far from the nucleus. A Rydberg wave packet is formed by a coherent superposition of highly excited states or Rydberg states. These wave packets play a fundamental role in our understanding of the bridge between quantum and classical concepts of the trajectory of a particle. When a Rydberg atom is excited by a short laser pulse, a state is created that has classical behavior for a limited time [1]. Short laser pulses (pump pulses) are used to excite a wide range of states simultaneously. For the purpose of detection, another pulse, called probe pulse is used as a function of the delay time from the first pulse. In experiments, initially one-electron-like atoms such as potassium and rubidium have been used. They have ionization potential of order 4eV, requiring laser wave length of order 2858Å, which produces the Rydberg wave packet around $\overline{n} = 65$.

Depending on the excitation scheme, either a radially localized wave packet [1, 12, 13] or a packet localized in the angular co-ordinate is produced [14]. In 1990, Geata *et al.* [15] studied another type of wave packet which is the circular wave packet. These are localized in both radial and angular co-ordinates.

Here we discuss circular Rydberg wave packets, which consist of a sum of fully aligned eigenstates with l = m = n - 1, where l, m and n are orbital, azimuthal and principle quantum numbers, respectively. These states have been widely used in the literature because of their largest magnetic moment, smallest Stark effect and longest radiative lifetime. Two methods have been studied to produce these states, (i) the adiabatic microwave transfer method and (ii) the use of crossed electric and magnetic fields [16]. We restrict our analysis here to wave packets for hydrogen, having energies $E = -\frac{1}{2n^2}$ (in a.u.).

1.2.2 Diatomic molecular system

Why study the revival dynamics of molecular wave packets?

A new field of molecular optics is emerging where lasers are used to manipulate the

internal and external degrees of freedom of molecules, to deflect beams of molecules, to control molecular dynamics, and to align molecules. However, our abilities are limited by time scales. Chemical reactions can be extremely fast, with durations of less than a picosecond. In the absence of suitable tools we would only uncover the initial and final states of reactions, and then the knowledge of any intermediate state could be obtained only indirectly (possible side products, fluorescence during the reaction etc.). Furthermore, without the tools, the steering of fast processes would not be easy, because if it required a careful sequence of external manipulations or events, the interval between the events would necessarily have to be less than the duration of the reaction. However, the recent development of ultra short laser pulses with durations so that they can be studied and perhaps even be controlled. Much of the early work in understanding bond breaking and making on these time scales was undertaken by Ahmed H. Zewail [17], who received the Nobel prize in 1999, for 'showing that it is possible with rapid laser technique to see how atoms in a molecule move during a chemical reaction'.

The idea of ultra short pulses sounds like a nightmare for a high precision spectroscopist. As we make pulses shorter and shorter, we enlarge the pulse bandwidth, and thus instead of interacting with a small, and very selected, group of molecular states we involve a very large number of states. Typically a femtosecond pulse interacting with a molecule excites several vibrational states simultaneously. As we gain localization in time, we lose localization in energy. As a result it becomes more meaningful to consider not single quantum states, but their superposition. In other words, we enter the world of wave packets and their time resolved dynamics.

As mentioned above, an important motivation for femtochemistry is the possibility to manipulate chemical reactions. However we prefer to take another view of the situation. Femtosecond pulses have given us a method to create and observe quantum mechanical superposition. The study of the time evolution of these superposition is a fascinating part of fundamental research in molecular physics (and chemistry), and other areas of physics too. Just as the invention of lasers quickly made it possible to discover a wealth of explicitly time dependent quantum phenomena in atomic systems, femtosecond pulses open up a new

regime in molecular dynamics.

Morse potential

The well known convenient model for describing the diatomic molecular system was first introduced by Morse [18] in 1929. There are a number of empirical functions in closed form that can be used to give potential energy curves that offer adequate approximations for many purposes. One of the best known model of these is the Morse potential. It is a better approximation for the vibrational structure of the molecule than the quantum harmonic oscillator because it explicitly includes the effects of bond breaking, such as the existence of unbound states. The potential describing the vibrational motion of a diatomic molecule has the form

$$V(x) = D(e^{-2\beta x} - 2e^{-\beta x}), \qquad (1.16)$$

where $x = r/r_0 - 1$, r_0 is the equilibrium value of the inter-nuclear distance r, D is the dissociation energy and β is a range parameter. The Morse potential, as a model, has a range of applicability for real systems. It is much used in spectroscopic applications as it is possible to solve Schrödinger equation for this system.

Solving Schrödinger equation for the Morse oscillator

Schrödinger equation for the Morse potential is given by

$$\frac{-\hbar^2}{2\mu r_0^2} \frac{d^2\psi}{dx^2} + D(e^{-2\beta x} - 2e^{-\beta x})\psi = E\psi, \qquad (1.17)$$

where μ is the reduced mass, $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

Then we get

$$\frac{d^2\psi}{dx^2} + (-\delta^2 + 2\gamma^2 e^{-\beta x} - \gamma^2 e^{-2\beta x})\psi = 0, \qquad (1.18)$$

where

$$\delta^2 = -\frac{2\mu E r_0^2}{\hbar^2}; \qquad \gamma^2 = \frac{2\mu D r_0^2}{\hbar^2}.$$
 (1.19)

Changing the variable with $\xi = 2\lambda e^{-\beta x}$, Eq. (1.17) becomes

$$\frac{d^2\psi}{d\xi^2} + \frac{1}{\xi}\frac{d\psi}{d\xi} + \frac{\lambda^2}{\xi^2}\left[E/D - \left(\frac{\xi}{2\lambda}\left(\frac{\xi}{2\lambda} - 2\right)\right)\right]\psi = 0, \qquad (1.20)$$

where

$$\lambda = \sqrt{\frac{2\mu Dr_0^2}{\beta^2 \hbar^2}}; \qquad 0 < \xi < \infty.$$
(1.21)

 ψ must be finite, single valued and continuous over this range. Assuming $\psi = e^{-\xi/2} \xi^{s/2} F(\xi)$, Eq. (1.20) gives

$$\xi \frac{d^2 F}{d\xi^2} + (s - \xi + 1)\frac{dF}{d\xi} + \left[\frac{s^2}{4\xi} + \frac{\lambda^2 E}{\xi D} + (\lambda - s/2 - 1/2)\right] = 0.$$
(1.22)

The solution will be a finite polynomial if $(\lambda - s/2 - 1/2) = n$, is an integer. The quantity s is given by

$$s = \sqrt{-\frac{8\mu r_0^2}{\beta^2 \hbar^2}}E,\tag{1.23}$$

and the corresponding $F(\xi) = L_n^s(\xi)$, is the associate Laguerre Polynomials. Eigen functions of the Morse potential can be written as

$$\psi_n^{\lambda}(\xi) = N e^{-\xi/2} \xi^{s/2} L_n^s(\xi), \qquad (1.24)$$

where N is the normalization constant. Normalization condition gives

$$\frac{r_0|N|^2}{\beta} \int_0^\infty \frac{[\psi_n^\lambda]^2(\xi)}{\xi} d\xi = 1.$$
 (1.25)

It yields

$$N = \left[\frac{\beta(2\lambda - 2n - 1)\Gamma(n + 1)}{\Gamma(2\lambda - n)}\right]^{1/2}.$$
(1.26)

Rotational correction of Morse formula

In the above section, we omitted the rotational energy term which is much smaller than that of vibration. In the study of many fields, e.g. astrophysical work, it becomes necessary to examine the effect of the rotational motion on the vibrational levels of a diatomic molecule in which the Morse potential plays the role of the internuclear potential. This rotational correction has been included by Pekeris in 1934 [19].

Solving Schrödinger equation for the Pekeris Model

A rotational correction term has to be added in the Schrödinger radial equation. If the rotational quantum number j is non-zero, the centrifugal potential is

$$V' = \frac{\hbar^2 j(j+1)}{2\mu r^2}.$$
(1.27)

Using $r/r_0 - 1 = x$ and the expression of γ from Eq. (1.19), we get

$$V' = \frac{j(j+1)}{\gamma^2} D \frac{1}{(1+x)^2}.$$
(1.28)

The nuclear distance r will not fluctuate very far from the equilibrium position at r_0 even for higher vibrational levels. We expand about $r = r_0$ in a power series and keep upto quadratic term:

$$V' = \frac{j(j+1)}{\gamma^2} D(1 - 2x + 3x^2).$$
(1.29)

As an alternative potential V' can be replaced as

$$\tilde{V}' = \frac{j(j+1)}{\gamma^2} D(C_0 + C_1 e^{-\beta x} + C_2 e^{-2\beta x}), \qquad (1.30)$$

where

$$C_0 = 1 - \frac{3}{\beta} + \frac{3}{\beta^2}; \quad C_1 = \frac{4}{\beta} - \frac{6}{\beta^2}; \quad C_2 = -\frac{1}{\beta} + \frac{3}{\beta^2}.$$
 (1.31)

With this rotational correction term the radial part of Scrödinger equation becomes

$$\frac{d^2 R_{\nu j}}{dx^2} + \left(-\delta_1^2 + 2\gamma_1^2 e^{-\beta x} - \gamma_2^2 e^{-2\beta x}\right) R_{\nu j} = 0, \qquad (1.32)$$

where

$$\beta_1^2 = \beta^2 + j(j+1)C_0; \quad \gamma_1^2 = \gamma^2 - \frac{1}{2}j(j+1)C_1; \quad \gamma_2^2 = \gamma^2 + j(j+1)C_2$$
(1.33)

and ν and j are vibrational and rotational quantum numbers. Solving the above equation with the scaled variable y, one obtains

$$R_{\nu j}(y) = N_{\nu j} \exp(-y/2) y^{b/2} L_{\nu}^{b}(y)$$
(1.34)

where

$$b = (2/\beta)[\gamma_1^2/\gamma_2 - \beta(\nu + 1/2)],$$

$$y = (2\gamma_2/\beta) \exp(-\beta x),$$

$$N_{\nu j} = [\beta b\nu! / \Gamma(b + \nu + 1)]^{1/2}.$$
(1.35)

The complete wave function $\psi_{\nu jm}(\mathbf{r})$, including both rotation and vibration, is given by

$$\psi_{\nu jm}(\mathbf{r}) = r^{-1} R_{\nu j}(y) Y_{jm}(\theta, \phi), \qquad (1.36)$$

where $Y_{jm}(\theta, \phi)$ are the spherical harmonics. Here, $L^b_{\nu}(y)$ is a generalized Laguerre polynomial and $N_{\nu j}$ is the normalization constant. The corresponding energy eigenvalues can be written in the form of a Dunham series:

$$E_{\nu j} = C \sum_{ik} (-1)^{i+k+1} \beta_{ik} (\nu + 1/2)^i j^k (j+1)^k, \qquad (1.37)$$

where $C = \hbar^2/(2Mr_0^2)$ and M is the reduced mass of the two nuclei. The coefficients β_{ik} are positive real quantities that depend on β and $\gamma = \sqrt{D/C}$ only,

$$\beta_{00} = \gamma^2, \quad \beta_{01} = 1, \quad \beta_{02} = 9(\beta - 1)^2 / (4\beta^4 \gamma^2),$$
(1.38)

$$\beta_{10} = 2\beta\gamma, \quad \beta_{20} = \beta^2, \quad \beta_{11} = 3(\beta - 1)/(\beta\gamma).$$
 (1.39)

In chap. 2, we will discuss the Morse coherent state involving vibrational levels and its time evolution in both co-ordinate space and phase space. We will study the well known Wigner phase space distribution to find the sub Planck scale structure.

1.3 Coherent state

In 1926, Schrdinger first introduced the coherent states to describe non-spreading wave packets for harmonic oscillators [20]. Harmonic oscillator coherent states arise in systems whose dynamical symmetry group is the Heisenberg-Weyl group. Coherent states of other symmetry groups, e.g., SU(1, 1), SU(2) have also found physical applications [21]. Two important properties of the coherent states are i) resolution of unity and ii) overcompleteness. Coherent states are defined in three different ways:

(i) These are displaced vacuum states:

$$|\alpha\rangle = D(\alpha)|0\rangle. \tag{1.40}$$

The displacement operator $D(\alpha)$, operating on the vacuum state, is given by

$$D(\alpha) = e^{-|\alpha|^2/2} e^{\alpha a^{\dagger}} e^{-\alpha^* a}.$$
 (1.41)

(ii) These are eigenstates of the annihilation operator:

$$a|\alpha\rangle = \alpha|\alpha\rangle. \tag{1.42}$$

Since light is, in general, detected by absorption, coherent states have the nice property that they remain coherent even after detection.

(iii) Harmonic oscillator coherent states are states of minimum uncertainty: $\Delta p \Delta x = \hbar/2$, and thus are most classical within the quantum framework.

These three definitions are equivalent for the harmonic oscillator coherent state. It is not the case for coherent states in general. Output from a well stabilised laser is a coherent state.

It was found that under the action of a Hamiltonian which is a non-linear function of the photon operator(s) only, an initial coherent state loses its coherent structure quickly due to quantum dephasing induced by the nonlinearity of the Hamiltonian; then regains it (revival) after an interval. At fractions of this time interval, the initial coherent state breaks up into a superposition of two or more coherent states which also can have a coherent structure [22]. This is an example of the quantum phenomenon of fractional revivals, or, the formation of Schrödinger cat and cat-like states [23, 24] which, unlike a coherent state, have many non-classical properties.

1.4 Phase space and Quasi-probability distribution

In classical physics, a particle has a definite position x and momentum p. It is common to build a 6N dimensional space, where N is the number of particles constituting the system. This space is called the phase space. Hence, it is possible to represent the state of the system by a point in phase space. For an ensemble or a collection of particles, the probability of finding a particle at (x, p) in phase space is given by a probability distribution, statistically. The average of any function f(x, p) is expressed as

$$\langle f \rangle_C = \int \int f(x,p) P(x,p) dx dp,$$
 (1.43)

where, P(x, p) gives the probability distribution. In quantum physics, this is not possible because of Heisenberg's uncertainty principle. A joint probability distribution of both these variables can be defined but simultaneous probability distribution for position and momentum cannot be interpreted i.e., one cannot define a true phase space probability distribution. For this reason, these distributions are named as quasi probability distribution. Similar to classical physics, the average value of any quantum mechanical operator can be defined as

$$\langle f \rangle_Q = \int \int f(x,p) P_Q(x,p) dx dp,$$
 (1.44)

where $P_Q(x, p)$ gives the quasi-probability distribution or phase space distribution. Thus this distributions provide closest quantum analogy of the classical phase space distribution and have proven to be a useful tool for studying many quantum systems.

1.4.1 Wigner distribution

The most widely used phase space distribution is Wigner distribution [25]. The Wigner function W(x, p; t) is the joint probability distribution for measuring both the quadratures. In terms of position space wave functions, it can be defined as

$$W(x,p;t) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x-z,t)\psi(x+z,t)e^{-2ipz/\hbar}dz,$$
 (1.45)

whereas in momentum space:

$$W(x,p;t) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \phi^*(p-z',t)\phi(p+z',t)e^{-2ixz'/\hbar}dz'.$$
 (1.46)

This Wigner function is a useful tool to visualize the correlated position-momentum behavior of quantum eigen states and wavepackets.

Important properties

(i) Wigner fuction is always real:

The definition of the Wigner function is given by

$$W(x,p;t) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x-z,t)\psi(x+z,t)e^{-2ipz/\hbar}dz.$$
 (1.47)

Now, we write

$$W^*(x,p;t) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi(x-z,t)\psi^*(x+z,t)e^{2ipz/\hbar}dz.$$
 (1.48)

Changing variable by $z = -\bar{z}$, above relation becomes

$$W^{*}(x,p;t) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi^{*}(x-\bar{z},t)\psi(x+\bar{z},t)e^{-2ip\bar{z}/\hbar}d\bar{z}$$

= $W(x,p;t).$ (1.49)

Of course, it is one of the desired properties of probability distributions.

(ii) Probability density in one variable can be obtained by integrating W(x, p; t) over the another variable. Making use of Dirac δ function, one can find

$$\int_{-\infty}^{\infty} W(x, p; t) dp = |\psi(x, t)|^{2}$$
$$\int_{-\infty}^{\infty} W(x, p; t) dx = |\psi(p, t)|^{2}.$$
(1.50)

This is another necessary condition for a joint probability distribution.

(iii) The Wigner function of a state can have negative values which indicates that the state has nonclassical nature. Two distinct quantum states, $\psi(x, t)$ and $\chi(x, t)$, satisfy the relation:

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp W(x,p;t)_{\psi} W(x,p;t)_{\chi} = \frac{2}{\pi\hbar} |\langle \psi | \chi \rangle|^2.$$
(1.51)

If ψ and χ are orthogonal states, then $\langle \psi | \chi \rangle = 0$.

Wigner functions have been studied under several physical conditions. It can be measured by tomography. Wigner function of molecular vibrational state can be reconstructed from the time-resolved fluorescence spectra via inverse random transform. This is known as emission tomography [26, 27, 28]. It employs time-resolved spectroscopic data, which can be inverted to obtain phase space quasi probability distribution that contain all the information about the vibrational states. The Wigner function of a Schrödinger cat state exhibits typical Gaussian-like probabilities located at two different regions of phase-space, with an additional interference term that takes negative values.



Figure 1.1: Scrödinger cat states.

1.4.2 Mesoscopic superposition

Schrödinger cat states

Mesoscopic superpositions of states has attracted a great deal of attention. They lie in between the macroscopic and microscopic world or at the interface of classical and quantum worlds. These superpositions exhibit very important interference effects [29, 30, 31]. The simplest superposition gives the well known Schrödinger cat states giving rise to the socalled "Cat paradox" of Scrödinger [20]. Such superposition is closely connected to the occurrence of fractional revivals in the non linear dynamics of quantum systems [32, 33, 34]. Quantum superposition of classically distinguishable state of a molecule can create such Scrödinger cat states. A fractional revival at one-fourth or three-fourth of revival time can produce such a superposition of two coherent states as shown in Fig. 1.4.1. The optical Scrödinger cat states are superposition of coherent states and are eigenstates of the operator a^2 [23, 31, 35, 36]. A vibrational analog of such states can be realized in an experiment of double pulse or chirped pulse excitation [37].



Figure 1.2: Sub-Planck scale structures produced in a superposition of four optical coherent states in phase space.

1.4.3 Sub-Planck scale structure and Decoherence

An unexpected sign of quantum interference in phase space can play a surprisingly important role in the distinguishbility of quantum states. A phase space structure associated with sub-Planck scale ($<<\hbar$) can exit in non-local quantum superpositions or Scrödinger cat states. Zurek [38] showed that appropriate superposition of some of these states with a classical action A can lead to sub-Planck-scale structures in phase space. These sub-Planck-scale structures in phase space are characterized by an area \hbar^2/A . Apart from their counterintuitive nature and theoretical significance, the above scale has been shown to control the effectiveness of decoherence [35, 39, 40, 41], a subject of tremendous current interest in the area of quantum computation and information [42]. Zurek's realization made use of dynamical systems which exhibit chaotic behavior in the classical domain. Recently a cavity QED realization involving the mesoscopic superposition of the compass states has been given [43, 44] (see Fig. 1.4.1). In principle, one could also use superpositions of cat-like states arising in quantum optical systems with large Kerr nonlinearity. In practice, such a large nonlinearity in not available though some proposals for the enhancement of the kerr nonlinearity exist [45]. The existence of such superpositions is closely connected to the occurrence of fractional revivals in the nonlinear dynamics of quantum systems [13, 32, 33, 34]. We demonstrate the possibility of realizing sub-Planck-scale structures

in the mesoscopic superposition of molecular coherent state wave packets, which involve vibrational levels. We study the spatiotemporal structure of these states, paying special attention to the fractional revival, which gives rise to four coherent states required for the observation of the sub-Planck structure. Very recently, sub Planck scale structures were also found in phase space using the Kirkwood-Rihaczek distribution [46]. It is also found [47] in two entangled cat states which are most robust against decoherence.

Two typical problems of small quantum parameter estimation are (i) high precision phase measurement and (ii) weak force measurement. These structures in the Wigner function can be used to achieve Heisenberg-limited sensitivity in weak force measurement [48]. Sensitivity of quantum states to small rotation or displacement is related to the smallest structure present in phase space—sub Planck scale structure.

It also determines the sensitivity of a quantum system to perturbation or decoherence. Decoherence occurs because of the interaction of the system with its surroudings. Any system, in reality, no matter how isolated it is, interacts with the environment. This interaction destroys the coherent structure of quantum superposition and leaves it as an incoherent mixture of those states. This is known as decoherence [41]. This process is almost instantenuous for open, macroscopic systems as they are always interacting with the environment e.g., air molecules or photons. In other words, the effect of decoherence on density matrix is essentially the decay or rapid vanishing of the off-diagonal elements of the partial trace of the joint system's density matrix. The main source of decoherence in vibrational molecular wavepacket is the coupling between the vibrational and rotational modes which can be minimized by making use of close control method [49].

In chap. 3, we discuss the revival dynamics of the system whose energy spectrum depends on two quantum numbers.

1.5 Two time scales: revival and fractional revivals

In the literature, most of the calculations explored the revival dynamics of a system whose energy spectrum depends on a single quantum number. But there are many systems for which the energy spectrum depends on more than one quantum number. A practical ex-

ample in this category is the ro-vibrational motion of diatomic molecules. The energy spectrum, in this case, depends on both the vibrational quantum number ν and the rotational quantum number j. The revival dynamics of wave packets depending on two quantum numbers is complicated [50, 51, 52] and thus one often resorts to simplified models or special cases. For example, most authors considered either the vibrational dynamics in an anharmonic model [9, 53, 54] or the rotational dynamics in a rigid rotator model [55, 56, 57]. We should note that this practice of treating vibration and rotation separately was quite common even in the earlier literature spanning over many decades. However, as noted by Tennyson et al [58], there was no a *priori* reason behind this practice except that it simplifies computation and also spectroscopic data suggested that the ro-vibrational coupling is small for many diatomic molecules.

1.5.1 Generalization of one time scale to two time scales

Consider a system whose energy $E_{n_1n_2}$ depends on two quantum numbers n_1 and n_2 . A wave packet $\Psi(t)$ is formed as a coherent superposition of states $\Phi_{n_1n_2}$ with energies $E_{n_1n_2}$:

$$\Psi(t) = \sum_{n_1 n_2} c_{n_1 n_2} \Phi_{n_1 n_2} exp(-iE_{n_1 n_2} t).$$
(1.52)

We assume that the weighting coefficients $c_{n_1n_2}$ are strongly peaked around $n_1 = \bar{n}_1$ and $n_2 = \bar{n}_2$ and that the wave packet consists of only those states for which $|n_1 - \bar{n}_1| \ll \bar{n}_1$ and $|n_2 - \bar{n}_2| \ll \bar{n}_2$. These conditions allow us to expand $E_{n_1n_2}$ about $E_{\bar{n}_1\bar{n}_2}$ in a Taylor series and retain a finite number of terms in the expansion. The energy can then be expanded in a Taylor series as

$$E_{n_{1}n_{2}} \simeq E_{\bar{n}_{1}\bar{n}_{2}} + \left(\frac{\partial E}{\partial n_{1}}\right)_{\bar{n}_{1},\bar{n}_{2}} (n_{1} - \bar{n}_{1}) + \left(\frac{\partial E}{\partial n_{2}}\right)_{\bar{n}_{1},\bar{n}_{2}} (n_{2} - \bar{n}_{2}) + \frac{1}{2} \left(\frac{\partial^{2} E}{\partial n_{1}^{2}}\right)_{\bar{n}_{1},\bar{n}_{2}} (n_{1} - \bar{n}_{1})^{2} + \frac{1}{2} \left(\frac{\partial^{2} E}{\partial n_{2}^{2}}\right)_{\bar{n}_{1},\bar{n}_{2}} (n_{2} - \bar{n}_{2})^{2} + \left(\frac{\partial^{2} E}{\partial n_{1} \partial n_{2}}\right)_{\bar{n}_{1},\bar{n}_{2}} (n_{1} - \bar{n}_{1})(n_{2} - \bar{n}_{2}) + \dots$$
(1.53)

Keeping terms to second order and neglecting an overall phase due to $E_{\bar{n}_1\bar{n}_2}$, we rewrite $\Psi(t)$ as a double sum in shifted indices $\mu = n_1 - \bar{n}_1$ and $k = n_2 - \bar{n}_2$:

$$\Psi(t) = \sum_{\mu k} \tilde{c}_{\mu k} \tilde{\Phi}_{\mu k} \exp\left[-2\pi i t \left(\frac{\mu}{T_{\rm cl}^{(n_1)}} + \frac{k}{T_{\rm cl}^{(n_2)}} - \frac{\mu^2}{T_{rev}^{(n_1)}} + \frac{k^2}{T_{rev}^{(n_2)}} - \frac{\mu k}{T_{rev}^{(n_1n_2)}}\right)\right], \quad (1.54)$$

where $\tilde{c}_{\mu k} = c_{\mu + \bar{n}_1, k + \bar{n}_2}$, $\tilde{\Psi}_{\mu k} = \Psi_{\mu + n_1, k + n_2}$. For each quantum number, there is a classical period and a revival time scale. The third time scale $T_{rev}^{(n_1 n_2)}$, is the cross revival time. These are defined as

$$T_{\rm cl}^{(n_1)} = 2\pi \left(\frac{\partial E_{n_1 n_2}}{\partial n_1}\right)_{\bar{n}_1 \bar{n}_2}^{-1}, \ T_{\rm cl}^{(n_2)} = 2\pi \left(\frac{\partial E_{n_1 n_2}}{\partial n_2}\right)_{\bar{n}_1 \bar{n}_2}^{-1},$$

$$T_{\rm rev}^{(n_1)} = -4\pi \left(\frac{\partial^2 E_{n_1 n_2}}{\partial n_1^2}\right)_{\bar{n}_1 \bar{n}_2}^{-1}, \ T_{\rm rev}^{(n_2)} = 4\pi \left(\frac{\partial^2 E_{n_1 n_2}}{\partial n_2^2}\right)_{\bar{n}_1 \bar{n}_2}^{-1},$$

$$T_{\rm rev}^{(n_1 n_2)} = -2\pi \left(\frac{\partial^2 E_{n_1 n_2}}{\partial n_1 \partial n_2}\right)_{\bar{n}_1 \bar{n}_2}^{-1}.$$
(1.55)

When t is small, the dominant phase terms in Eq. (1.54) are the first two. They produce beating between the classical periods $T_{\rm cl}^{(n_1)}$ and $T_{\rm cl}^{(n_2)}$. The two classical periods are commensurate with each other if

$$T_{\rm cl}^{(n_1)} = \frac{a}{b} T_{\rm cl}^{(n_2)}$$
(1.56)

where a and b are mutually prime integers. In that case, the wave packet displays a period on short time scales given by

$$T_{\rm cl} = bT_{\rm cl}^{(n_1)} = aT_{\rm cl}^{(n_2)}.$$
(1.57)

When the two classical periods are incommensurate, the initial motion of $\Psi(t)$ is not exactly periodic. On a longer time scale, the full revivals appear if the three revival times $T_{\rm rev}^{(n_1)}$, $T_{\rm rev}^{(n_2)}$ and $T_{\rm rev}^{(n_1n_2)}$ are commensurate and satisfy

$$T_{\rm rev}^{(n_1)} = \frac{c}{d} T_{\rm rev}^{(n_2)} = \frac{e}{f} T_{\rm rev}^{(n_1 n_2)}$$
(1.58)

where c, d and e, f are pairs of mutually prime integers. When Eq. (1.58) is satisfied, all three second-order terms in the phase become integer multiples of 2π . At this time, a full revival occurs and the phase is governed once more by the classical periods.

Fractional revivals will appear at $t = t_{\text{frac}}$, given by

$$t_{\rm frac} = \frac{p_1}{q_1} T_{\rm rev}^{(n_1)} = \frac{p_2}{q_2} T_{\rm rev}^{(n_2)} = \frac{p_{12}}{q_{12}} T_{\rm rev}^{(n_1 n_2)},$$
(1.59)

where the integer pairs (p_1, q_1) , (p_2, q_2) and (p_{12}, q_{12}) are mutually prime. To explain fractional revival phenomena, we define a doubly-periodic function in the following way:

$$\Psi_{cl}(t_1, t_2) = \sum_{\mu k} \tilde{c}_{\mu k} \tilde{\Phi}_{\mu k} \exp\left[-2\pi i \left(\frac{\mu t_1}{T_{cl}^{(n_1)}} + \frac{k t_2}{T_{cl}^{(n_2)}}\right)\right],$$
(1.60)

where $\Psi_{cl}(t_1, t_2)$ is periodic in t_1 and t_2 with periods $T_{cl}^{(n_1)}$ and $T_{cl}^{(n_2)}$ respectively and t_1, t_2 are dummy variables. Also it satisfies

$$\Psi_{cl}(t_1 + T_{rev}^{(n_1)}, t_2) = \Psi_{cl}(t_1, t_2)$$

$$\Psi_{cl}(t_1, t_2 + T_{rev}^{(n_2)}) = \Psi_{cl}(t_1, t_2).$$
(1.61)

At t = 0, $\Psi(0) = \Psi_{cl}(0,0)$. So when time is small, $\Psi(t)$ behaves in approximately the same way as $\Psi_{cl}(t,t)$. Following Bluhm *et.al* [50], we will show that at fractional revival times $t \approx t_{\text{frac}}$, $\Psi(t)$ can be written as a sum of doubly periodic classical wave packets.

To explore the cyclic properties in μ and k of the second-order contributions to the time-dependent phase in $\Psi(t)$ at $t = t_{\text{frac}}$, we write these contributions as $exp(-2\pi i\theta_{\mu,k})$, where

$$\theta_{\mu,k} = \frac{p_1}{q_1}\mu^2 + \frac{p_2}{q_2}k^2 + \frac{p_{12}}{q_{12}}\mu k \tag{1.62}$$

Let us assume that minimum periods are l_1 and l_2 , such that

$$\theta_{\mu+l_1,k} = \theta_{\mu,k}, \quad \theta_{\mu,k+l_2} = \theta_{\mu,k}.$$
 (1.63)

The revival time scales are

$$T_{\rm rev}^{n_1} = \frac{r_1}{s_1} T_{\rm rev}^{n_{12}}, \quad T_{\rm rev}^{n_2} = \frac{r_2}{s_2} T_{\rm rev}^{n_{12}}, \tag{1.64}$$

which follow from Eq. (1.59) with the conditions

$$\frac{r_1}{s_1} = \frac{q_1 p_{12}}{p_1 q_{12}}, \quad \frac{r_2}{s_2} = \frac{q_2 p_{12}}{p_2 q_{12}}.$$
(1.65)

The periods l_1 and l_2 must then satisfy

$$\frac{p_1}{q_1}l_1^2 + \frac{2p_1}{q_1}l_1\mu + \frac{p_1r_1}{q_1s_1}l_1k = 0 \pmod{1}, \frac{p_2}{q_2}l_2^2 + \frac{2p_2}{q_2}l_2k + \frac{p_2r_2}{q_2s_2}l_2\mu = 0 \pmod{1}.$$
(1.66)

These relations can be satisfied by choosing $l_1 = q_1 s_1$ and $l_2 = q_2 s_2$, where the secondorder contributions $\theta_{\mu,k}$ are cyclic in μ and k with periods l_1 and l_2 . The function $\Psi_{cl}(t + s_1 T_{cl}^{n_1}/l_1, t + s_2 T_{cl}^{n_2}/l_2)$ with shifted arguments have the same periodicities in μ and k, where Ψ_{cl} is defined in Eq. (1.60). Finally, the wave packet at times $t \approx t_{frac}$ can be written as

$$\Psi(t) = \sum_{s_1=0}^{l_1-1} \sum_{s_2=0}^{l_2-1} a_{s_1s_2} \Psi_{\rm cl}(t+s_1 T_{\rm cl}^{n_1}/l_1, t+s_2 T_{\rm cl}^{n_2}/l_2),$$
(1.67)

where the coefficients $a_{s_1s_2}$ are given by

$$a_{s_1s_2} = \frac{1}{l_1l_2} \sum_{s_1=0}^{l_1-1} \sum_{s_2=0}^{l_2-1} a_{s_1s_2} \exp(-2\pi i\theta_{\mu,k}) \exp(2\pi i\frac{s_1}{l_1}\mu) \exp(2\pi i\frac{s_2}{l_2}k).$$
(1.68)

Eq. (1.67) shows that at $t \approx t_{\text{frac}}$, the wave packet can be written as a sum of subsidiary wave functions which have distinct shifts in two arguments.

In chap. 4, we study the wavelet based time-frequency analysis of revival dynamics of Rydberg atomic wave packets and molecular vibrational wave packets.

1.6 Non stationary signal analysis

Signal processing is a fast growing area today and a desired effectiveness in utilization of bandwidth and energy makes the progress even faster. Signals for which the properties or the frequency content do not change in time, are called stationary signals. Most signals observed in nature are typically non-stationary. Autocorrelation function relates directly to the observable signal in the pump-probe type experiments for studying the wave packet dynamics. This observed signal is a time series, which is non-stationary and it requires suitable transformation to find the information contained in it.

1.6.1 Fourier Transform:

The Fourier Transform (FT) [59] provides a representation of functions defined over an infinite interval and having no particular periodicity. We define FT of f(t) as

$$\tilde{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt, \qquad (1.69)$$

and the inverse transform follows

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(\omega) e^{i\omega t} dt.$$
 (1.70)

Its utility lies in its ability to analyze a signal in the time domain for its frequency content. The transform works by first translating a function in the time domain into a function in the frequency domain. The signal can then be analyzed for its frequency content because the Fourier coefficients of the transformed function represent the contribution of each sine and cosine function at each frequency. It can be used for non-stationary signals, if we are only interested in what spectral components exist in the signal, but not interested in the time of their occurrence. Non-stationarity is often the most important part of the signal, and Fourier analysis is not suited for detecting it. It was proved insufficient due to the non-localized nature of the transform.

1.6.2 Short Time Fourier Transform:

For the purpose of time-frequency analysis of a signal, short-time Fourier transform (STFT) [60] has often been used in the literature. It is defined as

$$X(\omega,t) = \int_{-\infty}^{\infty} x(\tau)w(\tau-t)e^{-i\omega\tau}d\tau.$$
(1.71)

The function w(t) is the window function. This method divides the whole time series in several windows, each of certain fixed width. Then the FT is performed in each window for obtaining the frequency information. The STFT can be considered as sliding the window along the signal x(t) and then for each shift of the window, computing the Fourier transform. The plot of $|X(\omega, t)|^2$ or spectrograms for all shifts of the total signal duration gives us the time-frequency distribution as required. Unfortunately, the time-frequency information obtained by this method has not always been satisfactory as its fixed window

length does compromise on the frequency resolution. The method of wavelet transform overcomes the preset resolution problem of STFT by using a variable length window.

What sets wavelets apart, is that the wavelets were designed from first principles to study how the signal changes over time. Whereas Fourier methods usually involve analyzing the entire signal at once, wavelet analysis assumes that the signals may be of finite duration. So it is designed to study the spectrum of variability as a function of time.

1.6.3 Wavelet Transform

The wavelet transform [61, 62], by design provides good localisation in both time and frequency. The subject area of wavelets, developed mostly over the last fifteen years, is at the forefront of much current research in pure and applied mathematics, physics, computer science and engineering. It really began in the mid 1980s where it was developed to interrogate seismic signals (Goupillaud et al 1984) [63]. The application of wavelet transform analysis in science and engineering really began to take off at the beginning of the 1990s. This transform has emerged over recent years as a powerful time-frequency analysis. Now it is worthwhile asking *"What is a wavelet"*? A wavelet is a waveform of effectively limited duration that has an average value of zero.

Wavelet transforms, as they are in use today, come in essentially two distinct ways or classes: the continuous wavelet transform and the discrete wavelet transform. Here we discuss the continuous wavelet transform.

Continuous Wavelet Transform (CWT): Time-frequency analysis

The continuous wavelet transform (CWT) [60, 61, 62, 63, 64, 65, 66] is gaining wide acceptance as a convenient tool for time-frequency analysis that separates individual signal components more effectively than the traditional short time Fourier transform (STFT). CWT of a signal f(t) is defined as

$$T(s,\tau) = \frac{1}{\sqrt{s}} \int f(t)\phi^*\left(\frac{t-\tau}{s}\right) dt$$
(1.72)

This transformed signal is a function of two variables, s and τ that are used respectively to scale and translate the wavelet window whereas ϕ^* is the complex conjugate of the

transforming function known as the mother wavelet for the CWT. The mother wavelet used here is the Morlet wavelet. The Morlet wavelet is the most popular complex wavelet used in practice and it is defined as

$$\phi(t) = \pi^{-1/4} e^{i\omega_0 t} e^{-t^2/2}, \qquad (1.73)$$

where ω_0 is the central frequency of the Morlet wavelet. The transform can be related to the time-frequency representation with low scale corresponding to compressed mother wavelet and high scale corresponding to dilated mother wavelet. The effect of scaling is to change the area of the time-frequency plane with the value of the frequency related to the scale value. The square of the modulus of the transform plotted on a time-scale plane is called the *scalogram* [60, 62]. This transform overcomes the frequency resolution problem of the STFT by allowing variable length windows. Another important distinction from the STFT is that the CWT is not limited to using sinusoidal analysing functions.

In chap. 4, we choose the most widely used transform (CWT) to find the time-frequency information of a signal in the pump-probe type experiments or autocorrelation function of Rydberg atomic wavepacket and molecular vibrational wavepacket.

Chapter 2

Mesoscopic superposition and sub-Planck scale structure in molecular wave packets

2.1 Introduction

Mesoscopic states are lying at the interface between the classical and the quantum world i.e. macroscopic and microscopic world. Mesoscopic superposition of coherent states and their generalizations, such as cat-like states, have attracted considerable attention in the recent literature [23, 29, 30, 31, 36, 67], since they show a host of non-classical behaviors. Zurek [38] demonstrated that appropriate superposition of some of these states with a classical action A can lead to sub-Planck scale structures in phase space. These structures are characterized by an area \hbar^2/A . Apart from their counter intuitive nature and theoretical significance, the above scale has been shown to control the effectiveness of decoherence, a subject of tremendous current interest in the area of quantum computation and information. Zurek's realization made use of dynamical systems which exhibit chaotic behavior in the classical domain. Recently a cavity QED realization involving the mesoscopic superposition of the so-called compass states have been given [43, 44]. In principle, one could also use superpositions of cat-like states arising in quantum optical systems with large Kerr non-linearity [23].

In this chapter, we demonstrate the possibility of realizing sub-Planck scale structures in the mesoscopic superposition of molecular wave packets, which involves vibrational levels. The time evolution of an initial wave packet, taken here as the SU(2) coherent state (CS) of the Morse potential, produces cat-like states. These arise due to the quadratic dependence of the energy on the vibrational quantum number. The superposition of these states is responsible for the above phenomena. We study the spatio-temporal structure of these states, paying special attention to the fractional revival, which gives rise to four coherent states required for the observation of the sub-Planck structure. This structure can be clearly explained through the interference phenomena in phase space. For this, we investigate the phase space dynamics of the coherent state through the Wigner function approach and identify the optimal parameter ranges for a clear observation of these features.

The Morse potential is well-known to capture the vibrational dynamics of a number of diatomic molecules [9, 18, 68, 69, 70]. It is worth mentioning that the phenomena of revival and fractional revival [2, 4, 71] have been experimentally observed in wave packets involving vibrational levels [72]. Creation of the wave packets and observation of their dynamics are carried out through pump-probe method [73]. The control and analysis of molecular dynamics is achieved through ultrashort femto-second laser pulses [53]. Fractional revival can be probed by random-phase fluorescence interferometry [74]. Recently, cat-like states, arising in the temporal evolution of the Morse system, have been proposed for use in the quantum logic operations [75].

2.2 Symmetry generation and Perelomov coherent state of the Morse potential

2.2.1 Morse potential

The Morse potential describing the vibrational motion of a diatomic molecule has the form

$$V(x) = D(e^{-2\beta x} - 2e^{-\beta x})$$
(2.1)

where $x = r/r_0 - 1$, r_0 is the equilibrium value of the inter-nuclear distance r, D is the dissociation energy and β is a range parameter. We will be considering the hydrogen iodide molecule, as an example, which has 30 bound states, with $\beta = 2.07932$, reduced


Figure 2.1: Morse potential of HI molecule. $\beta = 2.07932$, $\mu = 1819.99 \ a.u.$, $r_0 = 3.04159 \ a.u.$ and $D = 0.1125 \ a.u.$

mass $\mu = 1819.99 \ a.u.$, $r_0 = 3.04159 \ a.u.$ and $D = 0.1125 \ a.u.$ Morse potential of hydrogen iodide molecule is shown in Fig. 2.1. Defining

$$\lambda = \sqrt{\frac{2\mu D r_0^2}{\beta^2 \hbar^2}} \quad \text{and} \quad s = \sqrt{-\frac{8\mu r_0^2}{\beta^2 \hbar^2} E}, \tag{2.2}$$

eigen functions of the Morse potential can be written as

$$\psi_n^{\lambda}(\xi) = N e^{-\xi/2} \xi^{s/2} L_n^s(\xi), \qquad (2.3)$$

where $\xi = 2\lambda e^{-\beta x}$; $0 < \xi < \infty$, and $n = 0, 1, ..., [\lambda - 1/2]$, with $[\rho]$ denoting the largest integer smaller than ρ , so that the total number of bound states is $[\lambda - 1/2]$. The parameters λ and s satisfy the constraint condition $s + 2n = 2\lambda - 1$.

Note that λ is potential dependent, s is related to energy E and, by definition, $\lambda > 0$, s > 0. In Eq. (2.3), $L_n^s(y)$ is the associated Laguerre polynomial and N is the normalization constant:

$$N = \left[\frac{\beta(2\lambda - 2n - 1)\Gamma(n + 1)}{\Gamma(2\lambda - n)r_0}\right]^{1/2}.$$
(2.4)



Figure 2.2: $|d_m|^2$ plotted as a function of m for the Morse potential of HI molecule for different values of α .

2.2.2 Morse Perelomov coherent state

Quite some time back, Nieto and Simmons gave a minimum uncertainty coherent state for the Morse oscillator considering suitable conjugate variables [76]. Later, Benedict and Molnár [77] also found the same coherent state through super symmetric quantum mechanical method. This was used to describe the cat states of the NO molecule [78]. This coherent state involves infinite number of bound states, not belonging to the same potential [7]. Morse potential has a finite number of bound states. Hence it is natural to expect an underlying SU(2) algebra. Recently, Dong *et al.*, [79] have obtained the SU(2) generators \hat{J}_+ , \hat{J}_- and \hat{J}_0 as follows

$$\hat{J}_{-} = -\left[\frac{d}{d\xi}(s+1) - \frac{1}{\xi}\frac{s}{2}(s+1) + \frac{2\lambda}{2}\right]\sqrt{\frac{s+2}{s}}$$
$$\hat{J}_{+} = \left[\frac{d}{d\xi}(s-1) + \frac{1}{\xi}\frac{s}{2}(s-1) - \frac{2\lambda}{2}\right]\sqrt{\frac{s-2}{s}}$$
$$\hat{J}_{0} = \left[\xi\frac{\xi^{2}}{d\xi^{2}} + \frac{d}{d\xi} - \frac{s^{2}}{4\xi} - \frac{\xi}{4} + n + \frac{1}{2}\right].$$
(2.5)

They satisfy the algebra at the level of wave function as

$$\left[\hat{J}_{+},\hat{J}_{-}\right]\psi_{n}^{\lambda}(\xi) = 2\hat{J}_{0}\psi_{n}^{\lambda}(\xi).$$
(2.6)

Definition of the Perelomov coherent state [21] is given in section 1.3. The SU(2) Perelomov coherent state of the Morse system is obtained by operating the displacement operator



Figure 2.3: (a),(b) and (c) gives the wave packets at t = 0 for different values of α (b) $\alpha = 0.2, \bar{m} = 29$, (c) $\alpha = 1.3, \bar{m} = 7$, (d) $\alpha = 2.5, \bar{m} = 2, \bar{m}$ is the value of m when $|d_m|^2$ is maximum.

 $e^{\alpha \hat{J}_+ - \alpha^* \hat{J}_-}$ on the highest bound state n', defined by $\hat{J}_+ \psi_{n'}^{\lambda}(\xi) = 0$. Using disentanglement theorem [21], the coherent state (modulo normalization) becomes

$$\chi(\xi) = e^{-\alpha \hat{J}_{-}} \psi_{n'}^{\lambda}(\xi)$$

= $\left[\psi_{n'}^{\lambda} - \alpha \sqrt{n'(s+n'+1)} \psi_{n'-1}^{\lambda} + \dots + \frac{(-\alpha)^{n'}}{(n')!} \times \sqrt{n'!(s+n'+1)(s+n'+2)\dots(s+2n')} \psi_{0}^{\lambda} \right].$ (2.7)

As is explicitly seen, the above coherent state involves only the bound states, which are finite in number. This is due to the fact that the underlying group here is a compact group [21]. For the purpose of our analysis, we consider this wave packet. We have checked that, superposition of Morse eigen states with suitable Gaussian weight factors, also reproduces the sub-Planck scale structure.

Simplifying the above expression, we can write it in a compact form:

$$\chi(\xi) = \sum_{m=0}^{n'} d_m \ \psi_m^{\lambda}(\xi),$$
(2.8)

where

$$d_m = \frac{(-\alpha)^{n'-m}}{(n'-m)!} \left[\frac{n'!\Gamma(2\lambda - m)}{m!\Gamma(2\lambda - n')} \right]^{\frac{1}{2}}.$$
 (2.9)

Fig. 2.2 shows $|d_m|^2$ distribution of HI molecule for various values of α and Fig. 2.3 show the probability distribution of the corresponding coherent state wave packet at time t = 0. For smaller values of α , $|d_m|^2$ is peaked at higher values of m, where the anharmonicity is larger. The corresponding initial coherent state wave packet is not well localized and has an oscillatory tail. With the increase of α , $|d_m|^2$ distribution moves towards the lower levels and the wave packet's oscillatory tail gradually disappears. For larger values of α , only the lower levels contribute to form the coherent state wave packet, where the effect of anharmonicity is rather small. Hence, it is clear that the choice of the distribution is quite crucial in the wave packet localization and its subsequent dynamics.

2.3 Coherent state wave packet time evolution in different representation

Temporal evolution of the coherent state state wave packet is given by

$$\chi(\xi,t) = \sum_{m} d_m \psi_m^\lambda(\xi) \exp[-iE_m t]$$
(2.10)

with $E_m = -(D/\lambda^2)(\lambda - m - 1/2)^2$. This quadratic energy spectrum yields the revival times as $T_{\rm cl} = T_{\rm rev}/(2\lambda - 1)$ and $T_{\rm rev} = 2\pi\lambda^2/D$ respectively.

2.3.1 Autocorrelation function



Figure 2.4: Plot of the auto correlation function $|A(t)|^2$ as a function of time, scaled by T_{rev} . Here $\beta = 2.81603$, $\alpha = 1.4$.

The autocorrelation function in Fig. 2.4 gives a striking illustration of revival and fractional revival phenomena. When $|A(t)|^2 = 1$, the wave packet revives and the fractional revival appears as periodic peaks in the auto correlation function. The oscillations occur initially at the orbital period T_{cl} . After some damping, the oscillations double in frequency. This doubling in frequency is characteristic of a one-half fractional revival.

2.3.2 Quantum carpet structure



Figure 2.5: Quantum carpet structure of Morse coherent state with parameter values $\beta = 2.81603$, $\alpha = 1.4$. Here time is scaled by T_{rev} .



Figure 2.6: Space-time contour plots describes (a) time evolution of fictitious coherent state wave packet, having only linear dependence in phase argument and (b) time evolution of coherent state wave packet considering the full energy expression. Here time is scaled by T_{cl} , with $\beta = 2.81603$, $\alpha = 1.4$.

The first striking example of a quantum carpet emerged from numerical simulations performed on a particle confined to an infinite potential well [80]. It describes the space-time structure of the modulus of a quantum mechanical wave packet. Similar structures appear in many fields of wave physics ranging from quantum mechanics, with applications in nuclear physics [81] and Bose–Einstein condensation [82], to electromagnetic waves



Figure 2.7: Wave packet distribution in coordinate space for HI molecule, where $\alpha = 1.4$, $\beta = 2.07932$. Plotted here is $|\chi(\xi, t)|^2$ as a function of x (where $\xi = 2\lambda \exp[-\beta x]$) for (a) t=0, (b) $t = T_{\rm rev}/8$, (c) $t = T_{\rm rev}/4$ and (d) $t = T_{\rm rev}/2$.

propagating in self-imaging waveguides. In Fig. 2.5, quantum carpets, i.e. plots of probability density, for the propagation of a Morse coherent state wavepacket is depicted. In Fig. 2.6(a), two classical periods (upto $2T_{cl}$) of a 'fictitious' or classical coherent state wave packet is shown i.e, we have considered here only the linear energy dependence whereas, Fig. 2.6(b) shows the same when we considered the full expression for the energy. Nonlinear dependence is clearly seen at the beginning of the second classical period.

2.3.3 Co-ordinate representation

More interestingly, when t takes the values $\frac{r}{q}T_{rev}$, where r, q are mutually prime integers, the original wave packet splits into several number of small copies or mini-packets, with well defined phase relationship. To explain fractional revival phenomena [2], we consider a 'fictitious' or classical coherent state wave packet,

$$\chi_{\rm cl}(\xi,t) = \sum_{m} d_m \psi_m^{\lambda}(\xi) \exp[-2\pi i m t/T_{\rm cl}].$$
(2.11)

which revives at $t = T_{cl} = \frac{2\pi\lambda^2}{D(2\lambda-1)}$. At fractional revival, using discrete Fourier transform (DFT) and changing the quadratic term into linear terms, the original coherent state wave packet can be written as a linear combination of fictitious coherent state wave packets as follows

$$\chi(\xi, t) = \sum_{p}^{l-1} a_p \,\chi_{\rm cl}[\xi, (r/q \, T_{\rm rev} - p/l \, T_{\rm cl})], \qquad (2.12)$$

The amplitudes are determined by

$$a_p = \frac{1}{l} \sum_{m}^{l-1} \exp\left[2\pi i (m^2 r/q - mp/l)\right],$$
(2.13)

where l = q/2 when q is an integer multiple of 4 and l = q, in all other cases.

Fig. 2.7 shows the coherent state wave packet in the co-ordinate representation, where the revival behaviors at $T_{rev}/4$ and $T_{rev}/8$ are not transparent. We will now clarify the phase space picture of the wave packet at fractional revival times by using the Wigner function approach. We will also show that the interference phenomenon in phase space involving the cat-like states gives rise to the sub-Planck scale structure.

2.4 Wigner distribution of coherent state wave packet at different times

The Wigner function [25] can be written as

$$W(x,p,t) = \frac{r_0}{\pi\hbar} \int_{-\infty}^{+\infty} \bar{\chi}^*(x-x',t)\bar{\chi}(x+x',t)e^{-2ipx'/\hbar}dx' , \qquad (2.14)$$

where x is the scaled co-ordinate and p is the corresponding scaled momentum and also $\bar{\chi}(x) = \chi(\xi)$.

Phase space pictures at these times are depicted in Fig. 2.8 which gives more clear idea compared to the co-ordinate space representation. At time $t = \frac{1}{4}T_{rev}$, it is quite clear from the phase space picture (Fig. 2.8(b)) that the individual wave packets are well separated producing a cat like state which has very important quantum mechanical properties like sub-Poissonian statistics, squeezing, etc. At $\frac{1}{8}T_{rev}$, the wave packets are not equispaced and the superposition structure gives a complicated structure.

At t = 0, the Wigner function of the Morse coherent state is on the left side of the Morse potential.

At $t = T_{rev}/2$, we use Eq. (2.10) to write

$$\chi(\xi, t = T_{rev}/2) = \sum_{m} d_m \psi_m^{\lambda}(\xi) e^{-2\pi i m \frac{t}{T_{cl}}} e^{\pi i m^2}$$
(2.15)



Figure 2.8: Wigner function plots of the coherent state wave packet at different times in x, p space for HI molecule, where $\alpha = 1.4$, $\beta = 2.81603$. (a) t=0, (b) $t = \frac{1}{4}T_{rev}$, (c) $t = \frac{1}{2}T_{rev}$ and (d) $t = \frac{1}{8}T_{rev}$.

Making use of the classical coherent state wave packets, we get

$$\chi_{cl}(\xi, t - T_{cl}/2) = \sum_{m} d_{m} \psi_{m}^{\lambda}(\xi) e^{-2\pi i m (t - T_{cl}/2)/T_{cl}}$$
$$= \sum_{m} d_{m} \psi_{m}^{\lambda}(\xi) e^{-2\pi i m \frac{t}{T_{cl}}} e^{i m \pi}.$$
(2.16)

Note that

$$e^{\pi i m^2} = (-1)^{m^2} = (-1)^m = e^{\pi i m}.$$
 (2.17)

Finally, we obtain

$$\chi(\xi, t = T_{rev}/2) = \chi_{cl}(\xi, t - T_{cl}/2).$$
(2.18)

Fig. 2.8(c) shows that it is shifted from the position of the initial wave packet.



Figure 2.9: The Wigner function W(x, p, t) as a function of x and p for (a) $\alpha = 1.4$ and (b) $\alpha = 2.5$, at time $\frac{1}{4}T_{rev}$.

2.4.1 Schrödinger cat states

At $T_{rev}/4$, we get

$$\chi(\xi, t = T_{rev}/4) = \frac{1}{\sqrt{2}} \left[e^{i\pi/4} \chi_{cl}(\xi, \frac{1}{4}T_{rev}) + e^{-i\pi/4} \chi_{cl}(\xi, \frac{1}{4}T_{rev} - \frac{1}{2}T_{cl}) \right], \quad (2.19)$$

which is similar to a Scrödinger cat state, simulated by a superposition of two coherent state wave packets that are separated by one-half of a vibrational period as shown in Fig. 2.7(c).

Wigner functions at various times, can also be explained by making use of the classical coherent state wave packets. For example at $\frac{1}{4}T_{rev}$, the Wigner function becomes

$$W(x, p, \frac{1}{4}T_{rev}) = \frac{r_0}{\pi\hbar} \int_{-\infty}^{+\infty} \bar{\chi}^*(x - x', \frac{1}{4}T_{rev})\bar{\chi}(x + x', \frac{1}{4}T_{rev})e^{-2ipx'/\hbar}dx'.$$
 (2.20)

The coherent state wave packet $\bar{\chi}(x + x', \frac{1}{4}T_{rev})$ can be written in terms of the classical coherent state wave packets as follows

$$\bar{\chi}(x+x',\frac{1}{4}T_{rev}) = \frac{1}{\sqrt{2}} \left[e^{i\pi/4} \bar{\chi}_{cl}(x+x',\frac{1}{4}T_{rev}) + e^{-i\pi/4} \bar{\chi}_{cl}(x+x',\frac{1}{4}T_{rev} - \frac{1}{2}T_{cl}) \right]$$
(2.21)

and the Wigner function at $\frac{1}{4}T_{rev}$ can be divided into three parts:

$$W(x, p, \frac{1}{4}T_{rev}) = W_1 + W_2 + W_3, \qquad (2.22)$$

where W_1 , W_2 and W_3 are

$$W_1 = \frac{r_0}{\pi\hbar} \int_{-\infty}^{+\infty} \bar{\chi}_{cl}^*(x - x', \frac{1}{4}T_{rev}) \bar{\chi}_{cl}(x + x', \frac{1}{4}T_{rev}) e^{-2ipx'/\hbar} dx', \qquad (2.23)$$

$$W_{2} = \frac{r_{0}}{\pi\hbar} \int_{-\infty}^{+\infty} \bar{\chi}_{cl}^{*}(x - x', \frac{1}{4}T_{rev} + \frac{1}{2}T_{cl})\bar{\chi}_{cl}(x + x', \frac{1}{4}T_{rev} + \frac{1}{2}T_{cl})e^{-2ipx'/\hbar}dx', \quad (2.24)$$

and

$$W_{3} = \frac{r_{0}}{\pi\hbar} \int_{-\infty}^{+\infty} e^{i\pi/2} \bar{\chi}_{cl}^{*}(x - x', \frac{1}{4}T_{rev}) \bar{\chi}_{cl}(x + x', \frac{1}{4}T_{rev} + \frac{1}{2}T_{cl}) + e^{-i\pi/2} \bar{\chi}_{cl}^{*}(x - x', \frac{1}{4}T_{rev} + \frac{1}{2}T_{cl}) \bar{\chi}_{cl}(x + x', \frac{1}{4}T_{rev}) e^{-2ipx'/\hbar} dx'. \quad (2.25)$$

 W_1 and W_2 give two distinct peaks at the two opposite ends of the orbit as shown in Fig. 2.8(b). W_3 gives the result of quantum interference between them. Fig. 2.9 shows Scrödinger cat states with their interference structure for different values of α . For larger values of α , the distribution $|d_m|^2$ starts including lower levels of Morse potential and the number of ripples decreases as the distance between the two coherent state get decreased. The ridges and valleys of such interference pattern are always parallel to the line joining them.

2.4.2 Sub-Planck scale structure

At $t = T_{\rm rev}/8$, the coherent state wave packet splits into four classical wave packets:

$$\chi(\xi, \frac{T_{\rm rev}}{8}) = \frac{1}{2} \left[e^{i\pi/4} \chi_{cl}(\xi, \frac{T_{\rm rev}}{8}) + \chi_{cl}(\xi, \frac{T_{\rm rev}}{8} - \frac{T_{\rm cl}}{4}) - e^{i\pi/4} \chi_{cl}(\xi, \frac{T_{\rm rev}}{8} - \frac{T_{\rm cl}}{2}) + \chi_{cl}(\xi, \frac{T_{\rm rev}}{8} - \frac{3T_{\rm cl}}{4}) \right].$$
(2.26)

Defining

$$\chi_{\rm cl}^{(\rm even, odd)}(\xi, t) = \sum_{\rm m_{even, odd}} d_m \psi_m^\lambda(\xi) \exp[-2\pi i m \frac{t}{T_{\rm cl}}]$$
(2.27)

Sub-Planck scale structure

expression Eq. (2.26) can be rewritten in a simpler form:

$$\chi(\xi, \frac{T_{\rm rev}}{8}) = \chi_{\rm cl}^{\rm even}(\xi, \frac{T_{\rm rev}}{8} - \frac{T_{\rm cl}}{4}) + e^{i\pi/4}\chi_{\rm cl}^{\rm odd}(\xi, \frac{T_{\rm rev}}{8}).$$
(2.28)



Figure 2.10: The Wigner function W(x, p, t) and its constituent parts at $t = T_{rev}/8$ as a function of x and p for $\alpha = 1.4$ (top row) and $\alpha = 2.5$ (bottom row). Shown here are the contour plots of (a) $W^{(even)}$; (b) $W^{(odd)}$; (c) $W^{(int)}$ and (d)W(x, p, t).

The above expression plays a crucial role in the explanation of the phase space behavior at $T_{\rm rev}/8$. Substituting this in Eq. (2.14), the Wigner function at $t = T_{\rm rev}/8$ can be written down as a sum of three terms: $W(x, p, T_{\rm rev}/8) = W^{(\rm even)} + W^{(\rm odd)} + W^{(\rm int)}$, where $W^{(\rm even)}$ and $W^{(\rm odd)}$ are the Wigner functions corresponding to the first and second terms on the right hand side of Eq. (2.28) and $W^{(\rm int)}$ is the contribution from the interference between these two terms. In Fig. 2.10, we have plotted $W(x, p, T_{\rm rev}/8)$ and its constituent parts for two values of α . Note that both $W^{(\rm even)}$ and $W^{(\rm odd)}$ are Wigner functions of cat-like states. Each consists of two distinct peaks corresponding to two mesoscopic wave packets, and an oscillatory structure at the middle due to quantum interference between them. Furthermore, $W^{(\rm even)}$ is along the east-west direction whereas $W^{(\rm odd)}$ is along the north-south. This is because the time arguments of $\chi^{\rm even}_{\rm cl}$ and $\chi^{\rm odd}_{\rm cl}$ differ by $T_{\rm cl}/4$ in Eq. (2.28). The superposition of the interference regions of $W^{(\rm even)}$ and $W^{(\rm odd)}$ gives rise to the sub-Planck structure in Fig. 2.10(d). It is worth pointing out that W^{int} , as plotted in Fig. 2.10(c), gives the off diagonal interferences of compass-like states produced at $T_{\text{rev}}/8$.

As seen in Fig. 2.2, for higher values of α , the initial wave packet involves lower vibrational levels for which the turning points are nearer, resulting in a decrease in the span of the phase space variables. In this case, the area of overlap between the two interference structure increases and the number of ripples become less. As a consequence, the sub-Planck scale structure at the middle becomes more prominent as shown in the bottom array of Fig. 2.10. The four mini-wave packets, produced at $T_{\rm rev}/8$, are not equi-spaced and not of same size. The asymmetrical nature of the Morse potential is the main reason behind this. We also analyze numerically the expectation values of position and momentum at $t = T_{\rm rev}/8$ for different values of α . The uncertainty product $(\Delta x \Delta p)$, obtained from this analysis, is 5.5914 for $\alpha = 1.4$ and 2.56404 for $\alpha = 2.5$ in the unit of $\hbar = 1$. The classical action is defined by $A \approx \Delta x \Delta p$ and the corresponding dimension of the sub-Planck scale structure is $a \approx \hbar^2/A$ [38], which easily comes out to be 0.179 for $\alpha = 1.4$ and 0.39 for $\alpha = 2.5$ respectively, implying the sub-Planck scale structure. Note that for smaller values of α the area becomes more sub-Planck.

It is worth pointing out that, the vibrational wave packets are prone to decoherence through coupling to rotational and other vibrational levels. To minimize docoherence, different methods were proposed: (i) error correcting code [83, 84, 85, 86], (ii) decoherence free subspace [87, 88] and (iii) open-loop control scheme [89, 90]. But all these methods have their own drawbacks. Recently, methods like closed-loop control [49] have been devised to minimize the decoherence effect.

On the experimental front, the quantum state of a one-dimensional molecular vibration can be reconstructed via molecular emission tomography (MET) even in the case of an anharmonic potential [26]. In MET, the time-frequency resolved fluorescence spectrum of the molecule is the quantity that yields information on the quantum state [27, 28, 91, 92, 93]. Phase space quasi probability distribution or Wigner function of moecular vibrational states can be reconstructed from the time-resolved fluorescence spectra via inverse randon transform. An interference technique, which is based on quantum state holography, has been treated for molecular system [94]. In [95], a heterodyne measurement of vibrational

Sub-Planck scale structure

wave packets of diatomic molecules has been studied.

Chapter 3

The role of ro-vibrational coupling in the revival dynamics of diatomic molecular wave packets

3.1 Introduction

In this chapter, we treat rotational and vibrational motions simultaneously and present an indepth analysis of the revival dynamics for a diatomic molecular wave packet. Furthermore, we provide a simple, quantitative criterion that determines if and when the rotational and vibrational motions can be decoupled.

The chapter is organized as follows. In section 3.2, we present the theory for the ro-vibrational dynamics of a diatomic molecular wave packet of circular states using the Morse-Pekeris model [19, 96] and extract all the relevant revival time scales.

In section 3.3, we use I_2 and H_2 as examples of heavy and light molecules and show that the interplay between the rotational and vibrational motions is governed by a parameter $\gamma = \sqrt{2DMr_0^2/\hbar^2}$, where D is the dissociation energy, M is the reduced mass of the two nuclei and r_0 is the equilibrium distance between them. Specifically, if the weighing coefficients of the wave packet are peaked about $\nu = \overline{\nu}$ and $j = \overline{j}$, then, for $\gamma \gg \overline{\nu}$, \overline{j} , the rotational and vibrational time scales are so far apart that the ro-vibrational motion gets decoupled and the revival dynamics depends essentially on one time scale. For $\gamma \sim \overline{\nu}$, \overline{j} , on the other hand, rotational vibrational coupling cannot be ignored. In the latter case, an interesting rotational vibrational fractional revival is predicted and explained. We explained the above for two different values of $\bar{\nu}$ and \bar{j} .

We confirm our analytical results visually by means of pictures showing the probability density as a function of time when the initial wave packet is a superposition of circular states (i.e. states for which the quantum number m corresponding to the z-component of angular momentum is equal to j).

In section 3.4, we obtain further confirmation of our results from an analysis based on the autocorrelation function for both the cases. In the concluding section, we present a brief summary followed by a discussion on the validity of our model and its extension to wave packets of non-circular states. We also outline how the initial wave packet can be prepared and how its evolution can be studied by various existing techniques. We end by mentioning some possible applications of our work.

3.2 Theory

We assume a single electronic state of the diatomic molecule and consider only its nuclear motion. The vibrational motion of the two nuclei about their center of mass is modelled by the Morse potential

$$V(r) = D(e^{-2\alpha x} - 2e^{-\alpha x})$$
(3.1)

where $x = r/r_0 - 1$, r_0 is the equilibrium inter-nuclear distance, D is the dissociation energy and α is a range parameter. When rotational corrections are included [19, 96], the eigenstates of a particle in the Morse potential are given as

$$\psi_{\nu jm}(\mathbf{r}) = r^{-1} R_{\nu j}(y) Y_{jm}(\theta, \phi), \qquad (3.2)$$

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

$$R_{\nu j}(y) = N \exp(-y/2) y^{b/2} L_{\nu}^{b}(y)$$
(3.3)

is the radial part in a scaled variable y. Here, $L_{\nu}^{b}(y)$ is a generalized Laguerre polynomial and N is the normalization constant. Defining [96]

$$\gamma_1^2 = \gamma^2 - j(j+1)(2/\alpha - 3/\alpha^2),$$

$$\gamma_2^2 = \gamma^2 + j(j+1)(-1/\alpha + 3/\alpha^2),$$
(3.4)

one obtains

$$b = (2/\alpha)[\gamma_1^2/\gamma_2 - \alpha(\nu + 1/2)],$$

$$y = (2\gamma_2/\alpha) \exp(-\alpha x),$$

$$N = [\alpha b\nu! / \Gamma(b + \nu + 1)]^{1/2}.$$
(3.5)

The corresponding energy eigenvalues can be written in the form of a Dunham series:

$$E_{\nu j} = C \sum_{ik} (-1)^{i+k+1} \alpha_{ik} (\nu + 1/2)^i j^k (j+1)^k,$$
(3.6)

where $C = \hbar^2/(2Mr_0^2)$ and M is the reduced mass of the two nuclei. The coefficients α_{ik} are positive real quantities that depend on α and $\gamma = \sqrt{D/C}$ only:

$$\alpha_{00} = \gamma^{2}, \quad \alpha_{01} = 1, \quad \alpha_{02} = 9(\alpha - 1)^{2}/(4\alpha^{4}\gamma^{2}), \\
\alpha_{10} = 2\alpha\gamma, \quad \alpha_{20} = \alpha^{2}, \quad \alpha_{11} = 3(\alpha - 1)/(\alpha\gamma).$$
(3.7)

Let us now consider the evolution of a ro-vibrational wave packet $\Psi(\mathbf{r}, t) = \sum_{\nu j} c_{\nu j} \psi_{\nu j j}(\mathbf{r}) \exp(-iE_{\nu j}t)$ formed of circular states $\psi_{\nu j j}$. We assume that the weighting coefficients $c_{\nu j} = c_{\nu}^{(1)}c_{j}^{(2)}$ are strongly peaked about $\nu = \overline{\nu}$ and $j = \overline{j}$ and that the wave packet consists of only those states for which $|\nu - \overline{\nu}| \ll \overline{\nu}$ and $|j - \overline{j}| \ll \overline{j}$. These conditions allow us to expand $E_{\nu j}$ about $E_{\overline{\nu j}}$ in a Taylor series and retain a finite number of terms in the expansion. Keeping terms to second order and neglecting an overall phase due to $E_{\overline{\nu j}}$, we rewrite $\Psi(\mathbf{r}, t)$ as a double sum in shifted indices $\mu = \nu - \overline{\nu}$ and $k = j - \overline{j}$:

$$\Psi(\mathbf{r},t) = \sum_{\mu k} \tilde{c}_{\mu k} \tilde{\psi}_{\mu k}(\mathbf{r}) \exp\left[-2\pi i t \left(\frac{\mu}{T_{\rm cl}^{(\rm V)}} + \frac{k}{T_{\rm cl}^{(\rm R)}} - \frac{\mu^2}{T_{rev}^{(\rm V)}} + \frac{k^2}{T_{rev}^{(\rm R)}} - \frac{\mu k}{T_{rev}^{(\rm N)}}\right)\right].$$
 (3.8)

Here, $\tilde{c}_{\mu k} = c_{\mu + \overline{\nu}, k + \overline{j}}$, $\tilde{\psi}_{\mu k} = \psi_{\mu + \overline{\nu}, k + \overline{j}}$ and the notation $T_X^{(Y)}$ is used to describe various time scales of evolution. The superscripts V, R and VR correspond to the vibrational, rotational and vibrational-rotational time scales whereas the subscripts cl and rev refer to the classical and revival time periods in standard nomenclature. These time periods are defined as

$$T_{\rm cl}^{(\rm V)} = 2\pi \left(\frac{\partial E_{\nu j}}{\partial \nu}\right)_{\overline{\nu j}}^{-1}, \ T_{\rm cl}^{(\rm R)} = 2\pi \left(\frac{\partial E_{\nu j}}{\partial j}\right)_{\overline{\nu j}}^{-1},$$
$$T_{\rm rev}^{(\rm V)} = -4\pi \left(\frac{\partial^2 E_{\nu j}}{\partial \nu^2}\right)_{\overline{\nu j}}^{-1}, \ T_{\rm rev}^{(\rm R)} = 4\pi \left(\frac{\partial^2 E_{\nu j}}{\partial j^2}\right)_{\overline{\nu j}}^{-1}, \ T_{\rm rev}^{(\rm VR)} = -2\pi \left(\frac{\partial^2 E_{\nu j}}{\partial \nu \partial j}\right)_{\overline{\nu j}}^{-1}.$$
(3.9)

Initially, the wave packet motion is governed by the classical periods $T_{\rm cl}^{(\rm V)}$ and $T_{\rm cl}^{(\rm R)}$. If these periods are commensurate, i.e., if $T_{\rm cl}^{(\rm V)} = (a/b)T_{\rm cl}^{(\rm R)}$, where a and b are mutually prime, then the wave packet motion has a period $T_{\rm cl} = bT_{\rm cl}^{(\rm V)} = aT_{\rm cl}^{(\rm R)}$.

On a longer time scale, the wave packet will revive if the three revival times $T_{rev}^{(V)}$, $T_{rev}^{(R)}$ and $T_{rev}^{(VR)}$ are such that $T_{rev}^{(V)} = (c/d)T_{rev}^{(R)} = (e/f)T_{rev}^{(VR)}$, where c, d and e, f are pairs of mutually prime integers. Fractional revivals will occur at times $t = t_{frac}$ provided that

$$t_{frac} = \frac{p_1}{q_1} T_{\rm rev}^{(\rm V)} = \frac{p_2}{q_2} T_{\rm rev}^{(\rm R)} = \frac{p_3}{q_3} T_{\rm rev}^{(\rm VR)},$$
(3.10)

where the pairs of integers (p_i, q_i) , i = 1..3, are relatively prime. In general, these conditions for revival and fractional revival are too restrictive to be obeyed exactly. However, since the time scales are simple functions of $\overline{\nu}$ and \overline{j} for a given molecule, it is easy to check through a numerical program if these conditions are satisfied, at least approximately.

In a system whose energy spectrum is a function of two quantum numbers, the ratios of the associated time scales play a major role in the wave packet dynamics [52]. Defining

$$\beta_{1}(\nu, j) = 1 - \alpha(\nu + 1/2)/\gamma - 3(\alpha - 1)j(j + 1)/(2\alpha^{2}\gamma^{2}),$$

$$\beta_{2}(\nu, j) = 1 - 3(\alpha - 1)(\nu + 1/2)/(\alpha\gamma) - 9(\alpha - 1)^{2}j(j + 1)/(2\alpha^{4}\gamma^{2}),$$

$$\beta_{3}(\nu, j) = \beta_{2}(\nu, j) - 9(\alpha - 1)^{2}(2j + 1)^{2}/(4\alpha^{4}\gamma^{2}),$$
(3.11)

we write the ratios of various time scales as follows:

$$T_{\rm cl}^{(\rm R)}/T_{\rm cl}^{(\rm V)} = \frac{2\alpha\gamma}{(2\overline{j}+1)} \frac{\beta_1(\nu,j)}{\beta_2(\overline{\nu},\overline{j})}$$

$$T_{\rm rev}^{(\rm VR)}/T_{\rm rev}^{(\rm R)} = \frac{\alpha\gamma}{(2\overline{j}+1)} \frac{\beta_3(\overline{\nu},\overline{j})}{3(\alpha-1)}$$

$$T_{\rm rev}^{(\rm VR)}/T_{\rm rev}^{(\rm V)} = \frac{\alpha\gamma}{(2\overline{j}+1)} \frac{\alpha^2}{3(\alpha-1)}$$

$$T_{\rm rev}^{(\rm R)}/T_{\rm rev}^{(\rm V)} = \alpha^2/\beta_3(\overline{\nu},\overline{j})$$

$$T_{\rm rev}^{(\rm R)}/T_{\rm cl}^{(\rm R)} = (2\overline{j}+1)\beta_2(\overline{\nu},\overline{j})/\beta_3(\overline{\nu},\overline{j}).$$
(3.12)

Note that $T_{\text{rev}}^{(\text{VR})}/T_{\text{rev}}^{(\text{V})}$ is independent of $\overline{\nu}$. In what follows, we consider the wave packet dynamics for two limiting cases: (i) $\alpha > 1$, $\gamma \gg \overline{j}$, \overline{v} and (ii) $\alpha > 1$, $\gamma \sim \overline{j}$, \overline{v} .

3.3 Results and Discussion

3.3.1 Wave packet dynamics for $\alpha > 1$, $\gamma \gg \overline{j}$, $\overline{\nu}$

A good example of this case is the I_2 molecule for which $\alpha = 4.954$ and $\gamma = 577.43$ [96] so that $\alpha^2 = 24.54$ and $\alpha\gamma = 2860.59$. In Table 3.1, we present some typical time scale ratios of I_2 for moderate values of $\overline{\nu}$ and \overline{j} .

$\overline{\nu}$	\overline{j}	$T_{\rm cl}^{\rm (R)}/T_{\rm cl}^{\rm (V)}$	$T_{\rm rev}^{\rm (VR)}/T_{\rm rev}^{\rm (R)}$	$T_{\rm rev}^{\rm (R)}/T_{\rm rev}^{\rm (V)}$	$T_{\rm rev}^{\rm (R)}/T_{\rm cl}^{\rm (R)}$
7	14	190.50	8.06	25.33	29.00
8	8	323.39	13.68	25.44	17.00
10	10	259.17	10.98	25.66	21.00
13	9	282.02	11.98	26.00	19.00
15	9	278.99	11.88	26.23	19.00

Table 3.1: Some typical time scale ratios for I_2 .

These ratios can be explained by noting that for $\alpha\gamma \gg 2\overline{j} + 1$ and $\alpha\gamma \gg \overline{\nu} + 1/2$, $\beta_i(\overline{\nu},\overline{j}) = 1 + O(\gamma^{-1})$. Thus, from Eq. (3.12), one obtains $T_{\rm cl}^{(\rm R)} \gg T_{\rm cl}^{(\rm V)}$, $T_{\rm rev}^{(\rm VR)} \gg T_{\rm rev}^{(\rm R)} \gg T_{\rm rev}^{(\rm V)}$. Also, $T_{\rm rev}^{(\rm R)}/T_{\rm rev}^{(\rm N)}$ is slightly greater than α^2 and $T_{\rm rev}^{(\rm R)}/T_{\rm cl}^{(\rm R)} \approx 2\overline{j} + 1$.

Case I : I₂ molecule, $\overline{\nu} = 7$, $\overline{j} = 14$; $\overline{\nu} - 1 \le \nu \le \overline{\nu} + 1$, $\overline{j} - 3 \le j \le \overline{j} + 3$

In the first case, we consider the values of $\overline{\nu}$ and \overline{j} , given in the first row in Table 3.1. When the rotational and the vibrational time scales are not of the same order of magnitude, the corresponding motions become decoupled and the overall wave packet dynamics depends essentially on one time scale only. For a wave packet of I_2 , this is visually demonstrated in Fig. 3.1 where we have plotted $|\Psi(\mathbf{r},t)|^2$ at various times for two different cases. In case (a), we have used the original wave packet of the form Eq. (3.8). The initial wave packet is a superposition of states for which $\overline{\nu} = 7$, $\overline{j} = 14$, $\overline{\nu} - 1 \le \nu \le \overline{\nu} + 1$ and $\overline{j} - 3 \le j \le \overline{j} + 3$. The weighing factors $|c_{\nu}^{(1)}|^2$ and $|c_{j}^{(2)}|^2$ are taken as Gaussian functions of unit width. In case (b), we have set $\nu = \overline{\nu}$ (i.e. $\mu = 0$) in the time dependence of the wave function.



Figure 3.1: The wave packet evolution for I_2 . Shown here is a plot of $|\Psi(\mathbf{r}, t)|^2$ at different times for two cases: In case (a), the wave packet is of the form Eq. (3.8). The initial wave packet is a superposition of states for which $\overline{\nu} = 7$, $\overline{j} = 14$, $\overline{\nu} - 1 \le \nu \le \overline{\nu} + 1$ and $\overline{j} - 3 \le j \le \overline{j} + 3$. The annular ring extends from $0.9r_0$ to $1.2r_0$; in case (b), we have fixed ν at $\overline{\nu}$ (i.e. set $\mu = 0$) in the time dependence of the wave function. The wave packet is then of the form Eq. (3.13) as shown below.

With the z-axis perpendicular to the molecular axis, the wave packet rotates and vibrates on the z = 0 plane. The rotational motion takes place in a circular orbit about the center of mass of the two nuclei with a period $T_{cl}^{(R)}$ whereas the vibrational motion is confined along the radial direction with a period $T_{cl}^{(V)}$. However, with $T_{cl}^{(R)} \gg T_{cl}^{(V)}$, details of the vibrational motion are averaged out within one classical rotational period. This is a case of 'slow-fast dynamics' in nonlinear physics. Thus the prominent features of the wave packet dynamics can be recovered (see case (b)) by freezing ν at $\overline{\nu}$ (i.e. setting $\mu = 0$) in the time dependence of the wave function. In that case, Eq. (3.8) will reduce to

$$\Psi(\mathbf{r},t) \approx \sum_{\mu k} \tilde{c}_{\mu k} \tilde{\psi}_{\mu k}(\mathbf{r}) \exp\left[-2\pi i t \left(k/T_{\rm cl}^{\rm (R)} + k^2/T_{\rm rev}^{\rm (R)}\right)\right].$$
(3.13)

The dynamics of such a wave packet is well understood [2] in terms of fictitious classical wave packets

$$\psi_{\rm cl}(\mathbf{r},t) = \sum_{\mu k} \tilde{c}_{\mu k} \tilde{\psi}_{\mu k}(\mathbf{r}) \exp(-2\pi i k t / T_{\rm cl}^{\rm (R)}).$$
(3.14)

For example, at $t = T_{\rm rev}^{\rm (R)}/4$, the full wave function can be written as

$$\Psi(\mathbf{r},t) = a_{+}\psi_{\rm cl}(\mathbf{r},t+T_{\rm cl}^{\rm (R)}/2) + a_{-}\psi_{\rm cl}(\mathbf{r},t), \qquad a_{\pm} = \exp(\pm i\pi/4)/\sqrt{2}, \qquad t = T_{\rm rev}^{\rm (R)}/4.$$
(3.15)

Since the time arguments in the classical wave packets differ by $T_{\rm cl}^{\rm (R)}/2$, the packets lie at opposite ends of the orbit.

Case II : I₂ molecule,
$$\overline{\nu} = 10$$
, $\overline{j} = 10$; $\overline{\nu} - 2 \le \nu \le \overline{\nu} + 2$, $\overline{j} - 2 \le j \le \overline{j} + 3$

In the second case, we have chosen $\overline{\nu} = 10$ and $\overline{j} = 10$ as given in third row of Table 3.1. The weighing factors are taken as Gaussian functions of unit width and the initial wave packet is a superposition of states for which $\overline{\nu} - 2 \le \nu \le \overline{\nu} + 2$ and $\overline{j} - 2 \le j \le \overline{j} + 2$. Time scales are far apart and gives the results similar to the previous case for I_2 . Fig. 3.2 shows the time evolution of I_2 (a) for the original wave packet and (b) when $\nu = \overline{\nu}$ (i.e., $\mu = 0$) in the time dependence of the wave function. At specific times of fractional revivals, same



Figure 3.2: The wave packet evolution for I_2 . Shown here is a plot of $|\Psi(\mathbf{r}, t)|^2$ at different times for two cases: In case (a), the wave packet is of the form Eq. (3.8). The initial wave packet is a superposition of states for which $\overline{\nu} = 10$, $\overline{j} = 10$, $\overline{\nu} - 2 \le \nu \le \overline{\nu} + 2$ and $\overline{j} - 2 \le j \le \overline{j} + 2$. In case (b), we have fixed ν at $\overline{\nu}$ (i.e. set $\mu = 0$) in the time dependence of the wave function. The wave packet is then of the form Eq. (3.13) as shown below.

explanations can be provided as described in the case-I. Here also, overall time evolution of wave packet depends essentially on one time scale.

3.3.2 Wave packet dynamics for $\alpha > 1$, $\gamma \sim \overline{j}$, $\overline{\nu}$

For H_2 , $\alpha = 1.44$, $\gamma = 25.09$, $\alpha^2 = 2.07$ and $\alpha\gamma = 36.1$ [96]. In this case, $\alpha\gamma$ is comparable to $2\overline{j} + 1$ and $\overline{\nu} + 1/2$ even for moderate values of $\overline{\nu}$ and \overline{j} . Thus the approximations and the subsequent conclusions of the previous paragraph are not applicable here. For example, the classical time scales will now be of the same order of magnitude. Thus the vibrational and rotational motions cannot be decoupled from each other. Similarly, the revival time scales will be comparable to one another and it is even possible to satisfy conditions Eq. (3.10) for small values of p_i and q_i . Some such cases in the range $(p_i, q_i) \leq 5$, i = 1..3,

and $7 \leq \overline{\nu}, \overline{j} \leq 15$ are shown in Table 3.2.

Table 3.2: Some typical time scale ratios for H_2 satisfying conditions Eq. (3.10) approximately.

$\overline{\nu}$	\overline{j}	p_{1}/q_{1}	p_2/q_2	p_{3}/q_{3}	$T_{\rm cl}^{({\rm R})}/T_{\rm cl}^{({\rm V})}$	$T_{\rm rev}^{\rm (VR)}/T_{\rm rev}^{\rm (R)}$	$T_{\rm rev}^{\rm (R)}/T_{\rm rev}^{\rm (V)}$	$T_{\rm rev}^{\rm (R)}/T_{\rm cl}^{\rm (R)}$
7	14	4	1	2	1.75	0.49	3.96	36.5
8	8	2	3/5	3/5	3.03	1.00	3.35	18.28
10	10	2	1/2	3/4	2.02	0.66	4.07	23.92
13	9	1	1/5	1/3	1.43	0.60	4.94	21.63
15	9	3	1/2	1	0.61	0.50	5.98	22.18

Case I: H₂ molecule, $\overline{\nu} = 7, \overline{j} = 14; \overline{\nu} - 1 \le \nu \le \overline{\nu} + 1, \overline{j} - 3 \le j \le \overline{j} + 3$

In the first case, we have taken the values given in the first row in Table 3.2.

We now consider the wave packet evolution for H_2 . In Fig. 3.3, we show the time evolution at the initial stage. Although the initial wave packet is constructed in exactly the same way as for I_2 , in case-I, its subsequent evolution is very different. Since $T_{\rm cl}^{(\rm V)} \sim T_{\rm cl}^{(\rm R)}$, the radial spreading of the wave packet due to its vibrational motion will be quite conspicuous even during one classical period of rotational motion. The effect is further enhanced by the fact that the range of the potential increases as the parameter α decreases. Thus the excursion range along the radial direction is more for H_2 ($\alpha = 1.44$) than for I_2 ($\alpha = 4.954$).

In Fig. 3.4, we show the time evolution on longer time scales. Revivals of the initial wave packet take place at $t = T_{\rm rev}^{(\rm R)}/2 \approx 2T_{\rm rev}^{(\rm VR)} \approx T_{\rm rev}^{(\rm VR)}$ and also at $t = T_{\rm rev}^{(\rm R)} \approx 4T_{\rm rev}^{(\rm V)} \approx 2T_{\rm rev}^{(\rm VR)}$. But since $T_{\rm rev}^{(\rm R)}/T_{\rm cl}^{(\rm R)} = 36.5$, the revived wave packet is shifted from its initial position by one quarter of the orbit for $t = T_{\rm rev}^{(\rm R)}/2$ and by half an orbit for $t = T_{\rm rev}^{(\rm R)}$. Full revival at the initial position will take place at $t = 2T_{\rm rev}^{(\rm R)}$.

Three-way fractional revivals occur at $t = T_{rev}^{(R)}/6$ and at $t = T_{rev}^{(R)}/3$. But they are not well separated due to the spread in the initial wave packet. In what follows, we analyze a more clear case of rotational-vibrational fractional revival that occurs at $t = T_{rev}^{(R)}/4 \approx T_{rev}^{(V)} \approx T_{rev}^{(VR)}/2$.



Figure 3.3: The wave packet evolution for H_2 at the initial stage. Shown here is a plot of $|\Psi(\mathbf{r},t)|^2$ at different times for a wave packet of the form Eq. (3.8). The initial wave packet is constructed in exactly the same way as for I_2 , but the annular ring extends from $0.9r_0$ to $3.5r_0$.

In terms of a doubly periodic function

$$\psi_{\rm cl}(t_1, t_2) = \sum_{\mu k} \tilde{c}_{\mu k} \tilde{\psi}_{\mu k} \exp[-2\pi i (\mu t_1 / T_{\rm cl}^{\rm (V)} + k t_2 / T_{\rm cl}^{\rm (R)})], \qquad (3.16)$$

the full wave function at $t=T_{\rm rev}^{\rm (R)}/4$ can be written as

$$\Psi(\mathbf{r},t) = \frac{1}{2} [\psi_{\rm cl}(t,t) - i\psi_{\rm cl}(t+T_{\rm cl}^{\rm (V)}/2,t)] + \frac{1}{2} [\psi_{\rm cl}(t,t+T_{\rm cl}^{\rm (R)}/2) + i\psi_{\rm cl}(t+T_{\rm cl}^{\rm (V)}/2,t+T_{\rm cl}^{\rm (R)}/2)], \qquad t = T_{\rm rev}^{\rm (R)}/4.$$
(3.17)



Figure 3.4: The wave packet evolution for H_2 on longer time scales. Shown here is a plot of $|\Psi(\mathbf{r},t)|^2$ at different times for a wave packet of the form Eq. (3.8). The initial wave packet is constructed in exactly the same way as for I_2 , but the annular ring extends from $0.9r_0$ to $3.5r_0$.

Note that the second argument in the bottom line on the right of Eq. (3.17) is advanced by an amount $T_{\rm cl}^{(\rm R)}/2$ with respect to the top. With reference to the plot at $t = T_{\rm rev}^{(\rm R)}/4$ in Fig. 3.4, this means that the top and bottom lines on the right of Eq. (3.17) correspond to the wave packet on the right and left respectively. Using a pair of doubly periodic functions

$$\psi_{\rm cl}^{(\rm odd,\, even)}(\mathbf{r}, t_1, t_2) = \sum_{\mu} \sum_{k \, \rm odd,\, even} \tilde{c}_{\mu k} \tilde{\psi}_{\mu k}(\mathbf{r}) \exp[-2\pi i (\mu t_1 / T_{\rm cl}^{(\rm V)} + k t_2 / T_{\rm cl}^{(\rm R)})], \quad (3.18)$$

it is easy to show that

$$2\psi_{\rm cl}^{(\rm even)}(t,t) = \psi_{\rm cl}(t,t) + \psi_{\rm cl}(t,t + T_{\rm cl}^{(\rm R)}/2)$$

$$2\psi_{\rm cl}^{(\rm odd)}(tT_{\rm cl}^{(\rm V)}/2,t) = \psi_{\rm cl}(t + T_{\rm cl}^{(\rm V)}/2,t) - \psi_{\rm cl}(t + T_{\rm cl}^{(\rm V)}/2,t + T_{\rm cl}^{(R)}/2). \quad (3.19)$$

Substituting in Eq. (3.17), the full wave function at $t = T_{\rm rev}^{(\rm R)}/4$ can also be written as

$$\Psi(t) = \psi_{\rm cl}^{(\rm even)}(t,t) - i\psi_{\rm cl}^{(\rm odd)}(t+T_{\rm cl}^{(\rm V)}/2,t), \qquad t = T_{\rm rev}^{(\rm R)}/4.$$
(3.20)

In this form, $\psi_{cl}^{(even)}(t,t)$ produces the outer peaks at $t = T_{rev}^{(R)}/4$ while $\psi_{cl}^{(odd)}(t+T_{cl}^{(V)}/2,t)$ produces the inner peaks. Note that the latter is squeezed because of its proximity to the steep repulsive wall of the Morse potential.

Case II : H₂ molecule, $\overline{\nu} = 10, \overline{j} = 10; \ \overline{\nu} - 2 \le \nu \le \overline{\nu} + 2, \ \overline{j} - 2 \le j \le \overline{j} + 2$



Figure 3.5: The wave packet evolution for H_2 on longer time scales. Shown here is a plot of $|\Psi(\mathbf{r},t)|^2$ at different times for a wave packet of the form Eq. (3.8). The initial wave packet is constructed in exactly the same way as for I_2 , but the annular ring extends from $0.9r_0$ to $3.5r_0$.

In this second case, we have chosen $\overline{\nu} = 10$ and $\overline{j} = 10$ as given in third row of Table 3.2. Here also time scale ratios are very close to each other similar to the case I. Revival of the initial wave packet takes place at $t = T_{\text{rev}}^{(\text{R})}/2 \approx 2T_{\text{rev}}^{(\text{V})} \approx \frac{3}{4}T_{\text{rev}}^{(\text{VR})}$ i.e., at $t = T_{\text{rev}}^{(\text{R})} \approx 4T_{\text{rev}}^{(\text{V})} \approx \frac{3}{2}T_{\text{rev}}^{(\text{VR})}$. At this time, $T_{\text{rev}}^{(\text{V})}$ and $T_{\text{rev}}^{(\text{R})}$ are reviving but $T_{\text{rev}}^{(\text{VR})}$ is not. Therefore, at $t = T_{\text{rev}}^{(\text{R})}$, complete revival is not possible as shown in Fig. 3.5. Full revival will take place at $t = 2T_{\text{rev}}^{(\text{R})}$ i.e., at $t = 2T_{\text{rev}}^{(\text{R})} \approx 8T_{\text{rev}}^{(\text{V})} \approx 3T_{\text{rev}}^{(\text{VR})}$, where all revival time scales will revive simultaneously. But since $2T_{\text{rev}}^{(\text{R})}/T_{\text{cl}}^{(\text{R})} = 47.84$, not an integer, the revived wave packet is slightly shifted from the initial position (see Fig. 3.6). Note that, at $t = T_{\text{rev}}^{(\text{R})}$, there is a two-way ro-vibrational fractional revivals that can be analyzed in the same way as in Case I.



Figure 3.6: The wave packet evolution for H_2 at some specific times. Time is scaled by $T_{\rm rev}^{(\rm R)}$ where the last one shows the complete revival but slightly shifted in its orbit from the initial position.

We end this section by noting that for the relatively small values of $\overline{\nu}$ and \overline{j} as used in this paper, the nuclear wave packet for I₂ rotates on a narrow ring about the center of mass and bears striking similarities with the electronic wave packet evolution of Rydberg atoms [15]. For H₂, however, the wave packet evolution is like the 'unfolding of the petals of a flower' due to the presence of competing time scales.

3.4 Analysis by autocorrelation function



Figure 3.7: Plot of $|A(t)|^2$ as a function of time for the wave packet of the iodine molecule using the full energy spectrum (solid line) and the approximate energy spectrum with $\nu = \overline{\nu}$ (dotted line).



Figure 3.8: Plot of $|A(t)|^2$ as a function of time for the wave packet of the hydrogen molecule using the full energy spectrum (solid line) and the approximate energy spectrum with $\nu = \overline{\nu}$ (dotted line).

A widely used method for probing the revival dynamics of diatomic molecular wave packets has been through the autocorrelation function [9, 11] as it relates directly to the observable signal in the pump-probe type experiments for studying the wave packet dynamics. The autocorrelation function for an evolving wave packet $\Psi(\mathbf{r}, t)$ is given by the overlap integral $A(t) = \langle \Psi(\mathbf{r}, t) | \Psi(\mathbf{r}, 0) \rangle$. It is, by now, well understood how the prominent features of revival and fractional revivals can be gauged from a plot of $|A(t)|^2$ as a function of time.

In this section, we plot $|A(t)|^2$ for the wave packets of I₂ and H₂ with $\overline{\nu} = 7$, $\overline{j} = 14$; and $\overline{\nu} - 1 \le \nu \le \overline{\nu} + 1$, $\overline{j} - 3 \le j \le \overline{j} + 3$. In each case, we have also plotted $|A(t)|^2$ by freezing the vibrational motion, that is, by setting $\nu = \overline{\nu}$ in the energy spectrum.

Fig. 3.7 shows the results for I_2 . It is clear that the macroscopic or coarse-grained features of $|A(t)|^2$ are obtained, to a good approximation, even when the vibrational motion is neglected. More precisely, the positions of the prominent peaks are predicted correctly by rotational motion alone. The role of the vibrational motion is to provide densely packed subsidiary peaks under each of these prominent peaks.

The situation is very different in the case of H₂ as shown in Fig. 3.8. In this case, the vibrational and rotational motions are so strongly coupled that the neglect of one or the other will drastically alter the shape of $|A(t)|^2$. Because the time scales of the two motions are comparable, $|A(t)|^2$ is a rather complicated function of time. Furthermore, as Fig. 3.9



Figure 3.9: Plot of $|A(t)|^2$ as a function of time for the wave packet of the hydrogen molecule using the full energy spectrum for a narrow window about $t = T_{rev}^{(R)}/4$.

shows, the ro-vibrational fractional revival at $t = T_{rev}^{(R)}/4$ that was shown in Fig. 3.4 and analytically explained in the previous section, is not at all obvious from the autocorrelation plot.

To make the scenario more transparent, we have shown plots of autocorrelation function in which the terms appearing in the argument of the exponential factor in Eq. (3.8) have been included progressively. Fig. 3.10(a) shows a plot of $|A(t)|^2$ where the phase term has only linear dependence i.e., contains only the first two terms in the phase argument. Here competitive time scales are $T_{cl}^{(R)}$ and $T_{cl}^{(V)}$. Next, we show plots of $|A(t)|^2$ in which the quadratic terms in phase are added successively to emphasize the role of different revival time scales. Figs. 3.10(b), (c) and (d) are plotted by considering respectively the first three terms, the first four terms and all the terms in the phase argument of Eq. (3.8). Thus, in Fig. 3.10(d), all time scales are present. Note that at $t = T_{rev}^{(R)}$ i.e., $t = T_{rev}^{(R)} \approx 4T_{rev}^{(V)} \approx$ $2T_{rev}^{(VR)}$, complete revival will not appear as $T_{rev}^{(R)}/T_{cl}^{(R)} = 36.5$. When time is $t = 2T_{rev}^{(R)}$, all time scales revive simultaneously and the full revival takes place (see Fig. 3.10(e)).

Similar explanation can be given for case II with the values $\overline{\nu} = 10, \overline{j} = 10; \overline{\nu} - 2 \le \nu \le \overline{\nu} + 2, \quad \overline{j} - 2 \le j \le \overline{j} + 2.$



Figure 3.10: Plot of $|A(t)|^2$ as a function of time for the wave packet of the hydrogen molecule with $\overline{\nu} = 7$, $\overline{j} = 14$; and $\overline{\nu} - 1 \le \nu \le \overline{\nu} + 1$, $\overline{j} - 3 \le j \le \overline{j} + 3$. Time is scaled by $T_{rev}^{(R)}$. (a) Phase term contains only the linear terms. Next, we have added upto third term in (b), upto forth term in (c) of Eq. (3.8). (d) Phase term contains all time scales as given in Eq. (3.8). (e) Full revival appear at $t = 2T_{rev}^{(R)}$.

3.5 Conclusion and applications

Our detailed analysis was based on the Morse-Pekeris model [96] which is sufficiently accurate for both I_2 [97] and H_2 [98] for the values of ν and j used in this work. For higher values of ν and j, our predictions can be used as a crude indicator and, ideally, more accurate inter-nucleon potentials should be used. However, as long as the energy eigenvalues can be written as a Dunham series and the initial wave packet is formed with sharply peaked weighing coefficients, our procedure will remain valid.

The choice of a circular state wave packet was to draw parallels with the evolution of a Rydberg electronic wave packet of circular states [15]. As shown above, our results depend on the various time scales which are derived from the energy spectrum. Since the energy eigenvalues are independent of m, the z-component of the angular momentum, our conclusions are equally as valid for non-circular states.

Exciting non-circular ro-vibrational wave packets is now a routine exercise [99, 100]. In principle, it should also be possible to generate circular state wave packets by spinning the molecule in an optical centrifuge [101, 102]. Finally, the revival dynamics of the ro-vibrational wave packet can be probed by a variety of existing techniques such as direct imaging [103], photo-ionization [104], fluorescence in time delayed pump-probe spectroscopy [105] or even by sub-laser cycle electron pulses [106]. Separation of time scales can be measured by femtosecond wavepacket spectroscopy [99].

The revival dynamics, ro-vibrational separability condition and the detailed spatial structure of the evolving wave packet as described above, should be relevant and useful in the emerging areas of molecular wave packet dynamics [53, 107], molecules in laser fields [108], laser-assisted molecular engineering [109], isotope separation [110] and quantum computation [111]. As molecules are nowadays being probed and imaged with unprecedented temporal precision [106, 112, 113], it may even be possible, in near future, to confirm experimentally the ro-vibrational fractional revival predicted in this work.

Chapter 4

A time frequency analysis of wave packet fractional revivals

4.1 Introduction

Quantum systems, with nonlinear energy spectra, show some interesting phenomena in the time evolution of a wave packet, called the revival and fractional revivals [2, 4]. It has been shown that the phenomena of revival and fractional revival occur in the wave packet dynamics of various atomic, molecular and optical systems such as Rydberg atoms [1, 8, 13, 14, 15, 114, 115, 116, 117], optical parametric oscillators [118, 119, 120], the Jaynes-Cummings model [121, 122, 123], transient signals from multilevel quantum systems [124], potential wells [7, 125, 126, 127] and molecular vibrational states [9, 10, 72, 128]. Extensions to systems for which the energy spectrum depends on two quantum numbers, have also been made in recent years [33, 34, 50, 51, 129, 130]. These phenomena have been experimentally observed in both atomic [13, 14, 115, 117] and molecular systems [72].

A widely used method for probing the revival dynamics of wave packets is based on a study of the autocorrelation function [8, 10, 131]. This method is directly related to the observable signal in the pump-probe type experiments for studying the wave packet dynamics. The autocorrelation function for an evolving wave packet $\Psi(r, t)$ is given by the overlap integral $A(t) = \langle \Psi(r, t) | \Psi(r, 0) \rangle$. The autocorrelation function is a time series whose Fourier transform (FT) will reveal all the frequencies, but will be unable to provide any information on when a particular frequency appears. This is important in the present context as the frequencies are time varying. In other words, fractional revivals of a particular order occur at particular instants of time. What is really desirable is a time-frequency analysis of the autocorrelation function such that we not only know all the frequencies, but also get information on when a particular frequency occurs. This is the objective of the present work.

For the purpose of time-frequency analysis, short-time Fourier transform (STFT) has often been used in the literature. This method divides the whole time series in several windows, each of certain fixed width. Then the FT is performed in each window for obtaining the frequency information. Unfortunately, the time-frequency information obtained by this method has not always been satisfactory as its fixed window length does compromise on the frequency resolution. The method of continuous wavelet transform (CWT) [61, 62, 64, 65, 132, 133, 134] overcomes the preset resolution problem of STFT by using a variable length window. This transform, by design, provides good localisation in both time and frequency. The subject area of wavelets, developed mostly over the last fifteen years, is at the forefront of much current research in pure and applied mathematics, physics, computer science and engineering. This transform has emerged over recent years as a powerful time-frequency analysis. A narrow window is used for the analysis of the high frequencies and gives a better time resolution. A wider window is used for the analysis of low frequencies and gives a better frequency resolution. The continuous wavelet transform (CWT) of a signal f(t) is defined as

$$T(s,\tau) = \frac{1}{\sqrt{s}} \int f(t)\phi^*\left(\frac{t-\tau}{s}\right) dt$$
(4.1)

This transformed signal is a function of two variables, s and τ , that are used respectively to scale and translate the wavelet window whereas ϕ^* is the complex conjugate of the transforming function known as the mother wavelet for the CWT. In our study we have used the Morlet wavelet as the mother wavelet. The contribution to the signal energy at the specific scale s and location τ is given by the two-dimensional wavelet energy density function known as the scalogram:

$$E(s,\tau) = |T(s,\tau)|^2.$$
(4.2)

The frequencies are inversely proportional to the scale parameter, and thus s and τ together help provide information in the time-frequency plane. In this work, we present a case study to show that a wavelet-based time-frequency analysis is superior in many ways to the standard time-domain analysis of the auto-correlation function.

4.2 Fractional Revivals of a Rydberg wave packet

We consider a Rydberg wave packet which is a superposition of circular hydrogenic states having l = m = n - 1 [114]. The time-dependent wave function for a localized wave packet formed as a superposition of eigenstates may be written as

$$\psi(\vec{r},t) = \sum_{n} c_n \psi_n(\vec{r}) e^{-iE_n t}$$
(4.3)

As a pre-requisite for obtaining fractional revivals, we assume that the weighting probabilities $|c_n|^2$ are strongly peaked around a mean value \bar{n} with a spread $\Delta n = n_{\text{max}} - n_{\text{min}} \ll \bar{n}$. This allows us to expand the energy eigenvalues $E_n = -(2n^2)^{-1}$ (in atomic unit) in a Taylor series in n as follows

$$E_n = E_{\bar{n}} + E'_{\bar{n}}(n-\bar{n}) + \frac{1}{2}E''_{\bar{n}}(n-\bar{n})^2 + \frac{1}{6}E_{\bar{n}}(n-\bar{n})^3 + \dots$$
(4.4)

Neglecting the overall time-dependent phase and considering up to the second order term, we may write E_n as

$$E_n = 2\pi \left\{ \frac{(n-\bar{n})}{T_{\rm cl}} - \frac{(n-\bar{n})^2}{T_{\rm rev}} \right\},\tag{4.5}$$

where each term in the expansion defines important characteristic time scale that depend on \bar{n} ;

$$T_{\rm cl} = \frac{2\pi}{|E'_{\bar{n}}|}, \qquad T_{\rm rev} = \frac{2\pi}{\frac{1}{2}|E''_{\bar{n}}|}.$$
 (4.6)



Figure 4.1: Autocorrelation function of a Rydberg wave packet with $\bar{n} = 320$, $\Delta n = 40$ and $\sigma = 2.5$. Time t is in a.u. (in the unit of 10^{10}).

Since the energy spectrum is known in this case, one obtains

$$T_{\rm cl} = 2\pi \bar{n}^3, \quad T_{\rm rev} = 2T_{\rm cl} \bar{n}/3.$$
 (4.7)

The absolute square of autocorrelation function is

$$f(t) = |A(t)|^2 = \sum_{n,m} |c_n|^2 |c_m|^2 e^{-iE_{nm}t/\hbar},$$
(4.8)

where $E_{nm} = E_n - E_m$.

Fig. 4.1 shows a plot of $|A(t)|^2$ as a function of time. This plot was generated by choosing $|c_n|^2$ as a Gaussian distribution with $\bar{n} = 320$, $\Delta n = 40$ and a FWHM given by $\sigma = 2.5$.

Peaks appearing in Fig. 4.1, are the signature of revivals and fractional revivals. Fast Fourier transform (FFT) of this time series data gives the individual spectral components in the frequency plane as shown in Fig. 4.2. Although we can get complete frequency information in this way, we do not have any idea on which frequency appears at what time. On the other hand, the autocorrelation time series can be recovered by using the inverse FFT, but the frequency information goes away completely.

Our goal is to acquire some frequency information in some particular times of interest. In the next section, we make use of continuous wavelet transform to investigate how one is able to resolve time and frequency in a better way.



Figure 4.2: (Color online) Spectral components present in the autocorrelation function of the Rydberg wave packet. Frequency is in a.u (in the unit of 10^{-8}).

4.3 Time-Frequency Analysis

Wavelet based time-frequency representation or scalogram of the time series data $f(t) = |A(t)|^2$ is shown in Fig. 4.3. The scalogram was computed by using the *Time-Frequency Tool Box (TFTB) for MatLab* [135]. Here, we have used the Morlet wavelet, described as a complex exponential modulated by a Gaussian envelope. It is a function of time and given by $\varphi(t) = \pi^{-1/4} e^{i\omega_0 t} e^{-t^2/2}$, with the central frequency ω_0 . Let Δt and $\Delta \omega$ be the RMS duration and bandwidth respectively of the mother wavelet $\varphi(t)$, where Δt is given by

$$\Delta t \equiv \sqrt{\frac{\int_{-\infty}^{\infty} (t - t_0)^2 |\varphi(t)|^2 dt}{\int_{-\infty}^{\infty} |\varphi(t)|^2 dt}},$$
(4.9)

The term inside the square root is the second moment of the wavelet centered at t_0 . Similarly the bandwidth of the wavelet is

$$\Delta\omega \equiv \sqrt{\frac{\int_{-\infty}^{\infty} (\omega - \omega_0)^2 |\varphi(\omega)|^2 d\omega}{\int_{-\infty}^{\infty} |\varphi(\omega)|^2 d\omega}}.$$
(4.10)

This mother wavelet is then used to build a set of daughter wavelets by translating $\varphi(t)$ in time, and by dilating or contracting $\varphi(t)$, which not only adjusts the mean frequency but also the spread of the daughter wavelet.

Consider the case when the mother wavelet is scaled by s. The Fourier transform of $\varphi(t/s)$ is $|s|\varphi(s\omega)$. The RMS duration becomes $\Delta t(s) = |s|\Delta t$ and the corresponding

RMS bandwidth is $\Delta\omega(s) = \Delta\omega/s$. It implies $\Delta t(s)\Delta\omega(s) = \Delta t\Delta\omega$, which is independent of the scaling parameter s. It is easy to show that the translation parameter τ merely affects the location of the wavelet and not the RMS duration. Similarly, the RMS bandwidth is also not affected by τ as translating a function does not affect the magnitude of its Fourier transform. Thus, it suffices to consider the RMS duration and bandwidth of the mother wavelet only.

Ability of the CWT to resolve events closely spaced in time increases with smaller values of Δt . Similarly, the smaller the value of $\Delta \omega$, better is the ability of the CWT to resolve events closely spaced in frequency. However, it is not possible to reduce the uncertainty in both dimensions simultaneously as the time-frequency resolution is governed by the uncertainty relation $\Delta \omega \Delta t \geq 1/2$ [62]. A wavelet with a smaller value of $\Delta \omega \Delta t$ provides better simultaneous localization in the time frequency plane than one with a larger value. For our chosen mother wavelet $\varphi(t)$, Eqs. (4.9) and (4.10) can be used to show that the time bandwidth product reaches its minimum value of 1/2.

Referring to Fig. 4.3, we note that several patches appear in a rectangular array on the time-frequency plane. Each patch is centered about a particular frequency and a particular time. To help us understand the occurrence of these patches, we undertake an analytical approach as described below. Recall that the absolute square of the autocorrelation function is given by Eq. (4.8). Writing $y = (t - \tau)/s$, the CWT of f(t) can be written as

$$T(\tau, s) = \sqrt{s} \int_{-\infty}^{\infty} f(ys + \tau)\phi^*(y)dy.$$
(4.11)

where $\phi(y)$ is the Morlet wavelet with shifted time τ and scaled by s:

$$\phi(y) = \pi^{-1/4} e^{i\omega_0 y} e^{-y^2/2}.$$
(4.12)

Substituting in Eq. (4.11) and performing the integration over y, we get

$$T(\tau, s) = \sqrt{2\pi s} \sum_{n,m} |c_n|^2 |c_m|^2 \pi^{-1/4} e^{-iE_{nm}\tau/\hbar} e^{-(\omega_0 + sE_{nm}/\hbar)^2/2}.$$
 (4.13)

Maximum values of $T(\tau, s)$ corresponding to a particular scale parameter s should occur whenever the factor $e^{-(\omega_0 + sE_{nm}/\hbar)^2/2}$ approaches unity. This gives rise to a constraint:

$$\omega_0 = -sE_{nm}/\hbar. \tag{4.14}$$


Figure 4.3: Time-frequency representation of the autocorrelation function of Rydberg atom. Time t (in the unit of 10^{10}) and frequency (in the unit of 10^{-8}) are in a.u.

Since the distribution functions $|c_n|^2$ and $|c_m|^2$ are peaked about \bar{n} , the central frequency of each frequency band in Fig. 4.1(b) can be obtained by setting $n = \bar{n}$ and $m = \bar{n} + p$, where p is an integer. Since ω_0 is positive, we must insist that p is a *positive* integer. Substituting in Eq. (4.14) and using the quadratic approximation (4.5) for the energy eigenvalues, we immediately get

$$\omega_0 = \frac{2\pi sp}{T_{\rm cl}} \left(1 - p \frac{T_{\rm cl}}{T_{\rm rev}} \right) \tag{4.15}$$

Since the scale parameter s is related to frequency f by the relation $s = \omega_0/(2\pi f)$ and $T_{\rm cl} \ll T_{\rm rev}$, we finally obtain the simple formulae

$$f_p = \frac{p}{T_{\rm cl}}, \qquad s = \frac{\omega_0}{2\pi f_p}.$$
(4.16)

The above formula correctly predicts the central frequencies around which the spectral components are clustered in the frequency plane as was shown earlier in Fig. 4.1(b). Note that each horizontal band in Fig. 4.3 has a spread about its central frequency. We will now show that the terms corresponding to these frequencies add up coherently in the expression for $T(\tau, s)$ at a particular time τ given by

$$\tau/T_{\rm rev} = \frac{k}{2p} \tag{4.17}$$

where k is an integer.

Coherent addition of terms would require that the phase factor $\exp(-iE_{nm}\tau/\hbar)$ be the same for these terms. That is, for arbitrary values of n and n', one should be able to satisfy the condition

$$\tau E_{n,n+p} = \tau E_{n',n'+p} + 2\pi N \tag{4.18}$$

where N is an integer number. Using the approximation (4.5), it is now easy to show that τ is indeed given by the expression Eq. (4.17). An equivalent and simpler way of deriving this result is to insist that the phase factor $\exp(-i\tau E_{n,n+p})$ is independent of n.

The expression Eq. (4.17) gives us the time instants at which $|A(t)|^2$ is peaked. Specifically, it tells us which frequency beats occur at what times. The lowest frequency beat f_1 occurs for p = 1 at times $t/T_{rev} = 1/2$, 1, 3/2, 2,.... Similarly, the frequency beat f_2 corresponding to p = 2, occurs at $t/T_{rev} = 1/4$, 1/2, 3/4, 1,.... Thus the patches appearing in the bottom row give the transition frequency between any two consecutive levels (p = 1); the ones on the next row are the transition frequencies corresponding to p = 2 and so on.

Thus interestingly, in time-frequency plane, one can find both time and frequency information from the two time scales $T_{\rm cl}$ and $T_{\rm rev}$ by using the expressions (4.17) and (4.16). In fact, these two expressions provide the location of each patch in the time-frequency plane. As an example, let us consider the fourth maximum or patch in the third harmonic appearing in Fig. 4.3. Here, the third harmonic corresponds to p = 3, so the frequency information corresponding to this patch can be obtained from Eq. (4.16), which is $f_3 = 3/T_{\rm cl} = 1.457 \times 10^{-8}$ a.u., as shown in Fig. 4.3. The corresponding value for time can be obtained from Eq. (4.17). In this case, k = 4, and p = 3, so the patch will appear at $t = \frac{2}{3}T_{\rm rev} = 2.928 \times 10^{10}$ a.u.

How do these time-frequency patches relate to fractional revivals? Fractional revivals occur whenever

$$\tau/T_{\rm rev} = \frac{r}{q} \pmod{q},$$
 (4.19)

where r and q are mutually prime integers [2]. By expressing Eq. (4.17) in the form (4.19), one can obtain the correspondence between a particular patch in the time-frequency plane and the fractional revival it contributes to. In this way, frequency bands, depicted in Fig. 4.3, trace out the signature of fractional revivals and determine the different harmonics that are expected to appear in fractional revivals of a given order.

We end this section by noting that a time-frequency analysis of fractional revivals has also been made previously for a different system, the vibrational wave packet of a diatomic molecule [72]. The authors used a spectrogram rather than a scalogram. A spectrogram is based on the short-time Fourier transform (STFT) whereas a scalogram is based on the continuous wavelet transform (CWT). Notwithstanding the shortcomings of STFT as outlined in Introduction, we found that for the present system, results from both methods are in reasonable agreement provided an appropriate window length is chosen for the spectrogram. The agreement probably stems from the fact that in both methods, as applied to fractional revivals, we have so far only been concerned with the location of the centre of time-frequency patches and not with the way each patch extends in the horizontal and vertical directions.

4.4 Fractional Revivals of a diatomic molecular system

For a diatomic molecular system, the vibrational energy spectrum [128] can be expressed as



Figure 4.4: Autocorrelation function of I_2 molecular wave packet with a Gaussian distribution. $\bar{n} = 56$, $\Delta n = 30$ and $\sigma = 3$. Time t is in a.u. (in the unit of 10^6).

$$E_n = -(D/\lambda^2)(\lambda - n - 1/2)^2, \qquad (4.20)$$

where D is the dissociation energy. This quadratic energy spectrum yields the revival times given by $T_{\rm cl} = T_{\rm rev}/(2\lambda - 1)$ and $T_{\rm rev} = 2\pi\lambda^2/D$ respectively, where $\lambda = \sqrt{\frac{2\mu D r_0^2}{\beta^2 h^2}}$. We will be considering the I_2 molecule, as an example, with $\beta = 4.954$, reduced mass $\mu = 11.56 \times 10^4$ a.u., equilibrium distance $r_0 = 5.03$ a.u. and D = 0.057 a.u. The autocorrelation function of I_2 molecular wave packet of vibrational states is depicted in Fig. 4.4 where the width of the Gaussian distribution is $\sigma = 3$. It includes 30 bound states around $\overline{n} = 56$ where $T_{cl} = 6.5 \times 10^3 a.u.$ and $T_{rev} = 1.5 \times 10^6 a.u.$ respectively. Similar analysis can be done for I_2 molecule in the time-frequency plane. In Fig. 4.5, we show the time frequency representation of the same autocorrelation function. The harmonics pull out information of both time and frequency that was not obvious in the time domain. As $T_{cl} << T_{rev}$, similar results can be acquired for time τ and frequency f_p , as obtained in the case of Rydberg atom. For the fourth harmonics, frequency patches appeared at $t = \frac{1}{8}T_{rev}$, $\frac{1}{4}T_{rev}, \frac{3}{8}T_{rev}, \frac{1}{2}T_{rev}$ etc. This wavelet analysis, made it possible to find the clear signature of higher order fractional revivals.



Figure 4.5: Time-frequency representation of the autocorrelation function of I_2 molecule. Time t (in the unit of 10^6) and frequency (in the unit of 10^{-4}) are in a.u.

4.5 Advantages of the time-frequency representation

It is seen that the wavelet-based time-frequency representation provides localisation in both time and frequency. Higher order fractional revivals and their localisation in time are



Figure 4.6: (a)Autocorrelation function of Rydberg atomic system with $\sigma = 2.5$, (b), (c), (d) and (e) show $|T(\tau,s)|^2$ for s = 1.96, 0.97, 0.65 and 0.48 (in unit of 10^8) respectively. Times are scaled by revival time and $|T(\tau,s)|^2$ is scaled by 10^6 .



Figure 4.7: (a) A short-lived time series of autocorrelation function and (b) its wavelet based time-frequency representation. Time (in the unit of 10^5) and frequency (in the unit of 10^{-4}) are in a.u.

clearly manifest in the time-frequency plane. We showed how T_{rev} and T_{cl} are themselves sufficient to explain the time-frequency plane completely.

Note also that the square of the autocorrelation function, plotted as a time series, does not resolve fractional revivals unambiguously. More precisely, the order of the fractional revival cannot always be determined. In contrast, the time-frequency representation introduces a parameter p through Eqs. (4.16) and (4.17) that clearly separates out the fractional revivals in a rectangular array on the time-frequency plane. In Fig. 4.6, we show how the corresponding s values filter out fractional revivals from the complicated plot of the autocorrelation function. For p = 1, one can find s using Eq. (4.16). This specific s value can filter out the signature of fractional revivals as shown in Fig. 4.6(b). This is also true for the higher order harmonics as shown in Fig. 4.6(c), (d) and (e) for p = 2, p = 3 and p = 4, respectively. These specific values of s filter out the signature of the corresponding higher order fractional revivals.

The time-frequency representation can be useful for a wave packet that decays before its revival time. Although the short-time evolution of $|A(t)|^2$ can still be used to estimate $T_{\rm cl}$ [115], no information can be gained about $T_{\rm rev}$ if the energy spectrum of the system is *not* known. However, as long as the wave packet survives long enough for some patches to occur in the scalogram (see Fig. 4.7), one can use Eq. (4.17) to estimate $T_{\rm rev}$.

For example, let us consider the first patch appearing in the sixth harmonics in Fig. 4.7

(b). Here, k = 1 and p = 6. Eq. (4.17) predicts that this patch should occur around $\tau = T_{rev}/12$. A close view of this patch in Fig. 4.8 shows that the patch is centered around $\tau = 1.25 \times 10^5$ a.u. Equating these two values of τ one immediately obtains $T_{rev} = 15 \times 10^5$ a.u. What makes this possible is the better resolution available in the time-frequency plane for the detection of fractional revivals.



Figure 4.8: A close view of first patch appearing in the sixth harmonics in Fig. 4.7(b). Time t (in the unit of 10^5) and frequency (in the unit of 10^{-4}) are in a.u.

Experimental observation reveals that the main source of decoherence of the vibrational molecular wave packets is the coupling between the vibrational and rotational modes. It causes dephasing and destroys the coherent structure of the wave packets. The characteristic time of dephasing process is γ^{-1} . It is comparable to the vibrational periods T_{cl} which appears in general $\sim 300 - 500$ fs. For the potassium dimer at 400°C, $\gamma^{-1} \simeq 8.6 T_{cl}$ for the ground state and $\gamma^{-1} \simeq 6.7 T_{cl}$ for the first excited electronic state respectively [49]. For longer time scales, the ratio of revival time T_{rev} and the characteristic dephasing time γ^{-1} is of order of 10^2 . Thus, the first revival would appear only after many cycles of their vibrational periods. This situation is practically irrelevant in most experimental realization. In such a case, this wave-based time-frequency method will be useful and can extract information about the revival time scales of such short lived signal.

4.6 Conclusion

In conclusion, we demonstrate the time-frequency representation of autocorrelation function for the wave packet dynamics of Rydberg atom and a diatomic molecular system. Frequency information at different fractional revivals times are found. We showed that the analytical results fully interpret our numerical results. In practice, decoherence causes dephasing in coherent structures which produces a short-lived output signal in pump-probe type experiments. In such a case, this analysis can extract information about the revival dynamics of a short-lived system even if the system decays before reaching its revival time.

Conclusions and Future Outlook

In conclusion the present thesis reports several new and interesting results in the area of different application of fractional revivals of a wave packet. Here we have taken both the atomic and diatomic molecular systems. Let us summarise the thesis in the following way:

In Chap. 2, we demonstrate that the interesting sub-Planck structure in mesoscopic quantum systems can indeed be realized in the temporal evolution of vibrational wave packets. This is clearly present, where four wave packets are produced in the temporal evolution. The coherence parameter α plays a crucial role in the formation of this structure. For smaller values of α , $|d_m|^2$ includes the higher vibrational levels of the Morse potential, where the anharmonicity is larger. With the increase of α , $|d_m|^2$ distribution moves towards the lower levels and the initial wave packet becomes well localized. Thus, one needs the low-lying states for a clear observation of this structure. The sub-Planck scale has been shown to control the effectiveness of decoherence, a subject of tremendous current interest in the area of quantum computation and information.

In Chap. 3, we have studied the time evolution of a ro-vibrational diatomic molecular wave packet of circular states. This is an example of a quantum system whose energy spectrum depends on two quantum numbers and whose revival structure will depend on two time scales. Using I_2 as an example of heavy molecules, we show that the rotational and vibrational time scales are so far apart that the ro-vibrational motion gets decoupled and the revival dynamics depends essentially on one time scale. For lightest molecules, H_2 , on the other hand, the evolution of the wave packet depends crucially on both the rotational and vibrational time scales of revival. In the latter case, an interesting rotational vibrational fractional revival is predicted and explained. We also obtain further confirmation of our result from an analysis based on the auto-correlation function. The revival dynamics, ro-vibrational separability condition and the detailed spatial structure of the evolving wave packet should be relevant and useful in the emerging areas of molecular wave packet dynamics, molecules in lasers fields, laser-assisted molecular engineering, isotope separation and quantum computation.

In Chap. 4, we have made use of the continuous wavelet transform to demonstrate the time-frequency representation of autocorrelation function for the wave packet dynamics of a Rydberg wave packet. An analytical approach is provided to interpret the time-frequency plane and explain our numerical observations. We have shown that the time-frequency representation not only provides a complementary method of analyzing fractional revivals, it is a better tool in resolving fractional revivals. Finally, it is shown that the time-frequency representation may be able to extract information about the revival dynamics of a short-lived system even if the system decays before reaching its revival time.

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List of Publications

I. Papers in Journals:

- Mesoscopic superposition and sub-Planck-scale structure in molecular wave packets, S. Ghosh, A. Chiruvelli, J. Banerji and P. K. Panigrahi, Phys. Rev. A 73, 013411 (2006).
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II. Papers In Conference Proceedings:

- Sub-Planck-scale structure in Morse system, S. Ghosh, J. Banerji and P. K. Panigrahi, Proceedings of 2nd International Conference on "Current Developments in Atomic, Molecular and Optical Physics With Applications", held in Delhi University, Delhi, India, March 21-23, 2006.
- 2. Rydberg wave packet in the time-frequency plane, S. Ghosh and J. Banerji, Proceedings of "International Symposium on Quantum Optics", held in PRL, Ahmedabad, India, July 24-27, 2006.

III. Abstracts Presented in Conferences/symposiums:

- 1. SERC School on Quantum Information and Quantum Optics, Physical Research Laboratory, Ahmedabad, India, Feb. 1-14, 2004.
- 2. XV National Conference on Atomic and Molecular Physics, held in Physical Research Laboratory, Ahmedabad, India, December 20-23, 2004.
- Workshop on Quantum Information, Computation and Communication (QICC 2005), February 15-18, 2005, Center for theoretical Studies, IIT Kharagpur, India.
- 4. Topical Conference on Atomic, Molecular and Optical Physics, held in Indian Association for the Cultivation of Science, Kolkata, India, December 13-15, 2005.
- 5. Current Developments in Atomic, Molecular and Optical Physics With Applications, held in Delhi University, Delhi, India, March 21-23, 2006.
- 6. International Symposium on Quantum Optics, held in PRL, Ahmedabad, India, July 24-27, 2006.
- International Conference on Laser and Nanomaterials, held in University of Calcutta, Kolkata, India, November 30-December 2, 2006.
- 8. XVI National Conference on Atomic and Molecular Physics, Tata Institute of Fundamental Research, Mumbai, India, Jan. 8-11, 2007.
- 9. The 38th annual meeting of the Division of Atomic, Molecular, and Optical Physics (DAMOP) of the American Physical Society, Calgary, Canada, June 5 9, 2007.