The non-linear lattice dynamical studies in solids has been an active field of research during the last few years. With the development of modern computers and new techniques for solving non-linear equations, the old physical problems are getting renewed attention.

The mechanism of ferroelectric phase transition in perovskite structure has been investigated using a diatomic lattice chain model with anharmonic polarisable anion and rigid cation by Bilz and his coworkers during the last two decades. The anharmonic polarisable anion consists of a core and a shell with shell-core negative quadratic and positive quadric force constants. Bilz and his co-workers explained softmode behaviour using the model with self consistent phonon approximation (SPA) linearisation procedure. In the absence of SPA approximation, non-linear periodic excitations called periodons were also identified along with the phonons which can be associated with incommensurate phases that occur in crystals during phase transition.

Meanwhile, continuum treatment of similar types of diatomic lattices has appeared in the literature. In these works, an anharmonic nonlinear onsite (double well) potential is associated with one of the atoms. Analytical treatment showed kink soliton and large amplitude phonon type solution. Again it was establishing that the large amplitude phonon in continuum regime is completely equivalent to periodon in the discrete regime.

The dynamics of hydrogen bonded chain has also attracted a lot of interest during the last decade. It has been established that proton motion is responsible for the electrical conductivity
in hydrogen bonded system such as biological systems and some superionic conductors. Again experimental evidence indicates that double well potential associated with the proton along with defects such as Ionic and Bjerrum defects are responsible for proton's motion along the lattice chain. Considering these facts Antonchenko and his co-workers proposed a diatomic chain model (ADZ model), which consists of two sublattices in which proton lies in an onsite double well potential. Pnevmatikos suggested a model which is a variation of the ADZ model. In this model proton moves in a double well and anion moves in a single well. The proton lattice and ionic lattice couple harmonically. The continuum model of Pnevmatikos suggests the existence of both kink and bell type solitons in these lattices. It also explains how the proton motion is a cooperative behaviour over several unit cells with an accommodating anionic lattice.

In this thesis, an attempt has been made to combine Bilz and ADZ model with some modifications so that the dynamics of proton transport and Bilz type lattice dynamics are studied together to explain the behaviour of ferroelectric protonic conductors or biopolymer chains containing polarisable groups like PO₄ etc. As the equations of motion (difference-differential equations) contain two nonlinear terms, no analytical solution seems to exist. Under very special conditions, one may get analytical solutions.

As the main aim is to solve general nonlinear difference - differential equations without any approximation, it is necessary to carry out molecular dynamics (MD) simulation studies so that different types of solutions can be obtained (with or without external force). The initial values for MD simulation can be taken from analytical solutions.

The thesis is divided into six chapters. In the first introductory chapter, past literature is reviewed. As a prelude to the proposed model in this work, the previous nonlinear lattice
dynamics studies of one dimensional monoatomic chain, diatomic chain and hydrogen bonded chains have been elaborated in both discrete and continuum regimes.

Chapter II sets forth the details of the proposed model and the associated Hamiltonian and the equations of motion are derived. The diatomic linear chain is represented by

\[ \ldots X-H \ldots X-H \ldots \]

where \( X \) is the anion and \( H \) is the hydrogen.

The substrate onsite double well potential associated with hydrogen is

\[ V(u_{2n}) = \varepsilon_0 \left( 1 - \frac{u_{2n}^2}{u_0^2} \right)^2 \]

Where \( u_{2n} \) is the \( n^{th} \) proton displacement
\( u_0 \) is the equilibrium distance between neighbouring protons
\( \varepsilon_0 \) is the barrier height of the potential

The anharmonic shell core potential associated with anion is

\[ V(w_n) = -\frac{1}{2} g_2 w_n^2 + \frac{1}{4} g_4 w_n^4 \]

Where \( w_n = u_{1n} - v_n \), the relative shell-core displacement
\( v_n \) is the shell displacement of the anion.
\( u_{1n} \) is the displacement of \( n^{th} \) anion core
\( g_2 \) is the Harmonic shell-core polarisation force constant (quadratic)
\( g_4 \) is the Anharmonic shell-core polarisation force constant (quadric)
The shell of the anion $X$ is coupled to the hydrogen harmonically with a force constant $f$. Anion - Anion cores and the proton-proton (second nearest neighbours) interactions are also harmonic represented by force constants $f_1$ and $f_2$ respectively.

The equations of motion are obtained by applying adiabatic approximation with respect to electron shell movement.

(i) The anharmonic polarisation term gets linearised using SPA approximation.

$$g_4 \, w_n^3 = 3 \, g_4 \, w_n < w_n^2 > = g_1 \, w_n$$

where $< w_n^2 >$ is the self-consistent thermal average over the squared shell-core displacement $w_n^2$ at temperature $T$.

$$g_4 + g_2 = g.$$

If $g$ is high, shell-core interaction is strong and the anion is said to be rigid. On the other hand if $g$ is small, the interaction is weak and the shell and the core move independently. Hence $g$ is a measure of polarisation of the anion.

(ii) Because of the SPA approximation, equations of motion contain only one non linear term associated with the proton. In the discrete regime, if one linearises this nonlinear term also using another kind of SPA approximation, one will arrive at

$$\frac{\partial V (u_{2n})}{\partial u_{2n}} = - \frac{4 \varepsilon_0 u_{2n}}{u_0^2} \left( 1 - \frac{u_{2n}^2}{u_0^2} \right)^2 = - \frac{4 \varepsilon_0 u_{2n}}{u_0^2} \cdot c$$

where $c = \left( 1 - \frac{k}{u_0^2} \right) \; ; \; \; k = < u_{2n}^2 >$
Oscillatory phonon solution has been found using these two approximations. This phonon solution is similar to the solution obtained by Bilz et.al. under certain conditions. Without SPA approximations, periodon like solutions are found for the protonic lattice. Under special conditions, the periodon solution agrees well with the solution found by Henry and Oitmaa in the continuum regime.

In the continuum regime, if one chooses \( g << f \), one gets uncoupled non linear differential equations which can be analytically solved. The solutions found in this case are kink type soliton solutions and it is comparable to solutions obtained by different workers.

The phonon and periodon solutions were simulated numerically in discrete regime using computers for various values of parameters (like \( g \), \( c \) and \( f \)) involved in this model.

It was found that as \( g \rightarrow 0 \), \( \omega_\tau \) (optical mode frequency) \( \rightarrow 0 \) mimicking the softmode. However, for \( c \rightarrow u_0^2 \) even if \( g \rightarrow 0 \), \( \omega_\tau \) will not tend to zero, thus preventing total softening. This is a realistic representation as in no hydrogen bonded systems complete mode softening has been observed.

For \( c < u_0^2 \), there is no instability in the lattice against acoustic modes (\( \omega_- \)) near the centre and at the edge of the Brillouin zone. The corresponding optical dispersion curve (\( \omega_+ \)) shows a drastic change near the centre and at the edge of the Brillouin zone mirroring the probable structural change during the ferroelectric phase transition. From the periodon solution, it was observed that the variation of amplitude (\( \Lambda \)) with wave vector \( k \) depends strongly on the dispersion of phonon and periodon frequencies. As the SPA phonon dispersion curves and the periodon dispersion curves are likely to cross each other at certain values of \( k \) and very small \( g \)'s,
one can very easily visualise incommensurate structures in the proton lattice close to the ferroelectric transition temperature.

In order to solve general nonlinear difference-differential equations, Molecular Dynamics (MD) simulation has been carried out. In this connection, the theory of constant temperature MD is discussed in chapter III. The algorithms for the implementation of constant temperature MD for the proposed model equations are discussed. For the purpose of MD simulation equivalent dimensionless equations for the equations of motion are derived. Constant temperature is maintained by scaling the velocity at every time step. The time integrating algorithm is chosen to be the verlet algorithm. The simulation is carried out for 1000 unit cells i.e. 2000 particles. End - To - End periodic boundary condition (PBC) has been implemented. Initial bias is eliminated by looking at the system after the first 10000 time steps. The computer codes were developed in C and the complete programs are presented.

Chapter IV deals with the execution of MD simulation of the proposed model. The results of the MD simulation obtained by changing the values of various parameters involved in this model are discussed in detail. The values of different double well parameters are taken from experimental results. The variable parameters are temperature (T) polarisation (g) and double well potential parameters (height \( \varepsilon_0 \) and width \( u_0 \)). Snapshots have been taken at \( 2^{14} \)th time step. At low dimensionless temperature (0.1) all protons are in the left well only. The thermal energy is not sufficient for the protons to cross the barrier. As the temperature increases (0.5) MD simulation shows phonon dressed solitons which represent cooperative motion of protons from left well to right well over several unit cells. If the temperature is further increased (0.8) large amplitude phonon is the result. The change in values of g has similar effect as the change in temperature on the solutions. One can visualise the effect of variation in g as follows. When g is
small the shell-core coupling is very weak and there is no interaction between the core and the proton as the proton is connected to the shell only. So, the core and the proton move independently. If $g$ is large, coupling between shell and core is strong and there is indirect interaction between the core and the proton. This is evident in the MD simulation results. At large $g$ value both the core and the proton motion show the similar behaviour. The effect of variation of well parameters (height and width) lead to similar results.

Phase portrait (displacement vs velocity) have been plotted for selected atom sites ($250^{th}$, $500^{th}$, $750^{th}$) for $2^{14}$ time steps. The results show that at low $g$ and low $T$, phonon is the only solution (small amplitude oscillation). At medium value of $g$, two equilibrium points have been found for protons and it can be interpreted as kink type of relaxation by the proton from one well to another well. At higher $g$ value, phonon, soliton and periodon type solution were found to exist together. This suggests the to and fro movement of the proton between the two wells along with the periodic excitations. At very large value of $g$, only periodons (large amplitude non-linear phonon) were observed.

In chapter V, external force is introduced in the proton lattice and MD simulation is carried out for different temperatures. Snapshots have been taken for every 1000 time steps, with slight modifications in the MD programme. The value of external force is taken to be $f_e = 1.72 \times 10^{-11}$ Joules/metre. With the evolution of time, number of solitons gets reduced faster than the case where there is no external force. It is also observed that because of the external force kinks and antikinks get accelerated and these can be clearly seen in the snapshots taken at different time steps. Even in the case of absence of external force kink and antikink move towards each other or away from each other but the motion is only due to thermal fluctuation and no acceleration is observed.
Chapter VI deals with the same model, but has different onsite proton potential i.e. doubly periodic potential.

\[
V(\eta_n) = \frac{2 S_0}{(1 - \alpha^2)} \left( \cos \left( \frac{\eta_n}{2} \right) - \alpha \right)^2
\]

where \( \eta_n = \frac{4 \pi u_{2n}}{2d} \), \( 2d \) - dimension of unit cell, \( S_0 \) corresponds to barrier height.

The height and width of the well depend on the parameter \( \alpha \), where \( 0 < \alpha < 1 \). The double well potential discussed in the previous chapters fail to account for both Ionic and Bjerrum defects, which are essential for the proton transport. The above model potential is devoid of such shortcoming. For this model the equations of motion are derived under the adiabatic approximation. In the continuum limit under special conditions two types of kink like solutions have been found. The first kink corresponds to the shifting of protons from one double well minimum to the next minimum cooperatively over several unit cells (Ionic defect). The second kink represents similar movement over the anion barrier (Bjerrum defect). Using these solutions as initial values MD simulation is carried out for the general nonlinear partial difference differential equations. Results for different temperature and various \( g \) values were obtained.

It is observed that only for particular values of \( T \) and \( g \), both simulations show kink type behaviour at the same time. It can be interpreted as that the Ionic defect and Bjerrum defect motions cooperate effectively so that the proton moves along the lattice overcoming small barrier maximum (due to Ionic defect) and large barrier maximum (due to Bjerrum defect) simultaneously by means of relaxation mechanisms.