

Preface

This thesis deals with the electronic and optical properties of some heteroconjugated systems. The first chapter of this thesis provides an introduction to the study of strongly correlated many body systems. The model Hamiltonians employed to study physical phenomena in many-body systems are discussed in some detail. First the Hückel model is introduced and the failures of the model and reasons for the failures are discussed. Incorporating electron-electron interactions at zero differential overlap level and interpolating the potential between U for on-site interaction to e^2/r for large electron-electron separation leads to the Pariser-Parr-Pople (PPP) model. Truncating the range of the interactions to 'on-site' repulsion 'U' alone gives rise to the Hubbard model, while retaining the nearest neighbour interaction yields the U-V model. Methods for studying these quantum cell models are discussed, with emphasis largely on numerical approaches. The numerical many-body technique - the Valence Bond (VB) method, for exact diagonalization studies is also discussed. Iterative methods for solution of eigenvalue equation for large sparse matrices that result in these studies, are also discussed in detail. In the final section of this chapter, various methods for the computation of static and dynamic polarizabilities and hyperpolarizabilities are also discussed.

The second chapter of this thesis reports investigations on the linear and nonlinear optical properties of the inorganic analogs of the polyenes, namely $(\text{PN})_x$ systems, (x varies from 3 to 7) theoretically using the Pariser-Parr-Pople model(PPP). The Nitrogen and Phosphorus parameters for the PPP model are fixed by fitting the low-lying spectrum known experimentally in a few systems. The optical gap in the thermodynamic limit of the $(\text{PN})_x$ system is much larger than that in polyene. The low-lying electronic excitation and dynamic linear and nonlinear optic responses are compared with those of polyenes. The $(\text{PN})_x$ systems exhibit linear and THG responses comparable with those of polyenes. However, they exhibit weaker

SHG response than the push-pull polyenes. This could be because $(\text{PN})_x$ system can be viewed as a polyene system with alternate push and pull groups introduced along the chain atoms. In the case of polyenes, such a substitution pattern has been shown to be less efficient for SHG than when the push and pull groups are introduced only on the terminal sites of the chain. These NLO coefficients are also found to have a weaker system size dependence than that in polyenes. If push-pull groups are introduced in the linear chain phosphazenes, then a pushing group at the P-terminal end and a pulling group at the N-terminal end would be desired.

The Chapter three of this thesis concerns with studies on ring current and hence the aromaticity of phosphazene molecules. Exact diagonalization technique namely, Diagrammatic Valence Bond method coupled with correction vector technique is employed to calculate the ring currents in phosphazene system for varying system size. Both optical and magnetic properties are studied as a function of variation of substituents. There is a symmetry crossover in the ground state of the system, with change in site energy difference between the Nitrogen and Phosphorus sites. At this cross-over point, the ring current shows a peak. The charge density, charge-charge correlations and spin-spin correlations calculations confirm this transition at $\Delta\epsilon \approx 3.5$ eV.

The Exact PPP calculations of the two-photon cross-section of *trans*-stilbene forms the contents of chapter four. The site energies in the PPP model are varied to simulate donor or acceptor substitution and have computed the two-photon cross-section in the 7 and 8 disubstituted stilbene with both substituent groups being identical. The results do not depend on the type of substituents i.e. whether both substituents are donors or both acceptors. The dependence of the two-photon cross-sections on the strength of donor groups is weak and monotonic. Introducing either a twist around the central double bond or a pedal like rotation on unsubstituted stilbene result in gradual decrease in the two-photon cross-section. This emphasizes the importance of planarity as with fluorenes. Similar effect is observed in 7,8 disubstituted stilbene and the rotation carried out corresponds to the pedal like motion.

However, twisting a substituted stilbene system around the central double bond shows a non-monotonic dependence of the two-photon cross-section on the twist angle. At a twist angle of about 60° the two-photon cross-section increases sharply ($\approx 70\%$). This increase is associated with near degeneracy of the one and two photon states together with non-vanishing transition dipole between the one photon state and both the ground and two photon states. This study shows that bulky electron donating or electron withdrawing substituents which can twist the stilbene molecule around the central double bond can lead to molecules with very large two-photon cross-sections.

The studies reported in chapter five demonstrate that $R_3\text{-P=N}$ group can be used as an efficient donor chromophore to enhance nonlinear optic response of stilbene and azobenzene π -backbones. Both the stilbene and azobenzene systems have similar optical gaps, to the strongly allowed excitation which for stilbenes is the first excited singlet state and for azobenzenes the second excited singlet state. The linear polarizability and the SHG coefficient are large for the triphenyl derivatives and least for the triamino derivatives. These are not strongly frequency dependent up to 1.17 eV excitation frequency. The monophenyl derivative has both α_{av} and $|\vec{\beta}_{av}|$ values which are comparable to the diphenyl and triphenyl derivatives. The THG coefficient is much larger at 1.17 eV than at 0.65 eV excitation frequency because of the proximity of the 1.17 eV excitation energy to the three photon resonance. At 1.17 eV all the THG coefficients are ten to fifty fold larger than those at 0.65 eV. The trimethyl azobenzene derivative shows the largest increase as it is closest to three photon resonance. The low frequency THG coefficient is largest for the trimethyl derivative both for stilbenes and azobenzenes, although, former have larger values for the same derivatization. The EFISH coefficients arising due to alignment of dipole is also large but not as large as that of thiophenes. The TPA in all these systems is strongest to the state to which OPA is also strong. This suggests strong asymmetry of the system. The TPA cross-section is larger for stilbene derivatives than for the azobenzene derivatives and trimethyl derivatized stilbene has the largest TPA cross-section among the systems studied. The high thermal stability and the

ease of chemical manipulation together with large NLO responses make the azaphosphane derivatives linked to stilbene backbone promising candidates in organic optical devices.

The chapter six of this thesis deals with the electronic structure and bonding properties of cyclophosphazene derivatives $P_3N_3X_6$, where X can be Hydrogen, Fluorine, Chlorine, Methyl or Amino group. Density Functional calculations for the structural investigations of some cyclotriphosphazenes show that all of these phosphazenes have planar structures. The P-N and P-X bond lengths and X-P-X angle in the cyclotriphosphazenes are shortened with the increase in electronegativity of the ligands attached to Phosphorus. Vibrational analysis carried out using the B3LYP optimized structures and 6-31G* basis set, characterized these optimized structures as minima on the potential energy surface. Natural bond orbital analysis showed that π - electrons are delocalized over all the ring atoms of cyclotriphosphazenes. Natural bond orbital analysis also support contribution from $d_{\pi}-p_{\pi}$ interaction to the bonding structure and stability of these cyclic phosphazenes.