PREFACE

The present thesis deals with a theoretical study of electronic structures in π-conjugated molecular materials with focus on their application in organic electronics. We also discuss a modified and efficient symmetrized DMRG algorithm for studying excited states in these systems. In recent times, organic conjugated systems have emerged as potential candidates in a wide range of fascinating fields by virtue of their tunable electronic properties, easy processability and low cost. Tunability in the electronic and optical properties primarily are centered on the ordering and nature of the low-lying excited states. Probing these important excited states also demands development of efficient and adaptable techniques.

Chapter 1 provides a basic overview of conjugated organic polymers which have been utilized over decades in diverse fields as in organic light emitting diodes (OLED), organic solar cells (OSC) and non-linear optical (NLO) devices. These systems also contribute significantly to theoretical understanding as they provide important insights of one and quasi-one dimensional systems. In this chapter, we have given basic description of the electronic processes in OLED and OSC along with a brief theoretical description of π-conjugated organic systems.

Chapter 2 gives an account of the numerical techniques which are necessary for the study of low-dimensional strongly correlated systems like π-conjugated systems. For this purpose, effective low-energy model Hamiltonians viz. Hückel, Hubbard and Pariser-Parr-Pople Hamiltonians are discussed. Exact diagonalization technique within the diagrammatic valence bond (DVB) basis and density matrix renormalization group (DMRG) technique are discussed in details. We have also

given brief accounts of the methods employed to study real-time dynamics. A short description of different computational techniques for the study of NLO properties in π-conjugated systems is also provided.

Engineering the position of the lowest triplet state (T_1) relative to the first excited singlet state (S_1) is of great importance in improving the efficiencies of organic light emitting diodes and organic photovoltaic cells. In **chapter 3**, we have carried out model exact calculations of substituted polyene chains to understand the factors that affect the energy gap between S_1 and T_1. The factors studied are backbone dimerization, different donor-acceptor substitutions and twisted backbone geometry. The largest system studied is an eighteen carbon polyene which spans a Hilbert space of about 991 million in the triplet subspace. We show that for reverse intersystem crossing (RISC) process, the best choice involves substituting all carbon sites on one half of the polyene with donors and the other half with acceptors.

Singlet fission (SF) is a potential pathway for significant enhancement of efficiency in OSC. In **chapter 4**, we study singlet fission in a pair of polyene molecules in two different stacking arrangements employing exact many-body wave packet dynamics. In the non-interacting model, SF is absent. The individual molecules are treated within Hubbard and Pariser-Parr-Pople (PPP) models and the interaction between them involves transfer terms, intersite electron repulsions and site-charge—bond-charge repulsion terms. Initial wave packet is constructed from excited singlet state of one molecule and ground state of the other. Time development of this wave packet under the influence of intermolecular interactions is followed within the Schrödinger picture by an efficient predictor-corrector scheme. In unsubstituted Hubbard and PPP chains, 2^1A state leads to significant SF yield

while the 1^1B state gives negligible fission yield. On substitution by donor-acceptor groups of moderate strength, the lowest excited state will have sufficient 2^1A character and hence gives significant SF yield. Because of rapid internal conversion, the nature of the lowest excited singlet will determine the SF contribution to OSC efficiency. Furthermore, we find the fission yield depends considerably on the stacking arrangement of the polyene molecules.

In **chapter 5**, we have given an account of a new modified algorithm for symmetry adaptation within symmetrized density matrix renormalization group (SDMRG) technique. SDMRG technique has been an efficient method for studying low-lying eigenstates in one and quasi-one dimensional electronic systems. However, SDMRG method until now, had bottlenecks involving construction of linearly independent symmetry adapted basis states as the symmetry matrices in the DMRG basis were not sparse. Our modified algorithm overcomes this bottleneck. The new method incorporates end-to-end interchange symmetry (C_2), electron-hole symmetry (J) and parity or spin-flip symmetry (P) in these calculations. The one-to-one correspondence between direct-product basis states in the DMRG Hilbert space for these symmetry operations renders the symmetry matrices in the new basis with maximum sparseness, just one non-zero matrix element per row. Using methods similar to those employed in exact diagonalization technique for Pariser-Parr-Pople (PPP) models, developed in the eighties, it is possible to construct orthogonal SDMRG basis states while bypassing the slow step of Gram-Schmidt orthonormalization procedure. The method together with the PPP model which incorporates long-range electronic correlations is employed to study the correlated excited states of 1,12-benzoperylene.

In **chapter 6**, we have studied the correlated excited states of coronene and ovalene within Pariser-Parr-Pople (PPP) model employing symmetry adapted density matrix renormalization group technique. These polynuclear aromatic hydrocarbons can be considered as graphene nanoflakes and study of their electronic structures will shed light on the electron correlation effects in these finite-size graphene analogues. The electron correlation effect usually diminishes on going from one-dimensional to higher-dimensional systems, yet, it is significant within these finite-size graphene derivatives where it depends on the molecular topology. We have characterized these low-lying energy states by calculating bond orders, spin densities in the lowest triplet state and two-photon absorption cross-sections for low-lying two-photon states.