

ABSTRACT

The research problem undertaken in this dissertation is focused on the theoretical description of the consequences of interactions between the molecular matter and the electric field under the spatial confinement (orbital compression). In particular, the main aim of this work is the qualitative and quantitative analysis on the spatial restriction influence on the linear and nonlinear properties of different type of molecules (polar diatomic molecules, π -electron molecules, noble gas compounds) as well as hydrogen bonded complexes. All results presented within this study have been obtained employing quantum chemistry methods based on the wave function, primarily those which go beyond the independent particles approximation.

The results of theoretical studies conducted for the considered molecular systems demonstrated that together with the increasing strength of spatial confinement one may observe an increase, decrease, or non-monotonic changes in the values of electrical properties. This conclusion is particularly true for the dipole moment and first hyperpolarizability of analysed π -electron molecules. It is worth to emphasise that the obtained results indicate the possibility of strengthening the nonlinear electrical response of molecular systems under the influence of spatial confinement of cylindrical symmetry. The presented results allows to formulate a thesis that the *pure* orbital compression effect causes a reduction of the linear dipole polarizability. On the basis of obtained data it was also shown that the orbital compression significantly reduces the electron correlation contribution to the values of dipole moment, polarizability, and in particular first hyperpolarizability. Moreover, the proper theoretical description of the molecular electric properties, in the presence of cylindrical harmonic potential, may be achieved within the approximation neglecting the core correlation effects.

Based on the systematic comparative analysis of the results obtained using different models of spatial restriction (harmonic oscillator potential, chemical cages in the form of carbon nanotubes and helium structures of topology which corresponds to the carbon nanotubes) it was demonstrated that the analytical potentials can provide adequate representation of the inert chemical environment. However, such models are too simplified to include all sources of changes in the electrical properties of molecules embedded inside more complex structures, like for instance carbon nanotubes. The most pronounced changes in the values of dipole moment, polarizability and first hyperpolarizability of studied molecules occur when the orbital compression effect is modelled by carbon nanotubes.

Analysis regarding the nature of interactions of spatially confined hydrogen bonded complexes indicate that the investigated systems became less stable under the influence of strong orbital compression. Moreover, the shape of the interaction energy curve of the studied two

body systems is dominated by the electrostatic and exchange repulsion terms. It has been also demonstrated that the basis set superposition error is significantly enhanced in the presence of external harmonic confining potential. Furthermore, the results of studies concerning the impact of orbital compression on the phenomenon of hydrogen bonding cooperativity suggests that the spatial confinement may have a significant influence on processes related to the formation of molecular structures of different complexity (eg. molecular crystals).

Another important finding of this study is that the presence of spatial limitation leads to the reduction of distances between atoms, which builds molecular systems. This applies to the interaction of both covalent or ionic nature, as well as to the hydrogen bonds. Additionally, the obtained results indicate that the proper theoretical description of the molecular electrical properties, under the strong confinement regime, requires the inclusion of effects connected with the structural relaxation.