About the electric properties of spatially confined molecular systems

Justyna Kozlowska [1] , Agnieszka Roztoczyńska [2], Wojciech Bartkowiak [3]

Department of Physical and Quantum Chemistry, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, PL50370 Wroclaw, Poland

Studies concerning the spatial confinement phenomenon and its influence on the variety of physical and chemical properties of quantum objects have been attracting an increasing research attention. This is triggered by the great advances in nanotechnology, as well as the rapid development of chemical synthesis methods, particularly in the supramolecular chemistry [1, 2, 3]. These factors open up a fascinating possibility of constructing molecular systems with entirely new properties, mostly determined by the size effects (e.g. endohedral complexes, inclusion compounds or low-dimensional semiconductor structures). One area of research of increasing prominence concerns the linear and nonlinear (L&NLO) electric properties of spatially restricted atoms, ions and molecules. Basically, it is expected that embedding of a quantum system in the confining cages will affect its electronic density distribution. This, in turn, may be reflected through changes in a variety of L&NLO phenomena.

In the present contribution we focus on the theoretical description of the interactions between the molecular matter and the electric field under the spatial confinement (orbital compression). Particularly, the main objective 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) [4, 5, 6, 7] as well as hydrogen bonded complexes [8]. Among the evaluated molecular quantities are properties that govern the NLO processes in the resonant (TPA probability) as well as nonresonant (dipole moment, polarizability, first hyperpolarizability) regime upon confinement. All results, presented within this study, are 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, demonstrate that together with the increasing strength of spatial confinement one may observe an increase, decrease, or non-monotonic changes in the values of studied electric properties [4, 5, 6, 7]. This conclusion is particularly true for the dipole moment and first hyperpolarizability of analyzed molecules. Moreover, the obtained data provide an evidence that the orbital compression might have a significant influence on the magnitude of two-photon absorption response of molecular system [8]. On the other hand, the presented results allow to formulate a thesis that the pure orbital compression effect causes a reduction of the linear dipole polarizability [4, 5, 6, 7].

Summing up, our results indicate the possibility of strengthening the nonlinear electrical response of molecular systems under the influence of spatial confinement of cylindrical symmetry.

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[1] *E-mail: justyna.kozlowska@pwr.edu.pl*
[2] *E-mail: agnieszka.roztoczynska@pwr.edu.pl*
[3] *E-mail: wojciech.bartkowiak@pwr.edu.pl*