

Quantum chemical description of the influence of spatial confinement on the electric properties of atomic and molecular systems

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Abstract

The aim of the studies presented in this dissertation was to characterize the influence of spatial confinement on the electric properties of atomic and molecular systems. The effect of spatial confinement was modeled by applying the harmonic potential of cylindrical and spherical symmetry. The available literature provides a lot of information about changes in the electric properties of chemical objects within restricted spaces. Nevertheless, despite numerous studies in this area, there are still many important aspects that have not been analyzed yet.

The analysis of changes in the electric properties of the CO, BF, LiH, LiF, HF, HCl, HCN, OCS, HArF, ClCCH, HCCCN, CO₂, HCCH molecules, under the influence of spherical harmonic potential, was carried out. The obtained results show that the behavior of electric properties upon spherical harmonic potential significantly differs, depending on the studied system. Moreover, the dipole moment and (hyper)polarizability dependence on the relative position of the linear molecule and spherical harmonic potential was described and an attempt to assess the effect of the topology of confining environment on the electric properties was made. In the vast majority of cases, the significant differences in the values of electric properties obtained in spherical and cylindrical confinement were observed for each orbital compression strength. Nevertheless, when comparing the results obtained in spherical and cylindrical harmonic potential, one should keep in mind the fact that dipole moment and (hyper)polarizability strongly depend on the relative position of the studied system and spherical harmonic potential (as confirmed by the calculations performed for the LiH molecule).

An important element of the research presented in this dissertation were the highly accurate calculations of the polarizability and second hyperpolarizability for the isolated and spatially confined H⁻ and also the analysis of the methodological aspects of these calculations. The H⁻ ion is a very interesting system and the quantum chemical studies of its electric properties are

still a challenge for modern computational methods. Based on the conducted research, it was shown that the selection of basis set as well as the amplitude of the electric field used for the numerical differentiation procedure are the crucial factors in the description of electric properties of the H^- ion. It was also observed that the spatial confinement, represented by the spherical harmonic potential, causes a diminishment of the polarizability and second hyperpolarizability of H^- .

The results of the performed calculations demonstrate that increasing the strength of spatial confinement, modeled by cylindrical harmonic potential, leads to a decrease of both electronic and vibrational contributions to the electric properties of $HCN\cdots HCN$ and $HCN\cdots HNC$ complexes. However, the electronic contributions are reduced to the greater extent by the spatial confinement. For this reason, the importance of vibrational contributions in the description of electric response of the molecular complexes is greater when they are subjected to the spatial confinement. The same behavior was observed previously for the polarizability and second hyperpolarizability of the $HCCCN$, HCN , $HCCH$ and CO_2 molecules.

An interesting aspect of the presented studies is an attempt to characterize the influence of spatial confinement on the two-photon absorption process. This process has been extensively studied experimentally and theoretically for many years and is now one of the most important spectroscopic tools. Based on the performed calculations, it was shown that the presence of cylindrical harmonic potential significantly modifies the two-photon response of the lithium hydride molecule. One of the most important observations is the fact that in a certain range of the LiH bond lengths, the increase of the orbital compression strength results in a large amplification of the two-photon response of the studied system.

A systematic analysis of the behavior of 35 different exchange-correlation functionals in the description of the electric properties of spatially limited molecules was also carried out. The results obtained for the isolated and spatially confined HF , HCN , OCS , $HArF$ and $ClCCH$ molecules demonstrate that the behavior of the analyzed functionals differs significantly depending on the studied property and molecule, as well as on the strength of spatial restriction, represented by the cylindrical harmonic potential. Therefore, based on the conducted analysis, it is not possible to select functionals which would be recommended for the calculations of electric properties for various molecules in the presence of confining potential and without

it. This clearly indicates that there is still a need for new functionals dedicated to the calculations of molecular electrical properties.

Summing up the studies discussed in this dissertation, one can conclude that the spatial confinement has very significant impact on the electric properties of atomic and molecular systems. The several valuable observations have been made based on the performed quantum chemical calculations. The obtained results serve as an important source of information and an inspiration for further research in this area.