When finite becomes infinite: a journey from molecules to crystals

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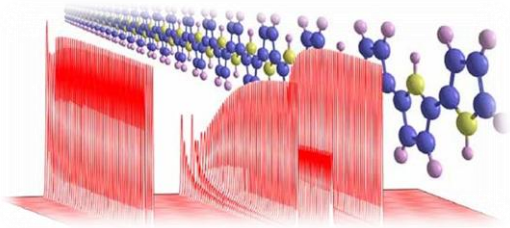
ABSTRACT

In old good days, when quantum chemistry dealt with molecules containing 10–20 atoms, it required certain intellectual bravery to ask how big should be the molecular system to resemble an infinite crystal or amorphous solid. Now, with dynamic development of computers and with rapid advances in theoretical algorithms, posing such questions became much easier. It is still rather ambiguous to define the term "resemble" in the context of structures containing different (indeed very different!) number of atoms. This difficulty can be circumvented by defining the similarity in terms of convergence of various physical and chemical properties for a series of finite molecules toward the properties corresponding to an infinite system. Getting an answer to this question is of big practical importance. Imagine, for instance, an infinite surface, on which a chemical reaction takes place. Such a system is usually modeled by imposing periodic boundary conditions. In practice it means that one is modeling infinitely many reactions at the same time and that these reactions occur at finite separation from each other. Are they influencing each other? How large should be local separation of each reacting domain to ensure lack of interference? Unfortunately, most questions of this type remain unanswered. I discuss here various physical and chemical properties of extended systems. The main question is how big should be the molecular model to display characteristics typical for an infinite system. It is hoped that the presented results[1–4] help to understand better the characteristics of materials that dwell in no man's land somewhere between quantum chemistry and solid state physics.



References

[1] W. Li, S. Irle, and H. A. Witek, "Convergence in the evolution of nanodiamond Raman spectra with particle size: A theoretical investigation", *ACS Nano* **4**, 4475–4486 (2010)

[2] W.-F. Li, M. Andrzejak, and H. A. Witek, "Evolution of physical properties of conjugated systems", *Phys. Status Solidi B* **249**, 306–316 (2012)

[3] H. A. Witek and S. Irle, "Diversity in electronic structure and vibrational properties of fullerene isomers correlates with cage curvature", *Carbon* **100**, 484–491 (2016)

[4] C.-P. Chou, H. A. Witek, and S. Irle, "When finite becomes infinite: convergence properties of vibrational spectra of oligomer chains", *J. Mol. Model.* **24**, 244 (2018)