Simulating Pressure on Molecules in Implicit Solvation Environments with the X-HCFF and GOSTSHYP methods

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The investigation of molecular properties under pressure in the gigapascal regime is significant for gaining a deeper understanding of materials under extreme circumstances. Theoretical methods are required to supplement experimental data because the latter can only provide indirect information about pressure-induced changes at the molecular level. Both combined allow complete insight into the effects of pressure on molecular systems. [1]

In this context, it is essential to consider the chemical surrounding of the desired molecular system. However, the simulation of pressure applied to liquid-phase compounds is far from straightforward. As a first approach to implicitly include solvent effects in pressure simulations, the pressure models eXtended Hydrostatic Compression Force Field (X-HCFF) [2] and Gaussians On Surface Tesserae Simulate HYdrostatic Pressure (GOSTSHYP) [3] were used together with the Conductor-like Polarizable Continuum Model (C-PCM). [4, 5] All of these methods require discretized molecular surfaces for their functionality. In previous implementations of X-HCFF and GOSTSHYP, the combination of these pressure models with C-PCM led to instabilities in the quantum chemical software Q-CHEM [6] due to simultaneous usage of the discretization routine. Therefore, an independent way of discretizing and handling molecular surfaces for X-HCFF and GOSTSHYP is introduced, enabling a stable way to include implicit solvent effects in high-pressure simulations.

To investigate the effects of implicit solvation on molecules, those that can occur in a zwitterionic and a neutral state are of special interest. For glycine and sulfamic acid, it could be shown that high pressure applied with the GOSTSHYP model tends to stabilize the solvated zwitterionic state of the compounds in an aqueous environment. Additionally, intramolecular proton transfers at high pressure could be identified for some compounds.

The improved way of handling molecular surfaces in the pressure models also allows the straightforward implementation of new surface grid methods. Vibrational frequency calculations under pressure could benefit from being performed with a static surface grid. This could allow a better reproduction of pressure-induced red shifts of selective modes in experimental vibrational spectra. A corresponding implementation is currently in progress.

[1]   F. Zeller, C.-M. Hsieh, W. Dononelli, T. Neudecker, *WIREs Comput. Mol. Sci.*, **2024**, *14*, e1708.
[2]   T. Stauch, *J. Chem. Phys.*, **2020**, *153*, 134503.
[3]   M. Scheurer, A. Dreuw, E. Epifanovsky, M. Head-Gordon, T. Stauch, *J. Chem. Theory Comput.*, **2021**, *17*, 583–597.
[4]   V. Barone, M. Cossi, *J. Phys. Chem. A*, **1998**, *102*, 1995–2001.
[5]   M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.*, **2003**, *24*, 669–681.
[6]   E. Epifanovsky *et al.*, *J. Chem. Phys.*, **2021**, *155*, 084801.