

# Electronic structure at high hydrostatic pressure

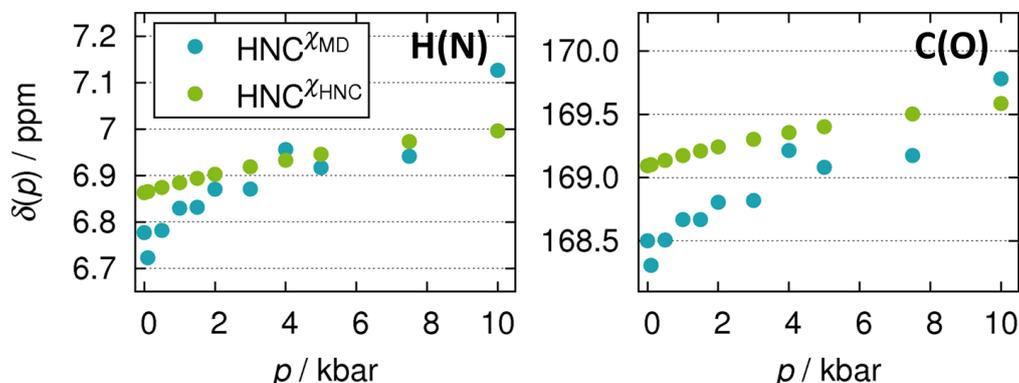
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While the majority of life on earth is adapted to ambient pressure conditions, on average about 88% of the oceanic water on earth is 3800 m deep, corresponding to a hydrostatic pressure of 380 bar, which is by far not the highest value on earth. [1] Biochemical processes for the vast number of lifeforms accommodated to these extreme conditions are barely understood.

Applying high hydrostatic pressure to biomolecules has substantial impact on their free energy surfaces that govern structure, function, dynamics, and thermodynamics. This poses a challenge to computational modeling approaches since the applicability of conventional empirical molecular interaction functions (force fields) is not known. As a step toward clarifying the situation, we need to account for high pressure in quantum-chemical calculations. A suitable methodology is provided by molecular integral equation theories, in particular the “embedded cluster reference interaction site model” (EC-RISM) [2,3] that combines statistical-mechanical 3D RISM integral equation theory and quantum-chemical calculations self-consistently. In this context the impact of pressure is naturally accounted for since the solvent susceptibility function that enters the theory contains the pure solvent correlation functions at the pressure chosen, derived from either an integral equation theory or molecular simulations. Here we illustrate the methodology for several benchmark applications in a pressure range of 1 bar up to 10 kbar, including the effect of pressure on molecular structure, the relevance of electronic polarizability under extreme conditions, and the pressure dependence of nuclear magnetic resonance shieldings.



[1] I. Daniel, P. Oger, R. Winter, *Chem. Soc. Rev.*, **2006**, 35, 858-875.

[2] T. Kloss, J. Heil, S. M. Kast, *J. Phys. Chem. B*, **2008**, 112, 4337-4343.

[3] R. Frach, S. M. Kast, *J. Phys. Chem. A*, **2014**, 118, 11620-11628.