Efficient global geometry optimization
of atomic and molecular clusters:
method and applications

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Finding global minimum energy structures of clusters is an NP-hard problem. Nevertheless, we have established a global geometry optimization method for atomic clusters that scales only cubically with cluster size [1]. With suitable enhancements, this method is also applicable to molecular clusters [2]. In combination with empirical potentials as guiding functions, we could also establish this approach as a practically viable method for global optimization on ab-initio and DFT potentials [3].

Using these methods, we are investigating structural transitions of clusters as a function of cluster size [4]. For mercury clusters [5], our results suggest a reinterpretation of the common picture of a transition from van-der-Waals to covalent bonding at $N = 13$. For alkali cation microhydration clusters [6], we offer interpretations for experimentally observed magic numbers, a critical assessment of the clathrate cage structure hypothesis, and an explanation for the complete lack of magic numbers in the sodium cation case.

In a recent application of these methods [7], we managed to locate the elusive transition from all-surface to water-centered cage structures in pure neutral water clusters. While simple model potentials like TIP4P can be surprisingly good at predicting the structures of small clusters, they start to fail qualitatively for larger clusters (at about $N = 17$). The results of our calculations with the sophisticated TTM2-F model potential, which quantitatively reproduces MP2 results for these systems, are more in line with expectations from related systems and also allow to link both the failure of the simpler models and the occurence of certain structural features to specific terms of the physical interaction between water molecules. Empirical simulations of IR spectra in the OH stretch region predict the possibility of an experimental detection of the structural transition to water-centered cage structures.

[1] B. Hartke, J. Comput. Chem. 20 (1999) 1752.
[2] B. Hartke, Z. Phys. Chem. 214 (2000) 1251.
[3] B. Hartke, Chem.Phys.Lett. 258 (1996) 144, Theor.Chem.Acc. 99 (1998) 241.
[4] B. Hartke, Angew.Chem. 114 (2002) 1534-1554 (Int.Ed. 41 (2002) 1468-1487).
[5] B. Hartke, H.-J. Flad and M. Dolg, Phys. Chem. Chem. Phys. 3 (2001) 5121.
[6] F. Schulz and B. Hartke, Chem. Phys. Chem. 3 (2002) 98.
[7] B. Hartke, Phys. Chem. Chem. Phys. 5 (2003), in press.