

Simulations of Neutral and Protonated Water Clusters with the SCC-DFTB Electronic Structure Method : Applications to $(\text{H}_2\text{O})_{21}\text{H}^+$, $(\text{H}_2\text{O})_{22}\text{H}^+$, and $(\text{H}_2\text{O})_8$

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Introduction

Recently an intriguing electronic structure method, Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB)¹, has been developed. This approach is comparable in computational speed to the AM1 and PM3 methods, but, in general, provides a more accurate description of geometries and energies of a wide variety of molecular systems. We have combined this approach with the basin hopping Monte Carlo² and parallel tempering Monte Carlo (PTMC)³ methods and applied to various neutral and protonated water clusters.

SCC-DFTB electronic structure method¹

The SCC-DFTB model is derived from density functional theory (DFT) by second-order expansion of the Kohn Sham total energy with respect to the charge density fluctuations.

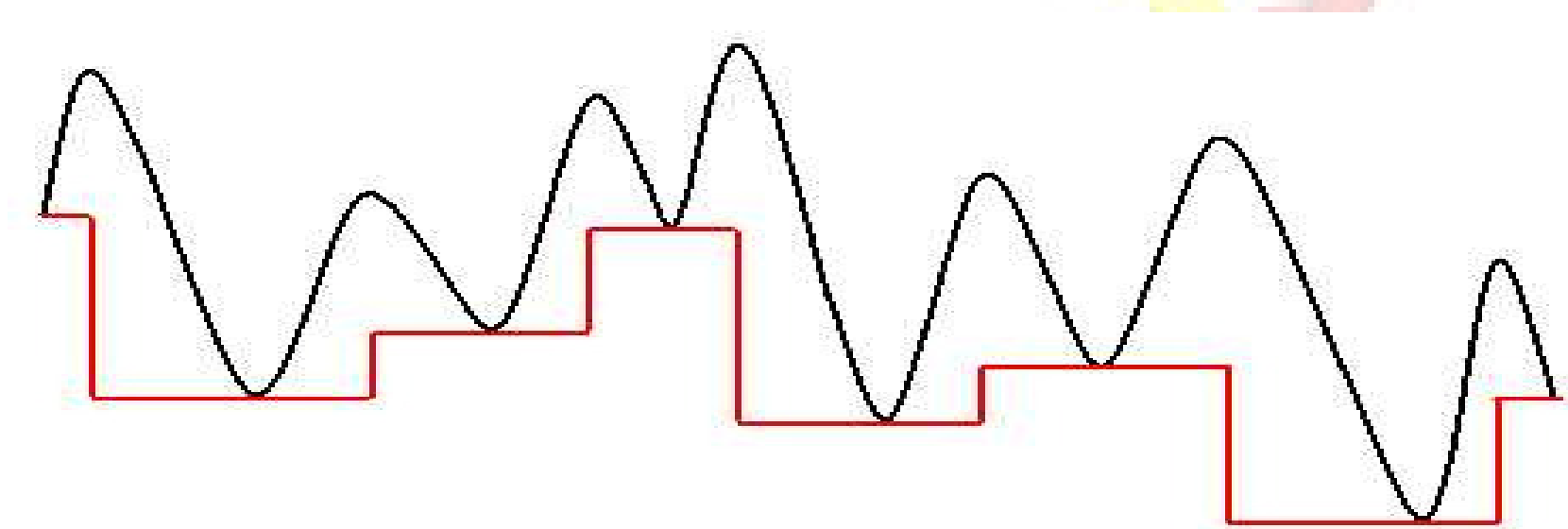
$$E_{tot} = \sum_{\mu\nu} c_{\mu}^i c_{\nu}^j H_{\mu\nu}^0 + E_{rep} + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta} + E_{dis}$$

$$E_{dis} = -\sum_{\alpha\beta} f(R_{\alpha\beta}) C_6^{\alpha\beta} (R_{\alpha\beta})^{-6}$$

Basin hopping Monte Carlo method²

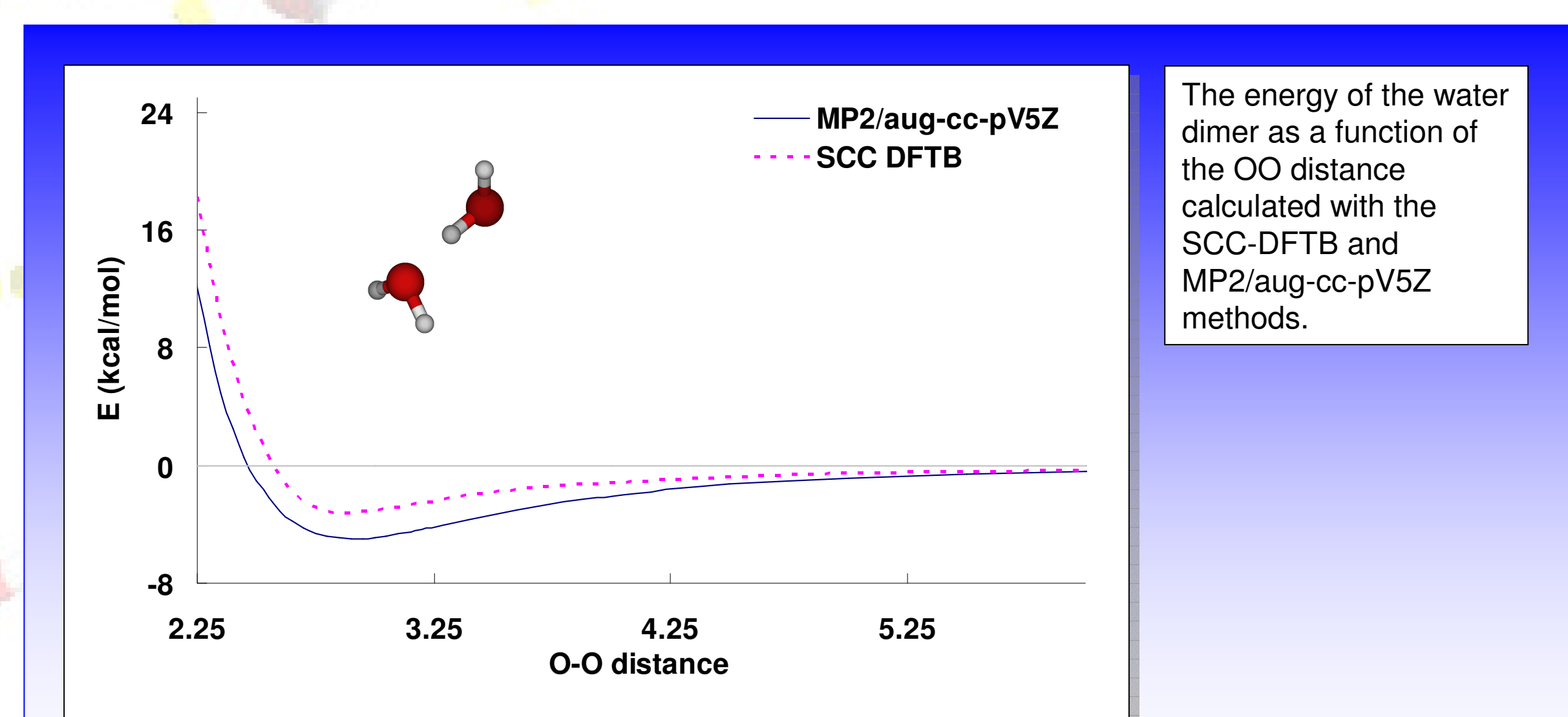
The basin hopping Monte Carlo method uses Monte Carlo walks combined with gradient based local optimization to locate local minima of the potential energy surface. Sampling in the Monte Carlo walks is based on the energies of the minima and, as a result, barriers are effectively removed. This is a very efficient algorithm for locating local minima.

$$\tilde{E}(X) = \min\{E(X)\}$$

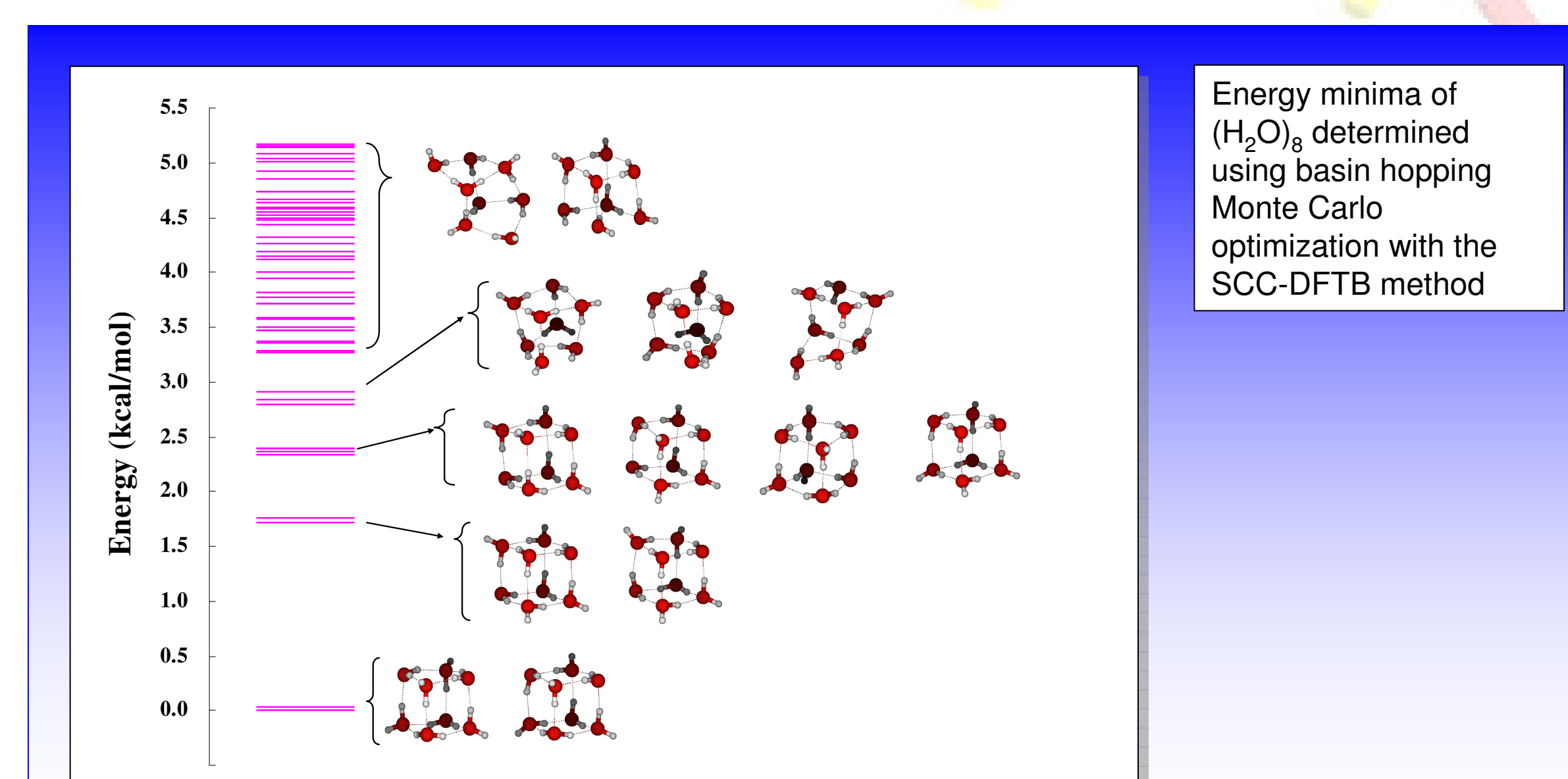


Results

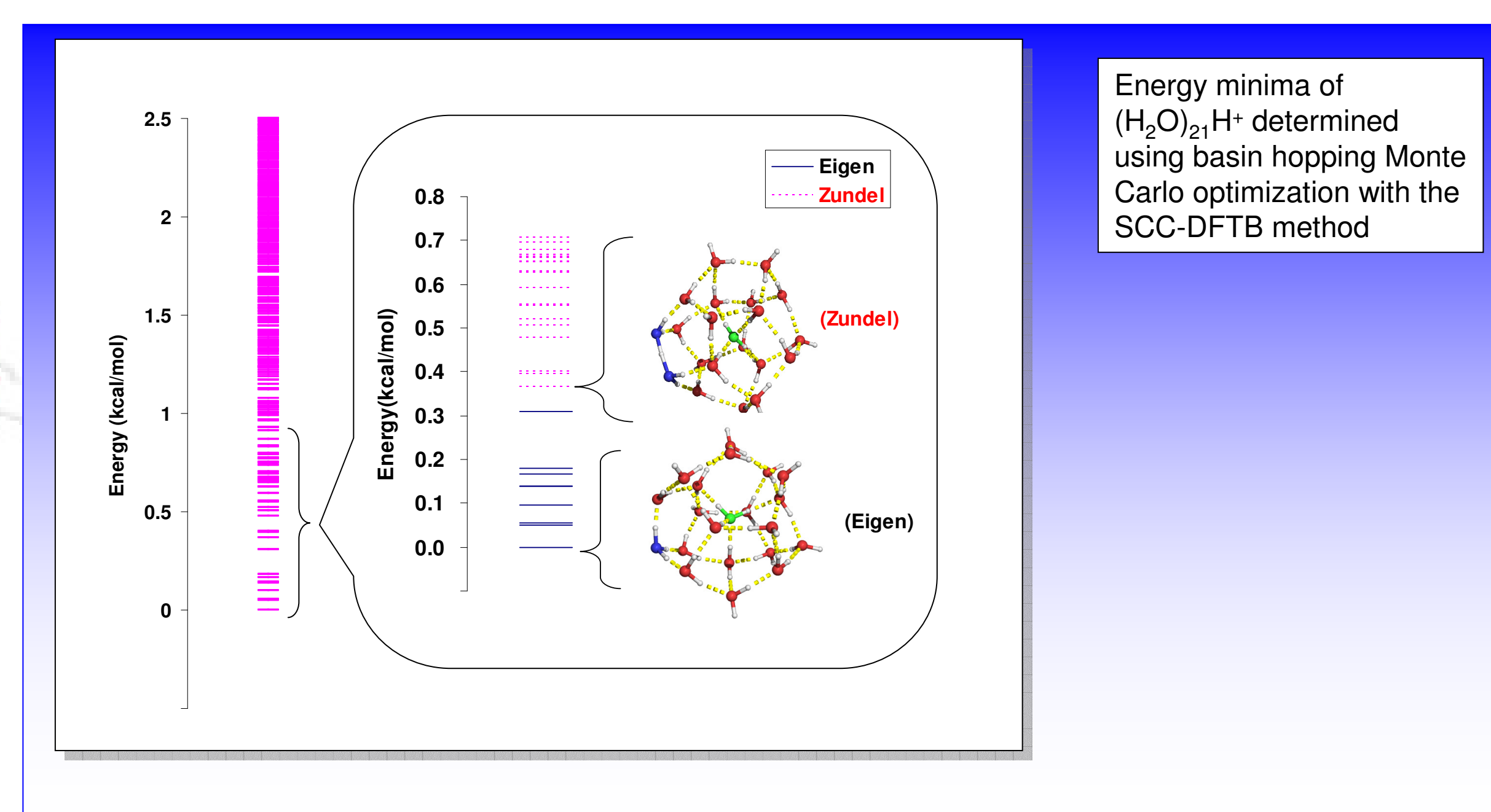
Binding Energy of water dimer



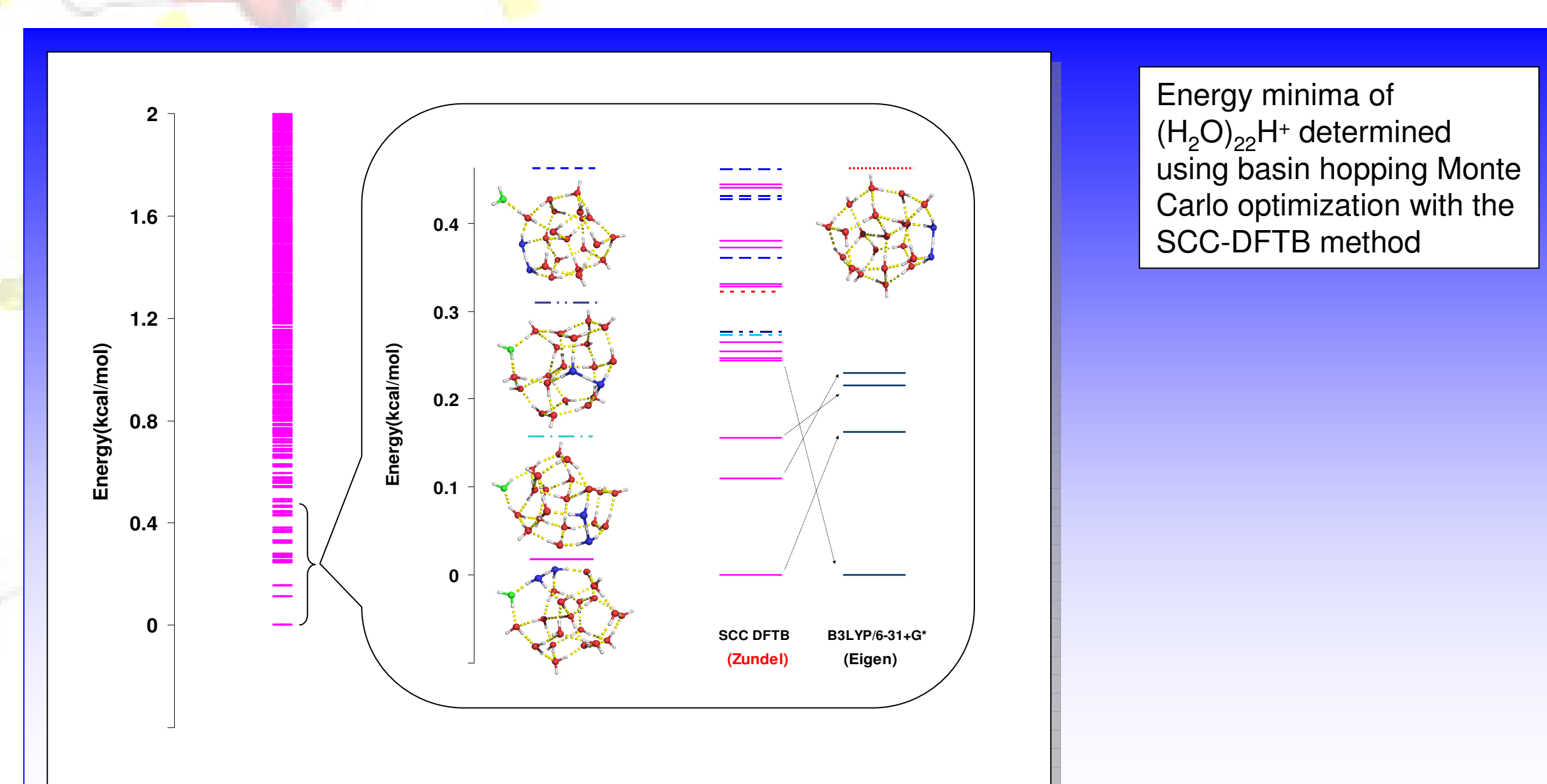
Energy diagram of $(\text{H}_2\text{O})_8$



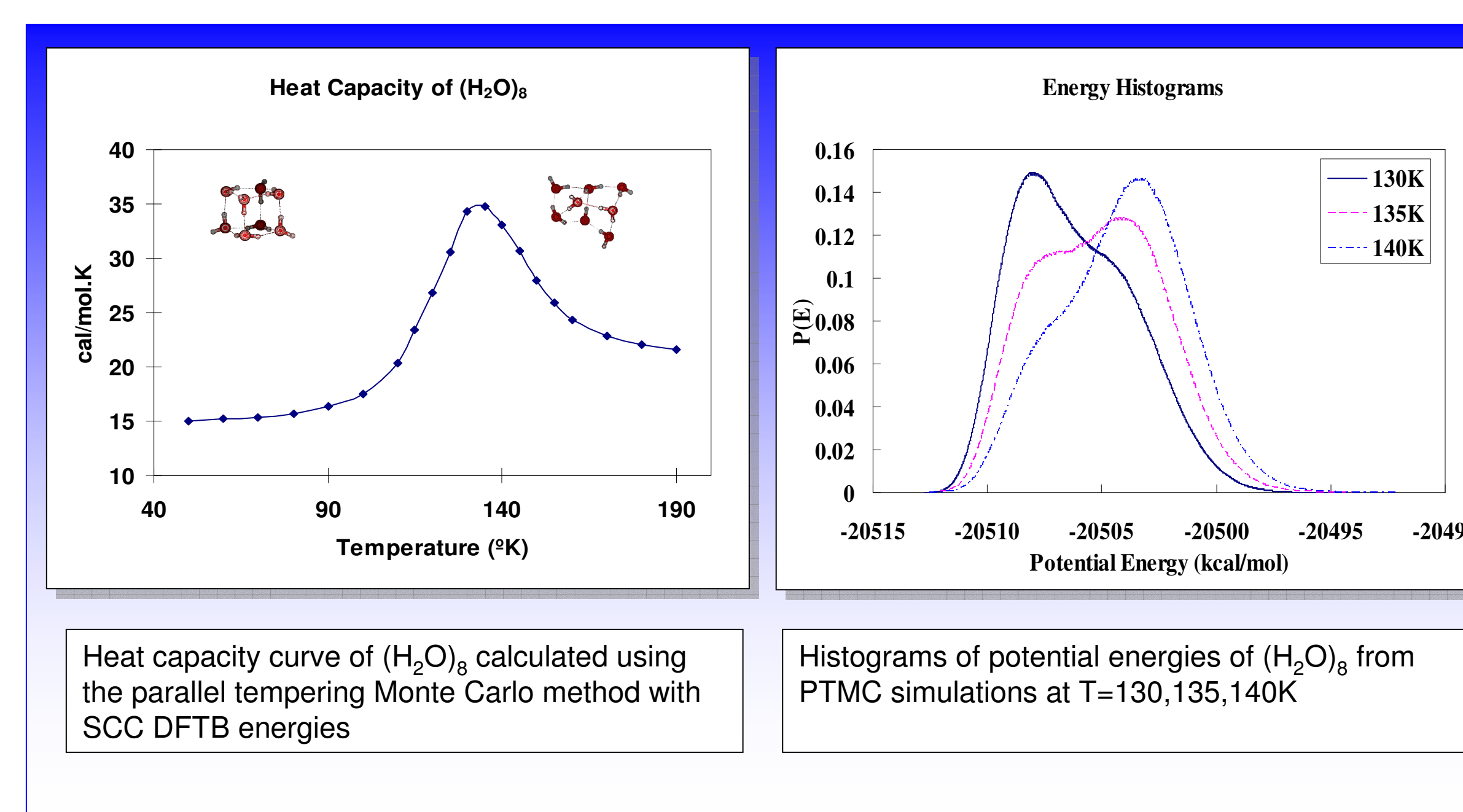
Low-energy minima of $(\text{H}_2\text{O})_{21}\text{H}^+$



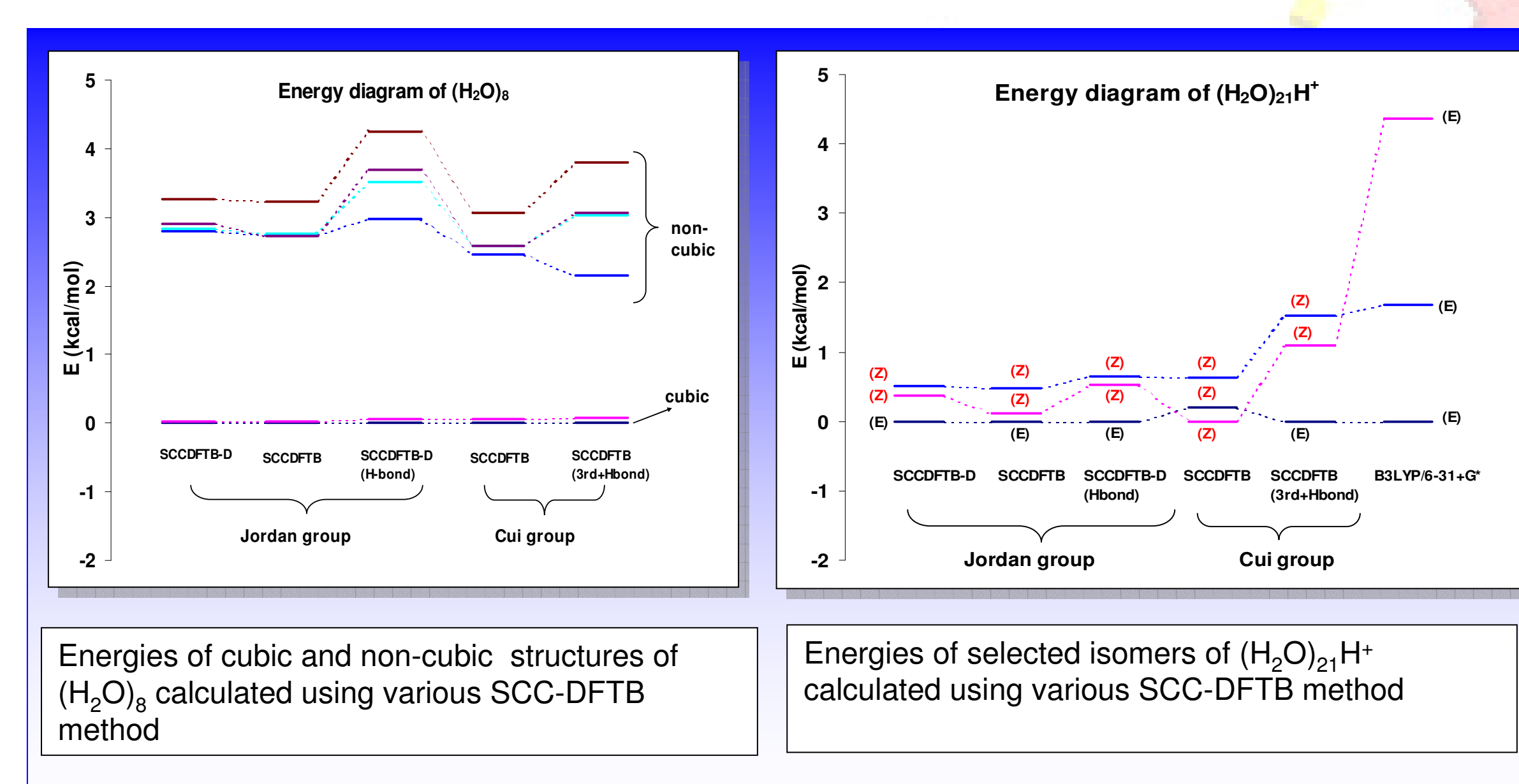
Low-energy minima of $(\text{H}_2\text{O})_{22}\text{H}^+$



Thermodynamic properties of $(\text{H}_2\text{O})_8$

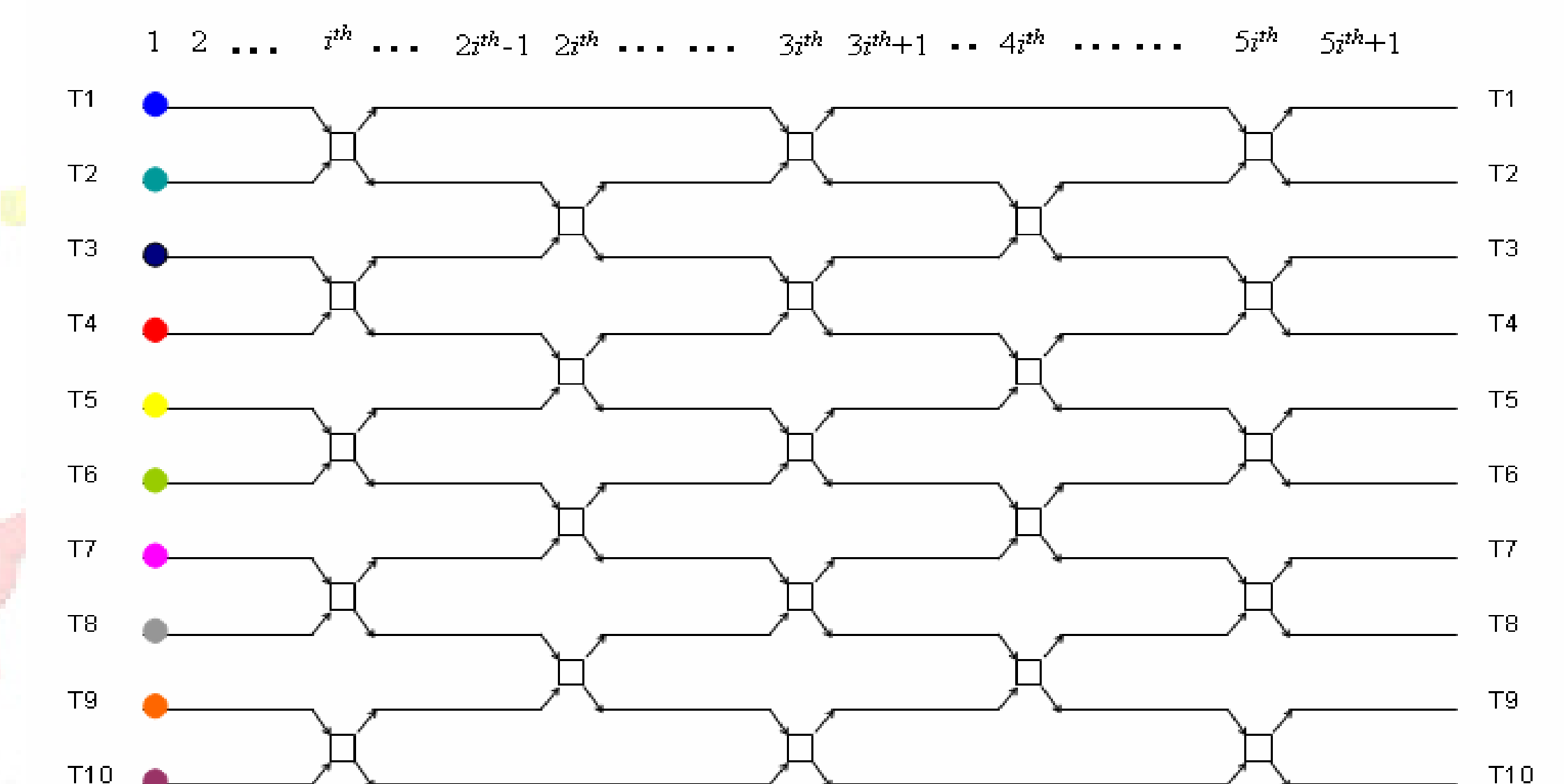


Ongoing Research



Parallel Tempering Monte Carlo simulations³

PTMC Simulations were carried out using the SCC-DFTB electronic structure method with 20 temperatures for $(\text{H}_2\text{O})_8$. Every 800th moves an exchange of configuration from replicas at adjacent temperature (T_i and T_{i+1}) was attempted.



Conclusions

The SCC-DFTB method predicts in agreement with earlier work that $(\text{H}_2\text{O})_8$ undergoes a melting transition. However, the melting temperature of the transition is far too low. Our calculations on $\text{H}^+(\text{H}_2\text{O})_{21}$ and $\text{H}^+(\text{H}_2\text{O})_{22}$ show that the SCC-DFTB method has a bias for Zundel structures.

Both of these problems appear to be due to an inadequate treatment of polarization in the SCC-DFTB method. Recently Cui, Elstner, and co worker⁴ introduced modifications of the SCC-DFTB procedure that improved its treatment of H-bonded systems. Preliminary results are shown in the adjacent figure. (The calculations with the new approaches were run in the Cui group.)



¹M. Elstner, S. Suhai, and G. Seifert, *Physical Review B*, **58**, 7260-7268 (1998)

²D.J. Wales and H.A. Scheraga, *Science*, **285**, 1368-1372 (1999)

³J.P. Neirotti, D. L. Freeman, J. D. Doll, *J. Chem. Phys.*, **112**, 10340 (2000)

⁴D. Riccard, P. Schaefer, Y. Yang, H. Yu, N. Ghosh, X. Prat-Resina, P. Konig, G. Li, D. Xu, H. Guo, M. Elstner, and Q. Cui, *J. Phys. Chem. B*, **110**, 6458-6469 (2006)

