Quantum Mechanical Correction of Lennard Jones Potential Parameters for Towhee Simulations

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Abstract

Area: Thermodynamics and Molecular Simulations

Purpose: Hydrogen trapped in lattice structures of ice can be an efficient method of storing hydrogen. Hydrogen hydrate structures of two types, sI and sII exist in nature. Both have different configurations with respect to the number of cages, cage occupancies, and coordination numbers. Through simulations, one can gauge the feasibility and existence of certain structures that may be difficult to determine experimentally. We intended to investigate the structure of sII hydrogen hydrates using numerical methods and Monte Carlo simulations. We have attempted to incorporate quantum mechanical effects in the classical Lennard Jones potential to improve the Monte Carlo simulations.

Method. A method has been devised to account for quantum mechanical corrections without changing the functional form of the classical Lennard Jones potential function. One of the existing approaches does something similar but needs a shift in r (position). A shift in r is not possible to incorporate in Towhee simulations software. Hence, we derived a numerical factor that will change the epsilon parameter of the LJ potential to account for the r shift. This numerical factor 'alpha' is derived using the minimization of the area between the corrected potential and the Feynmann-Hibbs function. We verify our results using the difference between the energy at the minima of the 2 functions.

Results: The alpha values at different temperatures (175K to 300K) have been obtained. The corrected quantities are less than classical values, which follow the correct trend. The alpha value suggested from analytical expressions (EQtEc>i -1) is less accurate than the one obtained from the numerical method proposed above. Hence, the use of this method provides a better estimate of the Feynmann-Hibbs quantum mechanical potential.

Conclusions: The incorporation of quantum effects agrees with the existing experimental data. This work can further be extended to calculate the order parameters of the hydrate and obtain the cage occupancies in the sII hydrate for which the work is underway.

Duration: Small part of a yearlong project

Contribution: Everything mentioned above was done by the two authors of this abstract.

References

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