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# *The Hydration Number of $\text{Li}^+$ in Liquid Water*

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## *Abstract*

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- **quasi-chemical theory and ‘ab initio’ molecular dynamics:** Li<sup>+</sup>(aq) has **4** inner shell water ligands at infinite dilution
  - interpretations of neutron scattering data on more concentrated solutions differ
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## *Why Study Ion Hydration in Water?*

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- fundamental physical chemistry but incompletely (!) understood
- inner shell exchange reactions decisive to selectivity of biological ion channels



## *Previous $\text{Li}^+$ Hydration Studies*

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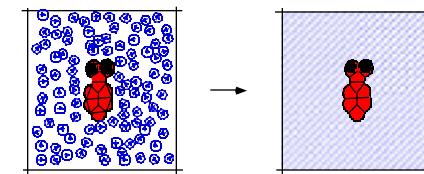
- neutron scattering expt. [Enderby and Neilson]
  - $\text{Li}^+(\text{aq})$  has **6 inner shell water** molecules [Friedman]
- electronic structure calc. [Feller, *et al.*]
  - minimum E hexamer has **4 inner + 2 outer shell waters**
- simulations [for example, Impey, *et al.*]
  - wide range of results including both **4 inner shell** and **6 inner shell** waters



# *Quasi-Chemical Treatment of Hydration*

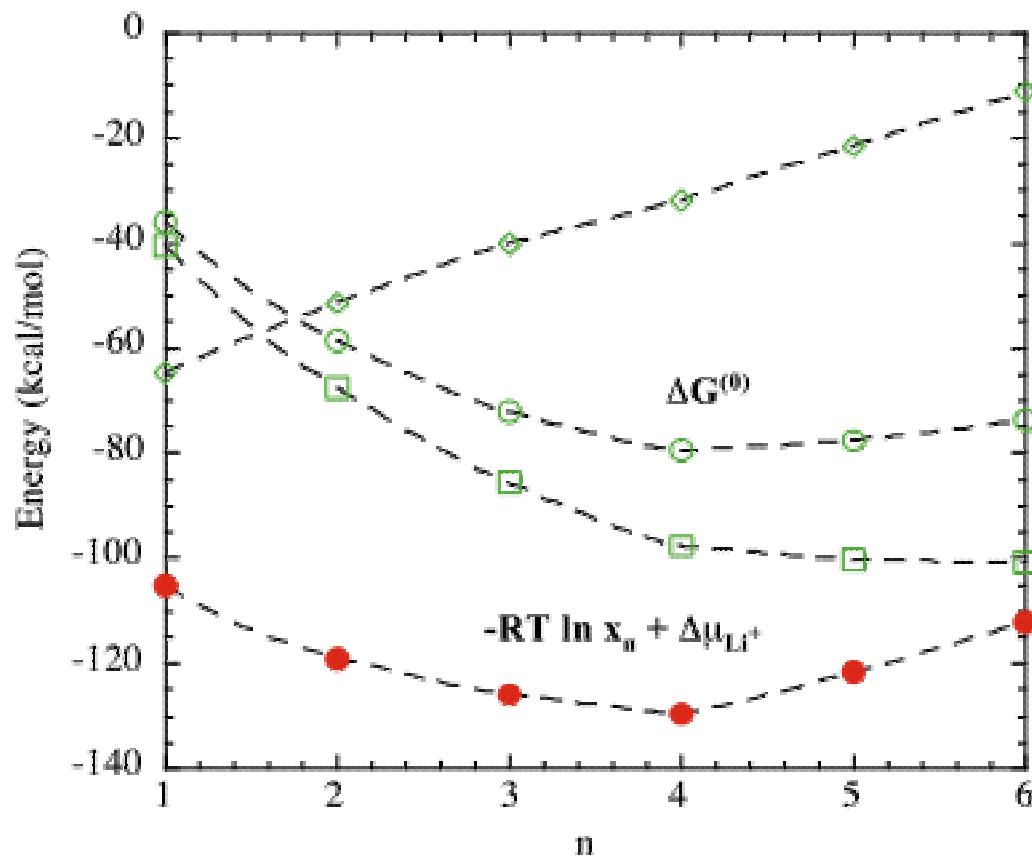
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- **Guggenheim, Bethe (1935):** Cooperative phenomena in crystals. **Pratt & LaViolette (1998)** specifically for fluid problems.
- **Explicit treatment of ion and nearest neighbors**
  - Avoid dielectric model with parameters and dubious T & p derivatives
  - Electronic structure calculations
- **Implicit treatment of all other solvent molecules**
  - Dielectric continuum model of solvent



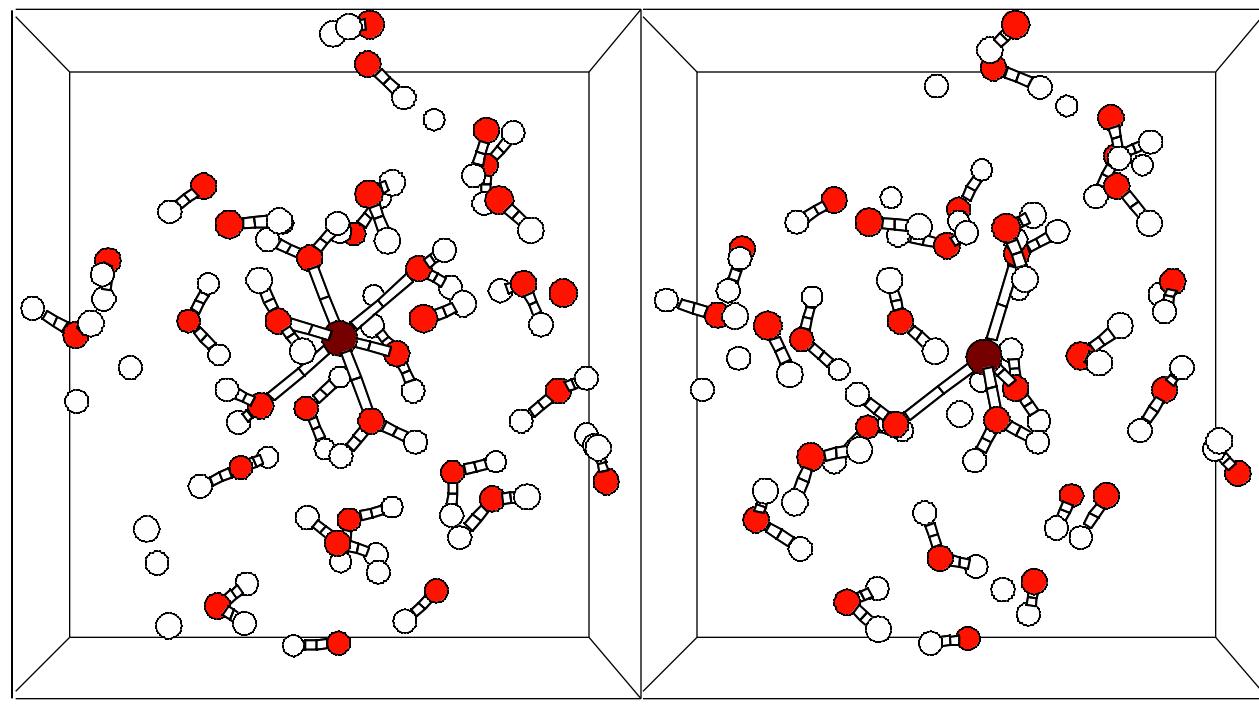
# *Calculation Results for Li<sup>+</sup> in Liquid Water*

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# *Ab Initio Molecular Dynamics Snapshots*

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**6 inner waters**

**0.125 ps**

**4 inner waters**

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## *Summary*

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- **quasi-chemical and molecular dynamics:** Li<sup>+</sup>(aq) has **4** inner shell water ligands at infinite dilution
- interpretations of neutron scattering data on more concentrated solutions differ

