A New Model for Charge Distributions in Molecular Systems

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Introduction
- Need electrode model for molecular modeling: Electron densities ≠ partial charges
- Parameters: Mulliken electronegativities, Per-Parr-Farrow hardnesses
- Popular and chemically intuitive, but has problems
- Objective: Fix Q Eq

What’s Wrong?
- No HOMO-LUMO band gap, metal bonding
- No difference between σ, π, metallic or ionic bonds
- No out-of-plane polarizability
- Physical difficulty in interpreting parameters, e.g. negative electron affinity of H

Our New Model, QTPIE
- Charge transfer postcess equilibrium
- Distance-dependent electronegativities
- Detailed balance

\[ E = \sum q_i \left( 1 + \frac{1}{2} \frac{\alpha}{\beta} \right) \]
\[ q_i = \left( 1 + \frac{1}{2} \frac{\alpha}{\beta} \right) \]
\[ \beta = \sum q_i \left( 1 + \frac{1}{2} \frac{\alpha}{\beta} \right) \]

\[ H = \sum \alpha_{\text{pair}} + \sum \beta_{\text{pair}} - \sum \gamma_{\text{pair}} \]

NaCl Dissociation
- Q Eq: fractional charges at infinite separation limit
- QTPIE: (this work) corrected asymptotic limit, wrong decay behavior
- ab initio: decay behavior arises from nonadiabatic curve-crossing effects
- Experimental dipole moment used to fit parameters

Water Dissociation
- Pull one hydrogen (H1) off to infinity slowly
- Charge on H1 converges exponentially to zero far away
- Remaining hydrogen/radical retains polarization

Future work
- Study adiabatic dissociation of sodium chloride-water hexamer cluster
- Understand the physical basis of this model: exp. in statistical mechanics
- Develop connections to quantum-mechanical observables
- Explore relationships to ensemble density functional theory
- Construct new models based on Janak’s Theorem and its consequences
- Look into statistical mechanical treatment of multiple configurations

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