# Computational Schemes for Predictive Modeling and Engineering of Materials

**Sandia National Laboratories**
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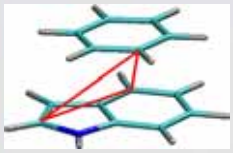
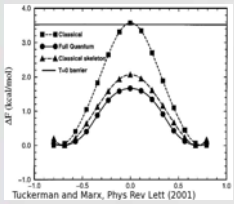
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

## Problem





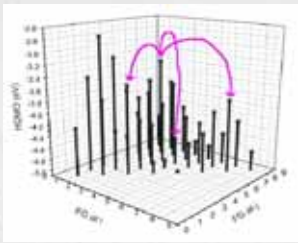

For many relevant properties and systems current atomistic modeling is not sufficiently predictive. Examples include:

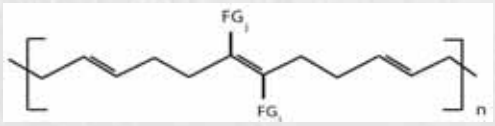
(A) Weak van-der-Waals binding using electronic structure methods such as density functional theory (DFT). Relevant to molecular crystals.

(B) Neglect of nuclear quantum effects (Tunneling/Zero Point Energies). Relevant to processes involving light atoms (protons, Li).

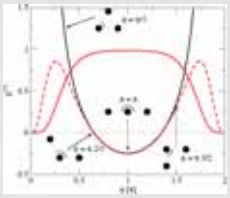
Virtual engineering on computer *prior* to experimental realization is in its infancy. Open questions include:

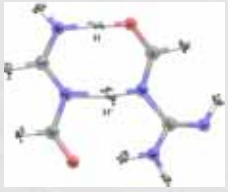
(C) Definition of chemical compound space. Can one define "alchemical" forces for gradient based optimization algorithms? If yes, are they sufficient or are Hessians necessary? How predictive are they?

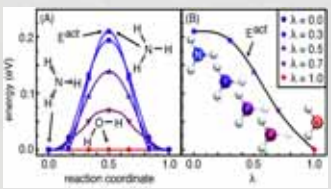





## Approach








(A) Compute 2 and 3-body interatomic dispersion contributions to van-der-Waals binding of realistic systems based on combination of London/Axilrod-Teller-Muto expression, and compare to reliable total values.

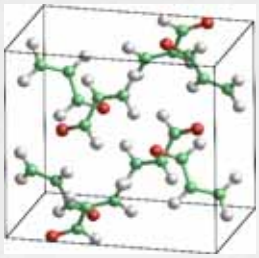
(B) Demonstrate significance of nuclear quantum effects in prototypical double proton transfer for DNA Watson-Crick base pair model using Car-Parrinello Path-Integral MD.

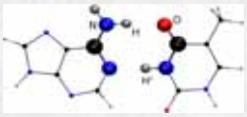
(C) Analytical first order derivatives wrt atomic number permit to control binding energies that are crucial for catalytic activities of nano-cluster metal particles.

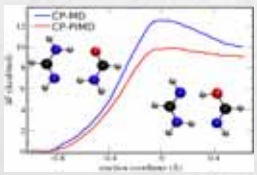
## Results

Virtual engineering on computer *prior* to experimental realization is in its infancy. Open questions include:

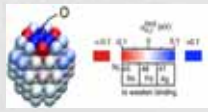
(A) For bi-graphene London and Axilrod-Teller-Muto dispersion energy respectively contribute up to 200 and 50% to binding. For other systems 3-body contributions frequently reach double digit % of total potential cohesive or interaction energies—substantial enough to affect energetical ranking such as competing molecular crystal polymorphs. Published: OAvL and A. Tkatchenko, *J. Chem. Phys* (2010).



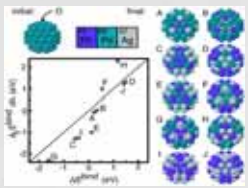





(B) Against all odds, tunneling renders the rare enol-tautomer models of Watson-Crick basepairs AT and GC metastable: Nuclear quantum effects enhance DNA's stability. Published: A. Perez, M. Tuckerman, H. Hjalmarson, OAvL, *J. Am. Chem. Soc.*, in press (2010)



(C) Predicted changes in oxygen binding due to alchemical mutations agree very well with actual changes in binding. A single calculation permits accurate control of catalytic activity. Published: D. Sheppard, G. Henkelman, OAvL, *J. Chem. Phys.*, in press (2010)



## Significance

Systematic quantification of inaccuracies is first step towards predictive materials modeling and design

Alchemical paths and derivatives hold great promise for highly efficient virtual materials improvement.

Progress made towards the eventual goal of computational engineering of materials' properties through stoichiometrical changes.

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