

# Multiscale schemes for the predictive description and virtual engineering of materials

Anatole Lilienfeld

Sandia National Laboratories

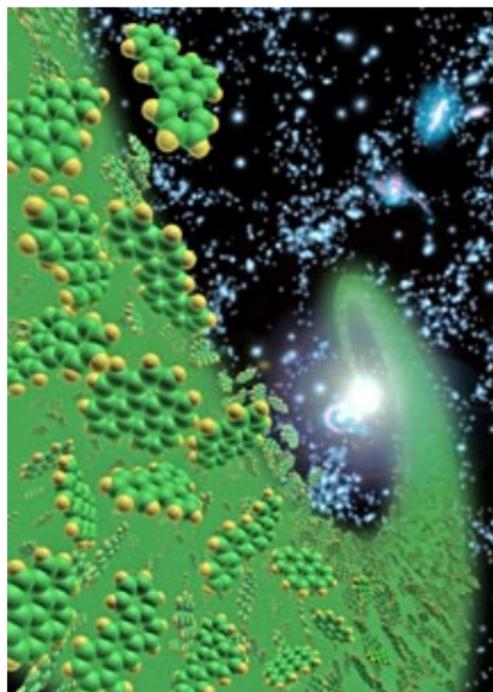
# Outline - going beyond description

## Design

Space  
Exploration

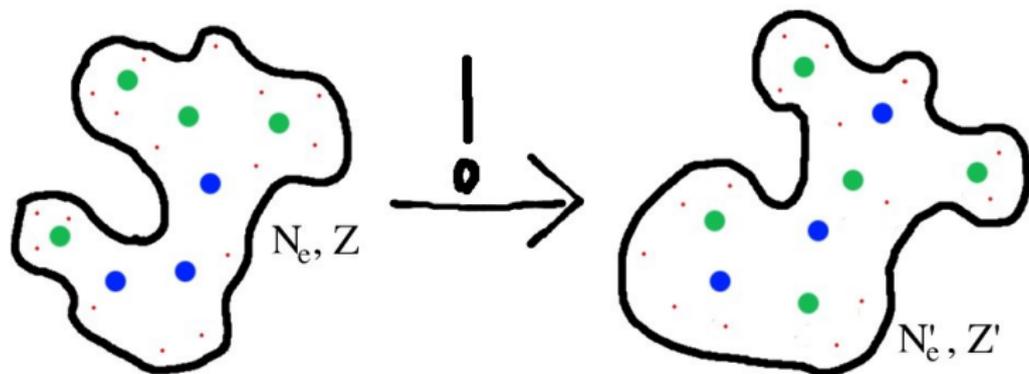
## Methods

Accuracy  
Multiscaling  
MGCE-DFT  
Application



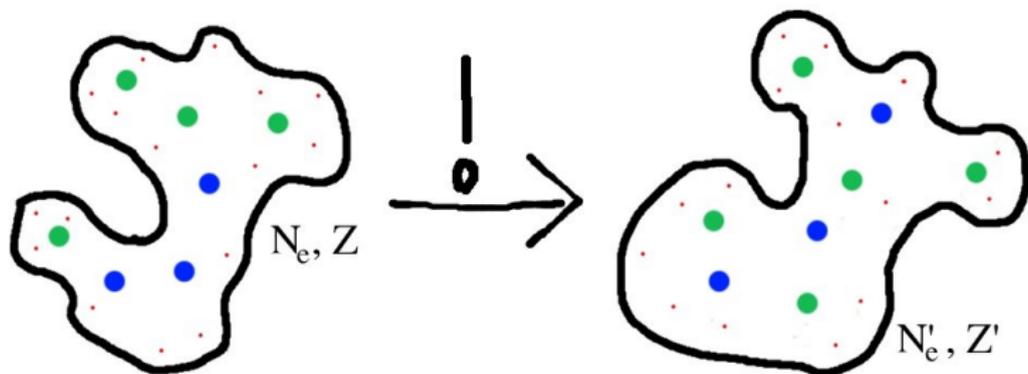
<http://www.rsc.org/>

# Materials design and the philosopher's stone?



- ▶ Render material's properties valuable through "alchemical" changes
- ▶ Properties of matter defined by composition

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- tune properties by variation of matter, *i.e.* composition
- ≡ optimize properties in "chemical space"

## What is chemical space?

Property hyper-space populated by all stable compounds

*Nature* **432** 823 (2004)

Property? - observable!

Compound? -

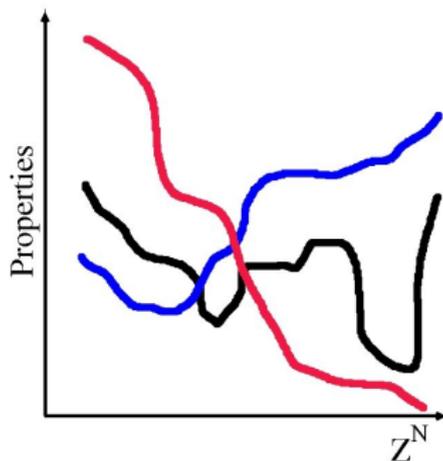
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Compound? -

- Stoichiometry + phase space  
within first principles picture





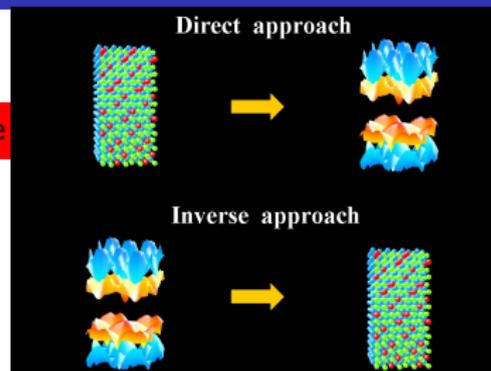
# “electronic screening”

Alex Zunger (Renewable Energy Lab) 'Inverse band-structure'

atomic configuration  $\Leftrightarrow$  band-structure

*Nature* **402** 60 (1999)

Simulated annealing of binary alloys for electronic properties



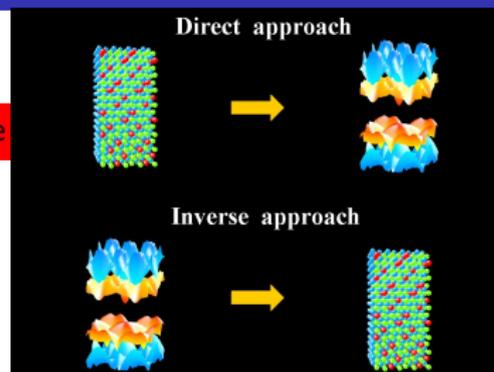
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Jens Nørskov 'genetic algorithm + DFT'  $\rightarrow$  enthalpy of formation

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## Combined Electronic Structure and Evolutionary Search Approach to Materials Design

G. H. Jóhannesson, T. Bligaard, A. V. Ruban, H. L. Skriver, K. W. Jacobsen, and J. K. Nørskov  
*Center for Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark,  
 DK-2800, Lyngby, Denmark*

(Received 20 February 2002; published 10 June 2002)

We show that density functional theory calculations have reached an accuracy and speed making it possible to use them in conjunction with an evolutionary algorithm to search for materials with specific properties. The approach is illustrated by finding the most stable four component alloys out of the

# “electronic” design

OAvL 'Variational particle number'  
[*PRL* **95** 153002 (2005)]

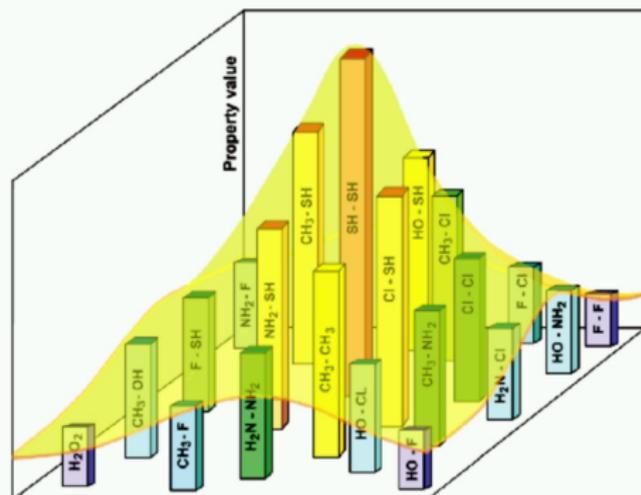


# “electronic” design

OAuL 'Variational particle number'  
[*PRL* **95** 153002 (2005)]



- ▶ Weitao Yang (Duke University)  
'Interpolating external potentials'  
[*JACS* **128** 3228 (2006)]



# The four grand challenges

In order to generally and reliably engineer materials for exhibiting predefined macroscopic properties we need to

- 1 have sufficient accuracy in describing it  
→ **Accuracy** of KS-DFT
- 2 rigorously link microscopic to macroscopic properties  
→ **Multiscaling**
- 3 devise combining scheme  
→ accurate **MGCE-DFT** within multiscaling
- 4 **Application** to materials design → a Holy Grail (verbatim)

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Perdew “Jacob’s ladder”

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Here *Conditio sine qua non* - accuracy **must** reflect right trends

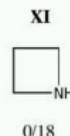
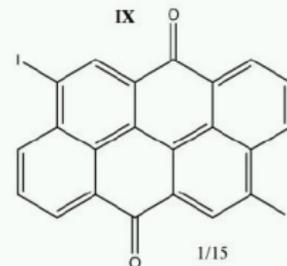
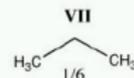
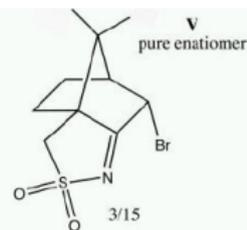
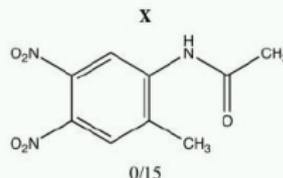
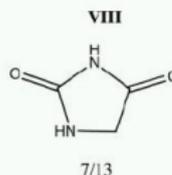
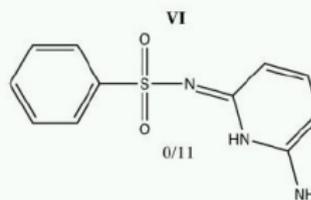
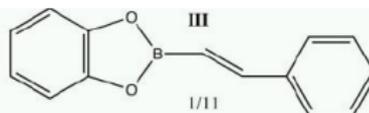
- ▶ intermolecular interactions (bulk) and Fermi level (band-structure)

# Molecular crystal structure prediction

- ▶ Maddox [*Nature* **335** 201 (1988)]: *One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition ...*

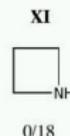
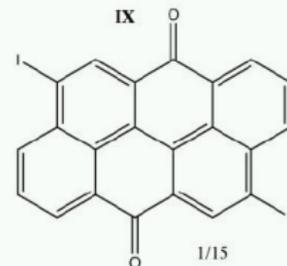
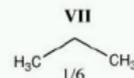
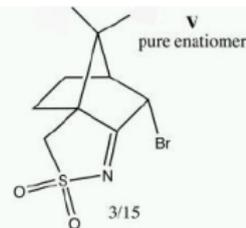
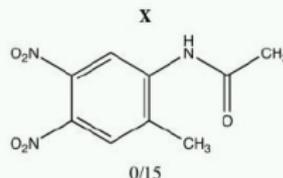
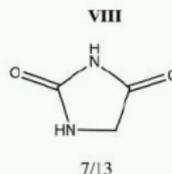
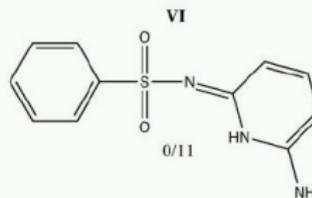
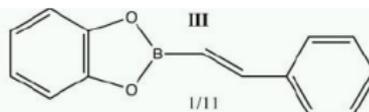
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- ▶ Dunitz (ETHZ) [*PNAS* **101** 14309 (2004)]
- ▶ **intermolecular potential?**



# From repulsive to attractive intermolecular energies

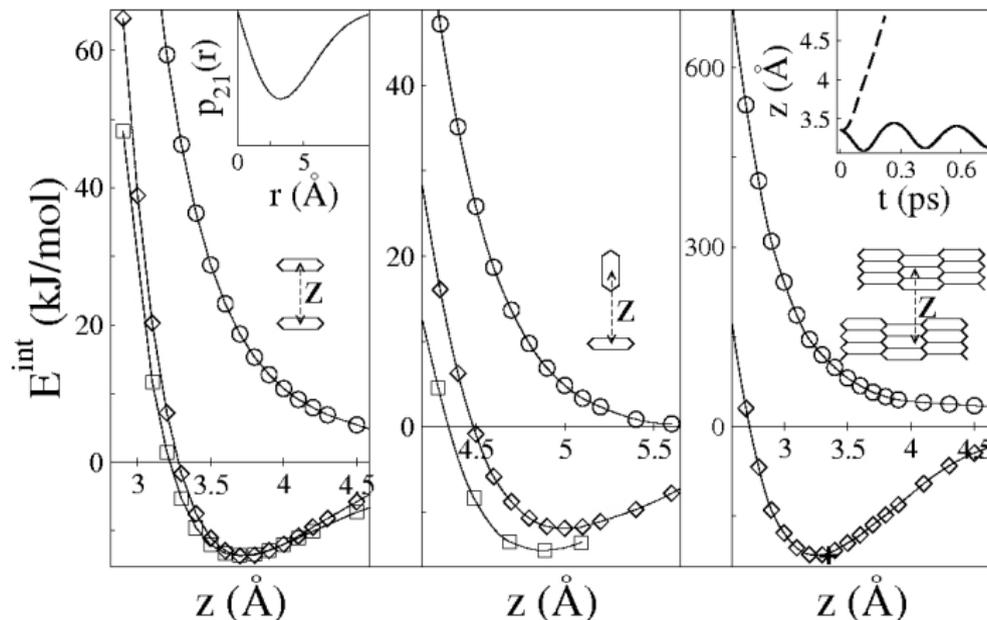
Dispersion corrected atom centered potentials (DCACP) augmented KS-DFT  
[OAvL et al. *PRL* **93** 153004 (2004), *PRB* **71** 195119 (2005)]

- ▶ parameterize for every atom (system, reference method, penalty)

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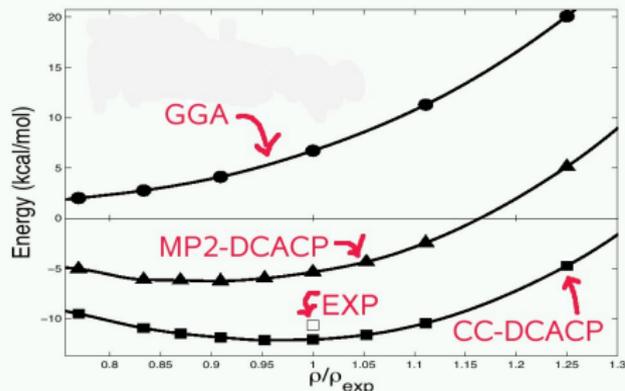
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- ▶  $\pi$ - $\pi$  stacking, rare-gases, hydrogen bonding

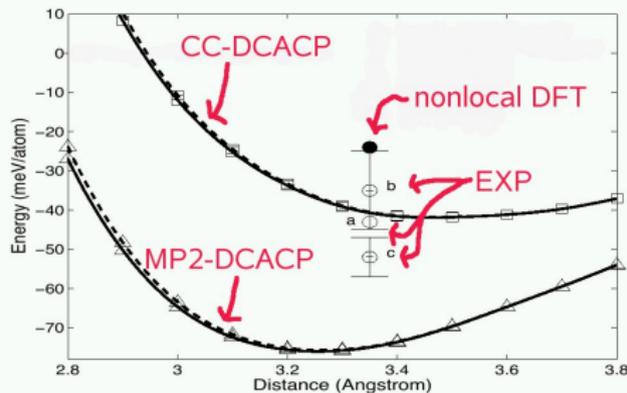


# From attractive intermolecular energies to bulk properties

Benzene crystal



Three graphene sheets



⇒ accurate input for sampling of (1) symmetry, (2) number of molecules per cell, (3) relative orientation

A Oganov (ETH Zürich, Moscow State University) [*JCP* **124** 244704 (2006)]

# Further improvements and tests

## Further

- ▶ Can we use atom centered corrections to the spin-ordering for transition metals, lanthanides, actinides?
- ▶ Can we use Ann Mattson's extension of LDA to electronic surfaces [*PRB* **72** 085108 (2005)]?
- ▶ Can we improve upon TDDFT?

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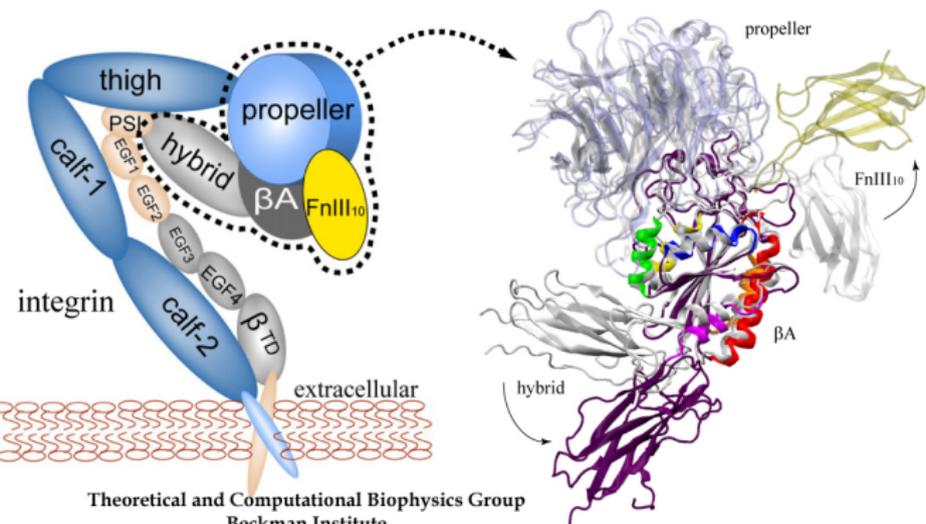
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## Tests to assess and exploit

- ▶ Can we do metals, oxides, fluids, semiconductors equally well?
  - ▶ How good are band-structures, defects, vacancies, adsorption, cohesive energies, bulk modulus, vaporization enthalpies?
  - ▶ Do we have an improved description of response to T and p vs. composition, phase-diagrams, various thermodynamic conditions?
- = direct impact on Sandia's mission (Peter Feibelman, Ann Mattsson, Peter Schultz)

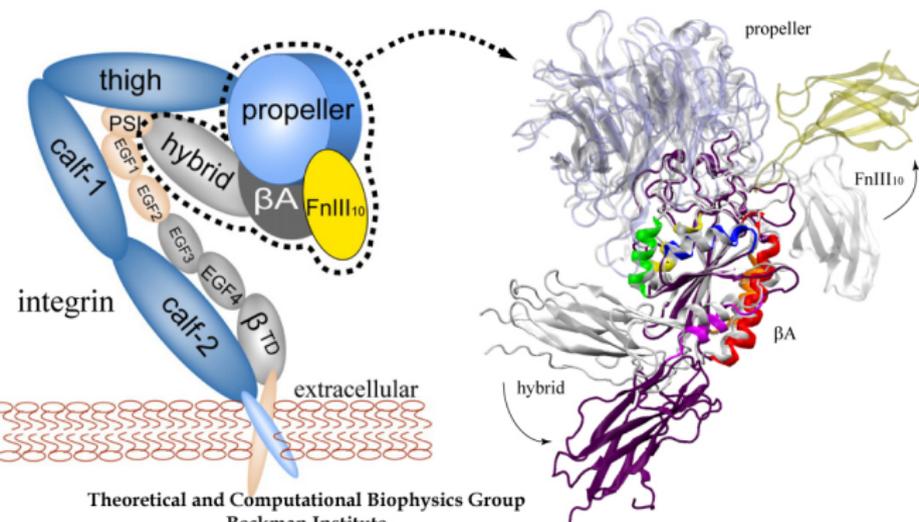
# Why multiscaling?



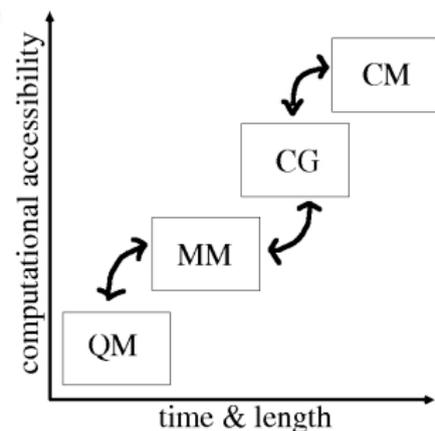
Theoretical and Computational Biophysics Group  
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ergodicity? resolution? ☹️

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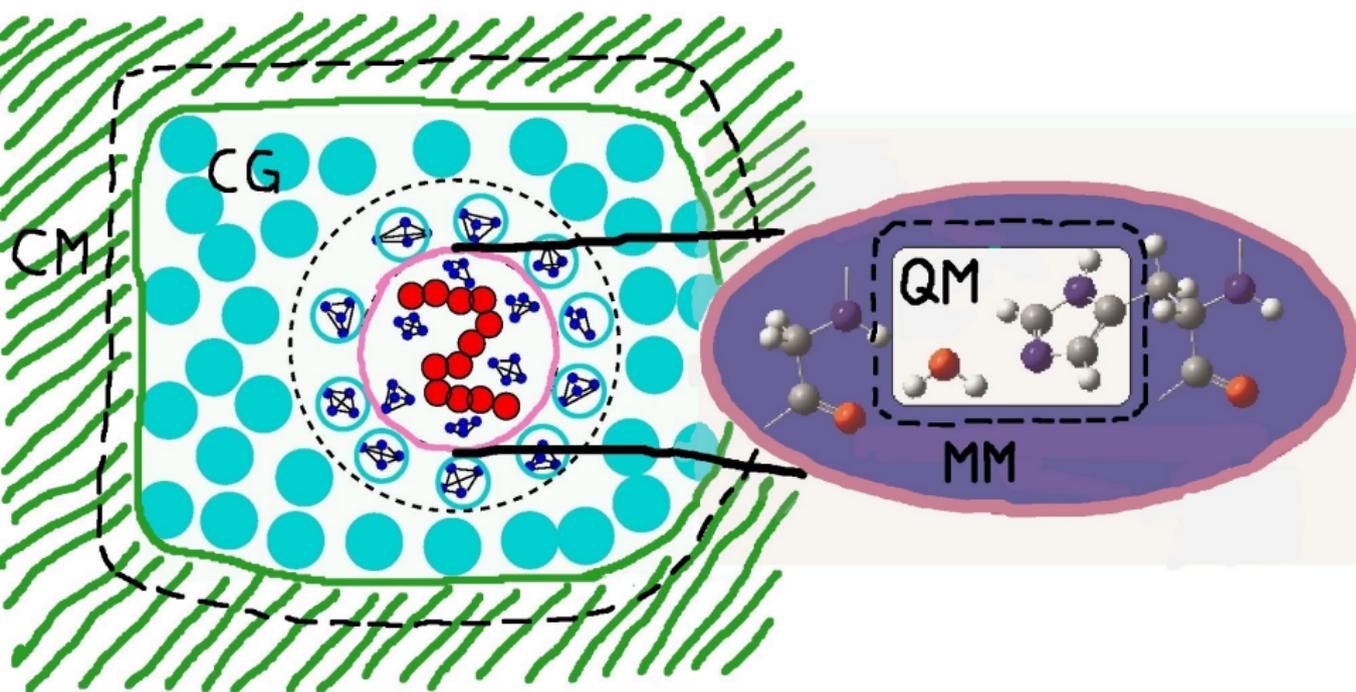
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→ 'Bridging Time and Length Scales in Materials Science and Bio-Physics'  
Fall 2005, IPAM, UCLA

# How to link QM to $\underbrace{\text{MM to CG to CM}}_{\text{FF}}$ ?



'adaptive resolution' [Matej Praprotnik, C Clementi, K Kremer **PRE** (2007)]

# Further improvements and tests

## Further

- ▶ QM/MM vs. QM/CG vs. QM/CM?
- ▶ Can we control boundary through value of  $\mu^{\text{QM}} = \mu^{\text{FF}}$  instead of spatially fixed regions?  
→ “self-adaptive” & multiple fragmentation?
- ▶ Role of dissipation, reversibility, thermostats, integrators?
- ▶ MD or MC? Multiple timesteps?

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## Tests to assess and exploit

- ▶ Reactions in liquids, solids, or on surfaces?
  - ▶ Nucleation of phase transformations?
- = direct impact on Sandia’s mission (Paul Crozier, Gary Grest, Kevin Leung, Susan Rempe)

# Variation of particles $\Rightarrow$ grand canonical ensemble

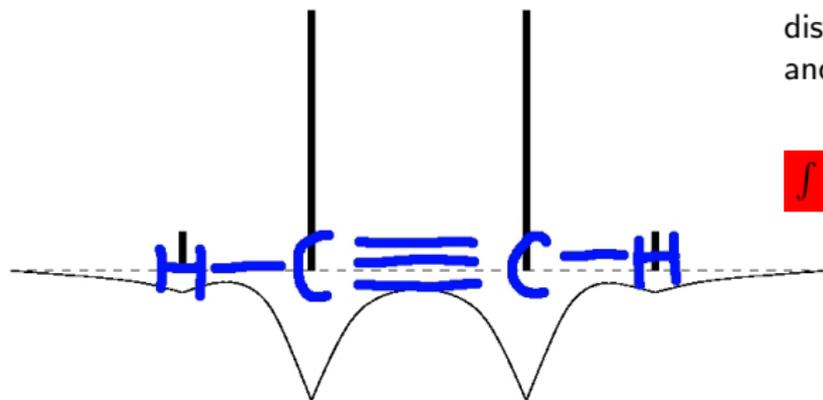
	canonical	grand-canonical
molecular model	molecular properties & processes	supra-molecular and $\lambda$ -path
first principles model	electronic properties & processes (reactions)	supra-molecular & $\lambda$ -path $\Rightarrow$ stoichiometry
space	phase space	phase & particle space chemical space from first principles <sup>†</sup>

<sup>†</sup> *Molecular grand-canonical ensemble DFT and exploration of chemical space*  
 OAvL and M. E. Tuckerman, *J Chem Phys* **125** 154104 (2006) **MGCE-DFT**

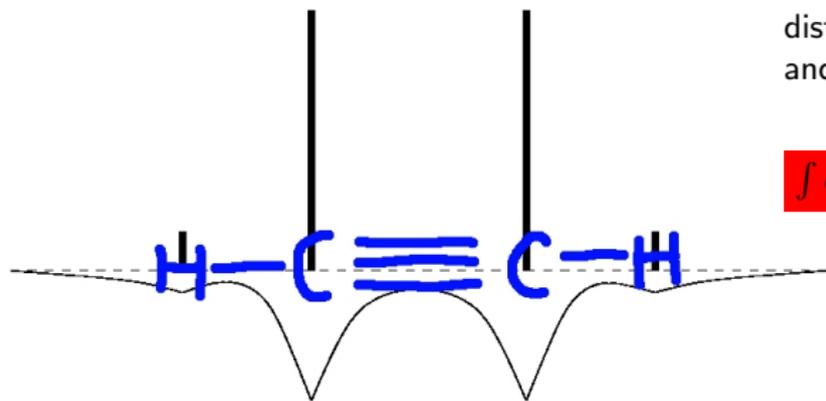
# MGCE-DFT - a DFT for electrons *and* nuclei

Back to the basics, matter consists of two particle distributions of  $N_e$  electrons and  $N_p$  protons, where

$$\int dr n(\mathbf{r}) = N_e \text{ and } \int dr Z(\mathbf{r}) = N_p$$



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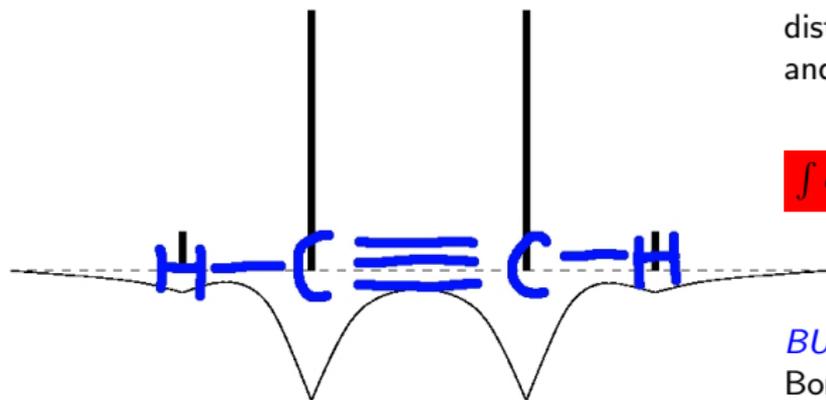
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So far, only for inclusion of nuclear quantum effects

- 'non-Born-Oppenheimer' [RG Parr et al. *JCP* **76** 568 (1982)]

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*BUT* still within Born-Oppenheimer

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# Chemical potentials - for variable particle distributions

Auxiliary variational functional with Lagrange multipliers  $\mu_e$  and  $\mu_n$ ,

$$\Omega = E[Z, n] - \mu_e \left( \int d\mathbf{r} n(\mathbf{r}) - N_e \right) - \int d\mathbf{r} \mu_n(\mathbf{r}) \left( Z(\mathbf{r}) - \sum_I N_I \delta(\mathbf{r} - \mathbf{R}_I) \right)$$

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- Variation of  $\Omega$  wrt  $n(\mathbf{r})$  yields Euler equation for electrons

$$\Rightarrow \mu_e = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\partial E[n]}{\partial N_e}$$

... electronegativity,  $\epsilon_{\text{HO}}$  [Janak *PRB* **18** 7165 (1978)]

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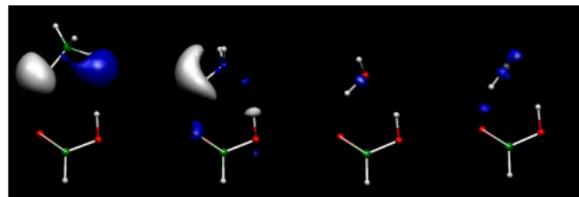
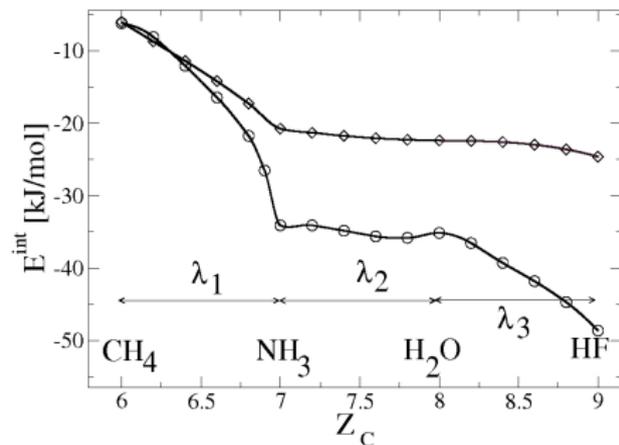
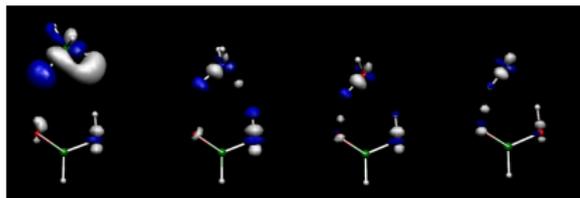
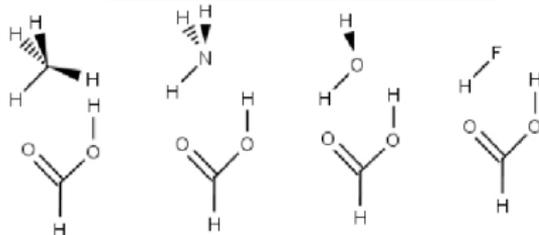
$$\text{RMD} \equiv \min_{\{Z(\mathbf{r}), N_e\}} \langle \mathcal{P}[Z, n] \rangle$$

# Example 1: intermolecular energies

$$\delta Z(\mathbf{r})|_{N_p=N_e=10}$$

$$E_{int} = E_{fa+s} - E_{fa} - E_s$$

$$\hookrightarrow \mathcal{P}[Z, n] = (E_{int} + \infty)^2$$



OAvL and ME Tuckerman *J Chem Theory Comput* **3** 1083 (2007)

## Example 2: tuning $\epsilon_{\text{HO}}$

consider Maxwell-relation,

$$\frac{\delta^2 E}{\delta Z(\mathbf{r}) \delta N_e} = \left( \frac{\delta \mu_e}{\delta Z(\mathbf{r})} \equiv \frac{\delta \epsilon_{\text{HO}}}{\delta Z(\mathbf{r})} \right) = \left( \frac{\partial \mu_n(\mathbf{r})}{\partial N_e} \equiv \frac{\partial \bar{V}_{\text{ESP}}(\mathbf{r})}{\partial N_e} \right) =: f_m(\mathbf{r})$$

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$$\frac{\delta^2 E}{\delta Z(\mathbf{r}) \delta N_e} = \left( \frac{\delta \mu_e}{\delta Z(\mathbf{r})} \equiv \frac{\delta \epsilon_{\text{HO}}}{\delta Z(\mathbf{r})} \right) = \left( \frac{\partial \mu_n(\mathbf{r})}{\partial N_e} \equiv \frac{\partial \bar{V}_{\text{ESP}}(\mathbf{r})}{\partial N_e} \right) =: f_m(\mathbf{r})$$

- ▶ Index of electronic response due to doping,  $Z_I \mapsto Z_I + dZ_I$

$$d\epsilon_{\text{HO}} = \frac{\bar{V}_{\text{ESP}}(\mathbf{R}_I, N_e + dN_e) - \bar{V}_{\text{ESP}}(\mathbf{R}_I, N_e)}{dN_e} dZ_I$$

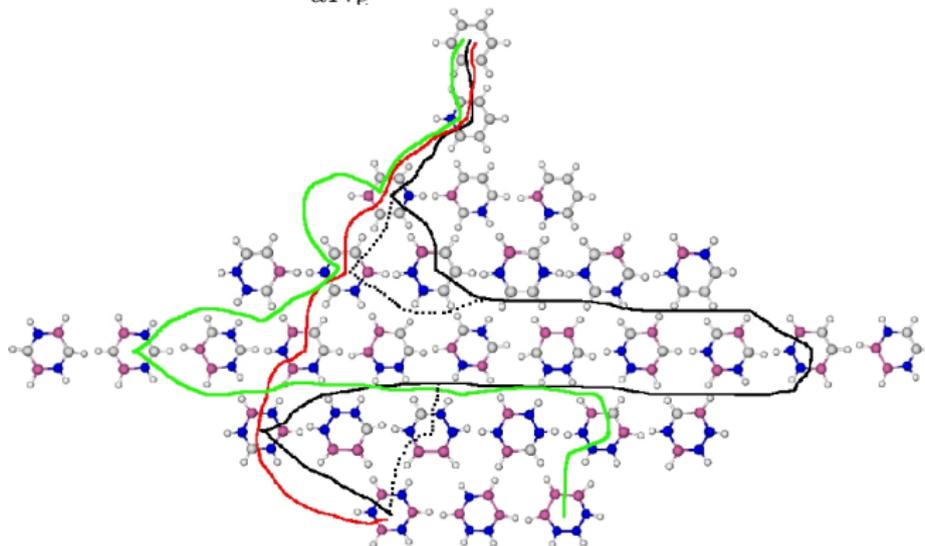
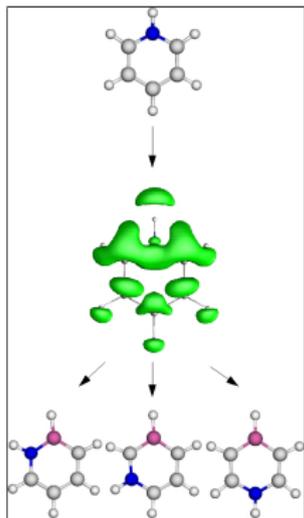
# Example 2: tuning $\epsilon_{\text{HO}}$

consider Maxwell-relation,

$$\frac{\delta^2 E}{\delta Z(\mathbf{r}) \delta N_e} = \left( \frac{\delta \mu_e}{\delta Z(\mathbf{r})} \equiv \frac{\delta \epsilon_{\text{HO}}}{\delta Z(\mathbf{r})} \right) = \left( \frac{\partial \mu_n(\mathbf{r})}{\partial N_e} \equiv \frac{\partial \bar{V}_{\text{ESP}}(\mathbf{r})}{\partial N_e} \right) =: f_m(\mathbf{r})$$

- ▶ Index of electronic response due to doping,  $Z_I \mapsto Z_I + dZ_I$

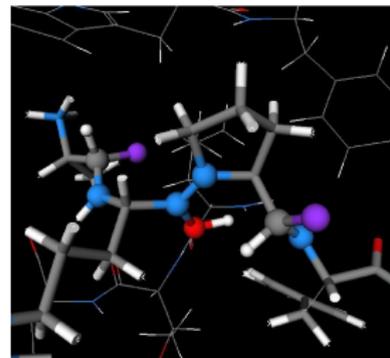
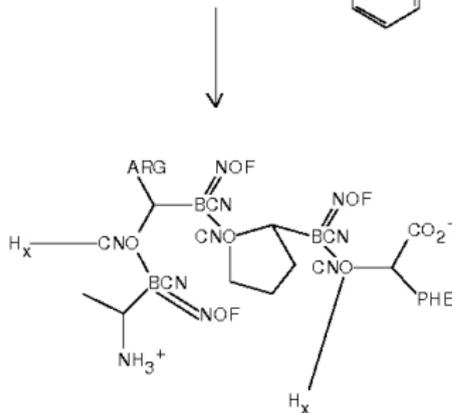
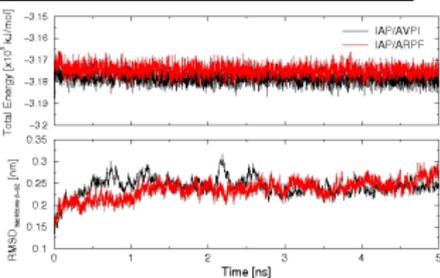
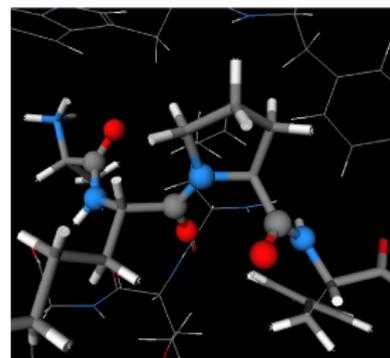
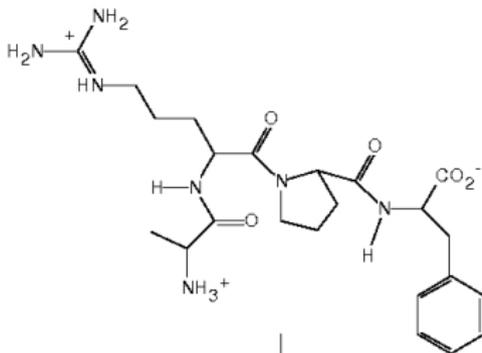
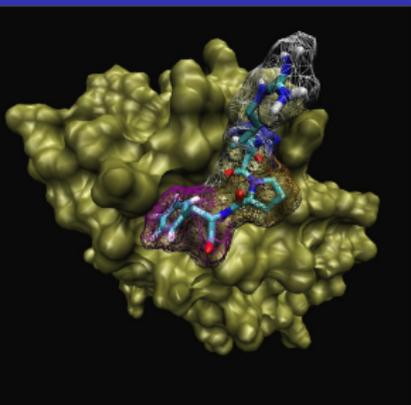
$$d\epsilon_{\text{HO}} = \frac{\bar{V}_{\text{ESP}}(\mathbf{R}_I, N_e + dN_e) - \bar{V}_{\text{ESP}}(\mathbf{R}_I, N_e)}{dN_e} dZ_I$$



Molecular electronics collaboration with MPI for polymer research, Mainz



# Example 3: drug discovery - inhibiting IAP



OAvL, R Lins, U Rothlisberger *PRL* **95** 153002 (2005)

# assembling the tools

Perform

$$\min_{\{N_e, Z\}} \langle \mathcal{P}[\hat{\mathcal{H}}^{\text{QM/FF}}] \rangle_{\text{ambient conditions}}$$

through sampling of chemical and phase space with

$$\text{QM} \equiv \hat{\mathcal{H}}^{\text{QM/FF}} = \hat{\mathcal{H}}^{\text{QM}} + \hat{V}_{\text{ESP}}^{\text{FF}} + \hat{V}_{\text{vdW}}^{\text{FF}}, \quad \hat{\mathcal{H}}^{\text{QM}} = \text{MGCE-}\hat{\mathcal{H}}^{\text{KS}}$$

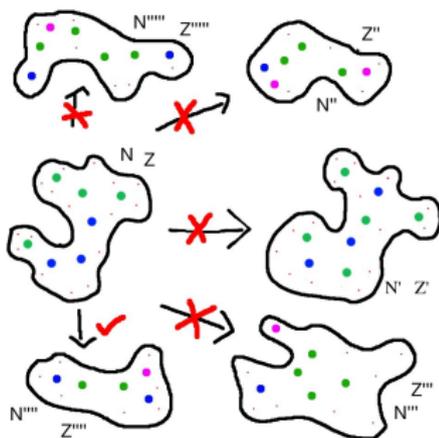
# assembling the tools

Perform

$$\min_{\{N_e, Z\}} \langle \mathcal{P}[\hat{\mathcal{H}}^{\text{QM/FF}}] \rangle_{\text{ambient conditions}}$$

through sampling of chemical and phase space with

$$\text{QM} \equiv \hat{\mathcal{H}}^{\text{QM/FF}} = \hat{\mathcal{H}}^{\text{QM}} + \hat{V}_{\text{ESP}}^{\text{FF}} + \hat{V}_{\text{vdW}}^{\text{FF}}, \quad \hat{\mathcal{H}}^{\text{QM}} = \text{MGCE-}\hat{\mathcal{H}}^{\text{KS}}$$



Multiscaling modular

→ “plug and play”

Entirely general

→ *any* property

The better initial guess

→ the faster converges  $\mathcal{P}$