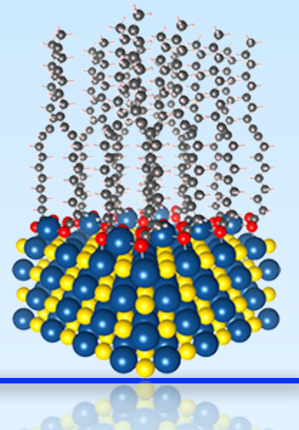
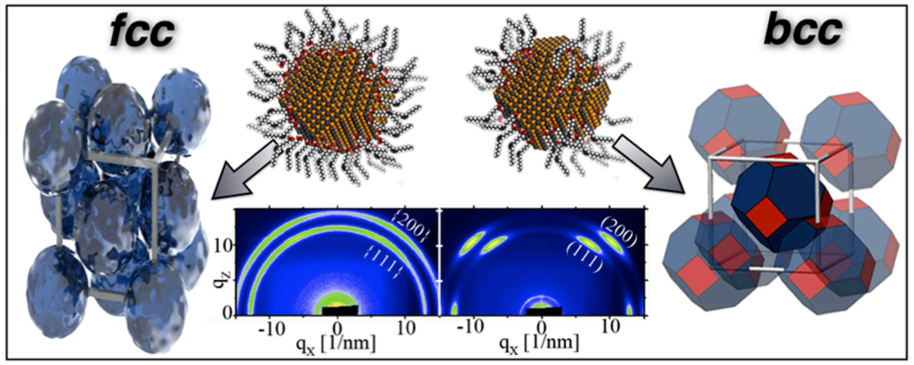
Control of Nanocrystal Morphology and Assembly and Quantum Monte Carlo Method for Solvation

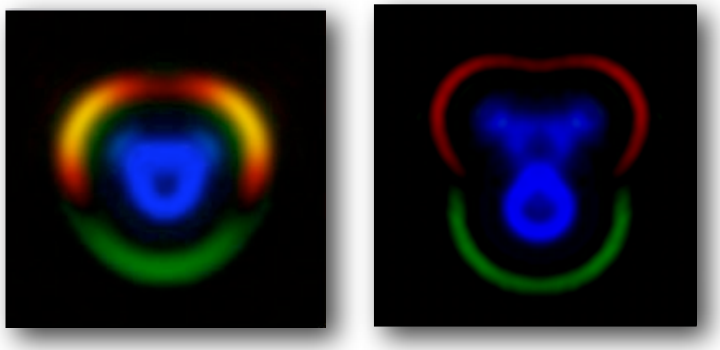
Richard G. Hennig, Cornell University



How can we predict the morphology and assembly of nanocrystals?
How can we include solvation effects in quantum Monte Carlo for molecules and surfaces?

- Shape control of ligand-stabilized nanocrystals core by modification of ligand coverage
- Anisotropic ligand coverage nanocrystals leads to anisotropy interactions and affects assembly
- Solvation can be included in QMC through external potential
- Successful for small molecules, promising for surfaces





ACS Nano 6, 2118 (2012), JACS 133, 3131 (2011), Phys. Rev. B 85, 201102 (R) (2012)

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Prediction and Design of Materials from Crystal Structures to Nanocrystal Morphology and Assembly

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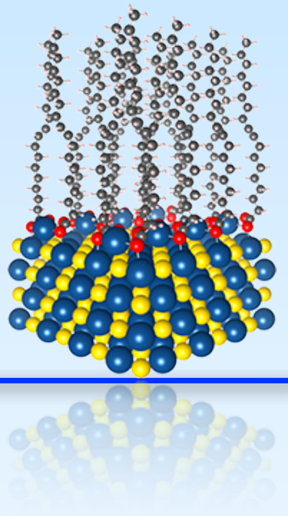

Acknowledgement

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- Quantum Monte Carlo Solvation Method: K. Schwarz, T. Arias
- Genetic algorithm development: W. Tipton, S. Wenner, A. Sanchez
- Battery materials: W. Tipton, C. Bealing, K. Matthew, M. Blonsky

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- Computational resources provided by XSEDE, Teragrid, CCNI, OSC

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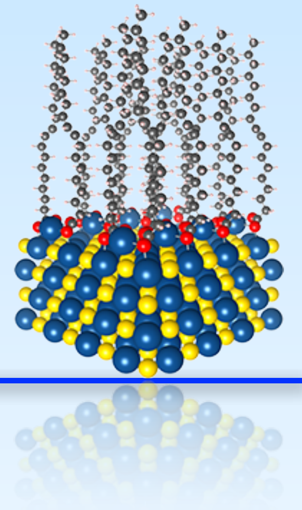
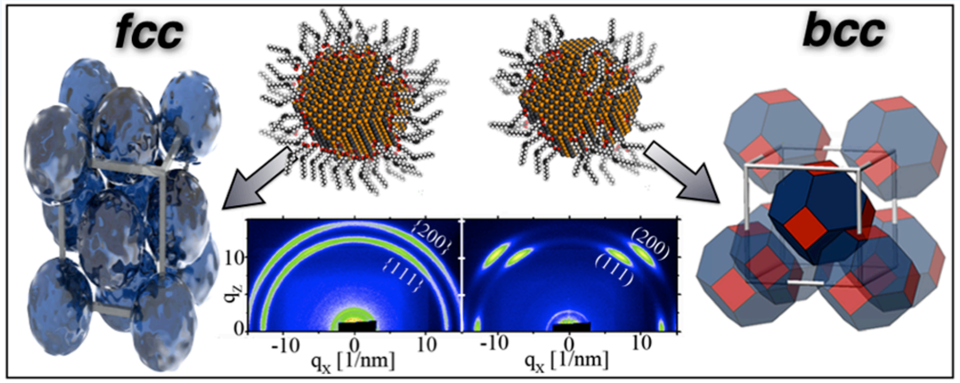
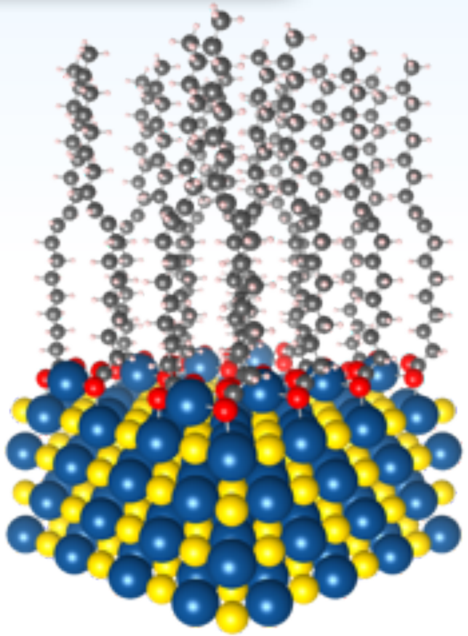
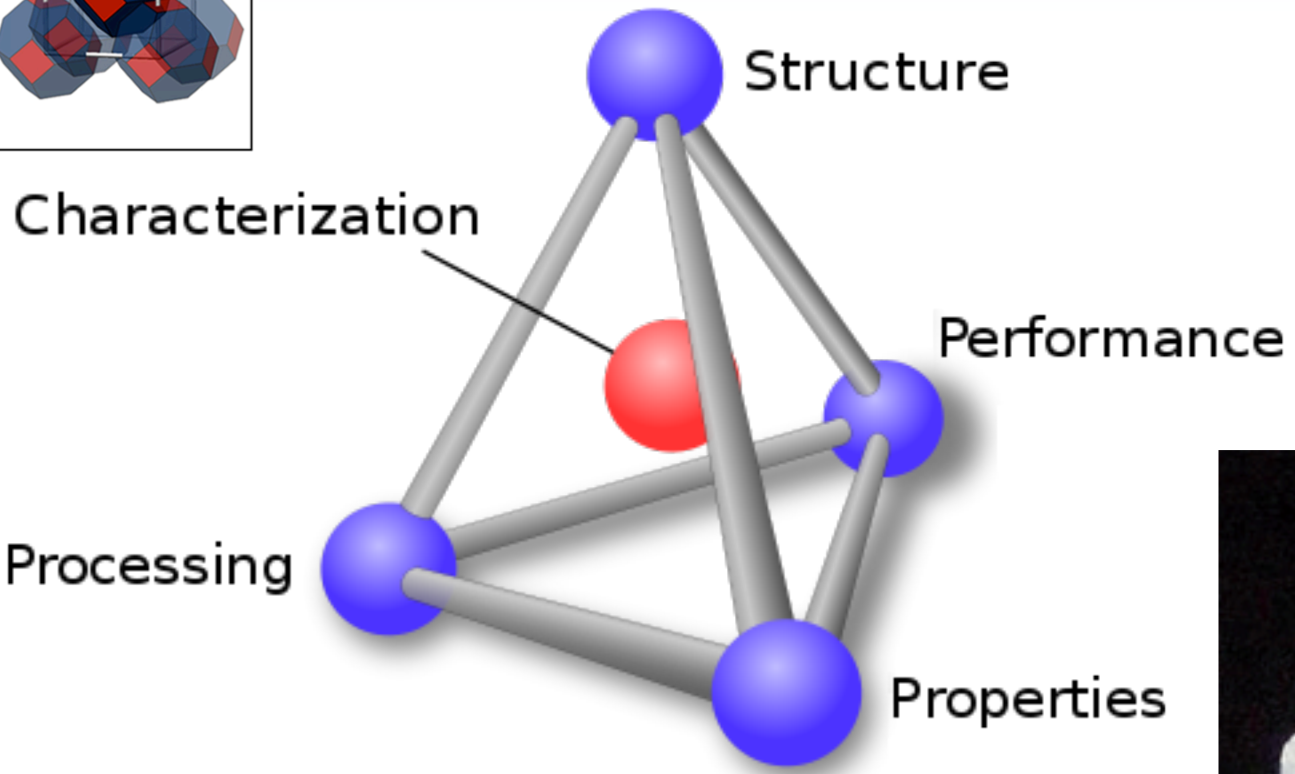


Materials Science = Structure - Property Relationships

Structure = Atomic structure + Microstructure







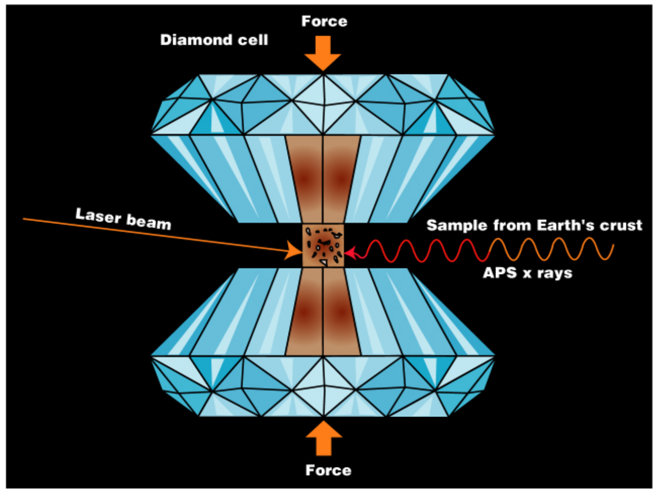
Structure

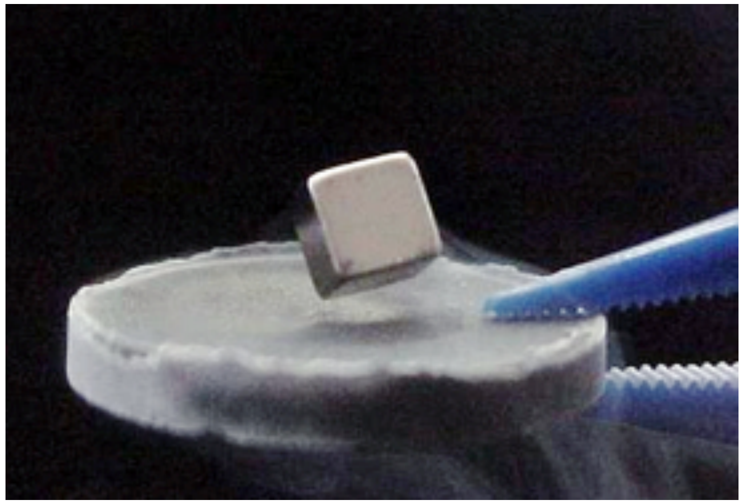
Characterization

Performance

Processing

Properties





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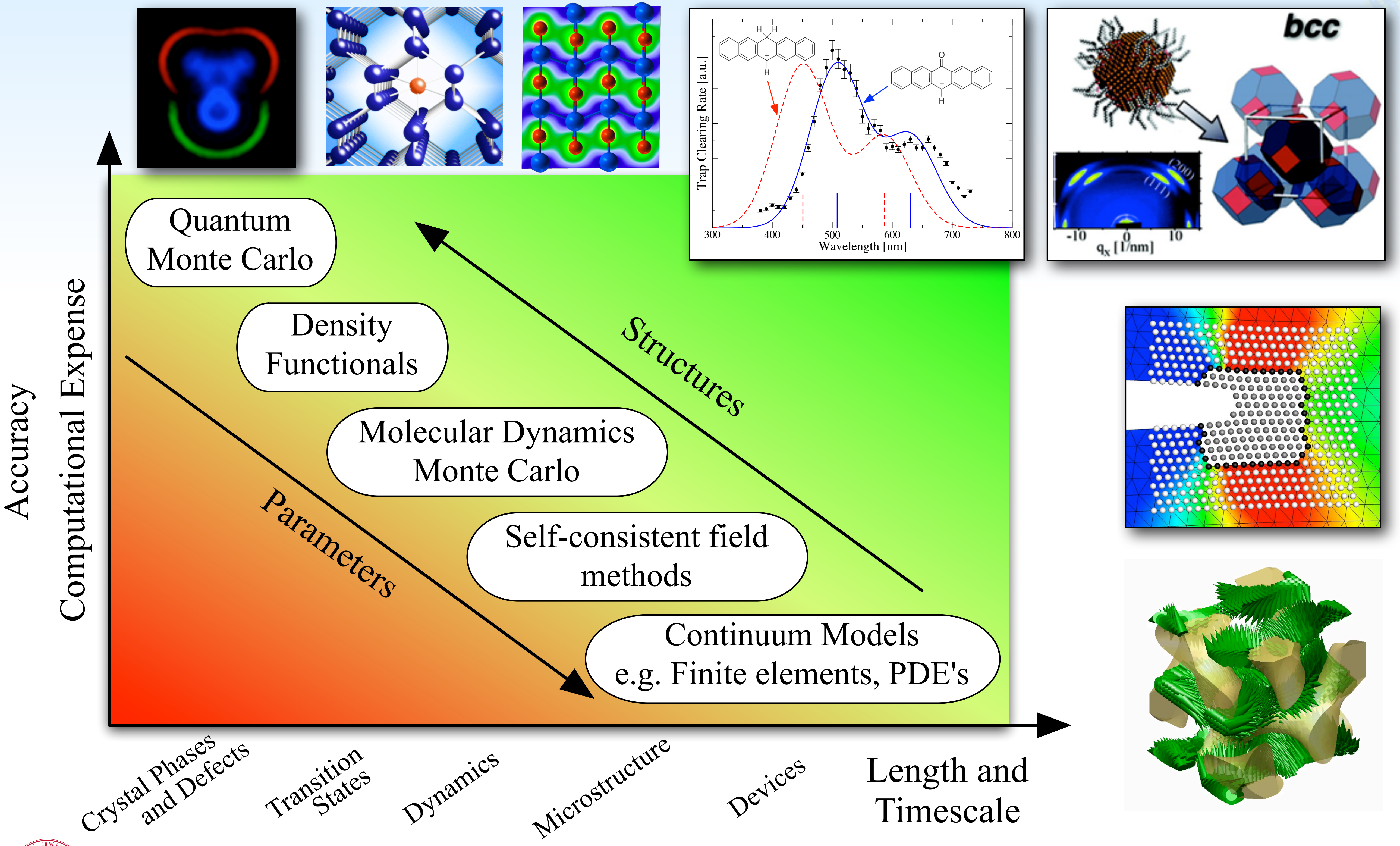
Computational Methods Across Length Scales



Accuracy

Computational Expense

Quantum Monte Carlo

Density Functionals

Molecular Dynamics Monte Carlo

Self-consistent field methods

Continuum Models e.g. Finite elements, PDE's

Structures

Parameters

Crystal Phases and Defects

Transition States

Dynamics

Microstructure

Devices

Length and Timescale

Nanocrystal Morphology and Assembly
Ligand-stabilized PbSe Nanocrystals

Clive R. Bealing, Richard G. Hennig
William J. Baumgardner, Joshua J. Choi, Tobias Hanrath

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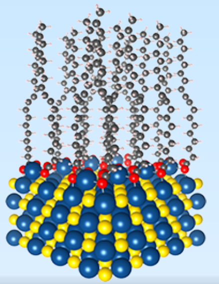
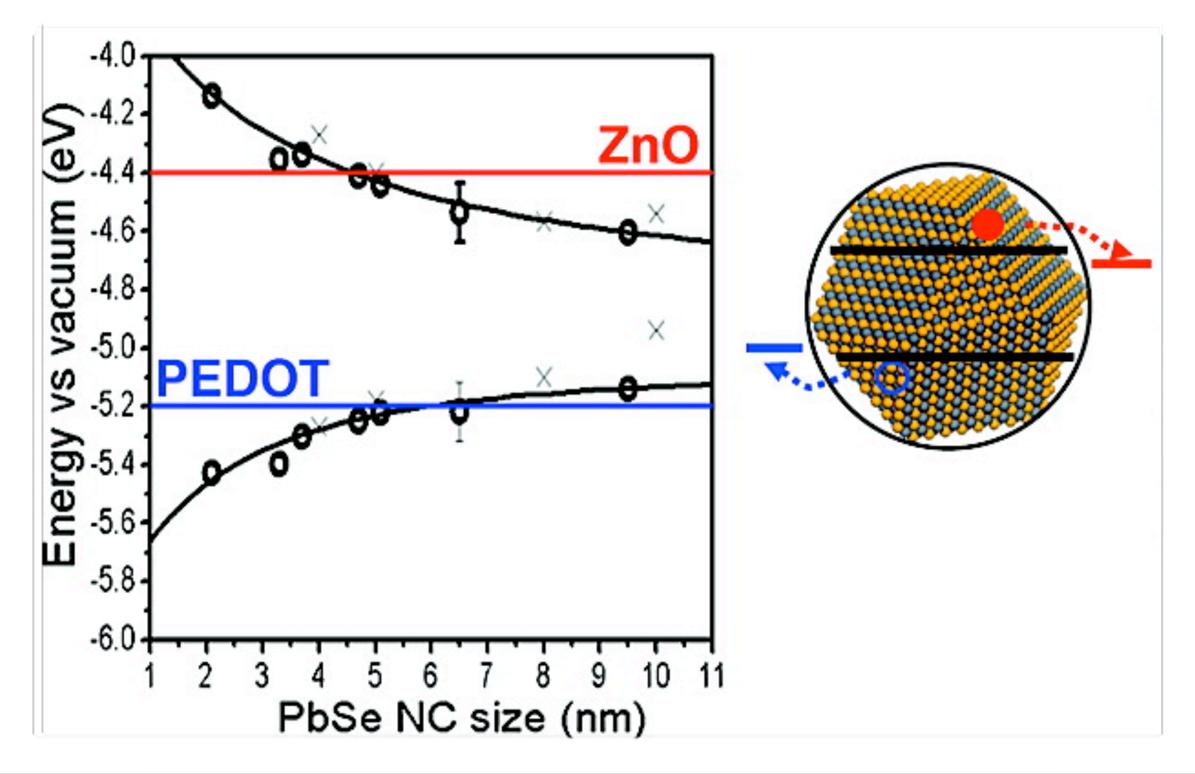
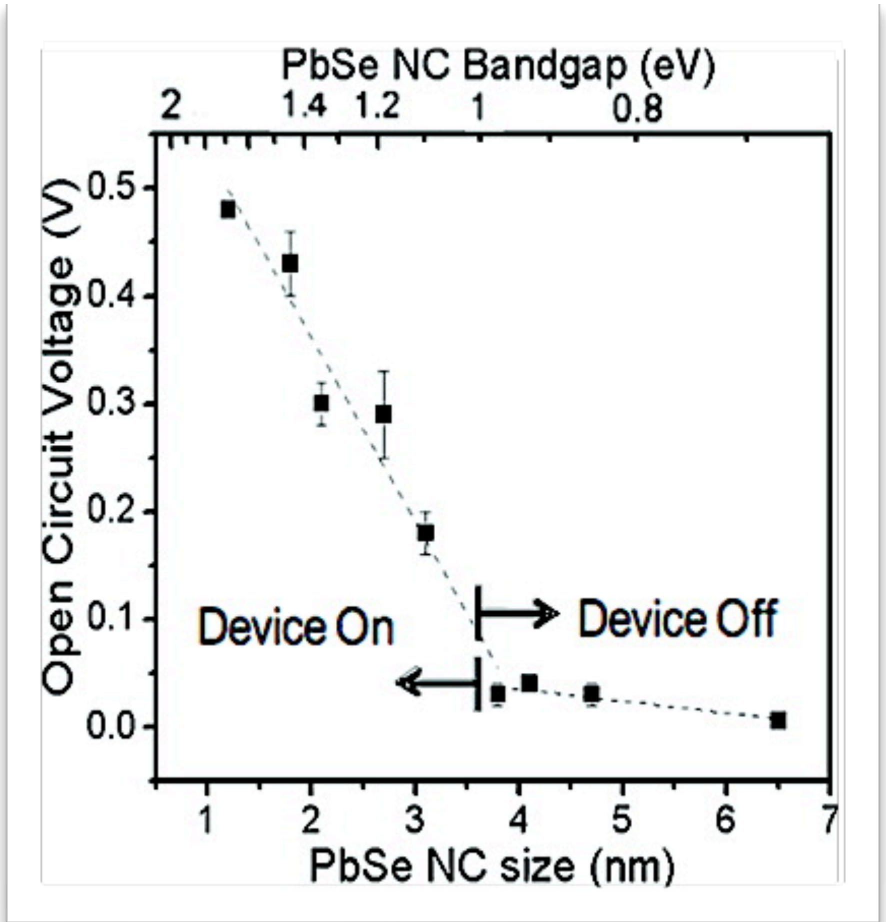
Importance of Lead-Salt Nanocrystals



- Promising candidates for photovoltaics
- Electronic and optical properties tunable through size
- Large exciton radius in PbSe of 46 nm ⇒ Energy gap tunable 1.4 – 0.4 eV

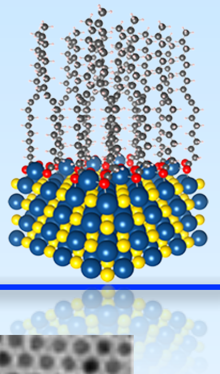




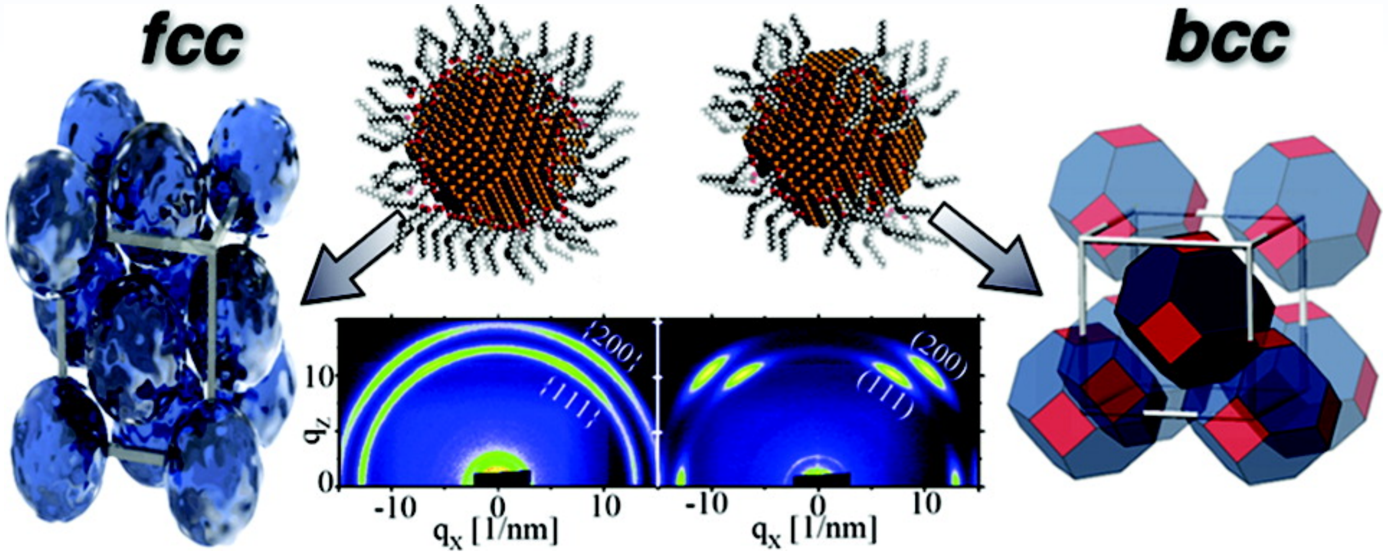
- Extension of solar energy conversion to near-infrared region
- Efficiency of excitonic solar cells of 3.4%

Nano Lett. 9, 3749 (2009)

Morphology of Lead-Salt Nanocrystals

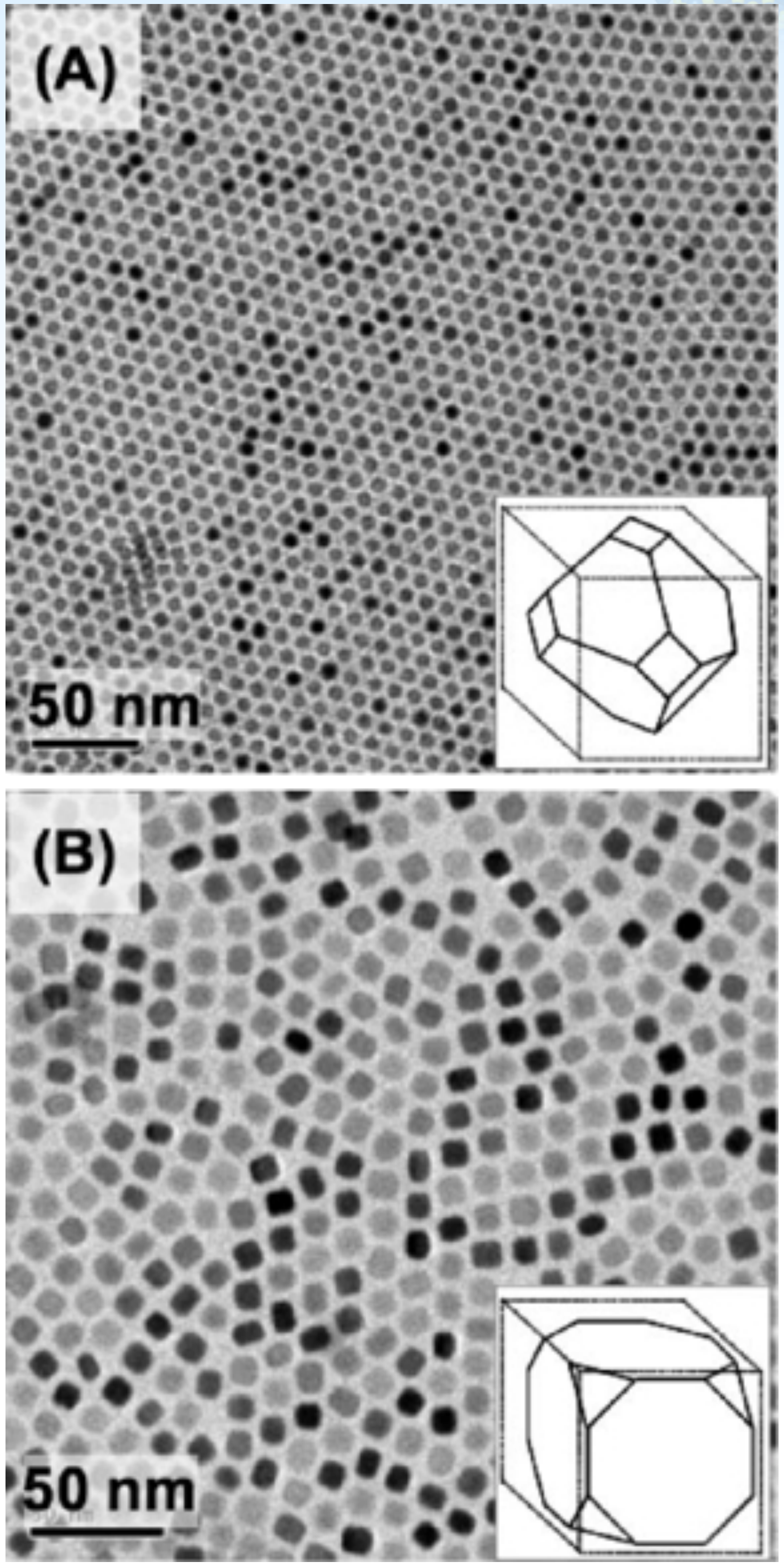


- Size and shape tunable in synthesis
- Nanocrystals stabilized by ligands like oleic acid
- Ligand loss of PbS nanocrystals
  ⇒ Transformation from *fcc* to *bcc* superlattice



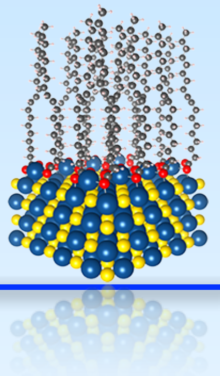
JACS, **133**, 3131 (2011)

Importance of control of size, shape and composition of individual nanocrystal, and tunability of nanocrystal assembly

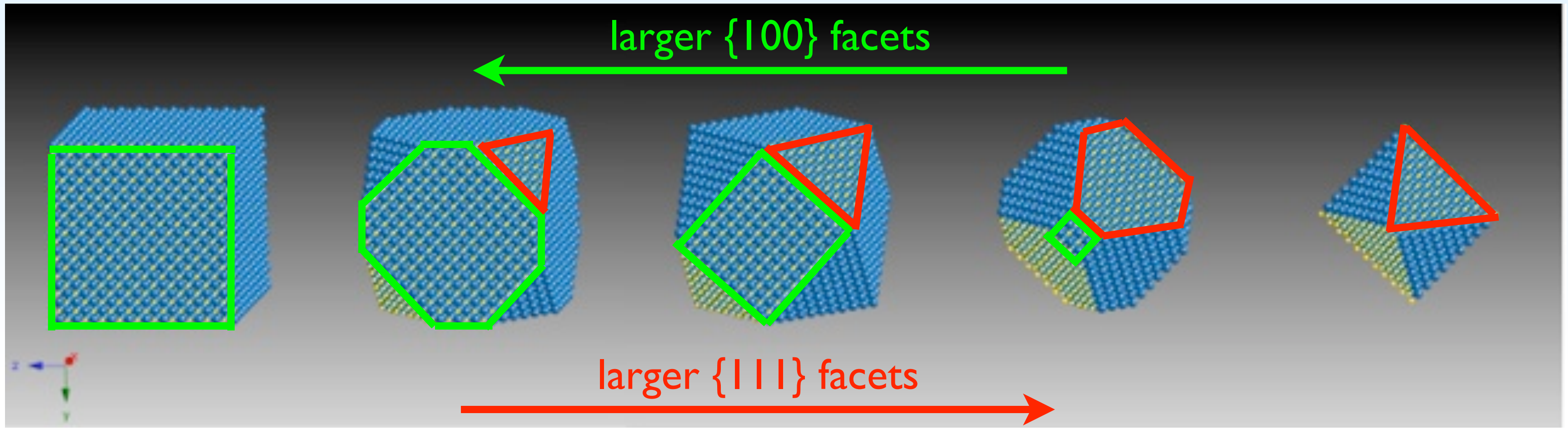


ACS Appl. Mater. Interfaces, **1**, 244 (2009)

Nanocrystal Shape



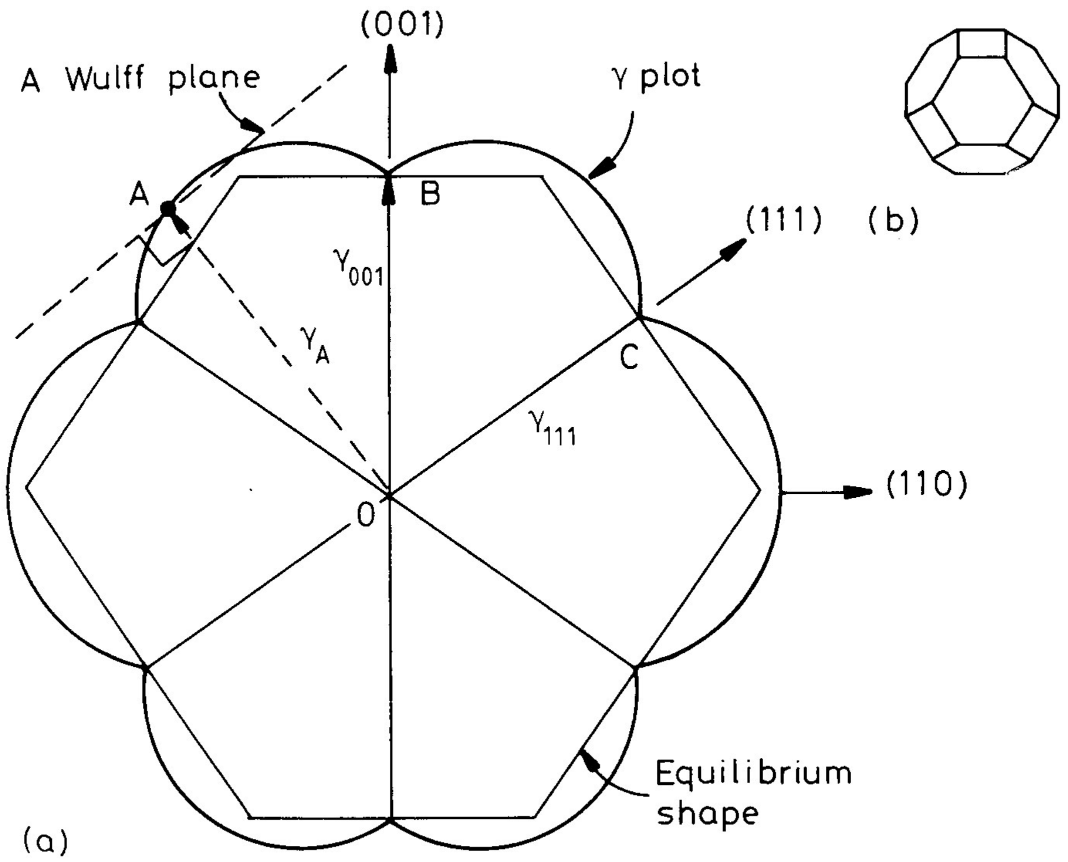
- Shape of nanocrystal core determined by size of {100} and {111} facets



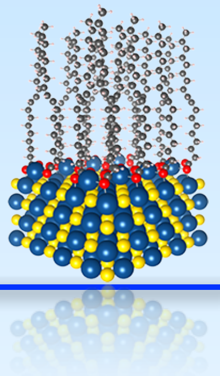
- Facet sizes related to surface energies $\sigma_{\{hkl\}}$ of the facets $\{hkl\}$
- Equilibrium shape of nanocrystal given by minimum of Gibbs energy

$$\min \sum_i A_i \cdot \gamma_i$$

- Simple geometric construction by Wulff

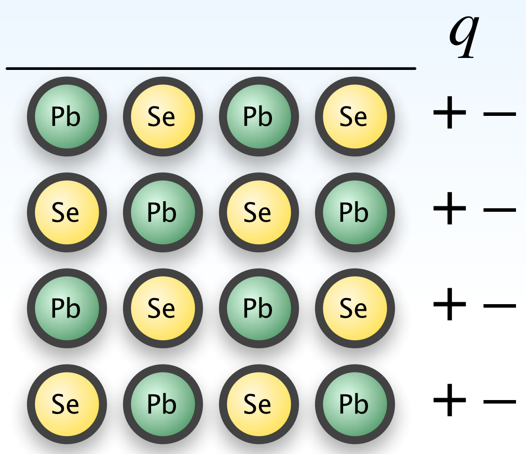


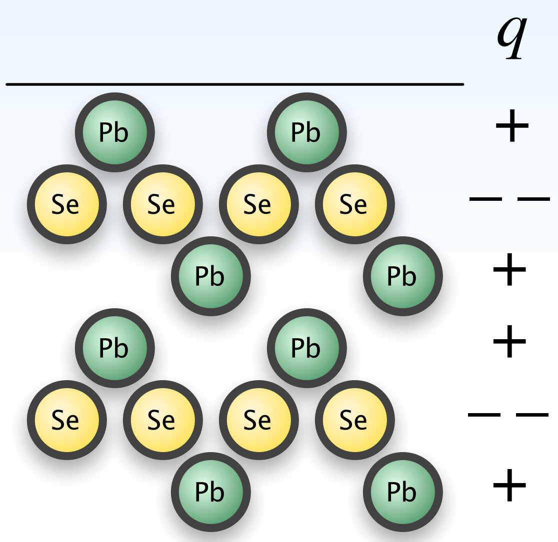
Surface Energy of Ionic Crystals



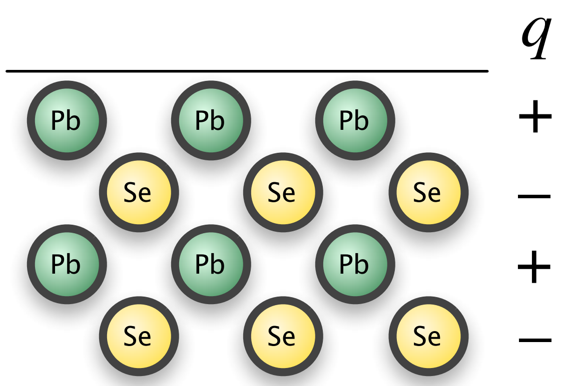
- Surface energy of ionic crystals depends on termination
- Two scenarios (Tasker '79)

Zero electric field
⇒ Low surface energy

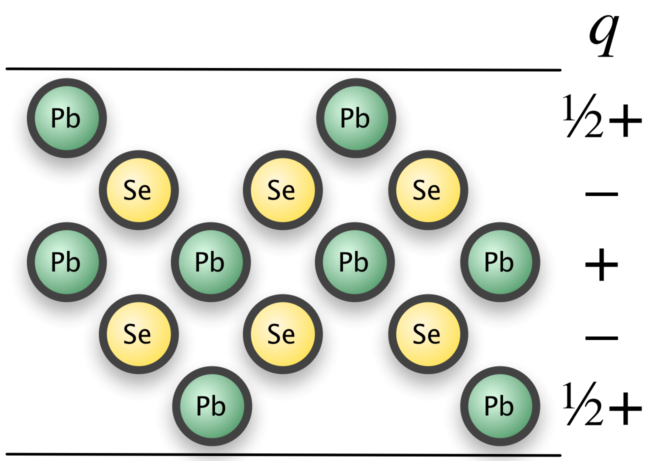


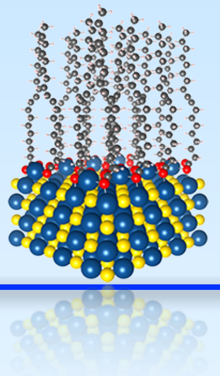


Finite electric field throughout
⇒ Infinite surface energy



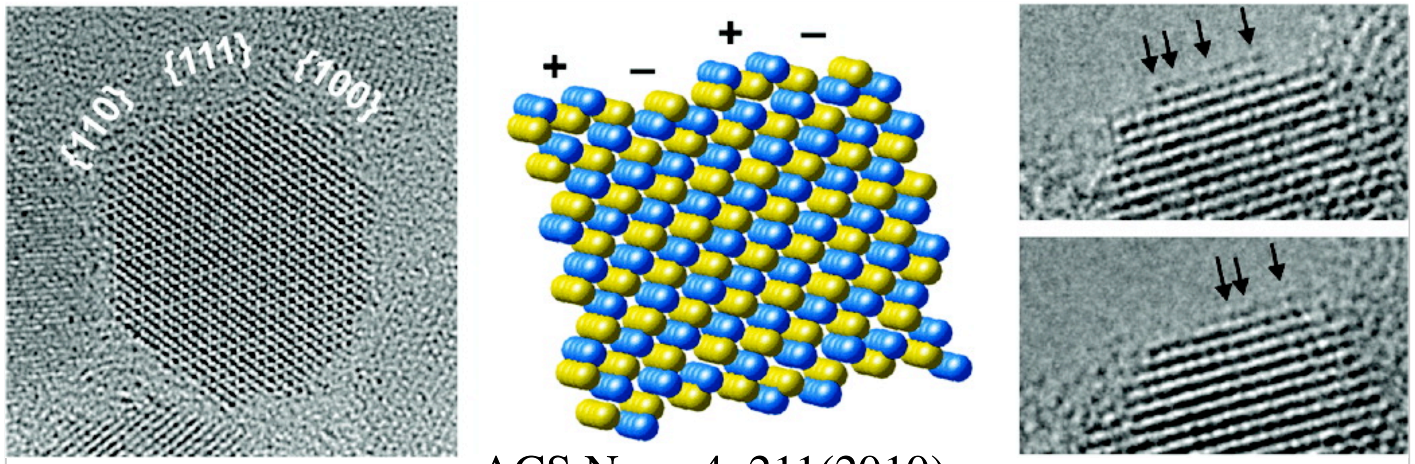
Surface reconstruction to remove electric dipole perpendicular to surface





Surface Energy of Nanocrystals

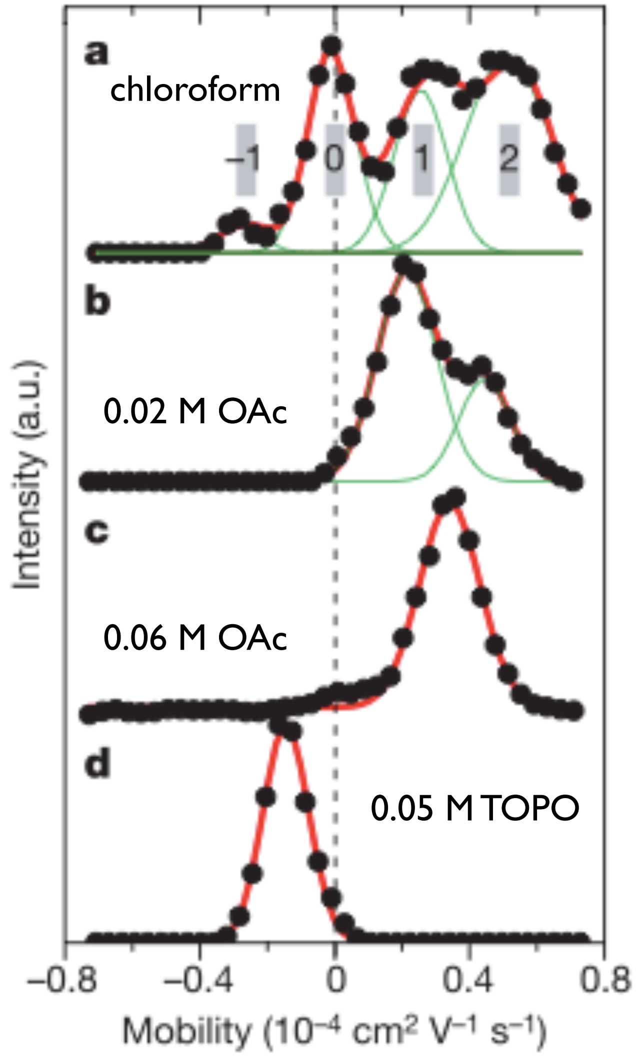
- PbSe exhibits rocksalt crystal structure
- {100} surface is uncharged, no dipole moment
- {111} cleavage plane is either Pb or Se terminated
- Charged surface reconstructs to remove surfae dipole



ACS Nano 4, 211(2010)

- Ligands modify the surface energy
- Oleate ligand is anionic but NCs exhibit little charge

  ⇒ Charge compensation by excess surface Pb^{2+}
- Pb incorporated into ligand **⇒ $PbOA_2$ ligands**



Shevchenko *et al.*, Nature Lett., **439**, 55 (2011)

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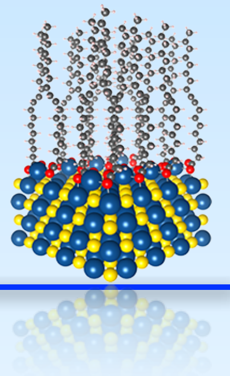
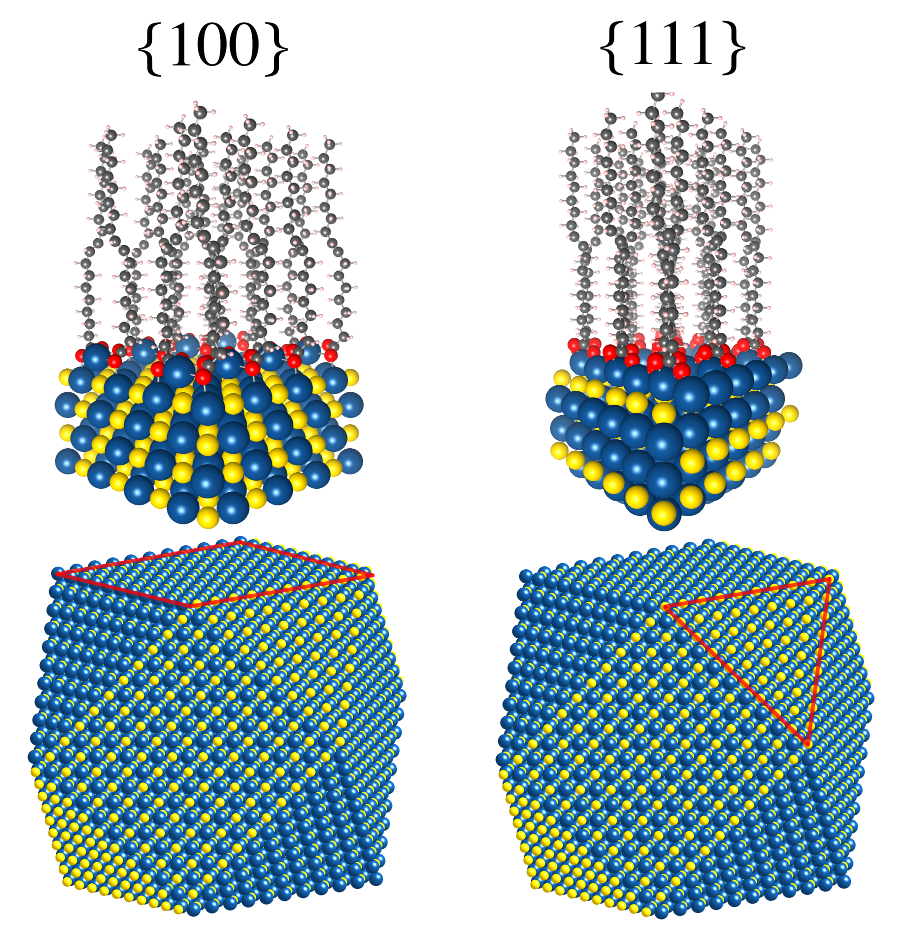
Ligand Binding and Surface Energies

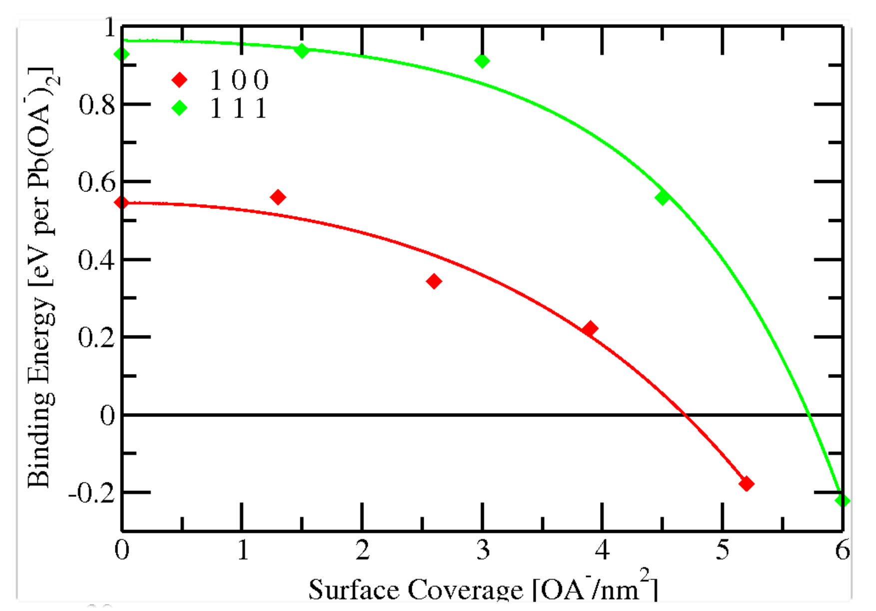


- Binding energies obtained through DFT (VASP)
- vdW interactions between ligands neglected

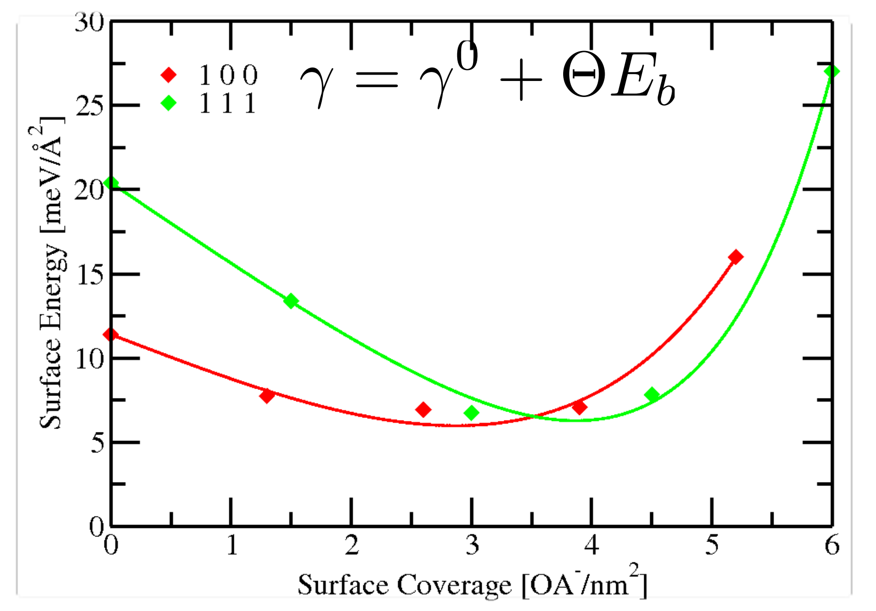


PbSe {100} and {111} surfaces capped by $Pb(OA)_2$

DFT binding energy decreases with coverage



Minimum in surface energy at 3 to 4 OA^{-}/nm^2



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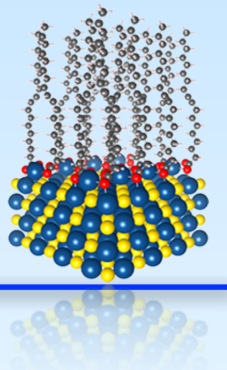
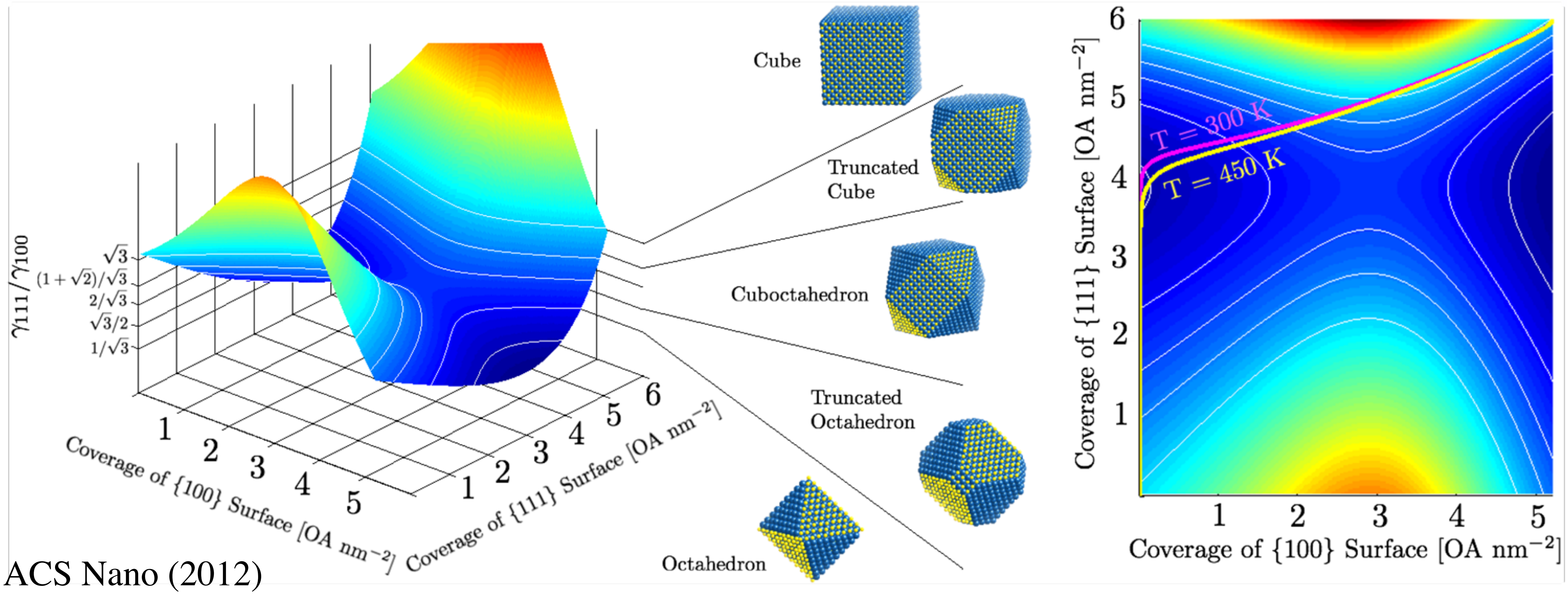
Predicted Nanocrystal Shapes



Wulff construction and equilibrium ligand coverage

- Ratio of the surface energies $\gamma_{111}/\gamma_{100}$ determines the equilibrium shape
- Isotherms for equilibrium coverage of facets show that **Shape can be tuned through ligand concentration during synthesis**



ACS Nano (2012)

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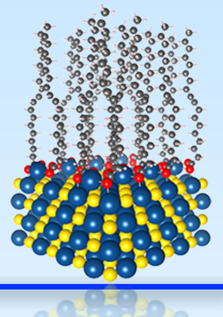
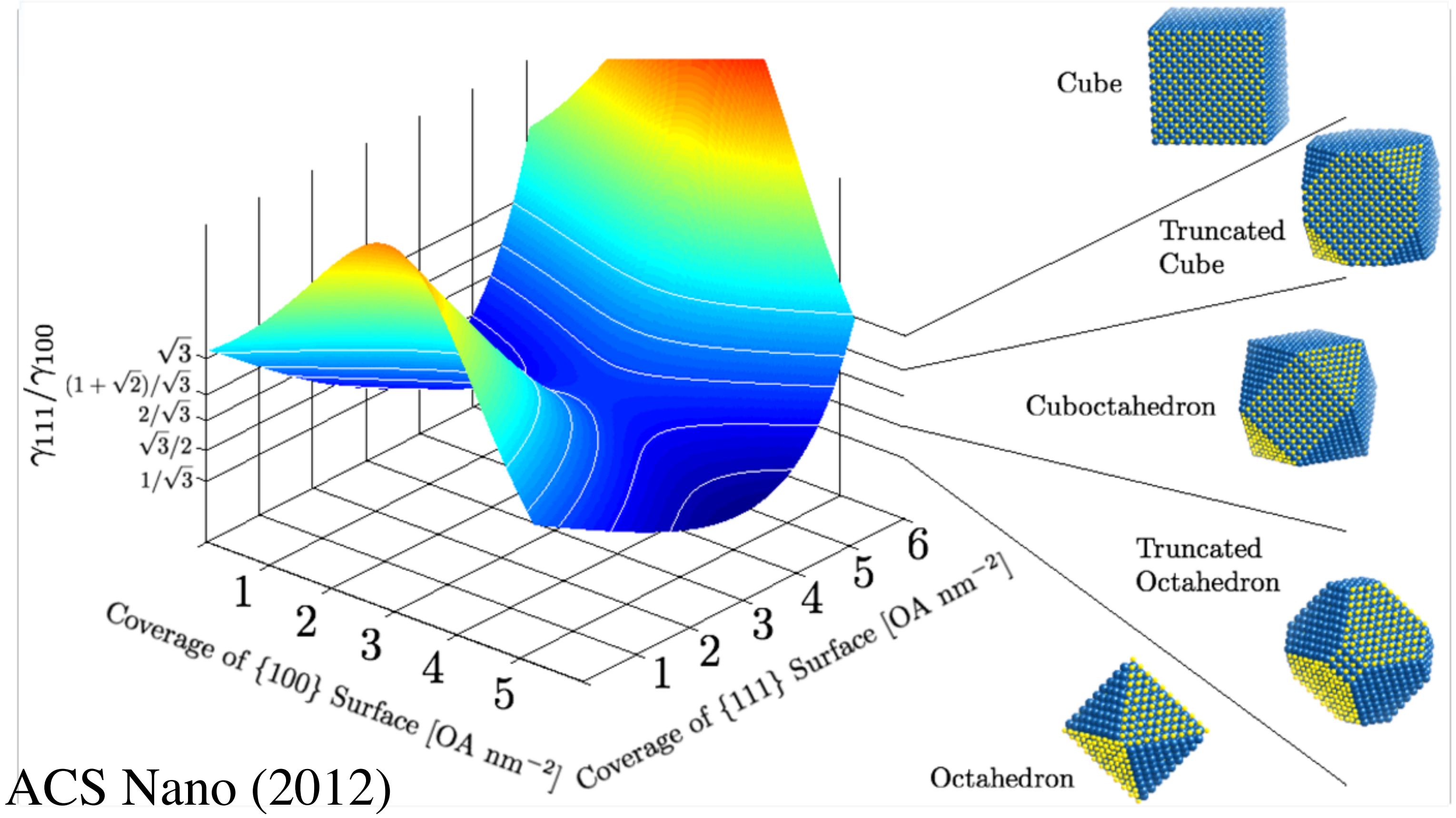
Experimental Confirmation

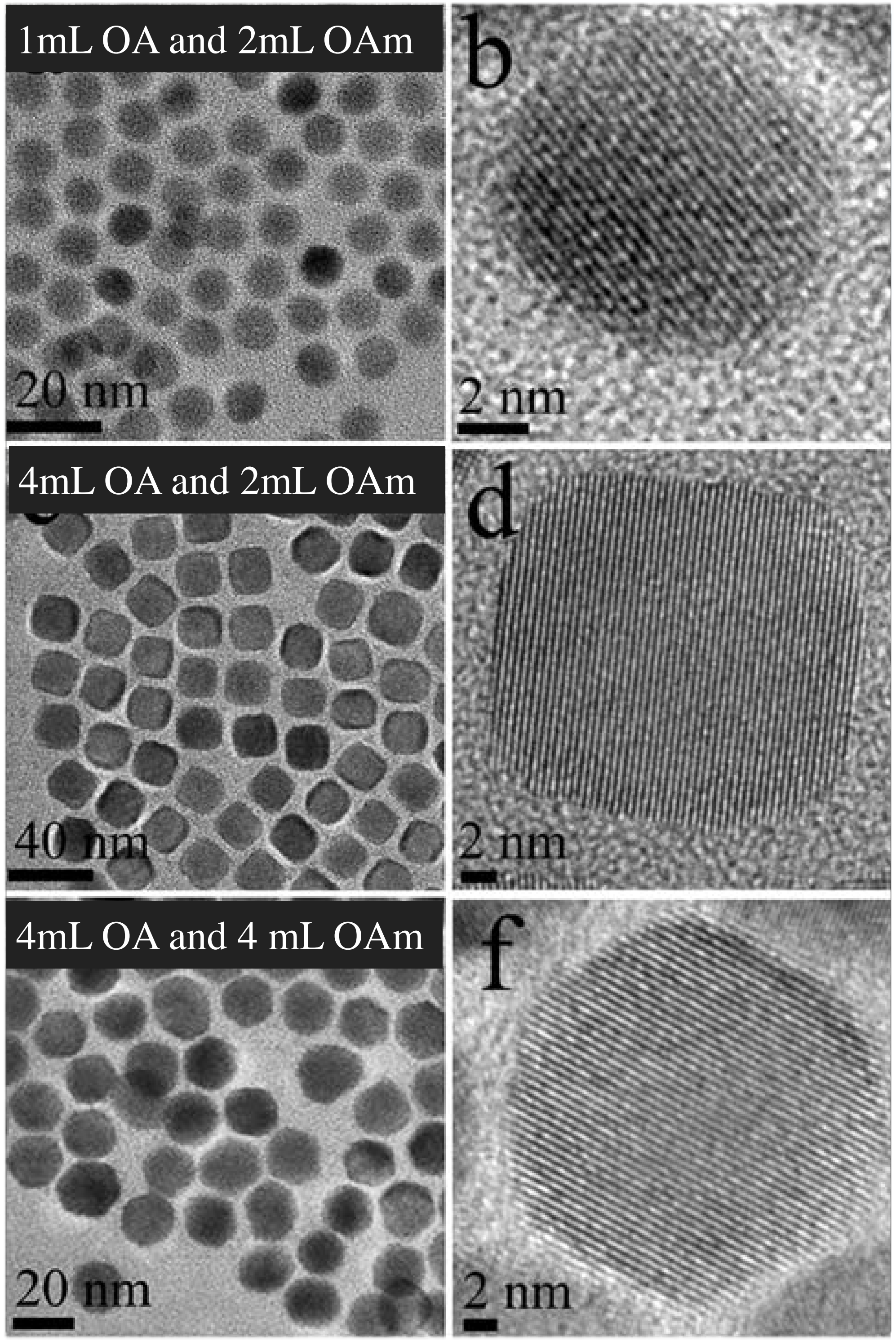


Li *et al*. *Cryst*. *Eng*. *Comm*. 12, 1127 (2010)

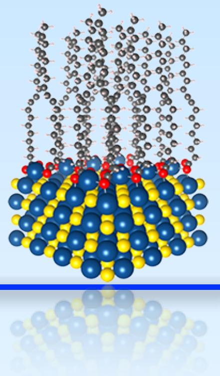
- Changing the amount of oleic acid and oleyamine with the same reaction time 1 min



ACS Nano (2012)

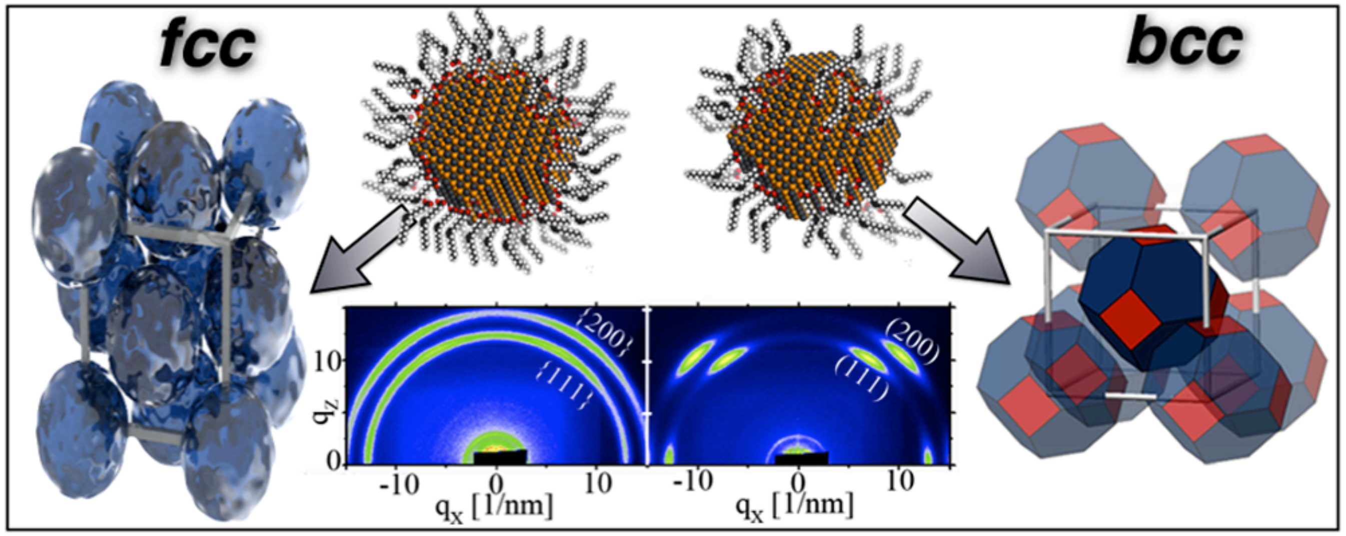


Nanocrystal Assembly

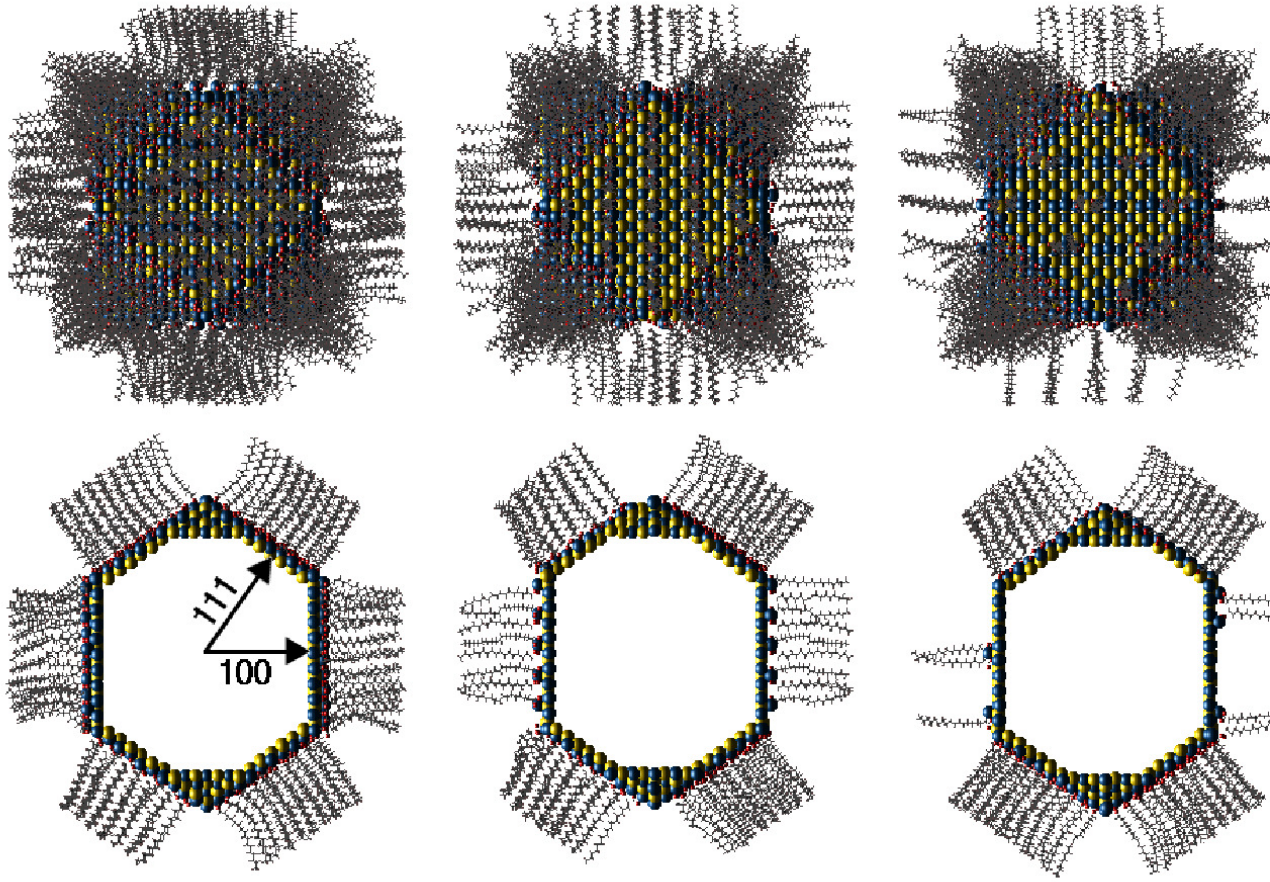


Aging of nanocrystals changes ligand coverage

- Ligands binding weaker on {100} than {111}
- Reduced coverage of {100} when aging in ligand poor condition
- Resulting change in "effective shape" from nearly spherical to preferred interactions in {111} direction
- Change in assembly
  ⇒ **Transformation from fcc to bcc**



JACS, **133**, 3131 (2011)



a b c

Quantum Monte Carlo Method for Solvation Energies

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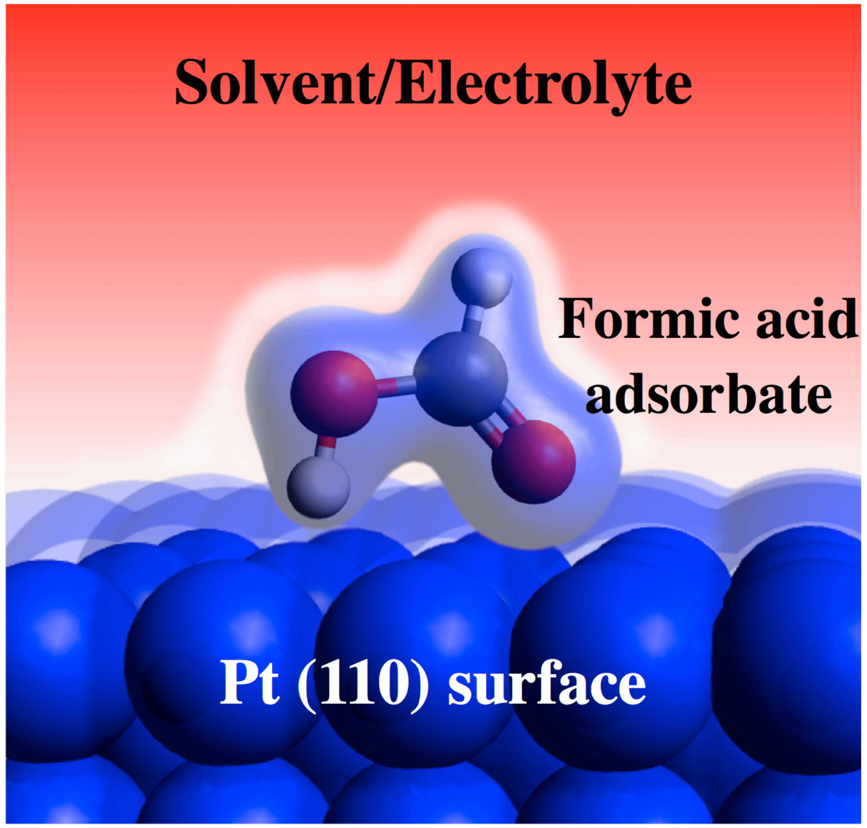
Importance of Solvent Effects

Motivation

- Energetics of chemical processes differ in vacuum and solution
- Importance of solvent effects in catalysis and electrochemistry
- Applications to energy technologies:
  Fuel cells and batteries
- Example:
  - Nucleophilic substitution (SN2) reaction

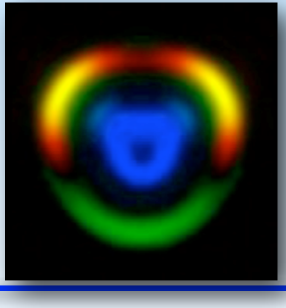
    $$Cl^{-} + CH_3Cl \rightarrow CH_3Cl + Cl^{-}$$

  - Hydration effects lower transfer rate by **20 orders of magnitude**



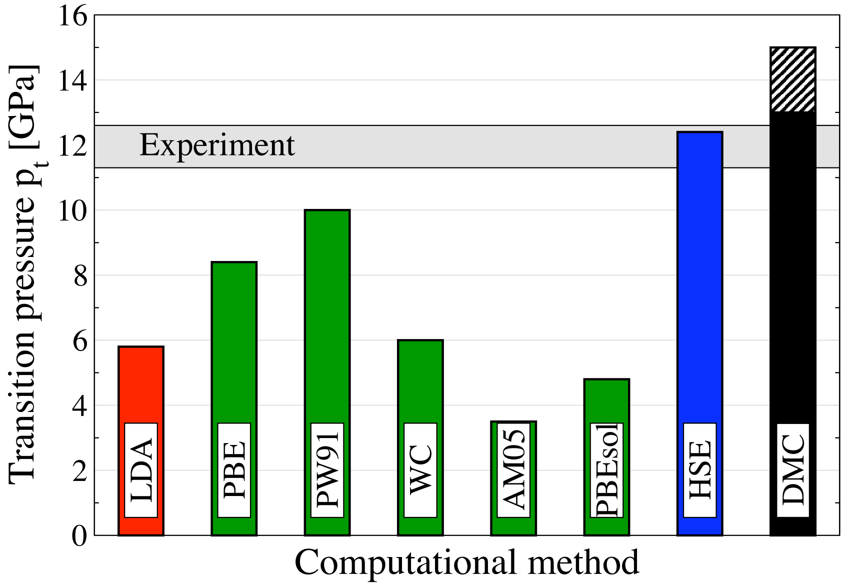
Solvation effects important for applications to energy technologies

Why Quantum Monte Carlo?



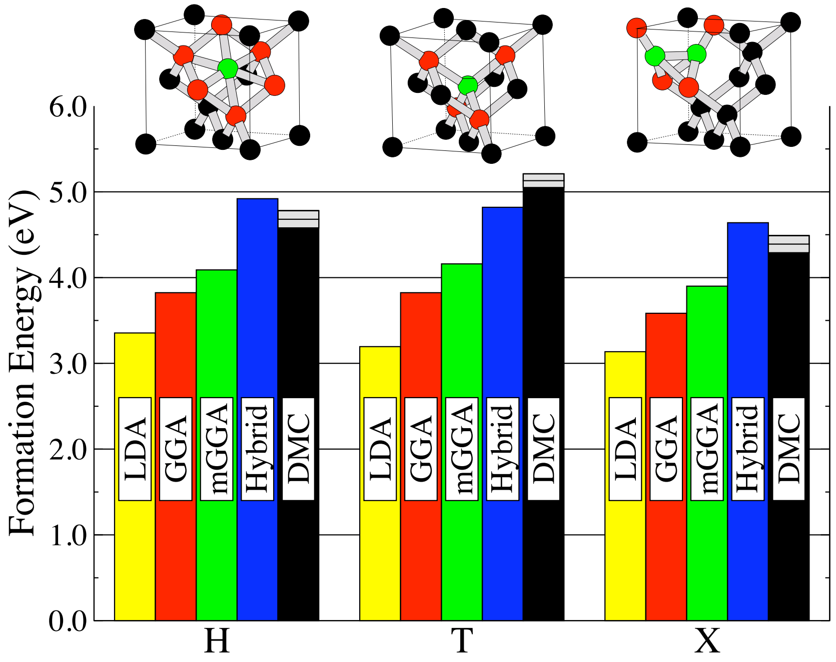
Limited accuracy of density functional theory for

- Solvated platinum surfaces with carbon monoxide adsorbates
- Surface energies in solution
- Van der Waals complexes in solution



Accuracy of quantum Monte Carlo for

- Structural and defect energies
- Bandgaps, optical excitations
- Reaction barriers and
- Weak dispersion forces
- In molecular and extended systems including metals



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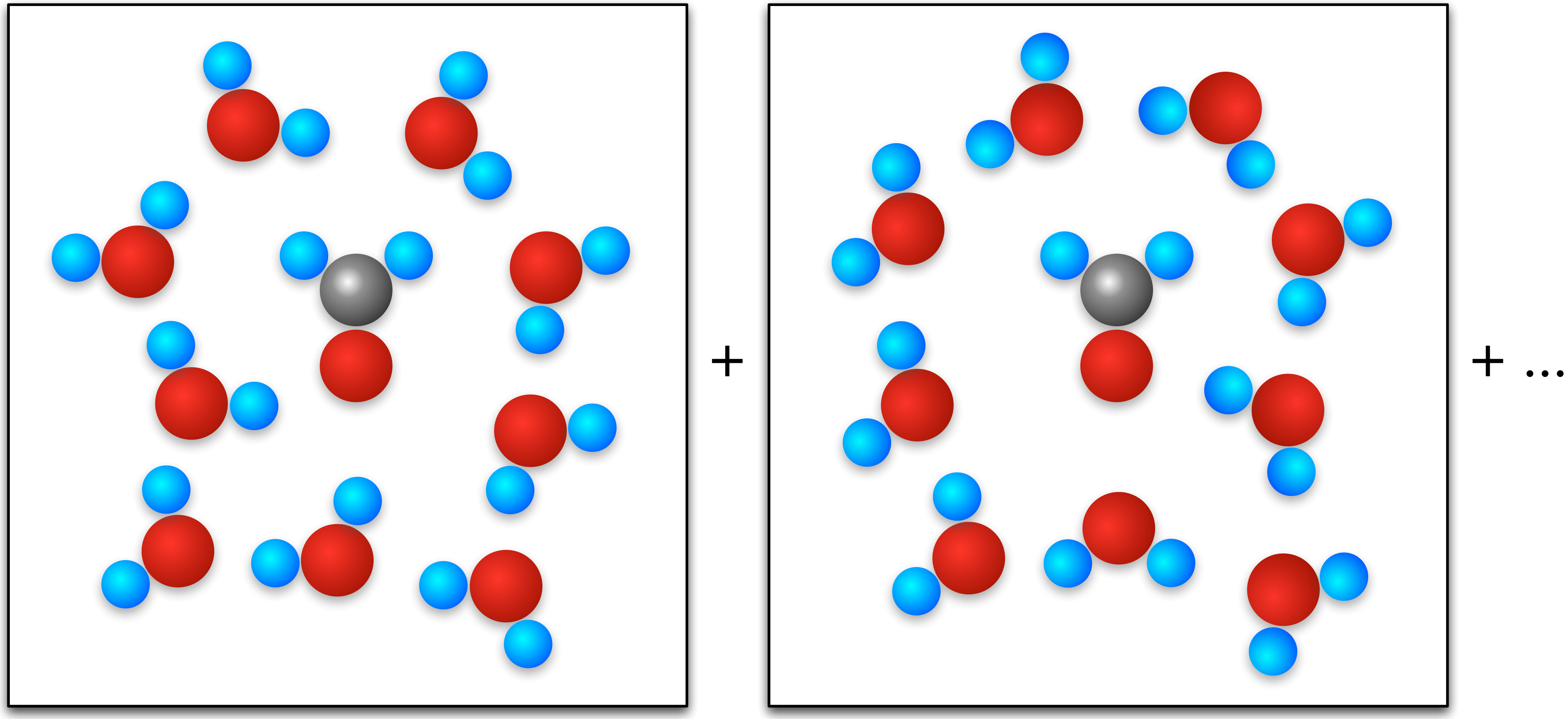
Why an Implicit Solvation Model?

Motivation

- Explicit solvation calculations require **many electrons** and **multiple nuclear configurations** of the solvent



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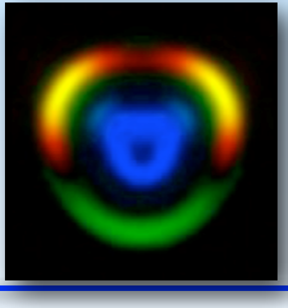
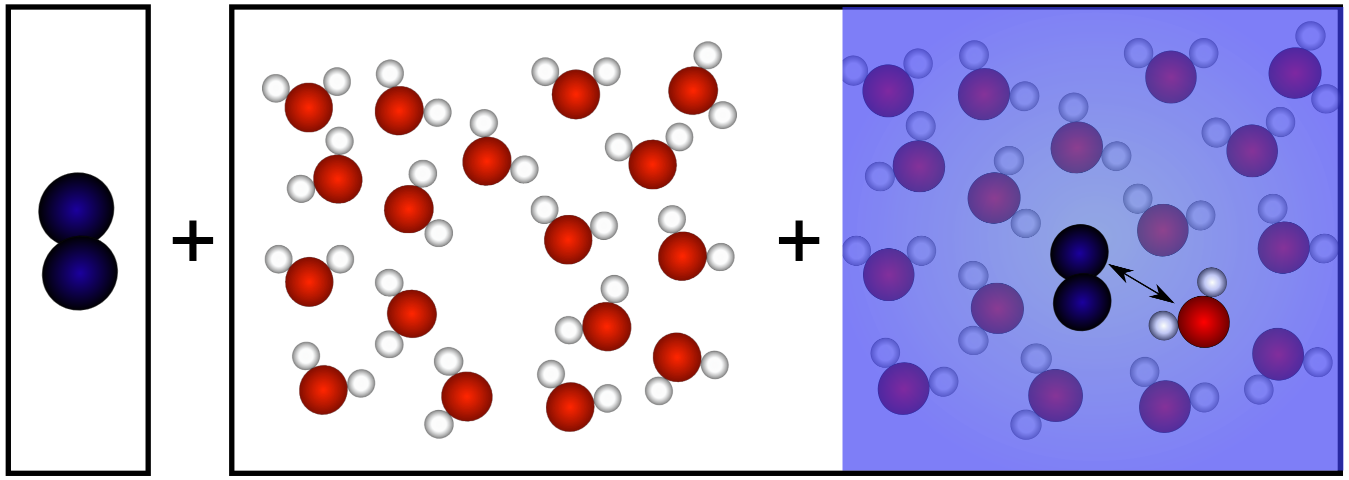
Joint Density Functional Theory



- Variational Principle of JDFT[1] - *A* is an exact free energy functional minimized by the fluid density N_α and electron density *n*

$$A[n,\{N_\alpha\}] = \underbrace{A_{\mathrm{HK}}[n]}_{\text{Electrons}} + \underbrace{\Omega_{\mathrm{lq}}[\{N_\alpha\}]}_{\text{Liquid}} + \underbrace{\Delta A[n,\{N_\alpha\}]}_{\text{Coupling}}$$



- The liquid and coupling terms are microscopically improvable
- Flexible, the model works with any electron basis set and can be used for surfaces and molecules

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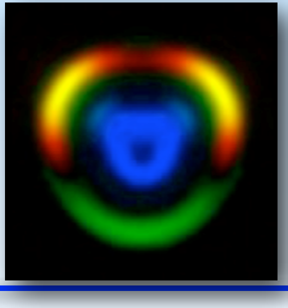
[1] S. Petrosyan, J.F. Briere, D. Roundy, and T. Arias, Phys. Rev B. 75, 205105 (2007)

Joint Density Functional Theory



- Combine terms related to the solvation into a single term

$$A[n,\{N_\alpha\}] = \underbrace{A_{\mathrm{HK}}[n]}_{\text{Electrons}} + \underbrace{\Omega_{\mathrm{lq}}[\{N_\alpha\}] + \Delta A[n,\{N_\alpha\}]}_{A_{\mathrm{solv}}}$$

solute electron density

average solvent site density

- Variational derivative with respect to the exact electron density *n*

$$\frac{\delta A}{\delta n} = \frac{\delta A_{\mathrm{HK}} + A_{\mathrm{env}}}{\delta n}$$

yields the usual Euler-Lagrange equation for the isolated electronic system with an **additional external potential**

$$V_{\mathrm{solv}}\left[n,\{N_\alpha\}\right] \equiv \left.\frac{\delta A_{\mathrm{solv}}\left[n,\{N_\alpha\}\right]}{\delta n}\right|_{N_\alpha}$$

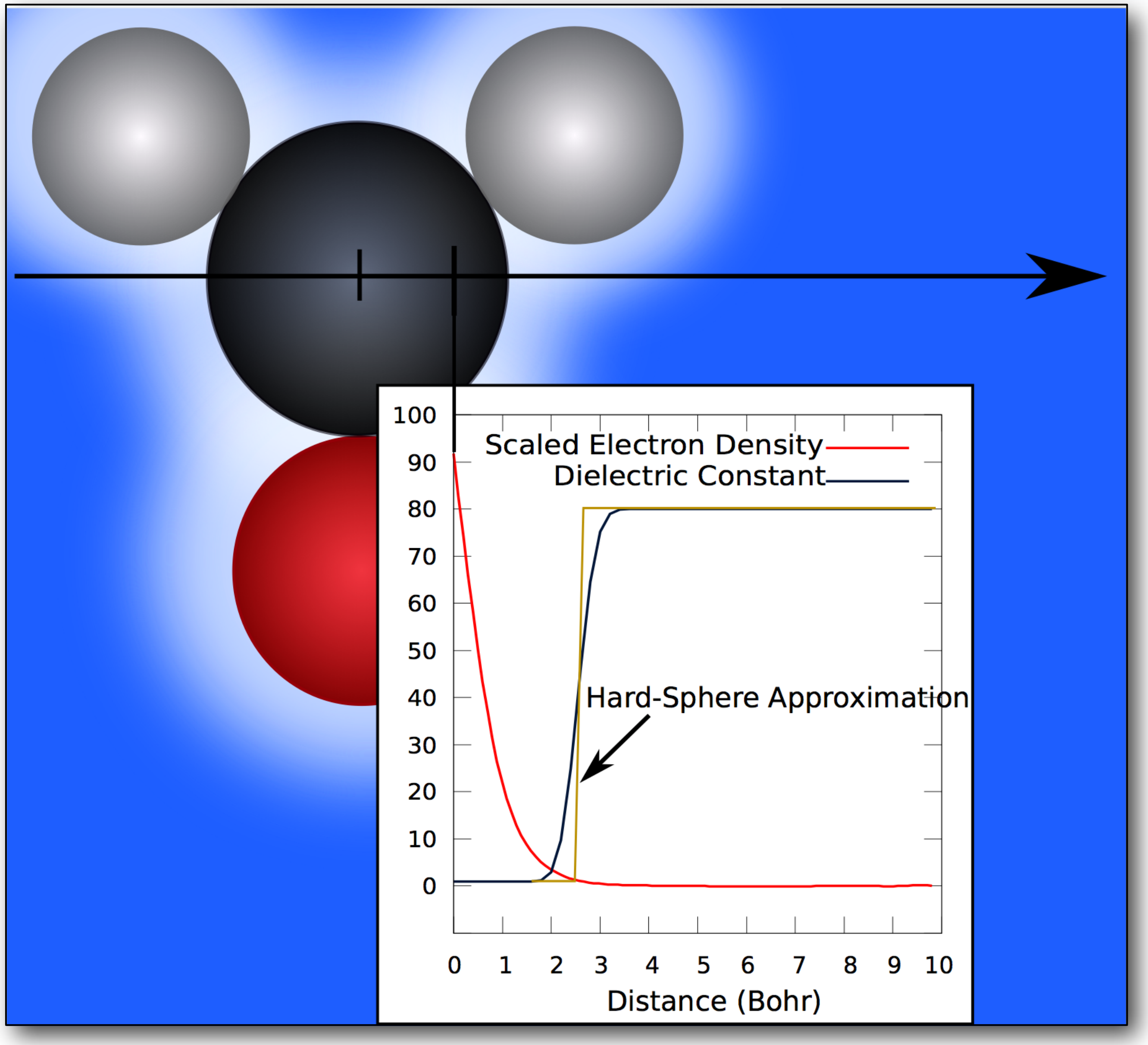
- Thermodynamic state of the system is given by **self-consistent solution** for which the electron density yields back the same potential

Simple Approximation for A_{env}

Linear dielectric continuum model

- Fluid and coupling modeled by dielectric continuum
- Dielectric constant determined by local electron density $n(r)$
- Switches smoothly from vacuum value at high density to value of liquid at low electron density
- Potential determined by modified Poisson equation

$$\boxed{\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi = -4\pi n(\mathbf{r})}$$



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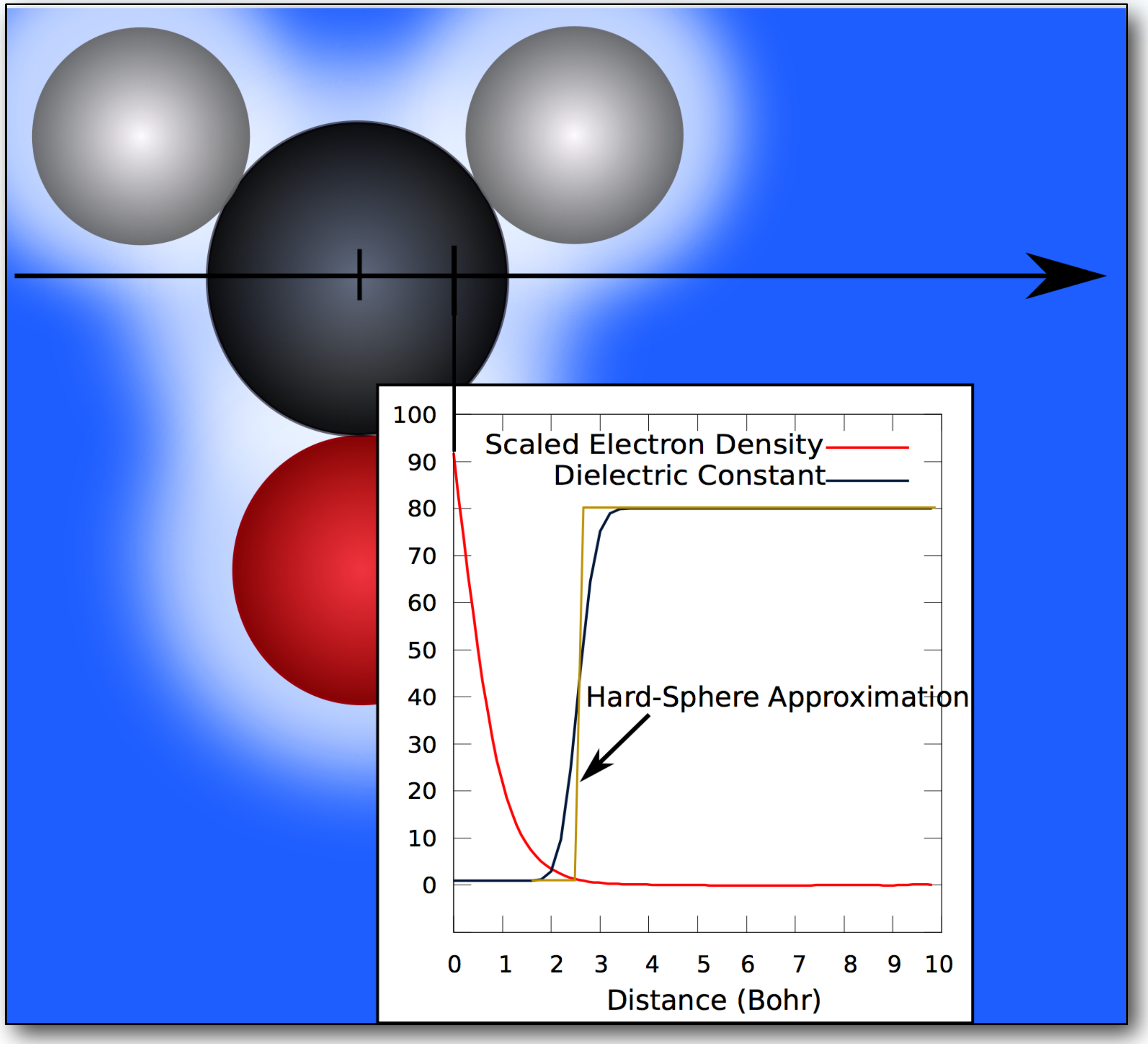
Linear Dielectric Continuum Model

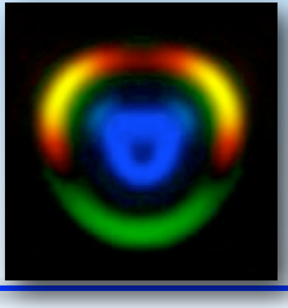
- Similar to Fattebert and Gygi,
  Int. J. Quantum Chem., 93, 139 (2003)
- Hard Sphere approximation by Amovilli, Filippi and Flores
  J. Chem. Phys. 129, 244106 (2008),
  J. Phys. Chem. B 110(51) (2006)



Advantages of our model

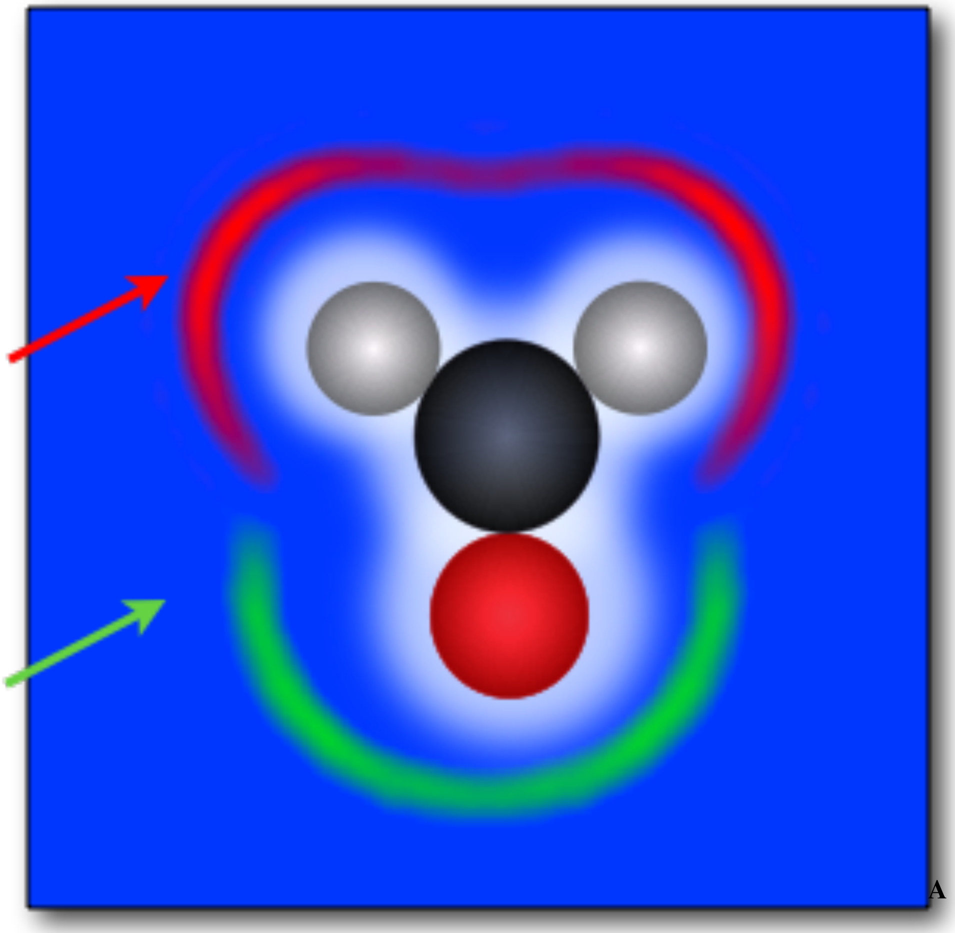
1) **Microscopically improvable:** Part of larger theoretical framework
2) **Ab initio:** Cavity forms itself from the electron density
3) **Flexible:** Model works with any electron basis set and can be used for surfaces and molecules

Linear Dielectric Continuum Model



Approximations

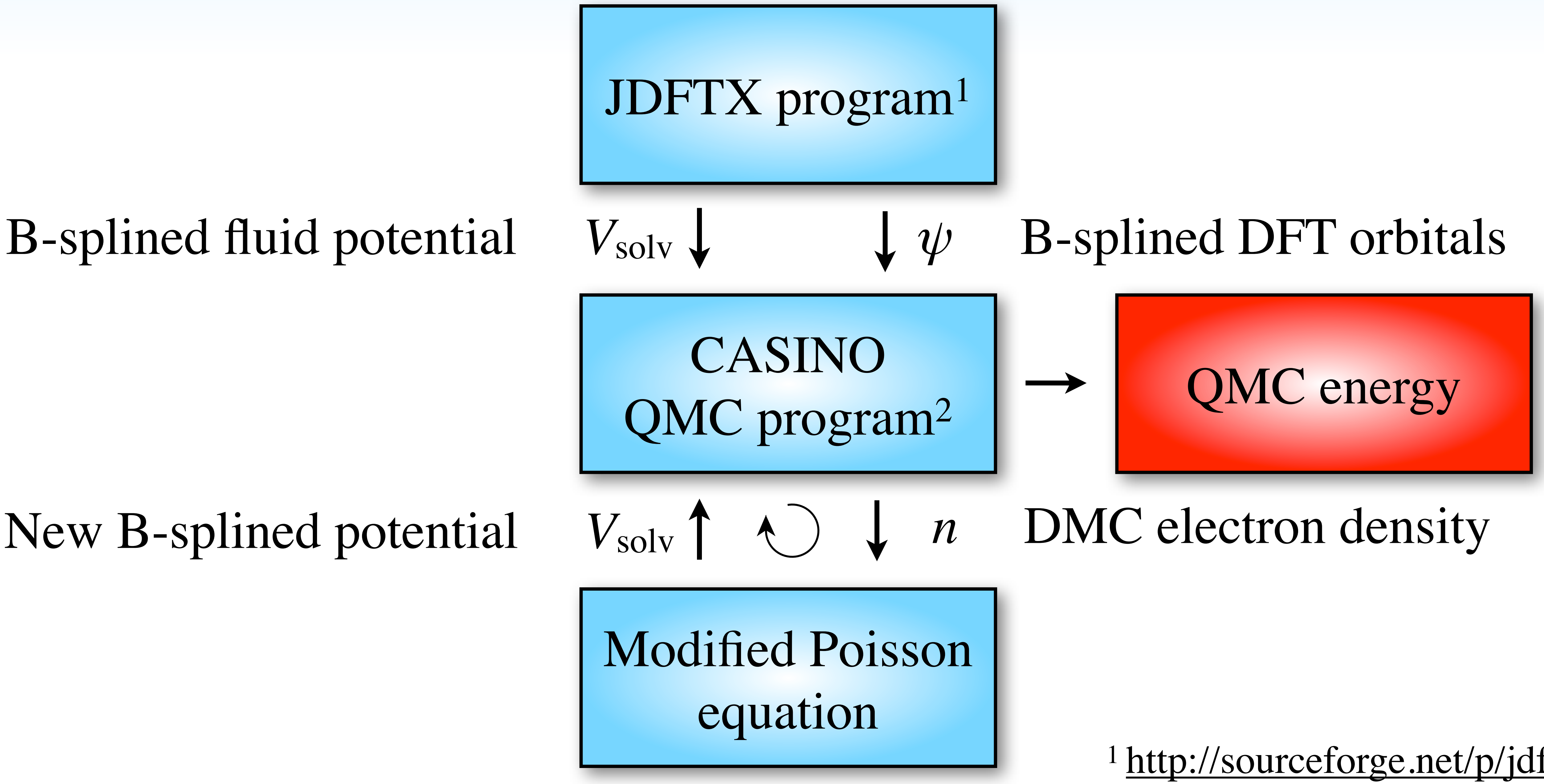
$$
\begin{aligned}
A_{\text{solv}}[n] &\equiv \min_{\{N_\alpha\}}\left(\underbrace{\Omega_{\text{lq}}[\{N_\alpha\}]}_{=0} + \Delta A[n,\{N_\alpha\}]\right)\\
&= \frac{1}{2}\int (n - N_\alpha)\left[\left(-\frac{\nabla\cdot\epsilon(n)\nabla}{4\pi}\right)^{-1} - \left(-\frac{\nabla^2}{4\pi}\right)^{-1}\right](n - N_\alpha)d^3r\\
V_{\text{solv}}[n] &= -\phi_{\text{Hartree}} + \phi + \mathcal{O}(10^{-2}) \approx \phi_{\text{bound}}
\end{aligned}
$$



Negative bound charge

Positive bound charge

Implementation



JDFTX program[1]

B-splined fluid potential $V_{\text{solv}} \downarrow$

$\downarrow \psi$ B-splined DFT orbitals

CASINO QMC program[2] → QMC energy

New B-splined potential $V_{\text{solv}} \uparrow$ ↻ $\downarrow n$ DMC electron density

Modified Poisson equation

[1] http://sourceforge.net/p/jdftx

[2] R. J. Needs *et al.*, Casino version 2.2 User Manual

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Zeroth-Order Estimate of Energy

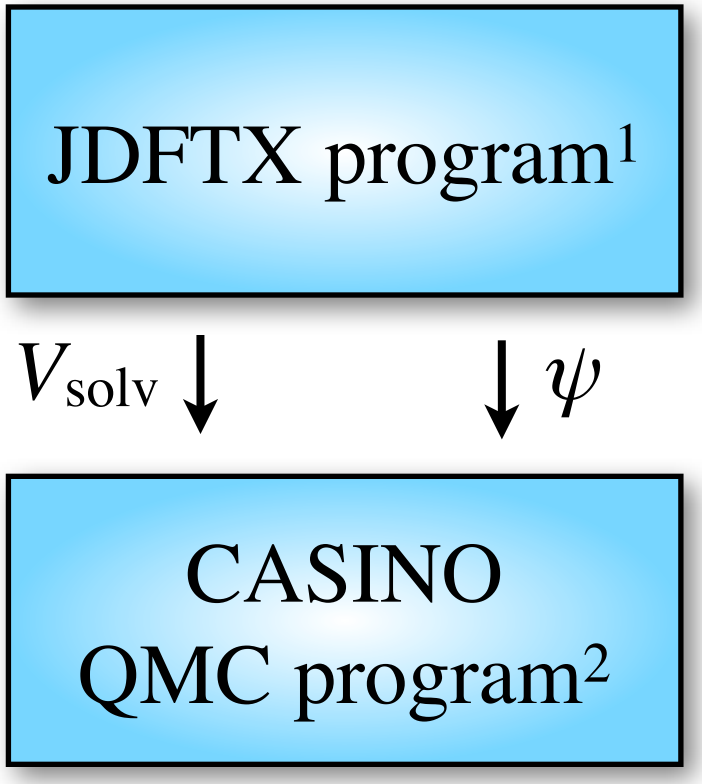
- Start from self-consistent JDFT calculation with LDA or GGA functional

$$V_{\text{solv}} = \frac{\delta A_{\text{solv}}[n_{\text{DFT}}]}{\delta n}$$

- Single QMC calculation of the solute within V_{sol}
  $\Rightarrow$ initial QMC density n_{QMC} and energy $A_{\text{QMC}}[n_{\text{QMC}}]$
- $A_{\text{QMC}}[n_{\text{QMC}}]$ is QMC estimate of functional A_{HK},
  energy of the solute *without* the energy associated with V_{sol}
- Zeroth order estimate of energy of solvated system

$$E = A_{\text{QMC}}[n_{\text{QMC}}] + A_{\text{env}}[n_{\text{DFT}}]$$

- Terms are not self-consistent, evaluated at different electron densities
- **No variational principle, error in energy is 1st order in density**

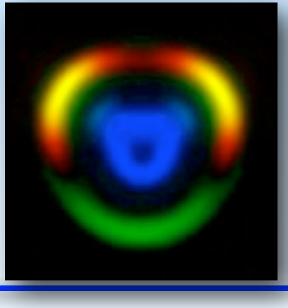


JDFTX program[1]

$V_{\text{solv}} \downarrow$ $\quad \downarrow \psi$

CASINO
QMC program[2]

First-Order Estimate of Energy



- Can correct the error in energy to second order in density by evaluating

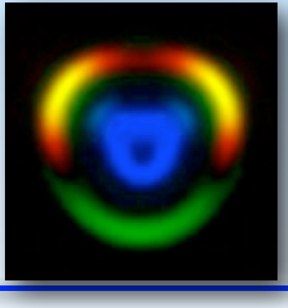
$$A_{\mathrm{solv}}[n_{\mathrm{QMC}}] = A_{\mathrm{env}}[n_{\mathrm{DFT}}] + \int V_{\mathrm{solv}}[n_{\mathrm{QMC}} - n_{\mathrm{DFT}}]\, d^3r$$

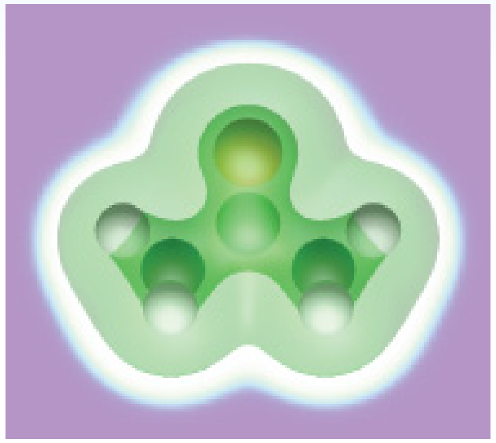
- Resulting energy estimate

$$E = A_{\mathrm{QMC}}[n_{\mathrm{QMC}}] + A_{\mathrm{env}}[n_{\mathrm{DFT}}] + \int V_{\mathrm{solv}}(r)\,[n_{\mathrm{QMC}}(r) - n_{\mathrm{DFT}}(r)]\, d^3r$$

- Errors are second order in *both* the difference between exact converged and DFT density *and* difference between exact and the first-iteration density
- In tests, this estimator is nearly as good as full self-consistency, but with the effort of only a single quantum Monte Carlo calculation

Application to Small Molecules

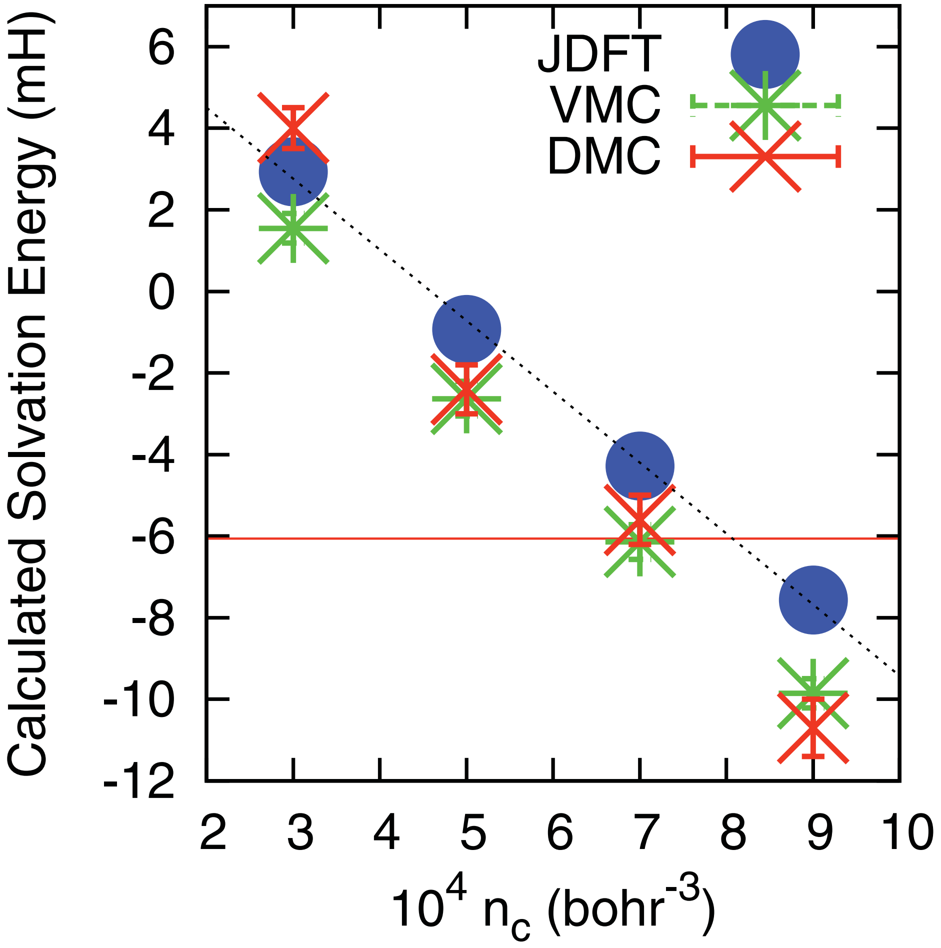




- Dielectric function contains 2 parameters σ and n_c

$$\epsilon[n(r)] = 1 + (\epsilon_b - 1)\,\mathrm{erfc}\left[\frac{1}{\sqrt{2}\sigma}\ln\left(\frac{n(r)}{n_c}\right)\right]$$

- Results not sensitive to σ, chose $\sigma = 0.6\ a_0$
- Dependence on n_c for acetone in water to select n_c
- VMC and DMC below DFT energies
- VMC energy without Jastrow factor (only exact exchange energy) close to DMC
- Primary corrections in solvation energy from exact treatment of the exchange
- Corrections to correlation beyond LDA largely cancel at least for acetone



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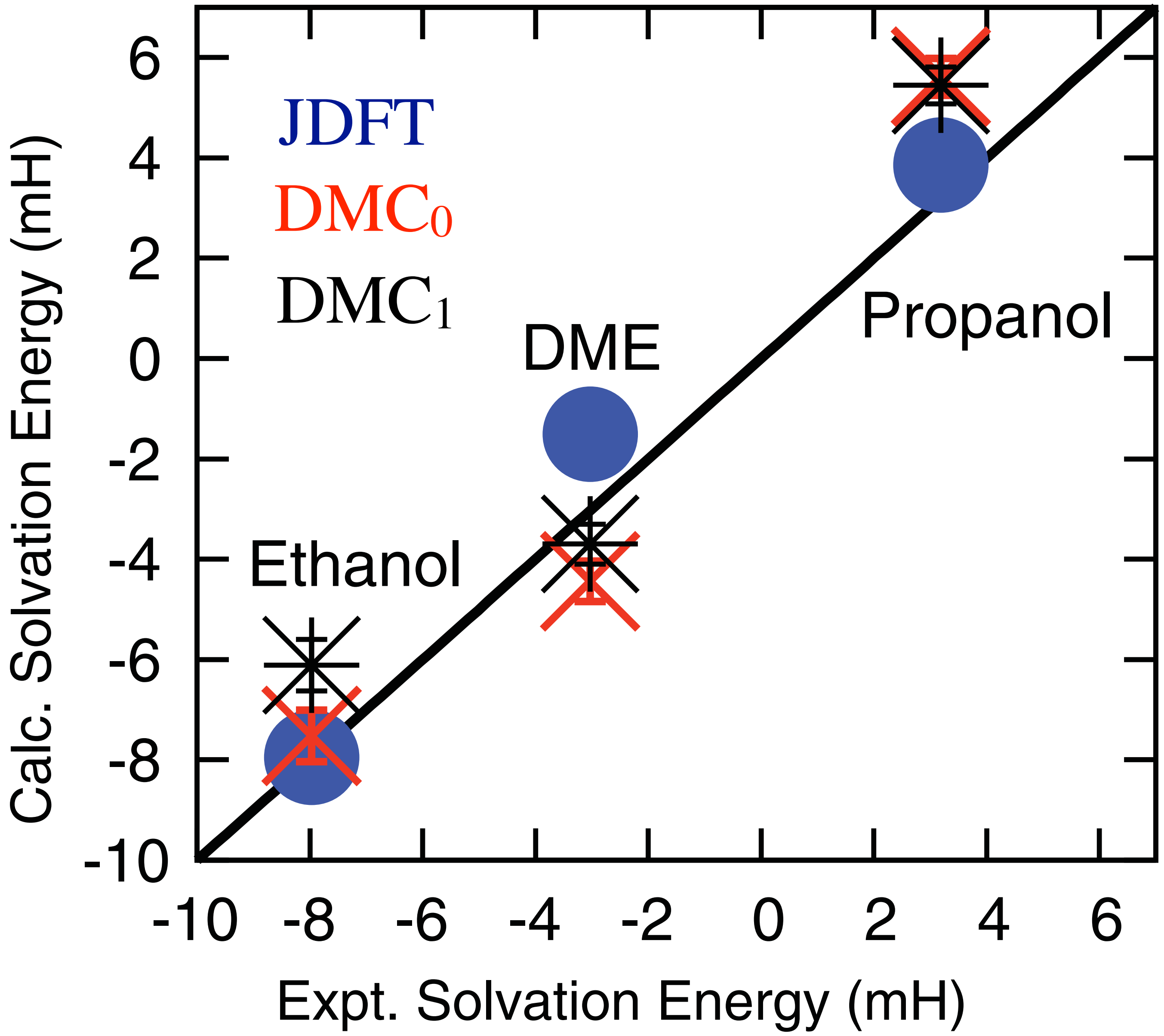
Application to Small Molecules

- Solvation energies for ethanol, dimethylether, and propanol in water
- Solvation energies include cavitation energy estimated from classical DFT



Agreement between QMC and experiment is encouraging given the simple fluid model

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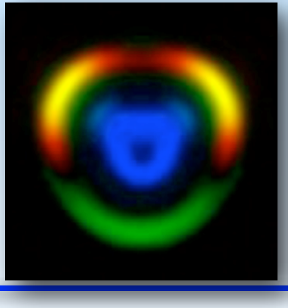
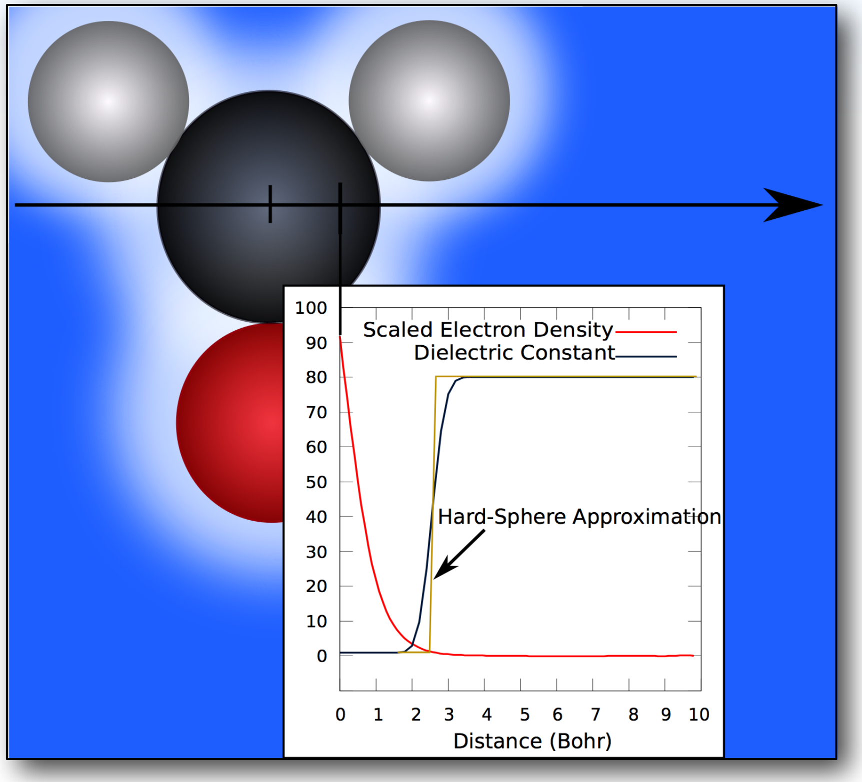
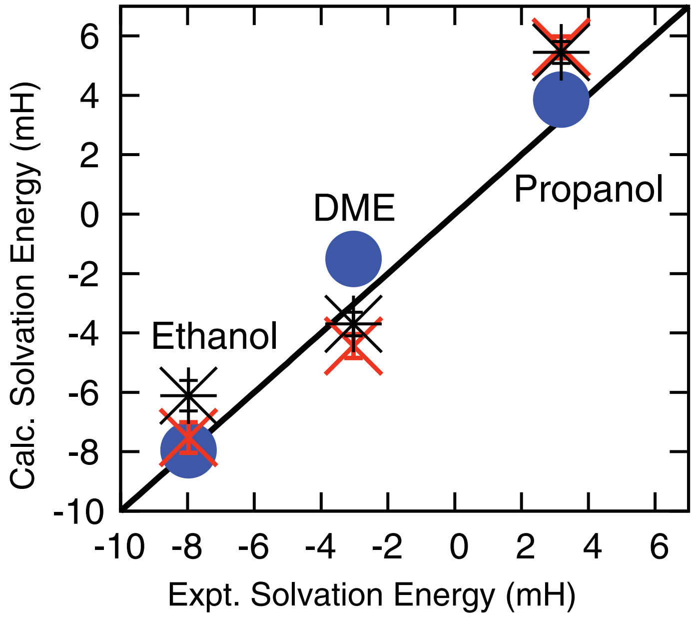
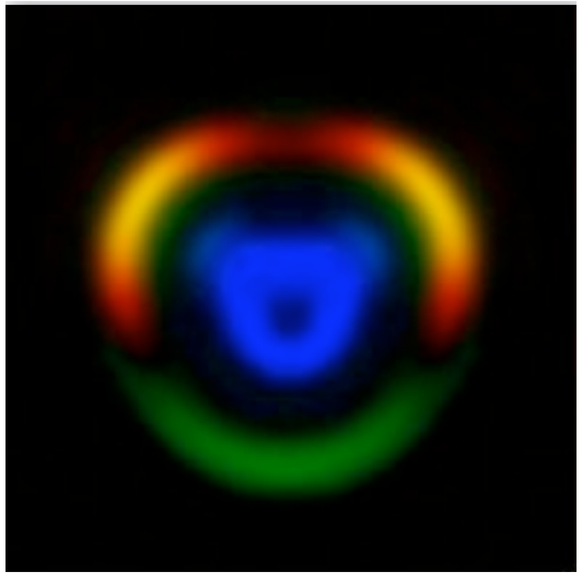
Summary of QMC Solvation Method

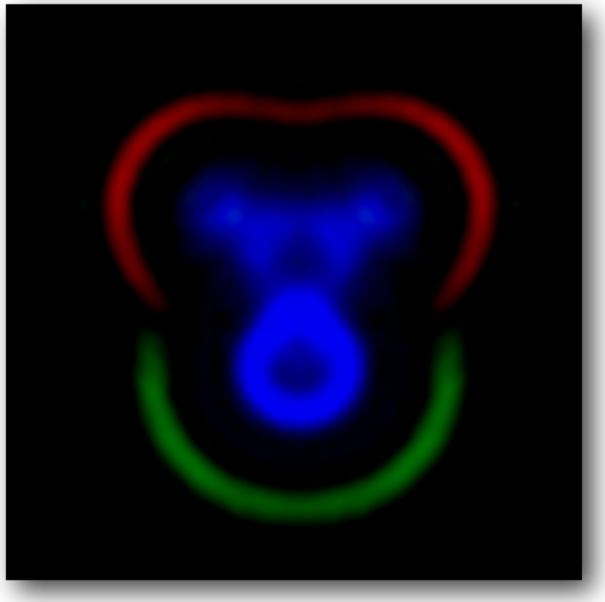


- Solvation of small molecules successfully described in QMC through use of external potential
- Method avoids need for phase space sampling of the fluid
- Accurate for molecules and promising for surfaces where QMC is needed









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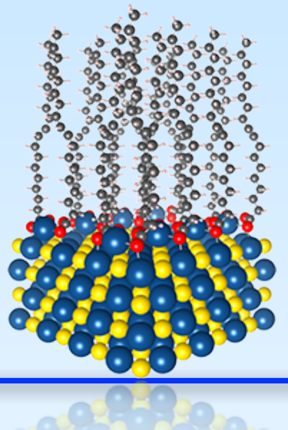
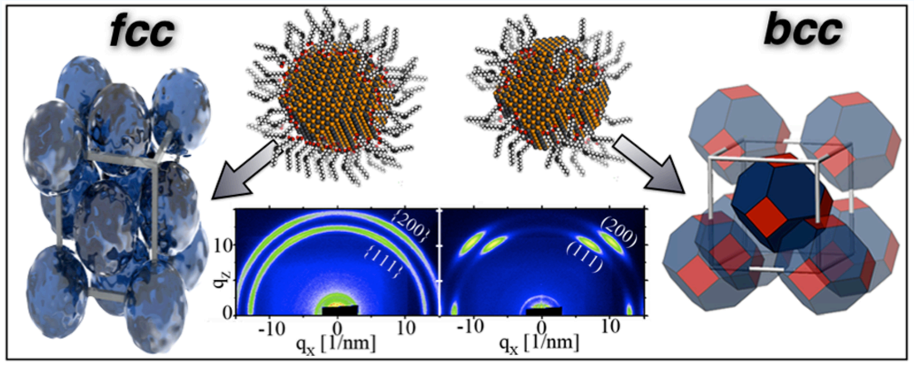
Control of Nanocrystal Morphology and Assembly and Quantum Monte Carlo Method for Solvation

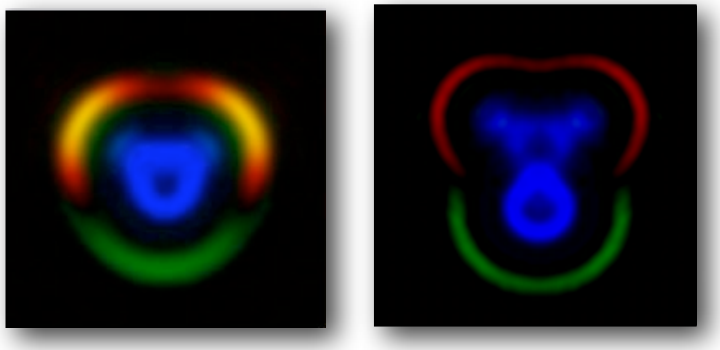
Richard G. Hennig, Cornell University



How can we predict the morphology and assembly of nanocrystals?
How can we include solvation effects in quantum Monte Carlo for molecules and surfaces?

- Shape control of ligand-stabilized nanocrystals core by modification of ligand coverage
- Anisotropic ligand coverage nanocrystals leads to anisotropy interactions and affects assembly
- Solvation can be included in QMC through external potential
- Successful for small molecules, promising for surfaces





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