Heidelberg Summer School
Applications: Extended Systems

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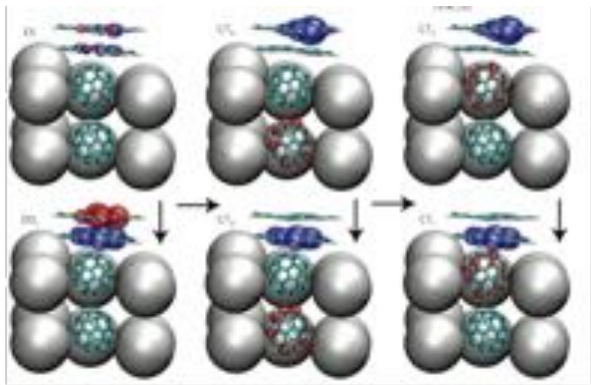
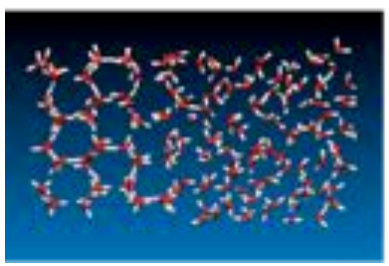
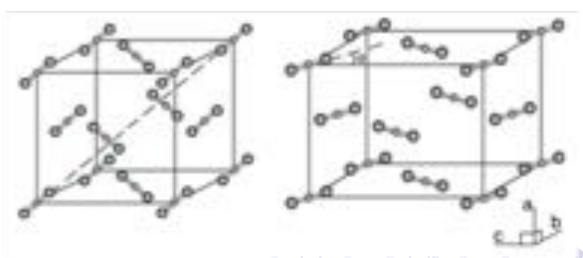
Extended Systems: What do I mean?

Macromolecules or molecular aggregates.

- Extended $\approx$ Extensive.
- Statistical fluctuations are often non-negligible, temperatures are important.
- Sometimes only qualitative accuracy is feasible







Outline

1. Survey of tools
2. A nibble of theory
3. Case studies (Crystals, Water)
4. Terra Incognita

Extended Systems Toolbox

- Linear scaling Gaussian SCF - to break bonds
- Linear scaling Plane-Wave DFT - cheap, infinite systems
- Ab-Initio Force Fields - high accuracy for MD
- Fragment Approaches - high accuracy for geometries
- Ab-initio Molecular Dynamics and Car-Parinello MD - reactive trajectories, disorder
- *The Leftovers:* Bethe-Salpeter, Density Matrix Renormalization Group, Quantum Monte Carlo for tough stuff.

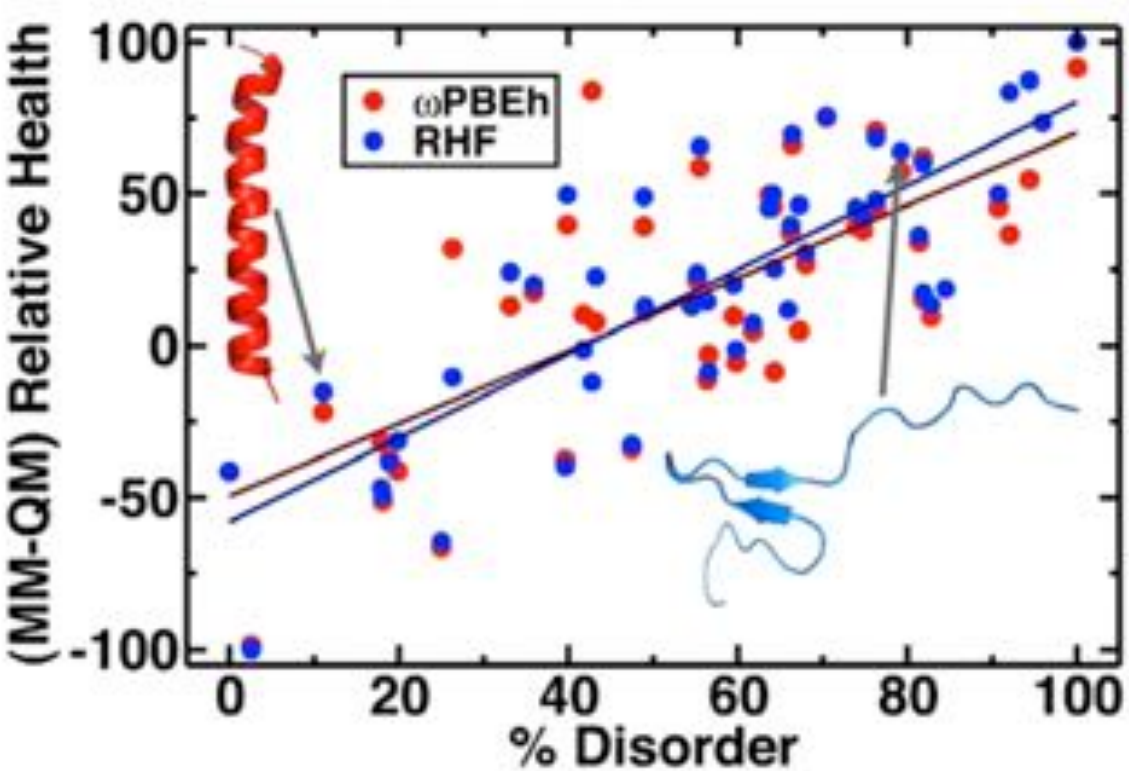
Free Tools for Your Reference

Free Extended Codes:

- Linear scaling Gaussian Basis SCF: Firefly, NWCHEM
- Linear scaling Plane-Wave DFT: ESPRESSO, NWCHEM, CP2K...
- Ab-Initio Force Fields: ForceBalance
- AIMD: CP2K, CPMD
- Excited States: YAMBO, BerkeleyGW

Linear Scaling SCF

SCF (6-31g*) optimized proteins are similar to AMBER when the protein has disorder... sometimes worse but is RHF better than ωPBEh? [1]



[1] Ab Initio Quantum Chemistry for Protein Structures,Heather J. Kulik Nathan Luehr, Ivan S. Ufimtsev, and Todd J. Martinez 2012.

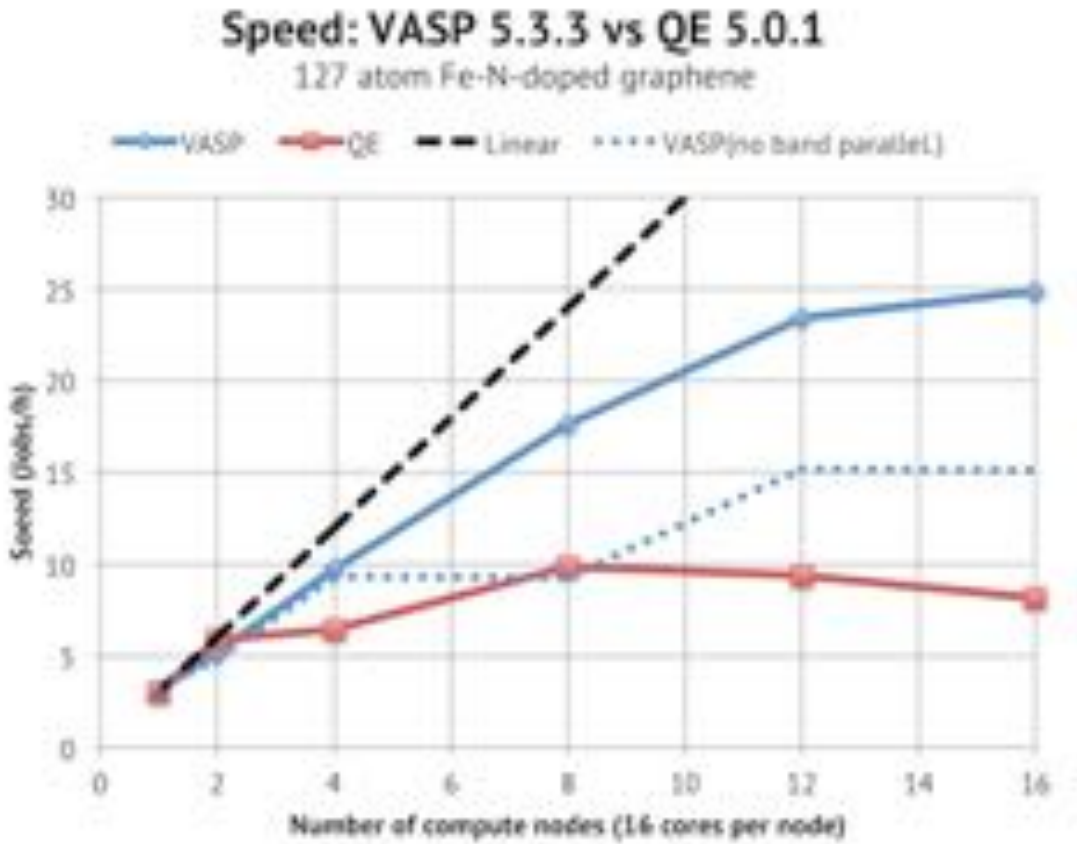
Correlation is not clearly the bottleneck

TABLE II. Wall times and scaling behavior with respect to the number of basis functions for SOS-RI-AO-MP2 calculations on linear alkanes in a def2-SVP and def2-TZVP basis on a computing node with two Intel Xeon E5-2620 processors (12 CPU cores) and four Nvidia GeForce GTX Titan GPUs. Timings and scaling exponents [$\mathcal{O}(N^x)$] are given for the whole calculation as well as selected steps of the algorithm defined in Table I.

def2 – SVP	# Basis	Total		Transformation (5)		Contraction (6) on GPU		Steps (1)–(4), (7), (8)	
system	functions	time [s]	$\mathcal{O}(N^x)$	time [s]	$\mathcal{O}(N^x)$	time [s]	$\mathcal{O}(N^x)$	time [s]	$\mathcal{O}(N^x)$
$C_{20}H_{42}$	490	98	...	51	...	39	...	8	...
$C_{40}H_{82}$	970	575	2.59	374	2.92	171	2.16	30	1.94
$C_{80}H_{162}$	1930	2248	1.98	1051	1.50	1048	2.64	149	2.33
$C_{160}H_{322}$	3850	14 134	2.66	6206	2.57	7127	2.78	801	2.44
$C_{320}H_{642}$	7690	95 765	2.77	33 881	2.45	56 358	2.99	5526	2.79
def2 – TZVP	# Basis	Total		Transformation (5)		Contraction (6) on GPU		Steps (1)–(4), (7), (8)	
system	functions	time [s]	$\mathcal{O}(N^x)$	time [s]	$\mathcal{O}(N^x)$	time [s]	$\mathcal{O}(N^x)$	time [s]	$\mathcal{O}(N^x)$
$C_{20}H_{42}$	872	406	...	261	...	120	...	25	...
$C_{40}H_{82}$	1732	1831	2.19	932	1.85	784	2.74	115	2.22
$C_{80}H_{162}$	3452	11 800	2.70	5790	2.65	5445	2.81	565	2.31

Linear Scaling SCF

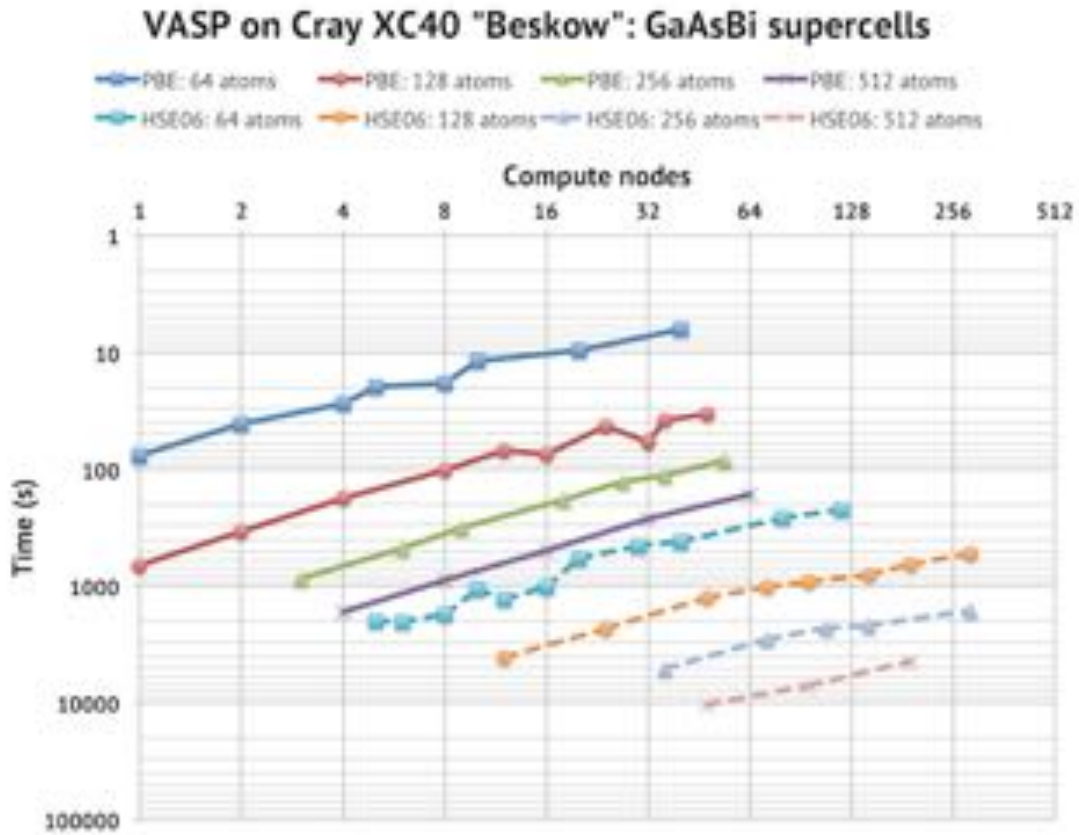
The main advantages of Gaussian basis SCF are core electrons, accuracy and exchange. However it is very difficult to parallelize and reach linear scaling, which only occurs with roughly more than 60 atoms. Plane wave DFT is linear scaling on small clusters.[2]



[2] Peter Larsson's blog

Linear Scaling SCF

Where these plots end, the parallel efficiency is lower than 50 percent, ie: these are max parallelizations you can get in 2015. Larger cells parallelize better. [3]



[3] Peter Larsson's blog

2015 Limitations.

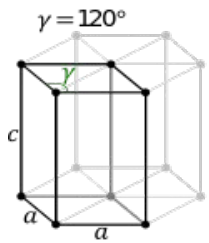
Very rough qualitative expectations:

What can be done:

- ∼500 atoms (total or unit cell) and you can run SCF several times qualitatively in a few weeks with PWSCF and many nodes
- For less than 200 atoms, a fast gaussian code may be a better option on one or two nodes.

Basic Periodic DFT: Bravais Lattices and Unit Cells.

- *Bravais lattice* - A set of points spread over space by discrete translations.
- $p_i = n_a\vec{a} + n_b\vec{b} + n_c\vec{c}$. Where n_i is an integer.
- The vectors are the edges of distorted cubes 'unit cells' that divide space.
- In 3d there are seven lattice systems with different symmetries, for applications purposes you only need to understand that these lattices have symbols and can be determined by crystallography.



Basic Periodic DFT: Bloch's theorem

- Periodic extended materials have unit cells containing one or more nuclei.
- Bloch theorem: The eigenfunctions of periodic potentials have the form: $\psi(\vec{r})_{n,k} = e^{i\vec{k}\cdot\vec{r}} \cdot u_{nk}(\vec{r})$. Where u has the translational symmetry of the unit cell:
- $u(\vec{r}) = u(\vec{r} + \vec{R})$, where $\vec{R}$ is any integer linear combination of lattice vectors. Thus $u(r)$ must only be known/stored within the unit cell.
- Obviously there are fewer atoms in the unit cell than the whole crystal, and so periodic DFT is efficient.
- There are also no 'edge effects' that would be caused by an aperiodic cluster model.

Basic Periodic DFT: G-vectors

- Within the unit cell $u_{nk}(\vec{r})$ is written as a linear combination of plane-waves: $u_{nk}(\vec{r}) = \sum_G u_{G,k} e^{iG\vec{r}}$, with G's chosen on a regular grid.
- The G-grid's lattice is the Fourier transform of the Bravais lattice (the *reciprocal lattice*).

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}} \therefore e^{i\mathbf{K}\cdot\mathbf{r}} e^{i\mathbf{K}\cdot\mathbf{R}} = e^{i\mathbf{K}\cdot\mathbf{r}} \Rightarrow e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \qquad (1)$$

Basic Periodic DFT: G-vectors

- The kinetic energy of a Bloch wave $\propto (k+G)^2$
- The magnitude of $u_{G,k}$ in a ground state decreases rapidly with energy.
- The dimension of PW basis is controlled by assuming $u_{G,k} = 0$ for waves above E_{cutoff}.
- E_{cutoff} implies a limit on the real-space resolution on ψ.
- Typically the cutoff is insufficient to resolve the shape of core orbitals.
- **good cancellation of errors requires that this remain constant within a model.**

Plane Waves are Efficient

For a system larger than Taxol, Plane-Wave integrals are much faster than a Gaussian basis. Q-Chem actually uses plane-waves for large systems, but saves the density in an atomic basis...

Table 1-3. Timings and energies for taxol, $C_{47}H_{51}NO_{14}$. See Table 1-1 for explanation

	6-31G(d,p)-dc (NBF = 1,484)		6-311G(2df,2pd)-dc (NBF = 2,860)	
Basis set	FTC	ERI	FTC	ERI
Coulomb	39.56	255.02	127.78	3,038.50
XC	34.42	56.04	126.19	140.85
Matrix	6.45	5.75	41.49	27.70
Total	80.50	317.00	295.68	3,208.27
Energy + 2,928	−0.615108	−0.615114	−1.442401	−1.442376

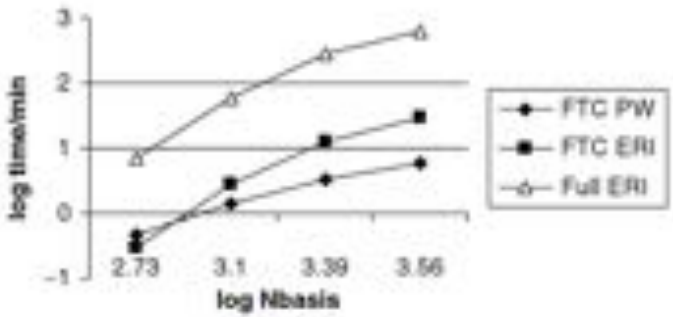


Figure 1-1. The scaling of the Coulomb time with respect to molecular size for a series of polyalanines, $n = 2-15$. FTC PW means the plane wave component of the FTC calculation (diffuse densities). FTC

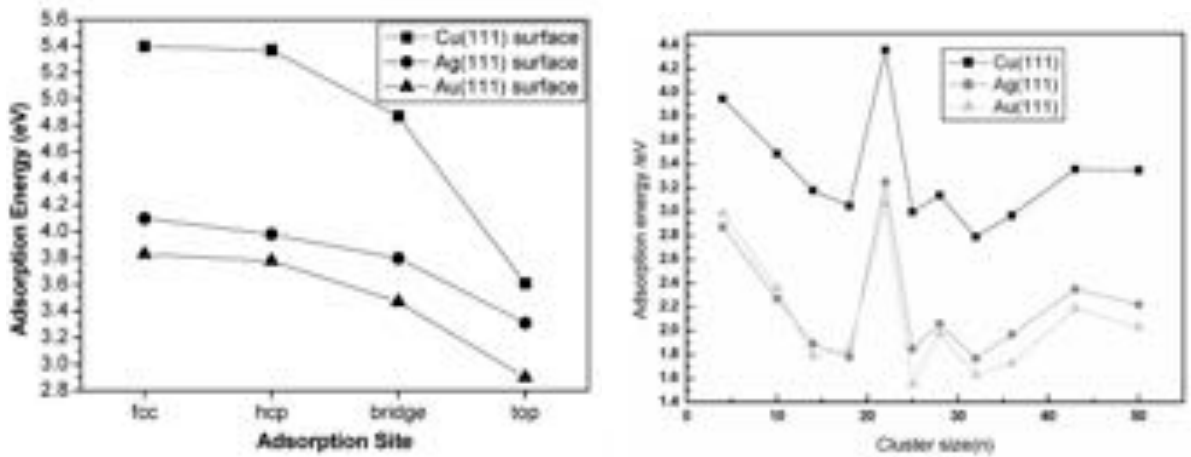
[4]

[4] P. Pulay '90's

Periodic DFT is Efficient

- Good speedups for typical 2-4 node parallel jobs. Dozens of metal atoms can be routinely treated.
- Free Packages (PW): Quantum Espresso, CP2K, CPMD + others.
- UnFree Packages: VASP, Siesta, FHI-AIMS (both periodic/aperiodic), Crystal, + others.

Periodic vs. APeriodic DFT



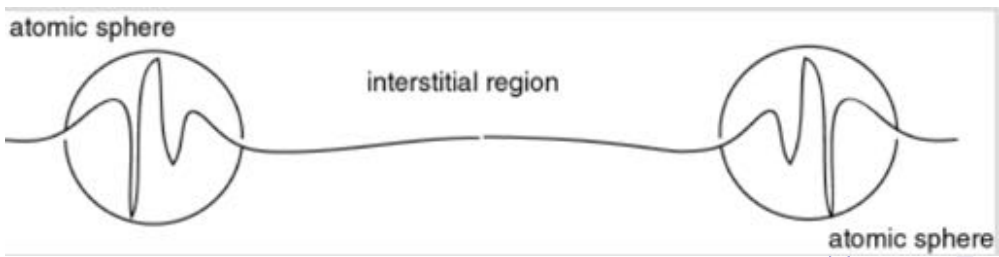
Nitrogen atom adsorption on metal surfaces. Even periodic calculations of aperiodic cluster models are qualitatively similar but quantitatively different. [5]

[5] Gui-Chang Wang, Ling Jiang, Xian-Yong Pang, and Junji Nakamura, J. Phys. Chem. B 2005, 109, 17943-17950

Periodic DFT: Pseudopotentials.

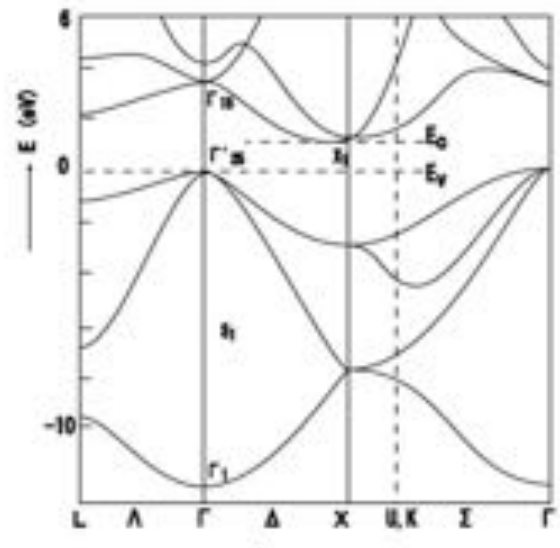
To converge PW grids for atoms would require intractable numbers of coefficients, so these calculations instead invoke *pseudopotentials* (PP) which replace core electrons with an effective potential.

- This results in accurate relative energies for low E_{cutoff}.
- PP come in many flavors (Norm-Conserving are theoretically more satisfying, Ultrasoft are cheaper.)
- PP can be calculated by most periodic codes for atomic references configurations, often determining your own for your application is good due-diligence.
- To have core properties Projector Augmented Wave (PAW) code must be used (VASP, Quantum Espresso)



Basic Periodic DFT: k-vectors

- Besides the Energy cutoff, several k-vectors must be sampled to obtain accurate wavefunctions.
- G-vectors represent the fine structure of the wavefunction within the cell, and k-vectors represent the slow variations between cells.
- 4x4x4 k-point sampling is a good rudimentary model for insulating systems. In metals and small unit cells many more may be required, and this number should be in-principle be converged.



An Example PWscf (ESPRESSO) input

```
&control
  calculation = 'scf',
  prefix = 'Si_exc1',
/
&system
  ibrav =  2,
  celldm(1) = 10.26,
  nat =  2,
  ntyp = 1,
  ecutwfc = 20
/
&electrons
  mixing_beta = 0.7
/
ATOMIC_SPECIES
 Si 28.086  Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
 Si 0.0 0.0 0.0
 Si 0.25 0.25 0.25
K_POINTS (automatic)
 6 6 6 1 1 1
```

Convergence of PW.

Table 1. Calculated Hartree-Fock Pseudo-Energy E_{HF}^{ps} Per Li-H Pair in LiH Crystal as Function of Plane-Wave Cut-Off Energy E_{cut} and Monkhorst-Pack k-Points Grid.

E_{cut} (E_h)	k-pts	E_{HF}^{ps} (E_h)
125	4 × 4 × 4	−0.829911
125	5 × 5 × 5	−0.829877
125	6 × 6 × 6	−0.829873
150	4 × 4 × 4	−0.829912

Results are for lattice parameter $a_0 = 4.084$ Å.

6

[6] M. J. Gillan, D. Alfe, S. De Gironcoli, F. R. Manby, High-Precision Calculation of Hartree-Fock Energy of Crystals, JCC 2008

Convergence of PW.

Table 5. HF Pseudo-Formation Energies (E_h units) of Li-H Clusters Obtained from Molpro With Different Decontracted Dunning Basis Sets, and Values Obtained by Extrapolation to Basis-Set Limit.

	Molpro				
Cluster	VTZ	VQZ	V5Z	V∞Z	PWSCF
1 × 1 × 2	−0.038942	−0.039354	−0.039441	−0.039464	−0.03943
1 × 2 × 2	−0.162266	−0.163057	−0.163210	−0.163247	−0.16318
1 × 2 × 3	−0.271008	−0.272150	−0.272347	−0.272388	–
1 × 2 × 4	−0.384287	−0.385766	−0.386011	−0.386060	−0.38629
1 × 2 × 5	−0.495737	−0.497572	−0.497869	−0.497926	–
1 × 2 × 6	−0.608092	−0.610285	−0.610637	−0.610704	–
1 × 2 × 7	−0.719907	−0.722457	−0.722865	−0.722943	–
1 × 2 × 8	−0.832060	−0.834970	−0.835434	−0.835522	−0.83586
1 × 3 × 4	−0.607733	−0.609951	−0.610309	−0.610378	–
1 × 4 × 4	−0.848890	−0.851825	−0.852298	−0.852389	−0.85262
2 × 2 × 2	−0.413537	−0.415051	−0.415349	−0.415422	−0.41545
2 × 2 × 3	−0.653911	−0.656175	−0.656591	−0.656685	–
2 × 2 × 4	−0.896014	−0.899000	−0.899537	−0.899655	−0.89984

[7]

[7] M. J. Gillan, D. Alfe, S. De Gironcoli, F. R. Manby, High-Precision Calculation of Hartree-Fock Energy of Crystals, JCC 2008

Crystal Structure Prediction

- Target:
  E_{QC} + ZPVE + (Rovibrational Enthalpy and Entropy)(T)
- Stillinger[8]: The number of local geometrical minima n_s in a system of N atoms divided into M unit cells goes as:

$$n_s(N) \sim e^{\alpha N} \tag{2}$$

Where α is a constant. The goal of crystal structure prediction is to predict the crystal geometry of lowest free-energy (with an accuracy $\sim k_b T \sim 0.001$Hartrees).

[8] F. H. Stillinger, Phys. Rev. E 59, 48 (1999).

Checkup

Somebody tell me...

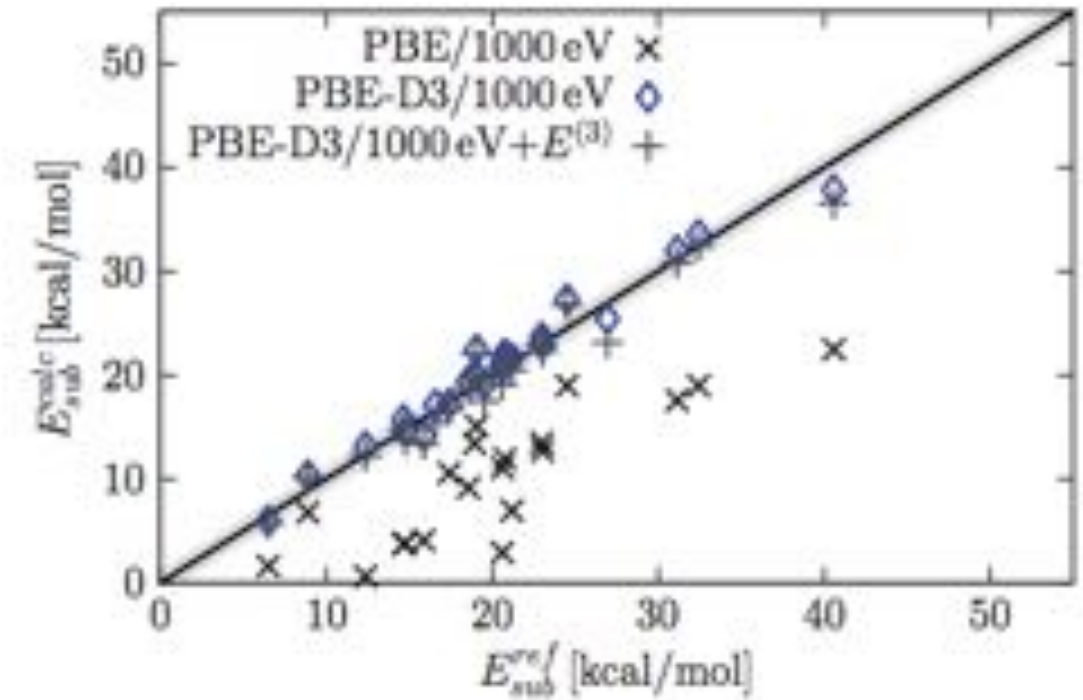
- What is a Hybrid Functional? Which of these are?
- PBE, BLYP, B3LYP, CAMB3LYP, $\omega B97$, PBE0, HSE.

Exchange in Solids

- The Hartree-Fock Exchange is much more costly than Coulomb, and also actually 'screened' in semiconducting solids.
- This cost is due to the integrable divergence of the Exchange kernel.[9]
- GGA Functionals (PBE/BLYP) are common in solids because exchange makes calculations comparable in cost to local-basis quantum chemistry. However these functionals are not as reliable as hybrids (PBE0, B3LYP,HSE)

[9] Self-consistent Hartree-Fock and screened-exchange calculations in solids: Application to silicon. F. Gygi and A. Baldereschi .Phys. Rev. B 34, 4405

PWDFT alone cannot predict crystal cohesion.



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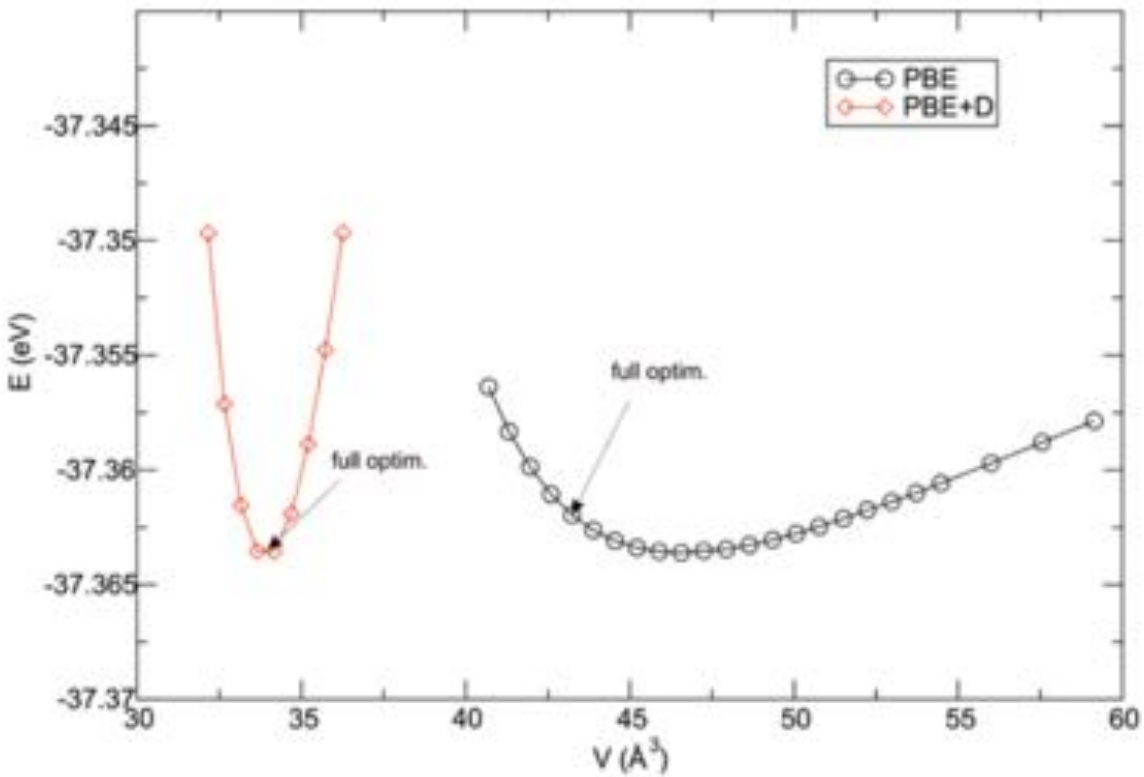
[10] Evernk and Aspuru-Guzik 2012

Beyond Periodic DFT.

- 'Bare' DFT completely misses dispersive interactions,
- Promising Extensions include: DFT-D, MBD, RPA.

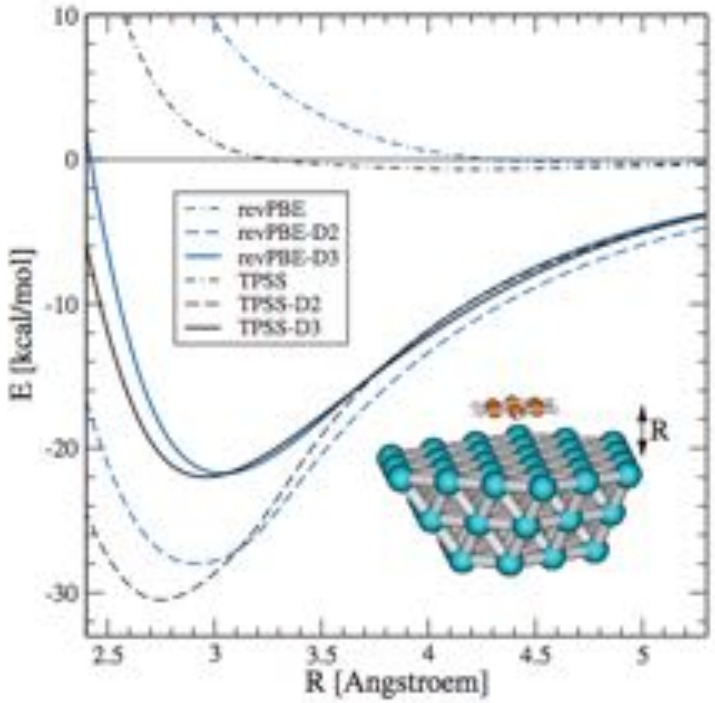


[11]

[11] Energy of graphite vs. V. - Janos G. Angyan J. Phys. Chem. A 2010, 114, 11814-11824

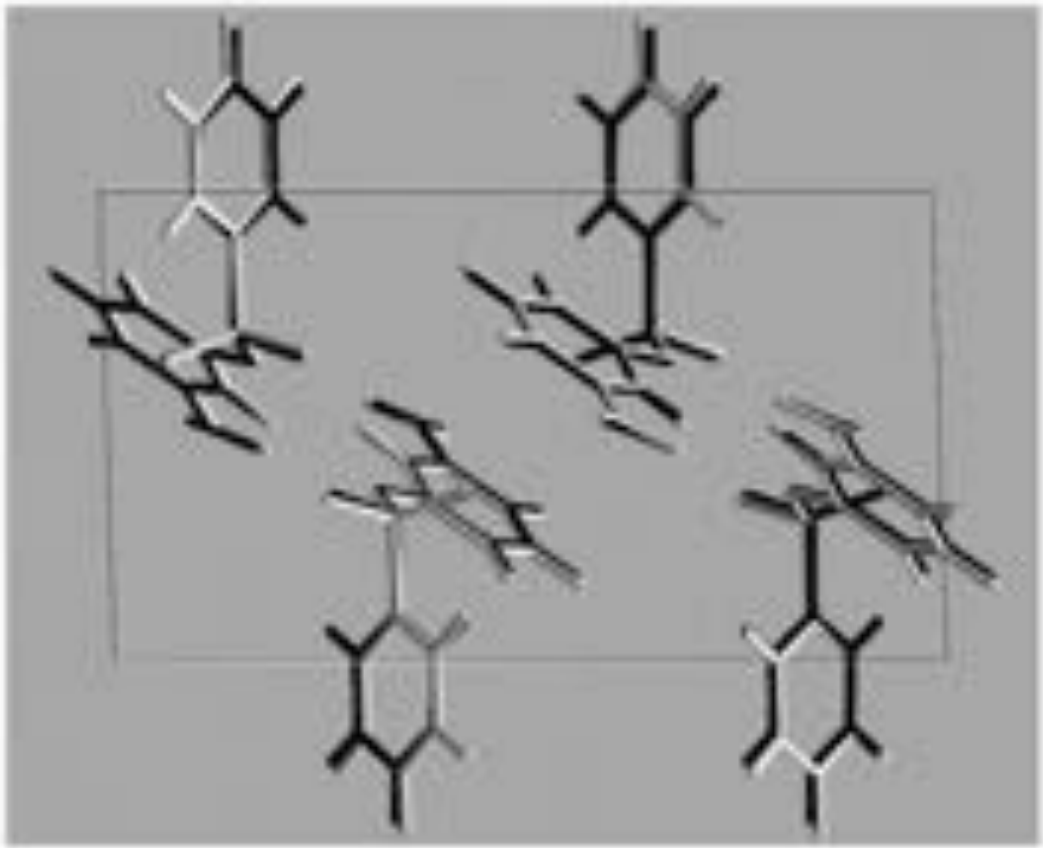
DFT-D

- Adds MM-style dispersion energy back into the molecular energy.
- $E = E_{\mathrm{DFT}} - \sum_{\mathrm{Atoms}} \frac{C^{AB}}{r^6} * \text{'damp'}$ [12]



[12] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg, The Journal Of Chemical Physics (2010)

Performance of DFT-D, Sulfonimide



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[13] H. C. Stephen Chan, John Kendrick, and Frank J. J. Leusen, Angew. Chem. Int. Ed. 2011, 50, 2979 ⊠2981

Performance of DFT-D, Sulfonimide

14

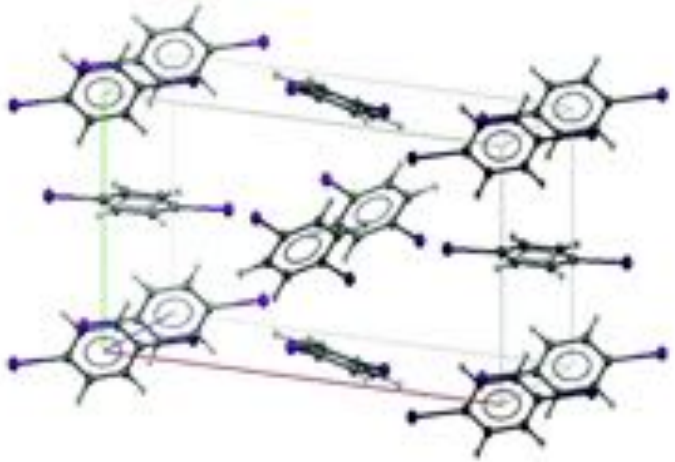
Table 1: The ten most stable predicted structures compared to the three experimental polymorphs.

CSP ranking		$\Delta E_{DFT(d)}$ [a] [kJ mol^{-1}]	Density [g cm^{-3}]	Z' [b]	Space group	Unit cell parameters [c]				RMSD [d] [Å]	HB [e]
DFT(d) rank	TMFF rank					a [Å]	b [Å]	c [Å]	β [°]		
form I [f]			1.464	1	$P2_1/c$	8.48	8.96	14.89	91.86		1D
1	1	0.000	1.452	1	$P2_1/c$	8.54	9.00	14.84	92.10	0.113	1D
form III [g]			1.452	1	*Pbca*	10.62	9.32	23.06	90.00		1D
2	20	0.887	1.428	1	*Pbca*	10.59	9.32	23.50	90.00	0.093	1D
form II [h]			1.463	2	$P2_1/c$	12.11	10.79	17.46	97.32		2D
3	140	0.911	1.471	2	$P2_1/c$	12.11	10.78	17.41	97.96	0.091	2D
4	18	1.144	1.417	2	$P2_1/c$	23.84	10.61	9.30	83.50		1D
5	21	1.357	1.438	2	*Pbca*	10.60	9.31	46.72	90.00		1D
6	2	1.362	1.445	1	$P2_1/c$	11.70	10.61	9.24	87.45		1D
7	5	1.524	1.425	2	*Pbca*	10.62	9.26	47.26	90.00		1D
8	16	1.679	1.408	1	*Pbca*	10.62	9.28	23.85	90.00		1D
9	17	1.726	1.428	2	*Pbca*	10.60	9.33	46.88	90.00		1D
10	111	1.820	1.436	2	$P2_1/c$	14.17	10.98	17.79	56.45		2D

[14] H. C. Stephen Chan, John Kendrick, and Frank J. J. Leusen, Angew. Chem. Int. Ed. 2011, 50, 2979-2981

Not all DFT-D's are created equal

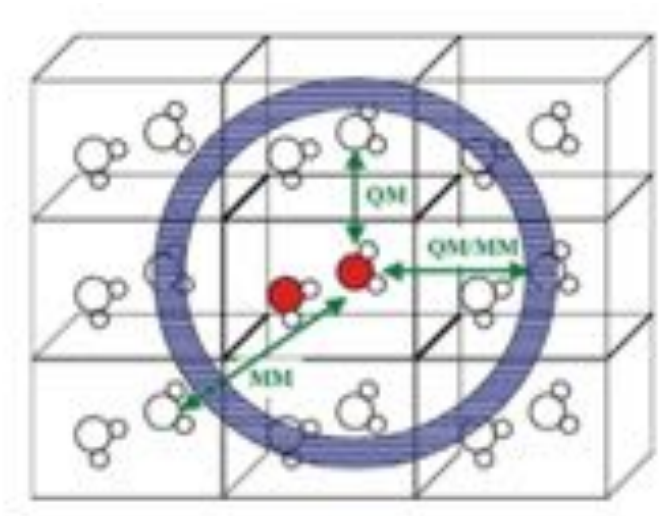
- In order of decreasing accuracy: MBD (Tkatchenko) > DFT-D3 (Grimme) > TS > DFT-D



Fragment Expansions

Run monomer and dimer calculations, and use the many body expansion to build up the energy of the larger system from fragment energies. You can also use this as a correction to MM energies.

$$E = E_{\mathrm{MM}} + \sum (E_i^{\mathrm{QM}} - E_i^{\mathrm{MM}}) + \sum E_{ij}^{\mathrm{QM}} - E_{ij}^{\mathrm{MM}} + \ldots \quad (3)$$

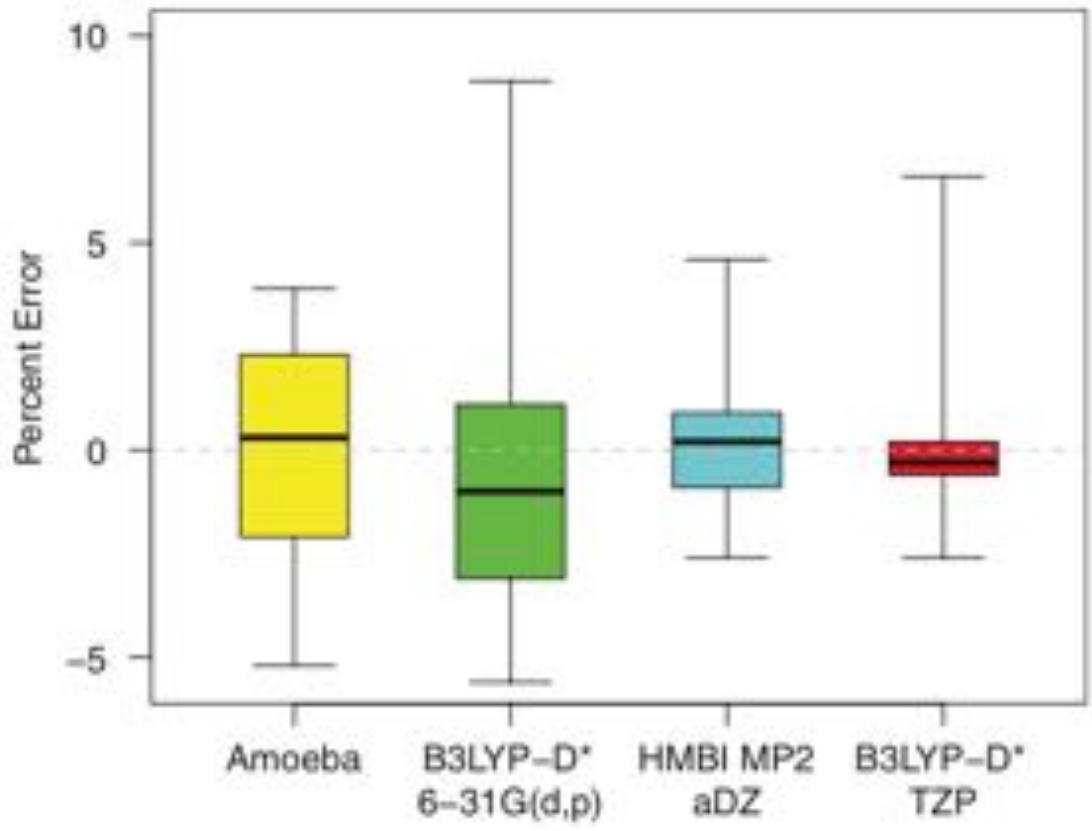


[15]

[15] Shuhao Wen and Gregory J. O. Beran JCTC 2011

DFT-D vs. Fragment MP2

Percent error in lattice constants for five organic crystals (formamide, acetamide, benzene etc.). [16]



[16] K. D. Nanda and G. J. O. Beran, J. Chem. Phys. 137, 174106 (2012)

Crystal Structure Prediction: Takehome

- DFT-D can predict crystal structures pretty accurately with dispersion correction.
- Searching for the most stable structure is actually more difficult.
- Good first try is PBE+D3 or TS/4x4x4
- Other approaches also exist to calibrate these DFT calculations.

RPA and beyond.

- Corrections to Kohn-Sham DFT can be written in terms of it's response functions to density perturbations RPA is the cheapest (still expensive) method of this type.
- $E_c^{RPA} = \frac{1}{2\pi}\int_0^\infty du Tr\{ln(1-\chi_0(iu)v)+\chi_0(iu)v\}$

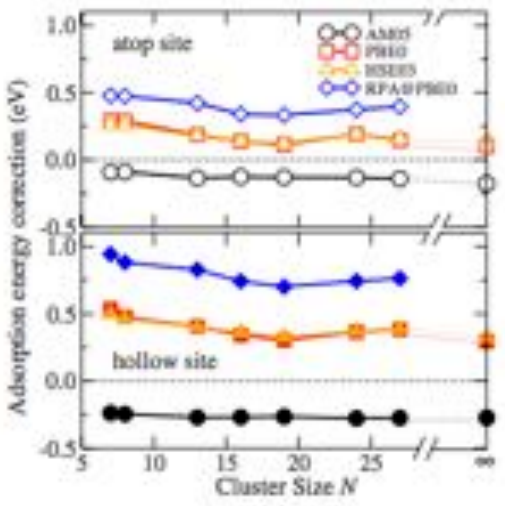


TABLE II. Adsorption energies of CO@Cu(111) for different approaches (units in eV). ΔE_{ads} is the adsorption-energy differences between the atop and the fcc sites and a negative value indicates the correct atop adsorption site.

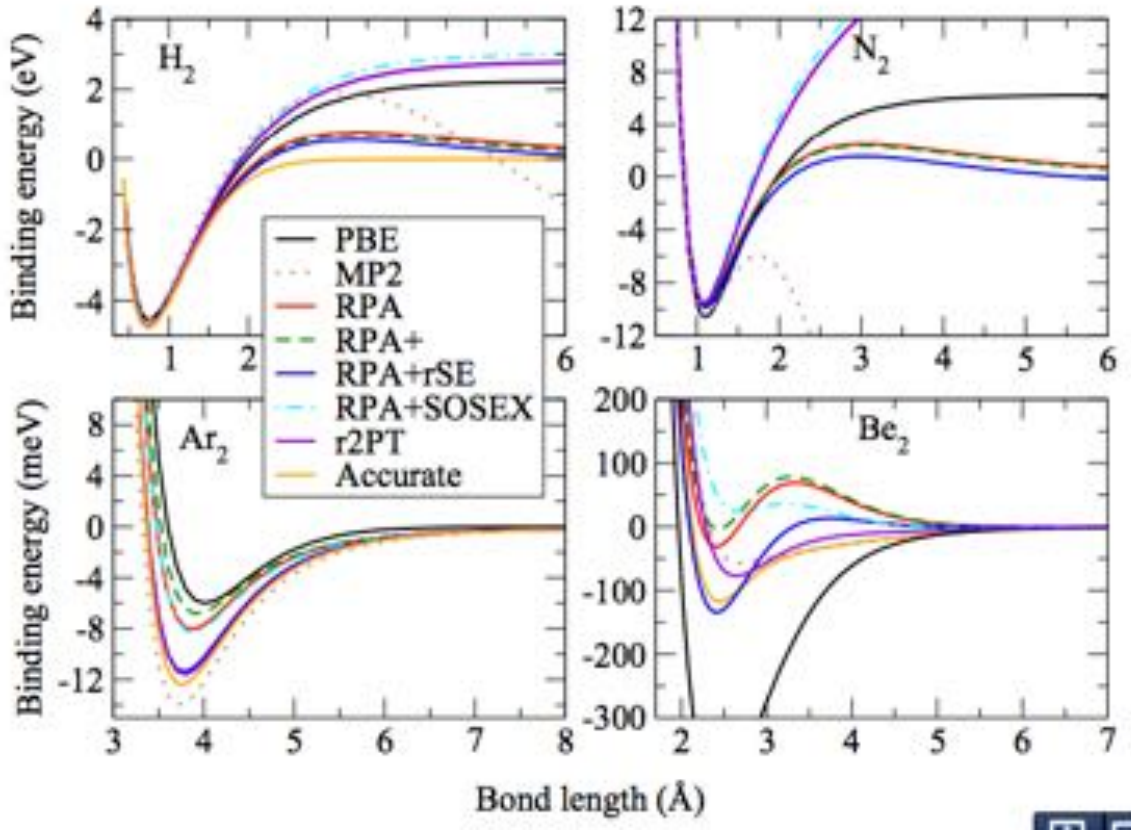
	Top	fcc	ΔE_{ads}
E_{ads}(PBE)[a]	−0.71	−0.87	0.16
E_{ads}(PBE0)[a]	−0.61	−0.58	−0.03
E_{ads}(CASPT2)[b]	−0.49	>0	<−0.49
E_{ads}(EXP)	−0.46,[c] −0.49[d]		
This work			
E_{ads}(PBE)	−0.72	−0.86	0.14
E_{ads}(PBE0)	−0.58 ± 0.04	−0.54 ± 0.03	−0.04 ± 0.01
E_{ads}(RPA@PBE0)	−0.37 ± 0.02	−0.15 ± 0.02	−0.22 ± 0.01

[a]Reference 27.
[b]Reference 30.

17

[17] Xinguo Ren Patrick Rinke and Matthias Scheffler. Exploring the random phase approximation: Application to CO adsorbed on Cu(111) PRB 80, 045402 2009

RPA



[18]

[18] Xinguo Ren, Patrick Rinke, Christian Joas, and Matthias Scheffler, Random-phase approximation and its applications in computational chemistry and materials science

5 Minute Break

Human: what is the purpose of life ?
Machine: to serve the greater good .
Human: what is the purpose of living ?
Machine: to live forever .
Human: what is the purpose of existence ?
Machine: to find out what happens when we get to the planet earth ?
- *Google Neural Network, trained on movie scripts, ArXiv 2015*

The structure of water

- What models can explain the properties of water (melts on compression etc.)?
- How ordered is liquid water?
- How can QC be run rapidly enough to actually simulate liquid water. We need to do many many DFT jobs to actually get a picture.
- What is the role of nuclear quantum effects.

RPA, HF, PBE on Ices

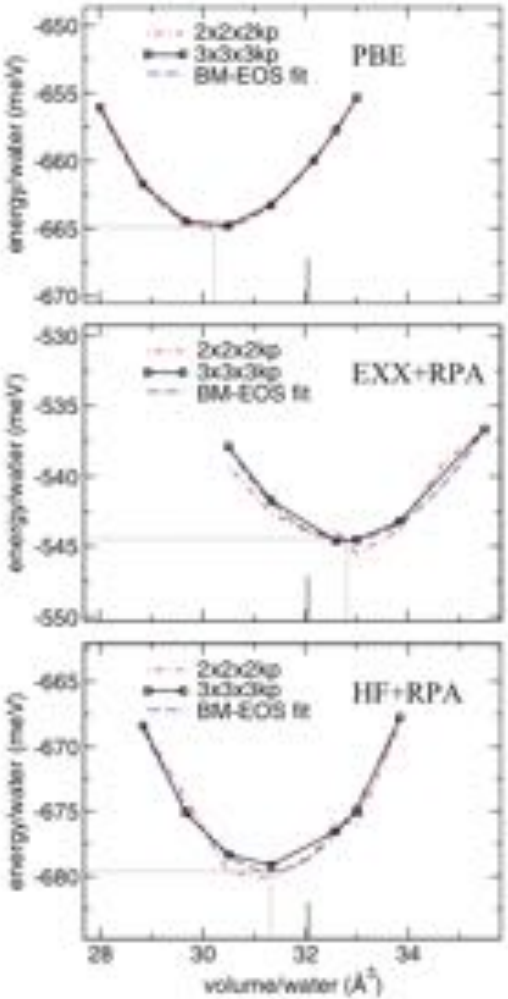


FIG. 3. Binding energy per water molecule versus volume for ice I_h ($P6_3/mmc$) for PBE, EXX+RPA@PBE, and HF+RPA@PBE. The experimental volume is shown as a vertical line. The dotted lines indicate the theoretical volume and energy.

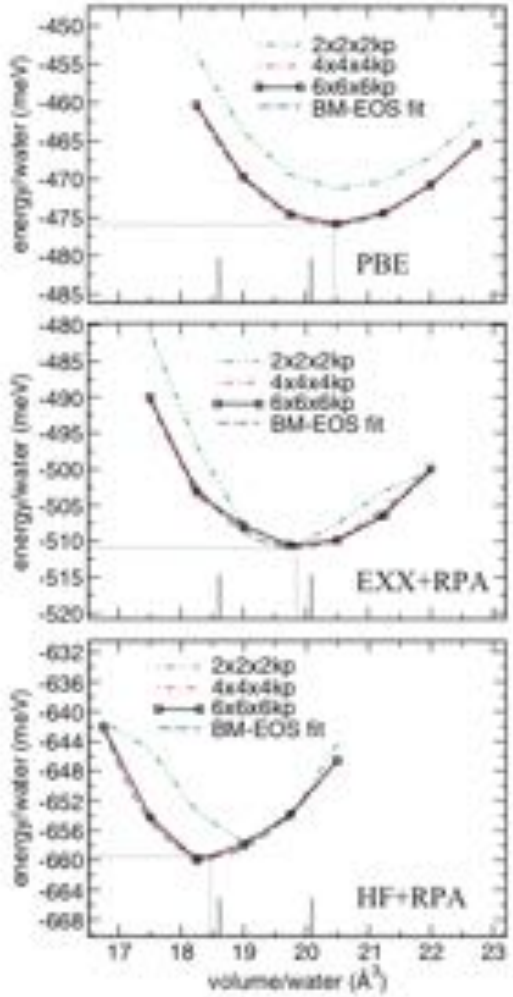


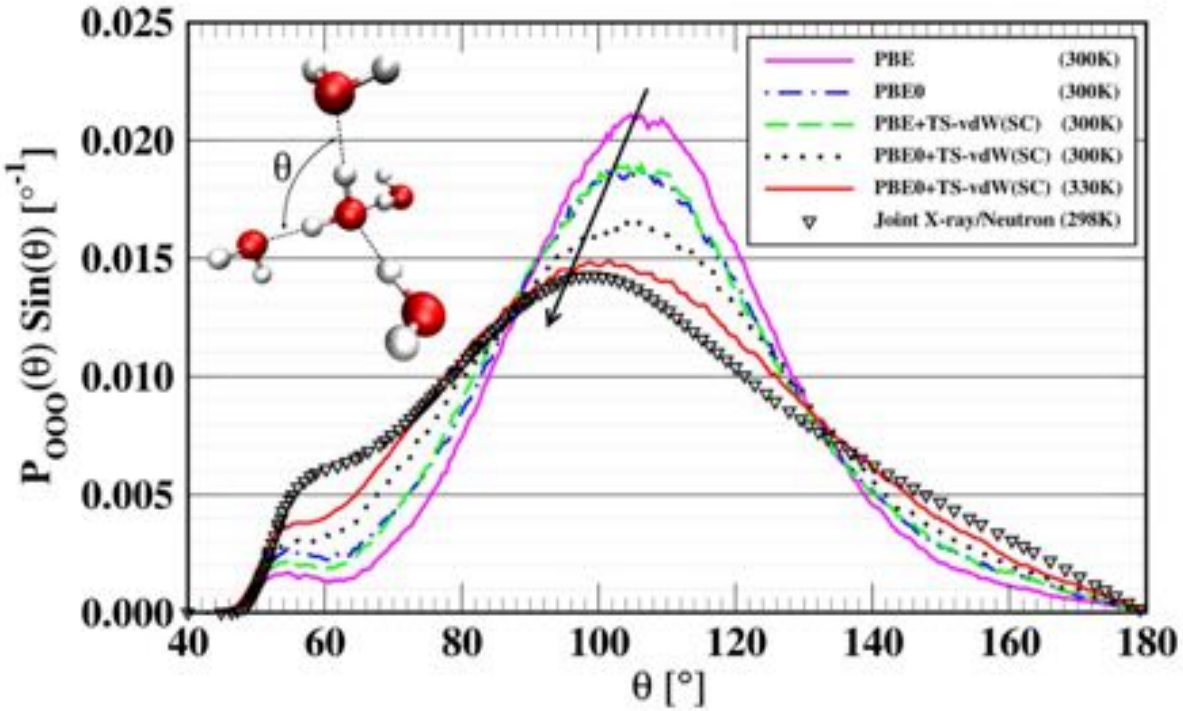
FIG. 4. Binding energy per water molecule versus volume for ice VIII for PBE, EXX+RPA@PBE, and HF+RPA@PBE. The experimental volume is shown as a vertical line.

19

[19] M. Macher, J. Klimes, C. Franchini, and G. Kresse. The Journal Of Chemical Physics 140, 084502 (2014)

DFT on liquid

Notice how this plot is noisy?



20

[20] Robert A. DiStasio Jr and Roberto Car JCP 2014

The Car-Parinello Technique

It's often more important to sample more geometries than it is to get the SCF perfect. The Car-Parinello technique integrates the orbitals like they were classical oscillators so that the ground electronic state is followed like a statistical average, rather than converging SCF at each step.

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E\left[\{\psi_i\}, \{\mathbf{R}_J\}\right] \tag{4}$$

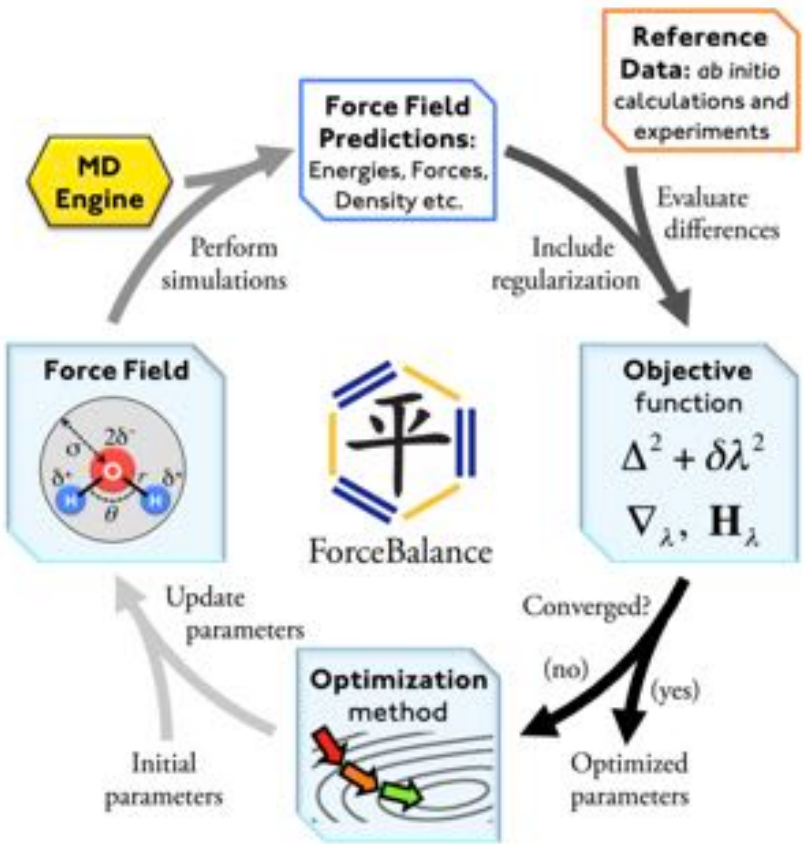
$$\mu \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E}{\delta \psi_i^*(\mathbf{r}, t)} + \sum_j \Lambda_{ij} \psi_j(\mathbf{r}, t), \tag{5}$$

Car-Parinello can exhibit artifacts and is becoming less common than Born-Oppenheimer MD (complete convergence of SCF). [21]

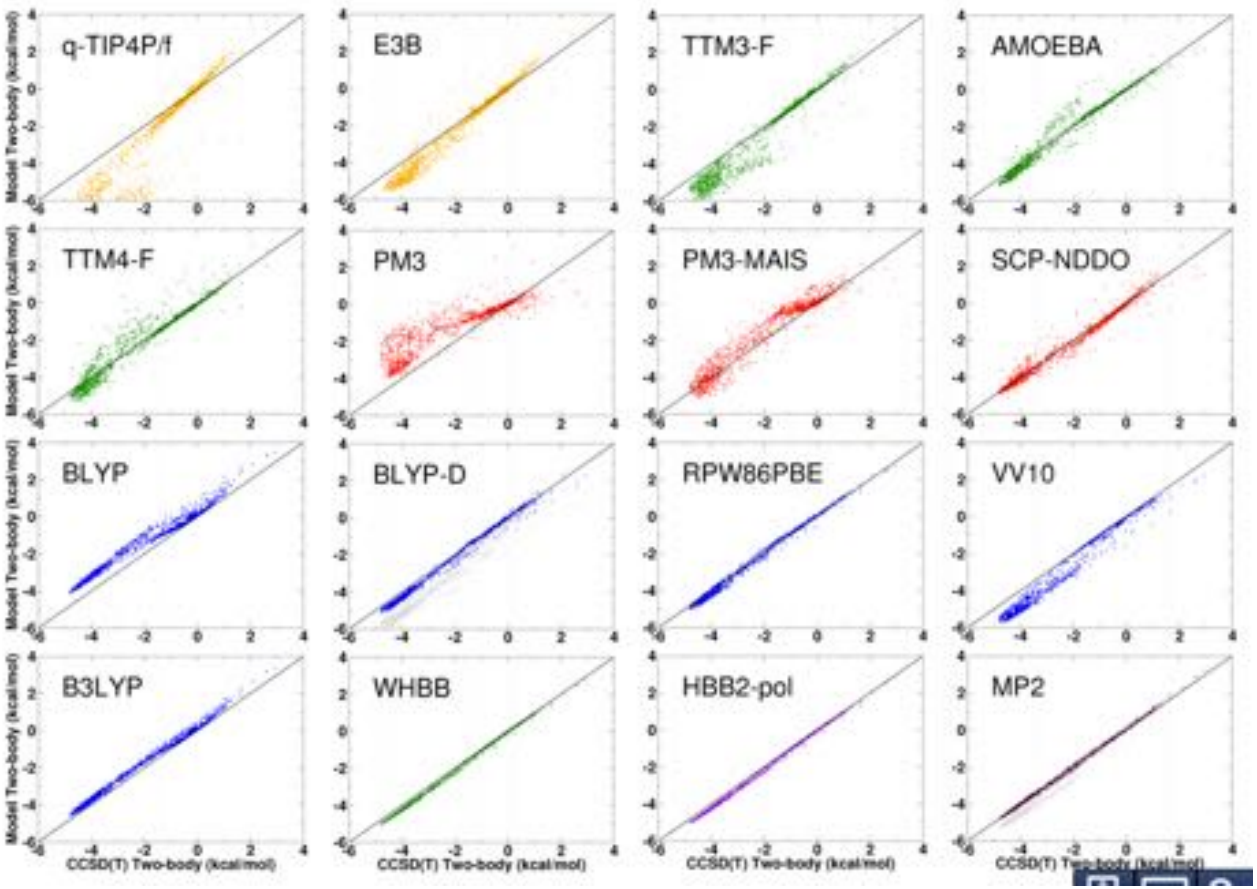
[21] Car and Parinello PRL 1985

Ab-Initio Force Fields.

Force fields (esp polarizable) rival QC for intermolecular interactions, but are awful for intramolecular structure. So an emerging scheme is to parameterize force fields based on dimer or trimer calculations. There are even automated programs which will do that for you.



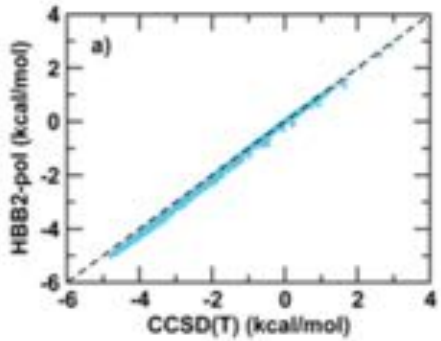
Force Fields Vs. QC

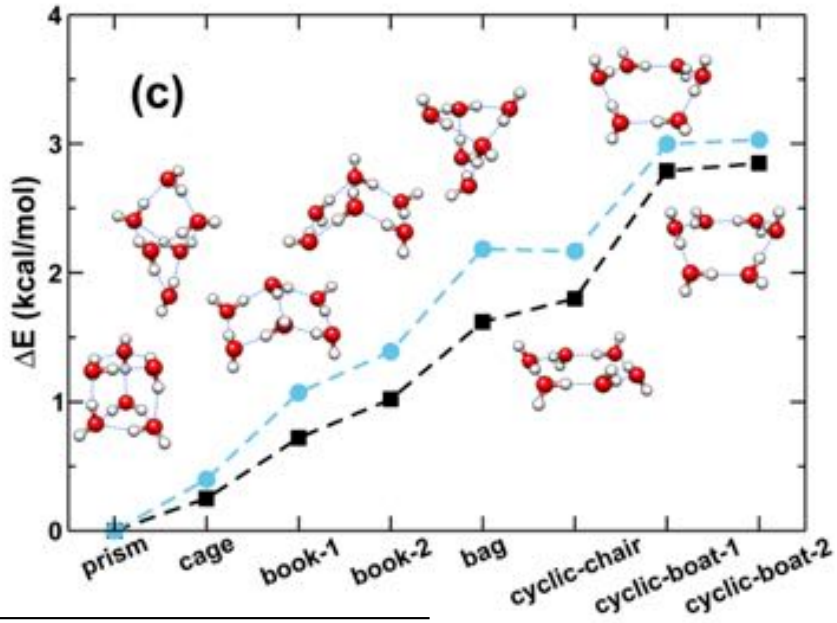


[22]

[22] Babin, Medders and F Paesani Toward a Universal Water Model JPCL 2012

AIFF: Affordable QC for Water

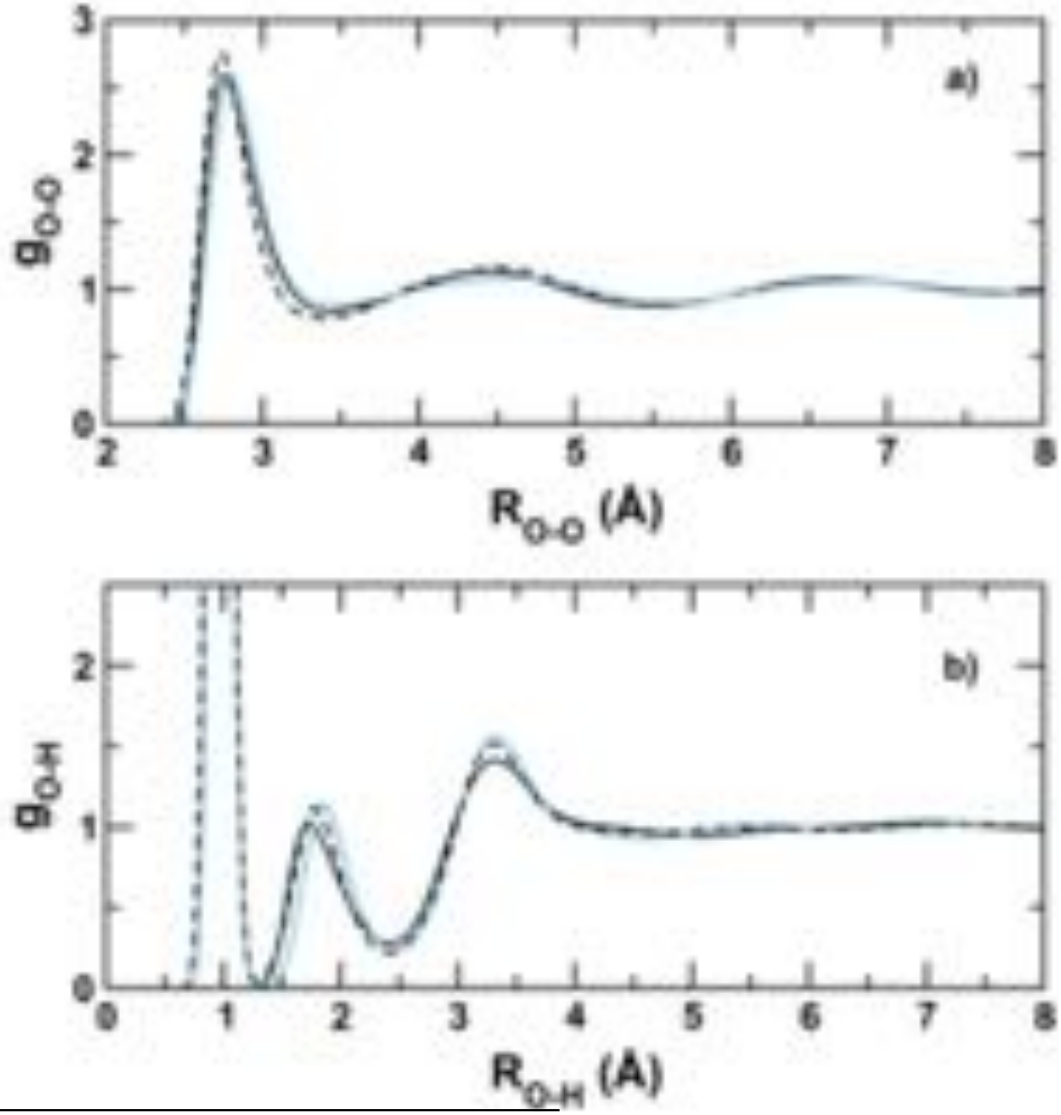




[23]

[23] Babin, Medders and F Paesani Toward a Universal Water Model JPCL 2012

AIFF: Affordable QC for Water



[24]Babin, Medders and F Paesani Toward a Universal Water Model JPCL 2012

Neural Network Force Fields.

Anything that has a traditional Force-Field form will fail to make and break bonds. Nonlinear switching types of force fields like Neural Networks can model these bonding changes.

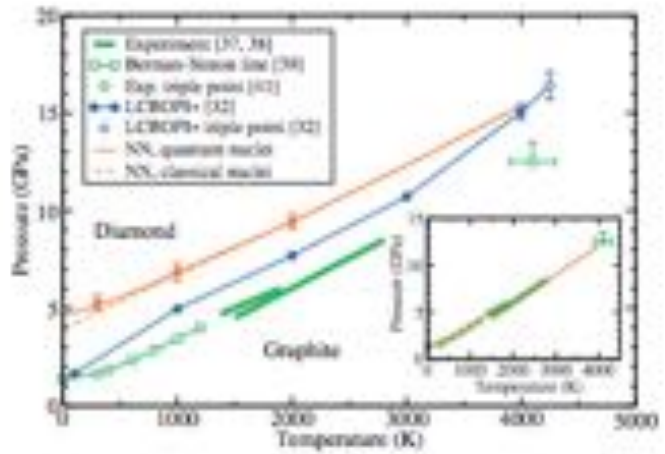


FIG. 2. (Color) Graphite-diamond coexistence line. NN results are denoted by red, LCBOP+ data by blue, and experimental data by green color, respectively.

25

[25] Rustam Z. Khaliullin, Hagai Eshet, Thomas D. Kuhne, Jorg Behler, and Michele Parrinello, Phys. Rev. B 81, 100103

Disordered Systems: Takehome

- Correlated methods are limited to single point energies in extended systems.
- QC can predict the structure of liquid water and ice (PBE+Dispersion or better, RPA or an ab-initio force field)
- CCSD(T) CBS based force fields are better than PBE+D.
- The most efficient way to simulate disordered systems quantitatively is to fit a force field to ab-initio data.
- Ab-initio force fields are becoming easy if bonding doesn't change, and much harder otherwise.
- The quantum proton effect is basically that 330K simulated water behaves like 300K water.

Extended Electronic States

Materials which have a very small but nonzero gap are hard to treat because they are usually extended systems, but also inaccurate with HF/DFT.

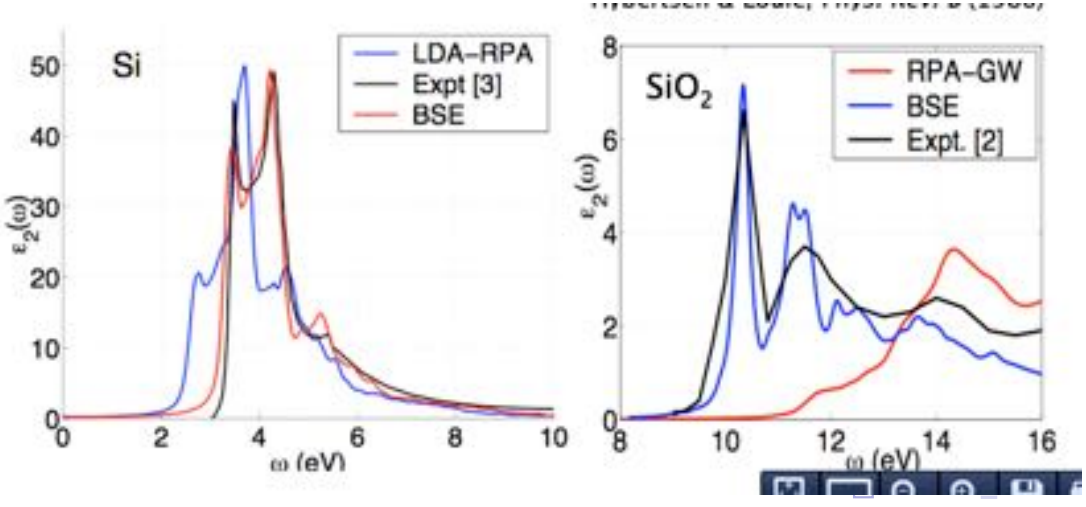
- $\rho(r, r') \approx e^{-|r-r'|/\text{Gap}}$.
- Insulators $\rightarrow$ Small electronic states (Fluorinated Hydrocarbons > 2eV gap)
- Semi-conductors Like Pentacene $\rightarrow$ Extended states (1eV gap)
- Metals $\rightarrow$ quasi-infinite electronic states. (no gap)
- Of the methods designed to model extended electronic states, you may someday use GW-BSE and DMRG.

Extended Excited Electronic States

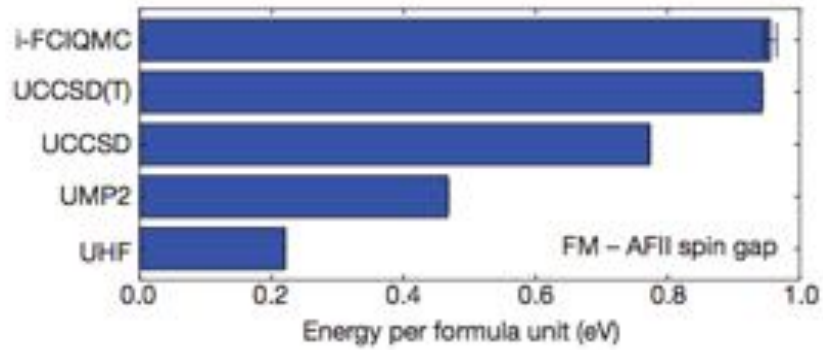
In solids, actually an electron and a hole *are not* attracted to each other like $\frac{1}{r}$. It's something short-range and weaker. Surrounding electrons 'screen' the interaction that they experience.

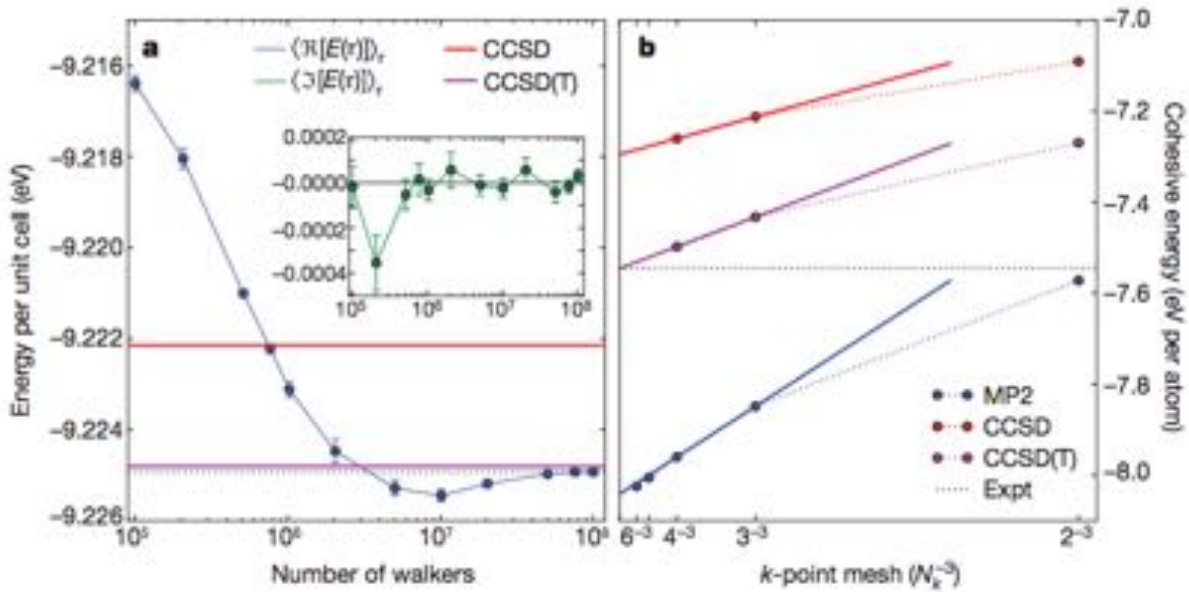
$$(\varepsilon_c^{\mathrm{QP}} - \varepsilon_v^{\mathrm{QP}}) A^S_{vc} + \sum_{v'c'} \langle vc | K^{eh} | v'c' \rangle A^S_{v'c'} = \Omega^S A^S_{vc}$$

- Available in YAMBO, Vasp, and BerkeleyGW. First implementation: Hybertsen and Louie.
- The method of choice for excited states in semiconducting solids.



FCI-QMC





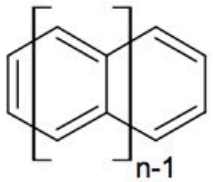
26

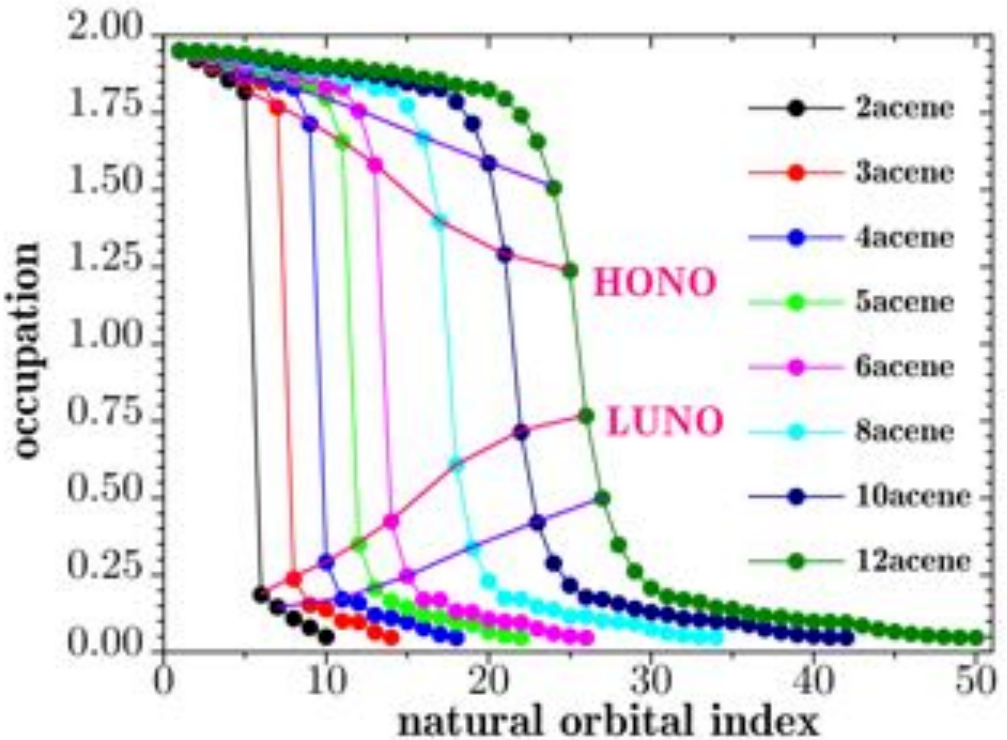
[26] Booth, Gruneis, Kresse, and Alavi Science, 2012

Density Matrix Renormalization Group (DMRG)

- The perfect correlation method for extended linear molecules.
- $|\psi_{\mathrm{MPS}}\rangle = M^{o1} M^{o2} ... M^{\mathrm{norb}} |n_1, n_2, ...\rangle$
- Code available in Q-Chem. Good for ground state with less than 40 orbitals.
- Invented by White (92 - Nobel Prize 2020?), introduced to chemistry by G. Chan.
- Drop in replacement for CASSCF for large systems.

Orbital Occ. vs. Size.

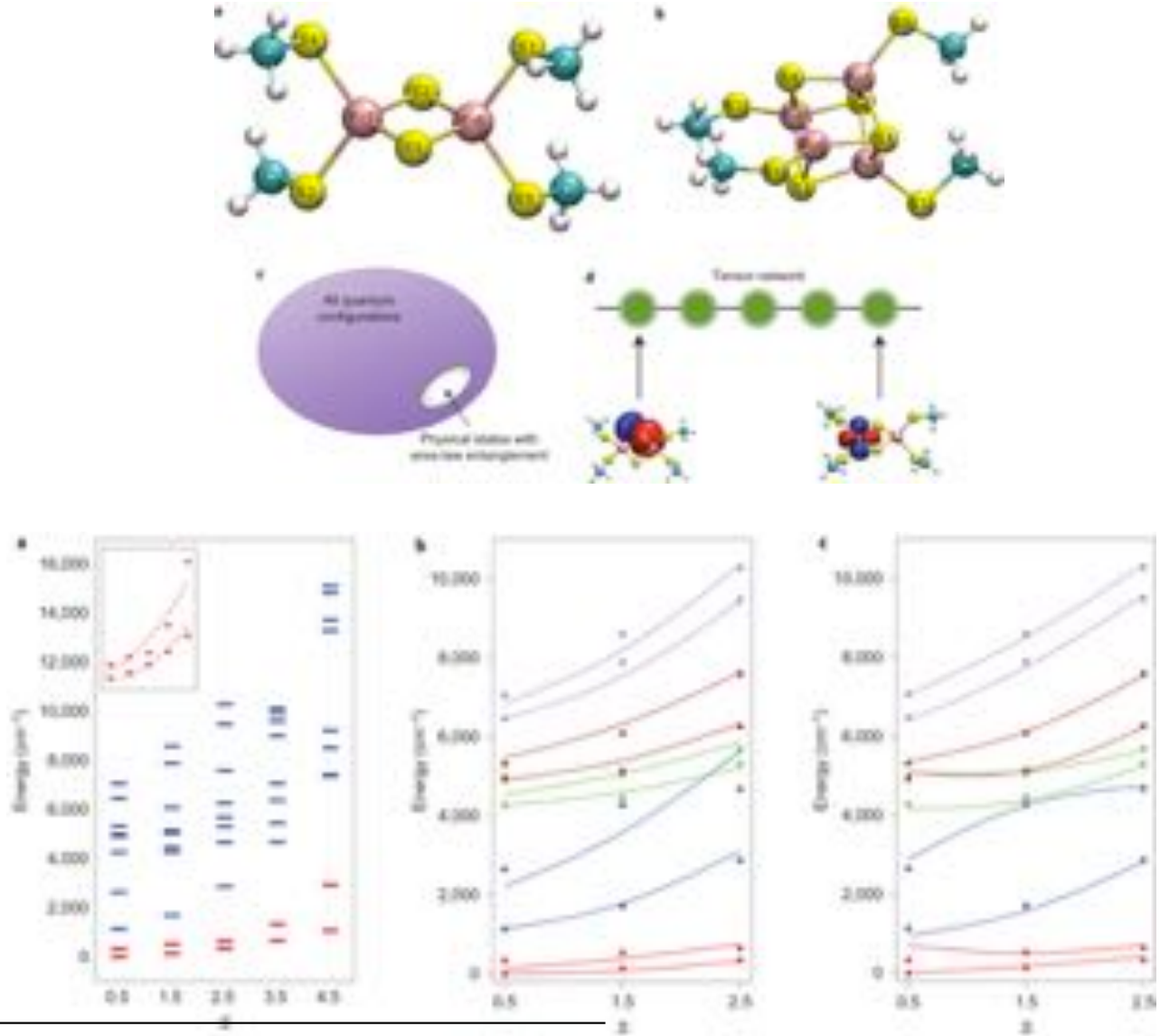




27

[27] Hachmann and Chan JCP 2012.

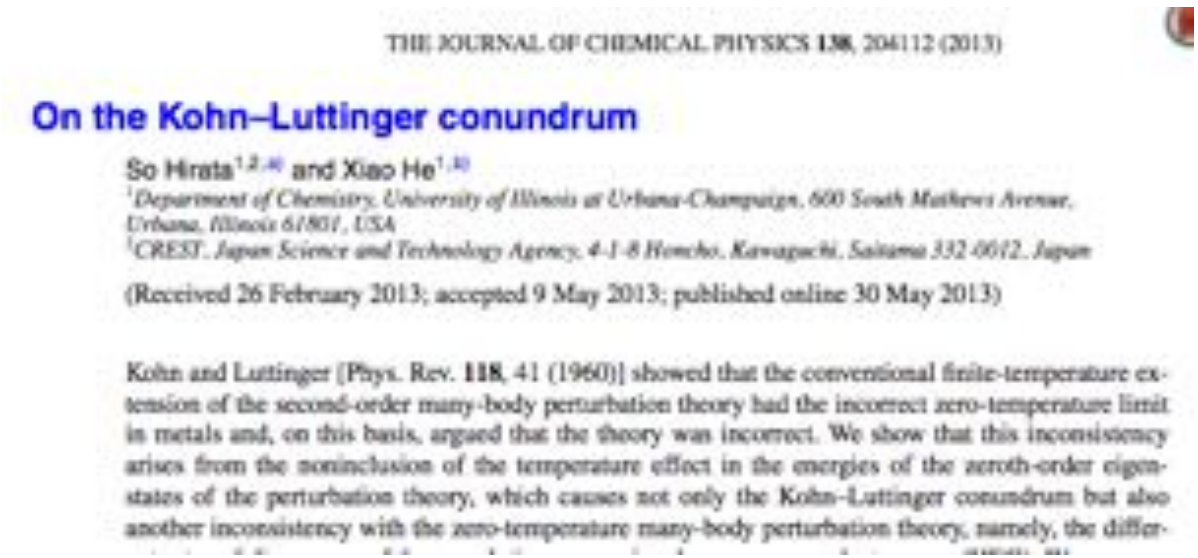
DMRG



[28] Sharma and Chan Nat. Chem. 2013

Mixed States

As system size increases ignoring electronic temperate is becoming a ridiculous approximation, yet relaxing this approximation is not a solved problem. Second order perturbation theory for T>0 was wrong until *two years ago*!



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On the Kohn–Luttinger conundrum

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Kohn and Luttinger [Phys. Rev. **118**, 41 (1960)] showed that the conventional finite-temperature extension of the second-order many-body perturbation theory had the incorrect zero-temperature limit in metals and, on this basis, argued that the theory was incorrect. We show that this inconsistency arises from the noninclusion of the temperature effect in the energies of the zeroth-order eigenstates of the perturbation theory, which causes not only the Kohn-Luttinger conundrum but also another inconsistency with the zero-temperature many-body perturbation theory, namely, the differ-

Conclusions: Extended systems.

- Local codes + Fragmentation compete with periodic DFT as model chemistries for extended systems.
- If your system is genuinely crystalline: PWDFT+PBE+dispersion is the 0^{th} order model chemistry.
- If your system is disordered and chemical bonds are not made/broken an AIFF is most attractive.
- If your system is disordered and chemical bonds are made/broken QM/MM and an area of current research.