Perspectives on many-body electronic structure

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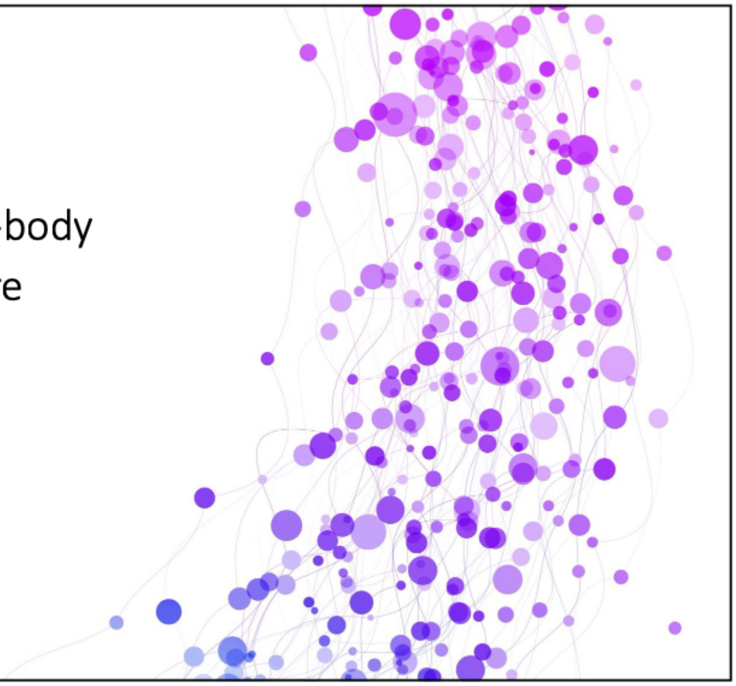
TYC Materials Modelling Course

UCL, 9th Nov 2022



Plan for the next hour…

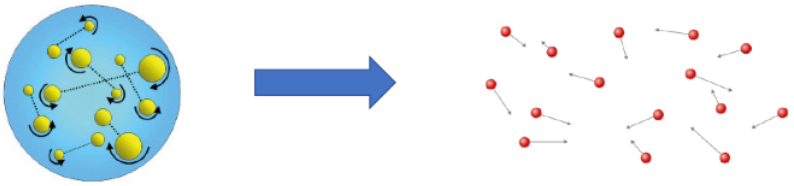
Starting point:

Electronic structure problem and its importance
Density Functional Theory and Hartree Fock. Why, how and practicalities.

From there:

- Does this solve all our problems in electronic structure?
- If not, why not?
- The nature of electron correlation.
- What else lies out there: LDA+U, Post-DFT, the spectrum of other methods, Embedding,…

(Static) mean-field theory



N-body problem

$$\Psi[\hat{H}]$$

N, 1-body independent particle problems

$$\gamma[F(\gamma)]$$

- HF/KS-DFT can be represented by single Slater determinant:
  No explicit correlation in this representation

Hartree-Fock theory

K.E., nuclear repulsion

Coulomb and exchange interaction with **average** of other electrons [Note, when electrons are the same, this cancels]

$$E_{IPM} = \sum_{\mu=1}^{N} E_{\mu} + \overbrace{\sum_{\mu<\nu}^{N} \tilde{J}_{\mu\nu} - \tilde{K}_{\mu\nu}}$$

$$E_{\mu} = \int \psi_{\mu}(1)\hat{H}_0\psi_{\mu}(1)\,d\tau$$

Dependent on orbitals: Solve self-consistently

$$\tilde{J}_{\mu\nu} \equiv \iint \psi_{\mu}^{*}(1)\psi_{\nu}^{*}(2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{\mu}(1)\psi_{\nu}(2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\sigma_1\,d\sigma_2$$

$$\tilde{K}_{\mu\nu} \equiv \iint \psi_{\mu}^{*}(1)\psi_{\nu}^{*}(2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{\mu}(2)\psi_{\nu}(1)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\sigma_1\,d\sigma_2$$

- One-body effective Hamiltonian
- No correlation effects (implicit or explicit)
- Symmetry breaking very powerful concept

Hartree-Fock to Kohn Sham-DFT…

$$E_{IPM} = \sum_{\mu=1}^{N} E_\mu + \sum_{\mu<\nu}^{N} \tilde{J}_{\mu\nu} - \cancel{\tilde{K}_{\mu\nu}} + E_{xc}[\rho]$$

$$E_\mu = \int \psi_\mu(1)\hat{H}_0\psi_\mu(1)\,d\tau$$

$$\tilde{J}_{\mu\nu} \equiv \iint \psi_\mu^*(1)\psi_\nu^*(2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_\mu(1)\psi_\nu(2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\sigma_1\,d\sigma_2$$

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1) Write energy as functional of **total** electron density

2) **Existence** proof of density functional for remaining neglected physics

- Still one-body effective Hamiltonian
- *Implicit* correlation effects

Hartree-Fock to Kohn Sham-DFT…

$$E_{IPM} = \sum_{\mu=1}^{N} E_\mu + \sum_{\mu<\nu}^{N} \tilde{J}_{\mu\nu} - \cancel{\tilde{K}_{\mu\nu}} + E_{xc}[\rho]$$

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1) Write energy as functional of **total** electron density

2) **Existence** proof of density functional for remaining neglected physics

- Still one-body effective Hamiltonian
- *Implicit* correlation effects

- Hybrid functionals [PBE0, B3LYP]: add back in a fraction (e.g. 25%) of 'exact exchange'.
- Back to HF cost

Hartree-Fock vs. Kohn Sham-DFT…

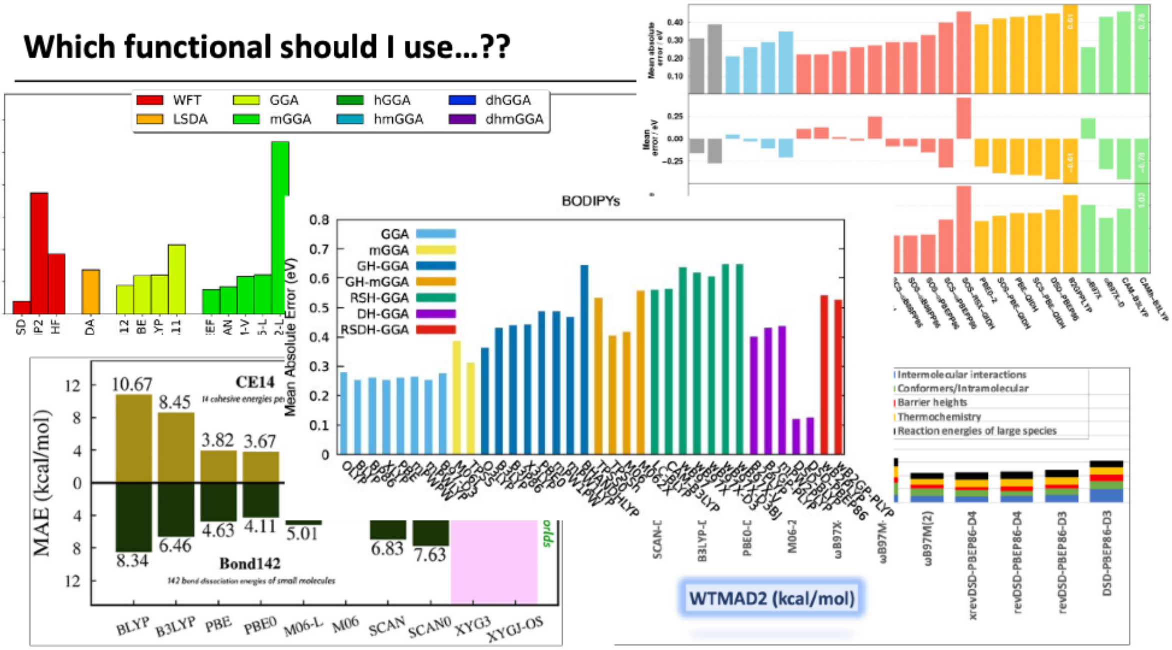
- HF is fully *ab initio*, while DFT is *semi-empirical* in practice
  - XC-functionals parameterized and optimized over data sets, giving (hopefully) a domain of applicability and transferability

KS-DFT often cheaper and *almost* always better

Property	HF accuracy	'Best' hybrid DFT accuracy
IPs and EAs	±0.5eV	±0.2eV [Delta SCF]
Bond lengths	-1%	±1 pm
Vibrational Frequencies	+10%	-3%
Barrier heights	+30-50%	-25%
Bond energies	-50%	±0.1eV

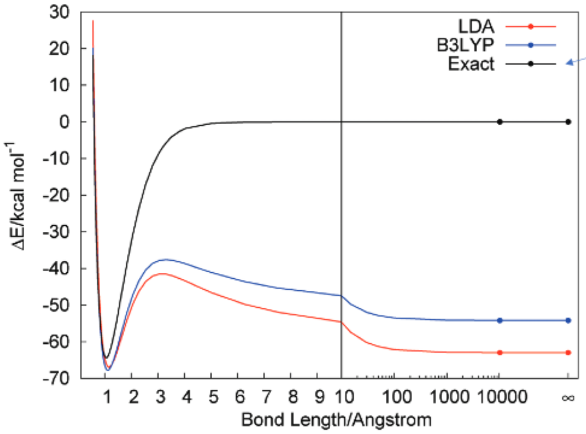
- **KS-DFT now overwhelmingly dominates materials (and molecular) modelling with excellent cost:accuracy ratio**

Which functional should I use…??



Lets start to think about errors a bit more systematically.

Stretched H_2^+



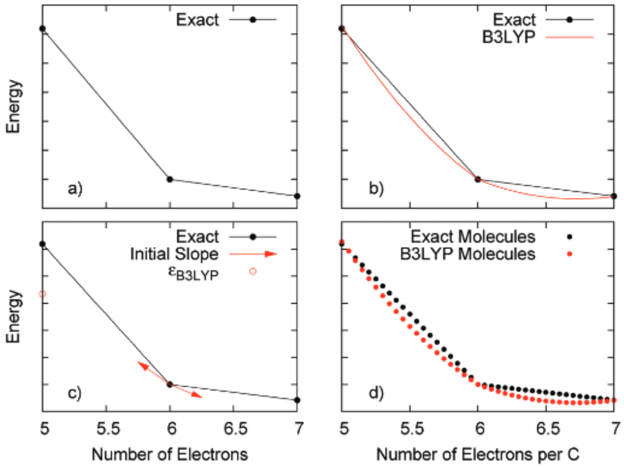
Hartree-Fock

Self-interaction / delocalization error

DFT can't describe $H^{0.5+}$

Cohen et. al., Chem. Rev. 2012

Delocalization error: Fractionally charged (sub)systems

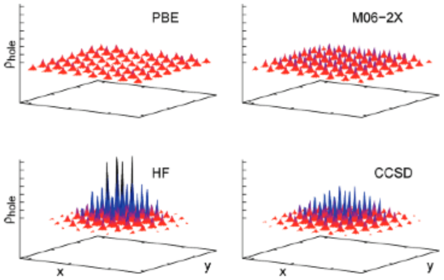


DFT has unphysical smooth change wrt variation in charge

Is this all completely abstract?

- Gaps significantly underestimated
- Excitations/charge spuriously delocalized
- Electron transport
- Absorption processes
- Coulomb blockade
- …and many more

H^{64} hole density



Cohen et. al., Chem. Rev. 2012

Delocalization error: Fractionally charged (sub)systems

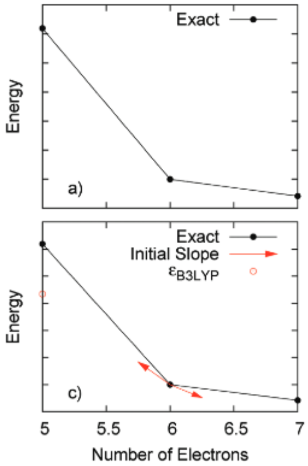


Table 4. Seeing the Delocalization Error in Organic Chemistry: Errors of Many Functionals for the Twist to Heart Isomerization Energy of [10]-Annulene, $C_{10}H_{10}$^{a}

functional	annulene	error[CH_4^{frac}]
LDA	−14.27	−15.97
GGA and Meta-GGA Functionals		
BLYP	−13.95	−15.62
HCTH	−14.37	−15.54
HCTH407	−14.47	−15.42
PBE	14.08	15.54
BP86	−14.12	−15.44
BPBE	−14.05	−15.48
OLYP	−14.93	−15.59
OPBE	−15.04	−15.45
TPSS	−14.47	−14.97
M06-L	−11.44	−14.61
Hybrid Functionals		
TPSSh	−12.75	−13.08
B3LYP	−10.60	−11.76
PBE0	−9.91	−10.66
B97−1	−10.34	−11.74
B97 2	10.60	11.70
B97−3	−9.35	−10.69
M06	−6.86	−10.92
M06−2X	−2.74	−6.23
M06-HF	2.66	1.19
HF	3.90	4.38
HFLYP	2.70	3.83

DFT has unphysical smooth c

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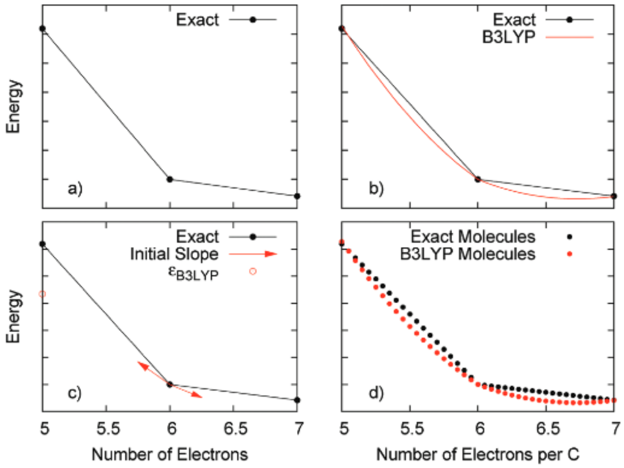
- Coulomb blockade
- …and many more

Comparing errors in isomers with different electron localization.

DFT spuriously stabilizes delocalized structures

Cohen et. al., Chem. Rev. 2012

Delocalization error: Fractionally charged (sub)systems



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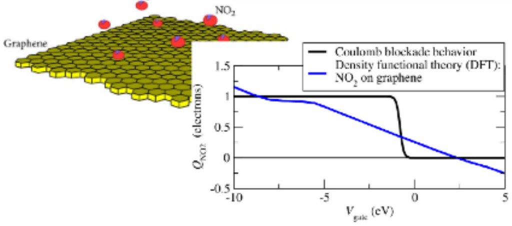
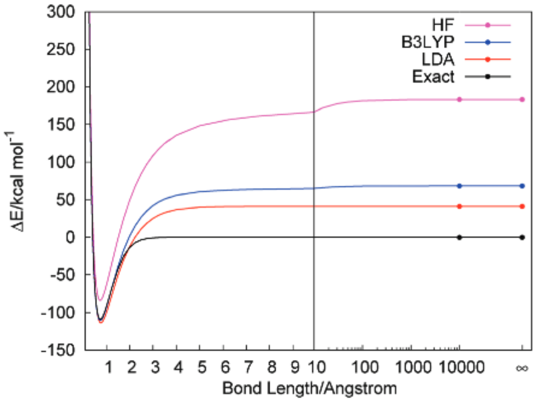
Absorption of NO_2 on graphene



Cohen et. al., Chem. Rev. 2012

Lets start to think about errors a bit more systematically.

Stretched H_2



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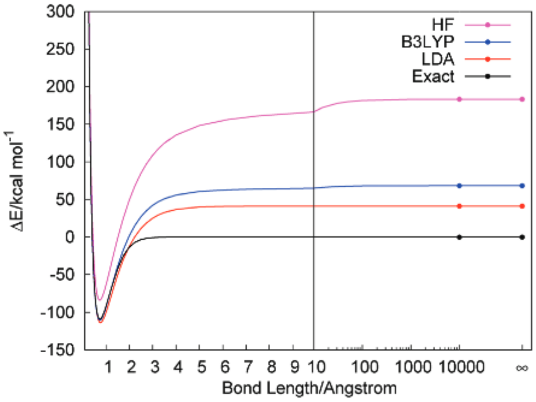

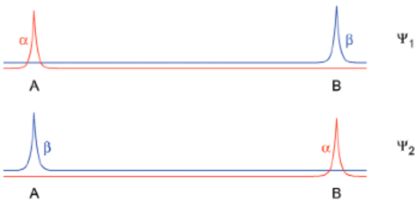

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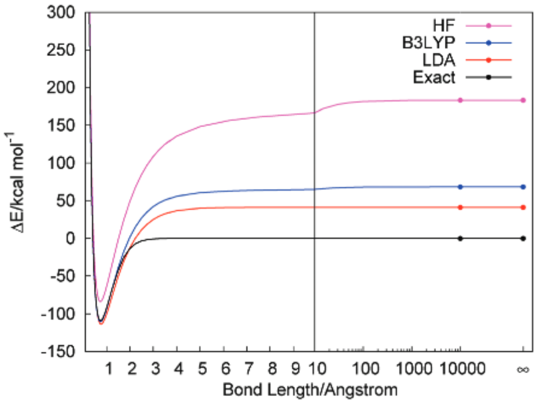
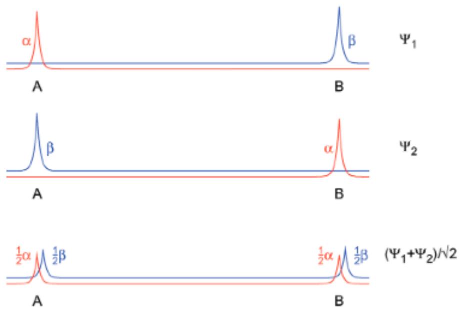
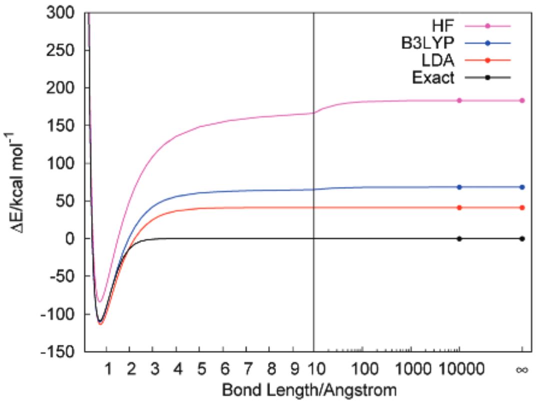


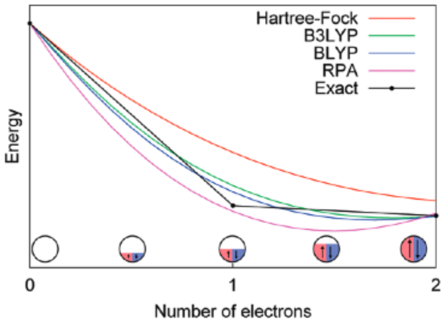


From a wave function perspective, this is a question of *conditional probability*, i.e. **electron correlation**

Lets start to think about errors a bit more systematically.

Stretched H_2





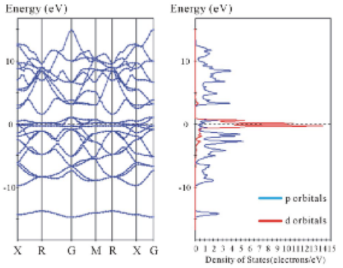
Despite the 'in principle exact' nature, due to viewing the N-electron density as a continuous (not discrete) variable, DFT still has the spirit of an average 'mean-field' method…

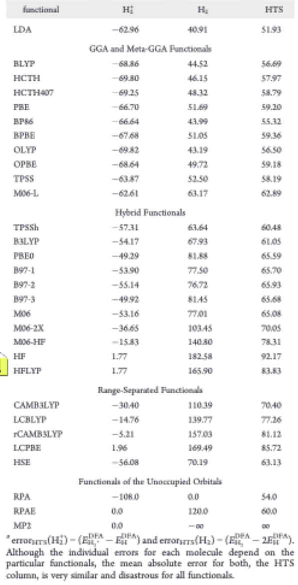
Fractional spin / strong correlation errors

Again, these abstract model manifest in *real* errors:

- Degenerate systems
- Competing spin states
- Bond-breaking
- Partially-filled transition metal d-shells
- f-electron systems
- …

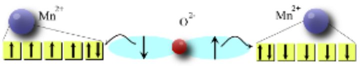
These errors are universal across DFT, and largely inherent in the approach





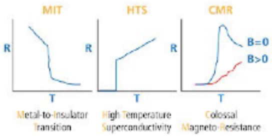
functional	H_2^+	H_2	HTS
LDA	−62.96	40.91	51.93
GGA and Meta-GGA Functionals			
BLYP	−68.86	44.52	56.69
HCTH	−69.80	46.15	57.97
HCTH407	−69.25	48.32	58.79
PBE	−66.70	51.69	59.20
BP86	−66.64	43.99	55.32
BPBE	−67.68	51.05	59.36
OLYP	−69.82	43.19	56.50
OPBE	−68.64	49.72	59.18
TPSS	−63.87	52.50	58.19
M06-L	−62.61	63.17	62.89
Hybrid Functionals			
TPSSh	−57.31	63.64	60.48
B3LYP	−54.17	67.93	61.05
PBE0	−49.29	81.88	65.59
B97-1	−53.90	77.50	65.70
B97-2	−55.14	76.72	65.93
B97-3	−49.92	81.45	65.68
M06	−53.16	77.01	65.08
M06-2X	−36.65	103.45	70.05
M06-HF	−15.83	140.80	78.31
HF	1.77	182.58	92.17
HFLYP	1.77	165.90	83.83
Range-Separated Functionals			
CAMB3LYP	−30.40	110.39	70.40
LCBLYP	−14.76	139.77	77.26
rCAMB3LYP	−5.21	157.03	81.12
LCPBE	1.96	169.49	85.72
HSE	−56.08	70.19	63.13
Functionals of the Unoccupied Orbitals			
RPA	−108.0	0.0	54.0
RPAE	0.0	120.0	60.0
MP2	0.0	−∞	∞

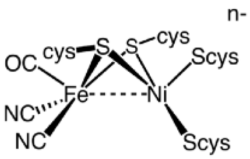
[a] $\text{error}_{\text{HTS}}(H_2^+) = (E^{\text{DFA}}_{H_2^+} - E^{\text{DFA}}_{H})$ and $\text{error}_{\text{HTS}}(H_2) = (E^{\text{DFA}}_{H_2} - 2E^{\text{DFA}}_{H})$. Although the individual errors for each molecule depend on the particular functionals, the mean absolute error for both, the HTS column, is very similar and disastrous for all functionals.



Other (related) universal difficulties:

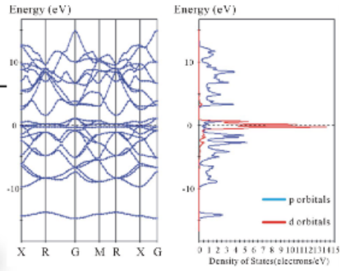
- Dispersion
- Excitations
- Charge transfer
- Multicenter bonds
- …

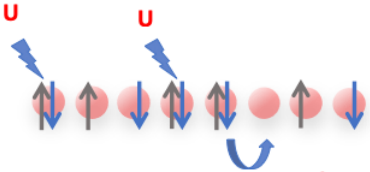




So, what can we do about this…?

1) Try to fix DFT: **LDA+U**





Electron Repulsion (correlated physics)

U

U

Lets consider a local description of strong correlation: **Hubbard model**

'Sites' ~ '3d shells' of Tm?

Kinetic Energy -t

$$H = \sum_{\langle ij\rangle\sigma} t a^{\dagger}_{i\sigma} a_{j\sigma} + \sum_{i} U n_{i\alpha} n_{i\beta}$$

weak coupling $t \gg U$ non-interacting electrons
electrons delocalize across atoms

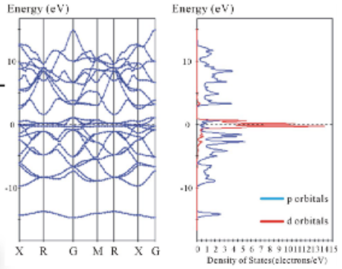
electrons localize
AFM ordering, Mott physics

strong coupling $U \gg t$

Unsolved problem in general

- High Dimension
- Lattice structure
- Filling
- Temperature
- …

So, what can we do about this…?



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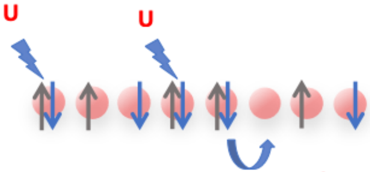

Electron Repulsion
(correlated physics)

Kinetic Energy -t

Lets consider a local description of strong correlation: **Hubbard model**

'Sites' ~ '3d shells' of Tm?

How can this fix DFT:

Remove contribution to
3d energy from DFT (not unique)

$$E_{\mathrm{LDA+U}}[\rho(\mathbf{r})] = E_{\mathrm{LDA}}[\rho(\mathbf{r})] + E_{\mathrm{Hub}}[U;\{n_m^{l\sigma}\}] - E_{\mathrm{dc}}[U;\{n^{l\sigma}\}]$$

Approximate solution as Hartree-Fock
i.e. <n n> ~ <n><n>

Depends on local occupation of e.g.
3d orbitals (moving away from density)
Note: choice of projector

LDA+U

Remove contribution to
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Approximate solution as Hartree-Fock
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Depends on local occupation of e.g.
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Differentiate to get potential:

$$V_{\mathrm{tot}}^{\sigma} = V_{\mathrm{LDA}}^{\sigma} + \sum_{l,m} U\left(\frac{1}{2} - n_m^{l\sigma}\right)|\phi_m^l\rangle\langle\phi_m^l|$$

Perspective 1: Get 3d filling right

- Repulsive potential if less than half-filled
- Attractive potential if more than half-filled
- Discourages fractional occupation of 3d shells
- Large *U* favours Mott localization (n -> 1)
- Note, only affects occupied bands, so changes energy of conduction relative to valence

Cococcioni and de Gironcoli, PRB, 2005

LDA+U

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3d energy from DFT (not unique)

$$E_{\mathrm{LDA+U}}[\rho(\mathbf{r})] = E_{\mathrm{LDA}}[\rho(\mathbf{r})] + E_{\mathrm{Hub}}[U;\{n^{l\sigma}_m\}] - E_{\mathrm{dc}}[U;\{n^{l\sigma}\}]$$

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Differentiate to get potential:

$$V^\sigma_{\mathrm{tot}} = V^\sigma_{\mathrm{LDA}} + \sum_{l,m} U \left(\frac{1}{2} - n^{l\sigma}_m\right) |\phi^l_m\rangle\langle\phi^l_m|$$

Perspective 2: *Local* Hybrid functional

- Include HF exchange on local subspace via empirical *U*
- HF opens up the gap at the chemical potential relative to DFT
- *Cheap* hybrid functional

Cococcioni and de Gironcoli, PRB, 2005

LDA+U

Remove contribution to
3d energy from DFT (not unique)

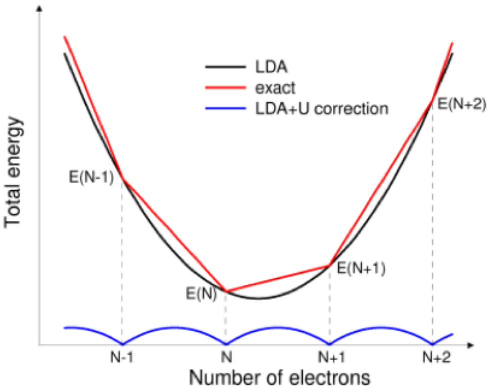
$$E_{\mathrm{LDA+U}}[\rho(\mathbf{r})] = E_{\mathrm{LDA}}[\rho(\mathbf{r})] + E_{\mathrm{Hub}}[U;\{n^{l\sigma}_m\}] - E_{\mathrm{dc}}[U;\{n^{l\sigma}\}]$$

Approximate solution as Hartree-Fock
i.e. <n n> ~ <n><n>

Differentiate to get potential:

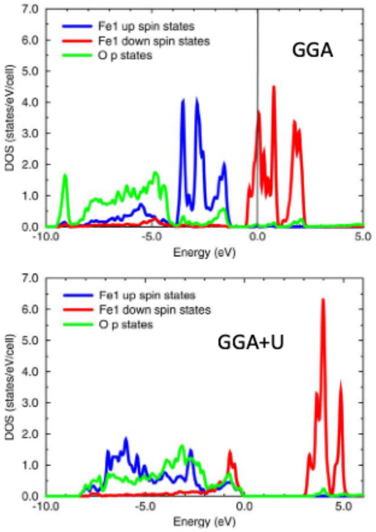
$$V^\sigma_{\mathrm{tot}} = V^\sigma_{\mathrm{LDA}} + \sum_{l,m} U \left(\frac{1}{2} - n^{l\sigma}_m\right.$$

Perspective 3: Balance fractional charge error by adding energy penalty quadratic in fractional electron number

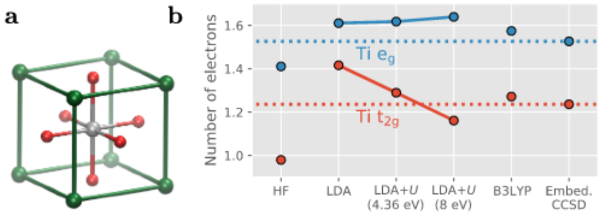


Cococcioni and de Gironcoli, PRB, 2005

LDA+U



Fe_2SiO_4. Himmetoglu et al. IJQC, 2014



$SrTiO_3$: Nusspickel, Booth, PRX 2022

LDA+U

$$E_{\mathrm{LDA+U}}[\rho(\mathbf{r})] = E_{\mathrm{LDA}}[\rho(\mathbf{r})] + E_{\mathrm{Hub}}[U;\{n_m^{l\sigma}\}] - E_{\mathrm{dc}}[U;\{n^{l\sigma}\}]$$

Considerations:

- Choice of *U* [fully empirical, get filling/gap to match experiment/hybrid DFT, energy differences, linear response…]
- Choice of double-counting correction
- Choice of projectors
- Is increasingly a method-of-choice for transition metal materials modelling

LDA+DMFT: Treat E_{Hub} term ‘exactly’ (not HF approx.)

- Requires *dynamical* mean-field picture, but gets true *quantum fluctuations*
- Same issues as above
- Beyond scope of this lecture

Can we avoid empiricism…?

2) 'Post-mean-field' methods

GW [Perturbation theory + Greens function]: Next term
QMC [Variational Principle + Wave function]: Next term

World of (important) variations on a theme:

Choose: **Perturbation theory** or **variational principle**

Choose quantum variable: **Greens/response function**, **Density matrix**, **Wave function**

Beyond this, choose *ansatz/deterministic vs. stochastic/infinite-order resummations/suitable for strong vs. weak correlation*:

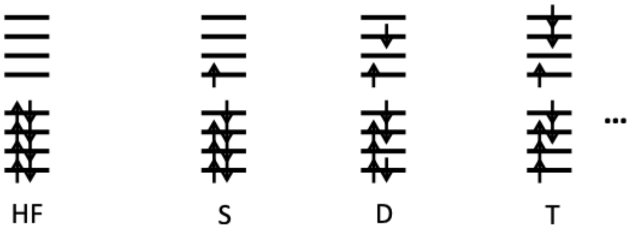
Random phase approximation (**RPA**, GF+PT), *Coupled-Cluster* (**CC**, WF+PT), *Configuration Interaction* (**CI**, WF+V), *Moller-Plesset* (**MP2**, WF+PT), *Algebraic Diagrammatic Construction* (**ADC**, WF+PT), **DMRG** (WF+V),…

Key starting point:

These methods (all?) remove any explicit reference to the exchange-correlation potential
Start from Hartree—Fock (know what you have to start from) [post-HF], or just the DFT orbitals [post-DFT]

A brief view of the (traditional) landscape of many-body quantum chemistry

- Return to rigorous and systematic hierarchy of approximations.
- No empiricism/fitting. Know how to improve (in principle).



$|\Psi_{HF}\rangle$ $\quad c_i^a|\Psi_i^a\rangle$ $\quad c_{ij}^{ab}|\Psi_{ij}^{ab}\rangle$ $\quad c_{ijk}^{abc}|\Psi_{ijk}^{abc}\rangle$

Reference determinant

Excited determinants

1) How to truncate this 'space' of configurations
2) How to find the coefficients

We conclude that traditional wavefunction methods, … are generally limited to a small number of electrons, $N < O(10)$.

Physical states and Hamiltonians are 'simple'

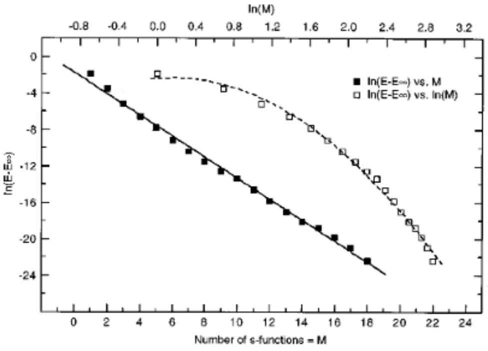
A brief view of the (traditional) landscape of many-body quantum chemistry

Lets converge wrt the explicit many-body effects to exactness,
by increasing #determinants / level of theory…?

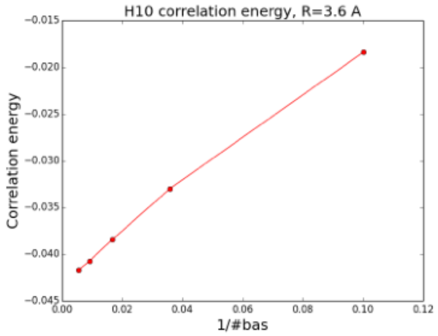
Level of Theory

HF **MP2** **CCSD** **CCSD(T)** **FCI**

A brief view of the (traditional) landscape of many-body quantum chemistry



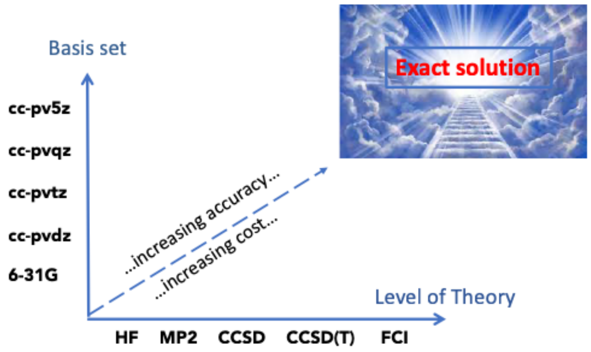
Mean-field methods converge **exponentially** with basis



Correlation energy converge as ~1/#basis

c.f. “F12” methods / explicit correlation

A brief view of the (traditional) landscape of many-body quantum chemistry



basis	orbitals	CCSD
cc-pVDZ	86	6.918
cc-pVTZ	204	6.660
cc-pVQZ	400	6.562
cc-pV5Z	694	6.474
cc-pV6Z	1106	6.428
CBS estimate	∞	6.365

CCSD ← Approximate many-body method

6.365 ← deviation due to further many-body effects

Butadiene (C_4H_6) lowest excitation (first optical peak) (eV)

Experimental excitation ~ 6.2 eV, resolution ~0.1 eV

Chan, Simon's electronic summerschool notes, 2016

A brief view of the (traditional) landscape of many-body quantum chemistry

MP2 (Moller—Plesset perturbation theory):

Property	HF accuracy	'Best' hybrid DFT accuracy	MP2
IPs and EAs	±0.5eV	±0.2eV [Delta SCF]	±0.2eV
Bond lengths	-1%	±1 pm	±1 pm
Vibrational Frequencies	+10%	-3%	+3%
Barrier heights	+30-50%	-25%	+10%
Bond energies	-50%	±0.1eV	±0.4 eV

https://ocw.mit.edu/: 5.61 Physical Chemistry

A brief view of the (traditional) landscape of many-body quantum chemistry

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Barrier heights	+30-50%	-25%	+10%
Bond energies	-50%	±0.1eV	±0.4 eV
Cost [canonical]	~N^4	~N^4	~N^5
Atoms [v. rough]	~1000	~1000	~50

- Similar accuracy to (hybrid) DFT. Higher cost.
- Can catastrophically fail [strong correlation, degeneracies, metals]

https://ocw.mit.edu/: 5.61 Physical Chemistry

A brief view of the (traditional) landscape of many-body quantum chemistry

Coupled-cluster

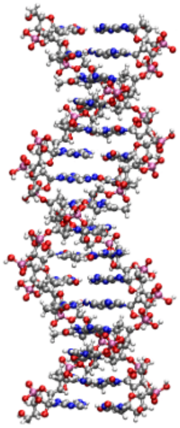
Property	HF accuracy	'Best' hybrid DFT accuracy	MP2	CCSD(T) [GOLD STANDARD]
IPs and EAs	±0.5eV	±0.2eV [Delta SCF]	±0.2eV	±0.02 eV
Bond lengths	-1%	±1 pm	±1 pm	±0.5 pm
Vibrational Frequencies	+10%	-3%	+3%	±5 cm^{-1}
Barrier heights	+30-50%	-25%	+10%	±2 kcal/mol
Bond energies	-50%	±0.1eV	±0.4 eV	±0.05eV
Cost [canonical]	~N^4	~N^4	~N^5	~N^{6-7}
Atoms [v. rough]	~1000	~1000	~50	~10

- **Gold standard** of many-body quantum chemistry
- Generally as good or better than many experiments

https://ocw.mit.edu/: 5.61 Physical Chemistry

But… huge progress…

MP2:

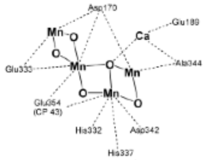


16 DNA base-pairs, Ochsenfeld, J. Chem. Phys. (2009)

Dynamics of liquid water, Del Ben et al., JCTC 2013

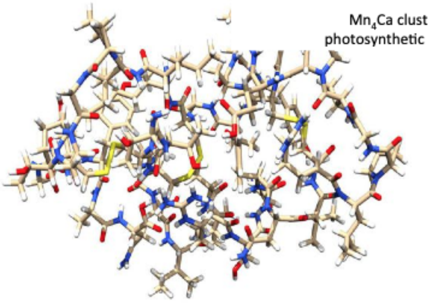
But… huge progress…

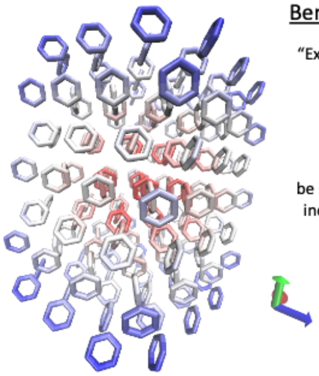
Coupled cluster:



$2H_2O + 4h\nu \rightarrow 4H^+ + 4e^- + O_2$

Mn_4Ca cluster:
photosynthetic center





Benzene molecular crystal

"Exact" theoretical lattice energy
55.97 ± 0.76 ± 0.1 kJ/mol

Exptal 0K extrapolation
51-53 kJ/mol

Expt. extrapolation must
be in error, revised extrapolation
increases lattice energy by 10%

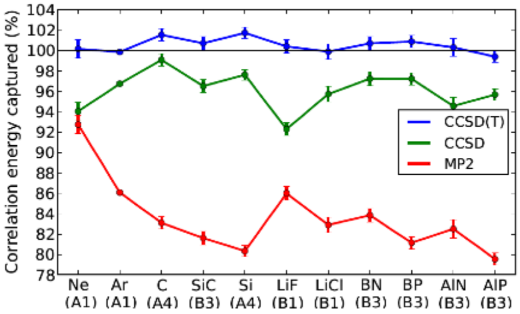
Yang, Hu, Usvyat, Matthews,
Schütz, and Chan, Science (2014)

Crambin protein fragment: 644 atoms, coupled cluster theory (CCSD)

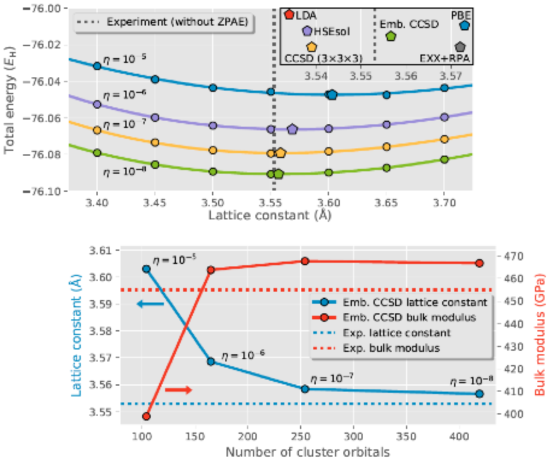
Riplinger and Neese J. Chem. Phys. (2013)

But… huge progress…

Towards application in solids:



Hierarchy still holds up…

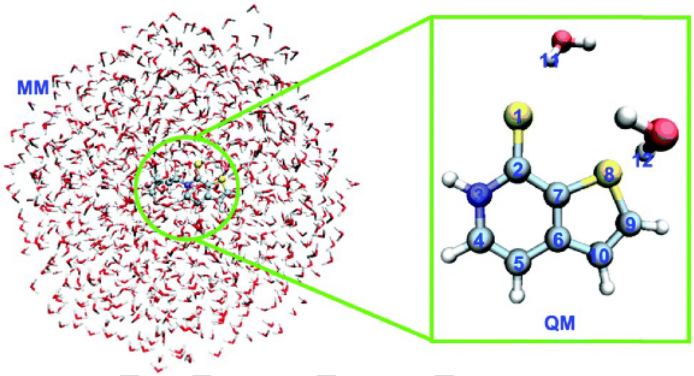


Can now converge results well within the spread of XC-fun

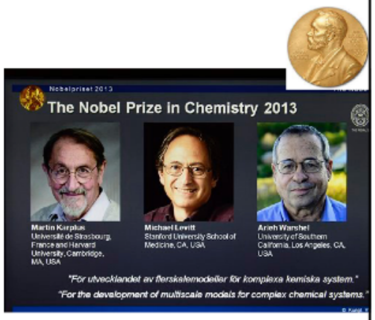
Locality of correlations

- Is a high-scaling of these many-body methods physical?
- Density matrix decays exponentially [insulators]: "nearsightedness"
- Even many-body correlations functions decay algebraically*

QM/MM approach



$$E = E_{MM} + E_{QM} + E_{QM-MM}$$



The Nobel Prize in Chemistry 2013

Martin Karplus
Université de Strasbourg, France and Harvard University, Cambridge, MA, USA

Michael Levitt
Stanford University School of Medicine, CA, USA

Arieh Warshel
University of Southern California, Los Angeles, CA, USA

"För utvecklandet av flerskalemodeller för komplexa kemiska system."

"For the development of multiscale models for complex chemical systems."

Can extend to e.g. CCSD(T):DFT:MM:Continuum layers
c.f. ONIOM

Locality of correlations

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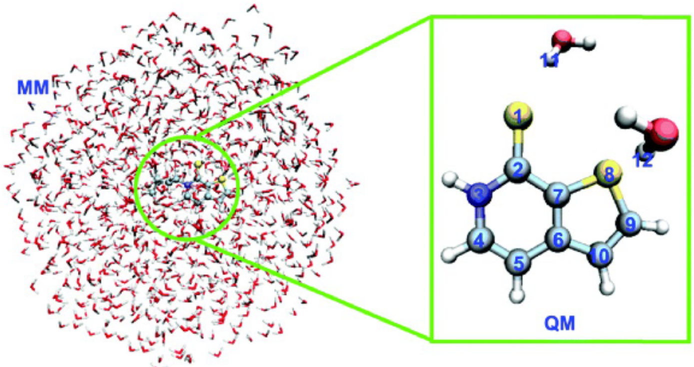


$$E = E_{MM} + E_{QM} + E_{QM-MM}$$

Significant challenge:
How to couple QM to environment

- *Mechanical embedding*

energy from interaction of charge densities

- *Electrostatic embedding*

MM forms potential felt by QM

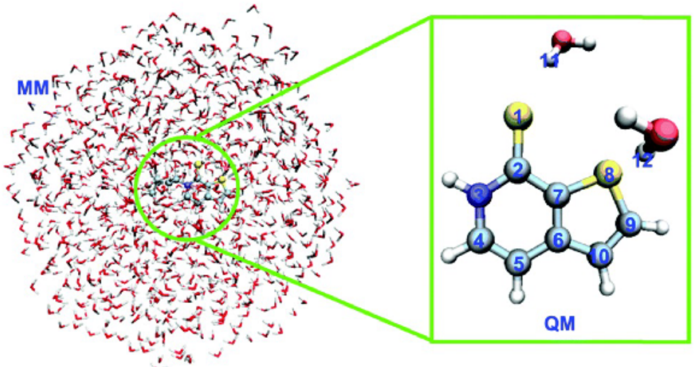
- *Polarizable embedding*

MM can relax due to QM

Locality of correlations

- Is a high-scaling of these many-body methods physical?

- Density matrix decays exponentially [insulators]: “nearsightedness”
- Even many-body correlations functions decay algebraically*



$$E = E_{MM} + E_{QM} + E_{QM-MM}$$

Significant challenge:
How to couple QM to environment

- However, these still neglect quantum entanglement (e.g. hybridization) between subsystems
  - especially important for **covalent bonds**

- Various ‘hacks’ to fix: Link atoms

Rigorous approach:
‘Quantum’ embedding
(c.f. DMFT and others)

…for ‘next time’…

Summary

- Failures and challenges of mean-field theory and DFT
- Emerging approaches to ‘fix’ DFT:
  - LDA+U, LDA+DMFT
  - ‘Rigorous’ many-body quantum chemistry
- Quantum chemistry in a nutshell
- Ideas behind multiscale and embedded approaches for large systems

Thanks!