

SCAN in context

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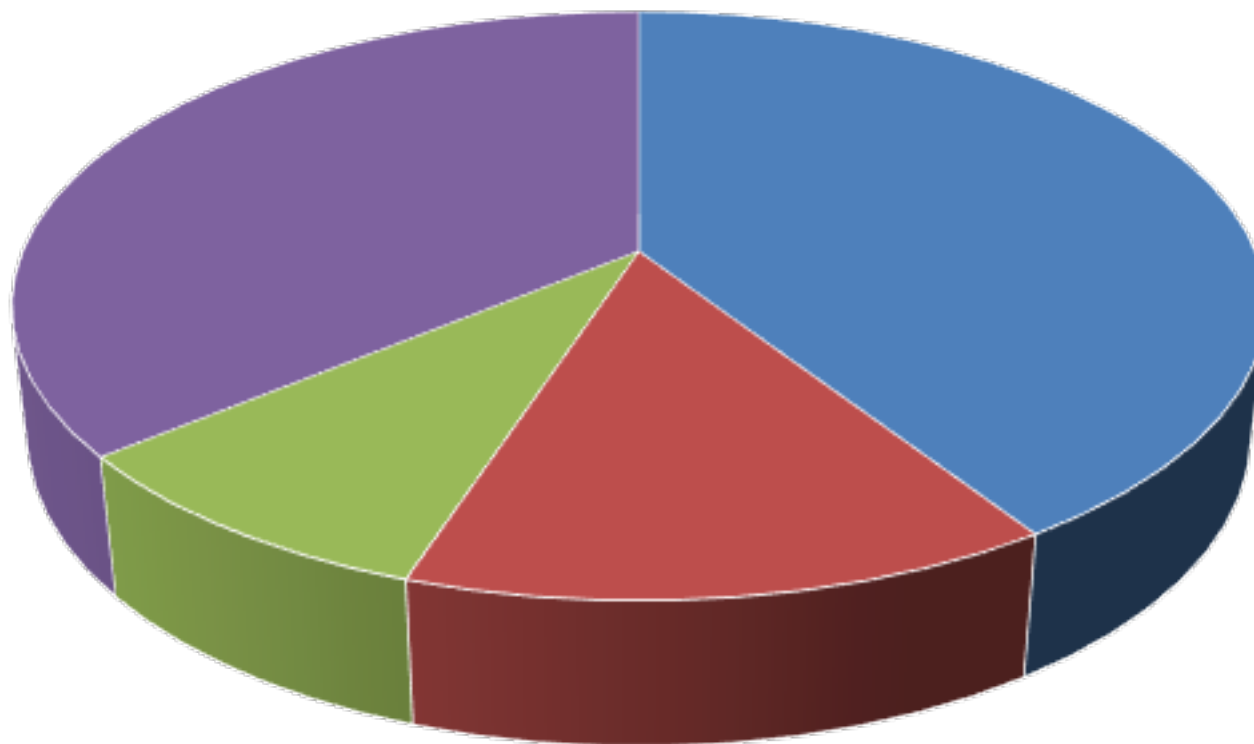
<http://dft.uci.edu>

Outline

- Brief history of DFT
- Popular approximations
- Today's uses of DFT
- Meta-GGA's
- My first use of SCAN:
 - Adiabatic spin energy differences for Fe(II) clusters

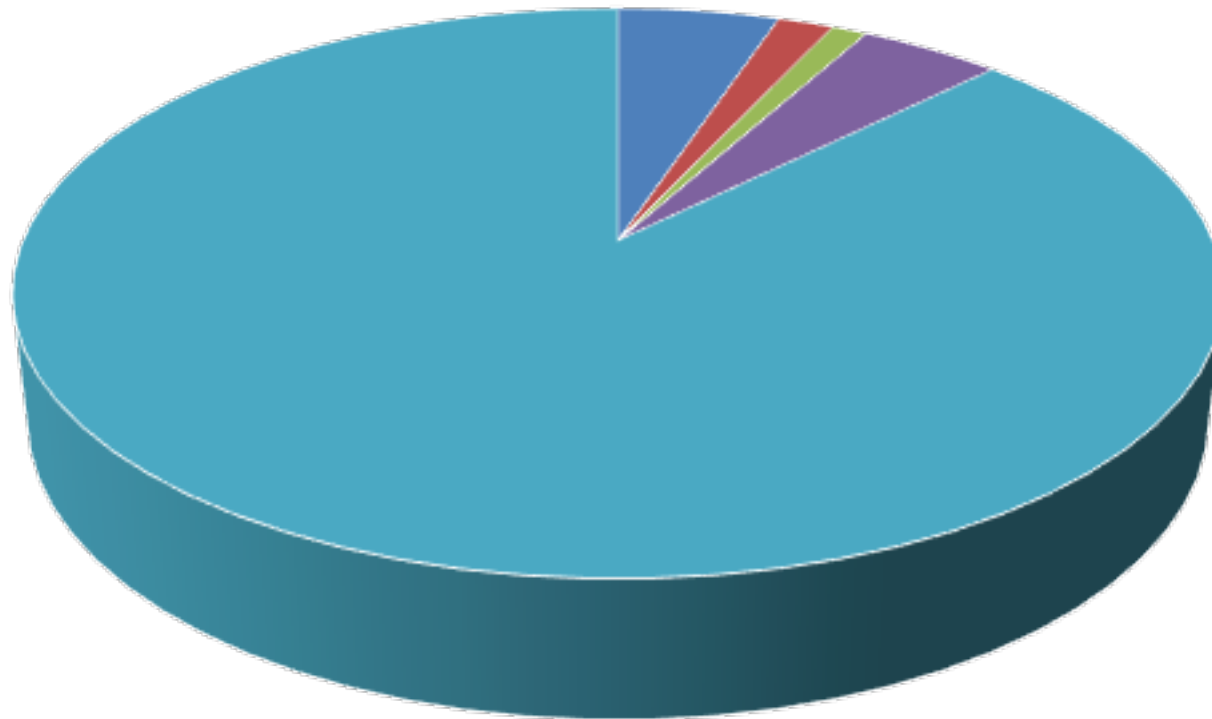
Non-DFT electronic structure methods

2000 papers in 2016

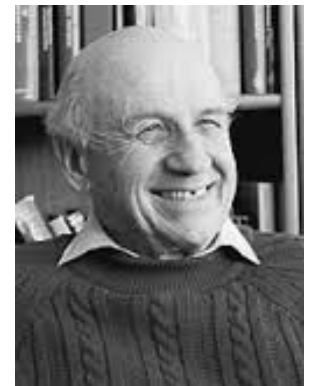


■ Quantum Monte Carlo ■ Dynamical mean field theory ■ Density Matrix renormalization group ■ coupled cluster

All electronic structure



- Quantum Monte Carlo
- Dynamical mean field theory
- Density Matrix renormalization group
- coupled cluster
- DFT



Thomas/Fermi Theory 1927

- Derived in 1926 without Schrodinger eqn.

The Calculation of Atomic Fields

L. H. THOMAS (*Proc. Camb. Phil. Soc.* 23, p. 542-548)

Trinity College

[Received 6 November, read 22 November 1926.]

- Thomas-Fermi Theory (TF):

- $T \approx T^{\text{TF}}$

- $V_{ee} \approx U = \text{Hartree energy}$

- $V = \int dr n(r) v(r)$

- $E_0 = T + V_{ee} + V$

- Minimize $E_0[n]$ for fixed N

$$T_s^{loc} = \frac{3(3\pi)^{2/3}}{10} \int d^3r n^{5/3}(r)$$

$$U = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|}$$

The theoretical calculation of observable atomic constants is often only possible if the effective electric field inside the atom is known. Some fields have been calculated to fit observed data* but for many elements no such fields are available. In the following paper a method is given by which approximate fields can easily be determined for heavy atoms from theoretical considerations alone.

- Properties:

- Typical error of order 10%

- Teller's unbinding theorem: Molecules don't bind.

KS equations (1965)

Define *fictitious* non-interacting electrons satisfying:

$$\left\{ -\frac{1}{2}\nabla^2 + v_S(\mathbf{r}) \right\} \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r}), \quad \sum_{j=1}^N |\phi_j(\mathbf{r})|^2 = n(\mathbf{r}).$$

where $v_S(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

Define T_S as the kinetic energy of the KS electrons, U as their Hartree energy and

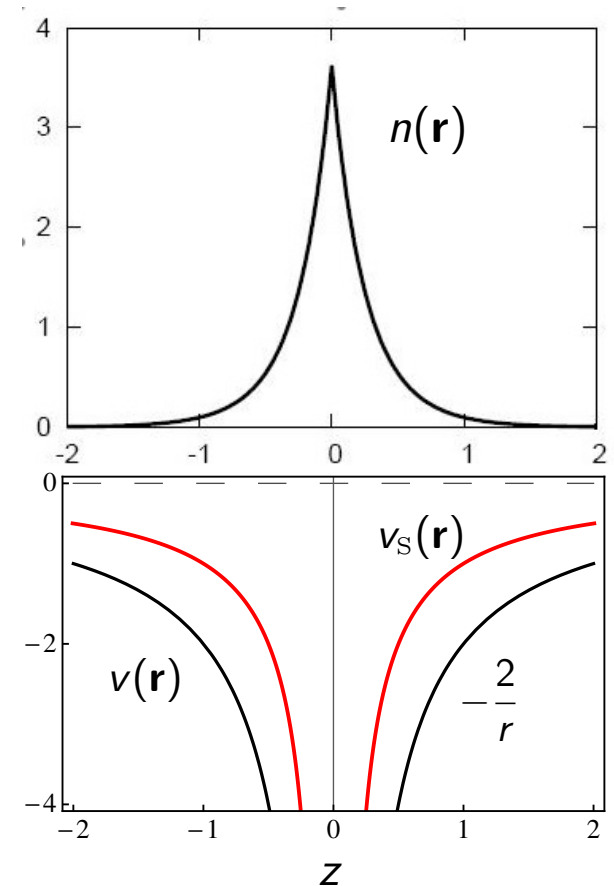
$$T + V_{ee} = T_S + U + E_{XC}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

$$v_S(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{XC}[n](\mathbf{r}), \quad v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}$$

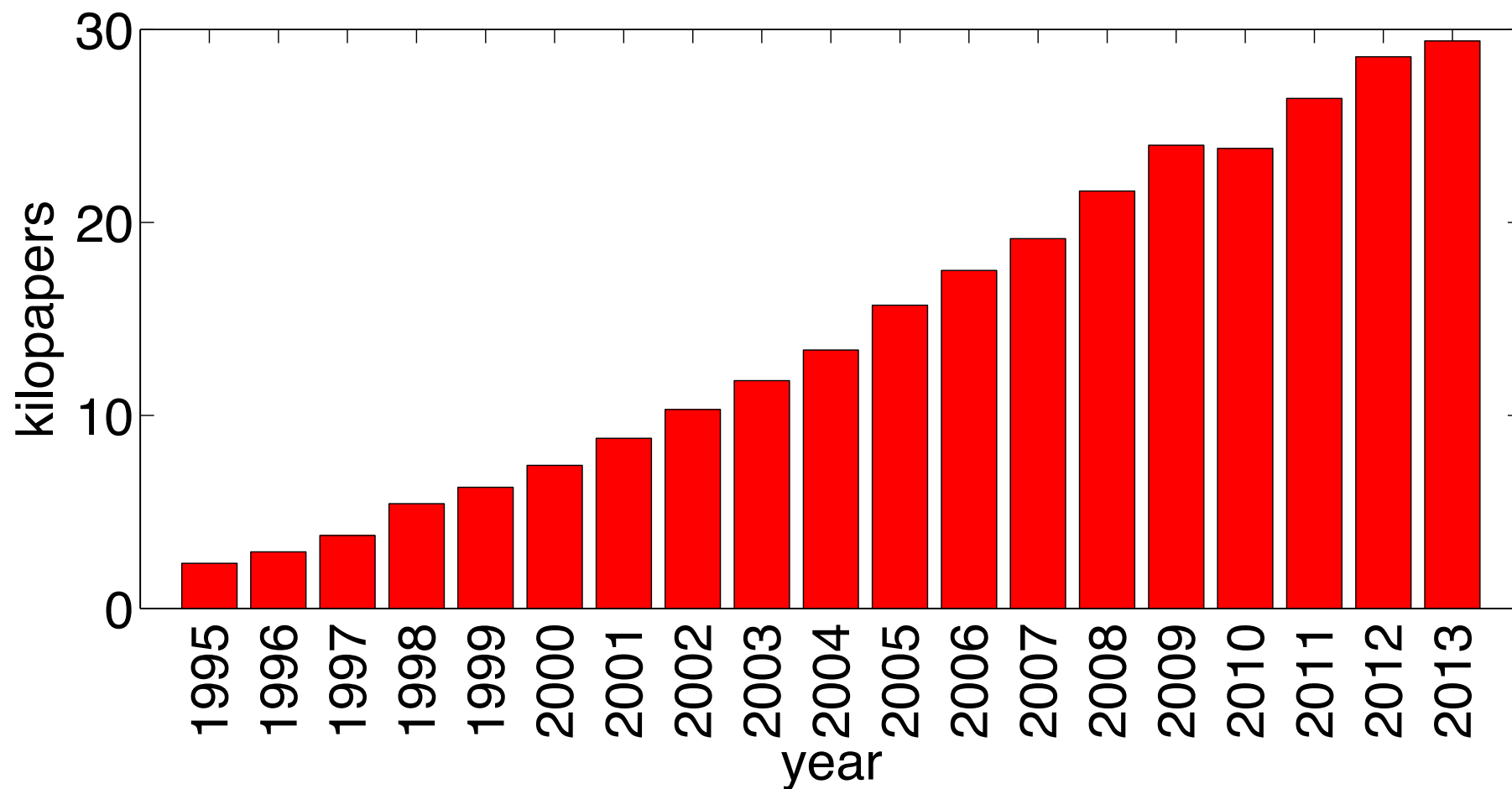
Knowing $E_{XC}[n]$ gives closed set of self-consistent equations.



Today's commonly-used functionals

- **Local density approximation (LDA)** $E_X^{\text{LDA}}[n] = A_X \int d^3r n^{4/3}(\mathbf{r})$
 - Uses only $n(\mathbf{r})$ at a point. $A_X = -(3/4)(3/\pi)^{1/3} = -0.738.$
- **Generalized gradient approx (GGA)**
 - Uses both $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$
 - Should be more accurate, corrects overbinding of LDA
 - Examples are PBE and BLYP
- **Hybrid:**
 - Mixes some fraction of HF
 - Examples are B3LYP and PBE0

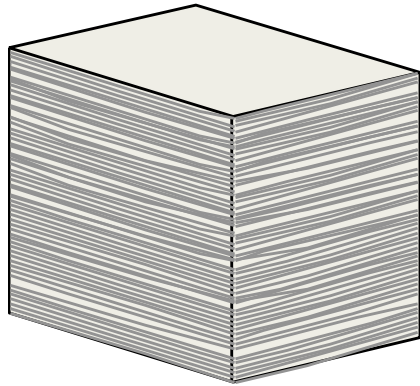
DFT papers



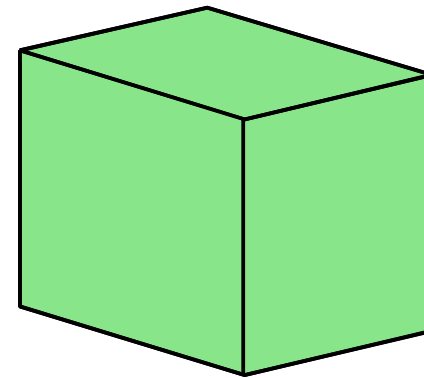
DFT: A Theory Full of Holes, Aurora Pribram-Jones, David A. Gross, Kieron Burke, Annual Review of Physical Chemistry (2014).

Key

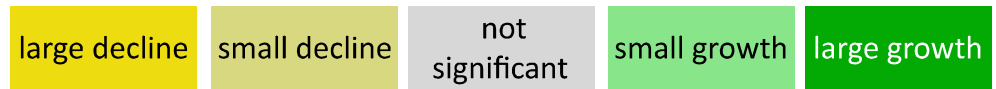
Paper Stacks:
Percentage of papers which
contribute to a discipline



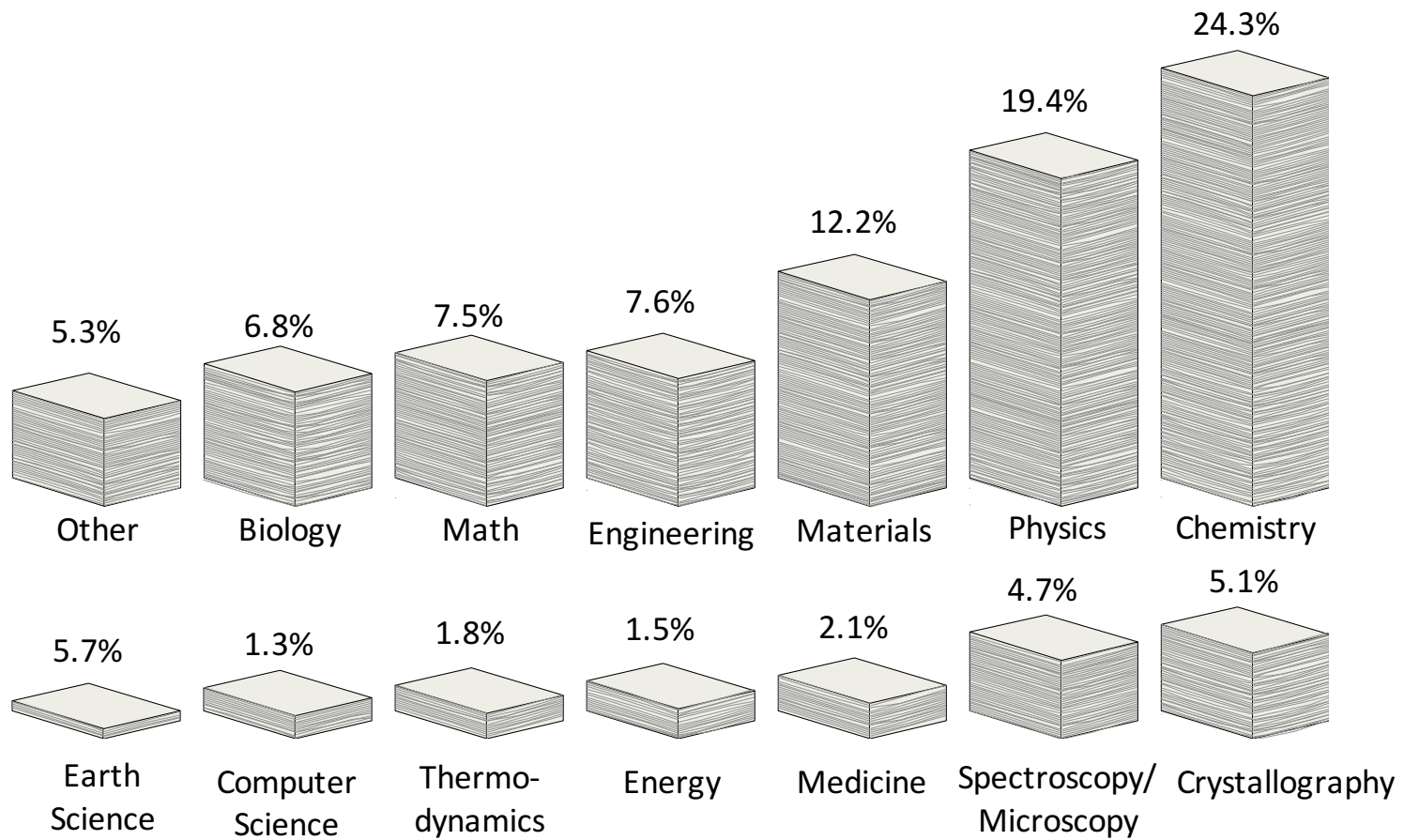
Colors indicate change in the
citation distribution
(market share)



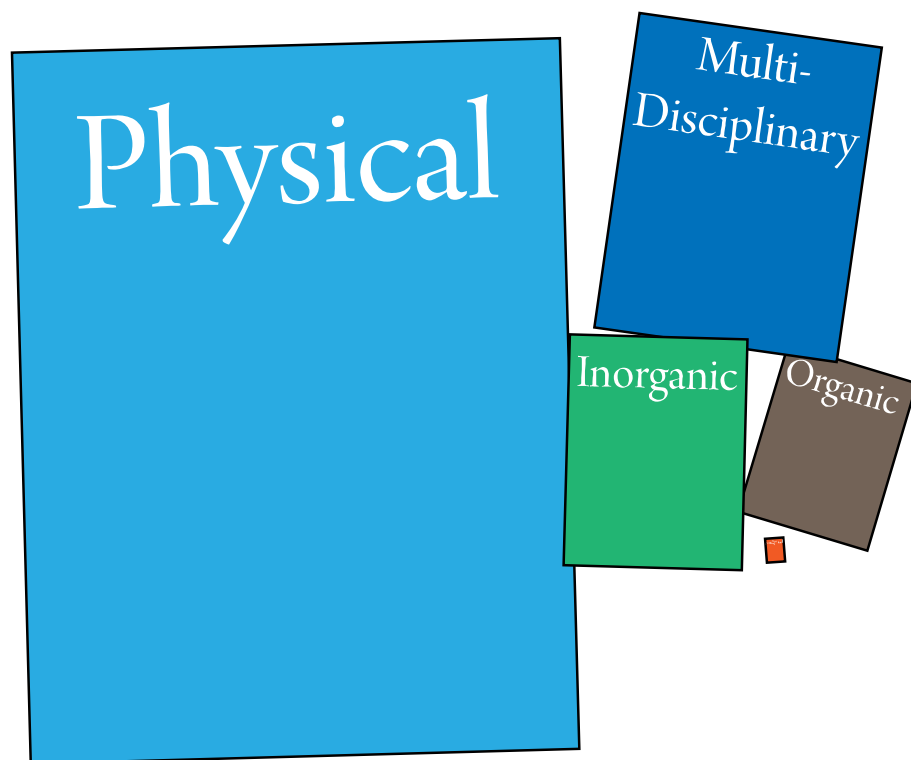
Color key:



Who uses DFT?



Chemistry (24%)



47% Physical

21% Multidisciplinary

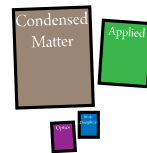
15% Inorganic

11% Organic

2% Analytical

Physics (19%)

Atomic/
Chemical



80% Atomic/Chemical

9% Condensed Matter

5% Applied

3% Optics

2% Multidisciplinary

Materials (12%)



53% Multidisciplinary

30% Nanomaterials

9% Polymers

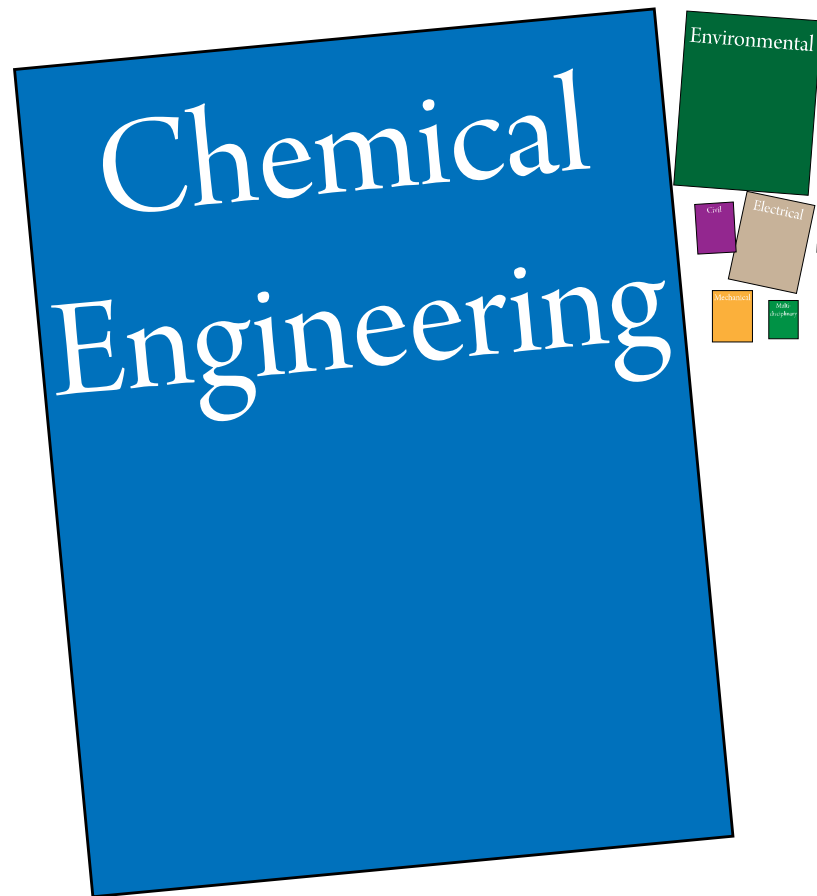
3% Films/coatings

2% Textiles

2% Metallurgy

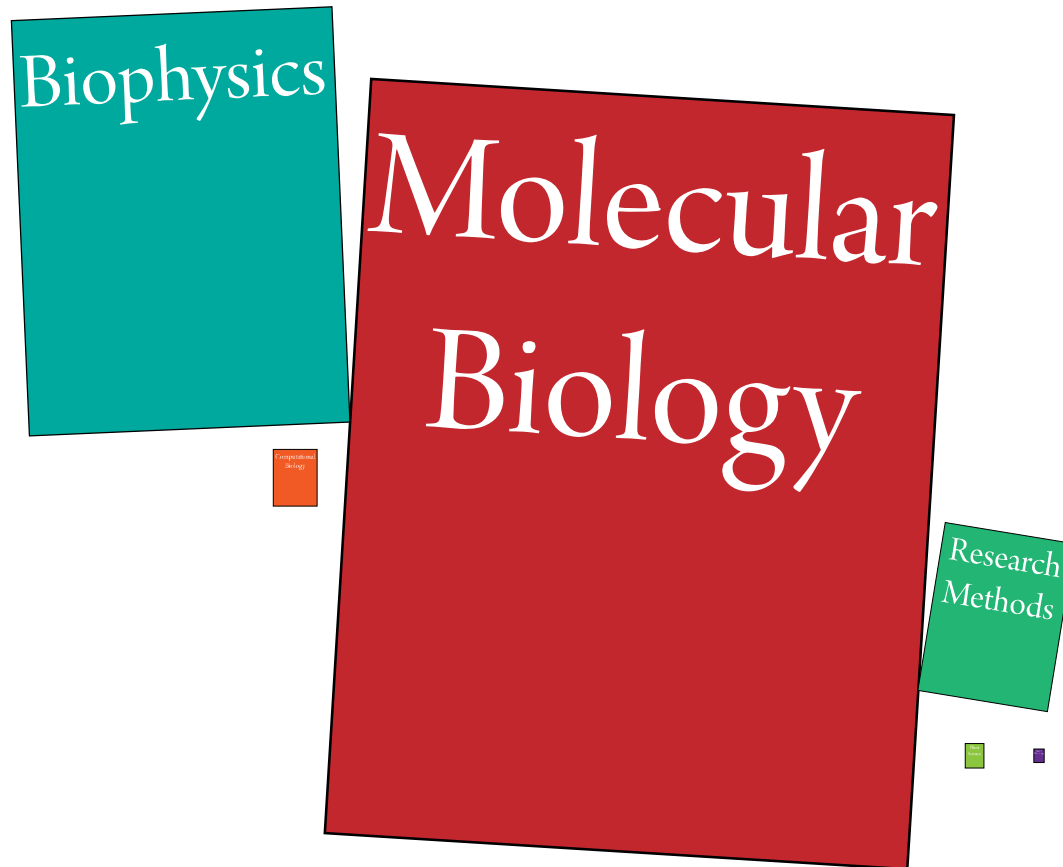
1% Ceramics

Engineering (8%)



- 65% Chemical
- 13% Environmental
- 7% Electrical
- 4% Mechanical
- 4% Civil
- 3% Multidisciplinary
- 1% Biomedical

Biology (7%)



51% Molecular Biology

28% Biophysics

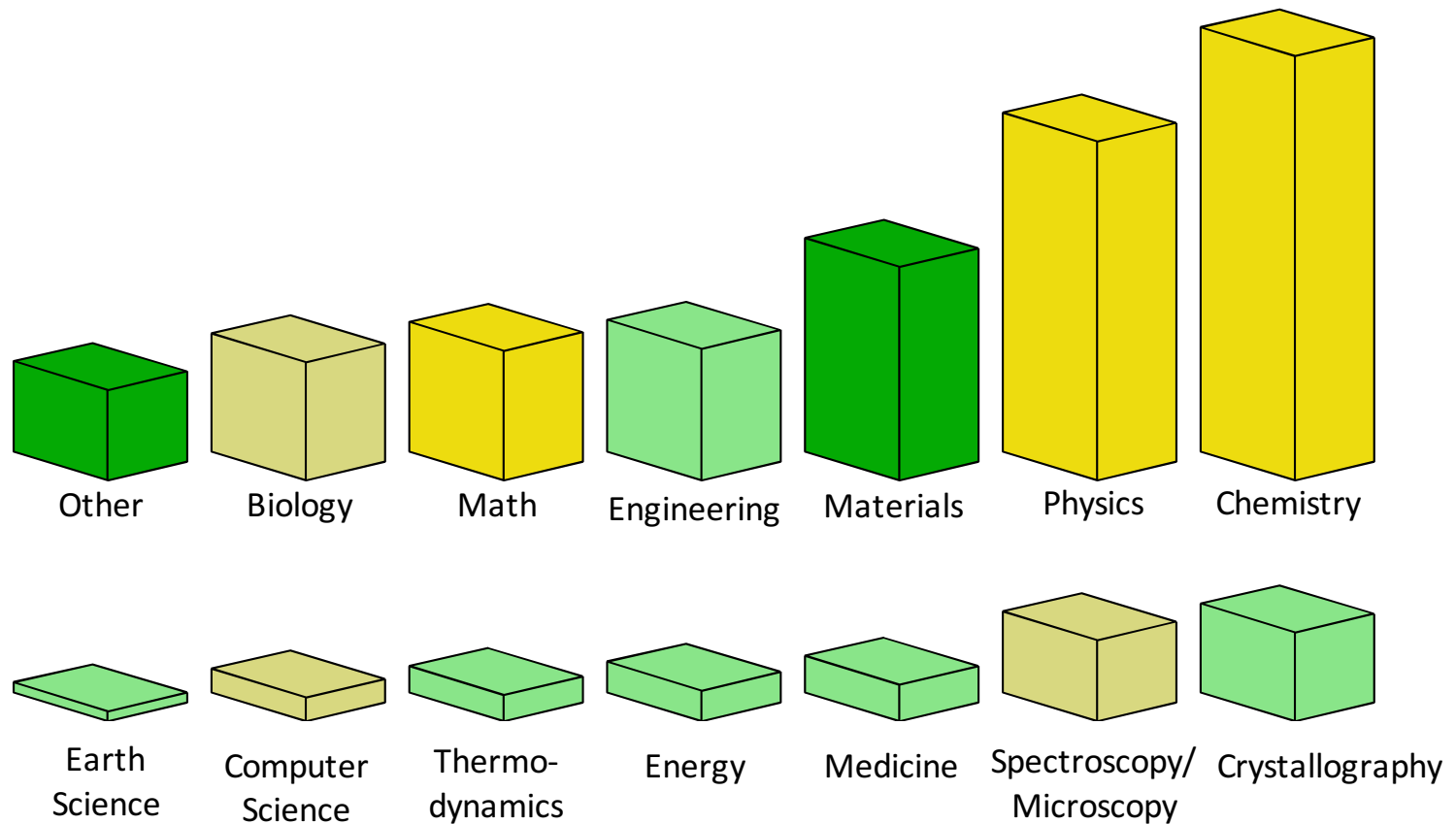
11% Research Methods

4% Computational Biology

2% Plant Science

1% Applied Microbiology

Who will be using DFT?



Meta-GGA

- Hybrids deliver higher accuracy (usually), but much more expensive for solids (HSE06)
- Meta-GGA is logical generalization of GGA
 - Uses kinetic energy density (semi-local ingredient)
 - Does not need total non-locality of Fock integral
- Goal:
 - Achieve hybrid-level accuracy (or better) without hybrid cost

The path to SCAN

- PBE (1996)
- PKZB (1999)
- TPSS (2003)
- revTPSS (2009)
- SCAN (2015)

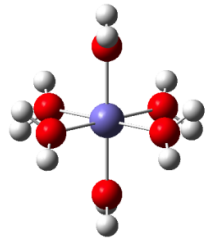
Naming scan

- Strongly constrained, appropriately trained (SCAT)
- Strongly constrained, appropriately normed (SCAN)
- Strongly constrained, appropriately meaned (SCAM)
- Strongly protected, appropriately meaned (SPAM)

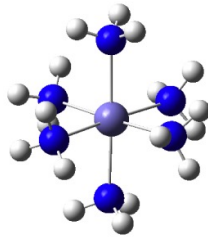
Density-corrected DFT

- In abnormal DFT calculations, energy error is dominated by delocalization error in density
- For molecules, often using the HF density improves results a lot
- Fixed anions, ions and radicals in solution, transition state barriers, molecular dissociation curves...
- But never tried it for spin before...
- All work by Suhwan Song and Eunji Sim, Yonsei

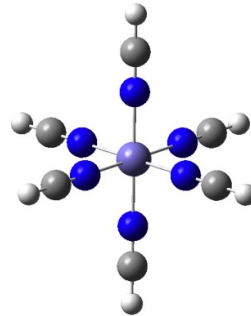
SCO complexes



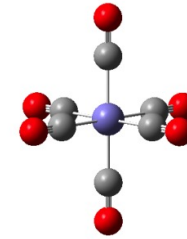
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



$[\text{Fe}(\text{NH}_3)_6]^{2+}$



$[\text{Fe}(\text{NCH})_6]^{2+}$



$[\text{Fe}(\text{CO})_6]^{2+}$

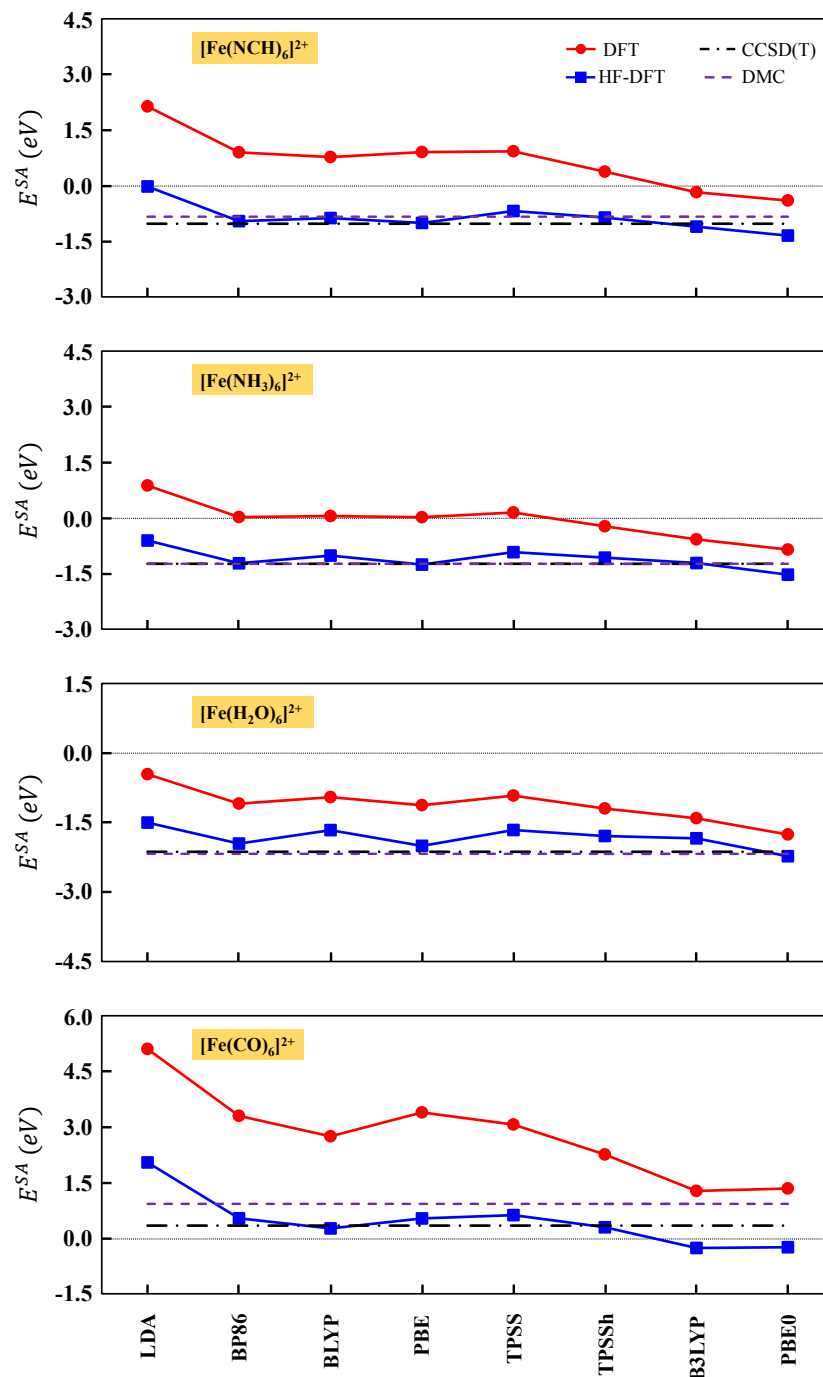
(exp.) HS stable Complexes

(exp.) LS stable Complex

- Fe (II) with 6 ligands attached
- FeL_6^{++}
- 'Small' ones have $\text{L}=\text{CO}, \text{H}_2\text{O}, \text{NCH}, \text{NH}_3$
- $E^{\text{SA}} = E^{\text{HS}} - E^{\text{LS}}$ is substantial
- Very important in spintronics and molecular magnets
- Size means DFT only game in town
- Here, ground-state depends crucially on spin state.

Prel

SCO's



Consistent DFT results for SCO complexes

Suhwan Song, Eunji Sim, Anouar Benali, Olle Heinonen, and Kieron Burke, in preparation

Rainbow slide

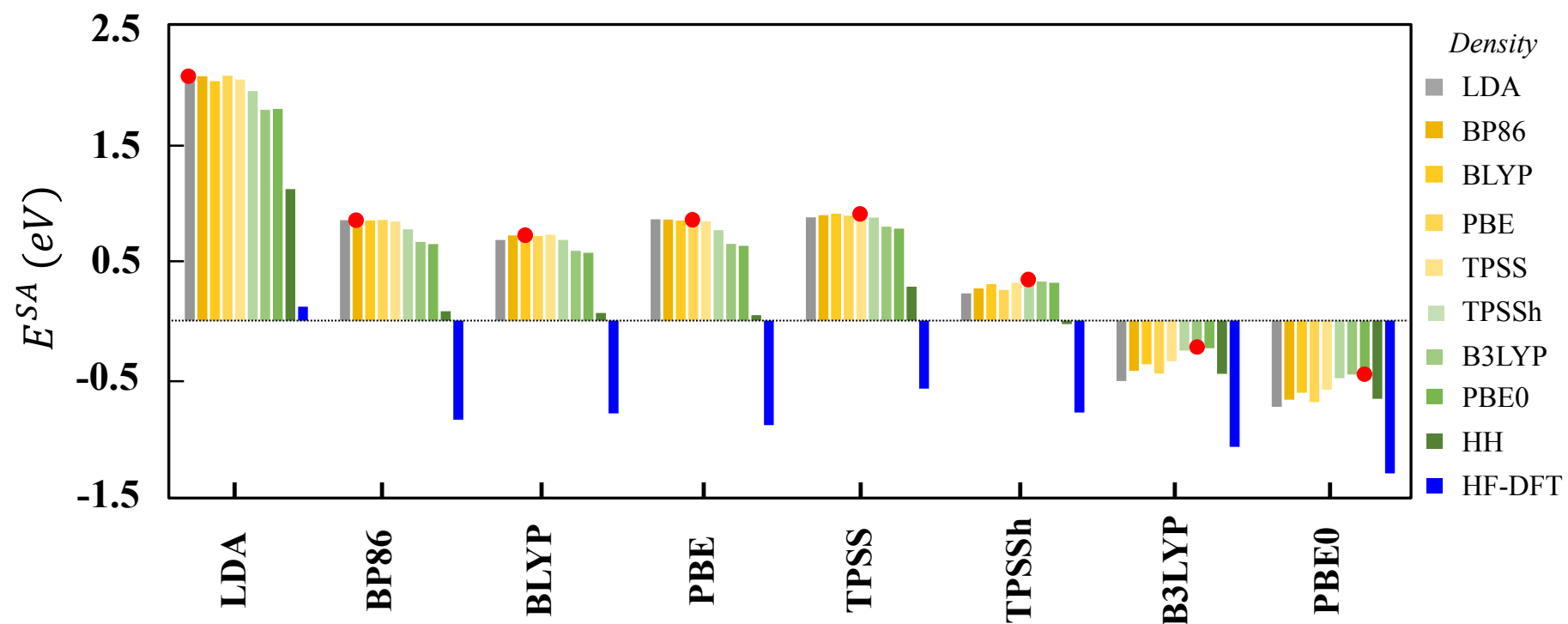


FIG. 2. SA of NCH complex evaluated with several different XC approximations on several different self-consistent densities (red dots) and the HF density (blue bar). The x-axis labels the energy functional, the colored bars indicate which density (grey is LDA, yellow is GGA/mGGA, green is hybrid, and blue is HF). The dark green bar uses the self-consistent density of Becke's half-and-half functional (HH), which contains 50% exact exchange. The purple horizontal line is DMC and black is CCSD(T).

Density difference for CO complex

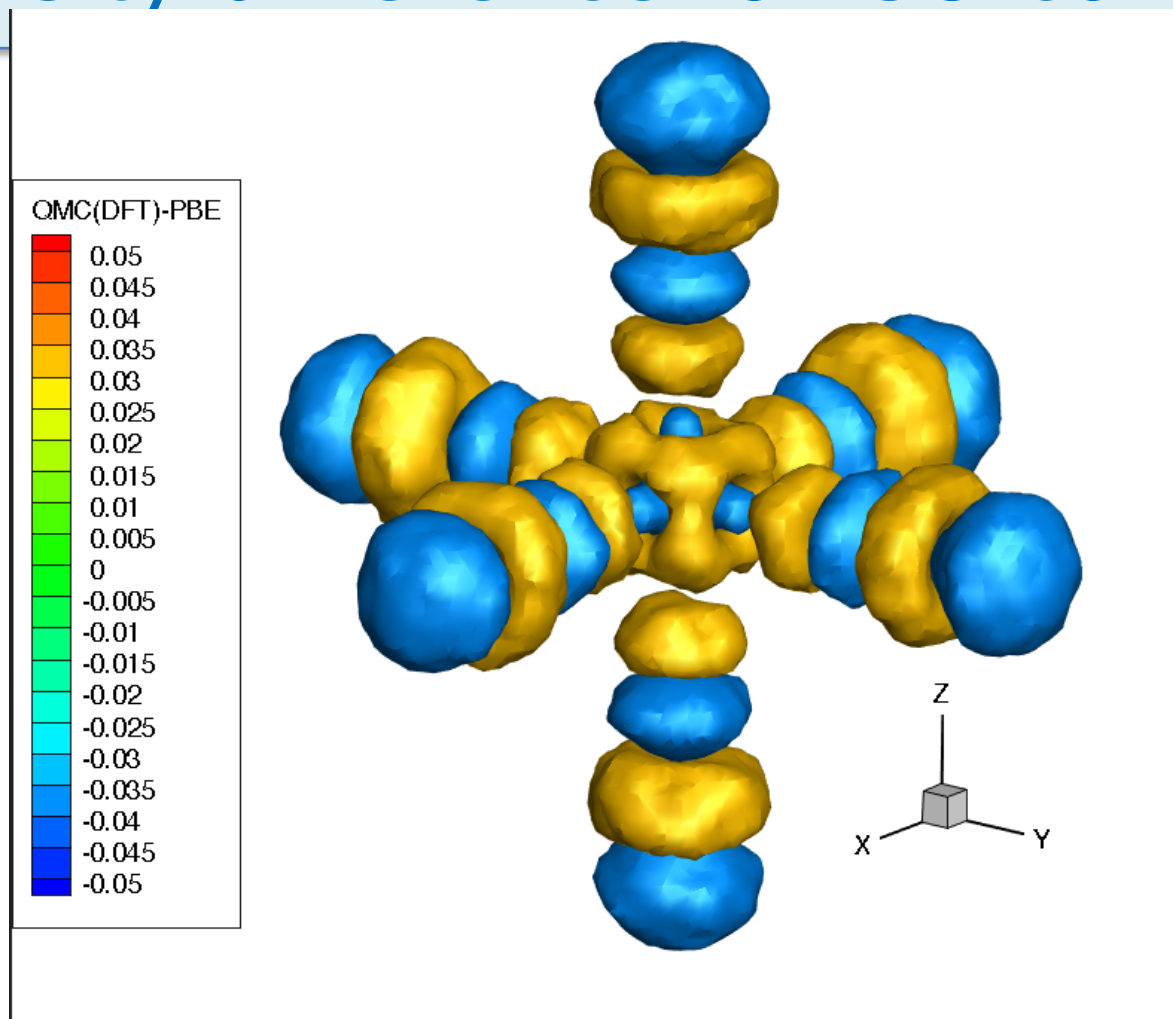
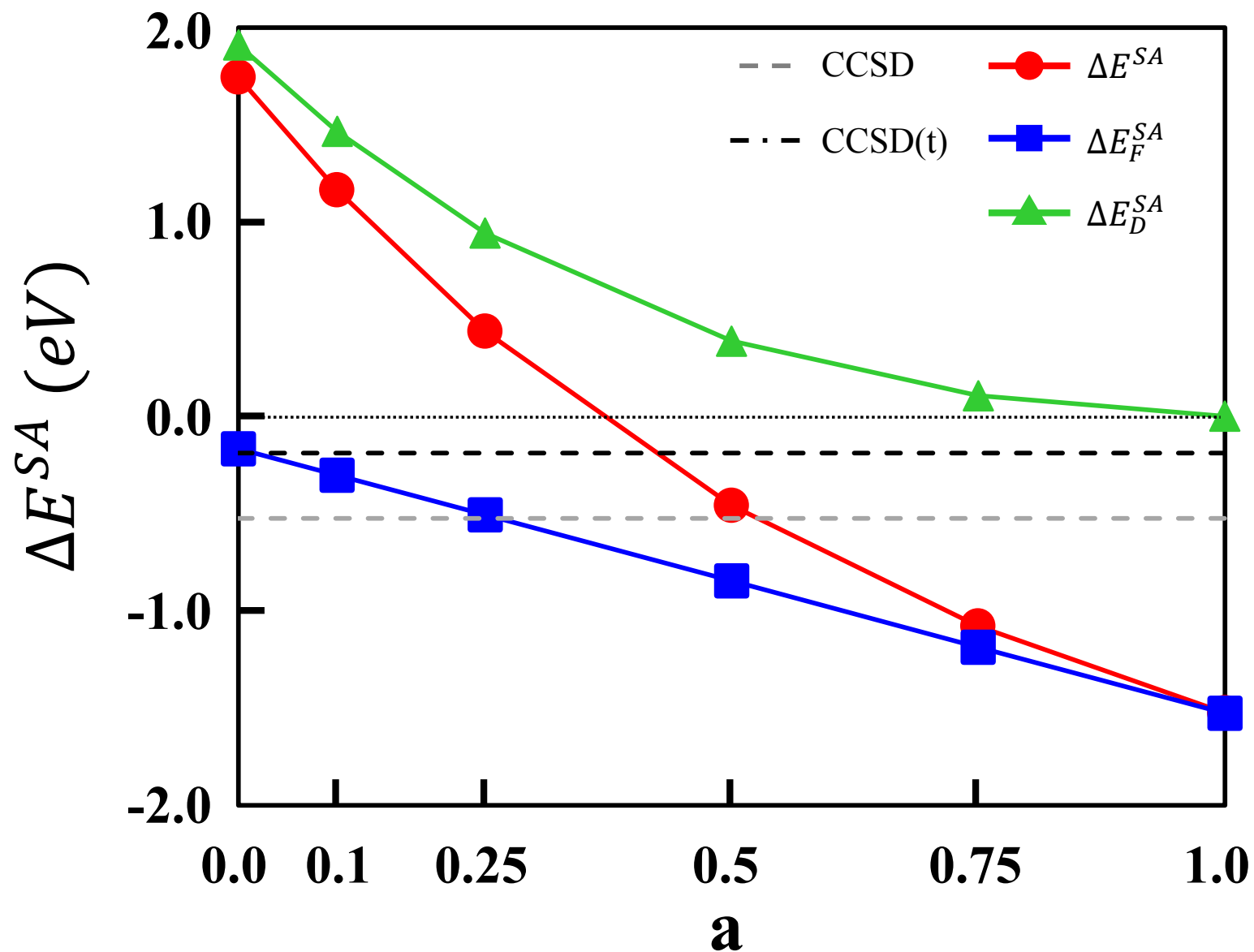
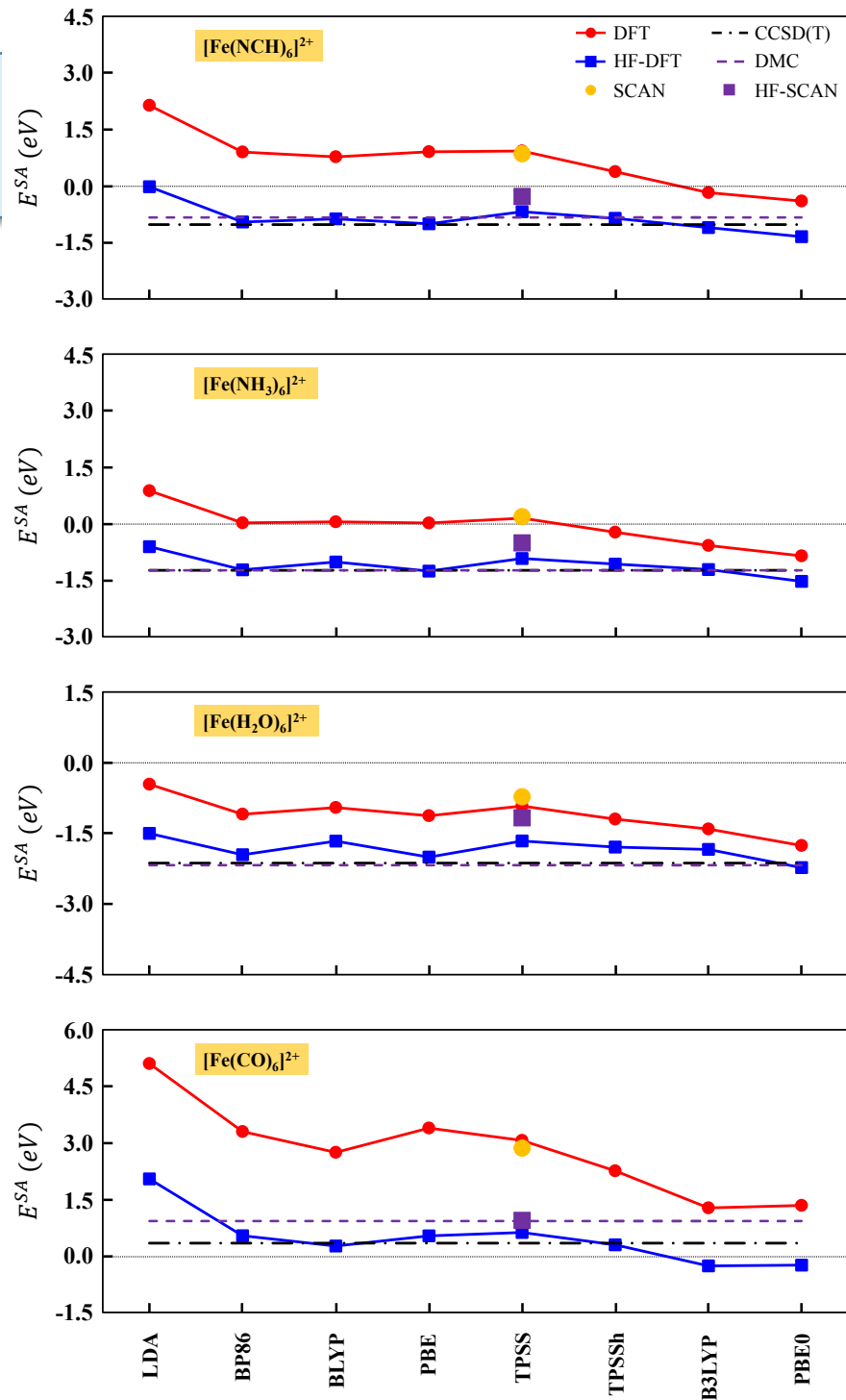


FIG. 3: Isosurfaces (left) and 2D contour plots (right) of the density difference in units of \AA^{-3} between QMC(DFT) and PBE densities for the HS (a) and the LS (b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ complex.

Escaping the parameter dilemma





Summary

- KS-DFT dominates electronic structure calculations in almost all fields
- SCAN has tremendous potential to improve ten's of thousands of published calculations per year (i.e., make PBE obsolete)
- Might need some more work on the spin-dependence.
- Thanks to NSF and Korea for funding.

My first SCAN

