

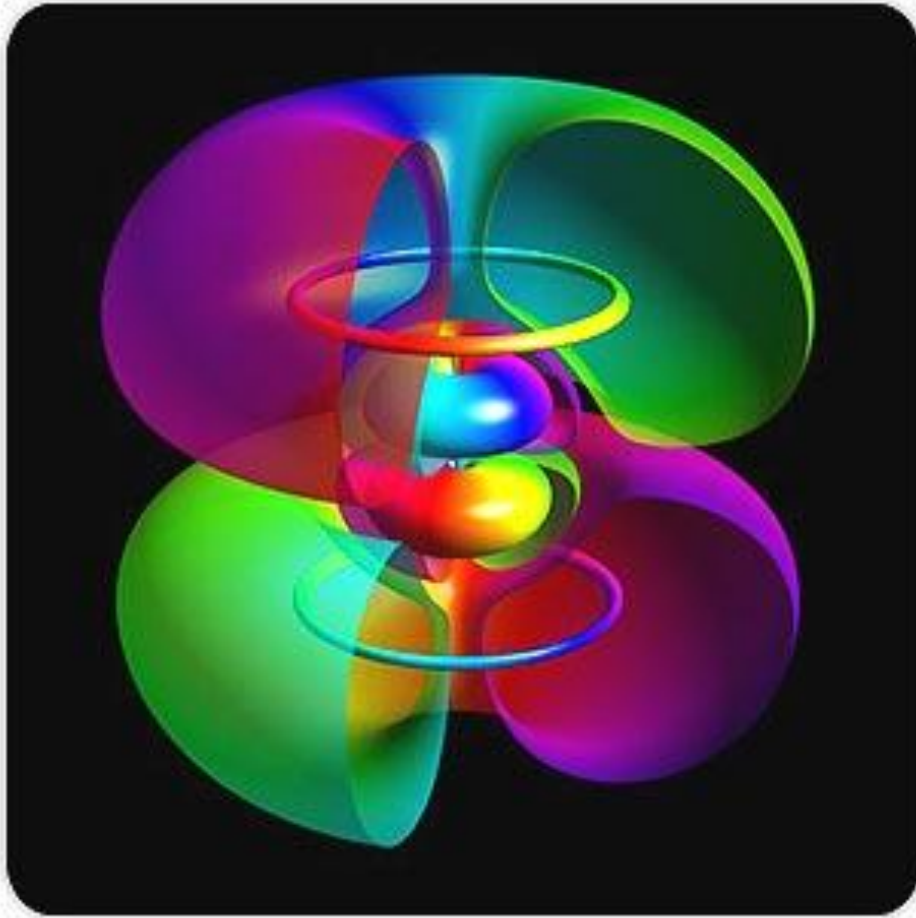
# Density Functional Theory (DFT)

$$E_{\text{🍫}} = \int_{\mathbb{R}^3}^{\text{🍫}} [\rho_{\alpha}(\vec{r}), \rho_{\beta}(\vec{r})] d\vec{r}$$

# Agenda

- The mechanism of DFT
- Derivation of KS-DFT
- The Many Flavors of KS-DFT
- Accuracy of DFT
- Pros/Cons of DFT
- References

# Wavefunction Approach



Hydrogen  $\psi_{421}$  Wavefunction at  
Density Isosurface.

Really hard to find

$$|\Psi(\vec{r}_1, \vec{r}_2, \dots)\rangle \rightarrow O(\vec{r})$$

Easy to do this

Why? Because of Hermitian Operators:

$$O(\vec{r}) = \Psi^\dagger(\vec{r}_1, \vec{r}_2, \dots) \hat{O}(\vec{r}) \Psi(\vec{r}_1, \vec{r}_2, \dots)$$

Kinetic Energy Density:

$$\tau(\vec{r}) = \Psi^\dagger(\vec{r}_1, \vec{r}_2, \dots) \left[ -\frac{1}{2} \nabla^2(\vec{r}) \right] \Psi(\vec{r}_1, \vec{r}_2, \dots)$$

# Density Functional Approach



Hydrogen  $\rho_{421}$  Density  
(Why is it grayscale?)

Probably easier to find

$$|\Psi(\vec{r}_1, \vec{r}_2, \dots)\rangle \rightarrow \rho_\alpha(\vec{r}), \rho_\beta(\vec{r}) \rightarrow O(\vec{r})$$

A bit less obvious

The density completely defines the observable state of the system:

$$O(\vec{r}) = f(\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}))$$

The way in which it does so (the *functional*) is very difficult to determine sometimes:

$$f = ?$$

Still, if we're going to fudge it anyways, we don't need to commit yet!

# How many $\rho$ and $\psi$ are there?

- There are infinitely many possible wavefunctions for any given density field, due to *phase factor*:

1 particle example:

$$\begin{aligned} |\psi(\vec{r}_1)\rangle &= A(\psi(\vec{r}_1))e^{i\phi(\psi(\vec{r}_1))} \Rightarrow \rho(\vec{r}) = \psi^\dagger(\vec{r}_1)\hat{1}(\vec{r})\psi(\vec{r}_1) \\ &= A(\psi(\vec{r}_1))e^{-i\phi(\psi(\vec{r}_1))} A(\psi(\vec{r}_1))e^{i\phi(\psi(\vec{r}_1))} = A^2(\vec{r}_1) \end{aligned}$$

- There are infinitely many possible density fields for any given electron count, due to geometric freedom.
- Some charge-constrained density fields are better than others, but all density-constrained wavefunctions give the same observables.

# Derivation of KS-DFT: Determining $\rho$

- How do we pick the right density field? Write the functional for energy in terms of density field, and minimize the energy variationally:

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}]$$

- This is mathematically justified by the Levy Constrained-Search formalism:

$$E_0 = \min_{\rho \rightarrow N} \left( \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} | \Psi \rangle \right)$$

# The Universal Functional

- Introduce the “Universal Functional” which encapsulates all electron-only physics:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

- Yields:

$$\Rightarrow E_0 = \min_{\rho \rightarrow N} \left( F[\rho] + \int_{R^3} \rho(\vec{r}_1) \hat{V}_{Ne} d\vec{r}_1 \right)$$

- The Universal Functional may be defined as:

$$F[\rho] = T[\rho] + J[\rho] + E_{\text{ncl}}[\rho]$$

Kinetic Energy  
Functional

Classical Coulomb  
Functional

Correlation (Nonclassical)  
Functional

# The Difficult Bit (Kinetic Energy)

- Functionals are able to be (at least approximately) developed for:
  - Nuclear-electron attraction (exact)
  - Classical Coulomb electron repulsion (exact)
  - Dynamical correlation (approximate)
  - Exchange (approximate)
- Functionals are very hard to define for:
  - **Kinetic Energy** ← Dealbreaker!  
(Almost)
  - Nondynamical correlation
  - Dispersion



# Breakthrough: The Kohn-Sham Witchcraft

- Build your density field from a noninteracting set of Slater orbitals (moving in an effective potential), and take the KE from there:

$$T_s = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle$$

- Such that

$$\sum_i^N |\phi_i(\vec{r})|^2 = \rho(\vec{r})$$

- These orbitals will not have the true kinetic energy, as the wavefunction we are aiming for is more complex, but the difference is small, and can be corrected with other functionals if needed.

# Do what you can and Fudge The rest (DFT)

- So now the energy functional reads:

$$E[\rho(\vec{r})] = E_{Ne}[\rho(\vec{r})] + T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$$

- And we know:

$$E_{Ne}[\rho(\vec{r})] = \int_{\mathbb{R}^3} \rho(\vec{r}) \sum_A \frac{Z_A}{r_A} d\vec{r}$$

$$T_s[\rho(\vec{r})] = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle$$

$$J[\rho(\vec{r})] = \frac{1}{2} \iint_{\mathbb{R}^6} \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

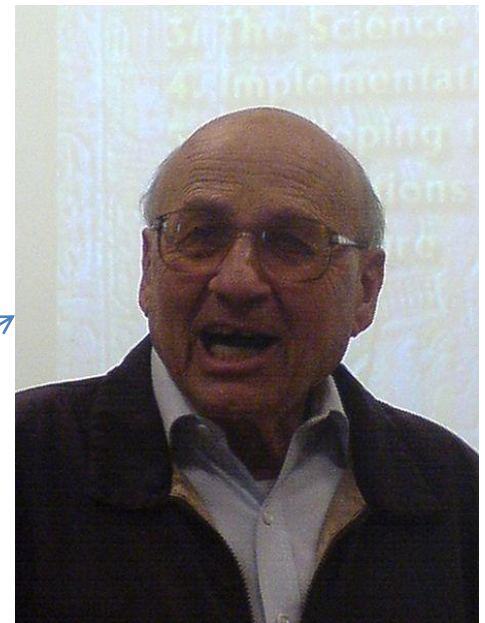
# The Exchange-Correlation Functional

$$\begin{aligned} E_{XC}[\rho(\vec{r})] &= (T[\rho(\vec{r})] - T_s[\rho(\vec{r})]) + E_{\text{ncl}}[\rho(\vec{r})] \\ &= E_{\Delta}[\rho(\vec{r})] + E_X[\rho(\vec{r})] + E_C[\rho(\vec{r})] \end{aligned}$$

So we now have three fudge factors to designate as we wish:

- KE correction functional (neglected)
- Exchange functional
- Correlation functional

Walter Kohn  
Epic Physicist



# The Kohn-Sham Equations:

- So finally, after all the mind games:

$$E[\rho(\vec{r})] = E_{Ne}[\rho(\vec{r})] + T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$$

- Now use Variational Calculus to force the first variation of E to zero under orthonormality/antisymmetry of the KS orbitals:

$$\Rightarrow \left\{ -\frac{1}{2}\nabla^2 - \sum_A^M \frac{Z_A}{r_{iA}} + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) \right\} \phi_i = \epsilon_i \phi_i$$

- Where the exchange-correlation function (what programmers call the functional) is abstractly:

$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho}$$

# Introduction of a Basis

- Introducing a finite basis as Roothaan did for HF:

$$\phi_i(\vec{r}) = \sum_{\mu=1}^L C_{\mu i} \eta_{\mu}(\vec{r})$$

- Applying the Galerkin Method:

$$F^{KS} C = S C \epsilon$$

$$F_{\mu\nu}^{KS} = -\frac{1}{2} \int \eta_{\nu}(\vec{r}_1) \nabla^2 \eta_{\mu}(\vec{r}_1) d\vec{r}_1 - \int \eta_{\nu}(\vec{r}_1) \sum_A^M \frac{Z_A}{r_{iA}} \eta_{\mu}(\vec{r}_1) d\vec{r}_1$$

$$+ \int \eta_{\nu}(\vec{r}_1) \sum_A^M \frac{\rho(\vec{r}_2)}{r_{12}} \eta_{\mu}(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 + \int \eta_{\nu}(\vec{r}_1) V_{XC}(\vec{r}_1) \eta_{\mu}(\vec{r}_1) d\vec{r}_1$$

- The electron density is:

$$\rho(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2 = \sum_i^N \sum_{\mu}^L \sum_{\nu}^L c_{\mu i} c_{\nu i} \eta_{\mu}(\vec{r}) \eta_{\nu}(\vec{r})$$

# Resultant (Finally!)


- We end up with the nonlinear eigenvalue problem:

$$F^{KS} C = SC\epsilon$$

- Just like Hartree-Fock, except exact exchange:

$$K_{\mu\nu} = \sum_{\lambda}^L \sum_{\sigma}^L D_{\lambda\sigma} \int \eta_{\nu}(\vec{r}_1) \eta_{\sigma}(\vec{r}_1) \frac{1}{r_{12}} \eta_{\mu}(\vec{r}_2) \eta_{\lambda}(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

- is replaced by:

$$V_{\mu\nu}^{XC} = \int \eta_{\nu}(\vec{r}_1) V_{XC}(\vec{r}_1) \eta_{\mu}(\vec{r}_1) d\vec{r}_1$$


This integral is not analytical for most functionals!

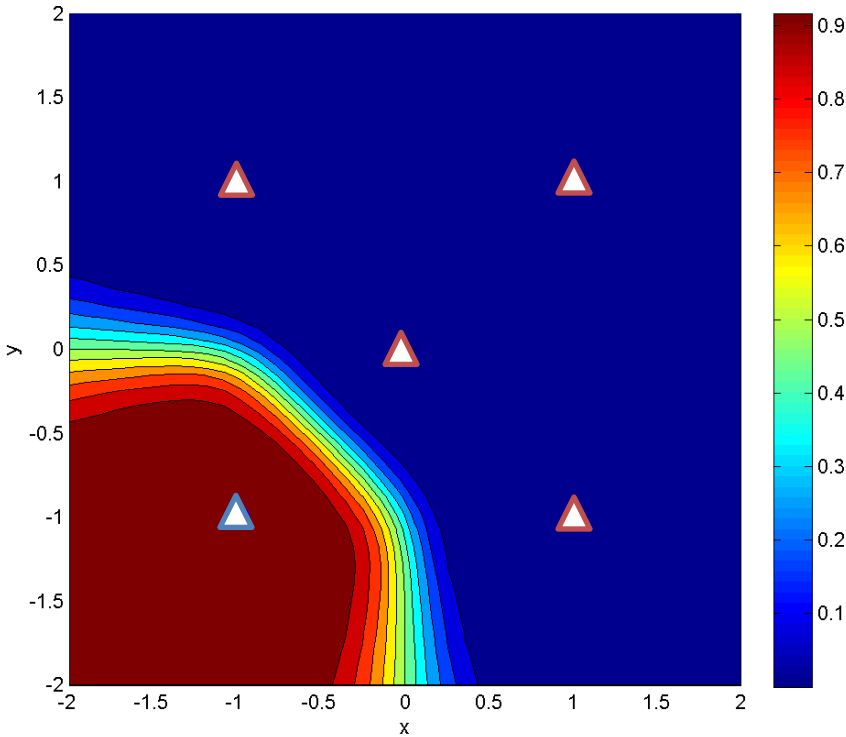
# Solution: Numerical Integration

$$\int_{R^3} f(\vec{r}_1) d\vec{r}_1 \approx \sum_n w_n \underbrace{\int_0^{4\pi} \int_0^\infty f(\Omega, r) r^2 dr d\Omega}_{I_n}$$
$$\approx \sum_n w_n \underbrace{\sum_\tau w_\tau \sum_\sigma w_\sigma r^2 f(\Omega, r, \vec{R}_n)}_{I_n}$$

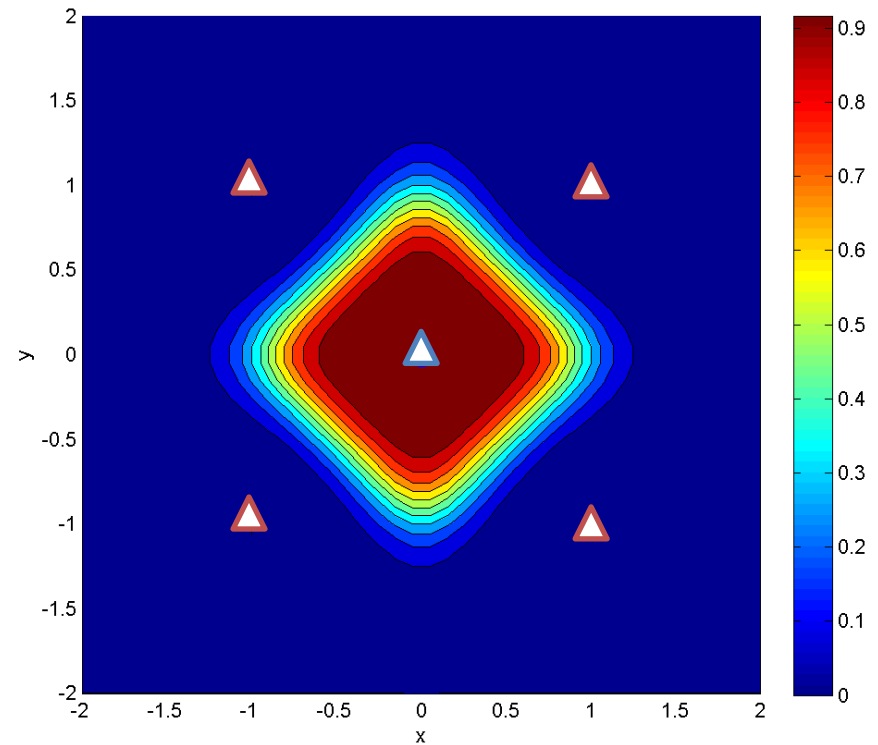
-Split the integration into a weighted sum of integrals of  $R^3$  over all nuclei. Then perform the integral about each nucleus via very accurate spherical integration techniques.

- $n_{nuc}$  integrals performed, reduced via a position and atom dependent weight function  $w_n$

# Atomic Integration: Fuzzy Voronoi Cells



Lower Left Nucleus (k=3, naïve)

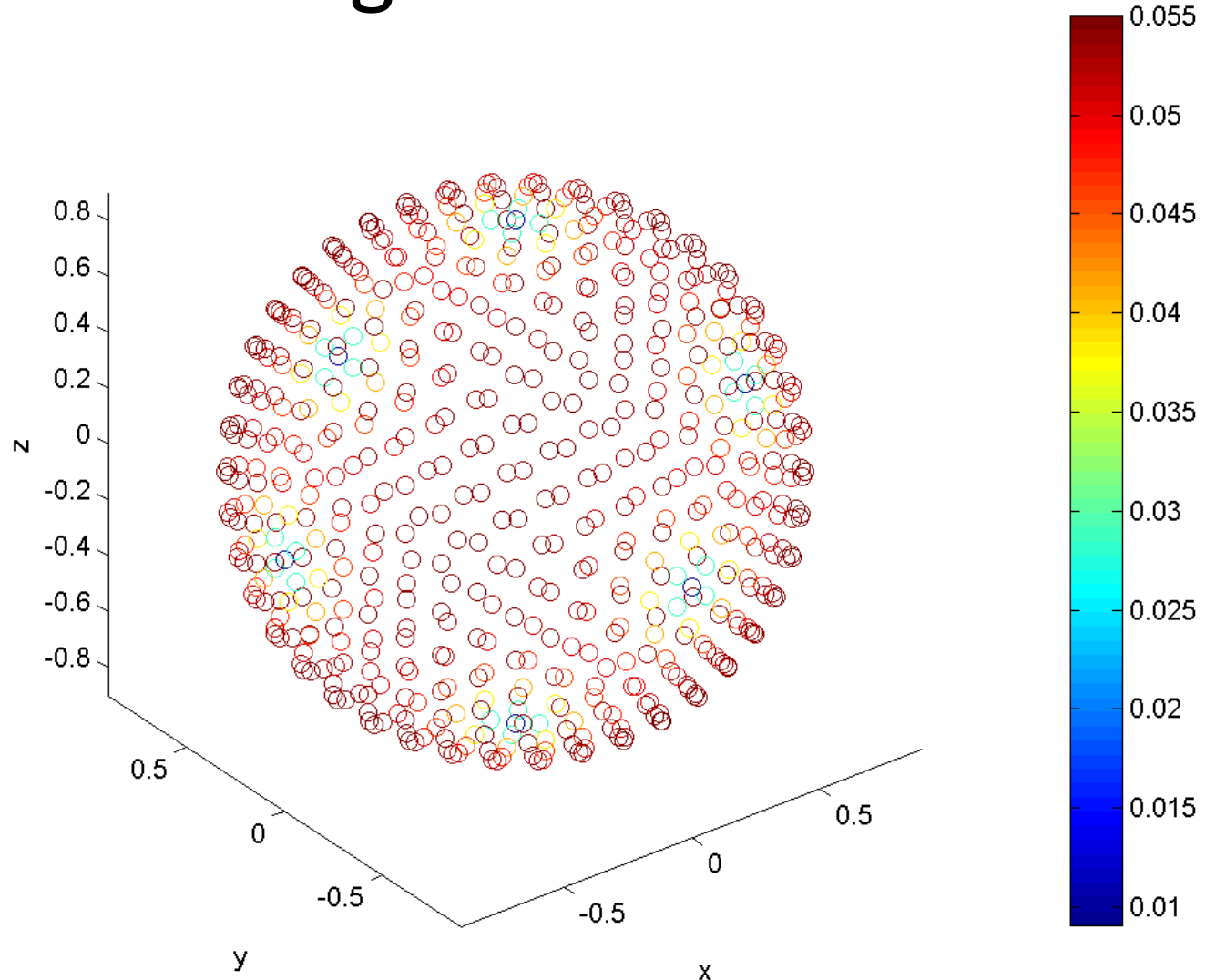


Center Nucleus (k=3, naïve)

Plots are of nuclear weights,  $w_n$ . Black stars represent nuclear positions.

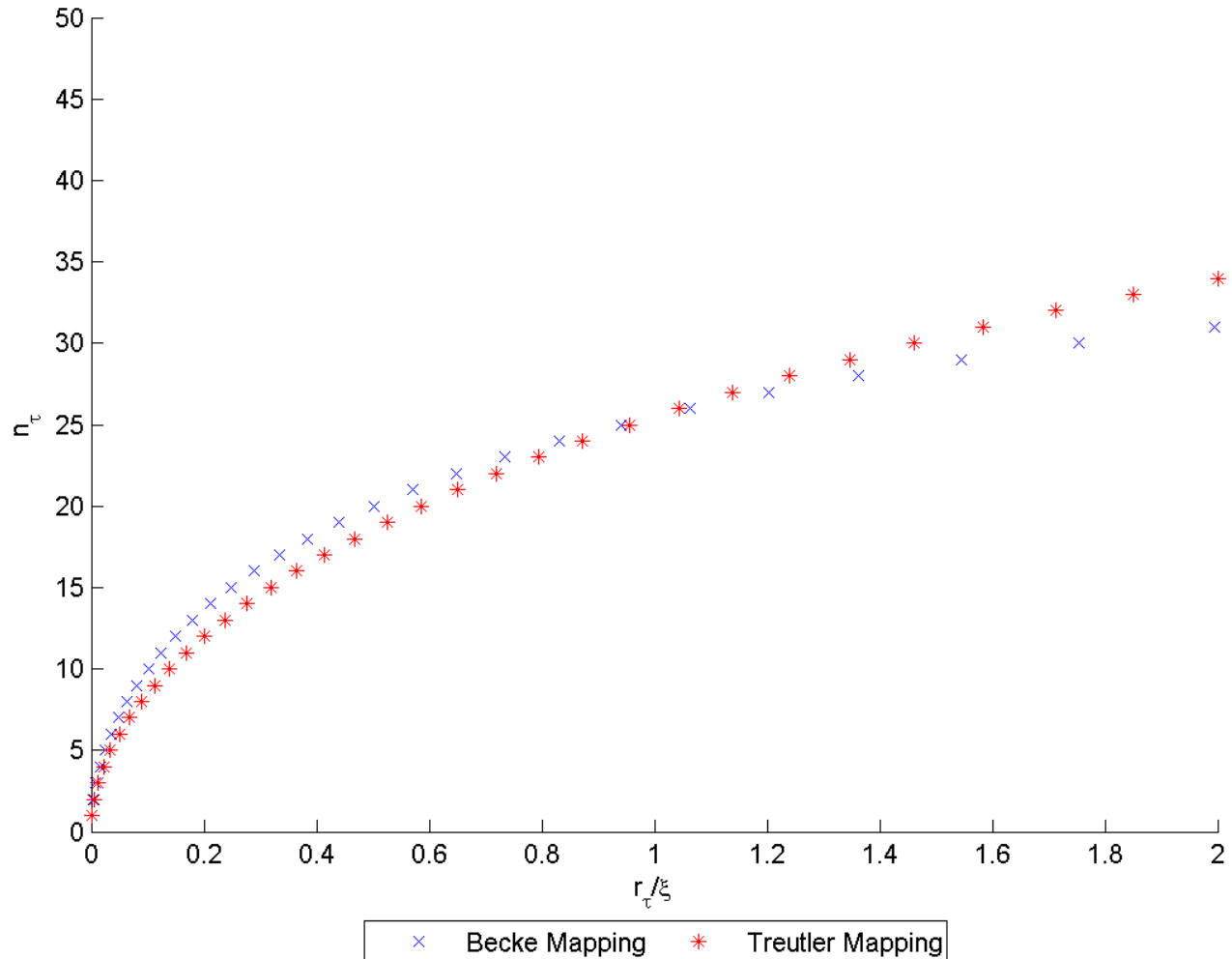


# Spherical Integration: Lebedev Grids

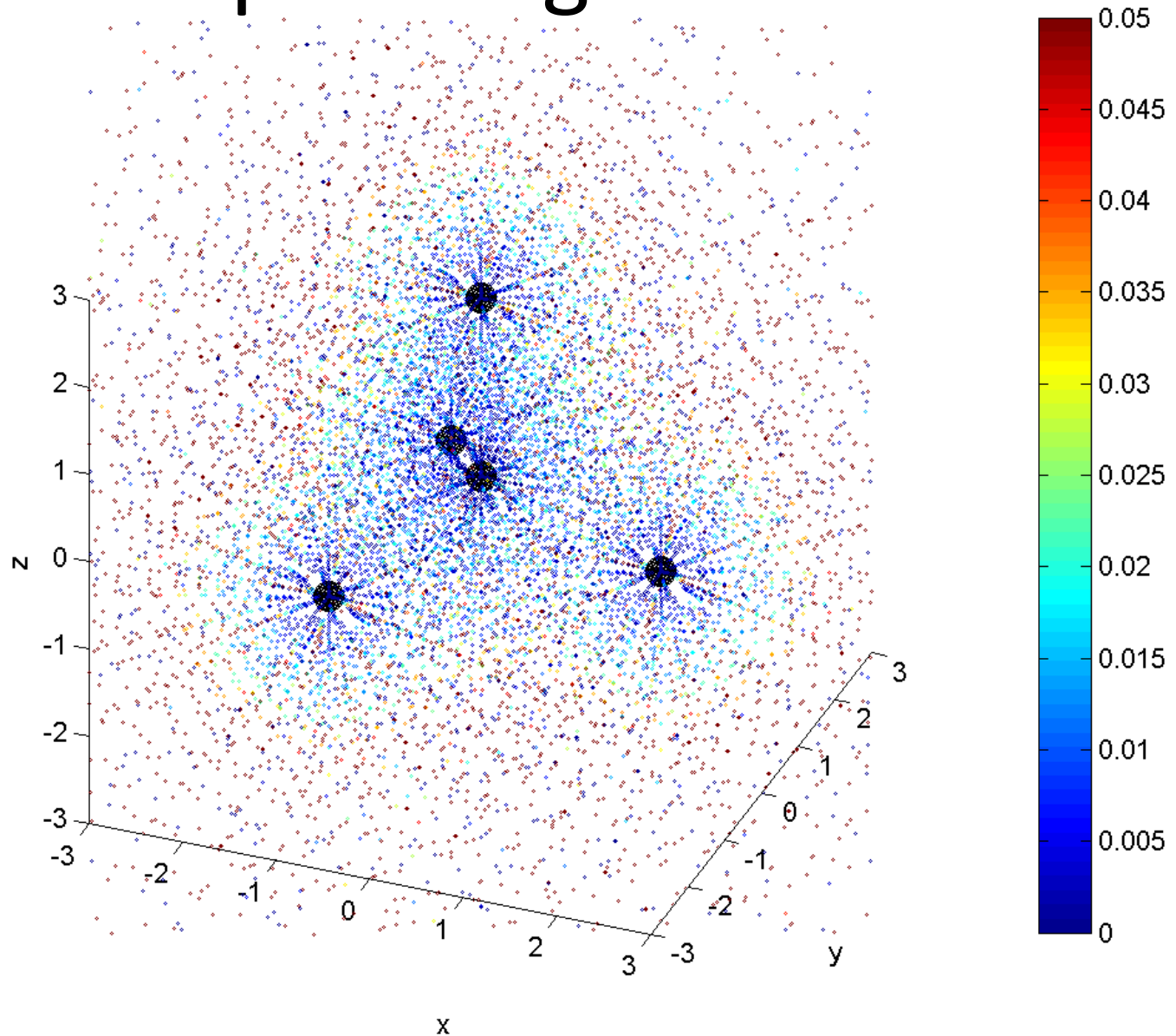


$-n = 590$ , corresponds to  $l = 41$ , can exactly integrate any function that has spherical harmonics of up to 41<sup>st</sup> order as a complete basis.

# Radial Integration: 1D Quadratures



# Example Integration Grid



# DFT Computational Costs

- Formation of H:  $O(N^3)$
- Formation of S:  $O(N^3)$
- Formation of J:  $O(N^4) \longrightarrow O(N^3)$  (Density –Fitting)
- Formation of K (Hybrid Only):  $O(N^4)$
- Formation of V:  $O(N^3)$ 
  - Number of Integration Points:  $O(N)$ 
    - Atomic Weight:  $O(N^2)$
    - Basis Points:  $O(N)$
    - Properties:  $O(N^2)$
    - Contributions to  $V_{xc}$ :  $O(N^2)$
- Eigendecomposition:  $O(N^3)$
- **Overall:**  $O(N^4) \longrightarrow O(N^3)$  (Density –Fitting)

Numerical integration makes for a large prefactor!

# Deriving Functionals

- We have:
  - An SCF procedure that we know how to solve.
  - Most of the components (electron-nucleus attraction, non-interacting electron kinetic energy, classical electron-electron repulsion) are exactly specified.
  - A rigorous way of adding the exchange correlation into the mix.
- We must specify the functional in one of two ways:
  - Model systems.
  - Empirical training.

# The Many Flavors of KS-DFT

- The functional should be based on the density, but that leaves a lot of freedom:

$$E_{XC} = f[\rho(\vec{r})] \quad (\text{LDA})$$

$$E_{XC} = f[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})] \quad (\text{LSDA})$$

$$E_{XC} = f[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}), \nabla\rho_\alpha(\vec{r}), \nabla\rho_\beta(\vec{r})] \quad (\text{GGA})$$

$$E_{XC} = f[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}), \nabla\rho_\alpha(\vec{r}), \nabla\rho_\beta(\vec{r}), K(\vec{r})] \quad (\text{Hybrid})$$

$$E_{XC} = f[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}), \nabla\rho_\alpha(\vec{r}), \nabla\rho_\beta(\vec{r}), K(\vec{r}), \tau(\vec{r})] \quad (\text{Meta})$$

# Common Exchange Functionals

- Slater [S]: LSDA Exchange, Poor asymptotic behavior.
- Becke 88 [B88] or [B]: GGA Exchange, Correct asymptotic behavior.

# Common Correlation Functionals

- Vokso–Wilk–Nusair [VWN3 and VWN5]: LSDA Correlation.
- Perdew-Zunger [PW92]: LSDA Correlation.
- Lee-Yang-Parr [LYP]: GGA Correlation.



# Common Mixed Functionals

- BLYP: **S** and **B88** LSDA/GGA Exchange, VWN3 and LYP LSDA/GGA Correlation. (Amongst the best pure DFT methods for general use).
- PBE: General Exchange/Correlation.
- B3LYP: **S**, **B88**, and **Exact** LSDA/GGA/Hybrid Exchange, **VWN3** and **LYP** LSDA/GGA Correlation. (Almost industry standard).
- BMK: Exchange/Correlation Meta-GGA.
- M05 and M06 Family: Exchange/Correlation Meta-GGA (Produces superb geometries for many systems, designed for thermochemistry. The -2X set is preferred, heavy in Exact Exchange).

# Dispersion Correction (-D)

Empirical Correction Suggested by Grimme:

$$E_{\text{disp}} = -s_6 \sum_A \sum_{B < A} \frac{C_6^{AB}}{R_{AB}^6} f_{\text{dmp}}(R_{AB}),$$

$$C_6^{AB} = \sqrt{C_6^A C_6^B},$$

$$f_{\text{dmp}}(R_{AB}) = \frac{1}{1 + e^{-d(R_{AB}/R_{AB}^0 - 1)}},$$

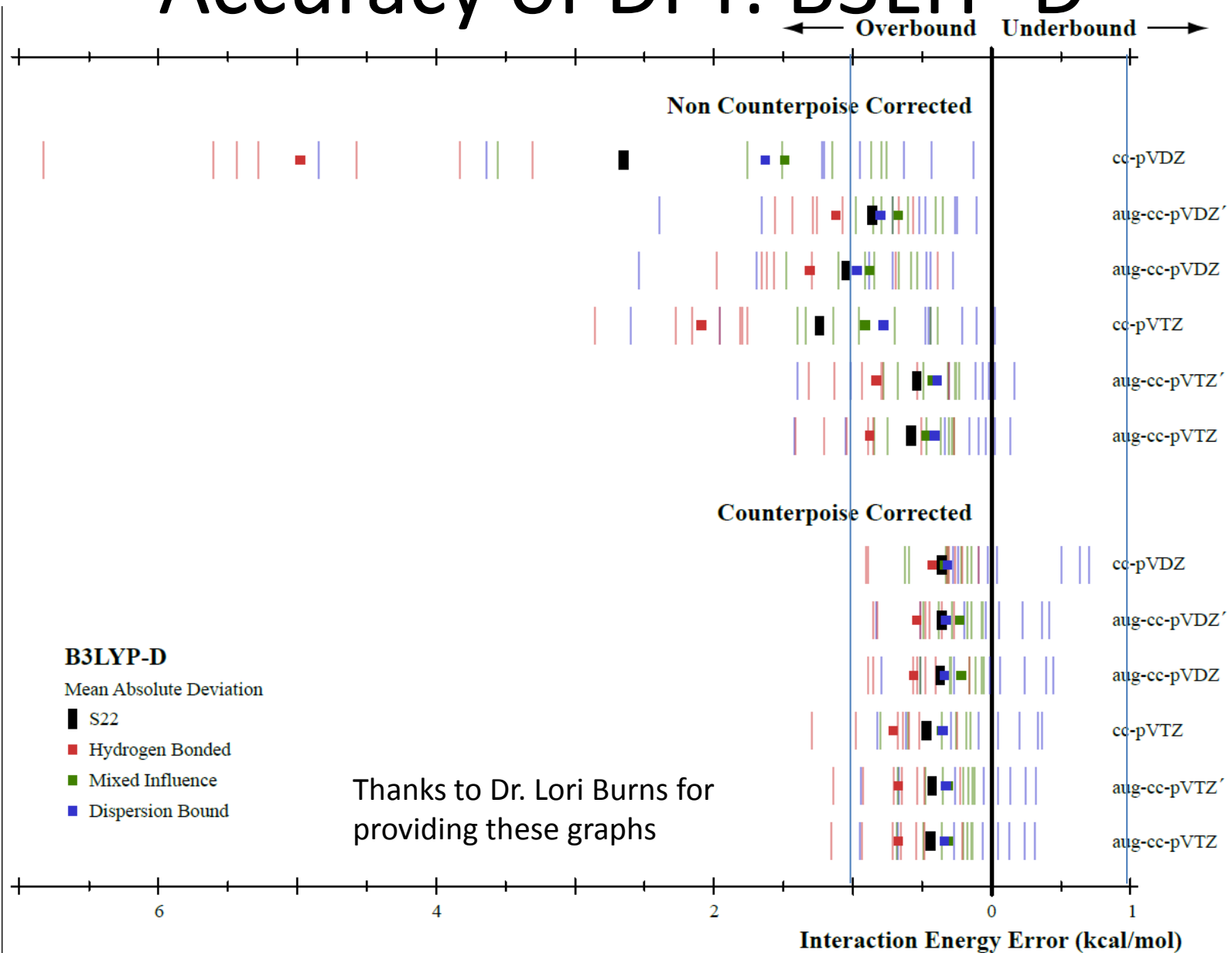
“Improved” -D3 involves  $R^8$  terms as well.

These may be applied (quite cheaply) to literally any conventional functional known. There are some cases where these induce more error than they correct!

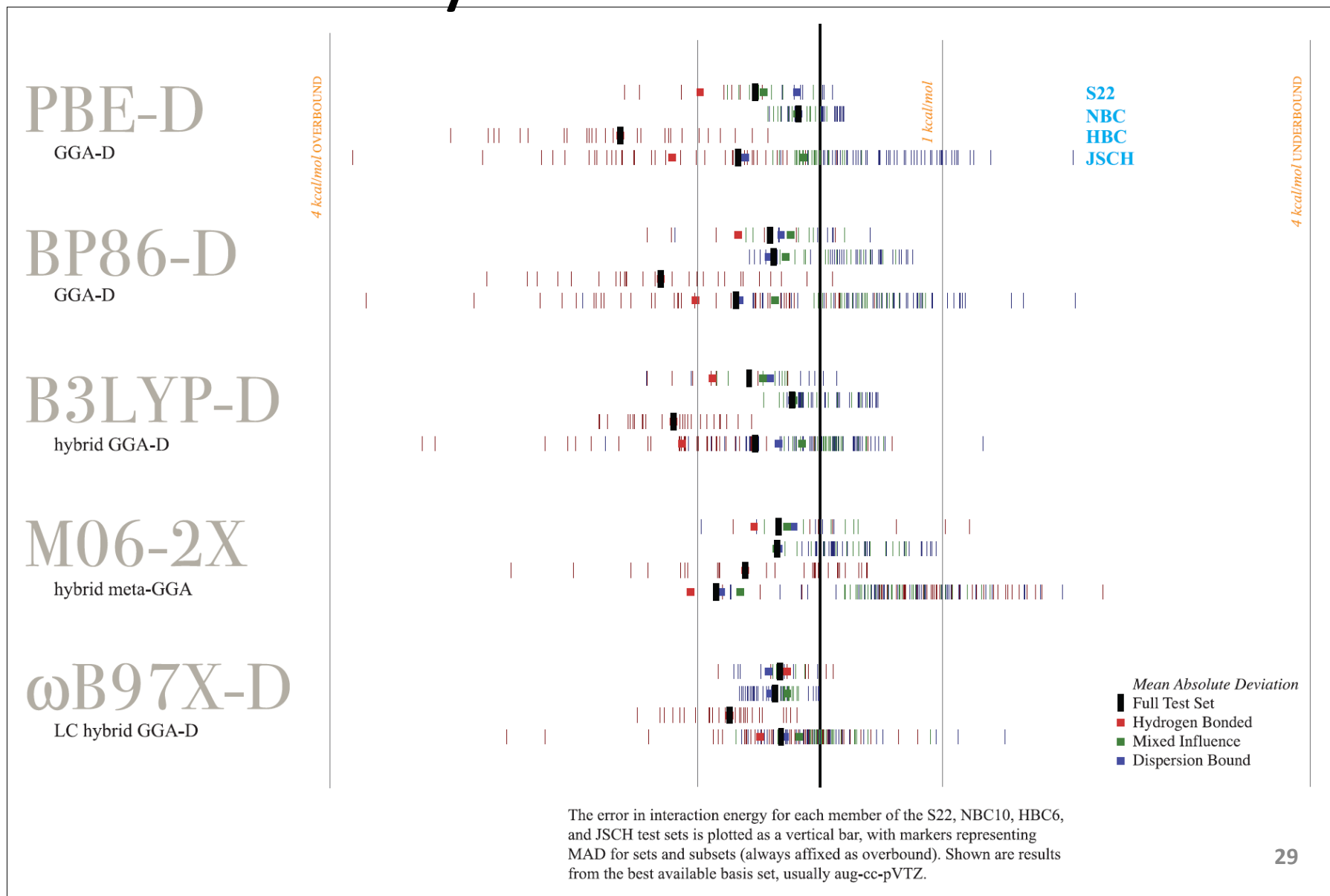
# Double Hybrids

- Add both Hartree-Fock Exchange and MP2 (PT2) long-range correlation into the functional.
- Generally quite expensive [ $O(N^5)$ ], but more accurate (not a huge difference, but can make or break chemical accuracy).
  - B2PLYP-D (Grimme)
  - XYG-3 (Ying Zang, Xin Xu, William Goddard)
  - $\omega$ B97X-2 (Jeng-Da Chai and Martin Head-Gordon)

# Accuracy of DFT: B3LYP-D



# Accuracy of DFT: Nonbonded



# Pros/Cons of KS-DFT

- Pros:
  - Quite fast (DF-MP2 is just starting to catch it).
  - Superb geometries in most cases.
  - Good energetics for covalently bound systems.
- Cons:
  - Dispersion (-D, -D3) treatments are very shaky theoretically.
  - Nondynamical (multireference) correlation is not treated correctly (DFT should not be applied to metals without careful benchmarking!)
  - Every functional goes nuts on some system or other.

# Some Names in the Field

- Kohn and Sham (Theory)
- Axel Becke (Integrals, B88, B3LYP)
- Truhlar (M05-2X)
- Stephen Grimme (-D, -D3)
- John Perdew (of P86 and PBE)
- Peter Gill (Metals, Correlation)
- Martin Head-Gordon (Linear scaling DFT, TD-DFT,  $\omega$ B97X-2)

# Key References

- Koch, W. and Holthausen, M.C., 2001, *A Chemist's Guide to Density Functional Theory*, 2<sup>nd</sup>, Wiley-VCH, Weinheim.
- Kohn, W. and Sham, L. J, *Phys. Rev.*, **140** (4a), pp. A1133-A1138, 1 November, 1965.
- Becke, A.D., *J. Chem. Phys.*, **88** (4), pp. 2547, 15 February, 1988.
- Treutler, O. and Ahlrichs, R., *J. Chem. Phys.*, **102** (1), pp. 346, 1 January 1995.
- Gill, P.M.W., Johnson, B.G., and Pople, J.A., *Chem. Phys. Lett.*, **209** (5), pp. 506, 16 July 1993.