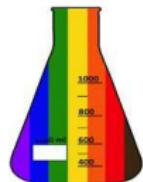


Molecular DFT and TD-DFT

John M. Herbert

Dept. of Chemistry & Biochemistry
The Ohio State University

i-CoMSE Workshop on DFT
Boise State University
7–8 June, 2023



Outline

1 Logistics

- Q-Chem & IQmol
- Philosophy

2 Intro to Molecular DFT

- Self-Consistent Field Theory
- Gaussian Basis Sets
- Physical Interpretation

3 Exchange-Correlation Functionals

- Jacob's Ladder
- Self-Interaction Error
- Recommendations

4 Contemporary Issues in DFT

- Dispersion Interactions
- Self-Interaction & Delocalization Errors
- HOMO/LUMO Gaps
- Range-Separated Hybrid Functionals

5 TD-DFT

- DFT for Excited States
- Charge-Transfer Problems

Outline

1 Logistics

- Q-Chem & IQmol
- Philosophy

2 Intro to Molecular DFT

- Self-Consistent Field Theory
- Gaussian Basis Sets
- Physical Interpretation

3 Exchange-Correlation Functionals

- Jacob's Ladder
- Self-Interaction Error
- Recommendations

4 Contemporary Issues in DFT

- Dispersion Interactions
- Self-Interaction & Delocalization Errors
- HOMO/LUMO Gaps
- Range-Separated Hybrid Functionals

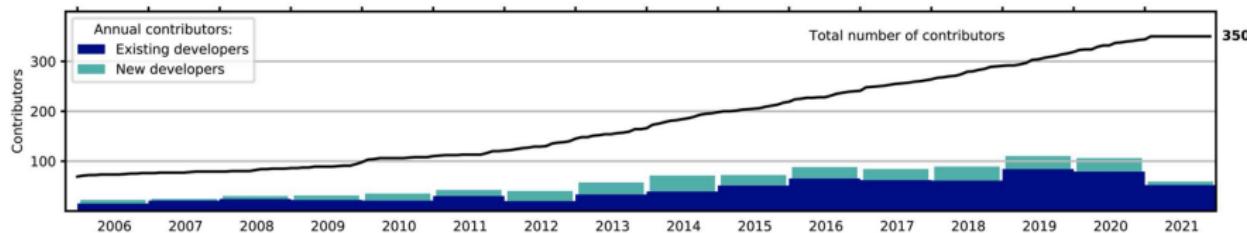
5 TD-DFT

- DFT for Excited States
- Charge-Transfer Problems

Q-Chem: A Molecular Quantum Chemistry Program



www.q-chem.com

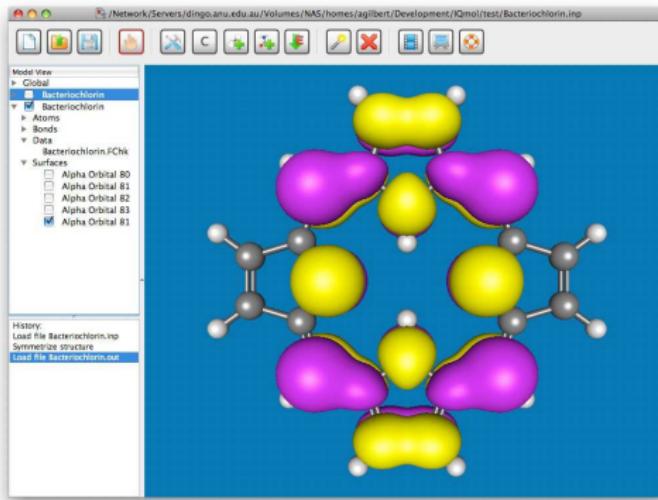


Q-Chem v. 6.0 overview: *J. Chem. Phys.* **155**, 084801 (2021)

Disclosure: J.M.H. serves on the board of directors of Q-Chem Inc.

IQmol: A Quantum Chemistry GUI

Download: www.iqmol.org



- Use for structure building and remote job submission
- Default server hosts fully functional Q-Chem with ~ 10 min. time limit
- Visualization using a formatted checkpoint file (.fchk)

Look for the Helpers

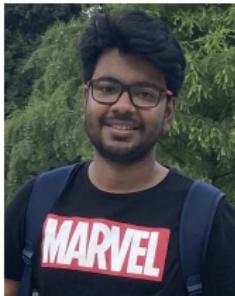
- I have three students at this workshop:



Aniket Mandal



Arnelle Fonlon



Avik Ojha

- Thanks also to Profs. **Neeraj Rai** and **Eric Jankowski** for the invitation, and for their **HUGE** amount of organizational work.

- Papers that include QC calculations should discuss methods not software.
 - ▶ Don't simply report which buttons you pushed.
 - ▶ QC software is a research instrument, don't treat it like you're ordering lunch.
 - ▶ Not all methods are implemented in every code, and not all implementations are equally efficient.

- Papers that include QC calculations should discuss methods not software.
 - ▶ Don't simply report which buttons you pushed.
 - ▶ QC software is a research instrument, don't treat it like you're ordering lunch.
 - ▶ Not all methods are implemented in every code, and not all implementations are equally efficient.
- There is no single calculation you should trust to provide the “right” answer.
 - ▶ Nevertheless, “*try all the functionals and see what agrees with experiment*” doesn't seem like science.
 - ▶ Can you rationalize the differences? What about methods other than DFT?
 - ▶ Repeating a previous student's protocol is a good starting point but shouldn't be the ending point.
 - ▶ Beware of “workflows”, as this is often code for “stop thinking and calculate”.

- Papers that include QC calculations should discuss methods not software.
 - ▶ Don't simply report which buttons you pushed.
 - ▶ QC software is a research instrument, don't treat it like you're ordering lunch.
 - ▶ Not all methods are implemented in every code, and not all implementations are equally efficient.
- There is no single calculation you should trust to provide the “right” answer.
 - ▶ Nevertheless, *“try all the functionals and see what agrees with experiment”* doesn't seem like science.
 - ▶ Can you rationalize the differences? What about methods other than DFT?
 - ▶ Repeating a previous student's protocol is a good starting point but shouldn't be the ending point.
 - ▶ Beware of “workflows”, as this is often code for “stop thinking and calculate”.
- Tip your server!
 - ▶ Please cite original method-development literature.

Outline

- 1 Logistics**
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT**
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals**
 - Jacob's Ladder
 - Self-Interaction Error
 - Recommendations
- 4 Contemporary Issues in DFT**
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - HOMO/LUMO Gaps
 - Range-Separated Hybrid Functionals
- 5 TD-DFT**
 - DFT for Excited States
 - Charge-Transfer Problems

Review: Kohn-Sham DFT

$$E[\{\psi_k\}] = T[\rho] + E_{\text{ne}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho]$$

- Kohn-Sham approach largely solves the problem of finding $T[\rho]$.
 - ▶ Map the N -electron Schrödinger equation onto an independent-electron problem.
 - ▶ $\rho(\mathbf{r}) = \sum_k^{\text{occ}} |\psi_k(\mathbf{r})|^2$

Review: Kohn-Sham DFT

$$E[\{\psi_k\}] = \textcolor{orange}{T[\rho]} + \textcolor{green}{E_{ne}[\rho]} + \textcolor{blue}{E_H[\rho]} + \textcolor{red}{E_{xc}[\rho]}$$

- Kohn-Sham approach largely solves the problem of finding $T[\rho]$.
 - ▶ Map the N -electron Schrödinger equation onto an independent-electron problem.
 - ▶ $\rho(\mathbf{r}) = \sum_k^{\text{occ}} |\psi_k(\mathbf{r})|^2$
- Variational theorem allows us to cast this as an SCF eigenvalue equation:

$$\hat{F}\psi_k = \varepsilon_k \psi_k \quad (\text{Kohn-Sham eqn.})$$

$$\hat{F} = -\frac{1}{2}\hat{\nabla}^2 + v_{ne} + v_H + v_{xc} \quad (\text{Fock operator})$$

- Each term is defined by functional derivatives of $E[\rho]$:

$$\hat{F}\psi_k = \underbrace{-\frac{1}{2}\hat{\nabla}^2\psi_k}_{=\delta T_s / \delta \psi_k} + \left[\underbrace{v_{ne}(\mathbf{r})}_{=\delta E_{ne} / \delta \rho(\mathbf{r})} + \underbrace{v_H(\mathbf{r})}_{=\delta E_H / \delta \rho(\mathbf{r})} + \underbrace{v_{xc}(\mathbf{r})}_{=\delta E_{xc} / \delta \rho(\mathbf{r})} \right] \psi_k$$

Self-Consistent Field (SCF) Procedure

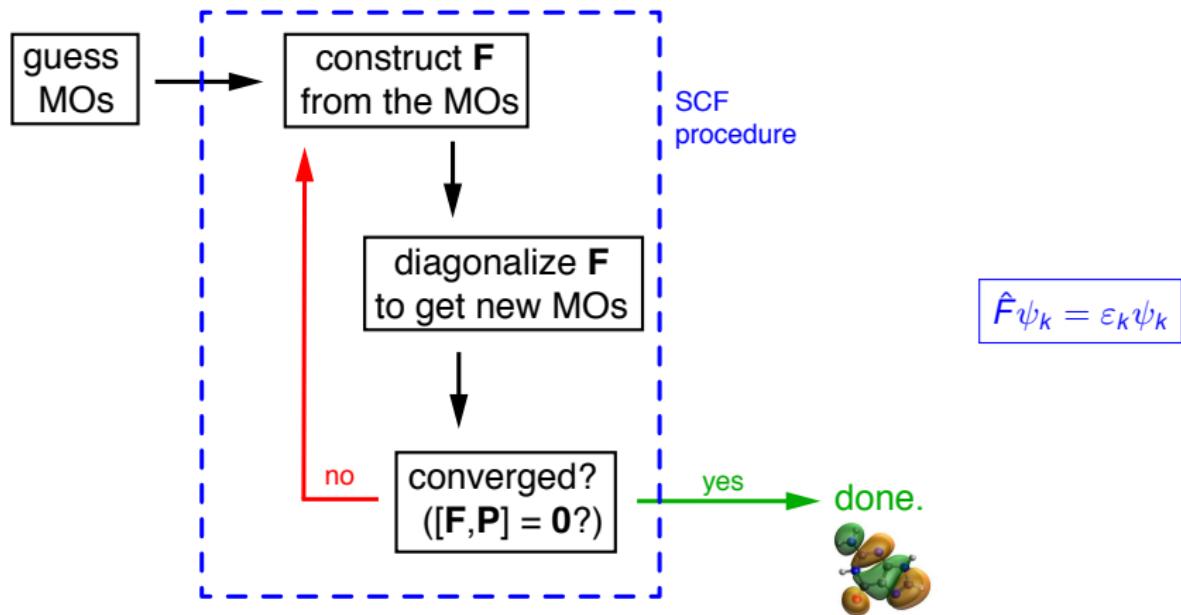


Figure: J. M. Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Linear Combination of Atomic Orbitals (LCAO) Framework

$$\psi(\mathbf{r}) \stackrel{\text{LCAO}}{=} \sum_A^{\text{atoms}} c_A \phi_A(\mathbf{r})$$

■ What to use for the basis functions $\{\phi_A\}$?

- ▶ *Slater-type functions* resemble actual atomic orbitals:

$$\phi_A(\mathbf{r}) = r^{n-1} e^{-\zeta_A r} Y_{\ell m}(\theta, \phi)$$

- ▶ Variational problem is non-linear if applied to $\{c_A, \zeta_A\}$.
 - ▶ Linear variation problem for $\{c_A\}$ (only) is much simpler.
- ## ■ *Gaussian-type functions* make it (relatively) easy to compute integrals.

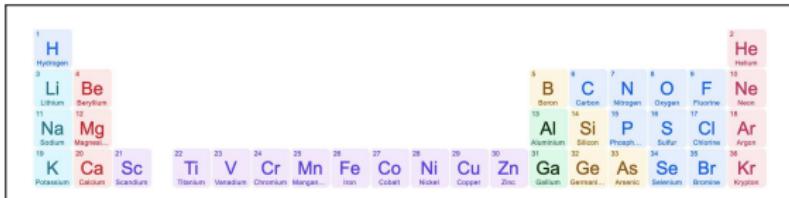
$$g(\mathbf{r}) \propto (x - x_0)^a (y - y_0)^b (z - z_0)^c e^{-\zeta r^2}$$

- ▶ “angular momentum” is $\ell = a + b + c$
- ▶ combinations $\{xx, xy, xz, yy, yz, zz\} \times e^{-\zeta r^2}$ resemble d functions ($\ell = 2$)

Introduction of a Fixed Basis Set

$$\psi(\mathbf{r}) \stackrel{\text{LCAO}}{=} \sum_A \sum_{\mu \in A} c_{A\mu} g_{A\mu}(\mathbf{r})$$

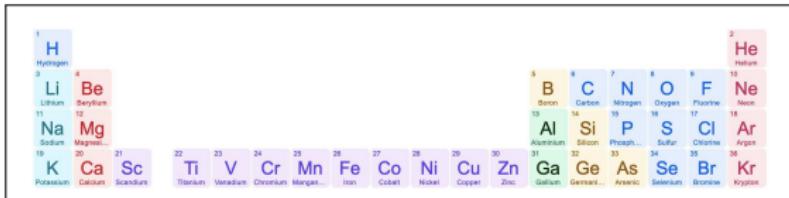
- LCAO *anatz* is exact **only** If we use a complete set of AOs on each atom.
 - ▶ This requires AOs that are unoccupied in the isolated atoms.
 - ▶ Atomic eigenfunctions are not eigenfunctions of the molecular Hamiltonian!



Introduction of a Fixed Basis Set

$$\psi(\mathbf{r}) \stackrel{\text{LCAO}}{=} \sum_A \text{atoms} \sum_{\mu \in A} \text{Gaussians} c_{A\mu} g_{A\mu}(\mathbf{r})$$

- LCAO *anatz* is exact **only** If we use a complete set of AOs on each atom.
 - ▶ This requires AOs that are unoccupied in the isolated atoms.
 - ▶ Atomic eigenfunctions are not eigenfunctions of the molecular Hamiltonian!



- Additional AOs beyond the minimal set increase the variational flexibility.
 - ▶ Higher- ℓ functions in polyatomics, to get bond angles right.
 - ▶ Additional values of ζ ("split valence") allow the orbital to change size.

Nuclear Cusps

- Exact wave function exhibits a cusp whenever $V \rightarrow \pm\infty$.
- This implies a cusp at each nucleus.

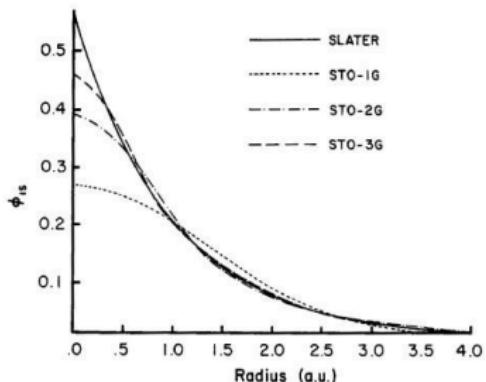


Figure 3.3 Comparison of the quality of the least-squares fit of a 1s Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure: Szabo & Ostlund, *Modern Quantum Chemistry* (1982)

Nuclear Cusps

- Exact wave function exhibits a cusp whenever $V \rightarrow \pm\infty$.
- This implies a cusp at each nucleus.

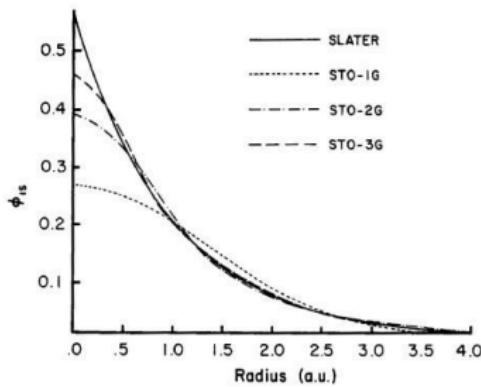


Figure 3.3 Comparison of the quality of the least-squares fit of a 1s Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

- Slater-type functions have a cusp but Gaussians do not.
- Approximate the cusp using a linear combination of Gaussian primitives.

- Plane-wave basis sets sidestep this issue via core-electron pseudopotentials
 - What to do for core-level spectroscopy?

Figure: Szabo & Ostlund, *Modern Quantum Chemistry* (1982)

Contracted Gaussian Basis Functions

- 1 Approximate the nuclear cusps using *contracted* Gaussians:

$$\psi_i(\mathbf{r}) = \sum_{\mu}^{N_{\text{basis}}} c_{\mu i} \underbrace{\left(\sum_{\nu}^{N_{\text{contraction}}} b_{\mu \nu} g_{\nu}(\mathbf{r}) \right)}_{\mu\text{th contracted Gaussian}}$$

- ▶ Coefficients $\{b_{\mu \nu}\}$ are fixed. (Pre-optimized for atoms.)
- ▶ MO coefficients $\{c_{\mu i}\}$ are optimized by the SCF procedure.
- ▶ SCF equation ($\mathbf{Fc} = \epsilon \mathbf{SC}$) is a linear variation problem for the $\{c_{\mu i}\}$.

Contracted Gaussian Basis Functions

- 1 Approximate the nuclear cusps using *contracted* Gaussians:

$$\psi_i(\mathbf{r}) = \sum_{\mu}^{N_{\text{basis}}} c_{\mu i} \underbrace{\left(\sum_{\nu}^{N_{\text{contraction}}} b_{\mu \nu} g_{\nu}(\mathbf{r}) \right)}_{\mu\text{th contracted Gaussian}}$$

- ▶ Coefficients $\{b_{\mu \nu}\}$ are fixed. (Pre-optimized for atoms.)
- ▶ MO coefficients $\{c_{\mu i}\}$ are optimized by the SCF procedure.
- ▶ SCF equation ($\mathbf{Fc} = \epsilon \mathbf{SC}$) is a linear variation problem for the $\{c_{\mu i}\}$.

- 2 There are also *electron coalescence cusps*, as $\|\mathbf{r}_1 - \mathbf{r}_2\| \rightarrow 0$.

- ▶ Important in for correlated wave functions that contain 2e information.
- ▶ Difficult to reproduce without very large Gaussian basis sets.
- ▶ Correlated wave function calculations require large (high- ℓ) basis sets.

Nomenclature for Gaussian Basis Sets

- Basis functions on a given atom have the form

$$g(\mathbf{r}) = \left\{ \underbrace{1}_{\text{s}}, \underbrace{x, y, z}_{\text{p}}, \underbrace{xx, xy, xz, yy, yz, zz, \dots}_{\text{d}} \right\} \times e^{-\zeta r^2}$$

Nomenclature for Gaussian Basis Sets

- Basis functions on a given atom have the form

$$g(\mathbf{r}) = \left\{ \underbrace{1,}_{\text{s}} \underbrace{x, y, z,}_{\text{p}} \underbrace{xx, xy, xz, yy, yz, zz, \dots}_{\text{d}} \right\} \times e^{-\zeta r^2}$$

1	H	Hydrogen	2	He	Helium
3	Li	Lithium	4	Be	Beryllium
5	Na	Sodium	6	Mg	Magnesium
7	K	Potassium	8	Ca	Calcium
9	Sc	Scandium	10	Ti	Titanium
11	V	Vanadium	12	Cr	Chromium
13	Mn	Manganese	14	Fe	Iron
15	Co	Cobalt	16	Ni	Nickel
17	Cu	Copper	18	Zn	Zinc
19	Ga	Gallium	20	Ge	Germanium
21	As	Arsenic	22	Si	Silicon
23	Se	Selenium	24	P	Phosphorus
25	Br	Bromine	26	O	Oxygen
27	Kr	Krypton	28	F	Fluorine
29			30	N	Nitrogen
31			32	C	Carbon
33			34	Al	Aluminum
35			36	Si	Silicon
37			38	P	Phosphorus
39			40	O	Oxygen
41			42	F	Fluorine
43			44	N	Nitrogen
45			46	C	Carbon
47			48	Al	Aluminum
49			50	Si	Silicon
51			52	P	Phosphorus
53			54	O	Oxygen
55			56	F	Fluorine

- Minimal basis:* Core + valence shell for each atom.

- For Li–Ne, this means:

- 1s Gaussian (core, $e^{-\zeta_1 r^2}$)
- 2s Gaussian ($e^{-\zeta_2 r^2}$, with $\zeta_2 < \zeta_1$)
- set of 2p Gaussians ($\{x, y, z\} \times e^{-\zeta_2 r^2}$).

- Split-valence basis:* Multiple shells (with different ζ) for the valence electrons.

Split-Valence Basis Sets

- **Minimal basis:** Core + valence shell for each atom.
- **Split-valence basis:** Multiple shells (with different ζ) for valence electrons.
 - ▶ Double- ζ basis (e.g., for C atom):
 - one 1s Gaussian (core)
 - two 2s Gaussians + two sets of 2p Gaussians (valence)
 - 9 functions total
 - ▶ Triple- ζ basis (e.g., for C atom):
 - 1s core
 - three sets of (2s,2p) valence
 - 13 functions total
 - ▶ Quadruple- ζ basis: What do you think?

Nomenclature: Pople Basis Sets

■ Minimal vs. split-valence

- ▶ **Minimal (STO- n G):** n represents the degree of contraction. These are toys.
- ▶ **Double- ζ (6-31G):** Contraction length is 6 for the core, and contraction lengths of 3 and 1 for the two valence shells.
- ▶ **Triple- ζ (6-311G):** You get the idea...

■ Polarization functions

- ▶ One additional value of ℓ beyond the minimal-basis requirement.
 - Provides angular flexibility (e.g., in geometry optimizations).
 - Describes electron correlation (e.g., polarization along the bond axis).
- ▶ **6-31G* \equiv 6-31G(d):** Includes $\ell = 2$ functions for 2nd-row atoms.
- ▶ **6-31G** \equiv 6-31G(d,p):** Consists of 6-31G* plus $\ell = 1$ functions for H.

Basis	N_{basis}	r_e (Å)	θ (deg)
STO-3G	7	0.989	100.0
6-31G	13	0.949	111.5
6-31G(d)	19	0.947	105.5
6-31G(d,p)	25	0.943	106.0
cc-pVQZ	115	0.940	106.2
Expt.		0.958	104.5

Hartree-Fock geometries for H₂O in various basis sets

■ Split-valence

- ▶ **Double- ζ** (6-31G): Two sets of valence functions, with different exponents ζ .
- ▶ **Triple- ζ** (6-311G): Three sets of valence functions.

■ Polarization functions

- ▶ 6-31G* \equiv 6-31G(d): Includes $\ell = 2$ functions for 2nd-row atoms (C, N, O, etc.)
- ▶ 6-31G** \equiv 6-31G(d,p): Consists of 6-31G* plus $\ell = 1$ functions for H.

■ Diffuse functions

- ▶ Add a valence shell with a much smaller exponent ($\zeta_{\text{diffuse}} \approx \frac{1}{3} \zeta_{\text{valence}}$).
- ▶ Crucial for anions and non-covalent interactions.
- ▶ Asymptotic decay of the wave function is $\psi(r) \sim e^{-r/\lambda}$, where $\lambda = \hbar/(2m \times \text{IE})^{1/2}$.*
- ▶ **6-31+G**: Consists of **6-31G** plus a diffuse **sp** shell for non-H atoms.
- ▶ **6-31++G**: Consists of **6-31+G** plus a diffuse **s** shell for H atoms.

* Herbert, "The quantum chemistry of loosely-bound electrons" [Rev. Comput. Chem. 28, 391 (2015)]

Nomenclature: **Karlsruhe** Basis Sets*

- Designed for SCF methods, as replacements for Pople basis sets.
 - Broad coverage of periodic table (unlike Pople basis sets).
 - The ones in current use are 2nd-generation versions (“def2-”).
-
- **Nomenclature:**
 - ▶ **def2-SV(P)**: Split-valence with polarization functions on heavy atoms. Analogous to 6-31G*.
 - ▶ **def2-SVP**: Split-valence polarization. Analogous to 6-31G**.
 - ▶ **def2-SVPD**: def2-SVP + diffuse functions. Analogous to 6-31++G**.
 - ▶ **def2-TZVP**: Valence triple- ζ with polarization. Analogous to 6-311G**.
 - ▶ **def2-TZVPD**: def-TZVP + diffuse functions. Analogous to 6-311++G**.
 - ▶ **def2-TZVPP**: def-TZVPP + second set of polarization functions. Analogous to 6-311G(2df,2pd).
 - ▶ **Partially augmented:**[†] def2-ma- and def2-ha- SVP, TZVP, QZVP

* Also known as “Ahrlrichs” basis sets, originally developed in the group of R. Ahrlrichs at U. of Karlsruhe.

† Gray & Herbert [*J. Chem. Theory Comput.* **18**, 2308 (2022)]

Exercise: Weakly-Bound Anion



M = indole-5,6-diquinone ($\mu = 9.1 \text{ D}$)

- μ is large enough to support the anion, M^-
- Note the charge (= -1) and multiplicity (= 2, meaning doublet).
 - ▶ multiplicity = $2S + 1$ for total spin S

sample input for M^-

```
$molecule
-1 2
note!
C 0.8290529 -0.7374209 -0.0000018
C 0.8648382 0.6447538 0.0000013
[snip]
H 2.4850716 -2.2001465 -0.0000086
$end

$rem
method b3lyp
basis 6-31G*
$end
```

Exercise: Weakly-Bound Anion



M = indole-5,6-diquinone ($\mu = 9.1$ D)

- μ is large enough to support the anion, M^-
- Note the charge (= -1) and multiplicity (= 2, meaning doublet).
 - ▶ multiplicity = $2S + 1$ for total spin S
- M^- is unbound(!!) What about 6-31++G*?

sample input for M^-

```
$molecule
-1 2          note!
C   0.8290529  -0.7374209  -0.0000018
C   0.8648382  0.6447538   0.0000013
[snip]
H   2.4850716  -2.2001465  -0.0000086
$end

$rem
method b3lyp
basis 6-31G*           good idea?
$end
```

output, B3LYP / 6-31G*

```
Alpha MOs
-- Occupied --
-18.9179 -18.9155 -14.2330 -10.0735 -10.0538 -10.0488 -10.0476 -10.0207
-10.0069 -9.9974 -9.9926 -0.8494 -0.8391 -0.8107 -0.6659 -0.6250
-0.5456 -0.5242 -0.4608 -0.4264 -0.3994 -0.3768 -0.3073 -0.2934
-0.2864 -0.2846 -0.2633 -0.2511 -0.2254 -0.2205 -0.2016 -0.1945
-0.1671 -0.1373 -0.1113 -0.0671 -0.0287 -0.0226 0.0256 !!!
-- Virtual --
0.1676  0.1882  0.2119  0.2532  0.2548  0.2773  0.2893  0.3132
```

Looking Under the Hood: 6-31+G*

Basis set information in a standardized format

O	0			
S	6	1.000000		
	5.48467170E+03	1.83110000E-03	exponent (in bohr ⁻²)	
	8.25234950E+02	1.39501000E-02		
	1.88046960E+02	6.84451000E-02		
	5.29645000E+01	2.32714300E-01		
	1.68975700E+01	4.70193000E-01		
	5.79963530E+00	3.58520900E-01		
SP	3	1.000000		
	1.55396160E+01	-1.10777500E-01	7.08743000E-02	scaling factor (sp functions only)
	3.59993360E+00	-1.48026300E-01	3.39752800E-01	
	1.01376180E+00	1.13076700E+00	7.27158600E-01	
SP	1	1.000000		
	2.70005800E-01	1.00000000E+00	1.00000000E+00	
SP	1	1.000000		
	8.45000000E-02	1.00000000E+00	1.00000000E+00	
D	1	1.000000		
	8.00000000E-01	1.00000000E+00		

H	0			
S	3	1.000000		
	1.87311370E+01	3.34946000E-02	contraction coefficient	
	2.82539370E+00	2.34726950E-01		
	6.40121700E-01	8.13757330E-01		
S	1	1.000000		
	1.61277800E-01	1.00000000E+00		

In Q-Chem, use `PRINT_GENERAL_BASIS = TRUE` to obtain this information.

Looking Under the Hood: 6-31+G*

Basis set information in a standardized format

```
      0      0
      S      6      1.000000
      5.48467170E+03   1.83110000E-03
      8.25234950E+02   1.39501000E-02
      1.88046960E+02   6.84451000E-02
      5.29645000E+01   2.32714300E-01
      1.68975700E+01   4.70193000E-01
      5.79963530E+00   3.58520900E-01
      SP     3      1.000000
      1.55396160E+01   -1.10777500E-01   7.08743000E-02
      3.59993360E+00   -1.48026300E-01   3.39752800E-01
      1.01376180E+00   1.13076700E+00   7.27158600E-01
      SP     1      1.000000
      2.70005800E-01   1.00000000E+00   1.00000000E+00
      SP     1      1.000000
      8.45000000E-02   1.00000000E+00   1.00000000E+00
      D      1      1.000000
      8.00000000E-01   1.00000000E+00
*****
      H      0
      S      3      1.000000
      1.87311370E+01   3.34946000E-02
      2.82539370E+00   2.34726950E-01
      6.40121700E-01   8.13757330E-01
      S      1      1.000000
      1.61277800E-01   1.00000000E+00
*****
```

diffuse

polarization

In Q-Chem, use `PRINT_GENERAL_BASIS = TRUE` to obtain this information.

Other Basis Sets

- This is not an exhaustive list.
- Consult the [Basis Set Exchange](#)

Basis Set Exchange

Download GitHub Feedback About Help Request a Basis set

All roles ▾ All

Total found: 565 basis sets

Select All Reset Selection

1	2																
H	He																
Li	Be																
Na	Mg																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Hf	Ta	W	Ta	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Pu	At	Rn	
Fr	Ra	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cu	Nb	Fl	Mc	Lv	Ts	Og	
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

search basis sets...

References for selected basis

Plain Text Get References

Download basis set

Format Q-Chem Get Basis Set Advanced

Basis-Set Superposition Error (BSSE)

- How to compute the interaction energy of noncovalent complex A · · · B?

$$\Delta E = E_{AB} - E_A - E_B$$

- **Problem:** This represents unbalanced approximation when atom-centered basis sets are used.

- ▶ In A · · · B, atoms on A can use basis functions centered on B.
 - ▶ This imbalance is known *basis-set superposition error* (BSSE).

Basis-Set Superposition Error (BSSE)

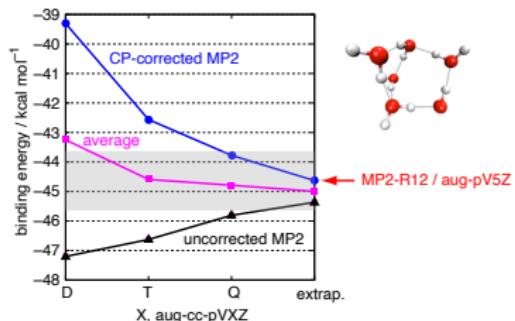
- How to compute the interaction energy of noncovalent complex A · · · B?

$$\Delta E = E_{AB} - E_A - E_B$$

- Problem:** This represents unbalanced approximation when atom-centered basis sets are used.

- In A · · · B, atoms on A can use basis functions centered on B.
- This imbalance is known *basis-set superposition error* (BSSE).

- Solution:** Use the dimer basis to compute all three energies.



- Use *ghost atoms* for the other monomer.
- This procedure is known as *counterpoise correction*.

Figure: Richard, Lao, and Herbert [*J. Phys. Chem. Lett.* 4, 2674 (2013)]

Exercise: Energy Lowering Via Ghost Atoms

- π -stacked configuration of (benzene)₂:



Benchmark
 $|\Delta E| \approx 1.5 \text{ kcal/mol}$

- ▶ Compare a monomer calculation...
- ▶ ...to one with “ghost atom” basis functions for the other monomer.

Benzene Monomer

```
$molecule
@ 1
C 1.394697 -0.000000 -1.745866
H 2.481097 0.000000 -1.737508
C 0.697348 1.207843 -1.745866
H 1.240548 2.148693 -1.737508
C -0.697348 1.207843 -1.745866
H -1.240548 2.148693 -1.737508
C -1.394697 0.000000 -1.745866
H -2.481097 -0.000000 -1.737508
C -0.697348 -1.207843 -1.745866
H -1.240548 -2.148693 -1.737508
C 0.697348 -1.207843 -1.745866
H 1.240548 -2.148693 -1.737508
$end
```

Monomer + Ghost Atoms

```
$molecule
@ 1
@C 1.394697 -0.000000 1.745866
@H 2.481097 0.000000 1.737508
@C 0.697348 1.207843 1.745866
@H 1.240548 2.148693 1.737508
@C -0.697348 1.207843 1.745866
@H -1.240548 2.148693 1.737508
@C -1.394697 0.000000 1.745866
@H -2.481097 0.000000 1.737508
@C -0.697348 -1.207843 1.745866
@H -1.240548 -2.148693 1.737508
@C 0.697348 -1.207843 1.745866
@H 1.240548 -2.148693 1.737508
C 1.394697 -0.000000 -1.745866
H 2.481097 0.000000 -1.737508
C 0.697348 1.207843 -1.745866
H 1.240548 2.148693 -1.737508
C -0.697348 1.207843 -1.745866
H -1.240548 2.148693 -1.737508
C -1.394697 0.000000 -1.745866
H -2.481097 -0.000000 -1.737508
C -0.697348 -1.207843 -1.745866
H -1.240548 -2.148693 -1.737508
C 0.697348 -1.207843 -1.745866
H 1.240548 -2.148693 -1.737508
$end
```

Exercise: Energy Lowering Via Ghost Atoms

- π -stacked configuration of (benzene)₂:



Benchmark
 $|\Delta E| \approx 1.5 \text{ kcal/mol}$

- ▶ Compare a monomer calculation...
 - ▶ ...to one with “ghost atom” basis functions for the other monomer.
-
- The difference is the BSSE:
 - ▶ B3LYP / 6-31G*: $\Delta CP = -1.2 \text{ kcal/mol}$
 - ▶ B3LYP / def2-TZVPD: $\Delta CP = -0.2 \text{ kcal/mol}$

Benzene Monomer

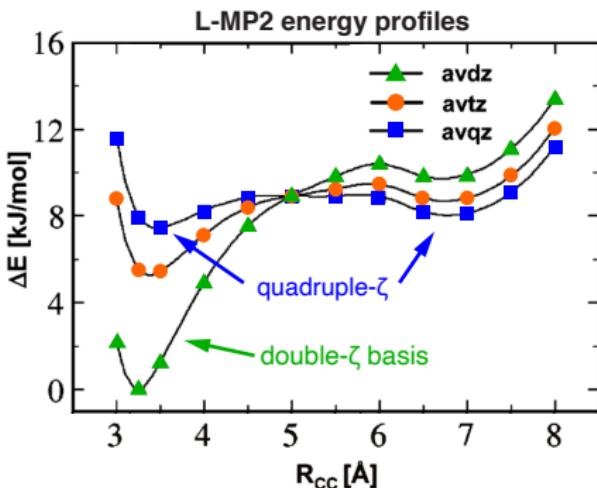
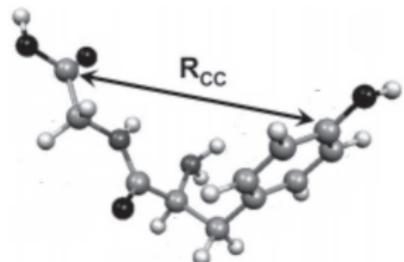
```
$molecule
@ 1
C 1.394697 -0.000000 -1.745866
H 2.481097 0.000000 -1.737508
C 0.697348 1.207843 -1.745866
H 1.240548 2.148693 -1.737508
C -0.697348 1.207843 -1.745866
H -1.240548 2.148693 -1.737508
C -1.394697 0.000000 -1.745866
H -2.481097 -0.000000 -1.737508
C -0.697348 -1.207843 -1.745866
H -1.240548 -2.148693 -1.737508
C 0.697348 -1.207843 -1.745866
H 1.240548 -2.148693 -1.737508
$end
```

Monomer + Ghost Atoms

```
$molecule
@ 1
@C 1.394697 -0.000000 1.745866
@H 2.481097 0.000000 1.737508
@C 0.697348 1.207843 1.745866
@H 1.240548 2.148693 1.737508
@C -0.697348 1.207843 1.745866
@H -1.240548 2.148693 1.737508
@C -1.394697 0.000000 1.745866
@H -2.481097 0.000000 1.737508
@C -0.697348 -1.207843 1.745866
@H -1.240548 -2.148693 1.737508
@C 0.697348 -1.207843 1.745866
@H 1.240548 -2.148693 1.737508
C 1.394697 -0.000000 -1.745866
H 2.481097 0.000000 -1.737508
C 0.697348 1.207843 -1.745866
H 1.240548 2.148693 -1.737508
C -0.697348 1.207843 -1.745866
H -1.240548 2.148693 -1.737508
C -1.394697 0.000000 -1.745866
H -2.481097 -0.000000 -1.737508
C -0.697348 -1.207843 -1.745866
H -1.240548 -2.148693 -1.737508
C 0.697348 -1.207843 -1.745866
H 1.240548 -2.148693 -1.737508
$end
```

Intramolecular BSSE

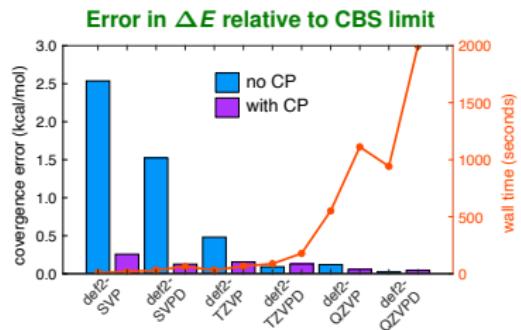
- For intramolecular BSSE there is no analogue to counterpoise correction.
- The only general solution is to increase the quality of the basis set
 - BSSE vanishes in the basis-set limit



Figures: Shields & van Mourik [*J. Phys. Chem. A* **111**, 13272 (2007)]

Choice of Basis Matters!

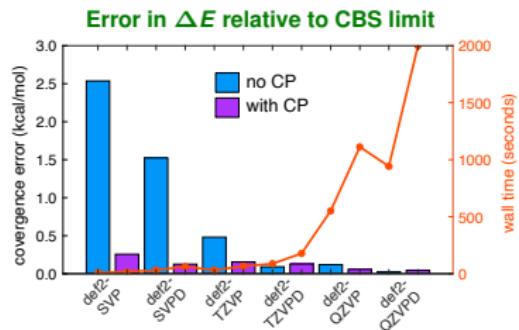
- DFT is **much less** sensitive to basis set than correlated wave functions.
 - ▶ Double- ζ geometries + triple- ζ single-point energies is a reasonable paradigm.
- Double- ζ energetics is still (too) prevalent in the literature.



- ▶ BLYP+D3(BJ) basis-set convergence errors
- ▶ S66 data set of small non-covalent dimers, $|\Delta E| \sim 1\text{--}19$ kcal/mol

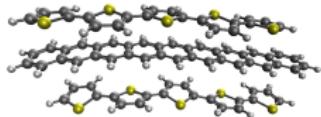
Choice of Basis Matters!

- DFT is **much less** sensitive to basis set than correlated wave functions.
 - ▶ Double- ζ geometries + triple- ζ single-point energies is a reasonable paradigm.
- Double- ζ energetics is still (too) prevalent in the literature.



- ▶ BLYP+D3(BJ) basis-set convergence errors
- ▶ S66 data set of small non-covalent dimers, $|\Delta E| \sim 1\text{--}19$ kcal/mol

- BSSE is extensive with system size!



- ▶ $\Delta CP \sim 50$ kcal/mol for def2-SVPD
- ▶ $\Delta CP \lesssim 5$ kcal/mol for def2-TZVPD

Synopsis: Basis Set Recommendations

- 6-31G* (or 6-31+G*, when diffuse functions are required) is the closest there is to a “default” Gaussian basis set.
- For SCF calculations, triple- ζ is a high-quality basis set.
 - ▶ 6-311G(3df,2pd) works well and is faster (per unit basis function) in Q-Chem as compared to open-source codes.
 - ▶ def2-TZVP has better coverage across the periodic table.
 - ▶ Add diffuse functions if appropriate.

Synopsis: Basis Set Recommendations

- 6-31G* (or 6-31+G*, when diffuse functions are required) is the closest there is to a “default” Gaussian basis set.
- For SCF calculations, triple- ζ is a high-quality basis set.
 - ▶ 6-311G(3df,2pd) works well and is faster (per unit basis function) in Q-Chem as compared to open-source codes.
 - ▶ def2-TZVP has better coverage across the periodic table.
 - ▶ Add diffuse functions if appropriate.
- “High quality” \neq CBS limit!
 - ▶ BSSE may not (quite) be negligible triple- ζ basis sets.
 - ▶ Basis-set error can mask DFT functional error in “benchmark” studies.*
 - ▶ For post-SCF wave function calculations, triple- ζ is a starting point.

* Jensen, “Method calibration or data fitting?” [*J. Chem. Theory Comput.* **14**, 4651 (2018)]

Synopsis: Issues to Consider

- Diffuse functions are expensive but sometimes necessary.
 - ▶ May need to tighten thresholds to avoid numerical linear dependencies.
- Is your conformational landscape skewed by intramolecular BSSE?

Synopsis: Issues to Consider

- Diffuse functions are expensive but sometimes necessary.
 - ▶ May need to tighten thresholds to avoid numerical linear dependencies.
- Is your conformational landscape skewed by **intramolecular BSSE**?
- ***Your conclusions should not depend on the use of a “special” basis set with the magical ability to produce results that conform to your preconceived expectations.***
 - ▶ Any conclusions drawn should be robust against modest variations.
 - ▶ This is even more true when it comes to choosing a density functional.
 - ▶ Error cancellation often helps, but do you understand its origins?

Synopsis: Issues to Consider

- Diffuse functions are expensive but sometimes necessary.
 - ▶ May need to tighten thresholds to avoid numerical linear dependencies.
- Is your conformational landscape skewed by **intramolecular BSSE**?
- ***Your conclusions should not depend on the use of a “special” basis set with the magical ability to produce results that conform to your preconceived expectations.***
 - ▶ Any conclusions drawn should be robust against modest variations.
 - ▶ This is even more true when it comes to choosing a density functional.
 - ▶ Error cancellation often helps, but do you understand its origins?
- **Justify your choices!**
 - ▶ ***“Anything better is too expensive!” is an excuse, not a rationale.***
 - ▶ “That’s what the previous grad student used” is an acceptable starting point but should not be an ending point.

Outline

1 Logistics

- Q-Chem & IQmol
- Philosophy

2 Intro to Molecular DFT

- Self-Consistent Field Theory
- Gaussian Basis Sets
- **Physical Interpretation**

3 Exchange-Correlation Functionals

- Jacob's Ladder
- Self-Interaction Error
- Recommendations

4 Contemporary Issues in DFT

- Dispersion Interactions
- Self-Interaction & Delocalization Errors
- HOMO/LUMO Gaps
- Range-Separated Hybrid Functionals

5 TD-DFT

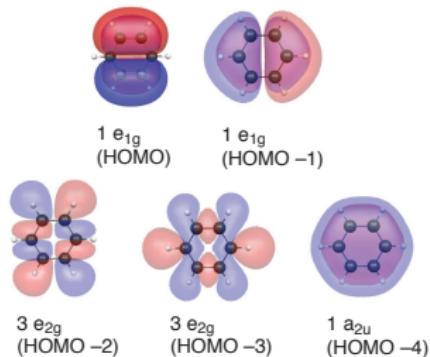
- DFT for Excited States
- Charge-Transfer Problems

What Do the SCF Orbitals Mean?

- SCF partitions the linear space into an *occupied space* and a *virtual space*.
 - ▶ $E_{\text{SCF}}(\mathbf{P})$ energy depends only on the span of the occupied MOs ($\mathbf{P} = \mathbf{c}\mathbf{c}^\dagger$) and is **invariant** to unitary transformations of them.
 - ▶ The *canonical MOs* diagonalize \mathbf{F} and have well-defined energy levels,

$$\hat{F}\psi_k = \varepsilon_k \psi_k$$

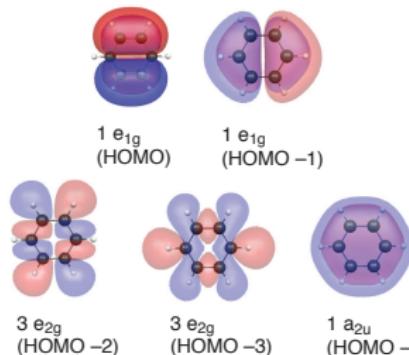
- ▶ Canonical MOs must transform like irreps of the symmetry group.



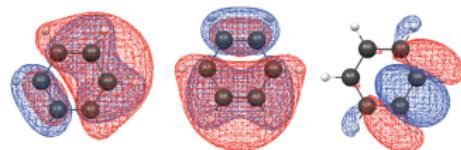
Canonical MOs for benzene

What Do the SCF Orbitals Mean?

- SCF partitions the linear space into an *occupied space* and a *virtual space*.
 - ▶ $E_{\text{SCF}}(\mathbf{P})$ energy depends only on the span of the occupied MOs ($\mathbf{P} = \mathbf{c}\mathbf{c}^\dagger$) and is **invariant** to unitary transformations of them.
 - ▶ The *canonical MOs* diagonalize \mathbf{F} and have well-defined energy levels,
- Analysis tools exploit orbital invariance to use a more convenient set of MOs.



Canonical MOs for benzene



Boys-localized MOs (maximize dist. between centroids),
similar to maximally-localized Wannier functions

What Do Hartree-Fock Energy Levels Mean?

- The right way to compute the first IE is by ΔSCF :*

$$\text{IE} = E(N - 1) - E(N).$$

- Koopmans' theorem:* neglecting orbital relaxation and electron correlation,

$$\text{IE}_k \stackrel{\text{def}}{=} E_k(N - 1) - E(N) \stackrel{\text{Koopmans}}{\approx} -\varepsilon_k$$

* Requires creating a charge state, which is problematic in a periodic code.

What Do Hartree-Fock Energy Levels Mean?

- The right way to compute the first IE is by ΔSCF :*

$$\text{IE} = E(N - 1) - E(N) .$$

- Koopmans' theorem:* neglecting orbital relaxation and electron correlation,

$$\text{IE}_k \stackrel{\text{def}}{=} E_k(N - 1) - E(N) \stackrel{\text{Koopmans}}{\approx} -\varepsilon_k$$

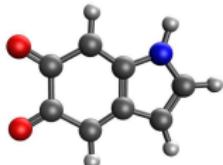
orbital	Koopmans' IE (eV)				Exptl. IE (eV)	
	Hartree-Fock		B3LYP			
	$-\varepsilon_k$	shifted ^a	$-\varepsilon_k$	shifted ^b		
$1b_1$	13.9	12.6	7.2	12.6	12.6	
$3a_1$	15.9	14.6	9.3	14.7	14.7	
$1b_2$	19.4	18.1	13.1	18.5	18.6	
$2a_1$	36.8	35.5	25.2	30.6	32.2	
$1a_1$	559.6	558.3	511.0	516.4	539.7	

^aEigenvalues shifted by 1.3 eV so that $-\varepsilon(1b_1)$ equals the first IE.
^bEigenvalues shifted by -5.4 eV so that $-\varepsilon(1b_1)$ equals the first IE.

Ionization energies for H_2O , aug-cc-pVQZ basis set

* Requires creating a charge state, which is problematic in a periodic code.

Exercise: ΔSCF Calculation of the Lowest IE



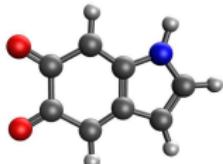
- 1 Build a molecular structure in IQmol
 - ▶ charge & multiplicity

\$molecule
0 1

			neutral singlet
C	-0.2315201	0.7114049	1.2539744
C	-1.6140257	0.6927947	1.2495809
C	-2.3600484	0.7850066	0.1365327
H	-3.4447499	0.7655403	0.1859391
C	-1.6561247	0.9145463	-1.1653513
C	-0.1680294	0.9343027	-1.1577024
C	0.5252062	0.8233273	0.1513040
H	1.6096200	0.8325801	0.2127946
O	-2.2848553	1.0019273	-2.2083477
O	0.4689883	1.0384721	-2.1941069
N	-2.0795357	0.5707452	2.5057235
C	-0.9980147	0.5111944	3.3141582
C	0.1699903	0.5959367	2.5681976
H	-3.0793963	0.5294212	2.8051944
H	-1.0512408	0.4113970	4.3902086
H	1.1844506	0.5752319	2.9446690

\$end

Exercise: ΔSCF Calculation of the Lowest IE



- 1 Build a molecular structure in IQmol
 - ▶ charge & multiplicity
- 2 Compute cation in a 2nd job
 - ▶ separated by "@@@"
 - ▶ new charge and multiplicity
 - ▶ can read in previous MOs as a guess
- 3 Check Q-Chem text output (see below)

```
$molecule
0 1
C   -0.2315201   0.7114049   1.2539744
C   -1.6140257   0.6927947   1.2495809
C   -2.3600484   0.7850066   0.1365327
H   -3.4447499   0.7655403   0.1859391
C   -1.6561247   0.9145463   -1.1653513
C   -0.1680294   0.9343027   -1.1577024
C   0.5252062   0.8233273   0.1513040
H   1.6096200   0.8325801   0.2127946
O   -2.2848553   1.0019273   -2.2083477
O   0.4689883   1.0384721   -2.1941069
N   -2.0795357   0.5707452   2.5057235
C   -0.9980147   0.5111944   3.3141582
C   0.1699903   0.5959367   2.5681976
H   -3.0793963   0.5294212   2.8051944
H   -1.0512408   0.4113970   4.3902086
H   1.1844506   0.5752319   2.9446690
$end

$rem
method b3lyp
basis 6-31G*
$end

@@@

$molecule
1 2
read
$end

$cation (+1)
doublet

$rem
scf_guess read
method b3lyp
basis 6-31G*
$end
```

Results: ΔSCF Calculation of the Lowest IE

Cycle	Energy	DIIS error
1	-515.9918941678	6.51e-02
2	-512.7626981202	7.86e-03
3	-512.2409988807	1.52e-02
4	-512.9550142741	2.74e-03
5	-512.9796495899	1.12e-03
6	-512.9829118452	6.90e-04
7	-512.9845549849	2.07e-04
8	-512.9847032232	4.62e-05
9	-512.9847099404	2.09e-05
10	-512.9847114772	6.40e-06 Convergence criterion met

SCF iterations and converged SCF energy

Orbital Energies (a.u.)								
Alpha MOs								
-- Occupied --								
-19.1439	-19.1409	-14.4096	-10.2733	-10.2685	-10.2617	-10.2530	-10.2112	
-10.2007	-10.1956	-10.1955	-10.0523	-10.0331	-10.0225	-0.8605	-0.8136	
-0.7398	-0.7167	-0.6468	-0.6171	-0.5894	-0.5646	-0.5031	-0.4821	
-0.4706	-0.4688	-0.4524	-0.4404	-0.4217	-0.4207	-0.4028	-0.3885	
-0.3625	-0.3212	-0.2916	-0.2761	-0.2366	-0.2040			
-- Virtual --								
-0.1216	-0.0126	0.0316	0.0413	0.0642	0.1101	0.1205	0.1284	

MO energy levels: $\epsilon_{\text{HOMO}} = -0.2040 \text{ Ha} = -5.55 \text{ eV}$

Results: ΔSCF Calculation of the Lowest IE

Cycle	Energy	DIIS error
1	-515.9918941678	6.51e-02
2	-512.7626981202	7.86e-03
3	-512.2409988807	1.52e-02
4	-512.9550142741	2.74e-03
5	-512.9796495899	1.12e-03
6	-512.9829118452	6.90e-04
7	-512.9845549849	2.07e-04
8	-512.9847032232	4.62e-05
9	-512.9847099404	2.09e-05
10	-512.9847114772	6.40e-06

SCF iterations and converged SCF energy

Orbital Energies (a.u.)								
Alpha MOs								
-- Occupied --								
-19.1439	-19.1409	-14.4096	-10.2733	-10.2685	-10.2617	-10.2530	-10.2112	
-10.2007	-10.1956	-10.1955	-10.0523	-1.0331	-1.0225	-0.8605	-0.8136	
-0.7398	-0.7167	-0.6468	-0.6171	-0.5894	-0.5646	-0.5031	-0.4821	
-0.4706	-0.4688	-0.4524	-0.4404	-0.4217	-0.4207	-0.4028	-0.3885	
-0.3625	-0.3212	-0.2916	-0.2761	-0.2366	-0.2040			
-- Virtual --								
-0.1216	-0.0126	0.0316	0.0413	0.0642	0.1101	0.1205	0.1284	

MO energy levels: $\varepsilon_{\text{HOMO}} = -0.2040 \text{ Ha} = -5.55 \text{ eV}$

■ B3LYP/6-31G*

- ΔSCF ionization energy = 7.5 eV
- Koopmans IE ($-\varepsilon_{\text{HOMO}} = 5.5 \text{ eV}$)
- $\varepsilon_{\text{LUMO}} = -3.3 \text{ eV}$

■ HF/6-31G*

- method = hf in the \$rem input section
- ΔSCF ionization energy = 6.0 eV
- Koopmans IE ($-\varepsilon_{\text{HOMO}} = 7.7 \text{ eV}$)
- $\varepsilon_{\text{LUMO}} = +0.2 \text{ eV}$

■ CCSD(T)/6-31G*

- ionization energy = 7.3 eV

Koopmans' Electron Affinities

$$\text{EA}_a \stackrel{\text{def}}{=} E(N) - E_a(N+1) \xrightarrow{\text{Koopmans}} \approx -\varepsilon_a$$

- Electron correlation and orbital relaxation have same sign for EAs.
 - ▶ No error cancellation \implies larger errors.
 - ▶ IEs are often ~ 10 eV for closed-shell molecules but EAs are generally < 1 eV.
 - ▶ Koopmans' approximation is not useful for EAs.

Koopmans' Electron Affinities

$$EA_a \stackrel{\text{def}}{=} E(N) - E_a(N+1) \stackrel{\text{Koopmans}}{\approx} -\varepsilon_a$$

- Electron correlation and orbital relaxation have same sign for EAs.
 - ▶ No error cancellation \implies larger errors.
 - ▶ IEs are often ~ 10 eV for closed-shell molecules but EAs are generally < 1 eV.
 - ▶ Koopmans' approximation is not useful for EAs.
- Additional considerations:
 - ▶ If $\varepsilon_a < 0$ then $EA_a > 0$ and the neutral molecule supports a stable anion.
 - ▶ HF virtual levels are subject to the full molecular (N -electron) Coulomb potential and are thereby upshifted relative to true affinity levels.
 - ▶ This upshift can be large enough to make the HF virtuals unbound, even if the real molecule supports a stable anion.

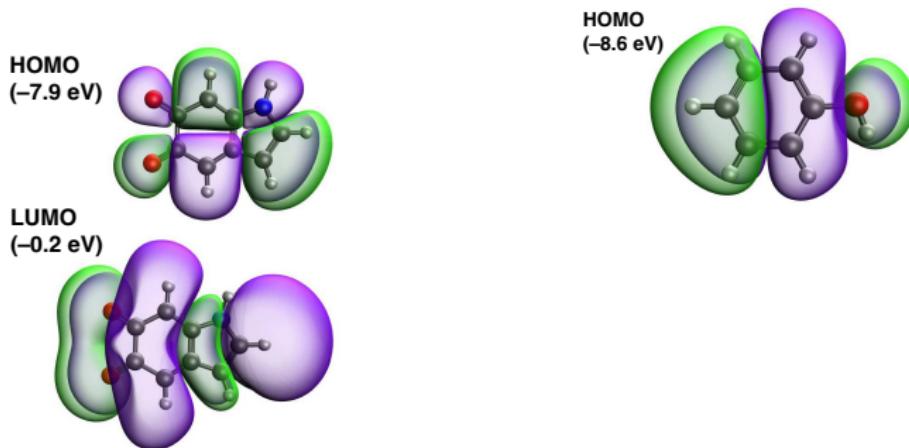
Continuum States

- Unbound levels ($\varepsilon_a > 0$) are *orthogonalized discretized continuum states*.*
- These are finite-basis approximations to continuum states and should not be taken seriously.
- The corresponding HOMO/LUMO gap should also not be taken seriously.

* Herbert, "The quantum chemistry of loosely-bound electrons" [*Rev. Comput. Chem.* **28**, 391 (2015)]

Continuum States

- Unbound levels ($\varepsilon_a > 0$) are *orthogonalized discretized continuum states*.*
- These are finite-basis approximations to continuum states and should not be taken seriously.
- The corresponding HOMO/LUMO gap should also not be taken seriously.

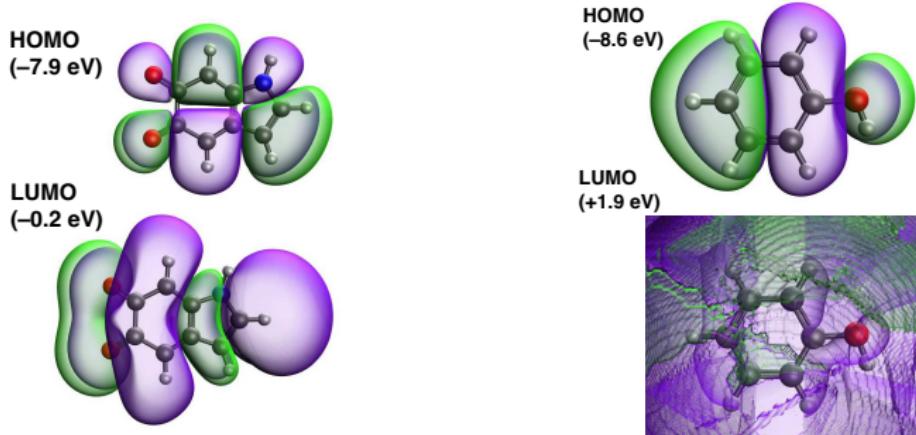


- These are 75% probability isocontours, meaning $\int_V |\psi(\mathbf{r})|^2 d\mathbf{r} = 0.75$

* Herbert, "The quantum chemistry of loosely-bound electrons" [Rev. Comput. Chem. 28, 391 (2015)]

Continuum States

- Unbound levels ($\varepsilon_a > 0$) are *orthogonalized discretized continuum states*.*
- These are finite-basis approximations to continuum states and should not be taken seriously.
- The corresponding HOMO/LUMO gap should also not be taken seriously.



- These are 75% probability isocontours, meaning $\int_V |\psi(\mathbf{r})|^2 d\mathbf{r} = 0.75$

* Herbert, "The quantum chemistry of loosely-bound electrons" [Rev. Comput. Chem. 28, 391 (2015)]

Kohn-Sham

- All orbitals computed from a common $(N - 1)$ -electron potential.
- Lowest few virtual orbitals are often bound ($\varepsilon_a < 0$).

Hartree-Fock

- Occupied orbitals determined by an $(N - 1)$ -electron potential but virtuals determined by N -electron potential.
- Frequently, all virtual orbitals are unbound ($\varepsilon_a > 0$).

Kohn-Sham

- All orbitals computed from a common $(N - 1)$ -electron potential.
- Lowest few virtual orbitals are often bound ($\varepsilon_a < 0$).
- KS orbitals are the appropriate ones for *excitation*, and $\Delta E \approx \varepsilon_a - \varepsilon_i$.¹

Hartree-Fock

- Occupied orbitals determined by an $(N - 1)$ -electron potential but virtuals determined by N -electron potential.
- Frequently, all virtual orbitals are unbound ($\varepsilon_a > 0$).
- Appropriate orbitals for *ionization* and *electron attachment*.

¹"Physical meaning of the virtual Kohn–Sham orbitals and orbital energies" [*J. Chem. Theory Comput.* **10**, 4432 (2014)]. Note that this is true of exact Kohn-Sham MOs may be severely degraded by XC approximations.

Kohn-Sham

- All orbitals computed from a common $(N - 1)$ -electron potential.
- Lowest few virtual orbitals are often bound ($\varepsilon_a < 0$).
- KS orbitals are the appropriate ones for *excitation*, and $\Delta E \approx \varepsilon_a - \varepsilon_i$.¹
- HOMO satisfies an exact condition

$$\varepsilon_{\text{HOMO}} = -\text{IE}$$

and lower-lying ε_i provide approximations to subsequent IEs.²

Hartree-Fock

- Occupied orbitals determined by an $(N - 1)$ -electron potential but virtuals determined by N -electron potential.
- Frequently, all virtual orbitals are unbound ($\varepsilon_a > 0$).
- Appropriate orbitals for *ionization* and *electron attachment*.
- $\varepsilon_{\text{HOMO}} \approx -\text{IE}$ is always an approximation.

¹“Physical meaning of the virtual Kohn–Sham orbitals and orbital energies” [*J. Chem. Theory Comput.* **10**, 4432 (2014)]. Note that this is true of exact Kohn-Sham MOs may be severely degraded by XC approximations.

²“Approximate Koopmans’ theorem of DFT” [*J. Chem. Phys.* **116**, 1760 (2002)].

Kohn-Sham vs. Hartree-Fock MOs

Kohn-Sham

- All orbitals computed from a common $(N - 1)$ -electron potential.
- Lowest few virtual orbitals are often bound ($\varepsilon_a < 0$).
- KS orbitals are the appropriate ones for *excitation*, and $\Delta E \approx \varepsilon_a - \varepsilon_i$.¹
- HOMO satisfies an exact condition

$$\varepsilon_{\text{HOMO}} = -\text{IE}$$

and lower-lying ε_i provide approximations to subsequent IEs.²

- Better energy levels for bonds between AOs of very different size?³

Hartree-Fock

- Occupied orbitals determined by an $(N - 1)$ -electron potential but virtuals determined by N -electron potential.
- Frequently, all virtual orbitals are unbound ($\varepsilon_a > 0$).
- Appropriate orbitals for *ionization* and *electron attachment*.
- $\varepsilon_{\text{HOMO}} \approx -\text{IE}$ is always an approximation.
- Orbitals distort to lower the total energy. (HF theory is energy-based, not density-based.)

¹"Physical meaning of the virtual Kohn–Sham orbitals and orbital energies" [*J. Chem. Theory Comput.* **10**, 4432 (2014)]. Note that this is true of exact Kohn-Sham MOs may be severely degraded by XC approximations.

²"Approximate Koopmans' theorem of DFT" [*J. Chem. Phys.* **116**, 1760 (2002)].

³"Kohn-Sham density functional theory: Predicting and understanding chemistry" [*Rev. Comput. Chem.* **15**, 1 (2000)]

Comparison of Orbital Energies: Excitation

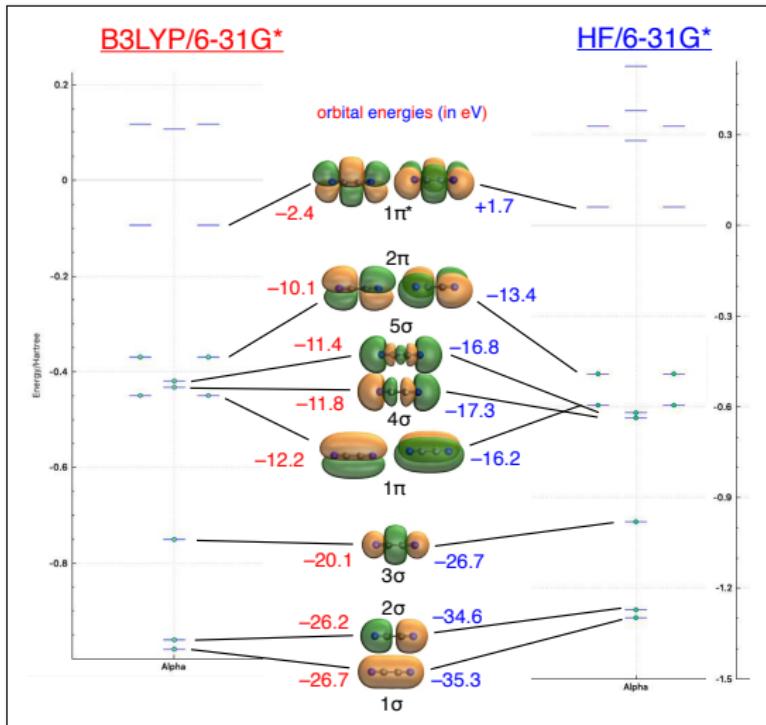
Comparison of HOMO/LUMO Gaps with Benchmark Excitation Energies (in eV).

Molecule	$\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$				Benchmark	
	HF	LDA	BLYP	Exact KS ¹	Singlet	Triplet
H ₂	17.6	10.6	10.5	12.5	12.7	11.7
H ₂ O	14.7	6.5	6.2	7.5	7.4–7.5	7.0–7.2
FH	18.5	8.9	8.5	10.5	10.3	9.9
N ₂	19.9	9.7	9.6	9.9	9.3–10.3 ²	7.8–8.9 ²
CO	17.0	6.9	7.1	7.5	8.5	6.3
HCN	15.4	7.9	7.8	8.0	8.8	5.5–6.0
FCN	14.8	7.3	7.0	7.6	8.4	7.8
HCl	13.8	7.0	6.8	7.4	7.8	7.4

¹ Numerical inversion of Kohn-Sham equation for a near-exact density.

² Includes the Π_g , Σ_u , and Δ_u states, each of which includes the $1\pi_u \rightarrow 1\pi_g$ transition.

Example: Valence MO Diagram for N≡C—C≡N



- Vertical IE (eV):
 - 13.5 (expt)
 - 13.0 (B3LYP/6-31G*)
 - 12.0 (HF/6-31G*)
- Vertical EA (eV):
 - 0.6 (expt)
 - 0.3 (B3LYP/6-31+G*)
 - <0 (HF/6-31+G*)

Outline

1 Logistics

- Q-Chem & IQmol
- Philosophy

2 Intro to Molecular DFT

- Self-Consistent Field Theory
- Gaussian Basis Sets
- Physical Interpretation

3 Exchange-Correlation Functionals

- Jacob's Ladder
- Self-Interaction Error
- Recommendations

4 Contemporary Issues in DFT

- Dispersion Interactions
- Self-Interaction & Delocalization Errors
- HOMO/LUMO Gaps
- Range-Separated Hybrid Functionals

5 TD-DFT

- DFT for Excited States
- Charge-Transfer Problems

HFX: “Exact” (Hartree-Fock) Exchange

- Despite the emphasis on correlation, **exchange** is the *sine qua non* of electronic structure.
 - ▶ **Exchange:** Originates in the antisymmetry requirement. A simple product wave function $\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots$ results in a variational catastrophe.
 - ▶ **Correlation:** Subtleties not captured by the mean-field description of $\sum_{i < j} r_{ij}^{-1}$.
- HF model describes exchange exactly.
 - ▶ \hat{K} is nonlocal so HFX is not equivalent to any scalar potential.
 - ▶ It can be written as an **orbital-dependent** scalar potential.

HFX: “Exact” (Hartree-Fock) Exchange

- Despite the emphasis on correlation, **exchange** is the *sine qua non* of electronic structure.
- HF model describes exchange exactly.
 - ▶ \hat{K} is nonlocal so HFX is not equivalent to any scalar potential.
 - ▶ It can be written as an **orbital-dependent** scalar potential.
- If we force

$$E_K = \sum_{\sigma} \int v_x^{\sigma}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) d\mathbf{r} \quad (\sigma = \alpha, \beta)$$

then

$$\begin{aligned} v_x^{\sigma}(\mathbf{r}) &\stackrel{\text{def}}{=} \frac{1}{\rho_{\sigma}(\mathbf{r})} \sum_j^{\text{occ}} \psi_{j\sigma}^*(\mathbf{r}) \hat{K} \psi_{j\sigma}(\mathbf{r}) \\ &= \frac{1}{2} \int \frac{h_x^{\sigma}(\mathbf{r}|\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r}' \end{aligned}$$

where h_x^{σ} is the **exchange hole** for σ -spin electrons.

Approximating Exact Exchange

- It's easy to compute $h_x^\sigma(\mathbf{r}_1|\mathbf{r}_2)$ given $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots)$, but harder to model the hole using only the density.
 - ▶ **Wave function theory:** $\hat{H}\Psi = E\Psi$ where \hat{H} is simple but Ψ is complicated.
 - ▶ **DFT:** $\hat{F}\psi_k = \varepsilon_k\psi_k$ where \hat{F} is complicated but ψ_k is simple.

Approximating Exact Exchange

- It's easy to compute $h_x^\sigma(\mathbf{r}_1|\mathbf{r}_2)$ given $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots)$, but harder to model the hole using only the density.
 - ▶ **Wave function theory:** $\hat{H}\Psi = E\Psi$ where \hat{H} is simple but Ψ is complicated.
 - ▶ **DFT:** $\hat{F}\psi_k = \varepsilon_k\psi_k$ where \hat{F} is complicated but ψ_k is simple.
- For the special case of a uniform electron gas (UEG),

$$v_x^\sigma(\mathbf{r}) \propto \rho_\sigma(\mathbf{r})^{1/3},$$

which is the exchange potential for the *local density approximation* (LDA).*

- Functionals beyond LDA are often based on an *exchange inhomogeneity factor*, $F_x[\rho]$:

$$E_x[\rho(\mathbf{r})] \propto \int F_x[\rho(\mathbf{r})] \rho(\mathbf{r})^{4/3} d\mathbf{r}.$$

* LDA or UEG exchange is called "Slater exchange" in many quantum chemistry programs.

How Does This Work in Practice?

- Given models for $v_x[\rho](\mathbf{r})$ and $v_c[\rho](\mathbf{r})$,

$$E_{xc}[\rho(\mathbf{r})] = \int v_{xc}[\rho](\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

- Even if each infinitesimal bit of $\rho(\mathbf{r})$ is treated like a (near-)homogeneous density, the whole thing is iterated to self-consistency

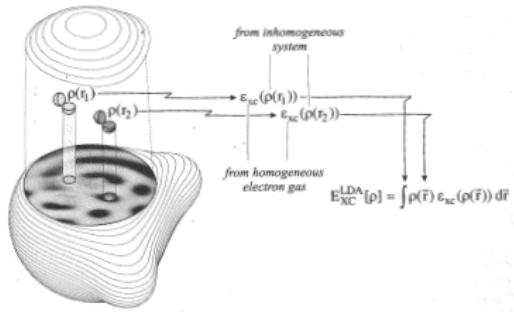


Fig. 6-2 of Koch & Holthausen,
*A Chemist's Guide to Density
Functional Theory* (2001)

How Does This Work in Practice?

- Given models for $v_x[\rho](\mathbf{r})$ and $v_c[\rho](\mathbf{r})$,

$$E_{xc}[\rho(\mathbf{r})] = \int v_{xc}[\rho](\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

- Even if each infinitesimal bit of $\rho(\mathbf{r})$ is treated like a (near-)homogeneous density, the whole thing is iterated to self-consistency

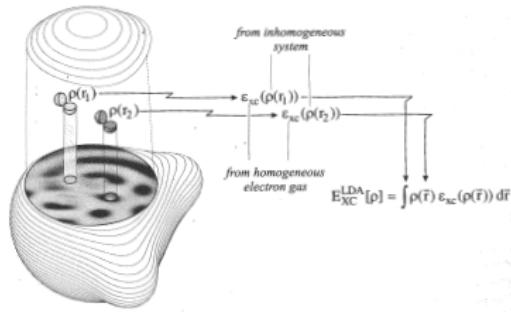


Fig. 6-2 of Koch & Holthausen,
A Chemist's Guide to Density
Functional Theory (2001)

- $E_{xc}[\rho]$ is evaluated on a numerical integration grid.*
 - Absolute energies can vary greatly from one grid (or basis set) to the next.
 - Energy differences should always be reported using same basis & grid.

* Grids for DFT: Dasgupta & Herbert [*J. Comput. Chem.* **38**, 869 (2017)]

1 Physics-based models:

Introduce an *ansatz* for $F_x[\rho]$ that satisfies known constraints on $E_{xc}[\rho]$.

- ▶ e.g., try to model the exchange hole.
- ▶ Becke '88 (B88)¹ and PBE² are the most widely-used examples.
- ▶ The SCAN functional³ satisfies all 17 known constraints but still has deficiencies (lack of long-range dispersion).

¹"Density-functional exchange-energy approximation with correct asymptotic behavior" [*Phys. Rev. A* **38**, 3098 (1988)]

²"Generalized gradient approximations made simple" [*Phys. Rev. Lett.* **77**, 3865 (1996)]

³"Strongly constrained and appropriately normed semilocal density functional" [*Phys. Rev. Lett.* **115**, 036402 (2015)]

1 Physics-based models:

Introduce an *ansatz* for $F_x[\rho]$ that satisfies known constraints on $E_{xc}[\rho]$.

- ▶ e.g., try to model the exchange hole.
- ▶ Becke '88 (B88)¹ and PBE² are the most widely-used examples.
- ▶ The SCAN functional³ satisfies all 17 known constraints but still has deficiencies (lack of long-range dispersion).

2 Empirical approach:

Series expansion of $F_x[\rho(\mathbf{r})]$, often in powers of $s(\mathbf{r}) = \|\hat{\nabla}\rho(\mathbf{r})\|/\rho(\mathbf{r})^{4/3}$ with empirical exponents and coefficients.

- ▶ Beware of overfitting!⁴

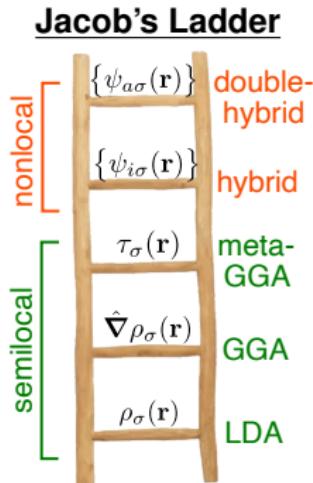
¹ "Density-functional exchange-energy approximation with correct asymptotic behavior" [*Phys. Rev. A* **38**, 3098 (1988)]

² "Generalized gradient approximations made simple" [*Phys. Rev. Lett.* **77**, 3865 (1996)]

³ "Strongly constrained and appropriately normed semilocal density functional" [*Phys. Rev. Lett.* **115**, 036402 (2015)]

⁴ "Characterizing and understanding the remarkably slow basis set convergence of several Minnesota density functionals for intermolecular interaction energies" [*J. Chem. Theory Comput.* **9**, 4453 (2013)]

Hierarchical Classification of XC Functionals



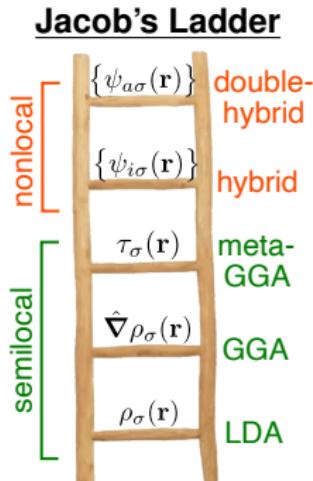
Rungs:

1. Local density approximation (LDA), $E_{xc}[\rho_\sigma]$.
2. Generalized gradient approximations (GGAs): $E_{xc}[\rho_\sigma, \hat{\nabla}\rho_\sigma]$.

Ingredients:

- $\rho_\sigma(\mathbf{r})$, spin density ($\sigma = \alpha$ or β)

Hierarchical Classification of XC Functionals

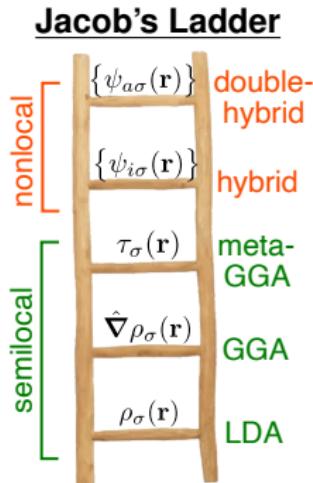


Rungs:

1. Local density approximation (LDA), $E_{xc}[\rho_\sigma]$.
2. Generalized gradient approximations (GGAs): $E_{xc}[\rho_\sigma, \hat{\nabla}\rho_\sigma]$.
3. Meta-GGAs: $E_{xc}[\rho_\sigma, \hat{\nabla}\rho_\sigma, \hat{\nabla}^2\rho_\sigma, \tau_\sigma]$.

Ingredients:

- $\rho_\sigma(\mathbf{r})$, spin density ($\sigma = \alpha$ or β)
- $\tau_\sigma(\mathbf{r}) = \sum_i^{\text{occ}} \|\hat{\nabla}\psi_{i\sigma}(\mathbf{r})\|^2$, kinetic energy density



Rungs:

1. Local density approximation (LDA), $E_{xc}[\rho_\sigma]$.
2. Generalized gradient approximations (GGAs): $E_{xc}[\rho_\sigma, \hat{\nabla}\rho_\sigma]$.
3. Meta-GGAs: $E_{xc}[\rho_\sigma, \hat{\nabla}\rho_\sigma, \hat{\nabla}^2\rho_\sigma, \tau_\sigma]$.
4. Hybrid functionals including HFX.
5. Double-hybrid functionals including MP2 correlation.

Ingredients:

- $\rho_\sigma(\mathbf{r})$, spin density ($\sigma = \alpha$ or β)
- $\tau_\sigma(\mathbf{r}) = \sum_i^{\text{occ}} \|\hat{\nabla}\psi_{i\sigma}(\mathbf{r})\|^2$, kinetic energy density
- $\{\psi_{i\sigma}\}, \{\psi_{a\sigma}\}$: occupied, virtual Kohn-Sham MOs

Outline

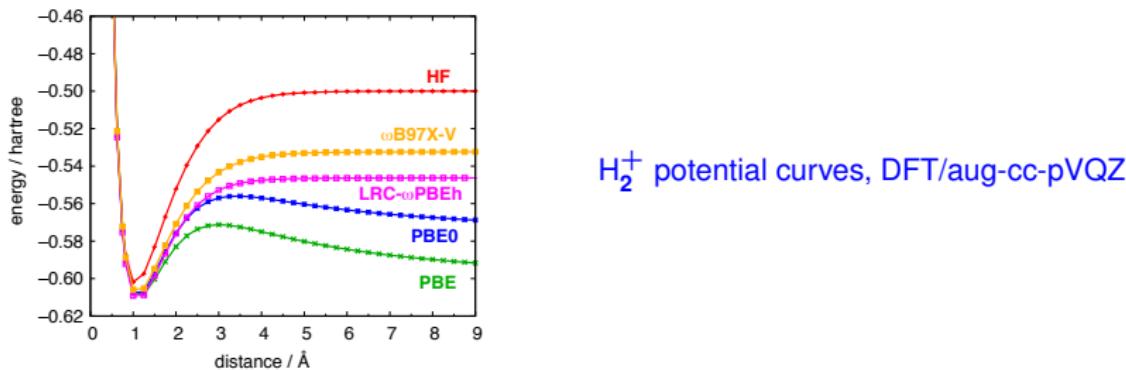
- 1 Logistics
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals
 - Jacob's Ladder
 - **Self-Interaction Error**
 - Recommendations
- 4 Contemporary Issues in DFT
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - HOMO/LUMO Gaps
 - Range-Separated Hybrid Functionals
- 5 TD-DFT
 - DFT for Excited States
 - Charge-Transfer Problems

Self-Interaction Error (SIE)

- In Hartree-Fock theory, $\hat{J} - \hat{K} = 0$ for any one-electron system.
- For most XC functionals, $E_H + E_{xc} \neq 0$ for one-electron densities.

Self-Interaction Error (SIE)

- In Hartree-Fock theory, $\hat{J} - \hat{K} = 0$ for any one-electron system.
- For most XC functionals, $E_H + E_{xc} \neq 0$ for one-electron densities.
- A main consequence of SIE is overstabilization of half-filled orbitals.
 - ▶ Fractional charges on separated atoms
 - ▶ Delocalization of unpaired electrons
 - ▶ Overstabilization of transition states \implies too-low reaction barriers



Rung 4: Hybrid Functionals

- Hybrids mix a fraction of HFX with a GGA exchange functional.

- ▶ Epitomized by Becke's three-parameter *ansatz*,¹

$$E_{xc}^{\text{B3LYP}} = E_x^{\text{LDA}} + a_1(E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_2(E_x^{\text{GGA}} - E_x^{\text{LDA}}) \\ E_c^{\text{LDA}} + a_3(E_c^{\text{GGA}} - E_c^{\text{LDA}})$$

where the GGA correlation functional is that of Lee, Yang, and Parr (LYP),² and $a_1 = 0.2$ (20% HFX).

¹ Becke, "Density-functional thermochemistry. III. The role of exact exchange" [*J. Chem. Phys.* **98**, 5648 (1993)]

² Lee, Yang, & Parr [*Phys. Rev. B* **37**, 785 (1988)]

Rung 4: Hybrid Functionals

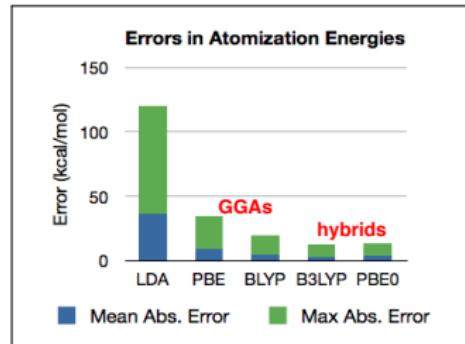
- Hybrids mix a fraction of HFX with a GGA exchange functional.

- ▶ Epitomized by Becke's three-parameter *ansatz*,¹

$$E_{xc}^{\text{B3LYP}} = E_x^{\text{LDA}} + a_1(E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_2(E_x^{\text{GGA}} - E_x^{\text{LDA}})$$
$$E_c^{\text{LDA}} + a_3(E_c^{\text{GGA}} - E_c^{\text{LDA}})$$

where the GGA correlation functional is that of Lee, Yang, and Parr (LYP),² and $a_1 = 0.2$ (20% HFX).

- This is what finally made DFT accurate enough for molecular applications.
- Figure: Errors in DFT/6-311+G(3df,2p) atomization energies.³



¹Becke, "Density-functional thermochemistry. III. The role of exact exchange" [J. Chem. Phys. 98, 5648 (1993)]

²Lee, Yang, & Parr [Phys. Rev. B 37, 785 (1988)]

³J. Chem. Phys. 110, 5029 (1999).

Role of HFX in DFT

- In hybrid DFT, v_{xc} is no longer a local potential since \hat{K} is nonlocal.
 - ▶ Mixes formal properties of HF and KS theories
- Depending upon whom you ask, the introduction of HFX in DFT was either:
 - 1 The thing that made DFT finally useful for chemistry.
 - 2 An abuse of the original idea of a scalar XC potential for all orbitals.

Role of HFX in DFT

- In hybrid DFT, v_{xc} is no longer a local potential since \hat{K} is nonlocal.
 - ▶ Mixes formal properties of HF and KS theories
- Depending upon whom you ask, the introduction of HFX in DFT was either:
 - 1 The thing that made DFT finally useful for chemistry.
 - 2 An abuse of the original idea of a scalar XC potential for all orbitals.
- Pros (☺) and cons (☹) of hybrid DFT:
 - ☺ Hybrid functionals reduce SIE and greatly improve reaction barriers.
 - ☺ In excited-state (TD-)DFT calculations, there is no electron–hole interaction unless \hat{K} is included.
 - ☺ In large systems, GGAs tend toward vanishing HOMO/LUMO gaps, which makes the SCF equations difficult to converge. Hybrids open up the gap.

- In hybrid DFT, v_{xc} is no longer a local potential since \hat{K} is nonlocal.
 - ▶ Mixes formal properties of HF and KS theories
- Depending upon whom you ask, the introduction of HFX in DFT was either:
 - 1 The thing that made DFT finally useful for chemistry.
 - 2 An abuse of the original idea of a scalar XC potential for all orbitals.

■ Pros (😊) and cons (😢) of hybrid DFT:

- 😊 Hybrid functionals reduce SIE and greatly improve reaction barriers.
- 😊 In excited-state (TD-)DFT calculations, there is no electron–hole interaction unless \hat{K} is included.
- 😊 In large systems, GGAs tend toward vanishing HOMO/LUMO gaps, which makes the SCF equations difficult to converge. Hybrids open up the gap.
- 😢 A nonlocal \hat{v}_{xc} means different potentials for occupied vs. virtual MOs.
- 😢 In periodic codes, hybrid functionals are 10–100× more expensive than GGAs.

Outline

1 Logistics

- Q-Chem & IQmol
- Philosophy

2 Intro to Molecular DFT

- Self-Consistent Field Theory
- Gaussian Basis Sets
- Physical Interpretation

3 Exchange-Correlation Functionals

- Jacob's Ladder
- Self-Interaction Error
- Recommendations

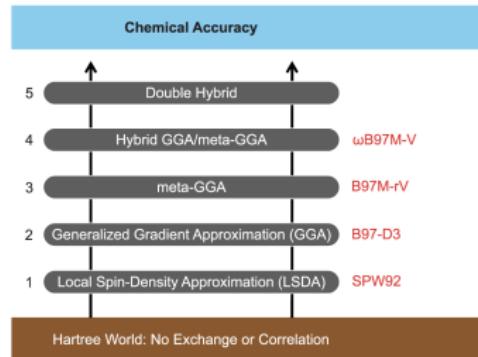
4 Contemporary Issues in DFT

- Dispersion Interactions
- Self-Interaction & Delocalization Errors
- HOMO/LUMO Gaps
- Range-Separated Hybrid Functionals

5 TD-DFT

- DFT for Excited States
- Charge-Transfer Problems

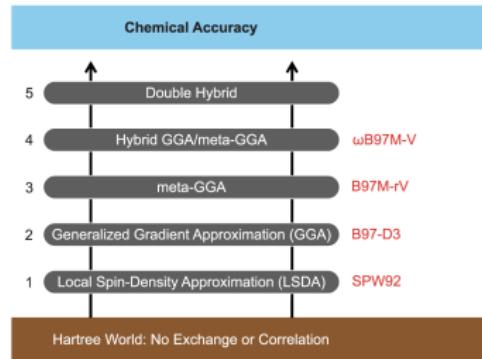
Systematic Assessment of Jacob's Ladder



Best-performing functional at each rung of Jacob's ladder

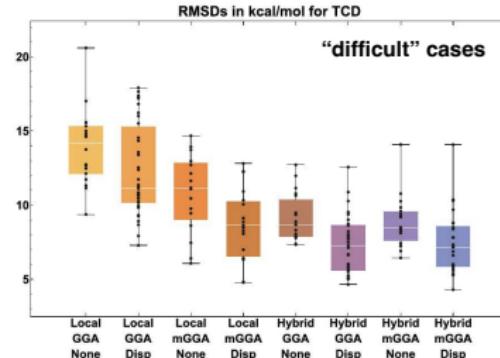
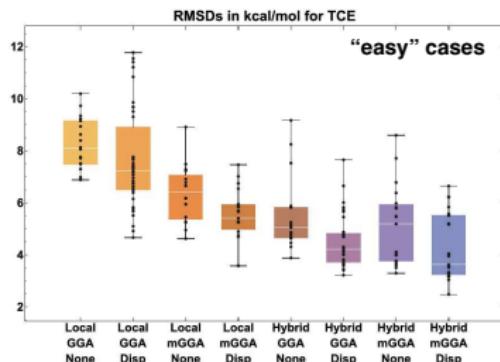
"Thirty years of density functional theory... assessment of 200 density functionals" [*Mol. Phys.* **115**, 2315 (2017)]

Systematic Assessment of Jacob's Ladder



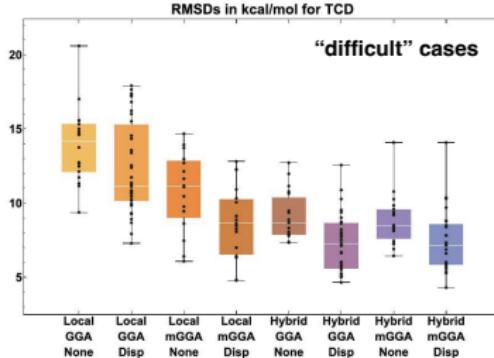
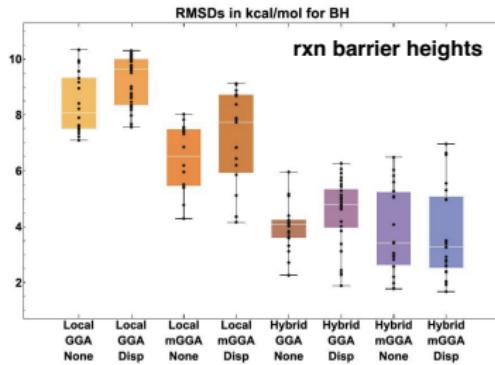
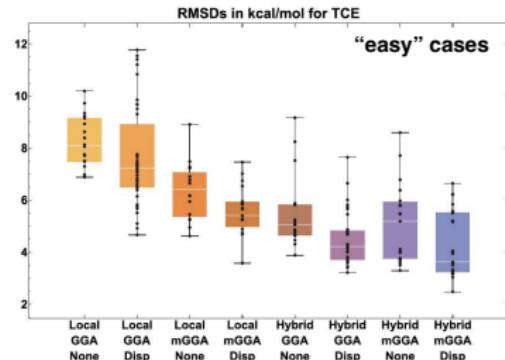
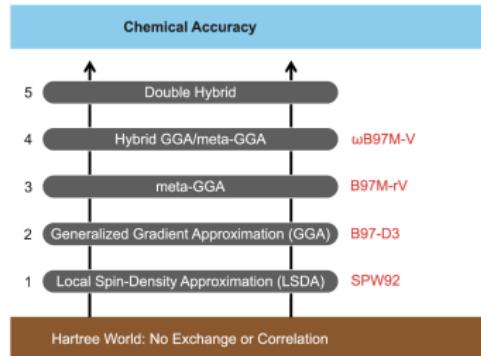
Best-performing functional at each rung of Jacob's ladder

Figure at right:
Thermochemical benchmarks (atomization energies, bond dissociation energies, electron affinities, ionization energies, and reaction enthalpies).



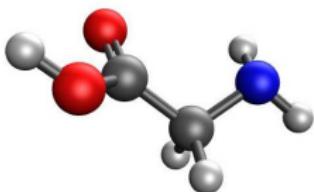
"Thirty years of density functional theory... assessment of 200 density functionals" [Mol. Phys. 115, 2315 (2017)]

Systematic Assessment of Jacob's Ladder

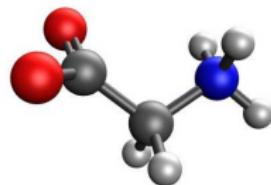


“Thirty years of density functional theory... assessment of 200 density functionals” [Mol. Phys. 115, 2315 (2017)]

Exercise: Tautomers of Glycine

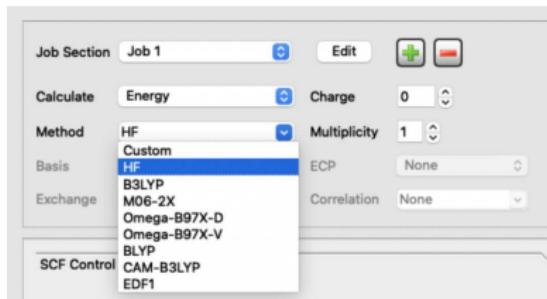


amino acid
 $\text{HOOC}-\text{CH}_2-\text{NH}_2$

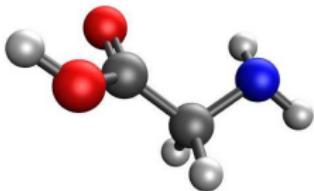


zwitterion
 $-\text{OOC}-\text{CH}_2-\text{NH}_3^+$

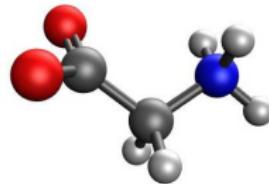
- **Question #1:** How does relative energy depend on XC functional?
 - ▶ e.g., using 6-31+G* basis set



Exercise: Tautomers of Glycine



zwitterion
 $\text{HOOC}-\text{CH}_2-\text{NH}_3^+$



amino acid
 $\text{HOOC}-\text{CH}_2-\text{NH}_2$

- **Question #1:** How does relative energy depend on XC functional?
 - ▶ e.g., using 6-31+G* basis set
- **Question #2:** Does this answer change with an implicit solvation model?

```
$rem
method      wB97X-D
basis       6-31+G*
solvent_method   SMD
$end
```

Which Functional to Use?

Caveats:

- 1 There are many functionals, nearly all of which can be safely ignored.
- 2 My recommendations are guidelines for general use.
- 3 For any particular application, it may be possible to find some esoteric functional that performs better for a given property.
 - ▶ This is especially true if you're willing to start adjusting parameters.

Which Functional to Use?

Caveats:

- 1 There are many functionals, nearly all of which can be safely ignored.
- 2 My recommendations are guidelines for general use.
- 3 For any particular application, it may be possible to find some esoteric functional that performs better for a given property.
 - ▶ This is especially true if you're willing to start adjusting parameters.
 - ▶ **How much should you trust the conclusions drawn from such an approach?**
Are they predictive?
 - ▶ Conclusions drawn from DFT calculations should be robust against modest variations, else they are not "conclusions".
 - ▶ There is no magic functional, and there should not be a "special" basis set that is required by a given functional.*

* Semi-empirical methods **are** parameterized for specific basis sets.

Recommendations: GGAs

- Hard to recommend for molecular applications.
- Delocalization error can make large GGA calculations difficult to converge in diagonalization-based codes.
- The ubiquitous ones are **BLYP**¹ and **PBE**,² which should be used as **BLYP+D3** and **PBE+D3**.³

¹ **BLYP**: B88 [Becke, *Phys. Rev. A* **38**, 3098 (1988)] + LYP [Lee, Yang, & Parr, *Phys. Rev. B* **37**, 785 (1988)]

² **PBE**: Perdew, Burke, & Ernzerhof, [*Phys. Rev. Lett.* **77**, 3865 (1996)]

³ **D3**: Grimme, "Density functional theory with London dispersion corrections" [*WIREs Comput. Mol. Sci.* **1**, 211 (2011)]

Recommendations: GGAs

- Hard to recommend for molecular applications.
- Delocalization error can make large GGA calculations difficult to converge in diagonalization-based codes.
- The ubiquitous ones are BLYP¹ and PBE,² which should be used as BLYP+D3 and PBE+D3.³
- B97+D3⁴ may be the best all-round GGA. (This is under-appreciated.)

Functional	Class	Error (kcal/mol) ⁵		
		$\Delta_f H$	$\Delta_{rxn} H$	noncovalent*
BLYP	GGA	7.1	15.5	0.7
PBE	GGA	16.7	7.9	1.0
B97-D	GGA	3.8	7.8	0.4
TPSS	meta-GGA	6.1	8.4	0.8
B3LYP	hybrid	3.6	9.8	0.8

* When +D3 is included

¹ BLYP: B88 [Becke, *Phys. Rev. A* **38**, 3098 (1988)] + LYP [Lee, Yang, & Parr, *Phys. Rev. B* **37**, 785 (1988)]

² PBE: Perdew, Burke, & Ernzerhof, [*Phys. Rev. Lett.* **77**, 3865 (1996)]

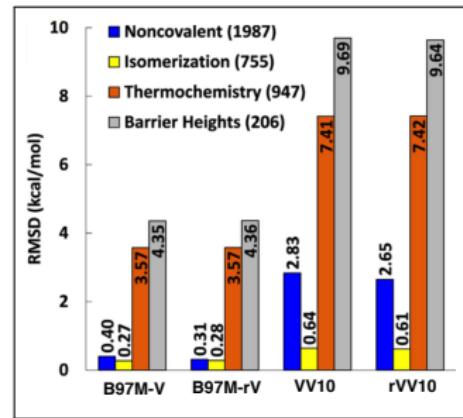
³ D3: Grimme, "Density functional theory with London dispersion corrections" [*WIREs Comput. Mol. Sci.* **1**, 211 (2011)]

⁴ B97: Becke [*J. Chem. Phys.* **107**, 8554 (1997)]

⁵ Data: *J. Comput. Chem.* **27**, 1787 (2006)

Recommendations: Meta-GGAs

- B97M-V¹ and B97M-rV² are the best all-around mGGAs.
- -V and -rV indicates use of VV10 or rVV10.³
 - ▶ these are nonlocal correlation functionals
 - ▶ in principle they have the right physics to describe dispersion “for the right reasons”
 - ▶ simplified variants of what physicists call “the” van der Waals functional (vdW-DF)⁴
- These are semilocal functionals (no HFX).
 - ▶ cheaper than hybrids for large molecules
 - ▶ efficient implementation in periodic codes



Error statistics for VV10-based functionals
[*J. Phys. Chem. Lett.* **8**, 35 (2017)]

¹ B97M-V: *J. Chem. Phys.* **142**, 074111 (2015)

² B97M-rV: *J. Phys. Chem. Lett.* **8**, 35 (2017)

³ VV10: *J. Chem. Phys.* **133**, 244103 (2010). rVV10: *Phys. Rev. B* **87**, 041108R (2013)

⁵ vdW-DF: *Phys. Rev. Lett.* **92**, 246401 (2004); *Phys. Rev. B* **76**, 125112 (2007)

Recommendations: Hybrids

- B3LYP¹ has long been the workhorse in molecular quantum chemistry.
 - ▶ Superior alternatives have emerged (e.g., ω B97X-D and ω B97X-D3)² but B3LYP remains competitive.
 - ▶ Use as B3LYP+D3.
- PBE0³ is the hybrid version of PBE; use as PBE0+D3.
 - ▶ $C_{HFX} = 0.25$ for PBE0 vs. $C_{HFX} = 0.20$ for B3LYP.
 - ▶ Very similar performance to B3LYP for main-group chemistry.

¹ B3: *J. Chem. Phys.* **98**, 5648 (1993). LYP: *Phys. Rev. B* **37**, 785 (1988)

² ω B97X-D: *Phys. Chem. Chem. Phys.* **10**, 6615 (2008). ω B97X-D3: *J. Chem. Theory Comput.* **9**, 263 (2013)

³ PBE0: *J. Chem. Phys.* **110**, 6158 (1999)

⁴ ω B97X-V: *Phys. Chem. Chem. Phys.* **16**, 9904 (2014)

⁵ ω B97M-V: *J. Chem. Phys.* **144**, 244110 (2016)

Recommendations: Hybrids

- B3LYP¹ has long been the workhorse in molecular quantum chemistry.
 - ▶ Superior alternatives have emerged (e.g., ω B97X-D and ω B97X-D3)² but B3LYP remains competitive.
 - ▶ Use as B3LYP+D3.
- PBE0³ is the hybrid version of PBE; use as PBE0+D3.
 - ▶ $C_{HFX} = 0.25$ for PBE0 vs. $C_{HFX} = 0.20$ for B3LYP.
 - ▶ Very similar performance to B3LYP for main-group chemistry.
- ω B97X-V⁴ (a hybrid GGA) outperforms all of these, but is somewhat more expensive to evaluate and requires larger basis sets (e.g., def2-TZVPD).
- ω B97M-V⁵ (a hybrid meta-GGA) is probably the single best all-around density functional to date, but a bit more expensive still.

¹ B3: *J. Chem. Phys.* **98**, 5648 (1993). LYP: *Phys. Rev. B* **37**, 785 (1988)

² ω B97X-D: *Phys. Chem. Chem. Phys.* **10**, 6615 (2008). ω B97X-D3: *J. Chem. Theory Comput.* **9**, 263 (2013)

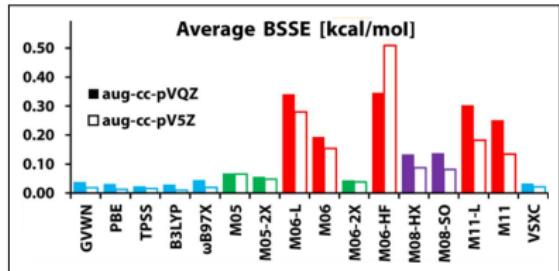
³ PBE0: *J. Chem. Phys.* **110**, 6158 (1999)

⁴ ω B97X-V: *Phys. Chem. Chem. Phys.* **16**, 9904 (2014)

⁵ ω B97M-V: *J. Chem. Phys.* **144**, 244110 (2016)

Why No “Minnesota” Functionals?

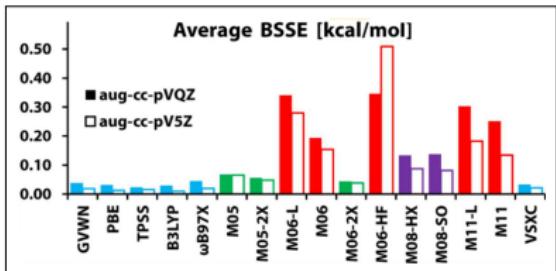
Difficult to reach the basis-set limit¹



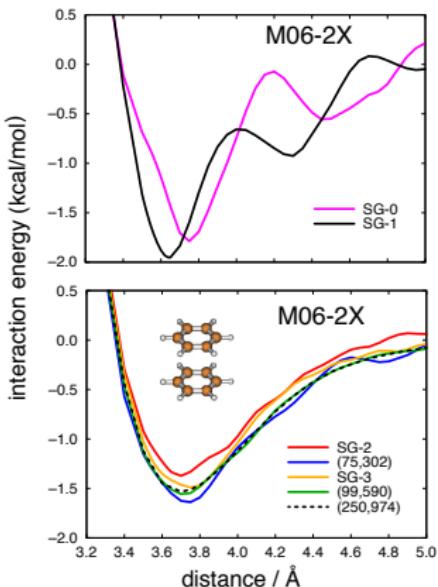
¹ Mardirossian & Head-Gordon, "Characterizing and understanding the remarkably slow basis set convergence of several Minnesota density functionals for intermolecular interaction energies" [*J. Chem. Theory Comput.* **9**, 4453 (2013)]

Why No “Minnesota” Functionals?

Difficult to reach the basis-set limit¹



Difficult to reach the XC grid limit²

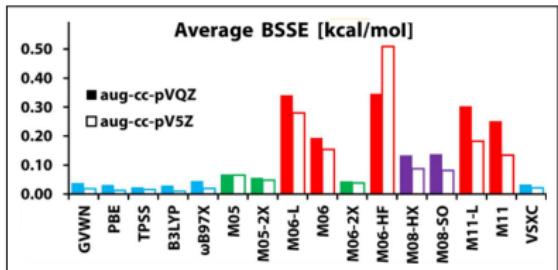


¹ Mardirossian & Head-Gordon, “Characterizing and understanding the remarkably slow basis set convergence of several Minnesota density functionals for intermolecular interaction energies” [*J. Chem. Theory Comput.* **9**, 4453 (2013)]

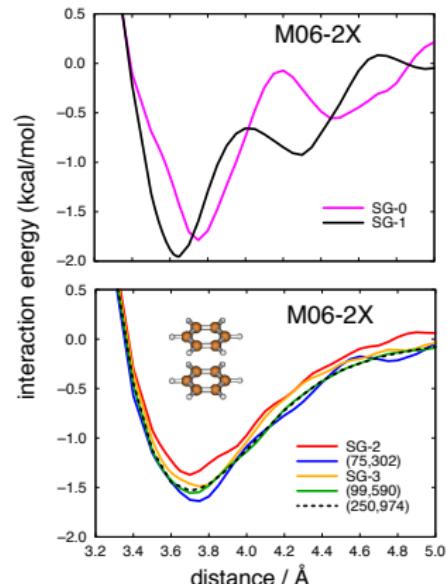
² Dasgupta & Herbert [*J. Comput. Chem.* **38**, 869 (2017)]

Why No “Minnesota” Functionals?

Difficult to reach the basis-set limit¹



Difficult to reach the XC grid limit²

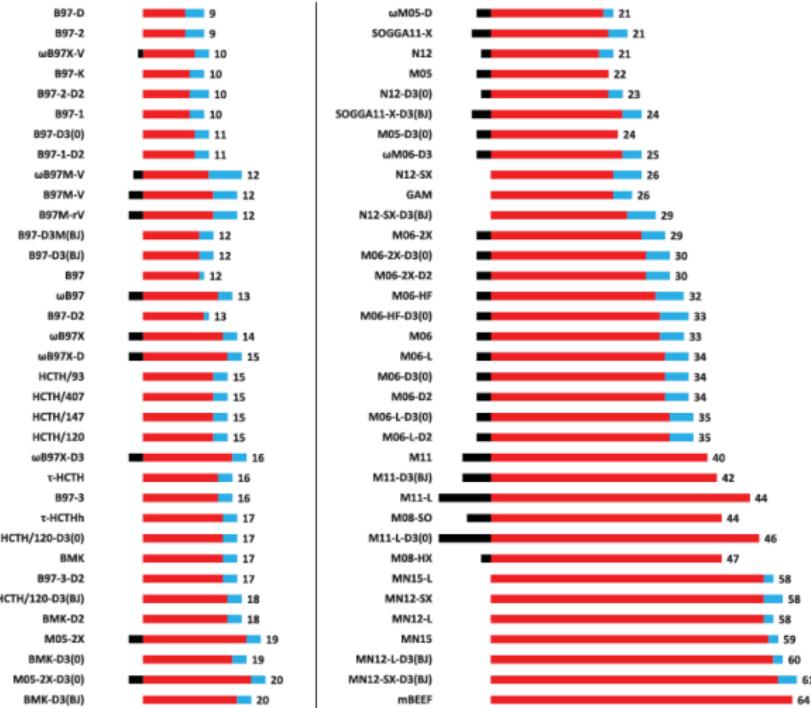


- Stability problems arise from an oscillatory integrand.
 - F_x is an 8th-order power series in $s(\mathbf{r})$
 - Fitted parameters have large values and alternating signs
- May cause problems in basis sets very different from the one used to parameterize.

¹ Mardirossian & Head-Gordon, “Characterizing and understanding the remarkably slow basis set convergence of several Minnesota density functionals for intermolecular interaction energies” [*J. Chem. Theory Comput.* **9**, 4453 (2013)]

² Dasgupta & Herbert [*J. Comput. Chem.* **38**, 869 (2017)]

Counting Adjustable Parameters



■ **Red:** indicates the number of fitted parameters.

■ **Blue:** indicates borrowed or preset parameters

■ **Black:** indicates number of exact constraints

■ Numerical values are

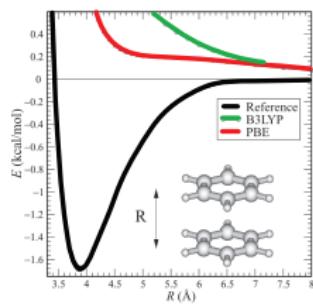
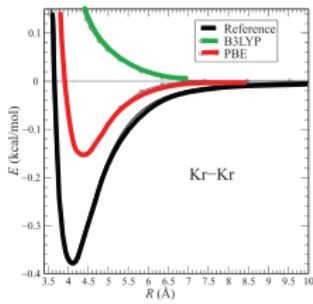
$$N_{\text{param}} = N_{\text{fitted}} - N_{\text{constr}}$$

Outline

- 1 Logistics**
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT**
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals**
 - Jacob's Ladder
 - Self-Interaction Error
 - Recommendations
- 4 Contemporary Issues in DFT**
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - HOMO/LUMO Gaps
 - Range-Separated Hybrid Functionals
- 5 TD-DFT**
 - DFT for Excited States
 - Charge-Transfer Problems

van der Waals (vdW) Interactions in DFT

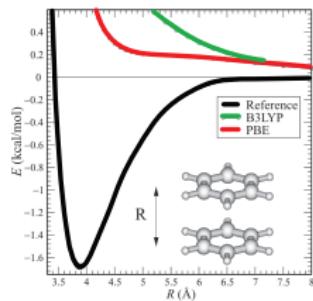
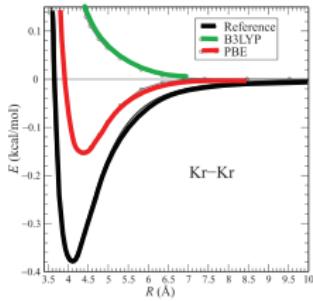
- “vdW” is often used synonymously with dispersion.
- E_{disp} comes from long-range **non-local** correlation.



Grimme, “DFT with London dispersion corrections” [WIREs Comput. Mol. Sci. 1, 211 (2011)]

van der Waals (vdW) Interactions in DFT

- “vdW” is often used synonymously with dispersion.
- E_{disp} comes from long-range **non-local** correlation.
 - ▶ “-V” functionals (containing VV10) do contain nonlocal correlation.
 - ▶ Semilocal functionals (including mGGAs like SCAN and Minnesota) **do not**.
 - ▶ With semilocal functionals, attraction is possible at vdW contact distances but this is not true (or at least, not pure) dispersion.*



Grimme, “DFT with London dispersion corrections” [WIREs Comput. Mol. Sci. 1, 211 (2011)]

* “Do semilocal density-functional approximations recover dispersion energies...?” [Phys. Rev. Lett. 121, 113402 (2018)]

Empirical Dispersion Corrections: DFT+D

■ **Problem:** Many functionals lack long-range, nonlocal correlation.

- ▶ Exchange energy of A \cdots B decays exponentially with distance in semilocal functionals, because that's how the density overlap decays.
- ▶ Recall that $E_{\text{disp}} \sim -\alpha_A \alpha_B / R_{AB}^6$ for well-separated A \cdots B.

Empirical Dispersion Corrections: DFT+D

■ **Problem:** Many functionals lack long-range, nonlocal correlation.

- ▶ Exchange energy of A · · · B decays exponentially with distance in semilocal functionals, because that's how the density overlap decays.
- ▶ Recall that $E_{\text{disp}} \sim -\alpha_A \alpha_B / R_{AB}^6$ for well-separated A · · · B.

■ **Solution:** Augment standard functionals with atom–atom C_6/R^6 potentials:¹

$$E_{\text{DFT+D}} = E_{\text{DFT}} - \underbrace{\sum_{A,B}^{\text{atoms}} \left(\frac{C_6^{AB}}{R_{AB}^6} + \frac{C_8^{AB}}{R_{AB}^8} + \dots \right) f_{\text{damp}}(R_{AB})}_{+\text{D}}$$

- ▶ $\{C_n^{AB}\}$ are generally taken to be empirical fitting parameters.
- ▶ Additional parameters in the damping function f_{damp} .

¹ Grimme, "DFT with London dispersion corrections" [*WIREs Comput. Mol. Sci.* **1**, 211 (2011)]

Empirical Dispersion Corrections: DFT+D

■ Problem: Many functionals lack long-range, nonlocal correlation.

- ▶ Exchange energy of A · · · B decays exponentially with distance in semilocal functionals, because that's how the density overlap decays.
- ▶ Recall that $E_{\text{disp}} \sim -\alpha_A \alpha_B / R_{AB}^6$ for well-separated A · · · B.

■ Solution: Augment standard functionals with atom–atom C_6/R^6 potentials:¹

$$E_{\text{DFT+D}} = E_{\text{DFT}} - \underbrace{\sum_{A,B}^{\text{atoms}} \left(\frac{C_6^{AB}}{R_{AB}^6} + \frac{C_8^{AB}}{R_{AB}^8} + \dots \right) f_{\text{damp}}(R_{AB})}_{+\text{D}}$$

- ▶ $\{C_n^{AB}\}$ are generally taken to be empirical fitting parameters.
- ▶ Additional parameters in the damping function f_{damp} .

■ Cautionary notes:

- ▶ Don't equate the value of the "+D" correction with the actual dispersion energy.
- ▶ M06-2X has been advertised as "DFT for vdW interactions", but includes (at best) only mid-range correlation.²

¹ Grimme, "DFT with London dispersion corrections" [*WIREs Comput. Mol. Sci.* **1**, 211 (2011)]

² "Do semilocal density-functional approximations recover dispersion...?" [*Phys. Rev. Lett.* **121**, 113402 (2018)]

- +D correction is crucial for conformational energies.
 - ▶ Stabilize compact structures with more close contacts.
 - ▶ Intramolecular BSSE has the same effect and can artificially compensate.
 - ▶ **Be wary of functionals that come with a small-basis recommendation.**

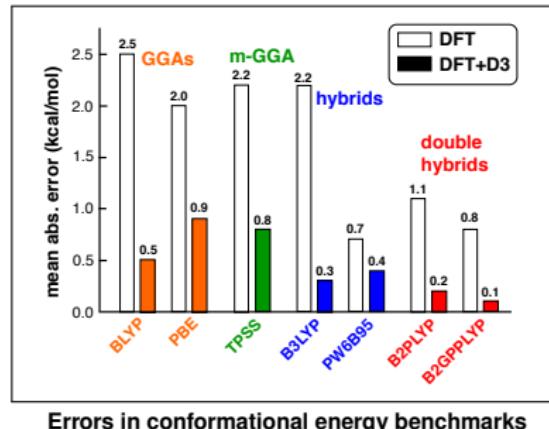
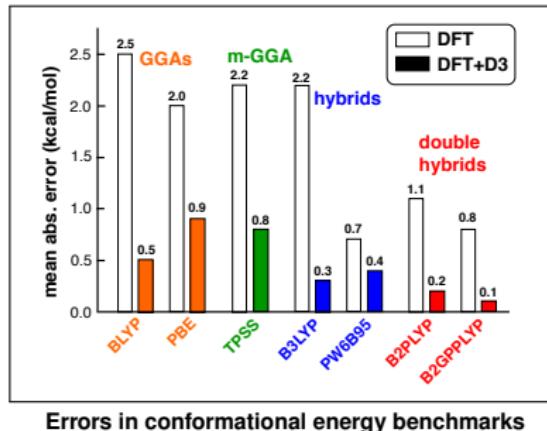


Figure: "DFT with London dispersion corrections" [*WIREs Comput. Mol. Sci.* 1, 211 (2011)]

- +D correction is crucial for conformational energies.
 - ▶ Stabilize compact structures with more close contacts.
 - ▶ Intramolecular BSSE has the same effect and can artificially compensate.
 - ▶ **Be wary of functionals that come with a small-basis recommendation.**



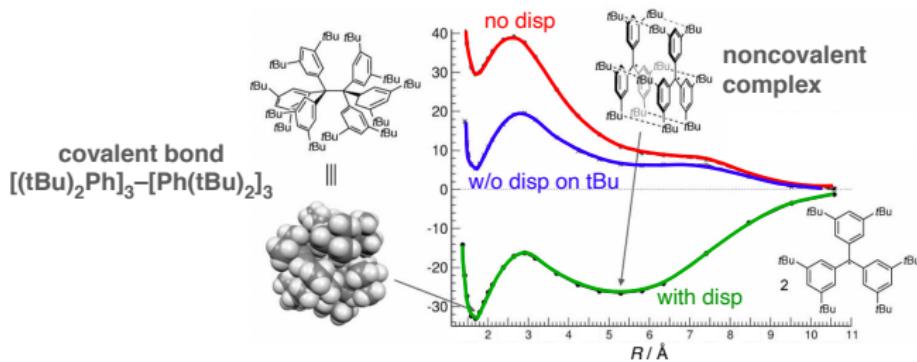
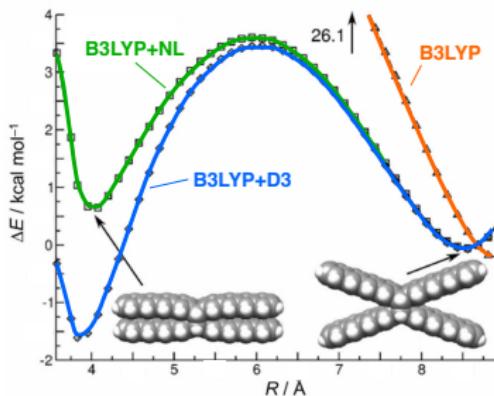
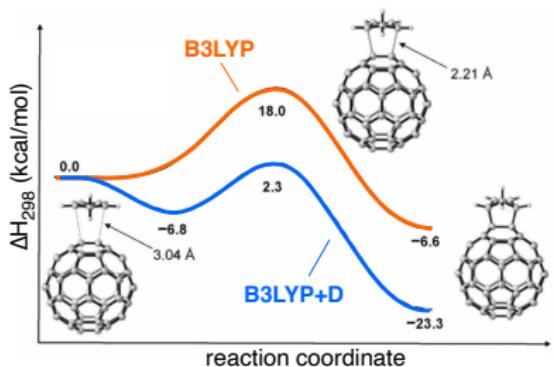
- In *ab initio* MD simulations of liquid water, inclusion of +D:
 - ▶ somewhat corrects ice-like overstructuring in $g(r)$.¹
 - ▶ increases melting temperature by ~ 50 K.²

Figure: "DFT with London dispersion corrections" [WIREs Comput. Mol. Sci. 1, 211 (2011)]

¹"Importance of van der Waals interactions in liquid water" [J. Phys. Chem. B 113, 1127 (2009)]

²"How van der Waals interactions determine the unique properties of water" [PNAS 113, 8368 (2016)]

Chemical Examples: DFT vs. DFT+D



Wagner & Schreiner, "London dispersion in molecular chemistry..." [Angew. Chem. 54, 12274 (2015)]

Performance of Grimme's +D3 Correction

Property	mean signed error (kcal/mol)					
	HF	LDA	PBE (GGA)	TPSS (mGGA)	PBE0 (hybrid)	TPSSh (hybrid)
ΔE (atomization)	112.8	-58.1	-12.2	-2.7	1.1	1.5
ΔE (vdW) ^a	6.0	-1.1	3.4	4.7	3.4	4.6
ΔE (H-bond) ^b	18.3	-30.7	-1.3	3.2	0.2	3.5

^aAlkane dimers. ^bWater clusters.

Performance of Grimme's +D3 Correction

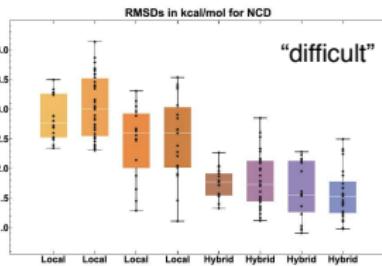
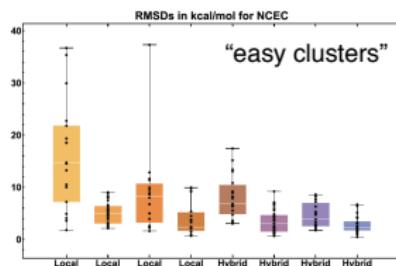
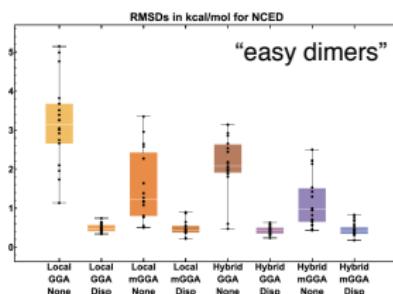
Property	mean signed error (kcal/mol)						
	HF	LDA	PBE (GGA) (+D3)	TPSS (mGGA) (+D3)	PBE0 (hybrid) (+D3)	TPSSh (hybrid) (+D3)	
ΔE (atomization)	112.8	-58.1	-12.2 (-13.1)	-2.7 (-3.9)	1.1 (0.3)	1.5 (0.4)	
ΔE (vdW) ^a	6.0	-1.1	3.4 (-0.1)	4.7 (0.2)	3.4 (-0.0)	4.6 (0.2)	
ΔE (H-bond) ^b	18.3	-30.7	-1.3 (-5.9)	3.2 (-2.4)	0.2 (-3.9)	3.5 (-1.8)	

^aAlkane dimers. ^bWater clusters.

Performance of Grimme's +D3 Correction

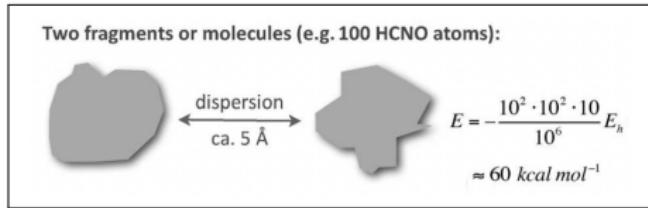
Property	mean signed error (kcal/mol)						
	HF	LDA	PBE (GGA)	TPSS (mGGA)	PBE0 (hybrid)	TPSSh (hybrid)	
ΔE (atomization)	112.8	-58.1	-12.2 (-13.1)	-2.7 (-3.9)	1.1 (0.3)	1.5 (0.4)	
ΔE (vdW) ^a	6.0	-1.1	3.4 (-0.1)	4.7 (0.2)	3.4 (-0.0)	4.6 (0.2)	
ΔE (H-bond) ^b	18.3	-30.7	-1.3 (-5.9)	3.2 (-2.4)	0.2 (-3.9)	3.5 (-1.8)	

^aAlkane dimers. ^bWater clusters.

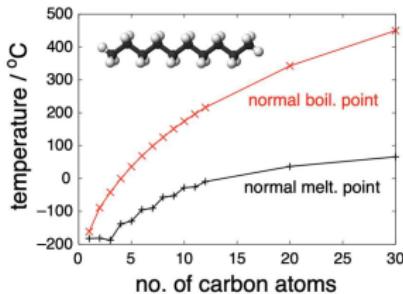


Dispersion Is Size-Extensive

- Dispersion is only a “weak” interaction for small molecules.



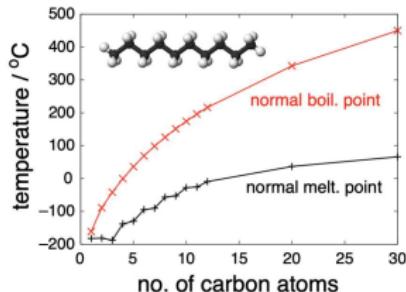
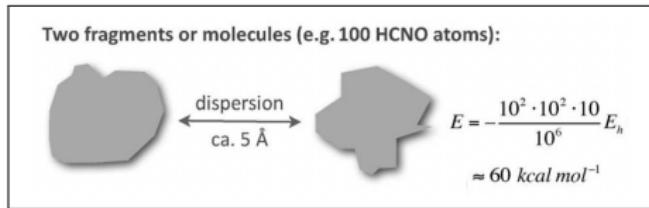
- $C_6(A \cdots B) \sim \alpha_A \alpha_B$ and polarizabilities α are size-extensive.



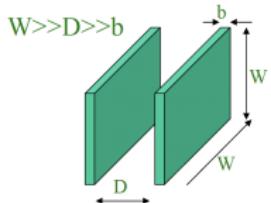
Top left: “London dispersion in molecular chemistry—reconsidering steric effects” [*Angew. Chem.* **54**, 12274 (2015)]

Dispersion Is Size-Extensive

- Dispersion is only a “weak” interaction for small molecules.



- $C_6(A \cdots B) \sim \alpha_A \alpha_B$ and polarizabilities α are size-extensive.
- In nanoscale systems, dipolar atomic C_6 interactions screen one another.*

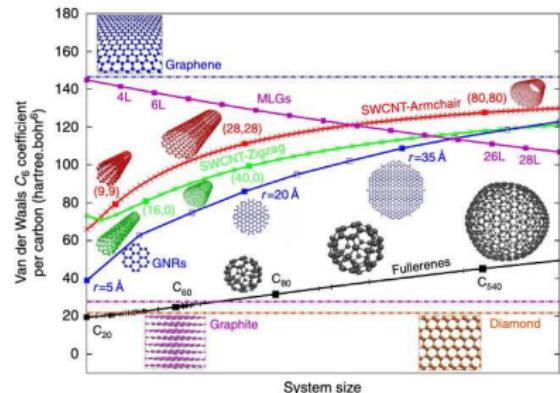


$$E_{\text{disp}}/\text{area} \propto D^{-5/2} \quad (\text{conductors})$$
$$\propto D^{-4} \quad (\text{insulators})$$
$$\propto D^{-3} \quad (\pi\text{-conjugated})$$

Top left: “London dispersion in molecular chemistry—reconsidering steric effects” [*Angew. Chem.* **54**, 12274 (2015)]

* Dobson, White, & Rubio [*Phys. Rev. Lett.* **96**, 073201 (2006)]

Dispersion Interactions in Materials Science



- Scaling laws (C_6 per carbon atom) for various classes of materials
- Gobre & Tkatchenko [*Nat. Commun.* 4, 2341 (2013)]

- Many-body dispersion (MBD) model includes density-dependent screening of the fluctuating dipoles.¹
- Based on an atoms-in-molecules model for *in situ* C_6 coefficients:²

$$C_{6,A}^{\text{eff}} = \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}} \right)^2 C_{6,A}^{\text{free}}$$

where V_A^{eff} is the effective volume of atom A in the molecular system.

¹ Ambrosetti, Reilly, DiStasio, & Tkatchenko [*J. Chem. Phys.* 140, 18A508 (2014)]

² Tkatchenko & Scheffler [*Phys. Rev. Lett.* 102, 073005 (2009)]

Outline

- 1 Logistics
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals
 - Jacob's Ladder
 - Self-Interaction Error
 - Recommendations
- 4 Contemporary Issues in DFT
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - HOMO/LUMO Gaps
 - Range-Separated Hybrid Functionals
- 5 TD-DFT
 - DFT for Excited States
 - Charge-Transfer Problems

Self-Interaction Correction (SIC)

- In practice, $E_H[\rho_k] + E_{xc}[\rho_k] \neq 0$ for a one-electron density $\rho_k = |\psi_k|^2$.
- A simple SIC was proposed long ago by Perdew and Zunger (PZ):¹

$$E_{\text{PZ}} = E_{\text{DFT}} + \sum_k^{\text{occ}} \underbrace{\left(E_H[\rho_k] - E_{xc}[\rho_k] \right)}_{E_{\text{SIC}}}$$

- E_{SIC} subtracts out the SIE orbital-by-orbital. **Simple!**

¹ Perdew & Zunger [*Phys. Rev.* **23**, 5048 (1981)]

Self-Interaction Correction (SIC)

- In practice, $E_H[\rho_k] + E_{xc}[\rho_k] \neq 0$ for a one-electron density $\rho_k = |\psi_k|^2$.
- A simple SIC was proposed long ago by Perdew and Zunger (PZ):¹

$$E_{\text{PZ}} = E_{\text{DFT}} + \sum_k^{\text{occ}} \underbrace{\left(E_H[\rho_k] - E_{xc}[\rho_k] \right)}_{E_{\text{SIC}}}$$

- E_{SIC} subtracts out the SIE orbital-by-orbital. **Simple!**
- **However,**
 - ▶ PZ-SIC is not invariant to unitary transformations of the occupied MOs, which is problematic for solving the SCF equations.
 - ▶ Except for LDA, thermochemistry is generally not improved by PZ-SIC.²
 - ▶ PZ-SIC is prone to “real → complex” symmetry breaking, with numerous quasi-degenerate solutions in complex orbital space.³

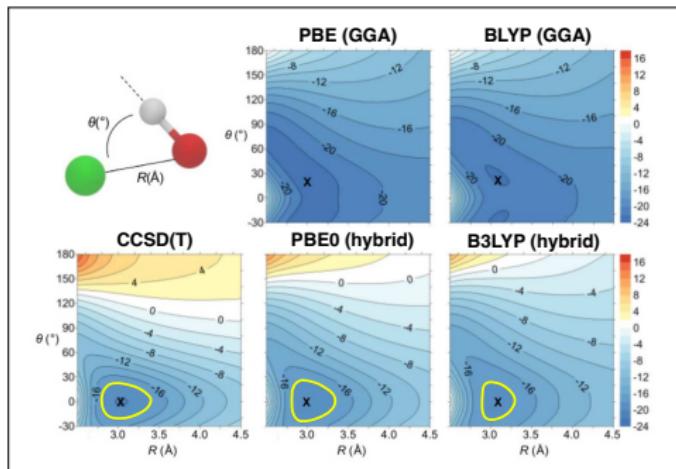
¹ Perdew & Zunger [*Phys. Rev.* **23**, 5048 (1981)]

² Vydrov & Scuseria [*J. Chem. Phys.* **121**, 8187 (2004)]

³ Lehtola, Head-Gordon, & Jónsson [*J. Chem. Theory Comput.* **12**, 3195 (2016)]

SIE \implies Delocalization of Radicals

- SIE is semi-synonymous with “delocalization error” for unpaired electrons.
- Artificially stabilizes (2c,3e) “hemibonds”, as in $(\text{HOCl})^-$:¹



- ▶ $\theta = 0^\circ$: Hydrogen-bonded $\text{Cl}^- \cdots \text{HO}$
- ▶ $\theta = 180^\circ$: Hemibonded $\text{Cl}^- \cdots \text{OH}$

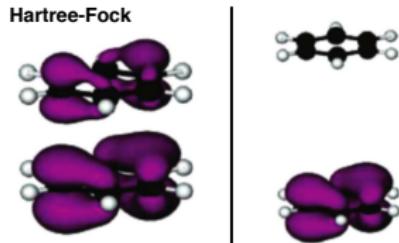
- There is experimental evidence for hemibonds in $(\text{H}_2\text{S})_n^+$ and $(\text{CH}_3\text{SH})_n^+$ clusters, but the case of $\text{OH}(\text{aq})$ is ambiguous.²

¹ Kim, Sim, & Burke [*J. Chem. Phys.* **140**, 18A528 (2014)]

² Rana & Herbert, “Hidden hemibonding in the aqueous hydroxyl radical” [*J. Phys. Chem. Lett.* **12**, 8053 (2021)]

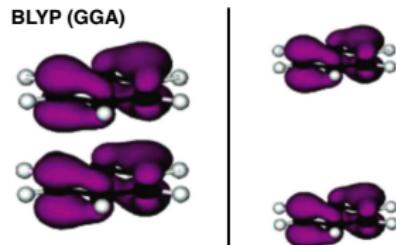
Delocalization of Radical Centers: $(C_6H_6)_2^+$

■ Spin densities ($\rho_\alpha - \rho_\beta$) from Hartree-Fock theory:



Hole delocalization at π -stacking distance (left)
but localization in the well-separated dimer (right).

■ GGA functional:

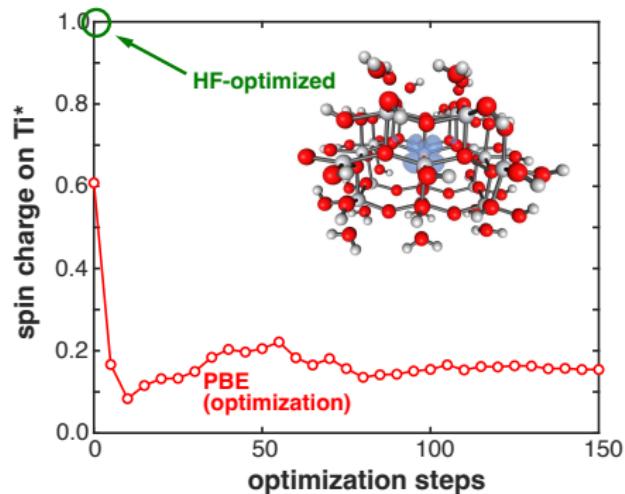


The unpaired electron remains delocalized even
at large intermolecular separation.

Figures: "Charge localization in stacked radical cation DNA base pairs..." [J. Phys. Chem. A 111, 105 (2007)]

Polaron Delocalization in TiO_2

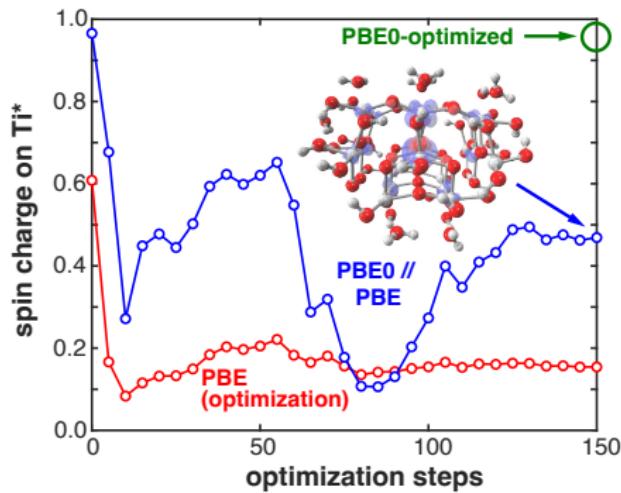
- Standard procedure is periodic GGA structure optimization, possibly followed by single-point hybrid DFT calculations.



■ **PBE optimization** starting from a spin-localized HF structure

Polaron Delocalization in TiO₂

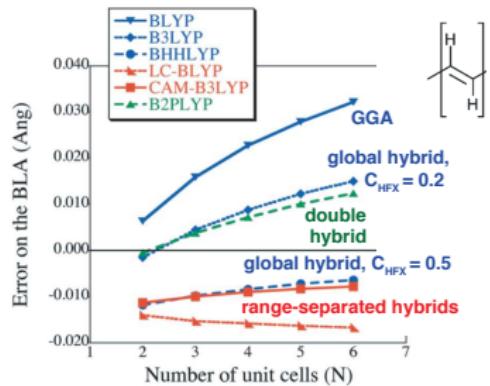
- Standard procedure is periodic GGA structure optimization, possibly followed by single-point hybrid DFT calculations.
- **PBE** drives the elongation of Ti–O bonds, from which **PBE0//PBE** cannot recover a localized polaron.



- **PBE** optimization starting from a spin-localized HF structure
- **PBE0** optimizes to a spin-localized (HF-like) polaron but **PBE0//PBE** does not

Overstabilization of π -Electron Delocalization

- GGAs underestimate bond-length alternation in conjugated π systems.¹

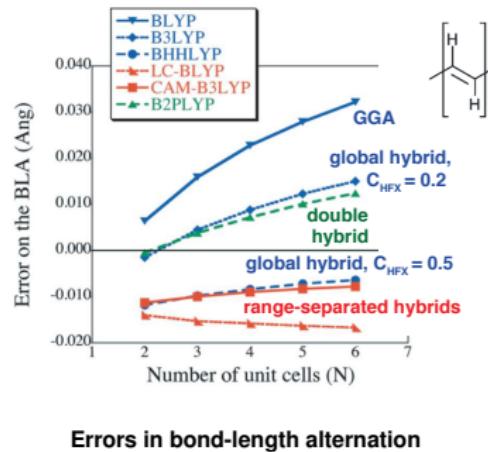


Errors in bond-length alternation

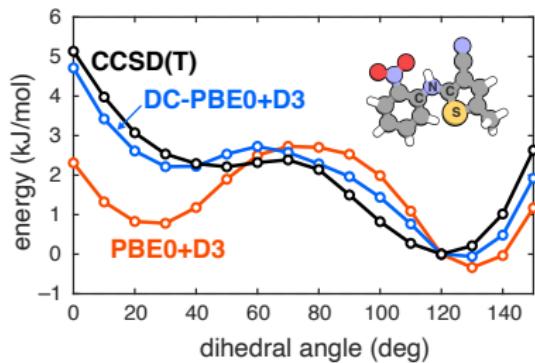
¹Figure @ left: Jacquemin & Adamo, "Bond length alternation..." [J. Chem. Theory Comput. 7, 369 (2011)]

Overstabilization of π -Electron Delocalization

- GGAs underestimate bond-length alternation in conjugated π systems.¹
- \Rightarrow overstabilization of geometries with longer conjugation lengths.²
- A partial solution is a non-self-consistent “density-corrected” (DC)-DFT, $E_{\text{DC-DFT}} = E_{\text{DFT}}[\rho_{\text{HF}}]$.³



Errors in bond-length alternation



Torsional profile in a conjugated system

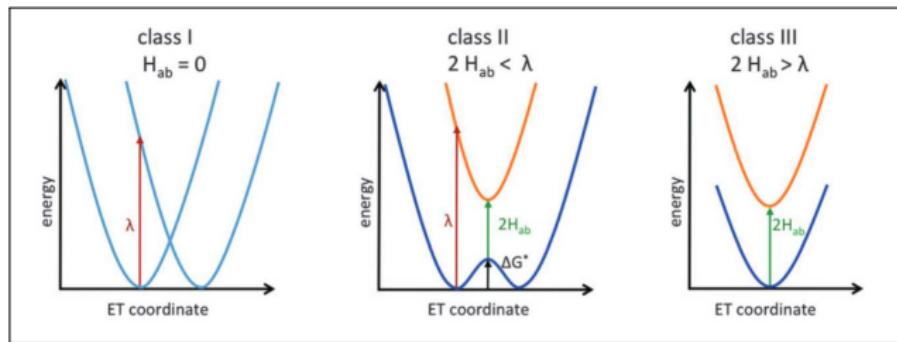
¹Figure @ left: Jacquemin & Adamo, “Bond length alternation...” [J. Chem. Theory Comput. 7, 369 (2011)]

²Figure @ right: Rana, Beran, & Herbert, “Correcting π -delocalisation errors...” [Mol. Phys. XX, e2138789 (2023)]

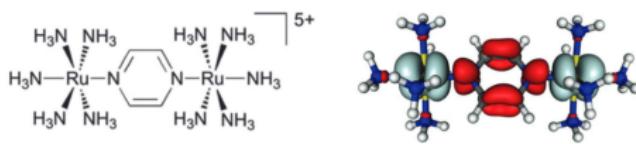
³Song, Vuckovic, Sim, & Burke, “DC-DFT explained...” [J. Chem. Theory Comput. 18, 817 (2022)]

(De)localization & Symmetry Breaking

- Mixed-valence transition metal systems present the possibility of symmetry breaking, which may be real or artificial.



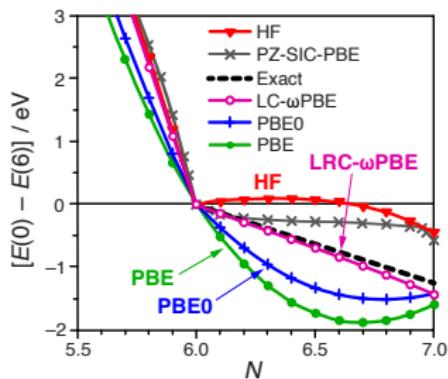
- Semilocal functionals make everything into class III (!)



Creutz-Taube Ru(II) / Ru(III) ion and spin density

Figures: "Quantum-chemical insights into mixed-valence systems..." [Chem. Soc. Rev. 43, 5067 (2014)]

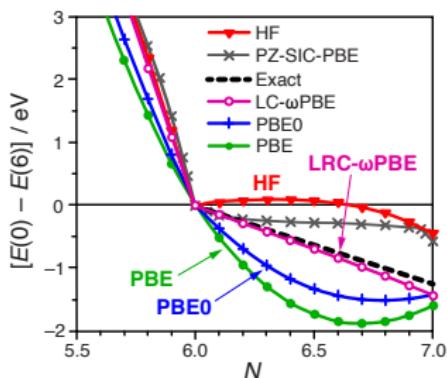
- For systems with fractional electrons, $E(N)$ should be a series of straight-line segments with a *derivative discontinuity* at integer values of N .



- $E(N)$ curves, set to a common value at $N = 6$
- Vydrov, Scuseria, & Perdew, "Tests of functionals for systems with fractional electron number" [*J. Chem. Phys.* **126**, 154109 (2007)]

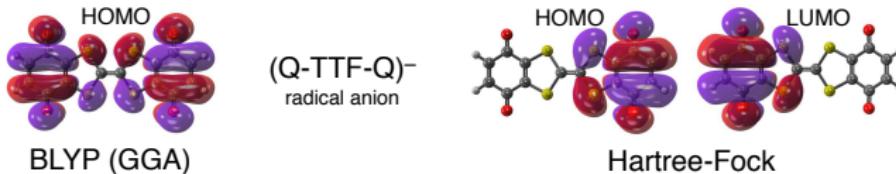
Fractional-Electron Analysis

- For systems with fractional electrons, $E(N)$ should be a series of straight-line segments with a *derivative discontinuity* at integer values of N .



- $E(N)$ curves, set to a common value at $N = 6$
- Vydrov, Scuseria, & Perdew, "Tests of functionals for systems with fractional electron number" [*J. Chem. Phys.* **126**, 154109 (2007)]

- For radicals, HF theory errs towards symmetry breaking (localization) whereas GGAs tend towards delocalization.*



* For a discussion of symmetry-breaking in $(\text{Q-TTF-Q})^{\cdot-}$, see *J. Phys. Chem. A* **116**, 10629 (2012)

Outline

- 1 Logistics
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals
 - Jacob's Ladder
 - Self-Interaction Error
 - Recommendations
- 4 Contemporary Issues in DFT
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - **HOMO/LUMO Gaps**
 - Range-Separated Hybrid Functionals
- 5 TD-DFT
 - DFT for Excited States
 - Charge-Transfer Problems

Long-Range Behavior of $v_{KS}(\mathbf{r})$

- Incomplete cancellation of Hartree self-interaction means that $v_{KS}(\mathbf{r})$ has the wrong asymptotic behavior as one electron is pulled away from the system.
 - Expect: $v_{KS}(r) \sim -(Z - N + 1)/r$

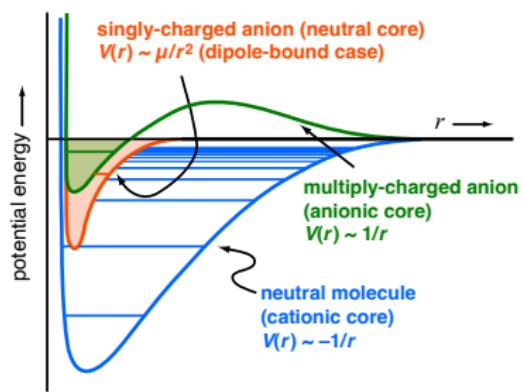


Figure @ left: Herbert, "The quantum chemistry of loosely-bound electrons" [Rev. Comput. Chem. 28, 391 (2015)]

Long-Range Behavior of $v_{KS}(\mathbf{r})$

- Incomplete cancellation of Hartree self-interaction means that $v_{KS}(\mathbf{r})$ has the wrong asymptotic behavior as one electron is pulled away from the system.
 - Expect:** $v_{KS}(r) \sim -(Z - N + 1)/r$
 - Find:** Insufficiently attractive and decays exponentially
 - Consequence:** ϵ_{HOMO} is insufficiently bound

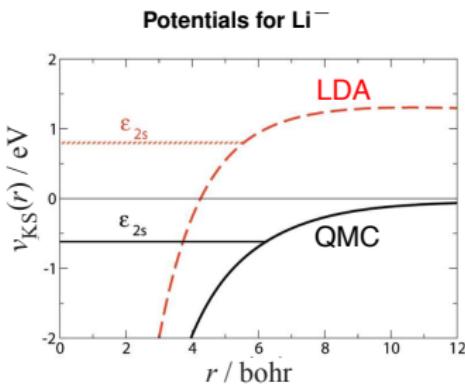
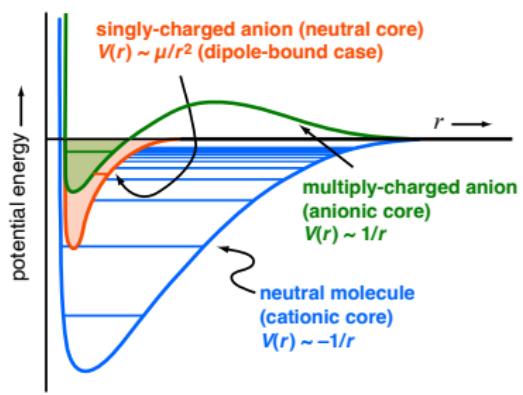


Figure @ left: Herbert, "The quantum chemistry of loosely-bound electrons" [Rev. Comput. Chem. 28, 391 (2015)]

Figure @ right: Lee, Furche, & Burke, "Accuracy of electron affinities..." [J. Phys. Chem. Lett. 1, 2124 (2010)]

Orbital Energies for Ionization

Koopmans Ionization Energies for H₂O (in eV).

Orbital	“Koopmans IE”, $-\varepsilon_k$				Exptl. IE
	HF ^a	B3LYP ^a	SAOP ^b	CAM-	
				QTP(00) ^c	
1b ₁	13.9	7.2		12.6	12.5
3a ₁	15.9	9.3		14.8	14.6
1b ₂	19.4	13.1		18.5	18.3
2a ₁	36.8	25.2		30.9	33.4
1a ₁	559.6	511.0		517.0	539.0
					539.7

^a aug-cc-pVQZ basis set.

^b SAOP functional is designed to have correct asymptotic behavior of $v_{xc}(\mathbf{r})$.

Data are from *J. Chem. Phys.* **116**, 1760 (2002).

^c CAM-QTP(00) functional is CAM-B3LYP reparameterized to reproduce these data.

Data are from *J. Chem. Phys.* **140**, 18A534 (2014).

Orbital Energies for Ionization

Koopmans Ionization Energies for H₂O (in eV).

Orbital	“Koopmans IE”, $-\varepsilon_k$					Exptl. IE	
	HF ^a		B3LYP ^a		SAOP ^b		
	HF	B3LYP	SAOP	CAM-QTP(00) ^c			
1b ₁	13.9	(12.6)	7.2	(12.6)	12.6	12.5	12.6
3a ₁	15.9	(14.6)	9.3	(14.7)	14.8	14.6	14.7
1b ₂	19.4	(18.1)	13.1	(18.5)	18.5	18.3	18.6
2a ₁	36.8	(35.5)	25.2	(30.6)	30.9	33.4	32.2
1a ₁	559.6	(558.3)	511.0	(516.4)	517.0	539.0	539.7

^a aug-cc-pVQZ basis set. Values in parenthesis are shifted so that $\varepsilon_{\text{HOMO}} = -\text{IE(expt)}$.

^b SAOP functional is designed to have correct asymptotic behavior of $v_{xc}(\mathbf{r})$.

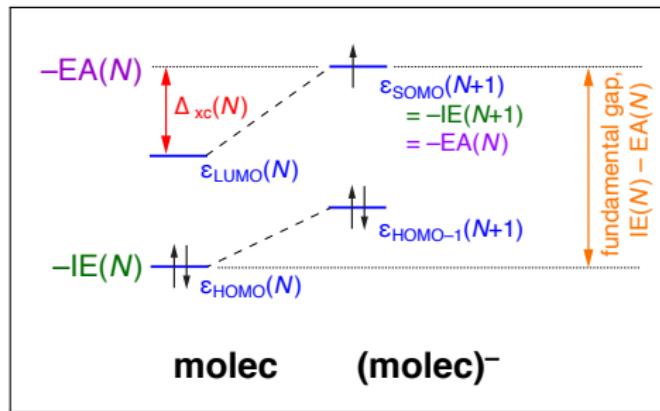
Data are from *J. Chem. Phys.* **116**, 1760 (2002).

^c CAM-QTP(00) functional is CAM-B3LYP reparameterized to reproduce these data.

Data are from *J. Chem. Phys.* **140**, 18A534 (2014).

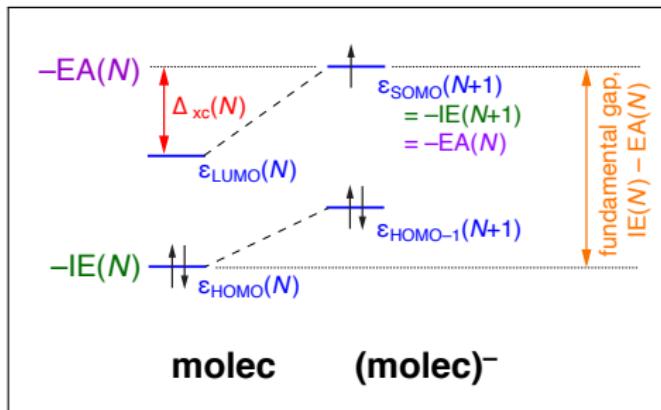
Meaning of the Kohn-Sham Energy Levels

- Apply the “IE theorem” ($\varepsilon_{\text{HOMO}} = -\text{IE}$) to an N -electron molecule and its $(N + 1)$ -electron anion:



Meaning of the Kohn-Sham Energy Levels

- Apply the “IE theorem” ($\varepsilon_{\text{HOMO}} = -\text{IE}$) to an N -electron molecule and its $(N + 1)$ -electron anion:



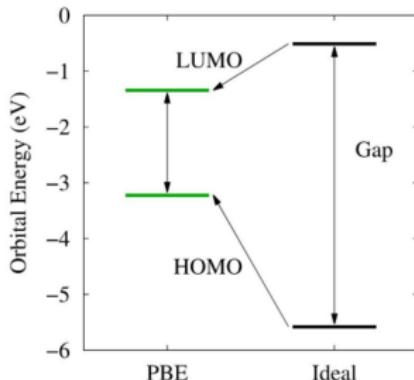
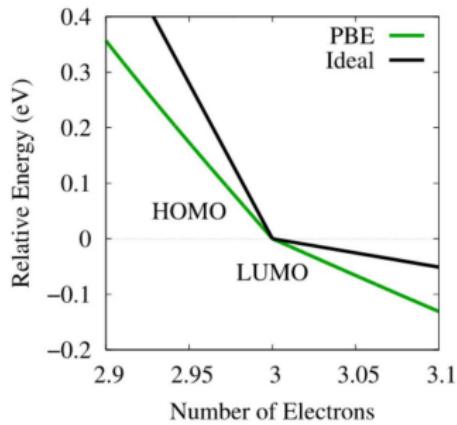
- Derivative discontinuity: $\Delta_{\text{xc}}(N) \stackrel{\text{def}}{=} \lim_{\xi \rightarrow 0} \left(\frac{\partial E}{\partial N} \Big|_{N+\xi} - \frac{\partial E}{\partial N} \Big|_{N-\xi} \right)$
- Fundamental gap:

$$-\text{EA}(N) + \text{IE}(N) = \Delta_{\text{xc}}(N) + \varepsilon_{\text{LUMO}}(N) - \varepsilon_{\text{HOMO}}(N)$$

Consequences for Band Gaps

- First, stipulate that by “band gap” we mean the fundamental gap ($= \text{IE} - \text{EA}$).
- Janak’s theorem ($\varepsilon_k = \partial E / \partial n_k$) implies that

$$\varepsilon_{\text{HOMO}} = (\partial E / \partial N)|_{N-\xi^+} \quad \varepsilon_{\text{LUMO}} = (\partial E / \partial N)|_{N+\xi^+}$$

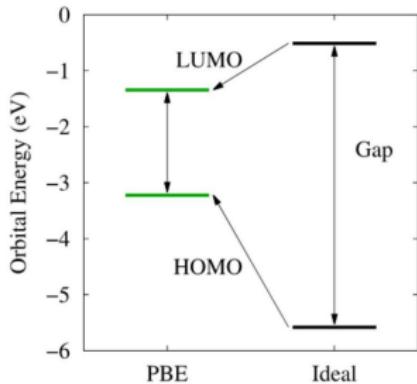
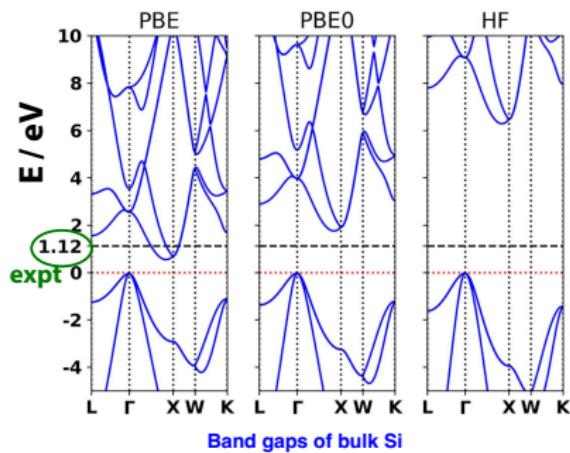


Figures: Bryenton, Adeleke, Dale, & Johnson, “Delocalization error...” [WIREs Comput. Mol. Sci. 13, e1631 (2023)]

Consequences for Band Gaps

- First, stipulate that by “band gap” we mean the fundamental gap ($= \text{IE} - \text{EA}$).
- Janak’s theorem ($\varepsilon_k = \partial E / \partial n_k$) implies that

$$\varepsilon_{\text{HOMO}} = (\partial E / \partial N)|_{N-\xi^+} \quad \varepsilon_{\text{LUMO}} = (\partial E / \partial N)|_{N+\xi^+}$$



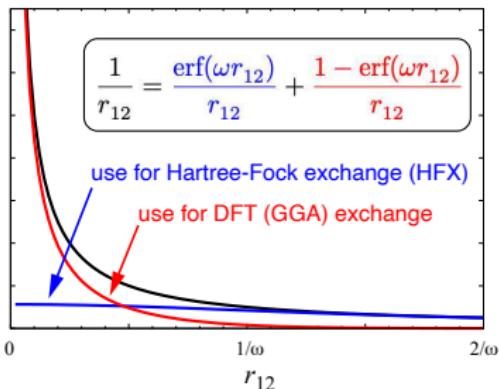
Figures: Bryenton, Adeleke, Dale, & Johnson, “Delocalization error...” [WIREs Comput. Mol. Sci. 13, e1631 (2023)]

Outline

- 1 Logistics**
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT**
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals**
 - Jacob's Ladder
 - Self-Interaction Error
 - Recommendations
- 4 Contemporary Issues in DFT**
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - HOMO/LUMO Gaps
 - Range-Separated Hybrid Functionals
- 5 TD-DFT**
 - DFT for Excited States
 - Charge-Transfer Problems

Long-Range Corrected (LRC) Functionals

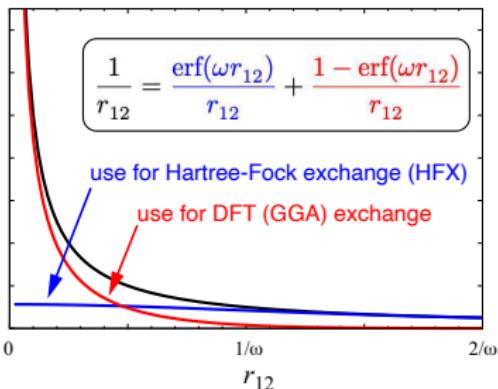
- Full HFX provides correct asymptotics but is incompatible with existing (local) correlation functionals.
- *Long-range corrected* (LRC) functionals attempt a compromise by including HFX only in the LR part of the Coulomb potential.



Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Long-Range Corrected (LRC) Functionals

- Full HFX provides correct asymptotics but is incompatible with existing (local) correlation functionals.
- *Long-range corrected* (LRC) functionals attempt a compromise by including HFX only in the LR part of the Coulomb potential.



$$E_{xc}^{\text{LRC}} = E_c + \underbrace{C_{\text{HFX}} E_x^{\text{HF},\text{SR}} + (1 - C_{\text{HFX}}) E_x^{\text{GGA},\text{SR}}}_{\text{short-range (GGA or hybrid) exchange}} + \underbrace{E_x^{\text{HF},\text{LR}}}_{\text{LRC}}$$

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Nomenclature for LRC Functionals

- Taking GGA = PBE for example,

$$E_{xc}^{\text{LRC}-\omega\text{PBEh}} = E_c + C_{\text{HFX}} E_x^{\text{HF,SR}} + \underbrace{(1 - C_{\text{HFX}}) E_x^{\text{PBE,SR}}}_{\omega\text{PBE}} + \underbrace{E_x^{\text{HF,LR}}}_{\text{LRC}}$$

- ▶ ωPBE refers to the short-range exchange part of the functional only, and ωPBEh is the corresponding short-range hybrid.
- ▶ **LRC** refers to the use of long-range HFX. Sometimes called “LC” instead.
- ▶ μPBE and μB88 are alternative constructions of short-range PBE and B88, leading for example to LRC- μ BLYP.

For an explanation of the nomenclature of RSH and LRC functionals, see *J. Phys. Chem. C* **124**, 24653 (2020)

Nomenclature for LRC Functionals

- Taking GGA = PBE for example,

$$E_{xc}^{\text{LRC}-\omega\text{PBEh}} = E_c + C_{\text{HFX}} E_x^{\text{HF,SR}} + \underbrace{(1 - C_{\text{HFX}}) E_x^{\text{PBE,SR}}}_{\omega\text{PBE}} + \underbrace{E_x^{\text{HF,LR}}}_{\text{LRC}}$$

- ▶ ωPBE refers to the short-range exchange part of the functional only, and ωPBEh is the corresponding short-range hybrid.
- ▶ **LRC** refers to the use of long-range HFX. Sometimes called “LC” instead.
- ▶ μPBE and μB88 are alternative constructions of short-range PBE and B88, leading for example to LRC- μ BLYP.
- The “ ω ” in the $\omega\text{B97*}$ functionals indicates a *range-separated hybrid* (RSH) functional.
 - ▶ In contrast, B3LYP and PBE0 are “global” hybrids
 - ▶ In RSH functionals, ω is included in the global fitting and **should not be modified**.

For an explanation of the nomenclature of RSH and LRC functionals, see *J. Phys. Chem. C* **124**, 24653 (2020)

Range-Separate Hybrid (RSH) Functionals

- LRCs were designed as asymptotic corrections for standard GGA exchange functionals.
 - ▶ Switches smoothly from GGA to HFX on a length scale $\sim 1/\omega$.
 - ▶ “Optimal tuning”:* adjust ω such that

$$\text{IE}(\omega) = -\varepsilon_{\text{HOMO}}(\omega).$$

where $\text{IE}(\omega)$ is computed by ΔSCF .

- ▶ This is an exact condition ensures that $v_{\text{xc}}(\infty) = 0$.
- ▶ Badly violated by most approximate functionals.

* Baer *et al.*, “Tuned range-separated hybrids in density functional theory” [*Annu. Rev. Phys. Chem.* **61**, 85 (2010)]

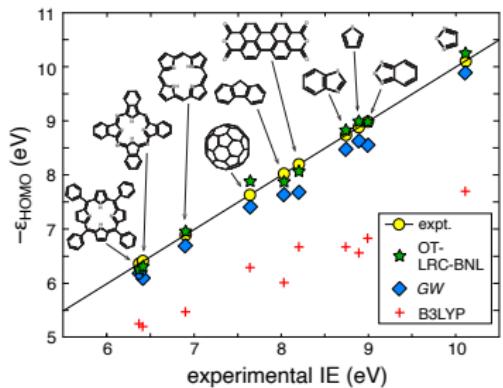
Range-Separate Hybrid (RSR) Functionals

- LRCs were designed as asymptotic corrections for standard GGA exchange functionals.
 - ▶ Switches smoothly from GGA to HFX on a length scale $\sim 1/\omega$.
 - ▶ “Optimal tuning”:* adjust ω such that

$$\text{IE}(\omega) = -\varepsilon_{\text{HOMO}}(\omega).$$

where $\text{IE}(\omega)$ is computed by ΔSCF .

- ▶ This is an exact condition ensures that $v_{\text{xc}}(\infty) = 0$.
- ▶ Badly violated by most approximate functionals.



Kronik *et al.*, “Excitation gaps of finite-sized systems from OT-RSH functionals”
[*J. Chem. Theory Comput.* **8**, 1515 (2012)]

* Baer *et al.*, “Tuned range-separated hybrids in density functional theory” [*Annu. Rev. Phys. Chem.* **61**, 85 (2010)]

Optimal Tuning and the Kohn-Sham Gap

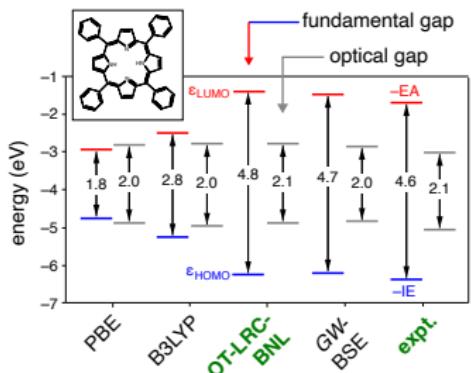
- Recall that $\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$ **should not** equal to the band gap in pure KS theory.
 - In hybrid DFT, the meaning of the orbital energy levels gets murky.
 - Generalized (G)KS theory* (with nonlocal \hat{v}_{xc}), may allow that $\text{IE} - \text{EA} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$.¹

¹ Perdew *et al.*, "Understanding band gaps of solids in generalized Kohn-Sham theory" [*PNAS* **114**, 2801 (2017)]

Optimal Tuning and the Kohn-Sham Gap

- Recall that $\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$ **should not** equal to the band gap in pure KS theory.
 - In hybrid DFT, the meaning of the orbital energy levels gets murky.
 - Generalized (G)KS theory (with nonlocal \hat{v}_{xc}), may allow that $\text{IE} - \text{EA} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$.¹
- To set both $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ in a non-empirical way, use²

$$\min_{\omega} \left([\varepsilon_{\text{HOMO}}(\omega) + \text{IE}(\omega)]^2 + [\varepsilon_{\text{LUMO}}(\omega) + \text{EA}(\omega)]^2 \right)$$

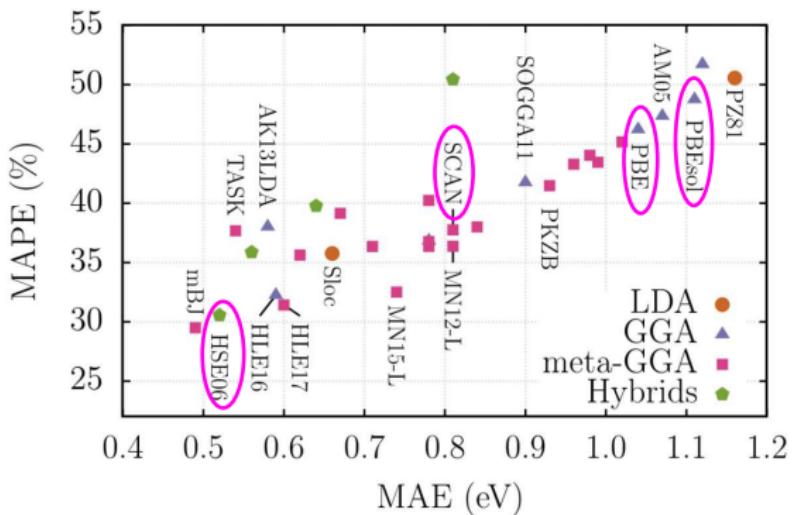


Kronik & Kümmel [*Adv. Mater.* **30**, 1706560 (2018)]

¹ Perdew *et al.*, "Understanding band gaps of solids in generalized Kohn-Sham theory" [*PNAS* **114**, 2801 (2017)]

² Baer, Livshits, & Salzner, "Tuned range-separated hybrids in DFT" [*Annu. Rev. Phys. Chem.* **61**, 85 (2010)]

Band Gaps in Solids



- $\text{HSE06} \equiv \omega\text{PBEh}$ with 25% short-range HFX (mimics PBE0 at short range)
- In periodic codes, hybrid functionals are $10\text{--}100\times$ more expensive than GGAs.

Figure: "Exchange-correlation functionals for band gaps of solids..." [NPJ Comput. Mater. 6, 96 (2020)]

Optimal Tuning: Caveats

- Optimally-tuned value of ω depends on system size (therefore OT-RSH is not size-extensive.)
- Tuning plots need to be recomputed for every system of interest.

Tuning plots for three different isomers of $(\text{H}_2\text{O})_{70}^-$

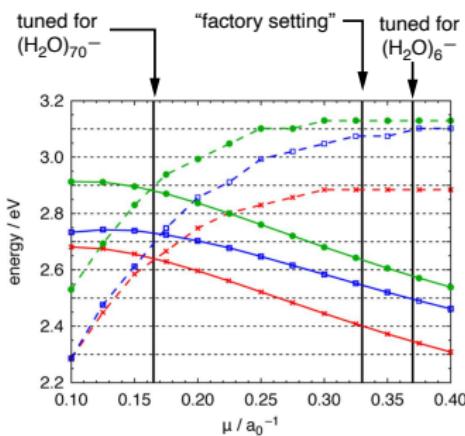
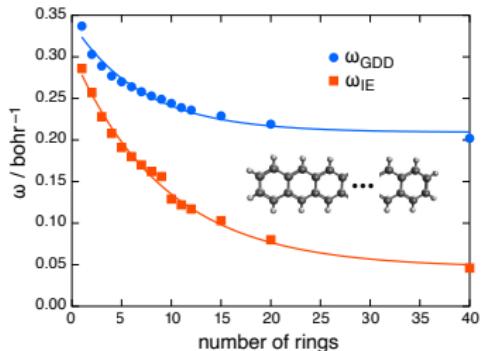


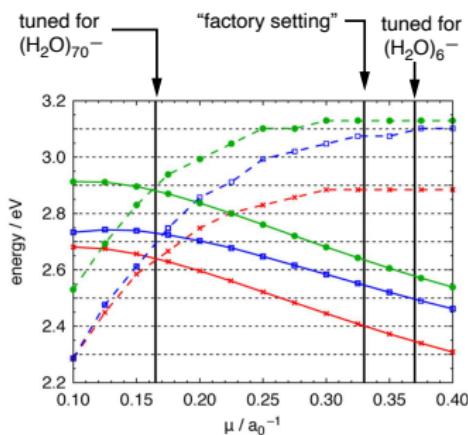
Figure @ top right: Uhlig, Herbert, Coons, & Jungwirth [J. Phys. Chem. A 118, 7507 (2014)]

Optimal Tuning: Caveats

- Optimally-tuned value of ω depends on system size (therefore OT-RSH is not size-extensive.)
- Tuning plots need to be recomputed for every system of interest.
- For large systems, it may be that $\omega \rightarrow 0$.



Tuning plots for three different isomers of $(\text{H}_2\text{O})_{70}^-$



← LRC- ω PBE / def2-TZVP tuning plots for acenes

Figure @ top right: Uhlig, Herbert, Coons, & Jungwirth [J. Phys. Chem. A 118, 7507 (2014)]

Figure @ bottom left: Gray & Herbert [J. Chem. Phys. 155, 034103 (2021)]

Exercise: ω_{GDD} Tuning

- Global density-dependent (GDD) tuning attempts to estimate the optimally-tuned value (ω_{IE}) based on the size of the exchange hole.*
 - ▶ Fitting set is small molecules

■ Input:

```
$rem
symmetry      false
exchange       lrc-wpbe
basis          6-31G*
lrc_dft        true
omega          300    ! starting value for search
omega_gdd      true
$end
```

* "Density-dependent onset of the long-range exchange..." [J. Phys. Chem. A 117, 11580 (2013)]

Exercise: ω_{GDD} Tuning

- Global density-dependent (GDD) tuning attempts to estimate the optimally-tuned value (ω_{IE}) based on the size of the exchange hole.*
 - ▶ Fitting set is small molecules

■ Input:

```
$rem
symmetry      false
exchange       lrc-wpbe
basis          6-31G*
lrc_dft        true
omega          300    ! starting value for search
omega_gdd      true
$end
```

■ Output:

```
*****
**   Tuning based on GDD scheme: w = 308 / 100 bohr^(-1)      **
*****
```

- **Question:** How well does LRC- ω PBE with ω_{GDD} satisfy the condition $\text{IE} = -\varepsilon_{\text{HOMO}}$, where IE is computed via Δ SCF?

* "Density-dependent onset of the long-range exchange..." [J. Phys. Chem. A 117, 11580 (2013)]

Outline

- 1 Logistics**
 - Q-Chem & IQmol
 - Philosophy
- 2 Intro to Molecular DFT**
 - Self-Consistent Field Theory
 - Gaussian Basis Sets
 - Physical Interpretation
- 3 Exchange-Correlation Functionals**
 - Jacob's Ladder
 - Self-Interaction Error
 - Recommendations
- 4 Contemporary Issues in DFT**
 - Dispersion Interactions
 - Self-Interaction & Delocalization Errors
 - HOMO/LUMO Gaps
 - Range-Separated Hybrid Functionals
- 5 TD-DFT**
 - DFT for Excited States
 - Charge-Transfer Problems

Three Methods for Obtaining Excited States from DFT

1 Excited-state Kohn-Sham theory (a.k.a. Δ SCF or ROKS)

- ▶ Find a non-*aufbau* solution of $\mathbf{Fc} = \varepsilon \mathbf{Sc}$.
- ▶ Typically needs a modified convergence algorithm.
- ▶ Not formally justified but often works well; uses ground-state gradients.
- ▶ *Requires a separate SCF for each state.*

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Three Methods for Obtaining Excited States from DFT

1 Excited-state Kohn-Sham theory (a.k.a. Δ SCF or ROKS)

- ▶ Find a non-*aufbau* solution of $\mathbf{Fc} = \epsilon \mathbf{Sc}$.
- ▶ Typically needs a modified convergence algorithm.
- ▶ Not formally justified but often works well; uses ground-state gradients.
- ▶ *Requires a separate SCF for each state.*

2 “Real-time” TD-DFT (a.k.a. TDKS)

- ▶ Create a time-evolving superposition by perturbing the ground state.
- ▶ Propagate MOs $\psi_k(\mathbf{r}, t)$ by solving one-electron analogue of time-dependent Schrödinger equation.
- ▶ Broadband spectrum computed by Fourier transform of dipole moment function.

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Three Methods for Obtaining Excited States from DFT

1 Excited-state Kohn-Sham theory (a.k.a. Δ SCF or ROKS)

- ▶ Find a non-*aufbau* solution of $\mathbf{Fc} = \epsilon \mathbf{Sc}$.
- ▶ Typically needs a modified convergence algorithm.
- ▶ Not formally justified but often works well; uses ground-state gradients.
- ▶ *Requires a separate SCF for each state.*

2 “Real-time” TD-DFT (a.k.a. TDKS)

- ▶ Create a time-evolving superposition by perturbing the ground state.
- ▶ Propagate MOs $\psi_k(\mathbf{r}, t)$ by solving one-electron analogue of time-dependent Schrödinger equation.
- ▶ Broadband spectrum computed by Fourier transform of dipole moment function.

3 Linear response DFT

- ▶ Most widespread approach and the only one discussed here.
- ▶ *This is what is usually meant by “TD-DFT”!*
- ▶ Iterative solution of an eigenvalue equation for a spectrum of states.

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Linear-Response TD-DFT Formalism

- The complete TD-DFT problem (sometimes called the *random-phase approximation* or RPA formulation),

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{x}^{(n)} \\ \mathbf{y}^{(n)} \end{pmatrix} = \omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{x}^{(n)} \\ \mathbf{y}^{(n)} \end{pmatrix}.$$

is an equation for amplitudes x_{ia} and y_{ia} , and excitation energy ω .

- ▶ i, j, k, \dots are occupied MOs; a, b, c, \dots are virtual MOs.
- ▶ n indexes excited states and will be omitted for convenience.
- Amplitudes \mathbf{x} and \mathbf{y} parameterize the *transition density matrix*,

$$T(\mathbf{r}, \mathbf{r}') = \sum_{ia} \left[x_{ia} \psi_a(\mathbf{r}) \psi_i^*(\mathbf{r}') + y_{ia} \psi_i(\mathbf{r}) \psi_a^*(\mathbf{r}') \right].$$

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Linear-Response TD-DFT Formalism

- The complete TD-DFT problem (sometimes called the *random-phase approximation* or RPA formulation),

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{x}^{(n)} \\ \mathbf{y}^{(n)} \end{pmatrix} = \omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{x}^{(n)} \\ \mathbf{y}^{(n)} \end{pmatrix}.$$

is an equation for amplitudes x_{ia} and y_{ia} , and excitation energy ω .

- ▶ i, j, k, \dots are occupied MOs; a, b, c, \dots are virtual MOs.
- ▶ n indexes excited states and will be omitted for convenience.
- Amplitudes \mathbf{x} and \mathbf{y} parameterize the *transition density matrix*,

$$T(\mathbf{r}, \mathbf{r}') = \sum_{ia} \left[x_{ia} \psi_a(\mathbf{r}) \psi_i^*(\mathbf{r}') + y_{ia} \psi_i(\mathbf{r}) \psi_a^*(\mathbf{r}') \right].$$

- Matrices $A_{ia,jb}$ and $B_{ia,jb}$ are *orbital Hessians*, related to the stability of the ground state.
 - ▶ *Thouless theorem*: For a Slater determinant wave function, any unitary transformation of the MOs can be parameterized as single excitations.

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Tamm-Dancoff Approximation

- Applying the *Tamm-Dancoff approximation* ($y_{ia} \approx 0$) affords

$$\boxed{\mathbf{A}\mathbf{x} = \omega\mathbf{x}} \quad (\star)$$

- ▶ Typically y_{ia} is $\sim 100\times$ smaller than x_{ia} .
- ▶ Triplet instabilities often preclude solution of full TD-DFT equation, especially near bond-breaking geometries.*

* "Troubleshooting TD-DFT for photochemical applications" [*J. Chem. Phys.* **127**, 164111 (2007)]

Tamm-Dancoff Approximation

- Applying the *Tamm-Dancoff approximation* ($y_{ia} \approx 0$) affords

$$\boxed{\mathbf{A}\mathbf{x} = \omega\mathbf{x}} \quad (*)$$

- ▶ Typically y_{ia} is $\sim 100\times$ smaller than x_{ia} .
- ▶ Triplet instabilities often preclude solution of full TD-DFT equation, especially near bond-breaking geometries.*
- For HFX, Eq. (*) is equivalent to configuration-interaction singles (CIS),

$$|\Psi_{\text{ex}}\rangle = \sum_{ia} x_{ia} |\Phi_i^a\rangle$$

where $|\Phi_i^a\rangle$ is a single excitation relative to the ground state.

* "Troubleshooting TD-DFT for photochemical applications" [J. Chem. Phys. 127, 164111 (2007)]

Tamm-Dancoff Approximation

- Applying the *Tamm-Dancoff approximation* ($y_{ia} \approx 0$) affords

$$\boxed{\mathbf{A}\mathbf{x} = \omega\mathbf{x}} \quad (*)$$

- ▶ Typically y_{ia} is $\sim 100\times$ smaller than x_{ia} .
- ▶ Triplet instabilities often preclude solution of full TD-DFT equation, especially near bond-breaking geometries.*
- For HFX, Eq. (*) is equivalent to configuration-interaction singles (CIS),

$$|\Psi_{\text{ex}}\rangle = \sum_{ia} x_{ia} |\Phi_i^a\rangle$$

where $|\Phi_i^a\rangle$ is a single excitation relative to the ground state.

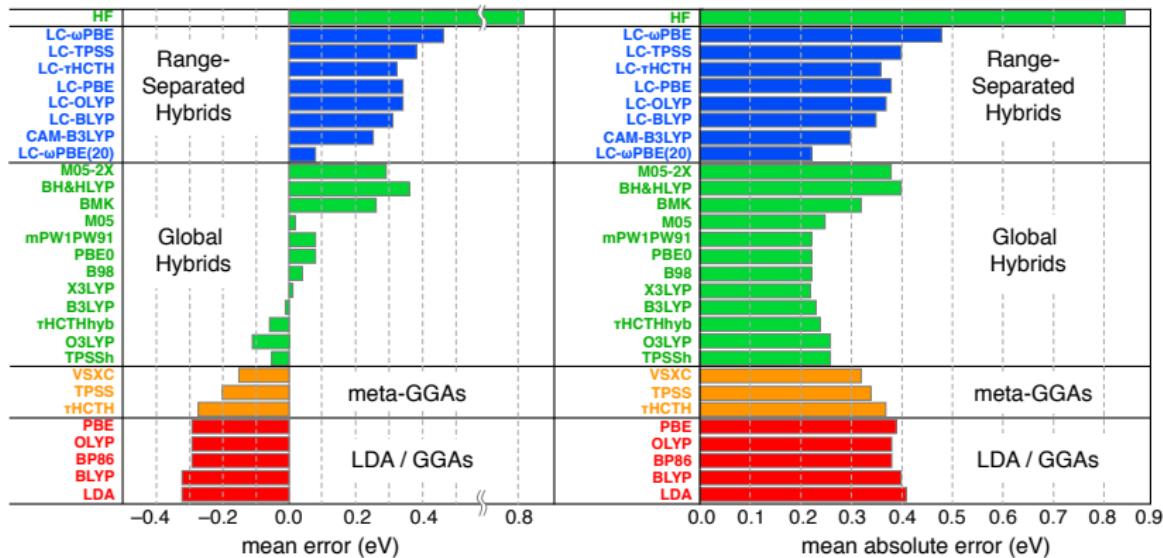
- Only full TDDFT satisfies the Thomas-Reiche-Kuhn sum rule ($\sum_n f_{0 \rightarrow n} = N$) for the *oscillator strengths* (intensities), which are

$$f_{0 \rightarrow n} = \left(\frac{2m_e \omega_{n0}}{3e^2 \hbar} \right) \|\langle 0 | \hat{\mu} | n \rangle\|^2$$

* "Troubleshooting TD-DFT for photochemical applications" [J. Chem. Phys. 127, 164111 (2007)]

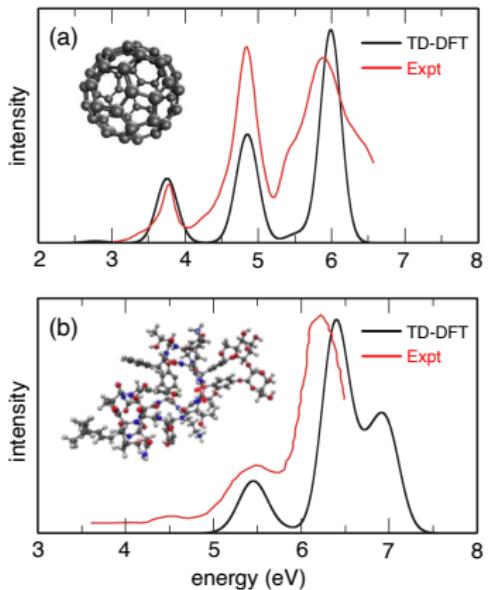
Statistical Assessment of Functionals

Statistical summary of errors in vertical excitation energies computed using TD-DFT



Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Proof of Concept and Cost



- (a) C_{60} , TD-PBE/6-31G*
- (b) 271 atoms, 2,483 basis functions (CAM-B3LYP/6-31G*)
- “Assessment of TD-DFT calculations with the restricted space approximation for excited state calculations of large systems” [*Mol. Phys.* **116**, 1452 (2018)]

- $A_{ia,jb}$ has dimension $ov \times ov$ so the cost of computing **all** states is $\mathcal{O}(N^6)$.
- In practice we use iterative eigensolvers whose cost is $n_{\text{roots}} \times \mathcal{O}(N^4)$.
- Compare this to ground state cost, which is $\mathcal{O}(N^3)$.

Understanding the TD-DFT Eigenvectors

TDDFT/TDA Excitation Energies

Excited state 1: excitation energy (eV) = 4.5530
Total energy for state 1: -457.75882631 au
Multiplicity: Singlet

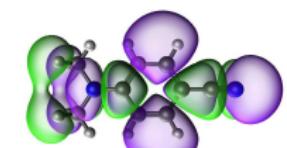
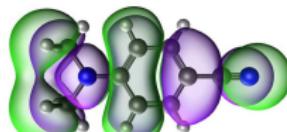
Trans. Mom.: -0.0001 X -0.5438 Y 0.0027 Z
Strength : 0.0329868812
D(38) --> V(1) amplitude = 0.3301
D(39) --> V(2) amplitude = 0.9358

1L_a

Excited state 2: excitation energy (eV) = 4.9621
Total energy for state 2: -457.74379172 au
Multiplicity: Singlet

Trans. Mom.: 2.5698 X 0.0002 Y 0.0110 Z
Strength : 0.8028474549
D(38) --> V(2) amplitude = -0.2383
D(39) --> V(1) amplitude = 0.9475

1L_b



PBE0 / 6-31+G^{*} for dimethylaminobenzonitrile (DMABN) molecule

Which Orbital Basis for Visualization?

- The canonical MO basis is not ideal for visualization.
 - ▶ Unbound orbitals ($\varepsilon_a > 0$) are diffuse continuum states.
 - ▶ Significant configuration mixing may be required to obtain valence virtuals that describe localized excitations such as $\pi \rightarrow \pi^*$, etc.
- *Natural transition orbitals* (NTOs) are the best possible particle/hole basis.
 - ▶ SVD of the linear response amplitudes:

$$\mathbf{U}_o(\mathbf{x} + \mathbf{y})\mathbf{U}_v^\dagger = \begin{pmatrix} \mathbf{\Lambda} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad \mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & 0 & \cdots \\ 0 & \lambda_2 & 0 & \cdots \\ & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \lambda_o \end{pmatrix}$$

Which Orbital Basis for Visualization?

- The canonical MO basis is not ideal for visualization.
 - ▶ Unbound orbitals ($\varepsilon_a > 0$) are diffuse continuum states.
 - ▶ Significant configuration mixing may be required to obtain valence virtuals that describe localized excitations such as $\pi \rightarrow \pi^*$, etc.
- *Natural transition orbitals* (NTOs) are the best possible particle/hole basis.
 - ▶ SVD of the linear response amplitudes:

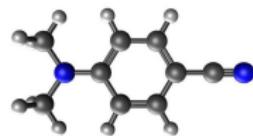
$$\mathbf{U}_o(\mathbf{x} + \mathbf{y})\mathbf{U}_v^\dagger = \begin{pmatrix} \Delta & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \quad \Delta = \begin{pmatrix} \lambda_1 & 0 & 0 & \cdots \\ 0 & \lambda_2 & 0 & \cdots \\ & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \lambda_o \end{pmatrix}$$

- ▶ Reduces the number of amplitudes from $o \times v$ to o without loss of information.
- ▶ Often just a single occ/virt pair describes $\gtrsim 90\%$ of the amplitude.
- ▶ Singular values $\pm \lambda_k$ are eigenvalues of the particle and hole components of ΔP .
- ▶ Unlike visualization of densities, the NTOs preserve nodal surfaces and phase.

NTOs: Example #1 (DMABN)

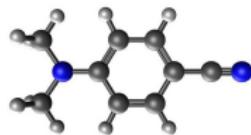
```
$rem
method      pbe0
basis       6-31+G*
cis_n_roots 2
cis_triplets false
cis_ampl_anal true
$end
```

sample input (needs \$molecule section)



NTOs: Example #1 (DMABN)

```
$rem
method          pbe0
basis           6-31+G*
cis_n_roots    2
cis_triplets   false
cis_ampl_anal true
$end
```



sample input (needs \$molecule section)

```
=====
TDA excitation amplitudes in the NTO basis
(Print if lampl > 0.15)
=====
```

```
Excited state 1:  4.5530 eV (singlet)
e-/hole pair 1:  ampl =  0.9372  (87.8 %)
e-/hole pair 2:  ampl =  0.3396  (11.5 %)
These amplitudes account for 99.4 % of total amplitude
```

```
Excited state 2:  4.9621 eV (singlet)
e-/hole pair 1:  ampl =  0.9544  (91.1 %)
e-/hole pair 2:  ampl =  0.2387  ( 5.7 %)
These amplitudes account for 96.8 % of total amplitude
```

relevant portion of output

NTOs: Example #1 (DMABN)

```
$rem
method          pbe0
basis           6-31+G*
cis_n_roots    2
cis_triplets   false
cis_ampl_anal true
$end
```

sample input (needs \$molecule section)

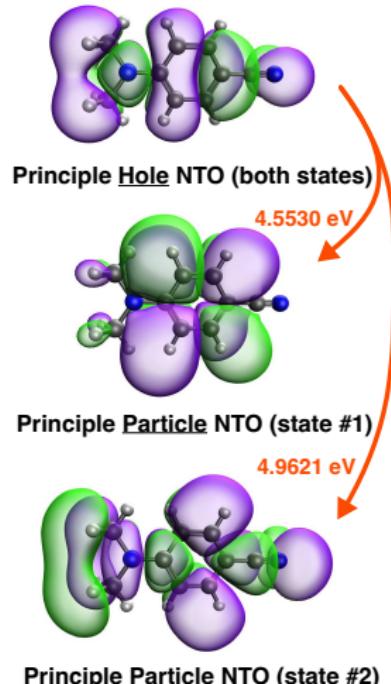
```
=====
TDA excitation amplitudes in the NTO basis
(Print if lampl > 0.15)
=====

Excited state 1: 4.5530 eV (singlet)
e-/hole pair 1: ampl = 0.9372 (87.8 %)
e-/hole pair 2: ampl = 0.3396 (11.5 %)
These amplitudes account for 99.4 % of total amplitude

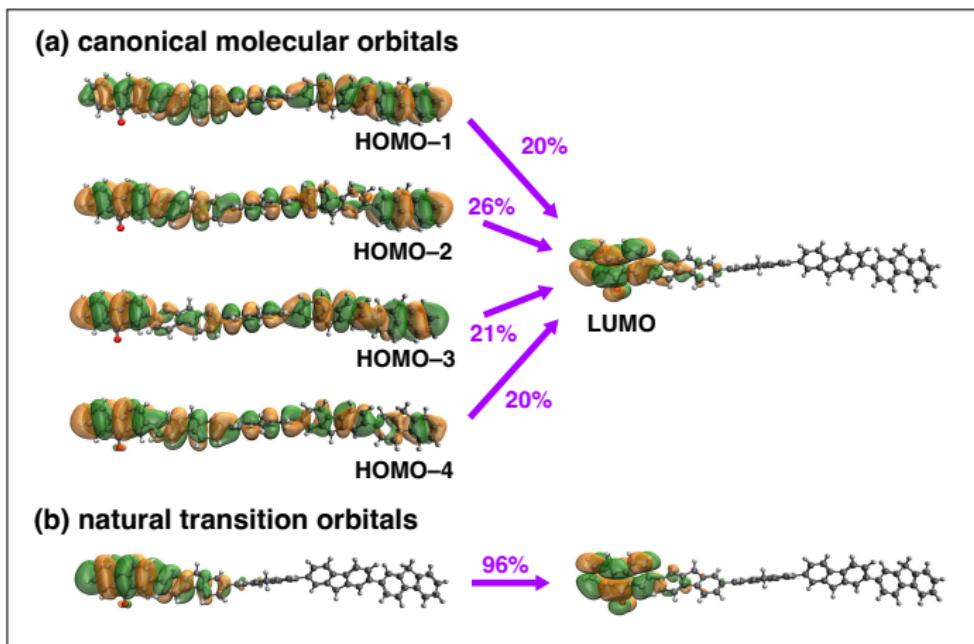
Excited state 2: 4.9621 eV (singlet)
e-/hole pair 1: ampl = 0.9544 (91.1 %)
e-/hole pair 2: ampl = 0.2387 ( 5.7 %)
These amplitudes account for 96.8 % of total amplitude
```

=====

relevant portion of output



NTOs: Example #2

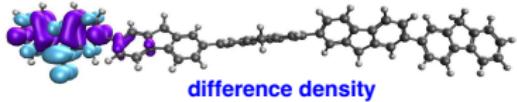


- $S_0 \rightarrow S_2$ excitation of fluorenone-terminated polyfluorene (CAM-B3LYP/3-21G*).
- Percentages represent $|x_{ia}|^2$ since $\sum_{ia} |x_{ia}|^2 = 1$.

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Other Visualization Tools

Various densities representing the $S_0 \rightarrow S_2$ excitation

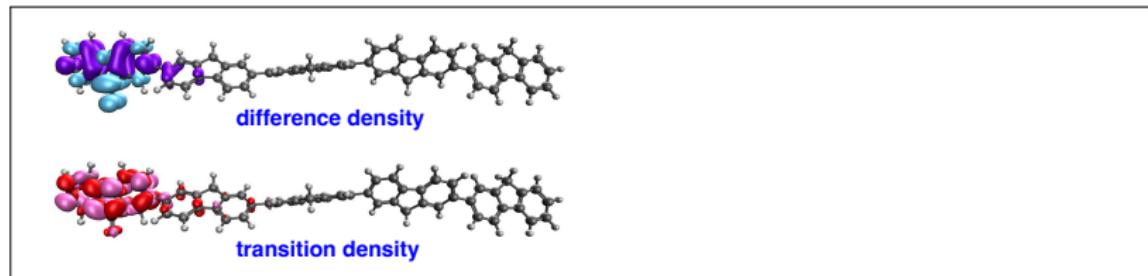


- Difference density, $\Delta\rho(\mathbf{r}) = \rho_{\text{exc}}(\mathbf{r}) - \rho_{\text{gnd}}(\mathbf{r})$

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Other Visualization Tools

Various densities representing the $S_0 \rightarrow S_2$ excitation

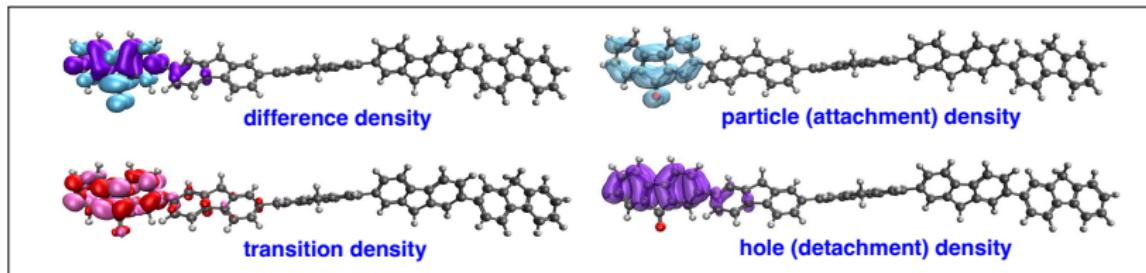


- Difference density, $\Delta\rho(\mathbf{r}) = \rho_{\text{exc}}(\mathbf{r}) - \rho_{\text{gnd}}(\mathbf{r})$
- Transition density

$$T(\mathbf{r}) = \int \Psi_{\text{exc}}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{\text{gnd}}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

Various densities representing the $S_0 \rightarrow S_2$ excitation



- Difference density, $\Delta\rho(\mathbf{r}) = \rho_{\text{exc}}(\mathbf{r}) - \rho_{\text{gnd}}(\mathbf{r})$

- Transition density

$$T(\mathbf{r}) = \int \Psi_{\text{exc}}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{\text{gnd}}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

- Particle/hole densities: $\Delta\rho(\mathbf{r}) = \Delta\rho_{\text{elec}}(\mathbf{r}) + \Delta\rho_{\text{hole}}(\mathbf{r})$.

- These are sums of squares of the particle/hole NTOs, e.g.:

$$\Delta\rho_{\text{elec}}(\mathbf{r}) = \sum_{k=1}^{\text{occ}} \lambda_k^2 |\psi_k^{\text{elec}}(\mathbf{r})|^2$$

Herbert, "Density-functional theory for electronic excited states", Ch. 3 of *Theoretical and Computational Photochemistry: Fundamentals, Methods, Applications and Synergy with Experimental Approaches*, pp. 69–118 (2023).

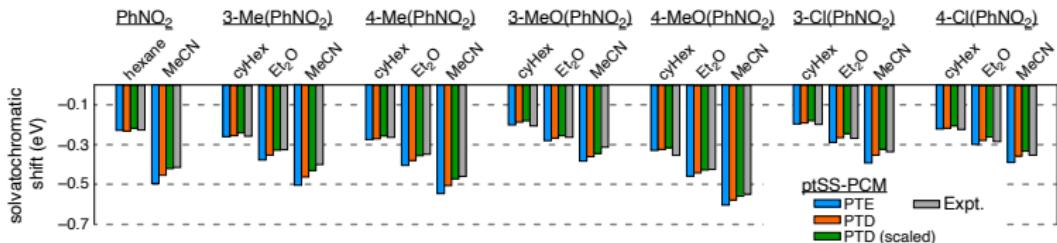
Dielectric Continuum Boundary Conditions

- *Polarizable continuum models* (PCMs) describe a class of methods for implementing dielectric (rather than vacuum) boundary conditions.
- “Nonequilibrium” PCMs use the static dielectric constant (ϵ_0) for the ground state and the optical dielectric constant (ϵ_∞) to repolarize with $\Delta\rho$.

Herbert, “Dielectric continuum models for quantum chemistry” [*WIREs Comput. Mol. Sci.* 11, e1519 (2021)]

Dielectric Continuum Boundary Conditions

- *Polarizable continuum models* (PCMs) describe a class of methods for implementing dielectric (rather than vacuum) boundary conditions.
- “Nonequilibrium” PCMs use the static dielectric constant (ϵ_0) for the ground state and the optical dielectric constant (ϵ_∞) to repolarize with $\Delta\rho$.
 - ▶ For localized excitations, solvatochromic shifts are often small.
 - ▶ For charged moieties, dielectric boundaries may be necessary even to converge the ground-state SCF.*



Herbert, “Dielectric continuum models for quantum chemistry” [WIREs Comput. Mol. Sci. 11, e1519 (2021)]

* Bowling, Broderick, & Herbert [J. Phys. Chem. Lett. 14, 3826 (2023)]

Figure: Mewes, You, Wormit, Kriesche, Herbert, & Dreuw [J. Phys. Chem. A 119, 5446 (2015)]

Outline

1 Logistics

- Q-Chem & IQmol
- Philosophy

2 Intro to Molecular DFT

- Self-Consistent Field Theory
- Gaussian Basis Sets
- Physical Interpretation

3 Exchange-Correlation Functionals

- Jacob's Ladder
- Self-Interaction Error
- Recommendations

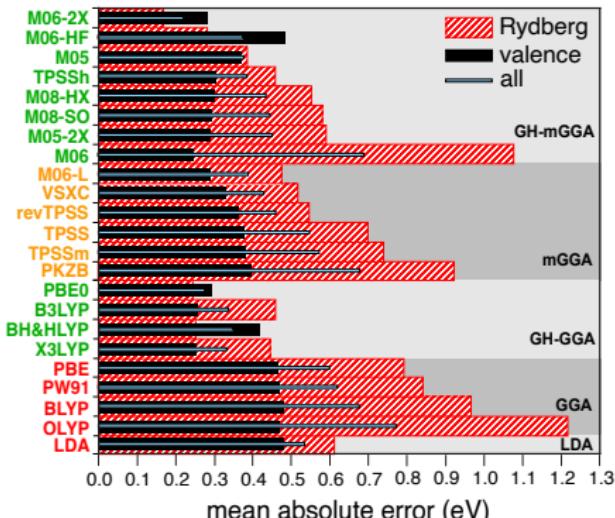
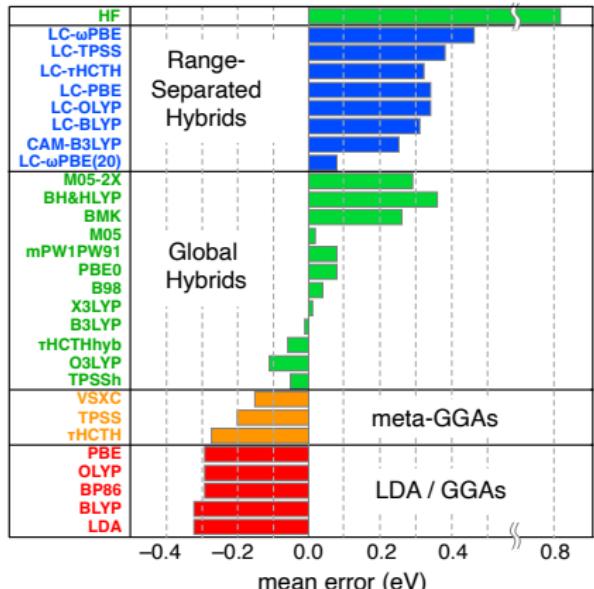
4 Contemporary Issues in DFT

- Dispersion Interactions
- Self-Interaction & Delocalization Errors
- HOMO/LUMO Gaps
- Range-Separated Hybrid Functionals

5 TD-DFT

- DFT for Excited States
- Charge-Transfer Problems

A Closer Look at Functional Performance



- GGAs systematically underestimate excitation energies
- Errors are larger for Rydberg excitations than for localized valence excitations
- LRC functionals overcorrect this problem

Long-Range Behavior of v_{xc}

- **Theory:** $v_{xc}(\mathbf{r}) \sim -1/r$ for removing an electron from a neutral molecule.
- **Practice:** $v_{xc}(\mathbf{r})$ decays exponentially for semilocal functionals.
- This has adverse effects on any property that depends on the tail of v_{xc} (polarizabilities, Rydberg excitations, . . .).
- CT excitations are **severely** underestimated

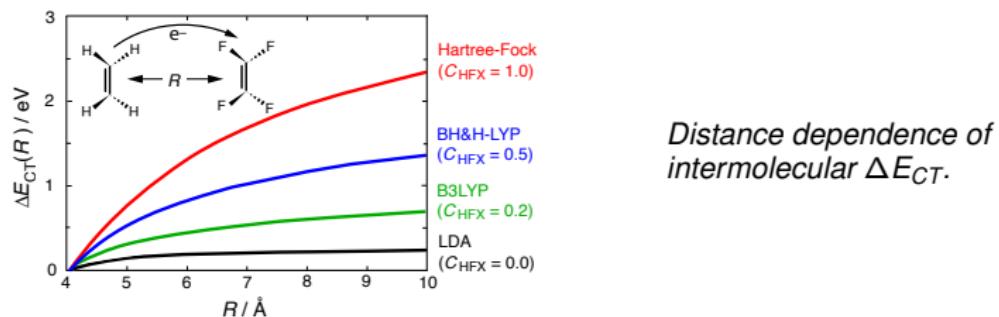


Figure @ left: Dreuw, Weisman, & Head-Gordon [*J. Chem. Phys.* **119**, 2943 (2003)]

Long-Range Behavior of v_{xc}

- **Theory:** $v_{xc}(\mathbf{r}) \sim -1/r$ for removing an electron from a neutral molecule.
- **Practice:** $v_{xc}(\mathbf{r})$ decays exponentially for semilocal functionals.
- This has adverse effects on any property that depends on the tail of v_{xc} (polarizabilities, Rydberg excitations, ...).
- CT excitations are **severely** underestimated ...*but LRC functionals can restore proper asymptotic behavior*:

$$\text{Mulliken: } \Delta E_{CT}(R) \sim IE_{\text{donor}} - EA_{\text{acceptor}} - 1/R$$

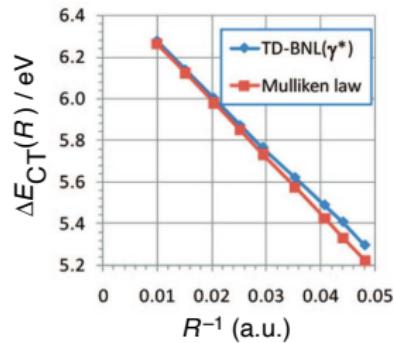
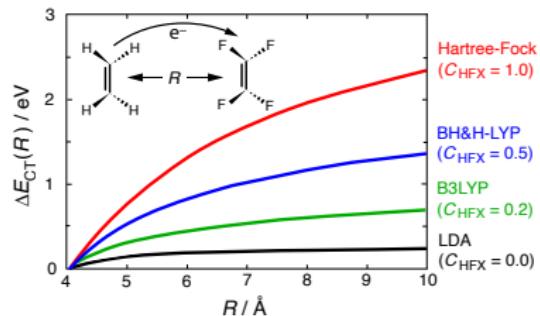
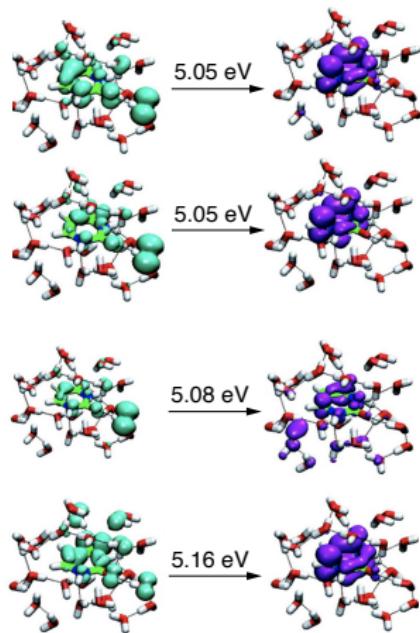


Figure @ left: Dreuw, Weisman, & Head-Gordon [*J. Chem. Phys.* **119**, 2943 (2003)]

Figure @ right: Stein, Kronik, & Baer [*J. Am. Chem. Soc.* **131**, 2818 (2009)]

Appearance of Spurious CT States

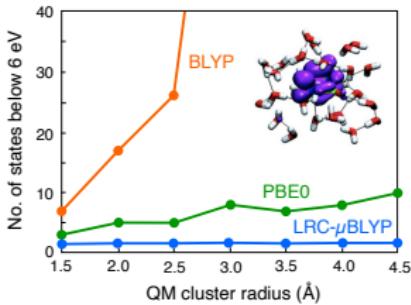
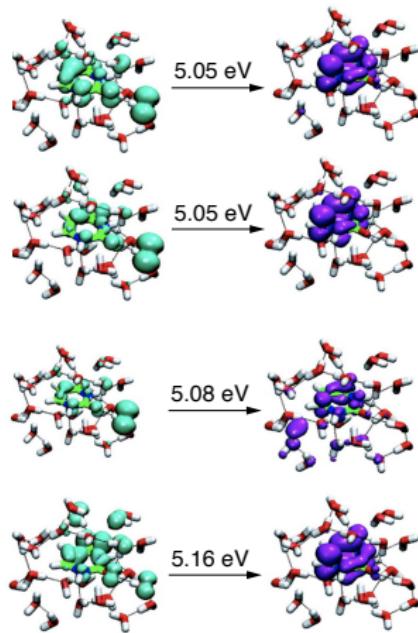
Underestimation of ΔE_{CT} is so severe that spurious, low-energy CT states appear in TD-DFT and mix with valence excitations.



Lange & Herbert [*J. Chem. Theory Comput.* **3**, 1680 (2007)]
Rohrdanz, Lange, & Herbert [*J. Phys. Chem. B* **112**, 6304 (2008)]

Appearance of Spurious CT States

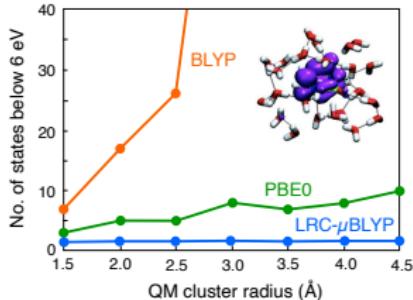
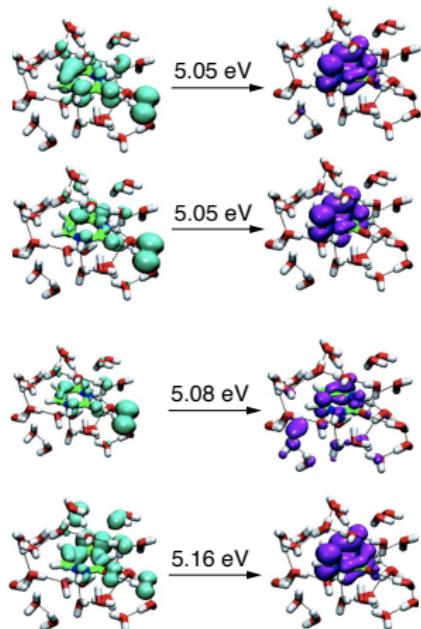
Underestimation of ΔE_{CT} is so severe that spurious, low-energy CT states appear in TD-DFT and mix with valence excitations.



Lange & Herbert [*J. Chem. Theory Comput.* **3**, 1680 (2007)]
Rohrdanz, Lange, & Herbert [*J. Phys. Chem. B* **112**, 6304 (2008)]

Appearance of Spurious CT States

Underestimation of ΔE_{CT} is so severe that spurious, low-energy CT states appear in TD-DFT and mix with valence excitations.



d/Å ^a	no. QM water molecules	no. states below 6 eV	ω_{40} /eV	first ${}^1\pi\pi^*$ state		
				state no.	ω /eV	oscillator strength
1.5	0	3	9.73	2	5.31	0.1396
2.0	4	5	8.66	2	5.25	0.1168
2.5	7	5	8.16	2	5.22	0.1707
3.0	15	8	7.59	2	5.15	0.1616
3.5	18	7	7.44	1	5.13	0.1041
4.0	25	8	7.15	1	5.09	0.1422
4.5	37	10	6.91	1	5.10	0.1624

^a Distance criterion for selecting the QM region.

TD-PBE0 / 6-31+G*

Lange & Herbert [*J. Chem. Theory Comput.* **3**, 1680 (2007)]

Rohrdanz, Lange, & Herbert [*J. Phys. Chem. B* **112**, 6304 (2008)]

- TD-DFT is generally more sensitive (as compared to ground-state DFT) to the choice of XC functional.
 - ▶ This is a result of the *adiabatic approximation* (locality in time), by means of which we can use ground-state XC functionals.
 - ▶ There are no production-level functionals that go beyond this approximation.

- TD-DFT is generally more sensitive (as compared to ground-state DFT) to the choice of XC functional.
 - ▶ This is a result of the *adiabatic approximation* (locality in time), by means of which we can use ground-state XC functionals.
 - ▶ There are no production-level functionals that go beyond this approximation.
- **Conjecture:** TD-DFT works much better in the hands of experimental chemists than it does in the hands of theoretical chemists.
 - ▶ Why do you suppose this might be true?

- TD-DFT is generally more sensitive (as compared to ground-state DFT) to the choice of XC functional.
 - ▶ This is a result of the *adiabatic approximation* (locality in time), by means of which we can use ground-state XC functionals.
 - ▶ There are no production-level functionals that go beyond this approximation.
- **Conjecture:** TD-DFT works much better in the hands of experimental chemists than it does in the hands of theoretical chemists.
 - ▶ Why do you suppose this might be true?
- The presence of pernicious, systemic problems means there are tremendous opportunities to improve the status quo!

