Molecular properties and spectra Using DFT and TDDFT

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Outline

1. **Introduction**

2. First order: dipoles, geometries

3. Second order: IR, NMR

4. Excited states by TDDFT and OODFT

Molecular properties are energy derivatives

- Properties are responses to applied fields / perturbations

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}^{(1)} + \dots$$

- First order properties:
  - Examples: electric dipole moment, nuclear forces
  - Perturbation theory to 1st order (variational wave functions only)

  $$E^{(1)} = <\Psi^{(0)} | \hat{V}^{(1)} | \Psi^{(0)} >$$

  - First derivative of the energy (all well-posed methods)

  $$E^{(1)} = \partial E / \partial \lambda \equiv E^{\lambda}$$

- Second order properties:
  - Examples: molecular magnetizabilities, magnetic shielding
  - Perturbation theory to 2nd order (variational wave functions)

  $$E^{(2)} = <\Psi^{(0)} | \hat{V}^{(2)} | \Psi^{(0)} > + <\Psi^{(0)} | \hat{V}^{(1)} | \Psi^{(1)} >$$

  - Second derivative of the energy (all well-posed methods)

  $$E^{(2)} = \partial^2 E / \partial \lambda^2 \equiv E^{\lambda\lambda}$$

Since properties are energy derivatives….

- Analytic evaluation of those derivatives is possible

"Analytic derivatives" transformed quantum chemistry!

- Peter Pulay: SCF gradients (1969)

Analytic gradients: efficient, precise and (relatively) easy

First order properties

$$E^\lambda = \text{Tr}(\mathbf{p}\mathbf{h}^\lambda) + \text{Tr}(\mathbf{w}\mathbf{s}^\lambda) + \text{Tr}(\mathbf{\Gamma}\mathbf{G}^\lambda)$$

p, G are   1, 2-electron density matrices. w is E-1-PDM

s, h, Γ, s are 0, 1, 2-electron matrix elements

Analytic hessians: (less) efficient, precise and (technically) harder

Second order properties

$$E^{\lambda\lambda} = \text{Tr}(\mathbf{p}\mathbf{h}^{\lambda\lambda}) + \text{Tr}(\mathbf{w}\mathbf{s}^{\lambda\lambda}) + \text{Tr}(\mathbf{\Gamma}\mathbf{G}^{\lambda\lambda})$$
$$+ \text{Tr}(\mathbf{p}^\lambda\mathbf{h}^\lambda) + \text{Tr}(\mathbf{w}^\lambda\mathbf{s}^\lambda) + \text{Tr}(\mathbf{\Gamma}^\lambda\mathbf{G}^\lambda)$$

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1. Introduction

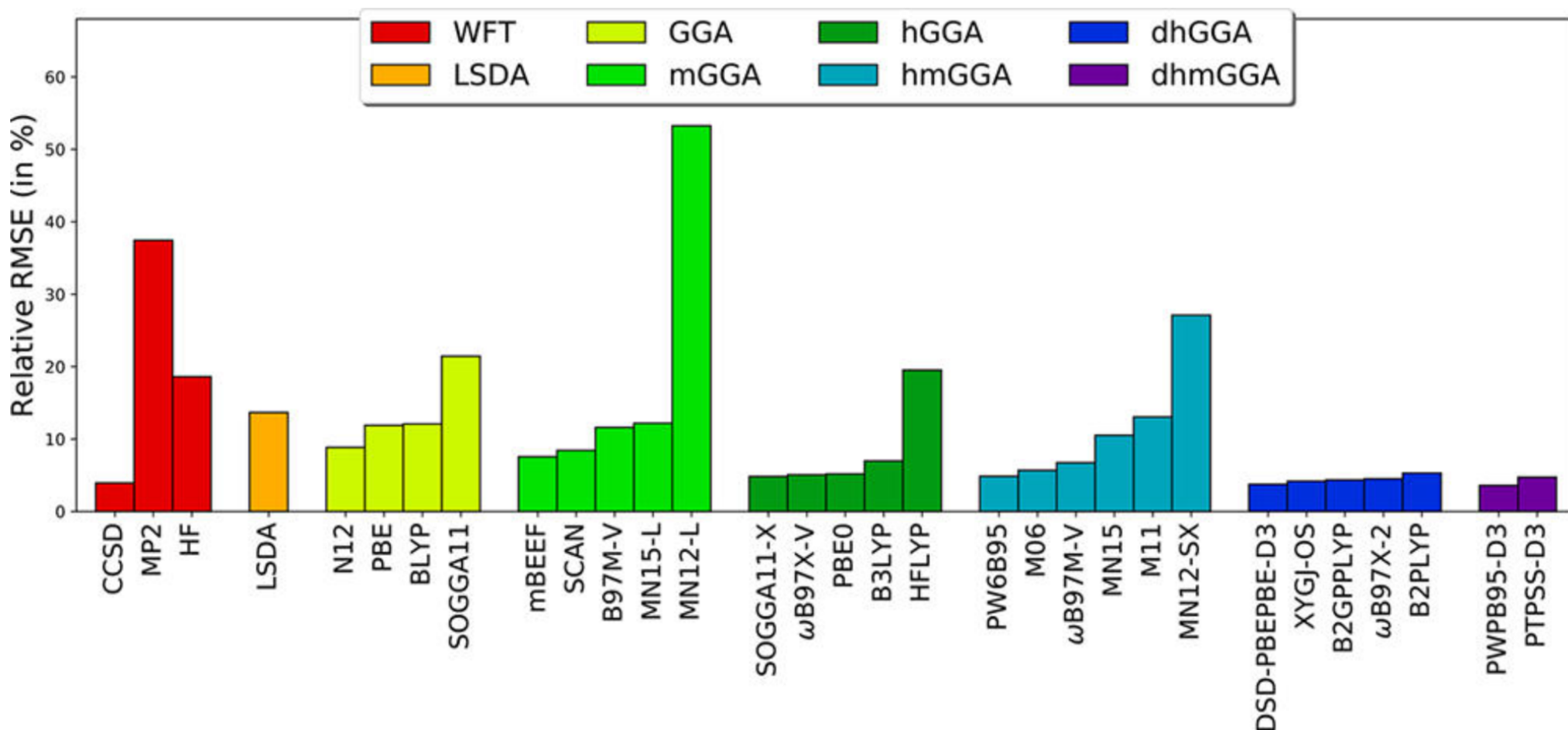**2. First order: dipoles, geometries**

3. Second order: IR, NMR

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Dipole moments (Diptarka Hait)

D. Hait and MHG, J. Chem. Theory Comput. 14, 1969 (2018)

Dipole moment is a measure of the electron density (1st moment)
200 CBS limit CCSD(T) dipole moments used to test 88 functionals

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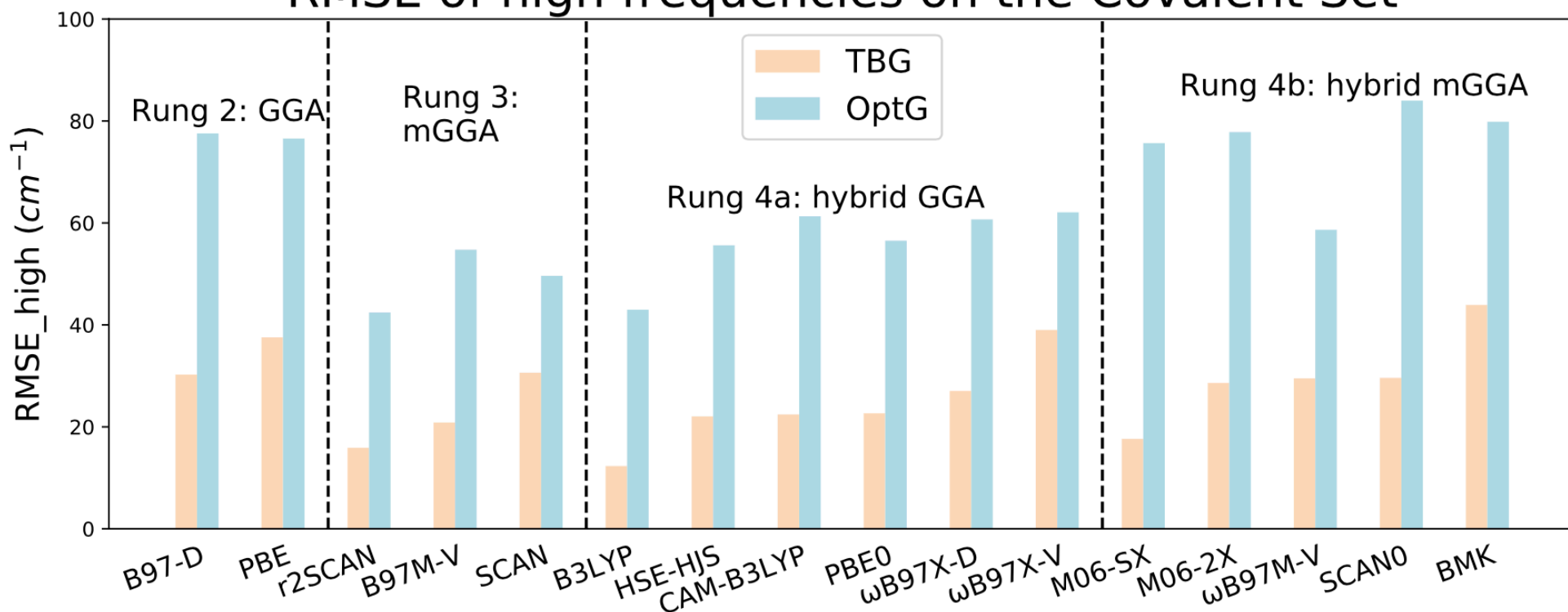2. First order: dipoles, geometries

3. **Second order: IR, NMR**

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Harmonic vibrational frequencies (Jiashu Liang)

J. Liang, X. Feng, and MHG, J. Chem. Phys. (Submitted, 2023)

Harmonic vibrational frequencies for some common functionals
Compared against CCSD(T) on 100 molecules / 182 frequencies

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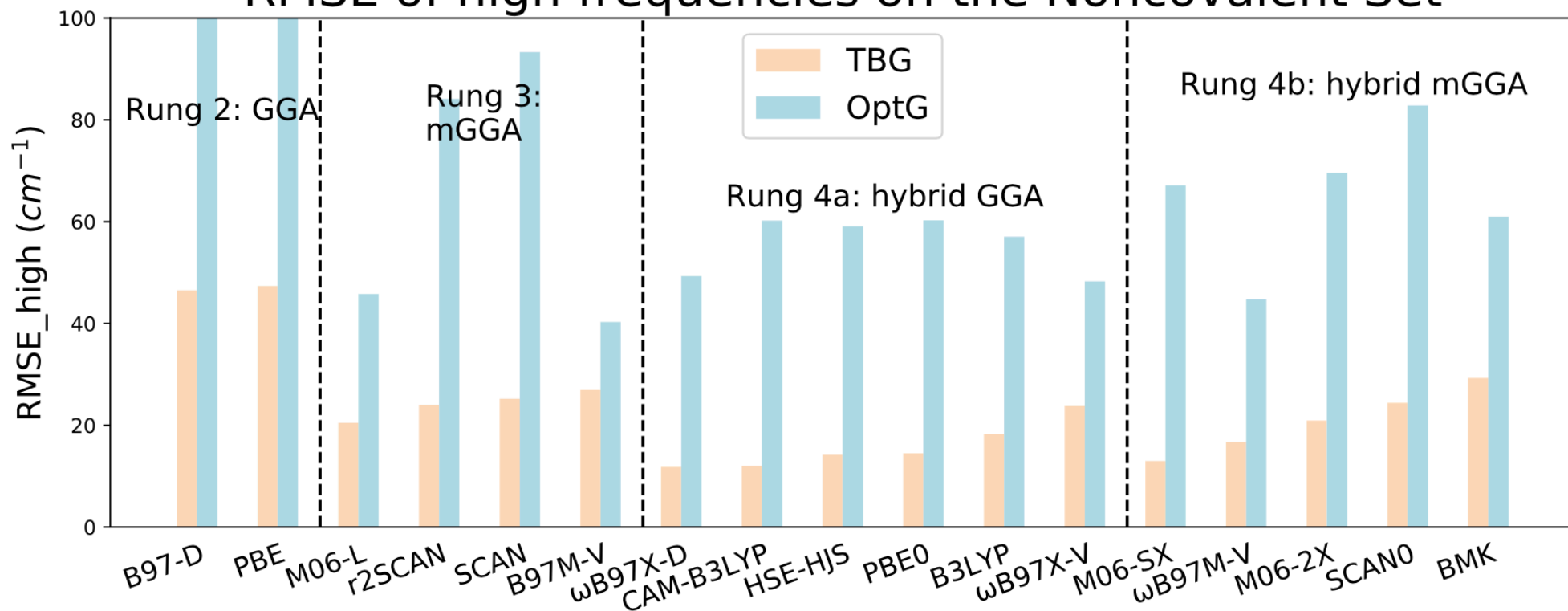
Harmonic vibrational frequencies: scaling factors.

Scaling improves agreement with experimental frequencies, ZPEs
112 data points from J.M.L. Martin et al, JPC A 119, 1701 (2014)

	scale(ω)	RMS(ω)	scale(ZPE)	RMS(ZPE)
B3LYP	0.967	19.4	0.990	0.092
ωB97M-V	0.958	24.5	0.983	0.115
ωB97X-V	0.954	25.4	0.978	0.128
r2SCAN	0.967	27.5	0.991	0.085

B3LYP is "too good"!
All methods perform remarkably well.

NMR chemical shifts (Jiashu Liang, Zhe Wang)

J. Liang, Z. Wang, et al, J. Chem. Theory Comput. 19, 514 (2023)
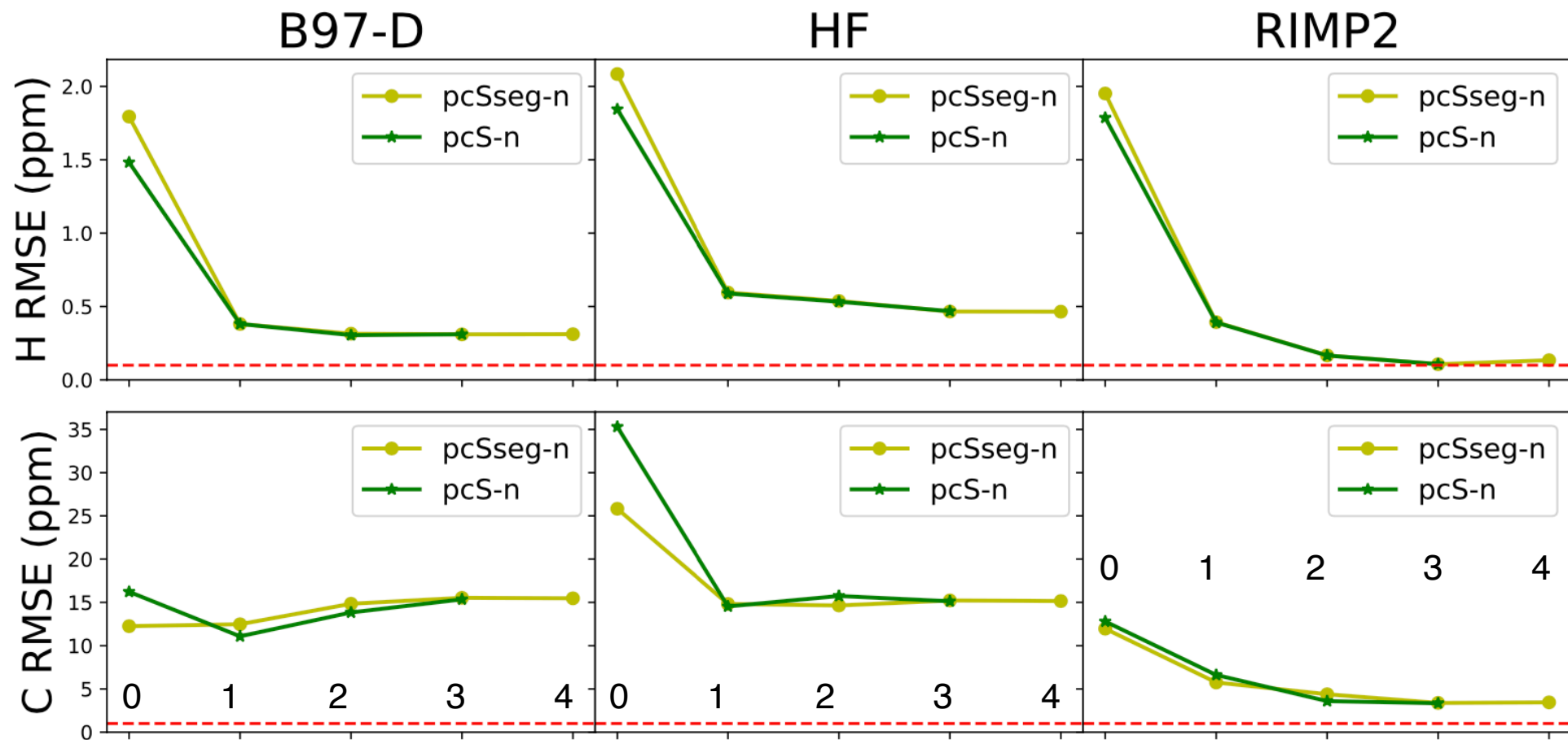
DFT is useful, but less accurate than WFT methods.
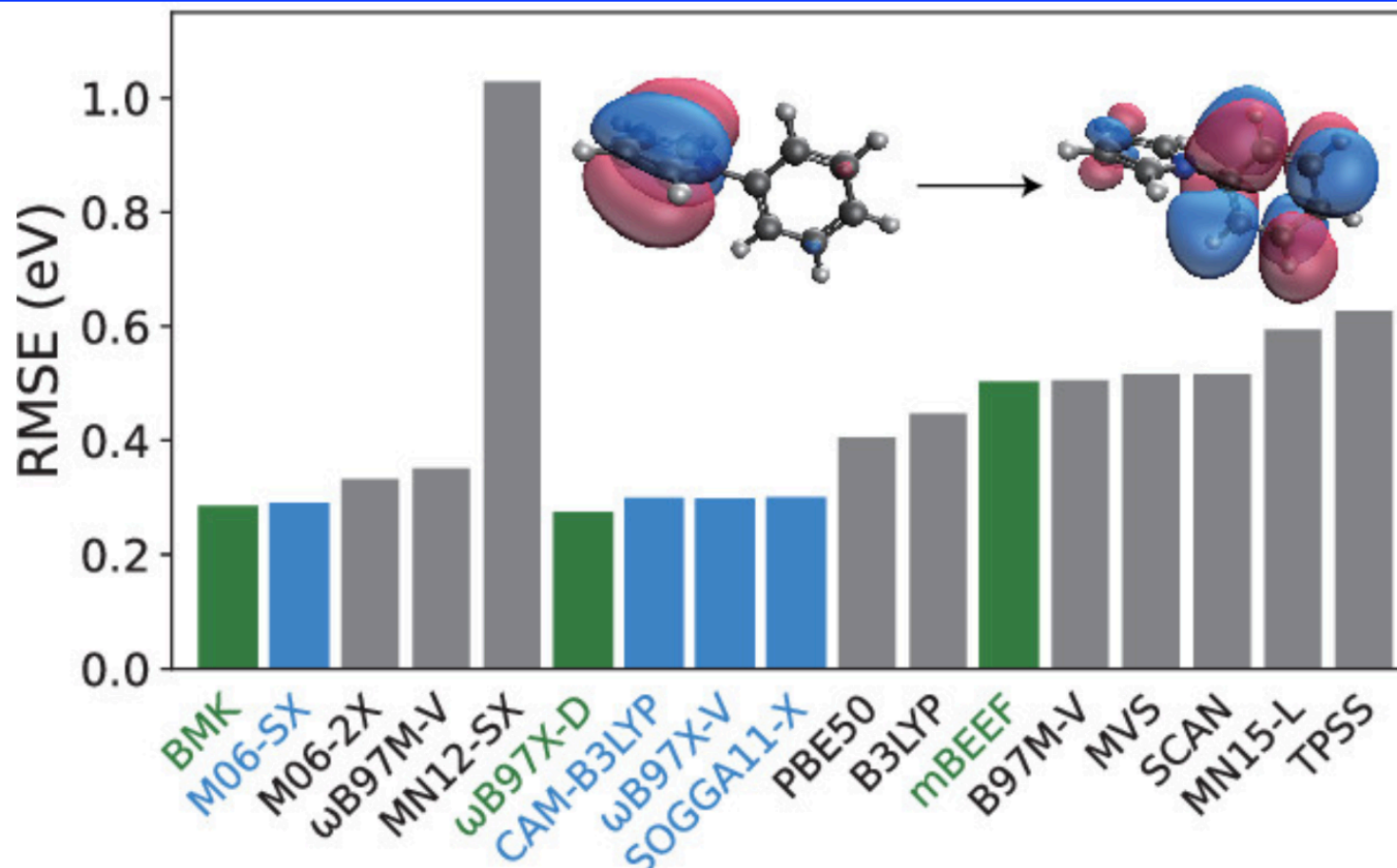The pcS1 basis set is a good compromise between cost and accuracy.

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Time-dependent DFT (Jiashu Liang)

J. Liang, X. Feng, D. Hait and MHG, J. Chem. Theory Comput. 18, 3460 (2022)

TDDFT is the workhorse for predicting UV-vis spectra
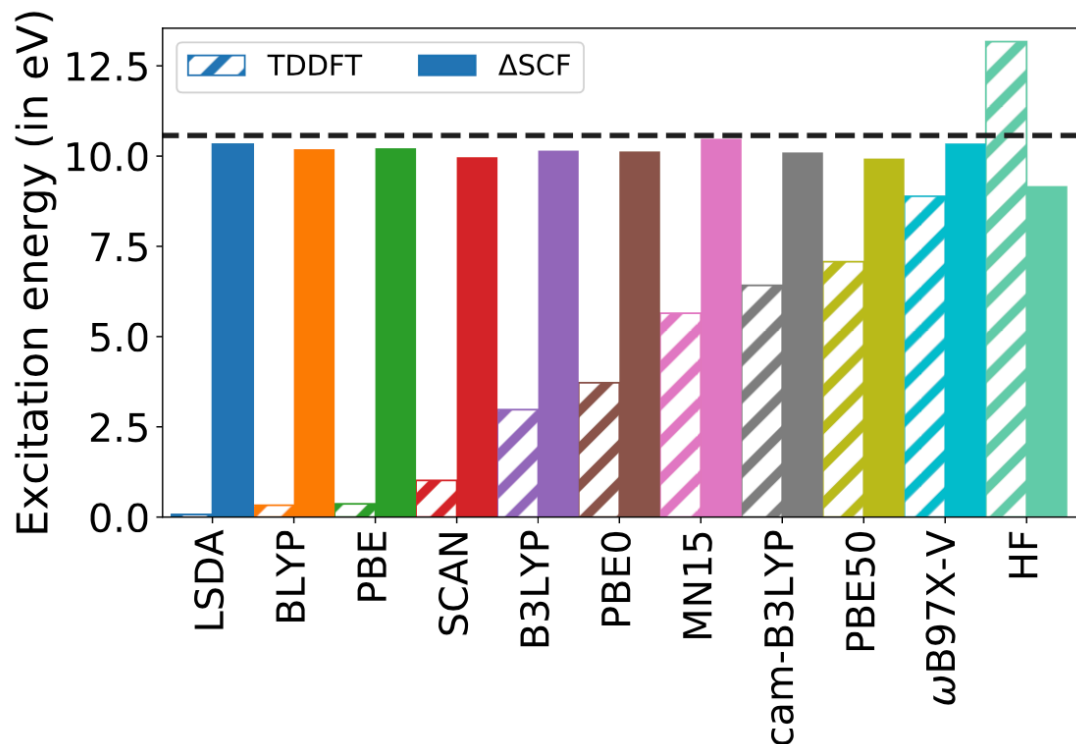RMS errors of ~ 0.3 eV across 463 transitions

Now it's on to the exercises!