Recent developments in exchange correlation functionals
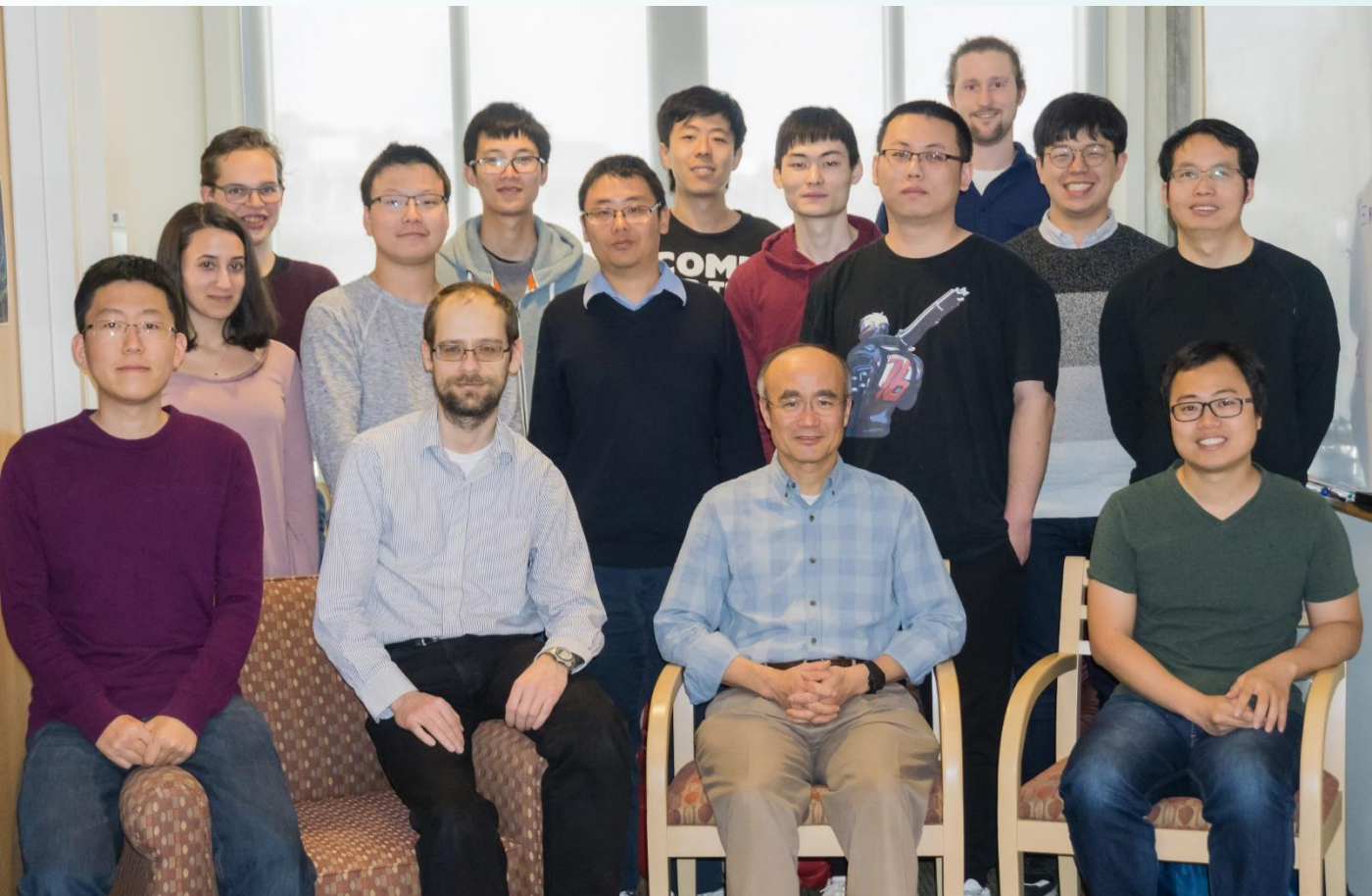
Weitao Yang
Duke University

HANDS-ON DFT AND BEYOND
Barcelona
August 30, 2019

1. **Systematic Errors in DFT from Fractional Perspectives**

2. **Localized Orbital Scaling Correction (LOSC) for Delocalization Error, and for Strong/Static Correlation Error**

3. **Quasiparticle and Excitation Energies from Ground-State DFT**

Density Functional Theory

- DFT is exact and should give agreement with experiment or high-level ab initio calculations in all situations.

- Approximate functionals perform well in many systems but can fail dramatically in other situations.

- This can be traced back to **errors of DFA (density functional approximation)**

- The understanding of these errors will hopefully lead to new and improved functionals.

- **The same challenges for other approximate QM methods.**

A large class of problems

- Wrong dissociation limit for molecules and ions
- Over-binding of charge transfer complex
- too low reaction barriers
- Overestimation of polarizabilities and hyperpolarizabilities
- Overestimation of molecular conductance in molecular electronics
- Incorrect long-range behavior of the exchange-correlation potential
- Charge-transfer excited states
- Band gaps too small
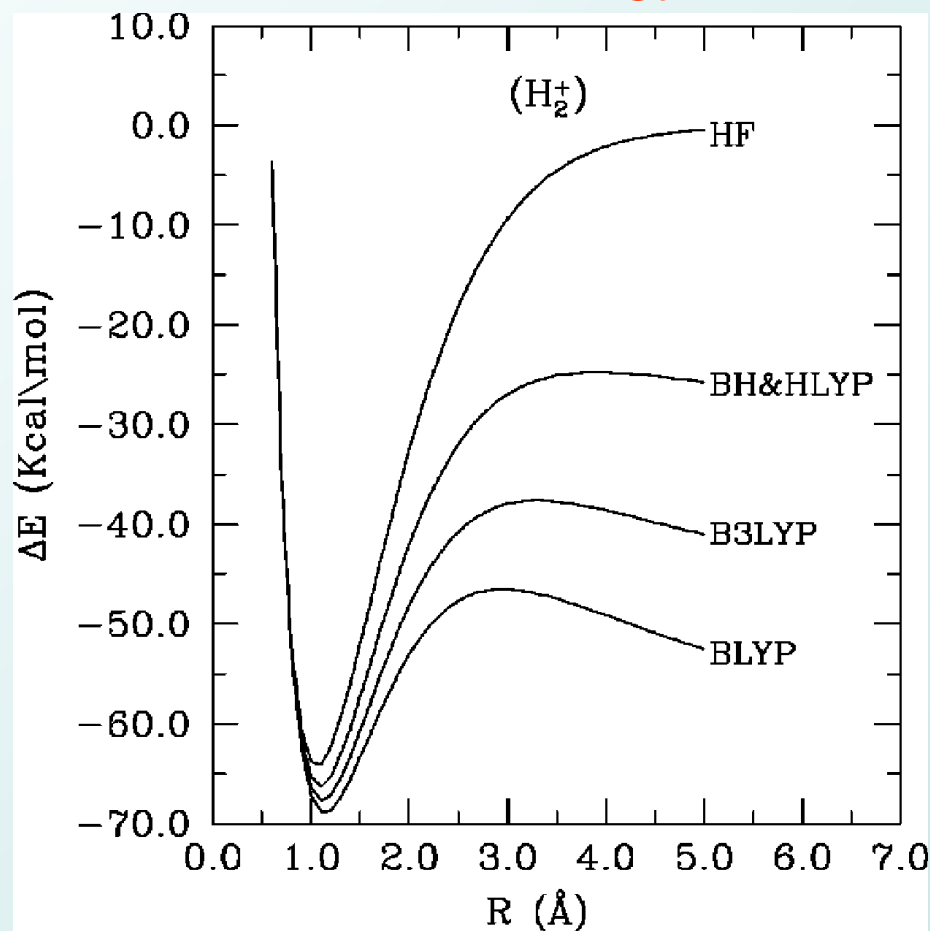- Diels-Alder reactions, highly branched alkanes, dimerization of aluminum complexes

Delocalization Error

H_2^+ **at the dissociation limit**
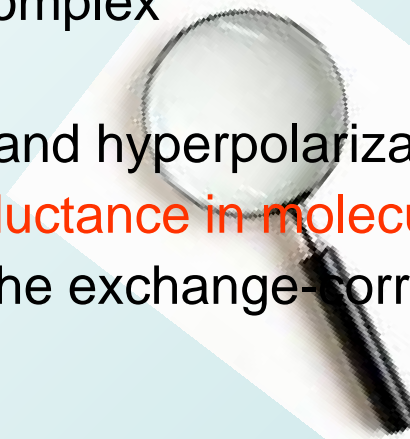
too low energy for delocalized electrons

DFT for fractional number of electrons

from grand ensembles,
Perdew, Parr, Levy, and Balduz, PRL. 1982

$$E_{N+\delta} = (1 - \delta)E_N + \delta E_{N+1}$$
$$\rho_{N+\delta} = (1 - \delta)\rho_N + \delta\rho_{N+1}$$

If

$$H\Psi_1 = E\Psi_1$$

$$H\Psi_2 = E\Psi_2$$

then

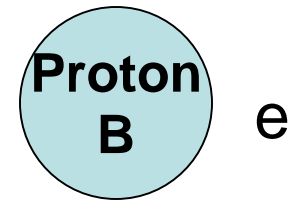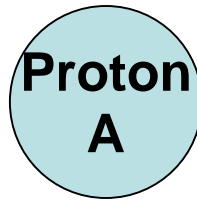$$H\left(c_1\Psi_1 + c_2\Psi_2\right) = E\left(c_1\Psi_1 + c_2\Psi_2\right)$$

Ground State Degeneracy in QM and in DFT

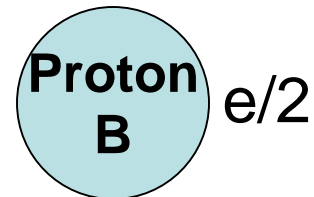WY, Yingkai Zhang and Paul Ayers, PRL, 2000 — pure states

$$\mathbf{H}_2^+ \quad \text{at the dissociation limit}$$

Ψ_α

$E_\alpha = E(0) + E(1)$

| Proton A | | Proton B | e |

Ψ_β
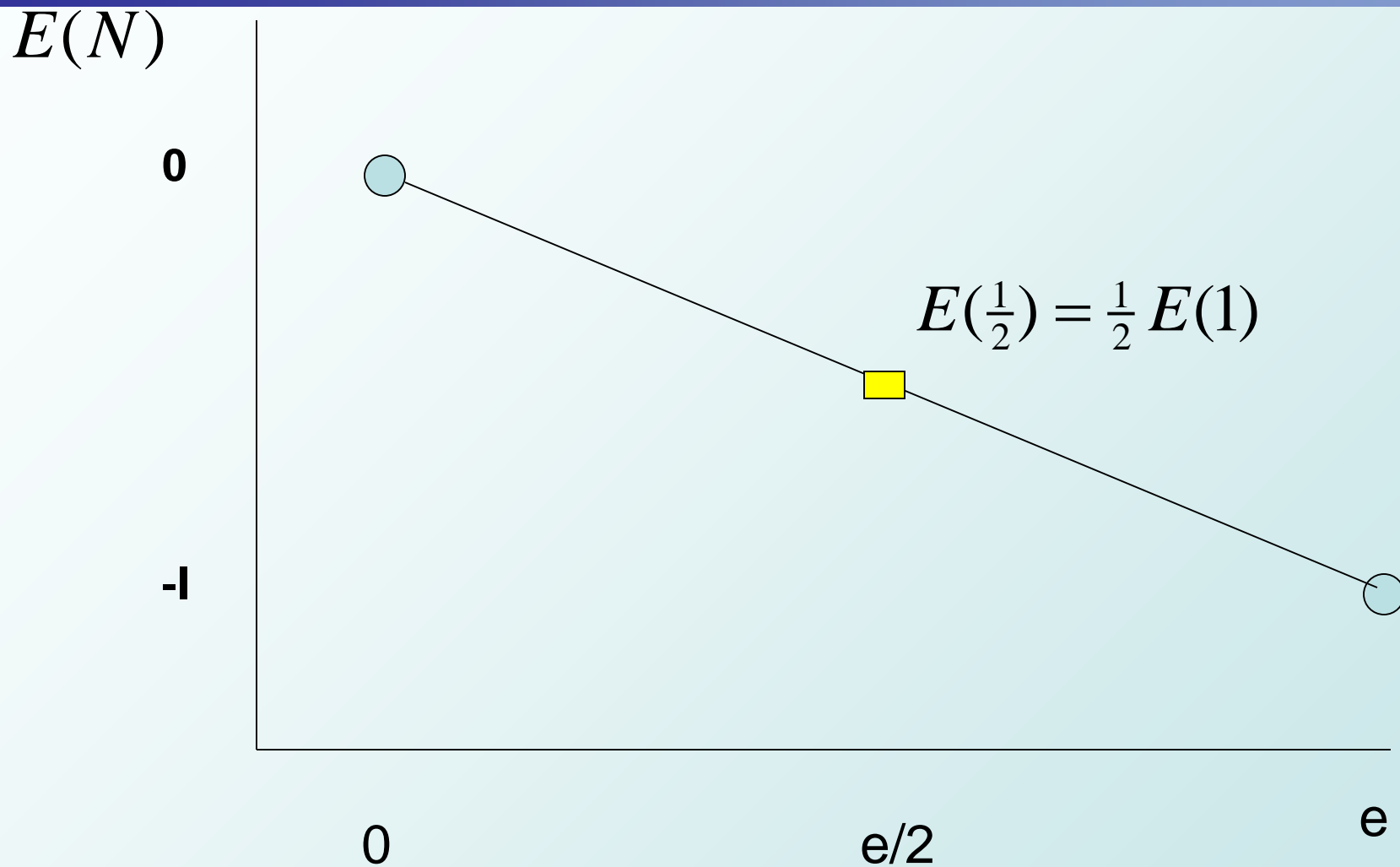
$E_\beta = E(1) + E(0)$

| Proton A | e | | Proton B |

$\Psi_\gamma = \tfrac{1}{\sqrt{2}}\left(\Psi_\alpha + \Psi_\beta\right)$
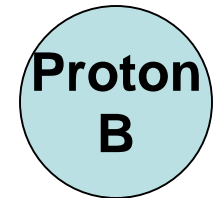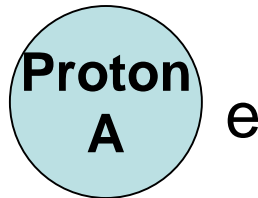
$E_\gamma = E(\tfrac{1}{2}) + E(\tfrac{1}{2}) = 2E(\tfrac{1}{2})$

| Proton A | e/2 | | Proton B | e/2 |
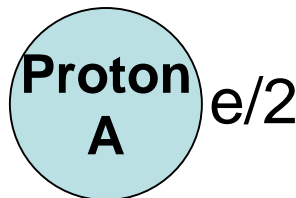
$$E(N): \quad E(\tfrac{1}{2}) = \tfrac{1}{2}E(0) + \tfrac{1}{2}E(1) = \tfrac{1}{2}E(1)$$

The linearity condition in fractional charges: The energy of e/2
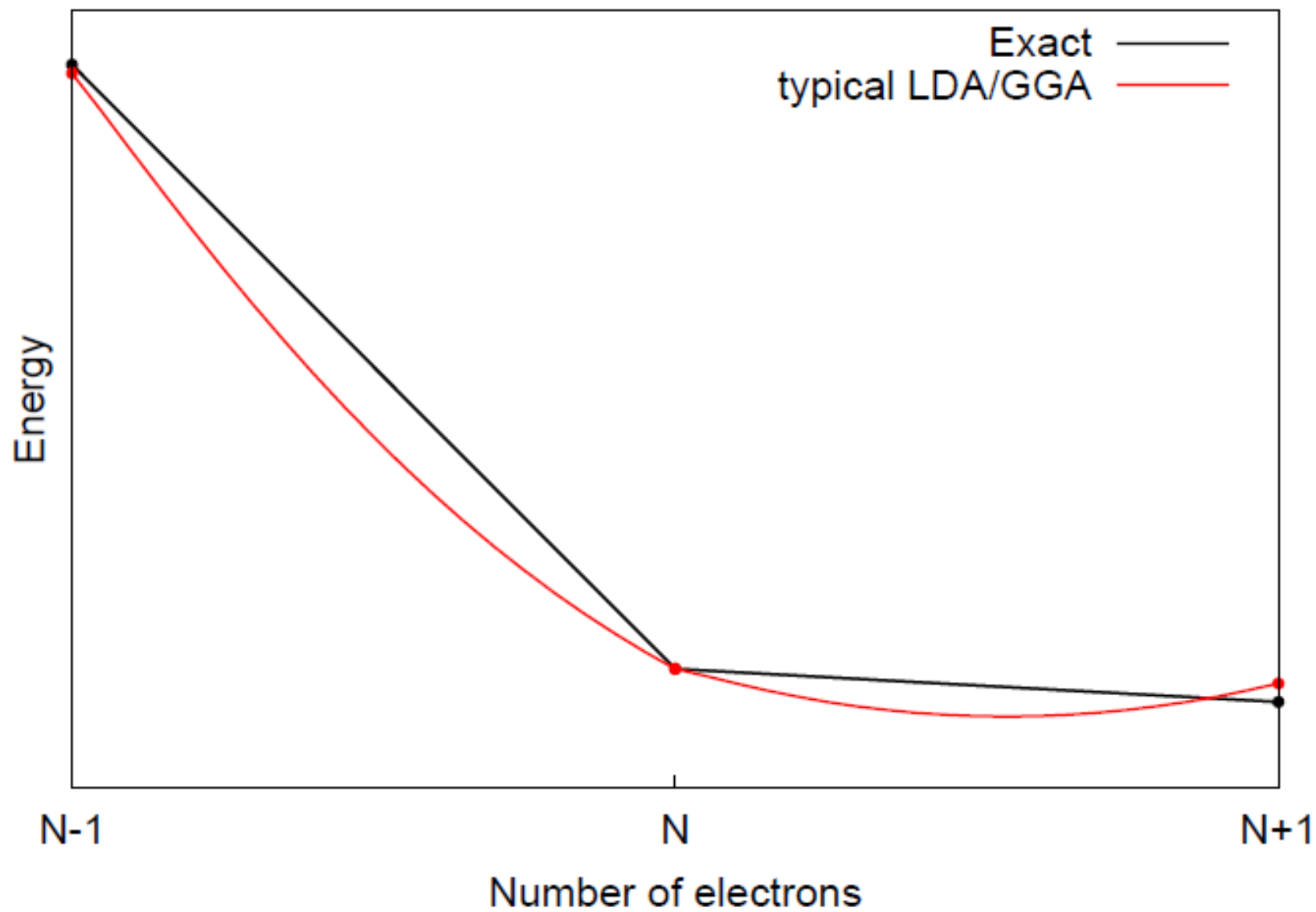
A dimer, with ∞ separation: each monomer has $E(N)$

2 x   **+ e**
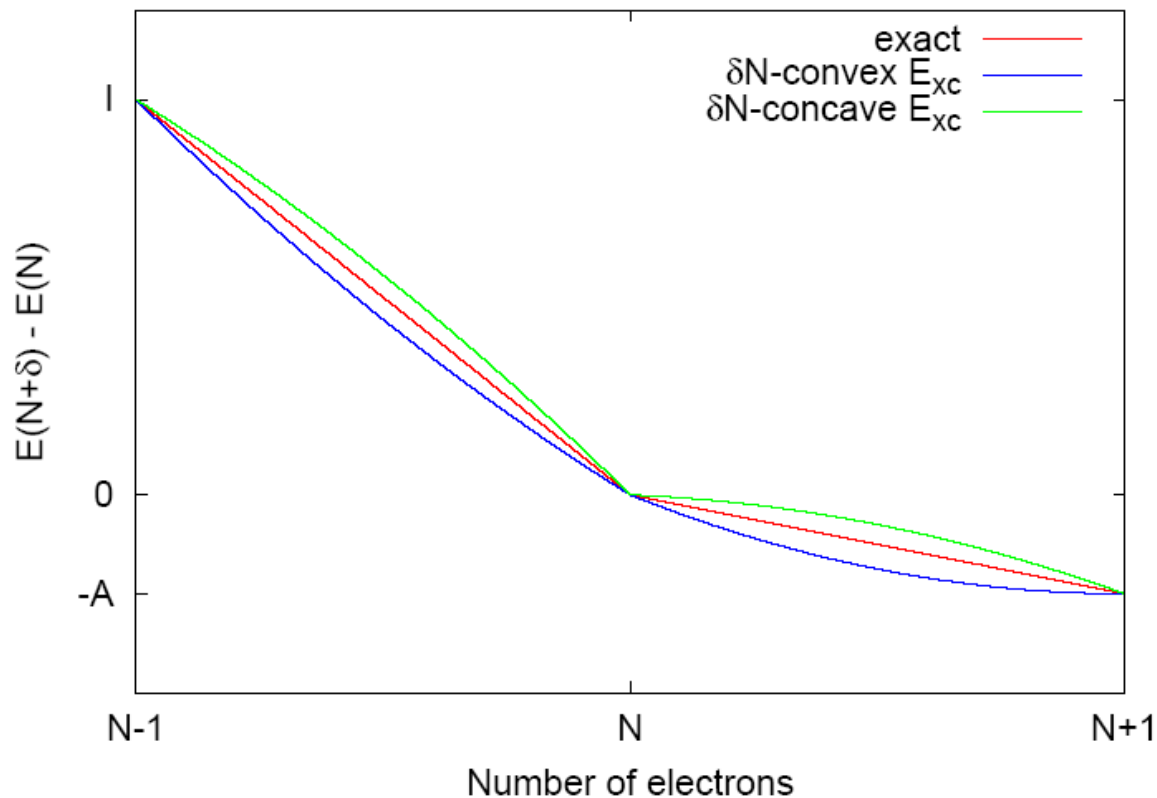
For δN-**convex**, $2E(N+\frac{1}{2}) < E(N)+E(N+1)$, **delocalized**

For δN-**concave**, $2E(N+\frac{1}{2}) > E(N)+E(N+1)$, **localized**

Delocalization and Localization Error
Paula Mori-Sanchez, Aron Cohen and WY, *PRL 2008*
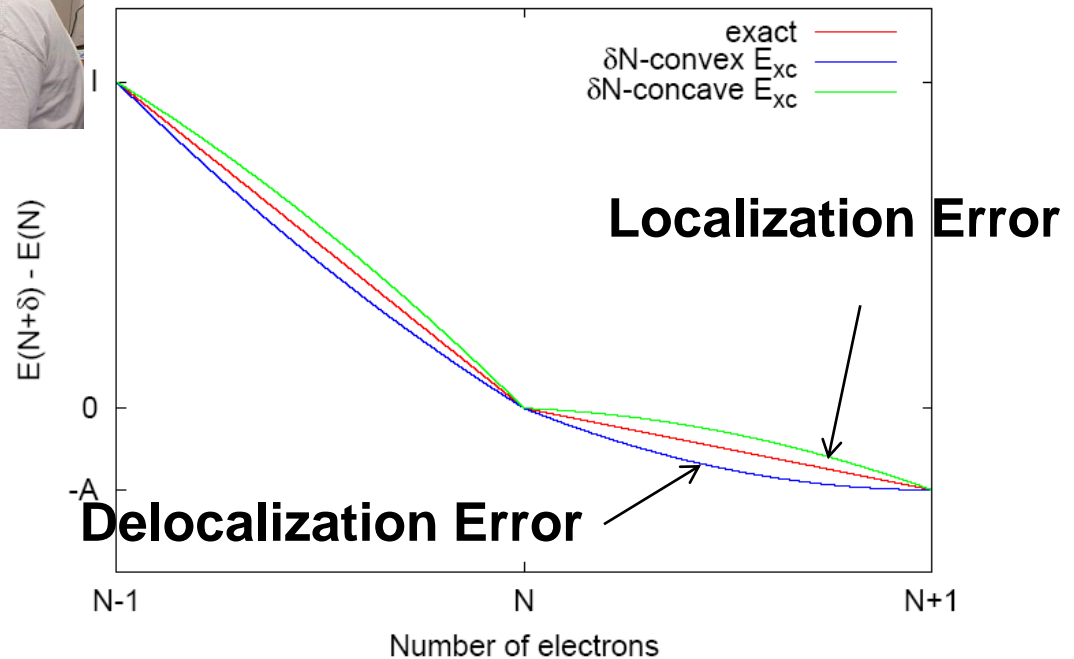
Consequence of Delocalization Error
1. predicts too low energy for delocalized distributions

2. gives too delocalized charge distributions

Delocalization Error

Define the Delocalization Error as the violation of the linearity condition for fractional charges

Cohen, Mori-Sanchez and Yang, 2008 Science

Where is the negative charge ?

Delocalization Error in GGA, LDA, B3LYP
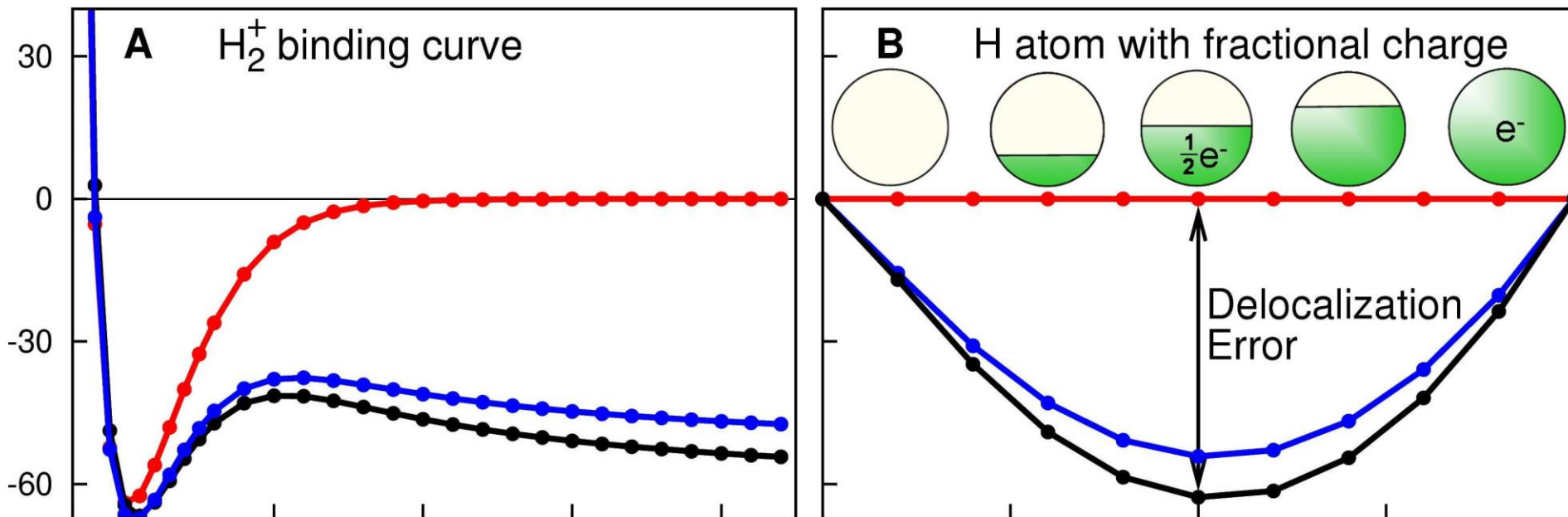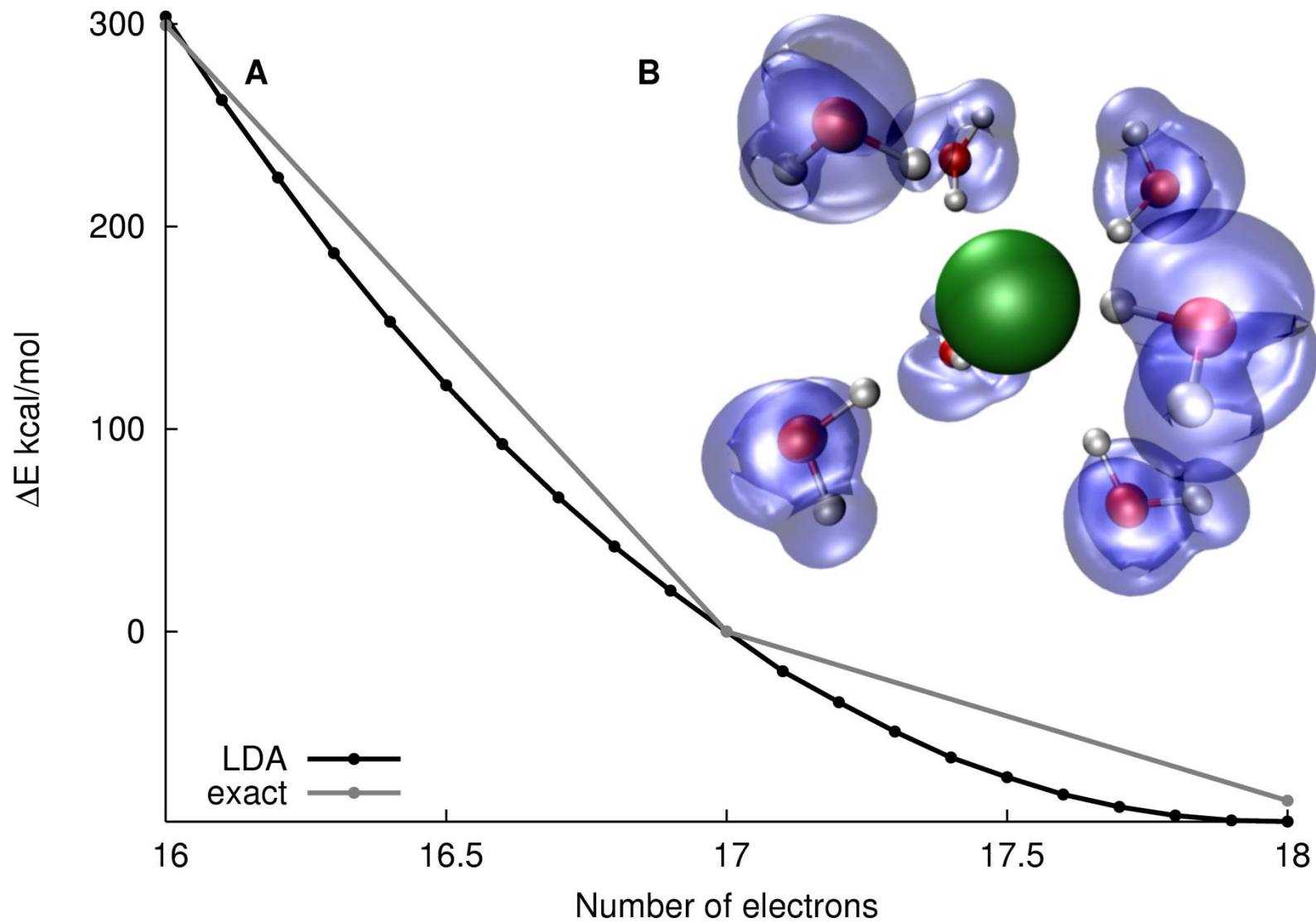
Delocalization Error in GGA, LDA, B3LYP

Too low energy for fractional charge systems

- Energy of dissociation of molecular ion: too low
- Charge transfer complex energy: too low
- Transition state energy: too low
- Charge transfer excitation energy: too low
- Band gap: too low
- Molecular conductance: too high
- (Hyper)polarizability for long molecules: too high
- Diels-Alder reaction products, highly branched alkanes, dimerization of aluminum complexes: too high

Cohen, Mori-Sanchez and Yang, 2008 Science

DFT: Chemical potentials

$$\mu = \left(\frac{\partial E_v(N)}{\partial N} \right)_v$$

The PPLB linearity conditions

$$E_v(N_0 + \delta) = (1 - \delta)E_v(N_0) + \delta E_v(N_0 + 1)$$

The chemical potentials

$$\mu(N) = \begin{cases} -I(N_0) = E(N_0) - E(N_0 - 1) \text{ if } N_0 - 1 < N < N_0 \\ -A(N_0) = E(N_0 + 1) - E(N_0) \text{ if } N_0 < N < N_0 + 1 \end{cases}$$

NOTE: **all ground states,** **no excited state**

DFT: How to calculate the chemical potentials

$$\mu(N) = \begin{cases} -I(N_0) = E(N_0) - E(N_0 - 1) \text{ if } N_0 - 1 < N < N_0 \\ -A(N_0) = E(N_0 + 1) - E(N_0) \text{ if } N_0 < N < N_0 + 1 \end{cases}$$

How to calculate chemical potential in DFT was NOT known until 2008.

What did we know about the meanings of orbital energies before 2008?

Janak's Theorem on Kohm-Sham eigenvalues

$$\varepsilon_i = \left(\frac{\partial E_v[n_i, \phi_i]}{\partial n_i} \right)$$

Based on asymptotic behavior of electron density, and the Kohm-Sham effective potential, for the exact KS HOMO

$$\varepsilon_{max} = -I$$

$$\left(\frac{\partial E_v}{\partial N}\right)_v = -\frac{1}{2}\langle \phi_f | \nabla^2 | \phi_f \rangle + \int \phi_f^*(\mathbf{r})\left[v(\mathbf{r}) + v_J(\mathbf{r})\right]\phi_f(\mathbf{r})d\mathbf{r} + \int \phi_f^*(\mathbf{r})v_{xc}^{\mathrm{NL}}(\mathbf{r}, \mathbf{r}')\phi_f(\mathbf{r}')d\mathbf{r}$$

$$\square = \varepsilon_f^{\mathrm{GKS}},$$

Before this work, no meaning for (G)KS LUMO has been given.

**A new meaning to the frontier eigenvalues of the HF theory, as the HF
chemical potentials of electron removal or addition,
different from Koopman's theorm on HF theory
(Yang, Cohen and Mori-Sanchez, JCP 2012)**

$$\left(\frac{\partial E_v^{HF}}{\partial N}\right)_v^{(-)} = \varepsilon_{HOMO}^{\mathrm{HF}}$$

$$\left(\frac{\partial E_v^{HF}}{\partial N}\right)_v^{(+)} = \varepsilon_{LUMO}^{\mathrm{HF}}.$$
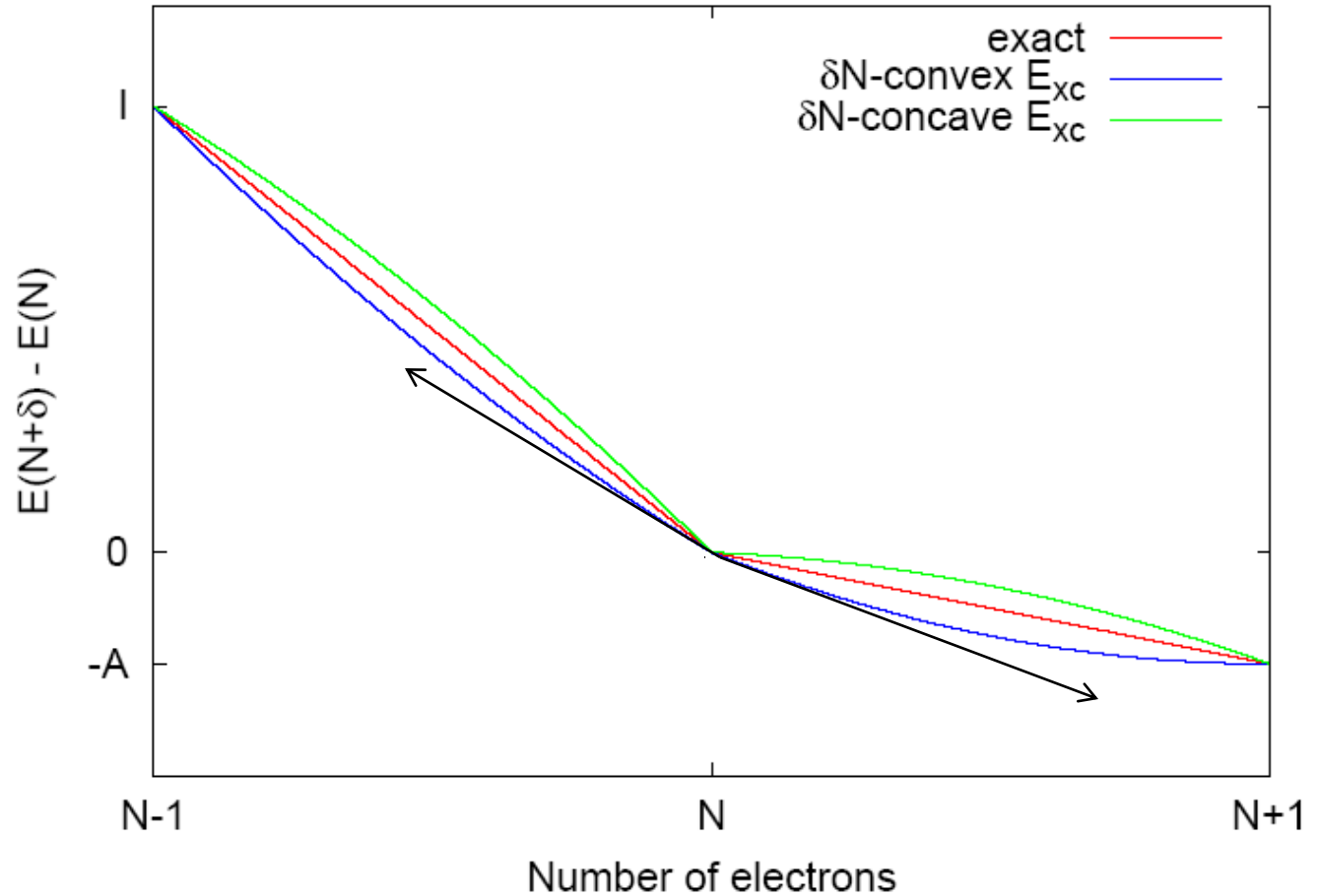
How can fundamental gap be predicted in DFT

For continuous and differentiable functionals of density/density matrix

- **HOMO** energy is the chemical potential for electron removal

- **LUMO** energy is the chemical potential for electron addition

- **Fundamental gaps** predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap

- For **orbital functionals**, the LUMO of the KS (OEP) eigenvalue is NOT the chemical potential of electron addition. The KS gap is not the fundamental gap predicted by the functional.

$$\frac{\partial E_v(N)}{\partial N} = \langle \phi_f | H_{\text{eff}} | \phi_f \rangle$$

WY, Mori-Sanchez and Cohen, PRB 2008, JCP 2012

For Linear E(N)

$$\Delta N = 1, \; \Delta E = \frac{\partial E}{\partial N}$$

Convex curve (LDA, GGA):
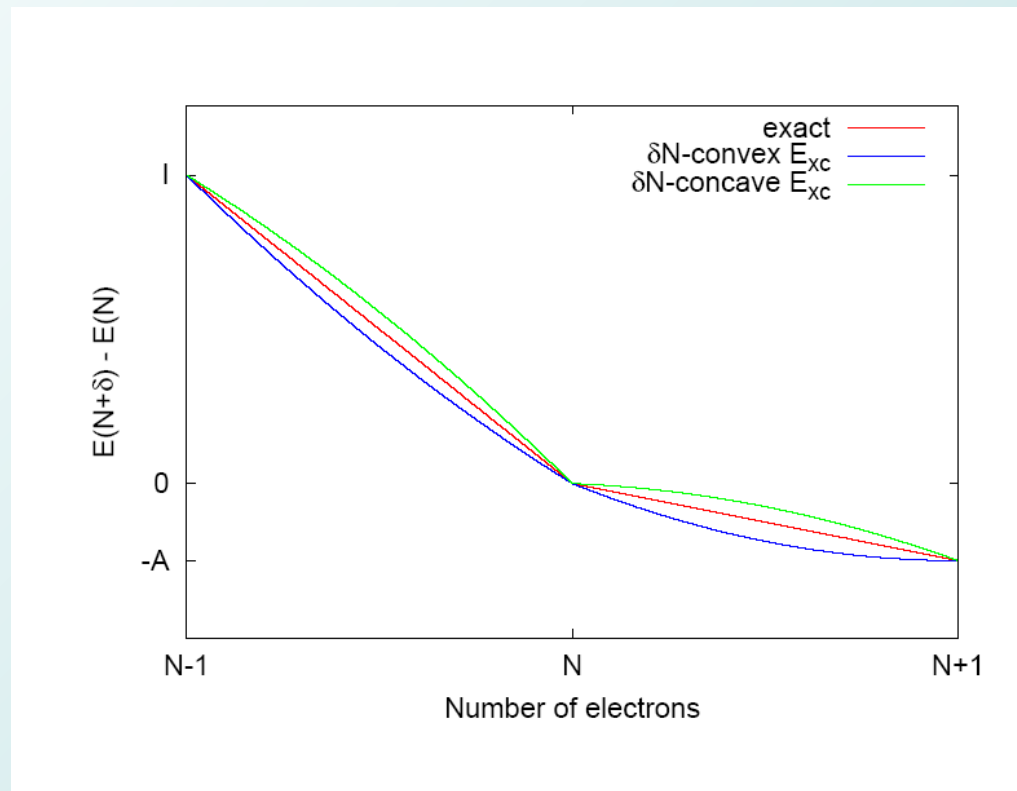   derivative underestimates I, overestimates A,   I-A is too small

Concave curve (HF):
   derivative overestimates I, underestimate A,   I-A is too large

- **Fundamental gaps** predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap

- Only works well if functionals have minimal delocalization/localization error.

Delocalization Error vs. Self-Interaction Error (SIE)

Self-Interaction Error (Perdew-Zunger 1982)

- Exc error for **one-electron** systems
- Self-Interaction Correction (**SIC**) forces the correction for every one-electron orbital, improves atomic systems.
- SIC does not improve molecular systems in general (sometime over corrections).
- SIE fractional extension (0<N<1, Zhang and Yang, JCP 1998) explained $\mathbf{H}_2^+$ problem)
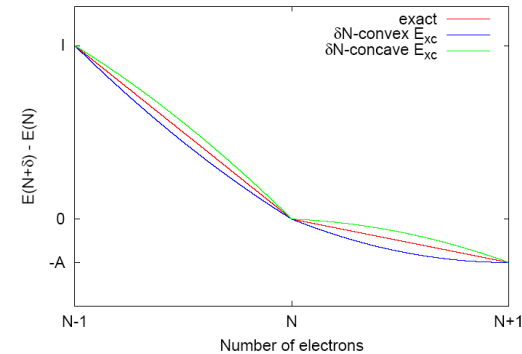
Delocalization Error (Mori-Sanchez, Cohen and Yang, PRL 2008)

- Two SIE-free functionals: Becke06, and MCY2 (2006) **did not solve** the problems (Self-interaction-free exchange-correlation functional for thermochemistry and kinetics, Mori-Sanchez, Cohen and Yang, JCP 2006)
- Many-electron SIE were used in 2006 (A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, JCP 2006, Mori-Sanchez, Cohen and Yang, JCP 2006)
- **Delocalization Error** agrees with SIE for one electron systems. For general systems, it reveals the true relevant mathematical error of approximate functionals, and captures the physical nature of the error—delocalization.

55

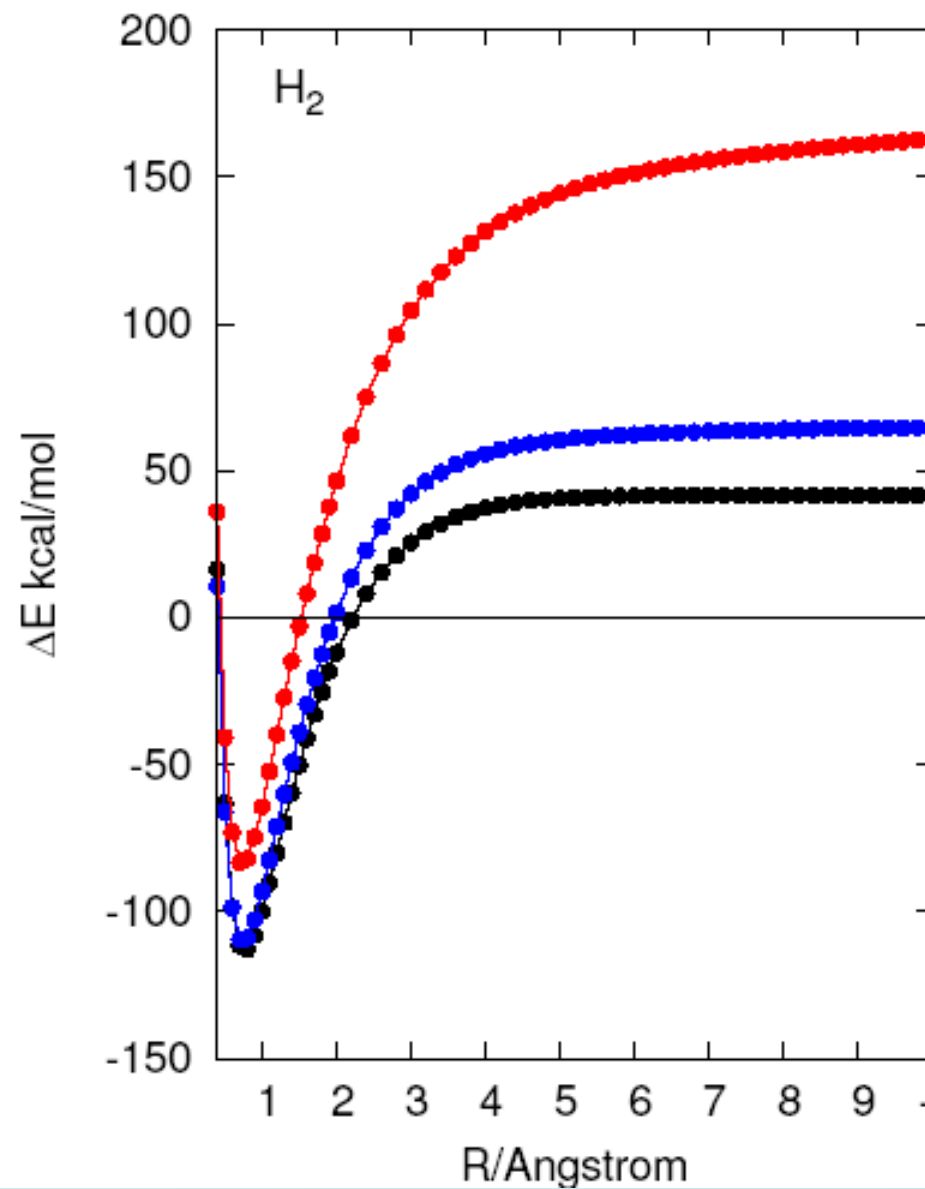**Fractional Spins**

Another large class of problems

- huge error dissociation of chemical bonds
- transition metal dimmers
- some magnetic properties
- strongly correlated systems
- Mott insulators, high T_c superconductors
- degeneracy and near degeneracy

Static Correlation Error

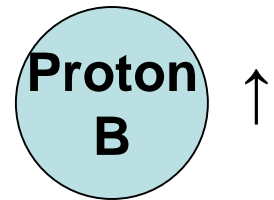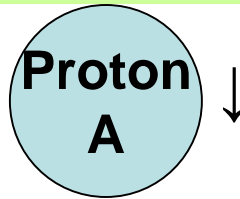# Where can you find fractional spins?

Aron Cohen, Paula Mori-Sanchez and Yang, 2008, JCP
Yang, Ayers and Zhang, PRL 2000

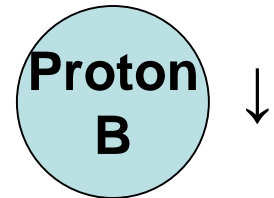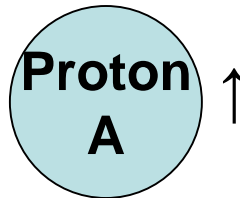**H_2**   **at the dissociation limit**

Ψ_α

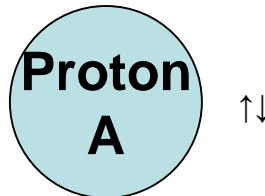$E_\alpha = E(\downarrow) + E(\uparrow)$

Proton A $\downarrow$ **Proton B** $\uparrow$

Ψ_β

$E_\beta = E(\uparrow) + E(\downarrow)$

Proton A $\uparrow$ **Proton B** $\downarrow$

$\Psi_\gamma = \frac{1}{\sqrt{2}}\left(\Psi_\alpha + \Psi_\beta\right)$

$E_\gamma = 2E(\uparrow) = 2E(\downarrow)$

Proton A $\uparrow\downarrow$ **Proton B** $\uparrow\downarrow$
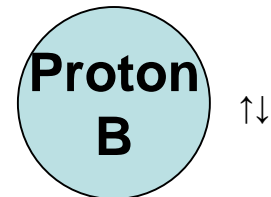
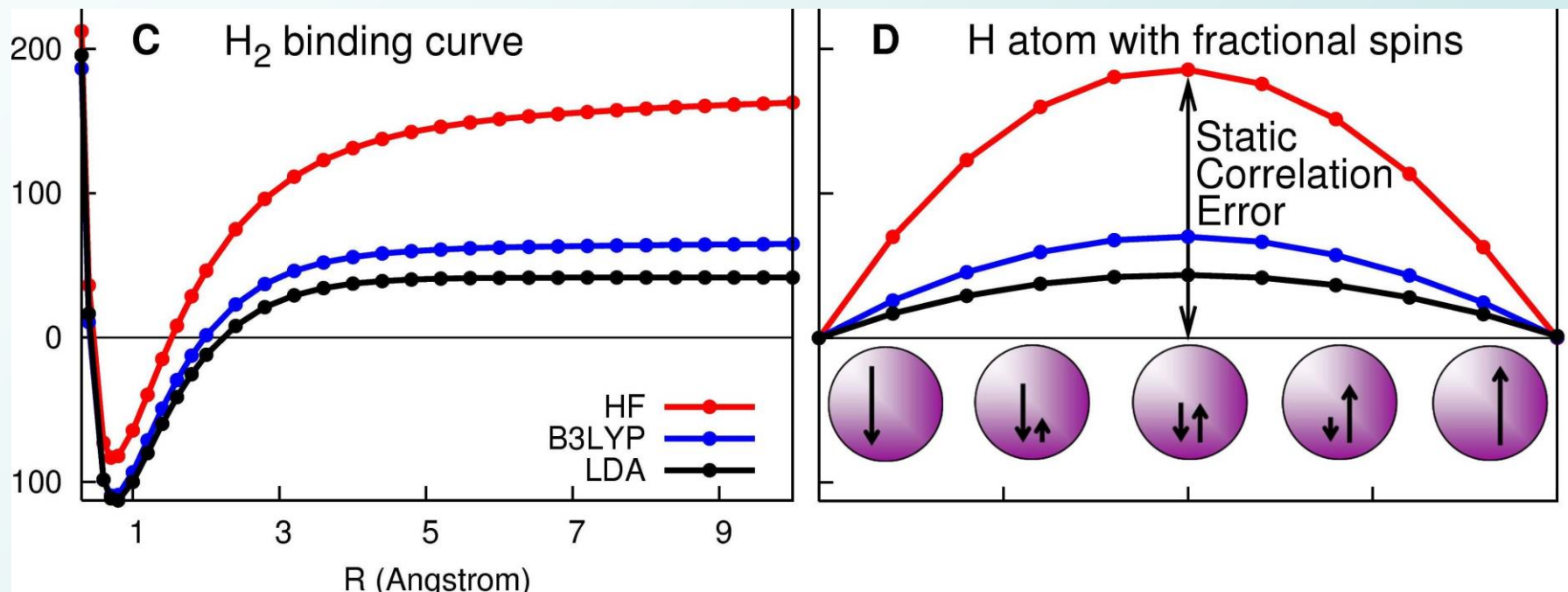**Fractional Spin H Atom: half spin up electron and half spin down electron**

$$E\left(\frac{\uparrow\downarrow}{2}\right) = E(\uparrow) = E(\downarrow)$$

The constancy condition: energy of fractional spins

$E(\gamma)$

$$E\left(\frac{\uparrow\downarrow}{2}\right) = E(\uparrow) = E(\downarrow)$$

$\downarrow$ $\qquad\qquad\qquad$ $\dfrac{\uparrow\downarrow}{2}$ $\qquad\qquad\qquad$ $\uparrow$
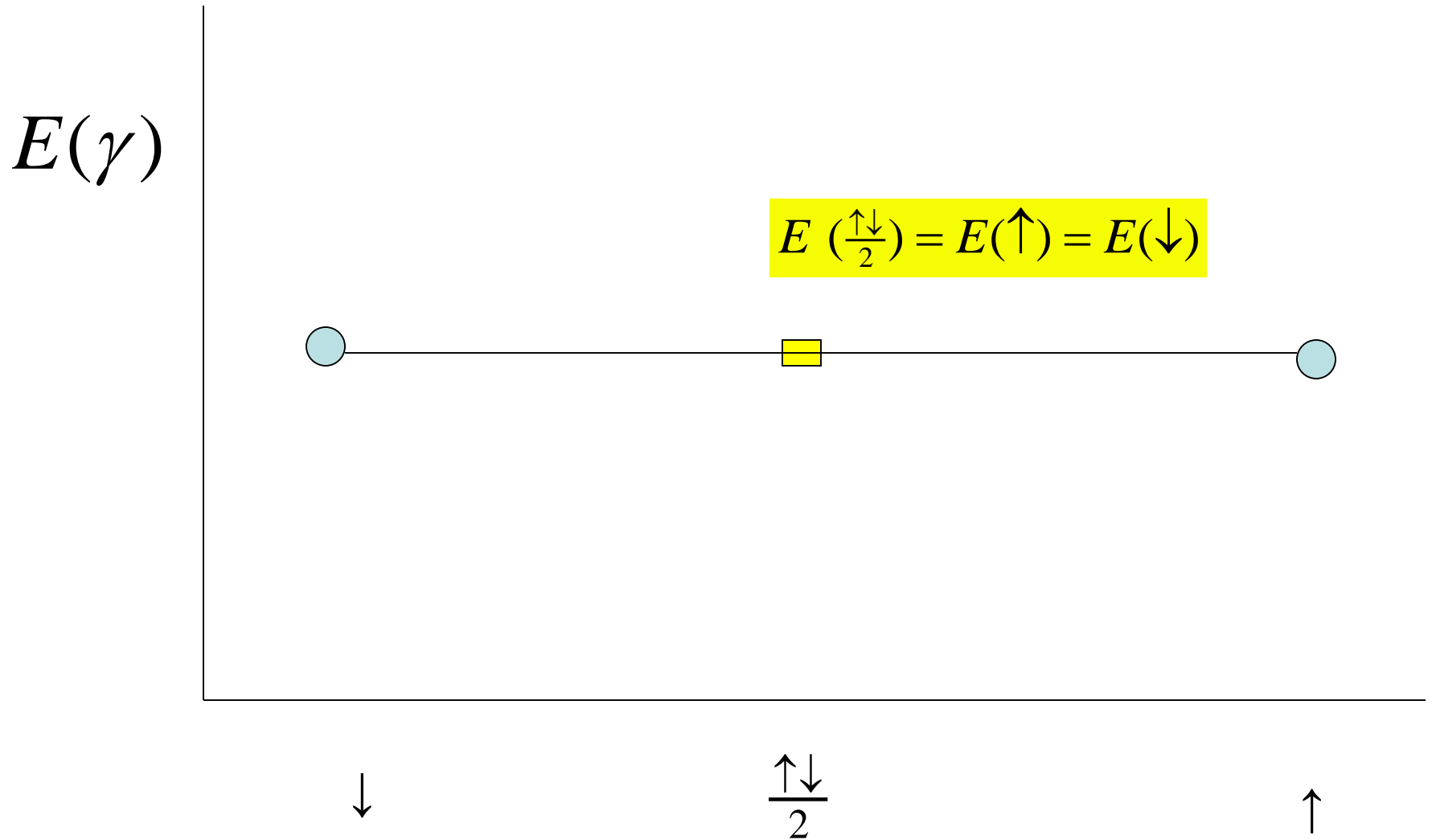
Static Correlation Error

Define the Static Correlation Error as the violation of the constancy condition for fractional spins

Cohen, Mori-Sanchez and Yang, 2008, JCP; 2008 Science

Exact conditions on DFT—all coming from QM for **degeneracy**

Fractional Charge: **1982: Perdew, Levy, Parr and Baldus**

$$E\left[(1-\delta)\rho_N + \delta\rho_{N+1}\right] = (1-\delta)E_N + \delta E_{N+1}$$

Fractional Spins: **2000, PRL, WY, Zhang and Ayers;**
2008, JCP, Cohen, Moris-Sanchez, and WY

$$E\left[\sum_i c_i \rho_{N,i}\right] = E[\rho_{N,i}] = E_N$$

Fractional Charges and Spins: **2009: PRL, Moris-Sanchez, Cohen and WY**

$$E\left[(1-\delta)\sum_i c_i \rho_{N,i} + \delta\sum_j d_j \rho_{N+1,j}\right] = (1-\delta)E_N + \delta E_{N+1}$$

- **!! The exact XC functional cannot be an explicit and differentiable functional of the electron density/density matrix, either local or nonlocal.**

- **Valid for density functionals, and also for 1-body density matrix functionals, 2-RDM theory, and other many-body theories.**

$$\rho(\mathbf{r})_{\llcorner} \Longleftrightarrow \Psi(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_N)$$

ve to deal with fractional num

$$E = E[\rho(\mathbf{r})]$$

Density Functional Theory

$$E = \langle \Psi | H | \Psi \rangle$$

Wavefunction Theory
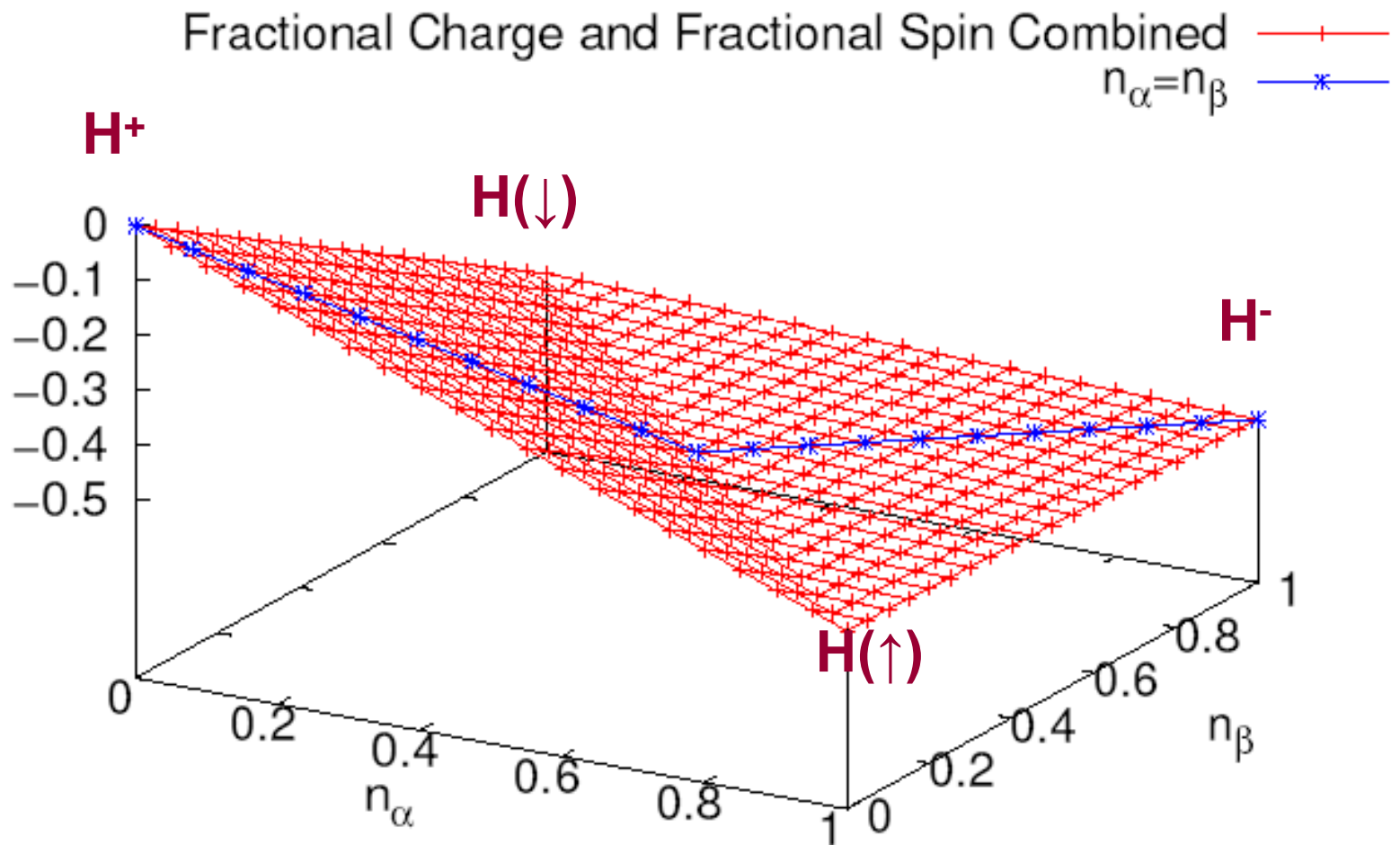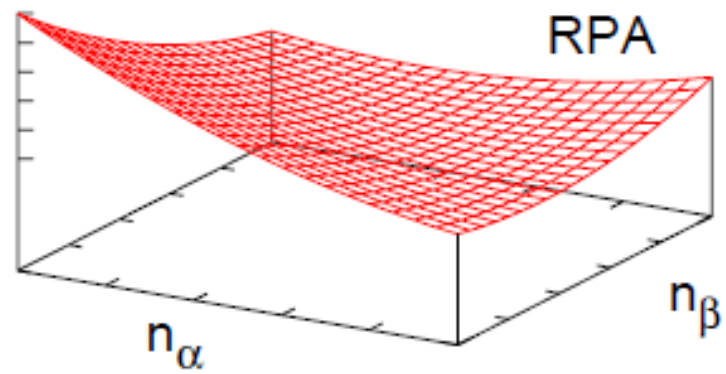
Fractional charges and spins
from degeneracy

Integers, always!

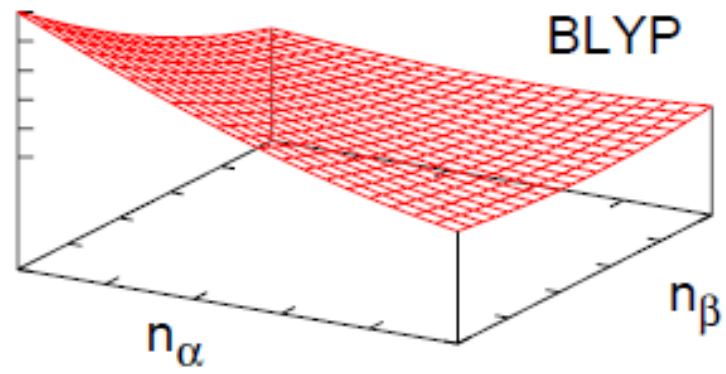Many-electron theories based on

•Green function
•Density matrix

62

Fractional Charges and Spins: **PRL 2009, Cohen, Moris-Sanchez, and WY**
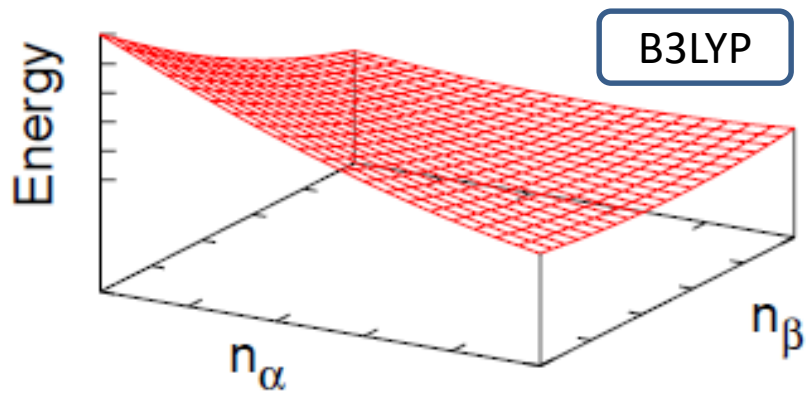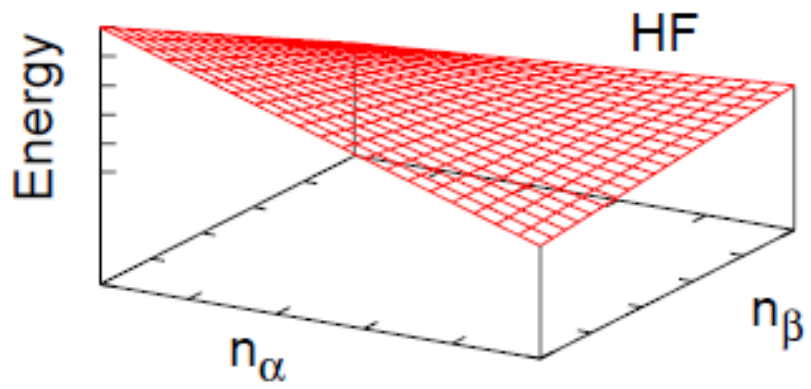
CHEMICAL REVIEWS

Challenges for Density Functional Theory

Aron J. Cohen,* Paula Mori-Sánchez,* and Weitao Yang*

2012

Improving band gap prediction in density functional theory from molecules to solids

PRL, 2011, Xiao Zheng, Aron J. Cohen, Paula Mori-Sanchez, Xiangqian Hu, and Weitao Yang

Xiao Zheng (USTC)

Aron J. Cohen (Cambridge)

Paula Mori-Sanchez (Univ. Autonoma Madrid)

Xiangqiang Hu

A Local Scaling Correction for Reducing Delocalization Error in Density Functional Approximations

Chen Li,[1] Xiao Zheng,[2,3,*] Aron J. Cohen,[4] Paula Mori-Sánchez,[5] and Weitao Yang[1,†]
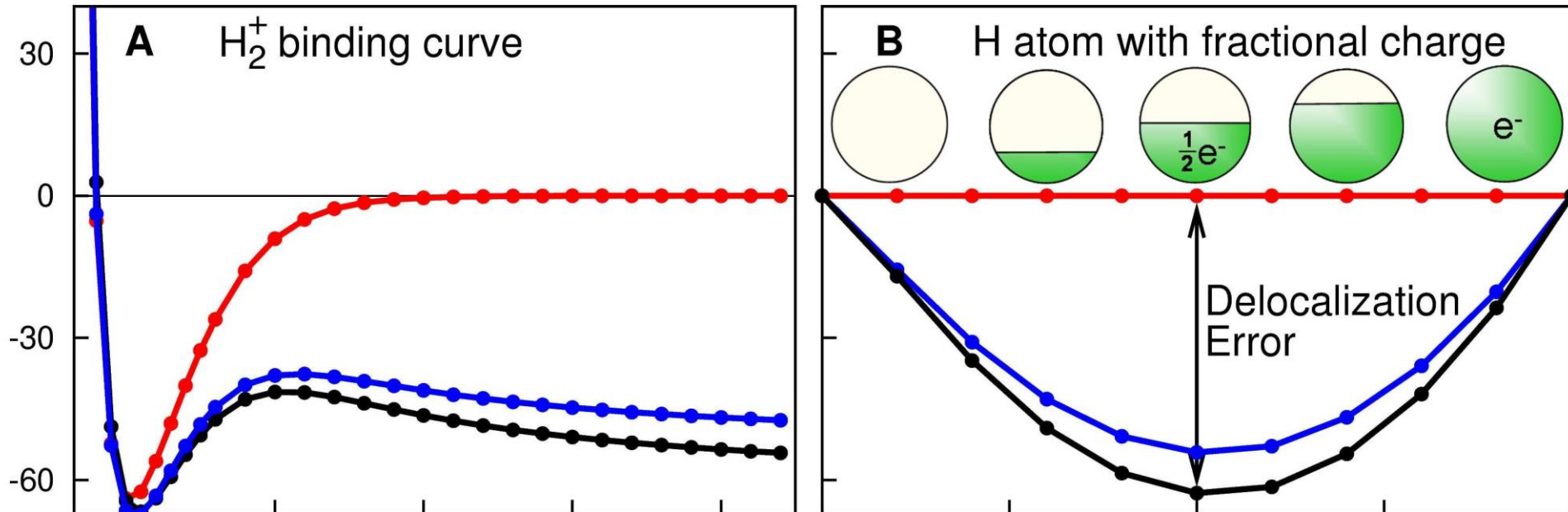
Chen Li (Duke)

Xiao Zheng (USTC)

Aron J. Cohen (Cambridge)

Paula Mori-Sanchez (Univ. Autonoma Madrid

A H$_2^+$ binding curve

B H atom with fractional charge

$\frac{1}{2}$e$^-$

e$^-$

Delocalization
Error

Challenges

- Error and correction are known in terms of factional charges -- but there is no fractional charge at any finite R!

- Correction is needed at large R, but not at small R -- what is difference between the electronic structures at small and large R ?
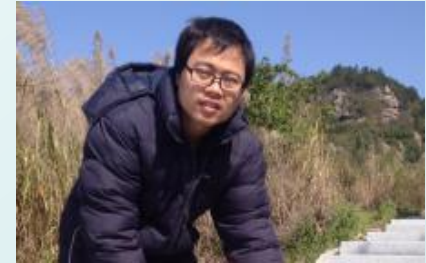
Localized Orbital Scaling Correction (LOSC)

Chen Li, Xiao Zheng, Neil Qiang Su and WY (arXiv:1707.00856v1)
National Science Review, 2018
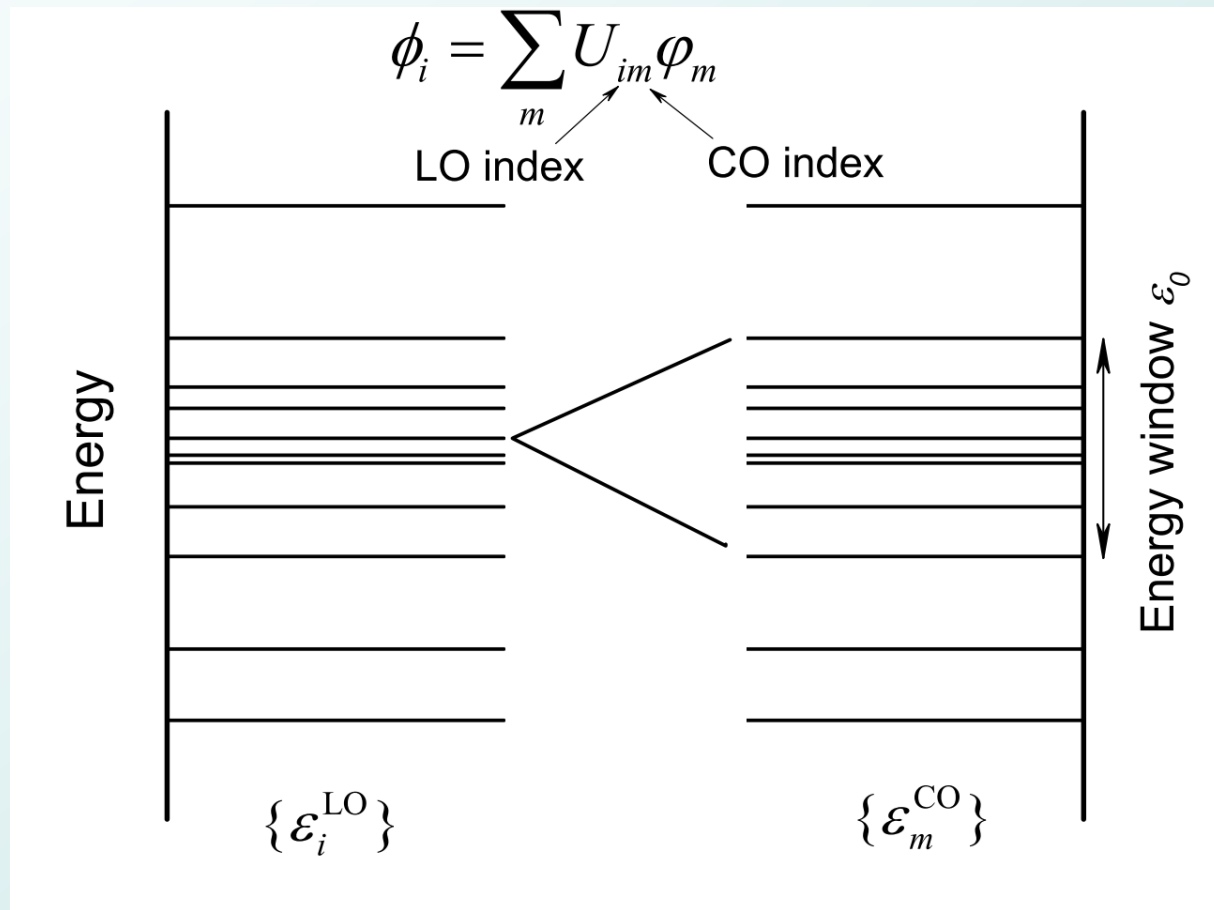
Chen Li   **Xiao Zheng**   **Neil Qiang Su**

- **Orbitalets: Novel localized orbitals** to represent density matrix.
- **Size-consistent**, functional of the GKS density matrix for corrections to common DFA.
- Accurately characterization of the distributions of **global** and **local** fractional electrons.
- **Systematic improvements**: the dissociation of cationic species, the band gaps of molecules and polymers, the energy and density changes upon electron addition and removal, and photoemission spectra.

Orbitalets: Novel Localized Orbitals

$$\rho_s = \sum_{ij} |\phi_i\rangle\langle\phi_i|\rho_s|\phi_j\rangle\langle\phi_j| = \sum_{ij} \lambda_{ij}|\phi_i\rangle\langle\phi_j| \qquad \lambda_{ij} = \langle\phi_i|\rho_s|\phi_j\rangle$$

$$\phi_i = \sum_m U_{im}\varphi_m$$

LO index   CO index

Energy

$\{\varepsilon_i^{\mathrm{LO}}\}$ $\{\varepsilon_m^{\mathrm{CO}}\}$
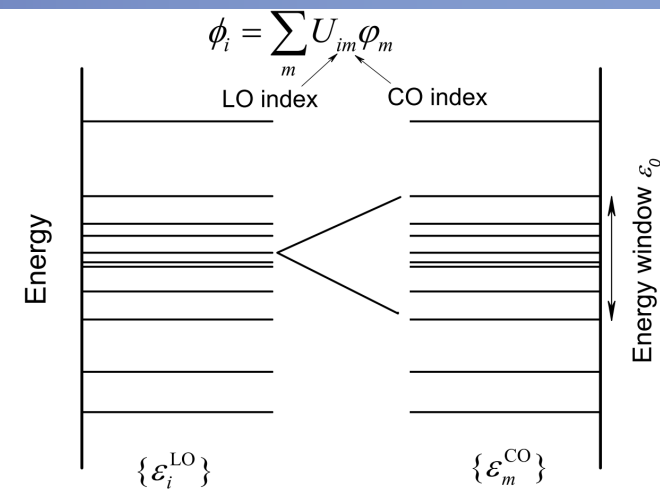
Energy window ε_0

E-Constrained Optimization $\quad F = \sum_i \left[\langle\phi_i|\mathbf{r}^2|\phi_i\rangle - \langle\phi_i|\mathbf{r}|\phi_i\rangle^2 \right] + \sum_{im} w_{im}|U_{im}|^2$

Novel Localized Orbitals

$$\phi_i = \sum_m U_{im} \varphi_m$$

LO index   CO index

Orbitalets

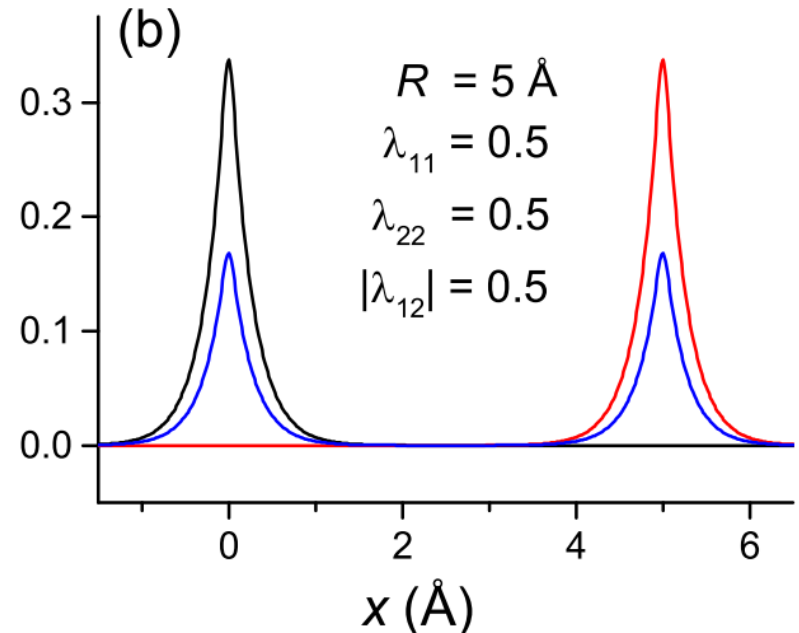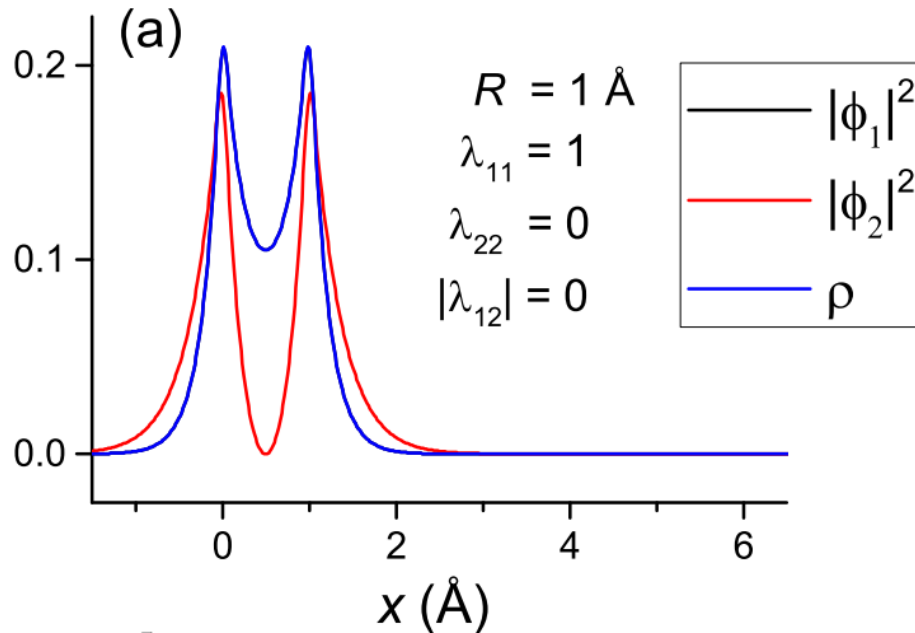-- Span **both occupied** and **virtual** space

-- Localization **both** in the **physical** space and in the **energy** space.

Traditional
-- localized orbitals -- localization in the physical space

-- canonical orbitals -- localization only in the energy space (energy eigenstates of an one-particle Hamiltonian)

Distribution of LO densities in H_2^+

At small R, R=1A
- Large energy gap between HOMO and LUMO
- Little mixing, LO ~ Canonical Orb, integer occupations

At large R, R=5A
- Small energy gap between HOMO and LUMO
- Much mixing, LO localized, fractional occupations

New LOSC, as correction to DFA

$$\Delta E^{\mathrm{LOSC}} = \sum_{ij} \frac{1}{2} \kappa_{ij} \lambda_{ij} \left(\delta_{ij} - \lambda_{ij} \right) = \frac{1}{2} \mathrm{tr}(\boldsymbol{\kappa \omega})$$

$$\frac{1}{2} \kappa_{ij} = \frac{1}{2} \iint \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{\tau C_{\mathbf{x}}}{3} \int [\rho_i(\mathbf{r})]^{\frac{2}{3}} [\rho_j(\mathbf{r})]^{\frac{2}{3}} d\mathbf{r}$$

Non-empirical parameter to get correct limit for H_2^+

$$\tau = 6(1 - 2^{-1/3}) \approx 1.2378$$
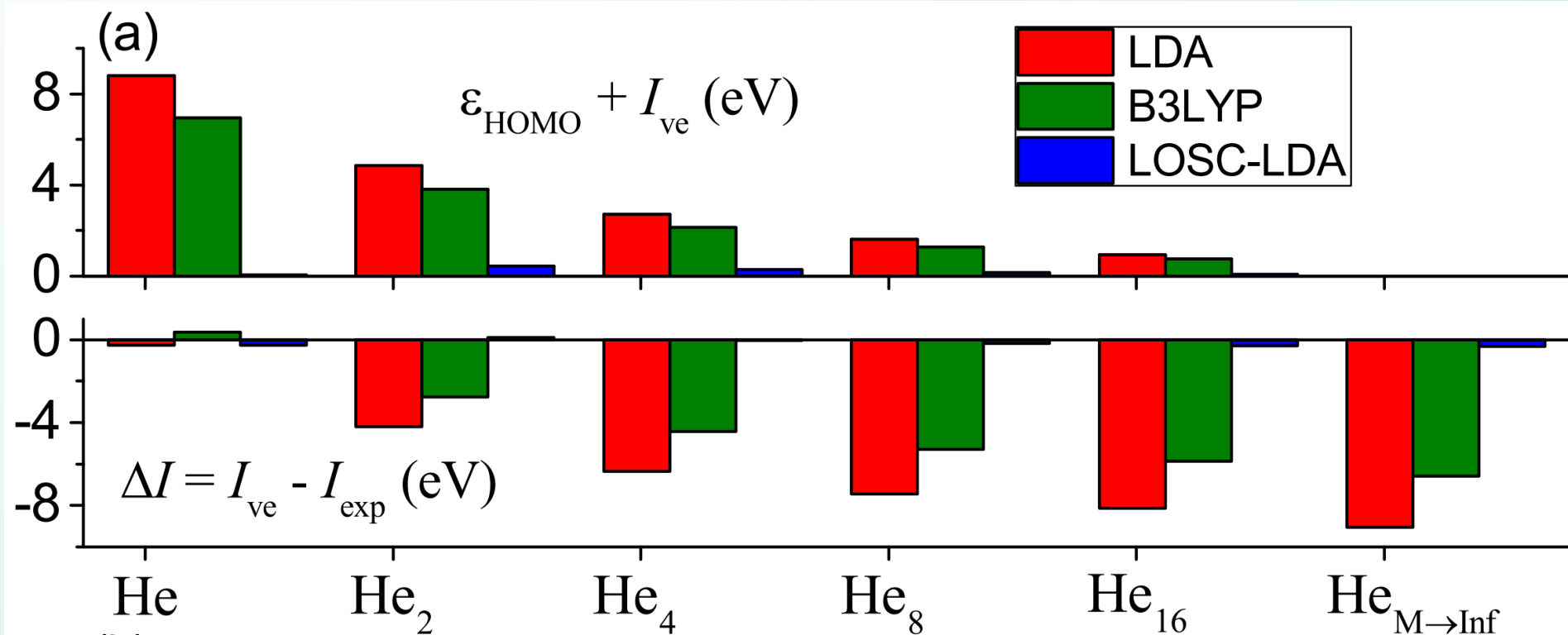
Orbital energy corrections

$$\Delta \epsilon_m = \sum_i \kappa_{ii} \left(\frac{1}{2} - \lambda_{ii} \right) |U_{im}|^2 - \sum_{i \neq j} \kappa_{ij} \lambda_{ij} U_{im} U_{jm}^*$$
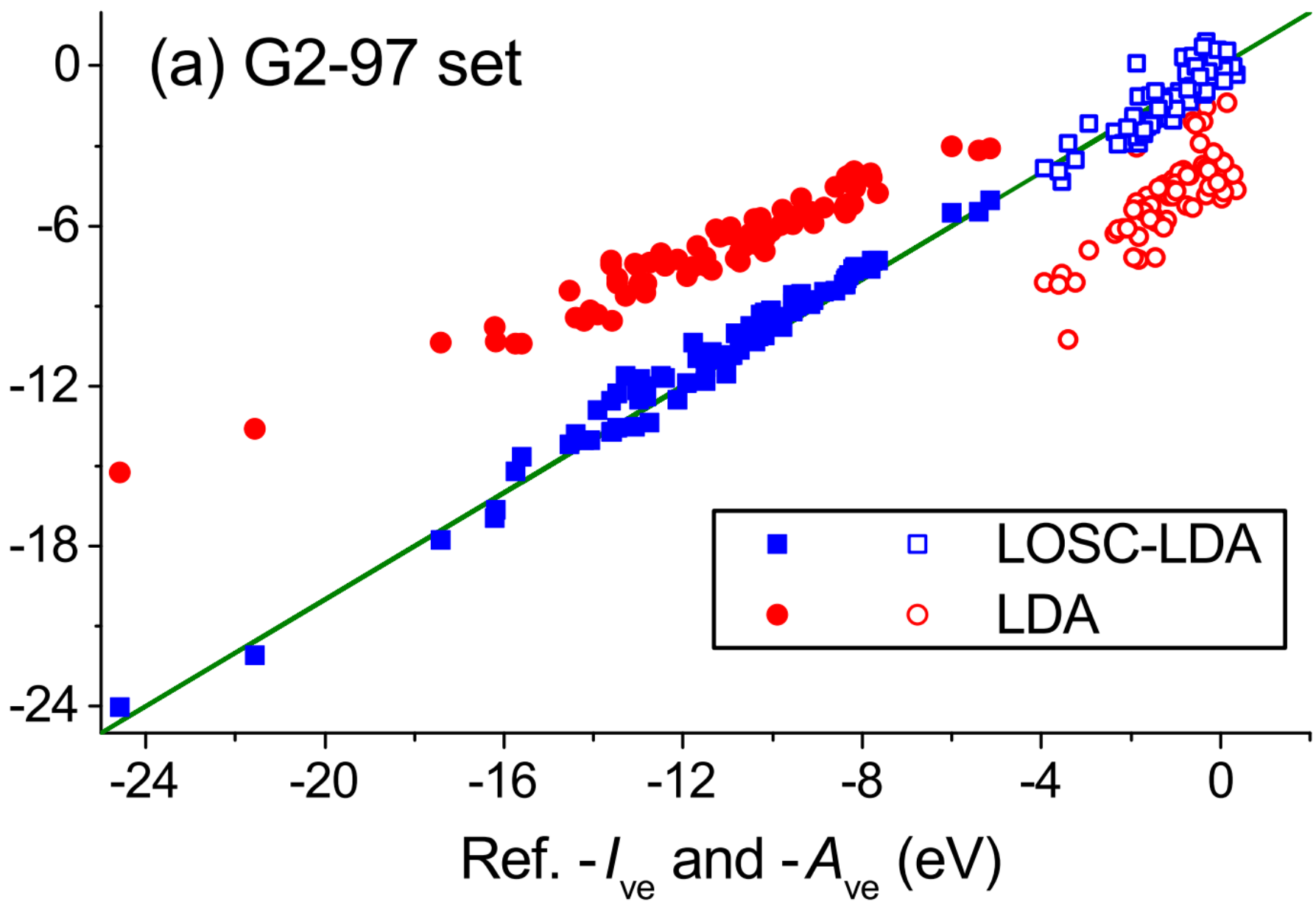
Deviations between the calculated ε_{HOMO} and $-I_{ve}$ and between I_{ve} and I_{exp} for a series of He_M clusters (non-interacting).

I_{ve}= E(N-1)-E(N)

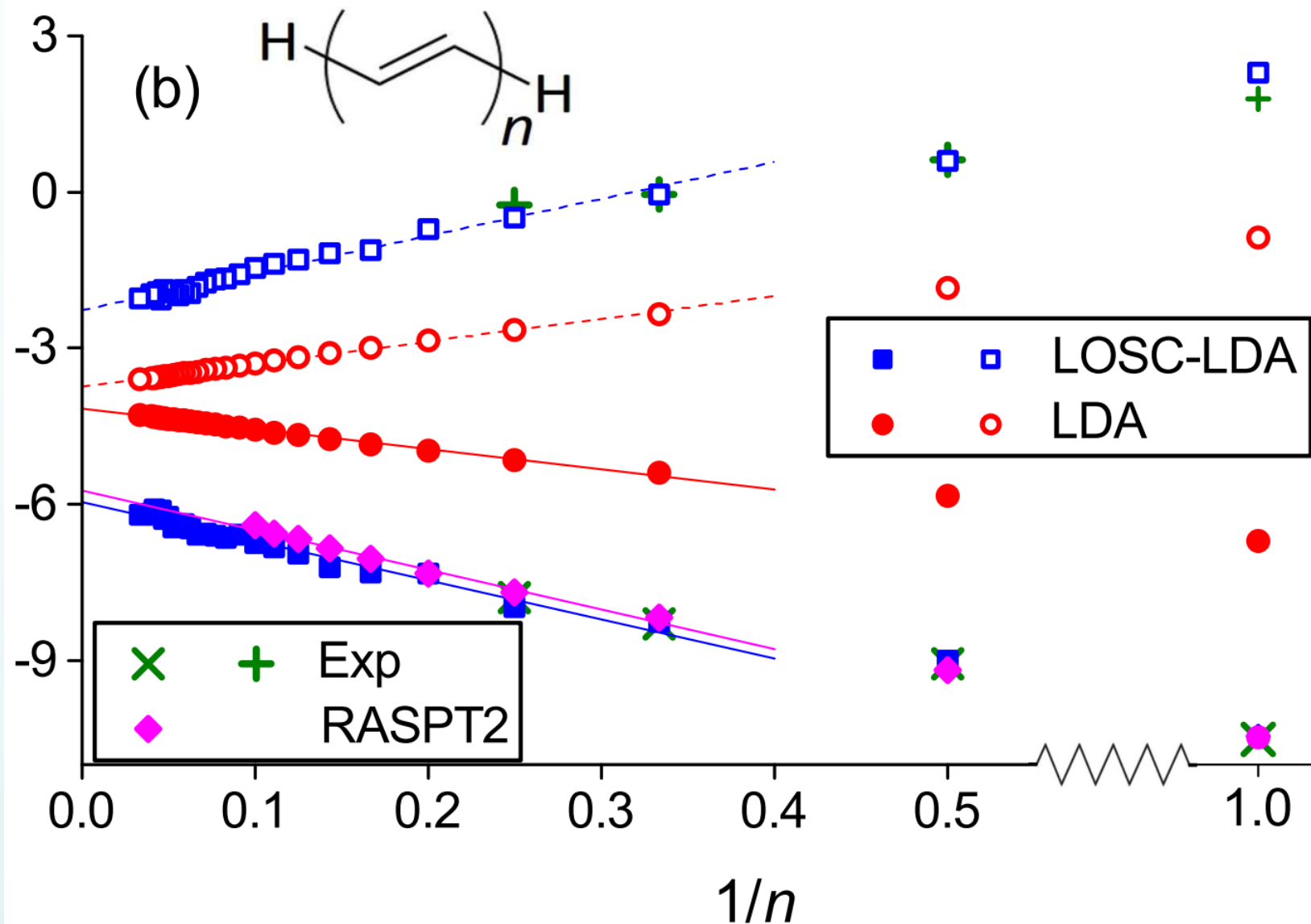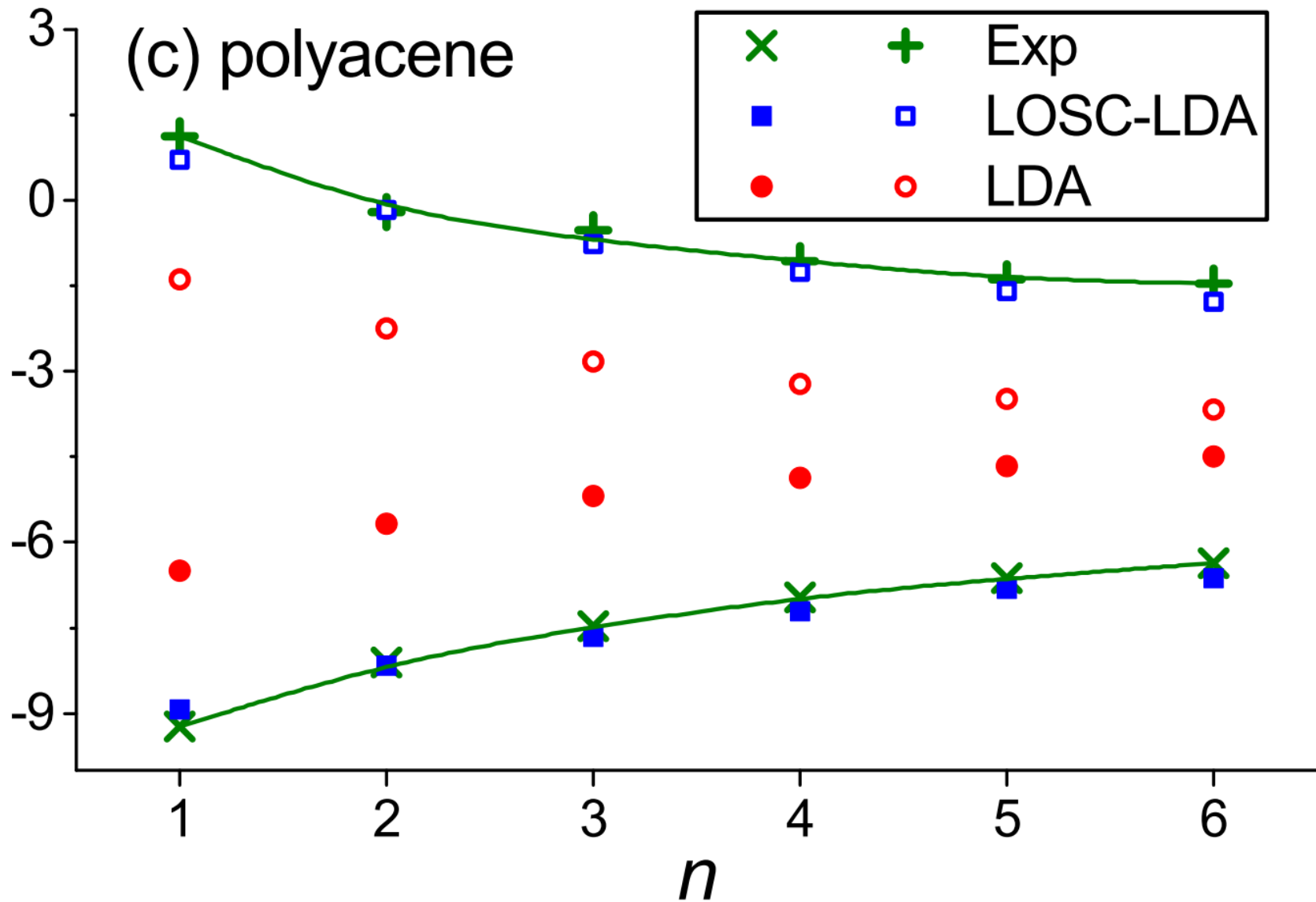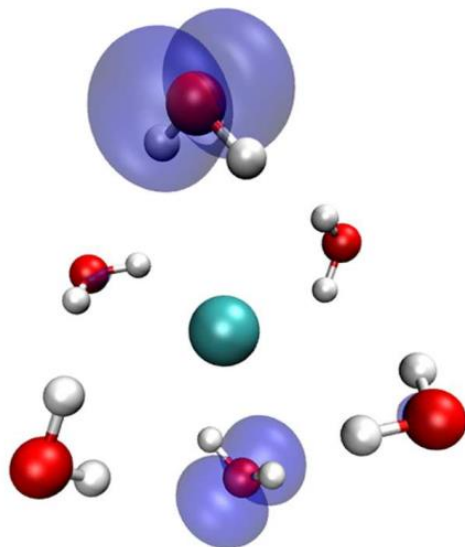$\varepsilon_{HOMO}= \left(\frac{\partial E(N)}{\partial N}\right)_v$

(a)

$\varepsilon_{\text{HOMO}} + I_{\text{ve}}$ (eV)

LDA
B3LYP
LOSC-LDA

$\Delta I = I_{\text{ve}} - I_{\text{exp}}$ (eV)

He   He$_2$ He$_4$ He$_8$ He$_{16}$ He$_{M\rightarrow\text{Inf}}$

(a) G2-97 set

LOSC-LDA
LDA

Ref. $-I_{ve}$ and $-A_{ve}$ (eV)

(c) polyacene

$Cl^-(H_2O)_6$
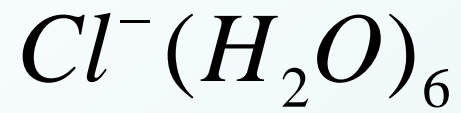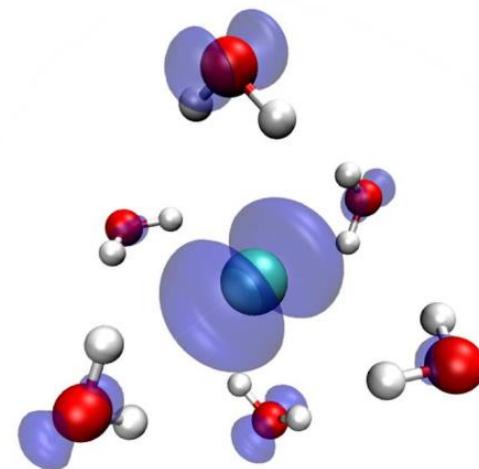
PBE $\triangle q(Cl)= 0.04$

B3LYP $\triangle q(Cl)= -0.67$
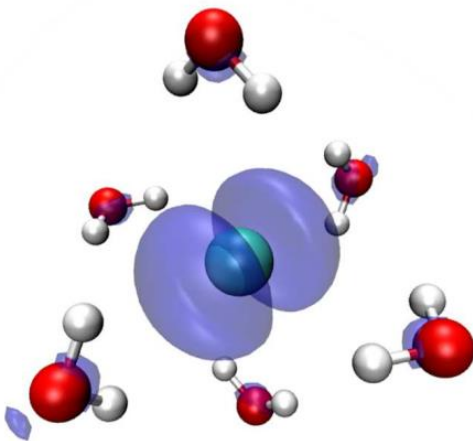
LOSC-PBE $\triangle q(Cl)= -0.92$
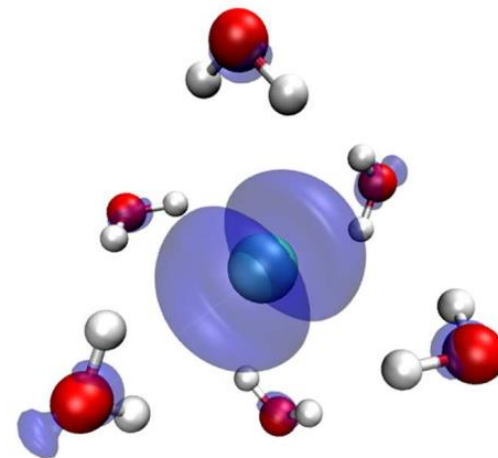
CCSD $\triangle q(Cl)= -0.96$

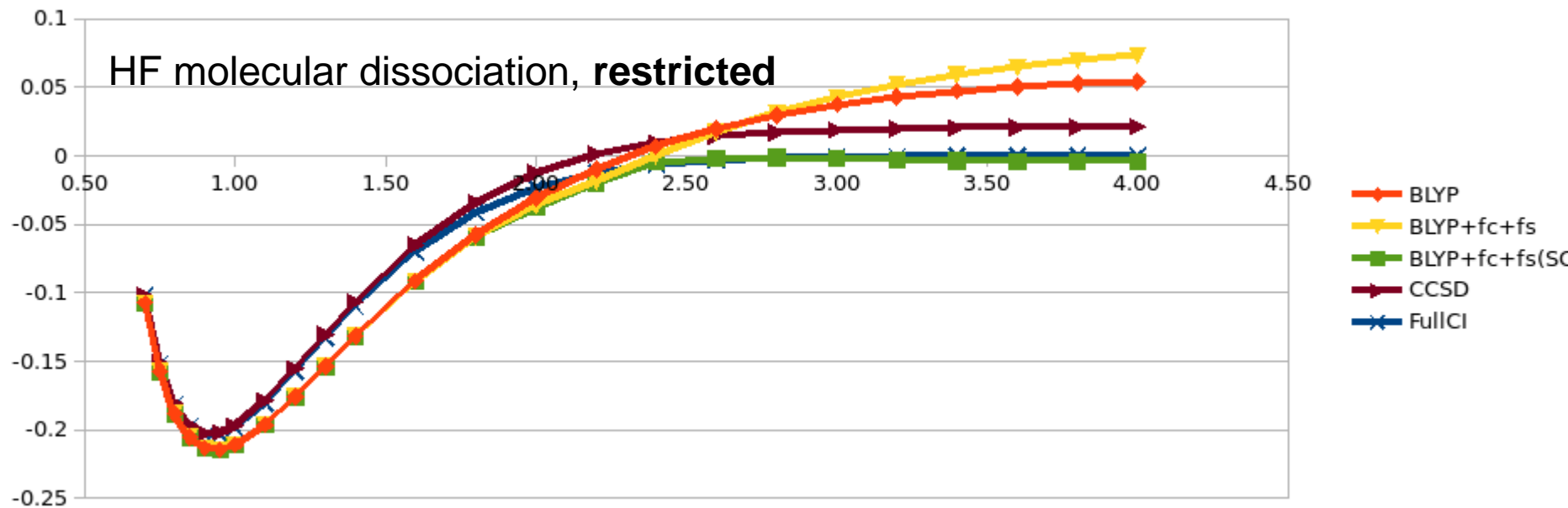# *Describing strong correlation within DFT*

Neil Su

Chen Li

HF molecular dissociation, **restricted**
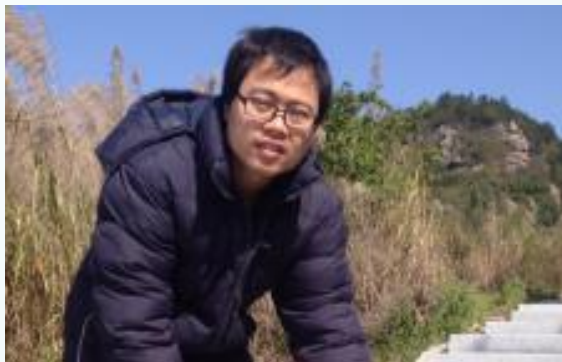
Legend:
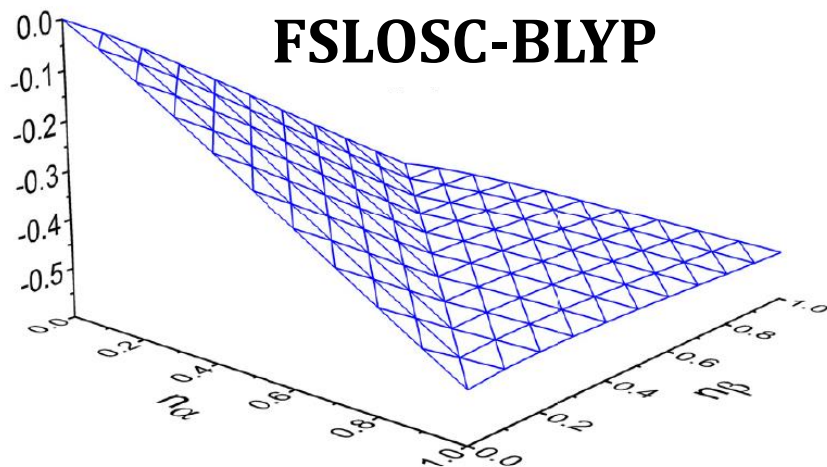- BLYP
- BLYP+fc+fs
- BLYP+fc+fs(SC
- CCSD
- FullCI
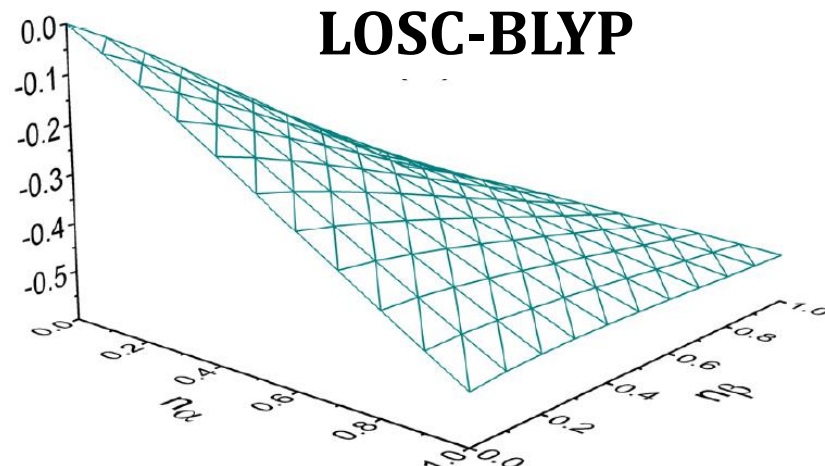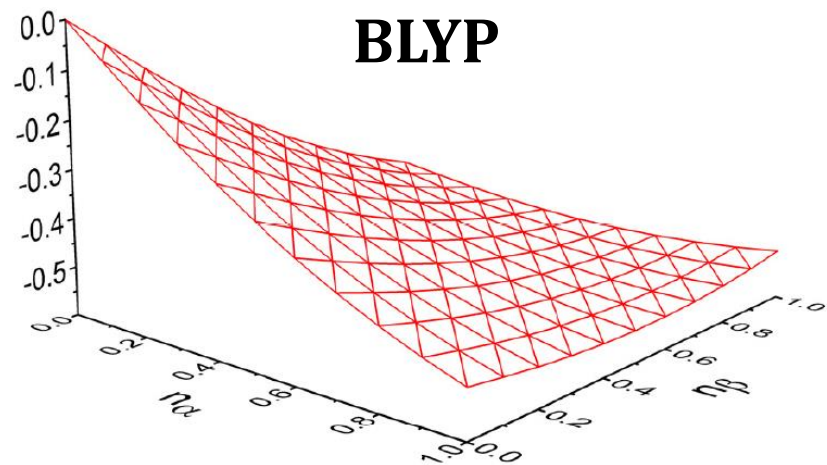
Neil Su, Chen Li, W. Yang, PNAS 2018

Fractional-spin correction

BLYP

LOSC-BLYP

FSLOSC-BLYP

$$\Delta E^{\text{FS}} = -\Lambda\left(n_f^{\alpha}, n_f^{\beta}\right)\kappa^{\text{FS}}\left[\rho_f\right]$$

$$\kappa^{\text{FS}}\left[\rho_f\right] = \iint d\mathrm{r}d\mathrm{r}' \frac{\rho_f\left(\mathrm{r}\right)\rho_f\left(\mathrm{r}'\right)}{\left|\mathrm{r}-\mathrm{r}'\right|}$$

$$+ 4\int \rho_f\left(\mathrm{r}\right)\left[\varepsilon_c^0\left(r_{s,f}\right) - \varepsilon_c^1\left(r_{s,f}\right)\right]d\mathrm{r}$$

$$\Lambda\left(n_f^{\alpha}, n_f^{\beta}\right) = \begin{cases} n_f^{\alpha}n_f^{\beta}, & n_f^{\alpha} + n_f^{\beta} \leq 1 \\ \left(1-n_f^{\alpha}\right)\left(1-n_f^{\beta}\right), & n_f^{\alpha} + n_f^{\beta} > 1 \end{cases}$$

N2

(d) C_2H_4

(b) N₂ & P₂
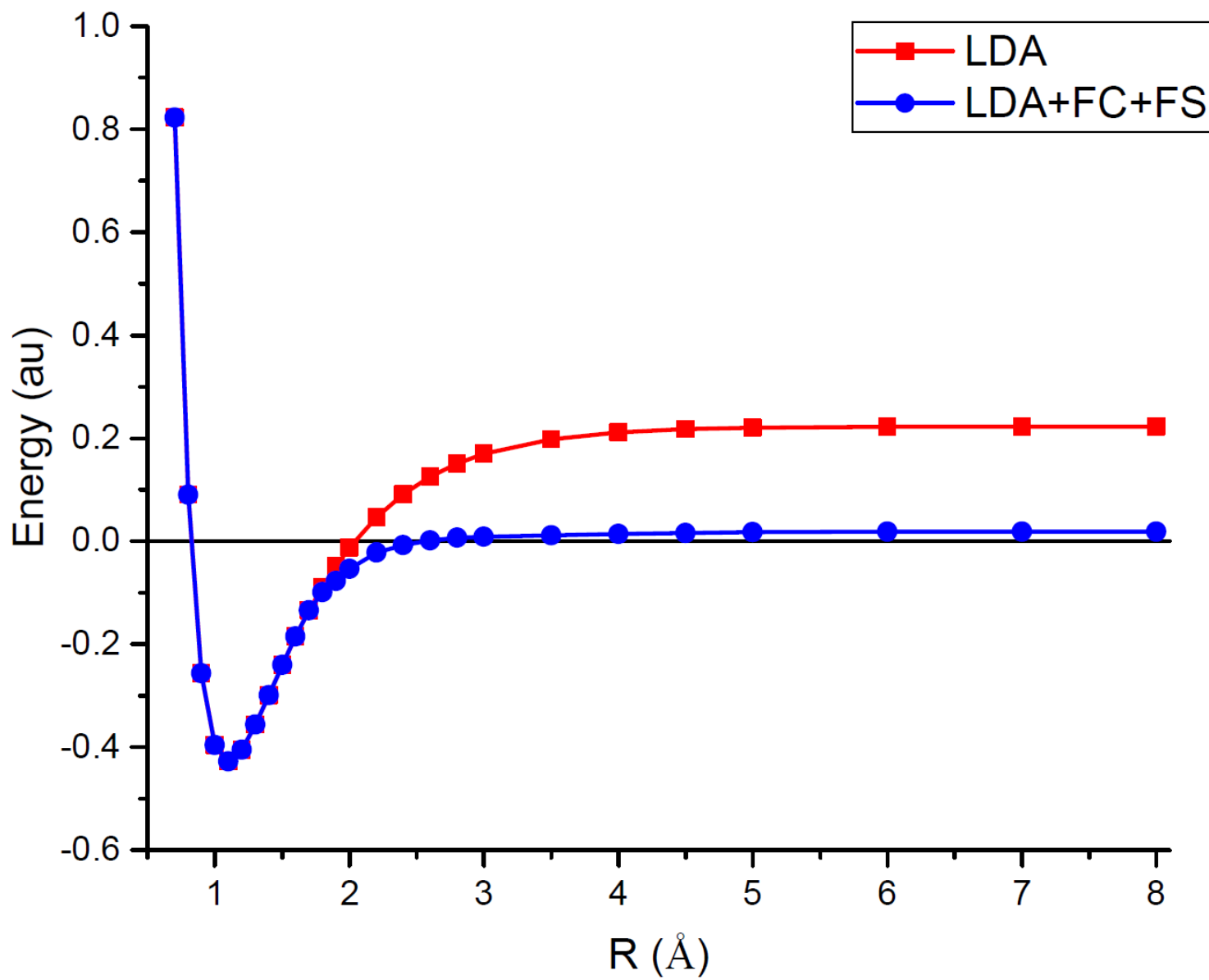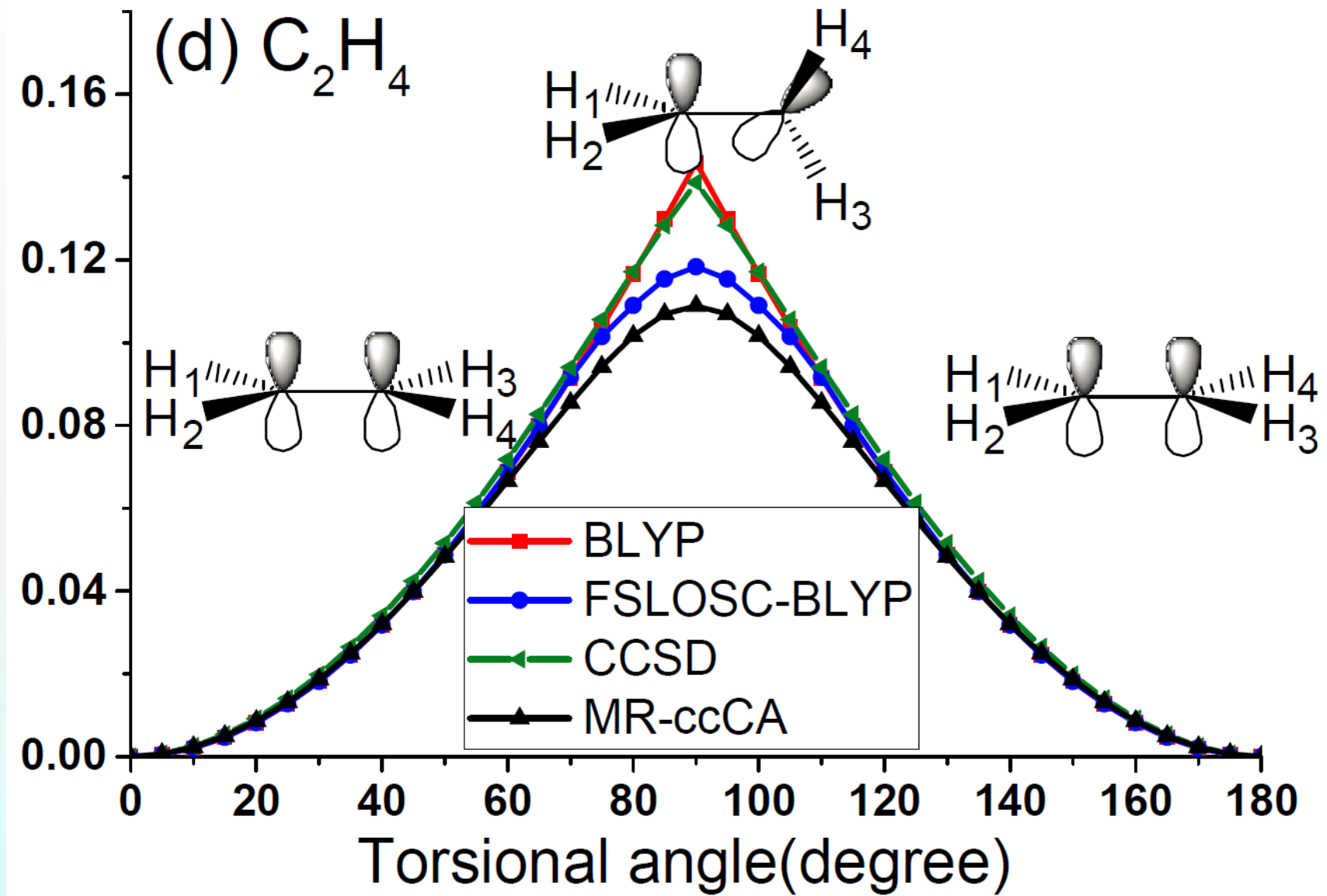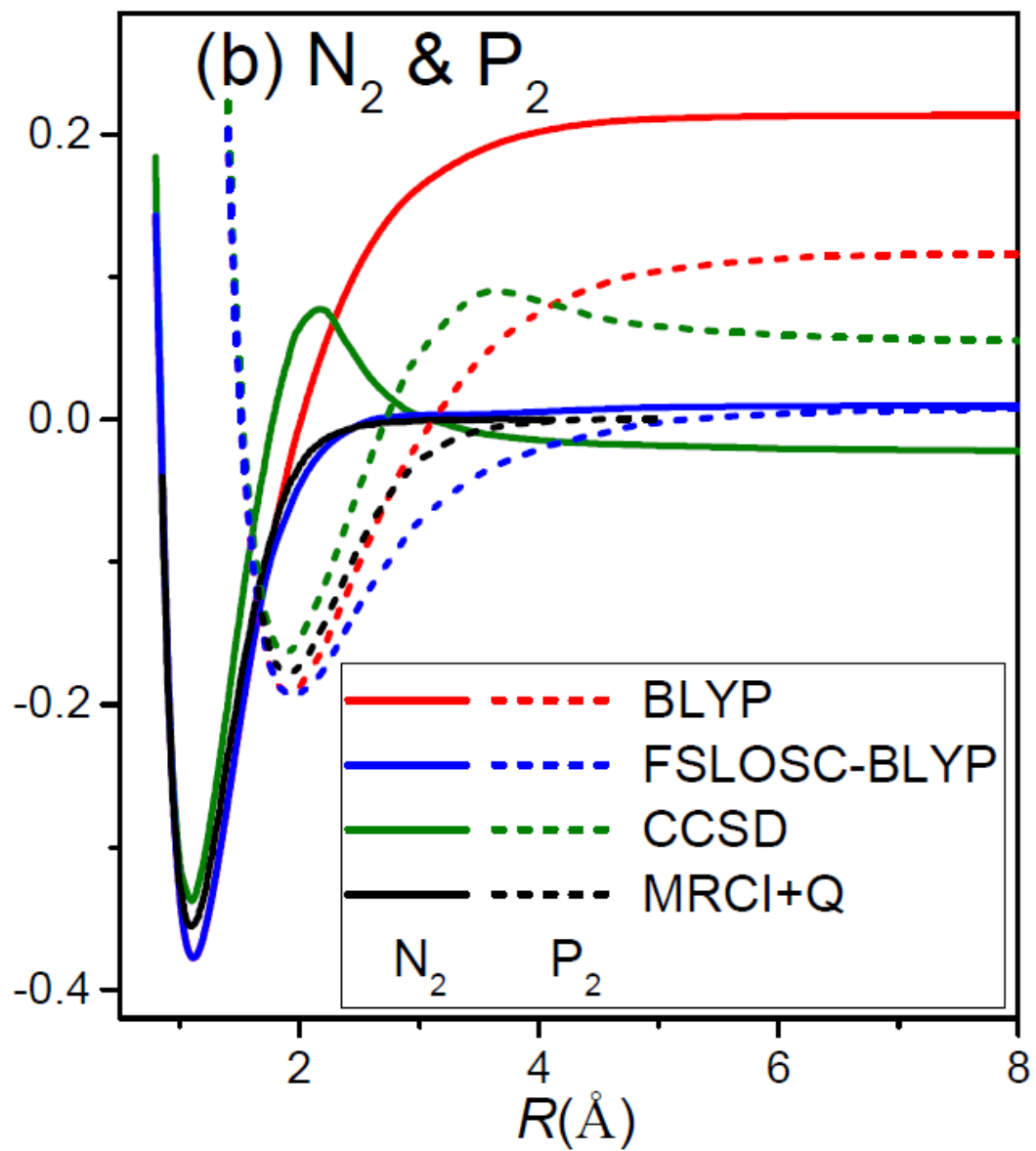
Approximating Quasiparticle and Excitation Energies from Ground State Generalized Kohn–Sham Calculations

Yuncai Mei,[†] Chen Li,[†] Neil Qiang Su,[†] and Weitao Yang[*,†,‡]

[†]Department of Chemistry, Duke University, Durham, North Carolina 27708, United States
[‡]Key Laboratory of Theoretical Chemistry of Environment, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

arXiv 2018,
Yuncia Mei, Chen Li, Neil Su and WY
JPC A 2019, 123, 3, 666

DFT: One electron equations in DFT

Kohn-Sham (KS)

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)|\phi_i\rangle = \varepsilon_i |\phi_i\rangle,$$

$$v_s(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} + v_J(\mathbf{r}) + v_{ext}(\mathbf{r})$$

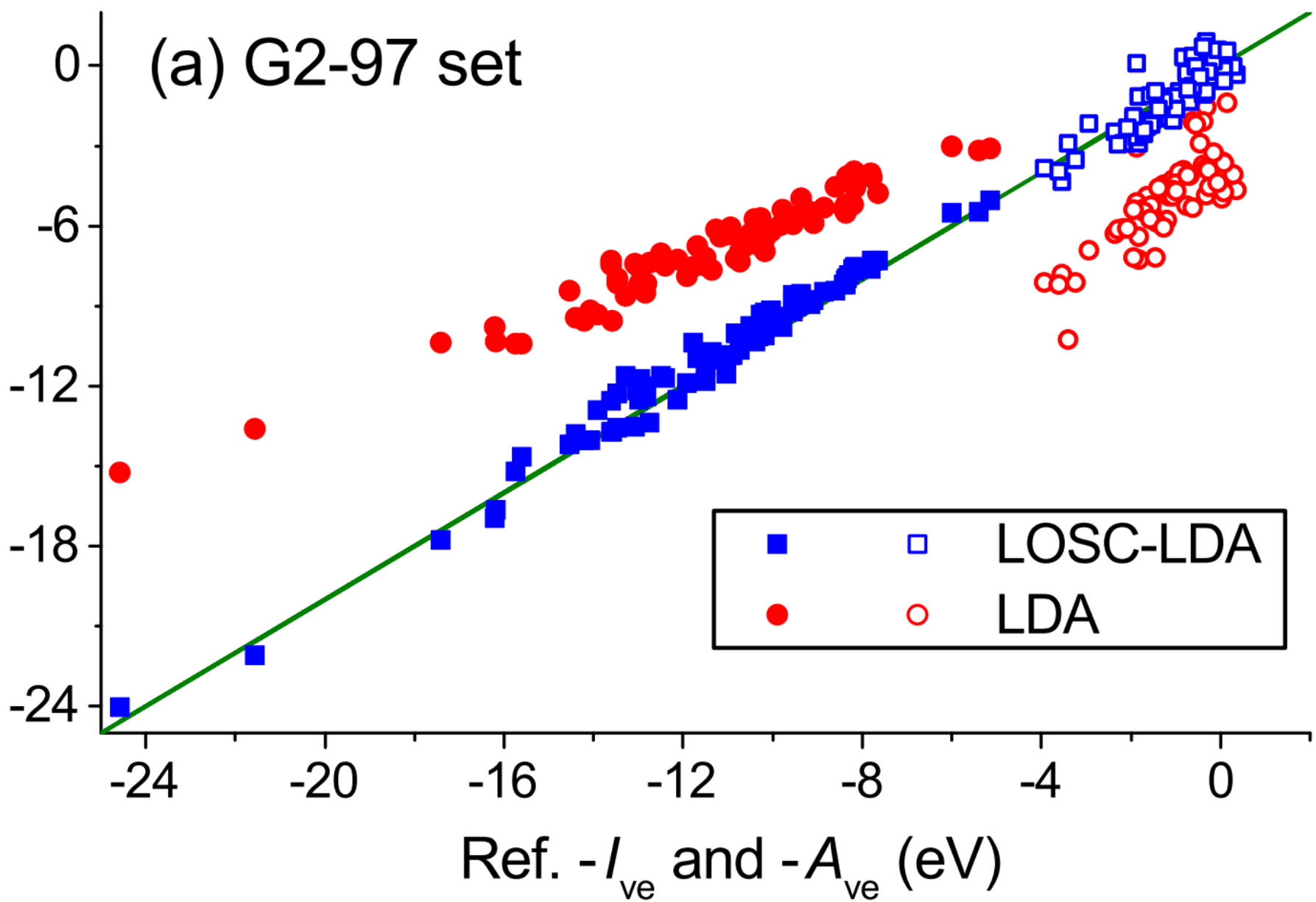**Generalized Kohn-Sham (GKS), Hartree-Fock-Kohm-Sham**

$$\left(-\frac{1}{2}\nabla^2 + v_s^{\mathsf{NL}}(\mathbf{r},\mathbf{r}')\right)|\phi_i\rangle = \varepsilon_i^{\mathsf{GKS}} |\phi_i\rangle.$$

$$v_s^{\mathsf{NL}}(\mathbf{r},\mathbf{r}') = \frac{\delta E_{xc}[\delta\rho_s(\mathbf{r}',\mathbf{r})]}{\delta\rho_s(\mathbf{r}',\mathbf{r})} + [v_J(\mathbf{r}) + v_{ext}(\mathbf{r})]\,\delta(\mathbf{r}' - \mathbf{r})$$

Compared to the quasiparticle equations

$$(T + V_{\mathrm{ext}} + V_{\mathrm{H}})\psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\,\Sigma(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

(a) G2-97 set

LOSC-LDA
LDA

Ref. $-I_{ve}$ and $-A_{ve}$ (eV)

Mean absolute error (eV) of ionization potential and electron affinity results on 40 test molecules.

Method	IP	EA
scGW	0.47	0.34
G_0W_0-PBE	0.51	0.37
LOSC-BLYP	0.47	0.32
LOSC-PBE	0.37	0.32
LOSC-B3LYP	0.26	0.27
LOSC-LDA	0.34	0.48
BLYP	2.98	1.99
PBE	2.81	2.17
B3LYP	2.00	1.58
LDA	2.58	2.44

HOMO, LUMO ⟷ Chemical potentials,
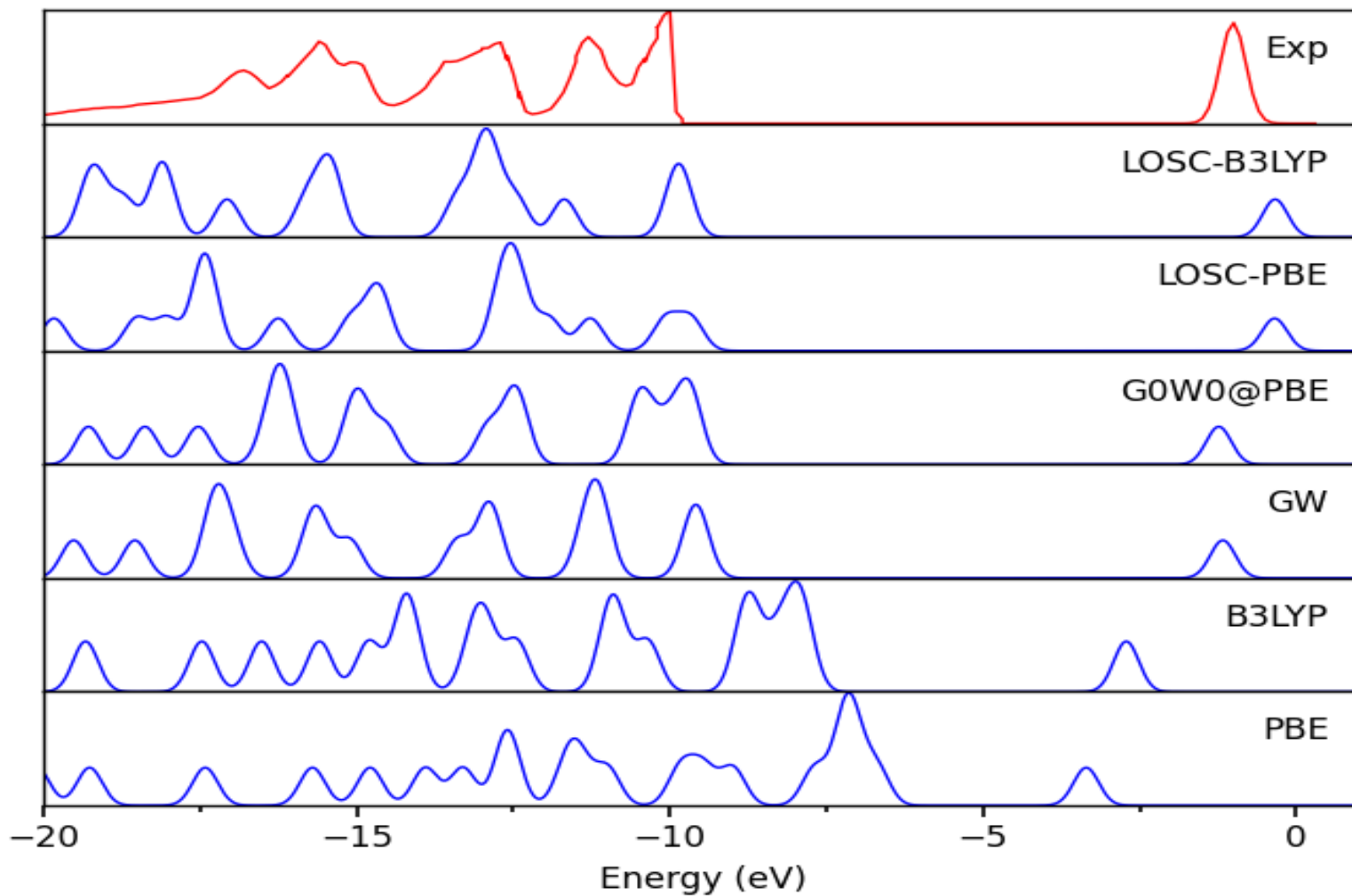Quarsiparticle energies

?

The rest of (G)KS
orbital energies ⟷ The rest of
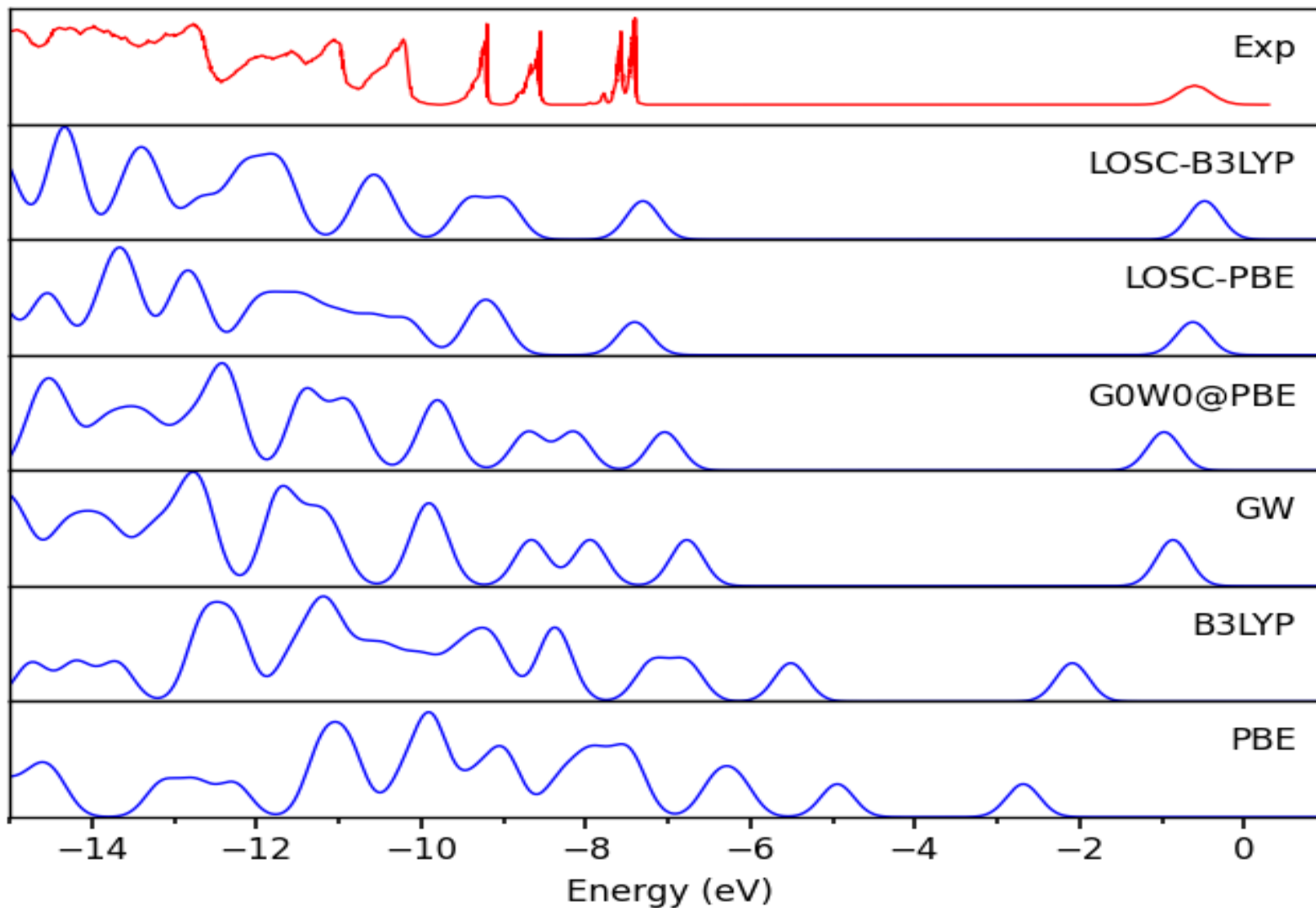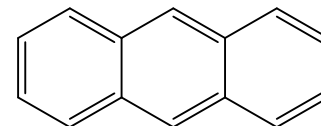Quarsiparticle
energies

Higher ionization energies of polyacene (n = 2,4,6) from GKS eigenvalues and ΔSCF calculation.

| Molecule	MO	Exp IP	Eigenvalues	
			LOSC-BLYP	BLYP
Naphthalene	Au	8.15	7.71	5.26
	B1u	8.87	8.84	5.97
	B2g	10.08	9.37	6.91
	B3g	10.83	11.12	7.81
	MAE		0.37	3.00
Tetracene	Au	6.97	6.86	4.44
	AB2g	8.41	8.50	5.72
	B1u	8.41	8.83	5.89
	Au	9.56	9.61	6.74
	B3g	9.70	10.06	7.02
	B2g	10.25	10.04	7.40
	MAE		0.21	2.68
Hexacene	Au	6.36	6.18	4.06
	B2g	7.35	7.56	5.03
	B3u	8.12	8.78	5.86
	Au	8.56	8.35	5.92
	B1g	9.36	9.55	6.60
	B2g	9.36	9.35	6.65
	Au	9.95	9.82	7.20
	B3u	9.95	10.57	7.55
	MAE		0.28	**2.52**

Photoemission spectrum of nitrobenzene
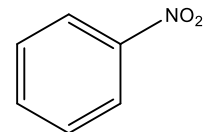
Photoemission spectrum of anthracene

Exp

LOSC-B3LYP

LOSC-PBE

G0W0@PBE

GW

B3LYP

PBE

Energy (eV)

Photoemission spectrum of C60
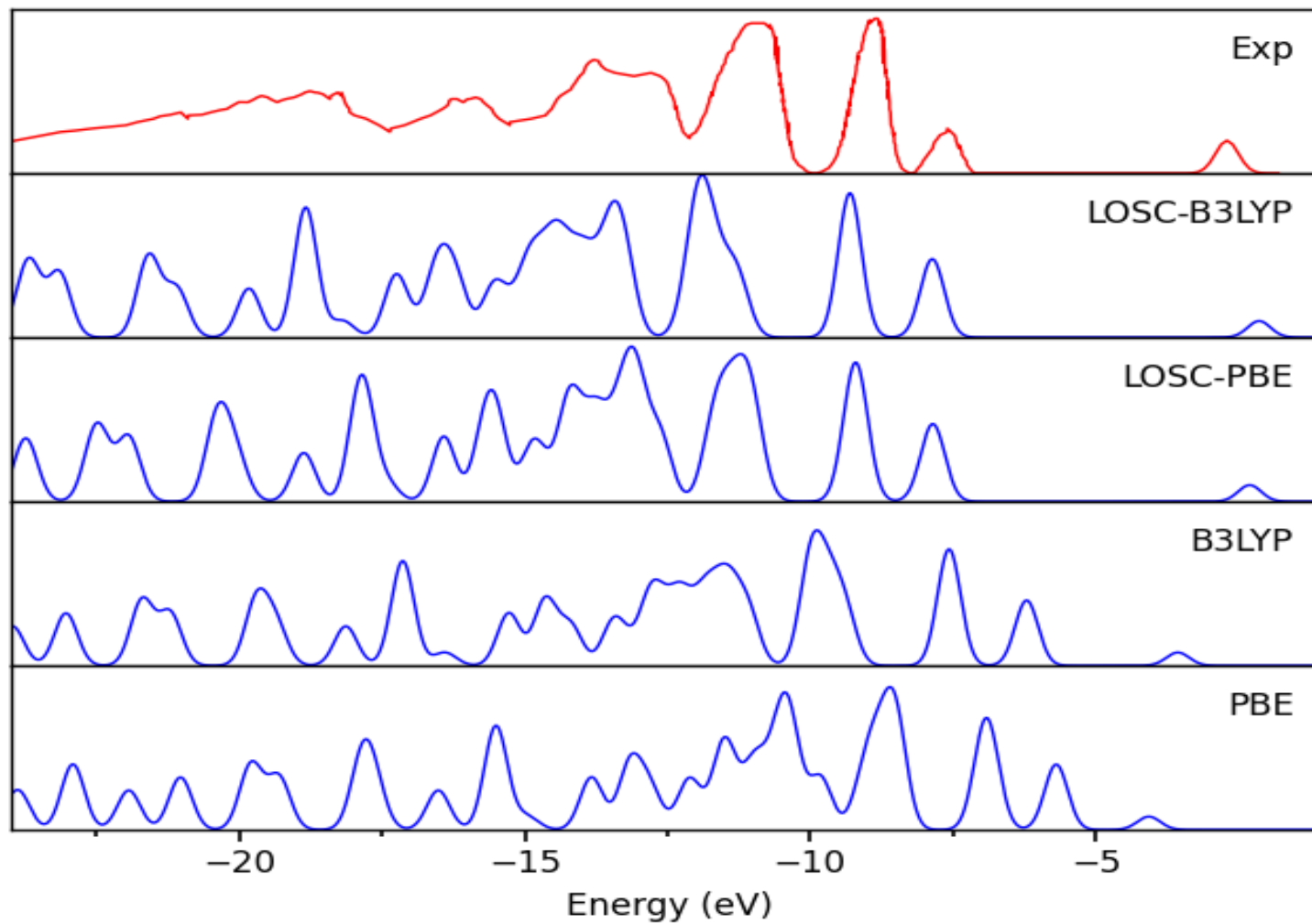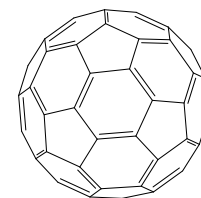
# Photoemission spectrum of H$_2$TPP
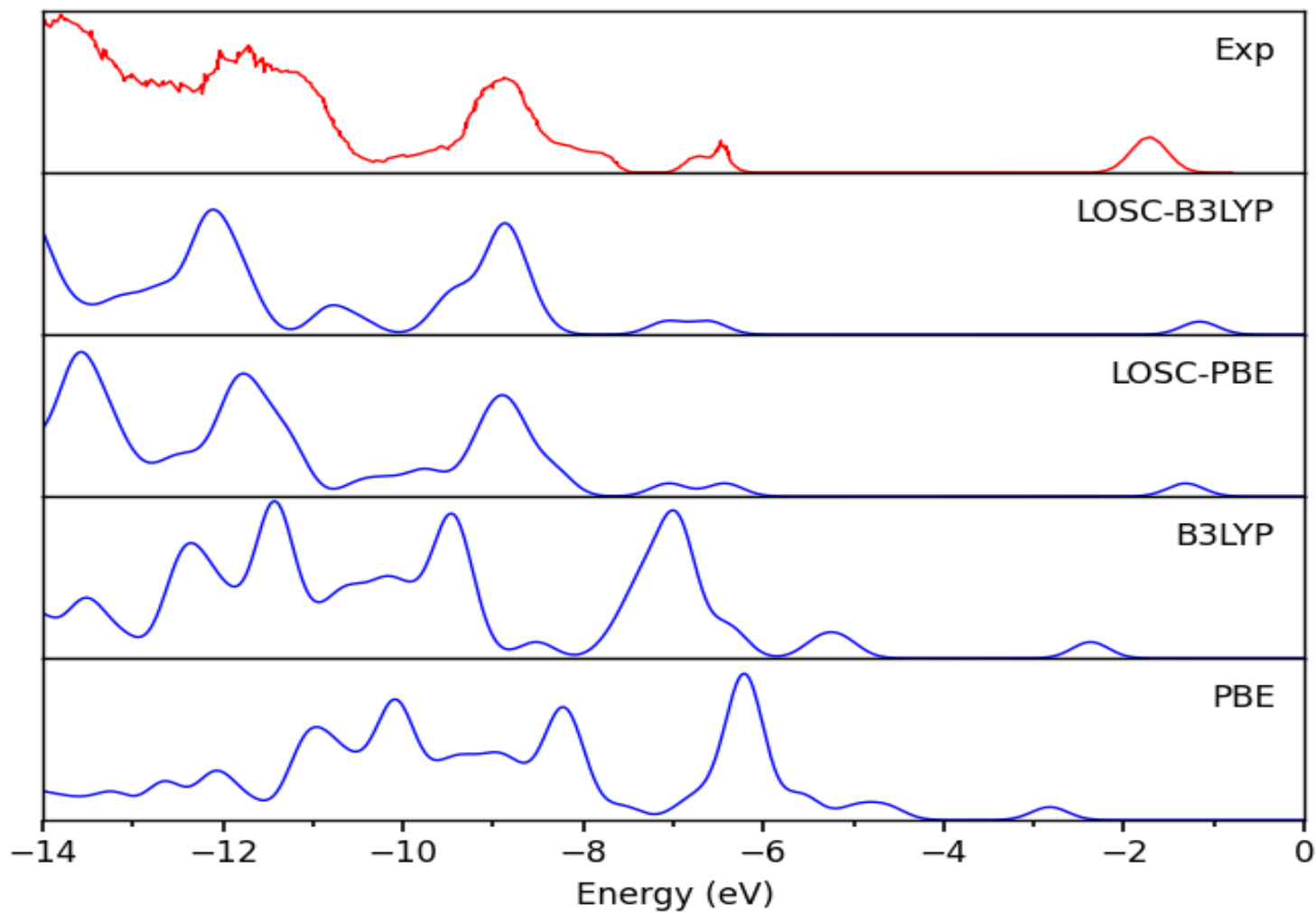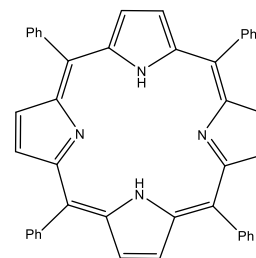
Orbital energy vs. quasiparticle energy

From extensive numerical results, (G)KS orbital energies are good approximation to the quasiparticle energies.

Unoccupied $\varepsilon_m(N) \approx \omega_m^+(N) = E_m(N+1) - E_0(N)$

Occupied $\varepsilon_n(N) \approx \omega_n^-(N) = E_0(N) - E_n(N-1)$

QE-DFT: Quasiparticle Energy-DFT for excitation energies from N-1 ground state calculation

E$_0$(N)
Ground State

E$_0$(N-1)
Ground State

E$_m$(N)
Excited State
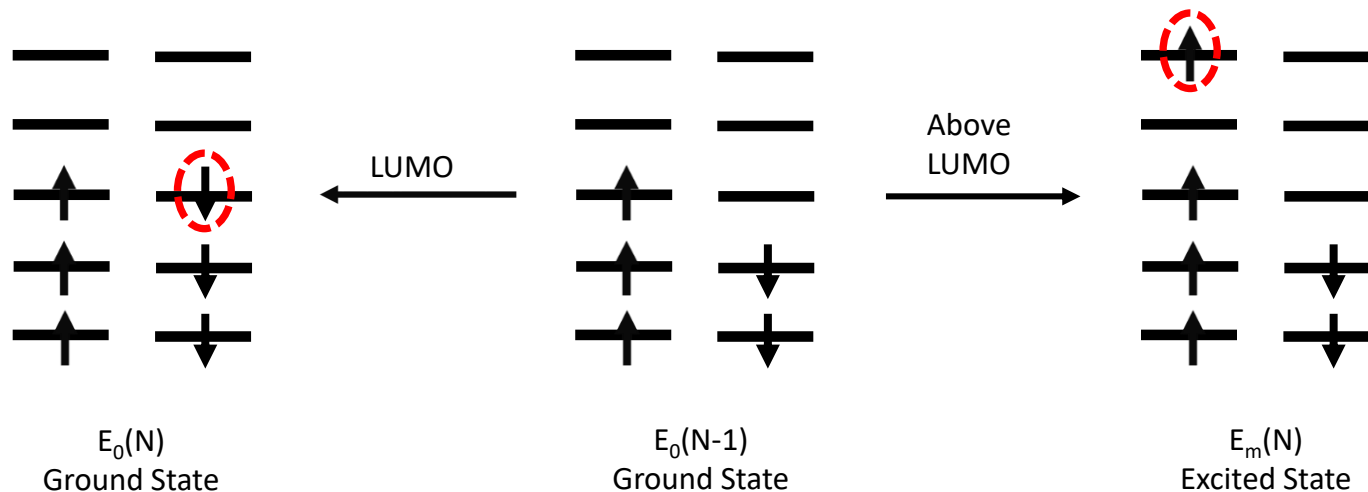
$$\Delta E_m(N) = E_m(N) - E_0(N)$$

$$= [E_m(N) - E_0(N-1)] - [E_0(N) - E_0(N-1)]$$

$$= \omega_m^+(N-1) - \omega_{min}^+(N-1)$$

$$\approx \varepsilon_m(N-1) - \varepsilon_{LUMO}(N-1)$$

Two groups independently:
Bartlett group: JCP, 2018, 149, 131101
Yang group: arXiv:1810.09906, 2018; JPC A 2019, 123, 3, 666-673

Low-lying excitation energies (eV) from different methods

Method	1st triplets		2nd triplets		1st singlets		2nd singlets		Total	
	MAE	MSE	MAE	MSE	MAE	MSE	MAE	MSE	MAE	MSE
HF	1.34	-1.10	1.13	-1.13	1.59	1.33	1.64	1.45	1.43	1.23
BLYP	0.21	0.15	0.46	0.41	0.76	0.76	0.32	0.02	0.46	0.25
B3LYP	0.39	0.08	0.58	0.54	0.71	0.41	0.46	-0.38	0.54	0.00
LDA	0.21	-0.06	0.57	0.57	0.67	0.65	0.34	0.03	0.46	0.10
LOSC-BLYP	0.63	0.47	0.69	0.43	1.09	1.09	0.64	0.15	0.80	0.48
LOSC-B3LYP	0.66	0.36	0.63	0.55	0.98	0.72	0.60	-0.22	0.75	0.21
LOSC-LDA	0.41	0.12	0.81	0.56	0.84	0.84	0.67	0.19	0.68	0.26
TD-B3LYP	0.48	0.48	0.31	0.31	0.31	0.17	0.37	0.33	0.36	0.31
ΔSCF-B3LYP	0.42	0.12	0.57	-0.43	0.83	0.63	0.55	0.13	0.62	0.25

Excitation energy (eV) of Li up to **Rydberg states**

AO	Exp	BLYP	LOSC-BLYP	LOSC-B3LYP	LOSC-LDA
2p	1.85	2.07 (-0.22)	2.18 (-0.33)	2.08(-0.23)	1.96(-0.12)
3s	3.37	4.80 (-1.43)	3.53 (-0.15)	3.46(-0.09)	2.78(0.60)
3p	3.83	5.33 (-1.50)	4.02 (-0.18)	3.90(-0.07)	3.15(0.68)
3d	3.88	5.56 (-1.69)	4.29 (-0.41)	4.15(-0.27)	3.43(0.45)
4s	4.34	6.23 (-1.89)	4.30 (0.04)	4.24(0.10)	3.31(1.03)
4p	4.52	6.42 (-1.89)	4.45 (0.07)	4.43(0.09)	3.43(1.09)
4d	4.54	6.52 (-1.98)	4.55 (-0.01)	4.53(0.01)	3.58(0.96)
5s	4.75	6.81 (-2.06)	4.66 (0.09)	4.39(0.35)	3.54(1.21)
5p	4.84	6.92 (-2.08)	4.78 (0.05)	4.72(0.12)	3.60(1.24)
5d	4.85	7.04 (-2.19)	5.00 (-0.15)	4.98(-0.13)	NA
6s	4.96	7.11 (-2.15)	4.74 (0.21)	4.69(0.26)	3.61(1.35)
6p	5.01	7.12 (-2.11)	4.71 (0.30)	4.76(0.25)	3.67(1.33)
MAE		1.77	0.17	0.16	0.91
MSE		-1.77	-0.04	0.03	0.89

Charge Transfer excitation

Acceptor

Donor

Ground
state

One electron transfer

-1

+
1

Excited state

$$E^{CT} = IP(D) - EA(A) - 1/R$$

1/R trend

(a) 4.65 Å (b) 6.65 Å

Y. Mei and WY, J. Phys. Chem., 2019

Origin of 1/R trend

From N-1

(a) LUMO (b) LUMO+1
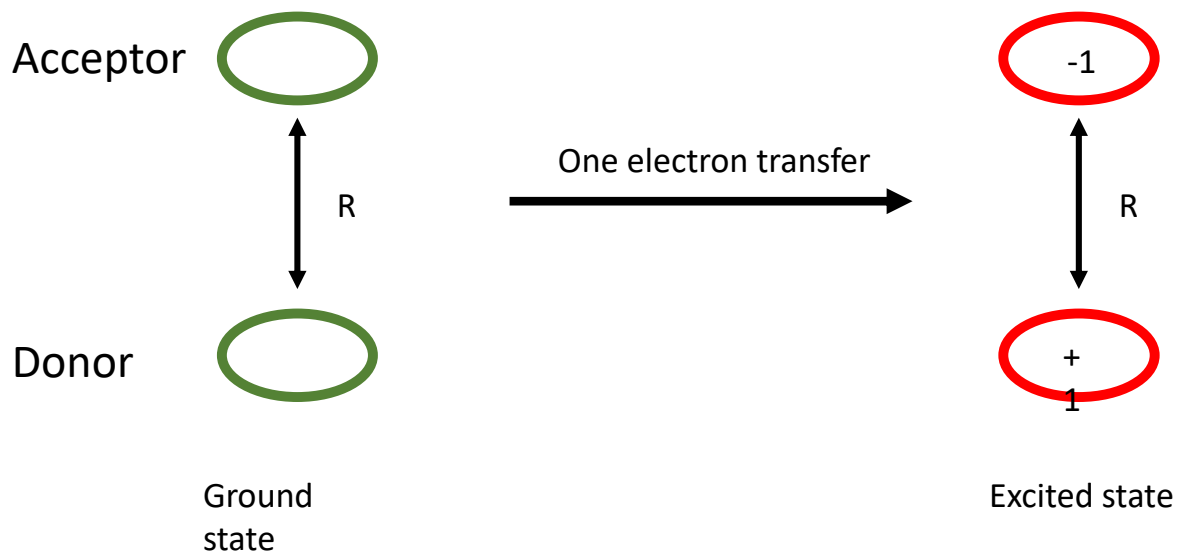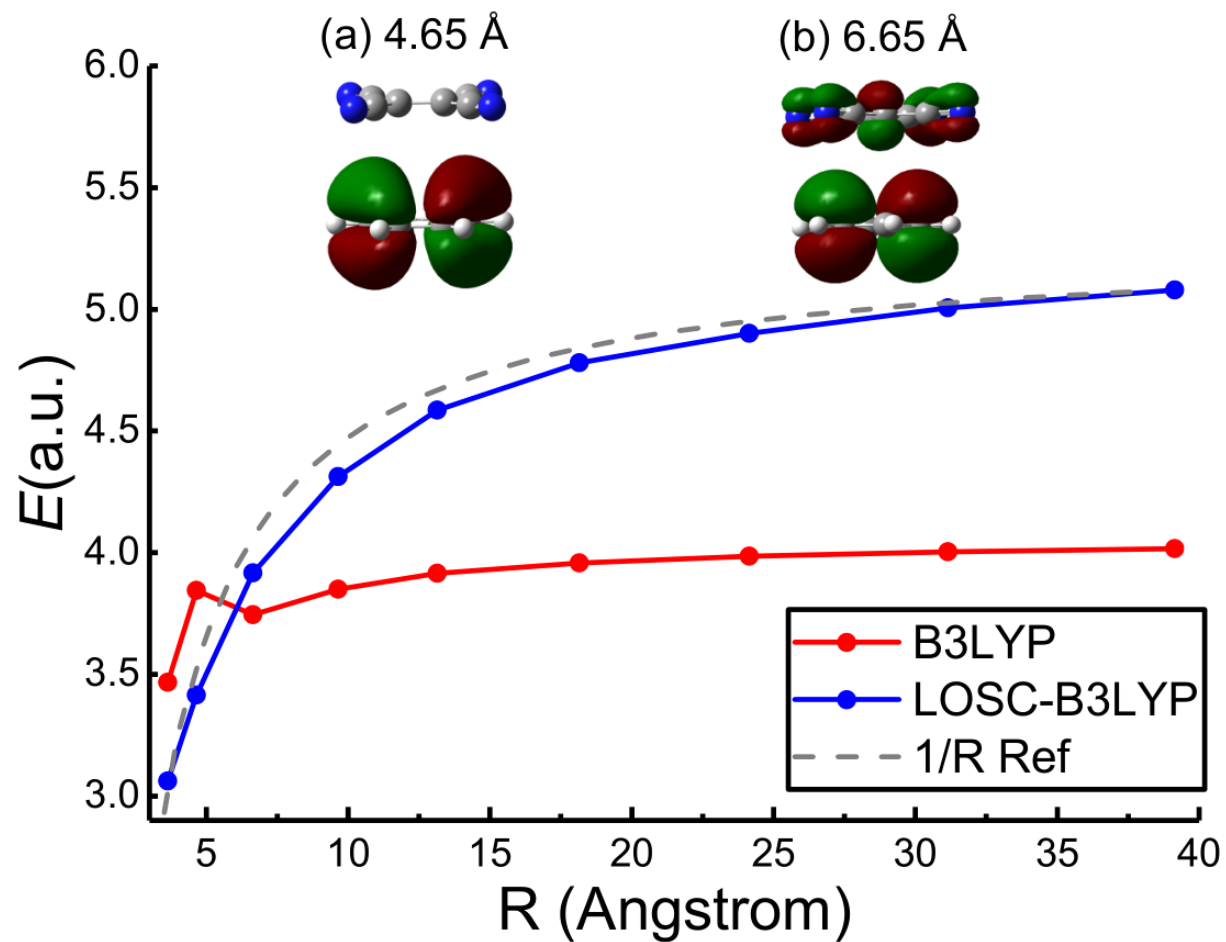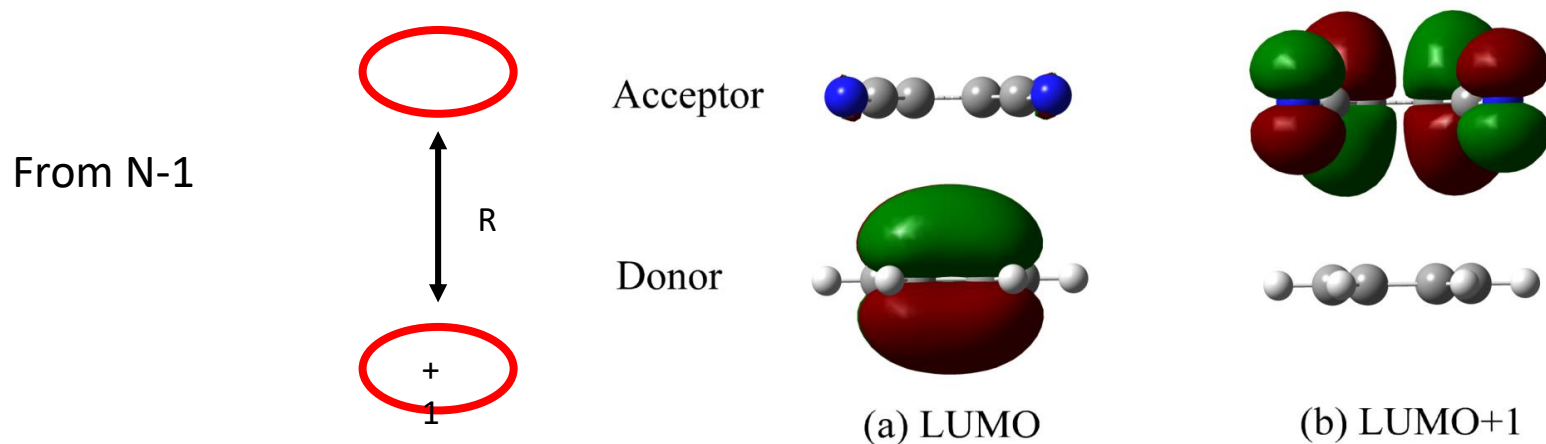
$$\Delta E^{exci} = \epsilon^{N-1}_{LUMO+1} - \epsilon^{N-1}_{LUMO}$$

$$\propto 1/R - 0 = 1/R$$

Excited-State Potential Energy Surfaces, Conical Intersections, and Analytical Gradients from Ground-State Density Functional Theory
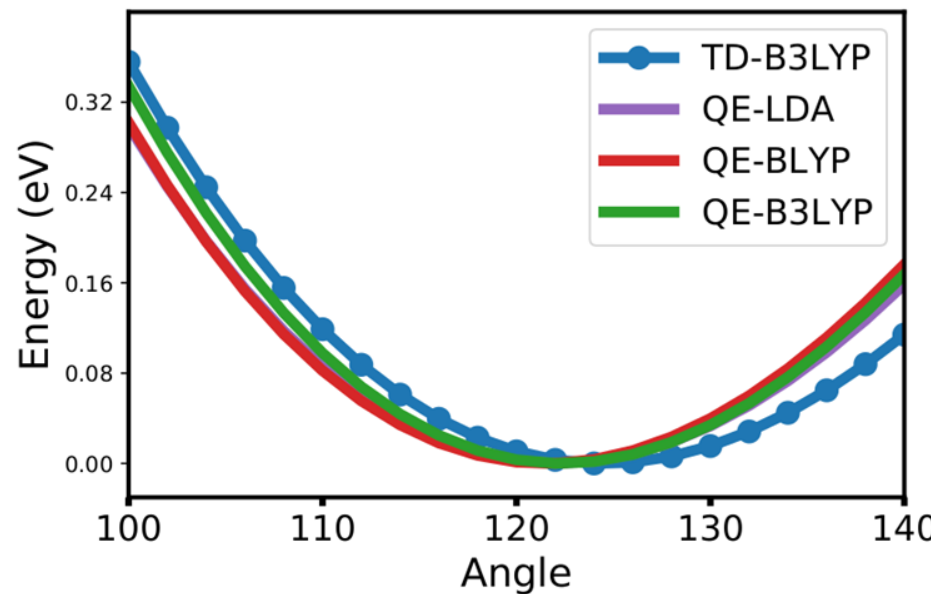
Yuncai Mei[†] and Weitao Yang*,[†,‡]

Excited-State Potential Energy Surface JPCL 2019

Excited-State Potential Energy Surfaces, Conical Intersections, and Analytical Gradients from Ground-State Density Functional Theory
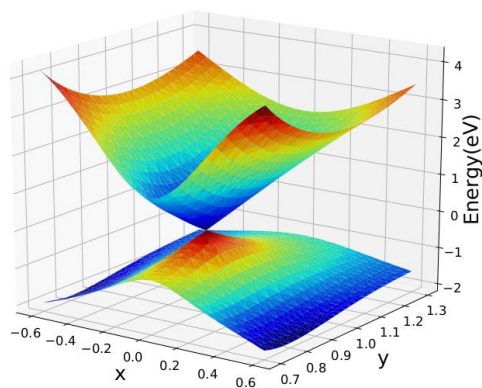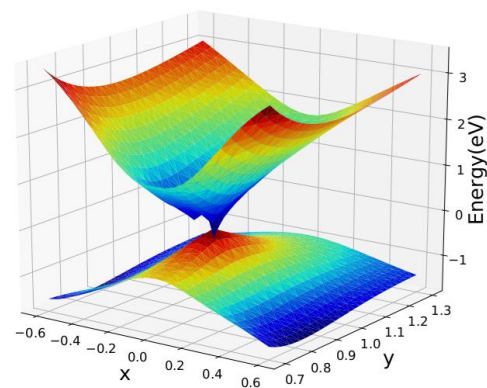
Yuncai Mei[†] and Weitao Yang[*,†,‡]
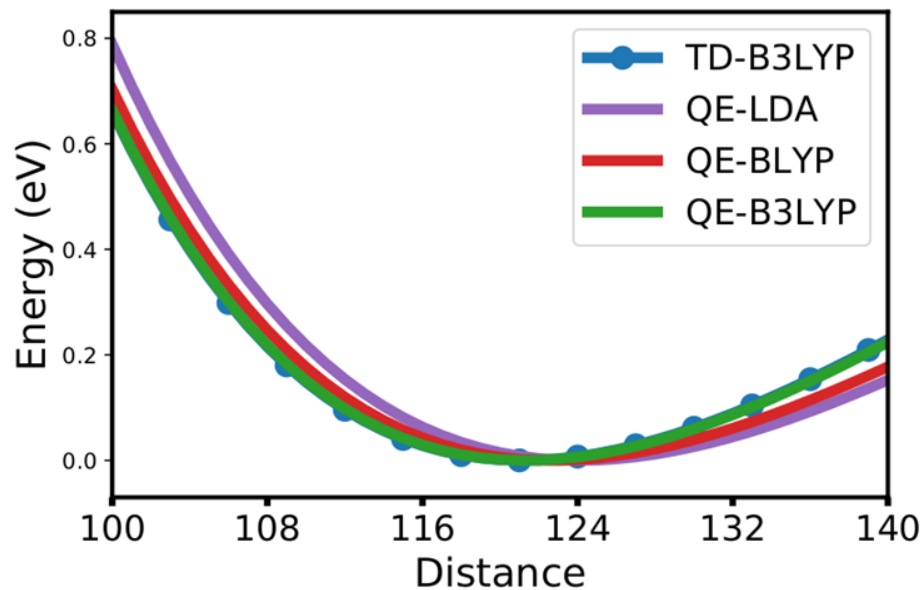
(a) BH

(b) C_2H_2

$$E_n(N) \approx En^{\mathrm{QE-DFT}}(N) = E_0(N-1) + \varepsilon_n(N-1)$$
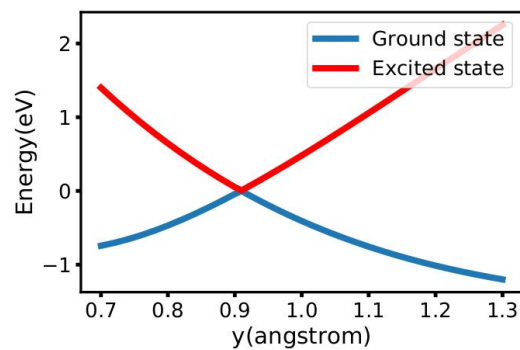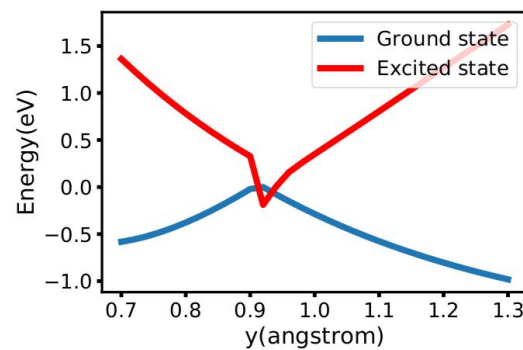
Conical Intersection

(a) QE-B3LYP

(b) TD-B3LYP

(c) QE-B3LYP (1D)

(d) TD-B3LYP (1D)

Summary

- Fractional perspective on the two main systematic errors in DFAs.

- LOSC approaches-- non-local corrections.

- Ground State DFT calculations, with accurate DFAs, can provide the following

  - Photoemission spectra -- quasiparticle energies, band gaps.

  - Photoabsorption spectra -- excitation energies (particle-hole) from the (N-1) ground state calculations.