

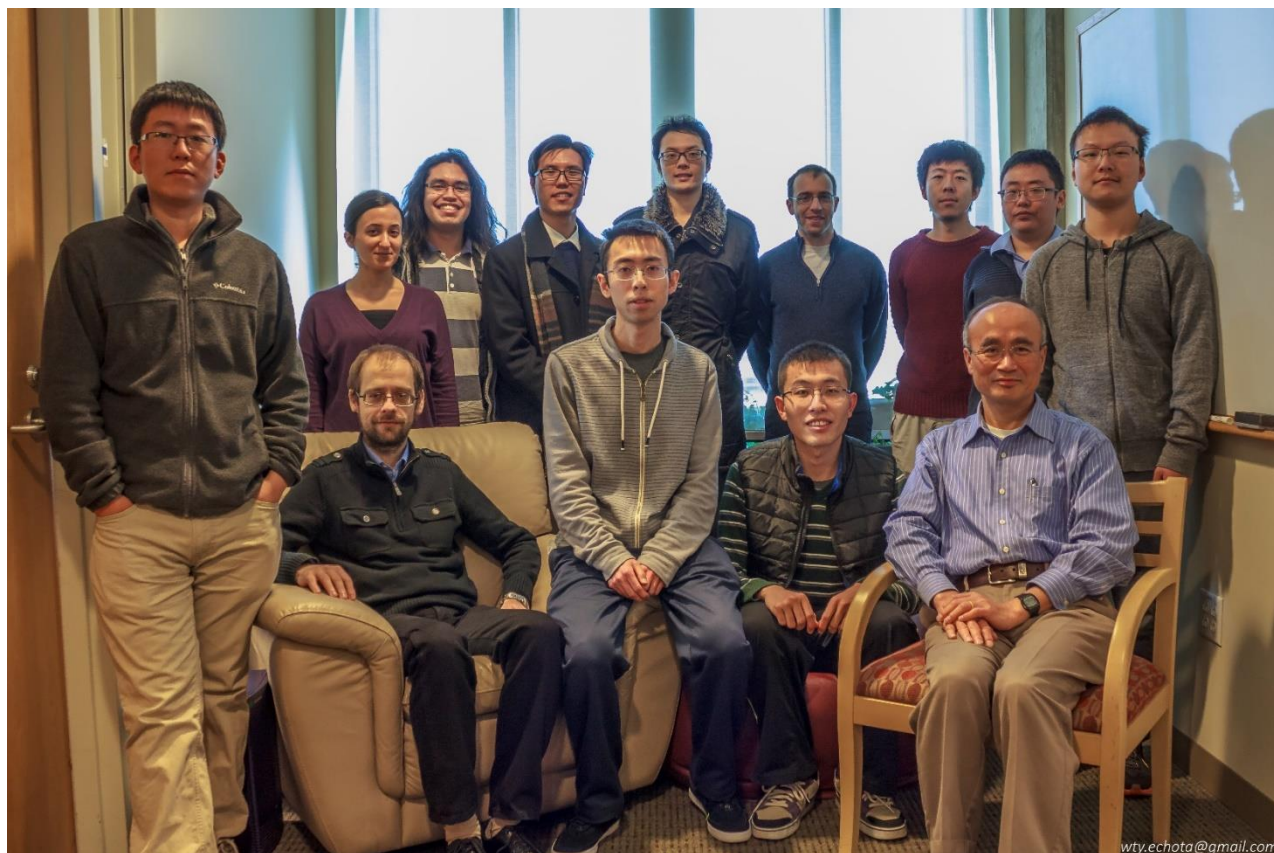
Exchange-Correlation Functionals in DFT

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Theory
Biological
Nano
Material

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Outline

- Kohn-Sham Equations
- Adiabatic Connection for XC: from wave function theory to DFT
- Commonly Used Functionals
- Challenges in DFT from **Fractional Perspectives**
- **LOSC** (Localized orbitals scaling correction)

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)

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

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

Features of Kohn-Sham theory

1. With N orbitals, the kinetic energy is treated rigorously. In comparison with the Thomas-Fermi theory in terms of density, it is a trade of computational difficulty for accuracy.
2. The KS or GKS equations are in the similar form as the Hartree-Fock equations and can be solved with similar efforts.
3. KS or GKS changes a N interacting electron problem into an N non-interacting electrons in an effective potential.
4. The E_{xc} is not known, explicitly. It is about 10% of the energy for atoms.

Adiabatic connection: from Kohn-Sham reference system to the true physical system

$$\begin{aligned} F[\rho] &= T[\rho] + V_{ee}[\rho] \\ &= T_s[\rho] + J[\rho] + E_{xc}[\rho] \end{aligned}$$

So far, the E_{xc} is expressed in a form that is not appealing, not revealing, not inspiring...

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

What is the relation of the Kohn-Sham reference system to the true physical system?

- The same electron density

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

- Anything else?

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	Kohn-Sham Reference System	Physical System
the same $\rho(\mathbf{r})$	$\sum_i n_i \phi_i(\mathbf{r}) ^2$	$N \int ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi(\mathbf{r}s_1, \mathbf{x}_2, \dots \mathbf{x}_N) ^2$
Hamiltonian	$H_s = \sum_j^N h_s(j) = \sum_j^N -\frac{1}{2} \nabla_j^2 + v_s(\mathbf{r}_j)$	$H = \hat{T} + \hat{V}_{ee} + \sum_i^N v_{ext}(\mathbf{r}_i)$
Energy	$E_s = \langle \Psi_s H_s \Psi_s \rangle$	$E = \langle \Psi H \Psi \rangle$
	$E_s = T_s[\rho] + \int d\mathbf{r} v_s(\mathbf{r}) \rho(\mathbf{r})$	$E = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r})$
connecting H_λ	$\sum_j^N -\frac{1}{2} \nabla_j^2 + \lambda \hat{V}_{ee} + \sum_i^N v_\lambda(\mathbf{r}_i)$, keeping fixed density $\rho_\lambda(\mathbf{r}) = \rho(\mathbf{r})$	
	$H_0 = H_s$	$H_1 = H$

Adiabatic connection: from Kohn-Sham reference system to the true physical system

$$H_\lambda = \sum_j^N -\frac{1}{2} \nabla_j^2 + \lambda \hat{V}_{ee} + \sum_i^N v_\lambda(\mathbf{r}_i)$$

$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= \frac{\partial \langle \Psi_\lambda | H_\lambda | \Psi_\lambda \rangle}{\partial \lambda} \\ &= \langle \Psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \hat{V}_{ee} + \sum_i^N \frac{\partial v_\lambda(\mathbf{r}_i)}{\partial \lambda} | \Psi_\lambda \rangle \\ &= \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle + \frac{\partial}{\partial \lambda} \int d\mathbf{r} v_\lambda(\mathbf{r}) \rho(\mathbf{r}) \end{aligned}$$

$$\begin{aligned} E_1 - E_0 &= \int_0^1 \frac{\partial E_\lambda}{\partial \lambda} d\lambda \\ &= \int_0^1 \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) - \int d\mathbf{r} v_s(\mathbf{r}) \rho(\mathbf{r}) \end{aligned}$$

	Kohn-Sham Reference System	Physical System
	$E_s = T_s[\rho] + \int d\mathbf{r} v_s(\mathbf{r}) \rho(\mathbf{r})$	$E = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r})$

$$J[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Finally,

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda - J[\rho]$$

Adiabatic connection: from Kohn-Sham reference system to the true physical system

$$E_{xc}[\rho] = \int_0^1 \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda - J[\rho]$$

- Exc in terms of wavefunction!

- Compared with

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

- What is the integrand at $\lambda = 0$?
- Starting point to make approximations – **DFA** (Density functional approximation)

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

$\varepsilon_{xc}(\rho(\mathbf{r}))$ is the XC energy per particle of a homogeneous electron gas of density ρ . It is a function of ρ .

Dirac exchange energy functional

$$E_x^{LDA}[\rho] = -C_D \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r}$$

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

LDA	$E_{xc} = \int d\mathbf{r} f(\rho)$	VWN, PW,
GGA	$E_{xc} = \int d\mathbf{r} f(\rho, \nabla \rho)$	BLYP, PW96, PBE
Hybrid	$E_{xc} = c_1 E_x^{HF} + c_2 E_{xc}^{GGA}$	B3LYP, PBE0
range-separated	

$$E_{\text{x}}^{\text{B88}} = - \sum_{\sigma=\alpha,\beta} \int \rho_{\sigma}^{4/3} \left[\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} + \frac{\beta x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma}} \right] \text{d}\mathbf{r}$$

$$E_{\text{x}}^{\text{PBE}} = - \int \rho^{4/3} \left[\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} + \frac{\mu s^2}{1 + \mu s^2 / \kappa} \right] \text{d}\mathbf{r}$$

$$E_{\text{x}}^{\text{HF}} = - \frac{1}{2} \sum_{ij\sigma} \int \int \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \text{d}\mathbf{r} \text{d}\mathbf{r}'$$

$$E_{\text{xc}}^{\text{B3LYP}} = 0.2E_{\text{x}}^{\text{HF}} + 0.8E_{\text{x}}^{\text{LDA}} + 0.72\Delta E_{\text{x}}^{\text{B88}} + 0.81E_{\text{c}}^{\text{LYP}} \\ + 0.19E_{\text{c}}^{\text{VWN}}$$

Atomization energies for a few selected molecules, mH

Mol.	Exp.	LSDA	PBE	UHF	MP2	B3LYP
H ₂	174.5	180.3	166.7	133.9	165.7	—
Li ₂	39.3	37.9	31.7	4.8	25.5	33.5
Be ₂	4.8	20.6	15.6	11.2	−1.6	—
N ₂	364.0	427.1	387.6	183.3	368.1	365.6
F ₂	62.1	124.6	85.1	−15.9	111.6	57.7
LiH	92.4	96.9	85.2	52.6	86.1	92.9
OH	169.6	197.9	175.0	108.4	165.7	172.3
HF	225.7	259.1	226.3	154.6	227.9	222.1
H ₂ O	370.0	424.9	373.2	245.4	366.5	368.1
NH ₃	473.9	537.5	480.8	318.7	462.1	478.4
CH ₄	668.2	737.2	669.0	522.7	661.3	670.4
CO	413.2	476.3	428.4	277.3	423.9	408.3
NO	243.7	316.2	273.9	84.5	242.2	248.0
Cl ₂	92.4	132.1	103.7	—	—	87.8

Most data from A. J. Cohen, P Mori-Sanchez, and
W. Yang, Chem. Rev, 2012

Mean Absolute Errors (MAE) Thermochemistry(G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

functional	post-B3LYP				
	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78

GGA and Meta-GGA

BLYP	6.64	7.37	0.0205	1.46	0.79
HCTH	5.59	4.15	0.0119	2.22	0.48
HCTH407	5.72	4.69	0.0107	1.05	0.50
PBE	15.99	8.29	0.0148	1.24	0.63
BP86	15.71	8.49	0.0158	1.39	0.66
BPBE	7.55	6.81	0.0155	1.67	0.53
OLYP	5.22	5.36	0.0142	2.21	0.53
OPBE	8.86	5.21	0.0121	2.55	0.31
TPSS	7.85	8.03	0.0123	1.16	0.44
M06-L	5.87	3.82	0.0056	0.58	0.40

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LDA	72.24	14.36	0.0107	3.02	0.78
Hybrid Functionals					
TPSSh	6.03	6.45	0.0082	0.98	0.30
B3LYP	4.28	4.50	0.0097	1.01	0.37
PBE0	6.37	4.11	0.0089	0.76	0.21
B97-1	3.90	3.88	0.0093	0.75	0.28
B97-2	4.31	2.79	0.0087	0.97	0.19
B97-3	3.70	2.22	0.0087	0.92	0.26
M06	4.78	2.03	0.0088	0.47	0.39
M06-2X	3.34	1.37	0.0110	0.34	0.35
M06-HF	6.26	3.14	0.0167	0.88	0.73
HF	132.38	15.12	0.0277	3.15	1.01
HFLYP	35.39	9.18	0.0423	1.13	1.36

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functional	post-B3LYP				
	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78
Range-Separated Functionals					
CAMB3LYP	4.04	2.51	0.0119	0.69	0.23
LCBLYP	16.91	3.73	0.0169	0.90	0.31
rCAMB3LYP	5.50	2.76	0.0225	0.78	0.37
LC-PBE	16.69	3.07	0.0245	0.75	0.53
HSE	4.37	3.43	0.0082	0.77	0.21

Density Functional Theory

- Structure of matter: atom, molecule, nano, condensed matter
- Chemical and biological functions
- Electronic
- Vibrational
- Magnetic
- Optical (TD-DFT)

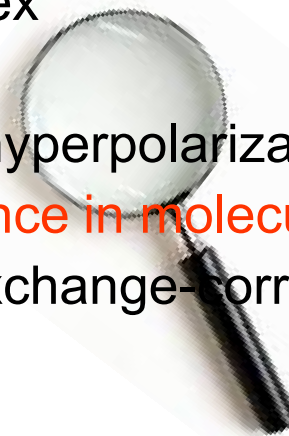
Density Functional Theory

- 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.**

Fractional Charges

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

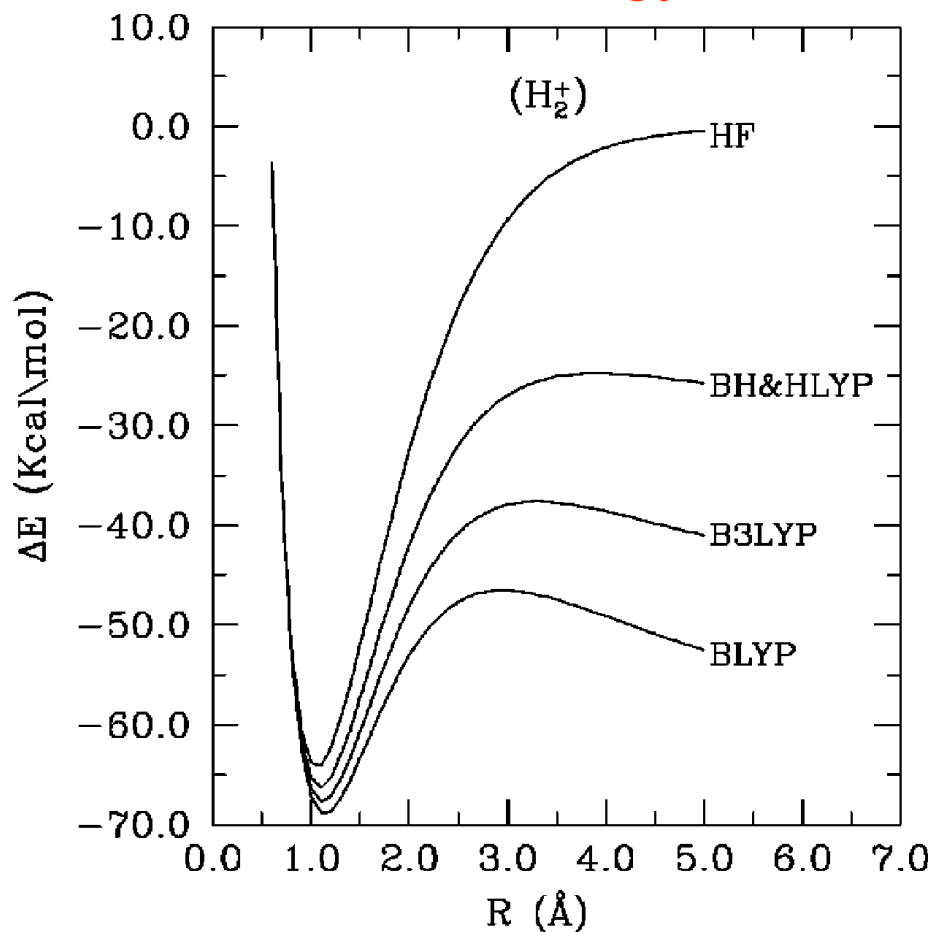


Delocalization Error

Error Increases for systems with fractional number of electrons: Yingkai Zhang and WY, JCP 1998

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

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

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

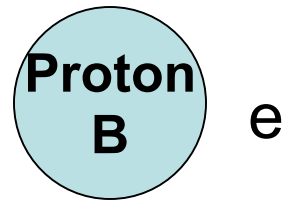
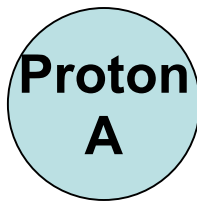
Ground State **Degeneracy** in QM and in DFT

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

H_2^+ at the dissociation limit

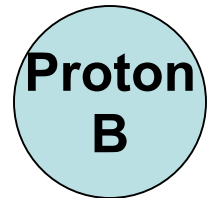
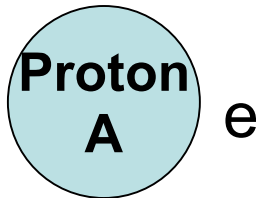
$$\Psi_\alpha$$

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



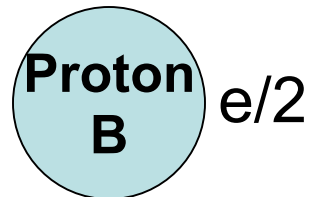
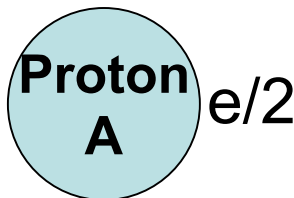
$$\Psi_\beta$$

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



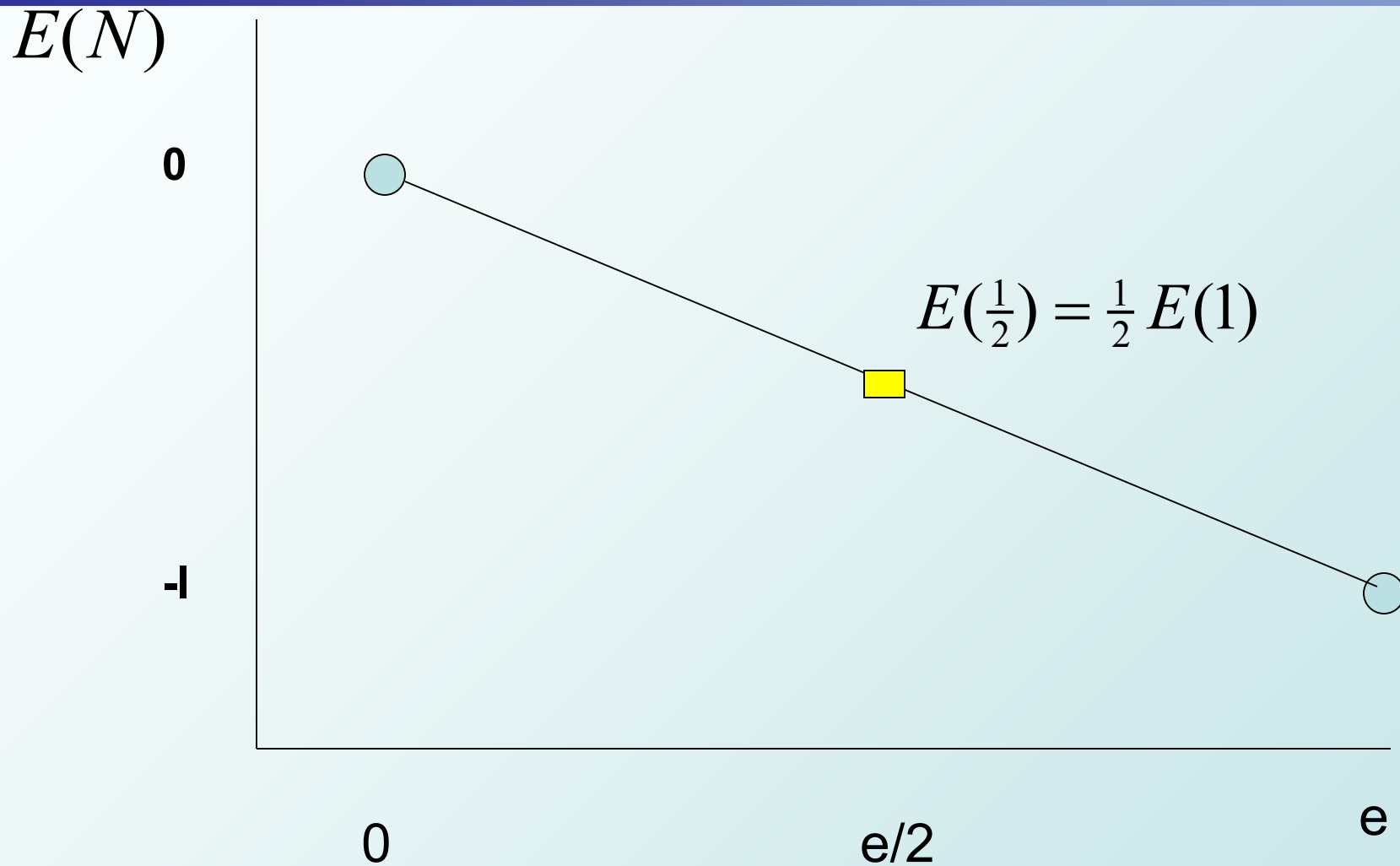
$$\Psi_\gamma = \frac{1}{\sqrt{2}} (\Psi_\alpha + \Psi_\beta)$$

$$E_\gamma = E(\tfrac{1}{2}) + E(\tfrac{1}{2}) = 2E(\tfrac{1}{2})$$

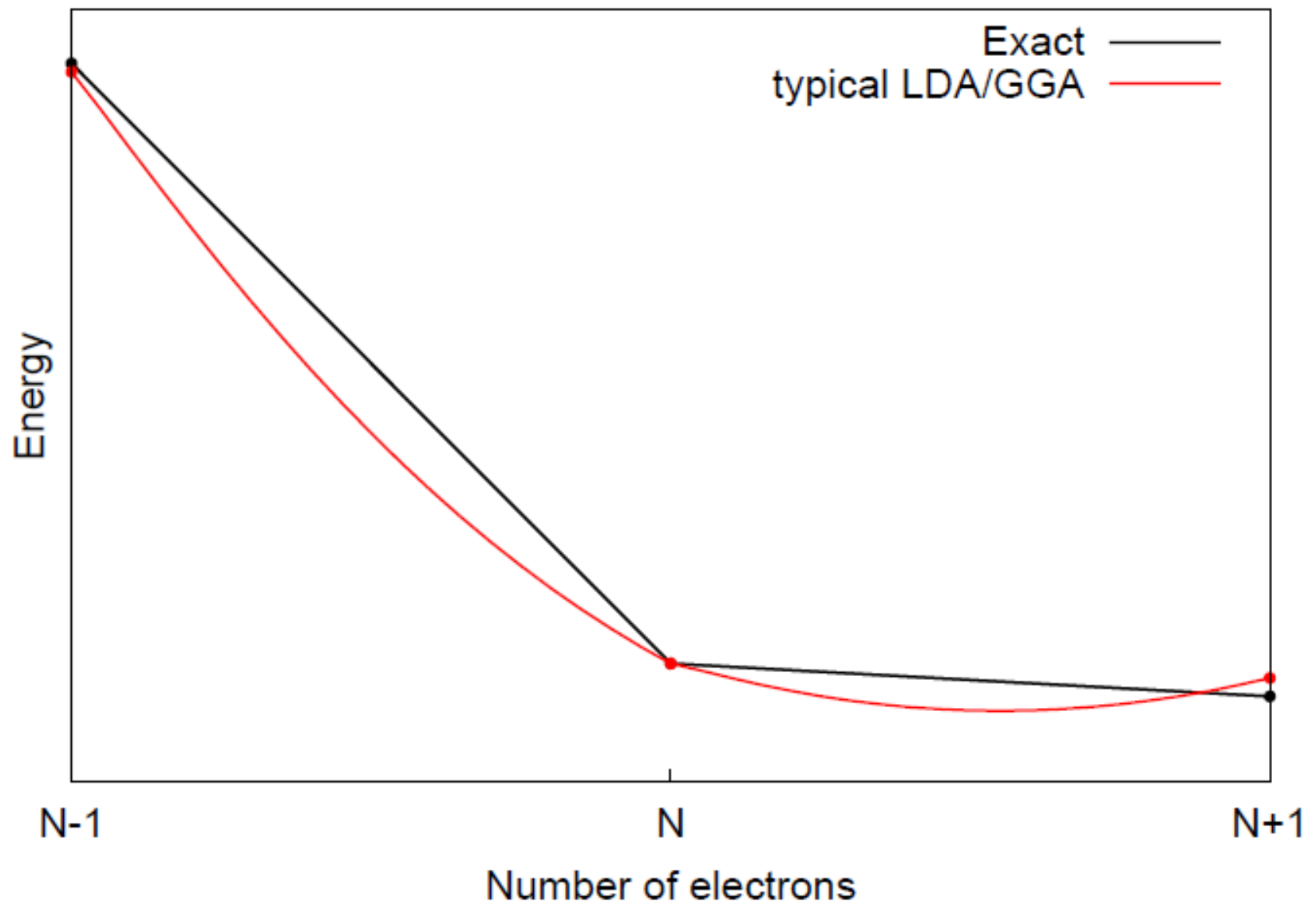


$$E(N): \quad E(\tfrac{1}{2}) = \tfrac{1}{2} E(0) + \tfrac{1}{2} E(1) = \tfrac{1}{2} E(1)$$

The linearity condition in fractional charges: The energy of $e/2$

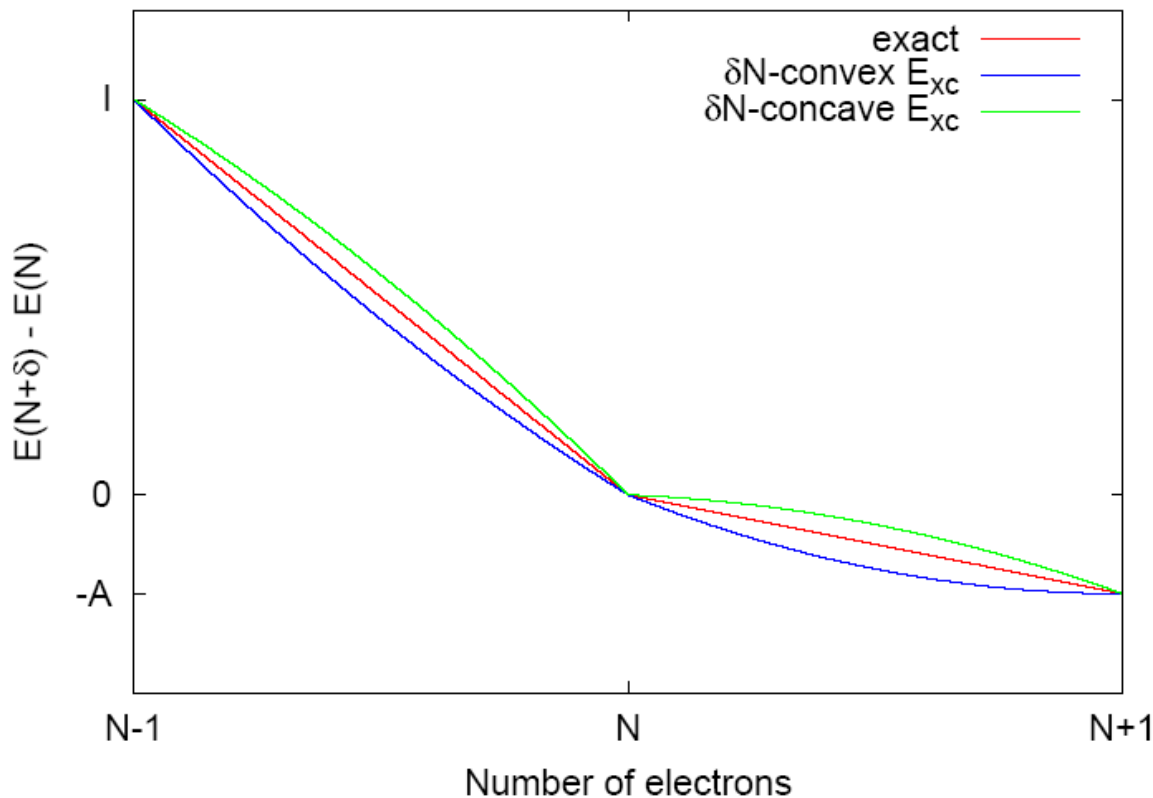


$$E(N)$$



A dimer, with ∞ separation: each monomer has $E(N)$

$2 \times$



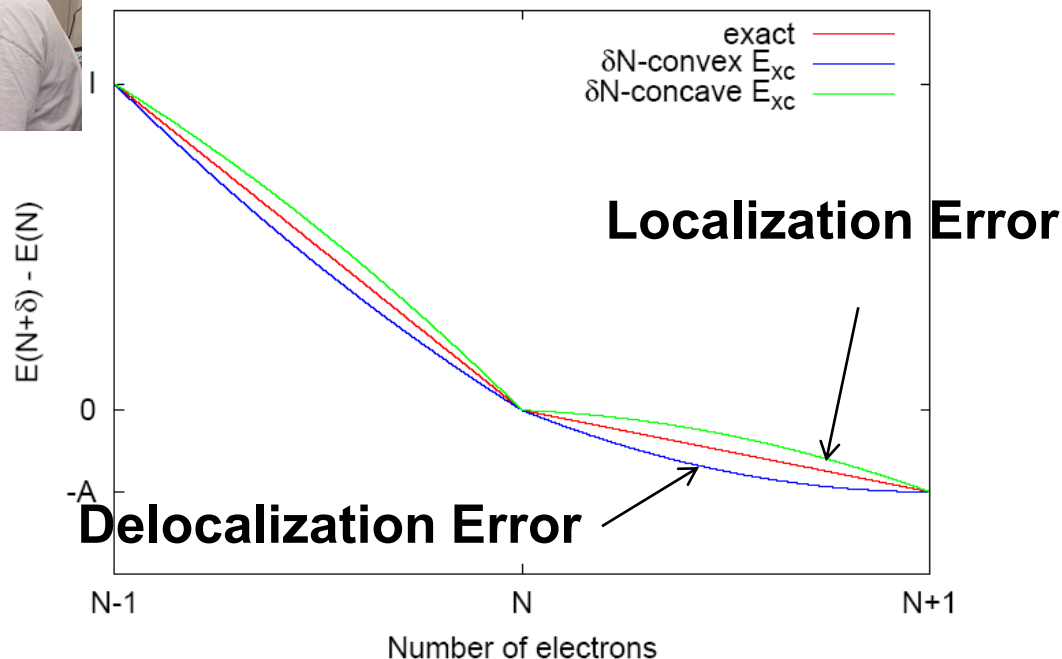
$+ e$

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

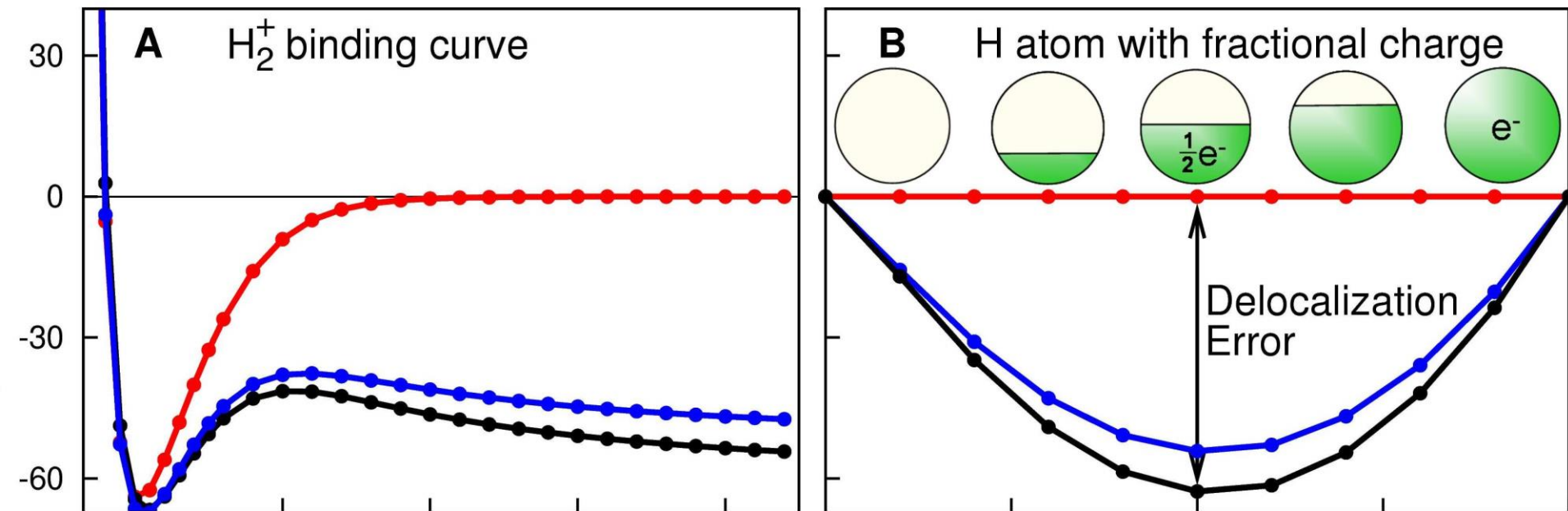


Consequence of Delocalization Error

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



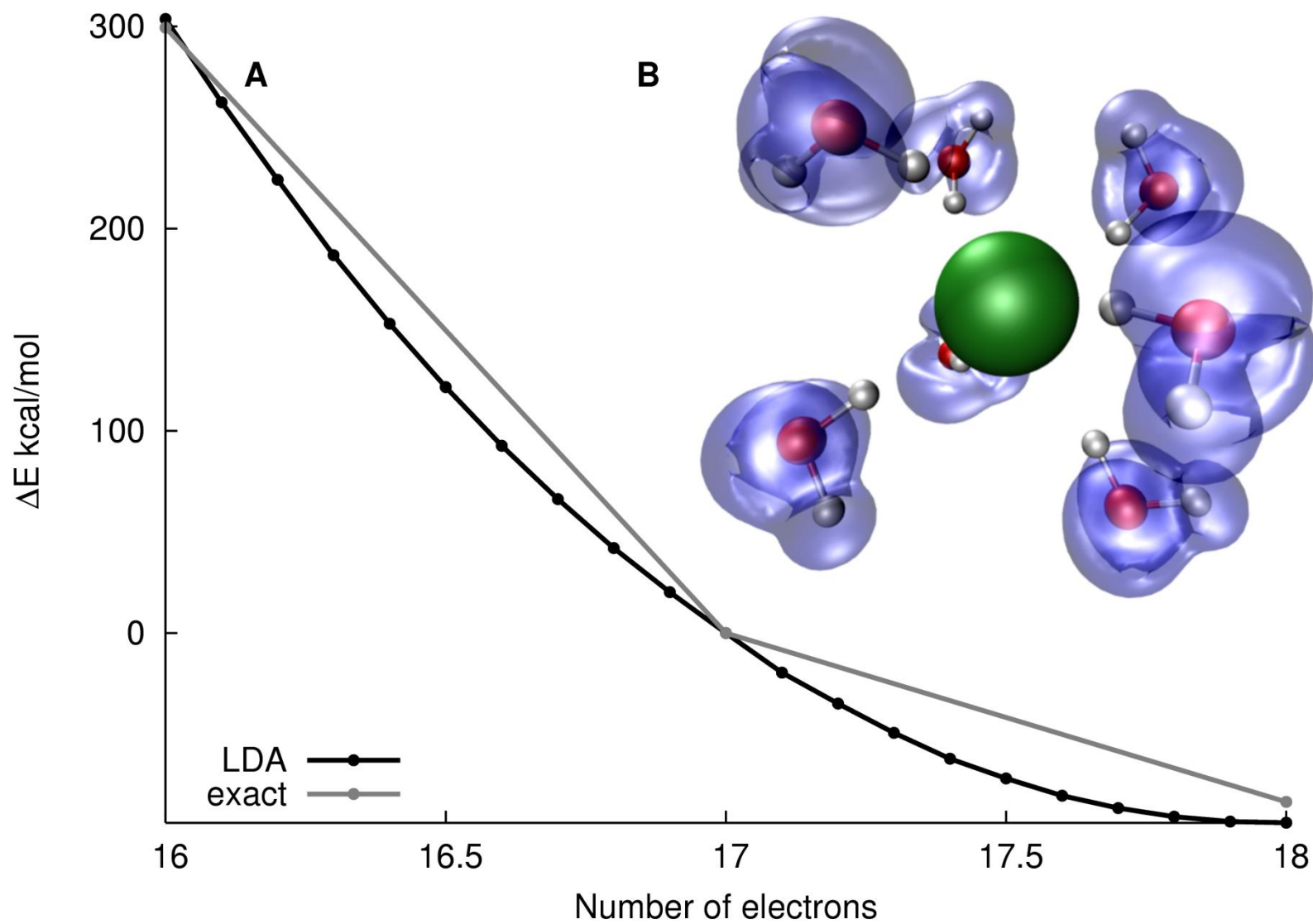
Too low energy for fractional charge systems

- 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

Seeing the delocalization error



Where is the negative charge ?

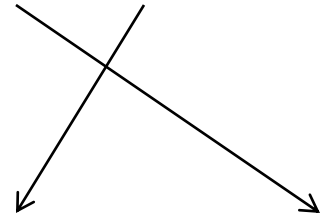


Band Gap

Definition of fundamental gap

$$\begin{aligned} E_{\text{gap}}^{\text{integer}} &= \{E(N-1) - E(N)\} - \{E(N) - E(N+1)\} \\ &= I - A \end{aligned}$$

derivative


$$E_{\text{gap}}^{\text{deriv}} = \left\{ \frac{\partial E}{\partial N} \Big|_{N+\delta} - \frac{\partial E}{\partial N} \Big|_{N-\delta} \right\}$$

$$E_{\text{gap}}^{\text{integer}} = E_{\text{gap}}^{\text{deriv}}, \text{ Only if } E(N + \delta) \text{ is linear.}$$

Unified expressions:

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

$$E_g^{\text{deriv}} = \langle \phi_{\text{lumo}} | H_{\text{eff}} | \phi_{\text{lumo}} \rangle - \langle \phi_{\text{homo}} | H_{\text{eff}} | \phi_{\text{homo}} \rangle$$

Functional	Calculation	$\frac{\partial E_v(N)}{\partial N}$	E_g^{deriv}
explicit density functional $E_{xc} = E_{xc}[\rho(\mathbf{r})]$	KS	ϵ_f^{KS}	$\epsilon_{\text{lumo}}^{\text{KS}} - \epsilon_{\text{homo}}^{\text{KS}}$
orbital functional $E_{xc} = E_{xc}[\rho_s(\mathbf{r}', \mathbf{r})]$	OEP	$\epsilon_f^{\text{OEP}} + \Delta_{xc}^f$	$\epsilon_{\text{lumo}}^{\text{OEP}} - \epsilon_{\text{homo}}^{\text{OEP}} + \Delta_{xc}$
orbital functional $E_{xc} = E_{xc}[\rho_s(\mathbf{r}', \mathbf{r})]$	GKS	ϵ_f^{GKS}	$\epsilon_{\text{lumo}}^{\text{GKS}} - \epsilon_{\text{homo}}^{\text{GKS}}$

–KS orbital gap is equal to the band gap, for any explicit density functional.

–OEP orbital gap is NOT equal to the band gap.

–GKS orbital gap is the band gap, for any orbital functional.

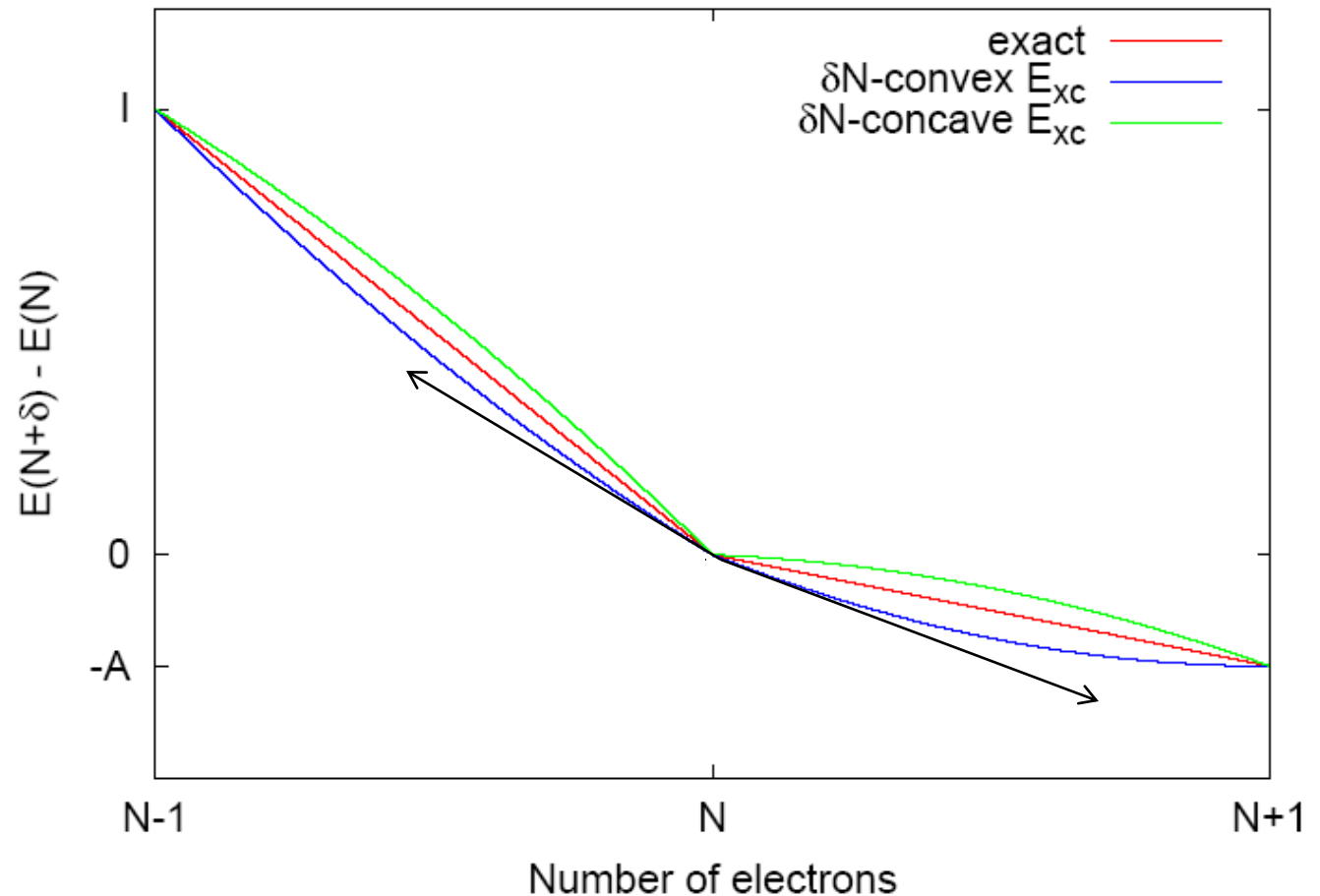
Gap as the discontinuity of energy derivatives- chemical potentials

How can fundamental gap be predicted in DFT

For continuous and differentiable functionals of density/density matrix

- **LUMO** energy is the chemical potential for electron addition
- **HOMO** energy is the chemical potential for electron removal
- **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.

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



For Linear $E(N)$

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

Convex curve (LDA, GGA):

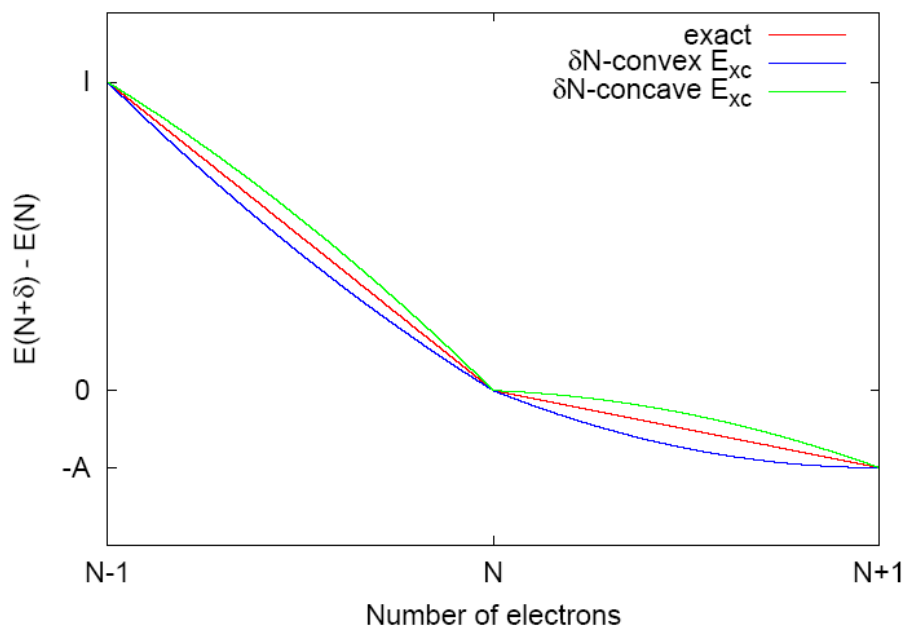
derivative underestimates I , overestimates A , **$I-A$ is too small**

Concave curve (HF):

derivative overestimates I , underestimate A , **$I-A$ is too large**

How *well* can fundamental gap be predicted in DFT

- **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.

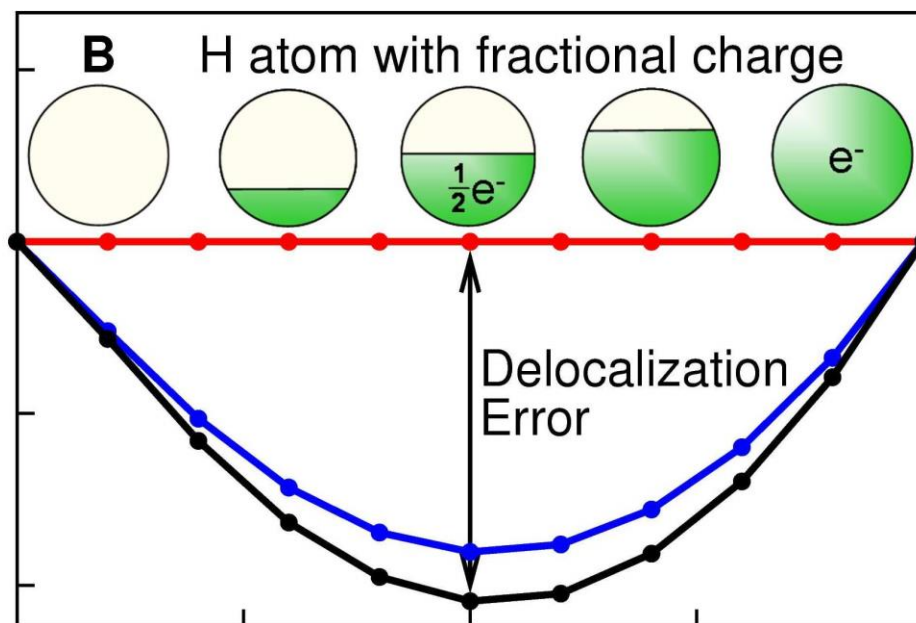
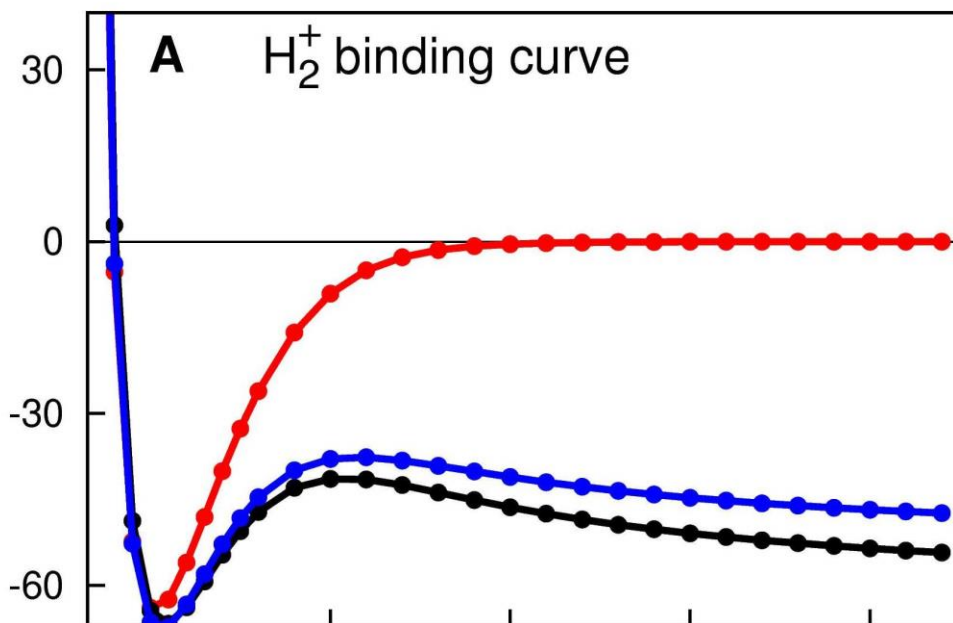


CHEMICAL REVIEWS

Challenges for Density Functional Theory

Aron J. Cohen,^{*} Paula Mori-Sánchez,^{*} and Weitao Yang^{*} 2012

Delocalization Error—Size dependent manifestation

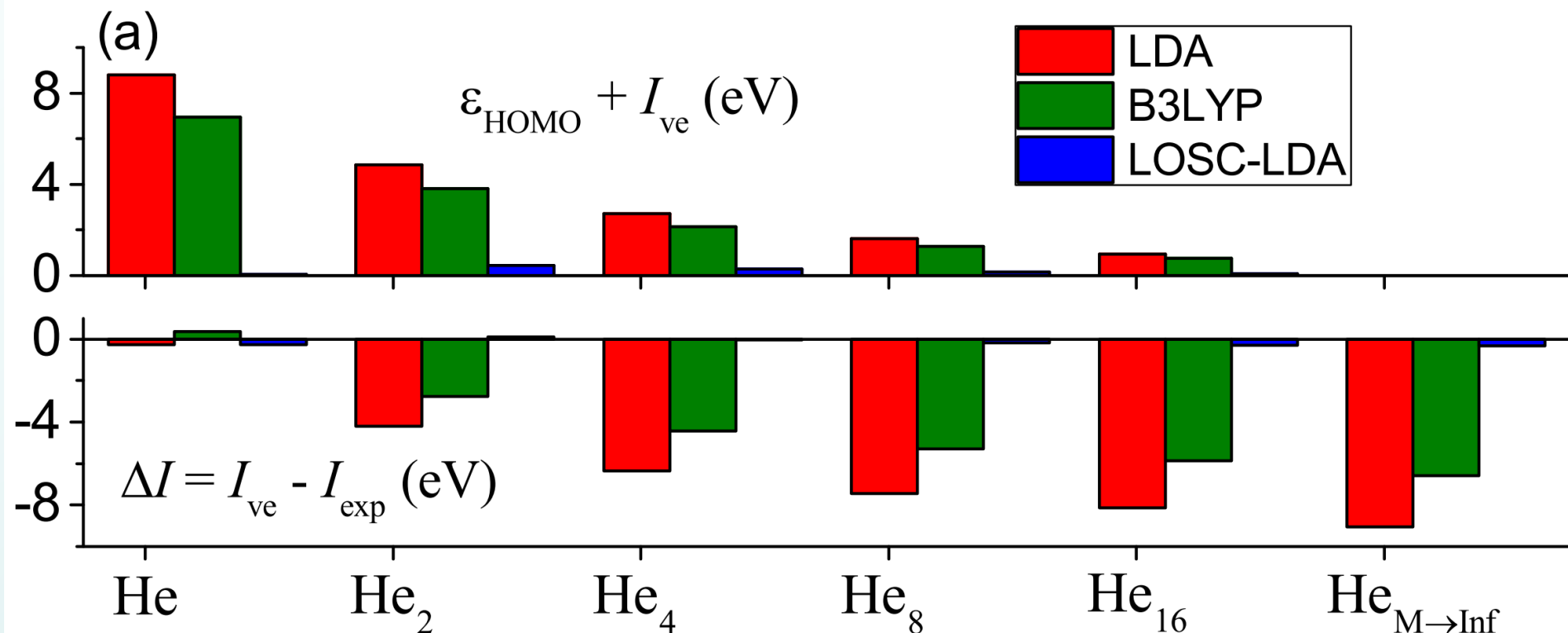


Delocalization Error—Size dependent manifestation

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).

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

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



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

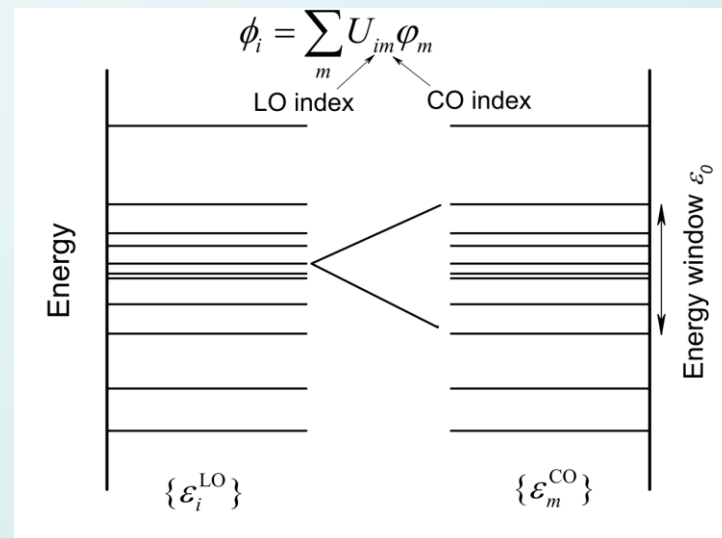
- **Orbitalets**: Novel localized orbitals to represent density matrix.
- **Size-consistent**, functional of the GKS density matrix for corrections to common DFA.
- Accurately characterization of the distributions of **global** and **local** fractional electrons.
- **Systematic improvements**: the dissociation 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

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

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

$$|\phi_{j\sigma}\rangle = \sum_m U_{jm}^\sigma |\psi_{m\sigma}\rangle$$



E-Constrained Optimization

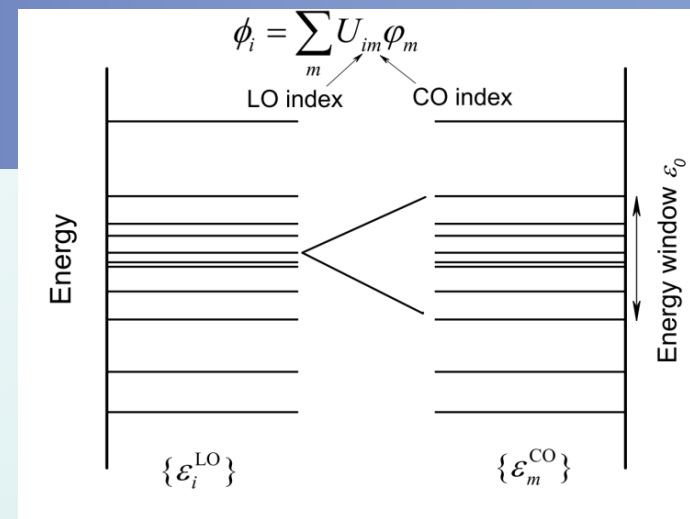
$$F = \sum_i \left[\langle \phi_i | \mathbf{r}^2 | \phi_i \rangle - \langle \phi_i | \mathbf{r} | \phi_i \rangle^2 \right] + \sum_{im} w_{im} |U_{im}|^2$$

Space and Energy localization

$$F = (1 - \gamma) \sum_p \Delta \mathbf{r}_p^2 + \gamma C \sum_p \Delta h_p^2$$

Novel Localized Orbitals

Orbitalets



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

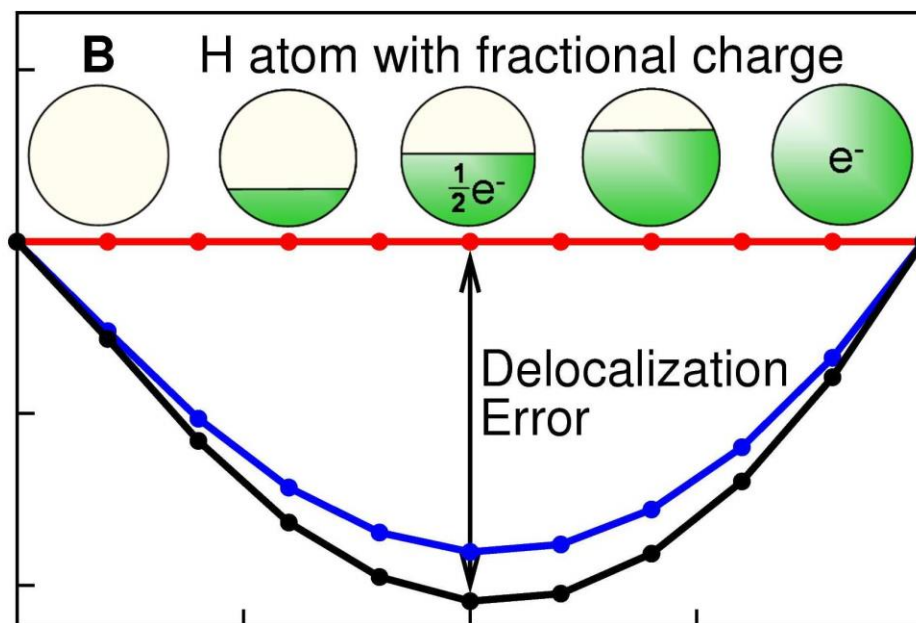
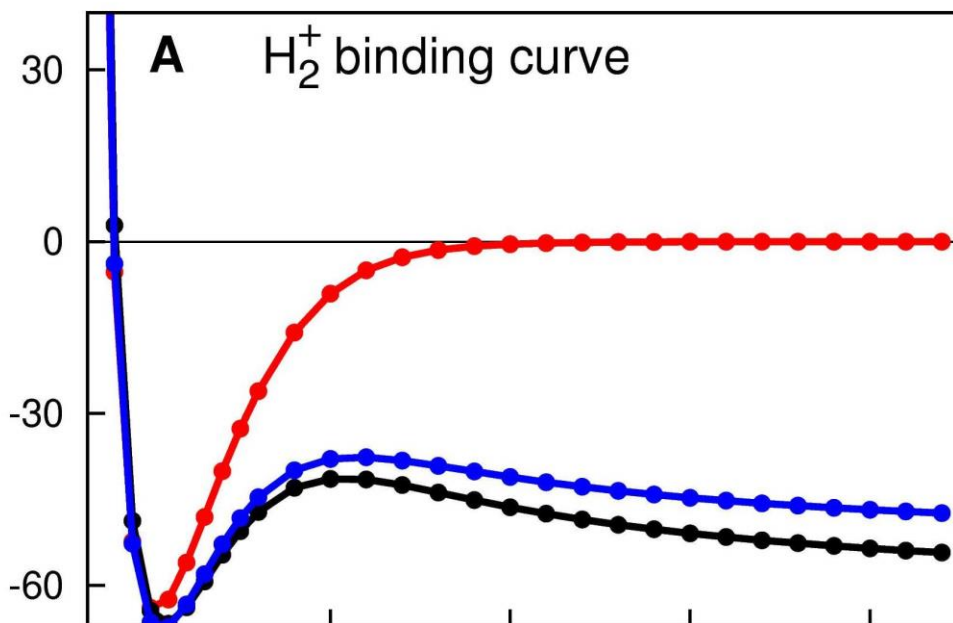
-- Localization **both** in the **physical** space and in the **energy** space.

Traditional

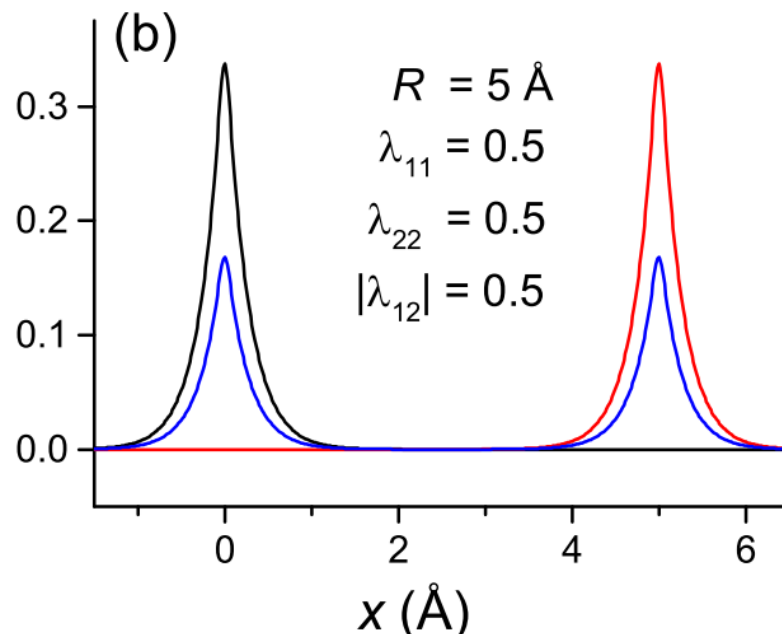
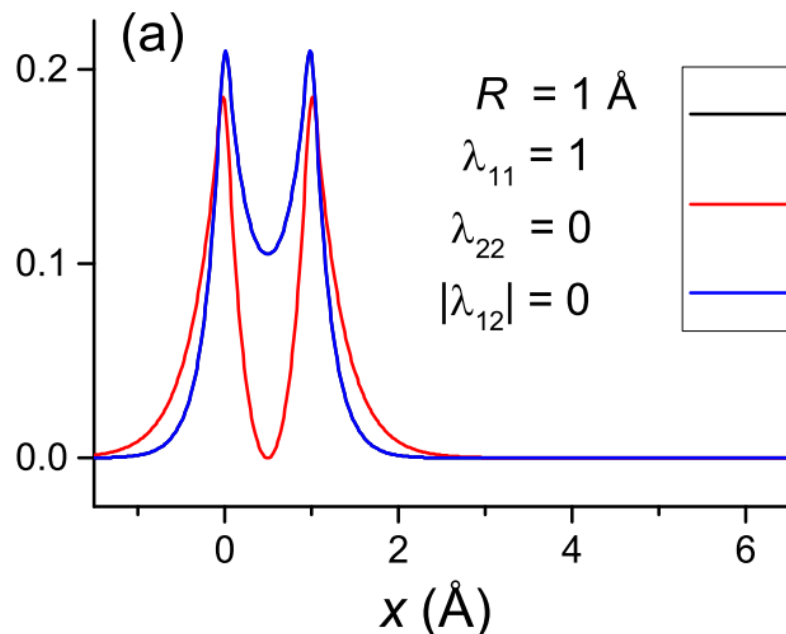
-- localized orbitals -- localization in the physical space

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

Delocalization Error—Size dependent manifestation



Distribution of LO densities in H_2^+



At small R, $R=1\text{Å}$

- Large energy gap between HOMO and LUMO
- Little mixing, LO ~ Canonical Orb, **integer occupations**

At large R, $R=5\text{Å}$

- Small energy gap between HOMO and LUMO
- Much mixing, LO localized, **fractional occupations**

Previous Global and Local Scaling Approach

PRL 2011 and PRL 2015

The GSC/LSC has the following asymptotic form,

$$\Delta E^{\text{GSC}} = \frac{1}{2} \kappa (n_f - n_f^2), \quad (2)$$

$$\Delta E^{\text{LSC}} \approx \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \tilde{n}_f(\mathbf{r}) [1 - \tilde{n}_f(\mathbf{r}')] \tilde{\kappa}(\mathbf{r}, \mathbf{r}'). \quad (3)$$

$$\frac{\partial^2 \Delta E^{\text{GSC}}}{\partial n_f^2} = -\kappa$$

$$\frac{1}{2} \kappa = \frac{1}{2} \iint \frac{\rho_f(\mathbf{r}) \rho_f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{C_x}{3} \int [\rho_f(\mathbf{r})]^{\frac{4}{3}} d\mathbf{r},$$

New LOSC, as correction to DFA

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

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

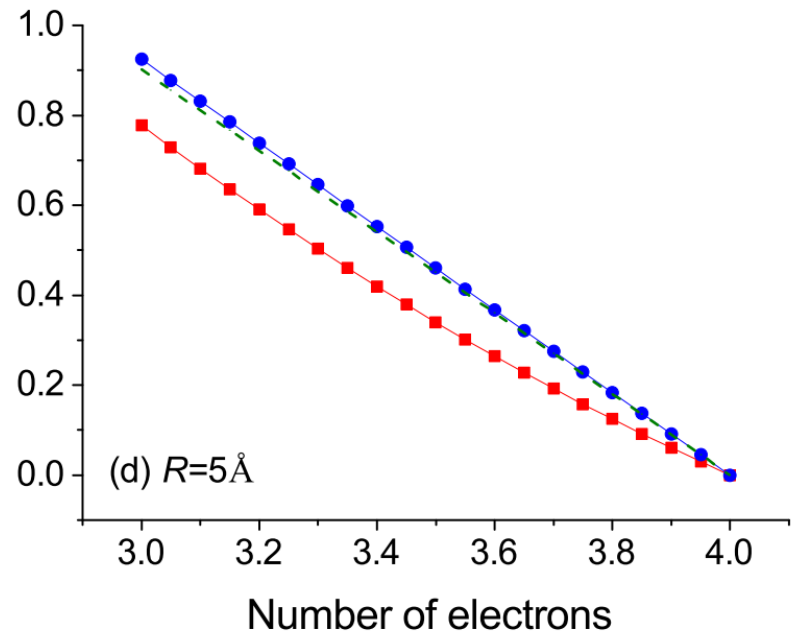
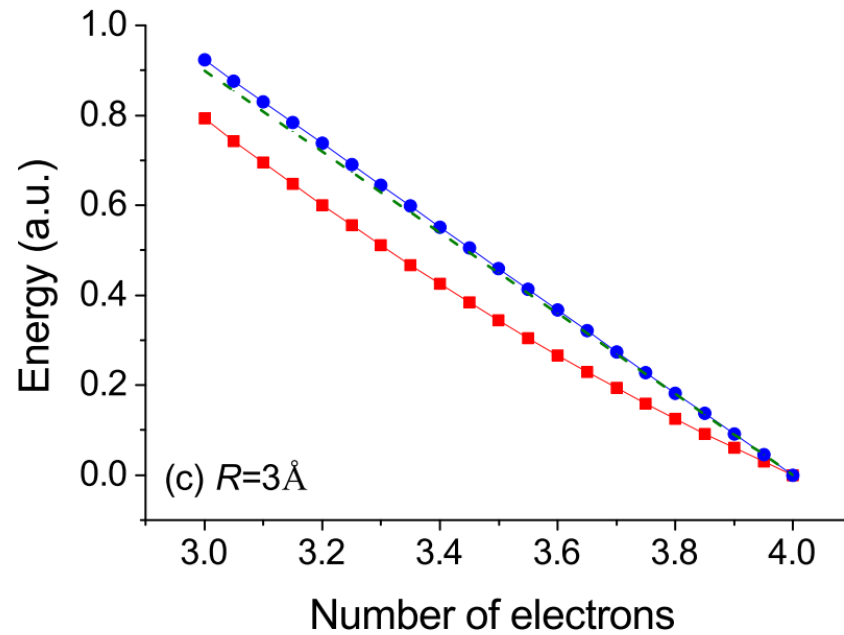
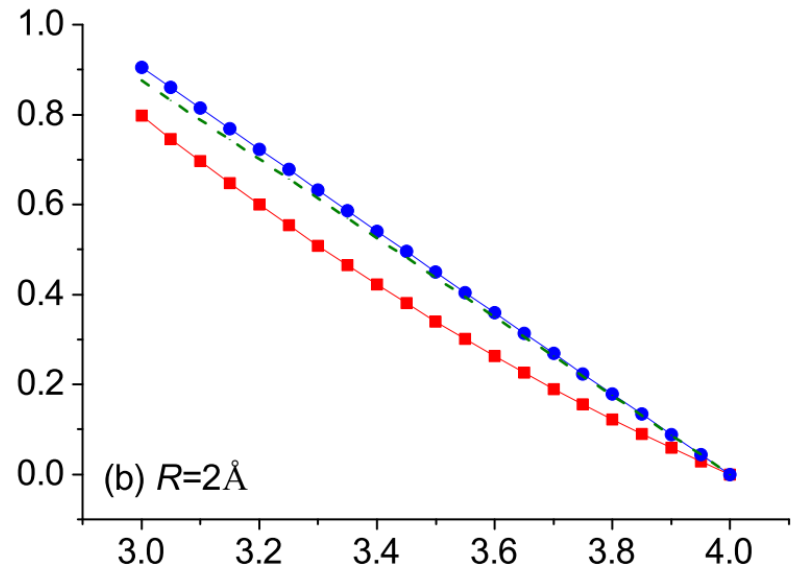
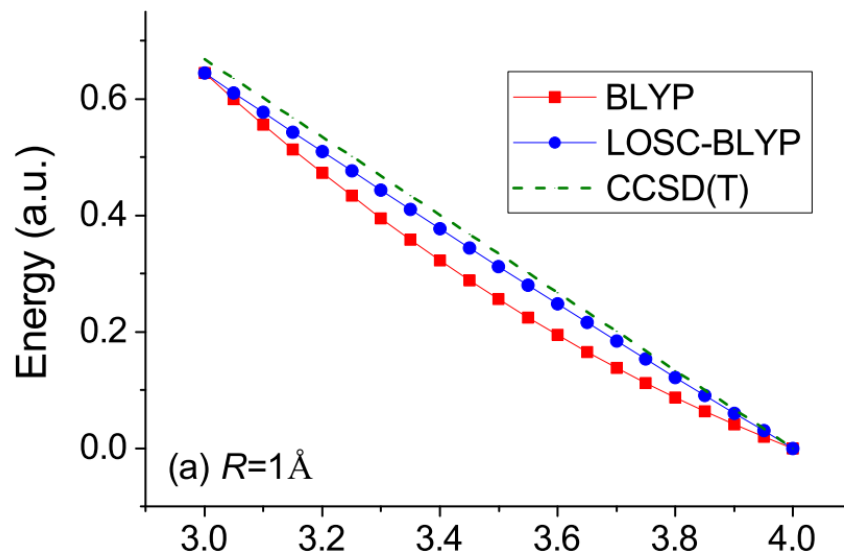
Non-empirical parameter to
get correct limit for H_2^+

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

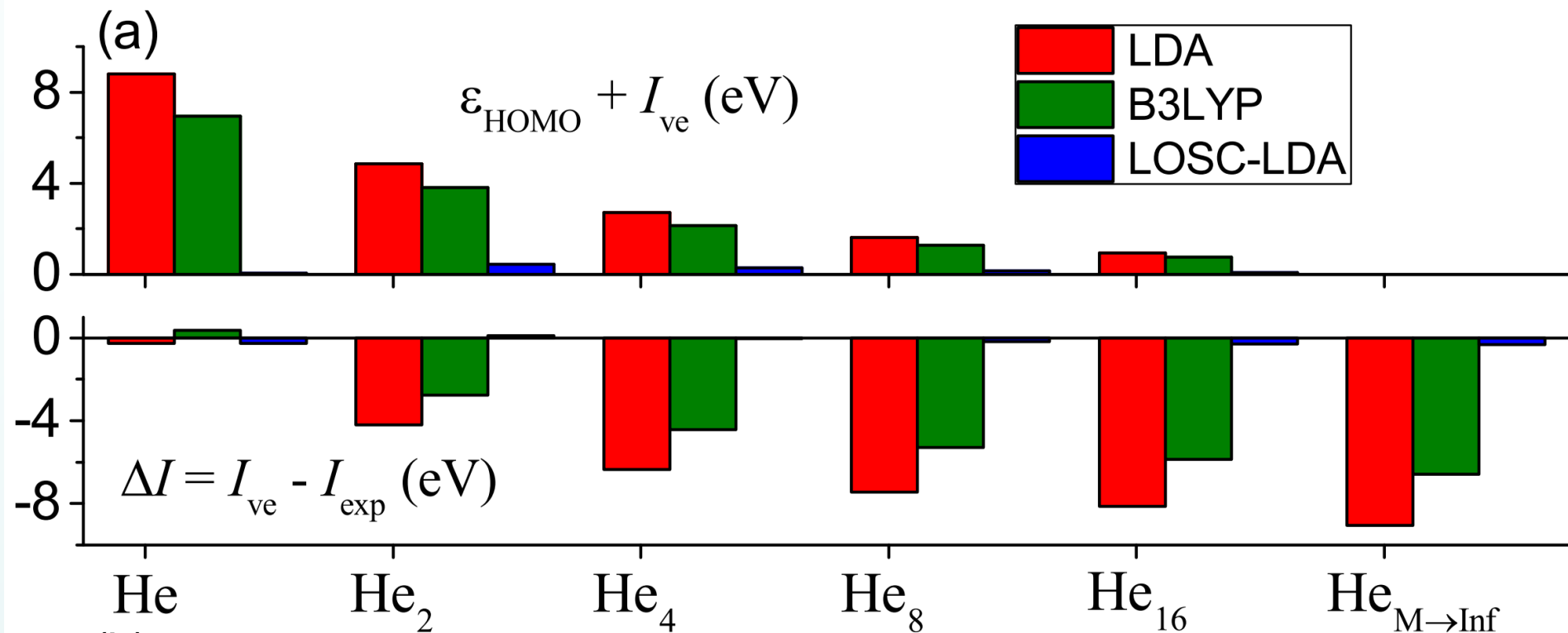
Orbital energy corrections

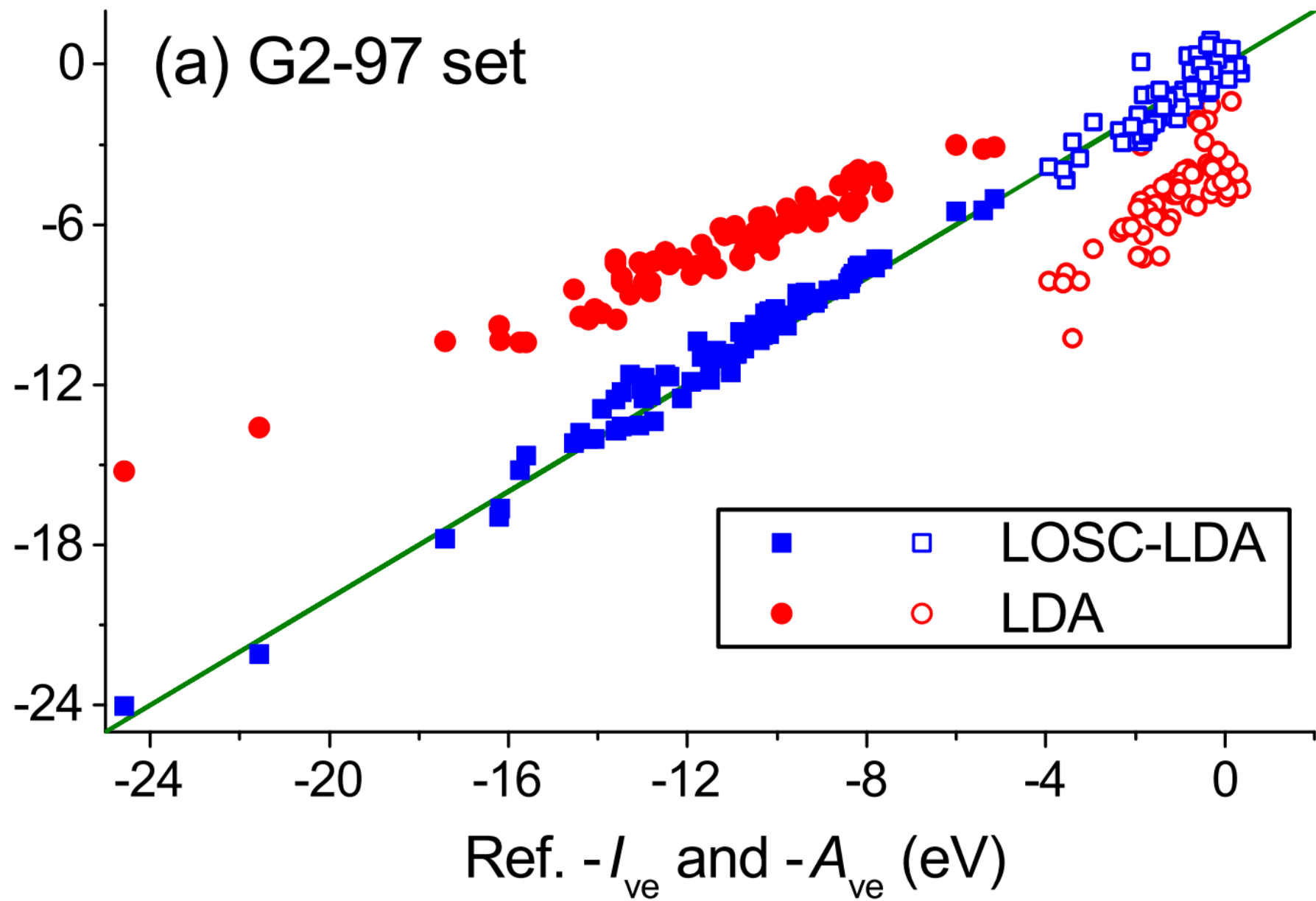
$$\Delta \epsilon_m = \sum_i \kappa_{ii} \left(\frac{1}{2} - \lambda_{ii} \right) |U_{im}|^2 - \sum_{i \neq j} \kappa_{ij} \lambda_{ij} U_{im} U_{jm}^*$$

Linear $E(N)$ and Size-Consistent: $He_2(R)$

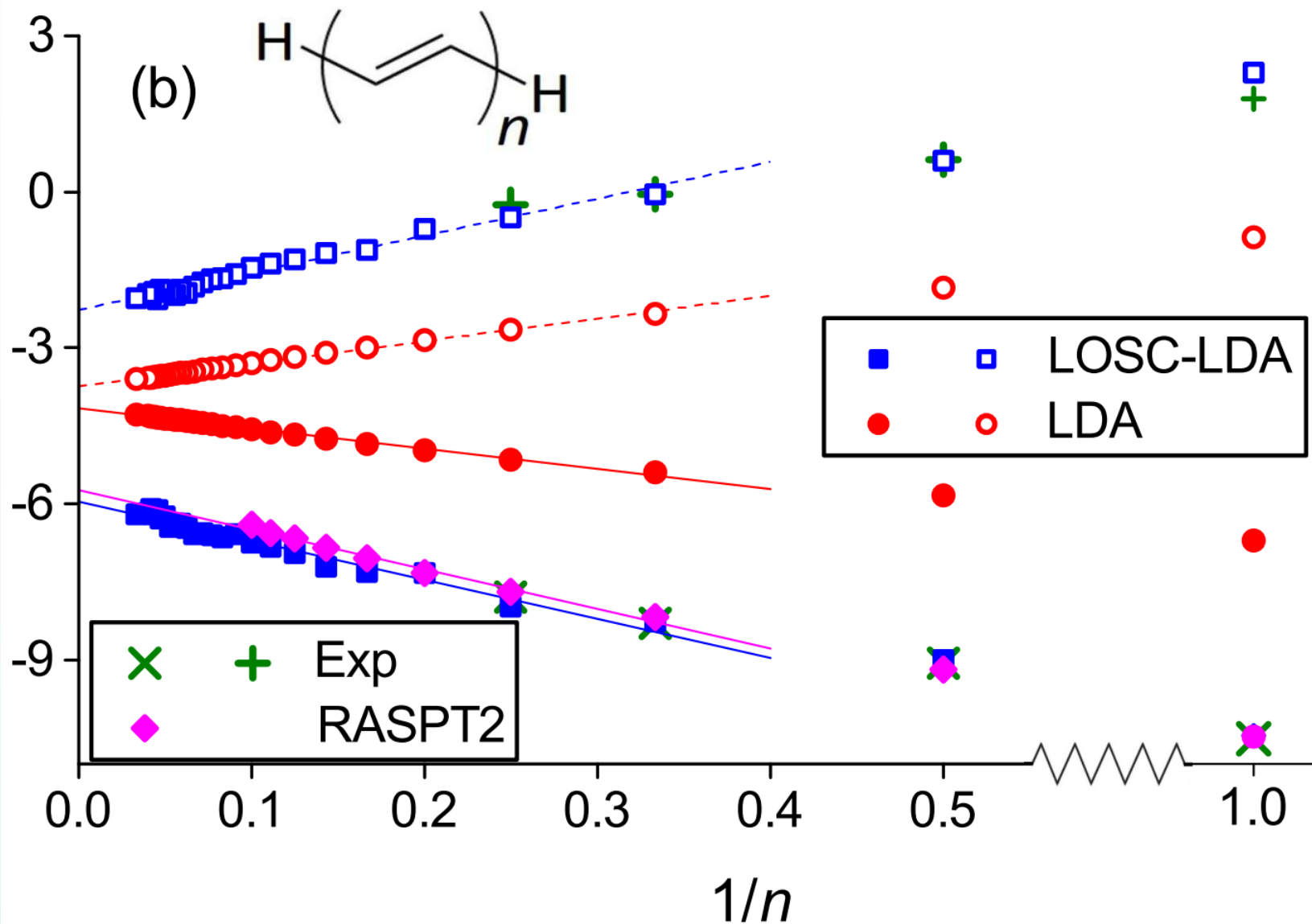


LOSC: Linear $E(N)$ and Size-Consistent

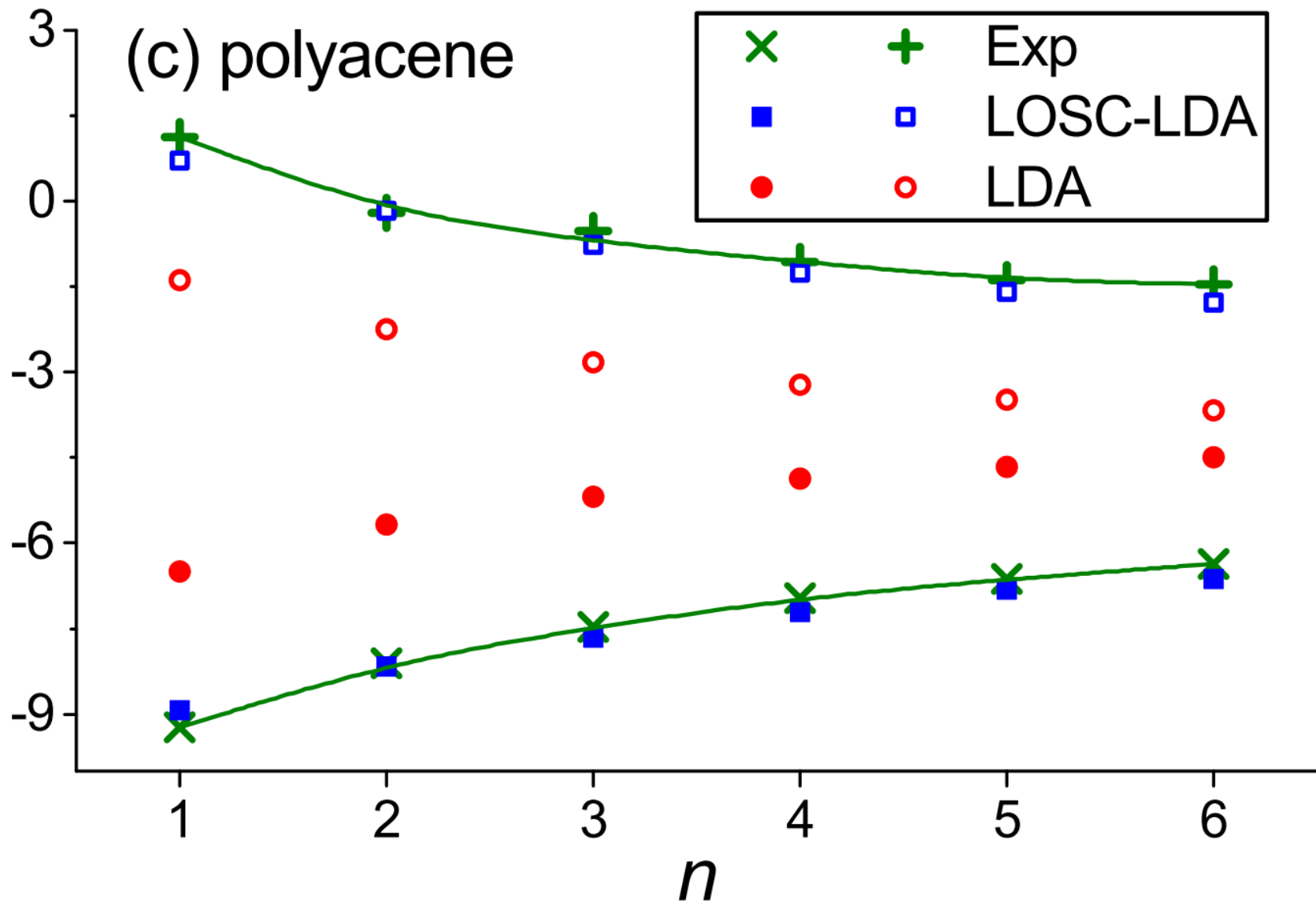




LOSC: HOMO, LUMO and Energy Gaps



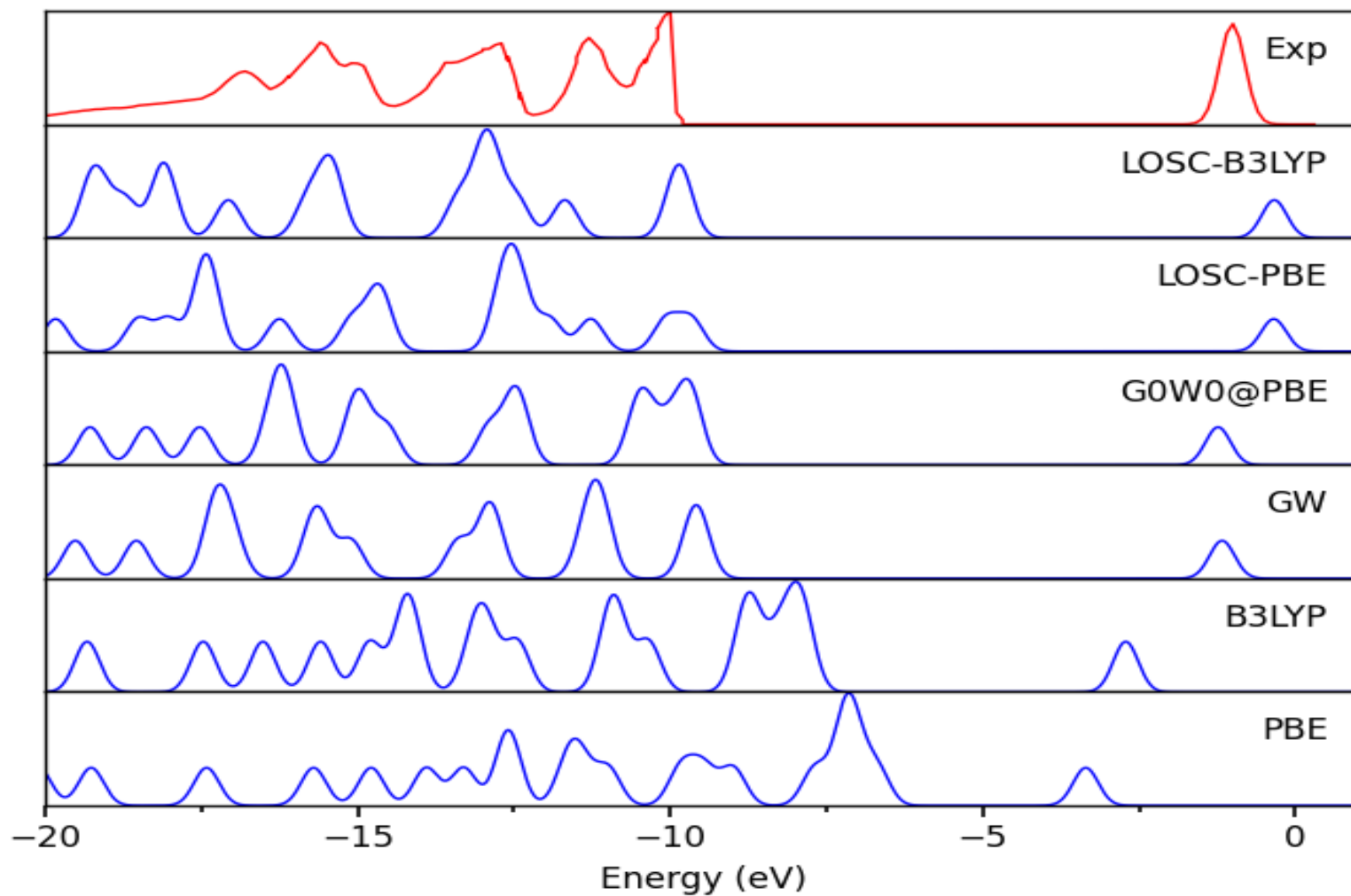
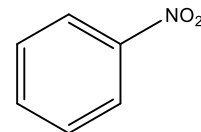
LOSC: HOMO, LUMO and Energy Gaps



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

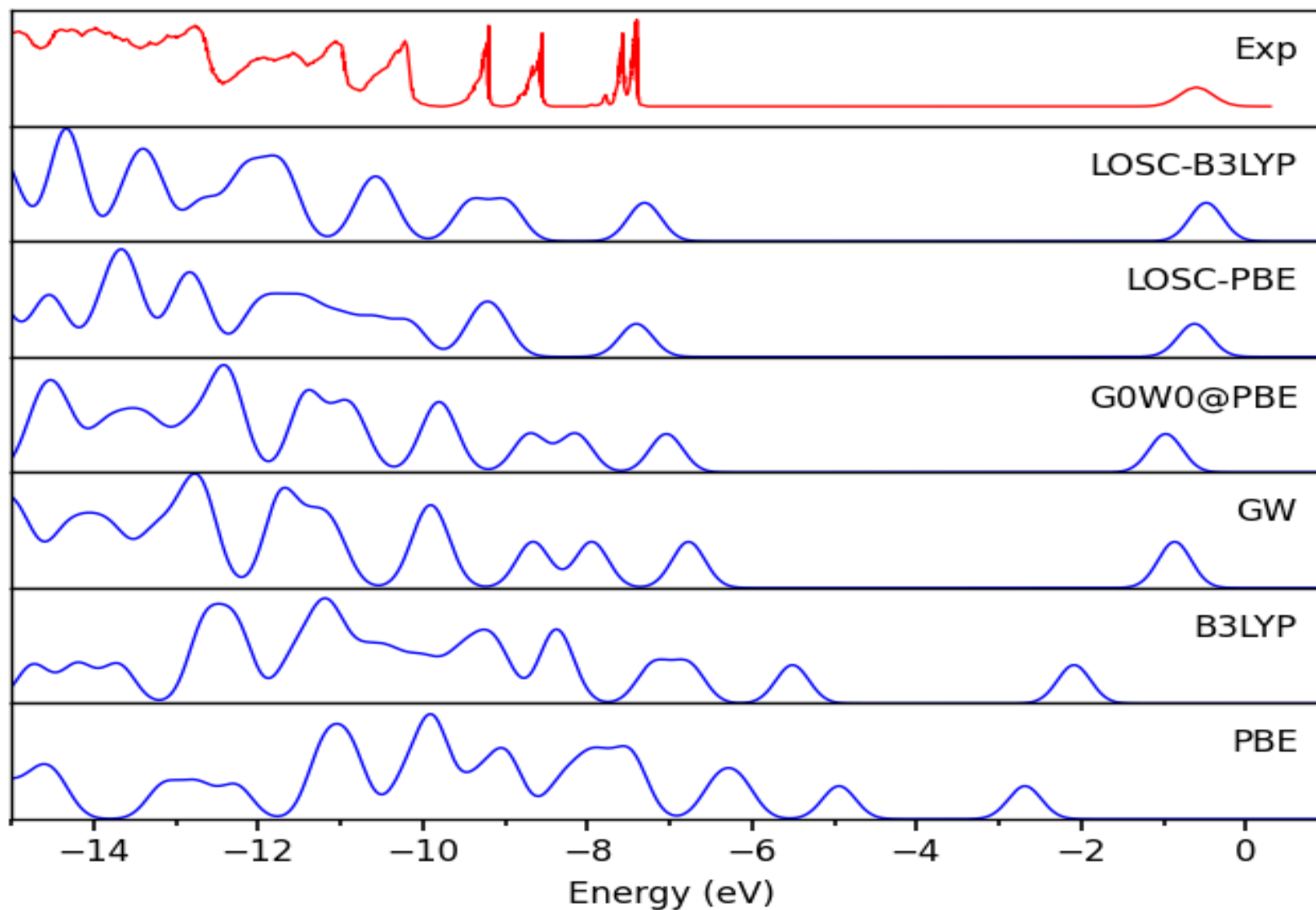
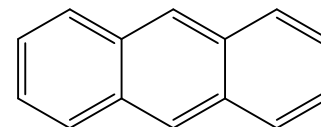
Method	IP	EA
scGW	0.47	0.34
G ₀ W ₀ -PBE	0.51	0.37
LOSC-BLYP	0.47	0.32
LOSC-PBE	0.37	0.32
LOSC-B3LYP	0.26	0.27
LOSC-LDA	0.34	0.48
BLYP	2.98	1.99
PBE	2.81	2.17
B3LYP	2.00	1.58
LDA	2.58	2.44

Photoemission spectrum of nitrobenzene

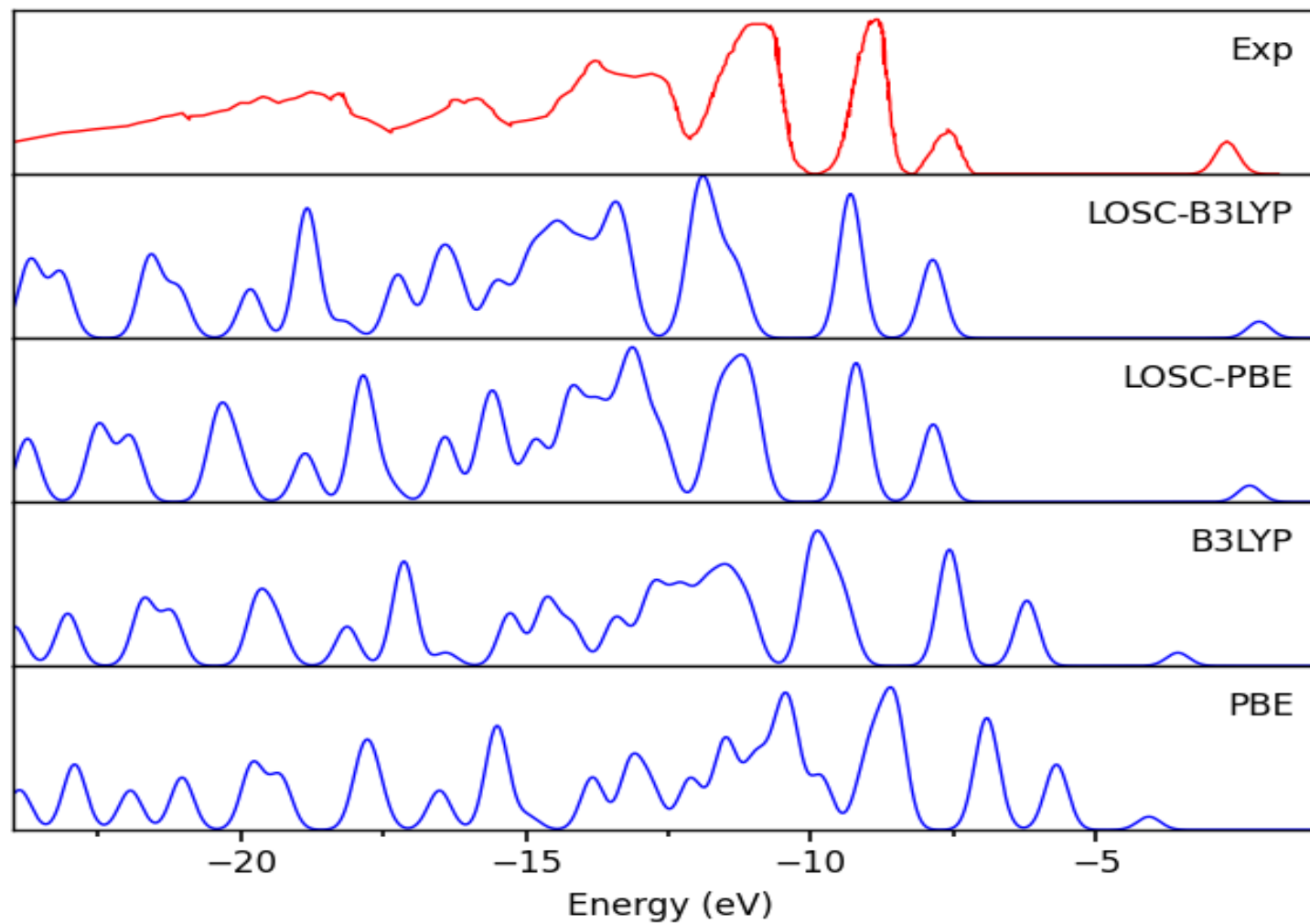
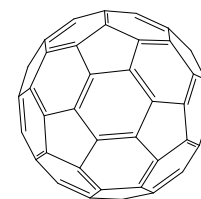


GW data: Knight, J. W.; Wang, X.; Gallandi, L.; Dolgounitchcheva, O.; Ren, X.; Ortiz, J. V.; Rinke, P.; Körzdörfer, T.; Marom, N. J. Chem. Theory Comput. 2016, 12, 615–626.

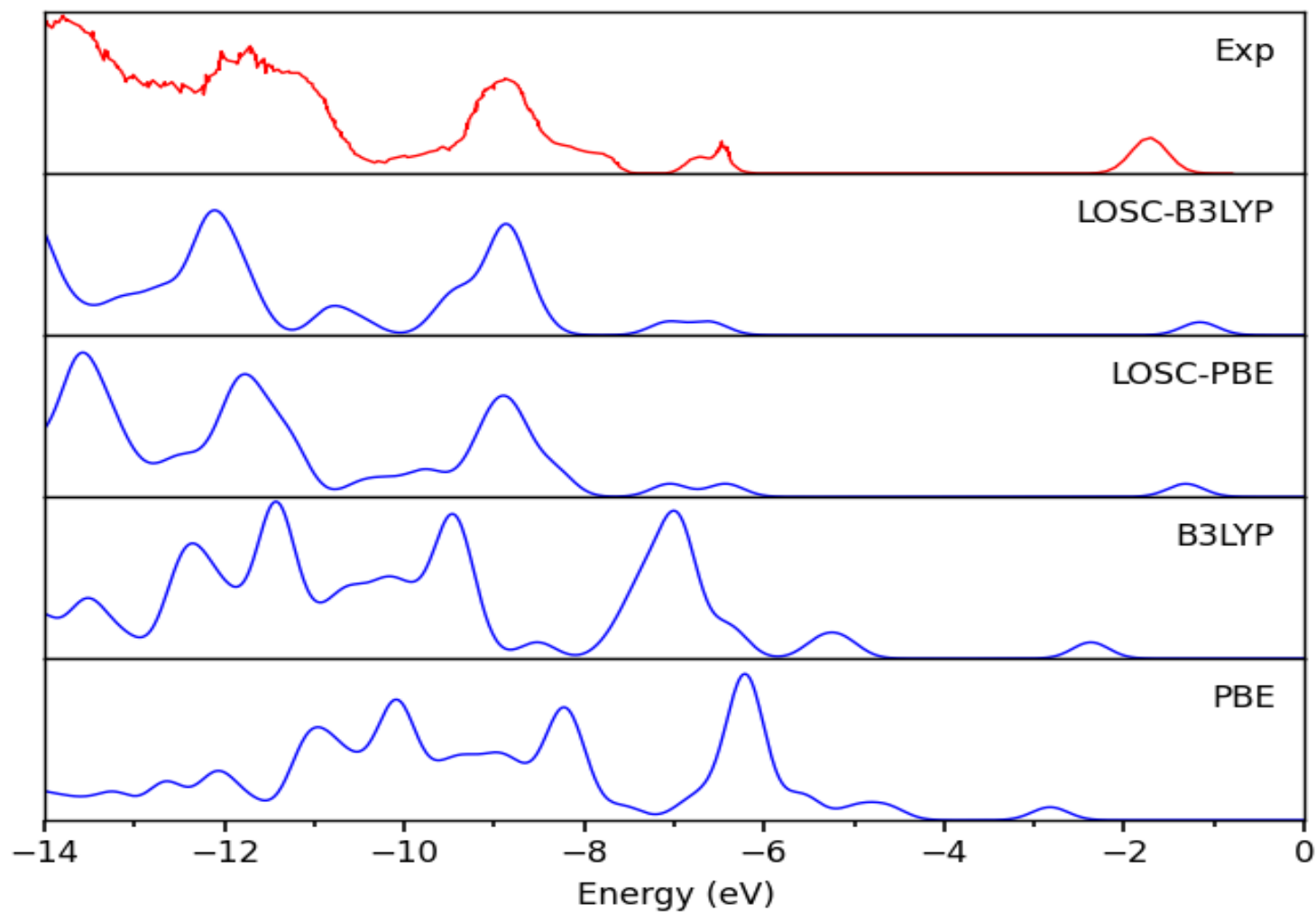
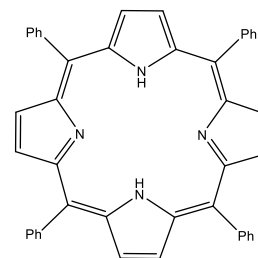
Photoemission spectrum of anthracene



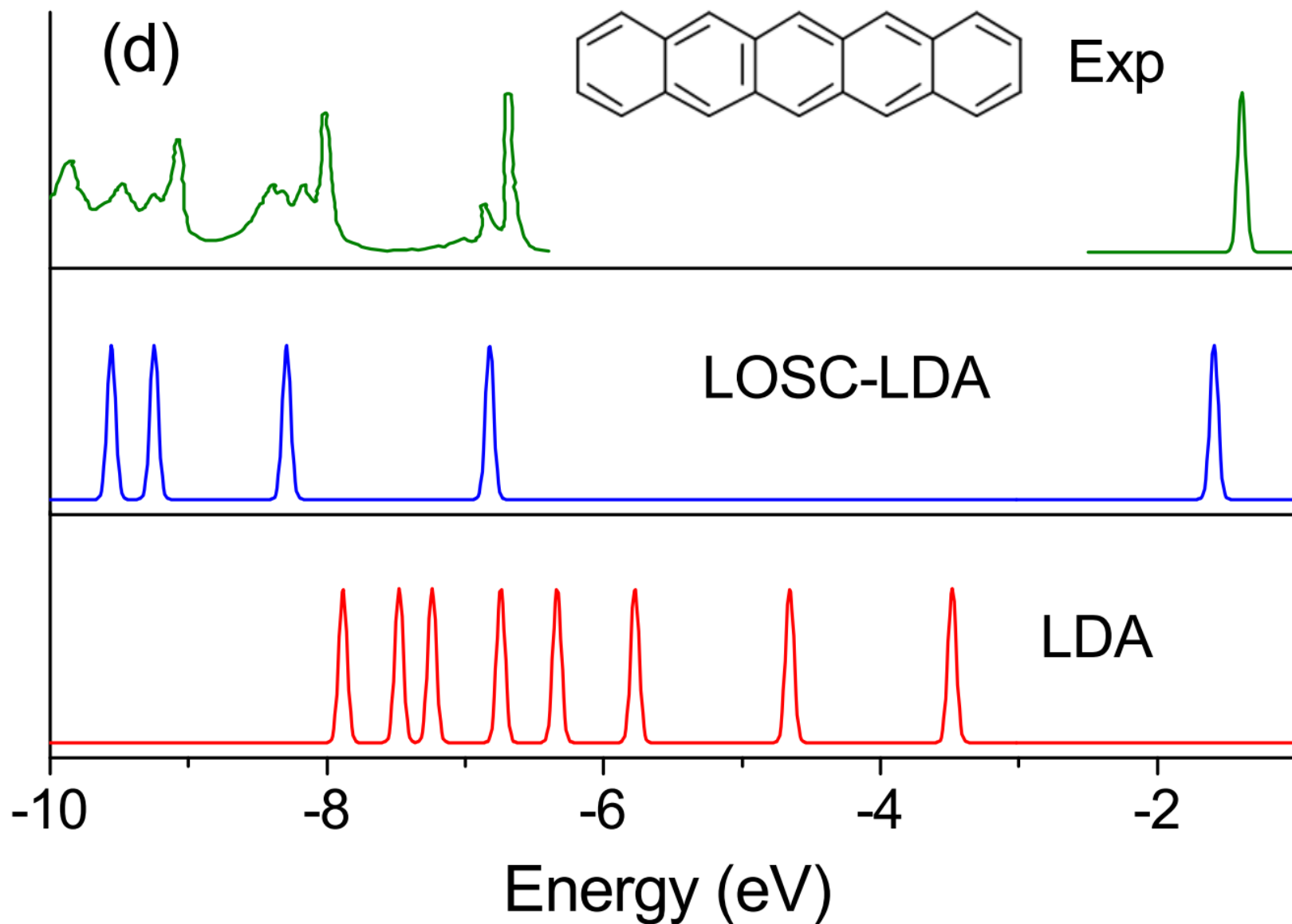
Photoemission spectrum of C₆₀



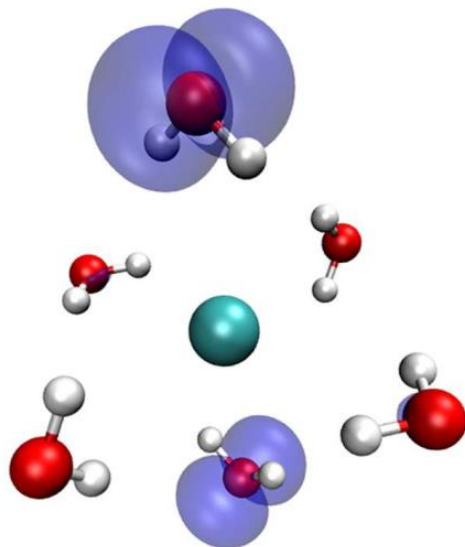
Photoemission spectrum of H₂TPP



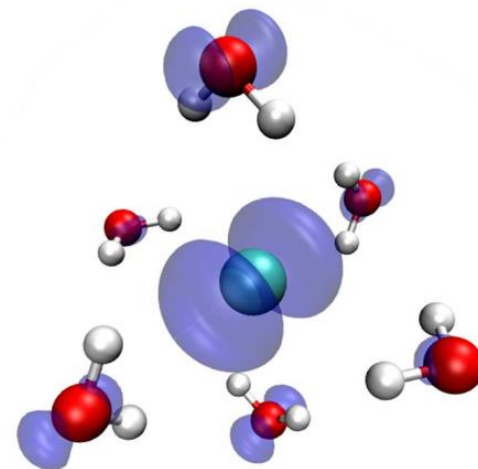
LOSC: photoemission spectra



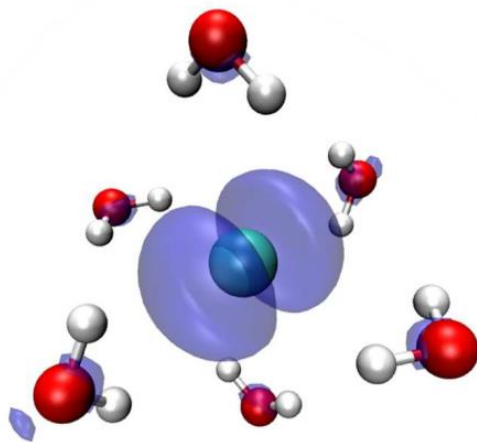
LOSC: corrections to electron density



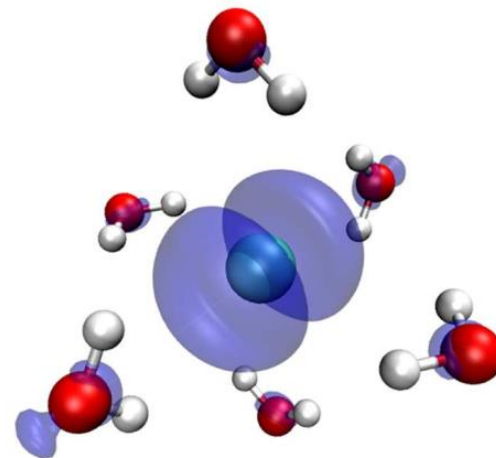
PBE $\Delta q(\text{Cl}) = 0.04$



B3LYP $\Delta q(\text{Cl}) = -0.67$



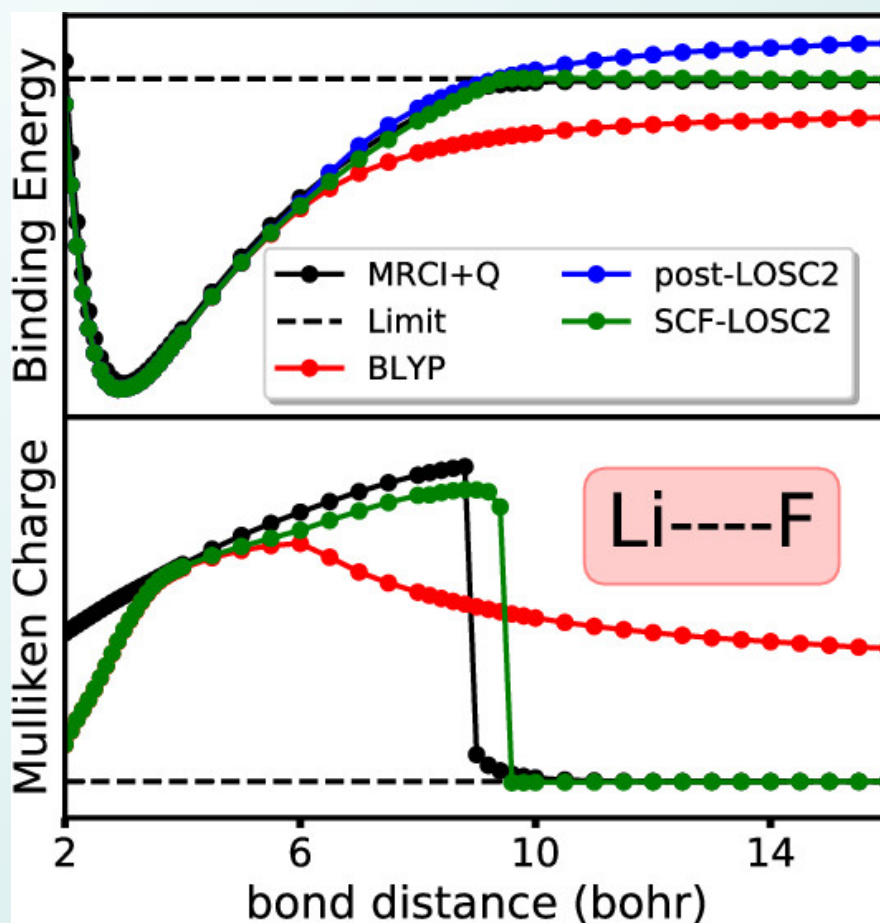
LOSC-PBE $\Delta q(\text{Cl}) = -0.92$



CCSD $\Delta q(\text{Cl}) = -0.96$

Self-Consistent Calculation of the Localized Orbital Scaling Correction for Correct Electron Densities and Energy-Level Alignments in Density Functional Theory

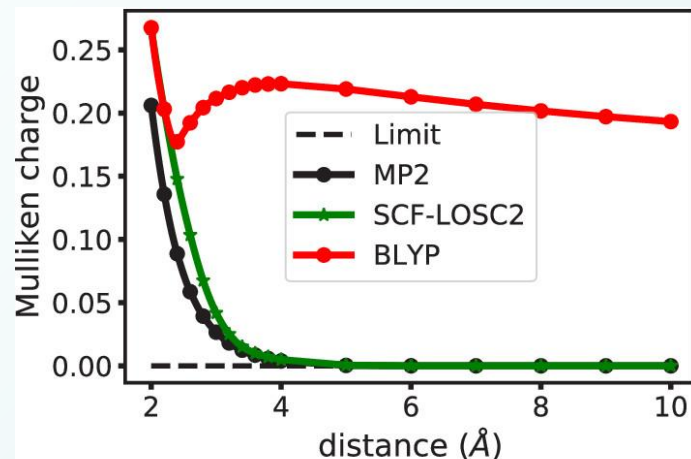
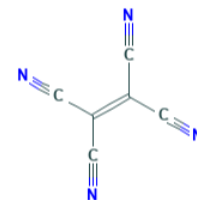
Yunca Mei,^{||} Zehua Chen,^{||} and Weitao Yang*



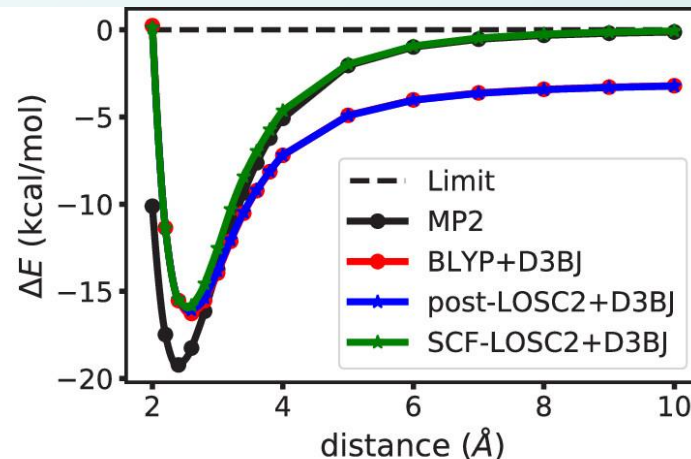
Donor (1,4-benzenediamine)



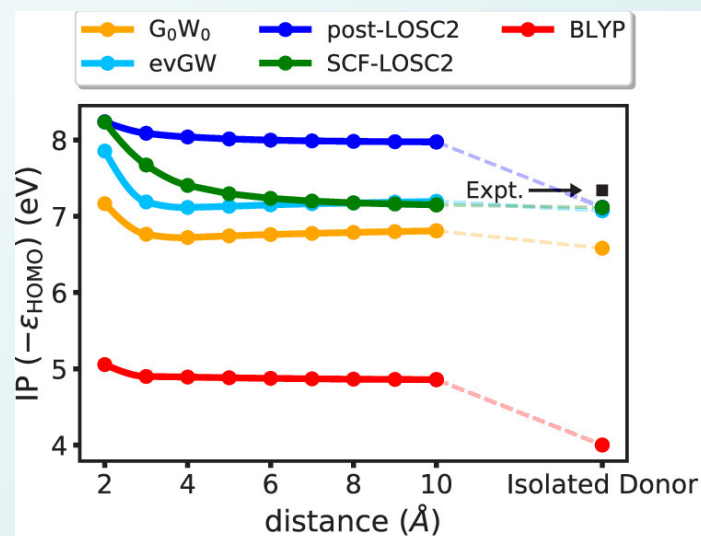
Acceptor (tetracyanoethylene)



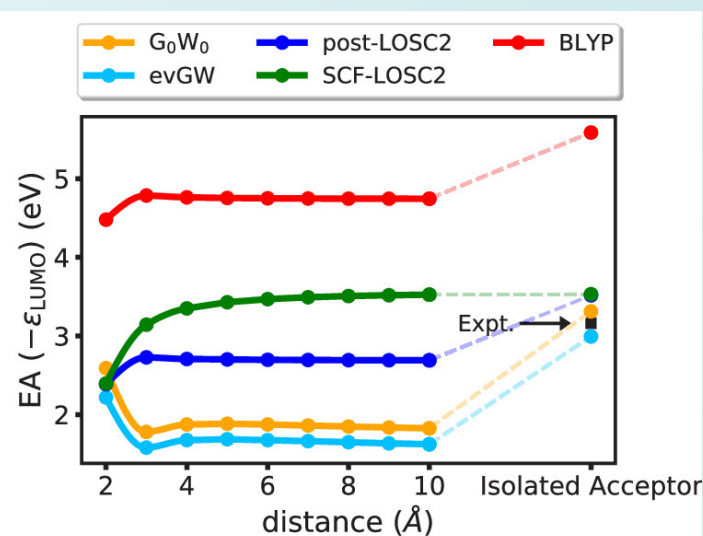
(a) Mulliken charge



(b) Relative total energy



(a) IP



(b) EA

LOSC: Summary

- Very different from conventional density functionals
- Novel localized Orbitals with energy and space localization – ***Orbitalets***
- Functional of the Generalized Kohn-Sham density matrix
- Size-consistent**

Prospective of DFT Approximations—bright future

Strategy of nonlocal corrections

---Imposing the exact constraints of fractional charges and fractional spins

Semilocal functionals + Nonlocal corrections

- LOSC: Eliminating delocalization error
 - Band gaps
 - Energy alignment
 - Charge transfer
 -
- Describing strong correlation (static correlation) — using fractional spins (**PNAS, 2018**)