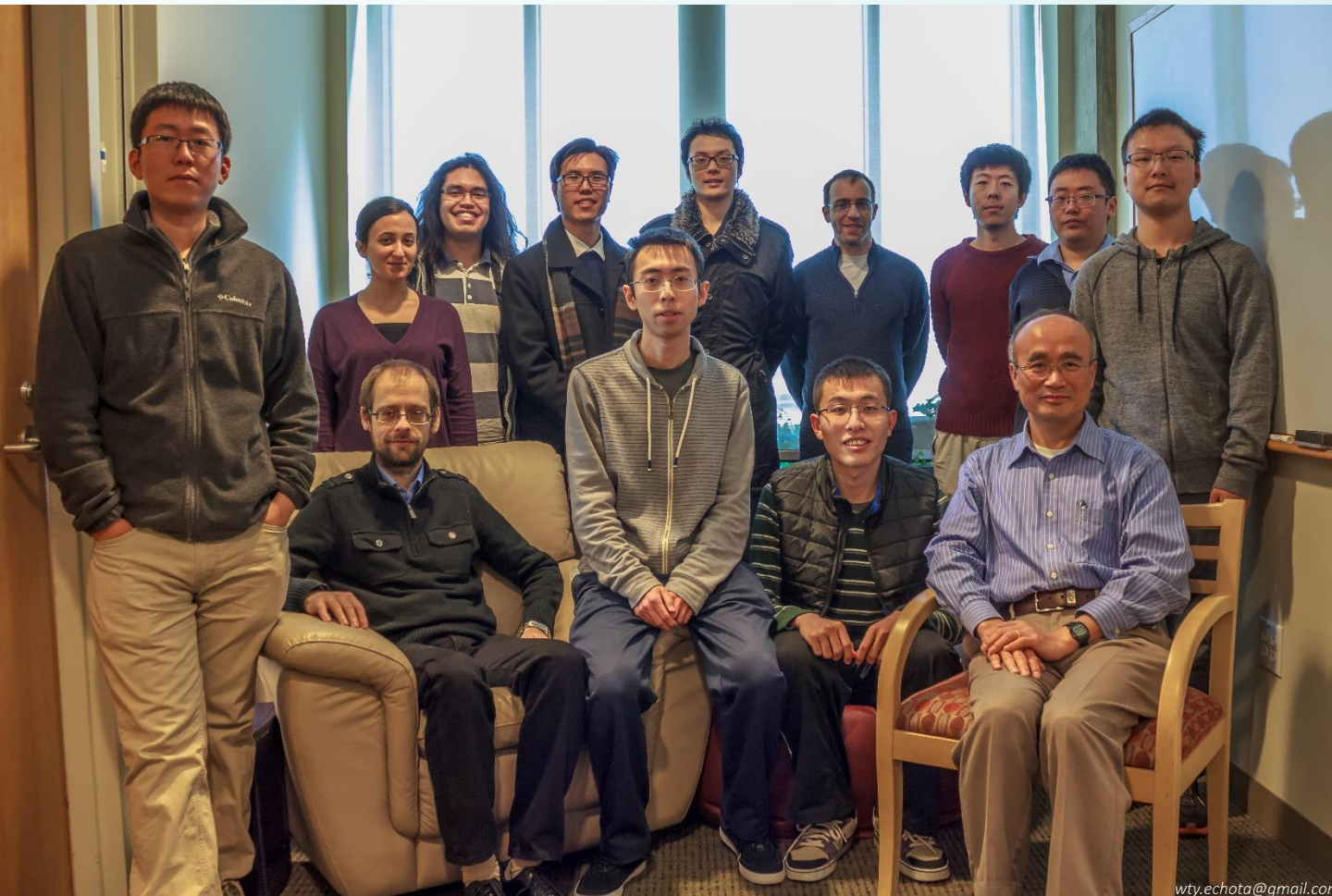# Going Beyond Conventional Functionals
with Local Scaling Corrections and Pairing Fluctuations

Pairing Fluctuations

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 Temple Univ.
NSF
NIH
Samsung

USTC-FHI, Hefei
June 15, 2016

Outline

- Challenges and Insight in DFT from Fractional Perspectives

- Scaling Corrections to Approximate Functionals

- Pairing Matrix Fluctuations--Connecting DFT to many-body theory through the pairing channel for electron correlation

    - Pp-RPA as an approximation of linear response to a pairing field perturbation

    - Capturing double, charge transfer and Rydberg excitations

   - Diradicals, Conical Intersections

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
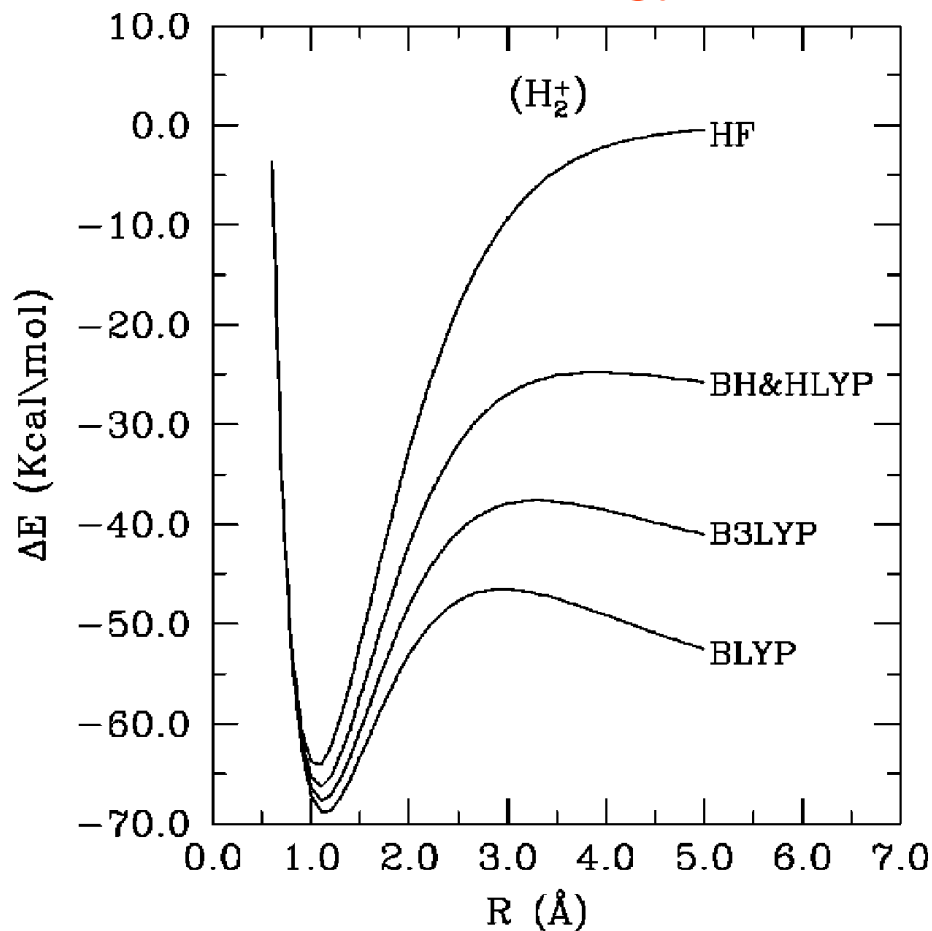- Diels-Alder reactions, highly branched alkanes, dimerization of aluminum complexes
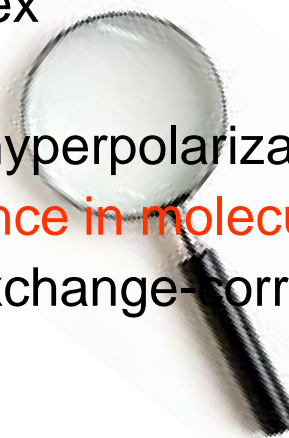
Delocalization Error

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

Savin, in Seminario, "Recent Developments and Applications of Modern DFT", 1996

DFT for fractional number of electrons

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

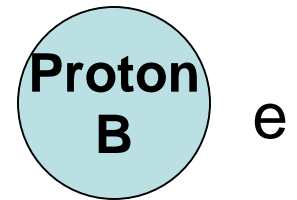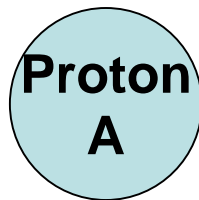$$E_{N+\delta} = (1 - \delta)E_N + \delta E_{N+1}$$
$$\rho_{N+\delta} = (1 - \delta)\rho_N + \delta\rho_{N+1}$$
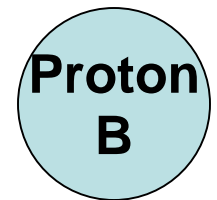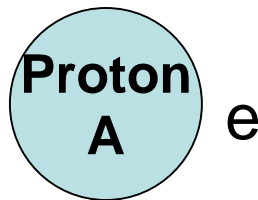
Where can you find fractional charges?

WY, Yingkai Zhang and Paul Ayers, PRL, 2000 – pure states
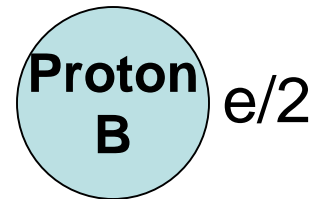
H_2^+ **at the dissociation limit**
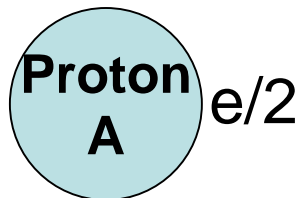
Ψ_α

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

Proton A   **Proton B** e

Ψ_β
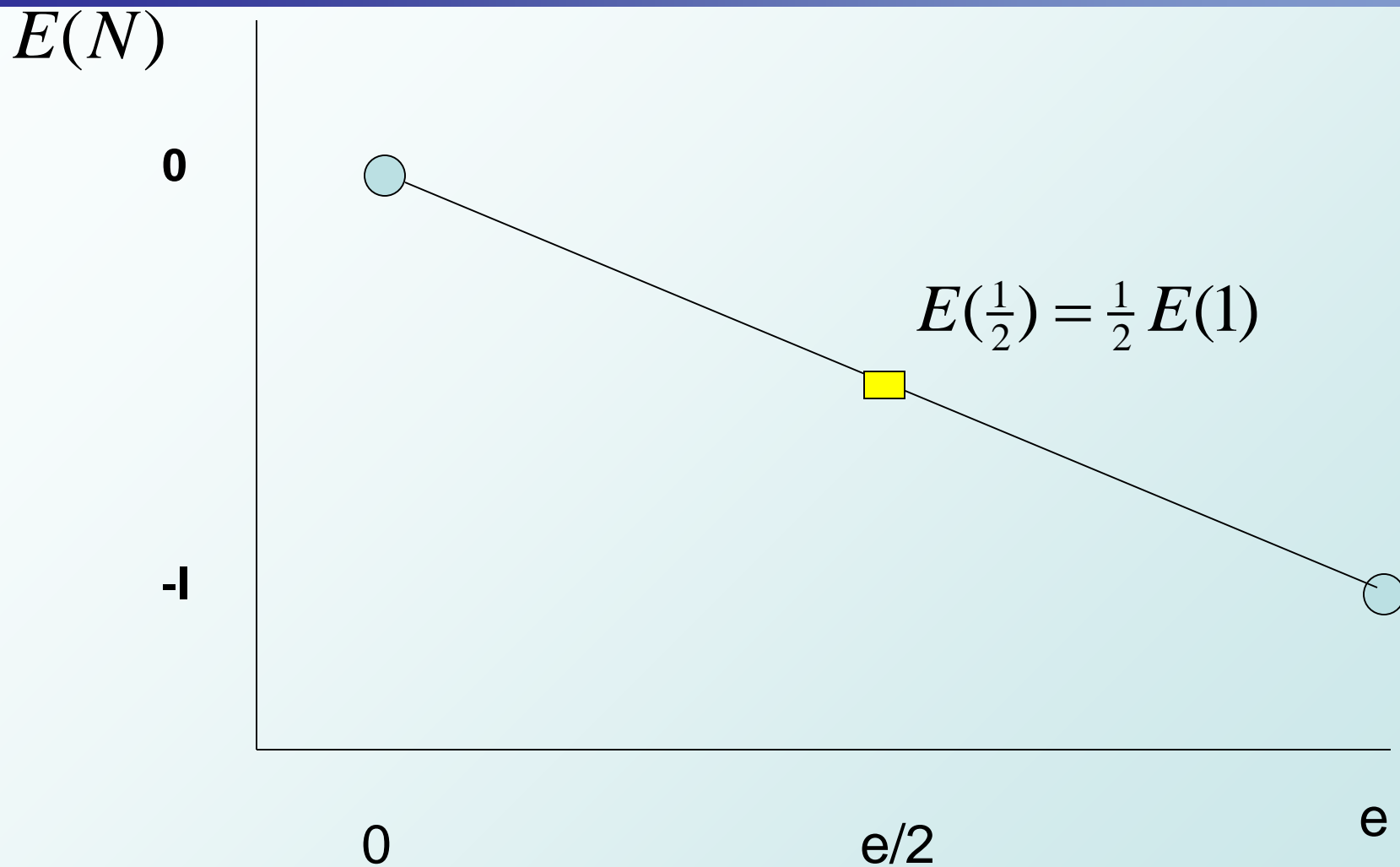
$E_\beta = E(1) + E(0)$

Proton A e   **Proton B**

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

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

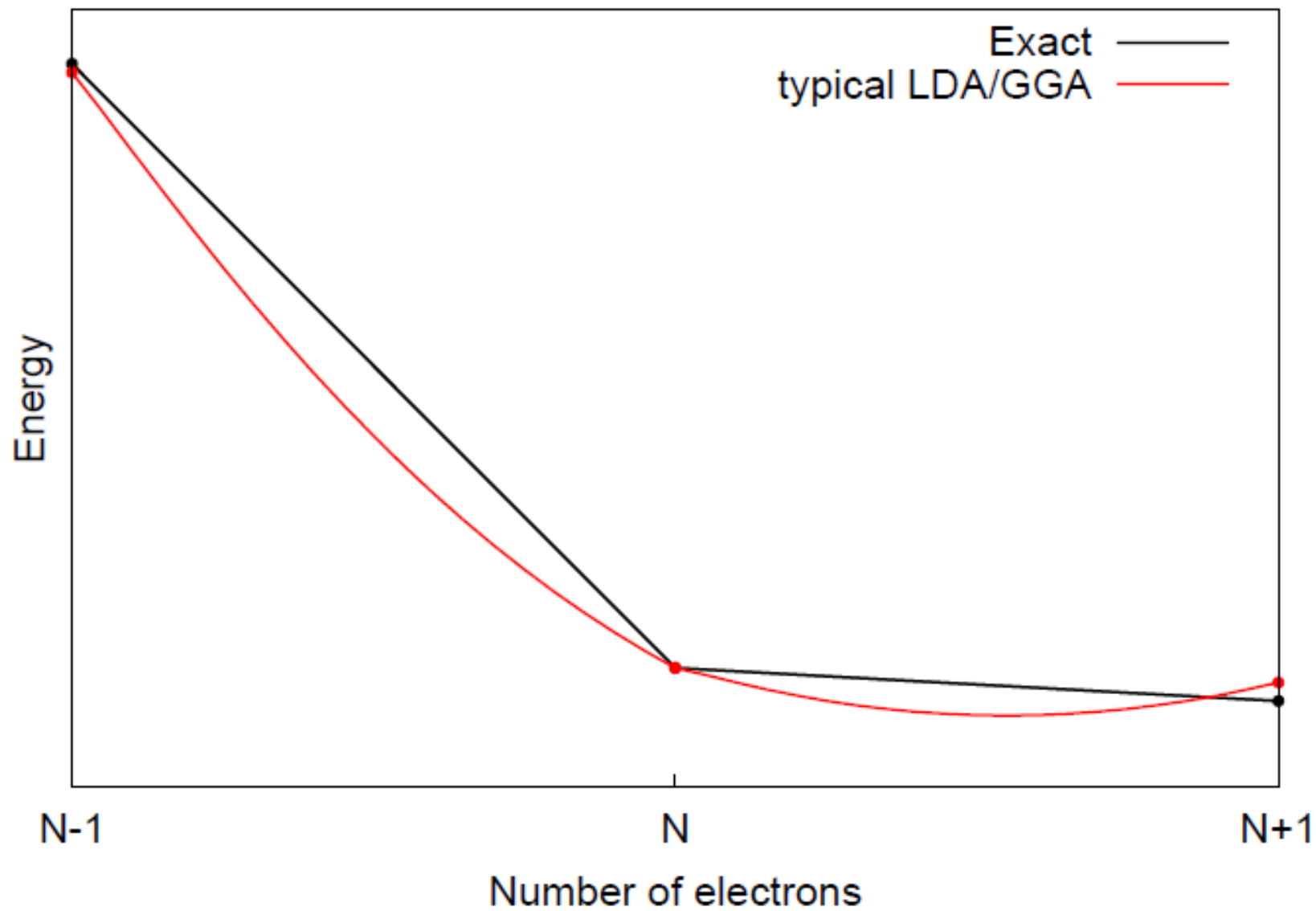**Proton A** e/2   **Proton B** e/2

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

$E(N)$

0

-I

$$E(\tfrac{1}{2}) = \tfrac{1}{2}\, E(1)$$

0   e/2   e

E(N)

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

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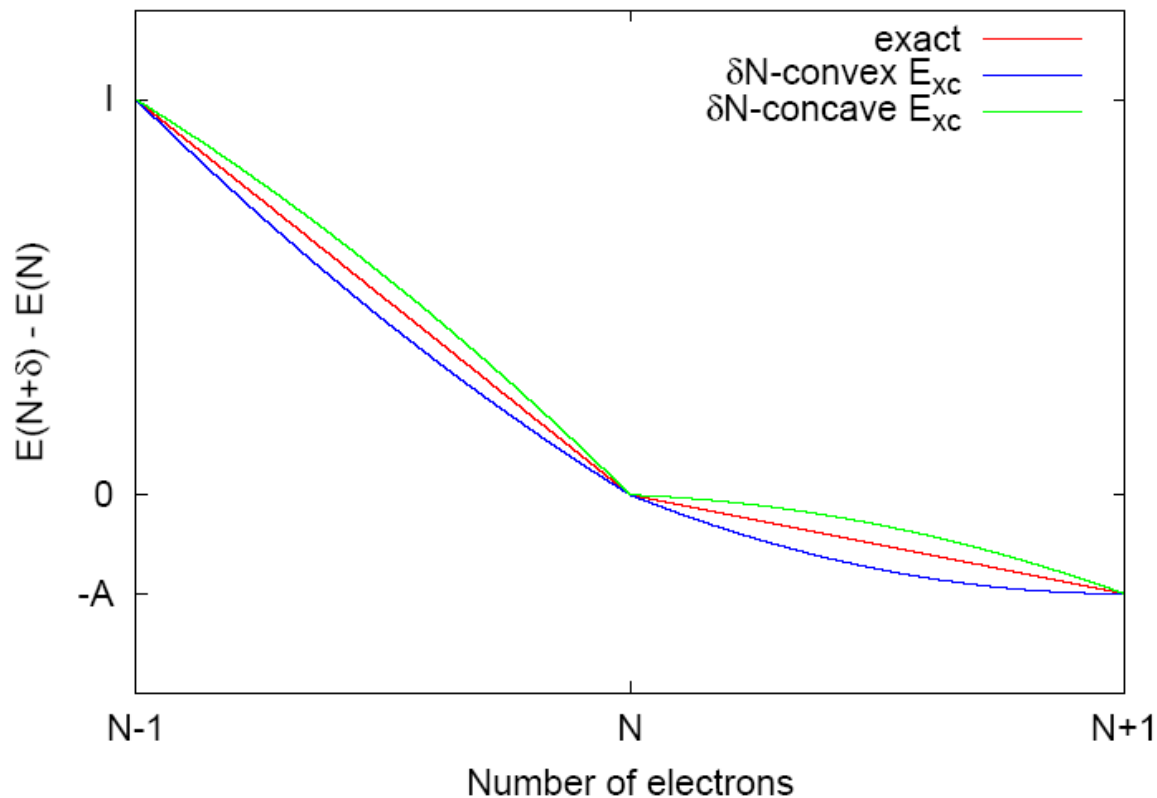
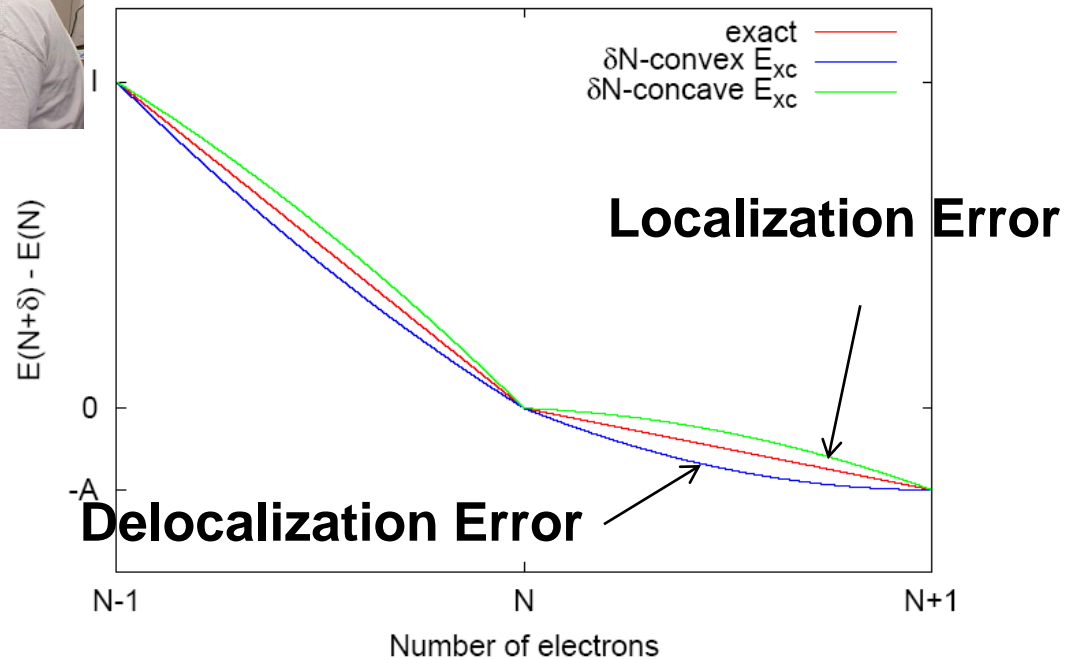For δN-**convex,** $2E(N + \dfrac{1}{2}) <\ E(N) + E(N+1),$ **delocalized**

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

Delocalization and Localization Error
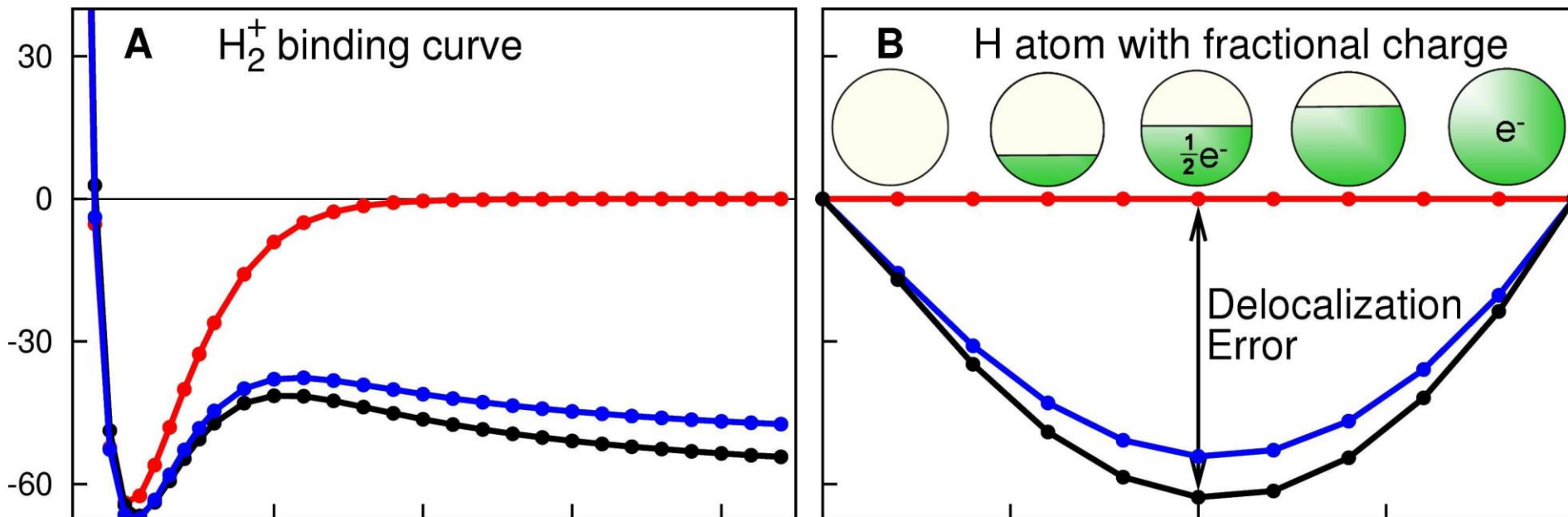Paula Mori-Sanchez, Aron Cohen and WY, *PRL 2008*

Consequence of Delocalization Error
1. predicts too low energy for delocalized distributions

2. gives too delocalized charge distributions
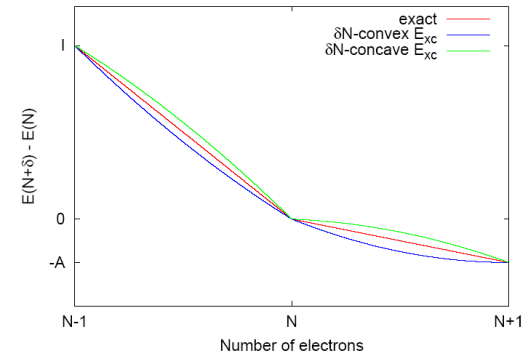
Delocalization Error

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

Cohen, Mori-Sanchez and Yang, 2008 Science

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 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.

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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

Where is the negative charge ?
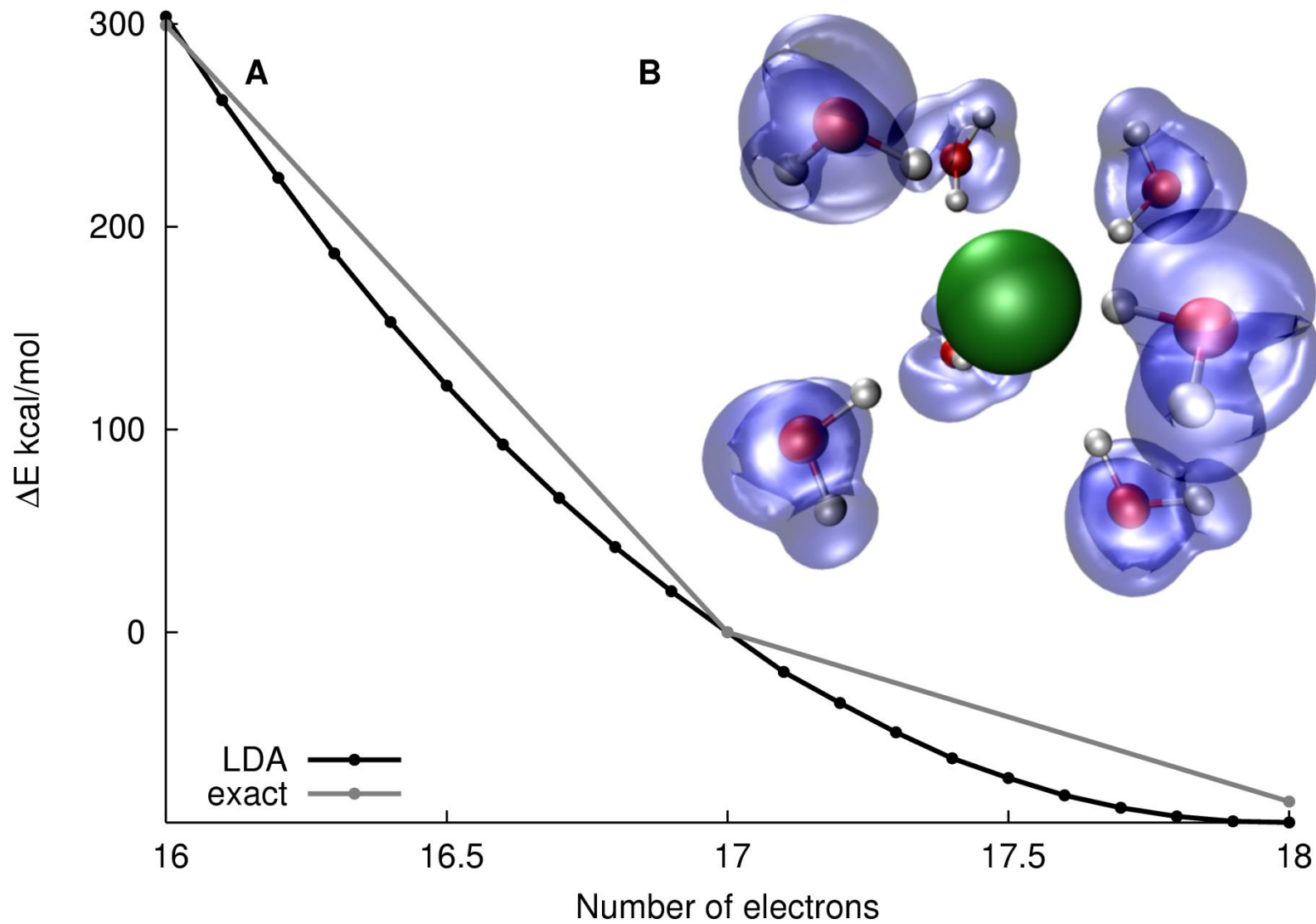
Fractional Spins
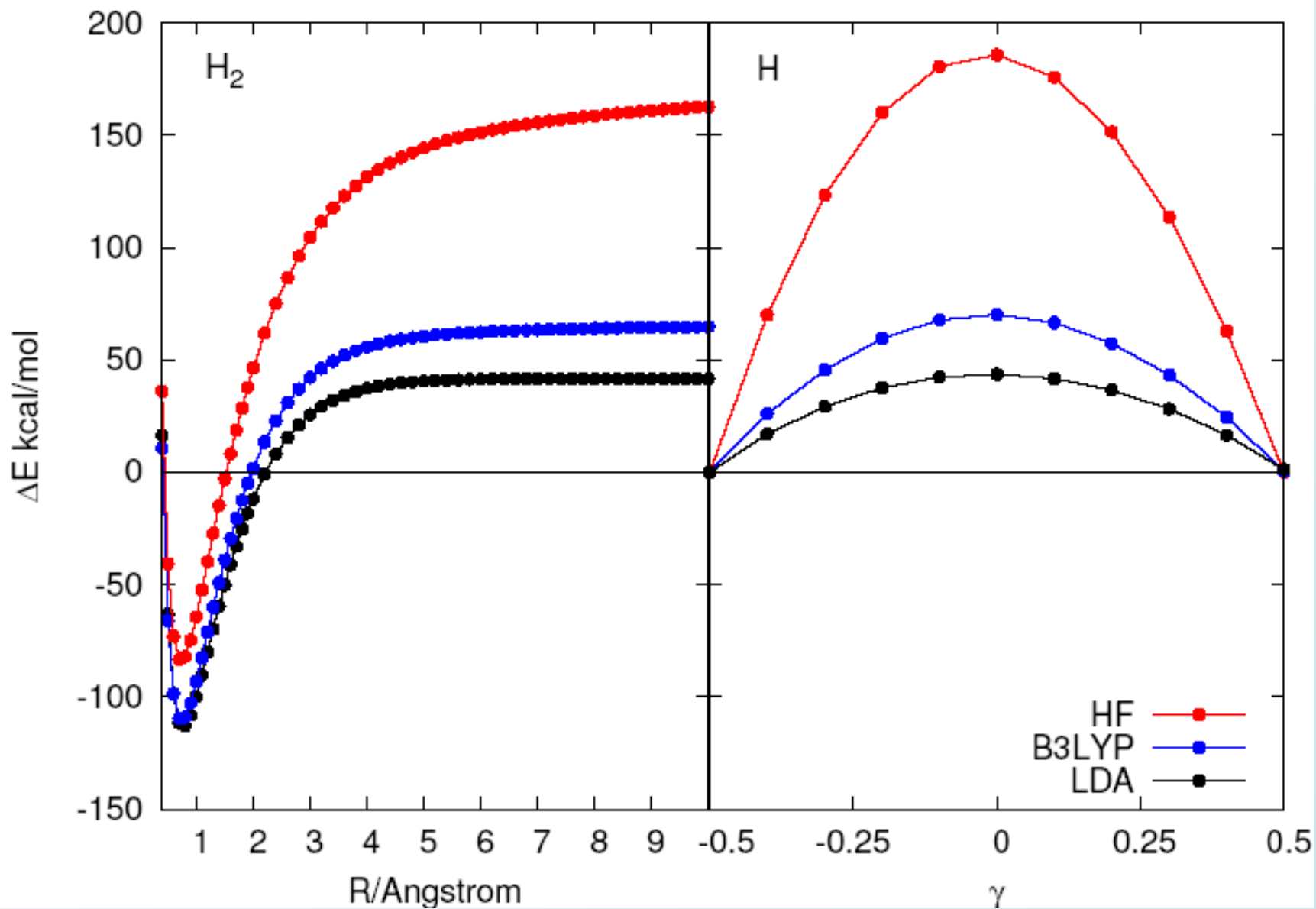
Another large class of problems

- 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

The huge error in breaking any bond

Where can you find fractional spins?

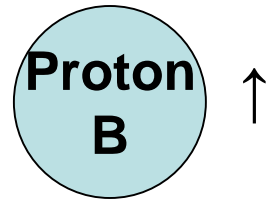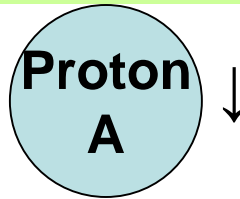Aron Cohen, Paula Mori-Sanchez and Yang, 2008, JCP
Yang, Ayers and Zhang, PRL 2000
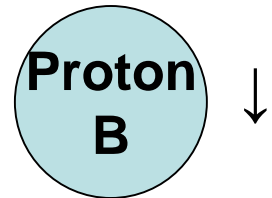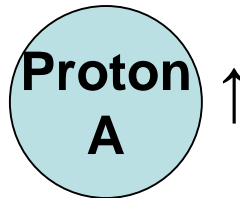
H_2 **at the dissociation limit**

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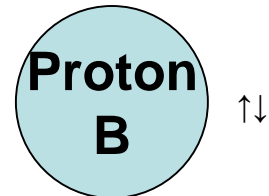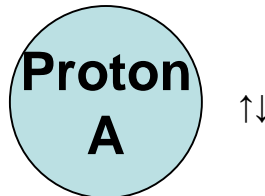
Fractional Spin H Atom: half spin up electron and half spin down electron

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

The constancy condition: energy of fractional spins

$E(\gamma)$

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

$\downarrow$　　　$\dfrac{\uparrow\downarrow}{2}$　　　$\uparrow$
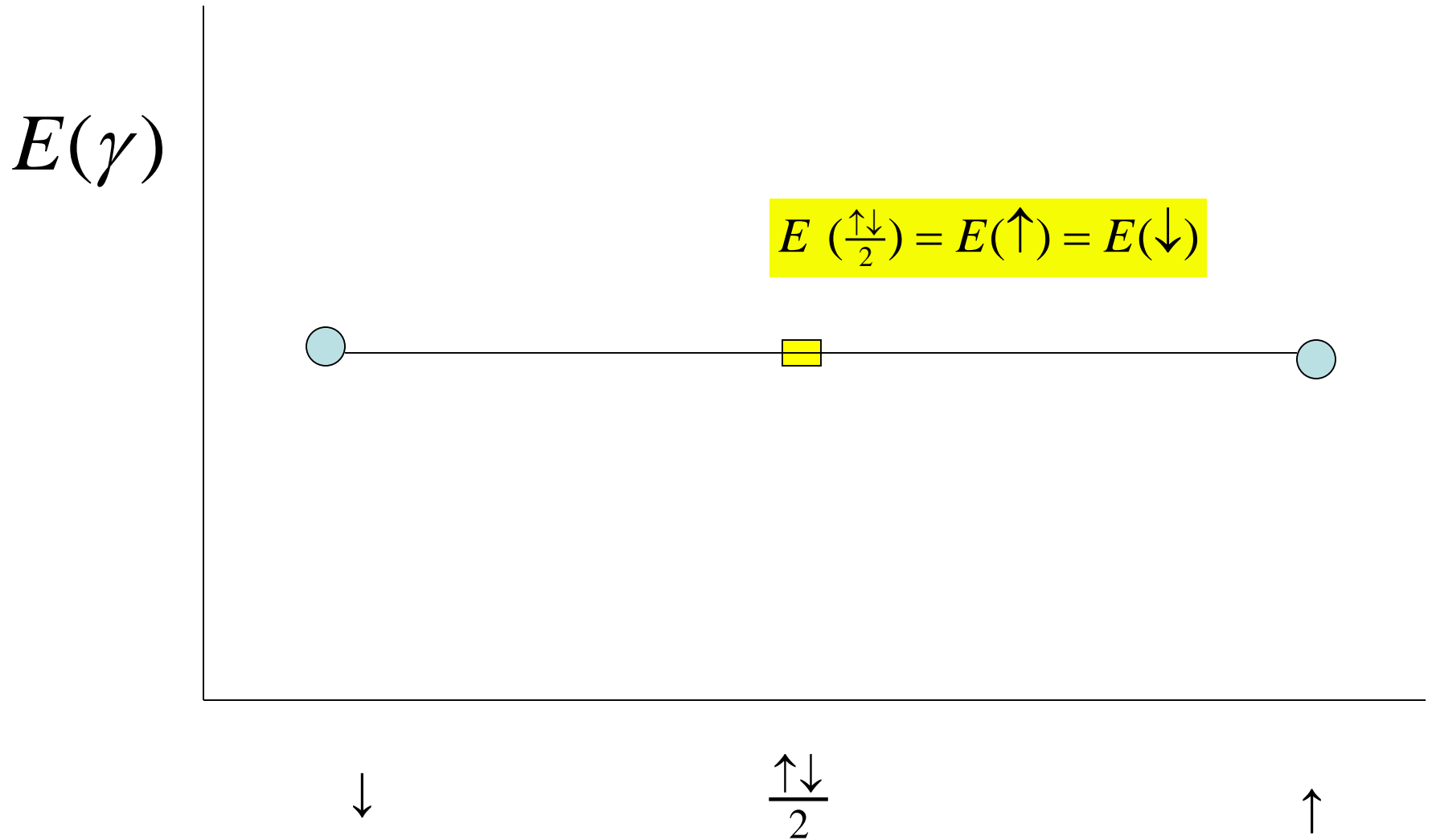
Define the Static Correlation Error as the violation of the constancy condition for fractional spins

Cohen, Mori-Sanchez and Yang, 2008, JCP; 2008 Science
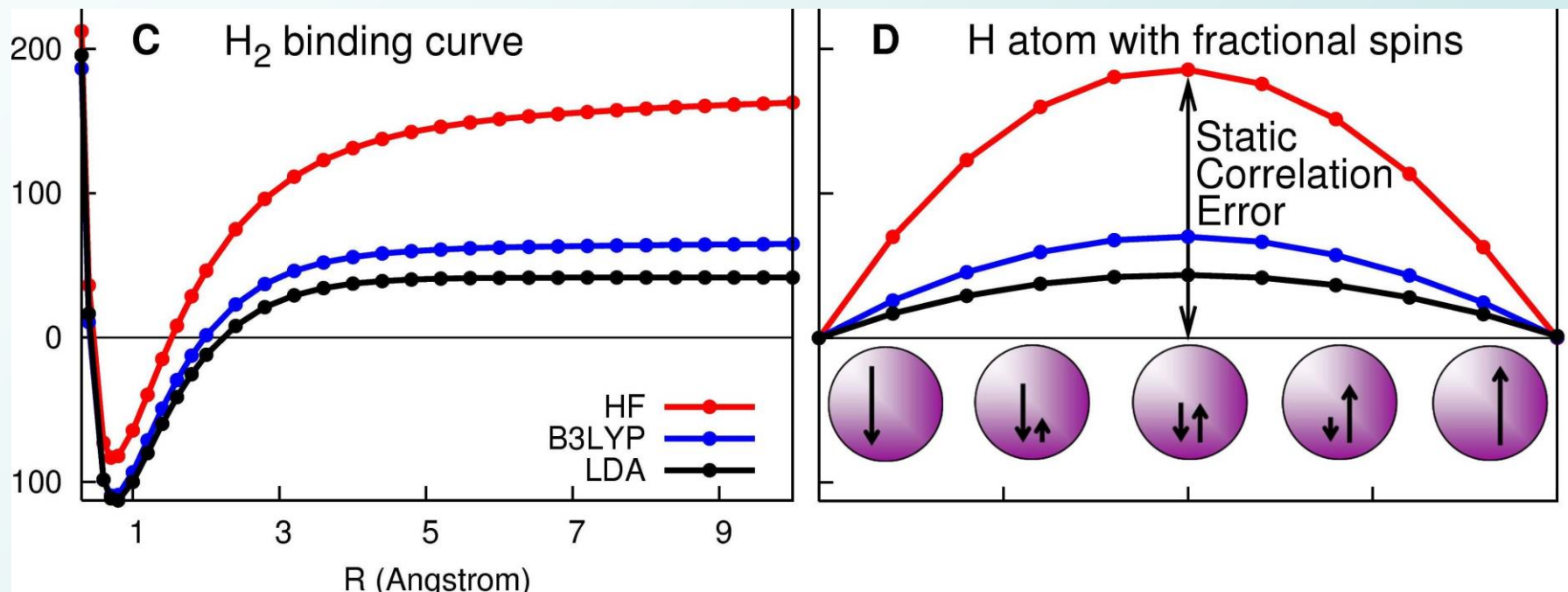
Exact conditions on DFT

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.**

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

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

Density Functional Theory

Fractional charge can occur

Many-electron theories based on

- Green function
- Density matrix

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

Wavefunction Theory

Integers, always!

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Fractional Charge and Fractional Spin Combined

$n_\alpha = n_\beta$

H⁺

H(↓)

H⁻

H(↑)

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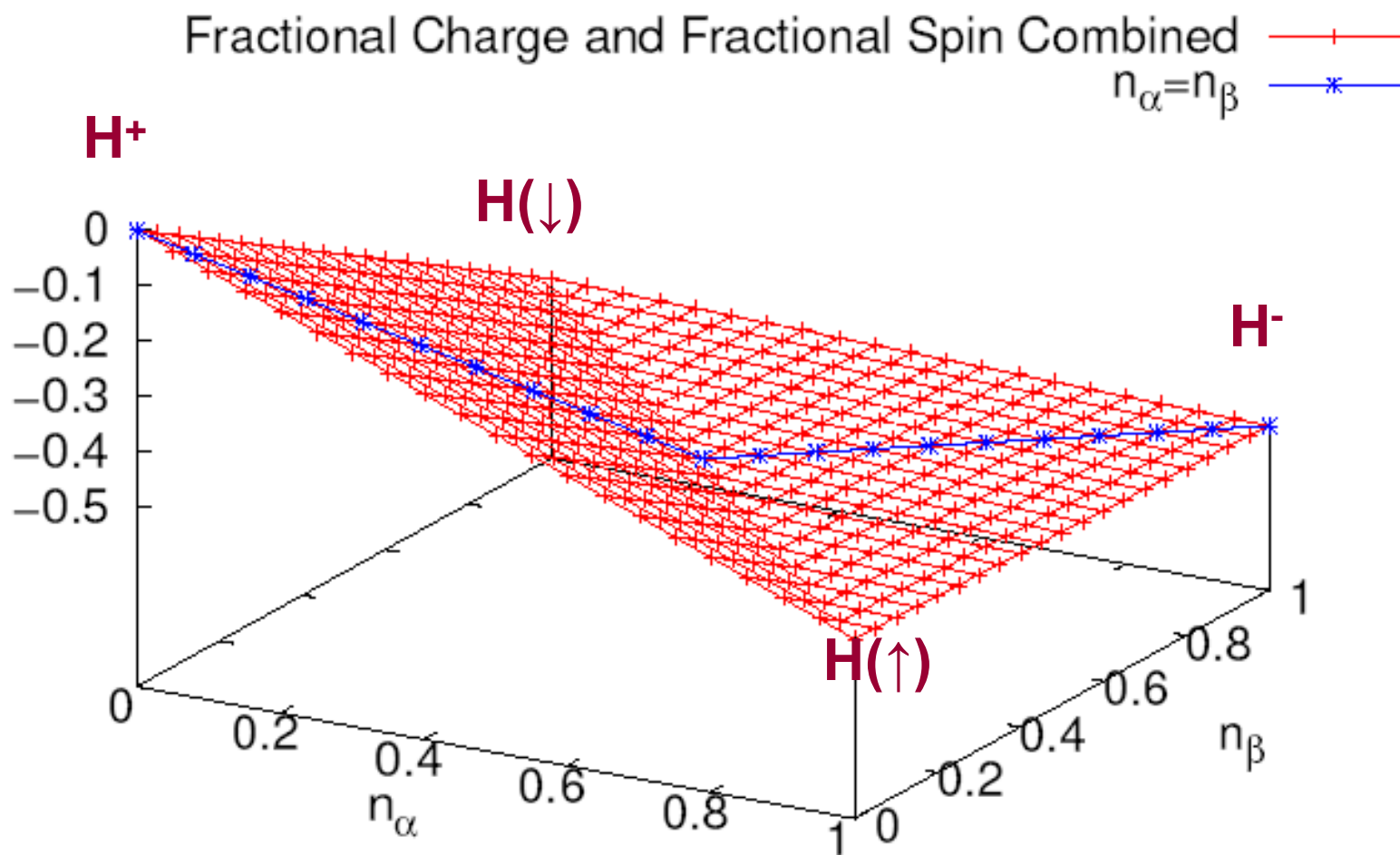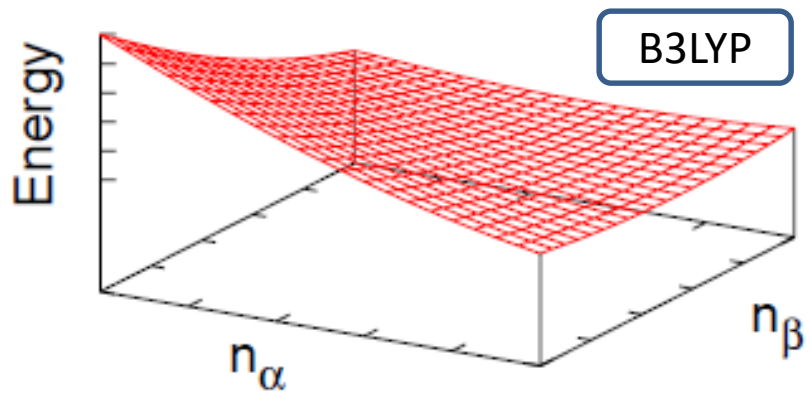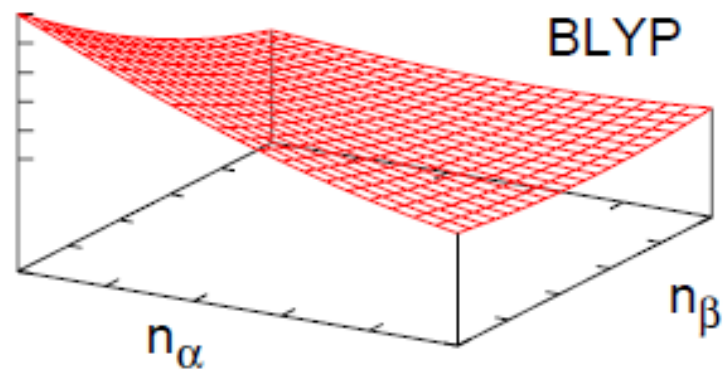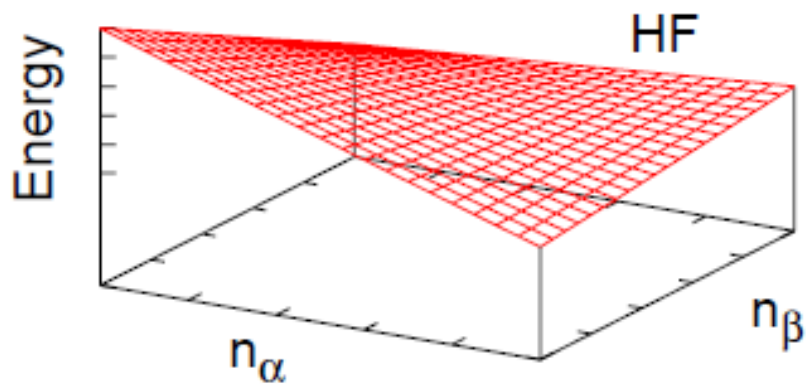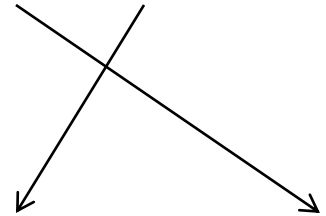
Band Gap

Definition of fundamental gap

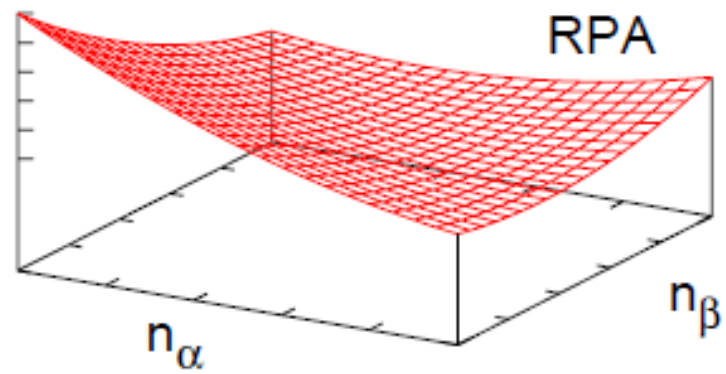$$E_{\text{gap}}^{\text{integer}} = \{E(N-1) - E(N)\} - \{E(N) - E(N+1)\}$$

$$= I - A$$

derivative

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

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

Cohen, Mori-Sanchez and Yang (PRB 2008), based on potential functional theory (PFT) (Yang, Ayers and Wu, PRL 2005)

Computing the chemical potential based on PFT

$$E_v(N) = \min_{v_s} E_v[v_s, N] = E_v[v_s^{\mathrm{gs}}, N]$$

The ground state energy is the minimum of the KS energy functional in terms of the KS potential.

$$\frac{\partial E_v[v_s, N]}{\partial N} = \int d\mathbf{r} \left. \frac{\delta E_v[v_s, N]}{\delta v_s(\mathbf{r})} \right|_N \frac{\partial v_s^{\mathrm{gs}}(\mathbf{r})}{\partial N} + \left(\frac{\partial E_v[v_s^{\mathrm{gs}}, N]}{\partial N} \right)_{v_s^{\mathrm{gs}}}$$

$$= \left(\frac{\partial E_v[v_s^{\mathrm{gs}}, N]}{\partial N} \right)_{v_s^{\mathrm{gs}}} \tag{1}$$

$$\frac{\partial E_v(N)}{\partial N} = \left(\frac{\partial E_v[\{\phi_i^{v_s^{gs}}, n_i\}]}{\partial n_{\mathrm{f}}} \right)_{\{\phi_i^{v_s^{gs}}\}}, \tag{2}$$

Unified expressions:

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

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

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

–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

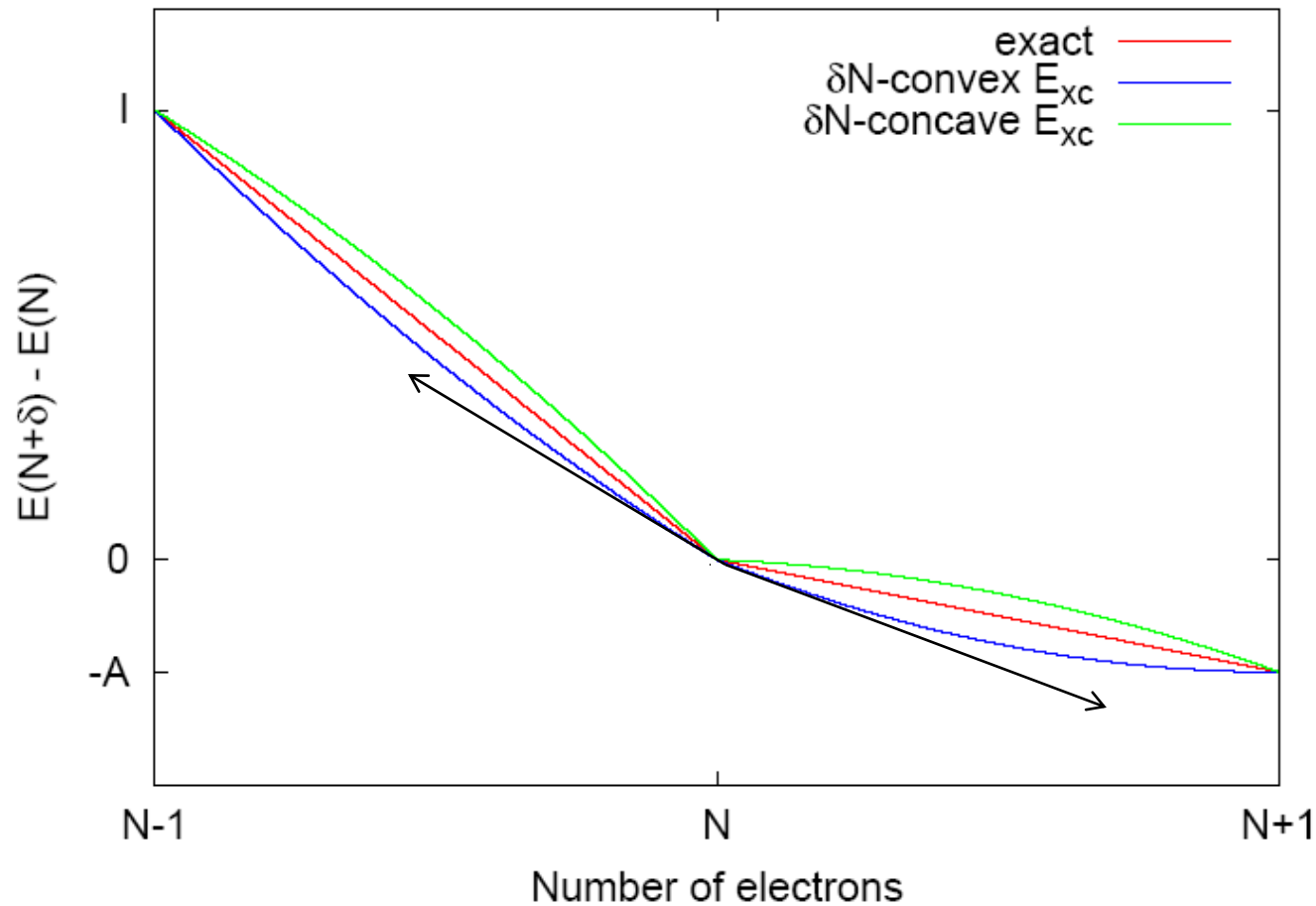# How can fundamental gap be predicted in DFT

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.

  Thus the KS gap is not the fundamental gap predicted by the functional.

$$\frac{\partial E_v(N)}{\partial N} = \langle \phi_{\mathrm{f}} | H_{\mathrm{eff}} | \phi_{\mathrm{f}} \rangle$$

For Linear E(N)

$$\Delta N = 1, \ \Delta E = \frac{\partial E}{\partial N}$$
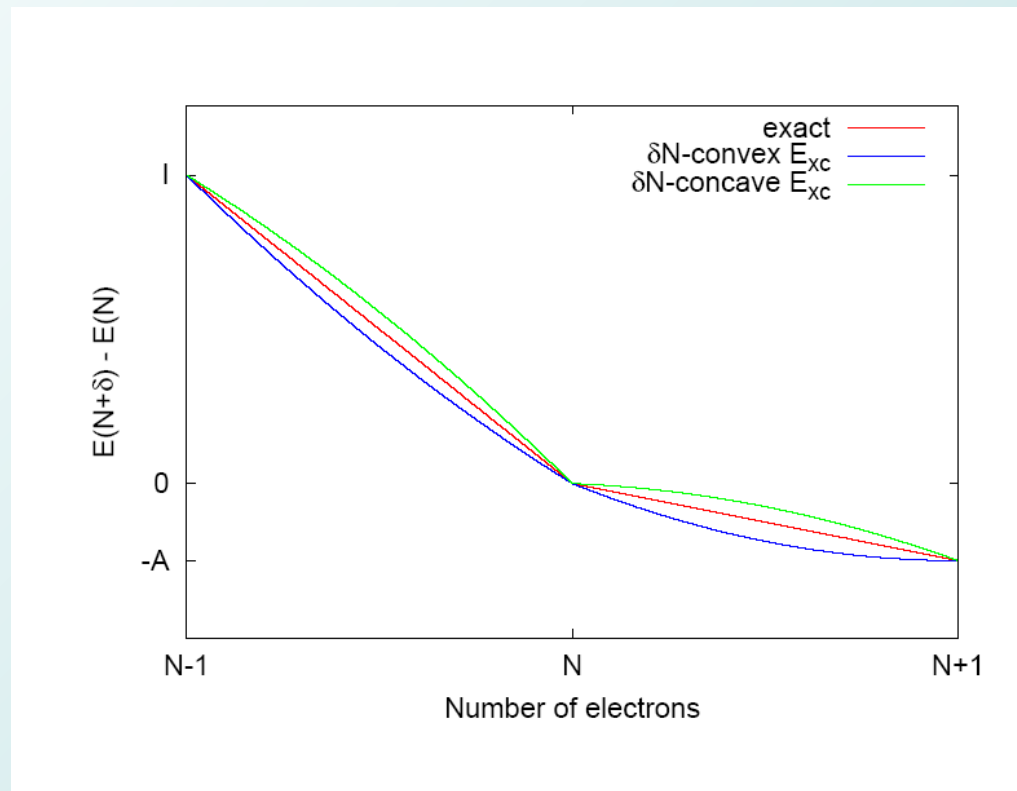
Convex curve (LDA, GGA):
   derivative underestimates I, overestimates A, **I-A is too small**

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

- **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.**

Challenges for Density Functional Theory

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

2012

What do we do?

1. **Use the exact conditions to improve existing approximations**

2. **Many-body theory**

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

Nonempirical Scaling correction

To linearize an energy component, E_{comp}, for a system of N + n (0 < n < 1) electrons, we construct

$$\tilde{E}_{\text{comp}}(N + n) = (1 - n)E_{\text{comp}}(N) + nE_{\text{comp}}(N + 1)$$

$\tilde{E}_{comp}(N + n)$ scales linearly with n, and reproduces E_{comp} at $n = 0$ and $n = 1$

The SC to E_{comp} is

$$\Delta E_{\text{comp}}(N + n) = \tilde{E}_{\text{comp}}(N + n) - E_{\text{comp}}(N + n)$$

It is then important to cast ΔE_{comp} into a functional form, so that it depends explicitly on ρ(**r**), or on Kohn-Sham first-order reduced density matrix ρ$_s$(**r,r'**)

Scaling correction to J[ρ]

At fractional electron number N + n, the electron density is

$$\rho_{N+n}(\mathbf{r}) \simeq \rho_N(\mathbf{r}) + nf(\mathbf{r}), \text{ where } f(\mathbf{r}) \equiv \lim_{n \to 0} \left. \frac{\partial \rho_{N+n}(\mathbf{r})}{\partial n} \right|_{v(\mathbf{r})} \text{ is the Fukui function.}$$

$$J(N+n) = \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}' \frac{[\rho_N(\mathbf{r}) + nf(\mathbf{r})][\rho_N(\mathbf{r}') + nf(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|}$$

The modified electron Coulomb energy which scales linearly with n is

$$\tilde{J}(N+n) = nJ[\rho_{N+1}(\mathbf{r})] + (1-n)J[\rho_N(\mathbf{r})]$$

$$= \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}' \left\{ \frac{n[\rho_N(\mathbf{r}) + f(\mathbf{r})][\rho_N(\mathbf{r}') + f(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} + \frac{(1-n)\rho_N(\mathbf{r})\rho_N(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\}$$

The SC to J[ρ] is

$$\Delta J(N+n) = \tilde{J}(N+n) - J(N+n) = \left(\frac{n - n^2}{2} \right) \iint d\mathbf{r}\, d\mathbf{r}' \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

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Scaling correction to J[ρ]

$$\rho(\mathbf{r}) = \sum_{m \in \text{occ}} n_m |\phi_m(\mathbf{r})|^2$$

$$g(\mathbf{r}) = -\rho(\mathbf{r}) \int d\mathbf{r}' \, h_{\text{x}}^{\text{HF}}(\mathbf{r}, \mathbf{r}')$$

HF exchange hole function

$$= \int d\mathbf{r}' \rho_s(\mathbf{r}, \mathbf{r}') \rho_s(\mathbf{r}', \mathbf{r}) = \sum_{m \in \text{occ}} n_m^2 |\phi_m(\mathbf{r})|^2$$

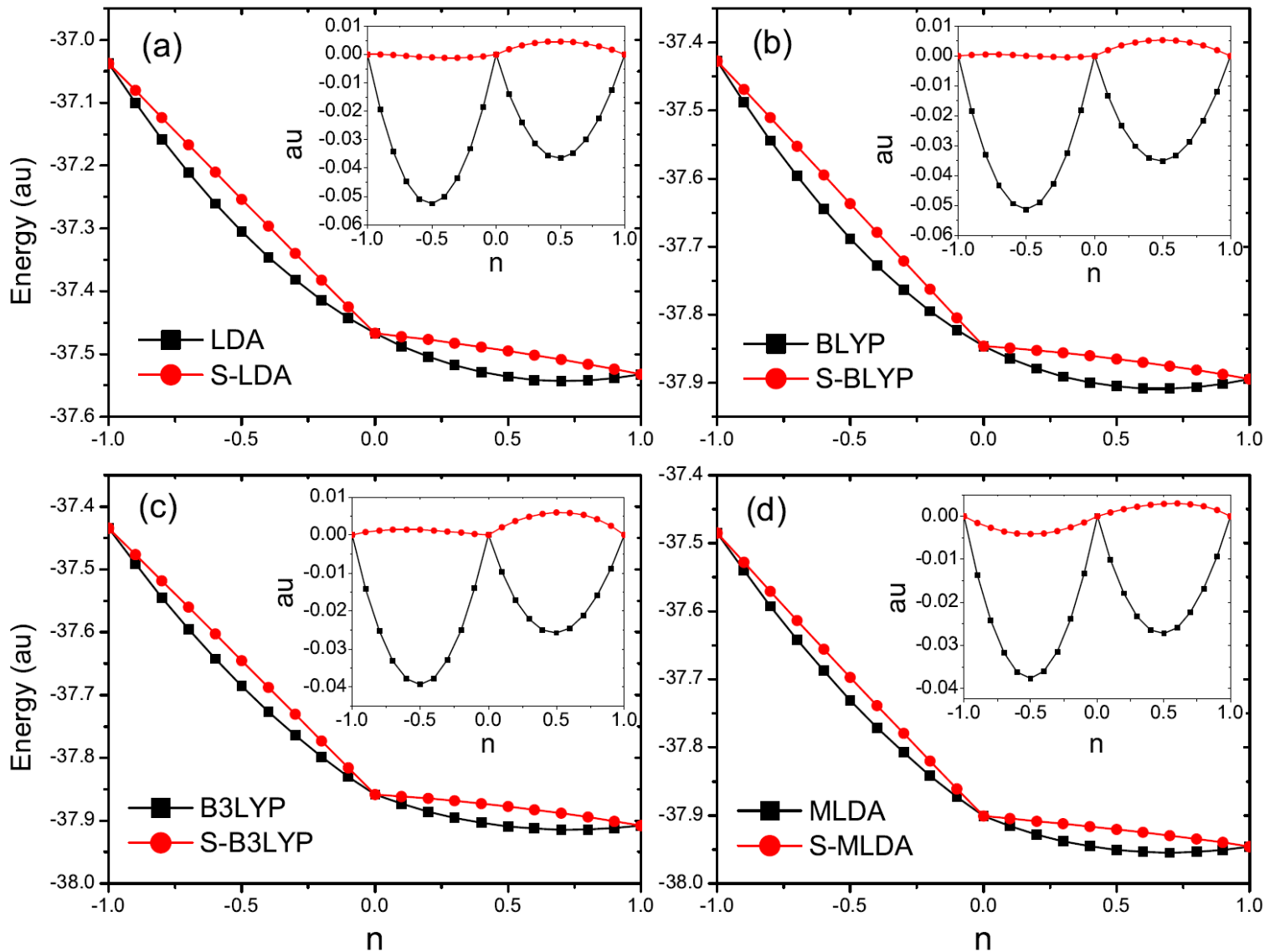At integer points, $n_m = 1$ for all occupied m, so that $\quad \rho(\mathbf{r}) = g(\mathbf{r})$

At fractional n: $\quad \rho(\mathbf{r}) - g(\mathbf{r}) = \rho(\mathbf{r}) \left[1 + \int d\mathbf{r}' \, h_{\text{x}}^{\text{HF}}(\mathbf{r}, \mathbf{r}') \right] = (n - n^2) |\phi_f(\mathbf{r})|^2$

Use Kohn–Sham frontier orbital density to approximate Fukui function,
$f(\mathbf{r}) \simeq |\phi_f(\mathbf{r})|^2$

$$\Delta J(N + n) \approx \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \, \frac{[\rho(\mathbf{r}) - g(\mathbf{r})] \, |\phi_f(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

Energy versus fractional electron number

**The SC significantly restores linearity condition for energy**

Band gaps by various DFA and S-DFA

Summary of band-gap prediction for a variety of systems

eV	MAE (# of data)	MLDA	S–MLDA	LDA	S–LDA	B3LYP	S–B3LYP
atom	I (18)	0.16	0.16	0.30	0.30	0.20	0.20
	A (15)	0.25	0.25	0.27	0.27	0.12	0.12
	ϵ_{HOMO} (18)	3.53	0.33	5.18	0.33	3.88	0.35
	ϵ_{LUMO} (15)	2.47	0.54	3.33	0.65	2.28	0.67
molecules	I_{ad} (70)	0.22	0.22	0.21	0.21	0.16	0.16
	A_{ad} (47)	0.25	0.25	0.24	0.23	0.13	0.13
	ϵ_{HOMO} (70)	3.10	0.21	4.19	0.35	3.09	0.31
	ϵ_{LUMO} (47)	2.78	0.27	3.66	0.34	2.59	0.39
solids	E_{gap} (18)	0.77	0.77	1.81	1.81	0.99	0.99

➢ The SC preserves the accuracy of *I*, *A*, and integer gaps, while it improves significantly on HOMO and LUMO energies, and derivative gaps

➢ S-MLDA predicts reasonable band gaps with consistent accuracy for systems of all sizes, ranging from atoms and molecules to solids

50

# Atoms and Molecules
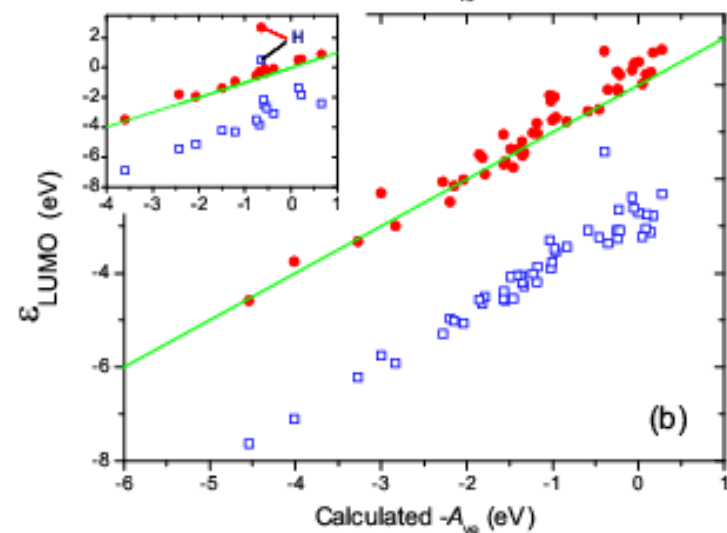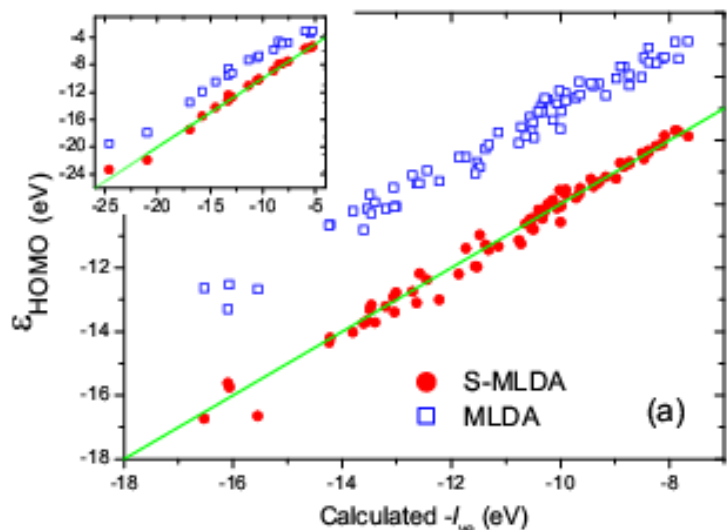
Bulk Solids
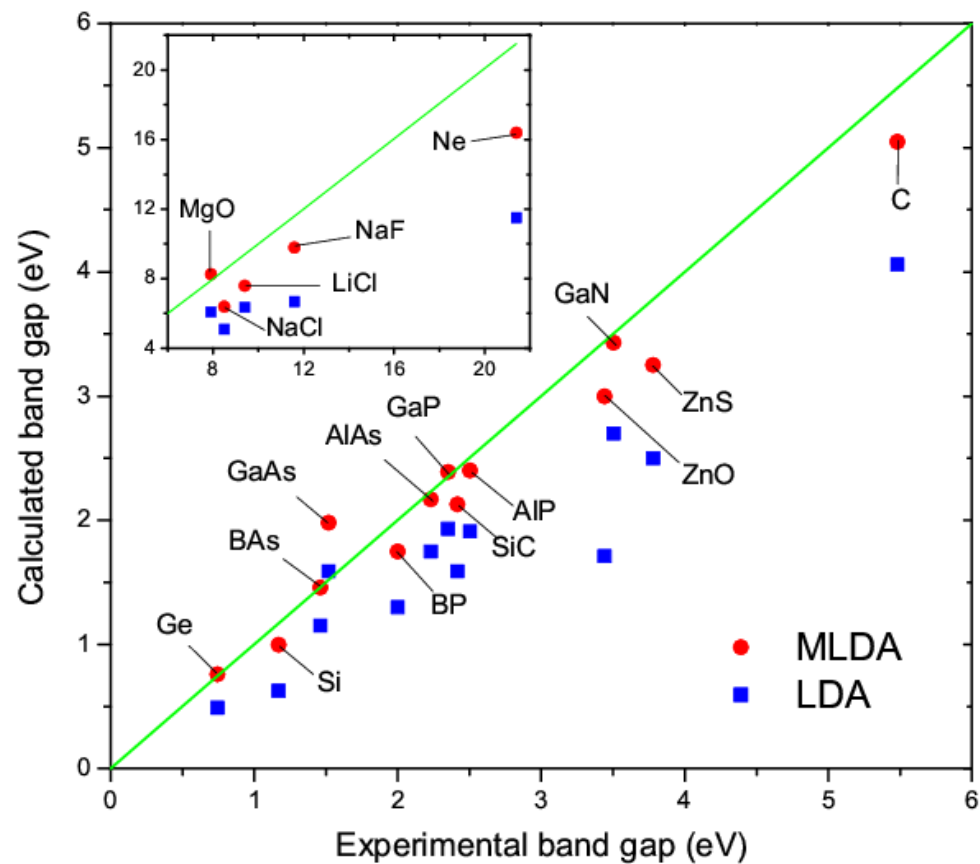
Band gaps of H-passivated Si nanocrystals

Computational details

➢ Systems under study: H-passivated spherical Si nanocrystals. The largest system is $Si_{191}H_{148}$ with a diameter of 20 angstrom

➢ Geometries optimized by B3LYP with Lanl2dz ECP basis set, except that the largest system $Si_{191}H_{148}$ is optimized with semiempirical PM3 method

➢ Diffusive basis functions are important to obtain accurate HOMO-LUMO gaps: 6-31G for H atoms; an sp-shell with an exponent of 0.0237 au and a d-shell with an exponent of 0.296 au added to Lanl2dz basis for Si atoms

Molecule	d (Å)	basis
$Si_{29}H_{36}$	9.0	Lanl2dz–spd
$Si_{35}H_{36}$	10.9	Lanl2dz–spd
$Si_{47}H_{60}$	11.8	Lanl2dz–spd
$Si_{71}H_{84}$	13.3	Lanl2dz–pd
$Si_{87}H_{76}$	14.1	Lanl2dz–pd
$Si_{99}H_{100}$	15.4	Lanl2dz–pd
$Si_{123}H_{100}$	16.1	Lanl2dz–d
$Si_{191}H_{148}$	19.4	Lanl2dz–d
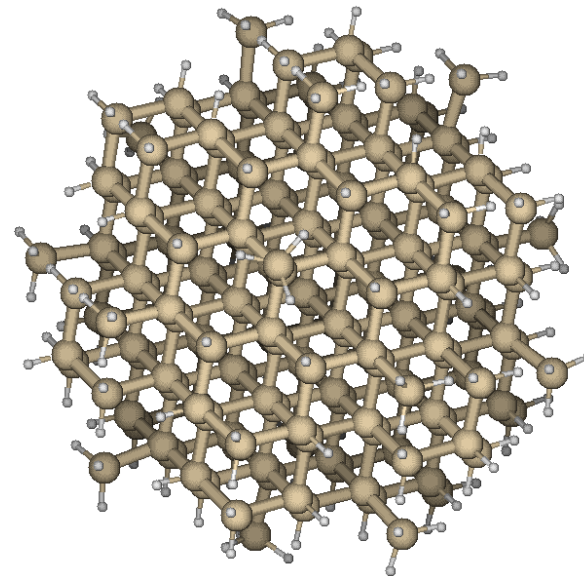
$Si_{191}H_{148}$

Band gaps of H-passivated Si nanocrystals
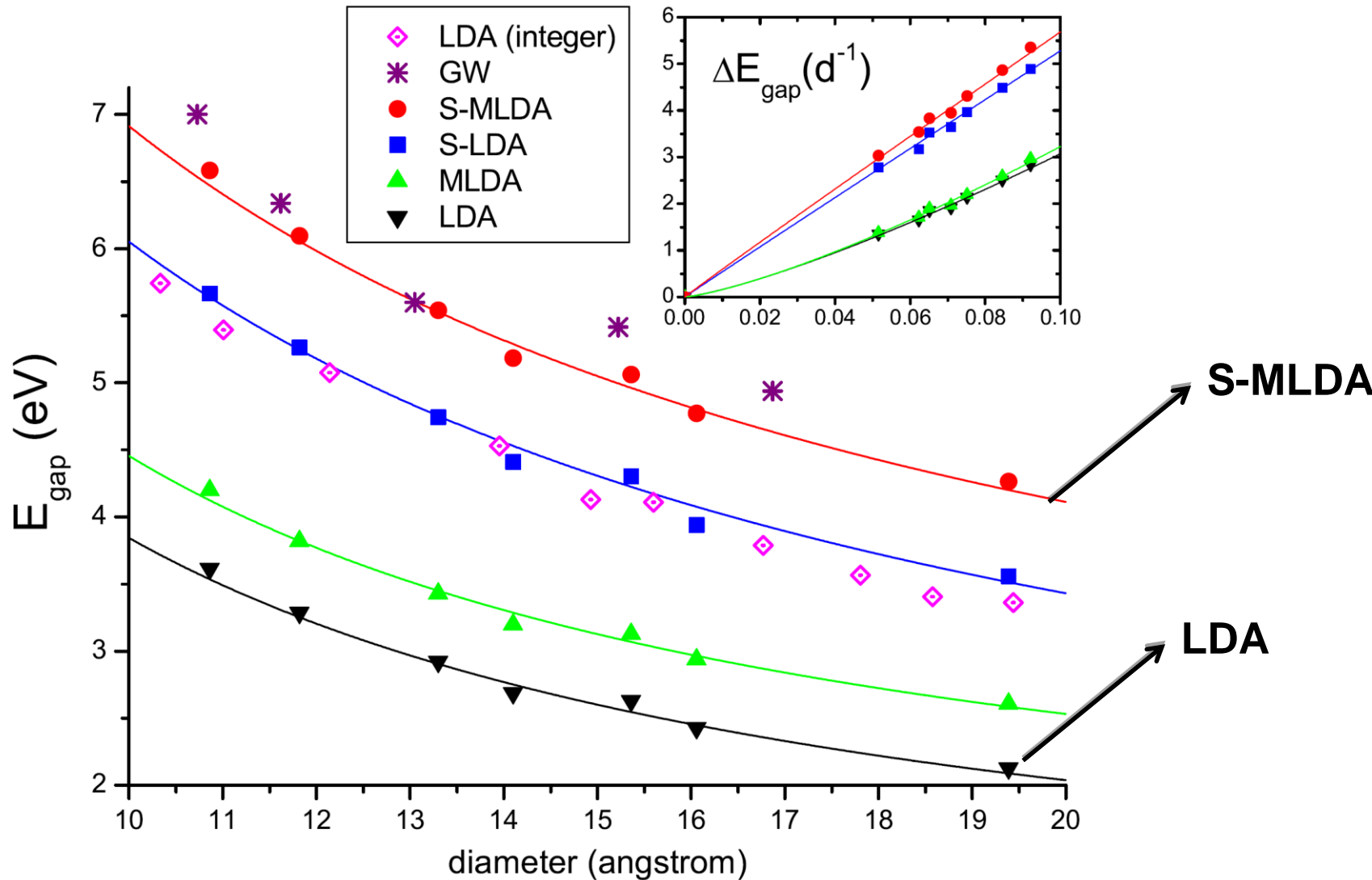
The S-MLDA HOMO-LUMO gaps agree well with the GW gaps

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,†]
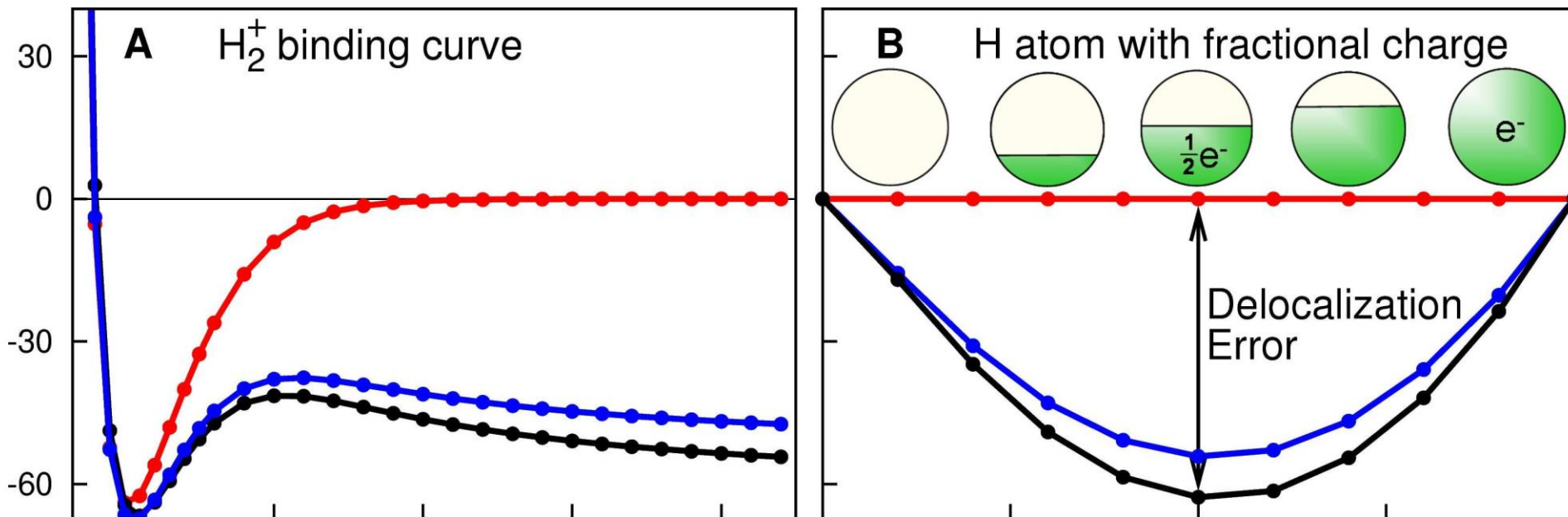

**Chen Li
(Duke)**

**Xiao Zheng
(USTC)**

**Aron J. Cohen
(Cambridge)**

**Paula Mori-Sanchez
(Univ. Autonoma Madrid**

Delocalization Error

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

Cohen, Mori-Sanchez and Yang, 2008 Science

Local Scaling Correction

- Motivation
  - Consider $M^{0.5+}$ (M is an atom)
  - Diagonize PS matrix

- PS $\rightarrow$
$$\begin{bmatrix} 1 & & & & \\ & \ddots & & 0 & & 0 \\ & & 1 & & & \\ 0 & & & 0.5 & & 0 \\ & & & & 0 & \\ 0 & & & 0 & & \ddots \\ & & & & & & 0 \end{bmatrix}$$

- $PS - (PS)^m$ $\rightarrow$
$$\begin{bmatrix} 0 & & & & \\ & \ddots & & 0 & & 0 \\ & & 0 & & & \\ 0 & & & 0.5 & & 0 \\ & & & & 0 & \\ 0 & & & 0 & & \ddots \\ & & & & & & 0 \end{bmatrix}$$

- Motivation
  - $S \Longrightarrow S_v$ (screened S to reflect locality)
  - In atomic basis representation,

$$l(r) = \lim_{m \to \infty} \chi^T(r)[P - (PS_v)^{m-1}P]\chi(r),$$

$$d(r) = \lim_{m \to \infty} \chi^T(r)[I - (PS_v)^m - (I - PS_v)^m](S_v)^{-1}\chi(r),$$

- Our key idea

  - Apply local linearity condition using f(r) and d(r)

Local fractional occupation numbers n(r)
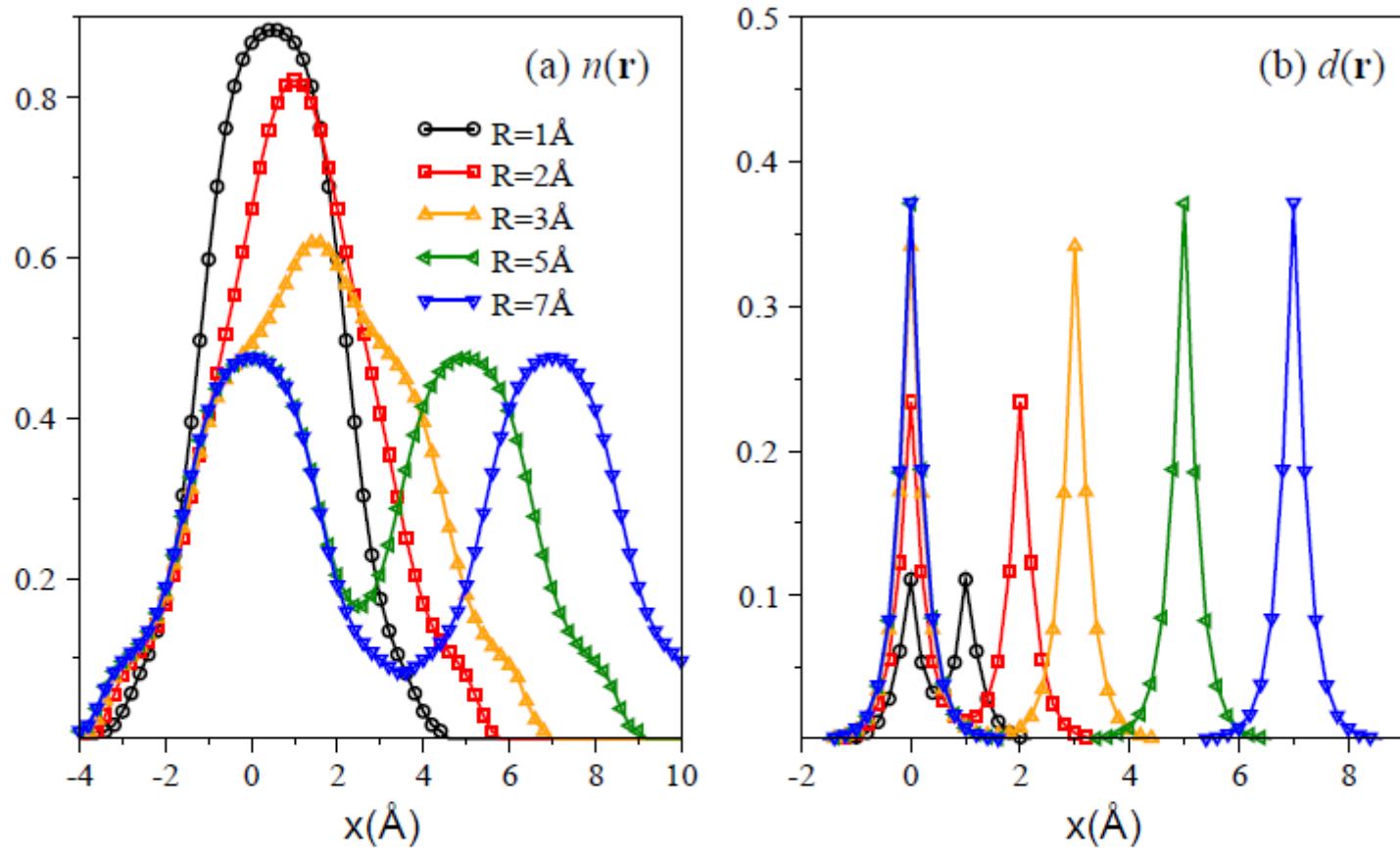
FIG. 1. (a) The local fractional occupation number $n(\mathbf{r})$ and (b) the local fractional orbital density $d(\mathbf{r})$ of a dissociating H_2^+ along the bonding axis at various internuclear distances R. A proton locates at $x = 0$, while the other proton resides

Results

- ## Reaction barrier heights

Test Set	MAE (kcal/mol)			
	BLYP	LSC-BLYP	B3LYP	LSC-B3LYP
HTBH38/08[11]	7.83	4.85	4.43	2.71
NHTBH38/08[11]	8.79	4.38	4.44	2.93
G2-97[12]	7.28	7.41	3.40	4.51

- ## LSC improves reaction barrier heights, maintains thermochemistry.

11. Zheng, J.; Zhao, Y.; Truhlar, D. G. J. Chem. Theory Comput. 2009, 5, 808-821.
12. L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. 1997, 106, 1063.
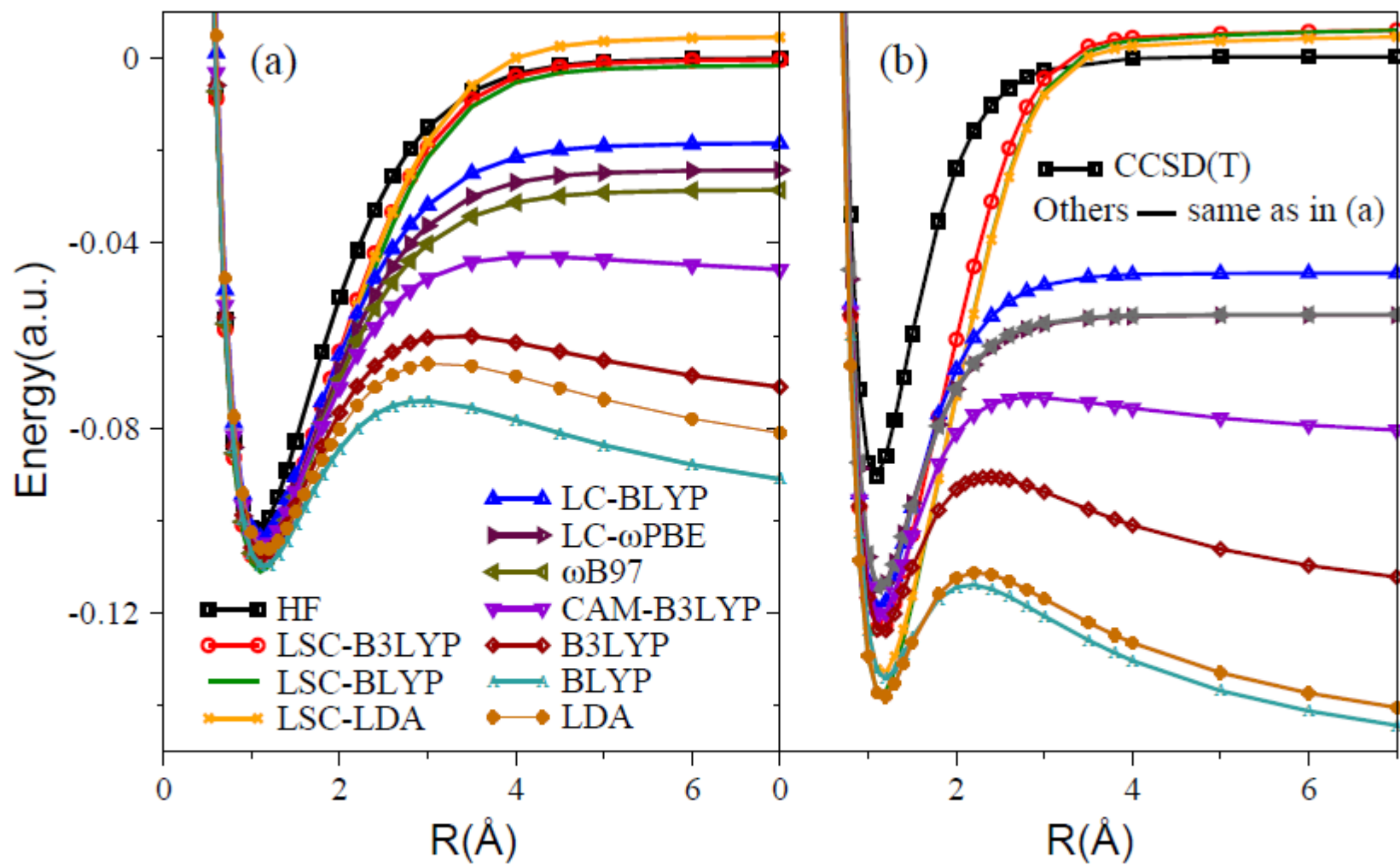
FIG. 2. Dissociation energy curves of (a) H_2^+ and (b) He_2^+.

Results

- Polarizablity (longitudinal)

2.0 a.u.

H — H

4.5 a.u.

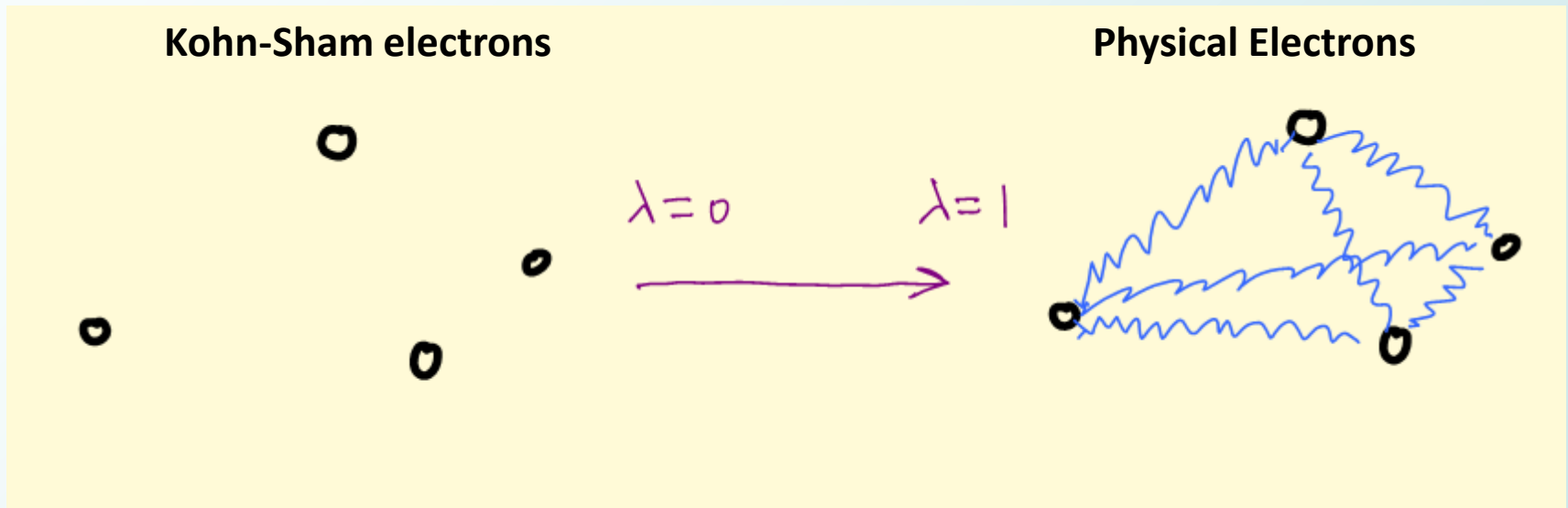Hydrogen chain

$(H_2)_n$
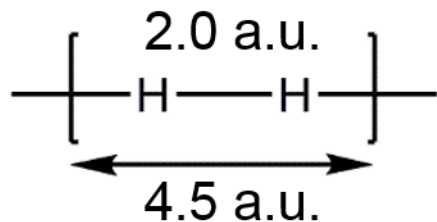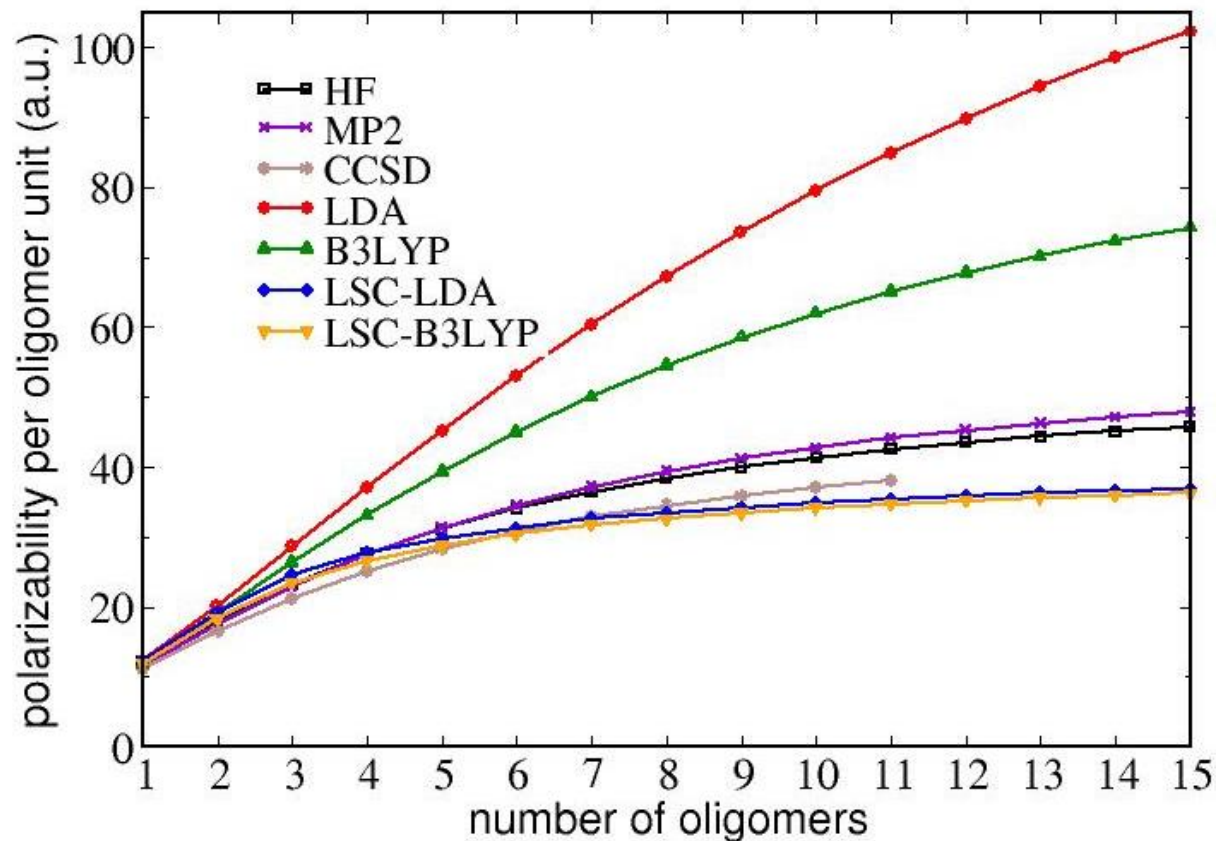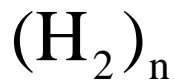
- Polarizablity (longitudinal)

Polythiophene (PT)

$$H(C_4H_2S)_nH$$
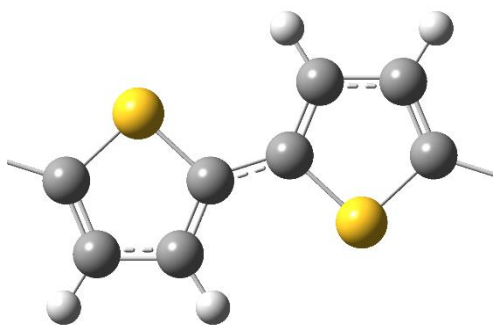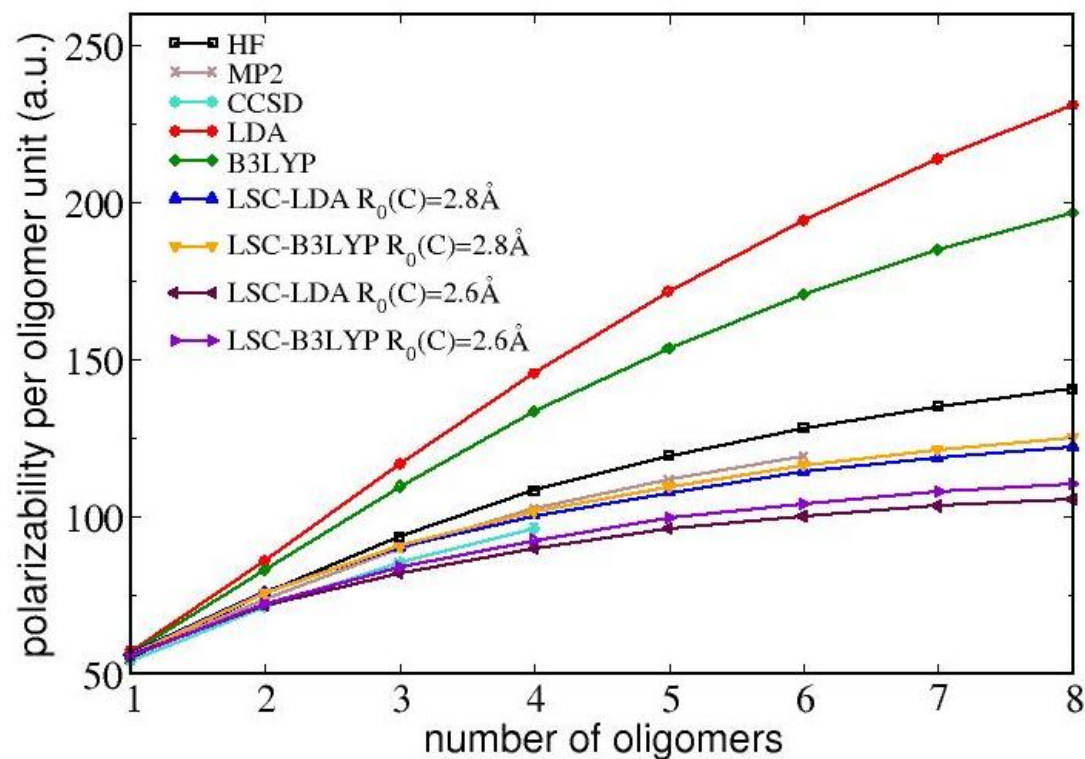
Results

- $OH(H_2O)_n$
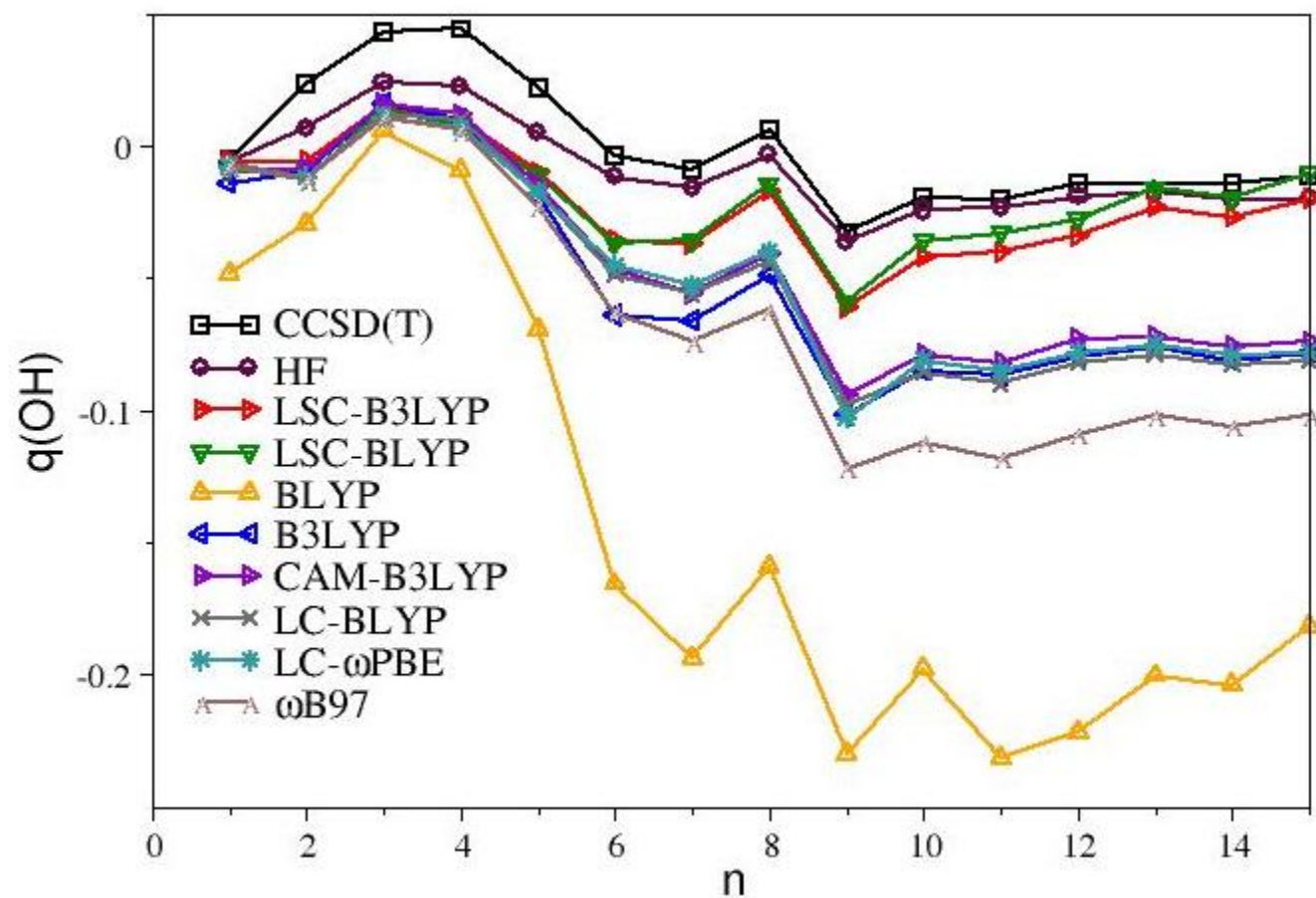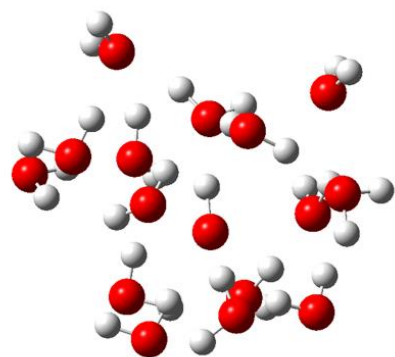
Second Approach: Many-Body Theory

Kohn-Sham electrons $\lambda = 0$ $\lambda = 1$ **Physical Electrons**

	Kohn-Sham **Noninteracting** System	Physical System
	$E_s = T_s[\rho] + \int d\mathbf{r}\, v_s(\mathbf{r})\rho(\mathbf{r})$	$E = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r}\, v_{ext}(\mathbf{r})\rho(\mathbf{r})$
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
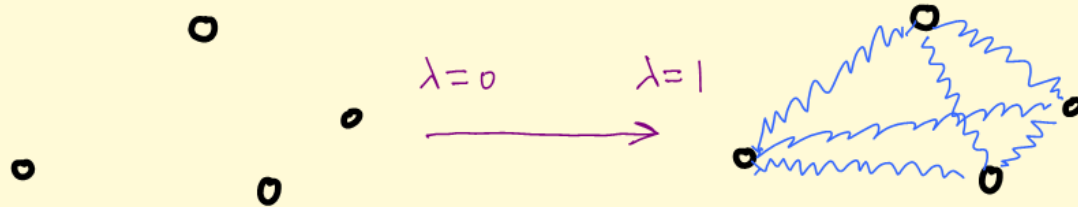
$$E_1 - E_0 = \int_0^1 \frac{\partial E_\lambda}{\partial \lambda} d\lambda$$

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

Two channels

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

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

$$V_{ee} = \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle a_i^\dagger a_j^\dagger a_l a_k$$

Particle-hole channel

$$G_{ijkl} = \langle \Psi | a_k^+ a_l a_j^+ a_i | \Psi \rangle$$

$$E^c = \mathrm{tr} \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G}^0) d\lambda .$$

Particle-particle channel (Hole-hole channel)

$$\Gamma_{ijkl} = \langle \Psi | a_k^+ a_l^+ a_j a_i | \Psi \rangle$$

$$Q_{ijkl} = \langle \Psi | a_k a_l a_j^+ a_i^+ | \Psi \rangle$$

$$E^c = \mathrm{tr} \int_0^1 \mathbf{V}(\mathbf{\Gamma}^\lambda - \mathbf{\Gamma}^0) d\lambda$$

$$E^c = \mathrm{tr} \int_0^1 \mathbf{V}(\mathbf{Q}^\lambda - \mathbf{Q}^0) d\lambda$$

Linear response in density

Particle-hole channel

$$G_{ijkl} = \langle \Psi | a_k^+ a_l a_j^+ a_i | \Psi \rangle.$$

$$E^c = \mathrm{tr} \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G^0}) d\lambda.$$

particle-number conserving field

$$\hat{F}(t) = \sum_{kl} f_{kl} a_{H_k}^+(t) a_{H_l}(t)$$

$$\delta v(\mathbf{r}, t)$$

$$\rho(\mathbf{r})$$

pertubation

$$\delta \rho(\mathbf{r}, t)$$
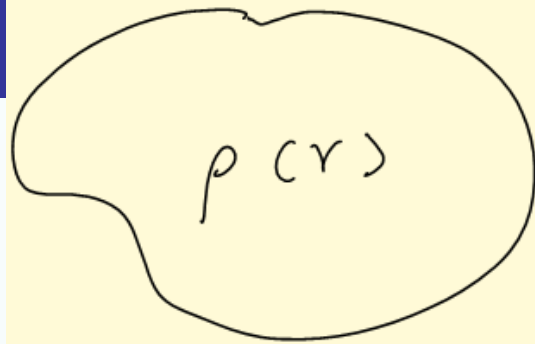
$$\langle \Psi_0^N | a_j^+ a_i | \Psi_0^N \rangle \longrightarrow \langle \Psi_0^N | a_{H_j}^+(t) a_{H_i}(t) | \Psi_0^N \rangle$$

Density at t=0

Density at t

$$\sum_{kl} \int_0^t \Pi_{ijkl}(t - t') f_{kl} dt'$$

Linear response
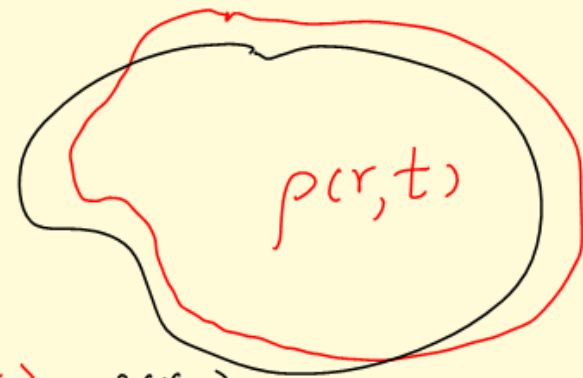
$$\Pi(\mathbf{x}_1, \mathbf{x}_2; E) = \sum_{n \neq 0} \frac{\langle \Psi_0^N | \hat{\rho}(\mathbf{x}_1) | \Psi_n^N \rangle \langle \Psi_n^N | \hat{\rho}(\mathbf{x}_2) | \Psi_0^N \rangle}{E - (E_n^N - E_0^N) + i\eta} - \sum_{n \neq 0} \frac{\langle \Psi_0^N | \hat{\rho}(\mathbf{x}_2) | \Psi_n^N \rangle \langle \Psi_n^N | \hat{\rho}(\mathbf{x}_1) | \Psi_0^N \rangle}{E - (E_0^N - E_n^N) - i\eta}$$

$$E^c = \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{-E\eta} \int d\mathbf{x} d\mathbf{x}' \int \frac{\Pi^\lambda(\mathbf{x}, \mathbf{x}', E) - \Pi^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE d\lambda$$

- **Exact expression (Langreth and Perdew, 1975)**

- **ACFDT –adiabatic connection fluctuation dissipation theorem**

- **Correlation from Dynamic linear response of electron density**

- **Simplest Approxmation is particle-hole Random Phase Approximation (ph-RPA)**

$$\Pi = \Pi^0 + \Pi^0 \tilde{V} \Pi$$

$$\Pi = \Pi^0 + \Pi^0 \tilde{V} \Pi^0 + \Pi^0 \tilde{V} \Pi^0 \tilde{V} \Pi^0 + \dots$$

- **Geometric summation of V, or Ring diagrams**

- **Direct-RPA, using only direct interaction, w/o exchange**

Helen van Aggelen

Yang Yang

Exchange-Correlation Energy from Pairing Matrix Fluctuation and the Particle-Particle Random Phase Approximation
Helen van Aggelen, Yang Yang, Weitao Yang, **arXiv:1306.4957 (2013), PRA (2013)**

$$\not{k}(r_1 \quad r_2) = 0 \qquad \xrightarrow{\;\delta D(r_1 \; r_2 \; t)\;} \qquad k(r_1 \; r_2 \; t)$$

$$\delta x(r_1 \; r_2 \; t) = \int K(r_1 \; r_2 \; , r_3 \; r_4 \quad t - t') \, \delta D(r_3 \; r_4 \; t')$$

$$F(t) = \sum_{kl} f_{kl} a^{+}_{H_k} a^{+}_{H_l} :$$

$$\langle \Psi^N_0 \mid a_j a_i \mid \Psi^N_0 \rangle \xrightarrow[\displaystyle \sum_{kl} \int_0^t K_{ijkl}(t-t') f_{kl} \, dt']{} \langle \Psi^N_0 \mid a_{H_j}(t) a_{H_i}(t) \mid \Psi^N_0 \rangle$$

$$k(r_1 \ r_2) = 0 \qquad \xrightarrow{\ \delta D(r_1 \ r_2 \ t)\ } \qquad k(r_1 \ r_2 \ t)$$

$$\delta \varkappa(r_1 \ r_2 \ t) = \int K(r_1 \ r_2 , r_3 \ r_4 \ t - t') \delta D(r_3 \ r_4 \ t')$$

$$K_{ijkl}(E) = -\sum_n \frac{\langle \Psi_0^N \mid a_k^+ a_l^+ \mid \Psi_n^{N-2}\rangle \langle \Psi_n^{N-2} \mid a_j a_i \mid \Psi_0^N \rangle}{E - \omega_n^{N-2} + i\eta} + \sum_n \frac{\langle \Psi_0^N \mid a_j a_i \mid \Psi_n^{N+2}\rangle \langle \Psi_n^{N+2} \mid a_k^+ a_l^+ \mid \Psi_0^N \rangle}{E - \omega_n^{N+2} + i\eta}$$

particle-hole

$$a^+ a$$
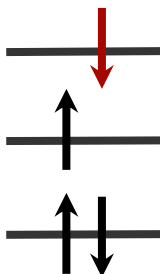
$$\omega_n = E_n^N - E_0^N$$
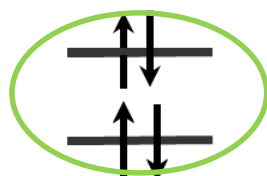
2 correlation/excitation channels
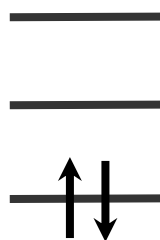
particle-particle

$$a^+ a^+$$
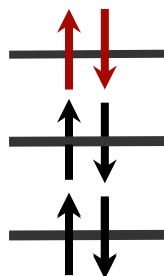
$$\omega_n^{N+2} = E_n^{N+2} - E_0^N$$

hole-hole

$$aa$$

$$\omega_n^{N-2} = E_0^N - E_n^{N-2}$$

The correlation energy can be written in terms of

pairing (matrix) fluctuations

$$E^c = \frac{1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{E\eta} \int d\mathbf{x} d\mathbf{x}' \frac{K^\lambda(\mathbf{x}, \mathbf{x}', E) - K^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE$$

van Aggelen, Yang, Yang, PRA (2013)

density (matrix) fluctuations

$$E^c = \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{-E\eta} \int d\mathbf{x} d\mathbf{x}' \int \frac{\Pi^\lambda(\mathbf{x}, \mathbf{x}', E) - \Pi^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE d\lambda$$

Langreth, Perdew (1975);
Gunnarsson, Lundqvist (1976)

The simplest approximation to K is the pp-RPA

$$K_{ijkl}(E) = -\sum_n \frac{\langle \Psi_0^N | a_k^+ a_l^+ | \Psi_n^{N-2} \rangle \langle \Psi_n^{N-2} | a_j a_i | \Psi_0^N \rangle}{E - \omega_n^{N-2} + i\eta} + \sum_n \frac{\langle \Psi_0^N | a_j a_i | \Psi_n^{N+2} \rangle \langle \Psi_n^{N+2} | a_k^+ a_l^+ | \Psi_0^N \rangle}{E - \omega_n^{N+2} + i\eta}$$

$$K = K^0 + K^0 V K$$

$$K = K^0 + K^0 V K^0 + K^0 V K^0 V K^0 + \ldots$$

pp-RPA has been used
- **double ionization energies for molecules**
- **correlation energy in nuclear physics, not in electronic structure before.**

The pp-RPA correlation energy from pairing matrix fluctuations:

$$E - E^{HF} = \frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{E\eta} tr\, V[K^\lambda(E) - K^0(E)] dE d\lambda$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{E\eta} \sum_{n=1} \lambda^n tr\, (VK^0(E))^{n+1} dE\, d\lambda$$

$$= \frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{E\eta} \sum_{n=1} \frac{1}{n+1} tr\, (VK^0(E))^{n+1} dE$$

$$= \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{E\eta} tr\, \, ln\, (I + VK^0(E)) + tr\, VK^0(E) dE$$

One way to get the pp-RPA correlation energy

$$\begin{pmatrix} A & B \\ B^\dagger & C \end{pmatrix} \begin{pmatrix} X^n \\ Y^n \end{pmatrix} = \omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X^n \\ Y^n \end{pmatrix}$$

$$A_{abcd} = \langle ab \| cd \rangle + \delta_{ac}\delta_{bd}(\epsilon_a + \epsilon_b - 2\nu)$$
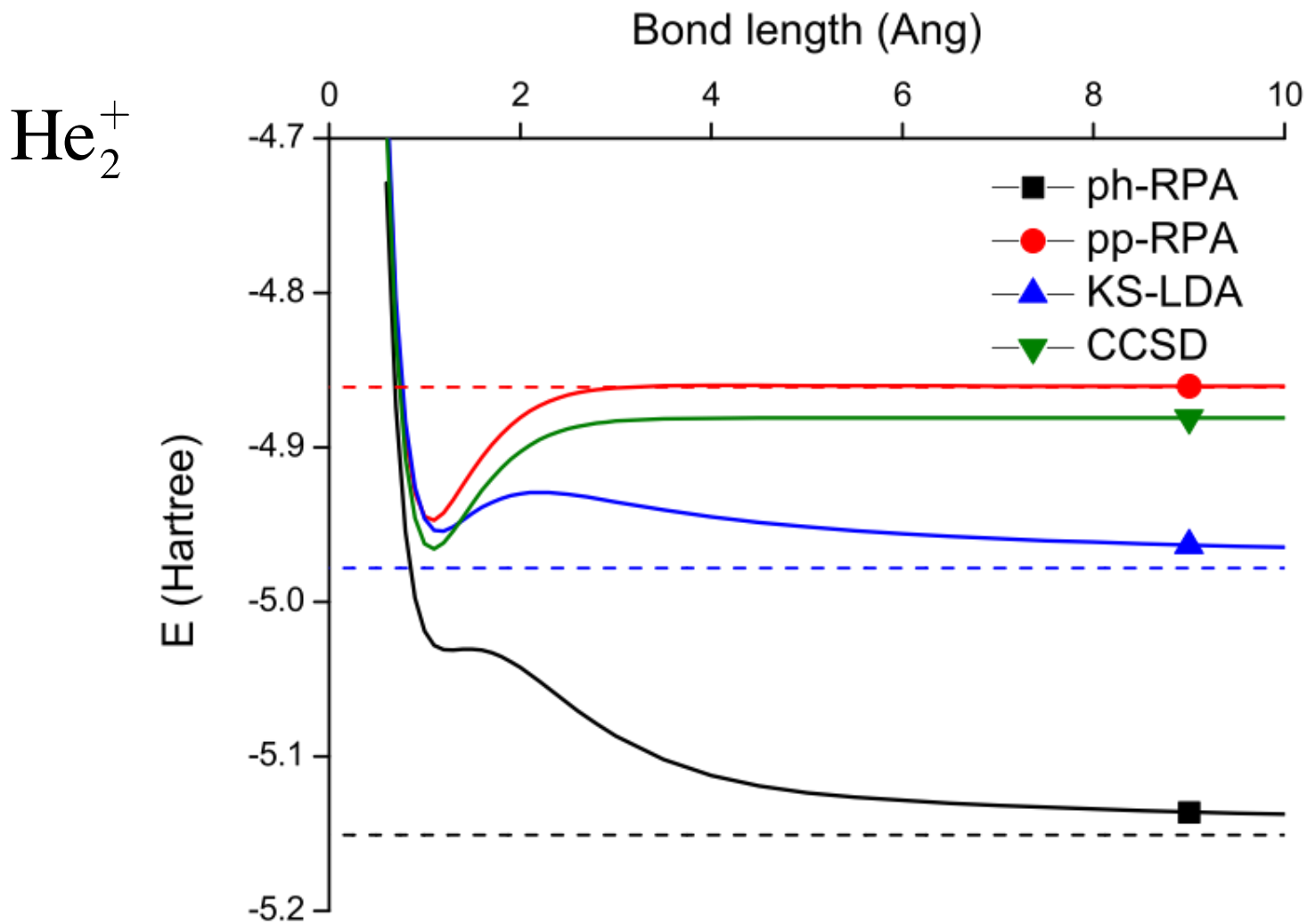$$B_{abij} = \langle ab \| ij \rangle$$
$$C_{ijkl} = \langle ij \| kl \rangle - \delta_{ik}\delta_{jl}(\epsilon_i + \epsilon_j - 2\nu).$$

$$E_{pp}^c = \sum_n^{N_{pp}} \omega_n^{N+2} - \sum_{a<b}^{N_p} (\epsilon_b + \epsilon_a) - \sum_{a<b}^{N_p} V_{abab}$$

$$= \sum_n^{N_{pp}} \omega_n^{N+2} - \mathrm{tr}\, A$$
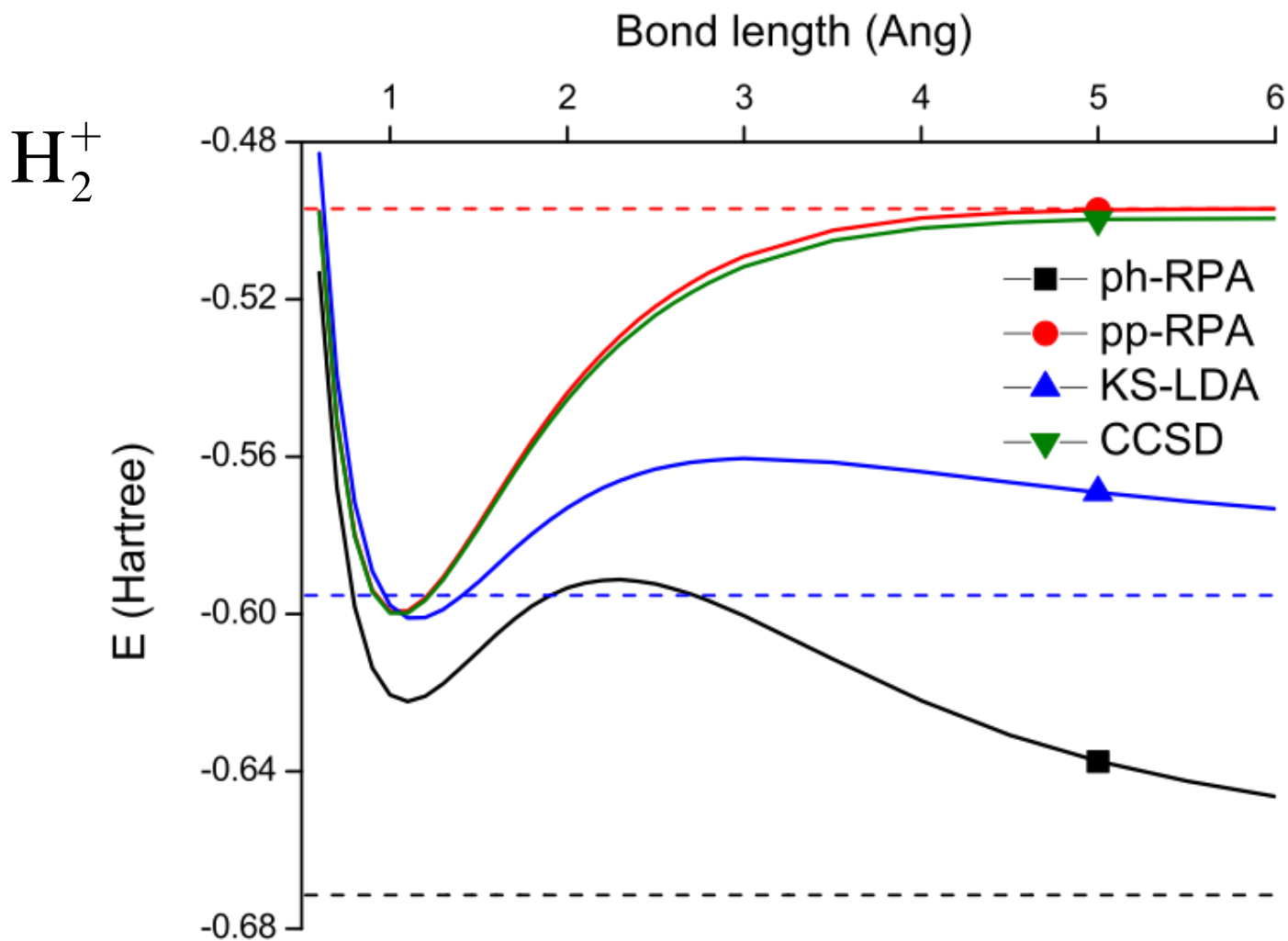
The ph-RPA has large fractional-charge errors

The ph-RPA has large fractional-charge errors

He_2^+

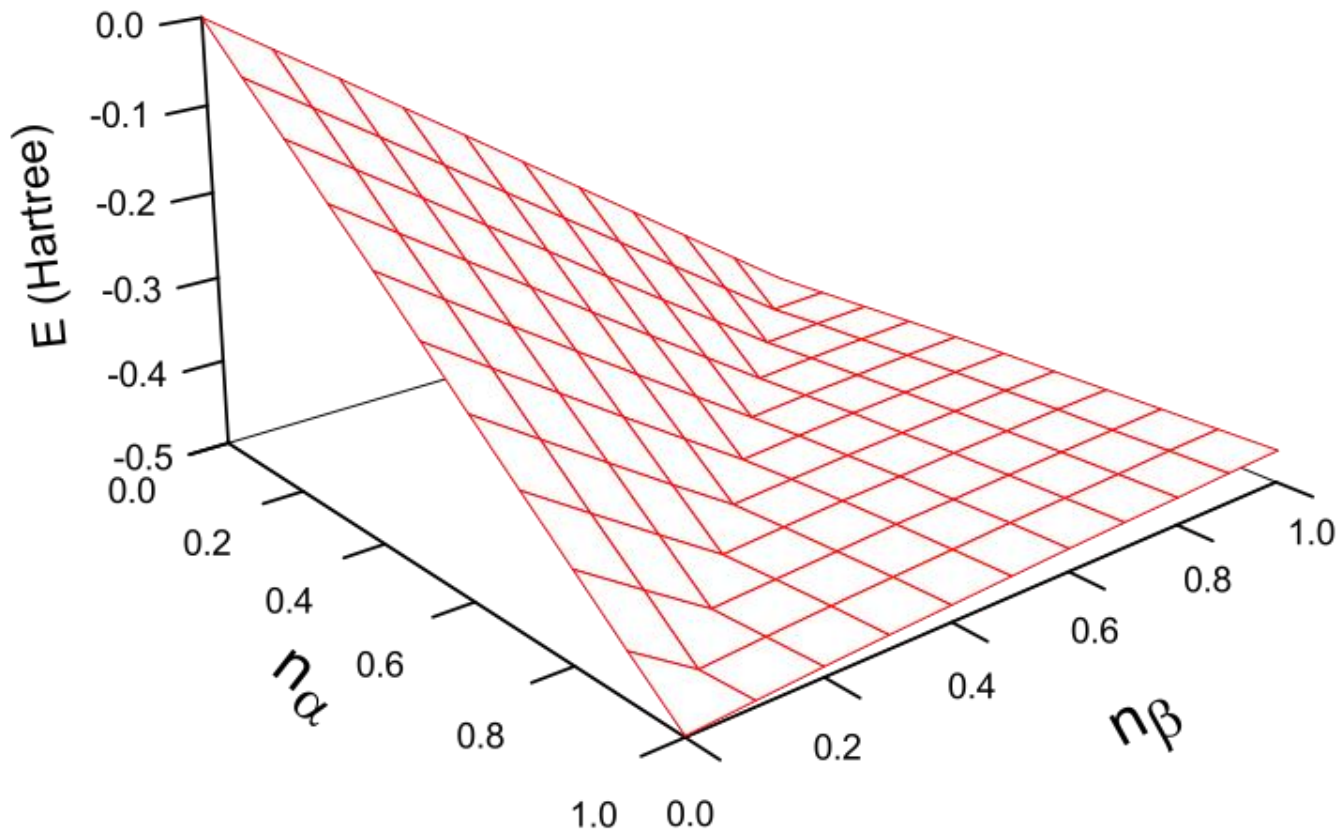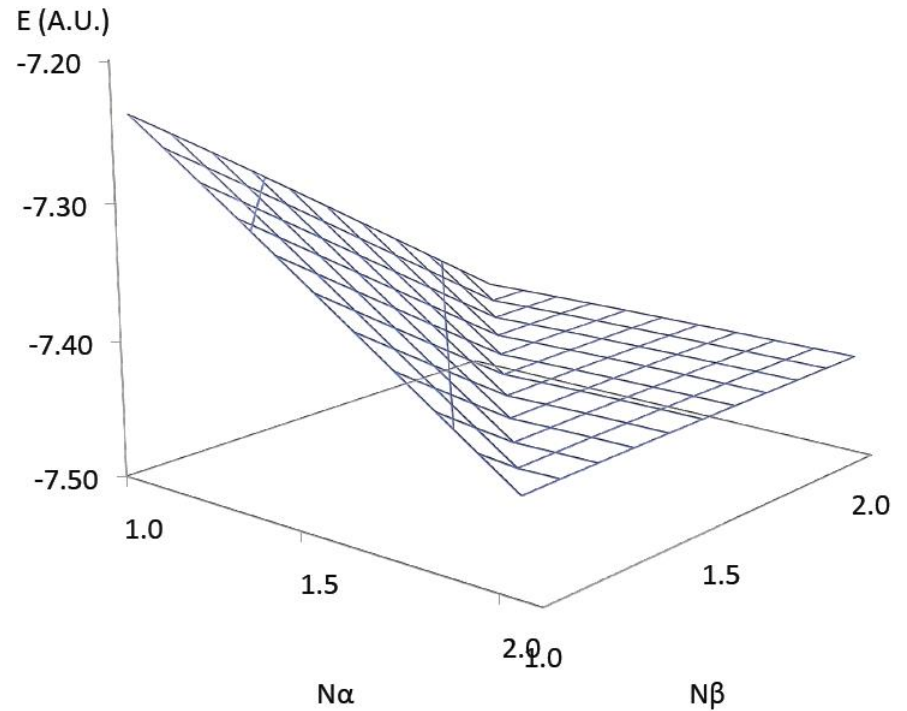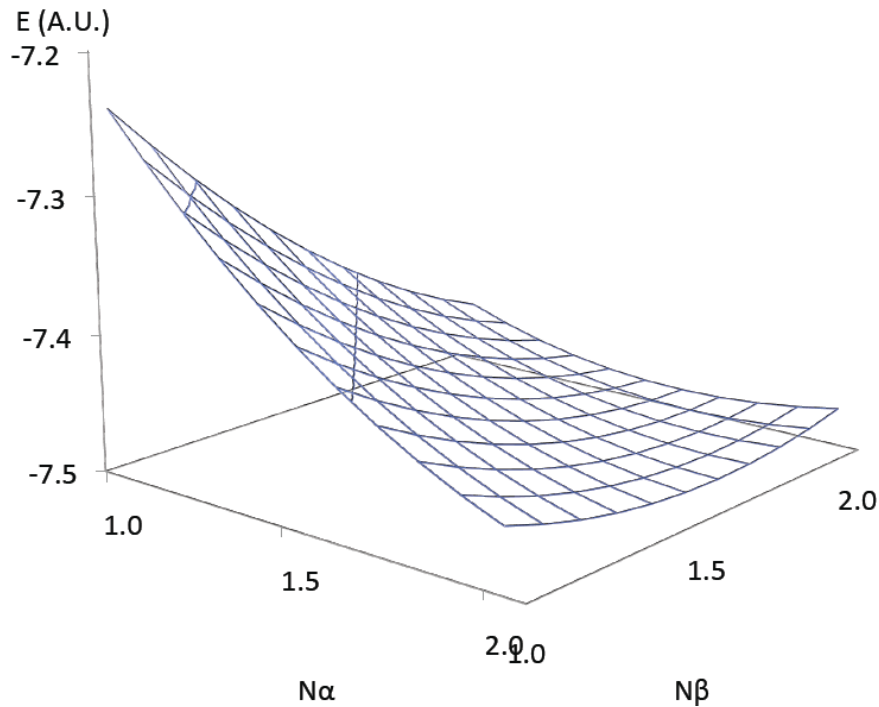# The ph-RPA violates the 'flat plane condition'
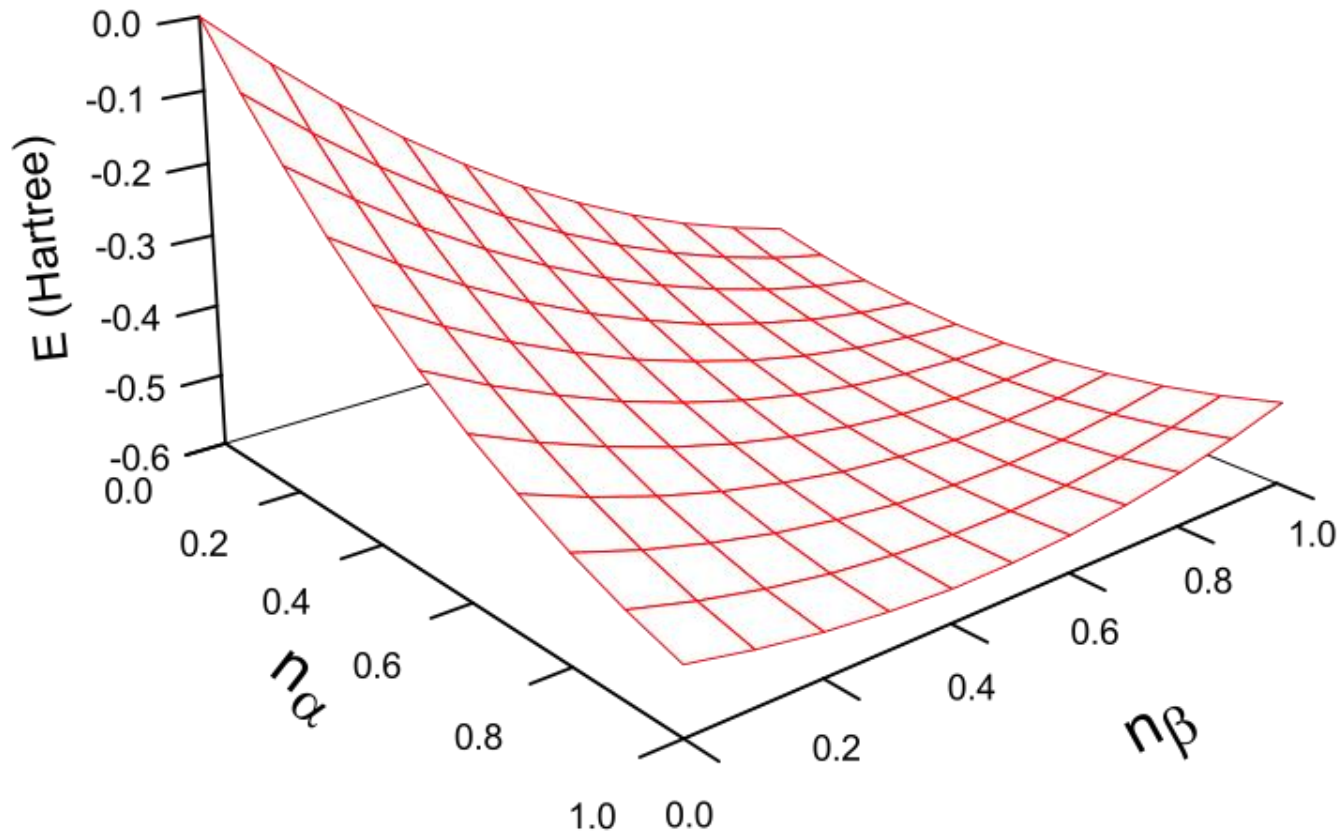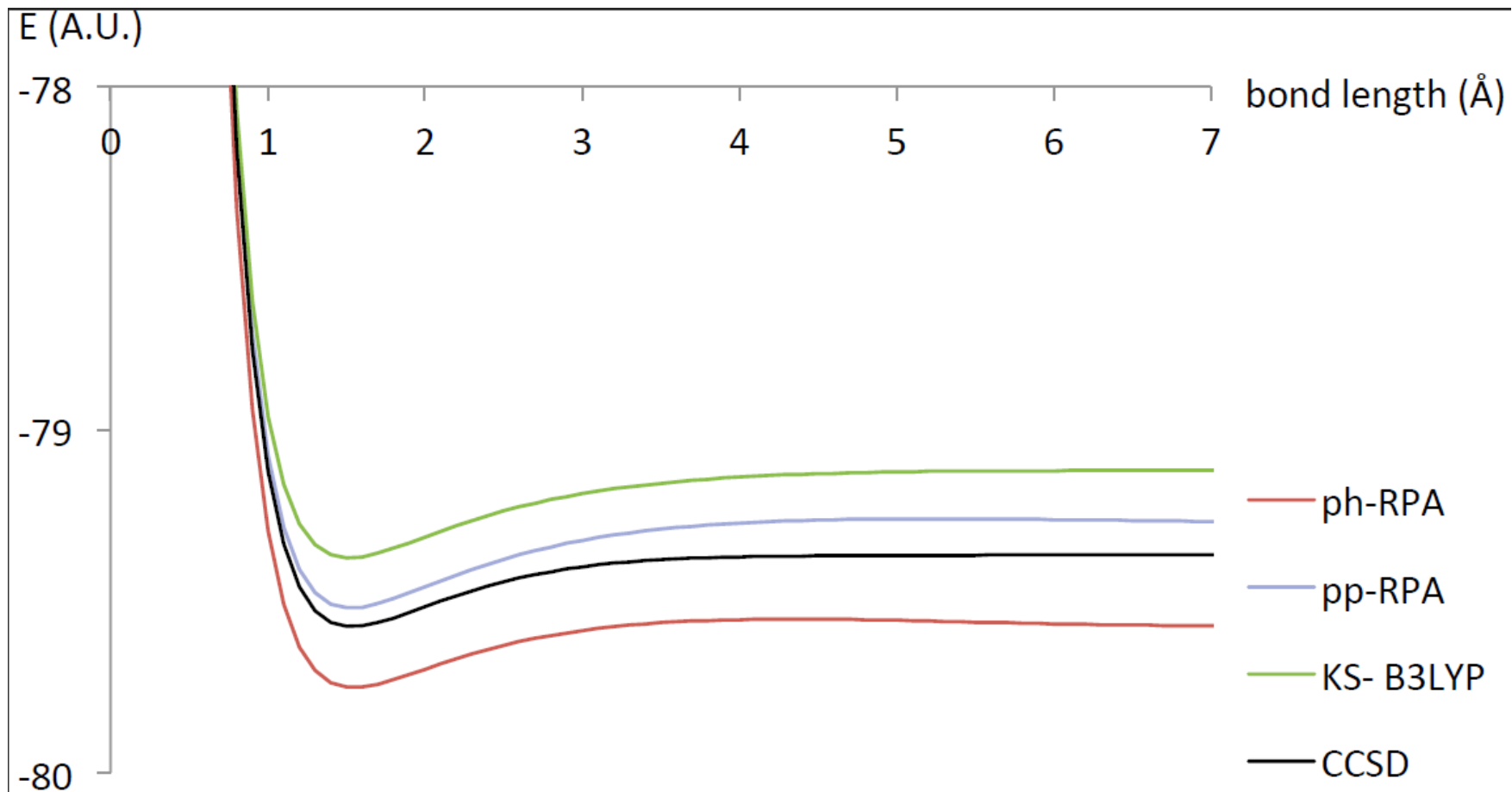
The pp-RPA satisfies the 'flat plane condition'

H

ph-RPA vs. pp-RPA

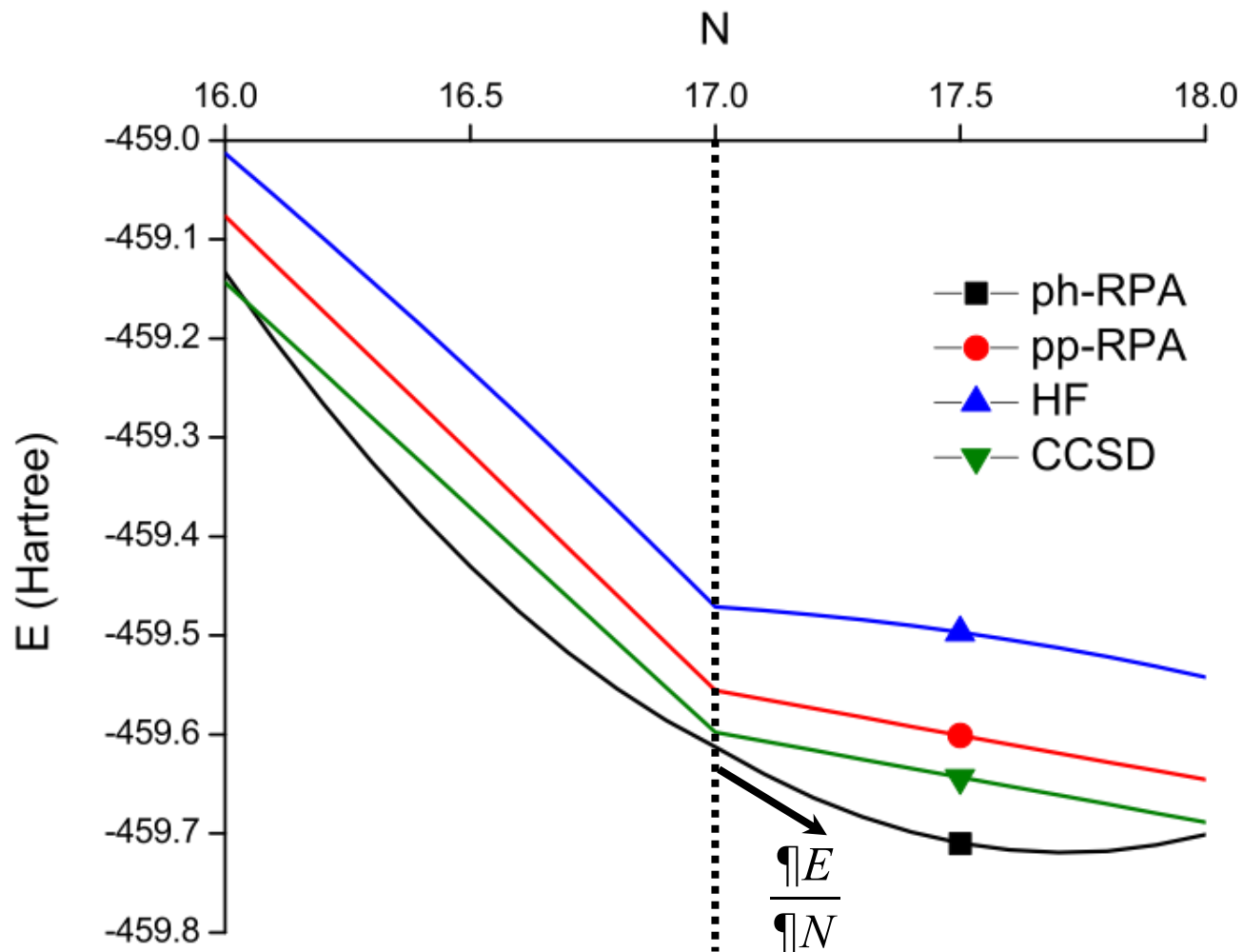
Li atom

CH3-CH3 dissociation

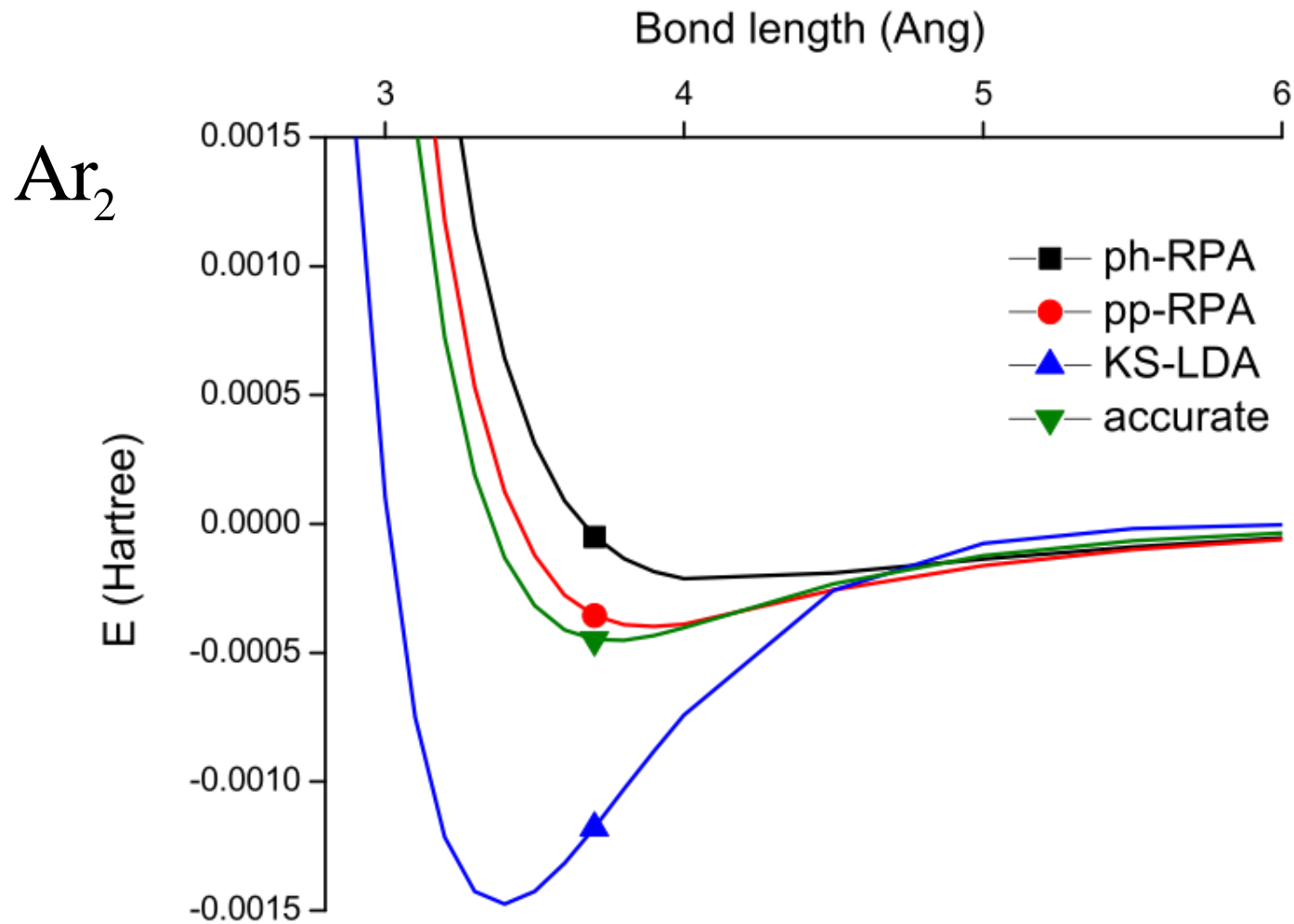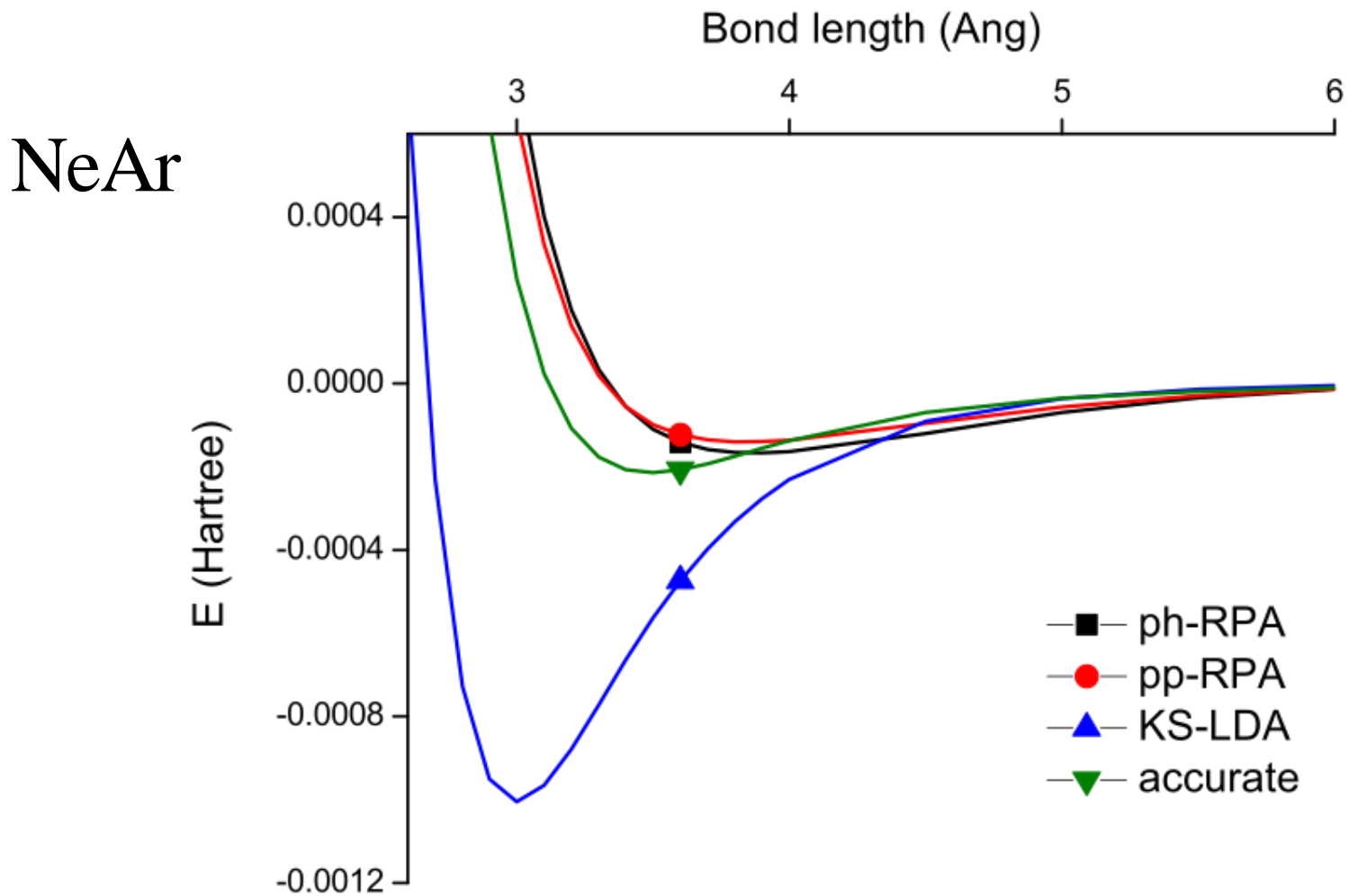# The pp-RPA has much better energy derivatives than the ph-RPA

The pp-RPA has much better energy derivatives than the ph-RPA

$$\left(\frac{\partial E}{\partial N} \right)_{N+d}$$

	pp-RPA	ph-RPA	LDA	expt.
Li	0.125	-3.013	-2.169	-0.618
Be	1.185	-2.811	-2.515	-0.295
B	0.772	-4.010	-3.812	-0.280
C	0.177	-4.131	-5.083	-1.262
N	0.959	-5.553	-4.910	-0.070
O	-1.395	-8.299	-7.709	-1.461
F	-4.206	-11.434	-10.812	-3.401
MAE	**0.945**	**4.552**	**4.232**	

The pp-RPA also recovers van der Waals interactions

Ar$_2$

The pp-RPA also recovers van der Waals interactions

NeAr

Error dependence on number of atoms

Reason?
May be change of electron pairs

ph-RPA: increase dramatically

pp-RPA: nearly constant

What is the exact theory behind pp-RPA?

Ph-excitation:

$$TDDFT \quad \xrightarrow{f_{xc} = 0} \quad RPA$$

Pp-excitation:
double ionization,
double electron affinity

$$TD\ ?\ theory \quad \xrightarrow{?_{xc} = 0} \quad pp\text{-}RPA$$
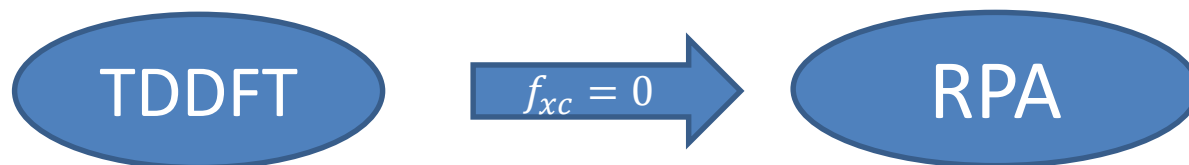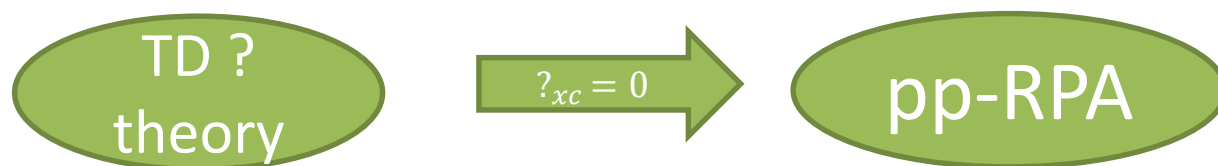
TDDDFT-P: TDDFT with pairing fields

$$\hat{D} = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' [D^*(\mathbf{x}, \mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}) + h.c.]$$

Linear-response TDDFT-P

- TDDFT with pairing field (TDDFT-P) at zero-pairing field limit

$$\mathbf{K}(\omega) = \mathbf{K}_s(\omega) + \mathbf{K}_s(\omega)\mathbf{L}\mathbf{K}(\omega)$$
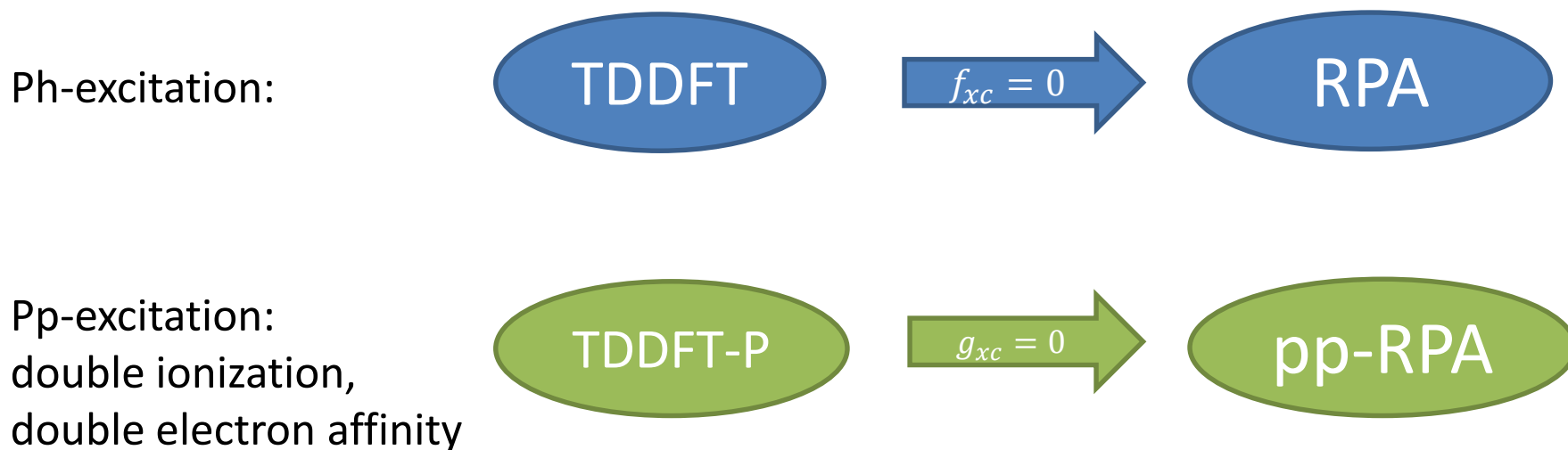
$$\lim_{\delta^2 E_{\mathrm{XC}}/\delta\kappa^*\delta\kappa \to 0} \mathrm{TDDFT\text{-}P} = \mathrm{pp\text{-}RPA}$$

- Extension and Restriction of work related to DFT/TDDFT for superconductors by Gross *et al.*

- Path forward

$$g_{xc} = \lim_{\kappa \to 0} \frac{\delta^2 E_{\mathrm{XC}}[\rho, \kappa]}{\delta\kappa^*(\mathbf{x}_1, \mathbf{x}_1')\delta\kappa(\mathbf{x}_2, \mathbf{x}_2')}$$

Peng, van Aggelen, Yang, Yang, *J. Chem. Phys.* 2014

--What is the exact theory behind pp-RPA?

Ph-excitation:

$$TDDFT \xrightarrow{f_{xc} = 0} RPA$$

Pp-excitation:
double ionization,
double electron affinity

$$TDDFT\text{-}P \xrightarrow{g_{xc} = 0} pp\text{-}RPA$$

--Justify the use of DFT reference in the pp-RPA calculations

Peng, van Aggelen, Yang, Yang, *J. Chem. Phys.* 2014

Capture Challenging Excitations with Particle-Particle Random Phase Approximation

Yang Yang, Helen v. Aggelen and WY

J. Chem. Phys. 2013

Reference shift
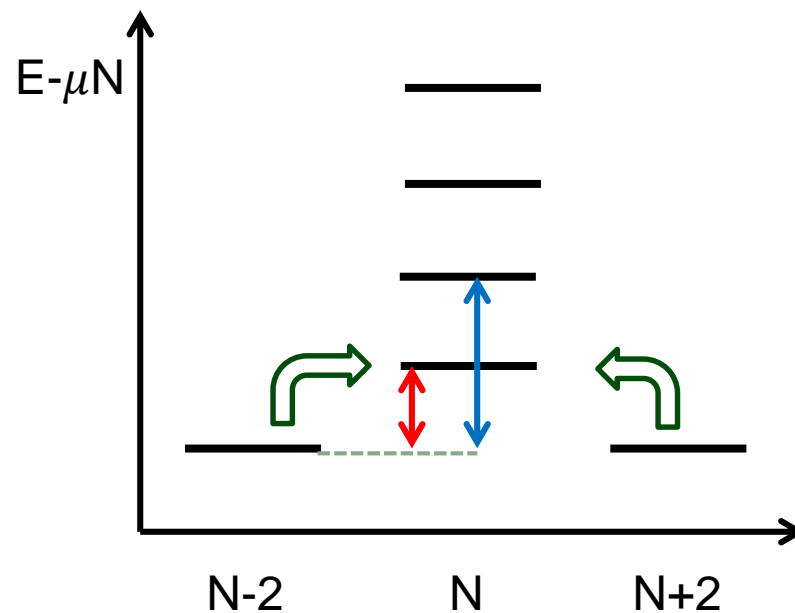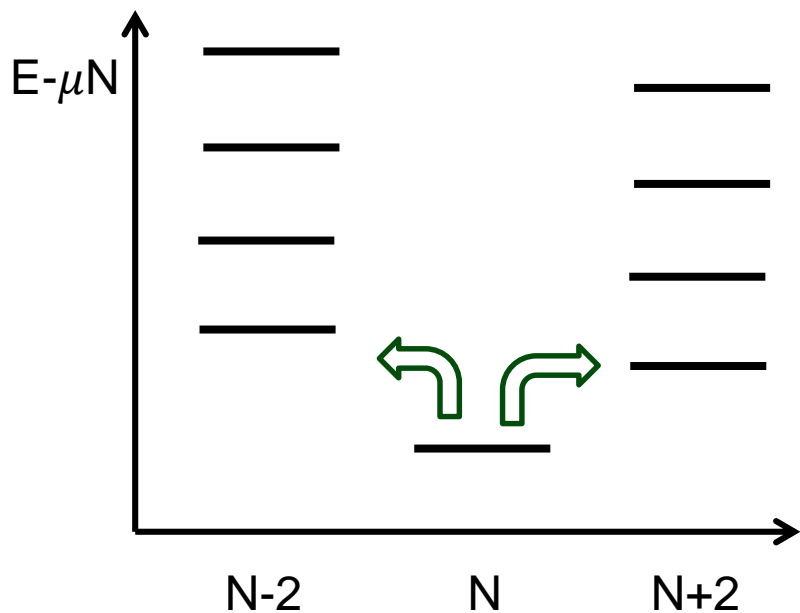
$$E_{excitation} = E_{blue} - E_{red}$$

TABLE I. Lowest double excitations or excitations with double excitation character (in eV).[a]

Term	Standard	RPA-HF	TDA-HF	RPA-B3LYP	RPA-HF*
Be					
^1D	7.05	7.06	7.06	7.97	7.06
^3P	7.40	7.45	7.45	7.84	7.45
BH					
$^3\Sigma$	5.04	5.51	5.48	5.12	5.53
$^1\Delta$	6.06	6.15	6.12	5.98	6.18
$^1\Sigma$	7.20	7.10	7.11	7.05	7.22
Butadiene					
^1A_g	6.55	5.93	5.83	6.47	7.93
Hexatriene					
^1A_g	5.21	5.43	5.34	5.01	7.46

TABLE II. Rydberg excitations (in eV).[a]

Transition	Term	Standard	RPA-HF	TDA-HF	RPA-HF*
Be					
$2s \rightarrow 6s$	^3S	8.82	8.79	8.79	8.79
$2s \rightarrow 6s$	^1S	8.84	8.81	8.81	8.81
$2s \rightarrow 6p$	^3P	8.89	8.87	8.87	8.87
$2s \rightarrow 6p$	^1P	8.90	8.87	8.87	8.87
$2s \rightarrow 6d$	^3D	8.93	8.91	8.91	8.91
$2s \rightarrow 6d$	^1D	8.96	8.95	8.95	8.95
Li					
$2s \rightarrow 6s$	^2S	4.96	4.97	4.97	…
$2s \rightarrow 6p$	^2P	5.01	5.05	5.05	…
$2s \rightarrow 6d$	^2D	5.01	5.03	5.03	…
N_2					
$\sigma_g \rightarrow 3s\sigma_g$	$^3\Sigma_g^+$	12.0	10.97	10.39	…
$\sigma_g \rightarrow 3s\sigma_g$	$^1\Sigma_g^+$	12.2	11.07	10.69	…
$\sigma_g \rightarrow 3p\pi_u$	$^1\Pi_u$	12.90	11.62	11.26	…
$\sigma_g \rightarrow 3p\sigma_u$	$^1\Sigma_u^+$	12.98	11.63	11.29	…

Accurate atomic quantum defects from particle-particle random phase approximation

Yang Yang

Department of Chemistry, Duke University, Durham, NC 27708, U.S.

Kieron Burke[*]

Weitao Yang[†]

The particle-particle random phase approximation with a Hartree-Fock reference accurately describes all the Rydberg excitations with a small error in quantum defect.
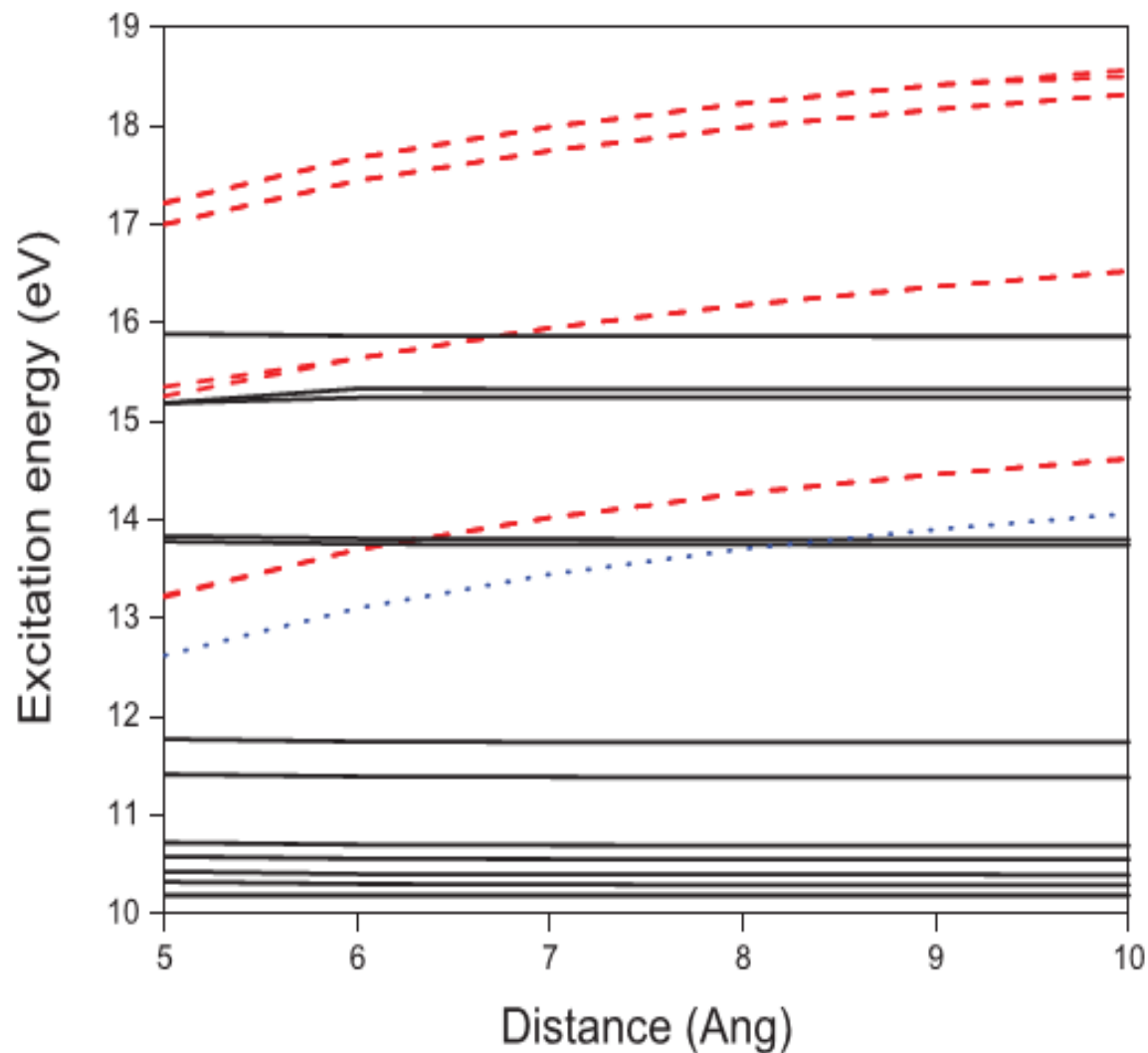
Mol. Phys. 2015

$C_2H_4 \cdot C_2F_4$
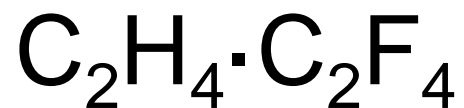
Black: non-CT

Red: CT

Blue: 1/r reference

Results: good single excitation

TABLE III. Single excitations (in eV).[a]

Term	Standard	RPA-HF	RPA-B3LYP	RPA-HF*	TDDFT
Mg					
^3P	2.71	2.57	3.43	2.58	2.61
^1P	4.53	4.27	5.68	4.28	4.25
^3S	5.11	4.99	6.96	5.00	5.06
^1S	5.39	5.27	7.21	5.28	5.45
CH^+					
$^3\Pi$	1.15	1.72	1.16	1.31	−1.24
$^1\Pi$	3.07	3.60	3.18	3.50	2.83
CO					
$^3\Pi$	6.32	5.59	5.84	6.44	5.96
$^1\Pi$	8.51	7.77	7.99	9.32	8.42

Ethene

E-Butadiene

all-*E*-Hexatriene

all-*E*-Octatetraene

Cyclopropene

Cyclopentadiene
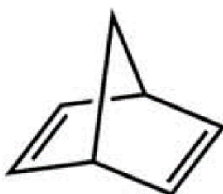
Norbornadiene

Furan
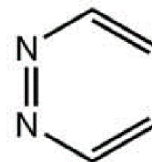
Pyridazine

s-Tetrazine

All-E-Decapentaene
not drawn

H_3C
$H_2C=O$
H_3C
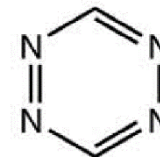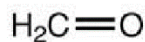
Formaldehyde
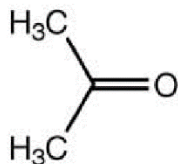
Acetone

p-Benzoquinone

16 molecules
46 excitations
27 Singlets
19 Triplets
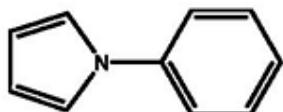
N-phenylpyrrole (PP)

NC

4-(N,N-dimethylamino)
benzonitrile (DMABN)

Benchmark tests: Error summary

eV		RPA-hf	RPA-b3lyp	RPA-pbe	TDA-hf	TDA-b3lyp	TDA-pbe	CIS	TD-hf	TD-b3lyp	TD-pbe
Total	MSE	0.02	0.04	-0.14	-0.14	-0.24	-0.44	0.34	-0.85	-0.34	-0.54
Total	MAE	0.88	0.38	0.38	0.85	0.41	0.60	0.79	1.74	0.38	0.54
Singlet	MSE	-0.17	0.10	-0.04	-0.33	-0.16	-0.30	0.82	0.61	-0.28	-0.63
Singlet	MAE	0.99	0.33	0.34	1.00	0.32	0.54	0.87	0.79	0.36	0.63
Triplet	MSE	0.29	-0.05	-0.27	0.12	-0.34	0.40	-0.36	-2.93	-0.42	-0.41
Triplet	MAE	0.71	0.46	0.44	0.64	0.54	0.43	0.67	3.08	0.42	0.41

Predictions of singlet-triplet gaps for diradicals through particle-particle random phase approximation

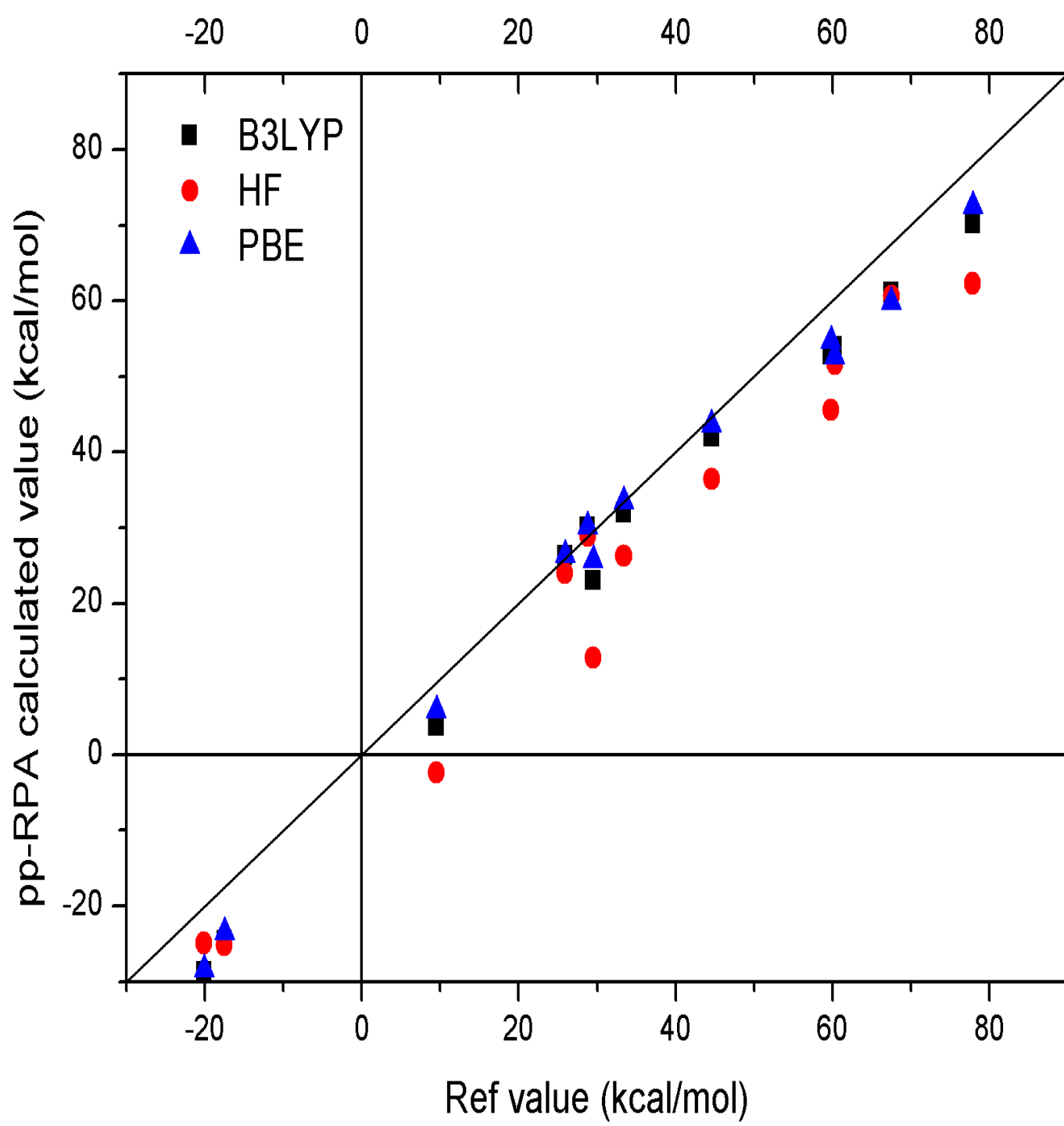JPC 2015

Diradicals

- Radical

- Diradical --- two radicals

  – To pair or not to pair?

p   q

q

p
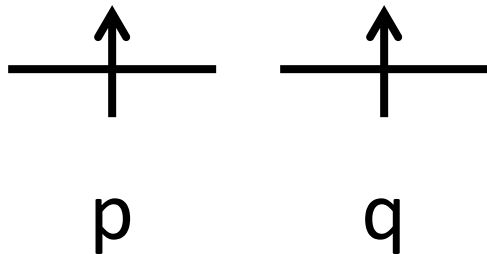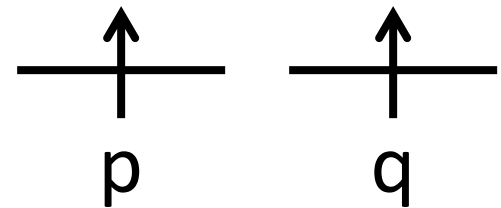
Degenerate

Hund's rule --- Exchange
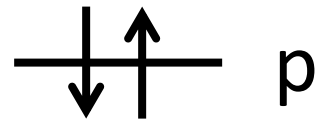
Energy far away

Orbital energy

TABLE III: Vertical singlet-triplet gaps (in kcal/mol) for disjoint diradicals[a]

		Ref.[b]	pp-HF	pp-B3LYP	pp-PBE	(V)FS-PBE[c]	SF-LDA[d]	SF-PBE[d]	SF-B3LYP[d]	SF-ωPBEh[d]
·CH$_2$CH$_2$CH$_2$·		1.8	2.4	4.4	5.4	20.4	-	-	-	-
·CH$_2$(CH$_2$)$_4$CH$_2$·	$^1A_1$	0.0	0.0	0.1	0.1	-	0.0	0.0	0.0	0.0
	$^1B_1$	160.8	79.9	147.4	159.2	-	35.1	38.2	67.8	133.2
	2^1A_1	163.1	80.6	149.0	161.9	-	35.2	38.3	67.9	133.6
·CH$_2$(CH$_2$)$_4$C(CH$_3$)H·	$^1A_1$	-0.2	-0.3	0.1	0.4	-	-1.5	-1.2	-1.1	-0.6
	2^1A_1	131.1	66.1	129.0	139.8	-	26.9	23.2	54.8	113.3
	3^1A_1	144.3	78.3	142.1	152.3	-	46.4	44.6	74.5	127.6

- Using DFT references are critical for pp-RPA.

- When there is no charge transfer ($^1A_1$), both pp-RPA and SF-TDDFT perform well.

- pp-RPA performs much better when there is charge transfer.

Singlet-triplet gaps (in eV) for acenes

Acene	2	3	4	5	6	7	8	9	10
pp-RPA/B3LYP S geo	2.90	2.01	1.41	1.00	0.71	0.51	0.37	0.28	0.22
pp-RPA/B3LYP T geo					0.39	0.25	0.17	0.12	0.09
Expt	2.65[a]	1.87[b]	1.27[c]	0.86[d]					
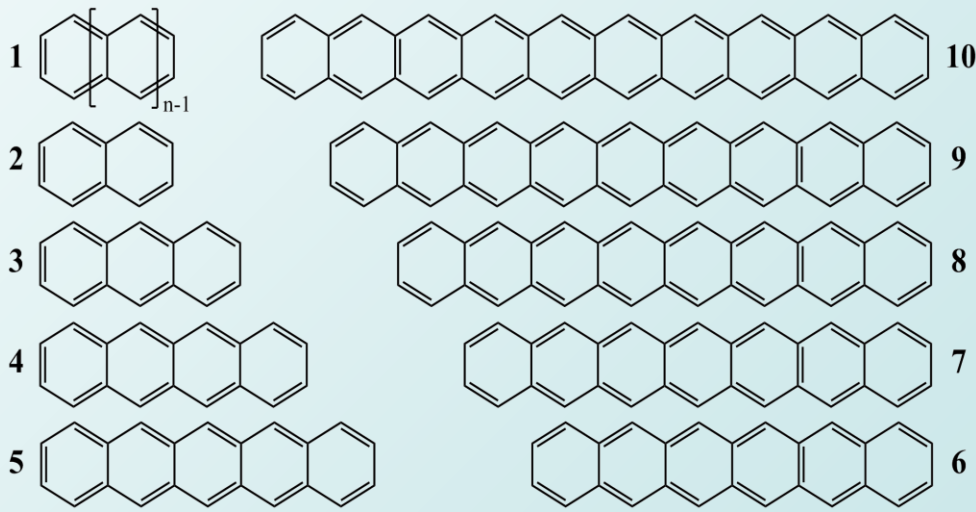
Adriel Dominguez Garcia

Thomas Frauenheim

1. *Excitations with double contributions*

	Ref.	pp-DFTB	pp-RPA	TD-camB3LYP
hexatriene Ag	5.21	5.19	5.01	6.64
butadiene Ag	6.55	6.61	6.47	7.71

2. Charge transfer excitations

--Need functionals with reduced delocalization error.
--Use the RS hybrid DFTB from Thomas Niehaus

Conical intersection

- two electronic states are degenerate and the potential energy surfaces intersect

- N^{int}-2 dimension space

- Often relates to charge transfer, ultrafast photochemical transitions
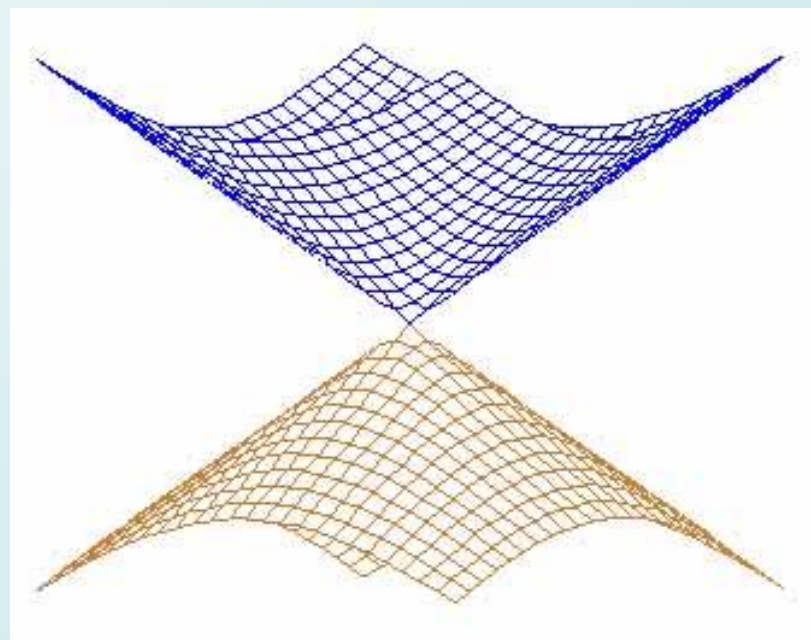
- TDDFT

  - Completely fails to get N^{int}-2 dimension

- Multi-reference methods

  - Usually expensive

- Recently developed methods

  - CIC-TDA, CDFT-CI, SI-SA-REKS, SF-TDDFT

A multi-configuration method that efficiently describes the ground and excited states on the same footing.
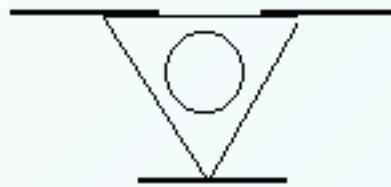
D_{3h}, Huckel's model
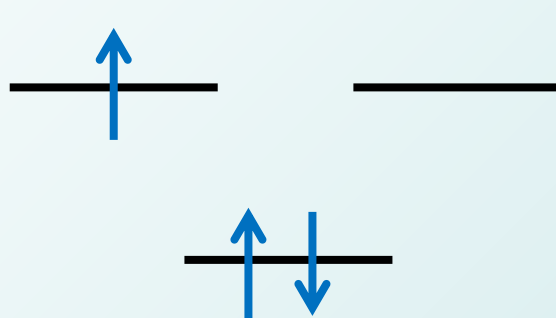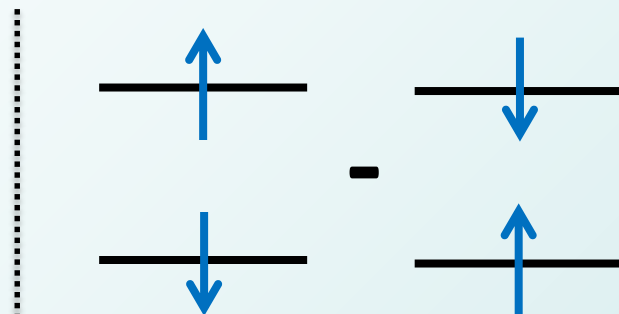
Ground state
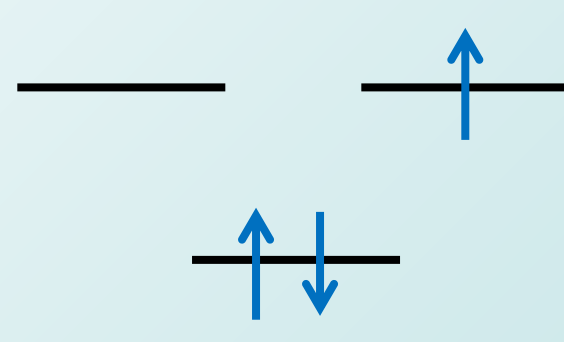
Excited state
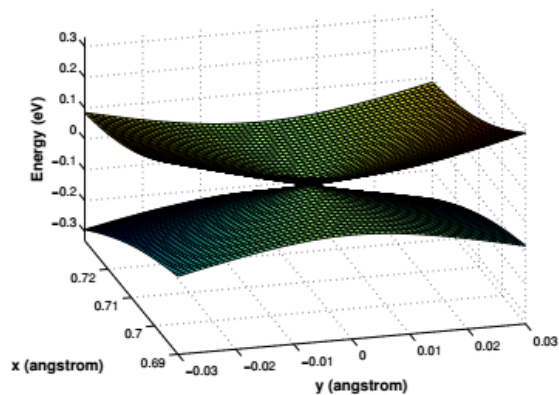
(a) CASSCF(3,6)
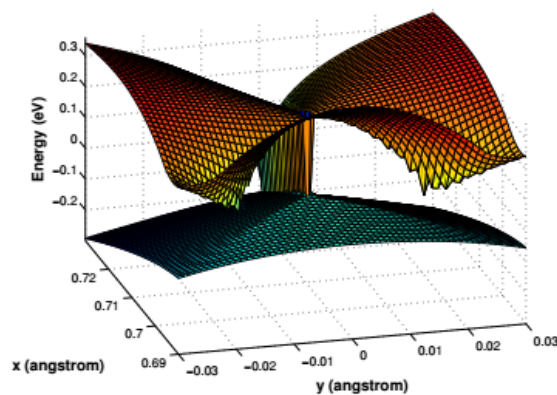
(b) TDDFT-B3LYP
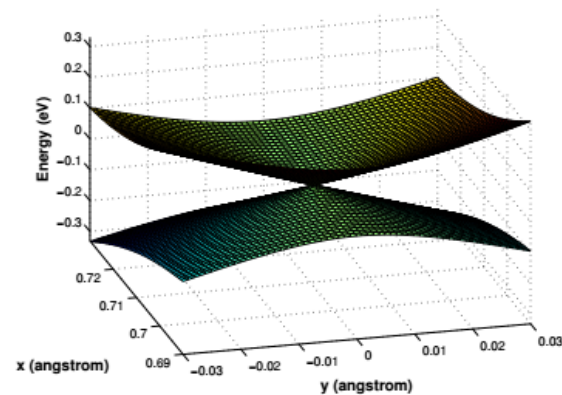
(c) pp-RPA-B3LYP (Same as pp-TDA-B3LYP here)
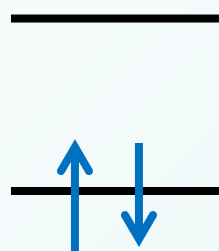
Accurate double-cone character

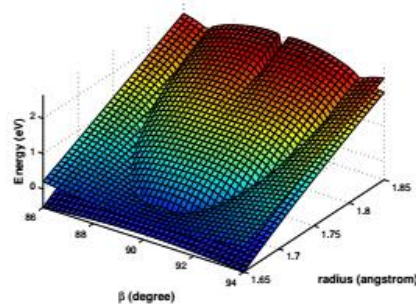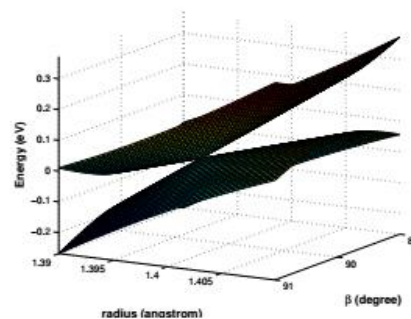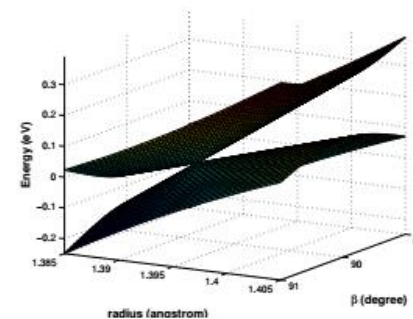Mori-Sanchez, Cohen and Yang, JCP 2006,

Ground state   Excited state
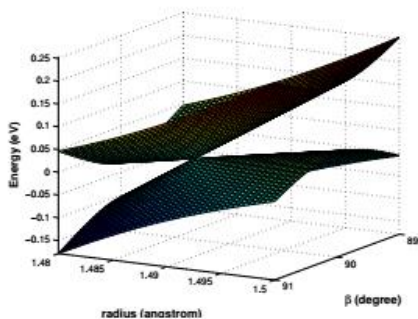
(a) CASSCF(6,6)   (b) TDDFT-B3LYP   (c) pp-RPA-B3LYP   (d) pp-TDA-B3LYP

J. Phys. Chem. Letters, in press 2016