Density Functional Theory: Moden Developments
Fractional Charge, Delocalization Error, Functional Approximation, Excited State Theory

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ACS
NIH
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Density Functional Theory

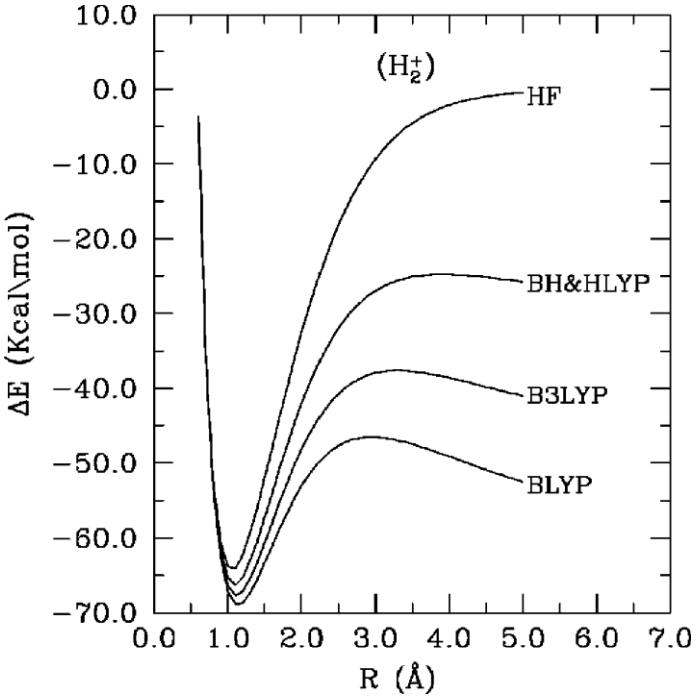
- DFT is exact and should give agreement with experiment or high-level ab initio calculations in all situations.
- Approximate functionals perform well in many systems but can fail dramatically in other situations.
- This can be traced back to **errors of DFA (density functional approximation)**
- The understanding of these errors will hopefully lead to new and improved functionals.
- **The same challenges for other approximate QM methods.**

Error Increases for systems with fractional number of electrons

Zhang and Yang, JCP 1998

H_2^+ **at the dissociation limit**

too low energy for delocalized electrons



Yingkai Zhang, NYU

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

DFT for fractional number of electrons

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

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

Yang, Zhang and Ayers, PRL, 2000 – pure states in molecular dissociation

$$H\Psi_1 = E\Psi_1$$
$$H\Psi_2 = E\Psi_2$$

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

Superposition of degenerate states

Ground State Degeneracy in QM and in DFT

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

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

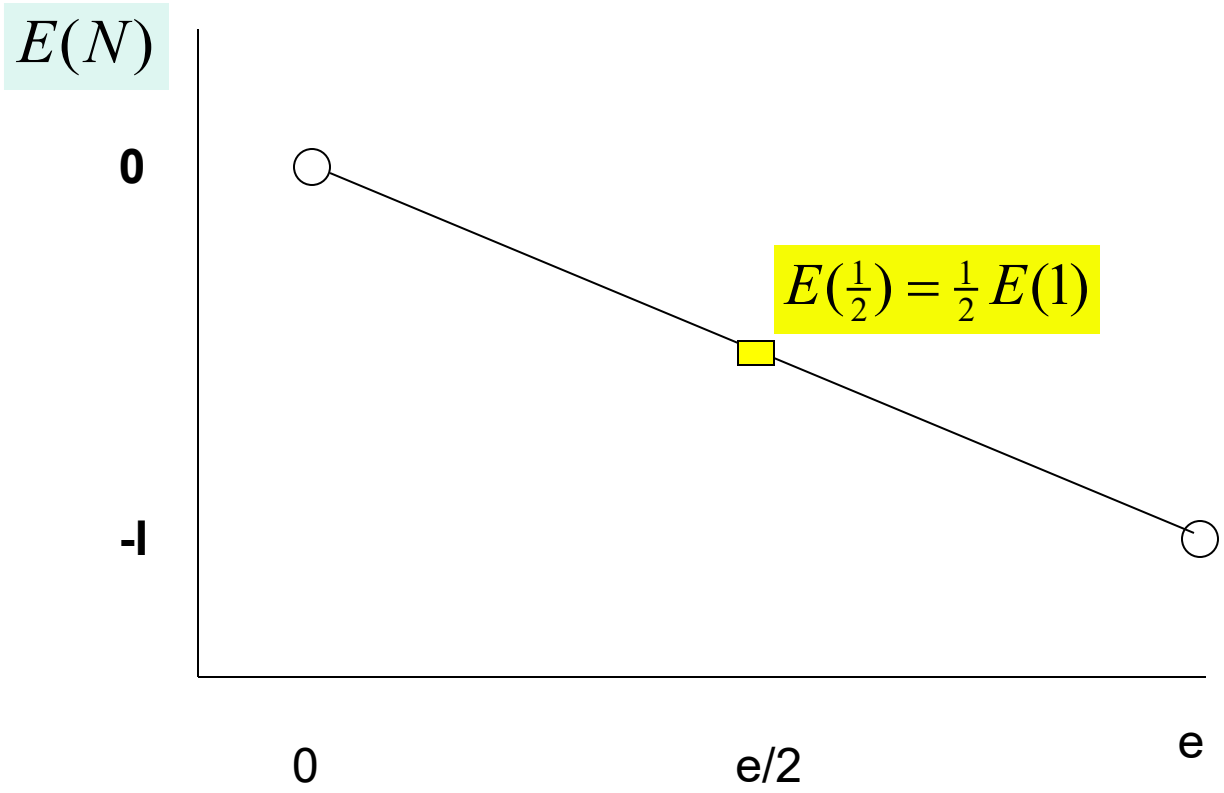
$E_\gamma = E(\frac{1}{2}) + E(\frac{1}{2}) = 2E(\frac{1}{2})$

Proton A e/2

Proton B e/2

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

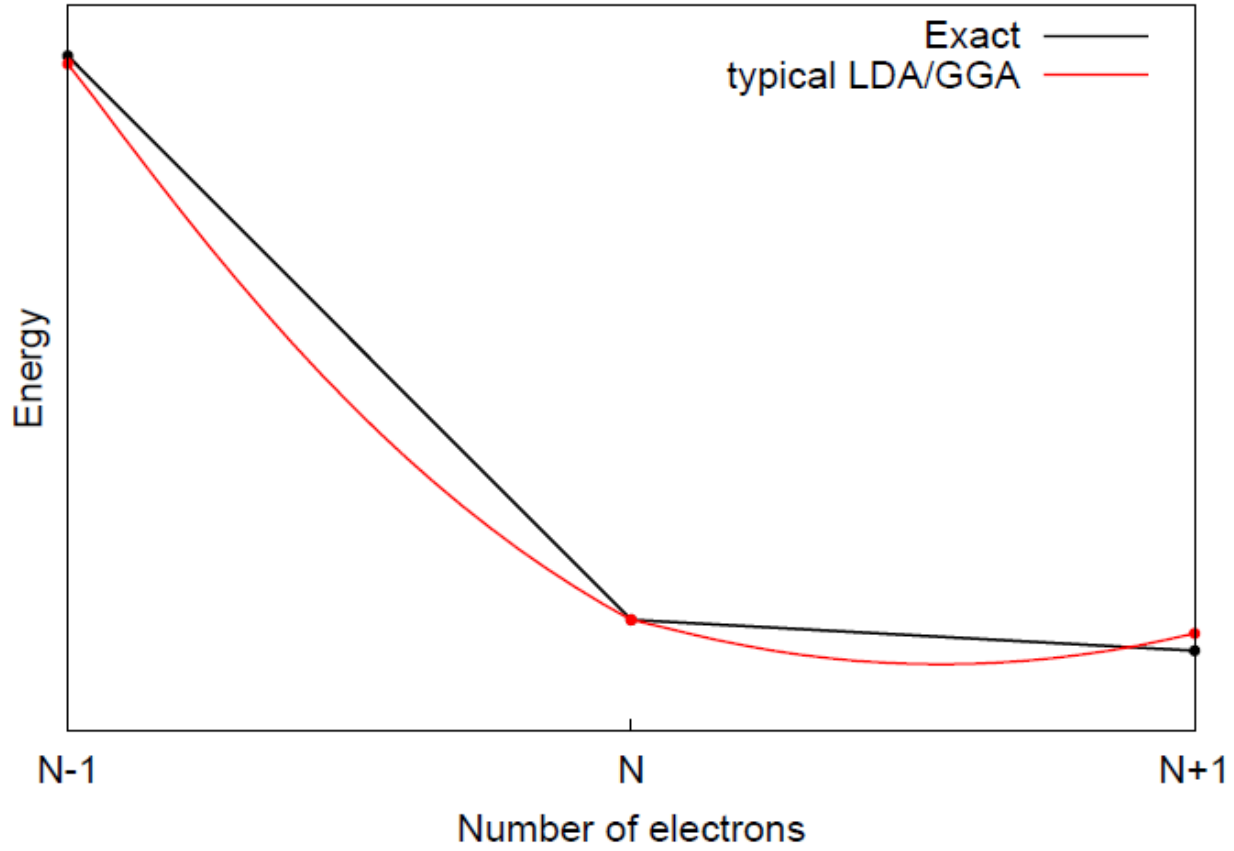
The linearity condition in fractional charges: The energy of e/2



A Homework Problem

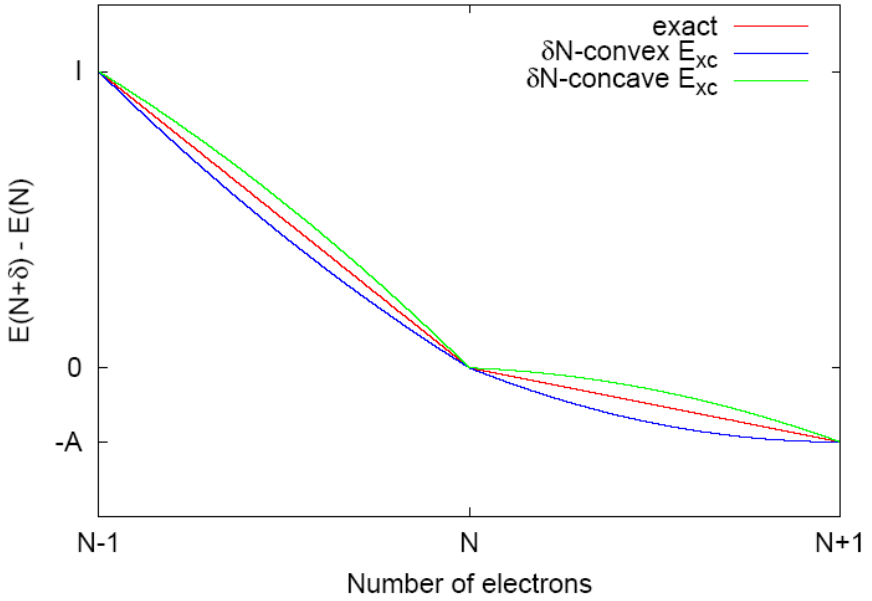
Using the same principles, can you derive the condition for the exact energy functional for 1/3 electron?

E(N)



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

2 x



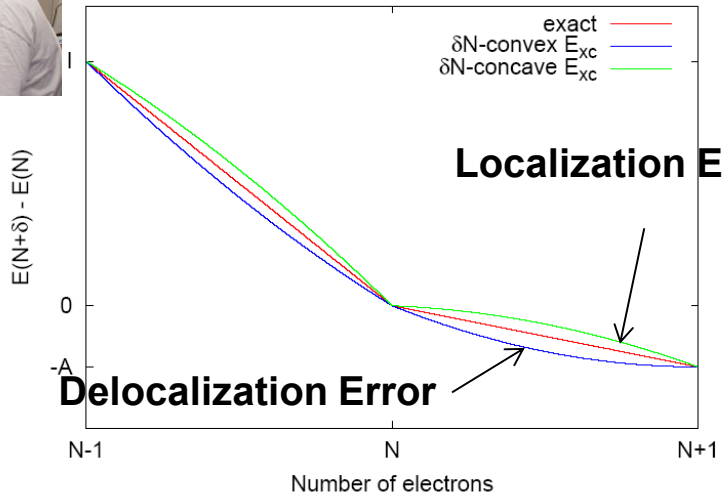
+ e

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, Science 2008***



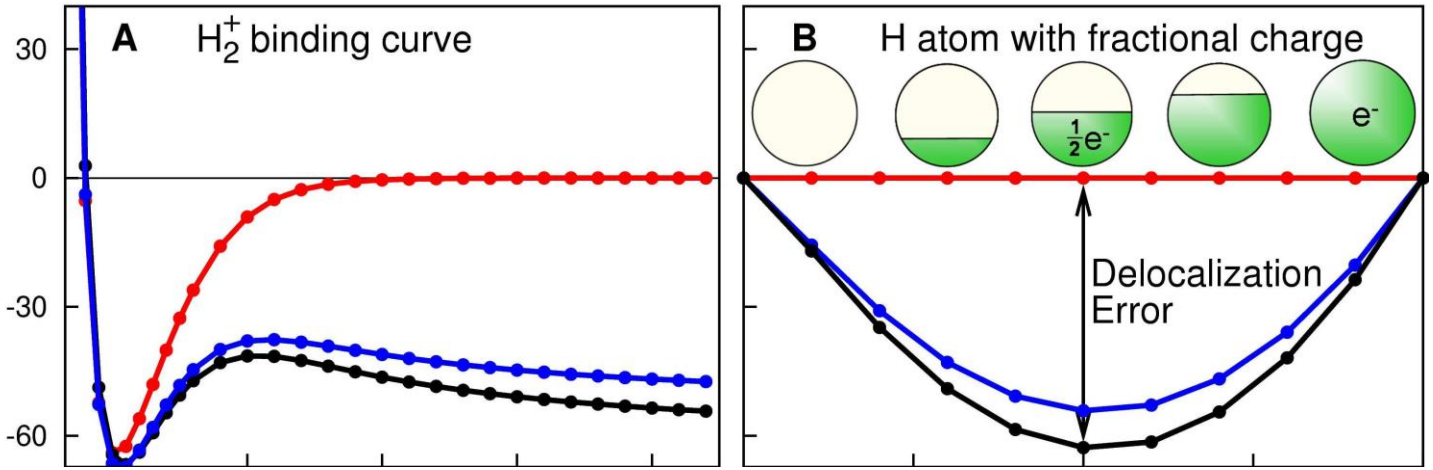
Consequence of Delocalization Error

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 for **small systems**



Cohen, Mori-Sanchez and Yang, 2008 Science

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

Delocalization Error in LDA, GGA, B3LYP

Too low energy for fractional charge systems

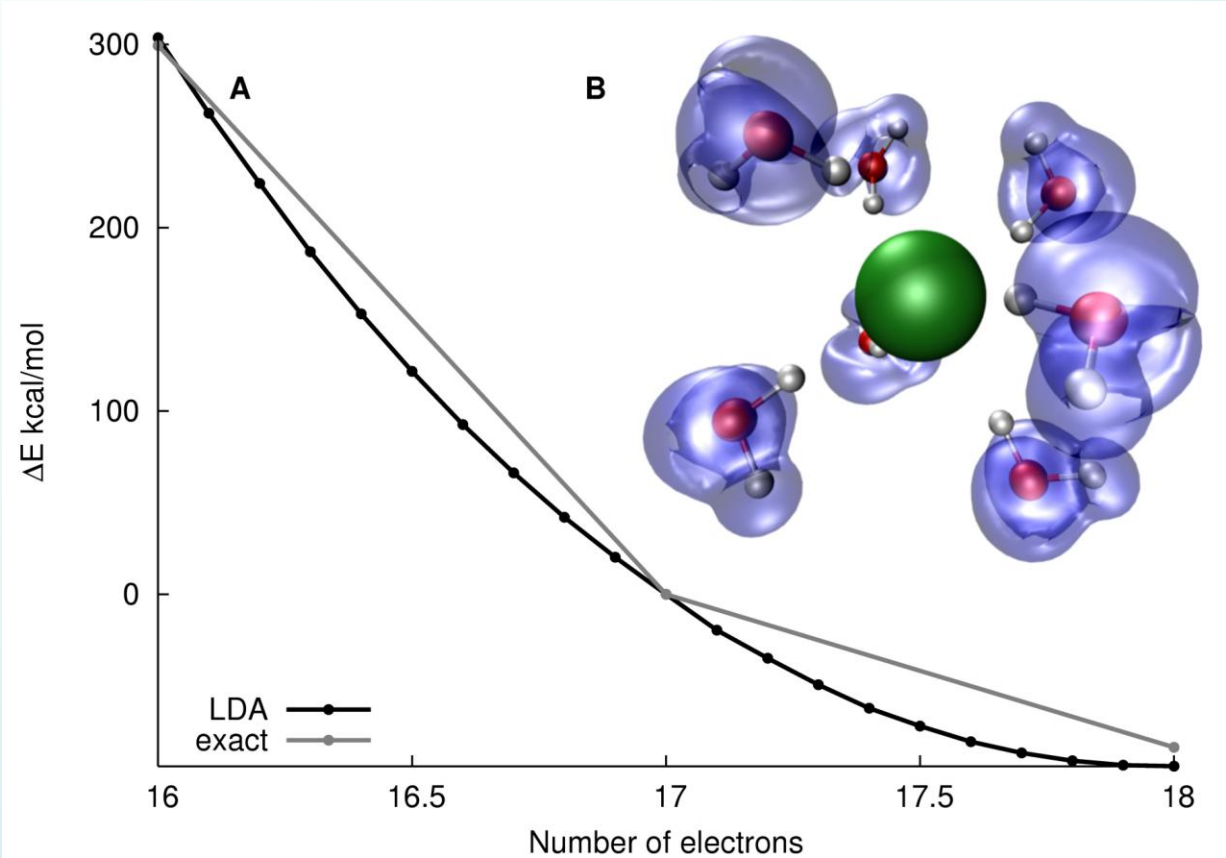
- Energy of dissociation of molecular ion: too low
- Charge transfer complex energy: too low
- Transition state energy: too low
- Charge transfer excitation energy: too low
- Band gap: too low
- Molecular conductance: too high
- (Hyper)polarizability for long molecules: too high
- Diels-Alder reaction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

Cohen, Mori-Sanchez and Yang, 2008 Science

Seeing the delocalization error

$Cl^-(H_2O)_7$

Where is the negative charge ?



DFT: Chemical potentials

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

Perdew, Parr, Levy, and Balduz, PRL. 1982

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**

Band Gap

Definition of fundamental gap

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

derivative

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

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

DFT: Chemical potentials

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

$$\mu = \frac{\partial E}{\partial N} = E^0(J) - E^0(J-1) \qquad \text{for } J > N > J-1 \qquad (4.3.43)$$

$$\mu_{\theta=0} = \begin{cases} -I, & N_0 - 1 < N < N_0 \\ -\dfrac{I+A}{2}, & N = N_0 \\ -A, & N_0 + 1 > N > N_0 \end{cases} \qquad (4.3.15)$$

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.

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

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

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

$$\begin{aligned}\frac{\partial E_v[v_s,N]}{\partial N} &= \int d\mathbf{r}\, \frac{\delta E_v[v_s,N]}{\delta v_s(\mathbf{r})}\bigg|_N \frac{\partial v_s^{\rm gs}(\mathbf{r})}{\partial N} + \left(\frac{\partial E_v[v_s^{\rm gs},N]}{\partial N}\right)_{v_s^{\rm gs}} \\ &= \left(\frac{\partial E_v[v_s^{\rm gs},N]}{\partial N}\right)_{v_s^{\rm gs}} \qquad (1)\end{aligned}$$

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

*Chemical potentials in DFT (PRB **77**, 115123, 2008, Cohen, Moris-Sancehz and Yang)*

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

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

Frontier orbital energies approximate IP and EA, and fundamental gap

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

A new meaning to the 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)

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

$$\left(\frac{\partial E_v^{HF}}{\partial N}\right)_v^{(+)} = \varepsilon_{LUMO}^{HF}.$$

How can fundamental gap be predicted in DFT

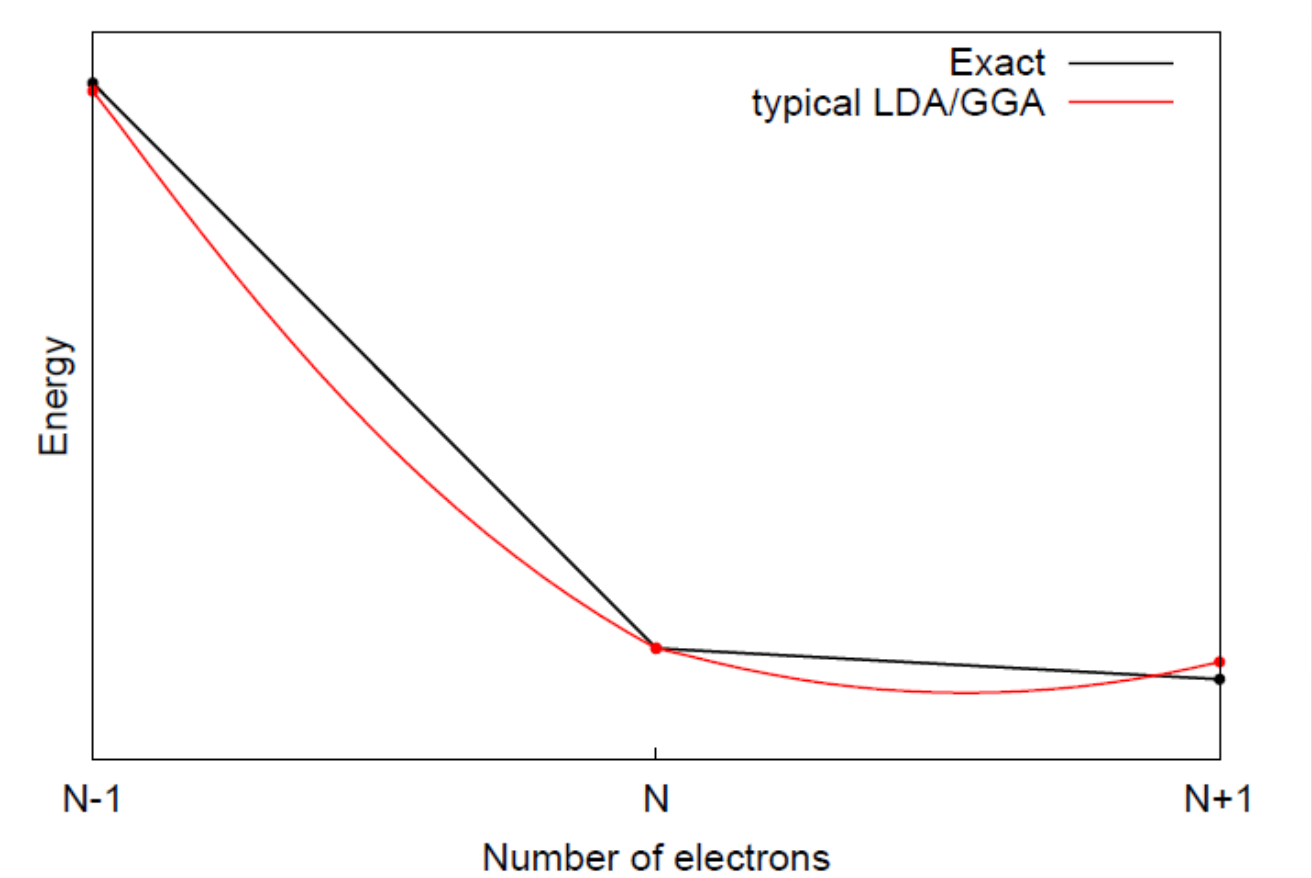
For continuous and differentiable functionals of density/density matrix

- **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.**

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

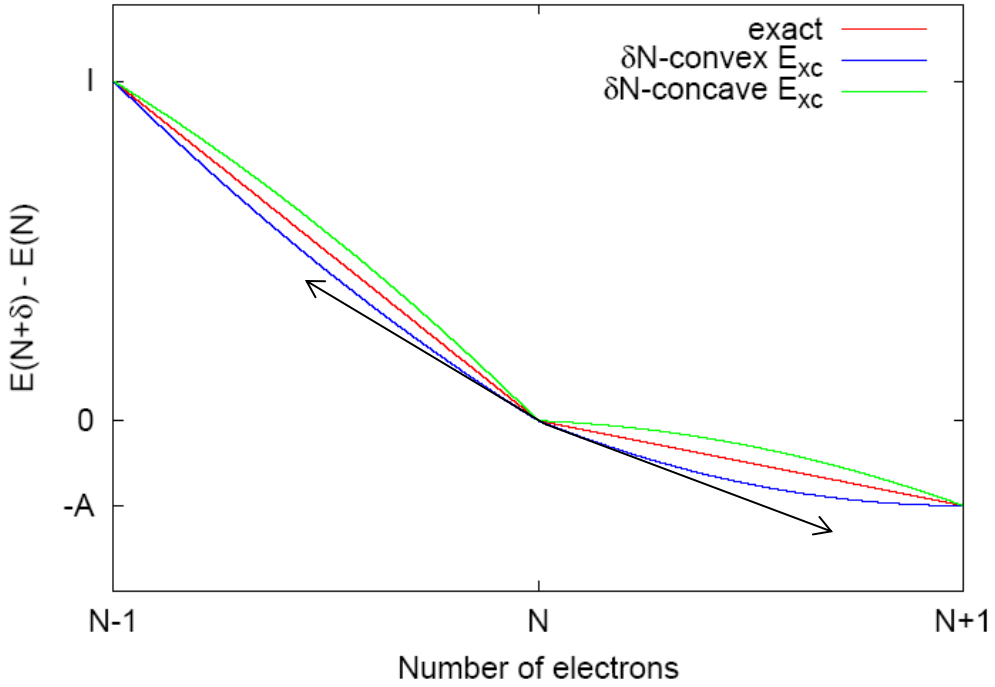
WY, Mori-Sanchez and Cohen, PRB 2008, JCP 2012

E(N)



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

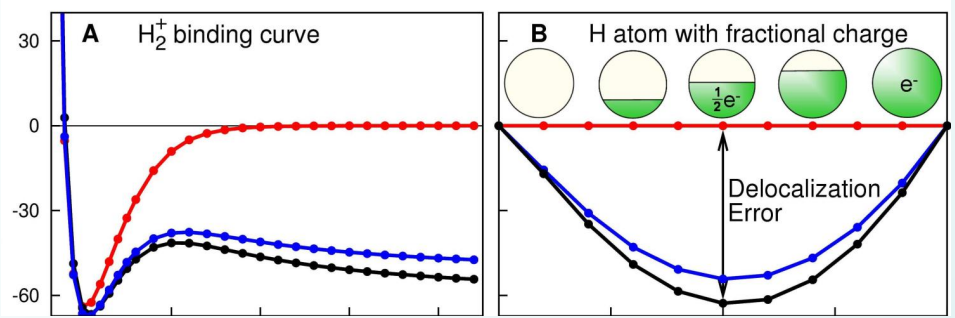
CHEMICAL REVIEWS

Challenges for Density Functional Theory

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

2012

Extensive Efforts in Correcting Delocalization Error



Hybrid
Range-Separate

FLOSIC: **Perdew, Peterson, Ruzsinszky**
Tuned Functionals: **Baer, Kronik, Neaton**
Koopmans Spectral Functional: **Marzari**

Challenges

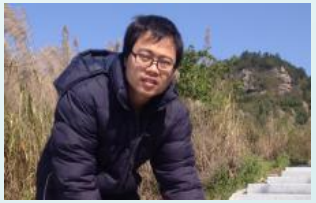
- Error and correction are known in terms of factional charges, but there is no fractional charge at any finite R
- Correction is size dependent, needed at large R, but not at small R. What is difference between the electronic structures at small and large R ?

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

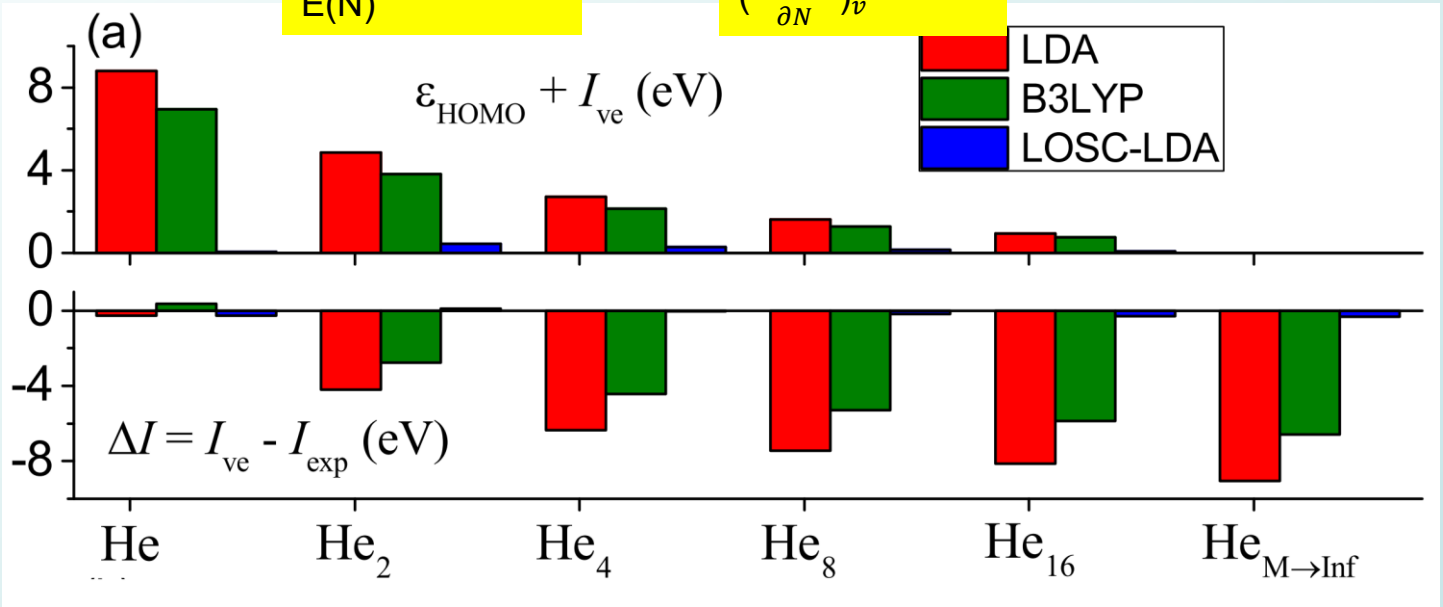
- **Orbitalets: Novel localized orbitals** to represent density matrix.
- **Size-consistent**, functional of the GKS density matrix for corrections to common DFA.
- Accurately characterization of the distributions of **global** and **local** fractional electrons.
- **Systematic improvements**: the dissociation,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

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)

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

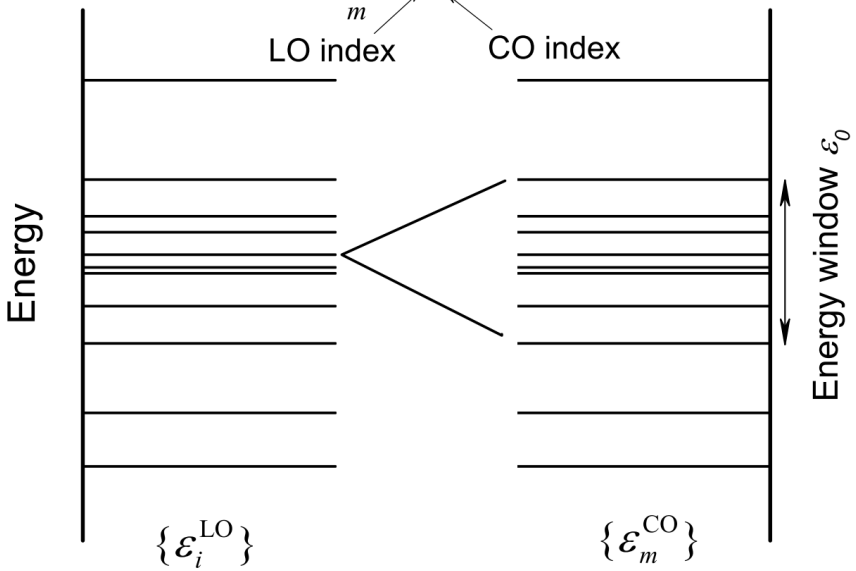


Orbitalets: Novel Localized Orbitals

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

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

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



E-Constrained Optimization

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

Orbitalets: Localized in Space and Energy

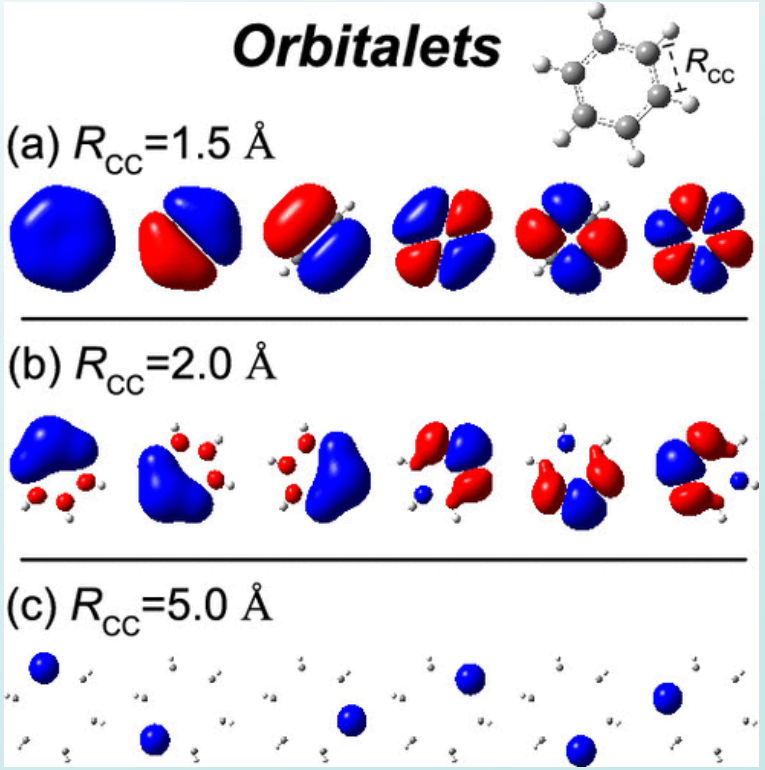
J. Phys. Chem. Lett. 2020

Sum over all orbs, occ and vir

$$\left|\phi_{j\sigma}\right\rangle = \sum_{m} U^{\sigma}_{jm} \left|\psi_{m\sigma}\right\rangle$$

Minimizing F w.r.t. U^{σ}_{jm}

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



LOSC, as correction to DFA

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

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

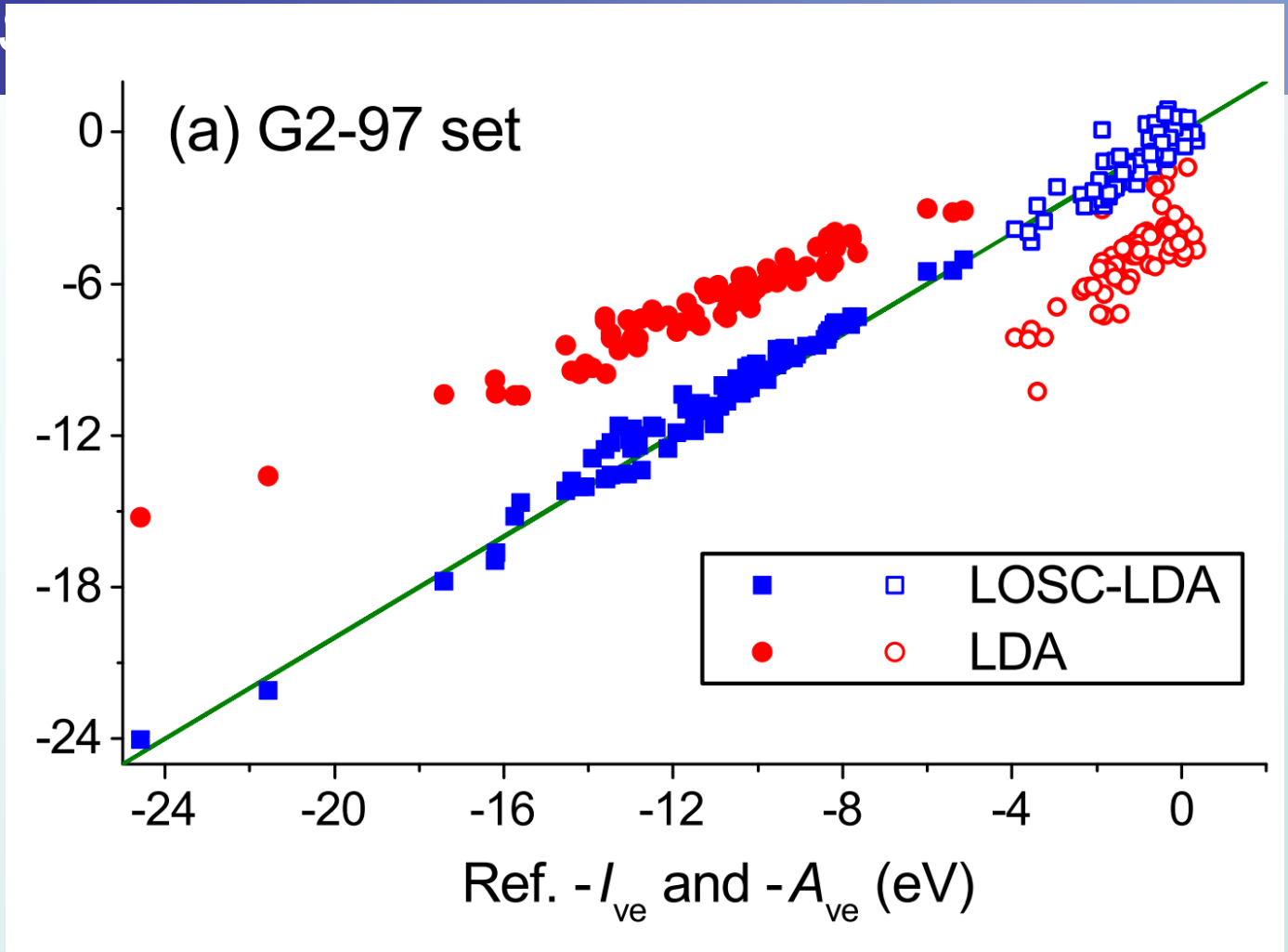
Non-empirical parameter
to get correct limit for H_2^+

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

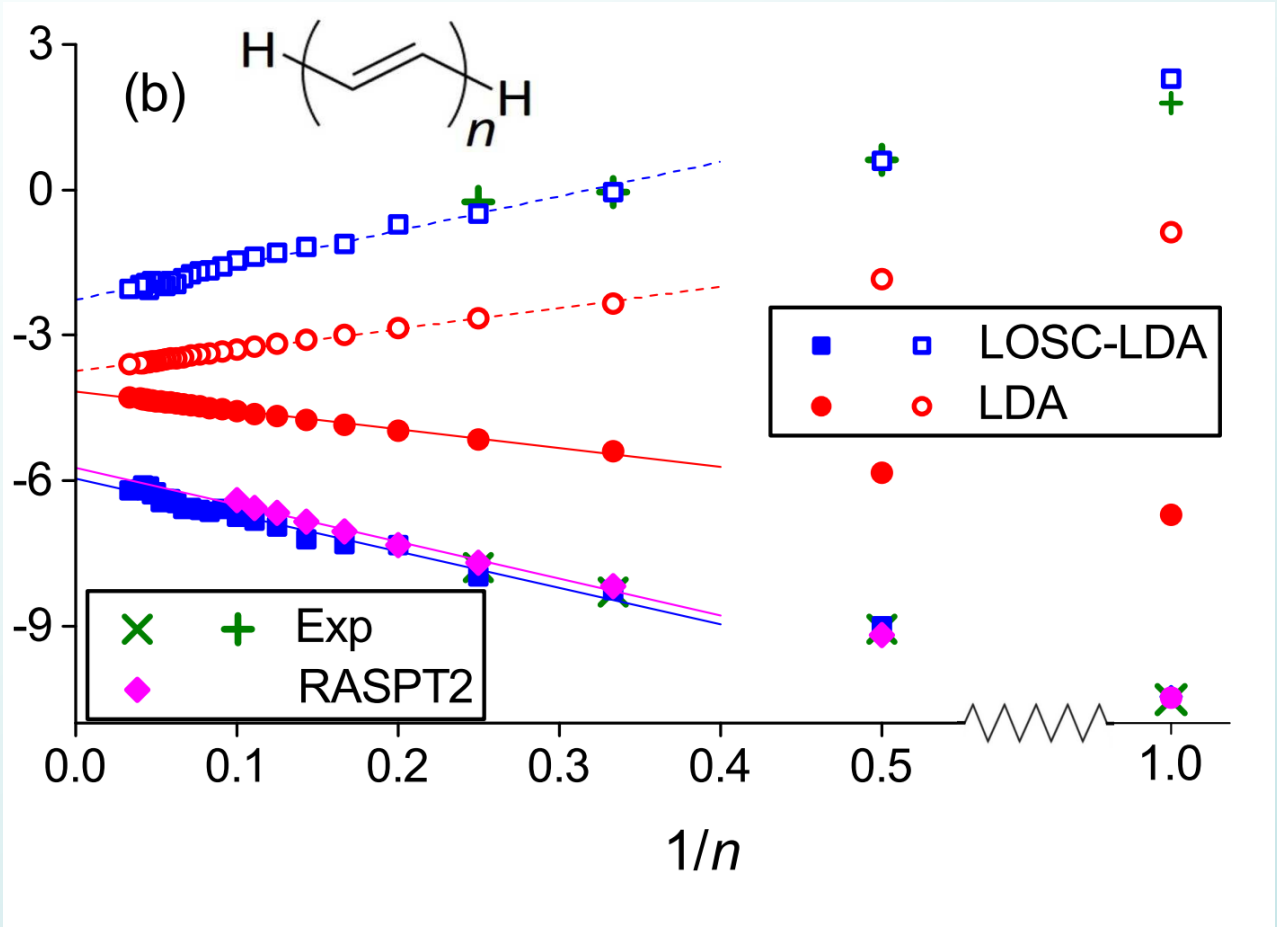
Orbital energy corrections

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

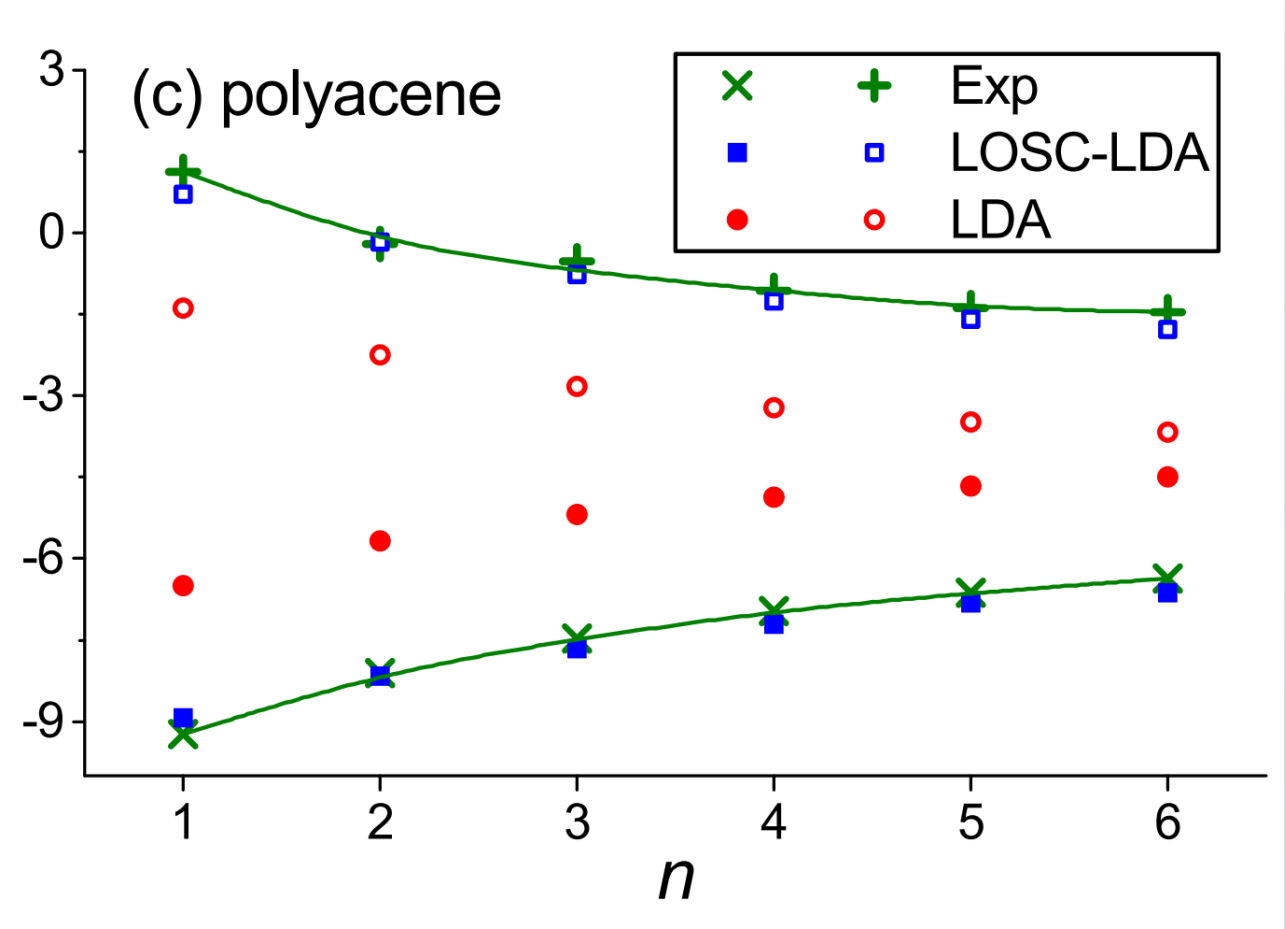
LOSC:


(a) G2-97 set
0
-6
-12
-18
-24
-24
-20
-16
-12
-8
-4
0
Ref. -I_{ve} and -A_{ve} (eV)
LOSC-LDA
LDA

LOSC: HOMO, LUMO and Energy Gaps

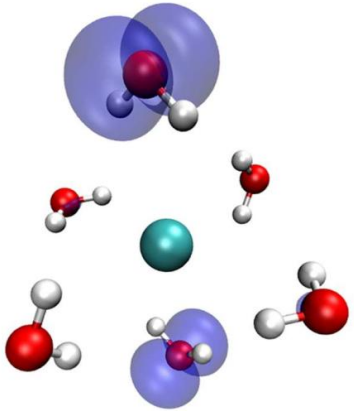


LOSC: HOMO, LUMO and Energy Gaps

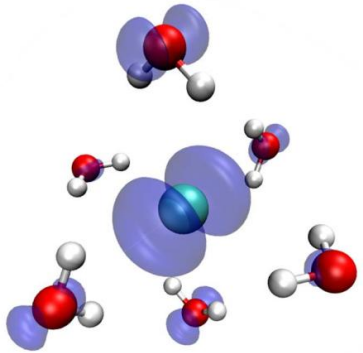


LOSC: corrections to electron density

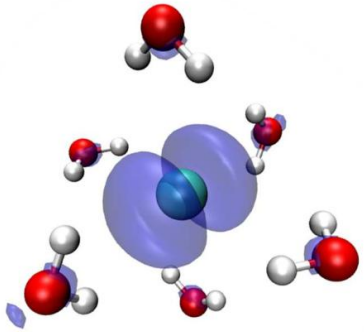
$Cl^{-}(H_2O)_6$



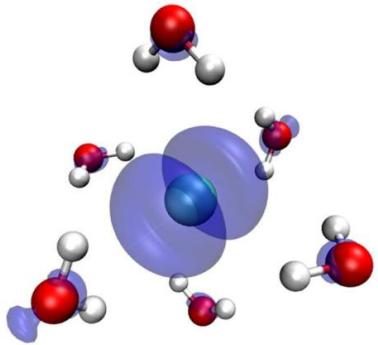
PBE $\Delta q(Cl)= 0.04$



B3LYP $\Delta q(Cl)= -0.67$



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

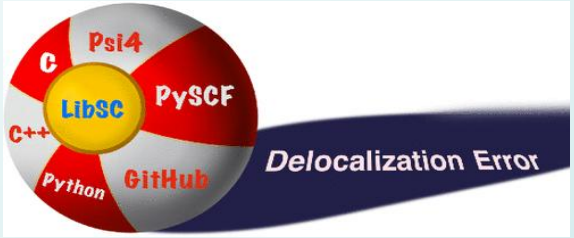


CCSD $\Delta q(Cl)= -0.96$

LibSC: Library for Scaling Correction Methods in Density Functional Theory

Yuncai Mei, Jincheng Yu, Zehua Chen, Neil Qiang Su, and Weitao Yang*

Cite this: *J. Chem. Theory Comput.* 2022, 18, 2, 840–850



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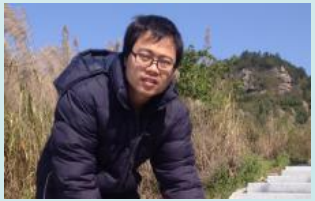


Neil Qiang Su

Orbital relaxation effect, Screening

Original LOSC, orbital frozen – excellent results for finite systems, and 1d infinite system

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

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

Orbital relaxation (screening effects), Zheng, Cohen, Mori-Sanchez, Hu and Yang PRL 2011

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

Fukui function $f(\mathbf{r}) = \lim_{n\to 0}\frac{\partial\rho_{N+n}(\mathbf{r})}{\partial n}\Big|_{v(\mathbf{r})}$

Frozen orbital app. $f(\mathbf{r}) \simeq |\phi_f(\mathbf{r})|^2$

Xiao Zheng

Orbital relaxation improves results
JCP 2013, 138, 174105; JCP 2015, 142, 154113; Molecular Physics 2018, 116, 927

Orbital relaxation effect

Orbital frozen – excellent results for finite systems, and 1d infinite system

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

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

Orbital relaxation (screening effects)

PRL 2011

JCP 2013, 138, 174105; JCP 2015, 142, 154113; Molecular Physics 2018, 116, 927

JPCL 2021, 12, 7236

$$\frac{\partial^2 E(\{n_{m\tau}\})}{\partial n_{p\sigma}^2} = \langle \psi_{p\sigma}\psi_{p\sigma}^* | K^{\sigma\sigma} + \sum_{\tau\upsilon} K^{\sigma\tau}\chi^{\tau\upsilon}K^{\upsilon\sigma} | \psi_{p\sigma}\psi_{p\sigma}^* \rangle$$

$$= K_{pp\sigma,pp\sigma} - \sum_{ia\tau,jb\upsilon} (K_{pp\sigma,ia\tau} + K_{pp\sigma,ai\tau}) M^{-1}_{ia\tau,jb\upsilon} K_{jb\upsilon,pp\sigma}$$

$$K^{\sigma\tau}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_3, \mathbf{r}_4) = \frac{\delta H_{\mathrm{s}}^{\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_{\mathrm{s}}^{\tau}(\mathbf{r}_3, \mathbf{r}_4)}$$

$$= \frac{\delta(\mathbf{r}_1, \mathbf{r}_2)\delta(\mathbf{r}_3, \mathbf{r}_4)}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{\delta^2 E_{\mathrm{xc}}}{\delta \rho_{\mathrm{s}}^{\sigma}(\mathbf{r}_2, \mathbf{r}_1)\delta \rho_{\mathrm{s}}^{\tau}(\mathbf{r}_3, \mathbf{r}_4)}$$

WY, Cohen, De Proft, and Geerlings JCP 2012, 136, 144110.

Also see Colonna, Nguyen,Ferretti and Marzari, JCTC. 2018, 14, 2549

lrLOSC

Linear Response Localized Orbital Scaling Corrections

-- Same novel localized orbitals with energy and space localization – ***Orbitalets***

-- **Accurate curvatures** (including screening/orbital relaxation effects)

--Improving LOSC results for small molecules, critical for large molecules and bulk systems

JPCL 2021, JCPL 2026, PRB 2026, JCP 2026 in press

Yuncai Mei

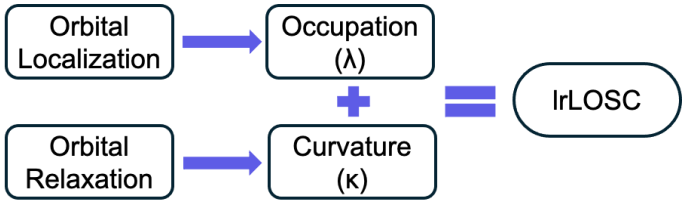
Zehua Chen

Jacob Z. Williams

Yichen Fan

Jincheng Yu

Capturing orbital relaxation through second derivative



Second derivative reflected through the screened interaction between orbitalets

$$\kappa_{pq} = \langle \phi_p(1)\phi_p(2)| \, (\varepsilon^{-1})K \, |\phi_q(3)\phi_q(4)\rangle \, ,$$

$$K(1,2;3,4) = \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(\mathbf{r}_3 - \mathbf{r}_4)}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{\delta^2 E_{xc}}{\delta\rho(2,1)\delta\rho(3,4)}$$

Generalized 4-point dielectric function:

$$\varepsilon^{-1}(1,2;3,4) = \frac{\delta v_s(1,2)}{\delta v(3,4)} = \delta(1,3)\delta(2,4) + K(1,2;5,6)\chi(5,6,3,4)$$

W. Yang, et al. *J. Chem. Phys.* **136**, 144110 (2012)
Y. Mei, et al. *J. Phys. Chem. Lett.* **12**, 7236 (2021)

IrLOSC in bulk materials

Jacob Z. Williams

arXiv 2024
PRB 2026

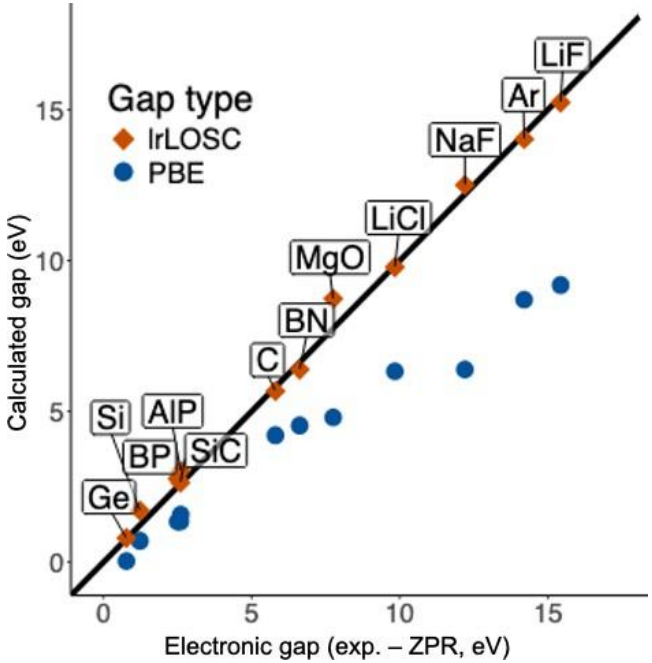


Figure: Band gaps for semiconductors and insulators in bulk materials

IrLOSC

Systematical elimination of DE- IrLOSC corrects DE, improve both orbital energies, total energies and electron densities.

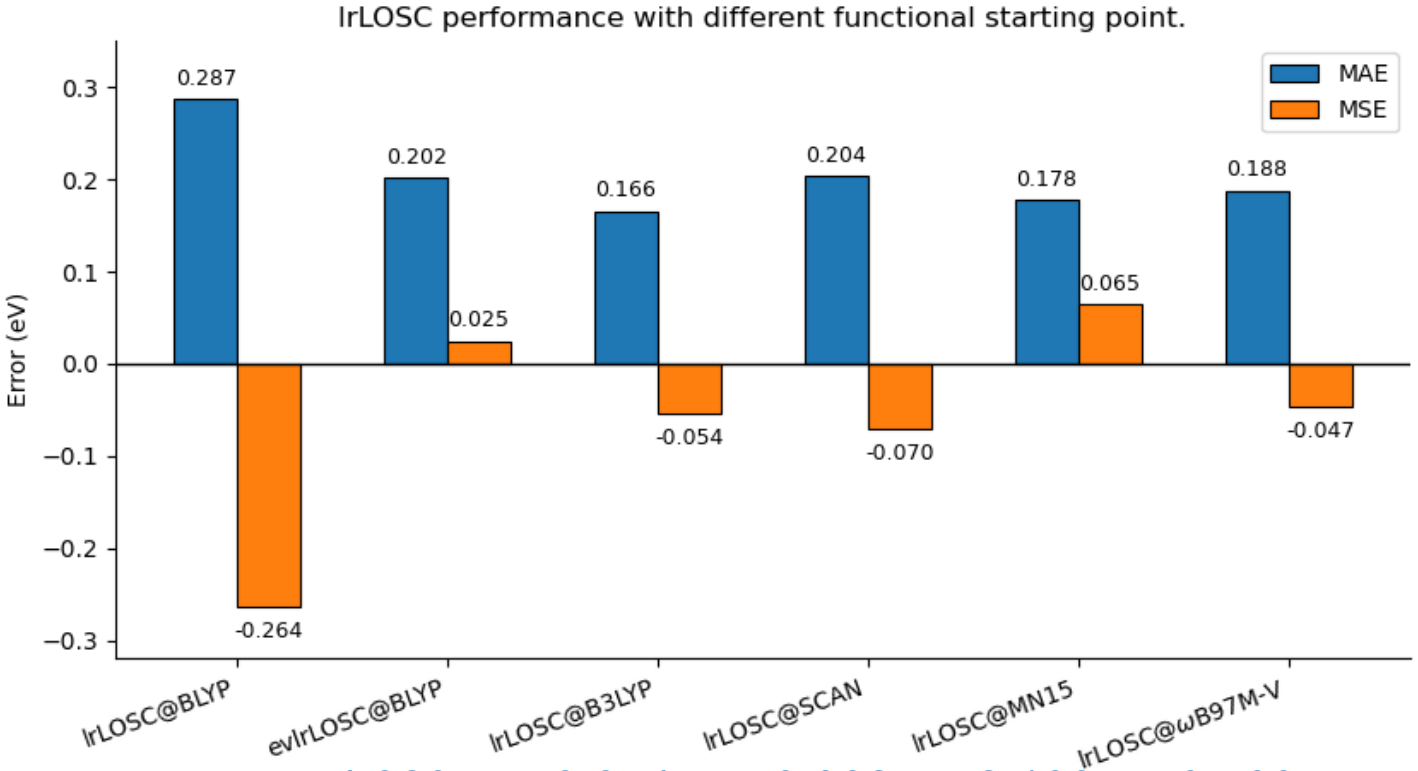
A universal functional approximation-

Results from Orbital Energies

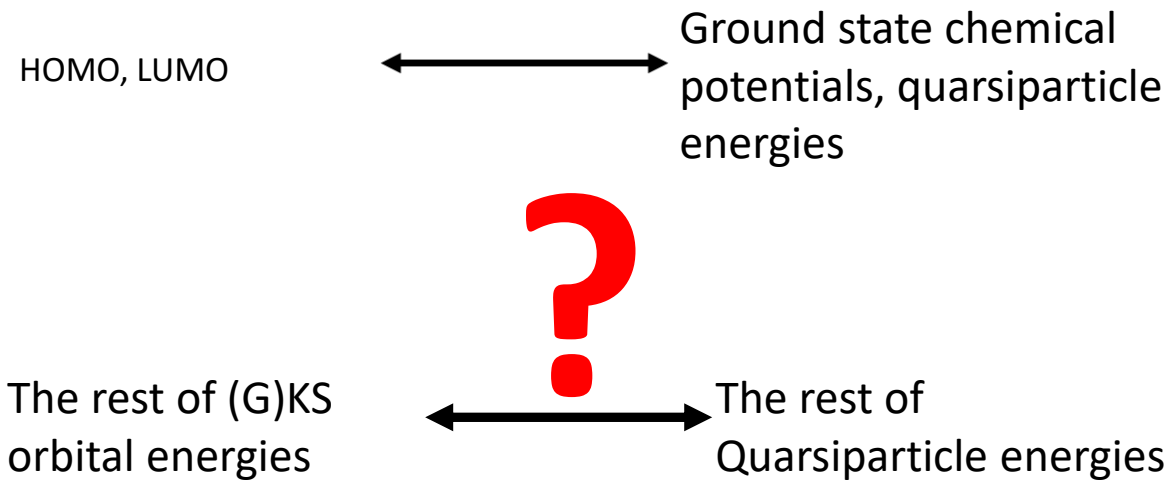
MAEs for …	IrLOSC@PBE
Small Molecules IPs	**0.25 eV**
Large Molecules IPs	**0.17 eV**
Bulk Materials Band Gaps	**0.23 eV**
Relative CLBEs	**0.17 eV**

Jincheng Yu et al, *JPCL* (2025)
Jacob Z. Williams and W. Yang, PRB (2026)
Yichen Fan, Jincheng Yu, Jiayi Du and W. Yang, *JCP (in press)*

Robustness with the density functional approximations



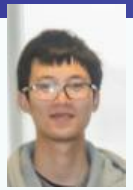
lrLOSC@BLYP	evlrLOSC@BLYP	lrLOSC@B3LYP	lrLOSC@SCAN	lrLOSC@MN15	lrLOSC@ωB97M-V
4.329	3.074	3.982	2.103	0.709	
-4.329	-3.074	-3.982	-2.103	-0.677	


HOMO, LUMO
Ground state 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	Eigenvalues 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**

arXiv 2018, **JPC A 2019**
Mei, Li, Su and WY



THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

Cite This: J. Phys. Chem. A XXXX, XXX, XXX−XXX

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Approximating Quasiparticle and Excitation Energies from Ground State Generalized Kohn−Sham Calculations

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

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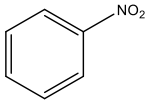
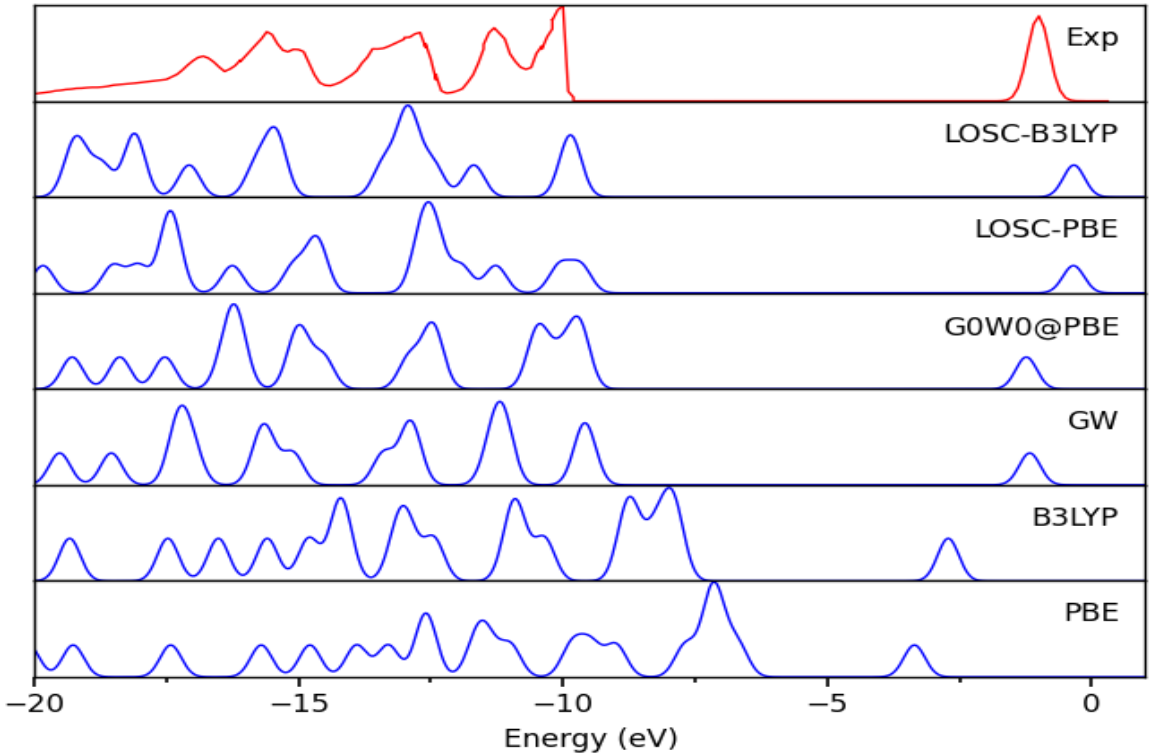
arXiv 2018,
Yuncia Mei, Chen Li, Neil Su and WY
JPC A 2019, 123, 3, 666

Photoemission spectrum of nitrobenzene

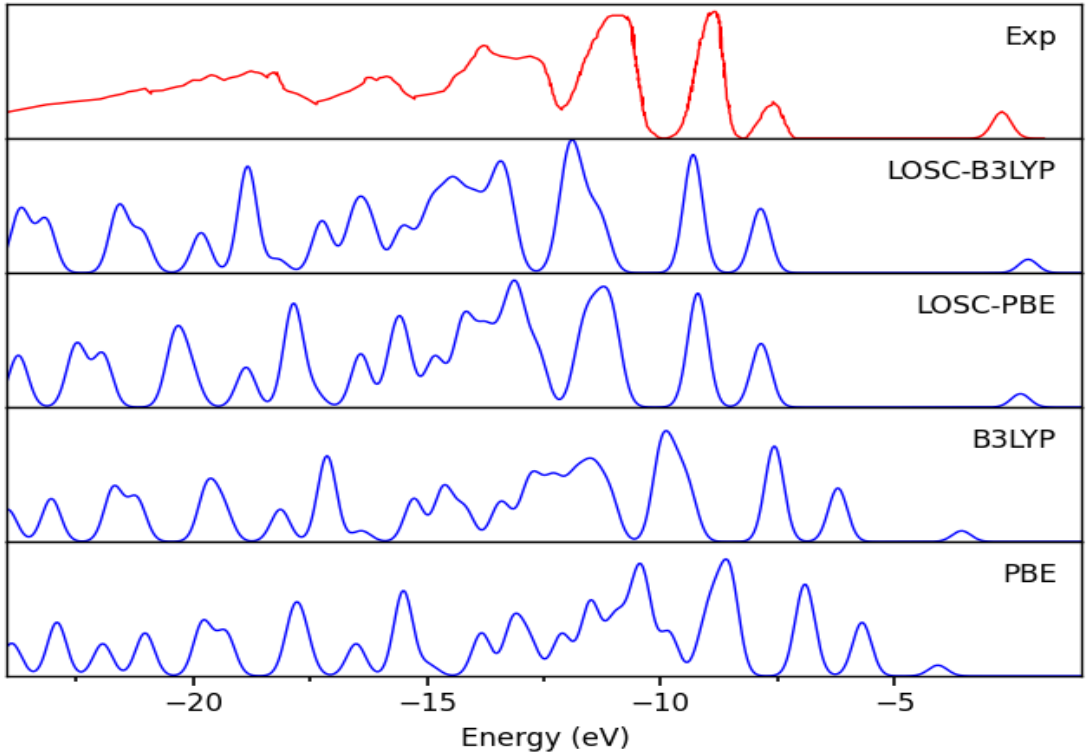




arXiv 2018, **JPC A 2019, 123, 3, 666**

Yuncia Mei, Chen Li, Neil Su and WY

Photoemission spectrum of C60



Excited State Energies from DFT – orbital energy data

Unoccupied

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

Occupied

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

- Approximate experimental excitation energies from orbital energies in DFT ground states-- abundance of data (since 2018…)
- **But**, DFT has been formulated only for ground states!
- For the quasiparticle energy interpretation of all orbital energies of a ground state to be true, **the DFT functional must contain excited-state information.**

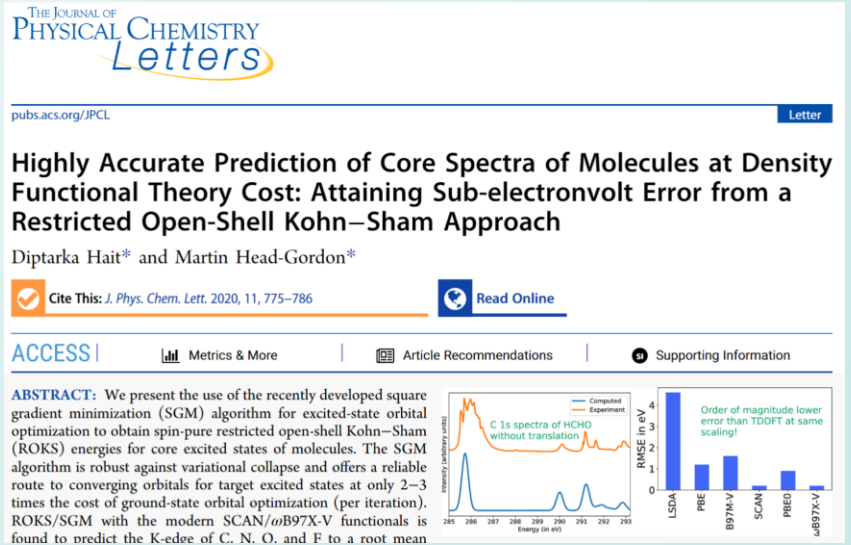
Excited State Energies from DFT – total energy data

ΔSCF method has been around since **Slater's work in the 70s**.

- Similar set of SCF Kohn-Sham equations with non-Aufbau occupations, the excited state of the noninteracting reference system
- Good accuracy for excited states, similar to ground states, better than TD-DFT for double, charge transfer excitations.
- Very active area:

Ziegler, Baerends, Jones, Gunnarsson, Mukamel, Van Voorhis, Gill, Head-Gordon, Herbert, Luber…

- **But DFT is established only for ground states!**



THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL Letter

Highly Accurate Prediction of Core Spectra of Molecules at Density Functional Theory Cost: Attaining Sub-electronvolt Error from a Restricted Open-Shell Kohn–Sham Approach

Diptarka Hait* and Martin Head-Gordon*

Cite This: *J. Phys. Chem. Lett.* 2020, 11, 775–786 Read Online

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ABSTRACT: We present the use of the recently developed square gradient minimization (SGM) algorithm for excited-state orbital optimization to obtain spin-pure restricted open-shell Kohn–Sham (ROKS) energies for core excited states of molecules. The SGM algorithm is robust against variational collapse and offers a reliable route to converging orbitals for target excited states at only 2–3 times the cost of ground-state orbital optimization (per iteration). ROKS/SGM with the modern SCAN/ωB97X-V functionals is found to predict the K-edge of C, N, O, and F to a root mean

Excited State DFT – no lack of efforts

Extensive theoretical effort to extend DFT to excited states

1. Use the same ground state functional, very limited class of excited states (Perdew, Levy, 1985)

2. Density and a real number, or pair of integers, specifying the excitation level, (Gorling, 1999)

3. Ground-state density and the excitation level (Levy and A. Nagy, 2012)

4. Ensemble (Theophilou, Gross, Kohn, Gidopoulos, Burke, Fromager, Gould, Kronik)

5. A matrix of densities (Lu and Gao)

But **“Despite the good performance of ΔSCF, there is no underlying theory to justify the method as used in applications”**
JCP perspective, Vandaele, M. Malis, and S. Luber, 2022

Perdew and Levy, PRB 1985

- with the **same** ground state **density** functional defined by the constrained search, the minimum is the ground state energy

- the stationary solutions can be the excited states of the same system

- **Critical issue**: very limited class of excited states—the electron density of the excited state cannot be the ground state of any potential. (not v representable)

Excited State DFT – no lack of efforts

Gorling, PRA 59, 3359, (1999) Replacing the minimization of the Levy constrained search with a stationary principle and labeled the stationary states with a real number ν

$$Q[\rho,\nu,\alpha] = \underset{\nu,\Psi\to\rho}{\text{stat}} \langle\Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle.$$

"The parameter ν labels all existing wavefunctions , $\Psi[\rho,\nu,\alpha]$ of a given density ρ in some arbitrary order"

- **Critical issue**: derivation of the stationary condition is based on variation of ρ, while keeping ν constant.

The functional derivative of $Q[\rho,\nu,\alpha]$ with respect to the electron density for fixed ν and α shall be denoted by

$$q([\rho,\nu,\alpha];\mathbf{r}) = \delta Q[\rho,\nu,\alpha]/\delta\rho(\mathbf{r}). \qquad (14)$$

- **But** ν characterizes the different possible potentials with the same electron density ρ. ν **depends on ρ!**

FUNCTIONALS OF REDUCED VARIABLES

The Hohenberg-Kohn Ground-State DFT

1. The unique mapping for ground state: $\rho \leftrightarrow \text{potential } w \rightarrow \Psi$
2. The energy for a trial ρ, a ground-state v−representable electron density

$$E_v^{HK}[\rho] = \left\langle \Psi_\rho | \hat{H}_v | \Psi_\rho \right\rangle$$

$\rho(\boldsymbol{x})$: ground-state v−representable, when $\Psi\rho$ exists

$\Psi\rho$: The ground-state wavefunction of some potential $w(\boldsymbol{x})$, which has the electron density ρ.

$$E_v^0 = \min_{\rho \in \mathcal{D}_v} E_v^{HK}[\rho]$$

Ground State Potential Functional Theory (PFT)

$$E_v^{HK}[\rho] = \left\langle \Psi_\rho | \hat{H}_v | \Psi_\rho \right\rangle \qquad E_v^0 = \min_{\rho \in \mathcal{D}_v} E_v^{HK}[\rho]$$

Pair of **Dual Variables**: $\langle \Psi | \Psi \rangle < \infty$ $\int d\mathbf{x}\, w(\mathbf{x})\rho(\mathbf{x}) < \infty$

Potential Functional Theory (PFT), Yang, Ayers and Wu, PRL 2004

- PFT changes the variable from a v-representable ρ, to the potential, $w(\boldsymbol{x})$, which yields ρ as its ground state from the wavefunction.
- Use $\rho_w(\mathbf{x})$ and Ψ_{ρ_w} to highlight the dependence on the potential $w(\mathbf{x})$

$$E_v^1[0,w] = \left\langle \Psi_w \middle| \hat{H}_v \middle| \Psi_w \right\rangle \qquad E_v^0 = \min_w E_v^1[0,w]$$

Excited –State Potential Functional Theory (nPFT)

Paul Ayers

Take the nth excited state of the potential $w(x)$

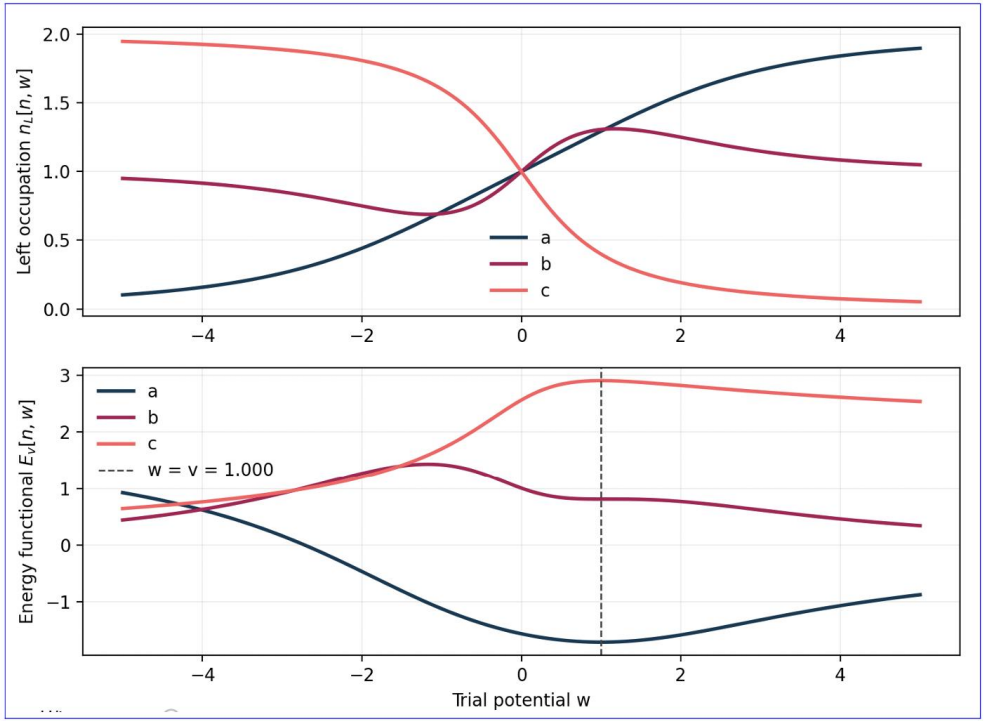
$$E_v[n,w] = \left\langle \Psi_{n,w} \middle| \hat{H}_v \middle| \Psi_{n,w} \right\rangle$$

Theorem 1: $E_v[n,w]$ is stationary with respect to variations in the trial potential, $w(\boldsymbol{x})$, if $w(\boldsymbol{x})$ and the physical potential, $v(\boldsymbol{x})$, differ by at most a constant.

Yang and Paul Ayers arXiv:2403.04604

Excited state potential functional for a two-site Hubbard model

$$\hat{H}_w = -\frac{w}{2}\sum_\sigma \hat{n}_{1\sigma} + \frac{w}{2}\sum_\sigma \hat{n}_{2\sigma} - t\sum_\sigma \left(\hat{c}^\dagger_{1\sigma}\hat{c}_{2\sigma} + \hat{c}^\dagger_{2\sigma}\hat{c}_{1\sigma}\right) + U\sum_{i=1}^{2} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow},$$



U=1, t=1, 3 singlet states

Density $\rho_w(\mathbf{x})$

Energy as Functional of Potential

$$E_v[n,w] = \left\langle \Psi_{n,w} \middle| \hat{H}_v \middle| \Psi_{n,w} \right\rangle$$

Figures from Yichen Fan

ΔSCF Excited-State Theory, not really a density functional theory

(1964, KS) Ground-State Kohn-Sham **Assumption**: the mapping of an interacting ground state to a noninteracting ground state

$$\rho(\mathbf{r}) = \sum_i n_i \left|\phi_i(\mathbf{r})\right|^2$$

Excited state KS **assumption**: the mapping of an interacting excited state $(n, w(\boldsymbol{x}))$ to a noninteracting excited states $(n_s, w_s(\boldsymbol{x}))$, with the same electron density.

a. Three equivalent sets of variables: $n_s, w_s(\boldsymbol{x})$, or the **density matrix** $\gamma_s(\boldsymbol{x}, \boldsymbol{x}')$ or **the wavefunction** Φ of the noninteracting reference system.

$$E_v[n_s, w_s(\boldsymbol{x})] = E_v[\gamma_s(\boldsymbol{x}, \boldsymbol{x}')] = E_v[\Phi]$$

b. Same functional, $E_v[\gamma_s(\boldsymbol{x}, \boldsymbol{x}')]$, for ground and excited states.

c. The *minimum* is the ground state, *stationary solutions* are excited states.

d. SCF Kohn-Sham equations, Aufbau for ground state, non-Aufbau for excited states.

Yang and Paul Ayers arXiv:2403.04604

Orbital Energies, previous work

All about ground states

(1) **Janak Theorem** for functional of density.

$$\frac{\partial \mathrm{E}}{\partial \mathrm{n_i}} = \varepsilon_\mathrm{i}$$

(2) **The ionization potential theorem**
For the exact and local Kohn-Sham potential, the KS HOMO energy is –IP (PPLB 1982).

(3) **The ground state chemical potential theorem** (Cohen, Mori-Sanchez and Yang, PRB 2008)

In any ground-state DFA calculation, HOMO/LUMO energy is the chemical potential of the electron removal/addition (approximating –IP/-EA)

Nothing about excited states

arXiv > physics > arXiv:2408.08443

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Physics > Chemical Physics

[Submitted on 15 Aug 2024]

Fractional Charges, Linear Conditions and Chemical Potentials for Excited States in ΔSCF Theory

Weitao Yang, Yichen Fan

Yichen Fan

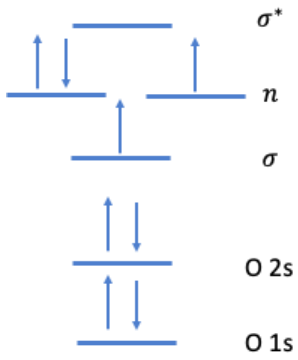
$E_v\left[\gamma_s(\mathbf{x},\mathbf{x}')\right]$ **degeneracy** and **size consistency**

1. Extension to fractional charges $0 \le \delta \le 1$ $\gamma_s = (1-\delta)\gamma_s^{n_s}(N) + \delta\gamma_s^{m_s}(N+1)$

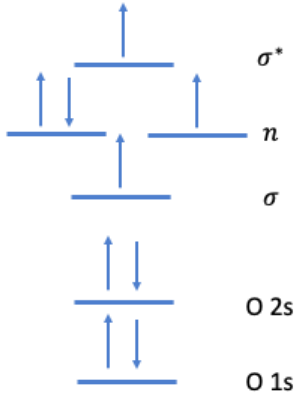
2. Proved the linear condition

$$E_v[(1-\delta)\gamma_s^{n_s}(N) + \delta\gamma_s^{m_s}(N+1)]$$
$$=(1-\delta)E_v^n(N) + \delta E_v^m(N+1).$$

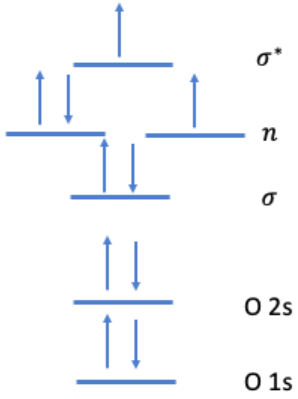
3. Generalize the PPLB condition for ground states in term of electron densities to **excited states in terms of density matrices**



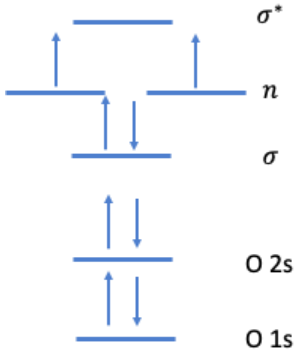
OH^+ (N=8) excited state



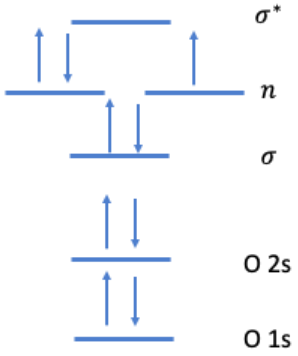
OH (N=9) excited state



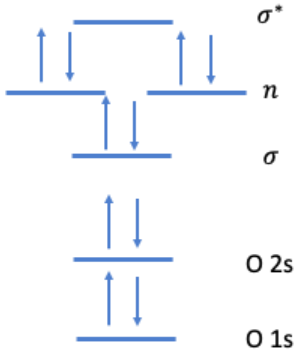
OH^- (N=10) excited state



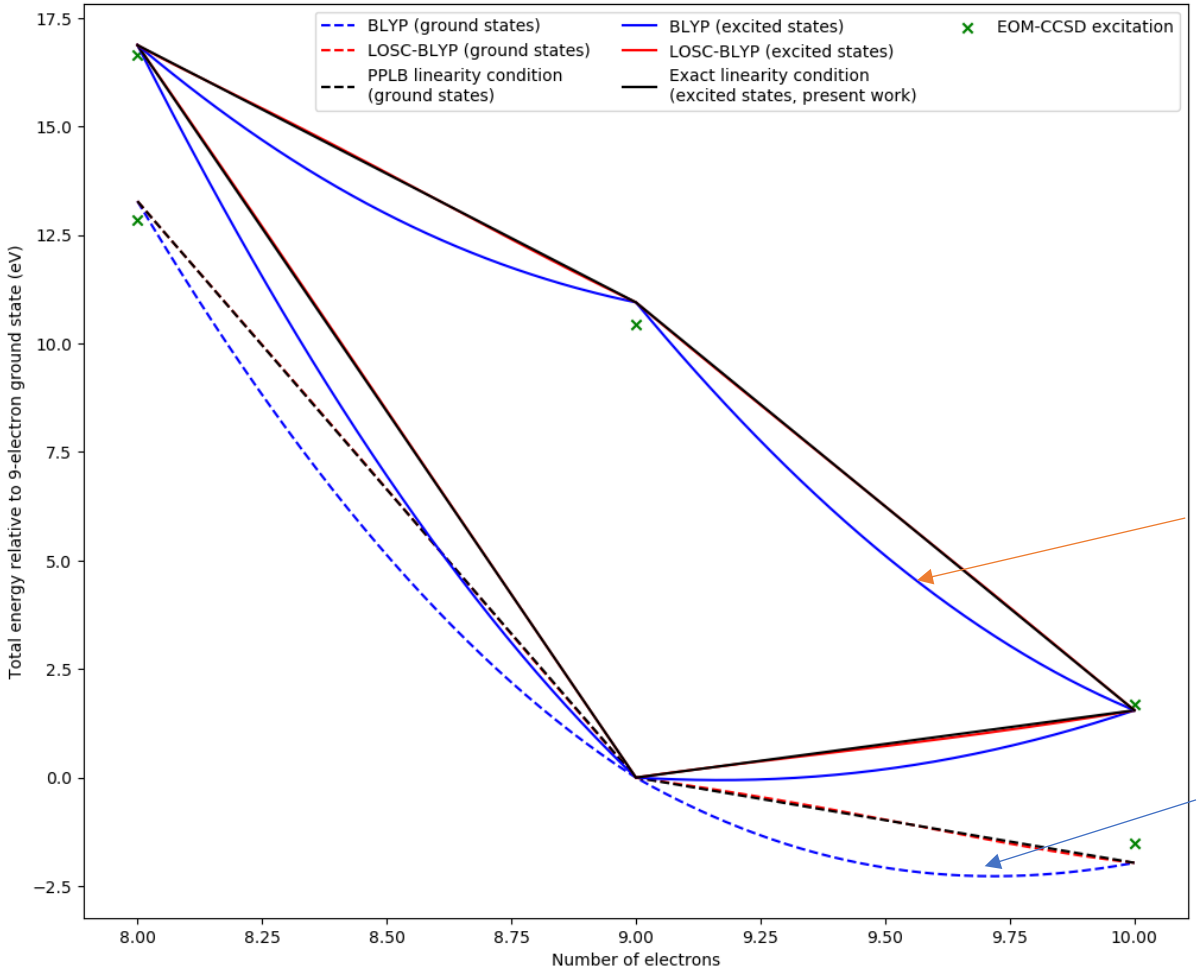
OH^+ (N=8) ground state



OH (N=9) ground state



OH^- (N=10) ground state

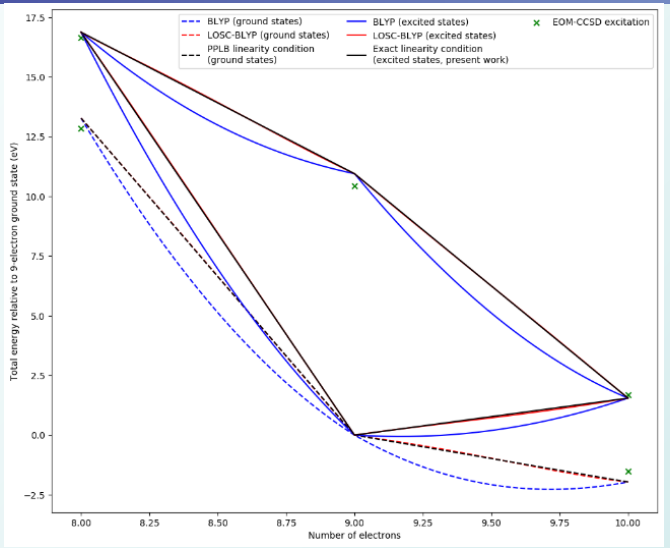


Excited-state delocalization error

Ground-state delocalization error

OH^+ OH OH^-

Excited-State Chemical Potentials: slopes of the lines



$$\mu^{+}_{n_s m_s} = \left(\frac{\partial E^{+}_{v}(n_s, m_s, \mathcal{N})}{\partial \mathcal{N}} \right)_{v} = E^{m}_{v}(N+1) - E^{n}_{v}(N),$$

$$\mu^{-}_{n_s l_s} = \left(\frac{\partial E^{-}_{v}(n_s, l_s, \mathcal{N})}{\partial \mathcal{N}} \right)_{v} = E^{n}_{v}(N) - E^{l}_{v}(N-1)$$

arXiv > physics > arXiv:2408.10059

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Physics > Chemical Physics

[Submitted on 19 Aug 2024]

Orbital Energies Are Chemical Potentials in Ground-State Density Functional Theory and Excited-State ΔSCF Theory

Weitao Yang, Yichen Fan

YichenFan

Proved **the general chemical potential theorem**

1. True for any approximate functional calculations

$$\mu^{-}_{n_s l_s}(N) = \left(\frac{\partial E^{-}_{v}(n_s, l_s, \mathcal{N})}{\partial \mathcal{N}}\right)_{v}\Bigg|_{f_i=1} = \frac{\partial E_v[\gamma_s]}{\partial f_i}\Bigg|_{f_i=1} = \varepsilon_i(N),$$

$$\mu^{+}_{n_s m_s}(N) = \left(\frac{\partial E^{+}_{v}(n_s, m_s, \mathcal{N})}{\partial \mathcal{N}}\right)_{v}\Bigg|_{f_a=0} = \frac{\partial E_v[\gamma_s]}{\partial f_a}\Bigg|_{f_a=0} = \varepsilon_a(N).$$

2. Approximate, depending on the functional approximation (delocalization error)

$$\varepsilon_i(N) = E^n_v(N) - E^l_v(N-1)$$

$$\varepsilon_a(N) = E^m_v(N+1) - E^n_v(N)$$

Orbital energies approximate excited state IP, EA, or excited state quasiparticle energies

Occupancy Extrapolation (OE) for Excited States

$$\gamma_s(\mathbf{x},\mathbf{x}') = \sum_{q\sigma} n_{q\sigma}\phi_{q\sigma}(\mathbf{x})\phi^*_{q\sigma}(\mathbf{x}').$$

The energy function of occupations

$$E_v(\{n_{q\sigma}\}) = \mathrm{Stat}_{\phi_{q\sigma}} E_v\left[\gamma_s(\mathbf{x},\mathbf{x}')\right],$$

(Landau, Slater, Janak)

QE-DFT Unoccupied

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

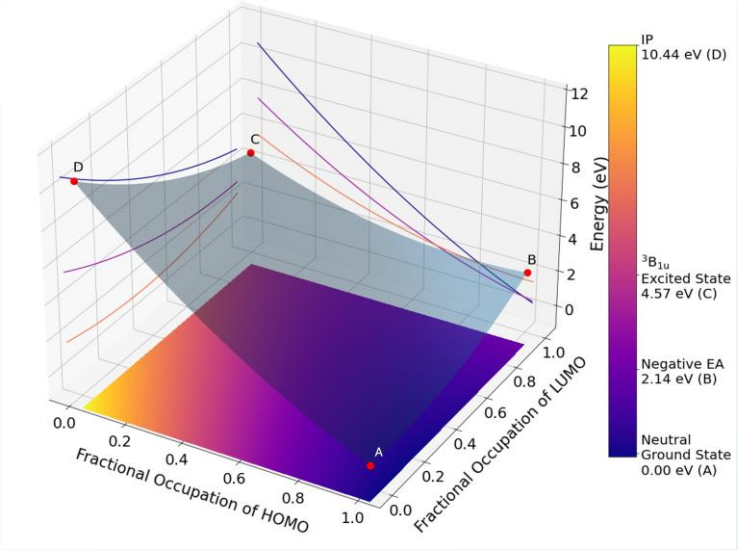
Occupied

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

General excitations beyond 1p or 1h?

Landau Fermi Liquid (LFL) Theory (homogeneous systems, semi-phenomenological)

$$\delta E = \sum_{\vec{k}} \varepsilon^0_{\vec{k}} \delta n(\vec{k}) + \frac{1}{2\mathcal{V}} \sum_{\vec{k},\vec{k}'} f(\vec{k},\vec{k}')\delta n(\vec{k})\delta n(\vec{k}'),$$



energy surface for ethylene (C2H4) as a function of fractional occupations of the HOMO and LUMO,

Yichen Fan

Occupancy Extrapolation

--- A Taylor expansion

$$E_v(\{n_{q\sigma}\}) - E_v(\{n^0_{q\sigma}\}) = \sum_q \left.\frac{\partial E_v}{\partial n_{q\sigma}}\right|_{n^0_{q\sigma}} \delta n_{q\sigma} + \frac{1}{2}\sum_{qr} \left.\frac{\partial^2 E_v}{\partial n_{q\sigma}\partial n_{r\sigma}}\right|_{n^0_{q\sigma}} \delta n_{q\sigma}\delta n_{r\sigma} + O(\delta n^3_{q\sigma})$$

$$\left.\frac{\partial E_v}{\partial n_{p\sigma}}\right|_{\{n^0_{p\sigma}\}} = \varepsilon_{p\sigma},$$

for functional of ρ, KS, Janak theorem,
for functional of γ_s: GKS, Cohen, Mori-Sanchez and Yang PRB 2008

$$\left.\frac{\partial^2 E_v}{\partial n_{p\sigma}\partial n_{q\tau}}\right|_{\{n^0_{p\sigma}\}} = \kappa_{p\sigma q\tau} = (\phi_{p\sigma}\phi^*_{p\sigma}|K^{\sigma\tau} + \sum_{\sigma\upsilon} K^{\sigma\sigma}\chi^{\sigma\upsilon}K^{\upsilon\tau}|\phi_{q\tau}\phi^*_{q\tau})$$

W. Yang, A. J. Cohen, F. De Proft, and P. Geerlings, JCP. (2012).
Y. Mei, Z. Chen, and W. Yang, JPCL. (2021).

Occupancy Extrapolation: Yichen Fan and WY, arXiv.2603.20055

N_p quasiparticles, N_h quasiholes and Interactions

$$\Delta E_v^{N_pN_h} = \sum_i^{N_h} \varepsilon_{i\sigma}\delta n_{i\sigma} + \sum_a^{N_h} \varepsilon_{a\sigma}\delta n_{a\sigma} + \frac{1}{2}\left(\sum_{ij}^{N_h} \kappa_{i\sigma j\tau}\delta n_{i\sigma}\delta n_{j\tau} + \sum_{ab}^{N_p} \kappa_{a\sigma b\tau}\delta n_{a\sigma}\delta n_{b\tau} + 2\sum_{ia}^{N_pN_h} \kappa_{i\sigma b\tau}\delta n_{i\sigma}\delta n_{b\tau}\right)$$
$$= -\sum_i^{N_h} \varepsilon_{i\sigma}^{QP} + \sum_a^{N_h} \varepsilon_{a\sigma}^{QP} + \frac{1}{2}\left(\sum_{i\sigma\neq j\tau}^{N_h} \kappa_{i\sigma j\tau} + \sum_{a\sigma\neq b\tau}^{N_p} \kappa_{a\sigma b\tau} - 2\sum_{i\sigma,a\tau}^{N_pN_h} \kappa_{i\sigma a\tau}\right), \qquad (8)$$

1 h $\Delta E(h) = -\varepsilon_{i\sigma} + \frac{1}{2}\kappa_{i\sigma,i\sigma},$

1 p $\Delta E_v(p) = \varepsilon_{a\sigma} + \frac{1}{2}\kappa_{a\sigma,a\sigma},$

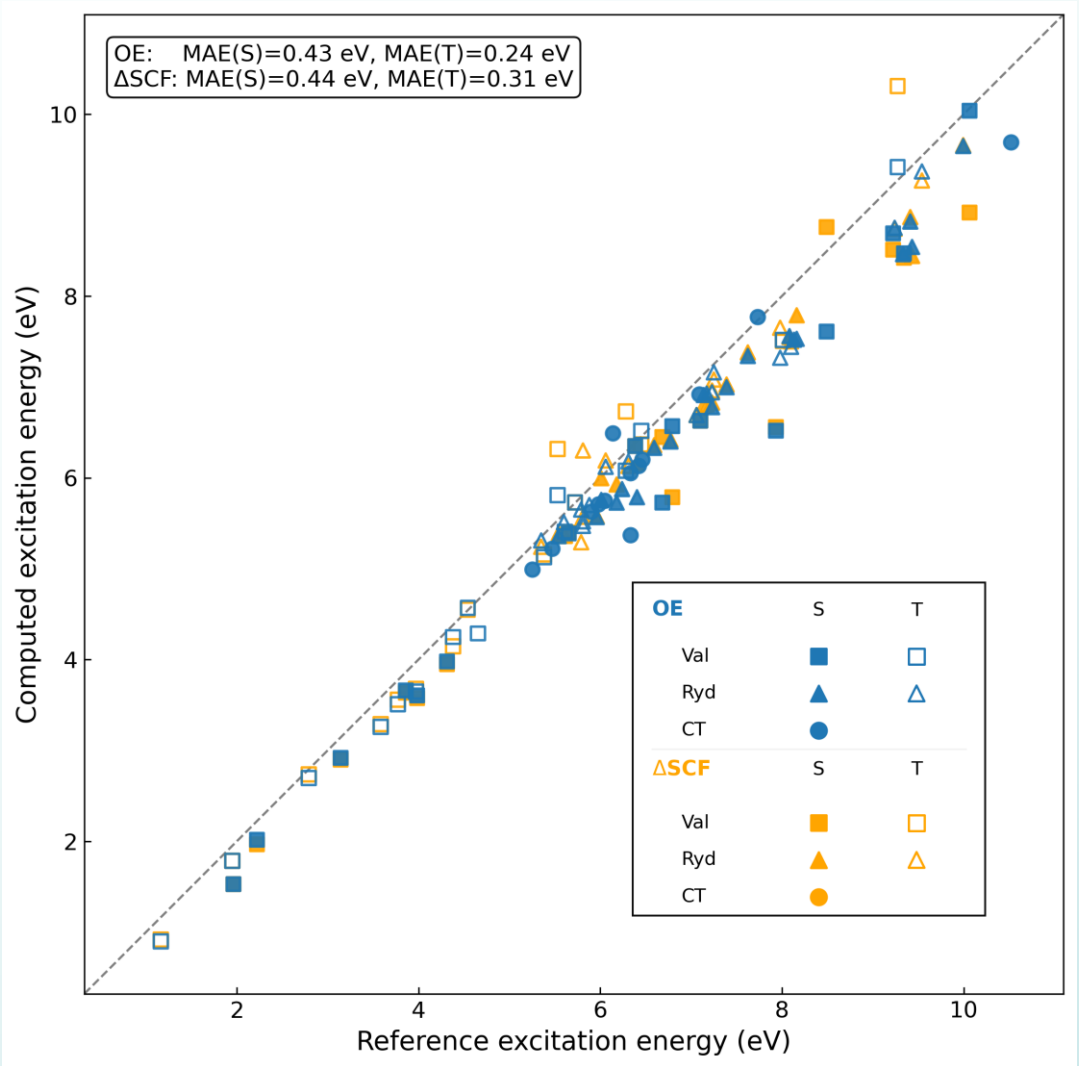
$$\varepsilon_{i\sigma}^{QP} = \varepsilon_{i\sigma} - \tfrac{1}{2}\kappa_{i\sigma i\sigma};\ \varepsilon_{a\sigma}^{QP} = \varepsilon_{a\sigma} + \tfrac{1}{2}\kappa_{a\sigma a\sigma}.$$

This is QE-DFT, with GSC2 quasiparticle energies

1p1h, particle-hole excitation, optical absorption

$$\Delta E(ph) = \varepsilon_{a\sigma}^{QP} - \varepsilon_{i\tau}^{QP} - \kappa_{a\sigma,i\tau},$$

- Reaching many excited states from ground state calculations.
- Many types of excited states
- Physical interpretation of excitation



OE captures ΔSCF excitation energies, directly from ground states, no ΔSCF.

Relations and Comparison

(1)the Landau Fermi Liquid theory

For homogeneous systems, the LFL theory has a similar Taylor expansion.
For inhomogeneous systems, the LFL theory involves expansions with respect to the one-particle density matrix.

(2) **Slater** developed a Taylor expansion within Xα. All the Taylor expansion coefficients have been calculated from the numerical ΔSCF calculations at fractional occupations.

(3) The **BSE** approach for 1p1h: the gap of quasiparticle energies and the screened Coulomb interaction:

OE: **quasiparticle energies** are all defined within DFT, with a **generalized screened interaction**, a four-point quantity, and include xc contributions.

OE: like ΔSCF, is based on a single determinant.

Quasiparticle Hamiltonian (QH) from OE

Yang Shen

Yichen Fan

Occupancy Extrapolation

1p1h, particle-hole excitation, optical absorption

$$\Delta E(ph) = \varepsilon^{QP}_{a\sigma} - \varepsilon^{QP}_{i\tau} - \kappa_{a\sigma,i\tau},$$

Define energy functional of the 1p1h wavefunction

$$\Delta E[\Psi_{\rm ph}(\mathbf{x}_{\rm p},\mathbf{x}_{\rm h})] = \langle\Psi_{\rm ph}|\sum_{i\sigma,a\tau}(\epsilon^{\rm QP}_{a\tau}-\epsilon^{\rm QP}_{i\sigma})|\Psi_{i\sigma,a\tau}\rangle\langle\Psi_{i\sigma,a\tau}|\Psi_{\rm ph}\rangle - \langle\Psi_{\rm ph}|\hat{W}|\Psi_{\rm ph}\rangle$$

Quasiparticle Hamiltonian $\hat{H}|\Psi_{\rm ph}\rangle = \frac{\delta\Delta E[\Psi_{\rm ph}]}{\delta\langle\Psi_{\rm ph}|}$

$$H_{(i\sigma,a\tau),(j\lambda,b\omega)} = \langle\Psi_{i\sigma,a\tau}|\hat{H}|\Psi_{j\lambda,b\omega}\rangle = (\epsilon^{\rm QP}_{a\tau}-\epsilon^{\rm QP}_{i\sigma})\delta_{ij}\delta_{ab}\delta_{\sigma\lambda}\delta_{\tau\omega} - (\phi_{i\sigma}\phi_{j\lambda}|W|\phi_{b\omega}\phi_{a\tau})$$

Yang Shen, Yichen Fan and WY arXiv:2604.27190v2

Restore the spin symmetry: matrix spin purification, or noncolinear XC

$$\mathbf{H} = (\epsilon_a^{\mathrm{QP}} - \epsilon_i^{\mathrm{QP}})\delta_{ij}\delta_{ab}\mathbf{I}_{4\times 4} - \begin{pmatrix} W_{ij,ab} & 0 & 0 & W_{i\bar{j},a\bar{b}} \\ 0 & W_{ij,\bar{a}\bar{b}} & 0 & 0 \\ 0 & 0 & W_{\bar{i}j,ab} & 0 \\ W_{\bar{i}j,\bar{a}b} & 0 & 0 & W_{\bar{i}\bar{j},\bar{a}\bar{b}} \end{pmatrix}.$$

QH vs **BSE** approach

$$\kappa_{p\sigma,q\tau} \equiv W_{pp\sigma,qq\tau} \equiv \frac{\partial^2 E_{\mathrm{tot}}^{\mathrm{DFA}}}{\partial n_{p\sigma}\partial n_{q\tau}} = (\psi_{p\sigma}\psi_{p\sigma}|K + K\chi K|\psi_{q\tau}\psi_{q\tau}).$$

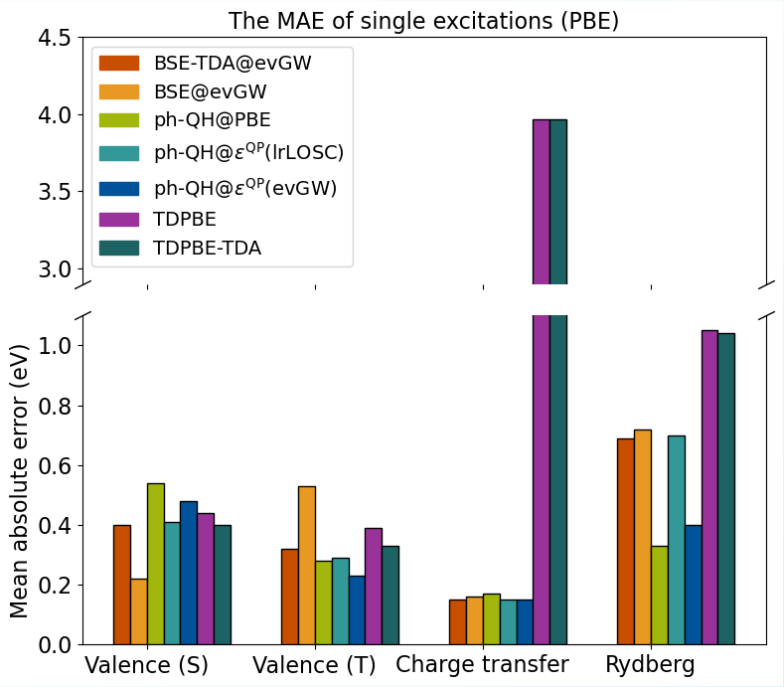
(1)The quasiparticle energies in BSE are typically GW

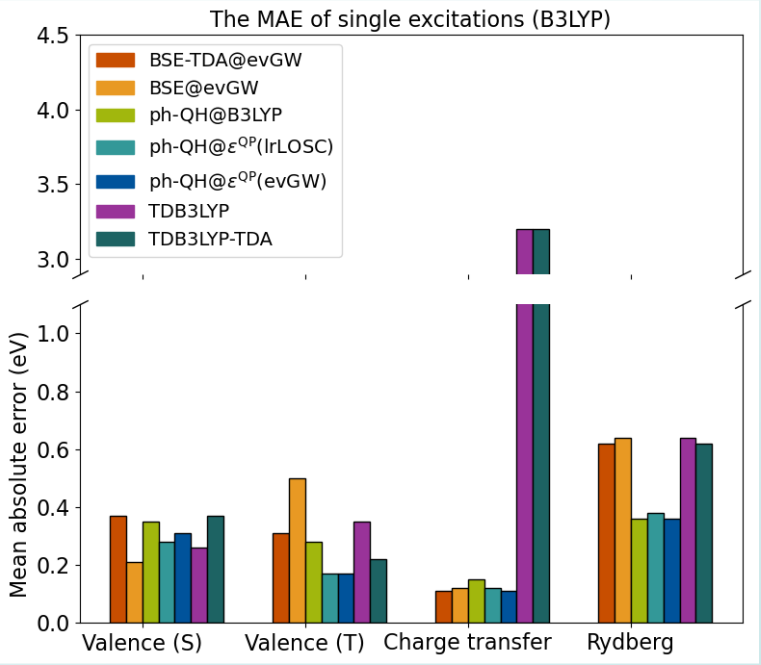
(2) **QH** incorporates XC contributions in the XC kernel in the particle-hole attraction, and in screening, beyond BSE

(3) Singlet and triplet splitting:

BSE $2\,(ia|v|jb)$

QH $2(W_{ij,ab} - W_{\bar{i}j,ab})$





Quasiparticle Hamiltonian – multideterminant excited states

- **comparable** to BSE for valence singlet and charge transfer excitations
- **significantly better** for valence triplet and Rydberg excitations

Summary

Beyond Commonly Used Functionals

- Corrections to systematic errors in DFT
- Unified functional for energy, charge density, band gaps of molecules and bulk systems

Beyond Ground States

- Foundation for excited-state theory -- ΔSCF
- Fractional charges, linear conditions, and chemical potentials
- Physical significance of all orbital energies

New Approaches to Excitations

- Occupancy Extrapolation (OE)
- Quasiparticle Hamiltonian (QH)