Fundamentals of DFT: Basics and Frontiers

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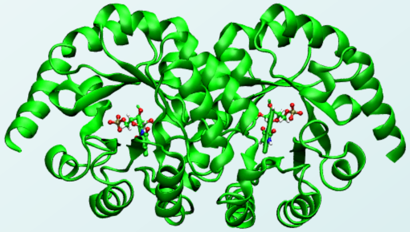
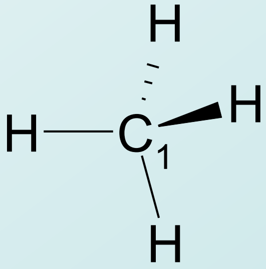
matter and changes

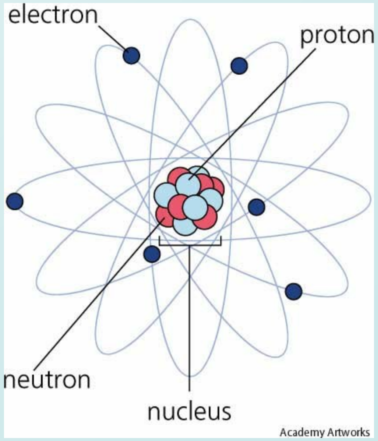


Matter

Materials, Molecules, Atoms

Nuclei, **Electrons**

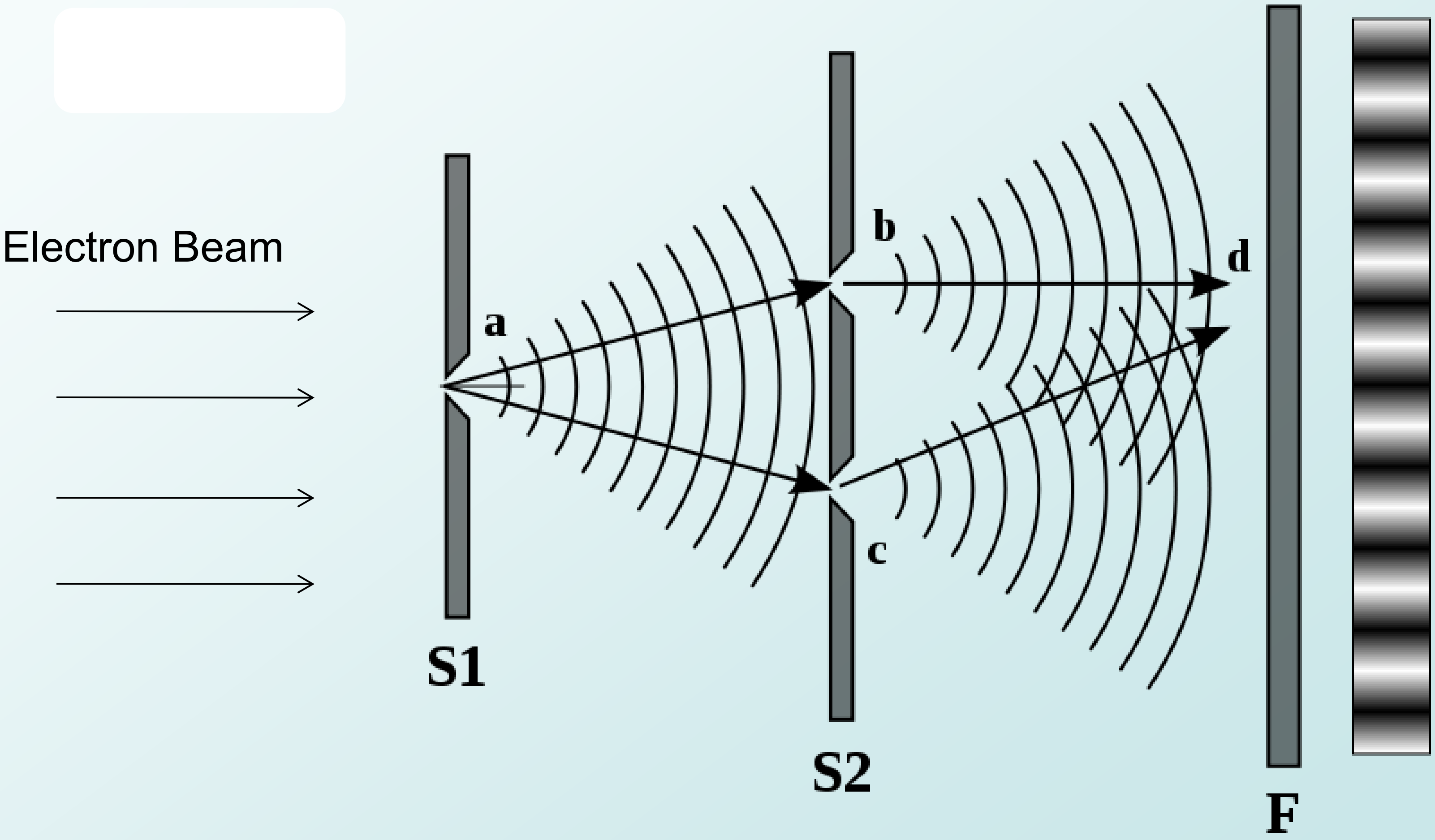




Electrons are the glue that bind the repulsive nuclei and determine the structure of matter, from molecules to macromolecules, to bulk materials.

Quantum Mechanics

The wave-like behavior of electrons



Quantum mechanics describes electrons

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi$$

$$H\Psi = E\Psi$$

Erwin Schrödinger

Wavefunction--the curse of dimensionality

$$\hat{H}\Psi(\mathbf{x}_{1,}\mathbf{x}_{2,}\dots\mathbf{x}_N) = E\Psi(\mathbf{x}_{1,}\mathbf{x}_{2,}\dots\mathbf{x}_N)$$

# of electrons	wavefunction	amount of data
1	$\Psi(\mathbf{x}_1)$	10^3
2	$\Psi(\mathbf{x}_{1,}\mathbf{x}_2)$	10^6
…	…	…
N	$\Psi(\mathbf{x}_{1,}\mathbf{x}_{2,}\dots\mathbf{x}_N)$	10^{3N}

- The amount of data contained in wavefunction grows exponentially with N, the number of electrons!   N can be very large.

- The problem is caused by the exponential increase in volume associated with adding extra dimensions to a (mathematical) space.

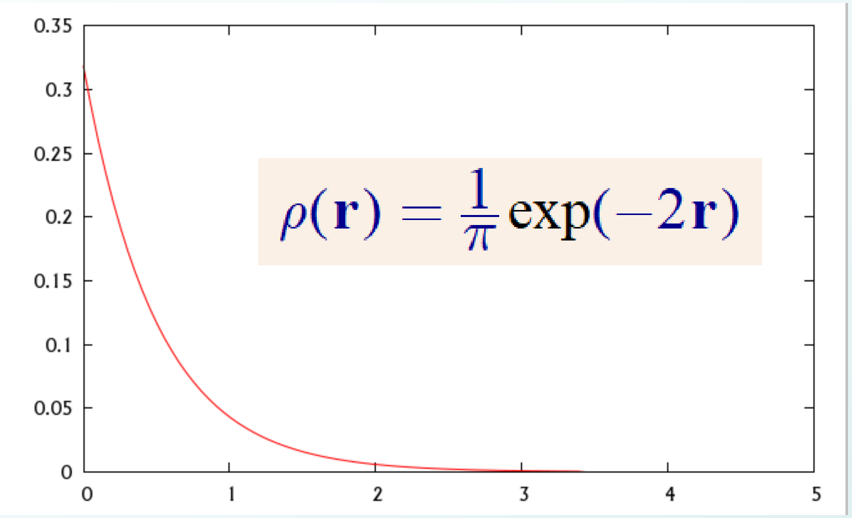
Exponential growth of information

$$\begin{tikzcd}
\text{N, positions and types of atoms} \arrow[r, Leftrightarrow] \arrow[d, Rightarrow] & N,\ v(\mathbf{r}) \arrow[dd, Leftrightarrow] \\
H \arrow[d, Rightarrow] & \\
10^{3N} \text{ in } \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) & ?
\end{tikzcd}$$

1. $v(\mathbf{r})$ is the electrostatic potential from the nuclei
2. $v(\mathbf{r}) = \sum^{Atoms} - \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$

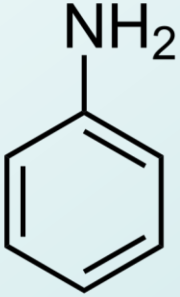
Electron density $\rho(\mathbf{r})$ *, 3-dimentional only*

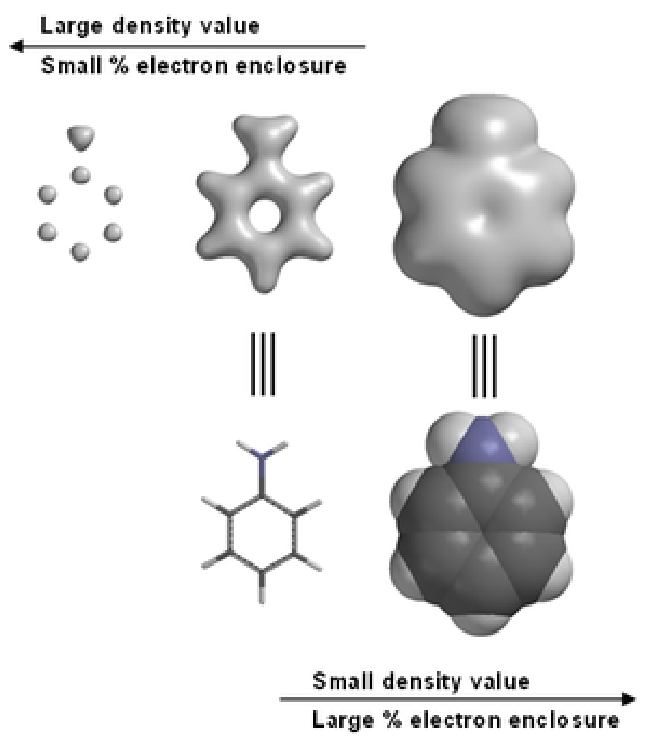
Electron density for the hydrogen atom



Distance from the nucleus

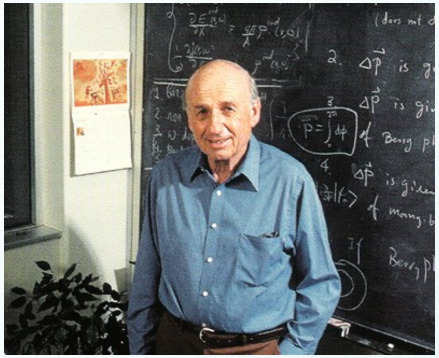
Electron density for aniline

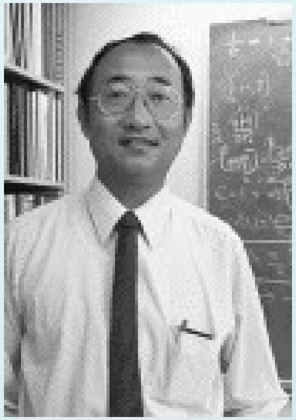




- **Electron density** $\rho(\mathbf{r})$ is the measure of the probability of an electron being present at a specific location.
- Experimental observables in X-ray diffraction for structural determination of small and large molecules

Density Functional Theory





Walter Kohn

Pierre C. Hohenberg

Lu J. Sham

The Nobel Prize in Chemistry 1998

Density functional theory (DFT) (1963, 1964)

1 $\rho(\mathbf{r}) \Longleftrightarrow N, v(\mathbf{r}) \Longleftrightarrow \Psi$

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

just the sum of molecular orbital densities

DFT: Exchange-correlation energy

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

E = Kinetic energy + potential energy
+ Coulomb interaction energy
+ $E_{xc}[\rho(\mathbf{r})]$

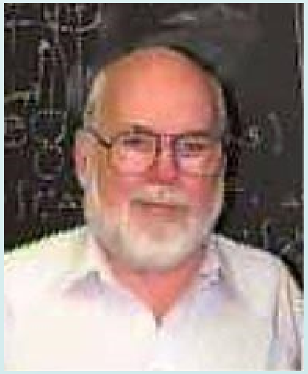
$$E_{xc}[\rho(\mathbf{r})]$$

- Exchange-correlation energy
- The only unknown piece in the energy
- About 10% of E

Approximations in exchange-correlation energy

$$E_{xc}[\rho(\mathbf{r})]$$

- 1965: Kohn and Sham, Local Density Approximation (LDA)
- 1980s-1990s: Axel Becke, Robert Parr, John Perdew



•Generalized Gradient Approximation (BLYP, PBE)

•Hybrid Functionals (B3LYP, PBE0)

Density Functional Theory

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

Introducing the electron density

$$\begin{aligned}
\langle\Psi|\sum_i^N v_{ext}(\mathbf{r}_i)\,|\Psi\rangle &= \int d\mathbf{x}^N\,|\Psi(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N)|^2\sum_i^N v_{ext}(\mathbf{r}_i)\\
&= \int d\mathbf{x}^N\,|\Psi(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N)|^2\int d\mathbf{r}v_{ext}(\mathbf{r})\sum_i^N\delta(\mathbf{r}-\mathbf{r}_i)\\
&= \int d\mathbf{r}v_{ext}(\mathbf{r})\int d\mathbf{x}^N\,|\Psi(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N)|^2\sum_i^N\delta(\mathbf{r}-\mathbf{r}_i)\\
&= \int d\mathbf{r}v_{ext}(\mathbf{r})\rho(\mathbf{r})
\end{aligned}$$

$$\rho(\mathbf{r}) = \int d\mathbf{x}^N\,|\Psi(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N)|^2\sum_i^N\delta(\mathbf{r}-\mathbf{r}_i)$$

For a determinant wave function

$$|\Phi_0\rangle = |\chi_1\chi_2 \cdots \chi_i\chi_j \cdots \chi_N\rangle$$

$$\begin{aligned}
\rho(\mathbf{r}) &= \langle\Phi_0|\sum_i^N \delta(\mathbf{r}-\mathbf{r}_i)\,|\Phi_0\rangle \\
&= \sum_i^N \langle\Phi_0|\,\delta(\mathbf{r}-\mathbf{r}_i)\,|\Phi_0\rangle \\
&= \sum_i^N \int d\mathbf{x}_i\,|\chi_i(\mathbf{x}_i)|^2\,\delta(\mathbf{r}-\mathbf{r}_i) \\
&= \sum_i^N \int d\mathbf{x}_i\,|\chi_i(\mathbf{x}_i)|^2\,\delta(\mathbf{r}-\mathbf{r}_i) \\
&= \sum_i^N \int d\mathbf{r}_i \sum_{s_i} |\phi_i(\mathbf{r}_i)\sigma(s_i)|^2\,\delta(\mathbf{r}-\mathbf{r}_i) \\
&= \sum_i^N |\phi_i(\mathbf{r})|^2
\end{aligned}$$

The variational principle for ground states

$$
\begin{aligned}
E^0 &= \min_{\Psi} \langle\Psi| H |\Psi\rangle \\
&= \min_{\Psi} \left\{ \langle\Psi| T + V_{ee} |\Psi\rangle + \langle\Psi| \sum_{i}^{N} v_{ext}(\mathbf{r}_i) |\Psi\rangle \right\} \\
&= \min_{\Psi} \left\{ \langle\Psi| T + V_{ee} |\Psi\rangle + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right\}
\end{aligned}
$$

Most QM methods use the wavefunction as the computational variable and work on its optimization.

The constrained-search formulation of DFT

$$
\begin{aligned}
E^0 &= \min_{\Psi} \left\{ \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} \min_{\Psi \to \rho(\mathbf{r})} \left\{ \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} \left\{ \min_{\Psi \to \rho(\mathbf{r})} \langle \Psi | \, T + V_{ee} \, | \Psi \rangle + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} \left\{ F[\rho(\mathbf{r})] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \\
&= \min_{\rho(\mathbf{r})} E_v[\rho(\mathbf{r})]
\end{aligned}
$$

Levy, 1979

The constrained search

A. We have a new $F[\rho(\mathbf{r})] = \min_{\Psi \to \rho(\mathbf{r})} \langle \Psi | T + V_{ee} | \Psi \rangle$

1. A functional of density; given a density, it gives a number.
2. A universal functional of density, independent of atoms, or molecules.

B. The ground state energy is the minimum

$$\begin{aligned} E^0 &= \min_{\rho(\mathbf{r})} E_v[\rho(\mathbf{r})] \\ &= \min_{\rho(\mathbf{r})} \left\{ F[\rho(\mathbf{r})] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \right\} \end{aligned}$$

C. $\rho(\mathbf{r})$ is the new reduced variable

Kohn-Sham theory, going beyond the Thomas-Fermi Approximation

Use a non-interacting electron system, —Kohn-Sham reference system, to calculate the electron density and kinetic energy

$$|\Phi_s\rangle = |\chi_1\chi_2\cdots\chi_i\chi_j\cdots\chi_N\rangle$$

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_i^N |\phi_i(\mathbf{r})|^2 \\ T_s[\rho] &= \langle\Phi_s| \sum_i^N -\frac{1}{2}\nabla_i^2 |\Phi_s\rangle \\ &= \sum_i^N \int d\mathbf{r}_i \phi_i^*(\mathbf{r}_i) \left(-\frac{1}{2}\nabla_i^2\right) \phi_i(\mathbf{r}_i) \\ &= \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle \end{aligned}$$

Kohn-Sham theory

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad T_s[\rho] = \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle$$

- $\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$ is the true electron density, but $T_s[\rho]$ is not $T[\rho]$. However, $T_s[\rho]$ is a very good approximation to $T_s[\rho]$

- The essence of KS theory is to solve $T_s[\rho]$ exactly in terms of orbitals

Kohn-Sham theory

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad T_s[\rho] = \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle$$

Introduce the exchange correlation energy functional

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

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

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

Kohn-Sham Equations

$$\rho(\mathbf{r}) \;=\; \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad\qquad T_s[\rho] \;=\; \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle$$

In terms of the orbitals, the KS total energy functional is now

$$E_v[\rho] = \sum_i^N \langle\phi_i| -\frac{1}{2}\nabla^2 |\phi_i\rangle + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r})$$

The g.s. energy is the minimum of the functional w.r.t. all possible densities. The minimum can be attained by searching all possible orbitals

$$W[\phi_i] = E_v[\phi_i] - \sum_i^N \varepsilon_i \{< \phi_i|\phi_i > -1\}$$

$$\frac{\delta W[\phi_i]}{\delta\phi_i(\mathbf{r})} = 0$$

The orbitals $\{|\phi_i\rangle\}$ are the eigenstates of an one-electron local potential $v_s(\mathbf{r})$ if we have explicit density functional for $E_{xc}[\rho]$ (KS equations)

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

or a nonlocal potential $v_s^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')$, if we have orbital functionals for $E_{xc}[\phi_i]$ (generalized KS equations)

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

One electron Equations

Kohn-Sham (KS)

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

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

Generalized Kohn-Sham (GKS)

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

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

Computational Scaling

In finite basis sets, KS and GKS equations turn into matrix eigenvalue problem. **The scaling is N^3**.

Feastures of Kohn-Sham theory

1. With N orbitals, the kinetic energy is treated rigorously. In comparison with the Thomas-Fermi theory in terms of density, it is a trade of computational difficulty for accuracy.

2. The KS or GKS equations are in the similar form as the Hartree-Fock equations and can be solved with similar efforts.

3. KS or GKS changes a N interacting electron problem into an N non-interacting electrons in an effective potential.

4. The E_xc is not known, explicitly. It is about 10% of the energy for atoms.

The Local Density Approximation (Kohn-Sham, 1964)

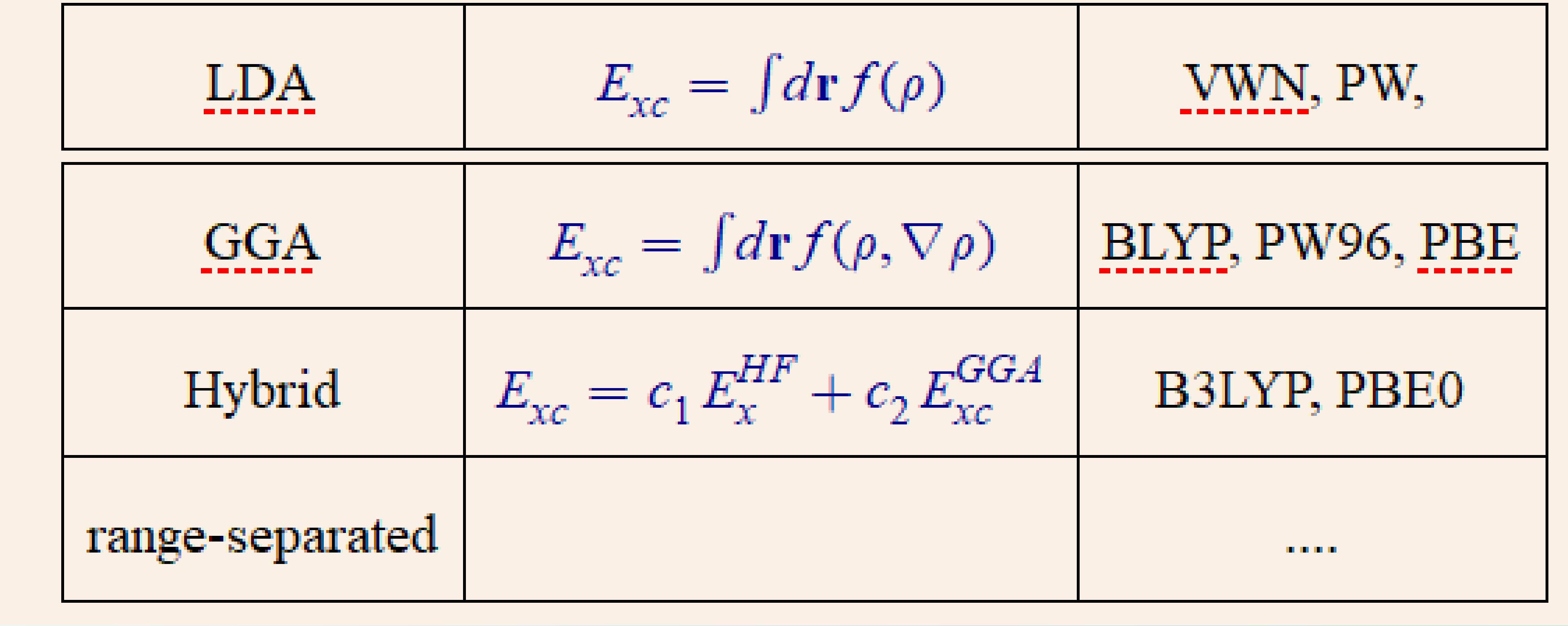
$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))$$

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

Dirac exchange energy functional

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

Beyond the Local Density Approximation



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

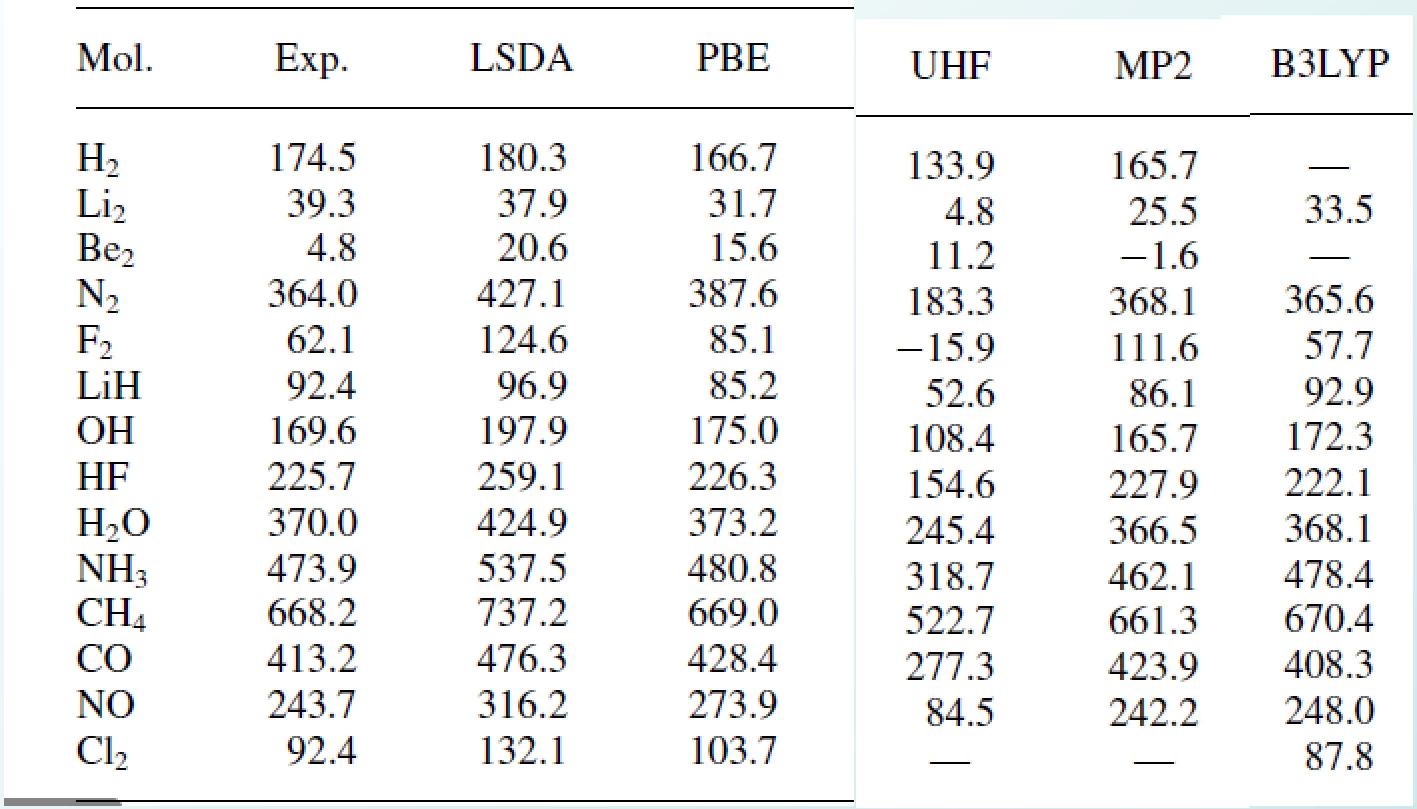
$$E_{\mathrm{x}}^{\mathrm{B88}} = - \sum_{\sigma=\alpha,\beta} \int \rho_{\sigma}{}^{4/3} \left[\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} + \frac{\beta x_{\sigma}{}^{2}}{1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma}} \right] \mathrm{d}\mathbf{r}$$

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

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

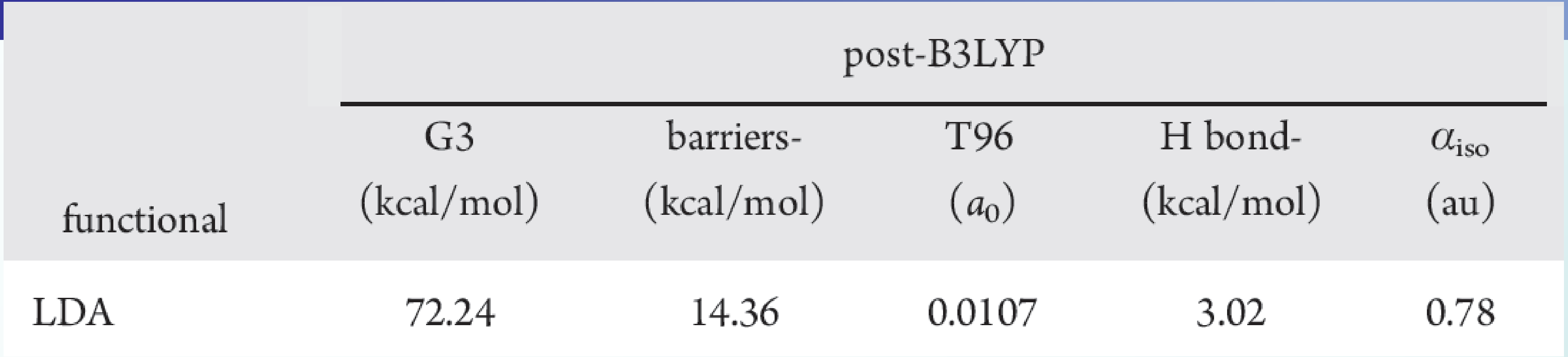
$$\begin{aligned} E_{\mathrm{xc}}^{\mathrm{B3LYP}} = {} & 0.2E_{\mathrm{x}}^{\mathrm{HF}} + 0.8E_{\mathrm{x}}^{\mathrm{LDA}} + 0.72\Delta E_{\mathrm{x}}^{\mathrm{B88}} + 0.81E_{\mathrm{c}}^{\mathrm{LYP}} \\ & + 0.19E_{\mathrm{c}}^{\mathrm{VWN}} \end{aligned}$$

Atomization energies for a few selected molecules, mH



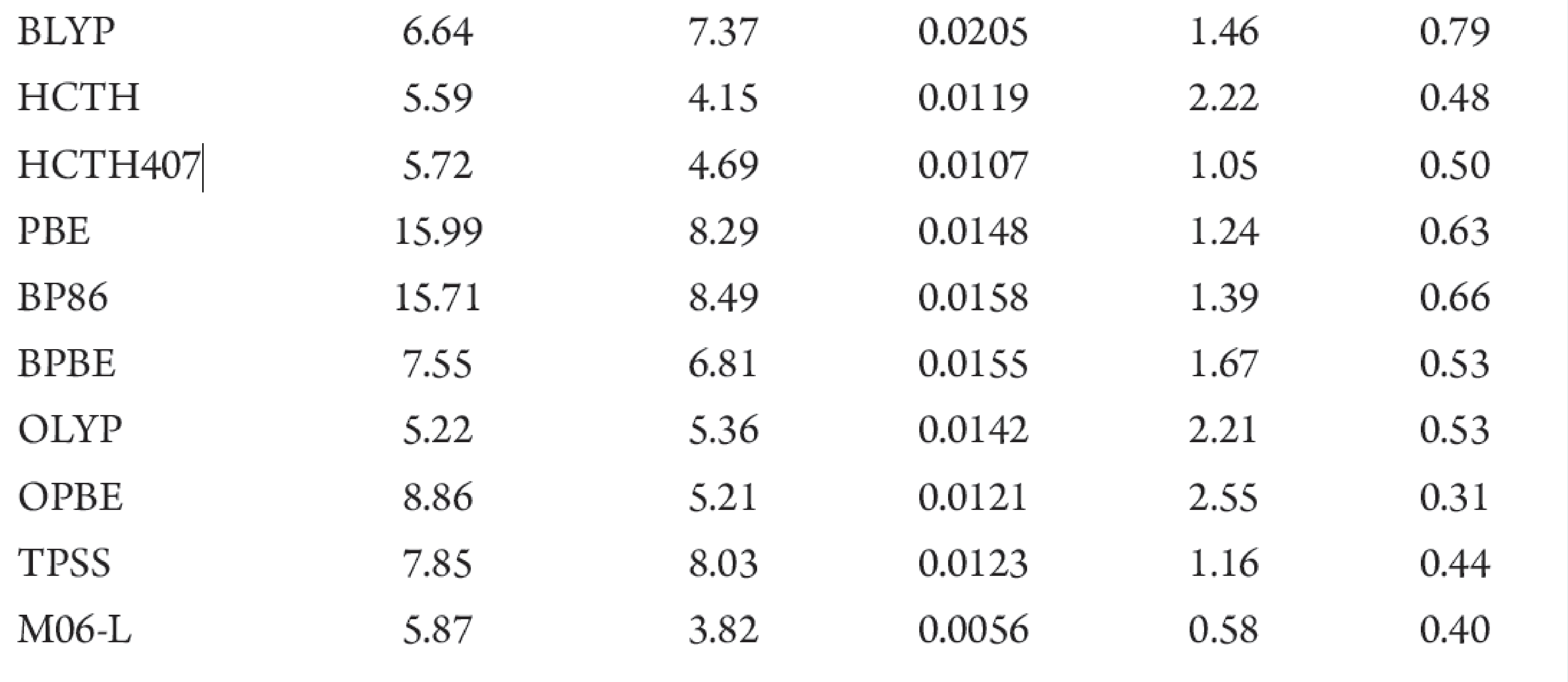
Mol.	Exp.	LSDA	PBE	UHF	MP2	B3LYP
H_2	174.5	180.3	166.7	133.9	165.7	—
Li_2	39.3	37.9	31.7	4.8	25.5	33.5
Be_2	4.8	20.6	15.6	11.2	−1.6	—
N_2	364.0	427.1	387.6	183.3	368.1	365.6
F_2	62.1	124.6	85.1	−15.9	111.6	57.7
LiH	92.4	96.9	85.2	52.6	86.1	92.9
OH	169.6	197.9	175.0	108.4	165.7	172.3
HF	225.7	259.1	226.3	154.6	227.9	222.1
H_2O	370.0	424.9	373.2	245.4	366.5	368.1
NH_3	473.9	537.5	480.8	318.7	462.1	478.4
CH_4	668.2	737.2	669.0	522.7	661.3	670.4
CO	413.2	476.3	428.4	277.3	423.9	408.3
NO	243.7	316.2	273.9	84.5	242.2	248.0
Cl_2	92.4	132.1	103.7	—	—	87.8

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



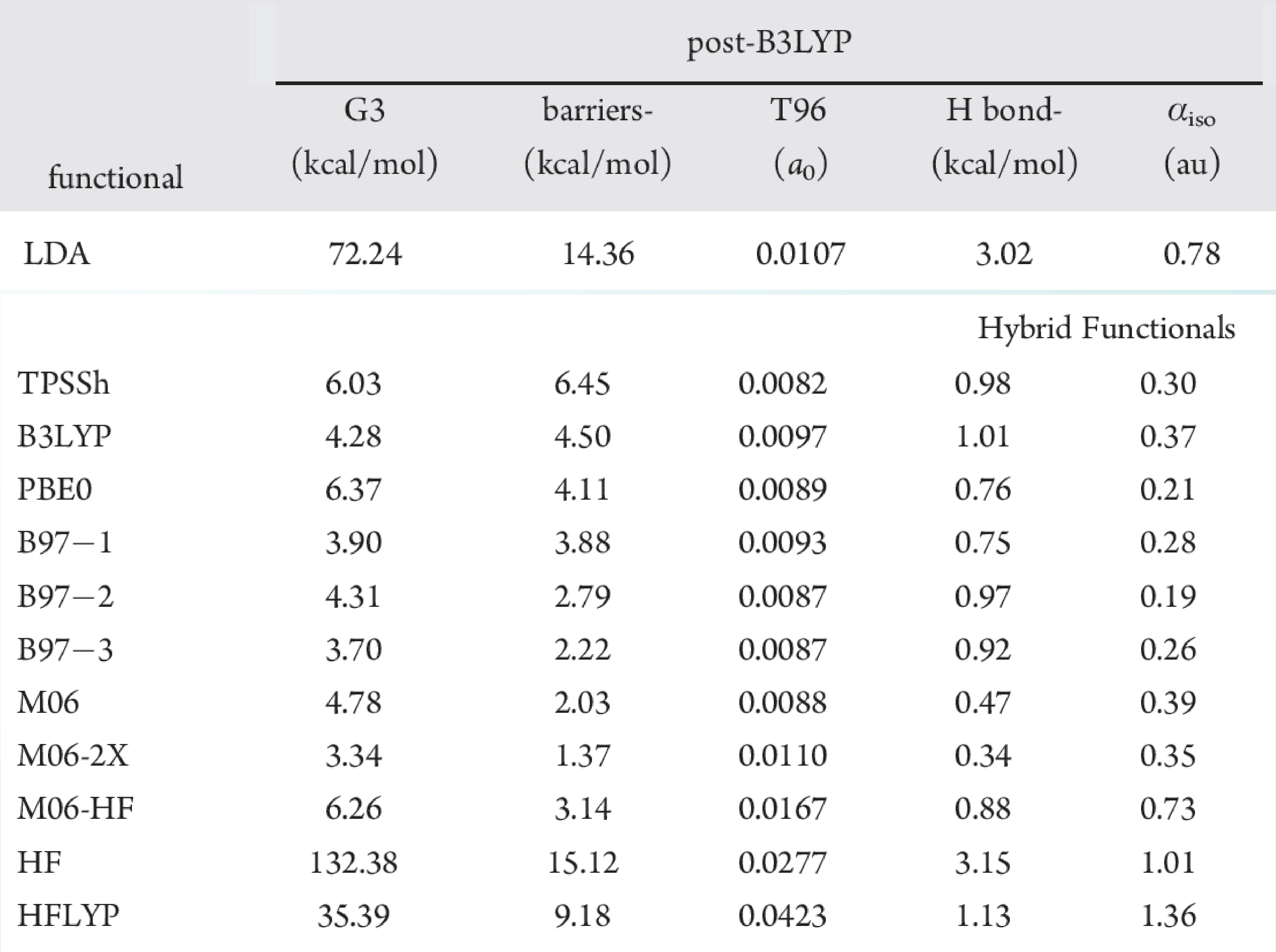
	post-B3LYP				
functional	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78

GGA and Meta-GGA



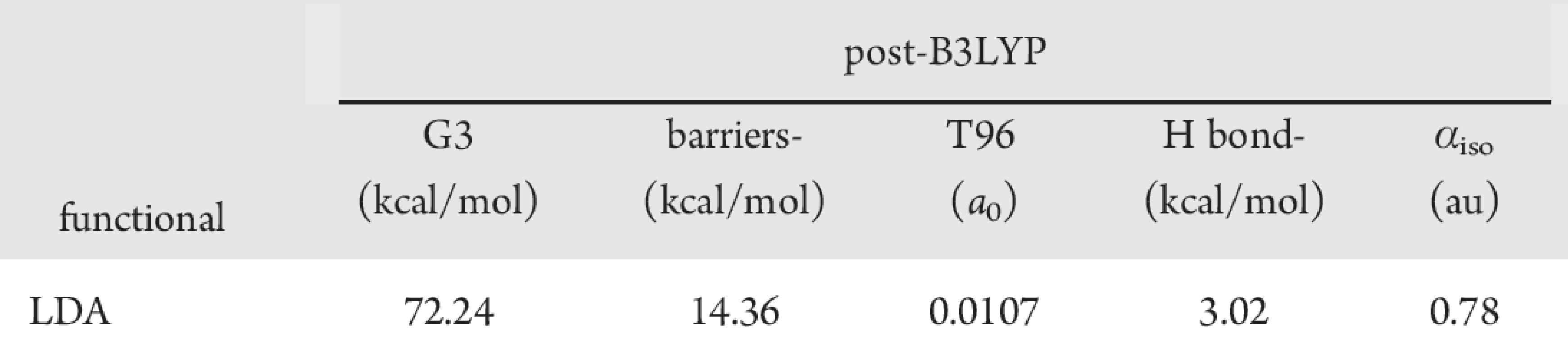
BLYP	6.64	7.37	0.0205	1.46	0.79
HCTH	5.59	4.15	0.0119	2.22	0.48
HCTH407	5.72	4.69	0.0107	1.05	0.50
PBE	15.99	8.29	0.0148	1.24	0.63
BP86	15.71	8.49	0.0158	1.39	0.66
BPBE	7.55	6.81	0.0155	1.67	0.53
OLYP	5.22	5.36	0.0142	2.21	0.53
OPBE	8.86	5.21	0.0121	2.55	0.31
TPSS	7.85	8.03	0.0123	1.16	0.44
M06-L	5.87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

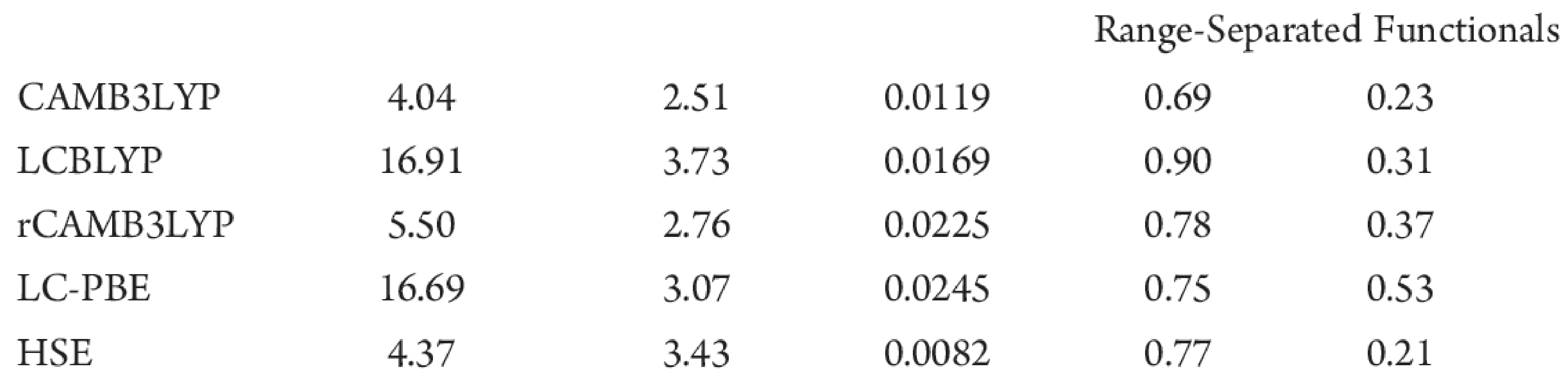
Mean Absolute Errors (MAE) Thermochemistry(G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities



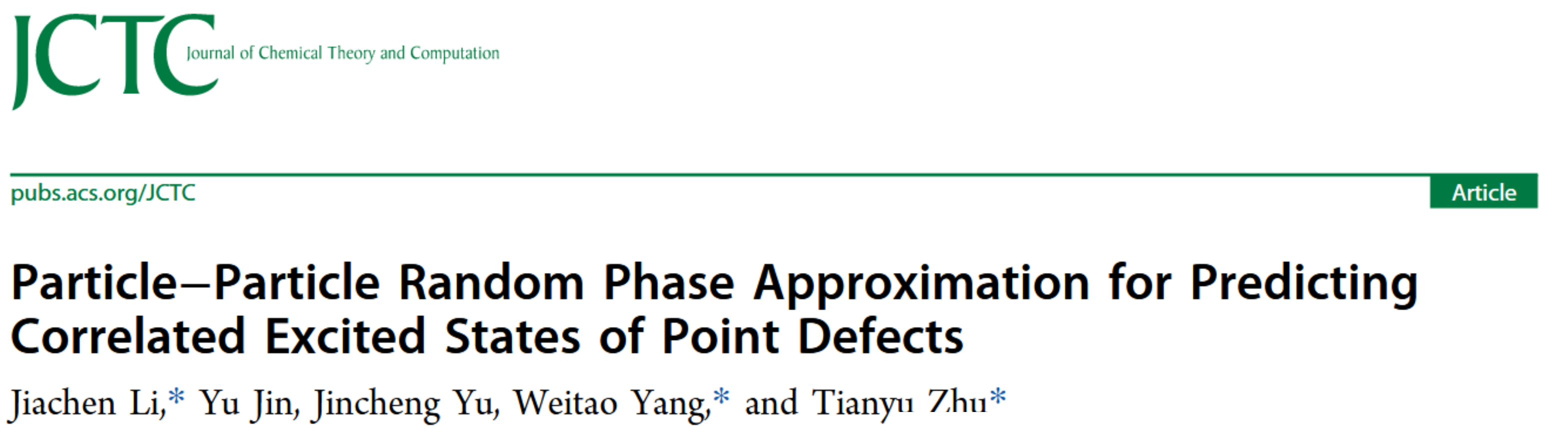
	post-B3LYP				
functional	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78
				Hybrid Functionals	
TPSSh	6.03	6.45	0.0082	0.98	0.30
B3LYP	4.28	4.50	0.0097	1.01	0.37
PBE0	6.37	4.11	0.0089	0.76	0.21
B97−1	3.90	3.88	0.0093	0.75	0.28
B97−2	4.31	2.79	0.0087	0.97	0.19
B97−3	3.70	2.22	0.0087	0.92	0.26
M06	4.78	2.03	0.0088	0.47	0.39
M06-2X	3.34	1.37	0.0110	0.34	0.35
M06-HF	6.26	3.14	0.0167	0.88	0.73
HF	132.38	15.12	0.0277	3.15	1.01
HFLYP	35.39	9.18	0.0423	1.13	1.36

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





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



JCTC Journal of Chemical Theory and Computation

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Particle–Particle Random Phase Approximation for Predicting Correlated Excited States of Point Defects

Jiachen Li,* Yu Jin, Jincheng Yu, Weitao Yang,* and Tianyu Zhu*

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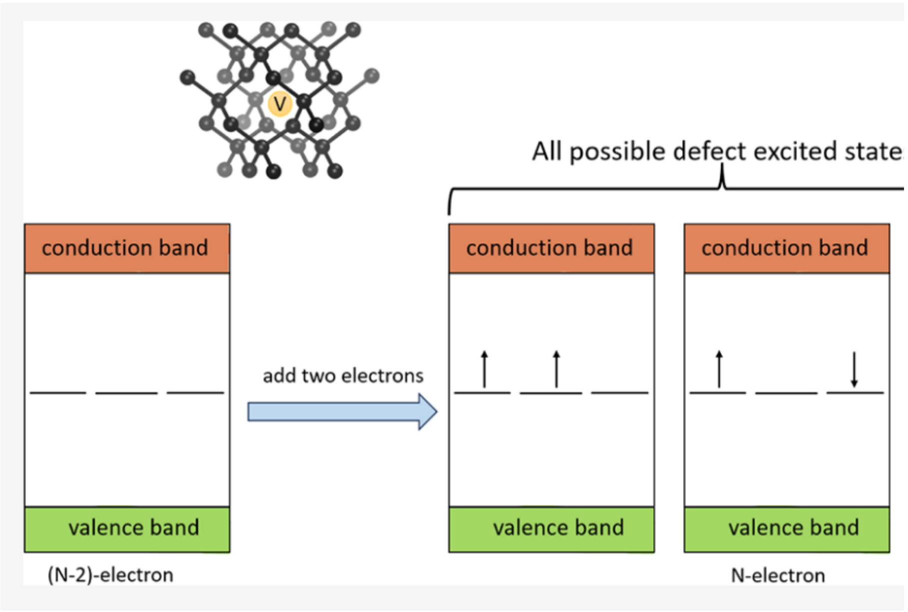


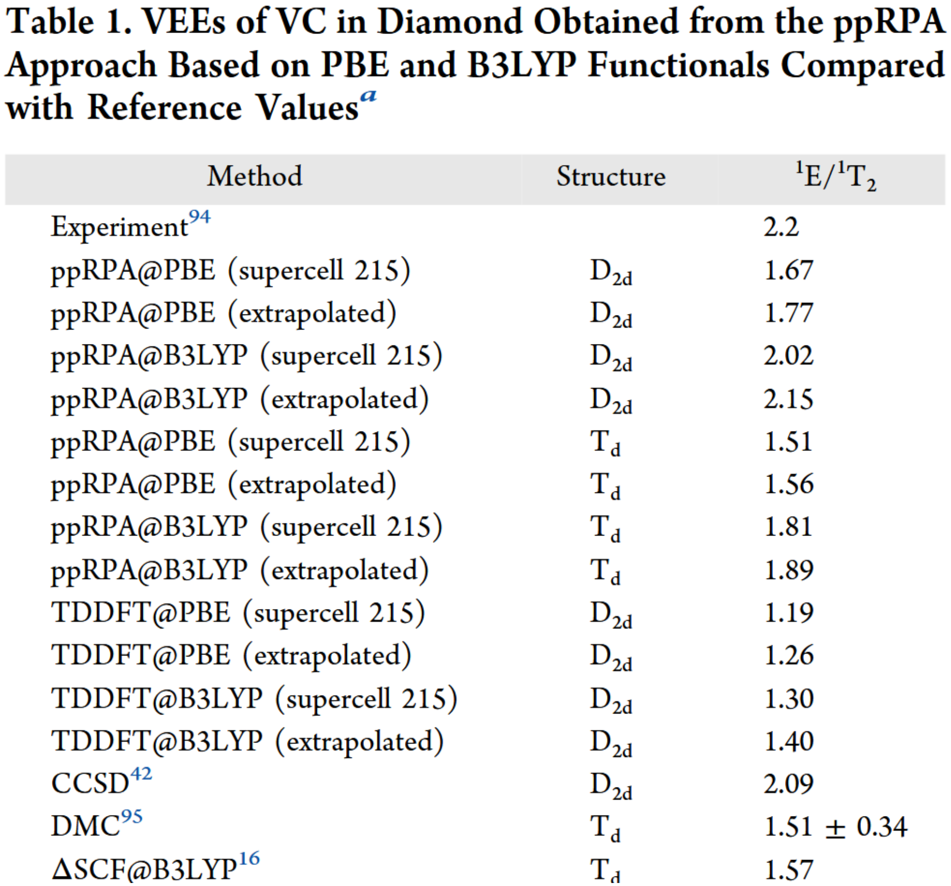


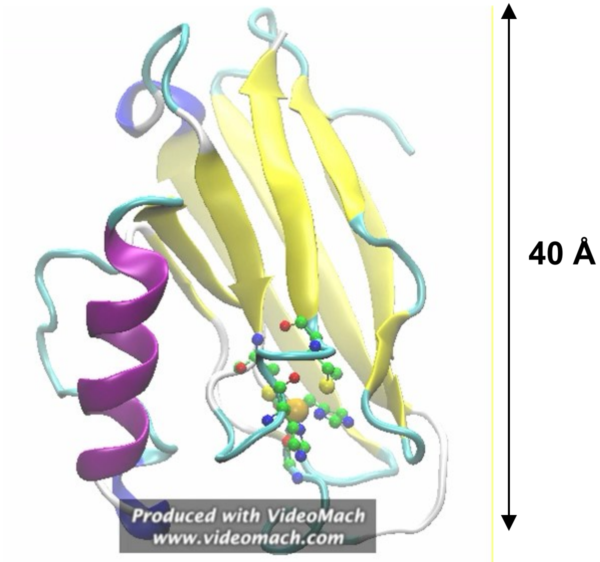
Table 1. VEEs of VC in Diamond Obtained from the ppRPA Approach Based on PBE and B3LYP Functionals Compared with Reference Values[a]

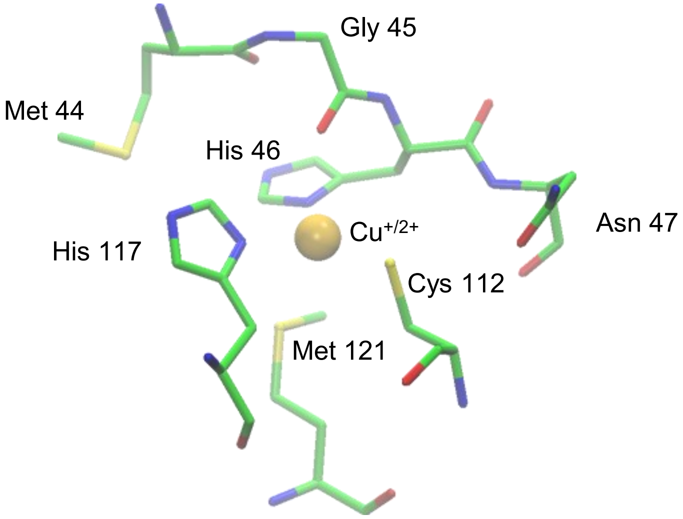
Method	Structure	$^1E/^1T_2$
Experiment[94]		2.2
ppRPA@PBE (supercell 215)	D_{2d}	1.67
ppRPA@PBE (extrapolated)	D_{2d}	1.77
ppRPA@B3LYP (supercell 215)	D_{2d}	2.02
ppRPA@B3LYP (extrapolated)	D_{2d}	2.15
ppRPA@PBE (supercell 215)	T_d	1.51
ppRPA@PBE (extrapolated)	T_d	1.56
ppRPA@B3LYP (supercell 215)	T_d	1.81
ppRPA@B3LYP (extrapolated)	T_d	1.89
TDDFT@PBE (supercell 215)	D_{2d}	1.19
TDDFT@PBE (extrapolated)	D_{2d}	1.26
TDDFT@B3LYP (supercell 215)	D_{2d}	1.30
TDDFT@B3LYP (extrapolated)	D_{2d}	1.40
CCSD[42]	D_{2d}	2.09
DMC[95]	T_d	1.51 ± 0.34
ΔSCF@B3LYP[16]	T_d	1.57

Carbon Vacancy in Diamond
Accuracy about 0.1 eV for the ecitation energy.

System and Computational Details

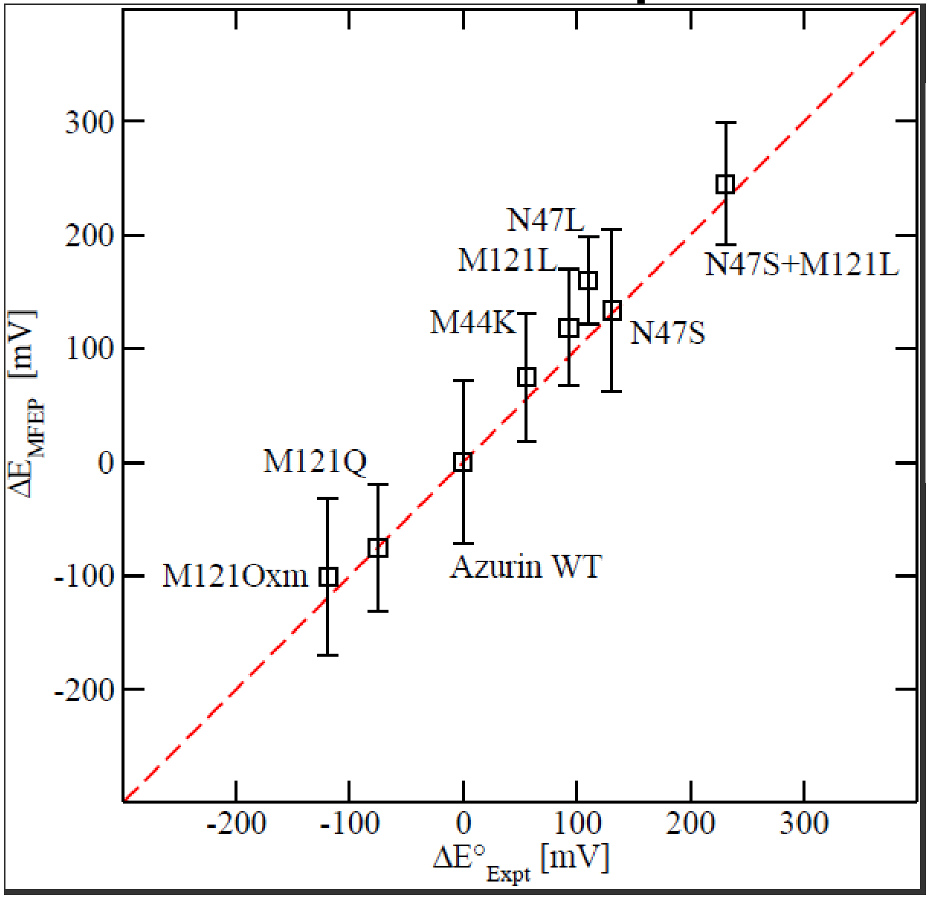
- System – Azurin 4AZU
  - 128 Residues, 43.5×33.1×41.4 Å^3
  - Water box, 90×90×90 Å^3
  - Mutants: Met44Lys, Asn47Leu, Met121Oxm (artificial)
  - Details
    - G03+Sigma, UBLYP/ccpv-dz
    - QM region: 5 coordination residue + 2 mutation sites (102~107 atoms)
    - MD time: 160 ps / ensemble
    - Cutoff: 20 Å for QM/MM, PME for MD sampling
    - Pseudo bond (Parks *et al.**)





Redox Potentials of Azurin and Mutants

- Relative redox potential (WT as reference)*



Mutant	ΔE_{MFEP}	$\Delta E^{0}_{\mathrm{Expt}}$	Error
WT	-	-	-
M44K	0.08	0.056	0.02
N47L	0.17	0.110	0.06
N47S	0.14	0.131	0.01
M121Q	-0.07	-0.075	0.01
M121L	0.12	0.093	0.03
M121Oxm	-0.10	-0.119	0.02
N47S+M121L	0.25	0.231	0.02

Units in V

Shen, Zeng, Hu, Hu and Yang, JCTC 2018

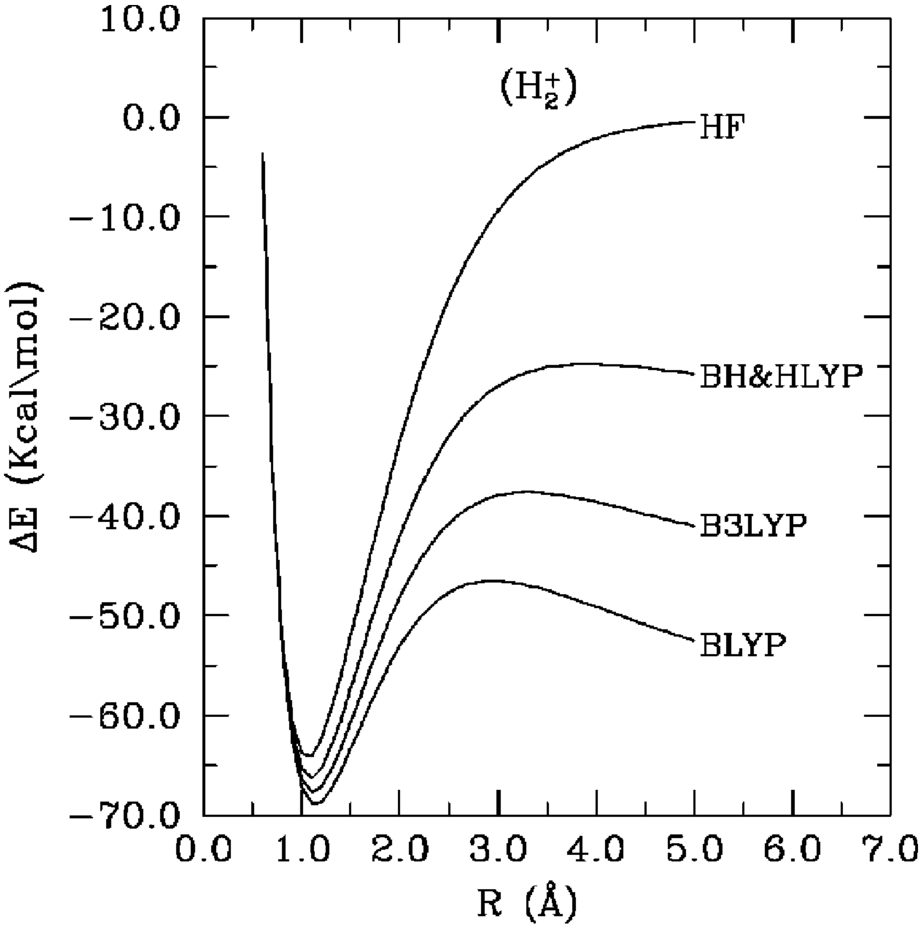
Density Functional Theory

- 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



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

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

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

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

Quantum Mechanics of Degeneracy

If

$$H\Psi_1 = E\Psi_1$$

$$H\Psi_2 = E\Psi_2$$

then

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

Ground State Degeneracy in QM and in DFT

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

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

$$\Psi_\alpha$$

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


Proton A

Proton B

e

$$\Psi_\beta$$

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


Proton A

e

Proton B

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

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


Proton A

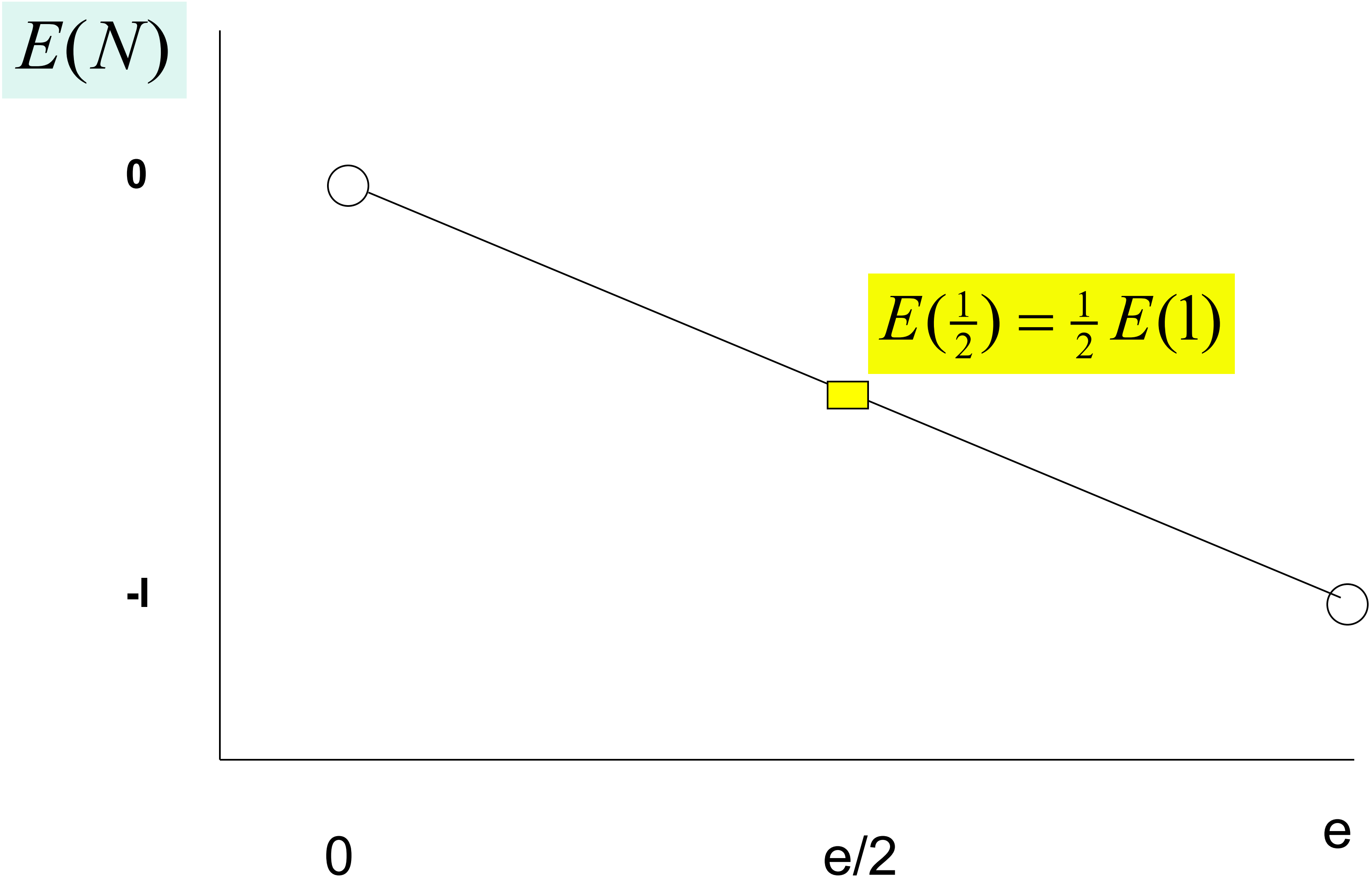
e/2

Proton B

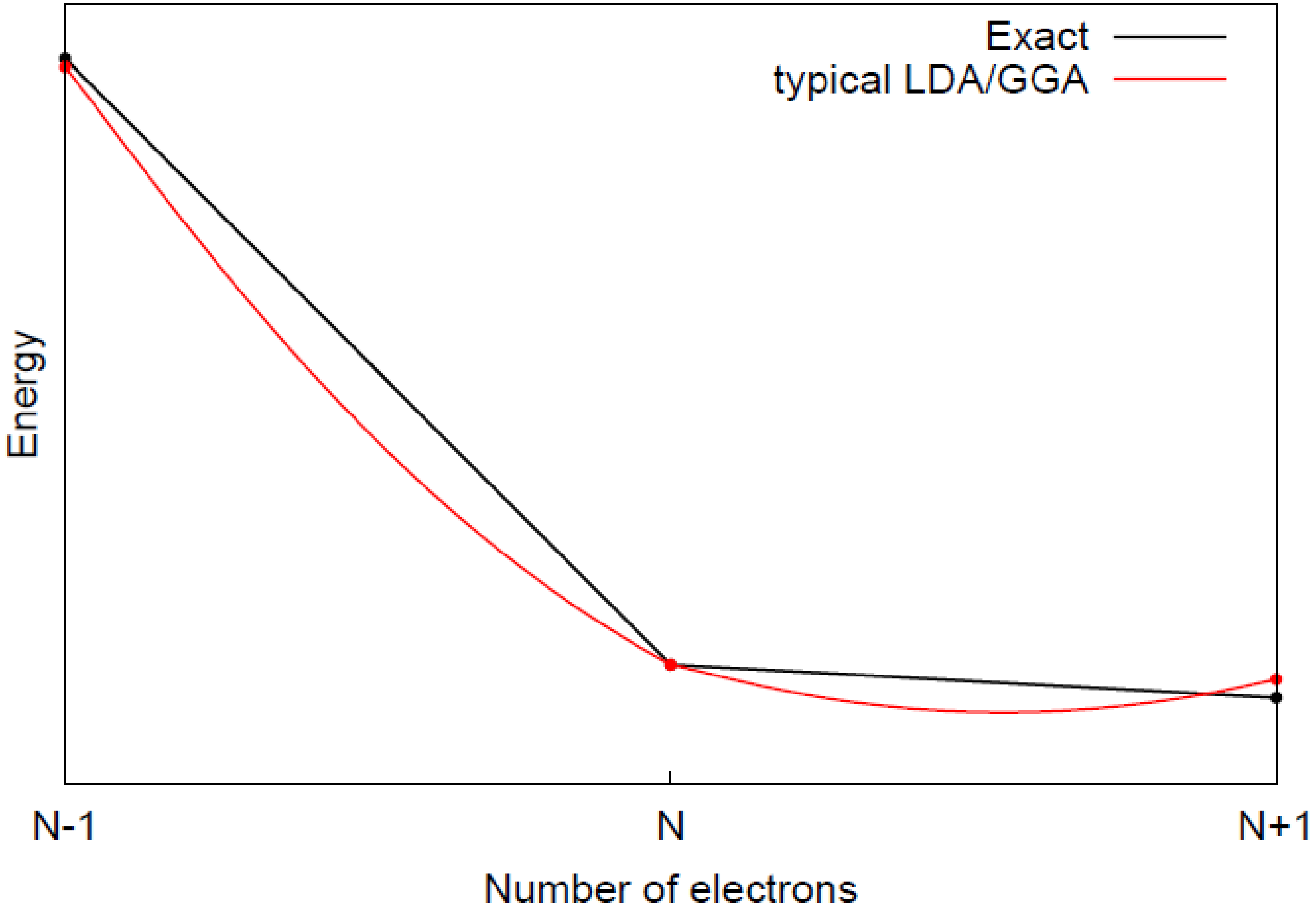
e/2

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

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

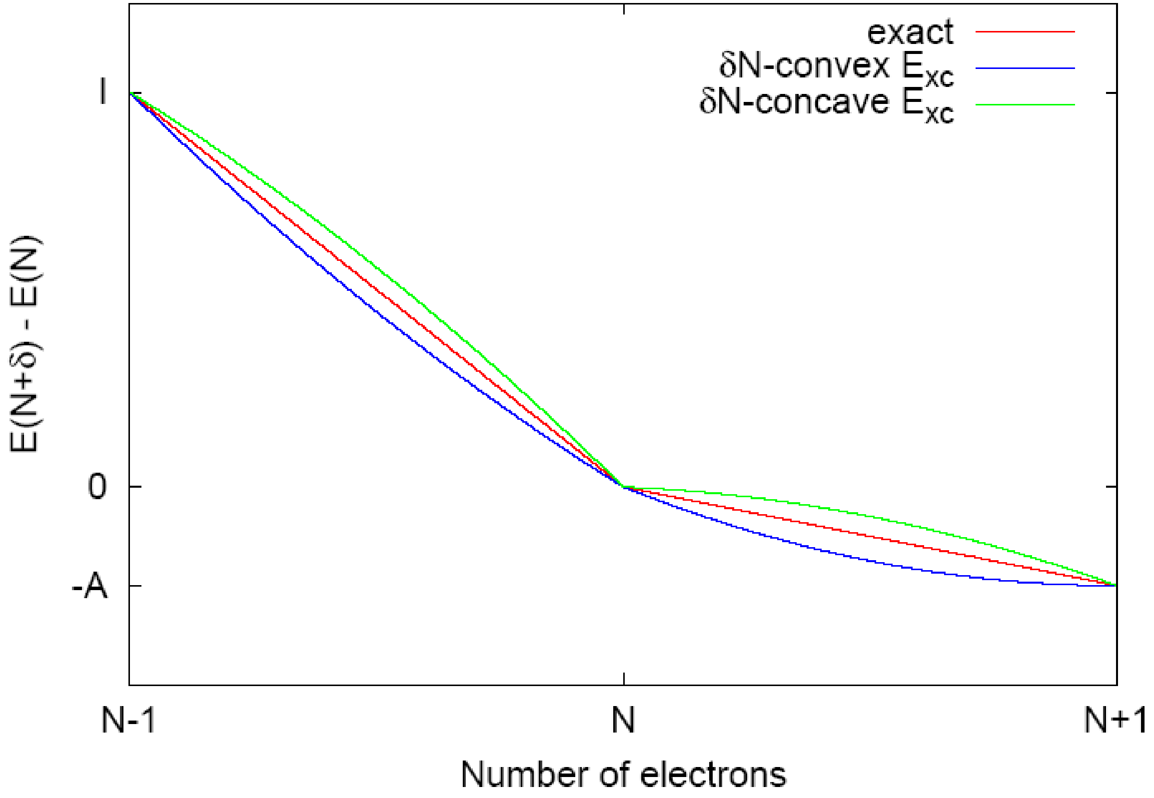


E(N)



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

2 x



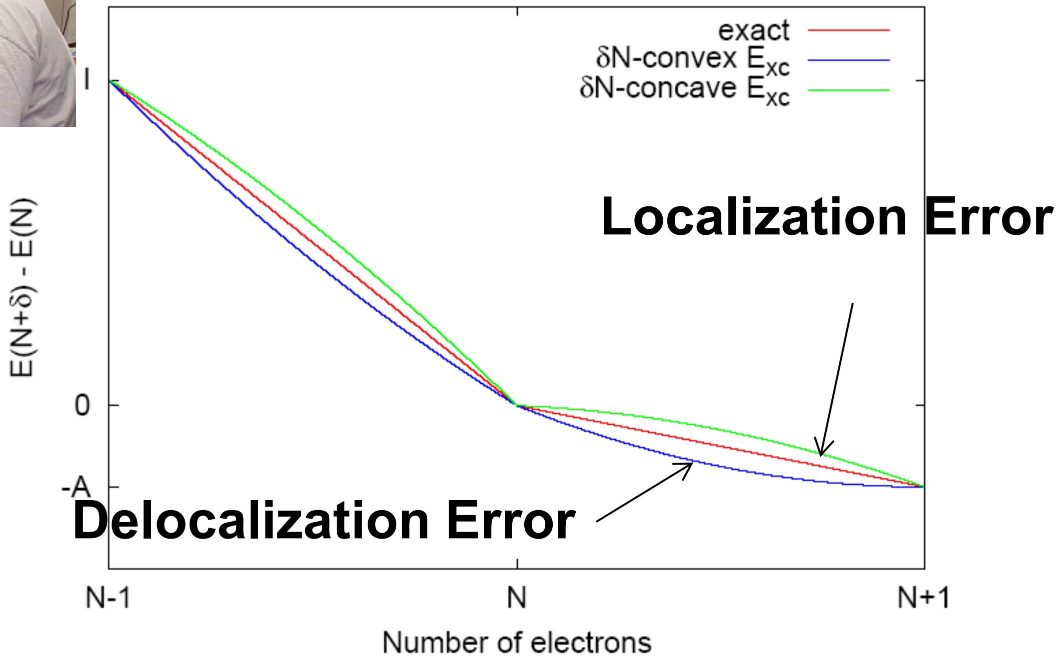
+ e

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***



Localization Error

Delocalization Error

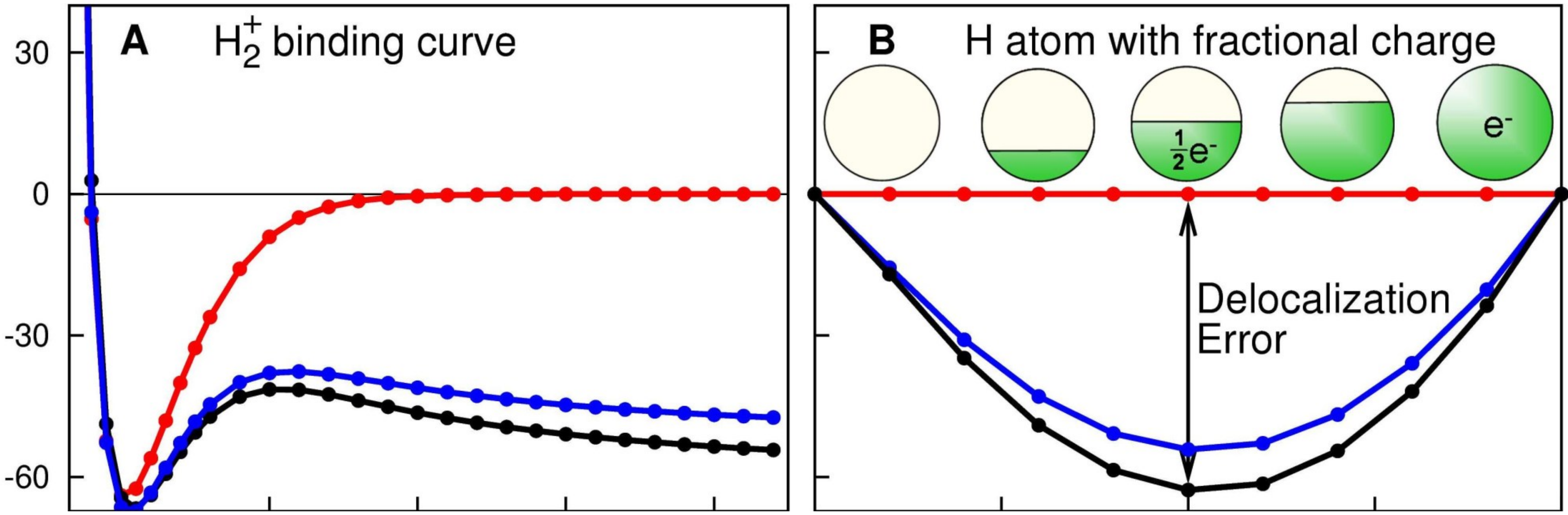
Consequence of Delocalization Error

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

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

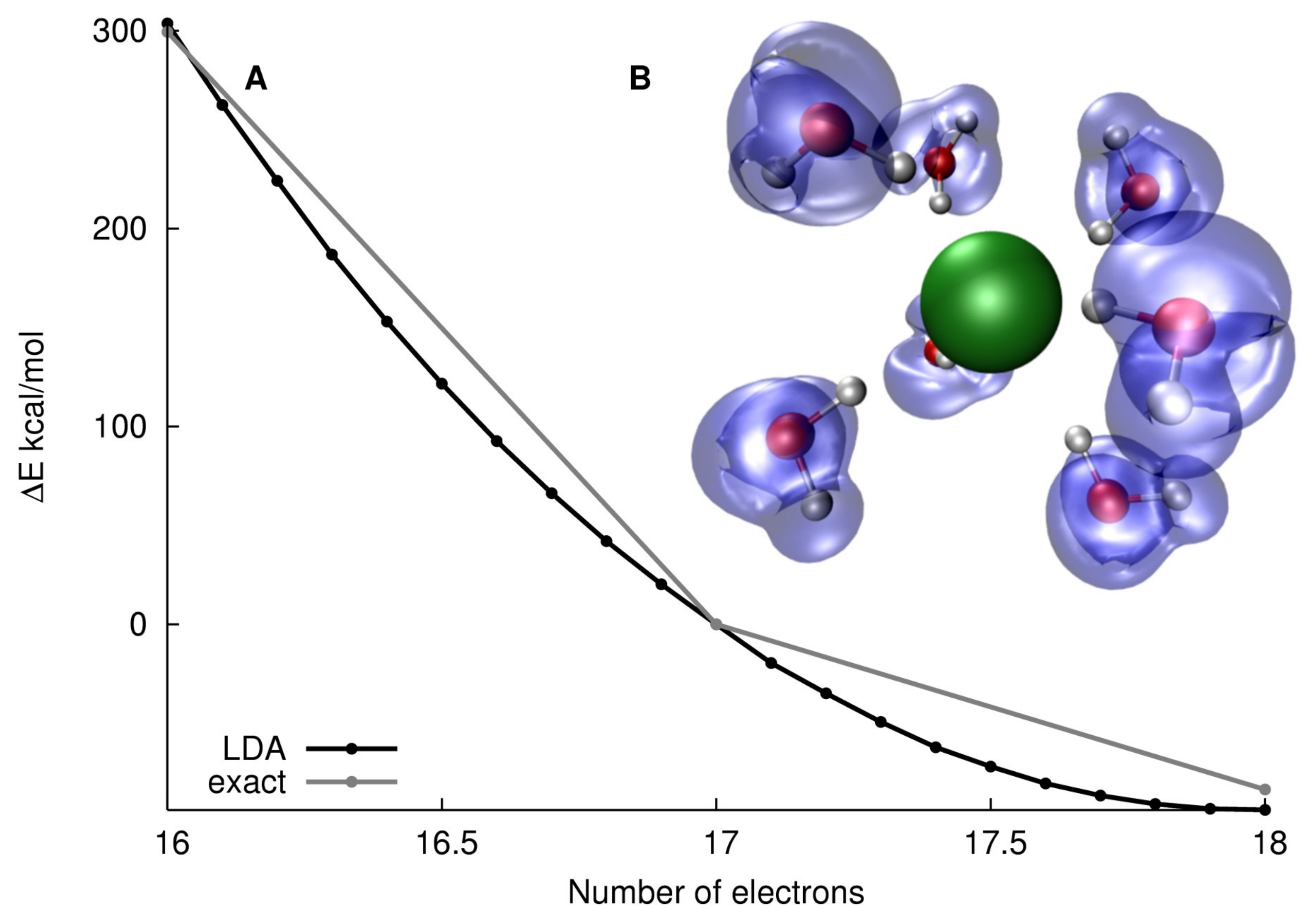
- Energy of dissociation of molecular ion: too low
- Charge transfer complex energy: too low
- Transition state energy: too low
- Charge transfer excitation energy: too low
- Band gap: too low
- Molecular conductance: too high
- (Hyper)polarizability for long molecules: too high
- Diels-Alder reaction 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

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

The PPLB linearity conditions

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

The chemical potentials

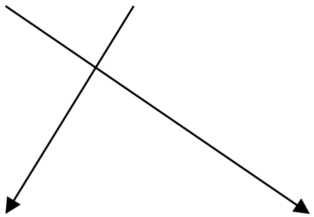
$$\mu(N) = \begin{cases} -I(N_0) = E(N_0) - E(N_0 - 1) \text{ if } N_0 - 1 < N < N_0 \\ -A(N_0) = E(N_0 + 1) - E(N_0) \text{ if } N_0 < N < N_0 + 1 \end{cases}$$

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

Band Gap

Definition of fundamental gap

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



derivative

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

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

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.

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

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

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

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

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

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

How can fundamental gap be predicted in DFT

For continuous and differentiable functionals of density/density matrix

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

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

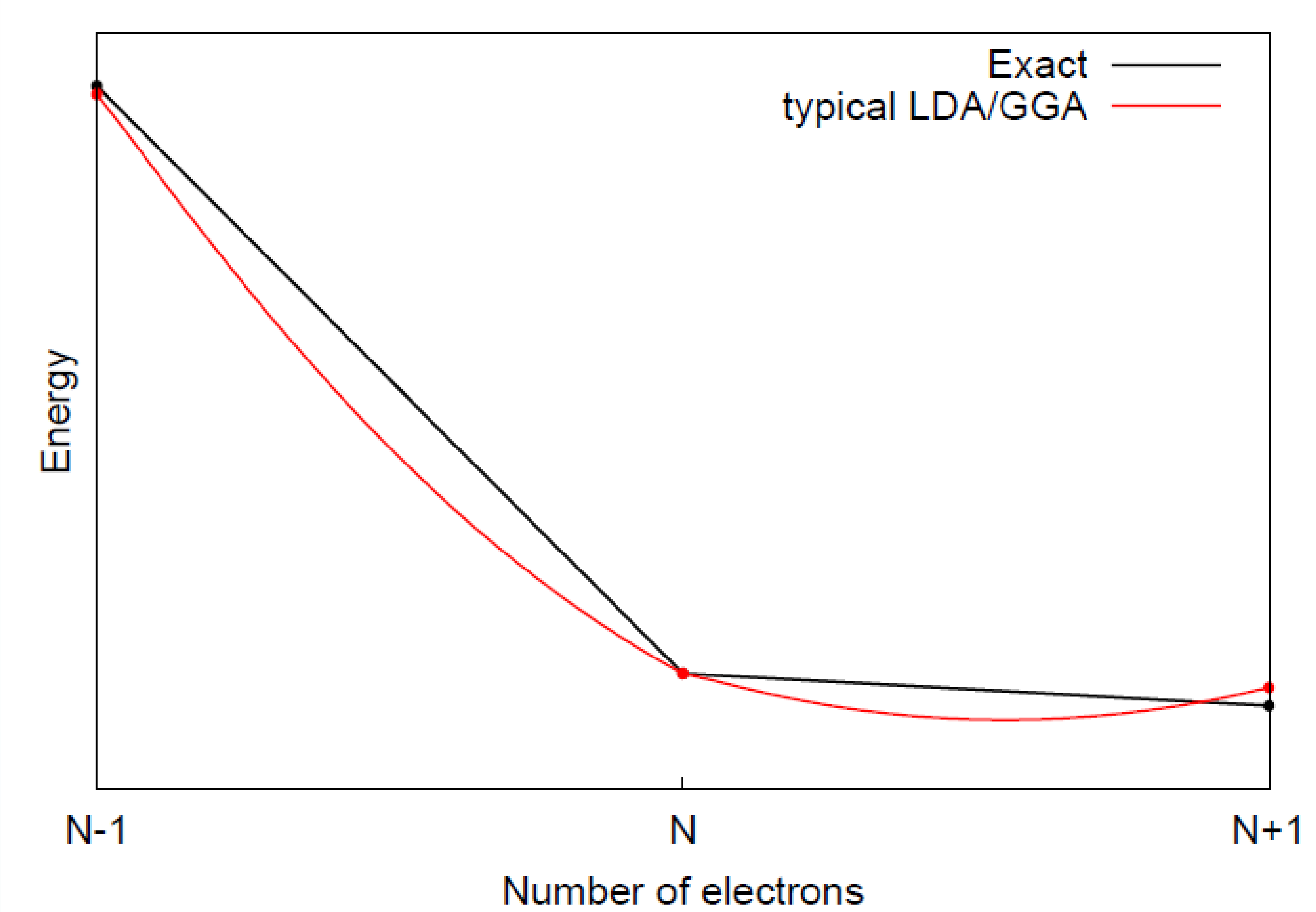
- **Fundamental gaps predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap**

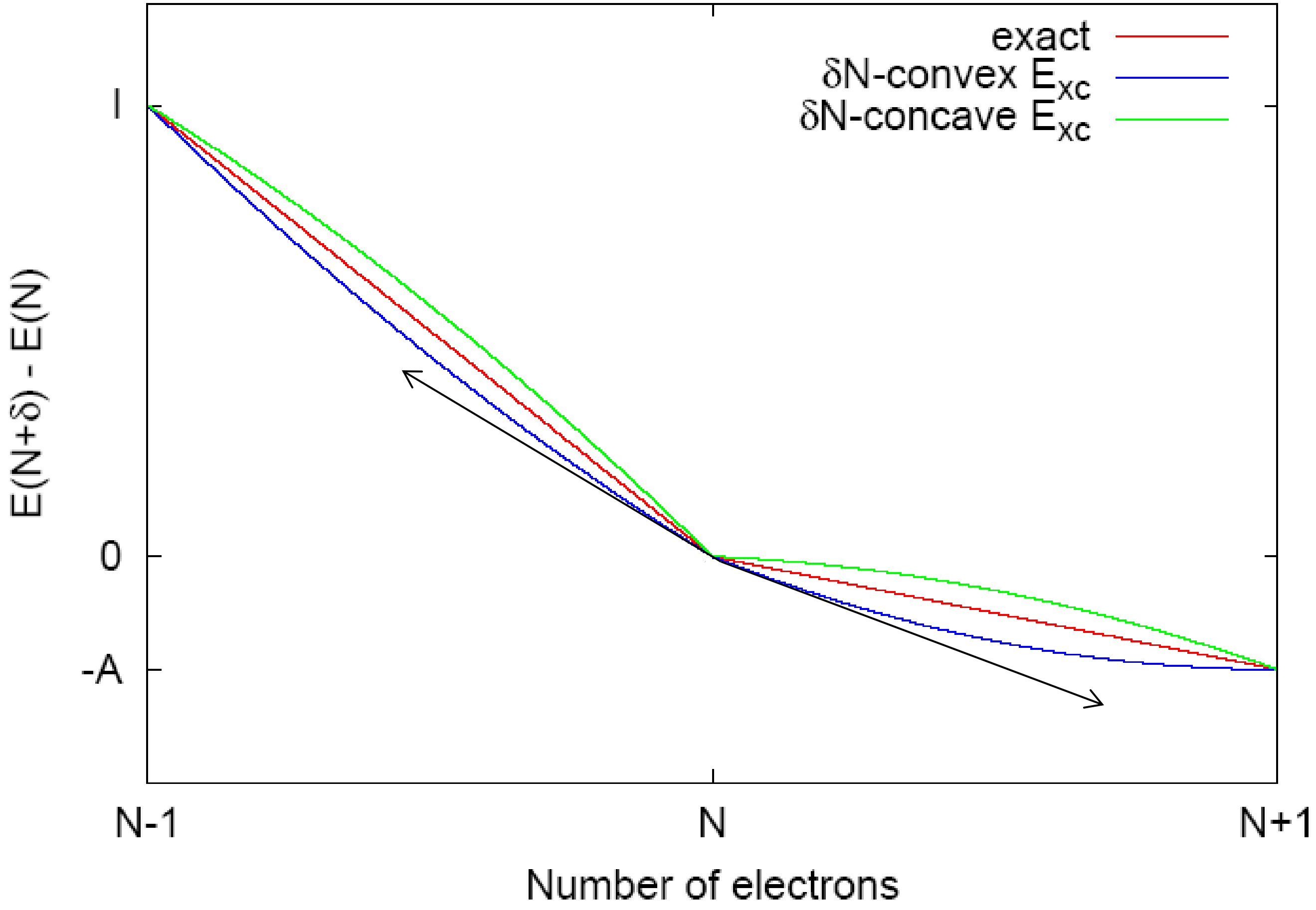
- **For orbital functionals, the LUMO of the KS (OEP) eigenvalue is NOT the chemical potential of electron addition. The KS gap is not the fundamental gap predicted by the functional.**

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

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

E(N)





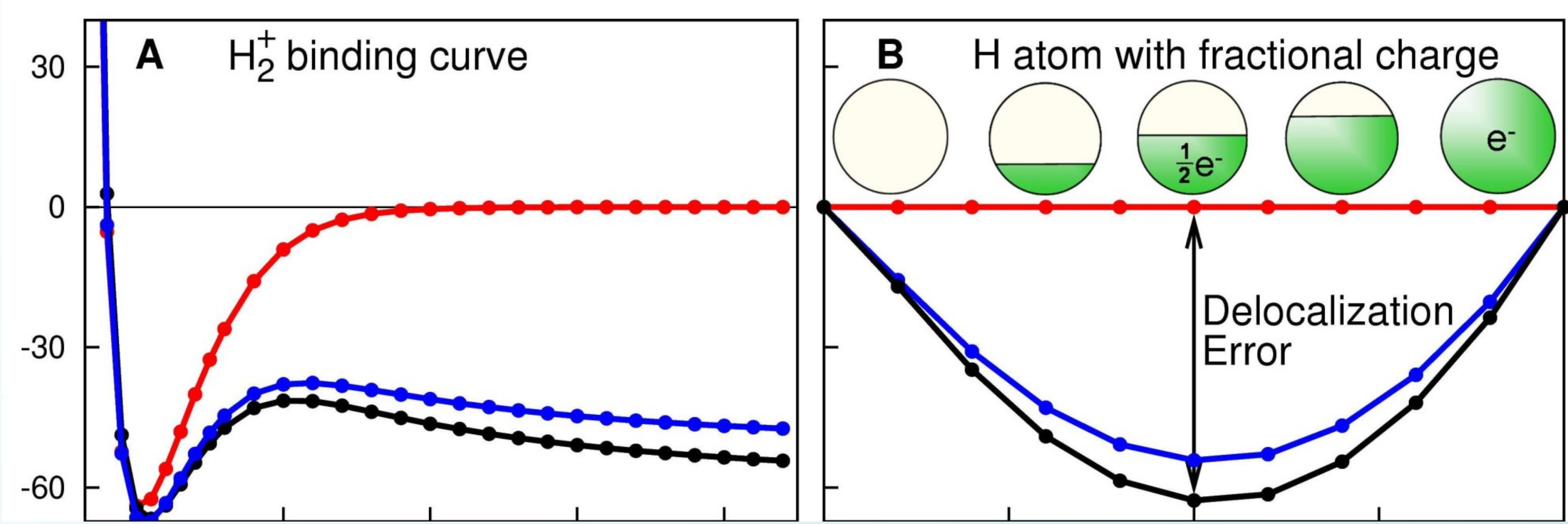
For Linear E(N)

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

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

Delocalization Error—Size dependent manifestation



Challenges

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

- Correction is needed at large R, but not at small R.

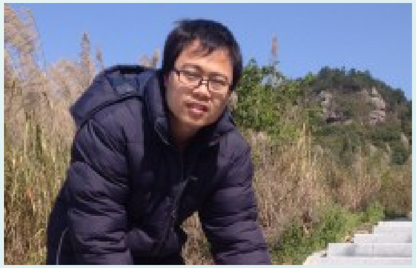
What is difference between the electronic structures at small and large R ?

Localized Orbital Scaling Correction (LOSC)

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


Chen Li

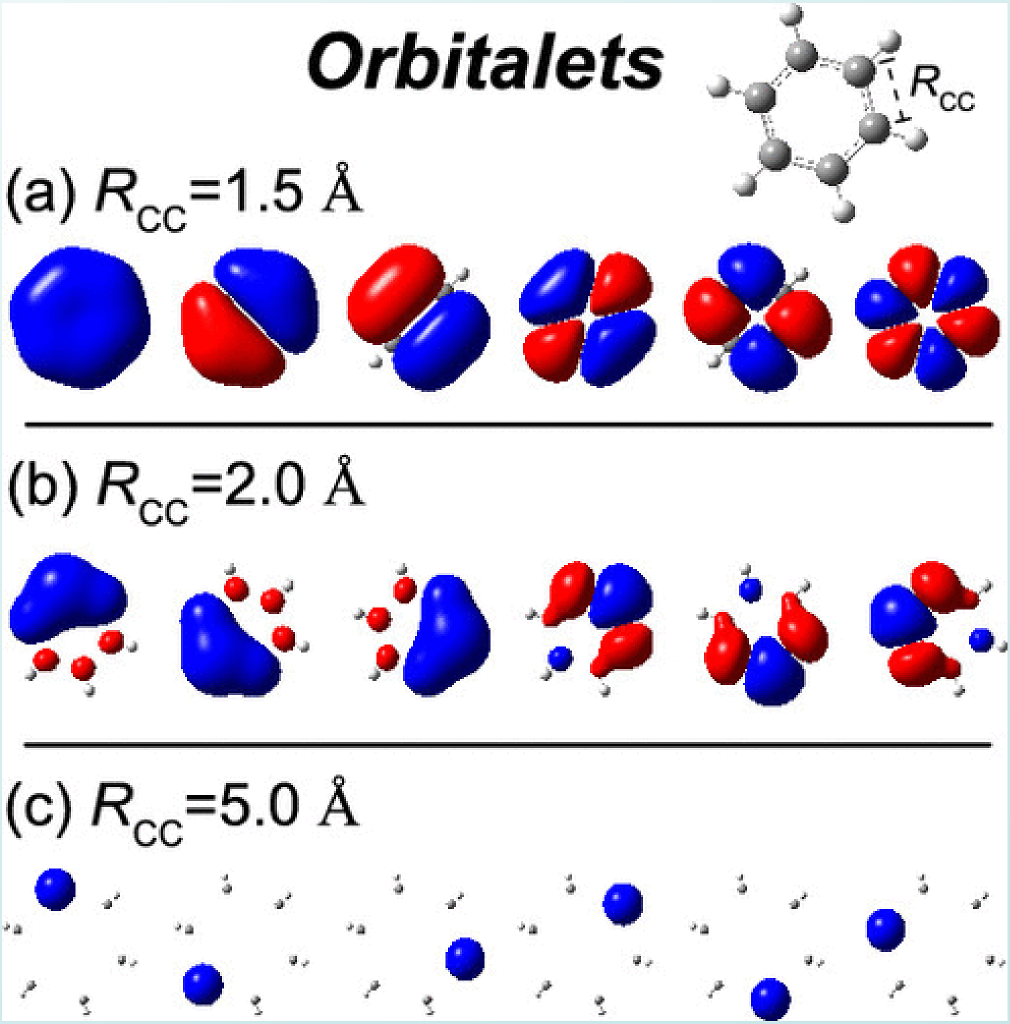

Xiao Zheng


Neil Qiang Su

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

Orbitalets: Localized in Space and Energy

Preserving Symmetry and Degeneracy in the Localized Orbital Scaling Correction Approach
Neil Qiang Su, Aaron Mahler, and Weitao Yang
J. Phys. Chem. Lett. 2020, 11, 1528-1535

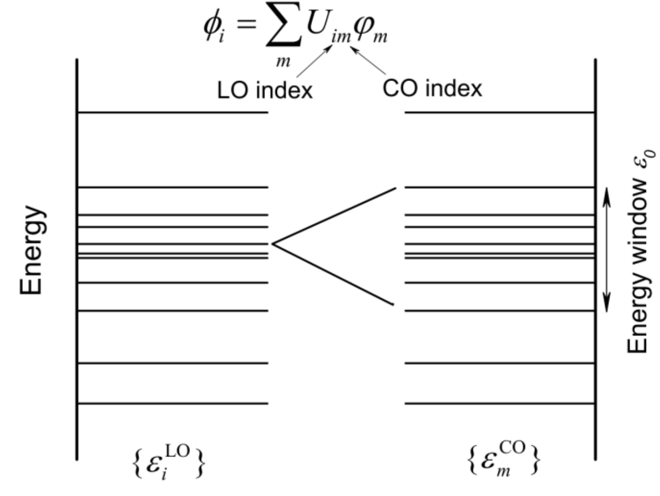


$$\left|\phi_{j\sigma}\right\rangle = \sum_m U^{\sigma}_{jm}\left|\psi_{m\sigma}\right\rangle$$

Minimizing *F* w.r.t. U^{σ}_{jm}

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

Novel Localized Orbitals



Orbitalets

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

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

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

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

New LOSC, as correction to DFA

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

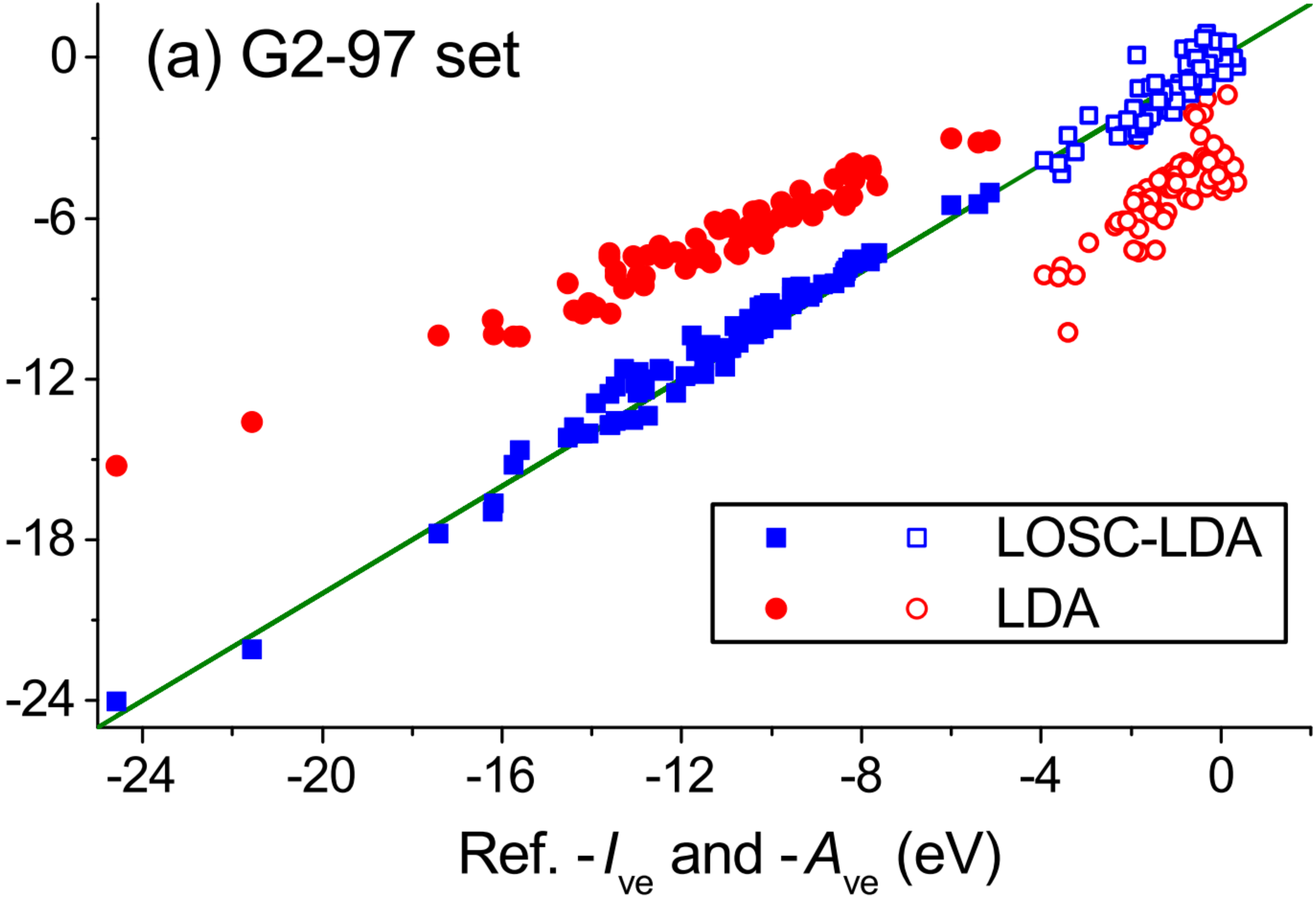
$$\frac{1}{2}\kappa_{ij} = \frac{1}{2}\iint \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{\tau C_{\mathrm{x}}}{3} \int [\rho_i(\mathbf{r})]^{\frac{2}{3}} [\rho_j(\mathbf{r})]^{\frac{2}{3}} d\mathbf{r}$$

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

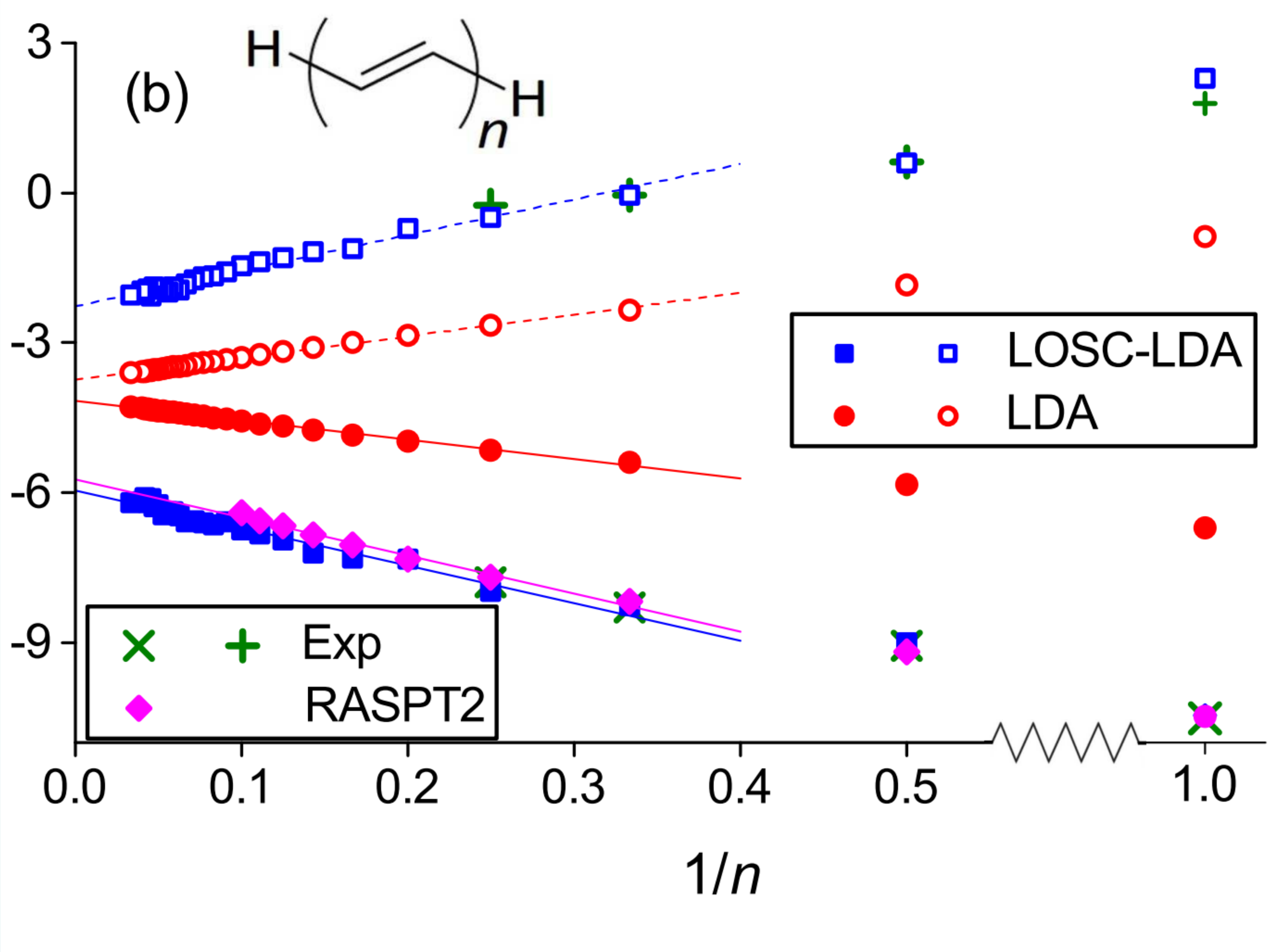
$$\tau = 6(1 - 2^{-1/3}) \approx 1.2378$$

Orbital energy corrections

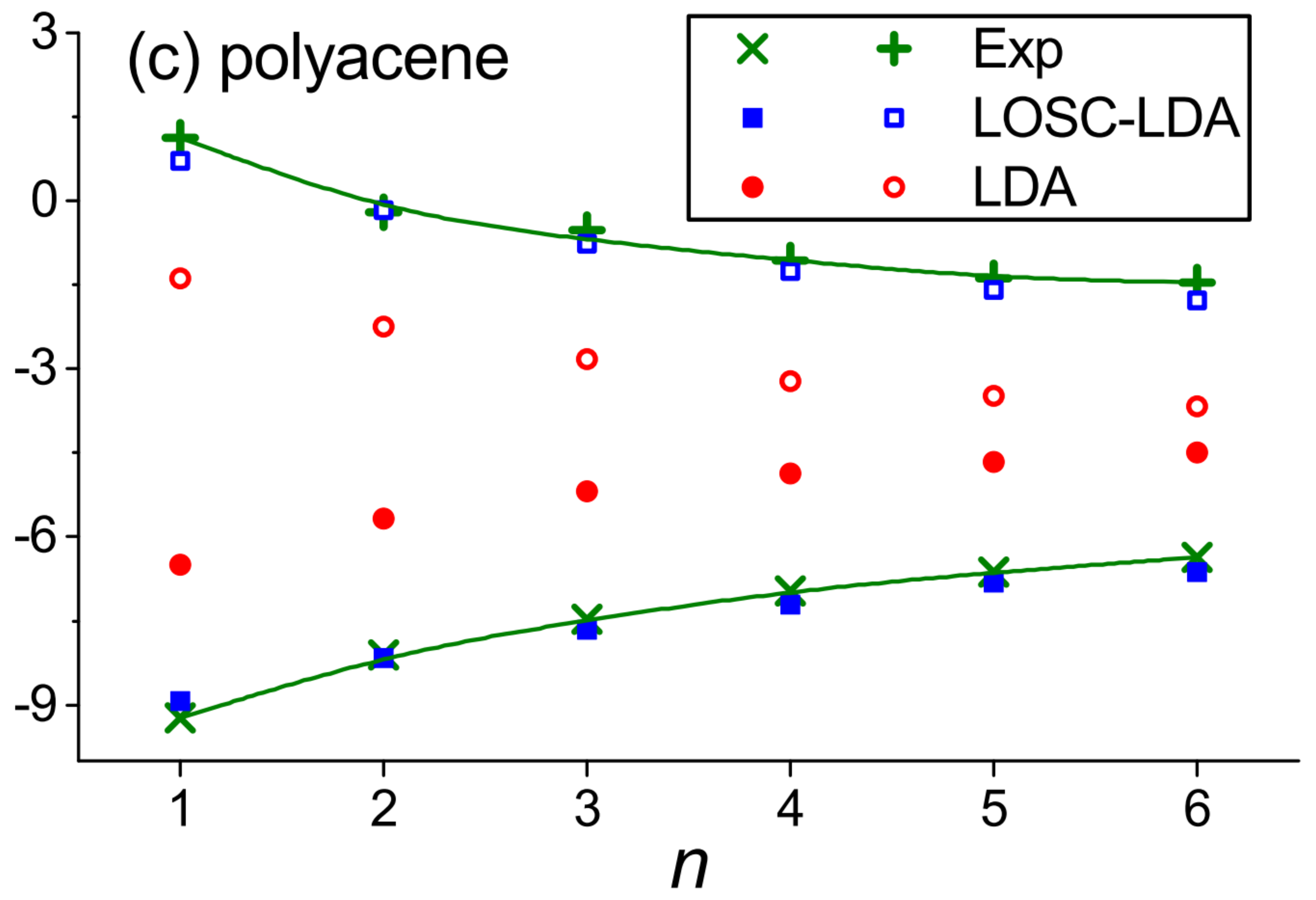
$$\Delta\epsilon_m = \sum_i \kappa_{ii} \left(\frac{1}{2} - \lambda_{ii}\right) |U_{im}|^2 - \sum_{i \neq j} \kappa_{ij} \lambda_{ij} U_{im} U_{jm}^*$$


(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

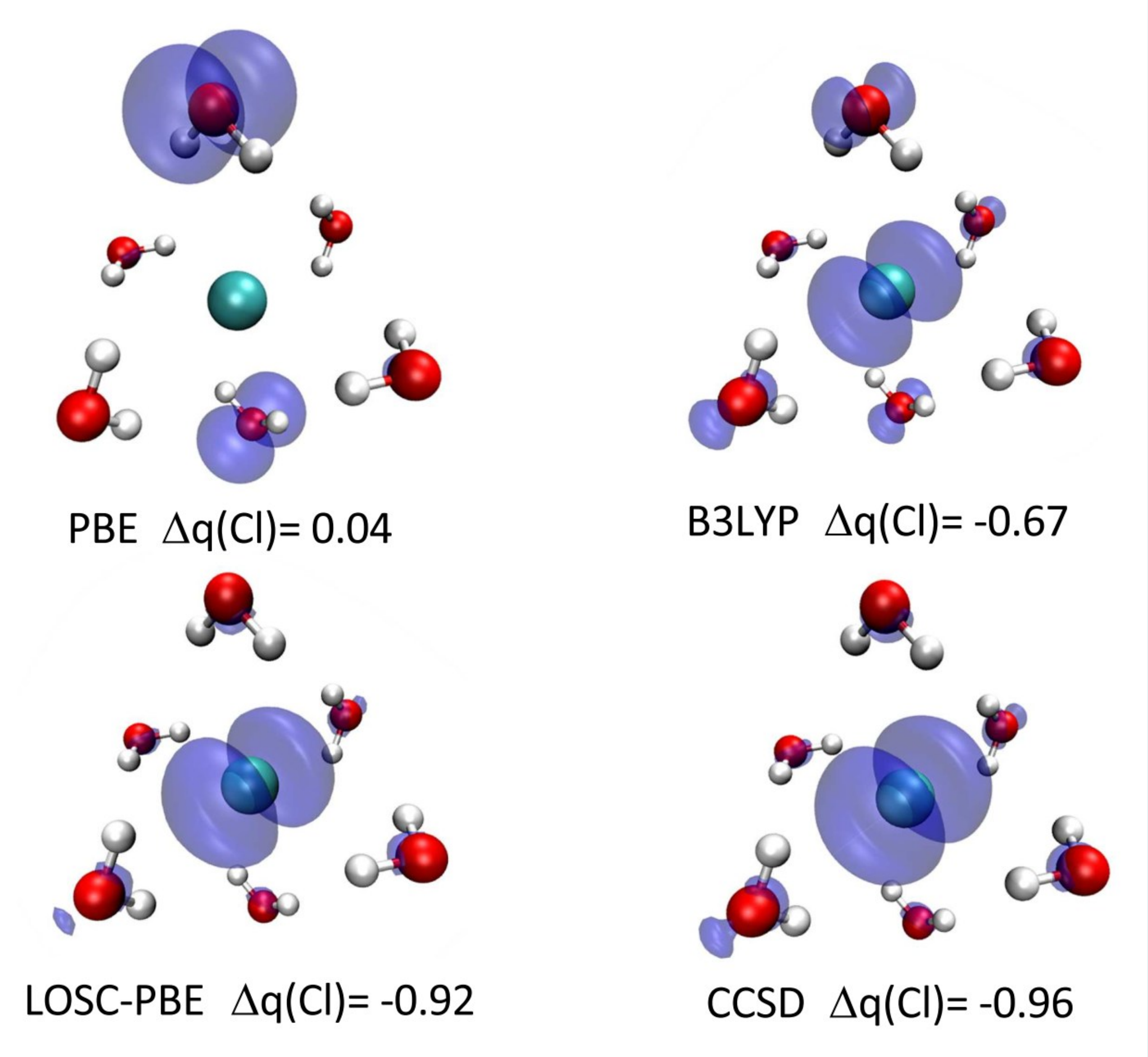


LOSC: HOMO, LUMO and Energy Gaps



LOSC: corrections to electron density

$Cl^-(H_2O)_6$



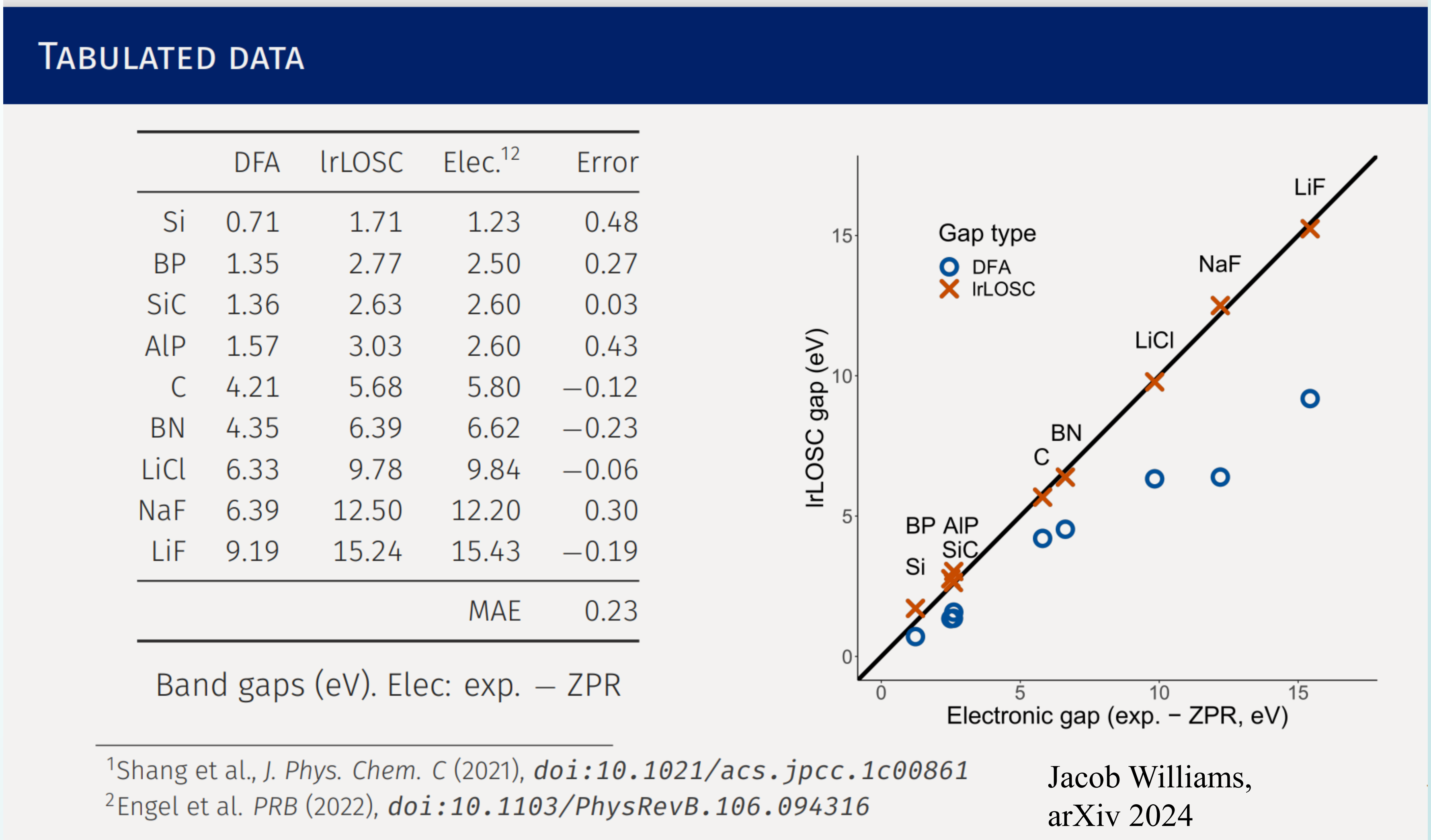
PBE $\Delta q(Cl)= 0.04$

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

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

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

Band Gaps of Bulk Systems



TABULATED DATA

	DFA	lrLOSC	Elec.[1,2]	Error
Si	0.71	1.71	1.23	0.48
BP	1.35	2.77	2.50	0.27
SiC	1.36	2.63	2.60	0.03
AlP	1.57	3.03	2.60	0.43
C	4.21	5.68	5.80	−0.12
BN	4.35	6.39	6.62	−0.23
LiCl	6.33	9.78	9.84	−0.06
NaF	6.39	12.50	12.20	0.30
LiF	9.19	15.24	15.43	−0.19
			MAE	0.23

Band gaps (eV). Elec: exp. − ZPR

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[1] Shang et al., *J. Phys. Chem. C* (2021), `doi:10.1021/acs.jpcc.1c00861`

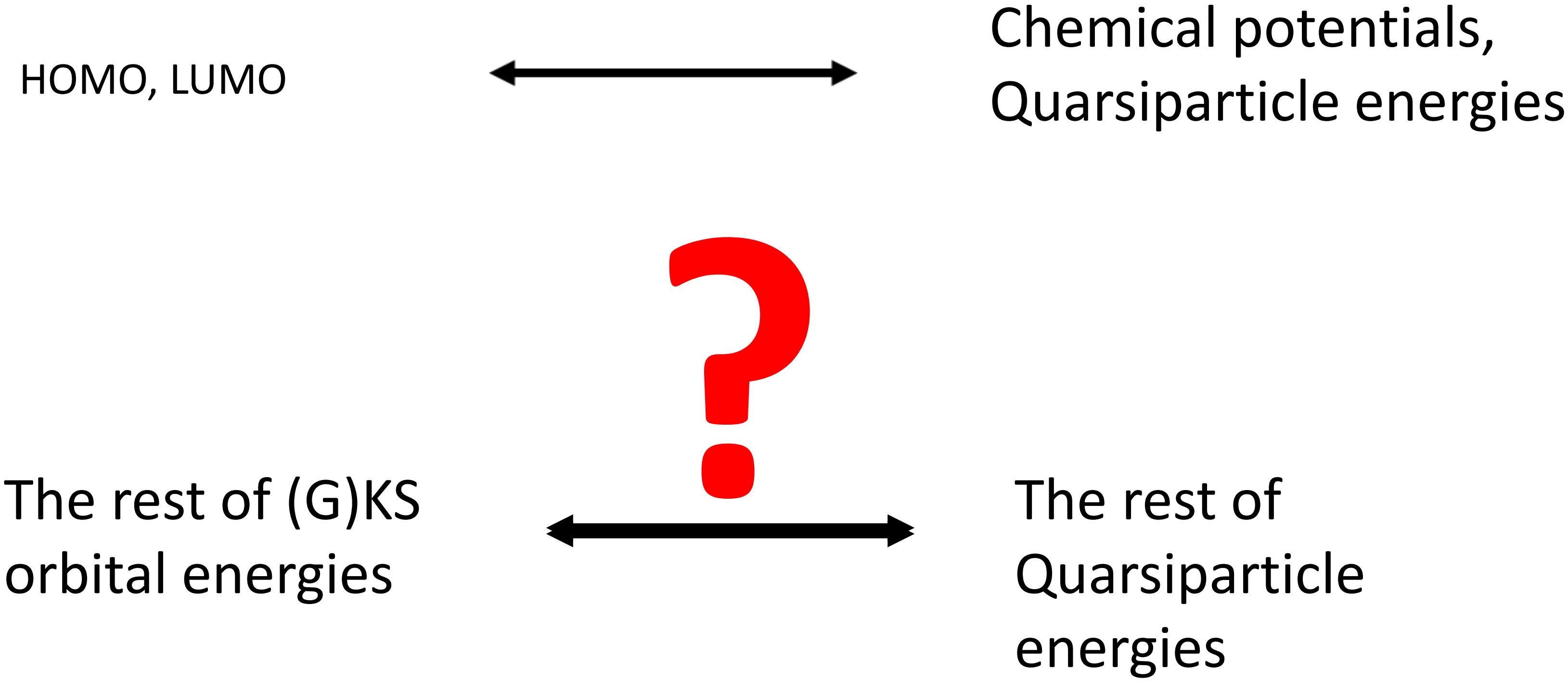
[2] Engel et al. *PRB* (2022), `doi:10.1103/PhysRevB.106.094316`

Jacob Williams,
arXiv 2024

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

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

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



HOMO, LUMO

Chemical potentials,
Quarsiparticle energies

?

The rest of (G)KS
orbital energies

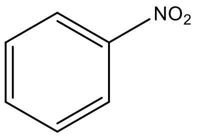
The rest of
Quarsiparticle
energies

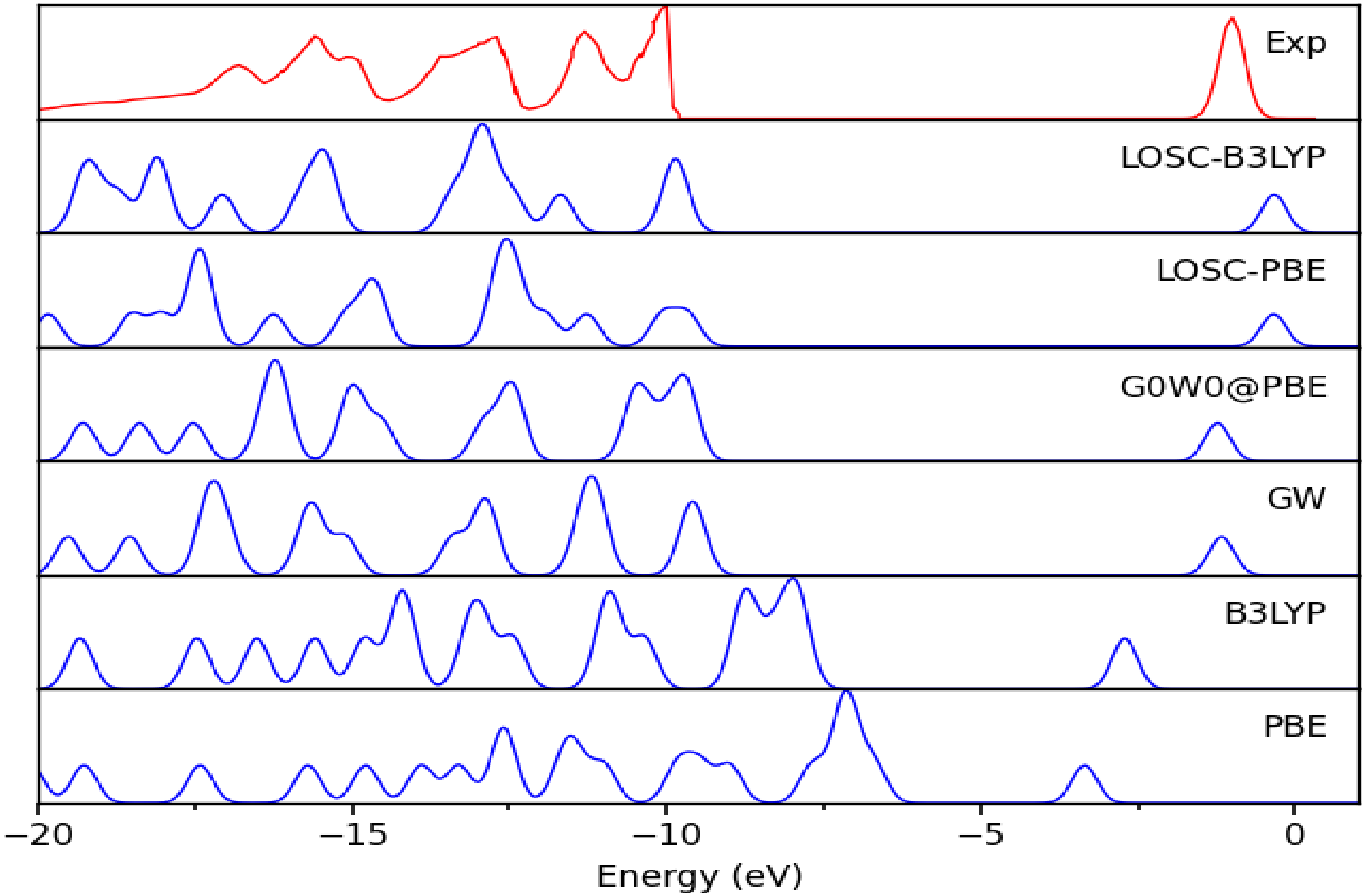
Higher ionization energies of polyacene (n = 2,4,6) from GKS eigenvalues and ΔSCF calculation.

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

arXiv 2018

Photoemission spectrum of nitrobenzene

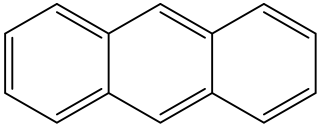


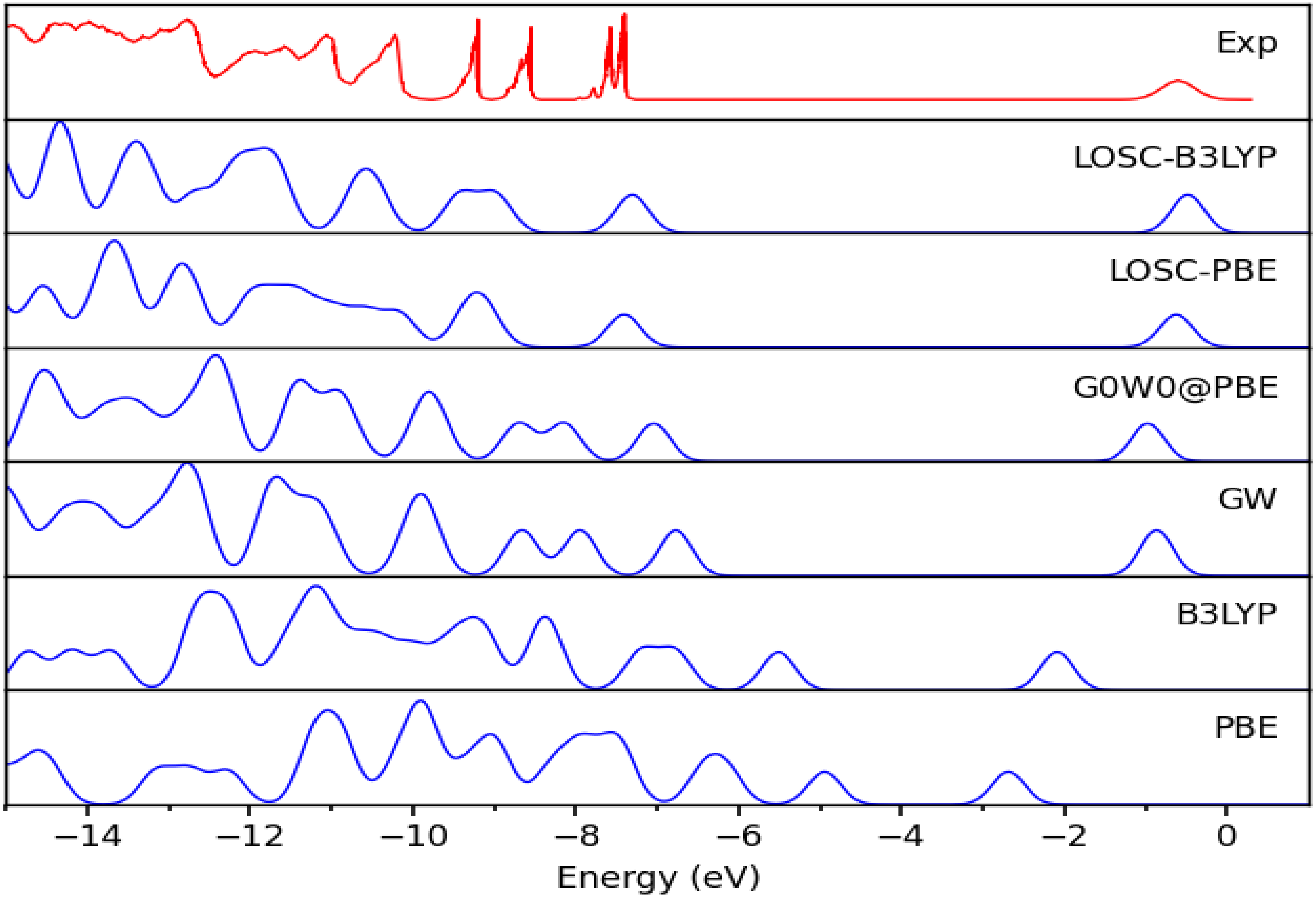


arXiv 2018, **JPC A 2019, 123, 3, 666**

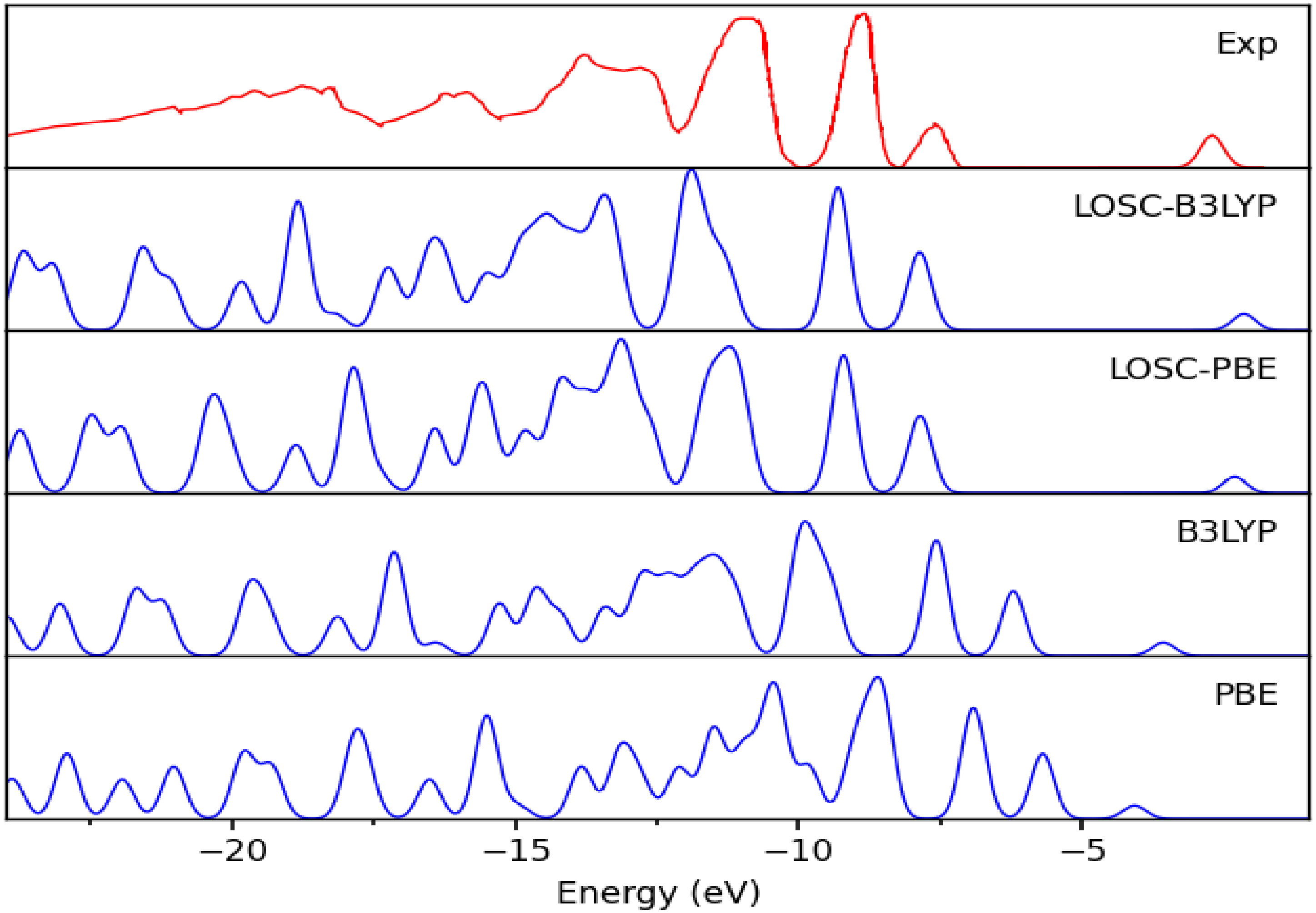
Yuncia Mei, Chen Li, Neil Su and WY

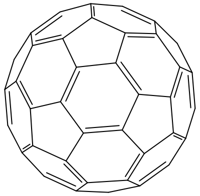
Photoemission spectrum of anthracene



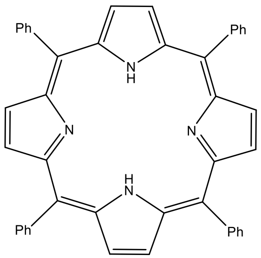


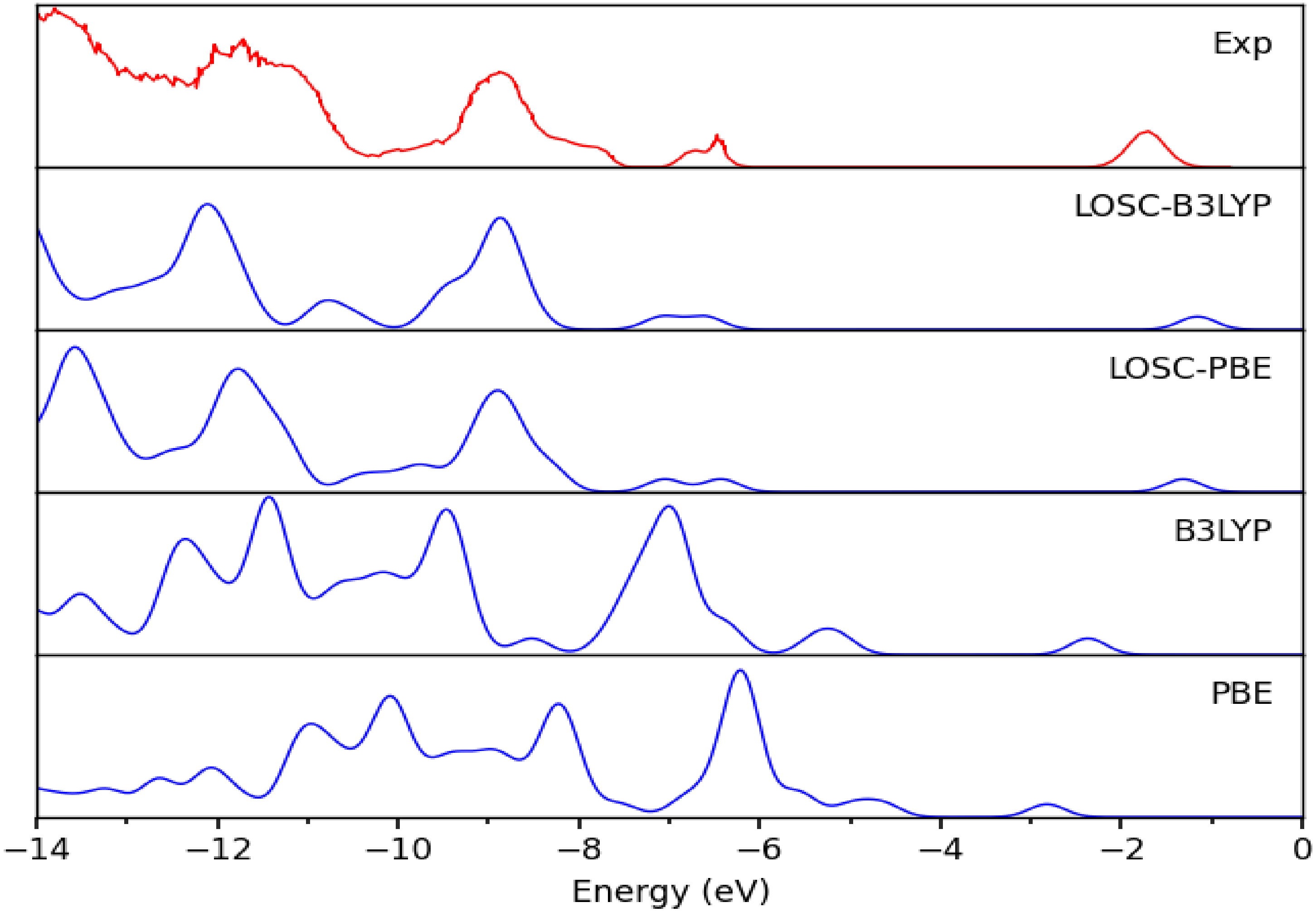
Photoemission spectrum of C60





Photoemission spectrum of H_2TPP





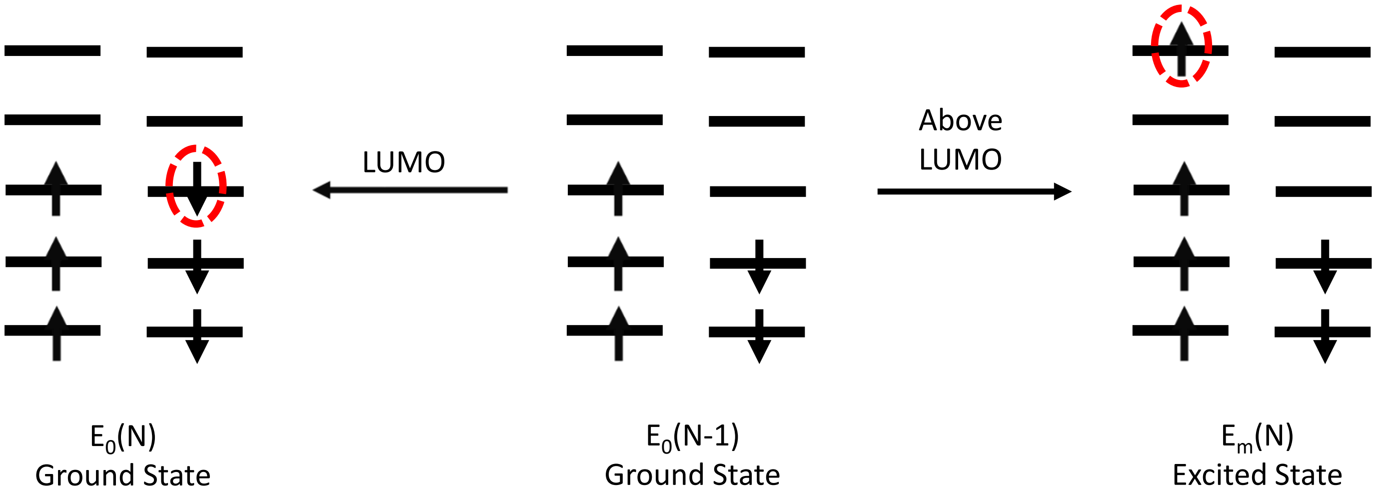
Orbital energy vs. quasiparticle energy

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

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

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

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



LUMO

Above LUMO

$E_0(N)$
Ground State

$E_0(N\text{-}1)$
Ground State

$E_m(N)$
Excited State

$$
\begin{aligned}
\Delta E_m(N) &= E_m(N) - E_0(N) \\
&= [E_m(N) - E_0(N-1)] - [E_0(N) - E_0(N-1)] \\
&= \omega_m^+(N-1) - \omega_{min}^+(N-1) \\
&\boxed{\approx \varepsilon_m(N-1) - \varepsilon_{LUMO}(N-1)}
\end{aligned}
$$

Two groups independently:

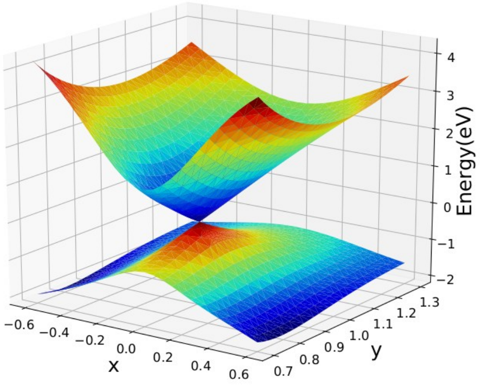
Bartlett group: JCP, 2018, 149, 131101

Yang group: arXiv:1810.09906, 2018; JPC A 2019, 123, 3, 666-673

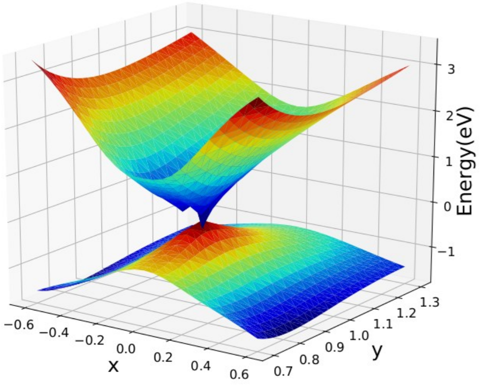
Low-lying excitation energies (eV) from different methods

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

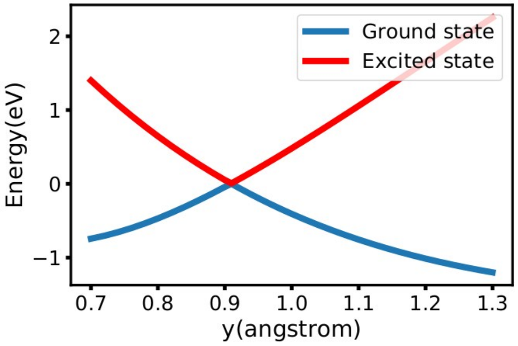
Conical Intersection



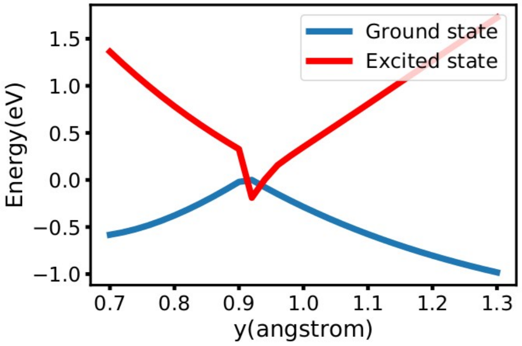
(a) QE-B3LYP



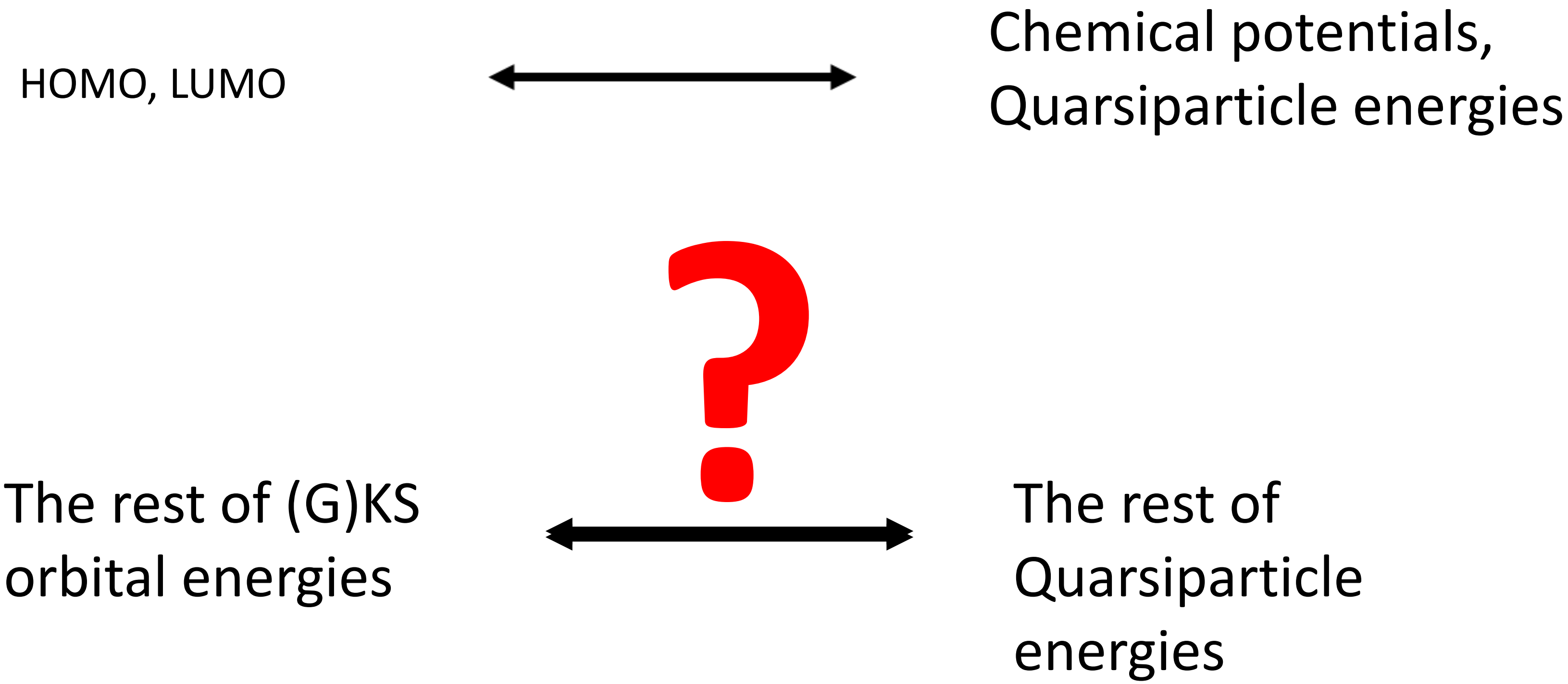
(b) TD-B3LYP



(c) QE-B3LYP (1D)



(d) TD-B3LYP (1D)



HOMO, LUMO

Chemical potentials,
Quarsiparticle energies

?

The rest of (G)KS
orbital energies

The rest of
Quarsiparticle
energies

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

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

arXiv 2018

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**.

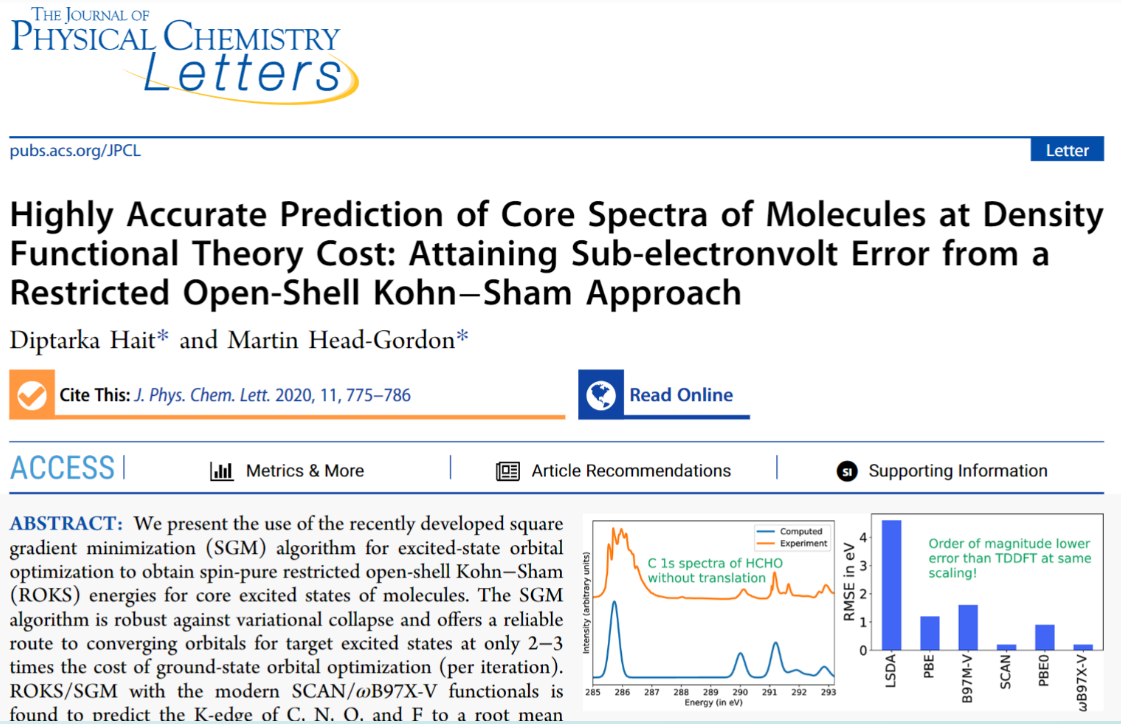
- Similar set of SCF Kohn-Sham equations with non-Aufbau occupations, the excited state of the noninteracting reference system

- 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

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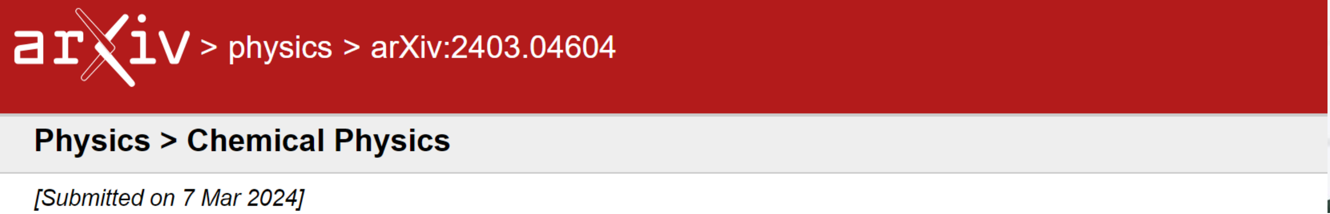
ABSTRACT: We present the use of the recently developed square gradient minimization (SGM) algorithm for excited-state orbital optimization to obtain spin-pure restricted open-shell Kohn–Sham (ROKS) energies for core excited states of molecules. The SGM algorithm is robust against variational collapse 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



Physics > Chemical Physics

[Submitted on 7 Mar 2024]

Foundation for the ΔSCF Approach in Density Functional Theory

Weitao Yang, Paul W. Ayers

Paul Ayers

Electron density is not sufficient. Not really a density functional.

1. (parallel to HK) **Theorem**: Define a functional of excitation number n, and trial **potential** $w(\boldsymbol{x})$:

   $E_v[n, w(\boldsymbol{x})]$ and variational principle for the nth excited state of $v(\boldsymbol{x})$

   excited state Potential Functional Theory (nPFT)

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

$$E_v[n_s, w_s(\boldsymbol{x})] = E_v[n, w(\boldsymbol{x})]$$

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.

b. The minimum is the ground state, the stationary solution is an excited state.

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

arXiv > physics > arXiv:2403.04604

Physics > Chemical Physics

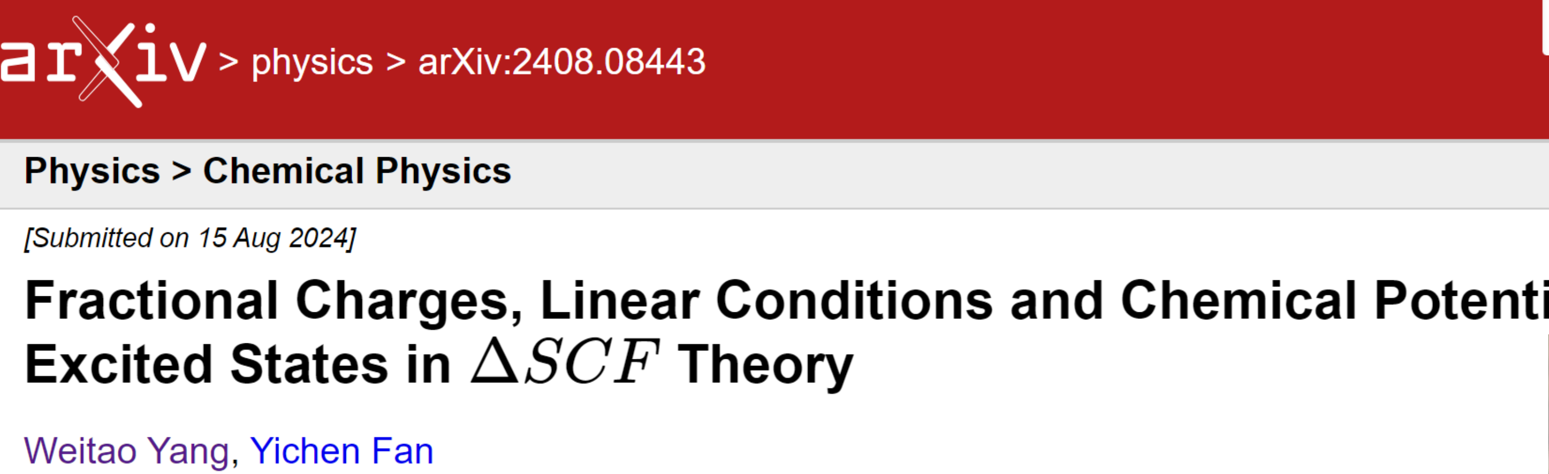
[Submitted on 7 Mar 2024]

Foundation for the ΔSCF Approach in Density Functional Theory

Weitao Yang, Paul W. Ayers

$$E_v\left[\gamma_s(\mathbf{x},\mathbf{x}')\right]$$

1. Both ground and excited state share the same functional
2. But for ground state, because the ground-state density uniquely determines the potential, and the density matrix or the wavefunction of the noninteracting system, $E_v\left[\gamma_s(\mathbf{x},\mathbf{x}')\right]$ is still a density functional (DFT!)
3. The rigor is same for ground and excited states.
4. **Total energies from ΔSCF DFA calculations for excited states is established.**
5. How about orbital energies?



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 $0 \le \delta \le 1$

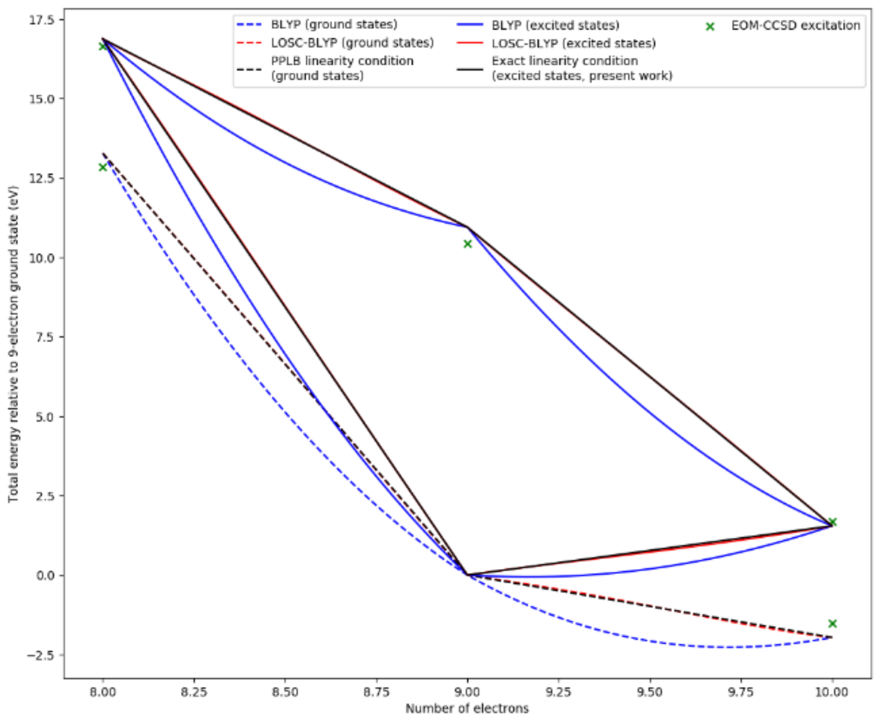
$$\gamma_s = (1-\delta)\gamma_s^{n_s}(N) + \delta\gamma_s^{m_s}(N+1)$$

2. Proved the linear condition

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

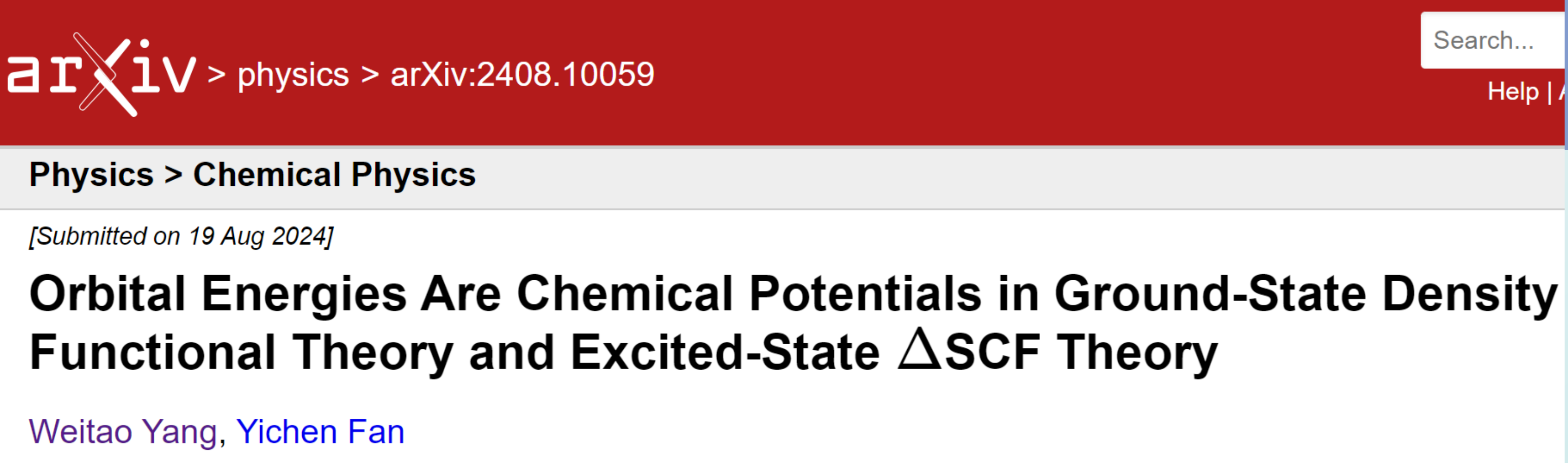
3. Generalize the PPLB condition for ground states in term of electron densities to **excited states in terms of density matrices**

Excited-State Chemical Potentials: slopes of the lines



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

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



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

Proved **the general chemical potential theorem**

1. True for any approximate functional calculations

$$\begin{aligned}\mu^-_{n_s l_s}(N) &= \left(\frac{\partial E^-_v(n_s, l_s, \mathcal{N})}{\partial \mathcal{N}}\right)_v\bigg|_{f_i=1}\\ &= \frac{\partial E_v[\gamma_s]}{\partial f_i}\bigg|_{f_i=1} = \varepsilon_i(N),\end{aligned}$$

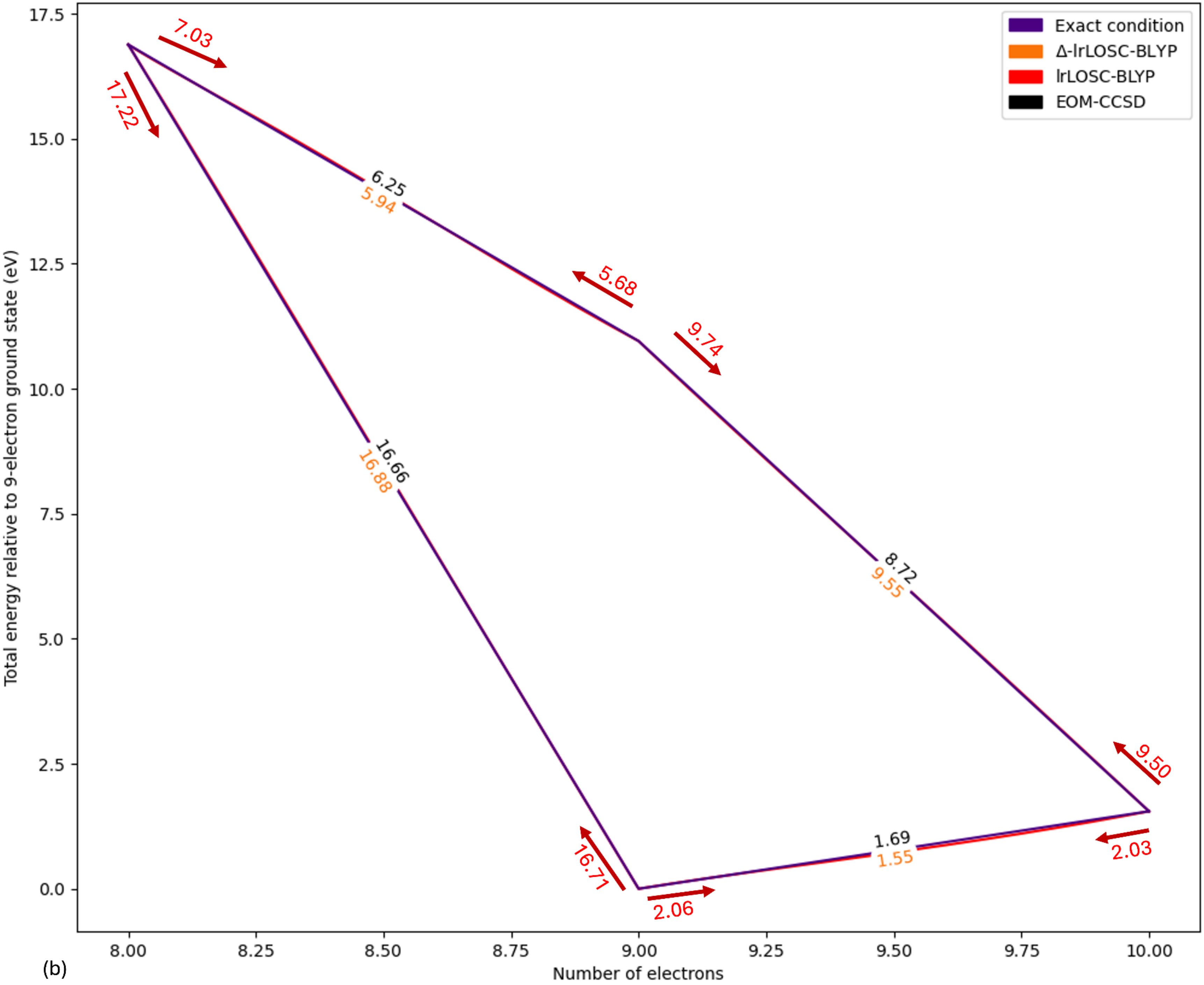
$$\begin{aligned}\mu^+_{n_s m_s}(N) &= \left(\frac{\partial E^+_v(n_s, m_s, \mathcal{N})}{\partial \mathcal{N}}\right)_v\bigg|_{f_a=0}\\ &= \frac{\partial E_v[\gamma_s]}{\partial f_a}\bigg|_{f_a=0} = \varepsilon_a(N).\end{aligned}$$

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. The equality holds for bulk systems.**


Exact condition
Δ-lrLOSC-BLYP
lrLOSC-BLYP
EOM-CCSD
7.03
17.22
6.25
5.94
5.68
9.74
16.66
16.88
8.72
9.55
9.50
1.69
1.55
2.03
16.71
2.06
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
Total energy relative to 9-electron ground state (eV)
8.00
8.25
8.50
8.75
9.00
9.25
9.50
9.75
10.00
Number of electrons

(b)

Theoretical Progress

Beyond Commonly Used Functionals

- **Exact conditions on fractional charges and spins based on QM degeneracy principle**
- **Corrections to systematic errors in DFT**
- **Computational optical spectroscopy from ground state calculations**
- **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 for excited-state ΔSCF theory**
- **Physical significance of all orbital energies in ground state DFT and excited-state ΔSCF theory**

Yang and Ayers, 2024 arXiv:2403.04604

Yang and Fan, 2024 arXiv:2408.08443

Yang and Fan, 2024 arXiv.2408.10059