

Orbital Density Dependent Functionals

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Outline:

Problems with GGA approximation (PBE, RPBE, ...)

Orbital density dependent (**ODD**) functionals:

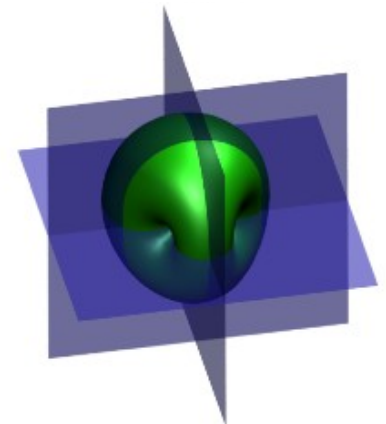
in particular Perdew-Zunger self-interaction correction;

CPU time can scale as for DFT/GGA;

Codes: Quantice (Gaussian orbitals),

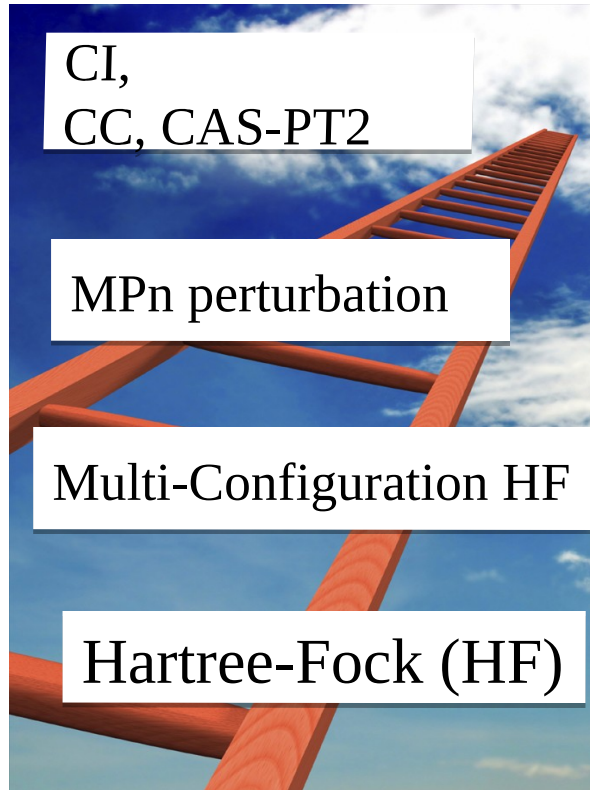
GPAW

Application to atoms, molecules and solids



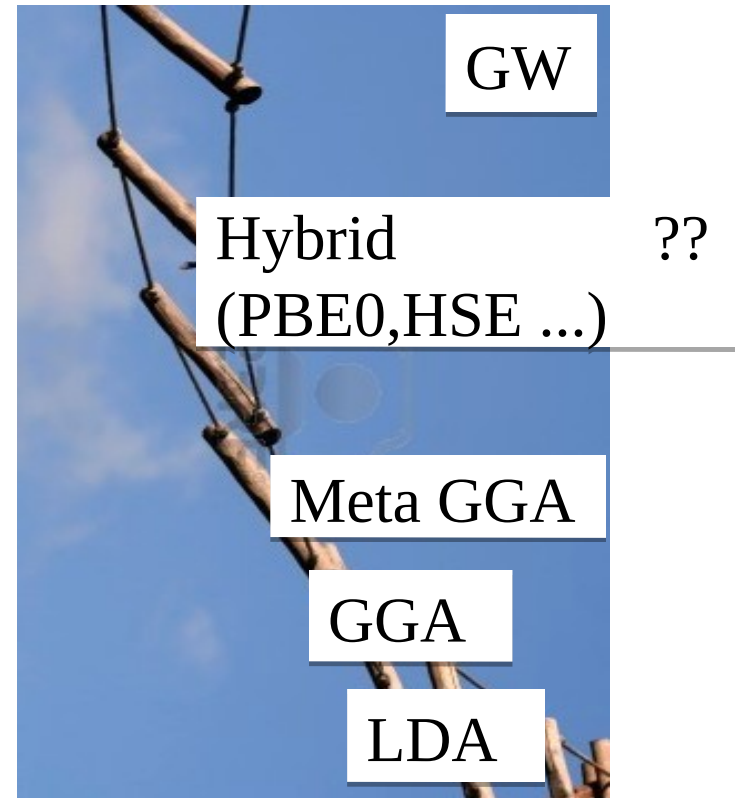
Electronic Structure Calculations

Wave function based Methods



**Exact solution obtained in principle, but effort scales $\sim N^7$.
Good for small systems ($N < 30$)**

DFT and beyond ...



Improved accuracy needed, keeping scaling of effort low ($\sim N^3$ for GGA which can be applied to large systems even $N \sim 1000$)

Hartree-Fock approximation

Each electron is subject to the *average* interaction with the other electrons – a mean field approximation

- \Rightarrow Wavefunction Ψ is a *Slater determinant* of orbitals
- Ground state is the set of orbitals that minimizes the energy of the Schrödinger equation.
- Electron-electron energy contributions:
 - E_H : Coulomb interaction of the electron density (positive)
 - E_X : *Exchange* energy, interaction of electrons of same spin (negative)

$$E_{\text{HF}} = E_{\text{kin}} + E_{\text{ext}} + E_H + E_X$$

- The effective Schrödinger equation is given by

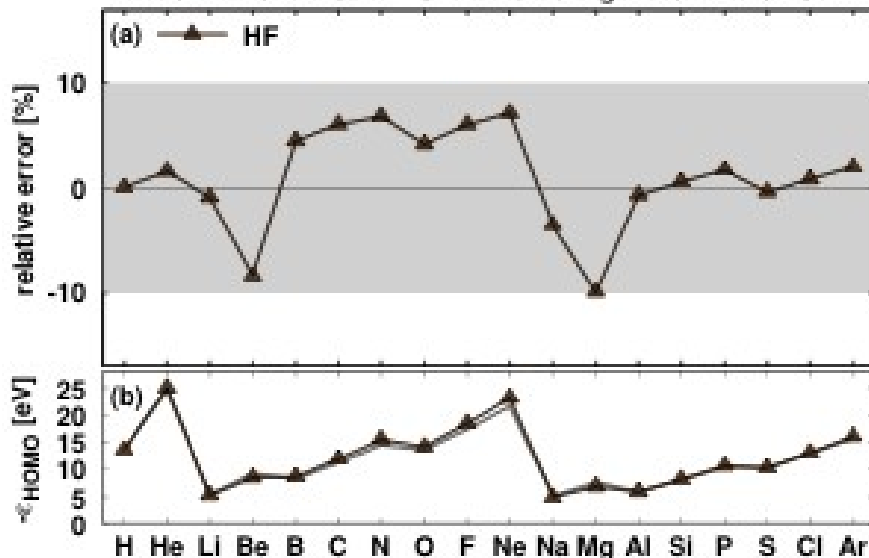
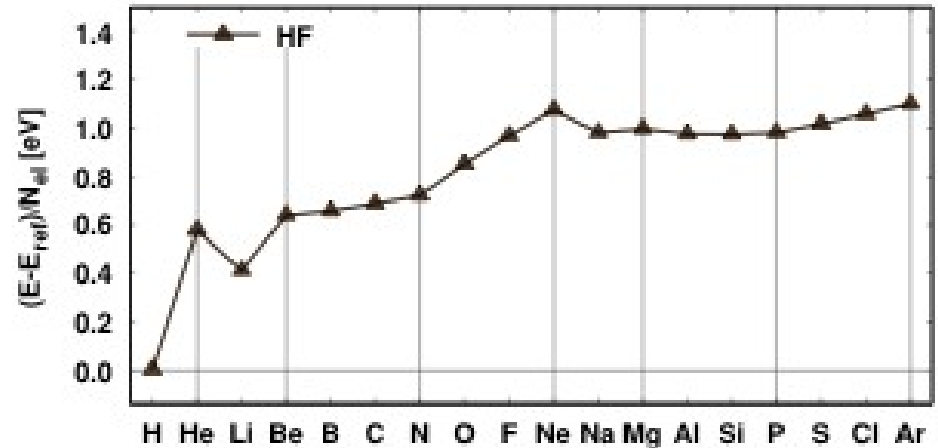
$$\hat{H}_{\text{HF}} \varphi_i = [\hat{T} + \hat{V}_{\text{ext}} + \hat{V}_H + \hat{V}_X] \varphi_i = \epsilon_i \varphi_i$$

↑orbital ↑orbital energy

Hartree-Fock *calculations of atoms*

Compare energy per electron with high level estimate of total energy, E_{ref} , by Chakravorty & Davidson, *JPC* **100**, 6167 (1996).

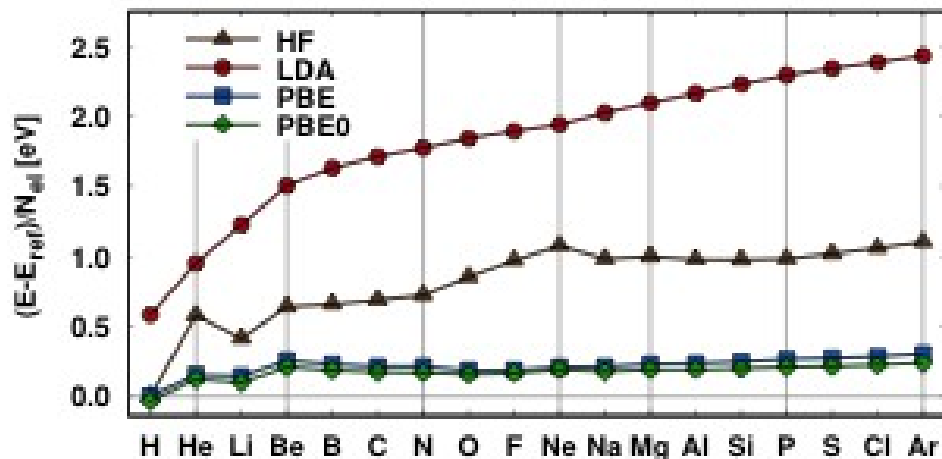
HF gives poor estimate of the total energy



But, HOMO energy agrees quite well with experimental ionization energy (Koopman).

Orbital energies correspond remarkably well with photo electron spectra ('orbitals are real' ???).

KS-DFT (cont.)

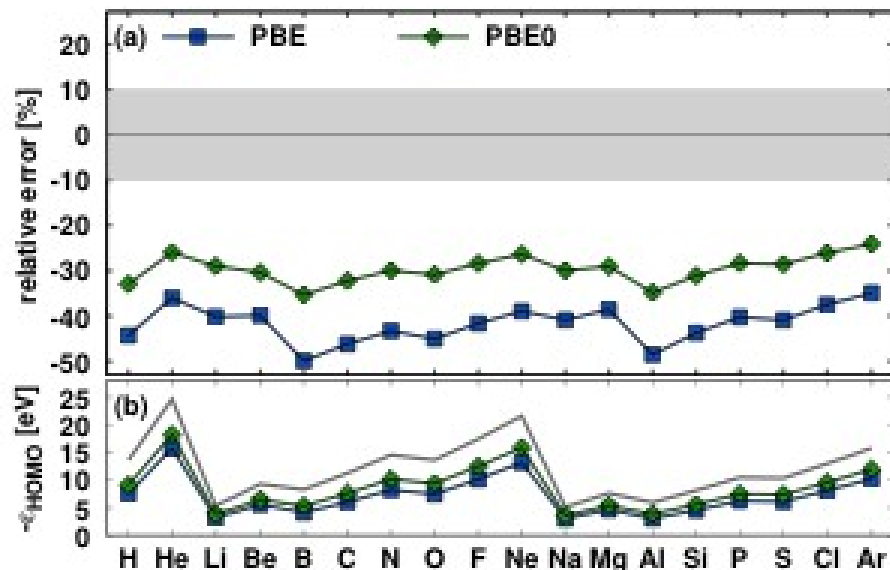


LDA worse than HF, but GGA (the PBE functional) which includes gradients is more accurate than HF.

Hybrid functional (PBE0) is only marginally better.

But, KS-DFT orbital energies are **not** good estimates of ionization energy

PBE0 hybrid functional again only marginally better than PBE



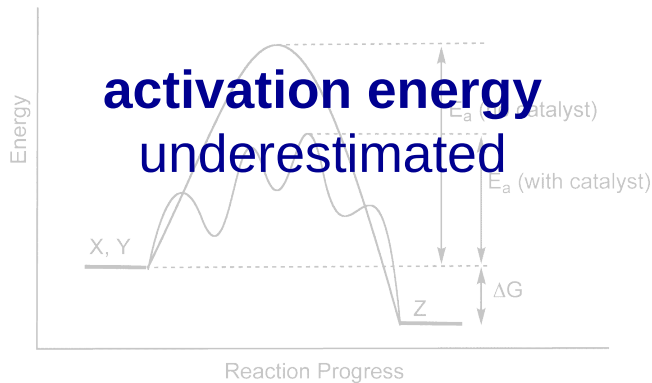
DFT/GGA and LDA calculations have several shortcomings

electron distribution:

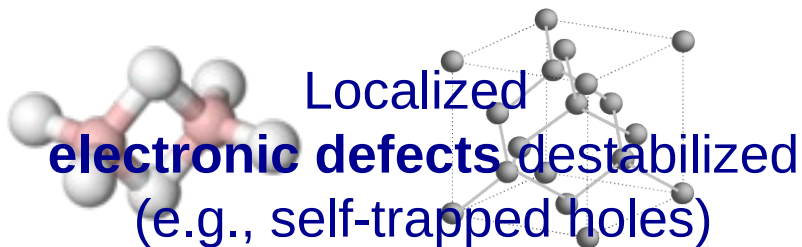
fractional charges in dissociated molecules



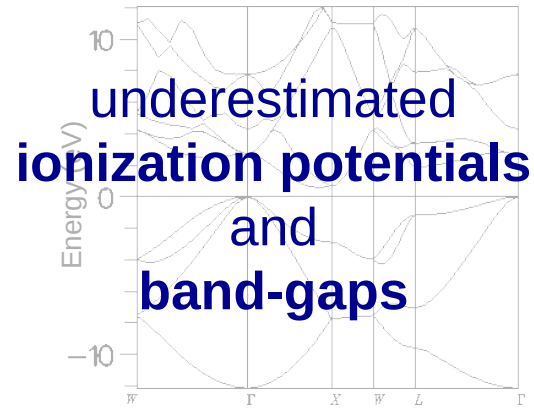
transition energy / reaction paths:



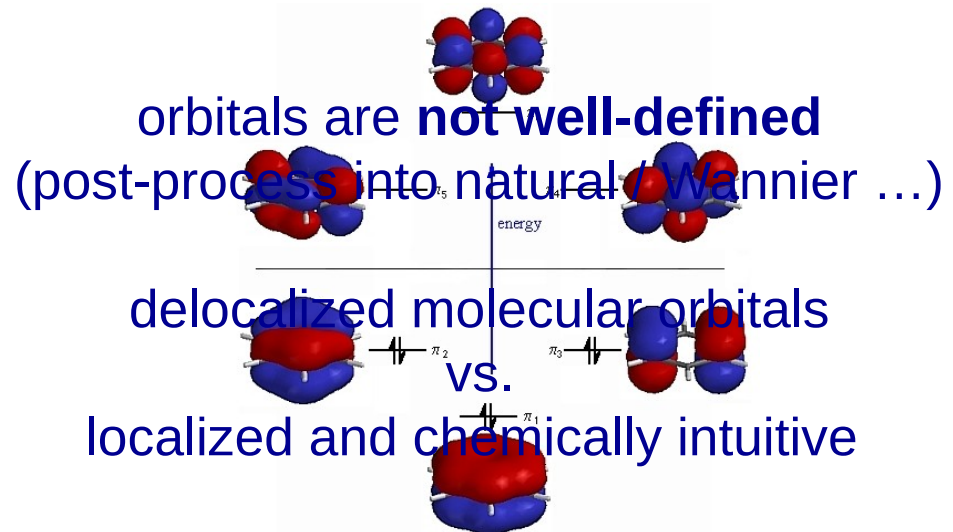
molecular geometry / crystal structure



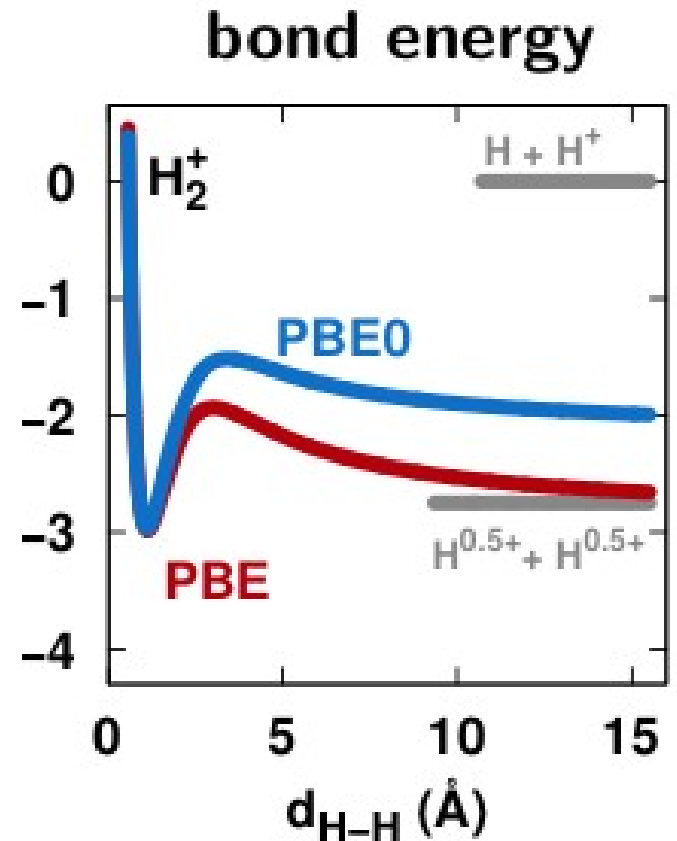
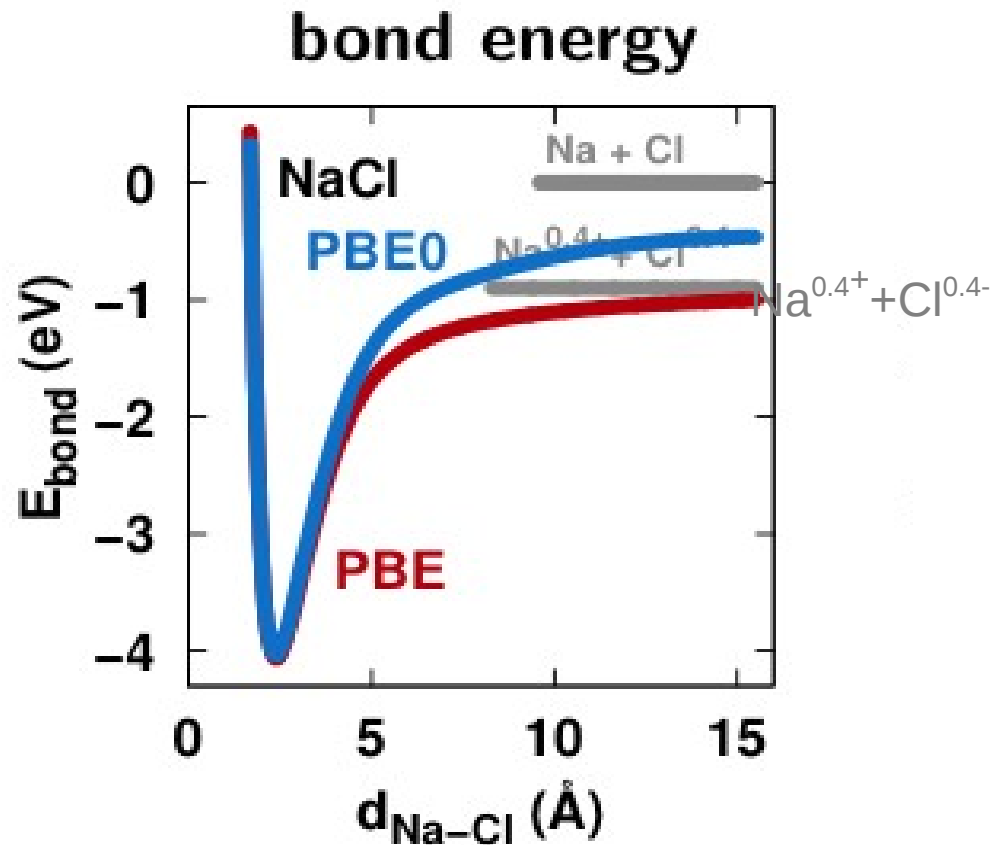
orbital energy / band structure:



orbital shape / chemical bonds



Functional Approximations – Qualitative Errors

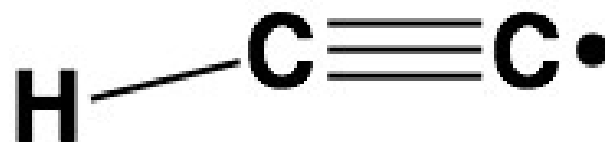


e.g.: Cohen, Mori-Sánchez, Yang, Chem. Ruzsinszky, Perdew, Csonka, Vydrov, Sci

alkynyl radical structure



experiment, PBE0



PBE

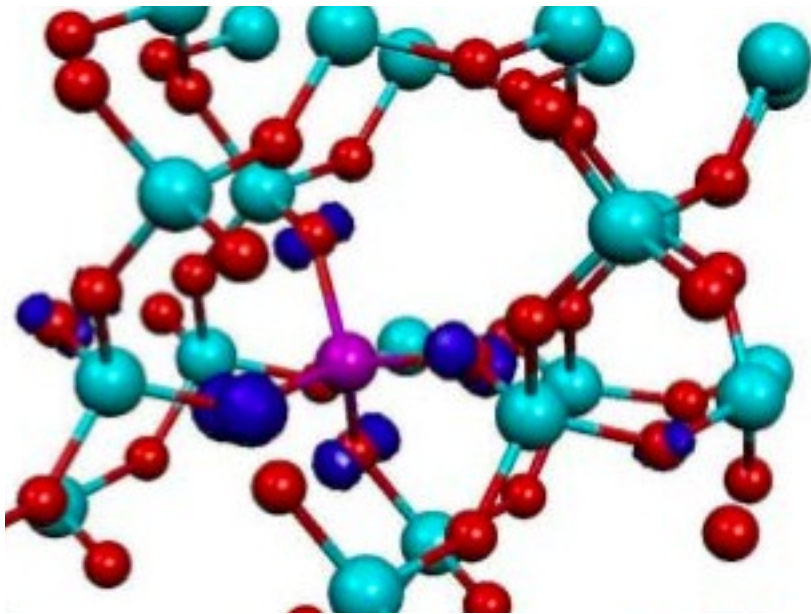
Examples of problems with GGA:

(Al,Si)O₂ system: Al substitutional defect in silica

Experiment: Structural symmetry breaking; spin density strongly localized on a single O atom; corresponding bond is longer than the bonds with three other O atoms.

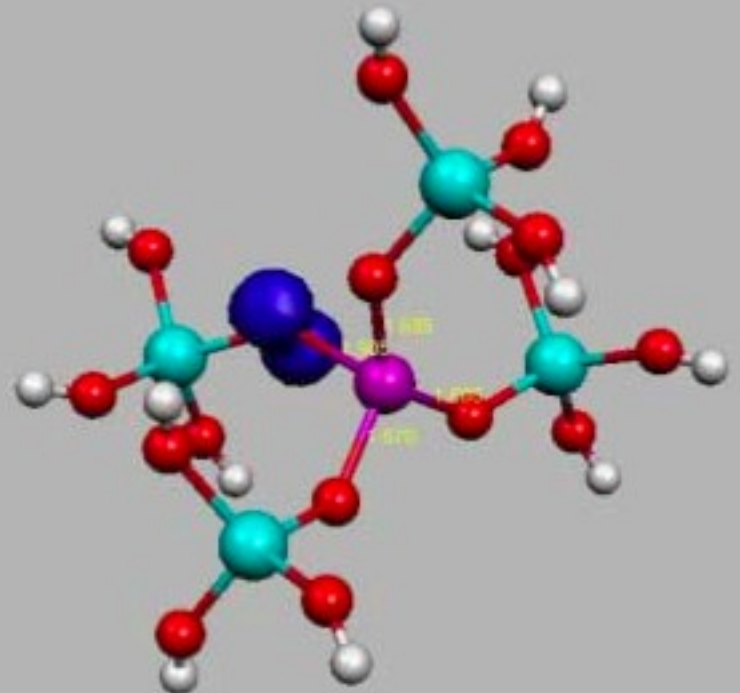
PBE calculation

Too delocalized spin density



Cluster calculation in Hartree-Fock

Properly localized spin density



Lægsgaard & Stokbro, PRL (2001)

Kohn-Sham density functional theory (KS-DFT)

Correlation can be included by Density Functional Theory (DFT):

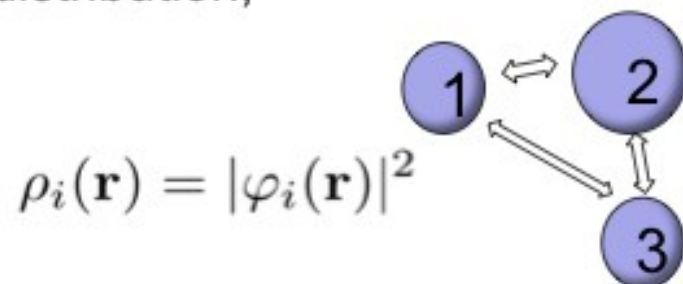
- Exact ground state energy of an electronic system is obtained from the electron density ρ by a *density functional* $E[\{\varphi_i\}]$
- Evaluation of this functional is as complicated as solving the Schrodinger equation, but approximations can be used
- Kohn-Sham DFT uses orbitals to estimate the kinetic energy; exchange and correlation are obtained from ρ approximately by an exchange-correlation functional $E_{xc}[\rho(\mathbf{r})]$

$$E[\rho(\mathbf{r})] = \sum_{i=1}^N \int d^3\mathbf{r} \frac{|\nabla\varphi_i(\mathbf{r})|^2}{2} + \int d^3\mathbf{r} \rho(\mathbf{r})v_{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r}d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

Can a functional lead to more meaningful orbitals and give better description of defect states?

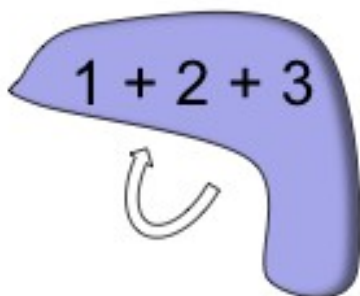
If orbitals are meaningful representations of electrons, then orbital densities should give an estimate of electron probability distribution,

$$E_H = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



excluding self-interaction.

$$E_H = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \sum_i \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



↑
estimate used
in HF and KS-DFT

↑
self-interaction correction

HF: Coulomb self-interaction compensated by equivalent term in exchange

DFT: Incomplete cancellation due to (semi)-local approximation of exchange

Self-Interaction Error

for a single electron

Energy of a single electron has no electron-electron contributions!

$$E[\rho^1] = V[\rho^1] + T_s[\rho^1] + \underbrace{E_H[\rho^1] + E_x[\rho^1] + E_c[\rho^1]}_{=0} = V[\rho^1] + T_s[\rho^1]$$

Exact exchange-correlation functional:

$$\begin{aligned} E_x^{\text{exact}}[\rho^1] &= -E_H[\rho^1] \\ E_c^{\text{exact}}[\rho^1] &= 0 \end{aligned}$$

Approximate functionals \Rightarrow Self-Interaction energy:

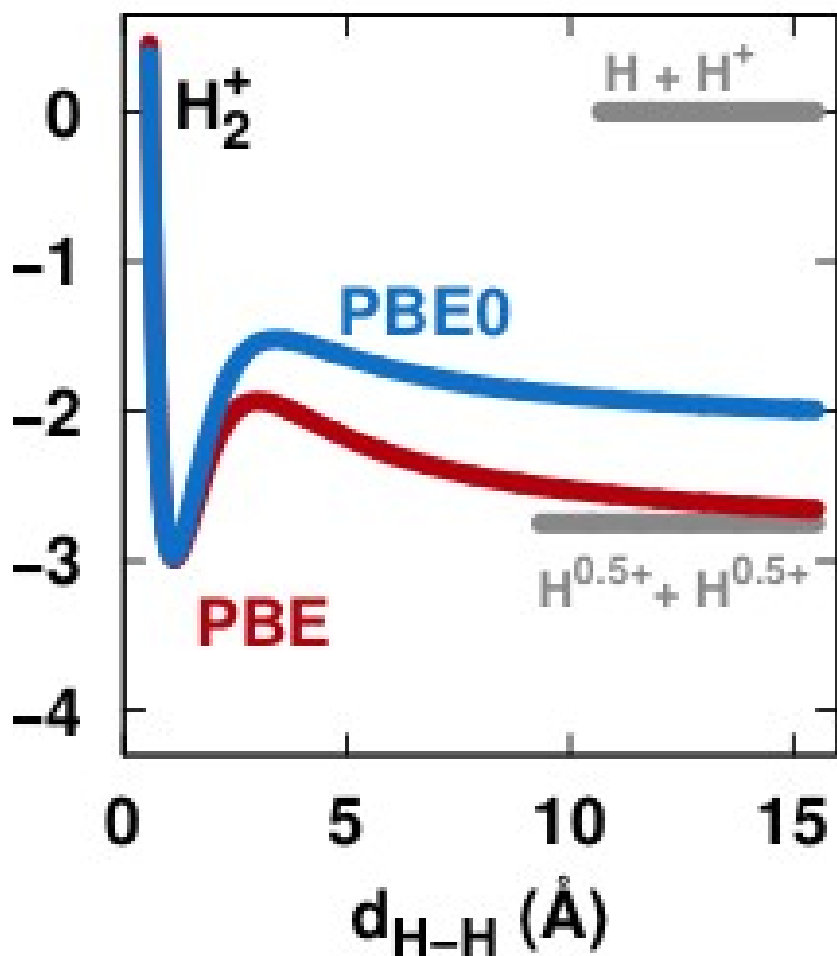
$$E^{\text{SI}}[\rho^1] = E_{\text{xc}}^{\text{appr.}}[\rho^1] + E_H[\rho^1] \neq 0$$

Correction:

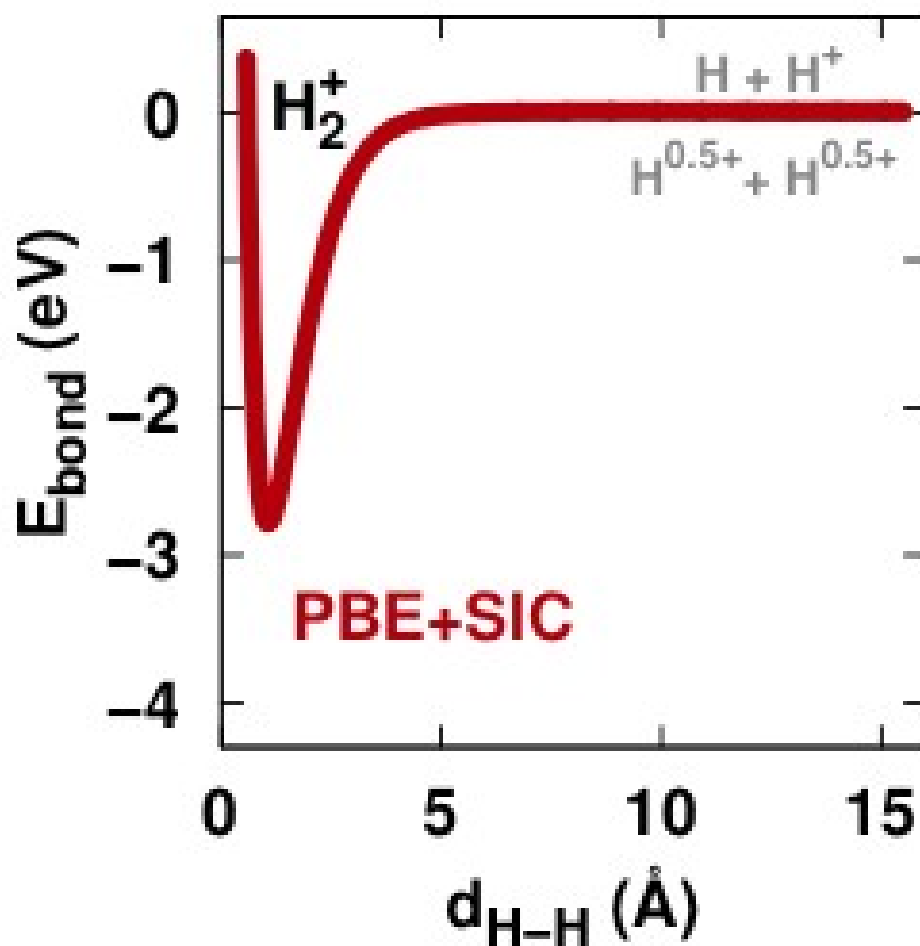
$$E^{\text{exact}}[\rho^1] = E^{\text{appr.}}[\rho^1] - E^{\text{SI}}[\rho^1]$$

Back to H_2^+

bond energy



bond energy



Perdew-Zunger Self-Interaction Correction (SIC)

Correct both Coulomb and E_{xc} orbital by orbital (1981)

$$E_{xc}[\{\varphi_i\}] = E_{xc}^{\text{DFT}}[\rho] - \underbrace{\sum_{i=1}^N \left[\frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}^{\text{DFT}}[\rho_i] \right]}_{\text{Orbital based estimate of self-interaction energy}}$$

Orbital based estimate of self-interaction energy

Compare computational cost with that of hybrids



$\sim N$

Hybrid-DFT / Hartree-Fock



$\sim N \times N$

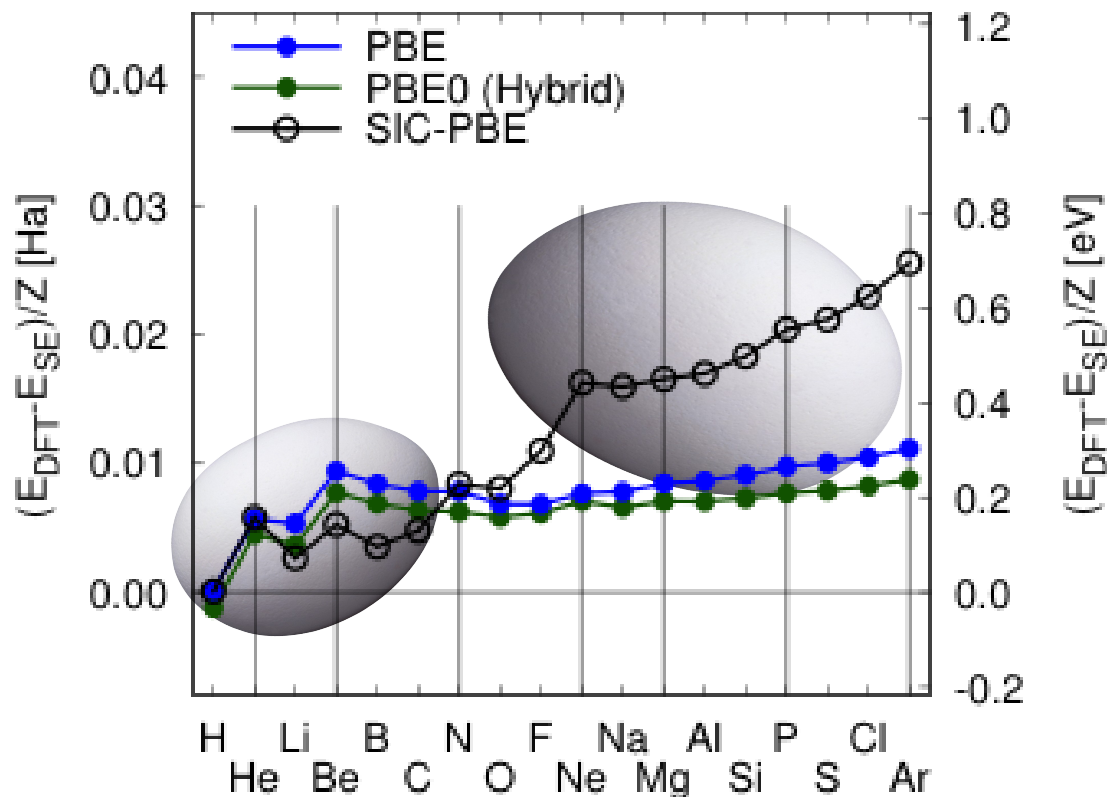
$$E_x^{\text{HF}}[\{\varphi_i\}] = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\varphi_i(\mathbf{r}')\varphi_j^*(\mathbf{r}')\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

In principle, PZ-SIC scales as N^3 , same as GGA and LDA,

But, how good is PZ-SIC?

Calculate the Energy of atoms

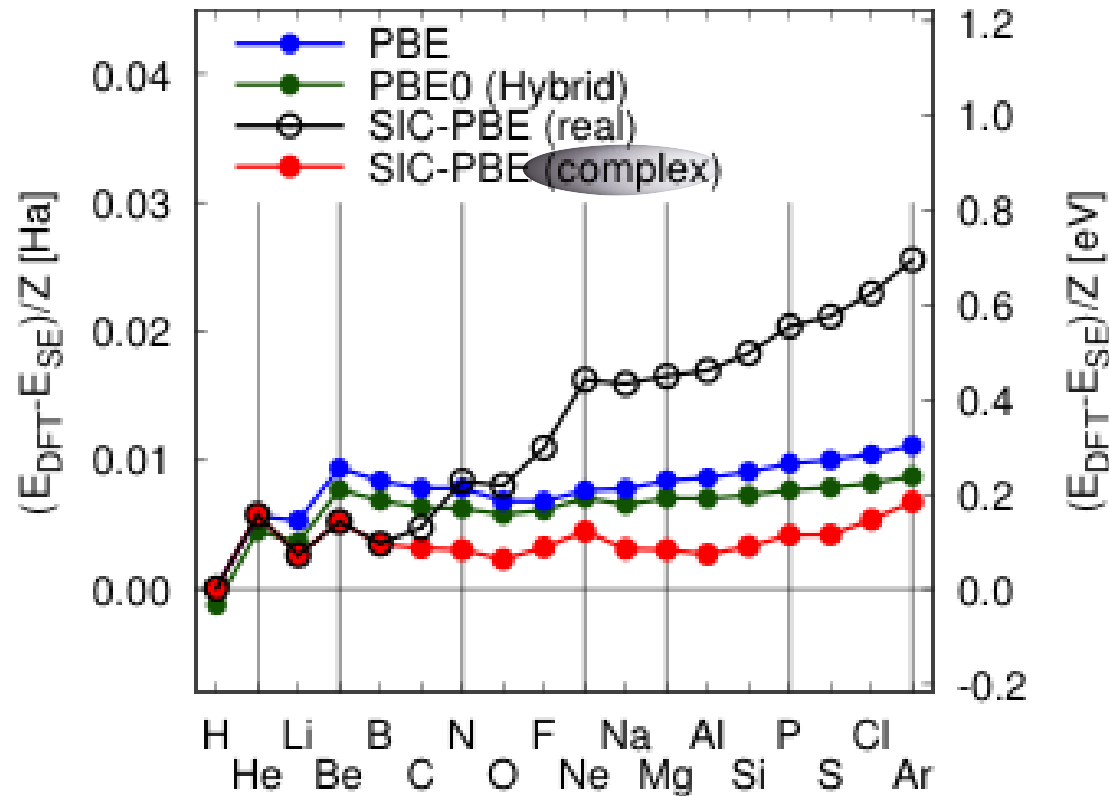
when real expansion coefficients are used in the orbitals:



- * SIC-PBE ... improves total energy for $Z < 7$
... but, for $Z \geq 7$ the total energy estimate becomes worse !!!
- * consistent with results reported by Vydrov and Scuseria, *JCP* **121** (2004).

Test SIC in atoms, (cont.)

Rather, use complex expansion coefficients

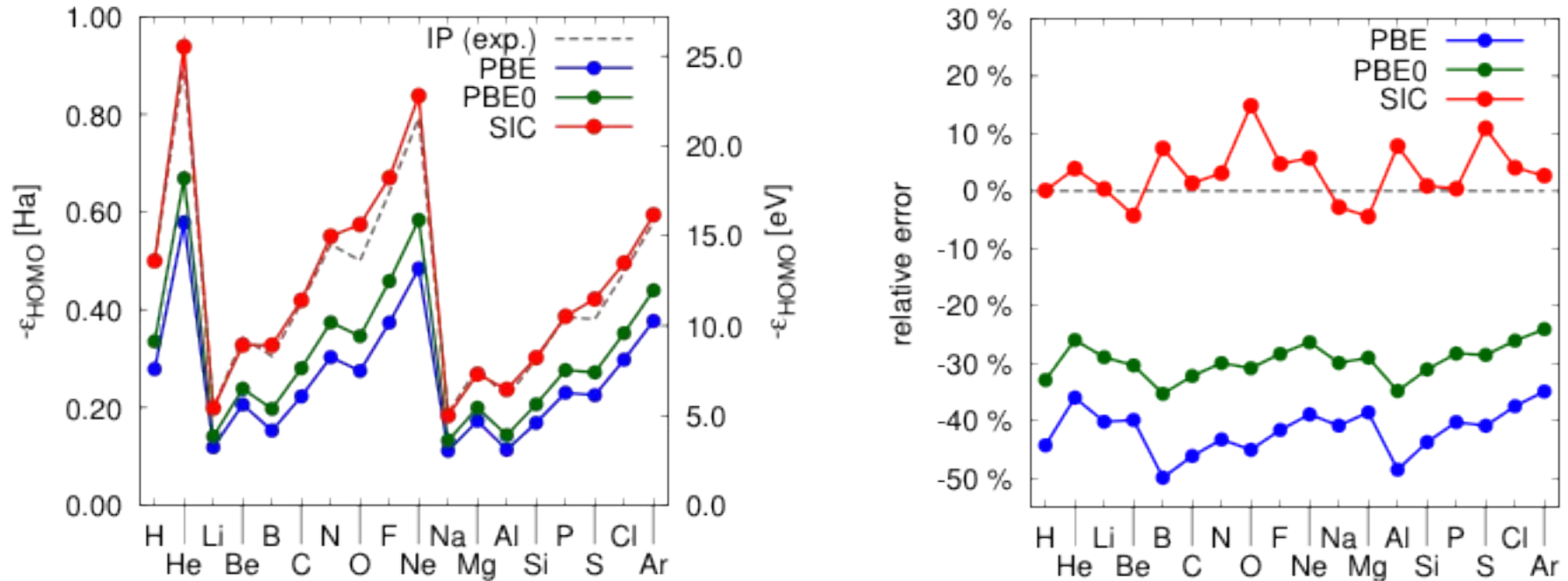


- * SIC-PBE ... improves total energies for all studied atoms
- * ... error reduced to about 0.15 eV / electron
- * Minimization of ODD functionals requires **complex orbitals**

(see S. Klüpfel, P. Klüpfel and HJ, *Phys.Rev.A (RC)* 84, 050501 (2011))

Ionization potentials of atoms

Obtained from the highest occupied orbital (HOMO)



- * PBE has ~40% errors
- * PBE0 (hybrid) gives some, but small improvement, error remains ~30%
- * **SIC-PBE has errors of ~5%, can give good estimates of orbital energies, also for deeper ionization (HOMO-1, HOMO-2, ...)**

Bond energy of diatomics

The SIC strongly affects the binding energy of molecules
Also here, real and complex orbitals can give significantly different values

$E_b[eV]$		H ₂	N ₂	O ₂
exp.		4.73	9.93	5.25
LDA		4.91	11.62	7.61
LDA-SIC	real	4.97	10.55	5.52
	cmpl.	4.97	10.94	5.82
PBE		4.54	10.58	6.26
PBE-SIC	real	4.46	9.50	4.19
	cmpl.	4.46	9.89	4.71

Molecules: Atomization Energy

Studied molecules:

H₂, LiH, Li₂, LiF, HF, N₂, O₂, F₂, P₂, CO, NO, CO₂, CH₄, NH₃, H₂O, C₂H₂, CH₂

Atomization energy:

$$E^{\text{atm}}(\text{A-B}) = [E(\text{A}) + E(\text{B})] - E(\text{A-B})$$

Error:

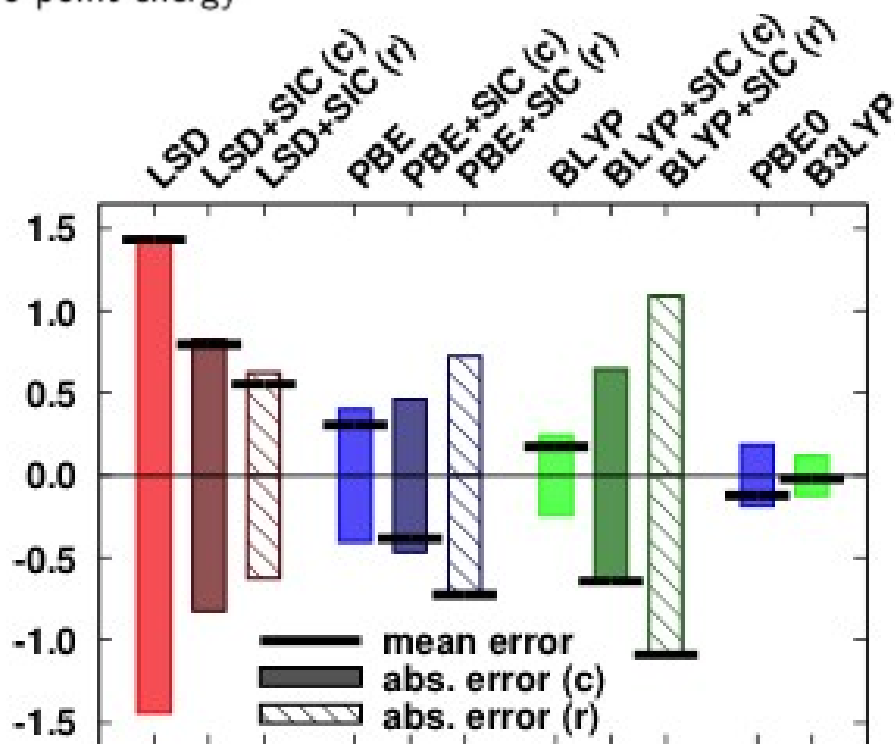
$$\Delta E^{\text{atm}}(\text{A-B}) = E_{\text{calc.}}^{\text{atm}} - E_{\text{ref.}}^{\text{atm}}$$

best estimates $E_{\text{ref.}}^{\text{atm}}$: Experiment corrected for zero-point energy

$$\text{Mean error: } ME = \frac{1}{N} \sum_i \Delta E^{\text{atm}}(i)$$

$$\text{Mean absolute error: } MAE = \frac{1}{N} \sum_i |\Delta E^{\text{atm}}(i)|$$

Cluepfel, Cluepfel and Jónsson,
JCP 137, 124102 (2012)



Scaled Self-Interaction Correction

Scaled Perdew-Zunger SIC:

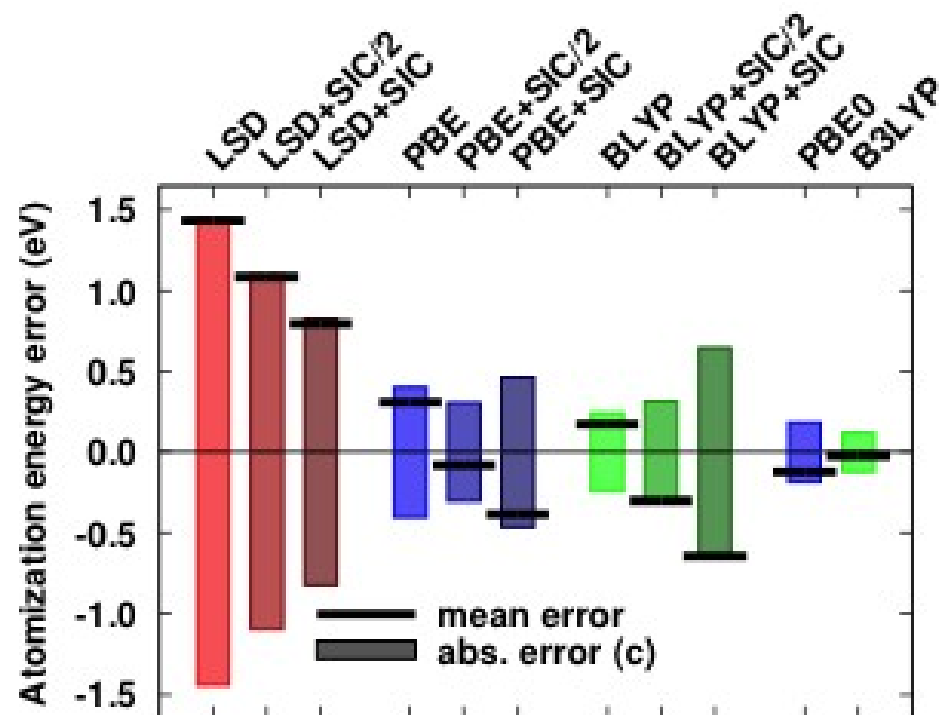
$$E_{\text{appr.}}^{\text{s-SIC}}[\rho] = E^{\text{appr.}}[\rho] - \sum_{i=1}^N \alpha_i E^{\text{SI}}[\rho_i]$$

SIC/2:

$$E_{\text{appr.}}^{\text{SIC}/2}[\rho] = E^{\text{appr.}}[\rho] - \frac{1}{2} \sum_{i=1}^N E^{\text{SI}}[\rho_i]$$

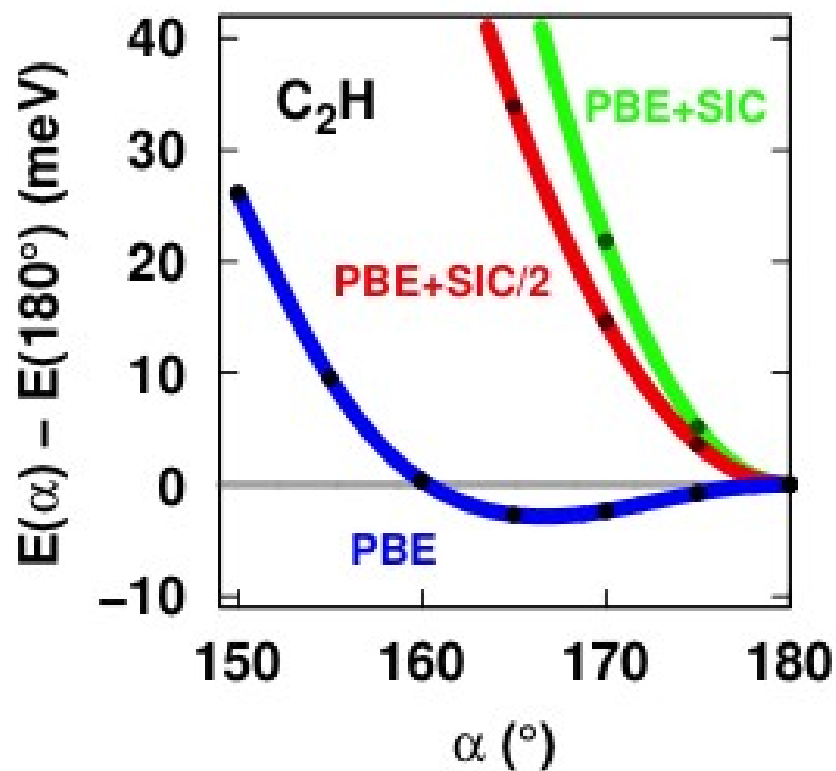
Bylaska, Tsemekhman, Jónsson, APS March Meeting abstract (2004)
Vydrov, Scuseria, Perdew, Ruzsinszky, Csonka, JCP 124, 094108 (2006)

Molecules: Atomization Energy



Cluepfel, Cluepfel and Jónsson, JCP 137, 124102 (2012)

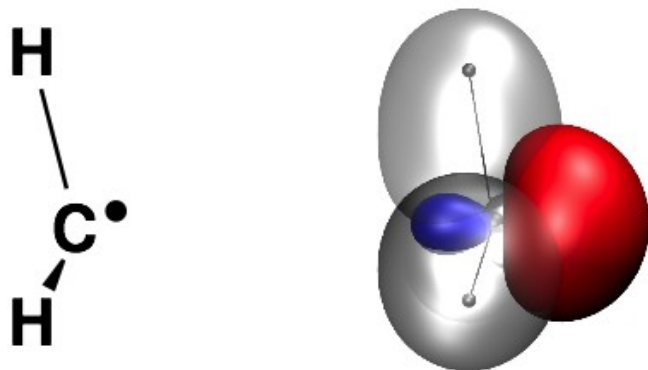
Molecular Radicals: C₂H



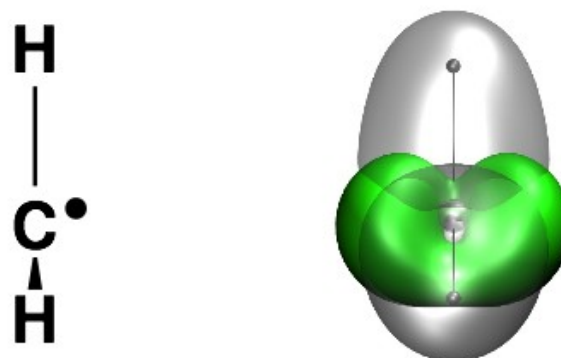
Cluepfel, Cluepfel and Jónsson, JCP 137, 124102 (2012)

Molecular geometry can become wrong when SIC is applied with real orbitals, resolved when complex orbitals are used

PBE+SIC — real orbitals

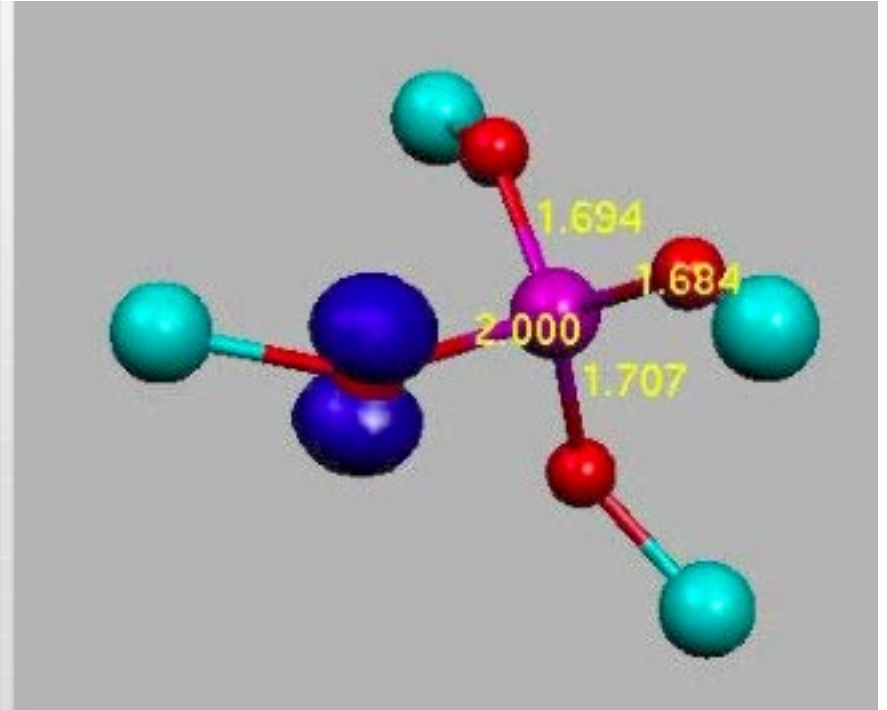
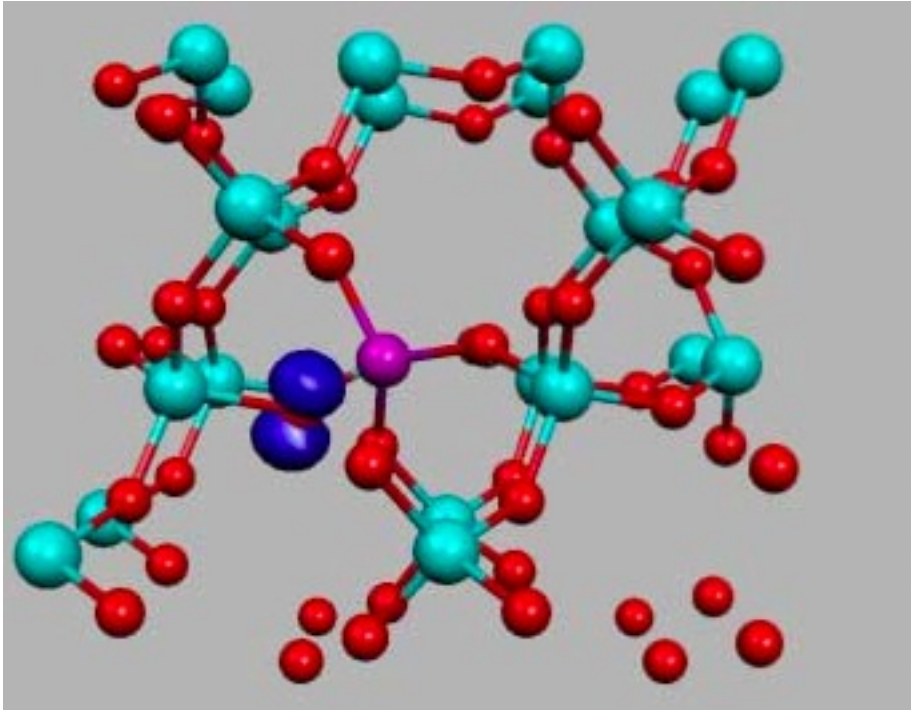


PBE+SIC — complex orbitals



Kluepfel, Kluepfel and Jónsson, JCP 137, 124102 (2012)

Apply to defects in oxides: Electron hole in quartz with Al



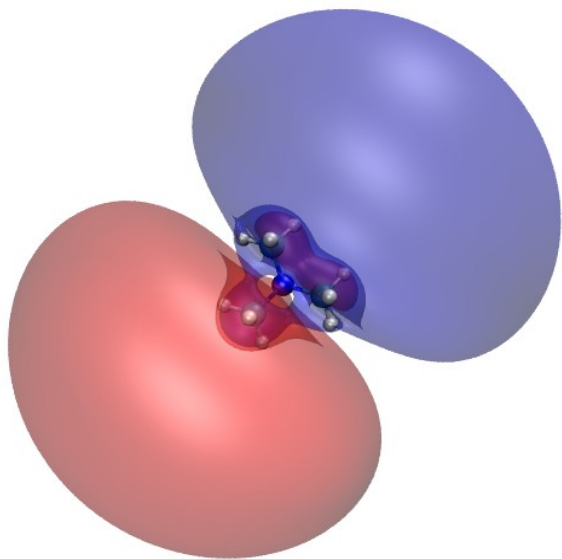
The DFT-SIC/2 correctly gives localized spin density and only one of the Al-O bonds is lengthened (by 0.3 Å).

Compare with EPR measurements, hyperfine constants:

Al:	0.32	0.18	0.50	PBE-SIC/2
	0.3	0.4	0.7	Exp
Si:	80	40	40	PBE-SIC/2
	85	41	44	Exp

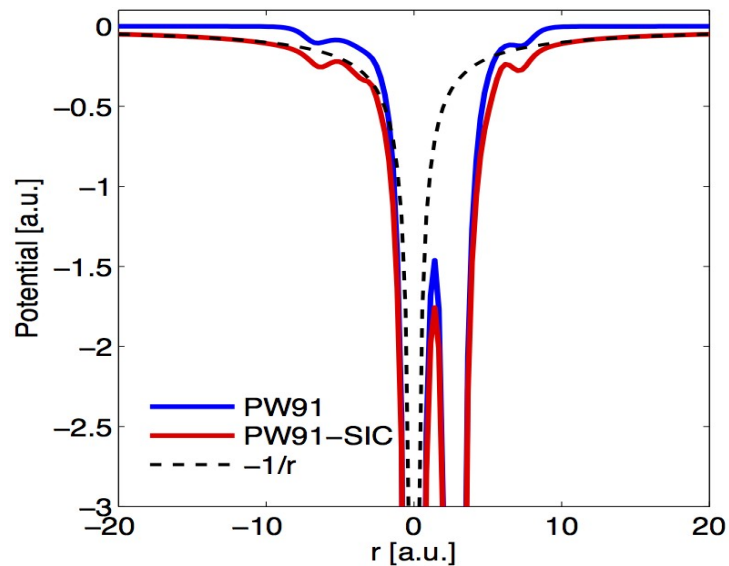
Application to excited states of large molecules

With SIC, the right $1/r$ dependence of the long range potential is built in, get the right Rydberg series of unoccupied states. Use solid-state approach to excited states of molecules, DFT-SIC energy functional, OEP for virtual.



$3p_{xy}$ orbital of trimethylamine

Collaboration with
Peter Weber at Brown
University.



Test:	NH_3	
Orb.	Exp.	Calc.
3s	6.392	6.391
$3p_{xy}$	7.927	7.946
$3p_z$	8.258	8.251

Minimization of ODD Energy Functionals

minimization under constrained orthonormalization of the orbitals:

$$S[\{\varphi_i\}] = E[\{\varphi_i\}] - \sum_{ij=1}^N \lambda_{ij} \left(\int d^3\mathbf{r} \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r}) - \delta_{ij} \right)$$

condition for
minimal energy

$$\left\{ -\frac{\Delta}{2} + \hat{v}[\rho] \right\} \tilde{\varphi}_i(\mathbf{r}) = \sum_{j=1}^N \lambda_{ij} \varphi_j(\mathbf{r}) \quad \& \quad \boldsymbol{\lambda} = \boldsymbol{\lambda}^\dagger$$

KS-DFT: $\hat{v}[\rho] = v[\rho](\mathbf{r})$ **HF:** $\hat{v}[\rho] = \hat{v}[\rho(\mathbf{r}, \mathbf{r}')]]$

Unitary invariance:

$$\tilde{\varphi}_i(\mathbf{r}) = \sum_{j=1}^N U_{ij} \varphi_j(\mathbf{r}) \implies \tilde{\rho} = \rho, \quad E[\tilde{\rho}] = E[\rho], \quad \hat{v}[\tilde{\rho}] = \hat{v}[\rho]$$

Constraint matrix always Hermitian:

$$\boldsymbol{\lambda} = \boldsymbol{\lambda}^\dagger$$

Choose canonical orbitals,

$$\boldsymbol{\lambda} = \mathbf{U}^\dagger \boldsymbol{\epsilon} \mathbf{U} \quad \epsilon_{ij} = \epsilon_i \delta_{ij}$$

Effective Schrödinger equation,
eigenvalue problem:

$$\left\{ -\frac{\Delta}{2} + \hat{v}[\rho] \right\} \tilde{\varphi}_i(\mathbf{r}) = \epsilon_i \tilde{\varphi}_i(\mathbf{r})$$

Minimization of PZ-SIC energy functional

$$\hat{H}_i \varphi_i(\mathbf{r}) = \left[\hat{H}_0 + v_i[\{\rho_i\}](\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \sum_{j=1}^N \lambda_{ji} \varphi_j(\mathbf{r})$$

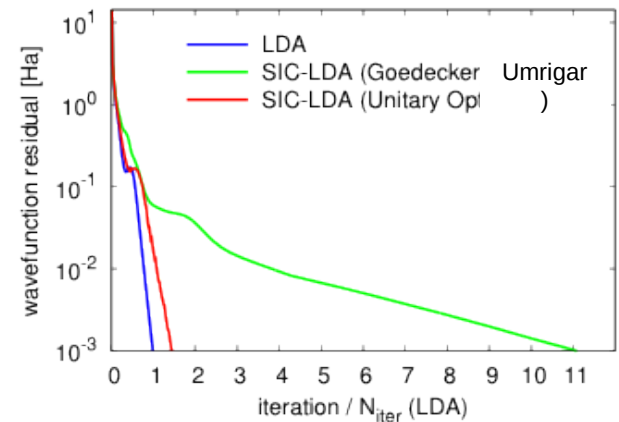
Energy/potential is not unitary invariant

Localized orbitals give larger SIC than delocalized orbitals

The equations for the orbitals are coupled
cannot choose orbitals to diagonalize λ :

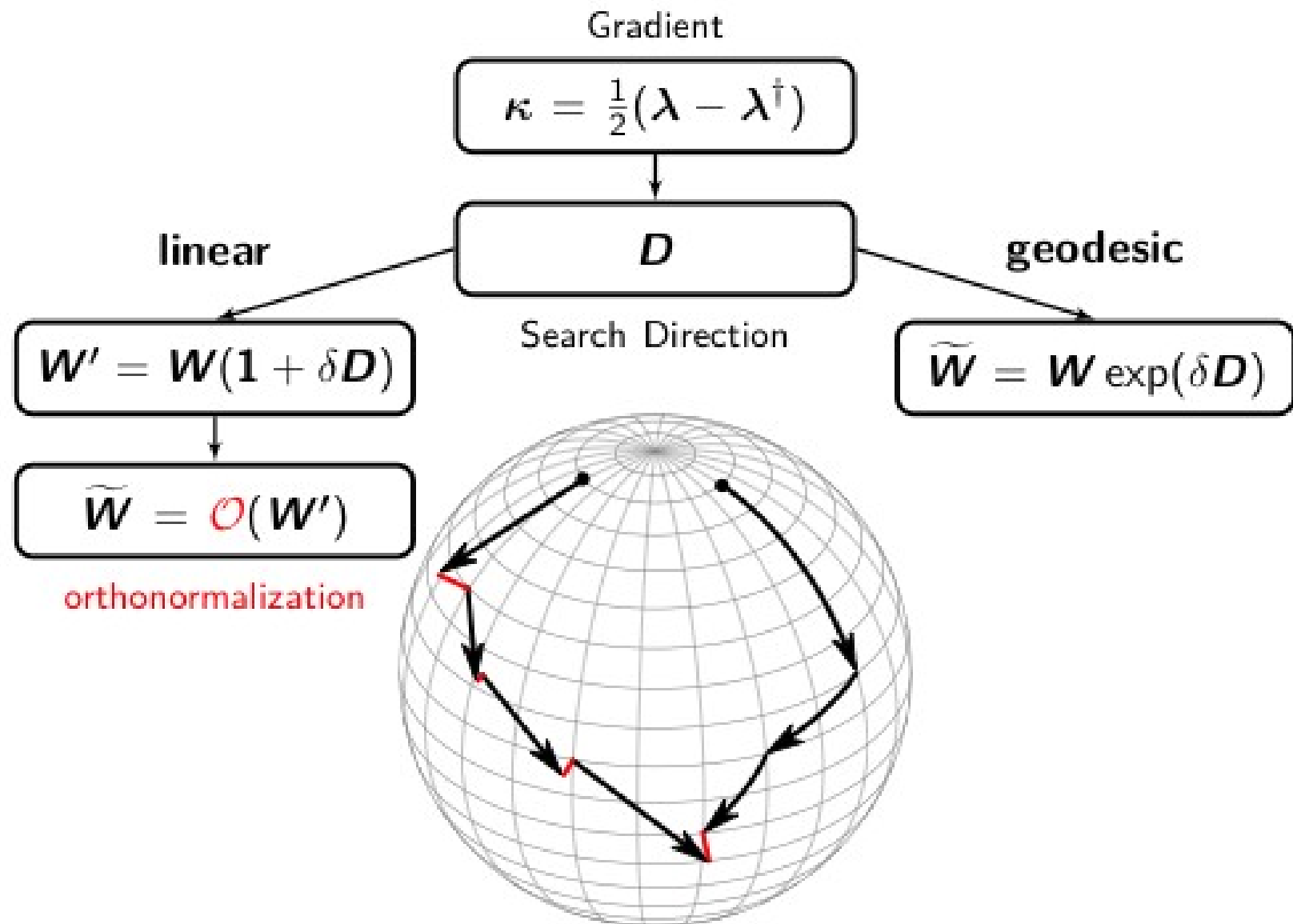
Hamiltonian depends on orbital index

This is in contrast to Kohn-Sham and HF
where the set of equations can be reduced to
several one-electron eigen value problems.

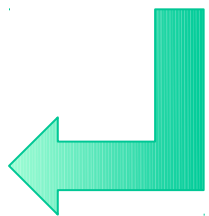


The lack of unitary invariance represents a problem in the minimization.
But, a set of unique orbitals is obtained, possibly more meaningful than MOs.

Unitary Optimization



Minimization of ODD functionals



Evaluate densities/potentials

$$\rho_i(\mathbf{r}) = |\varphi_i(\mathbf{r})|^2 \quad \rho(\mathbf{r}) = \sum_{i=1}^N \rho_i(\mathbf{r})$$
$$\hat{v}[\rho, \rho_i]$$



Optimize unitary transformation

$$\tilde{\varphi}_i(\mathbf{r}) \mapsto \sum_j U_{ij} \varphi_j(\mathbf{r})$$

Orthonormalization

$$\varphi_i(\mathbf{r}) \mapsto \hat{\mathcal{O}}\{\varphi_i(\mathbf{r})\}$$

Correction of the orbitals

$$\varphi_i(\mathbf{r}) \mapsto \varphi_i(\mathbf{r}) + \delta G_i(\mathbf{r})$$

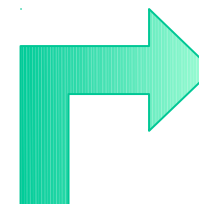
(Line Search, RMM-DIIS, ...)



Preconditioning of the search direction

$$G_i(\mathbf{r}) = \hat{\mathcal{P}}\{R_i(\mathbf{r})\}$$

(Conjugate Gradients, Davidson Methods,...)



Evaluate Lagrange Multipliers

$$\lambda_{ij} = \int d^3\mathbf{r} \varphi_j^*(\mathbf{r}) \left\{ -\frac{\Delta}{2} + \hat{v}[\rho, \rho_i] \right\} \varphi_i(\mathbf{r})$$

Evaluate Residual Vector

$$R_i(\mathbf{r}) = \left\{ -\frac{\Delta}{2} + \hat{v}[\rho, \rho_i] \right\} \varphi_i(\mathbf{r}) - \sum_{j=1}^N \lambda_{ij} \varphi_j(\mathbf{r})$$

Orbital Density Dependent (ODD) Functionals

Pros:

- ✓ scaling of CPU time same as GGA
- ✓ localized electronic states not penalized
- ✓ improved total/single-particle energy
- ✓ can give meaningful orbitals directly

Cons:

- ✗ inefficient minimization (not eigen value problem)
- ✗ several local minima

Progress: Improved minimization procedure:

P. Klüpfel, S. Klüpfel, K. Tsemekhman and HJ,
Lecture Notes In Computer Science (2012)).

Stage set for the development of an optimal ODD functional!

Summary

- PBE-SIC (or, better, PW91-SIC) is an alternative to hybrid functionals such as PBE0 giving **better estimate** of **total energy** of atoms and **ionization potentials**.
- **Complex wave functions have to be used** in self-consistent minimization of ODD functionals.
- Orbital-Density-Dependent functionals can give **meaningful, well-defined, localized orbitals** and this extended functional form opens the possibility for higher accuracy (defect states, band gaps, bond energy...) at computational cost that scales with N as DFT/GGA.
- Further development of ODD:
Construct new exchange correlation functional consistent with self-interaction free Hartree energy (need new PAW projectors).
Need to ensure size consistency, especially for solid state applications.
Improve the minimization algorithm (get stuck in local minima, large systems don't converge ...)