Electronic Structure: from BlackBoard to Source Code

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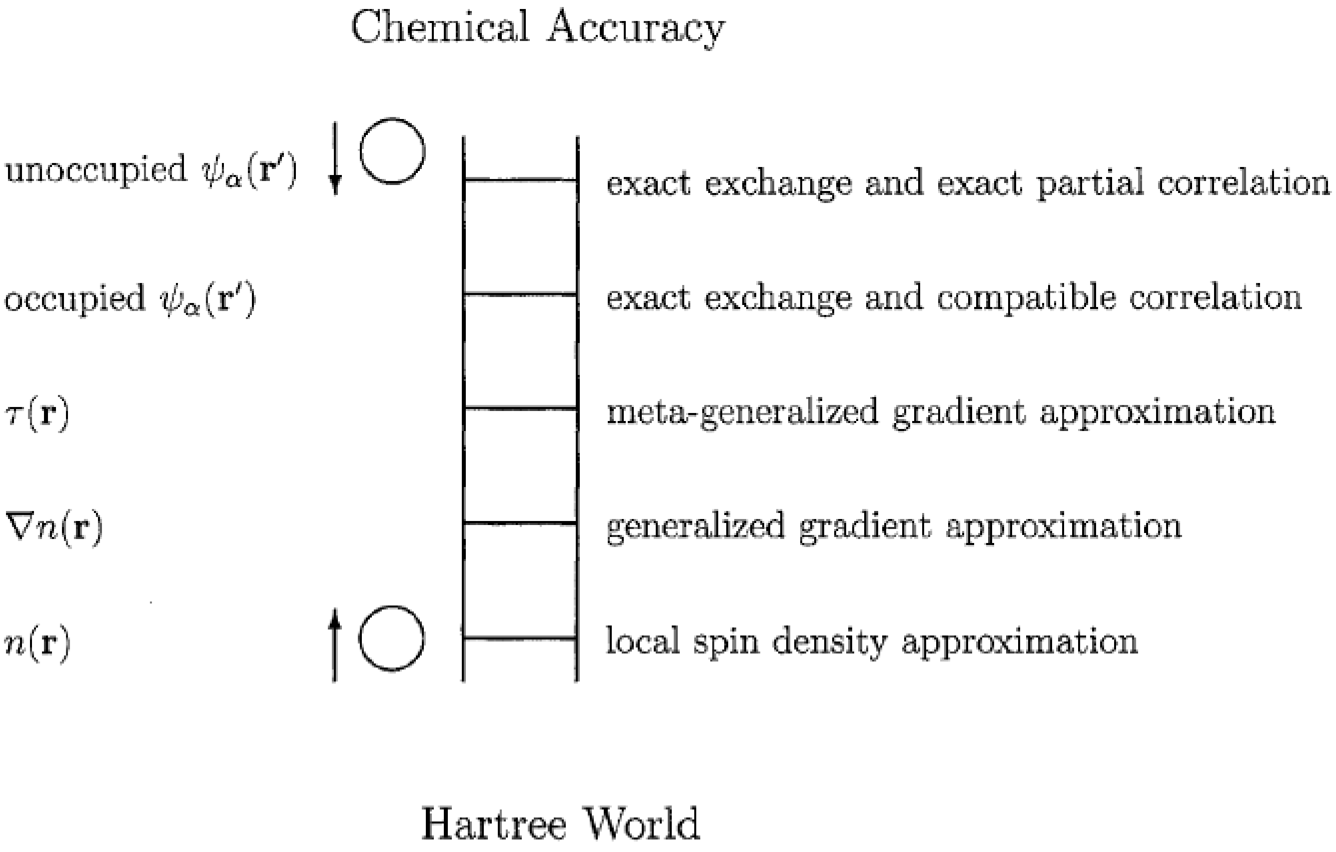
Going beyond Local Density and Gradient Corrected XC functionals in Quantum-ESPRESSO

Scuola Internazionale Superiore di Studi Avanzati

ma per seguir virtute e conoscenza

Jacob's ladder of Density Functional Theory



Chemical Accuracy

unoccupied $\psi_\alpha(\mathbf{r}')$	exact exchange and exact partial correlation
occupied $\psi_\alpha(\mathbf{r}')$	exact exchange and compatible correlation
$\tau(\mathbf{r})$	meta-generalized gradient approximation
$\nabla n(\mathbf{r})$	generalized gradient approximation
$n(\mathbf{r})$	local spin density approximation

Hartree World

FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

META-GGA: PKZB, TPSS,

SIC, DFT+U, hybrids

van der Waals functionals

...

exact DFT

LDA and LSDA ✓

GGA : PW91, PBE, revPBE, RPBE, BLYP ✓

~~META GGA: PKZB, TPSS,~~

SIC, DFT+U, hybrids

Van der Waals functionals ✓

...

exact DFT

simple approximations can work reasonably

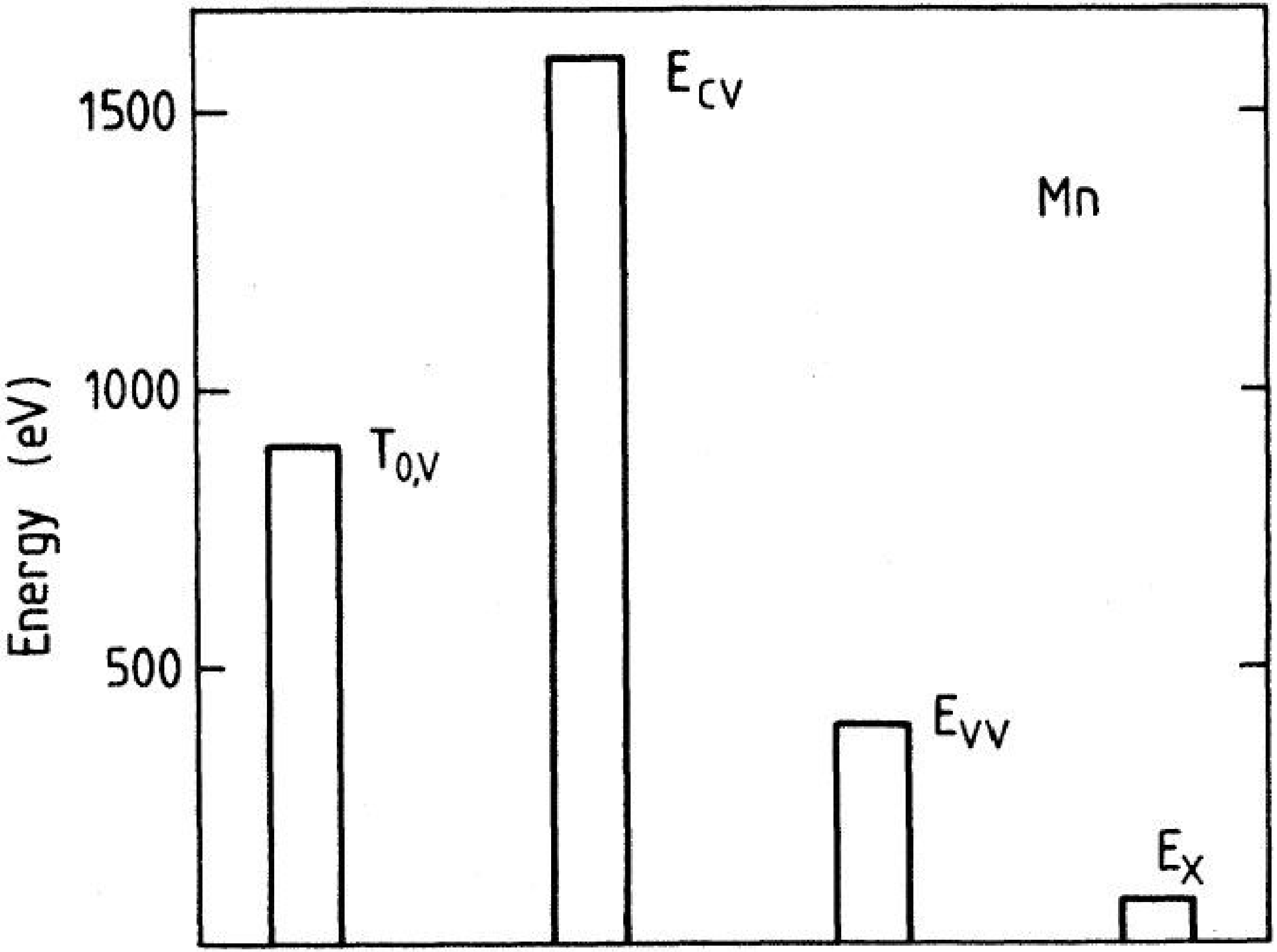


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

simple approximations can work reasonably

L(S)DA

$$E_{\rm XC}^{\rm LSD}[n_\uparrow, n_\downarrow] = \int d^3r\, n\, \epsilon_{\rm XC}^{\rm unif}(n_\uparrow, n_\downarrow)$$

GGA

$$E_{\rm XC}^{\rm GGA}[n_\uparrow, n_\downarrow] = \int d^3r\, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$$

Summary of Geometry Prediction

LDA under-predicts bond lengths (always ?)

GGA error is less systematic though over-prediction is common.

errors are in many cases < 1%, for transition metal oxides < 5%

Summary: Comparing Energy of Structures

For most elements, both LDA and GGA predict the correct structure for a material (as far as we know)

Notable exceptions: Fe in LDA; materials with substantial electron correlation effects (e.g. Pu)

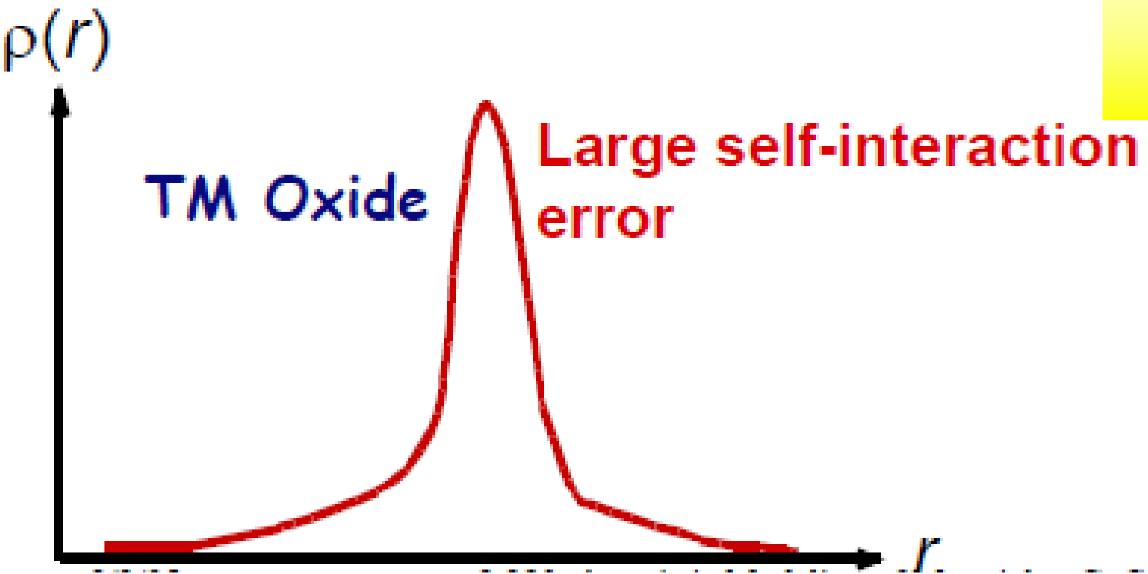
Redox Reactions can be more Problematic

	GGA	Exp
$FePO_4$ + Li -> $LiFePO_4$	2.8 eV	3.5 eV
MnO_2 + Li -> $LiMn_2O_4$	3.6 eV	4.1 eV
$V_2(PO_4)_3$ + Li -> $LiV_2(PO_4)_3$	3.3 eV	4.6 eV

All these reactions involve the transfer of an electron from a delocalized state in Li metal to a localized state in the transition metal oxide (phosphate)

In standard DFT an electron interacts with the effective potential generated by all the electrons (including itself)

$$H = \sum_i H_i = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{nuclear}(r_i) + \sum_{i=1}^{N_e} V_{effective}(r_i)$$



Self interaction in DFT is key problem in transition metal oxides

Problems with LDA / GGA functionals

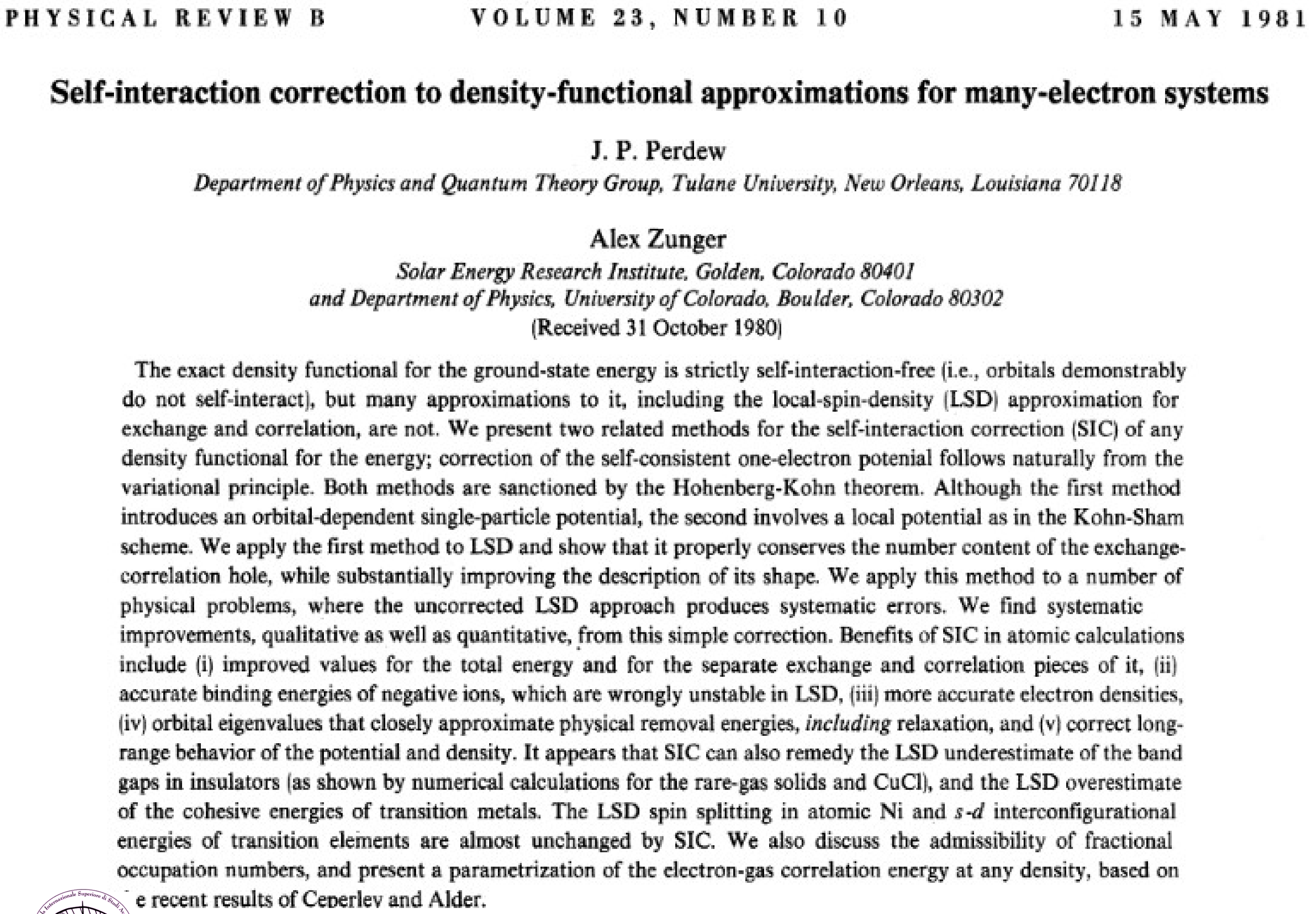
- Chemical accuracy (1 kcal/mol) is far.
  - trends are often accurate for strong bonds (covalent, ionic,metallic)
  - weak bonds/small overlaps are problematic
- Self interaction cancellation is only approximately verified in LDA and GGA.
  - molecular dissociation limit, TMO & RE and other atom-in-solid system.
- van der Waals interactions are not taken into account
  - occasional agreement with exp. from compensation of errors

SIC, DFT+U, hybrids

Self interaction correction was proposed as early as in 1981 by Perdew-Zunger. Conceptually important but not widely used.

DFT+U has been introduced by Anisimov, Zaanen and Andersen as an approximation to treat strongly correlated materials. It has been more recently been applied also in more normal system with encouraging results.

Hybrid functionals (like PBE0, B3LYB) mix a fraction of Self-interaction-free HF with LDA/GGA functionals.
Is the method preferred by chemists.
It is very expensive in a plane-wave basis.



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Self-interaction correction to density-functional approximations for many-electron systems

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(Received 31 October 1980)

The exact density functional for the ground-state energy is strictly self-interaction-free (i.e., orbitals demonstrably do not self-interact), but many approximations to it, including the local-spin-density (LSD) approximation for exchange and correlation, are not. We present two related methods for the self-interaction correction (SIC) of any density functional for the energy; correction of the self-consistent one-electron potenial follows naturally from the variational principle. Both methods are sanctioned by the Hohenberg-Kohn theorem. Although the first method introduces an orbital-dependent single-particle potential, the second involves a local potential as in the Kohn-Sham scheme. We apply the first method to LSD and show that it properly conserves the number content of the exchange-correlation hole, while substantially improving the description of its shape. We apply this method to a number of physical problems, where the uncorrected LSD approach produces systematic errors. We find systematic improvements, qualitative as well as quantitative, from this simple correction. Benefits of SIC in atomic calculations include (i) improved values for the total energy and for the separate exchange and correlation pieces of it, (ii) accurate binding energies of negative ions, which are wrongly unstable in LSD, (iii) more accurate electron densities, (iv) orbital eigenvalues that closely approximate physical removal energies, *including* relaxation, and (v) correct long-range behavior of the potential and density. It appears that SIC can also remedy the LSD underestimate of the band gaps in insulators (as shown by numerical calculations for the rare-gas solids and CuCl), and the LSD overestimate of the cohesive energies of transition metals. The LSD spin splitting in atomic Ni and *s-d* interconfigurational energies of transition elements are almost unchanged by SIC. We also discuss the admissibility of fractional occupation numbers, and present a parametrization of the electron-gas correlation energy at any density, based on e recent results of Ceperley and Alder.

$$Q[n_\uparrow, n_\downarrow] = T[n_\uparrow, n_\downarrow] + U[n] + E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]\,,$$

$$E_{\mathrm{xc}}^{\mathrm{SIC}} = E_{\mathrm{xc}}^{\mathrm{approx}}[n_\uparrow, n_\downarrow] - \sum_{\alpha\sigma} \delta_{\alpha\sigma}\,,$$

$$\delta_{\alpha\sigma} = U[n_{\alpha\sigma}] + E_{\mathrm{xc}}^{\mathrm{approx}}[n_{\alpha\sigma}, 0]$$

Hartree-Fock energy

$$\mathbf{E}_{HF} = -\frac{e^2}{2}\sum_{\substack{\mathbf{k}v\\ \mathbf{k}'v'}} \int \frac{\phi^*_{\mathbf{k}v}(\mathbf{r})\phi_{\mathbf{k}'v'}(\mathbf{r})\phi^*_{\mathbf{k}'v'}(\mathbf{r}')\phi_{\mathbf{k}v}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

- Hartree-Fock
- Exact Exchange (OEP)
- Hybrid Functionals: HH, B3LYP, PBE0
  (range separated) HSE

HF Vx using PWs

- FFT pseudo wfc to real space

$$\phi_{\mathbf{k}v}(\mathbf{k}+\mathbf{G}) \quad \overset{FFT}{\longrightarrow} \quad \phi_{\mathbf{k}v}(\mathbf{r})$$

- For each qpoint and each occupied band build “charge density”

$$\rho_{\mathbf{q}}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q}v'}(\mathbf{r})\phi_{\mathbf{k}v}(\mathbf{r})$$

- FFT charge to recip.space and solve Poisson eq.

$$\rho_{\mathbf{q}}(\mathbf{r}) \quad \overset{FFT}{\longrightarrow} \quad \rho_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) \quad \Longrightarrow \quad V_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) = \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}|^2} \quad \rho_{\mathbf{q}}(\mathbf{q}+\mathbf{G})$$

- FFT back to real space, multiply by wfc and add to result

$$V_{\mathbf{q}}(\mathbf{q}+\mathbf{G}) \quad \overset{FFT}{\longrightarrow} \quad V_{\mathbf{q}}(\mathbf{r}) \quad \Longrightarrow \quad V_x\phi_{\mathbf{k}v}(\mathbf{r}) = V_x\phi_{\mathbf{k}v}(\mathbf{r}) + \phi_{\mathbf{k}-\mathbf{q}v'}(\mathbf{r})V_{\mathbf{q}}(\mathbf{r})$$

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

$$\rho_{\substack{\mathbf{k}-\mathbf{q},v'\\ \mathbf{k},v}}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\phi_{\mathbf{k},v}(\mathbf{r}) \quad \Longrightarrow \quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\ \left|\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})\right|^2$$

$$= \frac{1}{N_\mathbf{k}}\sum_\mathbf{k} \left|\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})\right|^2$$

$$E_{HF} = -\frac{4\pi e^2}{2\Omega} \times \frac{\Omega}{(2\pi)^3}\int d\mathbf{q} \sum_\mathbf{G} \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2}$$

integrable divergence

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

$$\rho_{\mathbf{k}-\mathbf{q},v' \atop \mathbf{k},v}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\phi_{\mathbf{k},v}(\mathbf{r}) \quad \Longrightarrow \quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\ \ |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$= \frac{1}{N_{\mathbf{k}}}\sum_{\mathbf{k}} |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$E_{HF} = -\frac{4\pi e^2}{2\Omega}\times\left\{\frac{\Omega}{(2\pi)^3}\int d\mathrm{q}\sum_{\mathrm{G}}\frac{A(\mathbf{q}+\mathbf{G}) - A(0)e^{-\alpha|\mathrm{q}+\mathrm{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \frac{\Omega}{(2\pi)^3}\int d\mathrm{q}\sum_{\mathrm{G}}\frac{e^{-\alpha|\mathrm{q}+\mathrm{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2}A(0)\right\}$$

The q+G=0 divergence

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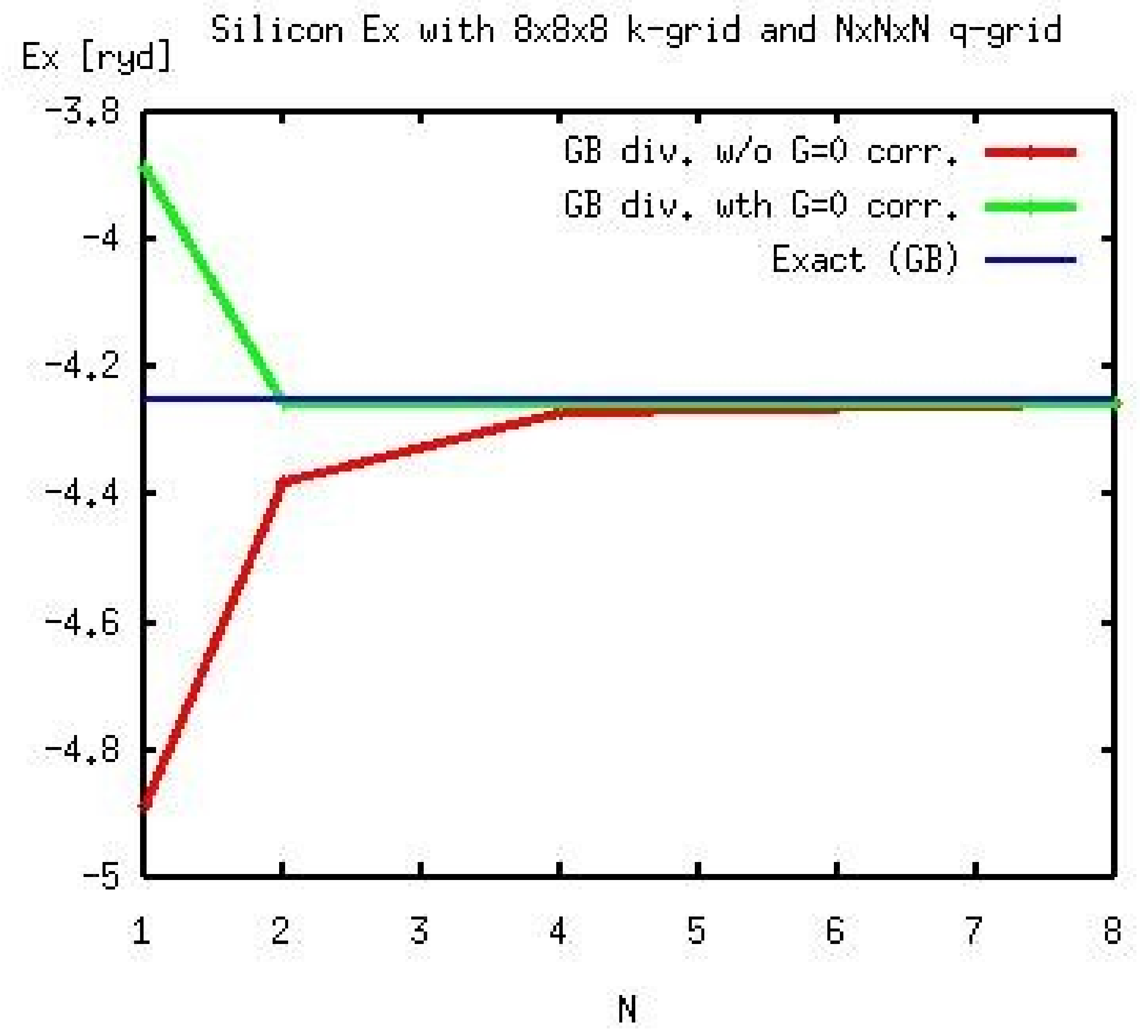
$$= \frac{1}{N_\mathbf{k}}\sum_\mathbf{k} |\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{q}+\mathbf{G})|^2$$

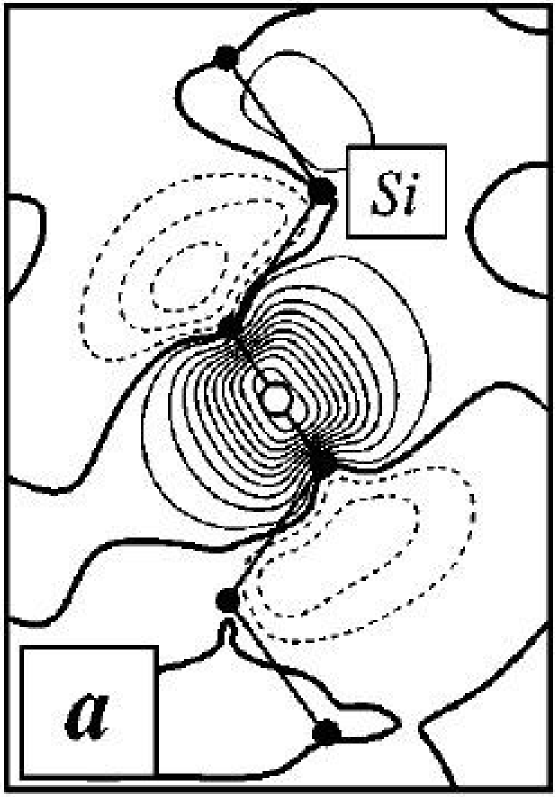
$$E_{HF} = -\frac{4\pi e^2}{2\Omega} \times \left\{ \frac{1}{N_\mathbf{q}} \left[{\sum_{\mathbf{q},\mathbf{G}}}' \frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} + \lim_{\mathbf{q}\to 0} \frac{A(\mathbf{q}) - A(0)}{\mathbf{q}^2} \right] + D \times A(0) \right\}$$

$$D = \frac{1}{N_\mathbf{q}} \left[-{\sum_{\mathbf{q},\mathbf{G}}}' \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} + \alpha \right] + \frac{\Omega}{(2\pi)^3}\sqrt{\frac{\pi}{\alpha}}$$

Silicon Bulk

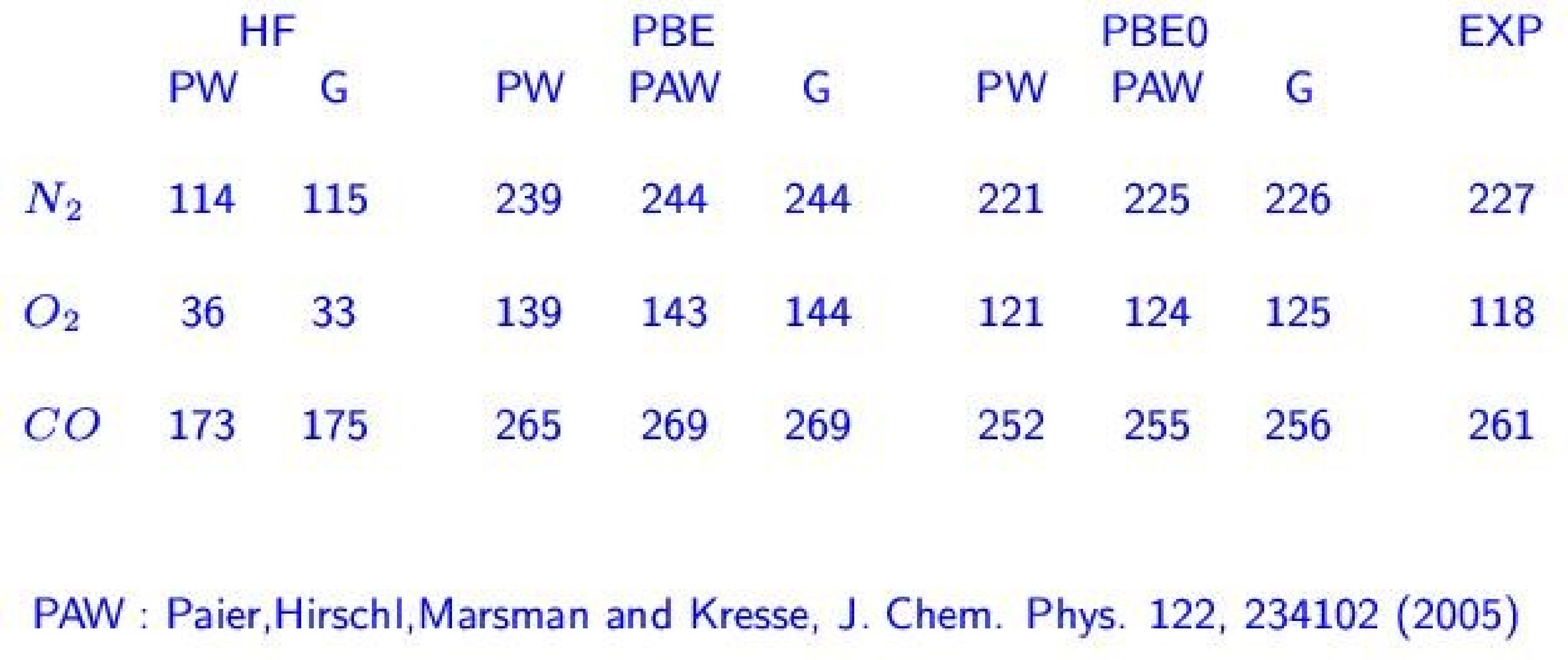


F.Gygi, EPFL PhD thesis (1988)



Fernandez, Dal Corso, Baldereschi,
PRB 58, R7480 (1998)

Simple Molecules



	HF		PBE			PBE0			EXP
	PW	G	PW	PAW	G	PW	PAW	G	
N_2	114	115	239	244	244	221	225	226	227
O_2	36	33	139	143	144	121	124	125	118
CO	173	175	265	269	269	252	255	256	261

PAW : Paier,Hirschl,Marsman and Kresse, J. Chem. Phys. 122, 234102 (2005)

Energies in kcal/mol = 43.3 meV

Scaling

- Kinetic energy and local Potential

$$NPW + 2 * FFT + NRXX$$

- Non local potential

$$2 * NBND * NPW$$

- Fock operator

$$2 * FFT + NBND * NQ * (NRXX + FFT) + 2 * NRXX$$

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From 10 to 100 times slower than standard case

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From 10 to 100 times slower than standard case

Moore's law: computer power doubles every 18 months
(a factor of 10 in 5 yrs)

Scaling

- Kinetic energy and local Potential

$$NPW + 2 * FFT + NRXX$$

- Non local potential

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- Fock operator

$$2 * FFT + NBND * NQ * (NRXX + FFT) + 2 * NRXX$$

From 10 to 100 times slower than standard case

Separation of long- and short-range part in X can help

the modified scf cycle

The HF energy is

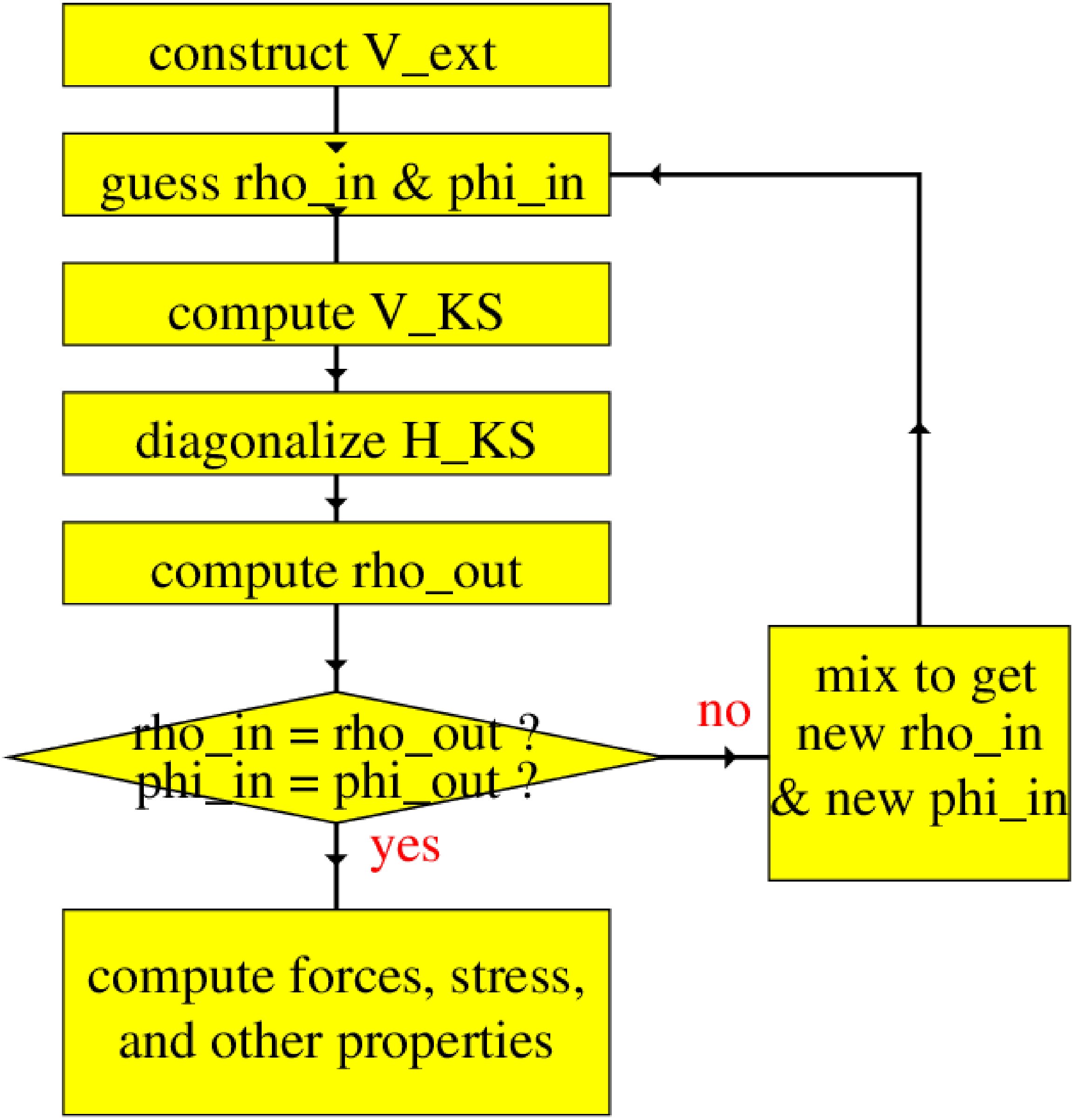
$$E_{HF}[\Phi] = \sum_i \langle\phi_i| - \frac{\hbar 2}{2m}\nabla^2|\phi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{WLD}$$
$$-\frac{e^2}{2}\int \frac{|\gamma_\phi(r,r')|^2}{|r-r'|}$$

with $\gamma_\phi(r,r') = \sum_i \phi_i(r)\phi_i^*(r')$

The HF equations are therefore

$$\left[-\frac{\hbar 2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) - e^2\int \frac{\gamma_\phi(r,r')}{|r-r'|}\right]\,|\phi_i\rangle = \varepsilon_i|\phi_i\rangle$$

the modified scf cycle



construct V_ext

guess rho_in & phi_in

compute V_KS

diagonalize H_KS

compute rho_out

rho_in = rho_out ?
phi_in = phi_out ?

no

mix to get
new rho_in
& new phi_in

yes

compute forces, stress,
and other properties

the modified scf cycle

Let's introduce an auxiliary set of functions

$$E_{HF}[\Phi,\Psi] = \sum_i \langle \phi_i | -\frac{\hbar 2}{2m}\nabla^2 |\phi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{WL}$$

$$-\frac{e^2}{2}\int \frac{|\gamma_\phi(r,r')|^2}{|r-r'|} \; + \; \frac{e^2}{2}\int \frac{|\gamma_\phi(r,r') - \gamma_\psi(r,r')|^2}{|r-r'|}$$

delta_exx > 0 !

with $\gamma_\phi(r,r') = \sum_i \phi_i(r)\phi_i^*(r'), \;\; \gamma_\psi(r,r') = \sum_i \psi_i(r)\psi_i^*(r')$

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$$-\frac{e^2}{2}\int\frac{|\gamma_\phi(r,r')|^2}{|r-r'|}+\frac{e^2}{2}\int\frac{|\gamma_\phi(r,r')-\gamma_\psi(r,r')|^2}{|r-r'|}$$

$$E_X^{HF}[\Phi]-E_X^{HF}[\Phi]+\sum_i\langle\phi_i|V_X^{HF}[\Psi]|\phi_i\rangle-E_X^{HF}[\Psi]$$

with $\gamma_\phi(r,r')=\sum_i\phi_i(r)\phi_i^*(r'),\quad \gamma_\psi(r,r')=\sum_i\psi_i(r)\psi_i^*(r')$

the modified scf cycle

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$$-\frac{e^2}{2}\int\frac{|\gamma_\phi(r,r')|^2}{|r-r'|} + \frac{e^2}{2}\int\frac{|\gamma_\phi(r,r')-\gamma_\psi(r,r')|^2}{|r-r'|}$$

$$\cancel{E_X^{HF}}[\Phi] - \cancel{E_X^{HF}}[\Phi] + \sum_i\langle\phi_i|V_X^{HF}[\Psi]|\phi_i\rangle - E_X^{HF}[\Psi]$$

with $\gamma_\phi(r,r') = \sum_i \phi_i(r)\phi_i^*(r'),\quad \gamma_\psi(r,r') = \sum_i \psi_i(r)\psi_i^*(r')$

the modified scf cycle

Let's introduce an auxiliary set of functions

$$E_{HF}[\Phi,\Psi] = \sum_i \langle\phi_i| -\frac{\hbar 2}{2m}\nabla^2|\phi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{WL}$$

$$+\sum_i \langle\phi_i|V_X^{HF}[\Psi]|\phi_i\rangle - E_X^{HF}[\Psi]$$

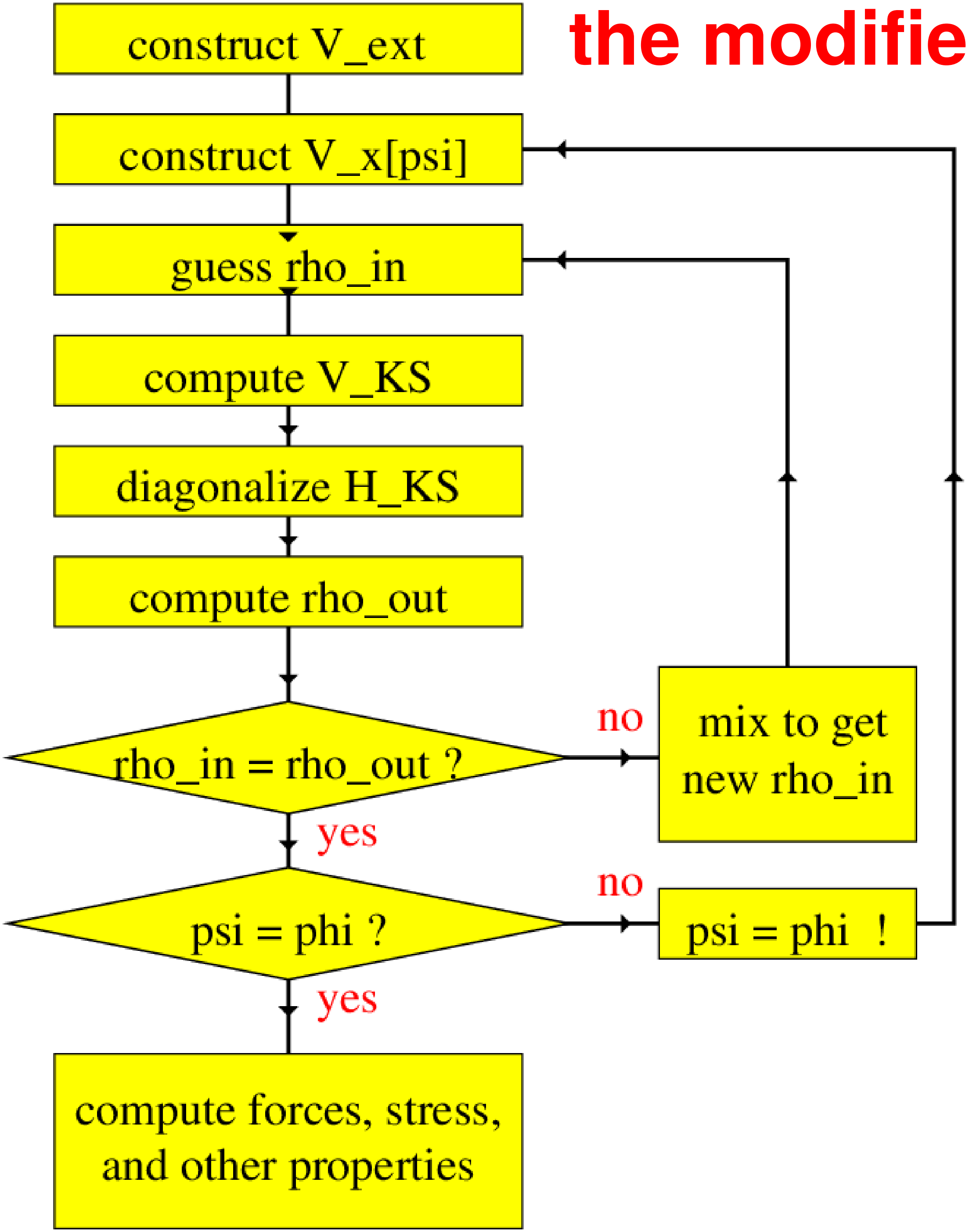
with $\gamma_\phi(r,r') = \sum_i \phi_i(r)\phi_i^*(r'),\ \ \gamma_\psi(r,r') = \sum_i \psi_i(r)\psi_i^*(r')$

The minimizing equations become

$$\left[-\frac{\hbar 2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) - e^2\int\frac{\gamma_\psi(r,r')}{|r-r'|}\right]\ |\phi_i\rangle = \varepsilon_i|\phi_i\rangle$$

and $\psi_i(r) = \phi_i(r),\ \forall i$

the modified scf cycle



Adaptively Compressed Exchenge (ACE)

Applying the Fock operator is estremely expensive !

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One can try to approximate it via a KB-type factorization in the inner loop of the nested scf-cycle (ACE)

$$V_X^{HF}[\Psi] \approx \sum_{i,j} |w_i\rangle a_{ij} \langle w_j|$$

such that it works exactly on the reference wfc $|\psi_k\rangle$

Lin Lin. Adaptively Compressed Exchange operator. arXiv, 2016.

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$$|w_k\rangle = V_X^{HF}[\Psi]|\psi_k\rangle \;\Rightarrow\; |w_k\rangle = \sum_{i,j} |w_i\rangle a_{ij} \langle \psi_j|V_X^{HF}[\Psi]|\psi_k\rangle$$

$$\sum_j a_{ij} \langle \psi_j|V_X^{HF}[\Psi]|\psi_k\rangle = \delta_{i,k}$$

$$\Rightarrow \quad a_{ij} = \langle \psi|V_X^{HF}[\Psi]|\psi\rangle^{-1}_{ij}$$

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such that it works exactly on the reference wfcs $|\psi_k\rangle$

$$|w_k\rangle = V_X^{HF}[\Psi]|\psi_k\rangle, \qquad a_{ij} = \langle\psi|V_X^{HF}[\Psi]|\psi\rangle_{ij}^{-1}$$

in this way the calculation of H_psi in the inner loop is comparable to a non-hybrid functional.

on the fully self-consistent wfcs the ACE operator is exact !

Lin Lin. Adaptively Compressed Exchange operator. arXiv, 2016.

LDA and LSDA ✓

GGA : PW91, PBE, revPBE, RPBE, BLYP ✓

~~META GGA: PKZB, TPSS,~~

SIC, DFT+U, hybrids ✓

van der Waals functionals ✓

...

exact DFT

... to be continued