Density functional theory in the solid state

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Summary

1. DFT
   - Repetition
   - Exchange-correlation functional
2. GIPAW-PP

Kohn-Sham method: Total energy

Let us write the total energy as:

$$E_{\mathrm{tot}}[n] = E_{\mathrm{kin}}[n] + E_{\mathrm{ext}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n]$$

- $E_{\mathrm{kin}}[n]$ = *QM* kinetic energy of electrons
- $E_{\mathrm{ext}}[n]$ = energy due to external potential (usually ions)
- $E_{\mathrm{H}}[n]$ = classical Hartree repulsion ($e^- - e^-$)
- $E_{\mathrm{xc}}[n]$ = exchange-correlation energy

Total energy expression

Kohn-Sham (total[1]) energy:

$$\begin{aligned} E_{\mathrm{KS}}[n] &= \sum_i -\frac{1}{2} f_i \left\langle \psi_i \mid \nabla^2 \mid \psi_i \right\rangle + \int_{\mathbf{r}} n(\mathbf{r})\, V_{\mathrm{ext}}(\mathbf{r})\; d\mathbf{r} \\ &+ \frac{1}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'\, d\mathbf{r} + E_{\mathrm{xc}} \end{aligned}$$

---

[1] without ion-ion interaction

Kohn-Sham equations

Vary the Kohn-Sham energy E_{KS} with respect to $\psi_j^*(\mathbf{r}'')$: $\frac{\delta E_{\mathrm{KS}}}{\delta \psi_j^*(\mathbf{r}'')}$

⇒ Kohn-Sham equations

$$\begin{aligned}
\left\{-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right\}\psi_i(\mathbf{r}) &= \varepsilon_i \psi_i(\mathbf{r}) \\
n(\mathbf{r}) &= \sum_i f_i \left|\psi_i(\mathbf{r})\right|^2 \\
V_{\mathrm{KS}}(\mathbf{r}) &= V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})
\end{aligned}$$

$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}$

Kohn-Sham equations: Notes

$$\left\{-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right\}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad ; \quad n(\mathbf{r}) = \sum_i f_i \left|\psi_i(\mathbf{r})\right|^2$$

- Equation looking like Schrödinger equation
- The Kohn-Sham potential, however, depends on density
- The equations are coupled and highly non-linear
- $\Rightarrow$ Self-consistent solution required
- ε_i and ψ_i are in principle only help variables (only $\varepsilon_{\mathrm{HOMO}}$ has a meaning)
- The potential V_{KS} is local
- The scheme is in principle exact

Kohn-Sham equations: Self-consistency

1. Generate a starting density n^{init}
2. Generate the Kohn-Sham potential $\Rightarrow V_{\mathrm{KS}}^{\mathrm{init}}$
3. Solve the Kohn-Sham equations $\Rightarrow \psi_i^{\mathrm{init}}$
4. New density n^1
5. Kohn-Sham potential V_{KS}^1
6. Kohn-Sham orbitals $\Rightarrow \psi_i^1$
7. Density n^2
8. $\ldots$

$\ldots$until self-consistency is achieved (to required precision)

Kohn-Sham energy: Alternative expression

- Take the Kohn-Sham equation, multiply from the left with $f_i \psi_i^*$ and integrate:

$$-\frac{1}{2} f_i \int_{\mathbf{r}} \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r})\ d\mathbf{r} + f_i \int_{\mathbf{r}} V_{\mathrm{KS}}(\mathbf{r}) \left|\psi_i(\mathbf{r})\right|^2 d\mathbf{r} = f_i \varepsilon_i$$

- Sum over i and substitute into the expression for Kohn-Sham energy:

$$E_{\mathrm{KS}}[n] \ = \ \sum_i f_i \varepsilon_i - E_{\mathrm{H}} + E_{\mathrm{xc}} - \int_{\mathbf{r}} n(\mathbf{r})\, V_{\mathrm{xc}} d\mathbf{r}$$

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- The exchange-correlation energy can be expressed using the exchange-correlation hole $n_{\mathrm{xc}}\left(\mathbf{r},\mathbf{r}'\right)$

$$\begin{aligned}
E_{\mathrm{xc}} &= \frac{1}{2}\int_{\mathbf{r}} n\left(\mathbf{r}\right)\int_{\mathbf{r}'}\frac{n_{\mathrm{xc}}\left(\mathbf{r},\mathbf{r}'-\mathbf{r}\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}'\,d\mathbf{r} \\
&= \frac{1}{2}\int_{\mathbf{r}} n\left(\mathbf{r}\right)\int_{R=0}^{\infty} R^2\frac{1}{R}\int_{\Omega} n_{\mathrm{xc}}\left(\mathbf{r},R\right)d\Omega\,dR\,d\mathbf{r}
\end{aligned}$$

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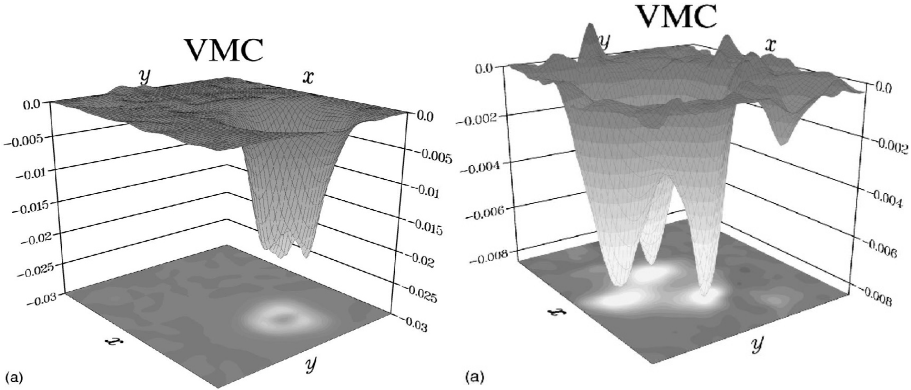
- Sum rule

$$\int_{\mathbf{r}'} n_{\mathrm{xc}}\left(\mathbf{r},\mathbf{r}'-\mathbf{r}\right)d\mathbf{r}' = -1$$

Exchange-correlation hole: Silicon



PP Rushton, DJ Tozer SJ Clark, Phys Rev B **65** (2002) 235203

Exchange-correlation functional: LDA

Local density approximation:

- Use the exchange-correlation energy functional for homogeneous electron gas at each point of space: $E_{\mathrm{xc}} \simeq \int_{\mathbf{r}} n(\mathbf{r})\, e_{\mathrm{xc}}^{\mathrm{heg}}[n(\mathbf{r})] d\mathbf{r}$

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Exchange-correlation functional: LDA

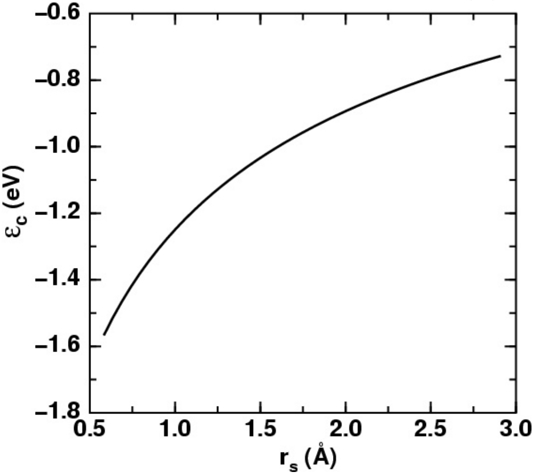
- The LDA exchange energy is due to Slater and Dirac,

$$\epsilon_x(n) = C_x n^{1/3} \,, \quad \text{where } C_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

- The exact analytical form of the correlation energy $\epsilon_c(n)$ of the homogeneous electron gas is not known. The correlation energy is therefore fitted to quantum Monte-Carlo results (Ceperley *&* Alder) and analytical high- and low-density limits
  - There are several parametrisations: Vosko, Wilk *&* Nusair (1980); Perdew *&* Zunger (1981); Perdew *&* Wang (1992))
  - Pade-interpolation reproducing the Perdew-Wang data S Goedecker, M Teter *&* J Hutter, Phys Rev B **54** (1996) 1703

Exchange-correlation functional: LDA

Correlation energy function $\epsilon_c(n)$

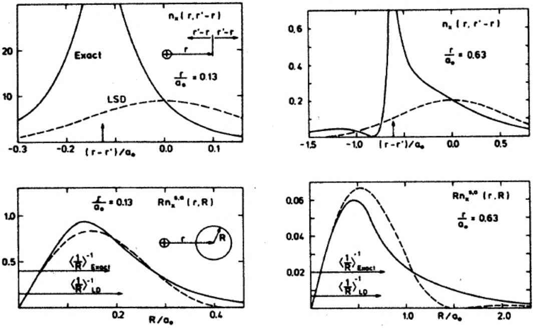


Exchange-correlation functional: LDA

Why does it albeit work so well?

- The XC contribution is the smallest (that's why it was packed aside in the first place)
- LDA, despite is simplicity, still fulfills many important requirements set for the exact functional; scaling relations, sum rules, . . .
- There is a major error cancellation between the exchange and correlation (Warning: Same occurs with many other functionals also; thereby best keeping the same “level of sophistication” in both parts)

Exchange-correlation functional: LDA



- The hole (top) is badly described, however the spherical average (bottom), which is the property needed, agrees reasonably
- LDA fulfills several sum rules

Exchange-correlation functional: LDA

Why does it *not* work so well?

- Missing integer discontinuity in the potential; thus bad excitation energies; the first place)
- Self-interaction not excluded: The electron interacts directly with itself
- Thus for example *d* and *f* functions underbound (*eg* density of states in fcc Cu)
- Wrong tail: no Rydberg states, image states at metal surfaces

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  - $\Rightarrow$ Negative ions normally not bound
  - Usually the best compromise between speed and accuracy in large systems

Exchange-correlation functional: GGA-PBE

J Perdew, KBurke & M Ernzerhof, Phys Rev Lett (1996):

- Like Perdew-Wang'91: "Analytical" function, only "natural constants"

$$E_{xc}^{\mathrm{PBE}} = E_{\mathrm{x}}^{\mathrm{PBE}} + E_{\mathrm{c}}^{\mathrm{PBE}}$$

$$\begin{aligned}
E_{\mathrm{x}}^{\mathrm{PBE}}(n, |\nabla n|) &= \int_{\mathbf{r}} n\, \varepsilon_{\mathrm{x}}^{\mathrm{LDA}}(n)\, F_{\mathrm{x}}^{\mathrm{PBE}}(s)\, d\mathbf{r}, \\
F_{\mathrm{x}}^{\mathrm{PBE}}(s) &= 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}, \\
\mu &= \beta \left(\frac{\pi^2}{3} \right)
\end{aligned}$$

Exchange-correlation functional: GGA-PBE

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{PBE}}\left(n,|\nabla n|\right) &= \int_{\mathbf{r}} d\mathbf{r}\, n\left[\varepsilon_{\mathrm{xc}}^{\mathrm{LDA}}\left(n\right)+H_{\mathrm{c}}^{\mathrm{PBE}}\left(r_s,\eta,t\right)\right],\\
H_{\mathrm{c}}^{\mathrm{PBE}}\left(r_s,\eta,t\right) &= \gamma\phi^3\ln\left[1+\frac{\beta}{\gamma}t^2\left(\frac{1+At^2}{1+At^2+A^2t^4}\right)\right],\\
A\left(r_s,\eta\right) &= \frac{\beta}{\gamma}\frac{1}{e^{-\varepsilon_{\mathrm{c}}^{\mathrm{LDA}}/\gamma\phi^3}-1},\\
\phi\left(\eta\right) &= \frac{1}{2}\left[\left(1+\eta\right)^{2/3}+\left(1-\eta\right)^{2/3}\right],
\end{aligned}
$$

$$\gamma=\frac{1-\ln 2}{\pi^2}; \qquad r_s=\left[\frac{3}{4\pi n}\right]^{1/3}$$ local Wigner-Seitz radius

Exchange-correlation functional: GGA-PBE

Here $s(\mathbf{r}) = \frac{|\nabla n|}{2k_F n}$ and $t(\mathbf{r}) = \frac{|\nabla n|}{2\phi k_s n}$, $k_s = \sqrt{4k_F/\pi}$, are dimensionless density gradients and β comes from the generalised gradient expansion for the correlation (Perdew *et al*, 1992) and $\approx 0.066\,725$ (Wang & Perdew, 1991). κ is formally set by the Lieb-Oxford bound (1981) for the exchange energy

$$E_{\mathrm{x}}[n] \geq E_{\mathrm{xc}}[n] \geq -1.679 \int_{\mathbf{r}} n^{4/3}(\mathbf{r})\, d\mathbf{r} \, .$$

Note: revPBE plays exactly with this parameter

Exchange-correlation functional: LDA+U/GGA+U

- Add on-site Hubbard term:

$$E_U = \frac{U}{2} \sum_{l,\sigma} \left[\lambda_m^{l\sigma} \left(1 - \lambda_m^{l\sigma} \right) \right]$$

- Improves description (energetics, magnetic moments, . . .) in many cases — but not always

Exchange-correlation functional: Meta-GGA

Meta-Generalised gradient approximation:

- In addition to the gradient, add also orbital kinetic energy

$$\tau\left(\mathbf{r}\right)=\sum_{i}\frac{1}{2}\left|\nabla\psi_{i}\left(\mathbf{r}\right)\right|^{2}$$

$$E_{\mathrm{xc}}\simeq\int_{\mathbf{r}}n\left(\mathbf{r}\right)e_{\mathrm{xc}}[n(\mathbf{r}),\left|\nabla n(\mathbf{r})\right|^{2},\tau(r)]d\mathbf{r}$$

Exchange-correlation functional: SIC

- The usual functionals include self-interaction: The electron interacts with itself because the functionals contain the full density, thus also that of a given orbital ψ_i

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  - M d'Avezac, M Calandra *&* F Mauri, Phys Rev B **71** (2005) 205210

$$E_{\mathrm{SIC,SPZ}} = E_{\mathrm{KS}} - E_{\mathrm{H}}\left[m\right] - E_{\mathrm{xc}}\left[m, 0\right]$$

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$$E_{\mathrm{SIC,US}} = E_{\mathrm{KS}} - E_{\mathrm{H}}\left[m\right] - E_{\mathrm{xc}}\left[n_\uparrow, n_\downarrow\right] + E_{\mathrm{xc}}\left[n_\uparrow - m, n_\downarrow\right]$$

Exchange-correlation functional: Hybrid functionals

Hybrid functionals

- Include partially the exact (Hartree-Fock) exchange: $E_{\mathrm{xc}} \simeq \alpha E_{\mathrm{HF}} + (1 - \alpha) E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{GGA}}$; again many variants

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- The method is no longer pure Kohn-Sham method: Fock operator is non-local; a mixed DFT-KS/Hartree-Fock scheme

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- This can be varied with respect to potential, leading to an integral equation for the exchange potential

$$\sum_i \int_{\mathbf{r}'} \left\{ \psi_i(\mathbf{r}') \left[V_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r}') - \frac{1}{\psi_p(\mathbf{r}')} \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}}{\delta \psi_i(\mathbf{r}')} \right] G_i(\mathbf{r}, \mathbf{r}') \psi_i(\mathbf{r}) + cc \right\} d\mathbf{r}' = 0$$

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_j \frac{\psi_j(\mathbf{r}) \psi_j(\mathbf{r}')}{\varepsilon_i - \varepsilon_j}$$

Exchange-correlation functional: ACDFT

$$E_{\mathrm{c}} = \int_{\lambda=0}^{1} \int_{\omega=0}^{\infty} \frac{1}{\pi} \mathrm{Tr} \left\{ V_{\mathrm{bare}} \left[\chi_{\mathrm{KS}} \left(i\omega \right) - \chi_{\lambda} \left(i\omega \right) \right] \right\} \, d\omega \, d\lambda$$

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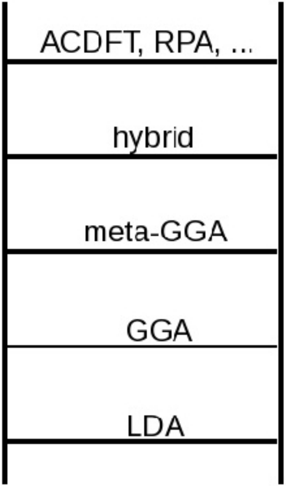
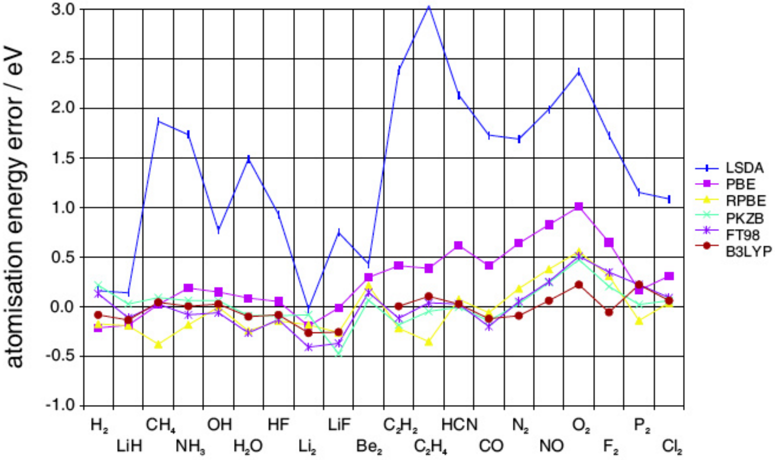
        - PBE0; among physicists
        - B3LYP; among chemists

Exchange-correlation functional: Jacob’s ladder



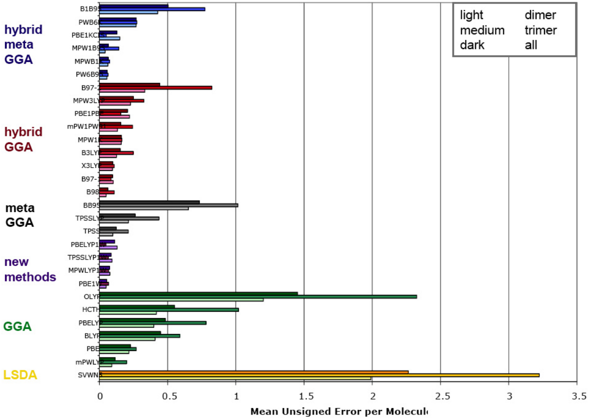
Exchange-correlation functional: Results

Small molecules



Exchange-correlation functional: Results

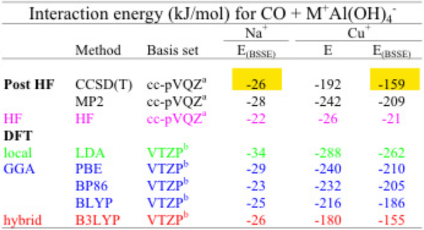
Water clusters



All DFT calculations use the MG3S (6-311+G(2df,2p)) basis set.

Dahlke, E. E.; Truhlar, D. G. *J. Phys. Chem. B* **2005**, *109*, 15677

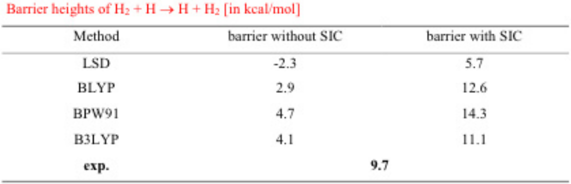
Exchange-correlation functional: Simple reactions



Interaction energy (kJ/mol) for CO + M$^+$Al(OH)$_4^-$

	Method	Basis set	Na$^+$	Cu$^+$	
			E$_{(BSSE)}$	E	E$_{(BSSE)}$
Post HF	CCSD(T)	cc-pVQZ^a	-26	-192	-159
	MP2	cc-pVQZ^a	-28	-242	-209
HF	HF	cc-pVQZ^a	-22	-26	-21
DFT					
local	LDA	VTZP^b	-34	-288	-262
GGA	PBE	VTZP^b	-29	-240	-210
	BP86	VTZP^b	-23	-232	-205
	BLYP	VTZP^b	-25	-216	-186
hybrid	B3LYP	VTZP^b	-26	-180	-155

1-T cluster model

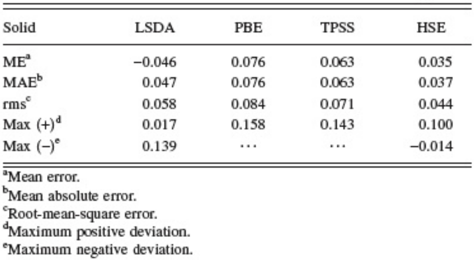


Barrier heights of $H_2 + H \rightarrow H + H_2$ [in kcal/mol]

Method	barrier without SIC	barrier with SIC
LSD	-2.3	5.7
BLYP	2.9	12.6
BPW91	4.7	14.3
B3LYP	4.1	11.1
exp.	**9.7**	

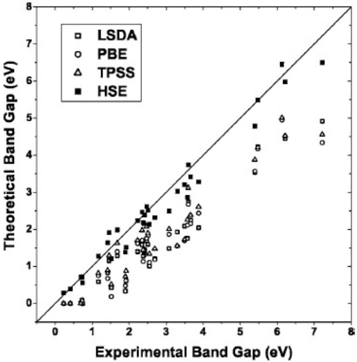
Exchange-correlation functional: Results

Solids



Solid	LSDA	PBE	TPSS	HSE
ME[a]	−0.046	0.076	0.063	0.035
MAE[b]	0.047	0.076	0.063	0.037
rms[c]	0.058	0.084	0.071	0.044
Max (+)[d]	0.017	0.158	0.143	0.100
Max (−)[e]	0.139	⋯	⋯	−0.014

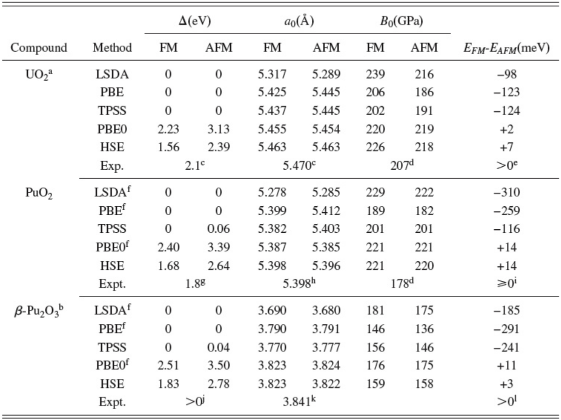
[a] Mean error.
[b] Mean absolute error.
[c] Root-mean-square error.
[d] Maximum positive deviation.
[e] Maximum negative deviation.



J Chem Phys **123** (2005) 174101

Exchange-correlation functional: Results

Magnetic oxides



		Δ(eV)		a_0(Å)		B_0(GPa)		
Compound	Method	FM	AFM	FM	AFM	FM	AFM	E_{FM}-E_{AFM}(meV)
UO_2[a]	LSDA	0	0	5.317	5.289	239	216	−98
	PBE	0	0	5.425	5.445	206	186	−123
	TPSS	0	0	5.437	5.445	202	191	−124
	PBE0	2.23	3.13	5.455	5.454	220	219	+2
	HSE	1.56	2.39	5.463	5.463	226	218	+7
	Exp.	2.1[c]		5.470[c]		207[d]		>0[e]
PuO_2	LSDA[f]	0	0	5.278	5.285	229	222	−310
	PBE[f]	0	0	5.399	5.412	189	182	−259
	TPSS	0	0.06	5.382	5.403	201	201	−116
	PBE0[f]	2.40	3.39	5.387	5.385	221	221	+14
	HSE	1.68	2.64	5.398	5.396	221	220	+14
	Expt.	1.8[g]		5.398[h]		178[d]		≥0[i]
β-Pu_2O_3[b]	LSDA[f]	0	0	3.690	3.680	181	175	−185
	PBE[f]	0	0	3.790	3.791	146	136	−291
	TPSS	0	0.04	3.770	3.777	156	146	−241
	PBE0[f]	2.51	3.50	3.823	3.824	176	175	+11
	HSE	1.83	2.78	3.823	3.822	159	158	+3
	Expt.	>0[j]		3.841[k]				>0[l]

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Functionals: Chemical shifts

Mean absolute deviation [ppm]

method	absolute	relative
HF	8.5	8.1
MP2	5.6	1.6
LDA	15.2	14.4
BLYP	15.0	7.8
B3LYP	13.0	7.9
PBE0	3.1	2.5

CH_4, NH_3, H_2O, C_2H_6, C_2H_4, C_2H_2, N_2, CF_4, …

Functionals: Chemical shifts in ozone

O_3 ; [ppm]

method	O_{terminal}	O_{central}
HF	-2793	-2717
MP2	$+1055$	$+2675$
CCSD(T)	-1208	-754
LDA	-1520	-914
BLYP	-1454	-892
B3LYP	-1673	-1115
PBE0	-1453	-1040
expr	-1290, -1254	-724, -688

DFT: Scaling

Scaling Behavior	Method
N^3	DFT(LSDA,GGA,meta)
N^4	HF, DFT(hybrid,hybrid meta)
N^5	MP2
N^6	MP3, CISD, MP4DQ, CCSD, QCISD
N^7	MP4,CCSD(T),QCISD(T)
N^8	MP5,CISDT,CCSDT
N^9	MP6
N^{10}	MP7,CISDTQ,CCSDTQ

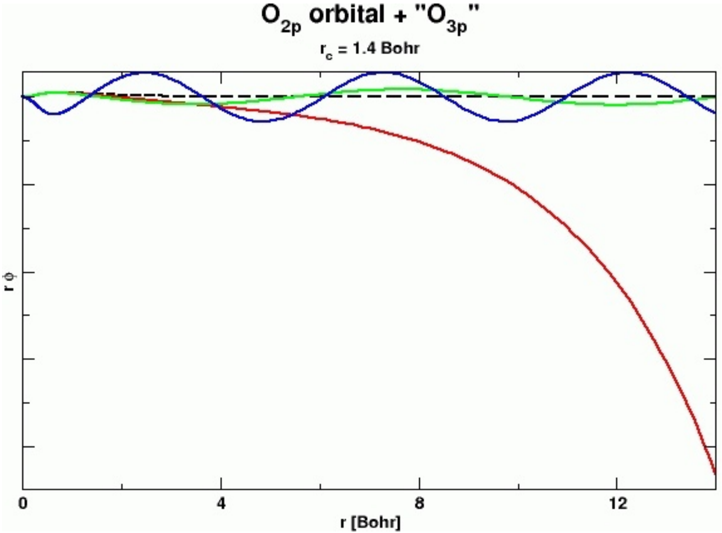
Summary

1. DFT
2. GIPAW-PP

Input for ld1.x

```
&input
  title = 'O'
  prefix = 'O'
  zed = 8.0
  rel = 1
  config = '1s2 2s2 2p4 3s-1 3p-1 3d-1'
  iswitch = 3
  dft = 'PBE'
/
&inputp
  pseudotype = 1
  tm = .true.
  lloc = 2
  file_pseudopw = 'O.pbe-tm-gipaw.UPF'
  lgipaw_reconstruction = .true.
/
3
 2S 1 0 2.00 0.00 1.40 1.40
 2P 2 1 4.00 0.00 1.40 1.40
 3D 3 2 -1.00 -0.30 1.40 1.40
&test
/
4
 2S 1 0 2.00 0.00 1.40 1.40
 2P 2 1 4.00 0.00 1.40 1.40
 3S 2 0 0.00 0.00 1.40 1.40
 3P 3 1 0.00 -0.10 1.40 1.40
```

Wave functions



Wave functions: Scaled