GOETHE UNIVERSITÄT FRANKFURT AM MAIN

Orbital-Dependent Exchange-Correlation Functionals in Density Functional Theory

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EMMI Workshop *From Ultracold Fermi Gases to Neutron-rich Many-Body Systems: Universal Aspects and Modern Approaches to Density Functional Theory*
(Darmstadt, March 21, 2013)

Kohn-Sham Equations

Idea: construct effective non-int. system with same n as int. system

$$n(\mathbf{r}) = \sum_k \Theta_k |\phi_k(\mathbf{r})|^2 \qquad \Theta_k = \begin{cases} 1 & \text{if } \epsilon_k \leq \epsilon_F \\ 0 & \text{else} \end{cases}$$

$\longrightarrow$ minimization of total energy $E[n]$ leads to (Kohn, Sham, 1965)

$$\left\{ -\frac{\nabla^2}{2m} + \underbrace{\underbrace{\sum_\alpha \frac{-Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}|}}_{= v_{\text{ext}}(\mathbf{r})} + \underbrace{\int d^3r' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{= v_{\text{H}}(\mathbf{r})} + \underbrace{\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}}_{= v_{\text{xc}}(\mathbf{r})}}_{v_s = v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}} \right\} \phi_k(\mathbf{r}) = \epsilon_k \, \phi_k(\mathbf{r})$$

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- yields exact n and E of int. system (for exact $E_{\text{xc}}[n]$), but not $|\Psi_0\rangle$
- extensions to spin-polarized, current-dependent, relativistic, time-dependent systems
  - presentation of formalism in simplest version
  - results based on Spin-DFT or relativistic DFT wherever necessary

Exchange-Correlation Energy

E_{xc} absorbs all non-trivial many-body effects

$$E_{\text{xc}}[n] \quad := \quad E[n] - T_{\text{s}}[n] - \int d^3r \, v_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r}) - E_{\text{H}}[n]$$

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$\uparrow$

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Basic idea behind decomposition of $E[n]$: Separate

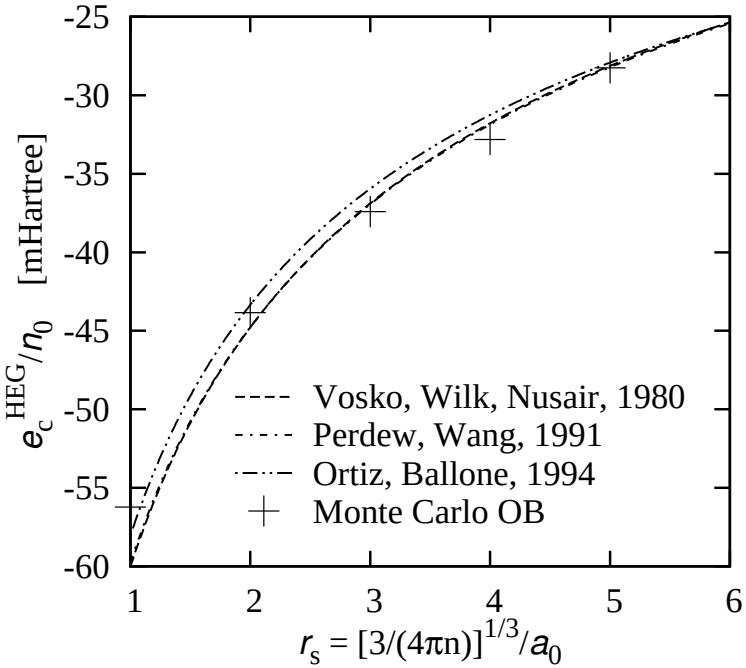
- managable and (hopefully) dominating contributions to $E[n]$
- more involved, but (hopefully) less important components, which can be dealt with by approximations

Local Density Approximation (LDA): 1st Generation E_{xc}

Idea: use available information on homogeneous electron gas (HEG)

$$e_{xc}^{HEG}(n_0) = \underbrace{-\frac{(3\pi^2 n_0)^{4/3}}{4\pi^3}}_{\text{exchange } e_x^{HEG}} + \underbrace{e_c^{HEG}(n_0)}_{\text{correlation}}$$

$e_c^{HEG}(n_0)$ known from Quantum Monte-Carlo studies, result used via analytical parameterization



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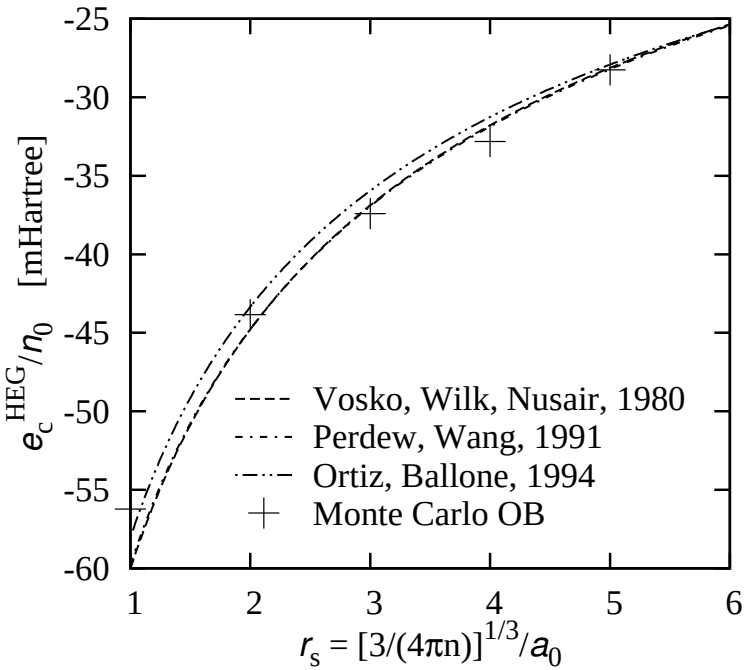

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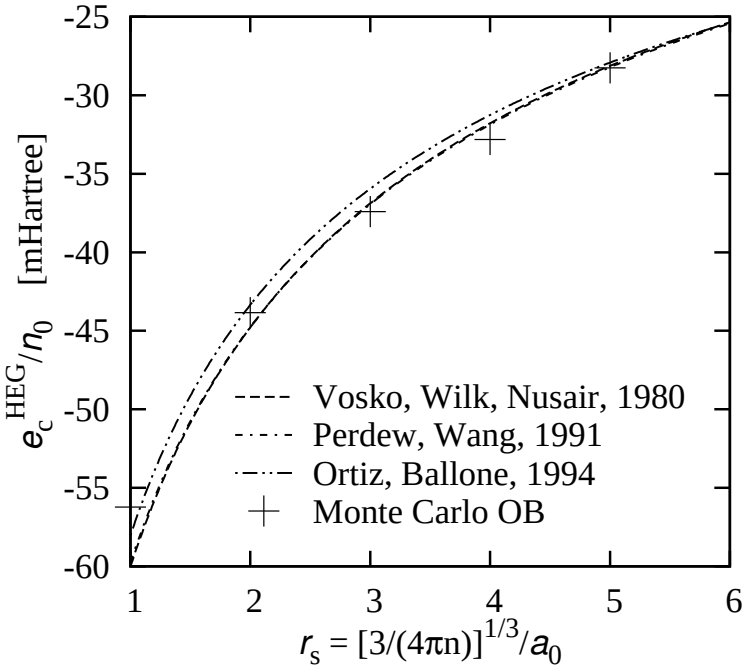

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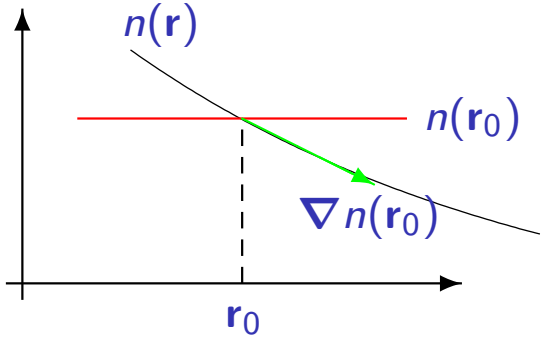
$$\Longrightarrow \quad v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(\mathbf{r})} = \frac{de_{xc}^{HEG}}{dn}(n(\mathbf{r})) \sim n^{1/3} + \ldots$$

{ extremely short-ranged

Gradient Corrections

Idea: use ∇n as local measure of inhomogenity



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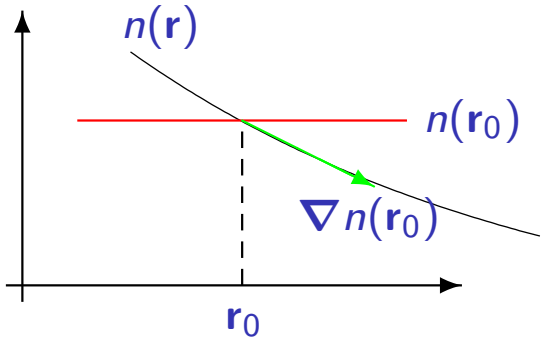

$$e_x(\mathbf{r}) \approx e_x^{\mathrm{HEG}}(n) \left[1 + \frac{10}{81} \xi + \ldots \right]$$

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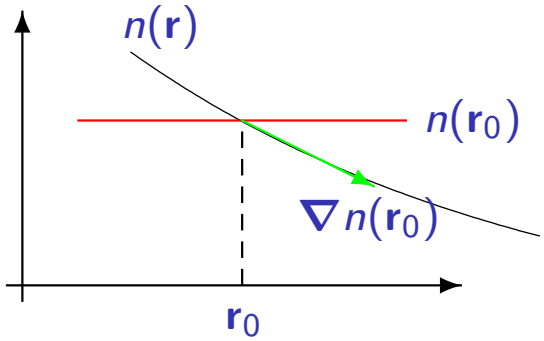

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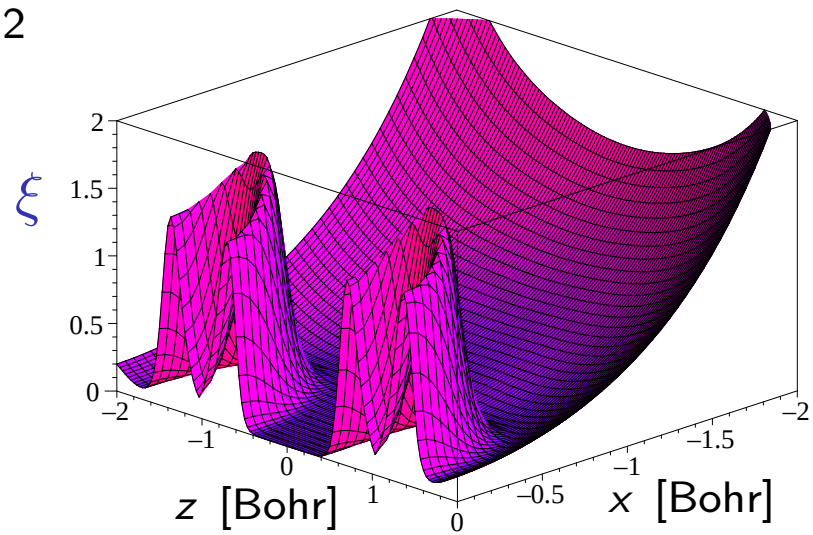
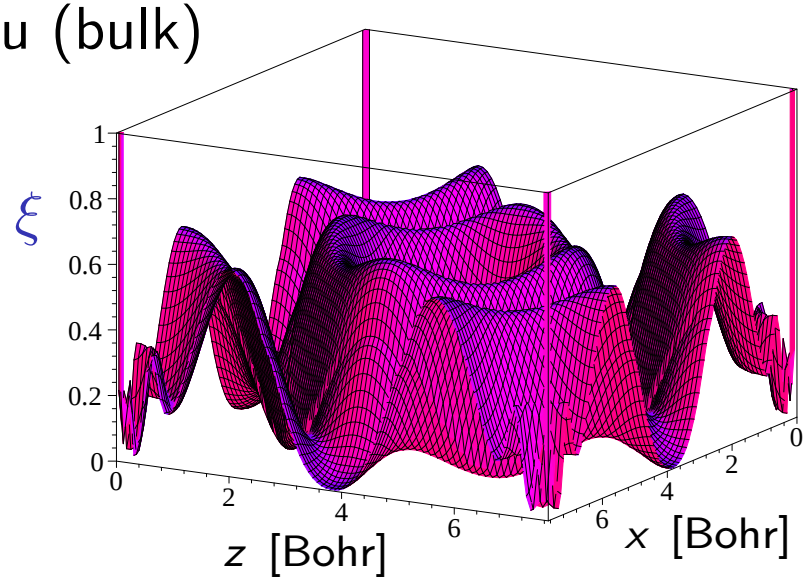
Convergence of gradient expansion?

N_2



Au (bulk)



Generalized Gradient Approximation: 2nd Generation E_{xc}

Problems with gradient expansion:

- v_x^{GE} diverges in asymptotic region of finite systems
- gradient expansion predicts incorrect ground state for metallic iron

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Solution: Partial resummation of gradient expansion

$$\underbrace{E_x^{GGA}[n]}_{\text{x-only (dominating source of error)}} = \int d^3r\, e_x^{HEG}(n) f(\xi) \quad ; \quad f(\xi) \underset{\xi<<1}{=} 1 + \underbrace{c_2\xi + \ldots}_{\text{to be determined}}$$

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Examples: (correlation even more complicated)

- Becke, PRA **38**, 3098 (1988)

$$f(\xi) = 1 + \frac{a\xi}{1 + b\sqrt{\xi}\,\mathrm{arsinh}(c\sqrt{\xi})}$$

a, b, c fitted to atomic E_x

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- Perdew, Burke, Ernzerhof, PRL **77**, 3865 (1996)

$$f(\xi) = 1 + \frac{a\xi}{1 + b\xi}$$

compatible with sum rules, etc:

$$\int d^3r'\, h_x(\mathbf{r}, \mathbf{r}') = -1$$

Full Potential LAPW Calculations for Metals

GGA = PW91 for exchange and correlation

System		a [Bohr]			B [GPa]		
		LDA	GGA	Expt.	LDA	GGA	Expt.
Li[a]	(bcc)	6.36	6.49	6.57	15	12	13
Al[a]	(fcc)	7.54	7.65	7.65	84	74	72
Fe[a]	(bcc)		5.36	5.41		215	172
Cu[b]	(fcc)	6.65	6.84	6.81	192	151	138
Pt[c]	(fcc)	7.37	7.53	7.40	308	247	283
Au[c]	(fcc)	7.65	7.89	7.67	217	154	171

[a] Dufek, Blaha, Schwarz, PRB **50**, 7279 (1994)

[b] Khein, Singh, Umrigar, PRB **51**, 4105 (1995)

[c] Schmid et al., Adv. Quant. Chem. **33**, 209 (1999)

Comparison of Various *Ab-Initio* Methods for Molecules

Johnson, Gill, Pople, JCP **98**, 5612 (1993)

- on basis of 32 experimentally well-studied molecules (H_2, NH_3, Li_2, OH_2, CO_2, H_3CCH_3, ...)
- technical treatment of DF and QC methods identical (basis sets etc)

Mean absolute error in spectroscopic constants: GGA = B88/VWN

		DF methods		QC methods		
		LDA	GGA	HF	MP2	QCISD
bond lengths	[Å]	0.021	0.018	0.020	0.014	0.013
bond angles	[Grad]	1.93	2.24	1.99	1.78	1.79
vibr. frequencies	[cm^{-1}]	75	61	168	99	42
bond energies	[eV]	1.55	0.19	3.73	0.97	1.25

for comparison: bond energy of OH_2=9.51 eV

Problems with LDA and GGA: Rydberg states

Consider Helium atom as an example

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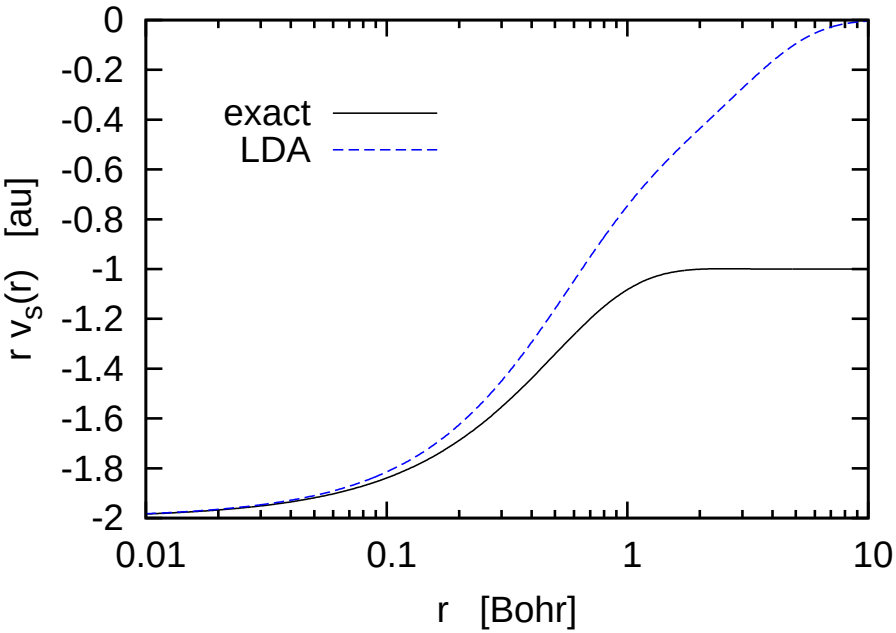

exact $\quad v_s(|\mathbf{r}| \to \infty) = -\dfrac{1}{|\mathbf{r}|}$

LDA $\quad v_s(|\mathbf{r}| \to \infty) \sim e^{-\alpha|\mathbf{r}|}$

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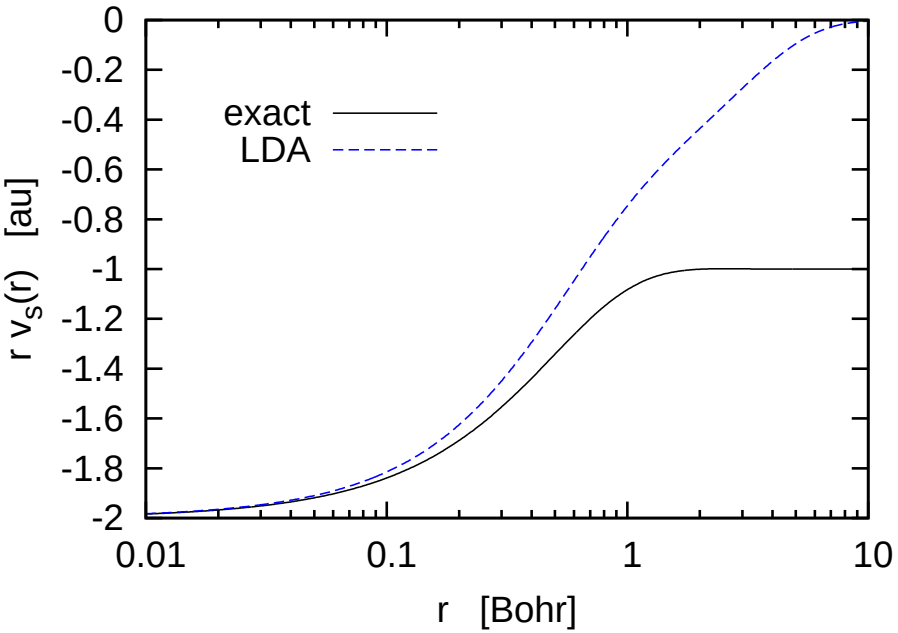

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individual components: $n \sim e^{-3\alpha|\mathbf{r}|}$

$$v_H(|\mathbf{r}| \to \infty) = \frac{2}{|\mathbf{r}|} = -v_{ext}(\mathbf{r})$$

$$v_x^{LDA}(|\mathbf{r}| \to \infty) \sim -e^{-\alpha|\mathbf{r}|}$$

since $\quad v_x^{LDA} = -(3\pi^2 n)^{1/3}/\pi$

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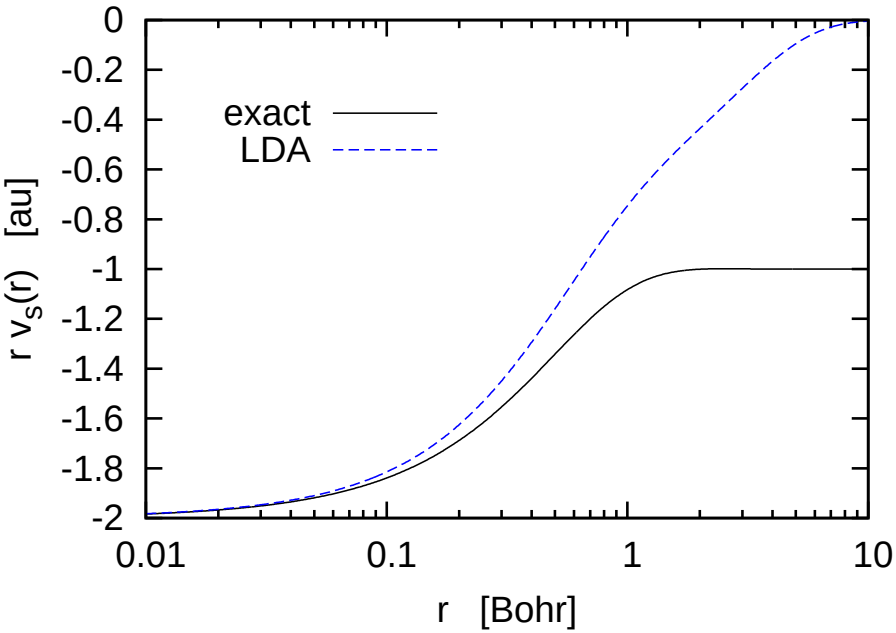

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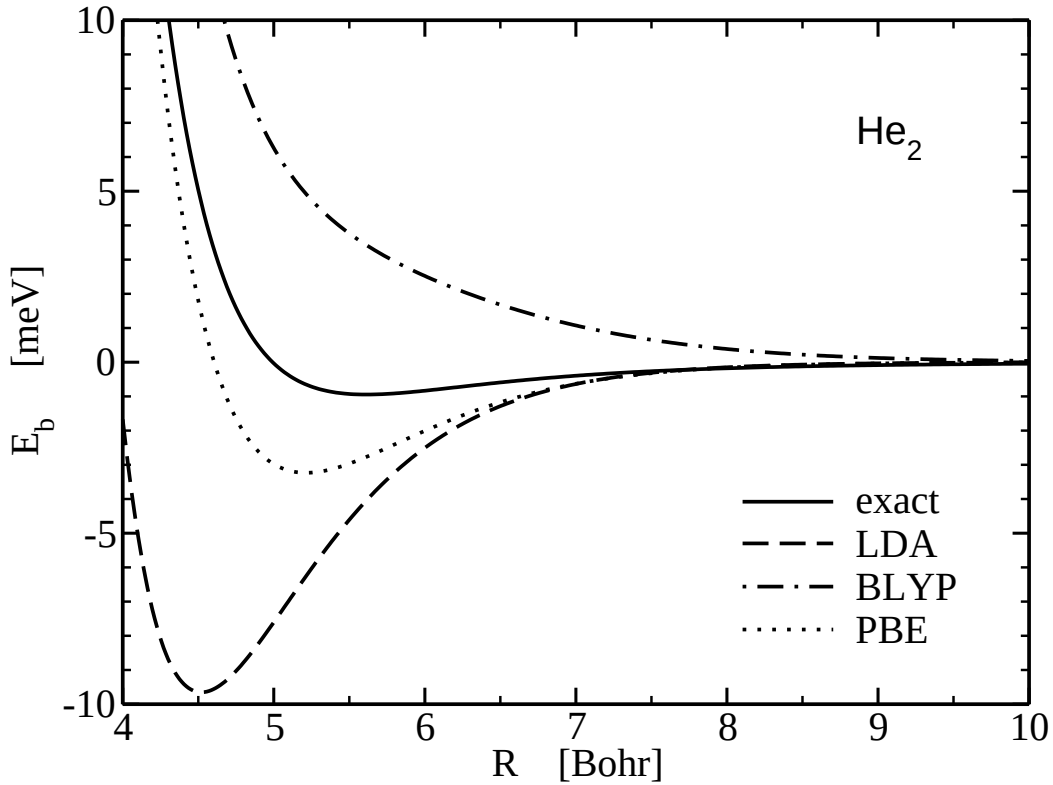
origin of problem: self-interaction in E_H cancelled only partially by E_x^{LDA}

$$E_H = \frac{1}{2}\int d^3r\, d^3r'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \to \quad E_H^{SI} = \frac{1}{2}\sum_i \Theta_i \int d^3r\, d^3r'\, \frac{|\phi_i(\mathbf{r})|^2 |\phi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

Problems with LDA and GGA: Dispersion forces

Consider He dimer as an example



dispersion: $E_{\text{int}}(R) \sim -\frac{C_6}{R^6}$

LDA: $E_{\text{int}}(R) \sim e^{-\alpha R}$

exact: Aziz, Slaman, JCP **94**, 8047 (1991)

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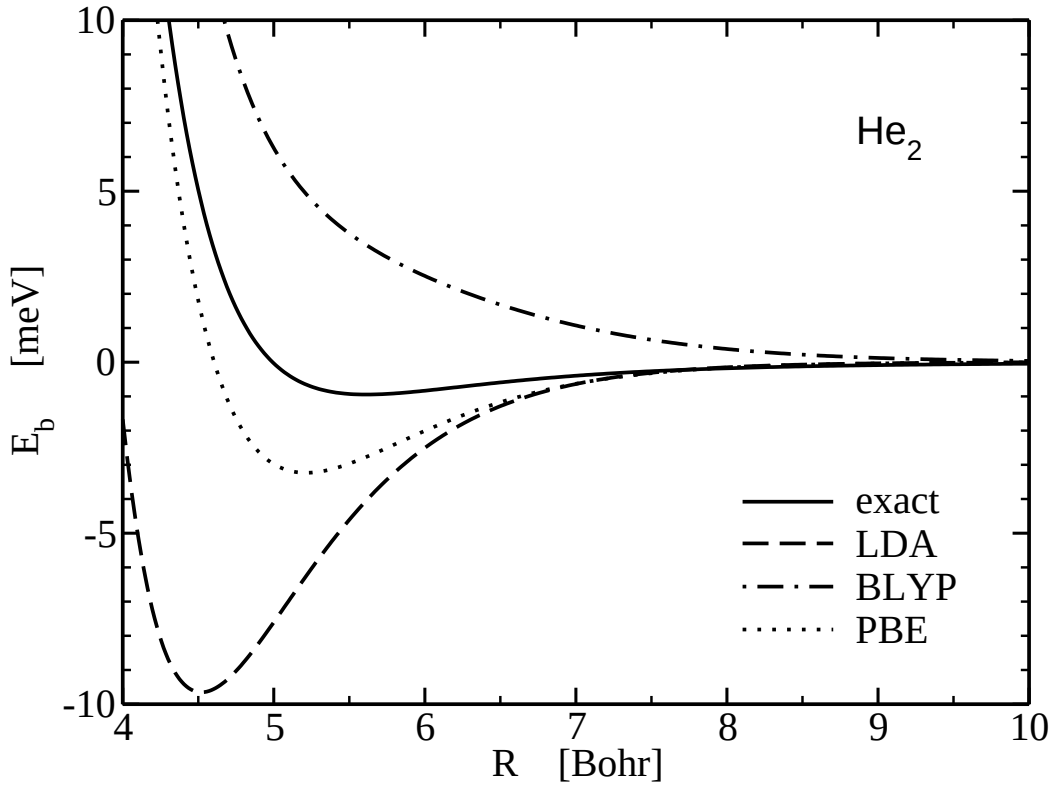

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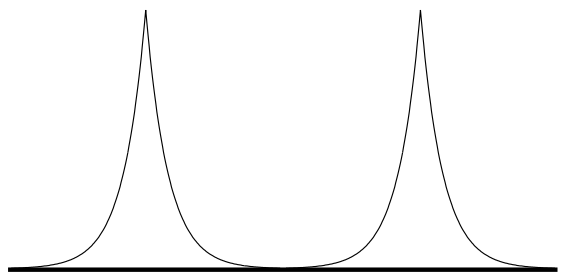
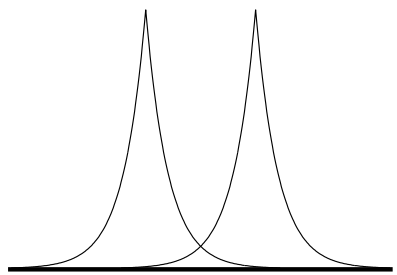


LDA:



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origin of problem: locality of LDA/GGA correlation functionals

Problems with LDA and GGA: Semiconductors

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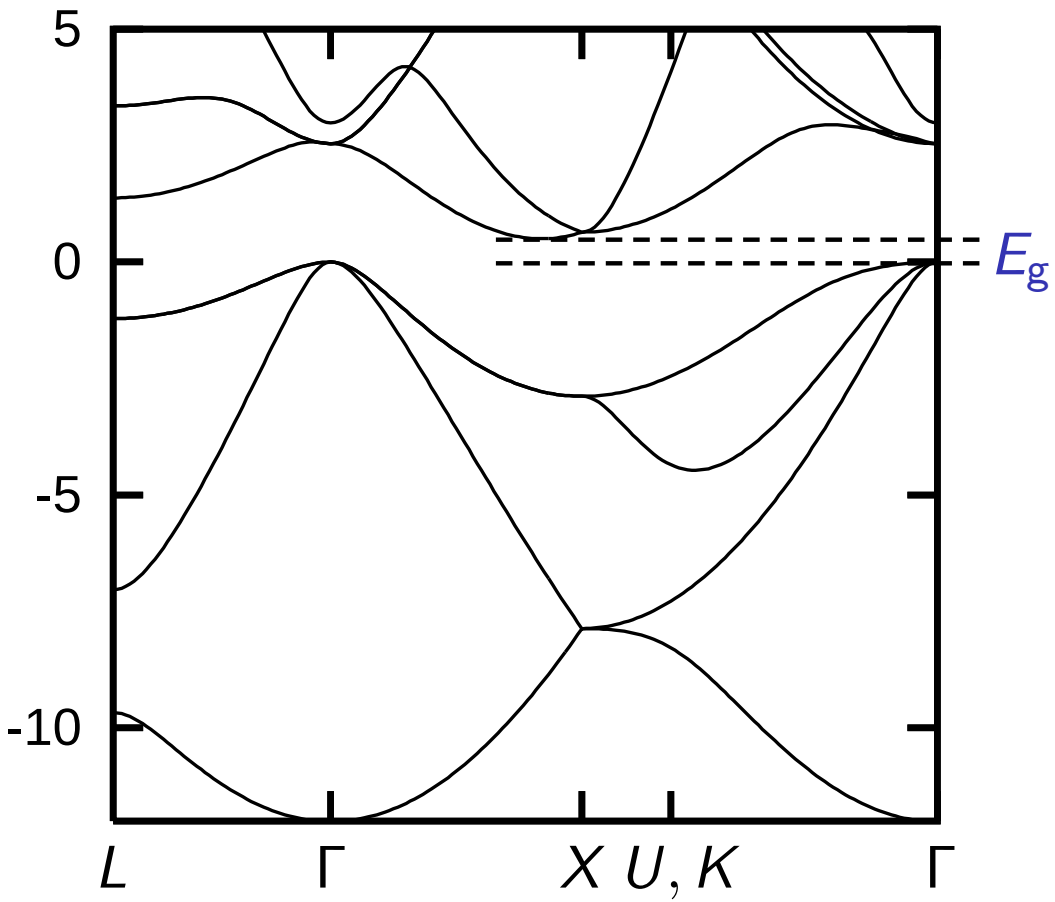

qualitatively correct, but

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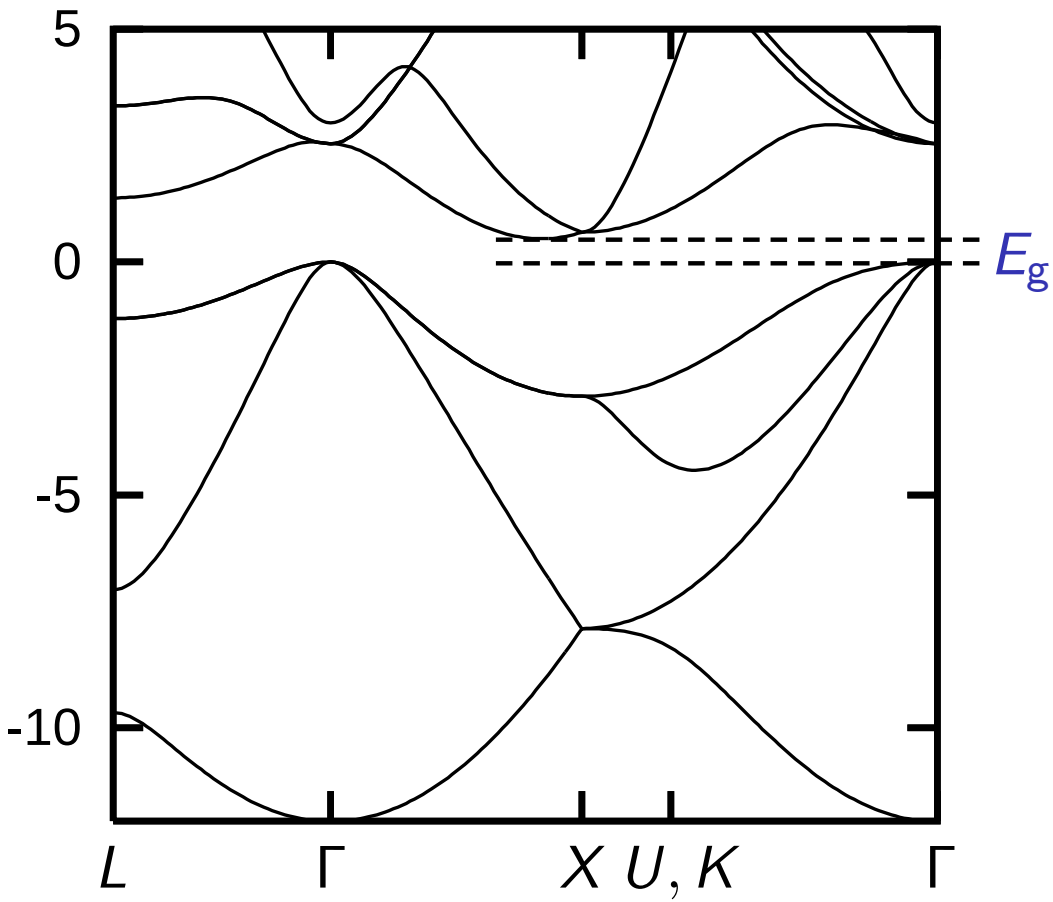

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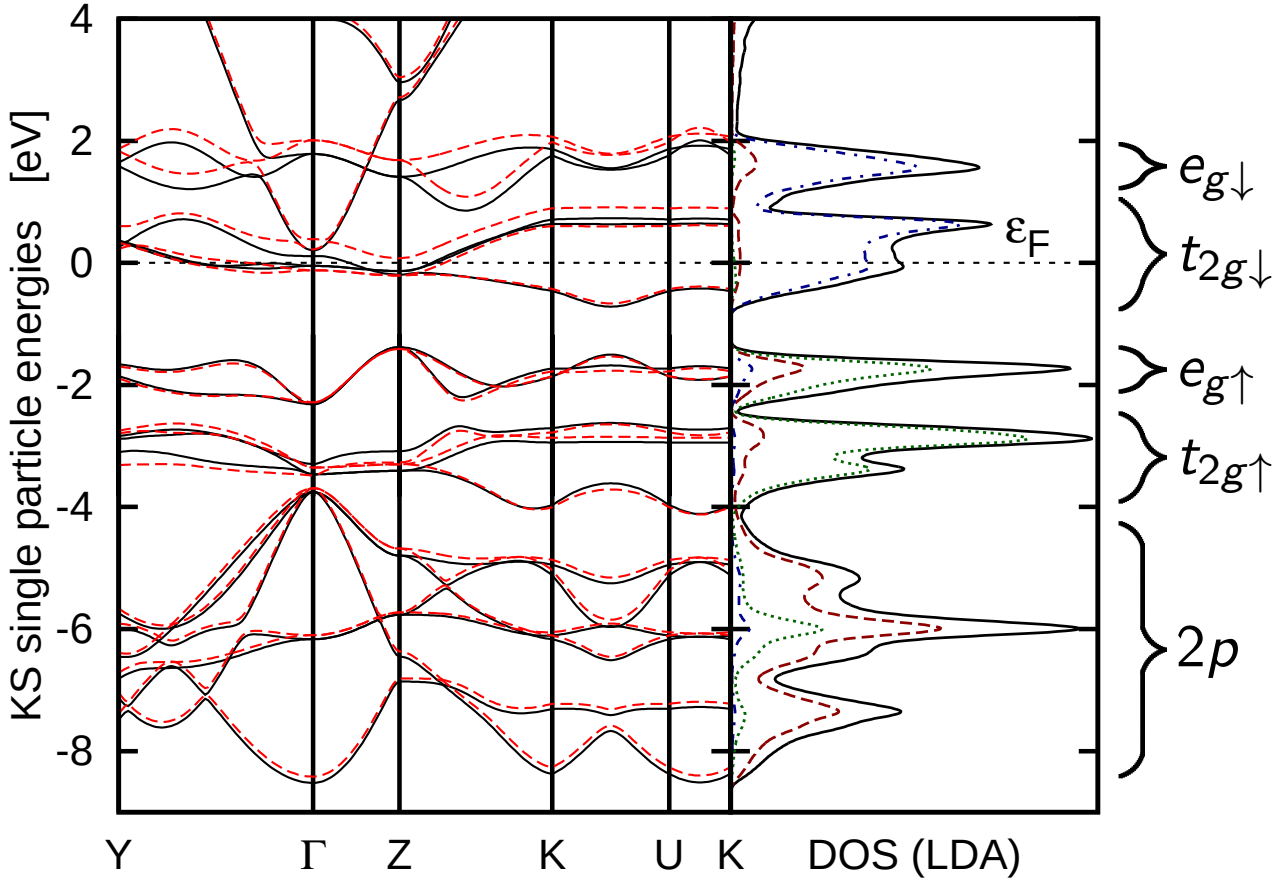
Problems with LDA and GGA: Highly correlated systems

Consider FeO in AF-II phase as an example



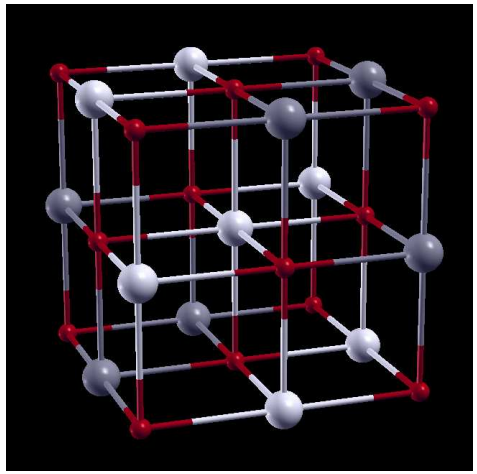
LDA = black
PBE GGA = red

FeO is insulating: $E_g = 2.4\,\text{eV}$

Bowen, Adler, Auker, J. Solid State Chem. **12**, 355 (1975)

Basic properties of prototype TMO: NiO

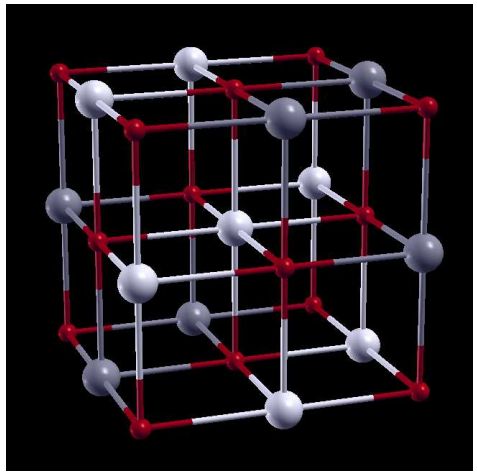
- rock-salt structure ($a = 7.88\,\text{Bohr}$)



qualitative band structure

Basic properties of prototype TMO: NiO

- rock-salt structure ($a = 7.88\,\text{Bohr}$)
- antiferromagnetic
  (Néel temperature $T_N = 523^\circ\,\text{K}$)
  $\longrightarrow$ two magnetic sublattices (AFII-type)
  $\longrightarrow$ local moments persist beyond T_N



qualitative band structure

Basic properties of prototype TMO: NiO

- rock-salt structure ($a = 7.88\,\text{Bohr}$)
- antiferromagnetic
  (Néel temperature $T_N = 523^\circ\,\text{K}$)
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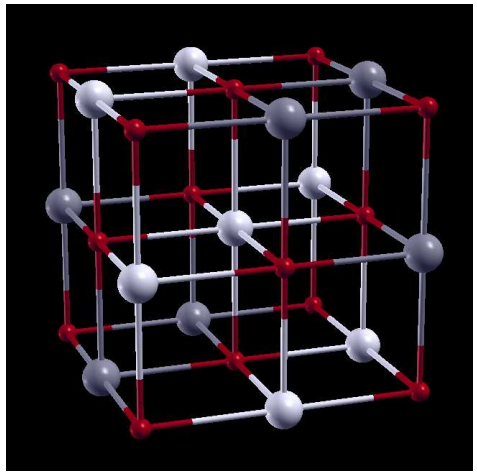
- insulating (up to $1400^\circ\,\text{K}$)
  $\longrightarrow$ large band gap ($\approx 4\,\text{eV}$ – indep. of T)



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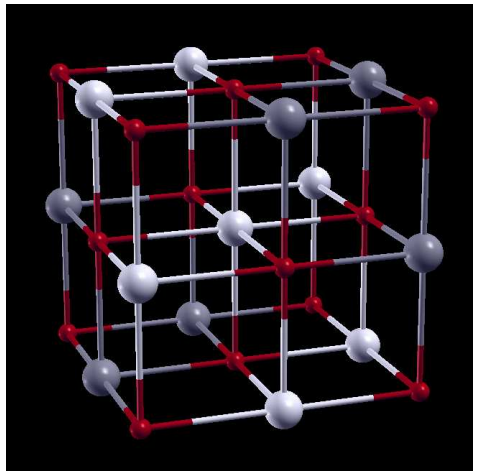

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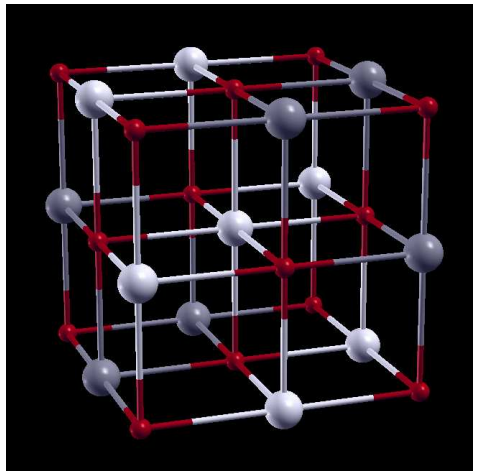

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Complications:

- rhombohedral distortion
- no pure samples in case of FeO
- spin-orbit coupling

$\longrightarrow$ irrelevant for existence of gap: ignored in the following

$\longrightarrow$ focus on ground state for $T = 0$

qualitative band structure

TMOs in AF-II phase: qualitative picture of band structure within single-particle picture

Starting point: transfer of TM $4s$ electrons to O $2p$ states
$\longrightarrow$ TM $3d$ experience octahedral crystal field

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atomic
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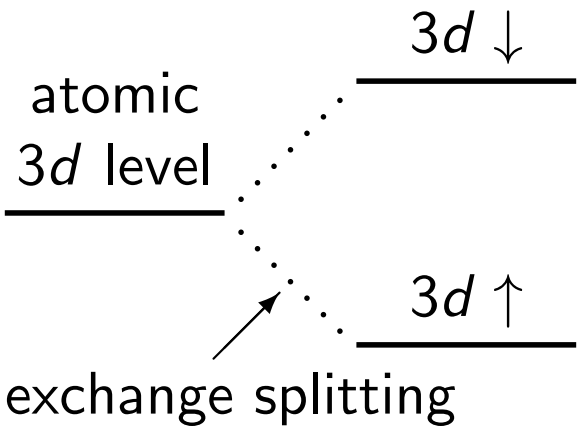

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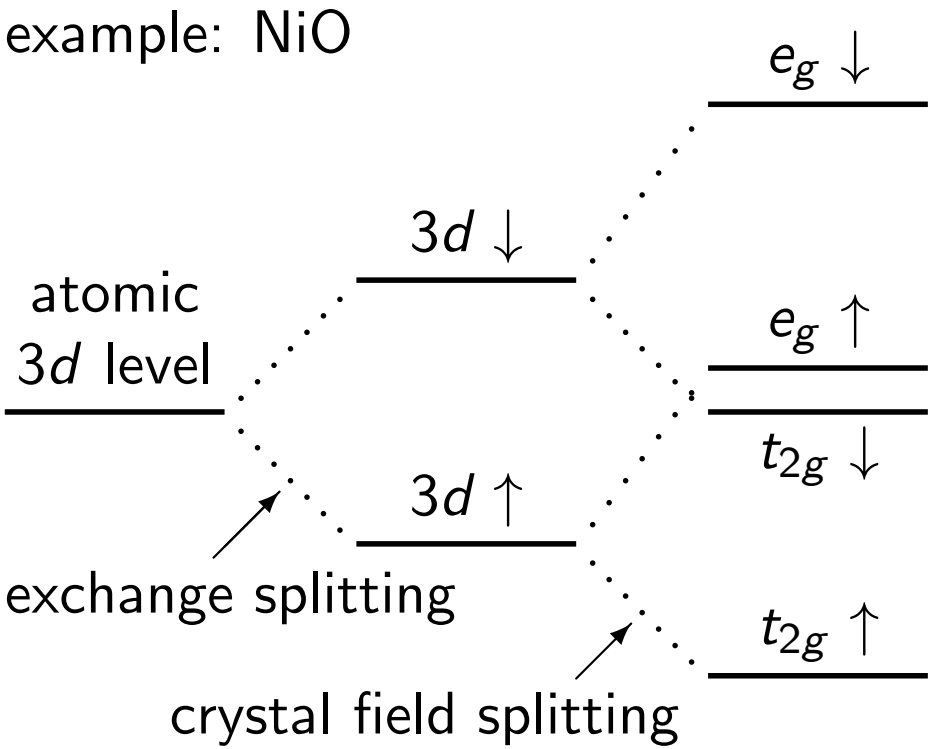

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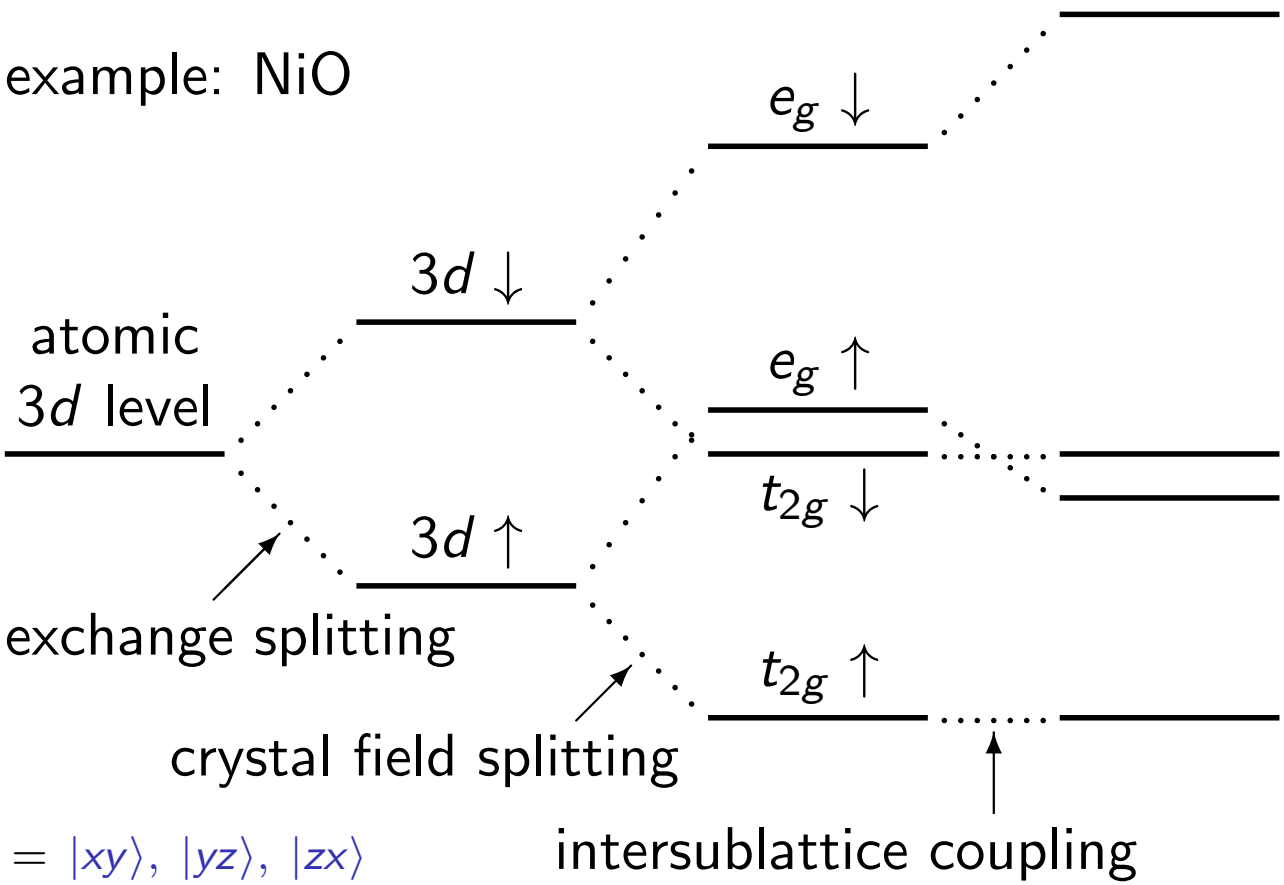

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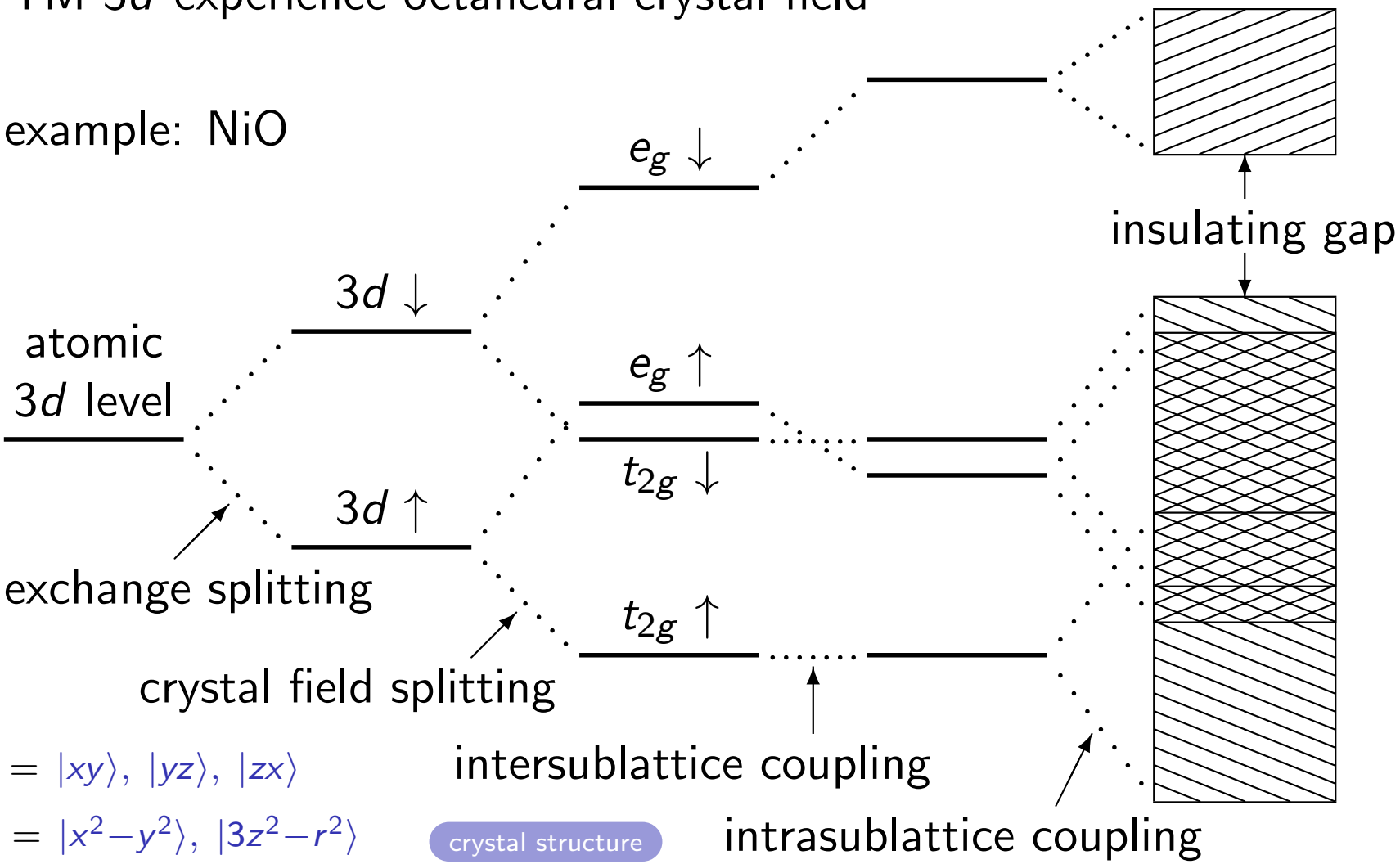

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Hints from successful methods:

- SIC-LDA Svane, Gunnarsson, PRL **65**, 1148 (1990)
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$\longrightarrow$ suggests that elimination of self-interaction is crucial

$\longrightarrow$ use exact E_x

Exact exchange

Definition of exact exchange (EXX): in terms of KS states

$$E_{\mathrm{x}} = -\frac{1}{2}\sum_{ij}\Theta_i\Theta_j\int^3 r\, d^3r'\,\frac{\phi_i^\dagger(\mathbf{r})\phi_j(\mathbf{r})\phi_j^\dagger(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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$\longrightarrow$ use chain rule for functional differentiation twice

$$\frac{\delta E_{\mathrm{x}}}{\delta n(\mathbf{r})} = \int d^3r'\,\frac{\delta v_{\mathrm{s}}(\mathbf{r}')}{\delta n(\mathbf{r})}\,\frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\mathbf{r}')}$$

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$\longrightarrow$ multiply by $\delta n(\mathbf{r}')/v_{\mathrm{s}}(\mathbf{r})$

$$\int d^3r'\,\frac{\delta n(\mathbf{r}')}{\delta v_{\mathrm{s}}(\mathbf{r})}\,\frac{\delta E_{\mathrm{x}}}{\delta n(\mathbf{r}')} = \sum_k\int d^3r'\,\frac{\delta\phi_k^\dagger(\mathbf{r}')}{\delta v_{\mathrm{s}}(\mathbf{r})}\,\frac{\delta E_{\mathrm{x}}}{\delta\phi_k^\dagger(\mathbf{r}')} + c.c.$$

$\longrightarrow$ basic derivative may be evaluated by variation of KS equations

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Optimized potential method (OPM) Talman, Shadwick, PRA **14**, 36 (1976)

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stationary response function of KS-system

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$\longrightarrow$ applicable to variety of other orbital-dependent functionals (eigenvalue-dependence of E_{xc} leads to additional term)

$\longrightarrow$ several schemes for solution

OPM equation on reciprocal lattice

$$
\begin{aligned}
v_{\mathrm{x}}(\mathbf{G}) &= \sum_{\mathbf{G}'} \chi_{\mathrm{s}}^{-1}(\mathbf{G},\mathbf{G}')\,\Lambda_{\mathrm{x}}(\mathbf{G}') \\
\chi_{\mathrm{s}}(\mathbf{G},\mathbf{G}') &= \int_{1\mathrm{BZ}} \frac{d^3k}{(2\pi)^3} \sum_{\alpha\alpha';\,\alpha'\neq\alpha} \frac{\Theta_{\mathbf{k}\alpha}-\Theta_{\mathbf{k}\alpha'}}{\epsilon_{\mathbf{k}\alpha}-\epsilon_{\mathbf{k}\alpha'}}\, O_{\mathbf{k}\alpha,\mathbf{k}\alpha'}(\mathbf{G})\, O_{\mathbf{k}\alpha',\mathbf{k}\alpha}(-\mathbf{G}') \\
\Lambda_{\mathrm{x}}(\mathbf{G}) &= \int_{1\mathrm{BZ}} \frac{d^3k}{(2\pi)^3} \sum_{\alpha\alpha';\,\alpha'\neq\alpha} \frac{\Theta_{\mathbf{k}\alpha}-\Theta_{\mathbf{k}\alpha'}}{\epsilon_{\mathbf{k}\alpha}-\epsilon_{\mathbf{k}\alpha'}}\, S_{\mathbf{k}\alpha\alpha'}\, O_{\mathbf{k}\alpha,\mathbf{k}\alpha'}(\mathbf{G}) \\
S_{\mathbf{k}\alpha\alpha'} &= -\int_{1\mathrm{BZ}} \frac{d^3k''}{(2\pi)^3} \sum_{\alpha''\mathbf{G}} \frac{4\pi e^2\,\Theta_{\mathbf{k}''\alpha''}}{(\mathbf{k}-\mathbf{k}''+\mathbf{G})^2}\, O^{\dagger}_{\mathbf{k}''\alpha'',\mathbf{k}\alpha'}(\mathbf{G})\, O_{\mathbf{k}''\alpha'',\mathbf{k}\alpha}(\mathbf{G}) \\
O_{\mathbf{k}\alpha,\mathbf{k}'\alpha'}(\mathbf{G}) &= \sum_{\mathbf{G}'} c^{\dagger}_{\mathbf{k}\alpha}(\mathbf{G}')\, c_{\mathbf{k}'\alpha'}(\mathbf{G}'+\mathbf{G}) \;=\; O^{\dagger}_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(-\mathbf{G}) \\
\phi_{\mathbf{k}\alpha}(\mathbf{r}) &= \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}\, c_{\mathbf{k}\alpha}(\mathbf{G}) \;=\; \text{Bloch states} \\
\Theta_{\mathbf{k}\alpha} &= \text{occupation factor}
\end{aligned}
$$

technical details

Krieger-Li-Iafrate approximation (KLI)

OPM computationally involved: approximate analytical solution of interest

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OPM computationally involved: approximate analytical solution of interest

$\longrightarrow$ simplest approach: closure approximation KLI, Phys. Lett. **146**A, 256 (1990)

$$G_k(\mathbf{r},\mathbf{r}') = \sum_{l\neq k} \frac{\phi_l(\mathbf{r})\phi_l^\dagger(\mathbf{r}')}{\epsilon_l - \epsilon_k} \approx \sum_{l\neq k} \frac{\phi_l(\mathbf{r})\phi_l^\dagger(\mathbf{r}')}{\Delta\overline{\epsilon}} = \frac{\delta^{(3)}(\mathbf{r}-\mathbf{r}') - \phi_k(\mathbf{r})\phi_k^\dagger(\mathbf{r}')}{\Delta\overline{\epsilon}}$$

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$\longrightarrow$ insertion into OPM integral equation: $\Delta\bar{\epsilon}$ drops out

$$\begin{aligned} v_{\mathrm{x}}^{\mathrm{KLI}}(\mathbf{r}) &= \frac{1}{2n(\mathbf{r})} \sum_k \left\{ \left[\phi_k^\dagger(\mathbf{r}) \frac{\delta E_{\mathrm{x}}}{\delta\phi_k^\dagger(\mathbf{r})} + c.c. \right] + |\phi_k(\mathbf{r})|^2 \Delta v_k \right\} \\ \Delta v_k &= \int d^3r \left[\Theta_k |\phi_k(\mathbf{r})|^2 v_{\mathrm{x}}^{\mathrm{KLI}}(\mathbf{r}) - \phi_k^\dagger(\mathbf{r}) \frac{\delta E_{\mathrm{x}}}{\delta\phi_k^\dagger(\mathbf{r})} \right] + c.c. \end{aligned}$$

- either solved iteratively or via linear equations for $\int d^3r |\phi_k|^2 v_{\mathrm{x}}^{\mathrm{KLI}}$
- preserves exact cancellation of self-interaction
- high accuracy observed for many systems

Exchange-only ground state energies: Atoms

Selfconsistent results for atoms with closed subshells (in mHartree).

Atom	E_{tot}	$E_{\text{tot}} - E_{\text{tot}}^{\text{OPM}}$			
	OPM[a]	KLI	LDA	GGA[c]	HF[b]
He	−2861.7	0.0	138.0	6.5	0.0
Be	−14572.4	0.1	349.1	18.2	−0.6
Ne	−128545.4	0.6	1054.7	−23.5	−1.7
Mg	−199611.6	0.9	1362.8	−0.5	−3.1
Ar	−526812.2	1.7	2294.8	41.2	−5.3
Ca	−676751.9	2.2	2591.8	25.7	−6.3
Zn	−1777834.4	3.7	3924.5	−252.6	−13.8

[a] Engel, Vosko, PRA **47**, 2800 (1993)

[b] Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977)

[c] PW91 — Perdew et al., PRB **46**, 6671 (1992)

- OPM and HF energies very close to each other
- KLI approximation very accurate
- GGA improves substantially over LDA

Exchange-only spectroscopic constants

Selfconsistent results for diatomic molecules

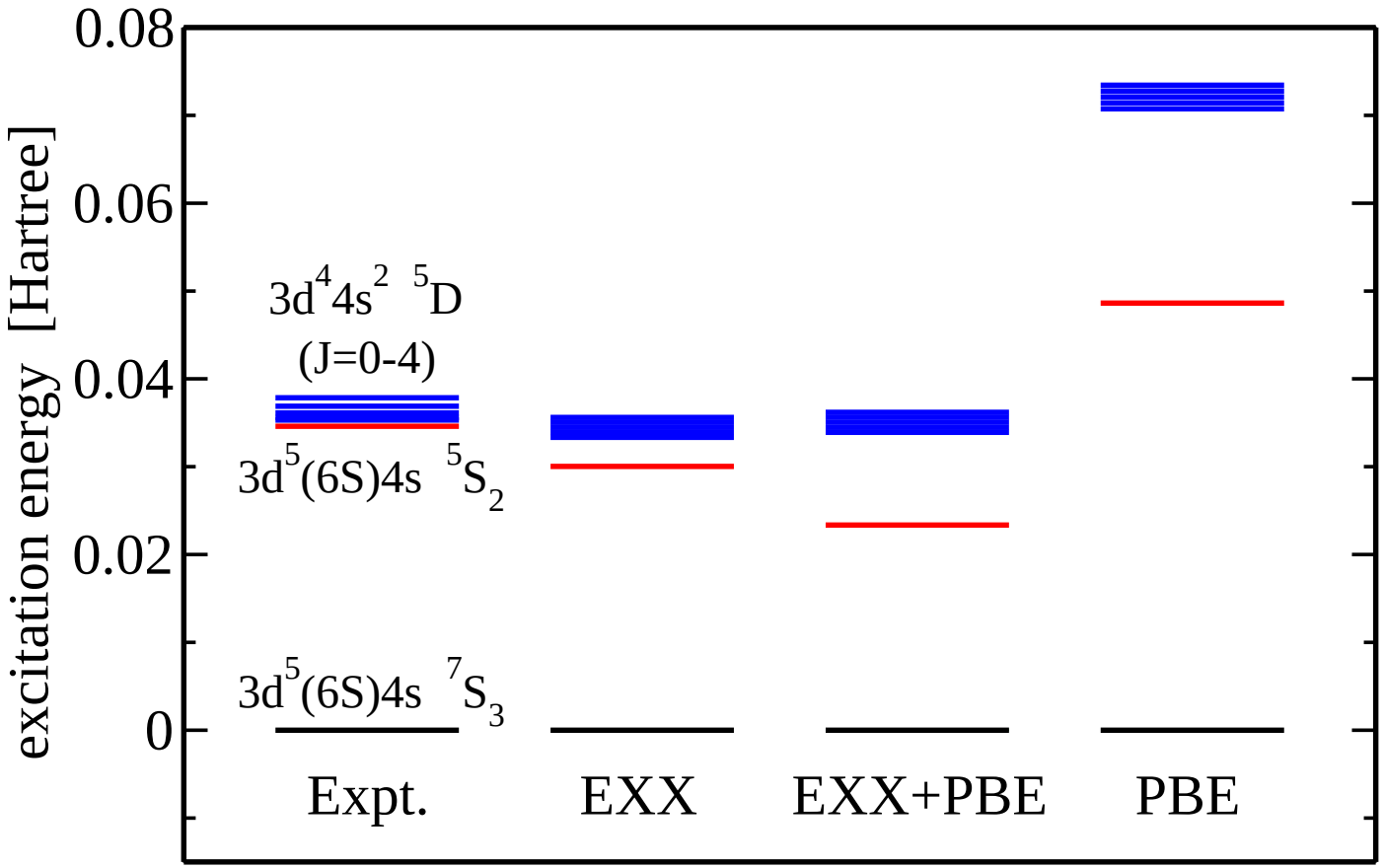
	method	R_e [Bohr]	D_e [eV]	ω_e [cm^{-1}]
H_2	KLI	1.386	3.638	4603
	HF	1.386	3.631	4583
N_2	KLI	2.011	4.972	2736
	HF	2.04	4.952	2738
O_2	KLI	2.184	1.441	1981
	HF	2.21	1.455	2002
CO	KLI	2.080	7.530	2444
	HF	2.105	7.534	2439
Cl_2	KLI	3.727	(1.083)	613
	HF	3.732	(1.23)	614

- only few full OPM data available
- agreement of KLI and HF results implies high accuracy of KLI

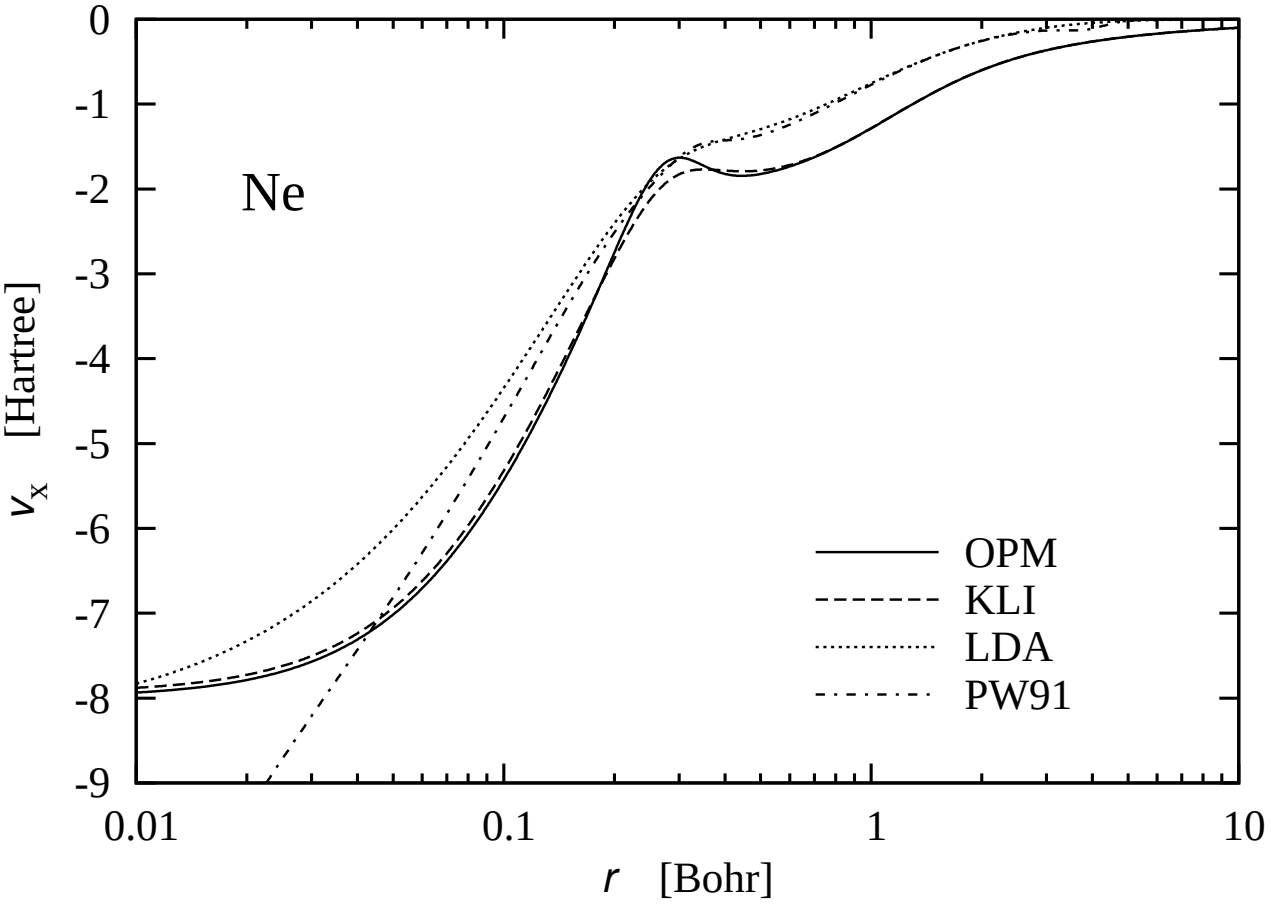
KLI data from Engel, Höck, Dreizler, PRA **62**, 042502 (2000)

HF data from various sources

Low-Lying Levels of Chromium Atom: Relative stability of different spin-states

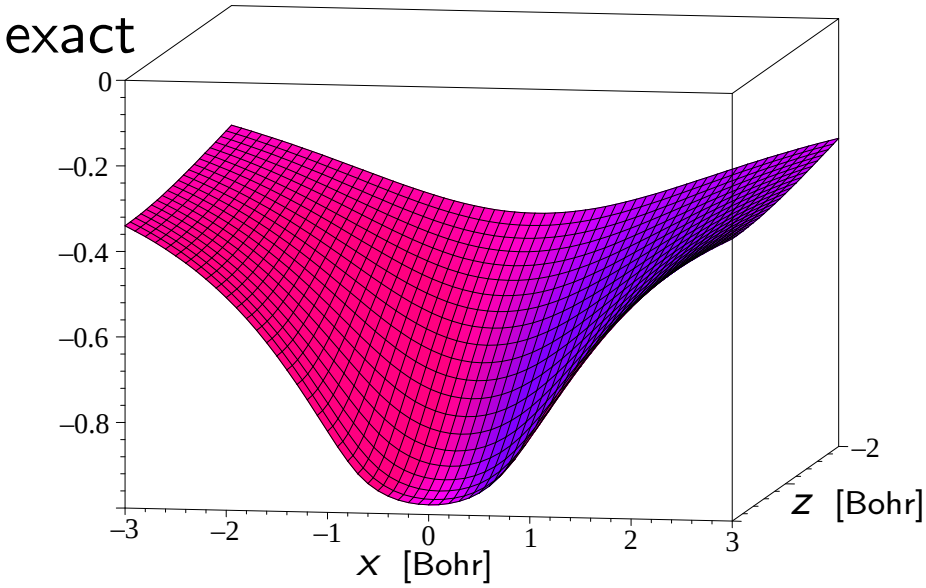


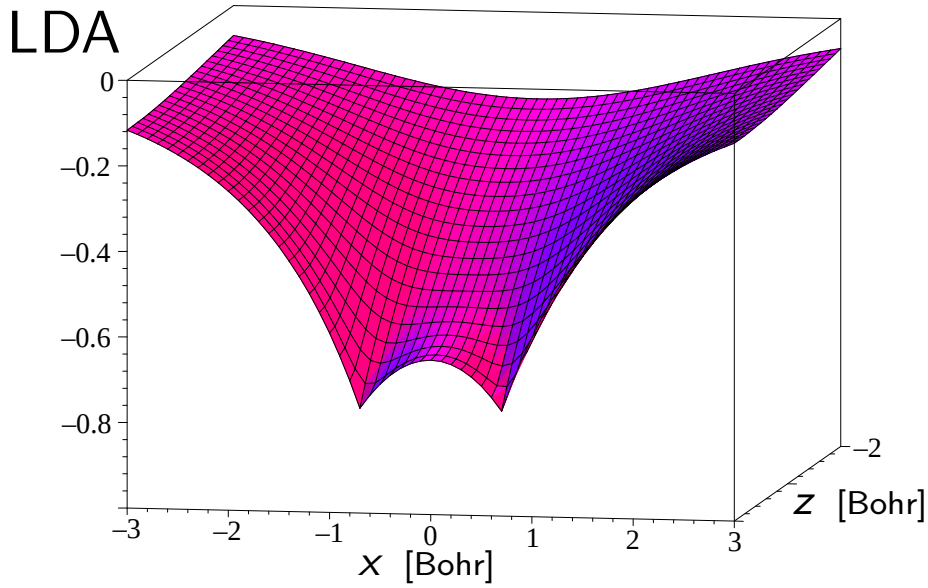
Exchange potentials: I) Atoms — Ne



- OPM and KLI potentials self-interaction free
- shell structure more pronounced in OPM potential
- KLI much more accurate than LDA or GGA

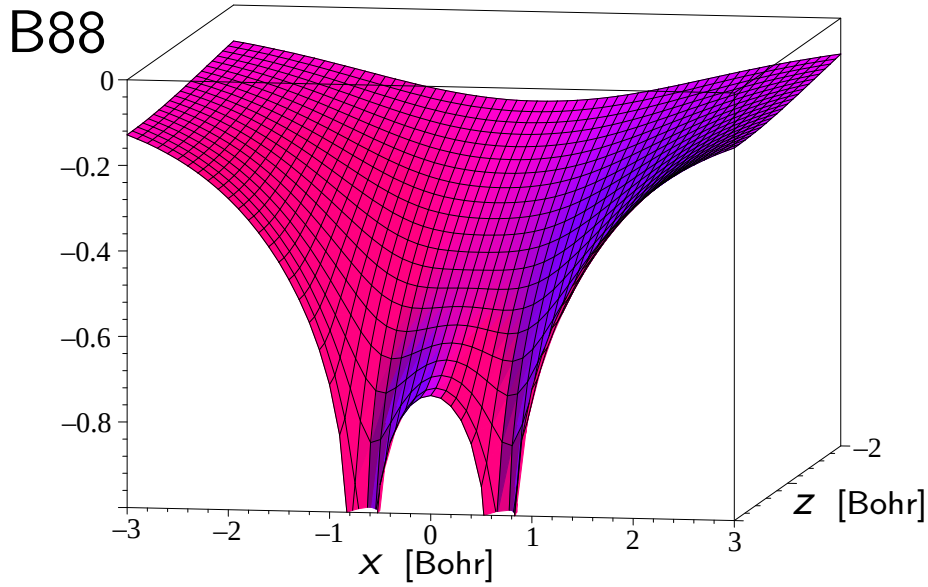
Exchange potentials: II) Molecules — H_2





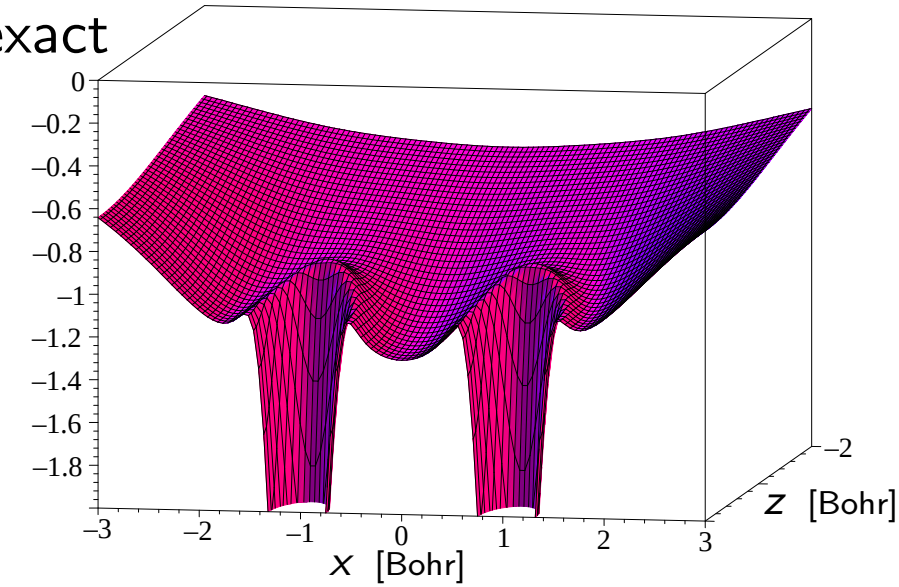
in case of H_2:

exchange reduces to pure SIC

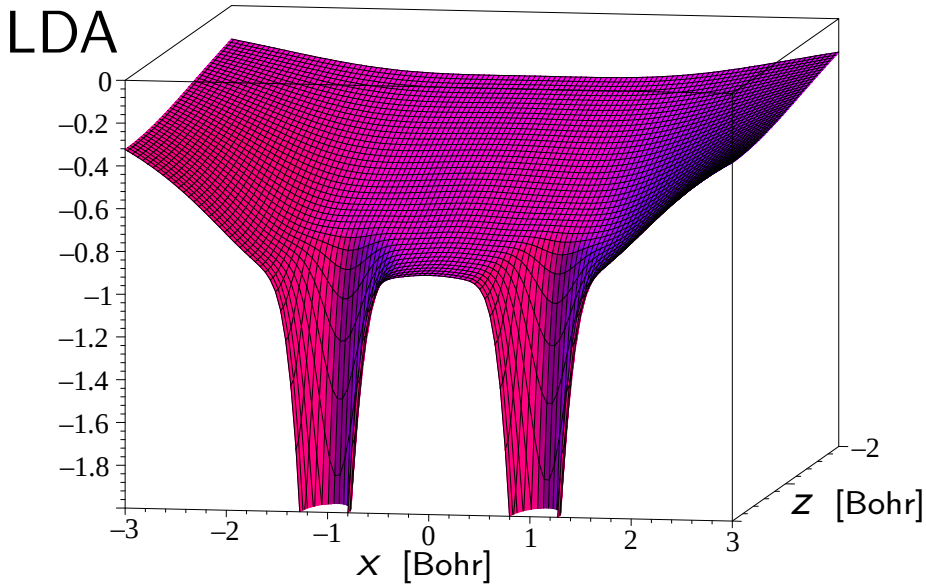


Exchange potentials: II) Molecules — N_2

exact

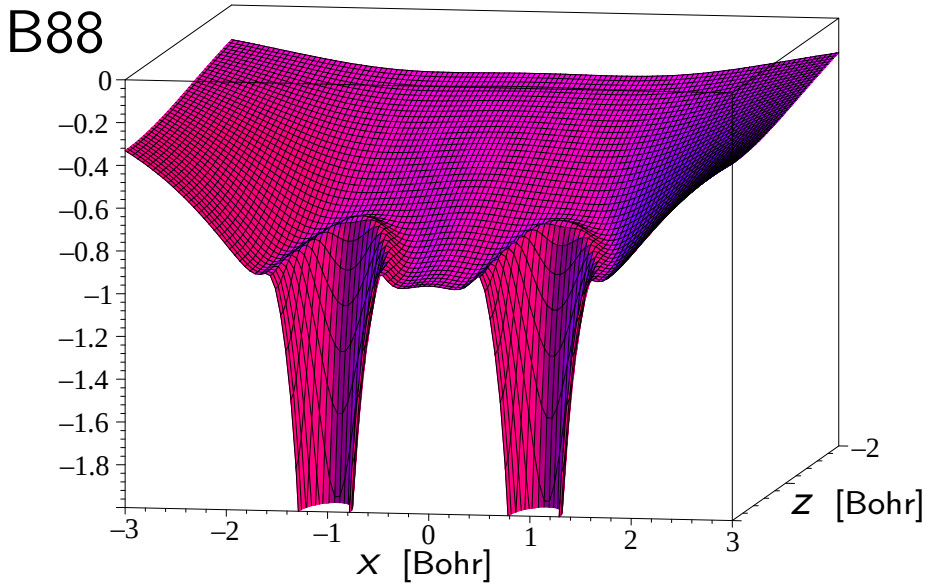


LDA



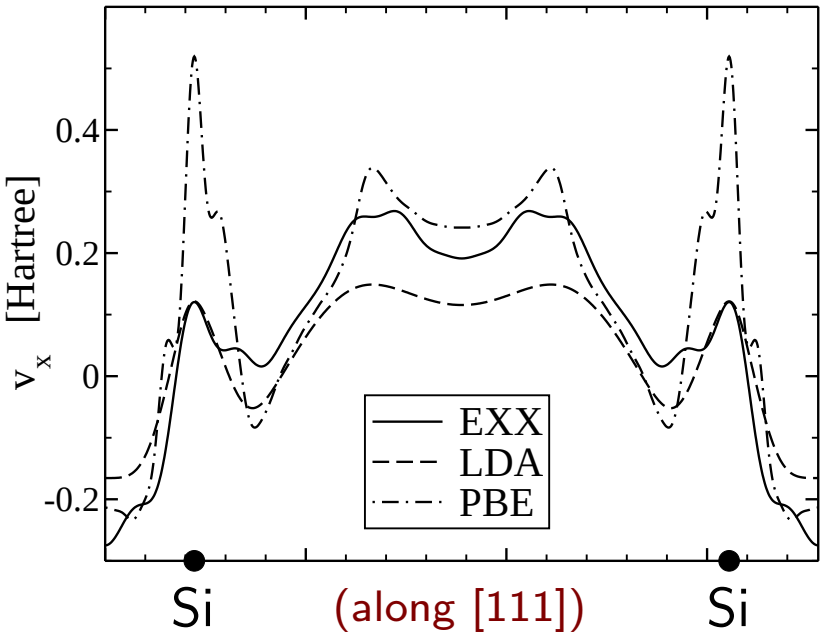
exact = exact E_x plus KLI

B88



Role of Exact Exchange: Semiconductors

Si



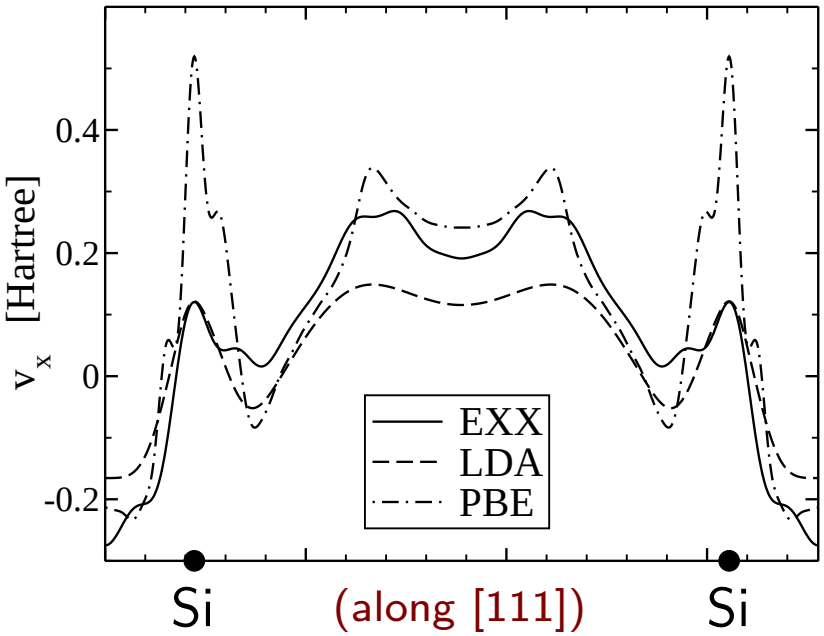
method		Δ
E_x	E_c	[eV]
LDA	LDA[a]	0.47
exact	LDA[b]	1.25
expt.		1.17

[a] Tran et al., JP: CM **19**, 196208 (2007)

[b] Kotani, Akai, PRB **54**, 16502 (1996)

Role of Exact Exchange: Semiconductors

Si



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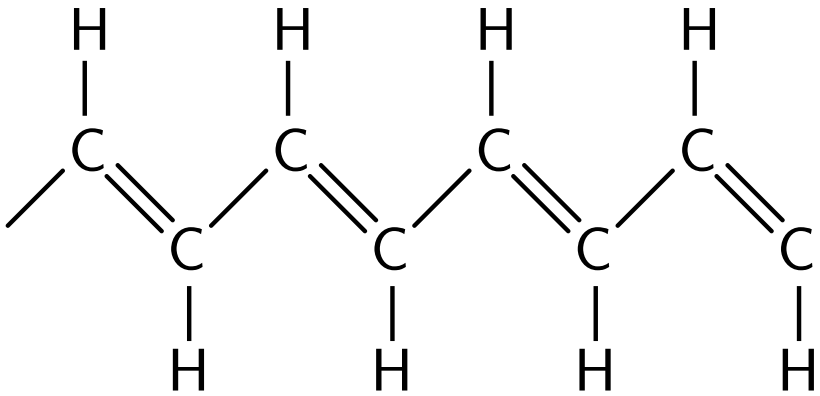
[a] Tran et al., JP: CM **19**, 196208 (2007)

[b] Kotani, Akai, PRB **54**, 16502 (1996)

trans-polyacetylene (monoclinic)

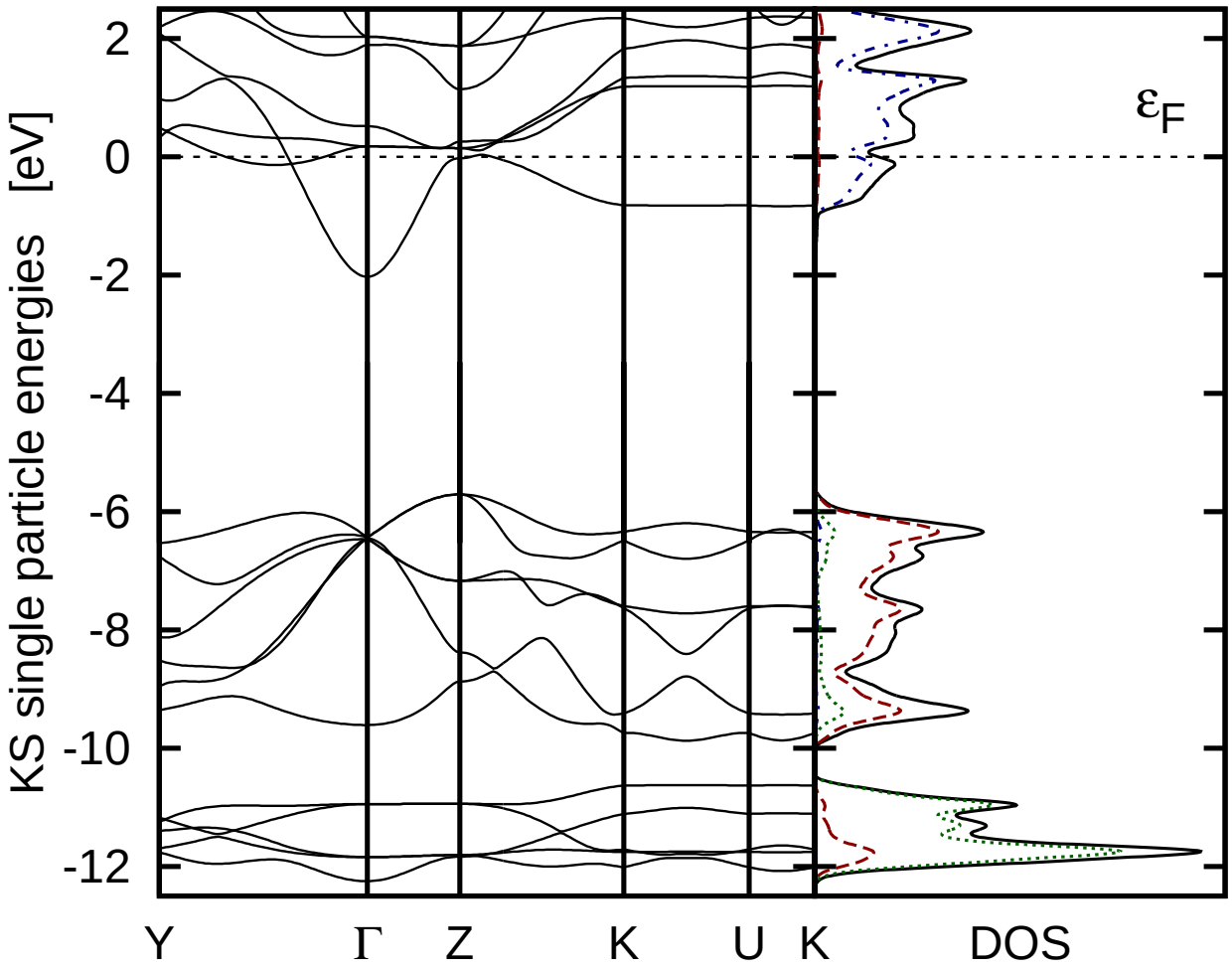


method		Δ
E_x	E_c	[eV]
LDA	LDA[a]	0.43
exact	LDA[a]	1.21
expt.[b]		1.5

[a] Rohra et al., PRB **73**, 045119 (2006)

[b] Leising, PRB **38**, 10313 (1988)

FeO in AF-II phase: exact exchange in KLI approximation



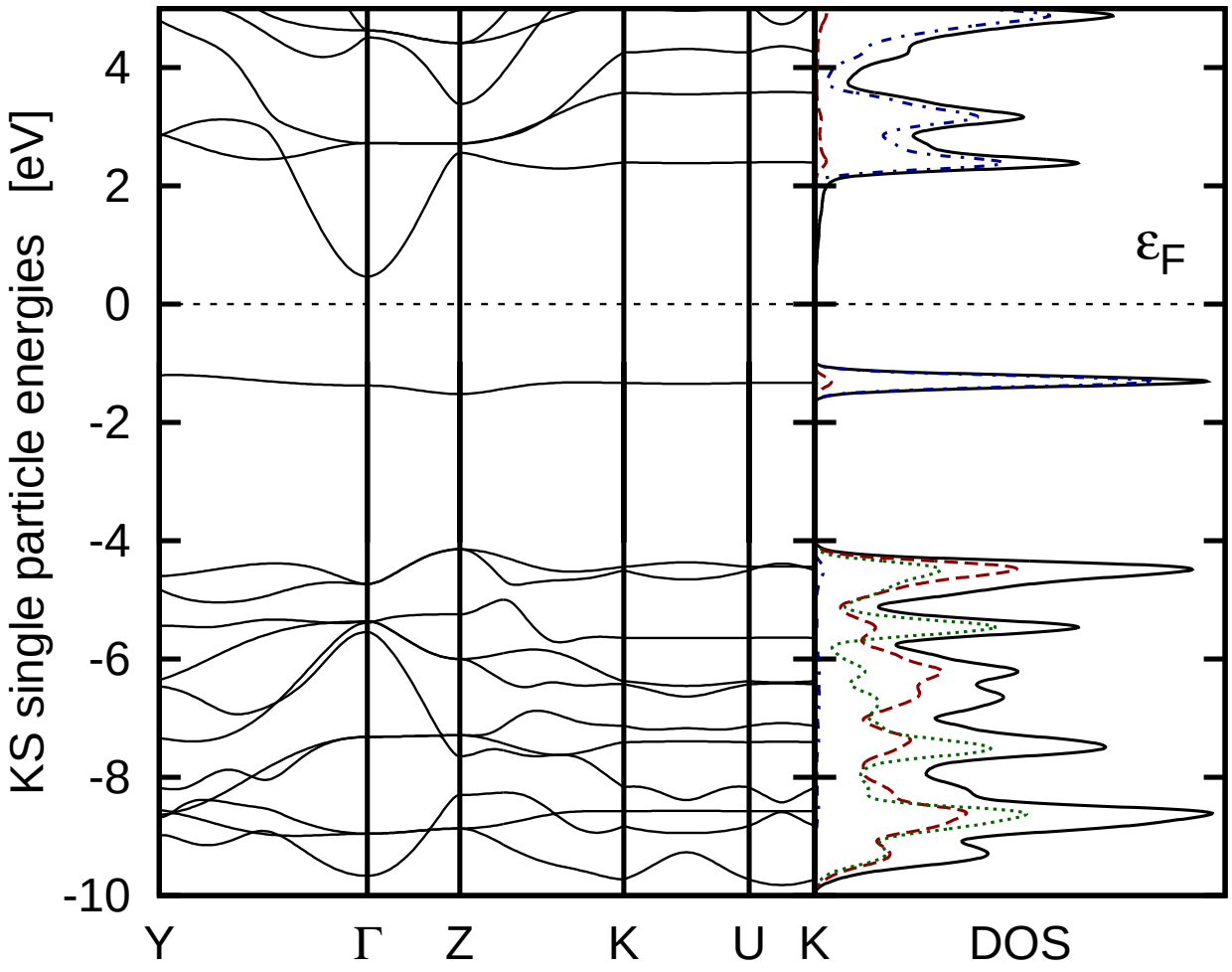
exact E_x plus
LDA correlation

total DOS = black
Fe $3d_\uparrow$ = green
Fe $3d_\downarrow$ = blue
O $2p$ = red

FeO: LDA/GGA

Schmid, PhD thesis, Frankfurt (1999), Schmid, Engel, Dreizler, in: *NIC Symposium 2001*, NIC-Series Vol. 9, ed. by Rollnik, Wolf (John von Neumann Institut, Jülich, 2002), p.213

FeO in AF-II phase: exact exchange plus full OPM



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Engel, Schmid,

PRL **103**, 036404 (2009)

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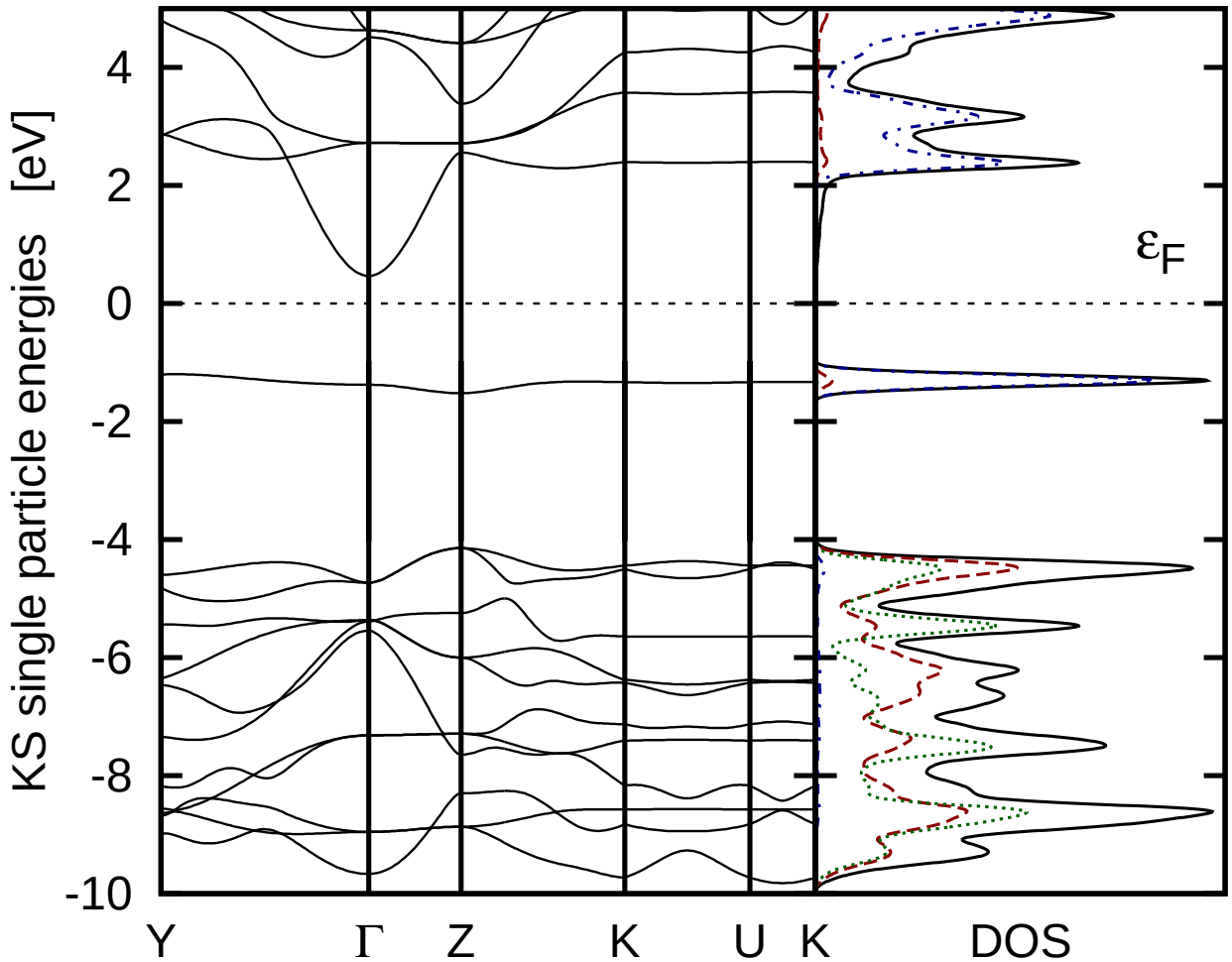

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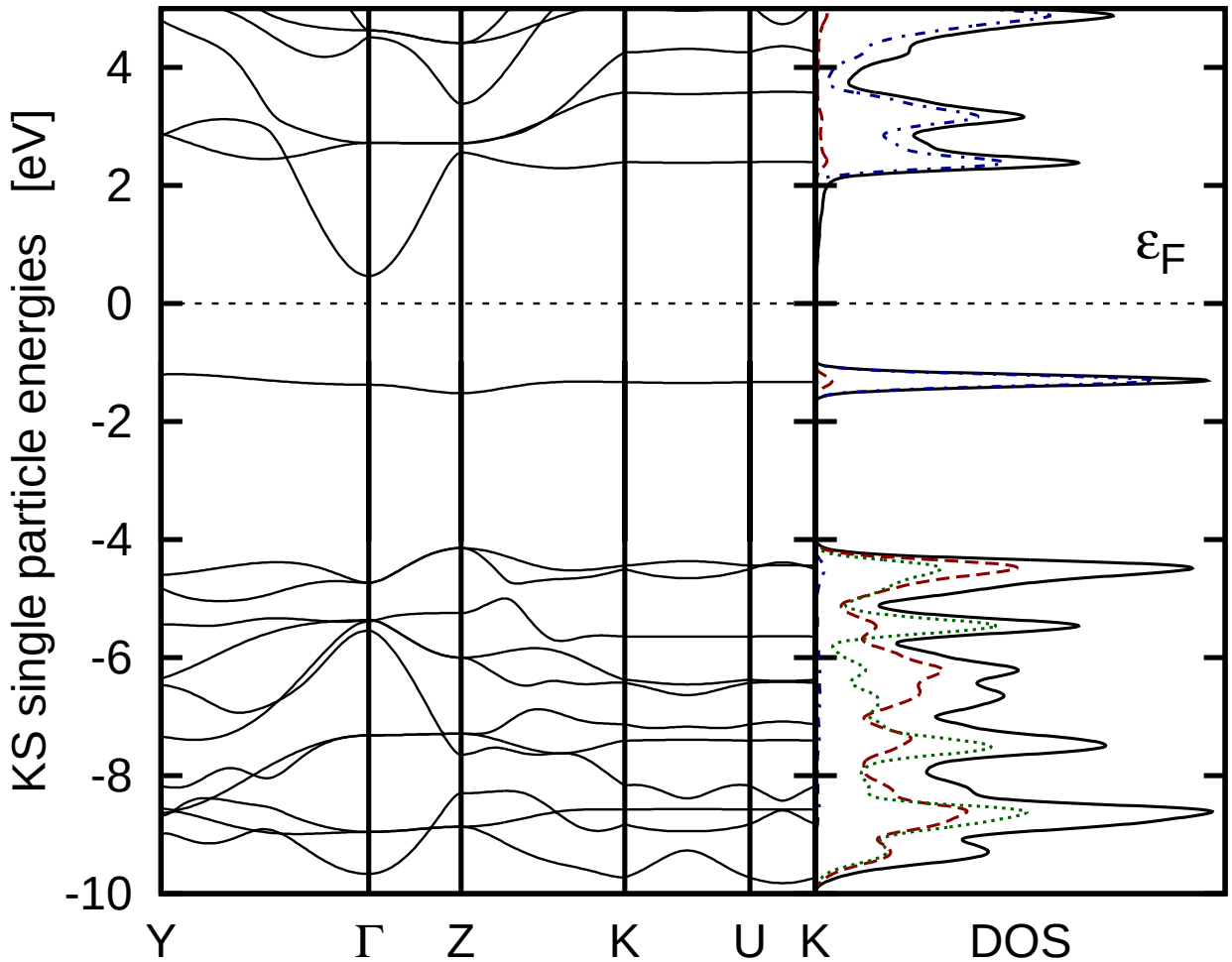
Engel, Schmid,

PRL **103**, 036404 (2009)

	magnetic moment
expt.:	$3.32, 4.2\,\mu_B$
EXX+VWN:	$3.8\,\mu_B$ (spin only)
orbital magnetic moment:	$\approx 0.7\,\mu_B$

Tran et al., PRB **74**, 155108 (2006)

FeO in AF-II phase: exact exchange plus full OPM



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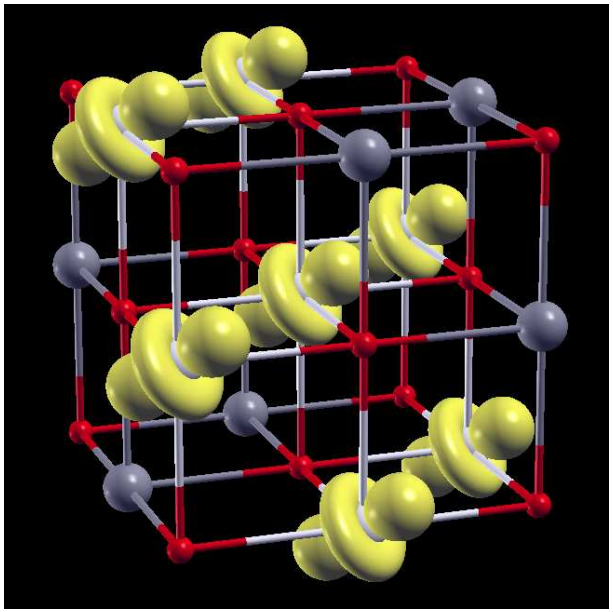
total DOS = black
Fe $3d_\uparrow$ = green
Fe $3d_\downarrow$ = blue
O $2p$ = red

Engel, Schmid,
PRL **103**, 036404 (2009)

	magnetic moment	fund. band gap
expt.:	$3.32, 4.2\,\mu_B$	2.4 eV
EXX+VWN:	$3.8\,\mu_B$ (spin only)	1.66 eV
orbital magnetic moment:	$\approx 0.7\,\mu_B$	

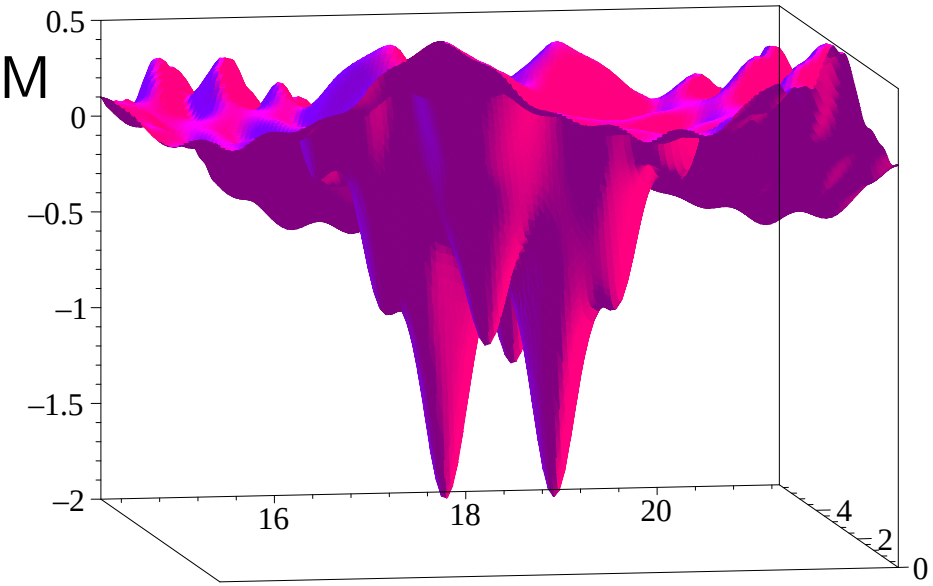
Tran et al., PRB **74**, 155108 (2006)

FeO (AF-II): minority spin exchange potential

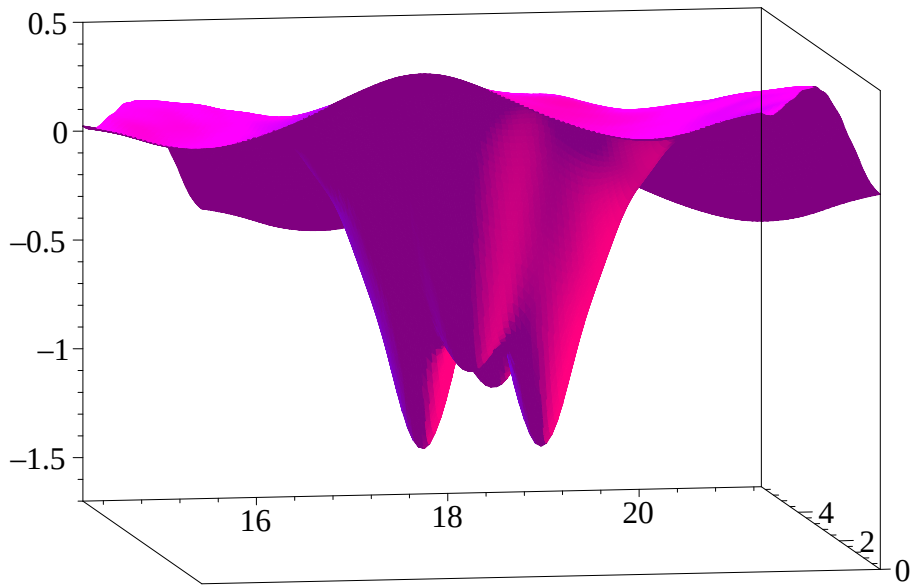


density of highest minority spin valence band (isosurface for $0.2\,\text{Å}^{-3}$)

OPM



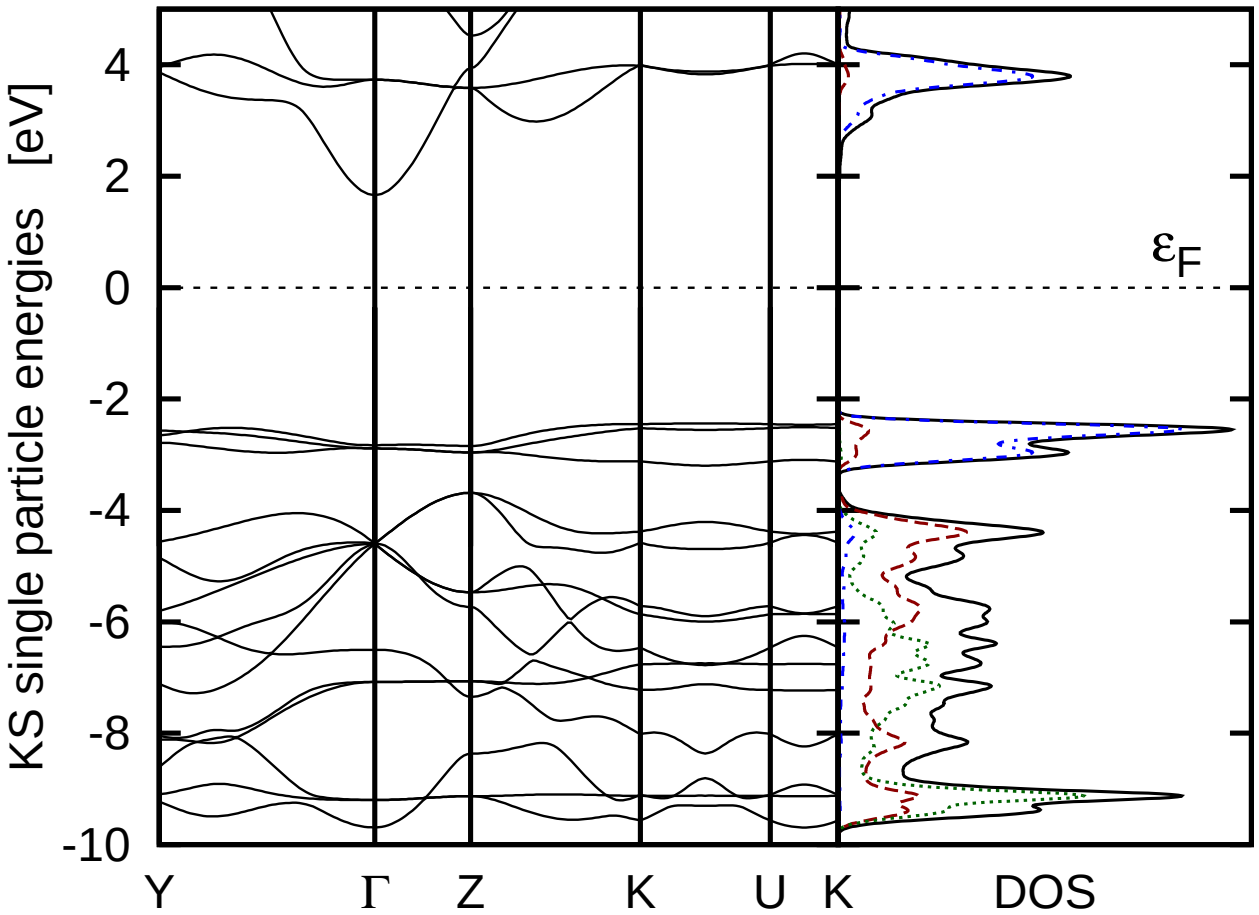
KLI



v_x in plane $\perp$ to AF-II planes

$\longrightarrow$ KLI averages over directions

NiO in AF-II phase: exact exchange plus full OPM

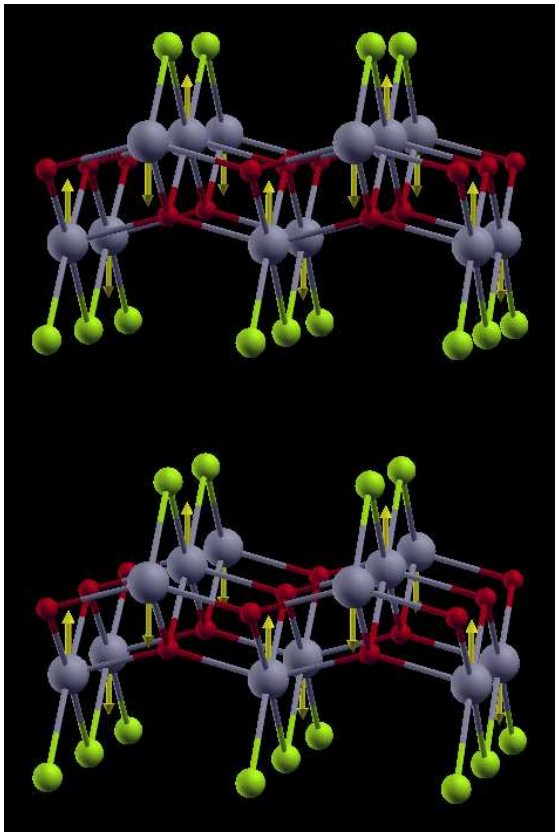


exact E_x plus
LDA correlation

total DOS = black
Ni $3d_\uparrow$ = green
Ni $3d_\downarrow$ = blue
O $2p$ = red

	magnetic moment	fund. band gap
expt.:	1.64,1.90 μ_B	4.0,4.3 eV
EXX+VWN:	1.9 μ_B	4.10 eV

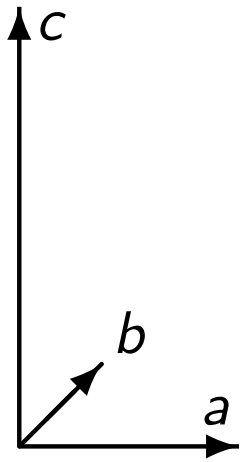
TiOCl in high temperature phase ($T > T_{c2}$)



Ti = grey dots

O = red dots

Cl = green dots



- for $T > T_{c2} \approx 91\,\mathrm{K}$: orthorhombic
- band gap: $\sim 2\mathrm{eV}$
- antiferromagnetic along b direction

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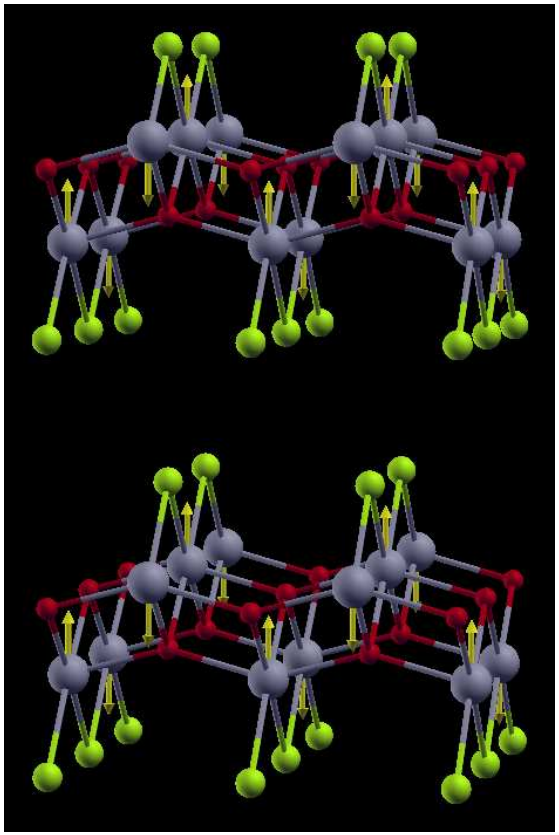

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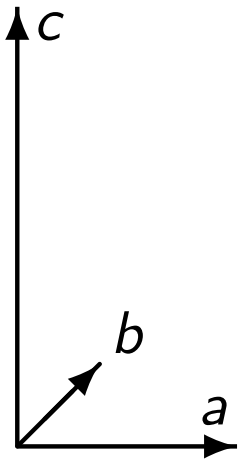

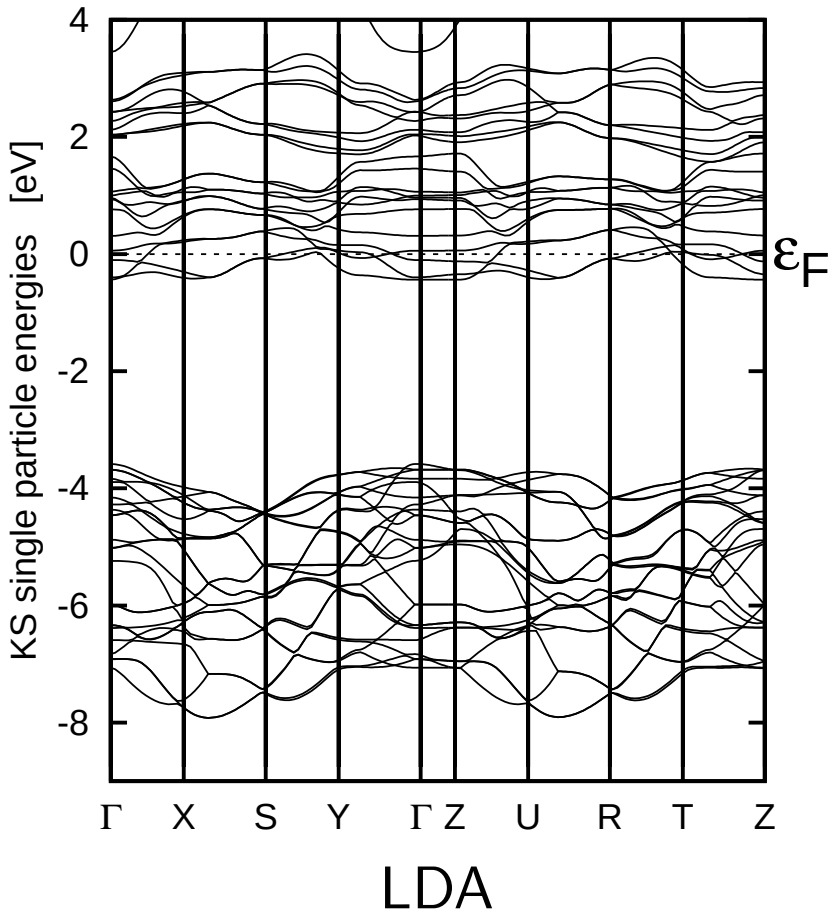

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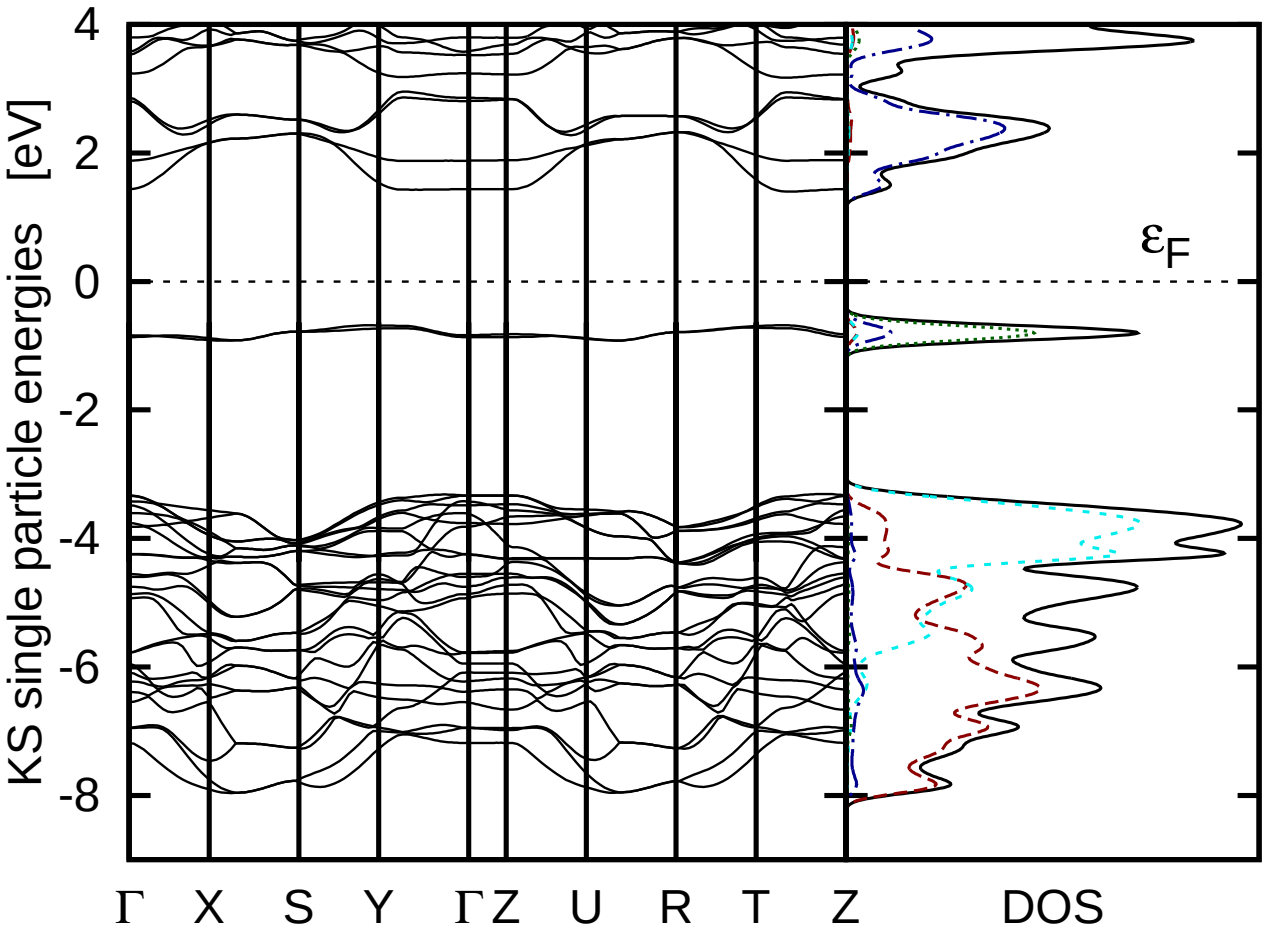


exact E_x plus
LDA correlation

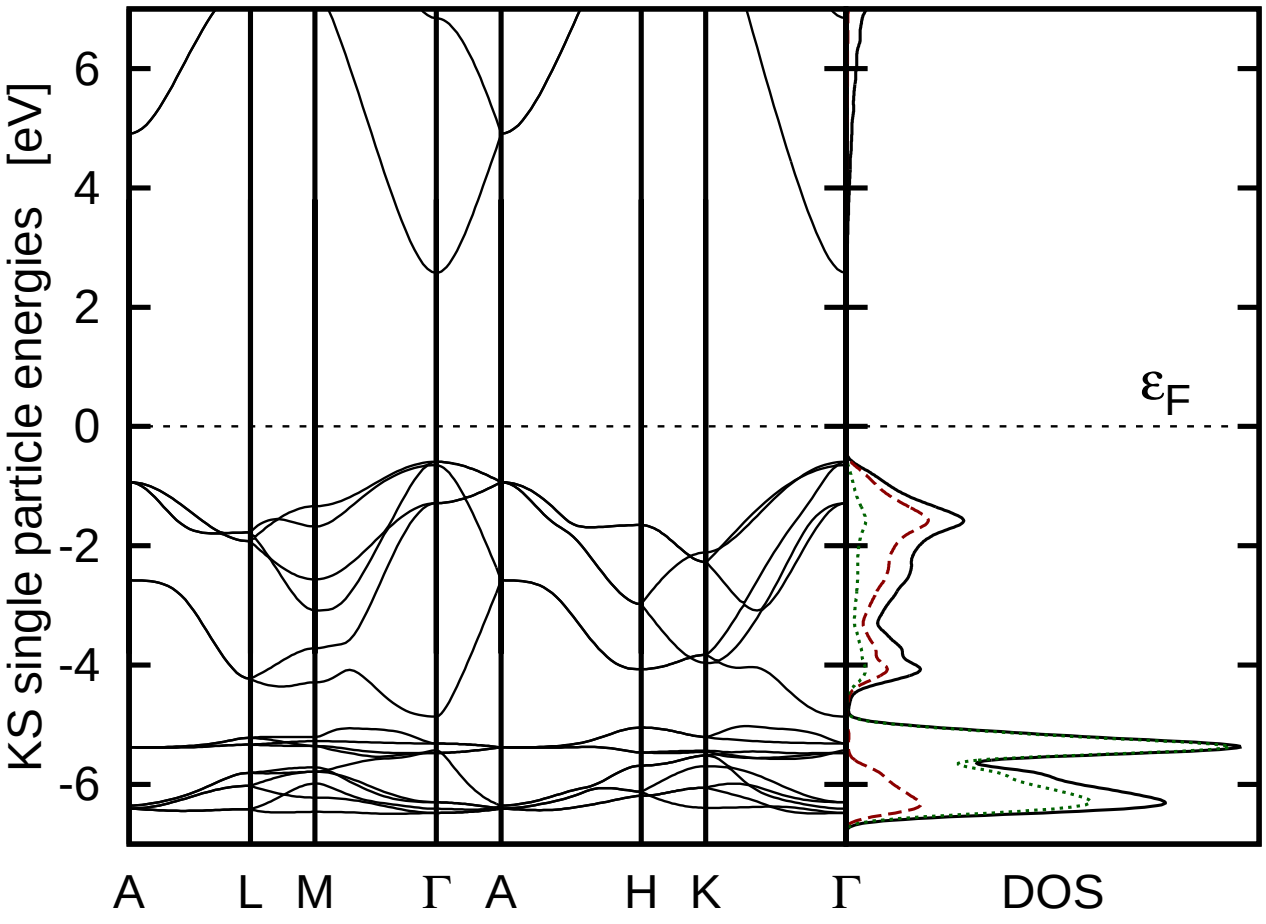
total DOS = black
Ti $3d_{\uparrow,xy}$ = green
Ti $3d_{\uparrow,z^2,x^2-y^2,yz,zx}$ = blue
O $2p$ = red
Cl $3p$ = cyan

highest valence band

	magn. mom.	opt. gap
expt.:	$1.0\,\mu_B$ [a]	$\sim 2\,\text{eV}$ [b]
EXX+VWN:	$1.0\,\mu_B$	$2.1\,\text{eV}$

[a] Seidel et al., PRB **67**, 020405(R) (2003)
[b] Rückamp et al., PRL **95**, 097203 (2005)

ZnO: exact exchange plus full OPM



exact E_x plus
LDA correlation

Zn $3d$ = green
O $2p$ = red

	band gap	
Expt.:	3.44 eV	
EXX+VWN:	3.17 eV	(LDA: 0.75 eV)

Green's Function Approach to Exact $E_{\mathrm{xc}}[n]$

Starting point: assume KS potential v_{s} to be known

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Concept: use conventional many-body theory with $\hat{H}_{\mathrm{s}}$ as noninteracting reference system together with perturbation

$$\hat{H}_1 = \underset{\uparrow}{\hat{W}} - \int d^3 r\, \hat{n}(\mathbf{r}) \left[v_{\mathrm{s}}(\mathbf{r}) - v_{\mathrm{ext}}(\mathbf{r}) \right]$$

Coulomb interaction

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Coulomb interaction

- leads to exact representation of E_{xc} in terms of the ϕ_k, ϵ_k
- all standard many-body techniques available for approximate evaluation

Perturbation Theory: Lowest Order Correlation Term

$\longrightarrow$ expansion of in powers of $\hat{H}_1$ and thus e^2

$$E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}^{(2)} + \ldots \qquad \Longrightarrow \qquad v_{\mathrm{xc}} = v_{\mathrm{x}} + v_{\mathrm{c}}^{(2)} + \ldots$$

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$\longrightarrow$ orbital- and eigenvalue-dependent functional for correlation

$$\begin{aligned}
E_{\mathrm{c}}^{(2)} &= E_{\mathrm{c}}^{\mathrm{MP2}} + E_{\mathrm{c}}^{\Delta\mathrm{HF}} \\
E_{\mathrm{c}}^{\mathrm{MP2}} &= \frac{1}{2} \sum_{ijkl} \Theta_i \Theta_j (1-\Theta_k)(1-\Theta_l) \frac{(ij||kl)[(kl||ij) - (kl||ji)]}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} \\
E_{\mathrm{c}}^{\Delta\mathrm{HF}} &= \sum_{il} \Theta_i (1-\Theta_l) \frac{|\langle i|v_{\mathrm{x}}|l\rangle + \sum_j \Theta_j (ij||jl)|^2}{\epsilon_i - \epsilon_l} \\
(ij||kl) &= \int d^3 r_1 \int d^3 r_2 \, \frac{\phi_i^\dagger(\mathbf{r}_1)\phi_k(\mathbf{r}_1)\, \phi_j^\dagger(\mathbf{r}_2)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}
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- $E_{\mathrm{c}}^{\mathrm{MP2}}$ = Møller-Plesset-type term ($E_{\mathrm{c}}^{\mathrm{MP2}} \gg E_{\mathrm{c}}^{\Delta\mathrm{HF}}$)
- agrees with 2nd order Görling-Levy E_{c} on basis of adiabatic connection

Correlation Energies of Atoms

	MP2[a]	exact[b]	$E_c^{(2)}$[c]	LDA[d]	GGA[e]
	[mHartree]				
H^-	27	40	55		
He	37	42	48	113	46
Be	76	94	124	225	94
F^-	400		530		
Ne	388	391	477	746	382
Mg	428	438	522	892	450
Ar	709	722	866	1431	771
Ca	798		996	1581	847
Zn	1678		2016	2668	1526

[a] Flores, JCP **98**, 5642 (1993); Termath et al., JCP **94**, 2002 (1991)

[b] Chakravorty et al., PRA **47**, 3649 (1993)

[c] Engel, Dreizler, JCC **20**, 31 (1999)

[d] LDA = VWN; [e] GGA = PW91

Correlation Potential on Basis of $E_c^{(2)}$

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Problem: OPM-equation does not have solution with $v_c^{(2)}(r \to \infty) = 0$, if positive continuum taken into account [Facco Bonetti et al., PRL **86**, 2241 (2001); PRL **90**, 219302 (2003); Engel et al., PRA **72**, 052503 (2005)]

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Solution: Discretize spectrum by boundary conditions (atom in large cavity)

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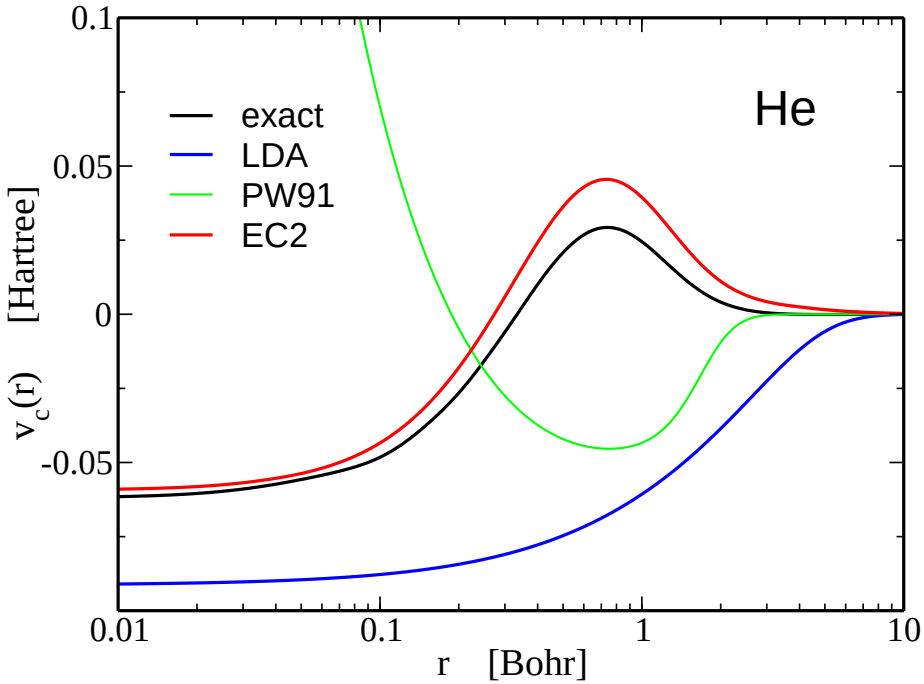

exact: Umrigar, Gonze, PRA **50**, 3827 (1994)

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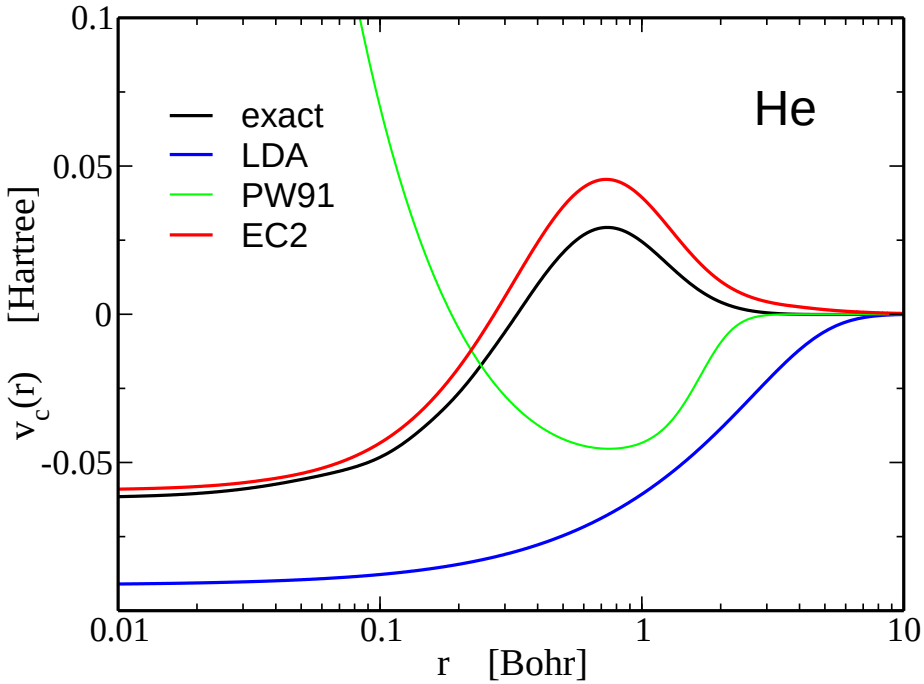

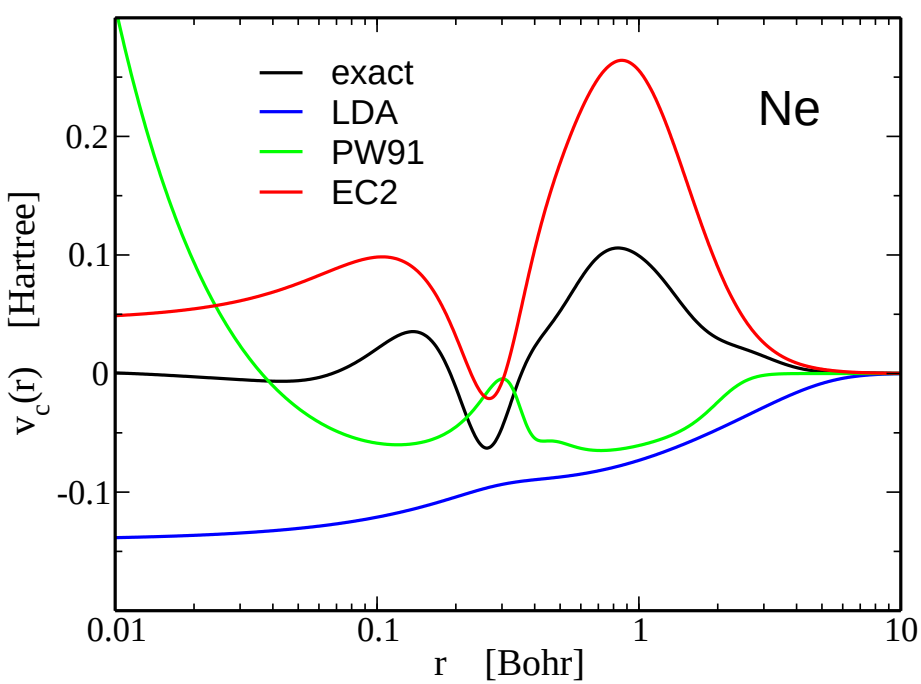

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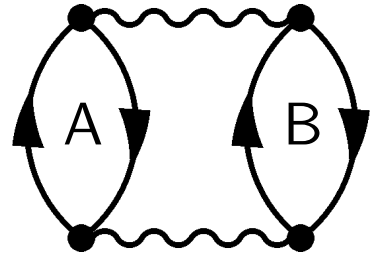
Description of Dispersion Forces by $E_c^{(2)}$?

Consider 2 neutral atoms A,B at large separation R



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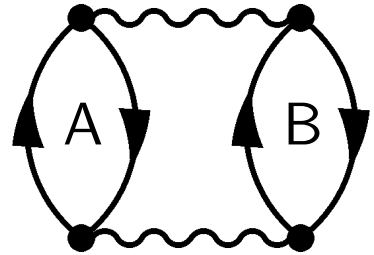


$\longrightarrow$ interaction between A and B reduces to (spherical case)

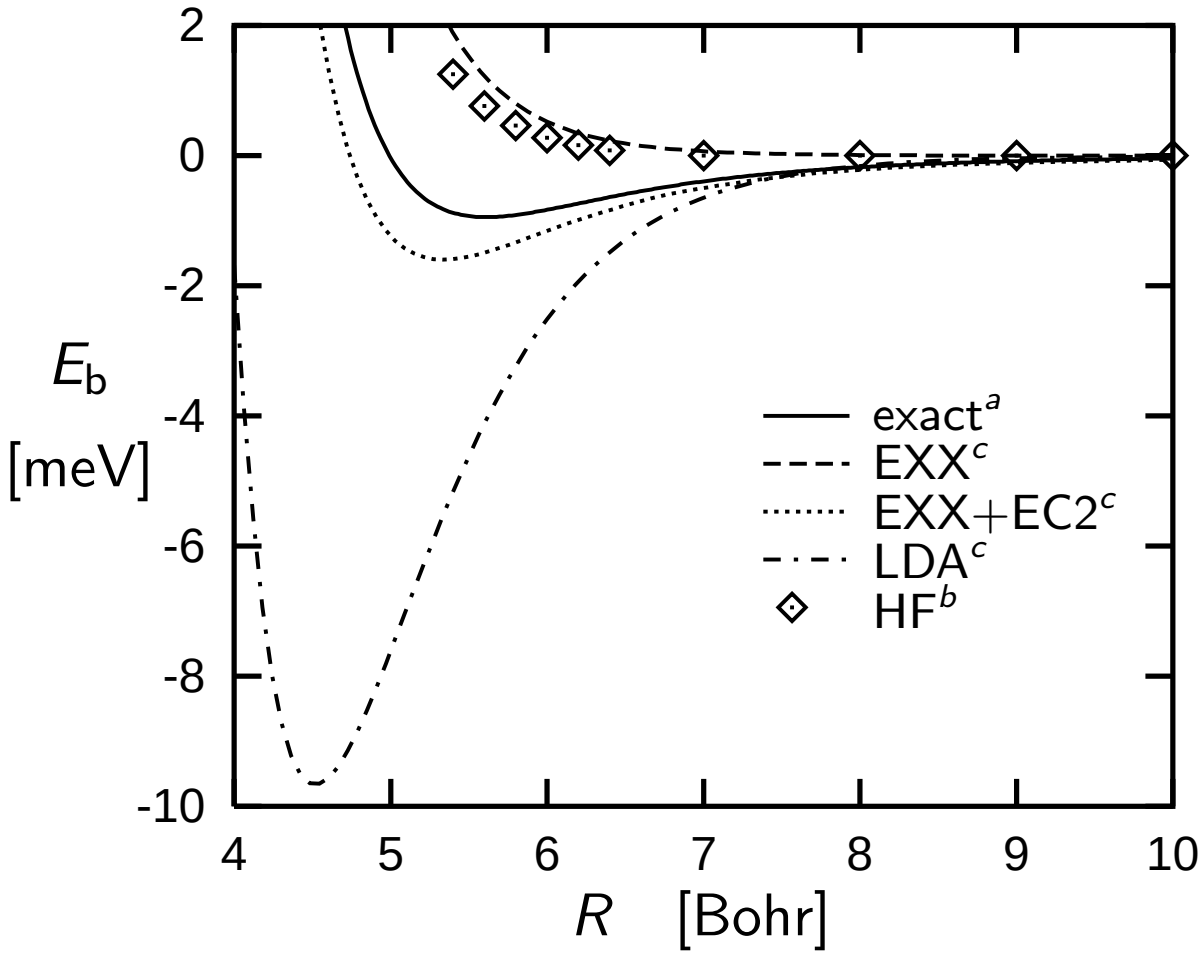
$$E_{c,\mathrm{int}}^{(2)} = -\frac{C_6}{R^6} = -3\frac{e^4}{R^6}\int_0^\infty \frac{du}{\pi}\,\alpha_A(iu)\alpha_B(iu)$$

$$\alpha(\omega) = \int d^3r_1 \int d^3r_2\; z_1\; z_2\; \chi_s^R(\mathbf{r}_1,\mathbf{r}_2,\omega) \qquad \leftarrow \text{KS polarizibility}$$

$$\chi_s^R(\mathbf{r}_1,\mathbf{r}_2,\omega) = \sum_{i,k}[\Theta_i-\Theta_k]\,\frac{\phi_i^\dagger(\mathbf{r}_1)\phi_k(\mathbf{r}_1)\phi_k^\dagger(\mathbf{r}_2)\phi_i(\mathbf{r}_2)}{\omega-\epsilon_k+\epsilon_i+i\eta}$$

Engel et al., PRA **58**, 964 (1998)

Energy Surface of He_2



[a] Aziz, Slaman, JCP **94**, 8047 (1991)

[b] Silver, PRA **21**, 1106 (1980)

[c] Engel, Höck, Dreizler, PRA **61**, 032502 (2000)

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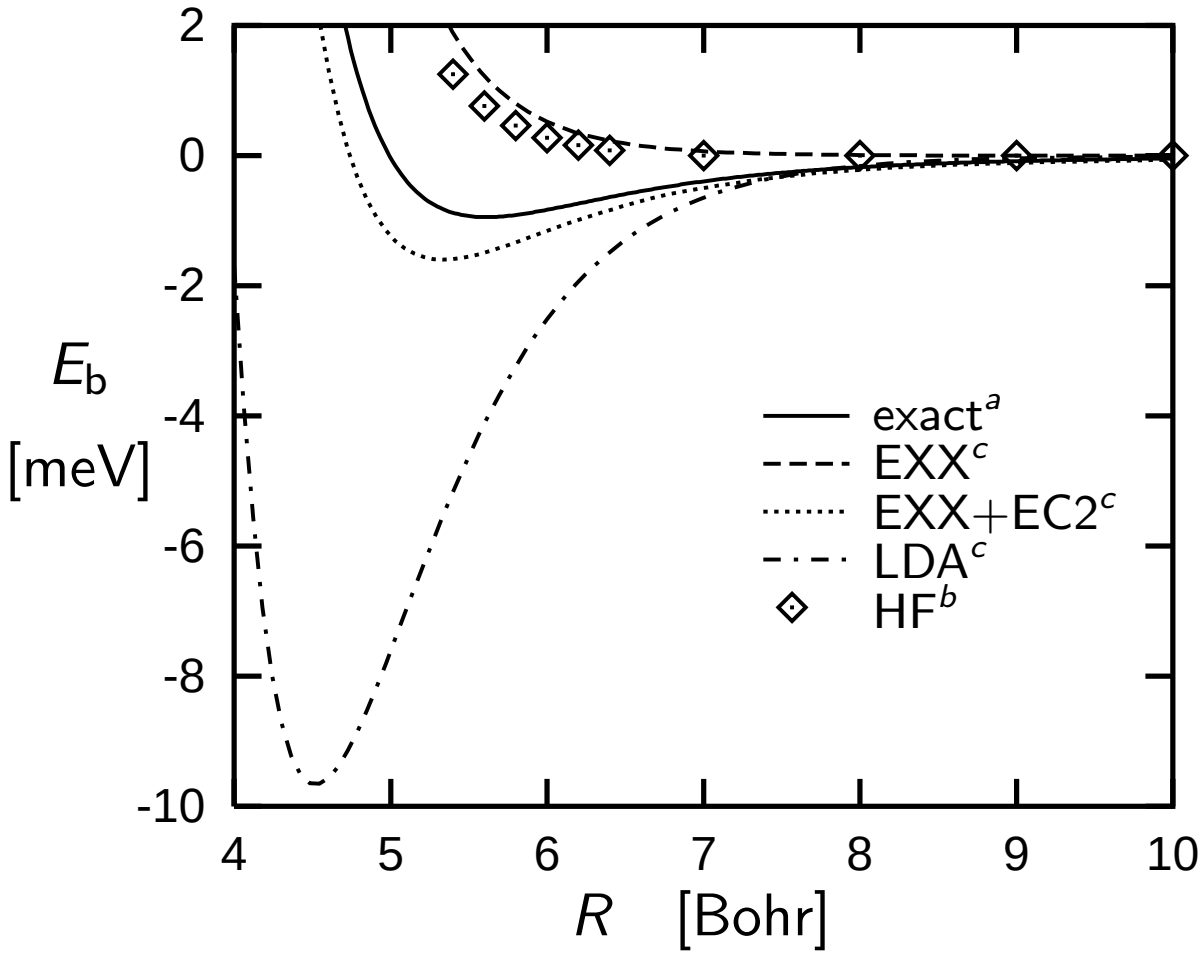

- EXX+$E_c^{(2)}$ realistic

C_6:	exact	$E_c^{(2)}$
	1.46	1.8

[a] Aziz, Slaman, JCP **94**, 8047 (1991)

[b] Silver, PRA **21**, 1106 (1980)

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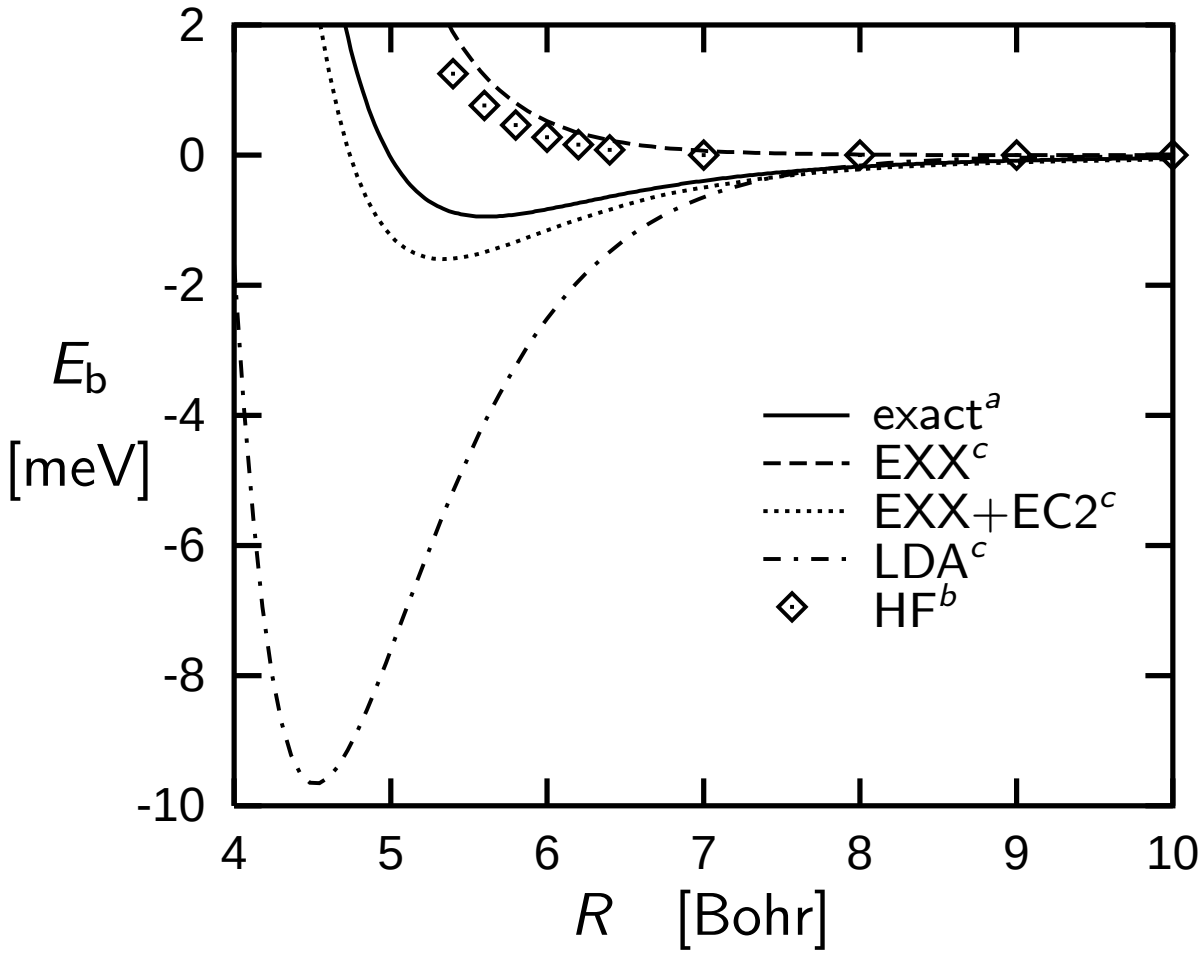
Energy Surface of He_2



skip zoom

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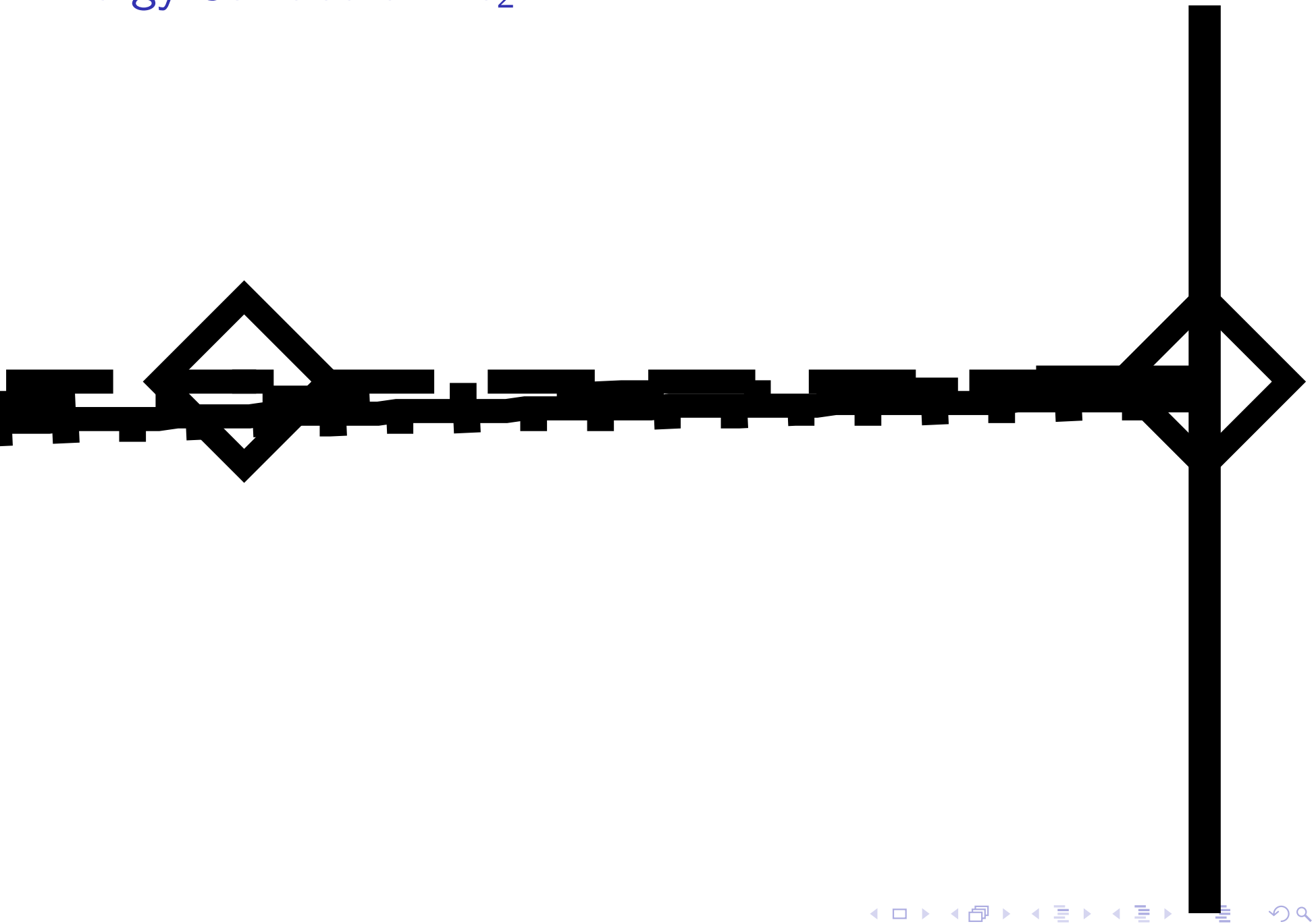

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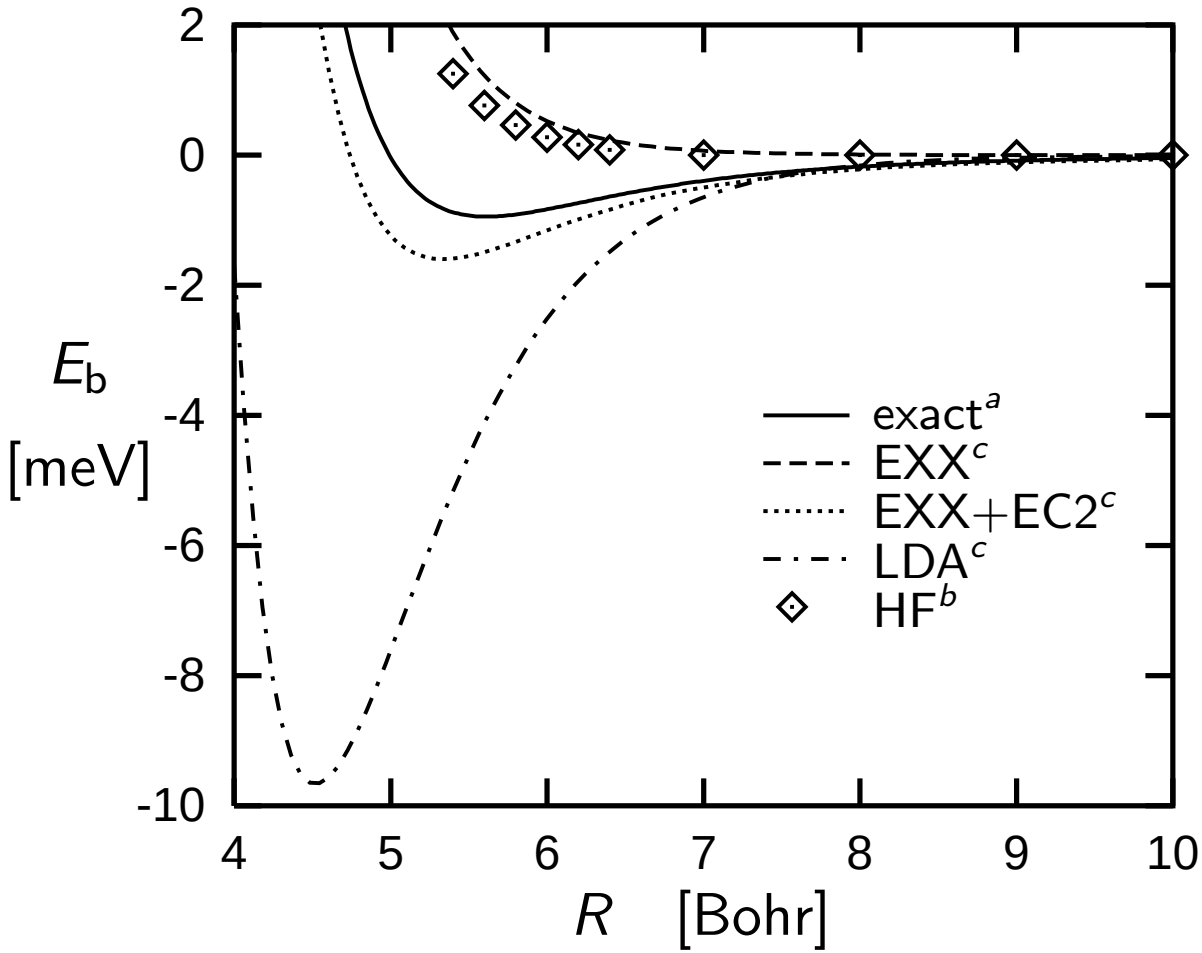

- EXX+$E_c^{(2)}$ realistic

C_6:	exact	$E_c^{(2)}$
	1.46	1.8

skip zoom

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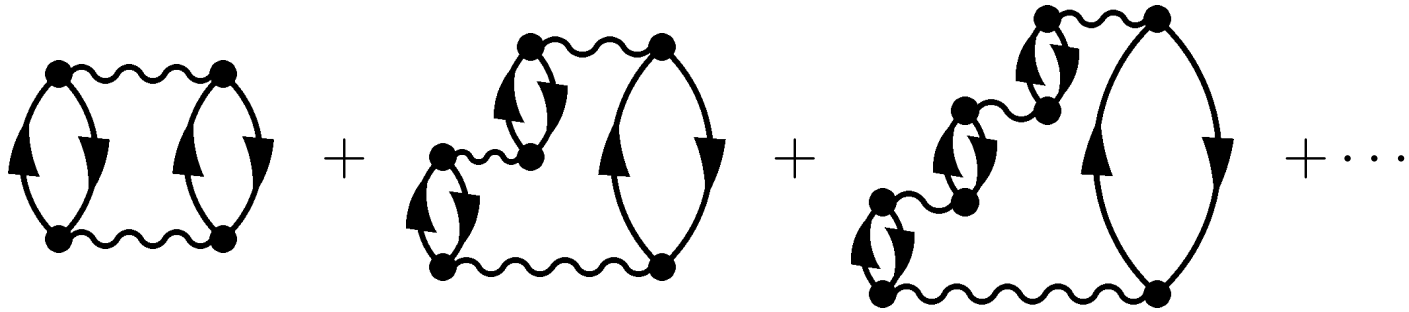
s-d-Transfer Energies of 3d-Elements: RPA

$E_c^{\mathrm{RPA}} =$  $+ \cdots$

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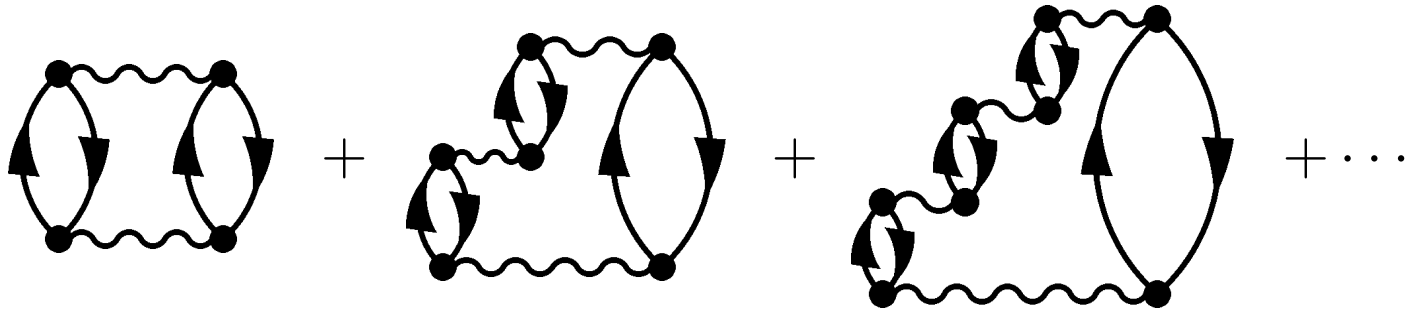
$E_c^{\mathrm{RPA}} =$  $+ \cdots$

transfer energy $= E[4s^1\,3d^n] - E[4s^2\,3d^{n-1}]$

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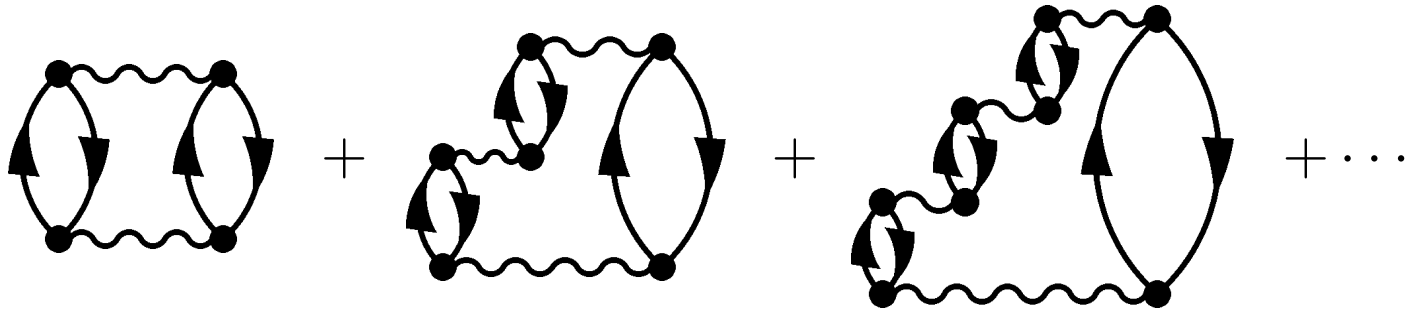
$E_c^{\mathrm{RPA}} =$  $+\cdots$

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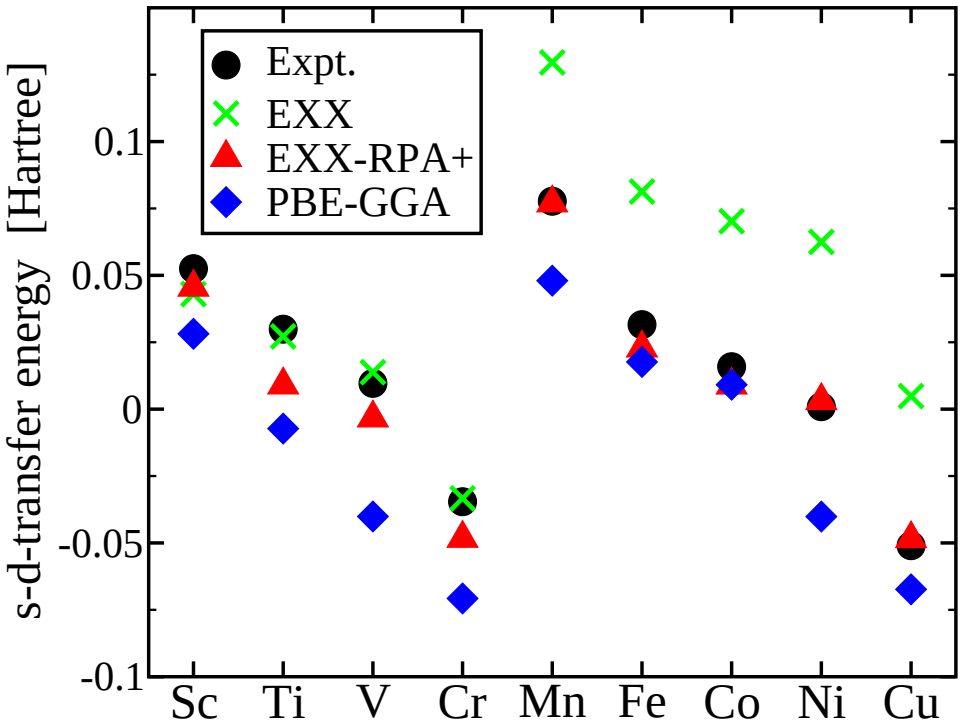

RPA+

= RPA + 2nd order exchange

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- reasonably accurate results for variety of properties
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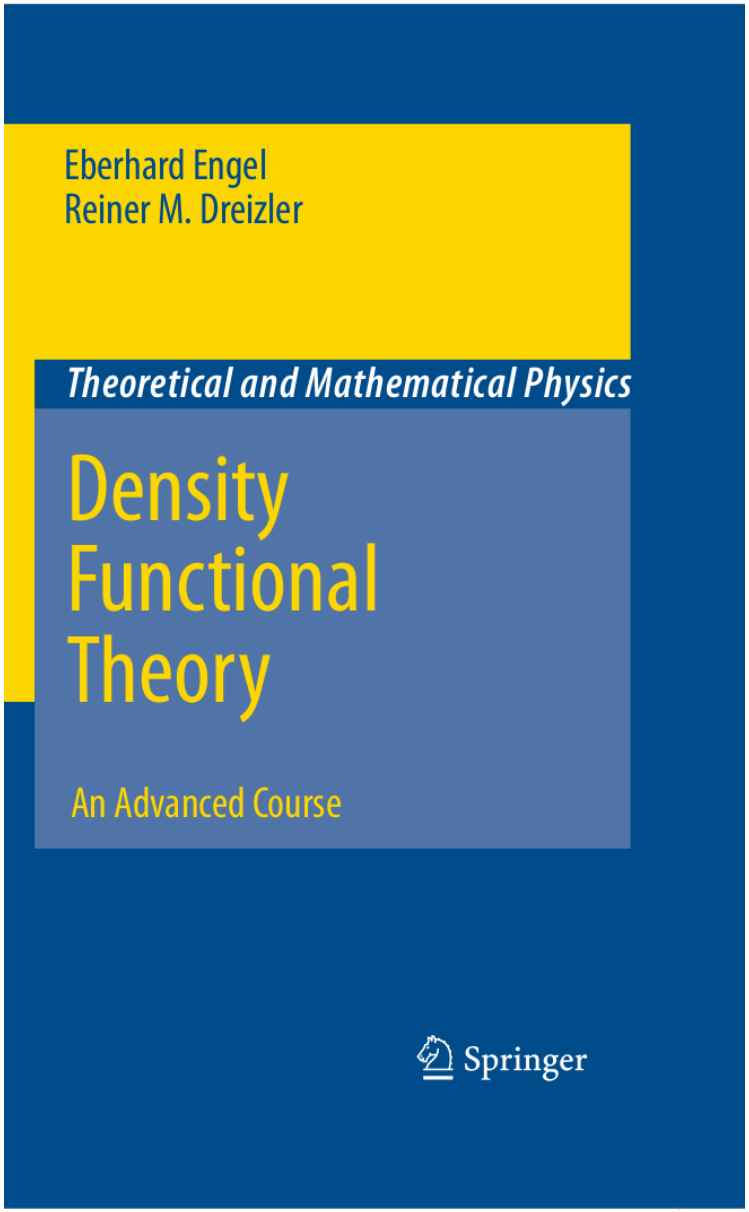
Relativistic extension of orbital-dependent functionals available

PRA **52**, 2750 (1995); PRA **58**, 964 (1998); PRB **63**, 125121 (2001);
PRB **64**, 235126 (2001); PRB **77**, 045101 (2008); PRB **78**, 235123 (2008)

many more details may be found in



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Existence theorem based on QED (Rajagopal, Callaway, 1973)

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- minimum principle for renormalized total energy

$$E[n,\mathbf{j}] \;<\; E[n',\mathbf{j}'] \qquad \forall \quad (n',\mathbf{j}') \;\neq\; (n,\mathbf{j})$$

$$(n,\mathbf{j}/c) \;=\; \text{true ground state four current}$$

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$$\mathbf{j}(\mathbf{r}) = c\sum_k \Theta_k \phi_k^\dagger(\mathbf{r})\boldsymbol{\alpha}\phi_k(\mathbf{r})$$

$$\Theta_k = \begin{cases} 0 & \text{for} \quad \epsilon_k \leq -mc^2 \\ 1 & \text{for} \quad -mc^2 < \epsilon_k \leq \epsilon_F \\ 0 & \text{for} \quad \epsilon_F < \epsilon_k \end{cases}$$

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$$

$\longrightarrow$ decompose total (no-pair) energy E as (definition of E_xc)

$$
\begin{aligned}
E &= T_\mathrm{s} + \int d^3r \left\{ n(\mathbf{r})\, v_\mathrm{ext}(\mathbf{r}) + \frac{e}{c}\mathbf{j}(\mathbf{r})\cdot\mathbf{A}_\mathrm{ext}(\mathbf{r}) \right\} + E_\mathrm{H} + E_\mathrm{xc} \\
T_\mathrm{s} &= \sum_k \Theta_k \int d^3r\, \phi_k^\dagger(\mathbf{r}) \big[-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta-1)mc^2 \big] \phi_k(\mathbf{r}) \\
E_\mathrm{H} &= \frac{e^2}{2}\int d^3r\, d^3r' \left\{ \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{\mathbf{j}(\mathbf{r})\cdot\mathbf{j}(\mathbf{r}')}{c^2|\mathbf{r}-\mathbf{r}'|} \right\}
\end{aligned}
$$

$\longrightarrow$ minimize E to determine effective four potential $v_s^\mu = (v_s, -e\mathbf{A}_s)$

$$\left\{-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta-1)mc^2 + v_s(\mathbf{r}) + e\boldsymbol{\alpha}\cdot\mathbf{A}_s(\mathbf{r})\right\}\phi_k(\mathbf{r}) = \epsilon_k\phi_k(\mathbf{r})$$

with

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v_H(\mathbf{r}) &= e^2\int d^3r'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
v_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}[n,\mathbf{j}]}{\delta n(\mathbf{r})} \\
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$\longrightarrow$ to be solved selfconsistently for given $E_{xc}[n,\mathbf{j}]$

Relativistic Optimized Potential Method (ROPM)

Exact (no-pair) exchange of RDFT (including transverse interaction)

$$E_x = -\frac{e^2}{2}\sum_{k,l}\Theta_k\Theta_l\int d^3r\, d^3r'\,\frac{\cos(|\epsilon_k-\epsilon_l|\,|\mathbf{r}-\mathbf{r}'|/c)}{|\mathbf{r}-\mathbf{r}'|}$$

$$\times\,\phi_k^\dagger(\mathbf{r})\alpha_\mu\phi_l(\mathbf{r})\,\phi_l^\dagger(\mathbf{r}')\alpha^\mu\phi_k(\mathbf{r}')$$

$$\alpha^\mu \equiv \gamma^0\gamma^\mu = (1,\boldsymbol{\alpha})$$

(Feynman gauge)

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How to determine $v_{xc}^\mu = \dfrac{\delta E_{xc}}{\delta j_\mu}$?

$\longrightarrow$ transform $\delta E_{xc}/\delta j_\mu$ into $\delta E_{xc}/\delta\phi_k$, using uniqueness $j^\mu \longleftrightarrow v_s^\mu$

$$\frac{\delta E_{xc}}{\delta v_s^\nu(\mathbf{r})} = \int d^3r'\,\frac{\delta j^\mu(\mathbf{r}')}{\delta v_s^\nu(\mathbf{r})}\,\frac{\delta E_{xc}}{\delta j^\mu(\mathbf{r}')}$$
$$= \sum_k\left\{\int d^3r'\left[\frac{\delta\phi_k^\dagger(\mathbf{r}')}{\delta v_s^\nu(\mathbf{r})}\,\frac{\delta E_{xc}}{\delta\phi_k^\dagger(\mathbf{r}')}+c.c.\right]+\frac{\delta\epsilon_k}{\delta v_s^\nu(\mathbf{r})}\,\frac{\partial E_{xc}}{\partial\epsilon_k}\right\}$$

$\longrightarrow$ requires linear response of ϕ_k to variation of v_s^ν

$$\frac{\delta \phi_k^\dagger(\mathbf{r}')}{\delta v_s^\nu(\mathbf{r})} = -\phi_k^\dagger(\mathbf{r})\,\alpha_\nu\,G_k(\mathbf{r},\mathbf{r}') \qquad G_k(\mathbf{r},\mathbf{r}') = \sum_{l\neq k} \frac{\phi_l(\mathbf{r})\,\phi_l^\dagger(\mathbf{r}')}{\epsilon_l - \epsilon_k}$$

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$$\int d^3r'\,\chi_s^{\mu\nu}(\mathbf{r},\mathbf{r}')\,v_{xc,\nu}(\mathbf{r}') = \Lambda_{xc}^\mu(\mathbf{r})$$

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$\longrightarrow$ $v_x^0(\mathbf{r}) \xrightarrow{r\to\infty} -1/|\mathbf{r}|$ for finite systems

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Dirac-type KS equations with magnetic field (Macdonald, Vosko, 1979)

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$$\mathbf{m}(\mathbf{r}) = \mu_{\mathrm{B}} \sum_k \Theta_k \, \phi_k^{\dagger}(\mathbf{r})\beta\boldsymbol{\Sigma}\phi_k(\mathbf{r}) \qquad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}$$

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$\longrightarrow$ approximation for $E_{\mathrm{xc}}[n, \mathbf{m}]$ required

KS Equations of RSDFT: Collinear Version

OPM Equations of RSDFT: Non-collinear version I

Evaluate required functional derivatives via chain rule

$$v_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n,\mathbf{m}]}{\delta n(\mathbf{r})}$$

$$= \sum_k \int d^3r' \int d^3r'' \left\{ \frac{\delta v_{\rm s}(\mathbf{r}')}{\delta n(\mathbf{r})} \frac{\delta \phi_k^\dagger(\mathbf{r}'')}{\delta v_{\rm s}(\mathbf{r}')} + \frac{\delta \mathbf{B}_{\rm s}(\mathbf{r}')}{\delta n(\mathbf{r})} \frac{\delta \phi_k^\dagger(\mathbf{r}'')}{\delta \mathbf{B}_{\rm s}(\mathbf{r}')} \right\} \frac{\delta E_{\rm xc}}{\delta \phi_k^\dagger(\mathbf{r}'')} + c.c.$$

$$\mathbf{B}_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n,\mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})}$$

$$= \sum_k \int d^3r' \int d^3r'' \left\{ \frac{\delta v_{\rm s}(\mathbf{r}')}{\delta \mathbf{m}(\mathbf{r})} \frac{\delta \phi_k^\dagger(\mathbf{r}'')}{\delta v_{\rm s}(\mathbf{r}')} + \frac{\delta \mathbf{B}_{\rm s}(\mathbf{r}')}{\delta \mathbf{m}(\mathbf{r})} \frac{\delta \phi_k^\dagger(\mathbf{r}'')}{\delta \mathbf{B}_{\rm s}(\mathbf{r}')} \right\} \frac{\delta E_{\rm xc}}{\delta \phi_k^\dagger(\mathbf{r}'')} + c.c.$$

(suppress possible dependence of $E_{\rm xc}$ on ϵ_k)

OPM Equations of RSDFT: Non-collinear version II

Determine variation of ϕ_k and ϵ_k with v_s and $\mathbf{B}_s$ from KS equations

$$\delta\phi_k(\mathbf{r}) = -\int d^3r'\, G_k(\mathbf{r},\mathbf{r}')\Big\{\delta v_s(\mathbf{r}') + \mu_B\beta\boldsymbol{\Sigma}\cdot\delta\mathbf{B}_s(\mathbf{r}')\Big\}\phi_k(\mathbf{r}')$$

with the Green's function

$$G_k(\mathbf{r},\mathbf{r}') = \sum_{l\neq k}\frac{\phi_l(\mathbf{r})\,\phi_l^\dagger(\mathbf{r}')}{\epsilon_l-\epsilon_k}$$

OPM Equations of RSDFT: Non-collinear version III

Consider inverse of $\delta v_s/\delta n$ etc: Stationary response functions of KS-system

$$\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \chi_{nn}(\mathbf{r}',\mathbf{r}) = -\sum_k \Theta_k \phi_k^\dagger(\mathbf{r}') G_k(\mathbf{r}',\mathbf{r})\phi_k(\mathbf{r}) + c.c.$$

$$\frac{\delta \mathbf{m}(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \chi_{mn}(\mathbf{r}',\mathbf{r}) = -\mu_B \sum_k \Theta_k \phi_k^\dagger(\mathbf{r}') \beta\boldsymbol{\Sigma} G_k(\mathbf{r}',\mathbf{r})\phi_k(\mathbf{r}) + c.c.$$

$$\frac{\delta n(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} = \chi_{nm}(\mathbf{r}',\mathbf{r}) = -\mu_B \sum_k \Theta_k \phi_k^\dagger(\mathbf{r}') G_k(\mathbf{r}',\mathbf{r})\beta\boldsymbol{\Sigma}\phi_k(\mathbf{r}) + c.c.$$

$$\frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} = \chi_{mm}(\mathbf{r}',\mathbf{r}) = -\mu_B^2 \sum_k \Theta_k \phi_k^\dagger(\mathbf{r}') \beta\boldsymbol{\Sigma} G_k(\mathbf{r}',\mathbf{r})\beta\boldsymbol{\Sigma}\phi_k(\mathbf{r}) + c.c.$$

OPM Equations of RSDFT: Non-collinear version IV

resulting OPM equations

$$\int d^3r' \left\{\chi_{nn}(\mathbf{r},\mathbf{r}')v_{\mathrm{xc}}(\mathbf{r}') + \chi_{nm}(\mathbf{r},\mathbf{r}')\cdot\mathbf{B}_{\mathrm{xc}}(\mathbf{r}')\right\}$$

$$= -\sum_k \int d^3r'\, \phi_k^\dagger(\mathbf{r}) G_k(\mathbf{r},\mathbf{r}') \frac{\delta E_{\mathrm{xc}}}{\delta\phi_k^\dagger(\mathbf{r}')} + c.c.$$

$$\int d^3r' \left\{\chi_{mn}(\mathbf{r},\mathbf{r}')v_{\mathrm{xc}}(\mathbf{r}') + \chi_{mm}(\mathbf{r},\mathbf{r}')\cdot\mathbf{B}_{\mathrm{xc}}(\mathbf{r}')\right\}$$

$$= -\mu_B \sum_k \int d^3r'\, \phi_k^\dagger(\mathbf{r}) \beta\boldsymbol{\Sigma} G_k(\mathbf{r},\mathbf{r}') \frac{\delta E_{\mathrm{xc}}}{\delta\phi_k^\dagger(\mathbf{r}')} + c.c.$$

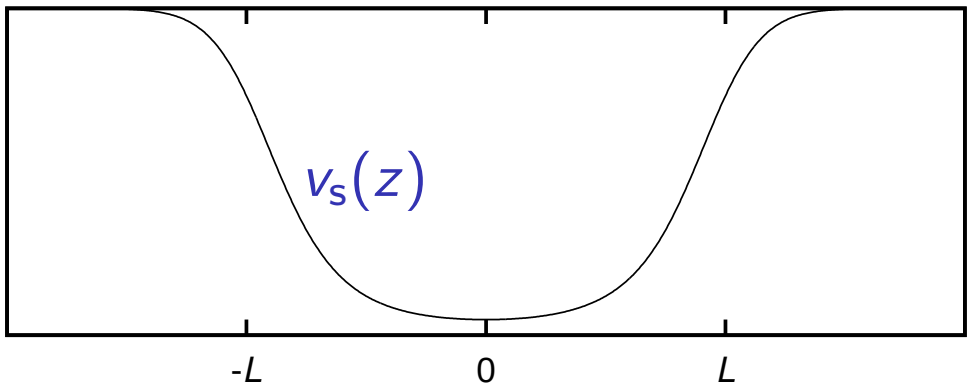
$\longrightarrow$ four coupled integral equations

$\longrightarrow$ to be solved together with the RKS equations

Back

EXX Potential at Surfaces: Slabs

Consider slab geometry: v_s forms potential well in z-direction



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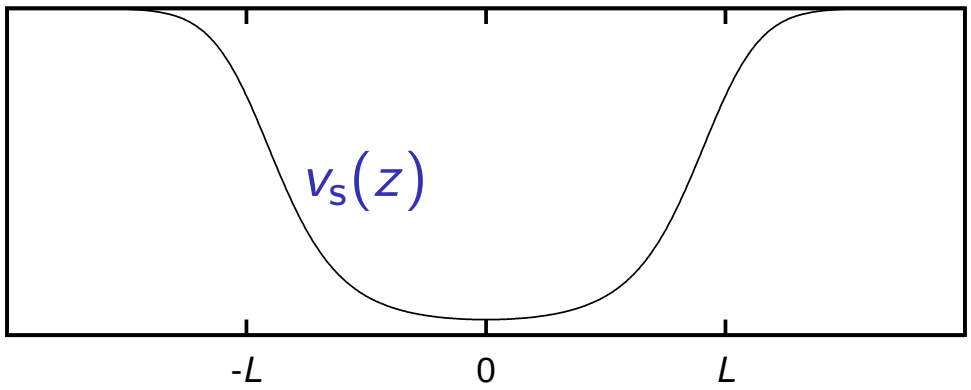

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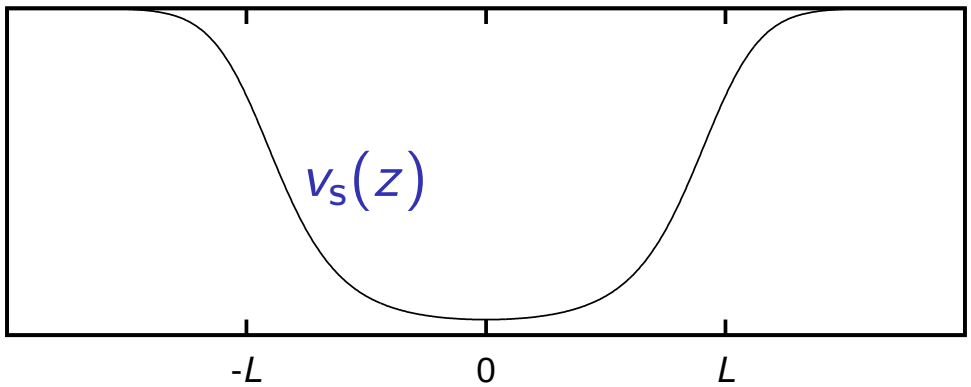

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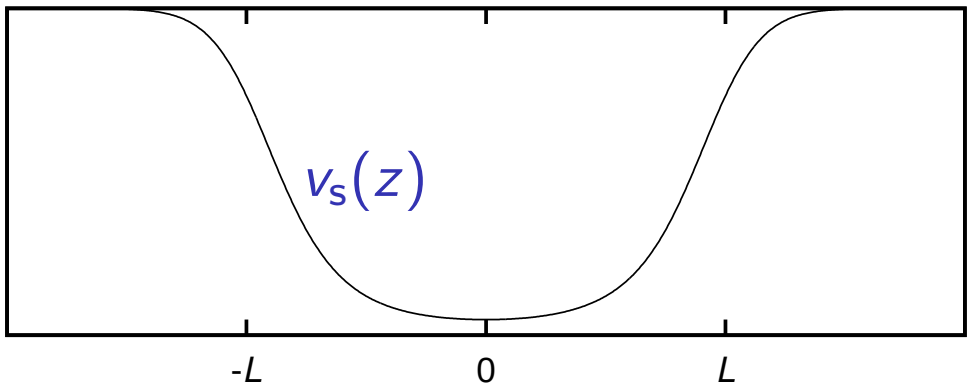

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density (spin-saturated)

$$n(\mathbf{r}) \equiv n(z) = \sum_\alpha \frac{k_\alpha^2}{2\pi}\Theta(\epsilon_F - \varepsilon_\alpha)\,\varphi_\alpha(z)^2 \qquad k_\alpha = \sqrt{2m(\epsilon_F - \varepsilon_\alpha)}$$

asymptotic behavior of density: $\alpha = h =$ highest band; $L =$ width of well

$$n(z \gg L) \;=\; \frac{k_h^2}{2\pi}\,\varphi_h(z)^2 \qquad \text{since} \quad \varphi_\alpha(z \gg L) \;\sim\; e^{-\sqrt{-2m\varepsilon_\alpha}\,z}$$

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exchange energy per unit area

$$\begin{aligned} E_{\mathrm{x}} \;=\; & -\int \frac{d^2k}{(2\pi)^2}\frac{d^2k'}{(2\pi)^2}\sum_{\alpha,\alpha'}\Theta(\epsilon_{\mathrm{F}}-\epsilon_{\mathbf{k}\alpha})\,\Theta(\epsilon_{\mathrm{F}}-\epsilon_{\mathbf{k}'\alpha'}) \\ & \times\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\,\frac{2\pi\,e^{-|\mathbf{k}-\mathbf{k}'||z-z'|}}{|\mathbf{k}-\mathbf{k}'|}\,\varphi_\alpha(z)\varphi_{\alpha'}(z)\varphi_{\alpha'}(z')\varphi_\alpha(z') \end{aligned}$$

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asymptotic exchange potential

$$\frac{\delta E_\mathrm{x}}{\delta n(z)} \;\xrightarrow{z\gg L}\; -\frac{4\pi}{k_h^2}\int\frac{d^2k}{(2\pi)^2}\frac{d^2k'}{(2\pi)^2}\Theta(\epsilon_\mathrm{F}-\epsilon_{\mathbf{k}h})\,\Theta(\epsilon_\mathrm{F}-\epsilon_{\mathbf{k}'h})$$
$$\times\int_{-\infty}^{\infty}dz'\,\frac{2\pi\,e^{-|\mathbf{k}-\mathbf{k}'||z-z'|}}{|\mathbf{k}-\mathbf{k}'|}\,\varphi_h(z')^2$$

$\longrightarrow$ z'-integral restricted to $-\bar{L} < z' < \bar{L}$ with $\bar{L} = L + \Delta L$ (surface width)

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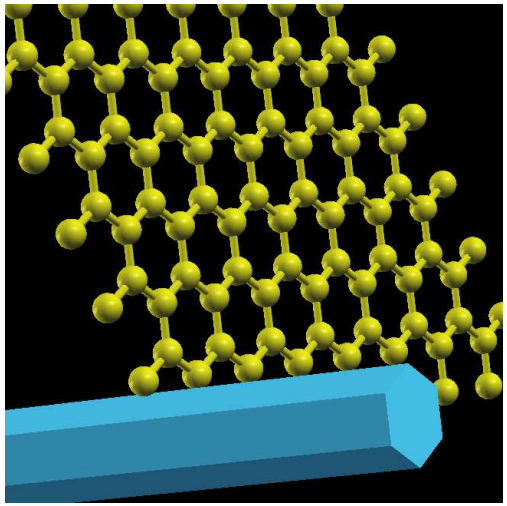
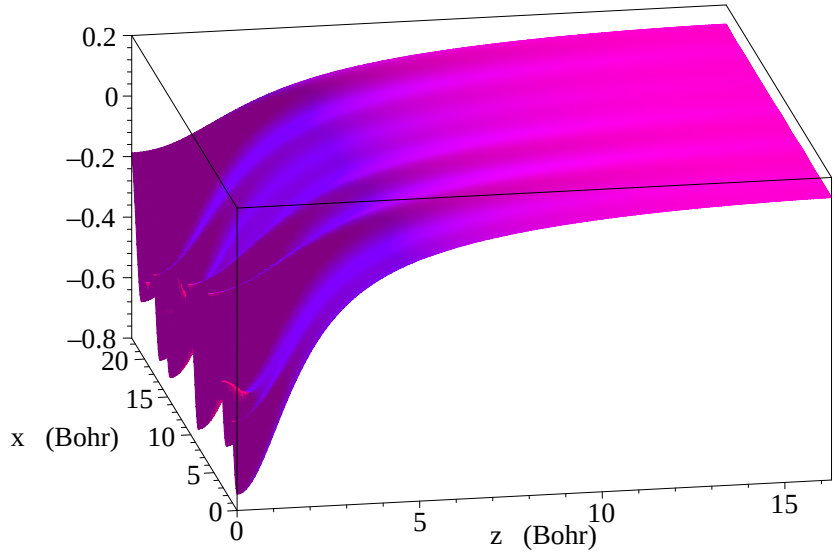
$\longrightarrow$ rapid convergence only for $z_0 = \langle z \rangle$

EXX Potential at Surfaces: Graphene





EXX-only PW-PP calculations; supercell of $7a$ vacuum ($a = 4.65$ Bohr)

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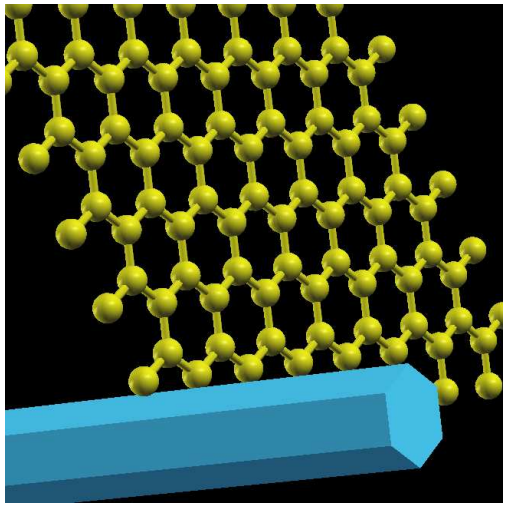

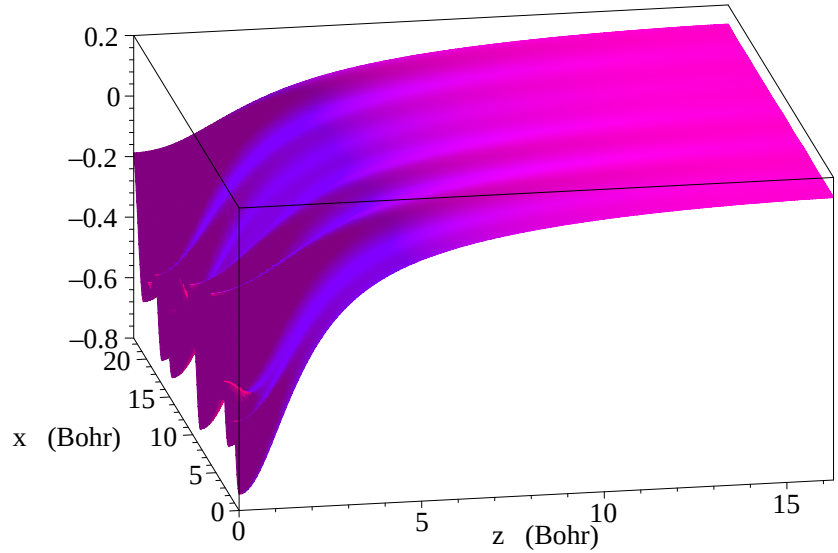

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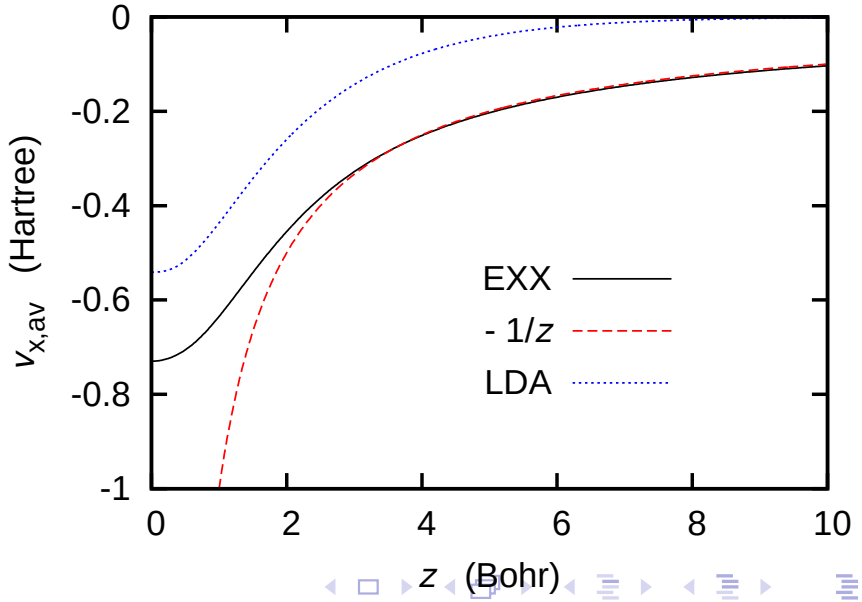
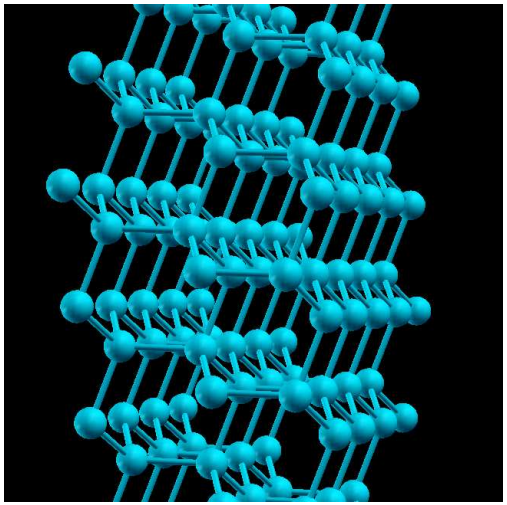
$$v_{x,av}(z) = \frac{1}{A}\int_A d^2 r_{\parallel}\, v_x(\mathbf{r})$$

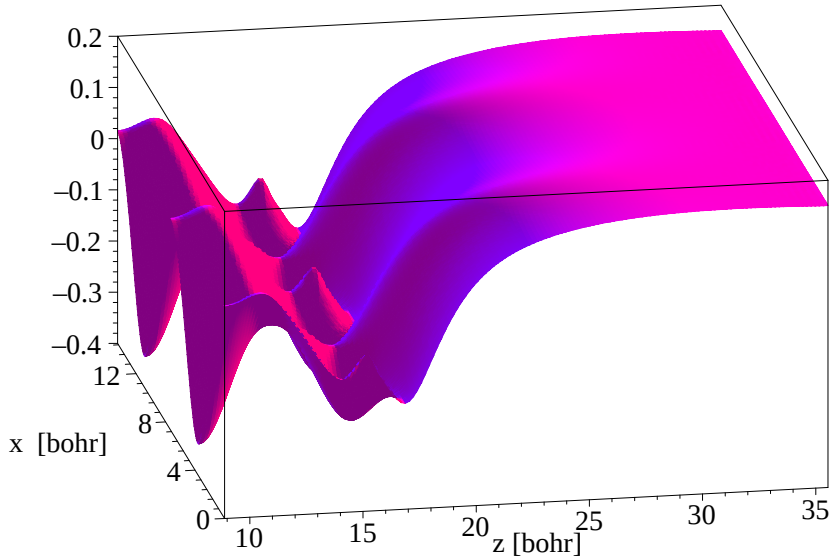
A = 2D unit cell of slab

$z_0 = 0$



EXX Potential at Surfaces: Si (111) slab





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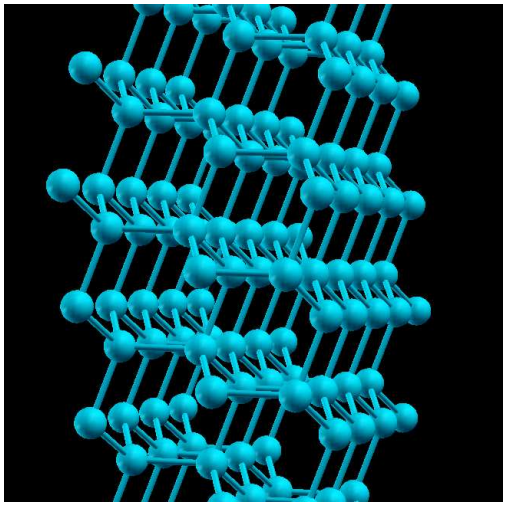

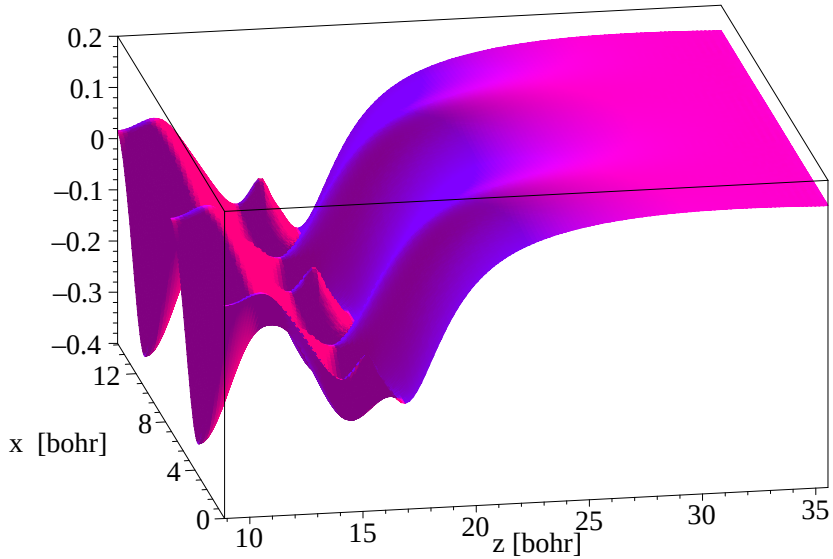

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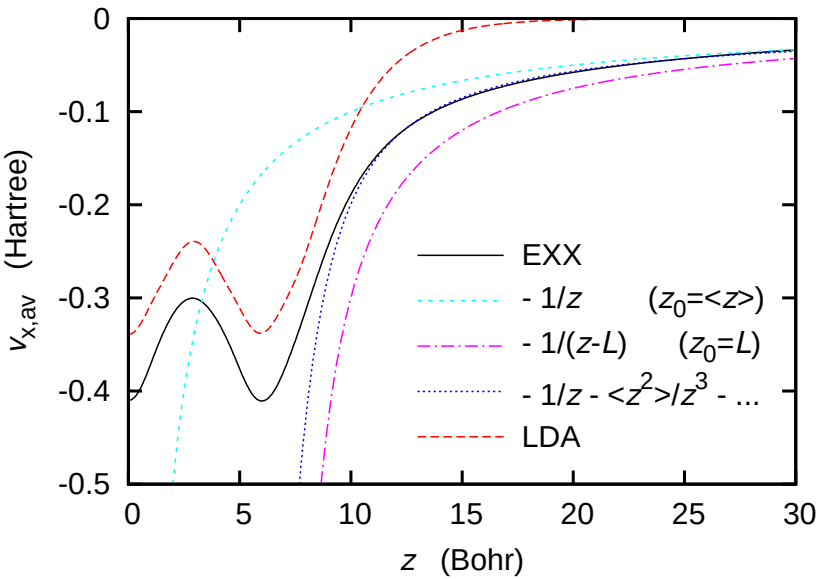

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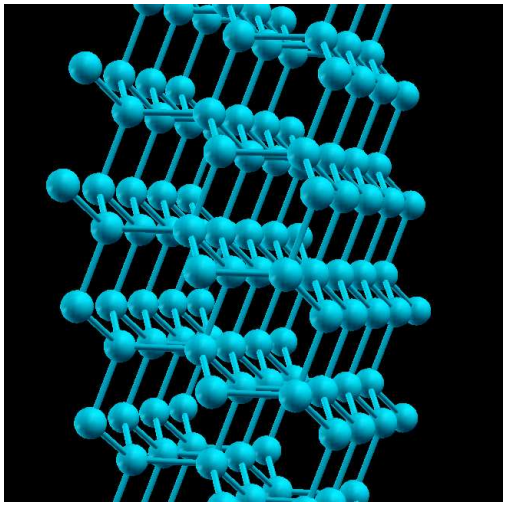

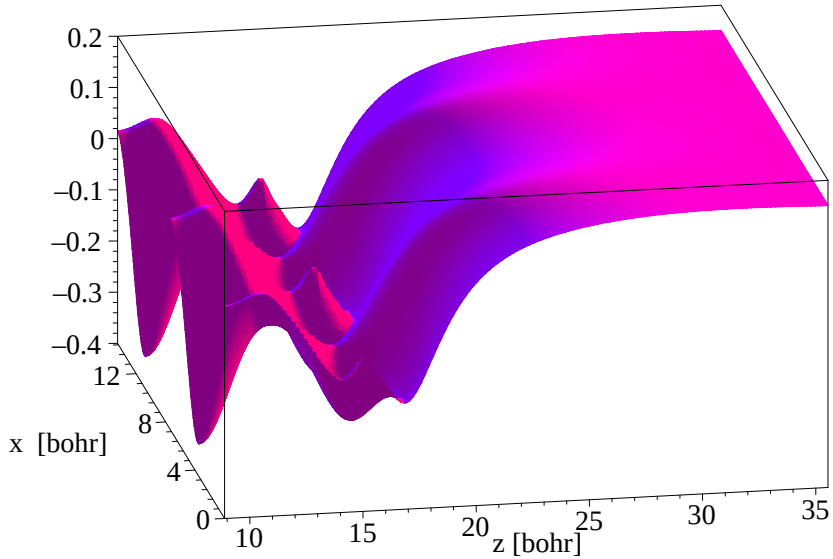

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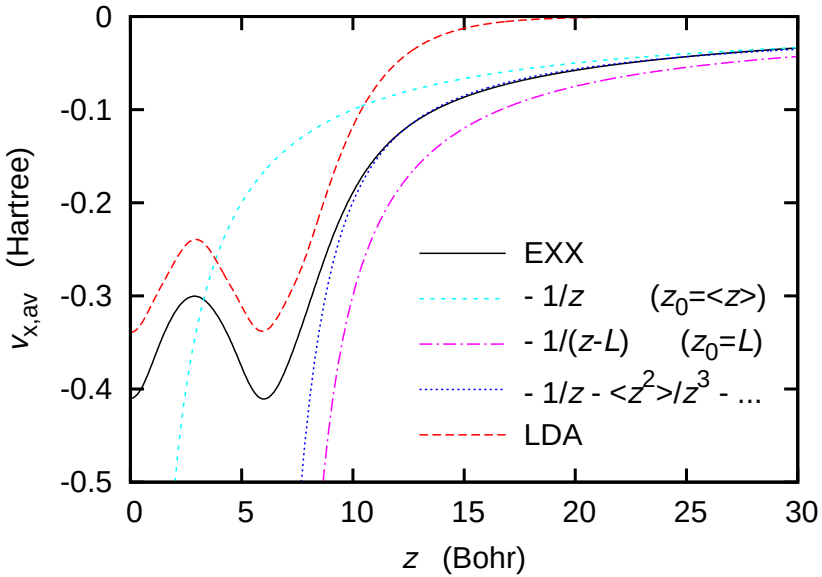

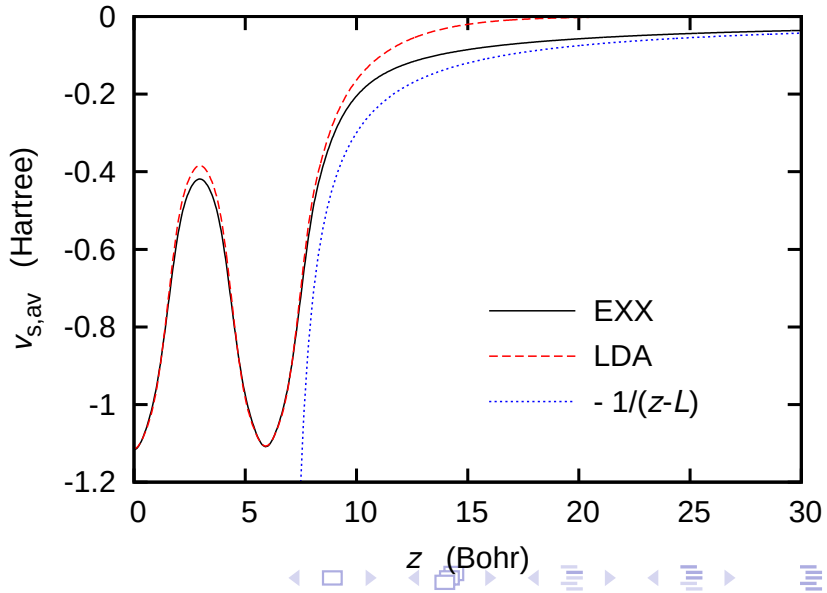

Interacting v-representability: Lieb Functional

Functional differentiability of $\langle \Psi[n] | \hat{H} | \Psi[n] \rangle$?

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Extension of $E[n]$ to proper set of n Lieb, IJQC **24**, 243 (1983)

$$E_{\mathrm{L}}[n] \;:=\; \inf_{\hat{D}\to n} \mathrm{tr}\left\{\hat{D}(\hat{T}+\hat{W}+\hat{V}_{\mathrm{ext}})\right\}$$

with ensemble density matrix $\hat{D}$

$$\hat{D} \;=\; \sum_k d_k\,|\Psi_k\rangle\langle\Psi_k|, \qquad d_k^* = d_k \geq 0, \qquad \sum_k d_k = 1$$

generated from arbitrary orthonormal set of N-particle states

$$\langle\Psi_k|\Psi_l\rangle \;=\; \delta_{kl} \qquad \Psi_k \in \mathcal{H}^1 \qquad \mathcal{H}^1 \;=\; \left\{f \;\middle|\; f \in \mathcal{L}^2, \boldsymbol{\nabla} f \in \mathcal{L}^2\right\}$$

and restricted to give desired density

$$n(\mathbf{r}) \;=\; \sum_k d_k\,\langle\Psi_k|\hat{n}(\mathbf{r})|\Psi_k\rangle$$

$\longrightarrow$ functional differentiability of $E_{\mathrm{L}}[n]$ guaranteed

Noninteracting v-representability: Lieb Kinetic Energy

Question: is there a KS system with same n for any interacting system?

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Solution: apply Lieb definition also to $T_s[n]$ Lieb, IJQC **24**, 243 (1983)

$$T_{s,L}[n] := \inf_{\hat{D}\to n} \text{tr}\{\hat{D}\hat{T}\} \qquad n(\mathbf{r}) = \sum_k d_k \langle\Psi_k|\hat{n}(\mathbf{r})|\Psi_k\rangle$$

$$\hat{D} = \sum_k d_k |\Psi_k\rangle\langle\Psi_k|, \quad d_k^* = d_k \geq 0, \quad \sum_k d_k = 1$$

$$\langle\Psi_k|\Psi_l\rangle = \delta_{kl} \qquad \Psi_k \in \mathcal{H}^1 \qquad \mathcal{H}^1 = \left\{f \;\middle|\; f \in \mathcal{L}^2, \nabla f \in \mathcal{L}^2\right\}$$

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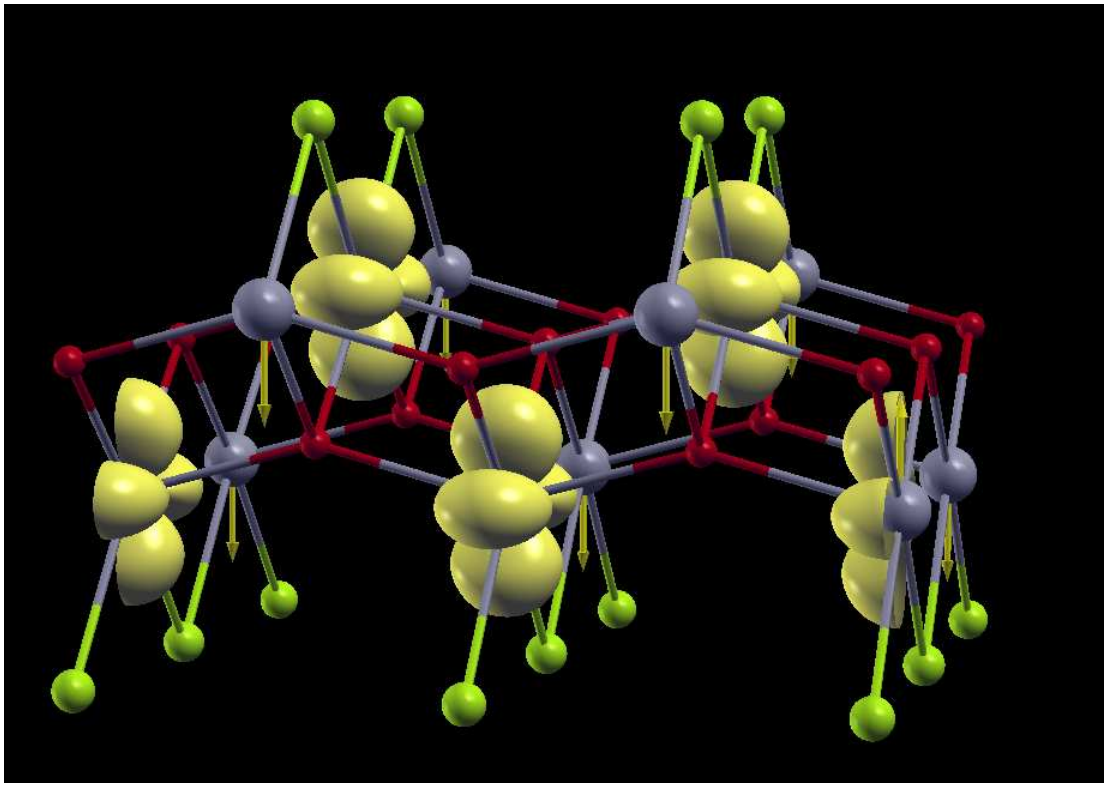
Back

TiOCl ($T > T_{c2}$): density of highest spin-up valence bands



Ti = grey dots
O = red dots
Cl = green dots
arrows = majority spin

(density isosurface
at $0.1\,\text{Å}^{-3}$)

$\longrightarrow$ rather pure d_{xy} character in coordinate system with x- and y-axes along diagonals of b-c-plane

$\longrightarrow$ consistent with experiment and LDA+U

back

Reliability of older EXX Results for solids?

$\longrightarrow$ has been questioned by first FP-LAPW all-electron calculations

Sharma, Dewhurst, Ambrosch-Draxl, PRL **95**, 136402 (2005)

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Example: band gap of diamond (values with * include LDA correlation)

Method	Δ_s	$\Gamma \rightarrow \Gamma$	
KKR-ASA*	4.58	5.87	Kotani, Akai, PRB, **54**, 16502 (1996)
LMTO-ASA*	4.65	5.92	Kotani, Akai, PRB, **54**, 16502 (1996)
PW-PP*	4.79	6.28	Städele et al., PRL **79**, 2089 (1997)
PW-PP	4.67	6.24	Engel, PRB **80**, 161205(R) (2009)
FP-LAPW	5.1	6.67	Sharma, et al., PRL **95**, 136402 (2005)

Reliability of older EXX Results for solids?

$\longrightarrow$ has been questioned by first FP-LAPW all-electron calculations

Sharma, Dewhurst, Ambrosch-Draxl, PRL **95**, 136402 (2005)

Example: band gap of diamond (values with * include LDA correlation)

Method	Δ_s	$\Gamma \rightarrow \Gamma$	
KKR-ASA*	4.58	5.87	Kotani, Akai, PRB, **54**, 16502 (1996)
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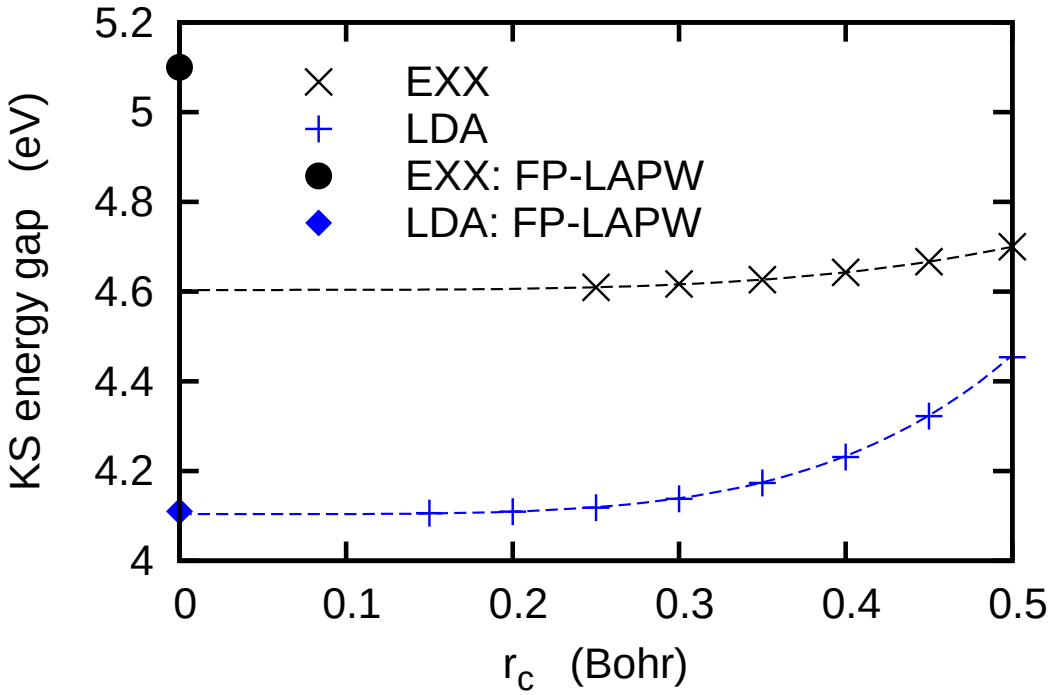
FP-LAPW	5.1	6.67	Sharma, et al., PRL **95**, 136402 (2005)
PW-AE	4.60	6.19	Engel, PRB **80**, 161205(R) (2009) details
FP-LAPW		6.21	Betzinger et al., PRB **83**, 045105 (2011)

Fundamental KS Band Gap of Diamond: Exact Exchange



PW all-electron calculations:

- use PP to smoothen nuclear potential at origin
- use large PW basis sets to ensure convergence (1200 Ry for EXX and $r_c = 0.25$ Bohr)

EXX: FP-LAPW — Sharma, Dewhurst, Ambrosch-Draxl, PRL **95**, 136402 (2005)

LDA: FP-LAPW — Tran, Blaha, Schwarz, JP: CM **19**, 196208 (2007)

EXX: PW-PP — Engel, PRB **80**, 161205(R) (2009)

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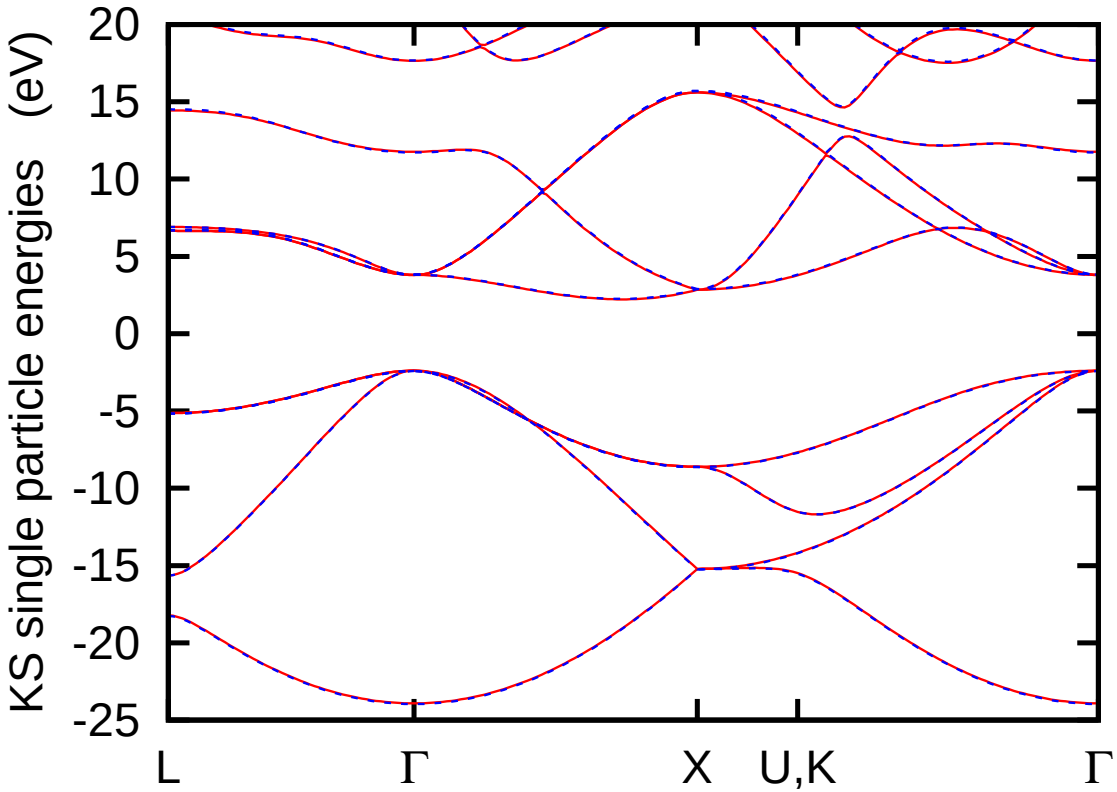
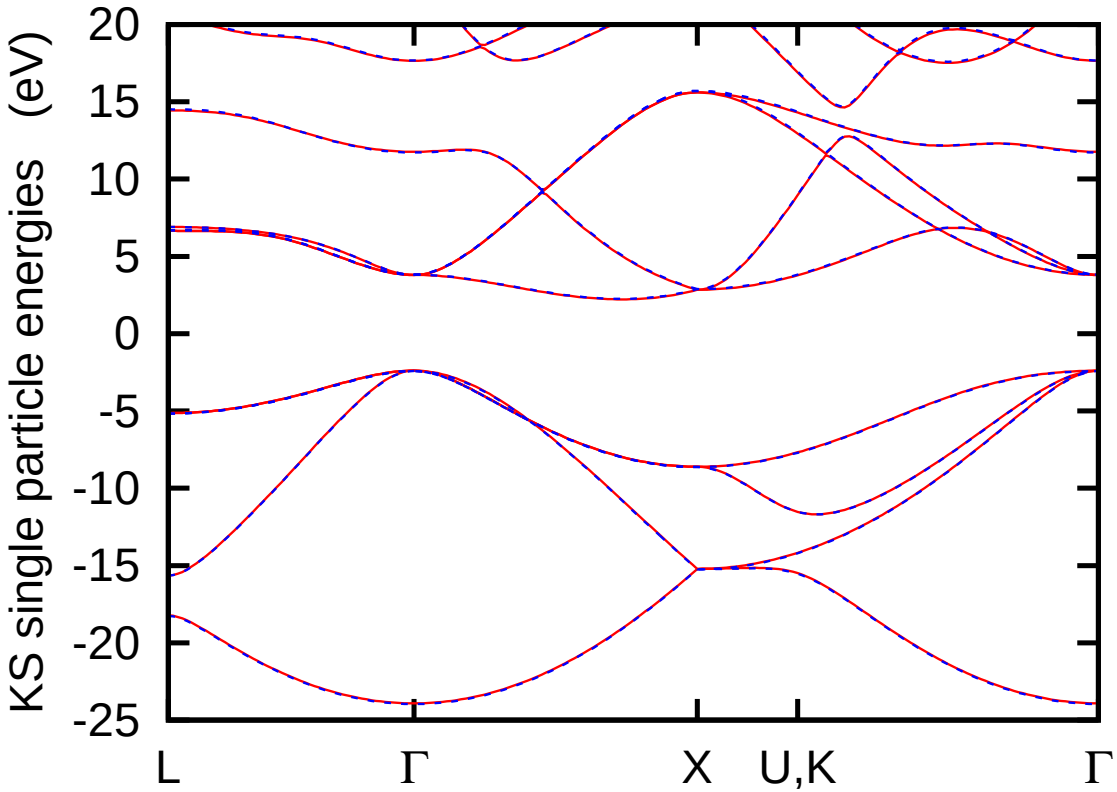
All-electron versus Pseudopotential Calculation: Diamond



dashed, blue = PP

solid, red = AE

All-electron versus Pseudopotential Calculation: Diamond



dashed, blue = PP
solid, red = AE

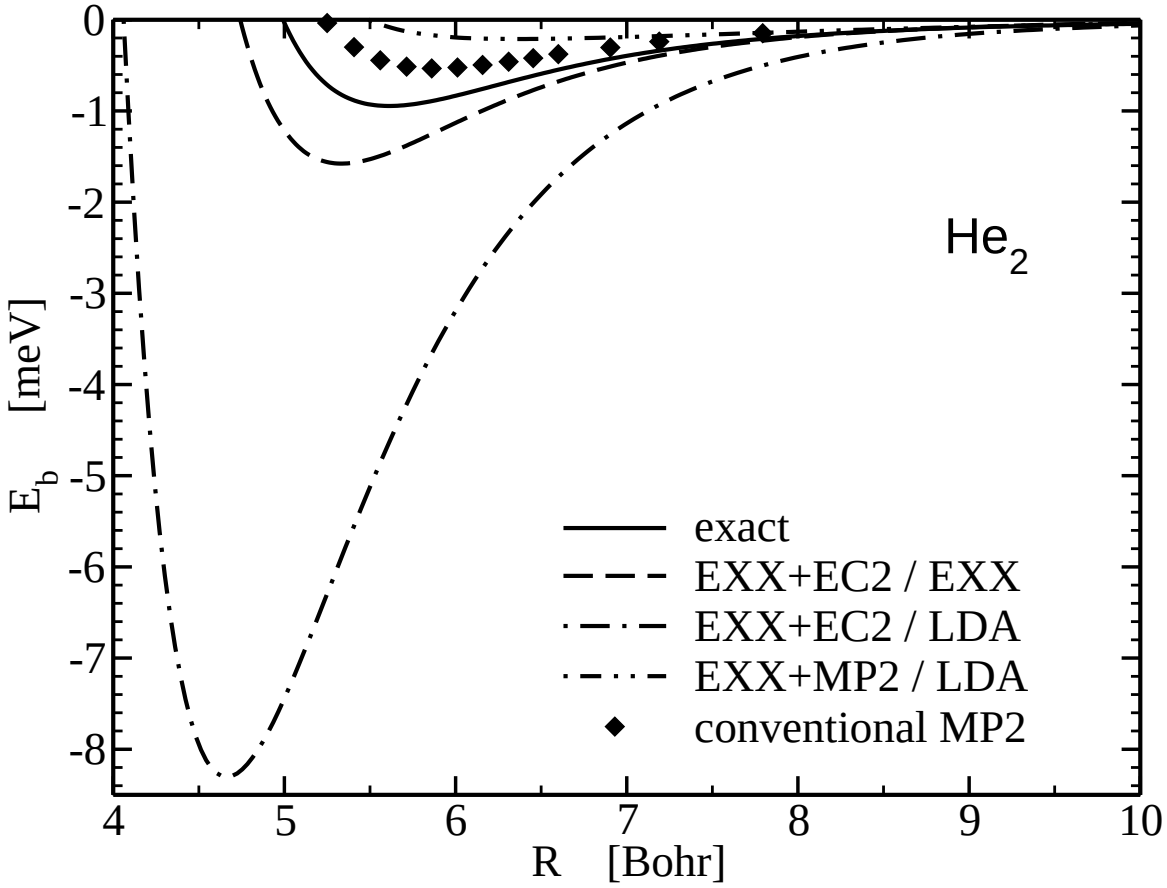
$\longrightarrow$ differences first FP-LAPW $\longleftrightarrow$ PW-PP even more dramatic if $3d$ electrons are involved

$\longrightarrow$ discrepancies attributed to core-valence contribution to exchange

Band Gap of Semiconductors: Exact Exchange

	E_x	E_c	Method	C	Si	Ge	GaAs	Ne
$\Delta_s(\Gamma)$	Exact	—	FP-LAPW	6.67	3.58	1.42	2.42	16.3
	Exact	—	PW-AE	6.19				
	Exact	—	PW-PP	6.24	3.17	1.46	2.06	14.72
	LDA	LDA	PW-PP	5.56	2.56	0.0	0.0	11.32
$E_g(\Gamma)$	Expt. ($T > 0$)			6.0	3.35	0.89	1.63	21.69
Δ_s	Exact	LDA	KKR-ASA	4.58	1.12	1.03		
	Exact	LDA	LMTO-ASA	4.65	1.25	1.12		
	Exact	LDA	PW-PP	4.81	1.35	1.22	2.11	14.76
	Exact	PBE	PW-PP	4.32	0.94	0.84	1.80	
	Exact	—	PW-PP	4.67	1.21	1.08	2.03	14.15
	Exact	—	PW-AE	4.60				
Δ_x	Exact	—	PW-PP	8.70	5.62	4.81	5.28	
E_g	HF	(LAPW/PW-PP)		12.4	6.3	6.4	7.7	
	Expt. ($T = 0$)			5.48	1.17	0.79	1.52	21.69

Energy Surface of He_2: Various Perturbation Expansions



exact: Aziz, Slaman, JCP **94**, 8047 (1991)

MP2: Woon, JCP **100**, 2838 (1994)

EXX+EC2,MP2: Engel, Höck, Dreizler, PRA **61**, 032502 (2000)

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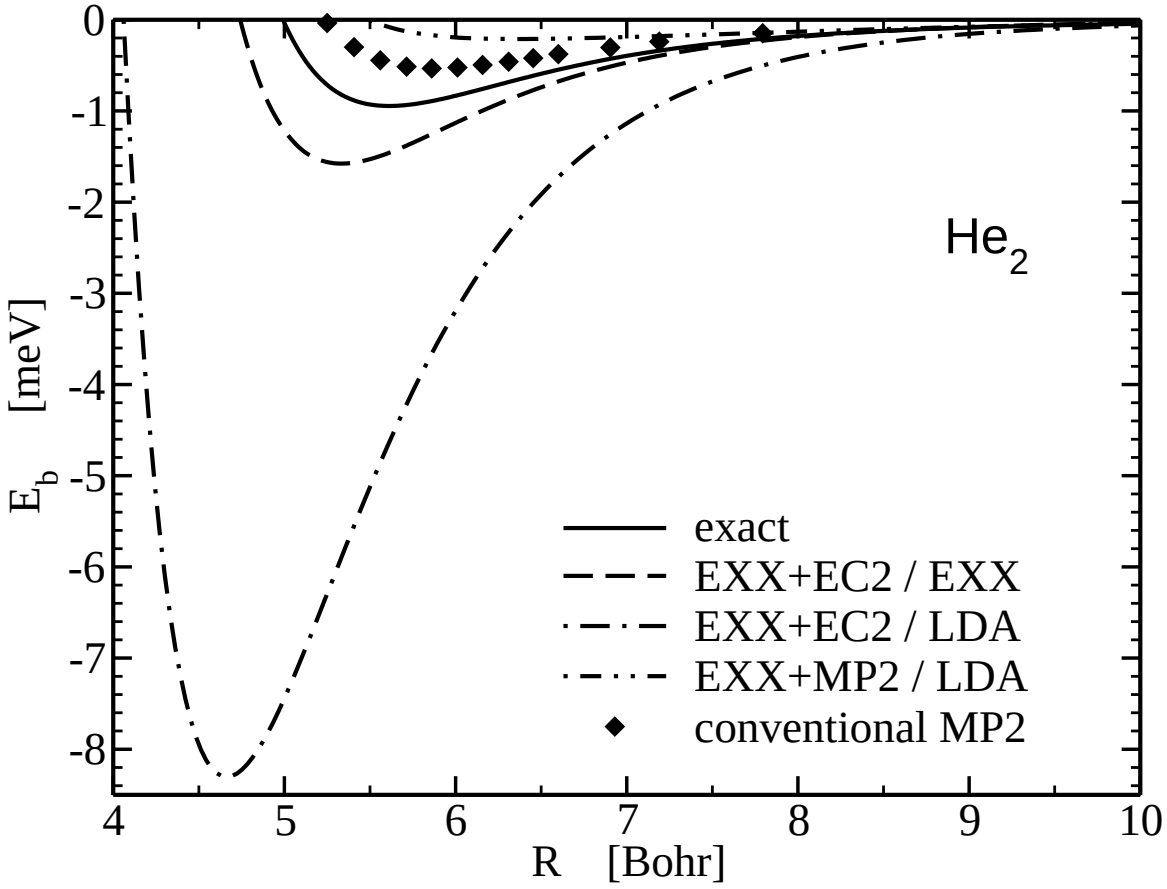

- KS Hamiltonian important

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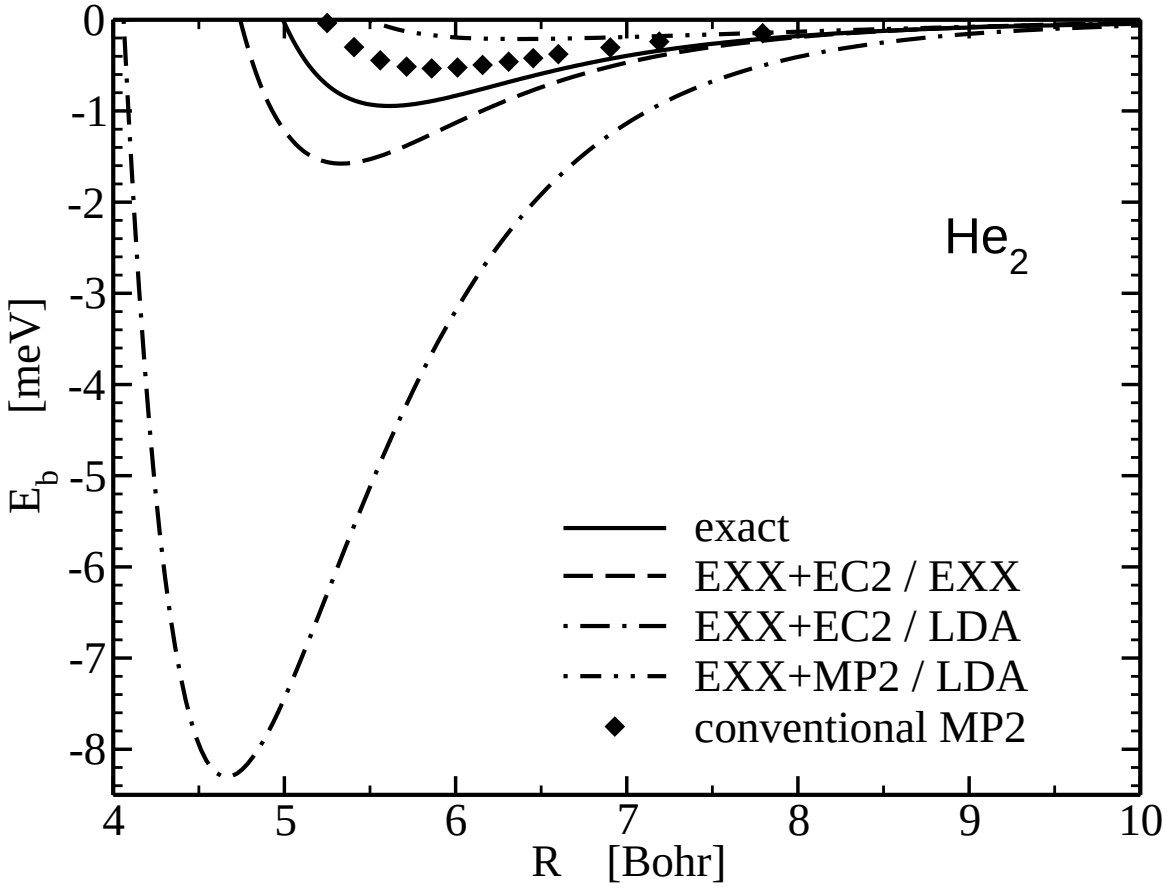

- KS Hamiltonian important
- role of $v_c^{(2)}$?

exact: Aziz, Slaman, JCP **94**, 8047 (1991)

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EXX+EC2,MP2: Engel, Höck, Dreizler, PRA **61**, 032502 (2000)

Van-der-Waals Coefficient C_6

Atoms	$E_c^{(2)}$ [a]	empirical [b,c]
He–He	1.66	1.46
He–Ne	3.49	3.03
Ne–Ne	7.45	6.38
Xe–Xe	730.7	285.9
H–He	3.02	2.82 ± 0.02
H–Na	81.14	71.8 ± 0.3

$E_c^{(2)}$ results on basis of x-only KS response function

$\longrightarrow$ reasonably accurate for light atoms

[a] Lein, Dobson, Gross, JCC **20**, 12 (1999)

[b] Kumar, Meath, JMP **54**, 823 (1985)

[c] Tang, Norbeck, Certain, JCP **64**, 3063 (1976)

Green's Function Approach to Exact $E_{xc}[n]$: I. Basics

Starting point: assume v_s to be known

Green's Function Approach to Exact $E_{\mathrm{xc}}[n]$: I. Basics

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- defines noninteracting Hamiltonian $\hat{H}_{\mathrm{s}} = \hat{T} + \int d^3 r\, \hat{n}(\mathbf{r}) v_{\mathrm{s}}(\mathbf{r})$

Green's Function Approach to Exact $E_{\mathrm{xc}}[n]$: I. Basics

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- KS ground state $|\Phi_0\rangle$ (Slater-determinant of the ϕ_k)
- complete KS spectrum available: KS field operator, Green's function

$$
\begin{aligned}
\hat{\psi}_0(\mathbf{r}t) &= e^{i\hat{H}_{\rm s}t}\, \hat{\psi}(\mathbf{r})\, e^{-i\hat{H}_{\rm s}t} \\
iG_{\rm s}(\mathbf{r}t, \mathbf{r}'t') &= \langle \Phi_0 | T \hat{\psi}_0(\mathbf{r}t) \hat{\psi}_0^\dagger(\mathbf{r}'t') | \Phi_0 \rangle \\
&= \sum_k \phi_k(\mathbf{r}) \phi_k^\dagger(\mathbf{r}')\, e^{-i\epsilon_k(t-t')} \\
&\qquad \times \left[\Theta(t-t')(1-\Theta_k) - \Theta(t'-t)\Theta_k \right]
\end{aligned}
$$

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\end{aligned}$$

Concept: use standard many-body-theory with $\hat{H}_s$ as noninteracting reference system together with perturbation

$$\hat{H}_1 = \hat{W} - \int d^3r\, \hat{n}(\mathbf{r}) \left[v_s(\mathbf{r}) - v_{\text{ext}}(\mathbf{r}) \right]$$

Green's Function Approach to Exact $E_{\rm xc}[n]$: II. Result

Coupling-constant-integration

Engel et al., PRA **58**, 964 (1998)

$$E_{\rm xc} = \frac{1}{2}\int d^3r \int d^3r' \, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left[\langle\Phi_0|\hat{\psi}^\dagger(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Phi_0\rangle - n(\mathbf{r})n(\mathbf{r}')\right]$$

$$+\sum_{n=1}^{\infty}\frac{(-i)^n}{(n+1)!}\int_{-\infty}^{\infty} dt_1\cdots dt_n \, \langle\Phi_0|T\hat{H}_{1,I}(0)\hat{H}_{1,I}(t_1)\cdots\hat{H}_{1,I}(t_n)|\Phi_0\rangle_I$$

Back

Green's Function Approach to Exact $E_{\rm xc}[n]$: II. Result

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Back

Green's Function Approach to Exact $E_{\mathrm{xc}}[n]$: II. Result

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Engel et al., PRA **58**, 964 (1998)

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- exact representation of E_{xc}
- further evaluation via Wick's theorem etc possible
- basic elements: G_{s}, v_{xc}: $\quad v_{\mathrm{s}} - v_{\mathrm{ext}} = v_{\mathrm{H}} + v_{\mathrm{xc}}$
- highly nonlinear relation for E_{xc}

Back

Spin-density Functional Theory

Extend Hamiltonian to include magnetic effects

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_{\text{ext}} + \int d^3 r \, \mathbf{B}_{\text{ext}}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r})$$

magnetization density

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Statements: (von Barth, Hedin, Rajagopal, Callaway, 1972)

- existence of unique map (nondegenerate ground state $|\Psi_0\rangle$)

$$|\Psi_0\rangle \overset{\text{one-to-one}}{\longleftrightarrow} \{n_0(\mathbf{r}), \mathbf{m}_0(\mathbf{r})\} \qquad \mathbf{m}_0(\mathbf{r}) = \langle \Psi_0 | \hat{\mathbf{m}}(\mathbf{r}) | \Psi_0 \rangle$$

$\Longrightarrow$ universal functional $|\Psi[n, \mathbf{m}]\rangle$

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- minimum principle for ground state energy functional

$$E[n, \mathbf{m}] = \langle \Psi[n, \mathbf{m}] | \hat{H} | \Psi[n, \mathbf{m}] \rangle$$

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Standard simplification: Reduce $\mathbf{B}, \mathbf{m}$ to one component

$\longrightarrow$ spin-densities $n_\sigma(\mathbf{r})$ can be used as basic variables

$$n = n_\uparrow + n_\downarrow \qquad m_z = \mu_B [n_\uparrow - n_\downarrow] \qquad \Longrightarrow \qquad |\Psi_0\rangle = |\Psi[n_\uparrow, n_\downarrow]\rangle$$

Kohn-Sham Equations of Spin-Density Functional Theory

1) represent spin-densities in terms of auxiliary orbitals $\phi_{k\sigma}$ $(\sigma = \uparrow, \downarrow)$

$$n_\sigma(\mathbf{r}) = \sum_k \Theta_{k\sigma} |\phi_{k\sigma}(\mathbf{r})|^2 \qquad \Theta_{k\sigma} = \begin{cases} 1 & \text{for} \quad \epsilon_{k\sigma} \leq \epsilon_F \\ 0 & \text{for} \quad \epsilon_F < \epsilon_{k\sigma} \end{cases}$$

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2) decompose total energy into suitable components ($B_z = 0$)

$$\begin{aligned} E &= T_\mathrm{s} + \int d^3r \, v_\mathrm{ext} n + E_\mathrm{H}[n] + E_\mathrm{xc}[n_\uparrow, n_\downarrow] \\ T_\mathrm{s} &= \frac{-1}{2m} \sum_{k\sigma} \Theta_{k\sigma} \int d^3r \, \phi^\dagger_{k\sigma}(\mathbf{r}) \boldsymbol{\nabla}^2 \phi_{k\sigma}(\mathbf{r}) \end{aligned}$$

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3) minimize E: coupled single-particle equations for both spins

$$\left\{ \frac{-\boldsymbol{\nabla}^2}{2m} + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + \underbrace{\frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})}}_{= v_{xc,\sigma}(\mathbf{r})} \right\} \phi_{k\sigma}(\mathbf{r}) = \epsilon_{k\sigma} \phi_{k\sigma}(\mathbf{r})$$

Relativistic Spin-Density Functional Theory (collinear)

Relativistic Spin-Density Functional Theory (collinear)

Dirac-type KS equations (ϕ_k = four spinors) (Macdonald, Vosko, 1979)

$$\left\{ -ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta-1)mc^2 + \sum_{\sigma=\pm} P_\sigma v_{s,\sigma}(\mathbf{r}) \right\} \phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{r})$$

$$P_\pm = \frac{1 \pm \beta\Sigma_z}{2} \qquad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} \qquad (\boldsymbol{\alpha}, \beta = \text{Dirac matrices})$$

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generalized spin-densities (no-pair)

$$n_\pm(\mathbf{r}) = \sum_k \Theta_k \, \phi_k^\dagger(\mathbf{r}) P_\pm \phi_k(\mathbf{r}) \qquad \Theta_k = \begin{cases} 1 & \text{if } \epsilon_F \geq \epsilon_k > -mc^2 \\ 0 & \text{else} \end{cases}$$

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total potential (no external magnetic field)

$$v_{\mathrm{s},\sigma}(\mathbf{r}) \;=\; v_\mathrm{ext}(\mathbf{r}) + v_\mathrm{H}(\mathbf{r}) + v_{\mathrm{xc},\sigma}(\mathbf{r}) \qquad v_{\mathrm{xc},\sigma}(\mathbf{r}) \;=\; \frac{\delta E_\mathrm{xc}[n_+, n_-]}{\delta n_\sigma(\mathbf{r})}$$

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$\longrightarrow$ approximation for $E_\mathrm{xc}[n_+, n_-]$ required

KS Equations of RSDFT: Non-collinear Version

OPM Equation of RSDFT: Collinear Version

Collinear approximation obtained from assumption $\mathbf{B}_s(\mathbf{r}) = (0, 0, B_s(\mathbf{r}))$

OPM Equation of RSDFT: Collinear Version

Collinear approximation obtained from assumption $\mathbf{B}_s(\mathbf{r}) = (0, 0, B_s(\mathbf{r}))$

$\longrightarrow$ spin-densities $n_\pm$ may be used as basic variables

$$n_\pm(\mathbf{r}) = \frac{1}{2}\left[n(\mathbf{r}) \pm \frac{m_z(\mathbf{r})}{\mu_B}\right] = \sum_k \Theta_k \phi_k^\dagger(\mathbf{r}) P_\pm \phi_k(\mathbf{r}) \qquad P_\pm = \frac{1 \pm \beta\Sigma_z}{2}$$

$$v_{\mathrm{xc}}^\pm(\mathbf{r}) = v_{\mathrm{xc}}(\mathbf{r}) \pm \frac{B_{\mathrm{xc},z}(\mathbf{r})}{\mu_B}$$

OPM Equation of RSDFT: Collinear Version

Collinear approximation obtained from assumption $\mathbf{B}_s(\mathbf{r}) = (0, 0, B_s(\mathbf{r}))$

$\longrightarrow$ spin-densities $n_\pm$ may be used as basic variables

$$n_\pm(\mathbf{r}) = \frac{1}{2}\left[n(\mathbf{r}) \pm \frac{m_z(\mathbf{r})}{\mu_B}\right] = \sum_k \Theta_k \phi_k^\dagger(\mathbf{r}) P_\pm \phi_k(\mathbf{r}) \qquad P_\pm = \frac{1 \pm \beta\Sigma_z}{2}$$

$$v_{\mathrm{xc}}^\pm(\mathbf{r}) = v_{\mathrm{xc}}(\mathbf{r}) \pm \frac{B_{\mathrm{xc},z}(\mathbf{r})}{\mu_B}$$

$\longrightarrow$ corresponding OPM equation (ignore ϵ_k-dependence of E_{xc})

$$\sum_{\sigma'} \int d^3r' \, \chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') v_{\mathrm{xc}}^{\sigma'}(\mathbf{r}') = -\sum_k \int d^3r' \, \phi_k^\dagger(\mathbf{r}) P_\sigma G_k(\mathbf{r}, \mathbf{r}') \frac{\delta E_{\mathrm{xc}}}{\delta \phi_k^\dagger(\mathbf{r}')} + c.c.$$

$$\chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = -\sum_k \Theta_k \phi_k^\dagger(\mathbf{r}) P_\sigma G_k(\mathbf{r}, \mathbf{r}') P_{\sigma'} \phi_k(\mathbf{r}') + c.c.$$

$$G_k(\mathbf{r}, \mathbf{r}') = \sum_{l \neq k} \frac{\phi_l(\mathbf{r}) \, \phi_l^\dagger(\mathbf{r}')}{\epsilon_l - \epsilon_k}$$