Constructing pseudopotentials for ABINIT:
about the use of the fhi98PP package

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Description of fhi98PP

1 Generate **norm-conserving** pseudopotentials (DFT) of
 − Hamann or Troullier–Martins type
 − test their transferability on the atomic level,
   including the fully-separable KB form

 by a free fortran77 code, operated through
 commandline interface using UNIX csh scripts

2 View data by GNU GPL plotting tool xmgrace
 http://plasma-gate.weizmann.ac.il/Grace/

3 Learn from **tutorial** (ps booklet) and background write-up
 M Fuchs, M Scheffler, Comput Phys Commun 119, 67–98 (1999)

➥ download from *http://www.FHI-Berlin.MPG.DE/th/fhi98md/fhi98PP/*

Interfaced to ABINIT . . .

. . . gives flexibility where needed

Part I: psatom

Free atom: all-electron full potential $\longrightarrow$ pseudo valence orbitals & pseudopotential

- Kohn-Sham equations for full potential $\rightarrow$ eigenstates $\phi_i^{AE}(\mathbf{r}) = \frac{u_{\nu l}^{AE}(r)}{r} Y_{lm}(\Omega)$ ... spherial

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V^{AE}[n^{AE};r] \right] u_{\nu l}^{AE}(r) = \epsilon_{\nu l}^{AE} u_{\nu l}^{AE}(r), \quad n^{AE}(r) = \sum_{occ} f_i |\phi_i^{AE}(\mathbf{r})|^2$$

▶ Relativity: Dirac $\rightarrow$ scalar relativistic $\rightarrow$ non-relativistic

▶ Full potential $\quad V^{AE}[n^{AE};r] = -\frac{Z}{r} + V^H[n^{AE};r] + \boxed{V^{XC}[n^{AE};r]}$

····· XC in LDA or GGA: **take same as in solid etc.**

- Pseudo atom $\rightarrow$ pseudo valence orbitals $\phi_i(\mathbf{r}) = \frac{u_l(r)}{r} Y_{lm}(\Omega)$ and density n

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l^{scr}[n;r] \right] u_l(r) = \epsilon_l u_l(r), \quad n(r) = \sum_{occ} f_i |\phi_i(\mathbf{r})|^2$$
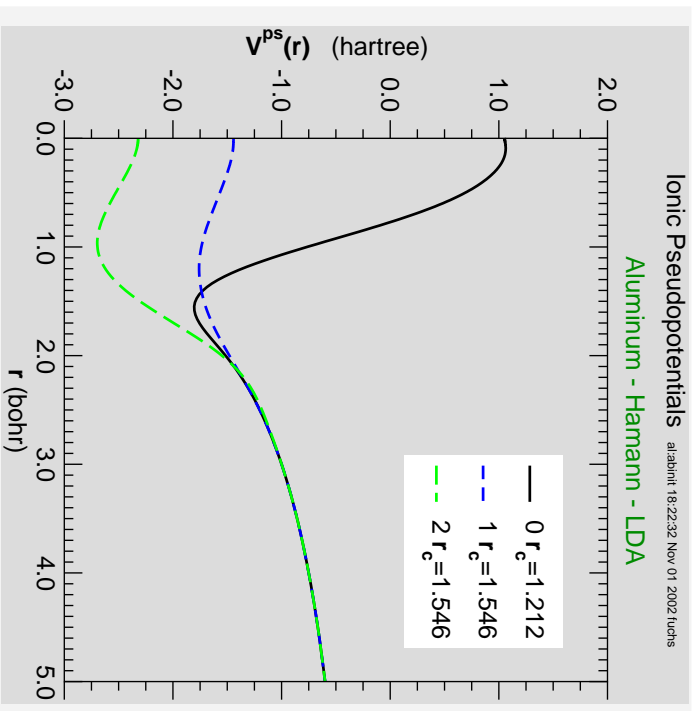
···· formally non-relativistic Schrödinger eq.

···· different for each valence state $\rightarrow$ l-dependent

↳ **Ionic pseudopotentials** $V_l^{ps}[n;r] = V_l^{scr}[n;r] - V^H[n;r] - \boxed{V^{XC}[n;r]}$

Part I: psatom

Pseudopotential on screen. . .

Ionic Pseudopotentials abinit 18:22:32 Nov 01 2002 fuchs

Aluminum - Hamann - LDA

$V^{ps}(r)$ (hartree)

r (bohr)

0 r_c=1.212
1 r_c=1.546
2 r_c=1.546

. . . is **transferable?**

- Start with default cutoff radii & neutral atom:

- Norm-conservation conditions

$$\epsilon_l = \epsilon_{\nu l}^{AE}$$
$$\langle \phi_l | \phi_l \rangle = \langle \phi_{\nu l}^{AE} | \phi_{\nu l}^{AE} \rangle$$

↘ ensure correct scattering properties around atomic valence energies
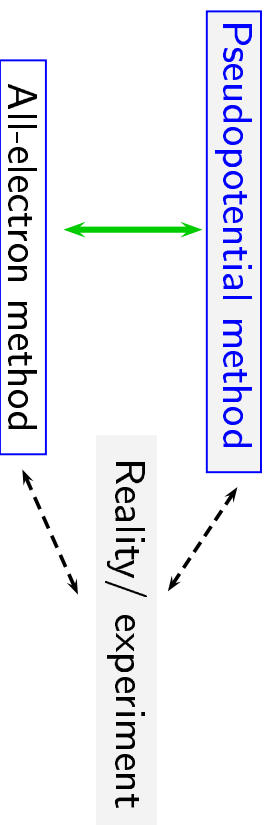
- But how about in the solid or molecule?

Must test!

. . . and if needed

improved!

- Proposal of how to . . .

All-electron method $\longleftrightarrow$ Pseudopotential method

Reality/ experiment

○ compromise with needed <u>smoothness</u>

● needed accuracy $\sim \mathcal{O}(0.1 \ldots 0.01 \text{ eV})$

  — electronic structure

  — cohesive properties

  — atomic structure, relaxation, phonons

  — formation enthalpies, activation energies, ...

● modifications

  — separable potentials (computational)

  — core corrections (methodic)

▶ <u>new materials</u> → GaN (with $3d$ or not), ...

▶ <u>new XC functionals</u> → GGA, ...
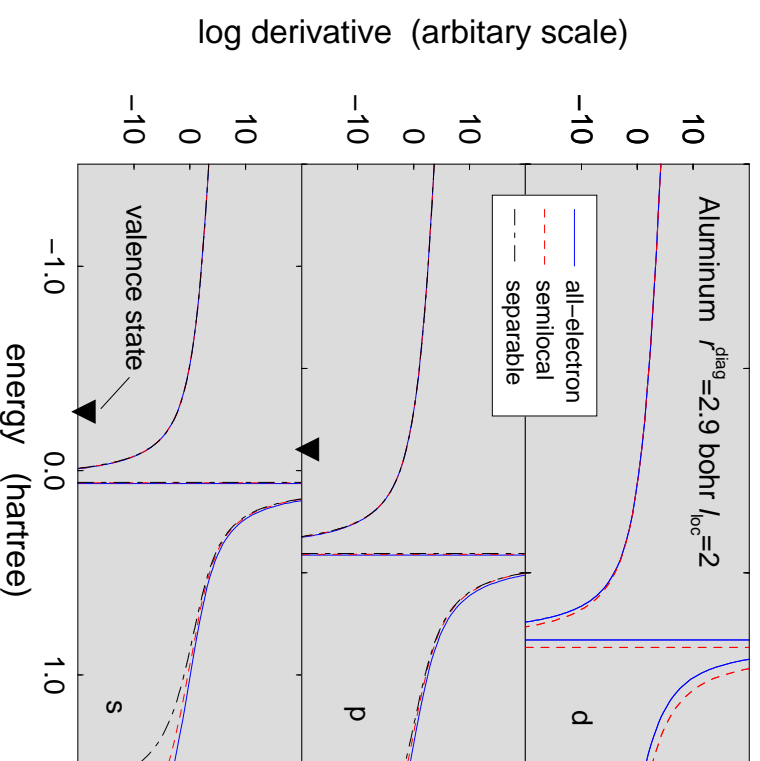
Characteristic tests of PP at atomic level?

Test: Logarithmic derivatives

$$D_l(r^{diag}, \epsilon) = \frac{1}{R_l(\epsilon)} \frac{d}{dr} R_l(r, \epsilon)\Big|_{r^{diag}}$$

norm conservation: o.k. for $\epsilon_l \pm \delta\epsilon$

... in practice: over range of valence bands?

log derivative (arbitary scale)

Aluminum r^{diag}=2.9 bohr l_{loc}=2

all–electron / semilocal / separable

valence state

energy (hartree)

s   p   d

Hardness tests - a „good" example

Test: Configurational changes (ΔSCF)
- $s \rightarrow p$ promotion (C, Si, Ge, ...)
- ionization (Li→Li$^+$, Na→Na$^+$, ...)

- total energy (excitations) $E[n(f_k)]$
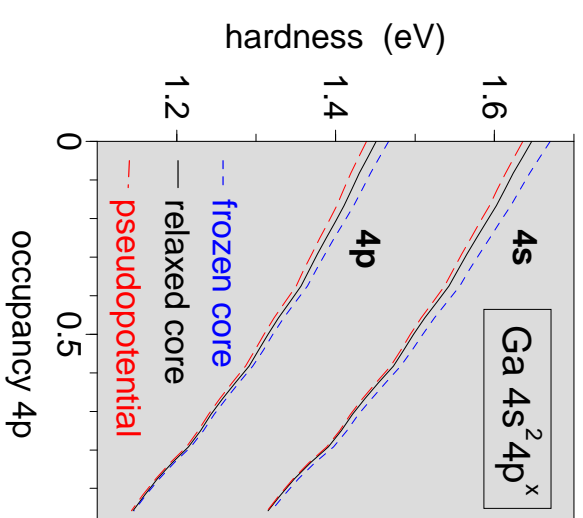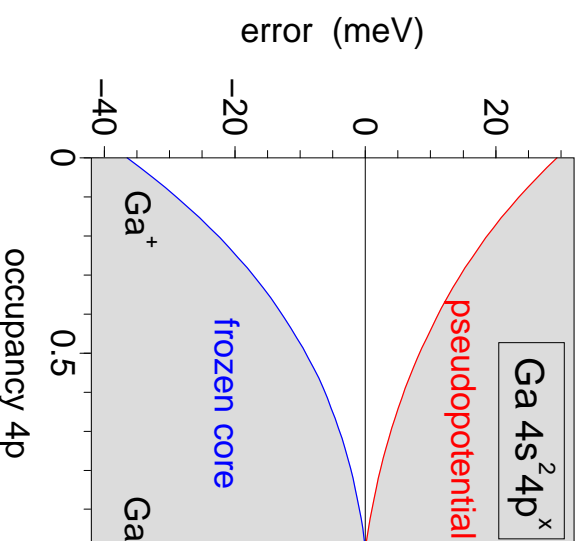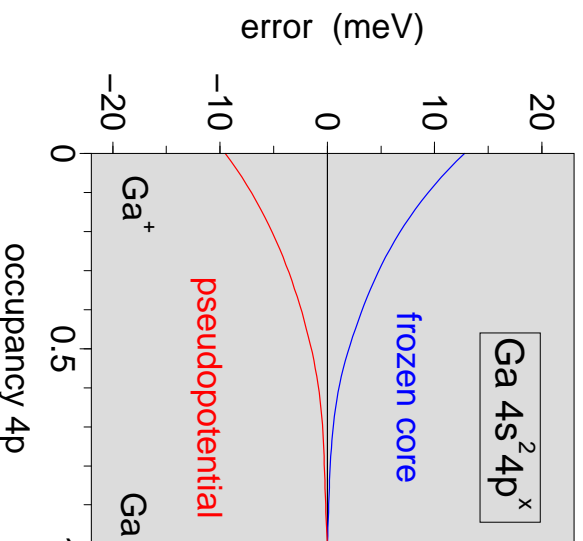
- eigenvalues (Janak theorem) $\dfrac{\partial E(f_k)}{\partial f_i} = \epsilon_i(f_k)$

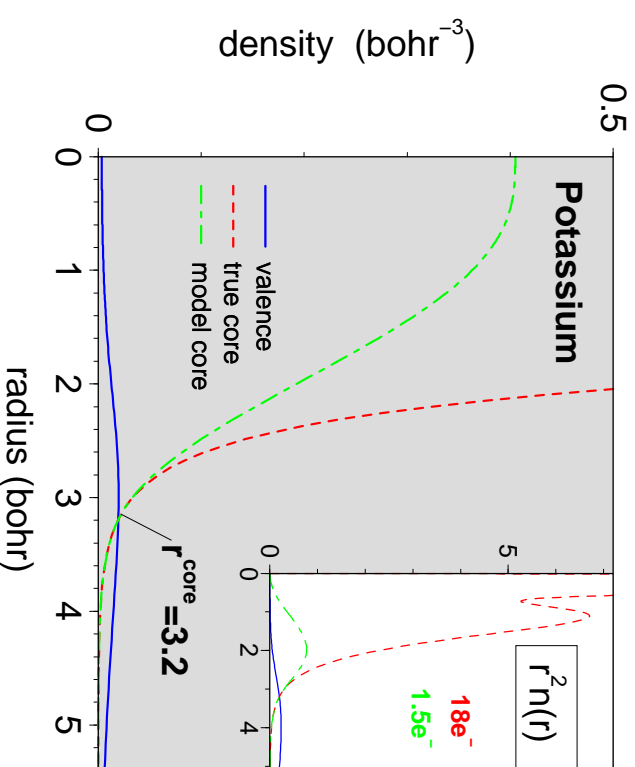- chemical hardness[1] $\dfrac{\partial^2 E(f_k)}{\partial f_i \partial f_j} = \dfrac{\partial \epsilon_i(f_k)}{\partial f_j}$

Plot 1: error (meV) vs occupancy 4p — Ga 4s^2 4p^x; curves: pseudopotential, frozen core.

Plot 2: error (meV) vs occupancy 4p — Ga 4s^2 4p^x; curves: frozen core, pseudopotential.

Plot 3: hardness (eV) vs occupancy 4p — Ga 4s^2 4p^x; 4p and 4s; curves: frozen core, relaxed core, pseudopotential.

1 Grinberg, Ramer, Rappe, Phys Rev B 63, 201102 (2001); Filipetti et al, Phys Rev B 52, 11793 (1995); Teter, Phys Rev B 48, 5031 (1993).

Nonlinear core-valence XC

- Pseudopotential mimicks also interactions of valence and core electrons

  ✓ electrostatic linear in n^v

  ✗ exchange-correlation **nonlinear**, terms like $(n^c + n^v)^{4/3}$ ....

- so far: linearized core-valence XC

  .... different in LDA & GGA [1]

- restoring nonlinear core-valence XC [2]

  $$E^{XC} = E^{XC}[n^c + n^v]$$

  different unscreening:

  $$V_l^{ps} = V_l^{scr} - V^H[n^v] - V^{XC}[n^c + n^v]\big|_{atom}$$

- a smooth model core density is used, replaces the true core density inside cutoff radius r^{core}
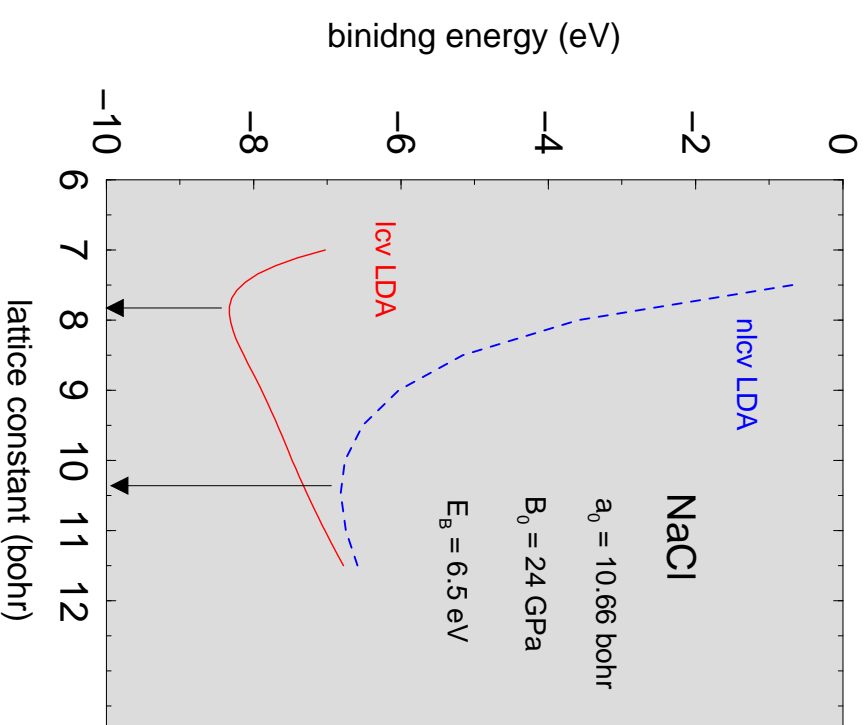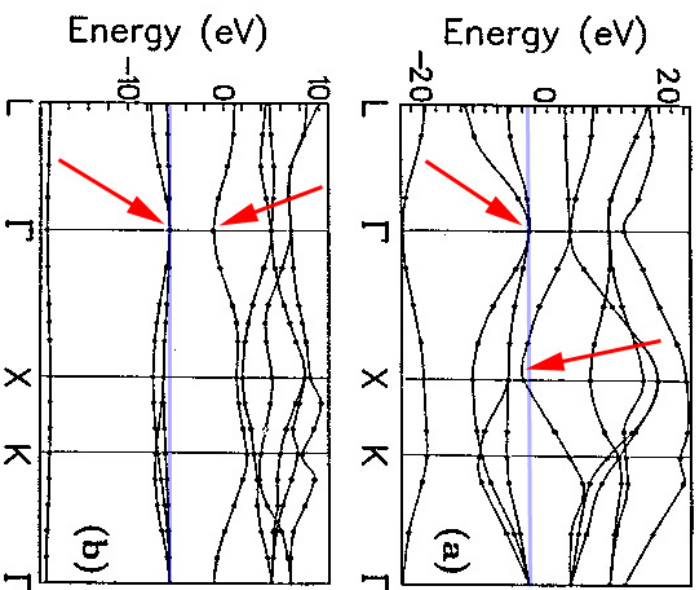
[1] M Fuchs et al, Phys Rev B 57, 2134 (1998)

[2] SG Louie et al, Phys Rev B 26, 1738 (1982)

density (bohr^{-3})

Potassium

valence — true core — model core

r^{core} =3.2

$r^2 n(r)$

18e$^-$ 1.5e$^-$

radius (bohr)

... where nonlinear core-valence XC makes a difference
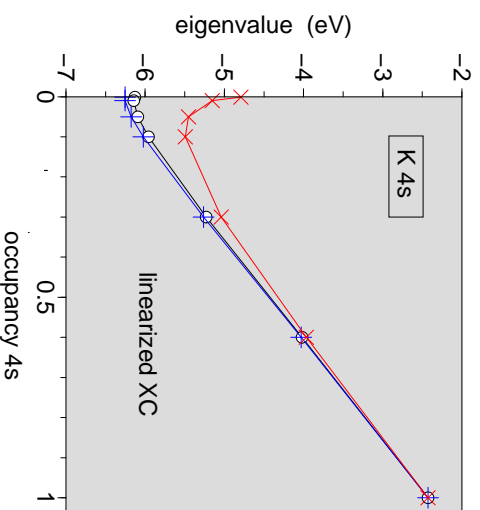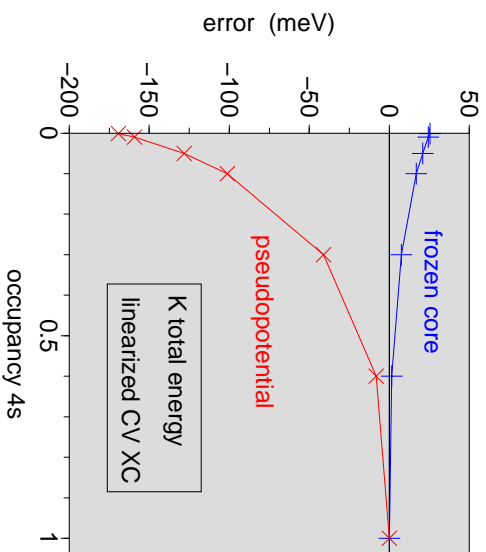
Rocksalt (NaCl): [1]

- ✗ semi-metal with linearized CV XC (a)
- ✓ insulator with nonlinear CV XC (b)

[1] Hebenstreit, Scheffler, Phys Rev B 46, 10134 (1992).

... and where linearized core-valence XC is fine

Transferability tests would tell. . . .

error (meV)

50
0
−50
−100
−150
−200

occupancy 4s

0   0.5   1

pseudopotential

frozen core

K total energy
linearized CV XC

eigenvalue (eV)

−2
−3
−4
−5
−6
−7

occupancy 4s

0   0.5   1

K 4s

linearized XC

☞ **linearized nlcv XC** mostly sufficient!

— 1st & 2nd row, As, Se, ...
— "two shell" cases → all transition metals,
    see Cu: 3–4 XC valence-valence interaction

A test calculation helps. . . .

✌ **nlcv XC** needed:

— "soft" valence shells (alkali's!)
— extended core states (Zn, Cd, ...)
    ↔ varying core-valence overlap
— spin-density functional calculations

✍ turning semi-core into valence states?

— Zn 3d, Ca 3d, Rb 4p, ...
— Ga 3d, In 4d in III-nitrides
    (but not GaP, GaAs, ...)
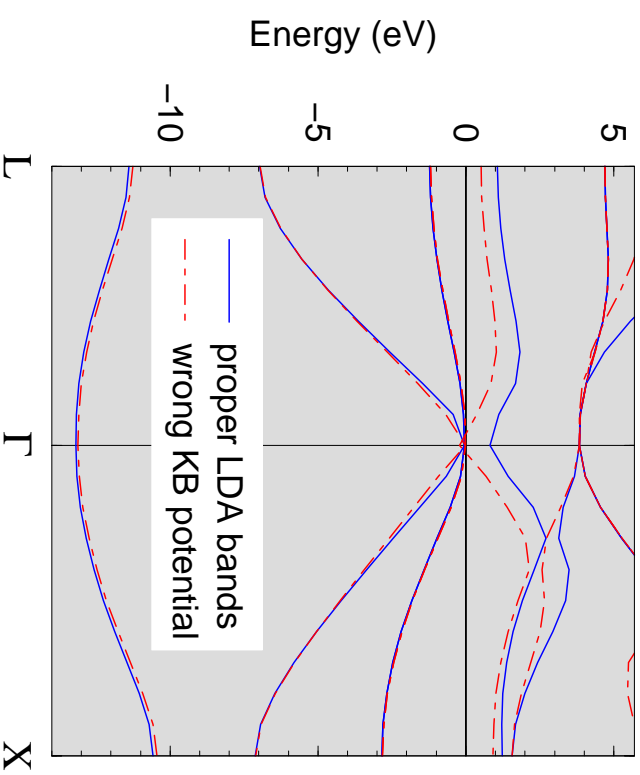
... a bit system dependent

Kleinman-Bylander potentials at work

Example: KB-pseudopotential for As
→ ZB GaAs bandstructure

✓ fully separable potentials are computational must

☞ full nonlocality → spectral order of states by radial nodes **not** guaranteed

⬇ <u>ghost states</u> above/below physical valence levels possible

❀ **Ghost states** detectable in free atom
⋮
● inspect <u>logarithmic derivatives</u>
● do <u>spectral analysis</u>
⋮
readily avoided by proper choice of local & nonlocal components

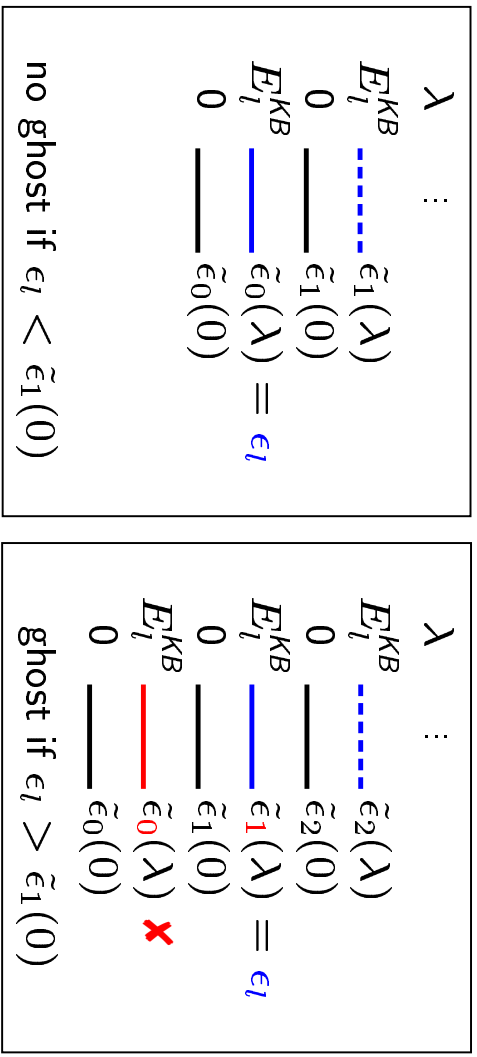$$V_i(r) \rightarrow \left\{ V^{loc}(r), \delta V_i(r) \right\}$$

Energy (eV) band structure along L – Γ – X with axis values 5, 0, −5, −10.

Legend:
— proper LDA bands
— · — wrong KB potential

Analysis of the spectrum of nonlocal Hamiltonians $\hat{H}_l = \hat{T}_l + \hat{V}^{loc} + |\chi_l\rangle\lambda\langle\chi_l|$

☞ $\lambda = E_l^{KB}$ gives the reference valence level $\boxed{\epsilon_l}$

☞ can compare spectra for
- $\square$ $\lambda = 0$ (local potential only) $\to \tilde{\epsilon}_i(0)$
- $\square$ λ arbitrary (with nonlocal potential) $\to \tilde{\epsilon}_i(\lambda)$

▶ Higher levels o.k. too?

s-state
AE SL NL

p-state
AE SL NL

🐾 not told by ghost state criteria, diagonalize H_l $\Rightarrow$ all bound levels

energy →

⬇ for any $\boxed{\lambda, E_l^{KB} > 0}$ spectra ordered like [1]

no ghost if $\epsilon_l < \tilde{\epsilon}_1(0)$

E_l^{KB}	...
0	
E_l^{KB}	$\tilde{\epsilon}_1(\lambda)$
0	$\tilde{\epsilon}_1(0)$
E_l^{KB}	$\tilde{\epsilon}_0(\lambda) = \epsilon_l$
0	$\tilde{\epsilon}_0(0)$

ghost if $\epsilon_l > \tilde{\epsilon}_1(0)$

E_l^{KB}	...
0	$\tilde{\epsilon}_2(\lambda)$
E_l^{KB}	
0	$\tilde{\epsilon}_2(0)$
E_l^{KB}	$\tilde{\epsilon}_1(\lambda)$
0	$\tilde{\epsilon}_1(0)$
E_l^{KB}	$\tilde{\epsilon}_0(\lambda) = \epsilon_l$ ✗
0	$\tilde{\epsilon}_0(0)$

⬇ for $\boxed{\lambda, E_l^{KB} < 0}$ have $\tilde{\epsilon}_0(\lambda) < \tilde{\epsilon}_0(0) < \tilde{\epsilon}_1(\lambda) < \tilde{\epsilon}_1(0) \dots$

no ghost if $\epsilon_l < \tilde{\epsilon}_0(0)$

ghost if $\epsilon_l > \tilde{\epsilon}_0(0)$
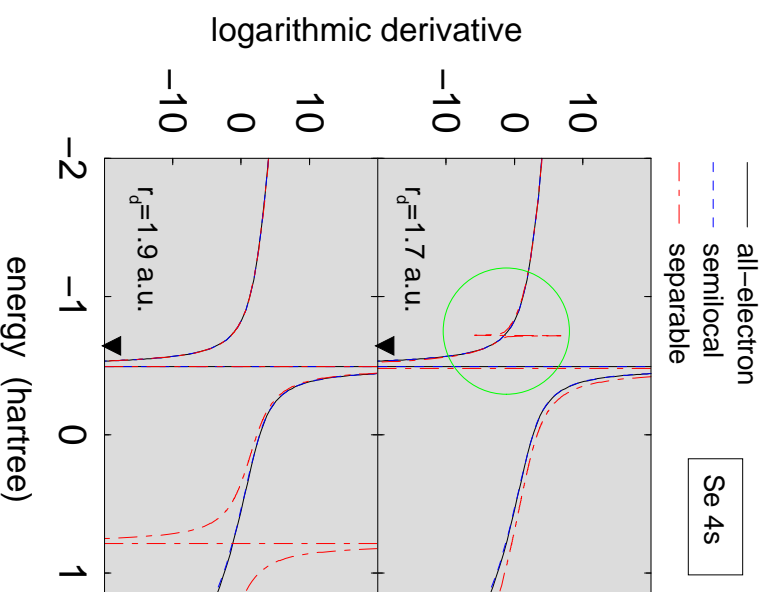
✿ used as **ghost state criteria** in fhi98PP (pswatch)

X Gonze, R Stumpf, M Scheffler, Phys Rev B 16, 8503 (1992)

. . . in case of ghost states

Seen in logarithmic derivatives . . .

. . . **where they occur, how to avoid them?**

☞ local potential $l_{loc} = l_{max} = 2$ saves computing

✓ unproblematic: 1st & 2nd row, (earth-) alkali's

☞ can cause strong nonlocality (large $|E_l^{KB}|$)

"artifically:" ≈ zero denominator in E_l^{KB} (KB-cos)

Ga, Ge, As, Se, ...

vary cutoff radii of local/ nonlocal components

"intrinsically:" numerator of E_l^{KB} large

Cu: deep $V_{3d}(r) \Rightarrow E_l^{KB} \gg 0$ to get 4s right

all $3,4,5d$-metals: Cu, Pd, Ag, ...

make local potential repulsive $\rightarrow E_l^{KB} < 0$

use to s - or p-component !

➥ KB-potentials work well in practice

Overview - fhi98PP covers "classic" pseudopotentials

- nucleus' Coulomb attraction + core-valence interaction (orthogonality, electrostatic, XC)

  Pseudopotential = electron-i on interaction

  - work throughout periodic table   (... almost)

✓ physically motivated approximation

  - Valence electrons rule chemical bonding
  - Frozen-core approximation   (depends on system)
  - Cancellation of potential and kinetic energy in core

✓ well controlled

  - norm-conservation   (built in)
  - nonlinear core-valence XC   (depends on system)

✓ Transferability properties & pseudopotential validation
  (scattering properties), chemical hardness

  - logarithmic derivatives
  ○ plane-wave convergence

✓ Fully separable, nonlocal potentials

  - analysis & removal of ghost states

✓ present XC: LDA & PW91,BP86,PBE,revPBE,RPBE,BLYP GGA . . . easy to add
- experimental XC: xOEP with KLI approximation, SIC, MGGA
✗ desirable: spin-polarization, $L \cdot S$-coupling,
  potential & performance database on the Web ?