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 $\phi_i^{AE}(\mathbf{r}) = \frac{u_{\nu l}^{AE}(r)}{r} Y_{lm}(\Omega)$ ... spherical

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

- ▲ 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

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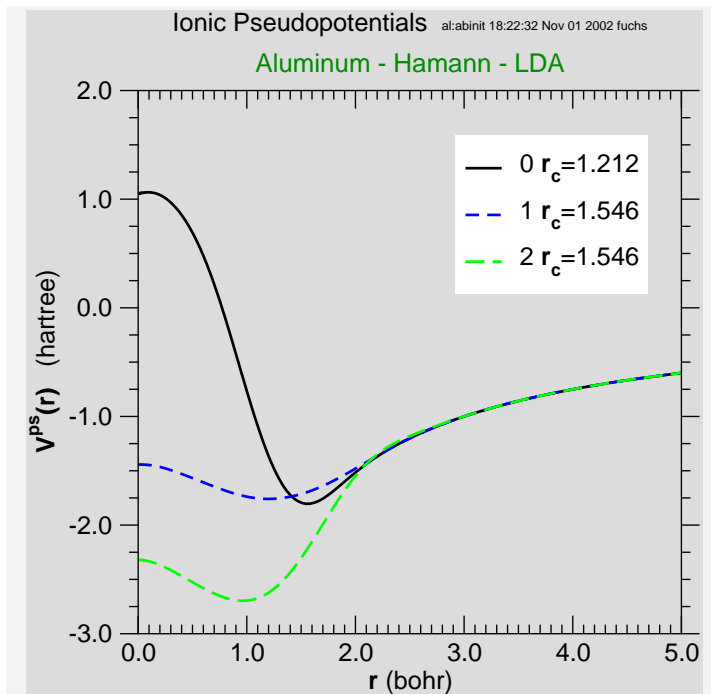
... formally non-relativistic Schrödinger eq.
... different for each valence state $\rightarrow$ l-dependent

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

Part I: psatom

Pseudopotential on screen. . .

. . . 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
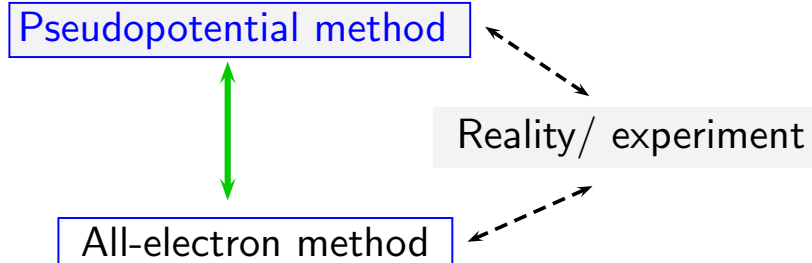
- But how about in the solid or molecule?

  Must test!

  . . . and if needed

  improved!

- Proposal of how to . . .

Part II: Monitoring transferability with pswatch

Pseudopotential method

Reality/ experiment

All-electron method

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

● needed <u>accuracy</u> $\sim \mathcal{O}(0.1 \ldots 0.01 \text{ eV})$
  – 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), ...

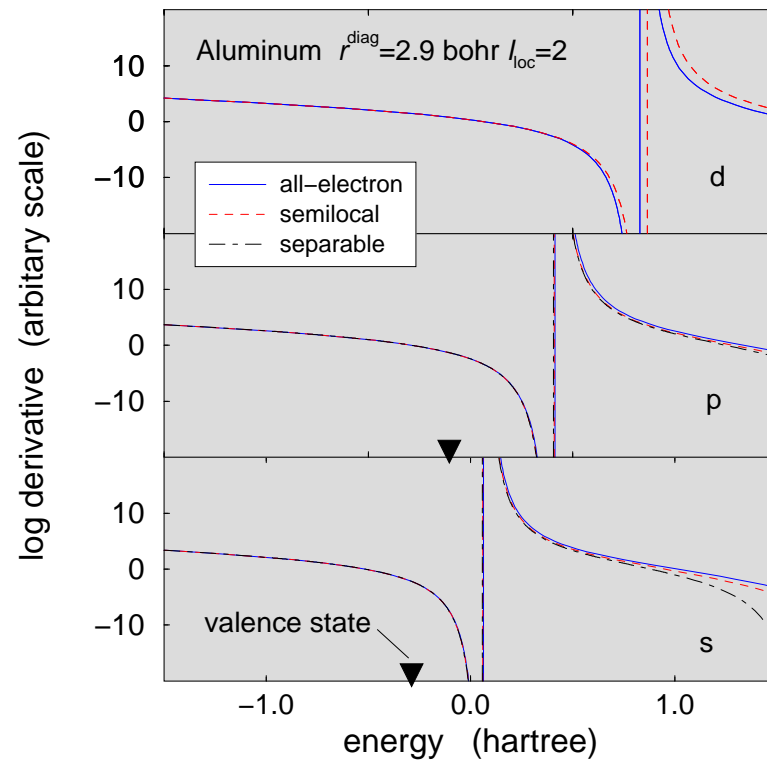▲ <u>new XC functionals</u> → GGA, ...

Characteristic tests of PP at atomic level?

Test: <u>Logarithmic derivatives</u>

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

norm conservation: o.k. for $\epsilon_l \pm \delta\epsilon$
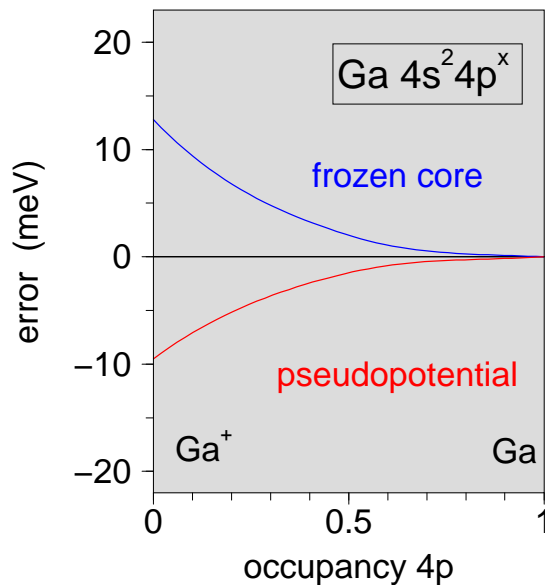
... in practice: over range of valence bands?

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

log derivative (arbitrary scale)

energy (hartree)

all–electron
semilocal
separable

d

p

s

valence state

Hardness tests - a ,,good'' example

Test: <u>Configurational changes</u> (ΔSCF)
- ❏ $s \rightarrow p$ promotion (C, Si, Ge, ...)
- ❏ ionization (Li→Li$^+$, Na→Na$^+$,...)
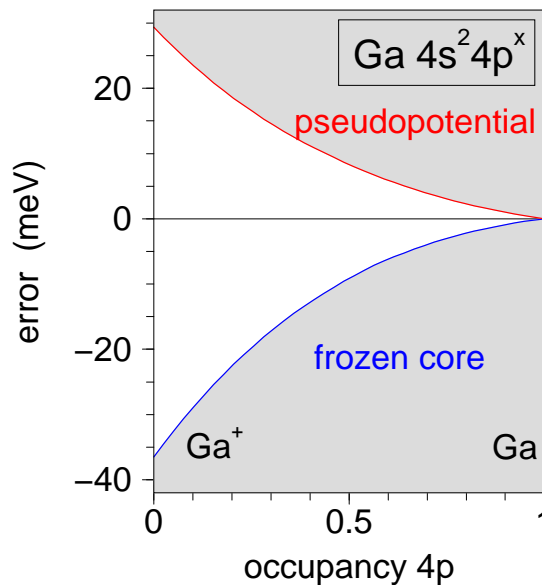
- $\boxed{\text{total energy (excitations)}}$

$$E[n(f_k)]$$

- $\boxed{\text{eigenvalues (Janak theorem)}}$

$$\frac{\partial E(f_k)}{\partial f_i} = \epsilon_i(f_k)$$

- $\boxed{\text{chemical hardness}^1}$

$$\frac{\partial^2 E(f_k)}{\partial f_i \partial f_j} = \frac{\partial \epsilon_i(f_k)}{\partial f_j}$$
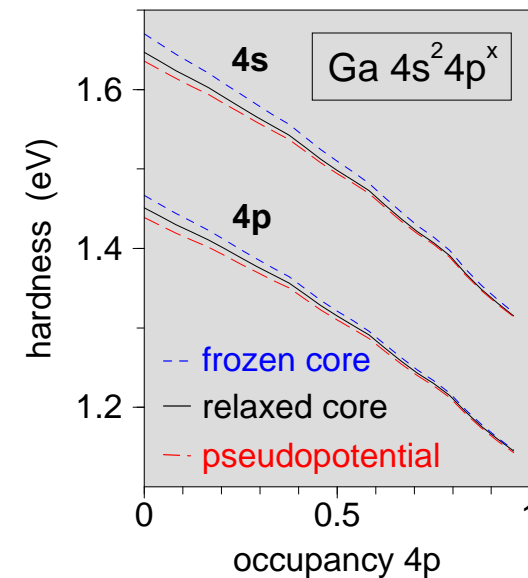
[1] Grinberg, Ramer, Rappe, Phys Rev B 63, 201102 (2001); Filipetti et al, Phys Rev B 52, 11793 (1995); Teter, Phys Rev B 48, 5031 (1993).
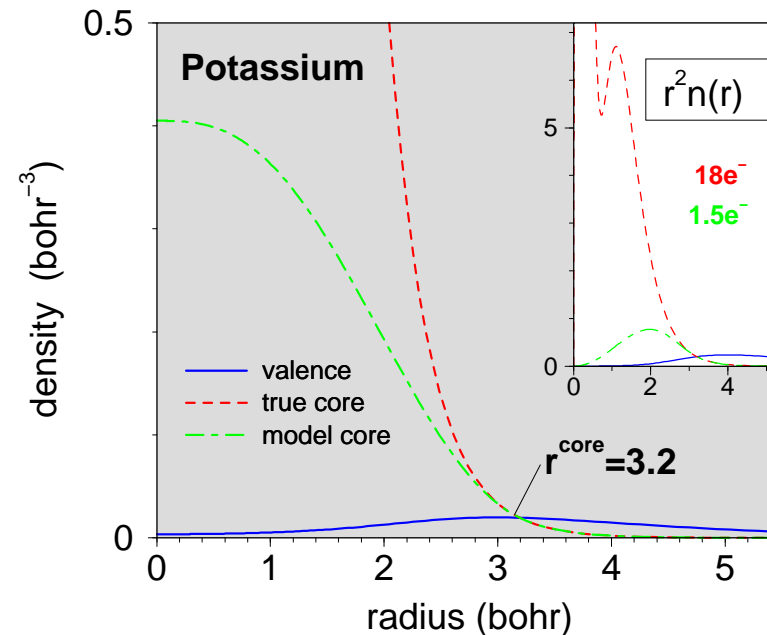
Nonlinear core-valence XC

- 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
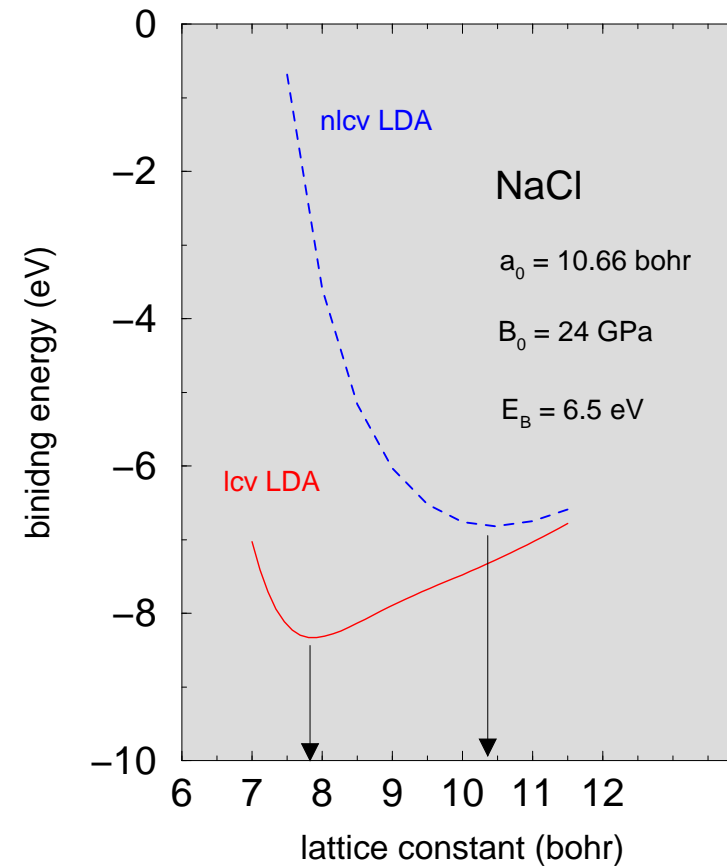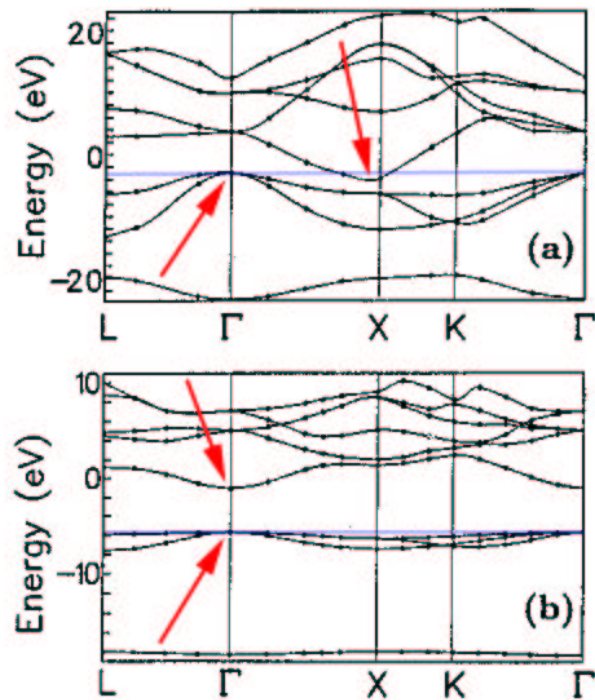 inside cutoff radius r^{core}

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[1] *M Fuchs et al, Phys Rev B 57, 2134 (1998)*

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

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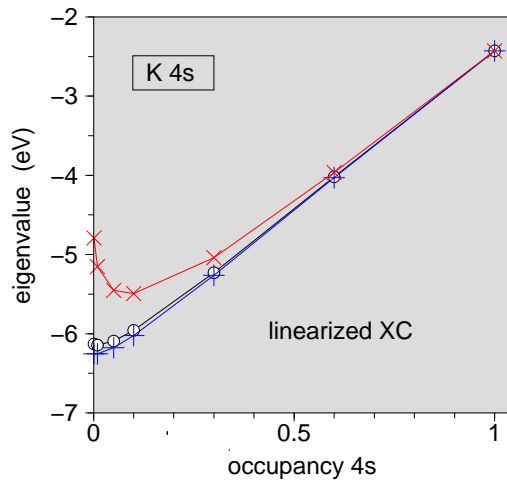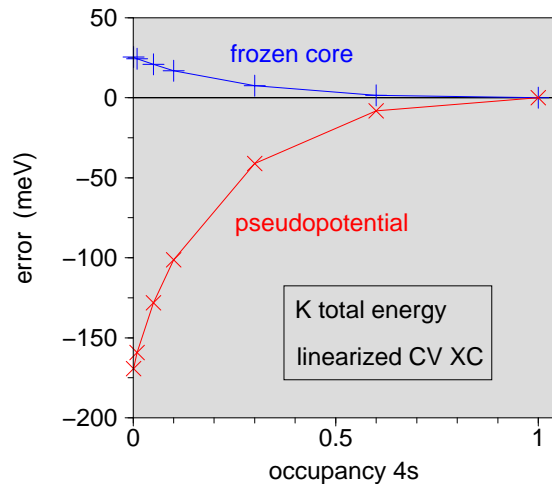
<u>Rocksalt (NaCl):</u> [1]

✗   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. . .

☞ **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

✓ fully separable potentials are computational must

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

➥ **ghost states** above/below physical valence levels possible

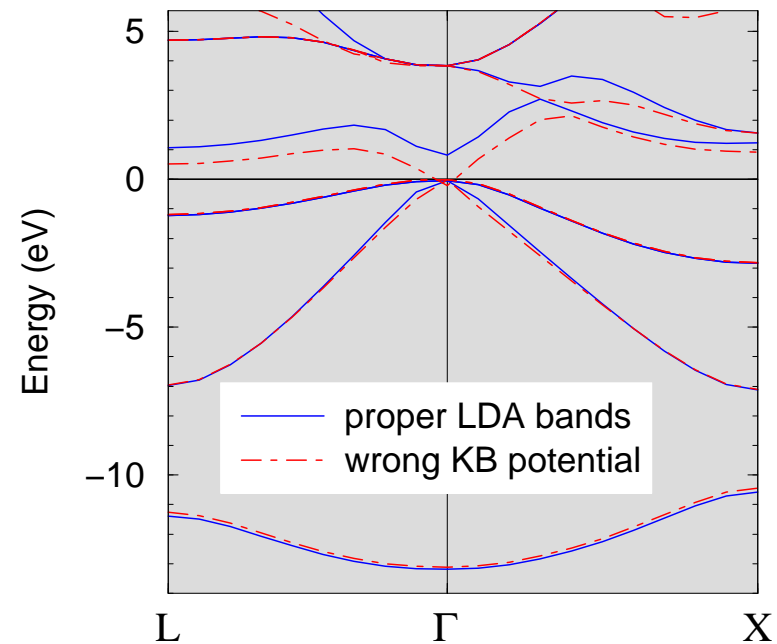❀ **Ghost states** detectable in free atom ...

- inspect logarithmic derivatives
- do spectral analysis

... readily avoided by proper choice of local & nonlocal components

$$V_l(r) \longrightarrow \left\{ V^{loc}(r), \delta V_l(r) \right\}$$

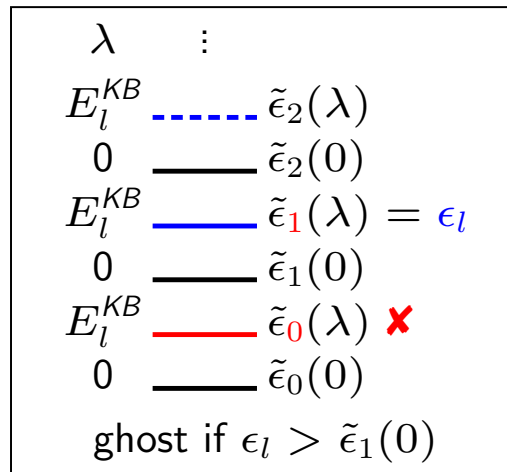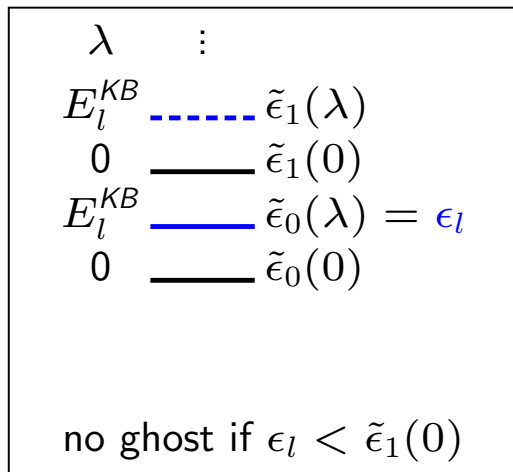Example: KB-pseudopotential for As
→ ZB GaAs bandstructure

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 ❑ $\lambda = 0$ (local potential only) $\rightarrow \tilde{\epsilon}_i(0)$

❑ λ arbitrary (with nonlocal potential) $\rightarrow \epsilon_i(\lambda)$

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

λ ⋮	λ ⋮
E_l^{KB} ------ $\tilde{\epsilon}_1(\lambda)$	E_l^{KB} ------ $\tilde{\epsilon}_2(\lambda)$
0 —— $\tilde{\epsilon}_1(0)$	0 —— $\tilde{\epsilon}_2(0)$
E_l^{KB} —— $\tilde{\epsilon}_0(\lambda) = \epsilon_l$	E_l^{KB} —— $\tilde{\epsilon}_1(\lambda) = \epsilon_l$
0 —— $\tilde{\epsilon}_0(0)$	0 —— $\tilde{\epsilon}_1(0)$
	E_l^{KB} —— $\tilde{\epsilon}_0(\lambda)$ ✗
	0 —— $\tilde{\epsilon}_0(0)$
no ghost if $\epsilon_l < \tilde{\epsilon}_1(0)$	ghost if $\epsilon_l > \tilde{\epsilon}_1(0)$

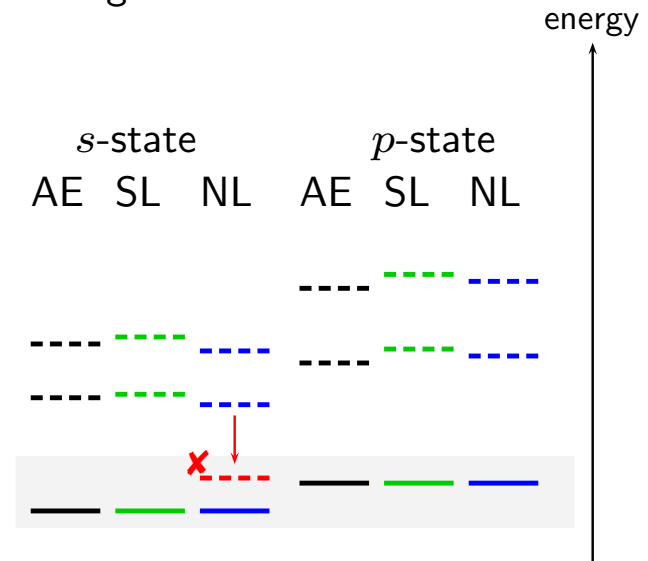➥ for $\boxed{\lambda, E_l^{KB} < 0}$ have $\tilde{\epsilon}_0(\lambda) < \tilde{\epsilon}_0(0) < \tilde{\epsilon}_1(\lambda) \ldots$

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

✿ used as **ghost state criteria** in fhi98PP (pswatch)

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

▲ Higher levels o.k. too?

energy

s-state p-state

AE SL NL   AE SL NL
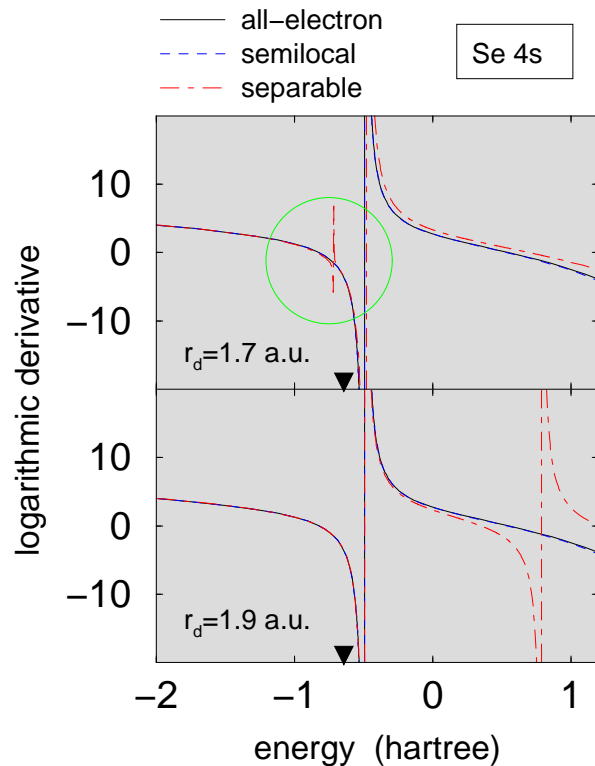

☞ not told by ghost state criteria, diagonalize H_l $\Rightarrow$ all bound levels

. . . 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:" $\approx$ 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

> Pseudopotential = electron-i on interaction

- nucleus' Coulomb attraction + core-valence interaction (orthogonality, electrostatic, XC)
  - 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
  - logarithmic derivatives   (scattering properties), chemical hardness
  ○ 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 ?