

Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry,
Engineering and Biology, Berlin, 23 July - 1 August 2001

L4

Pseudopotentials for ab initio electronic structure calculations

Martin Fuchs

Unité PCPM, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

Key words & ideas

“Bad idea”: Plane waves & Full-potential all-electron approach

- scale of orbitals
 - core: size of $1s \sim \frac{1}{Z}$ bohr
 - valence: same scale, due to orthogonality
 - ↳ number of plane waves $\propto Z^3$
- Hamiltonian matrix
 - size $\propto Z^6$, cpu time $\propto Z^9$
 - ↳ could do at most diamond (C)
- large total energy (components)
 - GaAs: $E_{\text{tot}} \simeq 10^5$ eV/pair
 - $\sim \omega_{\text{phonon}} \simeq 30$ meV
 - ↳ numerical precision possible but demanding

“Good news:” Chemical bonding, . . . determined by valence electrons

- core electrons matter only indirectly
 - ↳ removed within frozen core approximation
- effect on valence electrons can be described by a potential
 - ↳ “linearization” of core-valence interactions
- orthogonalization wiggles can be eliminated
 - smooth pseudo wavefunctions
 - weak pseudopotential
 - ↳ good efficiency with plane waves
- “pseudoization” should be independent of system
 - atom → molecule → solid
 - ↳ transferable pseudopotentials

Norm-conserving pseudopotentials \Leftrightarrow approximate electron-ion interaction potentials

. . . work accurately & effectively (almost) for all elements, because

- bonding happens outside the core region of ions
- norm conservation constraint leads to physical electron density & valence band energies
- clever “recipes” achieve smooth potentials, fully separable potentials, . . . improved efficiency!

. . . are well controlled by proper construction and testing of the pseudopotentials

From full potentials to pseudopotentials

Atom - Calculate eigenstates \rightarrow solve the (radial) Schrödinger equation: $\hat{T} + \hat{V}^{\text{AE}} |\phi_i^{\text{AE}}\rangle = \epsilon_i |\phi_i^{\text{AE}}\rangle$

- pick an energy $\epsilon < 0$ and integrate

outward $r R^{\text{out}}(\epsilon; 0) = 0 \rightarrow R^{\text{out}}(\epsilon; r) |_{r <} = 0 \dots r^{\text{match}}$

inward $R^{\text{in}}(\epsilon; \infty) = 0 \rightarrow R^{\text{in}}(\epsilon; r) |_{r >} = \infty \dots r^{\text{match}}$
 ... outside classical turning point

- if logarithmic derivatives match ... iterate ϵ until they do,

$$\left. \frac{1}{R^{\text{out}}(\epsilon; r)} \frac{d}{dr} R^{\text{out}}(\epsilon; r) \right|_{r^{\text{match}}} = \left. \frac{1}{R^{\text{in}}(\epsilon; r)} \frac{d}{dr} R^{\text{in}}(\epsilon; r) \right|_{r^{\text{match}}}$$

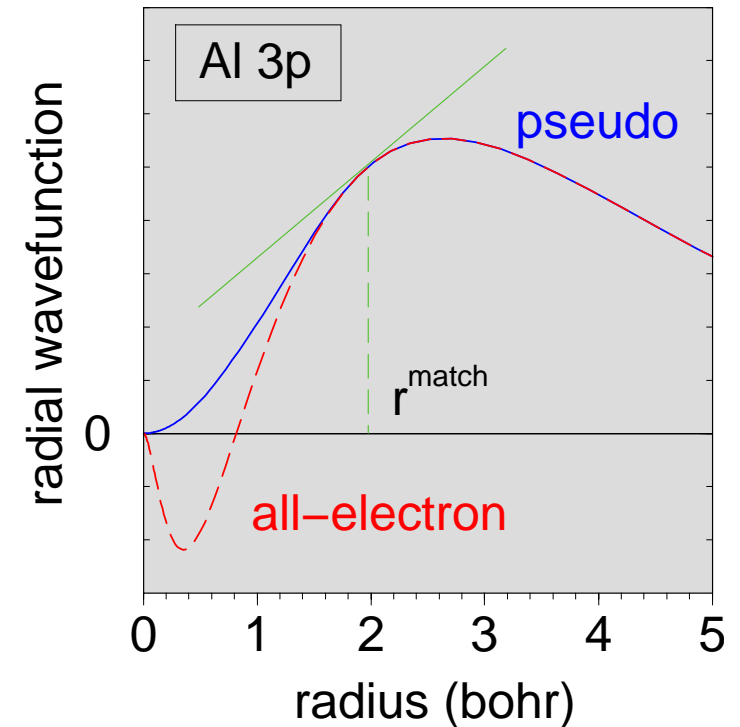
we get an eigenstate $R_{\nu l}$ with eigenvalue $\epsilon_{\nu l}$.

- Any potential $V^{\text{PS}}(r < r^{\text{match}})$ giving the same logarithmic derivative outside r^{match} gives the same eigenvalue

Pseudopotential = exact transformation of full potential

$$\hat{T} + \hat{V}^{\text{PS}} |\phi_i^{\text{PS}}\rangle = \epsilon_i |\phi_i^{\text{PS}}\rangle$$

- ! $r > r^{\text{match}}$: $\phi_i^{\text{PS}}(\mathbf{r}) \propto \phi_i^{\text{AE}}(\mathbf{r})$ what normalization?

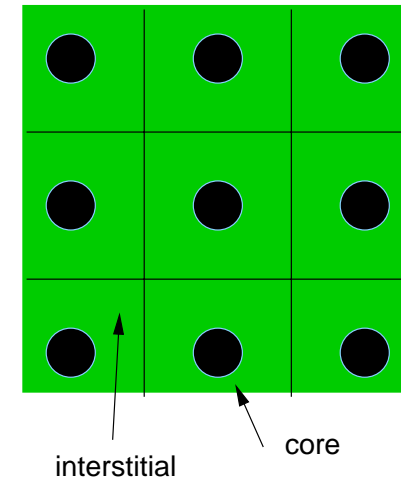


Solid: logarithmic derivatives \leftrightarrow boundary conditions

core: $\phi^{\text{core}} \rightarrow \sum c_{lm} R_l(r) Y_{lm}(\Omega)$

interstitial: $\phi^{\text{inter}} \rightarrow \sum c_{klm} j_l(kr) Y_{lm}(\Omega)$

Match $\left. \frac{\frac{d}{dr} R_l(r)}{R_l(r)} \right|_{\epsilon_{r^{\text{core}}}} = \left. \frac{\frac{d}{dr} \phi_l^{\text{inter}}(r)}{\phi_l^{\text{inter}}(r)} \right|_{\epsilon_{r^{\text{core}}}}$



The pseudopotential is “weak” - cancellation theorem

- can bind valence states, but not core states
- in the core region the potential and kinetic energy contributions nearly cancel:

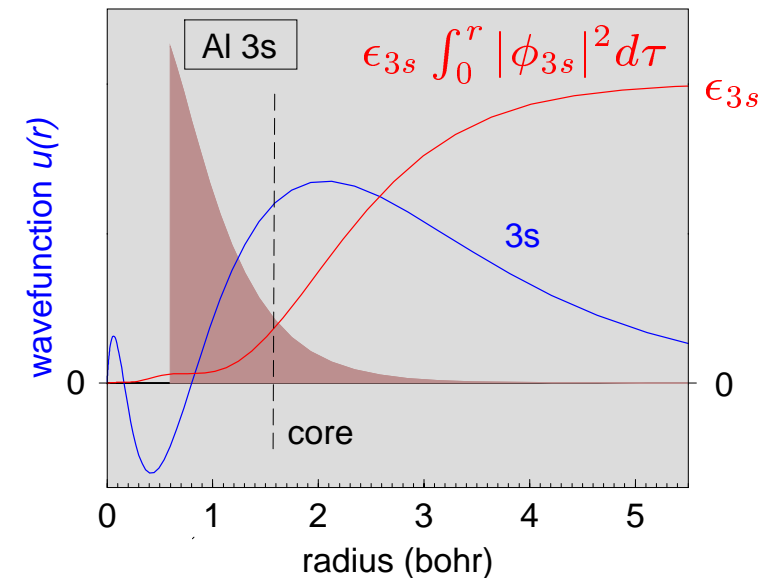
$$\int_0^{r^{\text{core}}} \bar{\phi}_i^{\text{AE}} [T + V^{\text{AE}}] \phi_i^{\text{AE}} d\tau \ll \epsilon_i$$

- the pseudopotential acts like¹

$$\hat{V}^{\text{PS}} |\phi^{\text{PS}}\rangle = \hat{V}^{\text{AE}} |\phi^{\text{PS}}\rangle - \sum_{\text{core}} |\phi_c\rangle \langle \phi_c | \hat{V}^{\text{AE}} | \phi^{\text{PS}}\rangle \approx 0$$

attractive repulsive, confined to core

... if there are core states with same angular momentum l



¹ Philips, Kleinman, Phys Rev 116, 287 (1959); Heine, in *Solid State Physics*, Vol 24 (Academic, 1970)

Accuracy aspect: Norm-conservation

- Pseudopotential must be **transferable**, i.e. perform correctly in different environments
 - ✿ PS \simeq AE eigenvalues \leftrightarrow band structure & one-particle energy $\sum_i^{\text{occ}} \epsilon_i$
 - ✿ electron density $\leftrightarrow V^{\text{eff}}[\mathbf{n}; \mathbf{r}]$ and total energy
- If we impose

$$\boxed{\phi_i^{\text{PS}}(\mathbf{r}) = \phi_i^{\text{AE}}(\mathbf{r}) \mid r > r^{\text{core}}} \Leftrightarrow \text{proper electron density outside core}$$

and **norm conservation**

$$\boxed{\int_0^{r^{\text{core}}} |\phi_i^{\text{AE}}(\mathbf{r})|^2 d\tau = \int_0^{r^{\text{core}}} |\phi_i^{\text{PS}}(\mathbf{r})|^2 d\tau \Leftrightarrow \langle \phi_i^{\text{PS}} \mid \phi_i^{\text{PS}} \rangle = \langle \phi_i^{\text{AE}} \mid \phi_i^{\text{AE}} \rangle \equiv 1}$$

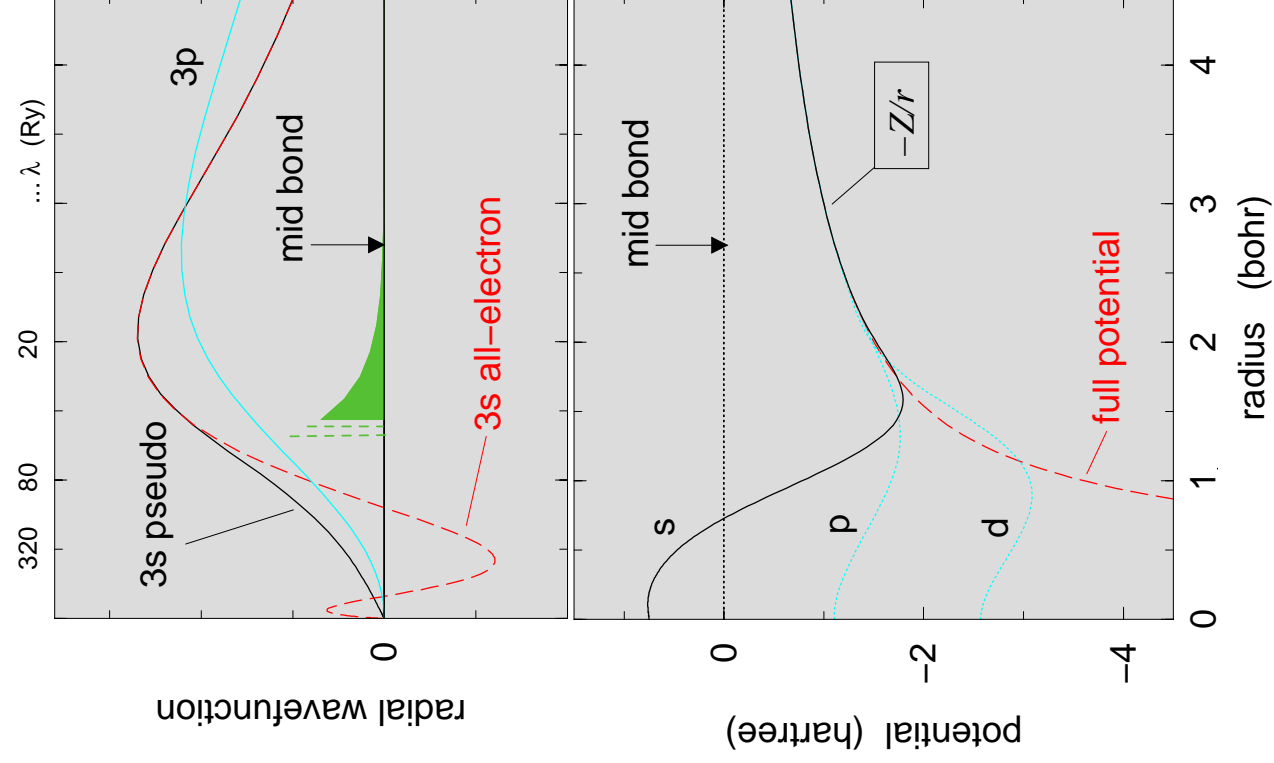
- ➔ correct “total charge inside core radius” \Leftrightarrow proper electrostatic potential for $r > r^{\text{core}}$
- ➔ boundary conditions of AE and PS wavefunctions change in the same way with energy $\epsilon_i \pm \delta\epsilon$

$$-\frac{1}{2} |\phi(\epsilon; \mathbf{r})|^2 \frac{d}{d\epsilon} \left[\frac{\partial}{\partial r} \ln \phi(\epsilon; \mathbf{r}) \right] \Big|_{r^{\text{core}}, \epsilon_i} = \int_0^{r^{\text{core}}} |\phi_i(\epsilon_i; \mathbf{r})|^2 d\tau$$

... over the width of the valence bands \rightarrow correct scattering properties

- ➔ PS wavefunctions change similar to AE wavefunctions
 - separately for each valence state $\rightarrow l$ -dependence

Pseudopotential for aluminum ...



An example ...

Accuracy aspect: Frozen-core approximation

☞ core orbitals change with chemical environment too! Effect on total energy?

Total energy:

$$E^{\text{tot}}[n] \rightarrow E^{\text{core}}[n^c] + E^{\text{valence}}[n^v] + E^{\text{valence-core}}[n^c; n^v]$$

two step view: change valence density \rightarrow change effective potential \rightarrow change core density

☞ second order error $\int \Delta V^{c,\text{eff}} \Delta n^c d\tau$
... cancels out in total energy differences ¹

¹von Barth, Gelatt, Phys Rev B 21, 2222 (1980).

Pseudopotential construction

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

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

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

▲ Relativity: Dirac \rightarrow scalar relativistic \rightarrow non-relativistic

▲ Full potential $V^{\text{AE}}[n^{\text{AE}}; r] = -\frac{Z}{r} + V^{\text{H}}[n^{\text{AE}}; r] + V^{\text{XC}}[n^{\text{AE}}; r]$
 . . . XC in LDA or GGA: **take same as in solid etc.**

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

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

. . . formally non-relativistic Schrödinger eq.

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

\rightarrow screened pseudopotentials $V_l^{\text{scr}}[n; r] = V_l^{\text{ion}}(r) + V^{\text{H}}[n; r] + V^{\text{XC}}[n; r]$

... pseudopotential construction

$u_l(r)$. . . nodeless radial pseudo wavefunctions \rightarrow must **meet conditions** ...

① same valence energy levels $\epsilon_l = \epsilon_{\nu l}$

② outside **cutoff radius** r_l^{cut} orbitals match $u_l(r > r^{\text{cut}}) = u_{\nu l}^{\text{AE}}(r)$

... implies matching of logarithmic derivatives $\frac{1}{u(r)} \frac{d}{dr} u(r)$

③ norm-conserving $\langle \phi_l | \phi_l \rangle = \langle \phi_l^{\text{AE}} | \phi_l^{\text{AE}} \rangle = 1$

+ constraints for good convergence

$V_l^{\text{scr}}(r)$. . . angular momentum dependent potential, regular for $r \rightarrow 0$

$n(r)$. . . pseudo valence density, what are $E^{\text{H}}[n]$, $E^{\text{XC}}[n]$?

\rightarrow parametrize $u_l(r)$ and **invert Schrödinger eq.** $V_l^{\text{scr}}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{d^2/dr^2 u_l(r)}{2u_l(r)}$

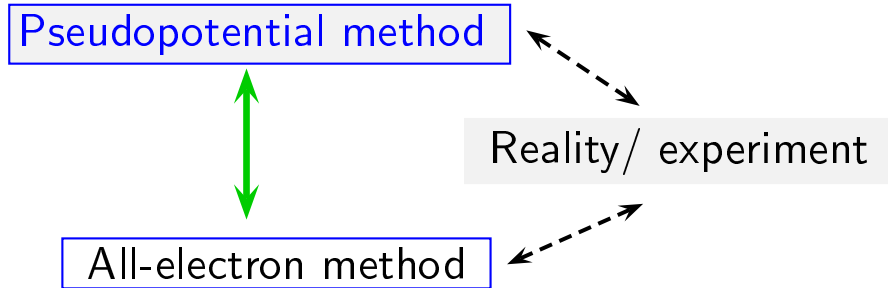
\rightarrow final **ionic pseudopotentials** \rightarrow unscreening

$$V_l^{\text{ion}}(r) = V_l^{\text{scr}}(r) - V^{\text{H}}[n; r] - V^{\text{XC}}[n; r]$$

▲ ... different schemes, e.g. Troullier-Martins: $u_l(r < r_l^{\text{cut}}) = r^{l+1} e^{c_0 + c_2 r^2 + \dots + c_{12} r^{12}}$

①: $\langle \phi_l | \phi_l \rangle = 1$ ②-⑥: $\frac{d^n}{dr^n} [u_l(r) - u_{\nu l}^{\text{AE}}(r)] |_{r_l^{\text{cut}}} = 0$, $n=0,1,\dots,4$ ⑦: $\frac{d^2}{dr^2} V_l^{\text{scr}}(0) = 0$

Transferability



- compromise with needed smoothness
- needed accuracy $\sim \mathcal{O}(0.1 \dots 0.01 \text{ eV})$
 - electronic structure
 - cohesive properties
 - atomic structure, relaxation, phonons
 - formation enthalpies, activation energies, ...
- modifications
 - separable potentials (computational)
 - core corrections (methodic)
- ▲ new materials \rightarrow GaN (with $3d$ or not), ...
- ▲ new XC functionals \rightarrow GGA, ...

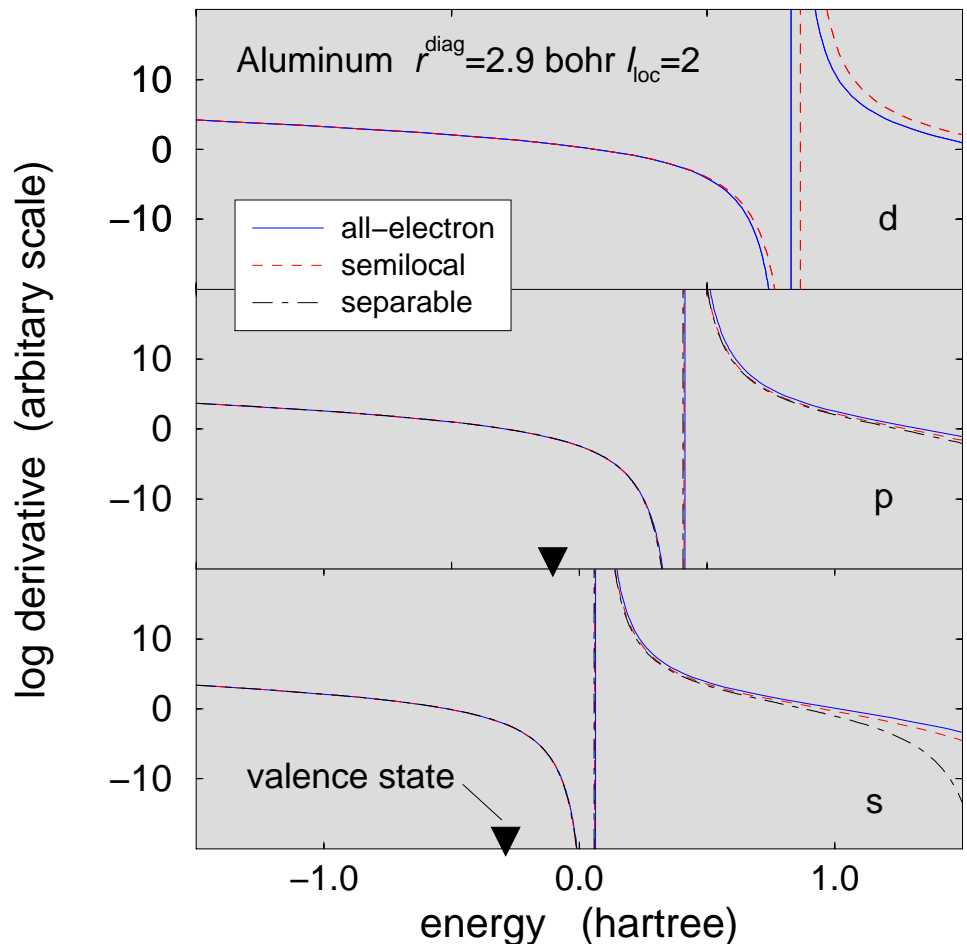
Characteristic tests of PP at atomic level?

Test: Logarithmic derivatives

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

norm conservation $\rightarrow D_l(\epsilon_l \pm \delta\epsilon) = D_l^{\text{AE}}(\epsilon_l \pm \delta\epsilon)$

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



Monitoring transferability

Test: Configurational changes (Δ SCF) $s \rightarrow p$ promotion (C, Si, Ge, ...)
 ionization ($\text{Li} \rightarrow \text{Li}^+$, $\text{Na} \rightarrow \text{Na}^+$, ...)

• total energy (“excitations”)

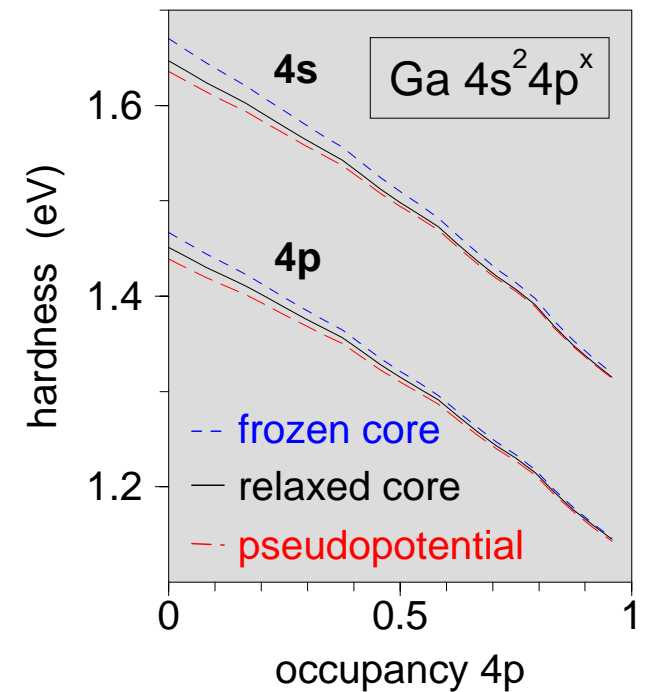
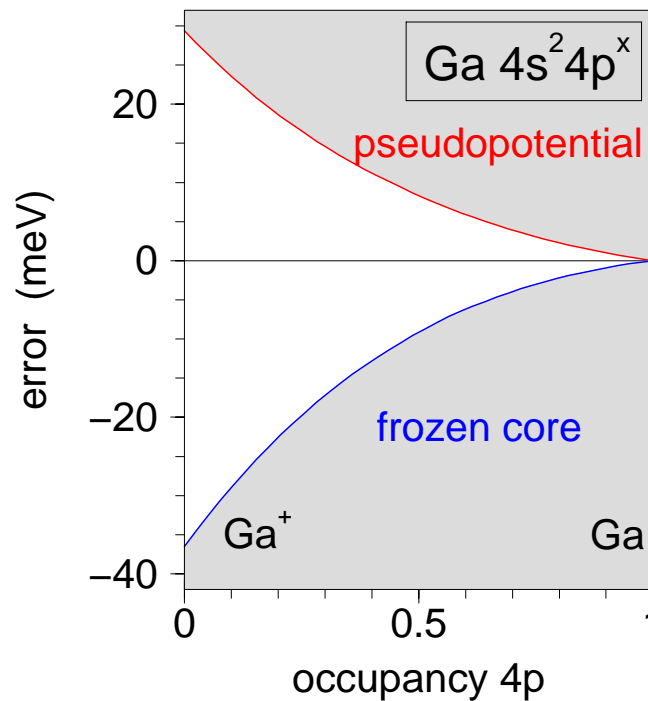
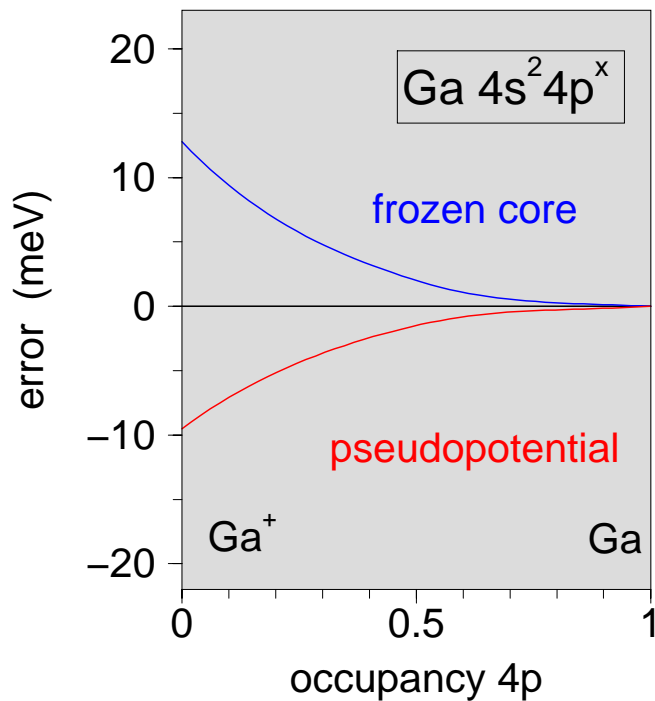
$$E[n(f_k)]$$

• eigenvalues (Janak theorem)

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

• chemical hardness¹ (response)

$$\frac{\partial^2 E(f_k)}{\partial f_i \partial f_j} = \frac{\partial \epsilon_i(f_k)}{\partial f_j}$$

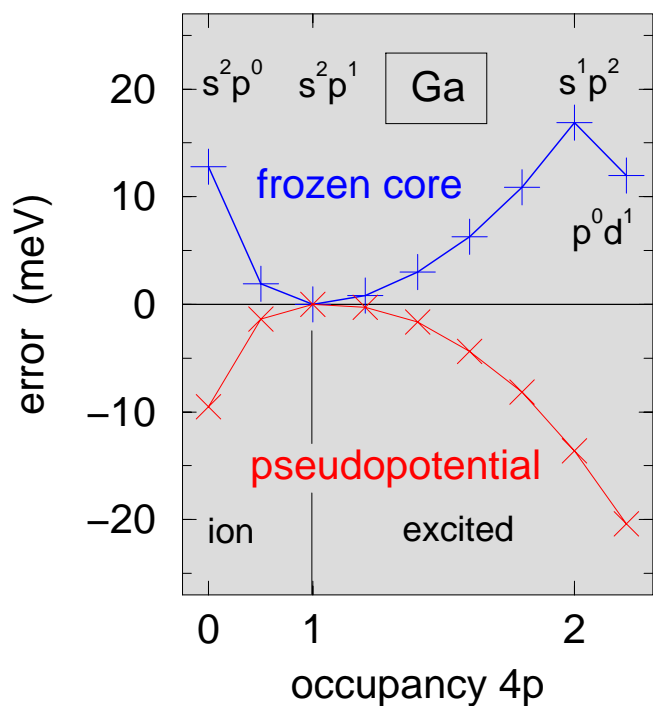


¹ Grinberg, Ramer, Rappe, Phys Rev B 63, 201102 (2001); Filipetti et al, Phys Rev B 52, 11793 (1995); Teter, Phys Rev B 48, 5031 (1993).

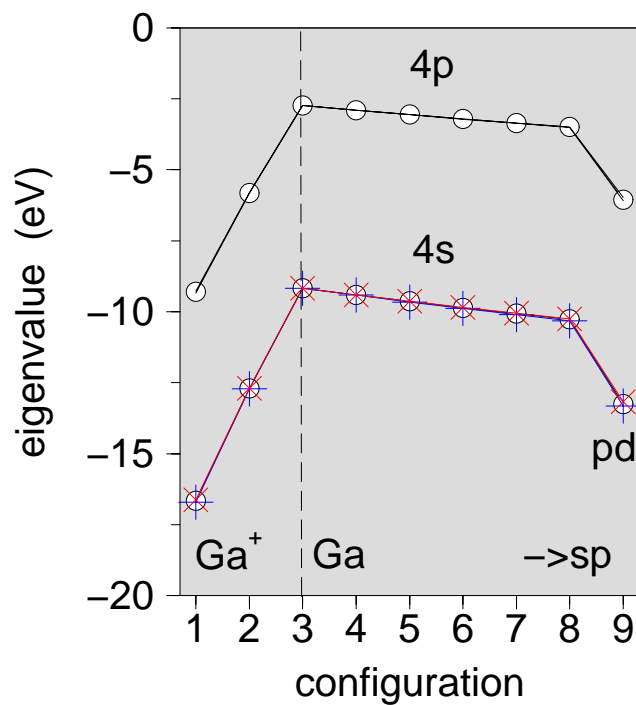
“Hardness tests” in practice

energy error $\mathcal{O}(\text{a few } 10 \text{ meV})?$

... PP not worse than frozen core

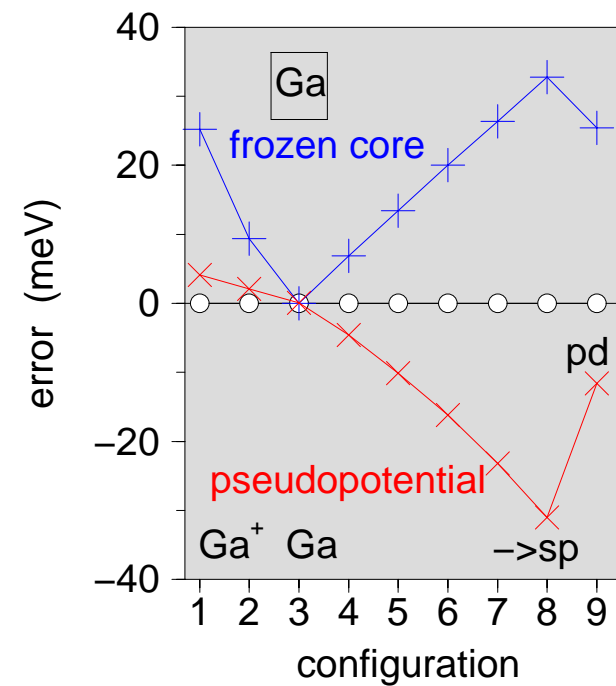


Eigenvalues match well?



Level splitting preserved?

$$\epsilon_p - \epsilon_s$$



Nonlinear core-valence XC (nlcv XC)

☛ total energy & electronic structure depend just on valence electron density

$$E[n^v] = \sum_i \langle \psi_i | \hat{T} + \delta \hat{V}_l^{\text{PS}} | \psi_i \rangle + \int V^{\text{PS}, \text{loc}}(\mathbf{r}) n^v(\mathbf{r}) d\tau + E^{\text{H}}[n^v] + E^{\text{XC}}[n^v]$$

- electronic core-valence interactions mimicked by pseudopotential → different in GGA & LDA! ¹
 - ✓ electrostatic part linear in n^v
 - ✗ exchange-correlation **nonlinear**, terms like $(n^c + n^v)^{4/3}$...

- pseudopotential → linearized core-valence XC

$$E^{\text{XC}} = E^{\text{XC}}[n^v] + \int n^v(\mathbf{r}) \sum_{\alpha} \Delta V^{\text{XC}}[n_{\alpha}^c + n_{\alpha}^v; \mathbf{r}] d\tau \quad \text{XC functional}$$

$$V_l^{\text{PS}, \alpha}(r) = V_l^{\text{scr}, \alpha}[n_{\alpha}; r] - V^{\text{H}}[n_{\alpha}^v; r] - V^{\text{XC}}[n_{\alpha}^v; r] \quad \text{PP unscreening, consistent in LDA or GGA}$$

- restoring nonlinear core-valence XC ²

$$E^{\text{XC}} = E^{\text{XC}}[n^v + n_{\{\alpha\}}^c]$$

$$V_l^{\text{PS}, \alpha}(r) = V_l^{\text{scr}, \alpha}[n_{\alpha}; r] - V^{\text{H}}[n_{\alpha}^v; r] - V^{\text{XC}}[n_{\alpha}^v + n_{\alpha}^c; r]$$

¹Fuchs, Bockstedte, Pehlke, Scheffler, Phys Rev B 57, 2134 (1998).

²Louie, Froyen, Cohen, Phys Rev B 26, 1738 (1982).

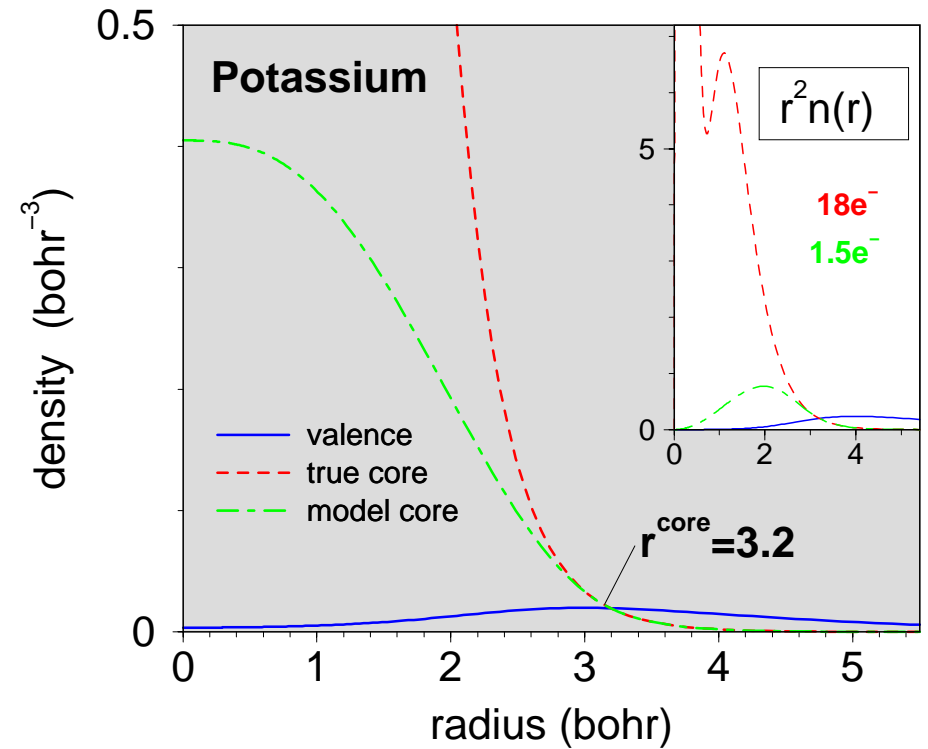
Partial core density for nlcv XC

Overlap matters only around core edge . . .

↳ can smoothen full core density inside the core
“partial core corrections”

$$n_{\alpha}^c(r) \rightarrow \left[1 - g(r)\theta(r^{\text{nlc}} - r) \right] n_{\alpha}^c(r)$$

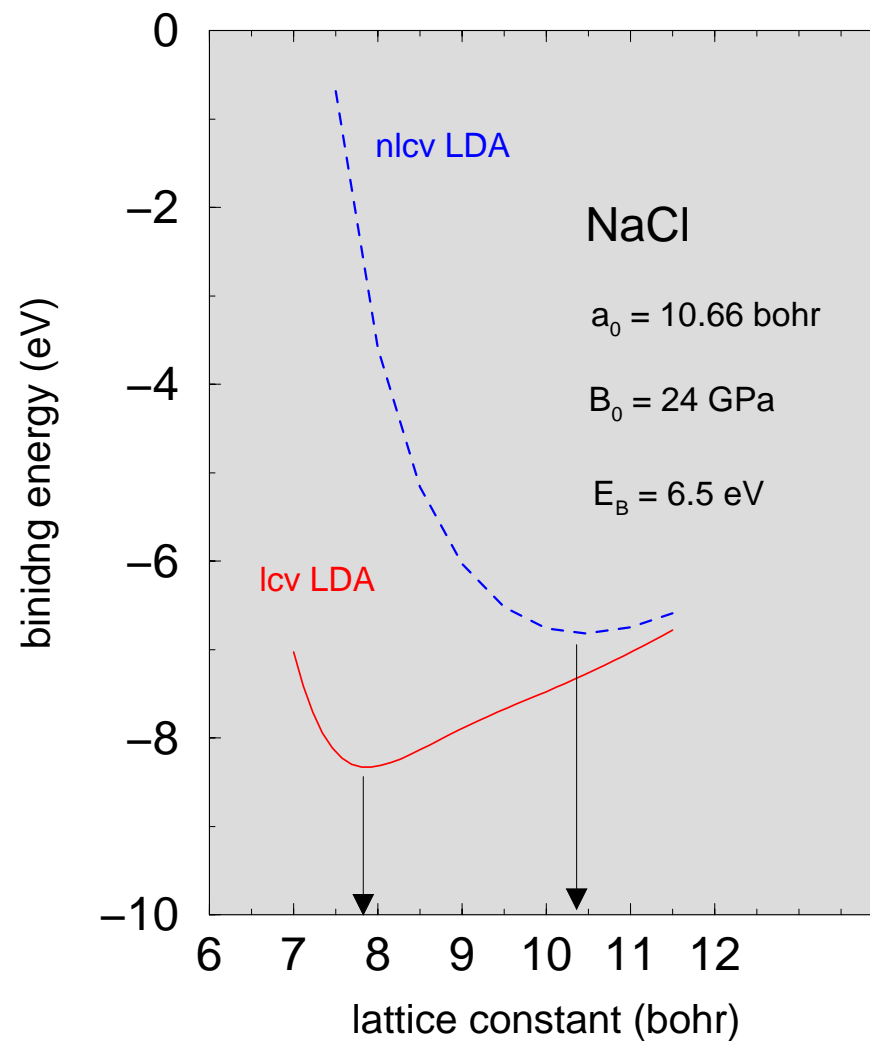
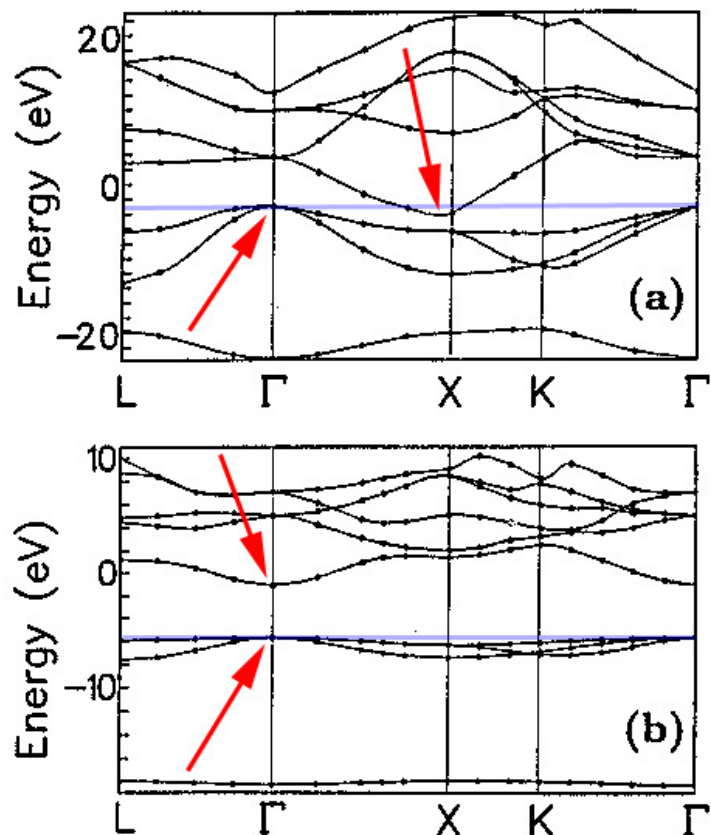
- where $0 < g(r) < 1$ e.g. a polynomial
- r^{nlcv} is the core cutoff radius



... where nonlinear core-valence XC makes a difference

Rocksalt (NaCl):¹

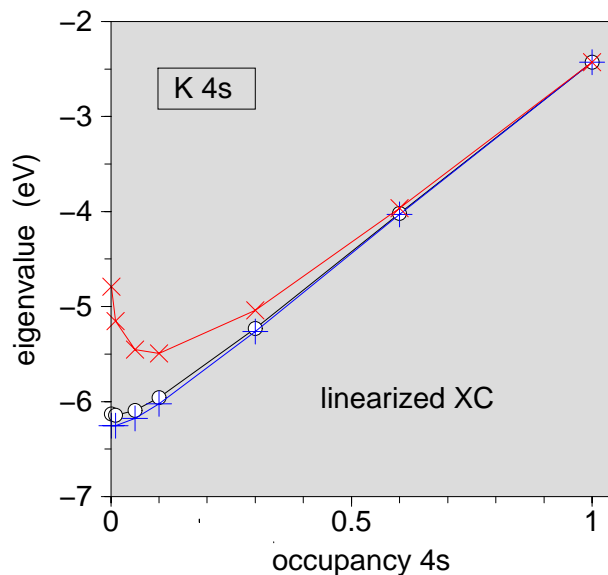
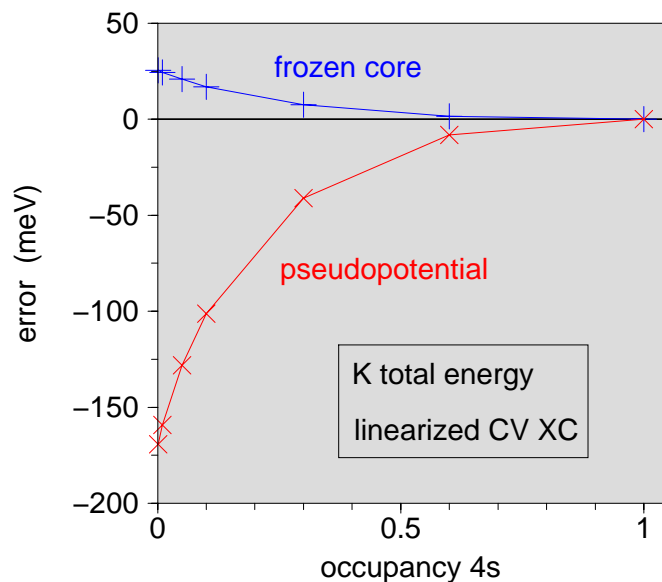
- ✗ semi-metal with linearized CV XC (a)
- ✓ insulator with nonlinear CV XC (b)



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

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

Transferability tests for K:



☞ **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 3*d*, Ca 3*d*, Rb 4*p*, ...
- Ga 3*d*, In 4*d* in III-nitrides (but not GaP, GaAs, ...)

... a bit system dependent

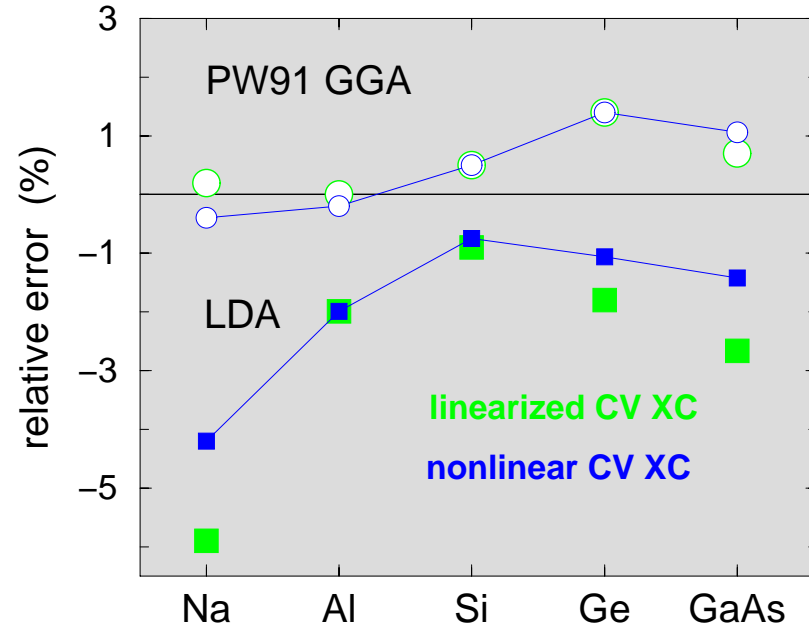
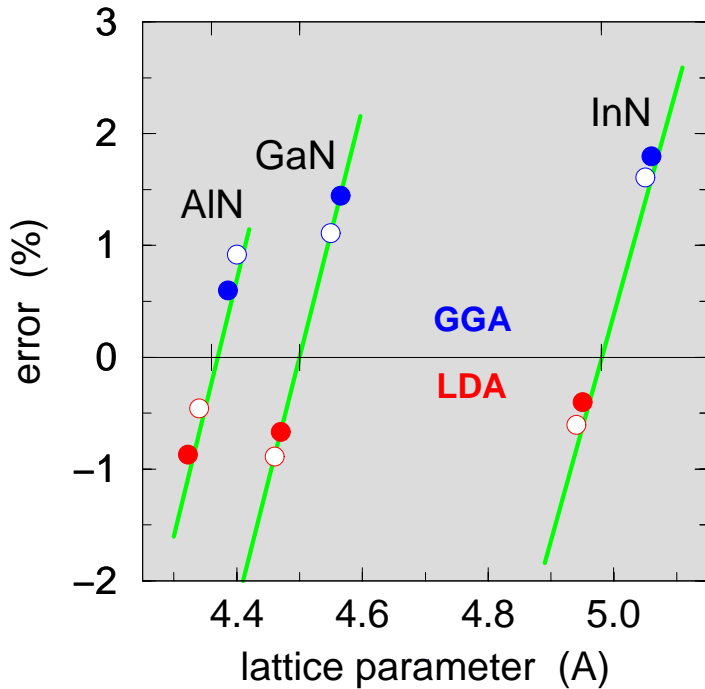
... core-valence interactions

Group-III nitrides: N $2s$ resonant with Ga $3d$

☞ Need for nlcv XC in GGA?

- all-electron
- pseudopotential

calculated vs. experimental lattice constants



☞ satisfactory only with cation $3, 4d$ states

nlcv XC not more important in GGA than in LDA!

Beware of frozen core approximation!

Plane-wave convergence – “smoothness”

✎ Nearly free electrons & perturbed plane-waves:
$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + \sum_{\mathbf{G}} \frac{V^{\text{PS}}(\mathbf{G})}{(\mathbf{k} + \mathbf{G})^2 - \mathbf{k}^2} e^{i(\mathbf{k} + \mathbf{G})\mathbf{r}}$$

➔ for fast convergence reduce high Fourier components of $\psi^{\text{PS}}(\mathbf{G})$ and $\langle \mathbf{G} | \hat{V}^{\text{PS}} | \mathbf{G}' \rangle$

- modern norm-conserving schemes are good already ¹
- ... not perfect: “coreless” $2p$ & $3d$ states still somewhat hard

Choose right scheme & (dare to) increase cutoff radii

- 1^{st} -row & $3, 4, 5d$ elements Troullier-Martins scheme (flat potential for $r \rightarrow 0$)
- Al, Si, Ga(4d), As, ... Troullier-Martins & Hamann scheme, ... perform much alike
- loss in accuracy \Leftrightarrow upper bound for r_l^{cut}
 - poor scattering properties, . . . \rightarrow atomic transferability tests tell
 - artificial overlap with neighbor “cores” ... total energy error $\Delta E \propto \int n(\mathbf{r}) \Delta V(\mathbf{r}) d\tau$,
N₂ dimer: $r_l^{\text{cut}} = 1.5$ a.u., bondlength $d/2 = 1.0$ a.u. \rightarrow binding energy error $\mathcal{O}(0.1 \text{ eV})$
... may be acceptable

¹Rappe, Raabe, Kaxiras, Joannopoulos, Phys Rev B 41, 1227 (1990); Troullier, Martins, Phys Rev B 43, 1993 (1991); Lin, Qteish, Payne, Heine, Phys Rev B 47, 4174 (1993).

Plane-wave cutoff in practice

Kinetic energy of valence electrons as measure for plane-wave cutoff energy $E^{\text{PW}} = G_{\text{PW}}^2$ (Ry):

For the free pseudo atom:

$$\Delta_l(G_{\text{PW}}) = \int_0^{G_{\text{PW}}} |u_l^{\text{PS}}(G)|^2 \frac{G^2}{2} dG - \int_0^\infty \dots$$

... for s, p, d electrons

Corresponding total energy convergence deficit:

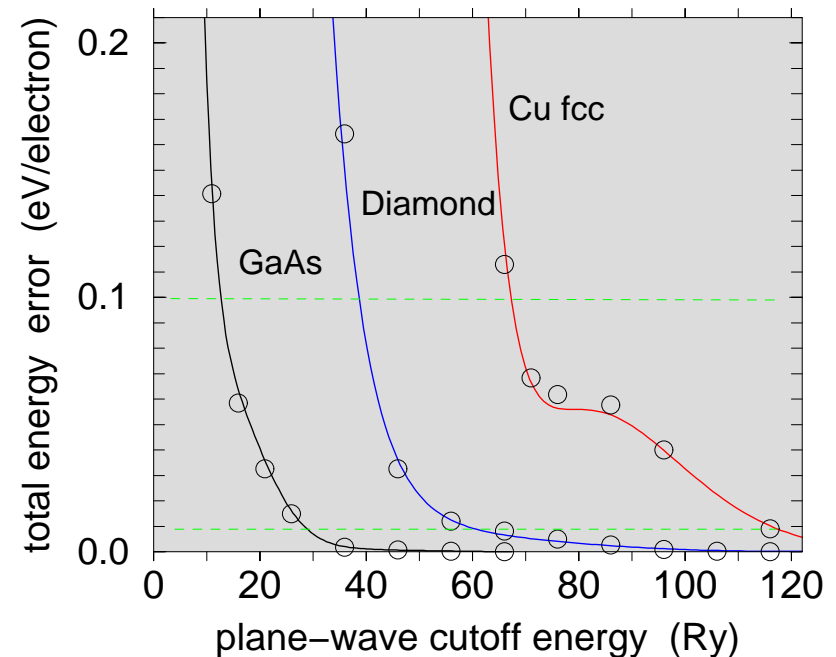
$$\Delta E(G_{\text{PW}}) = \sum_i^{\text{electrons}} w_i \Delta_{l_i}(G_{\text{PW}})$$

... for atom \approx same as in real system

↳ gives useful estimate .. too high/ too low?

▲ ... can't tell how much errors cancel out

Perform convergence tests on your system!



↳ typically we see converged properties for $\Delta_l \cdot 0.1$ eV

How to represent the pseudopotential operator

Atom: radial & angular momentum representation

$$\langle \mathbf{r} | \hat{V} | \mathbf{r}' \rangle = \sum_{lm, l'm'} \langle \mathbf{r} | rlm \rangle \langle rlm | \hat{V} | r'l'm' \rangle \langle r'l'm' | \mathbf{r}' \rangle = \sum_{lm, l'm'} \bar{Y}_{lm}(\Omega) \boxed{V_{ll'mm'}(r, r')} Y_{lm}(\Omega')$$

$$\rightarrow \boxed{V(r) \frac{\delta(r-r')}{r^2}} \sum_{lm} \bar{Y}_{lm}(\Omega) Y_{lm}(\Omega') = \boxed{V(r) \frac{\delta(r-r')}{r^2}} \dots \text{local potential}$$

- Coulomb, atomic, . . .
- same for all l

$$\rightarrow \sum_{lm} \bar{Y}_{lm}(\Omega) \boxed{V_l(r) \frac{\delta(r-r')}{r^2}} Y_{lm}(\Omega') \dots \text{semilocal pseudopotential}$$

- l -dependent/ angularly nonlocal, radially local
- $[T_l + V_l(r) - \epsilon] u_{nl}(r) = 0$
- nodeless $u_{nl} \leftrightarrow$ ground level for l (no core!)
- strict norm-conservation for ground state

Solid: reciprocal space representation, need $\langle \mathbf{G} | \hat{V} | \mathbf{G}' \rangle \rightarrow$ form factor \rightarrow like in atom

pseudopotential = local potential $\boxed{V^{\text{loc}}(r)}$ + short-range corrections $\boxed{\delta V_l(r) = V_l(r) - V^{\text{loc}}(r)}$

$$\rightarrow \boxed{V^{\text{loc}}(r)} \delta(\mathbf{r} - \mathbf{r}') + \sum_{l=0}^{l_{\text{max}}} \sum_{m=-l}^l \bar{Y}_{lm}(\Omega) \boxed{\delta V_l(r)} \frac{\delta(r-r')}{r^2} Y_{lm}(\Omega'), \boxed{\text{arbitrary } V^{\text{loc}}(r)} \text{ but...}$$

. . . semilocal pseudopotentials

Truncation of l -sum for $l > l_{\max}$ natural:

- $r > r^{\text{core}}$: $V_l(r) \propto -\frac{Z^{\text{ion}}}{r}$, all l
- high l : repulsive $+\frac{l(l+1)}{r^2}$ angular momentum barrier

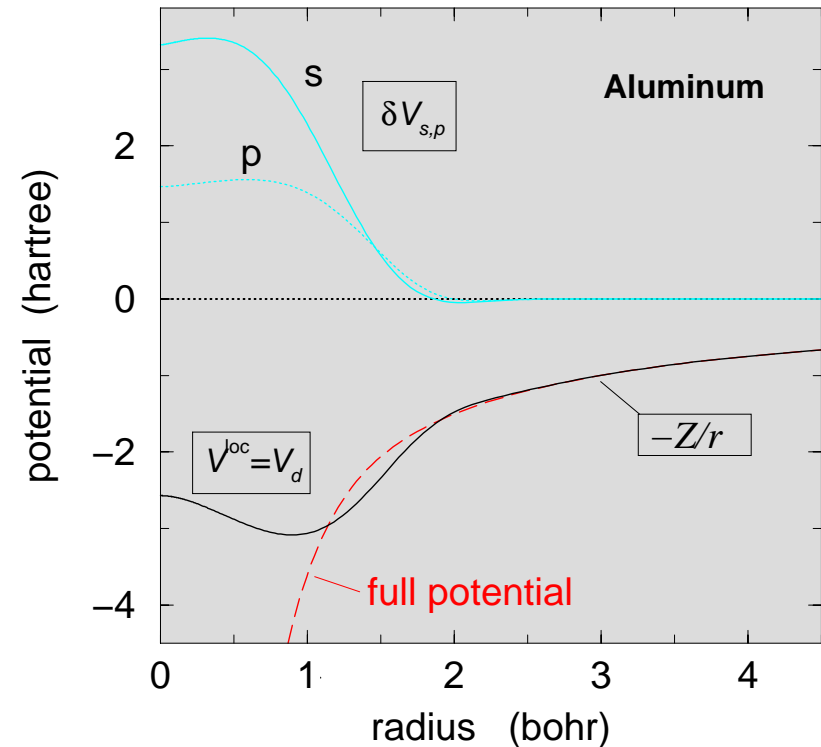
⇒ high- l partial waves see mostly local potential

↳ allows to save projections by local component

$$V^{\text{loc}}(r) = V_{l_{\text{loc}}}(r) \text{ with } l_{\text{loc}} = l_{\max}$$

- ✓ $l \leq l_{\max}$ see same $V_l(r)$ as before
- ▲ local potential ↔ scattering for $l > l_{\max}$
(norm-conservation not imposed)
- ▲ transferability of separable representation

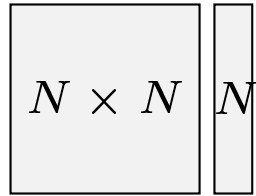
typically $l = 0, 1, 2, (3)$ $s, p, d, (f)$



Fully separable potentials

Semilocal potentials:

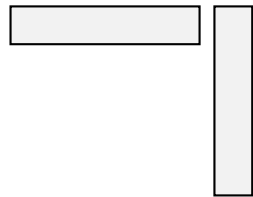
$$\langle \mathbf{G} | \delta \hat{V}_l | \mathbf{G}' \rangle \propto \int r^2 dr j_l(\mathbf{G}r) \underbrace{\delta V_l(r)} j_l(\mathbf{G}'r)$$



matrix multiplications
 $N \approx \mathcal{O}(10^{3\dots})$
 size $\approx \mathcal{O}(10^{6\dots})$

Separable potentials \leftrightarrow factorization:

$$\rightarrow \left[\int j_l(\mathbf{G}r) \chi_l(r) r^2 dr \right] \left[\int \chi_l(r) j_l(\mathbf{G}'r) r^2 dr \right]$$



only scalar products
 size $N \approx \mathcal{O}(10^{3\dots})$

- nonlocal, fully separable pseudopotential

$$\begin{aligned} \langle \mathbf{r} | \hat{V} | \mathbf{r}' \rangle &= \langle \mathbf{r} | \hat{V}^{\text{loc}} + \delta \hat{V}^{\text{NL}} | \mathbf{r}' \rangle \\ &= V^{\text{loc}}(r) \delta(\mathbf{r} - \mathbf{r}') + \sum_{lm} \langle \mathbf{r} | \chi_l lm \rangle E_l^{\text{KB}} \langle lm \chi_l | \mathbf{r}' \rangle \end{aligned}$$

- separable Kleinman-Bylander pseudopotential \leftrightarrow transformation of semilocal form

$$\delta \hat{V}_l^{\text{NL}} = \frac{|\delta V_l u_l\rangle \langle u_l \delta V_l|}{\langle u_l | \delta V_l u_l \rangle}$$

$$|\chi_l\rangle = \frac{|\delta V_l u_l\rangle}{\langle u_l \delta V_l | \delta V_l u_l \rangle^{1/2}}, \quad \delta \hat{V}_l^{\text{NL}} |\chi_l\rangle = E_l^{\text{KB}} |\chi_l\rangle$$

- KB-energy: strength of nonlocal vs. local part

$$E_l^{\text{KB}} = \frac{\langle u_l | \delta V_l^2 | u_l \rangle^{1/2}}{\langle u_l | \chi_l \rangle} = \frac{\text{average}}{\text{KB-cosine}}$$

- $|u_l\rangle$ eigenstates of semilocal & nonlocal Hamiltonian $\hat{H}_l = \hat{T}_l + \hat{V}^{\text{loc}} + |\chi_l\rangle E_l^{\text{KB}} \langle \chi_l|$

$$\langle \mathbf{r} | \delta \hat{V}_l^{\text{NL}} | u_l \rangle = \delta V_l(r) u_l(r) =: \langle \mathbf{r} | \tilde{\chi}_l \rangle$$

\Rightarrow KB-potentials norm-conserving!

- note: $|\tilde{\chi}_l\rangle = \epsilon_l - \hat{T}_l - \hat{V}^{\text{loc}} |u_l\rangle$ could be calculated directly from a chosen local potential

Kleinman-Bylander pseudopotentials at work

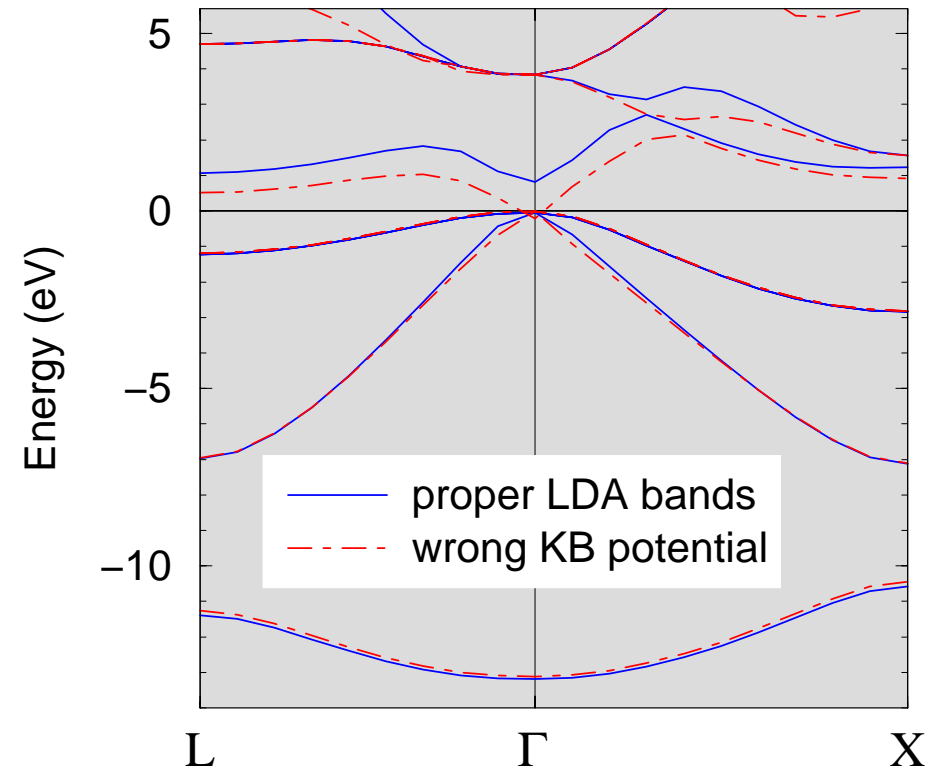
- ☞ **Price:** full nonlocality → spectral order of states by radial nodes **not** guaranteed
- ☞ **ghost states** above/below physical valence levels possible

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

- inspect logarithmic derivatives
 - do spectral analysis
- ... readily avoided by proper choice of local & nonlocal components

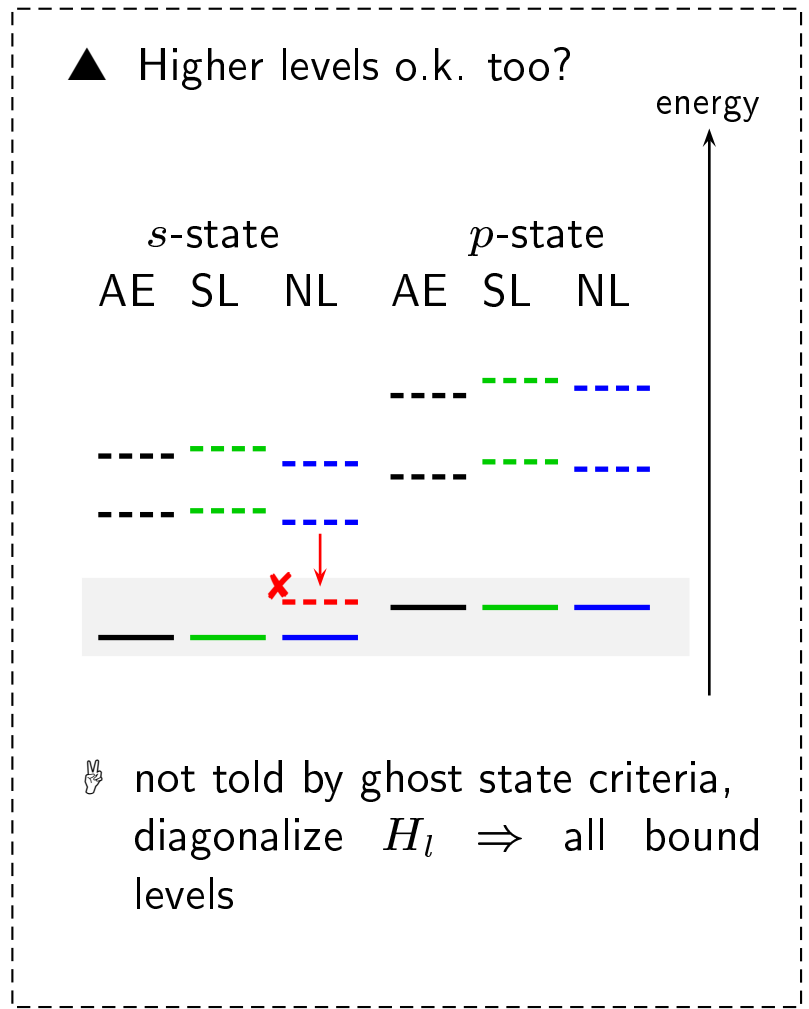
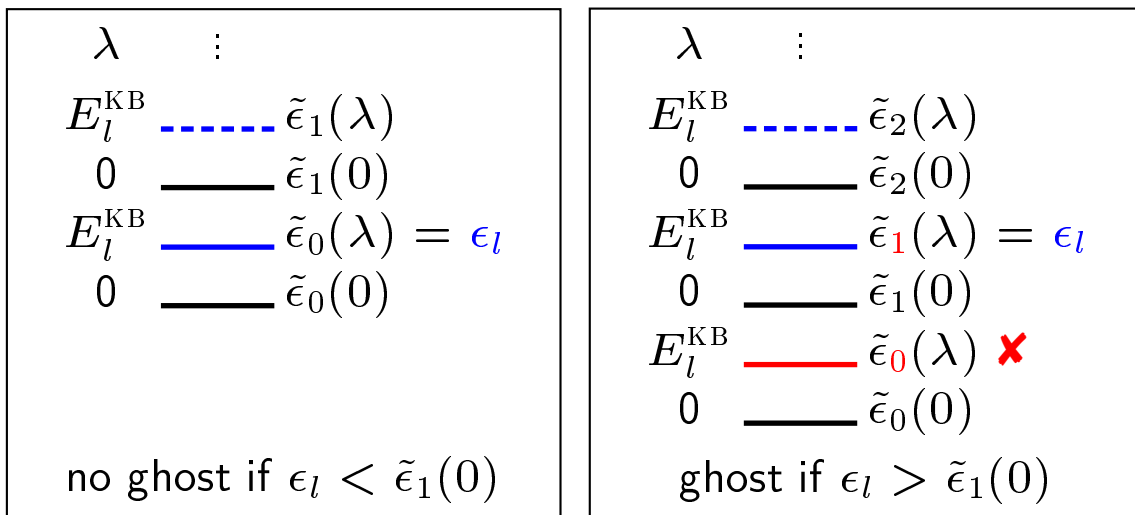
$$V_l(r) \rightarrow \left\{ V^{\text{loc}}(r), \delta V_l(r) \right\}$$

Example: KB-pseudopotential for As
→ ZB GaAs bandstructure



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

- ☞ $\lambda = E_l^{\text{KB}}$ gives the reference valence level ϵ_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 $\lambda, E_l^{\text{KB}} > 0$ spectra ordered like ¹



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

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

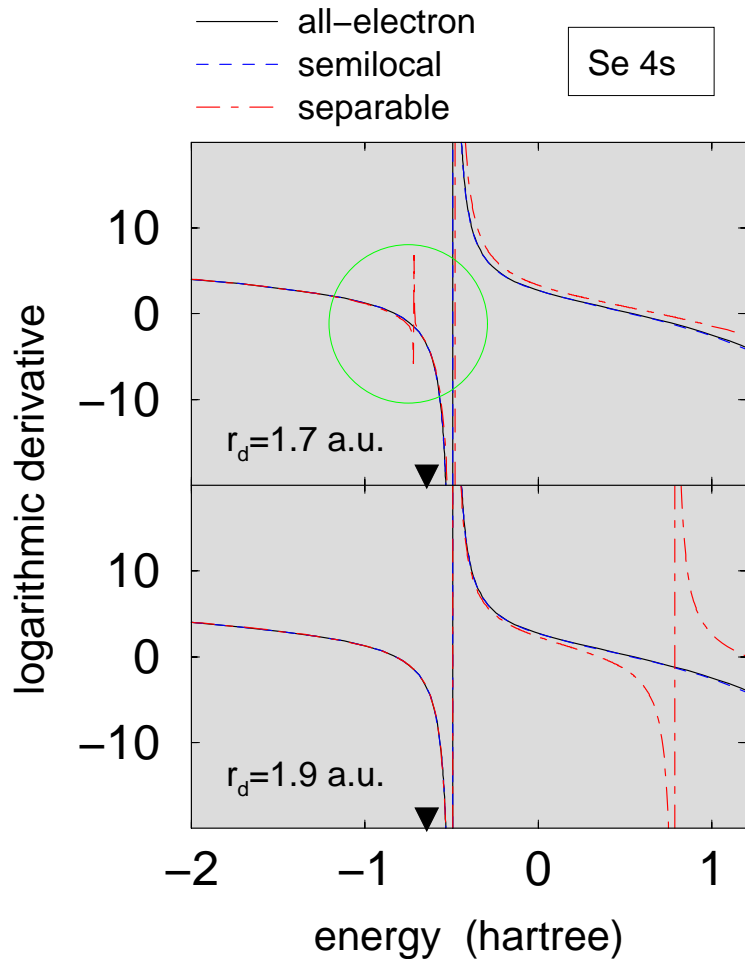
ghost if $\epsilon_l > \tilde{\epsilon}_0(0)$

✿ used as ghost state criteria in fhi98PP (pswatch)

¹Gonze, Stumpf, Scheffler, Phys Rev B 16, 8503 (1992)

Ghost states

Seen in logarithmic derivatives . . .



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

✎ local potential $l_{\text{loc}} = l_{\text{max}} = 2$ saves computing

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

✎ can cause strong nonlocality (large $|E_l^{\text{KB}}|$)

“artificially:” \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 $V_{3d}(r) \Rightarrow E_l^{\text{KB}} \gg 0$ to get 4s right
all 3,4,5d-metals: Cu, Pd, Ag, ...

make local potential repulsive $\rightarrow E_l^{\text{KB}} < 0$
use to s - or p -component!

→ KB-potentials work well in practice

Other forms of pseudopotentials

Motivation - an exact transformation between AE and PS wavefunctions is¹

$$|\phi^{\text{AE}}\rangle = |\phi^{\text{PS}}\rangle + \sum_n \left\{ |R_n^{\text{AE}}\rangle - |R_n^{\text{PS}}\rangle \right\} \langle \chi_n^{\text{PS}} | \phi^{\text{PS}} \rangle$$

$$|\phi^{\text{AE}}\rangle = \left\{ 1 + \hat{\mathcal{T}} \right\} |\phi^{\text{PS}}\rangle$$

. . . PS operators (acting on pseudo wavefunctions) act as

$$\begin{aligned} \hat{O}^{\text{PS}} &= \hat{\mathcal{T}}^\dagger \hat{O} \hat{\mathcal{T}} \\ &= \hat{O} + \sum_{nn'} |\chi_n^{\text{PS}}\rangle \left\{ \langle R_n^{\text{AE}} | \hat{O} | R_{n'}^{\text{AE}} \rangle - \langle R_n^{\text{PS}} | \hat{O} | R_{n'}^{\text{PS}} \rangle \right\} \langle \chi_{n'}^{\text{PS}} | \end{aligned}$$

$$\rightarrow \{ \dots \} \text{ looks like } \sum_{nn'} |\chi_n^{\text{PS}}\rangle V_{nn'} \langle \chi_{n'}^{\text{PS}} |$$

↪ Can make ansatz for *separable* pseudopotential with multiple projectors²

$$\langle r | \hat{V}_l | r' \rangle = \langle r | \hat{V}^{\text{loc}} | r' \rangle + \sum_{n,n'=1,2,\dots} \langle r | \chi_{nl} \rangle V_{l,nn'} \langle \chi_{n'l} | r' \rangle$$

. . . χ_{nl} : e.g. atomic functions derived from $|\tilde{\chi}_{nl}\rangle = \epsilon_n - \hat{T}_l - \hat{V}^{\text{loc}} | u_{nl} \rangle$

. . . $n = n' = 1$ like Kleinman-Bylander pseudopotentials

¹ Blöchl, Phys Rev B 50, 17953 (1994).

² Blöchl, Phys Rev B 41, 5414 (1990).

① **Norm-conserving:**

$$Q_{nn'} = \langle u_{nl}^{\text{AE}} | u_{n'l}^{\text{AE}} \rangle_{r^{\text{core}}} - \langle u_{nl} | u_{n'l} \rangle_{r^{\text{core}}} = 0$$

. . . several reference states possible!

② **“Quasi” norm-conserving:**

$$\langle u_{nl} | u_{n'l} \rangle_{r^{\text{core}}} + Q_{nn'} = \langle u_{nl}^{\text{AE}} | u_{n'l}^{\text{AE}} \rangle_{r^{\text{core}}}$$

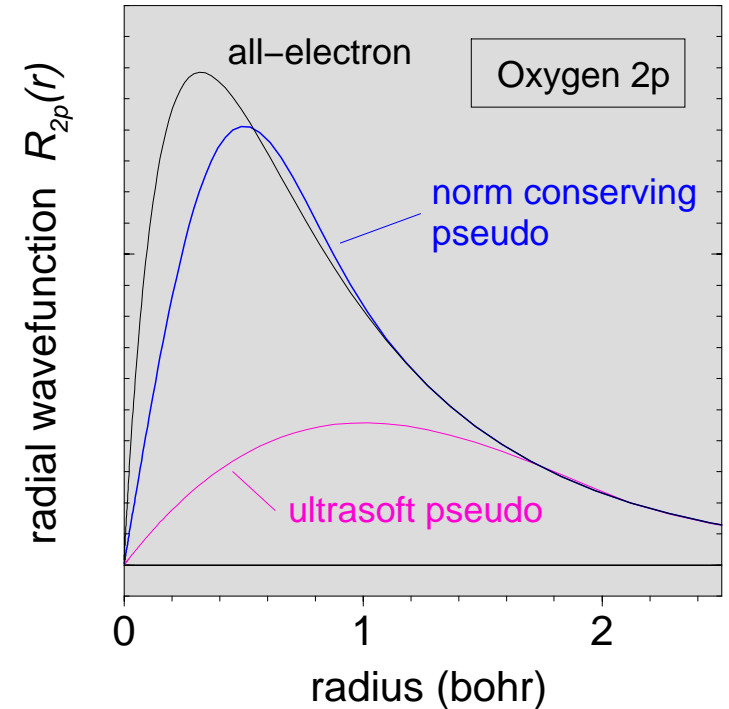
→ **Ultrasoft pseudopotentials**¹

- ↳ logarithmic derivative match as in norm-conserving case
- ↳ density & wavefunction → smooth part + augmentation
- ↳ gives generalized eigenvalue problem $\hat{H} - \epsilon \hat{S} | \phi_i \rangle = 0$

reduced plane-wave basis for 1st row & *d*-metal elements

↔

increase in projections, added complexity



¹ Vanderbilt, Phys Rev B 41, 7892 (1990); Laasonen *et al*, Phys Rev B 47, 10142 (1993); Kresse, Hafner, J Phys Cond Mat 6, 8245 (1994); Dong, Phys Rev B 57, 4304 (1998).

Summary

Pseudopotential = electron-ion 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
 - generalizations