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L4

Pseudopotentials for ab initio electronic structure calculations

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- We want to calculate electronic structure of many-atom systems using a plane wave basis
- . . . this is enabled by pseudopotentials
  "Where they come from and what they do in theory and practice"

Key words & ideas

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

- scale of orbitals

  core: size of $1s \sim \dfrac{1}{Z}$ 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_{tot}/pair	$\simeq$	10^5	eV
	$\hbar\omega_{phonon}$	$\simeq$	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 may be described by a potential

  ➥ *e-n* & *e-e* core-valence interactions are "linearized"

  work with valence electrons only = energy scale & degrees of freedom reduced

- eliminate orthogonalization wiggles in valence wavefunctions by transformation

  ○ to smooth pseudo wavefunctions seeing a weak pseudopotential

  ➥ good efficiency with plane waves

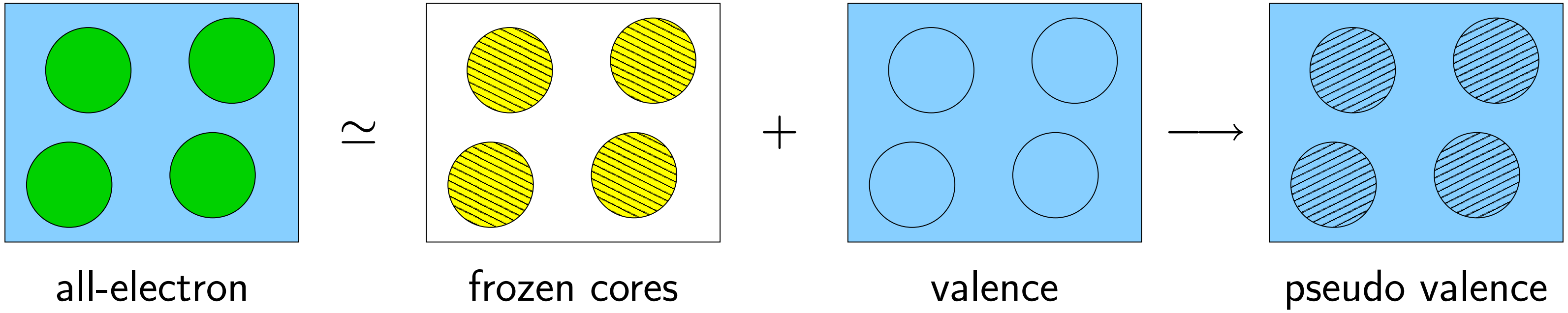
  ○ relativity can be included

- frozen-core & "pseudoization" are approximations

  should be independent of system: atom ⟶ molecule ⟶ solid

  ➥ transferable pseudopotentials

Pseudopotentials ⇔ approximate electron-ion interaction potentials



From full potentials to pseudopotentials

Atom - calculate eigenstates ⟶ solve (radial) Kohn-Sham equation: $\hat{T} + \hat{V}^{AE}|\phi_i^{AE}\rangle = \epsilon_i|\phi_i^{AE}\rangle$

- choose atomic configuration, for some $\epsilon < 0$ integrate …

  outward $rR^{out}(\epsilon;0) = 0 \quad \longrightarrow R^{out}(\epsilon;r)\big|\; r_< = 0\ldots r^{match}$

  inward $R^{in}(\epsilon;\infty) = 0 \quad \longrightarrow R^{in}(\epsilon;r)\big|\; r_> = \infty\ldots r^{match}$

  …outside classical turning point

- if $\boxed{\text{logarithmic derivatives}}$ match …iterate ϵ until they do,

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

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

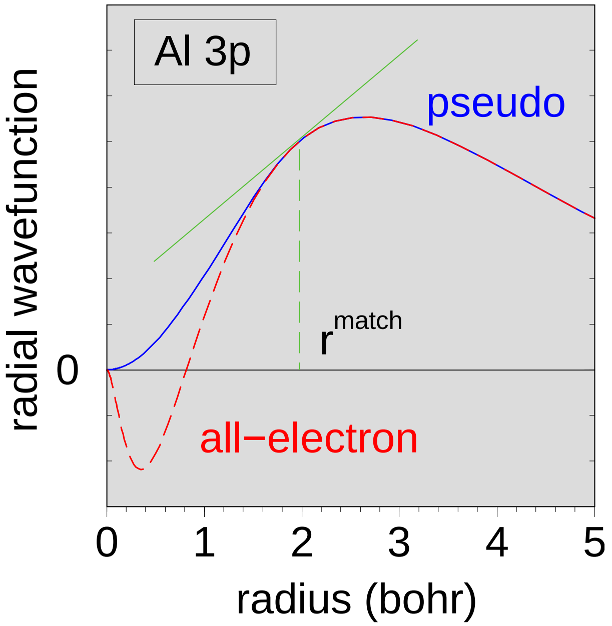
- Any potential $\hat{V}^{PS}$ giving the <u>same</u> logarithmic derivative for $r \geq r^{match}$ gives the <u>same</u> eigenvalue as $\hat{V}^{AE}$

Pseudopotential = exact transformation of full potential

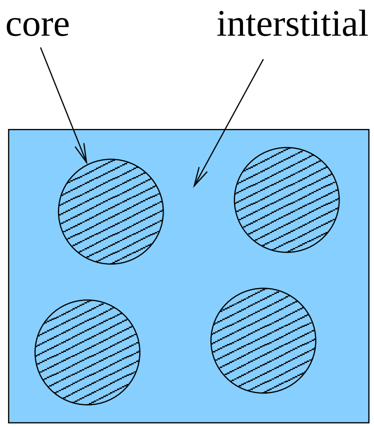
$$\hat{T} + \hat{V}^{PS}|\phi_i^{PS}\rangle = \epsilon_i|\phi_i^{PS}\rangle$$

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

Al $1s^2 2s^2 p^6$ $\mathbf{3s^2 3p^1}$



Solid - logarithmic derivatives ↔ boundary conditions



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

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

Match $$\left.\frac{\frac{d}{dr}R_l(r)}{R_l(r)}\right|_{\substack{\epsilon \\ r^{core}}} = \left.\frac{\frac{d}{dr}\phi_l^{inter}(r)}{\phi_l^{inter}(r)}\right|_{\substack{\epsilon \\ r^{core}}}$$ . . . like APW

The pseudopotential is “weak” - cancellation theorem

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

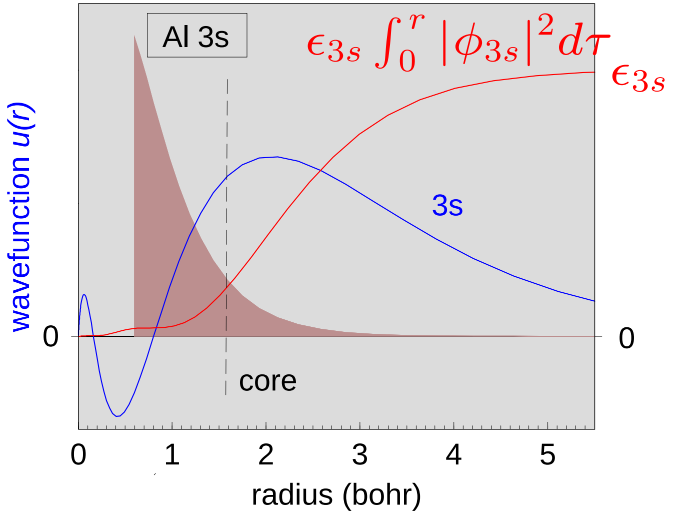
$$\int_0^{r^{core}} \bar{\phi}_i^{AE} \left[T + V^{AE} \right] \phi_i^{AE} d\tau \ll \epsilon_i$$

- the pseudopotential acts like[1]

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

attractive repulsive, confined to core

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



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

Accuracy aspect: Norm-conservation

- *So far:* Pseudopotential o.k. for atom in some chosen electronic configuration
- Pseudopotential must be **transferable**, i.e. perform correctly in different environments
  - ❈ PS $\simeq$ AE eigenvalues $\leftrightarrow$ band structure & one-particle energy $\sum_i^{occ} \epsilon_i$
  - ❈ electron density $\leftrightarrow$ $V^{eff}[n; \mathbf{r}]$ and total energy
- If we impose

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

and **norm conservation**

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

➥ get correct "total charge inside core radius" $\Leftrightarrow$ proper electrostatic potential for $r > r^{core}$

➥ boundary conditions of AE and PS orbitals in same way with energy $\epsilon_i \pm \delta\epsilon$

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

... over the width of the valence bands $\longrightarrow$ correct scattering properties

➥ PS wavefunctions change similar to AE wavefunctions

○ separately for each valence state $\longrightarrow$ l-dependence

Accuracy aspect: Frozen-core approximation

"Chemically inert core" . . . but in fact: core orbitals will change with chemical environment too!

- Effect on total energy?

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

two step view: change valence density ⟶ change effective potential ⟶ change core density

➥ second order error $\int \Delta V^{c,\mathit{eff}} \Delta n^c d\tau$

... cancels out in total energy differences [1]

- core regions of neighboring atoms do not overlap

- core/ valence separation often intuitive: core ⟶ all filled shells

  beware: this choice is not always adequate (semicore states of Ca, Zn, Ga, . . . see later)

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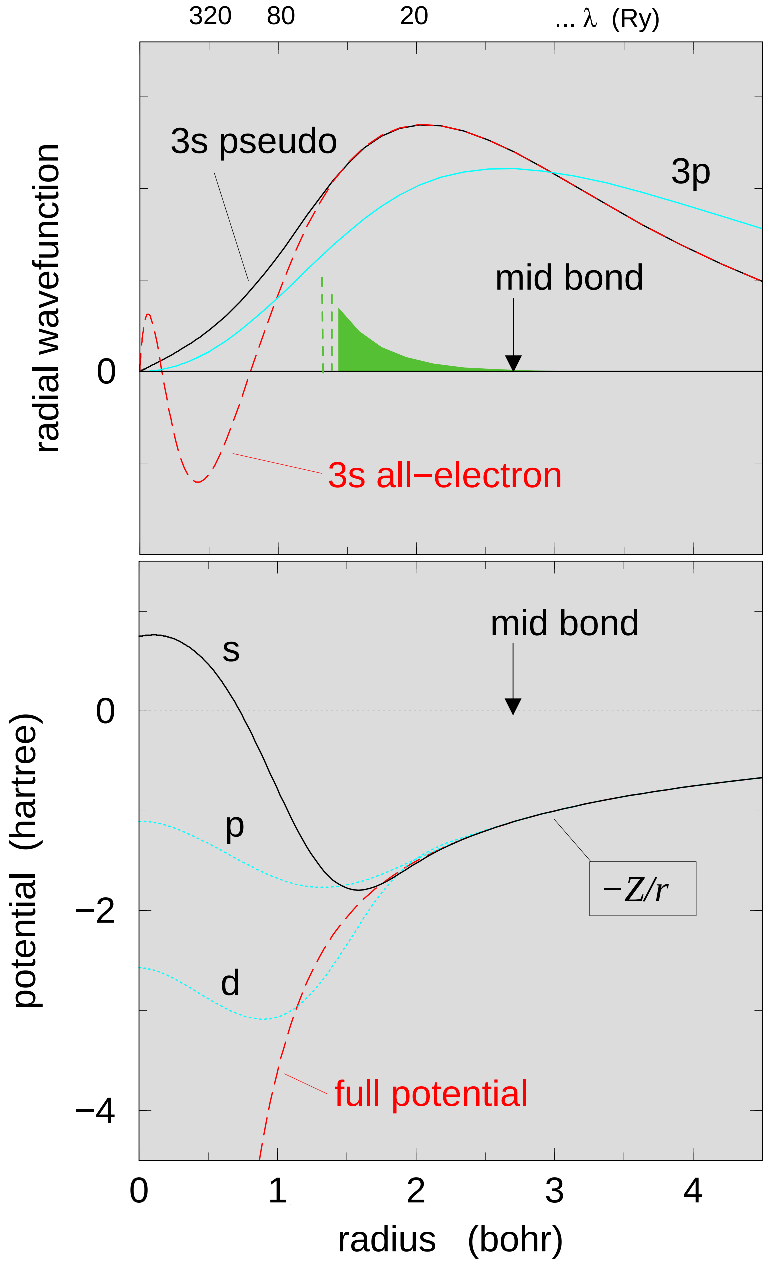
[1] von Barth, Gelatt, Phys Rev B 21, 2222 (1980).

Example: Pseudopotential for aluminum



Constructing normconserving pseudopotentials

Free atom - all-electron full potential ⟶ pseudo valence orbitals & pseudopotential

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

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

▲ Relativity: Dirac → scalar relativistic → non-relativistic

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

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

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

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

. . . formally non-relativistic Schrödinger eq.

. . . V_l^{scr} effective potential (screened pseudopotential)
different for each valence state → l-dependent

. . . lowest state for each l has no radial nodes → core states gone!

Actual steps in the construction

User chooses:

- Z
- electronic configuration
- valence states
- pseudopotential type
  - $\longrightarrow$ cutoff radii in each l
  - $\longrightarrow$ (reference energy)

○ (core-valence XC)

○ local potential

Program follows the recipe:

nodeless radial pseudo wavefunctions satisfy conditions ...

① same valence energy levels $\boxed{\epsilon_l = \epsilon_{\nu l}^{AE}}$ ...center of VB's

② outside **cutoff radius** $\boxed{r_l^{cut}}$ orbitals match

$$\boxed{u_l(r > r^{cut}) = u_{\nu l}^{AE}(r)}$$

...implies matching of logarithmic derivatives

③ norm-conservation $\boxed{\langle \phi_l | \phi_l \rangle = \langle \phi_l^{AE} | \phi_l^{AE} \rangle = 1}$

$+$ constraints for good plane-wave convergence

➥ pararametrize $u_l(r)$ and invert Schrödinger eq. $V_l^{scr}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{d^2/dr^2\, u_l(r)}{2u_l(r)}$

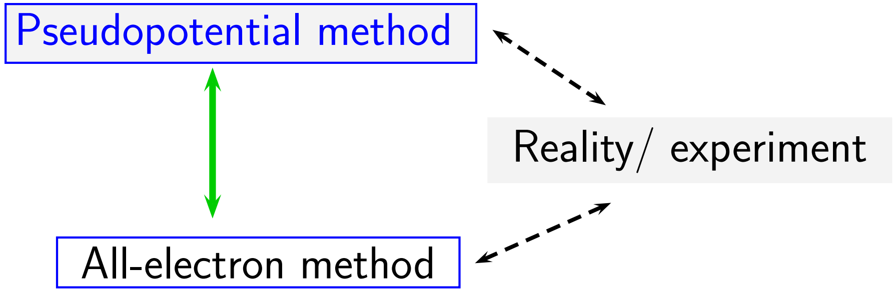
➥ unscreening with atom's pseudo valence density $\longrightarrow$ final ionic pseudopotentials for applications

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

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

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

Transferability



Pseudopotential method

Reality/ experiment

All-electron method

○ compromise with needed smoothness

● needed accuracy $\sim \mathcal{O}(0.1 \ldots 0.01 \text{ eV})$
  - electronic structure
  - cohesive properties
  - atomic structure, relaxation, phonons
  - formation & activation energies, ...

● modifications
  - separable potentials (computational)
  - core corrections (methodic)

▲ new materials → GaN (with $3d$ or not), ...

▲ new XC functionals → GGA, ...

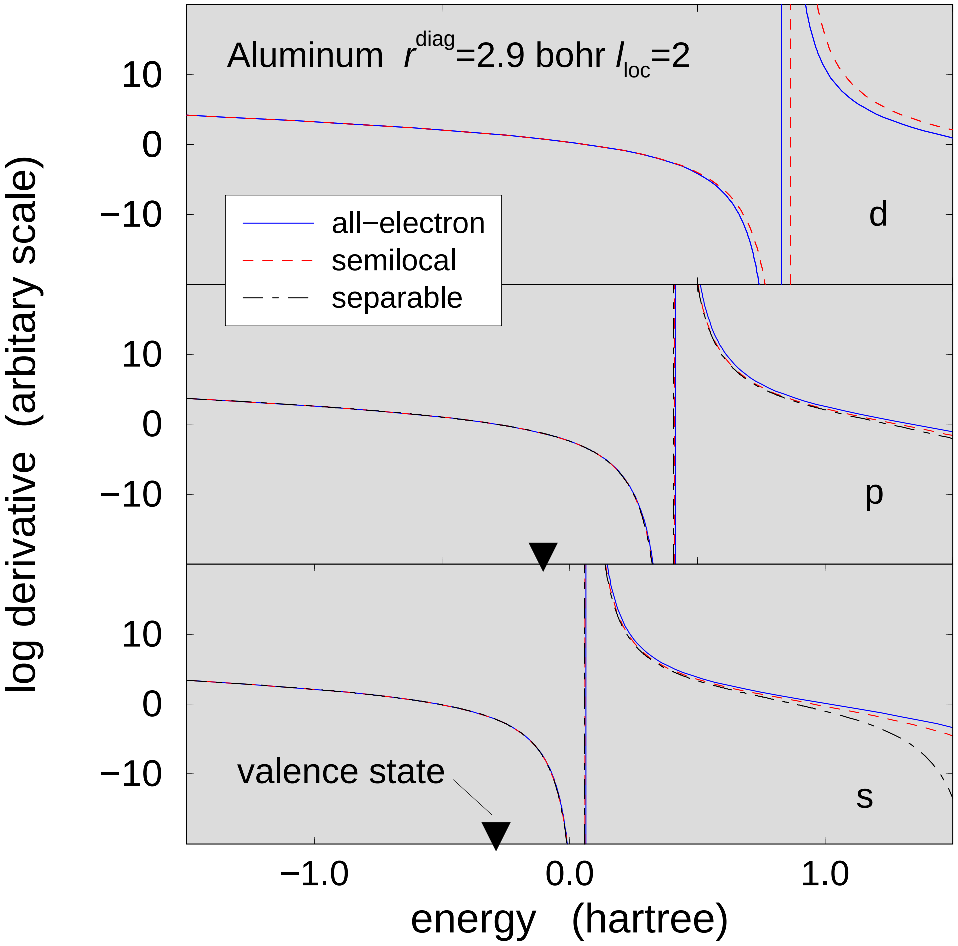
Characteristic tests of PP at atomic level?

Test: Logarithmic derivatives

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

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

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



Monitoring transferability

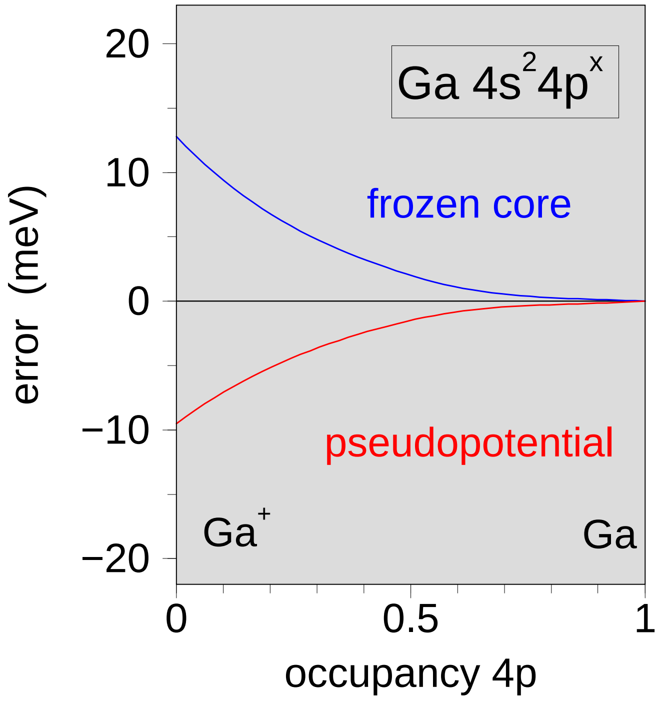
Test: Configurational changes (ΔSCF)

❑ $s \longrightarrow p$ promotion (C, Si, Ge, ...)

❑ ionization (Li⟶Li$^+$, Na⟶Na$^+$,...)

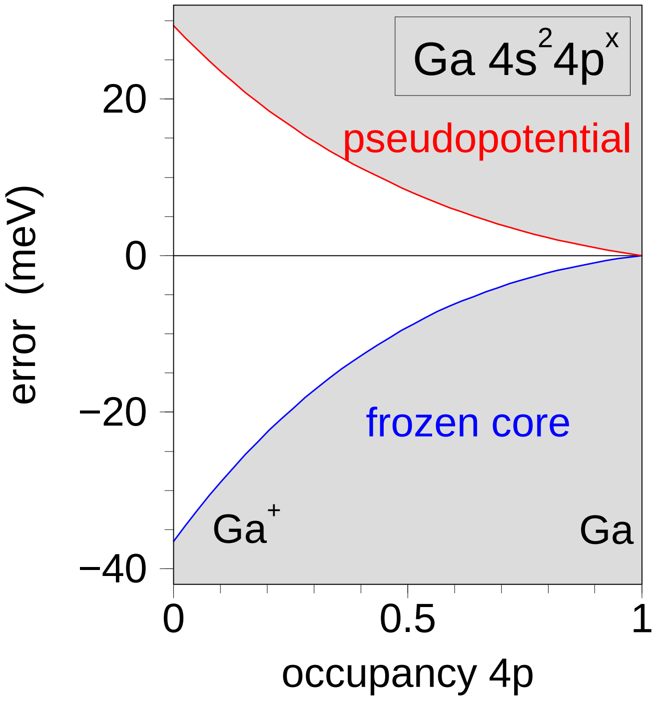
- total energy ("excitations")

$$E[n(f_k)]$$



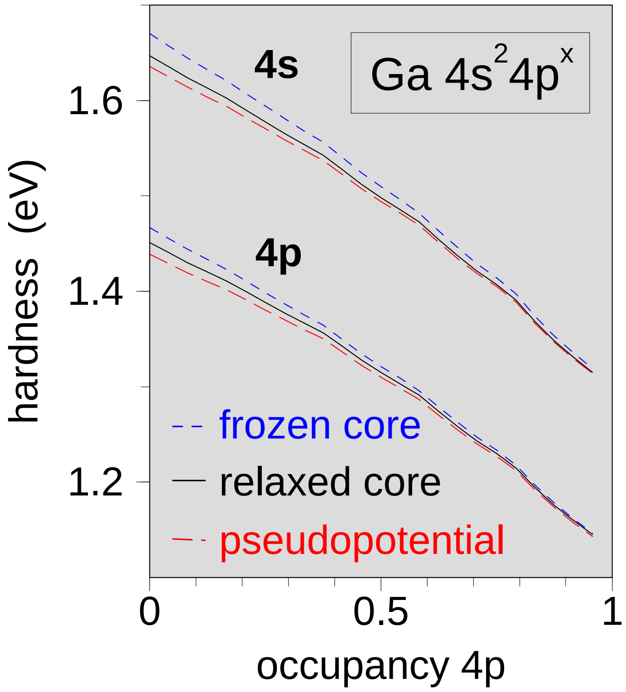
- eigenvalues (Janak theorem)

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



- chemical hardness[1] (response)

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



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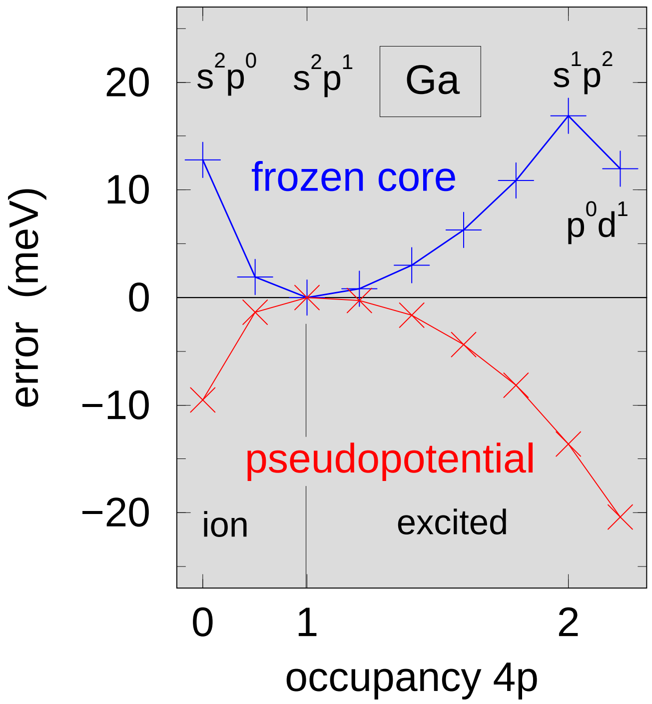
[1] Grinberg, Ramer, Rappe, Phys Rev B 63, 201102 (2001); Filipetti et al, Phys Rev B 52, 11793 (1995); Teter, Phys Rev B 48, 5031 (1993).

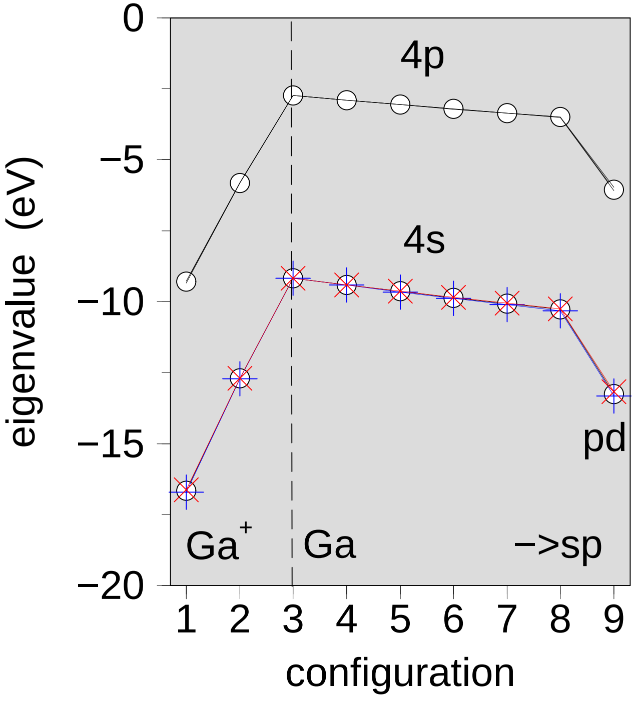
“Hardness tests” in practice

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

… PP not worse than frozen core

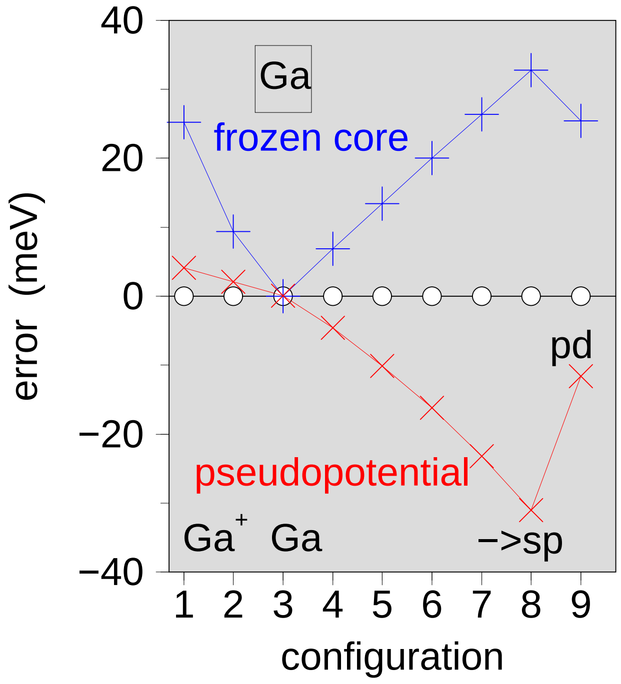


Eigenvalues match well?



Level splitting preserved?

$\epsilon_p - \epsilon_s$



Nonlinear core-valence XC (nlcv XC)

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

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

- electronic core-valence interactions mimicked by pseudoptential ⟶ 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

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

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

- restoring nonlinear core-valence XC[2]

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

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

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

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

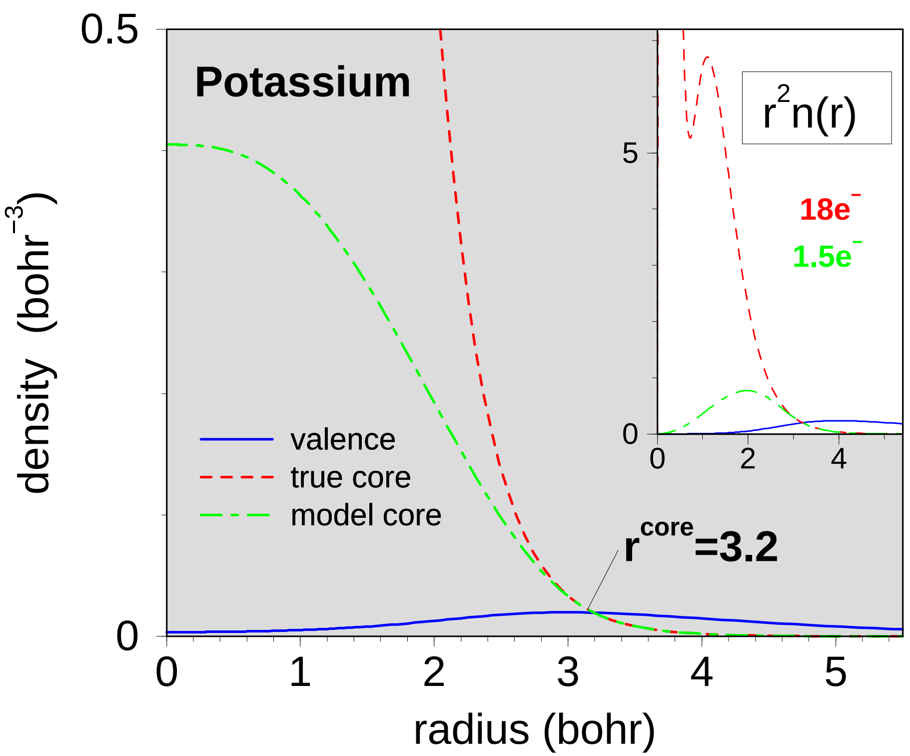
Partial core density for nlcv XC

Overlap matters only around core edge . . .

➥ can smoothen full core density inside the core
"partial core corrections"

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

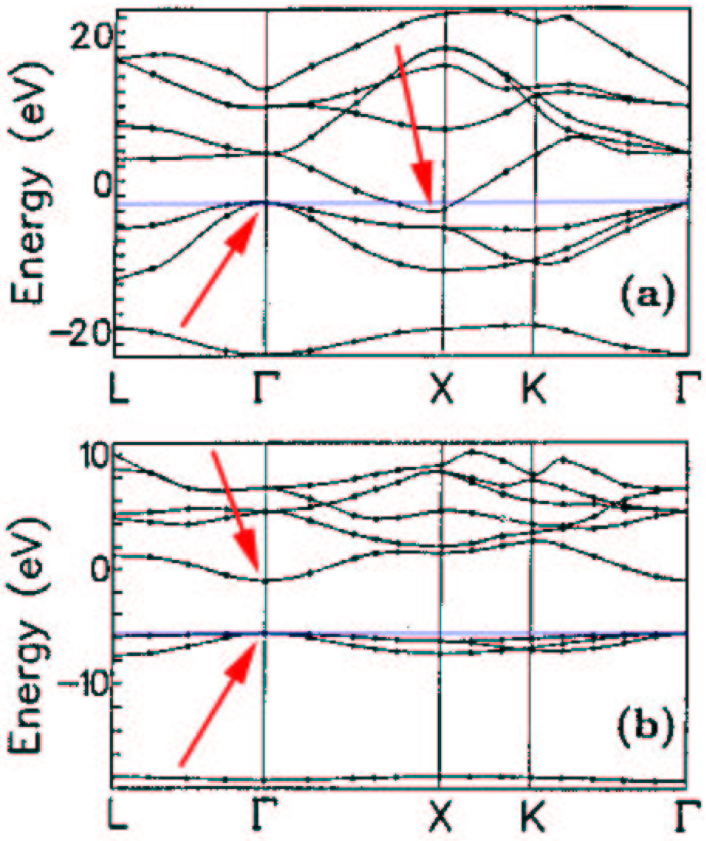
- where $0 < g(r) < 1$ e.g. a polynomial
- r^{nlcv} is the core cutoff radius

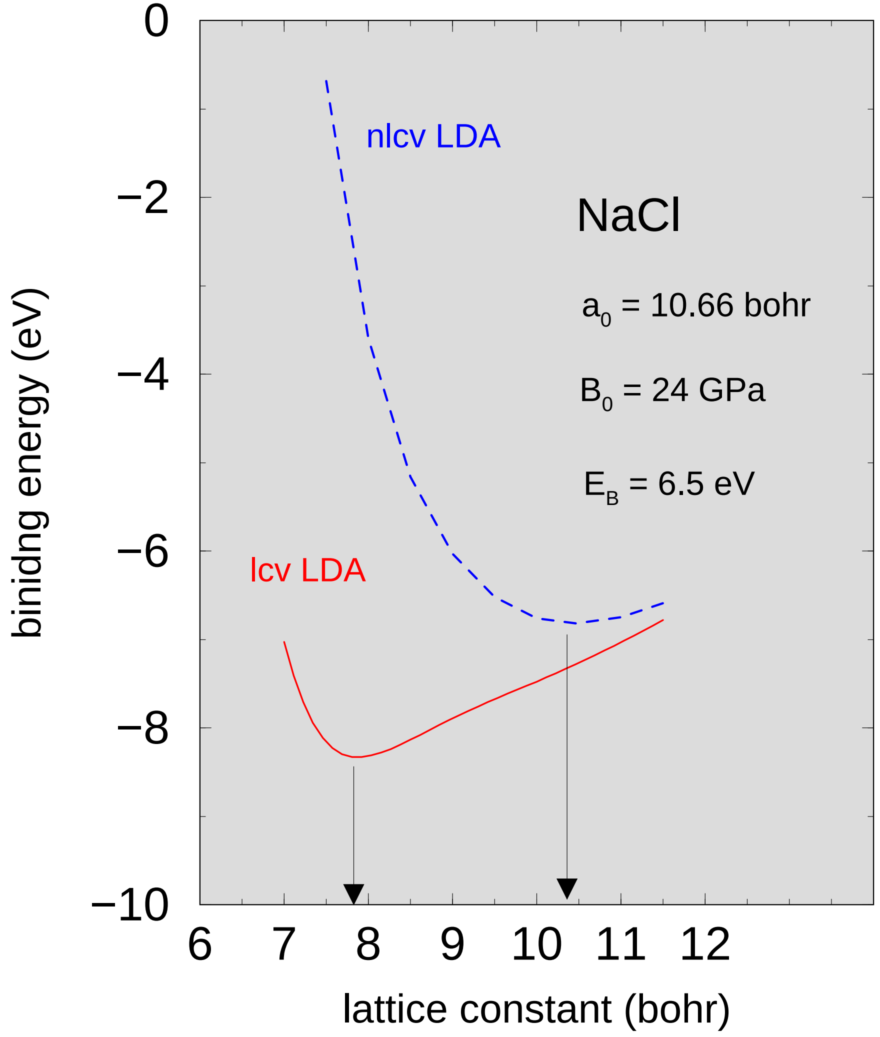


… where nonlinear core-valence XC makes a difference

Rocksalt (NaCl): [1]

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





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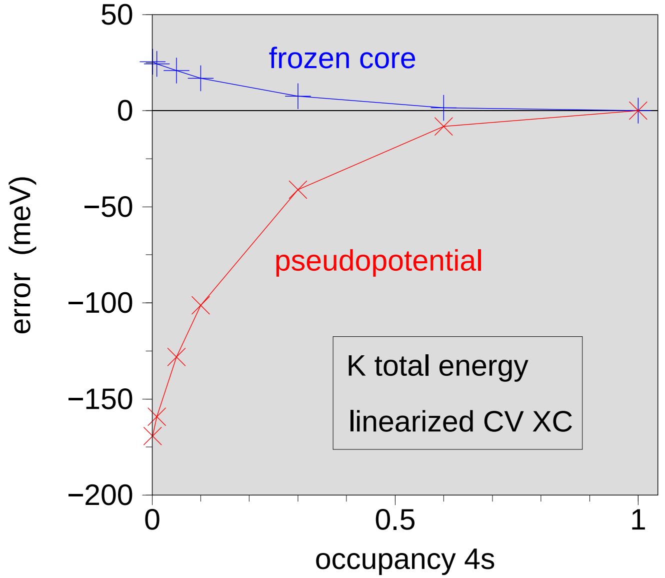
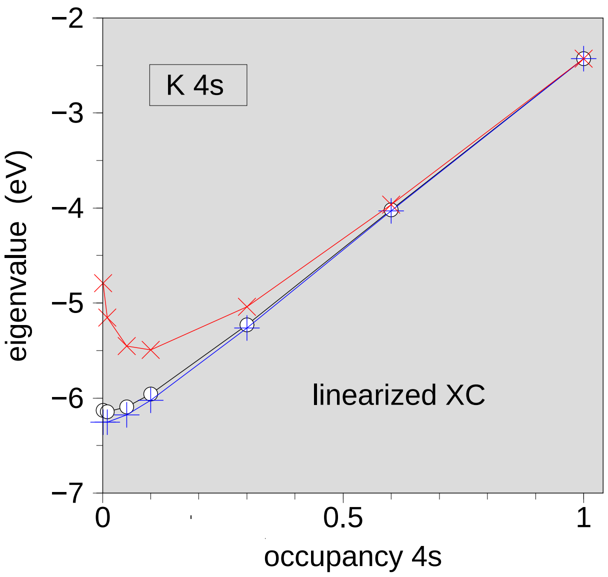
[1] Hebenstreit, Scheffler, Phys Rev B 46, 10134 (1992).

… and where linearized core-valence XC is fine

Transferability tests for K:





☛ **linearized nlcv XC** mostly sufficient!

- 1^{st} & 2^{nd} 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!** (open shell atoms, molecules, MnAs, …)

✌ turning semi-core into valence states?

- Zn $3d$, Ca $3d$, Rb $4p$, …
- Ga $3d$, In $4d$ in III-nitrides (but not GaP, GaAs, …)

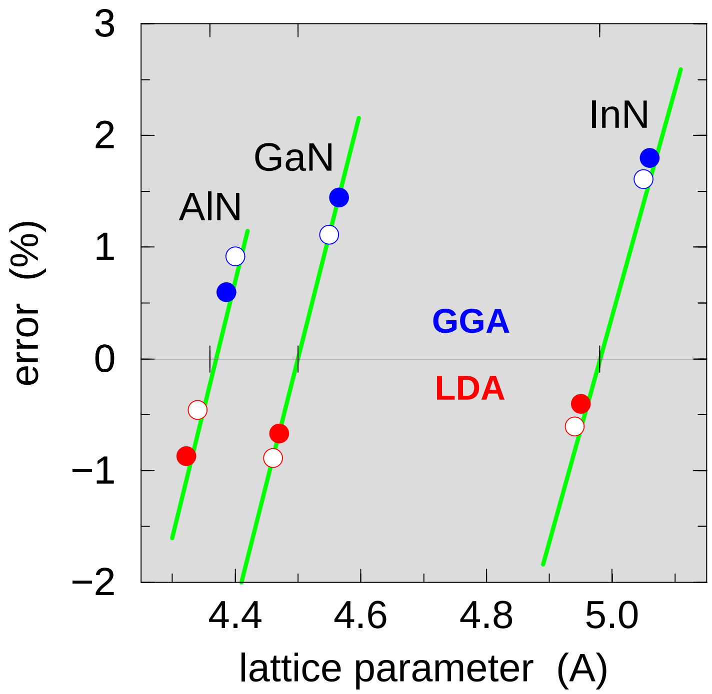
… a bit system dependent

… core-valence interactions

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

○ ○ all-electron

● ● pseudopotential

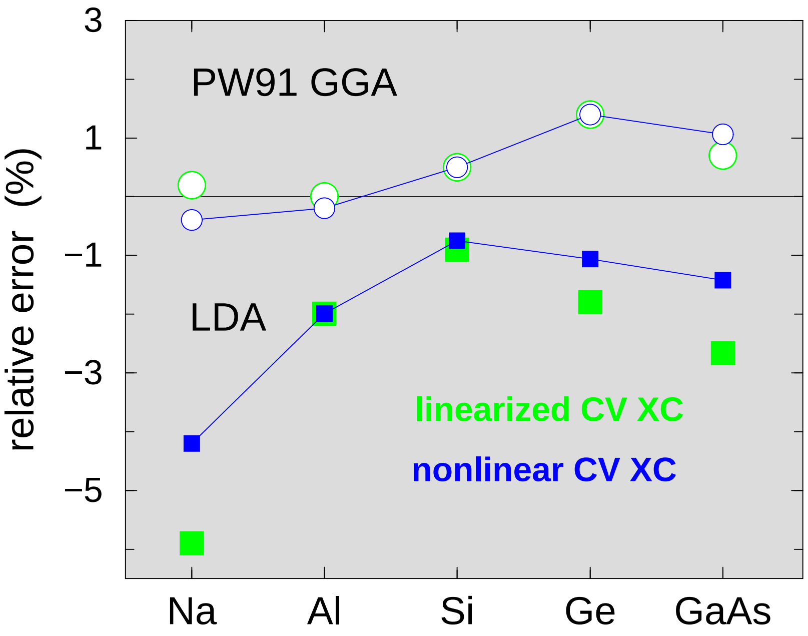


➥ satisfactory only with cation $3, 4d$ states

Beware of frozen core approximation!

☛ Need for nlcv XC in GGA ?

calculated vs. experimental lattice constants



nlcv XC not more important in GGA than in LDA!

Plane-wave convergence – "smoothness"

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

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

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

$\boxed{\text{Choose right scheme \& (dare to) increase cutoff radii}}$

- $\boxed{1^{st}\text{-row \& } 3,4,5d \text{ elements}}$ Troullier-Martins scheme (flat potential for $r \longrightarrow 0$)
- $\boxed{\text{Al, Si, Ga(4d), As, ...}}$ Troullier-Martins & Hamann scheme, ... perform much alike
- $\boxed{\text{loss in accuracy}}$ ⇔ upper bound for r_l^{cut}
  - poor scattering properties, $\ldots \longrightarrow$ $\boxed{\text{atomic transferability tests tell}}$
  - artificial overlap with neighbor "cores" ... total energy error $\Delta E \propto \int n(\mathbf{r}) \Delta V(\mathbf{r}) d\tau$,
    N_2 dimer: $r_l^{cut} = 1.5$ a.u., bondlength $d/2 = 1.0$ a.u. $\longrightarrow$ binding energy error $\mathcal{O}(0.1$ eV$)$
    ... may be acceptable

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[1] Rappe, 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 $\boxed{E^{PW} = {G_{PW}}^2 \text{ (Ry)}}$:

For the free pseudo atom:

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

... for s, p, d electrons

Corresponding total energy convergence error :

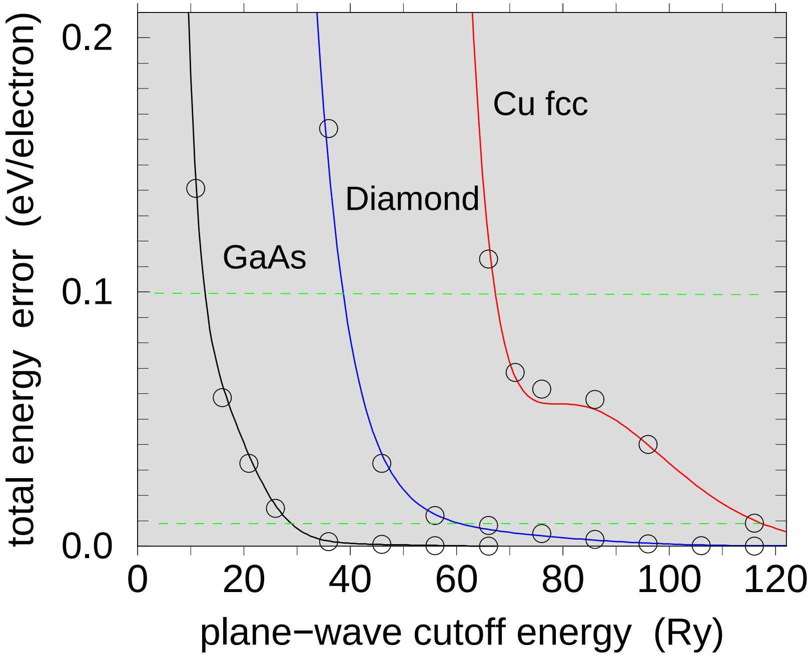
$$\Delta E(G_{PW}) \simeq \sum_i^{electrons} w_i \Delta_{l_i}(G_{PW})$$

... for atom ≈ 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 cohesive properties for $\Delta_l \lesssim 0.1$ eV

Form of pseudopotential operator in applications

Atom - radial & angular momentum representation

general but naive: $\hat{V} = \sum_{lm,l'm'} |rlm\rangle \boxed{V_{ll'mm'}(r,r')} \langle r'l'm'|$ …a projector, nonlocal in space

- $\langle \mathbf{r}|\hat{V}|\vec{\mathbf{r}}'\rangle = \boxed{V(r)\frac{\delta(r-r')}{r^2}} \sum_{lm} \bar{Y}_{lm}(\Omega) Y_{lm}(\Omega') = \boxed{V(r)\frac{\delta(\mathbf{r}-\mathbf{r}')}{r^2}}$ …local potential
  - Coulomb, atomic, …
  - same for all l
- $\langle \mathbf{r}|\hat{V}|\vec{\mathbf{r}}'\rangle = \sum_{lm} \bar{Y}_{lm}(\Omega) \boxed{V_l(r)\frac{\delta(r-r')}{r^2}} Y_{lm}(\Omega')$ …our semilocal pseudopotential

Solid etc. - $\langle \mathbf{r}|\hat{V}|\vec{\mathbf{r}}'\rangle = \sum_{\mathbf{R}_i} V_i(\mathbf{r}-\mathbf{R}_i, \mathbf{r}'-\mathbf{R}_i)$

…want reciprocal space representation $\langle \mathbf{G}|\hat{V}|\mathbf{G}'\rangle$ → form factor → like in atom

Need a finite infite sum over l! One could use

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

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

…note that one can choose an arbitrary $V^{loc}(r)$ but …

. . . semilocal pseudopotentials

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

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

$\Rightarrow$ high-l partial waves see mostly local potential

➥ allows to save projections by local component

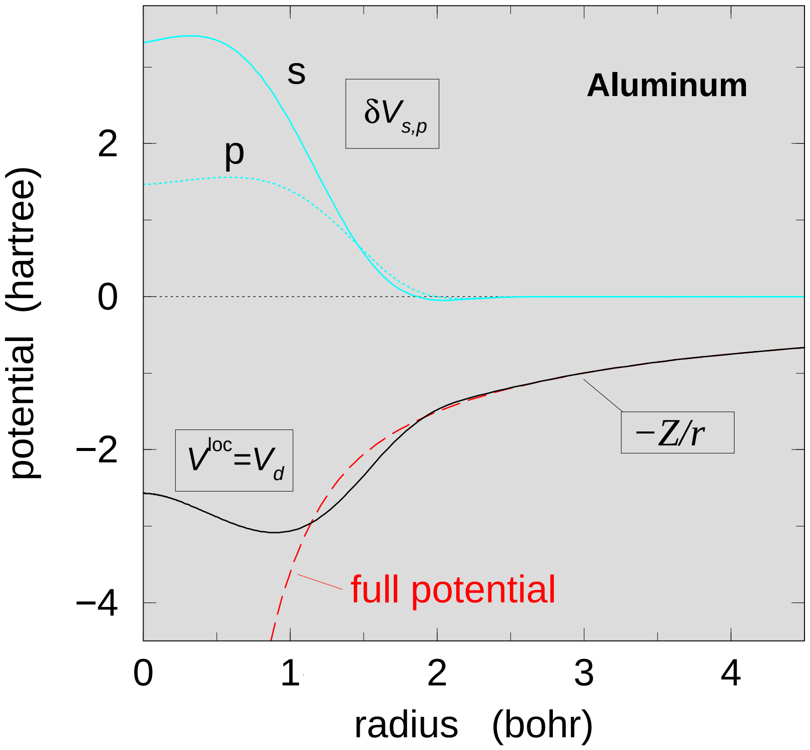
$$\boxed{V^{loc}(r) = V_{l_{loc}}(r) \text{ with } l_{loc} = l_{max}}$$

✓ $l \leq l_{max}$ see same $V_l(r)$ as before

▲ local potential ↔ scattering for $l > l_{max}$ (norm-conservation not imposed)

▲ transferability of separable representation

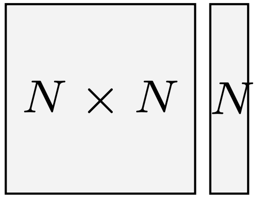
$$\boxed{\text{typically } l = 0, 1, 2, (3) \quad s, p, d, (f)}$$



Fully separable potentials

Semilocal potentials:

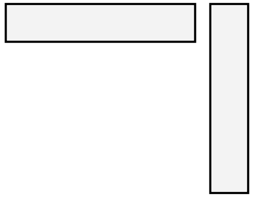
$$\langle \mathbf{G}|\delta\hat{V}_l|\mathbf{G}'\rangle \propto \int r^2 dr\, j_l(\underbrace{Gr)\delta V_l(r) j_l(G'}_{}r)$$



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

Separable potentials ↔ factorization:

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



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

- nonlocal, fully separable pseudopotential

$$\langle \mathbf{r}|\hat{V}|\mathbf{r}'\rangle = \langle \mathbf{r}|\hat{V}^{loc} + \delta\hat{V}^{NL}|\mathbf{r}'\rangle$$
$$= V^{loc}(r)\delta(\mathbf{r}-\mathbf{r}') + \sum_{lm}^{l_{max}} \langle \mathbf{r}|\chi_l lm\rangle E_l^{KB} \langle lm\chi_l|\mathbf{r}'\rangle$$

- separable Kleinman-Bylander pseudopotential
↔ transformation of semilocal $\delta\hat{V}_l = V_l - V_{loc}$

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

$$\delta\hat{V}^{NL} = |\chi_l\rangle E_l^{KB}\langle\chi_l|$$

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

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

- semilocal & nonlocal potential yield same (reference) valence states; also

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

⇒ KB-potentials norm-conserving !

- note: $|\tilde{\chi}_l\rangle = \epsilon_l - \hat{T}_l - \hat{V}^{loc}|u_l\rangle$ 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

➥ **unphysical states** above/below physical valence levels possible ⟶ "**ghost states**"

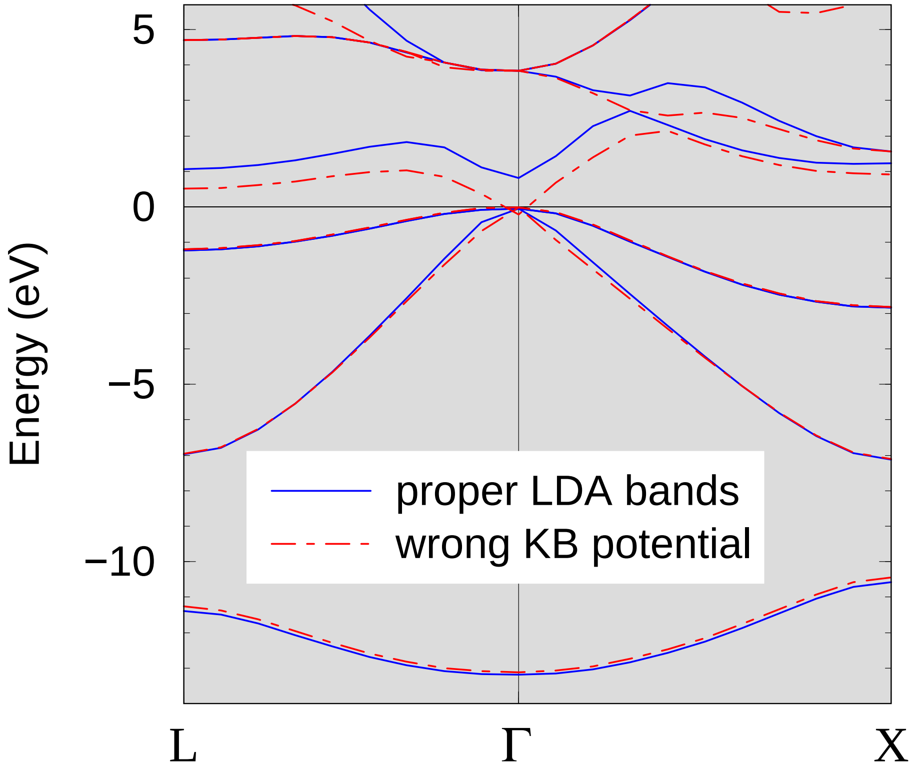
✾ **Ghost states** detectable in free atom …

- inspect logarithmic derivatives
- do analyze the atom's valence spectrum

… 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

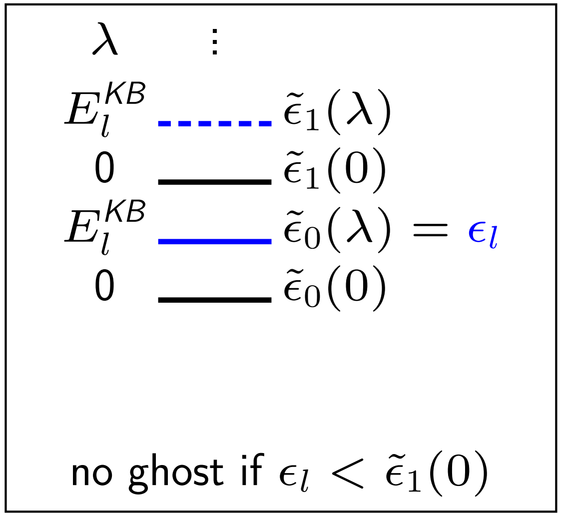


Analysis of the spectrum of nonlocal Hamiltonians $\hat{H}_l = \hat{T}_l + \hat{V}^{loc} + |\chi_l\rangle\lambda\langle\chi_l|$

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

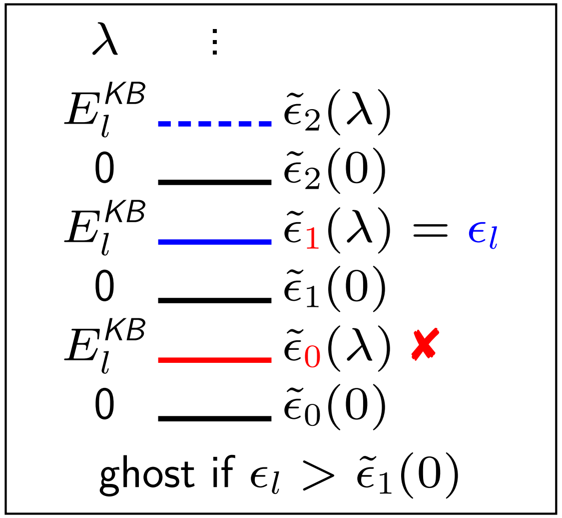
☞ can compare spectra for ☐ $\lambda = 0$ (local potential only) gives $\tilde{\epsilon}_i(0)$
☐ λ arbitrary (with nonlocal potential) gives $\tilde{\epsilon}_i(\lambda)$

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



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

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



λ $\vdots$
E_l^{KB} $\tilde{\epsilon}_2(\lambda)$
0 $\tilde{\epsilon}_2(0)$
E_l^{KB} $\tilde{\epsilon}_1(\lambda) = \epsilon_l$
0 $\tilde{\epsilon}_1(0)$
E_l^{KB} $\tilde{\epsilon}_0(\lambda)$ ✘
0 $\tilde{\epsilon}_0(0)$

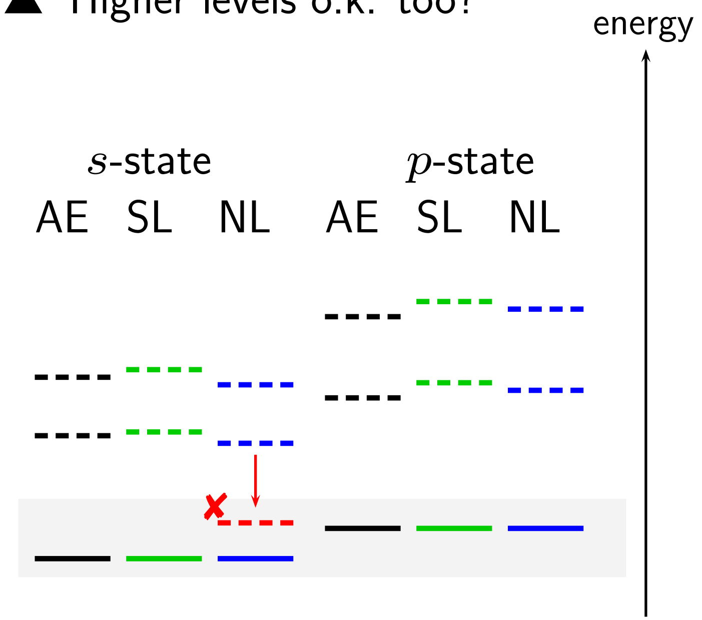
ghost if $\epsilon_l > \tilde{\epsilon}_1(0)$

➥ 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)

▲ Higher levels o.k. too?



✌ not told by ghost state criteria!
Instead diagonalize H_l
→ spectrum of bound states

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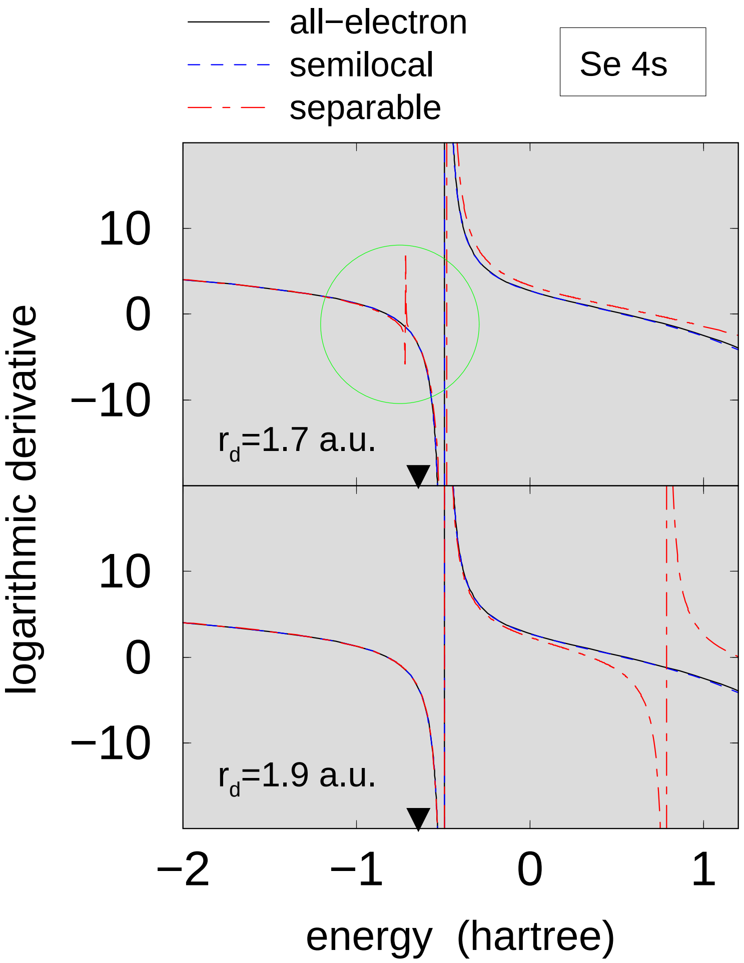
[1] Gonze, Stumpf, Scheffler, Phys Rev B 16, 8503 (1992)

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

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

"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 $\longrightarrow E_l^{KB} < 0$
use to s - or p-component !

➜ KB-potentials work well in practice

○ additional projectors in principle a cure too

Other forms of pseudopotentials

Motivation - an exact transformation between AE and PS wavefunctions is[1]

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

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

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

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

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

➥ Can make ansatz for *separable* pseudopotential with multiple projectors[2]

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

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

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

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

[2] Blöchl, Phys Rev B 41, 5414 (1990).

① $\boxed{\text{Norm-conserving:}}$

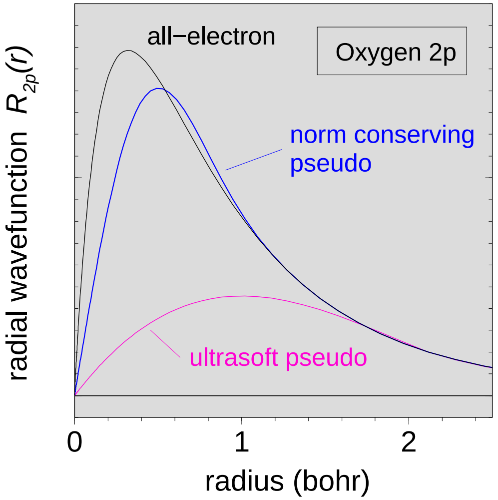
$$Q_{n\,n'} = \langle u^{AE}_{nl} | u^{AE}_{n'l} \rangle_{r^{core}} - \langle u_{nl} | u_{n'l} \rangle_{r^{core}} = 0$$

...several reference states possible!

② $\boxed{\text{“Quasi” norm-conserving:}}$

$$\langle u_{nl} | u_{n'l} \rangle_{r^{core}} + Q_{n\,n'} = \langle u^{AE}_{nl} | u^{AE}_{n'l} \rangle_{r^{core}}$$

➞ $\boxed{\text{Ultrasoft pseudopotentials}}$ [1]



➥ logarithmic derivative match as in norm-conserving case

➥ density & wavefunction ⟶ smooth part + augmentation

reduced plane-wave basis for 1^{st} row & d-metal elements

⟷ increase in projections, added complexity

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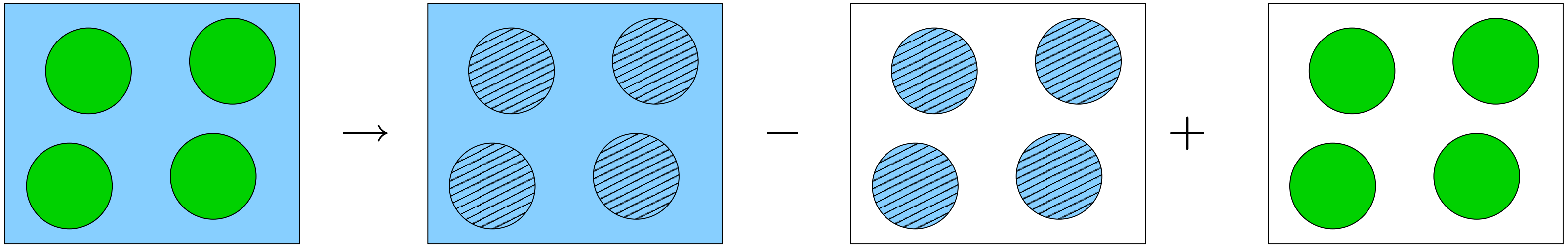
[1] Vanderbilt, Phys Rev B 41, 7892 (1990); Laasonen *et al*, Phys Rev B 47, 10142 (1993)

Outlook: pseudopotentials justified as approximations to PAW, an exact all-electron approach:



all-electron ⟶ pseudo valence − pseudo valence on site + all-electron on site

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)
  - **proper construction & testing** of the pseduopotential

✓ Transferability properties
  - logarithmic derivatives (scattering properties)
  - chemical hardness
  - plane-wave convergence

✓ Fully separable, nonlocal potentials
  - analysis & removal of ghost states
  - generalizations