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”
"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 $E_{\text{tot}}/\text{pair} \approx 10^5$ eV
  - $\hbar \omega_{\text{phonon}} \approx 30$ 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:

\[ \hat{T} + \hat{V}^{AE} \phi_i^{AE} = \epsilon_i \phi_i^{AE} \]

- choose atomic configuration, for some \( \epsilon < 0 \) integrate...

  **outward** \( r R^\text{out}(\epsilon; 0) = 0 \) \( \longrightarrow \) \( R^\text{out}(\epsilon; r) \mid r_\text{<} = 0 \ldots r^\text{match} \)

  **inward** \( R^\text{in}(\epsilon; \infty) = 0 \) \( \longrightarrow \) \( R^\text{in}(\epsilon; r) \mid r_\text{>} = \infty \ldots r^\text{match} \)

...outside classical turning point

- if logarithmic derivatives match ...iterate \( \epsilon \) 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 \( \hat{V}^{PS} \) giving the same logarithmic derivative for \( r \geq r^\text{match} \) gives the same eigenvalue as \( \hat{T}^{AE} \)

**Pseudopotential = exact transformation of full potential**

\[ \hat{T} + \hat{V}^{PS} \phi_i^{PS} = \epsilon_i \phi_i^{PS} \]

- \( r > r^\text{match} : \phi_i^{PS}(r) \propto \phi_i^{AE}(r) \) what normalization?
Solid - logarithmic derivatives $\leftrightarrow$ boundary conditions

core
\[ \phi_{\text{core}} \rightarrow \sum c_{lm} R_l(r) Y_{lm}(\Omega) \]

interstitial
\[ \phi_{\text{inter}} \rightarrow \sum c_{klm} \dot{R}_l(kr) Y_{lm}(\Omega) \]

\[ \frac{d}{dr} R_l(r) \bigg|_{r_{\text{core}}} = \frac{d}{dr} \phi_{\text{inter}}(r) \bigg|_{r_{\text{core}}} \]

...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:

\[ \int_{0}^{r_{\text{core}}} \phi_{\text{i}}^{AE} \left[ T + V^{AE} \right] \phi_{\text{i}}^{AE} d\tau \ll \epsilon_i \]

- the pseudopotential acts like\(^1\)
\[ \hat{V}^{PS} |\phi^{PS}\rangle = \hat{V}^{AE} |\phi^{PS}\rangle - \sum_{\text{core}} |\phi_c\rangle \langle \phi_c| \hat{V}^{AE} |\phi^{PS}\rangle \approx 0 \]

attractive repulsive, confined to core

...if there are core states with same angular momentum \( l \)

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 \( \approx \) AE eigenvalues \( \leftrightarrow \) band structure & one-particle energy \( \sum_i^{occ} \epsilon_i \)
  - electron density \( \leftrightarrow \) \( V^{\text{eff}}[n; \mathbf{r}] \) and total energy
- If we impose

\[
\phi_i^{PS}(\mathbf{r}) = \phi_i^{AE}(\mathbf{r}) \mid r > r^{\text{core}} 
\]

\( \Leftrightarrow \) proper electron density outside core

and norm conservation

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

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

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

... 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
Accuracy aspect: Frozen-core approximation

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

- Effect on 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 \(^1\)

- core regions of neighboring atoms do not overlap

- core/valence separation often intuitive: core \(\rightarrow\) all filled shells

*be aware:* 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 \( \phi_i^{AE}(r) = u_{\nu l}^{AE}(r) Y_{lm}(\Omega) \) ... central field

\[
\begin{bmatrix}
-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V^{AE}[n^{AE}; r] \\
\end{bmatrix}
\]
\[
\begin{align*}
u_{\nu l}^{AE}(r) &= \epsilon_{\nu l}^{AE} u_{\nu l}^{AE}(r), \\
n^{AE}(r) &= \sum_{occ} f_i \left| \phi_i^{AE}(r) \right|^2
\end{align*}
\]

△ Relativity: Dirac → scalar relativistic → non-relativistic

△ Full potential \( V^{AE}[n^{AE}; r] = -\frac{Z}{r} + V^{H}[n^{AE}; r] + V^{XC}[n^{AE}; r] \)

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

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

\[
\begin{bmatrix}
-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l^{scr}[n; r] \\
\end{bmatrix}
\]
\[
\begin{align*}u_l(r) &= \epsilon_l u_l(r), \\
n(r) &= \sum_{occ} f_i \left| \phi_i(r) \right|^2
\end{align*}
\]

... 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
  - → cutoff radii in each $l$
  - → (reference energy)
- (core-valence XC)
- local potential

**Program follows the recipe:**

nodeless radial pseudo wavefunctions satisfy conditions . . .

1. same valence energy levels $\epsilon_{l} = \epsilon_{l}^{AE}$ . . . center of VB’s
2. outside cutoff radius $r_{l}^{\text{cut}}$ orbitals match
   $$u_{l}(r > r_{l}^{\text{cut}}) = u_{l}^{AE}(r)$$
   . . . implies matching of logarithmic derivatives
3. norm-conservation
   $$\langle \phi_{l} | \phi_{l} \rangle = \langle \phi_{l}^{AE} | \phi_{l}^{AE} \rangle = 1$$

$+$ constraints for good plane-wave convergence

- pararametrize $u_{l}(r)$ and invert Schrödinger eq.
- unscreening with atom’s pseudo valence density → final ionic pseudopotentials for applications

\[
V_{l}^{\text{ion}}(r) = V_{l}^{\text{src}}(r) - V_{l}^{H}[n; r] - V_{l}^{XC}[n; r]
\]

\[\triangle \text{ ...different schemes around, e.g. Troullier-Martins:} \]

$u_{l}(r < r_{l}^{\text{cut}}) = r^{l+1}e^{c_{0}+c_{2}r^{2}+...+c_{12}r^{12}}$

$\Rightarrow$

- $\langle \phi_{l} | \phi_{l} \rangle = 1$
- $\frac{d^{n}}{dr^{n}} \left[ u_{l}(r) - u_{l}^{AE}(r) \right] |_{r_{l}^{\text{cut}}} = 0$, $n=0,1,\ldots,4$
- $\frac{d^{2}}{dr^{2}}V_{l}^{\text{scr}}(0) = 0$
Transferability

- compromise with needed smoothness
  - needed accuracy $\sim O(0.1 \ldots 0.01$ eV)
    - electronic structure
    - cohesive properties
    - atomic structure, relaxation, phonons
    - formation & 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

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

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

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

**Test:** Configurational changes (ΔSCF)

- s → 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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“Hardness tests” in practice

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

... 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

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

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

- **Pseudopotential** → linearized core-valence XC

\[ E^{XC} = E^{XC}[n^v] + \int n^v(r) \sum_\alpha \Delta V^{XC}[n^c_\alpha + n^v_\alpha; r] d\tau \]

\[ V^{PS, \alpha}_l(r) = V^{\text{scr, } \alpha}_l[n^c_\alpha; r] - V^H[n^c_\alpha; r] - V^{XC}[n^v_\alpha; r] \]

PP unscreening, consistent in LDA or GGA

- **Restoring nonlinear core-valence XC**

\[ E^{XC} = E^{XC}[n^v + n^c_{\{\alpha\}}] \]

\[ V^{PS, \alpha}_l(r) = V^{\text{scr, } \alpha}_l[n^c_\alpha; r] - V^H[n^v_\alpha; r] - V^{XC}[n^v_\alpha + n^c_\alpha; r] \]

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Partial core density for nlcv XC

Overlap matters only around core edge . . .

- can smoothen full core density inside the core

“partial core corrections”

\[ n^c_\alpha(r) \rightarrow \left[ 1 - g(r)\theta(r^{nlc} - r) \right] n^c_\alpha(r) \]

- 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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... 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

  ![Graph](image)

  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, ...)

  ![Graph](image)

  turning semi-core into valence states?
  - Zn 3d, Ca 3d, Rb 4p, ...
  - Ga 3d, In 4d in III-nitrides
    (but not GaP, GaAs, ...)

  ![Graph](image)

  ... a bit system dependent
... core-valence interactions

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

- o all-electron
- ■ pseudopotential

Need for nlcv XC in GGA?

Calculated vs. experimental lattice constants

- PW91 GGA
- LDA
- linearized CV XC
- nonlinear CV XC

>satisfactory only with cation 3, 4d states

Beware of frozen core approximation!
Plane-wave convergence – “smoothness”

Nearly free electrons & perturbed plane-waves: \( \psi_k(r) = e^{ikr} + \sum_G \frac{V^{PS}(G)}{(k+G)^2 - k^2} e^{i(k+G)r} \)

- for fast convergence reduce high Fourier components of \( \psi^{PS}(G) \) and \( \langle G|\hat{V}^{PS}|G'\rangle \)
  - modern norm-conserving schemes are good already \(^1\)
  - ... not perfect: “coreless” 2\(p\) & 3\(d\) states still somewhat hard

Choose right scheme & (dare to) increase cutoff radii

- 1\(^{st}\)-row & 3, 4, 5\(d\) elements Troullier-Martins scheme (flat potential for \( r \to 0 \))

- Al, Si, Ga(4d), As, ... Troullier-Martins & Hamann scheme, ... perform much alike

- loss in accuracy ⇔ upper bound for \( r_i^{cut} \)
  - poor scattering properties, ... → atomic transferability tests tell
  - artificial overlap with neighbor “cores” ... total energy error \( \Delta E \propto \int n(r)\Delta V(r) d\tau \),

N\(_2\) dimer: \( r_i^{cut} = 1.5 \) a.u., bondlength \( d/2 = 1.0 \) a.u. → binding energy error \( \mathcal{O}(0.1 \text{ eV}) \)

... may be acceptable

Plane-wave cutoff in practice

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

For the free pseudo atom:

\[
\Delta_l(G_{PW}) = \int_0^{G_{PW}} |u^P_l(G)|^2 \frac{G^2}{2} dG - \int_0^\infty \ldots
\]

... for s, p, d electrons

Corresponding total energy convergence error:

\[
\Delta E(G_{PW}) \approx \sum_{i} w_i \Delta_l(G_{PW})
\]

... 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 cohesive properties for \( \Delta_l \lesssim 0.1 \) eV
Form of pseudopotential operator in applications

Atom - radial & angular momentum representation

general but naive: \( \hat{V} = \sum_{lm, l'm'} |r'lm\rangle V_{\mu\mu'}(r, r') \langle r'l'm'| \) ... a projector, nonlocal in space

\[ \langle r | \hat{V} | r' \rangle = V(r) \frac{\delta(r-r')}{r^2} \sum_{lm} \bar{Y}_{lm}(\Omega) Y_{lm}(\Omega') = V(r) \frac{\delta(r-r')}{r^2} \] ... local potential

- Coulomb, atomic, ...
- same for all \( l \)

\[ \langle r | \hat{V} | r' \rangle = \sum_{lm} \bar{Y}_{lm}(\Omega) \bar{V}_{i}(r) \frac{\delta(r-r')}{r^2} Y_{lm}(\Omega') \] ... our semilocal pseudopotential

Solid etc. - \( \langle r | \hat{V} | r' \rangle = \sum_{R_i} V_i(r - R_i, r' - R_i) \)

... want reciprocal space representation \( \langle \mathbf{G} | \hat{V} | \mathbf{G}' \rangle \rightarrow \) form factor \( \rightarrow \) like in atom

Need a finite infinite sum over \( l \)! One could use

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

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

... note that one can choose an arbitrary \( V^{loc}(r) \) but ...
Truncation of \( l \)-sum for \( l > l_{\text{max}} \) natural:

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

\[ \Rightarrow \text{high-}l \text{ partial waves see mostly local potential} \]

\[ \nabla \text{allows to save projections by local component} \]

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

\[ \checkmark l \leq l_{\text{max}} \text{ see same } V_l(r) \text{ as before} \]

\[ \Delta \text{ local potential } \leftrightarrow \text{scattering for } l > l_{\text{max}} \]

\[ \text{(norm-conservation not imposed)} \]

\[ \Delta \text{ transferability of separable representation} \]

Typically \( l = 0, 1, 2, (3) \ s, p, d, (f) \)
Fully separable potentials

Semilocal potentials:
\[ \langle \mathbf{G} | \delta \hat{V}_l | \mathbf{G}' \rangle \propto \int r^2 dr j_i(Gr) \delta V_i(r) j_i(G'r) \]

- matrix multiplications
- \( N \times N \)
- \(N \approx O(10^3\ldots)\)
- size \( \approx O(10^6\ldots)\)

Separable potentials \( \leftrightarrow \) factorization:
\[ \rightarrow \left[ \int j_i(Gr) \chi_i(r) r^2 dr \right] \left[ \int \chi_i(r) j_i(G'r) r^2 dr \right] \]

- only scalar products
- size \( N \approx O(10^3\ldots)\)

- separable Kleinman-Bylander pseudopotential
- \( \leftrightarrow \) transformation of semilocal \( \delta \hat{V}_l = V_l - V_{loc} \)
\[ |\chi_i\rangle = \frac{|\delta V_i u_i\rangle}{\langle u_i | \delta V_i | u_i \rangle^{1/2}} \], \( \delta V_l^{NL} |\chi_i\rangle = E_l^{KB} |\chi_i\rangle \)
\[ \delta \hat{V}^{NL} = |\chi_i\rangle E_l^{KB} \langle \chi_i | \]

- KB-energy: strength of nonlocal vs. local part
\[ E_l^{KB} = \frac{\langle u_i | \delta V_i^2 | u_i \rangle^{1/2}}{\langle u_i | \chi_i \rangle} = \frac{\text{average}}{\text{KB-cosine}} \]

- semilocal & nonlocal potential yield same (reference) valence states; also
\[ \langle r | \delta \hat{V}_l^{NL} | u_i \rangle = \delta V_l(r) u_l(r) =: \langle r | \tilde{\chi}_i \rangle \]

\( \Rightarrow \) KB-potentials norm-conserving!

- note: \( |\tilde{\chi}_i\rangle = \epsilon_i - \hat{T}_l - \hat{V}_l^{loc} | u_i \rangle \) could be calculated directly from a chosen local potential
Kleinman-Bylander pseudopotentials at work

**Price:** full nonlocality $\rightarrow$ spectral order of states by radial nodes **not** guaranteed

- **unphysical states** above/below physical valence levels possible $\rightarrow$ “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

$$V_i(r) \rightarrow \{ \nabla V_{loc}(r), \delta V_i(r) \}$$

Example: KB-pseudopotential for As $\rightarrow$ ZB GaAs bandstructure
**Analysis** of the spectrum of nonlocal Hamiltonians $\hat{H}_l = \hat{T}_l + \hat{V}^{\text{loc}} + |\chi_l\rangle \lambda \langle \chi_l|$.

- $\lambda = E^{KB}_l$ gives the reference valence level $\epsilon_l$.
- Can compare spectra for:
  - $\lambda = 0$ (local potential only) gives $\tilde{\epsilon}_i(0)$.
  - $\lambda$ arbitrary (with nonlocal potential) gives $\tilde{\epsilon}_i(\lambda)$.
- For any $\lambda$, $E^{KB}_l > 0$, spectra ordered like $^1$.

<table>
<thead>
<tr>
<th>$\lambda$ :</th>
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<tbody>
<tr>
<td>$E^{KB}_l$</td>
<td>$E^{KB}_l$</td>
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<tr>
<td>$\tilde{\epsilon}_1(\lambda)$</td>
<td>$\tilde{\epsilon}_2(\lambda)$</td>
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<td>$\tilde{\epsilon}_1(0)$</td>
<td>$\tilde{\epsilon}_2(0)$</td>
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<td>$\tilde{\epsilon}_0(\lambda) = \epsilon_l$</td>
<td>$\tilde{\epsilon}_1(\lambda) = \epsilon_l$</td>
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<tr>
<td>$\tilde{\epsilon}_0(0)$</td>
<td>$\tilde{\epsilon}_1(0)$</td>
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- No ghost if $\epsilon_l < \tilde{\epsilon}_1(0)$.
- No ghost if $\epsilon_l < \tilde{\epsilon}_0(0)$.
- Ghost if $\epsilon_l > \tilde{\epsilon}_1(0)$.
- Ghost if $\epsilon_l > \tilde{\epsilon}_0(0)$.

- For $\lambda, E^{KB}_l < 0$ have $\tilde{\epsilon}_0(\lambda) < \tilde{\epsilon}_0(0) < \tilde{\epsilon}_1(\lambda)$... 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).

- Higher levels o.k. too?

- Not told by ghost state criteria! Instead diagonalize $H_l$ → spectrum of bound states.

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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 $|E_{KB}^l|$) can cause ghosts

“artificially:” $\approx$ zero denominator in $E_{KB}^l$ (KB-cos)
Ga, Ge, As, Se, ...
- vary cutoff radii of local/ nonlocal components

“intrinsically:” numerator of $E_{KB}^l$ large
Cu: deep $V_{3d}(r)$ $\Rightarrow$ $E_{KB}^l \gg 0$ to get 4s right
all 3,4,5d-metals: Cu, Pd, Ag, ...
- make local potential repulsive $\rightarrow E_{KB}^l < 0$
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\(^1\)

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

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

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

\[
\hat{O}^{PS} = \hat{T}^{\dagger} \hat{O} \hat{T}
\]

\[
= \hat{O} + \sum_{nn'} |\chi_i^{PS}\rangle \left\{ \langle R_n^{AE} | \hat{O} | R_{n'}^{AE} \rangle - \langle R_n^{PS} | \hat{O} | R_{n'}^{PS} \rangle \right\} \langle \chi_{n'}^{PS}|\n\]

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

\[\Rightarrow \text{Can make ansatz for separable pseudopotential with multiple projectors}^2\]

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

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

\[\ldots n = n' = 1 \text{ like Kleinman-Bylander pseudopotentials}\]

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1. Norm-conserving:
\[ Q_{nn'} = \langle u_{nl} | u_{n'l} \rangle_{r,\text{core}} = 0 \]
...several reference states possible!

2. “Quasi” norm-conserving:
\[ \langle u_{nl} | u_{n'l} \rangle_{r,\text{core}} + Q_{nn'} = \langle u_{nl}^{AE} | u_{n'l}^{AE} \rangle_{r,\text{core}} \]
→ Ultrasoft pseudopotentials

- logarithmic derivative match as in norm-conserving case
- density & wavefunction → smooth part + augmentation
  - reduced plane-wave basis for 1\textsuperscript{st} row & d-metal elements
  ↔ increase in projections, added complexity

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

![Diagram showing all-electron, pseudo valence, and on-site pseudo valence for Oxygen 2p](attachment:diagram.png)

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Summary

Pseudopotential \(=\) electron-ion interaction

- nucleus’ Coulomb attraction + core-valence interaction (orthogonality, electrostatic, XC)
- work throughout periodic table \(\ldots\) almost

✓ physically motivated approximation
- valence electrons rule chemical bonding
- frozen-core approximation \(\text{(depends on system)}\)
- cancellation of potential and kinetic energy in core

✓ well controlled
- norm-conservation \(\text{(built in)}\)
- nonlinear core-valence XC \(\text{(depends on system)}\)
- **proper construction & testing** of the pseudopotential

✓ Transferability properties
- logarithmic derivatives \(\text{(scattering properties)}\)
- chemical hardness
- plane-wave convergence

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