Pseudopotentials

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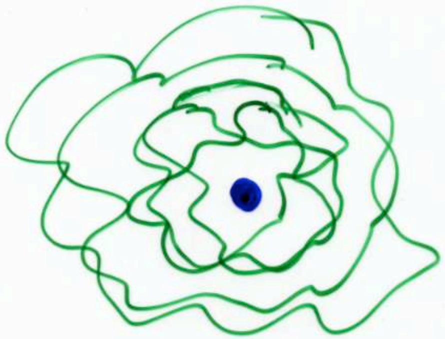
CECAM--Siesta Tutorial -- June 2007

- Atomic calculations using DFT



$$\left\{ -\nabla^2 + \underset{\displaystyle \downarrow \atop \displaystyle -\frac{Ze^2}{r}}{V_{nucleus}} + V_H + V_{xc} \right\} \psi_i = \varepsilon_i \psi_i$$

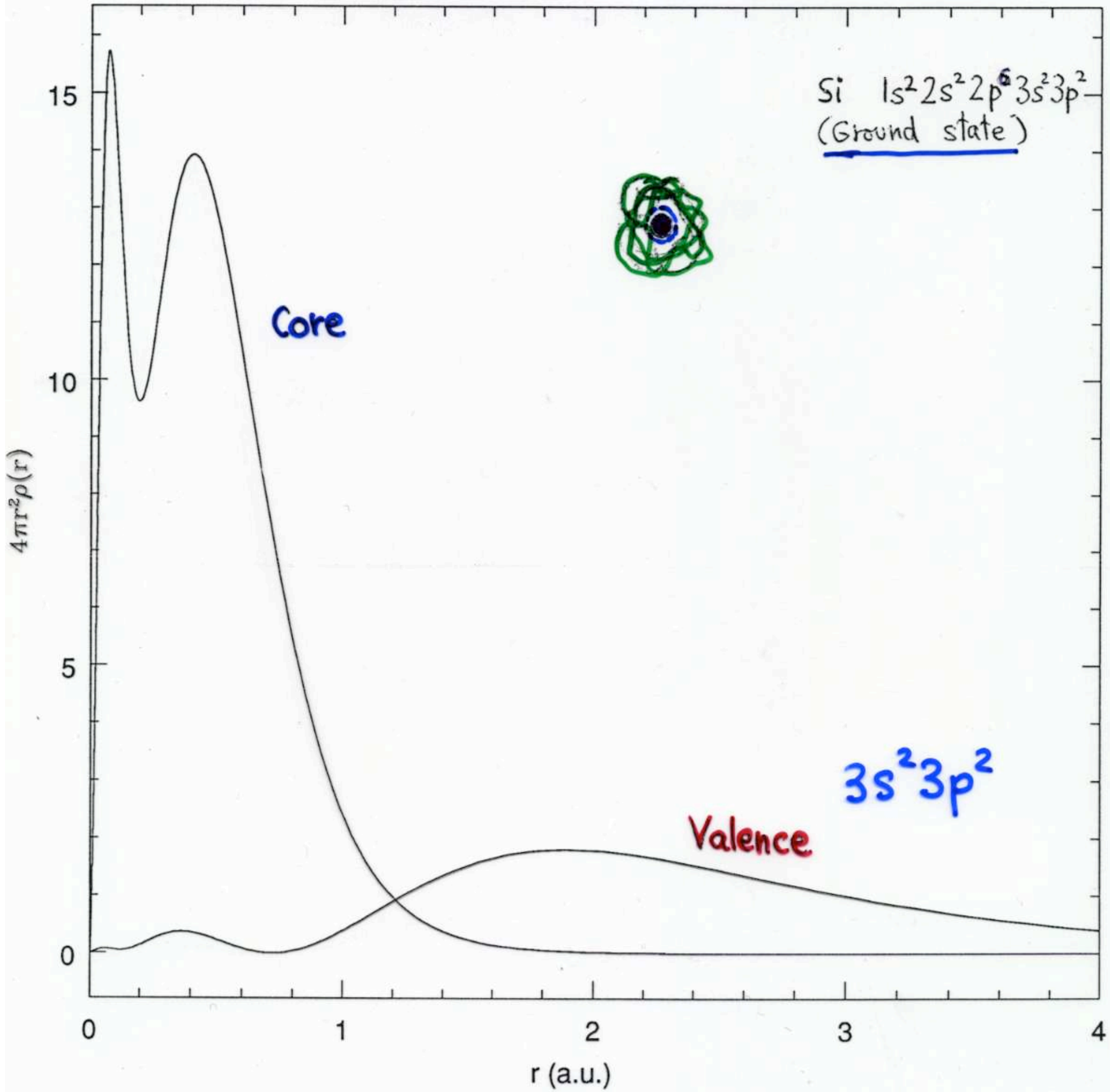
$$n_{el}(\vec{r}) = \sum_i |\psi_i|^2$$

- Example: Si

Ground state: $1s^2 2s^2 2p^6 3s^2 3p^2$

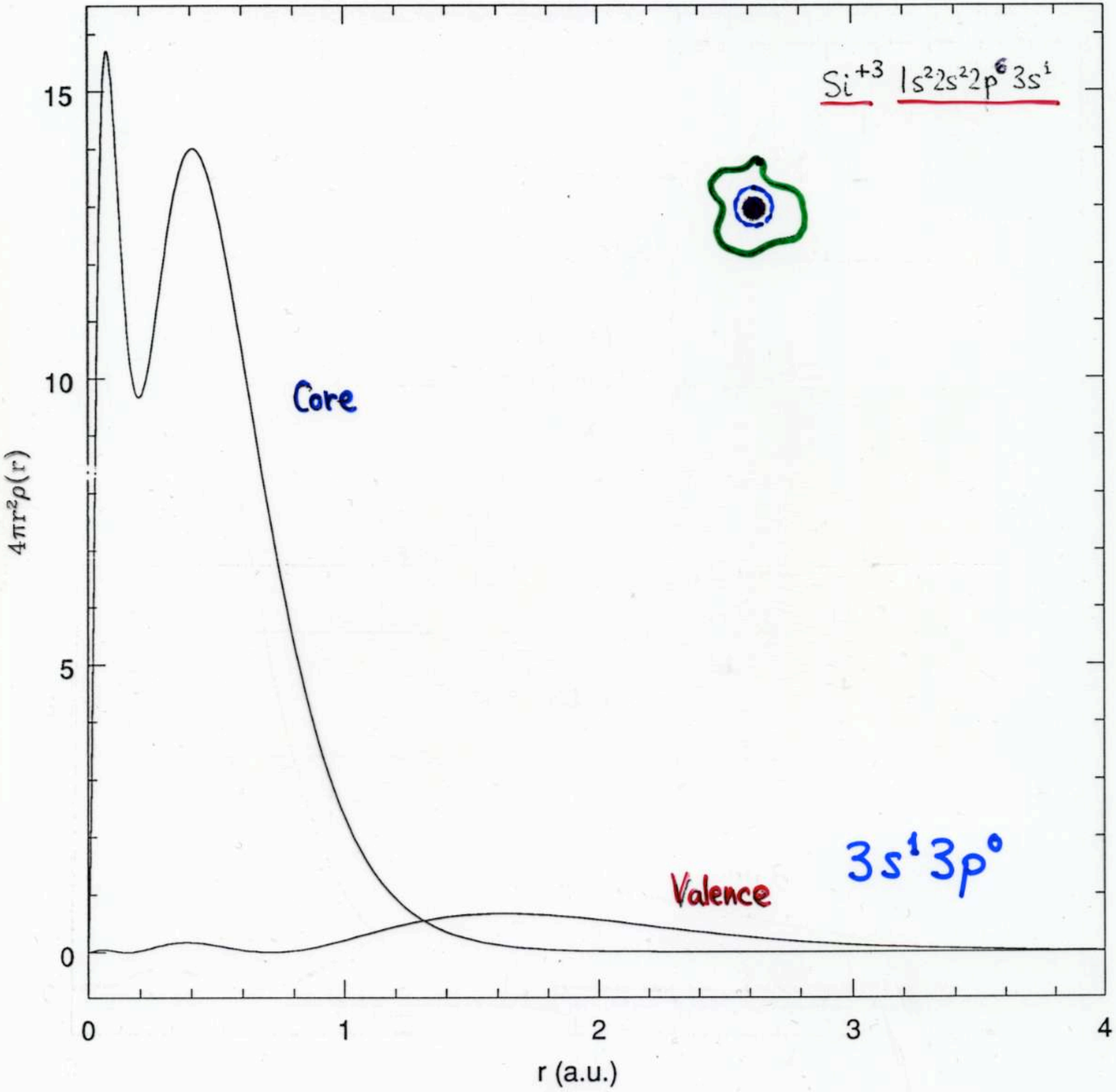
Charge density (Ground State)

$1s^2 2s^2 2p^6\ 3s^2 3p^2$



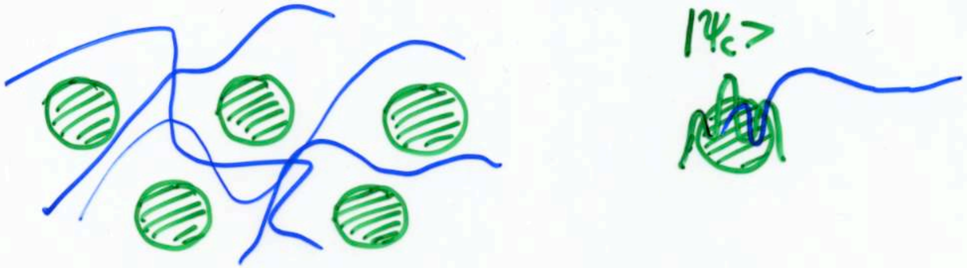
(triply ionized) $3s^1 3p^0$

Si^{+3} (triplemente ionizado)



- Core electrons are chemically inert
- Only the valence electrons are involved in bonding
- IDEA:
  - Ignore the dynamics of core electrons (freeze them)
  - Focus on the valence electrons and generate an effective potential for them

Orthogonalized plane-wave method (Herring, 1940)



Valence states: $|\vec{k}, \mathrm{OPW}\rangle = |\vec{k}\rangle - \sum_c |\psi_c\rangle\langle\psi_c|\vec{k}\rangle$

orthogonal to the core states $|\psi_c\rangle$

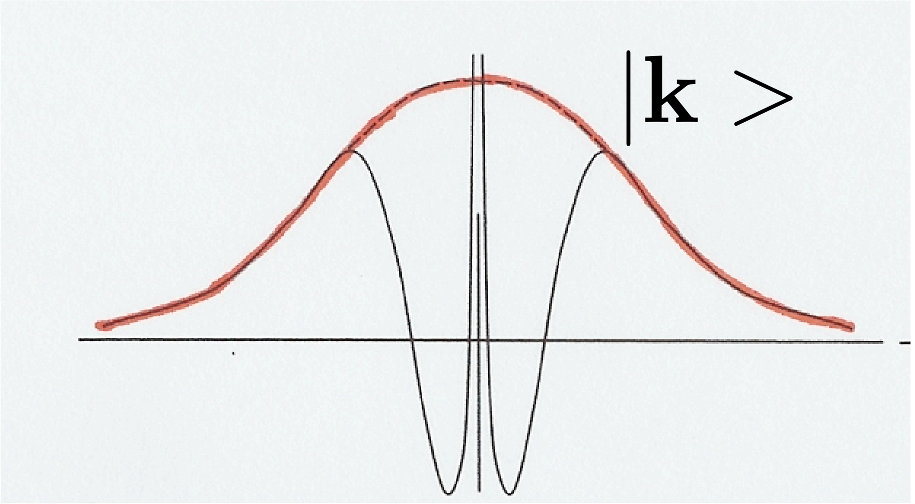
$\hat{H}|\mathrm{OPW}\rangle = \varepsilon|\mathrm{OPW}\rangle \Rightarrow$

$\Rightarrow (\hat{H} + \hat{V}_{\mathrm{Rep}})|\vec{k}\rangle = \varepsilon|\vec{k}\rangle$

where: $\hat{V}_{\mathrm{Rep}} = \sum_c (\varepsilon - \varepsilon_c)|\psi_c\rangle\langle\psi_c|$

is a repulsive potential

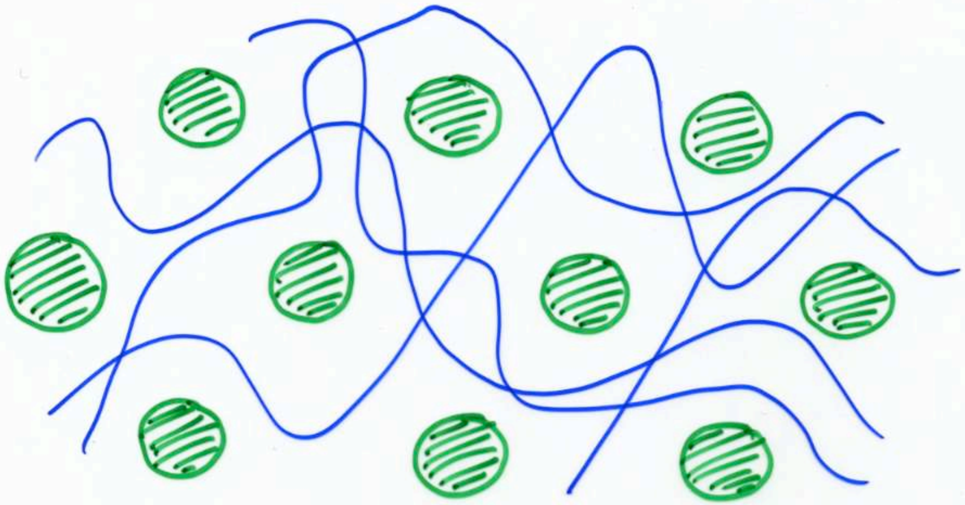
$\hat{H} = \hat{T} + \hat{V} \Rightarrow$ $\hat{V}_{\mathrm{eff}} = \hat{V} + \hat{V}_{\mathrm{Rep}}$ is a "soft" pseudopotential

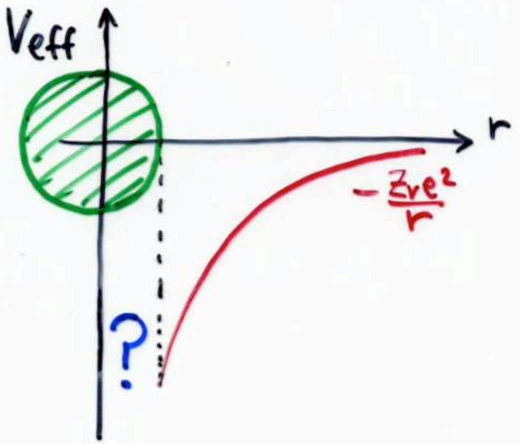


Phillips-Kleinman cancellation theorem

Common metal: Na

$\underbrace{1s^2 2s^2 2p^6}_{\text{core}} + \underset{\text{valence}}{3s^1}$



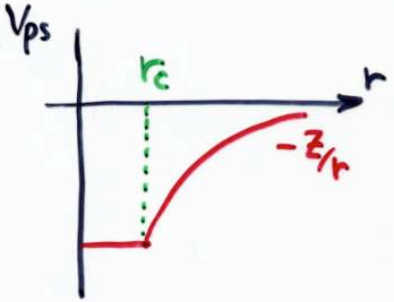


In the core zone, the effective potential will be softer than the coulomb $-\frac{Z_v e^2}{r}$ pot.

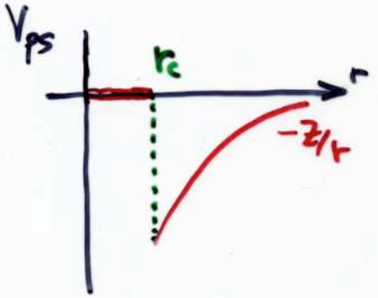
- Pseudopotential (pre) history

- Fermi (1934)

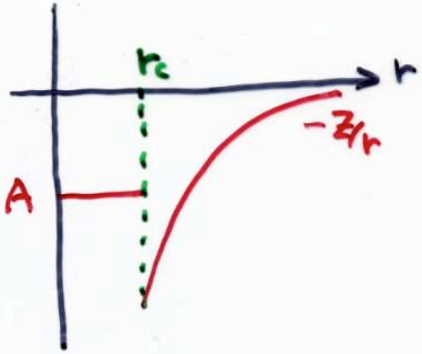
- Simple empirically-adjustable pseudopotentials



r_c adjusted to reproduce the valence eigenvalue



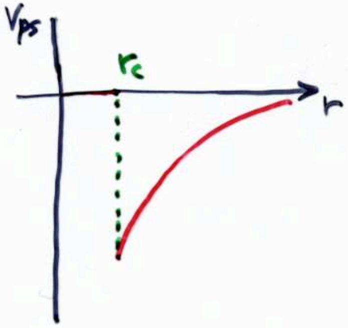
"Empty-core" pseudopotential
Ashcroft (1966)

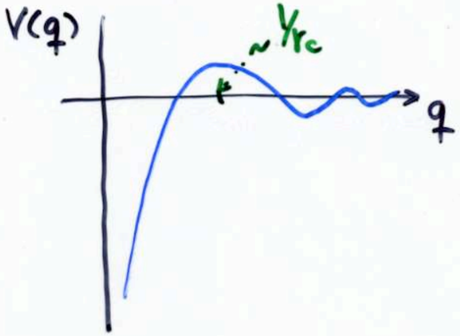


Heine - Abarenkov (~1964)

$A = A(\ell)$: angular-momentum-dependent

$A = A(E,\ell)$: energy-dependent





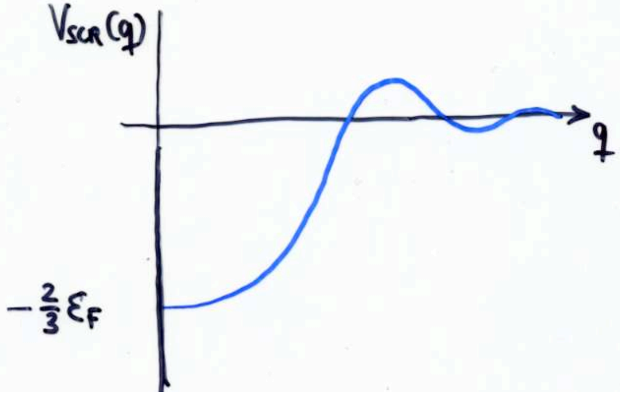
Fourier transform : $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

- Screening

$\frac{1}{r} \longrightarrow \frac{1}{r} e^{-K_{TF} \cdot r}$

K_{TF} : Thomas-Fermi wavevector

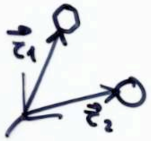
$$V_{scr}(q) = -\frac{4\pi e^2}{q^2 + K_{TF}^2} \cos q \cdot r_c$$



- In a periodic solid :

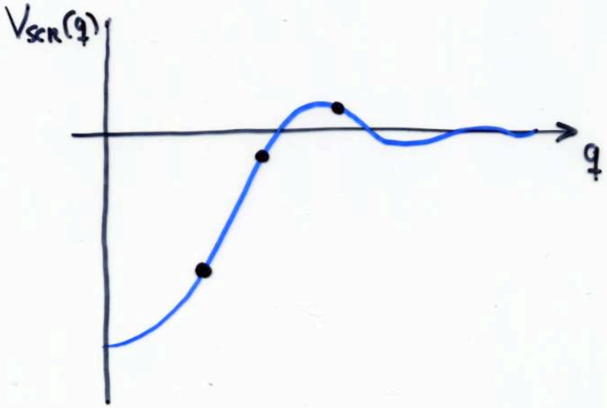
$$V(\vec{G}) = S(\vec{G}) \cdot V(q = |\vec{G}|)$$

$$S(\vec{G}) = \frac{1}{N_a} \sum_{\tau} e^{-i\vec{G}\cdot\vec{\tau}_i} \qquad \text{structure factor}$$



For highly symmetric structures, $S(\vec{G}) \neq 0$ for only relatively few $\vec{G}$'s

Diamond / Zinc Blende : $G^2 = 3, 8, 11, \ldots \quad (\times (\frac{2\pi}{a})^2)$



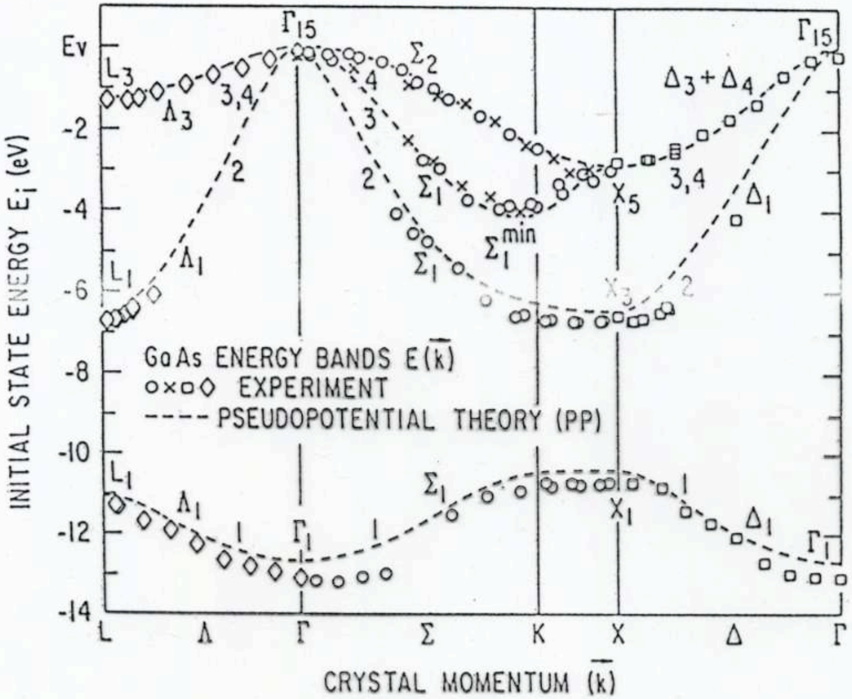
ONLY three parameters are needed for a reasonably good description

$$\{ -\nabla^2 + \underbrace{V_{ion} + V_H + V_{xc}}_{V_{eff}} \} \psi = \varepsilon \psi$$

$V_{eff}(G)$ fitted !

Empirical Pseudopotential Method (EPM)

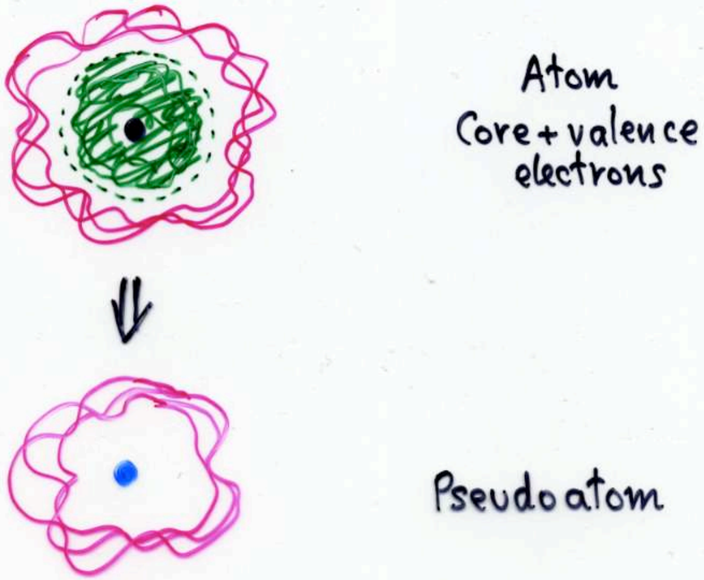
(Marvin L. Cohen et al. ~ 1962)

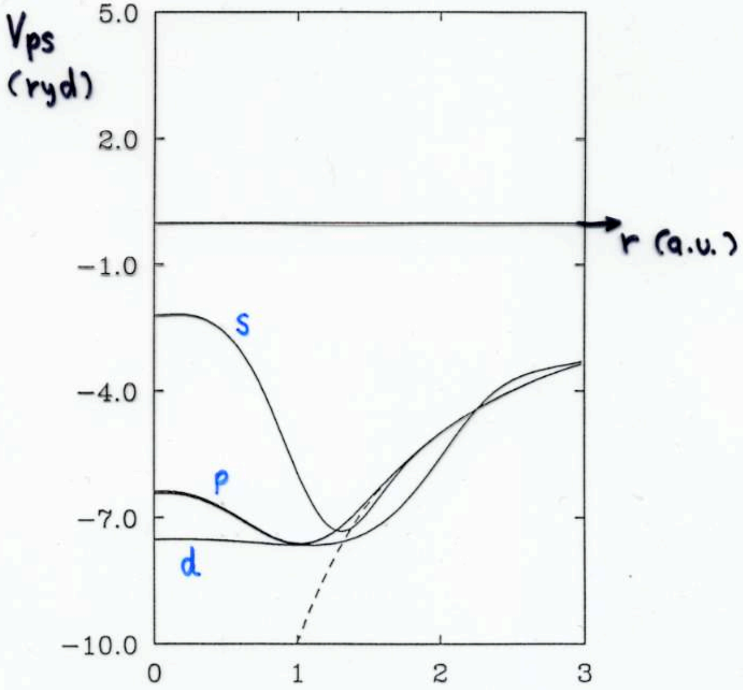


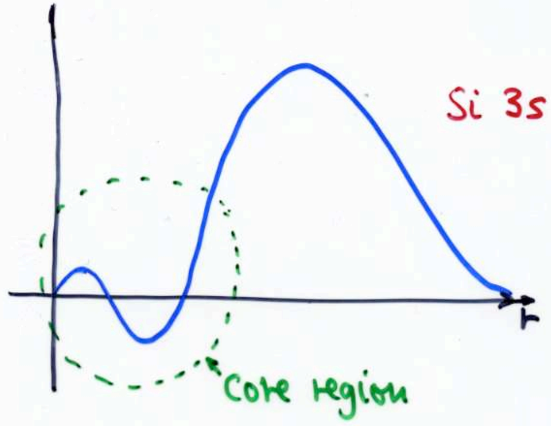
Band structure of GaAs

EPM needs a few experimental inputs
(absorption edge, reflectivity features...)
and provides the whole band structure

Ab-initio pseudopotentials



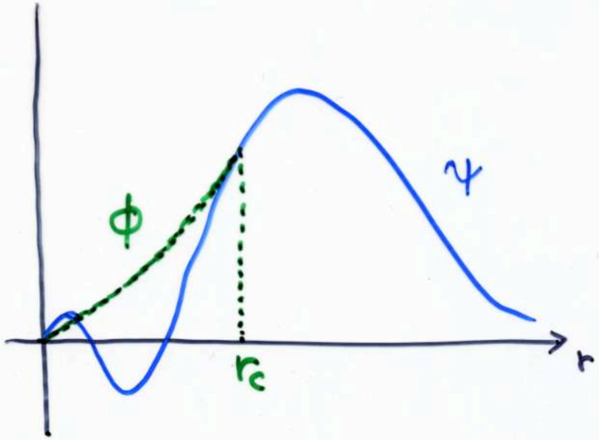




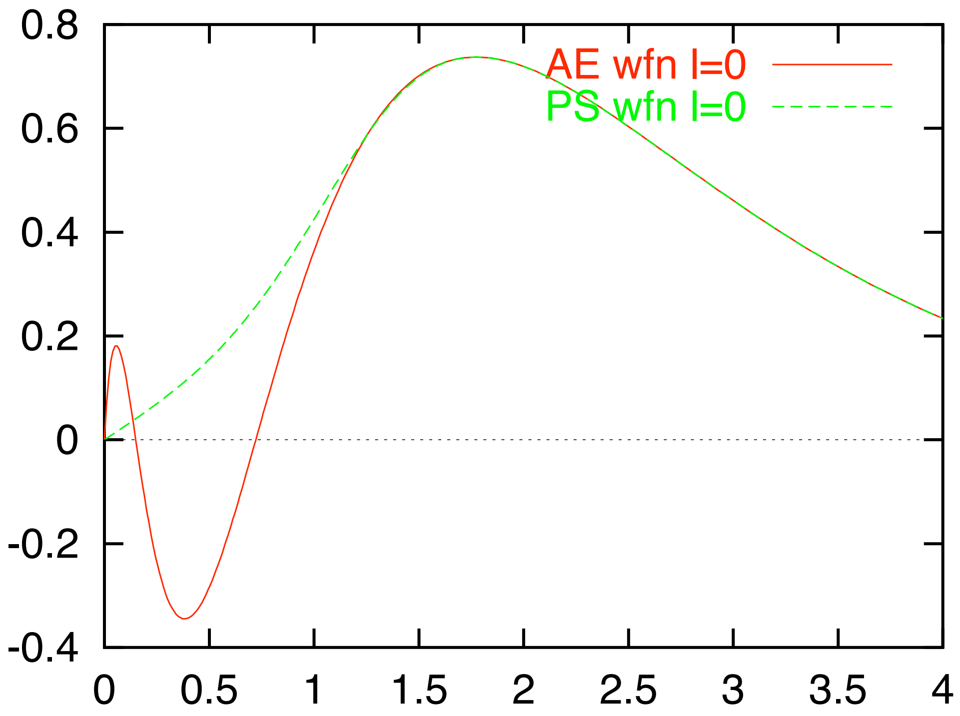
Si 3s orbital wfn.

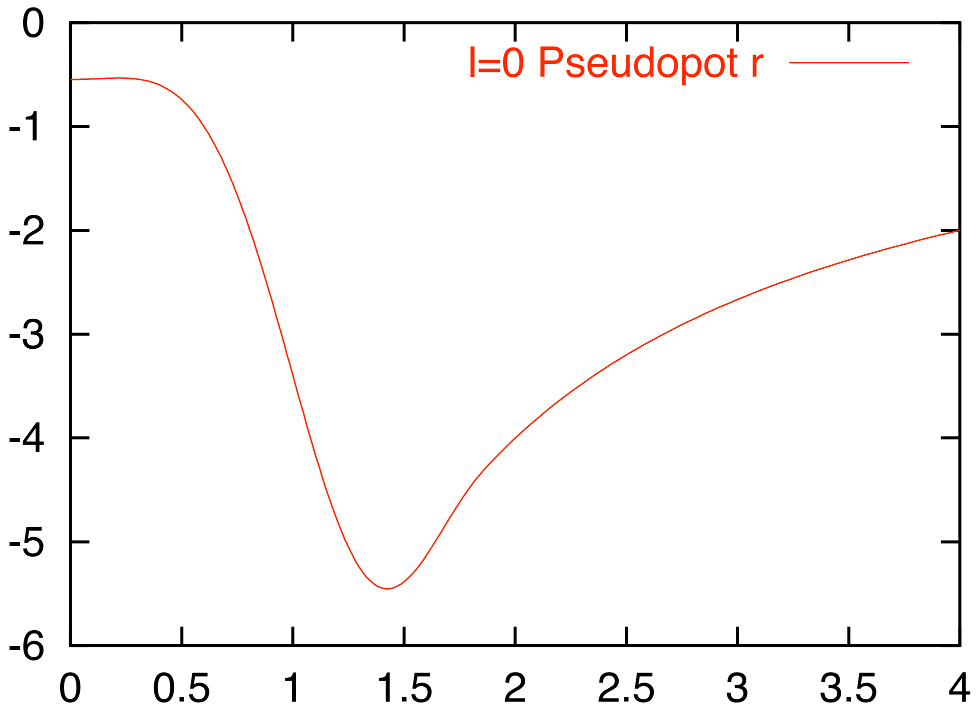
nodes : Imposed by orthogonality to the core states.

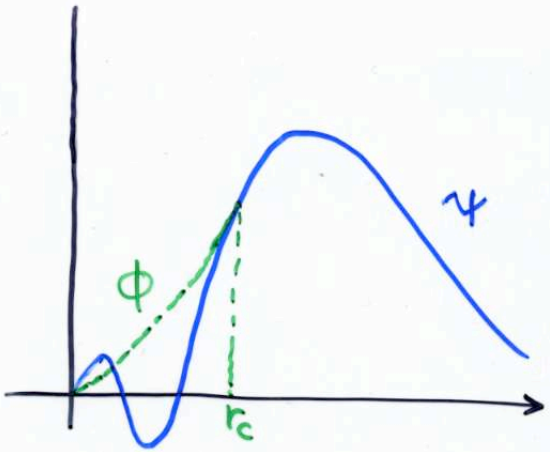
Idea: Eliminate the core electrons by "ironing out" the nodes:



Φ: Pseudowavefunction


AE wfn l=0
PS wfn l=0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4


l=0 Pseudopot r
0
-1
-2
-3
-4
-5
-6
0
0.5
1
1.5
2
2.5
3
3.5
4

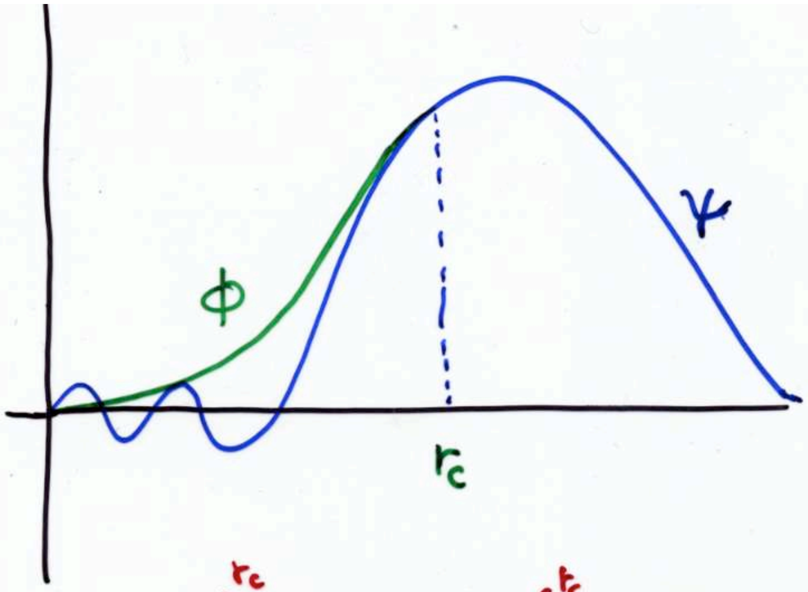


HOW does one get ϕ from Ψ ?

Essential steps:

- Pick r_c (typically between the last node and the maximum)
- Match ϕ and Ψ at or near r_c.
- Conserve the norm:

$$\int |\phi|^2 dV = \int |\Psi|^2 dV$$



$$\int_0^{r_c} |\phi|^2 r^2\, dr = \int_0^{r_c} |\psi|^2 r^2\, dr$$

Norm – conservation

- Preserves electrostatic potential outside r_c

- $$\frac{d}{d\varepsilon}\left(\frac{d}{dr} \ln (r\phi) \right)\Bigg|_R \propto \frac{1}{(r\phi)^2} \int_0^R (r\phi)^2\, dr$$

Preserves scattering properties
(and their first energy derivative)

$$\left\{-\nabla^2 + \hat{V}_{AE}\right\}\psi = \varepsilon\psi$$

$$\hat{V}_{AE} = V_{nuc}(r) + V_H^{[n]}(r) + V_{xc}^{[n]}(r)$$

$$\left\{-\nabla^2 + \hat{V}_{ps}^{[n]}\right\}\phi = \varepsilon\phi$$

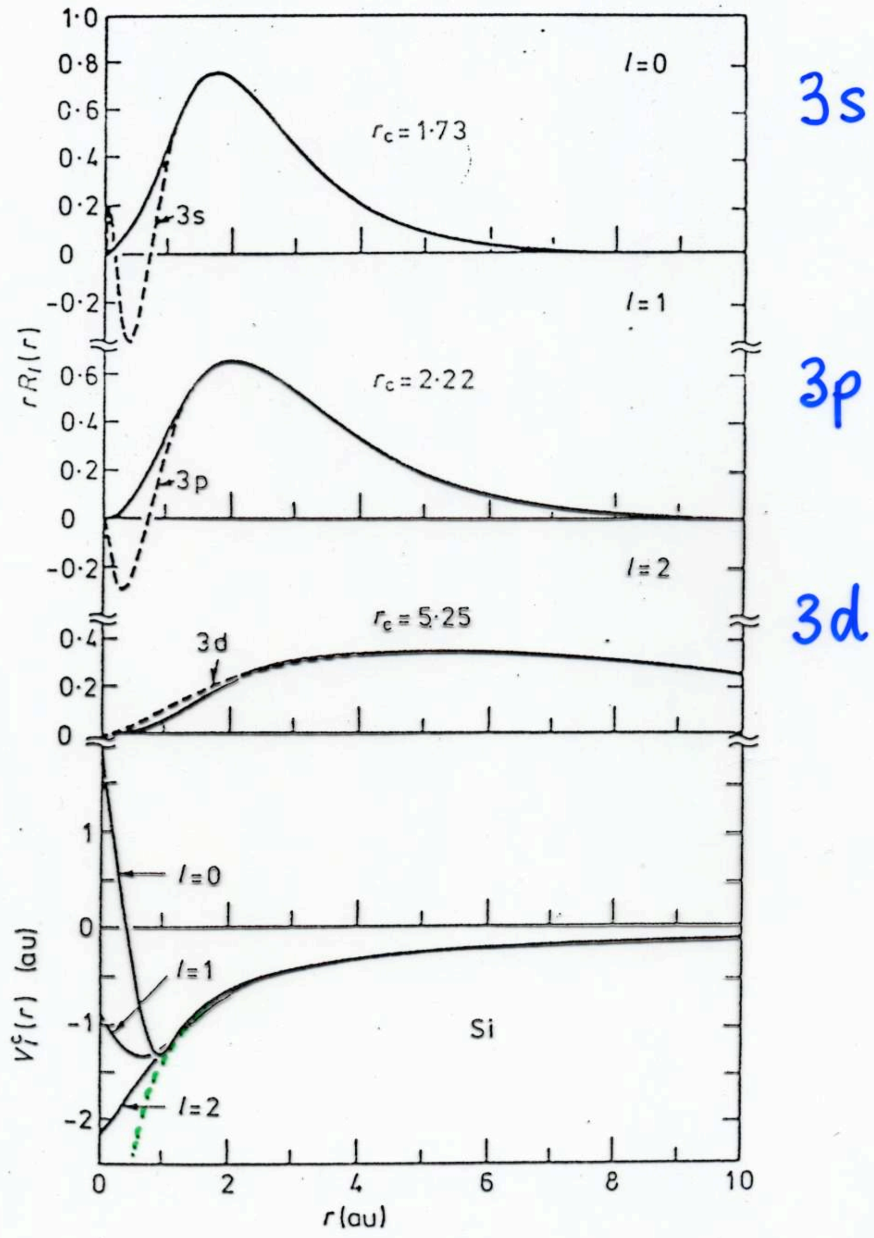
$\hat{V}_{ps}^{[n]}$: Screened pseudopotential

$$V_{ps}^{[n]} = \varepsilon + \frac{1}{\phi}\nabla^2\phi$$

"Bare" or ionic pseudopotential:

$$V_{ps}(r) = V_{ps}^{[n]} - V_H^{[n]} - V_{xc}^{[n]}$$

n: Valence charge density

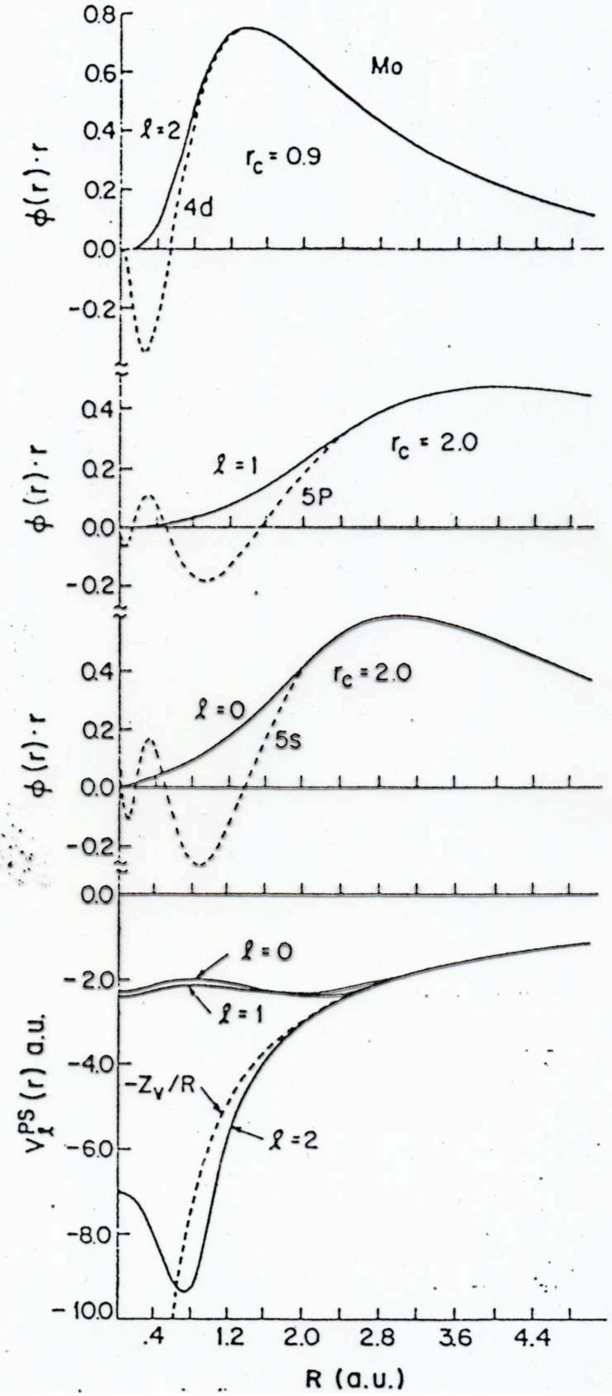


Si pseudopotential

(Kerker Method)

Mo pseudopotential

(Hamann - Schlüter - Chiang)



4d

5p

5s

Semi-local form:

$$\hat{V}_{ps} = \sum_{\ell} V_{\ell}(r) \underbrace{|\ell\rangle\langle\ell|}_{\text{Projector for } \ell}$$

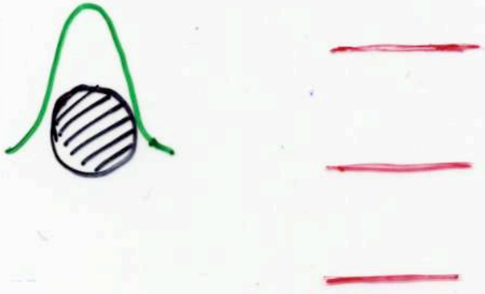
$$= V_{LOCAL}(r) + \sum_{\ell} \underbrace{\Delta V_{\ell}(r)}_{\text{Short ranged}} |\ell\rangle\langle\ell|$$

Kleinman-Bylander form:

$$\hat{V}_{ps} = V_{LOCAL}(r) + \sum_{\ell m} \frac{|\Delta V_{\ell}\,\phi_{\ell m}\rangle\langle\phi_{\ell m}\,\Delta V_{\ell}|}{\langle\phi_{\ell m}|\Delta V_{\ell}|\phi_{\ell m}\rangle}$$

(Fully non-local form)

Isolated atom

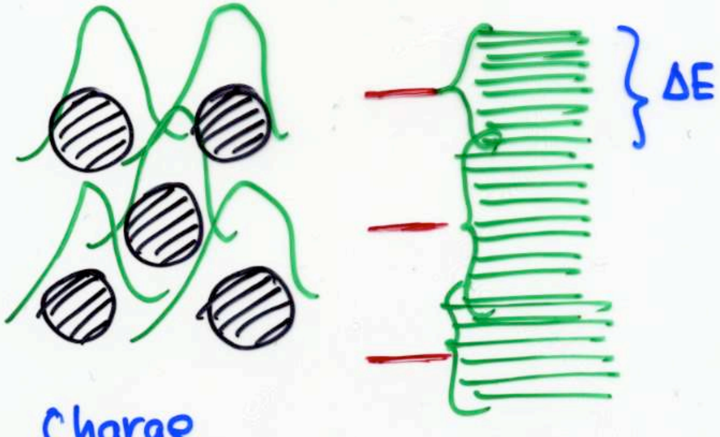


Atomic eigenvalues

V_{ps} "perfect"

TRANSFERABILITY

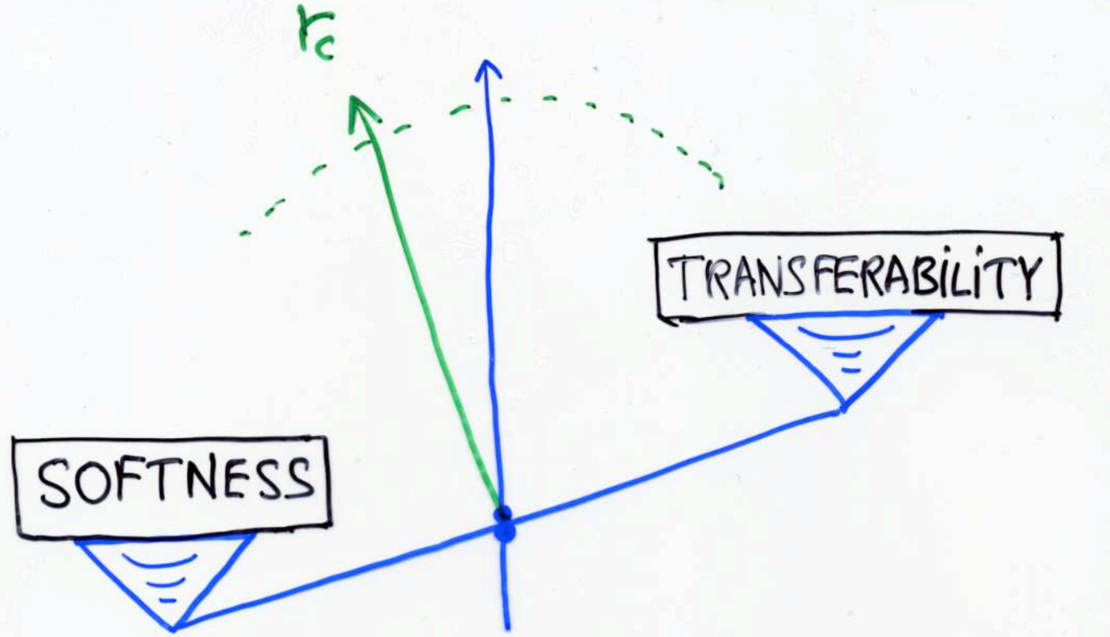
Solid



Bands

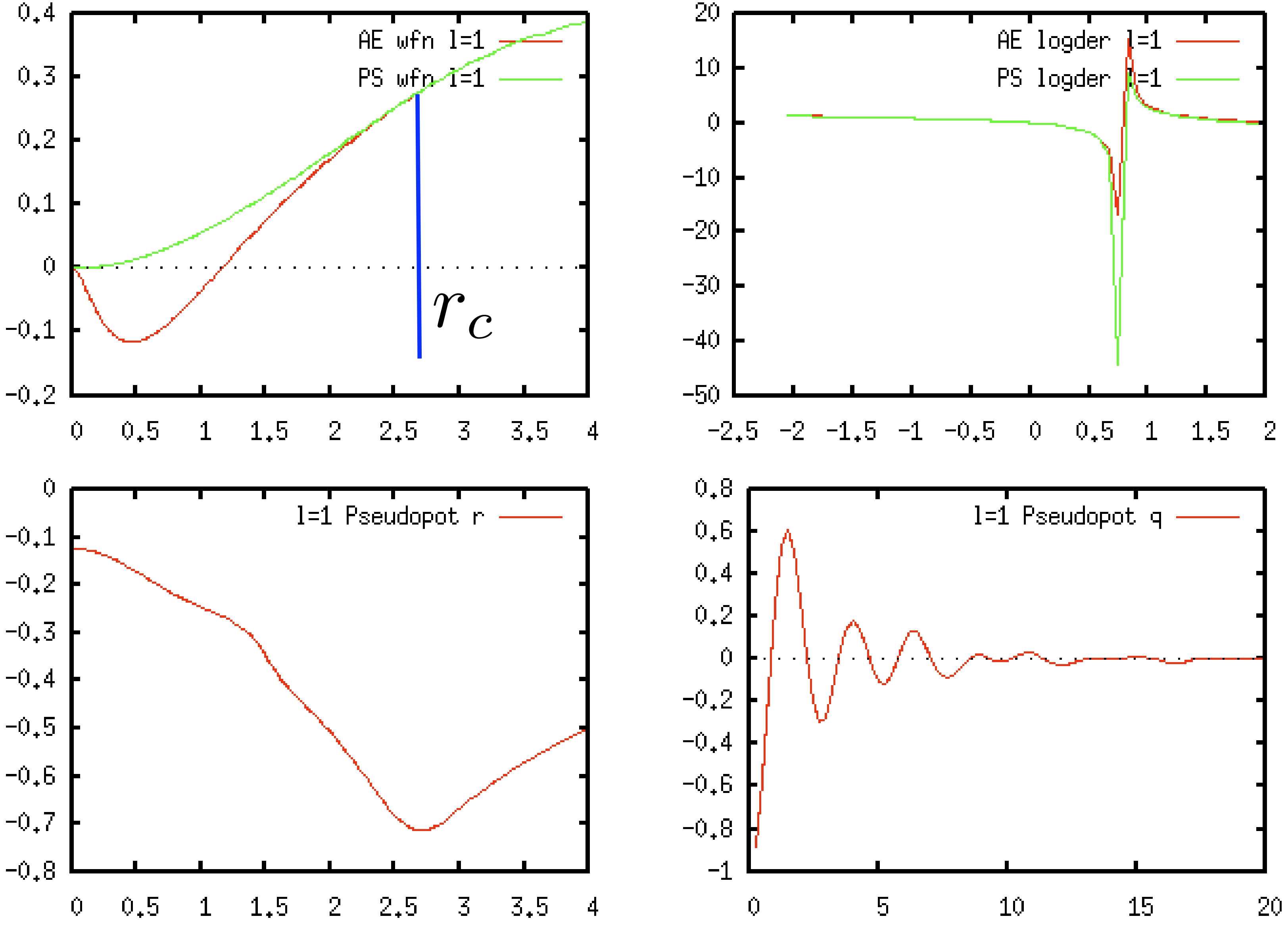
V_{ps} ?

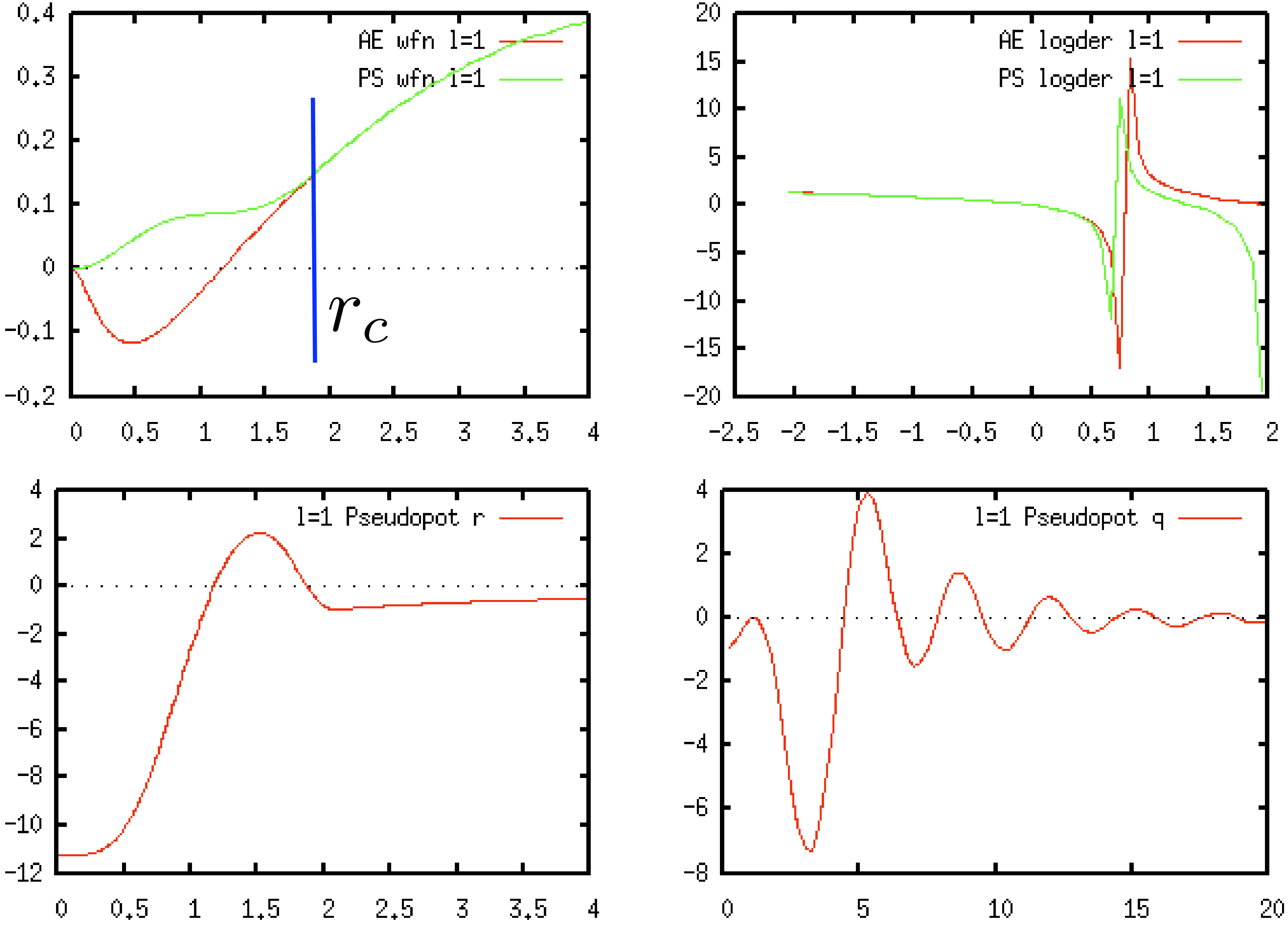
Charge
Transfer...



Essential Tradeoff

Transferability: Accuracy in varying environments
Softness: Representability by a reasonably small set of plane waves.


AE wfn l=1
PS wfn l=1
r_c
0.4
0.3
0.2
0.1
0
-0.1
-0.2
0
0.5
1
1.5
2
2.5
3
3.5
4
AE logder l=1
PS logder l=1
20
10
0
-10
-20
-30
-40
-50
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
l=1 Pseudopot r
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
0
0.5
1
1.5
2
2.5
3
3.5
4
l=1 Pseudopot q
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
5
10
15
20


AE wfn l=1
PS wfn l=1
r_c
0.4
0.3
0.2
0.1
0
-0.1
-0.2
0
0.5
1
1.5
2
2.5
3
3.5
4
AE logder l=1
PS logder l=1
20
15
10
5
0
-5
-10
-15
-20
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
l=1 Pseudopot r
4
2
0
-2
-4
-6
-8
-10
-12
0
0.5
1
1.5
2
2.5
3
3.5
4
l=1 Pseudopot q
4
2
0
-2
-4
-6
-8
0
5
10
15
20

Transferability Tests

The pseudopotential should:

- Reproduce eigenvalues
- Reproduce tails of wavefunctions

for configurations OTHER than the construction configuration

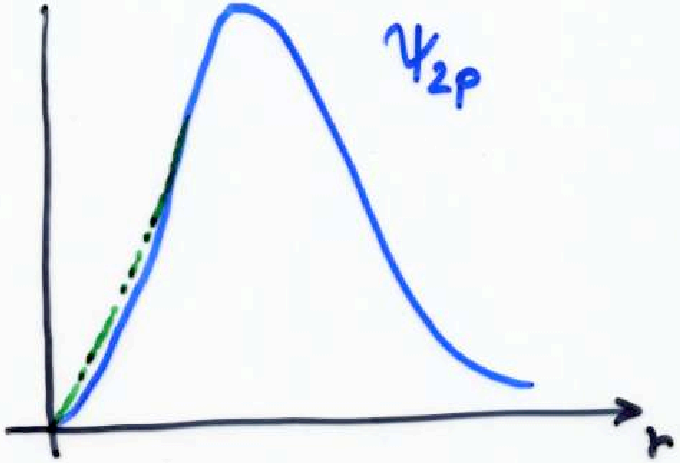
It should reproduce also excitation energies among different configurations

```
&d total energy differences in series
&d          1        2        3        4        5
&d  1    0.0000
&d  2    0.4308   0.0000
&d  3    0.4961   0.0653   0.0000
&d  4    0.9613   0.5305   0.4652   0.0000
&d  5    1.4997   1.0689   1.0036   0.5384   0.0000

                                 GS 3s2 3p2
                                 3s2 3p1 3d1
                                 3s1 3p3
                                 3s1 3p2 3d1
                                 3s0 3p3 3d1

&d          1        2        3        4        5
&d  1    0.0000
&d  2    0.4299   0.0000
&d  3    0.4993   0.0694   0.0000
&d  4    0.9635   0.5336   0.4642   0.0000
&d  5    1.5044   1.0745   1.0051   0.5409   0.0000
```

Problematic cases

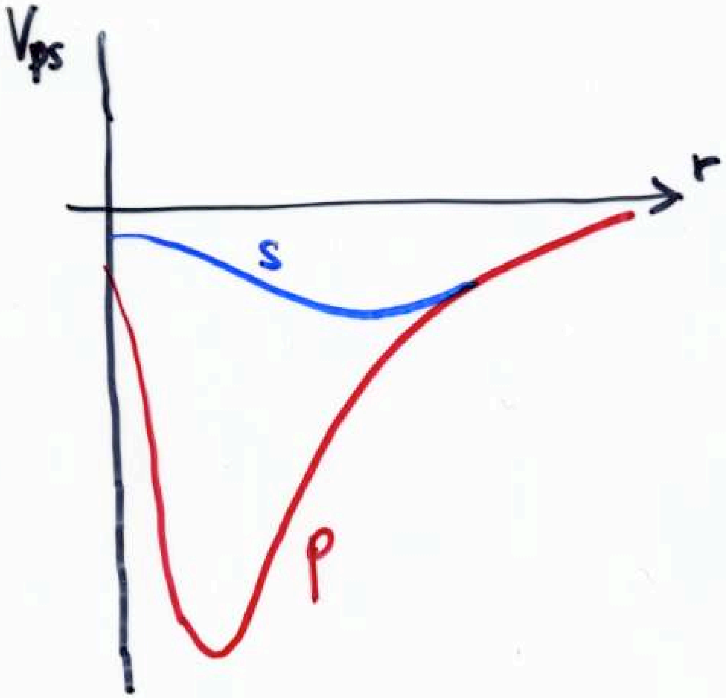
- First-row elements

Example: Oxygen: O: $1s^2 2s^2 2p^4$



There are no nodes because there are no p core states to be orthogonal to.

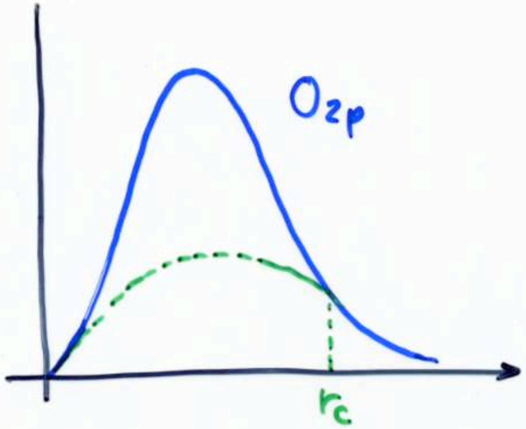
The resulting pseudopotential is hard :



The absence of inner p-states has very important consequences for chemistry (s-p hybridization)

- Pseudopotentials without norm-conservation (Vanderbilt, 1990)

(Ultrasoft)



- large r_c
- Several reference energies for each angular momentum channel

- The "missing charge/norm" needs to be accounted for in the solid-state calculation

- They allow the use of much smaller energy cutoffs in the plane-wave basis

- Can deal with several instances of the same angular momentum (Zn: 3d and 4d)