

Pseudopotential Approximation

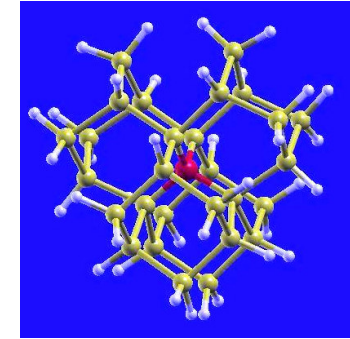
The concept of *Pseudopotential* (PP).

How to construct a PP (FHI98pp code)

The semilocal and separable (*Kleinman-Bylander*)
form of a PP.

Different PP description for Spectroscopies:
the problem of using pseudopotentials for
excited state calculations

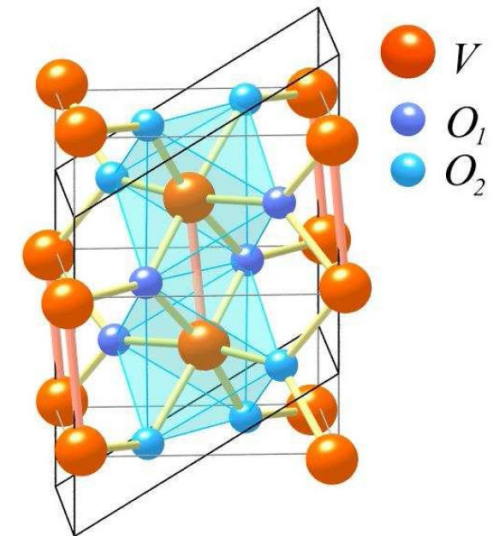
The Kohn-Sham equations:



$$\left(\frac{-\hbar^2}{2m} \nabla^2 + v_H + v_{xc} + v_{ext} \right) \phi_i(r) = \epsilon_i \phi_i(r)$$



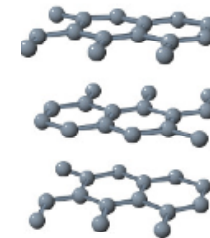
PP approach



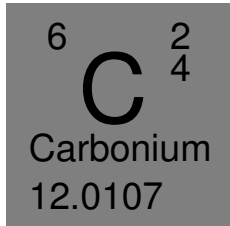
external
potential
QuickTime™ and a
decompressor
needed to see this picture.



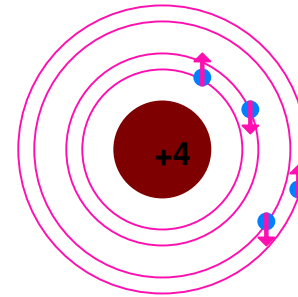
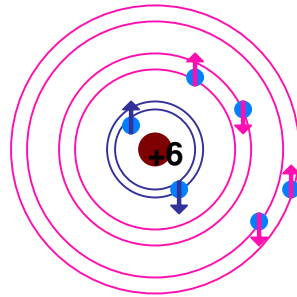
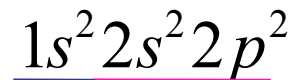
external
potential
QuickTime™ and a
decompressor
needed to see this picture.



We want to simulate a carbon system:



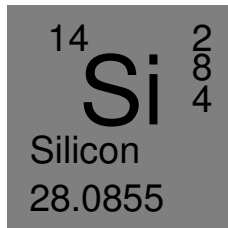
only valence electrons are responsible for bonding in solids



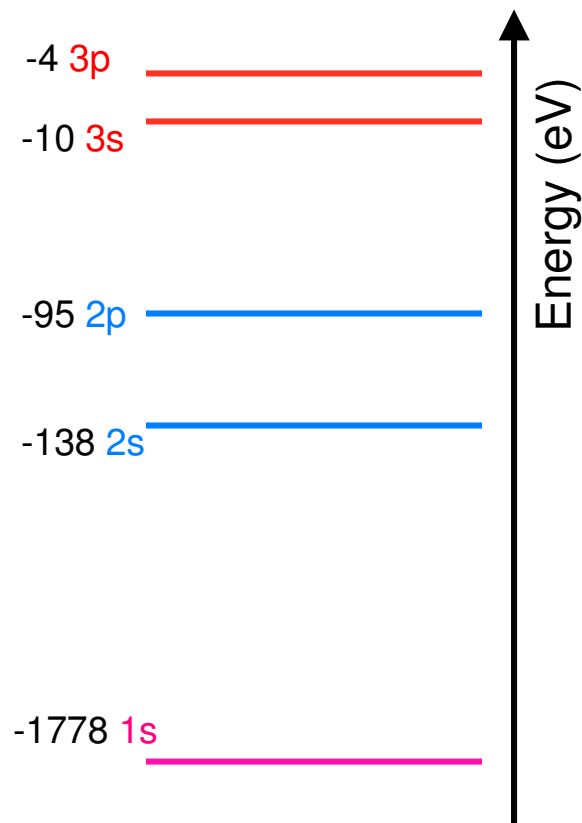
pseudo ATOME:

EFFECTIVE IONIC CORE + VALENCE ELECTRONS

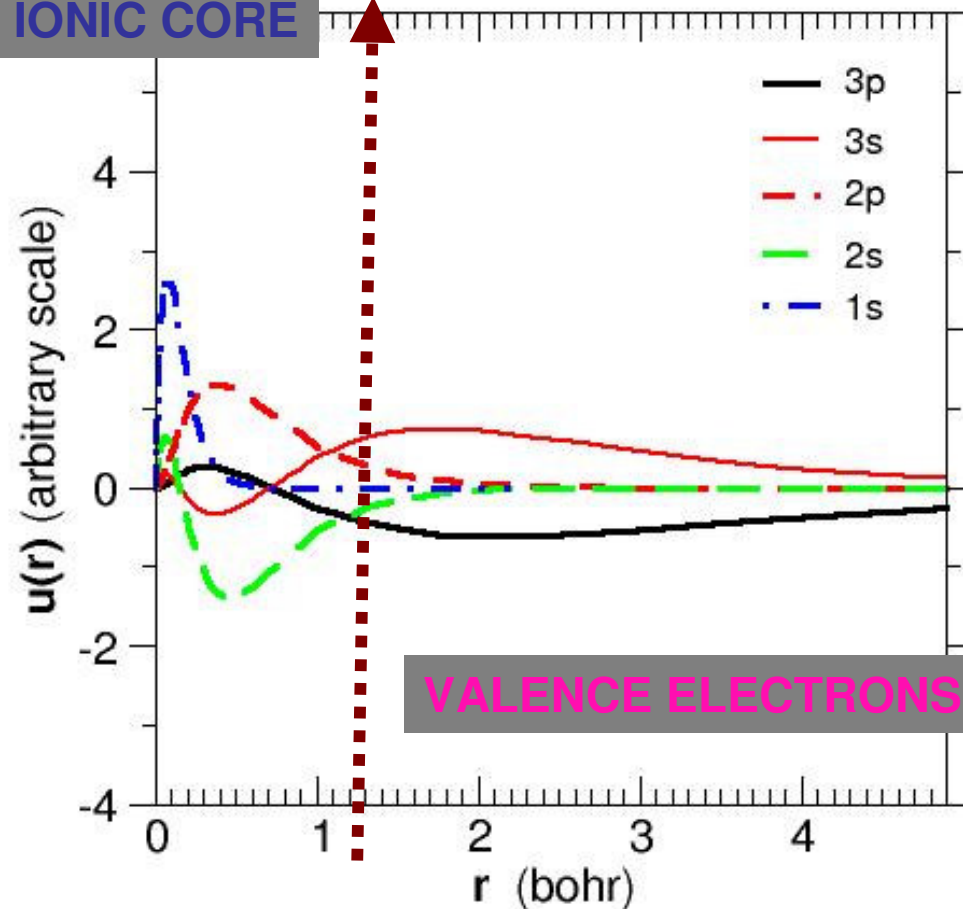
Silicon atom: all-electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$



All-electron wavefunctions: different spatial localization



EFFECTIVE IONIC CORE



How to generate a norm-conserving pseudopotential

The choice of a pseudopotential
is not unique:
*lots of freedom to construct a
computationally
efficient pseudopotential*

FH198pp code

M. Fuchs, M. Scheffler, Comput. Phys. Commun. 119, 67-98 (1999),
"Ab initio pseudopotentials for electronic structure calculations of poly-atomic
systems" using density-functional theory"

Pseudopotential generation

- 1) Atomic all-electron calculation in a reference configuration

$$\phi_i(r) = \frac{u_{n_i l_i}(r)}{r} Y_{l_i m_i}$$

$$\left[\frac{1}{2} \left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} \right) + V^{xc}[n] + V^H[n] - \frac{Z}{r} \right] u_{n_i l_i} = \epsilon_i u_{n_i l_i}$$

- 2) Screened norm-conserving pseudopotential

$$\phi_i^{PS}(r) = \frac{u_{l_i}(r)}{r} Y_{l_i m_i}$$

$$\left[\frac{1}{2} \left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} \right) + V_{l_i}^{PS,scr}(r) \right] u_{l_i}^{PS} = \epsilon_i^{PS} u_{l_i}^{PS}$$

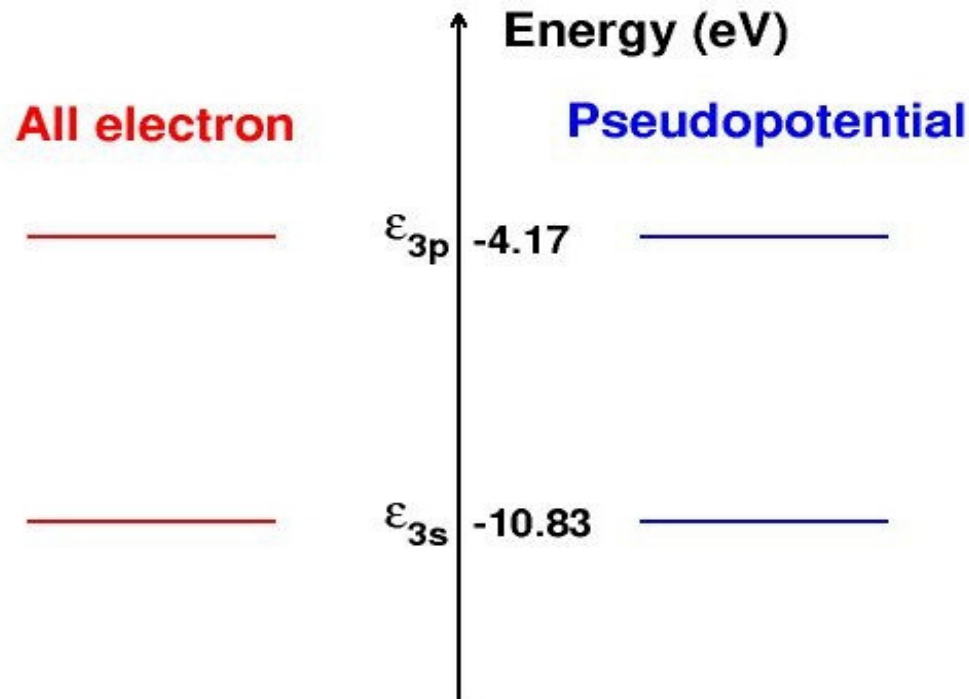
Inversion of the radial KS equation

Hamann

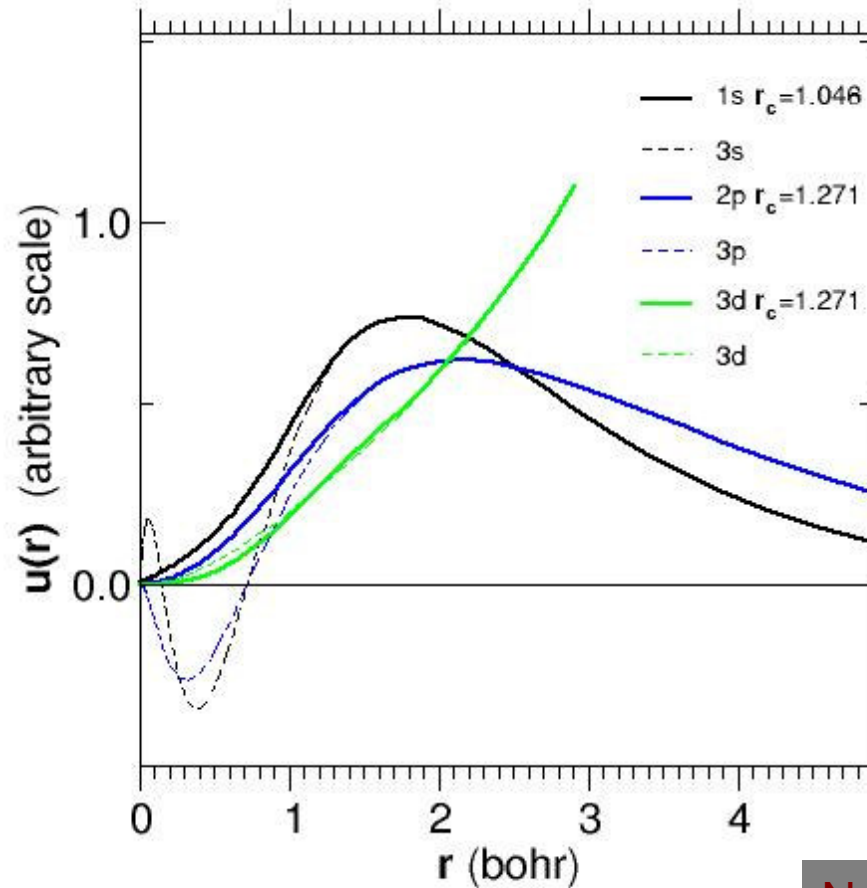
Martins-Trouiller

$$\mathcal{U}_l^{PS}$$

- A) The pseudo wavefunction contains no radial nodes.
- B) The pseudo wavefunction and all electron wavefunction corresponds to the same eigenvalue for a fixed l



C) The radial pseudo wavefunction and the all-electron wavefunction agree beyond a cutoff radius (r_c)



Norm conservation constraint

$$\int_0^{r'_c} \left| u_l^{PS}(\epsilon_l^{PS}; r) \right|^2 dr = \int_0^{r'_c} \left| u_{nl}(\epsilon_{nl}; r) \right|^2 dr \quad r'_c \leq r_l^c$$

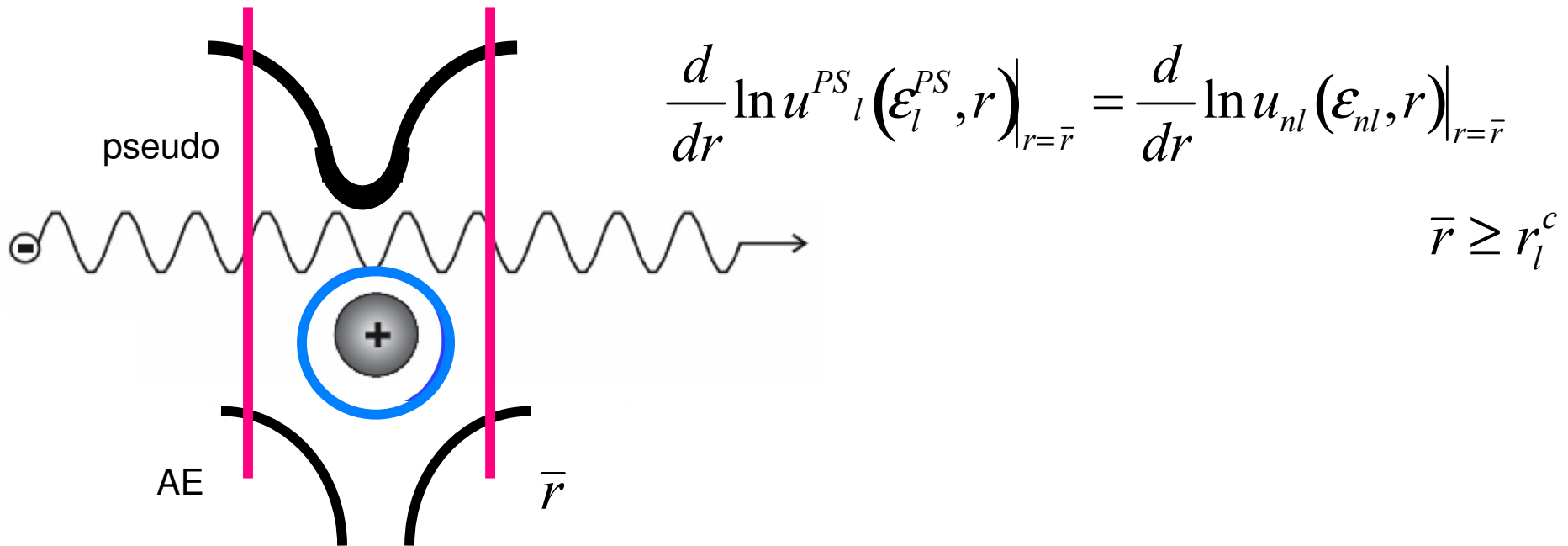
D) Logarithmic derivatives agrees beyond the r_c :

scattering properties

$$D_l(\epsilon, \bar{r}) = \left. \frac{d}{dr} \ln u_l(\epsilon_l, r) \right|_{r=\bar{r}}$$

Why LD ?

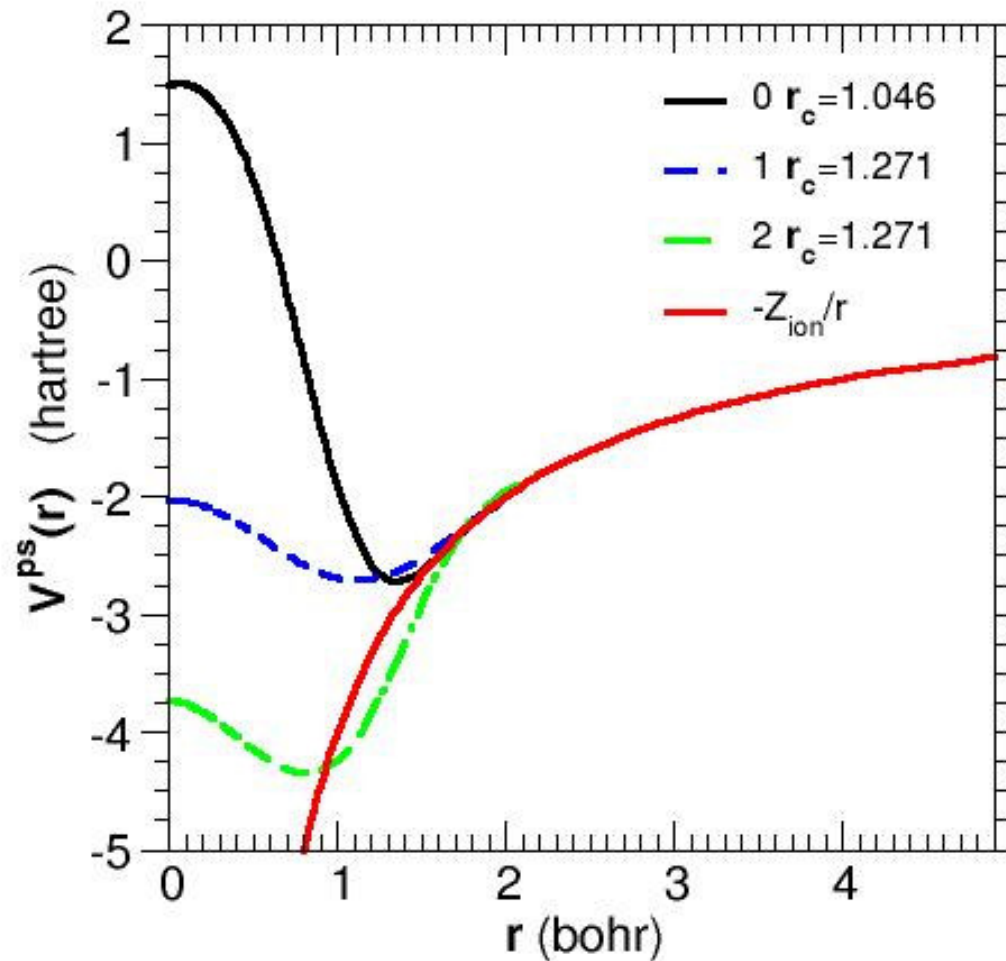
The logarithmic derivatives is a quantity which is related with the scattering properties of a system, so the idea is that the pseudopotential (if good) has to reproduce the same all-electron scattering properties for that system.



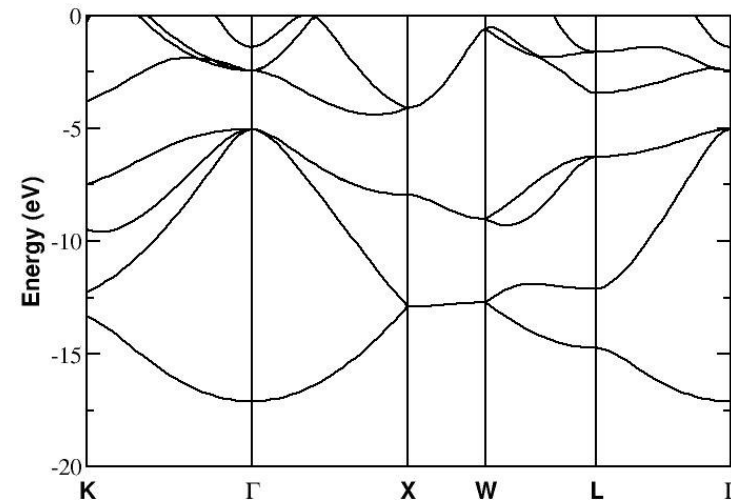
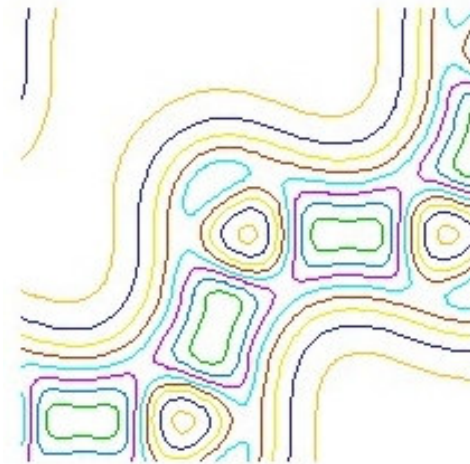
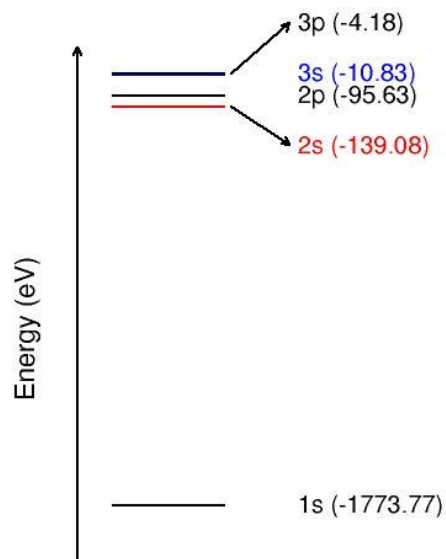
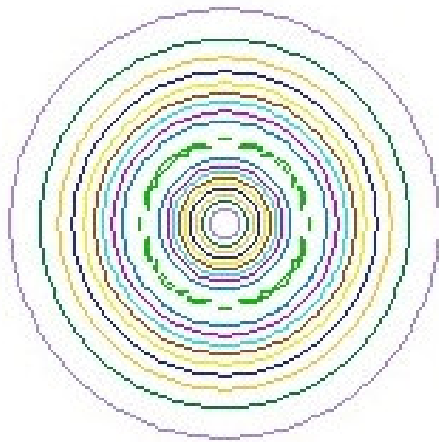
electron scattering in a localized spherical potential

3) Unscreened norm-conserving pseudopotential

$$V_l^{PS}(r) = V_l^{PS,scr}(r) - V^H(\hat{n}^{PS}; r) - V^{xc}(\hat{n}^{PS}; r)$$



A transferable pseudo will reproduce the AE energy levels and wave functions in arbitrary environments



Core electrons are highly localized and very depth energy

chemically inert

Pseudopotential

Ignore the dynamics of the core electrons (freeze them)

And replace their effects by an effective potential

PP are not unique:

Two overall competing factors:

transferability vs hardness

**Always test the pseudopotential
in well-known situations**

The semi-local and fully non-local PPs: the role of the local reference component

$$V^{PP} = \sum_{l=0}^{l=+\infty} v_l P_l$$

infinite sum of angularly dependent non local terms, being P_l the angular projectors operator

$$V^{PP} = \sum_{l=0}^{l=l_{\max}} u_l P_l + \sum_{l=l_{\max}+1}^{l=+\infty} v_l P_l = \sum_{l=0}^{l=l_{\max}} [v_l - v_{lref}] P_l + \underbrace{\sum_{l=l_{\max}+1}^{l=+\infty} v_l P_l}_{\substack{l > l_{\max} \\ v_l = v_{lref}}} + v_{lref} \sum_{l=0}^{l=l_{\max}} P_l =$$

$$\sum_{l=0}^{l=l_{\max}} [v_l - v_{lref}] P + v_{lref} = \underline{v_{nloc} + v_{lref}}$$

Semi-local form of a PP

$$u_{nloc}(r, \Omega, \Omega') = \sum_{l=0}^{l=l_{\max}} \underbrace{[v_l(r) - v_{lref}(r)]}_{\text{local}} \frac{\delta(r-r')}{r^2} \underbrace{P_l(\Omega, \Omega')}_{\text{nonlocal}}$$

Real space representation

$$\hat{P}_l(\Omega, \Omega') = \sum_{m=-l}^{+l} Y_{lm}^*(\Omega) Y_{lm}(\Omega')$$

Reciprocal space representation

G, G' coupled

$$v_{nloc}(k) = \sum_{l=0}^{l=l_{\max}} \sum_{m=-l}^{m=+l} \sum_{G, G'} \underbrace{|k+G\rangle \delta v_l(k+G, k+G') \langle k+G'|}_{\text{G, G' coupled}}$$

Fully non-local form of a PP:

Kleinman-Bylander

$$v_{nloc}^{KB} = \sum_{l=0}^{l=l_{\max}} \sum_{m=-l}^{+l} \frac{\delta v_l |\phi_{lm}\rangle \langle \phi_{lm}| \delta v_l}{\langle \phi_{lm} | \delta v_l | \phi_{lm} \rangle}$$

Real space representation

$$\phi_{lm} = Y_{lm}(\Omega) \frac{u_l(r)}{r}$$

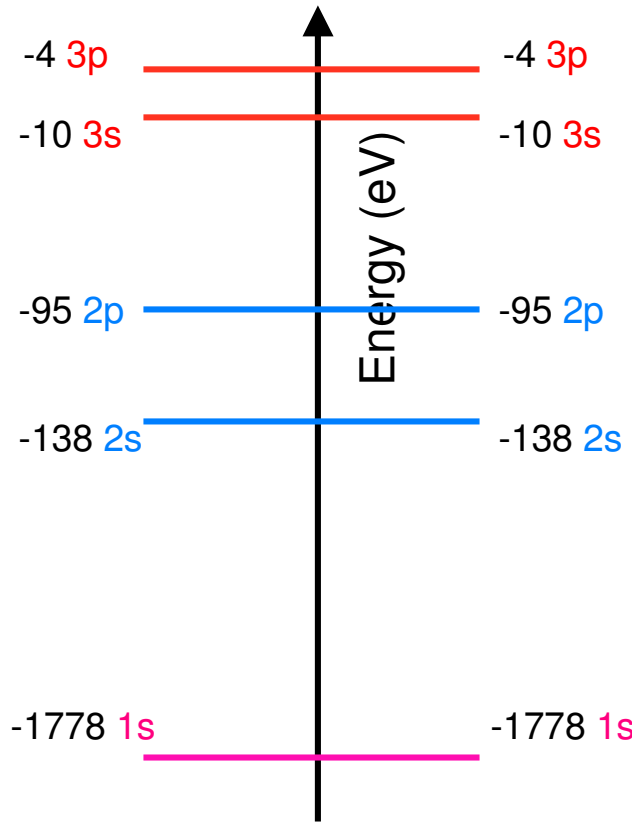
Reciprocal space representation

$$v_{nloc}^{KB}(k) = \sum_{l=0}^{l=l_{\max}} \sum_{m=-l}^{m=+l} \frac{\left[\sum_G |k+G\rangle \langle k+G| \delta v_l \phi_{lm} \right] \left[\sum_{G'} \langle \delta v_l \phi_{lm} | k+G' \rangle \langle k+G' \right]}{\langle \phi_{lm} | \delta v_l | \phi_{lm} \rangle}$$

**What happen using PPs
for excited state calculations?**

The set of pseudopotential considered:

1) *Standard*
Pseudopotential

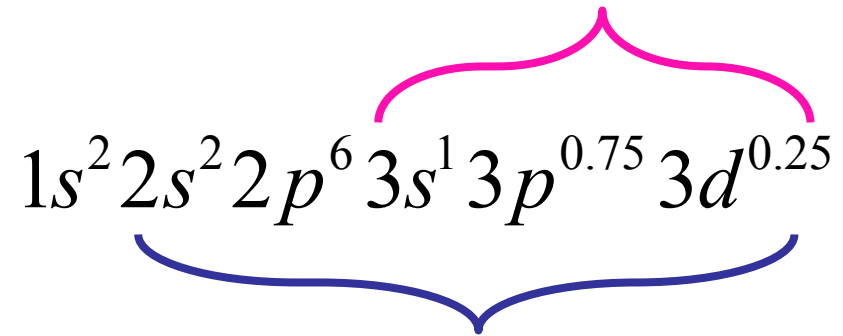
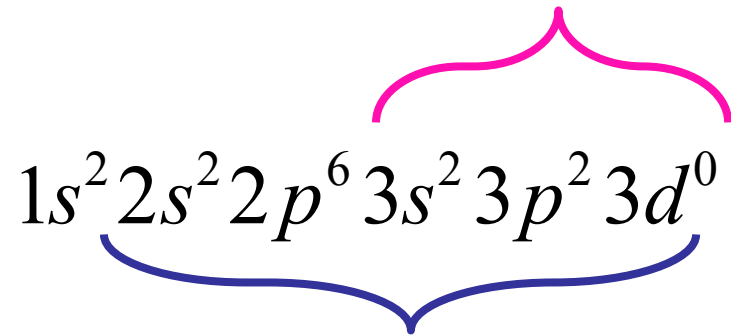


2) *Outercore*
Pseudopotential

Unbound d wavefunction: improving transferability for excited states

$$l_{\max} = 2$$

1) Standard Pseudopotential

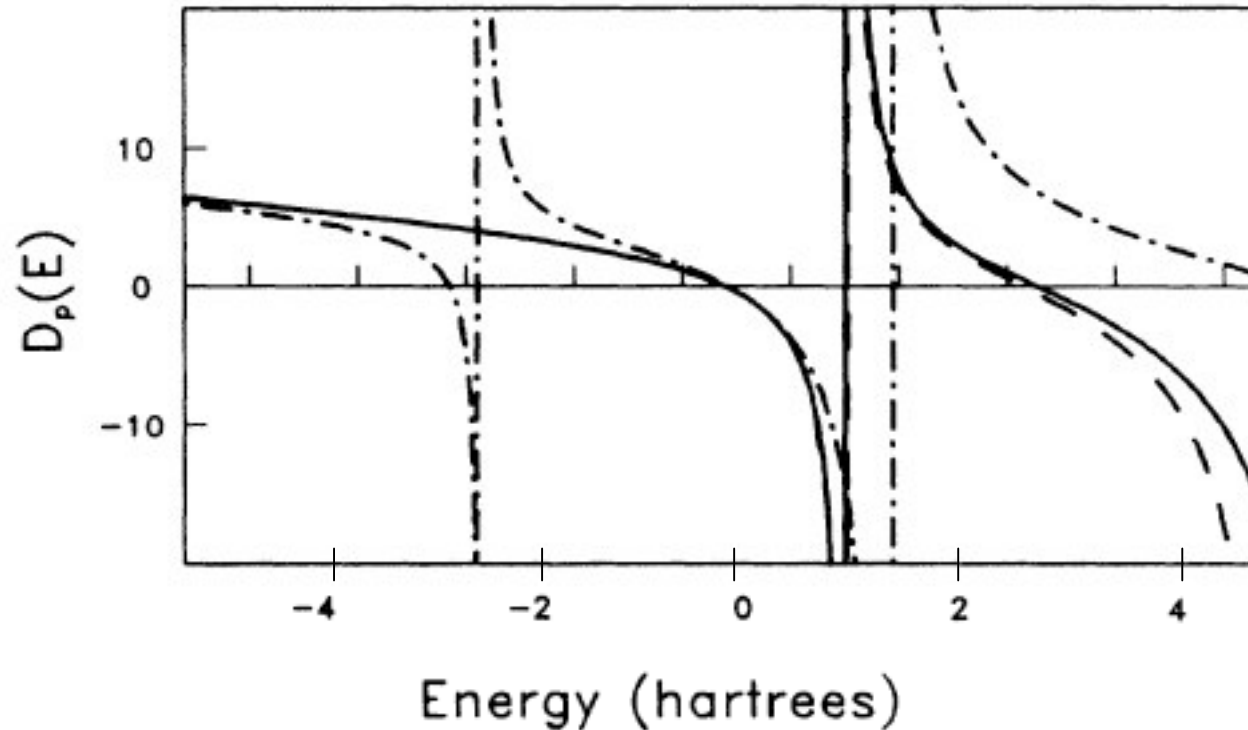


2) Outercore Pseudopotential

$$l_{\max} = 2$$

Logarithmic Derivatives:

- 1) Comparison with all-electron LD
- 2) Ghost states analysis



Only for the KB hamiltonian (nonlocal)
the Wronskian theorem is not valid anymore.

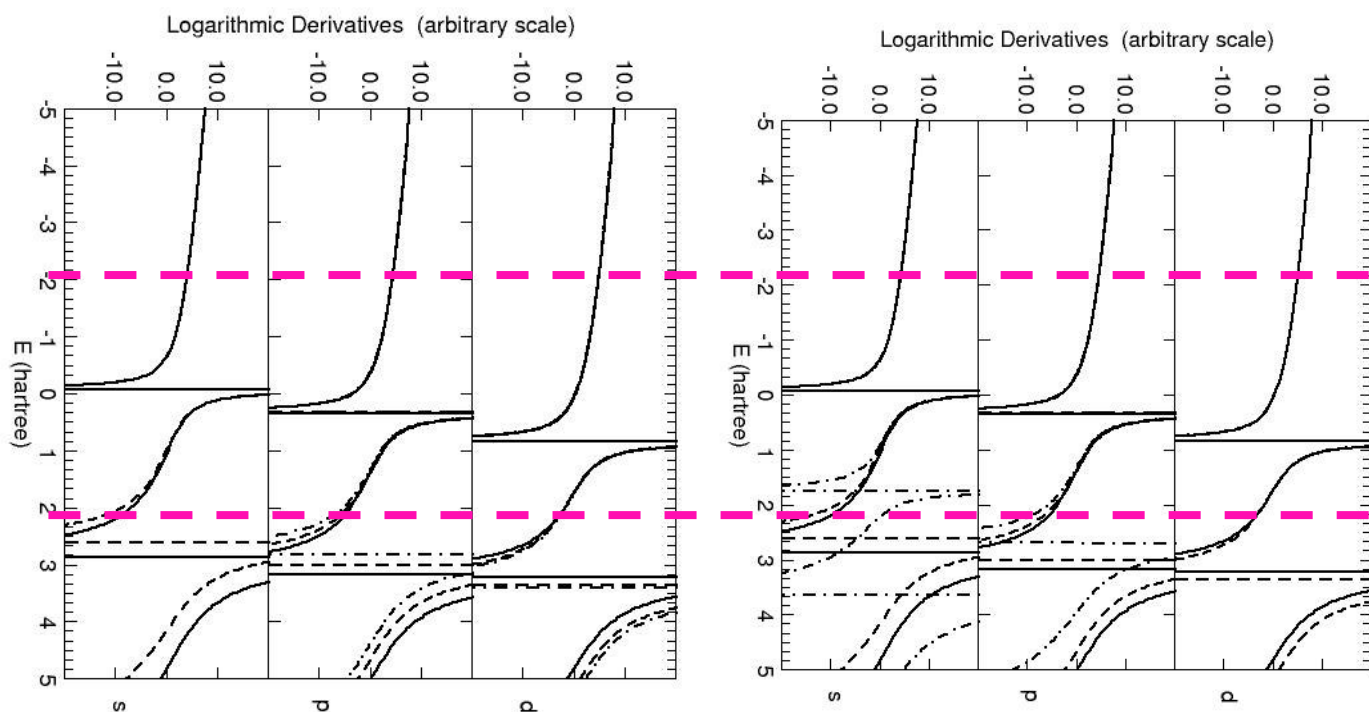
The Wronskian theorem: the number of nodes in the radial wavefunctions (at a fixed value of Angular momentum) increase with the energy of the state. The lowest energy state is nodeless.

And so because of the Wronskian theorem it is also the lowest energy state.

For the KB case it can happen that the others bound states appear lower the nodeless state.

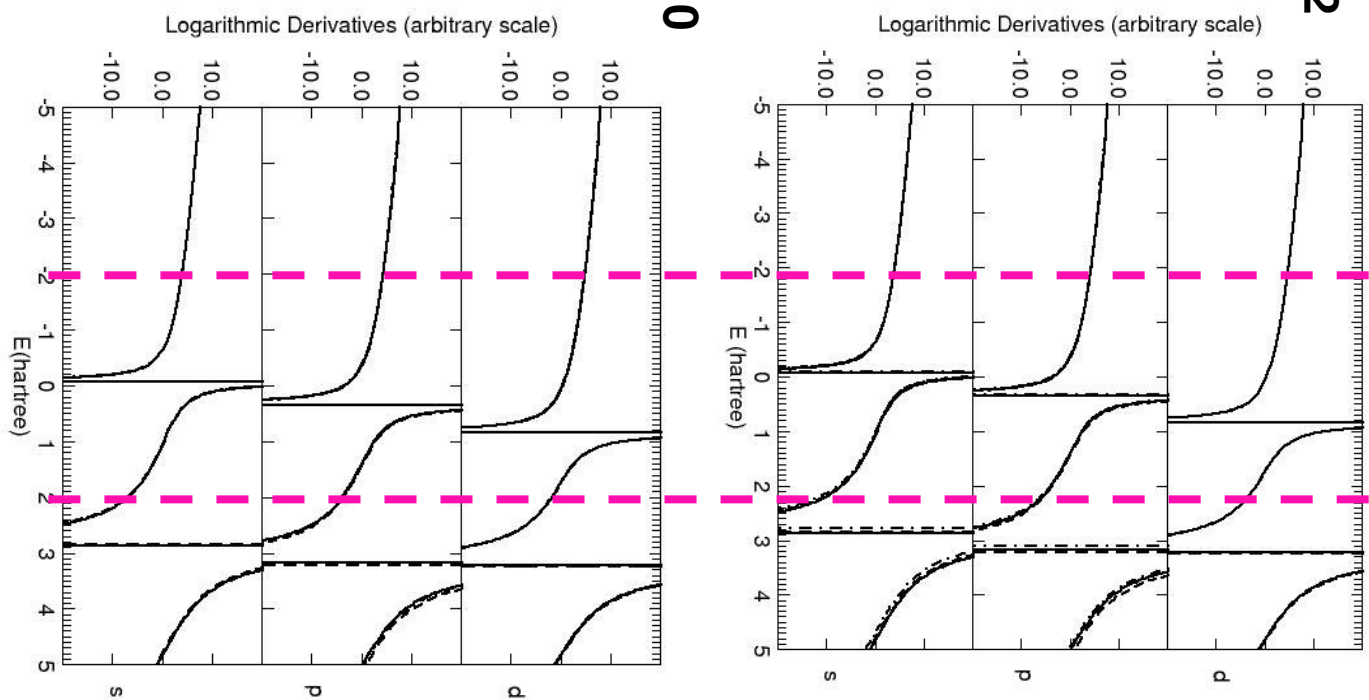
This is not good ;-)!!!!

Logarithmic Derivatives

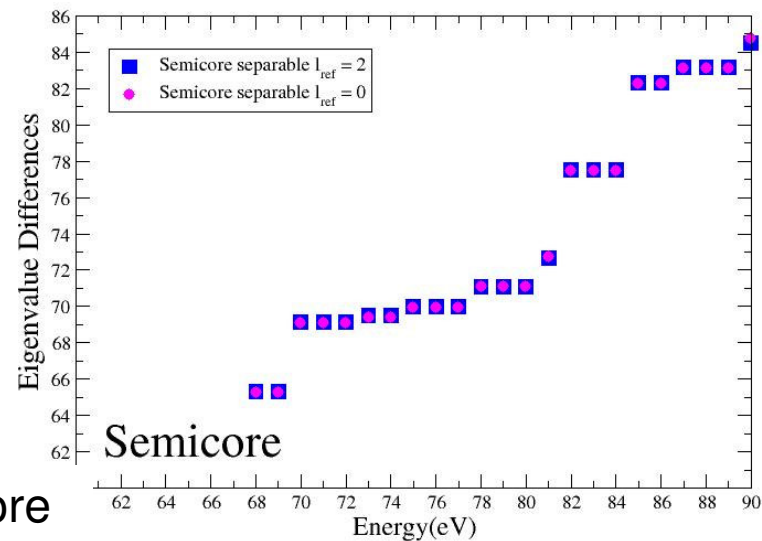
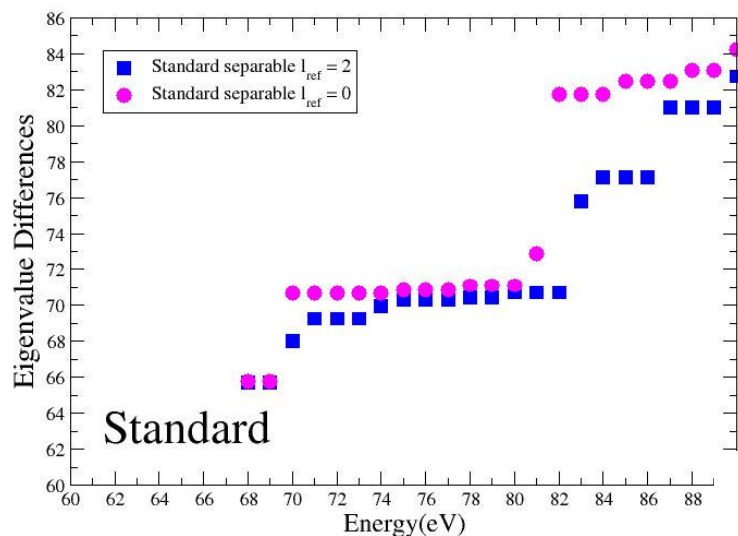


$l_{ref} = 2$

$l_{ref} = 0$

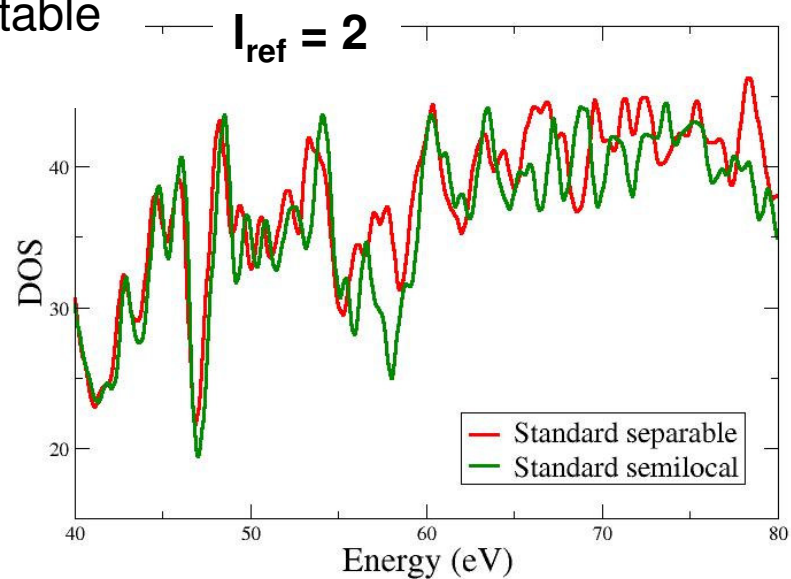
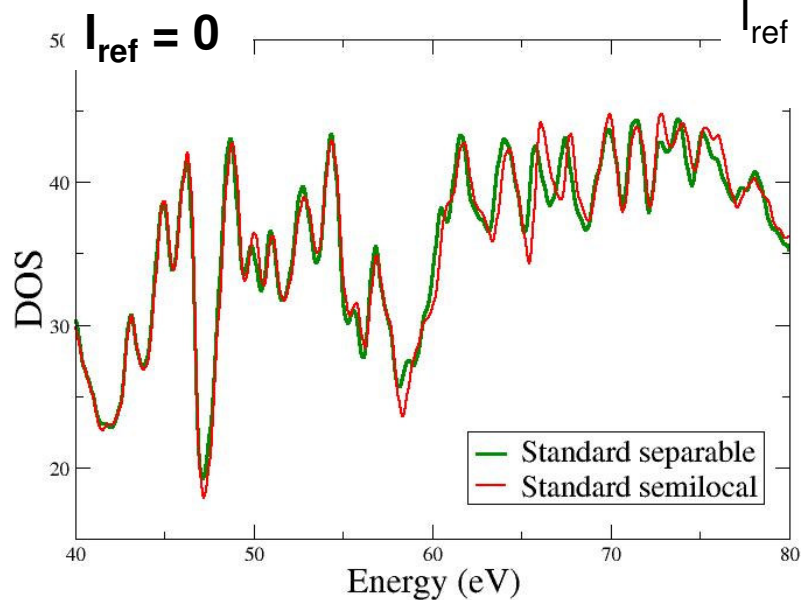


Kohn-Sham Band Structure



Outercore is more l_{ref} independent and

l_{ref} give more stable results



ALL OUR QUANTITIES ARE CALCULATED AS A SUM OVER STATES

$$\chi_0^1(r, r', \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_i^*(r) \psi_j(r) \psi_j^*(r') \psi_i(r')}{\epsilon_i - \epsilon_j + i\eta}$$

GW

$$\Sigma = GW$$

$$G(r, r', \omega) = \sum_i \frac{\psi_i^*(r) \psi_i(r')}{\omega - \epsilon_i}$$

$$W = \epsilon^{-1} v$$

$$\epsilon = 1 - v \chi_0^1$$

EELS

$$\epsilon_M(q, \omega) = \lim_{q \rightarrow 0} \epsilon^{-1}(q, \omega)$$

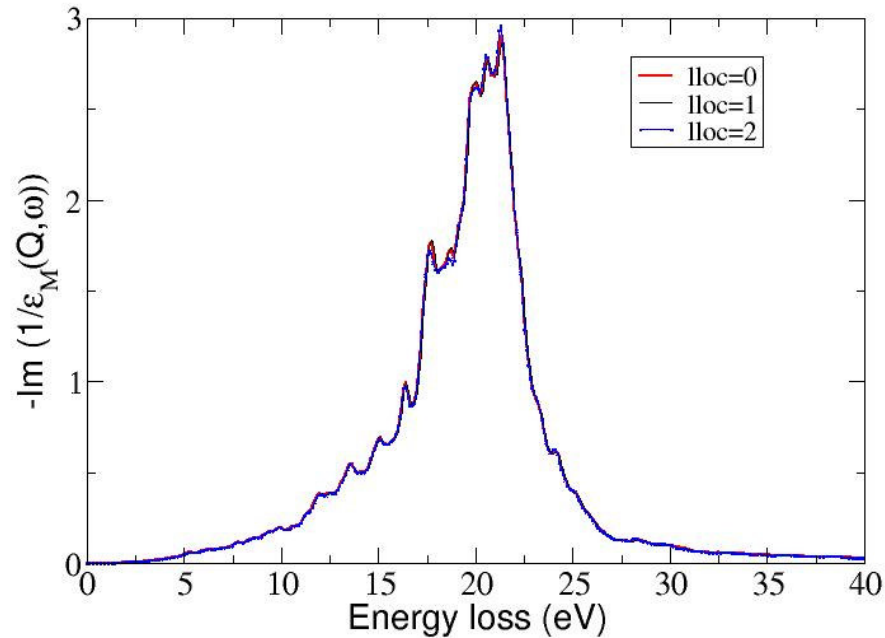
$$-\text{Im} \epsilon_M^{-1} = \frac{\text{Im} \epsilon_M}{|\epsilon_M|^2}$$

GW

		$\Gamma_c - \Gamma_v$	$X_c - X_v$	$L_c - L_v$	$X_c - \Gamma_v$	$L_c - \Gamma_v$
Si GW						
PP method:						
PP calculations	present work <i>Standard</i>	(2.56)3.23	4.18	3.31	1.31	2.09
	Aulbur	(2.56)3.25	4.27	3.38	1.31	2.13
	Rohlfing [?]	(2.57)3.36	4.36	3.44	1.43	2.19
	Olevano	(2.57)3.25			1.33	2.28
	M.S. Hybertsen and S.G.Louie [?]	(2.57)3.27		3.44	1.44	2.27
	E.L.Shirley et al [?]	(2.59)3.35			1.31	
	Bruneval et al [?]	(2.57)3.20			1.29	2.08
	Godby et al [?]	(2.57)3.30		3.49		2.30
	Rieger et al [?]	(2.58)3.24	4.14	3.31	1.34	2.14
	Fleszar et al [?]	(2.55)3.23	4.18	3.38	1.35	2.18
present work <i>Outercores</i>	(2.52)3.01	4.03	3.35	1.06	2.10	
M.L. Tiago et al [?]	(2.52)3.24			1.18		
All electron method:						
AE calculations	Hamada et al [?]	(2.55)3.30	4.17	3.41	1.14	2.15
	T.Kotani and M. van Schilfgaarde [?]	3.12				
	W.Ku and A.G.Eguiluz [?]	(2.53)3.12				
	Schindlmayr et al [?]	3.20	4.11	3.35		
	B. Arnaud and M. Alouani [?]	(2.53)3.13/3.17	4.13/4.17	3.41/3.42	1.15/1.20	2.16/2.17
	Lebegues et al [?]	(2.54)3.09/3.15	3.91/4.00	3.21/3.28	1.01/1.08	2.05/2.11
Exp		3.05-3.40			1.25	2.1(2.4±0.15)

Why the *Outercore* PP gives results so similar to all-electron calculations ? *later discussion*

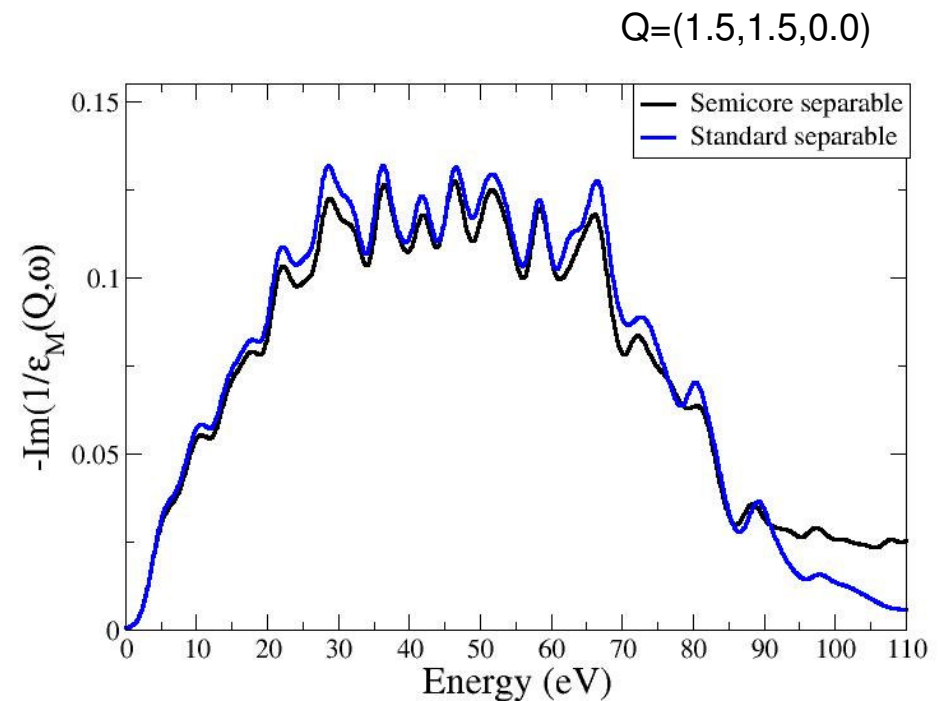
EELS



NO
reference component influence

Bigger differences for higher q

The difference comes from
the pseudo
not from the core levels

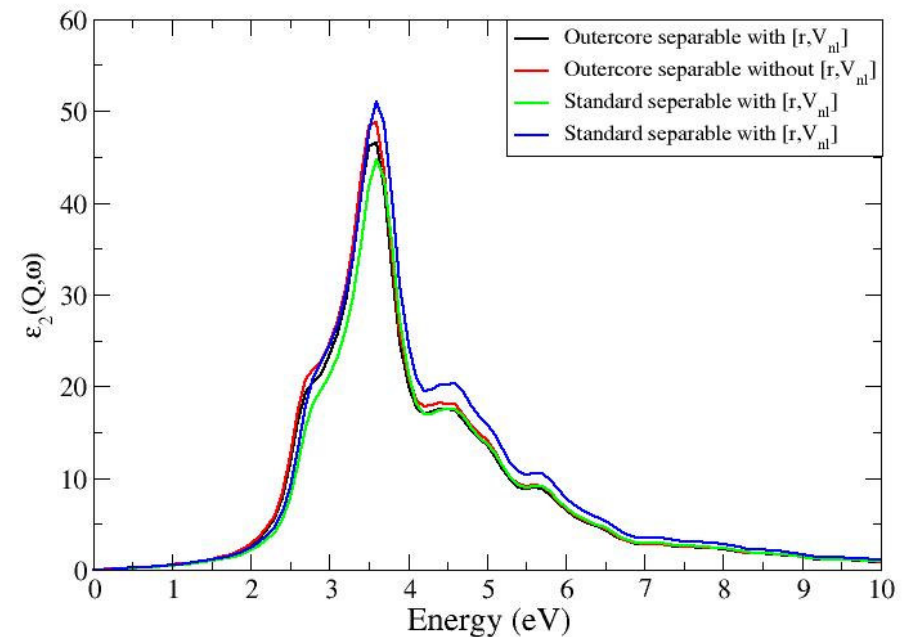
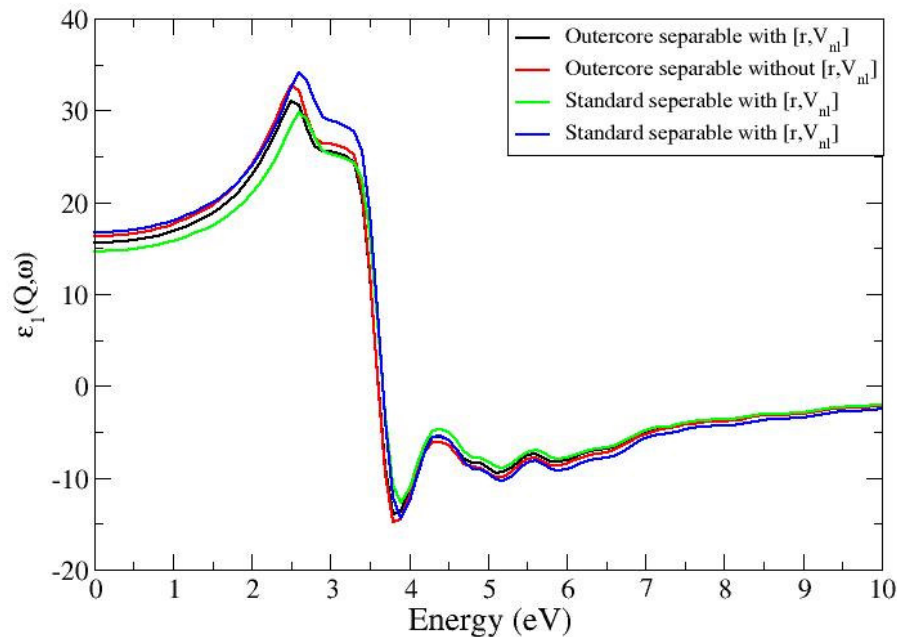


Optical matrix elements: the non-local contribution

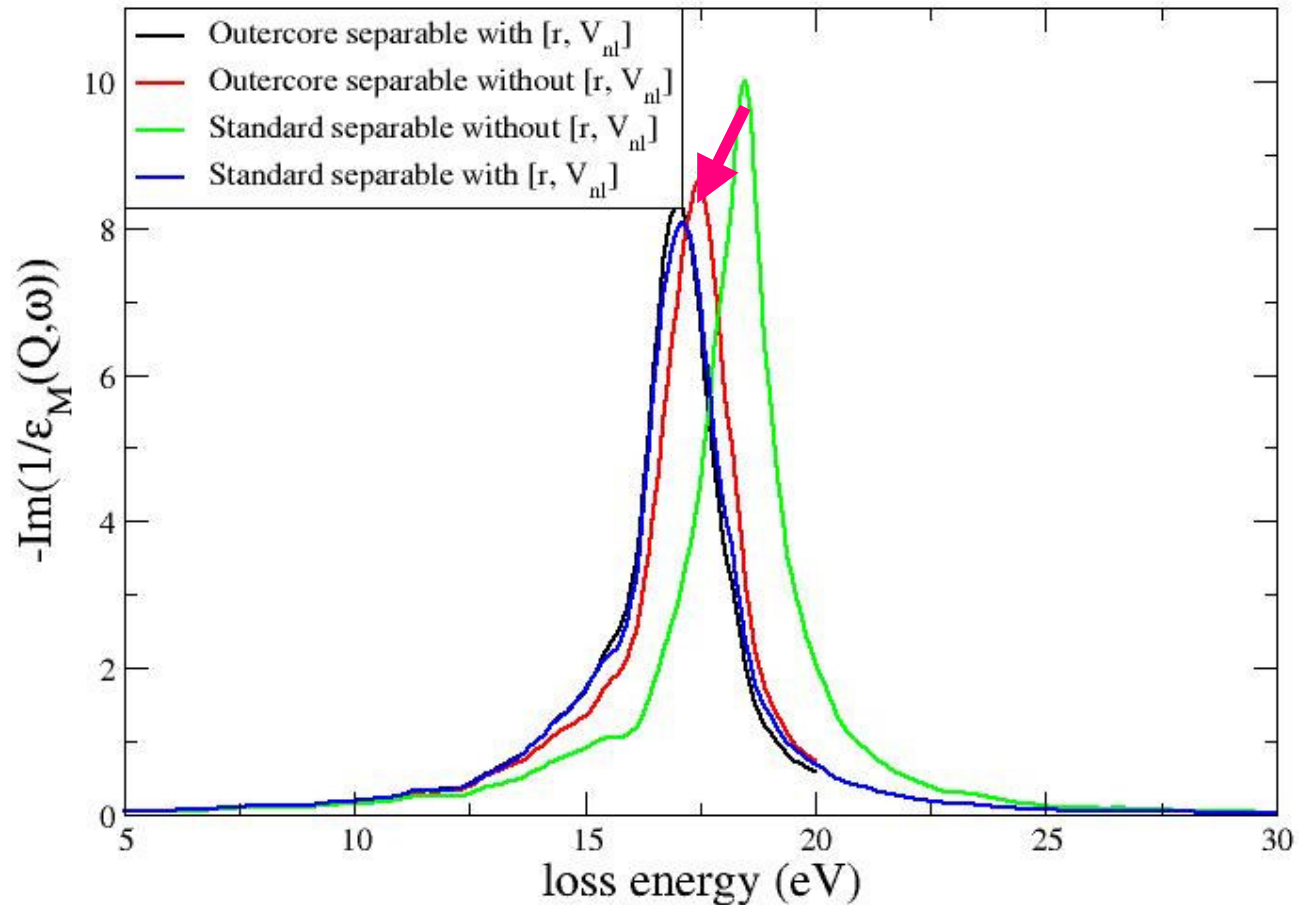
$$\lim_{q \rightarrow 0} \langle ck | e^{iqr} | vk + q \rangle = \lim_{q \rightarrow 0} \frac{\langle ck | v | vk + q \rangle}{\epsilon_c - \epsilon_v}$$

$$\langle ck | v | vk \rangle = \langle ck | p | vk \rangle + \langle ck | [r, V_{nl}] | vk \rangle$$

Reminder: Valerie seminar next week



Peak shift in the loss $\langle ck | [r, V_{nl}] | vk \rangle$



Standard: nonlocal contribution shifts the peak of about 2 eV

Outercore: less nonlocal contribution effects respect with Standard

All-electron: no nonlocal contribution

Non-linear optics: non-linear contribution for the optical matrix elements

$$\chi_0^{(2)}(2\mathbf{q}, \mathbf{q}, \mathbf{q}, \omega, \omega) = \frac{4}{V} \sum_{n, n', n'', \mathbf{k}} \frac{\langle \phi_{n, \mathbf{k}} | e^{-2i\mathbf{q}\mathbf{r}} | \phi_{n', \mathbf{k}+2\mathbf{q}} \rangle}{(E_{n, \mathbf{k}} - E_{n', \mathbf{k}+2\mathbf{q}} + 2\omega + 2i\eta)}$$

$$\left[(f_{n, \mathbf{k}} - f_{n'', \mathbf{k}+\mathbf{q}}) \frac{\langle \phi_{n', \mathbf{k}+2\mathbf{q}} | e^{i\mathbf{q}\mathbf{r}'} | \phi_{n'', \mathbf{k}+\mathbf{q}} \rangle \langle \phi_{n'', \mathbf{k}+\mathbf{q}} | e^{i\mathbf{q}\mathbf{r}''} | \phi_{n, \mathbf{k}} \rangle}{(E_{n, \mathbf{k}} - E_{n'', \mathbf{k}+\mathbf{q}} + \omega + i\eta)} \right.$$

$$\left. + (f_{n', \mathbf{k}+2\mathbf{q}} - f_{n'', \mathbf{k}+\mathbf{q}}) \frac{\langle \phi_{n', \mathbf{k}+2\mathbf{q}} | e^{i\mathbf{q}\mathbf{r}'} | \phi_{n'', \mathbf{k}+\mathbf{q}} \rangle \langle \phi_{n'', \mathbf{k}+\mathbf{q}} | e^{i\mathbf{q}\mathbf{r}''} | \phi_{n, \mathbf{k}} \rangle}{(E_{n'', \mathbf{k}+\mathbf{q}} - E_{n', \mathbf{k}+2\mathbf{q}} + \omega + i\eta)} \right]$$

