

# Pseudopotentials in DFT and VMC

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# Ahhh, pseudopotentials ...

Difficult subject ... why ?

- highly technical, difficult
- often the most complicated parts of the codes
- “only” an auxiliary concept, not really fundamental :-)

but

- it saves (b)illions of hours of computer time
- enables to do calculations/predictions which otherwise are impossible
- forces you to learn/understand electronic structure a lot deeper

# Outline of this talk

- Total energy as a function of  $Z$  (atomic number)
- Core vs valence: energy and length scales
- Idea of “pseudo-ion”: effective potential in the core + valence electrons
- Helps in DFT and basis set methods: smaller basis, less states
- Helps in QMC: smaller total energies, significant gain in efficiency
- PP (ECP in quantum chem.) norm-conserving construction
- Evaluation of PP terms in VMC/QMC
- Existing tables, accuracy, errors to watch
- Ideas on many-body construction of PP

# Reminder: one-particle electronic structure methods, DFT and HF

Density Functional Theory :

$$E_{tot} = \int F_{tot}[\rho(\mathbf{r})] d\mathbf{r}$$

self-consistent loop

$$[T_{kin} + V_{ext} + V_{eff,DFT}(\rho)]\phi_i = E_i \phi_i$$

$$\rho(r) = \sum_i^{occup} \phi_i^2(r)$$

Hartree-Fock:  $\psi_{HF}(\mathbf{r}_1, \mathbf{r}_2, \dots) = Det[\{\phi_i(\mathbf{r}_j)\}]$   $E_{HF} = \langle \psi_{HF} | H | \psi_{HF} \rangle = \mathbf{min}$

self-consistent loop

$$[T_{kin} + V_{ext} + V_{eff,HF}(\{\phi_j\})]\phi_i = E_i \phi_i$$

$$V_{eff,HF} = V_{Coul+Exch}[\{\phi_i\}]$$

# Atom with nuclear charge Z: energies of one-particle states

Eigenvalues/energies of the one-particle levels [ in a.u.  $\sim 27$  eV ]

Deep core qualitatively:  $E_n = -Z^2 / (2n^2)$ , n is the principal q. number  
**Valence different, strongly** modified by e-e interactions  $\sim$  **a few eVs**

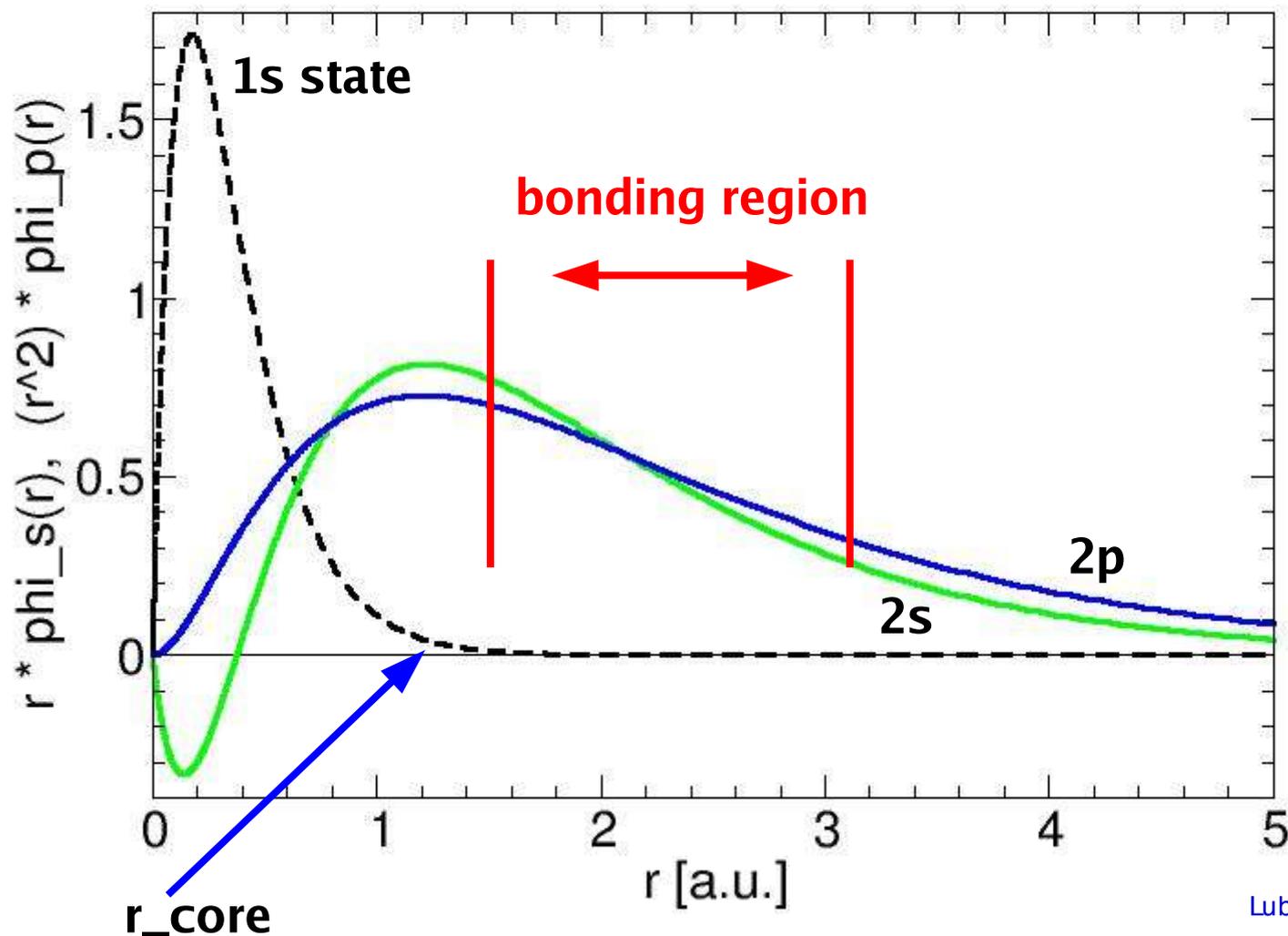
One-particle eigenvalues for carbon C (Z=6) and copper Cu (Z=29)

2p	$E_{2p} = -0.5$	<b>Valence</b>	4s	$E_{4s} = -0.2$
2s	$E_{2s} = -0.7$		3d	$E_{3d} = -0.5$
1s	$E_{1s} = -11.0$		3p	$E_{3p} = -3.5$
		<b>Core</b>	3s	$E_{3s} = -5.0$
			2p	$E_{2p} = -35.$
			2s	$E_{2s} = -41.$
			1s	$E_{1s} = -392.$

**Note: different energy scales in core vs. valence**

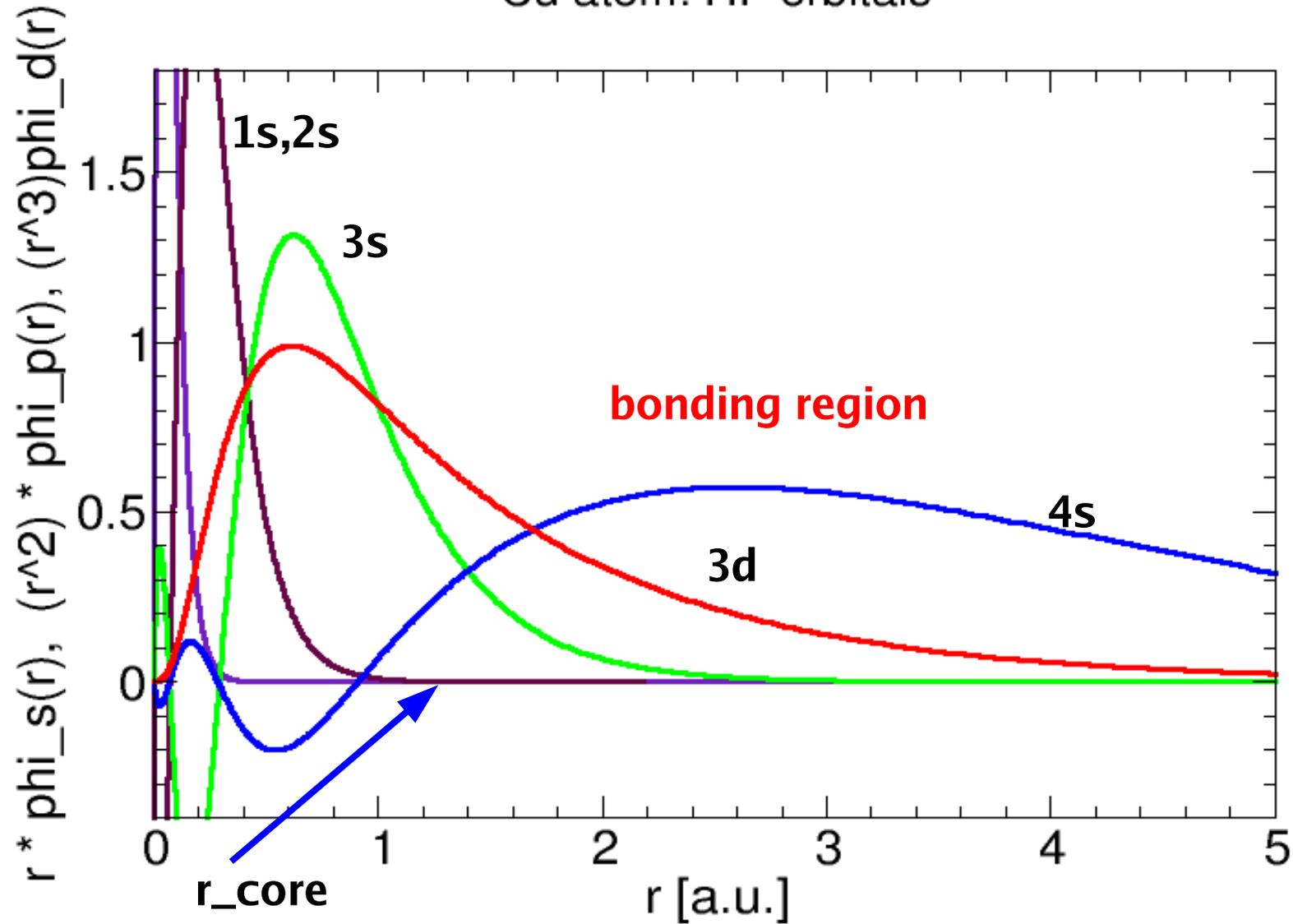
# Length scales of core vs valence electrons: carbon atom

Carbon atom: HF orbitals

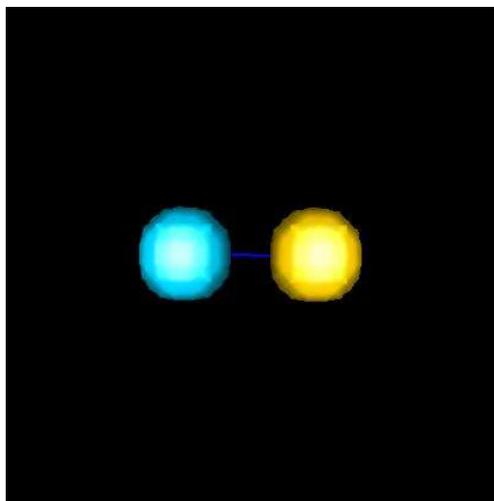
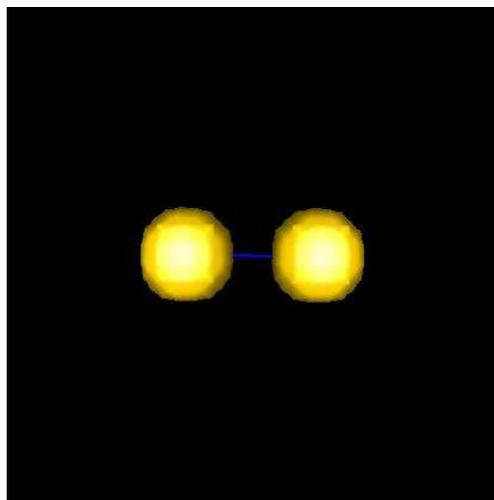


# Core vs valence electrons: copper atom, semicore states 3s,3p

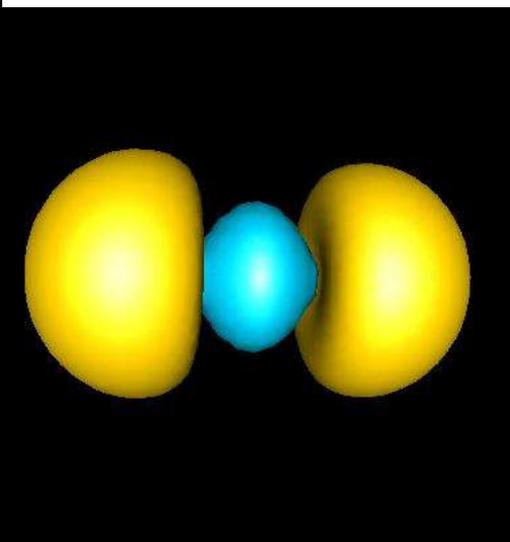
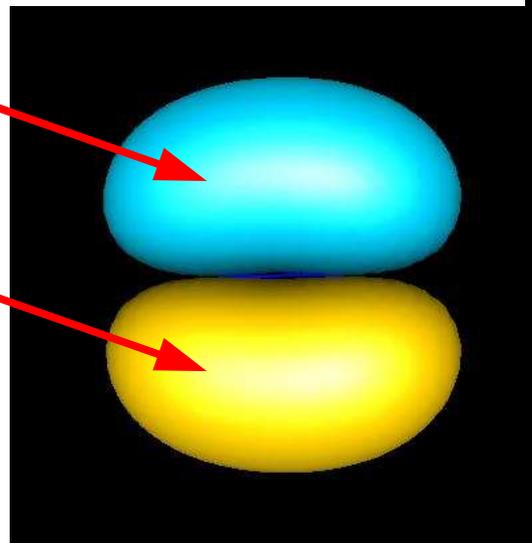
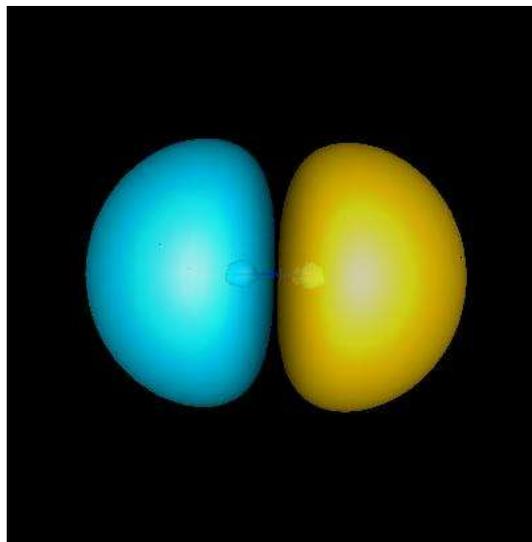
Cu atom: HF orbitals



# Core vs valence in bonds ( $C_2$ ): isosurfaces of molecular orbitals



1s core states (unchanged)



valence  
(hybridized, bond  
formation)

# Difficulties from cores for DFT (HF, etc): large/huge basis and/or combined basis necessary

Clearly difficult to describe **both** core and valence:

- **core** states/electrons are highly localized and have large energies:  
require very accurate description: nuclear cusp  $\rightarrow \phi_{core}(r) \approx \exp(-Zr)$ 
  - requires very localized description and basis
- **valence states have small energies**, affected significantly due to bonding; states at or above Fermi level in solids can be even completely delocalized like a free-particle wave, very smooth
  - calls for very smooth basis, plane wave almost ideal

# Difficulties from cores for DFT (and HF): large/huge basis and/or combined basis necessary II

The best all-electron basis sets for solids based on combination of two types of basis (FLAPW method):

- in spheres around atoms localized states: numerical radial meshes
  - between spheres plane waves
  - matching/continuity of orbitals on sphere surfaces very complicated
  - perfectly working approach within DFT but **could be expensive**
  - **development took a long time and was rather slow**
- ultimately, cores are inefficient if you are interested in valence properties (think about a heavy atom, most of the states are in core)
- can we get rid of the core electrons completely ?

# Idea of core – valence partitioning

- core states/electrons appear to be rigid and do not affect valence electronic structure (bonds, excitations, band gaps, conductivity) much due to the different energy and length scales
- get rid of the core states/electrons and keep only the valence ones
- **represent the core by an effective operator** (cannot be a simple potential, must be angular momentum dependent because of different number of core states in s, p, d angular momentum channels)
- valence electrons feel **a pseudopotential operator (instead of core e-)**

$$V_{ps-ion} = \sum_l v_l(r) \sum_m |lm\rangle \langle lm| = \sum_{l=0}^{l_{max}} [v_l(r) - v_{loc}] \sum_m |lm\rangle \langle lm| + v_{loc}(r)$$

# Dictionary and notations

In condensed matter physics: **pseudopotentials** or **PPs**

In quantum chemistry : **effective core potentials** or **ECPs**

$$V_{ps-ion} = \sum_l v_l(r) \sum_m |lm\rangle \langle lm| = \sum_{l=0}^{l_{max}} [v_l(r) - v_{loc}] \sum_m |lm\rangle \langle lm| + v_{loc}(r)$$

$v_l(r)$  - radial pseudopotential function for a given l-symmetry channel

$v_{loc}(r)$  - outside the core will be just  $-Z_{eff}/r = -(Z-Z_{core})/r$

$|lm\rangle \langle lm|$  projection operator onto a given  $|lm\rangle$  state -> nonlocal!!!

$l_{max}$  - number of different occupied channels -> number of nonlocal projection operators

# Nonlocality ? What does it mean ?

Remember the self-consistent loop/one-particle eigenfunction eq. ?

$$[T_{kin} + \underbrace{V_{ext=ion}} + V_{eff,HF}(\{\phi_j\})]\phi_i = E_i \phi_i$$

In the simplest atomic case the nonlocality means that each symmetry channel has **different ionic (pseudo)potential**

**s**

$$[T_{kin} + \underbrace{v_s} + V_{eff,HF}(\{\phi_j\})]\phi_s = E_s \phi_s$$

**p**

$$[T_{kin} + \underbrace{v_p} + V_{eff,HF}(\{\phi_j\})]\phi_p = E_p \phi_p$$

etc

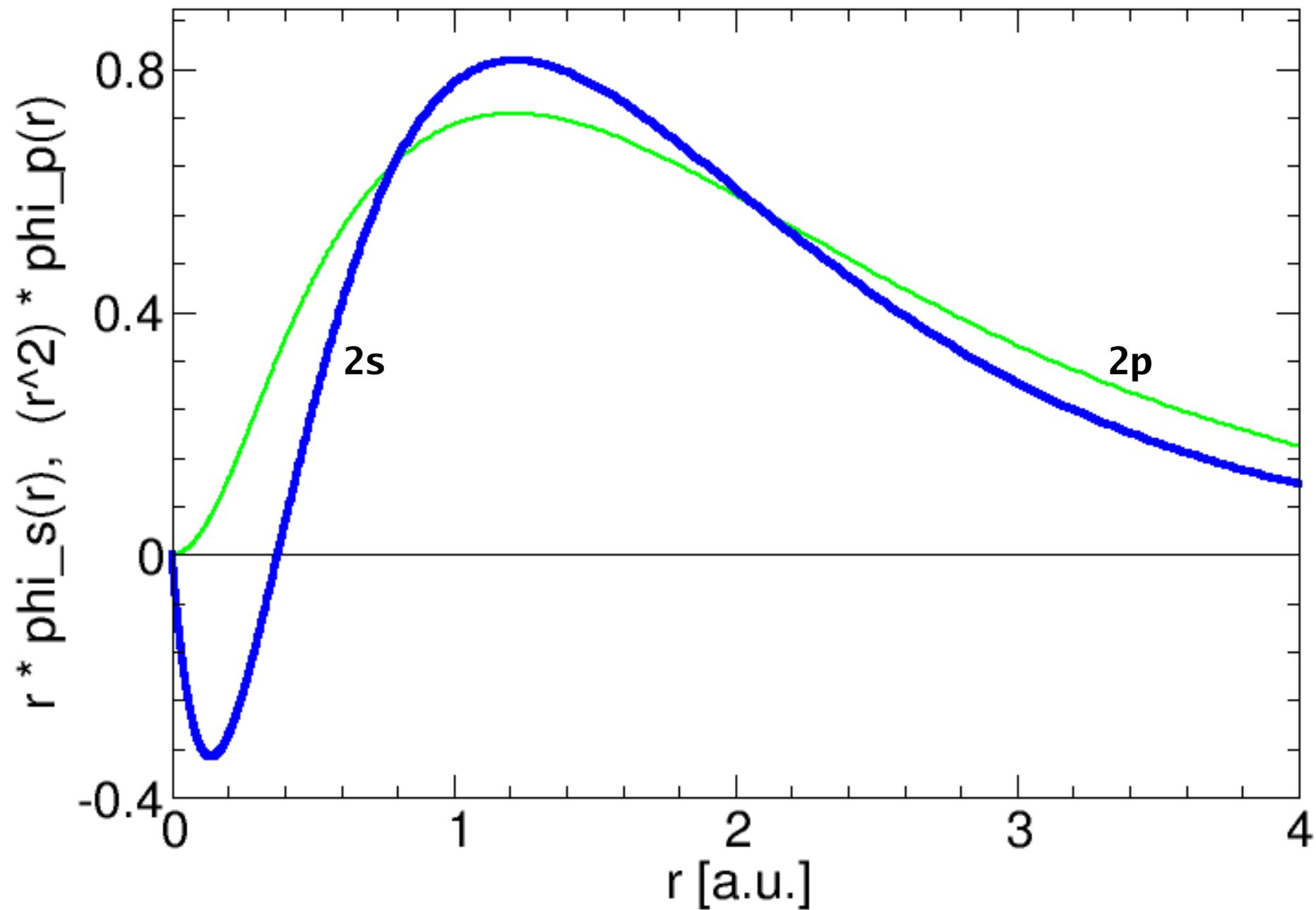
# One-particle construction of PP: norm-conservation

How to construct such an **operator** so as to represent the action of the core electrons **as closely as possible to the true atom**

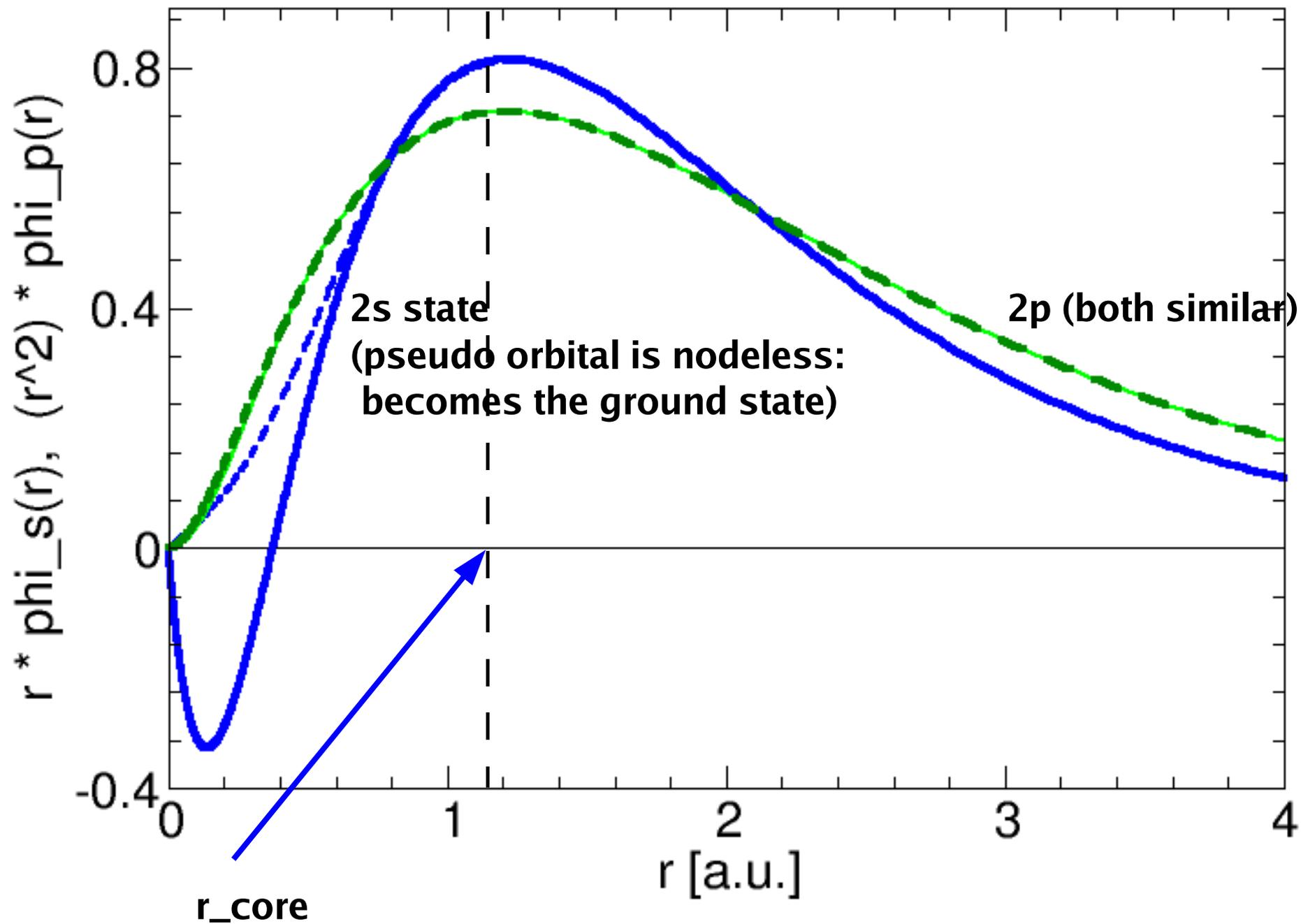
The most important is the charge: beyond certain  $r_{\text{core}}$  radius the valence states should look identical like if the core electrons were present

- outside the  $r_{\text{core}}$  the charge will then be the same as pseudo-charge, valence eigenvalues will be identical for both all-electron and pseudo atom
- number of clever clever and elaborated schemes (often used in condensed matter: Troullier-Martins construction)
- more complicated schemes exist (enable to save even more)

# Carbon atom: HF orbitals

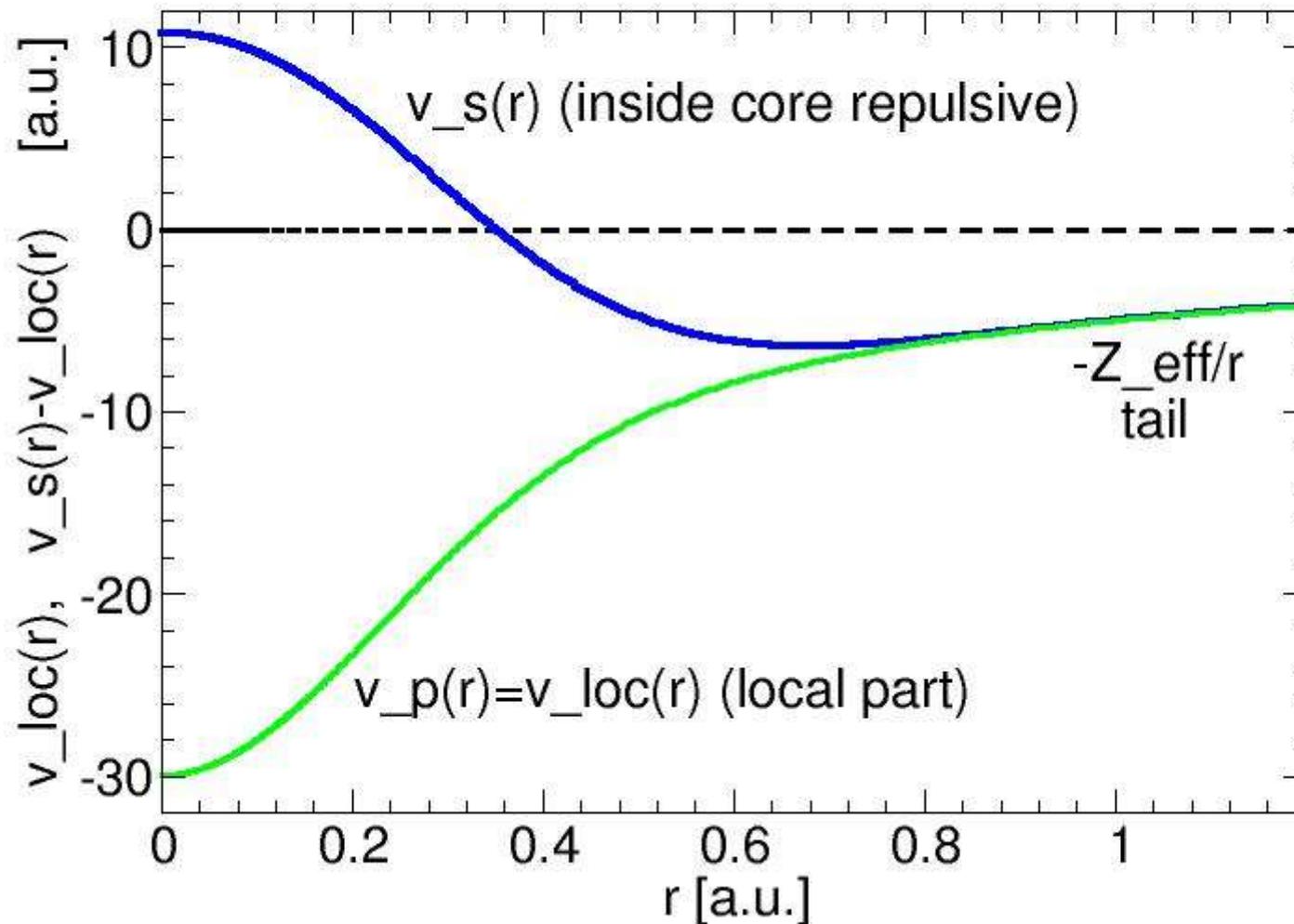


Carbon atom: HF (full) and pseudo-orbitals (dashed)



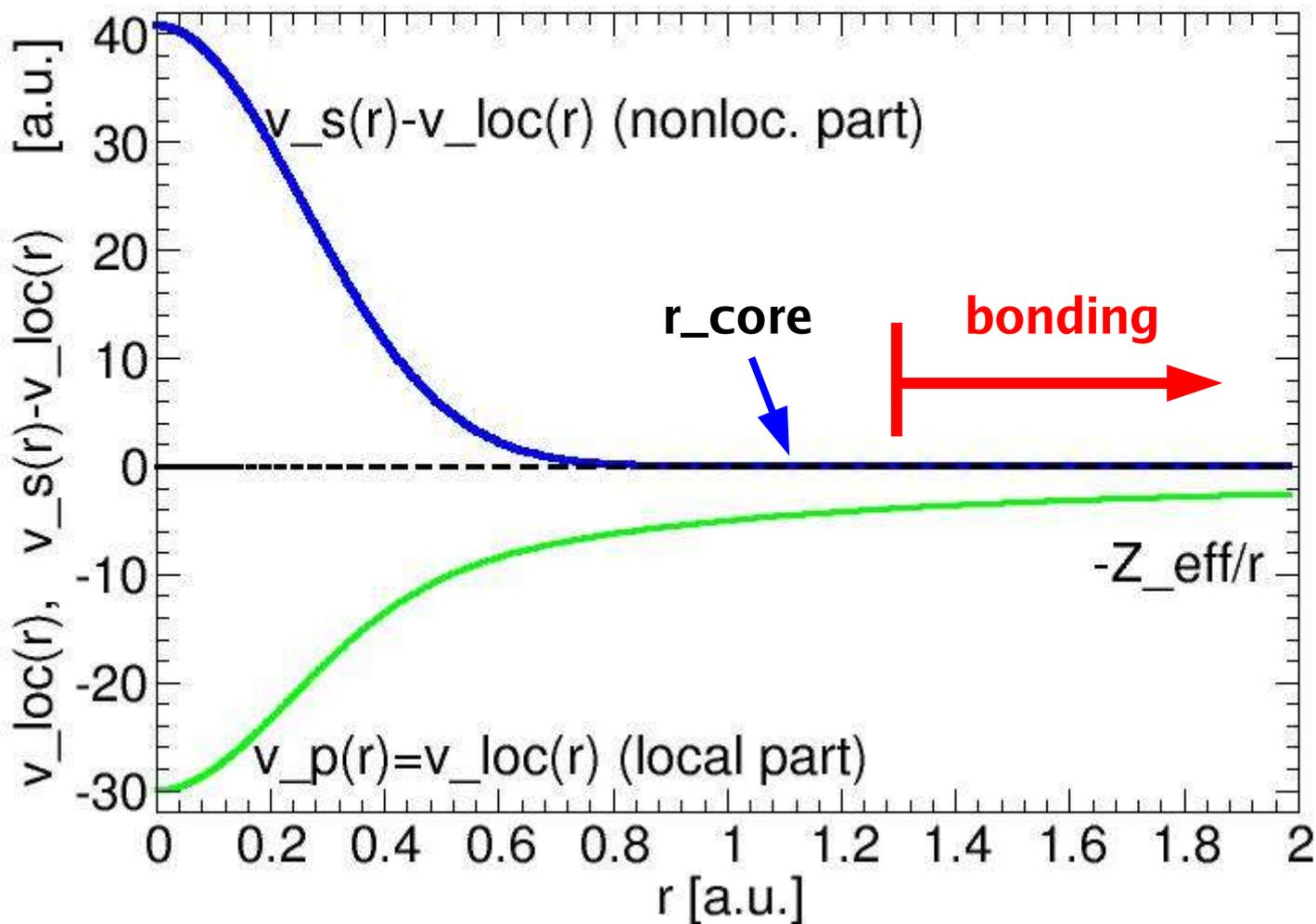
# Example of PPs for C atom (Lester et al, JCP 2003)

Carbon atom pseudopotentials



# Example of PPs for C atom

Carbon atom pseudopotentials



# Norm conservation conditions not very constraining inside the core: large flexibility in construction

- many of the PPs (ie, ECPs in quantum chemistry) can have singularities

$$v_l(r) = \text{const}/r^2 \text{ for } r \rightarrow 0, \quad v_{loc}(r) = -Z_{eff}/r \text{ for } r \rightarrow 0$$

- > not fundamental, the reason is in gaussian basis sets used in quantum chemistry, these are rather flexible to describe these, can be equally accurate as others
- in condensed matter physics all PPs are **smooth and bounded** since the key motivation was/is to simplify the basis and use only plane waves
- smoothness of PP helps in QMC, too ( as we will see)

# Norm conservation conditions not very constraining inside the core: large flexibility in construction

- figure of SBKs

$$v_{loc}(r) = -Z_{eff}/r \text{ for } r \rightarrow 0$$

# PPs in QMC: perhaps even more important for efficiency of the method -> energy fluctuations!

Energy of core states: scales as  $Z^2$

Energy of valence states: basically constant  $\sim 1-10$  eV (0.01 – 0.5 au)

Variance of energy in QMC is always determined by the largest energy scale present! Very crude estimation:

$$\sigma^2 = \langle \psi_{VMC} | (H - E_{VMC})^2 | \psi_{VMC} \rangle \approx Z^4$$

Efficiency of sampling of valence properties (bond energies, gaps etc) for heavy atoms therefore **can be very inefficient**

In reality: for He atom  $\sigma^2 \approx 0.2$  for Cu atom  $\sigma^2 \approx 100$   
**slowdown by a factor of  $\sim 500$**  (for heavier atoms: impractical)

**Huge hit on efficiency: while we are interested in valence properties all the time would be spent on sampling the fluctuations in the core**

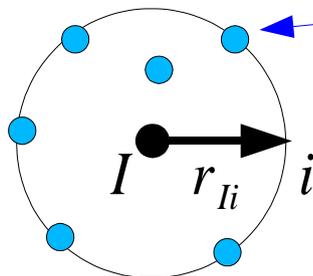
# PPs in VMC: straightforward but numerically involved

- $|lm\rangle \langle lm|$  projection operators mean that the pseudopotential operator is **nonlocal (ie, has off-diagonal matrix elements)**
- its action on an arbitrary trial wave function for many-particle system is a sum over electrons and ions (ie, sum of one-particle operators)

$$V_{ps} \psi(\mathbf{R}) = \sum_{iI} V_{ps}(iI) \psi(\mathbf{R})$$

$$\begin{aligned} V_{ps}(iI) \psi(\mathbf{R}) &= \sum_{lm} v_l(r_{iI}) Y_{lm}(\omega_{iI}) \int_{4\pi} Y_{lm}^*(\omega'_{iI}) \psi(\mathbf{r}_1, \dots, \mathbf{r}'_{iI}, \dots, \mathbf{r}_N) d\omega'_{iI} = \\ &= \sum_l \frac{2l+1}{4\pi} v_l(r_{iI}) \int_{4\pi} P_l[\cos(\theta'_{iI})] \psi(\mathbf{r}_1, \dots, \mathbf{r}'_{iI}, \dots, \mathbf{r}_N) d\omega'_{iI} \end{aligned}$$

The key numerical task is the integral over the spatial angle/sphere surface  
Done by using numerical quadratures of  $N_k$  points and weights on a sphere surface



$$J = \int_{4\pi} f(\omega) d\omega = \sum_k w_k f(\omega_k)$$

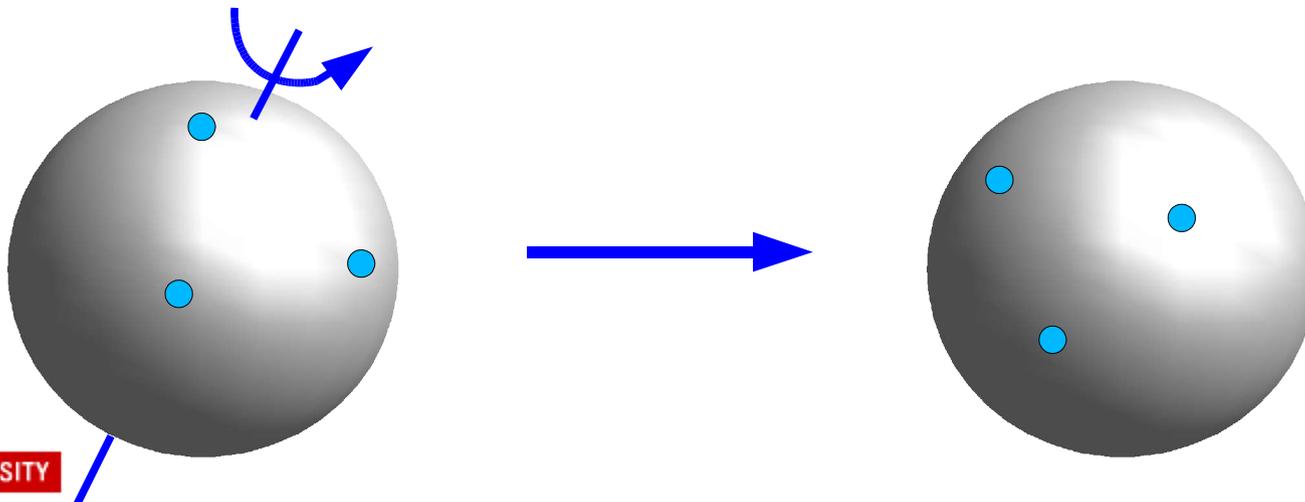
# PPs in VMC: elimination of the numerical bias

Quadratures are such that they integrate products of spherical harmonics up to a given  $l_{\max}$  exactly, eg,  $N_k=12$   $l_{\max}=5$

Quadratures by V. Lebedev from a russian math journal (available in original at UI Urbana-Champaign library :-)

- numerical bias from the integration: to the leading order eliminated by random rotations of the quadrature points on the sphere (Fahy et al, '88)

$$\omega_k^{rand} = R(\text{axis}^{rand}, \phi^{rand}) \omega_k$$



# PPs in QMC: some speed-up improvements

- high accuracy quadratures help because the nonlocal part can become the dominant part of the calculations
- typically it is about 50- 70% of the computational cost (costly but still much better than sampling core states)
- make sense to minimize the computational cost further:
  - improve the fluctuations of energy inside the core by smoothing out the PPs
  - shorten the radial range ( $r_{\text{core}}$ ) of the PPs
  - sample the exponentially small tails of PPs stochastically (ie, only occasionally) instead of each time

Most of these implemented in good QMC codes and PPs

# Do PP really work and how accurate are they

If you are careful the pseudopotentials work (and save millions of hours of computational time)

## - advantages:

- the key is the lower total energy -> smaller fluctuations
- smaller number of states/electrons to carry along
- scalar relativistic effects which are important beyond the third-row can be automatically included (by construction);
- formalism can be expanded to spin-orbit dependent PPs

## - disadvantages:

- always watch how accurate PP is
- might not work well in some cases: you have to watch whether the core does not affect the valence properties in special cases, eg at high pressures
- necessary to evaluate numerically the action of projectors (dominant cost in QMC calculation)

# Comparison efficiency/accuracy for Fe atom

Fe atom -> [Ne] 3s<sup>2</sup>3p<sup>6</sup>3d<sup>6</sup>4s<sup>2</sup> = [Ar] 3d<sup>6</sup>4s<sup>2</sup>

	all-electron	[Ne]-core	[Ar]-core
E_HF [au]	-1262.444	-123.114	-21.387
E_VMC[au]	-1263.20(2)	-123.708(2)	-21.660(1)
$\sigma_{VMC}^2$ [au]	~ 50	1.5	0.16
efficiency = $\frac{1}{\sigma^2 T_{decorr}}$	0.02	2.1	125
valence errors	0	< 0.1 eV	~ 0.5 eV !!!

Ne-core PPs represent the best compromise for QMC: **high accuracy, acceptable efficiency**

# Well-known limits of PPs

PPs are an “artificial” construction, Nature knows nothing about it, it is an auxiliary concept which helps to make many calculations practical and you should worry about accuracy: the key point is **when ?**

- when the **core** is “fat”, **polarizable and exhibit core relaxation** effects:  
example:  
Na = [Ne core] + single 3s electron is **not a good representation** of sodium (you need additional operators to capture these effects) or take more electrons to the valence space
- in general, **high pressures** (increase in core-valence overlaps)
- changes in **local magnetic moments from high to low** (eg MnO) in combination with methods used

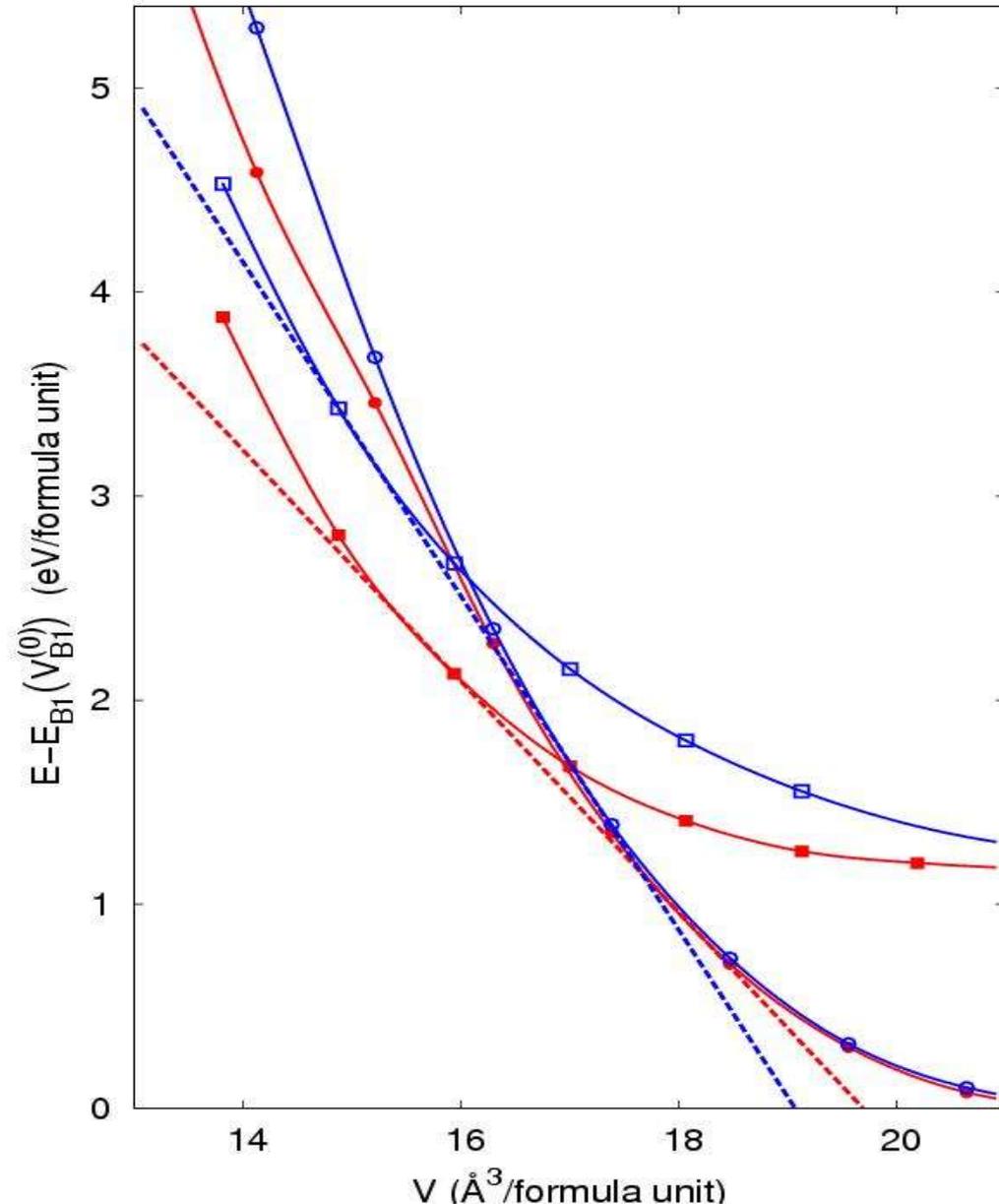
# MnO at high pressures B1 to B8 transition (J. Kolorenc, NCSU)

Comparison between  
all-electron (red) vs.  
PP (blue) calculations  
using DFT/GGA(PBE)

all-electron transition  
pressure: **43 GPa**

PP transition pressure:  
**67 GPa**

mainly DFT problem,  
read more about it in  
cond-mat/0608101  
(to appear in PRB)



# The basic input forms

**Inputs and forms:**

**a) gaussian times polynomial expansions**

**most of quantum chemistry calculations and codes  
(bodes well with gaussian basis sets)**

$$v_l(r) = \sum_i c_i r^{n_i} \exp(-\alpha_i r^2)$$

**b) generated numerically as radial meshes with agreed upon formats**

**many DFT codes, especially plane waves (qbox, qespresso, pwscf)**

**also generated by OPIUM utility**

# Pseudopotentials in condensed matter physics

**Some existing tables:**

**Bachelet Hamman Schlutter (PRB mid 80s) /DFT based, whole periodic table**

**Troullier-Martins/ DFT with better convergence in plane-wave cut off**

**Vanderbilt/DFT/"ultrasoft" additional technical improvements so that plane waves can be used**

**Easy to find: type the last name in Google Scholar**

**Alternative: existing codes to generate these, eg, OPIUM**

# Existing tables in quantum chemistry

Tables in quantum chemistry find at the gaussian basis set web page (at PNL)

[www.emsl.pnl.gov/forms/basisform.html](http://www.emsl.pnl.gov/forms/basisform.html)

- good standard for the first two rows / based on Hartree-Fock SBKJC (Stevens-Basch-Krauss)

basically whole periodic table by the Stuttgart group/Dirac-Fock

Stuttgart RLC (relativistic large core)

Stuttgart RSC (relativistic small core)

- transition metals and rare earth heavy atoms

New generation of these PPs might be coming (ask Claudia)

# Pseudopotentials in DFT and QMC: some useful papers and reviews

**Review of pseudopotentials in DFT: W. Pickett, *Comput. Physics Reports* (Google Scholar)**

**L. Mitas, E. L. Shirley, D.M. Ceperley, *J. Chem. Phys.*, Nonlocal pseudopotentials and quantum Monte Carlo, 95, 3467 (1991)**

M. Foulkes, L. Mitas, R. Needs, G. Rajagopal, *Quantum Monte Carlo for Solids*, *Rev. Mod. Phys.* 73, pp. 33-83 (2001)

D. M. Ceperley and L. Mitas, *Quantum Monte Carlo methods in chemistry*, *Adv. Chem. Phys.* Vol. XCIII, pp. 1-38, Ed. By I. Prigogine and S. A. Rice, Wiley, New York, 1996.

B.L. Hammond, W.A. Lester, Jr., and P.J. Reynolds, *Monte Carlo Methods in ab initio quantum chemistry*, World Scientific, Singapore, 1994

# More accurate and advanced PP constructions (many-body ideas)

## 1) Stuttgart group (especially Michael Dolg, U. Bonn now)

Use one-particle construction (eg, norm conservation) as a starting point.

Improve the PPs using correlated wavefunction methods (Configuration Interaction, Coupled Cluster) in such a way that PPs **reproduce energy differences** between various atomic states as closely as possible, eg,

- excited states
- positively ionized states
- negatively ionized states, etc

Some fits done to dozens of states

# More accurate and advanced PP constructions (many-body ideas) II

2) Acioli and Ceperley generalized the one-particle construction into a many-body one as follows. Instead of enforcing agreement between original and pseudo orbital they proposed to use agreement between the one-particle density matrix for all  $r > r_{\text{core}}$ .

Assume we can calculate very accurate atomic wavefunction  $\psi(R)$

$$\rho^{(1)}(r, r') = \int \psi(r, r_2, \dots, r_N) \psi(r', r_2, \dots, r_N) dr_2 \dots dr_N$$

$$\rho_{\text{all}}^{(1)}(r, r') = \rho_{\text{ps}}^{(1)}(r, r') \quad r, r' > r_{\text{core}}$$

Since the density matrix can be diagonalized in the so-called natural orbitals that effectively leads to fix agreement of natural orbitals for all-electron and pseudo cases.

Tested on the first row atoms, quite laborious method.

# Doing calculations with PPs: a few basic recommendations

- use appropriate PP
  - test or find the tests how accurate they are
  - be sure to use accurate basis sets
  - test whether PP does not affect your predictions
- if you find that PP is not good enough:
  - take more electrons from the core to the valence space
  - construct new PP
  - test vs all-electron at least for representative cases!
  - point out the differences or errors which you find so that others are aware of it
- there is no end to improvement of PP, each generation builds its own (note the aptly named code OPIUM)

# Notes to add/fix

- all states for Cu
- two figs with C orbs
- subindexes