

Pseudopotentials/effective core potentials

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CPSFM

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pseudopotentials ... difficult subject

- **highly technical**
 - **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

- total energy as a function of Z (atomic number)
- core vs valence: energy and length scales
- pseudoion: effective potential in the core + valence electrons
- QMC: **smaller total energies, significant gain in efficiency**
- evaluation of PP terms in VMC/QMC, localization, T-moves
- how do they look like
- how it is done: norm-conserving and ccECP constructions
- forms, existing tables, accuracy, errors to watch
- examples

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

self-consistent loop

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

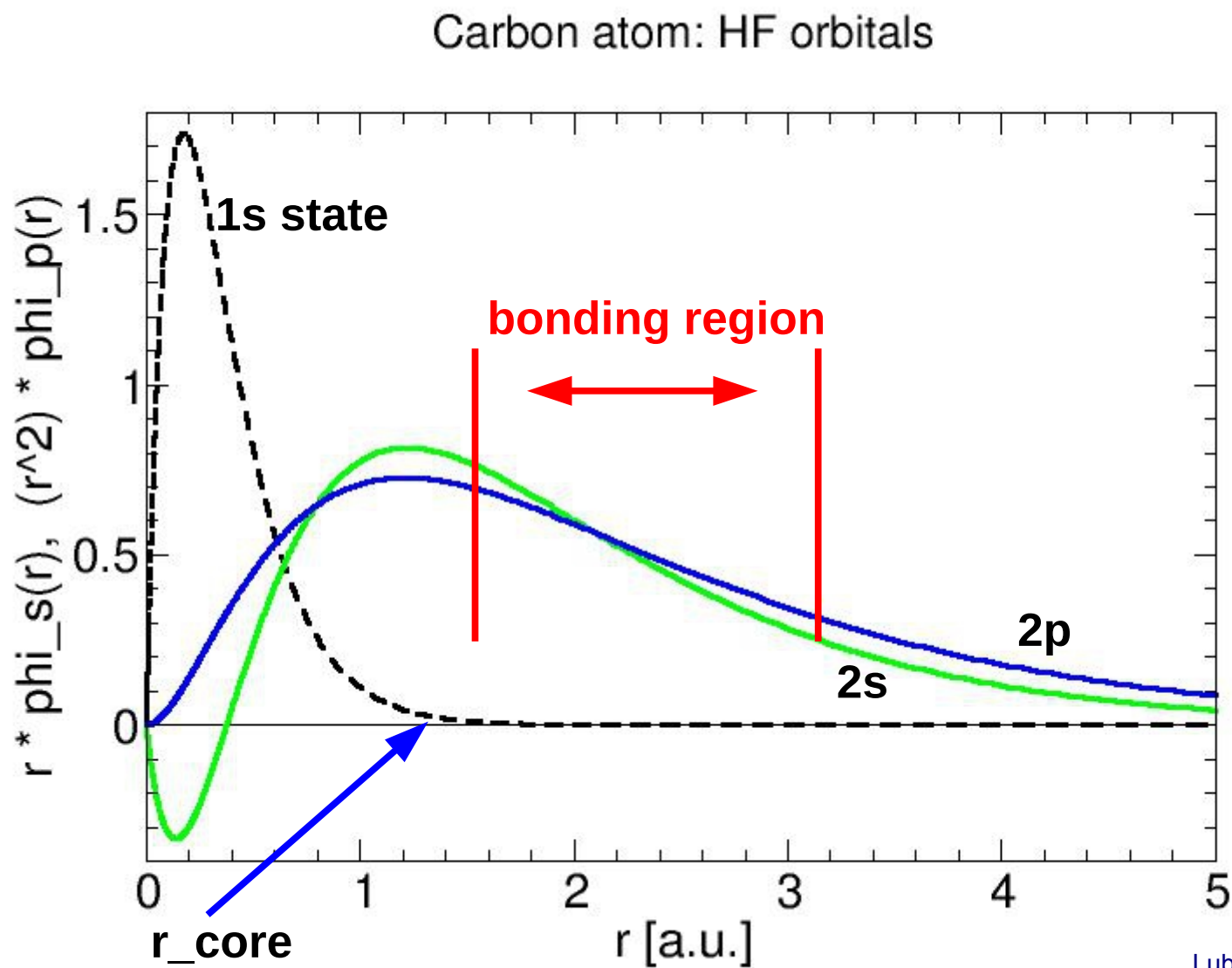
$$V_{eff}^{HF} = V_{Coul+Exch}[\{\phi_i\}]$$

core vs valence states

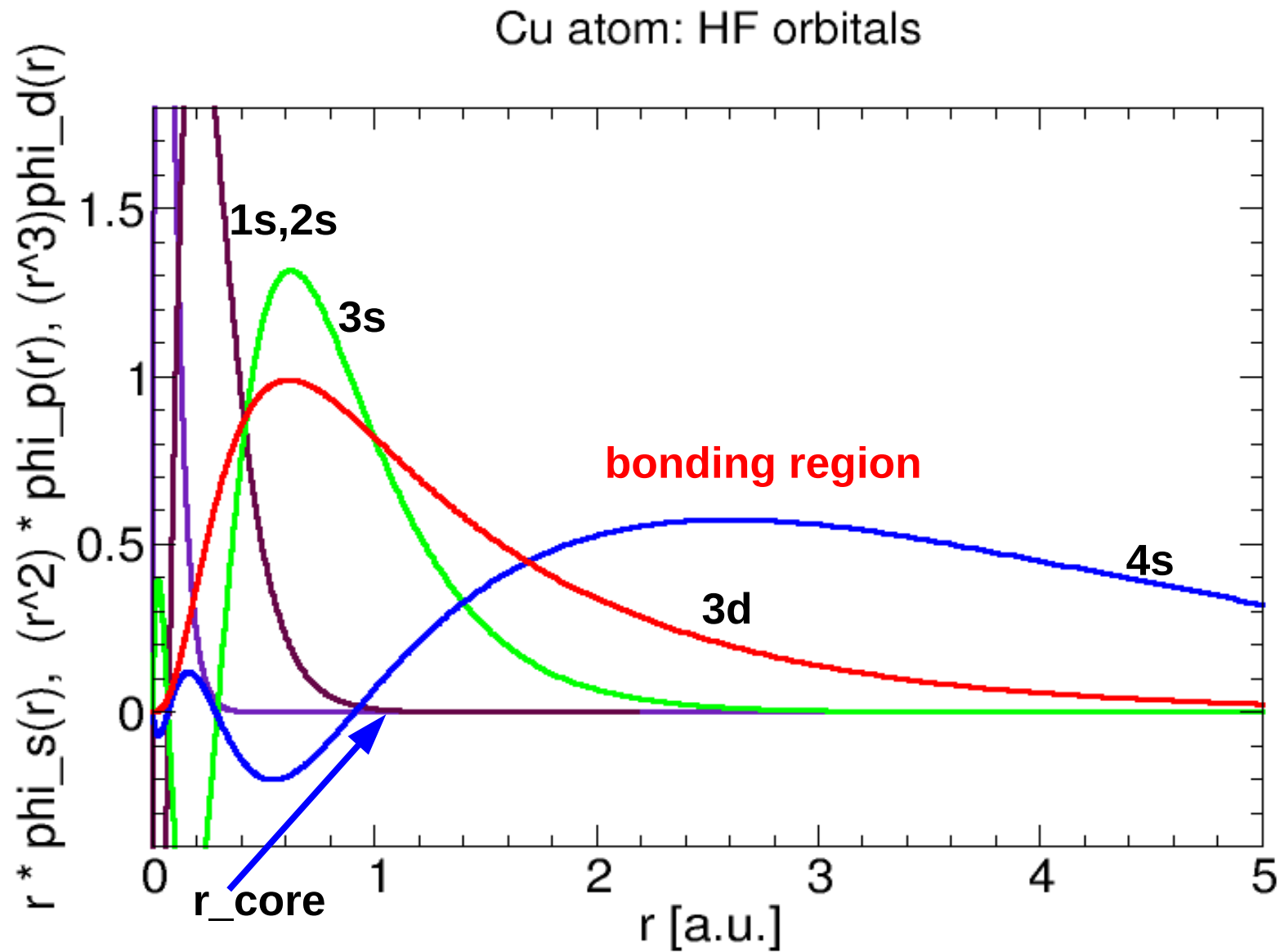
two fundamental differences:

- spatial distribution**
- energy scales**

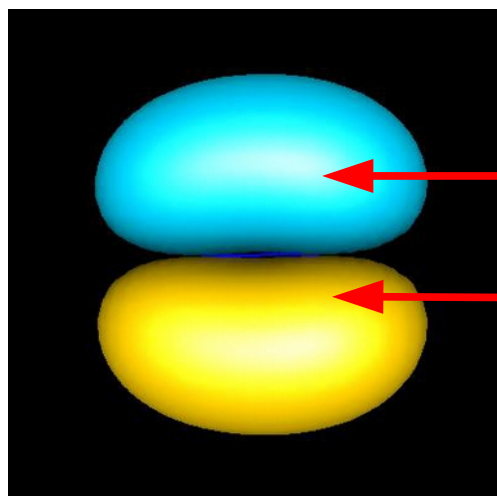
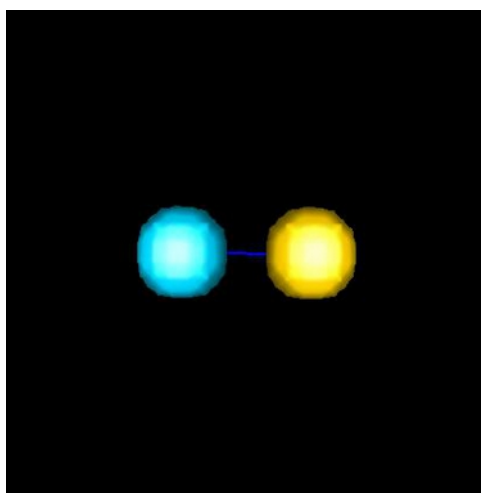
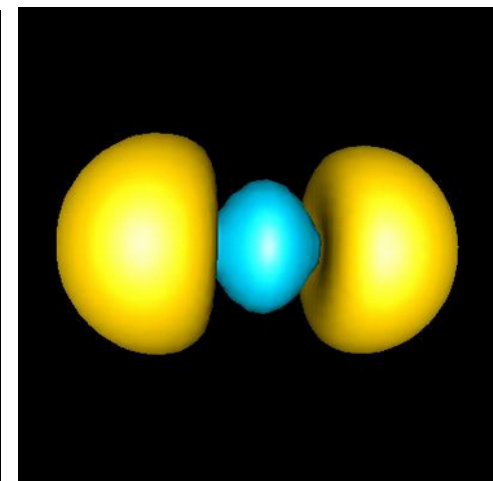
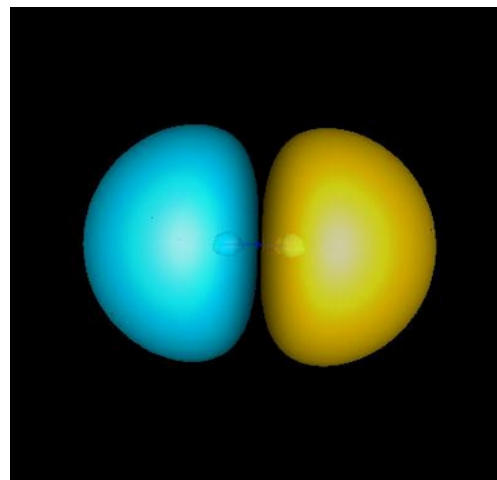
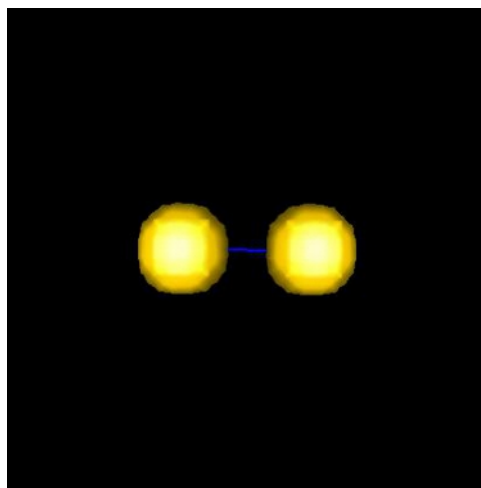
spatial range of core vs valence electrons: carbon atom



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



core vs valence in bonds: isosurfaces of molecular orbitals of C₂ dimer



—
+
valence
(hybridized, bonds)

1s core states (unchanged)

atom with nuclear charge Z : energies of one-particle states

core states qualitatively: $E_n = -Z^2/(2n^2)$, n is the principal q. number

$\sim 100 - 10^6$ eV

semicore states **$\sim 30 - 100$ eV**

valence states **$\sim 0.001 - 30$ eV**

crucial for efficiency of QMC → energy fluctuations

energy of core states scales as Z^2 , and energy variance is determined by the largest scale present!

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

efficiency of sampling of valence properties (bond energies, gaps etc) for heavy atoms therefore is **very low**

in reality: for He atom $\sigma^2 \approx 0.2$ for Cu atom $\sigma^2 \approx 100$

slowdown by a factor of ~ 500 (heavier atoms: impractical → impossible)

while we are interested in valence properties almost all the time would be spent on sampling irrelevant fluctuations in the core!!!

core – valence partitioning

- core states/electrons are rigid and affect valence electronic structure (bonds, excitations, band gaps, conductivity) only marginally
 - different energy and length scales
 - eliminate 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-)

$$W = \sum_l v_l(r) \sum_m |lm\rangle \langle lm| + v_{loc}(r)$$

dictionary and notations

in condensed matter physics: **pseudopotentials** or **PPs**
in quantum chemistry : **effective core potentials** or **ECPs**

$$W = \sum_l v_l(r) \sum_m^{l_{max}} |lm\rangle \langle lm| + v_{loc}(r)$$

$v_l(r)$ - 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 on lm ang. mom. state \rightarrow nonlocal!!!

l_{max} - number of different occupied channels \rightarrow number of nonlocal projection operators

nonlocality: (effective) potential depends of the lm -channel

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

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

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

s-channel

$$\left[T_{kin} + \underbrace{v_s + v_{loc}} + V_{eff}^{HF}(\{\phi_j\}) \right] \phi_s = E_s \phi_s$$

p-channel

$$\left[T_{kin} + \underbrace{v_p + v_{loc}} + V_{eff}^{HF}(\{\phi_j\}) \right] \phi_p = E_p \phi_p$$

etc

PPs in VMC: straightforward but numerically involved

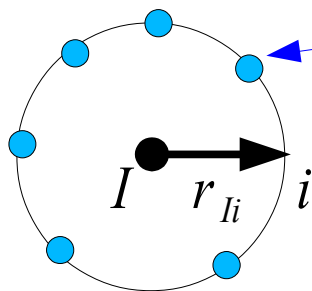
$|lm\rangle \langle lm|$ projectors are **nonlocal, ie, have off-diagonal matrix elements**

- action on a many-body trial wave function

$$W \psi = \sum_{\text{electrons } i, \text{ ions } I} \langle \mathbf{R} | W(iI) | \mathbf{R}' \rangle \psi(\mathbf{R}') d\mathbf{R}'$$

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

spherical surface integral \rightarrow numerical quadratures \rightarrow N_quad points



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

efficiency gain from pseudopotential vs accuracy Fe atom example

Fe atom \rightarrow [Ne] 3s²3p⁶3d⁶4s² = [Ar] 3d⁶4s²

	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)
σ_{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 !!!

additional important gain: scalar relativistic effects built-in pseudopots.
 \rightarrow differences are more accurate than using nonrel. all-electrons !!!

in DMC PPs/ECPs are more involved: localization approximation

- off-diagonal matrix elements imply non-local moves → could violate the fixed-node condition
- localization approximation by projection onto accurate trial function

$$W \rightarrow \frac{[W \psi_T]}{\psi_T} = W_{\psi_T, localized}(\mathbf{R})$$

- the result is a many-body effective operator, depends on the trial wf, its properties:
 - bias quadratic in trial function error, ie, converges quickly
→ zero variance property ($\psi_T \rightarrow \psi_{\text{exact}}$)
 - not necessarily an upper bound, however, small biases tend to cancel out in differences (buried in fixed-node bias)

alternative to localization approximation: T-moves → restore the upper bound property

- find out which moves break the fixed-node condition and which do not
- sample those that do not break it
- use the localization (“average \leftrightarrow spherical integral”) for those that do

$$\psi_T(\mathbf{R}) \langle \mathbf{R} | W | \mathbf{R}' \rangle \psi_T(\mathbf{R}') > 0 \quad \text{vs} \quad . . . < 0$$

properties:

- total energy is an upper bound
- but lost zero variance → even for an exact trial function there are statistical fluctuations (some increase in computational effort)

complementary: localization approximation \leftrightarrow T-moves

PP/ECP advantages

- smaller energy fluctuations (crucial)
- reduced # of degrees of freedom
- smaller/smoother bases (plane waves in particular)
- scalar relativity included, spin-orbit more straightforward

additional

-

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,
for plane waves basically impossible
- **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

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)

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

