

# Pseudopotentials/effective core potentials

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**Lubos Mitas, Gani Annaberdiyev**

**North Carolina State University**

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**CPSFM** | Center for Predictive Simulation  
of Functional Materials



## **pseudopotentials ... difficult subject**

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- **highly technical, complicated constructions**
- **often the most complicated parts of the codes**
- **typical example of well-defined, controlable, effective Hamiltonian**  
**and**
- **they save (b)illions of hours of computer time**
- **allow calculations/predictions which are otherwise impossible**

# outline

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- one-particle self-consistent methods
- core vs valence: length and energy scales, dependence on  $Z$  (atomic num.)
- (pseudo)ion: effective potential in the core + valence electrons
- QMC: impact on **total energies and fluctuations** → **efficiency gains**
- evaluation in VMC/DMC, localization approx., T-moves

## Gani Annaberdiyev's presentation:

- 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 self-consistent methods, DFT and HF

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**Density Functional Theory :**

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

**self-consistent loop**

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

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

**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**

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

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

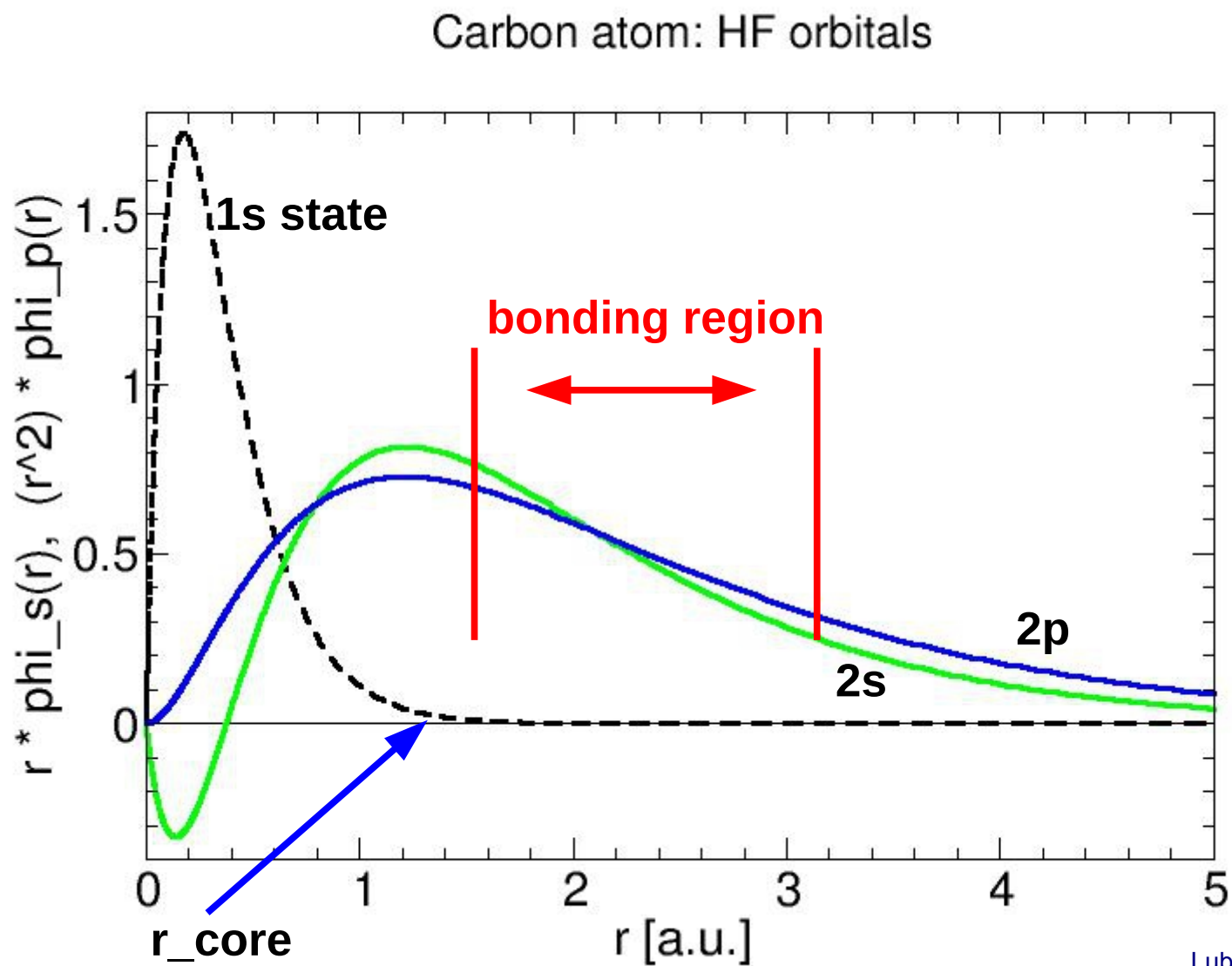
# core vs valence states

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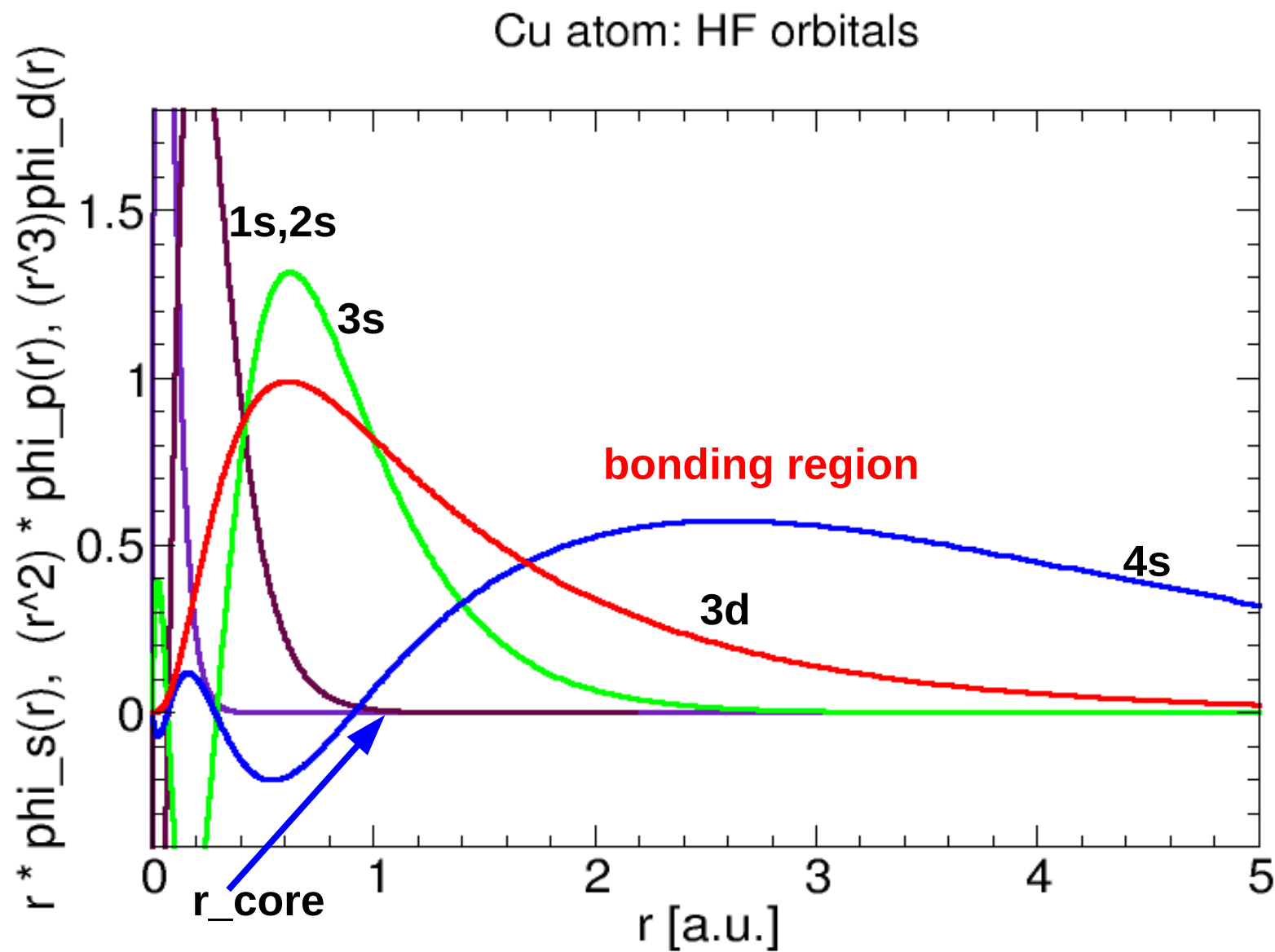
**two fundamental differences:**

- spatial distribution**
- energy scales**

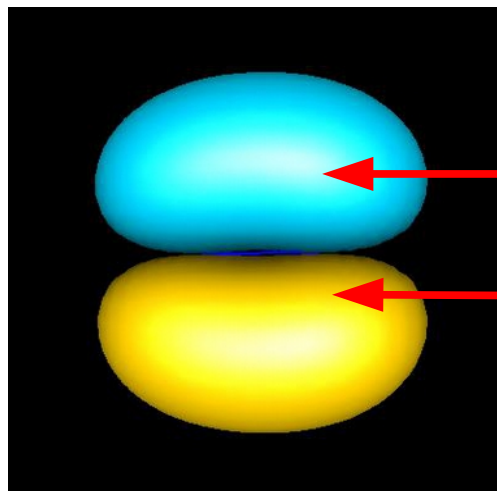
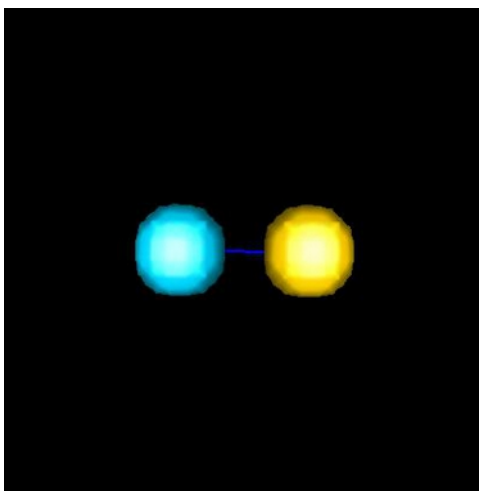
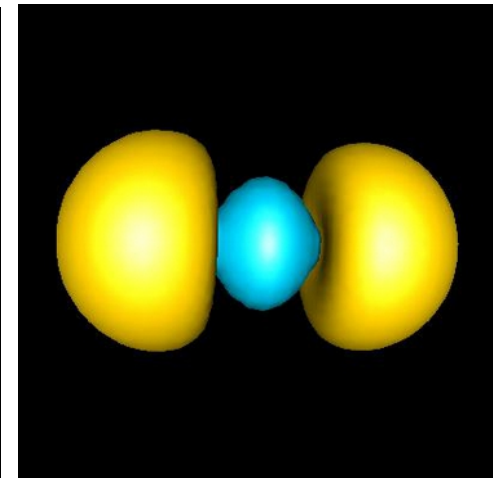
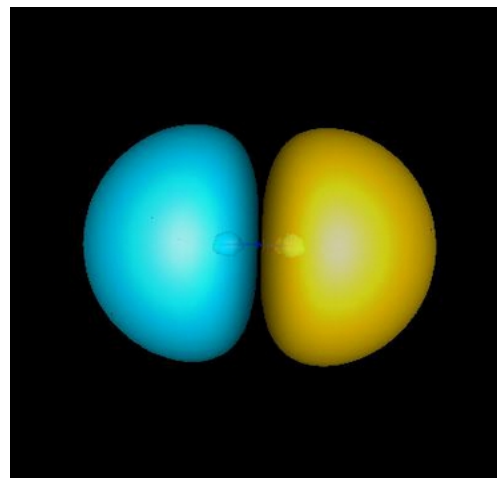
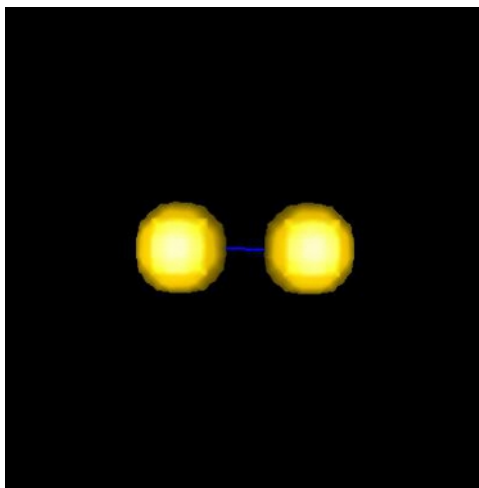
# spatial range of core vs valence electrons: carbon atom



## core vs valence one-particle orbitals: copper atom, semicore states 3s,3p



# core vs valence in bonds: isosurfaces of molecular orbitals of C<sub>2</sub> dimer



—  
+  
valence  
(hybridized, bonds)

1s core states (unchanged)



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

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**core states qualitatively:**  $\epsilon_n = -Z^2/(2n^2)$ ,  $n$  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

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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 is therefore **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

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

**Strategy:** eliminate the core states/electrons and keep only the valence!

- 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, ... 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

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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 is *lm*-dependent

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

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

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

**s-channel**

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

**p-channel**

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

etc

## PPs in VMC: straightforward but numerically involved

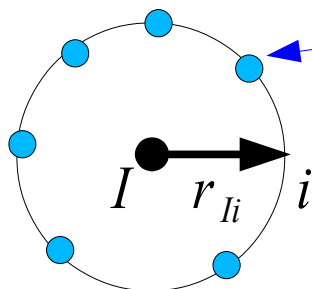
$|lm\rangle \langle lm|$  projectors are **nonlocal, ie, have off-diagonal matrix elements**

- 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] 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]	$\sim 50$	1.5	0.16
efficiency = $\frac{1}{\sigma^2 T_{decorr}}$	0.02	2.1	125
valence errors	"0"	< 0.1 eV	<b>~ 0.5 eV !!!</b>

**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

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- 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)

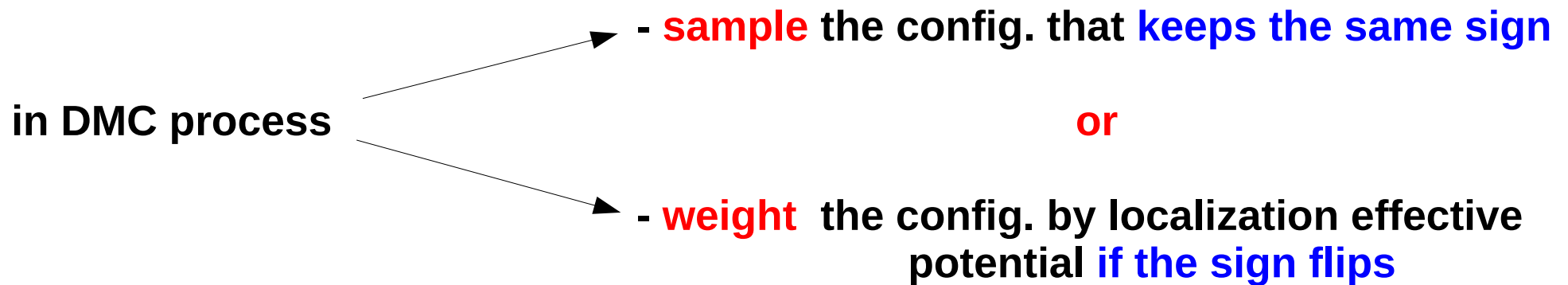


## alternative to localization approximation: T-moves → they restore the upper bound property

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- either the DMC move breaks the fixed-node condition or it does not:

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



T-moves properties:

- total energy is an upper bound
- but no zero variance → some increase in computational effort

**complementary properties: localization approximation ↔ T-moves**

## PP/ECP advantages

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

# additional

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## PPs in VMC: elimination of the numerical bias

- quadratures are such that they integrate products of spherical harmonics up to a given  $l_{\text{max}}$  exactly, eg,  $N_k=12$   $l_{\text{max}}=5$
- quadratures by V. I. Lebedev from a russian math journal
- numerical bias from the integration: to the leading order eliminated by random rotations of the quadrature points on the sphere (Fahy et al, '88)

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

