

DFT with plane waves, pseudopotentials

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Basis sets

- ★ In quantum chemistry, the base objects are the wavefunctions:

$$h_i(\mathbf{r}_m)\phi_i(\mathbf{r}_m) + [V_{ee} - V_{ex}](\mathbf{r}_m)\phi_i(\mathbf{r}_m) = \varepsilon_i\phi_i(\mathbf{r}_m) \qquad \left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}).$$

- ★ ... which we represent as linear combinations of basis functions:

$$\phi_i = \sum_{\alpha} C_{i\alpha}\psi_{\alpha}$$

- ★ This family has to be finite, limited in size
- ★ It maps a continuous problem to linear algebra:
 - ✓ Wavefunctions are vectors
 - ✓ Operators are matrices
- ★ The basis set should allow enough flexibility to represent the “real” wavefunctions

Atomic basis sets

- ★ Also called “localized basis sets”:
centered on nuclei (or sometimes ghost atoms)
- ★ Slater-types or Gaussian functions
- ★ Matches the “linear combination of atomic orbitals” ansatz;
also include “polarization” and “diffuse” orbitals
- ★ Thus, choices are:
 - ✓ Function type
 - ✓ Number of orbitals per atom
 - ✓ Including polarisation/diffuse orbitals (and how many)?

Atomic basis sets — Pros and cons

- ★ Correspond to chemical picture
- ★ Describe well the atoms, even with few orbitals
- ★ No so much harder to describe inner electrons
- ★ Easily tunable
- ★ No implicit periodicity
- ★ Non-orthogonal
- ★ Depend on atomic positions
- ★ Basis set superposition error
- ★ So many parameters... how do you optimize?

Plane-waves basis sets

- ★ We choose the basis functions as plane waves:

$$\varphi_{\alpha}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{G}_{\alpha} \cdot \vec{r}} \quad \phi_i(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} c_i(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

- ★ G is a vector of the reciprocal lattice.
For an orthorhombic unit cell:

$$\vec{G} = i \cdot \frac{2\pi}{L_x} \cdot \vec{x} + j \cdot \frac{2\pi}{L_y} \cdot \vec{y} + k \cdot \frac{2\pi}{L_z} \cdot \vec{z}$$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

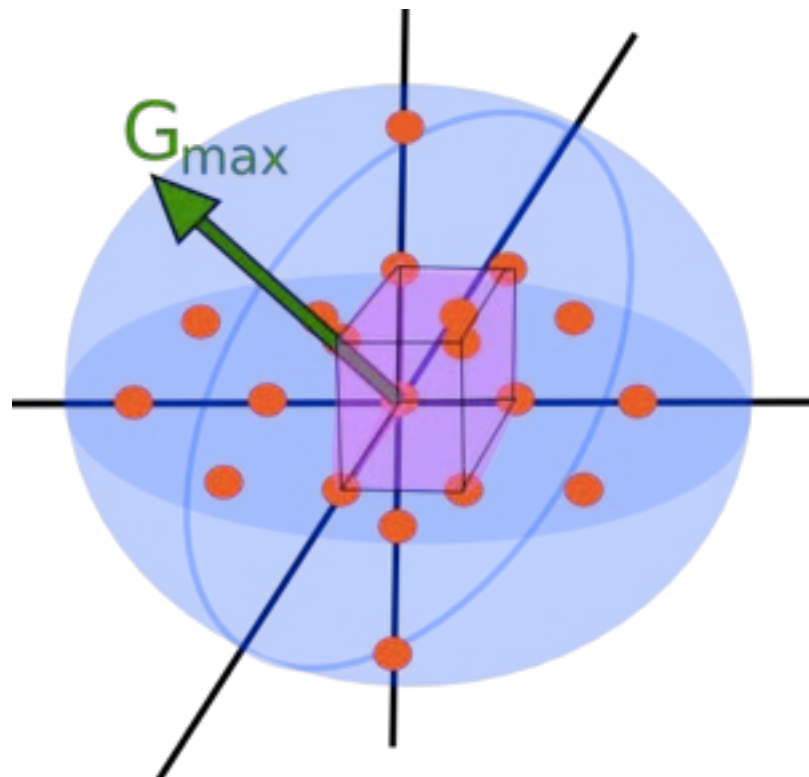
- ★ Infinite sum would be the Fourier series of the wavefunction
- ★ How many basis functions do we have?
Ruled by one parameter, \mathbf{G}_{\max}

Plane-waves sets — Pros and cons

- ★ Orthogonal
 - ★ Independent of atomic positions (no Pulay forces)
 - ★ Improving is easy: increase the cutoff
 - ★ Easy to use on any atomic type (no basis set optimization)
 - ★ Use of Fast Fourier Transform
-
- ★ Implicit periodicity
 - ★ All-or-nothing description (no spot favored)
-
- ★ Large number of basis functions needed
 - ★ How do you get back chemical information?
 - ★ Inner wavefunctions vary too rapidly:
Pseudopotentials are needed

Plane-waves basis sets

- ★ Number of plane waves used: described by an energy cutoff



kinetic energy associated with each plane wave

$$-\frac{1}{2}\nabla^2\varphi_{\vec{G}}(\vec{r}) = \frac{1}{2}\|\vec{G}\|^2\varphi_{\vec{G}}(\vec{r})$$

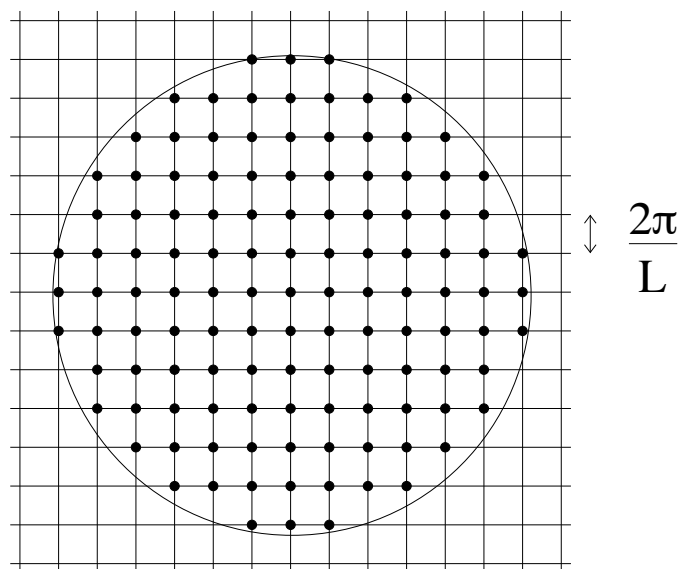
$$E_{cutoff} = \frac{G_{max}^2}{2}$$

Volume of the sphere containing all PW:

$$V_{sphere} = \frac{4\pi}{3} G_{max}^3$$

Volume of occupied by 1 single PW:

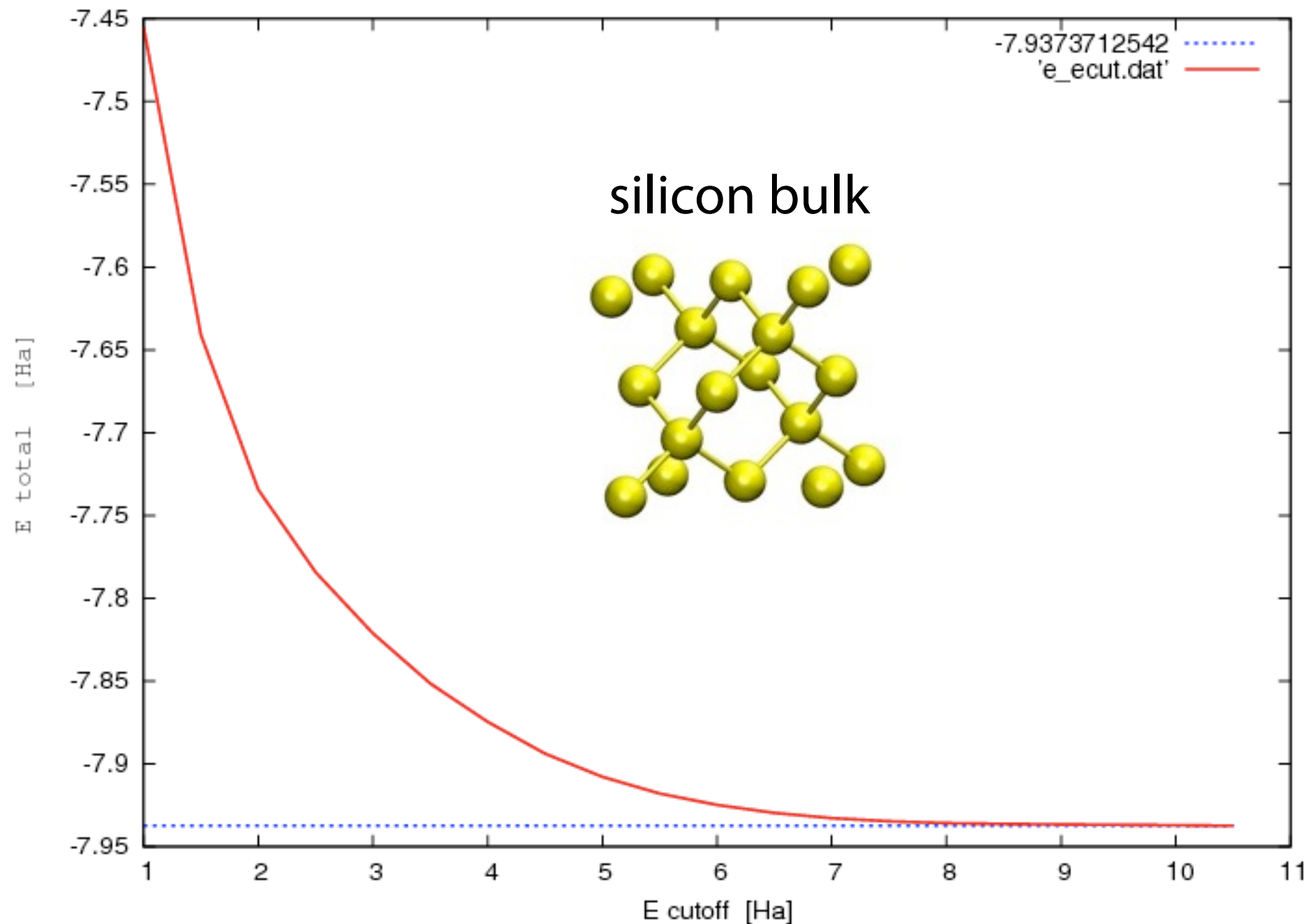
$$V_{PW} = \frac{(2\pi)^3}{\Omega}$$



$$N_G \propto \Omega E_{cutoff}^{3/2}$$

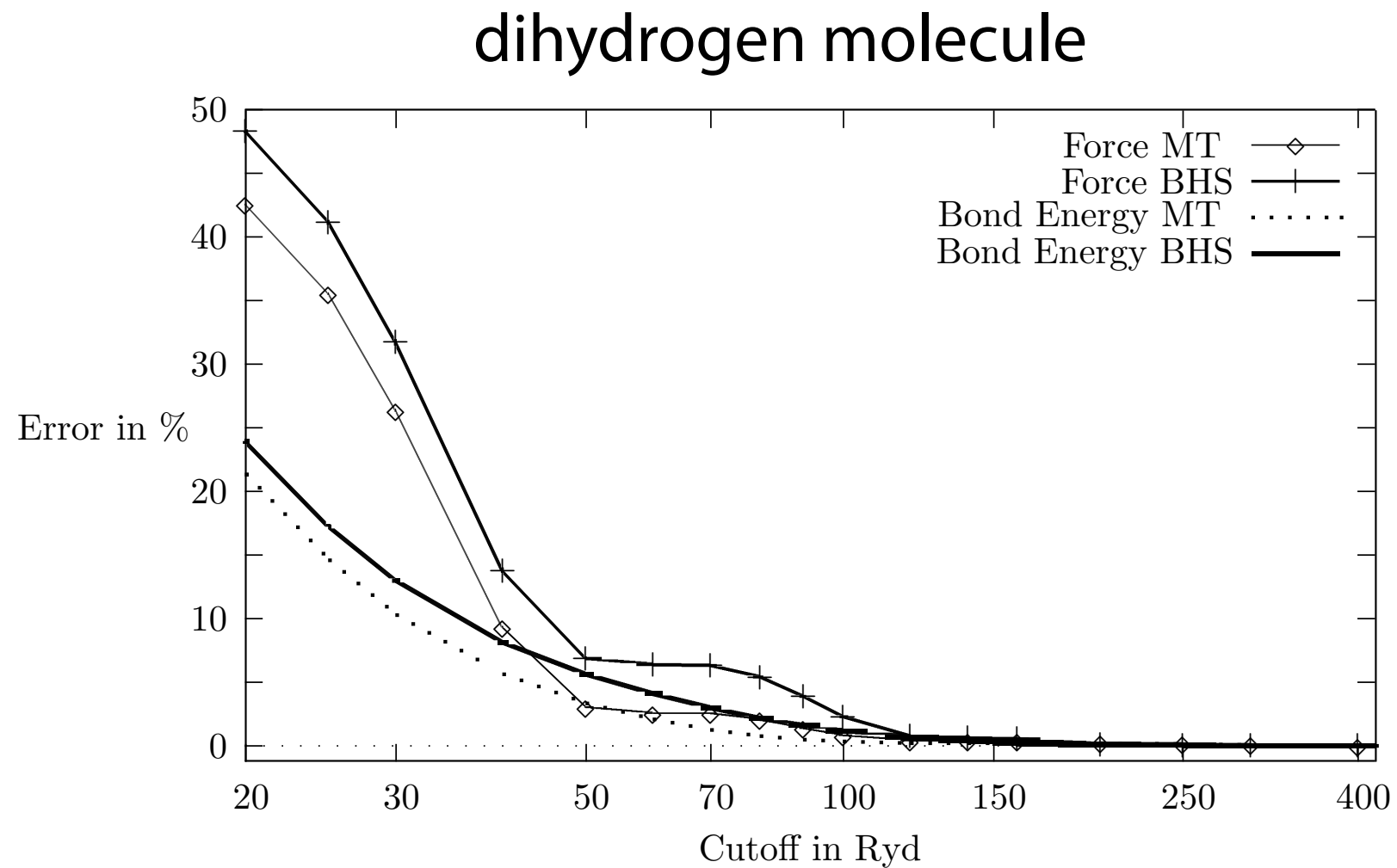
Plane-waves basis sets

★ Example of convergence



Plane-waves basis sets

★ Example of convergence



k-point sampling

- ★ Bloch's theorem:
eigenstates in a system under a periodic potential $U(r)$ can be written as

$$\phi_i(\vec{r}; \vec{k}) = e^{i\vec{k} \cdot \vec{r}} u_i(\vec{r}; \vec{k})$$

- ★ Operators such as the Hamiltonian are block-diagonal by k -point

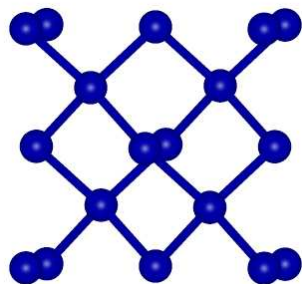
$$H = \begin{pmatrix} h_{\mathbf{k}_1} & 0 & 0 & \\ 0 & h_{\mathbf{k}_2} & 0 & \\ 0 & 0 & h_{\mathbf{k}_3} & \\ & & & \ddots \end{pmatrix}$$

- ★ Important to describe waves and correlation lengths longer than unit cell: solids (esp. conductors / semi-conductors)
- ★ What we described before: only the Γ point is sampled ($\mathbf{k} = 0$)
- ★ Use supercell to compensate for this

k-point sampling

★ Example for silicon bulk

Si₈:

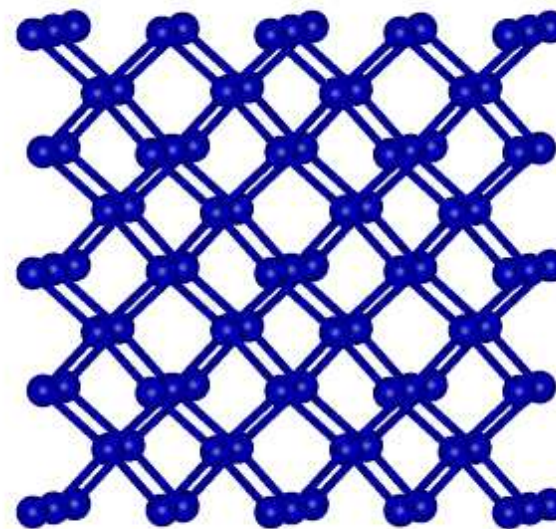


Point Γ : $E_{\text{Si}} = 3.90$ A.U.

4 points k : $E_{\text{Si}} = 3.948$ A.U.

32 points k : $E_{\text{Si}} = 3.951$ A.U.

Si₆₄:



Point Γ : $E_{\text{Si}} = 3.943$ A.U.

4 points k : $E_{\text{Si}} = 3.947$ A.U.

Fourier transforms

★ We use an auxiliary grid in real space for some calculations

★ Discrete Fourier Transform:

$$\begin{aligned}f(\mathbf{r}) &= \sum_{\mathbf{G}} \tilde{f}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \\ \tilde{f}(\mathbf{G}) &= \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{-i\mathbf{G} \cdot \mathbf{r}} f(\mathbf{r}) \\ &= \frac{1}{N_r} \sum_{\mathbf{r}_i \in \Omega} e^{-i\mathbf{G} \cdot \mathbf{r}_i} f(\mathbf{r}_i)\end{aligned}$$

★ Moving from a grid in real space: $x = \{0, 1, \dots, N\} * L/N$
to a grid in reciprocal space: $G = \{-N/2+1, \dots, N/2\} * 2\pi/L$

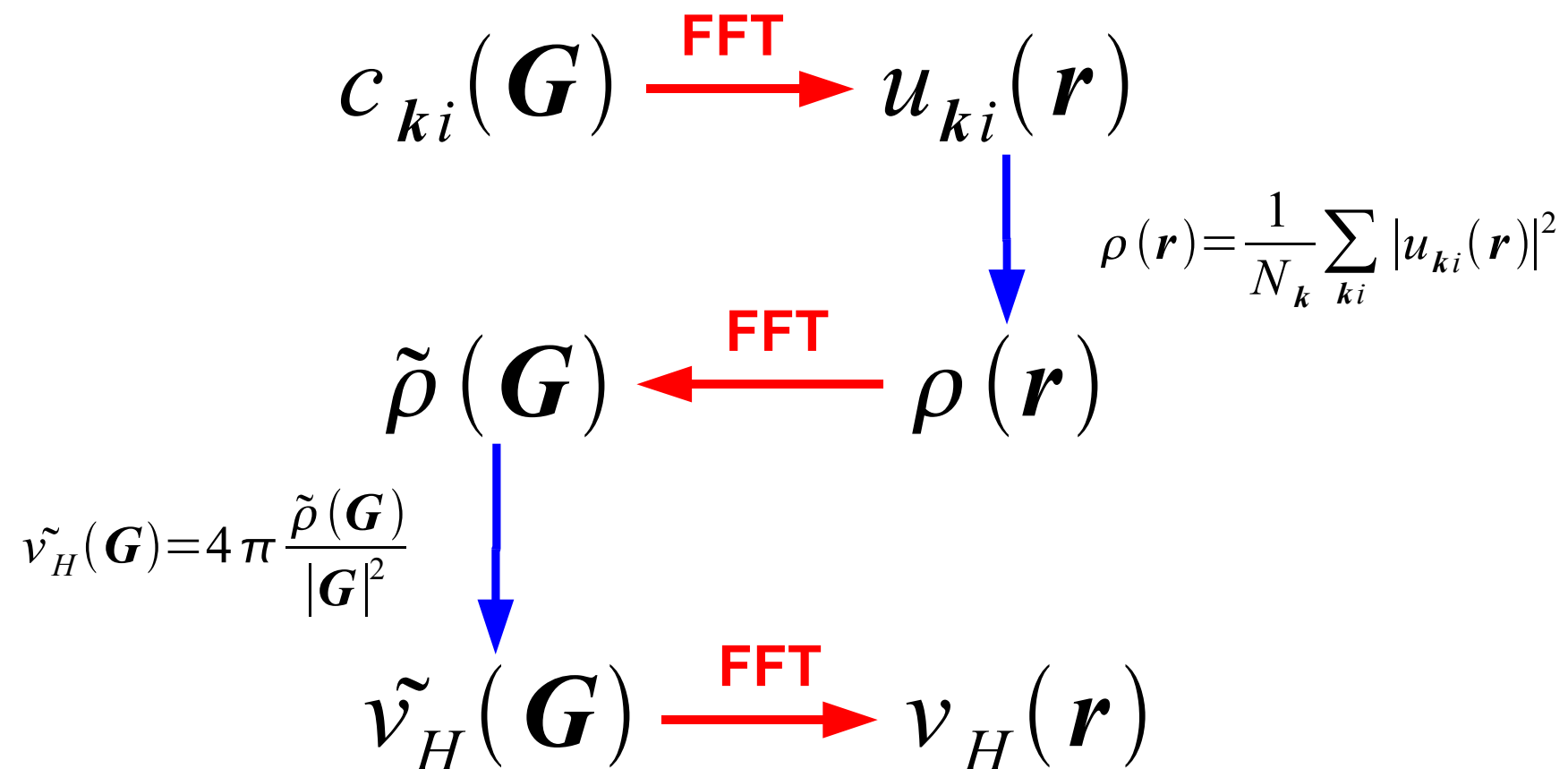
★ Transform is invertible if both have the same number of points.

★ If N is a product of small prime numbers, use FFT ($N \log N$)
instead of DFT (N^2)

Fourier transforms

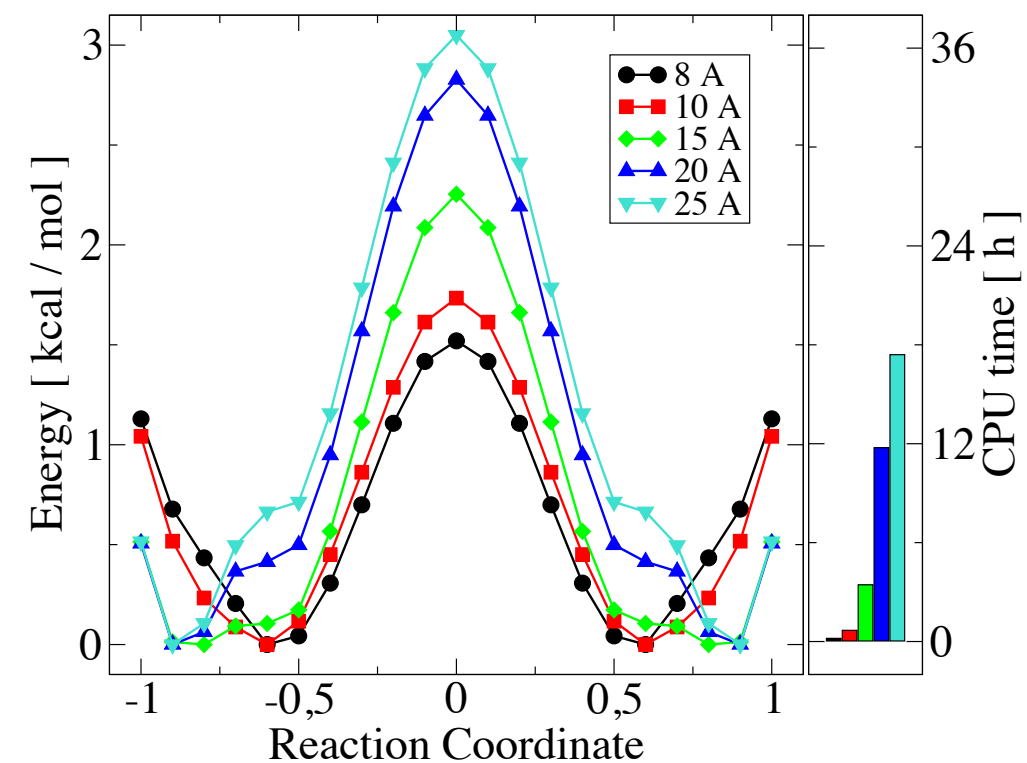
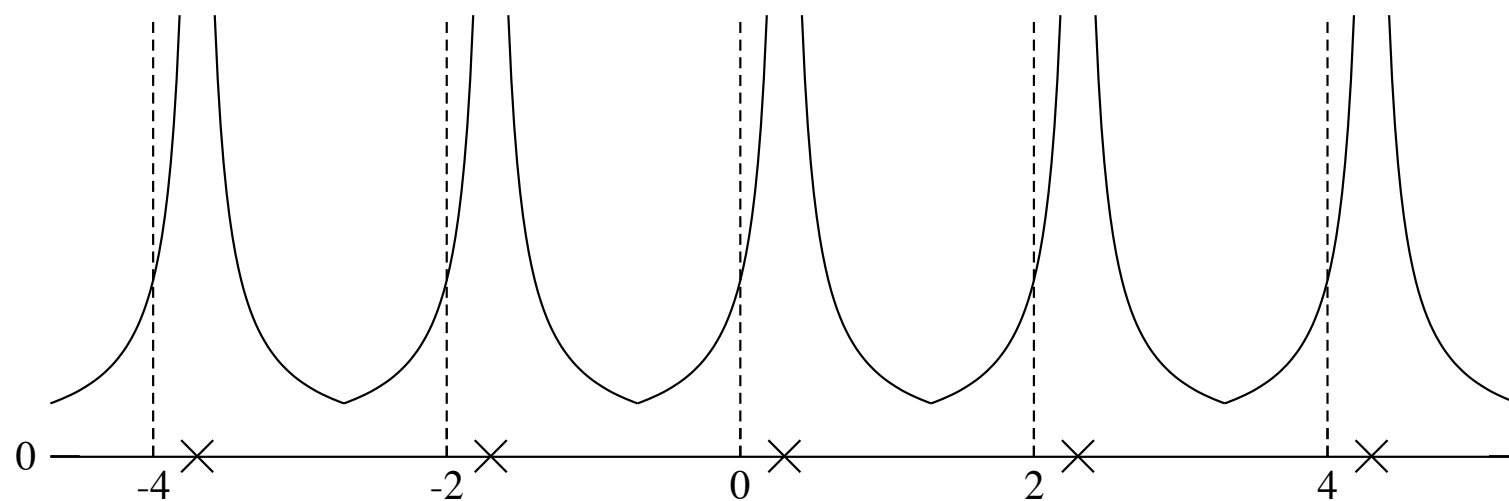
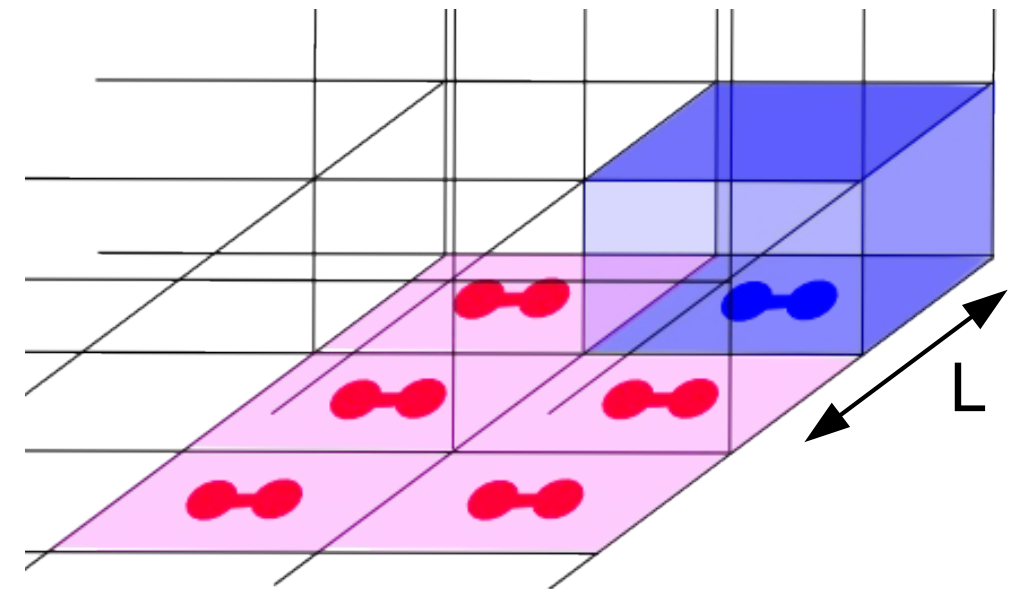
- ★ Example of the use of Fourier transforms:
calculating the Hartree potential

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



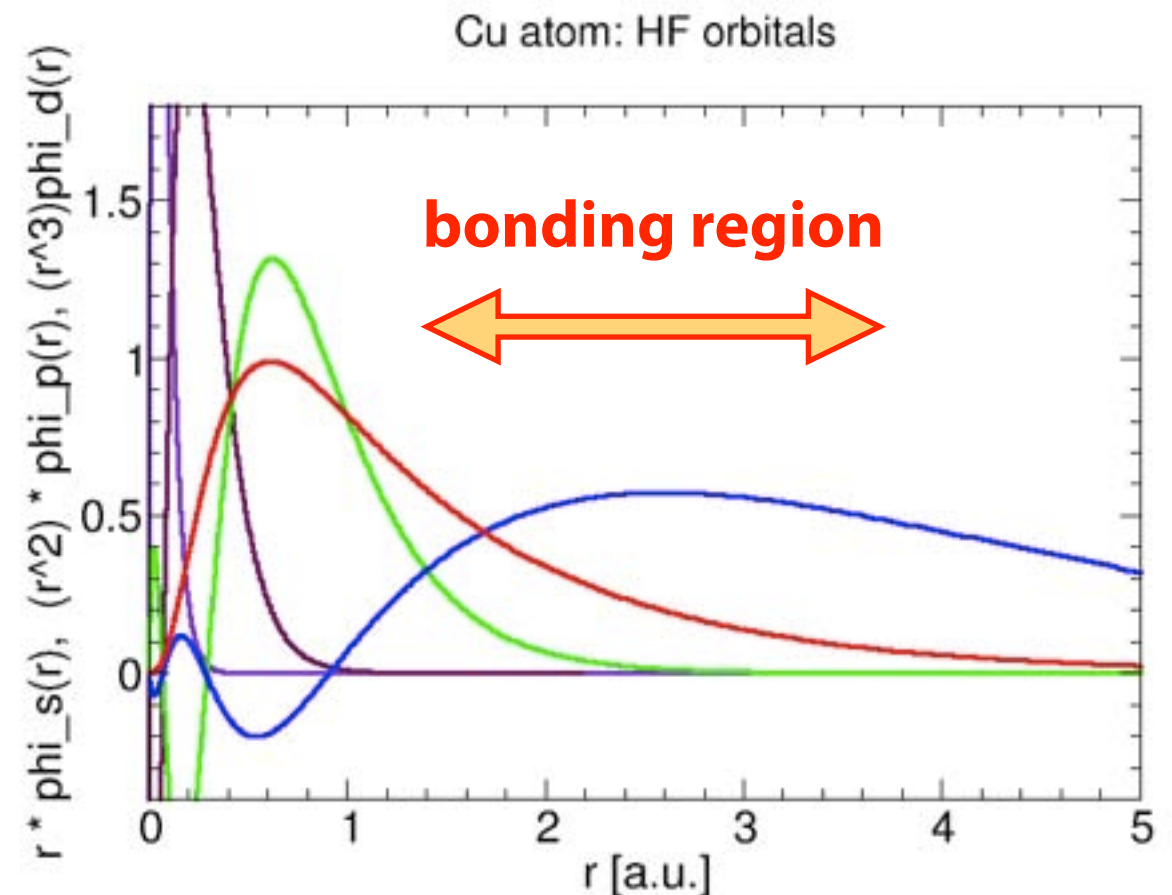
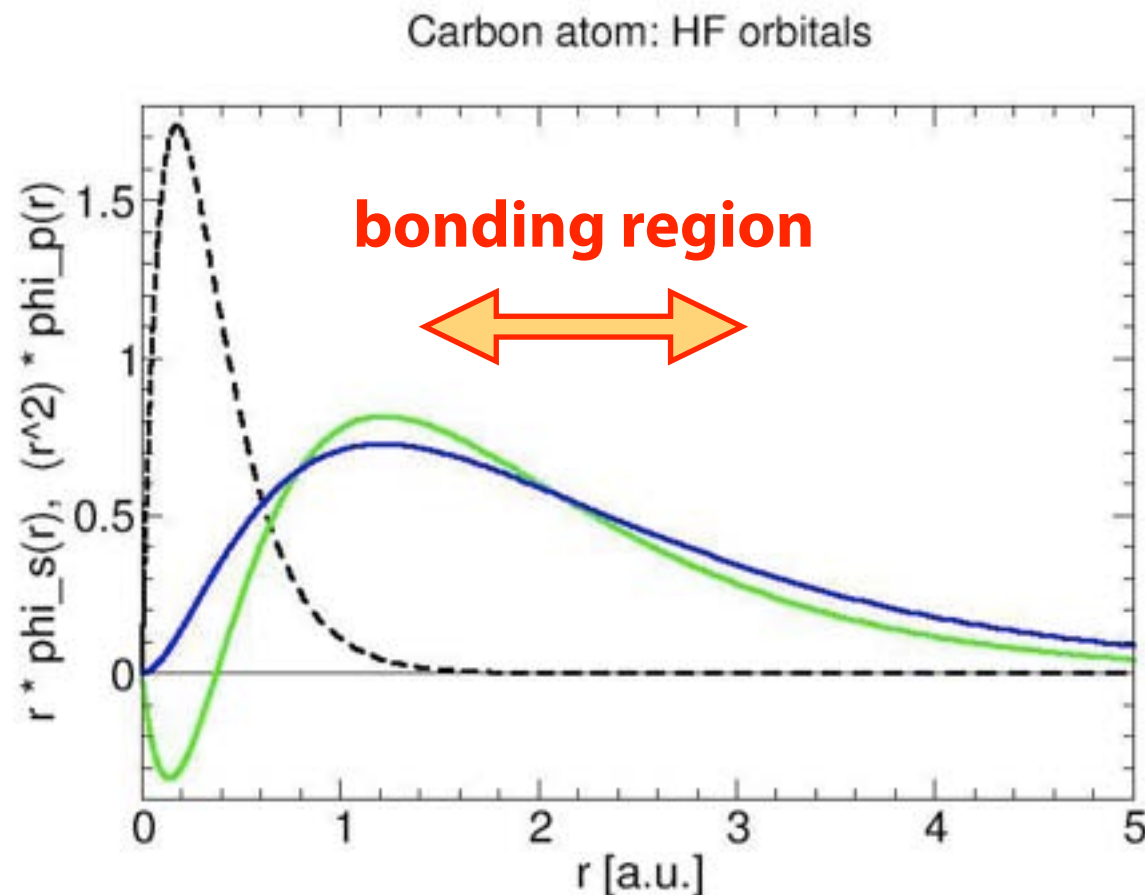
Avoiding PBC?

- ★ How to describe an isolated system with a plane-waves basis set?
- ★ Replicate the box, leave lots of space
- ★ Or truncate the Coulombic interaction using a nearest-neighbor convention



Pseudopotentials

- ★ Length scales of the core and valence electron orbitals:



- ★ Rapidly varying functions (core states) require high PW cutoff
- ★ Goal of cutoff is to "smooth things at the core"

Pseudopotentials

- ★ Core electrons do not participate in bonding, excitations, conductivity
- ★ Do not treat the core electrons explicitly any more
- ★ Instead of the nuclei Coulombic potential, use a core “nuclear + core electrons” potential,
- ★ Valence electrons will “feel” this pseudopotential

| C (Z=6) | | | Cu (Z=29) | | |
|---------|-------|--------|-----------|--------|--------|
| 2p | E_1s= | - 0.5 | 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 |
| | | | 3s | E_3s = | - 5.0 |
| | | | 2p | E_2p = | -35. |
| | | | 2s | E_2s = | - 41. |
| | | | 1s | E_1s = | - 392. |

Valence

Core

One-electron eigenstates energies (in a.u.)

Pseudopotentials

- ★ Pseudopotentials are nonlocal operators, i.e. they are not simple functions $V_{ps}(r)$
- ★ Because they represent core states, they have $s, p, d...$ components (we say "channels": they represent how they act on each symmetry-adapted projection of the valence electrons)

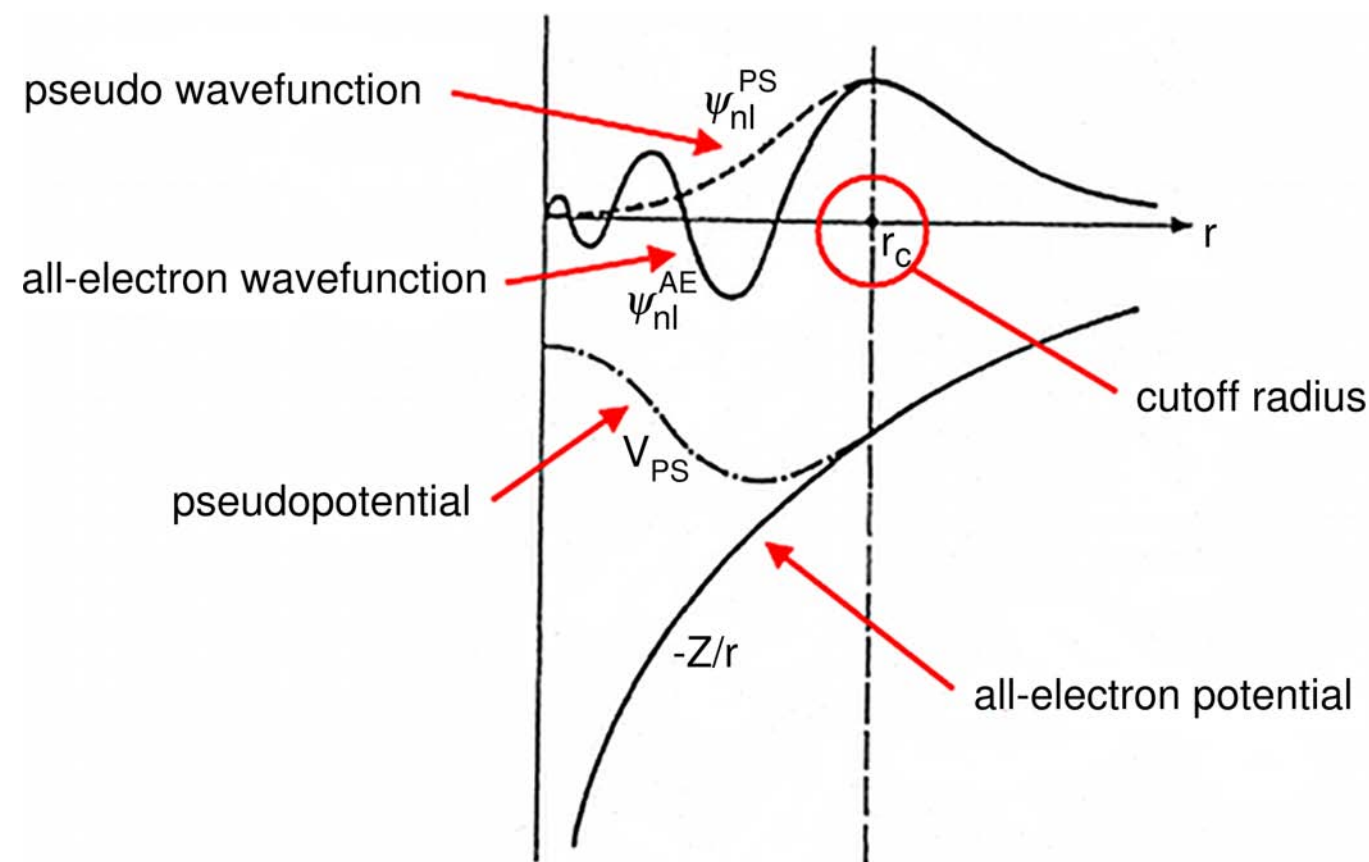
$$V_{ps-ion} = \sum_l v_l(r) \sum_m |lm\rangle \langle lm| = \sum_{l=0}^{l_{max}} [v_l(r) - v_{loc}] \sum_m |lm\rangle \langle lm| + v_{loc}(r)$$

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

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

Pseudopotentials

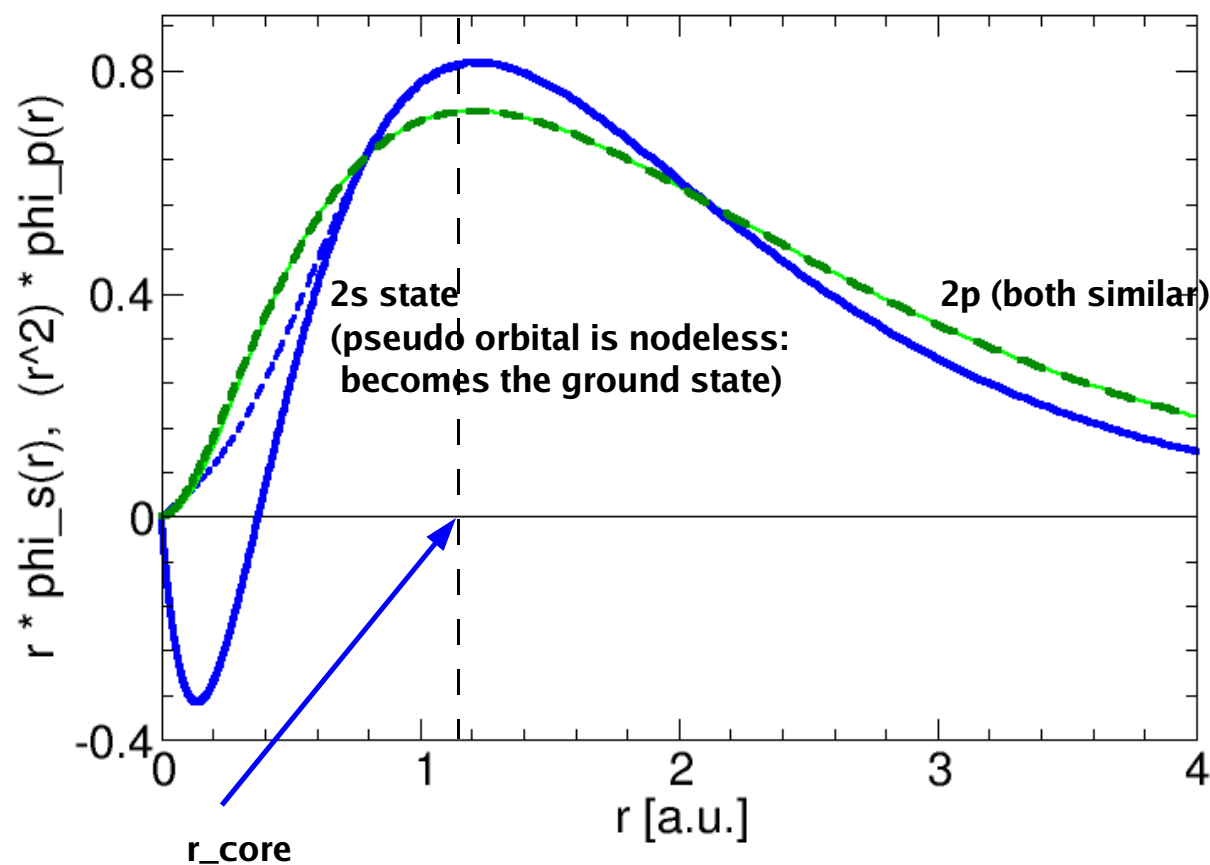
- ★ The valence states will thus be different around $r = 0$
- ★ Beyond a certain radius (r_{core}), valence states should be identical to all-electron results



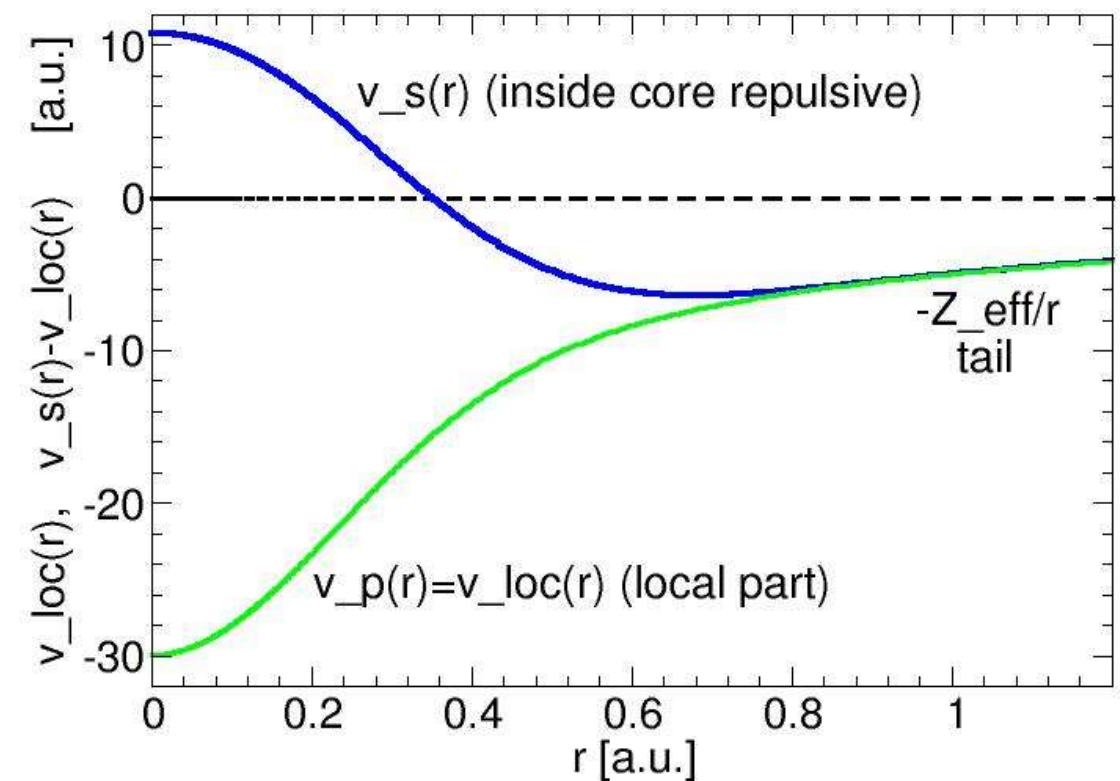
Pseudopotentials

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



Carbon atom pseudopotentials



Pseudopotentials — Pros and cons

- ★ Smaller energy, smaller cutoff
- ★ Smaller number of electrons/wavefunctions to calculate (think lanthanides)
- ★ Can include scalar relativistic effects (think lanthanides again)
- ★ Can be extended to include spin-orbit interactions (heavy nuclei)
- ★ For atomic basis sets: use basis set optimized together with PP
- ★ If your core is too fat, you describe your system badly (polarization, core relaxation)
- ★ Choice of core radius
- ★ Core–valence overlap might become larger, e.g. at high pressure
- ★ Cost of Y_{lm} projection operators (evaluated in real space)

Pseudopotentials — accuracy

★ Example: how do you choose a good core for an Fe atom?

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 !!! |

Courtesy L. Mitas, NCSU

★ Another example: Na = [He] 2s² 2p⁶ 3s¹ ; and not Na = [Ne] 3s¹

Pseudopotentials: summary

- ★ There are many families of pseudopotentials:
 - ✓ norm-conserving (conservative choice)
 - ✓ ultrasoft (lower energy cutoff)
- ★ Keep in mind:
 - ✓ pseudopotentials are technical, difficult topics
 - ✓ only an auxiliary concept
- ★ But...
 - ✓ they save a lot of CPU time
 - ✓ allow calculations otherwise impossible
- ★ **They can mess up your calculation for good...**
(but all might still look unsuspecting)