Calculation of nmr parameters in paramagnetic metal-organic materials

Jure Lapajne

10. februar 2019

Presentation plan

1. MOFs = Metal—organic frameworks

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2. NMR — what and why

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3. NMR parameter calculation

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5. Preliminary results

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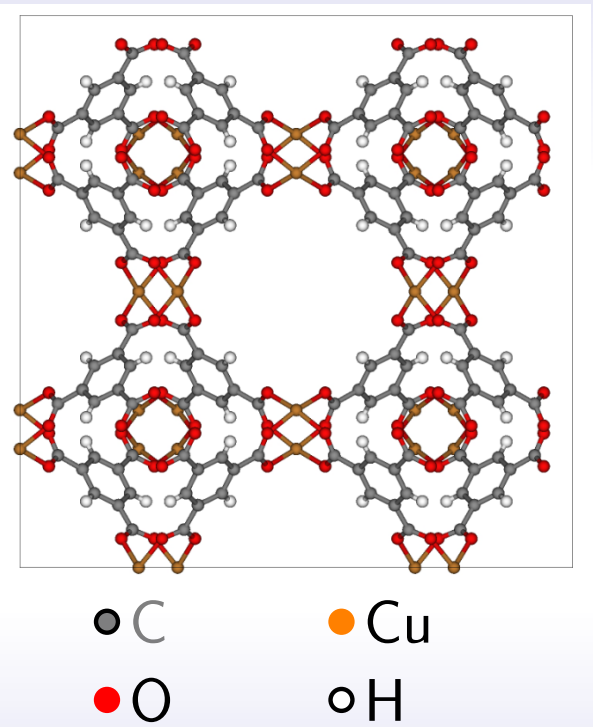
- crystal structure: central metallic ions + organic ligands



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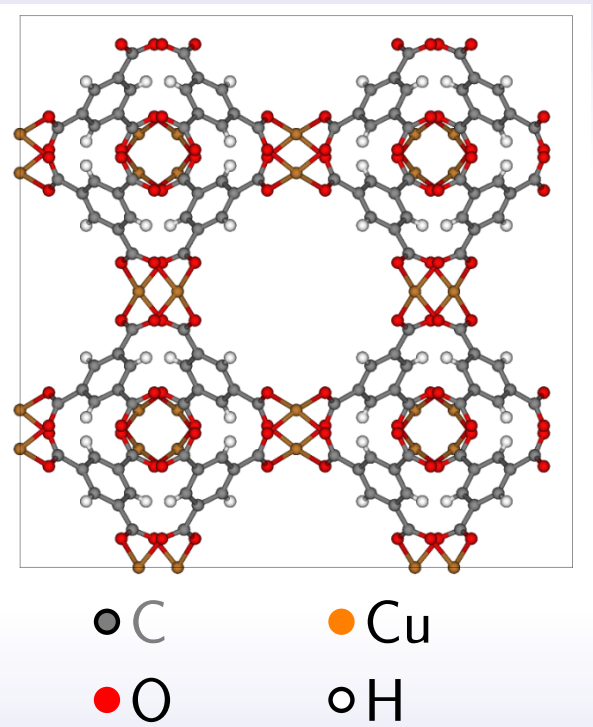
- diversity: large number of possible combinations



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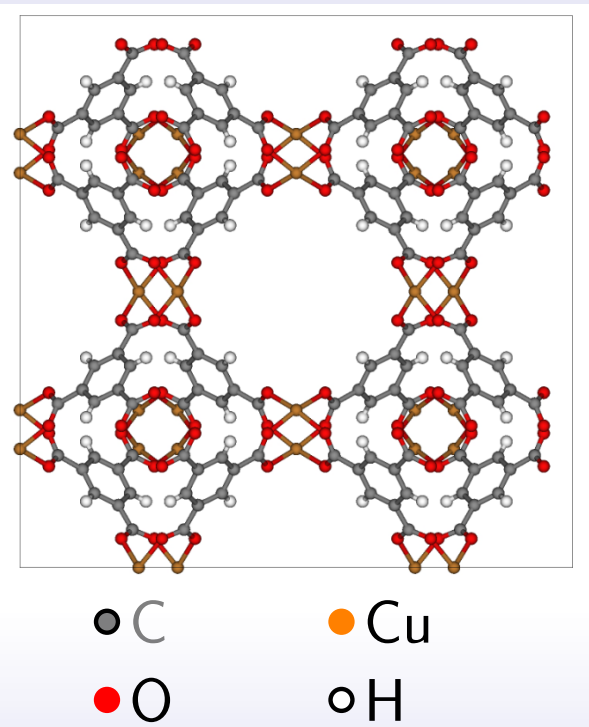

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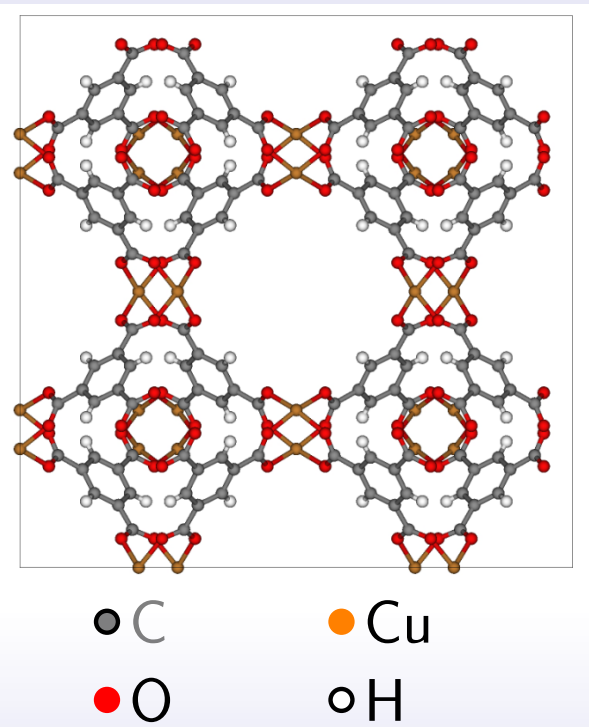

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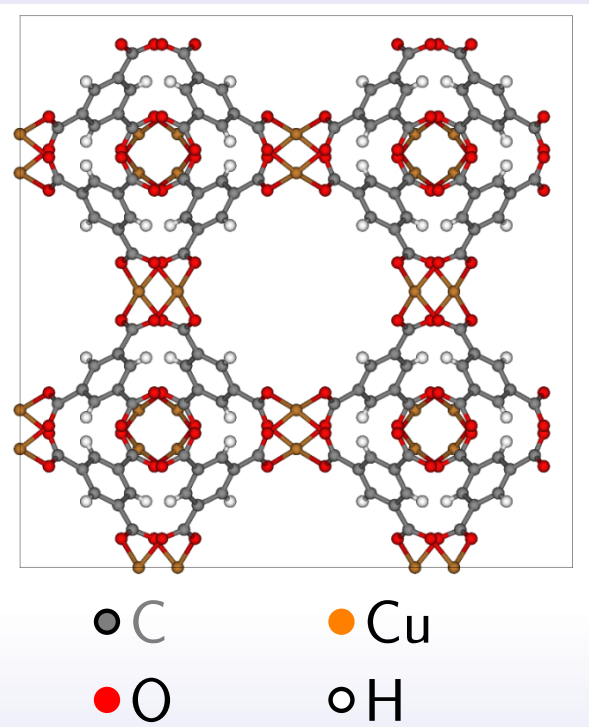
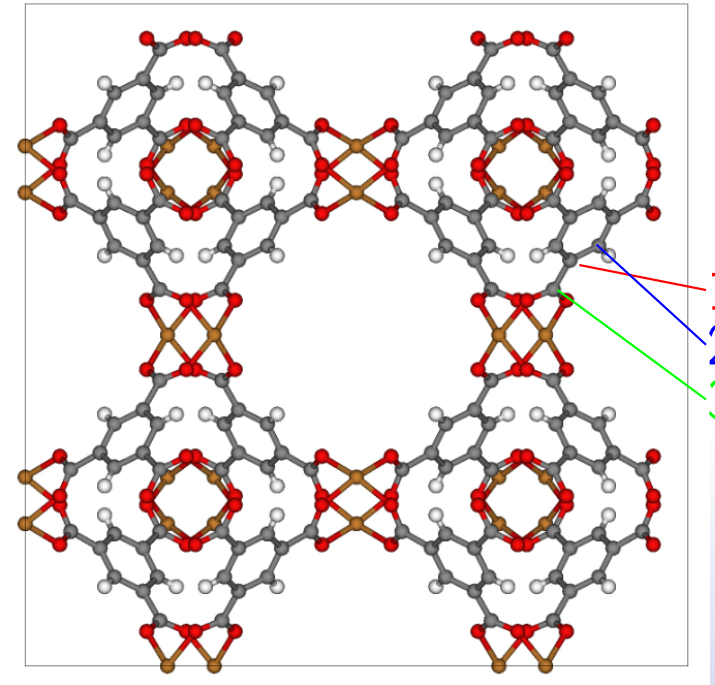
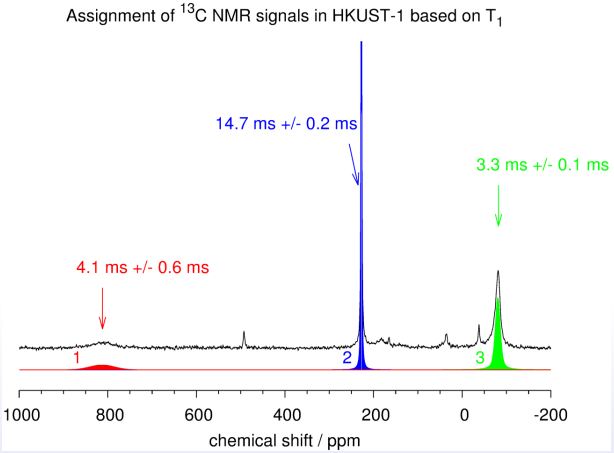
- NMR spectra feature large shifts caused by unpaired electrons



NMR spectra of MOFs

- usual organic molecules display shifts in range $[-200, 200]$ ppm
- MOF spectra display large shifts rarely seen in purely organic molecules





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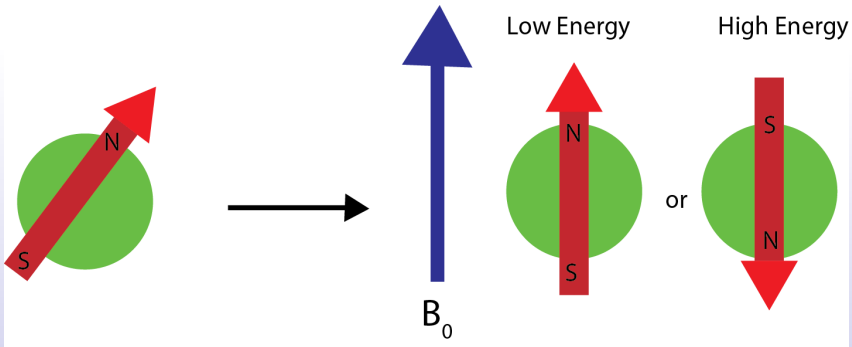

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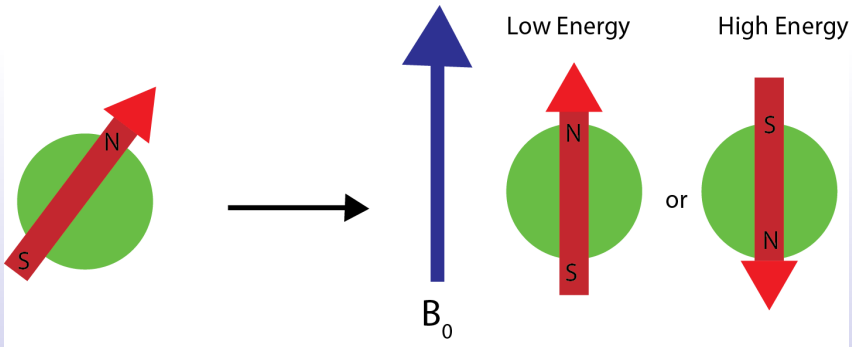

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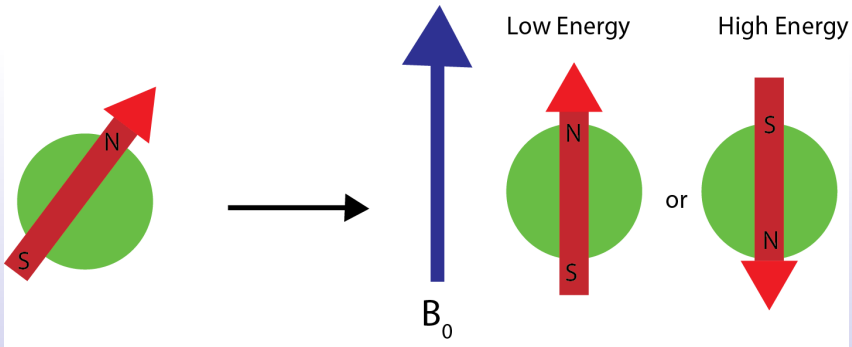

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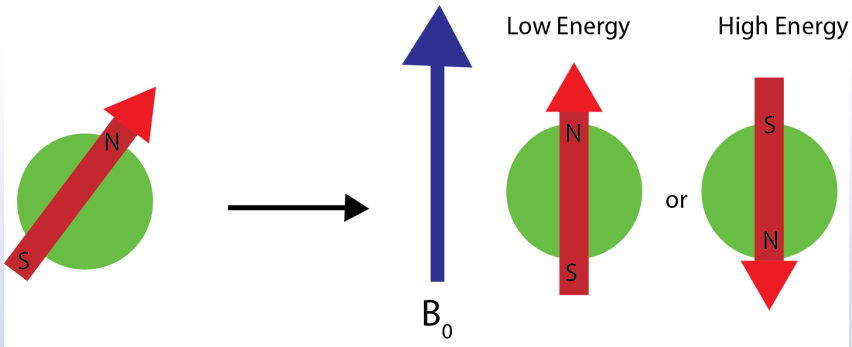
- absorption peak at $\Delta E = \hbar\omega_{res}$
- ω_{res} depends on $B_{eff}(observednucleus)$



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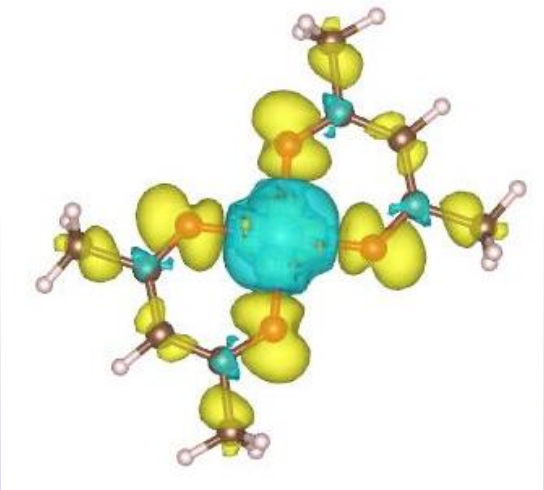

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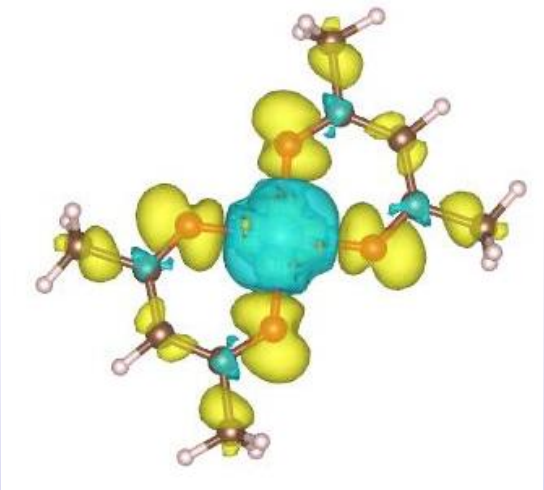

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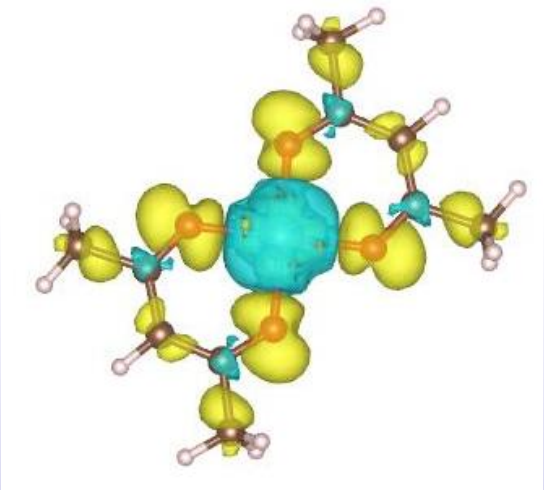

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Definition

Total shift tensor $\underline{\underline{\sigma}}$ is defined by:

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Two sources of chemical shifts:

- electron density change caused by applied external magnetic field
- depends on electron density $n(\vec{r})$
- coupling between unpaired electron and observed nuclei
- depends on spin density $n_{\uparrow}(\vec{r}_{nuclei}) - n_{\downarrow}(\vec{r}_{nuclei})$

Calculation of NMR parameters:

accurate electronic wave function needed!

electronic wave function calculation

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* Coupled-Cluster methods

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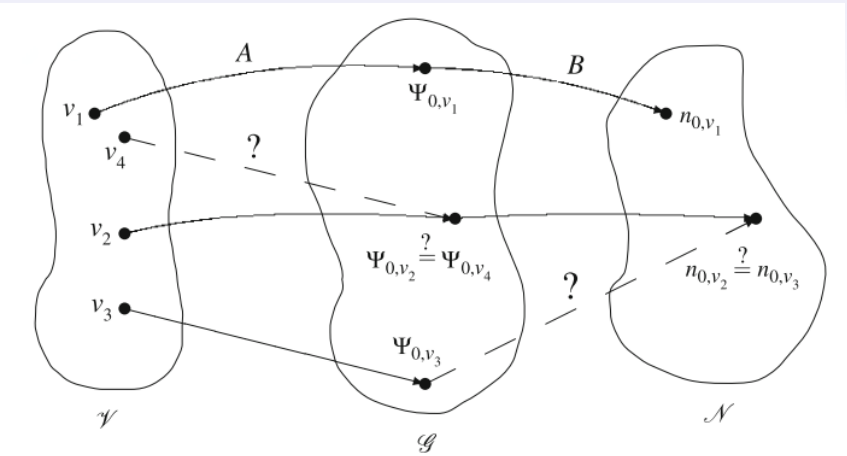
density functional theory — DFT

N-particle problem:

- DFT effectively reduces N-particle problem to 1-particle problem
- Kohn-Sham theorems: transition from $3N$ to 3 coordinates.



System of N–particles:

- bijection between the set of external potentials and corresponding non-degenerate ground states
- bijection between the set of ground states and the set of ground states electron densities

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Unfortunately the functional $\Psi[n_0(\vec{r})]$ not known!
$E[n(\vec{r})]$ is modelled emperically.

Energy functional

$E[n(\vec{r})]$ should contain:

* kinetic energy $T[n(\vec{r})]$
* coulomb interaction
* exchange – correlation term $E_{xc}[n(\vec{r})]$
* external potential

$$E_H[n] = \frac{1}{2}\int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}\mathrm{d}\vec{r}' \qquad V_{ext}[n] = \frac{1}{2}\int n(\vec{r})v_{ext}(\vec{r})\mathrm{d}\vec{r}$$

Issues:

- kinetic energy term
- Calculation on exchange-correlation part

Solution:

- use of Slater determinant
- various approaches, no general rule/solution

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solve $\left(T[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] + E_{ext}[n(\vec{r})]\right)\psi_i = \epsilon_i\psi_i$

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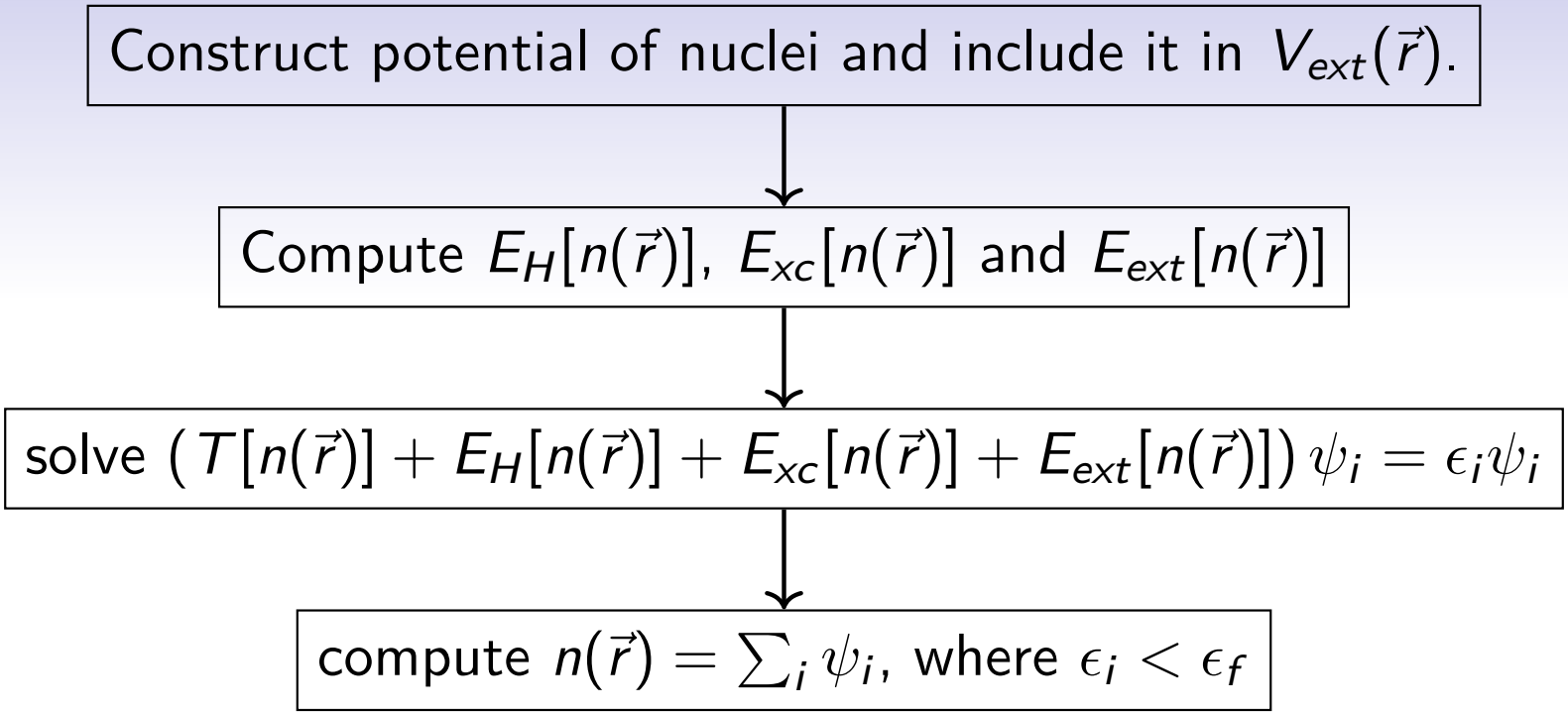

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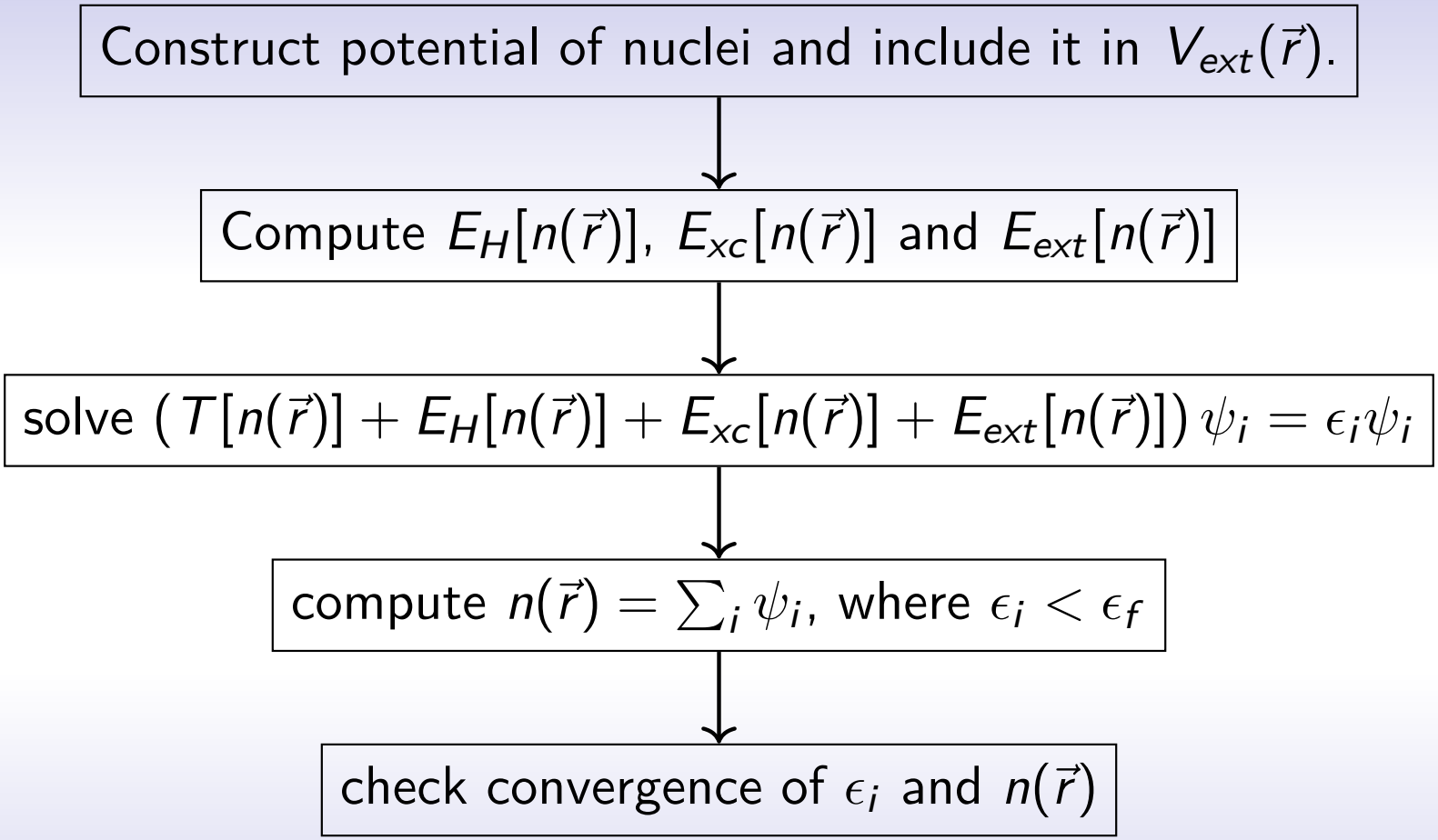

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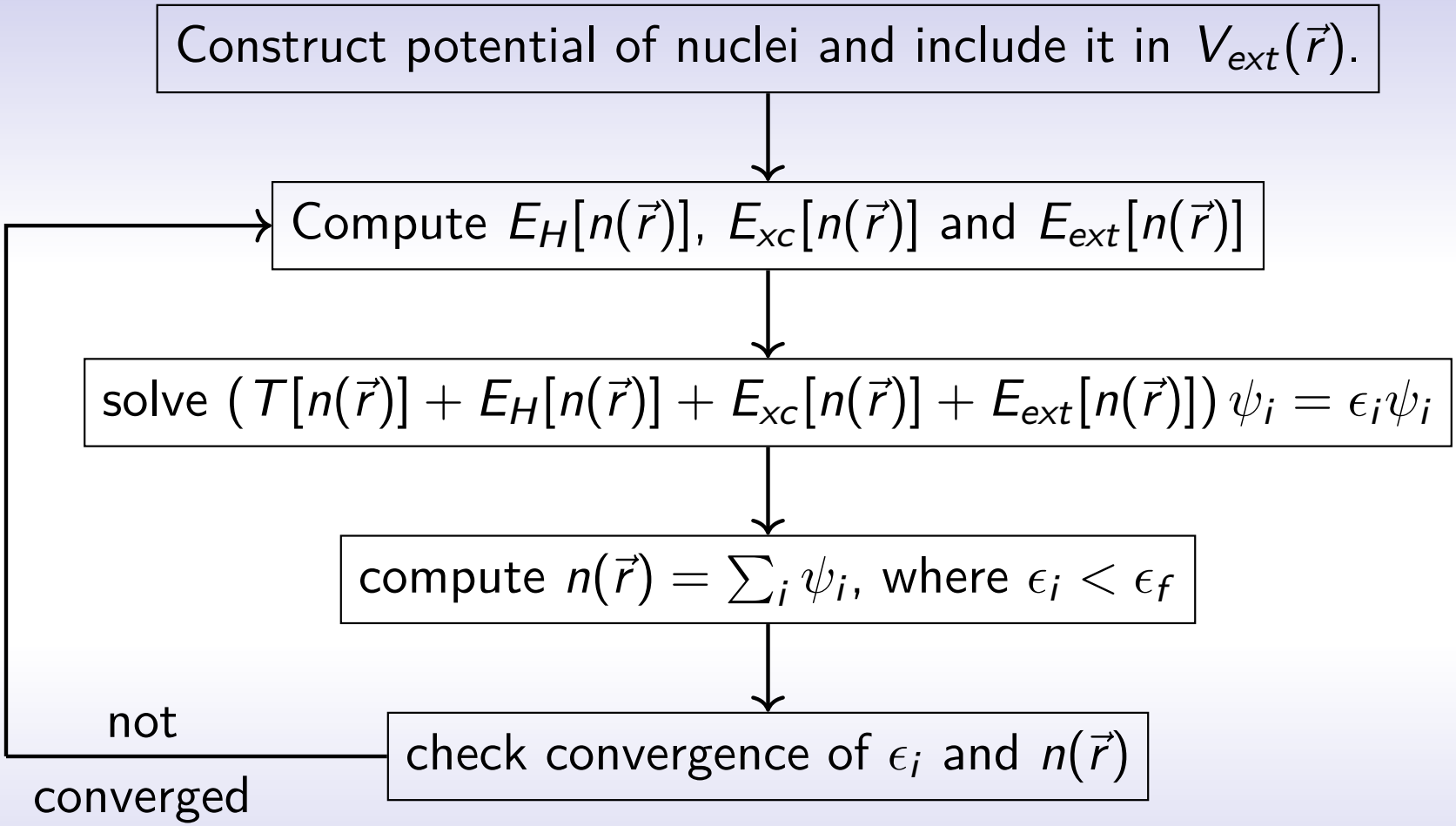

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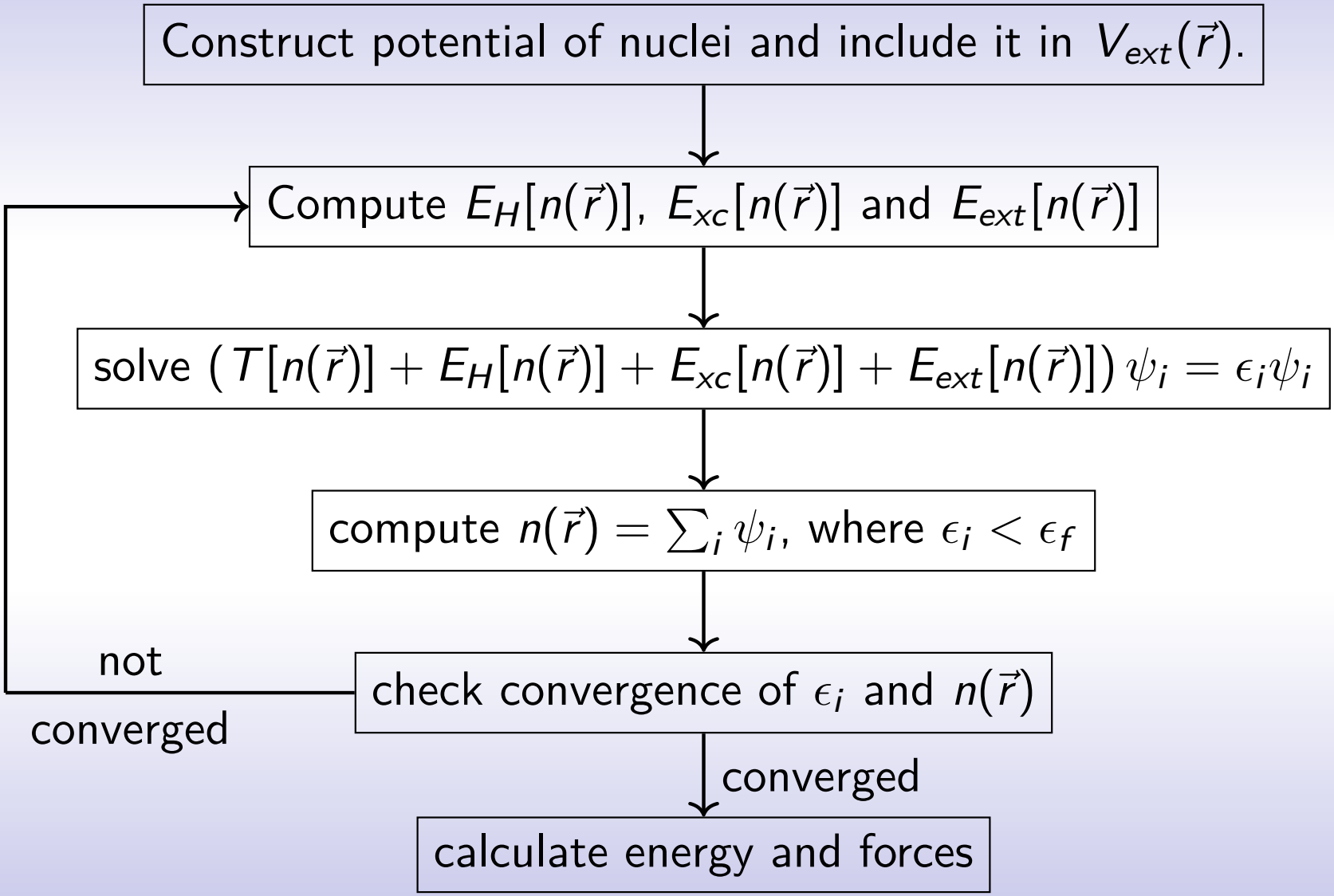

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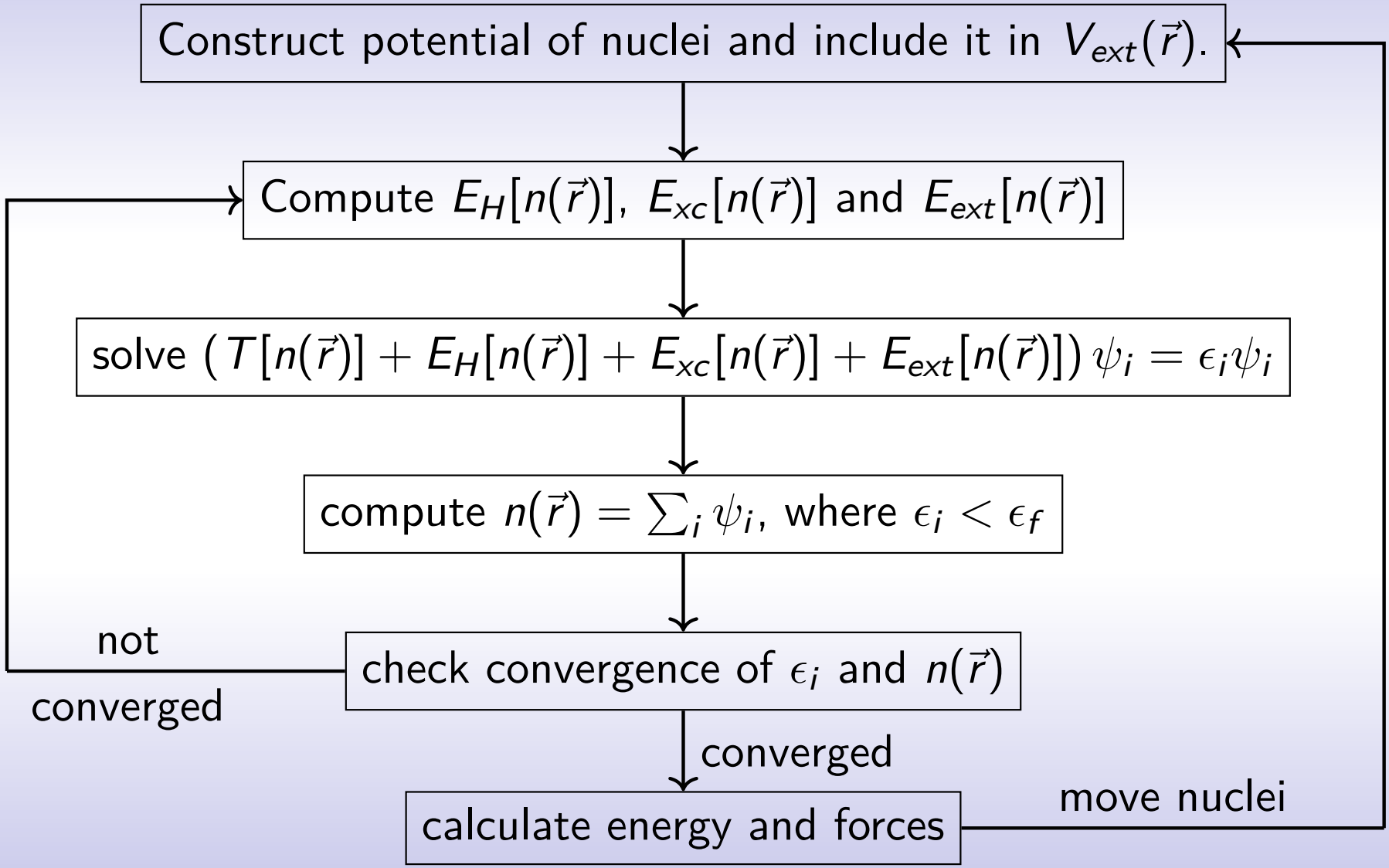
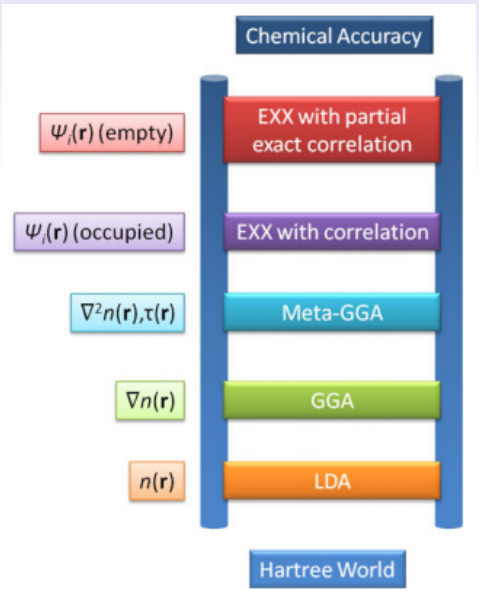


DFT flexibility

Large number of various exchange-correlation functionals:

- hybrid: GGA + hartree-fock exchange
  $-\frac{1}{2}\sum_{k,l}\int \frac{\phi_k^*(\vec{r},\sigma)\phi_l(\vec{r},\sigma)\phi_l^*(\vec{r'},\sigma')\phi_k(\vec{r'},\sigma')}{|\vec{r}-\vec{r'}|}\mathrm{d}\vec{r}\mathrm{d}\vec{r'}$
- meta–GGA: higher order derivatives
- GGA:
  $E_{xc}^{gga} = \int n(\vec{r})^{4/3} F(|\nabla n(\vec{r})|/n(\vec{r})^{4/3})$
- LDA: uniform gas
  $E_{xc}^{lda}[n] = -C\int n(\vec{r})^{4/3}\mathrm{d}\vec{r}$



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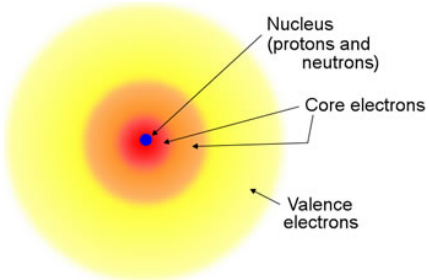

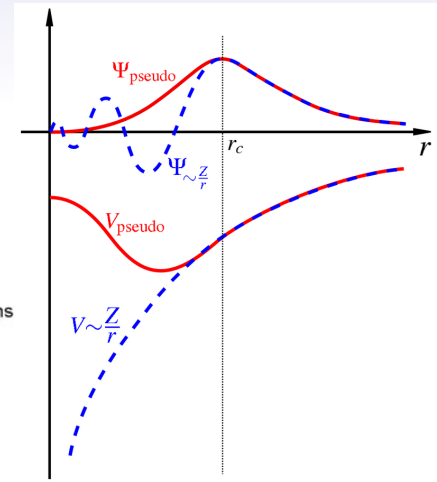

Conclusion

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