Numerical orbitals in DFT and beyond

Patrick Rinke

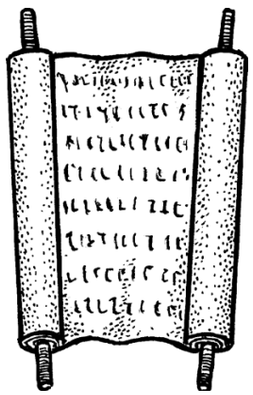
School of Science
Department of Applied Physics
Aalto University, Helsinki

Aalto University
School of Science

An important distinction

Computational Model

1. DFT is exact
2. We approximate E_{xc}
3. The approximation determines the:
   - level of sophistication
   - accuracy of results



Its numerical realisation

1. DFT equations need to be discretised.
2. Computational parameters determine the accuracy.
3. Parameters <u>should</u> not affect the result.

An important distinction

Computational Model

1. DFT is exact
2. We approximate E_{xc}
3. The approximation determines the:
   - level of sophistication
   - accuracy of results

Its numerical realisation

1. DFT equations need to be discretised.
2. Computational parameters determine the accuracy.
3. Parameters <u>should</u> not affect the result.

- Volker Blum
- Lixin He

An important distinction

Computational Model

1. DFT is exact
2. We approximate E_{xc}
3. The approximation determines the:
   - level of sophistication
   - accuracy of results

- Igor Ying Zhang

Its numerical realisation

1. DFT equations need to be discretised.
2. Computational parameters determine the accuracy.
3. Parameters <u>should</u> not affect the result.

- Volker Blum
- Lixin He

Kohn-Sham equations

KS orbitals/wave functions

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\mathrm{KS}}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

KS potential

KS eigenvalues

Density

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Kohn-Sham equations

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\mathrm{KS}}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$h_{\mathrm{KS}}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Kohn-Sham equations in a basis

Pick basis set {φ$_i$} and expand:

$$\phi_n(\mathbf{r}) = \sum_i c_{ni}\varphi_i(\mathbf{r})$$

Solve generalised eigenvalue problem:

$$\mathbf{hc}_n = \epsilon_n \mathbf{sc}_n$$

$$h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle$$

$$s_{ij} = \langle \varphi_i | \varphi_j \rangle$$

Basis function types

$$\phi_n(\mathbf{r}) = \sum_i c_{ni}\varphi_i(\mathbf{r})$$

Many basis choices:

- **plane waves or real space**
- **linear augmented plane waves (LAPW)**
- **projector augmented plane waves (PAW)**
- **local orbitals**
  - **Gaussian orbitals**
  - **numeric atom centered orbitals (NAOs)**

Basis function types

$$\phi_n(\mathbf{r}) = \sum_i c_{ni}\varphi_i(\mathbf{r})$$

Many basis choices:

- **plane waves or real space**
- **linear augmented plane waves (LAPW)**
- **projector augmented plane waves (PAW)**
- **local orbitals**
  - **Gaussian orbitals**
  - **numeric atom centered orbitals (NAOs)**

Atom-centred basis functions

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

radial function

spherical harmonic

Atom-centred basis functions

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

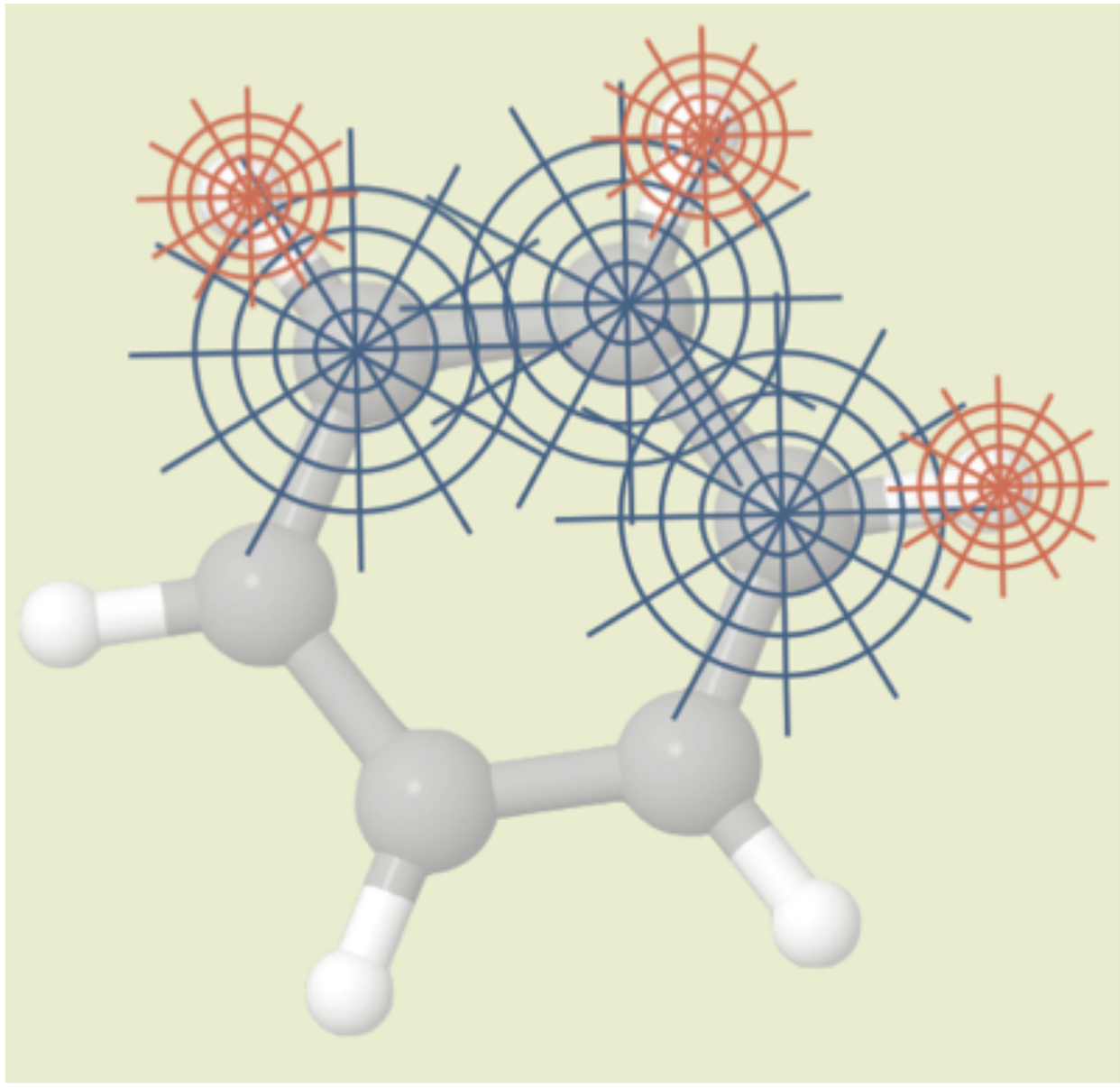
radial function

spherical harmonic

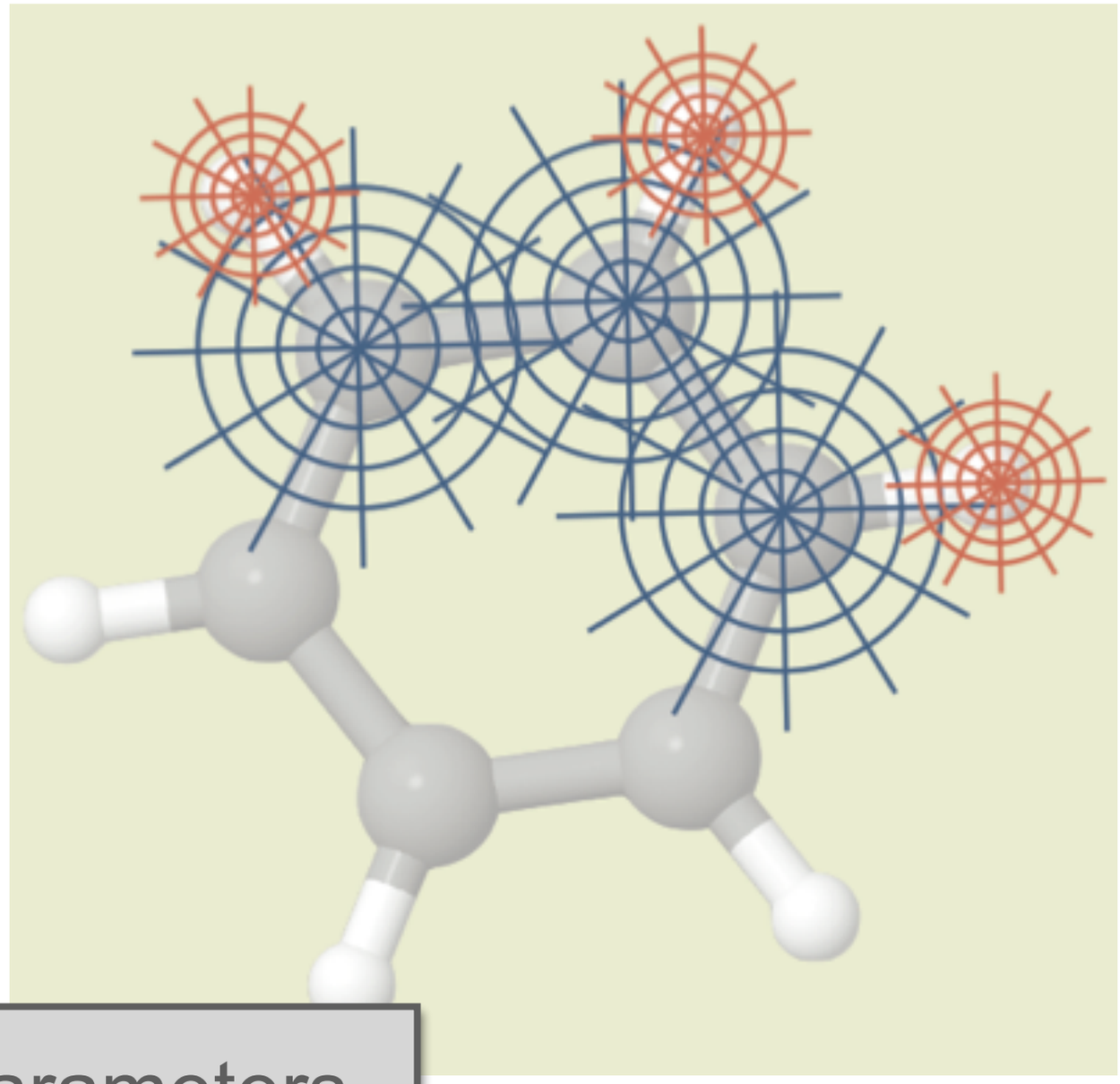
solution of a radial Schrödinger equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}} \right] u_i(r) = \epsilon_i u_i(r)$$

Real-space grid for basis functions

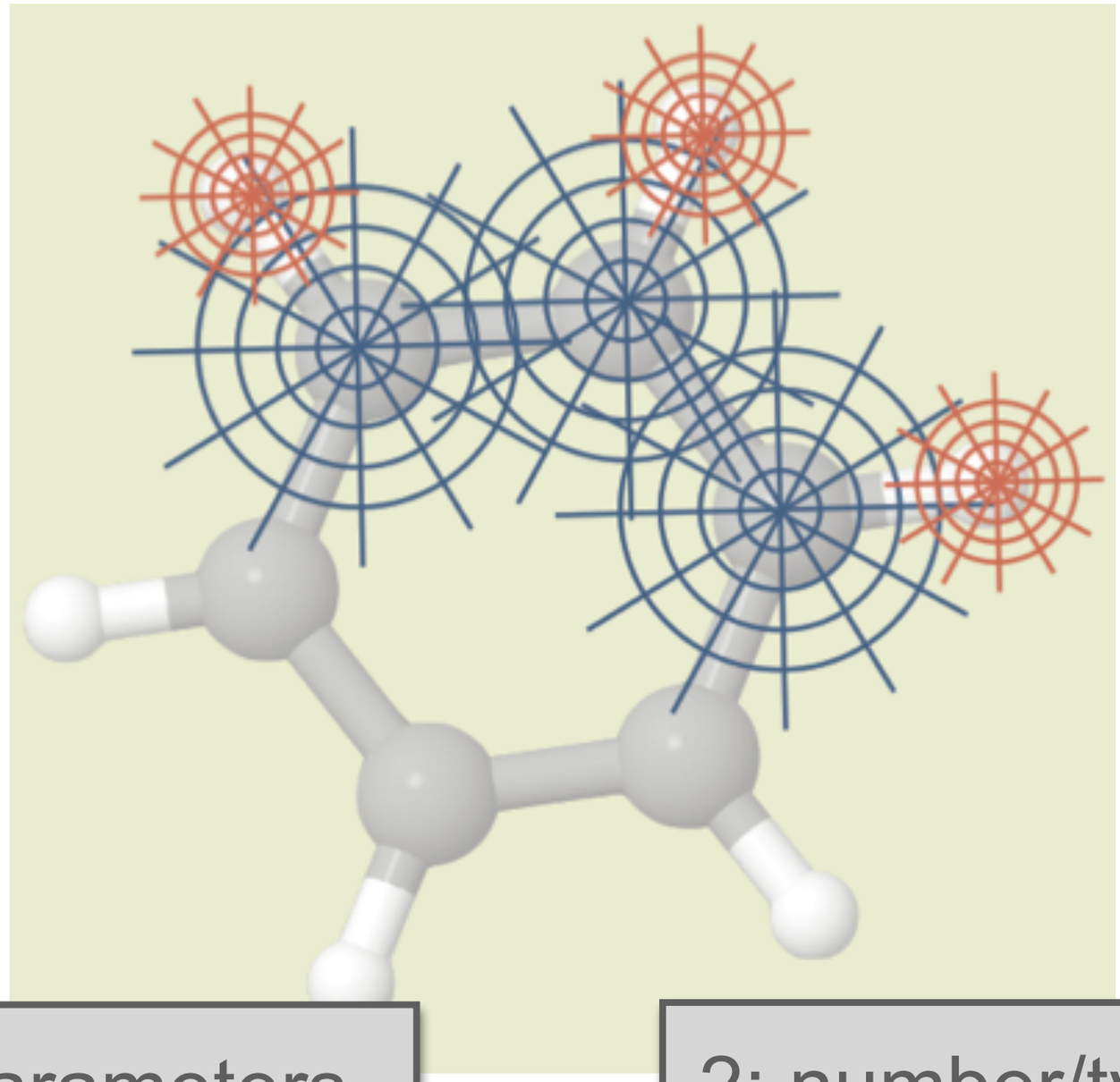


Real-space grid for basis functions



1: grid parameters

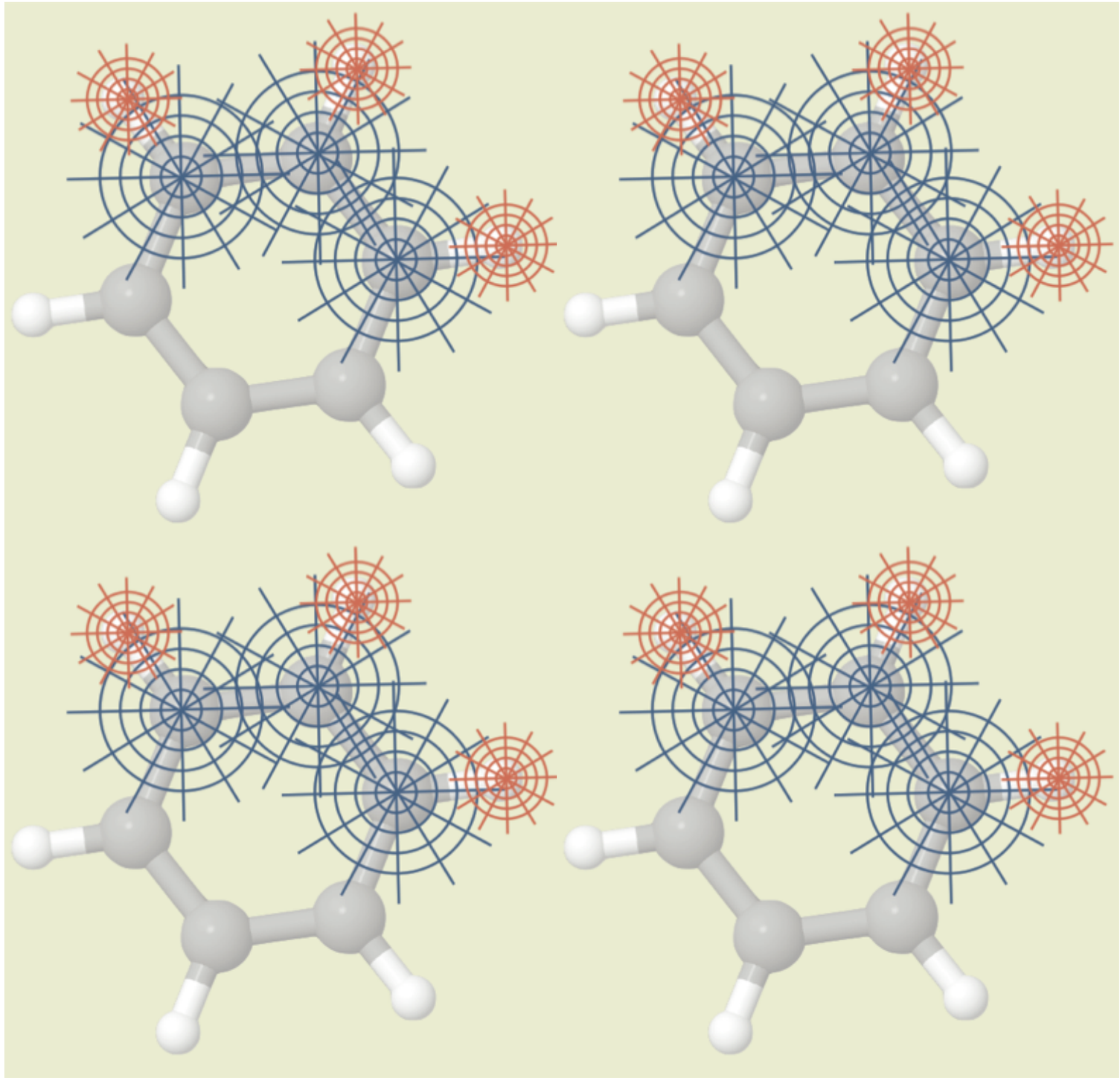
Real-space grid for basis functions



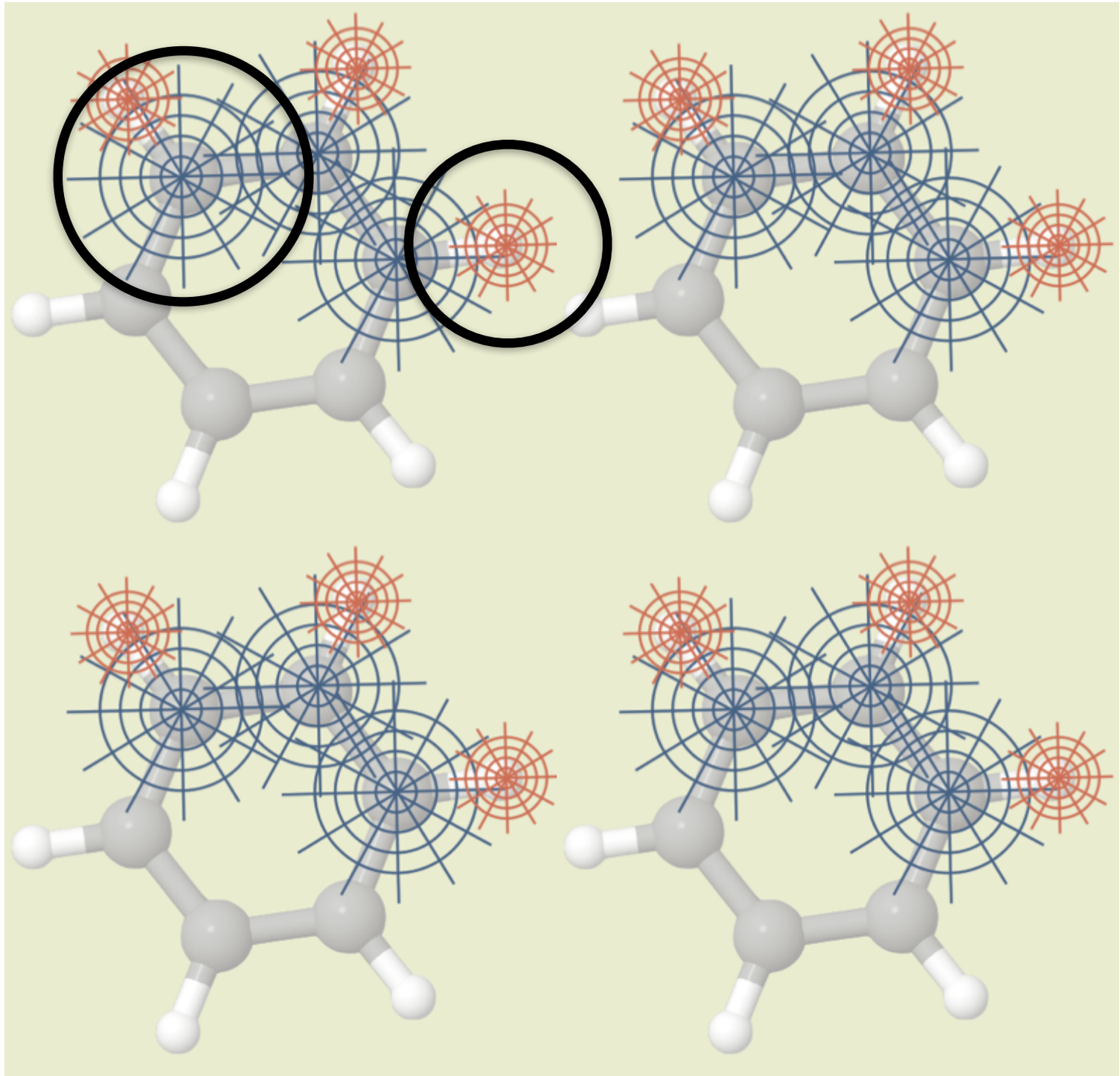
1: grid parameters

2: number/type of basis functions

Locality of the basis functions

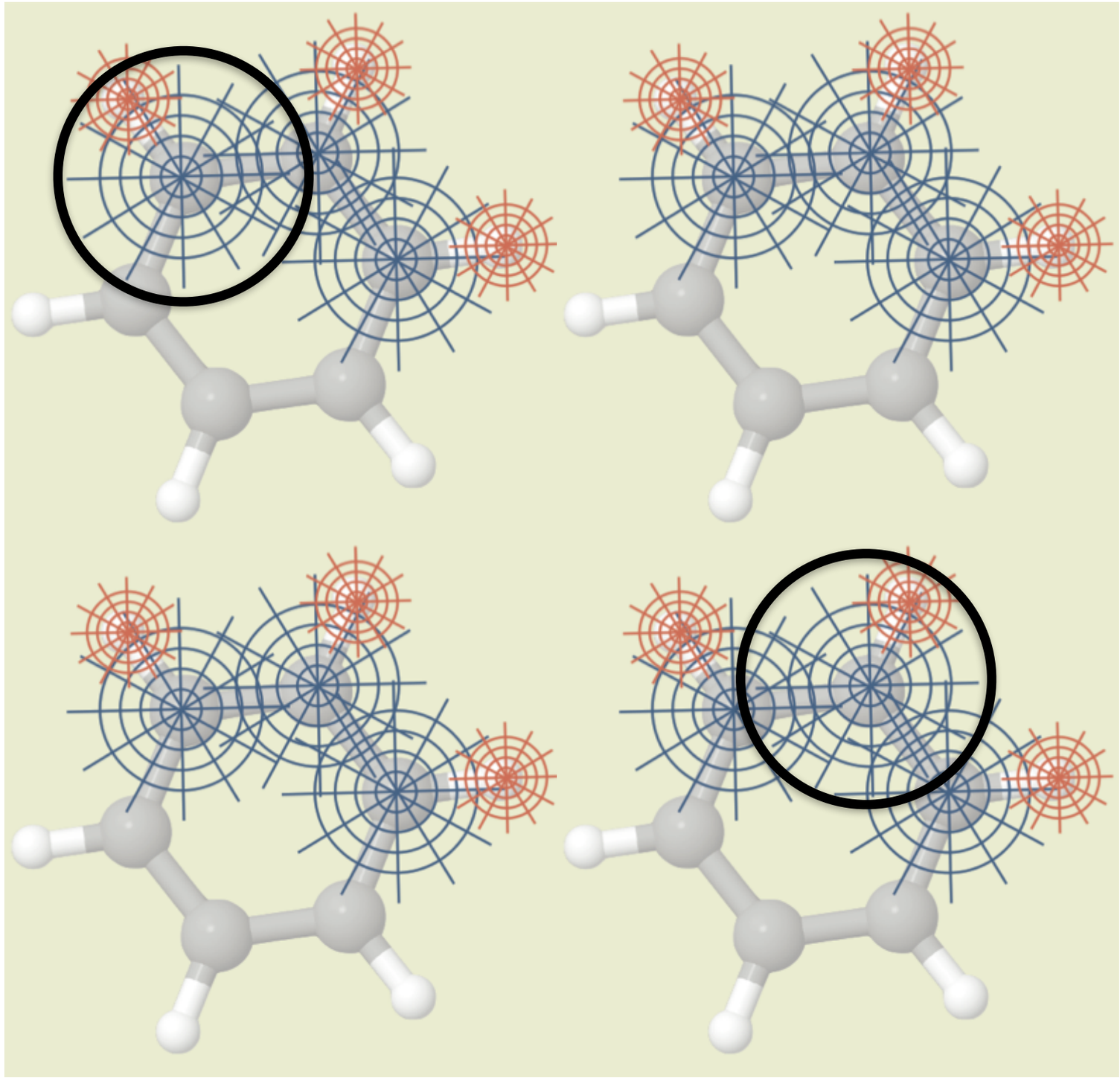


Locality of the basis functions



$$s_{ij} = 0$$

Locality of the basis functions

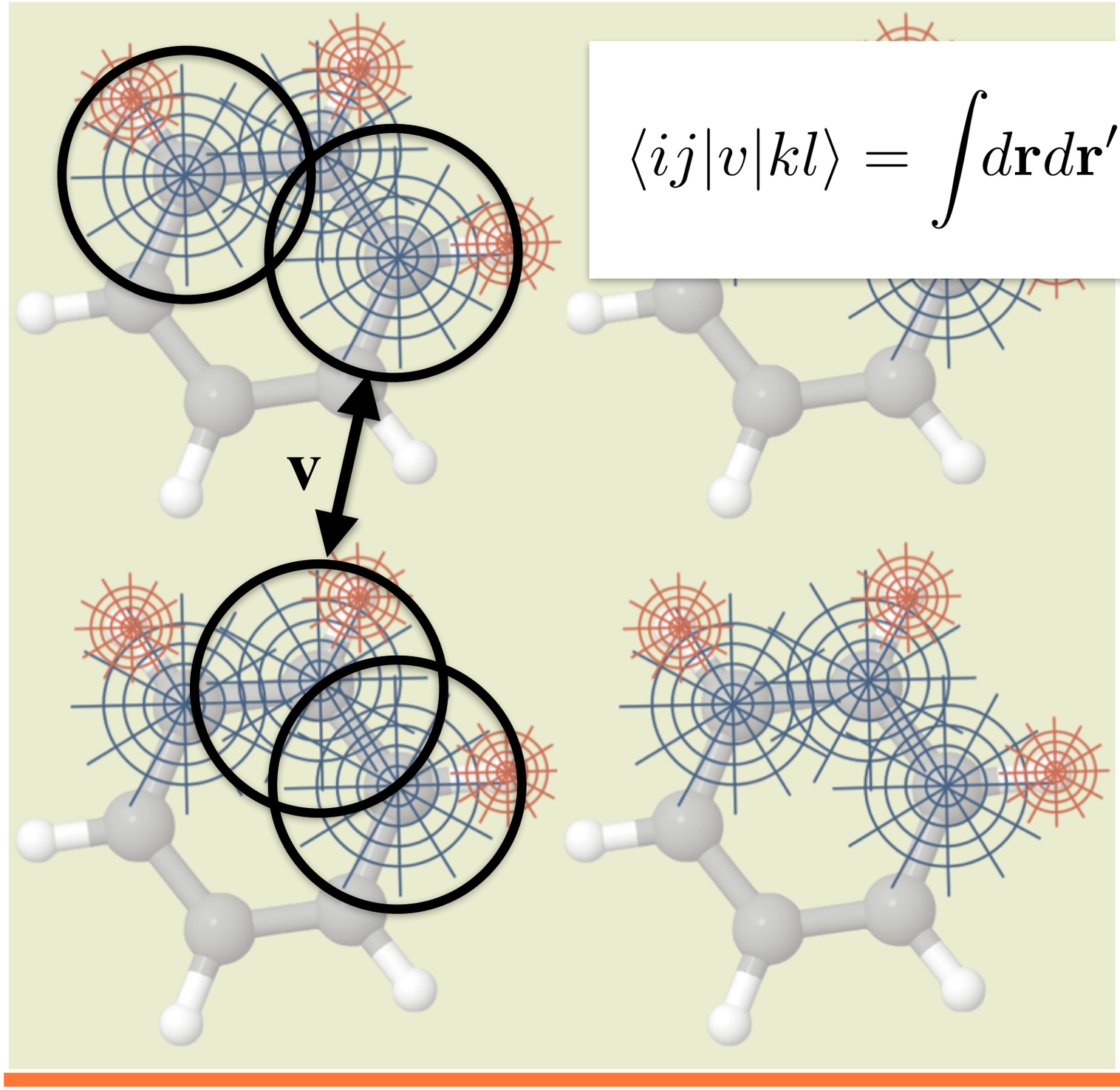


$$s_{ij} = 0$$

$$h_{ij} \ll 1$$

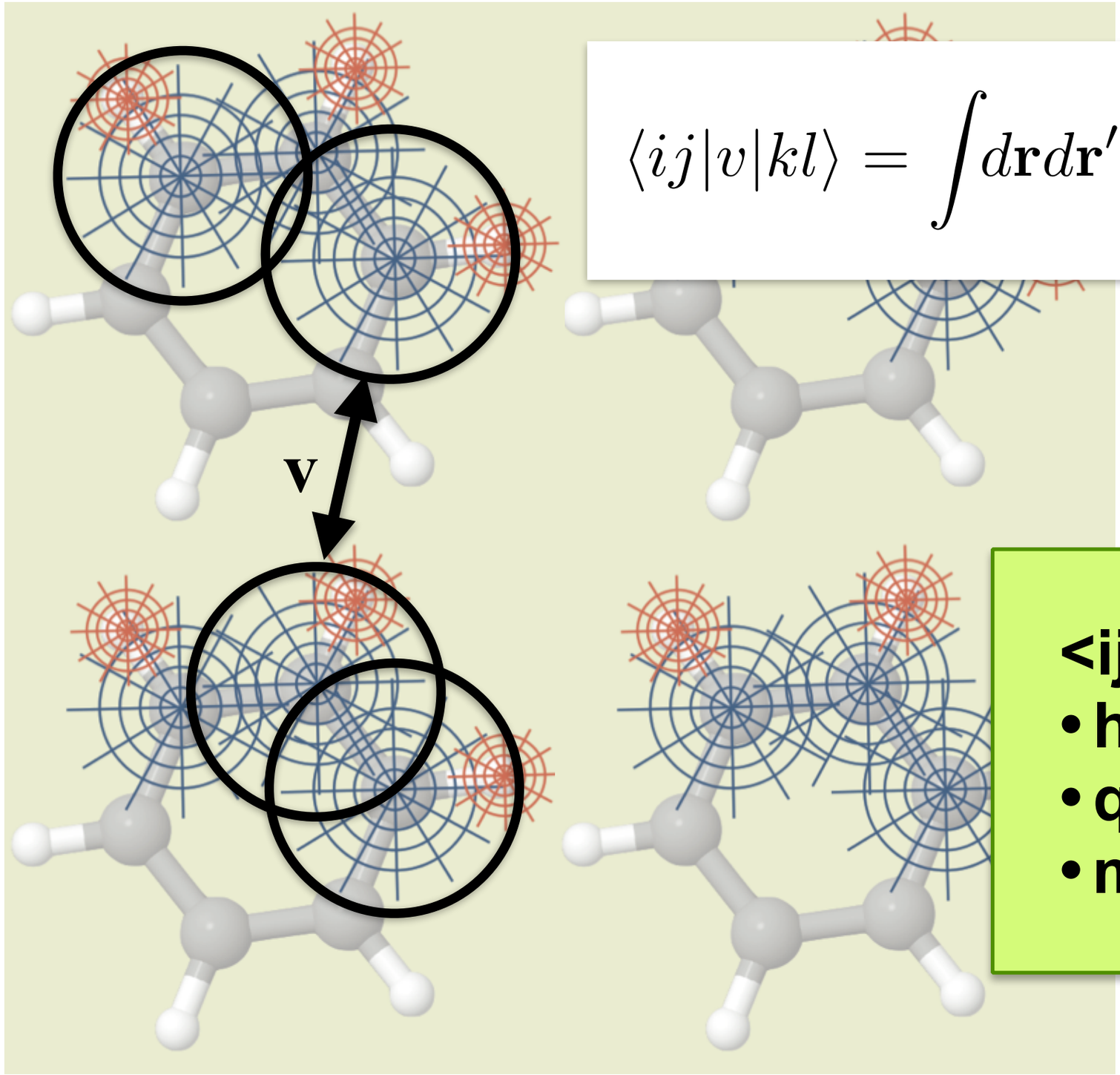
Interactions between far away basis functions become less important.

Problem for Coulomb matrix elements



$$\langle ij|v|kl\rangle = \int d\mathbf{r}d\mathbf{r}' \, \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Problem for Coulomb matrix elements



$$\langle ij|v|kl\rangle = \int d\mathbf{r}d\mathbf{r}' \, \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

<ij|v|kl> needed for:

- **hybrid functionals**
- **quantum chemistry**
- **many-body theory**

Please give me your questions after the talks or in the coffee break!