

Calculation of nmr parameters in paramagnetic metal-organic materials

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Presentation plan

- 1 MOFs = Metal—organic frameworks

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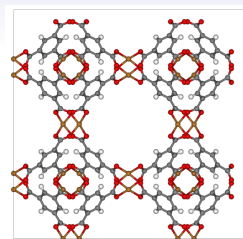
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- 1 MOFs = Metal—organic frameworks
- 2 NMR — what and why
- 3 NMR parameter calculation
- 4 DFT
- 5 Preliminary results

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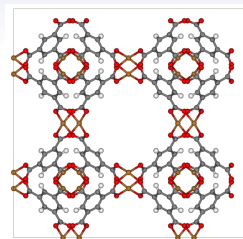
- crystal structure: central metallic ions + organic ligands



● carbon ● copper
● oxygen ○ hydrogen

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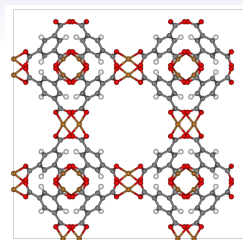
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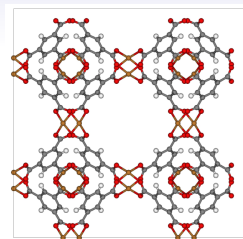
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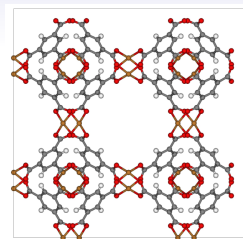
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- NMR spectra feature large shifts caused by unpaired electrons



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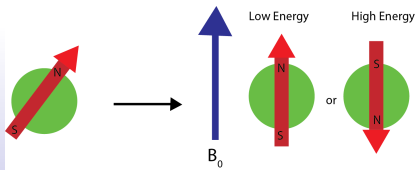
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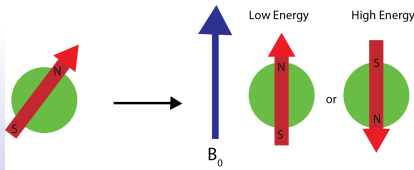
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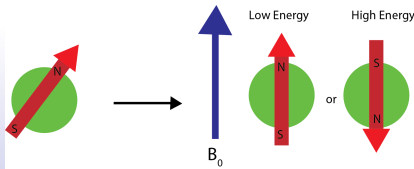
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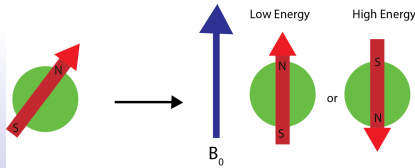
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- two new states ΔE apart
- radio frequency spectrum: excitations from low to high energy states
- absorption peak at $\Delta E = \hbar\omega_{res}$
- ω_{res} depends on $B_{eff}(\text{observed nucleus})$



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Several parameters affect $B_{\text{eff}}(\text{nucleus})$ and ω_{res} :

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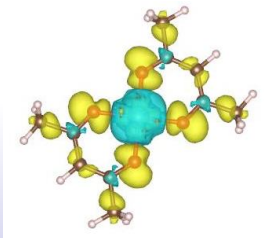
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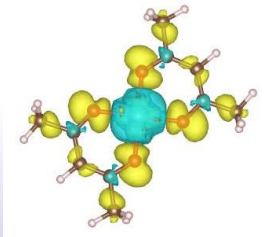


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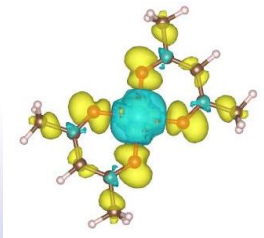


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Definition

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

$$\vec{B}_{eff} = \vec{B}_0 \left(\underline{\underline{I}} - \underline{\underline{\sigma}} \right).$$

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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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$$\hat{H} = T_n + T_e + W_{n-n} + W_{e-n} + W_{e-e} + V_{ext}$$

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- direct solution of coupled pde not feasible

electronic wave function calculation

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- Born-Oppenheimer approximation
- direct solution of coupled pde not feasible
- at a given accuracy level: time needed grows exponentially as a function of number of particles

density functional theory — DFT

Approximations

DFT

- most widely used
- good tradeoff between accuracy and speed
- highly customizable - suitable for various molecules

Alternatives

- * Hartree—Fock
- * Quantum Monte Carlo
- * Coupled-Cluster methods
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