MAX-PLANCK-INSTITUT
FÜR KOHLENFORSCHUNG

Theoretical Calculation Towards Molecular Properties

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Molecular Properties as Energy Derivatives

Hamiltonian subject to some external perturbation:

$$\hat{H} = \hat{H}(0) + \lambda \hat{O} + \dots \tag{1}$$

Example of external perturbations:

- $\mathbf{F}$: external electric field
- $\mathbf{B}$: external magnetic field
- $\mathbf{I}$: nuclear spin
- $\mathbf{R}$: nuclear geometric displacement

Energy expansion in terms of external perturbation:

$$E(\lambda) = E(0) + \lambda \frac{\mathrm{d}E}{\mathrm{d}\lambda}\Big|_{\lambda=0} + \frac{1}{2!}\lambda^2 \frac{\mathrm{d}^2 E}{\mathrm{d}\lambda^2}\Big|_{\lambda=0} + \dots \tag{2}$$

The n-th order property could be written as the n-th order derivative against perturbation.

Types of Molecular Properties

Some first and second order molecular properties, expressed as energy derivatives:

$$\frac{\partial^{n_1+n_2} E}{\partial^{n_1}\lambda_1 \partial^{n_2}\lambda_2}$$

$n_{\mathbf{F}}$	$n_{\mathbf{B}}$	$n_{\mathbf{I}}$	$n_{\mathbf{R}}$	Property
1	0	0	0	electric dipole moment
0	1	0	0	magnetic dipole moment
0	0	1	0	hyperfine coupling constant
0	0	0	1	nuclear gradient
2	0	0	0	electric polarizability
0	2	0	0	magnetizability
0	0	2	0	nuclear spin-spin coupling
0	0	0	2	harmonic vibrational frequencies
1	0	0	1	infrared absorption intensities
0	1	1	0	NMR shielding

[1]

[1] Introduction to computational chemistry - Jensen, 2007

Property Evaluation: Example - NMR Shielding Tensor

NMR Shielding Tensor:

$$\begin{aligned}\sigma^{K}_{\beta\alpha} =& \frac{\mathrm{d}^2 E}{\mathrm{d}B_\alpha \, \mathrm{d}m_{K_\beta}}\Big|_{\mathbf{B},\mathbf{m}_K=\mathbf{0}} \\ =& \sum_{\mu\nu} D_{\mu\nu} \frac{\mathrm{d}^2 h_{\mu\nu}}{\mathrm{d}B_\alpha \, \mathrm{d}m_{K_\beta}} + \sum_{\mu\nu} \frac{\mathrm{d}D_{\mu\nu}}{\mathrm{d}B_\alpha} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}}\end{aligned} \tag{3}$$

$D_{\mu\nu}$ is the density matrix specific to different levels of theory, e.g. D^{SCF}, D^{MP2}, D^{CC} ...

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Energy functionals:

$$\mathcal{L}_{\mathrm{MP2}} = E_{\mathrm{HF}} + E_{\mathrm{H}} + \sum_{ai} f_{ai} z_{ai} \tag{4}$$

$$\mathcal{L}_{\mathrm{CC}} = \langle \Phi_0 | (1 + \hat{\Lambda}) \mathcal{H} | \Phi_0 \rangle + \sum_{ai} f_{ai} z_{ai} \tag{5}$$

Corresponding (relaxed) density:

$$D_{\mu\nu}^{\mathrm{R}} = D_{\mu\nu}^{\mathrm{amp}} + D_{\mu\nu}^{z} \tag{6}$$

Current Progress

Have done:

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- Local approximation: DLPNO

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