Introduction: Evaluation of Electric and Magnetic Molecular Properties using Canonical Coupled Cluster Method

Hang Xu

Neese Department
Max-Planck-Institut für Kohlenforschung

February 10, 2022

Second-Order Electric and Magnetic Properties

Hamiltonian subject to perturbation:

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

E.g. $\hat{O} = -\boldsymbol{\mathcal{E}} \cdot \sum_\mu q_\mu \mathbf{r}_\mu$ for external electric field.

Second-Order Electric and Magnetic Properties

Hamiltonian subject to perturbation:

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

E.g. $\hat{O} = -\boldsymbol{\mathcal{E}} \cdot \sum_\mu q_\mu \mathbf{r}_\mu$ for external electric field.
Energy response subject to external perturbation (Taylor series):

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

Second-Order Electric and Magnetic Properties

Hamiltonian subject to perturbation:

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

E.g. $\hat{O} = -\boldsymbol{\mathcal{E}} \cdot \sum_\mu q_\mu \mathbf{r}_\mu$ for external electric field.
Energy response subject to external perturbation (Taylor series):

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

By definition of expectation value and Perturbation Theory:

$$\langle \hat{O} \rangle = \langle \hat{H}^{(1)} \rangle = \frac{\langle \Psi^{(0)} | \hat{H}^{(1)} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} = \frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda}\Big|_{\lambda=0} \tag{3}$$

Second-Order Electric and Magnetic Properties

Hamiltonian subject to perturbation:

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

E.g. $\hat{O} = -\boldsymbol{\mathcal{E}} \cdot \sum_\mu q_\mu \mathbf{r}_\mu$ for external electric field.
Energy response subject to external perturbation (Taylor series):

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

By definition of expectation value and Perturbation Theory:

$$\langle\hat{O}\rangle = \langle\hat{H}^{(1)}\rangle = \frac{\langle\Psi^{(0)}|\hat{H}^{(1)}|\Psi^{(0)}\rangle}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle} = \frac{\mathrm{d}E(\lambda)}{\mathrm{d}\lambda}\Big|_{\lambda=0} \tag{3}$$

Therefore we can evaluate many molecular properties with energy derivatives. For example:

- $\frac{\mathrm{d}^2E}{\mathrm{d}\mathcal{E}_\alpha \mathrm{d}\mathcal{E}_\beta}$: electric polarizability
- $\frac{\mathrm{d}^2E}{\mathrm{d}B_\alpha \mathrm{d}B_\beta}$: magnetizability
- $\frac{\mathrm{d}^2E}{\mathrm{d}B_\alpha \mathrm{d}m_{K\beta}}$: NMR shielding tensor
- $\frac{\mathrm{d}^2E}{\mathrm{d}B_\alpha \mathrm{d}S_\beta}$: electronic g-tensor

Canonical Coupled Cluster Ansatz

The Coupled Cluster wavefunction:

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle \tag{4}$$

$$\hat{T} = \sum_{\eta} \hat{T}_\eta \qquad \hat{T}_\eta = \frac{1}{(\eta!)^2} \sum_{\substack{ij\ldots \\ ab\ldots}} t_{ij\ldots}^{ab\ldots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} \tag{5}$$

Canonical Coupled Cluster Ansatz

The Coupled Cluster wavefunction:

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle \tag{4}$$

$$\hat{T} = \sum_{\eta} \hat{T}_\eta \qquad \hat{T}_\eta = \frac{1}{(\eta!)^2} \sum_{\substack{ij\ldots \\ ab\ldots}} t_{ij\ldots}^{ab\ldots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} \tag{5}$$

Energy expression:

$$\Delta E_{\mathrm{CC}} = \langle \Psi_{\mathrm{CC}}|\hat{H}_{\mathrm{N}}|\Psi_{\mathrm{CC}}\rangle = \langle \Phi_0|\mathcal{H}|\Phi_0\rangle \tag{6}$$

Canonical Coupled Cluster Ansatz

The Coupled Cluster wavefunction:

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle \tag{4}$$

$$\hat{T} = \sum_{\eta} \hat{T}_\eta \qquad \hat{T}_\eta = \frac{1}{(\eta!)^2} \sum_{\substack{ij\ldots \\ ab\ldots}} t_{ij\ldots}^{ab\ldots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} \tag{5}$$

Energy expression:

$$\Delta E_{\mathrm{CC}} = \langle \Psi_{\mathrm{CC}}|\hat{H}_{\mathrm{N}}|\Psi_{\mathrm{CC}}\rangle = \langle \Phi_0|\mathcal{H}|\Phi_0\rangle \tag{6}$$

Effective Hamiltonian (using BCH expansion):

$$\begin{aligned}
\mathcal{H} =& e^{-\hat{T}} \hat{H}_{\mathrm{N}} e^{\hat{T}} \\
=& \hat{H}_{\mathrm{N}} + [\hat{H}_{\mathrm{N}}, \hat{T}] + \frac{1}{2!}[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}] + \frac{1}{3!}[[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}], \hat{T}] \\
&+ \frac{1}{4!}[[[[\hat{H}_{\mathrm{N}}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] \\
=& \hat{H}_{\mathrm{N}} + (\hat{H}_{\mathrm{N}}\hat{T})_{\mathrm{C}} + \frac{1}{2!}(\hat{H}_{\mathrm{N}}\hat{T}^2)_{\mathrm{C}} + \frac{1}{3!}(\hat{H}_{\mathrm{N}}\hat{T}^3)_{\mathrm{C}} + \frac{1}{4!}(\hat{H}_{\mathrm{N}}\hat{T}^4)_{\mathrm{C}} \\
=& (\hat{H}_{\mathrm{N}} e^{\hat{T}})_{\mathrm{C}}
\end{aligned} \tag{7}$$

CC Lagrangian and Stationary Conditions

For non-variational methods, Lagrange's undetermined multipliers ansatz are used.

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \sum_{\eta}\lambda_\eta\langle\Phi_\eta|\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \\ =& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\nu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \end{aligned} \tag{8}$$

CC Lagrangian and Stationary Conditions

For non-variational methods, Lagrange's undetermined multipliers ansatz are used.

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \sum_{\eta}\lambda_\eta\langle\Phi_\eta|\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \\ =& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\nu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \end{aligned} \tag{8}$$

The following stationary conditions need to be imposed, resulting different sets of equations to solve:

- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\eta} = 0$: resulting the CC amplitude equations

CC Lagrangian and Stationary Conditions

For non-variational methods, Lagrange's undetermined multipliers ansatz are used.

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \sum_{\eta}\lambda_\eta\langle\Phi_\eta|\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \\ =& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\nu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \end{aligned} \tag{8}$$

The following stationary conditions need to be imposed, resulting different sets of equations to solve:

- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\eta} = 0$: resulting the CC amplitude equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial t_\eta} = 0$: resulting the CC Λ equations

CC Lagrangian and Stationary Conditions

For non-variational methods, Lagrange's undetermined multipliers ansatz are used.

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \sum_{\eta}\lambda_\eta\langle\Phi_\eta|\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \\ =& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\nu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \end{aligned} \tag{8}$$

The following stationary conditions need to be imposed, resulting different sets of equations to solve:

- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\eta} = 0$: resulting the CC amplitude equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial t_\eta} = 0$: resulting the CC Λ equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial z_{ai}} = 0$: resulting the Brillouin condition (HF equations)

CC Lagrangian and Stationary Conditions

For non-variational methods, Lagrange's undetermined multipliers ansatz are used.

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \sum_{\eta}\lambda_\eta\langle\Phi_\eta|\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \\ =& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\nu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \end{aligned} \tag{8}$$

The following stationary conditions need to be imposed, resulting different sets of equations to solve:

- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\eta} = 0$: resulting the CC amplitude equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial t_\eta} = 0$: resulting the CC Λ equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial z_{ai}} = 0$: resulting the Brillouin condition (HF equations)
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\kappa_{bj}} = 0$: resulting the z-vector equation

CC Lagrangian and Stationary Conditions

For non-variational methods, Lagrange's undetermined multipliers ansatz are used.

$$\begin{aligned}\mathcal{L}_{\mathrm{CC}} =& \langle\Phi_0|\mathcal{H}|\Phi_0\rangle + \sum_{\eta}\lambda_\eta\langle\Phi_\eta|\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\mu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \\ =& \langle\Phi_0|(1+\hat{\Lambda})\mathcal{H}|\Phi_0\rangle + \sum_{ai} f_{ai}z_{ai} + \sum_{pq} I_{pq}(\sum_{\mu\nu} C^*_{\nu p}S_{\mu\nu}C_{\nu q} - \delta_{pq}) \end{aligned} \tag{8}$$

The following stationary conditions need to be imposed, resulting different sets of equations to solve:

- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\lambda_\eta} = 0$: resulting the CC amplitude equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial t_\eta} = 0$: resulting the CC Λ equations
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial z_{ai}} = 0$: resulting the Brillouin condition (HF equations)
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial\kappa_{bj}} = 0$: resulting the z-vector equation
- $\frac{\partial\mathcal{L}_{\mathrm{CC}}}{\partial I_{pq}} = 0$: resulting the orthonormality condition

Evaluation of Derivatives: NMR Shielding Tensor

Expression for the shielding tensor:

$$\begin{aligned}\sigma^K_{\beta\alpha} &= \left(\frac{\mathrm{d}^2 E}{\mathrm{d}B_\alpha \, \mathrm{d}m_{K\beta}}\right)\Big|_{\mathbf{B},\mathbf{m}_K=\mathbf{0}} \\ &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial m_{K\beta}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\alpha} \frac{\partial h_{\mu\nu}}{\partial m_{K\beta}}\end{aligned} \tag{9}$$

Evaluation of Derivatives: NMR Shielding Tensor

Expression for the shielding tensor:

$$\begin{aligned}\sigma^K_{\beta\alpha} &= \left(\frac{\mathrm{d}^2 E}{\mathrm{d}B_\alpha \, \mathrm{d}m_{K\beta}}\right)\Big|_{\mathbf{B},\mathbf{m}_K=\mathbf{0}} \\ &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial m_{K\beta}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\alpha} \frac{\partial h_{\mu\nu}}{\partial m_{K\beta}}\end{aligned} \tag{9}$$

One-electron Hamiltonian in magnetic field:

$$h = \frac{\mathbf{p}^2}{2} + \mathbf{A}\cdot\mathbf{p} + \mathbf{B}\cdot\mathbf{s} + \frac{\mathbf{A}^2}{2} - \phi(\mathbf{r}) \tag{10}$$

Evaluation of Derivatives: NMR Shielding Tensor

Expression for the shielding tensor:

$$\begin{aligned}\sigma_{\beta\alpha}^{K} &= \left(\frac{\mathrm{d}^2 E}{\mathrm{d}B_\alpha \, \mathrm{d}m_{K\beta}}\right)\Big|_{\mathbf{B},\mathbf{m}_K=\mathbf{0}} \\ &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial m_{K\beta}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\alpha} \frac{\partial h_{\mu\nu}}{\partial m_{K\beta}}\end{aligned} \tag{9}$$

One-electron Hamiltonian in magnetic field:

$$h = \frac{\mathbf{p}^2}{2} + \mathbf{A}\cdot\mathbf{p} + \mathbf{B}\cdot\mathbf{s} + \frac{\mathbf{A}^2}{2} - \phi(\mathbf{r}) \tag{10}$$

Then the derivatives of the one-electron Hamiltonian could be worked out.
Taking derivatives of the Lagrangian $\mathcal{L}_{\mathrm{CC}}$ is not too difficult at this point, as the Lagrangian is already made stationary w.r.t most parameters.

Evaluation of Derivatives: NMR Shielding Tensor

Expression for the shielding tensor:

$$\begin{aligned}\sigma_{\beta\alpha}^{K} &= \left(\frac{\mathrm{d}^2 E}{\mathrm{d}B_\alpha \, \mathrm{d}m_{K\beta}}\right)\Big|_{\mathbf{B},\mathbf{m}_K=\mathbf{0}} \\ &= \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial m_{K\beta}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_\alpha} \frac{\partial h_{\mu\nu}}{\partial m_{K\beta}}\end{aligned} \tag{9}$$

One-electron Hamiltonian in magnetic field:

$$h = \frac{\mathbf{p}^2}{2} + \mathbf{A}\cdot\mathbf{p} + \mathbf{B}\cdot\mathbf{s} + \frac{\mathbf{A}^2}{2} - \phi(\mathbf{r}) \tag{10}$$

Then the derivatives of the one-electron Hamiltonian could be worked out.
Taking derivatives of the Lagrangian $\mathcal{L}_{\mathrm{CC}}$ is not too difficult at this point, as the Lagrangian is already made stationary w.r.t most parameters.
Note the derivatives of MO coefficient $\mathbf{C}$ are worked out by firstly solving the CPSCF equations for the orbital transformation parameter, then for example:

$$\frac{\partial C_{\mu p}}{\partial B_\alpha} = \sum_q C_{\mu q} U_{qp}^{B_\alpha} \tag{11}$$

Long-Term Goal: Evaluation of Properties with DLPNO-CC method

Method	Computational Scaling
CCSD	$\mathcal{O}(N^6)$
CCSD(T)	$\mathcal{O}(N^7)$
CCSDT	$\mathcal{O}(N^8)$

It's not impossible, but computationally unfriendly hence often not feasible to calculate properties for large molecular systems using canonical CC ansatz.

Long-Term Goal: Evaluation of Properties with DLPNO-CC method

Method	Computational Scaling
CCSD	$\mathcal{O}(N^6)$
CCSD(T)	$\mathcal{O}(N^7)$
CCSDT	$\mathcal{O}(N^8)$

It's not impossible, but computationally unfriendly hence often not feasible to calculate properties for large molecular systems using canonical CC ansatz.

Taking local correlation approximations would significantly reduce the amount of calculation, making the methods in previous slides applicable to real-life chemistry.

Long-Term Goal: Evaluation of Properties with DLPNO-CC method

Method	Computational Scaling
CCSD	$\mathcal{O}(N^6)$
CCSD(T)	$\mathcal{O}(N^7)$
CCSDT	$\mathcal{O}(N^8)$

It's not impossible, but computationally unfriendly hence often not feasible to calculate properties for large molecular systems using canonical CC ansatz.

Taking local correlation approximations would significantly reduce the amount of calculation, making the methods in previous slides applicable to real-life chemistry.

Thank you for your time!

Long-Term Goal: Evaluation of Properties with DLPNO-CC method

Method	Computational Scaling
CCSD	$\mathcal{O}(N^6)$
CCSD(T)	$\mathcal{O}(N^7)$
CCSDT	$\mathcal{O}(N^8)$

It's not impossible, but computationally unfriendly hence often not feasible to calculate properties for large molecular systems using canonical CC ansatz.

Taking local correlation approximations would significantly reduce the amount of calculation, making the methods in previous slides applicable to real-life chemistry.

Thank you for your time!

Acknowlegement: Prof. Dr. Frank Neese
Georgi Stoychev
Stan Papadopoulos