# Coupled cluster theory: Analytic derivatives, molecular properties, and response theory

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$C^4$ Tutorial, Zürich, 2–4 October 2006

## Variational and non-variational wavefunctions

- A wavefunction is referred to as variational if the electronic energy function $E(x, \lambda)$ fulfills the condition

$$\frac{\partial E(x,\lambda)}{\partial \lambda} = 0 \quad \text{for all } x$$

- $x$ is the molecular geometry or any other perturbational parameter and $\lambda$ represents the molecular electronic wavefuntion parameters (*e.g.*, MO coefficients, CC amplitudes).
- The electronic gradient vanishes at all geometries.
- The variational condition determines $\lambda$ as a function of $x$. The molecular electronic energy is obtained by inserting the optimal $\lambda_*$ into the energy function.

# Examples of variational wavefunctions

- The Hartree–Fock wavefunction is variational since the orbital rotation parameters $\kappa$ (MO coefficients) are variational,

$$\frac{\partial E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa} = 0 \quad \text{for all } x$$

- The MCSCF wavefunction is variational since the variational condition is fulfilled both for the orbital rotation parameters $\kappa$ (MO coefficients) and the state transfer parameters $p$ (CI coefficients),

$$\frac{\partial E_{\mathrm{MCSCF}}(x,\kappa,p)}{\partial \kappa} = 0, \qquad \frac{\partial E_{\mathrm{MCSCF}}(x,\kappa,p)}{\partial p} = 0 \quad \text{for all } x$$

- CI wavefunctions are *not* variational since the variational condition is not fulfilled for the orbital rotation parameters $\kappa$,

$$\frac{\partial E_{\mathrm{CI}}(x,\kappa,p)}{\partial \kappa} \neq 0, \qquad \frac{\partial E_{\mathrm{CI}}(x,\kappa,p)}{\partial p} = 0 \quad \text{for all } x$$

# Derivatives of variational wavefunctions

- The molecular electronic energy is obtained by inserting the optimal electronic wavefunction parameters ($\lambda_*$) into the energy function,

$$\varepsilon(x) = E(x,\lambda_*)$$

- We are interested in the first derivative

$$\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x} + \frac{\partial E(x,\lambda)}{\partial \lambda}\frac{\partial \lambda}{\partial x}$$

$$\text{If} \quad \frac{\partial E(x,\lambda)}{\partial \lambda} = 0, \quad \text{then} \quad \frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} = \frac{\partial E(x,\lambda)}{\partial x}$$

- We do not need the response of the variational wavefunction!

# Hellmann–Feynman theorem

- Assume that the (variational) energy function can be written as an expectation value,

$$E(x,\lambda) = \langle \lambda | \hat{H}(x) | \lambda \rangle$$

- We then obtain

$$\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} = \left\langle \lambda \left| \frac{\partial \hat{H}(x)}{\partial x} \right| \lambda \right\rangle$$

- This is the *Hellmann–Feynman theorem*.
  Although originally stated for geometrical distortions, it holds for any perturbation.

# Hellmann–Feynman theorem for Hartree–Fock

- Consider the Hamiltonian of a molecule in a static electric field $\boldsymbol{\mathcal{E}}$,

$$\hat{H}(\boldsymbol{\mathcal{E}}) = \hat{H}(0) - \boldsymbol{\mu} \cdot \boldsymbol{\mathcal{E}}$$

- Thus, in Hartree–Fock theory, the $z$-component of the molecule's dipole can be computed as

$$\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}\mathcal{E}_z} = \left\langle \lambda \left| \frac{\partial \hat{H}(\boldsymbol{\mathcal{E}})}{\partial \mathcal{E}_z} \right| \lambda \right\rangle = -\left\langle \lambda \left| \mu_z \right| \lambda \right\rangle$$

- Concerning Hartree–Fock calculations in a finite basis, note that the Hellmann–Feynman theorem does not hold for a geometrical distortion ($A_x$),

$$\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}A_x} \neq \left\langle \lambda \left| \frac{\partial \hat{H}(x)}{\partial A_x} \right| \lambda \right\rangle$$

# Hellmann–Feynman force and corrections

- In Hartree–Fock theory, a geometrical distortion ($A_x$) yields the Hellmann–Feynman force plus corrections,

$$\begin{aligned} \frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}A_x} &= \left\langle \lambda \left| \frac{\partial \hat{H}(x)}{\partial A_x} \right| \lambda \right\rangle + \text{corrections} \\ &= -Z_A \sum_{i=1}^{N} \left\langle \lambda \left| \frac{x_i - A_x}{r_A^3} \right| \lambda \right\rangle + \dots \end{aligned}$$

- The reason is that the parameters of the one-electron basis (exponents and contraction coefficients) are *non-variational* electronic wavefunction parameters.
- The corrections are sometimes called *Pulay terms*.

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# Second derivative of variational wavefunctions

- The variational condition also simplifies the calculation of second derivatives,

$$\frac{\mathrm{d}^2\varepsilon(x)}{\mathrm{d}x^2} = \frac{\partial^2 E}{\partial x^2} + 2\frac{\partial^2 E}{\partial x \partial \lambda}\left(\frac{\partial \lambda}{\partial x}\right) + \frac{\partial^2 E}{\partial \lambda^2}\left(\frac{\partial \lambda}{\partial x}\right)^2$$

- The term $\partial E/\partial\lambda(\partial\lambda^2/\partial x^2)$ is eliminated by the variational condition.
- We need the *first-order response* ($\partial\lambda/\partial x$) of the wave function to calculate the energy to second order.
- $2n$+1 rule: The derivatives of the wavefunction to order $n$ determine the derivatives of the energy to order $2n$+1.

## Response equations

- The calculation of second derivatives requires the knowledge of the first-order response $\partial\lambda/\partial x$.
- This first-order response is obtained by differentiating the equations that determine the electronic wavefunction parameters $\lambda$.
- For variational wavefunctions, the variational condition $\partial E/\partial\lambda = 0$ determines the parameters $\lambda$. Thus,

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial E}{\partial \lambda}\right) = \frac{\partial^2 E}{\partial x \partial \lambda} + \frac{\partial^2 E}{\partial \lambda^2}\left(\frac{\partial \lambda}{\partial x}\right) = 0$$

- We obtain a set of linear equations (*response equations*) from which the first-order response may be determined.

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## Derivatives of non-variational wavefunctions

- As an example, we consider the gradient of the CI energy, which is variational w.r.t. the configuration coefficients $p$, but not w.r.t. the orbital rotations $\kappa$,

$$\frac{\partial E_{\mathrm{CI}}(x,\kappa,p)}{\partial p} = 0, \qquad \frac{\partial E_{\mathrm{CI}}(x,\kappa,p)}{\partial \kappa} \neq 0$$

- Therefore, if we differentiate the CI energy function w.r.t. $x$, we do not obtain the simplifications of the $2n+1$ rule,

$$\frac{\mathrm{d}\varepsilon_{\mathrm{CI}}(x)}{\mathrm{d}x} = \frac{\partial E_{\mathrm{CI}}(x,\kappa,p)}{\partial x} + \frac{\partial E_{\mathrm{CI}}(x,\kappa,p)}{\partial \kappa}\frac{\partial \kappa}{\partial x}$$

- It appears that we need the first-order response of the orbitals, $\partial\kappa/\partial x$.

# First-order response of the orbitals

- The orbital rotation parameters $\kappa$ are determined by the variational Hartree–Fock condition

$$\frac{\partial E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa} = 0 \quad \text{for all } x$$

- Thus, the first-order response of the orbitals $\partial\kappa/\partial x$ can be determined by differentiating the Hartree–Fock condition with respect to $x$,

$$\frac{\partial^2 E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa^2}\left(\frac{\partial \kappa}{\partial x}\right) = -\frac{\partial^2 E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa \partial x}$$

- There is one set of response equations for each perturbation, that is, for each independent geometrical distortion.

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# Lagrange’s method of undetermined multipliers

- By regarding the variational Hartree–Fock condition as a set of constraints in the optimization of the CI energy, we introduce the Lagrangian function

$$L_{\mathrm{CI}}(x,\kappa,\bar{\kappa},p) = E_{\mathrm{CI}}(x,\kappa,p) + \bar{\kappa}\frac{\partial E_{\mathrm{HF}}(x,\kappa)}{\partial \kappa}$$

- $\bar{\kappa}$ are the Lagrange multipliers. The form of $L_{\mathrm{CI}}$ is different from $E_{\mathrm{CI}}$, but it gives the same energy when the Hartree–Fock condition is fulfilled.
- We adjust the multipliers so that $L_{\mathrm{CI}}$ becomes variational in *all* variables. The price we pay for this is that there is a larger number of variables.

# The variational Lagrangian

- The Lagrangian function is variational in all variables,

$$\begin{aligned}
\frac{\partial L_{\text{CI}}(x,\kappa,\bar{\kappa},p)}{\partial p} &= \frac{\partial E_{\text{CI}}(x,\kappa,p)}{\partial p} = 0 \\
\frac{\partial L_{\text{CI}}(x,\kappa,\bar{\kappa},p)}{\partial \bar{\kappa}} &= \frac{\partial E_{\text{HF}}(x,\kappa)}{\partial \kappa} = 0 \\
\frac{\partial L_{\text{CI}}(x,\kappa,\bar{\kappa},p)}{\partial \kappa} &= \frac{\partial E_{\text{CI}}(x,\kappa,p)}{\partial \kappa} + \bar{\kappa}\frac{\partial^2 E_{\text{HF}}(x,\kappa)}{\partial \kappa^2} = 0
\end{aligned}$$

- The last equation determines the Lagrange multipliers in such a way that the Lagrangian is variational in $\kappa$.
- With the Lagrangian function, we have a completely variational formulation of the CI energy, and the total derivative of the Lagrangian w.r.t. $x$ is simply the corresponding partial derivative.

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# The total derivative of the Lagrangian

- The total derivative of the CI energy can be computed from the Lagrangian,

$$\begin{aligned}
\frac{\mathrm{d}\varepsilon_{\text{CI}}(x)}{\mathrm{d}x} &= \frac{\mathrm{d}L_{\text{CI}}(x,\kappa,\bar{\kappa},p)}{\mathrm{d}x} = \frac{\partial L_{\text{CI}}(x,\kappa,\bar{\kappa},p)}{\partial x} \\
&= \frac{\partial E_{\text{CI}}(x,\kappa,p)}{\partial x} + \bar{\kappa}\frac{\partial^2 E_{\text{HF}}(x,\kappa)}{\partial x \partial \kappa}
\end{aligned}$$

- The multipliers $\bar{\kappa}$ are obtained from the equation

$$\frac{\partial^2 E_{\text{HF}}(x,\kappa)}{\partial \kappa^2}\bar{\kappa} = -\frac{\partial E_{\text{CI}}(x,\kappa,p)}{\partial \kappa}$$

  which does *not* depend on the perturbation $x$.
- The perturbation independent formulation is also known as "$Z$-vector" or "interchange" method.

# The coupled-cluster Lagrangian

- The coupled-cluster energy is neither variational in the orbital rotations $\kappa$ nor in the amplitudes $t_\mu$. Thus, we must introduce Langrange multipliers $\bar{\kappa}$ and $\bar{t}_\mu$,

  $$L_{\text{CC}}(x,\kappa,\bar{\kappa},t_\mu,\bar{t}_\mu) = E_{\text{CC}}(x,\kappa,t_\mu)+\bar{\kappa}\frac{\partial E_{\text{HF}}(x,\kappa)}{\partial\kappa}+\bar{t}_\mu\Omega_\mu(x,\kappa,t_\mu)$$

  where $\Omega_\mu(x,\kappa,t_\mu)$ is the coupled-cluster *vector function*

  $$\Omega_\mu(x,\kappa,t_\mu) = \langle\mu|\hat{H}^T(x)|\text{HF}\rangle = \langle\mu|\,\text{exp}(-\hat{T})\hat{H}(x)\,\text{exp}(\hat{T})|\text{HF}\rangle$$

  The coupled-cluster *amplitudes equations* are

  $$\Omega_\mu(x,\kappa,t_\mu) = 0 \quad \text{for all } \mu$$

# Orbital-unrelaxed coupled-cluster properties

- Let us first consider *orbital-unrelaxed* molecular properties. Imagine that the perturbation is switched on only *after* the Hartree–Fock calculation. Thus, the orbitals are not changed by the perturbation and it suffices to consider the unrelaxed Lagrangian

  $$L_{\text{CC,unrelaxed}}(x,\kappa,t_\mu,\bar{t}_\mu) = E_{\text{CC}}(x,\kappa,t_\mu)+\bar{t}_\mu\Omega_\mu(x,\kappa,t_\mu)$$

- The property can be obtained from

  $$\frac{\mathrm{d}L_{\text{CC,unrelaxed}}}{\mathrm{d}x} = \frac{\partial L_{\text{CC,unrelaxed}}}{\partial x} = \frac{\partial E_{\text{CC}}}{\partial x} + \bar{t}_\mu\frac{\partial\Omega_\mu}{\partial x}$$

  (Here and in the following we omit arguments for clarity.)

# A simple unrelaxed one-electron property

- Consider (again) the Hamiltonian of a molecule in a static electric field $\boldsymbol{\mathcal{E}}$,

$$\hat{H}(\boldsymbol{\mathcal{E}}) = \hat{H}(0) - \boldsymbol{\mu} \cdot \boldsymbol{\mathcal{E}}$$

- The (orbital-unrelaxed) $z$-component of the molecule's dipole can be computed as

$$\mu_z = \frac{\partial E_{\text{CC}}}{\partial \mathcal{E}_z} + \bar{t}_\mu \frac{\partial \Omega_\mu}{\partial \mathcal{E}_z}$$

- Note that the $z$-component of the molecule's dipole can also be computed by means of finite perturbation theory by adding the operator $-\mu_z \mathcal{E}_z$ after the Hartree–Fock calculation has finished and before the coupled-cluster calculation has begun.

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# The coupled-cluster multipliers

- The coupled-cluster multipliers are obtained by requiring that the coupled-cluster Lagrangian is variational in the amplitudes,

$$\frac{\partial L_{\text{CC,unrelaxed}}}{\partial t_\nu} = \frac{\partial E_{\text{CC}}}{\partial t_\nu} + \bar{t}_\mu \frac{\partial \Omega_\mu}{\partial t_\nu} = \frac{\partial E_{\text{CC}}}{\partial t_\nu} + \bar{t}_\mu \Omega_{\mu\nu} = 0$$

  where $\Omega_{\mu\nu}$ is the *coupled-cluster Jacobian*,

$$\Omega_{\mu\nu} = \langle \mu | \exp(-\hat{T}) \, [\hat{H}(x), \hat{\tau}_\nu] \, \exp(\hat{T}) | \text{HF} \rangle$$

- Furthermore,

$$\frac{\partial E_{\text{CC}}}{\partial t_\nu} = \langle \text{HF} | \hat{H}(x) \hat{\tau}_\nu | \text{CC} \rangle$$

# The coupled-cluster Hellmann–Feynman theorem

- Consider the following partial derivatives:

$$\begin{aligned}\frac{\partial E_{\text{CC}}}{\partial x} &= \left\langle \text{HF} \left| \frac{\partial \hat{H}(x)}{\partial x} \right| \text{CC} \right\rangle \\ \bar{t}_\mu \frac{\partial \Omega_\mu}{\partial x} &= \bar{t}_\mu \left\langle \mu \left| \exp(-\hat{T}) \frac{\partial \hat{H}(x)}{\partial x} \right| \text{CC} \right\rangle\end{aligned}$$

Thus, if we define a bra state

$$\langle \Lambda | = \langle \text{HF} | + \bar{t}_\mu \langle \mu | \exp(-\hat{T})$$

we can write the total derivative of the Lagrangian as

$$\frac{\mathrm{d} L_{\text{CC,unrelaxed}}}{\mathrm{d} x} = \left\langle \Lambda \left| \frac{\partial \hat{H}(x)}{\partial x} \right| \text{CC} \right\rangle$$

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# A variational coupled-cluster energy

- The usual expression for the coupled-cluster energy is (now omitting the $x$-dependence of $\hat{H}(x)$)

$$E_{\text{CC}} = \langle \text{HF} | \hat{H} | \text{CC} \rangle = \langle \text{HF} | \hat{H}^T | \text{HF} \rangle$$

- Alternatively, we may compute the energy from

$$E_{\text{CC,var}} = \langle \Lambda | \hat{H} | \text{CC} \rangle = \langle \text{HF} | \hat{H}^T | \text{HF} \rangle + \bar{t}_\mu \langle \mu | \hat{H}^T | \text{HF} \rangle$$

- $\langle \text{HF} | + \bar{t}_\mu \langle \mu |$ is the left eigenvector and $| \text{HF} \rangle$ is the right eigenvector of the similarity-transformed Hamiltonian $\hat{H}^T$.
- Of course, $E_{\text{CC,var}}$ is nothing but the CC Lagrangian.
- The CC energy is less sensitive to numerical errors in the amplitudes and multipliers when evaluated from $E_{\text{CC,var}}$.

# Coupled-cluster density matrices

- Recall that the Hamiltonian in second quantization is

$$\hat{H} = h_{\text{nuc}} + \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$$

Hence, the energy $E_{\text{CC}} = \langle \text{HF} | \hat{H} | \text{CC} \rangle$ can be written as

$$E_{\text{CC}} = \sum_{PQ} \bar{D}_{PQ} h_{PQ} + \tfrac{1}{2} \sum_{PQRS} \bar{d}_{PQRS} g_{PQRS}$$

$$\bar{D}_{PQ} = \langle \text{HF} | a_P^\dagger a_Q | \text{CC} \rangle, \quad \bar{d}_{PQRS} = \langle \text{HF} | a_P^\dagger a_R^\dagger a_S a_Q | \text{CC} \rangle$$

- The coupled-cluster density matrices are not Hermitian and may give complex eigenvalues upon diagonalization. For the energy, it is sufficient to consider the real symmetric part.

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# Coupled-cluster Lagrangian density matrices

- The energy $E_{\text{CC,var}} = \langle \Lambda | \hat{H} | \text{CC} \rangle$ can be written as

$$E_{\text{CC}} = \sum_{PQ} \bar{D}^{\Lambda}_{PQ} h_{PQ} + \tfrac{1}{2} \sum_{PQRS} \bar{d}^{\Lambda}_{PQRS} g_{PQRS}$$

$$\bar{D}^{\Lambda}_{PQ} = \langle \Lambda | a_P^\dagger a_Q | \text{CC} \rangle, \quad \bar{d}^{\Lambda}_{PQRS} = \langle \Lambda | a_P^\dagger a_R^\dagger a_S a_Q | \text{CC} \rangle$$

- In terms of the Lagrangian densities, we may calculate coupled-cluster first-order properties in the same way as for variational wavefunctions, contracting the density matrix elements with the molecular integrals.
- The Lagrangian density matrices are also known as the *variational* or *relaxed density matrices*.

# A biorthogonal basis

- We introduce the notation

$$\begin{aligned}(\mu| &= \langle\mu|\,\mathrm{exp}(-\hat{T}) = \langle \mathrm{HF}|\hat{\tau}_\mu^\dagger\,\mathrm{exp}(-\hat{T})\\ |\nu) &= \mathrm{exp}(\hat{T})|\nu\rangle = \mathrm{exp}(\hat{T})\hat{\tau}_\nu|\mathrm{HF}\rangle\end{aligned}$$

- These states form a biorthogonal set,

$$(\mu|\nu) = \delta_{\mu\nu}$$

- For convenience, we identify $\hat{\tau}_0$ as the identity operator,

$$\begin{aligned}(0| &= \langle \mathrm{HF}|\hat{\tau}_0^\dagger\,\mathrm{exp}(-\hat{T}) = \langle \mathrm{HF}|\,\mathrm{exp}(-\hat{T}) = \langle \mathrm{HF}| = (\mathrm{HF}|\\ |0) &= \mathrm{exp}(\hat{T})\hat{\tau}_0|\mathrm{HF}\rangle = \mathrm{exp}(\hat{T})|\mathrm{HF}\rangle = |\mathrm{CC}\rangle = |\mathrm{HF})\end{aligned}$$

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# Matrix representation of the Hamiltonian

- We consider the matrix representation of the molecular electronic Hamiltonian $\hat{H}$ in the biorthogonal basis,

$$\mathbf{H} = \begin{pmatrix} H_{00} & H_{0\nu} \\ H_{\mu 0} & H_{\mu\nu} \end{pmatrix} \qquad \text{with } \mu, \nu > 0$$

- $\hat{H}$ is an unsymmetric real matrix.
- It follows that

$$\begin{aligned}H_{00} &= (0|\hat{H}|0) = \langle \mathrm{HF}|\,\mathrm{exp}(-\hat{T})\hat{H}\,\mathrm{exp}(\hat{T})|\mathrm{HF}\rangle = E_{\mathrm{CC}}\\ H_{\mu 0} &= (\mu|\hat{H}|0) = \langle \mu|\,\mathrm{exp}(-\hat{T})\hat{H}\,\mathrm{exp}(\hat{T})|\mathrm{HF}\rangle = \Omega_\mu = 0\\ H_{0\nu} &= (0|\hat{H}|\nu) = \langle \mathrm{HF}|\,\mathrm{exp}(-\hat{T})\hat{H}\,\mathrm{exp}(\hat{T})|\nu\rangle = \partial E_{\mathrm{CC}}/\partial t_\nu\end{aligned}$$

# Left and right eigenvectors

Apparently, $\mathbf{H} = \begin{pmatrix} E_{\text{CC}} & \partial E_{\text{CC}}/\partial t_\nu \\ 0 & H_{\mu\nu} \end{pmatrix}$ with $\mu, \nu > 0$

- $E_{\text{CC}}$ is an eigenvalue of $\mathbf{H}$ with right eigenvector $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$.
- The left eigenvector $(1 \;\; \bar{t}_\mu)$ must fulfill

$$\frac{\partial E_{\text{CC}}}{\partial t_\nu} + \bar{t}_\mu (H_{\mu\nu} - \delta_{\mu\nu} E_{\text{CC}}) = 0$$

- Recall the multipliers equation,

$$\frac{\partial E_{\text{CC}}}{\partial t_\nu} + \bar{t}_\mu \Omega_{\mu\nu} = 0 \;\rightarrow\; \Omega_{\mu\nu} = H_{\mu\nu} - \delta_{\mu\nu} E_{\text{CC}}$$

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# The coupled-cluster Jacobian

- Earlier, we have encountered the Jacobian

$$\begin{aligned} \Omega_{\mu\nu} &= \frac{\partial \Omega_\mu}{\partial t_\nu} = \langle \mu | \exp(-\hat{T}) \, [\hat{H}, \hat{\tau}_\nu] \, \exp(\hat{T}) | \text{HF} \rangle \\ &= (\mu | \, [\hat{H}, \hat{\tau}_\nu] \, | \text{HF}) = (\mu | \hat{H} | \nu) - (\mu | \hat{\tau}_\nu \hat{H} | \text{HF}) \\ &= H_{\mu\nu} - (\mu | \hat{\tau}_\nu \hat{H} | \text{HF}) \end{aligned}$$

- We invoke the resolution of the identity to show that

$$\begin{aligned} (\mu | \, \hat{\tau}_\nu \hat{H} | \text{HF}) &= \langle \mu | \hat{\tau}_\nu \hat{H}^T | \text{HF} \rangle = \sum_\rho \langle \mu | \hat{\tau}_\nu | \rho \rangle \langle \rho | \hat{H}^T | \text{HF} \rangle \\ &= \langle \mu | \hat{\tau}_\nu | \text{HF} \rangle \langle \text{HF} | \hat{H}^T | \text{HF} \rangle = \delta_{\mu\nu} E_{\text{CC}} \end{aligned}$$

- Thus, the CC Jacobian occurs in the matrix representation of the similarity-transformed Hamiltonian.

# Equation-of-motion CC theory (EOM-CC)

- IN EOM-CC theory, we expand the excited states in the space spanned by all $|\mu)$,

$$\begin{aligned} |\mathbf{c}_k) &= \sum_\mu c^k_\mu |\mu) = \sum_\mu c^k_\mu \,\mathrm{exp}(\hat{T})|\mu\rangle \\ &= \sum_\mu c^k_\mu \,\mathrm{exp}(\hat{T})\hat{\tau}_\mu|\mathrm{HF}\rangle = \sum_\mu c^k_\mu \hat{\tau}_\mu \,\mathrm{exp}(\hat{T})|\mathrm{HF}\rangle \\ &= \sum_\mu c^k_\mu \hat{\tau}_\mu|\mathrm{CC}\rangle = \mathrm{exp}(\hat{T})\sum_\mu c^k_\mu \hat{\tau}_\mu|\mathrm{HF}\rangle \end{aligned}$$

- The EOM-CC excited state may be regarded as being generated from a conventional expansion in Slater determinants by the application of an exponential operator containing the ground-state amplitudes.

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# The EOM-CC eigenvalue problem

- In the biorthogonal basis, we may set up EOM-CC wavefunctions of the form

$$|\mathbf{c}_k) = \sum_\nu c^k_\nu \,|\nu), \qquad (\bar{\mathbf{c}}_k| = \sum_\mu \bar{c}^k_\mu \,(\mu|$$

and express the energy as a pseudo-expectation value

$$E_k = (\bar{\mathbf{c}}_k|\hat{H}|\mathbf{c}_k), \qquad \text{with} \quad \bar{\mathbf{c}}_i^{\mathsf{T}}\mathbf{c}_j = \delta_{ij}$$

- For the ground state, we have $c^0_0 = 1$ and $c^0_\nu = 0$ for $\nu > 0$. Also, $\bar{c}^0_0 = 1$ and $\bar{c}^0_\mu = \bar{t}_\mu$ for $\mu > 0$. Hence,

$$E_0 = (\bar{\mathbf{c}}_0|\hat{H}|\mathbf{c}_0) = \langle\Lambda|\hat{H}|\mathrm{CC}\rangle = E_{\mathrm{CC,var}}$$

# The EOM-CC eigenvalue problem

- Differentiating the EOM-CC pseudo-expectation value w.r.t. the ket and bra coefficients (assumed to be real), yields

  $$\begin{aligned}\mathbf{H}\mathbf{c}_k &= E_k\mathbf{c}_k \\ \bar{\mathbf{c}}_k^{\mathsf{T}}\mathbf{H} &= \bar{\mathbf{c}}_k^{\mathsf{T}}E_k\end{aligned}$$

  Note that

  $$(\bar{\mathbf{c}}_i|\mathbf{c}_j) = \langle\bar{\mathbf{c}}_i|\mathbf{c}_j\rangle = \bar{\mathbf{c}}_i^{\mathsf{T}}\mathbf{c}_j = \delta_{ij}$$
  $$(\bar{\mathbf{c}}_i|\hat{H}|\mathbf{c}_j) = \langle\bar{\mathbf{c}}_i|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathbf{c}_j\rangle$$

- The EOM-CC states are obtained by diagonalizing the unsymmetric matrix representation of the similarity-transformed Hamiltonian. The ground-state amplitudes are used in the similarity transformation.

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# Eigenvalues of the Jacobian

- We shall level-shift the similarity-transformed Hamiltonian by the ground-state energy $E_0$. The eigenvalues will then correspond to the excitation energies,

  $$\Delta\mathbf{H} = \mathbf{H} - E_0\mathbf{1} = \begin{pmatrix} 0 & \boldsymbol{\eta}^{\mathsf{T}} \\ \mathbf{0} & \boldsymbol{\Omega}\end{pmatrix}, \quad \eta_\nu = \frac{\partial E_0}{\partial t_\nu} = \langle \mathrm{HF}|\hat{H}\hat{\tau}_\nu|\mathrm{CC}\rangle$$

  Thus,

  $$\begin{pmatrix} 0 & \boldsymbol{\eta}^{\mathsf{T}} \\ \mathbf{0} & \boldsymbol{\Omega}\end{pmatrix}\begin{pmatrix} s_k \\ \mathbf{t}_k\end{pmatrix} = \begin{pmatrix} \boldsymbol{\eta}^{\mathsf{T}}\mathbf{t}_k \\ \boldsymbol{\Omega}\mathbf{t}_k\end{pmatrix} = \Delta E_k\begin{pmatrix} s_k \\ \mathbf{t}_k\end{pmatrix}$$

- The EOM-CC excitation energies correspond to the eigenvalues of the CC Jacobian $\boldsymbol{\Omega}$. Since $\boldsymbol{\Omega}$ is unsymmetric, there is no guarantee that the eigenvalues are real, but this is not a problem in practice.

# Some remarks on EOM-CC

- The EOM-CC states are eigenvectors of the similarity-transformed Hamiltonian (using ground-state amplitudes). The excitation energies are eigenvalues of the ground-state CC Jacobian.
- EOM-CC can be applied to the standard models CCSD, CCSDT, etc.
- An EOM-CC calculation on two non-interacting systems A and B will recover the excitation energies of A and B (size-intensivity), but simultaneous excitations in A and B are not size-intensive.
- For CCSD, CCSDT, etc., the EOM-CC excitation energies are equal to those obtained from CC response theory.

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# Molecular gradients

- So far, we have only considered *orbital-unrelaxed* molecular properties. CC first-order properties can easily be computed from the pseudo-expectation value $\langle \Lambda | \hat{V} | \mathrm{CC} \rangle$, that is, from the corresponding *variational density*.
- Next, consider a perturbation that changes the MOs (but not the AOs). The *orbital-relaxed* approach is now required. Consider, for example, a static electric field that is switched on already in the Hartree–Fock step.
- Matters become even more complicated when also the AO basis is perturbed. This happens, for example, when derivatives are taken w.r.t. nuclear coordinates (molecular gradients), when the metric is changed by relativistic perturbations, or when GIAOs (London orbitals) are used for calculations of magnetic properties.

# Hartree–Fock orbitals

- The MOs are expanded in a basis of AOs,

  $$\varphi_P = \sum_\mu c_\mu^P \chi_\mu \sigma$$

  Thus, the derivative w.r.t. a nuclear coordinate becomes

  $$\frac{\partial \varphi_P}{\partial x} = \sum_\mu \left\{ \frac{\partial c_\mu^P}{\partial x} \chi_u + c_\mu^P \frac{\partial \chi_\mu}{\partial x} \right\} \sigma$$

- Changes occur in the MO coefficients and in the AOs. The problem can be handled in a two-step procedure. At each geometry $x$, we write the orthonormal Hartree–Fock orbitals as

  $$\mathbf{C}_{\text{HF}}(x) = \mathbf{C}_{\text{OMO}}(x)\, \mathbf{U}(x)$$

  where $\mathbf{U}(x)$ is a unitary (or orthogonal) matrix and $\mathbf{C}_{\text{OMO}}(x)$ a basis of orthonormal molecular orbitals (OMOs).

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# OMOs and UMOs

- At the reference geometry $x_0$, we choose $\mathbf{U}(x_0) = \mathbf{1}$ and $\mathbf{C}_{\text{OMO}}(x_0) = \mathbf{C}_{\text{HF}}(x_0)$.
- If the geometry changes from $x_0$ to $x$, the *unmodified molecular orbitals* (UMOs) are no longer orthonormal,

  $$\mathbf{C}_{\text{UMO}}(x) = \mathbf{C}_{\text{OMO}}(x_0)$$
  $$\mathbf{S}(x) = \mathbf{C}_{\text{UMO}}^{\text{T}}(x)\mathbf{S}_{\text{AO}}(x)\mathbf{C}_{\text{UMO}}(x) \neq \mathbf{1}$$

- We define *orthonormalized molecular orbitals* (OMOs),

  $$\mathbf{C}_{\text{OMO}}(x) = \mathbf{C}_{\text{UMO}}(x)\mathbf{S}^{-1/2}(x)$$

  Of course,

  $$\mathbf{S}(x) = \mathbf{C}_{\text{OMO}}^{\text{T}}(x)\mathbf{S}_{\text{AO}}(x)\mathbf{C}_{\text{OMO}}(x) = \mathbf{S}^{-1/2}(x)\mathbf{S}(x)\mathbf{S}^{-1/2}(x) = \mathbf{1}$$

# An orthogonal orbital connection

- The *connection matrix* $\mathbf{S}^{-1/2}(x)$ connects orthonormal orbitals at neighbouring geometries. Rules that accomplish this are called *orbital connections*.
- We use the OMOs (not the Hartree–Fock orbitals) to define a Fock space, in which we represent the Hamiltonian in second quantization,

$$\hat{H}(x) = h_{\text{nuc}}(x) + \sum_{PQ} \tilde{h}_{PQ}(x)\tilde{a}^{\dagger}_{P}\tilde{a}_{Q} + \tfrac{1}{2} \sum_{PQRS} \tilde{g}_{PQRS}(x)\tilde{a}^{\dagger}_{P}\tilde{a}^{\dagger}_{R}\tilde{a}_{S}\tilde{a}_{Q}$$

with

$$\begin{aligned} \tilde{a}^{\dagger}_{P} &= \sum_{Q} a^{\dagger}_{Q} \left[\mathbf{S}^{-1/2}(x)\right]_{QP} \\ \tilde{a}_{P} &= \sum_{Q} a_{Q} \left[\mathbf{S}^{-1/2}(x)\right]_{PQ} \end{aligned}$$

---

# Second quantization

- *We may ignore the geometry dependence of the creation and annihilation operators*!

$$\hat{H}(x) = h_{\text{nuc}}(x) + \sum_{PQ} \tilde{h}_{PQ}(x)a^{\dagger}_{P}a_{Q} + \tfrac{1}{2} \sum_{PQRS} \tilde{g}_{PQRS}(x)a^{\dagger}_{P}a^{\dagger}_{R}a_{S}a_{Q}$$

- At each geometry, all matrix elements can be written as vacuum expectation values of strings of operators. According to Wick's theorem, only totally contracted terms contribute, depending only on the overlap between the orbitals. Since the OMOs are orthormal at all geometries, the vacuum expectation values are independent of the geometry.
- The geometry dependence of the Hamiltonian is isolated in the integrals.

# First derivative of the one-electron Hamiltonian

- Consider

$$\frac{\partial}{\partial x}\sum_{PQ}\tilde{h}_{PQ}(x)a_P^\dagger a_Q = \frac{\partial}{\partial x}\sum_{PQ}\left[\mathbf{S}^{-1/2}(x)\mathbf{h}(x)\mathbf{S}^{-1/2}(x)\right]_{PQ} a_P^\dagger a_Q$$

- $\mathbf{S}(x)$ and $\mathbf{h}(x)$ are the overlap and Hamiltonian matrices at the new geometry $x_0 + \Delta x$ in the basis of the UMOs.
- When we expand around $x_0$, we get

$$\begin{aligned}
\mathbf{h}(x_0+\Delta x) &= \mathbf{h}^{(0)}(x_0) + \mathbf{h}^{(1)}(x_0)\Delta x + \dots \\
\mathbf{S}(x_0+\Delta x) &= \mathbf{1} + \mathbf{S}^{(1)}(x_0)\Delta x + \dots \\
\mathbf{S}^{-1/2}(x_0+\Delta x) &= \mathbf{1} - \tfrac{1}{2}\mathbf{S}^{(1)}(x_0)\Delta x + \dots
\end{aligned}$$

where $\mathbf{h}^{(1)}(x_0)$ and $\mathbf{S}^{(1)}(x_0)$ are the first derivatives of $\mathbf{h}$ and $\mathbf{S}$ in the UMO basis, computed at the reference geometry $x_0$.

---

# One-index transformations

- Hence,

$$\left.\frac{\partial \tilde{h}_{PQ}(x)}{\partial x}\right|_{x=x_0} = \left[\mathbf{h}^{(1)}(x_0) - \tfrac{1}{2}\mathbf{S}^{(1)}(x_0)\mathbf{h}^{(0)}(x_0) - \tfrac{1}{2}\mathbf{h}^{(0)}(x_0)\mathbf{S}^{(1)}(x_0)\right]$$

- We may write this in a compact brace notation for *one-index transformations*,

$$\left.\frac{\partial \tilde{h}_{PQ}(x)}{\partial x}\right|_{x=x_0} = \tilde{h}^{(1)}_{PQ} = h^{(1)}_{PQ} - \tfrac{1}{2}\left\{S^{(1)}, h^{(0)}\right\}_{PQ}$$

where

$$\begin{aligned}
\{A,B\}_{PQ} &= \sum_T (A_{PT}B_{TQ} + A^*_{QT}B_{PT}) \\
\{A,B\}_{PQRS} &= \sum_T (A_{PT}B_{TQRS} + A^*_{QT}B_{PTRS} \\
&+ A_{RT}B_{PQTS} + A^*_{ST}B_{PQRT})
\end{aligned}$$

# The Hartree–Fock gradient

- With the AO-dependence isolated in the integrals of the second-quantization Hamiltonian, we may write the Hartree–Fock gradient as

$$\begin{aligned}
E^{(1)}_{\mathsf{HF}} &= E^{(1)}_{\mathsf{nuc}} + \sum_{PQ} \tilde{h}^{(1)}_{PQ} \bar{D}^{\mathsf{HF}}_{PQ} + \tfrac{1}{2} \sum_{PQRS} \tilde{g}^{(1)}_{PQRS}\, \bar{d}^{\mathsf{HF}}_{PQRS} \\
&= E^{(1)}_{\mathsf{nuc}} + \sum_{I} \tilde{h}^{(1)}_{II} + \tfrac{1}{2} \sum_{IJ} \left( \tilde{g}^{(1)}_{IIJJ} - \tilde{g}^{(1)}_{IJJI} \right) \\
&= E^{(1)}_{\mathsf{nuc}} + \sum_{I} h^{(1)}_{II} - \sum_{IT} h^{(0)}_{TI} S^{(1)}_{TI} \\
&\quad + \tfrac{1}{2} \sum_{IJ} \left( g^{(1)}_{IIJJ} - g^{(1)}_{IJJI} \right) - \sum_{IJP} \left( g^{(0)}_{TIJJ} - g^{(0)}_{TJJI} \right) S^{(1)}_{TI} \\
&= E^{(1)}_{\mathsf{nuc}} + \sum_{I} h^{(1)}_{II} + \tfrac{1}{2} \sum_{IJ} \left( g^{(1)}_{IIJJ} - g^{(1)}_{IJJI} \right) - \sum_{IT} f^{(0)}_{TI} S^{(1)}_{TI} \\
&= E^{(1)}_{\mathsf{nuc}} + \sum_{I} \left( h^{(1)}_{II} - \varepsilon^{(0)}_{I} S^{(1)}_{II} \right) + \tfrac{1}{2} \sum_{IJ} \left( g^{(1)}_{IIJJ} - g^{(1)}_{IJJI} \right)
\end{aligned}$$

---

# Parametrization of the Hartree–Fock state

- The HF orbitals are obtained from the OMOs by a unitary (or orhogonal) transformation,

$$\mathbf{C}_{\mathsf{HF}}(x) = \mathbf{C}_{\mathsf{OMO}}(x)\, \mathbf{U}(x), \quad \text{with} \quad \mathbf{U}(x_0) = \mathbf{1}$$

  We can write $\mathbf{U}(x) = \exp(-\boldsymbol{\kappa})$, with $\boldsymbol{\kappa}^\dagger = -\boldsymbol{\kappa}$.

- In second quantization, this translates into

$$\hat{\kappa} = \sum_{PQ} \kappa_{PQ}\, a^\dagger_P a_Q, \quad \hat{\kappa}^\dagger = -\hat{\kappa}$$

- Spin and spatial restrictions may apply. In closed-shell HF theory, one usually writes

$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} \sum_{\sigma} (a^\dagger_{p\sigma} a_{q\sigma} - a^\dagger_{q\sigma} a_{p\sigma}) = \sum_{p>q} \kappa_{pq} E^{-}_{pq}$$

# Orbitals at the displaced geometry

| Geometry | Orbital |
|---|---|
| $x_0$ | $a_P^\dagger\lvert\text{vac}\rangle = \varphi_P^{\text{HF}}$ |
| $x_0 + \Delta x$ | $\tilde{a}_P^\dagger\lvert\text{vac}\rangle = \varphi_P^{\text{OMO}}$ |
| $x_0 + \Delta x$ | $\exp(-\hat{\kappa})\varphi_P^{\text{OMO}} = \exp(-\hat{\kappa})\tilde{a}_P^\dagger\lvert\text{vac}\rangle = \varphi_P^{\text{HF}}$ |

- At the new geometry $x_0 + \Delta x$, the HF orbital $\varphi_P^{\text{HF}}$ orbital is replaced by $\varphi_Q^{\text{HF}}$ through

$$\begin{aligned} \varphi_Q^{\text{HF}} &= \exp(-\hat{\kappa})\tilde{a}_Q^\dagger\tilde{a}_P\tilde{a}_P^\dagger\lvert\text{vac}\rangle \\ &= \exp(-\hat{\kappa})\tilde{a}_Q^\dagger\tilde{a}_P\exp(\hat{\kappa})\exp(-\hat{\kappa})\tilde{a}_P^\dagger\lvert\text{vac}\rangle \end{aligned}$$

- Thus, the replacement operator is

$$\exp(-\hat{\kappa})\tilde{a}_Q^\dagger\tilde{a}_P\exp(\hat{\kappa})$$

---

# CC energy at the displaced geometry

- The CC energy at the displaced geometry is written as

$$E_{\text{CC}} = \langle\text{OMO}\rvert\exp(-\hat{T})\exp(\hat{\kappa})\hat{H}\exp(-\hat{\kappa})\exp(\hat{T})\lvert\text{OMO}\rangle$$

- The wavefunction parameters in $\hat{\kappa}$ and $\hat{T}$ do depend on the geometry.
- The change of the AO basis is accounted for in $\hat{H}$.
- In the following, we shall write

$$E_{\text{CC}} = \langle 0\rvert\exp(-\hat{T})\exp(\hat{\kappa})\hat{H}\exp(-\hat{\kappa})\exp(\hat{T})\lvert 0\rangle$$

with the Fermi vacuum $\lvert 0\rangle \equiv \lvert\text{HF}\rangle \equiv \text{OMO}\rangle$ at the reference geometry and expansion point $x_0$.

# The closed-shell CC Lagrangian

- We are now in the position to write the CC Lagrangian as

$$\begin{aligned} L_{\mathrm{CC}} &= \langle 0| \exp(-\hat{T}) \exp(\hat{\kappa}) \hat{H} \exp(-\hat{\kappa}) \exp(\hat{T}) |0\rangle \\ &+ \sum_{\mu} \bar{t}_{\mu} \langle \mu | \exp(-\hat{T}) \exp(\hat{\kappa}) \hat{H} \exp(-\hat{\kappa}) \exp(\hat{T}) |0\rangle \\ &+ \sum_{p \geq q} \bar{\kappa}_{pq} (F_{pq} - \delta_{pq} \varepsilon_p) \end{aligned}$$

  where we have introduced the *canonical condition*, which helps to implement the frozen-core approximation.

- The orbital energies $\varepsilon_p$ are treated as wavefuntion parameters. Derivatives of $\varepsilon_p$ are not required according to the $2n$+1 rule.

---

# The closed-shell CC gradient

- The CC gradient $E^{(1)}_{\mathrm{CC}}$ can be written as

$$\begin{aligned} E^{(1)}_{\mathrm{CC}} &= E^{(1)}_{\mathrm{nuc}} + \sum_{pq} \tilde{h}^{(1)}_{pq} D^{\mathrm{eff}}_{pq} + \tfrac{1}{2} \sum_{pqrs} \tilde{g}^{(1)}_{pqrs} d^{\mathrm{eff}}_{pqrs} \\ &= E^{(1)}_{\mathrm{nuc}} + \sum_{pq} h^{(1)}_{pq} D^{\mathrm{eff}}_{pq} + \tfrac{1}{2} \sum_{pqrs} g^{(1)}_{pqrs} d^{\mathrm{eff}}_{pqrs} \\ &- \sum_{pq} S^{(1)}_{pq} F^{\mathrm{eff}}_{pq} \end{aligned}$$

  where we have introduced *effective densities* $D^{\mathrm{eff}}_{pq}$ and $d^{\mathrm{eff}}_{pqrs}$ and the *effective Fock matrix*

$$F^{\mathrm{eff}}_{pq} = \sum_{o} D^{\mathrm{eff}}_{po} h_{oq} + \sum_{ors} d^{\mathrm{eff}}_{pors} g_{qors}$$

# Effective CC densities

- The effective CC densities contain the CC Lagrangian densities plus contributions from the orbital rotation multipliers $\bar{\kappa}_{pq}$,

$$\begin{aligned} D^{\text{eff}}_{pq} &= \langle \Lambda | E_{pq} | \text{CC} \rangle + \bar{\kappa}'_{pq} \\ d^{\text{eff}}_{pqrs} &= \langle \Lambda | e_{pqrs} | \text{CC} \rangle + 2\bar{\kappa}'_{pq} D^{\text{HF}}_{rs} - \bar{\kappa}'_{pr} D^{\text{HF}}_{qs} \end{aligned}$$

  with $\bar{\kappa}'_{pq} = \frac{1}{2}(1 + \delta_{pq})\bar{\kappa}_{pq}$.

- The effective CC densities depend on the zeroth-order wavefunction parameters and multipliers.
- The zeroth-order wavefunction parameters and multipliers are obtained by making the Lagrangian stationary.

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# Coupled-perturbed Hartree–Fock (CPHF)

- The diagonal zeroth-order orbital rotation multipliers are obtained from requiring that $\partial L / \partial \varepsilon_p = 0$.
- The off-diagonal zeroth-order orbital rotation multipliers are obtained from the CPHF or $Z$-vector equations, which follow from $\partial L / \partial \kappa_{rs} = 0$ for all $r > s$,

$$\sum_{p \geq q} \bar{\kappa}_{pq} A_{pqrs} + \langle \Lambda | [\hat{H}, E^-_{rs}] | \text{CC} \rangle = 0$$

  with

$$A_{pqrs} = -\sum_{\sigma} \langle 0 | [a^\dagger_{p\sigma}, [a_{q\sigma}, [E^-_{rs}, \hat{H}]]]_+ | 0 \rangle$$

# Second derivatives

- Wavefunction parameters follow the $2n$+1 rule.
- Multipliers follow the $2n$+2 rule (since the Lagrangian is linear in the multipliers).
- Hence, we need the first-order wavefunction parameters (amplitudes and orbital rotation parameters) to compute second derivatives, but only zeroth-order multipliers,

$$\begin{aligned} \varepsilon^{(2)} &= E^{(20)} + 2E^{(11)}\lambda^{(1)} + E^{(02)}\{\lambda^{(1)}\}^2 \\ &+ \bar{\lambda}^{(0)}\left[e^{(20)} + 2e^{(11)}\lambda^{(1)} + e^{(02)}\{\lambda^{(1)}\}^2\right] \end{aligned}$$

$$E^{(mn)} = \frac{\partial^{m+n}E}{\partial x^m \partial \lambda^n}, \qquad e^{(mn)} = \frac{\partial^{m+n}e}{\partial x^m \partial \lambda^n}$$

---

# The $2n$+1 and $2n$+2 rules

- The Lagrangian is written as

$$L = E + \bar{\lambda}e$$

  where $E$ is the energy and $e$ the constraint $e = 0$.
- For the first derivative, we obtain

$$\frac{\mathrm{d}L}{\mathrm{d}x} = \frac{\partial L}{\partial x} = E^{(10)} + \bar{\lambda}^{(0)}e^{(10)}$$

- The second derivative is obtained from

$$\frac{\mathrm{d}}{\mathrm{d}x}\left\{E^{(10)} + E^{(01)}\lambda^{(1)} + \bar{\lambda}^{(0)}e^{(10)} + \bar{\lambda}^{(0)}e^{(01)}\lambda^{(1)} + \bar{\lambda}^{(1)}e^{(00)}\right\}$$

  Note that $e^{(00)} = 0$ and $E^{(01)} + \bar{\lambda}^{(0)}e^{(01)} = \partial L/\partial\lambda = 0$.

# The 2$n$+1 and 2$n$+2 rules

- The first-order response of the wavefunction parameters is obtained from requiring that $\mathrm{d}e/\mathrm{d}x = 0$. This yields

$$e^{(10)} + e^{(01)}\lambda^{(1)} = 0$$

- The second derivative yields

$$\begin{aligned}
\varepsilon^{(2)} &= E^{(20)} + E^{(11)}\lambda^{(1)} + \bar{\lambda}^{(0)}e^{(20)} + \bar{\lambda}^{(0)}e^{(11)}\lambda^{(1)} + \bar{\lambda}^{(1)}e^{(10)} \\
&+ \bar{\lambda}^{(2)}e^{(00)} + E^{(01)}\lambda^{(2)} + \bar{\lambda}^{(0)}e^{(10)}\lambda^{(2)} \\
&+ E^{(11)}\lambda^{(1)} + E^{(02)}\left\{\lambda^{(1)}\right\}^2 + \bar{\lambda}^{(0)}e^{(11)}\lambda^{(1)} \\
&+ \bar{\lambda}^{(0)}e^{(02)}\left\{\lambda^{(1)}\right\}^2 + \bar{\lambda}^{(1)}e^{(01)}\lambda^{(1)} \\
&= E^{(20)} + 2E^{(11)}\lambda^{(1)} + E^{(02)}\left\{\lambda^{(1)}\right\}^2 \\
&+ \bar{\lambda}^{(0)}\left(e^{(20)} + 2e^{(11)}\lambda^{(1)} + e^{(02)}\left\{\lambda^{(1)}\right\}^2\right)
\end{aligned}$$

---

# The symmetric approach

- Thus far, we have used the *symmetric formula* for second derivatives w.r.t. 2 perturbations $x$ and $y$

$$2E^{(11)}\lambda^{(1)} \equiv \frac{\partial^2 E}{\partial x \partial \lambda}\left(\frac{\partial \lambda}{\partial y}\right) + \frac{\partial^2 E}{\partial y \partial \lambda}\left(\frac{\partial \lambda}{\partial x}\right)$$

- In order to compute the second derivatives (*e.g.*, the molecular Hessian) of the CC energy, we need to solve

$$\begin{aligned}
E^{(01)} + \bar{\lambda}^{(0)}e^{(01)} &= 0 \\
e^{(10)} + e^{(01)}\lambda^{(1)} &= 0
\end{aligned}$$

- The zeroth-order multipliers equation is independent of the perturbation, whereas the first-order wavefunction parameters are determined by a set of equations that involve the perturbation-dependent $e^{(10)}$ (w.r.t. $x$ and $y$).

# Dalgarno's interchange theorem

- The *asymmetric formula* is obtained by considering the total derivative of the gradient,

$$\begin{aligned}
\varepsilon^{(2)} &= \frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{\partial L}{\partial y}\right\} = \frac{\mathrm{d}}{\mathrm{d}x}\left\{E^{(010)} + \bar{\lambda}^{(00)} e^{(010)}\right\} \\
&= E^{(110)} + E^{(011)}\lambda^{(10)} + \bar{\lambda}^{(10)} e^{(010)} \\
&+ \bar{\lambda}^{(00)} e^{(110)} + \bar{\lambda}^{(00)} e^{(011)}\lambda^{(10)}
\end{aligned}$$

with

$$E^{(klm)} = \frac{\partial^{k+l+m} E}{\partial x^k \partial y^l \partial \lambda^m}, \qquad \lambda^{(mn)} = \frac{\partial^{m+n}\lambda}{\partial x^m \partial y^n}, \qquad \text{etc.}$$

- For mixed second derivatives (NMR chemical shifts, IR intensities) it is sufficient to consider only the responses $\lambda^{(10)} = \partial\lambda/\partial x$ and $\bar{\lambda}^{(10)} = \partial\bar{\lambda}/\partial x$.

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# Time-dependent perturbations

- In the following, we shall investigate a time-dependent Hamiltonian of the form

$$\hat{H}(t, \boldsymbol{\epsilon}) = \hat{H}^{(0)} + \hat{V}(t, \boldsymbol{\epsilon})$$

where $\hat{H}^{(0)}$ is the unperturbed molecular Hamiltonian and $\hat{V}(t, \boldsymbol{\epsilon})$ the time-dependent perturbation, written as sum of Fourier components

$$\hat{V}(t, \boldsymbol{\epsilon}) = \sum_{j=-N}^{N} \hat{X}_j \epsilon_j(\omega_j) \exp(-i\omega_j t)$$

- The $\hat{X}_j$ are time-independent Hermitian operators, $\omega_{-j} = -\omega_j$, and $\epsilon_j(\omega_{-j}) = \epsilon_j(\omega_j)^*$. Thus, $\hat{V}(t, \boldsymbol{\epsilon})$ is Hermitian.

# Frequency-dependent response functions

- The time evolution of the observable $A$ can be expressed by means of response functions,

$$\begin{aligned}\langle\hat{A}\rangle(t) &= \langle\hat{A}\rangle_0 + \sum_j \langle\langle\hat{A};\hat{X}_j\rangle\rangle_{\omega_j} e^{-i\omega_j t}\epsilon_j(\omega_j)\\ &+ \tfrac{1}{2}\sum_{jk}\langle\langle\hat{A};\hat{X}_j,\hat{X}_k\rangle\rangle_{\omega_j,\omega_k} e^{-i(\omega_j+\omega_k)t}\epsilon_j(\omega_j)\epsilon_k(\omega_k) + \ldots\end{aligned}$$

- Examples include the (frequency-dependent) polarizability $\langle\langle\hat{\mu}_x;\hat{\mu}_y\rangle\rangle_\omega$ and the first hyperpolarizability $\langle\langle\hat{\mu}_x;\hat{\mu}_y,\hat{\mu}_z\rangle\rangle_{\omega_1,\omega_2}$.

- Important symmetries:

$$\begin{aligned}\langle\langle\hat{A};\hat{B},\hat{C},\ldots\rangle\rangle_{\omega_B,\omega_C,\ldots} &= \langle\langle\hat{A};\hat{C},\hat{B},\ldots\rangle\rangle_{\omega_C,\omega_B,\ldots}\\ &= \langle\langle\hat{B};\hat{A},\hat{C},\ldots\rangle\rangle_{-(\omega_B+\omega_C+\ldots),\omega_C,\ldots}\\ \langle\langle\hat{A};\hat{B},\hat{C},\ldots\rangle\rangle_{\omega_B,\omega_C,\ldots} &= \langle\langle\hat{A};\hat{B},\hat{C},\ldots\rangle\rangle^*_{-\omega_B,-\omega_C,\ldots}\end{aligned}$$

---

# Time-dependent Schrödinger equation

- We write the time-dependent wavefunction $|\bar{0}\rangle$ in the phase-isolated form

$$|\bar{0}\rangle = e^{-iF(t)}|\tilde{0}\rangle$$

Note that also $|\tilde{0}\rangle$ is time-dependent.

- The time-dependent Schrödinger equation becomes

$$\left\{\hat{H}(t) - i\partial/\partial t - \partial F(t)/\partial t\right\}|\tilde{0}\rangle = 0$$

- Projection onto $\langle\tilde{0}|$ yields

$$\frac{\partial F(t)}{\partial t} \equiv Q(t) = \langle\tilde{0}|\left\{\hat{H}(t) - i\partial/\partial t\right\}|\tilde{0}\rangle$$

# Time-dependent quasi-energy

- We term $Q(t)$ the time-dependent quasi-energy. Note that in the time-independent limit, $F(t) = Et$ and $Q(t) = E$.
- In CC response theory, we write $|\tilde{0}\rangle$ as

$$|\tilde{0}\rangle \equiv |\widetilde{\mathrm{CC}}(t,\boldsymbol{\epsilon})\rangle = \exp\{\hat{T}(t,\boldsymbol{\epsilon})\}|\mathrm{HF}\rangle$$

- All time-dependence is contained in the cluster operator $\hat{T}(t,\boldsymbol{\epsilon})$ (cf. orbital-unrelaxed properties).
- The CC Lagrangian is

$$\begin{aligned} L(t,\boldsymbol{\epsilon}) &= \left\langle \tilde{\Lambda}(t,\boldsymbol{\epsilon}) \middle| \left\{ \hat{H}(t) - i\partial/\partial t \right\} \middle| \widetilde{\mathrm{CC}}(t,\boldsymbol{\epsilon}) \right\rangle \\ \langle \tilde{\Lambda}(t,\boldsymbol{\epsilon})| &= \langle \mathrm{HF}| + \sum_{\mu} \bar{t}_{\mu}(t,\boldsymbol{\epsilon}) \langle \mu| \exp\{-\hat{T}(t,\boldsymbol{\epsilon})\} \end{aligned}$$

# The Frenkel–Dirac variational principle

- In the spirit of the Frenkel–Dirac variational principle

$$\langle \delta\Psi | \hat{H}(t) - i\partial/\partial t | \Psi \rangle = 0$$

we project the time-dependent Schrödinger equation onto $\langle \mathrm{HF}|$ and the excitation manifold $\langle \mu| \exp\{-\hat{T}(t,\boldsymbol{\epsilon})\}$,

$$\begin{aligned} Q(t) &= \langle \mathrm{HF}|\hat{H}(t)|\widetilde{\mathrm{CC}}(t,\boldsymbol{\epsilon})\rangle \\ 0 &= \langle \mu| \exp\{-\hat{T}(t,\boldsymbol{\epsilon})\} \left\{ \hat{H}(t) - i\partial/\partial t \right\} |\widetilde{\mathrm{CC}}(t,\boldsymbol{\epsilon})\rangle \end{aligned}$$

- The CC equations can be written as

$$\Omega_{\mu}(t,\boldsymbol{\epsilon}) - i\frac{\partial t_{\mu}(t,\boldsymbol{\epsilon})}{\partial t} = 0$$

$$\Omega_{\mu}(t,\boldsymbol{\epsilon}) = \langle \mu| \exp\{-\hat{T}(t,\boldsymbol{\epsilon})\}\hat{H}(t)|\widetilde{\mathrm{CC}}(t,\boldsymbol{\epsilon})\rangle$$

# Response functions

- The response functions are defined as the $n^{\text{th}}$ derivative of the CC Lagrangian,

$$\langle\langle \hat{X}_1; \hat{X}_2, \ldots, \hat{X}_n \rangle\rangle_{\omega_2,\ldots,\omega_n} = \tfrac{1}{2}\hat{C}^{\pm\omega} \frac{\mathrm{d}^n L(t,\boldsymbol{\epsilon})}{\mathrm{d}\epsilon_1(\omega_1)\mathrm{d}\epsilon_2(\omega_2)\ldots\mathrm{d}\epsilon_n(\omega_n)}$$

with

$$\hat{C}^{\pm\omega} f(\omega_1, \omega_2, \ldots, \omega_n) = f(\omega_1, \omega_2, \ldots, \omega_n) + f(-\omega_1, -\omega_2, \ldots, -\omega_n)^*$$

- The cluster amplitudes are expanded in the Fourier components of the perturbation(s),

$$\begin{aligned} t_\mu(t,\boldsymbol{\epsilon}) &= t_\mu^{(0)} + \sum_j t_\mu^{\hat{X}_j}(\omega_j)\epsilon_j(\omega_j)e^{-i\omega_j t} \\ &+ \tfrac{1}{2}\sum_{jk} t_\mu^{\hat{X}_j\hat{X}_k}(\omega_j,\omega_k)\epsilon_j(\omega_j)\epsilon_k(\omega_k)e^{-i(\omega_j+\omega_k)t} + \ldots \end{aligned}$$

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# The CC Jacobian

- The amplitude responses are obtained from

$$(\boldsymbol{\Omega} - \omega\mathbf{1})\,\mathbf{t}^{\hat{X}_1\ldots\hat{X}_n}(\omega_1,\ldots,\omega_n) = -\boldsymbol{\xi}^{\hat{X}_1\ldots\hat{X}_n}(\omega_1,\ldots,\omega_n)$$

with $\omega = \omega_1 + \cdots + \omega_n$ and

$$\xi_\mu^{\hat{X}_1\ldots\hat{X}_n}(\omega_1,\ldots,\omega_n) = \frac{\partial^{n+1} L(t,\boldsymbol{\epsilon})}{\partial\bar{t}_\mu \partial\epsilon_1(\omega_1)\partial\epsilon_2(\omega_2)\ldots\partial\epsilon_n(\omega_n)}$$

- $\boldsymbol{\Omega}$ is the Jacobian of the *unperturbed* system.
- Similar equations determine the multiplier responses,

$$\bar{\mathbf{t}}^{\hat{X}_1\ldots\hat{X}_n}(\omega_1,\ldots,\omega_n)\,(\boldsymbol{\Omega} + \omega\mathbf{1}) = -\bar{\boldsymbol{\xi}}^{\hat{X}_1\ldots\hat{X}_n}(\omega_1,\ldots,\omega_n)$$

# Linear-response equations

- Consider the linear response function $\langle\langle \hat{X}; \hat{Y} \rangle\rangle_\omega$.
- The amplitude and multiplier responses are obtained from the equations

$$\begin{aligned}
(\mathbf{\Omega} - \omega\mathbf{1})\,\mathbf{t}^{Y}(\omega) &= -\boldsymbol{\xi}^{Y}(\omega) \\
\bar{\mathbf{t}}^{Y}(\omega)\,(\mathbf{\Omega} + \omega\mathbf{1}) &= -\bar{\boldsymbol{\xi}}^{Y}(\omega) = -\left(\boldsymbol{\eta}^{Y}(\omega) + \mathbf{F}\mathbf{t}^{Y}(\omega)\right)
\end{aligned}$$

with

$$\xi^{Y}_{\mu}(\omega) = \frac{\partial^2 L(t,\boldsymbol{\epsilon})}{\partial \bar{t}_\mu \partial \epsilon_Y(\omega)}, \quad \eta^{Y}_{\mu}(\omega) = \frac{\partial^2 L(t,\boldsymbol{\epsilon})}{\partial t_\mu \partial \epsilon_Y(\omega)}, \quad F_{\mu\nu}(\omega) = \frac{\partial^2 L(t,\boldsymbol{\epsilon})}{\partial t_\mu \partial t_\nu}$$

- The same equations are obtained for orbital-unrelaxed second derivatives except for the $\pm\omega\mathbf{1}$ level shifts, which are due to the term $-i\partial t_\mu(t,\boldsymbol{\epsilon})/\partial t$ in the amplitudes equation.

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# Linear-response functions

- Recall the (symmetric) expression for the static 2nd derivative,

$$\begin{aligned}
\varepsilon^{(2)} &= E^{(20)} + 2E^{(11)}\lambda^{(1)} + E^{(02)}\{\lambda^{(1)}\}^2 \\
&+ \bar{\lambda}^{(0)}\left[e^{(20)} + 2e^{(11)}\lambda^{(1)} + e^{(02)}\{\lambda^{(1)}\}^2\right] \\
&= L^{(20)} + 2L^{(11)}\lambda^{(1)} + L^{(02)}\{\lambda^{(1)}\}^2
\end{aligned}$$

- The frequency-dependent polarizability becomes

$$\begin{aligned}
\alpha_{xy}(-\omega,\omega) &= \langle\langle x; y \rangle\rangle_\omega = \tfrac{1}{2}\hat{C}^{\pm\omega}\left\{\mathbf{t}^{x}(-\omega)\boldsymbol{\eta}^{y}(\omega)\right. \\
&+ \left.\mathbf{t}^{y}(\omega)\boldsymbol{\eta}^{x}(-\omega) + \mathbf{t}^{x}(-\omega)\mathbf{F}\mathbf{t}^{y}(\omega)\right\} \\
&= \tfrac{1}{2}\hat{C}^{\pm\omega}\left\{\mathbf{t}^{y}(\omega)\boldsymbol{\eta}^{x}(-\omega) + \mathbf{t}^{x}(-\omega)\bar{\boldsymbol{\xi}}^{y}(\omega)\right\}
\end{aligned}$$

- The asymmetric formula is

$$\langle\langle x; y \rangle\rangle_\omega = \tfrac{1}{2}\hat{C}^{\pm\omega}\left\{\mathbf{t}^{y}(\omega)\boldsymbol{\eta}^{x}(-\omega) + \bar{\mathbf{t}}^{y}(\omega)\boldsymbol{\xi}^{x}(-\omega)\right\}$$

# Poles and residues

$$\begin{aligned}(\mathbf{\Omega} - \omega \mathbf{1})\, \mathbf{t}^{Y}(\omega) &= -\boldsymbol{\xi}^{Y}(\omega) \\ \bar{\mathbf{t}}^{Y}(\omega)\,(\mathbf{\Omega} + \omega \mathbf{1}) &= -\bar{\boldsymbol{\xi}}^{Y}(\omega) = -\left(\boldsymbol{\eta}^{Y}(\omega) + \mathbf{F}\mathbf{t}^{Y}(\omega)\right)\end{aligned}$$

- The response equations become singular when $\pm\omega$ is equal to an eigenvalue of the CC Jacobian. Thus, these eigenvalues refer to an excitation energy.
- The residues are related to transition moments.
- The 2$n$+1 and 2$n$+2 rules apply.
- $\langle\langle x; y\rangle\rangle_0$ is the *orbital-unrelaxed* static polarizability.
- Frequency-dependent properties are obtained by level-shifting the Jacobian in the response equations that determine the perturbed amplitudes and multipliers.