COUPLED CLUSTER THEORY

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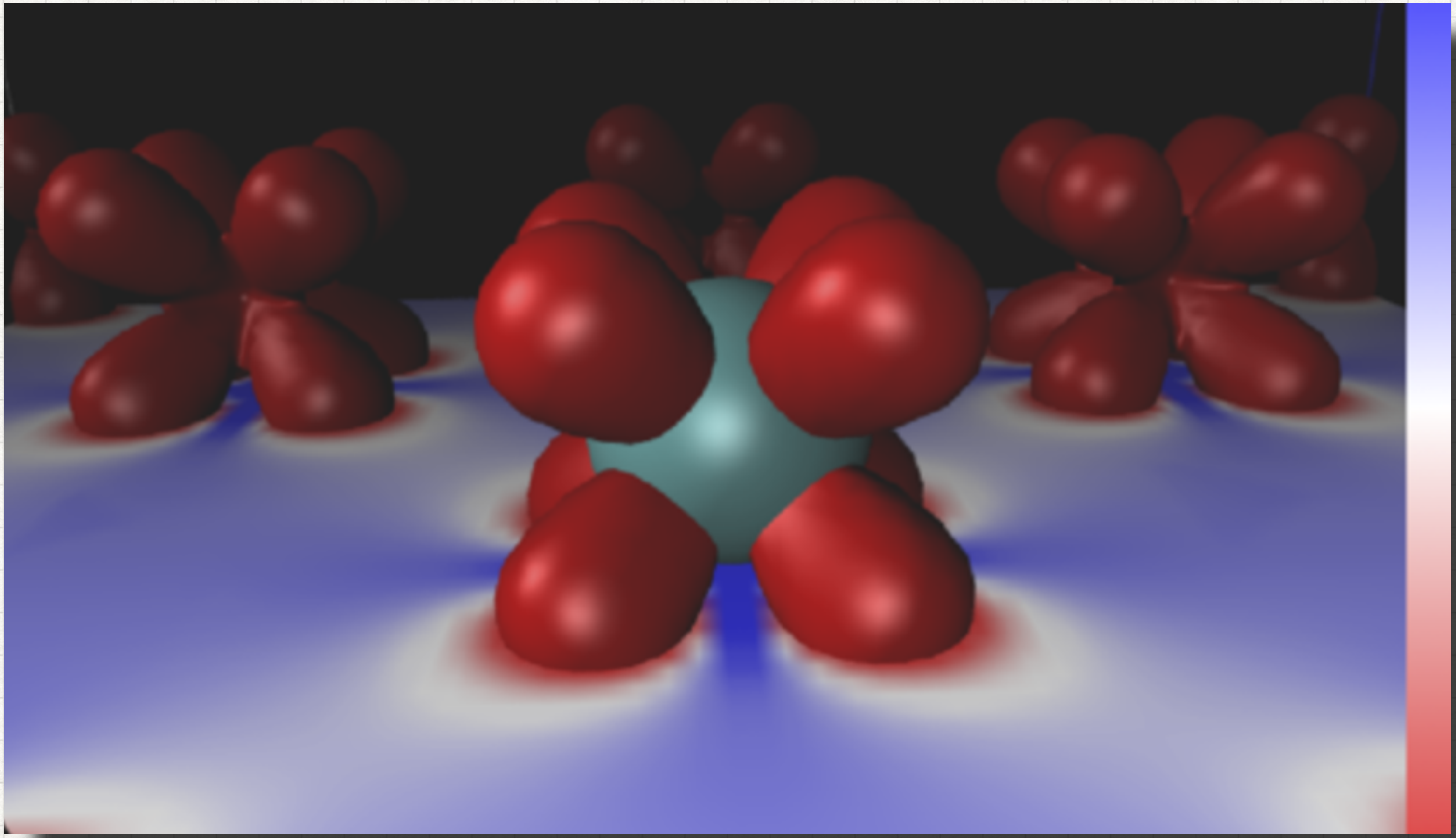


PROPERTIES FROM ANALYTIC GRADIENTS

$\dfrac{\partial E}{\partial \mathbf{R}_i}$	Force on the *i*th nucleus
$\dfrac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$	Quadratic force constants, harmonic vibrational frequencies
$\dfrac{\partial^3 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j \partial \mathbf{R}_k}$	Cubic force constants
$\dfrac{\partial^4 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j \partial \mathbf{R}_k \partial \mathbf{R}_l}$	Quartic force constants, anharmonicities

PROPERTIES FROM ANALYTIC GRADIENTS

$\frac{\partial E}{\partial \mathbf{F}}$	Dipole moment vector
$\frac{\partial^2 E}{\partial \mathbf{F}^2}$	Electric polarizability tensor
$\frac{\partial^3 E}{\partial \mathbf{F}^3}$	First hyperpolarizability tensor
$\frac{\partial^4 E}{\partial \mathbf{F}^4}$	Second hyperpolarizability tensor

PROPERTIES FROM ANALYTIC GRADIENTS

$\dfrac{\partial^2 E}{\partial \mathbf{F} \partial \mathbf{R}_i}$	Dipole moment derivatives, infrared intensities
$\dfrac{\partial^3 E}{\partial \mathbf{F}^2 \partial \mathbf{R}_i}$	Electric polarizability derivatives, Raman scattering intensities
$\dfrac{\partial^3 E}{\partial \mathbf{F} \partial \mathbf{R}_i \partial \mathbf{R}_j}$	Electrical anharmonicity, vibrational overtone intensities

PROPERTIES FROM ANALYTIC GRADIENTS

$\dfrac{\partial E}{\partial \mathbf{B}}$	Magnetic dipole moment vector
$\dfrac{\partial^2 E}{\partial \mathbf{B}^2}$	Magnetizability tensor
$\dfrac{\partial E}{\partial \mathbf{m}_A}$	Spin density on nucleus *A*
$\dfrac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{m}_A}$	NMR shielding tensor on nuclear *A*
$\dfrac{\partial^3 E}{\partial \mathbf{B} \partial \mathbf{F} \partial \mathbf{R}_i}$	Vibrational circular dichroism rotatory strength

DERIVATIVE OF THE CC ENERGY

- We may directly differentiate the coupled cluster energy expression with respect to a parameter x as:

$$\frac{\partial E_{\mathrm{CC}}}{\partial x} = \langle \Phi_0 | \frac{\partial \bar{H}}{\partial x} | \Phi_0 \rangle$$

- ***A key concept***: in this second-quantized expression, the role of $|\Phi_0\rangle$ is strictly for bookkeeping purposes: It merely allows us to keep track of the excitation level of the matrix element, and it carries no functional dependence on x. All of the of the orbital dependence is contained within the integrals and amplitudes in the $\hat{H}_N$ and $\hat{T}$ operators, respectively. Thus, we do not differentiate Φ_0 in this case.

- Similarly, derivatives of $\hat{H}_N$ and $\hat{T}$ operators do not involve differentiation of the annihilation/creation operators:

$$\frac{\partial H_N}{\partial x} = \sum_{pq} \frac{\partial f_{pq}}{\partial x} \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} \frac{\partial \langle pq || rs \rangle}{\partial x} \{a_p^\dagger a_q^\dagger a_s a_r\}$$

$$\frac{\partial T_2}{\partial x} = \frac{1}{4} \sum_{ijab} \frac{\partial t_{ij}^{ab}}{\partial x} \{a_a^\dagger a_b^\dagger a_j a_i\}$$

DERIVATIVE OF THE CC ENERGY

- It may be shown that the derivative of the similarity-transformed Hamiltonian may be written concisely as:

$$\frac{\partial \bar{H}}{\partial x} = e^{-\hat{T}} \frac{\partial \hat{H}_N}{\partial x} e^{\hat{T}} + \left[\bar{H}, \frac{\partial \hat{T}}{\partial x} \right] = \bar{H}^x + \left[\bar{H}, \frac{\partial \hat{T}}{\partial x} \right]$$

- Note that the derivative of a cluster operator is still a cluster operator, and thus $\hat{T}$ and its derivative commute:

$$\left[\hat{T}, \frac{\partial \hat{T}}{\partial x} \right] = 0$$

- The derivative of the coupled cluster energy is therefore:

$$\frac{\partial E_{\mathrm{CC}}}{\partial x} = \langle \Phi_0 | \bar{H}^x | \Phi_0 \rangle + \langle \Phi_0 | \left[\bar{H}, \frac{\partial T}{\partial x} \right] | \Phi_0 \rangle$$

- We may simplify this expression by expanding the commutator and introducing a resolution of the identity on the space of Slater determinants generated by $\hat{T}$.

DERIVATIVE OF THE CC ENERGY

- To make our task easier, once again we introduce new notation, starting with a normal-ordered excitation operator that generates excited determinants:

$$\hat{\tau}_\eta|\Phi_0\rangle = |\Phi_\eta\rangle \qquad\qquad \hat{T} = \sum_\eta t_\eta \hat{\tau}_\eta$$

where η denotes an excited determinant and the summation runs only over unique combinations so that we can avoid prefactors.

- In this notation, our cluster-operator derivative is written as:

$$\frac{\partial \hat{T}}{\partial x} = \sum_\eta \frac{\partial t_\eta}{\partial x}\hat{\tau}_\eta$$

- In the determinant space produced by $\hat{T}$, we have a resolution of the identity:

$$\hat{1} = |\Phi_0\rangle\langle\Phi_0| + \sum_\eta |\Phi_\eta\rangle\langle\Phi_\eta|$$

DERIVATIVE OF THE CC ENERGY

- Let's insert the resolution of the identity in between the Hamiltonian and the derivative of the cluster operator in the commutator in our energy derivative expression:

$$\langle\Phi_0|\left[\bar{H},\frac{\partial\hat{T}}{\partial x}\right]|\Phi_0\rangle = \langle\Phi_0|\bar{H}|\Phi_0\rangle\langle\Phi_0\xcancel{|}\frac{\partial\hat{T}}{\partial x}|\Phi_0\rangle + \sum_{\eta}\langle\Phi_0|\bar{H}|\Phi_\eta\rangle\langle\Phi_\eta|\frac{\partial\hat{T}}{\partial x}|\Phi_0\rangle$$

$$-\langle\Phi_0|\frac{\partial\hat{T}}{\partial x}\xcancel{|}\Phi_0\rangle\langle\Phi_0|\bar{H}|\Phi_0\rangle - \sum_{\eta}\langle\Phi_0|\frac{\partial\hat{T}}{\partial x}\xcancel{|}\Phi_\eta\rangle\langle\Phi_\eta\xcancel{|}\bar{H}|\Phi_0\rangle$$

- A few observations:
  1. The derivative of $\hat{T}$ in the first and third terms creates determinants that are orthogonal to Φ_0, and thus those terms vanish.
  2. In the fourth term, the derivative of $\hat{T}$ creates even higher excitations from Φ_η on the right, and thus that term vanishes.
  3. Also in the fourth term, the integral $\langle\Phi_\eta|\bar{H}|\Phi_0\rangle$ is zero because we've already solved the CC equations.

DERIVATIVE OF THE CC ENERGY

- The CC energy derivative now becomes:

$$\frac{\partial E_{\mathrm{CC}}}{\partial x} = \langle \Phi_0 | \bar{H}^x | \Phi_0 \rangle + \sum_\eta \langle \Phi_0 | \bar{H} | \Phi_\eta \rangle \langle \Phi_\eta | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle$$

- By our definition of the cluster operator and its derivative:

$$\langle \Phi_\eta | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle = \sum_{\eta'} \frac{\partial t_{\eta'}}{\partial x} \langle \Phi_\eta | \hat{\tau}_{\eta'} | \Phi_0 \rangle = \sum_{\eta'} \frac{\partial t_{\eta'}}{\partial x} \langle \Phi_\eta | \Phi_{\eta'} \rangle = \frac{\partial t_\eta}{\partial x}$$

- With this, our simplified expression for the gradient is:

$$\frac{\partial E_{\mathrm{CC}}}{\partial x} = \langle \Phi_0 | \bar{H}^x | \Phi_0 \rangle + \sum_\eta \langle \Phi_0 | \bar{H} | \Phi_\eta \rangle \frac{\partial t_\eta}{\partial x}$$

- If we were to evaluate the gradient using this form, we would need to compute explicitly the derivatives of the CC wave function amplitudes – a formidable task, because it requires solving the derivative amplitude equations for every perturbation (*e.g.*, for the nuclear position gradient, *3N* degrees of freedom). There is a better way…

DERIVATIVE OF THE CC ENERGY

- To obtain the derivatives of the $\hat{T}$ amplitudes, we must differentiate the equation from which they are defined, *i.e.*, in our new notation:

$$0 = \langle \Phi_\eta | \bar{H} | \Phi_0 \rangle$$

- Differentiation of this expression yields:

$$0 = \langle \Phi_\eta | \bar{H}^x | \Phi_0 \rangle + \langle \Phi_\eta | \left[\bar{H}, \frac{\partial \hat{T}}{\partial x} \right] | \Phi_0 \rangle$$

- Expanding the commutator in the last term and inserting the resolution of the identity gives:

$$\langle \Phi_\eta | \left[\bar{H}, \frac{\partial \hat{T}}{\partial x} \right] | \Phi_0 \rangle = \langle \Phi_\eta | \bar{H} | \Phi_0 \rangle \langle \Phi_0 | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle + \sum_{\eta'} \langle \Phi_\eta | \bar{H} | \Phi_{\eta'} \rangle \langle \Phi_{\eta'} | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle$$

$$- \langle \Phi_\eta | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle \langle \Phi_0 | \bar{H} | \Phi_0 \rangle - \sum_{\eta'} \langle \Phi_\eta | \frac{\partial \hat{T}}{\partial x} | \Phi_{\eta'} \rangle \langle \Phi_{\eta'} | \bar{H} | \Phi_0 \rangle$$

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = E_{CC}$$

$$= \sum_{\eta'} \langle \Phi_\eta | \bar{H} | \Phi_{\eta'} \rangle \langle \Phi_{\eta'} | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle - E_{\mathrm{CC}} \langle \Phi_\eta | \frac{\partial \hat{T}}{\partial x} | \Phi_0 \rangle$$

$$= \sum_{\eta'} \langle \Phi_\eta | \left(\bar{H} - E_{\mathrm{CC}} \right) | \Phi_{\eta'} \rangle \frac{\partial t_{\eta'}}{\partial x}$$

DERIVATIVE OF THE CC ENERGY

- The derivative of the amplitude equation becomes:

$$0 = \langle \Phi_\eta | \bar{H}^x | \Phi_0 \rangle + \sum_{\eta'} \langle \Phi_\eta | \left(\bar{H} - E_{\rm CC} \right) | \Phi_{\eta'} \rangle \frac{\partial t_{\eta'}}{\partial x}$$

- This is a system of linear equations for the derivatives of the cluster amplitudes, which we may solve by multiplying on the left by the inverse of the matrix on the right-hand side:

$$\frac{\partial t_\eta}{\partial x} = - \sum_{\eta'} \langle \Phi_\eta | \left(\bar{H} - E_{\rm CC} \right)^{-1} | \Phi_{\eta'} \rangle \langle \Phi_{\eta'} | \bar{H}^x | \Phi_0 \rangle$$

- Now insert this back into our energy derivative:

$$\frac{\partial E_{\rm CC}}{\partial x} = \langle \Phi_0 | \bar{H}^x | \Phi_0 \rangle - \sum_{\eta\eta'} \boxed{\langle \Phi_0 | \bar{H} | \Phi_\eta \rangle \langle \Phi_\eta | \left(\bar{H} - E_{\rm CC} \right)^{-1} | \Phi_{\eta'} \rangle} \langle \Phi_{\eta'} | \bar{H}^x | \Phi_0 \rangle$$

- Note that, in the second term, the product of the left-hand vector and the matrix inverse represent a de-excitation in that one starts (from the right) with an excited determinant, but ends with the Hartree-Fock reference.

- Also note that this de-excitation is independent of the perturbation, x.

THE LAMBDA EQUATIONS

- We can thus define a new de-excitation operator:

$$\langle\Phi_0|\hat{\Lambda}|\Phi_{\eta'}\rangle \equiv -\sum_{\eta}\langle\Phi_0|\bar{H}|\Phi_\eta\rangle\langle\Phi_\eta|\left(\bar{H}-E_{\mathrm{CC}}\right)^{-1}|\Phi_{\eta'}\rangle$$

- The "cluster de-excitation" operator, $\hat{\Lambda}$, may be expressed as:

$$\hat{\Lambda} = \sum_{\eta}\lambda_\eta\hat{\tau}_\eta^\dagger$$

where $\hat{\tau}_\eta^\dagger$ is a string of annihilation/creation operators arranged for de-excitation, $\{a_i^\dagger a_j^\dagger \ldots a_b a_a\}$, and λ_η is the corresponding amplitude.

- We can rearrange the definition of $\hat{\Lambda}$ to give:

$$\sum_{\eta'}\langle\Phi_0|\hat{\Lambda}|\Phi_{\eta'}\rangle\langle\Phi_{\eta'}|\left(\bar{H}-E_{\mathrm{CC}}\right)|\Phi_\eta\rangle = -\langle\Phi_0|\bar{H}|\Phi_\eta\rangle$$

- We can remove the sum over determinants to give:

$$\langle\Phi_0|\left(\hat{1}+\hat{\Lambda}\right)\left(\bar{H}-E_{\mathrm{CC}}\right)|\Phi_\eta\rangle = 0$$

- This is a system of ***perturbation independent*** linear equations that we need solve only once – not *3N* times!

A BETTER ENERGY DERIVATIVE

- Inserting the definition of $\hat{\Lambda}$ back into the energy derivative:

$$\frac{\partial E_{\rm CC}}{\partial x} = \langle \Phi_0 | \bar{H}^x | \Phi_0 \rangle + \sum_\eta \langle \Phi_0 | \hat{\Lambda} | \Phi_\eta \rangle \langle \Phi_\eta | \bar{H}^x | \Phi_0 \rangle$$

- Again removing the resolution of the identity:

$$\frac{\partial E_{\rm CC}}{\partial x} = \langle \Phi_0 | \left(1 + \hat{\Lambda} \right) \bar{H}^x | \Phi_0 \rangle$$

- We have demonstrated how we can avoid the computation and storage of the derivatives of the $\hat{T}$ amplitudes by instead solving a system of linear equations that do not depend on the perturbation.

- The cost of computing the $\hat{\Lambda}$ amplitudes is roughly the same as solving for $\hat{T}$ – indeed it's a little less expensive, because the $\hat{T}$ amplitude equations are non-linear.

- This is an example of the Wigner *2n+1* rule of perturbation theory in action!

THE LAGRANGIAN APPROACH

- An alternative approach to formulating the coupled cluster energy derivative begins by defining the coupled cluster Lagrangian, which we write as a function of the external parameters ($\mathbf{x}$), cluster amplitudes ($\mathbf{t}$), and Lagrange multipliers (λ):

$$\hat{\mathcal{L}}(\mathbf{x}, \mathbf{t}, \boldsymbol{\eta}) = \langle\Phi_0| \left(1 + \hat{\Lambda}\right) \bar{H}|\Phi_0\rangle = \langle\Phi_0|\bar{H}|\Phi_0\rangle + \sum_{\eta} \lambda_\eta \langle\Phi_\eta|\bar{H}|\Phi_0\rangle$$

- First, make the Lagrangian stationary with respect to the multipliers:

$$\frac{\partial\hat{\mathcal{L}}(\mathbf{x}, \mathbf{t}, \boldsymbol{\eta})}{\partial\lambda_\eta} = 0 = \langle\Phi_\eta|\bar{H}|\Phi_0\rangle$$

These are the CC amplitude equations.

- Next, make the Lagrangian stationary with respect to the $\hat{T}$ amplitudes:

$$\frac{\partial\hat{\mathcal{L}}(\mathbf{x}, \mathbf{t}, \boldsymbol{\eta})}{\partial t_\eta} = 0 = \langle\Phi_0| \left(1 + \Lambda\right) \bar{H}|\Phi_\eta\rangle$$

These are the CC Lambda equations.

THE LAGRANGIAN APPROACH

- One we make the Lagrangian stationary (by solving the $\hat{T}$ and Λ equations), we may differentiate it with respect to an external parameter and take advantage of the *2n+1* and *2n+2* rules:

$$\frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial x} = \frac{\partial E_{\mathrm{CC}}}{\partial x} = \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) e^{-\hat{T}} \frac{\partial \hat{H}_N}{\partial x} e^{\hat{T}} | \Phi_0 \rangle$$

This is exactly the same gradient expression we obtained before using direct differentiation of the coupled cluster energy expression, but the $\hat{\Lambda}$ operator arises naturally as an operator representation of the Lagrange multipliers.

COUPLED CLUSTER DENSITIES

- It is convenient to formulate energy gradient expressions in terms of one- and two-electron densities. This has significant advantages for computer implementations due to its generality and efficiency.
- While such densities are straightforwardly defined for variational methods, such as configuration interaction, they are not so obvious for non-variational methods.
- The coupled cluster Lagrangian is an ideal starting point for defining densities, and, if the Lagrangian is stationary:

$$\hat{\mathcal{L}} = E_{CC} = \langle \Phi_0 | \left(1 + \hat{\Lambda} \right) \bar{H} | \Phi_0 \rangle$$

- We expand the definition of $\bar{H}$ to obtain:

$$\hat{\mathcal{L}} = E_{CC} = \langle \Phi_0 | \left(1 + \hat{\Lambda} \right) e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle$$

- Aside: This form suggests that we may define left- and right-hand coupled cluster wave functions as, respectively:

$$\langle \Psi_{\text{CC}} | = \langle \Phi_0 | \left(1 + \hat{\Lambda} \right) e^{-\hat{T}} \qquad \text{and} \qquad | \Psi_{\text{CC}} \rangle = e^{\hat{T}} | \Phi_0 \rangle$$

COUPLED CLUSTER DENSITIES

- Now insert the second-quantized definition of $\hat{H}_N$:

$$\hat{\mathcal{L}} = E_{CC} = \sum_{pq} f_{pq} \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) e^{-\hat{T}} \{a_p^\dagger a_q\} e^{\hat{T}} | \Phi_0 \rangle$$

$$+ \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) e^{-\hat{T}} \{a_p^\dagger a_q^\dagger a_s a_r\} e^{\hat{T}} | \Phi_0 \rangle$$

- From this expression, we may define the coupled cluster one- and two-electron densities, respectively to be:

$$D_{pq} = \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) e^{-\hat{T}} \{a_p^\dagger a_q\} e^{\hat{T}} | \Phi_0 \rangle$$

and

$$\Gamma_{pqrs} = \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) e^{-\hat{T}} \{a_p^\dagger a_q^\dagger a_s a_r\} e^{\hat{T}} | \Phi_0 \rangle$$

- This leads to the convenient form for the energy:

$$E_{CC} = \sum_{pq} f_{pq} D_{pq} + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \Gamma_{pqrs}$$

COUPLED CLUSTER DENSITIES

- The CC energy gradient may therefore also be written in terms of these densities:

$$\frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial x} = \frac{\partial E_{\mathrm{CC}}}{\partial x} = \langle \Phi_0 | \left(1 + \hat{\Lambda} \right) e^{-\hat{T}} \frac{\partial \hat{H}_N}{\partial x} e^{\hat{T}} | \Phi_0 \rangle$$

$$= \sum_{pq} \frac{\partial f_{pq}}{\partial x} D_{pq} + \frac{1}{4} \sum_{pqrs} \frac{\partial \langle pq || rs \rangle}{\partial x} \Gamma_{pqrs}$$

- Equations for the densities may be obtained using the same algebraic and diagrammatic approaches we've discussed so far.

- This expression is sufficiently general that we may use it for *any* correlated method – CCSD, CCSD(T), etc. – as long as we can define the appropriate densities.

ORBITAL RELAXATION

- We're not quite finished, because we haven't addressed the evaluation of the derivatives of the Fock matrix elements and two-electron integrals in the Hamiltonian:

$$\frac{\partial f_{pq}}{\partial x} \qquad \frac{\partial \langle pq||rs\rangle}{\partial x}$$

- At first glance, these expressions require us to evaluate derivatives of the Hartree-Fock MO coefficients, *e.g.*:

$$\frac{\partial h_{pq}}{\partial x} = \frac{\partial}{\partial x}\sum_{\mu\nu} C^p_\mu h_{\mu\nu} C^q_\nu = \sum_{\mu\nu}\left(\frac{\partial C^p_\mu}{\partial x} h_{\mu\nu} C^q_\nu + C^p_\mu \frac{\partial h_{\mu\nu}}{\partial x} C^q_\nu + C^p_\mu h_{\mu\nu} \frac{\partial C^q_\nu}{\partial x}\right)$$

- However, we can avoid this by incorporating into our Lagrangian additional constraints for the MOs:

$$\hat{\mathcal{L}} = \langle\Phi_0|\left(1+\hat{\Lambda}\right)\bar{H}|\Phi_0\rangle + 2\sum_{ai} D_{ai}\boxed{f_{ai}} + \sum_{pq} I_{pq}\boxed{\left(\sum_{\mu\nu} C^p_\mu S_{\mu\nu} C^q_\nu - \delta_{pq}\right)}$$

- Requiring that the MOs obey the Brillouin equation and remain orthonormal provides additional stationarity conditions through which we can avoid computing derivatives of the orbital coefficients.

THE "FINAL" GRADIENT EXPRESSION

- After including orbital relaxation and ***much*** algebra, we arrive at the final expression for the CC energy derivative:

$$\frac{\partial E_{\rm CC}}{\partial x} = \sum_{pq} D_{pq} f_{pq}^{(x)} + \frac{1}{4}\sum_{pqrs} \Gamma_{pqrs} \langle pq||rs\rangle^{(x)} + \sum_{pq} I_{pq} S_{pq}^{(x)}$$

where the superscript "(x)" denotes derivatives of atomic-orbital-basis integrals transformed into the MO basis.

- However, we want to avoid transforming such derivative integrals into the MO basis because that would require us to carry out *3N* such expensive transformations and store the resulting tensors. Instead, we can "back-transform" the densities and the I_{pq} into the AO basis and directly contract them with the AO-basis derivative integrals:

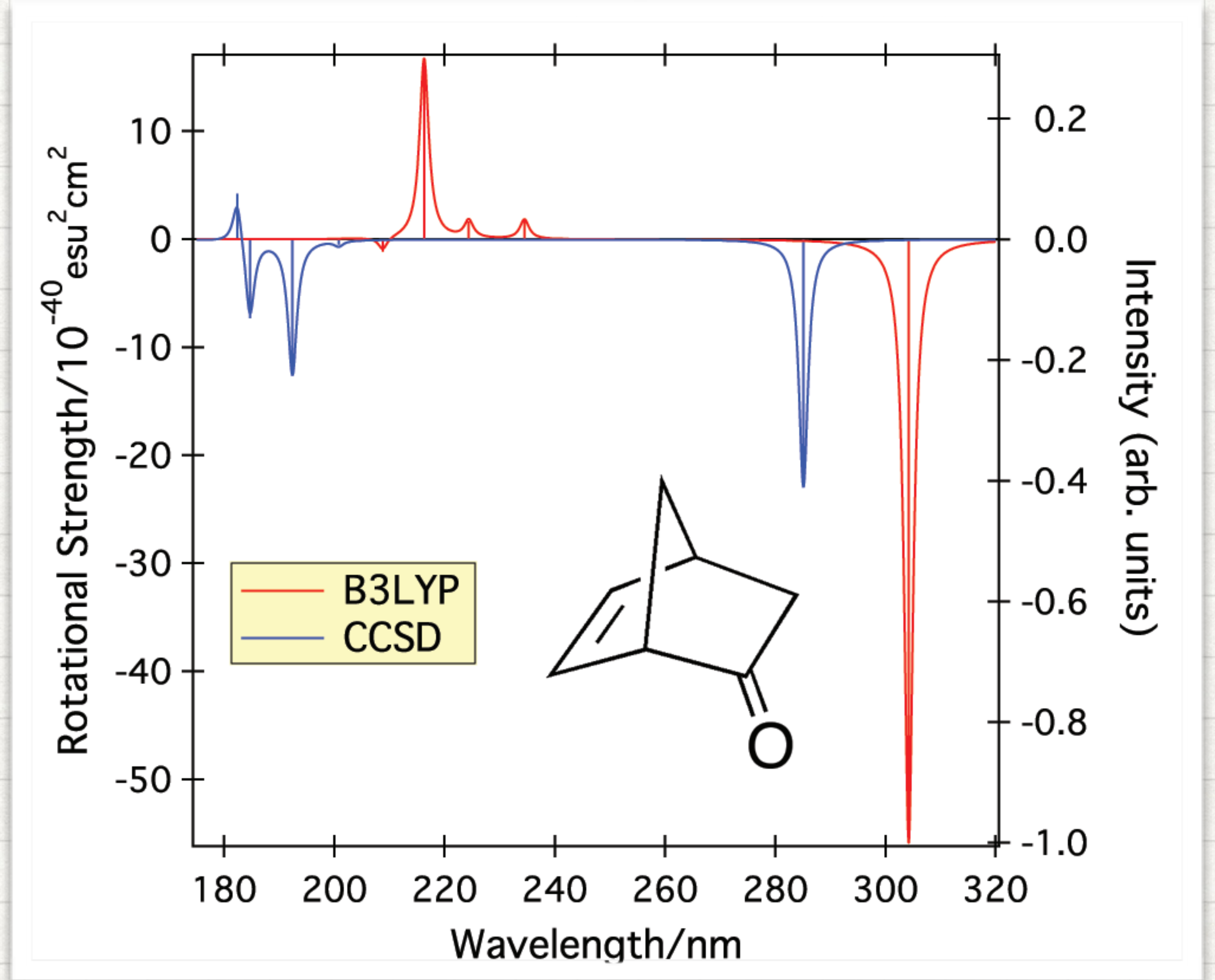
$$\frac{\partial E_{\rm CC}}{\partial x} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial x} + \frac{1}{4}\sum_{pqrs} \Gamma_{\mu\nu\lambda\sigma} \frac{\partial \langle \mu\nu||\lambda\sigma\rangle}{\partial x} + \sum_{\mu\nu} I_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial x}$$

STEPS IN A CC GRADIENT CALCULATION

1. Calculate the AO-basis one- and two-electron integrals.
2. Solve the Hartree-Fock equations for the MO coefficients.
3. Transform the one- and two-electron integrals to the MO basis.
4. Solve the CC $\hat{T}$ amplitude equations.
5. Solve the CC $\hat{\Lambda}$ amplitude equations.
6. Build the CC one- and two-electron densities.
7. Solve for the orbital relaxation parameters (the orbital *Z*-vector).
8. Back-transform the densities to the AO basis.
9. Contract the densities with the derivative integrals in the AO basis.

EXCITED STATES

- The CC equations we've examined so far describe the electronic ground state very well, but they do not provide access to excited states.
- Thus, we need to extend CC theory to excited states to obtain:
  - Excitation energies
  - Transition moments
  - Simulations of spectra
  - Excited-state properties



EQUATION-OF-MOTION CC THEORY

- We can parametrize excited states in coupled cluster theory using a linear wave function Ansatz acting on the CC ground state:

$$|\Psi_{\mathrm{ex}}\rangle = \hat{R}e^{\hat{T}}|\Phi_0\rangle$$

where $\hat{R}$ is yet another cluster operator:

$$\hat{R} = \hat{R}_0 + \hat{R}_1 + \hat{R}_2 + \ldots$$

- Inserting this into the Schrödinger equation, we obtain:

$$\hat{H}_N \hat{R} e^{\hat{T}}|\Phi_0\rangle = E_{\mathrm{ex}}\hat{R}e^{\hat{T}}|\Phi_0\rangle$$

- Since $\hat{R}$ is an excitation operator, it commutes with $\hat{T}$, so:

$$\hat{H}_N e^{\hat{T}}\hat{R}|\Phi_0\rangle = E_{\mathrm{ex}}e^{\hat{T}}\hat{R}|\Phi_0\rangle$$

- Now we multiply by the inverse of the exponential like we did in the ground-state CC equations:

$$e^{-\hat{T}}\hat{H}_N e^{\hat{T}}\hat{R}|\Phi_0\rangle = e^{-\hat{T}}E_{\mathrm{ex}}e^{\hat{T}}\hat{R}|\Phi_0\rangle$$

- Thus, we arrive at an eigenvalue equation for the excited-state energies:

$$\bar{H}\hat{R}|\Phi_0\rangle = E_{\mathrm{ex}}\hat{R}|\Phi_0\rangle$$

EQUATION-OF-MOTION CC THEORY

- We can modify the eigenvalue equation to yield the excitation energies directly by subtracting the ground state energy. First, apply $\hat{R}$ to the ground-state CC Schrödinger equation:

$$\hat{R}\bar{H}|\Phi_0\rangle = \hat{R}E_{\mathrm{CC}}|\Phi_0\rangle$$

- Subtract this from the excited-state Schrödinger equation:

$$\bar{H}\hat{R}|\Phi_0\rangle - \hat{R}\bar{H}|\Phi_0\rangle = E_{\mathrm{ex}}\hat{R}|\Phi_0\rangle - \hat{R}E_{\mathrm{CC}}|\Phi_0\rangle$$

- Combine terms:

$$\left(\bar{H}\hat{R} - \hat{R}\bar{H}\right)|\Phi_0\rangle = \Delta E_{\mathrm{ex}}\hat{R}|\Phi_0\rangle$$

- Insert the resolution of the identity between $\hat{R}$ and $\bar{H}$:

$$\bar{H}\hat{R}|\Phi_0\rangle - \hat{R}|\Phi_0\rangle\langle\Phi_0|\bar{H}|\Phi_0\rangle - \sum_{\eta}\hat{R}|\Phi_\eta\rangle\langle\Phi_\eta|\xcancel{\bar{H}}|\Phi_0\rangle = \Delta E_{\mathrm{ex}}\hat{R}|\Phi_0\rangle$$

- Rearrange:

$$\left(\bar{H} - \langle\Phi_0|\bar{H}|\Phi_0\rangle\right)\hat{R}|\Phi_0\rangle = \Delta E_{\mathrm{ex}}\hat{R}|\Phi_0\rangle$$

- And our final expression is:

$$\bar{H}_N\hat{R}|\Phi_0\rangle = \Delta E_{\mathrm{ex}}\hat{R}|\Phi_0\rangle$$

MATRIX REPRESENTATION

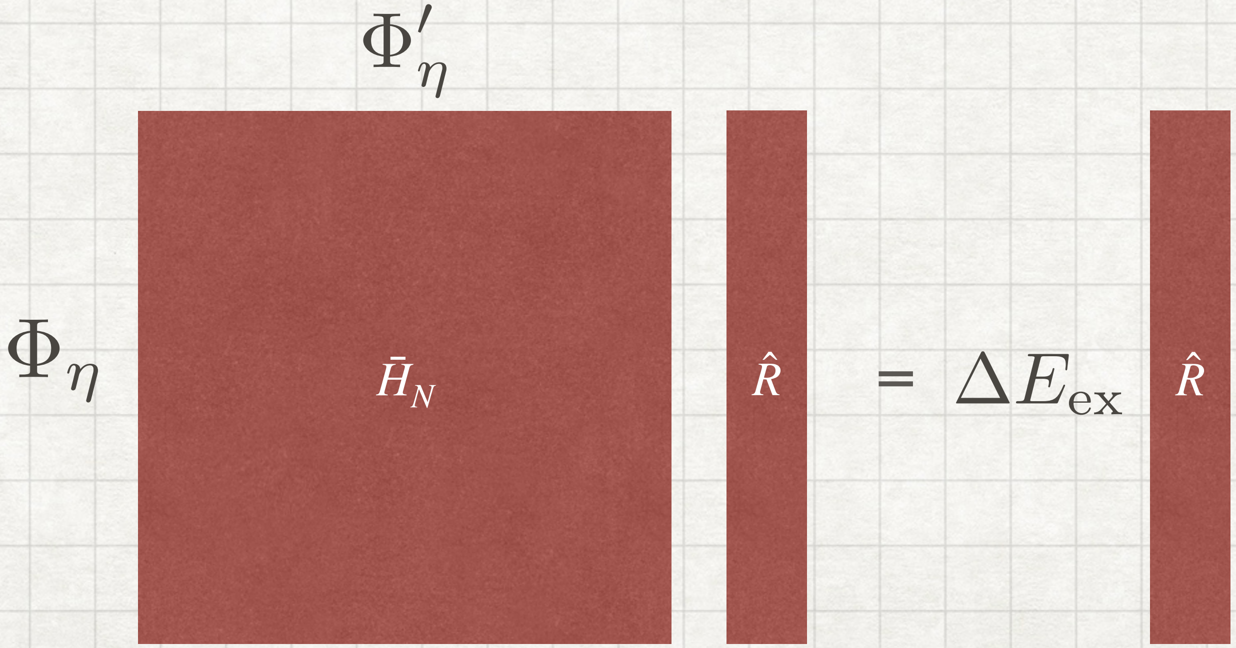
- We may project the eigenvalue equation onto excited determinants:

$$\langle\Phi_\eta|\bar{H}_N\hat{R}|\Phi_0\rangle = \Delta E_{\rm ex}\langle\Phi_\eta|\hat{R}|\Phi_0\rangle$$

- Inserting the resolution of the identity between $\hat{R}$ and $\bar{H}$ gives (after simplification):

$$\sum_{\eta'}\langle\Phi_\eta|\bar{H}_N|\Phi'_\eta\rangle\langle\Phi'_\eta|\hat{R}|\Phi_0\rangle = \Delta E_{\rm ex}\langle\Phi_\eta|\hat{R}|\Phi_0\rangle$$

- This is a matrix-based eigenvalue equation from which we may obtain algebraic expressions for subsequent computer implementation, *e.g.* using a Davidson diagonalization algorithm.

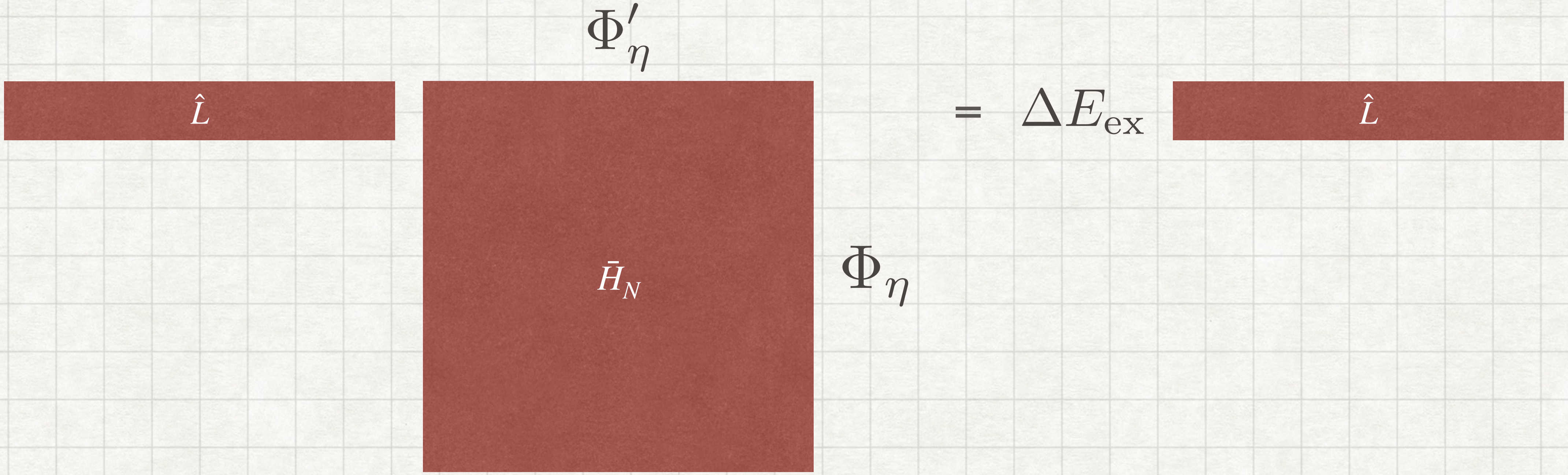


BIORTHONORMALITY

- If we do not truncate $\hat{R}$, then the eigenvalues of $\bar{H}$ are identical to those of the original Hamiltonian, but the similarity transformation removes Hermiticity, yielding distinct left- and right-hand eigenvalue equations:

$$\langle\Phi_0|\hat{L}\bar{H}_N = \langle\Phi_0|\hat{L}\Delta E_{\mathrm{ex}}$$

- Here we have introduced a new de-excitation cluster operator (analogous to $\hat{\Lambda}$) for the left-hand state: $\hat{L} = \hat{L}_0 + \hat{L}_1 + \hat{L}_2 + \dots$



- Note that the left- and right-hand states are orthonormal to each other, but not amongst themselves:

$$\langle\Phi_0|\hat{L}^i\hat{R}^j|\Phi_0\rangle = \delta_{ij} \quad \langle\Phi_0|\hat{L}^i\hat{L}^j|\Phi_0\rangle \neq \delta_{ij} \quad \langle\Phi_0|\hat{R}^i\hat{R}^j|\Phi_0\rangle \neq \delta_{ij}$$

EOM-CC ANALYTIC GRADIENTS

- The most straightforward approach to EOM-CC derivatives is via the Lagrangian formulation (skipping orbital response):

$$\mathcal{L}_{\text{EOM-CC}} = \langle\Phi_0|\hat{L}\bar{H}_N\hat{R}|\Phi_0\rangle + \Delta E_{\text{ex}}\langle\Phi_0|\hat{L}\hat{R}|\Phi_0\rangle + \sum_\eta Z_\eta\langle\Phi_\eta|\bar{H}|\Phi_0\rangle$$

- Differentiate with respect to each set of parameters:
  - Stationarity of the Lagrangian with respect to the $\hat{L}$ or $\hat{R}$ amplitudes gives the EOM-CC eigenvalue equations.
  - Stationarity with respect to the Z_η parameters gives the ground-state coupled cluster equations: $$\frac{\partial\hat{\mathcal{L}}_{\text{EOM-CC}}}{\partial Z_\eta} = 0 = \langle\Phi_\eta|\bar{H}|\Phi_0\rangle$$
  - Stationarity with respect the $\hat{T}$ amplitudes gives the “Zeta" equations:

$$\frac{\partial\mathcal{L}_{\text{EOM-CC}}}{\partial t_\eta} = 0 = \langle\Phi_0|\hat{L}\left[\bar{H},\tau_\eta\right]\hat{R}|\Phi_0\rangle + \langle\Phi_0|\hat{Z}\left[\bar{H},\tau_\eta\right]|\Phi_0\rangle$$

  - The $\hat{Z}$ equations are analogous to the $\hat{\Lambda}$ for ground-state gradients.

PERFORMANCE

CH^+	EOM-CCSD	FCI	Approximate Excitation Level
$^1\Sigma^+$	9.109	8.549	1.96
$^1\Sigma^+$	13.580	13.525	1.03
$^1\Sigma^+$	17.315	17.217	1.13
$^1\Pi$	3.261	3.230	1.03
$^1\Pi$	14.454	14.127	1.24

- The approximate excitation level is a measure of the number electrons excited relative to the ground state.

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[a] J. F. Stanton, J. Chem. Phys., 98, 7029 (1993). Excitation energies in eV.

PERFORMANCE

NH_3	Excitation Energy (eV)
EOM-CCSD	5.716
EOM-CCSDT	5.707
EOM-CCSDTQ	5.722
CISD	9.187
CISDT	5.937
CISDTQ	5.820

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[a] M. Kállay and J. Gauss, J. Chem. Phys., 121, 9257 (2004).

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