COUPLED CLUSTER THEORY

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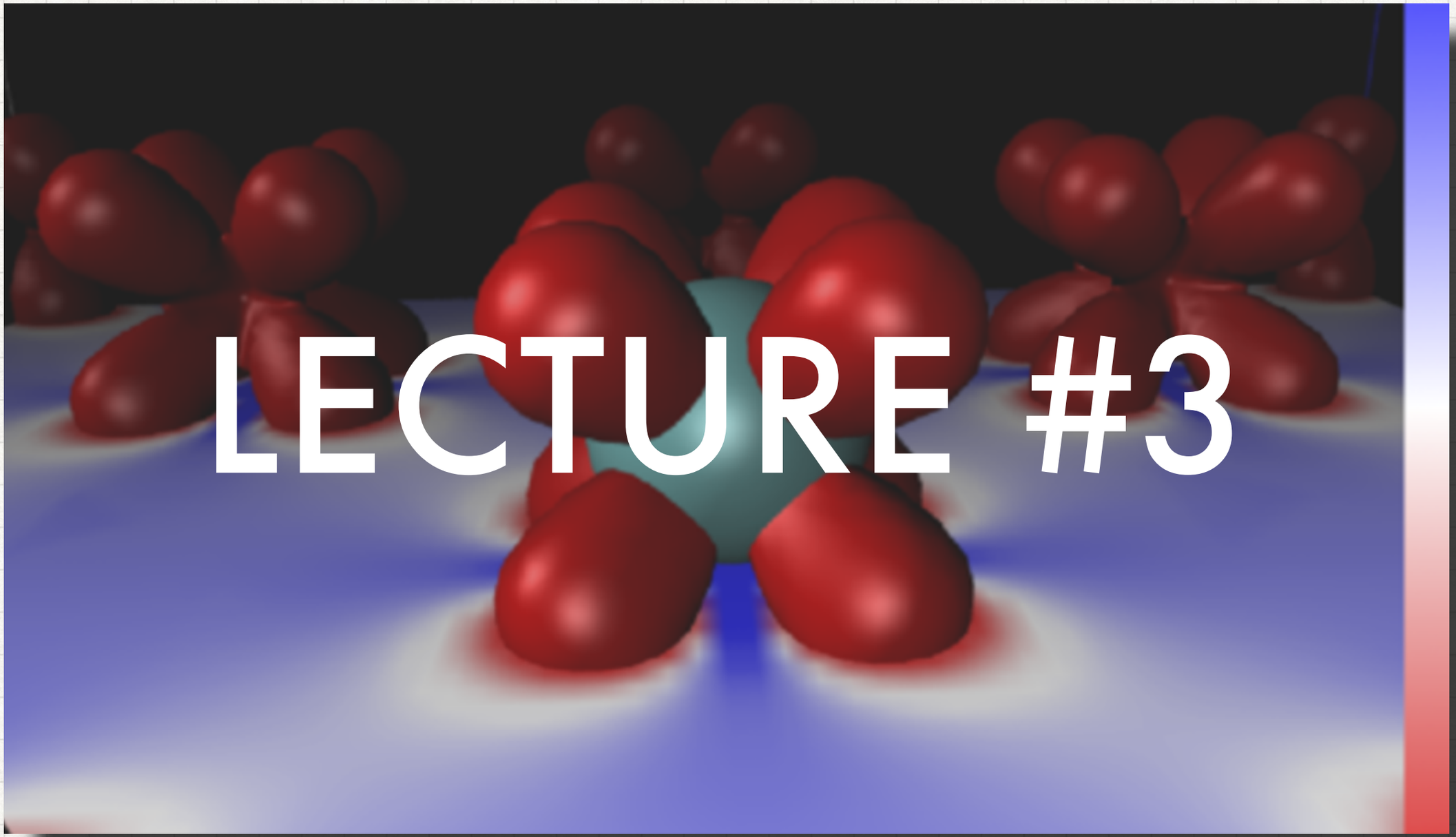


LECTURE #3

PERTURBATION THEORY

- Rayleigh-Schrödinger perturbation theory involves four key steps:
  1. Partition the Hamiltonian into a zeroth-order component and a perturbation/fluctuation potential:
  $$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}$$
  2. Expand the wave function and energy into orders of λ:
  $$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots$$
  $$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$
  3. Expand each perturbed wave function as a linear combination of a set of zeroth-order wave functions:
  $$|\Psi_0^{(n)}\rangle = \sum_{I \neq 0} c_I^{(n)} |\Psi_I^{(0)}\rangle$$
  which are often taken to be eigenfunctions of the zeroth-order Hamiltonian:
  $$\hat{H}^{(0)} |\Psi_I^{(0)}\rangle = E_I^{(0)} |\Psi_I^{(0)}\rangle$$
  4. Insert these expressions into the Schrödinger equation, collect terms by order of λ, and set λ=1 to obtain separate equations for each order.

MANY-BODY PERTURBATION THEORY

- In electronic-structure theory, we partition the second-quantized Hamiltonian into a zeroth-order component extracted from the Fock operator:

$$\hat{H}^{(0)} = \hat{F}_N = \sum_{ij} f_{ij}\{a_i^\dagger a_j\} + \sum_{ab} f_{ab}\{a_a^\dagger a_b\} = \sum_i \epsilon_i \{a_i^\dagger a_i\} + \sum_a \epsilon_a \{a_a^\dagger a_a\}$$

and place the remainder into the perturbation:

$$\hat{H}^{(1)} = \hat{V}_N = \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \{a_p^\dagger a_q^\dagger a_s a_r\}$$

where we have assumed canonical Hartree-Fock orbitals.

- With this choice, a natural candidate for the ground-state zeroth-order wave function is the Hartree-Fock determinant:

$$|\Psi_0^{(0)}\rangle = |\Phi_0\rangle$$

and the other zeroth-order wave functions are excited determinants:

$$\left\{|\Psi_I^{(0)}\rangle\right\} = \left\{|\Phi_{ij\ldots}^{ab\ldots}\rangle\right\}$$

MANY-BODY PERTURBATION THEORY

- This partitioning and choice of zeroth-order functions leads to the usual Møller-Plesset perturbational series, where the Hartree-Fock energy is the sum of the zeroth- and first-order energies:

$$E_{\mathrm{HF}} = \langle \Phi_0 | \hat{H}_N | \Phi_0 \rangle = \langle \Phi_0 | \left(\hat{H}^{(0)} + \hat{H}^{(1)} \right) | \Phi_0 \rangle = E_0^{(0)} + E_0^{(1)}$$

- The first-order Møller-Plesset wave function automatically includes only double excitations:

$$|\Phi_0^{(1)}\rangle = \frac{1}{4} \sum_{ijab} \left(t_{ij}^{ab}\right)^{(1)} |\Phi_{ij}^{ab}\rangle = \frac{1}{4} \sum_{ijab} \left(t_{ij}^{ab}\right)^{(1)} \{a_a^\dagger a_b^\dagger a_j a_i\} |\Phi_0\rangle = \hat{T}_2^{(1)} |\Phi_0\rangle$$

  where the first-order amplitudes have a concise form:

$$\left(t_{ij}^{ab}\right)^{(1)} = \frac{\langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- And the second-order (MP2) energy is:

$$E_{\mathrm{MP2}} = E_0^{(2)} = \frac{1}{4} \sum_{ijab} \left(t_{ij}^{ab}\right)^{(1)} \langle ij||ab\rangle = \frac{1}{4} \sum_{ijab} \frac{\langle ij||ab\rangle \langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- Note that only doubles appear in the first-order wave function, whereas singles, triples, and quadruples appear in the second-order wave function.

PERTURBATIONAL CC THEORY

- The contribution of excited determinants to various orders of perturbation theory suggests that we may decompose the cluster operators into perturbational orders:

$$\hat{T}_n = \hat{T}_n^{(1)} + \hat{T}_n^{(2)} + \hat{T}_n^{(3)} + \dots$$

  where only $\hat{T}_2$ includes a non-zero first-order term.

- We will adopt a common notation for the similarity-transformed Hamiltonian to simplify our equations somewhat:

$$\bar{H} = e^{-\hat{T}} \hat{H}_N e^{\hat{T}}$$

- The order-by-order expansion of $\hat{T}$ and the partitioning of $\hat{H}_N$ lead to a corresponding expansion of $\bar{H}$:

$$\bar{H} = \bar{H}^{(0)} + \bar{H}^{(1)} + \bar{H}^{(2)} + \dots$$

- The lowest few orders are:

$$\bar{H}^{(0)} = \hat{F}_N$$

$$\bar{H}^{(1)} = \hat{V}_N + \left(\hat{F}_N \hat{T}_2^{(1)} \right)_c$$

$$\bar{H}^{(2)} = \left(\hat{F}_N \hat{T}_1^{(2)} + \hat{F}_N \hat{T}_2^{(2)} + \hat{V}_N \hat{T}_2^{(1)} + \frac{1}{2} \hat{F}_N (\hat{T}_2^{(1)})^2 \right)_c$$

PERTURBATIONAL CC THEORY

- In this formulation, we can construct *n*-th order Schrödinger equations as:

$$\bar{H}^{(n)}|\Phi_0\rangle = E^{(n)}|\Phi_0\rangle$$

and then project these onto appropriate determinants to obtain energies and perturbed amplitudes.

- The perturbed energies arise from projection onto the Hartree-Fock state:

$$E^{(n)} = \langle\Phi_0|\bar{H}^{(n)}|\Phi_0\rangle$$

- The second-order energy, for example is:

$$E^{(2)} = \langle\Phi_0|\bar{H}^{(2)}|\Phi_0\rangle = \langle\Phi_0|\left(\hat{F}_N\hat{T}_1^{(2)} + \hat{F}_N\hat{T}_2^{(2)} + \hat{V}_N\hat{T}_2^{(1)} + \frac{1}{2}\hat{F}_N(\hat{T}_2^{(1)})^2\right)_c|\Phi_0\rangle$$

- However, the second and fourth terms on the right cannot contribute, because the Fock operator cannot cancel the +2 and +4 excitations produced by the cluster operators.

- Furthermore, the leading term is also zero, because only the f_{ia} component of $\hat{F}_N$ can connect with $\hat{T}_1^{(2)}$, and this term is zero by Brillouin's theorem.

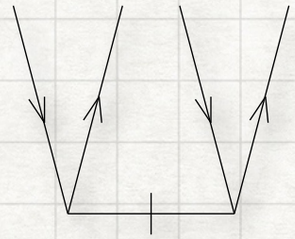
THE SECOND-ORDER ENERGY

- The simplified equation for the second-order (MP2) energy is:

$$E^{(2)} = \langle \Phi_0 | \left(\hat{V}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

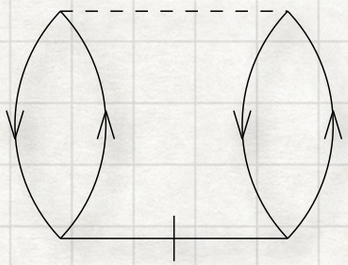
- We may write the first-order $\hat{T}_2$ operator as:

$$\hat{T}_2^{(1)} = \frac{1}{4} \sum_{ijab} \left(t_{ij}^{ab} \right)^{(1)} \{ a_a^\dagger a_b^\dagger a_j a_j \} =$$



where we indicate the order on the diagram using a hash mark on the interaction line.

- Then the second-order energy is similar to what we derived before for CCSD:



$$= \frac{1}{4} \sum_{ijab} \left(t_{ij}^{ab} \right)^{(1)} \langle ij || ab \rangle$$

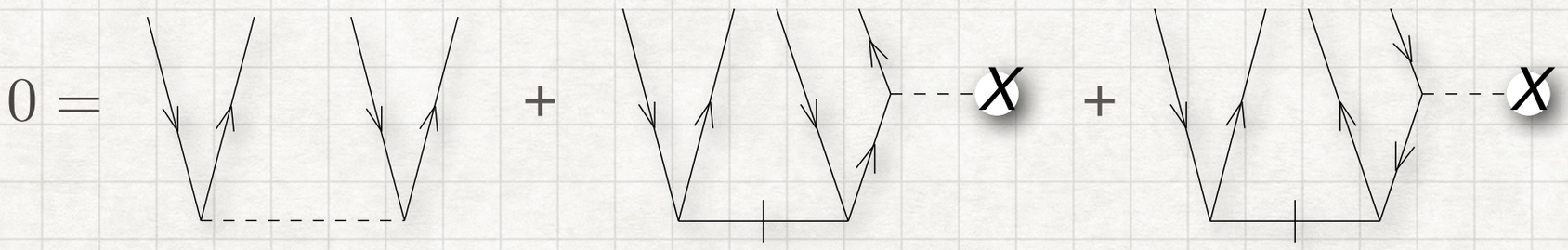
- Now we need an expression for the first-order doubles.

THE FIRST-ORDER WAVE FUNCTION

- We may obtain an equation for the $\hat{T}_2^{(1)}$ amplitudes by projecting the first-order Schrödinger equation onto the doubly excited Slater determinants:

$$0 = \langle \Phi_{ij}^{ab} | \bar{H}^{(1)} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{V}_N | \Phi_0 \rangle + \langle \Phi_{ij}^{ab} | \left(\hat{F}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

- Diagrammatically:



- Evaluating these diagrams gives:

$$0 = \langle ab||ij \rangle + P(ab) \sum_e f_{be} t_{ij}^{ae(1)} - P(ij) \sum_m f_{mj} t_{im}^{ab(1)}$$

- If the orbitals are canonical:

$$0 = \langle ab||ij \rangle + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) \, t_{ij}^{ab(1)}$$

- We may rearrange this to something familiar:

$$t_{ij}^{ab(1)} = \frac{\langle ab||ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

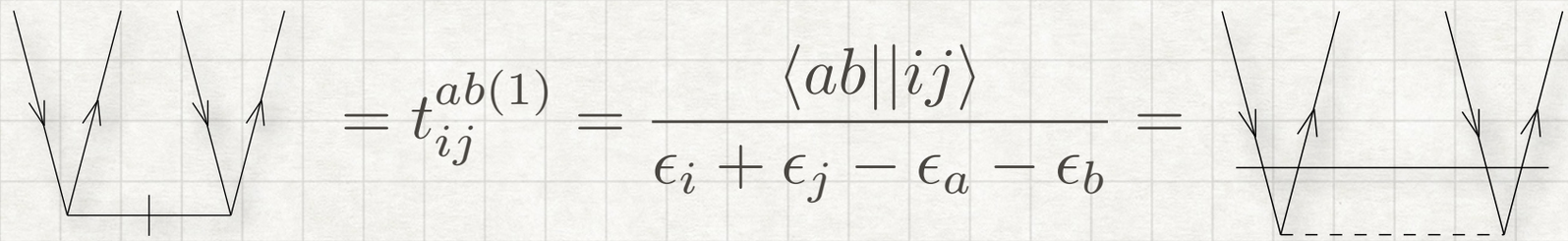
THE SECOND-ORDER ENERGY (AGAIN)

- With an expression for the first-order doubles, we may write the second-order energy in its final form:

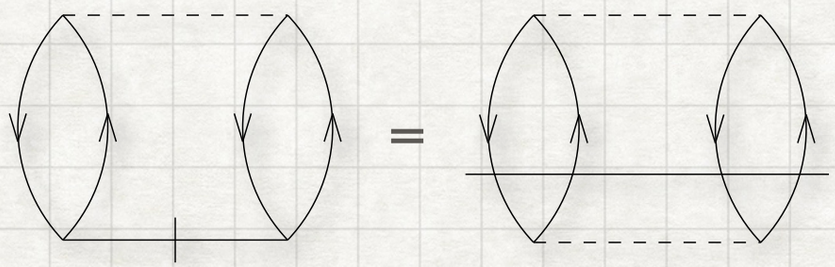
$$E_0^{(2)} = \frac{1}{4}\sum_{ijab} t_{ij}^{ab(1)} \langle ij||ab\rangle = \frac{1}{4}\sum_{ijab} \frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- This is identical to the MP2 expression we examined earlier, but was derived entirely via the coupled cluster equations.

- A notational convenience is to incorporate the energy denominator directly into the diagram for $\hat{T}_2^{(1)}$ as a horizontal line:



- This also leads to a modified diagram for the second-order energy:



HIGHER EXCITATIONS

- As noted earlier, if we go beyond the CCSD approximation to include triples via CCSDT, the cost of the computation becomes unmanageable for chemically significant systems. Can we incorporate the effects of triples without making an investment in the full triples equations?

- For this analysis, we'll choose $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ (CCSDT), which gives us a similarity-transformed Hamiltonian:

$$\bar{H}_{\mathrm{CCSDT}} = e^{-\hat{T}_1 - \hat{T}_2 - \hat{T}_3} \hat{H}_N e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_3}$$

- Triple excitations first appear in the second-order wave function and the fourth-order energy (MP4). That gives us a starting point for approximating the effects of full triples:

$$E_{\mathrm{T}}^{(4)} = \langle \Phi_0 | \bar{H}^{(4)} | \Phi_0 \rangle = \langle \Phi_0 | \left(\hat{V}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle$$

HIGHER EXCITATIONS

- The third-order doubles equation is:

$$0 = \langle \Phi_{ij}^{ab} | \bar{H}^{(3)} | \Phi_0 \rangle$$

$$= \langle \Phi_{ij}^{ab} | \left(\hat{F}_N \hat{T}_2^{(3)} + \hat{V}_N \hat{T}_1^{(2)} + \hat{V}_N \hat{T}_2^{(2)} + \hat{V}_N \hat{T}_3^{(2)} + \frac{1}{2} \hat{V}_N \left(\hat{T}_2^{(1)} \right)^2 \right)_c | \Phi_0 \rangle$$

and the only contribution we don't already have is $\hat{V}_N \hat{T}_3^{(2)}$.

- The contribution of $\hat{T}_3^{(2)}$ to $\hat{T}_2^{(3)}$ may be written as:

$$-\langle \Phi_{ij}^{ab} | \left(\hat{F}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \left(\hat{V}_N \hat{T}_3^{(2)} \right)_c | \Phi_0 \rangle$$

- We need second-order $\hat{T}_3^{(2)}$ for this expression, which comes from:

$$-\langle \Phi_{ijk}^{abc} | \left(\hat{F}_N \hat{T}_3^{(2)} \right)_c | \Phi_0 \rangle = \langle \Phi_{ijk}^{abc} | \left(\hat{V}_N \hat{T}_2^{(1)} \right)_c | \Phi_0 \rangle$$

- So the chain of perturbational levels we need to compute the contribution of $\hat{T}_3$ to the fourth-order energy is:

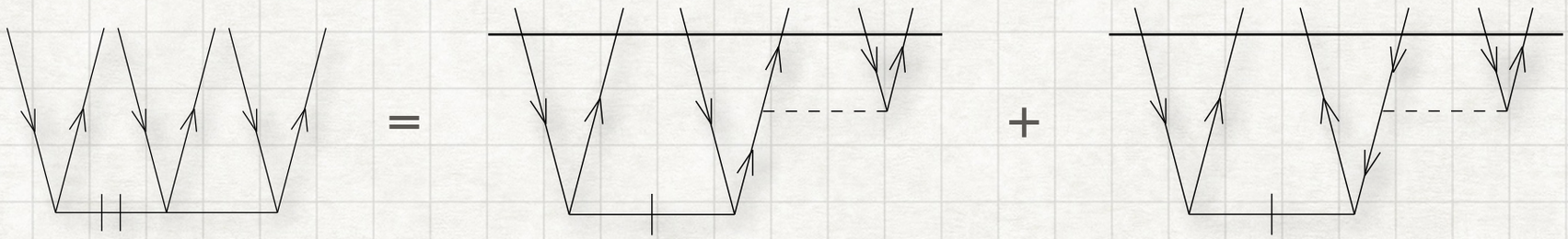
$$E_{\mathrm{T}}^{(4)} \leftarrow \hat{T}_2^{(3)} \leftarrow \hat{T}_3^{(2)} \leftarrow \hat{T}_2^{(1)}$$

HIGHER EXCITATIONS

- The contribution of $\hat{T}_2^{(1)}$ to $\hat{T}_3^{(2)}$ is:

$$-\langle \Phi_{ijk}^{abc}| \left(\hat{F}_N \hat{T}_3^{(2)} \right)_c |\Phi_0\rangle = \langle \Phi_{ijk}^{abc}| \left(\hat{V}_N \hat{T}_2^{(1)} \right)_c |\Phi_0\rangle$$

- Diagrammatically:



- Algebraically:

$$D_{ijk}^{abc} t_{ijk}^{abc(2)} = P(k/ij)P(a/bc) \sum_d \langle bc||dk\rangle t_{ij}^{ad(1)} - P(i/jk)P(c/ab) \sum_l \langle lc||jk\rangle t_{il}^{ab(1)}$$

- The permutation operators are defined as:

$$P(p/qr)f(pqr) = f(pqr) - f(qpr) - f(rqp)$$

- The energy denominators are defined as:

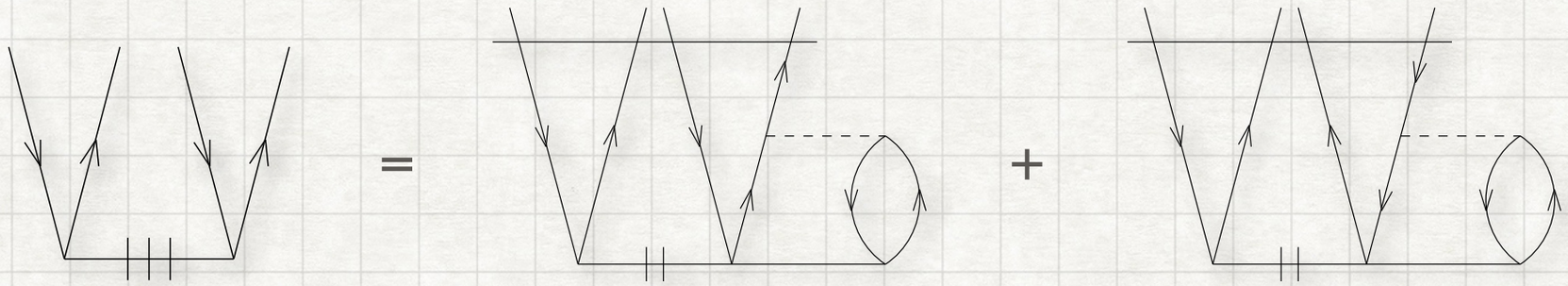
$$D_{ijk}^{abc} \equiv \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c$$

HIGHER EXCITATIONS

- The contribution of $\hat{T}_3^{(2)}$ to $\hat{T}_2^{(3)}$ may be written as:

$$-\langle \Phi_{ij}^{ab}| \left(\hat{F}_N \hat{T}_2^{(3)} \right)_c |\Phi_0\rangle = \langle \Phi_{ij}^{ab}| \left(\hat{V}_N \hat{T}_3^{(2)} \right)_c |\Phi_0\rangle$$

- Or, diagrammatically as:



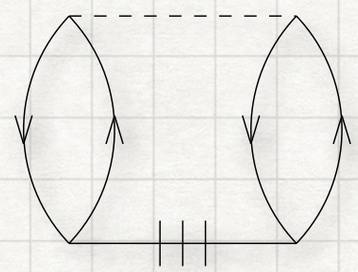
- And algebraically:

$$D_{ij}^{ab} t_{ij}^{ab(3)} = \frac{1}{2} P(ab) \sum_{mef} \langle bm||ef\rangle t_{ijm}^{aef(2)} - \frac{1}{2} P(ij) \sum_{mne} \langle mn||jb\rangle t_{imn}^{abe(2)}$$

HIGHER EXCITATIONS

- Finally, the contribution of $\hat{T}_2^{(3)}$ to $E_T^{(4)}$ is:

$$E_{\mathrm{T}}^{(4)} = \langle \Phi_0 | \left(\hat{V}_N \hat{T}_2^{(3)} \right)_c | \Phi_0 \rangle =$$



$$= \frac{1}{4} \sum_{ijab} \langle ij||ab\rangle t_{ij}^{ab(3)}$$

- Thus, we have a recipe for including the effects of triple-excitations via fourth-order perturbation theory. A few important observations are:
  - This approach is referred to as the CCSD+T(4) method.
  - Given that we are correcting E_{CCSD}, we already have the converged and $\hat{T}_2$ amplitudes. Thus, we can use them rather than $\hat{T}_2^{(1)}$, which gives the CCSD+T(CCSD) = CCSD[T] method.
  - It is not necessary to compute and store all the $t_{ijk}^{abc(2)}$ amplitudes. They are computed in batches, which are then immediately applied to the computation of $t_{ij}^{ab(3)}$, which is easier to store. ***This is key to the success of these methods.***

CCSD(T)

- In 1989, Raghavachari *et al.* recognized that, in addition to $E_T^{(4)}$, a particular fifth-order energy contribution involving $\hat{T}_1$ was important:

$$E_{\mathrm{ST}}^{(5)} = \frac{1}{4} \sum_{ijkabc} \langle jk||bc\rangle t_i^a t_{ijk}^{abc}$$

- They combined this term with $E_T^{(4)}$ (both computed using converged $\hat{T}_1$ and $\hat{T}_2$ amplitudes) to obtain the famous (T) correction:

$$E_{\mathrm{CCSD(T)}} = E_{\mathrm{CCSD}} + E_{\mathrm{T}}^{(4)} + E_{\mathrm{ST}}^{(5)}$$

- The computational cost of the CCSD(T) approach is a non-iterative $\mathcal{O}(n_o^3 n_v^4)$ step in addition to the iterative $\mathcal{O}(n_o^2 n_v^4)$ cost of CCSD.
- Due to its high accuracy, but significantly reduced cost (relative to the full CCSDT approach), CCSD(T) is widely regarded as the "gold standard" of coupled cluster theory.

OTHER APPROXIMATE TRIPLES METHODS

CCSDT-1	Similar in structure to (T), but iterative.
CCSDT-2	Adds $\hat{T}_2^2$ terms to CCSDT-1 (iterative).
CCSDT-3	Adds $\hat{T}_1$, $\hat{T}_1^2$, and, $\hat{T}_1^3$ terms to CCSDT-2 (iterative).
CC3	Similar to CCSDT-1, but includes all $\hat{T}_1$ terms at zeroth-order (iterative).
CCSDR(3)	Similar to CC3, but is non-iterative.

- All of these methods have $\mathcal{O}(N^7)$ cost, but vary in their prefactors and whether they are iterative or non-iterative. None require storage of the complete vector of $\hat{T}_3$ amplitudes.

PROPERTIES FROM ANALYTIC GRADIENTS

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

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

PROPERTIES FROM ANALYTIC GRADIENTS

$\frac{\partial E}{\partial \mathbf{B}}$	Magnetic dipole moment vector
$\frac{\partial^2 E}{\partial \mathbf{B}^2}$	Magnetizability tensor
$\frac{\partial E}{\partial \mathbf{m}_A}$	Spin density on nucleus *A*
$\frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{m}_A}$	NMR shielding tensor on nucleus *A*

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 formulation.

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

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

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

THE LAGRANGIAN APPROACH

- However, rather than directly differentiating the energy, a more elegant approach 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 ($\boldsymbol{\lambda}$):

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

- Here we've introduced a new notation for excited determinants and an associated general normal-ordered operator that generates them:

$$\hat{\tau}_{\eta} | \Phi_0 \rangle = | \Phi_{\eta} \rangle$$

- The second term in the Lagrangian provides the constraint that $\hat{T}$ satisfies the amplitude equations we derived earlier, *viz.*

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

- By defining a de-excitation operator, $\hat{\Lambda}$, we may write the Lagrangian as:

$$\hat{\mathcal{L}}(\mathbf{x}, \mathbf{t}, \boldsymbol{\lambda}) = \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) \bar{H} | \Phi_0 \rangle \qquad \text{where} \qquad \hat{\Lambda} = \sum_{\eta} \lambda_{\eta} \hat{\tau}_{\eta}^{\dagger}$$

THE LAMBDA EQUATIONS

- The equations governing $\hat{T}$ and $\hat{\Lambda}$ may then be determined by requiring that the Lagrangian be stationary with respect to variations in each:

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

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

These are the usual CC amplitude equations.

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

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

These are the CC Lambda equations.

THE LAGRANGIAN APPROACH

- One we make the Lagrangian stationary, we may differentiate it with respect to an external parameter and take advantage of the *2n+1* rule for the amplitudes and the *2n+2* rule for the multipliers:

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

Thus, the Lagrangian formation allows us to obtain the derivative of the CC energy without calculating the derivatives of the $\hat{T}$ amplitudes with respect to each perturbation parameter.

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:

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

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:

$$\frac{\partial \mathcal{L}_{CC}}{\partial x} = \frac{\partial E_{CC}}{\partial x} = \langle \Phi_0 | \left(1 + \hat{\Lambda}\right) e^{-\hat{T}} \frac{\partial \hat{H}_N}{\partial x} e^{\hat{T}} | \Phi_0 \rangle$$
$$= \sum_{pq} \frac{\partial f_{pq}}{\partial x} D_{pq} + \frac{1}{4} \sum_{pqrs} \frac{\partial \langle pq||rs \rangle}{\partial x} \Gamma_{pqrs}$$

- 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.*:

$$\frac{\partial h_{pq}}{\partial x} = \frac{\partial}{\partial x}\sum_{\mu\nu} C_\mu^p h_{\mu\nu} C_\nu^q = \sum_{\mu\nu}\left(\frac{\partial C_\mu^p}{\partial x} h_{\mu\nu} C_\nu^q + C_\mu^p \frac{\partial h_{\mu\nu}}{\partial x} C_\nu^q + C_\mu^p h_{\mu\nu}\frac{\partial C_\nu^q}{\partial x}\right)$$

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

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

- 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:

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

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:

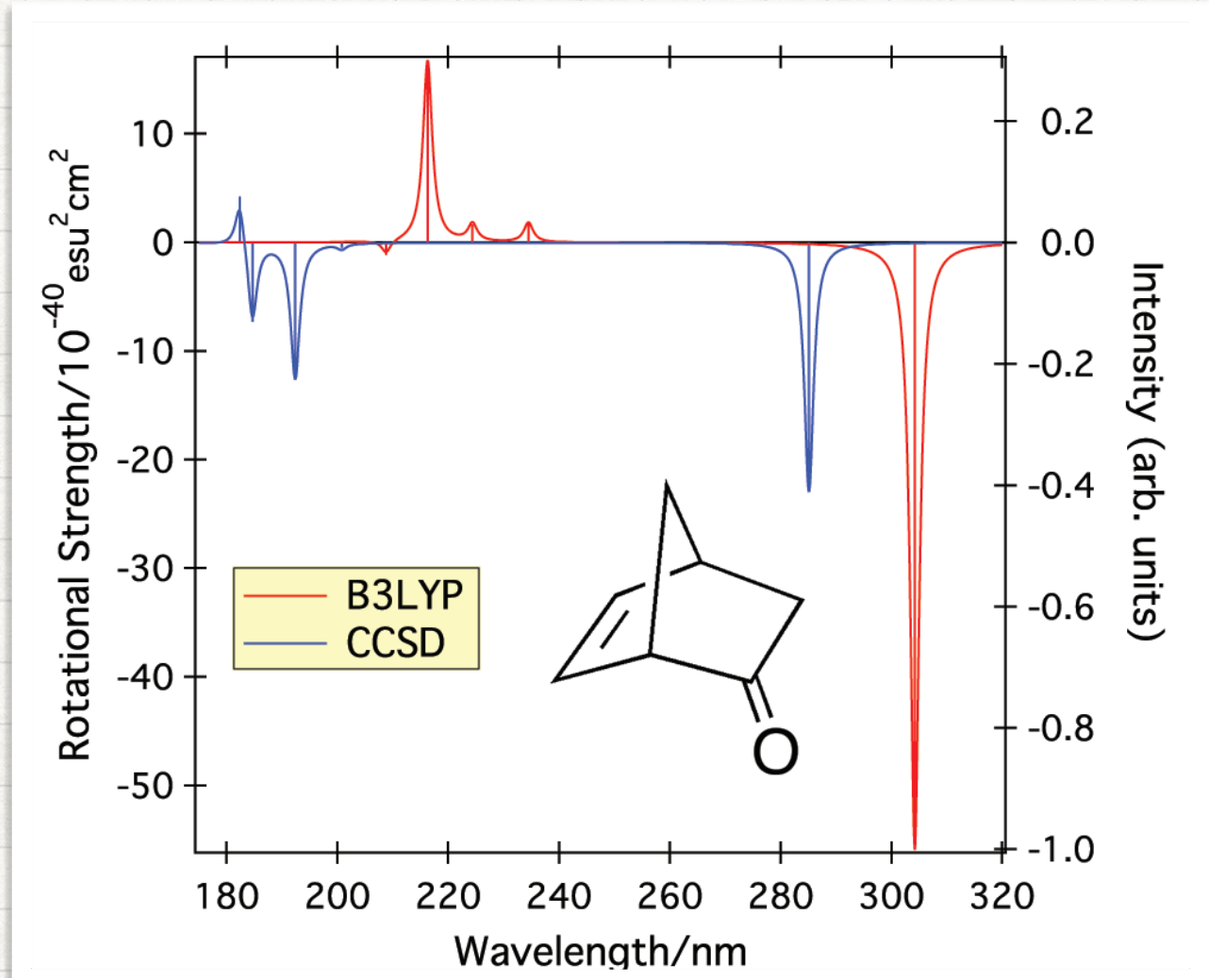
$$\frac{\partial E_{CC}}{\partial x} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial x} + \frac{1}{4} \sum_{pqrs} \Gamma_{\mu\nu\lambda\sigma} \frac{\partial \langle \mu\nu||\lambda\sigma \rangle}{\partial x} + \sum_{\mu\nu} I_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial x}$$

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:

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

- 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 $\bar{H}$:

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

- 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

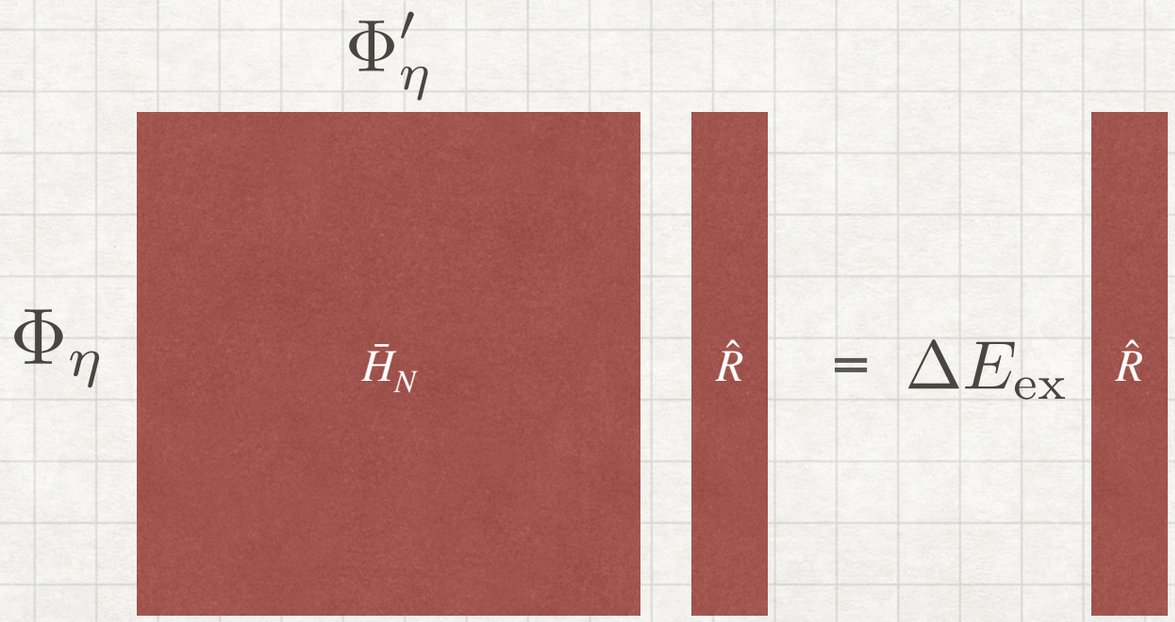
- We may project the eigenvalue equation onto excited determinants:

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

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

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

- 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.



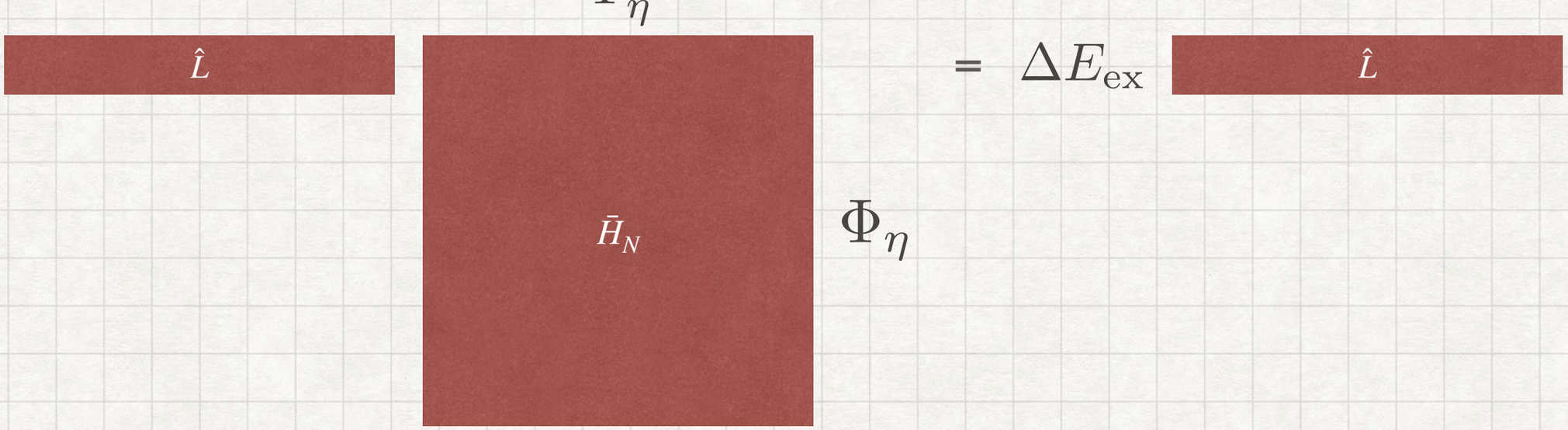
BIORTHONORMALITY

- 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.

[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

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

TIME-DEPENDENT COUPLED CLUSTER THEORY

- If the Hamiltonian contains a time-dependent contribution (e.g., an external, oscillating electric field), then we must begin from the time-dependent Schrödinger equation (in atomic units):

$$\hat{H}|\Psi\rangle = i\frac{d}{dt}|\Psi\rangle$$

- Choosing a coupled-cluster parametrization of the wave function yields distinct, time-dependent left- and right-hand states, for which we employ a phase-isolated form using a real function $\epsilon(t)$:

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

- This leads to distinct right- and left-hand Schrödinger equations:

$$\hat{H}e^{\hat{T}(t)}|\Phi_0\rangle e^{i\epsilon(t)} = i\frac{d}{dt}e^{\hat{T}(t)}|\Phi_0\rangle e^{i\epsilon(t)}$$

$$\langle\Phi_0|\left(1+\hat{\Lambda}(t)\right)e^{-\hat{T}(t)}e^{-i\epsilon(t)}\hat{H} = -i\frac{d}{dt}\langle\Phi_0|\left(1+\hat{\Lambda}(t)\right)e^{-\hat{T}(t)}e^{-i\epsilon(t)}$$

TIME-DEPENDENT COUPLED CLUSTER THEORY

- For the right-hand equation, explicit differentiation with respect to time yields (and assuming no time dependence of the reference state):

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle e^{i\epsilon} = i\frac{d\hat{T}}{dt}e^{\hat{T}}|\Phi_0\rangle e^{i\epsilon} - e^{\hat{T}}|\Phi_0\rangle\frac{d\epsilon}{dt}e^{i\epsilon}$$

- Multiplication on the left by $e^{-\hat{T}}$ gives:

$$\bar{H}|\Phi_0\rangle e^{i\epsilon} = i\frac{d\hat{T}}{dt}|\Phi_0\rangle e^{i\epsilon} - |\Phi_0\rangle\frac{d\epsilon}{dt}e^{i\epsilon}$$

- Finally, since the phase factor, $e^{i\epsilon}$, has no coordinate dependence, multiplication by its complex conjugate gives a somewhat simpler form:

$$\bar{H}|\Phi_0\rangle = i\frac{d\hat{T}}{dt}|\Phi_0\rangle - |\Phi_0\rangle\frac{d\epsilon}{dt}$$

TIME-DEPENDENT COUPLED CLUSTER THEORY

- Carrying out the same sequence of steps for the left-hand equation, explicit differentiation with respect to time yields:

$$\langle\Phi_0|\left(1+\hat{\Lambda}\right)e^{\bar{T}}e^{-i\epsilon}\hat{H} =$$

$$-i\langle\Phi_0|\frac{d\hat{\Lambda}}{dt}e^{-\hat{T}}e^{-i\epsilon} + i\langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\hat{T}}{dt}e^{-\hat{T}}e^{-i\epsilon} - \langle\Phi_0|\left(1+\hat{\Lambda}\right)e^{-\hat{T}}\frac{d\epsilon}{dt}e^{-i\epsilon}$$

- Multiplication on the left by $e^{-\hat{T}}$ gives:

$$\langle\Phi_0|\left(1+\hat{\Lambda}\right)e^{-i\epsilon}\bar{H} = -i\langle\Phi_0|\frac{d\hat{\Lambda}}{dt}e^{-i\epsilon} + i\langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\hat{T}}{dt}e^{-i\epsilon} - \langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\epsilon}{dt}e^{-i\epsilon}$$

- Finally, multiplication on the left by the complex conjugate of the phase factor:

$$\langle\Phi_0|\left(1+\hat{\Lambda}\right)\bar{H} = -i\langle\Phi_0|\frac{d\hat{\Lambda}}{dt} + i\langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\hat{T}}{dt} - \langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\epsilon}{dt}$$

TIME-DEPENDENT COUPLED CLUSTER THEORY

- We note that the time-derivative of the cluster operators retain the same excitation/de-excitation character as the original operators because only the amplitudes carry the time dependence:

$$\frac{d\hat{T}}{dt} = \sum_{\eta} \frac{dt_{\eta}}{dt} \tau_{\eta} \qquad \frac{d\hat{\Lambda}}{dt} = \sum_{\eta} \frac{d\lambda_{\eta}}{dt} \tau_{\eta}^{\dagger}$$

- Furthermore, as long as the sets of occupied and virtual orbitals are disjoint, then the cluster operators commute within excitation/de-excitation classes:

$$\left[\hat{T}_{\eta}, \hat{T}_{\nu}\right] = 0 \qquad \left[\hat{\Lambda}_{\eta}, \hat{\Lambda}_{\nu}\right] = 0$$

$$\left[\frac{d\hat{T}_{\eta}}{dt}, \hat{T}_{\nu}\right] = 0 \qquad \left[\frac{d\hat{\Lambda}_{\eta}}{dt}, \hat{\Lambda}_{\nu}\right] = 0$$

$$\left[\hat{\Lambda}_{\eta}, \hat{T}_{\nu}\right] \neq 0$$

THE TIME DEPENDENCE OF $\hat{T}$

- Starting from the right-hand coupled cluster Schrödinger equation:

$$\bar{H}|\Phi_0\rangle = i\frac{d\hat{T}}{dt}|\Phi_0\rangle - |\Phi_0\rangle\frac{d\epsilon}{dt}$$

- We may project onto the reference determinant to obtain the time dependence of the phase factor, i.e., the quasi-energy:*

$$\langle\Phi_0|\bar{H}|\Phi_0\rangle = i\langle\Phi_0|\frac{d\hat{T}}{dt}|\Phi_0\rangle - \langle\Phi_0|\Phi_0\rangle\frac{d\epsilon}{dt} = -\frac{d\epsilon}{dt}$$

- Similarly, projection onto excited determinants yields the time dependence of the cluster amplitudes:

$$\boxed{\langle\Phi_\mu|\bar{H}|\Phi_0\rangle = i\frac{dt_\mu}{dt}}$$

*This same result may be obtained by projecting the left-hand Schrödinger equation onto the reference determinant, though the derivation is more complicated.

THE TIME DEPENDENCE OF $\hat{\Lambda}$

- Projecting the left-hand Schrödinger equation onto the excited determinants yields:

$$\begin{aligned}
\langle\Phi_0|\left(1+\hat{\Lambda}\right)\bar{H}|\Phi_\mu\rangle &= -i\langle\Phi_0|\frac{d\hat{\Lambda}}{dt}|\Phi_\mu\rangle + i\langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\hat{T}}{dt}|\Phi_\mu\rangle - \langle\Phi_0|\left(1+\hat{\Lambda}\right)\frac{d\epsilon}{dt}|\Phi_\mu\rangle \\
&= -i\frac{d\lambda_\mu}{dt} + \sum_\nu \langle\Phi_0|\left(1+\hat{\Lambda}\right)\tau_\nu\tau_\mu|\Phi_0\rangle\left(i\frac{dt_\nu}{dt}\right) + \langle\Phi_0|\left(1+\hat{\Lambda}\right)|\Phi_\mu\rangle\langle\Phi_0|\bar{H}|\Phi_0\rangle \\
&= -i\frac{d\lambda_\mu}{dt} + \sum_\nu \langle\Phi_0|\left(1+\hat{\Lambda}\right)\tau_\mu|\Phi_\nu\rangle\langle\Phi_\nu|\bar{H}|\Phi_0\rangle + \langle\Phi_0|\left(1+\hat{\Lambda}\right)\tau_\mu|\Phi_0\rangle\langle\Phi_0|\bar{H}|\Phi_0\rangle \\
&= -i\frac{d\lambda_\mu}{dt} + \langle\Phi_0|\left(1+\hat{\Lambda}\right)\tau_\mu\bar{H}|\Phi_0\rangle
\end{aligned}$$

- If we subtract the second term on the right-hand side from both sides of the equation, we obtain the equation governing the time dependence of the $\hat{\Lambda}$ amplitudes:

$$\boxed{\langle\Phi_0|\left(1+\hat{\Lambda}\right)\left[\bar{H},\tau_\mu\right]|\Phi_\mu\rangle = -i\frac{d\lambda_\mu}{dt}}$$

TIME PROPAGATION IN COUPLED CLUSTER

- Now we have our governing equations for the time dependence of $\hat{T}$ and $\hat{\Lambda}$:

$$\boxed{\langle \Phi_\mu | \bar{H} | \Phi_0 \rangle = i \frac{dt_\mu}{dt}}$$

$$\boxed{\langle \Phi_0 | \left(1 + \hat{\Lambda}\right) \left[\bar{H}, \tau_\mu\right] | \Phi_\mu \rangle = -i \frac{d\lambda_\mu}{dt}}$$

- These equations may be cast into the general form:

$$\frac{dy}{dt} = f(t, y) \qquad y(t_0) = y_0$$

- A variety of algorithms exists for solving them through iterations (time steps) from a set of initial conditions, including the Runge-Kutta method, which follows the structure:

$$y_{n+1} = y_n + \Delta t \sum_{i=1}^{s} b_i k_{ni}$$

where

$$k_{ni} = f(t_n + c_i \Delta t, y_n + \Delta t \sum_{j=1}^{i-1} a_{ij} k_{nj})$$

and the coefficients are fixed for a given order of the algorithm.

WHY TD-CC?

- Explicitly time-dependent methods have a number of advantages over response (perturbation) methods:
  - Time- dependent methods allow straightforward connections to experimental conditions, such as fine-tuning the shape, duration, and intensity of external fields.
  - Time-dependent methods yield spectroscopic properties across a wide range of frequencies via Fourier transformation of, e.g., the time-dependent electric-dipole moment, rather than a relatively narrow window of frequencies produced by response techniques.
  - With careful propagation algorithms, time-dependent methods can permit simulation of more intense external fields than feasible with perturbation/response theory approaches.

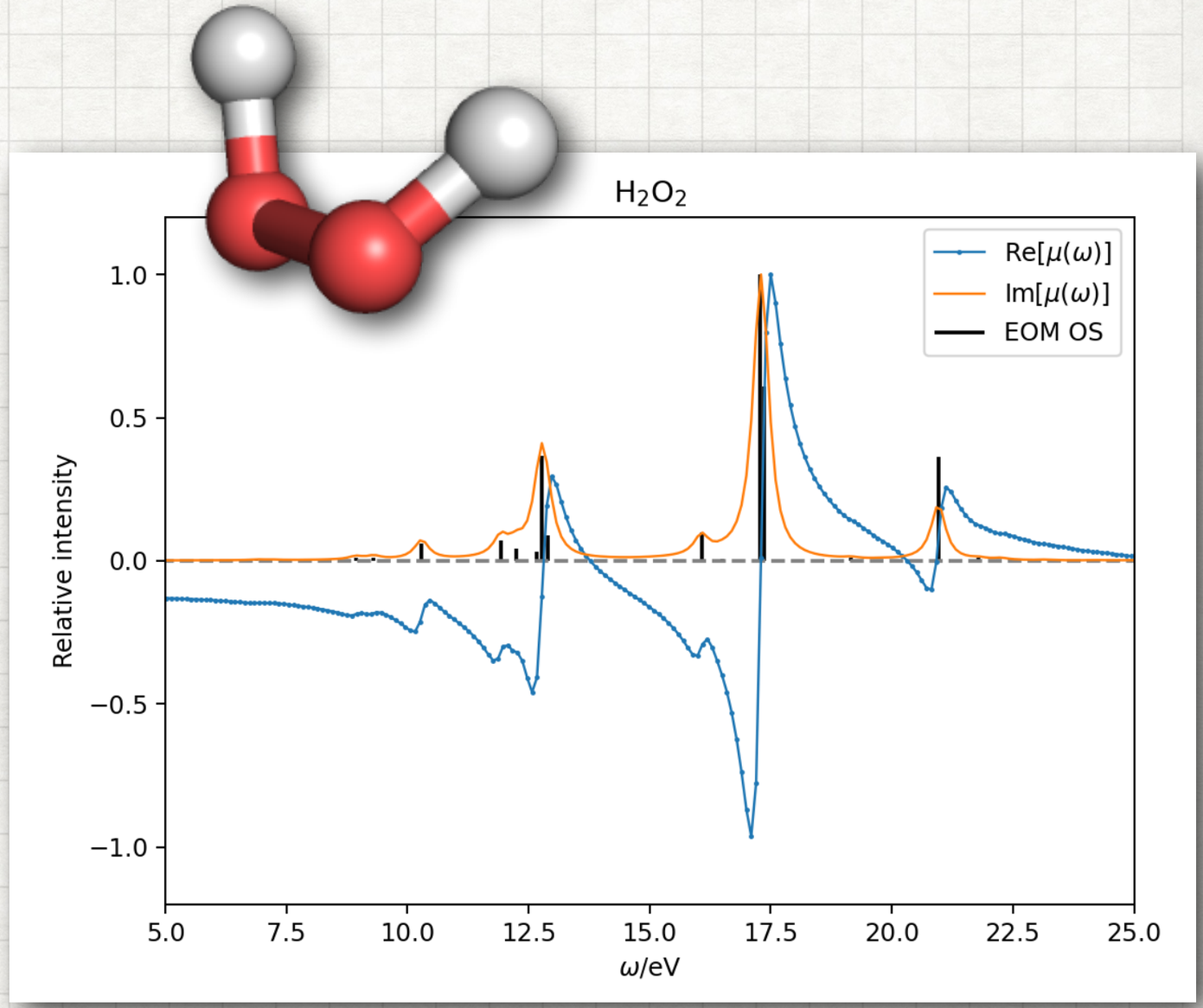
TD-CC: ABSORPTION SPECTRA

At each time step, we compute the time-dependent electric-dipole moment, which is related to the product of the polarizability and the electric field:

$$\mu_\alpha(t) = \langle \Psi_{\mathrm{CC}}(t) | \mu_\alpha | \Psi_{\mathrm{CC}}(t) \rangle$$
$$= \alpha_{\alpha\beta} \left(E_\beta(t) \right)_0$$

The dipole-strength function is thus obtained via the imaginary component of the Fourier transform of the polarizability:

$$S(\omega) \propto \mathrm{Im}\left[\mathrm{Tr}\{\alpha_{\alpha\beta}\} \right]$$
$$\propto \mathrm{Im}\left[\mathrm{Tr}\left\{ \frac{\mu_\alpha(\omega)}{E_\beta(\omega)} \right\} \right]$$



RT-CCSD/6-31G, Dirac delta pulse, Field strength = 0.01 a.u., Propagation time = 1000 a.u., Time step = 0.01 a.u.

TD-CC: CIRCULAR DICHROISM SPECTRA

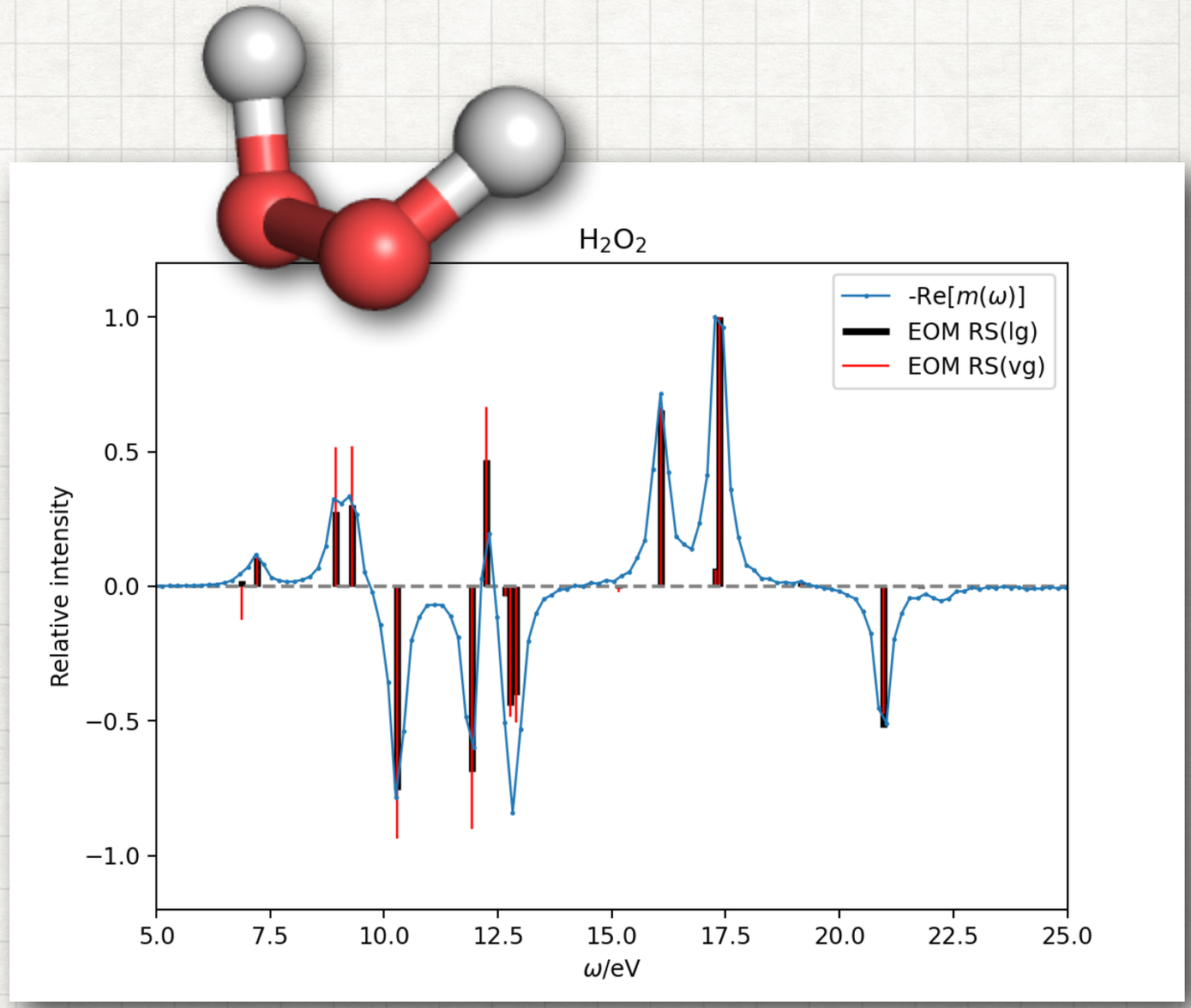
At each time step, we compute the time-dependent magnetic-dipole moment, which is related to the product of the polarizability and the time-derivative of the electric field:

$$m_\alpha(t) = -\frac{1}{\omega} G'_{\beta\alpha} \left(\dot{E}_\beta(t) \right)_0$$

The rotatory-strength function is thus obtained via the imaginary part of the Fourier transform of $G'_{\beta\alpha}$, which becomes the real part of the transform for a Dirac delta pulse:

$$R(\omega) \propto -\mathrm{Im}\left[\mathrm{Tr}\left\{G'_{\beta\alpha}\right\}\right]$$

$$\propto -\omega\ \mathrm{Re}\left[\mathrm{Tr}\left\{\frac{m_\alpha(\omega)}{\kappa_\beta}\right\}\right]$$



RT-CCSD/6-31G, Dirac delta pulse, Field strength = 0.01 a.u., Propagation time = 1000 a.u., Time step = 0.01 a.u.

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