Getting the amplitudes

We need to satisfy equation (61), but for a given set of trial amplitudes this will not be the case and a residue Ω_μ may be defined for each equation

$$\Omega_\mu = \langle \mu | e^{-\hat{T}} \hat{H} e^{\hat{T}} | HF \rangle \qquad (69)$$

This residue Ω_μ is of cause a function of the amplitudes t_μ so mathematically we may view this as a function of which we have to find the zero point. Since the starting point, MP2 amplitudes, is usually close to the optimal value we can use Newtons method in which we expand Ω and assume we only need to make a small step towards the point where it becomes zero:

$$\vec{\Omega}(\vec{t}^{(n)} + \Delta\vec{t}) = 0 \qquad (70)$$

in which we noted that all Ω_μ together form a vector function and denote the vector of all t_μ amplitudes in a given iteration (n) as $\vec{t}^{(n)}$.

Expanding this function gives

$$\vec{\Omega}(\vec{t}^{(n)} + \Delta\vec{t}) = \vec{\Omega}^{(0)}(\vec{t}^{(n)}) + \Omega^{(1)}(\vec{t}^{(n)})\Delta\vec{t} + \ldots \qquad (71)$$

in which $\Omega^{(1)}$ is the Jacobian matrix with first derivatives of the vector function.

We can calculate both terms using known amplitudes $t_\mu^{(n)}$:

$$\Omega_\mu^{(0)}(\vec{t}^{(n)}) = \langle \mu | e^{-\hat{T}^{(n)}} \hat{H} e^{\hat{T}^{(n)}} | HF \rangle \qquad (72)$$

$$\Omega_{\mu\nu}^{(1)}(\vec{t}^{(n)}) = \langle \mu | e^{-\hat{T}^{(n)}} [\hat{H}, \hat{\tau}_\nu] e^{\hat{T}^{(n)}} | HF \rangle \qquad (73)$$

and determine Δt from the equation

$$\Omega^{(1)}(\vec{t}^{(n)})\,\Delta t^{(n)} = -\Omega^{(0)}(\vec{t}^{(n)}) \qquad (74)$$

A problem is that it will be quite expensive to determine the full Jacobian in each CC iteration. In practice it is sufficient to approximate $\Omega^{(1)}$ by its diagonal part

$$\Omega^{(1)}_{\mu\nu}(\vec{t}) \approx \varepsilon_\mu \delta_{\mu\nu} \qquad (75)$$

in which ε_μ is simply the orbital energy difference, for instance for μ being a double excitation $\varepsilon_\mu = \varepsilon_{aibj} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$

that is easily calculated.

This then gives

$$\Delta t^{(n)}_\mu = -\varepsilon_\mu^{-1}\,\Omega^{(0)}(t^{(n)}) \qquad (76)$$

Convergence using this approximate Newton method is usually smooth, providing the CC energy in less than 50 iterations. Still better convergence can be obtained using the DIIS method to extrapolate the amplitudes.

Coupled cluster properties.

Now that we know how to calculate the energy, we may also consider energy derivatives as these give access to molecular properties and the geometry gradient (in this case the displacement of a nucleus from its fixed position is considered as the perturbation).

For exact wave functions we could calculate these via the Hellmann-Feynman Theorem:

$$\left.\frac{dE(\alpha)}{d\alpha}\right|_{\alpha=0} = \frac{d}{d\alpha}\langle \bar{\Psi}^{\text{exact}}(\alpha) | \hat{H}(\alpha) | \Psi^{\text{exact}}(\alpha) \rangle \qquad (77)$$

$$= \langle \Psi^{\text{exact}}(0) | \frac{d\hat{H}(\alpha)}{d\alpha} | \Psi^{\text{exact}}(0) \rangle \qquad (78)$$

which becomes for a Hamiltonian $\hat{H}(\alpha) = \hat{H} + \alpha\hat{V}$ simply the expectation value of the perturbation operator $\hat{V}$:

$$\left.\frac{dE(\alpha)}{d\alpha}\right|_{\alpha=0} = \langle \Psi^{\text{exact}}(0) | \hat{V} | \Psi^{\text{exact}}(0) \rangle \qquad (79)$$

While one could think of evaluating this expectation value for the coupled cluster wave function rather than the exact wave function a problem is that the CC approach is not variational so that the Hellmann-Feynman theorem does not hold. We should therefore first define a variational determined energy that allows us to use the simple expression (79). This can be done using the Lagrangian technique of introducing auxilliary variables $\bar{t}$ that make the energy variational.

We define first the normal energy

$$E^{cc}(\alpha, t) = \langle HF | \hat{H} + \alpha \hat{V} | cc \rangle$$

$$= \langle HF | (\hat{H} + \alpha \hat{V}) e^{\hat{T}} | cc \rangle \qquad (80)$$

and amplitudes fulfilling

$$\langle \mu | e^{-\hat{T}} (H + \alpha V) e^{\hat{T}} | HF \rangle = 0 \qquad (81)$$

and then the Lagrangian

$$L^{cc}(\alpha, t, \bar{t}) = E^{cc}(\alpha, t) + \sum_{\nu} \bar{t}_{\nu} \langle \nu | e^{-\hat{T}} (\hat{H} + \alpha \hat{V}) e^{\hat{T}} | HF \rangle \qquad (82)$$

(note that we suppress the vecter notation for $\vec{t}$ and $\vec{\bar{t}}$ to avoid confusion with the overbar for the Lagrange multipliers).

We then demand that the Lagrangian is a minimum in both sets of variables t and $\bar{t}$

$$\frac{dL}{d\bar{t}_{\mu}} = \langle \mu | e^{-\hat{T}} (\hat{H} + \alpha \hat{V}) e^{\hat{T}} | HF \rangle = 0 \qquad (82)$$

$$\frac{dL}{dt_{\mu}} = \underbrace{\langle HF | (\hat{H} + \alpha \hat{V}) \tau_{\mu} e^{\hat{T}} | HF \rangle}_{=0} + \sum_{\nu} \bar{t}_{\nu} \langle \nu | e^{-\hat{T}} [\hat{H} + \alpha \hat{V}, \tau_{\mu}] e^{\hat{T}} | HF \rangle \qquad (83)$$

The first set of equations (82) can be solved for $\alpha = 0$ and constitute the normal ~~energy~~ equations for the amplitudes. The second set of equations can be used to obtain the multipliers $\bar{t}$.

The Lagrangian is now variational be definition (in the minimum all first derivatives are zero) and we can invoke the Hellmann-Feynman theorem.

$$\left.\frac{dE}{d\alpha}\right|_{\alpha=0} = \left.\frac{\partial L}{\partial \alpha}\right|_{\alpha=0} = \langle HF|\hat{v}e^{\hat{T}}|HF\rangle + \sum_r \bar{t}_r \langle r|e^{-\hat{T}}\hat{v}e^{\hat{T}}|HF\rangle \quad (84)$$

One can also write this as an expectation value by defining the bra-vector

$$\langle \Lambda| = \langle HF| + \sum_r \bar{t}_r \langle r|e^{-\hat{T}} \quad (85)$$

such that

$$\left.\frac{dE}{d\alpha}\right|_{\alpha=0} = \langle \Lambda|\hat{v}|CC\rangle$$

In practice one forms a density matrix $D_{qp} = \langle \Lambda|a_p^\dagger a_q|CC\rangle$ that can be contracted with the matrix representation of $\hat{v}$ to calculate the expectation value.

In this way one may calculate first order properties such as dipole moments, geometry gradients, etc. in about twice the cost as a regular energy calculation. Extension to higher order properties is straightforward and coupled cluster Hessians are nowadays available.