A Whirlwind Introduction to Coupled Cluster Response Theory

T. Daniel Crawford, Virginia Tech, Blacksburg, Virginia, U.S.A.

1 Time-Independent Coupled Cluster Theory

If the Hamiltonian is independent of time, the corresponding Schrödinger equation is

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{1}$$

and the electronic wave function may be conveniently parametrized using the exponential form

$$|\Psi_{\rm CC}\rangle = e^{\hat{T}}|0\rangle, \tag{2}$$

where $|0\rangle$ is the reference determinant (usually Hartree-Fock), and $\hat{T}$ is a cluster operator that generates linear combinations of substituted determinants from $|0\rangle$:

$$\hat{T}|0\rangle = \sum_\mu \hat{T}_\mu|0\rangle = \sum_\mu t_\mu \tau_\mu |0\rangle = \sum_\mu t_\mu |\mu\rangle. \tag{3}$$

where μ denotes sets of singly, doubly, etc. substituted determinants, τ_μ is a second-quantized excitation operator, and the corresponding wave function amplitude/coefficient is t_μ. Insertion of Eq. (2) into Eq. (1) gives

$$\hat{H}e^{\hat{T}}|0\rangle = E_{\rm CC}e^{\hat{T}}|0\rangle, \tag{4}$$

where $E_{\rm CC}$ is still exact in a complete orbital basis and with untruncated $\hat{T}$. In the conventional coupled cluster method, the energy and wave function ampltidues are obtained by a projective approach rather than a variational one by multiplying both side by the inverse of the exponential,

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = E_{\rm CC}|0\rangle, \tag{5}$$

and projecting onto the reference determinant,

$$E_{\rm CC} = \langle 0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle, \tag{6}$$

or substituted determinants, *viz.*

$$0 = \langle \mu|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle, \tag{7}$$

where both equations require that the Slater determinants form an orthonormal set. The coupled cluster equations are typically expressed in terms of the non-Hermitian similarity transformed Hamiltonian,

$$\bar{H} \equiv e^{-\hat{T}}\hat{H}e^{\hat{T}}, \tag{8}$$

which may be interpreted as an effective Hamiltonian whose eigenspectrum is identical to the original Hamiltonian if $\hat{T}$ remains complete. This operator becomes convenient for several reasons, not least because it may be expressed as a finite commutator expansion,

$$\bar{H} = H + \left[\hat{H}, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{H}, \hat{T}\right], \hat{T}\right] + \ldots, \tag{9}$$

which truncates at the quartic terms in $\hat{T}$ due to the two-electron nature of the electronic Hamiltonian. In terms of $\bar{H}$, we obtain the governing equations for the energy

$$E_{\mathrm{CC}} = \langle 0|\bar{H}|0\rangle \tag{10}$$

and the cluster amplitudes

$$0 = \langle \mu|\bar{H}|0\rangle. \tag{11}$$

An alternative view of the non-variational coupled cluster equations arises through the variational optimization of Lagrangian function,

$$L_{\mathrm{CC}} = \langle 0|\bar{H}|0\rangle + \sum_{\mu} \lambda_{\mu}\langle \mu|\bar{H}|0\rangle, \tag{12}$$

where the λ_{μ} serve as the linear multipliers. If we recognize that

$$\langle \mu| = \langle 0|\tau_{\mu}^{\dagger}, \tag{13}$$

then we may define a cluster de-excitation operator analogous to $\hat{T}$ as

$$\langle 0|\hat{\Lambda} = \sum_{\mu}\langle 0|\hat{\Lambda}_{\mu} = \sum_{\mu}\langle 0|\lambda_{\mu}\tau_{\mu}^{\dagger} = \sum_{\mu}\langle \mu|\lambda_{\mu}. \tag{14}$$

This allows us to simplify the expression for the Lagrangian to obtain

$$L_{\mathrm{CC}} = \langle 0|\bar{H}|0\rangle + \langle 0|\hat{\Lambda}\bar{H}|0\rangle = \langle 0|\left(1+\Lambda\right)\bar{H}|0\rangle. \tag{15}$$

Variational optimization of L_{CC} with respect to the Λ amplitudes gives

$$0 = \frac{\partial L_{\mathrm{CC}}}{\partial \lambda_{\mu}} = \langle \mu|\bar{H}|0\rangle, \tag{16}$$

which identical to the defining equation for the $\hat{T}$ amplitudes in Eq. (11). Similar optimization of L_{CC} with respect to the $\hat{T}$ amplitudes gives

$$0 = \frac{\partial L_{\mathrm{CC}}}{\partial t_{\mu}} = \langle 0|\left(1+\hat{\Lambda}\right)\left[\bar{H}, \tau_{\mu}\right]|0\rangle, \tag{17}$$

which is the defining equation for the $\hat{\Lambda}$ amplitudes. The structure of the Lagrangian and the fact that the similarity transformed Hamiltonian is non-Hermitian leads naturally to the identification of left-hand coupled cluster wave function,

$$\langle \Psi_{\mathrm{CC}}| = \langle 0|\left(1+\hat{\Lambda}\right)e^{-\hat{T}}, \tag{18}$$

which is clearly distinct from its right-hand counterpart in Eq. (2).

2 Time-Dependent Coupled Cluster Theory

A time-dependent Hamiltonian requires us to use the corresponding time-dependent Schrödinger equation,

$$\hat{H}|\Psi\rangle = i\frac{d}{dt}|\Psi\rangle \qquad \text{(atomic units)} \tag{19}$$

As noted above, the coupled-cluster parametrization of the electronic wave function has distinct right-hand states,

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}(t)}|0\rangle e^{i\epsilon(t)}, \tag{20}$$

and left-hand states

$$\langle\Psi_{\mathrm{CC}}| = \langle 0| \left(1 + \hat{\Lambda}(t)\right) e^{-\hat{T}(t)} e^{-i\epsilon(t)}, \tag{21}$$

and, as before, the cluster operators generate linear combinations of substituted determinants from the left,

$$\hat{T}(t)|0\rangle = \sum_{\mu} \hat{T}_{\mu}(t)|0\rangle = \sum_{\mu} t_{\mu}(t)\tau_{\mu}|0\rangle = \sum_{\mu} t_{\mu}(t)|\mu\rangle, \tag{22}$$

or from the right,

$$\langle 0|\hat{\Lambda}(t) = \langle 0| \sum_{\mu} \hat{\Lambda}_{\mu}(t) = \langle 0| \sum_{\mu} \lambda_{\mu}(t)\tau_{\mu}^{\dagger} = \sum_{\mu} \lambda_{\mu}(t)\langle\mu|, \tag{23}$$

where the amplitudes, $t_{\mu}(t)$ and $\lambda_{\mu}(t)$ carry the time dependence. In addition, the wave function phase, $\epsilon(t)$, depends on time, though for now we take the reference determinant to be time-independent (no orbital response). This parametrization leads to distinct right- and left-hand Schrödinger equations, respectively,

$$\hat{H}e^{\hat{T}(t)}|0\rangle e^{i\epsilon(t)} = i\frac{d}{dt}e^{\hat{T}(t)}|0\rangle e^{i\epsilon(t)}, \tag{24}$$

and

$$\langle 0| \left(1 + \hat{\Lambda}(t)\right) e^{-\hat{T}(t)} e^{-i\epsilon(t)} \hat{H} = -i\frac{d}{dt}\langle 0| \left(1 + \hat{\Lambda}(t)\right) e^{-\hat{T}(t)} e^{-i\epsilon(t)}. \tag{25}$$

Explicit time differentiation of the amplitudes and phase factor leads to

$$\hat{H}e^{\hat{T}}|0\rangle e^{i\epsilon} = i\frac{d\hat{T}}{dt}e^{\hat{T}}|0\rangle e^{i\epsilon} - e^{\hat{T}}|0\rangle \frac{d\epsilon}{dt}e^{i\epsilon}, \tag{26}$$

for the right-hand Schrödinger equation and

$$\langle 0| \left(1 + \hat{\Lambda}\right) e^{\bar{T}} e^{-i\epsilon} \hat{H} =$$
$$- i\langle 0|\frac{d\hat{\Lambda}}{dt}e^{-\hat{T}}e^{-i\epsilon} + i\langle 0| \left(1 + \hat{\Lambda}\right) \frac{d\hat{T}}{dt}e^{-\hat{T}}e^{-i\epsilon} - \langle 0| \left(1 + \hat{\Lambda}\right) e^{-\hat{T}}\frac{d\epsilon}{dt}e^{-i\epsilon} \tag{27}$$

for the left-hand, and the notational time dependence has been supressed for simplicity. We may express these equations in terms of the similarity-transformed Hamiltonian,

$$\bar{H} \equiv e^{-\hat{T}} \hat{H} e^{\hat{T}} \tag{28}$$

to obtain

$$\bar{H}|0\rangle e^{i\epsilon} = i\frac{d\hat{T}}{dt}|0\rangle e^{i\epsilon} - |0\rangle \frac{d\epsilon}{dt} e^{i\epsilon} \tag{29}$$

and

$$\langle 0| \left(1+\hat{\Lambda}\right) e^{-i\epsilon}\bar{H} = -i\langle 0|\frac{d\hat{\Lambda}}{dt}e^{-i\epsilon} + i\langle 0| \left(1+\hat{\Lambda}\right) \frac{d\hat{T}}{dt}e^{-i\epsilon} - \langle 0| \left(1+\hat{\Lambda}\right) \frac{d\epsilon}{dt}e^{-i\epsilon}. \tag{30}$$

Furthermore, since the exponential phase factor contains no coordinate dependence, multiplication by its complex conjugate yields,

$$\bar{H}|0\rangle = i\frac{d\hat{T}}{dt}|0\rangle - |0\rangle \frac{d\epsilon}{dt} \tag{31}$$

and

$$\langle 0| \left(1+\hat{\Lambda}\right) \bar{H} = -i\langle 0|\frac{d\hat{\Lambda}}{dt} + i\langle 0| \left(1+\hat{\Lambda}\right) \frac{d\hat{T}}{dt} - \langle 0| \left(1+\hat{\Lambda}\right) \frac{d\epsilon}{dt}. \tag{32}$$

Note that the time-derivatives of the cluster operators retain their excitation/de-excitation character because the differentiation only affects the corresponding amplitudes, *i.e.*,

$$\frac{d\hat{T}}{dt} = \sum_{\mu} \frac{dt_\mu}{dt}\tau_\mu \quad \text{and} \quad \frac{d\hat{\Lambda}}{dt} = \sum_{\mu} \frac{d\lambda_\mu}{dt}\tau_\mu^\dagger. \tag{33}$$

Furthermore, as long as the orbital space is comprised of disjoint sets of occupied and virtual orbitals, the cluster operators communte within excitation/de-excitation classes, *e.g.*,

$$\left[\hat{T}_\mu, \hat{T}_\nu\right] = 0, \quad \left[\frac{d\hat{T}_\mu}{dt}, \hat{T}_\nu\right] = 0, \quad \left[\hat{\Lambda}_\mu, \hat{\Lambda}_\nu\right] = 0, \quad \text{and} \quad \left[\frac{d\hat{\Lambda}_\mu}{dt}, \hat{\Lambda}_\nu\right] = 0, \tag{34}$$

but

$$\left[\hat{\Lambda}_\mu, \hat{T}_\nu\right] \neq 0. \tag{35}$$

Projecting the right-hand Schrödinger equation, Eq. (31), onto the reference determinant gives an equation for the time dependence of the phase factor because

$$\langle 0|\bar{H}|0\rangle = i\langle 0|\frac{d\hat{T}}{dt}|0\rangle - \langle 0|0\rangle\frac{d\epsilon}{dt} = -\frac{d\epsilon}{dt}, \tag{36}$$

where we have taken advantage of the fact that the derivative of $\hat{T}$ is still an excitation operator and the set of Slater determinants are orthonormal. Similarly, projection of Eq. (31) onto substituted determinants yields the time dependence of the $\hat{T}$ amplitudes:

$$\langle \mu | \bar{H} | 0 \rangle = i \frac{dt_\mu}{dt}. \tag{37}$$

We may obtain corresponding results from the left-hand Schrödinger equation, though to do so requires some additional manipulation. Projecting Eq. (32) onto the reference determinant gives

$$\langle 0 | \left(1 + \hat{\Lambda}\right) \bar{H} | 0 \rangle = -i \langle 0 | \frac{d\hat{\Lambda}}{dt} | 0 \rangle + i \langle 0 | \left(1 + \hat{\Lambda}\right) \frac{d\hat{T}}{dt} | 0 \rangle - \langle 0 | \left(1 + \hat{\Lambda}\right) \frac{d\epsilon}{dt} | 0 \rangle. \tag{38}$$

The left-hand side may be manipulated by taking advantage of the fact that the set of Slater determinants is complete and thus provides an identity

$$1 = |0\rangle\langle 0| + \sum_\mu |\mu\rangle\langle\mu|. \tag{39}$$

Inserting this between $\hat{\Lambda}$ and $\hat{H}$ gives

$$\begin{aligned} \langle 0 | \left(1 + \hat{\Lambda}\right) \bar{H} | 0 \rangle &= \langle 0 | \bar{H} | 0 \rangle + \langle 0 | \hat{\Lambda} \bar{H} | 0 \rangle \\ &= \langle 0 | \bar{H} | 0 \rangle + \langle 0 | \hat{\Lambda} | 0 \rangle \langle 0 | \bar{H} | 0 \rangle + \sum_\mu \langle 0 | \hat{\Lambda} | \mu \rangle \langle \mu | \bar{H} | 0 \rangle \\ &= \langle 0 | \bar{H} | 0 \rangle + i \sum_\mu \langle 0 | \hat{\Lambda} | \mu \rangle \frac{dt_\mu}{dt}. \end{aligned} \tag{40}$$

where the final step arises due to Eq. (37).

The first term on the right-hand side of Eq. (38) is zero because the derivative of $\hat{\Lambda}$ is still a de-excitation operator, and the Slater determinants form an orthonormal set, while the final term collapses to only the derviative of the phase factor for similar reasons. This leaves only the second term of the right-hand side, which may be simplified as follows:

$$\begin{aligned} i \langle 0 | \left(1 + \hat{\Lambda}\right) \frac{d\hat{T}}{dt} | 0 \rangle &= i \langle 0 | \hat{\Lambda} \frac{d\hat{T}}{dt} | 0 \rangle \\ &= i \sum_\mu \langle 0 | \hat{\Lambda} | \mu \rangle \langle \mu | \frac{d\hat{T}}{dt} | 0 \rangle \\ &= i \sum_\mu \langle 0 | \hat{\Lambda} | \mu \rangle \frac{dt_\mu}{dt}, \end{aligned} \tag{41}$$

which exactly cancels the corresponding term from the left-hand side. Thus, we find that

$$\langle 0 | \bar{H} | 0 \rangle = -\frac{d\epsilon}{dt}, \tag{42}$$

which is identical to the result obtained from the right-hand Schrödinger equation.

Projecting the left-hand Schrödinger equation onto the substituted determinants requires similar manipulation,

$$\begin{aligned}\langle 0|\left(1+\hat{\Lambda}\right)\bar{H}|\mu\rangle &= -i\langle 0|\frac{d\hat{\Lambda}}{dt}|\mu\rangle + i\langle 0|\left(1+\hat{\Lambda}\right)\frac{d\hat{T}}{dt}|\mu\rangle - \langle 0|\left(1+\hat{\Lambda}\right)\frac{d\epsilon}{dt}|\mu\rangle \\ &= -i\frac{d\lambda_\mu}{dt} + i\langle 0|\hat{\Lambda}\frac{d\hat{T}}{dt}|\mu\rangle - \langle 0|\hat{\Lambda}|\mu\rangle\frac{d\epsilon}{dt} \\ &= -i\frac{d\lambda_\mu}{dt} + i\sum_\nu \langle 0|\hat{\Lambda}\frac{dt_\nu}{dt}\tau_\nu|\mu\rangle + \langle 0|\hat{\Lambda}|\mu\rangle\langle 0|\bar{H}|0\rangle, \end{aligned} \tag{43}$$

where we have used the definition of the $\hat{T}$ operator as well as Eq. (36) in the last step. A simpler, commutator-based expression may be obtained by adding a key term to both sides, *viz.*

$$\begin{aligned}\langle 0|\left(1+\hat{\Lambda}\right)\bar{H}|\mu\rangle - \langle 0|\left(1+\Lambda\right)\tau_\mu\bar{H}|0\rangle = -i\frac{d\lambda_\mu}{dt} + i\sum_\nu \langle 0|\hat{\Lambda}\frac{dt_\nu}{dt}\tau_\nu|\mu\rangle + \langle 0|\hat{\Lambda}|\mu\rangle\langle 0|\bar{H}|0\rangle \\ - \langle 0|\left(1+\Lambda\right)\tau_\mu\bar{H}|0\rangle. \end{aligned} \tag{44}$$

Then, recognizing that

$$\begin{aligned}|\mu\rangle &= \tau_\mu|0\rangle, \\ [\tau_\nu,\tau_\mu] &= 0,\end{aligned}$$

and

$$\langle 0|\tau_\mu\bar{H}|0\rangle = 0,$$

the equation may be further simplified as

$$\begin{aligned}\langle 0|\left(1+\hat{\Lambda}\right)\left[\bar{H},\tau_\mu\right]|0\rangle &= -i\frac{d\lambda_\mu}{dt} + \sum_\nu \langle 0|\hat{\Lambda}\tau_\nu|\mu\rangle\langle\nu|\bar{H}|0\rangle + \langle 0|\hat{\Lambda}|\mu\rangle\langle 0|\bar{H}|0\rangle - \langle 0|\Lambda\tau_\mu\bar{H}|0\rangle \\ &= -i\frac{d\lambda_\mu}{dt} + \sum_\nu \langle 0|\hat{\Lambda}\tau_\mu|\nu\rangle\langle\nu|\bar{H}|0\rangle + \langle 0|\hat{\Lambda}\tau_\mu|0\rangle\langle 0|\bar{H}|0\rangle - \langle 0|\Lambda\tau_\mu\bar{H}|0\rangle \\ &= -i\frac{d\lambda_\mu}{dt} + \langle 0|\hat{\Lambda}\tau_\mu\bar{H}|0\rangle - \langle 0|\Lambda\tau_\mu\bar{H}|0\rangle, \end{aligned} \tag{45}$$

where we have used the resolution of the identity [Eq. (39)] in the last step. Now we can see that the last two terms on the right-hand side cancel exactly, leaving a simpler final expression,

$$\langle 0|\left(1+\hat{\Lambda}\right)\left[\bar{H},\tau_\mu\right]|0\rangle = -i\frac{d\lambda_\mu}{dt}, \tag{46}$$

which is the time-dependence of the λ_μ amplitudes.

3 Coupled Cluster Response Theory

If the Hamiltonian is partitioned into a time-independent zeroth-order part and a time-dependent perturbation,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}(t), \tag{47}$$

where the perturbation is a Fourier transform of a frequency-dependent operator,

$$\hat{H}^{(1)}(t) = \int_{-\infty}^{\infty} d\omega \hat{H}^{(1)}(\omega) e^{-i\omega t}, \tag{48}$$

then the cluster operators may be expanded in orders of the perturbation, namely,

$$\hat{T} = \hat{T}^{(0)} + \hat{T}^{(1)} + \hat{T}^{(2)} + \dots \tag{49}$$

and

$$\hat{\Lambda} = \hat{\Lambda}^{(0)} + \hat{\Lambda}^{(1)} + \hat{\Lambda}^{(2)} + \dots \tag{50}$$

Note that the zeroth-order $\hat{T}^{(0)}$ and $\hat{\Lambda}^{(0)}$ amplitudes correspond to the time-independent quantities described in section 1, whose defining expressions are Eqs. (11) and (17), respectively. Similarity transformation of the Hamiltonian gives

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = e^{-\hat{T}^{(0)} - \hat{T}^{(1)} - \hat{T}^{(2)} - \dots} \hat{H} e^{\hat{T}^{(0)} + \hat{T}^{(1)} + \hat{T}^{(2)} + \dots} \tag{51}$$

Collecting the zeroth-order amplitudes together, we may define $\bar{H}$ in a manner consistent with Section 1,

$$\bar{H} \equiv e^{-\hat{T}^{(0)}} \hat{H} e^{\hat{T}^{(0)}}, \tag{52}$$

and then define the fully transformed Hamiltonian as

$$\bar{\bar{H}} = e^{-\hat{T}^{(1)} - \hat{T}^{(2)} \dots} \bar{H} e^{\hat{T}^{(1)} + \hat{T}^{(2)} \dots}. \tag{53}$$

Note that $\bar{H}$ contains only zeroth- and first-order terms with zeroth-order time-independent amplitudes, $\hat{T}^{(0)}$,

$$\bar{H} = \bar{H}^{(0)} + \bar{H}^{(1)}, \tag{54}$$

whereas $\bar{\bar{H}}$ contains all orders:

$$\bar{\bar{H}} = \bar{\bar{H}}^{(0)} + \bar{\bar{H}}^{(1)} + \bar{\bar{H}}^{(2)} \dots, \tag{55}$$

where, for example,

$$\bar{\bar{H}}^{(0)} = \bar{H}^{(0)} = e^{-\hat{T}^{(0)}} \hat{H}^{(0)} e^{-\hat{T}^{(0)}}, \tag{56}$$

$$\bar{\bar{H}}^{(1)} = \bar{H}^{(1)} + \left[\bar{H}^{(0)}, \hat{T}^{(1)} \right], \tag{57}$$

and

$$\bar{\bar{H}}^{(2)} = \left[\bar{H}^{(1)}, \hat{T}^{(1)} \right] + \frac{1}{2} \left[\left[\bar{H}^{(0)}, \hat{T}^{(1)} \right], \hat{T}^{(1)} \right] + \left[\bar{H}^{(0)}, \hat{T}^{(2)} \right]. \tag{58}$$

Amplitudes in each order may be obtained by similar expansion of the governing equations, Eqs. (37) and (46), in conjunction with the commutator expansion of $\bar{\bar{H}}$. For the $\hat{T}$ amplitudes, for example, the first few orders are derived from Eq. (37) to give

$$i\frac{dt_\mu^{(0)}}{dt} = \langle\mu|\bar{\bar{H}}^{(0)}|0\rangle = \langle\mu|\bar{H}^{(0)}|0\rangle = 0, \tag{59}$$

$$i\frac{dt_\mu^{(1)}}{dt} = \langle\mu|\bar{\bar{H}}^{(1)}|0\rangle = \langle\mu|\bar{H}^{(1)}|0\rangle + \langle\mu|\left[\bar{H}^{(0)}, \hat{T}^{(1)}\right]|0\rangle, \tag{60}$$

and

$$i\frac{dt_\mu^{(2)}}{dt} = \langle\mu|\bar{\bar{H}}^{(2)}|0\rangle = \langle\mu|\left[\bar{H}^{(1)}, \hat{T}^{(1)}\right]|0\rangle + \frac{1}{2}\langle\mu|\left[\left[\bar{H}^{(0)}, \hat{T}^{(1)}\right], \hat{T}^{(1)}\right]|0\rangle + \langle\mu|\left[\bar{H}^{(0)}, \hat{T}^{(2)}\right]|0\rangle. \tag{61}$$

Similarly, for the $\hat{\Lambda}$ amplitudes,

$$-i\frac{d\lambda_\mu^{(0)}}{dt} = \langle 0|\left(1 + \hat{\Lambda}^{(0)}\right)\left[\bar{H}^{(0)}, \tau_\mu\right]|0\rangle = 0, \tag{62}$$

$$-i\frac{d\lambda_\mu^{(1)}}{dt} = \langle 0|\left(1 + \hat{\Lambda}^{(0)}\right)\left[\bar{\bar{H}}^{(1)}, \tau_\mu\right]|0\rangle + \langle 0|\hat{\Lambda}^{(1)}\left[\bar{H}^{(0)}, \tau_\mu\right]|0\rangle, \tag{63}$$

and

$$-i\frac{d\lambda_\mu^{(2)}}{dt} = \langle 0|\left(1 + \hat{\Lambda}^{(0)}\right)\left[\bar{\bar{H}}^{(2)}, \tau_\mu\right]|0\rangle + \langle 0|\hat{\Lambda}^{(1)}\left[\bar{\bar{H}}^{(1)}, \tau_\mu\right]|0\rangle + \langle 0|\hat{\Lambda}^{(2)}\left[\bar{H}^{(0)}, \tau_\mu\right]|0\rangle. \tag{64}$$

We may define the time-dependent perturbed amplitudes in terms of Fourier transforms of their frequency-dependent counterparts in analogy to the frequency-dependent perturbation of Eq. (48) as, for example,

$$t_\mu^{(1)}(t) = \int_{-\infty}^{\infty} d\omega\; t_\mu^{(1)}(\omega)\; e^{-i\omega t} \tag{65}$$

and

$$t_\mu^{(2)}(t) = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2\; t_\mu^{(2)}(\omega_1, \omega_2)\; e^{-i\omega_1 t} e^{-i\omega_2 t}. \tag{66}$$

These expressions are trivially differentiated to give,

$$\frac{dt_\mu^{(1)}}{dt} = \int_{-\infty}^{\infty} d\omega\; (-i\omega)\; t_\mu^{(1)}(\omega)\; e^{-i\omega t} \tag{67}$$

and

$$\frac{dt_\mu^{(2)}}{dt} = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2\; (-i\omega_1 - i\omega_2)\; t_\mu^{(2)}(\omega_1, \omega_2)\; e^{-i\omega_1 t} e^{-i\omega_2 t}. \tag{68}$$

Comparing these expressions to the corresponding derivatives above and inserting the Fourier transforms of all time-dependent quantities gives

$$\begin{aligned}
i\frac{dt_\mu^{(1)}}{dt} &= \int_{-\infty}^{\infty} d\omega\ \omega\ t_\mu^{(1)}(\omega)\ e^{-i\omega t} = \langle\mu|\bar{\bar{H}}^{(1)}|0\rangle = \langle\mu|\bar{H}^{(1)}|0\rangle + \langle\mu|\left[\bar{H}^{(0)}, \hat{T}^{(1)}\right]|0\rangle \\
&= \langle\mu|\int_{-\infty}^{\infty} d\omega\ \bar{\bar{H}}^{(1)}(\omega)e^{-i\omega t}|0\rangle \\
&= \langle\mu|\int_{-\infty}^{\infty} d\omega\ \bar{H}^{(1)}(\omega)e^{-i\omega t}|0\rangle + \langle\mu|\left[\bar{H}^{(0)}, \int_{-\infty}^{\infty} d\omega\ \hat{T}^{(1)}(\omega)e^{-i\omega t}\right]|0\rangle.
\end{aligned} \tag{69}$$

We may equate the integration kernels of each term to obtain

$$\omega t_\mu^{(1)}(\omega) = \langle\mu|\bar{H}^{(1)}(\omega)|0\rangle + \langle\mu|\left[\bar{H}^{(0)}, \hat{T}^{(1)}(\omega)\right]|0\rangle, \tag{70}$$

where $\hat{T}^{(1)}(\omega)$ is a cluster operator built from the frequency-dependent first-order amplitudes and $\bar{H}^{(1)}(\omega)$ is the similarity transformation of the frequency-dependent perturbation $\hat{H}^{(1)}(\omega)$ using only the zeroth-order $\hat{T}^{(0)}$. This is the equation that must be solved to obtain the first-order, frequency-dependent cluster amplitudes.

Using a similar approach for the second-order derivatives, we see

$$\begin{aligned}
i\frac{dt_\mu^{(2)}}{dt} &= \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2\ (\omega_1+\omega_2)\ t_\mu^{(2)}(\omega_1,\omega_2)\ e^{-i\omega_1 t}e^{-i\omega_2 t} \\
&= \langle\mu|\left[\bar{H}^{(1)}, \hat{T}^{(1)}\right]|0\rangle + \frac{1}{2}\langle\mu|\left[\left[\bar{H}^{(0)}, \hat{T}^{(1)}\right], \hat{T}^{(1)}\right]|0\rangle + \langle\mu|\left[\bar{H}^{(0)}, \hat{T}^{(2)}\right]|0\rangle \\
&= \langle\mu|\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \frac{1}{2}\hat{P}(\omega_1,\omega_2)\left[\bar{H}^{(1)}(\omega_1), \hat{T}^{(1)}(\omega_2)\right] e^{-i(\omega_1+\omega_2)t}|0\rangle + \\
&\frac{1}{2}\langle\mu|\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \left[\left[\bar{H}^{(0)}, \hat{T}^{(1)}(\omega_1)\right], \hat{T}^{(1)}(\omega_2)\right] e^{-i(\omega_1+\omega_2)t}|0\rangle + \\
&\langle\mu|\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \left[\bar{H}^{(0)}, \hat{T}^{(2)}(\omega_1,\omega_2)\right] e^{-i(\omega_1+\omega_2)t}|0\rangle,
\end{aligned} \tag{71}$$

where the permutation operator $\hat{P}(\omega_1,\omega_2)$ gives a sum of two terms: one as written plus a second with the frequencies reversed. By equating the integrands on both sides, we obtain

$$\begin{aligned}
(\omega_1+\omega_2)t_\mu^{(2)}(\omega_1,\omega_2) = \frac{1}{2}\hat{P}(\omega_1,\omega_2)\langle\mu|\Big(\left[\bar{H}^{(1)}(\omega_1), \hat{T}^{(1)}(\omega_2)\right] + \\
\frac{1}{2}\left[\left[\bar{H}^{(0)}, \hat{T}^{(1)}(\omega_1)\right], \hat{T}^{(1)}(\omega_2)\right] + \left[\bar{H}^{(0)}, \hat{T}^{(2)}(\omega_1,\omega_2)\right]\Big)|0\rangle.
\end{aligned} \tag{72}$$

We may apply the same technique to the $\hat{\Lambda}$ amplitudes to give

$$-\omega\lambda_\mu^{(1)}(\omega) = \langle 0|\hat{\Lambda}^{(1)}(\omega)\left[\bar{H}^{(0)}, \tau_\mu\right]|0\rangle + \langle 0|\left(1+\hat{\Lambda}^{(0)}\right)\left[\bar{\bar{H}}^{(1)}(\omega), \tau_\mu\right]|0\rangle, \tag{73}$$

and

$$-(\omega_1+\omega_2)\lambda_\mu^{(2)} = \frac{1}{2}\hat{P}(\omega_1,\omega_2)\langle 0| \left(\hat{\Lambda}^{(2)}(\omega_1,\omega_2)\left[\bar{H}^{(0)},\tau_\mu\right] + \left(1+\hat{\Lambda}^{(0)}\right)\left[\bar{\bar{H}}^{(2)}(\omega_1,\omega_2),\tau_\mu\right] + \hat{\Lambda}^{(1)}(\omega_1)\left[\bar{\bar{H}}^{(1)}(\omega_2),\tau_\mu\right]\right)|0\rangle. \tag{74}$$

At long last, we are ready to define the coupled cluter response functions, starting from the Fourier expansion of the expectation value of a time-independent operator, $\hat{A}$,

$$\langle\hat{A}\rangle = \langle\hat{A}\rangle^{(0)} + \int_{-\infty}^{\infty} d_\omega \langle\langle\hat{A};\hat{H}^{(1)}(\omega)\rangle\rangle\ e^{-i\omega t} + \frac{1}{2}\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2\ \langle\langle\hat{A};\hat{H}^{(1)}(\omega_1),\hat{H}^{(1)}(\omega_2)\rangle\rangle\ e^{-i\omega_1 t}e^{-i\omega_2 t} + \ldots \tag{75}$$

Replacing the general expectation value with its coupled cluster counterpart yields

$$\langle\Psi_{\rm CC}|\hat{A}|\Psi_{\rm CC}\rangle = \langle 0|\left(1+\hat{\Lambda}(t)\right)e^{-T(t)}\hat{A}e^{T(t)}|0\rangle = \langle 0|\left(1+\hat{\Lambda}(t)\right)\bar{\bar{A}}|0\rangle,$$

where we have temporarily re-introduced the time-dependence notation for clarity. Inserting the order-by-order expansion in $\hat{H}^{(1)}(t)$ for the double similarity transformation of $\hat{A}$ gives

$$\bar{\bar{A}}^{(0)} = \bar{A}^{(0)},$$
$$\bar{\bar{A}}^{(1)} = \left[\bar{A}^{(0)},\hat{T}^{(1)}\right],$$
$$\bar{\bar{A}}^{(2)} = \frac{1}{2}\left[\left[\bar{A}^{(0)},\hat{T}^{(1)}\right],\hat{T}^{(1)}\right] + \left[\bar{A}^{0},\hat{T}^{(2)}\right],$$

etc. where the $\bar{A}^{(1)}$ terms are zero because of the time-independence of $\hat{A}$. Expanding the coupled cluster expectation value in orders of $\hat{H}^{(1)}$,

$$\langle\Psi_{\rm CC}|\hat{A}|\Psi_{\rm CC}\rangle = \langle 0|\left(1+\hat{\Lambda}^{(0)}\right)\bar{A}^{(0)}|0\rangle + \langle 0|\left[\left(1+\hat{\Lambda}^{(0)}\right)\bar{\bar{A}}^{(1)} + \hat{\Lambda}^{(1)}\bar{A}^{(0)}\right]|0\rangle + \langle 0|\left[\left(1+\hat{\Lambda}^{(0)}\right)\bar{\bar{A}}^{(2)} + \hat{\Lambda}^{(1)}\bar{\bar{A}}^{(1)} + \hat{\Lambda}^{(2)}\bar{A}^{(0)}\right]|0\rangle + \ldots \tag{76}$$

Inserting Fourier transforms of each time-dependent quantity above and equating the corresponding terms of each order in the general expectation value leads to expressions for the first few response functions, including the zeroth-order expectation value

$$\langle\hat{A}\rangle^{(0)} = \langle 0|\left(1+\hat{\Lambda}^{(0)}\right)\bar{A}^{(0)}|0\rangle, \tag{77}$$

the linear response function

$$\langle\langle\hat{A};\hat{H}^{(1)}(\omega)\rangle\rangle = \langle 0|\left[\left(1+\hat{\Lambda}^{(0)}\right)\left[\bar{A}^{(0)},\hat{T}^{(1)}(\omega)\right] + \hat{\Lambda}^{(1)}(\omega)\bar{A}^{(0)}\right]|0\rangle, \tag{78}$$

and the quadratic response function,

$$\langle\langle\hat{A};\hat{H}^{(1)}(\omega_1),\hat{H}^{(1)}(\omega_2)\rangle\rangle = \frac{1}{2}\hat{P}(\omega_1,\omega_2)\langle 0|\left[\left(1+\hat{\Lambda}^{(0)}\right)\bar{\bar{A}}^{(2)}(\omega_1,\omega_2)|0\rangle + \hat{\Lambda}^{(1)}(\omega_1)\bar{\bar{A}}^{(1)}(\omega_2) + \hat{\Lambda}^{(2)}(\omega_1,\omega_2)\bar{A}^{(0)}\right]|0\rangle \tag{79}$$

Recommended Reading

[1] H. Koch and P. Jørgensen, *J. Chem. Phys.*, **93**, 3333-3344 (1990). Coupled cluster response functions.

[2] O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quantum Chem.*, **68**, 1-52 (1998). Response functions from Fourier component variational perturbation theory applied to a time-averaged quasienergy.

[3] T. B. Pedersen and H. Koch, *J. Chem. Phys.*, **106**, 8059-8072 (1997). Coupled cluster response functions revisited.