Response Theory
A (hopefully) gentle introduction

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Contents

Response theory

Purpose of response theory

Twofold

1. Provide method for calculation the response of a molecule to a time-dependent external field(time-dependent perturbation), typically electromagnetic field.
    - Weak external field $\rightarrow$ linear response.
    - Strong external field $\rightarrow$ nonlinear response.
2. Properties of excited states.
    - Excitation energy from groundstate.
    - Transition moments, dipole moments, etc.

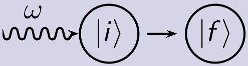
Motivation

1. Nonlinear response properties are of huge technological importance in electronics, photonics, ...
2. Information about excited states is impossible or difficult to obtain with standard quantum-chemical methods.

Types of response to external fields

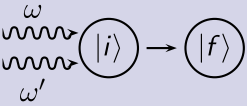
Transition occurs: Photon absorbtion

One-photon transition (linear response)



- $\omega = E_f - E_i$.

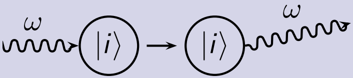
Two-photon transition (nonlinear response)



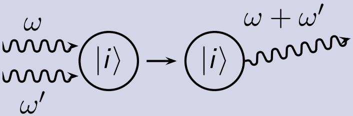
- $\omega + \omega' = E_f - E_i$

No transition occurs: Photon emission

Scattering (linear response)



Frequency doubling (nonlinear response)



Emission of photons from molecules in external field

Classically, a dipole oscillating with frequency ω emits light with frequency $\omega \rightarrow$ examine how dipole of a molecule oscillates.

Molecule with electromagnetic field

- $\hat{H}_0 \rightarrow \hat{H}_0 + \hat{V}^t$, $\hat{V}^t = \boldsymbol{\mu} \cos \omega t$, $\boldsymbol{\mu} = \mathbf{r}$.
- Time-dependent, ω is frequency.
- $|0\rangle \rightarrow |\tilde{0}(t)\rangle = e^{iF(t)} \left(|0^{(0)}\rangle + |0^{(1)}\rangle \cos \omega t + |0^{(2)}\rangle \cos 2\omega t + \ldots \right)$.

$$\langle \tilde{0}(t) | \boldsymbol{\mu} | \tilde{0}(t) \rangle = \langle 0 | \boldsymbol{\mu} | 0 \rangle + \underbrace{\left[\langle \tilde{0} | \boldsymbol{\mu} | \tilde{0} \rangle \right]^{(\omega)} \cos \omega t}_{\rightarrow photons, \omega} + \underbrace{\left[\langle \tilde{0} | \boldsymbol{\mu} | \tilde{0} \rangle \right]^{(2\omega)} \cos 2\omega t}_{\rightarrow photons, 2\omega} + \ldots$$

To predict emission of photons, expectation values and their time-development are important

Time-dependence of expectation values

Introduction to the mathematical treatment for exact states

General TD perturbation

- $\hat{H}_0 \rightarrow \hat{H}_0 + \hat{V}^t$, $\hat{V}^t = \int_{-\infty}^{\infty} d\omega \hat{V}^\omega e^{(i\omega+\epsilon)t}$.
- ϵ: a small positive number ($\rightarrow 0+$), perturbation $\rightarrow 0$ for t $\rightarrow -\infty$.

Time-development of $|\tilde{0}(t)\rangle$

- Solve the time-dependent Schrödinger equation (TDSE) $\hat{H}|\tilde{0}(t)\rangle = i\frac{\partial}{\partial t}|\tilde{0}(t)\rangle$ in orders of the perturbation.

$$|\tilde{0}(t)\rangle = |0\rangle + \int_{-\infty}^{\infty} d\omega e^{(-i\omega+\epsilon)t} \overbrace{|0_1^{(\omega)}\rangle}^{\text{linear in V}}$$

$$+ \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\omega_1 d\omega_2 e^{(-i(\omega_1+\omega_2)+2\epsilon)t} \overbrace{|0_1^{(\omega_1,\omega_2)}\rangle}^{\text{Quadratic in V}}$$

Time-dependence of expectation values

Introduction to the mathematical treatment for exact states, cont'd

Insert expansion of $|\tilde{0}(t)\rangle$ in $\langle\tilde{0}(t)|\hat{A}|\tilde{0}(t)\rangle$ for operator $\hat{A}$

$$\langle\tilde{0}(t)|\hat{A}|\tilde{0}(t)\rangle = \langle 0|\hat{A}|0\rangle + \int_{-\infty}^{\infty} \mathrm{d}\omega_1 e^{(-\mathrm{i}\omega+\epsilon)t} \overbrace{\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1}}^{\text{linear in V}}$$

$$+ \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1 \mathrm{d}\omega_2 e^{(-\mathrm{i}(\omega_1+\omega_2)+2\epsilon)t} \overbrace{\langle\langle A; V^{\omega_1}, V^{\omega_2}\rangle\rangle_{\omega_1\omega_2}}^{\text{Quadratic in V}} + \ldots$$

The response functions

- $\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega} = \langle 0_1^{(-\omega)}|\hat{A}|0\rangle + \langle 0|\hat{A}|0_1^{(\omega)}\rangle$ is the linear response function.
- $\langle\langle A; V^{\omega_1}, V^{\omega_2}\rangle\rangle_{\omega_1\omega_2}$ is the quadratic response function.
- Describes how expectation values changes as perturbation is added.
- Essential in the following!

Example of response functions

Time-dependent dipole-perturbation

The perturbation

- $\hat{A} = X$, $\hat{V}^t = Z(e^{i\omega t} + e^{-i\omega t})$.
- Electromagnetic field with frequency ω.

Expectation value

$$\langle \tilde{0}(t)|X|\tilde{0}(t)\rangle = \langle 0|X|0\rangle + \langle\langle X;Z\rangle\rangle_{\omega} e^{-i\omega t} + \langle\langle X;Z\rangle\rangle_{-\omega} e^{i\omega t}$$
$$+ \frac{1}{2}\langle\langle X;Z,Z\rangle\rangle_{\omega\omega} e^{-2i\omega t} + \frac{1}{2}\langle\langle X;Z,Z\rangle\rangle_{-\omega-\omega} e^{2i\omega t} + \langle\langle X;Z,Z\rangle\rangle_{\omega-\omega}.$$

The response functions

- $\langle\langle X;Z\rangle\rangle$: Dynamic polarizability($\times$ -1) $\rightarrow$ scattering.
- $\langle\langle X;Z,Z\rangle\rangle$: Dynamic first hyperpolarizability ($\times$ -1)$\rightarrow$ frequency doubling.

Excited states and response functions

Form of the linear response function

$$\langle\langle A; V^\omega \rangle\rangle_\omega = \sum_{n \neq 0} \frac{\langle 0|A|n\rangle\langle n|V^\omega|0\rangle}{\omega - (E_n - E_0)} - \sum_{n \neq 0} \frac{\langle 0|V^\omega|n\rangle\langle n|A|0\rangle}{\omega + (E_n - E_0)}$$

- $|n\rangle$: eigenstate of $\hat{H}_0$: $\hat{H}_0|n\rangle = E_n|n\rangle$.

Singularities (poles)

Identifies excitations energies $\omega_f = E_f - E_0$.

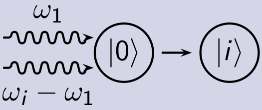
Residues

$$\lim_{\omega \to \omega_f} (\omega - \omega_f)\langle\langle A; V^\omega \rangle\rangle_\omega = \langle 0|A|f\rangle\langle f|V^\omega|0\rangle$$

- Gives information about transition moment between ground and excited state, e.g. $\langle 0|X|f\rangle$ (one-photon transition moments).

Two-photon transition moments from $\langle\langle A; B, C\rangle\rangle$

The two-photon transition moment (a,b are directions, say x,y)



$$\Gamma^{ba}(\omega_1) = \sum_n \frac{\langle 0|\mu_a|n\rangle\langle n|\left(\mu_b - \langle 0|\mu_b|0\rangle\right)|i\rangle}{\omega_n - \omega_1} + \sum_n \frac{\langle 0|\mu_b|n\rangle\langle n|\left(\mu_a - \langle 0|\mu_a|0\rangle\right)|i\rangle}{\omega_n - (\omega_i - \omega_1)}$$

A residue of the quadratic response function

$$\lim_{(\omega_2\to\omega_i)} (\omega_2 - \omega_i)\langle\langle \mu_b; \mu_a, \mu_c\rangle\rangle_{-\omega_i\ \omega_2} =$$

$$-\left[\sum_n \left(\frac{\langle 0|\mu_a|n\rangle\langle n|\left(\mu_b - \langle 0|\mu_b|0\rangle\right)|i\rangle}{\omega_n - \omega_1} + \frac{\langle 0|\mu_b|n\rangle\langle n|\left(\mu_a - \langle 0|\mu_a|0\rangle\right)|i\rangle}{\omega_n - (\omega_i - \omega_1)}\right]\right.$$

$$\langle i|\mu_c|0\rangle = -\Gamma^{ba}(\omega_1)\langle i|\mu_c|0\rangle$$

Transition moments between excited states from the quadratic response function

Second order residue

$$\lim_{\omega_B \to \omega_f} (\omega_B - \omega_f) \lim_{\omega_C \to -\omega_i} (\omega_C + \omega_i) \langle\langle A; B, C \rangle\rangle_{\omega_B\ \omega_C}$$
$$= -\langle 0^{(0)} | C | i \rangle \langle i | (A - \langle 0^{(0)} | A | 0^{(0)} \rangle) | f \rangle \langle f | B | 0^{(0)} \rangle$$

Allows identification of matrix element between two excited states.

Response functions will do it all !

- Transitions/No transitions.
- One-photon/Multi-photon transitions.
- polarizabilities and hyperpolarizabilities.
- Excitations energies and other properties of excited states.

Roy Orbison:

Everything you need, I got it..

Contents

Response theory

Equations for the time-development of a state

The time-dependent Schrödinger equation(TDSE)

- $\hat{H}|\bar{0}(t)\rangle = \mathrm{i}\frac{\partial}{\partial t}|\bar{0}(t)\rangle$.

General normalized wavefunction

- $|\bar{0}\rangle = e^{\mathrm{i}F}|\tilde{0}\rangle$.
- F is a phase-factor: real, depends on time but not on space.
- $|\tilde{0}\rangle$ is the *regular* wave function - eliminates annoying phase-factor.
- Fulfills a modified TDSE: $(\hat{H} + \dot{F})|\tilde{0}(t)\rangle = \mathrm{i}\frac{\partial}{\partial t}|\tilde{0}(t)\rangle$.
- Eliminate phase-factor: $\hat{P}_{\tilde{0}}(\hat{H} - \mathrm{i}\frac{\partial}{\partial t}|\tilde{0}(t)\rangle = 0, \hat{P}_{\tilde{0}} = |\tilde{0}\rangle\langle\tilde{0}|$.

Form of the regular wave function

- Introduce a orthonormal basis $\{|R\rangle, |I\rangle\}$.
- $|\tilde{0}\rangle = \frac{|R\rangle + \sum_I c_i|I\rangle}{\sqrt{1+\sum_I |c_I|^2}}$.
- $|R\rangle$ is the reference state, typical solution to the TISE.

Assume a periodic Hamiltonian

- $\hat{H}(t) = \hat{H}(t+T)$.
- The regular wave function is then also periodic: $|\tilde{0}(t)\rangle = |\tilde{0}(t+T)\rangle$.
- Period $T \rightarrow$ frequency $\omega = n2\pi/T, n = 1, 2, ...$

Periodic Hamiltonian

- Includes obviously a single harmonic perturbation $Ve^{i\omega t} + V^{\dagger}e^{-i\omega t}$.
- For a given finite set of frequencies, $\omega_1, \omega_2, ...$, a T can always found so $\omega_i = n_i 2\pi/T$ to arbitrary precision.
- Describes thus also multicolor perturbations(several frequencies).

Periodic Hamiltonians are assumed from now on

Equations for the time-development of a state

Introduce time-average of an expectationvalue

- $\{\hat{O}\}_T = \frac{1}{T}\int_0^T \mathrm{d}t \, \langle \tilde{0}(t)|\hat{O}|\tilde{0}(t)\rangle$.
- Integration both over space and time.
- Wave function in action is the regular wave function.

The time-averaged quasi-energy $\mathcal{E}$

- $\mathcal{E} = \{\hat{H} - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\}_T = \frac{1}{T}\int_0^T \mathrm{d}t \, \langle \tilde{0}|(\hat{H} - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t})|\tilde{0}\rangle$.

The variational principle for the exact time-averaged quasi-energy

- It may (easily) be shown that the TDSE is equivalent to

$$\delta\mathcal{E} = \delta\left(\frac{1}{T}\int_0^T \mathrm{d}t \, \langle \tilde{0}|(\hat{H} - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t})|\tilde{0}\rangle\right) = 0$$

- Is not a minimization- not even for the ground state.

Equations for the time-development of a state

The time-dependent Hellmann-Feynman theorem

$(\delta\mathcal{E} = \delta\{\langle\tilde{0}|H - \mathrm{i}\frac{\partial}{\partial t}|\tilde{0}\rangle\}_T = 0)$

Consider dependence of quasi-energy of a perturbation

- $H = H(\epsilon)$, ϵ may for example be the strength of an added electric field.
- The quasi-energy $\mathcal{E}$ as a function of ϵ.

$$
\begin{aligned}
\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\epsilon} &= \{\langle\tilde{0}|\frac{\partial H}{\partial\epsilon}|\tilde{0}\rangle\}_T + \{\langle\frac{\partial\tilde{0}}{\partial\epsilon}|H - \mathrm{i}\frac{\partial}{\partial t}|\tilde{0}\rangle\}_T + \{\langle\tilde{0}|H - \mathrm{i}\frac{\partial}{\partial t}|\frac{\partial\tilde{0}}{\partial\epsilon}\rangle\}_T \\
&= \{\langle\tilde{0}|\frac{\partial H}{\partial\epsilon}|\tilde{0}\rangle\}_T + \delta\mathcal{E}_{|\delta\tilde{0}=\frac{\partial\tilde{0}}{\partial\epsilon}} = \{\langle\tilde{0}|\frac{\partial H}{\partial\epsilon}|\tilde{0}\rangle\}_T
\end{aligned}
$$

Comments

- Is the time-dependent Hellmann-Feynman theorem.
- The derivative of the quasi-energy equals the expectation value of the derivative of the Hamiltionian.

Equations for the time-development of a state

Comparison of time-dependent and time-independent theory

	Time-dependent	Time-independent
Schrödinger equation	$P_{\tilde{0}}\left(H - \mathrm{i}\frac{\partial}{\partial t}\right)\lvert\tilde{0}\rangle = 0$	$P_{\tilde{0}} H \lvert\tilde{0}\rangle = 0$
Variational principle	$\delta\{\langle\tilde{0}\rvert H - \mathrm{i}\frac{\partial}{\partial t}\lvert\tilde{0}\rangle\}_T = 0$	$\delta\langle\tilde{0}\rvert H\lvert\tilde{0}\rangle = 0$
Hellmann-Feynman theorem	$\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\epsilon} = \{\langle\tilde{0}\rvert\frac{\partial H}{\partial \epsilon}\lvert\tilde{0}\rangle\}_T$	$\frac{\mathrm{d}E}{\mathrm{d}\epsilon} = \langle\tilde{0}\rvert\frac{\partial H}{\partial \epsilon}\lvert\tilde{0}\rangle$

$(\hat{P}_{\tilde{0}} = \lvert\tilde{0}\rangle\langle\tilde{0}\rvert)$

The quasi-energy $\mathcal{E}$ and response functions

Perturbation expansions

- The time-dependent state is expanded in orders of the perturbation.
- The equations for time-development may then be obtained from the various orders of the time-averaged quasi-energy.

Well, it has the response functions we were after..

- From the perturbation expansion, we obtain the quasi-energy in orders of the perturbation.
- The response functions are the perturbation expansion of a expectation value of an operator A.
- It may be shown that these are related as
  1. $\langle\langle A; B\rangle\rangle = 2\frac{\mathrm{d}^2\mathcal{E}}{\mathrm{d}\epsilon_A \mathrm{d}\epsilon_B}$.
  2. $\langle\langle A; B, C\rangle\rangle = 6\frac{\mathrm{d}^3\mathcal{E}}{\mathrm{d}\epsilon_A \mathrm{d}\epsilon_B \mathrm{d}\epsilon_C}$.
- - Just as the static polarizability is the second derivative of the normal energy.

Response Theory for SCF wave functions

Contents

- Form of time-dependent SCF wave-function.
- The SCF quasi-energy.
- Obtain wave-function corrections by minimizing the SCF quasi-energy.
- Expressions for the SCF linear response function.
- Identification of excitation energies and transition moments.
- Computational considerations.

The time-dependent SCF wave-function

Parameterization of the regular SCF wave function

$|\widetilde{\mathrm{HF}}\rangle = e^{\mathrm{i}\hat{\kappa}(t)}|\mathrm{HF}\rangle.$

The orbital rotation operator $e^{\mathrm{i}\hat{\kappa}(t)}$

- $\hat{\kappa} = \sum_{\mu}(\kappa_{\mu} q_{\mu}^{\dagger} + \kappa_{\mu}^{*} q_{\mu})$.
- $q_{\mu}^{\dagger}$ is spin-orbital excitation $a_P^{\dagger} a_Q$.
- $\hat{\kappa}$ is hermitian $\rightarrow$ $\mathrm{i}\hat{\kappa}$ is anti-hermitian $\rightarrow$ conservation of orthonormality of orbitals.
- Sum over μ is over non-redundant excitation operators.

The time-averaged quasi-energy

- $\mathcal{E} = \{\langle\widetilde{\mathrm{HF}}|(H - \mathrm{i}\frac{\partial}{\partial t})|\widetilde{\mathrm{HF}}\rangle\}_T$.
- $\delta\mathcal{E} = 0$ defines time-development of orbitals.

The (time-averaged) SCF quasi-energy

Arguments for variational approach

- This approach leads to a formalism where a number of important relations are fulfilled, also for approximate theory (example: equivalence between different forms of the oscillator strengths).
- However, no quasi-energy is systematically lowered when the variational space is enlarged.
- Becomes standard HF theory when the perturbation becomes time-independent.

Time-dependence from variational calculations on $\mathcal{E}$

Exact: Find the time-dependent operators parameters $\hat{\kappa}_\mu(t)$ that optimizes the quasi-energy.

Perturbative: Find the operators frequency-dependent parameters $\hat{\kappa}_\mu(\omega)$ that optimizes the quasi-energy through given order - used here.

Determination of the linear SCF response function

General considerations

Obtained from the quasi-energy

- The linear response function is equal (within a factor of two) to the second-order quasi-energy.
- The quasi-energy is variational $\rightarrow$ the first-order correction to the wave function is sufficient.

Expansion of perturbation and first-order wave function correction

- $V = \sum_B \epsilon_B V_B e^{-\mathrm{i}\omega_B t}$.
- $\hat{\kappa}(t) = \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + \cdots$.
- $\hat{\kappa}^{(1)} = \sum_B \epsilon_B \hat{\kappa}^B e^{-\mathrm{i}\omega_B t}$.
- $\hat{\kappa}^B = \sum_\mu (\kappa_\mu^B q_\mu^\dagger + \kappa_\mu^{B*} q_\mu)$
- V is Hermitian $\rightarrow$ operators comes in pairs with indices $B, -B$.

Unperturbed wave-function is assumed optimized

Determination of the linear SCF response function

The second-order time-dependent quasi-energy, $E^{(2)}(t)$

The equations

- $|\widetilde{\mathrm{HF}}\rangle = e^{\mathrm{i}\hat{\kappa}(t)}|\mathrm{HF}\rangle, E(t) = \langle\mathrm{HF}|e^{-\mathrm{i}\hat{\kappa}(t)}(H - \mathrm{i}\frac{\partial}{\partial t})e^{\mathrm{i}\hat{\kappa}(t)}|\mathrm{HF}\rangle.$

Insert expansion of $\hat{\kappa}$, use the BCH expansion and HF conditions

$$E^{(2)}(t) = -\mathrm{i}\langle\mathrm{HF}|[\hat{\kappa}^{(1)}, V(t)]|\mathrm{HF}\rangle - \frac{1}{2}\langle\mathrm{HF}|[\hat{\kappa}^{(1)}, [\hat{\kappa}^{(1)}, H_0 - i\frac{\partial}{\partial t}]]|\mathrm{HF}\rangle.$$

Introduce

- $\hat{\mathbf{T}} = \{\mathbf{q}^\dagger, \mathbf{q}\}, \boldsymbol{K^B} = \{\hat{\boldsymbol{\kappa}}^{\boldsymbol{B}}, \hat{\boldsymbol{\kappa}}^{\boldsymbol{B}\star}\}^T, \hat{\kappa}^B = \hat{\mathbf{T}}\boldsymbol{K^B} = \boldsymbol{K^B}{}^\dagger\hat{\mathbf{T}}^\dagger$
- $\mathbf{E}^{[2]} = \langle\mathrm{HF}|[\mathbf{T}^\dagger, [H_0, \mathbf{T}]]|\mathrm{HF}\rangle \leftarrow \langle\mathrm{HF}|[\hat{\kappa}^{(1)}, [\hat{\kappa}^{(1)}, H_0]]|\mathrm{HF}\rangle.$
- $\mathbf{S}^{[2]} = \langle\mathrm{HF}|[\mathbf{T}^\dagger, \mathbf{T}]|\mathrm{HF}\rangle \leftarrow \langle\mathrm{HF}|[\hat{\kappa}^{(1)}, [\hat{\kappa}^{(1)}, -\mathrm{i}\frac{\partial}{\partial t}]]|\mathrm{HF}\rangle.$
- ${\mathbf{V}^{[1]}}_B = \langle\mathrm{HF}|[\mathbf{T}^\dagger, V_B]|\mathrm{HF}\rangle \leftarrow \langle\mathrm{HF}|[\hat{\kappa}^{(1)}, V(t)]|\mathrm{HF}\rangle.$

Insert, time-average, minimize...$\rightarrow$ the SCF linear response function

$$\langle\langle A; B\rangle\rangle_{\omega_B} = 2\mathcal{E}^{(2)}_{A,B} = \mathbf{V}^{[1]\dagger}_{-A}(\mathbf{E}^{[2]} - \omega_B\mathbf{S}^{[2]})^{-1}\mathbf{V}^{[1]}_B$$

The linear SCF response function

$\langle\langle A; B\rangle\rangle_{\omega_B} = \mathbf{V}_{-A}^{[1]\dagger}(\mathbf{E}^{[2]} - \omega_B \mathbf{S}^{[2]})^{-1}\mathbf{V}_B^{[1]}$, the structure and form of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$

Our definition

- $\mathbf{E}^{[2]} = \langle \mathrm{HF}|[\mathbf{T}^\dagger, [H_0, \mathbf{T}]]|\mathrm{HF}\rangle$, $\mathbf{S}^{[2]} = \langle \mathrm{HF}|[\mathbf{T}^\dagger, \mathbf{T}]]|\mathrm{HF}\rangle$.
- $\mathbf{T} = \{\mathbf{q}^\dagger, \mathbf{q}\}$, Dimension = N(Occ.)xN(Virt.).

The two forms of T-operators defines blocks of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$

$$\mathbf{E}^{[2]} = \begin{pmatrix} \langle \mathrm{HF}|[\mathbf{q}, [H_0, \mathbf{q}^\dagger]]|\mathrm{HF}\rangle & \langle \mathrm{HF}|[\mathbf{q}, [H_0, \mathbf{q}]]|\mathrm{HF}\rangle \\ \langle \mathrm{HF}|[\mathbf{q}^\dagger, [H_0, \mathbf{q}^\dagger]]|\mathrm{HF}\rangle & \langle \mathrm{HF}|[\mathbf{q}^\dagger, [H_0, \mathbf{q}]]|\mathrm{HF}\rangle \end{pmatrix} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$$

- $\mathbf{A}$ is the matrix of single excitations.
- $\mathbf{B}$ is small and couples excitations and de-excitations.
- Neglecting $\mathbf{B}$ gives single-excited CI (Tamm-Dancoff).
- $\mathbf{S}^{[2]} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$
- The structure of $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ will give structures in eigenvalues.

Diagonal form of the linear response function

For analysis

Simultaneous diagonalization of $\mathbf{E}^{[2]}, \mathbf{S}^{[2]}$

- Consider the generalized eigenvalue problem $\mathbf{E}^{[2]}\mathbf{X}_i = \omega_i \mathbf{S}^{[2]}\mathbf{X}_i$.
- $\mathbf{X}_i = \begin{pmatrix} \mathbf{Z}_i \\ \mathbf{Y}_i \end{pmatrix}$.
- Two types of eigenvectors: $\mathbf{X}_i^\dagger \mathbf{S}^{[2]}\mathbf{X}_i = 1 \qquad , \mathbf{X}_i^\dagger \mathbf{S}^{[2]}\mathbf{X}_i = -1$.
- For eigenvectors with $\mathbf{X}_i^\dagger \mathbf{S}^{[2]}\mathbf{X}_i = 1$. define $\hat{O}_i^\dagger = \sum_k \mathbf{Z}_{\mu i} q_\mu^\dagger + \sum_\mu \mathbf{Y}_{\mu i} q_\mu$ (Excitation operator).

Allows rewrite of the linear response function

$$\langle\langle A; B\rangle\rangle_\omega = \sum_n \frac{\langle 0|[\hat{A}, \hat{O}_n^\dagger]|0\rangle\langle 0|[\hat{O}_n, B]|0\rangle}{(\omega - \omega_n)} - \sum_n \frac{\langle 0|[\hat{B}, \hat{O}_n^\dagger]|0\rangle\langle 0|[\hat{O}_n, A]|0\rangle}{(\omega + \omega_n)}$$

Identification of excitation energies and transition moments

The SCF linear response function

$$\langle\langle A; B\rangle\rangle_\omega = \sum_n \frac{\langle 0|[\hat{A}, \hat{O}_n^\dagger]|0\rangle\langle 0|[\hat{O}_n, B]|0\rangle}{(\omega - \omega_n)} - \sum_n \frac{\langle 0|[\hat{B}, \hat{O}_n^\dagger]|0\rangle\langle 0|[\hat{O}_n, A]|0\rangle}{(\omega + \omega_n)}$$

The exact linear response function

$$\langle\langle A; B\rangle\rangle_\omega = \sum_n \frac{\langle 0|\hat{A}|n\rangle\langle n|\hat{B}|0\rangle}{(\omega - \omega_n)} - \sum_n \frac{\langle 0|\hat{B}|n\rangle\langle n|\hat{A}|0\rangle}{(\omega + \omega_n)}$$

Suggests the identifications

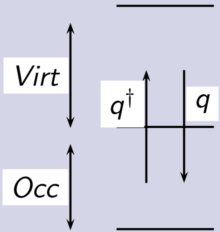
- The excitation energies are ω_k obtained as $\mathbf{E}^{[2]}\mathbf{X}_i = \omega_i \mathbf{S}^{[2]}\mathbf{X}_i$.
- The transition moments are $\langle 0|\hat{A}|k\rangle = \langle 0|[\hat{A}, \hat{O}_k^\dagger]|0\rangle$.

A bit more on the excitation operators

Z, Y

$$\hat{O}_k^\dagger = \overbrace{\sum_\mu Z_{\mu k} q_\mu^\dagger}^{\text{excitation}} + \overbrace{\sum_\mu Y_{\mu k} q_\mu}^{\text{deexcitation}}$$

- **Z**(order 0) > **Y**((order 1)



The transition moment

$$\langle 0|\hat{A}|k\rangle = \langle 0|[\hat{A}, \hat{O}_k^\dagger]|0\rangle = \overbrace{\langle 0|\hat{A}\hat{O}_k^\dagger|0\rangle}^{\text{from } \mathbf{Z}} - \overbrace{\langle 0|\hat{O}_k^\dagger \hat{A}_k|0\rangle}^{\text{from } \mathbf{Y}}$$

- Not of the form $\langle 0|\hat{A}|k\rangle \rightarrow$, no wave function for excited state.
- Instead: Recipe for construction transition moment.

Linear response HF/DFT calculations

Optimize reference state

Standard HF/DFT optimization.

Excitation energies

- Solve generalized eigenvalue problem $\mathbf{E}^{[2]}\mathbf{X}_i = \omega_i \mathbf{S}^{[2]}\mathbf{X}_i$.
- One excitation state = one eigenvector.
- Done iteratively, $\mathbf{E}^{[2]}$ is not constructed (Direct calculation of $\mathbf{E}^{[2]}\mathbf{V}$).
- May be performed in the AO basis $\rightarrow$ large molecules ($\approx$ 100 atoms).
- Linear scaling programs in development $\rightarrow$ even larger molecules ($\approx$ 1000-? atoms).

Transition moments

- From the excitation vector $\mathbf{X}_n = \begin{pmatrix} \mathbf{Z}_n & \mathbf{Y}_n \end{pmatrix}$ calculate transition moment as $\langle 0|\hat{A}|n\rangle = \langle 0|[\hat{A}, \hat{O}_n^\dagger]|0\rangle$.

Calculation of linear response function per se

$$\langle\langle A; B\rangle\rangle_\omega = -\mathbf{A}^{[1]T}(\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]})^{-1}\mathbf{B}^{[1]}$$

- Solve one sets of linear equations

$$\mathbf{N}^b(\omega) = (\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]})^{-1}\mathbf{B}^{[1]}$$

- Done by iterative techniques (Preconditioned Conjugate Gradient).
- Direct calculations of $\mathbf{E}^{[2]}\mathbf{V}, \mathbf{S}^{[2]}\mathbf{V}$.
- May also be done in the AO basis $\rightarrow$ large molecules ($\approx$ 100 atoms).
- May also be done in the AO basis using linear scaling. $\rightarrow$ even larger molecules ($\approx$ 1000 - ? atoms).

Contents

Response theory

- Introduction to response theory.
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The Runge-Gross theorem

- An extension of the standard Hohenberg-Kohn theorems to time-dependent theory.
- Says that the time-dependent density $\rho(\mathbf{r}, t)$ determines the time-dependent potential for a system evolving from a fixed initial state.

Fixed point theorem

Ruggenthaler and Van Leeuwen has recently devised a proof of the existence and uniqueness of the time-dependent XC-functional, (Europhysics Letters 95, 13001 (2011)).

Kohn-Sham formalism

- The time-dependent DFT calculations are typically done in the Kohn-Sham formulation.
- The kinetic energy is evaluated as the kinetic energy of an Slater-determinant plus a correction.

Very similar to Hartree-Fock Theory

- Same form of time-dependent equations.
- Linear response functions are very similar in HF and DFT.
- Only difference comes the use of exchange-correlation potential in DFT.
- The size of molecules that can be treated are thus similar in TDHF and TDDFT.

The adiabatic approximation

- Time-dependent density $\rightarrow$ time-dependent exchange-correlation pot.
- The **adiabatic approximation** neglects any explicit time-dependence of the exchange-correlation potential.

$$V_{xc}(\rho(r,t),t) = V_{xc}(\rho(r))|_{\rho(r)=\rho(r,t)} \quad (1)$$

- i.e. standard form of potential with the time-dependent density.

Standard exchange-correlation potentials are used

- GGA potentials like BLYP.
- Hybrid GGA potentials with exact exchange like B3LYP.
- GGA potentials with modified long-range exchange like CAM-B3LYP.
- A prefix A is sometimes used to stress that the adiabatic approximation is used.

Density Functional Response Theory: The linear Response Function

$$\langle\langle A; B\rangle\rangle_\omega = -\mathbf{V}_A^{[1]T}(\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]})^{-1}\mathbf{V}_B^{[1]}$$

$\mathbf{E}^{[2]}$ for functionals without exact exchange

$$\mathbf{E}^{[2]} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$$

$$A_{AI,BJ} = \delta_{IJ}\delta_{AB}(\epsilon_A - \epsilon_I) + (IA|BJ) + V_{xc}(AI, BJ)$$

$$B_{AI,BJ} = -(IA|JB) - V_{xc}(AI, BJ)$$

Compared to Hartree-Fock

- No exchange $\rightarrow$ no exchange integrals $(IJ|AB)$.
- Exchange-Correlation functional $\rightarrow V_{xc}(AI, BJ)$.
- $(\mathbf{A} + \mathbf{B})_{AI,BJ} = \delta_{IJ}\delta_{AB}(\epsilon_A - \epsilon_I)$
- Diagonal structure of $\mathbf{A} + \mathbf{B}$ allows simplifications.

Problems with the current xc-potentials 1: Charge-transfer excitations

Wrong long-range behaviour of standard xc-functionals

- Standard xc-potentials without exact exchange falls off too fast compared to the exact- typically exponential rather than $1/r$.
- xc-functionals that becomes exact exchange for large distances have been devised and exhibit the correct long-range behaviour.
- Wrong long-range behaviour $\rightarrow$ errors for charge-transfer states.

Analysis of the elements in A, B for charge transfer complex

- Assume excitation where occ. and virt. orbitals do not overlap.
  1. $A_{AI,BJ} = \delta_{IJ}\delta_{AB}(\epsilon_A - \epsilon_I) + (IA|BJ) + V_{xc}(AI, BJ) \rightarrow \delta_{IJ}\delta_{AB}(\epsilon_A - \epsilon_I)$
  2. $B_{AI,BJ} = -(IA|JB) - V_{xc}(AI, BJ) \rightarrow 0$

Therefore

- Excitation energy goes towards the orbital energy difference $\epsilon_A - \epsilon_I$.
- HF: Exchange term, $-(IJ|AB) \rightarrow$ correct $1/R$.

Problems with the current xc-potentials 2: Lack of double and higher excitations

The DFT linear response equations are single excitation equations

- The DFT and HF linear response equations are similar and solves a generalized eigenvalue problem in the space of single excitations.
- Doubly excited electronically states do therefore not occur.

Ways of introducing double excitations

- Introduce time-/frequency-dependent xc-functionals.
- Use ensemble or MCSCF-DFT rather than pure-state DFT.
- Develop DFT methods in analogy with the standard QC methods for obtaining double excitations.
- Density matrix rather than density methods.
- ...

Benchmarking DFT excitation energies: D. Jaquemin, W. Wathelet,E.A. Perpete, and C. Adamo (Namur), JCTC **5**, 2420-2435(2009)

Very extensive benchmark

- Contains more than 700 excitation energies.
- 29 Functionals.
- Compare both to theory and experiment.

Functionals in use

Type of functional	Examples
LDA	SVWN5
GGA	BP86, BLYP, OLEP, PBE
Meta-GGA	VSXC, τ-HCTC, TPSS
Global Hybrids	B3LYP, mPW91PW91, O3LYP X3LYP, ...
Long range corrected hybrids	LC versions of GGA and meta-GGA

Benchmarking DFT excitation energies: D. Jaquemin, W. Wathelet,E.A. Perpete, and C. Adamo (Namur), JCTC **5**, 2420-2435(2009)

Conclusions

- Most accurate results: Global hybrids 22 - 25 % exchange: X3LYP, B98, .. or long-range corrected hybrid.
- CAM-B3LYP does well, but does not in general outperform B3LYP
- Average errors of the best functionals: about 0.25 eV.
- Comparable to CC2.

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Coupled Cluster Theory

Standard Time-independent Coupled Cluster expansions

- $|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle$.
- $|\mathrm{CC}\rangle = |\mathrm{HF}\rangle + |Correlation\rangle \rightarrow$ intermediate normalized form.
- $\hat{T}$ includes all excitations up to a max excitation level m: $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_m$.
- The operator $\hat{T}$ is a weighted sum of excitations $\hat{T} = \sum_\mu t_\mu \tau_\mu$.
- The parameters t_μ are determined in the CC calculation.
- The excitation operators commute $[\tau_\mu, \tau_\nu] = 0$.

Problem

- $\langle \mathrm{CC}|H|\mathrm{CC}\rangle = \langle \mathrm{HF}| \exp \hat{T}^\dagger H \exp \hat{T}|\mathrm{HF}\rangle$ is cumbersome to evaluate $\rightarrow$ standard variational approaches are not feasible.
- $\langle \mathrm{HF}| \exp(-\hat{T}) H \exp(\hat{T})|\mathrm{HF}\rangle$ may be calculated.
- Use projection methods instead of variational methods.

Coupled Cluster Theory

The time-independent Coupled Cluster equations

- The Schrödinger equation: $H\exp(\hat{T})|\mathrm{HF}\rangle = E\exp(\hat{T})|\mathrm{HF}\rangle$.
- Multiply with $\exp(-\hat{T})$: $\exp(-\hat{T})H\exp(\hat{T})|\mathrm{HF}\rangle = E|\mathrm{HF}\rangle$ (manifestly extensive form).
- Projecting by $\langle\mathrm{HF}|$ gives the energy $E = \langle\mathrm{HF}|\exp(-\hat{T})H\exp(\hat{T})|\mathrm{HF}\rangle$.
- Projecting with $\langle\mathrm{HF}|\tau_\mu^\dagger$ gives the CC equations $\Omega_\mu = \langle\mathrm{HF}|\tau_\mu^\dagger\exp(-\hat{T})H\exp(\hat{T})|\mathrm{HF}\rangle = 0$.

In the following

- The $\hat{T}$ operator for the reference state is $\hat{T}^{(0)}$.
- The CC wave function for the reference state is $|\mathrm{CC}^{(0)}\rangle = \exp(\hat{T}^{(0)})|\mathrm{HF}\rangle$.

The EOM approach to excited states

EOM-CC?

- A simple way to obtain formulaes for the excitation energies.
- Same excitation energies as response, but different properties.

Explicit form of the excited state

- $|exc\rangle = \sum_\mu c_\mu \tau_\mu |\mathrm{CC}^{(0)}\rangle$.
- The unit operator is also included in the sum over μ.
- Linear parameterization of the excitation, will give problems later..

Equation for determining **c**

- Schrödinger equation for $|exc\rangle$: $H|exc\rangle = E_{exc}|exc\rangle$.
- Project from left with $\langle\bar{\mu}| = \langle\mathrm{HF}|\tau_\mu^\dagger \exp(-\hat{T}^{(0)})$.

$$\sum_\nu \langle\bar{\mu}|H\tau_\nu|\mathrm{CC}^{(0)}\rangle C_\nu = E_{exc} C_\mu.$$

The EOM approach to excited states

Matrix form of equations

$(\sum_\nu \langle\bar{\mu}|H\tau_\nu|\mathrm{CC}^{(0)}\rangle C_\nu = E_{exc} C_\mu)$

In matrix form

- $\boldsymbol{HC} = E_{exc}\boldsymbol{C}$, $H_{\mu\nu} = \langle\bar{\mu}|H\tau_\nu|\mathrm{CC}^{(0)}\rangle$.

The blocks of **H** - Partition into HF-part(0) and excitation part (μ)

- $H_{00} = \langle\mathrm{HF}|H|\mathrm{CC}^{(0)}\rangle = E_{CC}$.
- $H_{\mu 0} = \langle\bar{\mu}|H|\mathrm{CC}^{(0)}\rangle = 0$, $H_{0\mu} = \eta_\mu$.
- $H_{\mu,\nu} = \langle\bar{\mu}|H\tau_\nu|\mathrm{CC}^{(0)}\rangle = \langle\bar{\mu}|[H,\tau_\nu]|\mathrm{CC}^{(0)}\rangle + \langle\bar{\mu}|\tau_\nu H|\mathrm{CC}^{(0)}\rangle = A_{\mu\nu} + E_{cc}\delta_{\mu\nu}$, $A_{\mu\nu}$ is the CC Jacobian.
- $\boldsymbol{H} = \begin{pmatrix} H_{00} & H_{0\nu} \\ H_{\mu 0} & H_{\mu\nu} \end{pmatrix} = \begin{pmatrix} 0 & \boldsymbol{\eta} \\ \boldsymbol{0} & \boldsymbol{A} \end{pmatrix} + E_{CC}\mathbf{1}$

The EOM approach to excited states

Equivalence between excitation energies in EOM-CC and LR-CC

Conclusion on the form of $\boldsymbol{H}$

$$\boldsymbol{H} = \begin{pmatrix} 0 & \boldsymbol{\eta} \\ \boldsymbol{0} & \boldsymbol{A} \end{pmatrix} + E_{CC}\mathbf{1}$$

Excitation energies are obtained as

- In LR-CC (linear response CC), excitation energies are obtained as eigenvalues of $\boldsymbol{A}$.
- In EOM-CC, excitation energies are obtained as eigenvalues of $\boldsymbol{H}$

But

- Due to the simple form of the first column of $\boldsymbol{H}$, the (nontrivial) eigenvalues of $\boldsymbol{H}$, $\boldsymbol{A}$ are identical.
- So: EOM-CC and LR-CC gives identical excitation energies.

EOM-CC excitation energies and operators

The EOM-CC Hamiltonian matrix $\boldsymbol{A}$ is not symmetric

- A complete set of eigenvectors is not garanteed ($\boldsymbol{A}$ is not normal).
- Different left and right eigen-vectors, but common eigenvalues.

$$\boldsymbol{A}\boldsymbol{R}_i = \omega_i \boldsymbol{R}_i \tag{2}$$

$$\boldsymbol{L}_i^T \boldsymbol{A} = \omega_i \boldsymbol{L}_i^T \tag{3}$$

- Left and right eigenvectors are orthonormal, $\boldsymbol{L}_i^T \boldsymbol{R}_j = \delta_{ij}$
- If a complete basis exists, the resolution of the identity is $\sum_i \boldsymbol{L}_i^T \boldsymbol{R}_i$.

Left and right excited states differs

- $\langle i| = \sum_\mu L_{\mu i} \ \langle \bar{\mu}|$.
- $|i\rangle = \sum_\mu R_{\mu i} \ \tau_\mu |\mathrm{CC}^{(0)}\rangle$.
- Differs both in expansion coeffcients and vectors.
- Only small differences when the CC methods are accurate.

EOM-CC excitation energies and operators

Matrix elements between two states, i, f

- We have left and right representations of both states
  - $\langle \bar{i}| = \sum_\mu L_{\mu i} \langle \bar{\mu}|$, $\langle \bar{f}| = \sum_\mu L_{\mu f} \langle \bar{\mu}|$.
  - $|i\rangle = \sum_\mu R_{\mu i} \tau_\mu |\mathrm{CC}^{(0)}\rangle, |f\rangle = \sum_\mu R_{\mu f} \tau_\mu |\mathrm{CC}^{(0)}\rangle$.
- Several possible ways of defining a transition moment between i and f.

  1. $\langle \bar{i}|r|f\rangle$.
  2. $\langle \bar{f}|r|i\rangle$.
  3. $\sqrt{\langle \bar{i}|r|f\rangle\langle \bar{f}|r|i\rangle}$.
- The third form is normally used

Other terms in EOM-CC

- Start out from standard expression of exact states
- Insert forms for left and right states and energies
- Symmetrize as above

General comments on EOM-CC

- Problems with several ways of defining a transition property - ugly
- Also more fundamental problems:
  - Polarizabilities are not extensive
  - Transition moments are not intensive
- Usually, deviations are small
- Deviations are caused by the simple linear ansatz for the excited states
- So: EOM-CC is simple, but there is a price for this simplicity

The Response approach to CC theory - in brief

Solve time-dependent equations

- The CC state satisfies a modified TDSE
- Why modified? The TDSE conserves the norm of the wave function, in CC theory we have $\langle \mathrm{HF}|\mathrm{CC}\rangle = 1$, so the norm is not conserved.
- A Lagrangian form of the CC quasi-energy may then be constructed
- Stationary points of this Lagrangian is then obtained to give time-development of CC amplitudes
- From this, we may obtain CC response functions, and from these excitation energies, transition moments, polarizabilities..
- Formally, significantly more complex than EOM-CC, but in general similar scaling
- Excitation energies turn out to be identical in CC response and EOM-CC
- All terms have now the correct extensivity or intensivity

Coupled Cluster response models

The full models

- For the standard CCSD, CCSDT, CCSDTQ models, there is a corresponding response models
- The CCSD and CCSDT response models have been explicitly coded
- The CCSDTQ and higher models have been implemented using general techniques (spin-strings and/or the tensor-contraction engine)
- The operation counts are the same for the response and the energy models
- The CCSD/CCSDT models scales therefore as sixth/eigth power of the system size

Coupled Cluster response models

Approximate models

- In analogy with the standard energy approaches, methods that approximate the CCSD, CCSDT, ... full response models have been implemented
- Important approximate models are:

  CC2 MP2-like, fifth-order scaling

  CC3 CCSD(T)-like, seventh-order scaling

A convenient rewrite

- $\exp -(\hat{T}_1 + \hat{T}_2) H \exp(\hat{T}_1 + \hat{T}_2) = \exp -(\hat{T}_2) \tilde{H} \exp(\hat{T}_2)$
- $\tilde{H} = \exp -(\hat{T}_1) H \exp(\hat{T}_1)$ is like normal Hamiltonian - with modified integrals.
- Used in the following

The CCSD response model (1:singles, 2: doubles)

The A-matrix: $\langle \mathrm{HF}|\tau_\mu^\dagger \exp(-\hat{T}_2)[\tilde{H},\tau_\nu] \exp \hat{T}_2|\mathrm{HF}\rangle$

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$$

A_{11}

$$\langle \mathrm{HF}|\tau_1^\dagger \exp(-\hat{T}_2)[\tilde{H},\tau_1] \exp \hat{T}_2|\mathrm{HF}\rangle = \langle \mathrm{HF}|\tau_1^\dagger[\tilde{H},\tau_1]|\mathrm{HF}\rangle$$

$$+ \langle \mathrm{HF}|\tau_1^\dagger \underbrace{[[\tilde{H},\tau_1],\hat{T}_2]}_{\text{Single or higher}} |\mathrm{HF}\rangle + \langle \mathrm{HF}|\tau_1^\dagger \underbrace{[[[\tilde{H},\tau_1],\hat{T}_2],\hat{T}_2]}_{\text{Triple or higher} \rightarrow 0} |\mathrm{HF}\rangle$$

$$= \langle \mathrm{HF}|\tau_1^\dagger[\tilde{H},\hat{\tau}_1]|\mathrm{HF}\rangle + \langle \mathrm{HF}|\tau_1^\dagger[[\tilde{H},\hat{\tau}_1],\hat{T}_2]|\mathrm{HF}\rangle$$

The other blocks are obtained in a similar fashion

- $A_{21} = \langle \mathrm{HF}|\tau_2^\dagger[\tilde{H},\tau_1]|\mathrm{HF}\rangle + \langle \mathrm{HF}|\tau_2^\dagger[[\tilde{H},\tau_1],\hat{T}_2]|\mathrm{HF}\rangle$
- $A_{12} = \langle \mathrm{HF}|\tau_1^\dagger[\tilde{H},\tau_2]|\mathrm{HF}\rangle$
- $A_{22} = \langle \mathrm{HF}|\tau_2^\dagger[\tilde{H},\tau_2]|\mathrm{HF}\rangle + \langle \mathrm{HF}|\tau_2^\dagger[[\tilde{H},\tau_2],\hat{T}_2]|\mathrm{HF}\rangle$

The CC2 response model as an approximation to CCSD

The A-matrix

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$$

Simplifications from CCSD

- The sixth-order step in CCSD arises from the A_{22} block.
- Include only part of A_{22} that give second-order terms to single excit.
- Gives a diagonal form of A_{22} containing orbital energies.
- In A_{21} only the lowest order terms is retained.
- $hat T_1$, $\hat{T}_2$ are obtained in N^5 procedure, not CCSD.

Partitioned form of the CC2-equations (1:singles, 2: doubles)

- Allows a rewrite of the CC2 equation to an effective singles-equation

$$\sum_{\nu_1} \left(A_{\mu_1,\nu_1} - \sum_{\mu_2} \frac{A_{\mu_1,\mu_2} A_{\mu_2,\nu_1}}{(A^d_{\mu_2,\mu_2} - \omega)} \right) C_{\nu_1} = \omega C_{\mu_1}$$

Benchmarks of CC2, CCSD, CC3, CCSDT

Comparison with FCI for small molecules

- Predominately single excited states, but also som double excitations
- Both singlet and triplet excited states
- Singlet states are more often multiconfigurational than triplet states
- Singlet single excitation dominated states in table below

Method	Mean abs. deviation	Max deviation
CC2	0.46 eV	1.08 eV
CCSD	0.12 eV	0.23 eV
CC3	0.016 eV	0.071 eV
CCSDT	0.025 eV	0.050 eV

- Clear improvement CC2 $\rightarrow$ CCSD $\rightarrow$ CC3
- CC3 and CCSDT have here comparable accuracy

Benchmarks of CC2, CCSD, CC3, CCSDT

Benchmark with experiment: (W. Thiel *et al*, J. Chem. Phys. **128**, 134110 (2008)

- A group of 28 smaller organic molecules including unsaturated and aromatic compounds
- MP2/6-31G* basis set optimization
- Excitation energies calculated using the TZVP basis - no diffuse basis functions
- Compared to best experimental estimate

Method	Mean abs. deviation	Std. deviation	Max deviation
CC2	0.32 eV	0.41 eV	1.25 eV
CCSD	0.50 eV	0.58 eV	1.62 eV
CC3	0.22 eV	0.27 eV	0.83 eV
CASPT	0.35 eV	0.42 eV	1.02 eV

Systematic improvements less pronounced

Benchmarks of CC2, CCSD, CC3, CCSDT

Benchmark with experiment: (W. Thiel *et al*, J. Chem. Phys. **128**, 134110 (2008)

- Separate analysis was carried out for single excitation dominated states: $|T_1|$ atleast 90 % of total norm
- This should be the ideal show case for CC3

Method	Mean abs. deviation	Std. deviation	Max deviation
CC2	0.22 eV	0.27 eV	0.64 eV
CCSD	0.37 eV	0.42 eV	0.81 eV
CC3	0.22 eV	0.26 eV	0.49 eV
CASPT	0.36 eV	0.44 eV	0.99 eV

No significant improvement CC2 $\rightarrow$ CCSD $\rightarrow$ CC3!

Second-order approximations to CCSD

CC2

- Approximates CCSD Jacobian $\rightarrow$ asymmetric matrix, iterative N^5 step

ADC(2)

- Starts from standard energy form $\rightarrow$ symmetric matrix, standard MP-expansion, iterative N^5 step.
- Obtained from CC2 by eliminating T_1 and symmetrizing matrix.
- Results in general similar to CC2, but symmetric matrix is important for conical intersection.

CIS(D)

- Starts from CIS excitation energy, non-iterative N^5 step.

CPS(D-2)

- Starts from CCS (=CIS) excitation energy, non-iterative N^5 step

EOM-CC versus Response-CC

Excitation energies

- Obtained as eigenvalues of the Jacobian for both methods
- EOM-CC and Response-CC gives identical excitation energies

Explicit representation of excited states?

- In EOM-CC one has the explicit form of the excited states (in terms of excitations from $|\mathrm{CC}^{(0)}\rangle$)
- In response-CC there is no explicit representation of the excited states- but all properties may be calculated

Transition moments, polarizabilities, ...

- In Response-CC the properties are correctly intensive, due to the use of the exponential parameterization for the TD part of the wf
- In EOM-CC the properties are not intensive, due to the use of a linear parameterization of the TD part

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An overview of the most used response methods

Standard model → response model

Standard wavefunction	Corresponding linear response
HF	TDHF=RPA=LRHF
MCSCF	LR-MCSCF
DFT	TDDFT
MP2	CC2, SOPPA, ADC(2)
CCSD	LR-CCSD, EOM-CCSD
CCSD(T)	CC3

Similar computational complexity and limitations

- A response model and the corresponding wave-function model have typical identical scaling of operation counts
- Response models are typically iterative, many states are sought → higher timings and storage requirements

Conclusions

Theory

- A wealth of different physical properties may be obtained in a coherent fashion
- May be used for standard wave-function models including HF, DFT, CI, CC
- Highly excited states may be obtained

Still a lot to be done

1. High intensity lasers
    - Higher orders
    - Breakdown of perturbation theory (for time-dependent perturbation)
    - Solve equations directly in time-domain
    - Improved, nonadiabatic, TD exchange-correlation potential.
2. General Theories
    - Better CC theories to treat double excited states
    - Better CC theories to treat static correlation
    - CASPT-, NEVPT- based methods