Time-dependent linear response theory: exact and approximate formulations

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Response properties in the time-independent regime

- In the following we shall refer to $\hat{H} = \hat{T} + \hat{W}_{\rm ee} + \hat{V}_{\rm ne}$ as the unperturbed Hamiltonian with ground state Ψ_0.

- Let us introduce a perturbation operator $\hat{V}$ with strength ε. The Hamiltonian becomes ε-dependent: $\hat{H}(\varepsilon) = \hat{H} + \varepsilon\hat{V}$.

- Example: if the perturbation is a uniform electric field $\boldsymbol{\mathcal{E}}$ along the z axis, then

$\boldsymbol{\mathcal{E}} = \varepsilon\, \mathbf{e}_{\rm z}$ and $\hat{V} = \hat{\rm z}$ where $\hat{\rm z} = \int d\mathbf{r}\; {\rm z}\; \hat{n}(\mathbf{r})$ ← second-quantized notation !

- Response theory is nothing but perturbation theory formulated for both exact and approximate wavefunctions.

- Let $\Psi(\varepsilon)$ denote the exact normalized ground state of $\hat{H}(\varepsilon)$ with energy $E(\varepsilon)$.
- Linear and higher-order response functions:

$$\langle\hat{V}\rangle(\varepsilon) = \langle\Psi(\varepsilon)|\hat{V}|\Psi(\varepsilon)\rangle = \langle\Psi_0|\hat{V}|\Psi_0\rangle + \varepsilon\langle\langle\hat{V};\hat{V}\rangle\rangle + \frac{1}{2}\varepsilon^2\langle\langle\hat{V};\hat{V},\hat{V}\rangle\rangle + \ldots$$

Response properties in the time-independent regime

- In our example,

$\langle \Psi_0 | \hat{z} | \Psi_0 \rangle$ is the permanent dipole moment along the z axis

$\langle\langle \hat{z}; \hat{z} \rangle\rangle = \alpha_{zz}$ is the static polarizability

$\langle\langle \hat{z}; \hat{z}, \hat{z} \rangle\rangle = \beta_{zzz}$ is the static hyperpolarizability

- Hellmann–Feynman theorem:

$$\frac{\mathrm{d}E(\varepsilon)}{\mathrm{d}\varepsilon} = \left\langle \Psi(\varepsilon) \middle| \frac{\partial \hat{H}(\varepsilon)}{\partial \varepsilon} \middle| \Psi(\varepsilon) \right\rangle = \langle \hat{V} \rangle(\varepsilon)$$

- Exact response functions can be expressed as energy derivatives:

$$\langle\langle \hat{V}; \hat{V} \rangle\rangle = \left. \frac{\mathrm{d}^2 E(\varepsilon)}{\mathrm{d}\varepsilon^2} \right|_0, \qquad \langle\langle \hat{V}; \hat{V}, \hat{V} \rangle\rangle = \left. \frac{\mathrm{d}^3 E(\varepsilon)}{\mathrm{d}\varepsilon^3} \right|_0$$

Response theory for variational methods

- In variational methods, the energy is expressed as an expectation value. It depends on both the trial variational parameters $\boldsymbol{\lambda}$ and the perturbation strength ε:

$$E(\boldsymbol{\lambda}, \varepsilon) = \langle \Psi(\boldsymbol{\lambda}) | \hat{H}(\varepsilon) | \Psi(\boldsymbol{\lambda}) \rangle$$

- At the HF level of approximation, $\boldsymbol{\lambda}$ parameterizes orbital rotations.

- At the CI level (in the basis of perturbation-independent orbitals), $\boldsymbol{\lambda}$ contains all the CI coefficients.

- At the MCSCF level, it contains both orbital rotation and CI coefficients.

- Stationarity condition: $\boxed{\forall \varepsilon, \; \left. \dfrac{\partial E(\boldsymbol{\lambda}, \varepsilon)}{\partial \boldsymbol{\lambda}} \right|_{\boldsymbol{\lambda} = \boldsymbol{\lambda}(\varepsilon)} = 0} \quad \longrightarrow \quad \boldsymbol{\lambda}(\varepsilon)$

- In the following, we will use parameterizations such that $\boldsymbol{\lambda}(0) = 0$.

- Consequently $\boldsymbol{\lambda}(\varepsilon)$ quantifies the response of the electronic wavefunction to the perturbation.

Response theory for variational methods

- The converged ground-state energy only depends on the perturbation strength:

$$\mathcal{E}(\varepsilon) = E(\boldsymbol{\lambda}(\varepsilon), \varepsilon)$$

- The Hellmann–Feynman theorem remains valid for approximate variational methods:

$$\frac{\mathrm{d}\mathcal{E}(\varepsilon)}{\mathrm{d}\varepsilon} = \left[\frac{\partial \boldsymbol{\lambda}(\varepsilon)}{\partial \varepsilon}\right]^{\mathrm{T}} \underbrace{\left.\frac{\partial E(\boldsymbol{\lambda}, \varepsilon)}{\partial \boldsymbol{\lambda}}\right|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(\varepsilon)}}_{0} + \left.\frac{\partial E(\boldsymbol{\lambda}, \varepsilon)}{\partial \varepsilon}\right|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(\varepsilon)}$$

thus leading to

$$\boxed{\frac{\mathrm{d}\mathcal{E}(\varepsilon)}{\mathrm{d}\varepsilon} = \left\langle \Psi\Big(\boldsymbol{\lambda}(\varepsilon)\Big)\middle|\hat{V}\middle|\Psi\Big(\boldsymbol{\lambda}(\varepsilon)\Big)\right\rangle}$$

Conclusion: response functions obtained from variational wavefunctions can be expressed as energy derivatives.

Example: exact response theory

- We denote $\{\Psi_i\}_{i=0,1,\ldots}$ the exact orthonormal eigenvectors of the unperturbed Hamiltonian $\hat{H}$ with energies $\{E_i\}_{i=0,1,\ldots}$

- Exact wavefunction parameterization: $\boxed{|\Psi(\mathbf{S})\rangle = e^{\hat{S}}|\Psi_0\rangle}$

  where $\hat{S} = \sum_{i>0} S_i \left(\hat{R}_i^\dagger - \hat{R}_i\right)$ is anti-hermitian, $\hat{R}_i^\dagger = |\Psi_i\rangle\langle\Psi_0|$ and $\mathbf{S} \equiv \{S_i\}_{i=1,2,\ldots}$

- Linear response function: $\langle\langle\hat{V};\hat{V}\rangle\rangle = \left.\dfrac{\mathrm{d}^2\mathcal{E}(\varepsilon)}{\mathrm{d}\varepsilon^2}\right|_0$ where $\mathcal{E}(\varepsilon) = E(\mathbf{S}(\varepsilon),\varepsilon)$.

- BCH expansion:

$$
\begin{aligned}
\frac{\mathrm{d}\mathcal{E}(\varepsilon)}{\mathrm{d}\varepsilon} &= \langle\Psi_0|e^{-\hat{S}(\varepsilon)}\hat{V}e^{\hat{S}(\varepsilon)}|\Psi_0\rangle \\
&= \langle\Psi_0|\hat{V}|\Psi_0\rangle + \langle\Psi_0|[\hat{V},\hat{S}(\varepsilon)]|\Psi_0\rangle + \frac{1}{2}\langle\Psi_0|[[\hat{V},\hat{S}(\varepsilon)],\hat{S}(\varepsilon)]|\Psi_0\rangle + \ldots
\end{aligned}
$$

Example: exact response theory

- Using the condition $\mathbf{S}(0) = 0$ leads to $\langle\langle \hat{V}; \hat{V} \rangle\rangle = \left\langle \Psi_0 \left| \left[\hat{V}, \left. \dfrac{\partial \hat{S}(\varepsilon)}{\partial \varepsilon} \right|_0 \right] \right| \Psi_0 \right\rangle$
- Definition: $V_i^{[1]} = \left\langle \Psi_0 \left| \left[\hat{V}, \hat{R}_i^\dagger - \hat{R}_i \right] \right| \Psi_0 \right\rangle$ $\longleftarrow$ component i of the gradient property vector
- Usual expression for the linear response function:

$$\boxed{\langle\langle \hat{V}; \hat{V} \rangle\rangle = \left[\left. \frac{\partial \mathbf{S}(\varepsilon)}{\partial \varepsilon} \right|_0 \right]^{\mathrm{T}} V^{[1]}}$$

- The linear response of the wavefunction is obtained by differentiation of the stationarity condition with respect to the perturbation strength:

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left[\left. \frac{\partial E(\mathbf{S}, \varepsilon)}{\partial \mathbf{S}} \right|_{\mathbf{S}=\mathbf{S}(\varepsilon)} \right] \Bigg|_0 = 0$$

Example: exact response theory

- BCH expansion for the energy:

$$\begin{aligned} E(\mathbf{S},\varepsilon) &= \langle\Psi_0|e^{-\hat{S}}\hat{H}(\varepsilon)e^{\hat{S}}|\Psi_0\rangle \\ &= \langle\Psi_0|\hat{H}(\varepsilon)|\Psi_0\rangle + \langle\Psi_0|[\hat{H}(\varepsilon),\hat{S}]|\Psi_0\rangle + \frac{1}{2}\langle\Psi_0|[[\hat{H}(\varepsilon),\hat{S}],\hat{S}]|\Psi_0\rangle + \ldots \end{aligned}$$

which leads to

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\left[\left.\frac{\partial E(\mathbf{S},\varepsilon)}{\partial \mathbf{S}}\right|_{\mathbf{S}=\mathbf{S}(\varepsilon)}\right]\Bigg|_0 = V^{[1]} + E^{[2]}\left[\left.\frac{\partial \mathbf{S}(\varepsilon)}{\partial \varepsilon}\right|_0\right] = 0$$

where the hessian matrix elements equal

$$E^{[2]}_{ij} = \frac{1}{2}\left\langle\Psi_0\middle|\left[\left[\hat{H},\hat{R}_i^\dagger-\hat{R}_i\right],\hat{R}_j^\dagger-\hat{R}_j\right]\middle|\Psi_0\right\rangle + \frac{1}{2}\left\langle\Psi_0\middle|\left[\left[\hat{H},\hat{R}_j^\dagger-\hat{R}_j\right],\hat{R}_i^\dagger-\hat{R}_i\right]\middle|\Psi_0\right\rangle$$

Example: exact response theory

- In summary:

$$E^{[2]}\left[\frac{\partial \mathbf{S}(\varepsilon)}{\partial \varepsilon}\bigg|_0\right] = -V^{[1]} \qquad \longleftrightarrow \qquad \left[\frac{\partial \mathbf{S}(\varepsilon)}{\partial \varepsilon}\bigg|_0\right] = -\left(E^{[2]}\right)^{-1} V^{[1]}$$

$$\langle\langle \hat{V};\hat{V}\rangle\rangle = \left[\frac{\partial \mathbf{S}(\varepsilon)}{\partial \varepsilon}\bigg|_0\right]^{\mathrm{T}} V^{[1]} \qquad \longleftrightarrow \qquad \langle\langle \hat{V};\hat{V}\rangle\rangle = -\left(V^{[1]}\right)^{\mathrm{T}}\left(E^{[2]}\right)^{-1} V^{[1]}$$

Conclusion: in order to compute linear response functions, the gradient property vector and the hessian matrix are needed.

EXERCISE: Show that $V_i^{[1]} = 2\langle\Psi_i|\hat{V}|\Psi_0\rangle$, $E_{ij}^{[2]} = 2(E_i - E_0)\delta_{ij}$,

$$\frac{\partial S_i(\varepsilon)}{\partial \varepsilon}\bigg|_0 = \frac{\langle\Psi_i|\hat{V}|\Psi_0\rangle}{E_0 - E_i}, \quad \text{and} \quad \langle\langle \hat{V};\hat{V}\rangle\rangle = 2\sum_{i>0}\frac{\langle\Psi_i|\hat{V}|\Psi_0\rangle^2}{E_0 - E_i} \quad \leftarrow \text{second-order perturbation theory !}$$

Some comments before turning to the time-dependent regime

- Let us return to (approximate) variational methods.

- $\mathbf{X} = \left.\dfrac{\partial \boldsymbol{\lambda}(\varepsilon)}{\partial \varepsilon}\right|_0$ is usually referred to as the linear response vector. Like in the exact theory, the linear response equation writes

$$E^{[2]}\mathbf{X} = -V^{[1]}$$

- In the time-dependent regime, a linear response vector will be obtained for each frequency ω. We will show in the following that the linear response equation writes

$$\left(E^{[2]} - \omega S^{[2]}\right)\mathbf{X}(\omega) = -V^{[1]}$$

- What about non-variational methods such as MP2, CC, CI with ε-dependent HF orbitals ?

  We, in principle, do not have a stationarity condition anymore. How to proceed with the derivation of the response equations then ? What about the Hellmann–Feynman theorem ?

- Let us denote $\mathbf{t}$ the non-variational parameters (CC amplitudes for example).
- For each perturbation strength, a set of equations has to be solved:

$$\mathbf{f}(\mathbf{t}(\varepsilon),\varepsilon) = 0$$

- The non-variational energy is then determined for each perturbation strength: $\boxed{\mathcal{E}(\varepsilon) = E(\mathbf{t}(\varepsilon),\varepsilon)}$
- We introduce the Lagrangian function: $\boxed{L(\mathbf{t},\varepsilon,\bar{\mathbf{t}}) = E(\mathbf{t},\varepsilon) + \bar{\mathbf{t}}^{\mathrm{T}}\mathbf{f}(\mathbf{t},\varepsilon)}$

  and impose the following stationarity conditions:

$$\forall\varepsilon\ , \qquad \frac{\partial L(\mathbf{t},\varepsilon,\bar{\mathbf{t}})}{\partial\bar{\mathbf{t}}} = 0 = \mathbf{f}(\mathbf{t},\varepsilon) \qquad \text{and} \qquad \frac{\partial L(\mathbf{t},\varepsilon,\bar{\mathbf{t}})}{\partial\mathbf{t}} = 0 = \frac{\partial E(\mathbf{t},\varepsilon)}{\partial\mathbf{t}} + \bar{\mathbf{t}}^{\mathrm{T}}\frac{\partial\mathbf{f}(\mathbf{t},\varepsilon)}{\partial\mathbf{t}}$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$\mathbf{t}(\varepsilon) \qquad\qquad\qquad\qquad \bar{\mathbf{t}}(\varepsilon)$$

- Note that $\boxed{\mathcal{E}(\varepsilon) = L(\mathbf{t}(\varepsilon),\varepsilon,\bar{\mathbf{t}}(\varepsilon))}$
- Hellmann–Feynman theorem: $\dfrac{\mathrm{d}\mathcal{E}(\varepsilon)}{\mathrm{d}\varepsilon} = \left.\dfrac{\partial L(\mathbf{t},\varepsilon,\bar{\mathbf{t}})}{\partial\varepsilon}\right|_{\mathbf{t}(\varepsilon),\bar{\mathbf{t}}(\varepsilon)} = \left.\dfrac{\partial E(\mathbf{t},\varepsilon)}{\partial\varepsilon}\right|_{\mathbf{t}(\varepsilon)} + \bar{\mathbf{t}}^{\mathrm{T}}(\varepsilon)\left.\dfrac{\partial\mathbf{f}(\mathbf{t},\varepsilon)}{\partial\varepsilon}\right|_{\mathbf{t}(\varepsilon)}$

Time-dependent variational principle

- Time-dependent Schrödinger equation: $\hat{H}(t)|\overline{\Psi}(t)\rangle = \mathrm{i}\dfrac{\mathrm{d}}{\mathrm{d}t}|\overline{\Psi}(t)\rangle$

- Alternative formulation based on a change of phase: $|\overline{\Psi}(t)\rangle = e^{-\mathrm{i}\int_{t_0}^{t} Q(t)\mathrm{d}t}\,|\tilde{\Psi}(t)\rangle$

$$\longrightarrow \qquad \boxed{\hat{H}(t)|\tilde{\Psi}(t)\rangle - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\tilde{\Psi}(t)\rangle = Q(t)|\tilde{\Psi}(t)\rangle}$$

- Connection with the Runge–Gross theorem: two local potentials that differ by a real time-dependent function lead to the same time-dependent density for a given initial wavefunction $\overline{\Psi}(t_0)$:

$$\overline{\Psi}(t_0) = \tilde{\Psi}(t_0) \quad \text{and} \quad n_{\overline{\Psi}(t)}(\mathbf{r}) = \langle\overline{\Psi}(t)|\hat{n}(\mathbf{r})|\overline{\Psi}(t)\rangle = \langle\tilde{\Psi}(t)|\hat{n}(\mathbf{r})|\tilde{\Psi}(t)\rangle = n_{\tilde{\Psi}(t)}(\mathbf{r})$$

- In the particular case of a time-independent Hamiltonian $\hat{H}$, searching for time-independent solutions $\tilde{\Psi}(t) = \tilde{\Psi}$ and $Q(t) = E$ leads to the time-independent Schrödinger equation:

$$\hat{H}|\tilde{\Psi}\rangle = E|\tilde{\Psi}\rangle$$

- Returning to the time-dependent regime, $Q(t)$ is referred to as time-dependent quasienergy.

- Since $\dfrac{\mathrm{d}}{\mathrm{d}t}\langle\overline{\Psi}(t)|\overline{\Psi}(t)\rangle = \mathrm{i}\langle\hat{H}(t)\overline{\Psi}(t)|\overline{\Psi}(t)\rangle - \mathrm{i}\langle\overline{\Psi}(t)|\hat{H}(t)|\overline{\Psi}(t)\rangle = 0,$

  if $Q(t)$ is real then

  $$\langle\tilde{\Psi}(t)|\tilde{\Psi}(t)\rangle = \langle\overline{\Psi}(t)|\overline{\Psi}(t)\rangle = \langle\tilde{\Psi}(t_0)|\tilde{\Psi}(t_0)\rangle = 1 \quad \text{and} \quad \boxed{Q(t) = \left\langle\tilde{\Psi}(t)\left|\hat{H}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\right|\tilde{\Psi}(t)\right\rangle}$$

- The real character of the time-dependent quasienergy can be explicitly connected with the conservation of the norm:

  $$Q(t)^* = \left\langle\tilde{\Psi}(t)\left|\hat{H}(t)\right|\tilde{\Psi}(t)\right\rangle + \mathrm{i}\left\langle\frac{\mathrm{d}\tilde{\Psi}(t)}{\mathrm{d}t}\middle|\tilde{\Psi}(t)\right\rangle = \left\langle\tilde{\Psi}(t)\left|\hat{H}(t)\right|\tilde{\Psi}(t)\right\rangle - \mathrm{i}\left\langle\tilde{\Psi}(t)\middle|\frac{\mathrm{d}\tilde{\Psi}(t)}{\mathrm{d}t}\right\rangle = Q(t)$$

  since $$\left\langle\frac{\mathrm{d}\tilde{\Psi}(t)}{\mathrm{d}t}\middle|\tilde{\Psi}(t)\right\rangle = \underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\tilde{\Psi}(t)\middle|\tilde{\Psi}(t)\right\rangle}_{0} - \left\langle\tilde{\Psi}(t)\middle|\frac{\mathrm{d}\tilde{\Psi}(t)}{\mathrm{d}t}\right\rangle$$

Time-dependent variational principle

- For a given trial wavefunction $\Psi(t)$, we define the action integral as follows

$$\boxed{\mathcal{A}[\Psi] = \int_{t_0}^{t_1} Q[\Psi](t)\,\mathrm{d}t} \qquad \text{where} \qquad Q[\Psi](t) = \frac{1}{\langle\Psi(t)|\Psi(t)\rangle} \times \left\langle \Psi(t) \middle| \hat{H}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} \middle| \Psi(t) \right\rangle$$

- Note that $Q[\tilde{\Psi}](t) = Q(t)$.

- Stationarity condition:

$$\delta\mathcal{A}[\tilde{\Psi}] = 0 \qquad \leftrightarrow \qquad \hat{H}(t)|\tilde{\Psi}(t)\rangle - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\tilde{\Psi}(t)\rangle = Q(t)|\tilde{\Psi}(t)\rangle$$

variational formulation **non-variational formulation**

<u>Proof</u>: let us consider variations $\tilde{\Psi}(t) \rightarrow \tilde{\Psi}(t) + \delta\Psi(t)$ around the exact solution $\tilde{\Psi}(t)$ with the boundary conditions $\delta\Psi(t_0) = \delta\Psi(t_1) = 0$.

Consequently, the action integral varies as follows:

$$\delta\mathcal{A}[\tilde{\Psi}] = \mathcal{A}[\tilde{\Psi}+\delta\Psi] - \mathcal{A}[\tilde{\Psi}] = \int_{t_0}^{t_1}\Big(Q[\tilde{\Psi}+\delta\Psi](t) - Q[\tilde{\Psi}](t)\Big)\,\mathrm{d}t$$

$$= \int_{t_0}^{t_1}\left\langle \delta\Psi(t)\middle|\hat{H}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\middle|\tilde{\Psi}(t)\right\rangle \mathrm{d}t + \int_{t_0}^{t_1}\left\langle \tilde{\Psi}(t)\middle|\hat{H}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\middle|\delta\Psi(t)\right\rangle \mathrm{d}t$$

$$-\int_{t_0}^{t_1} Q(t)\Big(\langle\delta\Psi(t)|\tilde{\Psi}(t)\rangle + \langle\tilde{\Psi}(t)|\delta\Psi(t)\rangle\Big)\,\mathrm{d}t$$

where $\displaystyle\int_{t_0}^{t_1}\left\langle \tilde{\Psi}(t)\middle|\frac{\mathrm{d}\delta\Psi(t)}{\mathrm{d}t}\right\rangle \mathrm{d}t = \underbrace{\int_{t_0}^{t_1}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \tilde{\Psi}(t)\middle|\delta\Psi(t)\right\rangle \mathrm{d}t}_{\left[\left\langle \tilde{\Psi}(t)\middle|\delta\Psi(t)\right\rangle\right]_{t_0}^{t_1}=0} - \int_{t_0}^{t_1}\left\langle \frac{\mathrm{d}\tilde{\Psi}(t)}{\mathrm{d}t}\middle|\delta\Psi(t)\right\rangle \mathrm{d}t$

thus leading to

$$\delta\mathcal{A}[\tilde{\Psi}] = \int_{t_0}^{t_1}\left(\left\langle \delta\Psi(t)\middle|\hat{H}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - Q(t)\middle|\tilde{\Psi}(t)\right\rangle + \left\langle \delta\Psi(t)\middle|\hat{H}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - Q(t)\middle|\tilde{\Psi}(t)\right\rangle^{*}\right)\mathrm{d}t$$

Variational principle in adiabatic TD-DFT

- In time-dependent density-functional theory (TD-DFT), the physical time-dependent Hamiltonian is written as $\hat{H}(t) = \hat{T} + \hat{W}_{\rm ee} + \underbrace{\int {\rm d}\mathbf{r}\, v(\mathbf{r},t)\hat{n}(\mathbf{r})}_{\hat{V}(t)}$.

  $\hat{V}(t) \quad \longleftarrow \quad$ time-dependent local potential operator

- In standard TD-DFT, the exact time-dependent exchange-correlation (xc) potential is approximated with the ground-state xc density-functional potential calculated at the time-dependent density (adiabatic approximation):

$$\left(\hat{T} + \hat{V}(t) + \int {\rm d}\mathbf{r}\, \frac{\delta E_{\rm Hxc}\left[n_{\tilde{\Phi}^{\rm KS}(t)}\right]}{\delta n(\mathbf{r})}\hat{n}(\mathbf{r}) - {\rm i}\frac{\rm d}{{\rm d}t}\right)|\tilde{\Phi}^{\rm KS}(t)\rangle = Q^{\rm KS}(t)\,|\tilde{\Phi}^{\rm KS}(t)\rangle$$

where $n_{\tilde{\Phi}^{\rm KS}(t)}(\mathbf{r}) = \left\langle \tilde{\Phi}^{\rm KS}(t) \middle| \hat{n}(\mathbf{r}) \middle| \tilde{\Phi}^{\rm KS}(t) \right\rangle$ is an approximation to the exact physical time-dependent density $n_{\tilde{\Psi}(t)}(\mathbf{r})$.

EXERCISE: Show that, within the adiabatic approximation, the Kohn–Sham TD-DFT equation is equivalent to the stationarity condition $\delta\mathcal{A}_{\rm adia}[\tilde{\Phi}^{\rm KS}]=0$ where, for a trial wavefunction $\Psi(t)$,

$$\mathcal{A}_{\rm adia}[\Psi]=\int_{t_0}^{t_1}\frac{1}{\langle\Psi(t)|\Psi(t)\rangle}\times\left\langle\Psi(t)\left|\hat{T}+\hat{V}(t)-{\rm i}\frac{{\rm d}}{{\rm d}t}\right|\Psi(t)\right\rangle{\rm d}t+\int_{t_0}^{t_1}E_{\rm Hxc}[n_{\Psi(t)}]\,{\rm d}t$$

and $n_{\Psi(t)}(\mathbf{r})=\dfrac{\langle\Psi(t)|\hat{n}(\mathbf{r})|\Psi(t)\rangle}{\langle\Psi(t)|\Psi(t)\rangle}$.

Floquet theory

- In the following we consider a periodic Hamiltonian with period T: $\hat{H}(t+T) = \hat{H}(t)$.

- $\hat{H}(t)$ can be written as a Fourier series:

$$\hat{H}(t) = \hat{T} + \hat{W}_{\rm ee} + \hat{V}_{\rm ne} + \underbrace{\sum_x \sum_{k=-N}^{N} e^{-{\rm i}\omega_k t} \varepsilon_x(\omega_k) \hat{V}_x}_{\hat{\mathcal{V}}(t)},$$

$\longleftarrow$ time-dependent perturbation

where $\omega_k = \dfrac{2\pi k}{T}$ and $\varepsilon_x(\omega_k)$ is the strength of the perturbation $\hat{V}_x$ at frequency ω_k.

- $\hat{V}_x$ is any kind of (hermitian) operator, not necessarily a one-electron operator even though in practice it usually is.

- In order to apply TD-DFT, $\hat{V}_x$ should in principle be a (one-electron) local potential operator: $\hat{V}_x \rightarrow \int {\rm d}\mathbf{r}\; v_x(\mathbf{r})\hat{n}(\mathbf{r})$

Floquet theory

- **Example**: in the presence of a dynamic uniform electric field,

$$\mathbf{E}(t) = E_{\mathrm{x}}(t)\ \mathbf{e}_{\mathrm{x}} + E_{\mathrm{y}}(t)\ \mathbf{e}_{\mathrm{y}} + E_{\mathrm{z}}(t)\ \mathbf{e}_{\mathrm{z}} = \sum_{k=-N}^{N} e^{-\mathrm{i}\omega_k t}\Big(\varepsilon_{\mathrm{x}}(\omega_k)\mathbf{e}_{\mathrm{x}} + \varepsilon_{\mathrm{y}}(\omega_k)\mathbf{e}_{\mathrm{y}} + \varepsilon_{\mathrm{z}}(\omega_k)\mathbf{e}_{\mathrm{z}}\Big),$$

the perturbation is $\boxed{\hat{\mathcal{V}}(t) = \hat{\mathbf{r}}\,.\,\mathbf{E}(t)} = \hat{\mathrm{x}}\ E_{\mathrm{x}}(t) + \hat{\mathrm{y}}\ E_{\mathrm{y}}(t) + \hat{\mathrm{z}}\ E_{\mathrm{z}}(t)$ thus leading to

$$\hat{\mathcal{V}}(t) = \sum_{k=-N}^{N} e^{-\mathrm{i}\omega_k t}\Big(\varepsilon_{\mathrm{x}}(\omega_k)\ \hat{\mathrm{x}} + \varepsilon_{\mathrm{y}}(\omega_k)\ \hat{\mathrm{y}} + \varepsilon_{\mathrm{z}}(\omega_k)\ \hat{\mathrm{z}}\Big).$$

Comment: note that $\hat{\mathbf{r}}$ is written in second quantization as $\hat{\mathbf{r}} = \int \mathbf{r}\ \hat{n}(\mathbf{r})\mathrm{d}\mathbf{r}$ so that

$$\hat{\mathcal{V}}(t) = \int \mathbf{r}\,.\,\mathbf{E}(t)\ \hat{n}(\mathbf{r})\ \mathrm{d}\mathbf{r}$$ $\longleftarrow$ local potential operator !

Floquet theory

- Let us collect all perturbation strengths into the vector $\quad \boldsymbol{\varepsilon} = \begin{bmatrix} \vdots \\ \varepsilon_x(\omega_k) \\ \vdots \end{bmatrix}$

- $\hat{\mathcal{V}}^\dagger(t) = \hat{\mathcal{V}}(t) \quad \rightarrow \quad \varepsilon_x(-\omega_k)^* = \varepsilon_x(\omega_k)$

- The time-dependent wavefunction varies with the perturbation strengths: $\quad \tilde{\Psi}(t) \equiv \tilde{\Psi}(\boldsymbol{\varepsilon}, t)$

- Choice of the phase: we want the time-dependent wavefunction to become the (time-independent) ground-sate wavefunction Ψ_0 in the absence of perturbation,

$$\tilde{\Psi}(\boldsymbol{\varepsilon} = 0, t) = \Psi_0.$$

- In the following, the action integral will be calculated over a period: $\quad t_0 = 0 \quad$ and $\quad t_1 = T.$

Response functions

- Taylor expansion of the time-dependent expectation value for the perturbation $\hat{V}_x$:

$$\langle \hat{V}_x \rangle(\boldsymbol{\varepsilon}, t) = \langle \tilde{\Psi}(\boldsymbol{\varepsilon}, t) | \hat{V}_x | \tilde{\Psi}(\boldsymbol{\varepsilon}, t) \rangle =$$

$$\langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle \qquad \longleftarrow \text{zeroth order}$$

$$+ \sum_y \sum_k e^{-\mathrm{i}\omega_k t} \varepsilon_y(\omega_k) \langle\langle \hat{V}_x ; \hat{V}_y \rangle\rangle_{\omega_k} \qquad \longleftarrow \boxed{\textbf{linear response}}$$

$$+ \frac{1}{2} \sum_{y,z} \sum_{k,l} e^{-\mathrm{i}(\omega_k + \omega_l)t} \varepsilon_y(\omega_k) \varepsilon_z(\omega_l) \langle\langle \hat{V}_x ; \hat{V}_y, \hat{V}_z \rangle\rangle_{\omega_k, \omega_l} \qquad \longleftarrow \text{quadratic response}$$

$$+ \ldots$$

- We will focuse in the following on the exact and approximate description of the linear response functions $\langle\langle \hat{V}_x ; \hat{V}_y \rangle\rangle_{\omega_k}$.

Hellmann–Feynman theorem in the time-dependent regime

- The exact action integral depends both implicitly (through the time-dependent wavefunction) and explicitly (through the perturbation) on the perturbation strengths $\boldsymbol{\varepsilon}$:

$$\boxed{\mathcal{A}(\boldsymbol{\varepsilon}) = \mathcal{A}\left[\tilde{\Psi}(\boldsymbol{\varepsilon}), \boldsymbol{\varepsilon}\right]} \qquad \text{where}$$

$$\mathcal{A}\left[\Psi, \boldsymbol{\varepsilon}\right] = \int_0^T \frac{1}{\langle \Psi(t)|\Psi(t)\rangle} \times \left\langle \Psi(t) \middle| \hat{H} + \hat{\mathcal{V}}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} \middle| \Psi(t) \right\rangle \mathrm{d}t$$

and $\quad \hat{H} = \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} \quad \longleftarrow$ unperturbed Hamiltonian

- $\tilde{\Psi}(\boldsymbol{\varepsilon}, t)$ is determined from the variational principle: $\boxed{\forall \boldsymbol{\varepsilon}, \quad \delta\mathcal{A}\left[\tilde{\Psi}(\boldsymbol{\varepsilon}), \boldsymbol{\varepsilon}\right] = 0}$,

thus leading to the Hellmann–Feynman theorem

$$\boxed{\frac{\mathrm{d}\mathcal{A}(\boldsymbol{\varepsilon})}{\mathrm{d}\varepsilon_x(\omega_k)} = \left.\frac{\partial \mathcal{A}[\Psi, \boldsymbol{\varepsilon}]}{\partial \varepsilon_x(\omega_k)}\right|_{\Psi = \Psi(\boldsymbol{\varepsilon})}}$$

- $$\frac{\partial\hat{\mathcal{V}}(t)}{\partial\varepsilon_x(\omega_k)} = e^{-\mathrm{i}\omega_k t}\,\hat{V}_x \qquad \longrightarrow \qquad \boxed{\frac{\mathrm{d}\mathcal{A}(\boldsymbol{\varepsilon})}{\mathrm{d}\varepsilon_x(\omega_k)} = \int_0^T e^{-\mathrm{i}\omega_k t}\,\langle\hat{V}_x\rangle(\boldsymbol{\varepsilon},t)\,\mathrm{d}t}$$

- **Important consequence:** response functions can be expressed as action integral derivatives !

- zeroth order: $$\left.\frac{\mathrm{d}\mathcal{A}(\boldsymbol{\varepsilon})}{\mathrm{d}\varepsilon_x(\omega_k)}\right|_0 = \int_0^T e^{-\mathrm{i}\omega_k t}\,\langle\Psi_0|\hat{V}_x|\Psi_0\rangle\,\mathrm{d}t = T\langle\Psi_0|\hat{V}_x|\Psi_0\rangle\delta(\omega_k)$$ thus leading to

$$\boxed{\langle\Psi_0|\hat{V}_x|\Psi_0\rangle = \frac{1}{T}\left.\frac{\mathrm{d}\mathcal{A}(\boldsymbol{\varepsilon})}{\mathrm{d}\varepsilon_x(0)}\right|_0}$$

- Linear response:

$$\left.\frac{\mathrm{d}^2\mathcal{A}(\boldsymbol{\varepsilon})}{\mathrm{d}\varepsilon_y(\omega_l)\mathrm{d}\varepsilon_x(\omega_k)}\right|_0 = \int_0^T e^{-\mathrm{i}(\omega_k+\omega_l)t}\,\langle\langle\hat{V}_x;\hat{V}_y\rangle\rangle_{\omega_l}\,\mathrm{d}t = T\langle\langle\hat{V}_x;\hat{V}_y\rangle\rangle_{\omega_l}\delta(\omega_k+\omega_l)$$

thus leading to $$\boxed{\langle\langle\hat{V}_x;\hat{V}_y\rangle\rangle_{\omega_l} = \frac{1}{T}\left.\frac{\mathrm{d}^2\mathcal{A}(\boldsymbol{\varepsilon})}{\mathrm{d}\varepsilon_y(\omega_l)\mathrm{d}\varepsilon_x(-\omega_l)}\right|_0}$$

Some general statements before deriving more equations ...

- (Linear) response functions can be expressed as derivatives of the action integral with respect to the perturbation strengths.

- Such a formulation is convenient for deriving exact and approximate expressions for the response functions. In the latter case, non-variational methods such as Coupled-Cluster (CC) theory can also be considered (Lagrangian formalism).

- Various (approximate) parameterizations of the time-dependent wavefunction $\tilde{\Psi}(\boldsymbol{\varepsilon}, t)$ will lead to various response theories.

- Variational methods such as HF and MCSCF will be considered in the following.

- Adiabatic TD-DFT equations (Casida equations) can be obtained similarly.

- TD linear response CC theory can be derived by means of a Lagrangian formalism (in analogy with time-independent CC response theory).

- In the exact theory,

$$\langle\langle \hat{V}_x;\hat{V}_y\rangle\rangle_{\omega_l}=\frac{1}{T}\int_0^T e^{\mathrm{i}\omega_l t}\left[\left\langle \underbrace{\left.\frac{\partial\tilde{\Psi}(\boldsymbol{\varepsilon},t)}{\partial\varepsilon_y(\omega_l)}\right|_0}\right|\hat{V}_x\left|\Psi_0\right\rangle+\left\langle \left.\frac{\partial\tilde{\Psi}(\boldsymbol{\varepsilon},t)}{\partial\varepsilon_y(\omega_l)}\right|_0\right|\hat{V}_x\left|\Psi_0\right\rangle^*\right]\mathrm{d}t$$

$\downarrow$

linear response of the wavefunction

(first order in perturbation theory)

- Note that, in the static case, the action integral over T becomes the energy. Consequently, the standard second-order energy correction $\langle\Psi_0|\hat{V}_x|\Psi^{(1)}\rangle$ is recovered.

- Linear and higher-order responses of the wavefunction are obtained through differentiations of the stationarity condition with respect to the perturbation strengths:

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_l)}\left(\delta\mathcal{A}\left[\tilde{\Psi}(\boldsymbol{\varepsilon}),\boldsymbol{\varepsilon}\right]\right)\Big|_0=0\quad\longrightarrow\quad\left.\frac{\partial\tilde{\Psi}(\boldsymbol{\varepsilon},t)}{\partial\varepsilon_y(\omega_l)}\right|_0$$

Wavefunction parameterization

- **Double-exponential** parameterization of a trial wavefunction: $|\Psi(t)\rangle = e^{\mathrm{i}\hat{\kappa}(t)} e^{\mathrm{i}\hat{S}(t)} |\Psi_0\rangle$

- The hermitian operators $\hat{\kappa}(t)$ and $\hat{S}(t)$ ensure **rotations** in the orbital and configuration spaces, respectively.

- Fourier series:

$$\hat{\kappa}(t) = \sum_{l,i} e^{-\mathrm{i}\omega_l t} \kappa_i(\omega_l) \hat{q}_i^\dagger + e^{-\mathrm{i}\omega_l t} \kappa_i^*(-\omega_l) \hat{q}_i \qquad \text{where} \qquad \hat{q}_i^\dagger = \hat{E}_{pq} \qquad \text{and} \qquad p > q,$$

$$\hat{S}(t) = \sum_{l,i} e^{-\mathrm{i}\omega_l t} S_i(\omega_l) \hat{R}_i^\dagger + e^{-\mathrm{i}\omega_l t} S_i^*(-\omega_l) \hat{R}_i \qquad \text{where} \qquad \hat{R}_i^\dagger = |i\rangle\langle\Psi_0|.$$

- The time-dependent wavefunction is fully determined from the Fourier component vectors

$$\mathbf{\Lambda}(\omega_l) = \begin{bmatrix} \kappa_i(\omega_l) \\ S_i(\omega_l) \\ \kappa_i^*(-\omega_l) \\ S_i^*(-\omega_l) \end{bmatrix} \qquad \longleftarrow \text{ to be used as } \textbf{variational parameters} \text{ !}$$

Such a parameterization will enable us to derive

- an **exact response theory** when

$$\hat{\kappa}(t) = 0 \quad \text{and} \quad \hat{R}_i^\dagger = |\Psi_i\rangle\langle\Psi_0| \quad \text{with} \quad i > 0 \quad \text{and} \quad \forall k \geq 0, \quad \hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle.$$

- **HF response theory** (RPA) when

$$\hat{S}(t) = 0, \quad \Psi_0 \rightarrow \Phi_0 \text{ (HF determinant)},$$

$$\text{and} \quad \hat{q}_i^\dagger \rightarrow \hat{E}_{aj} \quad \text{(single excitation from the occupied } j \text{ orbital to the unoccupied } a \text{ orbital)}$$

- **MCSCF response theory** when

$$\Psi_0 \rightarrow \Psi^{(0)} \text{ (MCSCF wavefunction)}, \quad \hat{R}_i^\dagger \rightarrow |\text{det}_i\rangle\langle\Psi^{(0)}| \quad \text{(rotation within the active space)},$$

$$\text{and} \quad \hat{q}_i^\dagger \rightarrow \hat{E}_{uj}, \hat{E}_{aj}, \hat{E}_{au}.$$

Response properties from adiabatic TD-DFT

The HF parameterization enables also to derive standard TD-DFT response equations:

- for **pure exchange** functionals, the action integral expression to be used is

$$\mathcal{A}_{\text{adia}}[\Psi,\boldsymbol{\varepsilon}] = \int_0^T \left\langle \Psi(t) \left| \hat{T} + \hat{V}_{\text{ne}} + \hat{\mathcal{V}}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} \right| \Psi(t) \right\rangle \mathrm{d}t + \int_0^T E_{\text{Hxc}}[n_{\Psi(t)}]\, \mathrm{d}t$$

- for **hybrid exchange** functionals, the action integral expression to be used is

$$\mathcal{A}^{\alpha}_{\text{adia}}[\Psi,\boldsymbol{\varepsilon}] = \int_0^T \left\langle \Psi(t) \left| \hat{T} + \hat{V}_{\text{ne}} + \alpha\hat{W}_{\text{ee}} + \hat{\mathcal{V}}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} \right| \Psi(t) \right\rangle \mathrm{d}t + \int_0^T (1-\alpha) E_{\text{Hx}}[n_{\Psi(t)}]\, \mathrm{d}t + \int_0^T E_{\text{c}}[n_{\Psi(t)}]\, \mathrm{d}t$$

- For the sake of generality, we will derive, in the following, response equations for a mixed wavefunction/density-functional **variational** action integral:

$$\boxed{\mathcal{A}[\Psi,\boldsymbol{\varepsilon}] \rightarrow \mathcal{A}_{\text{var}}[\Psi,\boldsymbol{\varepsilon}] = \int_0^T \left\langle \Psi(t) \left| \hat{\mathcal{H}} + \hat{\mathcal{V}}(t) - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} \right| \Psi(t) \right\rangle \mathrm{d}t + \int_0^T \overline{E}_{\text{Hxc}}[n_{\Psi(t)}]\, \mathrm{d}t}$$

Hellmann–Feynman theorem for time-dependent variational methods

$$\mathcal{A}_{\rm var}\left[\Psi,\boldsymbol{\varepsilon}\right]=\int_0^T\left\langle\Psi(t)\left|\hat{\mathcal{H}}+\hat{\mathcal{V}}(t)-{\rm i}\frac{{\rm d}}{{\rm d}t}\right|\Psi(t)\right\rangle{\rm d}t+\int_0^T\overline{E}_{\rm Hxc}[n_{\Psi(t)}]\,{\rm d}t$$

- Let us keep in mind that the wavefunction Ψ is determined from the vector $\boldsymbol{\Lambda}\equiv\{\boldsymbol{\Lambda}(\omega_l)\}_l$

- The action integral will therefore be denoted $\mathcal{A}_{\rm var}(\boldsymbol{\Lambda},\boldsymbol{\varepsilon})$ in the following.

- For any perturbation strength $\boldsymbol{\varepsilon}$, $\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})$ is obtained from the stationarity condition:

$$\forall\boldsymbol{\varepsilon},\qquad\left.\frac{\partial\mathcal{A}_{\rm var}(\boldsymbol{\Lambda},\boldsymbol{\varepsilon})}{\partial\boldsymbol{\Lambda}}\right|_{\boldsymbol{\Lambda}=\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})}=0$$

- Consequently, the Hellmann-Feynman theorem is fulfilled for the variational action integral $\mathcal{A}_{\rm var}(\boldsymbol{\varepsilon})=\mathcal{A}_{\rm var}(\boldsymbol{\Lambda}(\boldsymbol{\varepsilon}),\boldsymbol{\varepsilon})$, **exactly like in the exact theory**:

$$\frac{{\rm d}\mathcal{A}_{\rm var}(\boldsymbol{\varepsilon})}{{\rm d}\boldsymbol{\varepsilon}}=\left.\frac{\partial\mathcal{A}_{\rm var}(\boldsymbol{\Lambda},\boldsymbol{\varepsilon})}{\partial\boldsymbol{\varepsilon}}\right|_{\boldsymbol{\Lambda}=\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})}$$

Linear response functions

- Therefore, in analogy with the exact theory, $\langle\langle \hat{V}_x ; \hat{V}_y \rangle\rangle_{\omega_l} = \dfrac{1}{T} \dfrac{d^2 \mathcal{A}_{\text{var}}(\boldsymbol{\varepsilon})}{d\varepsilon_y(\omega_l) d\varepsilon_x(-\omega_l)}\Big|_0$

  where

$$\frac{d\mathcal{A}_{\text{var}}(\boldsymbol{\varepsilon})}{d\varepsilon_x(-\omega_l)} = \int_0^T e^{i\omega_l t} \left\langle \Psi(t) \middle| \hat{V}_x \middle| \Psi(t) \right\rangle \, dt$$

$$= \int_0^T e^{i\omega_l t} \left\langle \Psi_0 \middle| e^{-i\hat{S}(t)} e^{-i\hat{\kappa}(t)} \hat{V}_x e^{i\hat{\kappa}(t)} e^{i\hat{S}(t)} \middle| \Psi_0 \right\rangle \, dt$$

  thus leading to

$$\frac{d\mathcal{A}_{\text{var}}(\boldsymbol{\varepsilon})}{d\varepsilon_x(-\omega_l)} = \int_0^T e^{i\omega_l t} \left[\left\langle \Psi_0 \middle| \hat{V}_x \middle| \Psi_0 \right\rangle + i \left\langle \Psi_0 \middle| \left[\hat{V}_x, \hat{\kappa}(t) \right] \middle| \Psi_0 \right\rangle + i \left\langle \Psi_0 \middle| \left[\hat{V}_x, \hat{S}(t) \right] \middle| \Psi_0 \right\rangle + \ldots \right] dt$$

$$= T\delta(\omega_l) \left\langle \Psi_0 \middle| \hat{V}_x \middle| \Psi_0 \right\rangle + iT \, V_x^{[1]\dagger} \boldsymbol{\Lambda}(\omega_l) + \ldots$$

Linear response functions

where the gradient property vector is defined as

$$V_x^{[1]} = \begin{bmatrix} \langle \Psi_0 | [\hat{q}_i, \hat{V}_x] | \Psi_0 \rangle \\ \langle \Psi_0 | [\hat{R}_i, \hat{V}_x] | \Psi_0 \rangle \\ \langle \Psi_0 | [\hat{q}_i^\dagger, \hat{V}_x] | \Psi_0 \rangle \\ \langle \Psi_0 | [\hat{R}_i^\dagger, \hat{V}_x] | \Psi_0 \rangle \end{bmatrix}$$

Conclusion:

$$\boxed{\langle\langle \hat{V}_x ; \hat{V}_y \rangle\rangle_{\omega_l} = \mathrm{i}\, V_x^{[1]\dagger} \left. \frac{\partial \mathbf{\Lambda}(\omega_l)}{\partial \varepsilon_y(\omega_l)} \right|_0}$$

We now need to derive the linear response equation that is fulfilled by the linear response vector $\mathbf{X}_y(\omega_l) = \left. \dfrac{\partial \mathbf{\Lambda}(\omega_l)}{\partial \varepsilon_y(\omega_l)} \right|_0$.

Linear response equation

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)}\left[\left.\frac{\partial \mathcal{A}_{\mathrm{var}}(\boldsymbol{\Lambda},\boldsymbol{\varepsilon})}{\partial \boldsymbol{\Lambda}^{\dagger}(-\omega_l)}\right|_{\boldsymbol{\Lambda}=\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})}\right]_0 = 0$$

where

$$\mathcal{A}_{\mathrm{var}}\left[\boldsymbol{\Lambda},\boldsymbol{\varepsilon}\right]$$

$$||$$

$$\underbrace{\int_0^T \left\langle \Psi(t)\middle|\hat{\mathcal{H}}\middle|\Psi(t)\right\rangle \mathrm{d}t}_{\mathcal{A}_{\hat{\mathcal{H}}}\left[\boldsymbol{\Lambda}\right]} + \underbrace{\int_0^T \overline{E}_{\mathrm{Hxc}}[n_{\Psi(t)}]\,\mathrm{d}t}_{\overline{\mathcal{A}}_{\mathrm{Hxc}}\left[\boldsymbol{\Lambda}\right]} + \underbrace{\int_0^T \left\langle \Psi(t)\middle|\hat{\mathcal{V}}(t)\middle|\Psi(t)\right\rangle \mathrm{d}t}_{\mathcal{A}_{\hat{\mathcal{V}}}\left[\boldsymbol{\Lambda},\boldsymbol{\varepsilon}\right]} + \underbrace{\int_0^T \left\langle \Psi(t)\middle|-\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\middle|\Psi(t)\right\rangle \mathrm{d}t}_{\mathcal{A}_{\mathrm{d}/\mathrm{d}t}\left[\boldsymbol{\Lambda}\right]}$$

Linear response equation

- $$\mathcal{A}_{\hat{\mathcal{V}}}\left[\boldsymbol{\Lambda},\boldsymbol{\varepsilon}\right]=\sum_{x}\sum_{k=-N}^{N}\sum_{p}\varepsilon_x(\omega_k)\Bigg[T\delta(\omega_k)\left\langle\Psi_0\left|\hat{V}_x\right|\Psi_0\right\rangle+\mathrm{i}T\delta(\omega_k+\omega_p)\;\underbrace{V_x^{[1]\dagger}\boldsymbol{\Lambda}(\omega_p)}_{\frac{1}{2}V_x^{[1]\dagger}\boldsymbol{\Lambda}(\omega_p)-\frac{1}{2}\boldsymbol{\Lambda}^{\dagger}(-\omega_p)V_x^{[1]}}+\ldots\Bigg]$$

$$\longrightarrow\qquad\frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)}\left[\left.\frac{\partial\mathcal{A}_{\hat{\mathcal{V}}}(\boldsymbol{\Lambda},\boldsymbol{\varepsilon})}{\partial\boldsymbol{\Lambda}^{\dagger}(-\omega_l)}\right|_{\boldsymbol{\Lambda}=\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})}\right]_0=-\frac{\mathrm{i}T}{2}\delta(\omega_m+\omega_l)\;V_y^{[1]}$$

EXERCISE: Let $\hat{f}(x,t)=e^{-x\hat{A}(t)}\dfrac{\mathrm{d}}{\mathrm{d}t}e^{x\hat{A}(t)}$.

Show that $$\hat{f}(1,t)=\int_0^1\frac{\partial\hat{f}(x,t)}{\partial x}\,\mathrm{d}x=\frac{\mathrm{d}\hat{A}(t)}{\mathrm{d}t}+\frac{1}{2}\left[\frac{\mathrm{d}\hat{A}(t)}{\mathrm{d}t},\hat{A}(t)\right]+\ldots$$

Linear response equation

- Using

$$e^{-\mathrm{i}\hat{S}(t)}e^{-\mathrm{i}\hat{\kappa}(t)}\frac{\mathrm{d}}{\mathrm{d}t}\left(e^{\mathrm{i}\hat{\kappa}(t)}e^{\mathrm{i}\hat{S}(t)}\right)=e^{-\mathrm{i}\hat{S}(t)}\left(e^{-\mathrm{i}\hat{\kappa}(t)}\frac{\mathrm{d}}{\mathrm{d}t}e^{\mathrm{i}\hat{\kappa}(t)}\right)e^{\mathrm{i}\hat{S}(t)}+e^{-\mathrm{i}\hat{S}(t)}\frac{\mathrm{d}}{\mathrm{d}t}e^{\mathrm{i}\hat{S}(t)}$$

leads to

$$\mathcal{A}_{\mathrm{d}/\mathrm{d}t}\left[\mathbf{\Lambda}\right] = \int_0^T\left\langle\Psi_0\middle|\frac{\mathrm{d}\hat{\kappa}(t)}{\mathrm{d}t}+\frac{\mathrm{d}\hat{S}(t)}{\mathrm{d}t}\middle|\Psi_0\right\rangle\mathrm{d}t$$

$$+\mathrm{i}\int_0^T\left\langle\Psi_0\middle|\frac{1}{2}\left[\frac{\mathrm{d}\hat{\kappa}(t)}{\mathrm{d}t},\hat{\kappa}(t)\right]+\frac{1}{2}\left[\frac{\mathrm{d}\hat{S}(t)}{\mathrm{d}t},\hat{S}(t)\right]+\left[\frac{\mathrm{d}\hat{\kappa}(t)}{\mathrm{d}t},\hat{S}(t)\right]\middle|\Psi_0\right\rangle\mathrm{d}t+\ldots$$

$$\longrightarrow \quad \frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)}\left[\left.\frac{\partial\mathcal{A}_{\mathrm{d}/\mathrm{d}t}\left[\mathbf{\Lambda}\right]}{\partial\mathbf{\Lambda}^\dagger(-\omega_l)}\right|_{\mathbf{\Lambda}=\mathbf{\Lambda}(\boldsymbol{\varepsilon})}\right]_0=\frac{T}{2}\omega_l\;S^{[2]}\left.\frac{\partial\mathbf{\Lambda}(-\omega_l)}{\partial\varepsilon_y(\omega_m)}\right|_0$$

Linear response equation

where

$$S^{[2]} = \begin{bmatrix} \Sigma & \Delta \\ -\Delta^* & -\Sigma^* \end{bmatrix},$$

$$\Sigma = \begin{bmatrix} \langle\Psi_0|[\hat{q}_i, \hat{q}_j^\dagger]|\Psi_0\rangle & \langle\Psi_0|[\hat{q}_i, \hat{R}_j^\dagger]|\Psi_0\rangle \\ \langle\Psi_0|[\hat{R}_i, \hat{q}_j^\dagger]|\Psi_0\rangle & \langle\Psi_0|[\hat{R}_i, \hat{R}_j^\dagger]|\Psi_0\rangle \end{bmatrix},$$

$$\Delta = \begin{bmatrix} \langle\Psi_0|[\hat{q}_i, \hat{q}_j]|\Psi_0\rangle & \langle\Psi_0|[\hat{q}_i, \hat{R}_j]|\Psi_0\rangle \\ \langle\Psi_0|[\hat{R}_i, \hat{q}_j]|\Psi_0\rangle & \langle\Psi_0|[\hat{R}_i, \hat{R}_j]|\Psi_0\rangle \end{bmatrix}.$$

Linear response equation

- Using the BCH expansion leads to

$$\mathcal{A}_{\hat{\mathcal{H}}}[\boldsymbol{\Lambda}] = \int_0^T \left\langle \Psi_0 \middle| \hat{\mathcal{H}} + \mathrm{i}\left[\hat{\mathcal{H}}, \hat{\kappa}(t)\right] + \mathrm{i}\left[\hat{\mathcal{H}}, \hat{S}(t)\right] \middle| \Psi_0 \right\rangle \mathrm{d}t$$

$$- \int_0^T \left\langle \Psi_0 \middle| \frac{1}{2}\left[\left[\hat{\mathcal{H}}, \hat{\kappa}(t)\right], \hat{\kappa}(t)\right] + \frac{1}{2}\left[\left[\hat{\mathcal{H}}, \hat{S}(t)\right], \hat{S}(t)\right] + \left[\left[\hat{\mathcal{H}}, \hat{\kappa}(t)\right], \hat{S}(t)\right] \middle| \Psi_0 \right\rangle \mathrm{d}t + \ldots$$

$$\longrightarrow \quad \frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)} \left[\left. \frac{\partial \mathcal{A}_{\hat{\mathcal{H}}}[\boldsymbol{\Lambda}]}{\partial \boldsymbol{\Lambda}^\dagger(-\omega_l)} \right|_{\boldsymbol{\Lambda}=\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})} \right]_0 = \frac{T}{2}\, E^{[2]} \left. \frac{\partial \boldsymbol{\Lambda}(-\omega_l)}{\partial \varepsilon_y(\omega_m)} \right|_0$$

Linear response equation

where

$$E^{[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix},$$

$$A = \begin{bmatrix} \langle\Psi_0|[\hat{q}_i, [\hat{\mathcal{H}}, \hat{q}_j^\dagger]]|\Psi_0\rangle & \langle\Psi_0|[[\hat{q}_i, \hat{\mathcal{H}}], \hat{R}_j^\dagger]|\Psi_0\rangle \\ \langle\Psi_0|[\hat{R}_i, [\hat{\mathcal{H}}, \hat{q}_j^\dagger]]|\Psi_0\rangle & \langle\Psi_0|[\hat{R}_i, [\hat{\mathcal{H}}, \hat{R}_j^\dagger]]|\Psi_0\rangle \end{bmatrix},$$

$$B = \begin{bmatrix} \langle\Psi_0|[\hat{q}_i, [\hat{\mathcal{H}}, \hat{q}_j]]|\Psi_0\rangle & \langle\Psi_0|[[\hat{q}_i, \hat{\mathcal{H}}], \hat{R}_j]|\Psi_0\rangle \\ \langle\Psi_0|[\hat{R}_i, [\hat{\mathcal{H}}, \hat{q}_j]]|\Psi_0\rangle & \langle\Psi_0|[\hat{R}_i, [\hat{\mathcal{H}}, \hat{R}_j]]|\Psi_0\rangle \end{bmatrix}.$$

Linear response equation

- DFT-type contribution:

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)}\left[\left.\frac{\partial\overline{\mathcal{A}}_{\mathrm{Hxc}}\left[\mathbf{\Lambda}\right]}{\partial\mathbf{\Lambda}^\dagger(-\omega_l)}\right|_{\mathbf{\Lambda}=\mathbf{\Lambda}(\boldsymbol{\varepsilon})}\right]_0=\frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)}\left[\int_0^T\mathrm{d}t\int\mathrm{d}\mathbf{r}\,\frac{\delta\overline{E}_{\mathrm{Hxc}}[n_{\Psi(t)}]}{\delta n(\mathbf{r})}\left.\frac{\partial n_{\Psi(t)}(\mathbf{r})}{\partial\mathbf{\Lambda}^\dagger(-\omega_l)}\right|_{\mathbf{\Lambda}=\mathbf{\Lambda}(\boldsymbol{\varepsilon})}\right]_0$$

$$=\int_0^T\mathrm{d}t\int\mathrm{d}\mathbf{r}\,\frac{\delta\overline{E}_{\mathrm{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r})}\frac{\mathrm{d}}{\mathrm{d}\varepsilon_y(\omega_m)}\left[\left.\frac{\partial n_{\Psi(t)}(\mathbf{r})}{\partial\mathbf{\Lambda}^\dagger(-\omega_l)}\right|_{\mathbf{\Lambda}=\mathbf{\Lambda}(\boldsymbol{\varepsilon})}\right]_0 \qquad \longleftarrow \textbf{potential !}$$

$$+\int_0^T\mathrm{d}t\int\mathrm{d}\mathbf{r}'\int\mathrm{d}\mathbf{r}\,\frac{\delta^2\overline{E}_{\mathrm{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})}\left.\frac{\partial n_{\Psi(t)}(\mathbf{r})}{\partial\mathbf{\Lambda}^\dagger(-\omega_l)}\right|_0\left.\frac{\partial n_{\Psi(t)}(\mathbf{r}')}{\partial\varepsilon_y(\omega_m)}\right|_0 \qquad \longleftarrow \textbf{kernel !}$$

- The "**potential**" term is simply taken into account with the substitution,

$$\hat{\mathcal{H}}\rightarrow\hat{\mathcal{H}}+\int\mathrm{d}\mathbf{r}\,\frac{\delta\overline{E}_{\mathrm{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r})}\hat{n}(\mathbf{r})$$

Linear response equation

- Using the expressions $\left.\dfrac{\partial n_{\Psi(t)}(\mathbf{r}')}{\partial \varepsilon_y(\omega_m)}\right|_0 = \mathrm{i}\sum_p e^{-\mathrm{i}\omega_p t} n^{[1]\dagger}(\mathbf{r}')\left.\dfrac{\partial \mathbf{\Lambda}(\omega_p)}{\partial \varepsilon_y(\omega_m)}\right|_0$

and $\left.\dfrac{\partial n_{\Psi(t)}(\mathbf{r})}{\partial \mathbf{\Lambda}^{\dagger}(-\omega_l)}\right|_0 = -\dfrac{\mathrm{i}}{2} e^{-\mathrm{i}\omega_l t} n^{[1]}(\mathbf{r}),$

the "**kernel**" contribution can be rewritten as follows,

$$\underbrace{\frac{T}{2}\int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}\, \frac{\delta^2 \overline{E}_{\mathrm{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} n^{[1]}(\mathbf{r}) n^{[1]\dagger}(\mathbf{r}')}_{\overline{K}_{\mathrm{Hxc}}} \left.\frac{\partial \mathbf{\Lambda}(-\omega_l)}{\partial \varepsilon_y(\omega_m)}\right|_0$$

$\longleftarrow$ kernel matrix

Linear response equation

Conclusion: in the particular case of **wavefunction linear response theory** (no DFT contributions), the linear response equations to be solved are

$$\left(E^{[2]}+\omega_l S^{[2]}\right)\left.\frac{\partial \boldsymbol{\Lambda}(-\omega_l)}{\partial \varepsilon_y(\omega_m)}\right|_0 = \mathrm{i}\delta(\omega_m+\omega_l)\, V_y^{[1]}$$

thus leading to

$$\boxed{\left(E^{[2]}-\omega_l S^{[2]}\right)\left.\frac{\partial \boldsymbol{\Lambda}(\omega_l)}{\partial \varepsilon_y(\omega_l)}\right|_0 = \mathrm{i}\, V_y^{[1]}}$$

and

$$\langle\langle \hat{V}_x;\hat{V}_y\rangle\rangle_{\omega_l} = \mathrm{i}\, V_x^{[1]\dagger}\left.\frac{\partial \boldsymbol{\Lambda}(\omega_l)}{\partial \varepsilon_y(\omega_l)}\right|_0 = -V_x^{[1]\dagger}\left(E^{[2]}-\omega_l S^{[2]}\right)^{-1} V_y^{[1]}$$

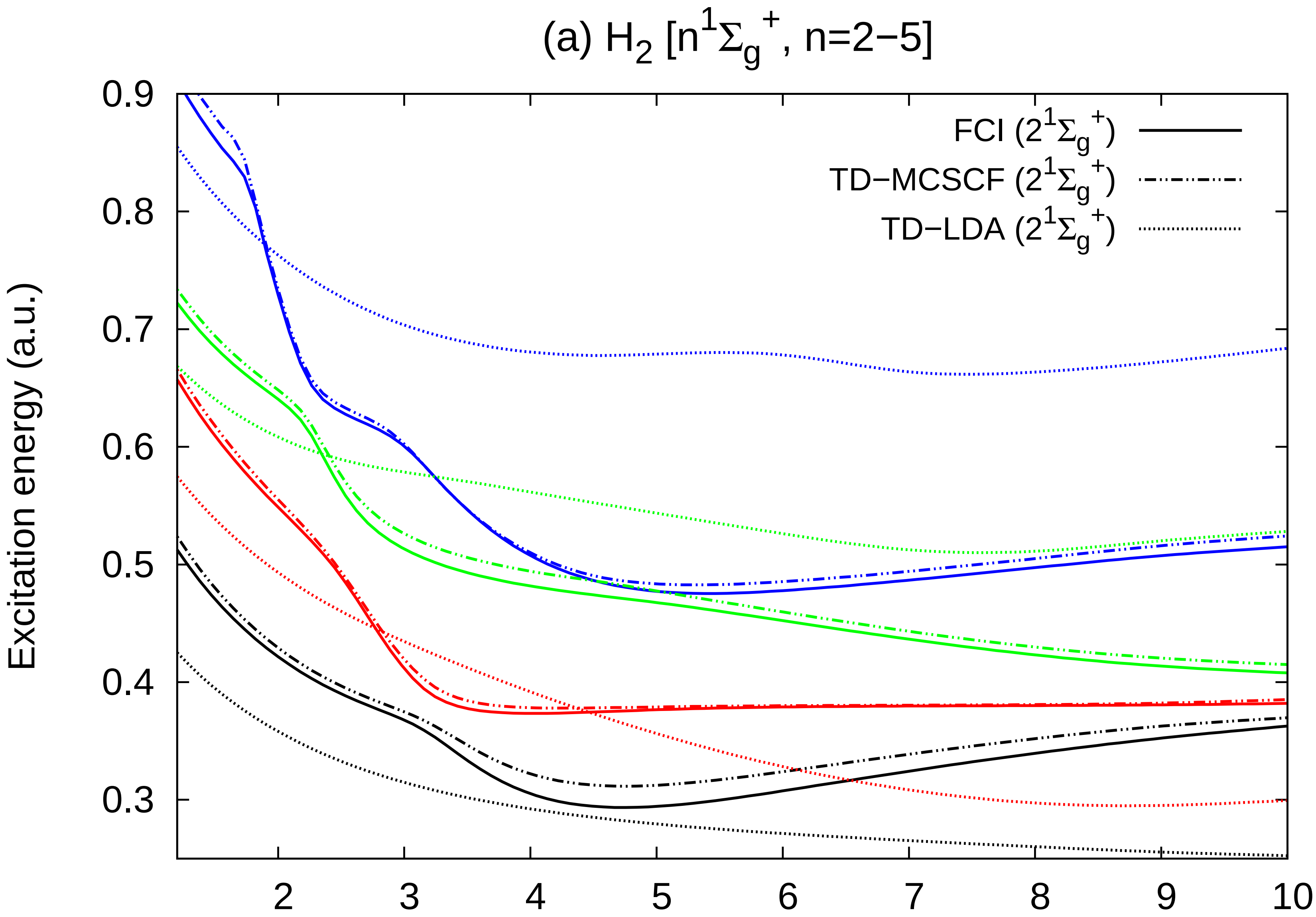
EXERCISE: **(1)** Show that, in exact response theory, $\Sigma_{ij}=\delta_{ij}$, $\Delta_{ij}=0$, $A_{ij}=\delta_{ij}(E_i-E_0)$, and $B_{ij}=0$.

(2) Show that $V_x^{[1]}=\begin{bmatrix}\langle\Psi_i|\hat{V}_x|\Psi_0\rangle\\ -\langle\Psi_0|\hat{V}_x|\Psi_i\rangle\end{bmatrix}$

(3) Conclude that

$$\langle\langle\hat{V}_x;\hat{V}_y\rangle\rangle_\omega=-\sum_{i>0}\left(\frac{\langle\Psi_0|\hat{V}_x|\Psi_i\rangle\langle\Psi_i|\hat{V}_y|\Psi_0\rangle}{E_i-E_0-\omega}+\frac{\langle\Psi_i|\hat{V}_x|\Psi_0\rangle\langle\Psi_0|\hat{V}_y|\Psi_i\rangle}{E_i-E_0+\omega}\right)$$

Comment: the so-called "density-density response function" (or polarizability) used in Physics is defined as $\chi(\mathbf{r},\mathbf{r}',\omega)=\langle\langle\hat{n}(\mathbf{r});\hat{n}(\mathbf{r}')\rangle\rangle_\omega$.


(a) H_2 [$n^1\Sigma_g^+$, n=2−5]
Excitation energy (a.u.)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
2
3
4
5
6
7
8
9
10
FCI ($2^1\Sigma_g^+$)
TD−MCSCF ($2^1\Sigma_g^+$)
TD−LDA ($2^1\Sigma_g^+$)

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