

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 $\hat{H} = \hat{T} + \hat{W}_{ee} + \hat{V}_{ne}$ 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 \mathcal{E} along the z axis, then

$$\mathcal{E} = \varepsilon \mathbf{e}_z \quad \text{and} \quad \hat{V} = \varepsilon \hat{z} \quad \text{where} \quad \hat{z} = \int d\mathbf{r} z \hat{n}(\mathbf{r}) \quad \leftarrow \text{second-quantized notation !}$$

- 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:

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

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:

$$\frac{dE(\epsilon)}{d\epsilon} = \left\langle \Psi(\epsilon) \left| \frac{\partial \hat{H}(\epsilon)}{\partial \epsilon} \right| \Psi(\epsilon) \right\rangle = \langle \hat{V} \rangle(\epsilon)$$

- Exact response functions can be expressed as **energy derivatives**:

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

Response theory for variational methods

- In variational methods, the energy is expressed as an expectation value. It depends on both the trial variational parameters λ and the perturbation strength ε :

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

- At the **HF** level of approximation, λ parameterizes orbital rotations.
- At the **CI** level (in the basis of perturbation-independent orbitals), λ contains all the CI coefficients.
- At the **MCSCF** level, it contains both orbital rotation and CI coefficients.

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

- In the following, we will use parameterizations such that $\lambda(0) = 0$.
- Consequently $\lambda(\varepsilon)$ 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:

$$\frac{d\mathcal{E}(\varepsilon)}{d\varepsilon} = \left[\frac{\partial \boldsymbol{\lambda}(\varepsilon)}{\partial \varepsilon} \right]^T \underbrace{\frac{\partial E(\boldsymbol{\lambda}, \varepsilon)}{\partial \boldsymbol{\lambda}} \Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(\varepsilon)}}_0 + \frac{\partial E(\boldsymbol{\lambda}, \varepsilon)}{\partial \varepsilon} \Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(\varepsilon)}$$

thus leading to

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

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

Example: exact response theory

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

- Exact wavefunction parameterization:

$$|\Psi(\mathbf{S})\rangle = e^{\hat{S}} |\Psi_0\rangle$$

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

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

- BCH expansion:

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

Example: exact response theory

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

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

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

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

Example: exact response theory

- BCH expansion for the energy:

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

which leads to

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

where the **hessian** matrix elements equal

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

Example: exact response theory

- In summary:

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

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

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

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

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

Some comments before turning to the time-dependent regime

- Let us return to (approximate) **variational** methods.
- $\mathbf{X} = \left. \frac{\partial \lambda(\varepsilon)}{\partial \varepsilon} \right|_0$ 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 ?

Time-dependent linear response theory: exact and approximate formulations

- 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:

$$\mathcal{E}(\varepsilon) = E(\mathbf{t}(\varepsilon), \varepsilon)$$

- We introduce the **Lagrangian function**:

$$L(\mathbf{t}, \varepsilon, \bar{\mathbf{t}}) = E(\mathbf{t}, \varepsilon) + \bar{\mathbf{t}}^T \mathbf{f}(\mathbf{t}, \varepsilon)$$

and impose the following stationarity conditions:

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

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

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

- Note that $\mathcal{E}(\varepsilon) = L(\mathbf{t}(\varepsilon), \varepsilon, \bar{\mathbf{t}})$

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

Time-dependent variational principle

- Time-dependent Schrödinger equation: $\hat{H}(t)|\bar{\Psi}(t)\rangle = i \frac{d}{dt} |\bar{\Psi}(t)\rangle$
- Alternative formulation based on a change of phase: $|\bar{\Psi}(t)\rangle = e^{-i \int_{t_0}^t Q(t) dt} |\tilde{\Psi}(t)\rangle$

→

$$\hat{H}(t)|\tilde{\Psi}(t)\rangle - i \frac{d}{dt} |\tilde{\Psi}(t)\rangle = Q(t)|\tilde{\Psi}(t)\rangle$$

- 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 $\bar{\Psi}(t_0)$:

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

- 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 $\frac{d}{dt} \langle \bar{\Psi}(t) | \bar{\Psi}(t) \rangle = i \langle \hat{H}(t) \bar{\Psi}(t) | \bar{\Psi}(t) \rangle - i \langle \bar{\Psi}(t) | \hat{H}(t) | \bar{\Psi}(t) \rangle = 0$,

if $Q(t)$ is real then

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

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

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

$$\text{since} \quad \left\langle \frac{d\tilde{\Psi}(t)}{dt} \left| \tilde{\Psi}(t) \right\rangle = \underbrace{\frac{d}{dt} \left\langle \tilde{\Psi}(t) \left| \tilde{\Psi}(t) \right\rangle}_0 - \left\langle \tilde{\Psi}(t) \left| \frac{d\tilde{\Psi}(t)}{dt} \right\rangle$$

0

Time-dependent variational principle

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

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

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

- **Stationarity condition:**

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

variational formulation

non-variational formulation

Proof: 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:

$$\begin{aligned}
 \delta\mathcal{A}[\tilde{\Psi}] &= \mathcal{A}[\tilde{\Psi} + \delta\Psi] - \mathcal{A}[\tilde{\Psi}] = \int_{t_0}^{t_1} \left(Q[\tilde{\Psi} + \delta\Psi](t) - Q[\tilde{\Psi}](t) \right) dt \\
 &= \int_{t_0}^{t_1} \left\langle \delta\Psi(t) \left| \hat{H}(t) - i \frac{d}{dt} \right| \tilde{\Psi}(t) \right\rangle dt + \int_{t_0}^{t_1} \left\langle \tilde{\Psi}(t) \left| \hat{H}(t) - i \frac{d}{dt} \right| \delta\Psi(t) \right\rangle dt \\
 &\quad - \int_{t_0}^{t_1} Q(t) \left(\langle \delta\Psi(t) | \tilde{\Psi}(t) \rangle + \langle \tilde{\Psi}(t) | \delta\Psi(t) \rangle \right) dt
 \end{aligned}$$

where

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

thus leading to

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

Variational principle in adiabatic TD-DFT

- In time-dependent density-functional theory (TD-DFT), the physical time-dependent Hamiltonian is

written as
$$\hat{H}(t) = \hat{T} + \hat{W}_{ee} + \underbrace{\int d\mathbf{r} v(\mathbf{r}, t) \hat{n}(\mathbf{r})}_{\hat{V}(t)}$$

$\hat{V}(t)$ ← 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):

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

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

EXERCISE: (1) Show that, within the adiabatic approximation, the Kohn–Sham TD-DFT equation is equivalent to the stationarity condition $\delta\mathcal{A}_{\text{adia}}[\tilde{\Phi}^{\text{KS}}] = 0$ where, for a trial wavefunction $\Psi(t)$,

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

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

(2) Within the adiabatic approximation, the equation to be solved in TD range-separated DFT is

$$\left(\hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \hat{V}(t) + \int d\mathbf{r} \frac{\delta E_{\text{Hxc}}^{\text{sr},\mu}[n_{\tilde{\Psi}^\mu(t)}]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}) - i \frac{d}{dt} \right) |\tilde{\Psi}^\mu(t)\rangle = Q^\mu(t) |\tilde{\Psi}^\mu(t)\rangle.$$

Show that it is equivalent to $\delta\mathcal{A}_{\text{adia}}^\mu[\tilde{\Psi}^\mu] = 0$ where

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

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:

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

← time-dependent **perturbation**

where $\omega_k = \frac{2\pi k}{T}$ 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:

$$\hat{V}_x \rightarrow \int d\mathbf{r} v_x(\mathbf{r}) \hat{n}(\mathbf{r})$$

Floquet theory

- **Example 1:** in the presence of a dynamic uniform **electric field**,

$$\mathbf{E}(t) = E_x(t) \mathbf{e}_x + E_y(t) \mathbf{e}_y + E_z(t) \mathbf{e}_z = \sum_{k=-N}^N e^{-i\omega_k t} \left(\varepsilon_x(\omega_k) \mathbf{e}_x + \varepsilon_y(\omega_k) \mathbf{e}_y + \varepsilon_z(\omega_k) \mathbf{e}_z \right),$$

the perturbation is $\hat{\mathcal{V}}(t) = \hat{\mathbf{r}} \cdot \mathbf{E}(t) = \hat{x} E_x(t) + \hat{y} E_y(t) + \hat{z} E_z(t)$ thus leading to

$$\hat{\mathcal{V}}(t) = \sum_{k=-N}^N e^{-i\omega_k t} \left(\varepsilon_x(\omega_k) \hat{x} + \varepsilon_y(\omega_k) \hat{y} + \varepsilon_z(\omega_k) \hat{z} \right).$$

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

$$\hat{\mathcal{V}}(t) = \int \mathbf{r} \cdot \mathbf{E}(t) \hat{n}(\mathbf{r}) d\mathbf{r} \quad \longleftarrow \text{local potential operator !}$$

Floquet theory

- **Example 2:** in the presence of a dynamic uniform **magnetic field**,

$$\mathbf{B}(t) = B_x(t) \mathbf{e}_x + B_y(t) \mathbf{e}_y + B_z(t) \mathbf{e}_z = \sum_{k=-N}^N e^{-i\omega_k t} \left(b_x(\omega_k) \mathbf{e}_x + b_y(\omega_k) \mathbf{e}_y + b_z(\omega_k) \mathbf{e}_z \right),$$

the perturbation equals $\hat{\mathcal{V}}(t) = \frac{1}{2} \hat{\mathbf{L}} \cdot \mathbf{B}(t)$ thus leading to

$$\hat{\mathcal{V}}(t) = \sum_{k=-N}^N e^{-i\omega_k t} \left(b_x(\omega_k) \frac{\hat{L}_x}{2} + b_y(\omega_k) \frac{\hat{L}_y}{2} + b_z(\omega_k) \frac{\hat{L}_z}{2} \right).$$

Comment: note that $\hat{\mathbf{L}}$ can be written as $\hat{\mathbf{L}} = -i \sum_{\sigma} \int \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \mathbf{r} \times \nabla_{\mathbf{r}} \hat{\Psi}_{\sigma}(\mathbf{r}) d\mathbf{r}$ so that

$$\hat{\mathcal{V}}(t) = -\frac{i}{2} \int \mathbf{B}(t) \cdot \left(\mathbf{r} \times \nabla_{\mathbf{r}} \hat{n}_1(\mathbf{r}', \mathbf{r}) \Big|_{\mathbf{r}'=\mathbf{r}} \right) d\mathbf{r} \quad \longleftarrow \text{non-local potential operator !}$$

EXERCISE:

(1) By using the hermiticity of $\hat{\mathbf{L}}$ show that $\hat{\mathbf{L}} = \int \mathbf{r} \times \hat{\mathbf{j}}(\mathbf{r}) \, d\mathbf{r}$ where the **current density operator** equals

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma} \left(\hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla_{\mathbf{r}} \hat{\Psi}_{\sigma}(\mathbf{r}) - (\nabla_{\mathbf{r}} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r})) \hat{\Psi}_{\sigma}(\mathbf{r}) \right)$$

(2) Show that the perturbation can be expressed as $\hat{\mathcal{V}}(t) = -\hat{\boldsymbol{\mu}}_{\text{mag}} \cdot \mathbf{B}(t)$ where the **magnetic dipole moment operator** equals

$$\hat{\boldsymbol{\mu}}_{\text{mag}} = -\frac{1}{2} \int \mathbf{r} \times \hat{\mathbf{j}}(\mathbf{r}) \, d\mathbf{r}$$

(3) Explain why TD-DFT is in principle not adequate for modeling such a perturbation. Show that the **paramagnetic current density**

$$\mathbf{j}_p(\mathbf{r}, t) = \langle \tilde{\Psi}(t) | \hat{\mathbf{j}}(\mathbf{r}) | \tilde{\Psi}(t) \rangle$$

would be a better variable to consider (rather than the density).

Floquet theory

- Let us collect all perturbation strengths into the **vector** $\boldsymbol{\varepsilon} = \begin{bmatrix} \vdots \\ \varepsilon_x(\omega_k) \\ \vdots \end{bmatrix}$
- $\hat{\mathcal{V}}^\dagger(t) = \hat{\mathcal{V}}(t) \quad \rightarrow \quad \varepsilon_x(-\omega_k)^* = \varepsilon_x(\omega_k)$
- The time-dependent wavefunction varies with the perturbation strengths: $\tilde{\Psi}(t) \equiv \tilde{\Psi}(\boldsymbol{\varepsilon}, t)$
- Choice of the **phase**: we want the time-dependent wavefunction to reduce to the (time-independent) ground-state 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**: $t_0 = 0$ and $t_1 = T$.

Response functions

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

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

$$\langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle$$

← zeroth order

$$+ \sum_y \sum_k e^{-i\omega_k t} \varepsilon_y(\omega_k) \langle \langle \hat{V}_x; \hat{V}_y \rangle \rangle_{\omega_k}$$

← **linear response**

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

← quadratic response

+ ...

- We will focus 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 ϵ :

$$\boxed{\mathcal{A}(\epsilon) = \mathcal{A}[\tilde{\Psi}(\epsilon), \epsilon]}$$

where

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

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

- $\tilde{\Psi}(\epsilon, t)$ is determined from the **variational principle**:

$$\boxed{\forall \epsilon, \quad \delta \mathcal{A}[\tilde{\Psi}(\epsilon), \epsilon] = 0}$$

Hellmann–Feynman theorem in the time-dependent regime

- Let us consider the variation $\varepsilon_x(\omega_k) \rightarrow \varepsilon_x(\omega_k) + d\varepsilon_x(\omega_k)$:

$$\begin{aligned}
 d\mathcal{A}(\boldsymbol{\varepsilon}) &= \mathcal{A}\left(\varepsilon_x(\omega_k) + d\varepsilon_x(\omega_k)\right) - \mathcal{A}\left(\varepsilon_x(\omega_k)\right) \\
 &= \frac{\partial \mathcal{A}[\Psi, \boldsymbol{\varepsilon}]}{\partial \varepsilon_x(\omega_k)} \Big|_{\Psi=\Psi(\boldsymbol{\varepsilon})} d\varepsilon_x(\omega_k) + \underbrace{\mathcal{A}\left[\tilde{\Psi}(\boldsymbol{\varepsilon}) + \frac{\partial \tilde{\Psi}(\boldsymbol{\varepsilon})}{\partial \varepsilon_x(\omega_k)} d\varepsilon_x(\omega_k), \boldsymbol{\varepsilon}\right] - \mathcal{A}\left[\tilde{\Psi}(\boldsymbol{\varepsilon}), \boldsymbol{\varepsilon}\right]}_{\delta \mathcal{A}\left[\tilde{\Psi}(\boldsymbol{\varepsilon}), \boldsymbol{\varepsilon}\right] = 0}
 \end{aligned}$$

thus leading to the **Hellmann–Feynman theorem**

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

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

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

- zeroth order:**
$$\frac{d\mathcal{A}(\boldsymbol{\varepsilon})}{d\varepsilon_x(\omega_k)} \Big|_0 = \int_0^T e^{-i\omega_k t} \langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle dt = T \langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle \delta(\omega_k) \quad \text{thus leading to}$$

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

- Linear response:**

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

thus leading to

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

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 $\tilde{\Psi}(\epsilon, t)$ 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**,

$$\langle\langle \hat{V}_x; \hat{V}_y \rangle\rangle_{\omega_l} = \frac{1}{T} \int_0^T e^{i\omega_l t} \left[\left\langle \underbrace{\frac{\partial \tilde{\Psi}(\boldsymbol{\varepsilon}, t)}{\partial \varepsilon_y(\omega_l)} \Big|_0}_{\text{linear response of the wavefunction}} \Big| \hat{V}_x \Big| \Psi_0 \right\rangle + \left\langle \frac{\partial \tilde{\Psi}(\boldsymbol{\varepsilon}, t)}{\partial \varepsilon_y(\omega_l)} \Big|_0 \Big| \hat{V}_x \Big| \Psi_0 \right\rangle^* \right] dt$$

↓

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:

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

Wavefunction parameterization

- **Double-exponential** parameterization of a trial wavefunction:

$$|\Psi(t)\rangle = e^{i\hat{\kappa}(t)} e^{i\hat{S}(t)} |\Psi_0\rangle$$

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

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

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

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

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

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

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

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

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

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

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

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

Response properties from adiabatic TD-DFT

- The **MCSCF parameterization** enables also to derive **multiconfiguration** range-separated **TD-DFT** equations: the action integral expression to be used is, in this case,

$$\mathcal{A}_{\text{adia}}^{\mu}[\Psi, \epsilon] = \int_0^T \left\langle \Psi(t) \left| \hat{T} + \hat{W}_{\text{ee}}^{\text{lr}, \mu} + \hat{V}_{\text{ne}} + \hat{\mathcal{V}}(t) - i \frac{d}{dt} \right| \Psi(t) \right\rangle dt + \int_0^T E_{\text{Hxc}}^{\text{sr}, \mu}[n_{\Psi(t)}] dt$$

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

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

Hellmann–Feynman theorem for time-dependent variational methods

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

- 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 $\mathcal{A}_{\text{var}}(\boldsymbol{\Lambda}, \boldsymbol{\varepsilon})$ in the following.

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

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

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

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

Linear response functions

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

where

$$\begin{aligned} \frac{d\mathcal{A}_{\text{var}}(\boldsymbol{\varepsilon})}{d\varepsilon_x(-\omega_l)} &= \int_0^T e^{i\omega_l t} \langle \Psi(t) | \hat{V}_x | \Psi(t) \rangle dt \\ &= \int_0^T e^{i\omega_l t} \langle \Psi_0 | e^{-i\hat{S}(t)} e^{-i\hat{\kappa}(t)} \hat{V}_x e^{i\hat{\kappa}(t)} e^{i\hat{S}(t)} | \Psi_0 \rangle dt \end{aligned}$$

thus leading to

$$\begin{aligned} \frac{d\mathcal{A}_{\text{var}}(\boldsymbol{\varepsilon})}{d\varepsilon_x(-\omega_l)} &= \int_0^T e^{i\omega_l t} \left[\langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle + i \langle \Psi_0 | [\hat{V}_x, \hat{\kappa}(t)] | \Psi_0 \rangle + i \langle \Psi_0 | [\hat{V}_x, \hat{S}(t)] | \Psi_0 \rangle + \dots \right] dt \\ &= T\delta(\omega_l) \langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle + iT V_x^{[1]\dagger} \boldsymbol{\Lambda}(\omega_l) + \dots \end{aligned}$$

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:

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

We now need to derive the linear response equation that is fulfilled by the linear response vector

$$\mathbf{X}_y(\omega_l) = \left. \frac{\partial \mathbf{\Lambda}(\omega_l)}{\partial \varepsilon_y(\omega_l)} \right|_0.$$

Linear response equation

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

where

$$\mathcal{A}_{\text{var}}[\boldsymbol{\Lambda}, \boldsymbol{\varepsilon}]$$

||

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

Linear response equation

$$\bullet \mathcal{A}_{\hat{y}}[\boldsymbol{\Lambda}, \boldsymbol{\varepsilon}] = \sum_x \sum_{k=-N}^N \sum_p \varepsilon_x(\omega_k) \left[T\delta(\omega_k) \langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle + iT\delta(\omega_k + \omega_p) \underbrace{V_x^{[1]\dagger} \boldsymbol{\Lambda}(\omega_p)} + \dots \right]$$

$$\frac{1}{2} V_x^{[1]\dagger} \boldsymbol{\Lambda}(\omega_p) - \frac{1}{2} \boldsymbol{\Lambda}^\dagger(-\omega_p) V_x^{[1]}$$

$$\rightarrow \frac{d}{d\varepsilon_y(\omega_m)} \left[\frac{\partial \mathcal{A}_{\hat{y}}(\boldsymbol{\Lambda}, \boldsymbol{\varepsilon})}{\partial \boldsymbol{\Lambda}^\dagger(-\omega_l)} \Big|_{\boldsymbol{\Lambda}=\boldsymbol{\Lambda}(\boldsymbol{\varepsilon})} \right]_0 = -\frac{iT}{2} \delta(\omega_m + \omega_l) V_y^{[1]}$$

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

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

Linear response equation

- Using

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

leads to

$$\begin{aligned} \mathcal{A}_{d/dt} [\mathbf{\Lambda}] &= \int_0^T \left\langle \Psi_0 \left| \frac{d\hat{\kappa}(t)}{dt} + \frac{d\hat{S}(t)}{dt} \right| \Psi_0 \right\rangle dt \\ &+ i \int_0^T \left\langle \Psi_0 \left| \frac{1}{2} \left[\frac{d\hat{\kappa}(t)}{dt}, \hat{\kappa}(t) \right] + \frac{1}{2} \left[\frac{d\hat{S}(t)}{dt}, \hat{S}(t) \right] + \left[\frac{d\hat{\kappa}(t)}{dt}, \hat{S}(t) \right] \right| \Psi_0 \right\rangle dt + \dots \end{aligned}$$

$$\rightarrow \frac{d}{d\varepsilon_y(\omega_m)} \left[\frac{\partial \mathcal{A}_{d/dt} [\mathbf{\Lambda}]}{\partial \mathbf{\Lambda}^\dagger(-\omega_l)} \Big|_{\mathbf{\Lambda}=\mathbf{\Lambda}(\varepsilon)} \right]_0 = \frac{T}{2} \omega_l S^{[2]} \frac{\partial \mathbf{\Lambda}(-\omega_l)}{\partial \varepsilon_y(\omega_m)} \Big|_0$$

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

$$\mathcal{A}_{\hat{\mathcal{H}}}[\mathbf{\Lambda}] = \int_0^T \langle \Psi_0 | \hat{\mathcal{H}} + i [\hat{\mathcal{H}}, \hat{\kappa}(t)] + i [\hat{\mathcal{H}}, \hat{S}(t)] | \Psi_0 \rangle dt$$

$$- \int_0^T \langle \Psi_0 | \frac{1}{2} [[\hat{\mathcal{H}}, \hat{\kappa}(t)], \hat{\kappa}(t)] + \frac{1}{2} [[\hat{\mathcal{H}}, \hat{S}(t)], \hat{S}(t)] + [[\hat{\mathcal{H}}, \hat{\kappa}(t)], \hat{S}(t)] | \Psi_0 \rangle dt + \dots$$

$$\rightarrow \frac{d}{d\varepsilon_y(\omega_m)} \left[\frac{\partial \mathcal{A}_{\hat{\mathcal{H}}}[\mathbf{\Lambda}]}{\partial \mathbf{\Lambda}^\dagger(-\omega_l)} \Big|_{\mathbf{\Lambda}=\mathbf{\Lambda}(\varepsilon)} \right]_0 = \frac{T}{2} E^{[2]} \frac{\partial \mathbf{\Lambda}(-\omega_l)}{\partial \varepsilon_y(\omega_m)} \Big|_0$$

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:

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

$$= \int_0^T dt \int d\mathbf{r} \frac{\delta \bar{E}_{\text{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r})} \frac{d}{d\varepsilon_y(\omega_m)} \left[\left. \frac{\partial n_{\Psi(t)}(\mathbf{r})}{\partial \Lambda^\dagger(-\omega_l)} \right|_{\Lambda=\Lambda(\varepsilon)} \right]_0 \quad \leftarrow \text{potential !}$$

$$+ \int_0^T dt \int d\mathbf{r}' \int d\mathbf{r} \frac{\delta^2 \bar{E}_{\text{Hxc}}[n_{\Psi_0}]}{\delta n(\mathbf{r}') \delta n(\mathbf{r})} \left. \frac{\partial n_{\Psi(t)}(\mathbf{r})}{\partial \Lambda^\dagger(-\omega_l)} \right|_0 \left. \frac{\partial n_{\Psi(t)}(\mathbf{r}')}{\partial \varepsilon_y(\omega_m)} \right|_0 \quad \leftarrow \text{kernel !}$$

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

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

Linear response equation

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

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

the "kernel" contribution can be rewritten as follows,

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

\bar{K}_{Hxc}

← 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

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

thus leading to

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

and

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

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

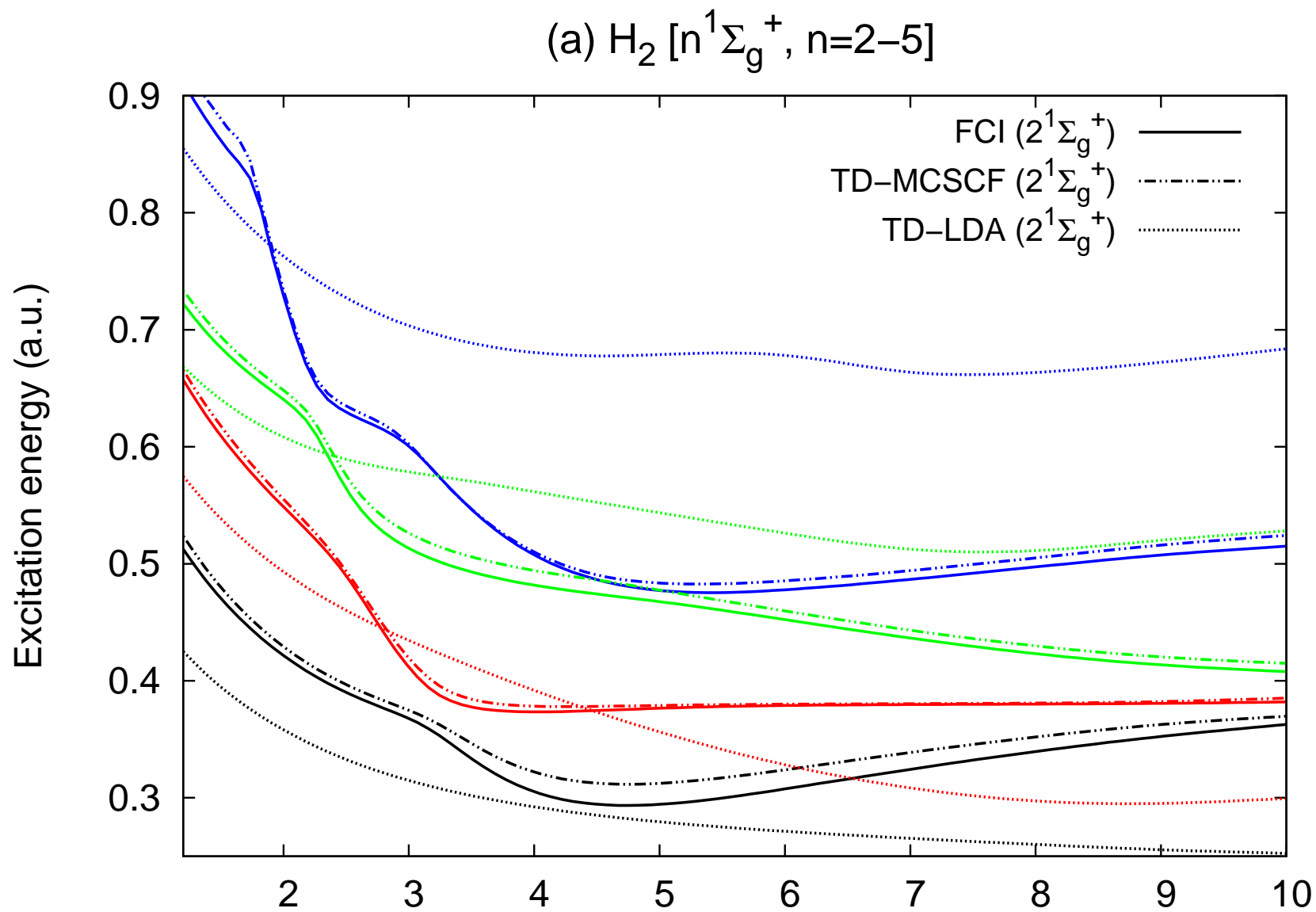
$$\langle\langle \hat{V}_x; \hat{V}_y \rangle\rangle_\omega = - \sum_{i>0} \left(\frac{\langle \Psi_0 | \hat{V}_x | \Psi_i \rangle \langle \Psi_i | \hat{V}_y | \Psi_0 \rangle}{E_i - E_0 - \omega} + \frac{\langle \Psi_i | \hat{V}_x | \Psi_0 \rangle \langle \Psi_0 | \hat{V}_y | \Psi_i \rangle}{E_i - E_0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

(4) Using real algebra and the formula $\int_0^{+\infty} \frac{a}{a^2 + \omega^2} d\omega = \frac{\pi}{2}$, prove the **fluctuation dissipation theorem**

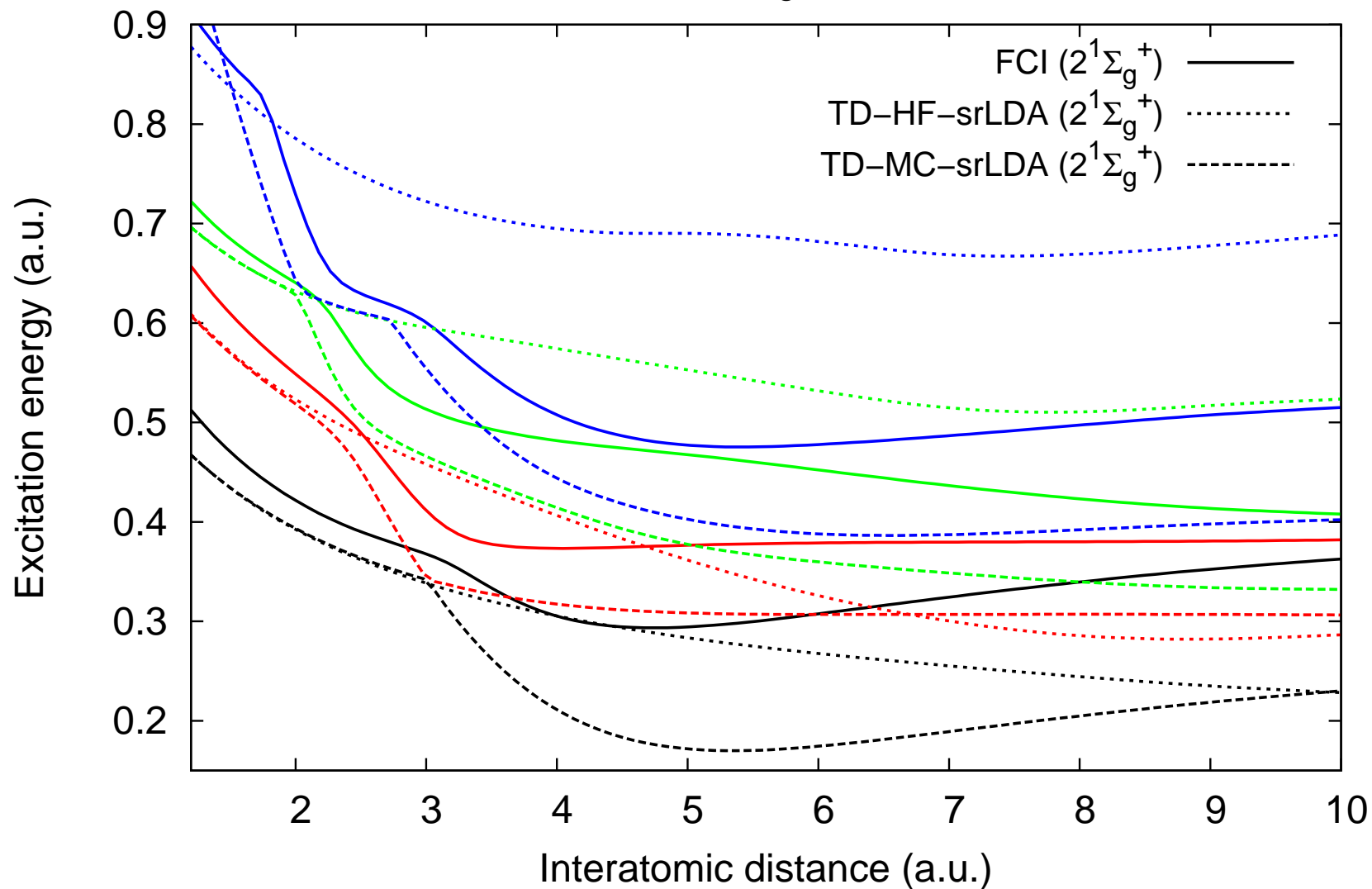
$$\langle \Psi_0 | \hat{V}_x \hat{V}_y | \Psi_0 \rangle - \langle \Psi_0 | \hat{V}_x | \Psi_0 \rangle \langle \Psi_0 | \hat{V}_y | \Psi_0 \rangle = -\frac{1}{\pi} \int_0^{+\infty} \langle\langle \hat{V}_x; \hat{V}_y \rangle\rangle_{i\omega}$$

(5) The so-called "response function" is defined in Physics as $\chi(\mathbf{r}, \mathbf{r}', \omega) = \langle\langle \hat{n}(\mathbf{r}); \hat{n}(\mathbf{r}') \rangle\rangle_\omega$. Conclude that

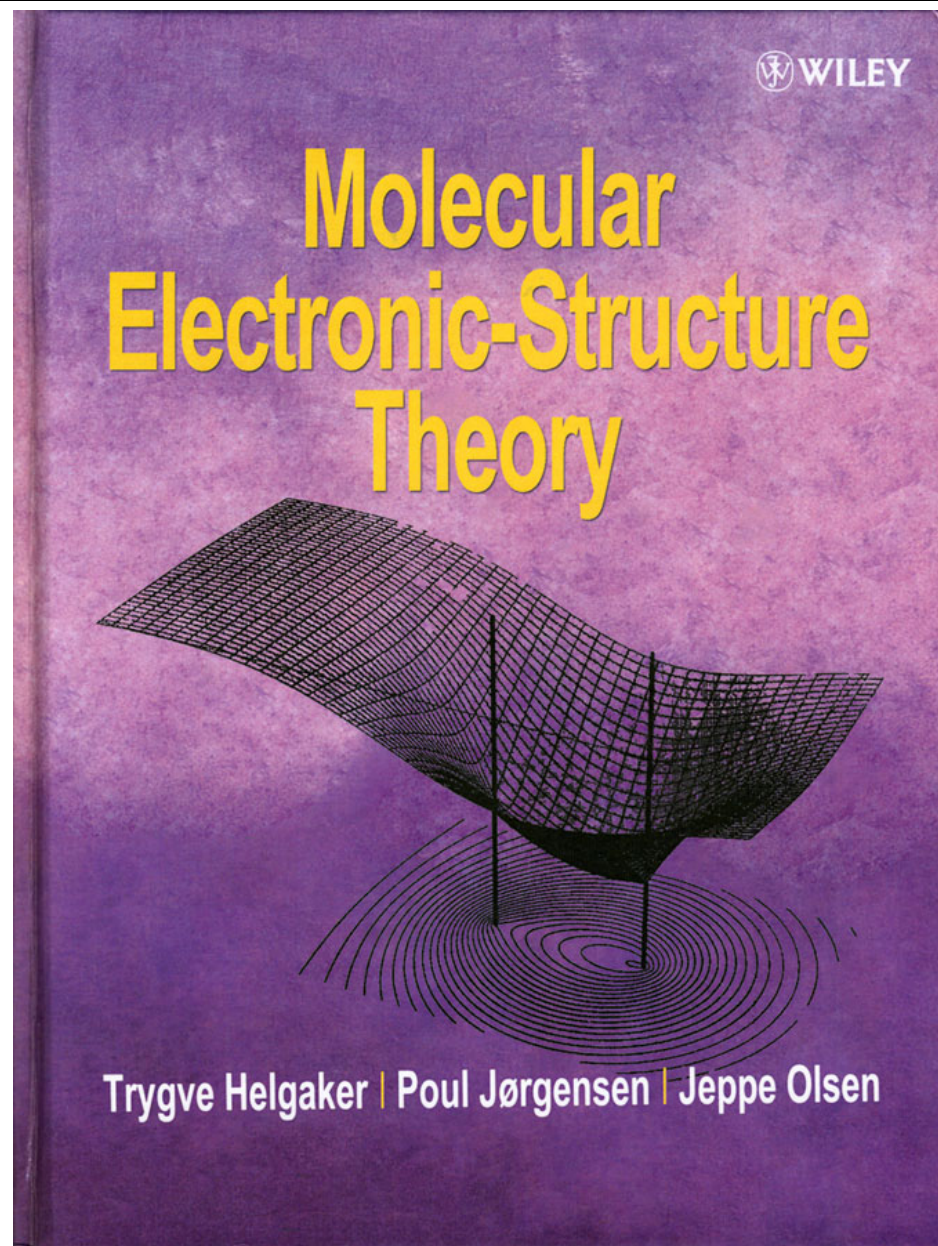
$$\langle \Psi_0 | \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') | \Psi_0 \rangle - n_0(\mathbf{r}) n_0(\mathbf{r}') = -\frac{1}{\pi} \int_0^{+\infty} \chi(\mathbf{r}, \mathbf{r}', i\omega)$$



(b) $H_2 [n^1\Sigma_g^+, n=2-5]$



E. Fromager, S. Knecht and H. J. Aa. Jensen, *J. Chem. Phys.* **138**, 084101 (2013)



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