

Calculation of molecular properties by response theory

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Books:

- ▶ Roy McWeeny, *Methods of Molecular Quantum Mechanics*, Academic Press, 1992.
- ▶ Stephan Sauer, *Molecular Electromagnetism: A Computational Chemistry*, Oxford Graduate Texts, 2011.
- ▶ Patrick Norman, Kenneth Ruud, Trond Saue, *Principles and Practices of Molecular Properties: Theory, Modeling and Simulations*, Wiley, 2018.

Review articles:

- ▶ M. Casida, *Time-dependent density-functional theory for molecules and molecular solids*, Journal of Molecular Structure: THEOCHEM 914, 3, 2009.
- ▶ T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen, K. Ruud, *Recent Advances in Wave Function-Based Methods of Molecular-Property Calculations*, Chemical Review 112, 543, 2012.

My lecture notes:

www.lct.jussieu.fr/pagesperso/toulouse/enseignement/molecular_properties.pdf

- 1 Static molecular properties
 - Definition and examples
 - General static response theory
 - Linear response HF and DFT

- 2 Dynamic molecular properties
 - Definition from the quasi-energy
 - Polarizability from dynamic response theory
 - Linear response TDHF and TDDFT

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Definition of static molecular properties

- Consider the isolated **molecular Hamiltonian** $\hat{H}_0 = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}$ and apply a **static perturbation** $\hat{V}(x)$

$$\hat{H}(x) = \hat{H}_0 + \hat{V}(x)$$

where x represents the strength of the perturbation. The perturbation vanishes for $x = 0$, i.e. $\hat{V}(x = 0) = 0$

- The **perturbed energy** for the perturbed state considered $\Psi(x)$ (usually the ground state) can be expanded with respect to x

$$\mathcal{E}(x) = \frac{\langle \Psi(x) | \hat{H}(x) | \Psi(x) \rangle}{\langle \Psi(x) | \Psi(x) \rangle} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)}x + \frac{1}{2}\mathcal{E}^{(2)}x^2 + \dots$$

where $\mathcal{E}^{(0)}$ is the unperturbed energy and the **energy derivatives with respect to x**

$$\mathcal{E}^{(1)} = \left. \frac{d\mathcal{E}}{dx} \right|_{x=0}; \quad \mathcal{E}^{(2)} = \left. \frac{d^2\mathcal{E}}{dx^2} \right|_{x=0}; \quad \text{etc...}$$

are called **static (or time-independent) molecular properties**

Examples of static molecular properties

- ▶ **Geometrical derivatives:** perturbation strengths x are the variations of the nuclei positions $R_i - R_i^0$ (in the Born-Oppenheimer approximation). For example, the **molecular gradient and Hessian** are

$$\frac{\partial \mathcal{E}}{\partial R_i}$$

and

$$\frac{\partial^2 \mathcal{E}}{\partial R_i \partial R_j}$$

which are needed for geometry optimization and calculating harmonic vibrational frequencies

- ▶ **Electric properties:** perturbation strengths x are the components of the external static electric field E_i . For example, the **electric dipole moment and polarizability** are

$$\left. \frac{\partial \mathcal{E}}{\partial E_i} \right|_{\mathbf{E}=0} = -\mu_i$$

and

$$\left. \frac{\partial^2 \mathcal{E}}{\partial E_i \partial E_j} \right|_{\mathbf{E}=0} = -\alpha_{i,j}$$

- ▶ **NMR magnetic properties:** perturbation strengths x are the nuclear magnetic dipole moments m_a and the external magnetic field B . For example, the **NMR shielding constants and spin-spin coupling constants** are

$$\frac{\partial^2 \mathcal{E}}{\partial m_a \partial B} = -1 + \sigma_a$$

and

$$\frac{\partial^2 \mathcal{E}}{\partial m_a \partial m_b} = J_{a,b}$$

Similarly, we could define **EPR hyperfine coupling constants and g values**

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There are two ways of calculating energy derivatives:

- ▶ **Numerical differentiation:** the derivatives are calculated by finite differences or by polynomial fitting
 - It is simple to implement.
 - The numerical precision is limited.
 - The computational efficiency is low.
 - It is not general. Usually, only real-valued and static perturbations can be done.
- ▶ **Analytical differentiation:** the derivatives are calculated explicitly from the analytical expressions
 - It is difficult to implement.
 - The precision is higher.
 - The computational efficiency is higher.
 - It is more general. In particular, time-dependent perturbations are possible.

⇒ Overall, analytical differentiation is preferable

- ▶ For “exact” wave functions (full configuration interaction in a basis), we can use straightforward **perturbation theory** to find the expression of the energy derivatives
- ▶ For example, for a perturbation linear in x ,

$$\hat{H}(x) = \hat{H}_0 + x\hat{V}$$

the **first-order energy derivative** is

$$\mathcal{E}^{(1)} = \langle \Psi_0 | \hat{V} | \Psi_0 \rangle$$

and the **second-order energy derivative** is

$$\mathcal{E}^{(2)} = -2 \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V} | \Psi_n \rangle \langle \Psi_n | \hat{V} | \Psi_0 \rangle}{\mathcal{E}_n - \mathcal{E}_0}$$

where $\{\Psi_n\}$ and $\{\mathcal{E}_n\}$ are the eigenstates and eigenvalues of the unperturbed Hamiltonian $\hat{H}_0$

- ▶ However, these expressions cannot be applied for methods like HF or KS DFT
 $\implies$ we need a more **general response theory**

- In an electronic-structure method, the **energy** $\mathcal{E}(x)$ is obtained by optimizing parameters $\mathbf{p} = (p_1, p_2, \dots)$ in an **energy function** $E(x, \mathbf{p})$ for each fixed value of x . The energy is thus

$$\mathcal{E}(x) = E(x, \mathbf{p}^\circ(x))$$

where $\mathbf{p}^\circ(x)$ are the optimal values of the parameters

Note that the optimization is not necessarily variational!

- Examples:

- HF and KS DFT: $\mathbf{p}$ are the orbital parameters (variational)
- MCSCF: $\mathbf{p}$ are the coefficients of the configurations (variational) and the orbital parameters (variational)
- CI: $\mathbf{p}$ are the coefficients of the configurations (variational) and the orbital parameters (non variational)
- CC: $\mathbf{p}$ are the cluster amplitudes (non variational) and the orbital parameters (non variational)

General static response theory (2/3)

- ▶ The **first-order derivative** of $\mathcal{E}(x)$ with respect to x is

$$\frac{d\mathcal{E}(x)}{dx} = \underbrace{\frac{\partial E(x, \mathbf{p}^o)}{\partial x}}_{\text{explicit dependence on } x} + \underbrace{\sum_i \frac{\partial E(x, \mathbf{p})}{\partial p_i} \bigg|_{\mathbf{p}=\mathbf{p}^o} \frac{\partial p_i^o}{\partial x}}_{\text{implicit dependence on } x}$$

- ▶ $\partial p_i^o / \partial x$ is called the **linear-response vector** and contains information about how the wave function changes when the system is perturbed. It is not straightforward to calculate it since we do not know explicitly the dependence of p_i^o on x .
- ▶ If all the parameters are **variational**, the zero electronic gradient condition simplifies the derivative

$$\left. \frac{\partial E(x, \mathbf{p})}{\partial p_i} \right|_{\mathbf{p}=\mathbf{p}^o} = 0 \quad \Rightarrow \quad \frac{d\mathcal{E}(x)}{dx} = \frac{\partial E(x, \mathbf{p}^o)}{\partial x}$$

i.e., we do not need the linear-response vector

- ▶ If all the parameters are **variational**, the second-order derivative of $\mathcal{E}(x)$ is then

$$\frac{d^2 \mathcal{E}(x)}{dx^2} = \frac{\partial^2 E(x, \mathbf{p}^o)}{\partial x^2} + \sum_i \frac{\partial^2 E(x, \mathbf{p})}{\partial x \partial p_i} \bigg|_{\mathbf{p}=\mathbf{p}^o} \frac{\partial p_i^o}{\partial x}$$

We need now the linear-response vector $\partial p_i^o / \partial x$

- ▶ To obtain the linear-response vector $\partial p_i^o / \partial x$ when all the parameters are variational, we start from the **stationary condition** which is true for all x

$$\forall x, \left. \frac{\partial E(x, \mathbf{p})}{\partial p_i} \right|_{\mathbf{p}=\mathbf{p}^o} = 0$$

- ▶ We can thus take the derivative of this equation with respect to x

$$\left. \frac{\partial^2 E(x, \mathbf{p})}{\partial x \partial p_i} \right|_{\mathbf{p}=\mathbf{p}^o} + \sum_j \left. \frac{\partial^2 E(x, \mathbf{p})}{\partial p_i \partial p_j} \right|_{\mathbf{p}=\mathbf{p}^o} \frac{\partial p_j^o}{\partial x} = 0$$

or

$$\sum_j \left. \frac{\partial^2 E(x, \mathbf{p})}{\partial p_i \partial p_j} \right|_{\mathbf{p}=\mathbf{p}^o} \frac{\partial p_j^o}{\partial x} = - \left. \frac{\partial^2 E(x, \mathbf{p})}{\partial x \partial p_i} \right|_{\mathbf{p}=\mathbf{p}^o}$$

which are the **linear-response equations**

- This is a linear system of equations for the linear-response vector $\partial p_i^o / \partial x$
- Since we are interested in energy derivatives evaluated at $x = 0$, we need to calculate the unperturbed **electronic Hessian** $\partial^2 E(x = 0, \mathbf{p}) / \partial p_i \partial p_j$

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Linear-response HF: Coupled-perturbed Hartree-Fock (CPHF) (1/3)

- ▶ The HF single-determinant wave function is parametrized by **orbital rotation parameters** κ

$$|\Phi(\kappa)\rangle = e^{\hat{\kappa}(\kappa)}|\Phi\rangle$$

where $e^{\hat{\kappa}(\kappa)}$ performs orbital rotations and is written with the orbital excitation operator

$$\hat{\kappa}(\kappa) = \sum_a^{\text{occ}} \sum_r^{\text{vir}} \left(\kappa_{ar} \hat{c}_r^\dagger \hat{c}_a - \kappa_{ar}^* \hat{c}_a^\dagger \hat{c}_r \right)$$

For the static case, we can take real-valued orbital rotation parameters, i.e. $\kappa_{ar} = \kappa_{ar}^*$

- ▶ Without perturbation, the **HF energy function** is

$$E_{\text{HF}}(\kappa) = \frac{\langle \Phi(\kappa) | \hat{H}_0 | \Phi(\kappa) \rangle}{\langle \Phi(\kappa) | \Phi(\kappa) \rangle}$$

- ▶ For linear response theory, we need first to calculate the **HF electronic Hessian**

$$\left. \frac{\partial^2 E_{\text{HF}}(\kappa)}{\partial \kappa_{ar} \partial \kappa_{bs}} \right|_{\kappa=0} = 2 (A_{ar,bs} + B_{ar,bs})$$

where

$$A_{ar,bs} = (\varepsilon_r - \varepsilon_a) \delta_{ab} \delta_{rs} + \langle rb|as \rangle - \langle rb|sa \rangle$$

and

$$B_{ar,bs} = \langle rs|ab \rangle - \langle rs|ba \rangle$$

where ε_k are the HF spin orbital energies and $\langle rb|as \rangle$ are the two-electron Coulomb integrals over the HF spin orbitals

- ▶ We consider the perturbation by a static electric field $\mathbf{E}$. The **perturbed HF energy** is

$$E_{\text{HF}}(\mathbf{E}, \kappa) = \frac{\langle \Phi(\kappa) | \hat{H}_0 - \hat{\mu} \cdot \mathbf{E} | \Phi(\kappa) \rangle}{\langle \Phi(\kappa) | \Phi(\kappa) \rangle}$$

where $\hat{\mu}$ is the dipole moment operator

- ▶ The **CPHF electric dipole polarizability** is

$$\alpha_{i,j}^{\text{CPHF}} = - \left. \frac{\partial^2 \mathcal{E}_{\text{HF}}}{\partial E_i \partial E_j} \right|_{\mathbf{E}=0} = - \left[\frac{\partial^2 E_{\text{HF}}}{\partial E_i \partial E_j} + \sum_a^{\text{occ}} \sum_r^{\text{vir}} \left. \frac{\partial^2 E_{\text{HF}}}{\partial E_i \partial \kappa_{ar}} \right|_{\kappa=0} \frac{\partial \kappa_{ar}}{\partial E_j} \right]$$

- ▶ Since the explicit dependence of $E_{\text{HF}}(\mathbf{E}, \kappa)$ on $\mathbf{E}$ is linear, we have $\partial^2 E_{\text{HF}} / \partial E_i \partial E_j = 0$

- ▶ The **HF perturbed electronic gradient** is

$$\left. \frac{\partial^2 E_{\text{HF}}}{\partial E_i \partial \kappa_{ar}} \right|_{\kappa=0} = -2 \langle r | \hat{\mu}_i | a \rangle$$

where $\langle r | \hat{\mu}_i | a \rangle$ are the transition dipole moment one-electron integrals

- ▶ The **CPHF polarizability** is thus

$$\alpha_{ij}^{\text{CPHF}} = \sum_a^{\text{occ}} \sum_r^{\text{vir}} 2 \langle r | \hat{\mu}_i | a \rangle \frac{\partial \kappa_{ar}}{\partial E_j}$$

- ▶ The linear-response vector $\partial \kappa_{ar} / \partial E_j$ is obtained from the **HF linear-response equations**

$$\sum_b^{\text{occ}} \sum_s^{\text{vir}} (A_{ar,bs} + B_{ar,bs}) \frac{\partial \kappa_{bs}}{\partial E_j} = \langle r | \hat{\mu}_j | a \rangle$$

- ▶ In vector/matrix notations, we obtain finally

$$\alpha_{ij}^{\text{CPHF}} = 2 \boldsymbol{\mu}_i^{\text{T}} (\mathbf{A} + \mathbf{B})^{-1} \boldsymbol{\mu}_j$$

where $\boldsymbol{\mu}_i$ is the vector of components $\mu_{i,ar} = \langle r | \hat{\mu}_i | a \rangle$ and $\mathbf{A} + \mathbf{B}$ is the matrix of elements $A_{ar,bs} + B_{ar,bs}$

- ▶ The **KS-DFT energy function** is

$$E_{\text{KS-DFT}}(\kappa) = \frac{\langle \Phi(\kappa) | \hat{T} + \hat{V}_{\text{ne}} | \Phi(\kappa) \rangle}{\langle \Phi(\kappa) | \Phi(\kappa) \rangle} + E_{\text{H}}[\rho_{\Phi(\kappa)}] + E_{\text{xc}}[\rho_{\Phi(\kappa)}]$$

where $E_{\text{H}}[\rho]$ is the Hartree density functional and $E_{\text{xc}}[\rho]$ is the exchange-correlation density functional

- ▶ The **KS-DFT electronic Hessian** has a similar expression as in HF

$$\left. \frac{\partial^2 E_{\text{KS-DFT}}(\kappa)}{\partial \kappa_{ar} \partial \kappa_{bs}} \right|_{\kappa=0} = 2(A_{ar,bs} + B_{ar,bs})$$

where

$$A_{ar,bs} = (\varepsilon_r - \varepsilon_a) \delta_{ab} \delta_{rs} + \langle rb | as \rangle + \langle rb | f_{\text{xc}} | as \rangle \quad \text{and} \quad B_{ar,bs} = \langle rs | ab \rangle + \langle rs | f_{\text{xc}} | ab \rangle$$

where ε_k are the KS spin orbital energies, $\langle rb | as \rangle$ are the two-electron Coulomb integrals over the KS spin orbitals, and $\langle rb | f_{\text{xc}} | as \rangle$ are the two-electron integrals over the **exchange-correlation kernel** $f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) = \delta^2 E_{\text{xc}}[\rho] / \delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)$

- ▶ All the rest is identical to CPHF

Example of calculations of polarizabilities

- ▶ If we neglect electron-electron interaction, we have $A_{ar,bs} = (\epsilon_r - \epsilon_a) \delta_{ab} \delta_{rs}$ and $B_{ar,bs} = 0$, and we obtain **uncoupled Hartree-Fock (UCHF)** or **uncoupled Kohn-Sham (UCKS)** polarizabilities

$$\alpha_{i,j}^{\text{UCHF/UCKS}} = 2 \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{\langle r | \hat{\mu}_i | a \rangle \langle a | \hat{\mu}_j | r \rangle}{\epsilon_r - \epsilon_a}$$

- ▶ Spherically averaged polarizabilities of atoms at the UCHF/CPHF and UCKS/CPKS levels (LDA functional, uncontracted d-aug-cc-pCV5Z basis sets):

	UCHF	CPHF	UCKS	CPKS	Estimated exact
He	1.00	1.32	1.81	1.66	1.38
Ne	1.98	2.38	3.48	3.05	2.67
Ar	10.1	10.8	18.0	12.0	11.1
Kr	15.9	16.5	27.8	18.0	16.8
Be	30.6	45.6	80.6	43.8	37.8
Mg	55.2	81.6	122	71.4	71.3
Ca	125	185	277	149	157

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Time-dependent Schrödinger equation and quasi-energy

- ▶ We consider now a **periodic time-dependent perturbation**

$$\hat{H}(t) = \hat{H}_0 + x^+ \hat{V} e^{-i\omega t} + x^- \hat{V}^\dagger e^{+i\omega t}$$

where x^+ and x^- represent the perturbation strengths (ultimately $x^+ = x^-$)

- ▶ The associated wave function $|\bar{\Psi}(t)\rangle$ satisfies the time-dependent Schrödinger equation

$$\left[\hat{H}(t) - i \frac{\partial}{\partial t} \right] |\bar{\Psi}(t)\rangle = 0$$

After extracting a phase factor, $|\bar{\Psi}(t)\rangle = e^{-i\mathcal{F}(t)} |\Psi(t)\rangle$, it can be reformulated as

$$\left[\hat{H}(t) - i \frac{\partial}{\partial t} \right] |\Psi(t)\rangle = \dot{\mathcal{F}}(t) |\Psi(t)\rangle \quad (1)$$

where $\dot{\mathcal{F}}(t) = d\mathcal{F}/dt$ is the **time-dependent quasi-energy**.

- ▶ The **quasi-energy** $\mathcal{Q}$ is defined as the time average of $\dot{\mathcal{F}}(t)$ over a period $T = 2\pi/\omega$:

$$\mathcal{Q} = \frac{1}{T} \int_0^T dt \dot{\mathcal{F}}(t) = \frac{1}{T} \int_0^T dt \frac{\langle \Psi(t) | \left[\hat{H}(t) - i \frac{\partial}{\partial t} \right] | \Psi(t) \rangle}{\langle \Psi(t) | \Psi(t) \rangle}$$

It satisfies a **stationary principle** similar to the time-independent one:

$$\delta_{\Psi(t)} \mathcal{Q} = 0 \iff \Psi(t) \text{ is a solution to (1)}$$

Definition of dynamic molecular properties

- ▶ The quasi-energy can be expanded with respect to the perturbation strengths x^+ and x^- :

$$Q = Q^{(0)} + Q^{(10)}x^+ + Q^{(01)}x^- + \frac{1}{2}Q^{(20)}x^{+2} + Q^{(11)}x^+x^- + \frac{1}{2}Q^{(02)}x^{-2} + \dots$$

where $Q^{(0)} = \mathcal{E}^{(0)}$ is the unperturbed energy and the quasi-energy derivatives

$$Q^{(10)} = \left. \frac{\partial Q}{\partial x^+} \right|_{x=0}; \quad Q^{(01)} = \left. \frac{\partial Q}{\partial x^-} \right|_{x=0}; \quad Q^{(20)} = \left. \frac{\partial^2 Q}{\partial x^{+2}} \right|_{x=0}; \quad Q^{(11)} = \left. 2 \frac{\partial^2 Q}{\partial x^+ \partial x^-} \right|_{x=0}; \quad \text{etc...}$$

are ω -**dependent dynamic molecular properties**

- ▶ We will consider the specific case of the **electric dipole interaction perturbation**

$$\hat{H}(t) = \hat{H}_0 - \mathbf{E}^+ \cdot \hat{\boldsymbol{\mu}} e^{-i\omega t} - \mathbf{E}^- \cdot \hat{\boldsymbol{\mu}} e^{+i\omega t}$$

where $\hat{\boldsymbol{\mu}}$ is the dipole moment operator and $\mathbf{E}^+ = \mathbf{E}^-$ is the amplitude of the oscillating electric field. The **dynamic electric dipole polarizability** is defined as:

$$\alpha_{i,j}(\omega) = - \left. \frac{\partial^2 Q}{\partial E_i^- \partial E_j^+} \right|_{\mathbf{E}=0}$$

- ▶ Using time-dependent perturbation theory, we obtain the exact expression:

$$\alpha_{i,j}(\omega) = - \left[\sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{\mu}_i | \Psi_n \rangle \langle \Psi_n | \hat{\mu}_j | \Psi_0 \rangle}{\omega - \omega_n} - \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{\mu}_j | \Psi_n \rangle \langle \Psi_n | \hat{\mu}_i | \Psi_0 \rangle}{\omega + \omega_n} \right]$$

where $\{\Psi_n\}$ are the states of $\hat{H}_0$ and $\{\omega_n\}$ are the **excitation energies**

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- ▶ In a time-dependent electronic-structure method, the quasi-energy $\mathcal{Q}(\mathbf{E}^+, \mathbf{E}^-)$ is obtained by plugging optimal parameters $\mathbf{p}^o(\mathbf{E}^+, \mathbf{E}^-)$ in a quasi-energy function $Q(\mathbf{E}^+, \mathbf{E}^-; \mathbf{p})$

$$\mathcal{Q}(\mathbf{E}^+, \mathbf{E}^-) = Q(\mathbf{E}^+, \mathbf{E}^-; \mathbf{p}^o(\mathbf{E}^+, \mathbf{E}^-))$$

- ▶ In contrast to the static case, the parameters now depend on time and take complex values. They can be decomposed in Fourier modes

$$\mathbf{p} = \mathbf{p}^+ e^{-i\omega t} + \mathbf{p}^{-*} e^{+i\omega t}$$

- ▶ We will consider only the case where all the parameters are **variational**, i.e. fulfilling the stationary conditions

$$\left. \frac{\partial Q}{\partial \mathbf{p}^{+*}} \right|_{\mathbf{p}=\mathbf{p}^o} = 0 \quad \text{and} \quad \left. \frac{\partial Q}{\partial \mathbf{p}^{-*}} \right|_{\mathbf{p}=\mathbf{p}^o} = 0$$

Polarizability from dynamic response theory (2/2)

- Thanks to the stationarity of the parameters, only the explicit dependence on $\mathbf{E}^+$, $\mathbf{E}^-$ in Q contributes for first-order properties:

$$\frac{\partial Q}{\partial E_i^-} = \frac{\partial Q}{\partial E_i^-} + \underbrace{\left[\frac{\partial Q}{\partial \mathbf{p}^+} \frac{\partial \mathbf{p}^+}{\partial E_i^-} + \frac{\partial Q}{\partial \mathbf{p}^-} \frac{\partial \mathbf{p}^-}{\partial E_i^-} + \text{c.c.} \right]}_{=0}$$

- For second-order properties, the implicit dependence on $\mathbf{E}^+$, $\mathbf{E}^-$ via the parameters contributes. In particular, for the **dynamic polarizability**, we get:

$$\alpha_{i,j}(\omega) = -\frac{\partial^2 Q}{\partial E_i^- \partial E_j^+} = -\frac{\partial^2 Q}{\partial \mathbf{p}^+ \partial E_i^-} \boxed{\frac{\partial \mathbf{p}^+}{\partial E_j^+}} - \frac{\partial^2 Q}{\partial \mathbf{p}^- \partial E_i^-} \boxed{\frac{\partial \mathbf{p}^-}{\partial E_j^+}}$$

- The linear-response vector $(\partial \mathbf{p}^+ / \partial E_j^+, \partial \mathbf{p}^- / \partial E_j^+)$ is found from the **linear-response equations**:

$$\begin{pmatrix} \frac{\partial^2 Q}{\partial \mathbf{p}^{+*} \partial \mathbf{p}^+} & \frac{\partial^2 Q}{\partial \mathbf{p}^{+*} \partial \mathbf{p}^-} \\ \frac{\partial^2 Q}{\partial \mathbf{p}^{-*} \partial \mathbf{p}^+} & \frac{\partial^2 Q}{\partial \mathbf{p}^{-*} \partial \mathbf{p}^-} \end{pmatrix} \begin{pmatrix} \frac{\partial \mathbf{p}^+}{\partial E_j^+} \\ \frac{\partial \mathbf{p}^-}{\partial E_j^+} \end{pmatrix} = - \begin{pmatrix} \frac{\partial^2 Q}{\partial E_j^+ \partial \mathbf{p}^{+*}} \\ \frac{\partial^2 Q}{\partial E_j^+ \partial \mathbf{p}^{-*}} \end{pmatrix}$$

- The **dynamic polarizability** has thus the general expression:

$$\alpha_{i,j}(\omega) = \begin{pmatrix} \frac{\partial^2 Q}{\partial \mathbf{p}^+ \partial E_i^-} \\ \frac{\partial^2 Q}{\partial \mathbf{p}^- \partial E_i^-} \end{pmatrix}^T \begin{pmatrix} \frac{\partial^2 Q}{\partial \mathbf{p}^{+*} \partial \mathbf{p}^+} & \frac{\partial^2 Q}{\partial \mathbf{p}^{+*} \partial \mathbf{p}^-} \\ \frac{\partial^2 Q}{\partial \mathbf{p}^{-*} \partial \mathbf{p}^+} & \frac{\partial^2 Q}{\partial \mathbf{p}^{-*} \partial \mathbf{p}^-} \end{pmatrix}^{-1} \begin{pmatrix} \frac{\partial^2 Q}{\partial E_j^+ \partial \mathbf{p}^{+*}} \\ \frac{\partial^2 Q}{\partial E_j^+ \partial \mathbf{p}^{-*}} \end{pmatrix}$$

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Linear-response time-dependent Hartree-Fock (TDHF)

- ▶ The **TDHF quasi-energy function** is

$$Q_{\text{TDHF}}(\mathbf{E}^+, \mathbf{E}^-; \kappa) = \frac{1}{T} \int_0^T dt \frac{\langle \Phi(\kappa) | \hat{H}(t) - i \frac{\partial}{\partial t} | \Phi(\kappa) \rangle}{\langle \Phi(\kappa) | \Phi(\kappa) \rangle}$$

- ▶ After calculating all the derivatives of Q_{TDHF} with respect to the orbital rotation parameters κ_{ar} , we get the **TDHF polarizability** (for real-valued orbitals):

$$\alpha_{i,j}^{\text{TDHF}}(\omega) = \begin{pmatrix} \mu_i \\ \mu_i \end{pmatrix}^T \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1} \begin{pmatrix} \mu_j \\ \mu_j \end{pmatrix}$$

where **A** and **B** are the same matrices introduced in static response theory (i.e., CPHF)

- ▶ The **TDHF excitation energies** ω_n corresponds to the poles of $\alpha_{i,j}^{\text{TDHF}}(\omega)$ in ω (i.e., the values of ω where $\alpha_{i,j}^{\text{TDHF}}(\omega)$ diverges). They are found by solving the **pseudo-Hermitian eigenvalue equation**:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}$$

- ▶ The **oscillator strengths** can be calculated from the eigenvectors $(\mathbf{X}_n, \mathbf{Y}_n)$

$$f_n = \frac{2}{3} \omega_n \sum_i \left[(\mathbf{X}_n + \mathbf{Y}_n)^T \boldsymbol{\mu}_i \right]^2$$

Linear-response time-dependent DFT (TDDFT)

- ▶ The **TDDFT quasi-energy function** is

$$Q_{\text{TDDFT}}(\mathbf{E}^+, \mathbf{E}^-; \kappa) = \frac{1}{T} \int_0^T dt \left(\frac{\langle \Phi(\kappa) | \hat{h}(t) - i \frac{\partial}{\partial t} | \Phi(\kappa) \rangle}{\langle \Phi(\kappa) | \Phi(\kappa) \rangle} + E_{\text{H}}[\rho_{\Phi(\kappa)}] \right) + Q_{\text{xc}}[\rho_{\Phi(\kappa)}]$$

where $\hat{h}(t)$ is the one-electron Hamiltonian and $Q_{\text{xc}}[\rho]$ is the **exchange-correlation quasi-energy functional** depending on the time-dependent density $\rho : t \mapsto \rho(t)$

- ▶ In practice, we always use the **adiabatic approximation**

$$Q_{\text{xc}}[\rho] \approx \frac{1}{T} \int_0^T dt E_{\text{xc}}[\rho(t)]$$

where $E_{\text{xc}}[\rho]$ is the ground-state exchange-correlation functional (defined for a static ρ).

- ▶ We then obtain the same equations as in TDHF with the same matrices **A** and **B** as in CPKS

$$A_{ar,bs} = (\varepsilon_r - \varepsilon_a) \delta_{ab} \delta_{rs} + \langle rb | as \rangle + \langle rb | f_{\text{xc}} | as \rangle \quad \text{and} \quad B_{ar,bs} = \langle rs | ab \rangle + \langle rs | f_{\text{xc}} | ab \rangle$$

In exact TDDFT the exchange-correlation kernel f_{xc} should depend on ω , but in the adiabatic approximation it does not. This has the consequence that double or higher electronic excitations are not described

Tamm-Dancoff approximation (TDA)

- ▶ The **Tamm-Dancoff approximation (TDA)** corresponds to neglecting the matrix **B**. The TDHF or TDDFT linear-response equations then simplifies to

$$\mathbf{A} \mathbf{X}_n = \omega_n \mathbf{X}_n$$

- ▶ In TDHF, the matrix **A** corresponds to the matrix of the Hamiltonian (shifted by the HF energy) in the basis of the single-excited determinants: $A_{ar,bs} = \langle \Phi_a^r | \hat{H}_0 - E_{\text{HF}} | \Phi_b^s \rangle$. We thus recover a **configuration-interaction singles (CIS)** calculation.
- ▶ In the TDA, we obtain **excited-state wave functions** as

$$|\psi_n\rangle = \sum_a^{\text{occ}} \sum_r^{\text{vir}} X_{n,ar} |\Phi_a^r\rangle$$

where $X_{n,ar}$ is the coefficient for the single orbital excitation $a \rightarrow r$. Usually, one orbital excitation dominates over all the other orbital excitations, and this is used to “assign” the excited-state state to this orbital excitation.

Example of calculations of excitation energies

Valence and Rydberg excitation energies of the CO molecule (Sadlej+ basis set)

State	Transition	TDHF	TDHF-TDA	TDLDA	TDLDA-TDA	EOM-CCSD	Expt
Valence excitation energies (eV)							
$^3\Pi$	$5\sigma \rightarrow 2\pi^*$	5.28	5.85	5.95	6.04	6.45	6.32
$^3\Sigma^+$	$1\pi \rightarrow 2\pi^*$	6.33	7.79	8.38	8.54	8.42	8.51
$^1\Pi$	$5\sigma \rightarrow 2\pi^*$	8.80	9.08	8.18	8.42	8.76	8.51
$^3\Delta$	$1\pi \rightarrow 2\pi^*$	7.87	8.74	9.16	9.20	9.39	9.36
$^3\Sigma^-$	$1\pi \rightarrow 2\pi^*$	9.37	9.73	9.84	9.84	9.97	9.88
$^1\Sigma^-$	$1\pi \rightarrow 2\pi^*$	9.37	9.73	9.84	9.84	10.19	9.88
$^1\Delta$	$1\pi \rightarrow 2\pi^*$	9.96	10.15	10.31	10.33	10.31	10.23
$^3\Pi$	$4\sigma \rightarrow 2\pi^*$	13.05	13.31	11.40	11.43	12.49	
Rydberg excitation energies (eV)							
$^3\Sigma^+$	$5\sigma \rightarrow 6\sigma$	11.07	11.18	9.55	9.56	10.60	10.40
$^1\Sigma^+$	$5\sigma \rightarrow 6\sigma$	12.23	12.27	9.93	9.95	11.15	10.78
$^3\Sigma^+$	$5\sigma \rightarrow 7\sigma$	12.40	12.42	10.26	10.26	11.42	11.30
$^1\Sigma^+$	$5\sigma \rightarrow 7\sigma$	12.78	12.79	10.47	10.50	11.64	11.40
$^3\Pi$	$5\sigma \rightarrow 3\pi$	12.52	12.60	10.39	10.39	11.66	11.55
$^1\Pi$	$5\sigma \rightarrow 3\pi$	12.87	12.88	10.48	10.50	11.84	11.53
Ionization threshold: $-\epsilon_{\text{HOMO}}$ (eV)							
		15.11	15.11	9.12	9.12		15.58
Mean absolute deviations of excitation energies with respect to EOM-CCSD (eV)							
Valence		0.89	0.49	0.37	0.33		
Rydberg		0.93	0.97	1.21	1.19		
Total		0.91	0.69	0.73	0.70		

There are on-going efforts for improving the approximations used in linear-response TDDFT:

- ▶ **Hybrid** approximations (mixing HF exchange and DFT exchange) and **range-separated hybrid** approximations (mixing long-range HF exchange and short-range DFT exchange) improve the description of **nonlocal excitations** (e.g., Rydberg and charge transfer)
- ▶ A number of **double-hybrid** approximations (mixing PT2 correlation and DFT correlation) for TDDFT have been proposed
- ▶ The TDDFT-like approach known as the **Bethe-Salpeter equation** (BSE), originally coming from condensed-matter physics, is increasingly applied to molecules. It is similar to TDHF but with a screened HF exchange kernel accounting for correlation
- ▶ Situations with **static/strong correlation** (bond dissociation, transition metals, conical intersection, ...) are usually a problem in TDDFT with the usual approximations. A number of approaches combining **multideterminant wave function methods** (e.g., MCSCF) with TDDFT are being developed.