Excited states in density-functional theory: time-dependent and time-independent approaches

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Electronic Hamiltonian

- The following lecture deals with the calculation of electronic excited state properties (excitation energies, oscillator strengths, ...)

- We will work within the Born–Oppenheimer approximation which means that the nuclei (indexed as A, B, C, ...) will be at fixed positions $\mathbf{R}_A$, $\mathbf{R}_B$, $\mathbf{R}_C$, ...

- Therefore the electronic Schrödinger equation reads $\boxed{\hat{H}\Psi_I = E_I\Psi_I}$,

  where $\Psi_I(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ is either the ground-state $(I = 0)$ N-electron wavefunction, that we assume to be non-degenerate in the following, or any of the excited-state N-electron wavefunctions $(I = 1, 2, 3, \ldots)$.

- The (non-relativistic) electronic Hamiltonian equals (in atomic units)

$$\hat{H} \equiv \underbrace{\sum_{i=1}^{N} -\frac{1}{2}\nabla^2_{\mathbf{r}_i}}_{\hat{T}} + \left(\underbrace{\sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{W}_{\mathrm{ee}}} + \underbrace{\sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i)}_{} \right) \times$$

with $v_{\mathrm{ne}}(\mathbf{r}) = -\sum_{A}^{\mathrm{nuclei}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$

Two (completely) different paths towards excited states: state-averaging or response theory

- Ground and excited states (up to the state of interest) can actually be determined simultaneously (all of them forming an ensemble) and variationally (Gross–Oliveira–Kohn variational principle).

- This approach is used in the so-called State-Averaged Complete Active Space Self-Consistent Field (SA-CASSCF) method where a single (state-averaged) set of molecular orbitals is used to construct all the states belonging to the ensemble of interest. It becomes the method of choice when states are nearly-degenerate.

- Note that, even though it did not draw much attention so far, an exact density-functional theory (DFT) relying on state-averaging can be formulated, thus leading to an extension of DFT to the excited states (will be discussed in the last part of the lecture).

- In most quantum chemical calculations a completely different approach is actually adopted: time-dependent linear response theory. This is what standard time-dependent DFT (TD-DFT) calculations rely on.

Time-dependent Schrödinger equation

- Time-dependent Schrödinger equation in atomic units: $\boxed{\hat{H}(t)|\Psi(t)\rangle = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle}$

  where the time-dependent Hamiltonian reads $\hat{H}(t) = \hat{H} + \hat{\mathcal{V}}(t)$.

- The unperturbed time-independent Hamiltonian is the usual electronic Hamiltonian $\hat{H} \equiv \hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i)\times$

- In the following, the time-dependent perturbation operator $\hat{\mathcal{V}}(t)$ is an arbitrary linear hermitian operator that does not contain any derivatives with respect to time.
- Example: in classical mechanics, the force applied to an electron at position $\mathbf{r} \equiv (x, y, z)$ in the presence of a dynamical electric field $\boldsymbol{E}(\mathbf{r}, t)$ equals (in a.u.)

$$\mathbf{F}(\mathbf{r}, t) = -\boldsymbol{E}(\mathbf{r}, t).$$

- If the electric field is uniform and along the z axis, $\boldsymbol{E}(\mathbf{r}, t) = \mathcal{E}(t)\mathbf{e_z}$, then the potential interaction energy equals $\boxed{V(\mathbf{r}, t) = \mathcal{E}(t)z}$. Indeed, one can see that

$$\mathbf{F}(\mathbf{r}, t) = -\boldsymbol{\nabla} V(\mathbf{r}, t) = -\mathcal{E}(t)\mathbf{e_z}.$$

Time-dependent Schrödinger equation

- Therefore, for N electrons, the potential energy that describes the interaction with the uniform electric field can be expressed as

$$\mathcal{V}(t) = \mathcal{E}(t) \sum_{i=1}^{N} z_i,$$

which leads, in quantum mechanics, to the operator

$$\hat{\mathcal{V}}(t) = \mathcal{E}(t)\hat{\mathcal{V}} \qquad \text{where} \qquad \hat{\mathcal{V}} \equiv \sum_{i=1}^{N} z_i \times .$$

- Note that, in the presence of an electric field, $\hat{\mathcal{V}}(t)$ is a time-dependent local potential (*i.e.* multiplicative) operator that will be denoted as follows later on,

$$\hat{\mathcal{V}}(t) \rightarrow \sum_{i=1}^{N} \mathcal{V}(\mathbf{r}_i, t)\times$$

- It should therefore be possible to describe the interaction between a time-dependent electric field and electrons in a time-dependent extension of DFT (this will be discussed after the "exact response theory" part).

Time-dependent Schrödinger equation

- If the electronic wave function is normalized at the initial time $t = 0$ then it remains normalized at any time $t > 0$. Indeed,

$$\frac{\mathrm{d}\langle\Psi(t)|\Psi(t)\rangle}{\mathrm{d}t} = -\frac{1}{\mathrm{i}}\langle\hat{H}(t)\Psi(t)|\Psi(t)\rangle + \frac{1}{\mathrm{i}}\langle\Psi(t)|\hat{H}(t)|\Psi(t)\rangle = 0.$$

- Adding a real multiplicative time-dependent function $\mathcal{Q}(t)$ to the time-dependent perturbation operator $\hat{\mathcal{V}}(t)$ is equivalent to multiplying the wavefunction by a phase factor:

$$\left(\hat{H}(t) + \mathcal{Q}(t)\times\right)|\Psi_{\mathcal{Q}}(t)\rangle = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi_{\mathcal{Q}}(t)\rangle \quad\Leftrightarrow\quad \hat{H}(t)|\Psi(t)\rangle = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle$$

where

$$\boxed{|\Psi_{\mathcal{Q}}(t)\rangle = e^{-\mathrm{i}\int_0^t \mathcal{Q}(\tau)\mathrm{d}\tau} \times |\Psi(t)\rangle}.$$

- Consequently, for any observable A,

$$\langle\Psi_{\mathcal{Q}}(t)|\hat{A}|\Psi_{\mathcal{Q}}(t)\rangle = e^{+\mathrm{i}\int_0^t \mathcal{Q}(\tau)\mathrm{d}\tau}e^{-\mathrm{i}\int_0^t \mathcal{Q}(\tau)\mathrm{d}\tau}\langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \langle\Psi(t)|\hat{A}|\Psi(t)\rangle.$$

Time-dependent Schrödinger equation

- In particular, the N-electron density is not affected by a time-dependent shift in the local potential $\mathcal{V}(\mathbf{r},t) \rightarrow \mathcal{V}(\mathbf{r},t) + C(t)$. Indeed, in the latter case, $\mathcal{Q}(t) = NC(t)$.

- In case of a periodic uniform electric field with frequency ω and strength ϵ,

$$\mathcal{E}(t) = 2\epsilon\cos(\omega t) = \epsilon\left(e^{\mathrm{i}\omega t} + e^{-\mathrm{i}\omega t}\right),$$

  so that the time-dependent perturbation operator reads

$$\hat{\mathcal{V}}(t) = 2\epsilon\cos(\omega t)\hat{\mathcal{V}}.$$

- We assume in the following that the exact ground ($i=0$) and excited ($i>0$) states of the electronic unperturbed Hamiltonian are known, hence the name exact response theory:

$$\hat{H}|\Psi_i\rangle = E_i|\Psi_i\rangle, \quad i = 0, 1, 2, \ldots$$

Linear response theory

- Let us decompose the solution to the TD Schrödinger equation (TDSE) in the (orthonormal) eigenvector basis of $\hat{H}$: $\boxed{|\Psi(t)\rangle = \sum_i \tilde{C}_i(t)|\Psi_i\rangle.}$
- We assume that the system is in the ground state at time $t = 0$: $|\Psi(0)\rangle = |\Psi_0\rangle$.
- The probability of the transition $0 \rightarrow j$ is $\mathcal{P}_j(t) = |\langle\Psi_j|\Psi(t)\rangle|^2 = |\tilde{C}_j(t)|^2$.
- It comes from the TDSE

$$\sum_i \tilde{C}_i(t)\Big(E_i + \hat{\mathcal{V}}(t)\Big)|\Psi_i\rangle = \mathrm{i}\sum_i \left[\frac{\mathrm{d}}{\mathrm{d}t}\tilde{C}_i(t)\right]|\Psi_i\rangle$$

or, by introducing $\tilde{C}_i(t) = e^{-\mathrm{i}E_i t}C_i(t)$,

$$\boxed{-2\mathrm{i}\epsilon\cos(\omega t)\sum_i e^{-\mathrm{i}(E_i - E_k)t}C_i(t)\mathcal{V}_{ki} = \frac{\mathrm{d}}{\mathrm{d}t}C_k(t)}$$

where $\mathcal{V}_{ki} = \langle\Psi_k|\hat{\mathcal{V}}|\Psi_i\rangle$.

Linear response theory

- There is no simple analytical solution since the various time-dependent coefficients $C_i(t)$ are coupled by the perturbation.

- Note that the coefficients $C_i(t)$ are functions of both time and perturbation strength ϵ.

- In response theory (also known as time-dependent perturbation theory), the perturbation is assumed to be weak enough so that the coefficients can be Taylor-expanded in ϵ:

$$C_i(t) = C_i(t)\big|_{\epsilon=0} + \epsilon \left.\frac{\partial C_i(t)}{\partial \epsilon}\right|_{\epsilon=0} + \frac{\epsilon^2}{2} \left.\frac{\partial^2 C_i(t)}{\partial \epsilon^2}\right|_{\epsilon=0} + \ldots$$

↙ unperturbed

↓ linear response

↘ quadratic response

- Inserting this expansion into the TDSE leads, through zeroth order, to

$$\left.\frac{\mathrm{d}}{\mathrm{d}t} C_k(t)\right|_{\epsilon=0} = 0 \quad \rightarrow \quad \boxed{C_k(t)\big|_{\epsilon=0} = \delta_{k0}} \quad \rightarrow \quad |\Psi(t)\rangle\big|_{\epsilon=0} = e^{-\mathrm{i}E_0 t}|\Psi_0\rangle \ .$$

Linear response theory

- We then obtain through first order,

$$-2\mathrm{i}\cos(\omega t)\sum_i e^{-\mathrm{i}(E_i-E_k)t}\, C_i(t)\big|_{\epsilon=0}\,\mathcal{V}_{ki} = \frac{\mathrm{d}}{\mathrm{d}t}\left.\frac{\partial C_k(t)}{\partial\epsilon}\right|_{\epsilon=0}$$

  thus leading to, for $j>0$ (since we are interested in transitions),

$$\frac{\mathrm{d}}{\mathrm{d}t}\left.\frac{\partial C_j(t)}{\partial\epsilon}\right|_{\epsilon=0} = -\mathrm{i}\mathcal{V}_{j0}\left[e^{\mathrm{i}(\omega+\omega_j)t}+e^{-\mathrm{i}(\omega-\omega_j)t}\right],$$

  where $\omega_j = E_j - E_0$ is the jth exact electronic excitation energy.

- Therefore, the linear response coefficients can be expressed as

$$\begin{aligned}\left.\frac{\partial C_j(t)}{\partial\epsilon}\right|_{\epsilon=0} &= \int_0^t \frac{\mathrm{d}}{\mathrm{d}\tau}\left.\frac{\partial C_j(\tau)}{\partial\epsilon}\right|_{\epsilon=0}\mathrm{d}\tau \\ &= X_j(\omega)\left[e^{\mathrm{i}(\omega+\omega_j)t}-1\right]+X_j(-\omega)\left[e^{-\mathrm{i}(\omega-\omega_j)t}-1\right]\end{aligned}$$

  where $\boxed{X_j(\omega) = -\mathcal{V}_{j0}/(\omega+\omega_j)}$.

Linear response theory

- The time dependence of the linear response (LR) coefficients is completely determined by the frequency-dependent coefficients $X_j(\omega)$.

- Note that the exact excitation energies are poles of the LR coefficients. In other words, the latter diverge when $\omega = \omega_j$ (absorption) or $\omega = -\omega_j$ (emission).

- These divergences correspond to resonances since
$$\mathcal{P}_j(t) = |C_j(t)|^2 = \epsilon^2 \left| \frac{\partial C_j(t)}{\partial \epsilon} \right|^2_{\epsilon=0} + \ldots$$

- In order to describe resonances, the use of so-called damped response theory has become increasingly popular in recent years. It consists in considering the following (more realistic) description of the electric field,
$$\mathcal{E}(t) = 2\epsilon\, e^{-\gamma t} \cos(\omega t) = \epsilon \left(e^{\mathrm{i}(\omega + \mathrm{i}\gamma)t} + e^{-\mathrm{i}(\omega - \mathrm{i}\gamma)t} \right),$$
where $\gamma > 0$ is the damping parameter. Physically, $1/\gamma$ can be interpreted as a lifetime for the pulse that is applied to the molecule.

Linear response theory

- In damped response theory, the LR coefficients become

$$\left.\frac{\partial C_j(t)}{\partial \epsilon}\right|_{\epsilon=0} \quad \rightarrow \quad X_j^{\gamma}(\omega)\left[e^{\mathrm{i}(\omega+\omega_j+\mathrm{i}\gamma)t}-1\right]+X_j^{\gamma}(-\omega)\left[e^{-\mathrm{i}(\omega-\omega_j-\mathrm{i}\gamma)t}-1\right]$$

  where $X_j^{\gamma}(\omega)=-\mathcal{V}_{j0}/(\omega+\omega_j+\mathrm{i}\gamma)$.

- Note that, at resonances, the frequency-dependent LR coefficients do not diverge anymore: $X_j^{\gamma}(-\omega_j)=\mathrm{i}\mathcal{V}_{j0}/\gamma$.

- In physics, it is common to consider an infinite lifetime as a limit which means $\gamma \rightarrow 0^+$.

- Of course, the transition is only possible if the coupling term $\mathcal{V}_{j0}$ is nonzero (transition rules).

- It is common to relate the intensity of the transition to the so-called "oscillator strength" $f_j=2\omega_j|\mathcal{V}_{j0}|^2$.

Linear response theory

- Note that, for a single electron, $[\hat{H},\hat{z}]=\dfrac{1}{2}[\hat{p}_z^2,\hat{z}]=-\mathrm{i}\hat{p}_z$ since $[\hat{p}_z,\hat{z}]=-\mathrm{i}$. Therefore,

  $$\langle\Psi_j|[\hat{H},\hat{z}]|\Psi_0\rangle=\omega_j\langle\Psi_j|\hat{z}|\Psi_0\rangle=\omega_j\mathcal{V}_{j0}=-\mathrm{i}\langle\Psi_j|\hat{p}_z|\Psi_0\rangle.$$

  By using

  $$\langle\Psi_0|[\hat{p}_z,\hat{z}]|\Psi_0\rangle=-\mathrm{i}=\sum_{j>0}\Bigg(\langle\Psi_0|\hat{p}_z|\Psi_j\rangle\langle\Psi_j|\hat{z}|\Psi_0\rangle-\langle\Psi_0|\hat{z}|\Psi_j\rangle\langle\Psi_j|\hat{p}_z|\Psi_0\rangle\Bigg),$$

  we finally obtain the sum rule $\boxed{\sum_{j>0}f_j=1}$.

- Let us return to the N-electron case. In order to calculate the linear response of the electron density, it is convenient to rewrite it as $\boxed{n_{\Psi(t)}(\mathbf{r})=\langle\Psi(t)|\hat{n}(\mathbf{r})|\Psi(t)\rangle}$

  where the density operator equals $\hat{n}(\mathbf{r})=\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\times\longleftarrow$ Dirac distribution !

Linear response theory

- The exact time-dependent density reads

$$n_{\Psi(t)}(\mathbf{r}) = \sum_{ik} \tilde{C}_k^*(t)\tilde{C}_i(t)\langle\Psi_k|\hat{n}(\mathbf{r})|\Psi_i\rangle$$

which gives through first order in ϵ,

$$\begin{aligned} n_{\Psi(t)}(\mathbf{r}) &= n_{\Psi_0}(\mathbf{r}) \\ &+\epsilon\sum_{i>0}\left(e^{\mathrm{i}\omega_i t}\left.\frac{\partial C_i(t)}{\partial\epsilon}\right|^*_{\epsilon=0}\langle\Psi_i|\hat{n}(\mathbf{r})|\Psi_0\rangle + e^{-\mathrm{i}\omega_i t}\left.\frac{\partial C_i(t)}{\partial\epsilon}\right|_{\epsilon=0}\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_i\rangle\right) \\ &+\ldots \end{aligned}$$

- **Important conclusion:** the exact excitation energies are poles of the electron density.

Linear response equation

- Let us return to standard (non damped) linear response theory. In order to explore approximate response theory (which is not discussed in this lecture), it is convenient to rewrite the exact theory in matrix form.
- We first collect all frequency-dependent LR coefficients $X_j(\omega) = -\mathcal{V}_{j0}/(\omega + \omega_j)$ into one single linear response column vector as follows,

$$\begin{bmatrix} X_1(-\omega) \\ X_2(-\omega) \\ \vdots \\ X_j(-\omega) \\ \vdots \\ X_1^*(\omega) \\ X_2^*(\omega) \\ \vdots \\ X_j^*(\omega) \\ \vdots \end{bmatrix} = \begin{bmatrix} \boldsymbol{X}(-\omega) \\ \boldsymbol{X}^*(\omega) \end{bmatrix}.$$

Linear response equation

- The linear response vector is solution of the so-called "linear response equation":

$$\left(\underbrace{\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{bmatrix}}_{\boldsymbol{E}_0^{[2]}} - \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix}\right) \begin{bmatrix} \boldsymbol{X}(-\omega) \\ \boldsymbol{X}^*(\omega) \end{bmatrix} = -\underbrace{\begin{bmatrix} \boldsymbol{\mathcal{V}} \\ \boldsymbol{\mathcal{V}}^* \end{bmatrix}}_{\boldsymbol{\mathcal{V}}^{[1]}},$$

where $\boldsymbol{\mathcal{V}}_j = \mathcal{V}_{j0} = \langle \Psi_j | \hat{\mathcal{V}} | \Psi_0 \rangle, \quad \boldsymbol{A}_{ij} = \delta_{ij}\omega_j, \quad \boldsymbol{B}_{ij} = 0.$

- $\boldsymbol{E}_0^{[2]}$ and $\boldsymbol{\mathcal{V}}^{[1]}$ are usually referred to as **energy hessian** matrix and gradient property vector, respectively.

- Indeed, if we introduce the normalized trial wavefunction

$$|\Psi(\boldsymbol{C})\rangle = \frac{|\Psi_0\rangle + \sum_{k>0} C_k |\Psi_k\rangle}{\sqrt{1 + \sum_{k>0} C_k^* C_k}} \quad \text{where } \boldsymbol{C} \equiv \{C_k\}_{k>0},$$

Linear response equation

it comes

$$A_{ij} = \frac{\partial^2}{\partial C_i^* \partial C_j} \left[\langle \Psi(\boldsymbol{C}) | \hat{H} | \Psi(\boldsymbol{C}) \rangle \right] \Big|_{\boldsymbol{C}=0}$$

$$B_{ij} = \frac{\partial^2}{\partial C_i \partial C_j} \left[\langle \Psi(\boldsymbol{C}) | \hat{H} | \Psi(\boldsymbol{C}) \rangle \right] \Big|_{\boldsymbol{C}=0}$$

$$\mathcal{V}_j = \frac{\partial}{\partial C_j^*} \left[\langle \Psi(\boldsymbol{C}) | \hat{\mathcal{V}} | \Psi(\boldsymbol{C}) \rangle \right] \Big|_{\boldsymbol{C}=0}$$

- Note that exact excitation energies are obtained by solving the generalized diagonalization problem

$$\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{bmatrix} \begin{bmatrix} \boldsymbol{Y} \\ \boldsymbol{Z} \end{bmatrix} = \Omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \boldsymbol{Y} \\ \boldsymbol{Z} \end{bmatrix},$$

whose solutions are $\Omega = \{\omega_j\}_{j=1,2,\dots}$ (absorption) and $\Omega = \{-\omega_j\}_{j=1,2,\dots}$ (emission).

- In the exact theory, the hessian matrix is diagonal. This will not be the case anymore if approximate wavefunctions (HF, CASSCF, CC, ...) are used.

Runge and Gross theorem

- Let us consider the time-dependent Hamiltonian $\hat{H}(t) = \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v(\mathbf{r}_i, t)\times$ and a fixed initial electronic wavefunction $\Psi(t=0)$.

- By varying the time-dependent local potential $v(\mathbf{r}, t)$ we obtain a map of time-dependent densities $n[v](\mathbf{r}, t) = n_{\Psi[v](t)}(\mathbf{r})$ where $\Psi[v](t)$ is the solution to the time-dependent Schrödinger equation with potential $v(\mathbf{r}, t)$ and $\Psi[v](t=0) = \Psi(t=0)$.

- If two potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ differ by a time-dependent function, then $\Psi[v](t)$ and $\Psi[v'](t)$ will have the same density at any time.

E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

Runge and Gross theorem

- According to the Runge and Gross theorem[*], the map of time-dependent densities can be inverted (up to an additive time-dependent function in the potential). This is nothing but the extension of the Hohenberg–Kohn theorem to the time-dependent regime.

- In the following, we will consider that $v(\mathbf{r},t) = v_{\rm ne}(\mathbf{r}) + \mathcal{V}(\mathbf{r},t)$ where $\mathcal{V}(\mathbf{r},t)$ is a local time-dependent perturbation.

- We will also assume that the system is in the ground state at time $t = 0$.

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[*] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

Time-dependent KS equations

- Like in the static case, the non-interacting N-electron time-dependent Schrödinger equation can be simplified into one-electron equations.

- For example, in the case of two electrons, the exact solution can be written as

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, t) = \varphi(\mathbf{r}_1, t)\varphi(\mathbf{r}_2, t)$$

  where $\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + v(\mathbf{r}, t)\right]\varphi(\mathbf{r}, t) = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\varphi(\mathbf{r}, t)$.

- The basic idea in standard TD-DFT is to make a mapping in the time-dependent regime between the real interacting (and therefore difficult to describe) system with Hamiltonian $\hat{H}(t)$ and a non-interacting system, in complete analogy with KS-DFT.

- Therefore, by solving $\left[\hat{T} + \sum_{i=1}^{N} v^{\mathrm{KS}}(\mathbf{r}, t) \times\right]\Phi^{\mathrm{KS}}(t) = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\Phi^{\mathrm{KS}}(t)$,

  where $\Phi^{\mathrm{KS}}(t)$ is a time-dependent Slater determinant, we should be able, in principle, to reproduce the exact time-dependent electron density $n(\mathbf{r}, t)$ of the molecule.

- Therefore, for two electrons, we should have $n(\mathbf{r}, t) = 2\left|\varphi^{\mathrm{KS}}(\mathbf{r}, t)\right|^2$.

Linear response regime and adiabatic approximation

- Consequently, if a time-dependent perturbation is applied to the molecule, the linear (and higher-order) response of the KS and real densities should be the same
- In particular, the poles of the KS density (which correspond to the poles of the KS orbitals), should be the exact excitation energies of true molecule (!).
- The exact time-dependent KS potential is in general unknown and difficult to model (memory effects).
- In the standard adiabatic approximation, it is simplified as follows,

$$v^{\mathrm{KS}}(\mathbf{r},t) \rightarrow v_{\mathrm{ne}}(\mathbf{r}) + \mathcal{V}(\mathbf{r},t) + \frac{\delta E_{\mathrm{Hxc}}[n_{\Phi^{\mathrm{KS}}(t)}]}{\delta n(\mathbf{r})},$$

  where $E_{\mathrm{Hxc}}[n]$ is the (time-independent) ground-state Hartree-exchange-correlation (Hxc) functional.

- Note that, within the adiabatic approximation, the KS potential is local in time (no memory effects are taken into account).

Casida equation

- Therefore, the (approximate) time-dependent KS equation to be solved for two electrons is

$$\hat{h}\left[\varphi^{\mathrm{KS}}\right](t)\left|\varphi^{\mathrm{KS}}(t)\right\rangle = \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\left|\varphi^{\mathrm{KS}}(t)\right\rangle$$

where $\hat{h}\left[\varphi^{\mathrm{KS}}\right](t) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}} + \left[v_{\mathrm{ne}}(\mathbf{r}) + \mathcal{V}(\mathbf{r},t) + \dfrac{\delta E_{\mathrm{Hxc}}\left[2\left|\varphi^{\mathrm{KS}}(\mathbf{r},t)\right|^2\right]}{\delta n(\mathbf{r})}\right]\times$

- Note that, in contrast to conventional wavefunction-based response theory, we have to solve a self-consistent time-dependent equation (time-dependent density functional perturbation theory).

- In the following, the time-dependent local potential perturbation will be written as

$$\mathcal{V}(\mathbf{r},t) = 2\epsilon\cos(\omega t)\mathcal{V}(\mathbf{r}).$$

- In the presence of a uniform electric field along the z axis, $\mathcal{V}(\mathbf{r}) = z$.

Casida equation

- Let us first consider the KS system in the absence of perturbation ($\epsilon = 0$). The time-dependent KS orbital simply reads $\varphi^{\mathrm{KS}}(\mathbf{r}, t)\Big|_{\epsilon=0} = e^{-\mathrm{i}\varepsilon_0 t}\varphi_0(\mathbf{r})$ where $\varphi_0(\mathbf{r})$ is the ground-state KS orbital with energy ε_0:

$$\underbrace{\left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + \left[v_{\mathrm{ne}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}\left[2\left|\varphi_0(\mathbf{r})\right|^2\right]}{\delta n(\mathbf{r})}\right] \times\right)}_{\hat{h}} \varphi_0(\mathbf{r}) = \varepsilon_0 \varphi_0(\mathbf{r})$$

- Consequently, in TD-DFT, the unperturbed Hamiltonian is the KS Hamiltonian $\hat{h}$.

- The perturbation in the KS system will be

$$\mathcal{V}(\mathbf{r}, t) + \frac{\delta E_{\mathrm{Hxc}}\left[2\left|\varphi^{\mathrm{KS}}(\mathbf{r}, t)\right|^2\right]}{\delta n(\mathbf{r})} - \frac{\delta E_{\mathrm{Hxc}}\left[2\left|\varphi_0(\mathbf{r})\right|^2\right]}{\delta n(\mathbf{r})}.$$

Casida equation

- In the following, we will use the ground (occupied) and excited (virtuals) KS orbitals $\{\varphi_i(\mathbf{r})\}_{i=0,1,2,\dots}$ with energies $\{\varepsilon_i\}_{i=0,1,2,\dots}$ as a basis for expanding the time-dependent KS orbital in the presence of the perturbation. Note that $\hat{h}\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$.

- By analogy with exact response theory, we therefore obtain

$$\varphi^{\mathrm{KS}}(\mathbf{r},t) = \sum_i e^{-\mathrm{i}\varepsilon_i t} C_i(t)\varphi_i(\mathbf{r}).$$

- The derivation of the linear response TD-DFT equation (known as Casida equation) requires the expansion of the Hxc potential through first order in the perturbation strength ϵ.

- By definition, the variation of the Hxc potential around a given density $n_0(\mathbf{r})$ equals, through first order in the time-dependent density variation $\delta n(\mathbf{r}',t)$,

$$\frac{\delta E_{\mathrm{Hxc}}\left[n_0+\delta n(t)\right]}{\delta n(\mathbf{r})} - \frac{\delta E_{\mathrm{Hxc}}\left[n_0\right]}{\delta n(\mathbf{r})} = \int \mathrm{d}\mathbf{r}' \underbrace{\frac{\delta^2 E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})}}_{\text{kernel ! } \leftarrow \; f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r})} \delta n(\mathbf{r}',t)$$

Mathematical interlude on functional derivatives

- Let $f : x \longmapsto f(x)$ be a function of x. The derivative of f at $x = x_0$ is obtained from the Taylor expansion (δx is a small variation of x around x_0)

$$f(x_0 + \delta x) = f(x_0) + \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} \times \delta x + \frac{1}{2}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_0} \times \delta x^2 + \ldots$$

- Let $S : n \longmapsto S[n]$ be a functional of the density n. The functional derivative of S at $n = n_0$ is by definition a function of $\mathbf{r}$ that is denoted $\dfrac{\delta S}{\delta n(\mathbf{r})}[n_0]$. The latter is obtained from the Taylor expansion [$\delta n(\mathbf{r})$ is a small variation of the density around n_0]:

$$S[n_0 + \delta n] = S[n_0] + \int \mathrm{d}\mathbf{r}\, \frac{\delta S[n_0]}{\delta n(\mathbf{r})} \times \delta n(\mathbf{r}) + \frac{1}{2}\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \frac{\delta^2 S[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} \times \delta n(\mathbf{r}')\delta n(\mathbf{r}) + \ldots$$

- Example: for the Hartree (or Coulomb) functional $E_{\mathrm{H}}[n] = \dfrac{1}{2}\displaystyle\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\,\mathbf{r} - \mathbf{r}'\,|}$,

$$\frac{\delta E_{\mathrm{H}}[n_0]}{\delta n(\mathbf{r})} = \int \mathrm{d}\mathbf{r}'\, \frac{n_0(\mathbf{r}')}{|\,\mathbf{r} - \mathbf{r}'\,|} \qquad \text{and} \qquad \frac{\delta^2 E_{\mathrm{H}}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} = \frac{1}{|\,\mathbf{r} - \mathbf{r}'\,|}$$

Casida equation

- In our case, $n_0(\mathbf{r}) = 2\left|\varphi_0(\mathbf{r})\right|^2$ and, by using $C_i(t)\big|_{\epsilon=0} = \delta_{i0}$, we obtain

$$\begin{aligned}\delta n(\mathbf{r}',t) &= 2\left|\varphi^{\mathrm{KS}}(\mathbf{r}',t)\right|^2 - 2\left|\varphi_0(\mathbf{r}')\right|^2 \\ &= 2\sum_{ij} e^{-\mathrm{i}(\varepsilon_i-\varepsilon_j)t} C_i(t)C_j^*(t)\varphi_i(\mathbf{r}')\varphi_j^*(\mathbf{r}') - 2\left|\varphi_0(\mathbf{r}')\right|^2 \\ &= 2\epsilon\sum_{i>0}\left(e^{-\mathrm{i}\Delta\varepsilon_i t}\left.\frac{\partial C_i(t)}{\partial\epsilon}\right|_{\epsilon=0}\varphi_i(\mathbf{r}')\varphi_0^*(\mathbf{r}') + e^{\mathrm{i}\Delta\varepsilon_i t}\left.\frac{\partial C_i^*(t)}{\partial\epsilon}\right|_{\epsilon=0}\varphi_0(\mathbf{r}')\varphi_i^*(\mathbf{r}')\right)\end{aligned}$$

where $\Delta\varepsilon_i = \varepsilon_i - \varepsilon_0$.

- Note that the two-electron KS wavefunction reads through first order

$$\begin{aligned}\varphi^{\mathrm{KS}}(\mathbf{r}_1,t)\varphi^{\mathrm{KS}}(\mathbf{r}_2,t) &= e^{-2\mathrm{i}\varepsilon_0 t}\varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2) \\ &\quad +\epsilon\sum_i e^{-\mathrm{i}(\varepsilon_i+\varepsilon_0)t}\left.\frac{\partial C_i(t)}{\partial\epsilon}\right|_{\epsilon=0}\underbrace{\Big(\varphi_0(\mathbf{r}_1)\varphi_i(\mathbf{r}_2)+\varphi_i(\mathbf{r}_1)\varphi_0(\mathbf{r}_2)\Big)}_{\text{single electron excitation !}} \\ &\quad +\ldots\end{aligned}$$

Casida equation

- Finally, the (local) perturbation in the KS system equals through first order

$$2\epsilon\cos(\omega t)\mathcal{V}(\mathbf{r}) \quad +2\epsilon\sum_{i>0}e^{-\mathrm{i}\Delta\varepsilon_i t}\left.\frac{\partial C_i(t)}{\partial\epsilon}\right|_{\epsilon=0}\int \mathrm{d}\mathbf{r}'\; f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r})\varphi_i(\mathbf{r}')\varphi_0^*(\mathbf{r}')$$
$$+2\epsilon\sum_{i>0}e^{\mathrm{i}\Delta\varepsilon_i t}\left.\frac{\partial C_i^*(t)}{\partial\epsilon}\right|_{\epsilon=0}\int \mathrm{d}\mathbf{r}'\; f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r})\varphi_0(\mathbf{r}')\varphi_i^*(\mathbf{r}')$$

- By analogy with the exact response theory, we obtain for $j>0$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left.\frac{\partial C_j(t)}{\partial\epsilon}\right|_{\epsilon=0} &= -\mathrm{i}\mathcal{V}_{j0}\left[e^{\mathrm{i}(\omega+\Delta\varepsilon_j)t}+e^{-\mathrm{i}(\omega-\Delta\varepsilon_j)t}\right]\\ &-2\mathrm{i}\sum_{i>0}e^{-\mathrm{i}(\Delta\varepsilon_i-\Delta\varepsilon_j)t}\left.\frac{\partial C_i(t)}{\partial\epsilon}\right|_{\epsilon=0}\langle j0|f_{\mathrm{Hxc}}|0i\rangle\\ &-2\mathrm{i}\sum_{i>0}e^{\mathrm{i}(\Delta\varepsilon_i+\Delta\varepsilon_j)t}\left.\frac{\partial C_i^*(t)}{\partial\epsilon}\right|_{\epsilon=0}\langle ji|f_{\mathrm{Hxc}}|00\rangle\end{aligned}$$

where $\langle ij|f_{\mathrm{Hxc}}|kl\rangle=\int\mathrm{d}\mathbf{r}\int\mathrm{d}\mathbf{r}'\;\varphi_i^*(\mathbf{r})\varphi_j^*(\mathbf{r}')f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r})\varphi_k(\mathbf{r})\varphi_l(\mathbf{r}')$.

Casida equation

- When the Hxc kernel is neglected, the TD-DFT linear response equation reduces to the exact linear response equation for the KS-DFT system. In this case, we obtain (approximate) excitation energies which are simply equal to the KS excitation energies $\varepsilon_j - \varepsilon_0$ with $j > 0$.

- In a sense, KS excitation energies can be viewed as "zeroth order" excitation energies if the Hxc kernel is considered as a perturbation.

- In (non-relativistic) molecular calculations, the KS orbitals are real. Consequently,

$$\begin{aligned}\langle j0|f_{\mathrm{Hxc}}|0i\rangle &= \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\; \varphi_0(\mathbf{r})\varphi_j(\mathbf{r}) f_{\mathrm{Hxc}}(\mathbf{r}',\mathbf{r})\varphi_0(\mathbf{r}')\varphi_i(\mathbf{r}') = \langle ji|f_{\mathrm{Hxc}}|00\rangle \\ &= f^{ji}_{\mathrm{Hxc}}\end{aligned}$$

- In case of a charge transfer excitation $0 \rightarrow j$, the KS orbitals $\varphi_0(\mathbf{r})$ and $\varphi_j(\mathbf{r})$ have no overlap i.e. $\varphi_0(\mathbf{r})\varphi_j(\mathbf{r}) = 0$, thus leading to $\boxed{f^{ji}_{\mathrm{Hxc}} = 0}$.

- Consequently, in TD-DFT, the charge transfer excitation energy is essentially equal to the KS excitation energy $\varepsilon_j - \varepsilon_0$ (usually lower than the true physical value).

Casida equation

- The Hxc kernel couples the time-dependent linear response coefficients. Consequently, there is no simple analytical solution to the problem.
- Casida* has shown that a linear response-type equation can be written in matrix form for TD-DFT, like in exact response theory. An important difference though is that the hessian matrix is not diagonal anymore.
- Indeed, by inserting into the TD-DFT linear response equations the decomposition

$$\left.\frac{\partial C_j(t)}{\partial \epsilon}\right|_{\epsilon=0} = \tilde{X}_j(\omega)e^{\mathrm{i}(\omega+\Delta\varepsilon_j)t} + \tilde{X}_j(-\omega)e^{-\mathrm{i}(\omega-\Delta\varepsilon_j)t},$$

where $\tilde{X}_j(\omega)$ and $\tilde{X}_j(-\omega)$ have to be determined, we obtain by identification for $i > 0$,

$$\Big(\Delta\varepsilon_i - \omega\Big)\tilde{X}_i(-\omega) = -\mathcal{V}_{i0} - 2\sum_{j>0} f^{ij}_{\mathrm{Hxc}}\Big(\tilde{X}_j(-\omega) + \tilde{X}^*_j(\omega)\Big)$$

and, with the substitution $\omega \to -\omega$ and complex conjugation,

$$\Big(\Delta\varepsilon_i + \omega\Big)\tilde{X}^*_i(\omega) = -\mathcal{V}^*_{i0} - 2\sum_{j>0} f^{ij}_{\mathrm{Hxc}}\Big(\tilde{X}_j(-\omega) + \tilde{X}^*_j(\omega)\Big).$$

*M. Casida in Recent Advances in Density Functional Methods, edited by D. P. Chong (World Scientific, Singapore, 1995).

Casida equation

- The latter equations can be rewritten in matrix form as follows,

$$\left(\begin{bmatrix} \tilde{\boldsymbol{A}} & \tilde{\boldsymbol{B}} \\ \tilde{\boldsymbol{B}}^* & \tilde{\boldsymbol{A}}^* \end{bmatrix} - \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix}\right)\begin{bmatrix} \tilde{\boldsymbol{X}}(-\omega) \\ \tilde{\boldsymbol{X}}^*(\omega) \end{bmatrix} = -\begin{bmatrix} \tilde{\boldsymbol{\mathcal{V}}} \\ \tilde{\boldsymbol{\mathcal{V}}}^* \end{bmatrix},$$

  where $\tilde{\boldsymbol{\mathcal{V}}}_i = \mathcal{V}_{i0} = \langle \varphi_i | \hat{\mathcal{V}} | \varphi_0 \rangle = \int \mathrm{d}\mathbf{r}\ \varphi_i(\mathbf{r})\mathcal{V}(\mathbf{r})\varphi_0(\mathbf{r})$ with, for example, $\mathcal{V}(\mathbf{r}) = z$ for an electric field along the z axis,

  $\tilde{\boldsymbol{A}}_{ij} = \delta_{ij}\Delta\varepsilon_i + 2f^{ij}_{\mathrm{Hxc}}$ and $\tilde{\boldsymbol{B}}_{ij} = 2f^{ij}_{\mathrm{Hxc}} \neq 0.$

- Approximate excitation energies $\tilde{\omega}_I$ can therefore be computed in TD-DFT (within the adiabatic approximation) by solving the following linear generalized eigenvalue equation,

$$\underbrace{\begin{bmatrix} \tilde{\boldsymbol{A}} & \tilde{\boldsymbol{B}} \\ \tilde{\boldsymbol{B}}^* & \tilde{\boldsymbol{A}}^* \end{bmatrix}} \tilde{\boldsymbol{\Lambda}}_I = \tilde{\omega}_I \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \tilde{\boldsymbol{\Lambda}}_I,$$

dimension: $\Big(2\times \text{ number of virtuals}\Big)^2$

Casida equation

- Note that single (i.e. one-electron) excitation and deexcitation energies only can be obtained from the Casida equation.

- Therefore, multiple electron excitations are simply absent from standard TD-DFT spectra.

- This limitation is due to the adiabatic approximation.

- In exact TD-DFT, the Hxc "energy" $\mathcal{E}_{\rm Hxc}[n]$ is a functional of the density n which is itself a function of both space coordinates and time. Therefore, it incorporates the evolution of the density over the time interval of interest $[t_0, t_1]$.

- Consequently, any deviation $\delta n(\mathbf{r}, t)$ from the ground-state density $n_0(\mathbf{r})$ will modify the Hxc "energy" as follows,

$$\begin{aligned}\mathcal{E}_{\rm Hxc}[n_0+\delta n] &= \mathcal{E}_{\rm Hxc}[n_0] + \int_{t_0}^{t_1} \mathrm{d}t \int \mathrm{d}\mathbf{r}\, \frac{\delta \mathcal{E}_{\rm Hxc}[n_0]}{\delta n(\mathbf{r}, t)} \\ &+ \frac{1}{2}\int_{t_0}^{t_1} \mathrm{d}t \int_{t_0}^{t_1} \mathrm{d}t' \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\, \underbrace{\frac{\delta^2 \mathcal{E}_{\rm Hxc}[n_0]}{\delta n(\mathbf{r}', t')\delta n(\mathbf{r}, t)}}_{f_{\rm Hxc}(\mathbf{r}', t', \mathbf{r}, t) \rightarrow f_{\rm Hxc}(\mathbf{r}', \mathbf{r}, \omega)} + \ldots\end{aligned}$$

Casida equation

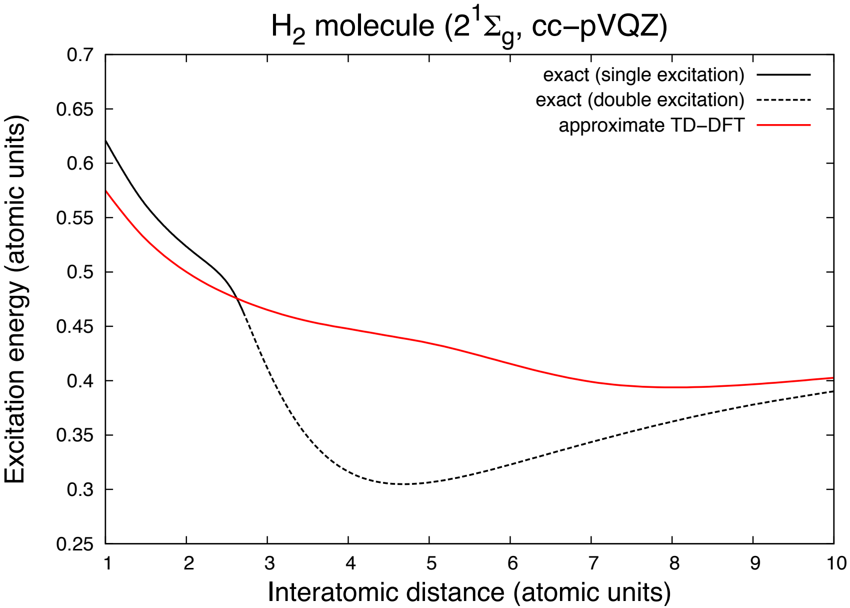
- Using the adiabatic approximation simply consists in expressing the Hxc "energy" in terms of the time-independent ground-state Hxc density functional:

$$
\begin{aligned}
\mathcal{E}_{\mathrm{Hxc}}[n] &\rightarrow \int_{t_0}^{t_1} \mathrm{d}t\, E_{\mathrm{Hxc}}\left[n(t)\right] \\
\frac{\delta \mathcal{E}_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r}, t)} &\rightarrow \frac{\delta E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r})} \\
\frac{\delta^2 \mathcal{E}_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r}', t')\delta n(\mathbf{r}, t)} &\rightarrow \frac{\delta^2 E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} \underbrace{\delta(t' - t)}_{}
\end{aligned}
$$

no frequency dependence !

- Returning to exact TD-DFT, the frequency-dependent kernel makes both $\tilde{\boldsymbol{A}}$ and $\tilde{\boldsymbol{B}}$ matrices in Casida equations frequency-dependent too, thus leading to a non-linear eigenvalue equation which can now give higher-order excitation energies, even though single excitations only are described explicitly:

$$
\begin{bmatrix} \tilde{\boldsymbol{A}}(\omega) & \tilde{\boldsymbol{B}}(\omega) \\ \tilde{\boldsymbol{B}}^*(\omega) & \tilde{\boldsymbol{A}}^*(\omega) \end{bmatrix} \tilde{\boldsymbol{\Lambda}}(\omega) = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \tilde{\boldsymbol{\Lambda}}(\omega)
$$



H_2 molecule ($2^1\Sigma_g$, cc−pVQZ)
Excitation energy (atomic units)
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
1
2
3
4
5
6
7
8
9
10
Interatomic distance (atomic units)
exact (single excitation)
exact (double excitation)
approximate TD−DFT

Excited states in time-independent DFT

- DFT can be extended to excited states when considering an ensemble of ground and excited states, like in statistical physics*.
- An ensemble is characterized by the total number of states and the weights assigned to these states.
- The simplest ensemble consists of the ground Ψ_0 and first excited Ψ_1 states, with weights $(1-w)$ and w, respectively.
- Variational principle for an equi-ensemble (*Theophilou*): if Ψ and Ψ' are orthonormal then

$$\langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi'|\hat{H}|\Psi'\rangle \geq E_0 + E_1$$

- Generalization: for a given ensemble weight w,

$$(1-w)\langle\Psi|\hat{H}|\Psi\rangle + w\langle\Psi'|\hat{H}|\Psi'\rangle = (1-2w)\underbrace{\langle\Psi|\hat{H}|\Psi\rangle}_{\geq E_0} + w\Big(\underbrace{\langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi'|\hat{H}|\Psi'\rangle}_{\geq E_0+E_1}\Big)$$

- *Gross-Oliveira-Kohn* (GOK) variational principle:

$$\boxed{\text{for } 0 \leq w \leq 1/2, \quad (1-w)\langle\Psi|\hat{H}|\Psi\rangle + w\langle\Psi'|\hat{H}|\Psi'\rangle \geq (1-w)E_0 + wE_1}$$

---

* E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2805

Excited states in time-independent DFT

- The w-dependent lower bound $\boxed{E^w = (1-w)E_0 + wE_1}$ is the exact ensemble energy.

- It is reached when the trial wavefunctions Ψ and Ψ' are equal to the exact ground- and first-excited-state wavefunctions Ψ_0 and Ψ_1, respectively.

- Note that the ensemble energy is linear in w so that the exact first excitation energy $\omega = E_1 - E_0$ can be expressed as

$$\boxed{\omega = \frac{\mathrm{d}E^w}{\mathrm{d}w} \quad \text{or} \quad \omega = 2\left(E^{w=1/2} - E^{w=0}\right).}$$

- Hohenberg–Kohn theorem for a two-state ensemble: there is a one-to-one correspondance (up to a constant) between the local (nuclear) potential and the ensemble density $\boxed{n^w(\mathbf{r}) = (1-w)n_{\Psi_0}(\mathbf{r}) + w\,n_{\Psi_1}(\mathbf{r})}$.

- Consequently, the ensemble energy is a functional of the ensemble density.

E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809

Excited states in time-independent DFT

Proof: like in ground-state DFT, the proof is obtained in two steps.

step 1: Let us consider two local potentials $u(\mathbf{r})$ and $v(\mathbf{r})$ that differ by more than a constant [i.e. $u(\mathbf{r}) - v(\mathbf{r})$ varies with $\mathbf{r}$]. The corresponding Hamiltonians,

$$\hat{H}[u] \equiv \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} u(\mathbf{r}_i) \times \quad \text{and} \quad \hat{H}[v] \equiv \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$$

cannot have the same eigenfunctions. Indeed, if Ψ is eigenfunction of both Hamiltonians with energies E_u and E_v, respectively, then

$$\begin{aligned}\left(\hat{H}[u] - \hat{H}[v]\right)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) &= (E_u - E_v) \times \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \\ &= \sum_{i=1}^{N} \left(u(\mathbf{r}_i) - v(\mathbf{r}_i)\right) \times \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N),\end{aligned}$$

which, after dividing by the wavefunction and taking $\mathbf{r}_1 = \mathbf{r}_2 = \ldots = \mathbf{r}_N = \mathbf{r}$, leads to

$$u(\mathbf{r}) - v(\mathbf{r}) = (E_u - E_v)/N \quad \leftarrow \text{constant}$$

which is absurd !

step 2: As a consequence of **step 1**, if we denote $\Psi_i[v]$ $(i=0,1)$ the exact ground- and first-excited-state wavefunctions of $\hat{H}[v]$, it comes

$$(1-w)\langle\Psi_0[v]|\hat{H}[u]|\Psi_0[v]\rangle + w\langle\Psi_1[v]|\hat{H}[u]|\Psi_1[v]\rangle > E^w[u]$$

where $E^w[u]$ is the exact ensemble energy of $\hat{H}[u]$.

Using $\hat{H}[u] \equiv \hat{H}[v] + \sum_{i=1}^{N}\Big(u(\mathbf{r}_i) - v(\mathbf{r}_i)\Big)\times$ leads to

$$E^w[v] + \int \Big[u(\mathbf{r}) - v(\mathbf{r})\Big] \times n^w[v](\mathbf{r})\,\mathrm{d}\mathbf{r} > E^w[u]$$

where $n^w[v]$ is the exact ensemble density of $\hat{H}[v]$. From the substitution $u \leftrightarrow v$, we also have

$$E^w[u] + \int \Big[v(\mathbf{r}) - u(\mathbf{r})\Big] \times n^w[u](\mathbf{r})\,\mathrm{d}\mathbf{r} > E^w[v]$$

thus leading by summation to the final inequality

$$\int \Big[u(\mathbf{r}) - v(\mathbf{r})\Big] \times \underbrace{\Big[n^w[v](\mathbf{r}) - n^w[u](\mathbf{r})\Big]}_{\neq 0}\,\mathrm{d}\mathbf{r} > 0$$

Ensemble density-functional theory

- Like in conventional KS-DFT, a Hartree-exchange-correlation (Hxc) density functional $E^w_{\mathrm{Hxc}}[n]$ describes the two-electron repulsion in the ensemble. Note that it is in principle w-dependent.
- Exact ensemble density-functional xc energies can be calculated for model systems like the Hubbard dimer*.
- KS equations in ensemble DFT (eDFT):

$$\left(-\frac{\nabla^2_{\mathbf{r}}}{2}+v_{\mathrm{ne}}(\mathbf{r})+\int d\mathbf{r}'\,\frac{n^w(\mathbf{r}')}{\mid\mathbf{r}-\mathbf{r}'\mid}+\frac{\delta E^w_{\mathrm{xc}}[n^w]}{\delta n(\mathbf{r})}\right)\varphi^w_p(\mathbf{r})=\varepsilon^w_p\varphi^w_p(\mathbf{r}),$$

  where

$$n^w(\mathbf{r})=2\left(\sum_{p=1}^{H-1}\left|\varphi^w_p(\mathbf{r})\right|^2\right)+(2-w)\left|\varphi^w_H(\mathbf{r})\right|^2+w\left|\varphi^w_L(\mathbf{r})\right|^2,$$

  if the first excitation is a single electron one from the HOMO (H) to the LUMO (L).

- Note that the ensemble weight w controls the partial occupations of the HOMO and the LUMO.
- Conventional (ground-state) KS-DFT is recovered when $w=0$.

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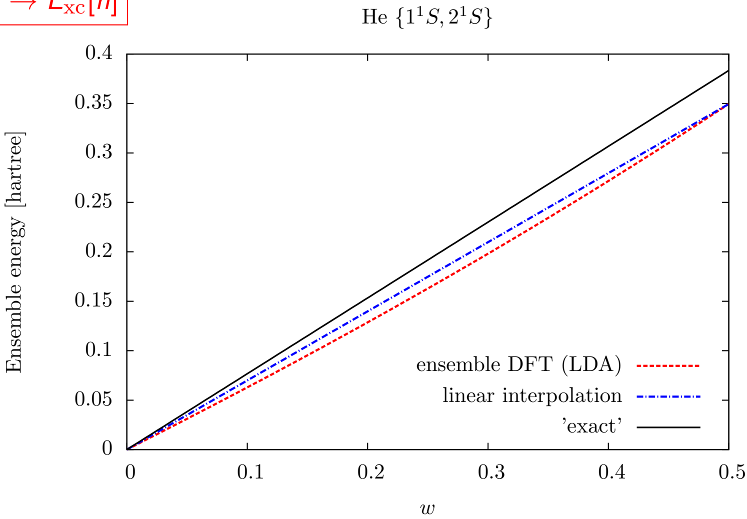
* K. Deur, L. Mazouin, and E. Fromager, *Phys. Rev. B* **95**, 035120 (2017).

$\boxed{E_{\rm xc}^{w}[n] \rightarrow E_{\rm xc}[n]}$



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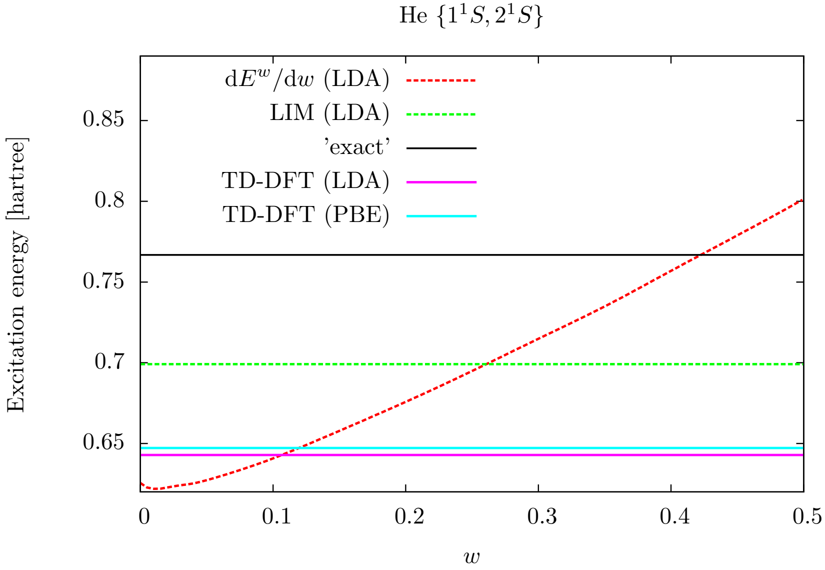

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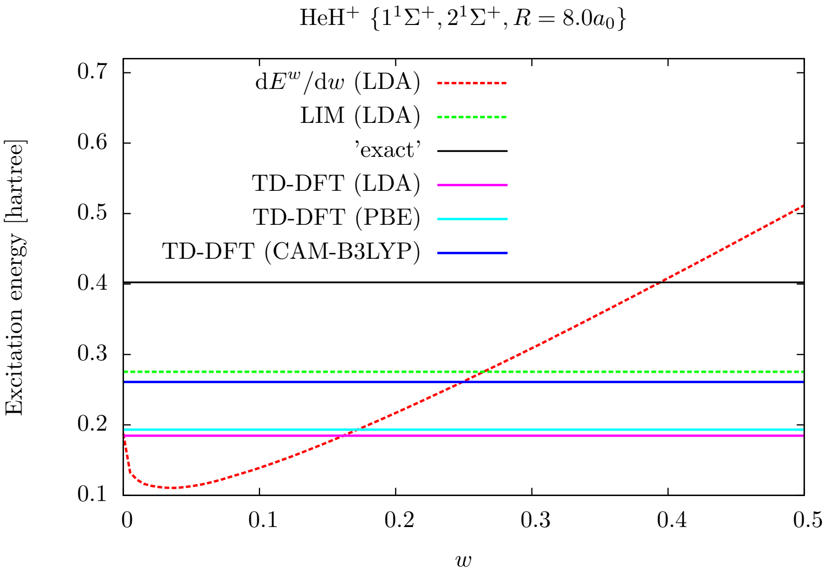

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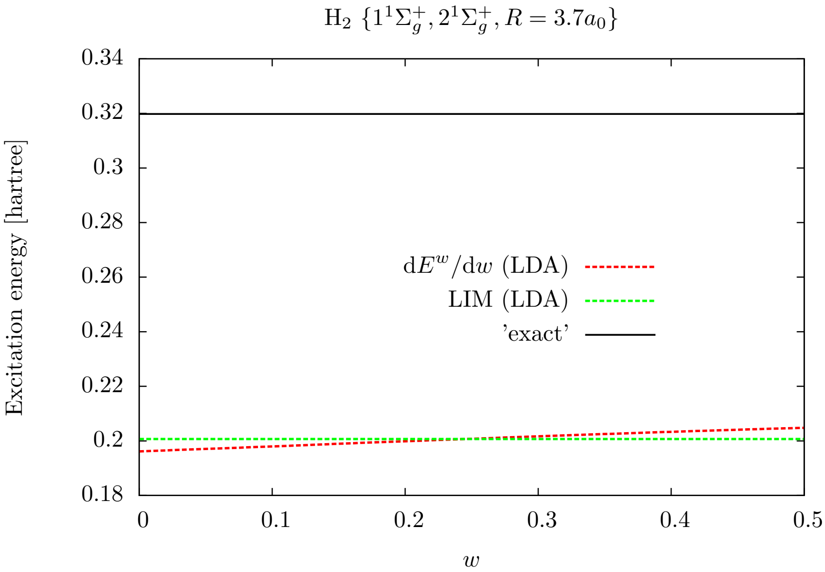

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