TDDFT II

Problem set

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Outline

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Problem 1: Time-dependent Linear Response Theory

1 A system is governed by the Hamiltonian $\hat{H}(t) = \hat{H}_0(t) + f(t)\hat{V}$, so that its evolution is given by:

$$\mathrm{i}\frac{\partial}{\partial t}\hat{\rho}(t) = \left[\hat{H}(t), \hat{\rho}(t)\right] ,$$

Show that, to first order in f, the change in the value of the expectation value of some observable $\hat{A}$ due to the presence of the *perturbation* $f(t)\hat{V}$ is given by:

$$\delta A(t) = \langle \hat{A} \rangle(t) - \langle \hat{A} \rangle_{f=0}(t) = \int_{-\infty}^{\infty} \mathrm{d}t' \, f(t') \chi_{\hat{A},\hat{V}}(t,t') ,$$

where the *linear response function* is given by:

$$\chi_{\hat{A},\hat{V}}(t,t') = -\mathrm{i}\theta(t-t')\mathrm{Tr}\{\hat{\rho}(t_0)\left[\hat{A}_H(t), \hat{V}_H(t')\right]\} .$$

$\hat{X}_H(t) = \hat{U}(t_0,t)\hat{X}\hat{U}(t,t_0)$ is the Heisenberg representation of $\hat{X}$, where $\hat{U}(t,t_0)$ is the evolution operator in the absence of the perturbation.

Problem 1: Time-dependent Linear Response Theory

Solution:

1. Expand $\hat{\rho}(t)$ in a power series in f:

$$\hat{\rho}(t) = \sum_{n=0}^{\infty} \hat{\rho}_n(t) \,,$$

where $\hat{\rho}_0$ is the unperturbed solution, $\hat{\rho}_1$ is linear in f, etc.

2. Find the differential equations that verify $\hat{\rho}_0$ and $\hat{\rho}_1$, and verify that they are equivalent to the integral equations:

$$\begin{aligned} \hat{\rho}_0(t) &= \hat{U}(t,t_0)\hat{\rho}(t_0)\hat{U}(t_0,t) \,, \\ \hat{\rho}_1(t) &= -\mathrm{i}\int_{t_0}^{t} \mathrm{d}t' \; \hat{U}(t,t') \left[f(t')\hat{V}, \hat{\rho}_0(t')\right] \hat{U}(t',t) \,, \end{aligned}$$

3. To first order in f,

$$\delta A(t) = \mathrm{Tr}\{\hat{\rho}_1(t)\hat{A}\} \,.$$

Substituting $\hat{\rho}_1(t)$, after some algebra one arrives to the final result.

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Problem 1: Time-dependent Linear Response Theory

2 Show that, at equilibrium ($\hat{H}_0$ is time-independent and $\left[\hat{H}_0, \hat{\rho}(t_0)\right] = 0$), the response function is *translationally invariant in time*, i.e.:

$$\chi_{\hat{A},\hat{V}}(t,t') = \chi_{\hat{A},\hat{V}}(t+\Delta, t'+\Delta)\,.$$

and therefore it only depends on the time-difference $t - t'$. One can then define a single-valued response function:

$$\chi_{\hat{A},\hat{V}}(\tau) := \chi_{\hat{A},\hat{V}}(t+\tau, t)\,.$$

Prove that this function is given by:

$$\chi_{\hat{A},\hat{V}}(\tau) = -\mathrm{i}\theta(\tau)\mathrm{Tr}\{\hat{\rho}(t_0)\left[\mathrm{e}^{\mathrm{i}\tau\hat{H}_0}\hat{A}\mathrm{e}^{-\mathrm{i}\tau\hat{H}_0}, \hat{V}\right]\}$$

Problem 1: Time-dependent Linear Response Theory

3 Sum-over-states. Derive the sum-over-states formula, i.e.:

$$\chi_{\hat{A},\hat{V}}(\omega) = \frac{1}{\sqrt{2\pi}} \sum_I \{ \frac{A_{I0} V_{0I}}{\omega - (E_I - E_0) - \mathrm{i}\eta} - \frac{A_{0I} V_{I0}}{\omega + (E_I - E_0) - \mathrm{i}\eta} \}$$

for the Fourier transform of the equilibrium response function:

$$\chi_{\hat{A},\hat{V}}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \chi_{\hat{A},\hat{V}}(\tau) \,,$$

assuming a pure system perturbed from its ground state $|\Psi_0\rangle$.

Solution:

1. Insert the resolution of the identity in the expression for the response function given in the previous problem,
2. Apply the following formula for the Fourier transform of the Heaviside function:

$$\theta(\omega) = \frac{1}{\sqrt{2\pi}} \frac{1}{\delta + \mathrm{i}\omega} \,.$$

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Problem 1: Time-dependent Linear Response Theory

4 In density-functional theories what we like is the “density-density” response function:

$$\chi(\mathbf{r}.\mathbf{r}',\omega) := \chi_{\hat{n}(\mathbf{r}),\hat{n}(\mathbf{r}')}(\omega)\,.$$

Prove that

$$\chi(\mathbf{r}.\mathbf{r}',\omega) = \frac{\delta n(\mathbf{r},\omega)}{\delta v(\mathbf{r}',\omega)}\,.$$

Outline

Problem 2: Quantum Optimal Control Theory

1 A system is governed by the Hamiltonian $\hat{H}[u](t) = \hat{\mathcal{H}} + \epsilon[u](t)\hat{V}$, so that its evolution is given by:

$$\mathrm{i}\frac{\partial}{\partial t}\hat{\rho}[u](t) = \left[\hat{H}[u](t), \hat{\rho}[u](t)\right] \ , \hat{\rho}[u](t_0) = \hat{\rho}_{\mathrm{init}} \ ,$$

where u is a real parameter that determine the precise shape of the real function ϵ.
Given the function $G[u] = \mathrm{Tr}\{\hat{\rho}[u](t_f)\hat{A}\}$ (the expectation value of some observable $\hat{A}$ at some final time t_f), show that:

$$\frac{\partial G}{\partial u}[u] = -i\int_{t_0}^{t_f} \mathrm{d}\tau \ \frac{\partial \epsilon}{\partial u}[u](\tau)\mathrm{Tr}\{\hat{\rho}[u](\tau)\left[\hat{A}[u](\tau), \hat{V}\right]\} \ .$$

where $\hat{A}[u]$ is defined as:

$$\begin{aligned} \frac{\partial}{\partial t}\hat{A}[u](t) &= -i\left[\hat{H}[u](t), \hat{A}[u](t)\right] \ , \\ \hat{A}[u](t_f) &= \hat{A} \ . \end{aligned}$$

These are the "QOCT equations".

Problem 2: Quantum Optimal Control Theory

Solution:

1. Obviously, $\frac{\partial G}{\partial u}[u] = \lim_{\Delta u \to 0} \Delta u^{-1}(G[u+\Delta u] - G[u])$.
2. Note that $G[u]$ corresponds to the propagation of the system with the Hamiltonian $\hat{H}[u](t)$, whereas $G[u+\Delta u]$ corresponds to the propagation of the system with:

$$\hat{H}[u+\Delta u](t) = \hat{H}[u](t) + \Delta u \frac{\partial \epsilon}{\partial u}[u]\hat{V}\,.$$

3. Now we can use directly the LRT result of the previous problem, by making the identifications,

$$\hat{H}_0(t) = \hat{H}[u](t), \quad f(t) = \Delta u \frac{\partial \epsilon}{\partial u}[u](t)\,.$$

and we arrive at:

$$\frac{\partial G}{\partial u}[u] = \int_{t_0}^{\infty} \mathrm{d}\tau \; \frac{\partial \epsilon}{\partial u}[u](\tau)\chi_{\hat{A},\hat{V}}(t_f,\tau)\,.$$

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Problem 2: Quantum Optimal Control Theory

2 Show that, for pure systems ($\hat{\rho}[u](t) = |\Psi[u](t)\rangle\langle\Psi[u](t)|$), the previous result is:

$$\frac{\partial G}{\partial u}[u] = 2\mathrm{Im}\int_{t_0}^{t_f} \mathrm{d}\tau \; \frac{\partial \epsilon}{\partial u}[u](\tau)\langle\chi[u](\tau)|\hat{V}|\Psi[u](\tau)\rangle \, .$$

$$\begin{aligned} \frac{\partial}{\partial t}|\chi(t)\rangle &= -i\hat{H}[u](t)|\chi(t)\rangle \, , \\ |\chi(t_f)\rangle &= \hat{A}|\Psi[u](t_f)\rangle \, , \end{aligned}$$

Outline

Problem 3: Optical absorption with TDDFT in the time domain

1 Consider an atom or molecule (assume, for the sake of simplicity, clamped nuclei and the Born-Oppenheimer approximation). The linear response function, in the case in which $\hat{A}$ is the (i-th component of the dipole moment operator),

$$\hat{R}^i = \sum_{n=1}^{N} \hat{r}_n^i$$

and $\hat{V} = -\hat{R}^j$ is (minus) the j-th component of the dipole moment operator,

$$\hat{R}^j = \sum_{n=1}^{h} \hat{r}_n^j$$

receives the special name of *(i,j) component of the (dynamical) (dipole-dipole) (linear) polarizability tensor*, $\alpha_{ij}(\omega)$.
It measures the (dipole) response of the system to a (weak) light interaction in the dipole approximation.

Problem 3: Optical absorption with TDDFT in the time domain

Prove that:

$$\alpha_{ij}(\omega) = -\int\int \mathrm{d}^3 r \mathrm{d}^3 r' \; x_i x_j \chi(\mathbf{r}, \mathbf{r}', \omega) \, .$$

Solution:

1. You just need to remember that the linear polarizability happens to be linear, and that for any one-body local operator:

$$\hat{A} = \sum_{n=1}^{N} a(\hat{\mathbf{r}}_i) \, .$$

it holds that:

$$\hat{A} = \int \mathrm{d}^3 r \hat{n}(\mathbf{r}) a(\mathbf{r}) \, .$$

Problem 3: Optical absorption with TDDFT in the time domain

2 Let us describe the physical system by its Kohn-Sham counterpart. We compute the ground-state Kohn-Sham orbitals $\{\varphi_i^{\mathrm{gs}}(\mathbf{r})\}_{i=1}^{N/2}$ (assume a spin-restricted case), and we define the following transformation, that preserves the ground state density $n_0(\mathbf{r})$:

$$\varphi_i(\mathbf{r}, t=0) = e^{-i\kappa x_j}\varphi_i^{\mathrm{gs}}(\mathbf{r})\,.$$

We now propagate the TDKS equations for this set of orbitals $\{\varphi_i(\mathbf{r},t)\}_{i=1}^{N/2}$, and compute

$$\delta n(\mathbf{r},\omega) = n(\mathbf{r},\omega) - n_0(\mathbf{r})\,,$$

where n is the density of the time-dependent Kohn-Sham system, $n(\mathbf{r},t) = \sum_{n=1}^{N/2} 2|\varphi_n(\mathbf{r},t)|^2$.

Prove that:

$$\alpha_{ij}(\omega) = \frac{1}{\kappa}\int \mathrm{d}^3 r\; \delta n(\mathbf{r},\omega) x_i\,.$$

Problem 3: Optical absorption with TDDFT in the time domain

Solution:

1. If we apply an instantaneous perturbation of the form $\kappa\delta(t-t_0)\hat{V}$ on a system that is at its ground state $|\Psi_0\rangle$ at $t=0$, it holds that (prove!):

$$|\Psi(0^+)\rangle = e^{-i\kappa\hat{V}}|\Psi_0\rangle\,.$$

2. The equilibrium response function can then be computed as:

$$\chi_{\hat{A},\hat{V}}(t) = \lim_{\kappa\to 0}\frac{1}{\kappa}\delta A(t)\,.$$

   This provides a very intuitive picture of what the linear response function represents.

3. If the measured observable is the dipole operator, the only thing we need is the time-dependent density, and therefore we can solve the TDKS equations instead:

$$\langle\hat{R}_i\rangle(t) = \int \mathrm{d}^3 r\; n(\vec{r})x_i\,.$$

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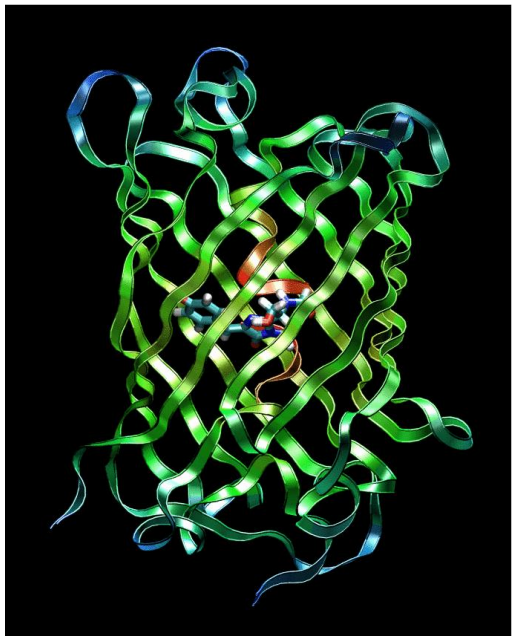
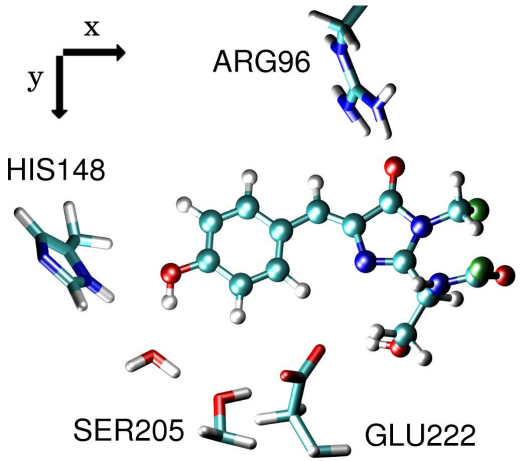
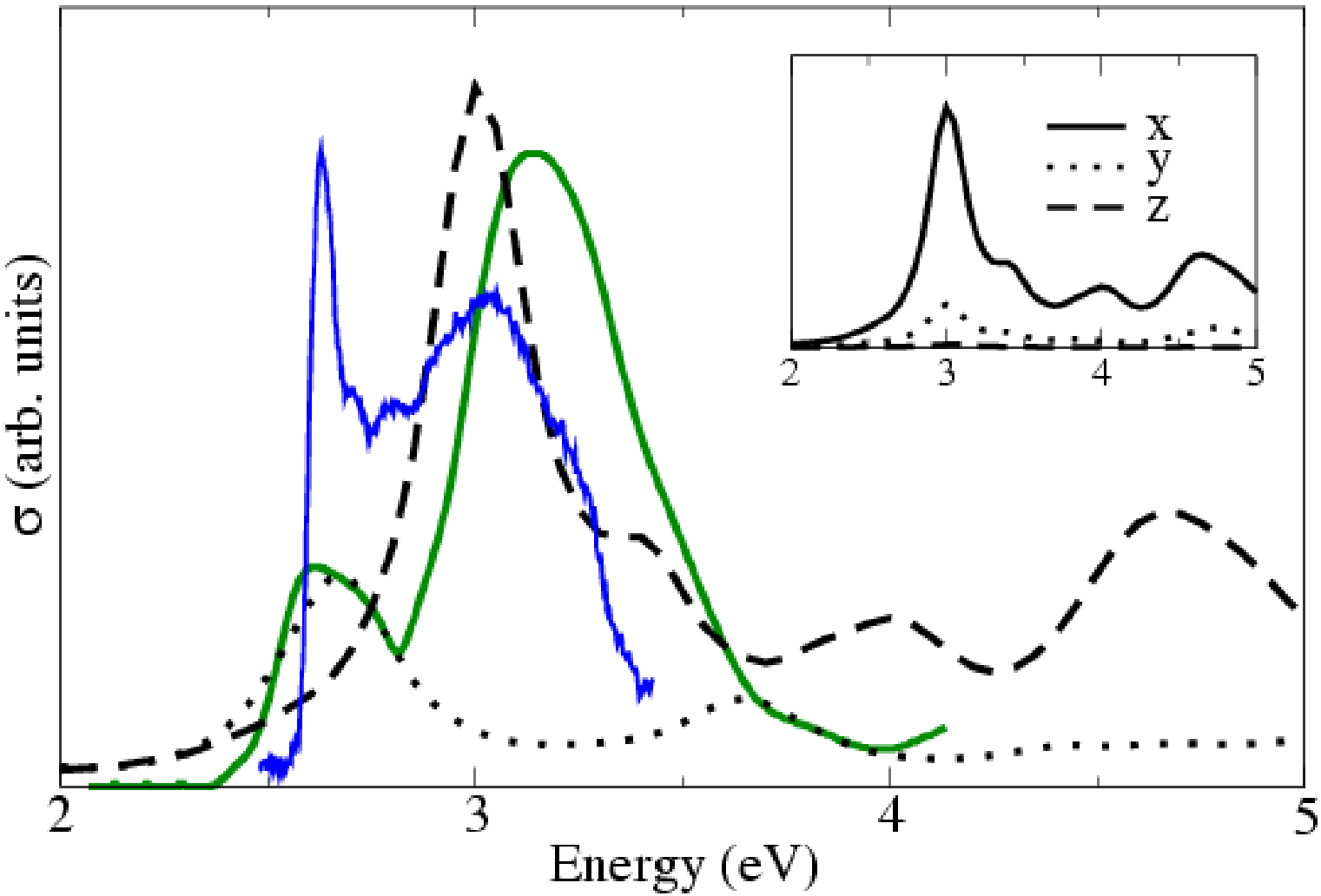
Example





1. The Green Fluorescent Protein (GFP) and its mutants



Marques et al., Phys. Rev. Lett. **90**, 258101 (2003).

Outline

Problem 4: The “time-dependent energy”

1 A system of electrons evolves from its ground state at time zero according to a time-dependent Hamiltonian in the form:

$$\hat{H}(t) = \hat{T} + \hat{W} + \sum_{n=1}^{N} v(\hat{\mathbf{r}}_i, t) \, .$$

We define the “time-dependent energy” as:

$$E(t) = \langle \Psi(t) | \hat{H}(t) | \Psi(t) \rangle \, .$$

Prove that it is an explict density functional:

$$\frac{\mathrm{d}}{\mathrm{d}t} E(t) = \int \mathrm{d}^3 r n(\mathbf{r}, t) \frac{\partial v}{\partial t}(\mathbf{r}, t) \, ,$$

or, in other words:

$$E(t) = E_0 + \int_0^t \mathrm{d}\tau \int \mathrm{d}^3 r n(\mathbf{r}, t) \frac{\partial v}{\partial t}(\mathbf{r}, t) \, ,$$

Problem 4: The "time-dependent energy"

2 $E(t)$ can therefore be computed *exactly* with *exact* TDDFT.

However, we will normally use an approximate, normally *adiabatic* exchange and correlation potential "A". This is usually derived from a ground state xc energy functional, $E_{\rm xc}^{A}[n]$, from which the ground state xc potential functional is derived by functional derivation:

$$v_{\rm xc}^{A}[n](\mathbf{r}) = \frac{\delta E_{\rm xc}^{A}}{\delta n(\mathbf{r})} \, .$$

The *time-dependent* adiabatic extension of A will be defined as:

$$v_{\rm tdxc}^{A}[n](\mathbf{r},t) = v_{\rm xc}^{A}[n(t)](\mathbf{r}) \, .$$

The time-dependent energy obtained with this approximation will be $E^{A}(t)$.

Problem 4: The “time-dependent energy”

The ground state DFT energy *density* functional is defined as:

$$E^A_{\mathrm{gsDFT}}[n] = T_S[n] + U[n] + V[n] + E^A_{\mathrm{xc}}[n] \,.$$

We can redefine it as a functional of the orbitals:

$$E^A_{\mathrm{gsDFT}}[\varphi] = T_S[\varphi] + U[\varphi] + V[\varphi] + E^A_{\mathrm{xc}}[\varphi] \,.$$

Is it true that

$$E^A(t) = E^A_{\mathrm{gsDFT}}[\varphi(t)] \;?$$

Problem 4: The “time-dependent energy”

Solution (1, brute force):

1. One has to prove that the time-derivatives of the two quantities coincide (and just assume the initial value, which is irrelevant anyways, coincides).
2. It may be useful to prove first the following identity:

$$E^A_{\mathrm{gsDFT}}[\varphi(t)] = \sum_{i=1}^{N} \varepsilon_i[\varphi(t)] - U[\varphi(t)] + E^A_{\mathrm{xc}}[\varphi(t)] - \int \mathrm{d}^3 r\, n(\vec{r},t) v_{\mathrm{xc}}[n(t)](\vec{r})\,.$$

3. The TDKS system is a system of non-interacting electrons whose energy is:

$$E^A_{\mathrm{KS}}(t) = \sum_{i=1}^{N} \varepsilon_i[\varphi(t)]\,.$$

Its time derivative is related to that of the true system by:

$$\frac{\mathrm{d}}{\mathrm{d}t} E^A_{\mathrm{KS}}(t) = \frac{\mathrm{d}}{\mathrm{d}t} E^A(t) + \int \mathrm{d}^3 r\, n(\vec{r},t) \{ \frac{\partial}{\partial t} v_{\mathrm{Hartree}}[n(t)] + \frac{\partial}{\partial t} v^A_{\mathrm{xc}}[n(t)] \}$$

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Problem 4: The "time-dependent energy"

Solution (2, Lagrangian formulation):

1. Prove that the TDKS equations can be derived from the following Lagrangian, assuming a time-independent external potential:

$$\mathcal{L}[\varphi(t), \dot{\varphi}(t)] = \frac{\mathrm{i}}{2} \int \mathrm{d}^3 r \sum_{n=1}^{N} \{\varphi_n^*(\vec{r}, t)\dot{\varphi}_n(\vec{r}, t) - \dot{\varphi}_n^*(\vec{r}, t)\varphi_n(\vec{r}, t)\} - E^A_{\mathrm{gsDFT}}[\varphi(t)]$$

   I.e., the TDKS equations are the Euler-Lagrange equations:

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial \mathcal{L}}{\partial \dot{\varphi}^*(\vec{r}, t)} = \frac{\partial \mathcal{L}}{\partial \varphi^*(\vec{r}, t)}$$

2. Once we have a Lagrangian, we can apply Noether's theorem to find conserved quantities. The time-independence of the Lagrangian, in this case, prescribes the time-independence of $E^A_{\mathrm{gsDFT}}[\varphi(t)]$.

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Solution (2, Lagrangian formulation):

1. Prove that the TDKS equations can be derived from the following Lagrangian, assuming a time-independent external potential:

$$\mathcal{L}[\varphi(t), \dot{\varphi}(t)] = \frac{\mathrm{i}}{2} \int \mathrm{d}^3 r \sum_{n=1}^{N} \{\varphi_n^*(\vec{r}, t)\dot{\varphi}_n(\vec{r}, t) - \dot{\varphi}_n^*(\vec{r}, t)\varphi_n(\vec{r}, t)\} - E^A_{\mathrm{gsDFT}}[\varphi(t)]$$

   I.e., the TDKS equations are the Euler-Lagrange equations:

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial \mathcal{L}}{\partial \dot{\varphi}^*(\vec{r}, t)} = \frac{\partial \mathcal{L}}{\partial \varphi^*(\vec{r}, t)}$$

2. Once we have a Lagrangian, we can apply Noether's theorem to find conserved quantities. The time-independence of the Lagrangian, in this case, prescribes the time-independence of $E^A_{\mathrm{gsDFT}}[\varphi(t)]$.

Problem 4: The “time-dependent energy”

1. Now add a time-dependent external local field, $v_{\text{ext}}(\vec{r}, t)$:

$$\tilde{\mathcal{L}}[\varphi(t), \dot{\varphi}(t), t] = \mathcal{L}[\varphi(t), \dot{\varphi}(t)] - \int \mathrm{d}^3 r \; n(\vec{r}, t) v_{\text{ext}}(\mathbf{r}, t) \; .$$

2. By making use of the chain rule, and Euler’s Lagrange equations, compute the *total* time derivative of $\tilde{\mathcal{L}}$, and compare it to its *partial* derivative.
   See how the partial derivative of the Lagrangian is related to the total derivative of $E^A_{\text{gsDFT}}[\varphi(t)]$, and this relationship in fact completes the proof.

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Problem 4: The “time-dependent energy”

3 Given a Hermitian NxN matrix (N is the number of KS orbitals), we consider the transformation:

$$\varphi'_m = \sum_{n=1}^{N} (\mathrm{e}^{-\mathrm{i}S})_{mn} \varphi_n \ .$$

Prove that the Lagrangian is invariant under this transformation. Prove that this fact leads, through the use of Noether’s theorem, to conclude that the time-dependent Kohn-Sham orbitals are orthonormal at all times.

Outline

Problem 5: Ehrenfest dynamics with TDDFT

1 Given a system formed by classical nuclei and quantum electrons, the Ehrenfest model for the description of the dynamics of this system is given by:

$$\begin{aligned} \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Phi(t)\rangle &= \{\hat{T}+\hat{V}(\hat{\mathbf{r}},\mathbf{R}(t),t)\}|\Phi(t)\rangle\,, \\ M_\alpha\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{R}_\alpha &= \mathbf{P}_\alpha\,, \\ \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}_\alpha &= -\langle\Phi(t)|\nabla_{\mathbf{R}_\alpha}\hat{V}(\hat{\mathbf{r}},\mathbf{R}(t),t)|\Phi(t)\rangle\,. \end{aligned}$$

$\hat{\mathbf{r}}$ is the full set of N electron coordinate operators, $\mathbf{R}$ is the full set of (classical) nuclear coordinates, $\mathbf{P}$ the nuclear momenta, and $V(\mathbf{r},\mathbf{R}(t),t)$ is the full potential, including the electron-electron, nucleus-nucleus, electron nucleus, and external (time-dependent) potential:

$$\begin{aligned} \hat{V}(\hat{\mathbf{r}},\mathbf{R}(t),t) = &\sum_{m<n}\frac{1}{|\hat{\mathbf{r}}_m-\hat{\mathbf{r}}_n|}+\sum_{\alpha<\beta}\frac{z_\alpha z_\beta}{|\mathbf{R}_\alpha(t)-\hat{\mathbf{R}}_\beta(t)|}-\sum_{\alpha,m}\frac{z_\alpha}{|\hat{\mathbf{r}}_m-\hat{\mathbf{R}}_\alpha(t)|} \\ &+\sum_m v_{\mathrm{ext}}^{\mathrm{electrons}}(\hat{\mathbf{r}}_m)+\sum_\alpha v_{\mathrm{ext}}^{\mathrm{nuclei}}(\hat{\mathbf{R}}_\alpha(t))\,. \end{aligned}$$

Problem 5: Ehrenfest dynamics with TDDFT

Project these equations into the adiabatic basis,

$$\{\hat{T} + V_{\text{int}}(\mathbf{r}, \mathbf{R})\}|\Phi_k(\mathbf{R})\rangle = E_k(\mathbf{R})|\Phi_k(\mathbf{R})\rangle \,,$$

and prove that, in the absence of external fields, Ehrenfest dynamics reduces to ground state Born-Oppenheimer Molecular Dynamics,

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}_\alpha = -\nabla_{\mathbf{R}_\alpha} E_0(\mathbf{R}(t)) \,,$$

if the system starts starts its evolution from the electronic ground state, and either the non-adiabatic couplings,

$$\mathbf{d}^\alpha_{jk}(\mathbf{R} = \langle\Phi_j(\mathbf{R})|\nabla_{\mathbf{R}_\alpha}|\Phi_k(\mathbf{R})\rangle$$

are negligible or the electronic gap,

$$\Delta(\mathbf{R}) = E_1(\mathbf{R}) - E_0(\mathbf{R}) \,,$$

is very large.

Problem 5: Ehrenfest dynamics with TDDFT

2 Prove that within the Ehrenfest model, the nuclear dynamics can be followed exactly within exact TDDFT, without the need of propagating the real interacting wave function.

Solution

One just needs to prove that the force is an explicit functional of the time-dependent density:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}_\gamma &= -\langle\Phi(t)|\nabla_{\mathbf{R}_\gamma} V(\mathbf{r},\mathbf{R}(t),t)|\Phi(t)\rangle\,. \\ &= -\nabla_{\mathbf{R}_\gamma}\sum_{\alpha<\beta}\frac{z_\alpha z_\beta}{|\mathbf{R}_\alpha(t)-\hat{\mathbf{R}}_\beta(t)|} - \int \mathrm{d}^3 r\, n(\mathbf{r},t)\nabla_{\mathbf{R}_\alpha}\sum_\alpha \frac{1}{|\mathbf{r}-\mathbf{R}_\alpha(t)|} \\ &\quad - \int \mathrm{d}^3 r\, n(\mathbf{r},t) v_{\mathrm{ext}}^{electrons}(\mathbf{r},t)\,.\end{aligned}$$

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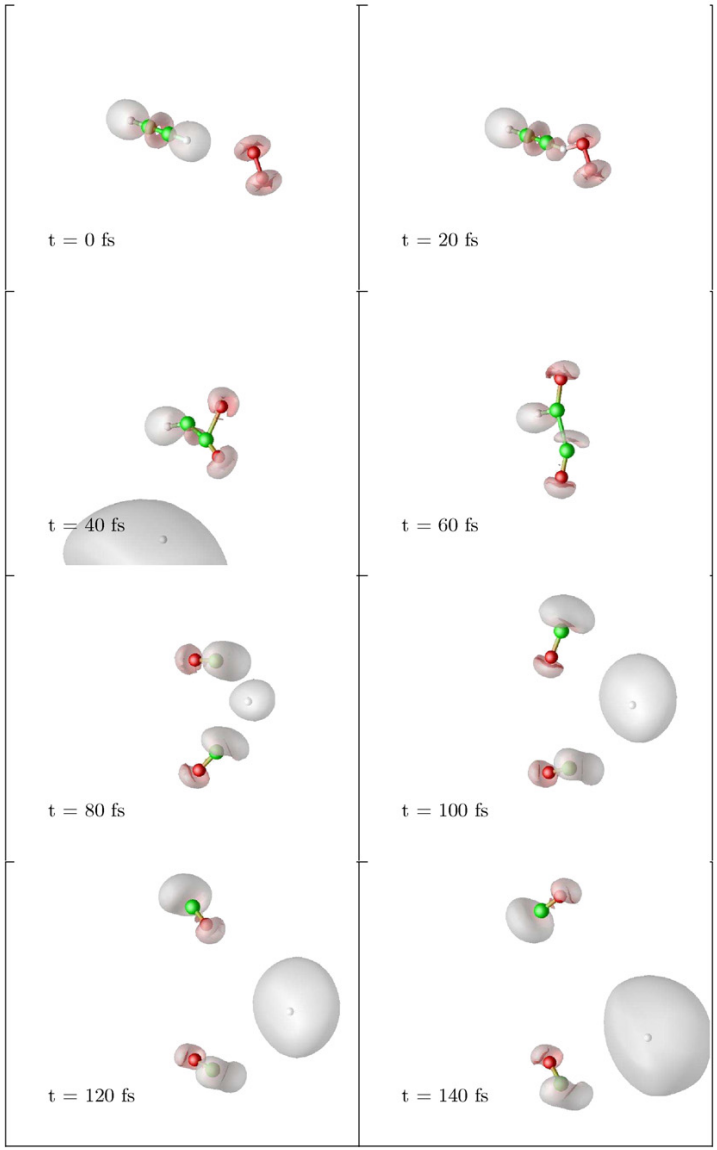
&\quad - \int \mathrm{d}^3r\, n(\mathbf{r},t) v_{\mathrm{ext}}^{electrons}(\mathbf{r},t)\,.
\end{aligned}$$

Example



- Combustion of acetylene.
- Calculation performed with Ehrenfest-MD based on TDDFT.
- The “clouds” represent the time-dependent electron localization function.