New Optimal Control Problems in Density Functional Theory motivated by Photovoltaics

Michael Kniely

joint work with Gero Friesecke

Annual Meeting of the GAMM Activity Group MOANSI
Zuse Institute Berlin, October 25–26, 2018

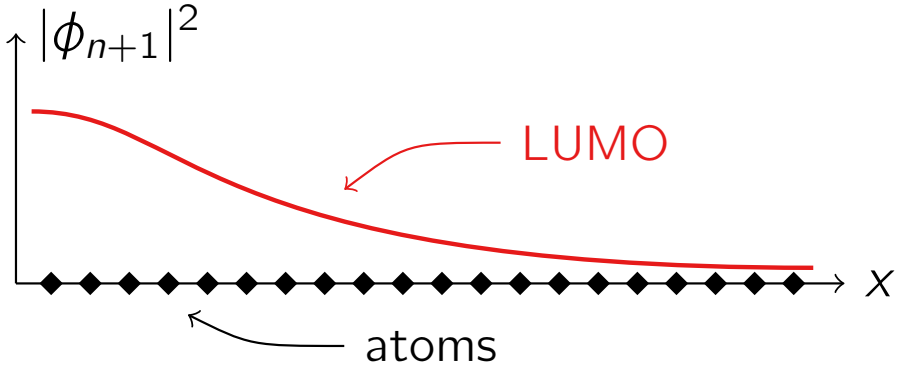
- G. Friesecke, M. K.
  New optimal control problems in density functional theory motivated by photovoltaics
  arXiv:1808.04200 [math.OC]

Table of Contents

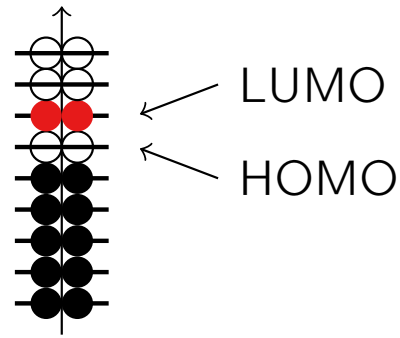
Motivation

- Photovoltaic devices convert light (photons) into current (electron motion).
- We employ a Kohn–Sham-DFT model with electronic orbitals ϕ_i.

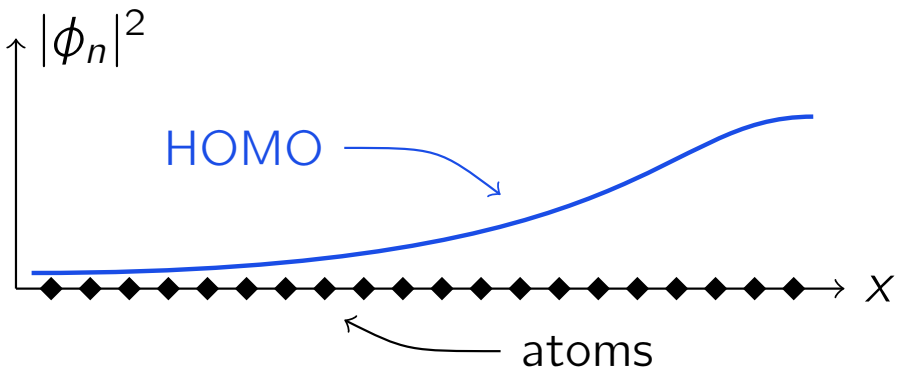
Excited state with occupied orbital $n+1$:



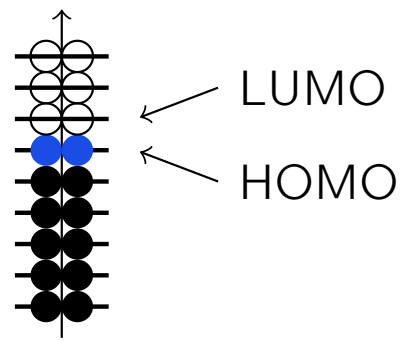
Energy of ϕ_i



Ground state with occupied orbital n:

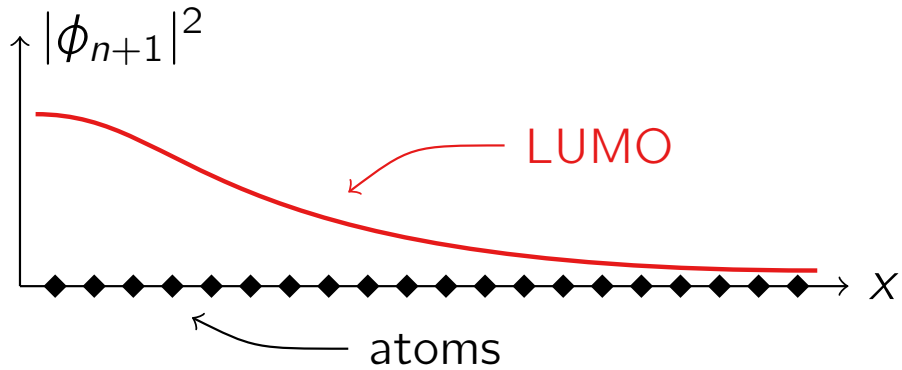


Energy of ϕ_i

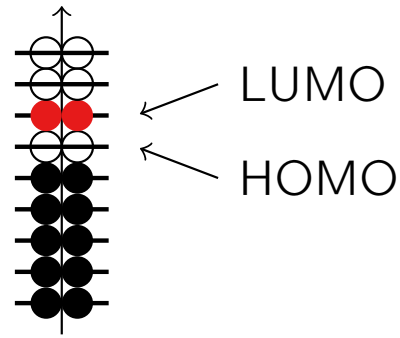


Motivation

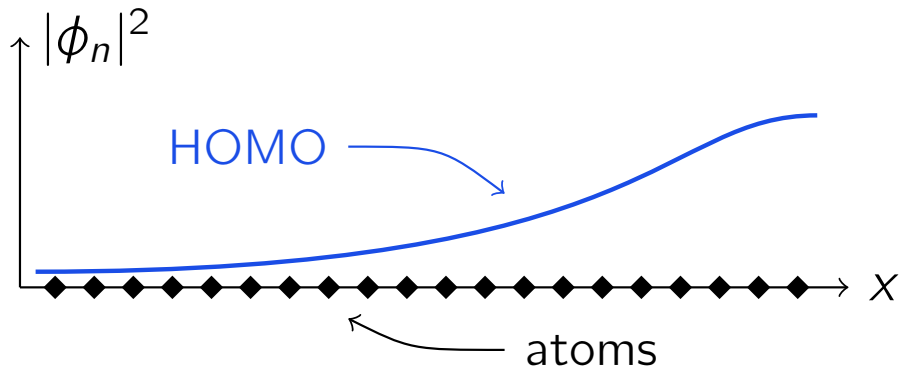
Excited state with occupied orbital $n+1$:



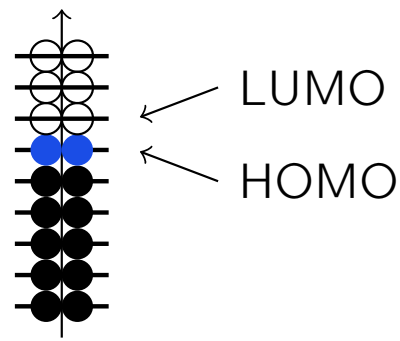
Energy of ϕ_i



Ground state with occupied orbital n:



Energy of ϕ_i



- We restrict ourselves to closed-shell electron configurations (no spin).
- Find a material such that the charge transfer from ϕ_n to ϕ_{n+1} is large.

Variational Principle for the Ground State Orbitals ϕ_i

Ground state orbitals satisfy $(\phi_1, \dots, \phi_n) \in \operatorname{argmin} \left\{ \mathcal{E}_\mu[\psi] \,\middle|\, \psi \in \mathcal{A} \right\}$ where

$$\mathcal{E}_\mu[\phi_1, \dots, \phi_n] := \underbrace{\sum_{i=1}^{n} \int_{\mathbb{R}^3} |\nabla \phi_i|^2}_{T[\phi]} \underbrace{- \int_{\mathbb{R}^3} \left(\frac{1}{|\cdot|} * \mu \right) \rho}_{V_{ext}[\rho]} \underbrace{+ \frac{1}{2} \int_{\mathbb{R}^3} \left(\frac{1}{|\cdot|} * \rho \right) \rho}_{J_H[\rho]}$$

denotes the Kohn–Sham energy functional (without exchange–correlation) and

$$\mathcal{A} := \left\{ \phi \in H_0^1(\Omega)^n \;\middle|\; \langle \phi_i, \phi_j \rangle_{L^2(\Omega)} = \delta_{ij} \right\}$$

equals the set of admissible electronic orbitals. The electronic density is given by $\rho := 2 \sum_{i=1}^{n} |\phi_i|^2$ and the nuclear density is contained in the set of admissible nuclear charge distributions supported in $\Omega_{nuc} \subset\subset \Omega$ ($\Omega \subset \mathbb{R}^3$ open, bounded):

$$\mu \in \mathcal{A}_{nuc} := \left\{ \nu \in \mathcal{M}(\Omega_{nuc}) \;\middle|\; \nu \geq 0,\ \nu(\Omega_{nuc}) = 2n \right\}.$$

Kohn–Sham Equations

Let $(\phi_1, \dots, \phi_n) \in \mathcal{A}$ be a minimizer of the unitary invariant

$$\mathcal{E}_\mu[\phi_1, \dots, \phi_n] := \underbrace{\sum_{i=1}^{n} \int_{\mathbb{R}^3} |\nabla \phi_i|^2}_{T[\phi]} \underbrace{- \int_{\mathbb{R}^3} \left(\frac{1}{|\cdot|} * \mu\right)\rho}_{V_{ext}[\rho]} \underbrace{+ \frac{1}{2} \int_{\mathbb{R}^3} \left(\frac{1}{|\cdot|} * \rho\right)\rho}_{J_H[\rho]}.$$

We perform a variation of each ϕ_i under the orthonormality constraints $\langle \phi_i, \phi_j \rangle_{L^2(\Omega)} = \delta_{ij}$. By a unitary transformation of $\phi_1, \dots, \phi_n$, one obtains $\varepsilon_i \in \mathbb{R}$ such that $\phi_1, \dots, \phi_n$ satisfy the Kohn–Sham equations

$$h_\phi \phi_i := \left(-\frac{1}{2}\Delta \underbrace{- \frac{1}{|\cdot|} * \mu}_{v_{ext}} \underbrace{+ \frac{1}{|\cdot|} * \rho}_{v_H} \right) \phi_i = \varepsilon_i \phi_i.$$

The operator h_ϕ is the Kohn–Sham Hamiltonian (without exchange–correlation).

Schrödinger Equation vs. Kohn–Sham Equations

Consider a system of n electrons in $\mathbb{R}^3$.

Schrödinger equation	Kohn–Sham equations
$H\psi = \varepsilon\psi, \quad \psi : \mathbb{R}^{3n} \to \mathbb{C},$	$h_\phi \phi_i = \varepsilon_i \phi_i, \ \phi_i : \mathbb{R}^3 \to \mathbb{C}, \ 1 \le i \le n$
$H = \sum_{i=1}^{n} -\frac{1}{2}\Delta_i + \sum_{i=1}^{n} V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j)$	$h_\phi = -\frac{1}{2}\Delta + v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{xc}[\rho(\vec{r})]$

Schrödinger Equation vs. Kohn–Sham Equations

Consider a system of n electrons in $\mathbb{R}^3$.

Schrödinger equation	Kohn–Sham equations
$H\psi = \varepsilon\psi, \quad \psi : \mathbb{R}^{3n} \to \mathbb{C},$	$h_\phi \phi_i = \varepsilon_i \phi_i, \ \phi_i : \mathbb{R}^3 \to \mathbb{C}, \ 1 \le i \le n$
$H = \sum_{i=1}^{n} -\frac{1}{2}\Delta_i + \sum_{i=1}^{n} V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j)$	$h_\phi = -\frac{1}{2}\Delta + v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{xc}[\rho(\vec{r})]$

Now, discretize $\mathbb{R}$ with 100 points.

Schrödinger equation	Kohn–Sham equations
$\overline{H}\,\overline{\psi} = \varepsilon\overline{\psi},$	$\overline{h_\phi}\,\overline{\phi}_i = \varepsilon\overline{\phi}_i, \quad \overline{\phi}_i \in \mathbb{C}^{10^6}$
$\overline{\psi} \in \mathbb{C}^{10^{6n}}$	$\overline{\phi} := (\overline{\phi}_i)_i \in \mathbb{C}^{10^6 n}$

- Kohn–Sham equations are much more efficient for many-body systems.

HOMO and LUMO

We set $\rho_\chi = |\chi|^2$ and introduce the excitation functional

$$\mathcal{E}_{\mu,\phi}[\chi] := \langle \chi,\, h_\phi \chi \rangle = \frac{1}{2}\int_\Omega |\nabla \chi|^2 - \int_\Omega \Big(\frac{1}{|\cdot|} * \mu\Big)\rho_\chi + \int_\Omega \Big(\frac{1}{|\cdot|} * \rho\Big)\rho_\chi.$$

A HOMO is then defined by $\phi_H \in \operatorname{argmax}\Big\{\mathcal{E}_{\mu,\phi}[\chi] \,\Big|\, \chi \in \mathcal{A}_\phi^H\Big\}$ where

$$\mathcal{A}_\phi^H := \Big\{\phi_H \in \operatorname{Span}\{\phi_1, \ldots, \phi_n\} \,\Big|\, \langle \phi_H, \phi_H\rangle = 1\Big\},$$

and a LUMO is defined by $\phi_L \in \operatorname{argmin}\Big\{\mathcal{E}_{\mu,\phi}[\chi] \,\Big|\, \chi \in \mathcal{A}_\phi^L\Big\}$ where

$$\mathcal{A}_\phi^L := \Big\{\phi_L \in \operatorname{Span}\{\phi_1, \ldots, \phi_n\}^\perp \,\Big|\, \langle \phi_L, \phi_L\rangle = 1\Big\}.$$

Obviously, $h_\phi \phi_H = \varepsilon_H \phi_H$ and $h_\phi \phi_L = \varepsilon_L \phi_L$ with $\varepsilon_H, \varepsilon_L \in \mathbb{R}$. Typically, we have $\varepsilon_H = \varepsilon_n$ and $\varepsilon_L = \varepsilon_{n+1}$, where $\varepsilon_1 \le \varepsilon_2 \le \ldots$ are the eigenvalues of h_ϕ [FG2018].

Optimal Control Problem

We start with a desirable physical property of the excitation, and formulate a mathematical goal functional J measuring the presence of the desired property.

We then solve the following OPC to find an optimal nuclear density $\mu \in \mathcal{A}_{nuc}$:

$$\min J[\phi, \phi_H, \phi_L, \mu]$$

over all $(\phi, \phi_H, \phi_L, \mu) \in \mathcal{A} \times \mathcal{A}_\phi^H \times \mathcal{A}_\phi^L \times \mathcal{A}_{nuc}$ such that

(i) $(\phi_1, \ldots, \phi_n)$ are ground state orbitals,

(ii) ϕ_H is a HOMO,

(iii) ϕ_L is a LUMO

corresponding to μ.

Among other choices, we will later specify J to be the charge transfer functional which measures the spatial separation between HOMO and LUMO.

Properties of the Kohn–Sham Energy Functional

We have the following bounds and continuity properties for

$$\mathcal{E}_\mu[\phi_1,\dots,\phi_n] := \underbrace{\sum_{i=1}^n \int_{\mathbb{R}^3} |\nabla\phi_i|^2}_{T[\phi]} \underbrace{- \int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \mu\Big)\rho}_{V_{ext}[\rho]} \underbrace{+ \frac{1}{2}\int_{\mathbb{R}^3} \Big(\frac{1}{|\cdot|} * \rho\Big)\rho}_{J_H[\rho]}.$$

Lemma

- $T[\phi] \geq \frac{1}{2} T[\phi] + c\|\rho\|_3$ with some $c > 0$, and

  $\phi \mapsto T[\phi]$ is continuous and weakly lower semicontinuous on $H^1(\Omega)^n$.

- $V_{ext}[\rho] \geq -\|\mu\|_{\mathcal{M}} \sup_{a\in\mathbb{R}^3} \Big\| \frac{1}{|\cdot - a|} \Big\|_2 \|\rho\|_1^{1/4} \|\rho\|_3^{3/4}$, and

  $(\phi, \mu) \mapsto V_{ext}[\rho]$ is strong $\times$ weak* continuous on $L^4(\Omega)^n \times \mathcal{M}(\Omega_{nuc})$.

- $J_H[\rho] \geq 0$, and $\phi \mapsto J_H[\rho]$ is continuous on $L^{12/5}(\mathbb{R}^3)^n$.

Properties of the Excitation Functional

Together with $\rho_\chi = |\chi|^2$, similar results are valid for

$$\mathcal{E}_{\mu,\phi}[\chi] := \langle \chi,\, h_\phi \chi \rangle = \frac{1}{2}\int_\Omega |\nabla\chi|^2 - \int_\Omega \Big(\frac{1}{|\cdot|} * \mu\Big)\rho_\chi + \int_\Omega \Big(\frac{1}{|\cdot|} * \rho\Big)\rho_\chi.$$

Lemma

- $\displaystyle\int_\Omega |\nabla\chi|^2 \geq \frac{1}{2}\int_\Omega |\nabla\chi|^2 + c\|\rho_\chi\|_3$ with some $c > 0$, and

  $\chi \mapsto \int_\Omega |\nabla\chi|^2$ is continuous and weakly lower semicontinuous on $H^1(\Omega)$.

- $\displaystyle\int_\Omega v_{ext}\,\rho_\chi \geq -\|\mu\|_{\mathcal{M}} \sup_{a\in\mathbb{R}^3} \Big\|\frac{1}{|\cdot - a|}\Big\|_2 \|\rho_\chi\|_1^{1/4}\|\rho_\chi\|_3^{3/4}$, and

  $(\chi,\mu) \mapsto \int v_{ext}\,\rho_\chi$ is strong $\times$ weak* continuous on $L^4(\Omega)\times\mathcal{M}(\Omega_{nuc})$.

- $\displaystyle\int_\Omega \Big(\frac{1}{|\cdot|} * \rho\Big)\rho_\chi \geq 0$ and $(\phi,\chi) \mapsto \int \big(\frac{1}{|\cdot|} * \rho\big)\rho_\chi$ is continuous on $L^{12/5}(\Omega)^{n+1}$.

Existence of Ground State Orbitals, HOMO and LUMO

Lemma

- $\mathcal{A}$ is weakly closed in $H^1(\Omega)^n$.
- For any $\phi \in \mathcal{A}$, the sets $\mathcal{A}_\phi^H$ and $\mathcal{A}_\phi^L$ are weakly closed in $H^1(\Omega)$.

Existence of Ground State Orbitals, HOMO and LUMO

Lemma

- $\mathcal{A}$ is weakly closed in $H^1(\Omega)^n$.
- For any $\phi \in \mathcal{A}$, the sets $\mathcal{A}_\phi^H$ and $\mathcal{A}_\phi^L$ are weakly closed in $H^1(\Omega)$.

Proposition

For any $\mu \in \mathcal{A}_{nuc}$, there exists a minimizing set of orbitals ϕ for the Kohn–Sham energy functional $\mathcal{E}_\mu[\phi]$ on the admissible set $\mathcal{A}$.

Proposition

For any $\mu \in \mathcal{A}_{nuc}$ and any set of orbitals $\phi \in \mathcal{A}$, the excitation functional $\mathcal{E}_{\mu,\phi}[\chi]$ possesses a maximizer ϕ_H on $\mathcal{A}_\phi^H$ and a minimizer ϕ_L on $\mathcal{A}_\phi^L$.

The Set of HOMO–LUMO Excitations

Theorem

The joint solution set for occupied KS orbitals, HOMO, and LUMO parametrized by the set of nuclear charge distributions μ,

$$\mathcal{B} := \Big\{ (\phi, \phi_H, \phi_L, \mu) \,\Big|\, \mu \in \mathcal{A}_{nuc},\ \phi \in \operatorname{argmin} \Big\{ \mathcal{E}_\mu[\psi] \,\Big|\, \psi \in \mathcal{A} \Big\},$$
$$\phi_H \in \operatorname{argmax} \Big\{ \mathcal{E}_{\mu,\phi}[\chi] \,\Big|\, \chi \in \mathcal{A}_\phi^H \Big\}$$
$$\phi_L \in \operatorname{argmin} \Big\{ \mathcal{E}_{\mu,\phi}[\chi] \,\Big|\, \chi \in \mathcal{A}_\phi^L \Big\} \Big\},$$

has the following properties:

(1) It is weak $\times$ weak* closed in $H^1(\Omega)^{n+2} \times \mathcal{M}(\Omega_{nuc})$.

(2) It is strong $\times$ weak* compact in $H^1(\Omega)^{n+2} \times \mathcal{M}(\Omega_{nuc})$.

The Set of HOMO–LUMO Excitations

Sketch of Proof for (1). Let $\left(\phi^{(k)}, \phi_H^{(k)}, \phi_L^{(k)}\right) \rightharpoonup (\phi, \phi_H, \phi_L)$ in $H^1(\Omega)^{n+2}$ and $\mu^{(k)} \overset{*}{\rightharpoonup} \mu$ in $\mathcal{M}(\Omega_{nuc})$. We need to check that (a) $\phi \in \operatorname{argmin}_{\mathcal{A}} \mathcal{E}_\mu$, (b) $\phi_H \in \operatorname{argmax}_{\mathcal{A}_\phi^H} \mathcal{E}_{\mu,\phi}$, (c) $\phi_L \in \operatorname{argmin}_{\mathcal{A}_\phi^L} \mathcal{E}_{\mu,\phi}$, (d) $\mu \in \mathcal{A}_{nuc}$.

We only prove (a). For fixed $\psi \in \mathcal{A}$, we have

$$\mathcal{E}_{\mu^{(k)}}[\phi^{(k)}] \leq \mathcal{E}_{\mu^{(k)}}[\psi] \to \mathcal{E}_\mu[\psi]$$

and, hence, $\limsup_{k\to\infty} \mathcal{E}_{\mu^{(k)}}[\phi^{(k)}] \leq \mathcal{E}_\mu[\psi]$. Since $\psi \in \mathcal{A}$ was arbitrary, we obtain

$$\limsup_{k\to\infty} \mathcal{E}_{\mu^{(k)}}[\phi^{(k)}] \leq \inf_{\mathcal{A}} \mathcal{E}_\mu.$$

And the weak $\times$ weak* lower semicontinuity of $(\phi, \mu) \mapsto \mathcal{E}_\mu[\phi]$ gives rise to

$$\liminf_{k\to\infty} \mathcal{E}_{\mu^{(k)}}[\phi^{(k)}] \geq \mathcal{E}_\mu[\phi].$$

By the weak closedness of $\mathcal{A}$, we know that $\phi \in \mathcal{A}$ and, hence, $\mathcal{E}_\mu[\phi] = \inf_{\mathcal{A}} \mathcal{E}_\mu$.

The Set of HOMO–LUMO Excitations

Sketch of Proof for (2). Let $\left(\phi^{(k)}, \phi_H^{(k)}, \phi_L^{(k)}, \mu^{(k)}\right) \in \mathcal{B}$. First, $\phi^{(k)}$, $\phi_H^{(k)}$ and $\phi_L^{(k)}$ are bounded in $H^1(\Omega)^n$ and $H^1(\Omega)$, respectively. As $\mu^{(k)} \in \mathcal{A}_{nuc}$, we have

$$\left\|\mu^{(k)}\right\|_{\mathcal{M}} = \mu^{(k)}(\Omega_{nuc}) = 2n.$$

Thus, along a subsequence, $\left(\phi^{(k)}, \phi_H^{(k)}, \phi_L^{(k)}\right) \rightharpoonup \left(\phi, \phi_H, \phi_L\right) \in H^1(\Omega)^{n+2}$ and $\mu^k \overset{*}{\rightharpoonup} \mu \in \mathcal{M}(\Omega_{nuc})$. From the proof of (1), we further conclude that

$$\mathcal{E}_{\mu^{(k)}}[\phi^{(k)}] \to \mathcal{E}_{\mu}[\phi].$$

But as $V_{ext}^k[\rho^k] \to V_{ext}[\rho]$ and $J_H[\rho^k] \to J_H[\rho]$, the kinetic energy satisfies

$$T[\phi^{(k)}] \to T[\phi].$$

Now, $\nabla\phi^{(k)} \rightharpoonup \nabla\phi$ in L^2 and $||\nabla\phi^{(k)}||_2 \to ||\nabla\phi||_2$. This implies $\nabla\phi^{(k)} \to \nabla\phi$ in L^2, $\phi^{(k)} \to \phi$ in $(H^1)^n$ and $\phi_H^{(k)} \to \phi_H$ in H^1. Similarly, $\phi_L^{(k)} \to \phi_L$ in H^1. □

Existence of Optimal Excitations

Theorem

The optimal control problem to maximize or minimize $J[\phi, \phi_H, \phi_L, \mu]$ over

$$\mathcal{B} = \Big\{ (\phi, \phi_H, \phi_L, \mu) \,\Big|\, \mu \in \mathcal{A}_{nuc},\ \phi \in \operatorname{argmin} \Big\{ \mathcal{E}_\mu[\psi] \,\Big|\, \psi \in \mathcal{A} \Big\},$$
$$\phi_H \in \operatorname{argmax} \Big\{ \mathcal{E}_{\mu,\phi}[\chi] \,\Big|\, \chi \in \mathcal{A}_\phi^H \Big\}$$
$$\phi_L \in \operatorname{argmin} \Big\{ \mathcal{E}_{\mu,\phi}[\chi] \,\Big|\, \chi \in \mathcal{A}_\phi^L \Big\} \Big\},$$

possesses a solution whenever $J[\phi, \phi_H, \phi_L, \mu]$ is continuous on $\mathcal{B}$ with respect to strong $\times$ weak* convergence in $H^1(\Omega)^{n+2} \times \mathcal{M}(\Omega_{nuc})$.

Time Evolution of Excited States

We assume that the time evolution after excitation is governed by

time-dependent density functional theory (TDDFT),

with the static map from density to exchange-correlation potential known as the

adiabatic local density approximation (ALDA).

With the KS orbitals ϕ, the HOMO ϕ_H, and the LUMO ϕ_L, we have

$$i\partial_t \phi'_j(\cdot, t) = h_{\phi'(\cdot,t)}\phi'_j(\cdot, t), \qquad \phi'_j(\cdot, 0) = \phi'_j$$

for all $1 \leq j \leq n$. The new electronic density contributing to $h_{\phi'(\cdot,t)}$ reads

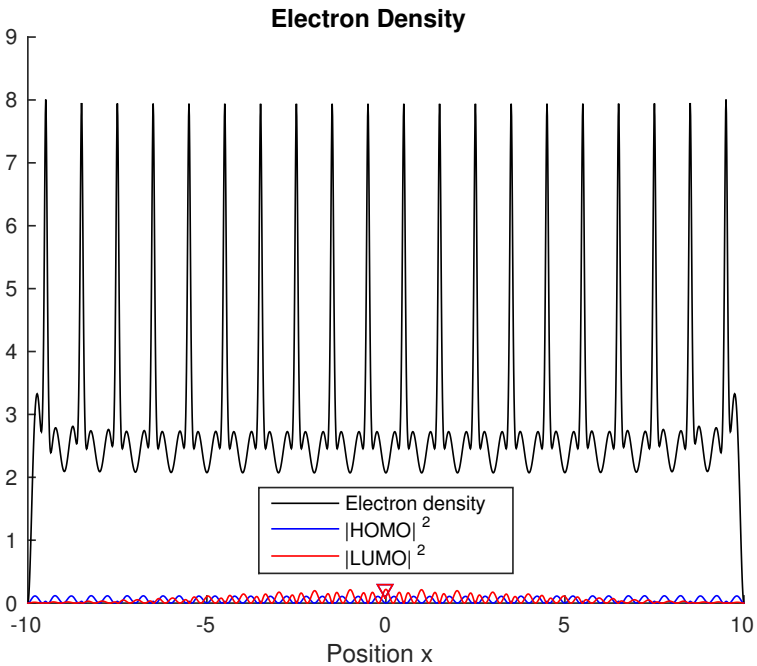
$$\rho'(\cdot, t) = 2\sum_{j=1}^{n} |\phi'_j(\cdot, t)|^2$$

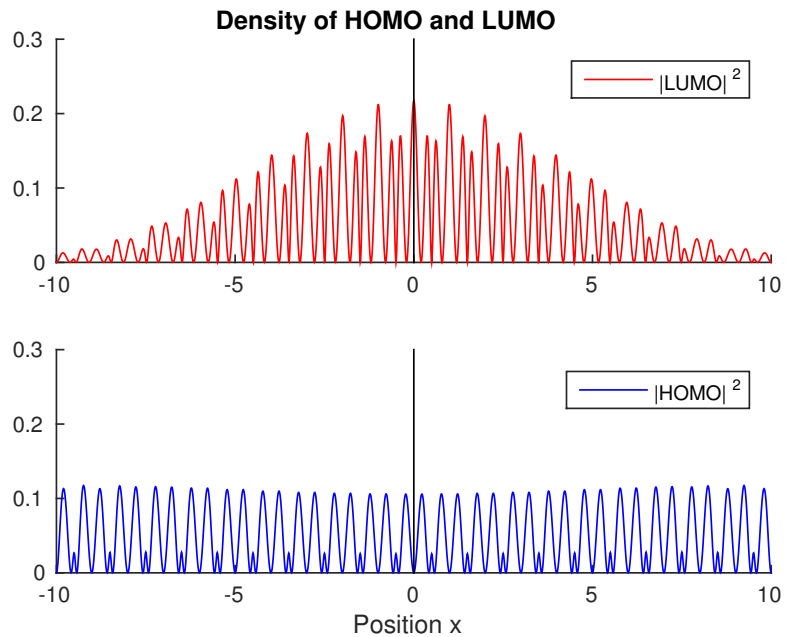
and the initial conditions are given by the new orbitals after excitation:

$$\begin{cases} \phi'_1, ..., \phi'_{n-1} \text{ form an ONB of } \left\{\chi \in \operatorname{Span}\{\phi_1, ..., \phi_n\} \,\middle|\, \langle \phi_H, \chi\rangle = 0\right\}, \\ \phi'_n = \phi_L. \end{cases}$$

Electronic Orbitals of a Pure Carbon Chain

- Ground State: Orbitals 1 – 60 doubly occupied

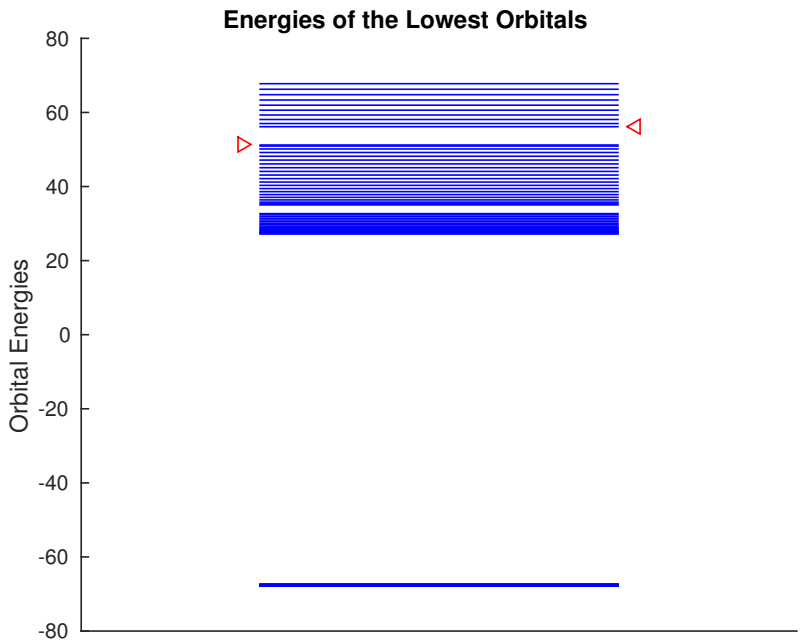


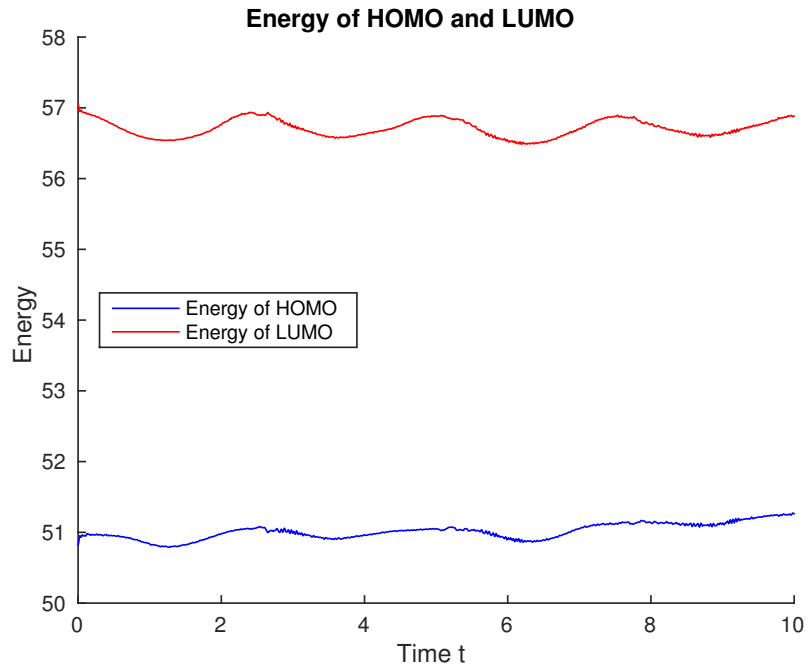


- Electronic density is almost periodic up to the boundary
- HOMO and LUMO are symmetric with respect to the origin

Orbital Energies of a Pure Carbon Chain

- Excited State: Orbitals 1 – 59 and 61 doubly occupied



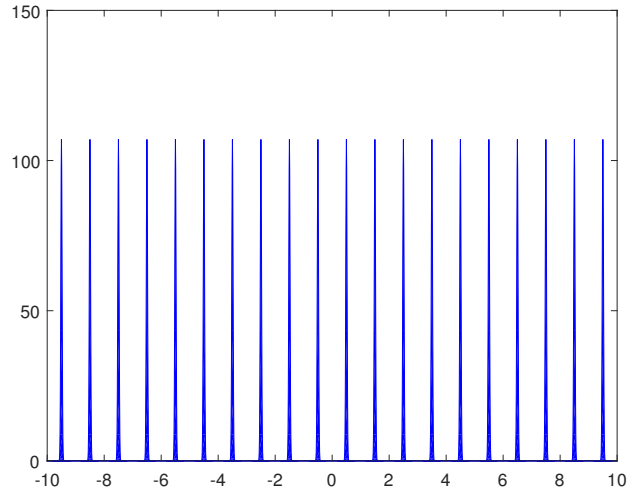


- Band structure with core states and a pronounced bandgap
- Bandgap between HOMO and LUMO is stable under time evolution

1D Optimal Control Problem

We consider

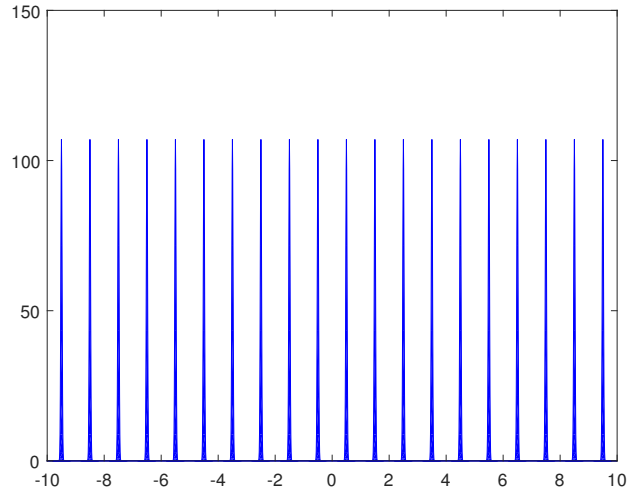
- 20 equidistant atoms at $p_j \in [-10, 10]$
- atomic cores as sharply peaked Gaussians
- a pure carbon chain as the starting point



1D Optimal Control Problem

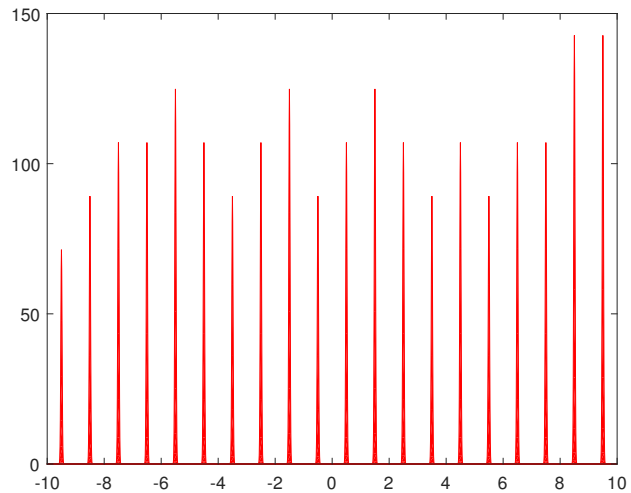
We consider

- 20 equidistant atoms at $p_j \in [-10, 10]$
- atomic cores as sharply peaked Gaussians
- a pure carbon chain as the starting point



Within the optimization procedure, we

- only vary the proton numbers of the atoms
- preserve the total number of protons
- stick to the elements Lithium, . . . , Fluorine



1D Optimal Control Problem

$$\max J[\mu] = \left| \int_{-10}^{10} x \left(|\phi_{60}|^2 - |\phi_{61}|^2 \right) \, dx \right|$$

where ϕ_i is the i-th electronic eigenstate of the Kohn–Sham Hamiltonian

$$h_\phi = -\frac{1}{2}\frac{d^2}{dx^2} + V$$

corresponding to the i-th lowest eigenvalue ε_i. Hence, $h_\phi \phi_i = \varepsilon_i \phi_i$. For the Kohn–Sham potential V, we only take the Coulomb part into account:

$$V = v_d * (\rho - \mu)$$

with an effective potential [BSCA2003, CF2015]

$$v_d(x) = \frac{\sqrt{\pi}}{2d} \exp\left(\frac{x^2}{4d^2}\right) \operatorname{erfc}\left(\frac{x}{2d}\right).$$

1D Optimal Control Problem

$$\max J[\mu] = \left| \int_{-10}^{10} x \left(|\phi_{60}|^2 - |\phi_{61}|^2 \right) \, dx \right|$$

where

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + v_d * (\rho - \mu) \right) \phi_i = \varepsilon_i \phi_i$$

and

$$\rho = 2 \sum_{i=1}^{60} |\phi_i|^2, \qquad \mu = \sum_{j=1}^{20} a_j \mathcal{N}(p_j, \sigma^2).$$

We optimize J w.r.t. $(a_j)_{j=1}^{20}$, the proton numbers of the corresponding atoms, while preserving the number of protons and restricting to seven elements:

$$\sum_{j=1}^{20} a_j = 120 \quad \text{and} \quad 3 \leq a_j \leq 9.$$

Numerical Scheme for the 1D Problem

Algorithm 1: Find a "local maximum" of the charge transfer functional J

Input: n, p, $iter$

Output: a

begin

$a \leftarrow (6)_{i=1}^{20}$

for $i = 1 : iter$ **do**

generate $n(i)$ random directions $h \in \{-1, 0, 1\}^{20}$ with $P(1) = P(-1) = p(i)$, $\sum_{k=1}^{20} h_k = 0$ and $a + h \in ([3, 9] \cap \mathbb{Z})^{20}$

$a \leftarrow a + t_* h_*$ where $t_* \in \{-1, 0, 1\}$ and $a + t_* h_*$ yields the maximal $J[a + th]$ among all admissible $t \in \{-1, 0, 1\}$ and h generated so far

Numerical Scheme for the 1D Problem

We perform four iterations using the following values for $n(i)$ and $p(i)$:

i	1	2	3	4
Number of directions $n(i)$	10	20	40	80
Probability $p(i)$ for $h_j = 1$	1/3	1/6	1/12	1/24

$p(i) = 1/3 \cdot 2^{-i+1}$

- $p(5) = 1/48 < 1/20 \;\Rightarrow$ almost no difference between the fourth and a fifth step concerning the sparsity of the search directions

$n(i) = 10 \cdot 2^{i-1}$

- more detailed exploration of the approximately 3^{20} admissible directions in the space $\{3, \ldots, 9\}^{20}$ for smaller step sizes

Output of the Optimization Algorithm

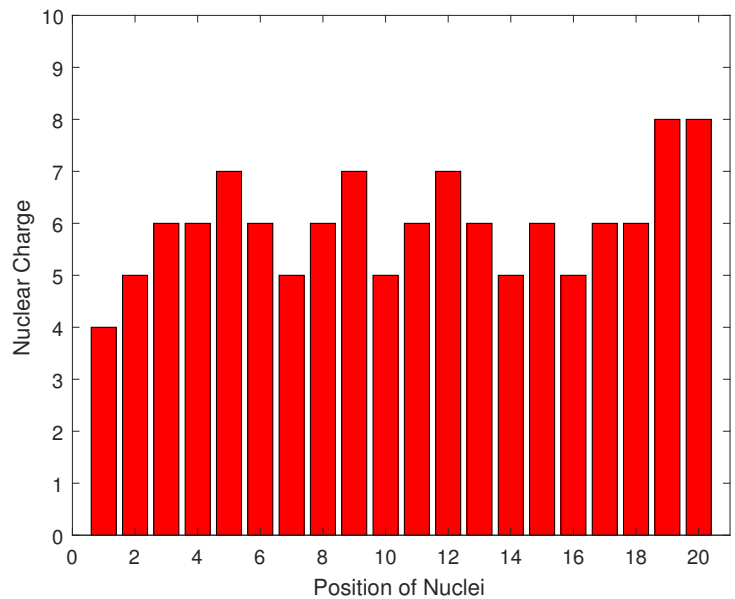
Our optimization technique iteratively improves the atomic configuration and finishes after four iterations. We initialize the algorithm with $a^{(0)} = (6)_{i=1}^{20}$.

$$\begin{cases} a^{(1)} = (5\ 5\ 7\ 5\ 6\ 5\ 5\ 6\ 7\ 5\ldots \\ \qquad 6\ 7\ 5\ 5\ 6\ 7\ 7\ 7\ 7\ 7) \\ J[a^{(1)}] = 12.2992 \end{cases}$$

$$\begin{cases} a^{(2)} = (4\ 4\ 6\ 5\ 7\ 5\ 5\ 6\ 7\ 5\ldots \\ \qquad 6\ 7\ 6\ 5\ 6\ 6\ 7\ 7\ 8\ 8) \\ J[a^{(2)}] = 15.2400 \end{cases}$$

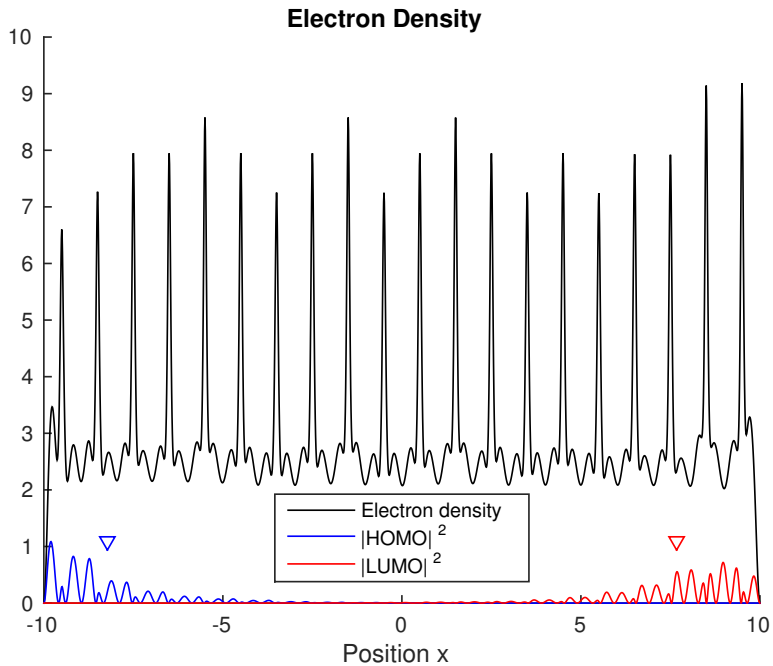
$$\begin{cases} a^{(3)} = (4\ 4\ 7\ 6\ 7\ 6\ 5\ 6\ 7\ 5\ldots \\ \qquad 6\ 7\ 6\ 5\ 6\ 5\ 6\ 6\ 8\ 8) \\ J[a^{(3)}] = 15.8363 \end{cases}$$

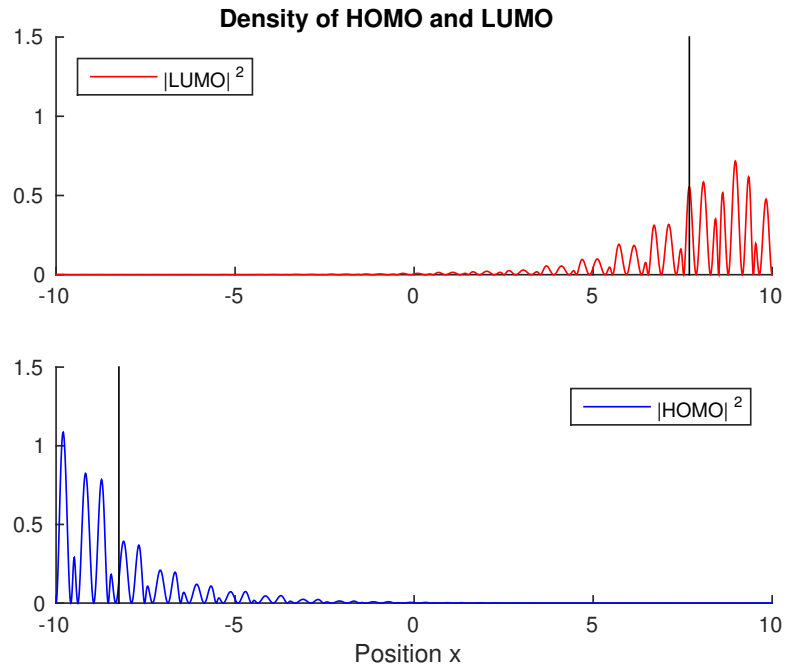
$$\begin{cases} a^{(4)} = (4\ 5\ 6\ 6\ 7\ 6\ 5\ 6\ 7\ 5\ldots \\ \qquad 6\ 7\ 6\ 5\ 6\ 5\ 6\ 6\ 8\ 8) \\ J[a^{(4)}] = 15.9321 \end{cases}$$



Ground State for the "Optimal" Nuclear Density

- Ground State: Orbitals 1 – 60 doubly occupied

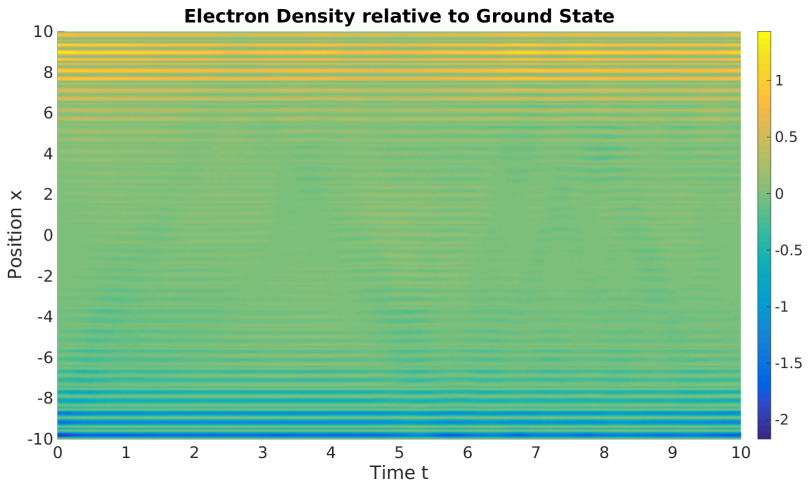


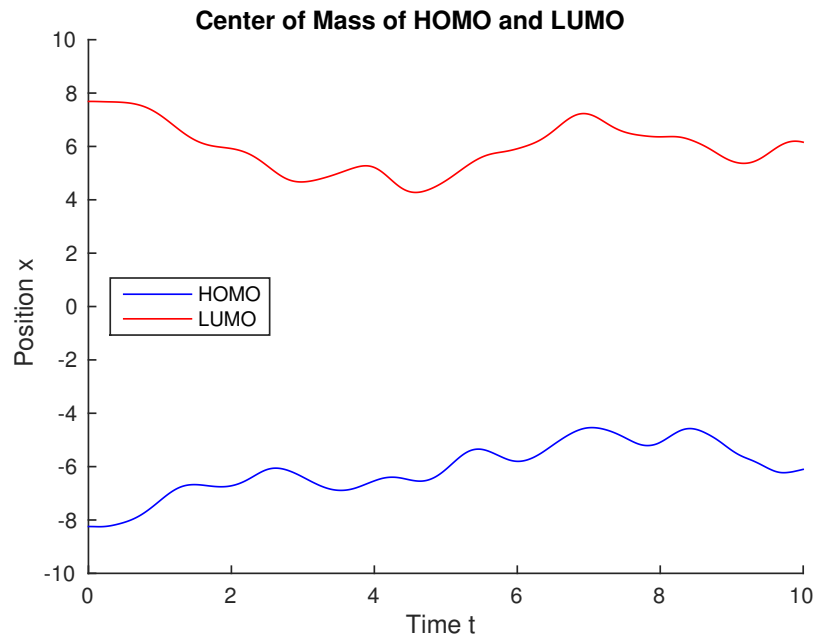


- Electronic density resembles the distribution of nuclear charges
- HOMO and LUMO are accumulated to opposite sides of the system

Temporal Evolution of the Excited State

- Excited State: Orbitals 1 – 59 and 61 doubly occupied





- Charge transfer persistent over (at least) 10 atomic units of time
- Average position of CoM of HOMO and LUMO slightly varies with time

Maximal Lifetime

We minimize the inverse lifetime functional L of a nuclear configuration:

$$L(\phi, \phi_h, \phi_L) := \left\| [h_{exc}, \gamma_{exc}] \right\|_{HS}^2 = 2 \sum_{i \ occ.exc.} \left\| (I - \gamma_{exc})(h_{exc} - h_{grd})\phi_i \right\|_2^2$$

where γ_{exc} is the density matrix of occupied orbitals in the excited state.

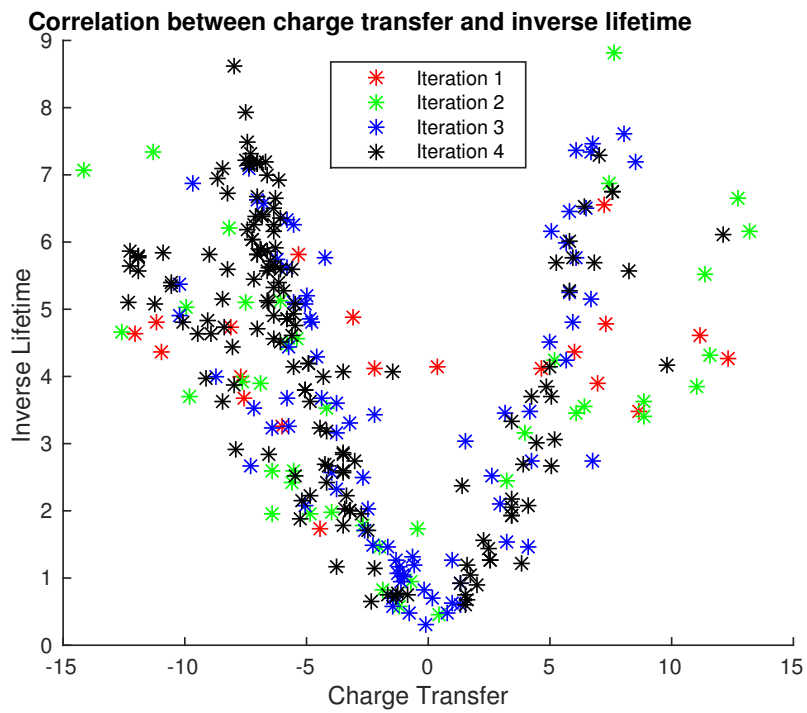
Maximal Lifetime

We minimize the inverse lifetime functional L of a nuclear configuration:

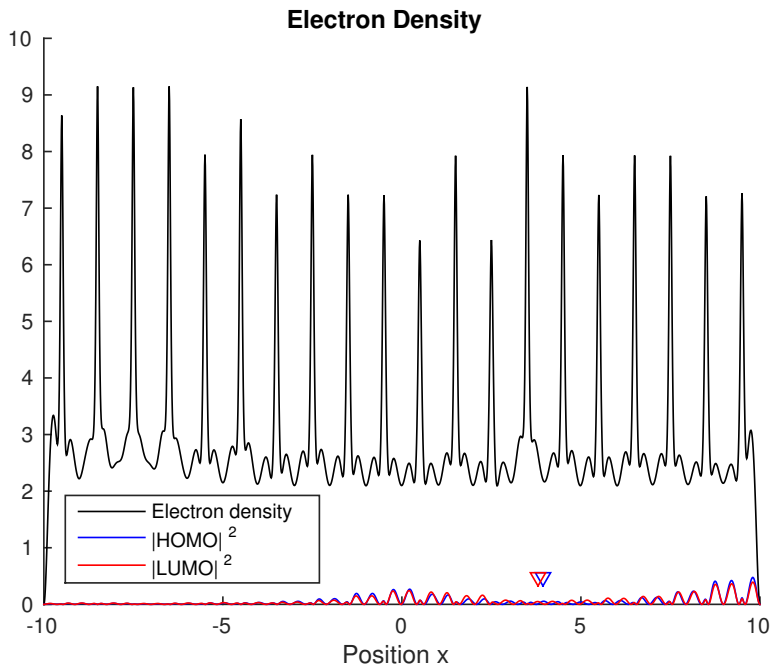
$$L(\phi, \phi_h, \phi_L) := \left\| [h_{exc}, \gamma_{exc}] \right\|_{HS}^2 = 2 \sum_{i \ occ.exc.} \left\| (I - \gamma_{exc})(h_{exc} - h_{grd})\phi_i \right\|_2^2$$

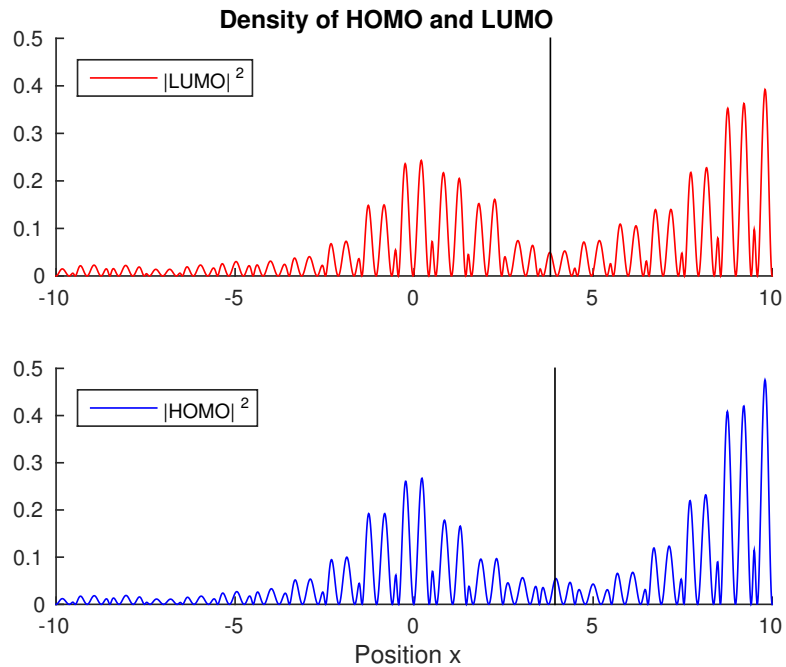
where γ_{exc} is the density matrix of occupied orbitals in the excited state.

- Simplified structure of L due to $[h_{grd}, \gamma_{exc}] = 0$
- Remarkable correlation between inverse lifetime and charge transfer
- Upper bound for lifetime for given charge transfer?



Maximal Lifetime





- Nuclear charge is asymmetric and "opposite" to HOMO and LUMO
- Nearly identical shapes of HOMO and LUMO $\Rightarrow h_{exc} \approx h_{grd} \Rightarrow L$ small

Minimal Overlap

It might also be feasible to minimize the spatial overlap functional O:

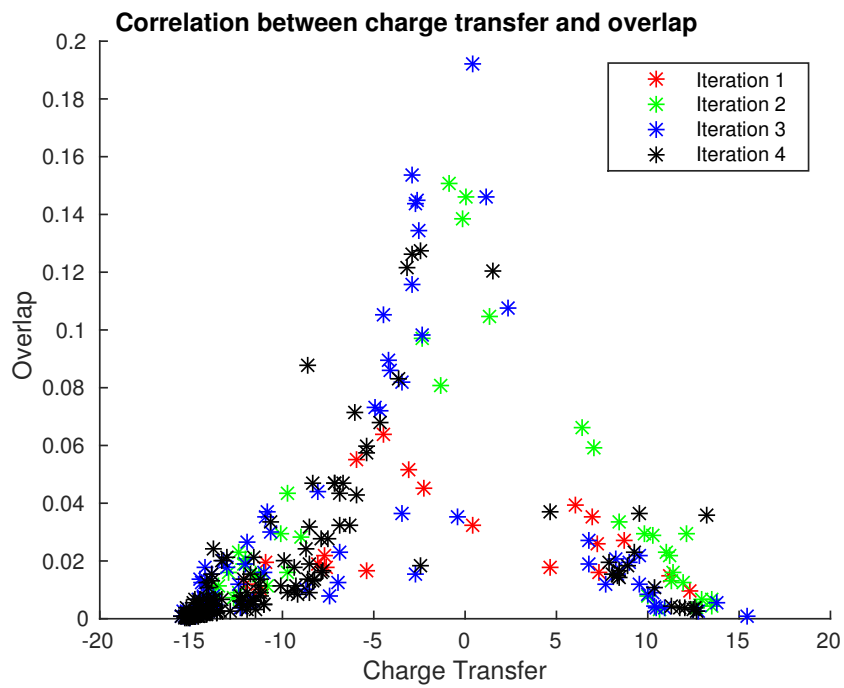
$$O(\phi_H, \phi_L) := \int_\Omega |\phi_H|^2 |\phi_L|^2 \, dx.$$

Minimal Overlap

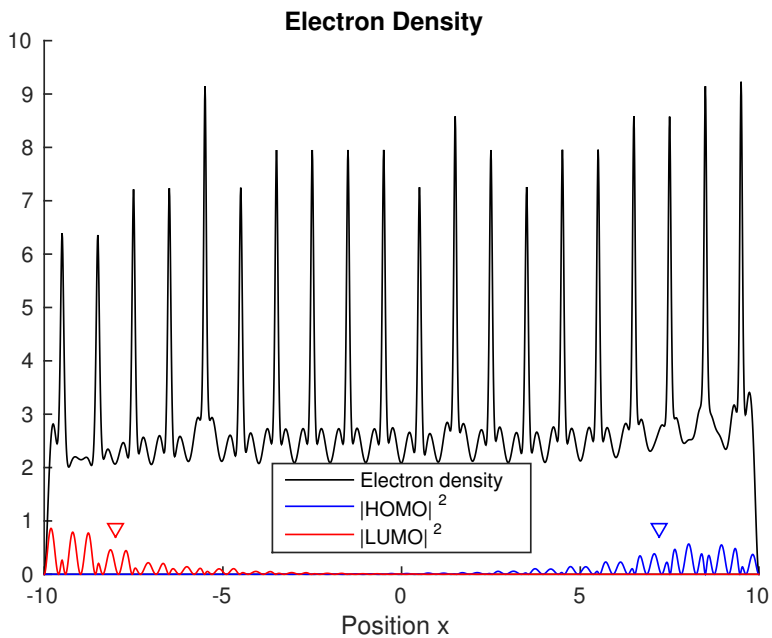
It might also be feasible to minimize the spatial overlap functional O:

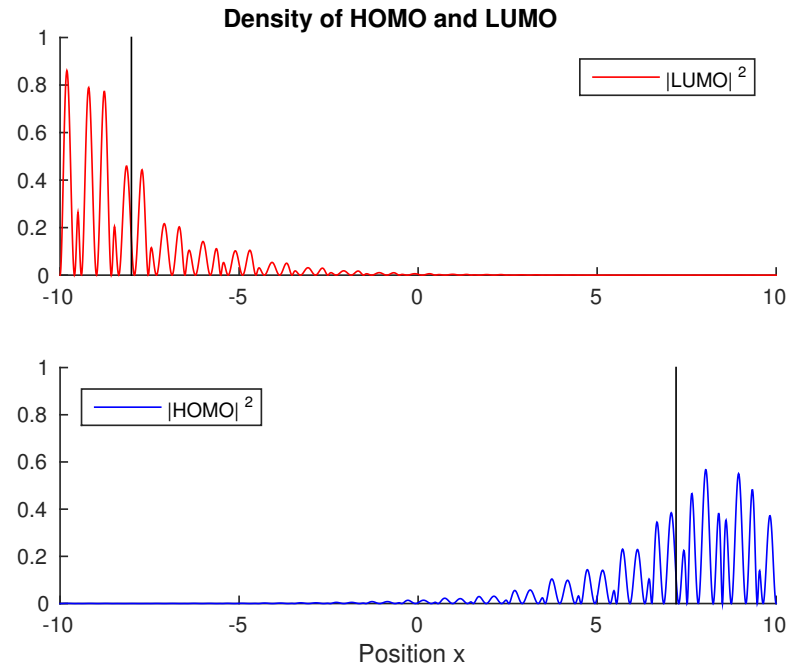
$$O(\phi_H, \phi_L) := \int_\Omega |\phi_H|^2 |\phi_L|^2 \, dx.$$

- $|\cdot|^2$ due to orthogonality of ϕ_H and ϕ_L
- Inverse correlation between spatial overlap and charge transfer
- Increasing concentration of iterates to certain regions?



Minimal Overlap





- HOMO and LUMO are separated on opposite sides of the domain
- Similar results as in the case of maximal charge transfer

Bandgap Design

In analogy to the position separation, one can also design the energy separation:

$$B(\phi, \phi_H, \phi_L, \mu) := \langle \phi_L \mid h_{grd} \mid \phi_L \rangle - \langle \phi_H \mid h_{grd} \mid \phi_H \rangle.$$

In fact, $J = \mathrm{tr}(x(\gamma_{exc} - \gamma_{grd}))$ and $B = \mathrm{tr}(h_{grd}(\gamma_{exc} - \gamma_{grd}))$.

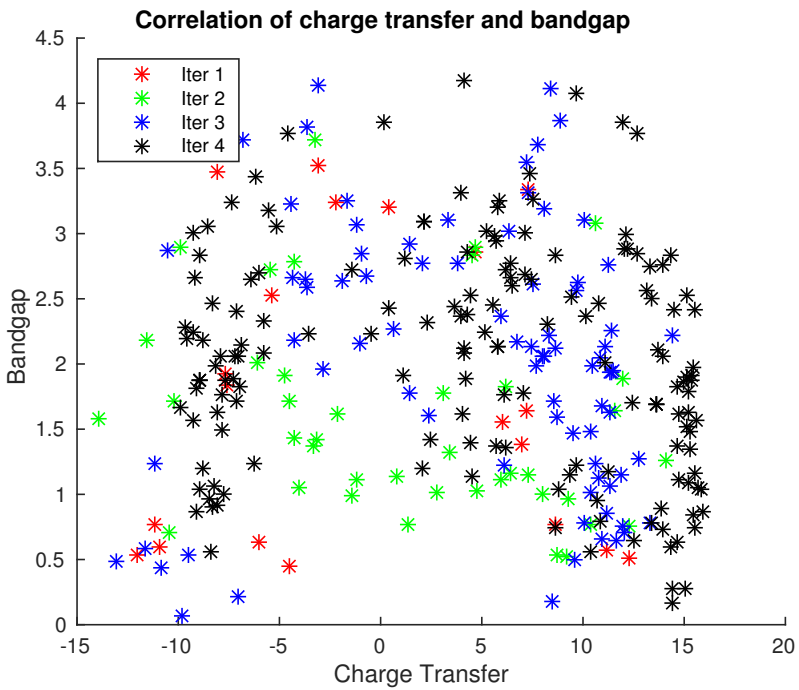
Bandgap Design

In analogy to the position separation, one can also design the energy separation:

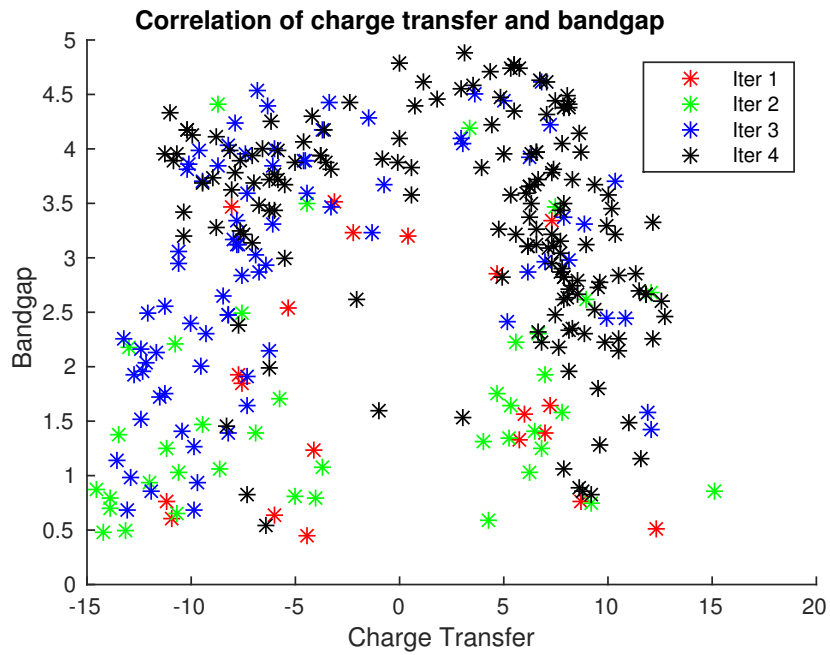
$$B(\phi, \phi_H, \phi_L, \mu) := \langle \phi_L \mid h_{grd} \mid \phi_L \rangle - \langle \phi_H \mid h_{grd} \mid \phi_H \rangle.$$

In fact, $J = \mathrm{tr}(x(\gamma_{exc} - \gamma_{grd}))$ and $B = \mathrm{tr}(h_{grd}(\gamma_{exc} - \gamma_{grd}))$.

- Minimize $|B - 3|$



- Maximize B



Conclusion and Outlook

Our optimal control problems reveal a remarkable multi-scale structure:

- Atoms located on an equidistant grid (order 1)
- Internal wavelength of HOMO and LUMO (order 0.1)
- Possible separation of HOMO and LUMO (order 10)

Future Work

- Generalize the optimization approach
- Investigate also 2D- and 3D-versions of the problem
- Harvest the charge separation to generate an electric current

References

[1] S. Bednarek, B. Szafran, T. Chwiej, and J. Adamowski.
Effective interaction for charge carriers confined in quasi-one-dimensional nanostructures
Phys. Rev. B 68, 2003.

[2] H. Chen, and G. Friesecke.
Pair Densities in Density Functional Theory
Multiscale Model. Simul. 13(4), 2015.

[3] G. Friesecke, and B. Graswald.
A proof that the minimizing orbitals of some common Kohn–Sham energy functionals are lowest eigenstates
to appear.

[4] P. Hohenberg, and W. Kohn.
Inhomogeneous electron gas
Phys. Rev. B 136, 1964.

[5] W. Kohn, and L. J. Sham.
Self-consistent equations including exchange and correlation effects
Phys. Rev. A 140, 1965.

[6] R. G. Parr, and W. Yang.
Density-Functional Theory of Atoms and Molecules
Oxford University Press, 1989.