QUANTUM OPTIMAL CONTROL OF MANY-ELECTRON SYSTEMS WITH TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

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Outline

1 Motivation

2 QOCT + TDDFT Formalism
   - Essential equations
   - QOCT for a system of independent electrons
   - QOCT for the (time-dependent) Kohn-Sham system

3 Some results
   - Design of maximal ionization laser pulses
   - Design of bond-breaking laser pulses
   - “DFT-like” mixing for QOCT algorithms

4 Conclusions and outlook
“Selective bond rearrangement” with tailored light

[R. J. Levis et al, Science 292, 709 (2001)]
What makes experimental “control” possible

- Existence of laser sources, since the 1960’s.
- Femto-second laser sources, which allow for fast processes (avoiding decoherence), and extending the band-width.
- High-intensities.
- Laser shapers.
- Application of algorithms for closed-loop learning control directly in the laboratory.
The learning loop algorithms

[H. Rabitz *et al.*, Science **288**, 824 (2000)]
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Quantum optimal control theory (QOCT) answers the following question:

A system can be driven, during some time interval, by one or various external fields whose temporal dependence is determined by a set of “control” functions $\varepsilon_k(t)$:

$$i \frac{d}{dt} |\Psi(t)\rangle = \hat{H}[\varepsilon_k(t)] |\Psi(t)\rangle.$$

Given an objective (e.g., transition probability to a target state), what are the control functions that best achieve this objective?

Usually, the control function is the electric field of a laser pulse:

$$\hat{H}(t) = \hat{H}_0 + \varepsilon(t) \hat{D}.$$
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$$\hat{H}(t) = \hat{H}_0 + \varepsilon(t)\hat{D}.$$
Essential equations

Variational formulation: Find the extremal points of the functional:

\[ J[\Psi, \chi, \varepsilon] = J_1[\Psi] + J_2[\varepsilon] + J_3[\Psi, \chi, \varepsilon] . \]

- **Target functional:**
  \[ J_1[\Psi] = \langle \Psi(T) | \hat{O} | \Psi(T) \rangle . \]
  Usually, \( \hat{O} \) is a projector operator: \( \hat{O} = |\Psi_{\text{target}}\rangle \langle \Psi_{\text{target}}| \), and the objective is to populate that state.

- **Constrain on the external control field.**
  \[ J_2[\varepsilon] = -\alpha \int_0^T dt |\varepsilon(t)|^2 . \]

- **Fulfillment of Schrödinger’s equation:**
  \[ J_3[\Psi, \chi, \varepsilon] = -2\Im \left[ \int_0^T dt \langle \chi(t) | i \frac{d}{dt} - \hat{H}(t) | \Psi(t) \rangle \right] . \]
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**Essential equations**

\[
\delta J = 0.
\]

\[
\frac{\delta J}{\delta \Psi} = 0,
\]

\[
\frac{\delta J}{\delta \epsilon} = 0.
\]

\[
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Essential equations

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Essential equations

- **QOCT equations**
  - **Forward propagation for** $|\Psi(t)\rangle$:
    \[
    i \frac{d}{dt} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle, \\
    |\Psi(0)\rangle = |\Psi_0\rangle,
    \]
  - **Backward propagation for** $|\chi(t)\rangle$:
    \[
    i \frac{d}{dt} |\chi(t)\rangle = \hat{H}^\dagger(t) |\chi(t)\rangle, \\
    |\chi(T)\rangle = \hat{O} |\chi(T)\rangle,
    \]
  - **Solution field**:
    \[
    \alpha\varepsilon(t) = \Im \left[ \langle \chi(t)| \frac{\partial \hat{H}}{\partial \varepsilon} |\Psi(t)\rangle \right].
    \]

- This set of self-consistent must be solved by iterative solution algorithms.
 Essential equations

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4. Conclusions and outlook
QOCT for a system of independent electrons

If the system is a set of independent electrons (e.g. the Kohn-Sham system), we must write QOCT equations for a set of spin-orbitals that form a single Slater determinant: \( \Psi = \det[\psi_1, \ldots, \psi_N] \).

- **Target functional:** \( J_1[\Psi] = \langle \Psi(T)|\hat{\mathcal{O}}|\Psi(T)\rangle \)
- \( \hat{\mathcal{O}} \) is a one-body operator: \( \hat{\mathcal{O}} = \sum_{i=1}^{N} \hat{o}_i \),

\[
J_1[\Psi] = \langle \Psi(T)|\hat{\mathcal{O}}|\Psi(T)\rangle = \sum_{i=1}^{N} \langle \psi_i|\hat{o}_i|\psi_i\rangle .
\]

E.g. the density at a given point \( r_0 \): \( J_1[\Psi] = \langle \Psi(T)|\hat{n}(r_0)|\Psi(T)\rangle = n(r_0, T) \)

- \( \hat{\mathcal{O}} \) is the projection operator onto a linear combination of Slater determinants:

\[
|\Psi_{\text{target}}\rangle = \sum_{I} c_I |\Phi^I\rangle ,
\]

\[
J_1[\Psi] = \langle \Psi(T)| \left[ \sum_{I} \sum_{J} c_I^* c_J |\Phi^I\rangle \langle \Phi^J| \right] |\Psi(T)\rangle .
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QOCT for a system of independent electrons

- Constrain on the external control field:

\[ J_2[\varepsilon] = -\alpha \int_0^T dt |\varepsilon(t)|^2. \]

- Fulfillment of Schrödinger’s equation for each spin-orbital:

\[ J_3[\Psi, \chi, \varepsilon] = -2 \Im \sum_{i=1}^N \left[ \int_0^T dt \langle \chi_i(t) | i \frac{d}{dt} - \hat{H}(t) | \psi_i(t) \rangle \right]. \]
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QOCT equations (target is a one-body operator, \( \hat{O} = \sum_{i=1}^{N} \hat{o}(i) \))

- Forward propagation for \( |\psi_i(t)\rangle \) \( (i = 1, \ldots, N) \):
  \[
  \frac{i}{\hbar} \frac{d}{dt} |\psi_i(t)\rangle = \hat{H}(t) |\psi_i(t)\rangle ,
  \]
  \[
  |\psi_i(0)\rangle = |\psi_{i0}\rangle ,
  \]

- Backward propagation for \( |\chi_i(t)\rangle \) \( (i = 1, \ldots, N) \):
  \[
  \frac{i}{\hbar} \frac{d}{dt} |\chi_i(t)\rangle = \hat{H}^\dagger(t) |\chi_i(t)\rangle ,
  \]
  \[
  |\chi_i(T)\rangle = \hat{o} |\chi_i(T)\rangle ,
  \]

- Solution field:
  \[
  \alpha \varepsilon(t) = \Im \left[ \sum_{i=1}^{N} \langle \chi_i(t) | \frac{\partial \hat{H}}{\partial \varepsilon} | \psi_i(t) \rangle \right] .
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QOCT for a system of independent electrons

- QOCT equations (target is the projection operator onto $\sum_I c_I |\Phi^I\rangle$)
  - Forward propagation for $|\psi_i(t)\rangle$:
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    i \frac{d}{dt} |\chi_i(t)\rangle = \hat{H}^\dagger(t) |\chi_i(t)\rangle ,
    \]
    \[
    |\chi_i(T)\rangle = \sum_I \lambda_{IJ} |m_i^J\rangle ,
    \]
    \[
    |m_i^J\rangle = \sum_j (M_I)_{ij}^{(-1)} |\Phi_i^J\rangle ,
    \]
    \[
    (M_I)_{ij} = \langle \Phi_i^J | \psi_j \rangle ,
    \]
  - Solution field:
    \[
    \alpha \epsilon(t) = \Im \left[ \langle \chi(t) | \frac{\partial \hat{H}}{\partial \epsilon} | \Psi(t) \rangle \right] .
    \]
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The Schrödinger equation (Kohn-Sham) is now **non-linear**: it depends on the spin-orbitals $\psi_i$ through the density $n(r, t)$.

The functional to minimize is:

$$J[\Psi, \chi, \epsilon] = \langle \Psi(T) | \hat{O} | \Psi(T) \rangle - \alpha \int_0^T dt \epsilon^2(t)$$

$$- 2 \Im \left[ \sum_{i=1}^N \langle \chi_i(t) | i \frac{d}{dt} - \hat{H}_{KS}[n](t) | \psi_i(t) \rangle \right]$$

where:

$$\hat{H}_{KS}[n](t) = \hat{T} + \hat{v}_{\text{Hartree}}[n] + \hat{v}_{\text{xc}}[n] + \epsilon(t) \hat{d}.$$
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J[\Psi, \chi, \epsilon] = \langle \Psi(T)|\hat{O}|\Psi(T)\rangle - \alpha \int_0^T dt \epsilon^2(t)
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-2\Im \left[ \sum_{i=1}^N \langle \chi_i(t)|i\frac{d}{dt} - \hat{H}_{KS}[n](t)|\psi_i(t)\rangle \right].
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$$
QOCT for the (time-dependent) Kohn-Sham system

- **QOCT equations with TDKS Hamiltonian**
  - **Forward propagation for $|\psi_i(t)\rangle$ (KS equations):**
    \[
    i\frac{d}{dt}|\psi_i(t)\rangle = \hat{H}_{KS}[n](t)|\psi_i(t)\rangle,
    \]
    \[
    |\psi_i(0)\rangle = |\psi_{i0}\rangle,
    \]
  - **Backward propagation for $|\chi(t)\rangle$:**
    \[
    i\frac{d}{dt}|\chi_i(t)\rangle = \hat{H}_{KS}^{\dagger}(t)|\chi_i(t)\rangle - D_{KS}^i(r, t),
    \]
    \[
    |\chi_i(T)\rangle = |\frac{\delta J_1}{\delta \psi_i(T)}\rangle
    \]
  - The most important difference is the appearance of an inhomogeneous term in the evolution of $\chi_i$:
    \[
    D_{KS}^i(r, t) = -2\Im \left[ \sum_{k=1}^{N} \int d^3r' \chi_k(r', t) \left[ \frac{1}{|r - r'|} + f_{xc}(r, r') \right] \psi_k(r', t) \psi_i(r, t) \right]
    \]
  - **Solution field:**
    \[
    \alpha\varepsilon(t) = \Im \left[ \sum_{i=1}^{N} \langle \chi(t) | \frac{\partial \hat{H}}{\partial \varepsilon} | \Psi(t) \rangle \right].
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Optimal Control of Multiphoton Ionization Processes in Aligned I₂ Molecules with Time-Dependent Polarization Pulses

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(Received 19 September 2003; published 2 April 2004)

Multiphoton ionization processes in aligned I₂ molecules are actively controlled by the homemade pulse shaping system, with which a time-dependent polarization pulse can be generated and controlled. We find a correlation between a femtosecond time-dependent polarization pulse and the production efficiency of evenly or oddly charged molecular ions. We achieve much better controllability of the correlation with a time-dependent polarization pulse than with a pulse having a fixed ellipticity. The results suggest the existence of an unknown tunnel ionization mechanism which is characteristic of a time-dependent polarization pulse. Our experiments point to new directions in optimal control studies with molecular systems, as discussed in the text.
Design of maximal ionization laser pulses

- Ionization functional:

\[ J_1[\Psi] = \langle \Psi(T) | \left[ \hat{1} - \sum_{k}^{\text{bound}} |\Psi_k\rangle \langle \Psi_k| \right] |\Psi(T)\rangle. \]

- An approximation can be done for the TDDFT case:

\[ J_1[\Psi] = \langle \Psi(T) | \int d^3r \, w(r) \, \hat{n}(r) \, |\Psi(T)\rangle = \int d^3 \, w(r) \, n(r, T), \]

where \( w = 1 \) in an “outer” region, and \( w = 0 \) in the “bound-states” region:
Case studied: H$_2$.
Laser polarized along the molecule axis.
Exact exchange.

Target functional: $J_1[\psi] = \langle \psi(T) | \left[ \hat{1} - \sum_{i=0}^{5} |\psi_i\rangle\langle\psi_i| \right] |\psi(T)\rangle$.

Fixed fluence mode: the total fluence of the optimal field must be equal to that of the initial, input laser.
Initial laser frequency tuned to the ionization potential.
Design of maximal ionization laser pulses

- Design of maximal ionization laser pulses
  - $Z_{\text{inside}} d^3 r n(r, t)_{\text{inside}}$
  - $\sum_{\text{bound}} |\langle \psi(t) | \psi_j \rangle|^2$
- Design of bond-breaking laser pulses
  - $2 \sum_{\text{bound}} |\langle \psi(t) | \psi_j \rangle|^2$

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Coherent control of bond breaking in amino acid complexes with tailored femtosecond pulses

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Intense femtosecond laser pulses, judiciously tailored in an adaptive, optimal control feedback loop were used to break preferentially the acyl-N (“peptide”) bond of Ac-Phe-NHMe that may be regarded as a dipeptide model. We show that coherent excitation of complex wave packets in the strong-field regime allows to cleave strong backbone bonds in the molecular system preferentially, while keeping other more labile bonds intact. These results show the potential of pulse shaping as a powerful complementary analytical tool for protein sequencing of large biopolymers in addition to the well-known mass spectrometry and chemical analysis. © 2007 American Institute of Physics.
Design of bond-breaking laser pulses

If the AB bond is breaking,

\[ \vec{r}_{BA} \cdot \vec{F}_B > 0 \]
\[ \vec{r}_{BA} \cdot \vec{F}_A < 0 \]
\[ \Rightarrow \]
\[ \vec{r}_{BA} \cdot \vec{F}_B - \vec{r}_{BA} \cdot \vec{F}_A > 0 \]
\[ \Rightarrow \]
\[ \vec{r}_{BA} \cdot \vec{F}_{BA} > 0 \]

\[ (\vec{F}_{BA} = \vec{F}_B - \vec{F}_A) \]
Design of bond-breaking laser pulses

- Bond-breaking target:

\[ J_1[\Psi] = \frac{1}{t_f - t_0} \int_{t_0}^{t_f} dt \langle \Psi(t) | \hat{r}_{BA} | \hat{F}_{BA}(t) | \left( 1 + \hat{r}_{BA} \cdot \hat{F}_{BA}(t) \right) | \Psi(t) \rangle. \]

- In an even more naïve approach, one can look at the force at the end of the pulse:

\[ J_1[\Psi] = \langle \Psi(T) | \hat{r}_{BA} | \hat{F}_{BA}(T) | \left( 1 + \hat{r}_{BA} \cdot \hat{F}_{BA}(T) \right) | \Psi(T) \rangle. \]

- Within TDDFT, \( \hat{F}_A \) is a local density operator: the necessary expectation values can be written as simple density integrals.

\[ \hat{F}_A(t) = \int d^3 r \, n(r) \, \nabla_{\vec{r}_A} v_{KS}(r, t). \]
Design of bond-breaking laser pulses

- Bond-breaking target:
  \[ J_1[\Psi] = \frac{1}{t_f - t_0} \int_{t_0}^{t_f} dt \langle \Psi(t)|\hat{\mathbf{r}}_{BA}|\hat{\mathbf{F}}_{BA}(t)\rangle \left( 1 + \mathbf{r}_{BA} \cdot \hat{\mathbf{F}}_{BA}(t) \right) |\Psi(t)\rangle. \]

- In an even more naïve approach, one can look at the force at the end of the pulse:
  \[ J_1[\Psi] = \langle \Psi(T)|\hat{\mathbf{r}}_{BA}|\hat{\mathbf{F}}_{BA}(T)\rangle \left( 1 + \mathbf{r}_{BA} \cdot \hat{\mathbf{F}}_{BA}(T) \right) |\Psi(T)\rangle. \]

- Within TDDFT, \( \hat{\mathbf{F}}_A \) is a local density operator: the necessary expectation values can be written as simple density integrals.
  \[ \hat{\mathbf{F}}_A(t) = \int d^3r \hat{n}(\mathbf{r}) \nabla_{\mathbf{r}_A} v_{KS}(\mathbf{r}, t). \]
Design of bond-breaking laser pulses

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\[
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Zhu-Rabitz algorithm for QOCT equations

- QOCT require iterative algorithms to find the optimal field: $\epsilon^{(1)}, \epsilon^{(2)}, \ldots$. In general, $\epsilon^{(k+1)} = F[\epsilon^{(k)}]$.
  1. Propagate, from $|\Psi(0)\rangle = |\Psi_0\rangle$ to $|\Psi(T)\rangle$ with $\epsilon^{(k)}$.
  2. Propagate backwards, from $|\chi(T)\rangle = \hat{O}|\Psi(T)\rangle$ to $|\chi(0)\rangle$, with $\tilde{\epsilon}$ defined as:
     $$\alpha\tilde{\epsilon}(t) = \Im \langle \chi(t) | \hat{V} | \Psi(t) \rangle . \tag{1}$$
     $\tilde{\epsilon}$ must be obtained “on the fly”, from the values of the propagating $|\chi(t)\rangle$ and the previously obtained $|\Psi(t)\rangle$.
  3. Propagate forward, from $|\Psi'(0)\rangle = |\Psi_0\rangle$ to $|\Psi'(T)\rangle$, using the output field $F[\epsilon^{(k)}](t)$, which is now defined as:
     $$\alpha F[\epsilon^{(k)}](t) = \Im \langle \chi(t) | \hat{V} | \Psi'(t) \rangle . \tag{2}$$
  4. Define $\epsilon^{(k+1)} = F[\epsilon^{(k)}]$, and repeat from step 1 until convergence is reached ($F[\epsilon] = \epsilon$).
The problem is a fixed-point search problem analogous to the DFT ground-state search problem. Why not using the same “mixing” schemes (Anderson, Pulay, Broyden, etc)?

\[ \epsilon^{(k+1)} = G_{\text{mixing}} \left[ \{ \epsilon^{(k-s)}, F[\epsilon^{(k-s)}] \}_{j=0}^{s-1} \right]. \] (3)

The functional \( G_{\text{mixing}} \) is chosen in some way designed to minimize the distance \( D \) between input and output:

\[ D(F[\epsilon], \epsilon) = \langle F[\epsilon] - \epsilon \mid F[\epsilon] - \epsilon \rangle^{1/2}. \] (4)
Transition from the $v = 0$ to the $v = 1$ vibrational state in a OH bond modeled by a Morse potential
Conclusions and outlook

- TDDFT may be used to perform the propagations required by QOCT theory for many-electron systems.
- The equations to propagate are similar to the TDKS equations, although some extra terms arise that may complicate the problem numerically. Fortunately, in some cases those terms are unimportant.
- The most used target in QOCT (projection onto an excited state) may be problematic to define when using TDDFT.
- We have performed TDDFT+QOCT calculations to obtain laser pulses that yield maximum molecular ionization.
- We have defined a possible target, defined as a function of the classical forces on the nuclei, that attempts to find the pulses that optimize the breaking of a certain bond.
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Motivation

QOCT + TDDFT Formalism

Some results

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Collaborators

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