Models for Time-Dependent Phenomena

I. Laser-matter interaction: atoms
II. Laser-matter interaction: molecules
III. Model systems and TDDFT

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Outline

Laser-matter interaction: atoms

- Classical models and quantum description
- Floquet theory, Volkov states
- Multiphoton processes, tunneling ionization
- Recollision, high-harmonic generation, double ionization
- Strong-field approximation
- Recent examples of research on atoms in strong fields
Laser-matter interaction

“Weak” light field
(normal light, synchrotron)

Strong light field
(laser pulses)

Single-photon absorption

\[ P \sim |\langle 1| r \cdot E |0 \rangle|^2 \]

Multiphoton absorption
perturbative or
nonperturbative
Femtosecond pulses are available:

- cause ionization of atoms, fragmentation of molecules
- allow ultrafast time-resolved measurements (pump-probe)
- “carrier-envelope phase” becomes important
Classical preliminaries

Free classical electron in a monochromatic laser field

Equation of motion: \[ \ddot{\mathbf{r}}(t) = -E_0 \sin(\omega t) \]

(using dipole approximation; \( E_0 \sin(\omega t) \) = electric field, linearly polarized)

Velocity: \( \dot{\mathbf{r}}(t) = \mathbf{v}_{\text{drift}} + \frac{E_0}{\omega} \cos(\omega t) \)

Position: \( \mathbf{r}(t) = \mathbf{r}_0 + \mathbf{v}_{\text{drift}} t + \frac{E_0}{\omega^2} \sin(\omega t) \)

Oscillation amplitude: \( \alpha = \frac{E_0}{\omega^2} \)
Kinetic energy: \( T(t) = \frac{v_{\text{drift}}^2}{2} + v_{\text{drift}} \cdot \frac{E_0}{\omega} \cos(\omega t) + \frac{E_0^2}{2\omega^2} \cos^2(\omega t) \)

Average kinetic energy:  
\[
\overline{T} = \frac{v_{\text{drift}}^2}{2} + \frac{E_0^2}{4\omega^2}
\]

→ Define **ponderomotive potential**:  
\[
U_p = \frac{E_0^2}{4\omega^2}
\]

If field amplitude is position dependent, there will be a ponderomotive force \( F_p = -\nabla U_p(\mathbf{r}) \).

(But in an ultrashort laser pulse, the electron has not enough time to follow this force).
Quantum mechanical description

Time evolution is described by the time-dependent Schrödinger equation (TDSE):
\[ i \frac{\partial}{\partial t} \Psi(t) = H(t) \Psi(t). \]

Hamiltonian in dipole approximation (\( \lambda \gg \text{system size} \)):
\[ H(t) = H_0 + \mathbf{E}(t) \cdot \sum_j \mathbf{r}_j \]
with \( \mathbf{E}(t) = \text{electric field}. \)
This is called \textit{length gauge}.

Alternatively:
\[ H'(t) = H_0 + \mathbf{A}(t) \cdot \sum_j [\mathbf{p}_j + \mathbf{A}(t)/2] \]
with
\[ \mathbf{A}(t) = - \int_{-\infty}^{t} \mathbf{E}(t')dt'. \]
This is called \textit{velocity gauge}. 
Quantum mechanical description

The velocity-gauge wave function $\Psi'(t)$ is related to the length-gauge wave function $\Psi(t)$ by

$$\Psi'(t) = e^{-i\mathbf{A}(t) \cdot \sum_j \mathbf{r}_j} \Psi(t)$$

Are there problems with TDDFT and velocity gauge (momentum-dependent interaction)?

No, because gauge transformation does not change density. → TDKS equations may be solved in either gauge.

But: orbitals change under gauge transformation.
Floquet theory

Consider monochromatic field \( E(t) = E_0 \sin(\omega t) \)

\( \rightarrow \) periodic Hamiltonian \( H(t + T) = H(t) \)

\( \rightarrow \) Floquet theorem (cf. Bloch theorem in solid-state physics):

TDSE has solutions of the form

\[
\Psi(t) = e^{-i\mathcal{E}t} \Phi(t)
\]

with time-periodic wave functions \( \Phi(t) \),

\[
\Phi(t + T) = \Phi(t).
\]
The Floquet states $\Phi(t)$ are eigenstates of the Floquet operator $\mathcal{H}(t) = H(t) - i \frac{\partial}{\partial t}$, where $\mathcal{H}(t)\Phi(t) = \mathcal{E}\Phi(t)$, where $\mathcal{E}$ is the quasienergy.

If $\mathcal{E}$ and $\Phi(t)$ are solutions, then also $\mathcal{E}' = \mathcal{E} + n\omega$ and $\Phi'(t) = \Phi(t)e^{in\omega t}$ are solutions.

$\Phi(t)$ are called dressed states (analog to stationary eigenstates for time-independent Hamiltonian).
**Volkov states**

Free electron in the presence of a time-dependent electric field is described by the Hamiltonian (length gauge):

$$H(t) = -\frac{\nabla^2}{2} + \mathbf{E}(t) \cdot \mathbf{r}$$

Possible solutions of the TDSE are **Volkov states**:

$$\Psi^V_p(\mathbf{r}, t) = e^{-iS(p, t, t')} e^{i[\mathbf{p} + \mathbf{A}(t)] \cdot \mathbf{r}}$$

with the action integral $S(\mathbf{p}, t, t') = \frac{1}{2} \int_{t'}^t [\mathbf{p} + \mathbf{A}(t'')]^2 dt''$ and arbitrary, fixed $t'$.

These are plane waves with momenta depending on time as in classical mechanics.
Volkov states

For a monochromatic field, the Volkov states can be written as

$$\Psi_p^V(r, t) = e^{-i(p^2/2 + U_p)t} \Phi_p(r, t)$$

with a time periodic function $\Phi_p$, i.e. this is a Floquet state with quasienergy

$$\mathcal{E}_p = p^2/2 + U_p.$$ 

The ponderomotive potential is the ac Stark shift of plane waves!
Static electric field $E \rightarrow$ potential barrier, allows tunneling.

Tunneling rate for the hydrogen atom (see Landau & Lifshitz):

$$w = \frac{4}{E} e^{-2/(3E)}$$

(derived from quasiclassical theory)
Over-barrier ionization

For sufficiently large field $E > \text{critical field } E_{BS}$ → ground-state energy above barrier maximum

$E_{BS} = \text{barrier suppression field strength}$

H atom: $E_{BS} = 0.113$ a.u.

(corresponds to laser intensity $I_{BS} = 4.5 \times 10^{14}$ W/cm$^2$)
Ionization regimes

**Multiphoton ionization**

\[ \gamma = \frac{\omega}{\omega_t} > 1 \]

**Tunnel ionization**

\[ \gamma = \frac{\omega}{\omega_t} < 1 \]

**Over-barrier ionization**

\[ E > E_{BS} \]

\[ \gamma = \frac{\text{tunneling time}}{\text{laser period}} \] (Keldysh parameter)

**H atom:**

\[ \gamma = \frac{\omega}{E} \]

**In general:**

\[ \gamma = \sqrt{\frac{I_p}{2U_p}} \]

\( I_p = \) ionization potential, \( U_p = \) ponderomotive potential
Simple man’s model of ionization

- At each instant $t_0$, the ionization rate is given by a simple estimate (e.g. tunneling formula) using the instantaneous field strength.
- Electron appears with zero velocity at position zero.
- Subsequent dynamics is described classically.
Simple man’s model of ionization

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For monochromatic field: $\dot{r}(t) = \frac{E_0}{\omega} [\cos(\omega t) - \cos(\omega t_0)]$

i.e. drift velocity $v_{\text{drift}} = -\frac{E_0}{\omega} \cos(\omega t_0)$

$\rightarrow$ Estimate of maximum photoelectron energy:

$|\cos(\omega t_0)| = 1 \rightarrow E_{\text{max}} = \frac{E_0^2}{2\omega^2} = 2U_p$
Above-threshold ionization

Absorption of more photons than needed to overcome the ionization threshold

→ Peaks separated by the photon energy in the electron spectrum


FIG. 2. Electron energy spectra for different laser intensities and pulse durations. (a) reference spectrum, $I = 2.2 \times 10^{13}$ W cm$^{-2}$; (b) and (c) $I = 7.5 \times 10^{12}$ W cm$^{-2}$. 

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Above-threshold ionization

Ponderomotive shift of the ATI peaks

- Continuum dressed states have energies \( \mathcal{E}_k^d = \frac{k^2}{2} + U_p \)
- Shift of ground-state energy is small: \( \mathcal{E}_g^d \approx E_g \), so absorption of \( n \) photons yields electrons with energy \( E_g + n\omega \).

\[ k^2/2 = E_g + n\omega - U_p \]

→ Photoelectron kinetic energies
Recollision mechanism

3-step process:

1. ionization
2. acceleration by the field
3. return to the core
Recollision mechanism

3-step process:
1. ionization
2. acceleration by the field
3. return to the core

Possible consequences:
- recombination (high harmonic generation – coherent light)
- elastic scattering $\rightarrow$ fast photoelectrons
- inelastic scattering $\rightarrow$ e.g. double ionization
High-harmonic generation

Photon picture

N photons of frequency $\omega$ → 1 photon of frequency $N\omega$. 

$\Omega = N\omega$
**High-harmonic generation**

**Recollision picture**

- **Ionization**
- **Free acceleration**
- **Recombination**

Maximum return energy: \( E_{\text{max}} = 3.17U_p \)

\[ \leftrightarrow \text{Cut-off at } \hbar \omega = 3.17U_p + I_p \]

[Corkum, PRL 71, 1994 (1993)]
Calculation of spectra

Calculation of the time-dependent dipole acceleration

\[ a(t) = \langle \psi(t)|\nabla V_0 + E(t)|\psi(t) \rangle \]

and Fourier transform

\[ a(\Omega) = \int a(t)e^{i\omega t} \]

gives emission spectrum

\[ S(\Omega) \sim |a(\Omega)|^2 \]

In practice: time integration over pulse duration \( T \),

\[ a(\Omega) = \int_0^T a(t)f(t)e^{i\omega t} \]

with some window function \( f(t) \).

Alternatively: \( a(t) = \ddot{D}(t) \) from time-dependent dipole moment \( D(t) \)
or: \( a(t) = \dot{v}(t) \) from time-dependent dipole velocity \( v(t) \)
Rescattered photoelectrons

Scattered electrons (high-order above-threshold ionization)

G.G. Paulus et al. PRL 72, 2851 (1994)
Double ionization is enhanced due to electron correlations by orders of magnitude.

Identification of the recollision mechanism:

R. Moshammer et al., PRL 84, 447 (2000)
Quantum mechanical methods for ultrashort pulses

- Numerical solution of the TDSE (or TDKS) equations
  - accurate,
  - but time consuming and hard to interpret,
  - approximations for TDDFT xc potential have deficiencies

- Strong-field approximation
  (“Keldysh-Faisal-Reiss theory”, “intense field S-matrix formalism”)
  - less reliable (e.g. strong dependence on gauge),
  - but fast and amenable to physical interpretation.
**Strong-field approximation for ionization**

Time evolution operator $U(t, t')$ obeys Schrödinger equation:

$$i \frac{\partial}{\partial t} U(t, t') = [H_0 + H_{\text{int}}(t)] U(t, t'),$$

where $H_{\text{int}}$ is the system-field interaction.

The solution can be written in integral form:

$$U(t, t') = U_0(t, t') - i \int_{t'}^{t} U(t, t'') H_{\text{int}}(t'') U_0(t'', t') dt''.$$

Goal: calculation of transition amplitudes from ground state to continuum states with momentum $p$ at final time $t_f$:

$$M_p(t_f, t_i) = \langle \Psi_p(t_f) | U(t_f, t_i) | \Psi_0(t_i) \rangle$$
**Strong-field approximation for ionization**

**Assumption 1**: time evolution after ionization is governed by the laser field only, not by the binding potential, i.e. $U(t, t'') \approx U_V(t, t'')$ (Volkov-Propagator). Then

$$U(t, t') = U_0(t, t') - i \int_{t'}^{t} U_V(t, t'') H_{\text{int}}(t'') U_0(t'', t') dt''.$$

**Assumption 2**: final state with momentum $p$ is approximated as a Volkov state.

$\rightarrow$ Ionization amplitude in strong-field approximation (SFA):

$$M_{p}^{\text{SFA}}(t_i, t_f) = -i \int_{t_i}^{t_f} \langle \Psi_p^V(t) | H_{\text{int}}(t) | \Psi_0(t) \rangle \, dt$$
Strong-field approximation for ionization

SFA is not gauge invariant: results for ionization of $N_2$


Length gauge $(r \cdot E(t))$ appears favourable (except for large molecules)
Two examples of recent research in laser-atom interactions

• Low-energy structure in electron spectra from long-wavelength irradiation

• Lateral momentum width in strong-field ionization
Low-energy structure in electron spectra

Figure 4 | Comparison of calculated and measured LES distributions for argon ionized by 150 TW cm$^{-2}$, 2 μm pulses. The experiment is remarkably well reproduced by the three-dimensional TDSE. For comparison, the KFR using Volkov states fails in this region. The calculated distributions are obtained using intensity averaged, 10-cycle flat-top pulses (see the Methods section).

Blaga et al., Nat. Phys. 5, 335 (2009)
Low-energy structure in electron spectra

Explanation: caustics from soft recollisions

Yan et al., PRL 105, 253002 (2010)
Lateral momentum distribution in strong-field ionization

Measured widths of lateral distributions (circularly polarized light)

→ Widths are larger than predicted by a simple tunneling formula

\[ |\Psi(k_\perp)|^2 = |\Psi(k_\perp)|^2 \exp\left(-k_\perp^2 \sqrt{2I_p/E}\right). \]
**Lateral momentum distribution in strong-field ionization**

Calculated widths and comparison to experiment:

- Very good agreement between TDSE, SFA, experiment.
- Simple tunneling model is inaccurate.

I. Dreissigacker, M.L., submitted; experimental data by Arissian et al. PRL 2010
Conclusions

• Strong laser fields require nonperturbative description and large grids.
• In general, theoretical description is not quantitative and relies heavily on models.
• TDDFT is the only tractable first-principles approach, already for atoms.

Next part:
• Laser-matter interaction: molecules