Nonperturbative quantum dynamics

I. Laser interactions with atoms/molecules

II. Model systems and TDDFT

Manfred Lein, TDDFT school Benasque 2014
Laser interactions with atoms/molecules

- Classical models and quantum description
- Multiphoton processes, tunneling ionization
- Recollision, high-harmonic generation, double ionization
- Strong-field approximation
- Molecules, laser-induced alignment
- Examples of open problems in strong-field dynamics
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
Ultrashort laser pulses

Few-femtosecond light pulses are available:

\[
I = 5 \times 10^{14} \, \text{W/cm}^2
\]

FWHM = 6 fs

→ cause ionization of atoms, fragmentation of molecules
→ allow ultrafast time-resolved measurements (pump-probe)
→ “carrier-envelope phase” becomes important
Free classical electron in a monochromatic laser field

Equation of motion: \[ \ddot{r}(t) = -E_0 \sin(\omega t) \] (using dipole approximation; \( E_0 \sin(\omega t) = \) electric field, linearly polarized)

Velocity: \[ \dot{r}(t) = v_{\text{drift}} + \frac{E_0}{\omega} \cos(\omega t) \]

Position: \[ r(t) = r_0 + v_{\text{drift}} t + \frac{E_0}{\omega^2} \sin(\omega t) \]

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: \( \bar{T} = \frac{v_{\text{drift}}^2}{2} + \frac{E_0^2}{4\omega^2} \)

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

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

(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 (\( \lambda \gg \) system size):

\[ H(t) = H_0 + \mathbf{E}(t) \cdot \sum_j r_j \]

with \( \mathbf{E}(t) = \) electric field.

This is called length gauge.

Alternatively:

\[ H'(t) = H_0 + \mathbf{A}(t) \cdot \sum_j [p_j + \mathbf{A}(t)/2] \]

with

\[ \mathbf{A}(t) = - \int_{-\infty}^{t} \mathbf{E}(t') dt'. \]

This is called velocity gauge.
Quantum mechanical description

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

\[
\Psi'(t) = e^{-iA(t) \cdot \sum_j r_j} \Psi(t)
\]

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

No, because gauge transformation does not change density.

\( \rightarrow \) TDKS equations may be solved in either gauge.

But: orbitals change under gauge transformation.
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:

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

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.
Tunneling

Static electric field $E$ → 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

$V(z)$

→ Classical escape of the electron.

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

H atom: $E_{BS} = 0.113 \text{ a.u.}$
(corresponds to laser intensity $I_{BS} = 4.5 \times 10^{14} \text{ W/cm}^2$)
Ionization regimes

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

\[ I_p = \text{ionization potential}, \quad U_p = \text{ponderomotive potential} \]
Above-threshold ionization

Absorption of more photons than needed to overcome the ionization threshold

→ Peaks separated by the photon energy in the electron spectrum

Example:
experiment with Xe atoms,

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

- p. 15
High-harmonic generation

Recollision picture

Ionization  Free acceleration  Recombination

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

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

[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 \( v(t) \)
Attosecond pulses

Currently shortest achieved coherent light pulses: 67as

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.

\[ M_{p}^{\text{SFA}}(t_i, t_f) = -i \int_{t_i}^{t_f} \langle \Psi_p^V(t) | H_{\text{int}}(t) | \Psi_0(t) \rangle dt \]

→ Ionization amplitude in strong-field approximation (SFA):
Molecules

Set of nuclear and electronic coordinates $\mathbf{R}_j$ and $\mathbf{r}_k$.

Hamiltonian:

$$H_0 = \sum_j \frac{p_j^2}{2M_j} + \sum_k \frac{p_k^2}{2} + \sum_{j,k} w_{j,e}(\mathbf{R}_j, \mathbf{r}_k) + \sum_{j_1 \neq j_2} w_{j_1,j_2}(\mathbf{R}_{j_1}, \mathbf{R}_{j_2}) + \sum_{k_1 \neq k_2} w_{ee}(\mathbf{r}_{k_1}, \mathbf{r}_{k_2})$$

with $w_{j_1,j_2}$ nucleus-nucleus interaction, $w_{j,e}$ nucleus-electron interaction, and $w_{ee}$ electron-electron interaction.

Light-molecule interaction:

$$H(t) = H_0 - \mathbf{D} \cdot \mathbf{E}(t)$$

with dipole moment $\mathbf{D} = (\sum_j Z_j \mathbf{R}_j) - (\sum_k \mathbf{r}_k)$.
Born-Oppenheimer approximation

Separation of time scales for nuclear and electronic motion due to great mass difference

→ Electrons adjust “instantaneously” to nuclear positions.

Born-Oppenheimer (BO) Ansatz for wave function:

\[ \Psi(R, r, t) = \sum_m \chi_m(R, t) \Phi_m(R, r), \]

\[ \Phi_m(R, r) = \text{electronic eigenstates at fixed nuclear positions.} \]

Inserting into the field-free TDSE yields

\[ i \frac{\partial}{\partial t} \chi_m(R, t) = \left[ T_n + V_m^{BO}(R) \right] \chi_m + \sum_{m'} \langle \Phi_m | T_n | \Phi_{m'} \rangle \chi_{m'} \]

← BO approximation

Nonadiabatic couplings

\( T_n \) acting on both \( \Phi_{m'} \) and \( \chi_{m'} \)
Including the laser-molecule interaction, the BO TDSE becomes:

\[ i \frac{\partial}{\partial t} \chi_m(\mathbf{R}, t) = \left[ T_n + V_{BO}^m(\mathbf{R}) \right] \chi_m(\mathbf{R}, t) - \mathbf{E} \cdot \sum_{m'} \langle \Phi_m | \mathbf{D} | \Phi_{m'} \rangle \chi_{m'} \]

→ Functions \( \chi_m \) coupled only by the dipole matrix elements.

BO approximation breaks down for highly excited electrons:

- Rydberg molecules
- Electrons in the continuum
Controlling harmonic generation with molecular alignment

$\text{CS}_2$, $\text{H}_2$, $\text{N}_2$

9th harmonic, adiabatic alignment

Hay et al. PRL 87, 183901 (2001)

impulsive alignment

Itatani et al., PRL 94, 123902 (2005)
Adiabatic alignment of molecules

Linear molecule with dipole moment $\mu$ and polarizabilities $\alpha_{||}$, $\alpha_{\perp}$ interacts with laser field $E = E_0 \cos(\omega t)$ as

$$V_\mu(\theta) = -\mu E \cos \theta, \quad V_\alpha(\theta) = -\frac{1}{2} E^2 (\alpha_{||} \cos^2 \theta + \alpha_{\perp} \sin^2 \theta)$$

Sufficiently high frequencies: $\langle E \rangle \to 0$, $\langle E^2 \rangle \to E_0^2 / 2$

Aligning laser field is switched on slowly $\to$ pendular states

Friedrich and Herschbach, PRL 74, 4623 (1995)

experiment: Larsen et al., JCP 111, 7774 (1999)
**Impulsive alignment**

Kick with a femtosecond pulse shorter than the rotational period → Rotational revival structure exhibits times of *field-free alignment*.

Seideman, PRL 83, 4971 (1999), Rosca-Pruna/Vrakking, PRL 87, 153902 (2001)

Detection by Coulomb explosion of $\text{N}_2$ in circularly polarized pulse / ion detection:

Dooley et al., PRL 68, 023406 (2003)
Two examples of open problems in laser atom/molecule interactions

- Tunneling times from the attoclock
- Photoelectron circular dichroism
Tunneling times from the attoclock

Attoclock principle:
- ionization by near-circular polarized pulses
- measurement of angular offset of the distribution peak

Pfeiffer et al., Nat. Phys. 8, 76 (2011)
Previous experiment: consistent with instantaneous tunneling

Pfeiffer et al., Nat. Phys. 8, 76 (2011)
Recent experiment: appears to indicate non-zero real tunneling time

Landsman et al., arXiv:13012766v2 (2013)
Strong-field photoelectron circular dichroism

- Ionization of chiral molecules with circularly polarized laser pulses
- Observable: three-dimensional photoelectron distribution
- Search for forward-backward asymmetry

[Ritchie, PRA 13, 1411 (1976); Cherepkov, CPL 87, 344 (1982); Powis, JCP 112, 301 (2000); Böwering et al., PRL 86, 1187 (2001)]
Strong-field photoelectron circular dichroism

Femtosecond pulse PECD [Lux et al., Angew. Chem. Int. Ed. 51, 5001 (2012)]
Camphor and fenchone HOMOs

R-camphor

R-fenchone
Calculated electron distributions (SFA+Born approximation)

R-fenchone, single orientation, LCP pulse (total length 20 cycles)

- Three-, four- and five-photon rings are visible.
- Asymmetry due to single orientation.
Photoelectron distributions

R-fenchone, random orientation (numerically averaged over Euler angles)

- Asymmetry is reduced by angle averaging.
- Camphor distribution looks practically the same as in fenchone.
Forward-backward asymmetries

- Nodal structure in good agreement with experiment
- Asymmetries smaller and of different sign compared to experiment
- Fenchone gives stronger asymmetry (matches experiment)
Conclusions

- Strong laser fields require nonperturbative description; even one-electron problem is demanding.
- In general, theoretical description relies heavily on models; open problems in simple systems
- TDDFT is the only tractable first-principles approach, already for atoms.

Next part:

- Model systems and TDDFT