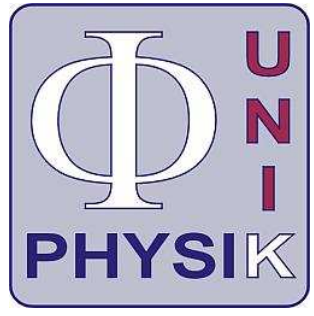
Models for Time-Dependent Phenomena

I. Physical phenomena in laser-matter interaction

II. Model systems and TDDFT

Manfred Lein, University of Kassel



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Outline

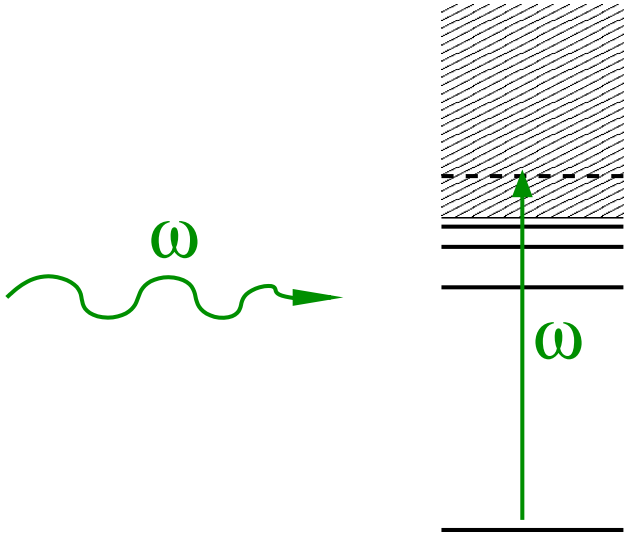
Physical phenomena in laser-matter interaction

- Classical and quantum description
- Floquet theory, Volkov states
- Multiphoton processes, tunneling
- Recollision - harmonics, ATI, double ionization
- Strong-field approximation
- Molecules, Born-Oppenheimer approximation
- Bond softening, enhanced ionization, Coulomb explosion

Laser-matter interaction

Weak light field

(normal light, synchrotron)

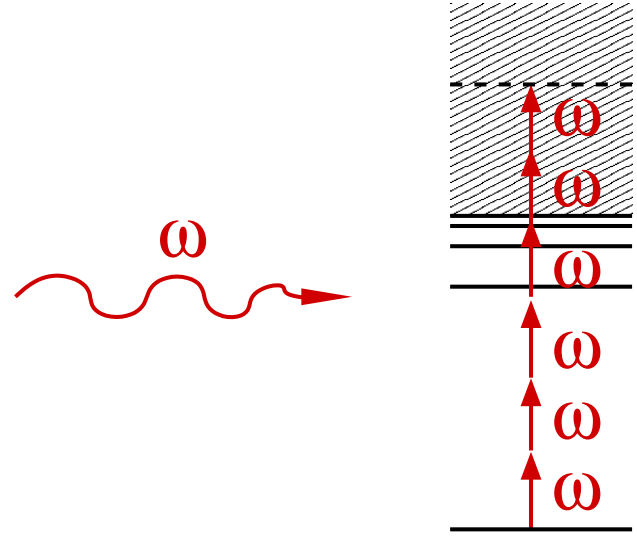


Single-photon absorption

$$P \sim |\langle 1|\mathbf{r}\cdot\mathbf{E}|0\rangle|^2$$

Strong light field

(laser pulses)



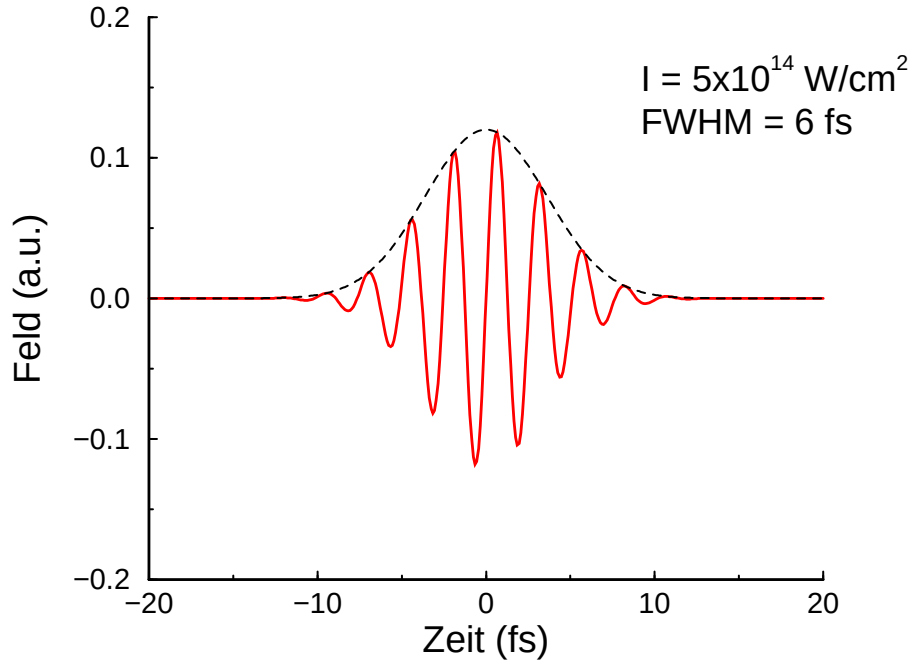
Multiphoton absorption

perturbative or

nonperturbative

Ultrashort laser pulses

State-of-the-art “few-cycle” pulse:



$\longrightarrow$ allows ultrafast time-resolved measurements (pump-probe)

$\longrightarrow$ “carrier-envelope phase” becomes important

Classical preliminaries

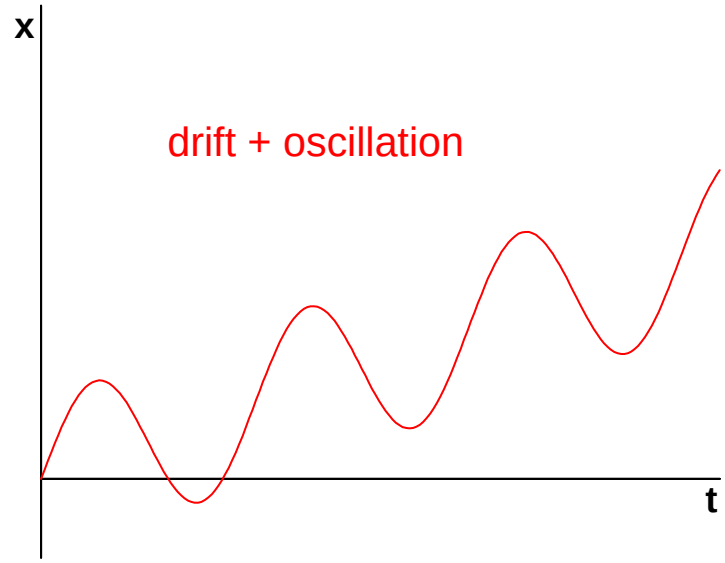
Classical electron in a monochromatic laser field

Equation of motion: $\boxed{\ddot{\mathbf{r}}(t) = -\mathbf{E}_0 \sin(\omega t)}$

(using dipole approximation; $\mathbf{E}_0 \sin(\omega t) =$ electric field, linearly polarized)

Velocity: $\dot{\mathbf{r}}(t) = \mathbf{v}_{\mathrm{drift}} + \frac{\mathbf{E}_0}{\omega} \cos(\omega t)$

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



Oscillation amplitude: $\alpha = \mathbf{E}_0/\omega^2$

Classical preliminaries

Kinetic energy: $T(t) = \frac{v_{\mathrm{drift}}^2}{2} + \mathbf{v}_{\mathrm{drift}} \cdot \frac{\mathbf{E}_0}{\omega} \cos(\omega t) + \frac{E_0^2}{2\omega^2} \cos^2(\omega t)$

Average kinetic energy: $\boxed{\bar{T} = \frac{v_{\mathrm{drift}}^2}{2} + \frac{E_0^2}{4\omega^2}}$

$\rightarrow$ Define **ponderomotive potential**: $\boxed{U_{\mathrm{p}} = \frac{E_0^2}{4\omega^2}}$

If field amplitude is position dependent, there will be a ponderomotive force $\mathbf{F}_{\mathrm{p}} = -\nabla U_{\mathrm{p}}(\mathbf{r})$.

(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): $\boxed{i\frac{\partial}{\partial t}\Psi(t) = H(t)\Psi(t).}$

Hamiltonian in dipole approximation ($\lambda >>$ system size):

$\boxed{H(t) = H_0 + \mathbf{E}(t)\sum_j \mathbf{r}_j}$ with $\mathbf{E}(t)$ = electric field.

This is called *length gauge*.

Alternatively:

$\boxed{H'(t) = H_0 + \mathbf{A}(t)\sum_j [\mathbf{p}_j + \mathbf{A}(t)/2]}$ 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

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

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

No, because gauge transformation does not change density .

$\longrightarrow$ TDKS equations may be solved in either gauge.

Floquet theory

Consider monochromatic field $\mathbf{E}(t) = \mathbf{E}_0 \sin(\omega t)$

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

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

TDSE has solutions of the form

$$\boxed{\Psi(t) = e^{-i\mathcal{E}t}\Phi(t)}$$

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

$$\boxed{\Phi(t+T) = \Phi(t).}$$

Floquet theory

The Floquet states $\Phi(t)$ are eigenstates of the **Floquet operator** $\mathcal{H}(t) = H(t) - i\frac{\partial}{\partial t}$,

$$\boxed{\mathcal{H}(t)\Phi(t) = \mathcal{E}\Phi(t),}$$

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**:

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

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.

Volkov states

For monochromatic field, the Volkov states can be written as

$$\Psi^{\mathrm{V}}_{\mathbf{p}}(\mathbf{r},t) = e^{-i(p^2/2+U_{\mathrm{p}})t}\ \Phi_{\mathbf{p}}(\mathbf{r},t)$$

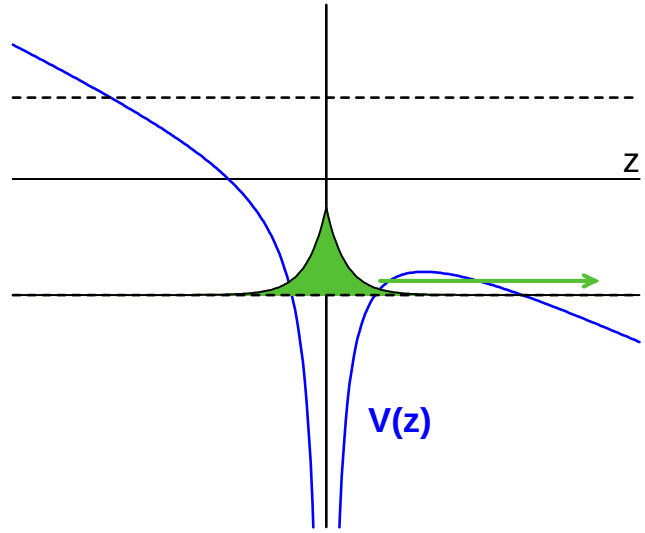
with a time periodic function $\Phi_{\mathbf{p}}$, i.e. this is a Floquet state with quasienergy

$$\boxed{\mathcal{E}_{\mathbf{p}} = p^2/2 + U_{\mathrm{p}}.}$$

The ponderomotive potential is the ac Stark shift of plane waves!

Tunneling

Static electric field $E \rightarrow$ potential barrier, allows tunneling.



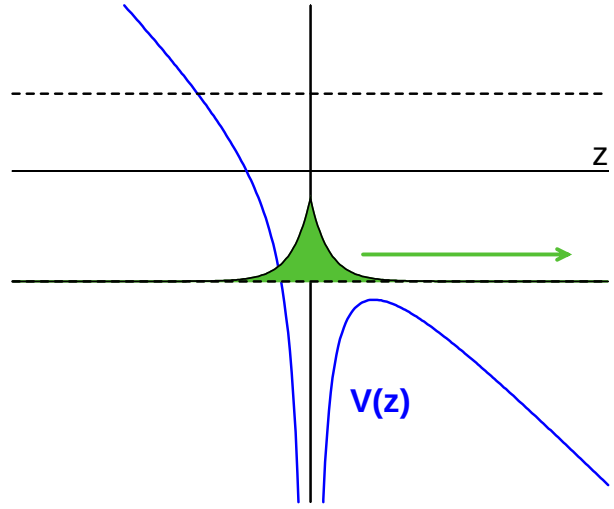
Tunneling rate for the hydrogen atom (see Landau & Lifshitz):

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

(derived from quasiclassical theory)

Over-barrier ionization

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

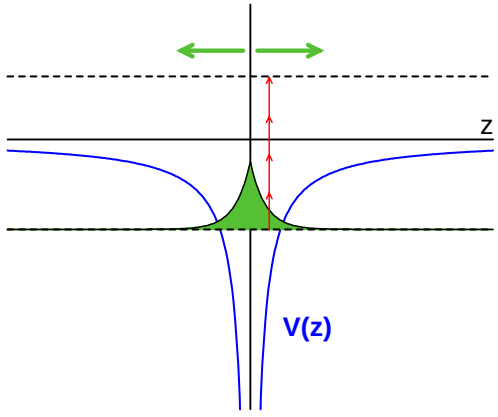


$\longrightarrow$ Classical escape of the electron.

$E_{\rm BS} =$ **barrier suppression field strength**
H atom: $E_{\rm BS} = 0.113$ a.u.
(corresponds to laser intensity $I_{\rm BS} = 4.5 \times 10^{14}$ W/cm^2)

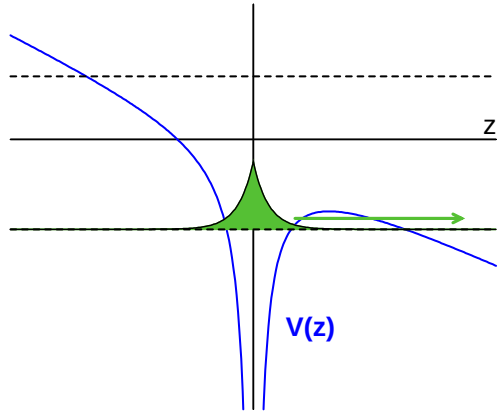
Ionization regimes

multiphoton ionization



$\gamma = \omega/\omega_{\rm t} > 1$

tunnel ionization



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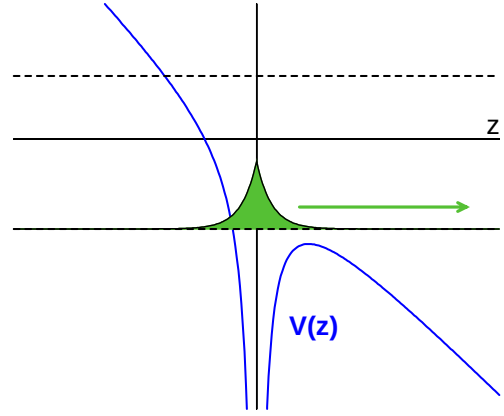
over-barrier ionization



$E > E_{\rm BS}$

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

H atom: $\gamma = \omega/E$

in general: $\gamma = \sqrt{I_{\rm p}/(2U_{\rm p})}$,

$I_{\rm p}$ = ionization potential, $U_{\rm p}$ = 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.

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For monochromatic field: $\dot{\mathbf{r}}(t) = \frac{\mathbf{E}_0}{\omega}[\cos(\omega t) - \cos(\omega t_0)]$

i.e. drift velocity $\mathbf{v}_{\mathrm{drift}} = -\frac{\mathbf{E}_0}{\omega}\cos(\omega t_0)$

$\longrightarrow$ Estimate of maximum photoelectron energy:

$$|\cos(\omega t_0)| = 1 \quad \rightarrow \quad \boxed{E_{\mathrm{max}} = \frac{E_0^2}{2\omega^2} = 2U_{\mathrm{p}}}$$

Above-threshold ionization

Absorption of more photons than needed to overcome the ionization threshold

$\rightarrow$ Peaks separated by the photon energy in the electron spectrum

Example:

experiment with Xe atoms,

Agostini et al. PRA **36**, R4111 (1987).

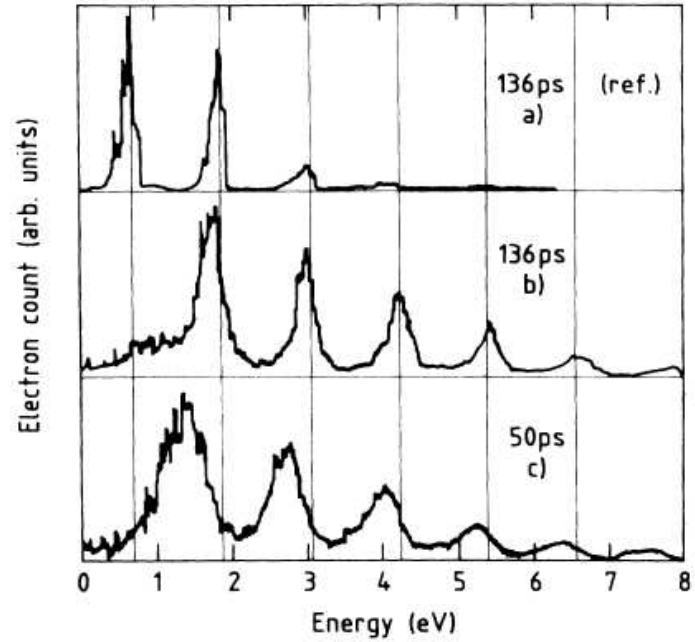

FIG. 2. Electron energy spectra for different laser intensities and pulse durations. (a) reference spectrum, $I = 2.2 \times 10^{12}$ W cm^{-2}; (b) and (c) $I = 7.5 \times 10^{12}$ W cm^{-2}.

Above-threshold ionization

Ponderomotive shift of the ATI peaks

- continuum dressed states have energies $\mathcal{E}_k^{\mathrm{d}} = k^2/2 + U_{\mathrm{p}}$

- shift of ground-state energy is small: $\mathcal{E}_{\mathrm{g}}^{\mathrm{d}} \approx E_{\mathrm{g}}$,
  so absorption of n photons yields electrons with energy $E_{\mathrm{g}} + n\omega$.

$\rightarrow$ Photoelectron kinetic energies $\boxed{k^2/2 = E_{\mathrm{g}} + n\omega - U_{\mathrm{p}}}$

Recollision mechanism

3-step process:

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

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2. acceleration by the field
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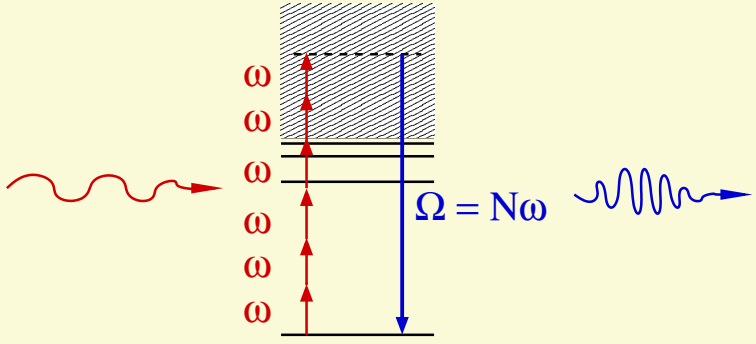
Possible consequences:

- recombination (high harmonic generation – coherent light)
- elastic scattering $\longrightarrow$ fast photoelectrons
- inelastic scattering $\longrightarrow$ e.g. double ionization

Mechanism of high-harmonic generation

Photon picture



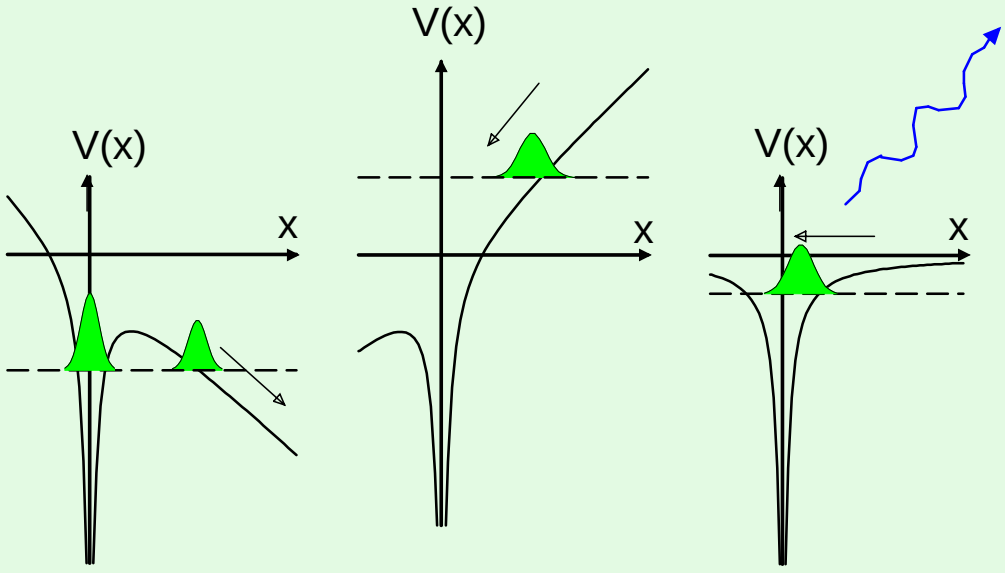
N photons of frequency ω

$\longrightarrow$ 1 photon of frequency $N\omega$.

Mechanism of high-harmonic generation

Recollision picture

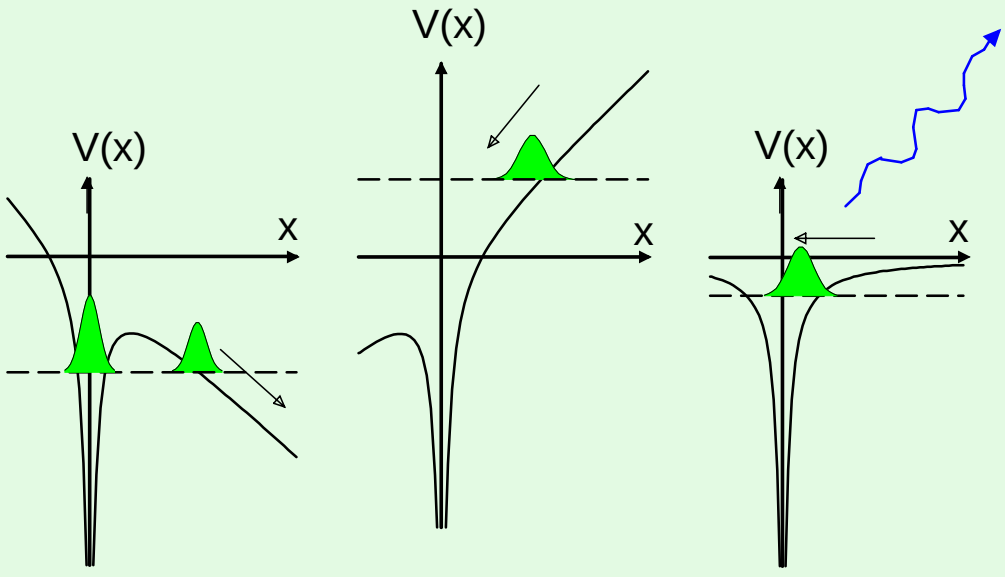
Ionization ***Free acceleration*** ***Recombination***



Mechanism of high-harmonic generation

Recollision picture

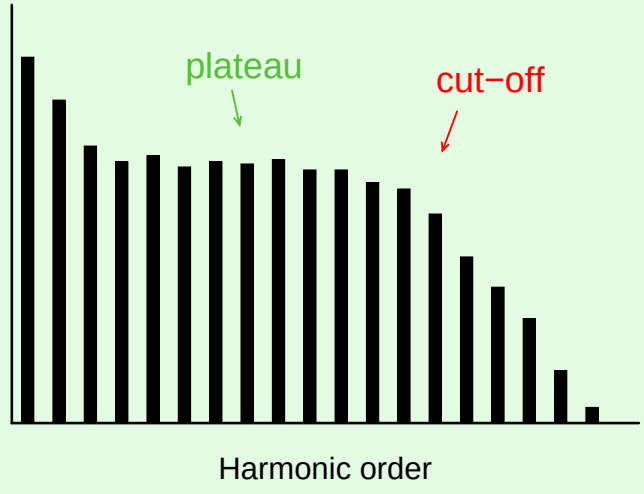
Ionization ***Free acceleration*** ***Recombination***



Maximum return energy: $E_{\max} = 3.17$

$\hookrightarrow$ Cut-off at $\boxed{\hbar\omega = 3.17U_{\mathrm{p}} + I_{\mathrm{p}}}$

[Corkum, PRL **71**, 1994 (1993)]



Calculation of spectra

Calculation of the time-dependent dipole acceleration

$$\boxed{\mathbf{a}(t) = \langle \psi(t) | \nabla V_0 + \mathbf{E}(t) | \psi(t) \rangle}$$

and Fourier transform

$$\boxed{\mathbf{a}(\Omega) = \int \mathbf{a}(t) e^{i\omega t}}$$

gives emission spectrum

$$\boxed{S(\Omega) \sim |\mathbf{a}(\Omega)|^2}$$

In practice: time integration over pulse duration T,

$$\boxed{\mathbf{a}(\Omega) = \int_0^T \mathbf{a}(t) f(t) e^{i\omega t}}$$

with some window function $f(t)$.

Alternatively: $\mathbf{a}(t) = \ddot{\mathbf{D}}(t)$ from time-dependent dipole moment $\mathbf{D}(t)$

or: $\mathbf{a}(t) = \dot{\mathbf{v}}(t)$ from time-dependent dipole velocity $\mathbf{v}(t)$

Application of high harmonics

- source of coherent extreme UV radiation and attosecond pulses

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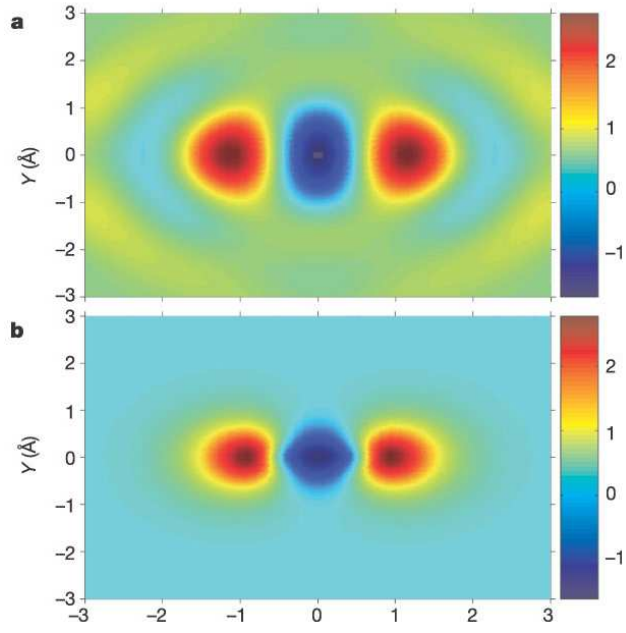
- investigation of molecular properties:

  molecular tomography: J. Itatani et al., Nature **432**, 867 (2004)

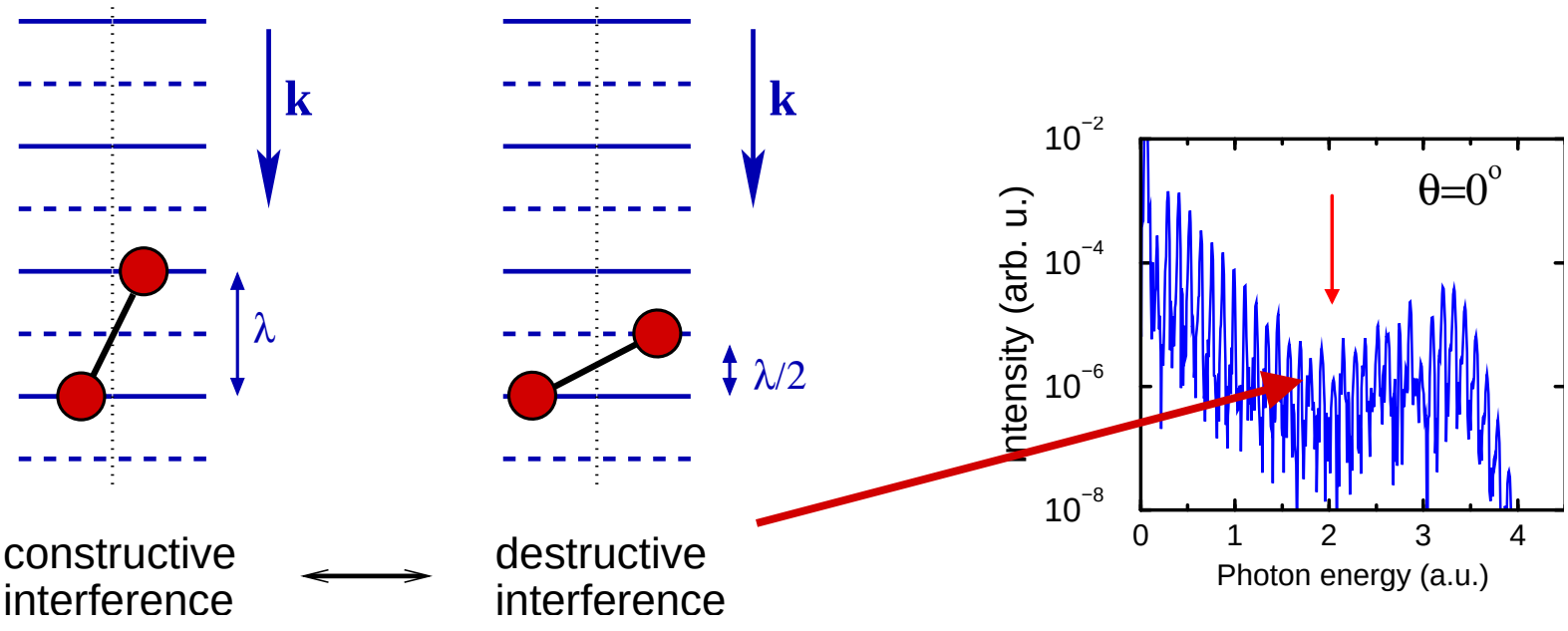


measured N_2 orbital

ab-initio N_2 orbital

Two-center interference

Recolliding electron with wave vector $\mathbf{k}$ in H_2 or H_2^+



Minimum occurs when $R\cos\theta = \lambda/2$ with $\lambda = 2\pi/k$ = electron wavelength

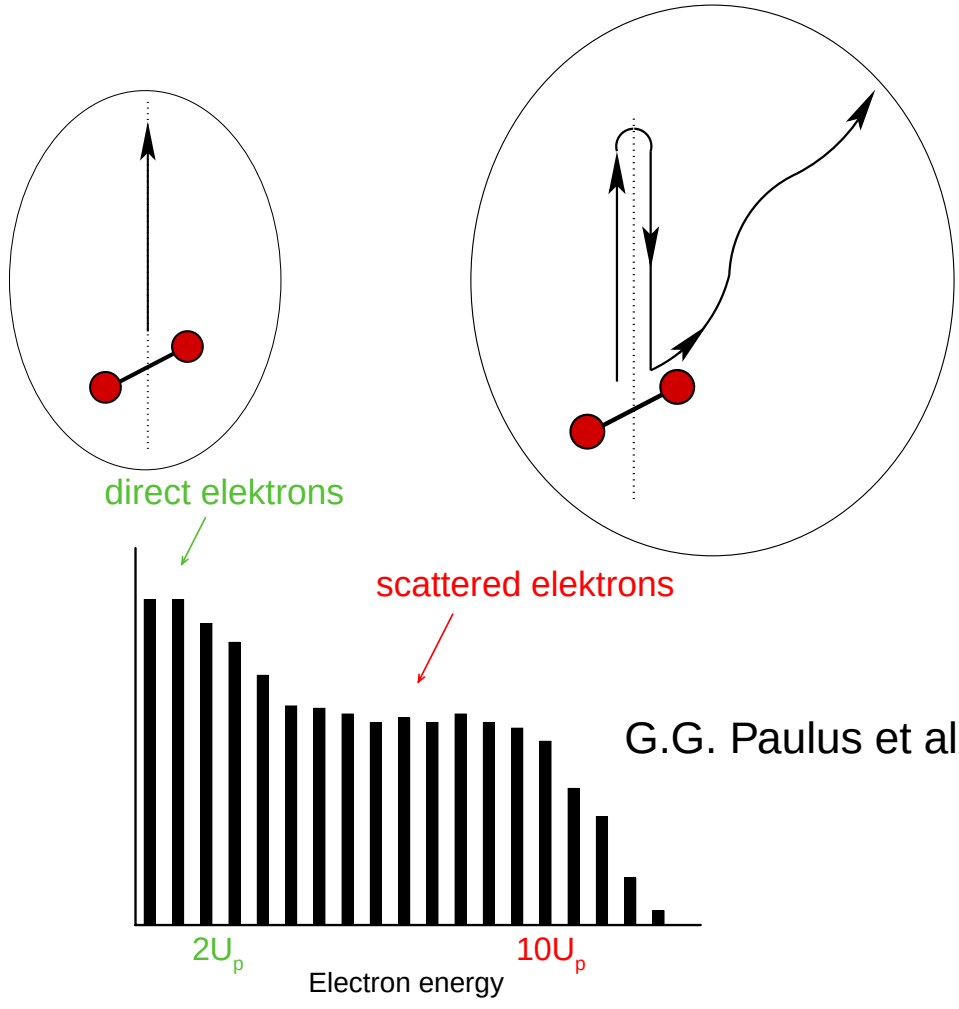
[Fixed-nuclei TDSE calculations:

M.L., N. Hay, R. Velotta, J.P. Marangos, P.L. Knight, PRL **88**, 183903 (2002)

Experimental confi rmation for CO_2: *T. Kanai et al., Nature **435**, 470 (2005)*]

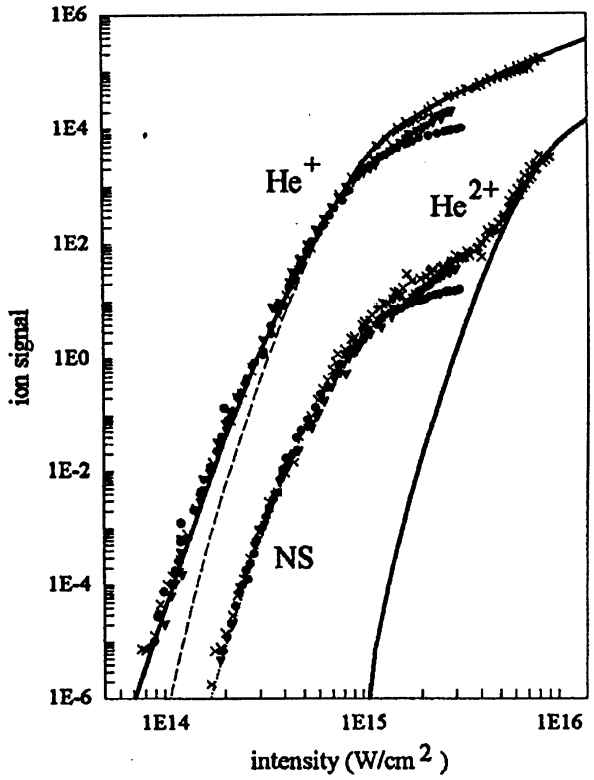
Rescattered photoelectrons

Scattered elektrons (*high-order above-threshold ionization*)



G.G. Paulus et al. PRL **72**, 2851 (1994)

Double ionization



Walker et al., PRL **73**, 1227 (1994)

Double ionization is enhanced due to electron correlations by orders of magnitude.

Identification of the recollision mechanism:

A. Becker, F.H.M. Faisal, J. Phys. B **29**, L197 (1996)

R. Moshammer et al., PRL **84**, 447 (2000)

T. Weber et al., Nature **405**, 658 (2000)

M.L., E.K.U. Gross, V. Engel, PRL **85**, 4707 (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 interpretation.

Strong-field approximation for ionization

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

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

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

The solution can be written in integral form:

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

Goal: calculation of transition amplitudes from ground state to continuum states with momentum $\mathbf{p}$ at final time $t_{\rm f}$:

$$M_{\mathbf{p}}(t_{\rm f},t_{\rm i}) = \langle\Psi_{\mathbf{p}}(t_{\rm f})|U(t_{\rm f},t_{\rm i})|\Psi_0(t_{\rm i})\rangle$$

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. $U(t,t'') \approx U_{\mathrm{V}}(t,t'')$ (Volkov-Propagator). Then

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

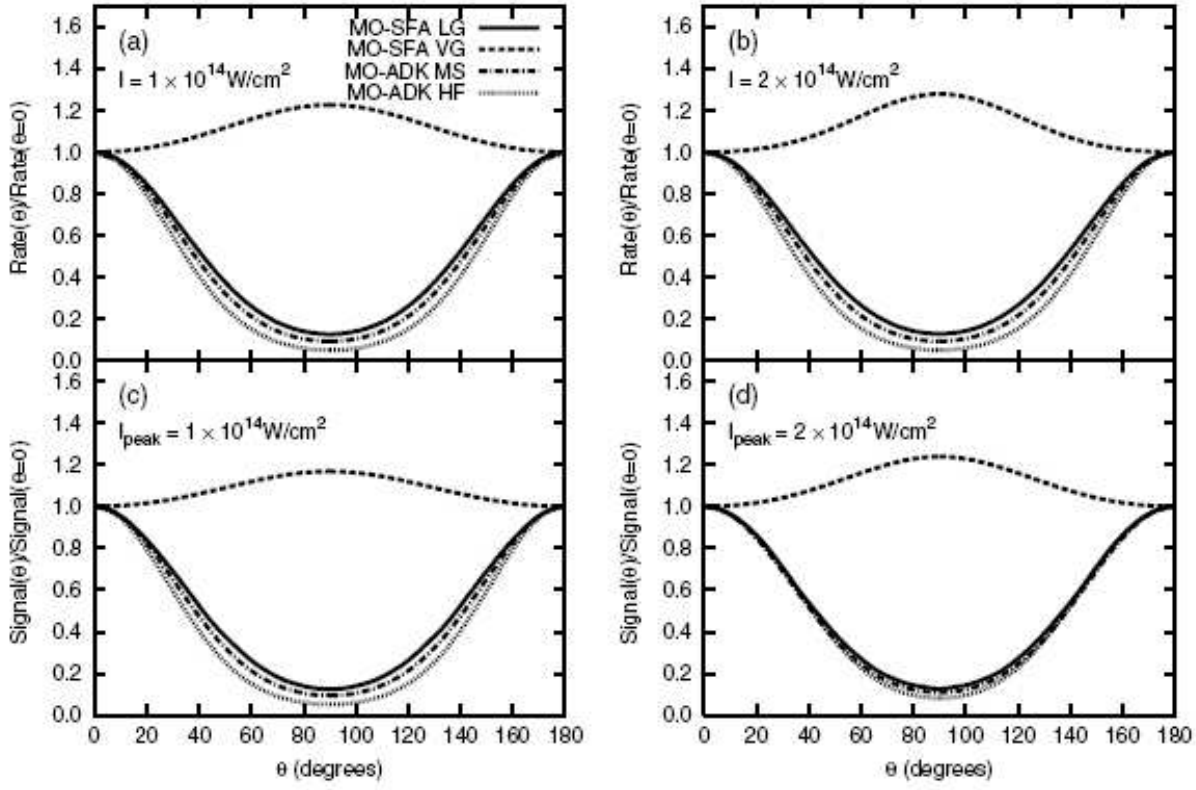
Assumption 2: final state with momentum $\mathbf{p}$ is approximated as a Volkov state.

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

$$M_{\mathbf{p}}^{\mathrm{SFA}}(t_{\mathrm{i}},t_{\mathrm{f}}) = -i\int_{t_{\mathrm{i}}}^{t_{\mathrm{f}}} \langle \Psi_{\mathbf{p}}^{\mathrm{V}}(t)|H_{\mathrm{int}}(t)|\Psi_0(t)\rangle\, dt$$

Strong-field approximation for ionization

SFA is not gauge invariant: results for ionization of N_2



T.K. Kjeldsen and L.B. Madsen, J. Phys. B **37**, 2033 (2004)

Length gauge ($\mathbf{r} \cdot \mathbf{E}(t)$) appears favourable (except for large molecules)

Strong-field approximation for high-harmonic generation

(Also known as Lewenstein model)

$$\mathbf{D}(t) = i\int_0^t dt'\, E(t') \int d^3p\, \langle \mathbf{p}+\mathbf{A}(t')|x|0\rangle\langle 0|\mathbf{r}|\mathbf{p}+\mathbf{A}(t)\rangle \exp[-iS(\mathbf{p},t,t')] \; + \text{c.c}$$

where $S(\mathbf{p},t,t') = \int_{t'}^{t} dt'' \left[\frac{(\mathbf{p}+\mathbf{A}(t''))^2}{2} + I_\mathrm{p}\right]$

(length-gauge form) [Lewenstein et al., Phys. Rev. A **49**, 2117 (1994)]

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(length-gauge form) [Lewenstein et al., Phys. Rev. A **49**, 2117 (1994)]

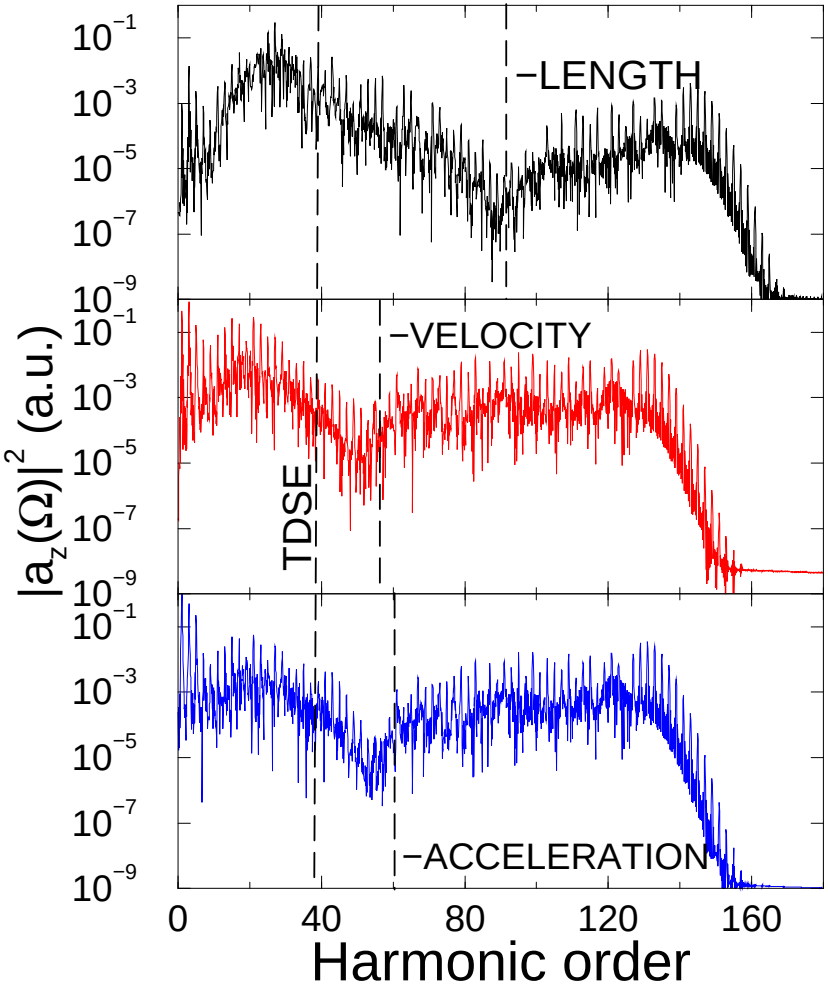
In addition to gauge problem, there is a ***choice of recombination operator***:

velocity (or acceleration) form preferable to length form

[A. Gordon, F.X. Kärtner, PRL **95**, 223901 (2005),

C.C. Chirilă, M.L., submitted]

Results for harmonic generation in H_2^+



$\theta = 40^{\circ}$

curves: full SFA results

dashed lines: minima from

- TDSE
- recombination elements only

Molecules

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

Hamiltonian:

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

with w_{j_1,j_2} nucleus-nucleus interaction, $w_{j,\mathrm{e}}$ 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

Idea: separation of time scales for nuclear and electronic motion due to great mass difference

$\rightarrow$ Electrons adjust "instantaneously" to nuclear positions.

Born-Oppenheimer (BO) Ansatz for wave function:

$$\boxed{\Psi(\mathbf{R},\mathbf{r},t) = \sum_m \chi_m(\mathbf{R},t)\,\Phi_m(\mathbf{R},\mathbf{r}),}$$

$\Phi_m(\mathbf{R},\mathbf{r}) =$ electronic eigenstates at fixed nuclear positions.

Inserting into the field-free TDSE yields

$$\begin{aligned} i\tfrac{\partial}{\partial t}\chi_m(\mathbf{R},t) = &\left[T_\mathrm{n} + V_m^\mathrm{BO}(\mathbf{R})\right]\chi_m && \leftarrow \textbf{BO approximation} \\ &+ \textstyle\sum_{m'} \langle \Phi_m | T_\mathrm{n} | \Phi_{m'} \rangle \chi_{m'} && \leftarrow \text{non-BO couplings} \\ &- T_\mathrm{n}\chi_m && (T_\mathrm{n} \text{ acting on both } \Phi_{m'} \text{ and } \chi_{m'}) \end{aligned}$$

Born-Oppenheimer approximation

Including the laser-molecule interaction, the BO TDSE becomes:

$$i\frac{\partial}{\partial t}\chi_m(\mathbf{R},t) = \left[T_{\rm n} + V_m^{\rm BO}(\mathbf{R})\right]\chi_m(\mathbf{R},t) \; - \; \mathbf{E}\cdot\sum_{m'}\langle\Phi_m|\mathbf{D}|\Phi_{m'}\rangle\chi_m$$

$\longrightarrow$ Functions χ_m coupled only by the dipole matrix elements.

BO approximation breaks down for highly excited electrons:

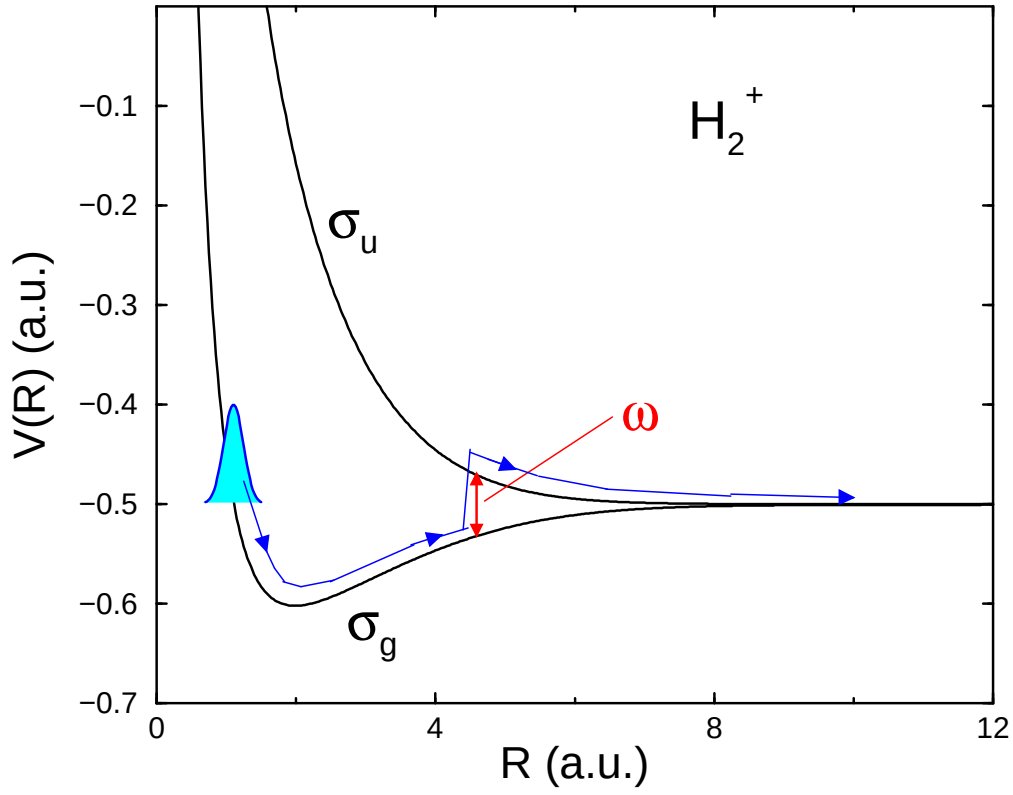
- Rydberg molecules
- Electrons in the continuum (from laser-molecule interaction)

Fragmentation mechanisms in H_2^+

- Bond softening
- “Above-threshold” dissociation
- Charge resonance enhanced ionization
- Coulomb explosion

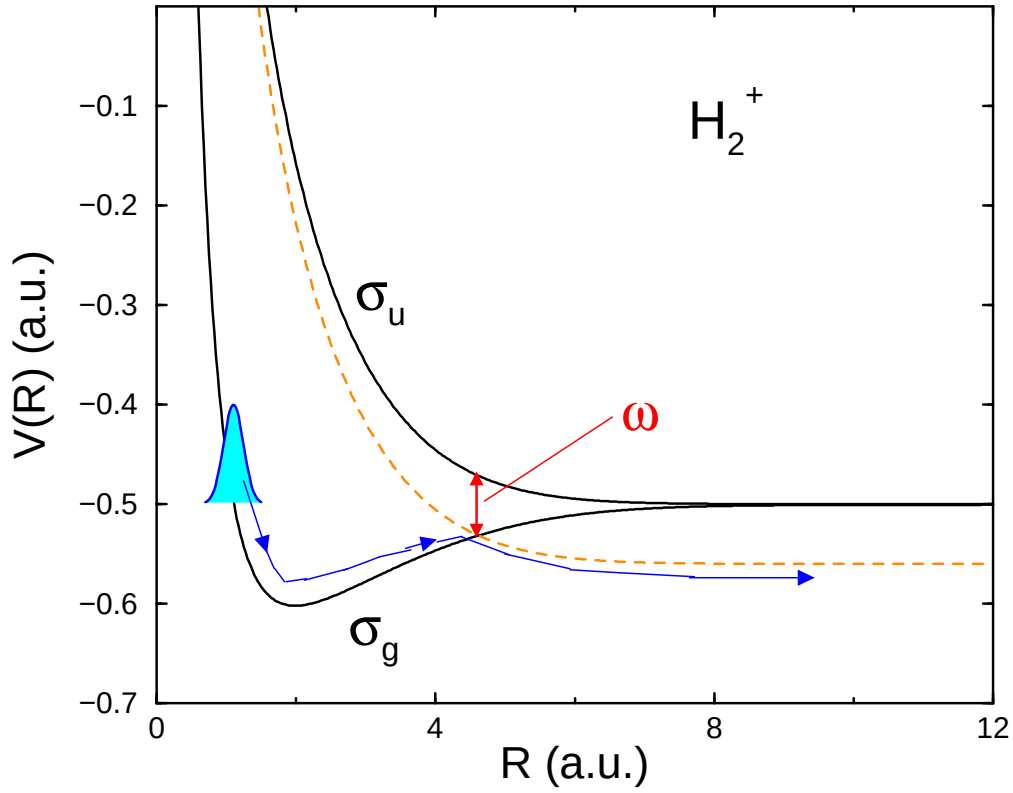
Bond softening

Transitions between BO states occur at nuclear positions where photon energy is resonant.



Bond softening

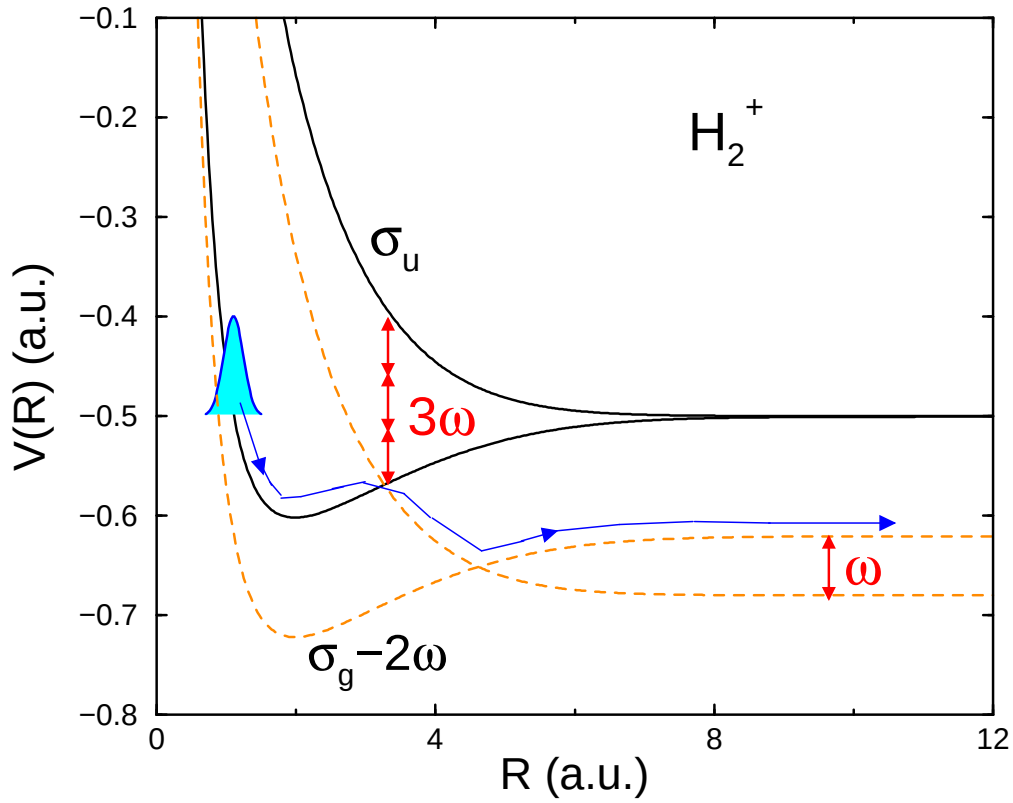
Alternative picture: potential surfaces shifted by multiples of the photon energy ($\longrightarrow$ **diabatic potentials**)



Lowering of dissociation threshold = **bond softening**

"Above-threshold" dissociation

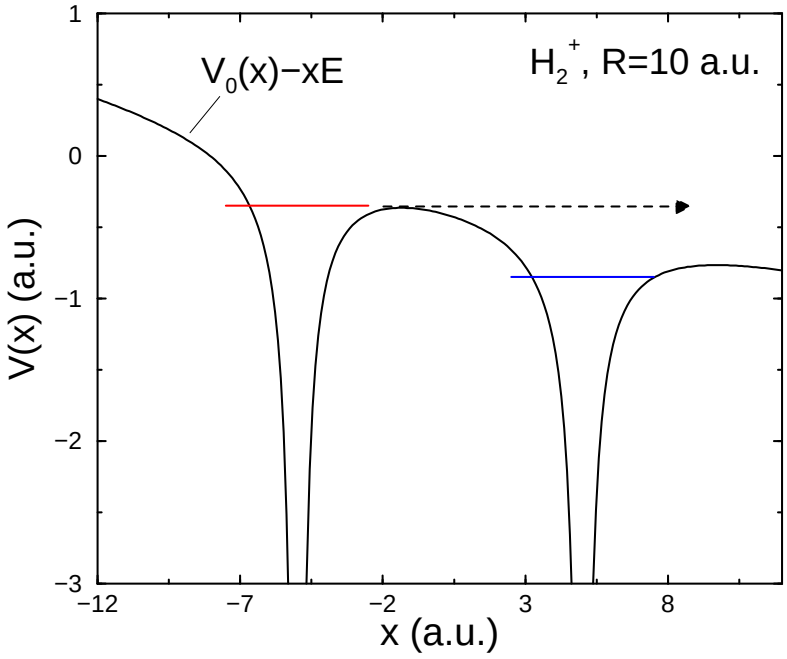
3-photon absorption + 1-photon emission
= effective 2-photon absorption



Charge-resonance enhanced ionization

At a range of internuclear distances, the tunneling barrier is suppressed by the presence of the second center.

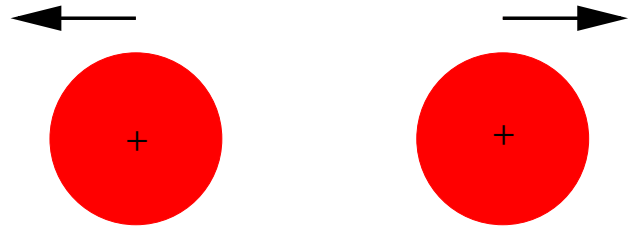
$\longrightarrow$ **enhancement of ionization**



Seideman, Ivanov, Corkum, PRL **75**, 2819 (1995),
Zuo, Bandrauk, PRA **52**, R 2511 (1995).

Coulomb explosion

Ionization of H_2^+ and other molecular ions can create two charged centers $\rightarrow$ rapid fragmentation due to Coulomb repulsion.



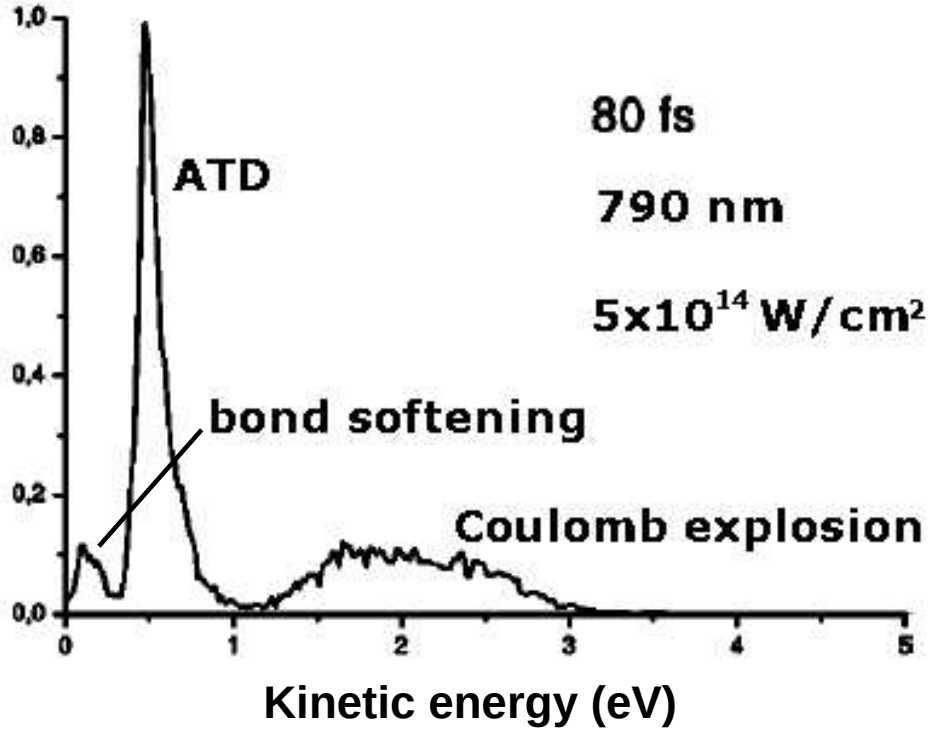
Kinetic energy release indicates initial internuclear distance by energy conservation:

$$E_{\mathrm{kin}} \approx 1/R_{\mathrm{initial}}$$

$\rightarrow$ **Coulomb explosion imaging**

Typical fragment spectrum

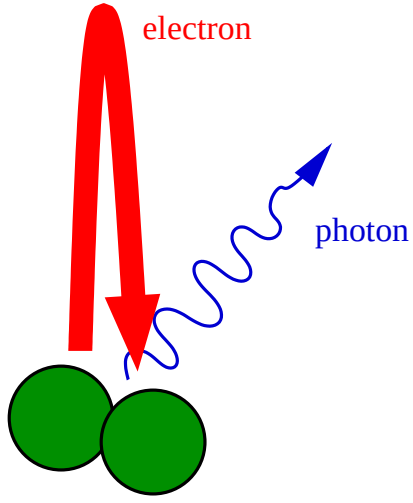
Energies of D^+ ions from D_2 in a strong pulse



[Trump et al. PRA **62**, 063402 (2000)]

Harmonic generation in molecules

For small molecules: electron excursion $>>$ molecular size



Atom-like mechanism

Influence of molecular properties on ionization and recombination

$\rightarrow$ *Probing of molecular structure / dynamics*

SFA for harmonics in vibrating molecules

Assume

- Born-Oppenheimer motion of core electrons,
- transition matrix element independent of internuclear distance

  (suffi cient is $d(\mathbf{k}, R) = f(\mathbf{k})\, g(R)$)

$\longrightarrow$ Creation of a nuclear wave packet χ that evolves on the BO potential surface of the ion between t' and t.

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$\longrightarrow$ Creation of a nuclear wave packet χ that evolves on the BO potential surface of the ion between t' and t.

$$\longrightarrow \mathbf{P}(t) = 2 \int_0^t dt'\, E(t') \int dR\, \chi(R,0)^* \chi(R, t-t')$$
$$\times \int d^3p\, \langle \mathbf{p}+\mathbf{A}(t')|x|0\rangle \langle 0|\nabla|\mathbf{p}+\mathbf{A}(t)\rangle \exp[-iS(\mathbf{p}, t, t')] \; + \; \text{c.c}$$

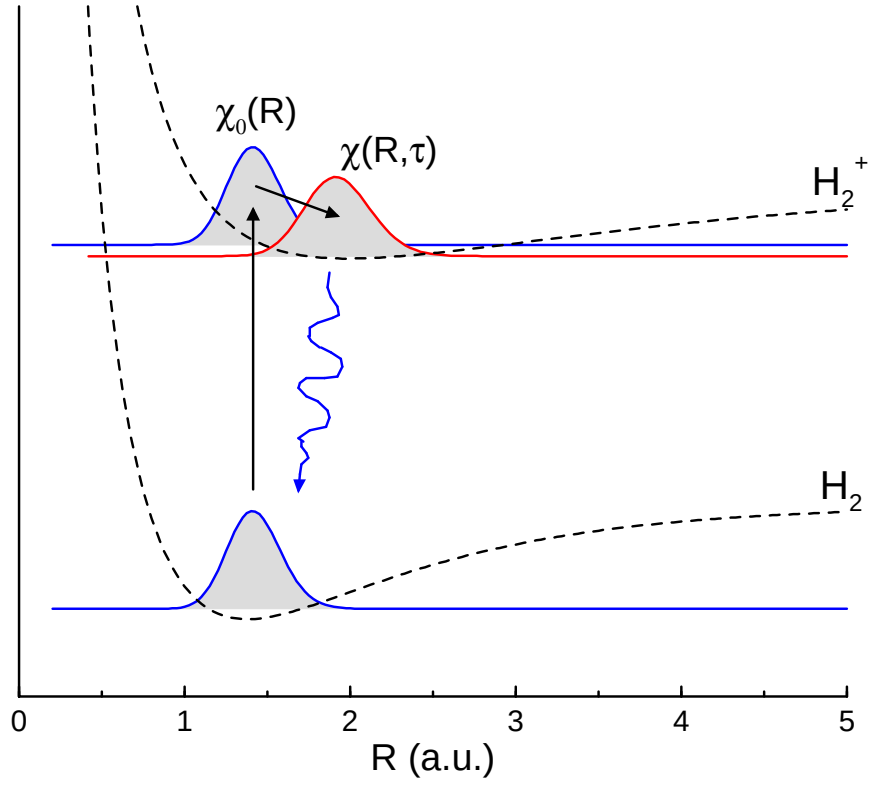
with vibrational wave packet $\chi(R, \tau)$.

$\longrightarrow$ Harmonics are sensitive to the vibrational autocorrelation function

$$C(\tau) = \int dR\, \chi(R,0)^* \chi(R, \tau)$$

Vibrational autocorrelation function

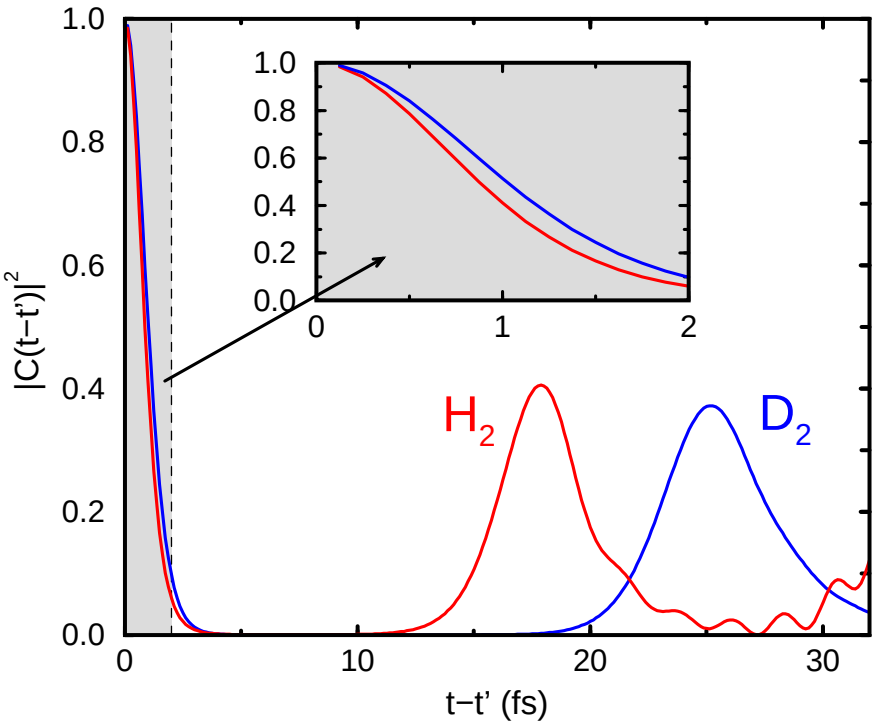
Illustration of physical mechanism:



Vibrational autocorrelation function

Calculate field-free evolution of a vibrational wave packet in the BO potential of H_2^+/D_2^+,

$$i\frac{\partial\chi(R,t)}{\partial t} = \left[-\frac{\partial_R^2}{M} + V_{\rm BO}^+(R)\right]\chi(R,t), \quad \chi(R,0) = \chi_0^{\rm H_2}(R)$$



→ More intense harmonics in heavier isotope D_2.

SFA for harmonics vibrating molecules

Generalization to matrix elements depending on internuclear distance and momentum:

$$d_{\rm ion}(\mathbf{k},R)\,\chi_0^{\rm H_2}(R) =: \bar{d}_{\rm ion}(\mathbf{k})\,\xi_{\mathbf{k}}(R,t=0)$$
$$d_{\rm rec}(\mathbf{k},R)\,\chi_0^{\rm H_2}(R) =: \bar{d}_{\rm rec}(\mathbf{k})\,\eta_{\mathbf{k}}(R,t=0)$$

$$\rightarrow P_x(t) = 2i\int_0^t dt'\,E(t')\int d^3p\;\; C(\mathbf{p},t',t)$$
$$\times\,\bar{d}_{\rm ion}(\mathbf{p}+A(t'))\;\bar{d}_{\rm rec}(\mathbf{p}+A(t))\exp[-iS(\mathbf{p},t,t')]\;+\;\text{c.c}$$

where

$$C(\mathbf{p},t',t) = \int dR\,[\eta_{\mathbf{p}+\mathbf{A}(t)}(R,0)]^*\,\xi_{\mathbf{p}+\mathbf{A}(t')}(R,t-t')$$

is the overlap between the evolved wave packet $\xi_{\mathbf{p}+\mathbf{A}(t')}(R,t-t')$ and the "target wave packet" $\eta_{\mathbf{p}+\mathbf{A}(t)}(R,0)$.

SFA for harmonics in vibrating molecules

Approximately: $\xi_{\mathbf{k}}(R) \approx \chi_0^{H_2}(R)$ (initial wave packet)

$$\rightarrow C(\mathbf{p}, t, t') = \int dR\, \chi_0^{H_2}(R)\, \frac{d_{\rm rec}(\mathbf{p}+\mathbf{A}(t),R)}{\bar{d}_{\rm rec}(\mathbf{p}+\mathbf{A}(t))}\, \chi(R, t-t')$$

H_2 with LCAO: $d_{\rm rec}(\mathbf{k}, R) = N(R) k_x \cos(\mathbf{k}\cdot\mathbf{R}/2) \langle 0|\mathbf{k}\rangle_{\rm atom}$

Harmonics are proportional to

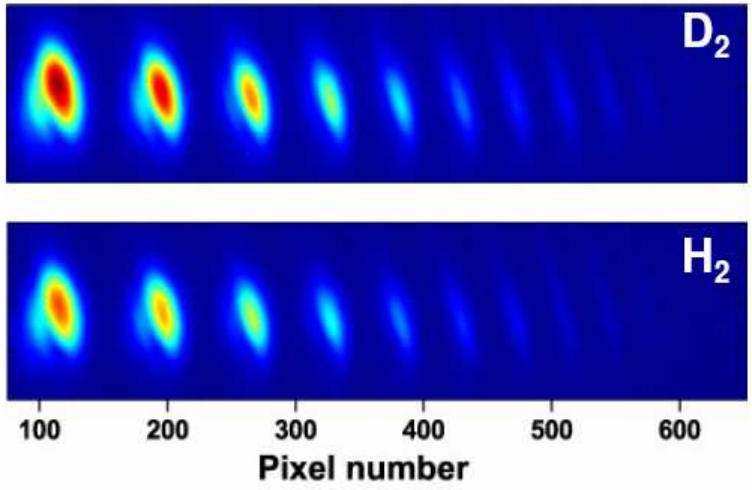
$$\boxed{\left| \int dR\, \chi_0^{H_2}(R)\, \cos(\mathbf{k}\cdot\mathbf{R}/2)\, \chi(R, t-t') \right|^2}.$$

(This incorporates interference + vibration.)

Comparison with experiment

8 fs pulses, wavelength 775 nm, intensity 2×10^{14} W/cm^2

Raw data of harmonics in D_2 and H_2



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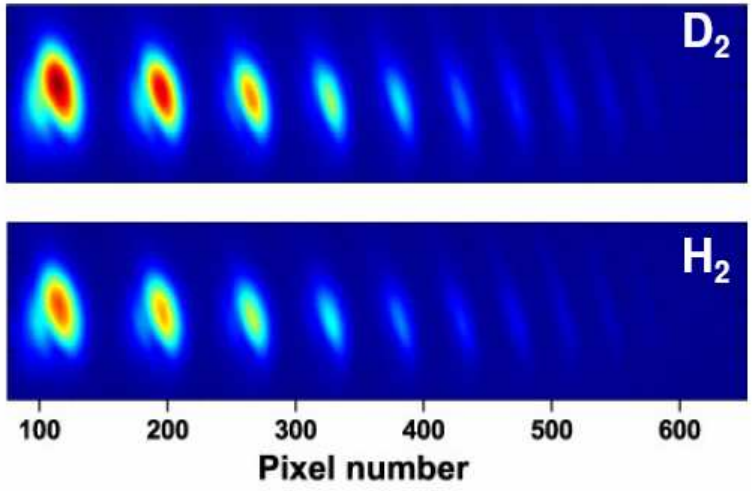
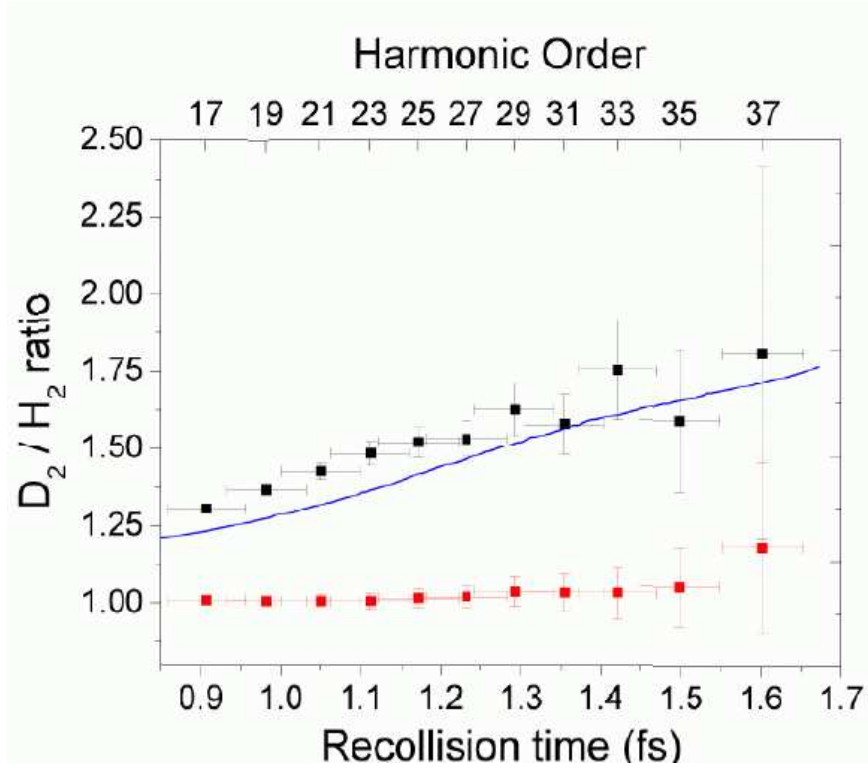


Ratio D_2/H_2



Blue: theory

Baker, Robinson, Haworth, Teng, Smith, Chirilă, Lein, Tisch, Marangos, Science **312**,424 (2006)

Conclusions

- There is a whole zoo of phenomena in intense-laser matter interactions
- In general, theoretical description is far from being quantitative.
- TDDFT is the only tractable first-principles approach, already for atoms. Many-body wave-function methods are restricted to 2 particles.

Next part:

- Learning about TDDFT and physical mechanisms from model systems