Time-dependent density functional theory

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OUTLINE

LECTURE I
- **Phenomena to be described by TDDFT**

LECTURE II
- **Review of ground-state DFT**

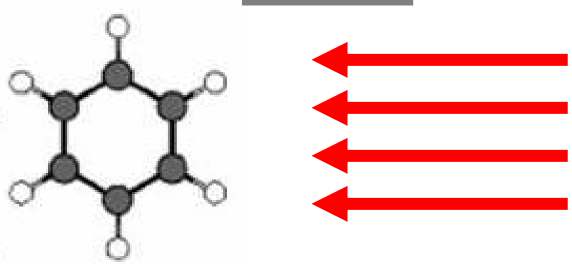
LECTURE III
- **Basic theorems of TDDFT**
- **TDDFT in the linear-response regime: Calculation of optical excitation spectra**

LECTURE IV: TDDFT beyond the regime of linear response
- **TD Electron Localization Function (TDELF)**
- **Calculating electronic transport using TDDFT**
- **Optimal control theory**

PHENOMENA TO BE DESCRIBED WITH TDDFT

Time-dependent systems

Generic situation:
Molecule in laser field



$$\hat{H}(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{j,\alpha} -\frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \vec{E}\cdot\vec{r}_j \cdot \sin\omega t$$

Strong laser ($v_{laser}(t) \geq v_{en}$) :

Non-perturbative solution of full TDSE required

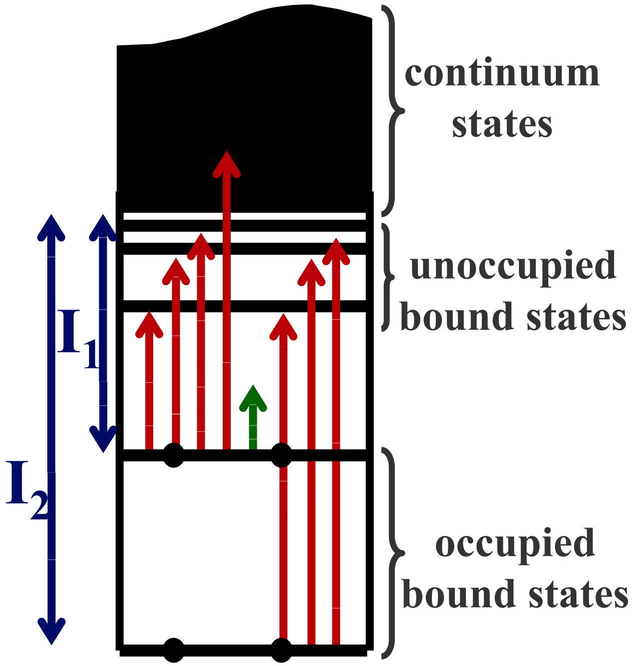
Weak laser ($v_{laser}(t) << v_{en}$) :

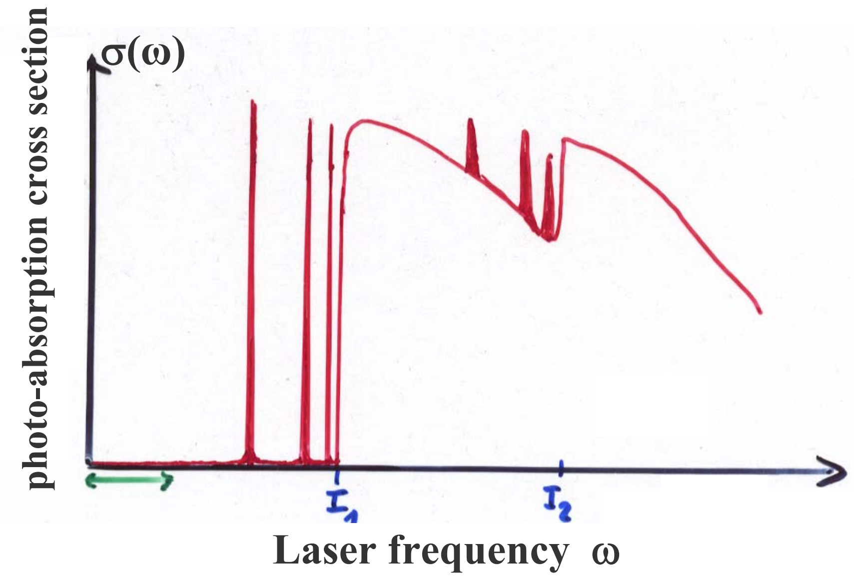
Calculate **1. Linear density response** $\rho_1(\vec{r}\ t)$

2. Dynamical polarizability $\alpha(\omega) = -\frac{e}{E}\int z\,\rho_1(\vec{r},\omega)\,d^3r$

3. Photo-absorption cross section $\sigma(\omega) = -\frac{4\pi\omega}{c}\,\mathrm{Im}\,\alpha$

Photo-absorption in weak lasers





No absorption if ω < lowest excitation energy

Standard linear response formalism

$H(t_0)$ = full static Hamiltonian at t_0

$$H(t_0)|m\rangle = E_m|m\rangle$$

← **exact many-body eigenfunctions and energies of system**

full response function

$$\chi(r,r';\omega) = \lim_{\eta\to 0^+}\sum_m\left(\frac{\langle 0|\hat{\rho}(r)|m\rangle\langle m|\hat{\rho}(r)|0\rangle}{\omega-(E_m-E_0)+i\eta}-\frac{\langle 0|\hat{\rho}(r')|m\rangle\langle m|\hat{\rho}(r')|0\rangle}{\omega+(E_m-E_0)+i\eta}\right)$$

⇒ The exact linear density response

$$\rho_1(\omega) = \chi(\omega)\, v_1$$

has poles at the exact excitation energies $\Omega = E_m - E_0$

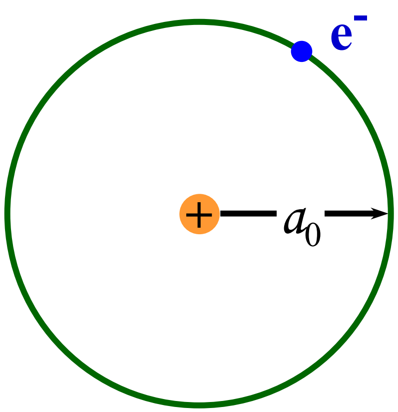
Strong Laser Fields

Intensities in the range of 10^{13} …10^{16} W/cm^2

Comparison: Electric field on 1st Bohr-orbit in hydrogen

$$E = \frac{1}{4\pi\varepsilon_0}\frac{e}{a_0^2} = 5.1\times10^9\ \mathrm{V/m}$$

$$I = \frac{1}{2}\varepsilon_0 c E^2 = 3.51\times10^{16}\ \mathrm{W/cm^2}$$



Three quantities to look at:

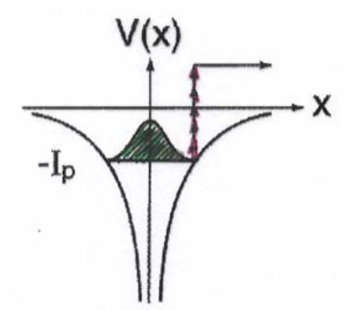
I. **Emitted ions**
II. **Emitted electrons**
III. **Emitted photons**

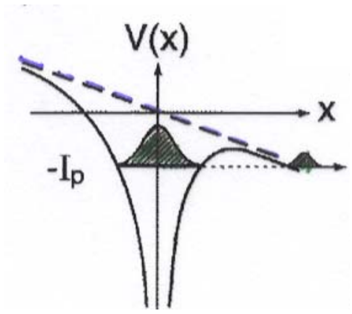
I. Emitted Ions

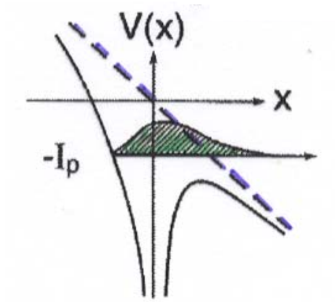
Three regimes of ionization, depending on Keldysh parameter

$$\gamma := \frac{\omega}{E} (\text{a.u.})$$

Multiphoton | **Tunneling** | **Over the barrier**



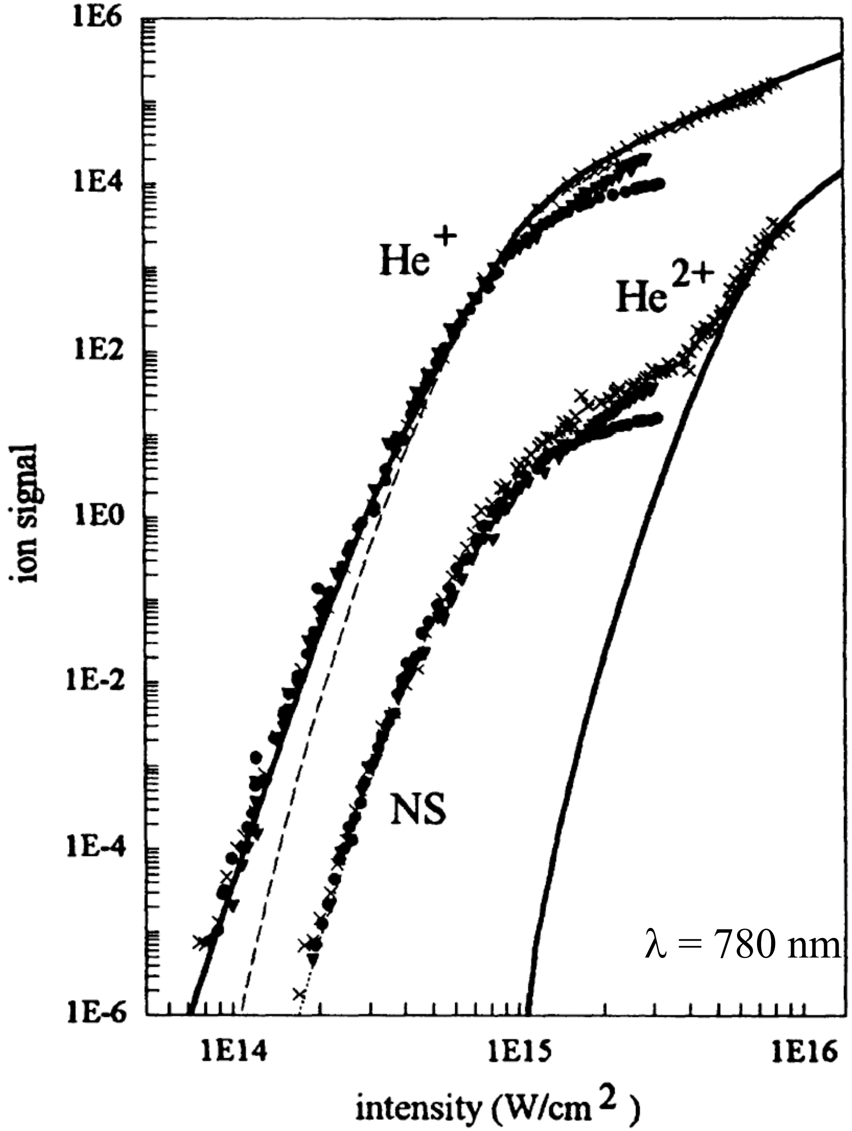




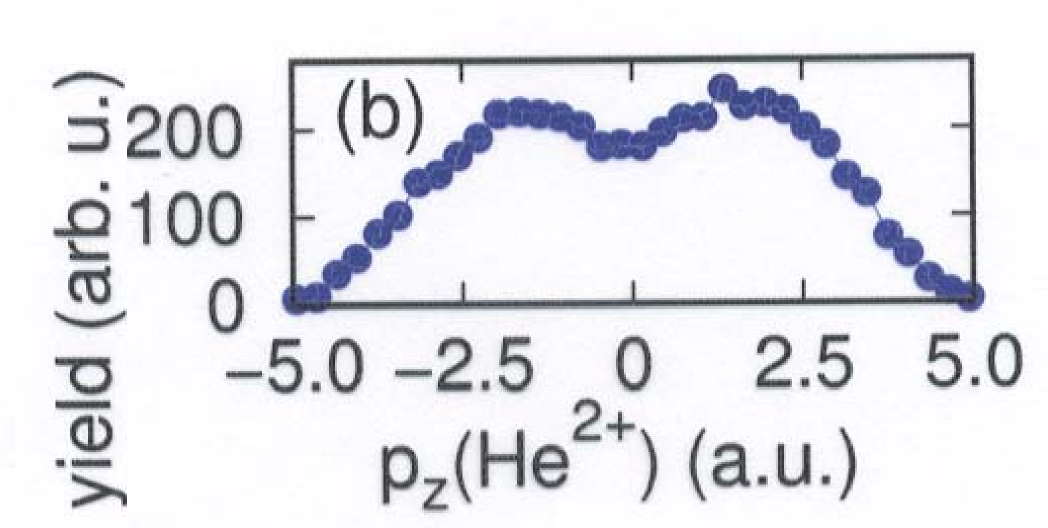
$\gamma >> 1$ | $\gamma \approx 1$ | $\gamma << 1$

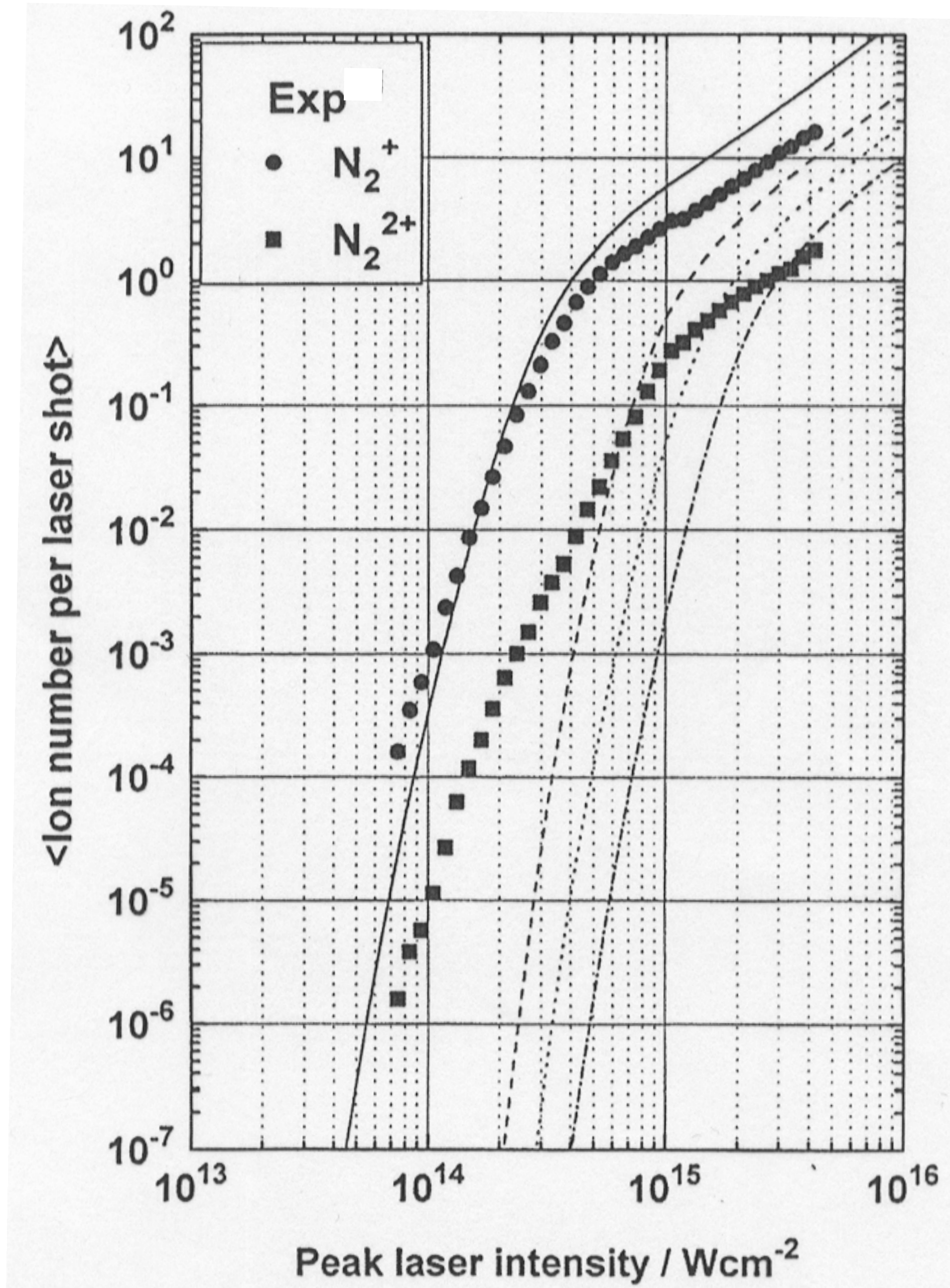
Multiphoton-Ionization (He)

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



Momentum Distribution of the He^{2+} recoil ions

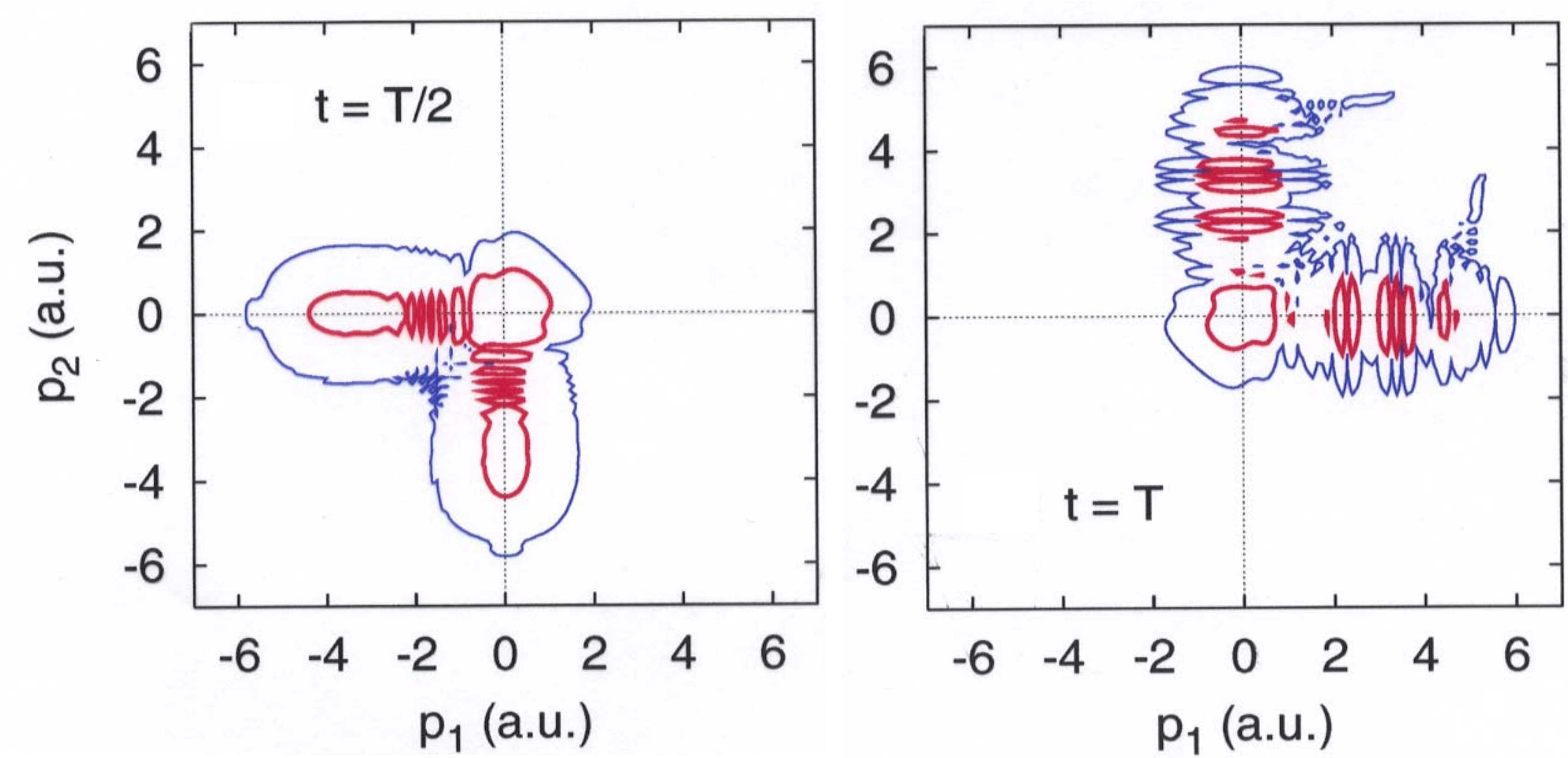




Exp
N_2^+
N_2^{2+}
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
<Ion number per laser shot>
10^{13}
10^{14}
10^{15}
10^{16}
Peak laser intensity / Wcm^{-2}

$$\left|\Psi\left(p_1, p_2, t\right)\right|^2 \quad \text{of the He atom}$$

(M. Lein, E.K.U.G., V. Engel, J. Phys. B 33, 433 (2000))



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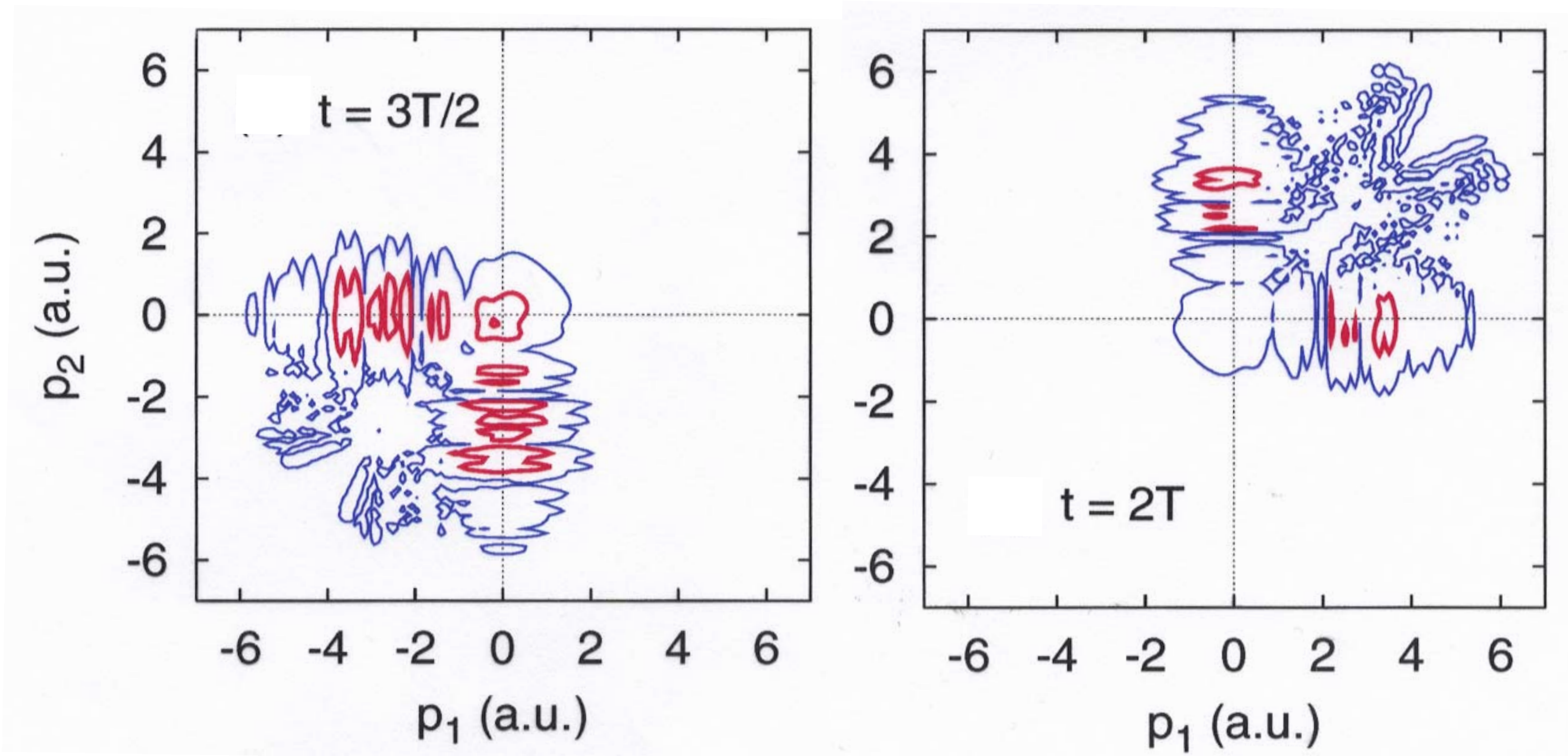
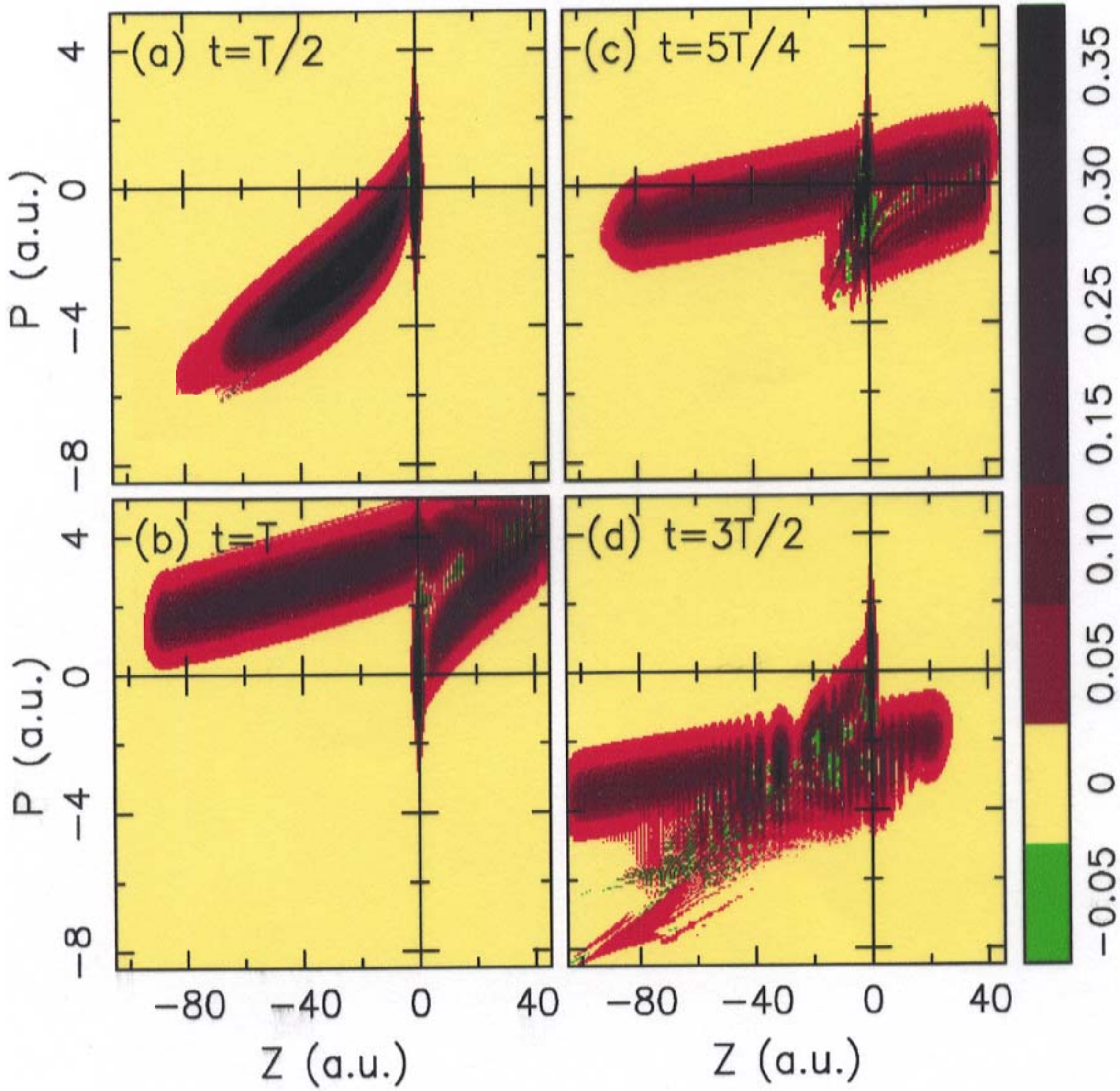


Wigner distribution W(Z,P,t) of the electronic center of mass for He atom

(M. Lein, E.K.U.G., V. Engel, PRL 85, 4707 (2000))



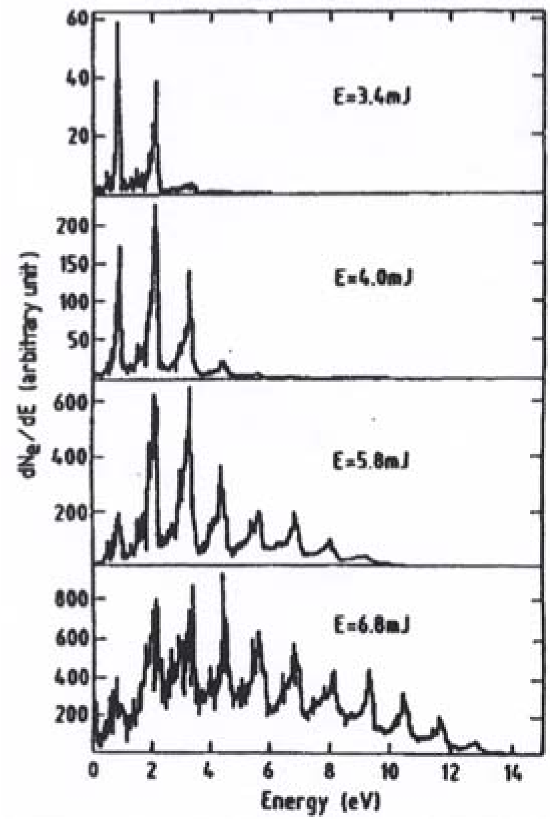
$v_{Laser}(z,t) = E\, z \sin \omega t$ $I = 10^{15}$ W/cm^2 $\lambda = 780$ nm

II. Electrons: Above-Threshold-Ionization (ATI)

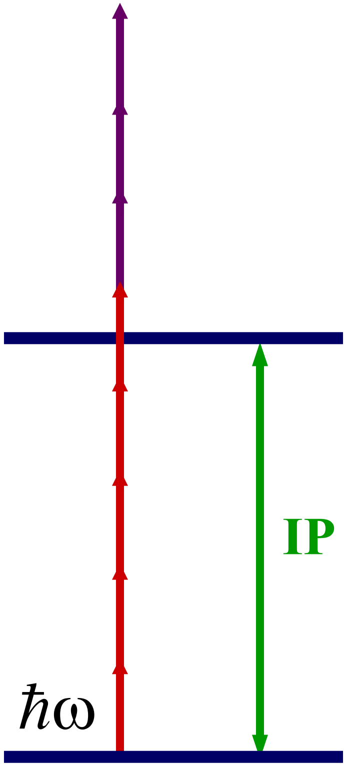
Ionized electrons absorb more photons than necessary to overcome the ionization potential (IP)

Photoelectrons: $E_{kin} = (n+s)\hbar\omega - IP$

⇒ Equidistant maxima in intervals of $\hbar\omega$:

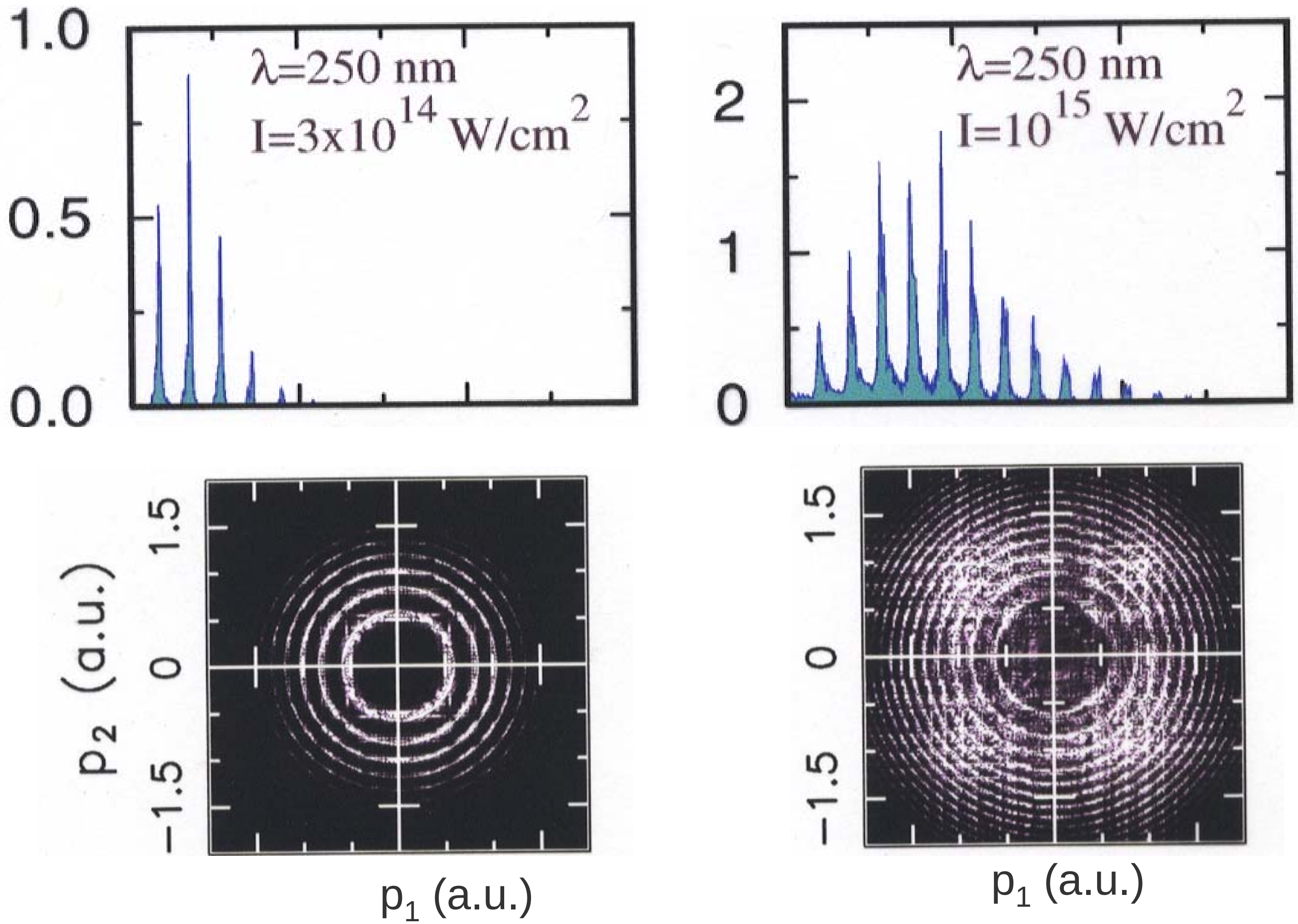


Agostini et al., PRL 42, 1127 (1979)



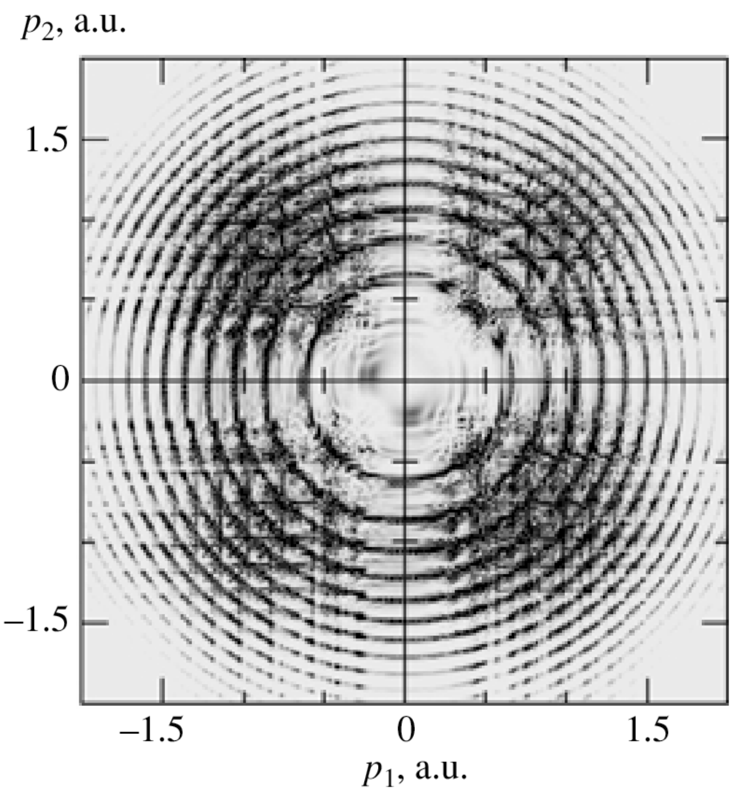
He: Above threshold double ionization

M. Lein, E.K.U.G., V. Engel, PRA 64, 23406 (2001)

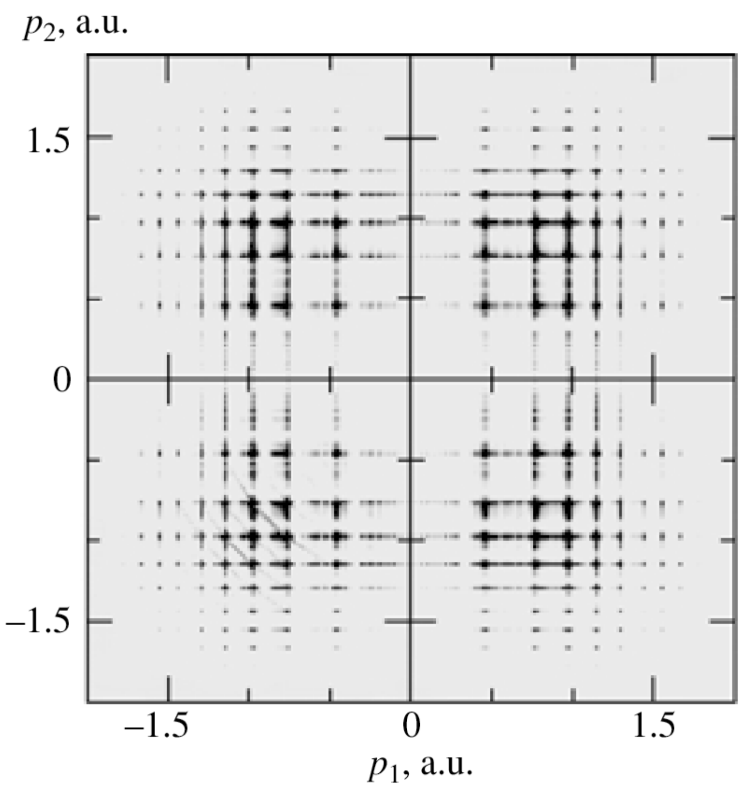


Role of electron-electron interaction

M. Lein, E.K.U.G., and V. Engel, Laser Physics <u>12</u>, 487 (2002)



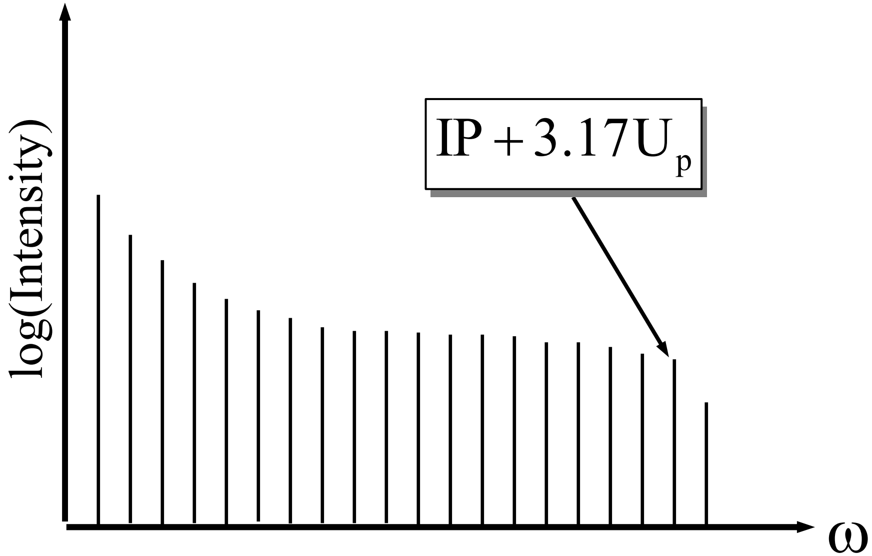
Two-electron momentum distribution for double ionization of the He model atom by a 250 nm pulse with intensity 10^{15} W/cm^2.

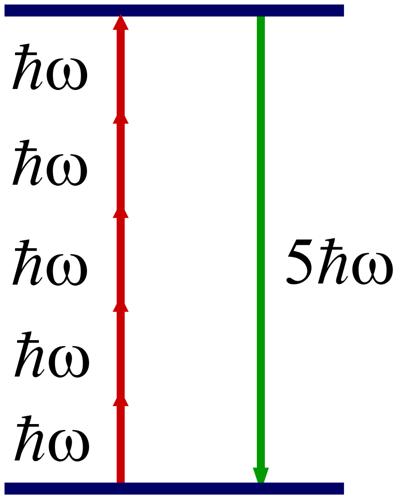


Two-electron momentum distribution for double ionization of the He model atom with non-interaction electrons by a 250 nm pulse with intensity 10^{15} W/cm^2.

III. Photons: High-Harmonic Generation

Emission of photons whose frequencies are integer multiples of the driving field. Over a wide frequency range, the peak intensities are almost constant (plateau).

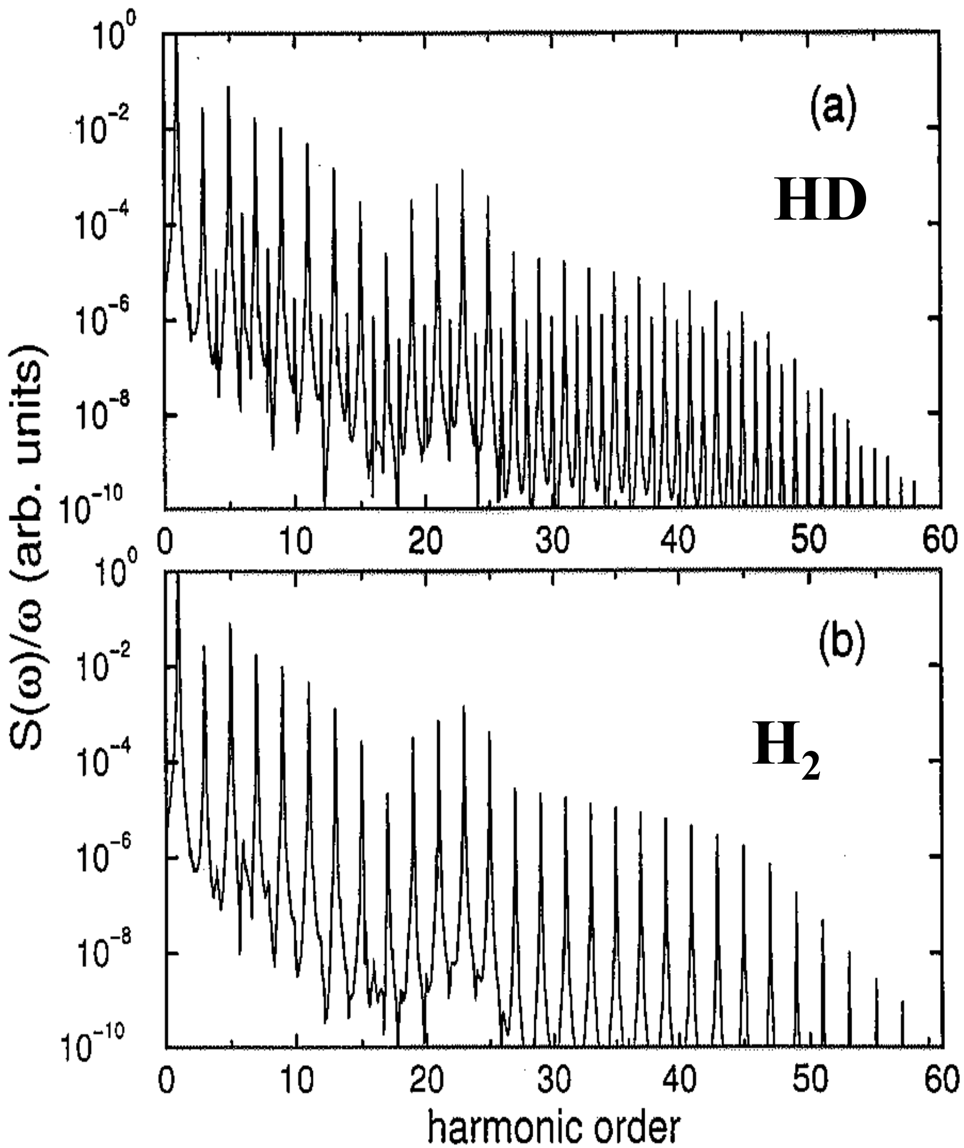




Even harmonic generation due to nuclear motion

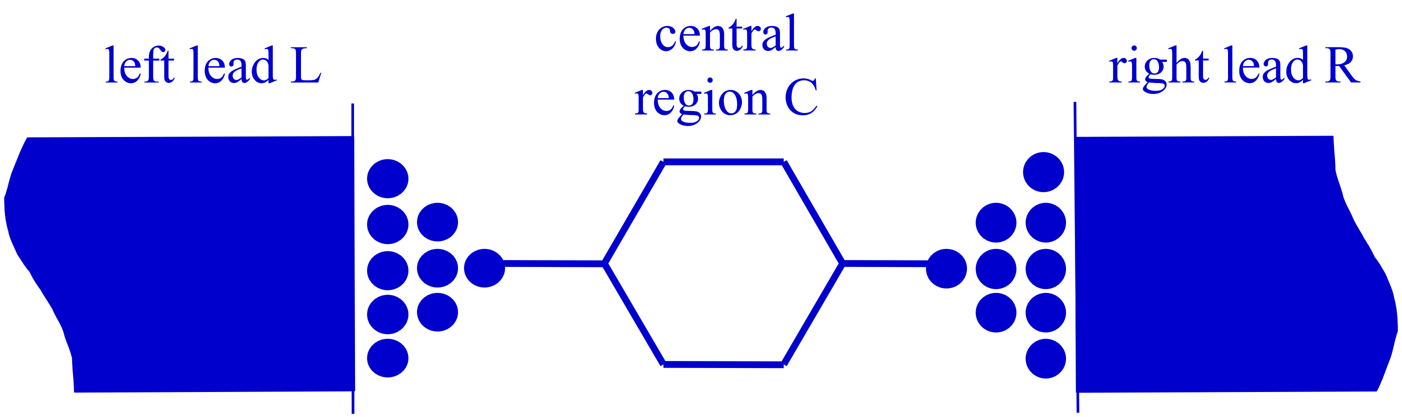
(a) Harmonic spectrum generated from the model HD molecule driven by a laser with peak intensity 10^{14} W/cm^2 and wavelength 770 nm. The plotted quantity is proportional to the number of emitted phonons. (b) Same as panel (a) for the model H_2 molecule.

T. Kreibich, M. Lein, V. Engel, E.K.U.G., PRL 87, 103901 (2001)



Molecular Electronics

Dream: Use single molecules as basic units (transistors, diodes, …) of electronic devices



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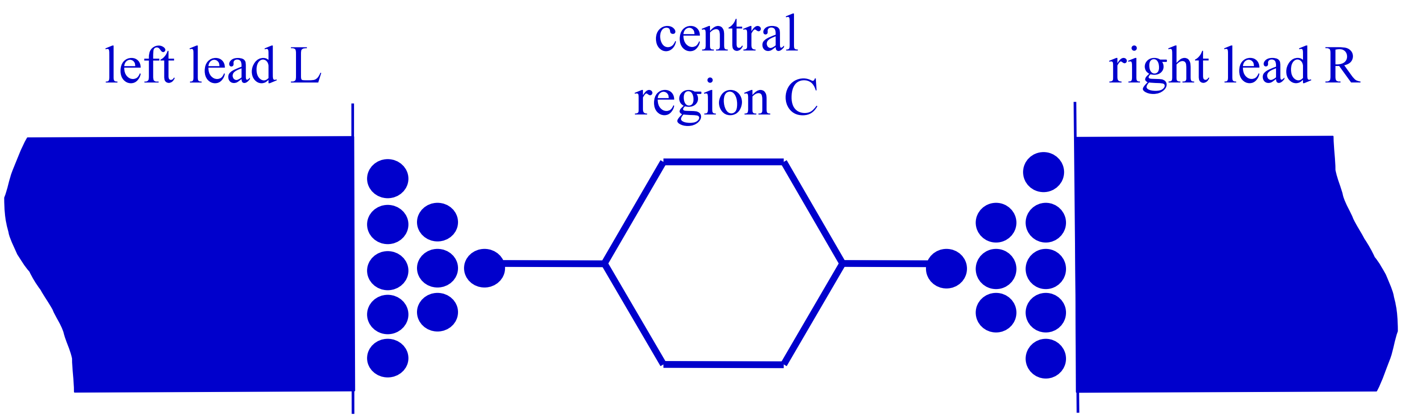

Bias between L and R is turned on: U(t) ⟶ V for large t

A steady current, I, may develop as a result.

- **Calculate current-voltage characteristics I(V)**

Hamiltonian for the complete system of N_e electrons with coordinates $(r_1 \cdots r_{N_e}) \equiv \underline{\underline{r}}$ and N_n nuclei with coordinates $(R_1 \cdots R_{N_n}) \equiv \underline{\underline{R}}$, masses $M_1 \cdots M_{N_n}$ and charges $Z_1 \cdots Z_{N_n}$.

$$\hat{H} = \hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{T}_e(\underline{\underline{r}}) + \hat{W}_{ee}(\underline{\underline{r}}) + \hat{U}_{en}(\underline{\underline{R}}, \underline{\underline{r}})$$

with $\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu}$ $\quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}$ $\quad \hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$

$$\hat{W}_{ee} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}}^{N_e} \frac{1}{|r_j - r_k|} \qquad \hat{U}_{en} = \sum_{j=1}^{N_e}\sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$$

Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\underline{\underline{r}}, \underline{\underline{R}}, t) = \left(H(\underline{\underline{r}}, \underline{\underline{R}}) + V_{external}(\underline{\underline{r}}, \underline{\underline{R}}, t)\right)\ \psi(\underline{\underline{r}}, \underline{\underline{R}}, t)$$

Why don't we just solve the many-particle SE?

Example: Oxygen atom (8 electrons)

$$\Psi\left(\vec{r}_1, \cdots, \vec{r}_8\right) \text{ depends on 24 coordinates}$$

rough table of the wavefunction

10 entries per coordinate:	$\Rightarrow$ **10^{24} entries**
1 byte per entry:	$\Rightarrow$ **10^{24} bytes**
10^{10} bytes per DVD:	$\Rightarrow$ **10^{14} DVDs**
10 g per DVD:	$\Rightarrow$ **10^{15} g DVDs**
	= 10^{9} t DVDs

ESSENCE OF DENSITY-FUNTIONAL THEORY

- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE**

- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles**