

Time-dependent density functional theory



E.K.U. Gross

**Max-Planck Institute for
Microstructure Physics**



OUTLINE

LECTURE I

- Phenomena to be described by TDDFT
- Some generalities on “functional theories”

LECTURE II

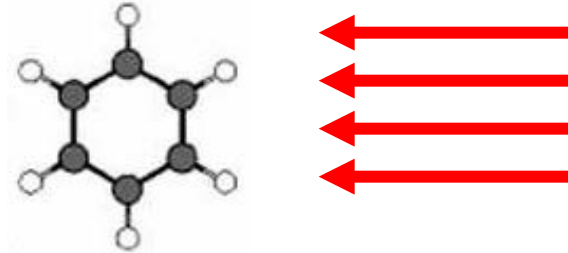
- Basic theorems of TDDFT

LECTURE III

- TDDFT in the linear-response regime: Calculation of optical excitation spectra
- Beyond linear response: TD Electron Localization Function

Time-dependent systems

Generic situation:
Molecule in laser field



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

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

Non-perturbative solution of full TDSE required

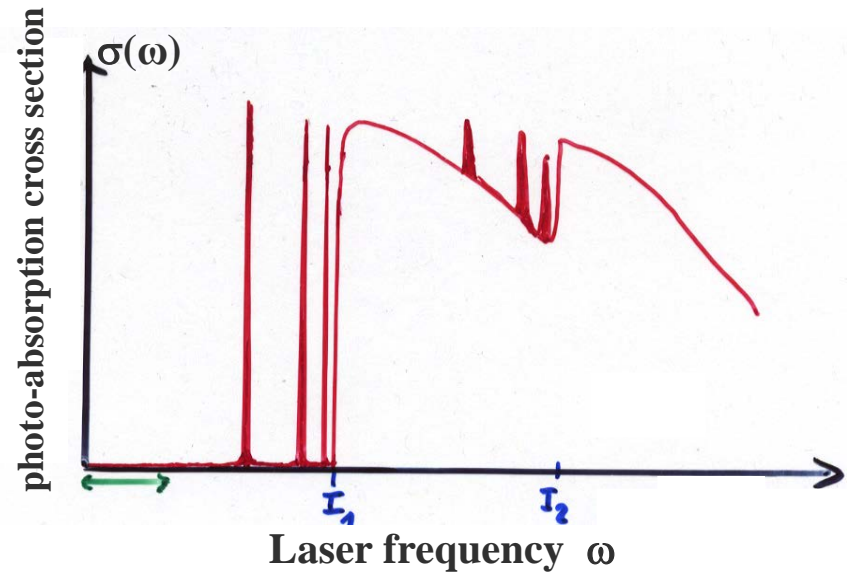
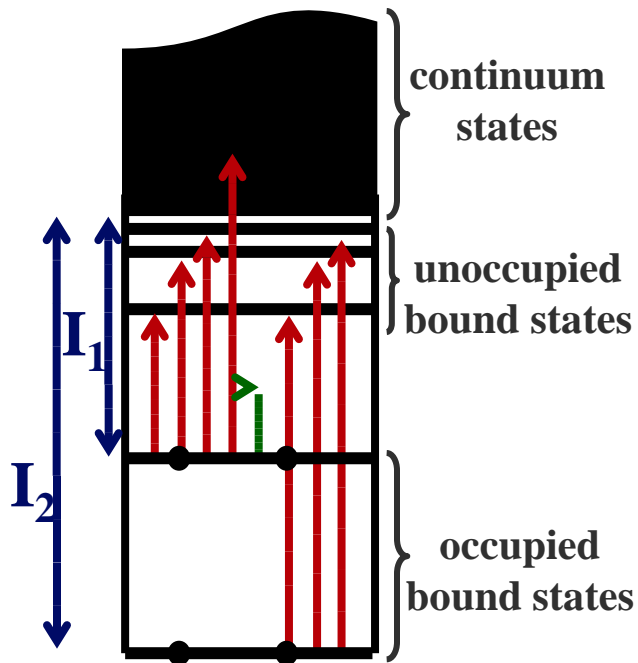
Weak laser ($v_{\text{laser}}(\mathbf{t}) \ll v_{\text{en}}$):

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

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

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

Reminder: Photo-absorption in weak lasers



No absorption if $\omega < \text{lowest excitation energy}$

Standard linear response formalism

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

$$H(t_0)|m\rangle = E_m|m\rangle \quad \leftarrow \text{exact many-body eigenfunctions and energies of system}$$

full response function

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

\Rightarrow The exact linear density response

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

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

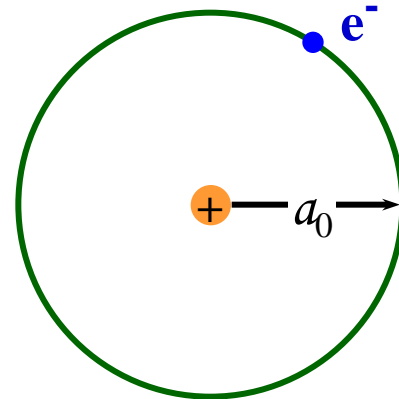
Strong Laser Fields

Intensities in the range of $10^{13} \dots 10^{16} \text{ W/cm}^2$

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

$$E = \frac{1}{4\pi\epsilon_0} \frac{e}{a_0^2} = 5.1 \times 10^9 \text{ V/m}$$

$$I = \frac{1}{2} \epsilon_0 c E^2 = 3.51 \times 10^{16} \text{ W/cm}^2$$



Three quantities to look at:

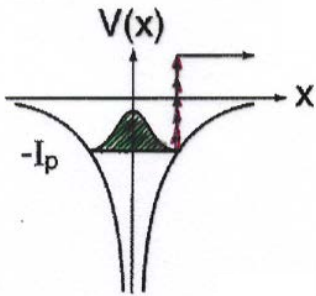
- I. Emitted ions**
- II. Emitted electrons**
- III. Emitted photons**

I. Emitted Ions

Three regimes of ionization,
depending on Keldysh parameter

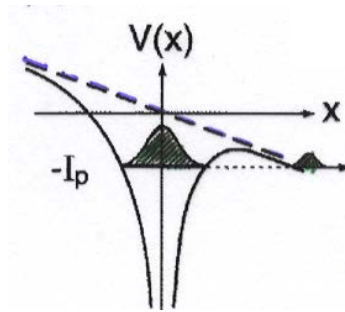
$$\gamma := \frac{\omega}{E} \text{ (a.u.)}$$

Multiphoton



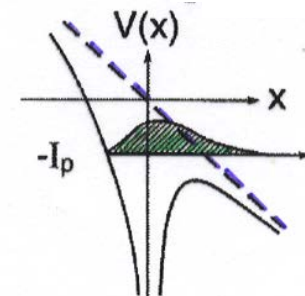
$$\gamma \gg 1$$

Tunneling



$$\gamma \approx 1$$

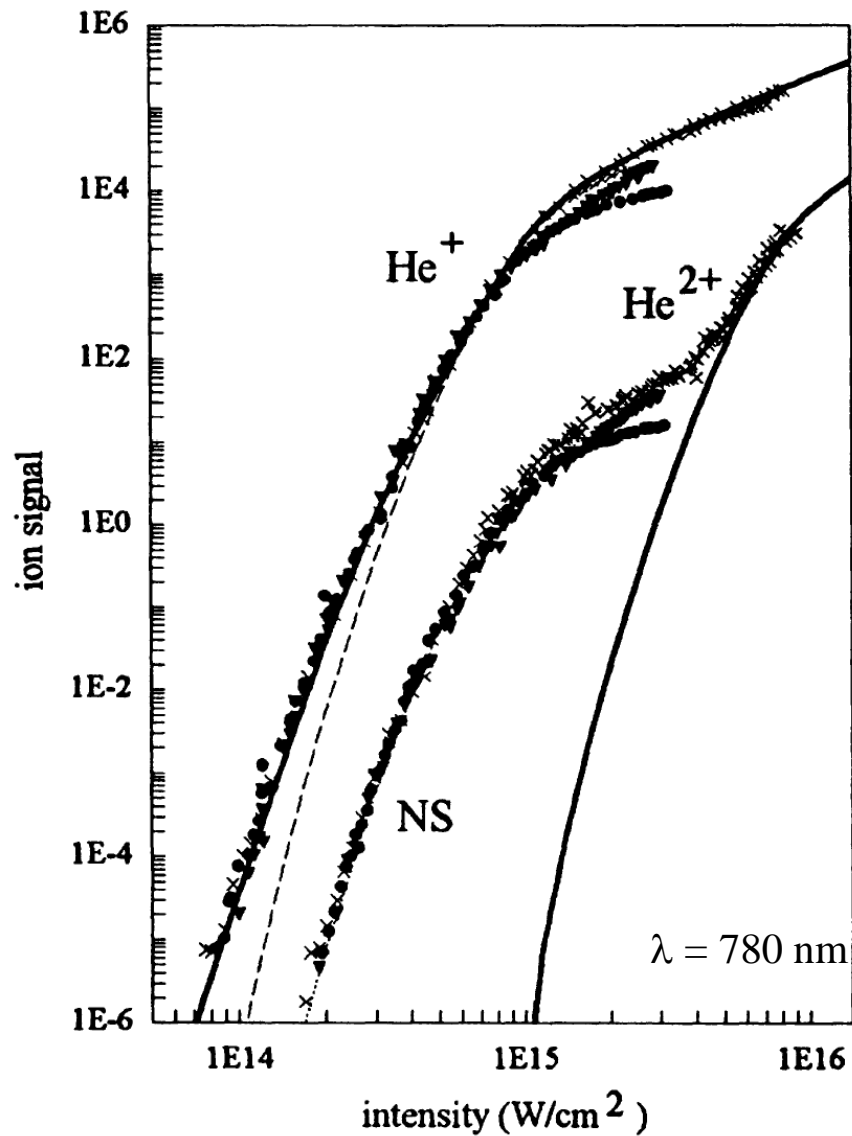
Over the barrier



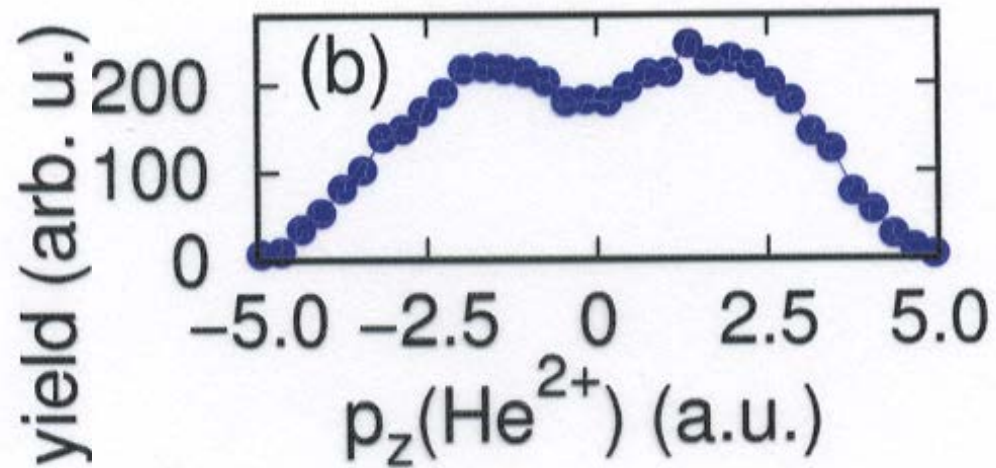
$$\gamma \ll 1$$

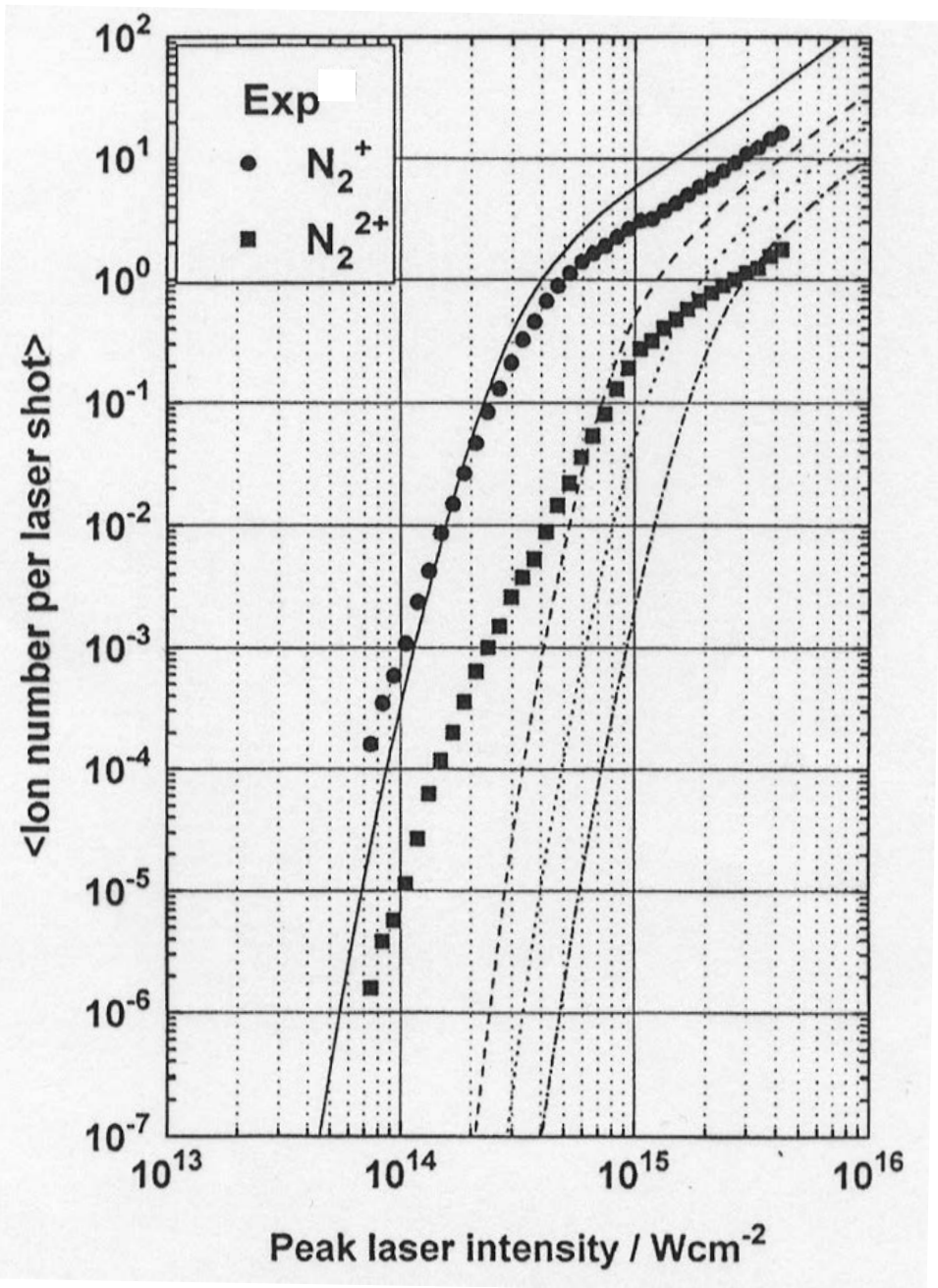
Multiphoton-Ionization (He)

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



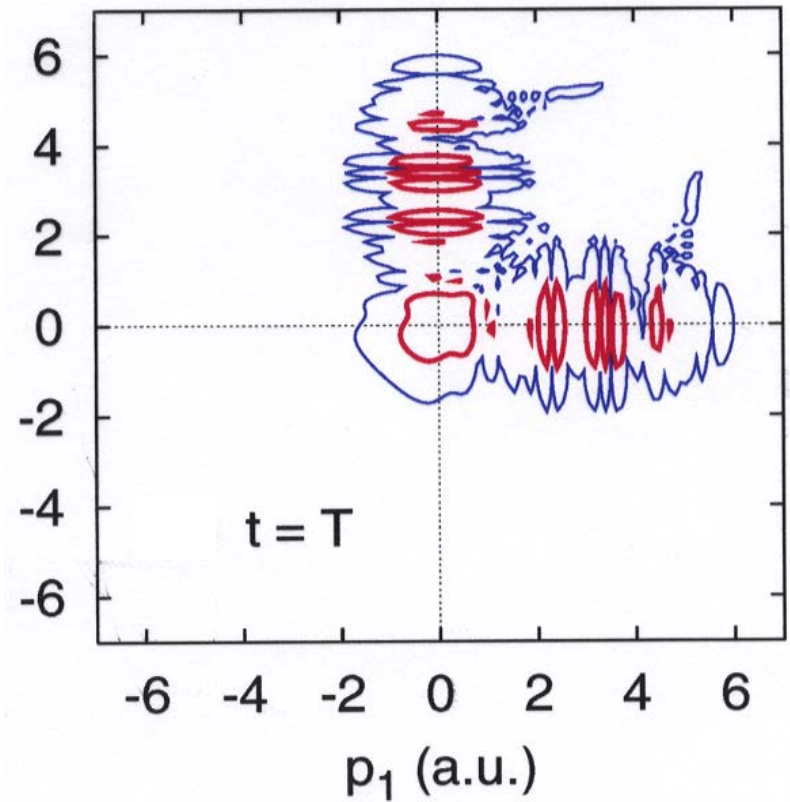
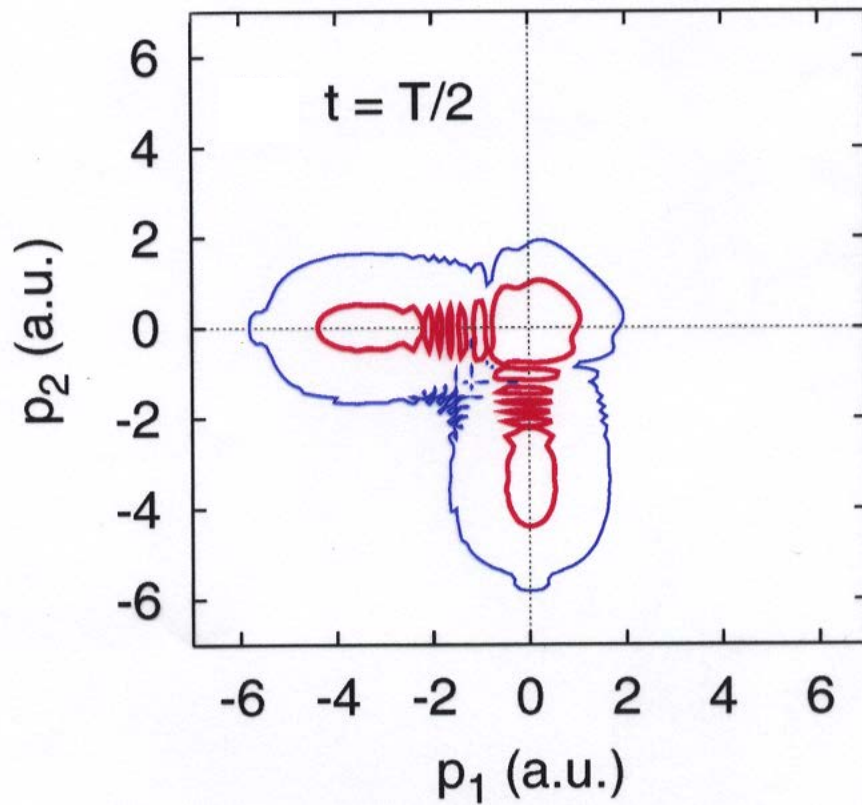
Momentum Distribution of the He^{2+} recoil ions





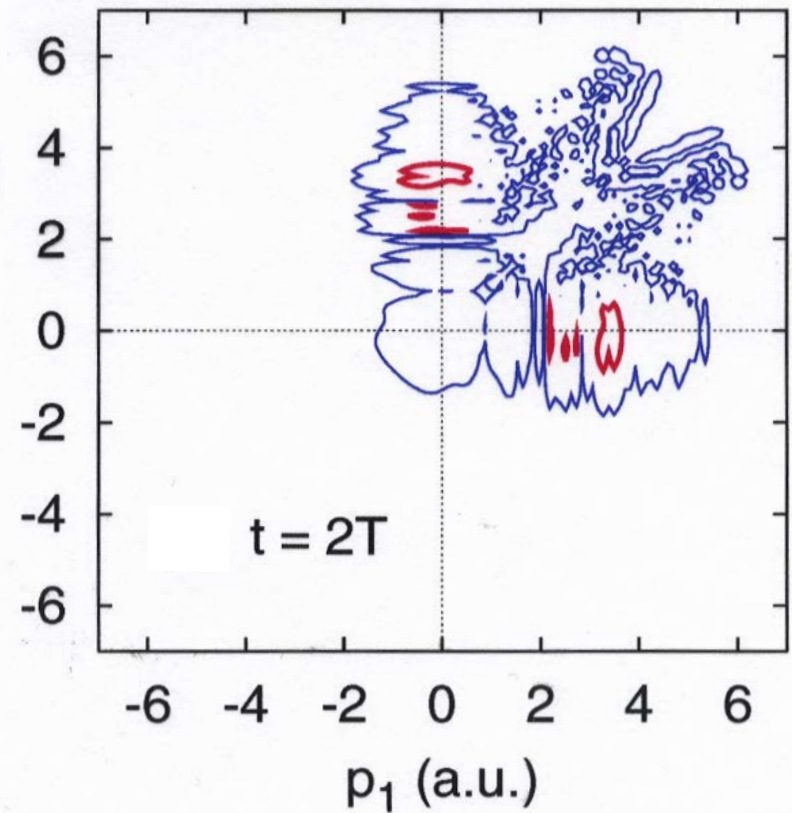
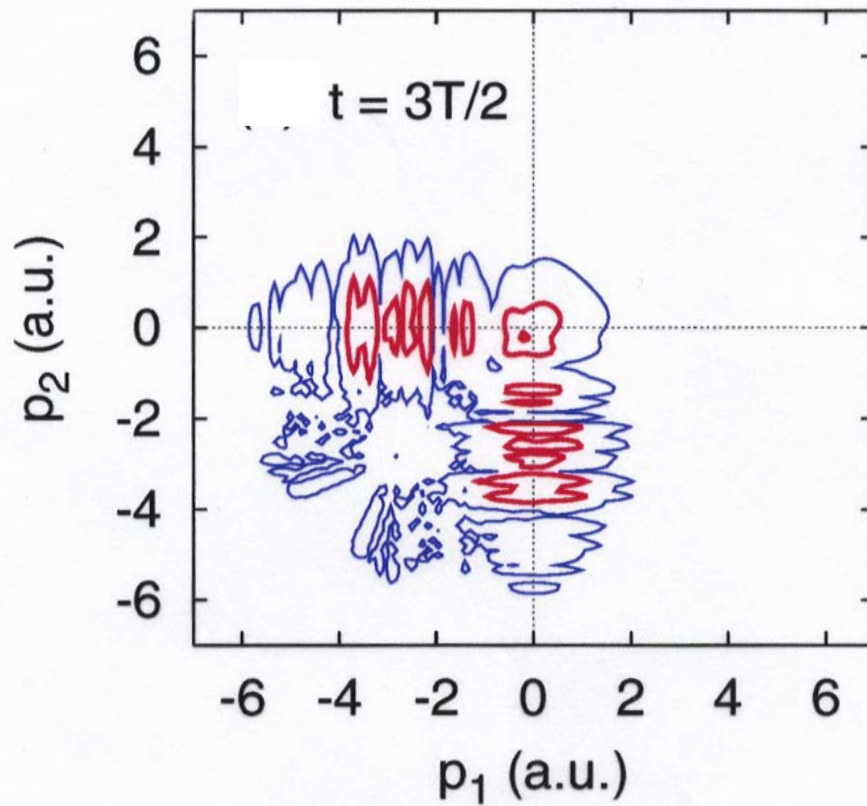
$$|\Psi(p_1, p_2, t)|^2 \text{ of the He atom}$$

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



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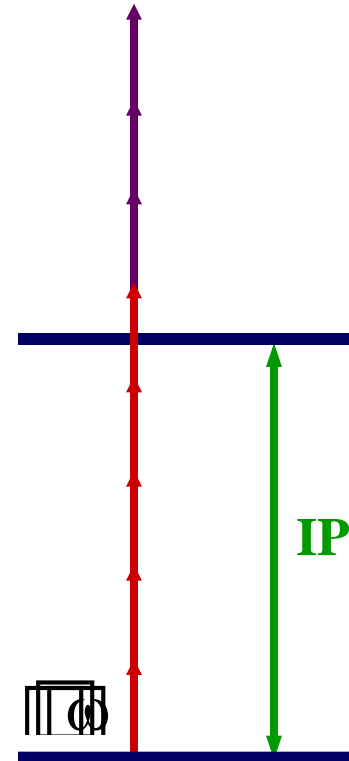
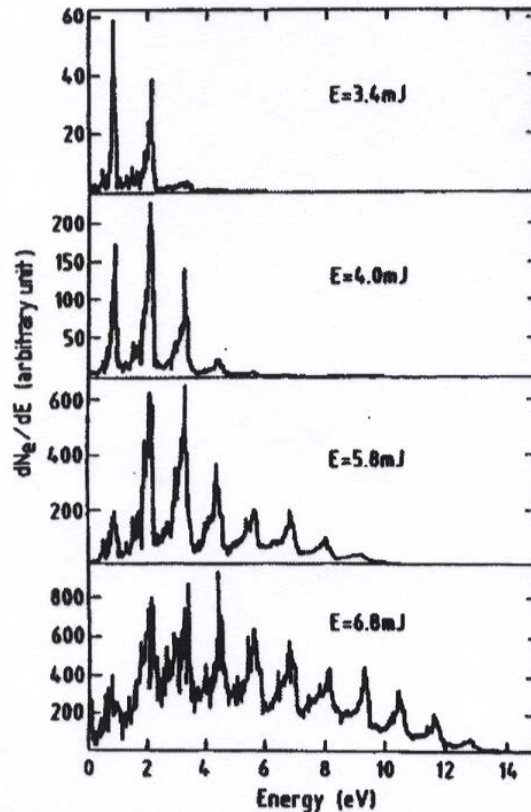


II. Electrons: Above-Threshold-Ionization (ATI)

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

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

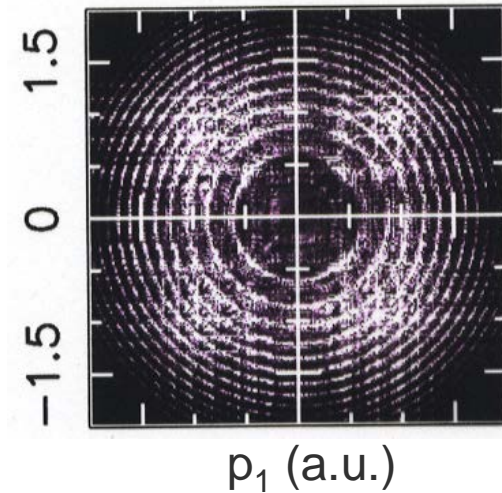
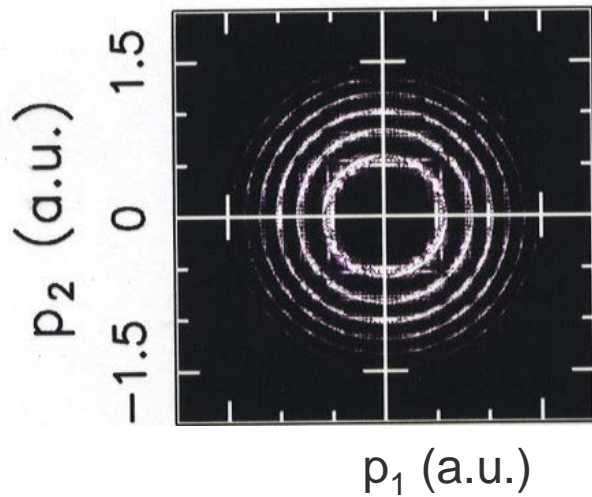
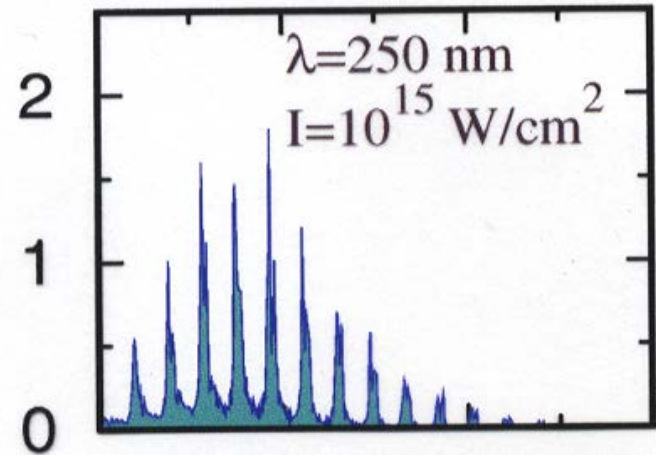
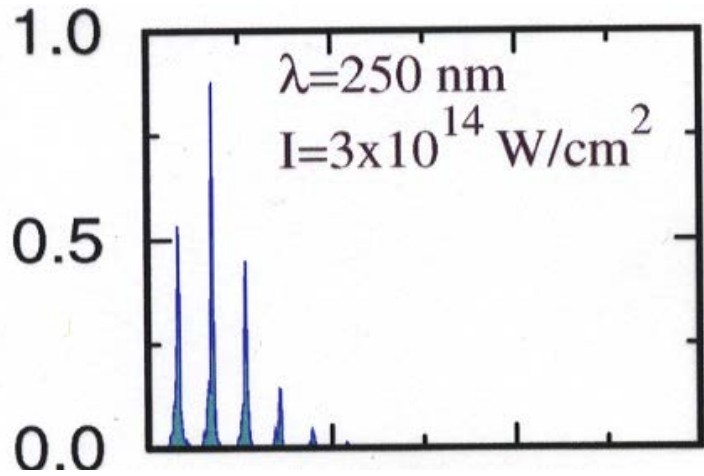
⇒ Equidistant maxima in intervals of $\hbar\omega$:



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

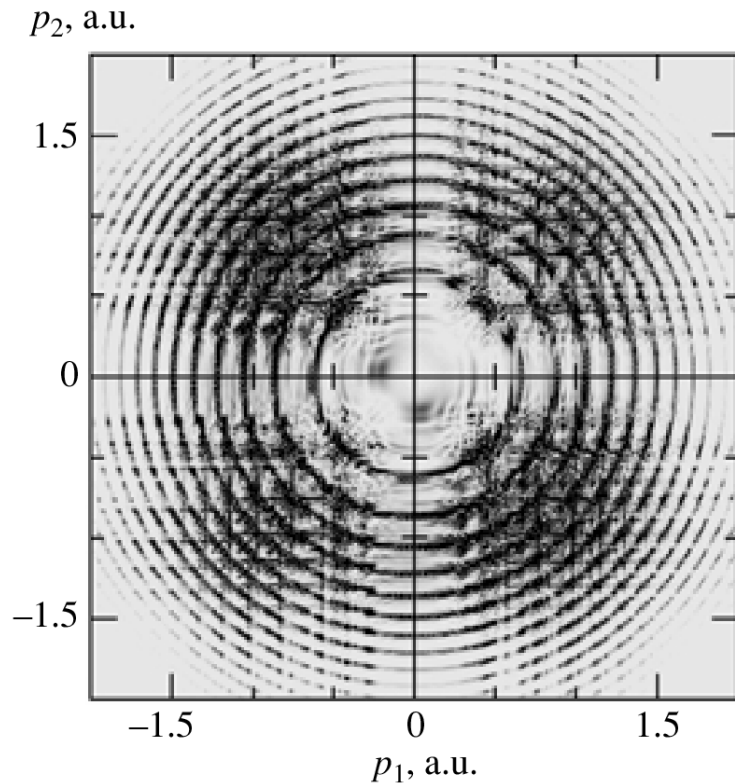
He: Above threshold double ionization

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

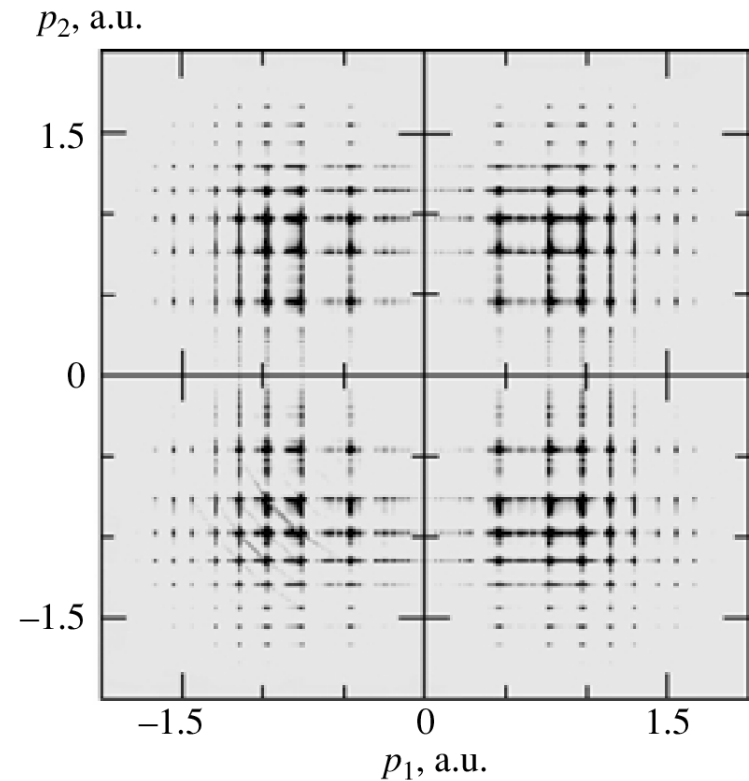


Role of electron-electron interaction

M. Lein, E.K.U.G., and V. Engel, *Laser Physics* **12**, 487 (2002)



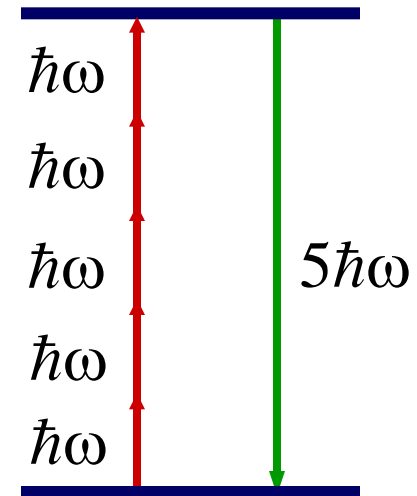
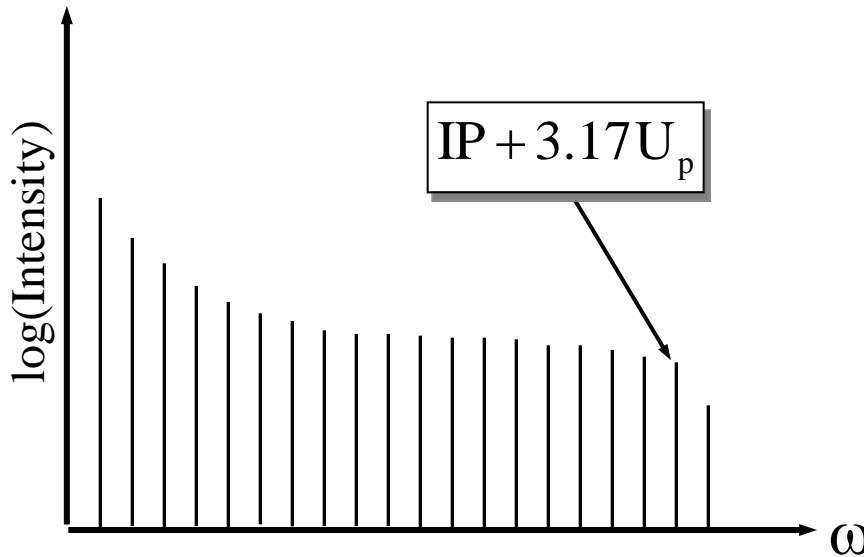
Two-electron momentum distribution for double ionization of the He model atom by a 250 nm pulse with intensity 10^{15} W/cm^2 .



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

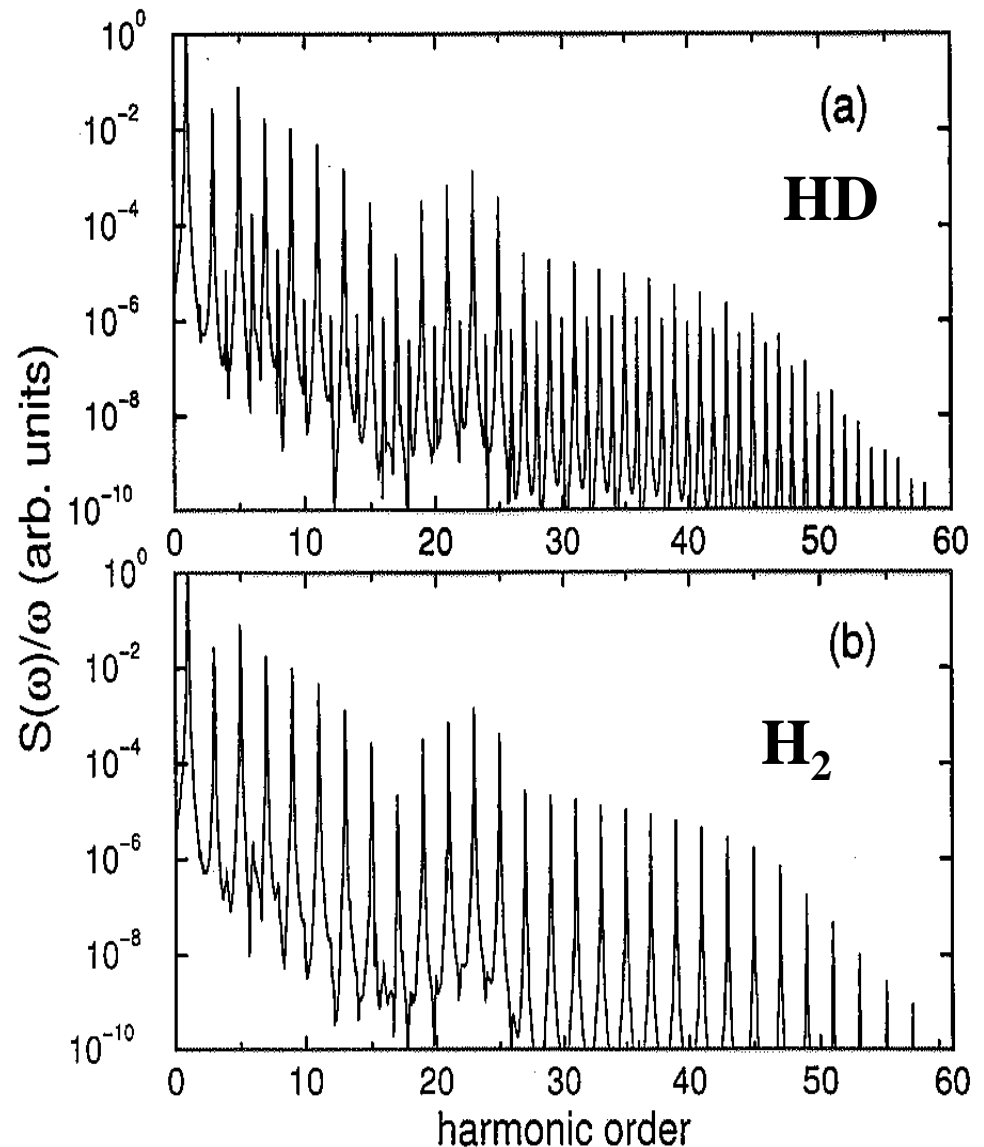
Emission of photons whose frequencies are integer multiples of the driving field. **Over a wide frequency range, the peak intensities are almost constant (plateau).**



Even harmonic generation due to nuclear motion

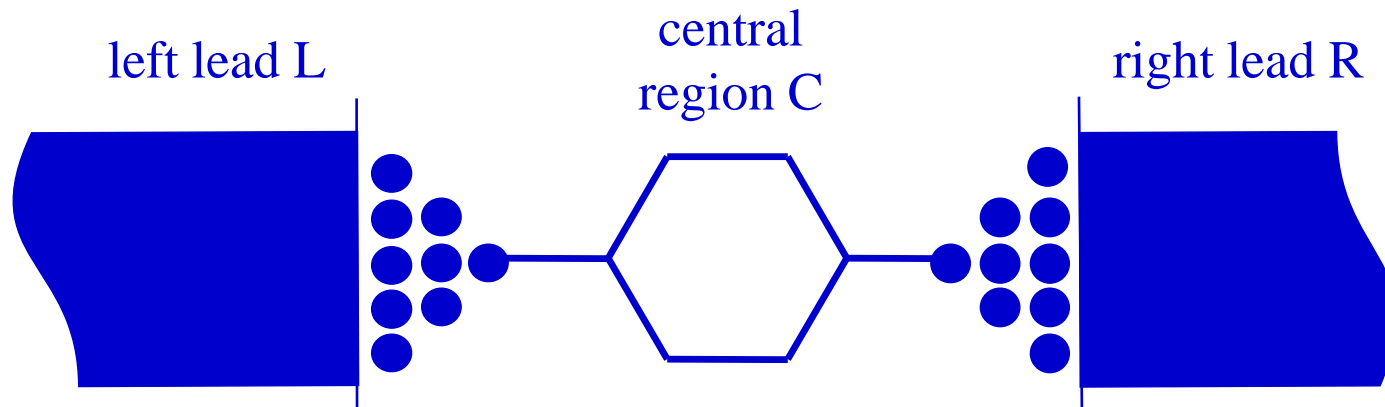
(a) Harmonic spectrum generated from the model HD molecule driven by a laser with peak intensity 10^{14} W/cm² and wavelength 770 nm. The plotted quantity is proportional to the number of emitted phonons. (b) Same as panel (a) for the model H₂ molecule.

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



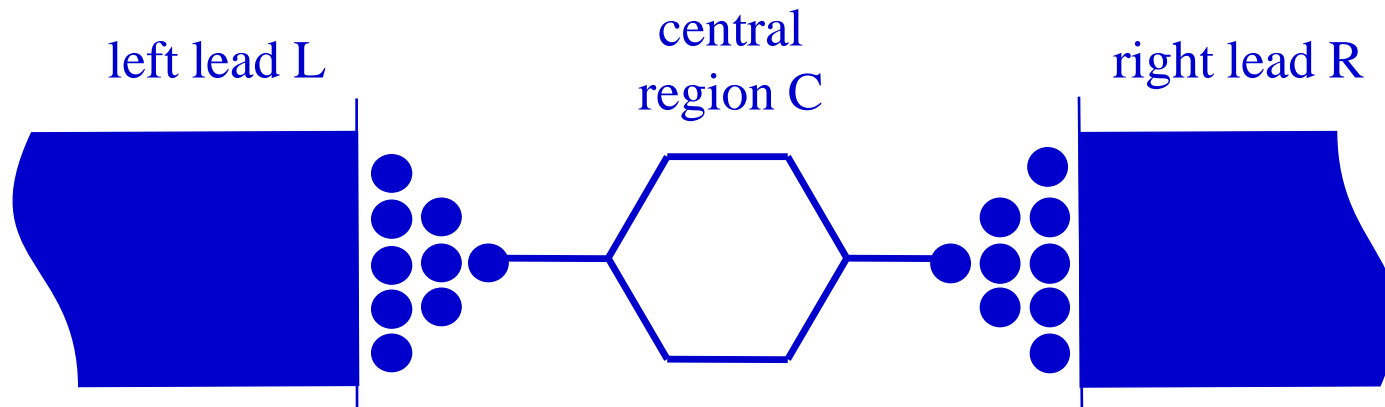
Molecular Electronics

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



Molecular Electronics

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Bias between L and R is turned on: $U(t) \longrightarrow V$ 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 $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{\mathbf{r}}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{\mathbf{R}}}$, masses $M_1 \cdots M_{N_n}$ and charges $Z_1 \cdots Z_{N_n}$.

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

with

$$\hat{T}_n = \sum_{v=1}^{N_n} -\frac{\nabla_v^2}{2M_v} \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m} \quad \hat{W}_{nn} = \frac{1}{2} \sum_{\substack{\mu, v \\ \mu \neq v}}^{N_n} \frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu - \mathbf{R}_\nu|}$$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{\substack{j, k \\ j \neq k}}^{N_e} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \quad \hat{U}_{en} = \sum_{j=1}^{N_e} \sum_{v=1}^{N_n} -\frac{Z_\nu}{|\mathbf{r}_j - \mathbf{R}_\nu|}$$

Time-dependent Schrödinger equation

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

First approximation: Clamp the nuclei or treat them classically

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

Example: Oxygen atom (8 electrons)

$\Psi(\vec{r}_1, \dots, \vec{r}_8)$ 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

“Functional Theories”

MBPT

RDMFT

DFT

$$G(\mathbf{r}, \mathbf{r}', t - t') \quad \gamma(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}, \mathbf{r}', 0^+) \quad \rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

“Functional Theories”

MBPT

RDMFT

DFT

$$G(r, r', t - t')$$

$$\gamma(r, r') = G(r, r', 0^+)$$

$$\rho(r) = \gamma(r, r)$$

Functional:

$$\Phi_{xc}[G]$$

or $\Sigma_{xc}[G]$

Functional:

$$E_{xc}[\gamma]$$

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

“Functional Theories”

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Functional:

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or $\Sigma_{xc}[G]$

easy (e.g. GW)

Functional:

$$E_{xc}[\gamma]$$

difficult

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

very difficult

“Functional Theories”

MBPT

$$G(r, r', t - t')$$

Functional:

$$\Phi_{xc}[G]$$

or $\Sigma_{xc}[G]$

easy (e.g. GW)

numerically

heavy

RDMFT

$$\gamma(r, r') = G(r, r', 0^+)$$

Functional:

$$E_{xc}[\gamma]$$

difficult

moderate

DFT

$$\rho(r) = \gamma(r, r)$$

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

very difficult

light

“Functional Theories”

MBPT

RDMFT

DFT

$$G(r, r', t - t')$$

$$\gamma(r, r') = G(r, r', 0^+)$$

$$\rho(r) = \gamma(r, r)$$

Functional:

$$\Phi_{xc}[G]$$

or $\Sigma_{xc}[G]$

easy (e.g. GW)

Functional:

$$E_{xc}[\gamma]$$

difficult

Functional:

$$E_{xc}[\rho]$$

or $v_{xc}[\rho]$

very difficult

For each of these functional theories there exist static and TD versions

Four steps needed

Step 1: Basic Theorems, exact features

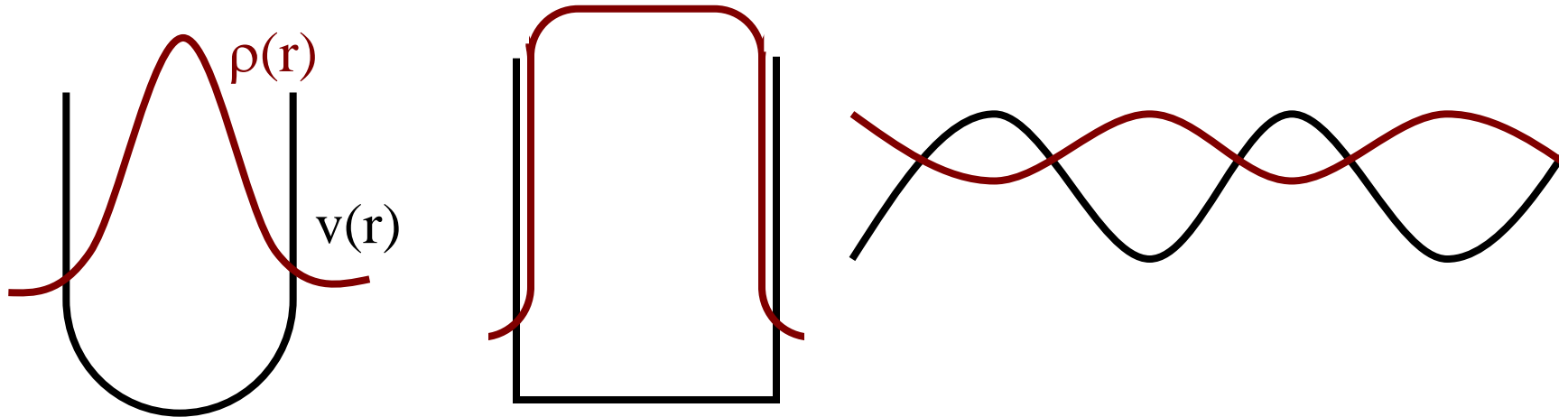
Step 2: Find approximate functionals for $v_{xc}[\rho(\mathbf{r}'t')](\mathbf{r}t)$

Step 3: Write code that solves the TDKS equations

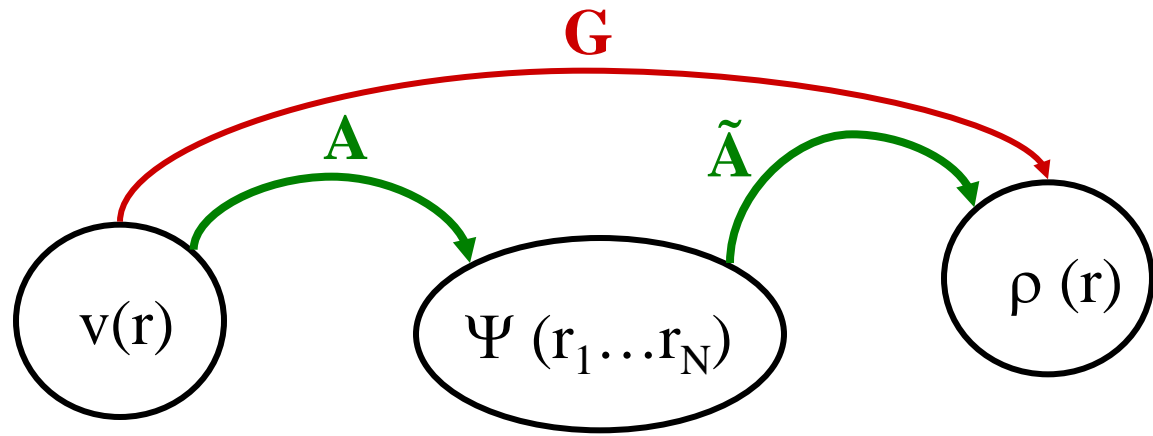
Step 4: Run code for interesting systems/questions

Static Density Functional Theory: Some remarks

compare **ground-state densities** $\rho(r)$ resulting from different external potentials $v(r)$.



QUESTION: Are the ground-state densities coming from different potentials always different?



single-particle
potentials having
nondegenerate
ground state

ground-state
wavefunctions

ground-state
densities

Hohenberg-Kohn-Theorem (1964)

$G: v(\mathbf{r}) \rightarrow \rho(\mathbf{r})$ is invertible

HOHENBERG-KOHN THEOREM

1. $v(\mathbf{r}) \xleftrightarrow{1-1} \rho(\mathbf{r})$

one-to-one correspondence between external potentials $v(\mathbf{r})$ and ground-state densities $\rho(\mathbf{r})$

2. Variational principle

Given a particular system characterized by the external potential $v_0(\mathbf{r})$. Then the solution of the Euler-Lagrange equation

$$\frac{\delta}{\delta \rho(\mathbf{r})} E_{\text{HK}}[\rho] = 0$$

yields the exact ground-state energy E_0 and ground-state density $\rho_0(\mathbf{r})$ of this system

3. $E_{\text{HK}}[\rho] = F[\rho] + \int \rho(\mathbf{r}) v_0(\mathbf{r}) d^3r$

$F[\rho]$ is UNIVERSAL. **In practice, $F[\rho]$ needs to be approximated**

Expansion of $F[\rho]$ in powers of e^2

$$F[\rho] = F^{(0)}[\rho] + e^2 F^{(1)}[\rho] + e^4 F^{(2)}[\rho] + \dots$$

where: $F^{(0)}[\rho] = T_s[\rho]$ (kinetic energy of non-interacting particles)

$$e^2 F^{(1)}[\rho] = \frac{e^2}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_x[\rho] \quad (\text{Hartree + exchange energies})$$

$$\sum_{i=2}^{\infty} (e^2)^i F^{(i)}[\rho] = E_c[\rho] \quad (\text{correlation energy})$$

$$\Rightarrow F[\rho] = T_s[\rho] + \frac{e^2}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_x[\rho] + E_c[\rho]$$

By construction, the HK mapping is well-defined for all those functions $\rho(\mathbf{r})$ that are ground-state densities of some potential (so called V-representable functions $\rho(\mathbf{r})$).

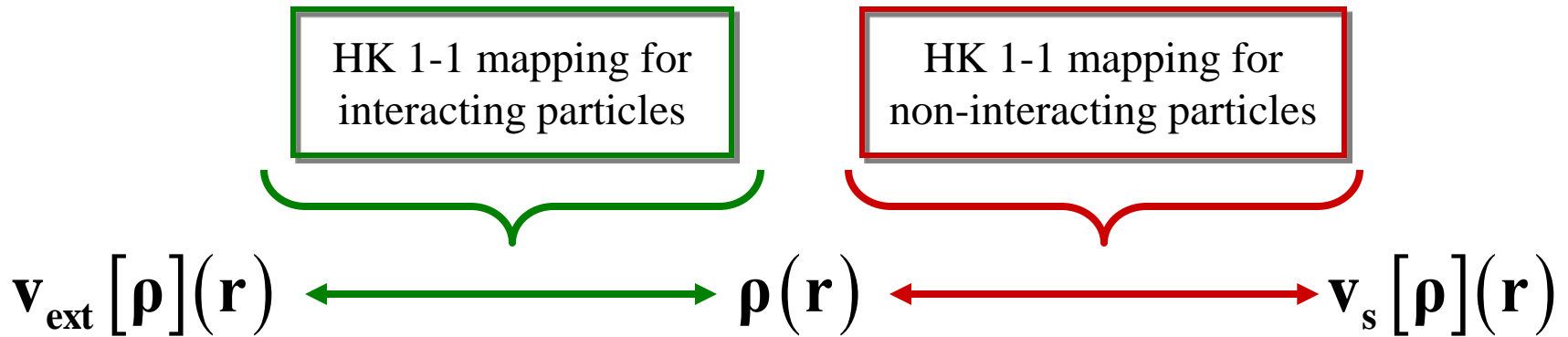
QUESTION: Are all “reasonable” functions $\rho(\mathbf{r})$ V-representable?

V-representability theorem (Chayes, Chayes, Ruskai, J Stat. Phys. 38, 497 (1985))

On a lattice (finite or infinite), any normalizable positive function $\rho(\mathbf{r})$, that is compatible with the Pauli principle, is (both interacting and non-interacting) ensemble-V-representable.

In other words: For any given $\rho(\mathbf{r})$ (normalizable, positive, compatible with Pauli principle) there exists a potential, $v_{\text{ext}}[\rho](\mathbf{r})$, yielding $\rho(\mathbf{r})$ as interacting ground-state density, and there exists another potential, $v_{\text{s}}[\rho](\mathbf{r})$, yielding $\rho(\mathbf{r})$ as non-interacting ground-state density.

In the worst case, the potential has degenerate ground states such that the given $\rho(\mathbf{r})$ is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).



Kohn-Sham Theorem

Let $\rho_0(\mathbf{r})$ be the ground-state density of interacting electrons moving in the external potential $v_0(\mathbf{r})$. Then there exists a local potential $v_{s,0}(\mathbf{r})$ such that non-interacting particles exposed to $v_{s,0}(\mathbf{r})$ have the ground-state density $\rho_0(\mathbf{r})$, i.e.

$$\left(-\frac{\nabla^2}{2} + v_{s,0}(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r}), \quad \rho_0(\mathbf{r}) = \sum_{j(\text{with lowest } \epsilon_j)}^N |\varphi_j(\mathbf{r})|^2$$

proof: $v_{s,0}(\mathbf{r}) = v_s[\rho_0](\mathbf{r})$

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

Define $v_{xc}[\rho](\mathbf{r})$ by the equation

$$v_s[\rho](\mathbf{r}) =: v_{\text{ext}}[\rho](\mathbf{r}) + \underbrace{\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'}_{v_H[\rho](\mathbf{r})} + v_{xc}[\rho](\mathbf{r})$$

$v_s[\rho]$ and $v_{\text{ext}}[\rho]$ are well defined through HK.

KS equations

$$\left(-\frac{\nabla^2}{2} + \underbrace{v_{\text{ext}}[\rho_o](\mathbf{r}) + v_H[\rho_o](\mathbf{r}) + v_{xc}[\rho_o](\mathbf{r})}_{v_o(\mathbf{r})} \right) \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r})$$

$v_o(\mathbf{r})$
fixed

to be solved selfconsistently with $\rho_o(\mathbf{r}) = \sum |\varphi_j(\mathbf{r})|^2$

Note: The KS equations do not follow from the variational principle. They follow from the HK 1-1 mapping and the V-representability theorem.

Variational principle gives an additional property of v_{xc} :

$$\mathbf{v}_{xc}[\rho_o](\mathbf{r}) = \left. \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho_o}$$

where $E_{xc}[\rho] := F[\rho] - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' - T_s[\rho]$

Consequence:

Approximations can be constructed either for $E_{xc}[\rho]$ or directly for $v_{xc}[\rho](\mathbf{r})$.