

Time-dependent DFT: Successes and Perspectives

E. K. U. GROSS

Freie Universität Berlin



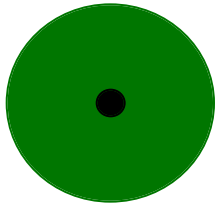
www:

<http://www.physik.fu-berlin.de/~ag-gross>

TIME-DEPENDENT SYSTEMS

Example:

atom in laser field



$$\hat{H}(\mathbf{t}) = \hat{T}_e + \hat{W}_{ee} + \sum_{j=1}^N -\frac{Ze^2}{r_j} + \vec{E} \cdot \vec{r}_j \cos \omega t$$

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

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

2. Dynamical polarizability

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

3. Photo-absorption cross section

$$\sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im } \alpha$$

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

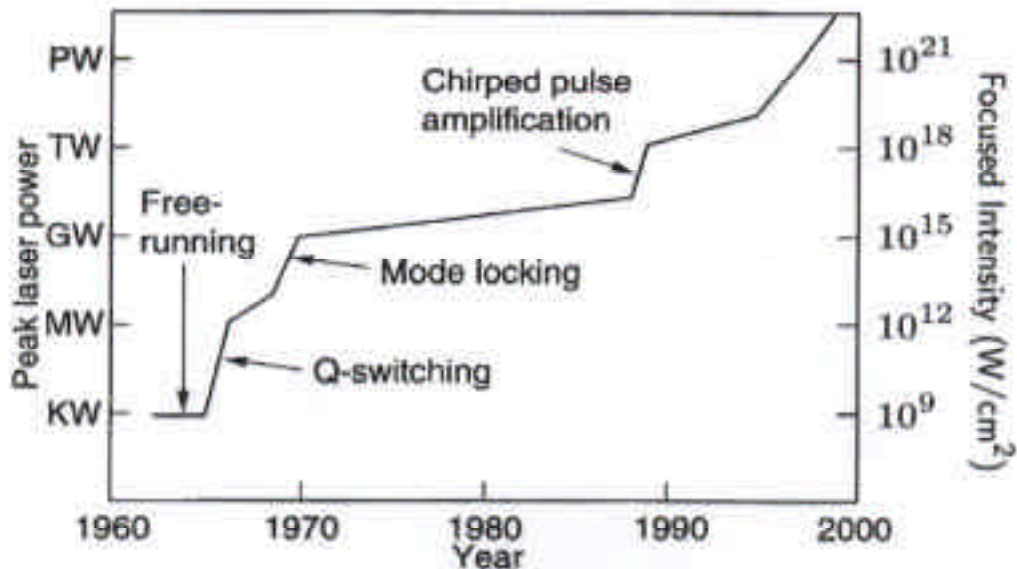
Aim: “Replace” full TDSE by TDKS scheme

Topics (linear-response regime)

- **Excitation spectra of atoms and molecules**
- **Optical spectra of semiconductors**
- **Dichroism in superconductors**

Strong Laser-Fields

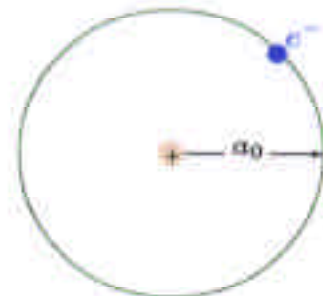
The peak-power of pulsed lasers has increased by **12 orders of magnitude** during the past 4 decades:



“Strong Laser-Field”: Intensities in the Range of $10^{13} \dots 10^{16} \text{W/cm}^2$ Comparison: Electric field on 1st Bohr-Orbit in Hydrogen

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

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

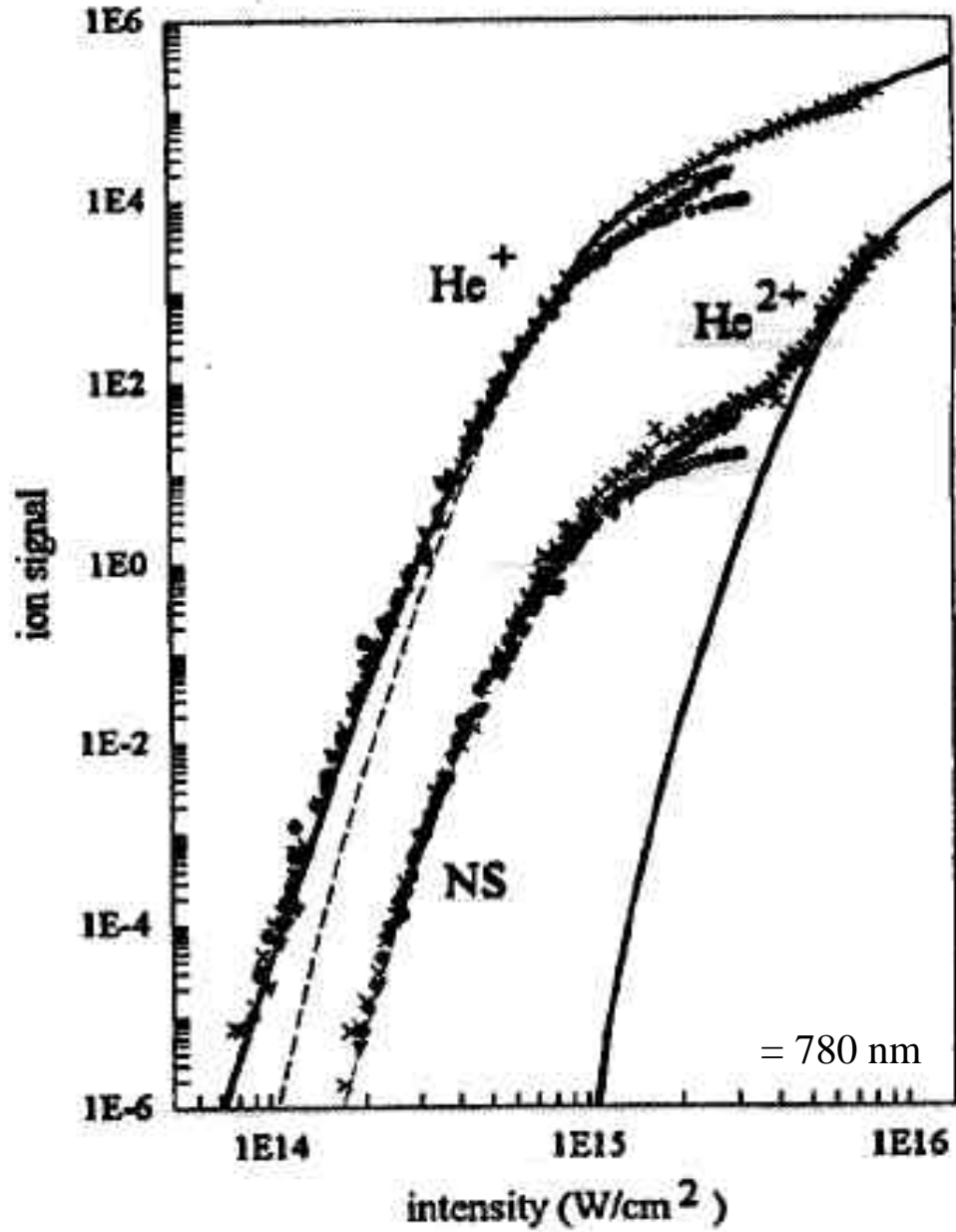


At the same time: **very short** pulses possible:

$$\approx 5 \text{ fs (1 fs} = 10^{-15} \text{ s)}$$

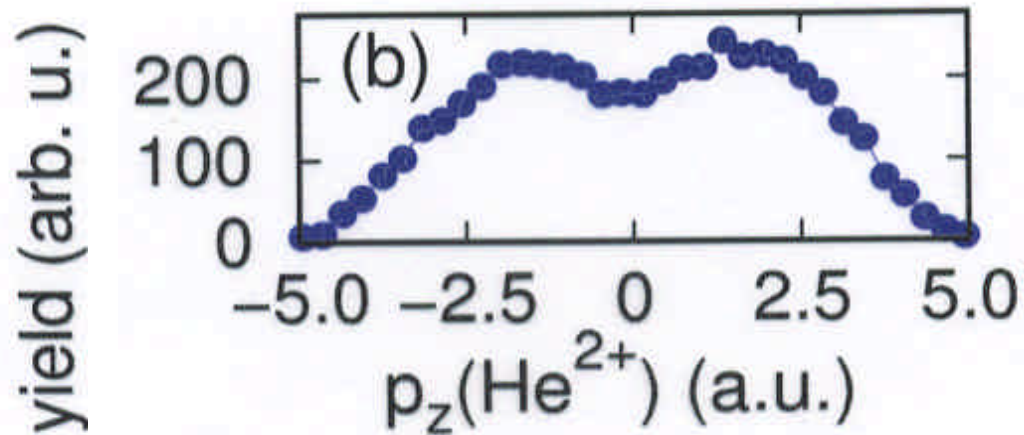
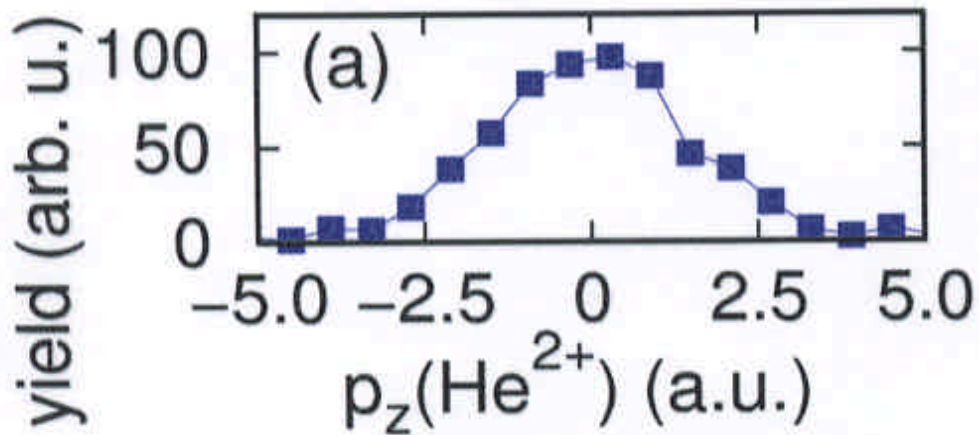
$$\approx 2 \dots 4 \text{ optical cycles in the visible region}$$

Multiphoton-Ionization (He)



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

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



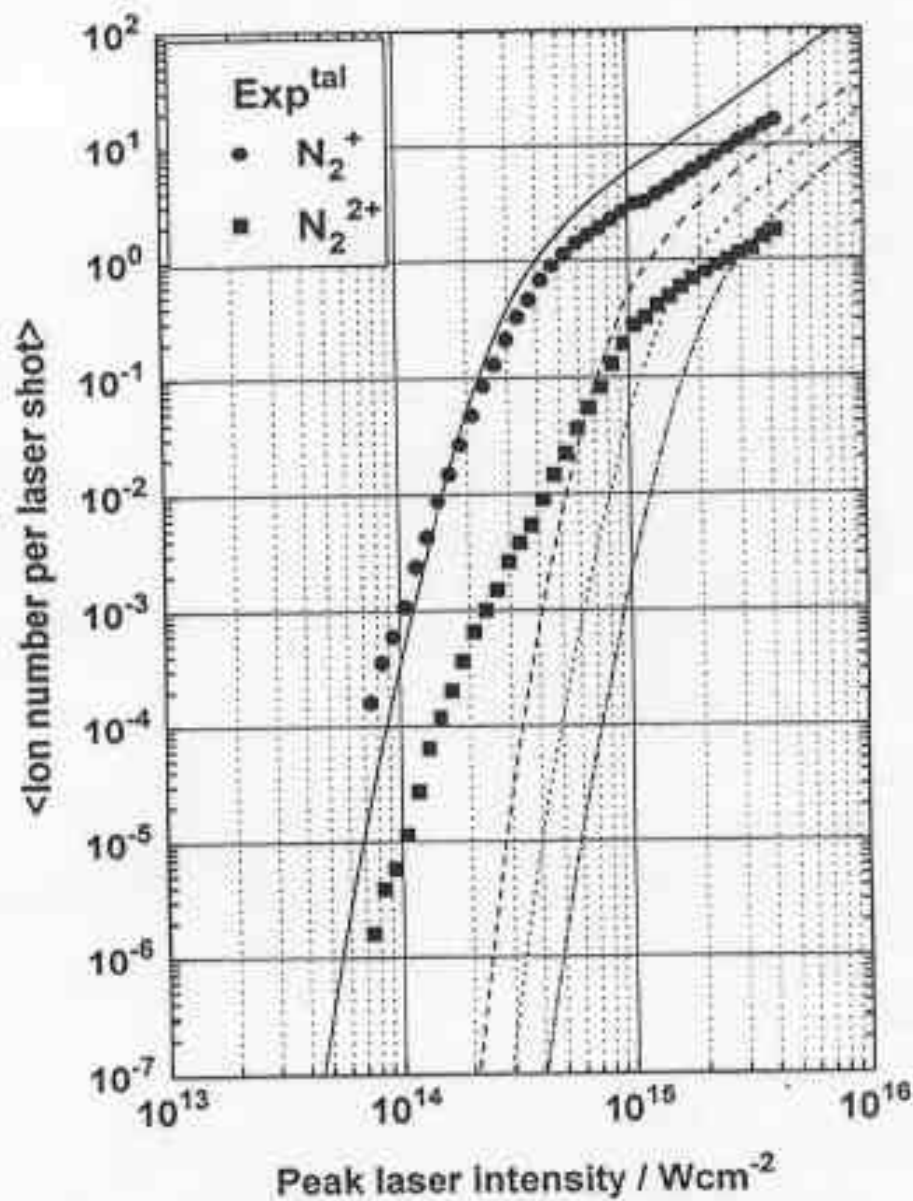


Figure 1. Experimental N_2^+ (\bullet) and N_2^{2+} (\blacksquare), and calculated N_2^+ (—) and N_2^{2+} (---, ·····, — · —) average ion number per laser shot for a reference pressure of $p(N_2) = 10^{-9}$ Torr as a function of the peak laser intensity for linearly polarized laser light. The ionization potentials introduced in the sequential ADK rates are 15.58 eV for $N_2 + \text{laser} \rightarrow N_2^+ + e^-$ (—), and 27.12 eV (---), 30.85 eV (·····) and 37.84 eV (— · —) for $N_2^+ + \text{laser} \rightarrow N_2^{2+} + e^-$ (see text).

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

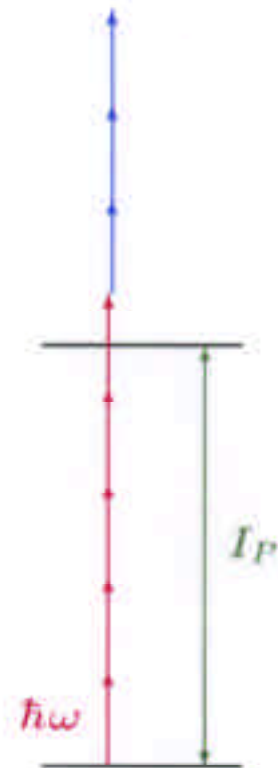
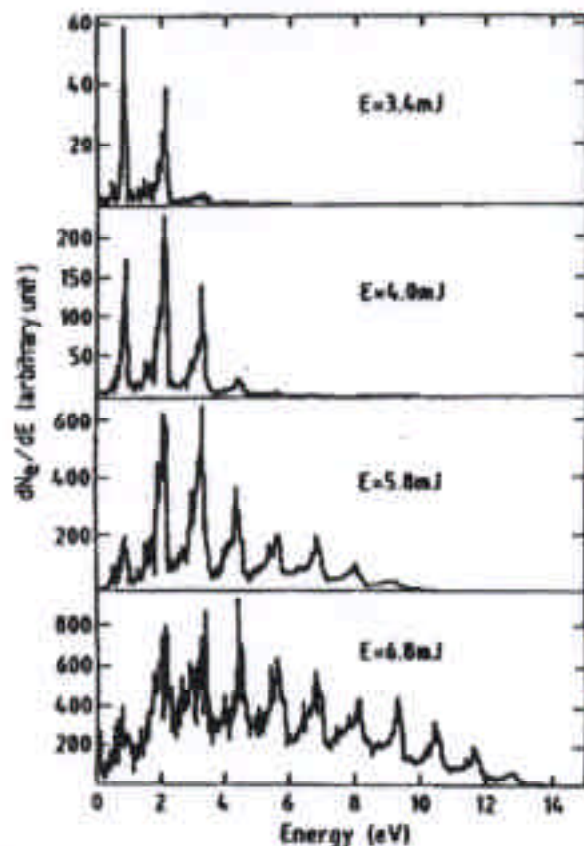
Agostini et al. Phys. Rev. Lett. 42, 1127 (1979)

Ionized electrons absorb **more photons than necessary**:

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

Important: During the absorption of the excess photons, the freed electron still feels the influence of the parent ion (conservation of momentum)

Measured energy spectra of photoelectrons (Yergeau 1986): **Equidistant maxima in intervals of $\hbar\omega$**



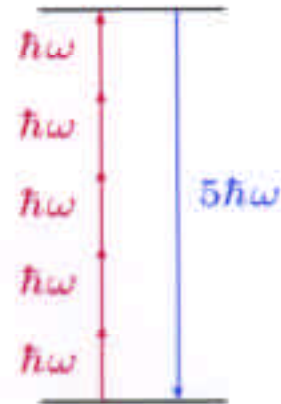
III. Photons: High-Harmonic Generation

L'Huillier et al., J. Phys. B 21, L31 (1988)

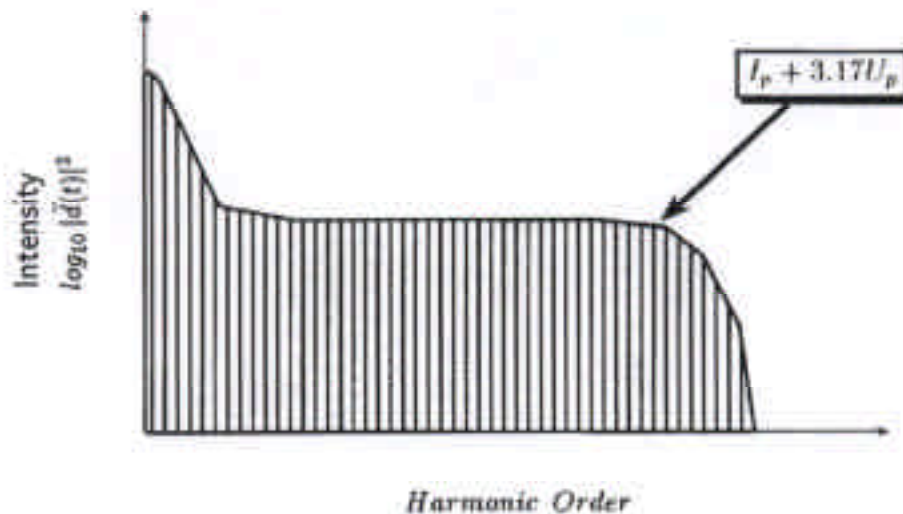
McPherson et al. J. Opt. Soc. Am. B 4, 595 (1987)

High intensities: atomic response (time-dependent dipole-moment) is highly nonlinear

⇒ Photoemission-spectra with characteristic peaks at (odd) multiples of the frequency of the driving field.



Typically nonlinear effect: Over a wide frequency range, the peak-intensities are almost constant (Plateau):



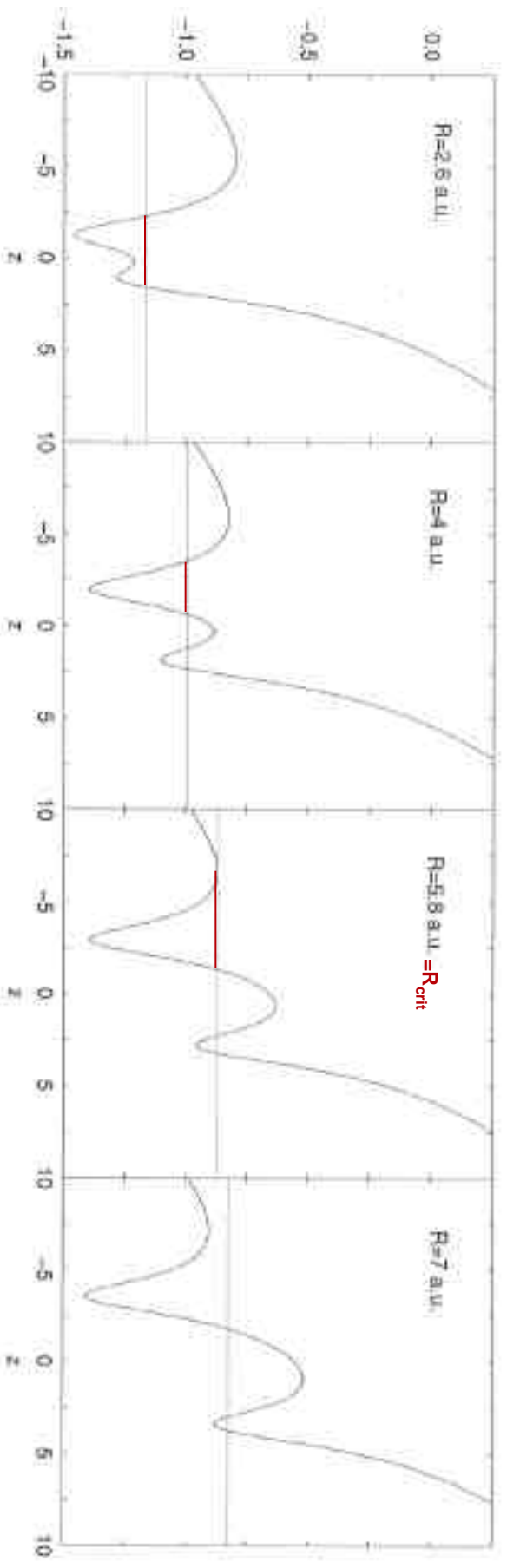
Allows generation of pulsed and coherent Radiation in the XUV c.f. weak X-ray regime with Table-Top laboratory systems.

Record: $\lambda = 2.5 \text{ nm}$ (0.5 keV) "water-window"

Schnürer et al., PRL 80, 3236 (1998)

H_2^+ in 1D

$$\nu_{\text{nuc}}(z) + E_0 z$$



consequence: ionization-induced Coulomb explosion

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

$$\hat{T}_n = \sum_{\mu=1}^{N_n} -\frac{\hbar^2}{2M_{\mu}} \nabla_{\mathbf{R}_{\mu}}^2 \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2$$

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

$$\hat{U}_{en} = \sum_{j=1}^{N_e} \sum_{\nu=1}^{N_n} -\frac{Z_{\nu}}{|\mathbf{r}_j - \mathbf{R}_{\nu}|}$$

Time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = (H(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) + V_{laser}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)) \psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)$$

$$V_{laser}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \sum_{j=1}^{N_e} \frac{1}{|\mathbf{r}_j - \mathbf{R}_v|} - \sum_{v=1}^{N_n} \frac{Z_v}{|\mathbf{R}_v|} E f(t) \cos \omega t$$

1D MODEL

- **Restrict motion of electrons and nuclei to 1D (along polarization axis of laser)**
- **Replace in $H(\underline{r}, \underline{R})$ all 3D coulomb interactions by soft 1D interactions (Eberly et al)**

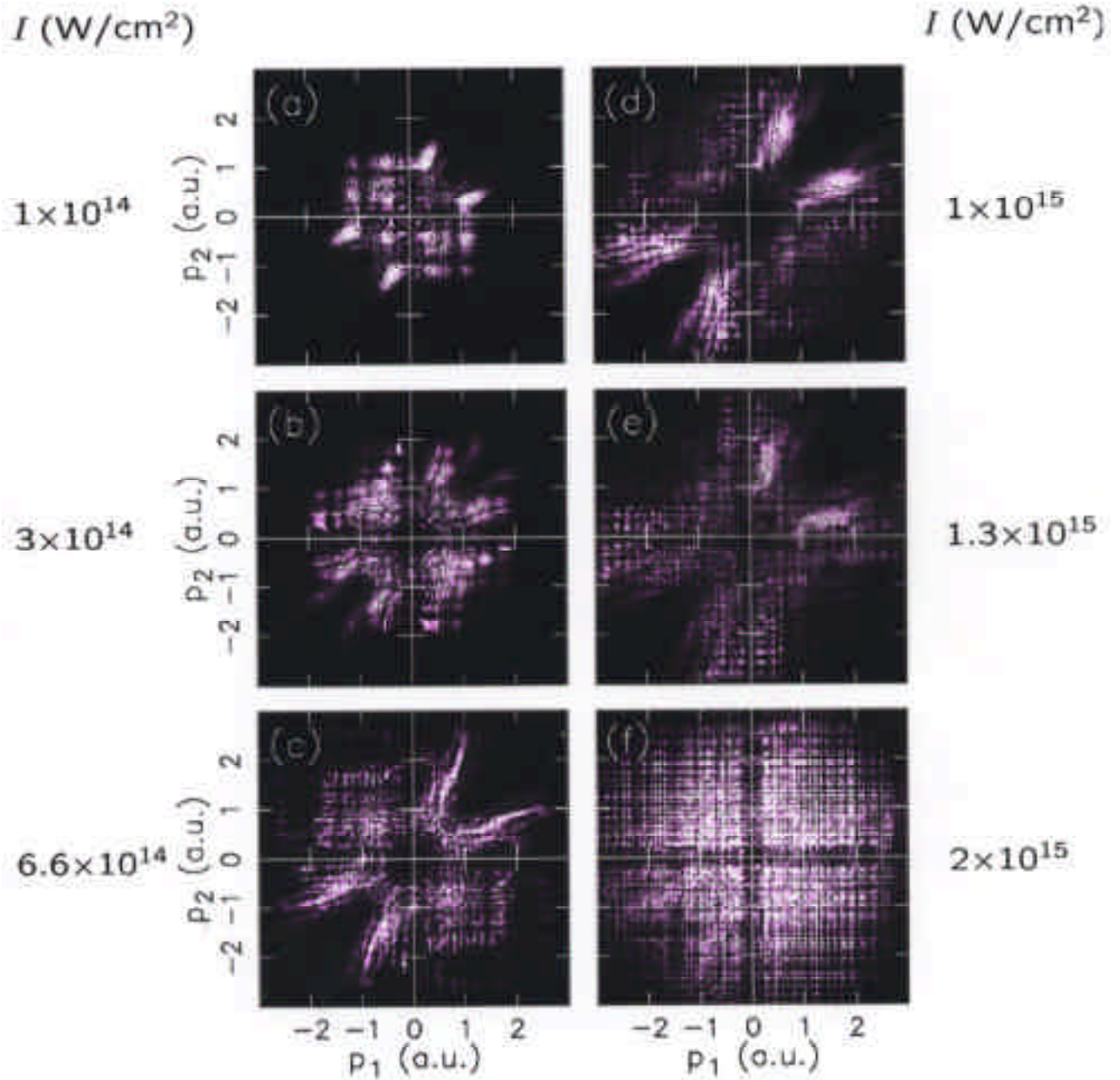
$$\frac{1}{\sqrt{x^2 + y^2 + z^2}} \longrightarrow \frac{1}{\sqrt{^2 + z^2}}$$

= constant

Two goals of 1D calculations

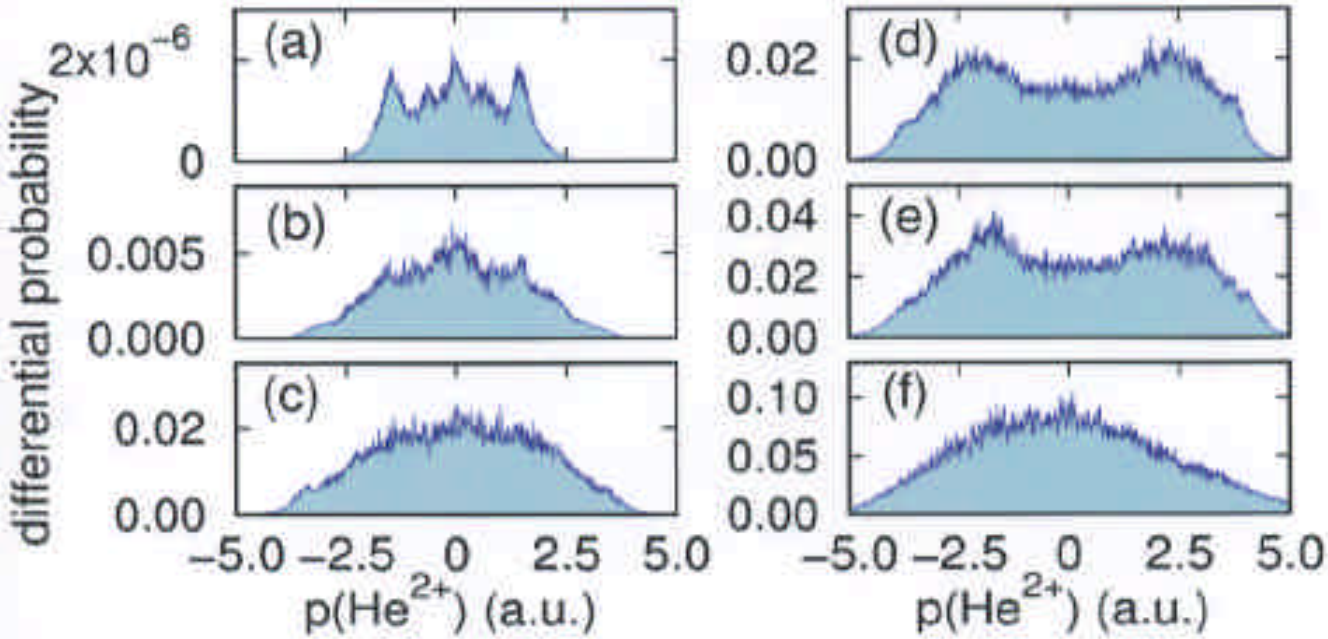
1. Qualitative understanding of physical processes, such as double ionization of He
2. Exact reference to test approximate xc functionals of time-dependent density functional theory

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



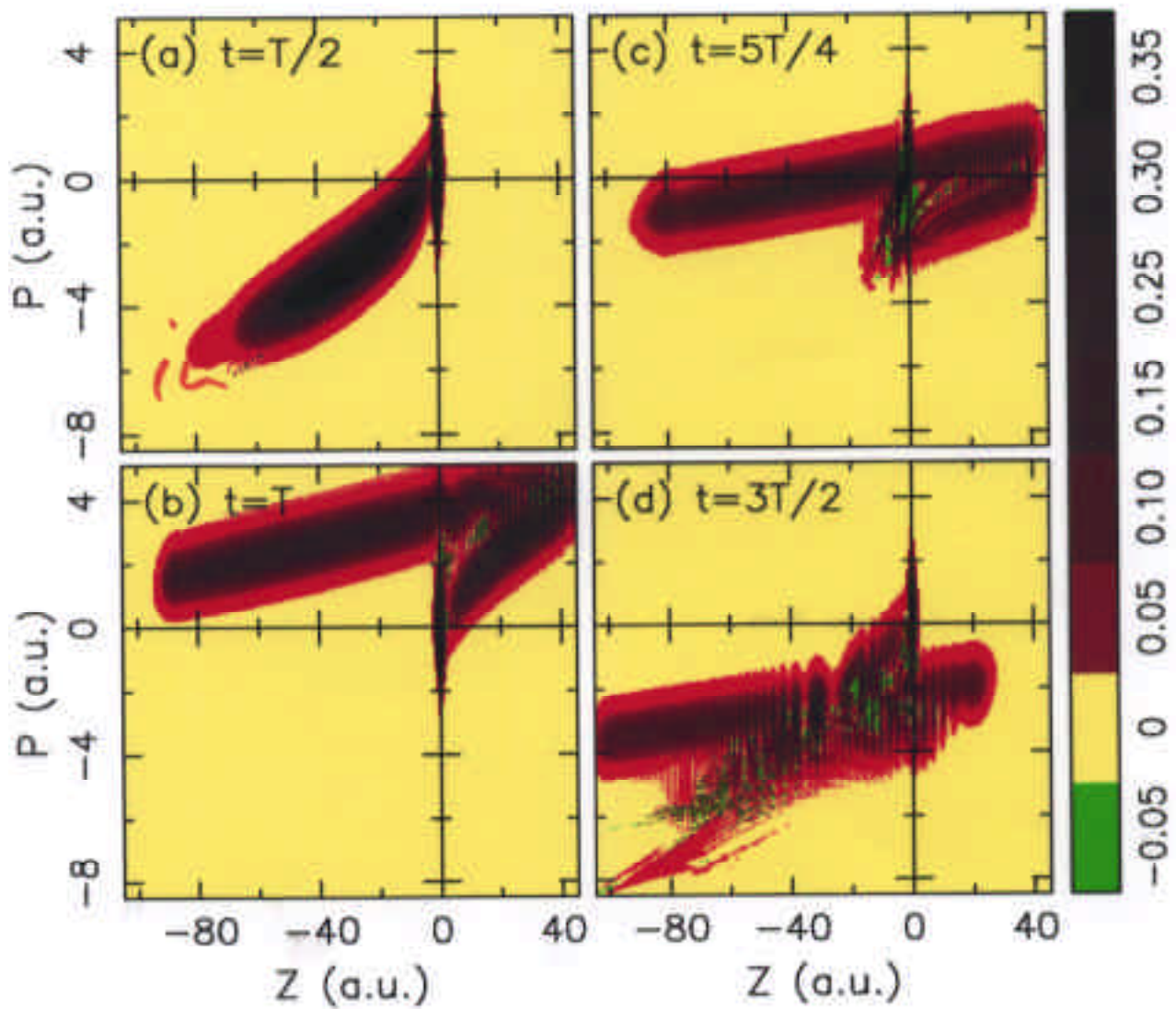
$|\Psi(p_1, p_2)|^2$ 16 fs after end of pulse

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



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

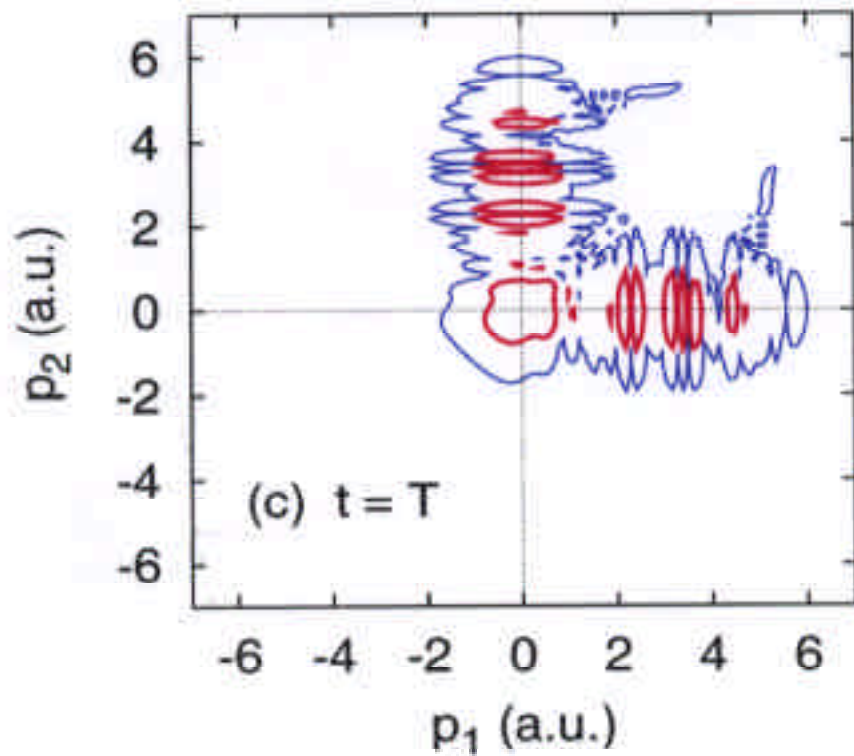
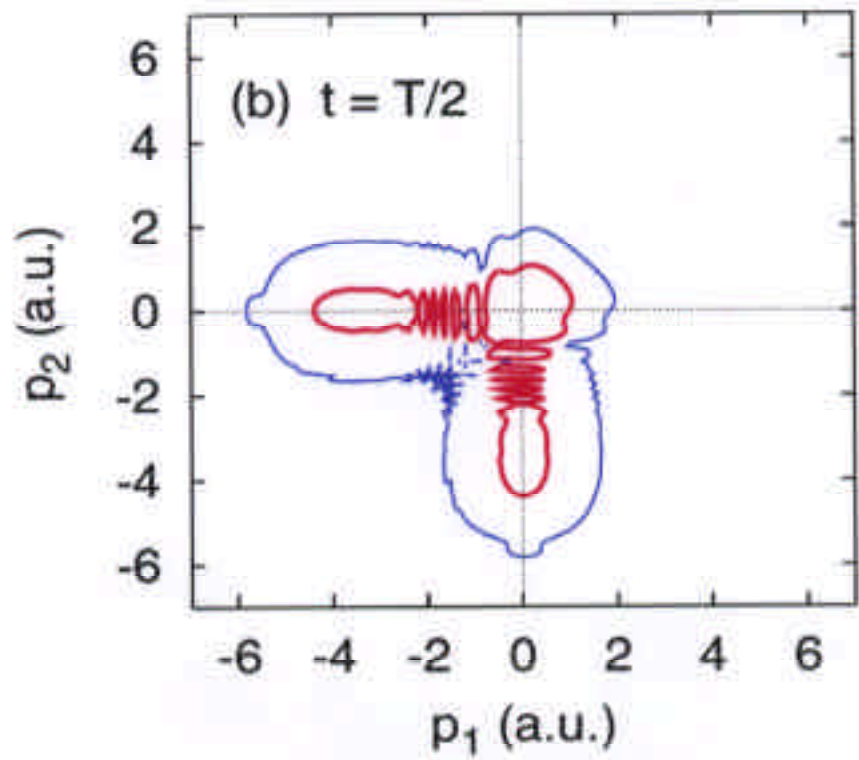
$w(Z, P)$



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

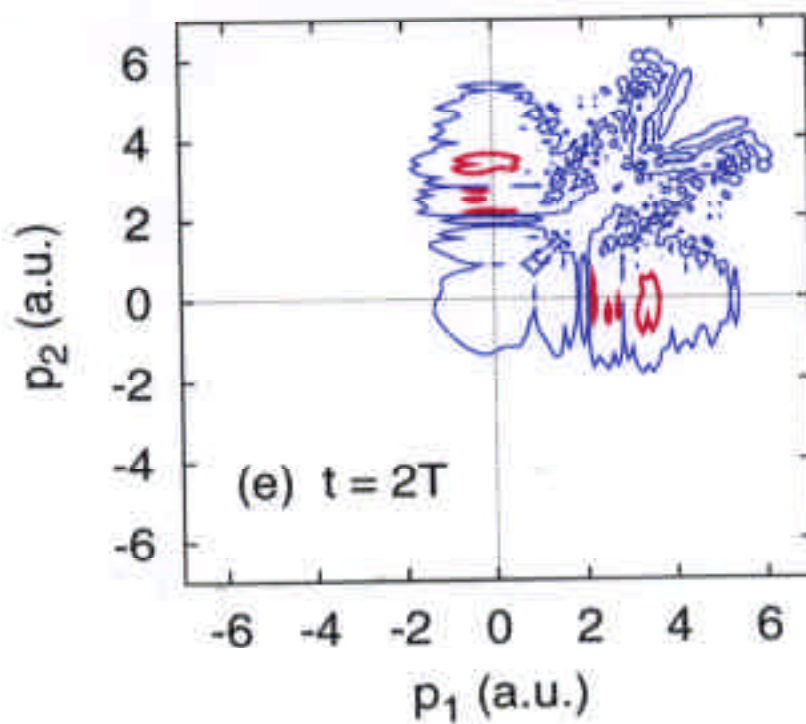
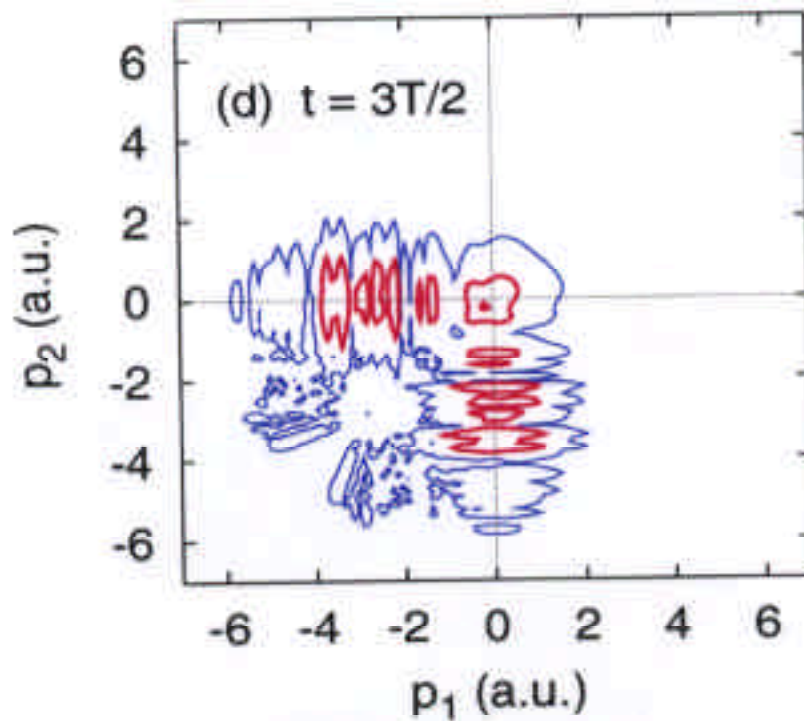
M. Lein, E. K. U. G., V. Engel, J. Phys. B 33, 433 (2000)

$$|\Psi(p_1, p_2, t)|^2$$

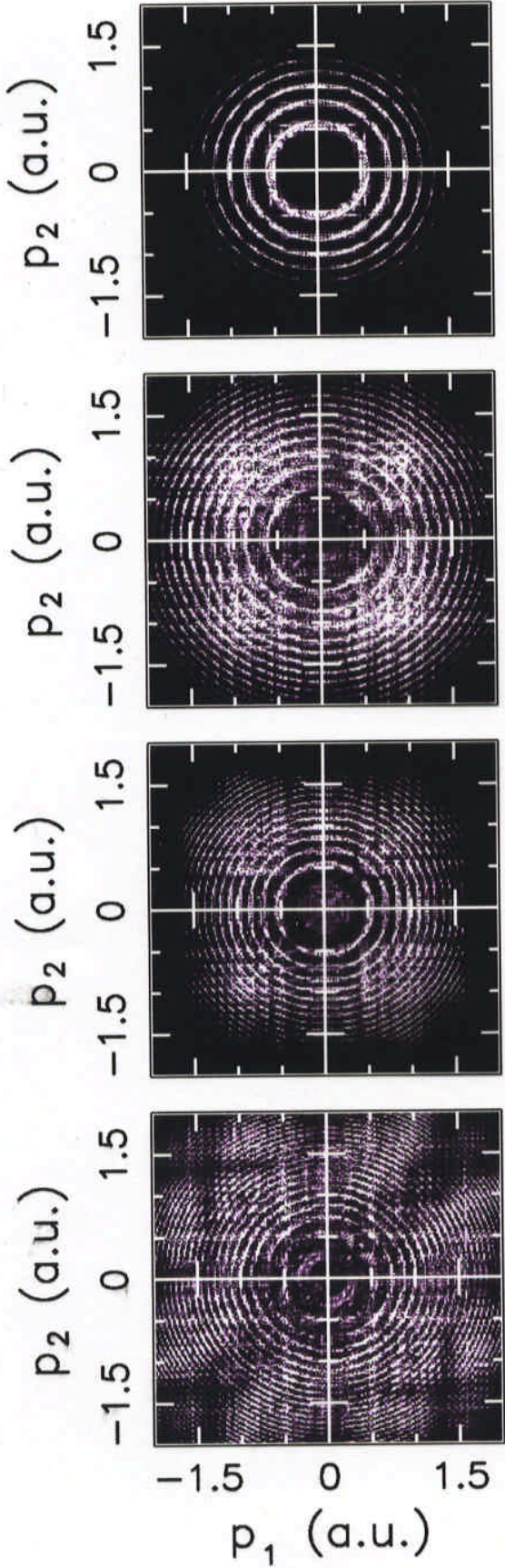


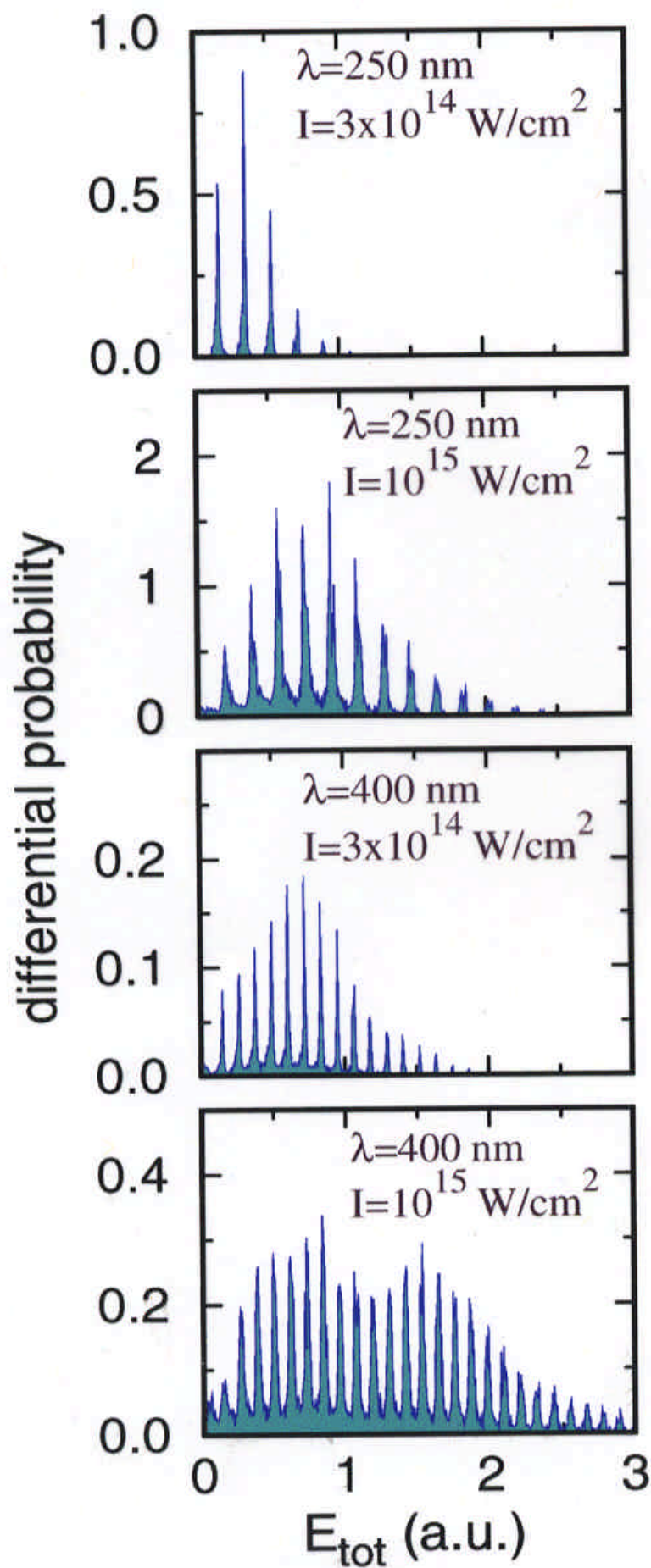
M. Lein, E. K. U. G., V. Engel, J. Phys. B 33, 433 (2000)

$$|\Psi(p_1, p_2, t)|^2$$



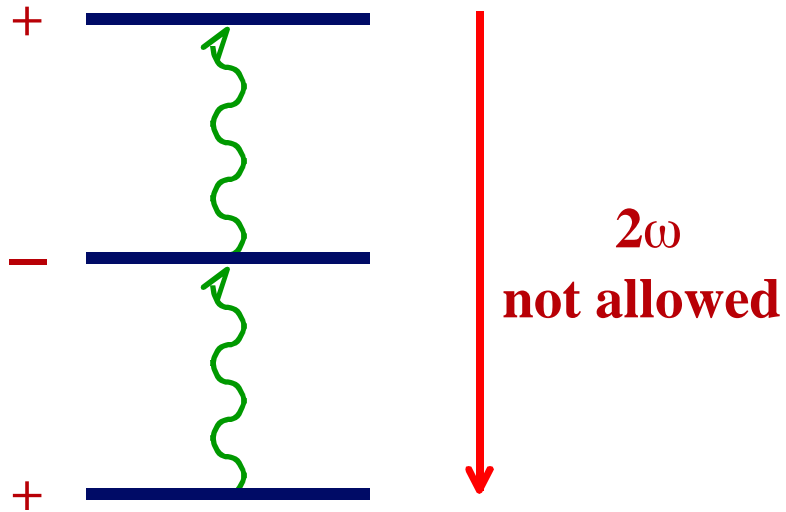
M. Lein, E. K. U. G., V. Engel, PRA 64, 23406 (2001)





Even-harmonic generation due to beyond-Born-Oppenheimer dynamics

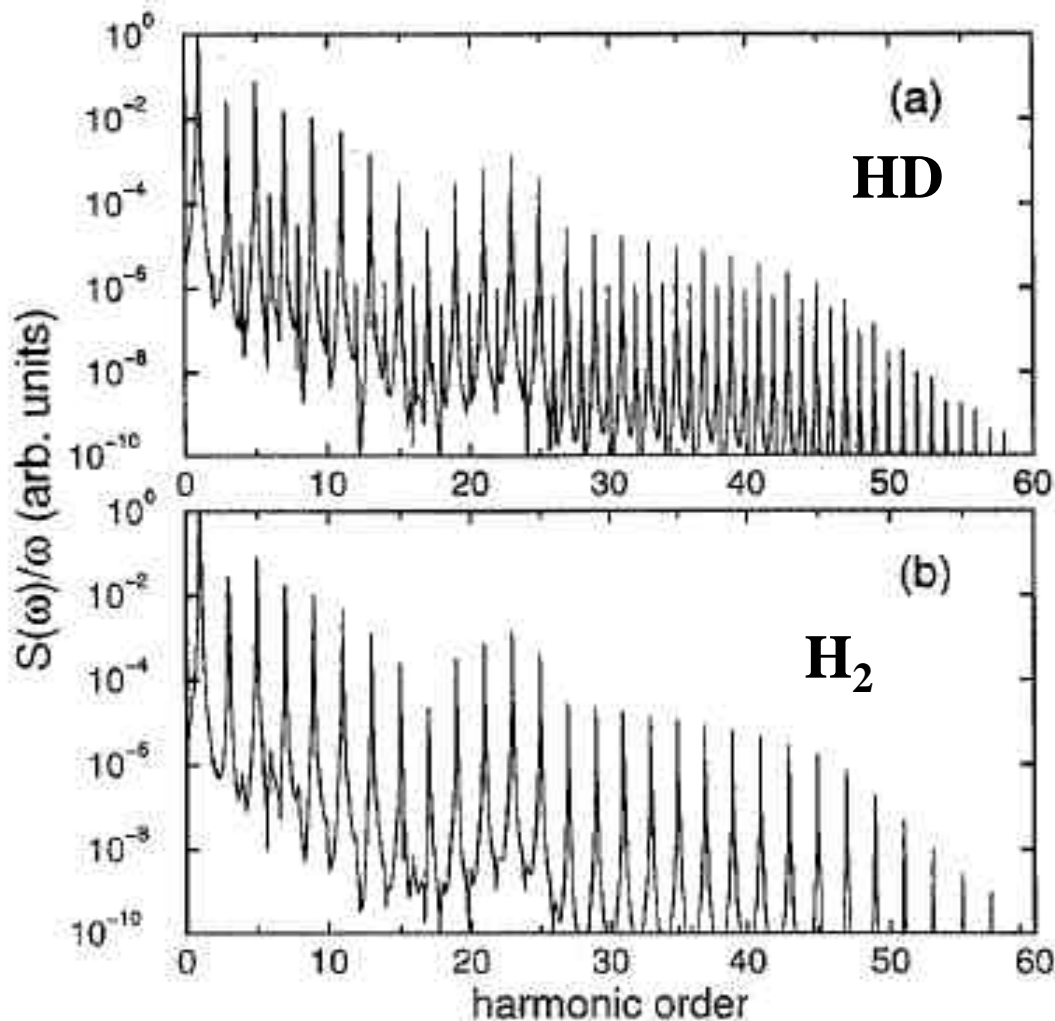
- even harmonic generation is parity forbidden



- regard oriented H_2 , D_2
- symmetry breaking for HD, not for H_2

HHG Spectrum

$$S(\omega) \sim \left| \int e^{i\omega t} \frac{d^2}{dt^2} \langle (t) | D | (t) \rangle dt \right|^2$$



(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 photons. (b) Same as panel (a) for the model H_2 molecule.

Time-dependent density-functional formalism

E. Runge, E.K.U.G., Phys. Rev. Lett. 52, 997 (1984)

HK theorem: $v(r, t) \xleftrightarrow{1-1} \rho(r, t)$

The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables

KS theorem:

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(r, t) = \sum_{j=1}^N \left| \varphi_j(r, t) \right|^2$$

of an auxiliary non-interacting (KS) system

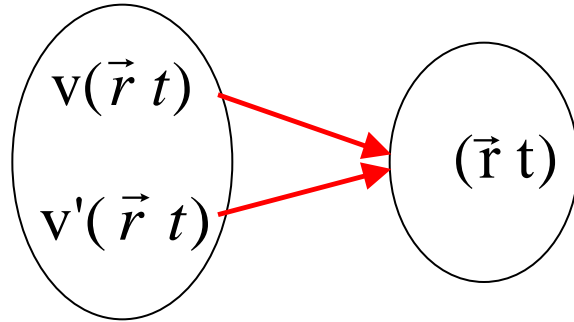
$$i\hbar \frac{\partial}{\partial t} \varphi_j(r, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{KS}}[\rho](r, t) \right] \varphi_j(r, t)$$

with the local potential

$$v_{\text{KS}}[\rho](r, t) = v(r, t) + \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}', t) + v_{\text{xc}}[\rho](\mathbf{r}, t)$$

proof (basic idea):

to be shown that



is impossible

i.e. $\mathbf{v}(\mathbf{r}, t) \neq \mathbf{v}'(\mathbf{r}, t) + \mathbf{c}(t) \Rightarrow \rho(\mathbf{r}, t) \neq \rho'(\mathbf{r}, t)$

$$\mathbf{v}(\vec{r}, t) \xrightarrow{\text{blue}} \vec{j}(\vec{r}, t) \xrightarrow{\text{green}} \rho(\vec{r}, t)$$

$$\mathbf{v}'(\vec{r}, t) \xrightarrow{\text{blue}} \vec{j}'(\vec{r}, t) \xrightarrow{\text{green}} \rho'(\vec{r}, t)$$

use

$$i \partial_t \vec{j}(\vec{r}, t) = \langle \phi(t) | [\hat{j}(\vec{r}), \hat{H}(t)] | \phi(t) \rangle$$

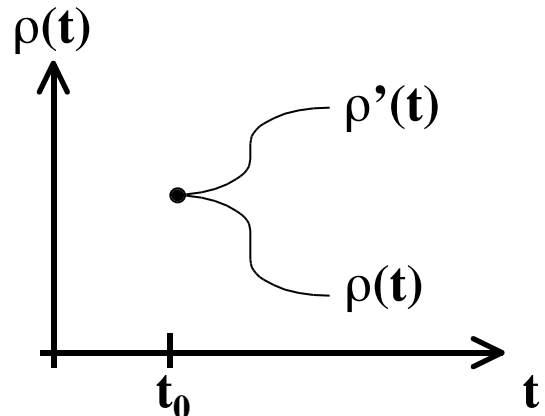
equation of motion for \vec{j}

and

$$\frac{1}{t} = -\text{div } \vec{j}(\vec{r}, t) \quad \text{continuity equation}$$

to show that $\left. \frac{\partial \vec{j}}{\partial t} \right|_{t=t_0}$ $\left. \frac{\partial \vec{j}'}{\partial t} \right|_{t=t_0}$ **and** $\left. \frac{1}{t^2} \right|_{t_0}$ $\left. \frac{1}{t^2} \right|_{t_0}$

$\Rightarrow \rho$ and ρ' will become different from each other infinitesimally later than t_0



Simplest possible approximation for $v_{xc}[\rho](\vec{r}, t)$

Adiabatic Local Density Approximation (ALDA)

$$v_{xc}^{ALDA}(\vec{r}, t) := v_{xc,stat}^{hom}(n) \Big|_{n=\rho(\vec{r}, t)}$$

$v_{xc,stat}^{hom}$ = xc potential of static homogeneous e-gas

Approximation with correct asymptotic $-1/r$ behavior: time-dependent optimized effective potential

C. A. Ullrich, U. Gossmann, E.K.U.G., PRL 74, 872 (1995)

Time-dependent DFT in the linear response regime and excited states

For times $t \leq t_0$:

System in ground state of $v_0(\mathbf{r})$
Density is the ground-state density $\rho_0(\mathbf{r})$

For times $t > t_0$:

Total external potential: $v(\mathbf{r}, t) = v_0(\mathbf{r}) + \mathbf{v}_1(\mathbf{r}, t)$
(with $\mathbf{v}_1(\mathbf{r}, t_0) = \mathbf{0}$)

density: $\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t)$

$$\delta\rho(\mathbf{r}, t) = \rho_1(\mathbf{r}, t) + \rho_2(\mathbf{r}, t) + \rho_3(\mathbf{r}, t) + \dots$$

↑
linear

↑
second order . . . density response to
the perturbation v_1

Standard Response Equation

$$v_1(\mathbf{r}, t) = \int dt' \int d^3r' \underbrace{\chi(\mathbf{r}, t, \mathbf{r}', t')}_{\text{full response function of the interacting (inhomogeneous) system}} v_1(\mathbf{r}', t')$$

full response function of the interacting (inhomogeneous) system

→ very hard to calculate

KS - Alternative

$$v_1(\mathbf{r}, t) = \int dt' \int d^3r' \underbrace{\chi_s(\mathbf{r}, t, \mathbf{r}', t')}_{\text{response function of the noninteracting (KS) system}} v_s^{(1)}(\mathbf{r}', t')$$

response function of the noninteracting (KS) system

→ relatively easy to calculate

self-consistent

$$\begin{aligned} v_s^{(1)}(\mathbf{r}, t) &= v_1(\mathbf{r}, t) + v_H^{(1)}(\mathbf{r}, t) + v_{xc}^{(1)}(\mathbf{r}, t) \\ &= v_1(\mathbf{r}, t) + \int d^3r' w(\mathbf{r}, \mathbf{r}') v_1(\mathbf{r}', t) + \int dt' \int d^3r' f_{xc}(\mathbf{r}, t, \mathbf{r}', t') v_1(\mathbf{r}', t') \end{aligned}$$

$f_{xc}(\mathbf{r}, t, \mathbf{r}', t')$ is the 1st-order term in a functional

Taylor expansion of $v_{xc}[\rho](\mathbf{r}, t)$ around $\rho_0(\mathbf{r})$:

$$v_{xc}[\rho](\mathbf{r}, t) = v_{xc}[\rho_0](\mathbf{r}, t) + \int dt' \int d^3r' \left. \frac{\delta v_{xc}(\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} (\rho(\mathbf{r}', t') - \rho_0(\mathbf{r}'))$$

Note: This is an exact representation of the linear density response

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

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

\Rightarrow The exact linear density response

$$\rho_1(\omega) = \hat{\chi}(\omega) v_1(\omega)$$

has poles at the exact excitation energies

$$\Omega = E_m - E_0$$

goal: Use the TDDFT representation of $\rho_1(\omega)$ to calculate the excitation energies $\Omega = E_m - E_0$

Single-pole approximation

Expand all quantities about one KS pole $(j_0 - k_0)$

$$\hat{\chi}_{\text{KS}}(\omega) = \frac{M_{j_0 k_0}}{-\omega + (j_0 - k_0) + i\eta} + \text{higher-order terms}$$

$$= \frac{1}{-\omega + (j_0 - k_0) + i\eta} + K$$

$$K = \int d^3r \int d^3r' \chi_{j_0}(\mathbf{r}) \chi_{j_0}^*(\mathbf{r}') \chi_{k_0}(\mathbf{r}') \chi_{k_0}^*(\mathbf{r})$$

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}')$$

Atom	Experimental Excitation Energies $^1S \rightarrow ^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	$\Delta\epsilon_{KS} + K$
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

$$\Delta E = \underbrace{\Delta\epsilon_{KS}}_{\epsilon_j - \epsilon_k} + K$$

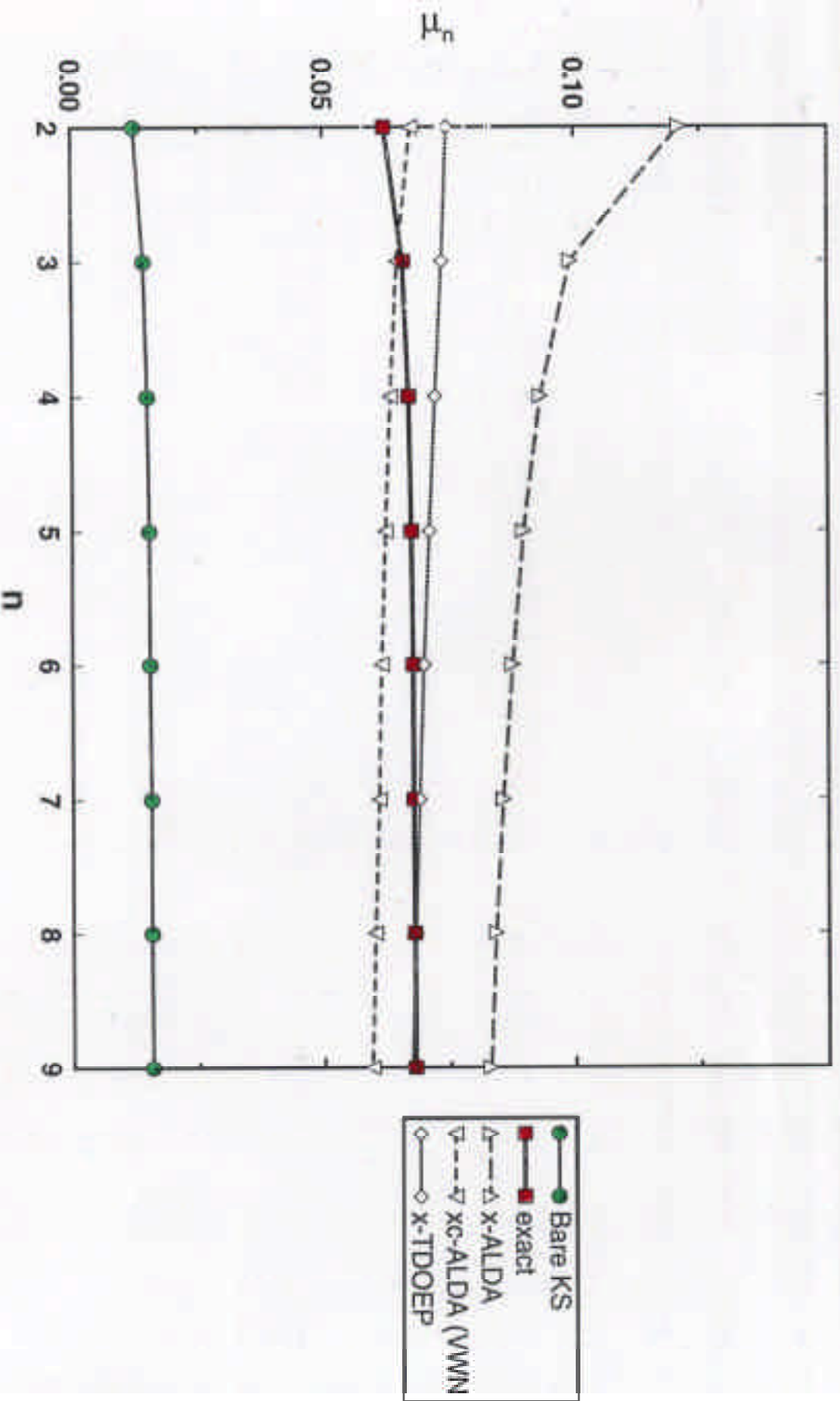
$$K = \int d^3r \int d^3r' \varphi_j^*(r) \varphi_j(r') \varphi_k(r) \varphi_k^*(r') \left(\frac{1}{|r-r'|} + f_{xc}(r, r') \right)$$

Excitation energies of CO molecule

State	Ω_{expt}	KS-transition	$\Delta\epsilon_{\text{KS}}$	$\Delta\epsilon_{\text{KS}} + \text{K}$
A	$^1\Pi$ 0.3127	$5\Sigma \rightarrow 2\Pi$	0.2523	0.3267
a	$^3\Pi$ 0.2323			0.2238
I	$^1\Sigma^-$ 0.3631	$1\Pi \rightarrow 2\Pi$	0.3626	0.3626
D	$^1\Delta$ 0.3759			0.3812
a'	$^3\Sigma^+$ 0.3127			0.3181
e	$^3\Sigma^-$ 0.3631			0.3626
d	$^3\Delta$ 0.3440			0.3404

approximations made: $v_{\text{xc}}^{\text{LDA}}$ and $f_{\text{xc}}^{\text{ALDA}}$

Quantumdefects in Helium 3P Series



Three approximations necessary

- a) approximation for v_{xc} to calculate $\{\varphi_j\}, \{\varepsilon_j\}$
- b) approximation for f_{xc}
- c) single-pole approximation (truncation of Laurent expansion)

Which one is most important? To investigate use

(a): exact v_{xc} (from Umrigar) for He and compare

(b): • $f_{xc}^{ALDA}(r, r') = (r - r') \frac{d^2}{dn^2} \left(n \left. \begin{matrix} \text{hom} \\ v_{xc} \end{matrix} \right| \right)_{(r)}$

• $f_{xc}^{TDOEP \text{ x-only}}(r, r') = \frac{\left| \sum_k^N \frac{\varphi_k(r) \varphi_k^*(r')}{|r - r'|} \right|^2}{\sum_k^N \frac{\varphi_k(r) \varphi_k^*(r')}{|r - r'|}}$

(c): • **Single-pole approximation**

$$\hat{v}_{xc}^{KS} = \frac{M_{j_0 k_0}}{-\left(\frac{1}{j_0} - \frac{1}{k_0} \right) + i}$$

• **Multiple-pole approximation**

$$\hat{v}_{xc}^{KS} = \sum_{j,k}^{J,K} \frac{M_{jk}}{-\left(\frac{1}{j} - \frac{1}{k} \right) + i}$$

Comparison of the excitation energies of neutral helium, calculated from the exact xc potential by using approximate xc kernels. All values are in Hartrees.

State	$k \rightarrow j$	$\Delta\omega_{KS}$	ALDA (xc)		TDOEP (x-only)		exact ^b
			SPA	full ^a	SPA	full ^a	
2^3S	$1s \rightarrow 2s$	0.7460	0.7357	0.7351	0.7232	0.7207	0.7285
2^1S			0.7718	0.7678	0.7687	0.7659	0.7578
3^3S	$1s \rightarrow 3s$	0.8392	0.8366	0.8368	0.8337	0.8343	0.8350
3^1S			0.8458	0.8461	0.8448	0.8450	0.8425
4^3S	$1s \rightarrow 4s$	0.8688	0.8678	0.8679	0.8667	0.8671	0.8672
4^1S			0.8714	0.8719	0.8710	0.8713	0.8701
5^3S	$1s \rightarrow 5s$	0.8819	0.8814	0.8815	0.8808	0.8811	0.8811
5^1S			0.8832	0.8835	0.8830	0.8832	0.8825
6^3S	$1s \rightarrow 6s$	0.8888	0.8885	0.8885	0.8882	0.8883	0.8883
6^1S			0.8895	0.8898	0.8894	0.8896	0.8892
7^3S	$1s \rightarrow 7s$	0.8929	0.8927	0.8927	0.8925	0.8926	0.8926
7^1S			0.8933	0.8935	0.8932	0.8934	0.8931
8^3S	$1s \rightarrow 8s$	0.8955	0.8954	0.8954	0.8952	0.8953	0.8953
8^1S			0.8958	0.8959	0.8957	0.8958	0.8956
9^3S	$1s \rightarrow 9s$	0.8972	0.8972	0.8972	0.8971	0.8971	0.8971
9^1S			0.8975	0.8976	0.8974	0.8975	0.8974
2^3P	$1s \rightarrow 2p$	0.7772	0.7702	0.7698	0.7693	0.7688	0.7706
2^1P			0.7764	0.7764	0.7850	0.7844	0.7799
3^3P	$1s \rightarrow 3p$	0.8476	0.8456	0.8457	0.8453	0.8453	0.8456
3^1P			0.8483	0.8483	0.8500	0.8501	0.8486
4^3P	$1s \rightarrow 4p$	0.8722	0.8714	0.8715	0.8712	0.8713	0.8714
4^1P			0.8726	0.8726	0.8732	0.8733	0.8727
5^3P	$1s \rightarrow 5p$	0.8836	0.8832	0.8832	0.8831	0.8831	0.8832
5^1P			0.8838	0.8838	0.8841	0.8842	0.8838
6^3P	$1s \rightarrow 6p$	0.8898	0.8895	0.8895	0.8895	0.8895	0.8895
6^1P			0.8899	0.8899	0.8901	0.8901	0.8899
7^3P	$1s \rightarrow 7p$	0.8935	0.8933	0.8933	0.8933	0.8933	0.8933
7^1P			0.8935	0.8936	0.8937	0.8937	0.8936
8^3P	$1s \rightarrow 8p$	0.8959	0.8958	0.8958	0.8958	0.8958	0.8958
8^1P			0.8959	0.8959	0.8960	0.8960	0.8959
9^3P	$1s \rightarrow 9p$	0.8975	0.8975	0.8975	0.8974	0.8975	0.8975
9^1P			0.8976	0.8976	0.8976	0.8976	0.8976
Mean abs. dev. ^c			0.0011	0.0010	0.0010	0.0010	
Mean percentage error			0.15%	0.13%	0.13%	0.13%	

^aUsing the lowest 34 unoccupied orbitals of s and p symmetry, respectively.

^bNonrelativistic variational calculation [38].

^cMean value of the absolute deviations from the exact values.

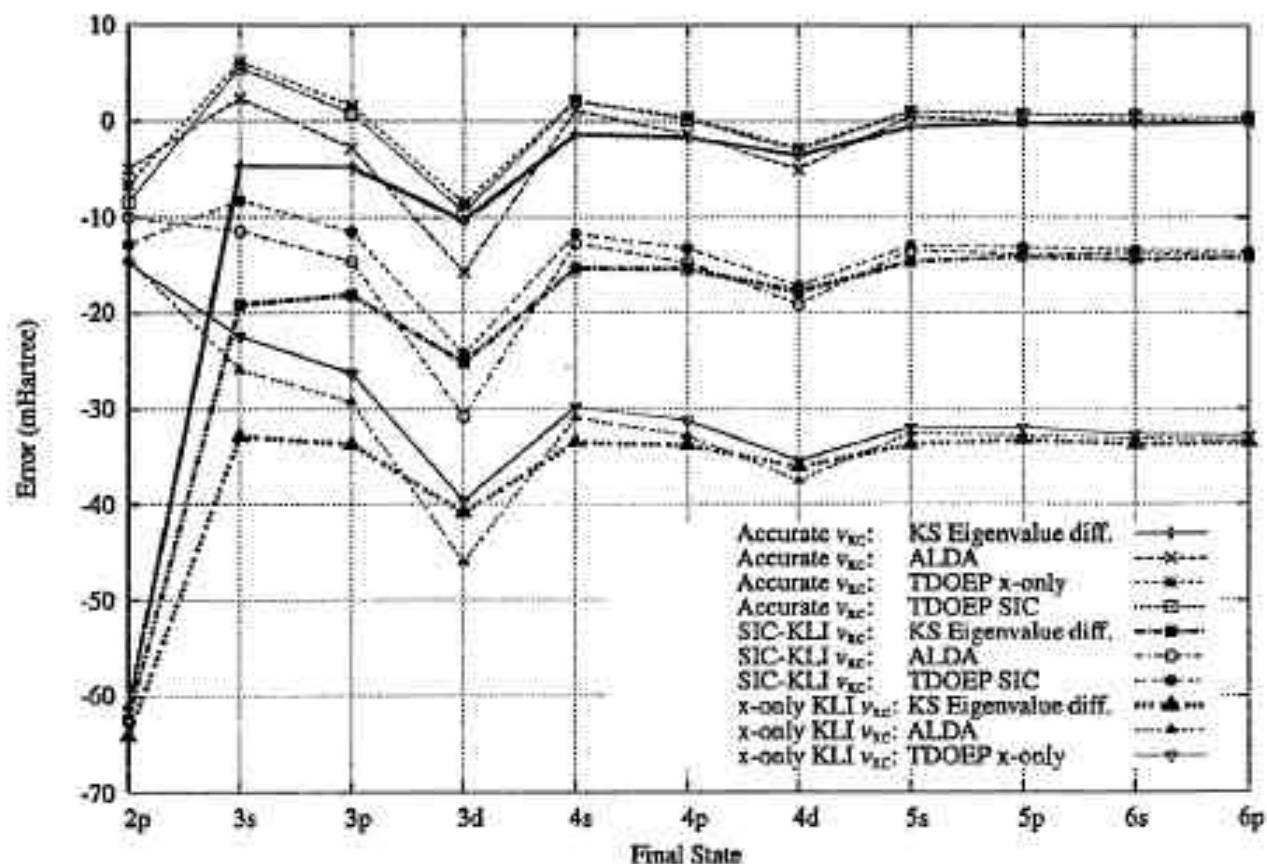
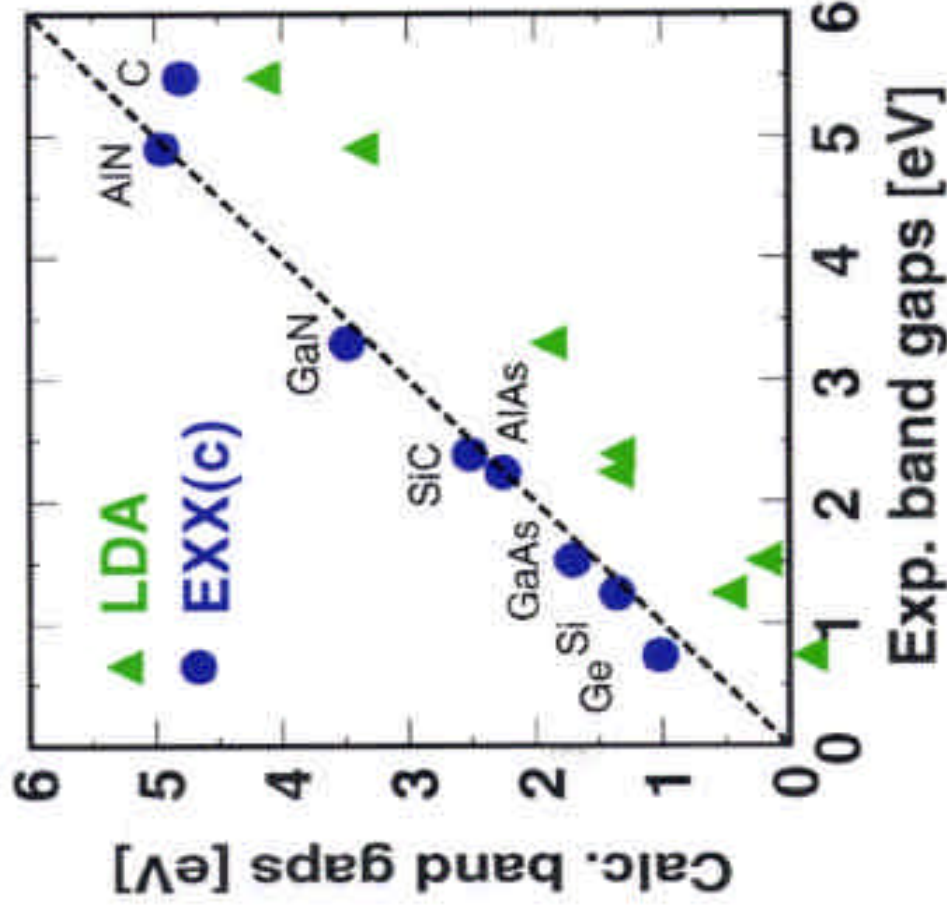


Figure 3.3: Errors of singlet excitation energies from the ground state of Be, calculated from the accurate, the OEP-SIC and x-only KLI exchange correlation potential and with different approximations for the exchange-correlation kernel (see text). The errors are given in mHartrees. To guide the eye, the errors of the discrete excitation energies were connected with lines.

Fundamental Energy gaps



- **EXX** gives excellent band gaps: larger than LDA by ~1 eV
- Small influence of correlation
- **EXX** pseudopotential important for Ge: minimum of conduction band in L

from: M. Städele, M. Morokuma, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B 59, 10031 (1999)

TABLE IX. Comparison of energy gaps between occupied and empty states with experiment. All energies in eV.

	LDA	GW-LDA	EXX	GW-EXX	Experiment
Si					
E_g	0.51	1.19	1.43	1.54	1.17 ^a
E'_0	2.55	3.23	3.28	3.57	3.35 ^b
E_1	2.69	3.38	3.35	3.72	3.46 ^b
E'_1	4.52	5.26	5.08	5.57	5.38 ^b
E_2	3.48	4.18	4.12	4.51	4.32 ^b
Ge					
$E_g(L_c - \Gamma_v)$	0.06	0.62	0.86	0.94	0.74 ^a
E_0	-0.07	0.57	0.81	0.94	0.90 ^c
\bar{E}'_0	2.59	3.17	3.16	3.40	3.16 ^c
E_1	1.44	2.03	2.14	2.32	2.22 ^c
E_2	3.75	4.31	4.37	4.56	4.45 ^c
GaAs					
E_0	0.49	1.22	1.49	1.65	1.52 ^d
E'_0	3.55	4.24	4.16	4.51	4.51 ^d
E_1	2.02	2.73	2.80	3.09	3.04 ^d
E_2	3.98	4.65	4.72	4.99	5.13 ^d
BeSe					
E_0	4.04	5.46	5.25	5.92	5.55 ^e
\bar{E}'_0	5.01	6.48	5.78	6.75	7.29 ^e
E_1	5.18	6.57	6.00	6.95	6.15 ^e
E'_1	6.81	8.31	7.48	8.64	8.47 ^e
E_2	5.02	6.43	5.86	6.82	6.56 ^e
BeTe					
$E_g(X_c - \Gamma_v)$	1.60	2.59	2.47	2.88	2.7 ^f , 2.8 ^g
E_0	3.28	4.33	3.91	4.58	4.20 ^h
E_1	3.97	4.97	4.61	5.28	4.69 ^h
E_2	4.33	5.37	4.99	5.68	5.04 ^h
MgSe					
E_0	2.47	4.08	3.72	4.71	4.23 ⁱ
MgTe					
E_0	2.29	3.66	3.33	4.20	3.67 ⁱ

Failures of ALDA in the linear response regime

- **H₂ dissociation is incorrect:**

$$E\left(1^+_{\text{u}}\right) - E\left(1^+_{\text{g}}\right)_{\text{R}} = 0 \quad \text{(in ALDA)}$$

(see: Gritsenko, van Gisbergen, Görling, Baerends, J. Chem. Phys. 113, 8478 (2000))

- **response of long chains strongly overestimated**

(see: Champagne et al., J. Chem. Phys. 109, 10489 (1998) and 110, 11664 (1999))

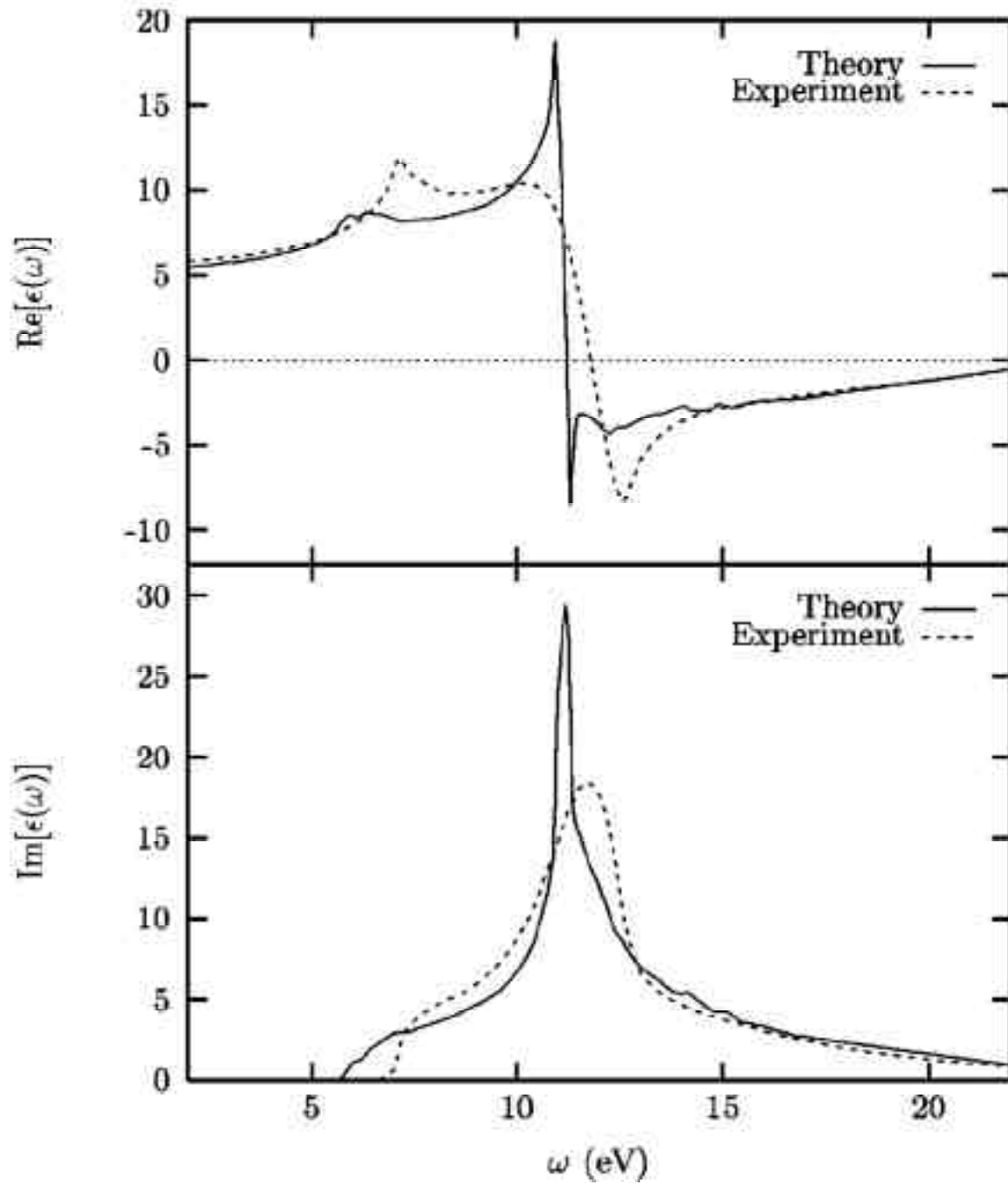
- **in periodic solids,** $f_{\text{xc}}^{\text{ALDA}}(q, \omega) = c(\omega)$

whereas, for insulators, $f_{\text{xc}}^{\text{exact}}(q, \omega) \sim 1/q^2$

divergent.

Dielectric Function Diamond

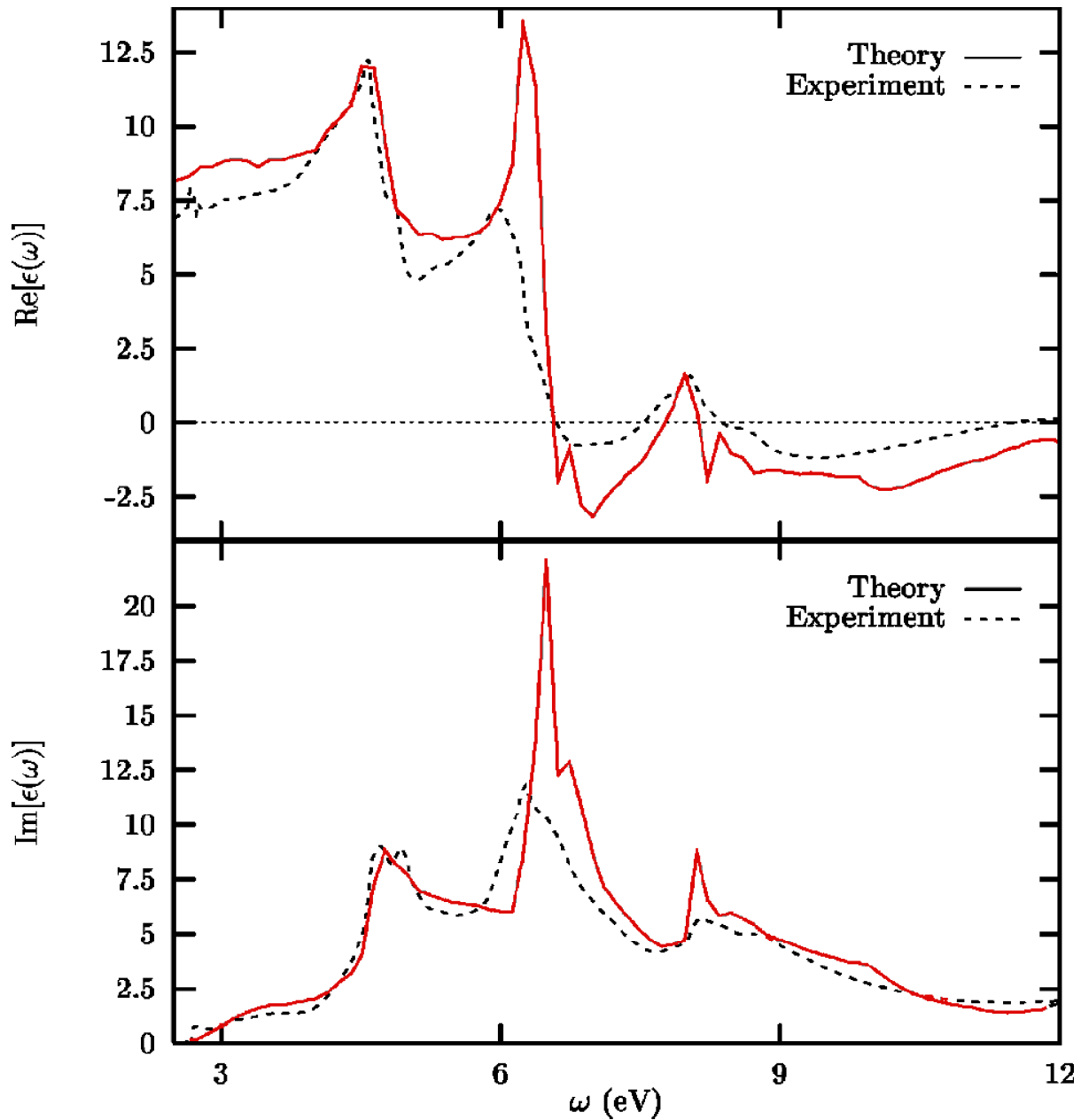
Kootstra, de Boeij, Snijders, *J. Chem. Phys.* **112**, 6517 (2000) & *Phys. Rev. B* **62**, 7071 (2000)



Experimental data taken from: P.E. Aspnes and A.A. Studna, *Phys. Rev. B* **27**, 985 (1983)

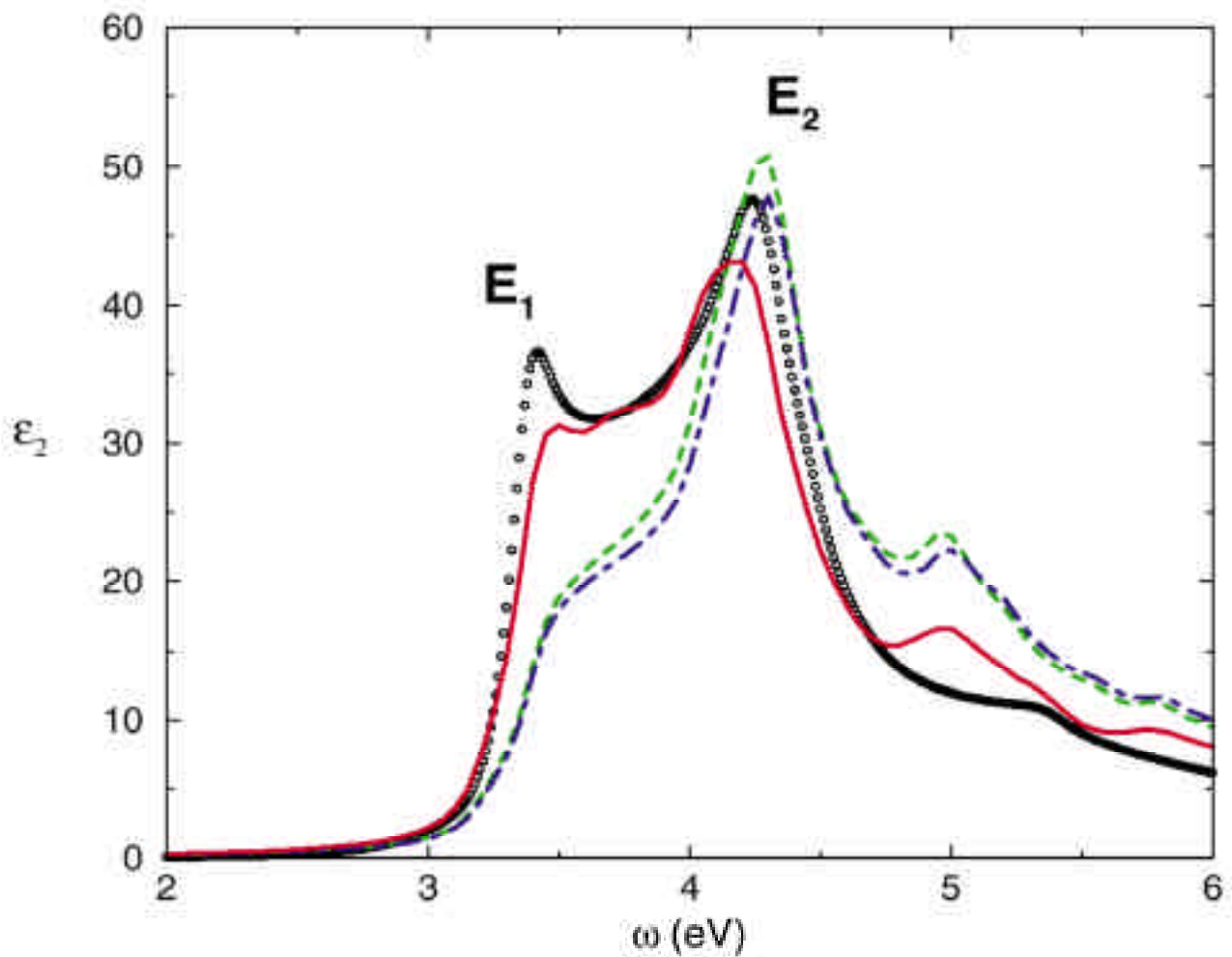
Dielectric Function Zinc selenide (ZnSe)

Kootstra, de Boeij, Snijders, Phys. Rev. B 62, 7071 (2000)



Experimental data taken from: J.L. Freilouf, Phys. Rev. B 7, 3810 (1973)

Calculated optical absorption spectrum of Si from EXX (dashed line), EXX+TDLDA (dot-dashed line), and EXX+TDEXX (solid line). Circles denotes experimental data from C.M. Herzinger et al., J.Appl. Phys. 83, 3323 (1998)



Y.-H. Kim, A. Göring, PRL 89, 096402 (2002).

Review articles on time-dependent DFT/excitation energies

Density-functional theory of time-dependent phenomena. E. K. U. Gross, J. F. Dobson. M. Petersilka, in: *Topics in Current Chemistry*, vol. 181, edited by R. Nalewajski (Springer, 1996), p. 81-172

A guided tour of time-dependent DFT. K. Burke, E. K. U. Gross, in: *Springer Lectures Notes in Physics*, vol. 500 (1998), p. 116-146

What is circular dichroism?

$P^{L/R}(\omega)$ = power absorption of L/R circularly polarized light with frequency ω

The occurrence of $P(\omega) = P^L(\omega) - P^R(\omega) \neq 0$ is called circular dichroism.

Where is dichroism observed?

A: materials where parity is broken (sugar)

B: simulations where time-reversal symmetry is broken

1. either by an external magnetic field
2. or by an “internal” magnetic field
(due to ferromagnetic order)

type B dichroism is a relativistic effect.

Relativistic Effects in Superconductors

$$\hat{H}^{nonrel} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \left[\frac{\left(-i\vec{\nabla} + \frac{e}{c} \vec{A} \right)^2}{2m} + (v(\mathbf{r}) - \mu) \right] \hat{\psi}_{\sigma}(\mathbf{r})$$

$$- \int d^3r \int d^3r' \left(\Delta^*(\mathbf{r}, \mathbf{r}') \hat{\chi}(\mathbf{r}, \mathbf{r}') + \Delta(\mathbf{r}, \mathbf{r}') \hat{\chi}^{\dagger}(\mathbf{r}, \mathbf{r}') \right)$$

$$\hat{H}^{rel} = \int d^3r \hat{\Psi}^{\dagger}(\mathbf{r}) \left[c\vec{\gamma} \cdot (-i\vec{\nabla}) + mc^2 + \gamma_{\mu} A^{\mu} \right] \hat{\Psi}(\mathbf{r})$$

+ ?

$\hat{\Psi}(\mathbf{r}) =$ Dirac spinor field operator

QUESTION: What is the correct relativistic generalization of the non-relativistic order parameter $\hat{\chi}(\mathbf{r}, \mathbf{r}')$?

non-relativistic order parameter

homogeneous case: $\vec{k} = \langle \hat{a}_{\vec{k}} \hat{a}_{-\vec{k}} \rangle$

spherical case: $l,m = \langle \hat{a}_{l,m} \hat{a}_{l,-m} \rangle$

general case: $= \langle \hat{a}_{\text{state}} \hat{a}_{\text{time-reversed state}} \rangle$

(Kramers pair)

require relativistic generalization of order Parameter to be a Kramers pair

$$\hat{\alpha}_{\text{rel}}(\mathbf{r}, \mathbf{r}') = \hat{\alpha}^t(\mathbf{r}) T \hat{\alpha}(\mathbf{r}')$$

with time reversal operator

$$T = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$$

Resulting relativistic order parameter $\hat{\alpha}_{\text{rel}}$ is Lorentz scalar

$$\hat{H}_{\text{rel}} = \int d^3r \hat{\alpha}(\mathbf{r}) \left(c \left(-i \frac{\partial}{\partial t} \right) + mc^2 + A \right) \hat{\alpha}(\mathbf{r}) - \int d^3r \int d^3r' \left(\hat{\alpha}^*(\mathbf{r}, \mathbf{r}') \hat{\alpha}_{\text{rel}}(\mathbf{r}, \mathbf{r}') + \text{H.C.} \right)$$

DIRAC EQUATION FOR SUPERCONDUCTORS

$$\hat{\gamma}^0 \left[c \vec{\gamma} \cdot \vec{p} + mc^2 (1 - \hat{\gamma}^0) + q \gamma^\mu A_\mu \right] u_n(\mathbf{r}) + \int d^3 \mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \hat{\eta}_0 v_n(\mathbf{r}') = E_n u_n(\mathbf{r})$$

$$-\hat{\gamma}^0 \left[c \vec{\gamma} \cdot \vec{p} + mc^2 (1 - \hat{\gamma}^0) + q \gamma^\mu A_\mu \right]^* v_n(\mathbf{r}) - \int d^3 \mathbf{r}' \Delta^*(\mathbf{r}, \mathbf{r}') \hat{\eta}_0 u_n(\mathbf{r}') = E_n v_n(\mathbf{r})$$

Particle amplitudes u_n }
 Hole amplitudes v_n } are Dirac spinors

$$\hat{\eta}_0 = \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix}_y$$

Non-relativistic limit of Dirac BdG equations

$$\underbrace{\begin{pmatrix} \left[\frac{(\vec{\sigma} \cdot \vec{\pi})^2}{2m} + (v(r) - \mu) \right] & \Delta(r)(i\sigma_y) \\ (-i\sigma_y)\Delta^*(r) & -\left[\frac{(\vec{\sigma}^* \cdot \vec{\pi}^*)^2}{2m} + (v(r) - \mu) \right] \end{pmatrix}}_{H_0} \begin{pmatrix} u(r) \\ v(r) \end{pmatrix} = E \begin{pmatrix} u(r) \\ v(r) \end{pmatrix}$$

$u(r)$ and $v(r)$ are PAULI spinors, and

weakly relativistic limit, up to order $(v/c)^2$

$$(H_0 + H_2) \begin{pmatrix} u \\ v \end{pmatrix} = E \begin{pmatrix} u \\ v \end{pmatrix}$$

$$H_2 = \begin{pmatrix} h_2 & d_2 \\ d_2^+ & -h_2^* \end{pmatrix}$$

$$h_2 = \frac{1}{4m^2 c^2} \left(\frac{\hbar^2}{2} \nabla^2 v + \hbar \vec{\sigma} \cdot (\vec{\nabla} v) \times \vec{p} - \frac{p^4}{2m} \right)$$

$$d_2 = \frac{1}{4m^2 c^2} \left(\frac{\hbar^2}{2} \nabla^2 \Delta + \hbar \vec{\sigma} \cdot (\vec{\nabla} \Delta) \times \vec{p} \right)$$

Off-diagonal spin-orbit and Darwin terms

Perturbation Theory

A) Stationary perturbations

Zeeman:	$\vec{m} \vec{B}_0$	→	exact	
currents:	$\vec{j} \vec{A}_0$	}		1st order pert. theory
diag. SOC:	$\vec{v} \times$			
offdiag. SOC:	\times			
	$]$			

B) Time-dependent perturbation

$$\vec{A}(\vec{r}, t) = \vec{A}_1(\vec{r}) e^{i t} + \text{c.c.}$$

$$\vec{A}_1 = i \frac{c}{2} \frac{E_0}{\omega} \vec{e}^{-i \vec{q} \cdot \vec{r}}$$

use dipole approximation ($q \rightarrow 0$) and

golden rule:

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H}^+ | i \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)$$

where

$$\hat{H} = \frac{\hat{p}^2}{2m} - \hbar \omega \hat{n} - \hbar \omega \hat{n}^\dagger$$

and

$$\hat{h} = \frac{q}{mc} \vec{A} \cdot \hat{p}$$

}

absorption
only

Power absorption:

$$P(\vec{\mu}, \mathbf{H}, T, \vec{\nu}) = \sum_{fi} W_{if} (E_f - E_i) f(E_i) f(-E_f)$$

Dichroism:

$$P = P(\vec{\mu}, \mathbf{H}, T, \vec{\nu}_L) - P(\vec{\mu}, \mathbf{H}, T, \vec{\nu}_R)$$

$$\vec{\nu}_{L,R} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix}$$

$P = 0$ without the stationary perturbations
 $\vec{j} \vec{A}_0$, diag./offdiag. SOC

Mechanisms for Dichroism

1. Mechanism known from the normal state

(strongly modified by superconductivity)

- (a) diagonal spin-orbit coupling
(+ Zeeman splitting)

- (b) orbital currents

2. Mechanism which show up only in superconductors

- (a) offdiagonal spin-orbit coupling
(+ Zeeman splitting)

- (b) unconventional pair potential (order parameter)
 - complex time reversal breaking
 - inversion symmetry breaking

- (c) supercurrents [already verified experimentally]

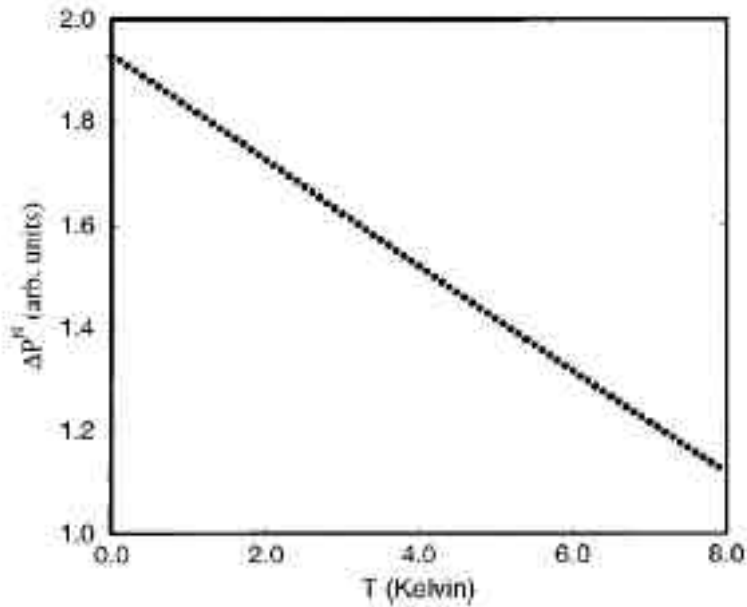


FIG. 1. Dichroism in the normal state vs temperature T . This and all other figures display only the contribution of SOC-induced dichroism. The other mechanisms are excluded from the calculation, as discussed in the main text. The numerical values of the parameters specifying the system are given in the main text.

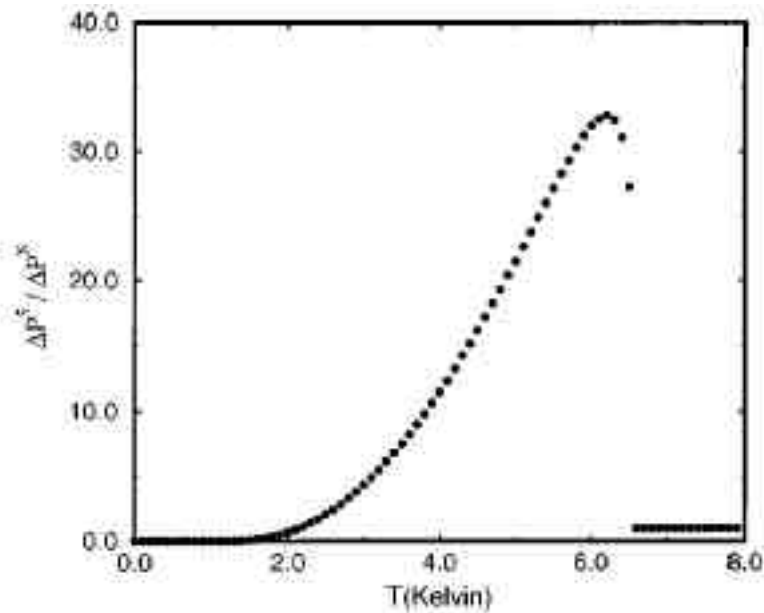


FIG. 2. Dichroism ratio vs T at small magnetic fields. A strong coherence peak is seen close to T_c , while near $T=0$ the curve approaches 0.

K. Capelle, E.K.U.G., B. L. Györfy, Phys.Rev. Lett. 78, 3753 (1997)

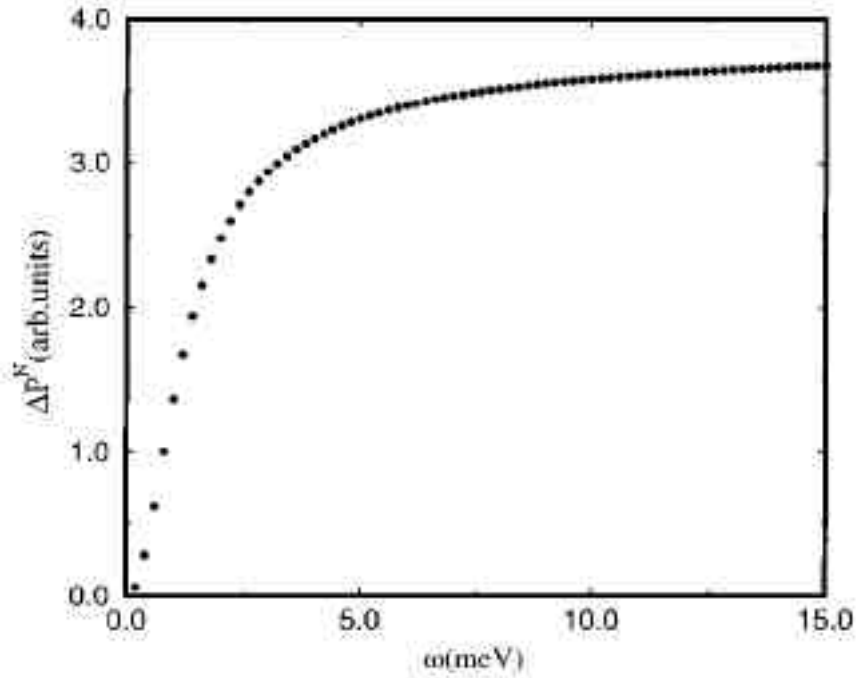


FIG. 7. Dichroism in the normal state vs frequency ω .

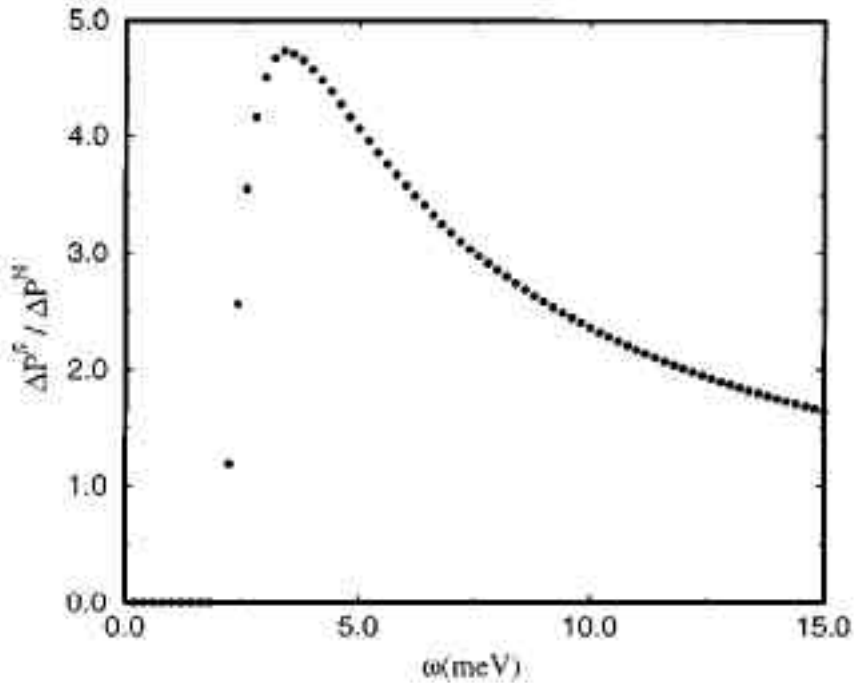


FIG. 8. Dichroism ratio vs ω . The absorption edge at $\omega=2\Delta$ has a mixed type I-II character, reflecting the behavior of the perturbations under time reversal.

K. Capelle, E.K.U.G., B. L. Györfy, Phys.Rev. Lett. 78, 3753 (1997)

General non-relativistic pairing potential

$$\hat{V} = \int d^3r \int d^3r' \left(\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}') \right) \mathbf{D}_{2 \times 2}(\mathbf{r}, \mathbf{r}') \hat{\psi} \begin{pmatrix} \mathbf{r}' \\ \mathbf{r}' \end{pmatrix}$$

$$\mathbf{D}_{2 \times 2}(\mathbf{r}, \mathbf{r}') = \sum_{i=0}^3 d_i(\mathbf{r}, \mathbf{r}') \mathbf{m}_i$$

$\{\mathbf{m}_i\}$ = basis in the space of 2×2 matrices

$$\hat{V} = \int d^3r \int d^3r' \sum_{i=0}^3 d_i(\mathbf{r}, \mathbf{r}') \hat{\psi}_i(\mathbf{r}, \mathbf{r}') \hat{\psi}_i(\mathbf{r}, \mathbf{r}')$$

Order parameters

$$\hat{\psi}_i(\mathbf{r}, \mathbf{r}') = \left(\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}') \right) \mathbf{m}_i \hat{\psi} \begin{pmatrix} \mathbf{r}' \\ \mathbf{r}' \end{pmatrix}$$

If $\{\mathbf{m}_i\}$ are chosen to be the Balian-Werthammer matrices then one obtains

1 OP (spin singlet BCS OP) : **scalar**

3 OP (spin triplet) : **3-vector under Galilei transformations**

General Relativistic Pairing Potential

$$\hat{\chi}^{\text{rel}} = \int d^3 r \int d^3 r' \hat{\chi}^T(\mathbf{r}) D_{4 \times 4}(\mathbf{r}, \mathbf{r}') \hat{\chi}(\mathbf{r}')$$

$$D_{4 \times 4}(\mathbf{r}, \mathbf{r}') = \sum_{i=0}^{15} M_i(\mathbf{r}, \mathbf{r}')$$

$\{M_i\}$ = basis in the space of 4×4 matrices

$$\hat{\chi}^{\text{rel}} = \int d^3 r \int d^3 r' \sum_{i=0}^{15} M_i(\mathbf{r}, \mathbf{r}') \hat{\chi}_i^{\text{rel}}(\mathbf{r}, \mathbf{r}')$$

Relativistic order parameters

$$\hat{\chi}_i^{\text{rel}}(\mathbf{r}, \mathbf{r}') = M_i(\mathbf{r}, \mathbf{r}') \hat{\chi}(\mathbf{r}, \mathbf{r}')$$

With a suitably chosen basis $\{M_i\}$ one obtains

1 OP : **scalar**

1 OP : **pseudoscalar**

4 OPs : **four-vector**

4 OPs : **axial four-vector**

6 OPs : **antisymmetric tensor of rank 2**

under Lorentz transformations

Further details on the relativistic framework

- K. Capelle, E.K.U.G., Phys.Lett. A198, 261 (1995)
- K. Capelle, E.K.U.G., Phys.Rev. B 59, 7140 (1999)
& 7155 (1999)

Further details on dichroism in superconductors

- K. Capelle, E.K.U.G., B. L. Györffy, PRL 78, 3753 (1997)
- K. Capelle, E.K.U.G., B. L. Györffy, Phys.Rev. B 58, 473 (1998)