Ionisation of atoms within TDDFT

Nuclear effects on the TRPES

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nano-bio spectroscopy group

Science at FELs, Villigen, Switzerland 16/09/2014

Ionisation of atoms within TDDFT

Time-Dependent Density-Functional Theory of Strong-Field Ionization of Atoms under Soft X-Rays

A. Crawford-Uranga et al

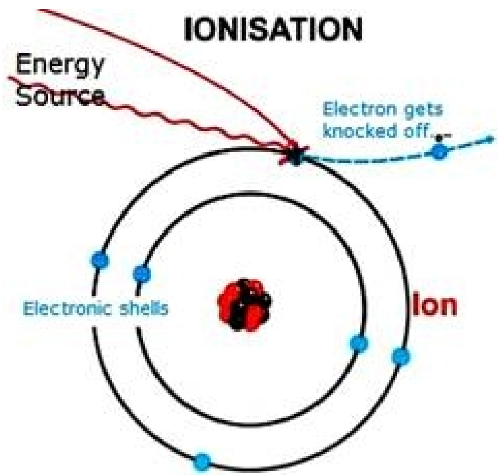
Physical Review A (accepted), (2014)

Outline

- Motivation
- Introduction to soft X-ray ionisation
  - Test atoms: neon and argon
- Theory: LOPT vs TDDFT
- Results
  - Neon
  - Argon
- Conclusions

Motivation

- Ionisation of atoms with FEL



- LOPT accurate vs experiment Ne and Ar atoms
  - Perturbative: It fails when FEL ↑ I ↑ ω
- Non-perturbative approach → TDDFT
  - Previously thought to fail (He “knee”)

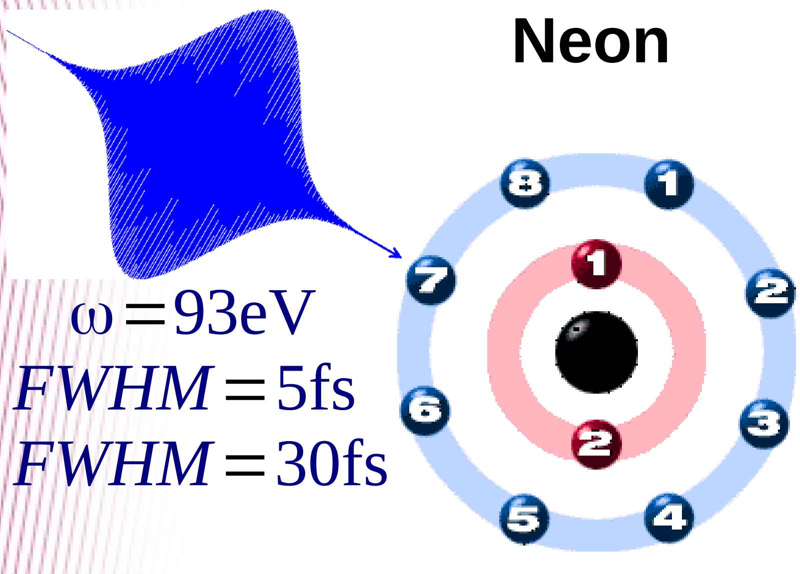
Introduction to soft X-ray ionisation

$$V_{FEL}(\mathbf{r},t) = A\, f(t) \sin(\omega t)\, \mathbf{r}\, \alpha$$

$$I(t) = I_0 e^{-\frac{(t-t_0)^2}{2\tau_0^2}} = I_0 f(t)$$

$$FWHM = 2\sqrt{ln2}\,\tau_0$$

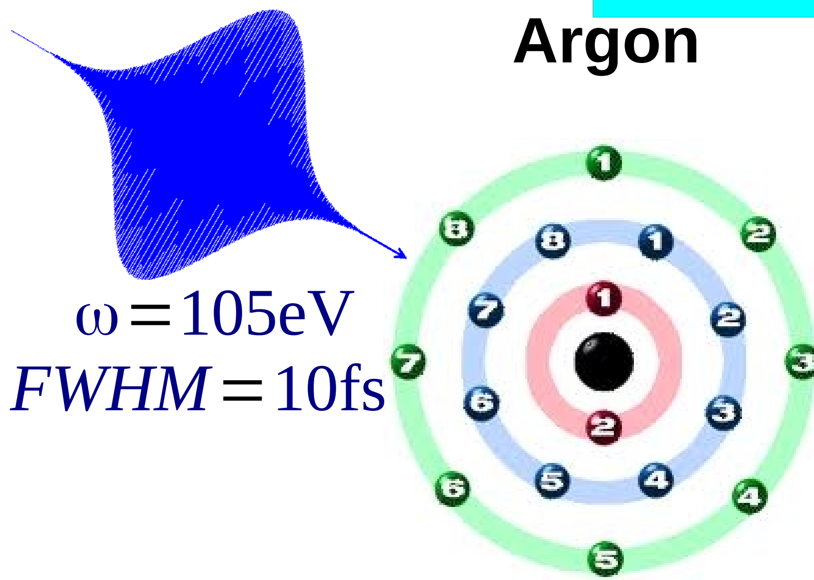
- Soft X-rays: laser $I \sim 10^{13} - 10^{16}\, W/cm^2$



$\omega = 93\text{eV}$

$FWHM = 5\text{fs}$

$FWHM = 30\text{fs}$



$\omega = 105\text{eV}$

$FWHM = 10\text{fs}$

Total and Individual electrons ejected

- Freeze $1s^2$ (Neon) and $1s^2$, $2s^2$, $2p^6$ (Argon)

Theory: LOPT

- Rate equations Neon

G. M. Nikolopoulos and P. Lambropoulos, J. Phys. B: At. Mol. Opt. Phys. 47, 115001 (2014)

$$\frac{dN_0}{dt} = -\sigma_{0,1} F N_0 - \sigma_{0,1} F^8 N_0 - \sigma_{0,8} F^{11} N_0 - \sum_{n=2}^{6} \sigma_{0,n} F^n N_0 ; \frac{dN_1}{dt} = \sigma_{0,1} F N_0 - \sigma_{1,2} F N_1$$

- Rate equations Argon

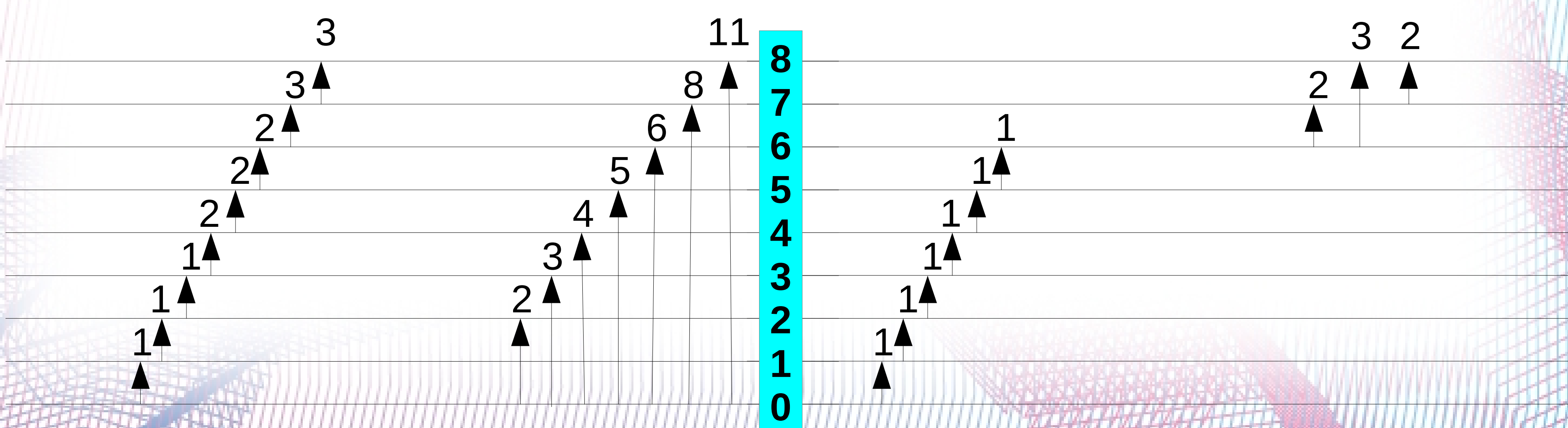
M. Ilchen et al, (2014), private communication to be published

Cross sections σ
Photon flux F

$$\frac{dN_6}{dt} = \sigma_{5,6} F N_5 - \sigma_{6,7} F^2 N_6 - \sigma_{6,8} F^3 N_6 ; \frac{dN_7}{dt} = \sigma_{6,7} F^2 N_6 - \sigma_{7,8} F^2 N_7$$

Neon 93 eV

Argon 105 eV



Theory: TDDFT

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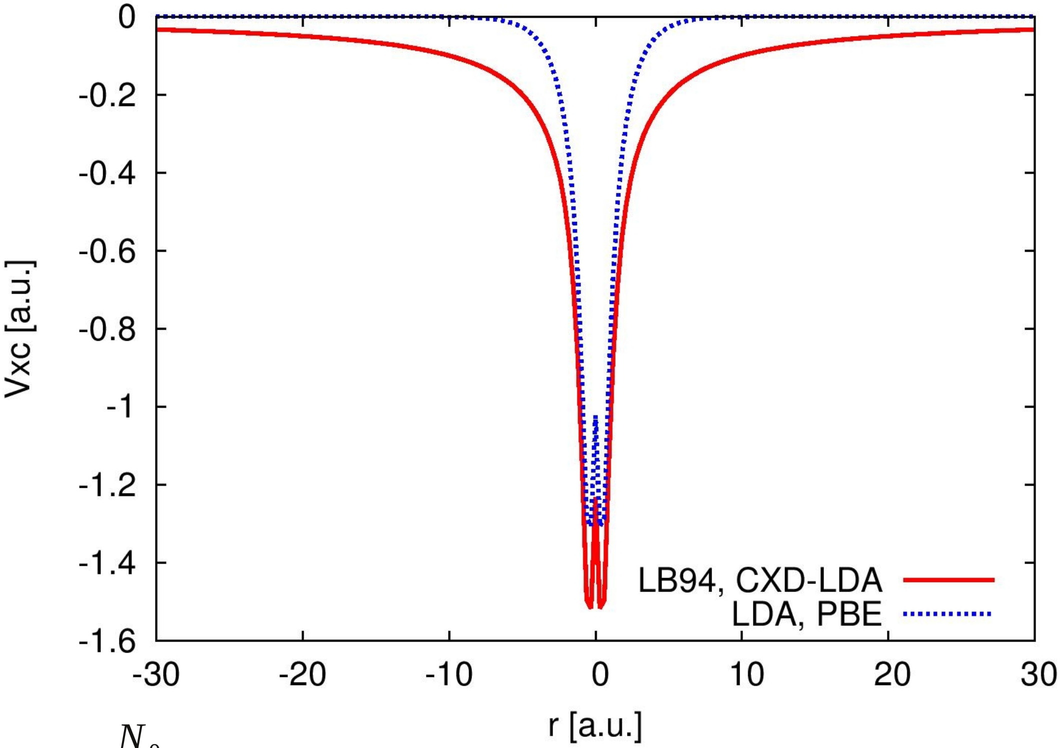
- TDDFT: Describe many-electron systems with KS non-interacting evolution

$$i\frac{\partial \varphi_i(\boldsymbol{r},t)}{\partial t}=\left(-\frac{1}{2}\nabla^2-\sum_j^M \frac{Z_j}{|\boldsymbol{R_j}-\boldsymbol{r}|}+\int d\boldsymbol{r}\frac{n(\boldsymbol{r},t)}{|r-r'|}+V_{FEL}(\boldsymbol{r},t)+V_{xc}[n](\boldsymbol{r},t)\right)\varphi_i(\boldsymbol{r},t)$$

$$n(\boldsymbol{r},t)=\sum_{i=1}^N |\varphi_i(\boldsymbol{r},t)^2|$$

- DFT functionals

LDA, CXD-LDA, PBE, LB94

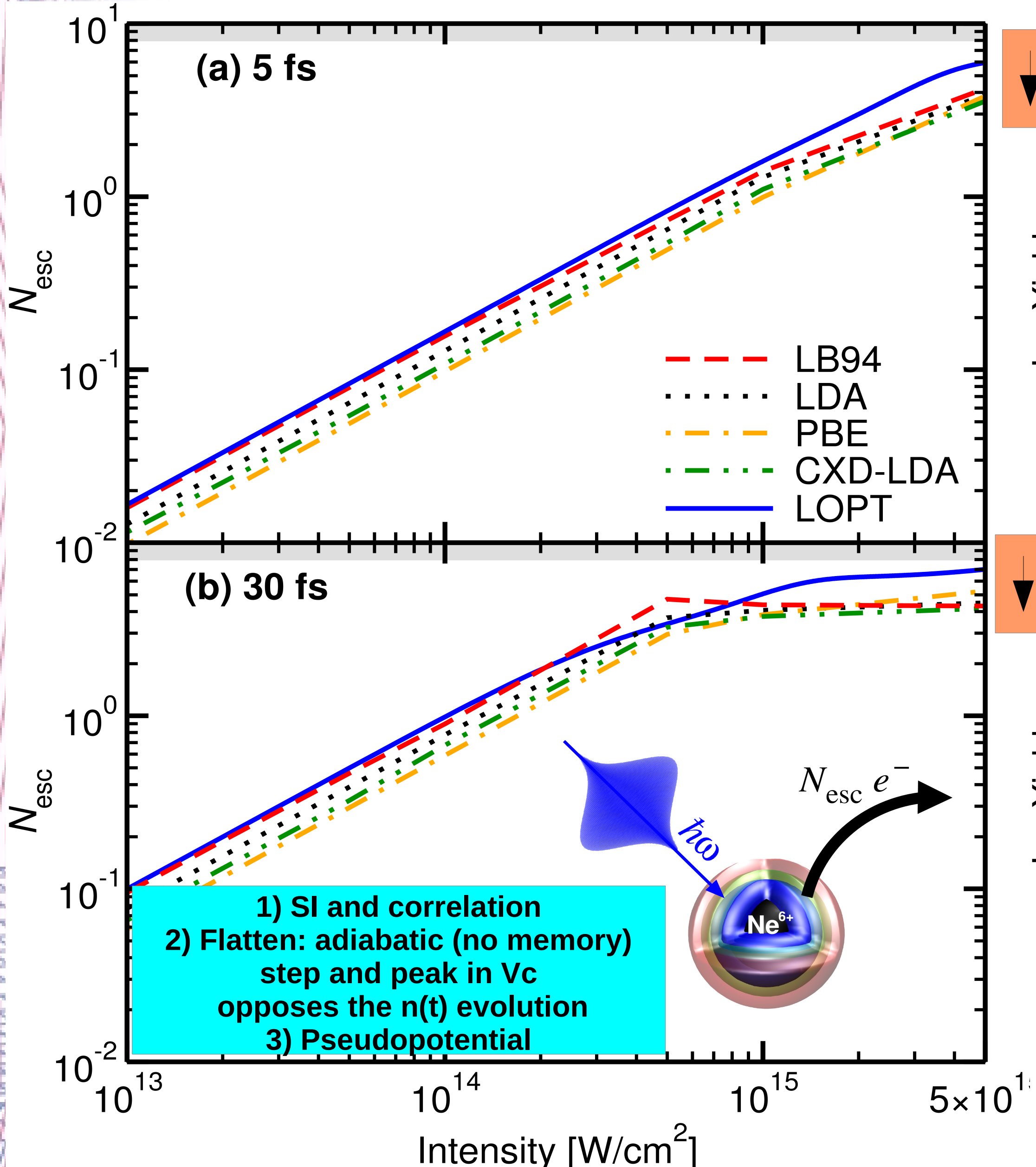


- Absorbing Boundary

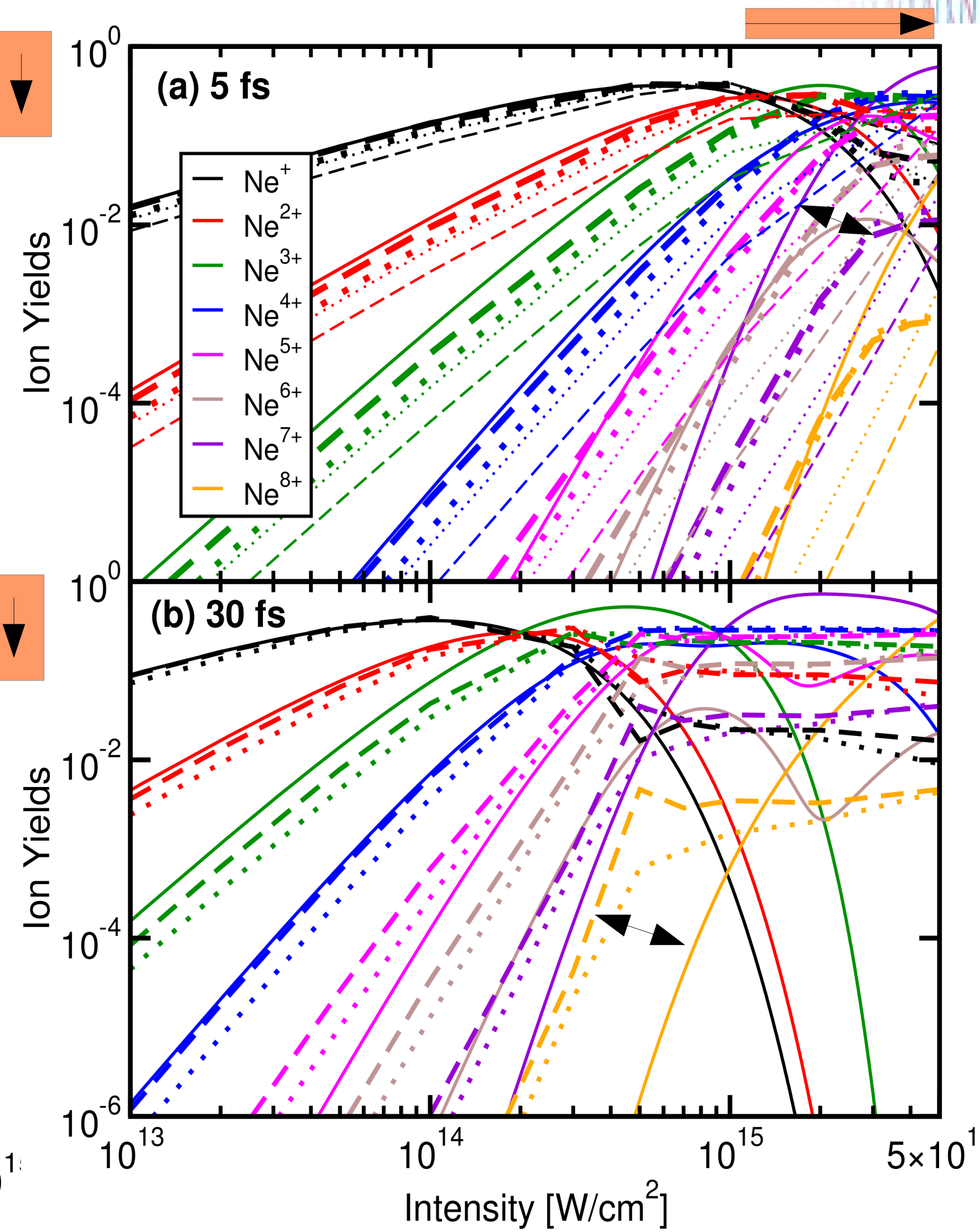
$$N_{esc}(t)=N_0-\int_{V_{inside}} dr\, n(r,t)=N_0-\sum_{n=1}^{N_0} N_n$$

Results: Neon

Total yields



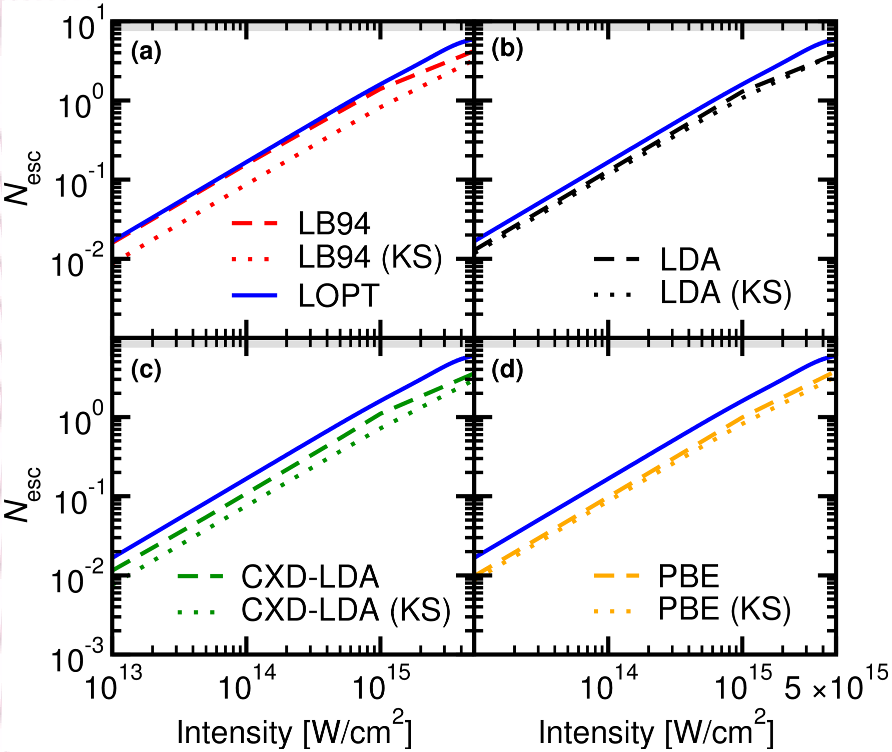
Individual yields



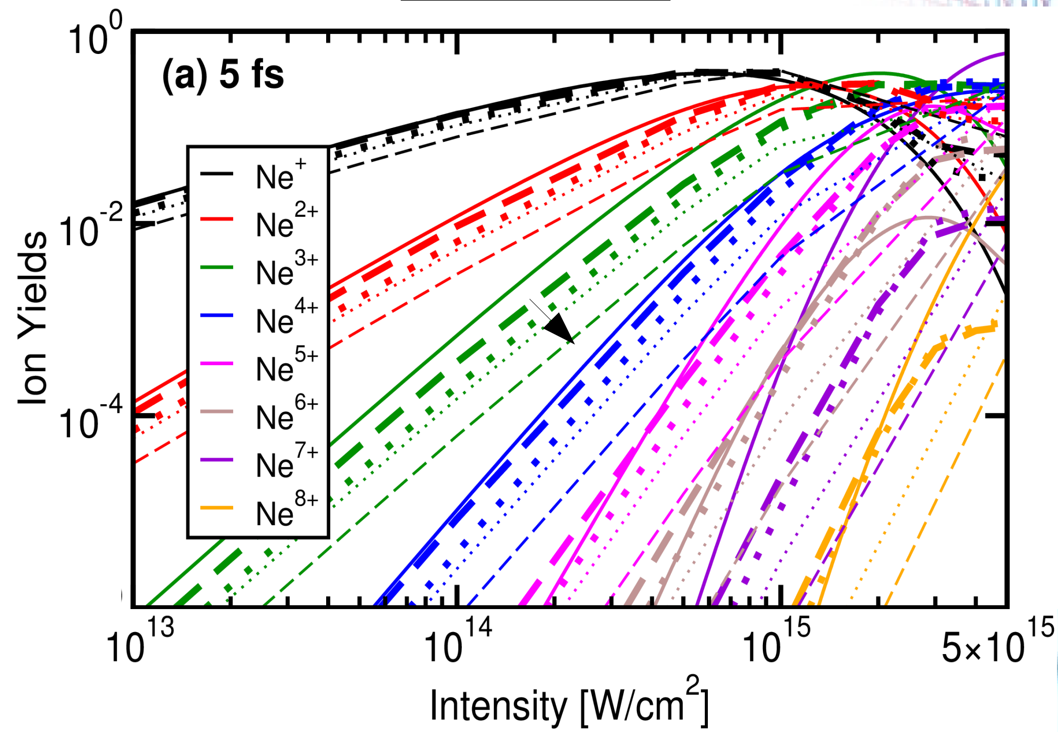
Results: Neon

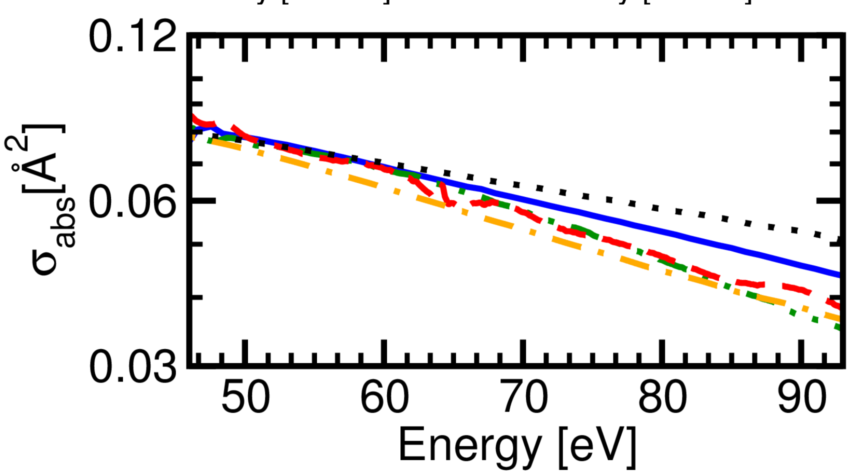
Frozen vs Non frozen yields

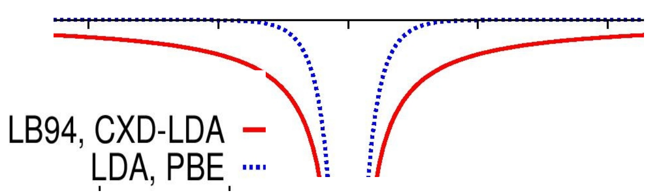
Total



Individual



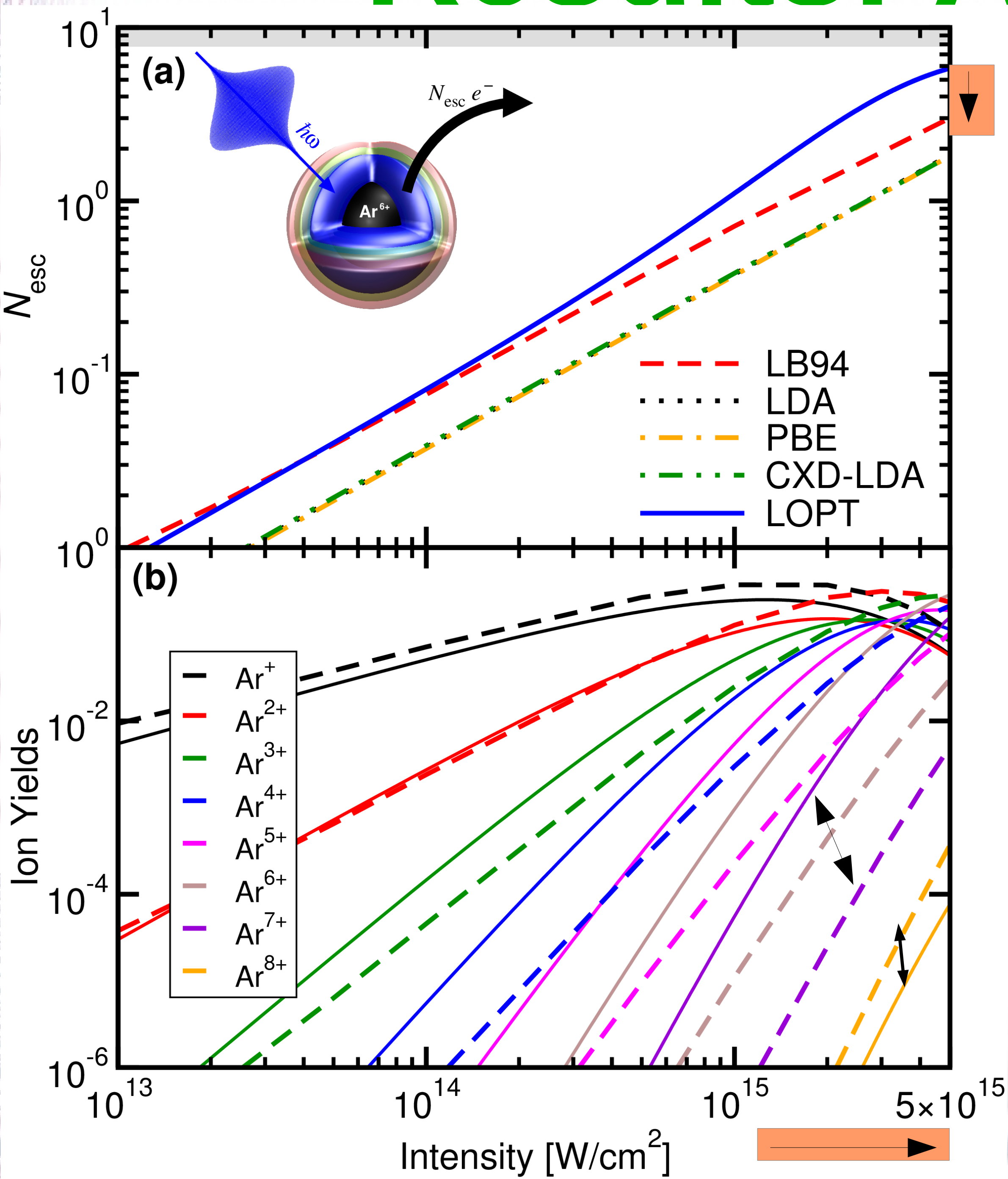




Time dependence of hxc

LB94(F) < LDA(F) ~ LDA < LB94

Results: Argon



Ar^{7+} self-interaction

Ar^{8+} TDDFT correlation

Conclusions

- LOPT vs TDDFT agreement (different methods) ↓ I ↓ ω
- Predictive power of TDDFT
  - Stabler xc-long ranged potentials
  - Sources of error (to check / improve)
    - Transferability pseudopotential
    - Adiabatic functionals
    - Self interaction and correlation
- Non-perturbative photoionisation Exp. with TDDFT ?

Nuclear effects on the TRPES

Modelling the effect of nuclear motion on the attosecond time-resolved photoelectron spectra of ethylene

A. Crawford-Uranga, et al

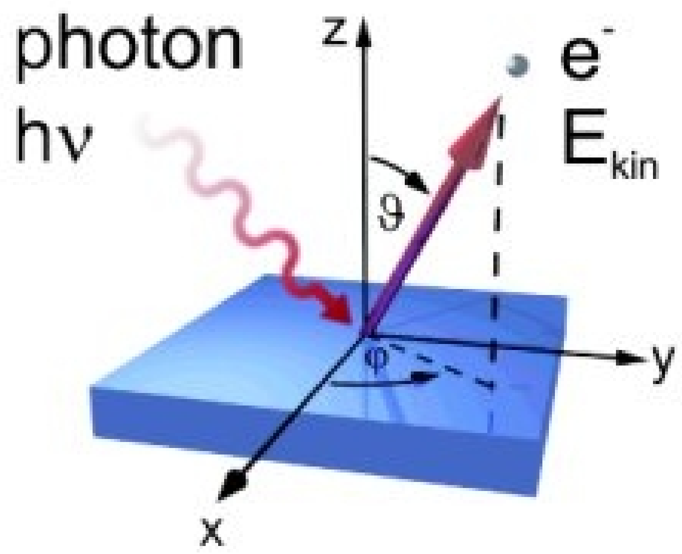
Journal of Physics B: Atomic Molecular and Optical Physics 47, 124018 (2014)

Outline

- Motivation
- Test case: ethylene
- Introduction to TRPES (pump + probe)
  - TDDFT + Ehrenfest
- Results
- Conclusions

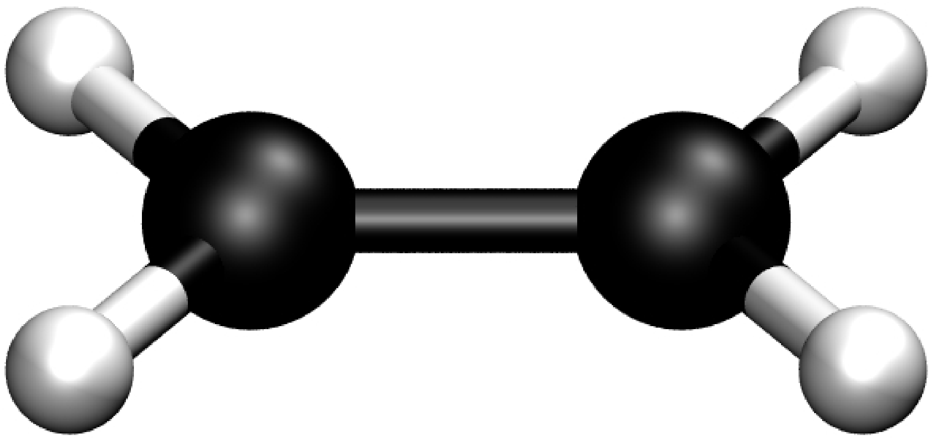
Motivation

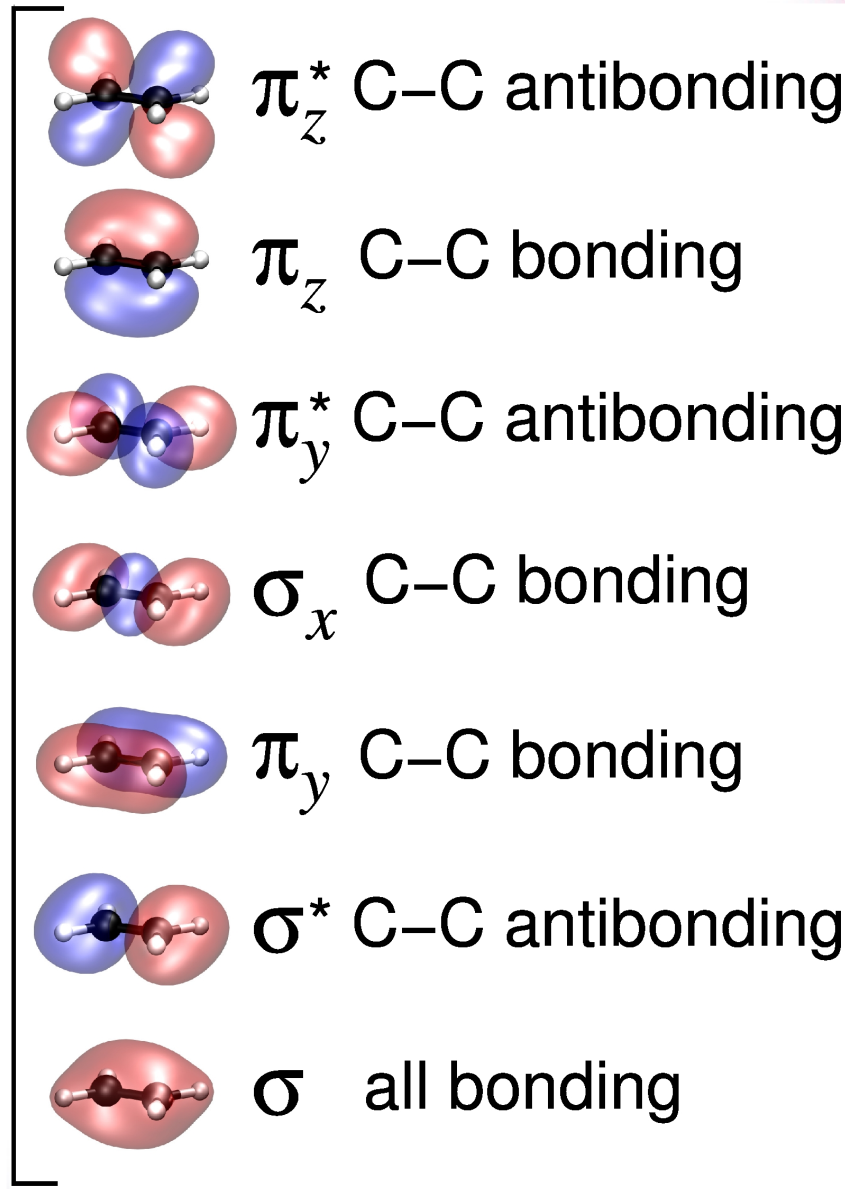
- TRPES/TRPAD: visualise kinetic energy and angular distribution



- Experiments: difficult alignment of the molecule

Test case: ethylene

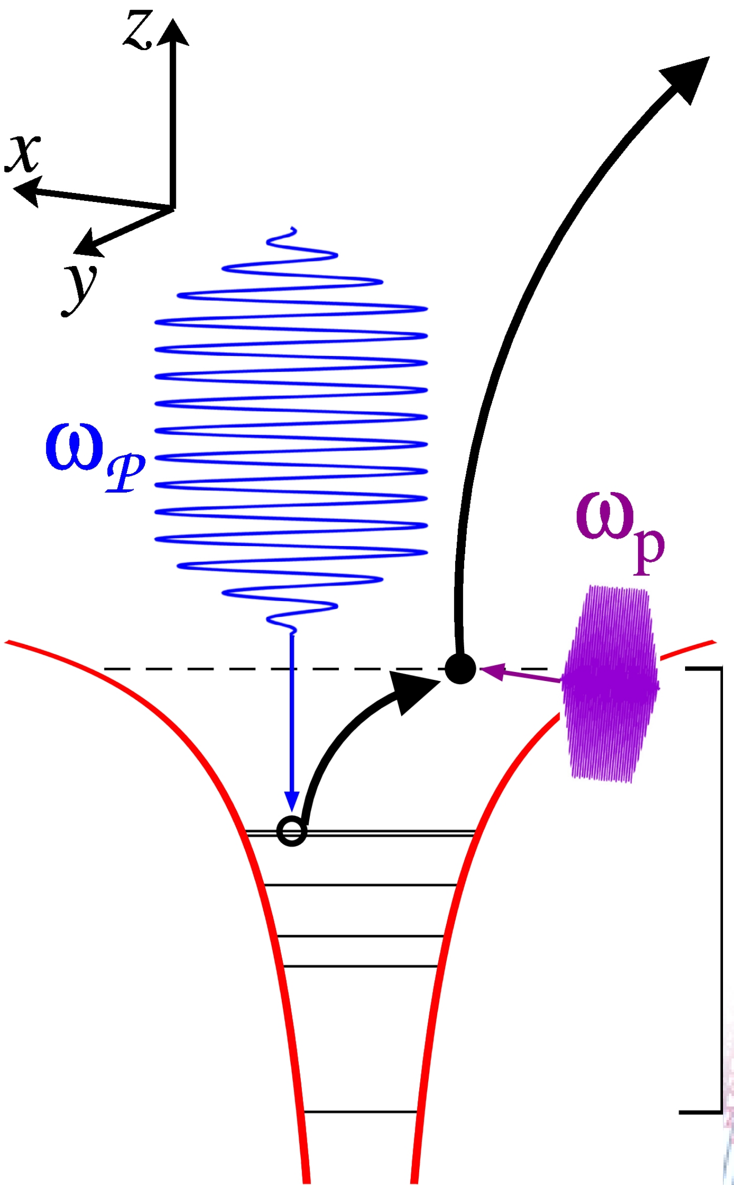




Test case: ethylene

Pump → $I \sim 10^{11} W/cm^2; \omega_P = 0.326\, Ha$ "tuned"

Probe → $I \sim 10^{11} W/cm^2; \omega_p = 1.8\, Ha$



$\pi_z \rightarrow \pi_z^*$

Introduction to TRPES

- Coupled electron-nuclear motion
  - **TDDFT: KS system electron evolution**

$$i\frac{\partial \varphi_i(\mathbf{r},t)}{\partial t}=\left(-\frac{1}{2}\nabla^2+V_{las}(\mathbf{r},t)-\sum_j^M \frac{Z_j}{|\mathbf{R}_j(t)-\mathbf{r}|}+\int d\mathbf{r}\frac{n(\mathbf{r},t)}{|r-r'|}+V_{xc}[n](r,t)\right)\varphi_i(\mathbf{r},t)$$

$$n(\mathbf{r},t)=\sum_{i=1}^{N/2} 2|\varphi_i(\mathbf{r},t)|^2$$

$$V_{xc}=\frac{\partial E^{LDA+ADSIC}}{\partial n(\mathbf{r},t)}=\frac{\partial}{\partial n(\mathbf{r},t)}\left(E^{LDA}[n(\mathbf{r},t)]-N(E_H+E_{xc})[n(\mathbf{r},t)/N]\right)$$

  - **Ehrenfest: nuclear evolution**

$$M_j\frac{\partial^2 \mathbf{R}_j(t)}{\partial t^2}=-\int dr\, n(\mathbf{r},t)\nabla_j\left[\sum_j^M \frac{Z_j}{|\mathbf{R}_j(t)-r|}+V_{las}(\mathbf{r},t)\right]+\nabla_j\sum_{l\neq j}\frac{Z_l Z_j}{|\mathbf{R}_j(t)-\mathbf{R}_l(t)|}$$

Introduction to TRPES

- **Obtain simultaneously $(\mathbf{r},\mathbf{p})$-space → C.M. Wigner Transform)**

$$\omega(\mathbf{r},\mathbf{r}',\mathbf{p},t)=\int \frac{d\,\mathbf{s}}{(2\pi)^{d/2}}\, e^{i\,\mathbf{p}\,\mathbf{s}}\,\rho_{KS}(\mathbf{r},\mathbf{r}',t)$$

$$\mathcal{P}(\mathbf{p})=\int d\,\mathbf{R}\,\omega(\mathbf{r},\mathbf{r}',\mathbf{p},t)$$

$$P(E)_{PES}=\int_0^{4\pi} d\,\Omega\,\mathcal{P}(\mathbf{p})$$

$$P(E,\theta)_{PAD}=\int_0^{2\pi} d\,\phi\,\mathcal{P}(\mathbf{p})$$

- **The KS orbitals in $(\mathbf{r},\mathbf{p})$-space ?**

U. De Giovannini et al, Physical Review A 85, 062515 (2012)

Introduction to TRPES

- Region A (interacting) → $\boldsymbol{r}$ - space
    - TDKS (electrons) + EHRENFEST (nuclei)
- Region B (ionized out A + in B) → $\boldsymbol{p}$ - space
- Absorbing M(r) → separation only outgoing

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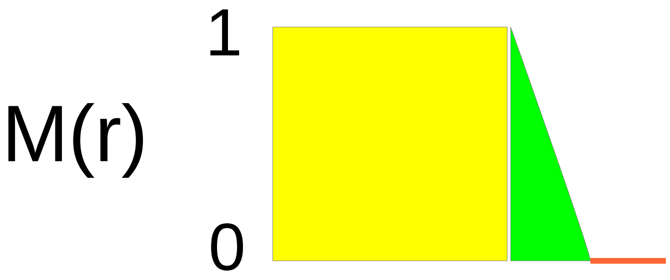
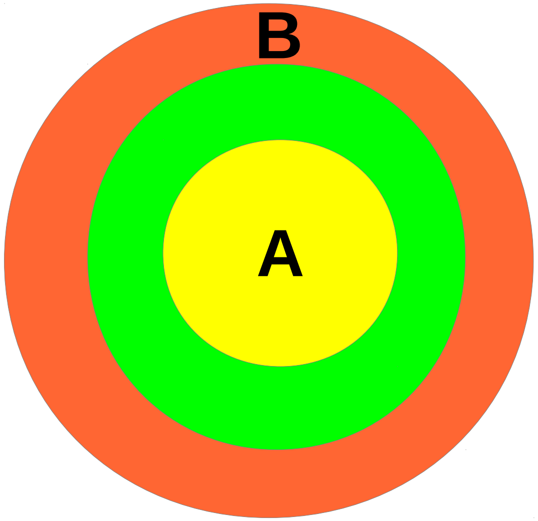




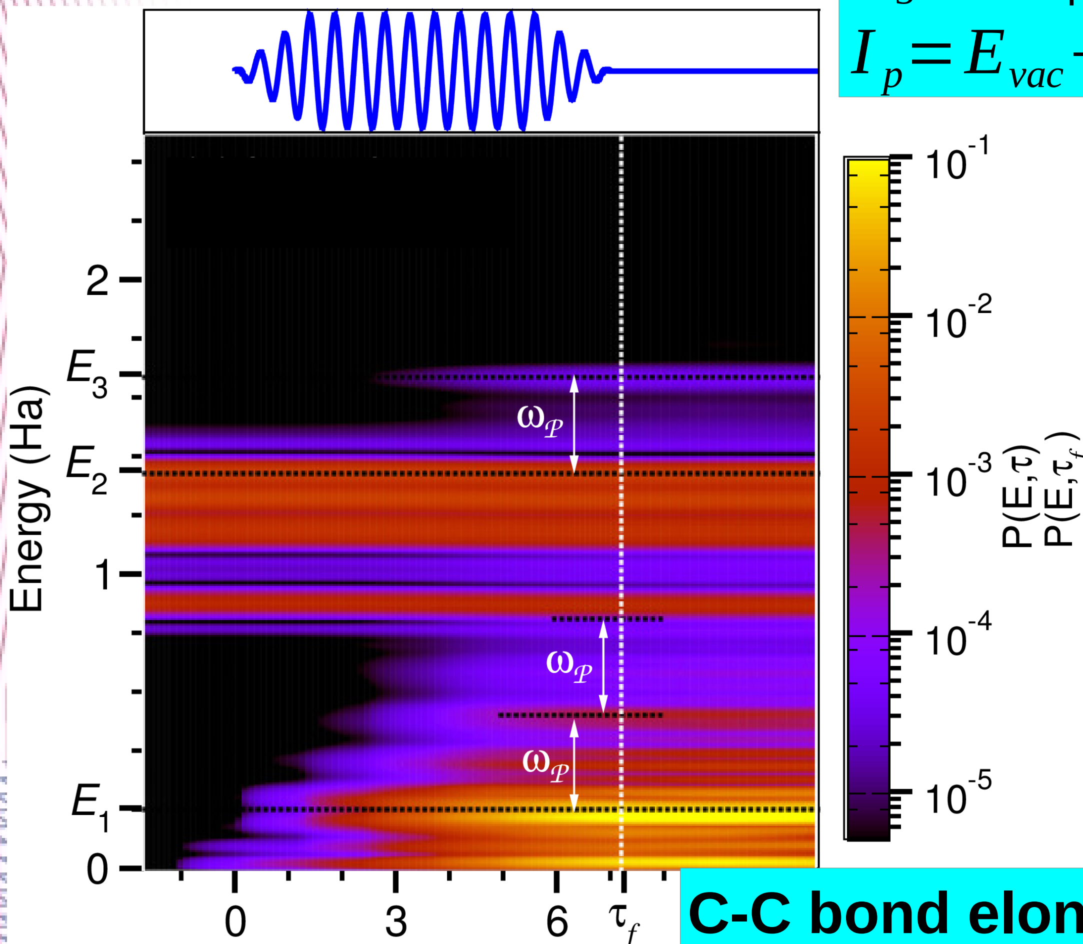
$$\varphi_i(\boldsymbol{r},t)=\varphi_i^A(\boldsymbol{r},t)+\varphi_i^B(\boldsymbol{r},t)$$

$$\mathcal{P}(\boldsymbol{p})_{\lim t\rightarrow\infty}=\sum_{i=1}^{N/2}2\left|\varphi_i^B(\boldsymbol{p},t)\right|^2$$

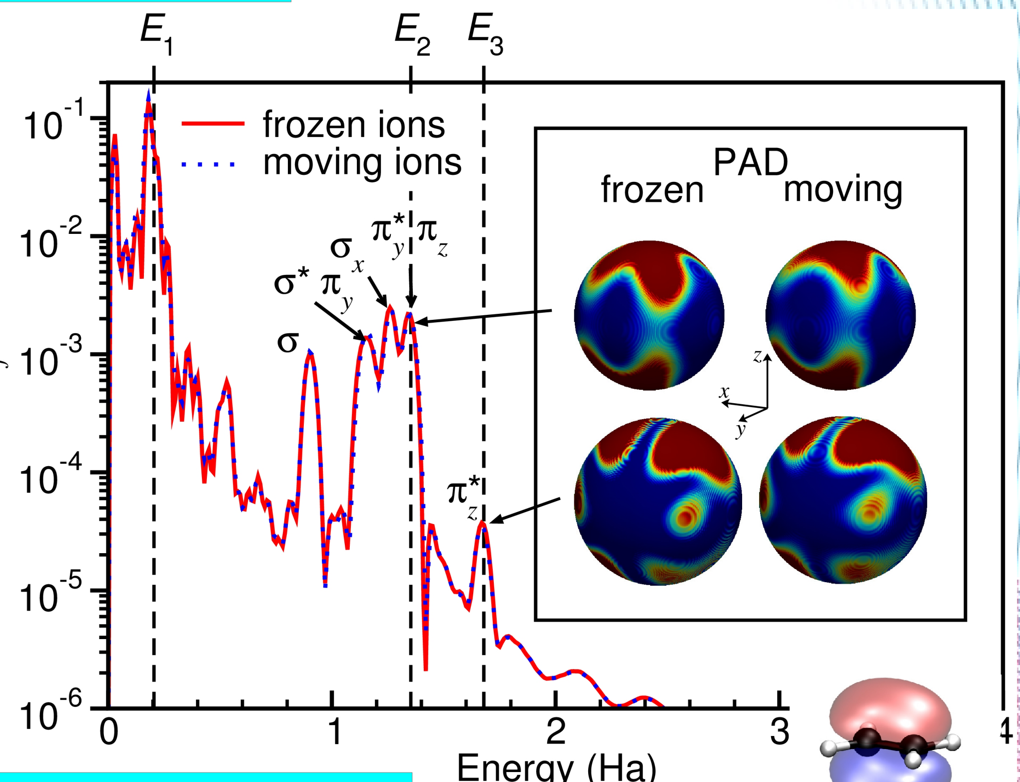
Pump/Probe

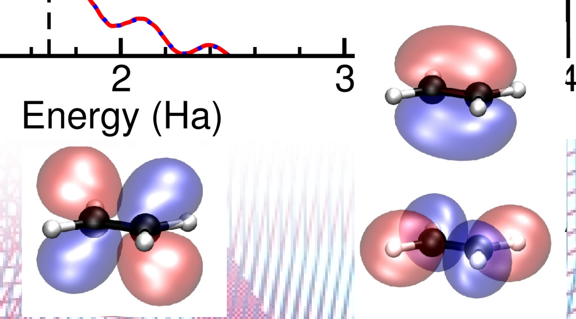
$$E_1 = 2\hbar\omega_{\mathcal{P}} - I_p$$
$$E_2 = \hbar\omega_p - I_p$$
$$E_3 = \hbar\omega_{\mathcal{P}} + \hbar\omega_p - I_p$$
$$I_p = E_{vac} - \varepsilon_{HOMO}$$

TRPES P(E,τ)



PES/PAD P(E,τ_f)



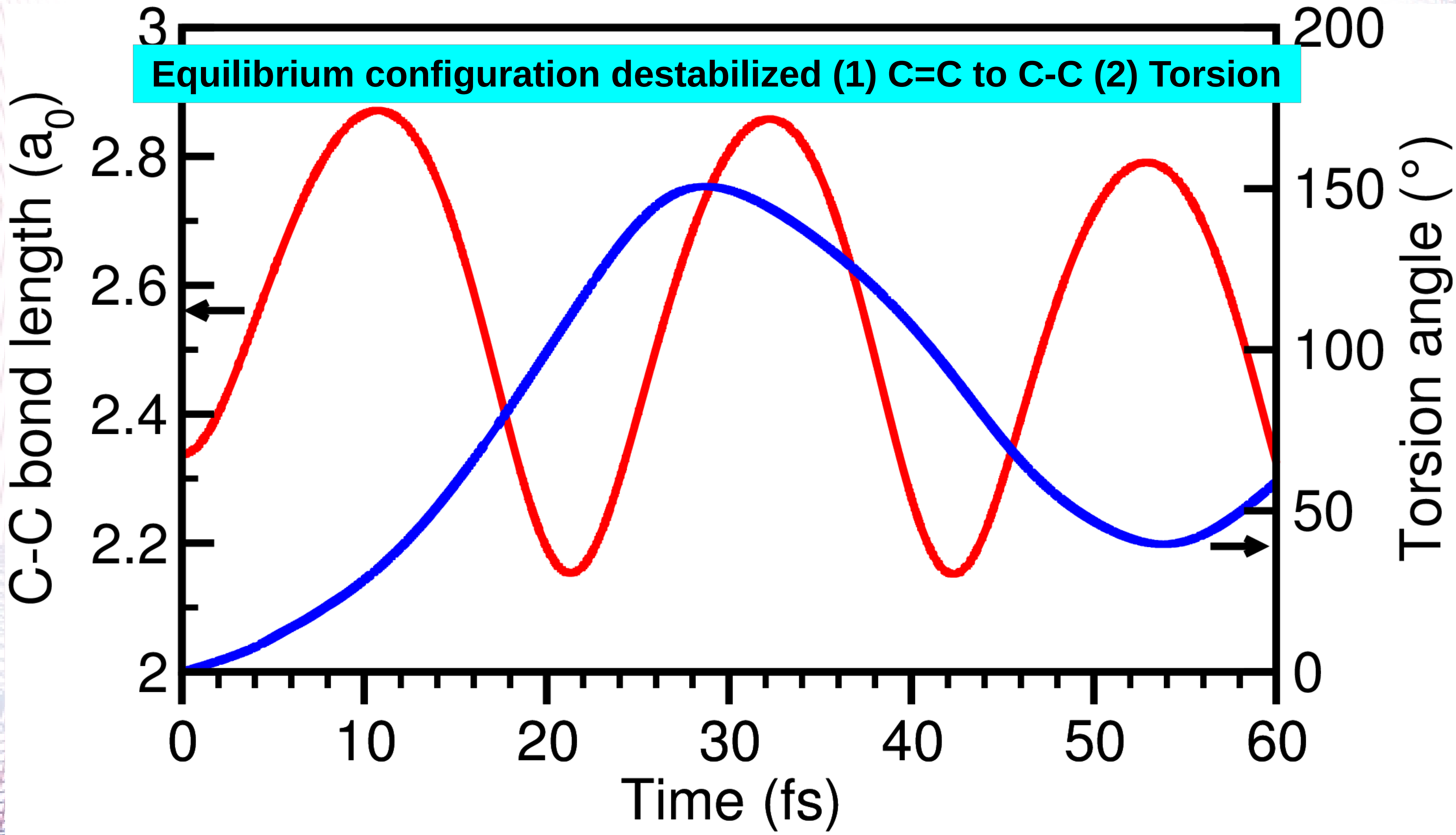


C-C bond elongates 0.03 a.u.
No torsion

U. De Giovannini et al, Chemphyschem 14, 1363 - 1376 (2013)

Artificial Pump/Probe

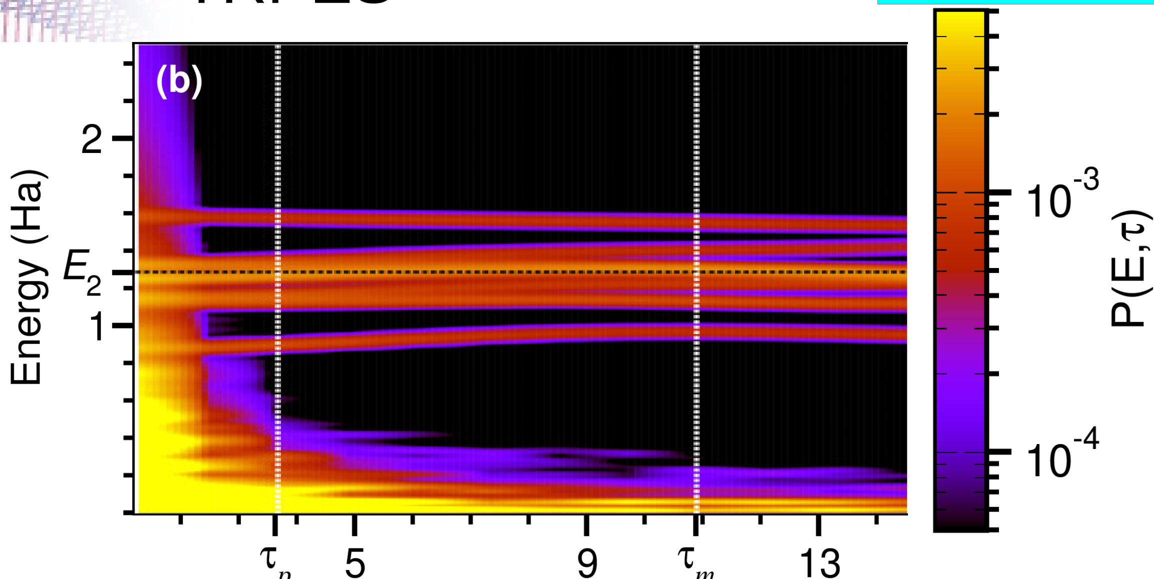
Artificial pump HOMO→LUMO half-occupied during time evolution

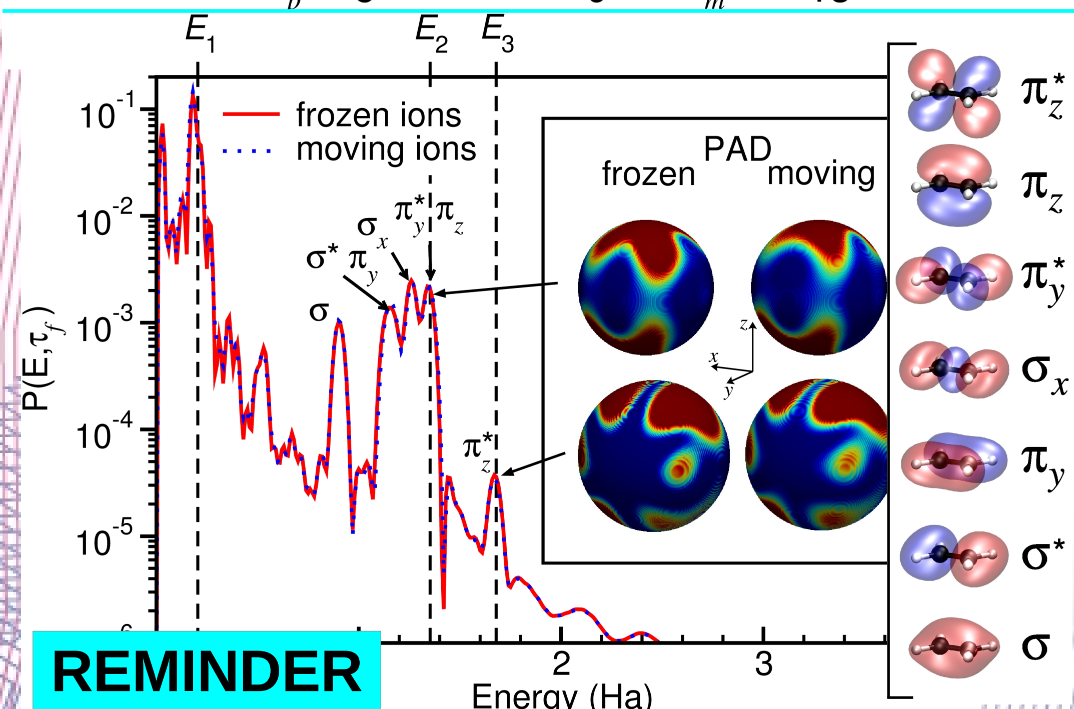


Artificial Pump/Probe

$$E_2 = \hbar\omega_p - I_p$$

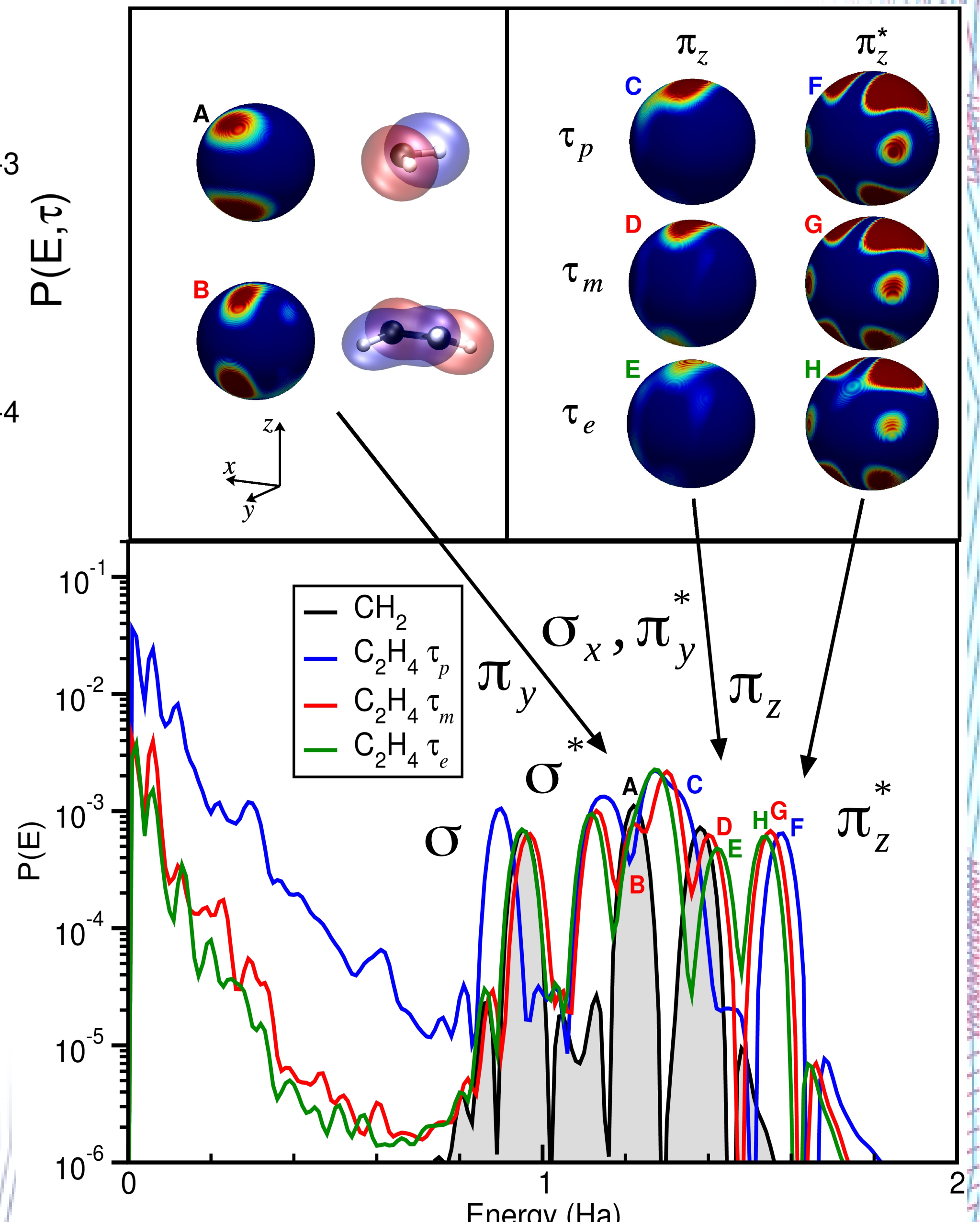
TRPES





REMINDER

PES/PAD



Conclusions

- Nuclear motion pump → occupation π_z^*
- Understood in terms of PADs and orbitals
- See photochemical dissociation
    - Elongation
    - Torsion

Ionisation of atoms within TDDFT

Nuclear effects on the TRPES

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Extra slides

Yields: LOPT vs TDDFT

LOPT		TDDFT
Individual	$P^{+n}(t)$	$P^{0}(t)=N_1(t)\ldots N_8(t)$ $P^{1}(t)=\sum_{n=1}^{N} N_1(t)\ldots \bar{N}_n(t)\ldots N_8(t)$ **ASSUME Ψ_{KS} GOOD REPRESENTATION Ψ_{MB}**
Total	$N_{esc}=\sum_{n=1}^{N_0} n P^{+n}(t)$	$N_{esc}(t)=N_0-\int_{V_{inside}} dr\, n(r,t)=N_0-\sum_{n=1}^{N_0} N_n$ $N_{esc}(t)=\sum_{n=1}^{N_0} n P^{+n}(t)=\sum_{n=1}^{N_0} \bar{N}_n$

DFT functionals

$$V_{xc}=\frac{\partial E_{xc}}{\partial n[\mathbf{r},t]}$$

- LDA

$$E_x^{LDA}[n]=-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n[r]^{4/3}d^3r$$

$$E_c^{LDA}[r_s,\zeta]=\varepsilon_c(r_s,0)+\alpha_c(r_s)\frac{f(\zeta)}{f''(\zeta)}(1-\zeta^4)+[\varepsilon_c(r_s,1)-\varepsilon_c(r_s,0)]f(\zeta)\zeta^4 \longrightarrow \text{fitted}$$

- PBE (GGA)

$$E_x^{GGA}[n]=\int d^3r\, n(r)\varepsilon_x[n](1+\kappa-\frac{\kappa^2}{1+\mu s^2}) \longrightarrow s=\frac{|\nabla n|}{2k_F n}$$

$$E_c^{GGA}[n]=\int d^3r\, n(r)[\varepsilon_c[n]+\frac{e^2\gamma\phi}{a_0}\ln[1+\frac{\beta}{\gamma}t^2(\frac{1+At^2}{1+At^2+A^2t^4})]] \longrightarrow t=\frac{|\nabla n|}{2\phi k_s n}$$

- LB94 (GGA)

$$E_c^{LB94}[r_s,\zeta]=E_c^{LDA}[r_s,\zeta] \quad V_x^{LB94}=V_x^{LDA}[n]-\beta n^{1/3}[r]\frac{x^2}{1+3\beta x\sinh^{-1}(x)} \longrightarrow x=\frac{|\nabla n|}{n^{4/3}}$$

- CXD-LDA

$$V_{xc}^{CXDLDA}=V_{xc}^{LDA}[n]-V_{xc}[n_{xc}] \longrightarrow n_{xc}=-\frac{\nabla^2 V_{xc}}{4\pi}+\frac{\Delta n_{xc}}{q_{xc}(\eta)}$$

$$\begin{cases}\Delta n_{xc}=0 \; if\; n(r)\geqslant\eta \\ \Delta n_{xc}=\frac{\Delta^2 V_{xc}}{4\pi}\; if\; n(r)<\eta\end{cases}$$

$$q_{xc}(\eta)=\int -\frac{\Delta^2 V_{xc}}{4\pi}+\Delta n_{xc}$$

Theory: LOPT neon

- Rate equations for each species (0 → 8)

$$\frac{dN_0}{dt} = -\sigma_{0,1} F N_0 - \sigma_{0,7} F^8 N_0 - \sigma_{0,8} F^{11} N_0 - \sum_{n=2}^{6} \sigma_{0,n} F^n N_0 ; \quad \frac{dN_1}{dt} = \sigma_{0,1} F N_0 - \sigma_{1,2} F N_1$$

$$\frac{dN_2}{dt} = \sigma_{0,2} F^2 N_0 + \sigma_{1,2} F N_1 - \sigma_{2,3} F N_2 ; \quad \frac{dN_3}{dt} = \sigma_{0,3} F^3 N_0 + \sigma_{2,3} F N_2 - \sigma_{3,4} F^2 N_3$$

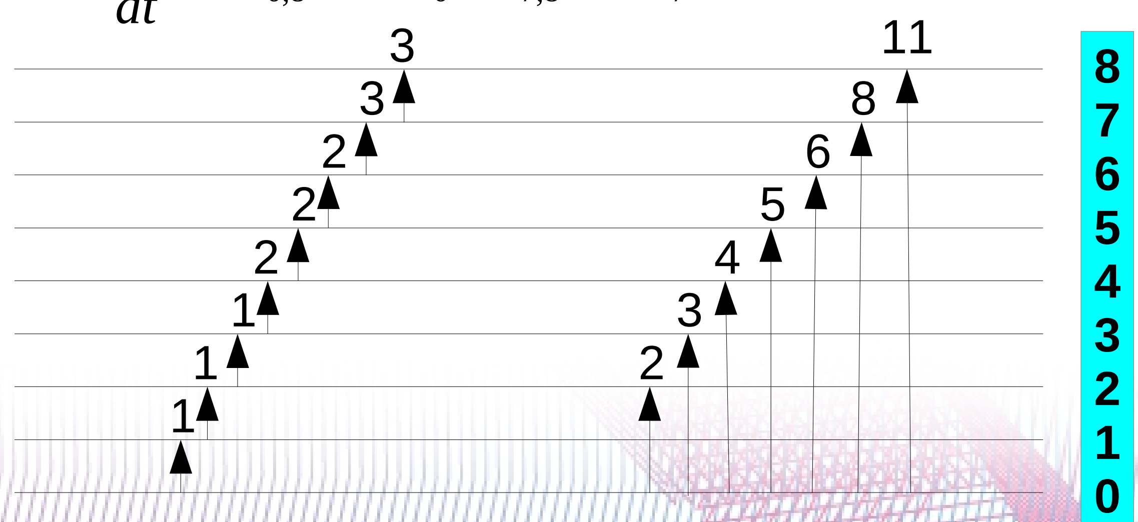
$$\frac{dN_4}{dt} = \sigma_{0,4} F^4 N_0 + \sigma_{3,4} F^2 N_3 - \sigma_{4,5} F^2 N_4 ; \quad \frac{dN_5}{dt} = \sigma_{0,5} F^5 N_0 + \sigma_{4,5} F^2 N_4 - \sigma_{5,6} F^2 N_5$$

$$\frac{dN_6}{dt} = \sigma_{0,6} F^6 N_0 + \sigma_{5,6} F^2 N_5 - \sigma_{6,7} F^3 N_6 ; \quad \frac{dN_7}{dt} = \sigma_{0,7} F^8 N_0 + \sigma_{6,7} F^3 N_6 - \sigma_{7,8} F^3 N_7$$

$$\frac{dN_8}{dt} = \sigma_{0,8} F^{11} N_0 + \sigma_{7,8} F^3 N_7$$

Cross sections σ
Photon flux F

Dominant sequential and direct photoionisation processes



Theory: LOPT argon

- Rate equations for each species (0 → 8)

$$\frac{dN_0}{dt} = -\sigma_{0,1} F N_0 ; \frac{dN_1}{dt} = \sigma_{0,1} F N_0 - \sigma_{1,2} F N_1$$

$$\frac{dN_2}{dt} = \sigma_{1,2} F N_1 - \sigma_{2,3} F N_2 ; \frac{dN_3}{dt} = \sigma_{2,3} F N_2 - \sigma_{3,4} F N_3$$

$$\frac{dN_4}{dt} = \sigma_{3,4} F N_3 - \sigma_{4,5} F N_4 ; \frac{dN_5}{dt} = \sigma_{4,5} F N_4 - \sigma_{5,6} F N_5$$

$$\frac{dN_6}{dt} = \sigma_{5,6} F N_5 - \sigma_{6,7} F^2 N_6 ; \frac{dN_7}{dt} = \sigma_{6,7} F^2 N_6 - \sigma_{7,8} F^2 N_7$$

$$\frac{dN_8}{dt} = \sigma_{7,8} F^2 N_7 + \sigma_{6,8} F^3 N_6$$

2e- (correlation) up to Ar^{+6}
part ionised specie excited 3d
Ar^{+6} excited 3d large effect
Ar^{+7} and Ar^{+8} ions negligible