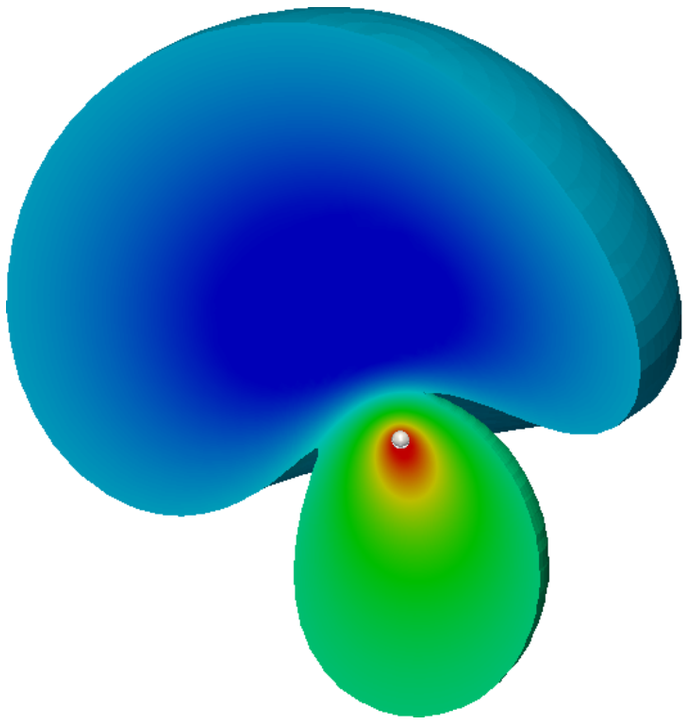
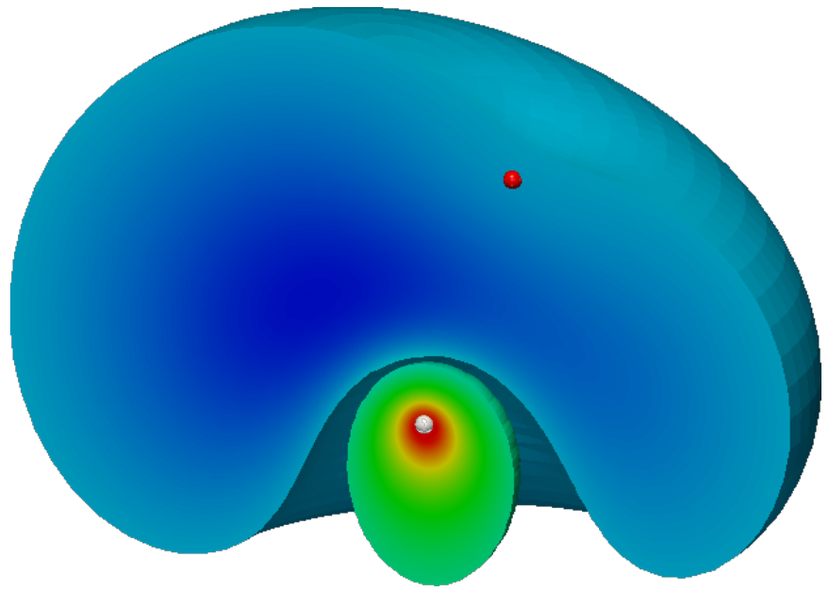
New TDCC programs for atomic and molecular ionization



2018

Oct 29, Daejon, Korea



Luca Argenti

University of Central Florida, Orlando, FL, U.S.A.

UCF

Outline

- Motivation for *ab initio* many-body TDSE
- New Stock atomic code
- XCHEM: molecular ionization

Acknowledgments

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C.-T. Liao
N. Harkema

Columbus

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T. Scarborough
T. Gorman

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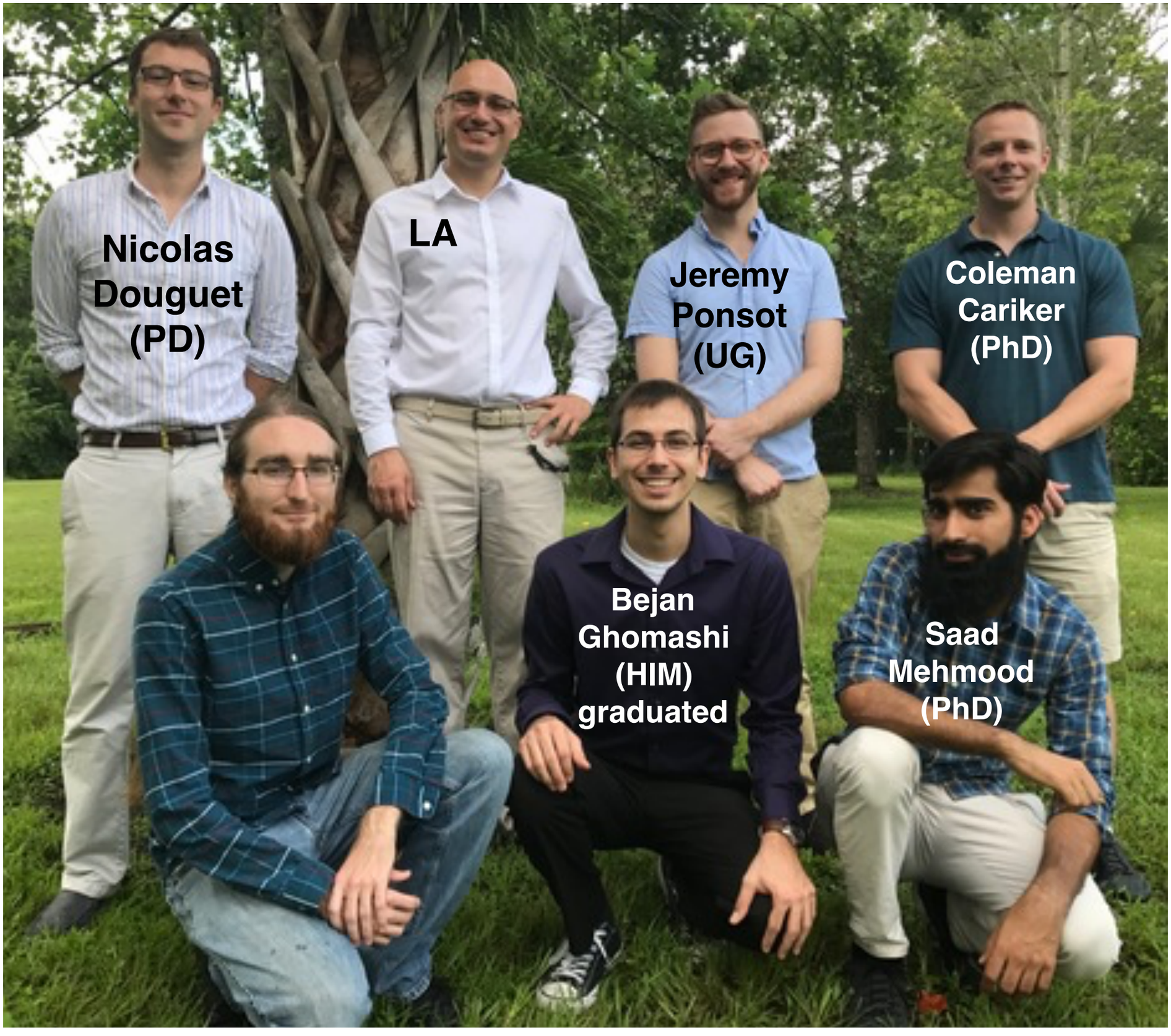
A. Palacios

Carlos Marante

M. Klinker
J. González-Vazquez
I. Corral

Theoretical Attosecond Spectroscopy @ UCF



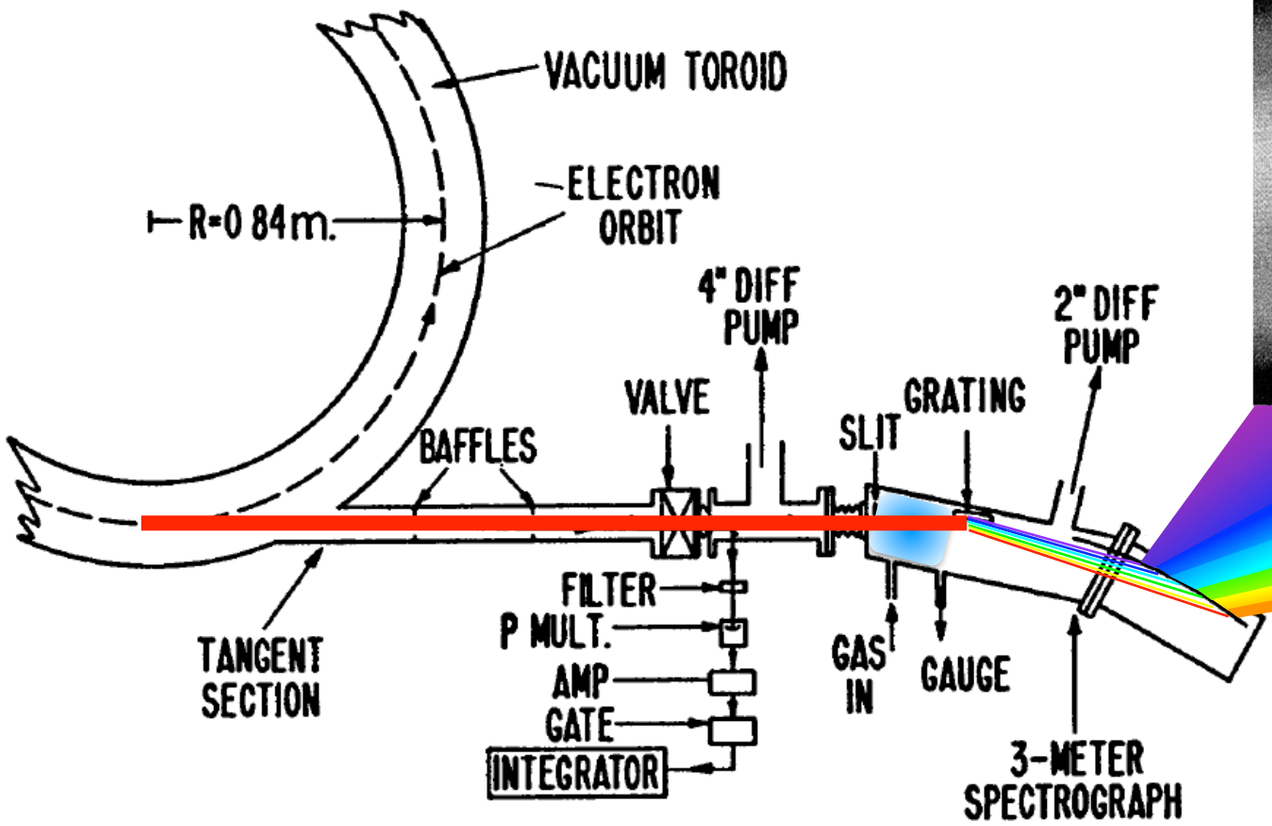
Didarul Ahlam (PhD)

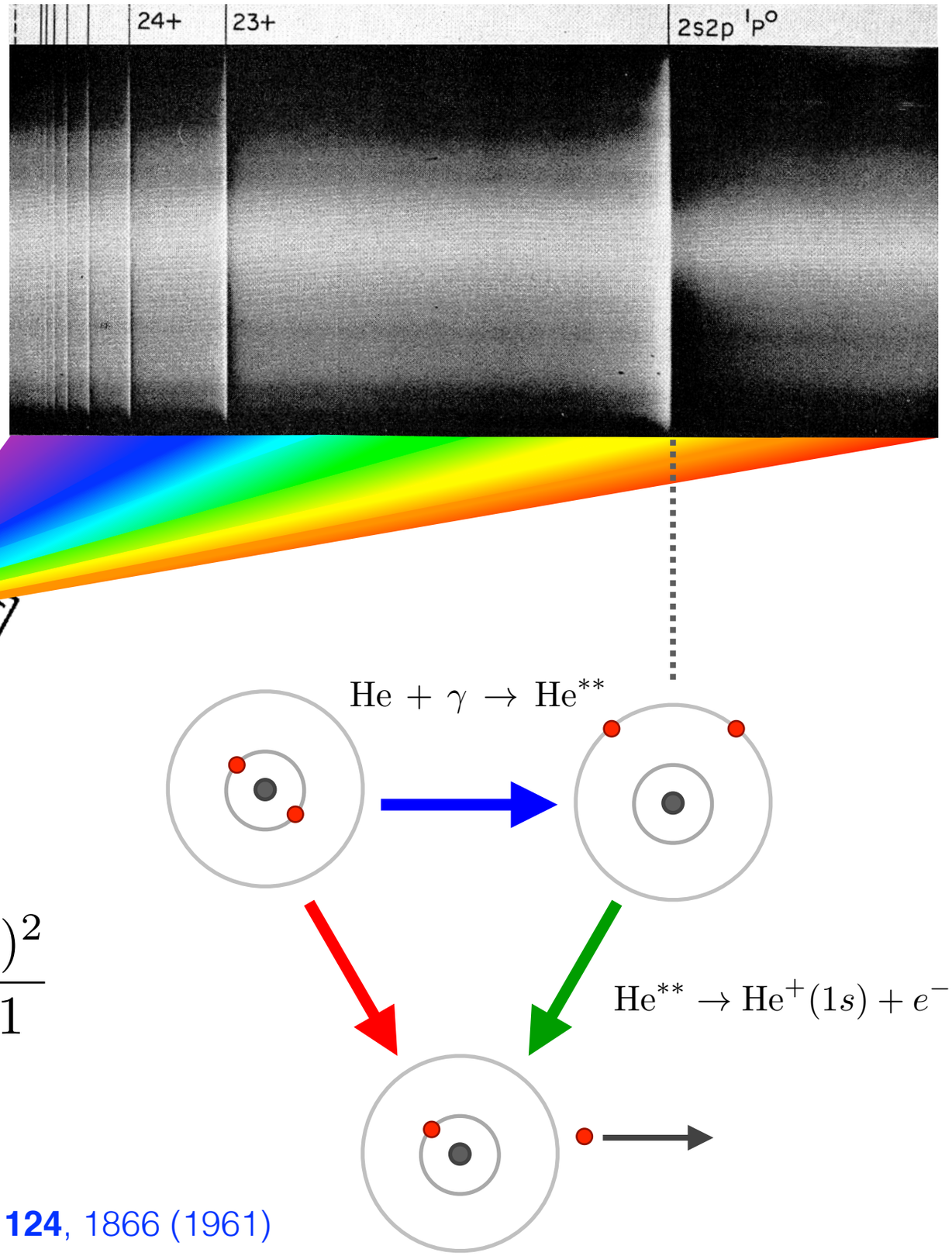
UCF

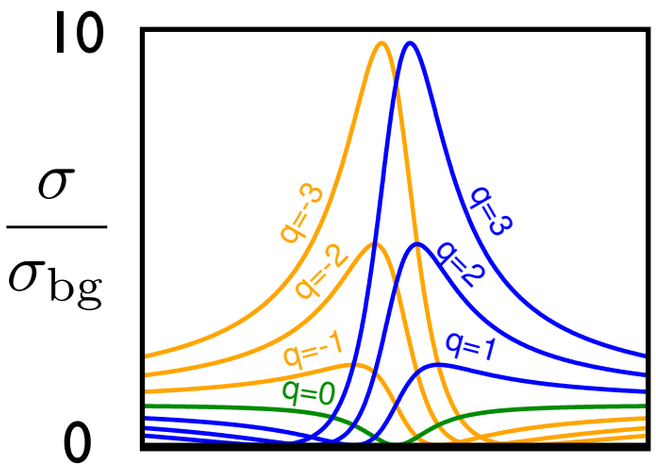
NSF

Electronic Continuum has structure

$$\mathrm{He} + \gamma \rightarrow \mathrm{He}^{+}(1s) + e^{-}$$







$$\sigma = \sigma_{\mathrm{bg}} \frac{(\epsilon + q)^2}{\epsilon^2 + 1}$$

$$\epsilon_E = \frac{E - \bar{E}_a}{\Gamma/2}$$

U Fano, Phys. Rev. **124**, 1866 (1961)

E

SCATTERING STATES

$|1s\,\epsilon\ell\rangle$

$|2s\,np\rangle + |2p\,ns\rangle$

Thr

BOUND STATES

$|1s2\ell\rangle$

$|1s^2\rangle$

E

SCATTERING STATES

$|1s\,\epsilon\ell\rangle$

$|2s\,np\rangle + |2p\,ns\rangle$

Thr

BOUND STATES

$|1s2\ell\rangle$

$|1s^2\rangle$

E

SCATTERING STATES

$|1s\,\epsilon\ell\rangle$

$|2s\,np\rangle + |2p\,ns\rangle$

Thr

BOUND STATES

DIRECT IONIZATION

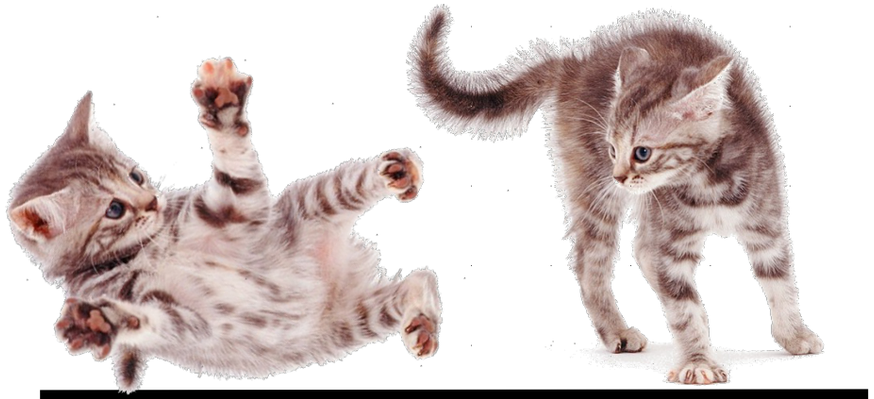
$|1s2\ell\rangle$

$|1s^2\rangle$

E

SCATTERING STATES

$|1s\,\epsilon\ell\rangle$



$|2s\,np\rangle + |2p\,ns\rangle$

Thr

BOUND STATES

$|1s2\ell\rangle$

$|1s^2\rangle$

DOUBLE EXCITATION

E

SCATTERING STATES

$|1s\,\epsilon\ell\rangle$

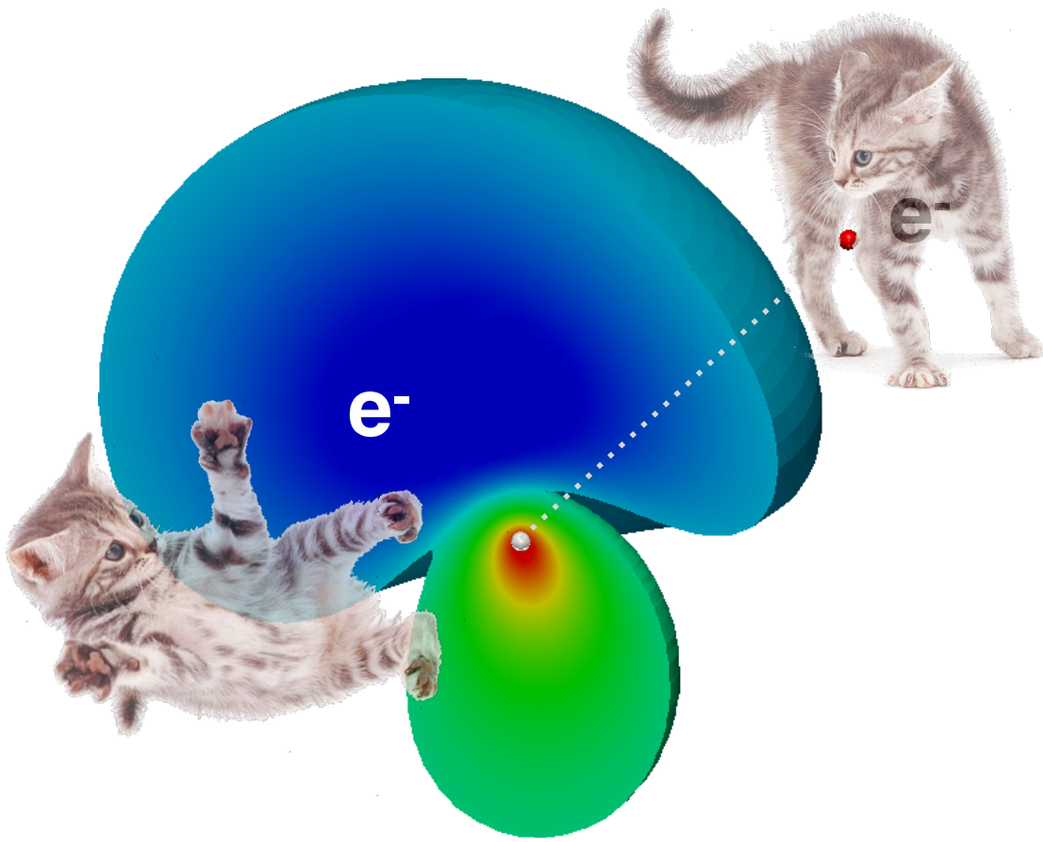
$|2s\,np\rangle + |2p\,ns\rangle$

Thr

BOUND STATES

$|1s2\ell\rangle$

$|1s^2\rangle$



E

SCATTERING STATES

$|1s\,\epsilon\ell\rangle$

AUGER DECAY

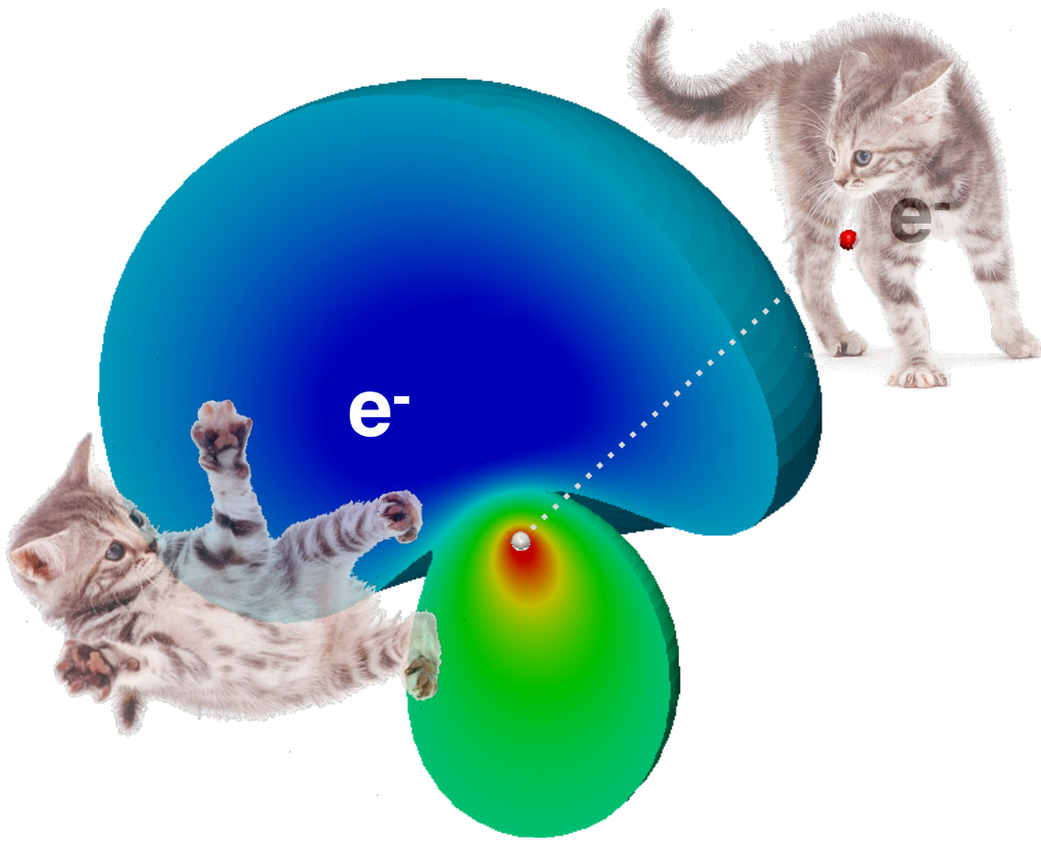
$|2s\,np\rangle + |2p\,ns\rangle$

Thr

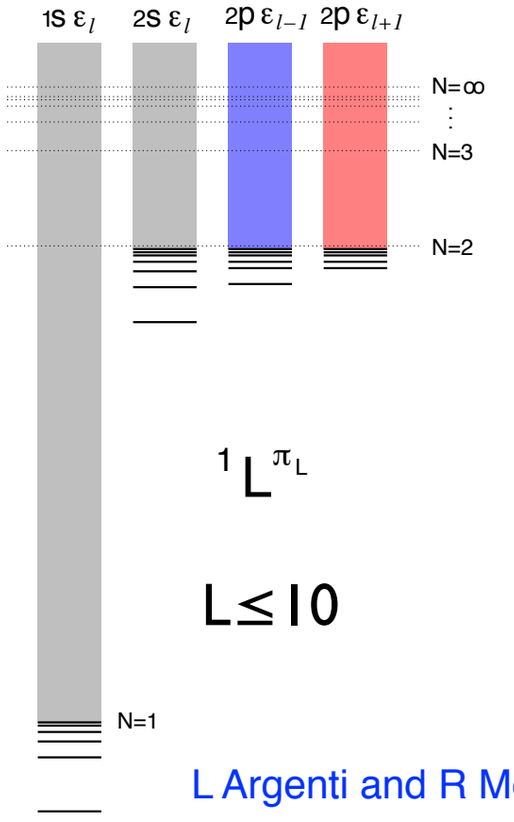
BOUND STATES

$|1s2\ell\rangle$

$|1s^2\rangle$



Basis



B-splines

Close coupling

Full-CI loc. channel

$^1L^{\pi_L}$

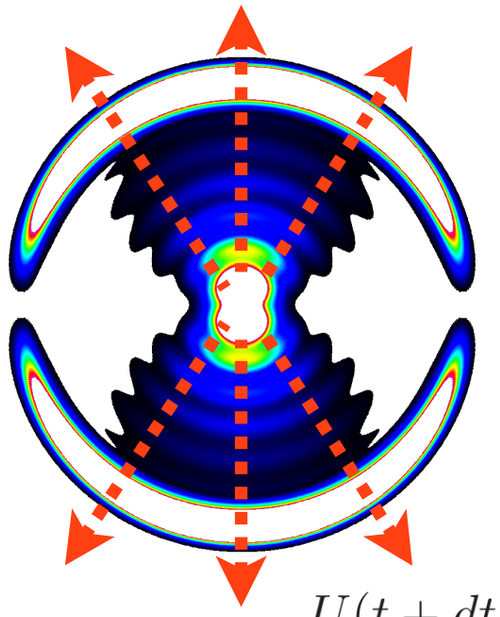
$L \leq 10$

R_{max} ~ 400 au (ATAS)

R_{max} ~1200 au (APES)

L Argenti and R Moccia, J. Phys. B **39**, 2773 (2006)

TDSE



$$\Psi(t+dt) = U(t+dt,t)\,\Psi(t)$$

SPLIT

Spectral resolution

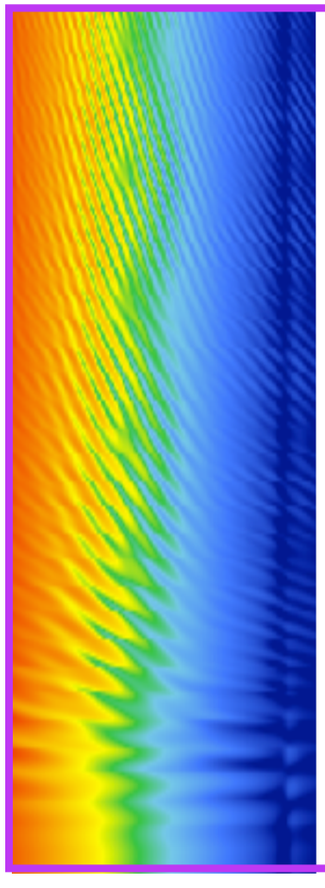
Magnus I + Krylov

$$U(t+dt,t) \simeq e^{-i\,dt\,V}\; e^{-i\,dt\,H(t+dt/2)}$$

$$H(t) = H_o + \alpha \vec{A}(t)\cdot\vec{P} \;+ \text{CAP}$$

L Argenti and E Lindroth, Phys. Rev. Lett. **105**, 053002 (2010)

Photoelectrons



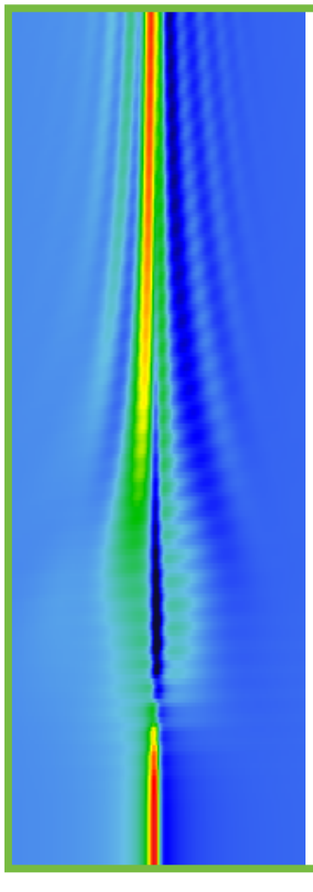
Photoelectron distributions

$$P_\alpha(E,\hat{\Omega}) = \sum_{M_\alpha \Sigma_\alpha \sigma'} \left| \langle \psi^-_{\alpha;E,\hat{\Omega},\sigma'} | \Psi(t) \rangle \right|^2$$

Scattering states from K-matrix method

$$\psi^-_{\alpha E} = \phi_{\alpha E} + G^-(E) H' \psi^-_{\alpha E}$$

Dipolar Response



$$\sigma(\boldsymbol{\omega}, \boldsymbol{t_d}) = \frac{4\pi\omega}{c}\, Im\left[\frac{\tilde{d}(\boldsymbol{\omega};\boldsymbol{t_d})}{\tilde{\mathcal{E}}_{\text{xuv}}(\boldsymbol{\omega};\boldsymbol{t_d})}\right]$$

"Exact" dipole FT

$$\tilde{d}(\omega;t_d) = \tilde{d}_-(\omega;t_d) + \tilde{d}_+(\omega;t_d)$$

NUMERICAL

ANALYTICAL

L Argenti *et al.* arXiv:**1211**.2566 (2012)

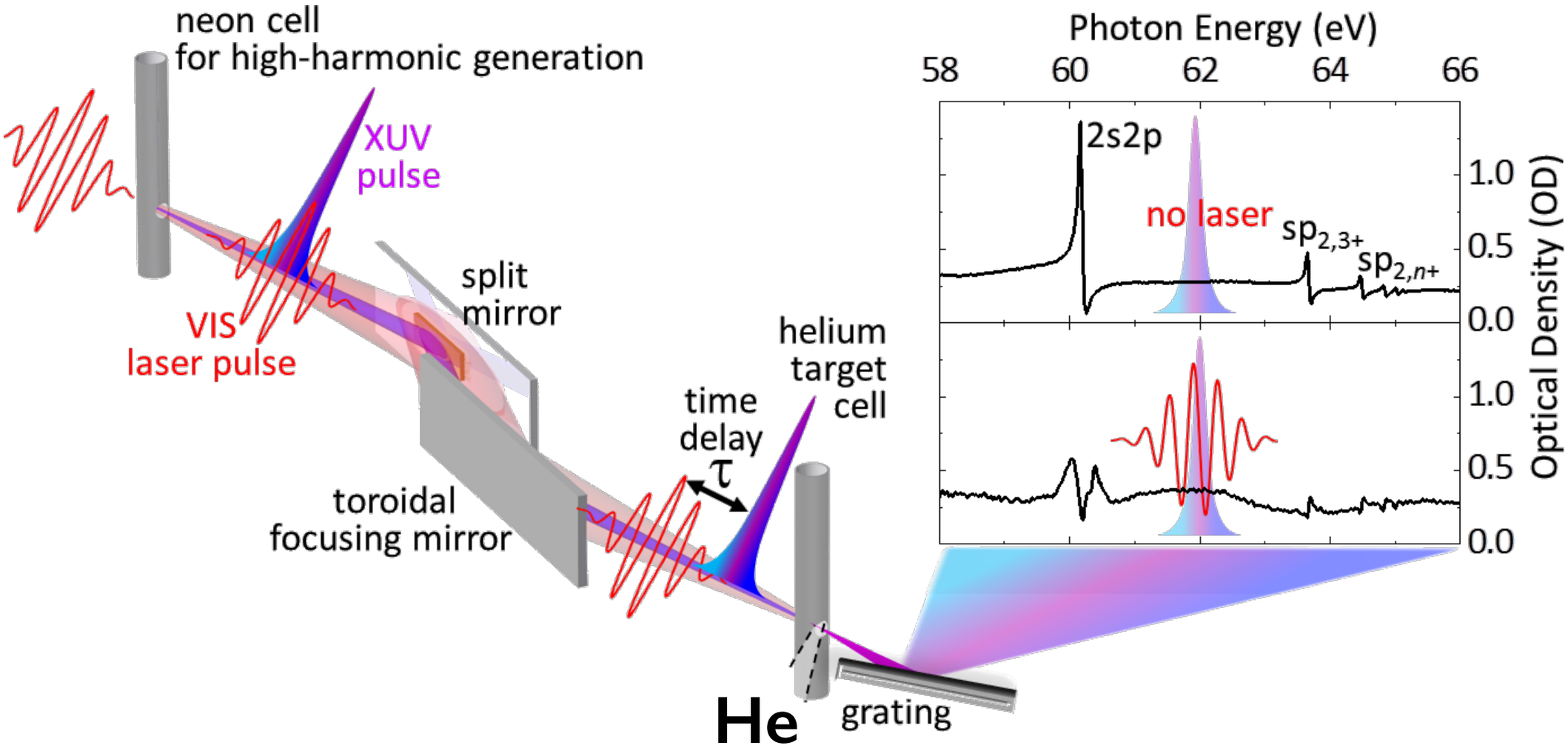
C Ott *et al.* Nature **516**, 374 (2014)

L Argenti *et al.* Phys. Rev. A **91**, 061403 (2015)

Reconstruction and control of a time-dependent two-electron wave packet

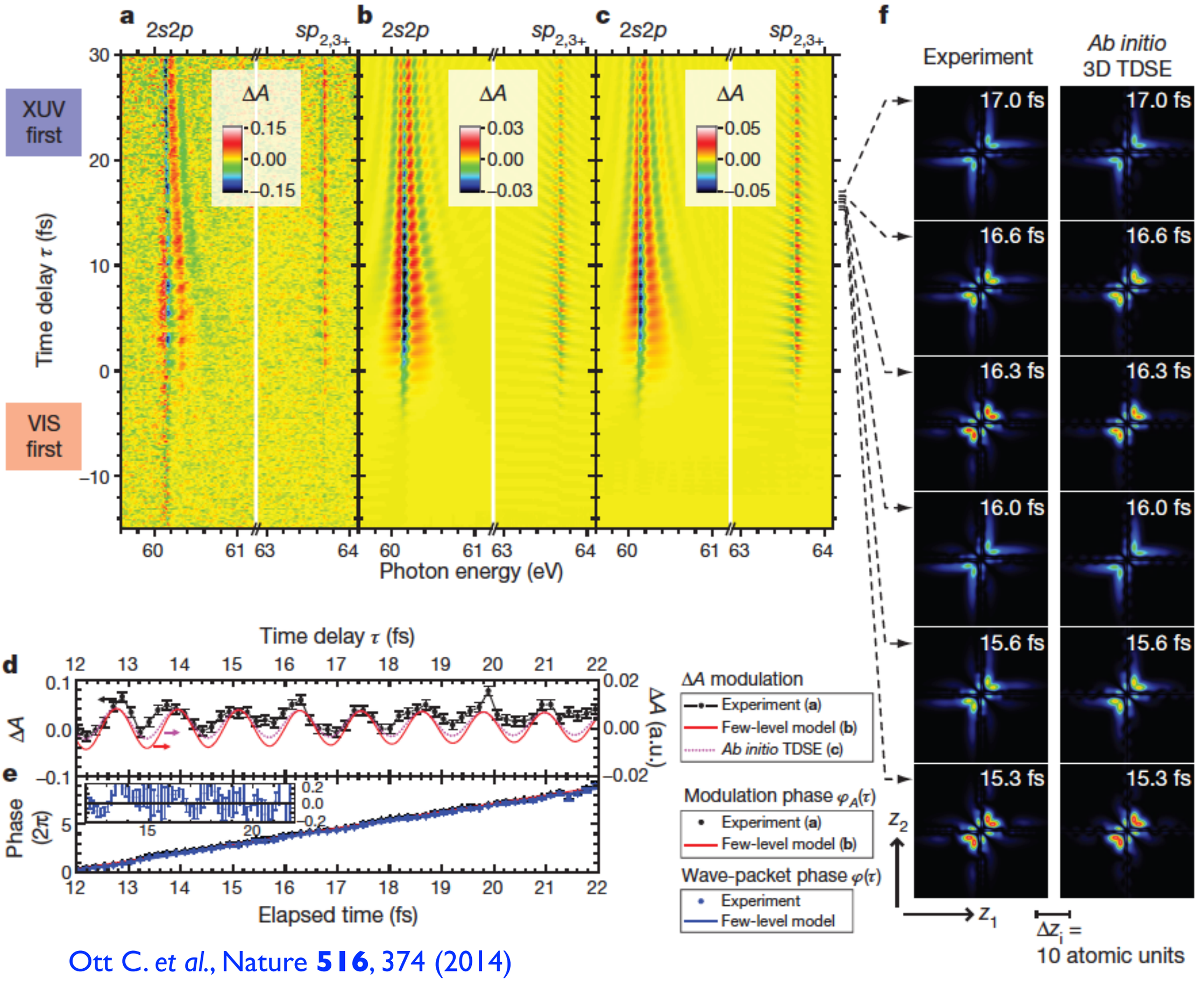
Christian Ott[1]†, Andreas Kaldun[1], Luca Argenti[2], Philipp Raith[1], Kristina Meyer[1], Martin Laux[1], Yizhu Zhang[1], Alexander Blättermann[1], Steffen Hagstotz[1], Thomas Ding[1], Robert Heck[1], Javier Madroñero[3]†, Fernando Martín[2,4] & Thomas Pfeifer[1,5]

374 | NATURE | VOL 516 | 18/25 DECEMBER 2014



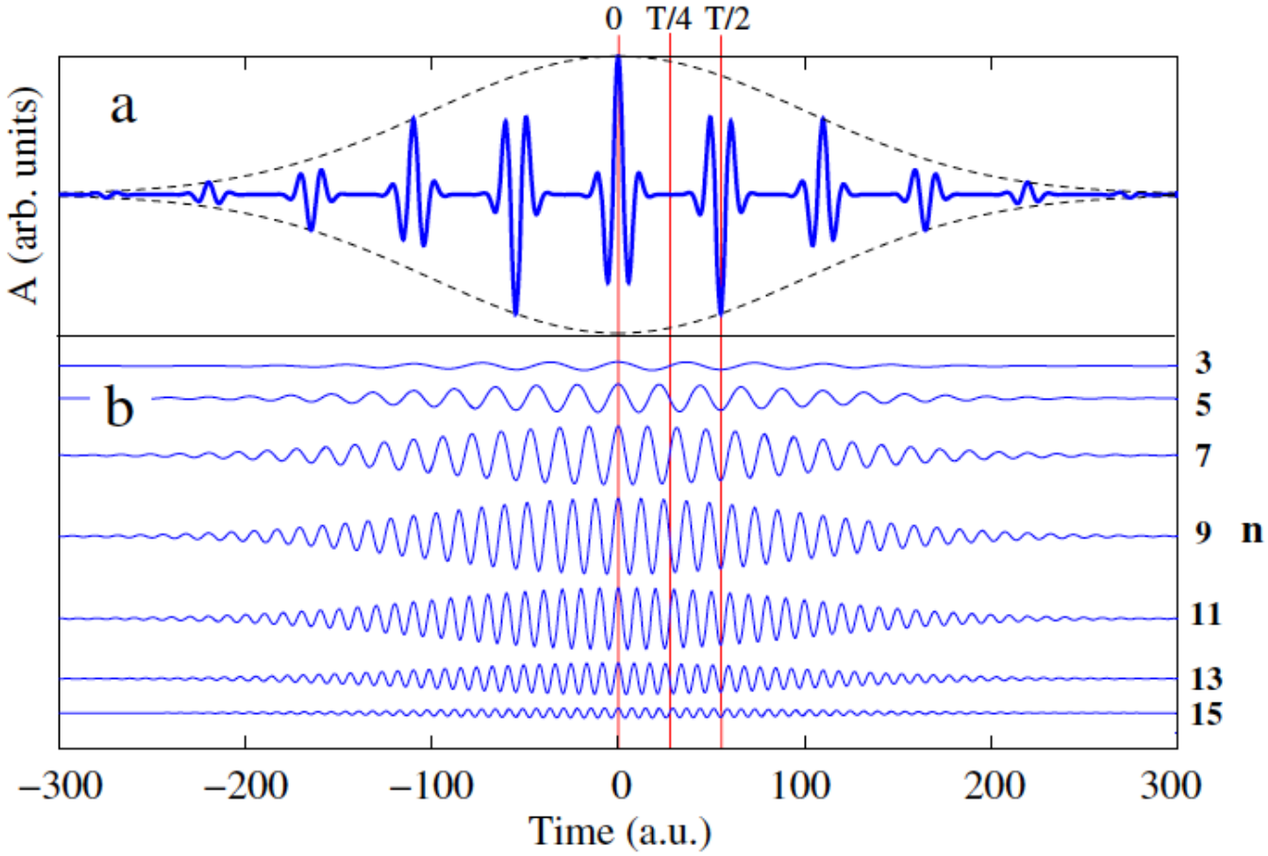
No Laser: measure all frequencies at once, but otherwise it is the same as with synchrotron radiation

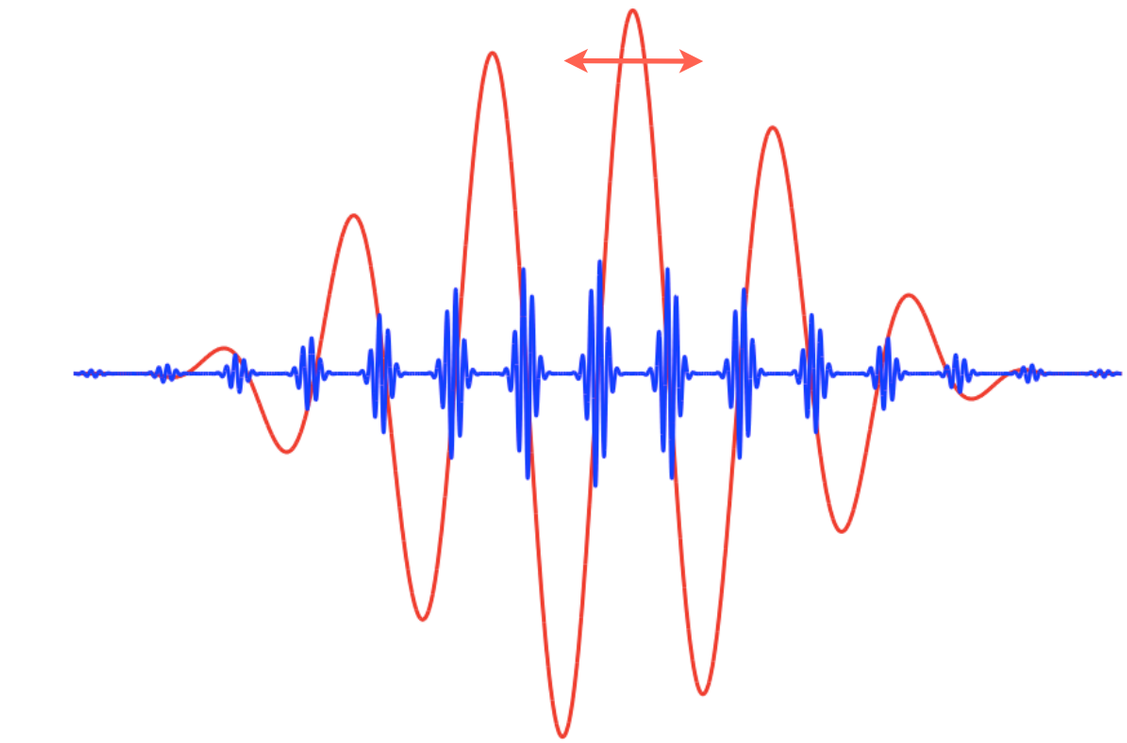
With Laser: strong dependence on time delay; each excitation frequency affects the dipolar response at far-away frequencies



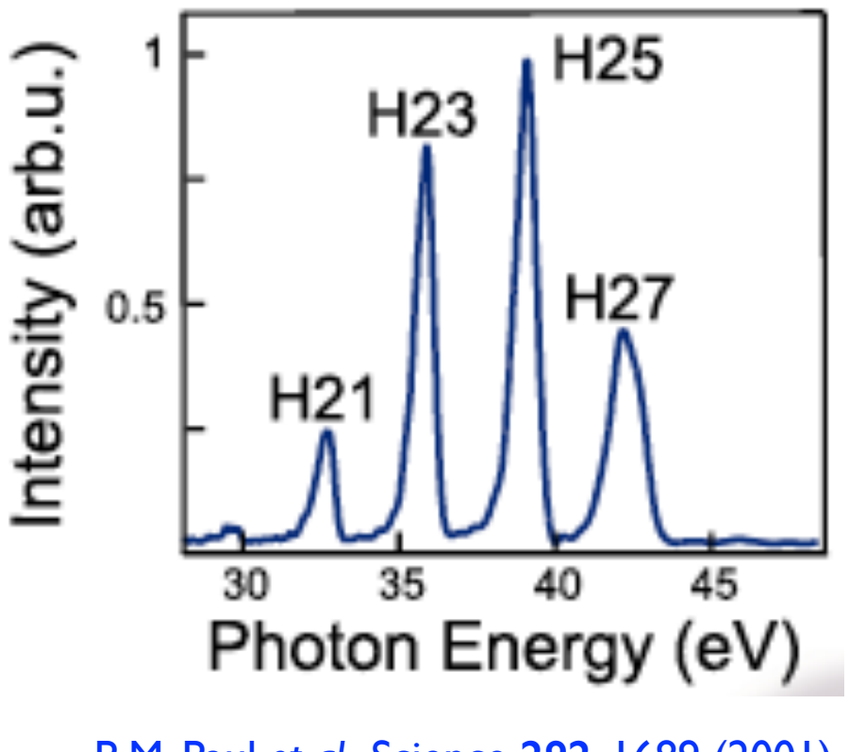
Ott C. *et al.*, Nature **516**, 374 (2014)

RABBIT



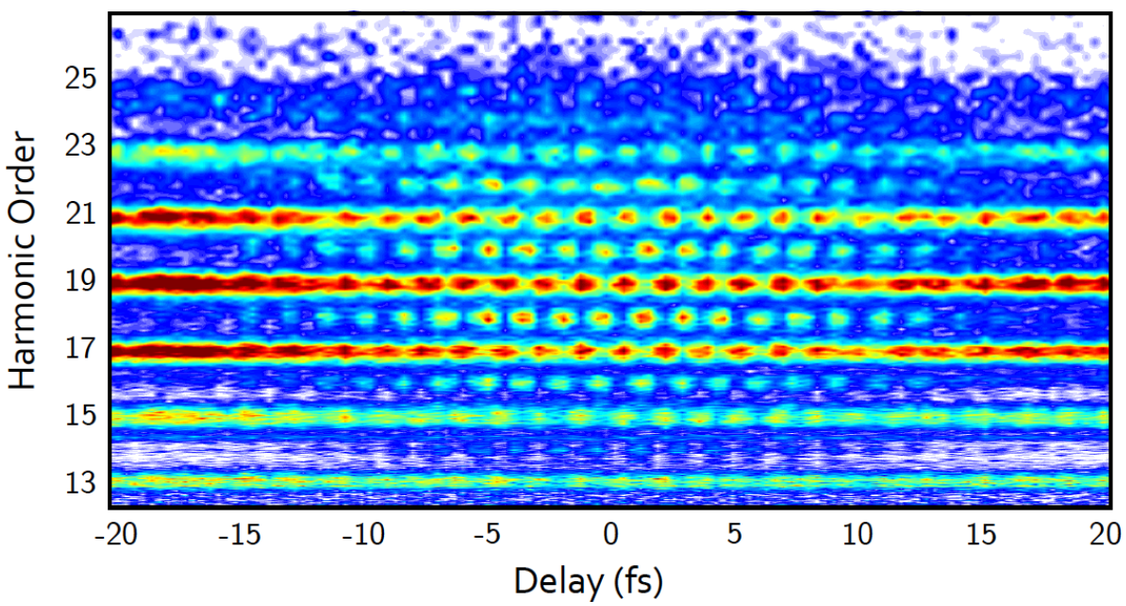


$$A + \Upsilon_{Hn} \longrightarrow A^+ + e^-$$



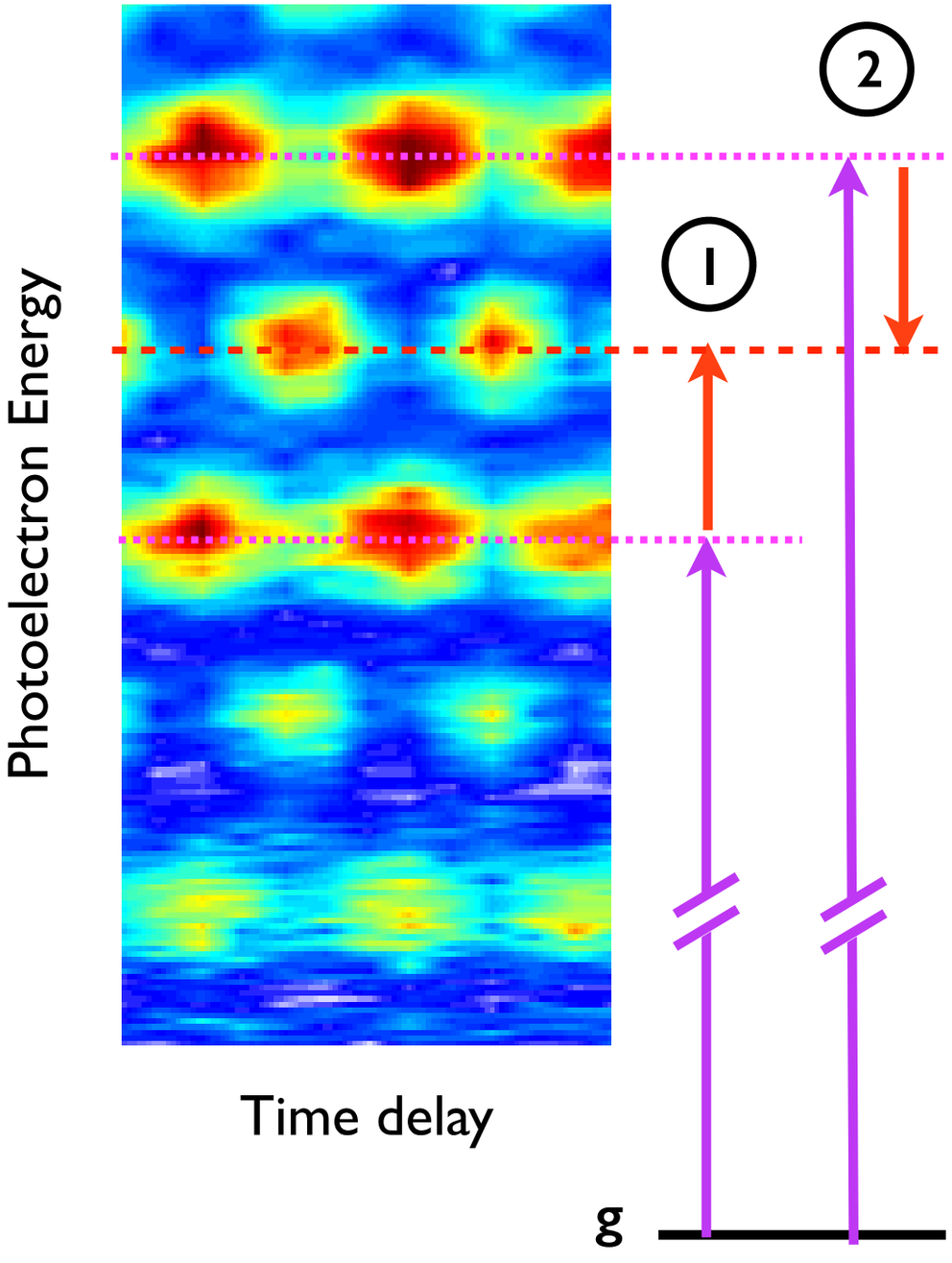
P. M. Paul *et al.*, Science **292**, 1689 (2001)

$$A + \Upsilon_{Hn} \pm \Upsilon_{IR} \longrightarrow A^+ + e^-$$



M. Swoboda, PhD Thesis, Lund (2010)

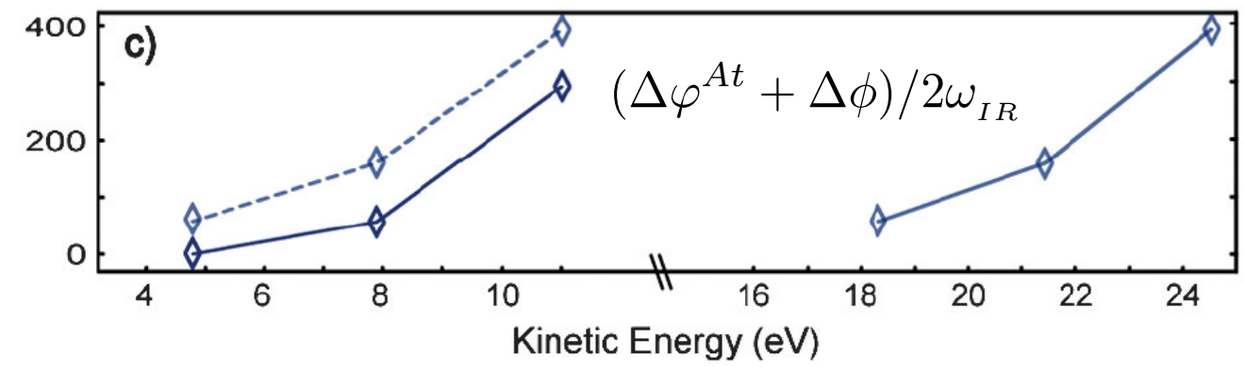
RABBIT's sense for the phase

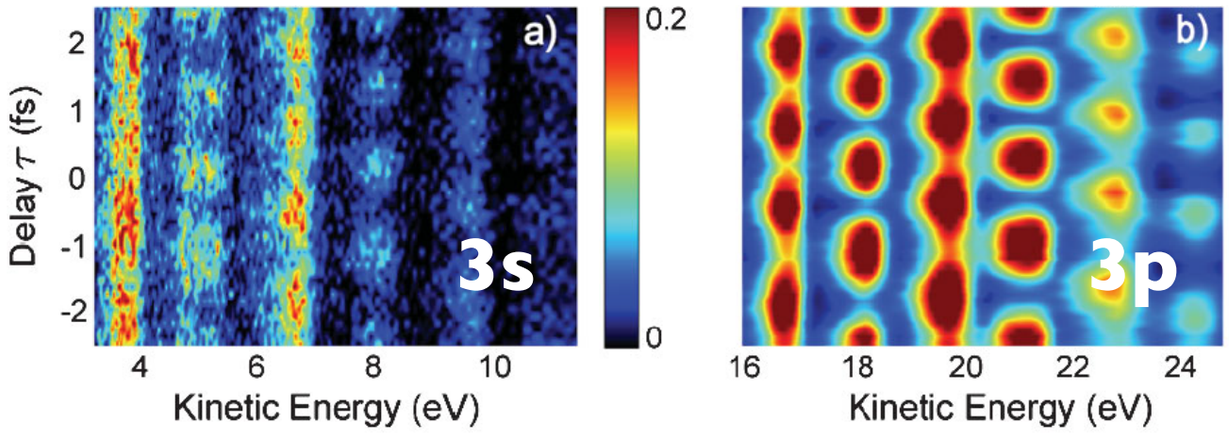


$$\Delta W^{(2)}_{2n\omega} \propto \cos\left(2\,\omega_{\mathrm{IR}}\tau - \Delta\phi_{2n} - \Delta\varphi^{At}_{2n} \right)$$

$$\Delta\phi_{2n} \equiv \phi_{2n+1} - \phi_{2n-1}$$ **Pulse**

$$\Delta\varphi^{\mathrm{At}}_{2n} = \varphi^{\mathrm{At}}_{2n+1} - \varphi^{\mathrm{At}}_{2n-1}$$ **Atom**





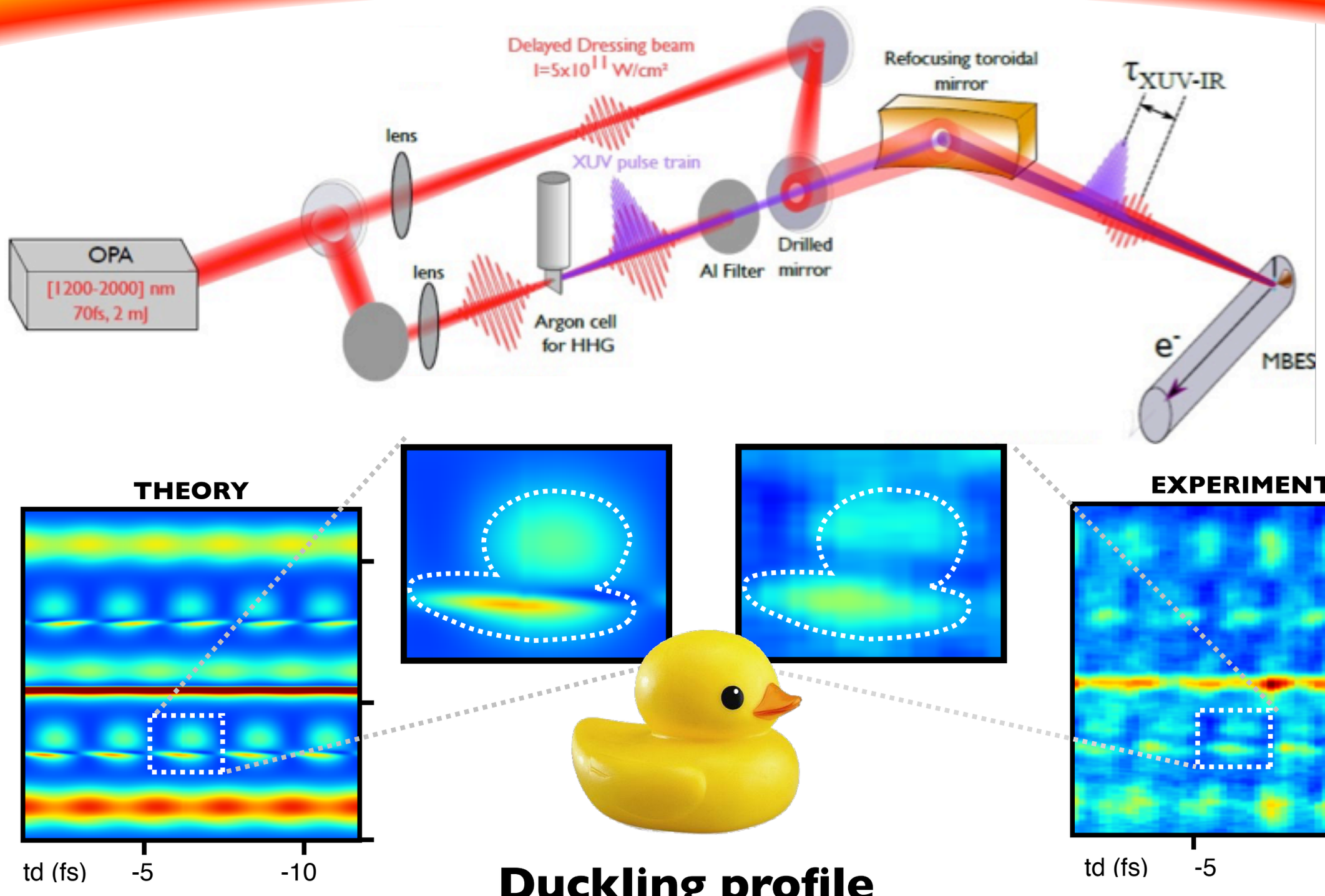
A + Υ_{Hn} ± Υ_{IR} ⟶ A^+ + e^-

M. Swoboda, PhD Thesis, Lund (2010)

Ar + Υ_{Hn} ± Υ_{IR} ⟶ $Ar^+(3l^{-1})$ + e^-

K. Klünder *et al.*, PRL **106**, 143002 (2011)

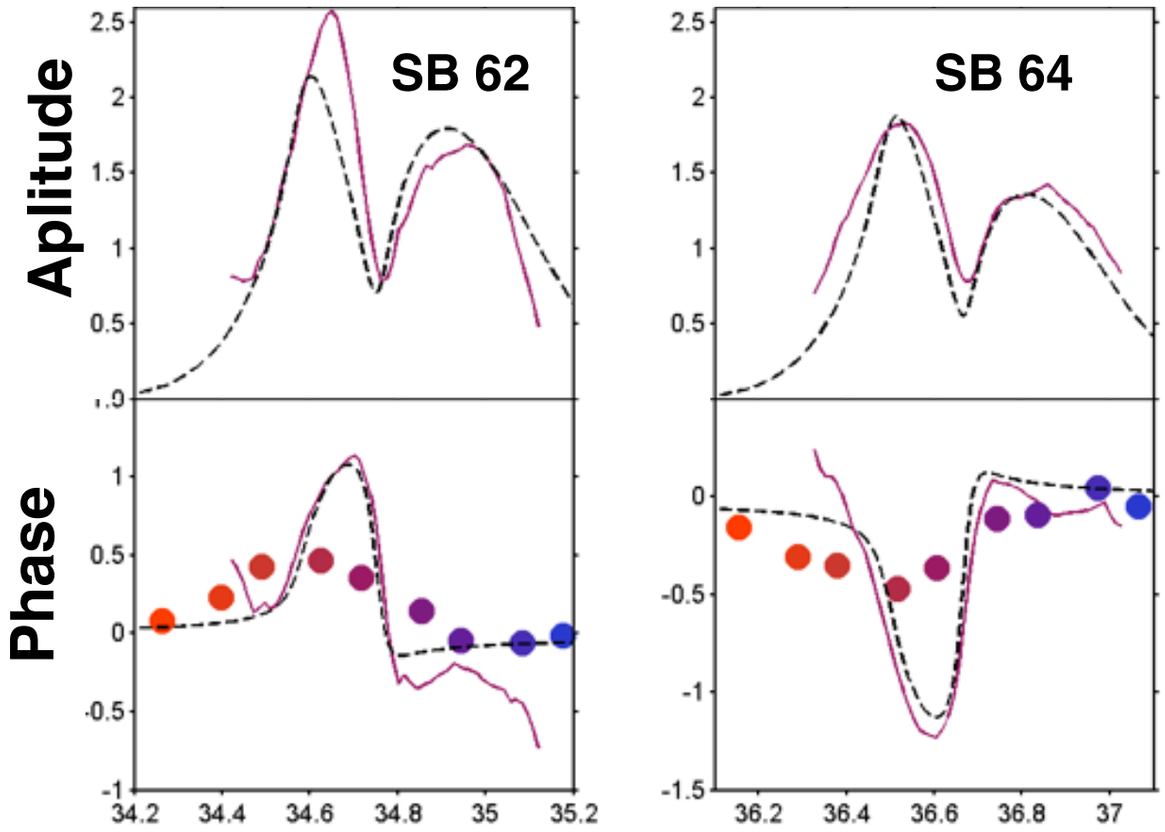
Rainbow RABBIT

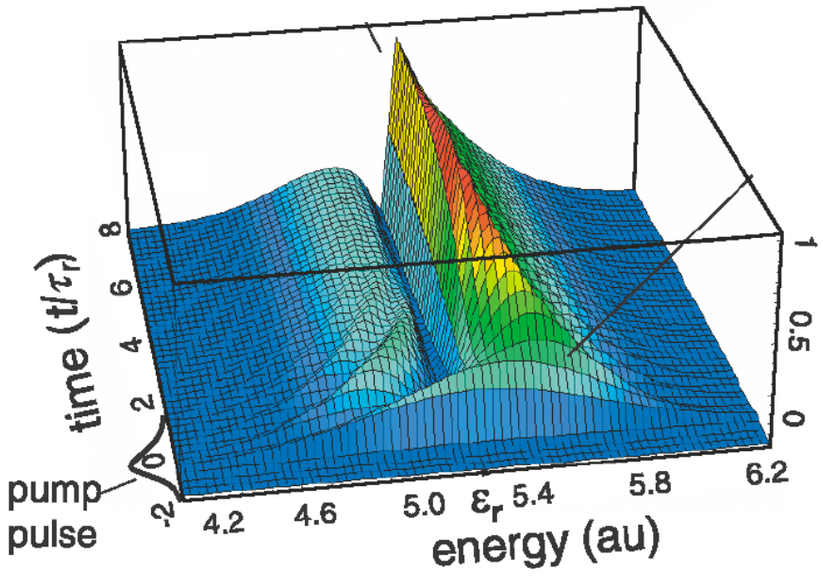


Duckling profile

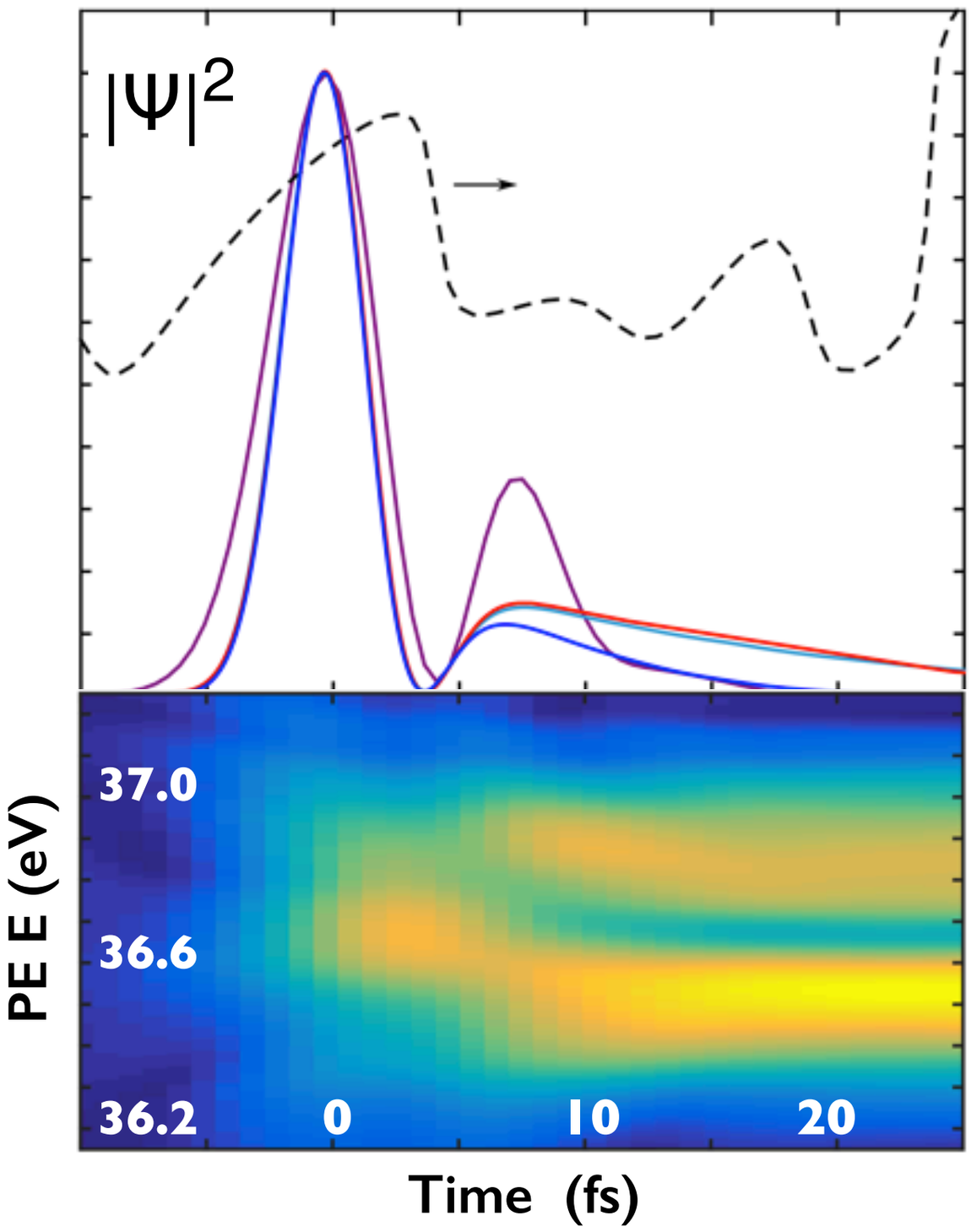
Gruson V. *et al.*, Science **354**, 734 (2016)

Buildup of Fano Profile





Wickenhauser *et al.*, PRL **94**, 023002 (2005)



Gruson V. *et al.*, Science **354**, 734 (2016)

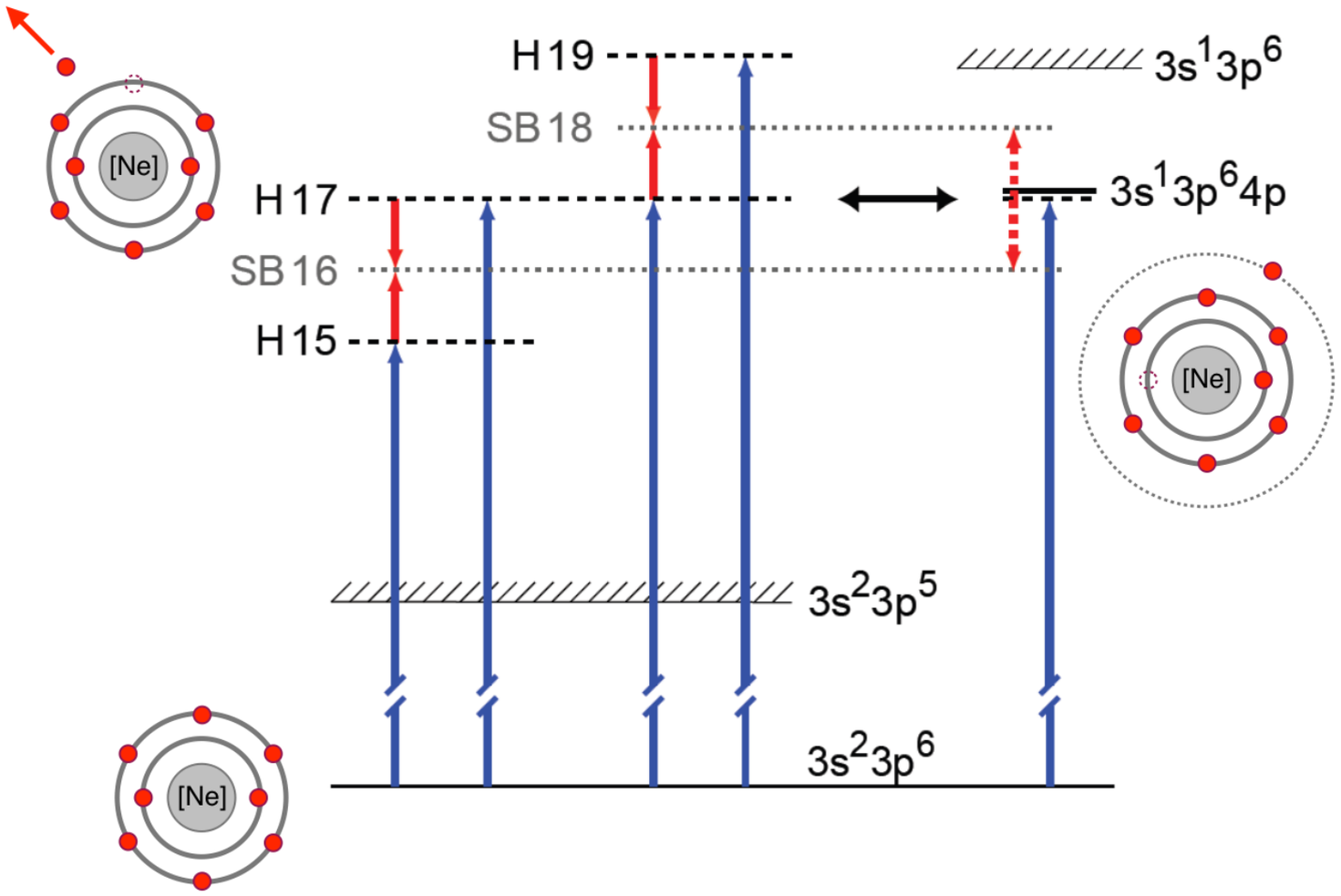
Resonant RABBIT: Argon

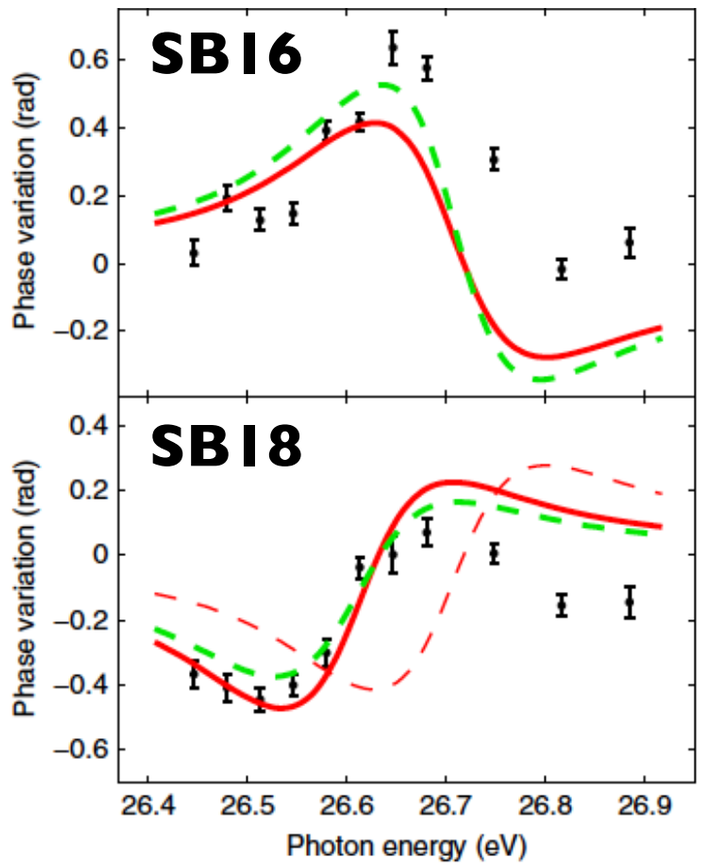
$$\mathrm{Ar} + \gamma \rightarrow \mathrm{Ar}^+ + e^-$$

$$\mathrm{Ar}^+ + e^- \pm \gamma \rightarrow \mathrm{Ar}^+ + e^-$$

$$\mathrm{Ar} + \gamma \rightarrow \mathrm{Ar}^*(3s^{-1}14p)$$

$$\mathrm{Ar}^*(3s^{-1}4p) \pm \gamma \rightarrow \mathrm{Ar}^+ + e^-$$





Model: the right-ish answer for the right-ish reason

DOI: 10.1038/ncomms10566

nature COMMUNICATIONS

Collab. with Anne L'Huillier's group

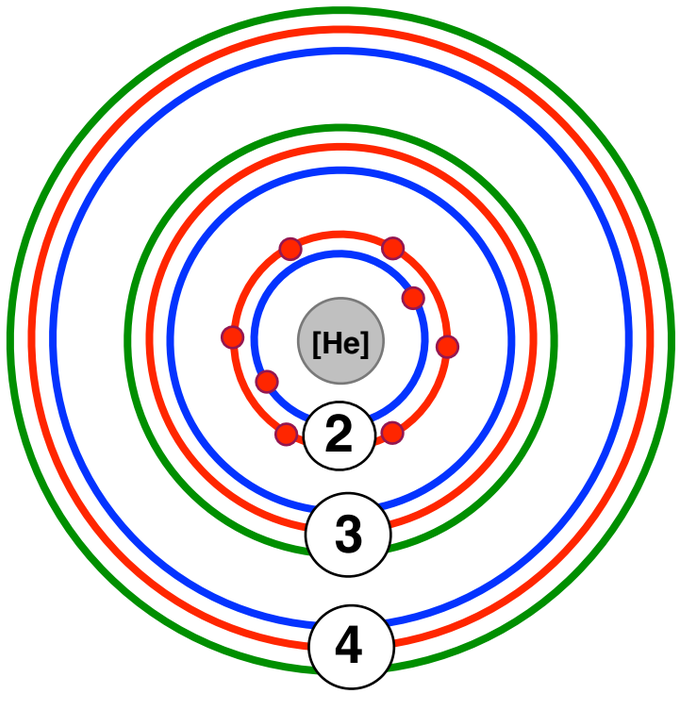
M. Kotur *et al.*, Nature Communication **7**, 10566 (2016)

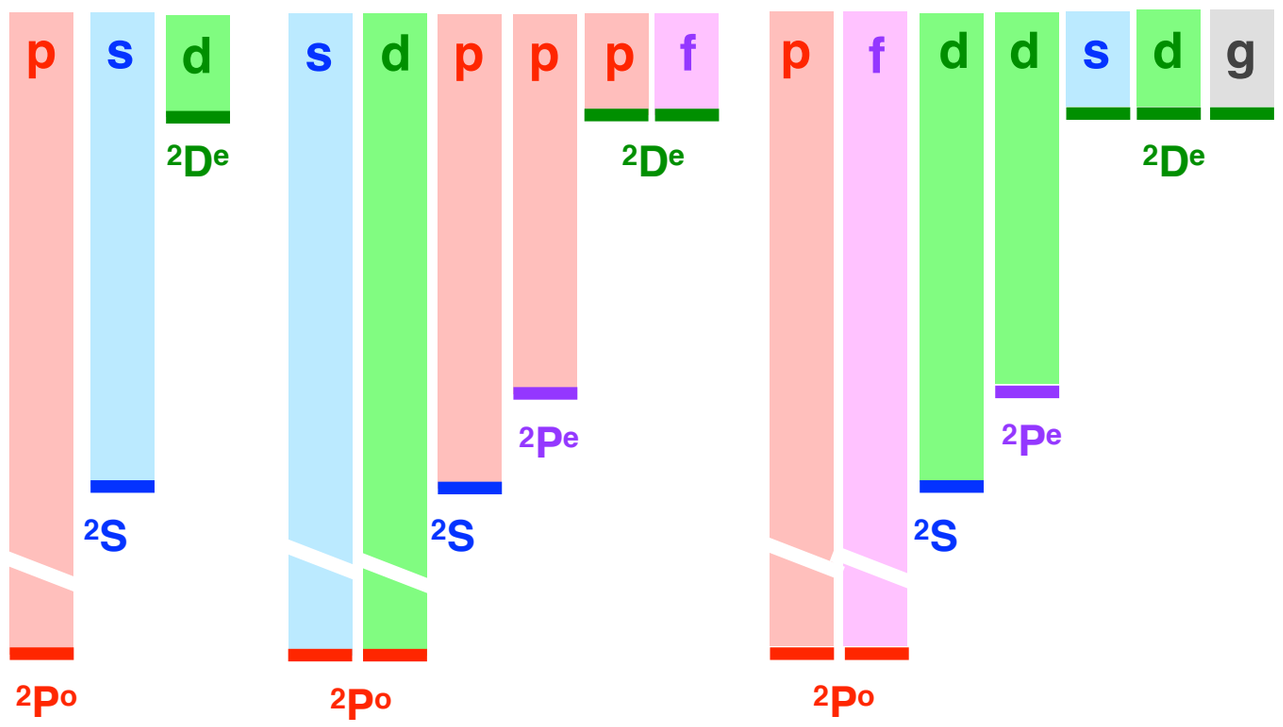
NewStock TDCC atomic code

$$\Psi(t) = \sum_{\Gamma} \Psi^{\Gamma}(t) \qquad \Gamma = (\Pi, L, S, M, \Sigma)$$

$$\Psi^{\Gamma}(t) = \sum_{i} \chi_i^{\Gamma}\, c_i^{\Gamma}(t) + \sum_{\alpha} \sum\!\!\!\!\!\!\int dE\, \phi_{\alpha E}^{\Gamma}\, c_{\alpha E}^{\Gamma}(t)$$

Neon





Carette T *et al.*, Phys. Rev. A **87**, 023420 (2013).

Argenti L *et al.*, *in preparation.*

Partial-Wave Channel

$$\phi^{\Gamma}_{\alpha E} = f\mathcal{A}\ \Phi^{\Gamma}_{\alpha}(\mathbf{x}_1, \cdots, \mathbf{x}_{N-1}; \hat{r}_N, \zeta_N)\ \varphi^{\Gamma}_{\alpha E}(r_N)$$

$$\Phi^{\Gamma}_{\alpha} = {}^{2S+1}\left[\Phi_{I_\alpha}(\mathbf{x}_1 - \mathbf{x}_{N-1}) \otimes {}^{2}\chi(\zeta_N) Y_{\ell_\alpha}(\hat{r}_N)\right]_L$$

MCHF parent-ions

$$\Phi_{I_\alpha} = \sum_j c_{j,\alpha} \Phi_j^{L_\alpha S_\alpha}$$

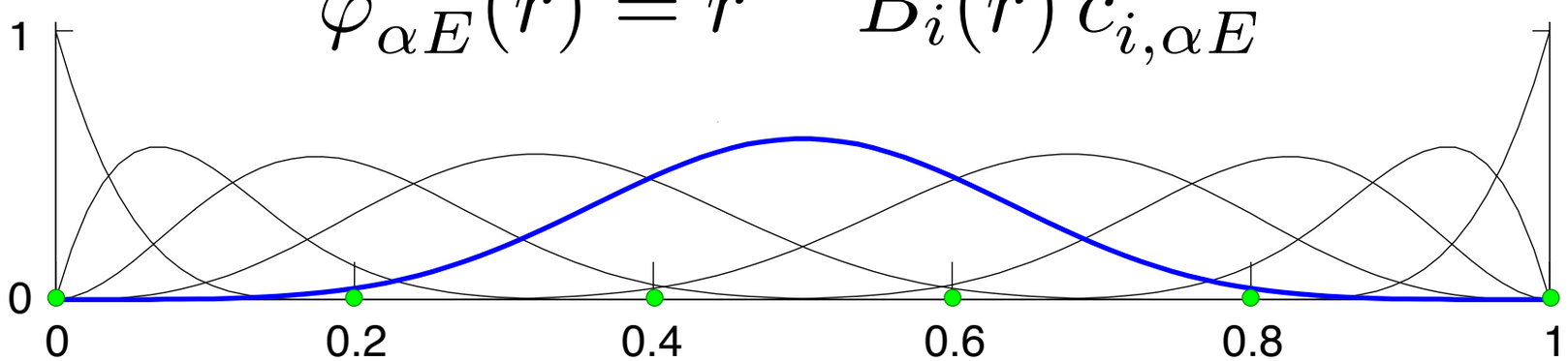
ATSP2K

Froese Fischer et al.
CPC **176**, 559 (2007)

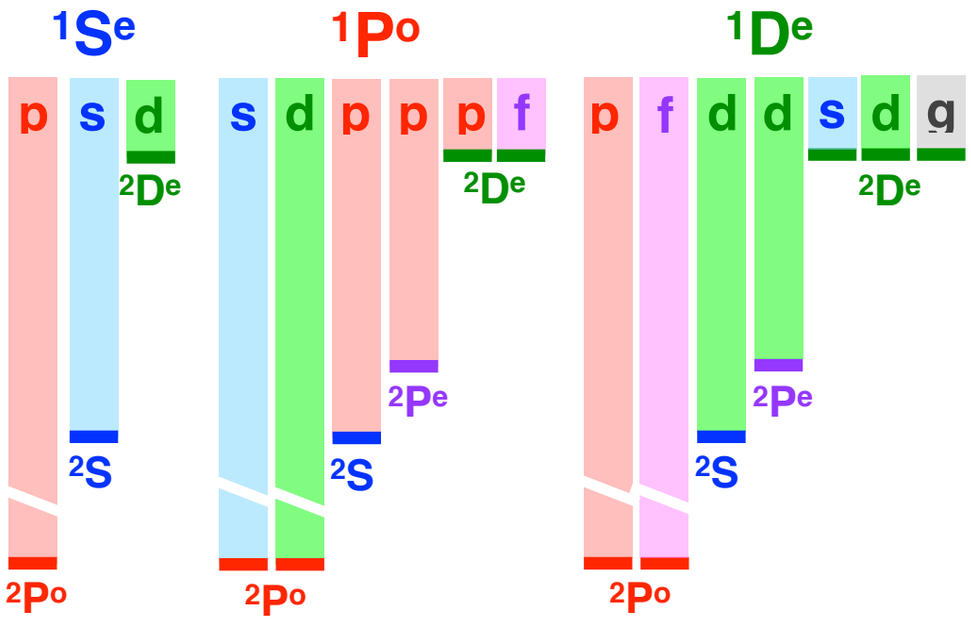
$1s^2\ 2s^2\ 2p^5$
$1s^2\ 2s^2\ 2p^4$ **nl**
$1s^2\ 2s^1\ 2p^6$
$1s^2\ 2s^1\ 2p^5\ 3p$
$1s^2\ 2p^6\ 3s$
$1s^2\ 2s^2\ 2p^3\ 3s\ 3p$

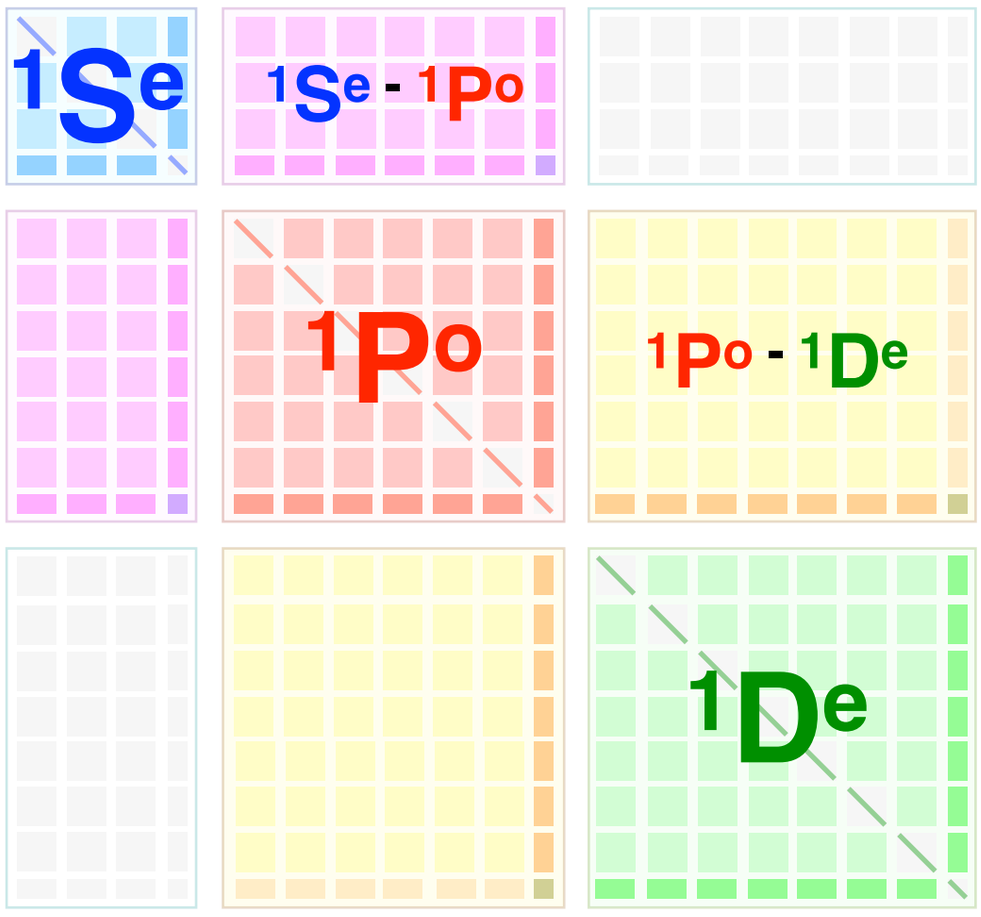
B-spline Radial Basis

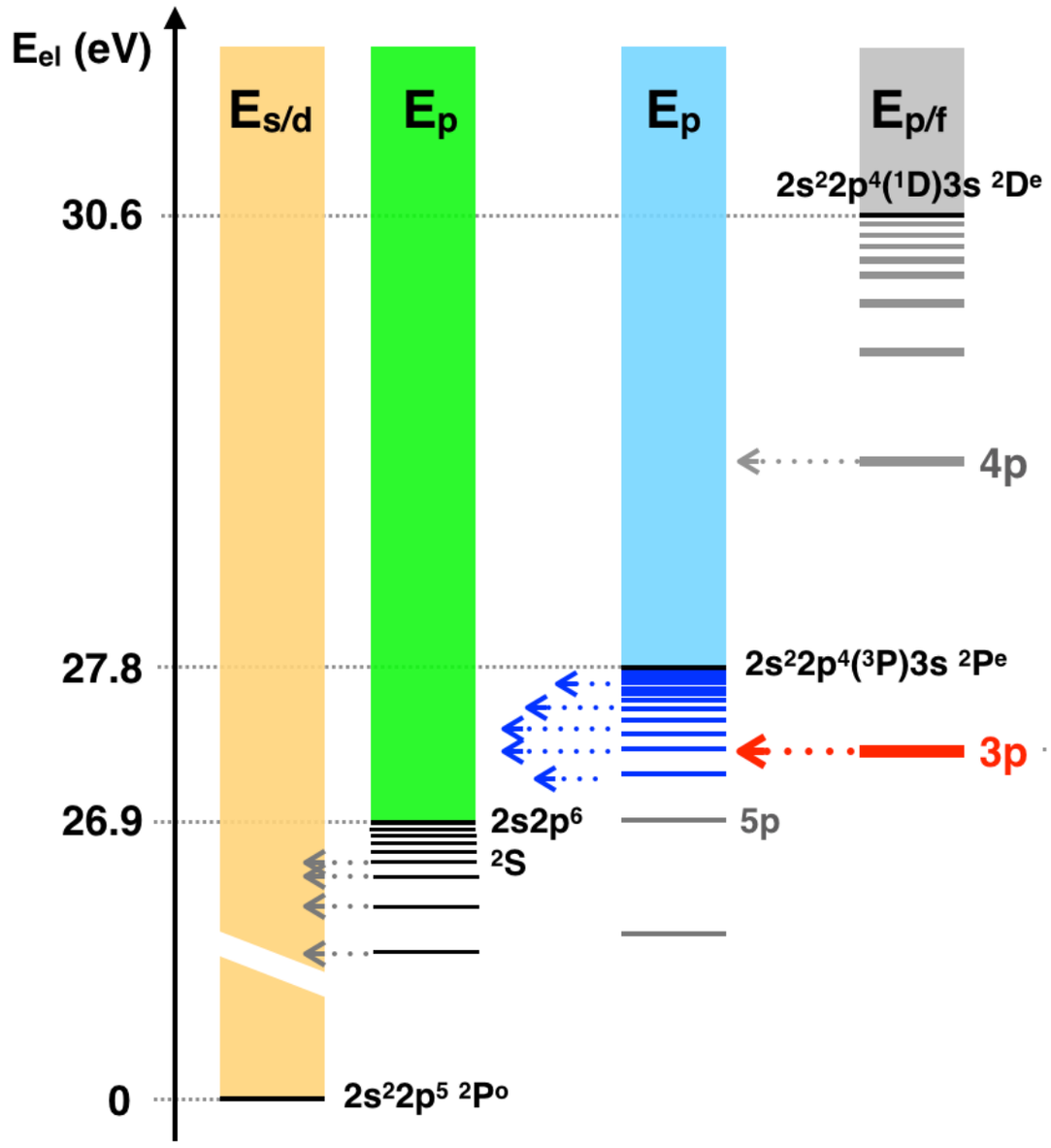
$$\varphi^{\Gamma}_{\alpha E}(r) = r^{-1}\, B_i(r)\, c^{\Gamma}_{i,\alpha E}$$



CC Energy spectrum







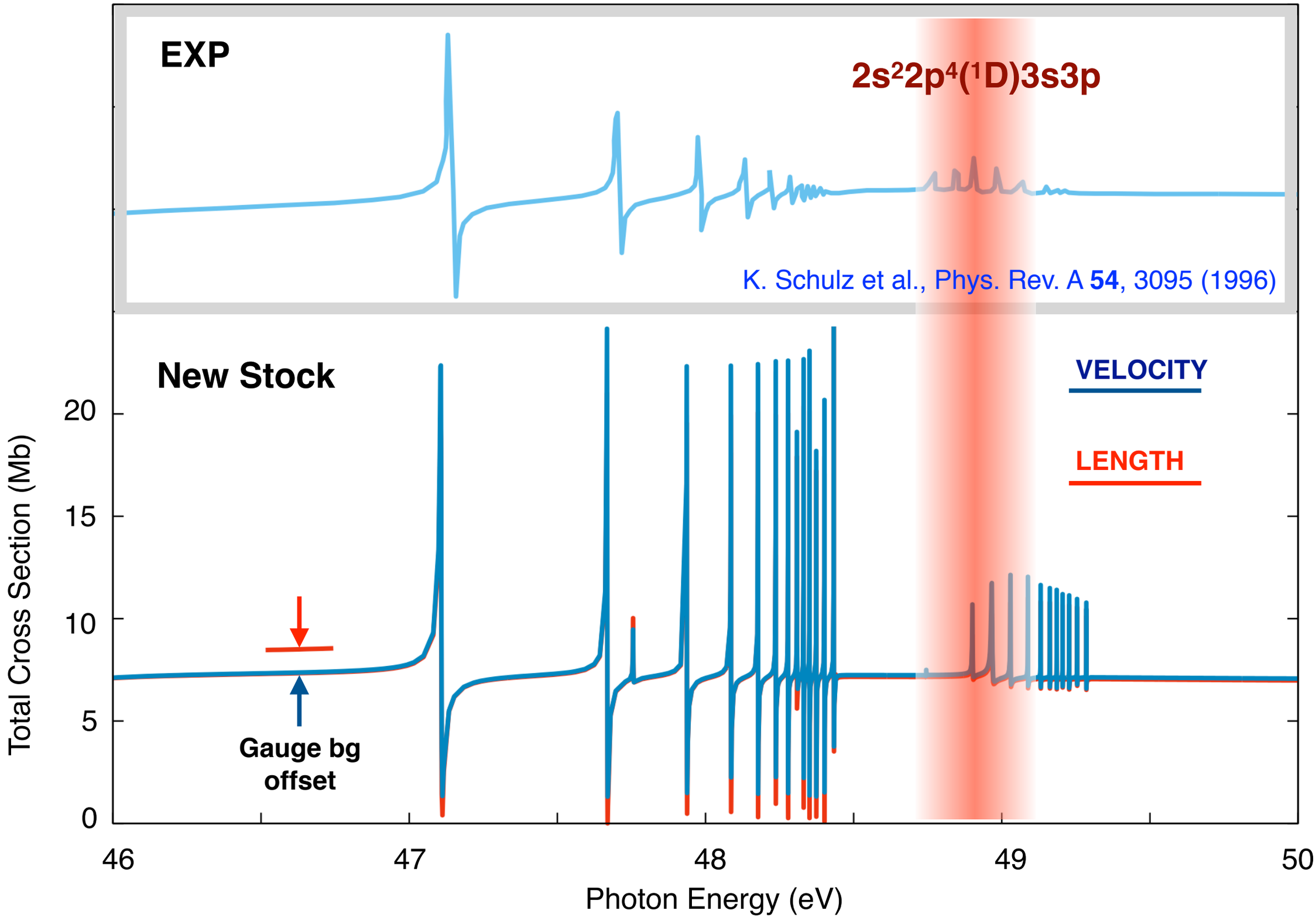
$$(E-H)|\Psi_E\rangle = 0 \qquad |\psi_E\rangle = |\boldsymbol{\psi}\rangle\mathbf{c} + \sum_\beta |\beta B\rangle b_\beta$$

$$\mathbf{c}_{\alpha E} = (E-\mathbf{E})^{-1}\langle\boldsymbol{\psi}|(H-E)|\alpha B\rangle$$

$$[\langle \boldsymbol{x}|\Psi^{\Gamma\,(-)}_{\alpha E}\rangle]_{out,\,k_\alpha r_N\gg 1} = \sqrt{N_e}\hat{\mathcal{A}}\Phi_\alpha(x_1\text{-}x_{N-1};\zeta_N,\Omega_N)\mathcal{W}^+_{\ell,E-E_a}(r_N)$$

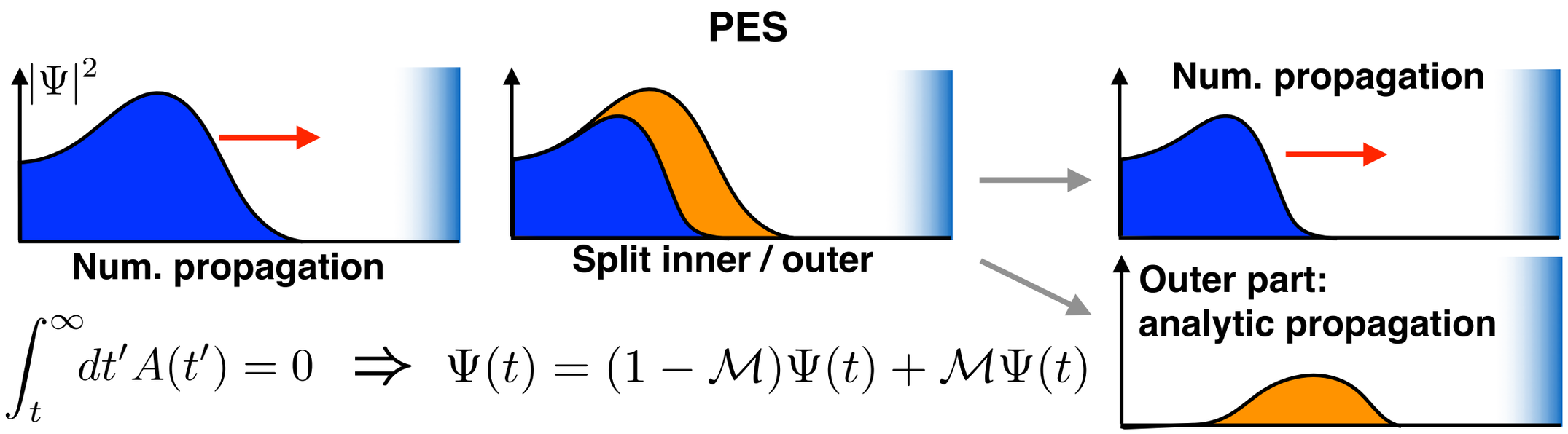
$$\mathcal{W}^+_{\ell E}(r) = \frac{e^{i\theta_{\ell k}(r)}}{\sqrt{2\pi k}\,r} \qquad \theta_{\ell k}(r) = kr + \frac{Z}{k}\log(2kr) - \frac{\ell\pi}{2} + \sigma_\ell(k)$$

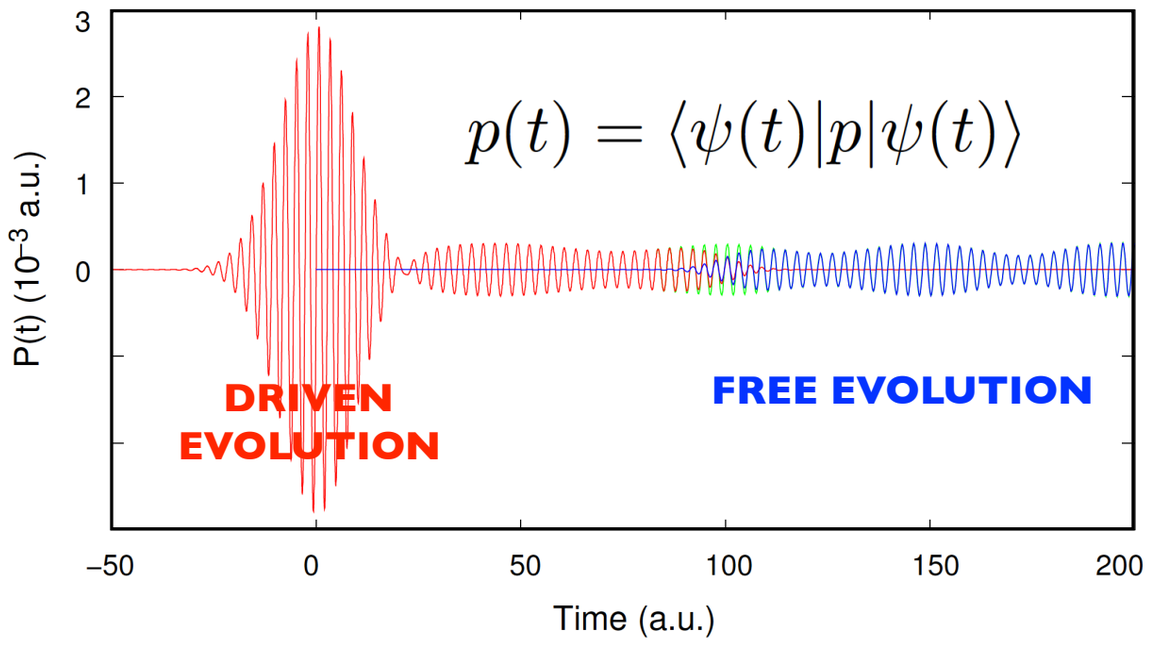
Neon PI Cross Section near an intruder state



TDSE

$$\Psi(t+dt) = e^{-iH_0 dt/2}\, e^{-iH_I(t+dt/2)dt}\, e^{-iH_0 dt/2}\, e^{-iV_{caps}dt}\, \Psi(t)$$





$$\sigma(\omega) = \frac{4\pi}{\omega}\,\mathrm{Im}\,\frac{\tilde{p}(\omega)}{\tilde{A}(\omega)}$$

$$p(t) = p^-(t) + p^+(t)$$

$$\tilde{p}(\omega) = \tilde{p}^-(\omega) + \tilde{p}^+(\omega)$$

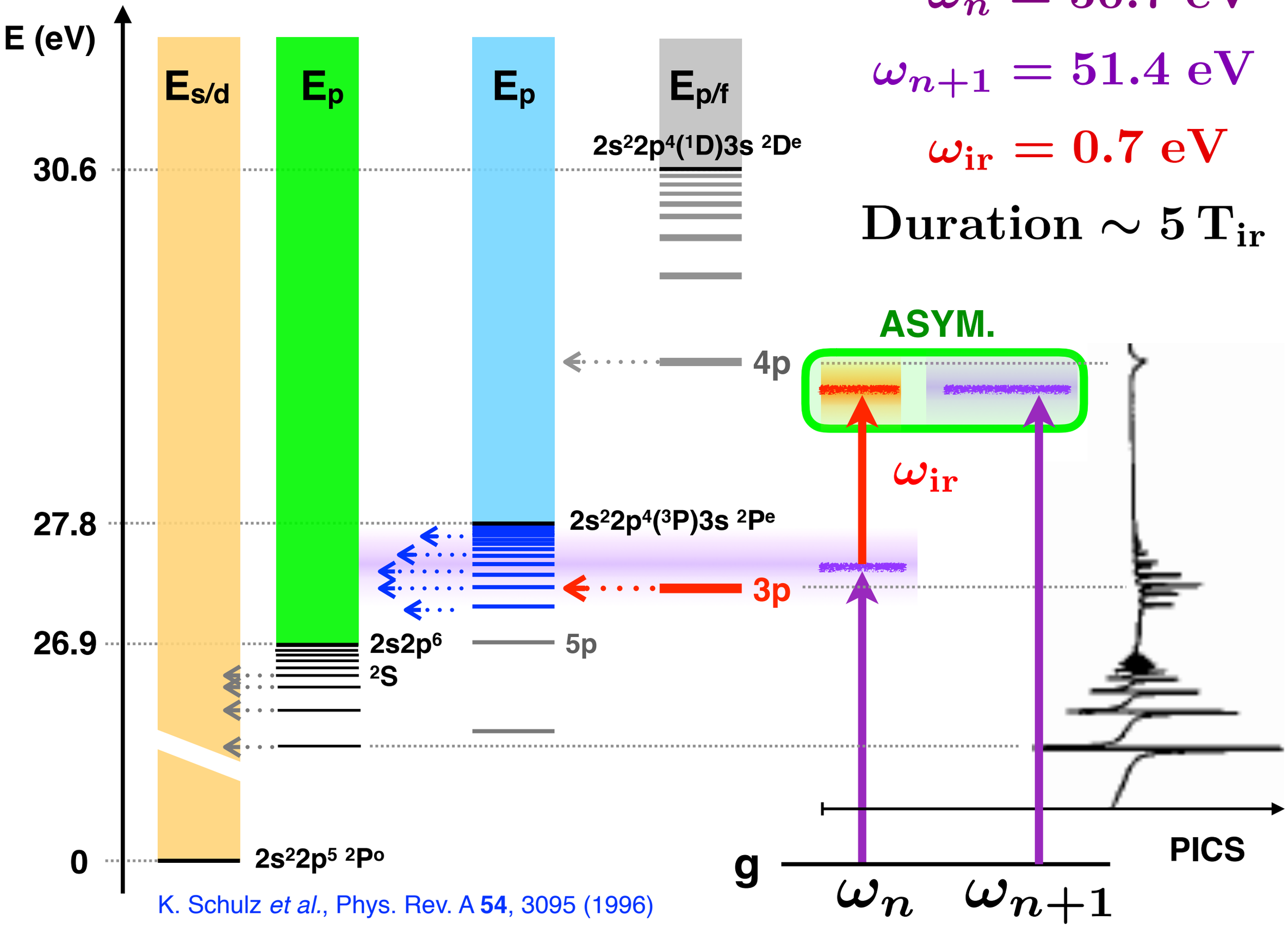
Intruder States: Neon

$$\omega_n = 50.7 \text{ eV}$$

$$\omega_{n+1} = 51.4 \text{ eV}$$

$$\omega_{ir} = 0.7 \text{ eV}$$

$$\text{Duration} \sim 5\, T_{ir}$$

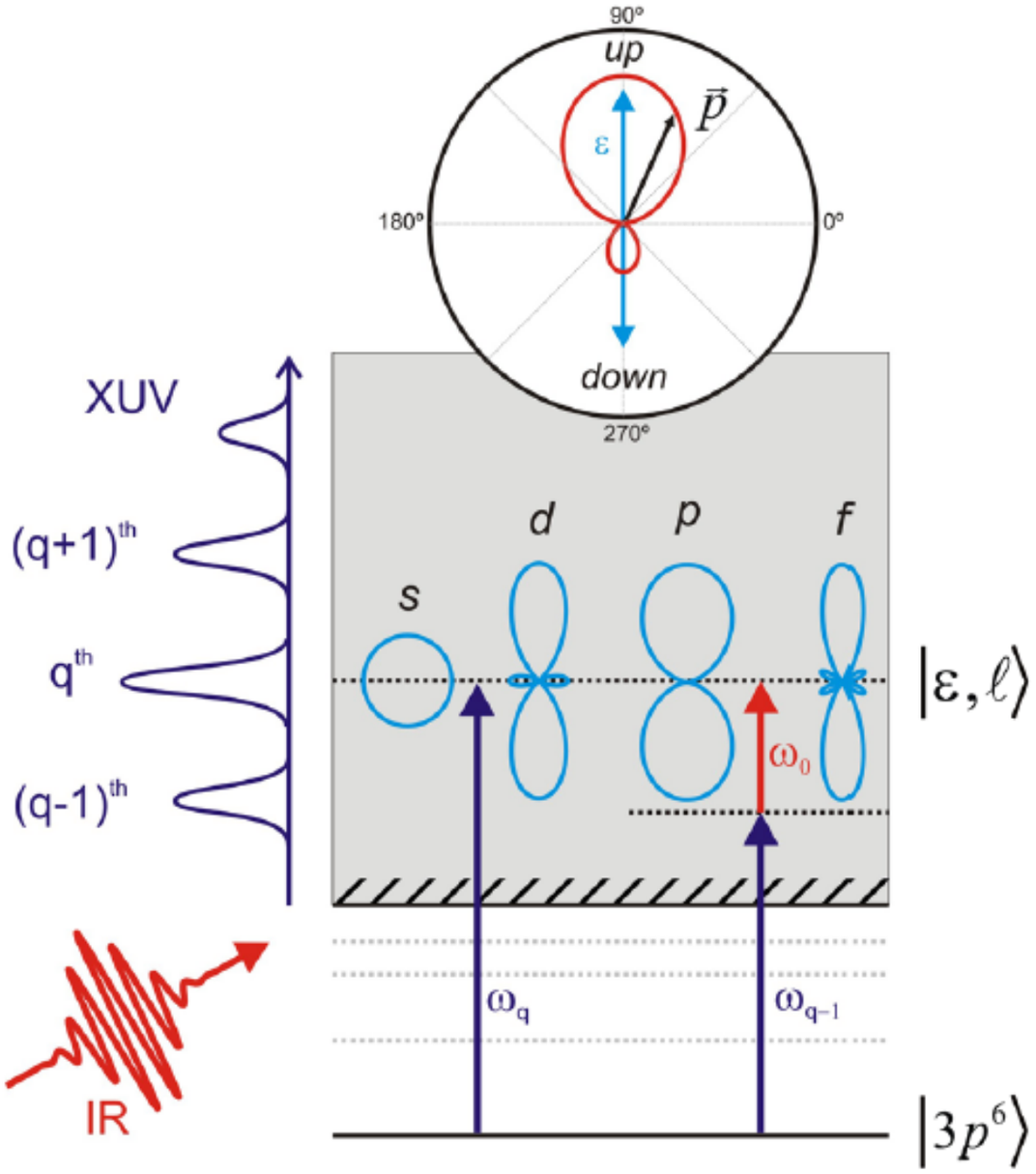


K. Schulz *et al.*, Phys. Rev. A **54**, 3095 (1996)

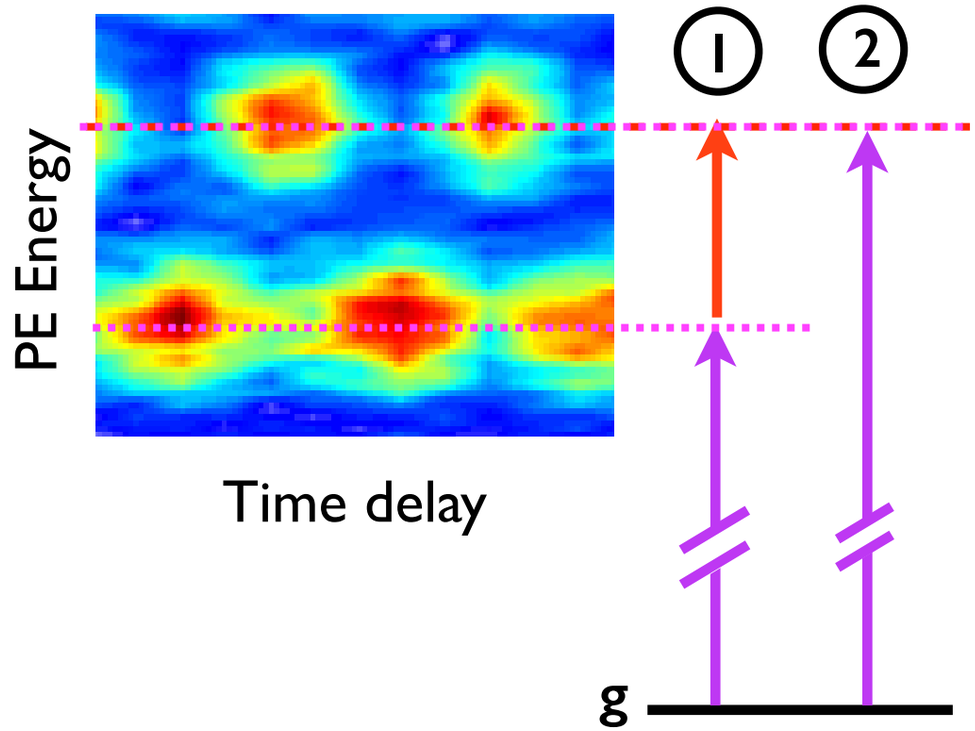
Checkerboard Rabbit

① $A + \Upsilon_{Hn} + \Upsilon_{IR} \longrightarrow A^+ + e^-$

② $A + \Upsilon_{Hn+I} \longrightarrow A^+ + e^-$



G. Laurent *et al.*, PRL **109**, 083001 (2012)



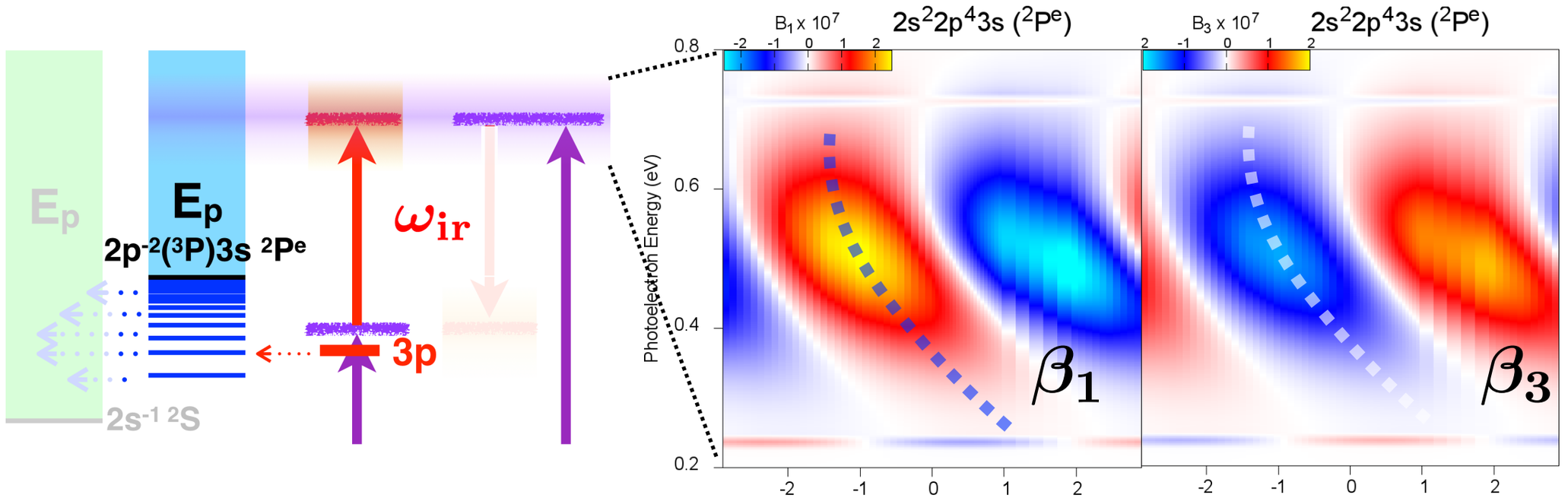
$$\mathcal{W}_{up} - \mathcal{W}_{down} \propto \cos\left[\omega_{\mathrm{IR}}\tau - \Delta\phi_{\mathrm{APT}} - \varphi_{n+1}^{At(1)} + \varphi_{n,IR}^{At(2)}\right]$$

$\varphi_{n+1}^{At(1)}$ ⟷ **one-photon PE-emission delay**

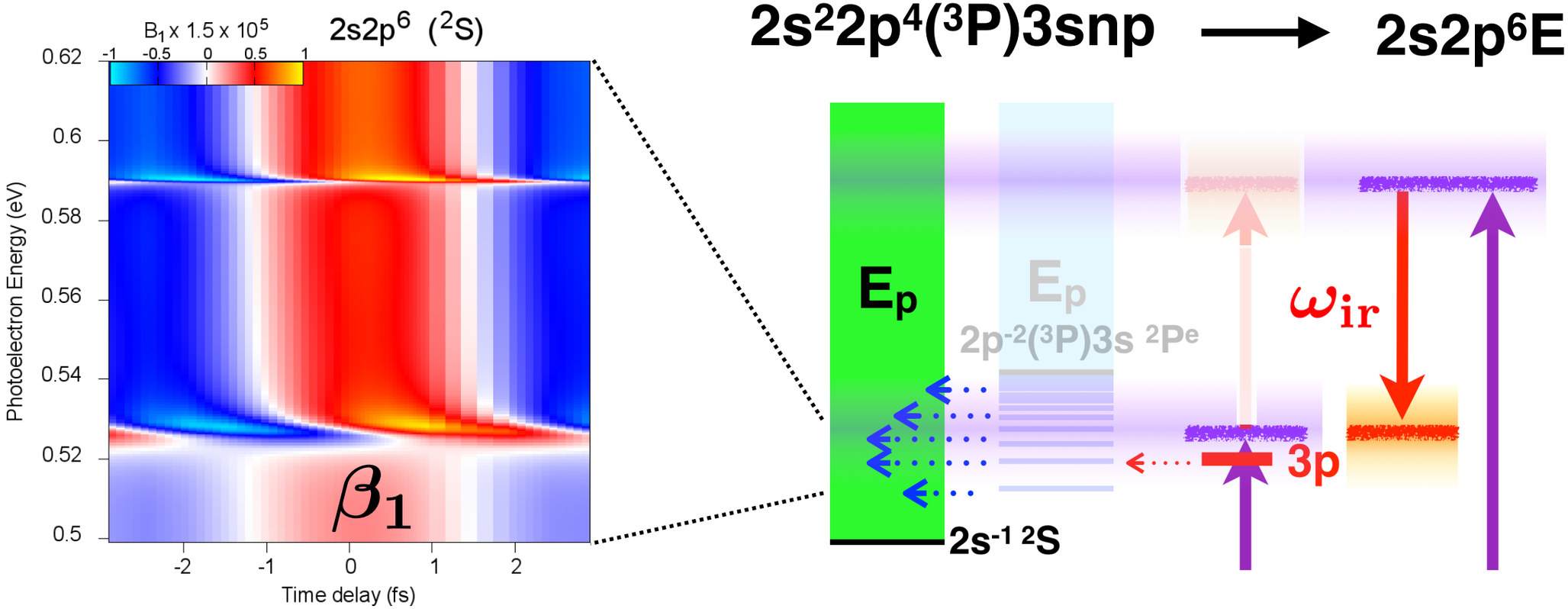
$\varphi_{n,IR}^{At(2)}$ ⟷ **two-photon PE-emission delay**

Photoelectron Angular Distribution

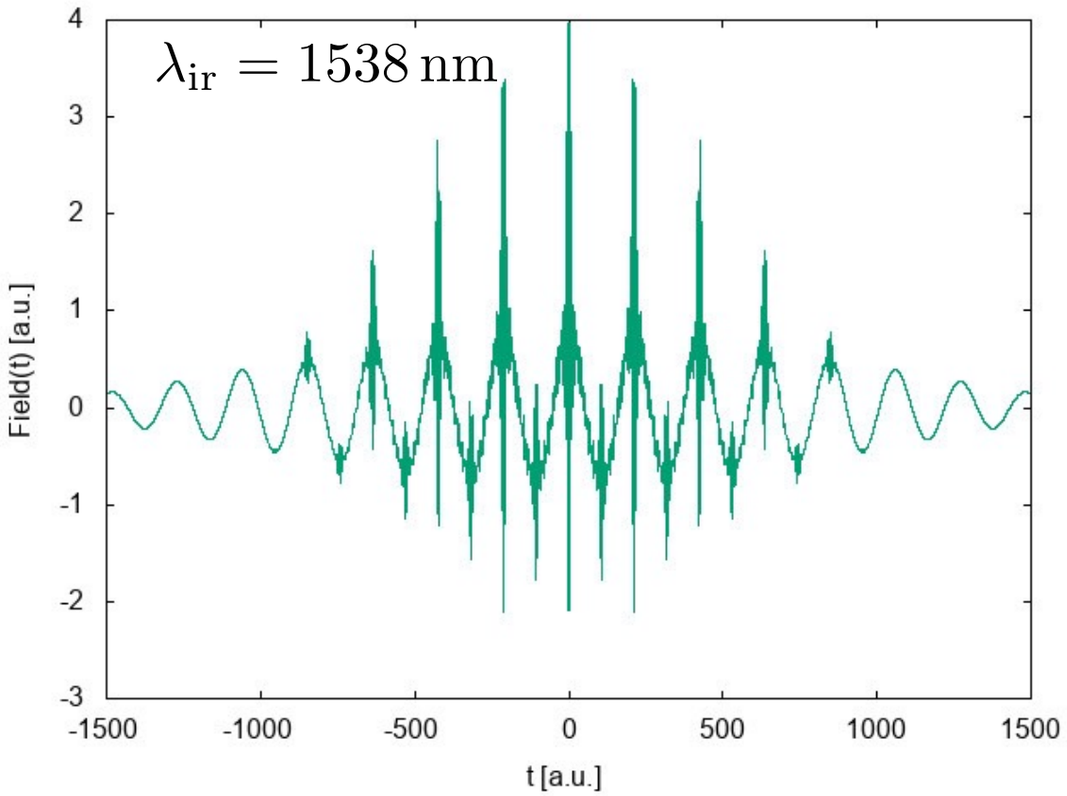
$2s^22p^4(^1D)3s3p \longrightarrow 2s^22p^4(^3P)3snp$

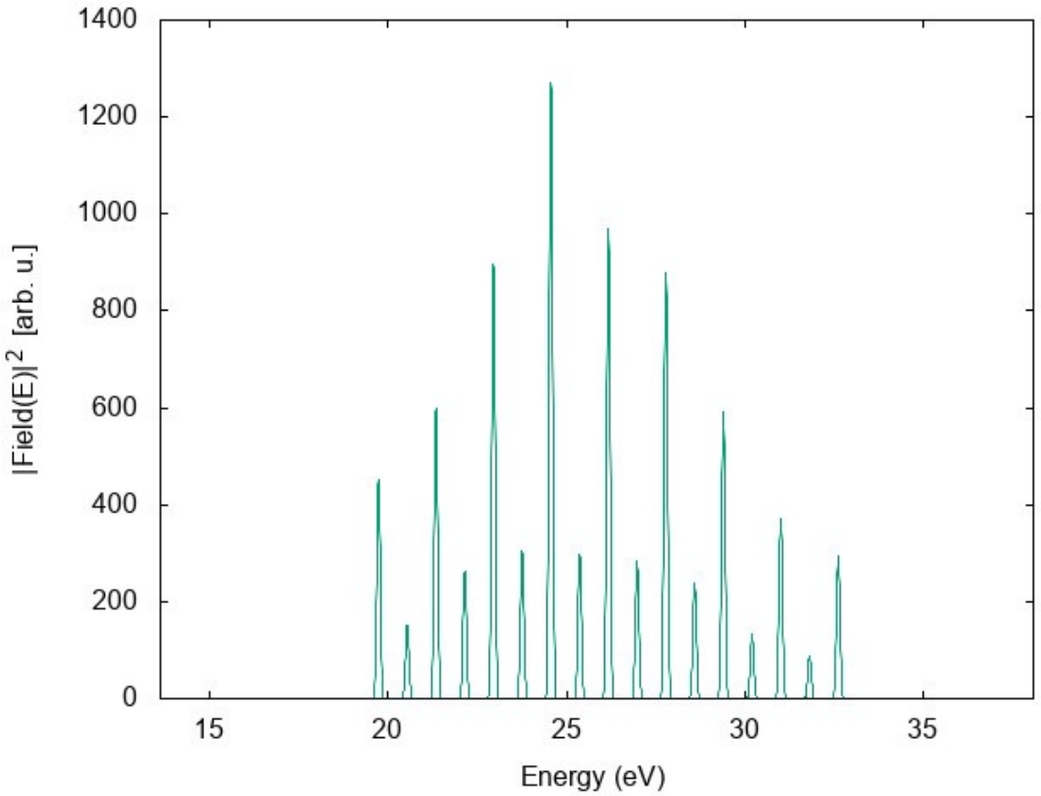


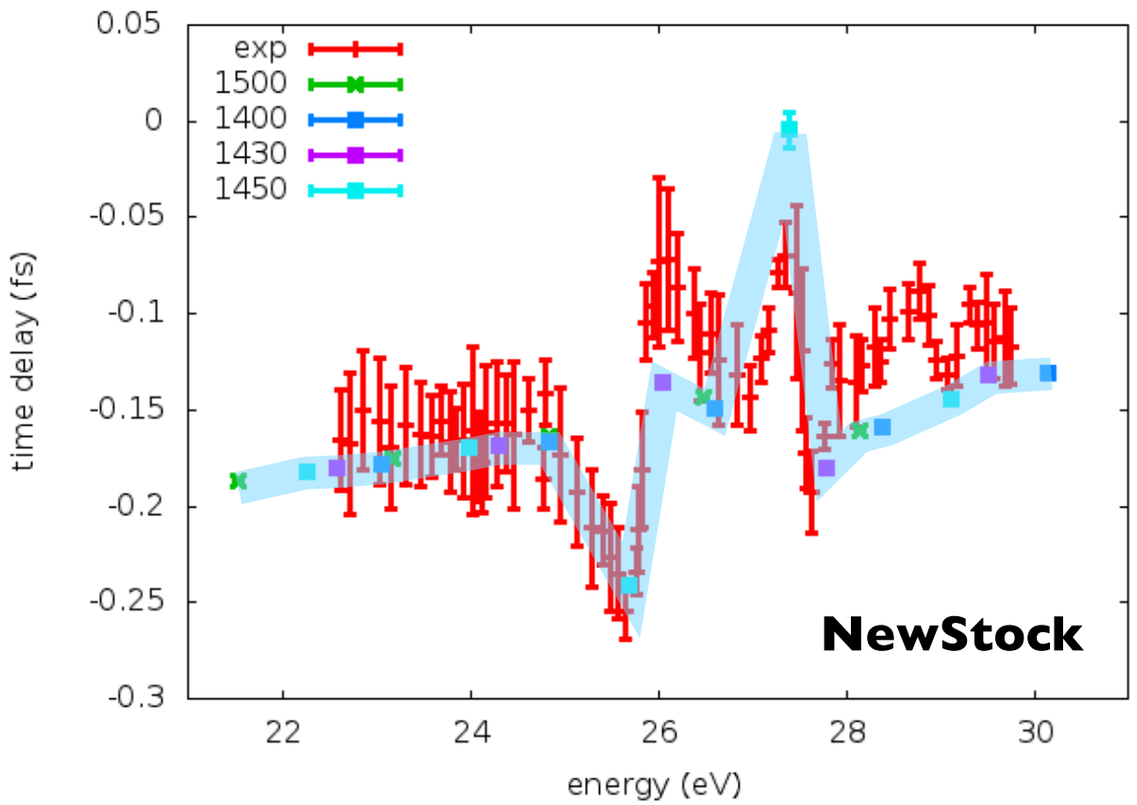
$2s^22p^4(^3P)3snp \longrightarrow 2s2p^6Ep$



Argon resonant RABBIT, long NIR Pulses







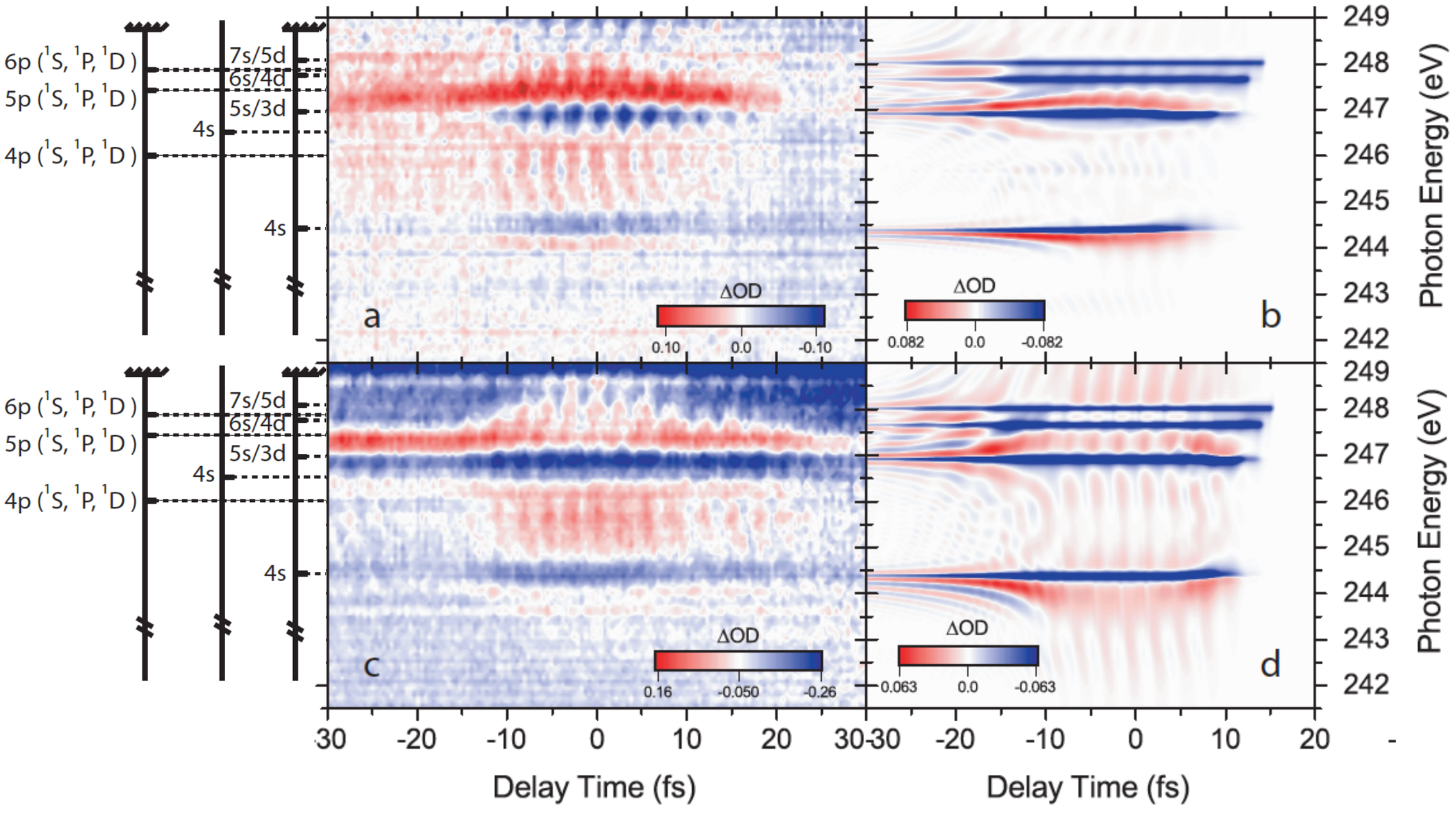
Phase of the integral sideband beating in RABBIT, as a function of the IR wavelength

Th. sims using **NewStock**, within a collab with
E. Lindroth, S. Donsa and J. Burgdörfer (2018)

Exp data by: T. Gorman, T. Scarborough, D. Tuthill,
A. Piper, D. Kiesewetter, and L. DiMauro (OSU)
Guillaume Laurent (AU) *priv. com.* (2017)

Attosecond Transient Absorption Spectrum of Argon at the $L_{2,3}$-edge

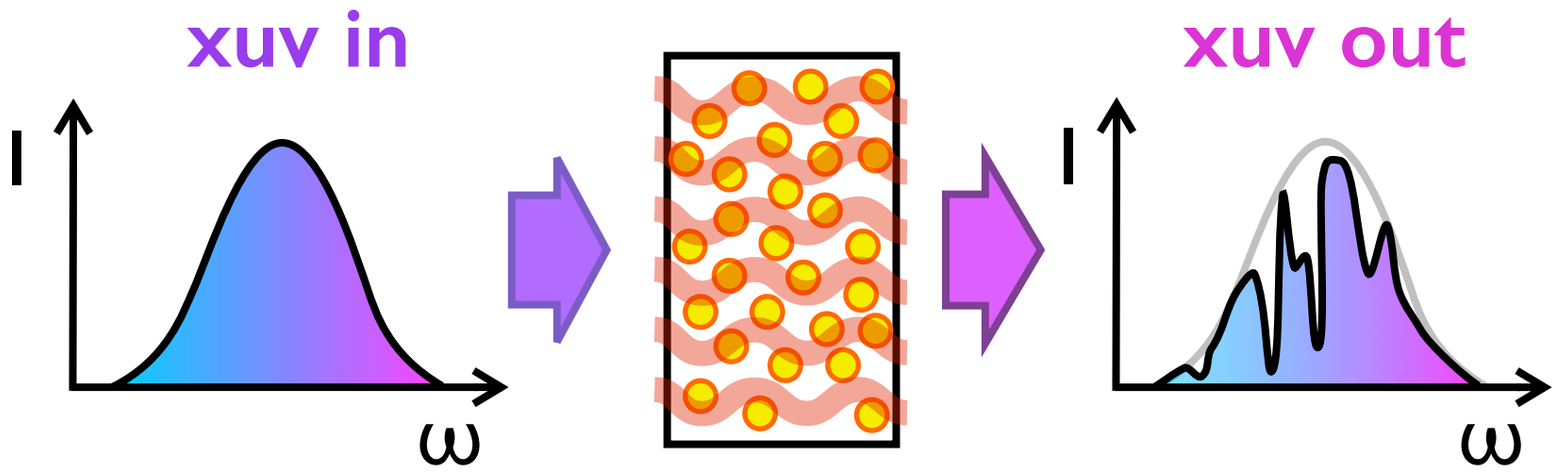
Andrew Chew,[1] Nicolas Douguet,[1] Coleman Cariker,[1] Jie Li,[1] Eva Lindroth,[2] Xiaoming Ren,[1] Yanchun Yin,[1] Luca Argenti,[1] Wendell T. Hill, III,[3] and Zenghu Chang[1,*]

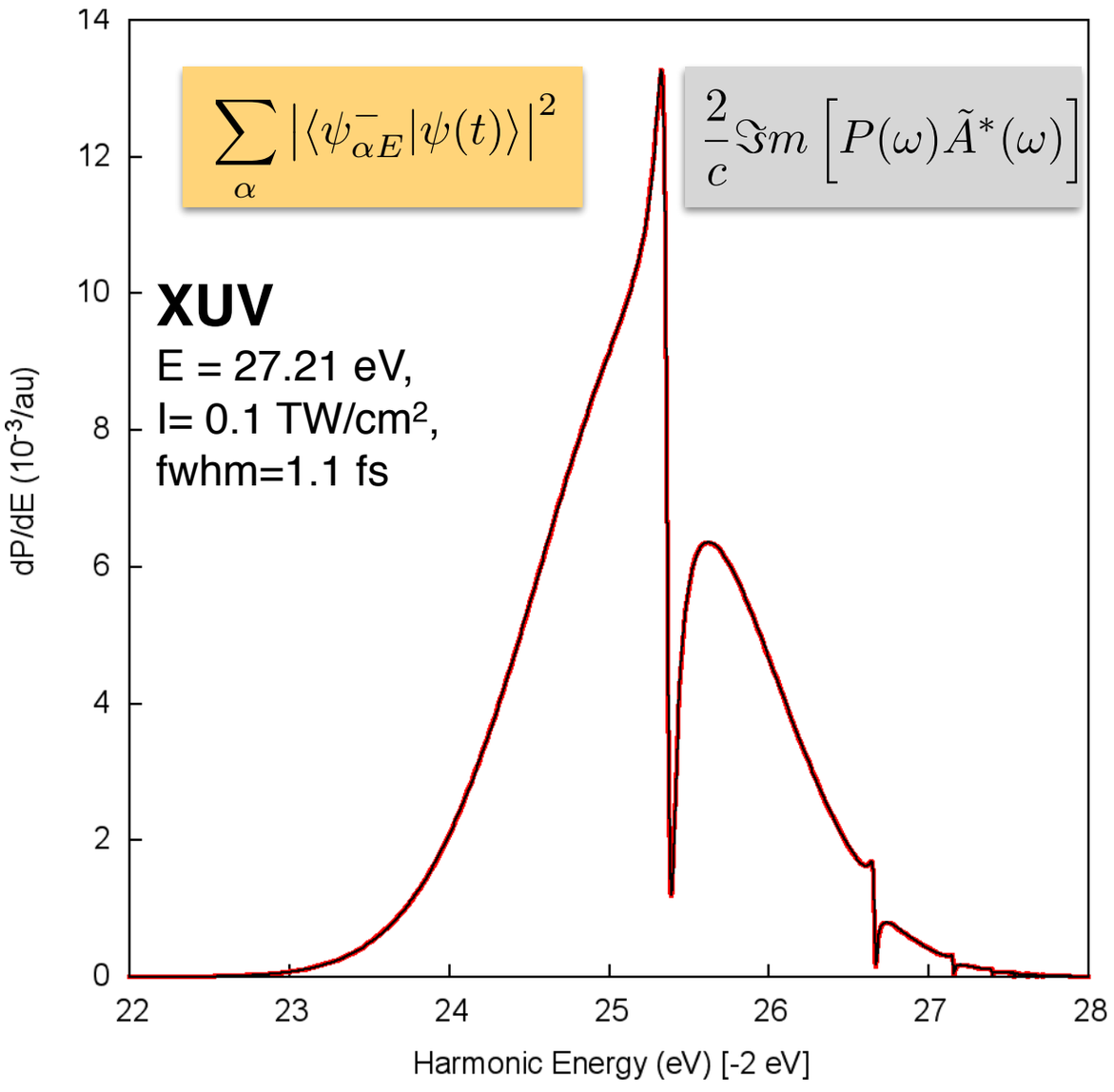


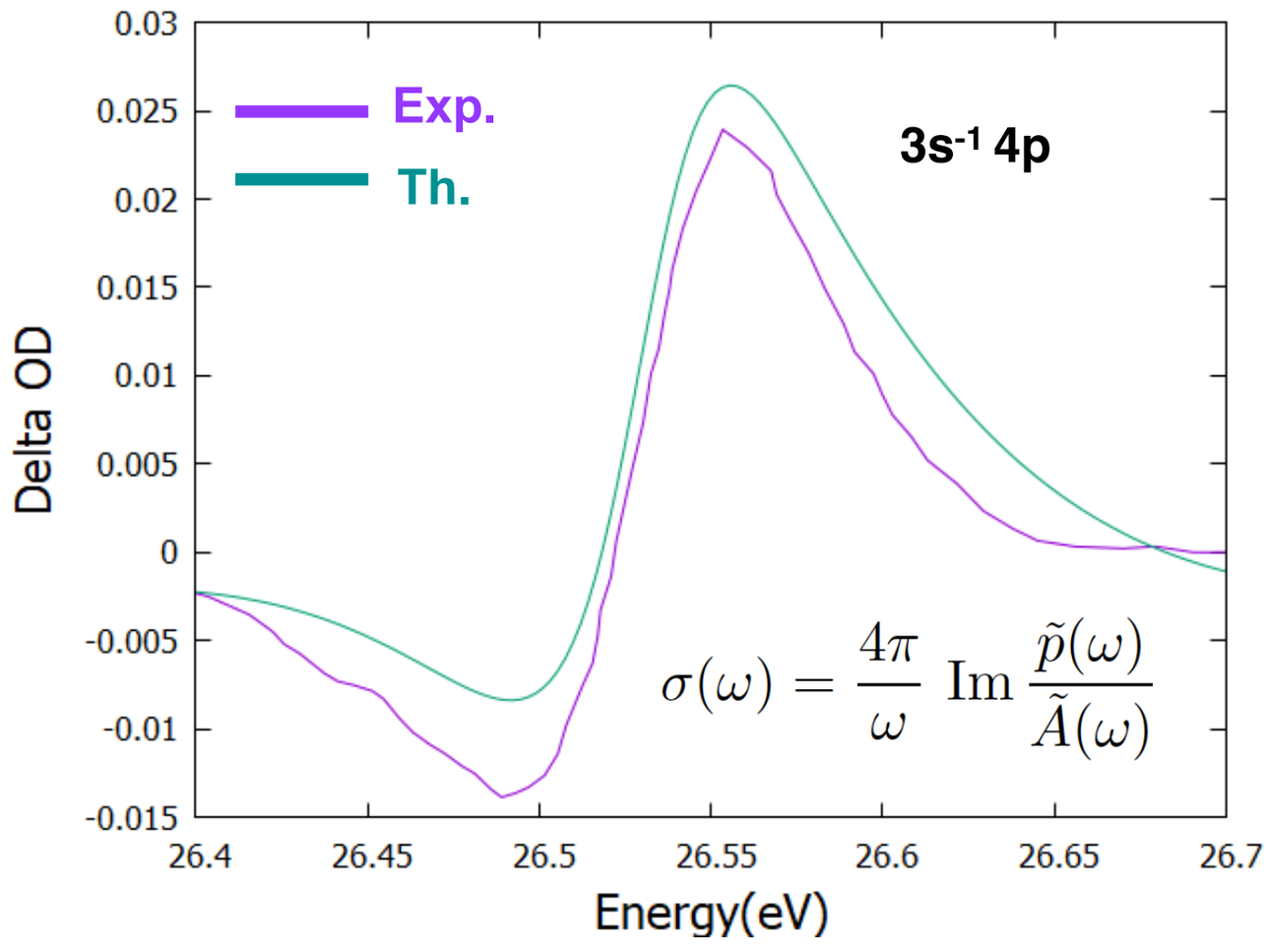
A Chew et al., PRA **97**, 031407(R) (2018)

Essential-state model from New Stokes + ADK tunnel ionization

ab initio ATAS of argon







Exp: Arvinder Sandhu *et al.* (ASU), *priv. com.*

C. Cariker & L.A., *in preparation*

XCHEM close-coupling

$$\Psi^{-}_{\alpha E} = \sum_{i} \chi_i \, c_{i,\alpha E} + \sum_{\beta i} \psi_{\beta i} \, c_{\beta i,\alpha E}$$

LC PWC

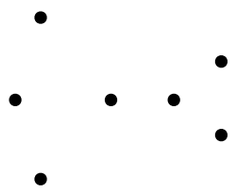
$$\psi_{\alpha i} = \hat{\mathcal{A}} \left[\Phi_a(\mathrm{x}_1, -, \mathrm{x}_{n-1}) \, \varphi_i(\mathrm{x}_n) \right] \quad \text{PWC}$$

$$\langle \Psi_{\alpha i} | \mathcal{O} | \Psi_{\beta j} \rangle = \langle \Phi_\alpha(1, -, N-1) \varphi_i(N) | \mathcal{O}[1 - (N-1)\mathcal{P}_{N-1,N}] | \Phi_\beta(1, -, N-1) \varphi_j(N) \rangle$$

$$\varphi_i = \begin{cases} \phi_i & \text{poly-centric Gaussian} \\ G_i & \text{mono-centric Gaussian} \\ B_i & \text{mono-centric B-spline} \end{cases}$$

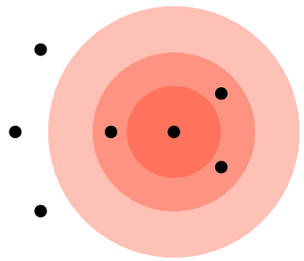
Marante C et al., J. Chem. Th. Comput. 13 , 499 (2017).

Orbital basis



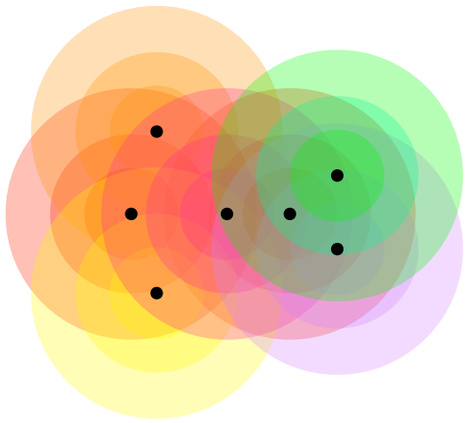
Orbital basis

PC Gauss



Orbital basis

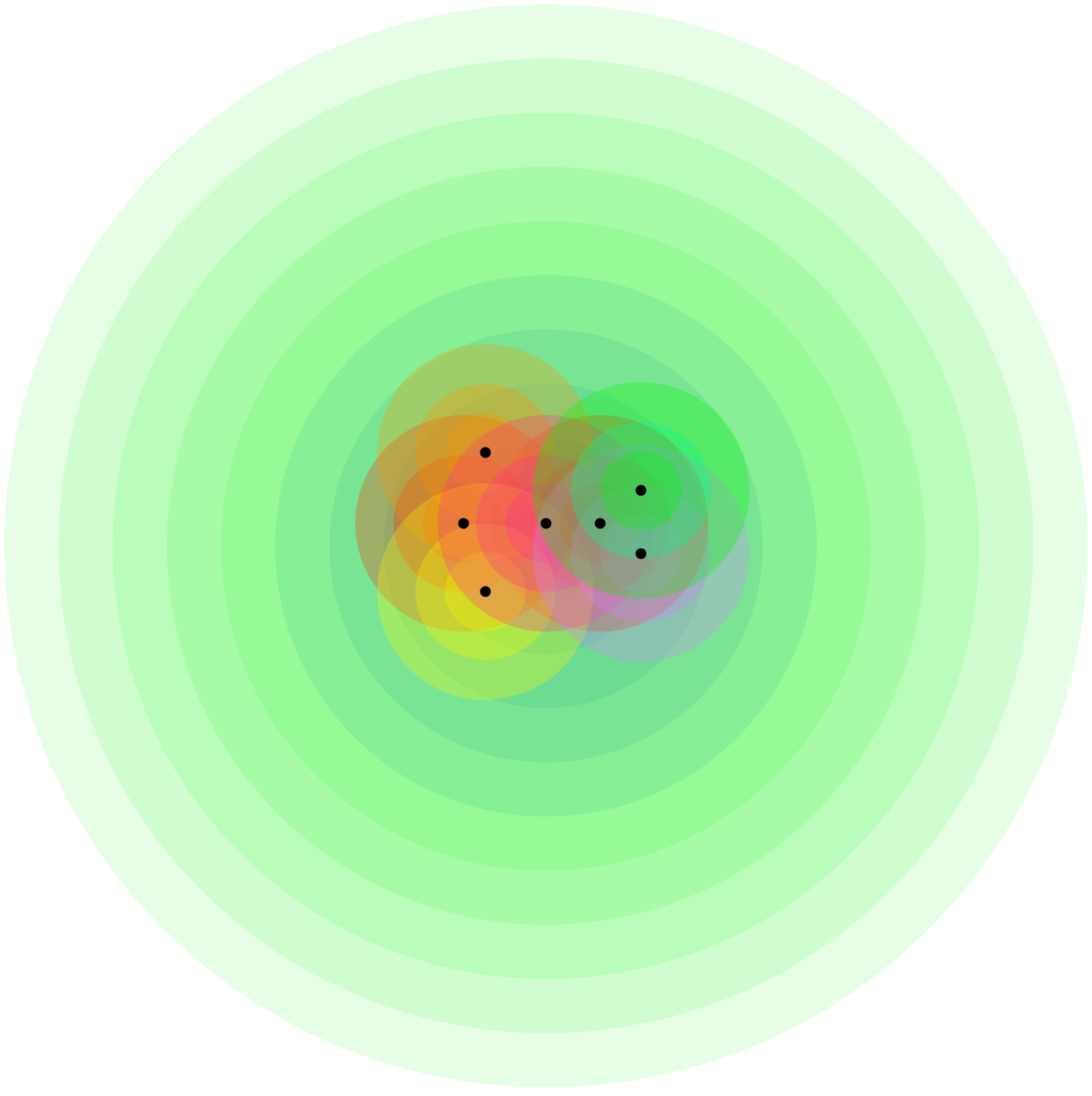
PC Gauss



Orbital basis

PC Gauss

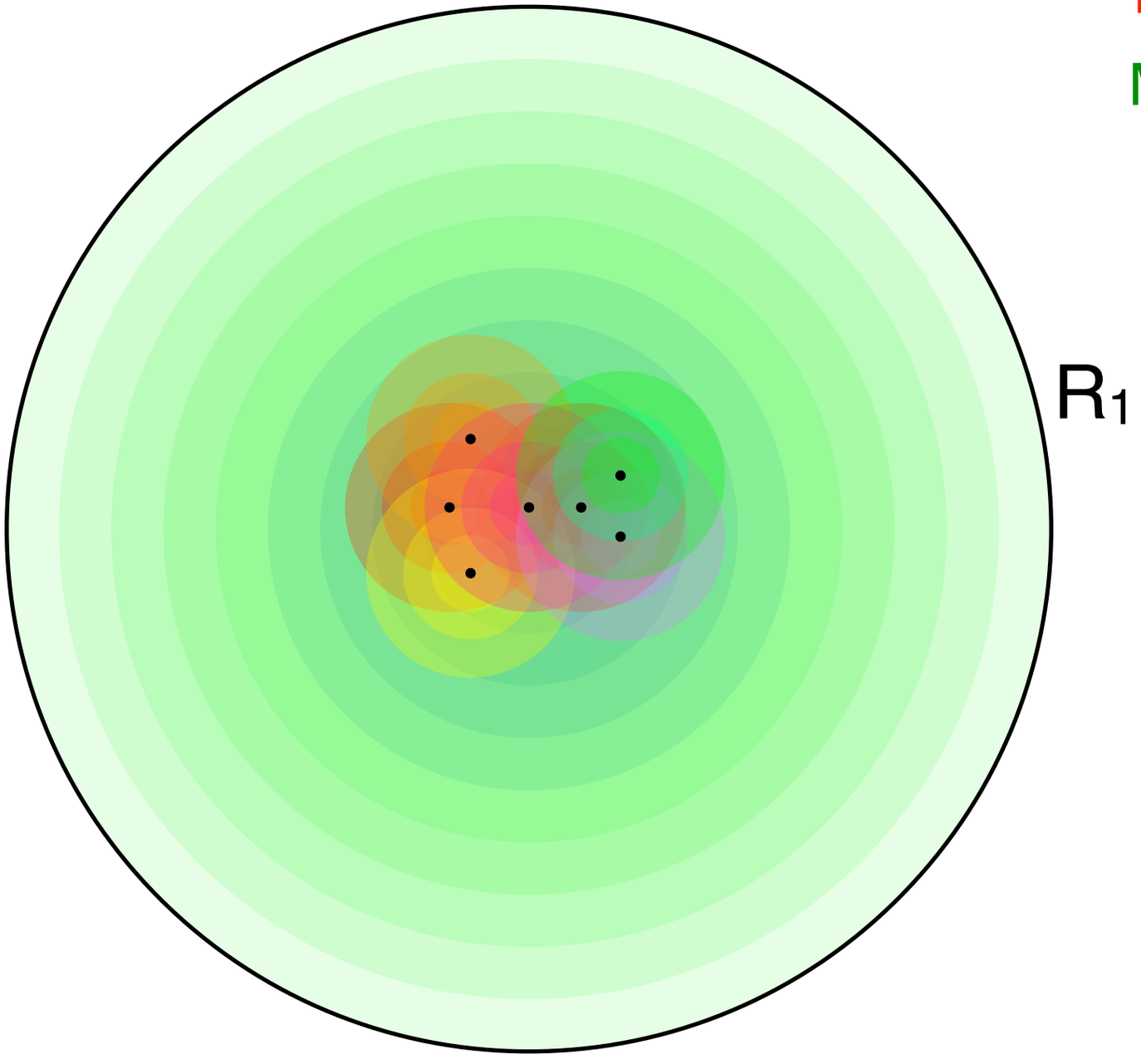
MC Gauss



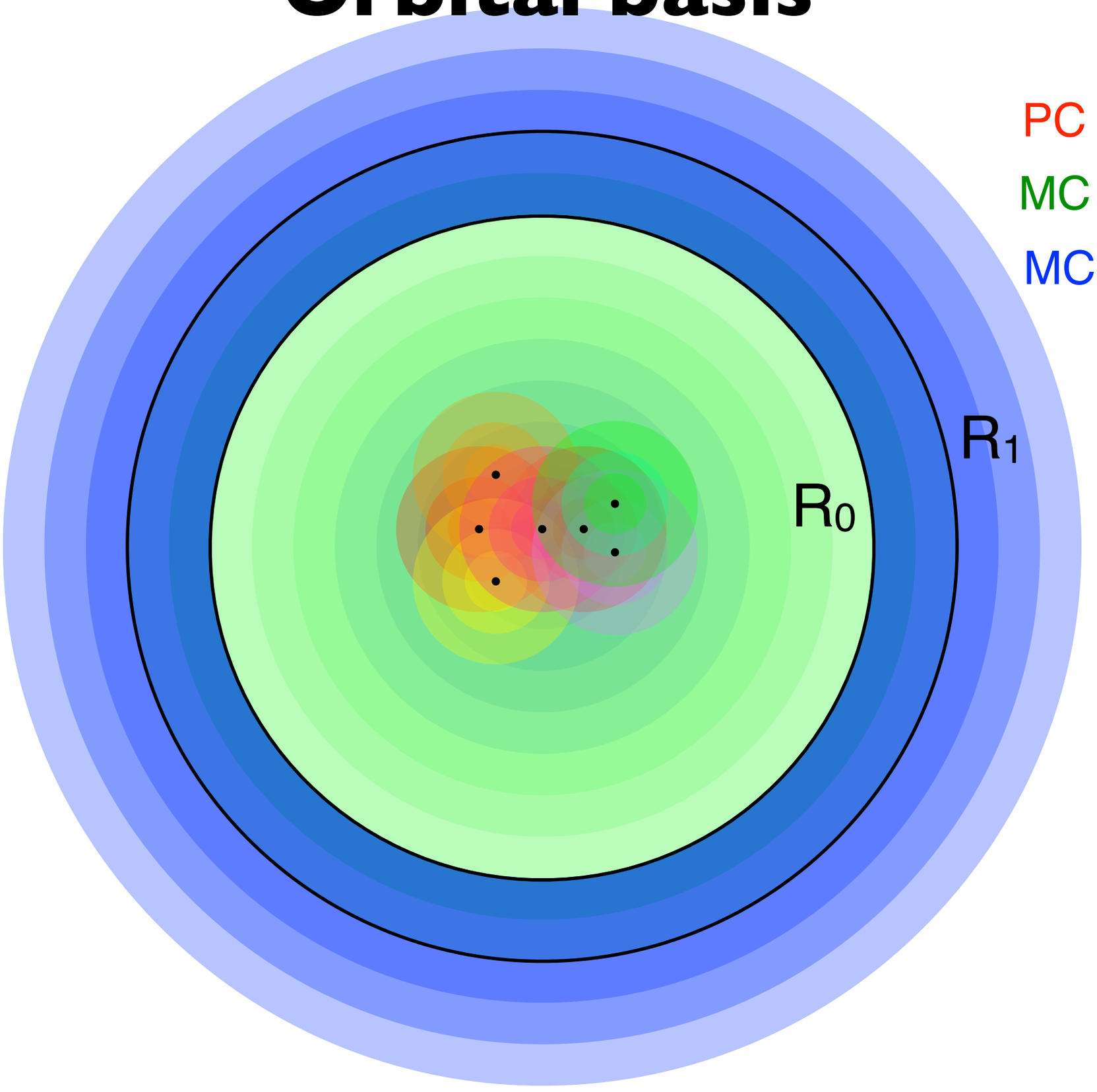
Orbital basis

PC Gauss

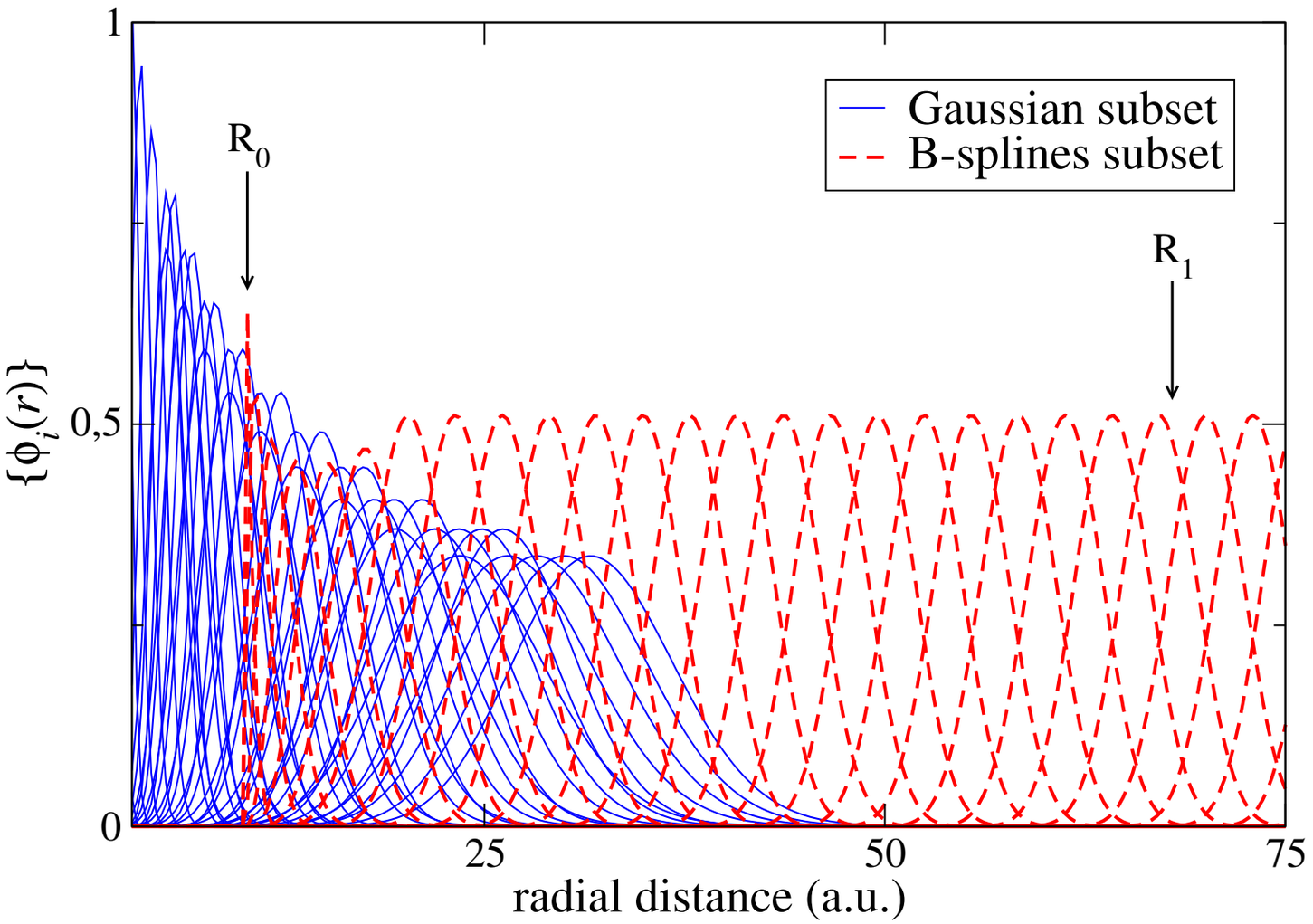
MC Gauss



Orbital basis



GABS hybrid-basis



C. Marante, L. Argenti and F. Martín, Phys. Rev. A **90**, 012506 (2014)

Gaussian functions

$$g_{\alpha lk}(\vec{r}) \propto r^{l+2k} \exp(-\alpha r^2) Y_{lm}(\hat{r})$$

✓ Poly-centric bi-electronic integrals are computed rapidly.

✓ Standard in all chemistry packages.

✳ Unsuited to reproduce the characteristic oscillatory behavior of continuum orbitals

B-splines functions

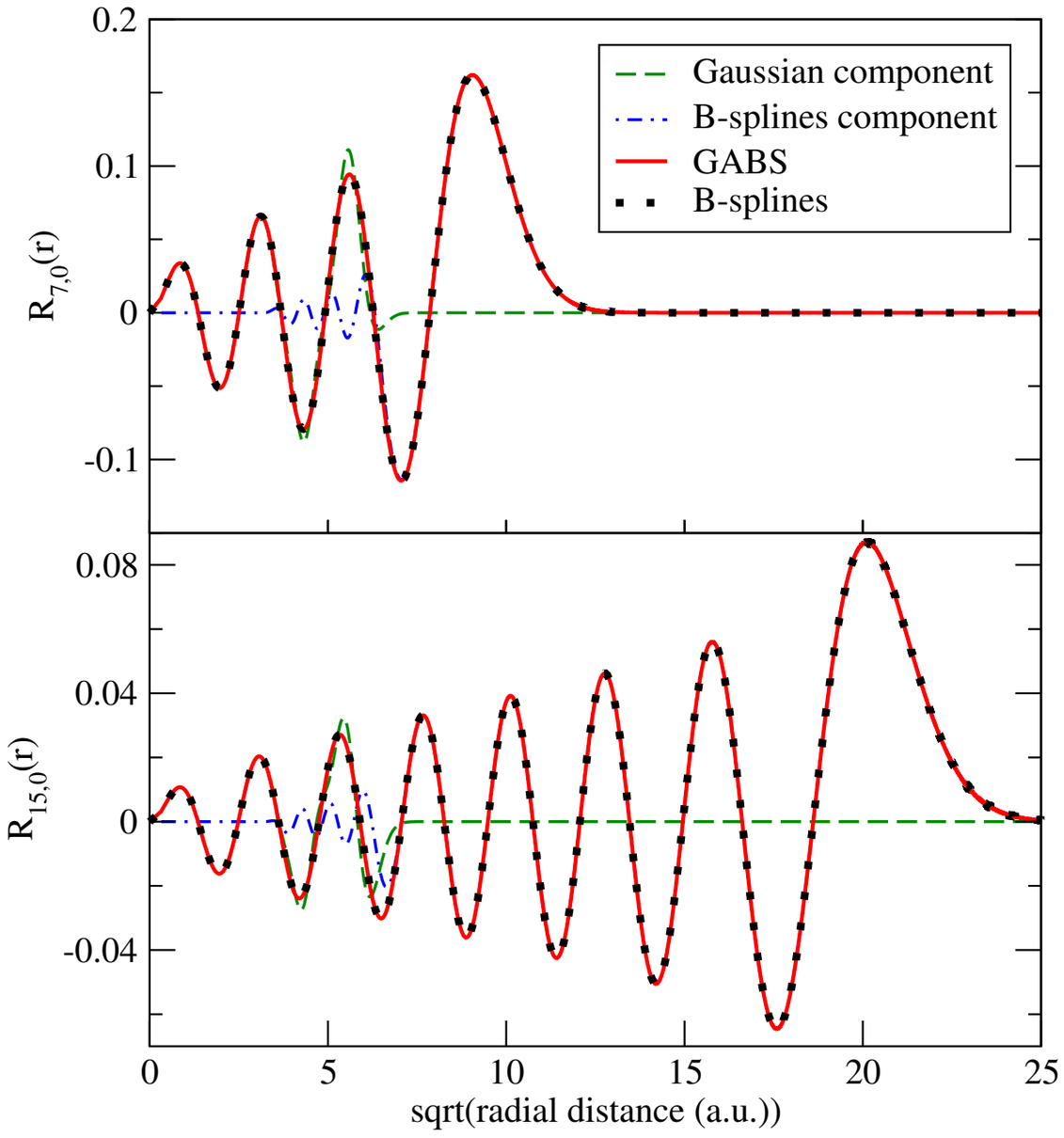
$$b_{il}(\vec{r}) \propto \frac{B_i(r)}{r} Y_{lm}(\hat{r})$$

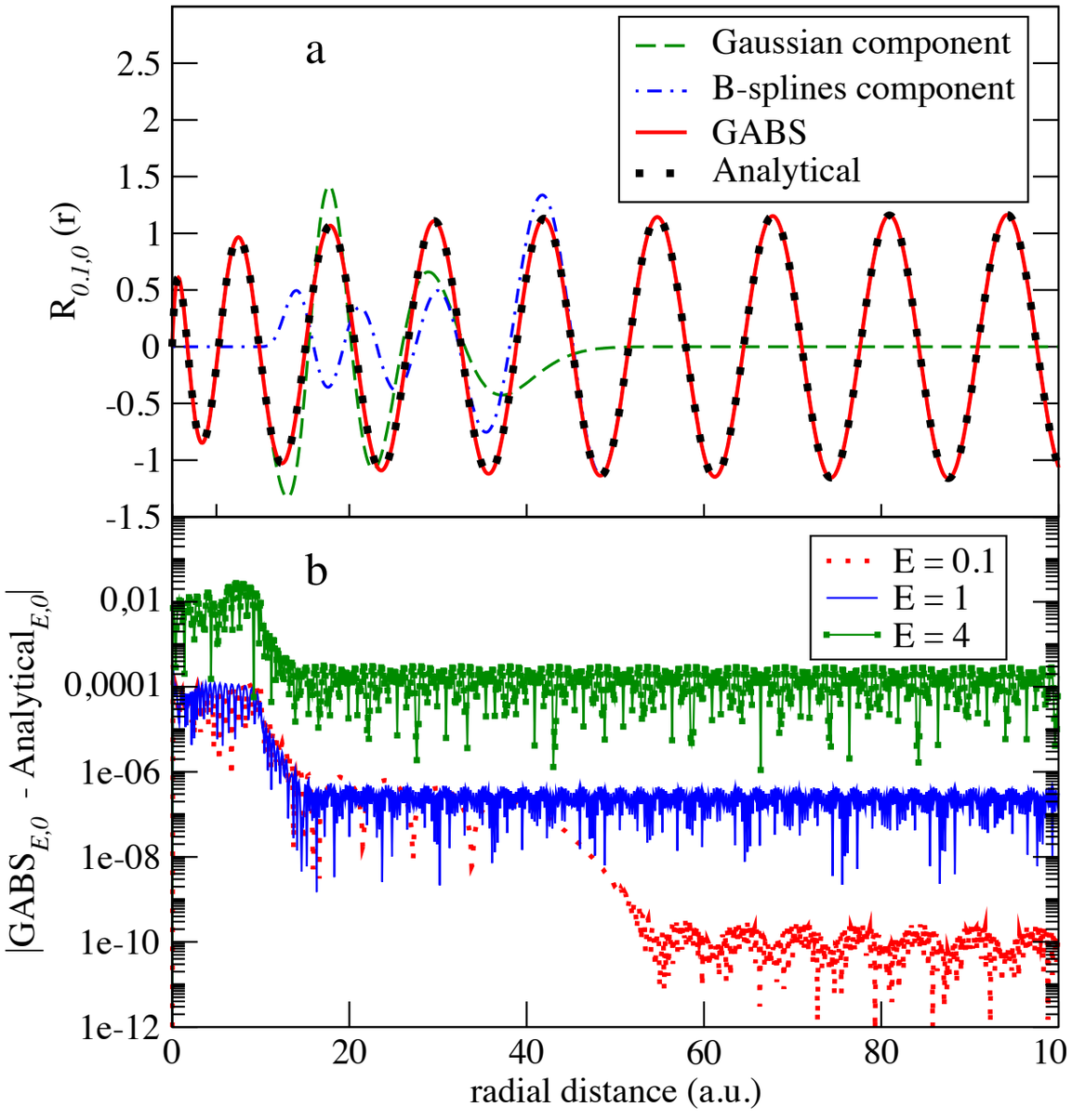
✓ Describe well the continuum orbitals rapid oscillations within a wide range of energies.

✓ Sparse matrices.

✳ Computationally expensive for poly-electronic molecules, due to poly-centric bi-electronic integrals.

GABS hybrid-basis

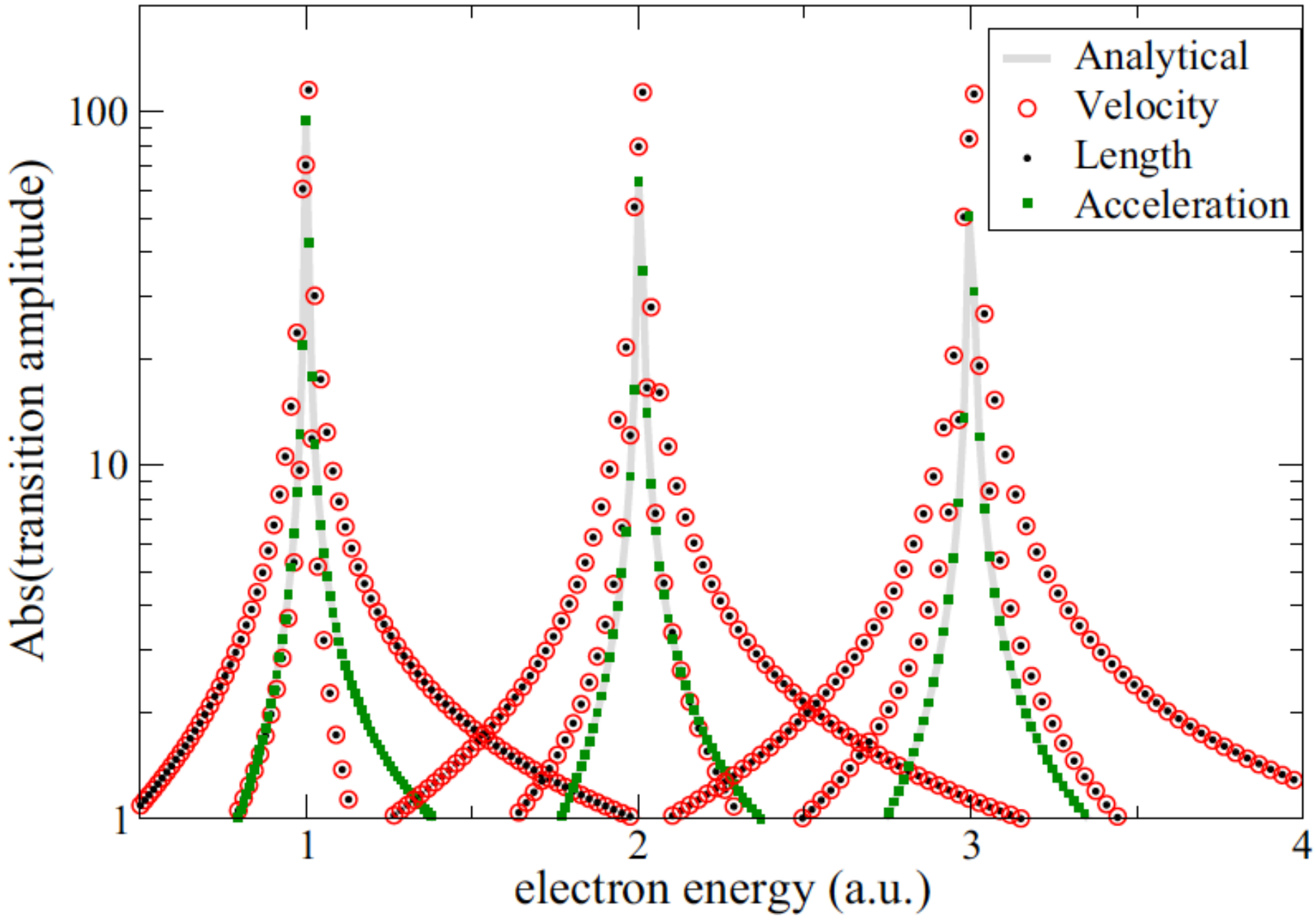




C. Marante, L. Argenti and F. Martín, Phys. Rev. A **90**, 012506 (2014)

GABS hybrid-basis

continuum-continuum transitions



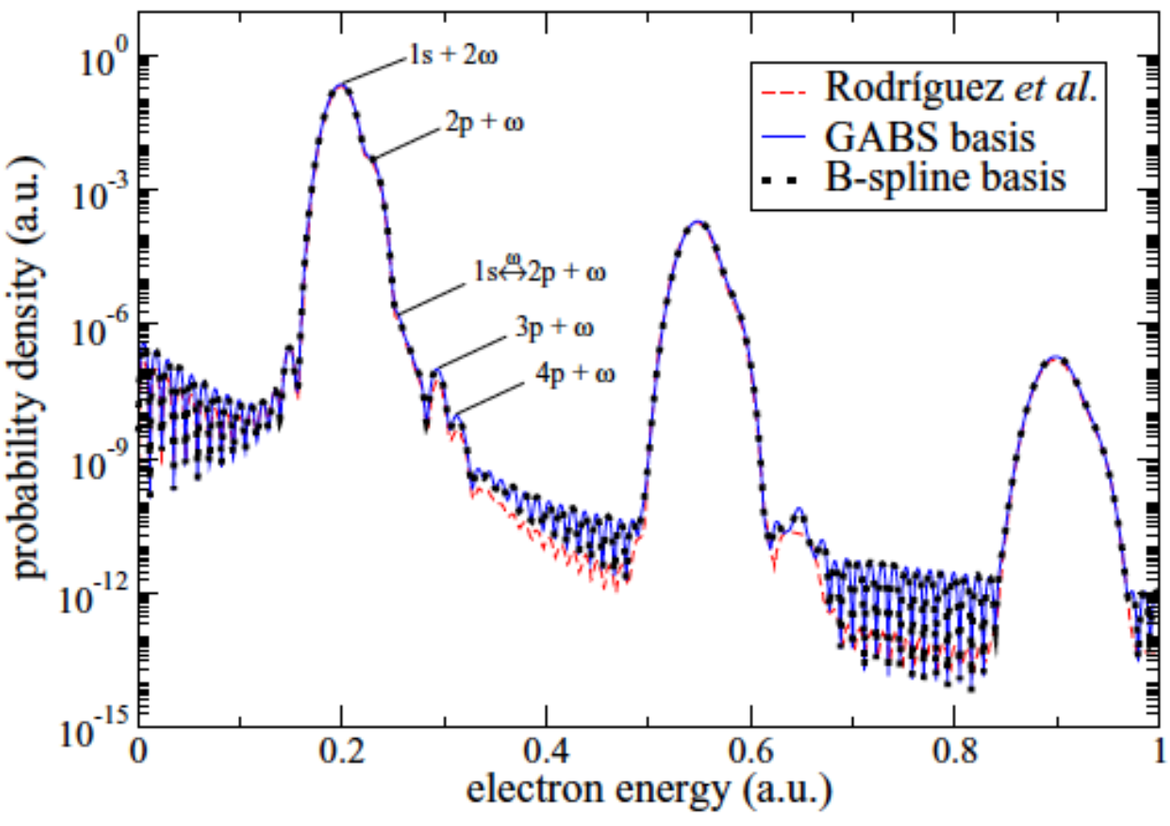
C. Marante, L. Argenti and F. Martín, Phys. Rev. A **90**, 012506 (2014)

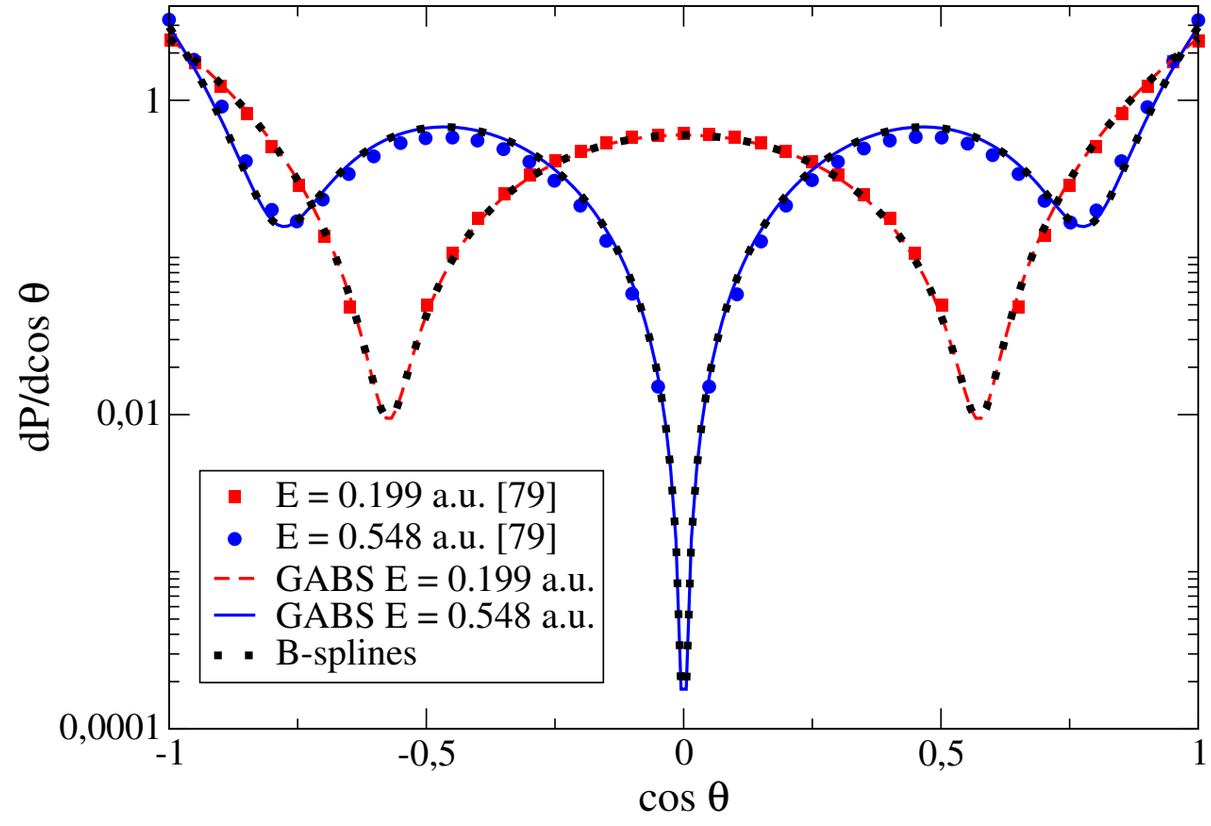
GABS hybrid-basis

$$\mathrm{H}(1s) + n\gamma_{\mathrm{UV}} \rightarrow \mathrm{H}^{+} + e^{-}_{\vec{k}}$$

$$\omega = 0.35 \text{ a.u.}$$

$$I = 14 \text{ TW/cm}^2$$





V. D. Rodriguez et al., JPB **44**, 125603 (2011)

C. Marante, L. Argenti and F. Martín, Phys. Rev. A **90**, 012506 (2014)

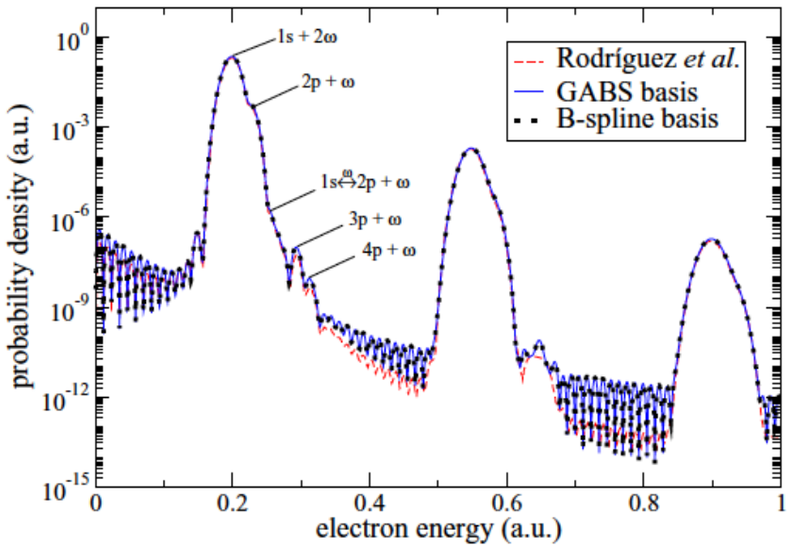
XCHEM CC atomic benchmarks

Hydrogen ATI

$$\mathrm{H}(1s) + n\gamma_{\mathrm{UV}} \rightarrow \mathrm{H}^+ + e^-_{\vec{k}}$$

$$\omega = 0.35 \text{ a.u.}$$

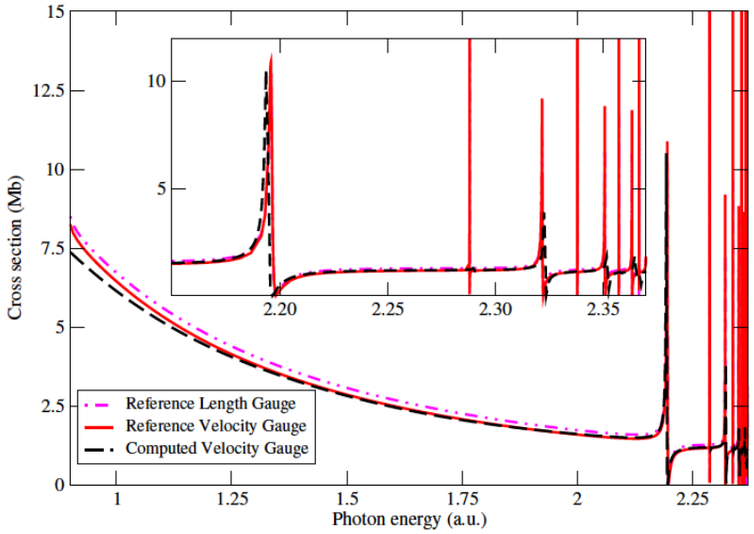
$$I = 14 \text{ TW/cm}^2$$



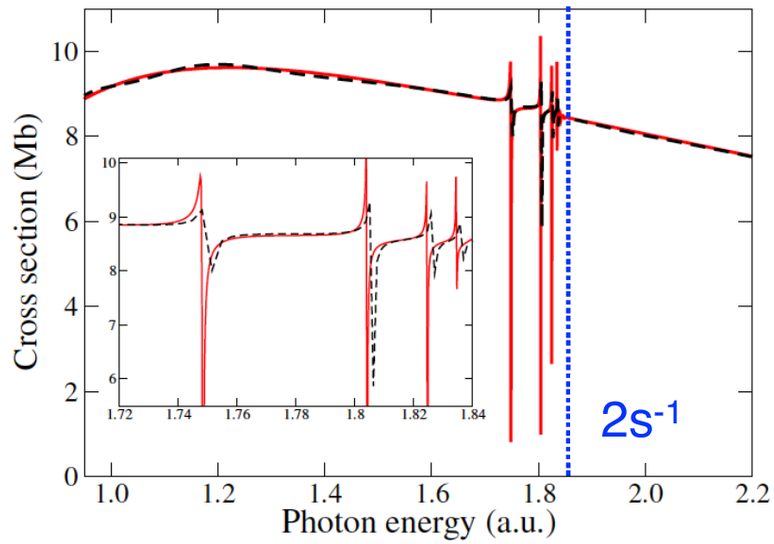
Photoionization Cross Section

$$\sigma_{\alpha E} = \frac{4\pi^2}{c(E - E_g)} |\langle \Psi^-_{\alpha E} | \hat{\varepsilon} \cdot \mathbf{P} | \Psi_g \rangle|^2$$

Helium



Neon



XCHEM

STOCK

V. D. Rodriguez et al., JPB **44**, 125603 (2011)

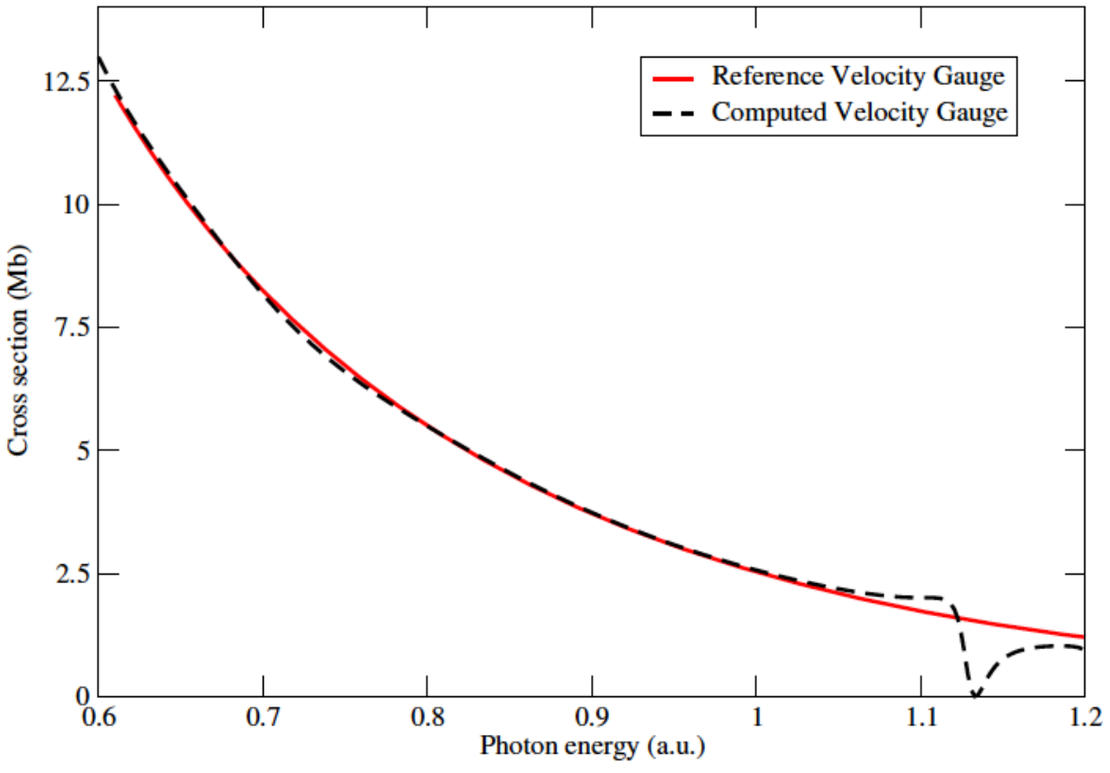
C. Marante, L. Argenti and F. Martín, Phys. Rev. A **90**, 012506 (2014)

C. Marante *et al.*, Phys. Rev. A **96**, 022507 (2017)

XCHEM CC molecular benchmarks

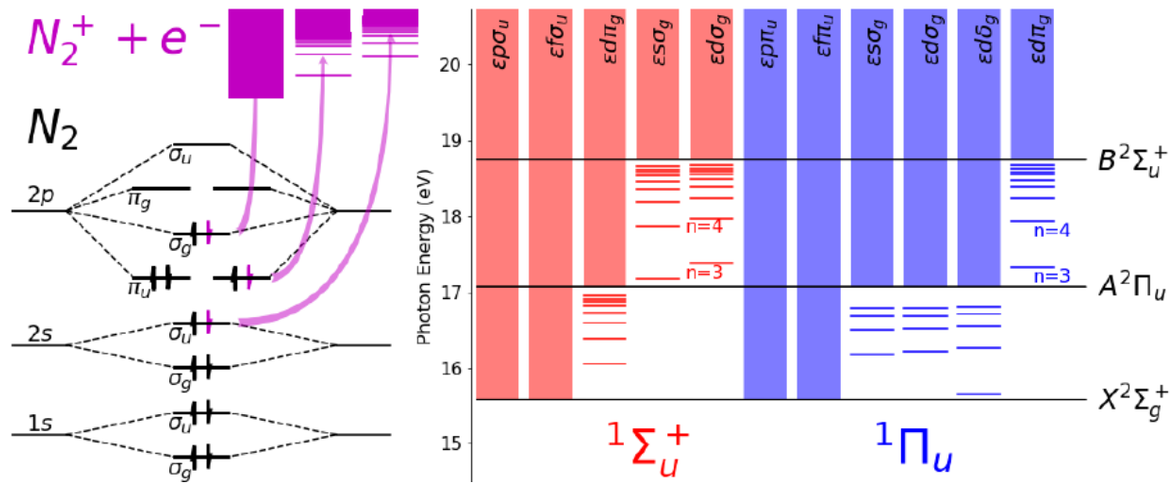
H_2 Resonances and PICS

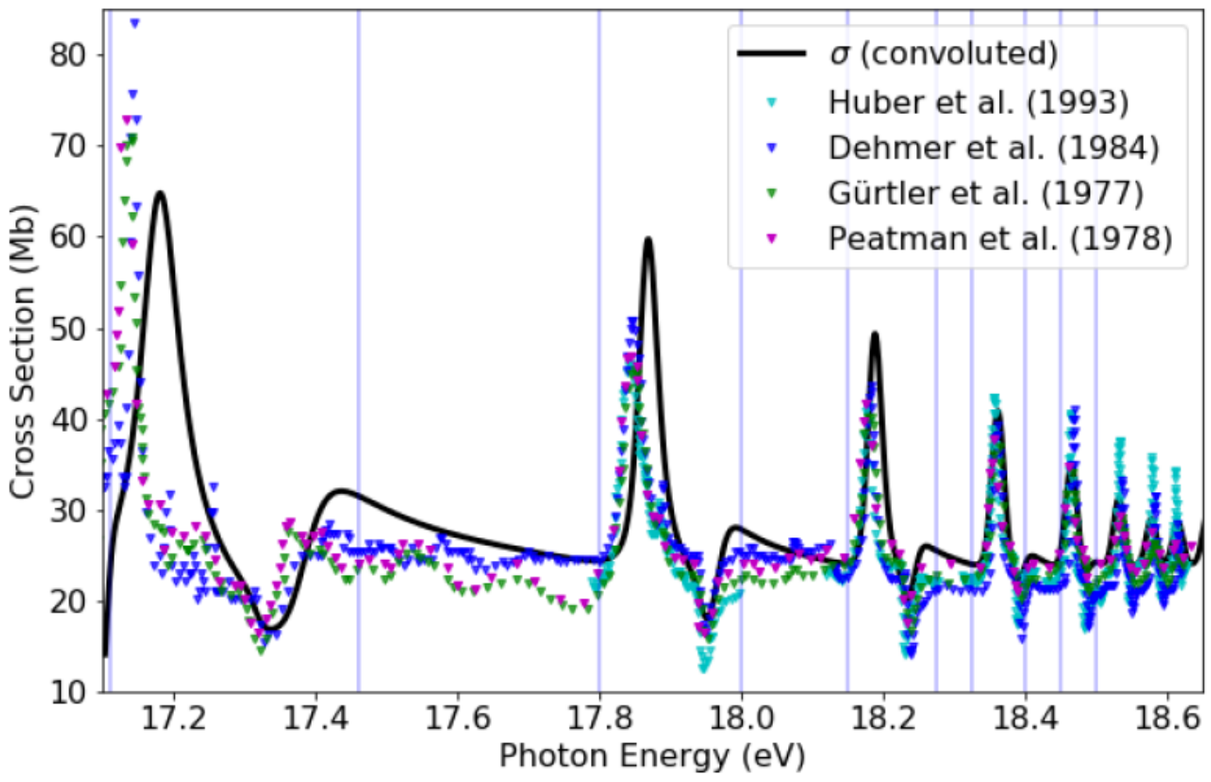
R	Resonance	E_{ref}	Γ_{ref}	E	Γ
1.0	1	0.2853	8.74(-3)	0.2847	8.94(-3)
1.0	2	0.3708	1.89(-3)	0.3703	1.97(-3)
1.0	3	0.3808	2.71(-4)	0.3809	2.86(-4)
1.4	1	-3.592(-2)	1.54(-2)	-3.602(-2)	1.45(-2)
1.4	2	4.237(-2)	3.58(-3)	4.206(-2)	3.89(-3)
1.4	3	4.794(-2)	6.21(-4)	4.792(-2)	5.88(-4)
2.0	1	-0.2926	2.55(-2)	-0.2899	2.33(-2)
2.0	2	-0.2236	3.52(-3)	-0.2225	1.39(-3)
2.0	3	-0.2212	3.94(-3)	-0.2223	6.45(-3)
3.0	1	-0.4783	4.10(-2)	-0.4673	3.67(-2)
3.0	2	-0.4238	2.80(-3)	-0.4230	2.21(-3)
3.0	3	-0.4177	1.15(-2)	-0.4170	9.73(-3)



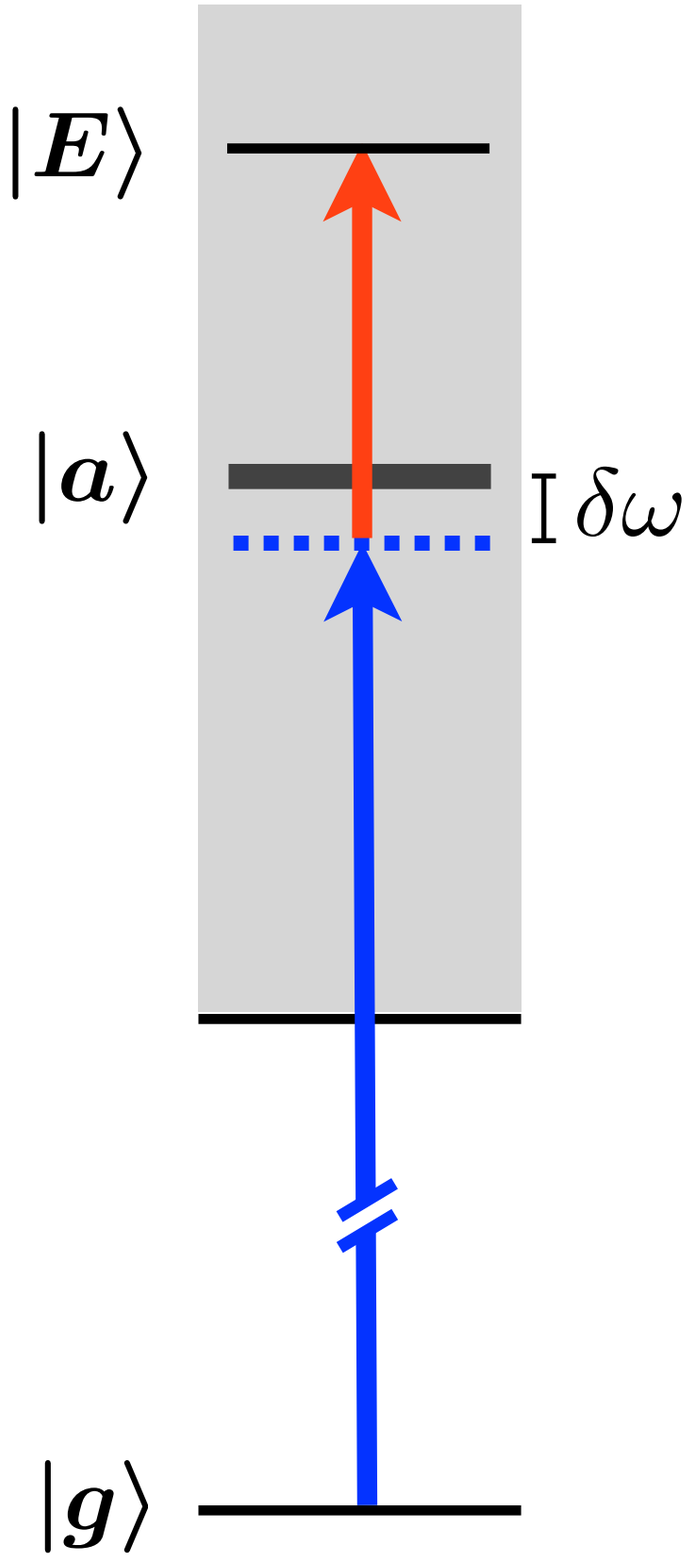
C. Marante *et al.*, J. Chem. Theory Comput. **13**, 499 (2017)

N_2 Resonances and PICS





M. Klinker *et al.*, J. Phys. Chem. Lett. **9**, 756 (2018)



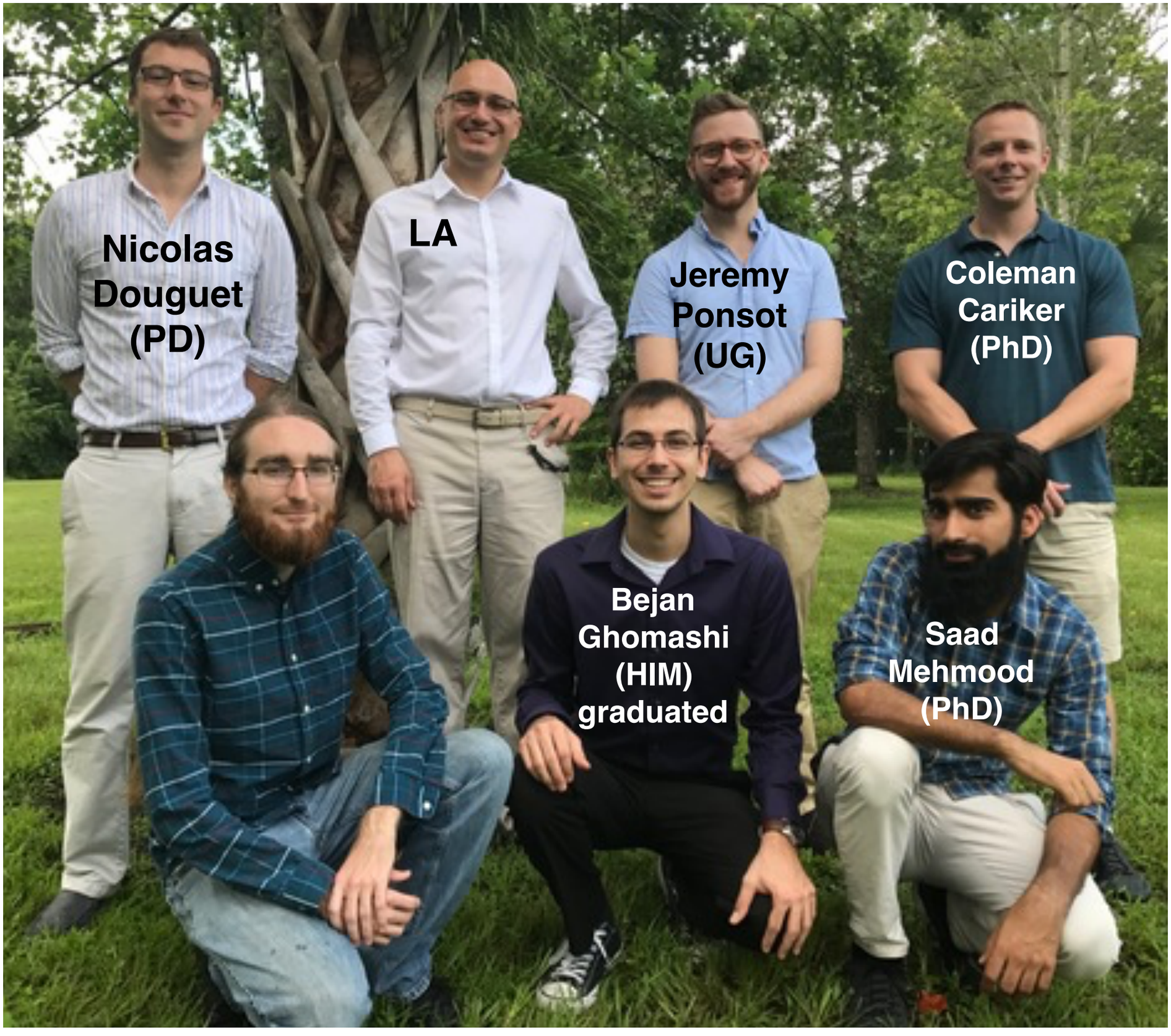
Conclusions

1. attosecond pump-probe spectroscopies in perturbative regimes allow to reconstruct coherent resonant dynamics in the electronic continuum.

2. In poly-electronic systems, B-spline close-coupling approaches can provide quantitative predictions, which often require explicit TDSE simulations.

3. A large set of electronic-structure software for bound and stationary transitions can be (and is being) leveraged to compute time dependent processes: application from several competing tools will soon come to fruition.

Theoretical Attosecond Spectroscopy @ UCF



Didarul Ahlam (PhD)

UCF

NSF