Quantum chemistry approaches for electronic structure II: single- and many-electron bound-continuum transitions

Vitali Averbukh

Quantum Optics and Laser Science, Blackett Laboratory, Imperial College London

Single-electron transition: Photoionization

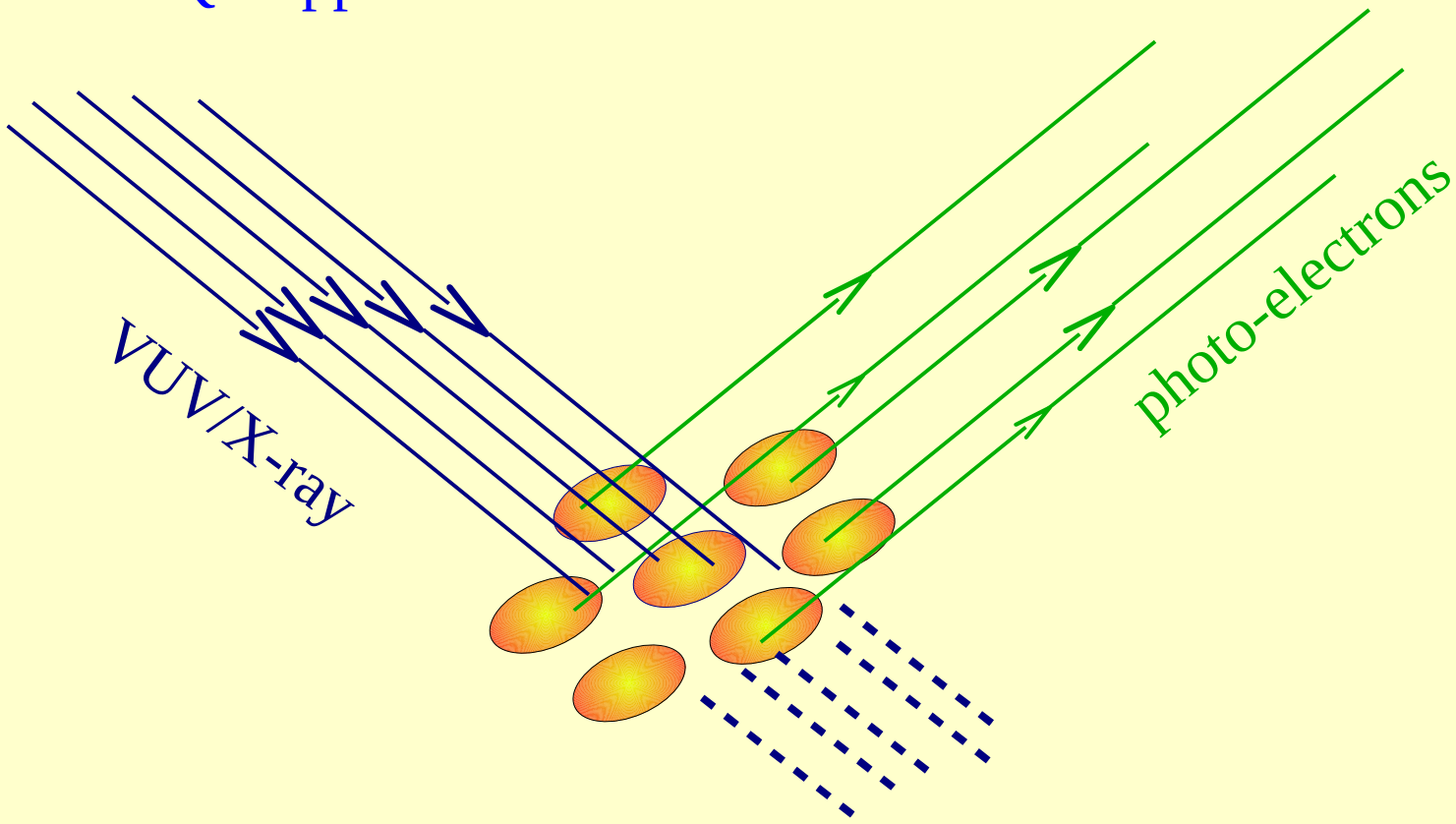
$$\sigma_E \propto E \left| \langle \Phi | \sum_i \vec{r}_i | \chi_E \rangle \right|^2$$

A bound (typically the ground) state
$\langle \Phi | \Phi \rangle = 1$

A continuum state
$\langle \chi_E | \chi_{E'} \rangle = \delta(E' - E)$

✔ Standard QC applies

✗ Standard QC does not apply



Ab initio approach: ADC

The purpose: *ab initio* calculation of Φ, χ wave functions in $\sigma_E \propto E \left| \langle \Phi | \Sigma \vec{r}_i | \chi_E \rangle \right|^2$

The method: Algebraic Diagrammatic Construction (**ADC**)
in the Intermediate State Representation (**ISR**)

$$\Psi = \sum_{ia} Y_i^a \Psi_i^a + \sum_{ijab} Y_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{ijkabc} Y_{ijk}^{abc} \Psi_{ijk}^{abc} + \ldots$$

CI-like expansion

1h1p single excitations

2h2p double excitations

3h3p triple excitations

$$\Psi_i^a = c_a^\dagger c_i \Psi_0, \; \Psi_{ij}^{ab} = c_a^\dagger c_b^\dagger c_i c_j \Psi_0, \ldots, \text{where } \Psi_0 = \Phi_0^{HF} + \Psi_0^{(1)} + \Psi_0^{(2)} + \ldots$$

ADC: Schirmer and Cederbaum (since 1980s)
ISR: Schirmer and Trofimov (since 1990s)

MBPT for The ground state

ADC-ISR for photoionization: Averbukh, Cederbaum, and co-workers (2009)

The problems

☹ *Problem №1:* $\langle \chi_E | \chi_{E'} \rangle = \delta(E'-E)$ is not fulfilled in an $\mathscr{L}^2$ *basis*, instead we have $\langle \chi_j | \chi_{j'} \rangle = \delta_{j,j'}$

☹ *Problem №2:* the energies ε_j obtained in an $\mathscr{L}^2$ *basis* are discrete ⇒ σ_E can not be obtained at an arbitrary E

Substitution of χ_ε obtained in $\mathscr{L}^2$ *basis* into $A=\left|\langle \Phi | \hat{A} | \chi_E \rangle\right|^2$ would give wrong dimensions for the physical quantity A

!!!

A solution: Stieltjes-Chebyscheff moment theory

Spectral moments of $\hat{H}$ with $\hat{A}|\Phi\rangle$ can be calculated using either true or discretized continuum functions:

$$M_n = \langle \Phi | \hat{A}^\dagger \hat{H}^n \hat{A} | \Phi \rangle = \int dE \, \langle \Phi | \hat{A}^\dagger \hat{H}^n | \chi_E \rangle \langle \chi_E | \hat{A} | \Phi \rangle = \int dE \, E^n |\langle \Phi | \hat{A} | \chi_E \rangle|^2$$

$$M_n = \langle \Phi | \hat{A}^\dagger \hat{H}^n \hat{A} | \Phi \rangle = \Sigma_j \langle \Phi | \hat{A}^\dagger \hat{H}^n | \chi_j \rangle \langle \chi_j | \hat{A} | \Phi \rangle = \Sigma_j \, E_j^{\,n} |\langle \Phi | \hat{A} | \chi_j \rangle|^2$$

Convergence problems ⇒ negative n

One can use the techniques of moment theory to obtain the best approximation for $f(E)=|\langle \Phi | \hat{A} | \chi_E \rangle|^2$ using a finite number of M_n's

P. W. Langhoff (1973)

☹ The *apparent* price: full spectrum of $\{\chi_j\}$ is required to calculate the M_n's

Not feasible for large systems!

Overcoming the full diagonalizaiton bottleneck: Stieljes imaging with Lanczos pseudospectrum

Krylov states: $\varphi_k = \hat{H}^k|\Phi\rangle$, $k = 0, ..., N$

Gram-Schmidt orthonormalization → Lanczos basis $\{\psi_j\}$, $j = 0, ..., N$

Representation of $\hat{H}$ in Lanczos basis: $\hat{H}^{(N)} = \Sigma_{j,k} |\psi_j\rangle\langle\psi_j| \hat{H} |\psi_k\rangle\langle\psi_k|$

Approximation [Meyer & Pal, 1989]:

$$F(\hat{H}) \approx F(\hat{H}^{(N)})$$

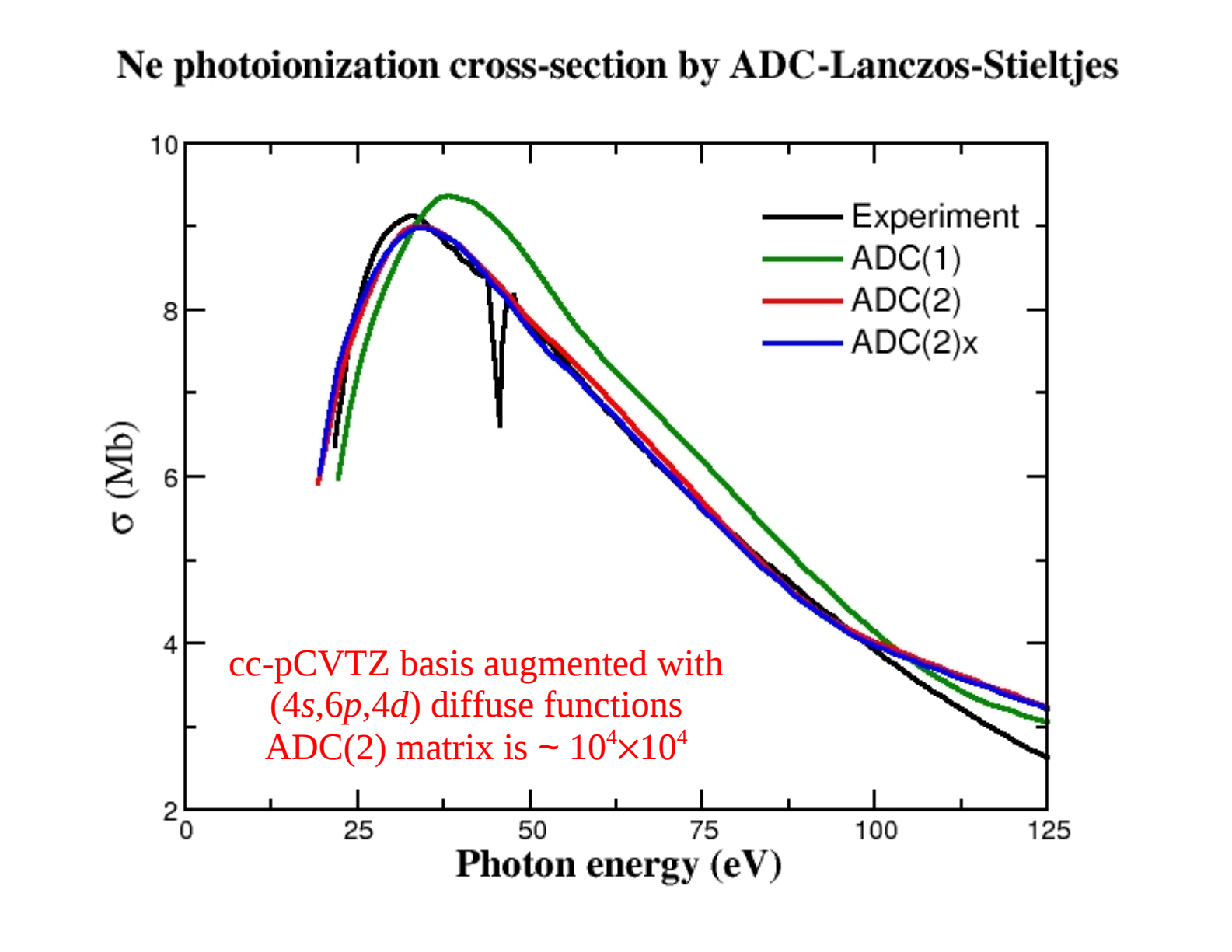
(exact for $\langle\Phi| F(\hat{H}) |\Phi\rangle$, if $F(x)=x^n$, $n=0, ..., 2N$)

Application to Stieltjes imaging:

$$M_n \approx \Sigma^N_{j=0} (E_j^{(N)})^n |\langle\Phi|\hat{A}|\chi_j\rangle|^2,$$

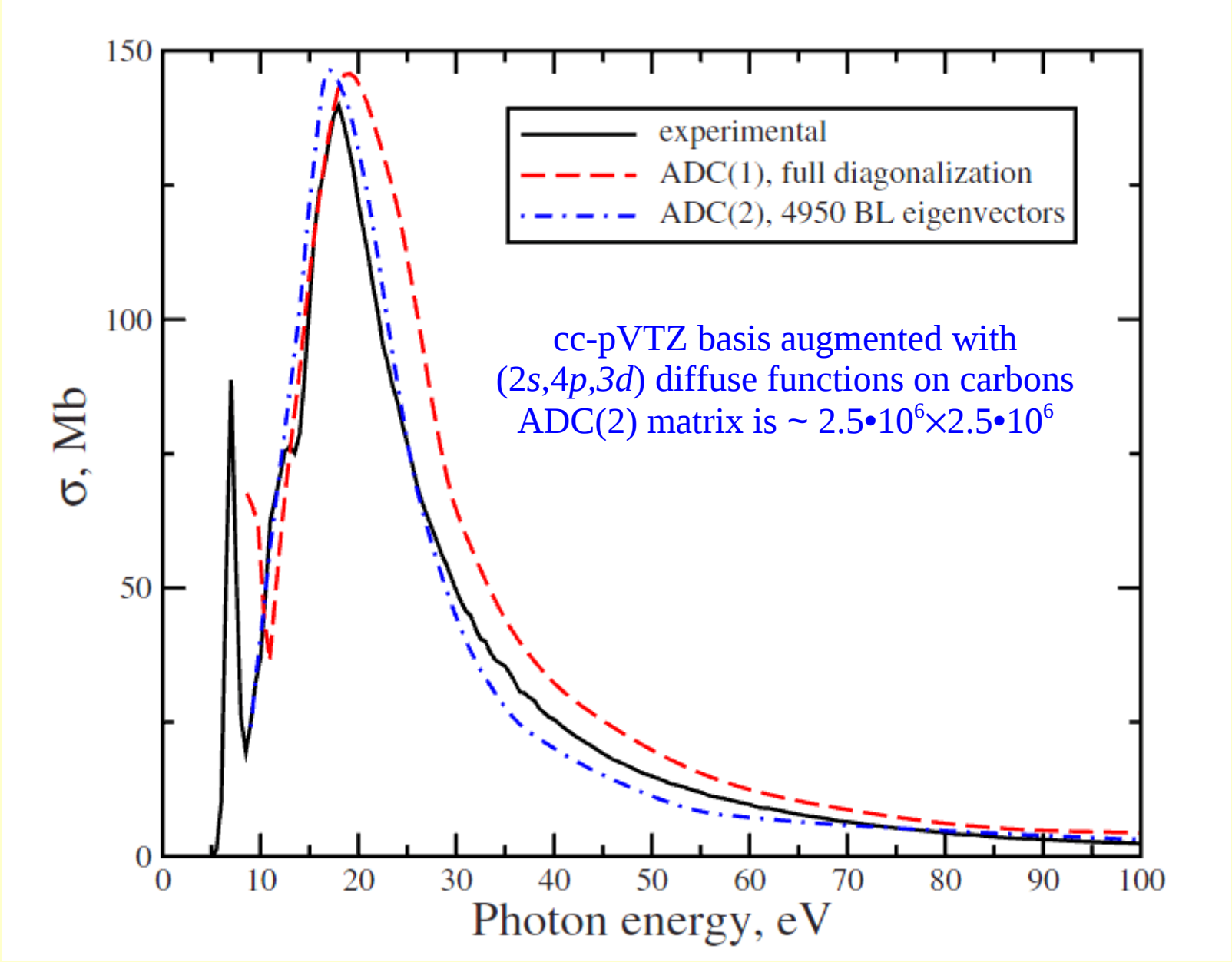
where $|\chi_j\rangle$ are obtained by Lanczos diagonalization after N iterations

Testing the use of Lanczos pseudospectrum in Stieltjes imaging



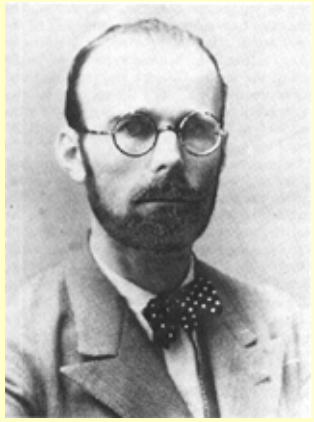
[Gokhberg, Vysotskiy & Cederbaum, Storchi & Tarantelli, Averbukh, JCP **130**, 064104 (2009)]

Application to photoionization cross-section: Benzene



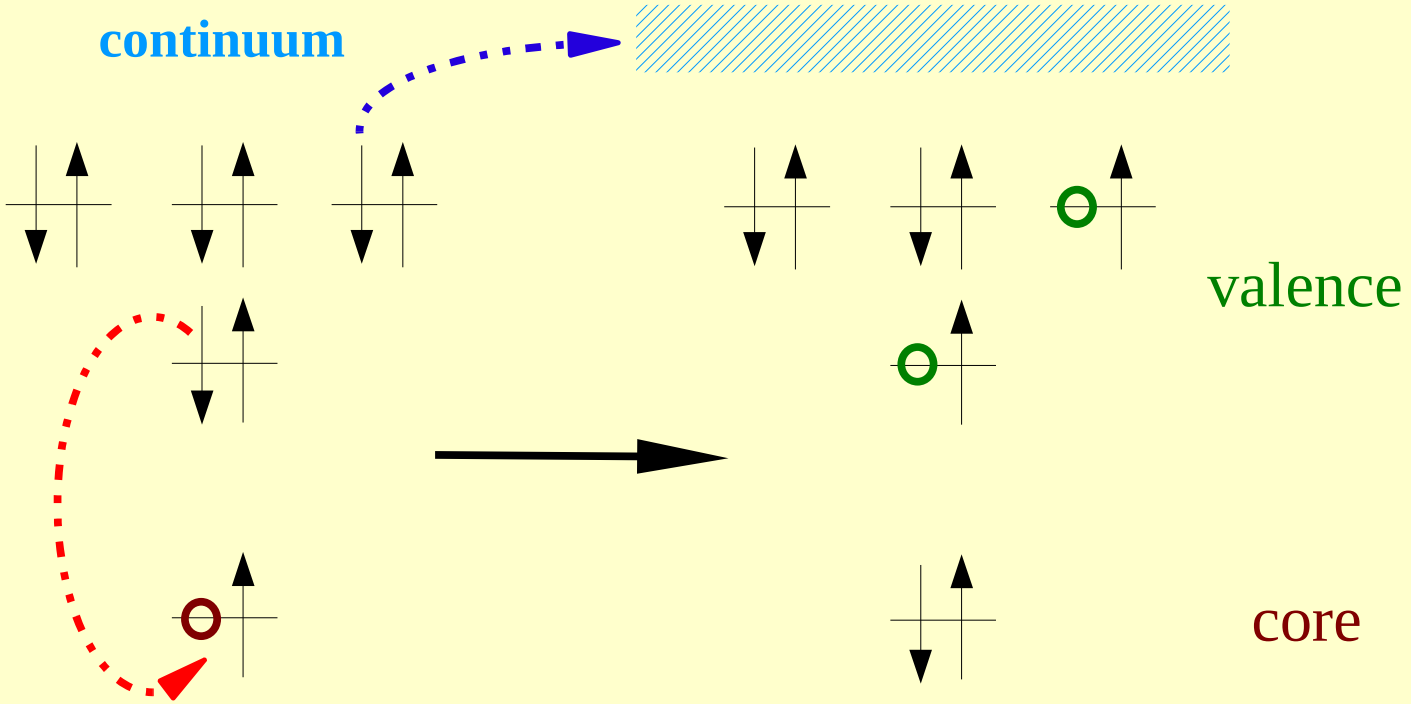
[Gokhberg, Vysotskiy & Cederbaum, Storchi & Tarantelli, Averbukh, JCP **130**, 064104 (2009)]

The basic two-electron process: Auger effect



Pierre Auger

"Sur L'effet Photoélectrique Composé" (1925)



Photoelectrons: $E_k = \hbar\omega - E(A^+)$

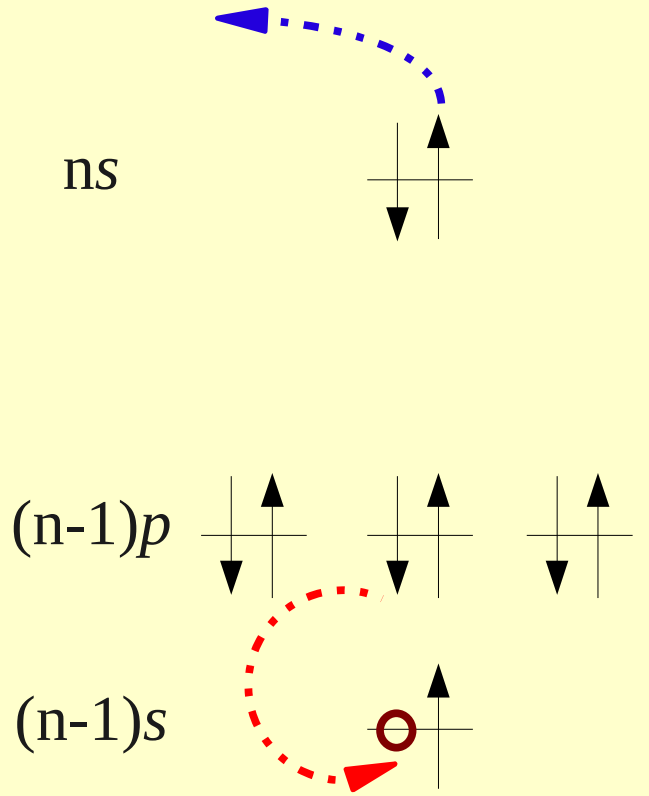
Auger electrons: $E_k = E(A^+) - E(A^{++})$

Gregor Wentzel

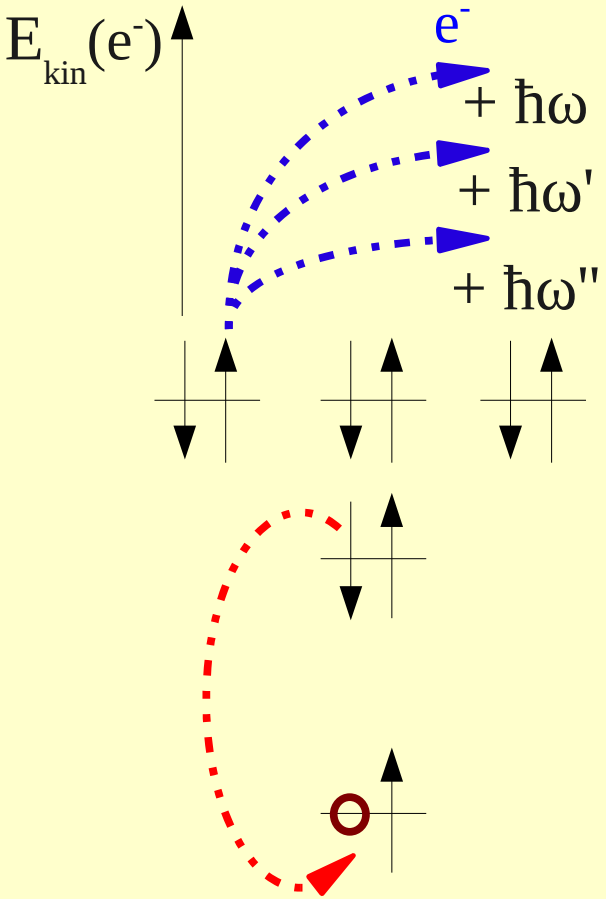
$$\Gamma_{\text{Auger}} = 2\pi \left| \langle \psi_{v1}(r_1)\, \psi_{v2}(r_2) \,|\, e^2/r_{12} \,|\, \psi_{\text{core}}(r_1)\, \psi_{\text{continuum}}(r_2) \rangle \right|^2$$

"Über strahlunglose Quantensprűnge" (1927)

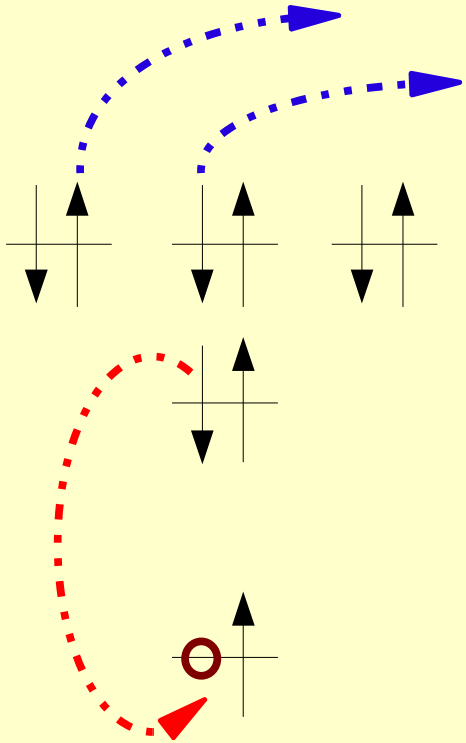
More Auger processes



Coster-Kronig decay
(sub-fs lifetimes)



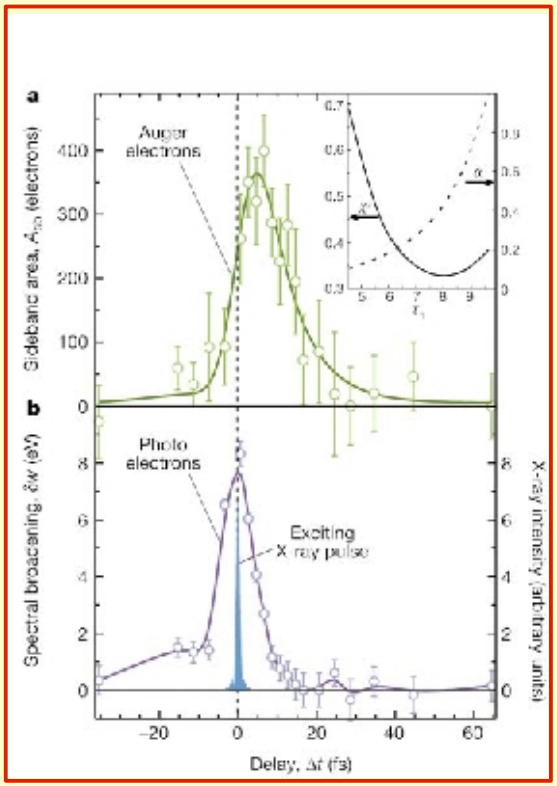
Radiative Auger decay

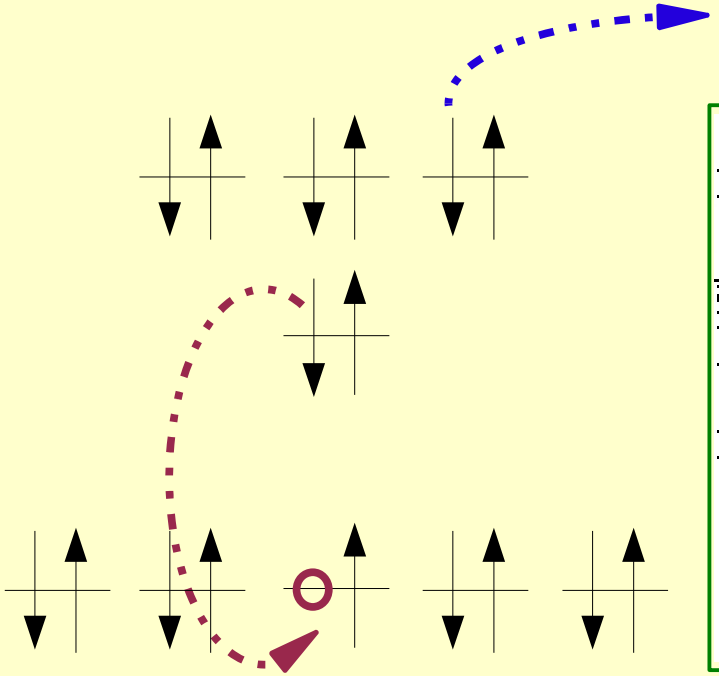


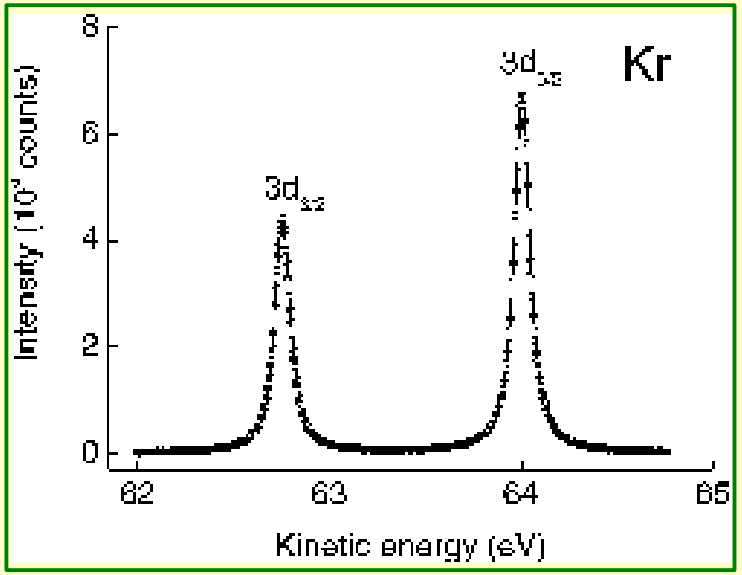
Double Auger decay

Motivation: Attosecond science

Time-resolved vs. energy-resolved Auger decay in ($3d^{-1}$) Kr^{+}







[Drescher *et al.*, Nature **419**, 803 (2002)]

[Jurvansuu *et al.*, PRA **64**, 012503 (2001)]

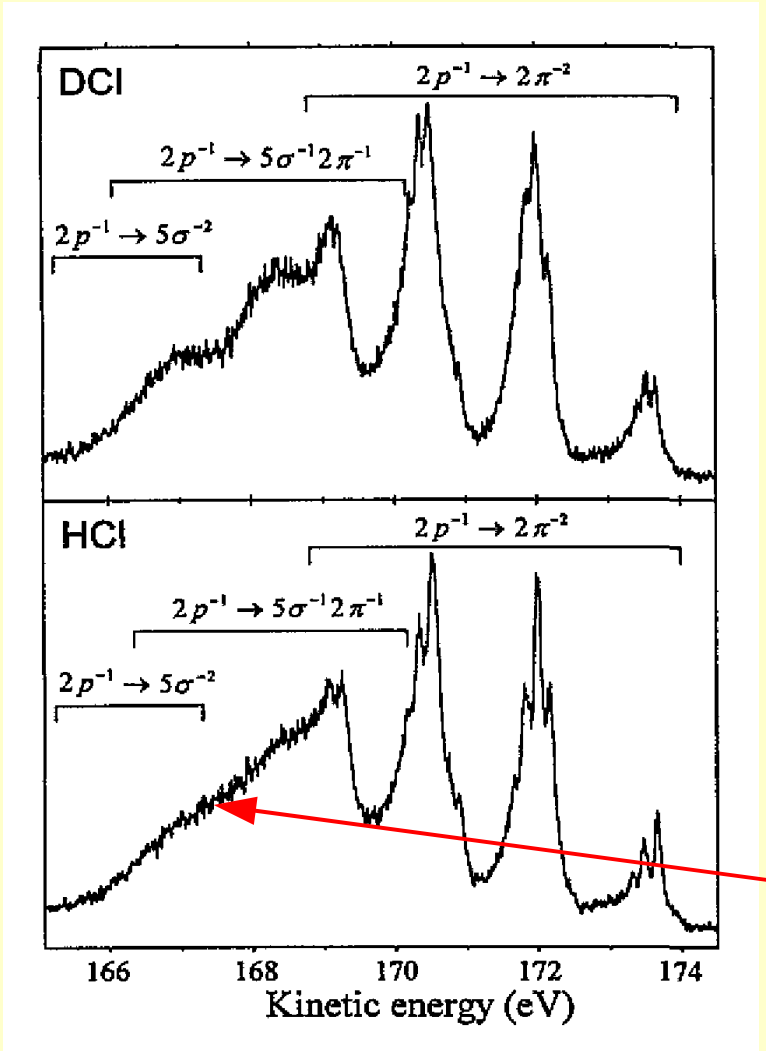
$\tau \approx 7.9$ fs

$\Gamma \approx 88$ meV

Is it always straightforward to draw such a correspondence

???

Molecular Auger decay: The effect of nuclear motion



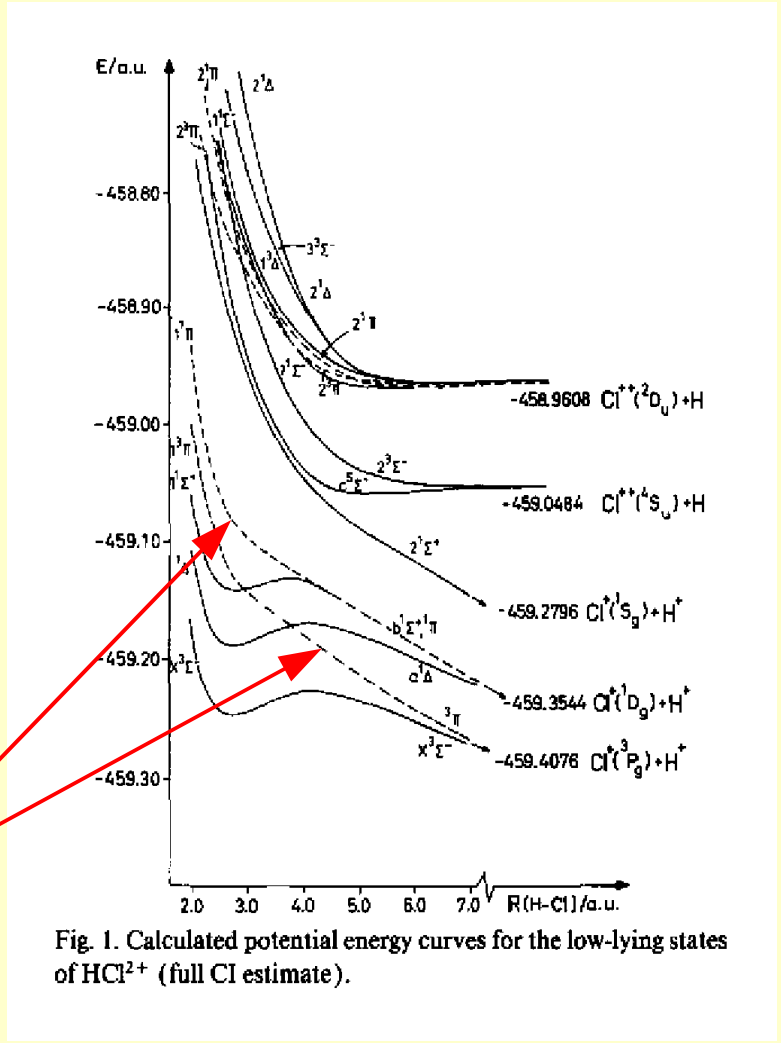
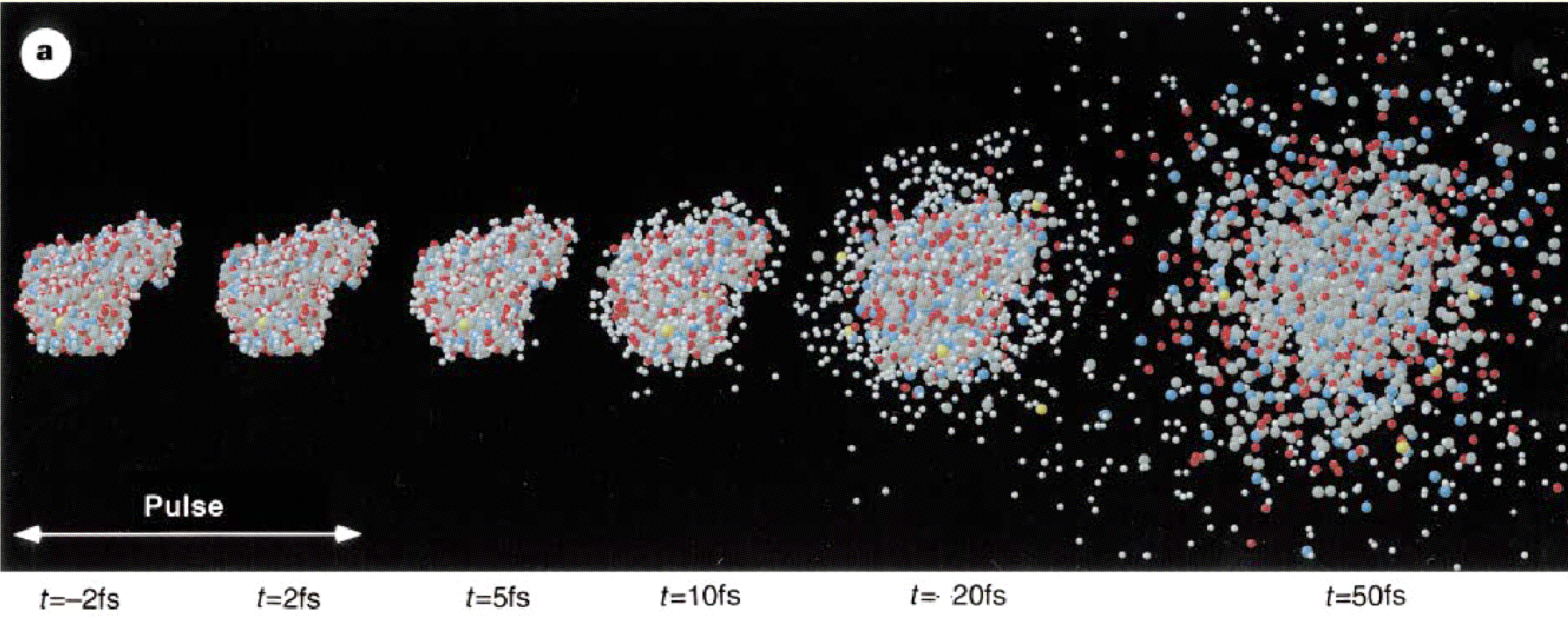


Fig. 1. Calculated potential energy curves for the low-lying states of HCl^{2+} (full CI estimate).

[Aksela *et al.*, JPB **28**, 4259 (1995)] [Banichevich *et al.*, CP **121**, 351 (1988)]

Auger transitions to dissociative states "produce very wide ... lineshapes, ... which rules out the possibility of their detailed study".

Motivation: XFEL science

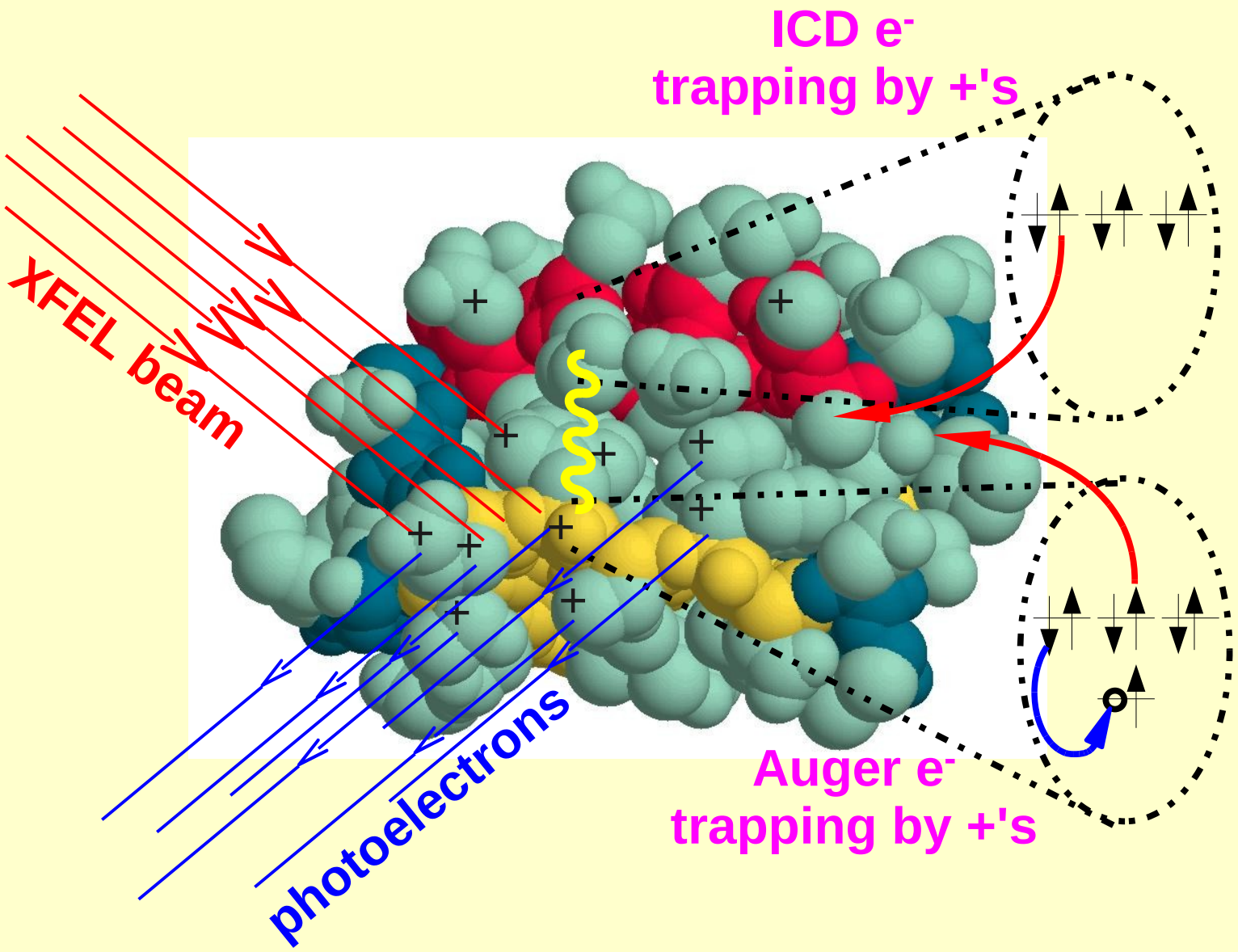


"*Potential for biomolecular imaging with femtosecond X-ray pulses*",
R. Neutze, R. Wouts, D. van der Spoel, E. Weckert & J. Hajdu, *Nature* **406**, 752 (2000).

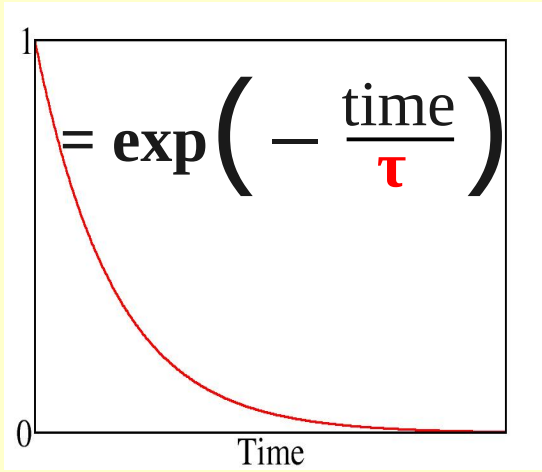
Obtain a diffraction image of a single molecule using a short pulse of high-intensity X-rays before the molecule is destroyed by radiation damage

"**Radiation damage**" - Coulombic explosion due to accumulation of a large number of positive charges

Macromolecule-XFEL interaction: Schematic picture



Survival probability $\{ \uparrow\downarrow \; \circ \} =$



State of the art radiation damage simulations rely on the isolated-species lifetimes (**τ**) for the intra-atomic processes and disregard the inter-atomic processes completely...

Open questions

- How different is the ***time scale*** of a core hole decay in a charged environment from the one in a singly ionized species**?**

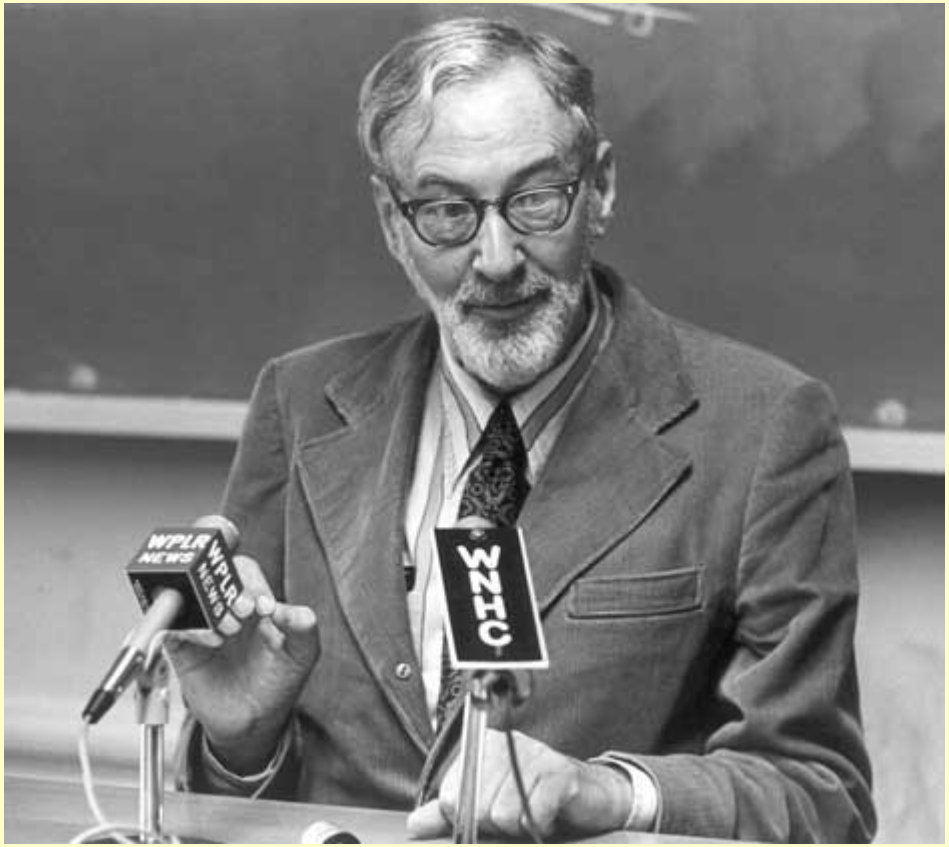
- Does the core hole dynamics in a highly charged environment follow the familiar ***exponential pattern*****?**

- Can one ***control*** the time scale of the electronic decay by shaping the XFEL pulse or by using an additional laser source**?**

- Can we follow the electronic decay dynamics in ***molecules and clusters*** directly using the ***attosecond streaking*** technique?

- What ***new electronic decay processes*** are possible in multiply charged and/or laser-driven systems?

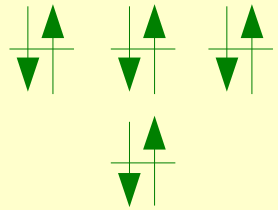
Simple quantum chemical theory for singly ionized states: Koopmans theorem



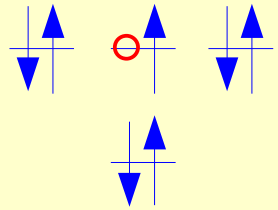
Tjalling C. Koopmans (Nobel prize winner in *economics*, 1975)

If both the ground state of the neutral and the eigenstate of the cation are approximated by single HF configurations:

$$\Psi_0^{(N)} = \Phi_0^{HF}$$



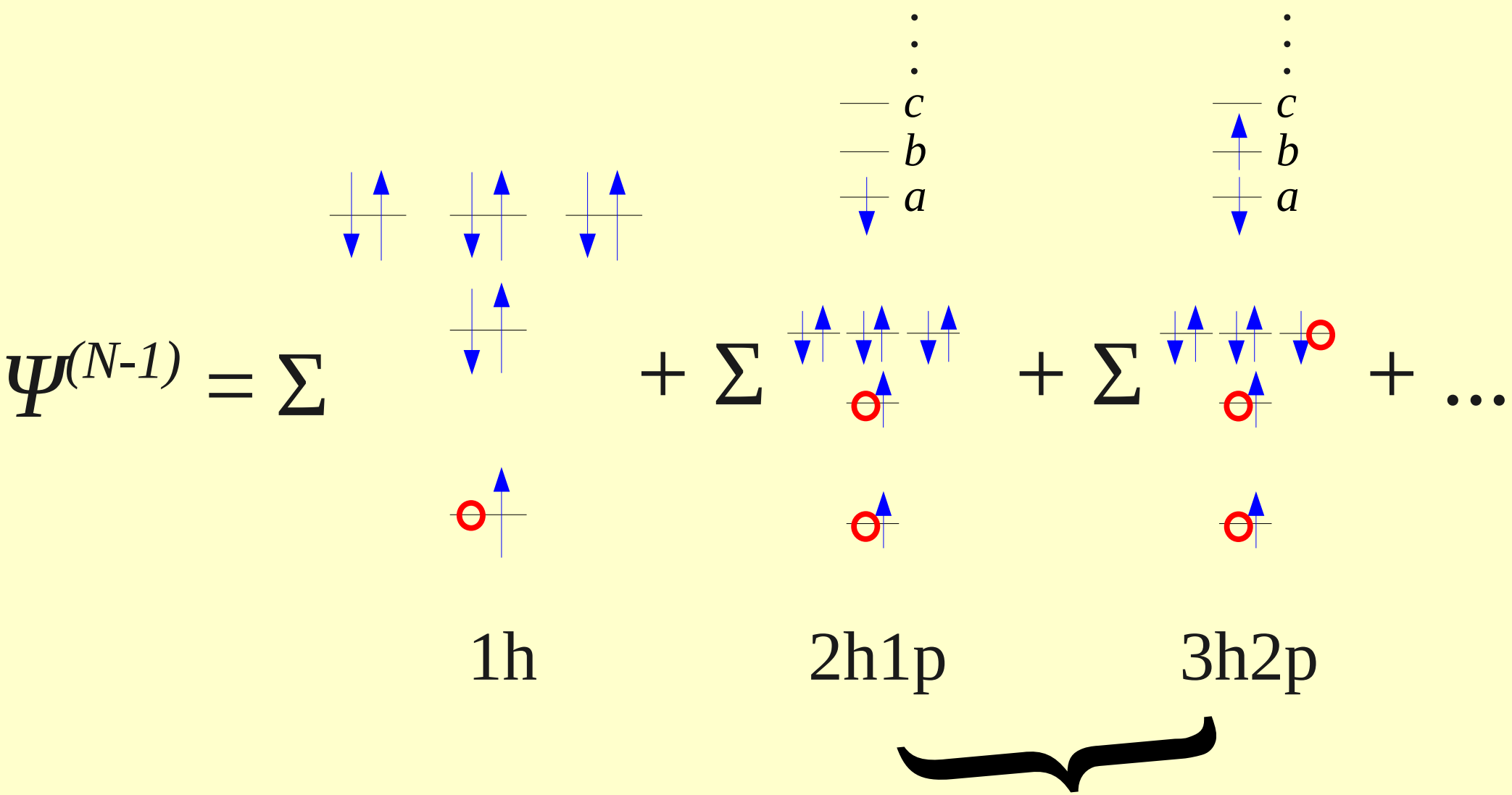
$$\Psi_0^{(N-1)} = \hat{a}_i \Phi_0^{HF}$$



then the corresponding ionization potential is given by the HF orbital energy:

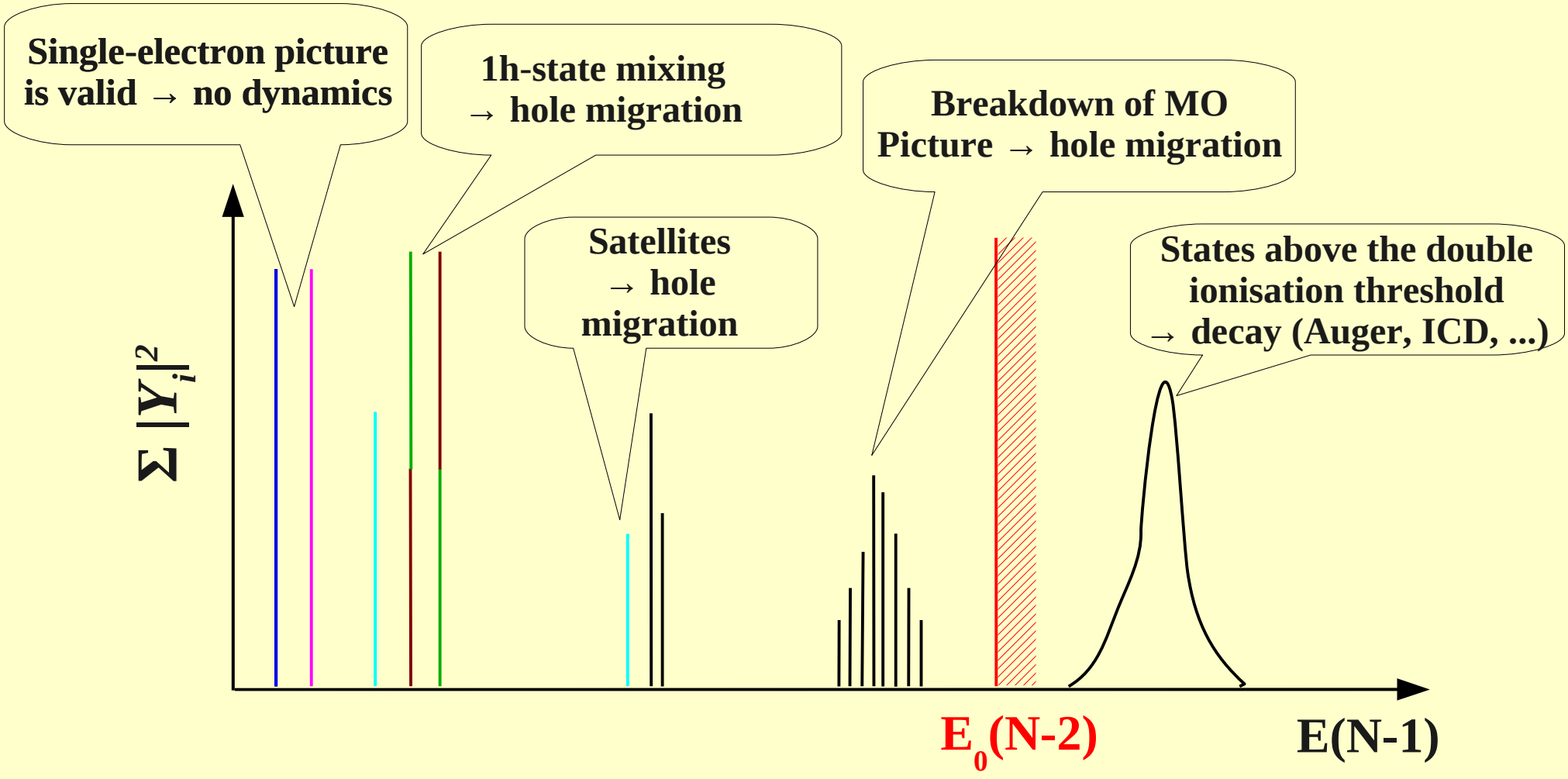
$$\mathbf{IP} = E_i(N-1) - E_0(N) = -\varepsilon_i$$

The real world: CI for singly ionised states



What is the physical effect of this contribution?

Effects of the CI: From spectral patterns to physical phenomena



$$\Psi^{(N-1)} = \sum Y_i \Psi_i + \sum Y_{ij}^{\ a} \Psi_{ij}^{\ a} + \sum Y_{ijk}^{\ ab} \Psi_{ijk}^{\ ab} + \ldots$$

1h 2h1p 3h2p

Quantitative approach to Γ_{Auger}: Fano theory of resonances

$$\Psi_E = a(E)\,\Phi + \int b(E,\varepsilon)\,\chi_\varepsilon\,d\varepsilon$$

exact wave function at energy E in the continuum

bound-like part

continuum part

Assumption: no continuum-continuum interaction

$$\langle \chi_{\varepsilon'} | \hat{H} - E | \chi_\varepsilon \rangle = (\varepsilon - E)\,\delta(\varepsilon' - \varepsilon)$$

No orthogonality requirement (unlike in Feshbach theory): $\langle \Phi | \chi_\varepsilon \rangle \neq 0$

$$\text{Solving } (\hat{H} - E)\Psi_E = 0 \text{ gives } |a(E)|^2 = \frac{\Gamma/2\pi}{(E - E_r)^2 + \Gamma^2/4}$$

Lorentzian width ⇒ decay rate

$$\Gamma = 2\pi \left| \langle \Phi | \hat{H} - E_r | \chi_{E_r} \rangle \right|^2$$

Fano (1961), Howat, Åberg & Goscinski (1978)

Fano-ADC approach: Configuration selection scheme

$$\Gamma = 2\pi \left| \langle \Phi | \hat{H} - E_r | \chi_{E_r} \rangle \right|^2$$

$$\Phi = \sum_i Y_i \Psi_i + \sum_{ija} Y_{ij}^{\ a} \Psi_{ij}^{\ a}$$

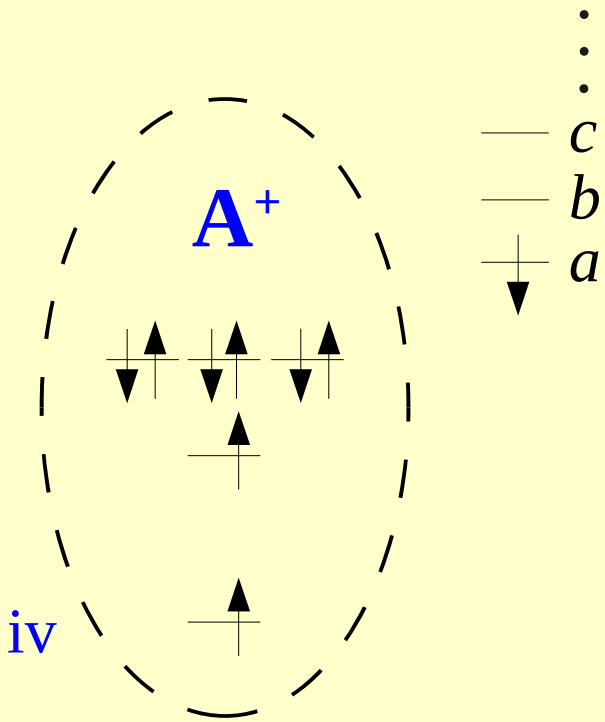
$E_{i,j}(A^{2+}) > E_{iv}(A^{+})$

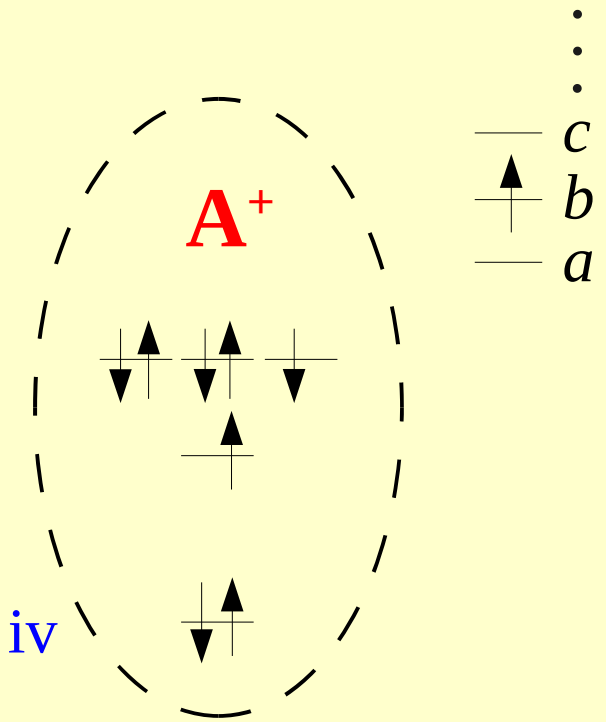
$E_r \approx \langle \Phi | \hat{H} | \Phi \rangle$

$$\chi_n = \sum_i Y_i \Psi_i + \sum_{ija} Y_{ij}^{\ a} \Psi_{ij}^{\ a}$$

$E_{i,j}(A^{2+}) < E_{iv}(A^{+})$

$\sum_i |Y_i|^2 \ll 1$





[Averbukh & Cederbaum, JCP **123**, 204107 (2005)]

Testing the theory on the ADC(2)x level

Ne ($2s^{-1}np$) autoionization

TABLE I. Experimental and theoretical decay widths Γ for the autoionizing $2s^{-1}np$ (n=3,4,5) states of Ne.

	n=3	n=4	n=5
$\Gamma_{expt.}$[a] (meV)	13 (±2)	4.5 (±1.5)	2 (±1)
Γ_{TDA} (meV)	30.48	9.31	5.59
$\Gamma_{ADC(2)}$ (meV)	8.93	2.86	1.72
$\Gamma_{ADC(2_x)}$ (meV)	11.46	3.78	1.94
Γ_{TDLDA}[b] (meV)	13.90	3.86	1.62
Γ_{RM}[c] (meV)	34.9	6.65	2.47

[a]Data taken from Ref. 13.
[b]Data taken from Ref. 17.
[c]Data taken from Ref. 16.

Ar ($3s^{-1}np$) autoionization

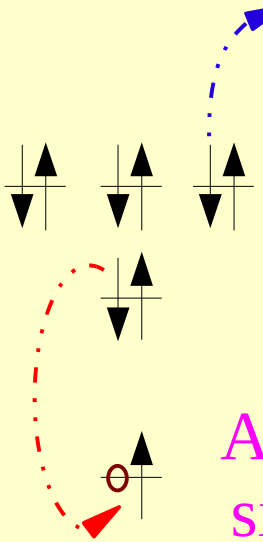
TABLE II. Experimental and theoretical decay widths Γ for the autoionizing $3s^{-1}np$ (n=4,5,6) states of Ar.

	n=4	n=5	n=6
$\Gamma_{expt.}$[a] (meV)	76 (±5)	25 (±7)	16 (±7)
Γ_{TDA} (meV)	50.61	13.52	5.59
$\Gamma_{ADC(2)}$ (meV)	61.5	18.42	8.05
$\Gamma_{ADC(2_x)}$ (meV)	67.76	25.85	12.14
Γ_{TDLDA}[b] (meV)	183.4	42.8	18.2

[a]Data taken from Ref. 15.
[b]Data taken from Ref. 17.

[Gokhberg, Averbukh & Cederbaum, JCP **126**, 154107 (2007)]

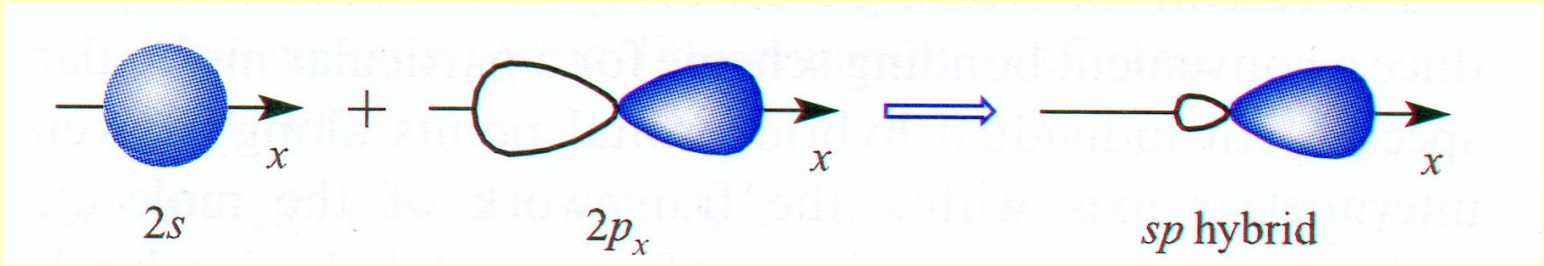
Auger effect in multiply charged systems: Effect of a single neighboring charge



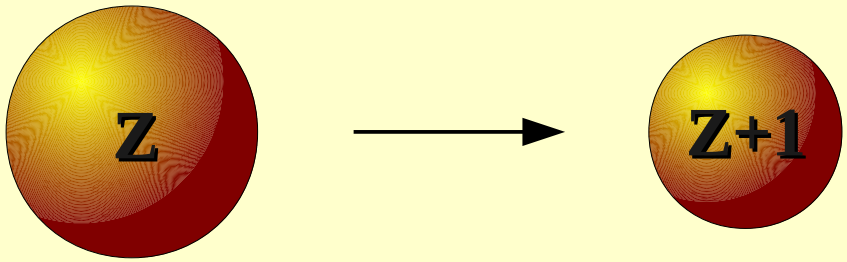
Wentzel's ansatz:

$$\Gamma_{\text{Auger}} = 2\pi \left| \left\langle \psi_{v1}(r_1)\, \psi_{v2}(r_2) \left| e^2/r_{12} \right| \psi_{\text{core}}(r_1)\, \psi_{\text{continuum}}(r_2) \right\rangle \right|^2$$

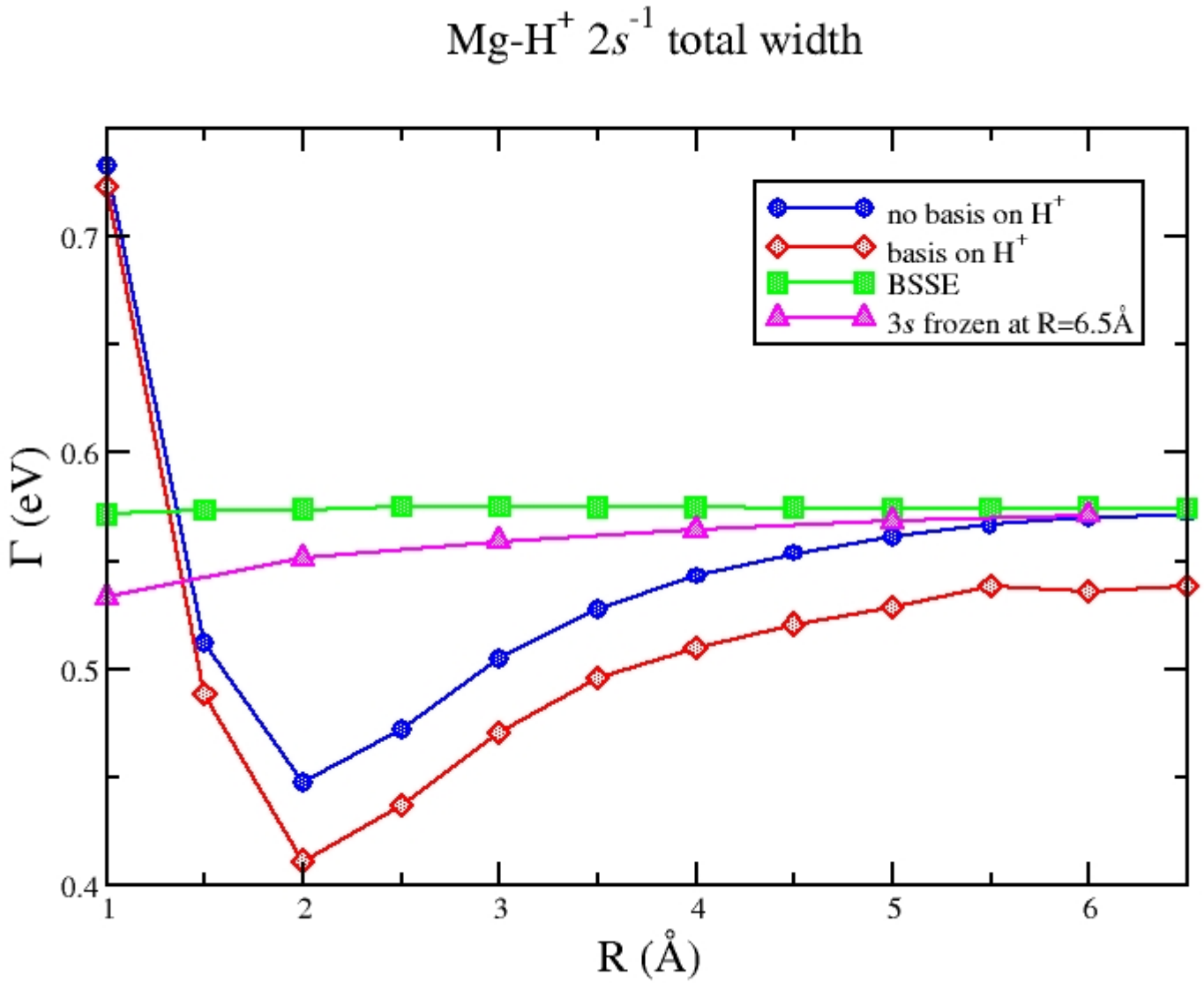
At large distances, a single charge causes *orbital mixing*, similar to hybridization in the theory of chemical bond:



At small distances, the charge penetrates the electron cloud causing orbital contraction:



Auger decay in the field of a charge: $2s^{-1}Mg^{+}...H^{+}$



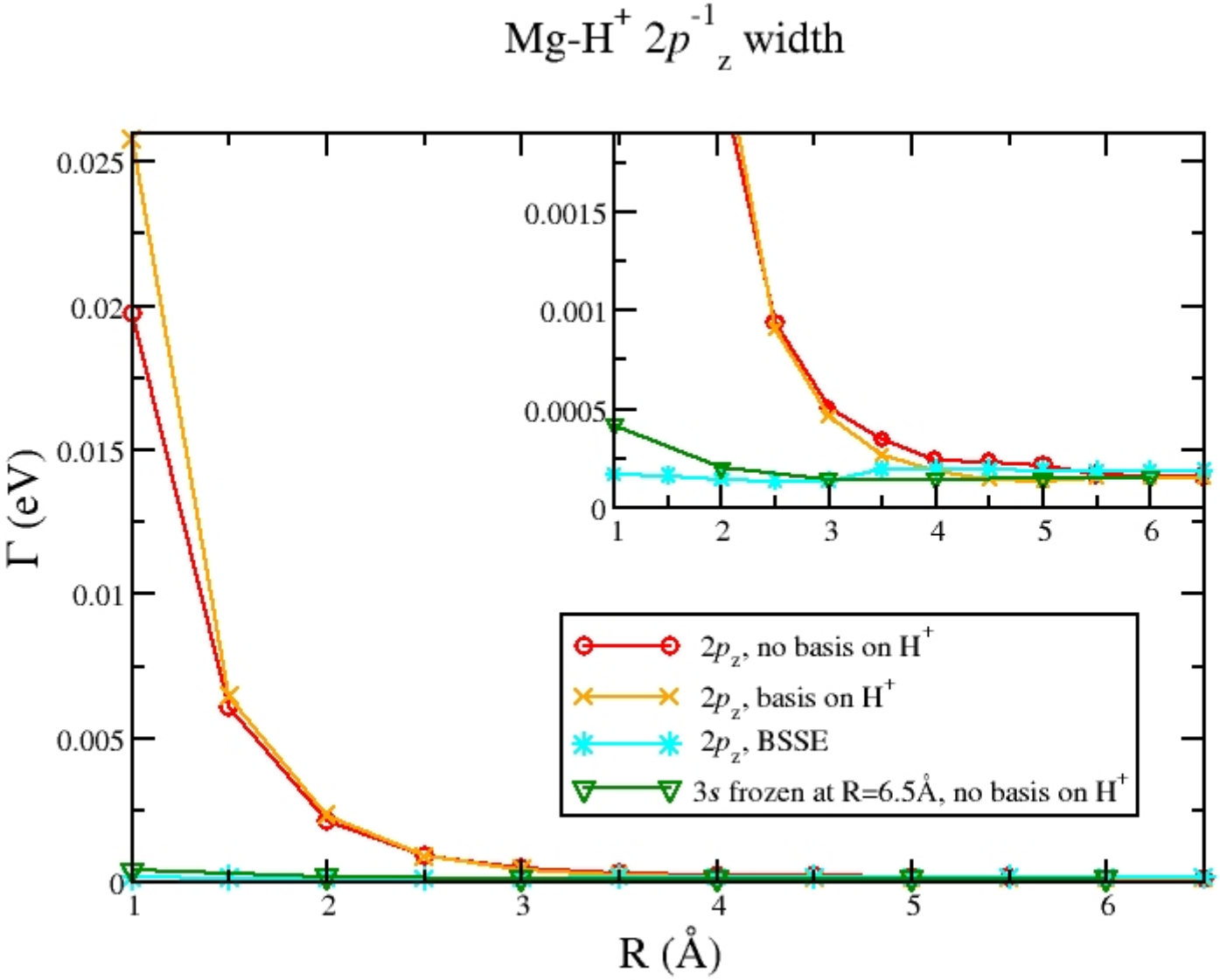
The leading decay channel is $2p_z^{-1}3s^{-1}$ singlet

Calculation is done using Fano-ADC(2)x-Stieltjes method [Averbukh & Cederbaum JCP **123**, 204107 (2005)]

The outermost (3*s*) orbital determines the Auger rate

[Averbukh, Saalmann & Rost, Phys. Rev. A **85**, 063405 (2012)]

Auger decay in the field of a charge: $2p^{-1}Mg^{+}...H^{+}$



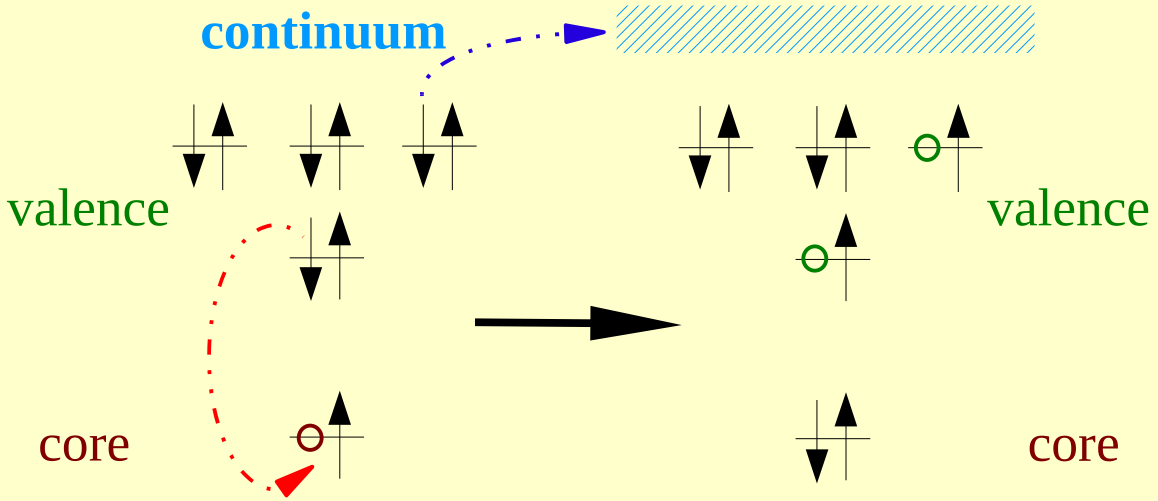
The single open decay channel is $3s^{-2}$ singlet

Calculation is done using Fano-ADC(2)x-Stieltjes method [Averbukh & Cederbaum JCP **123**, 204107 (2005)]

The outermost (3*s*) orbital determines the Auger rate

[Averbukh, Saalmann & Rost, Phys. Rev. A **85**, 063405 (2012)]

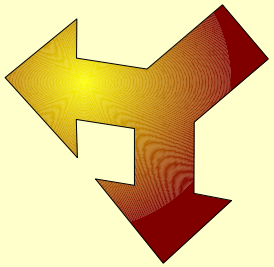
Auger decay in the field of a single charge: a more detailed interpretation



$$\Gamma_{\text{Auger}} = 2\pi\,|V|^2,\; V = \langle\, \psi_{v1}(r_1)\,\psi_{v2}(r_2)\,|\,e^2/r_{12}\,|\,\psi_{\text{core}}(r_1)\,\psi_{\text{continuum}}(r_2)\,\rangle$$

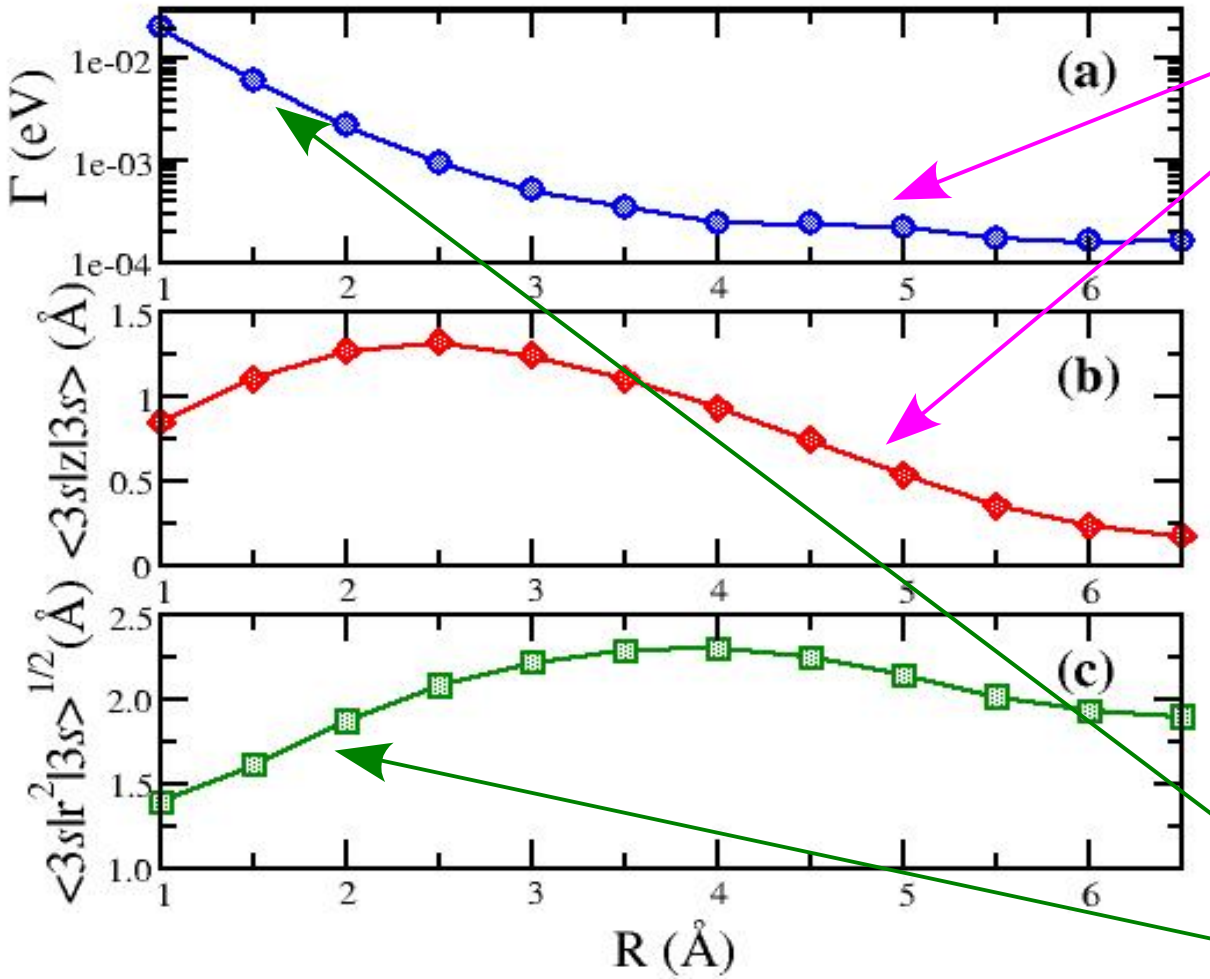
$$V = \sum_{l,m} \frac{4\pi}{(2l+1)} \langle \psi_{v1}(r_1)|r_1^{\,l}\,Y^*_{lm}(1)|\psi_{\text{core}}(r_1)\rangle\langle \psi_{v2}(r_2)|Y_{lm}(2)\,/r_2^{\,l+1}|\psi_{\text{continuum}}(r_2)\rangle$$

Contraction of ψ_{v2}
leads to higher Auger rate



Transitions described by lower-order
multipole transition moments lead to higher Auger rate

Auger decay in the field of a single charge: a more detailed interpretation



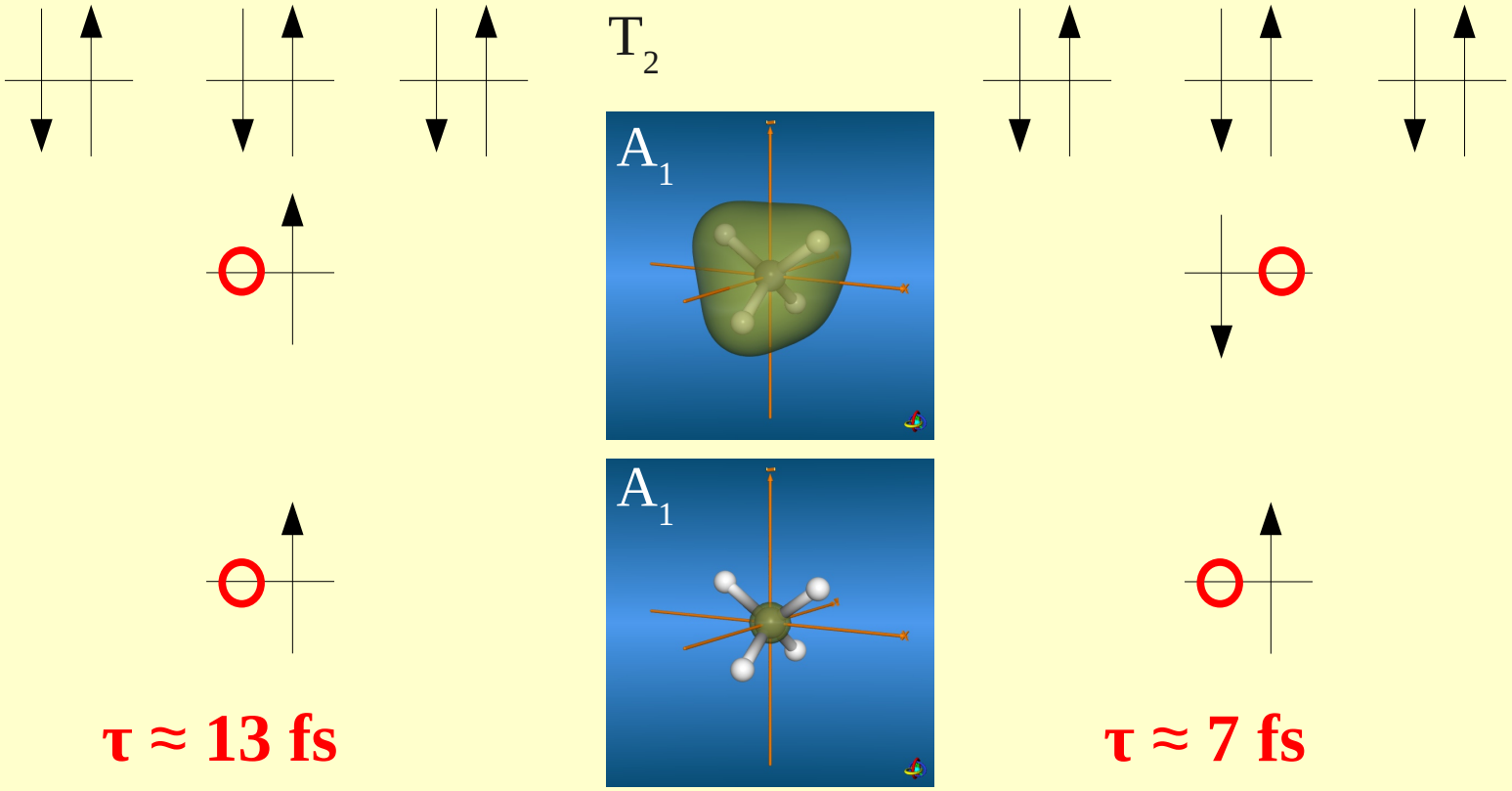
3*s*-3*p* hybridization turns the dipole-dipole transition into monopole-monopole

Contraction of 3*s* orbital further increases the Auger rate

[Averbukh, Saalmann & Rost, Phys. Rev. A **85**, 063405 (2012)]

Auger decay rate modified by an on-site charge: The spin effect

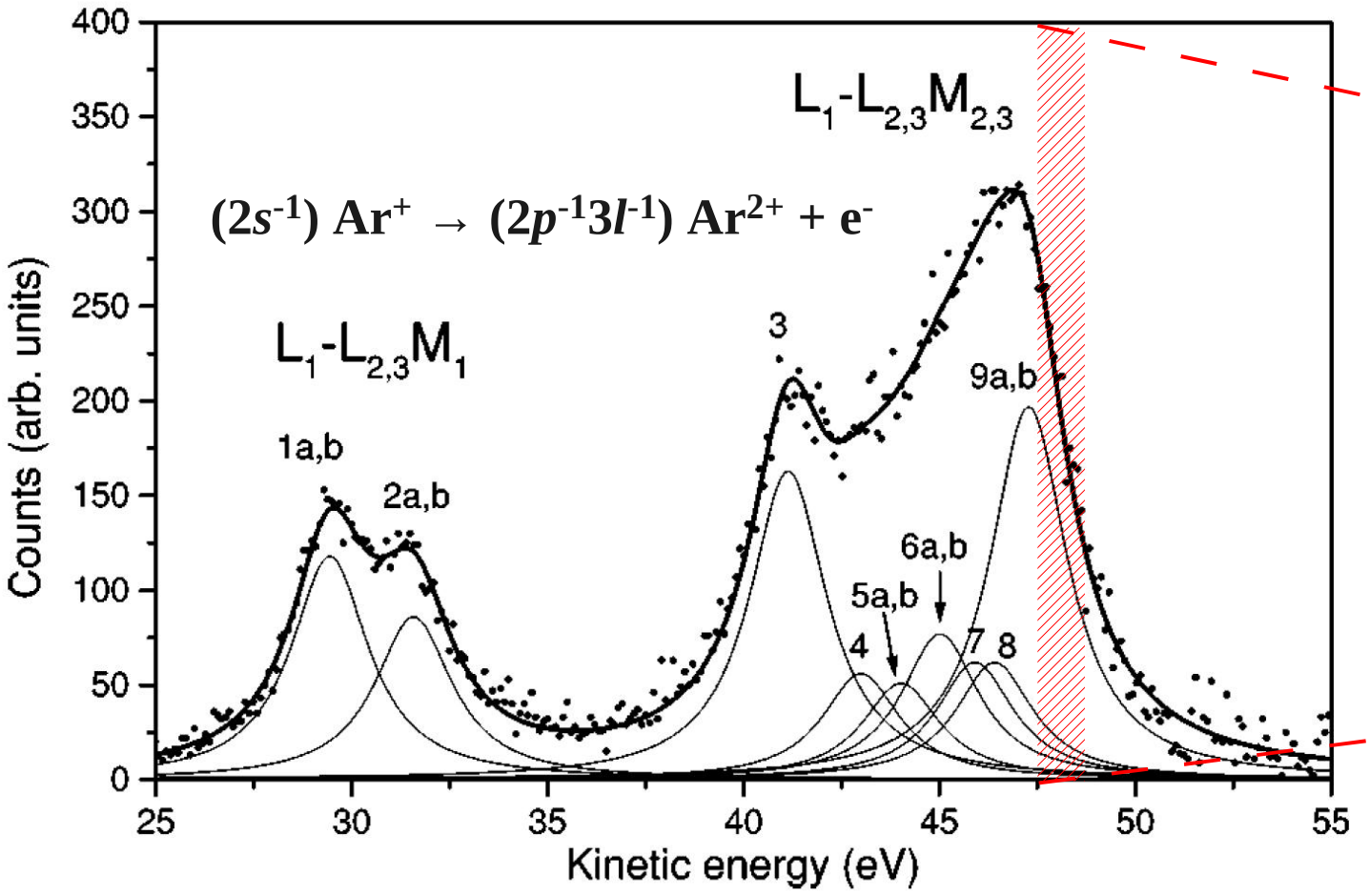
1*s* Auger in $1s^{-1}2s^{-1}$ CH_4

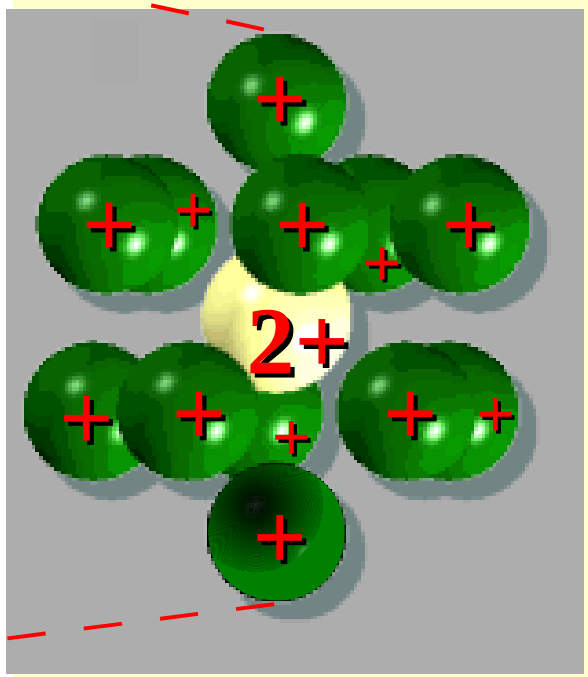


A similar effect is predicted for NH_3 and H_2O molecules

[Averbukh and Kolorenč, J. Chem. Phys. **135**, 134314 (2011)]

Adding more charges: trapping of secondary electrons





[Kylli *et al.*, PRA **59**, 4071 (1999)]

12 charges around $(2s^{-1})\ Ar^+$ in Ar^+_{13} close the Coster-Kronig channels!

Exponential decay without a true continuum?

Bixon & Jortner (1968): Exponential decay without a true continuum can take place only for a finite time

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 48, NUMBER 2 15 JANUARY 1968

Intramolecular Radiationless Transitions

MORDECHAI BIXON AND JOSHUA JORTNER

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(Received 7 August 1967)

$$\begin{pmatrix} E_s & v & v & \cdots \\ & \cdot & & \\ v & \cdot & & 0 \\ & & \cdot & \\ v & & E_i & \\ \cdot & & & \cdot \\ \cdot & & & & \cdot \\ \cdot & 0 & & & & \cdot \end{pmatrix} \begin{pmatrix} a_n \\ \cdot \\ \cdot \\ \cdot \\ b_i{}^n \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} = E_n \begin{pmatrix} a_n \\ \cdot \\ \cdot \\ \cdot \\ b_i{}^n \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}$$

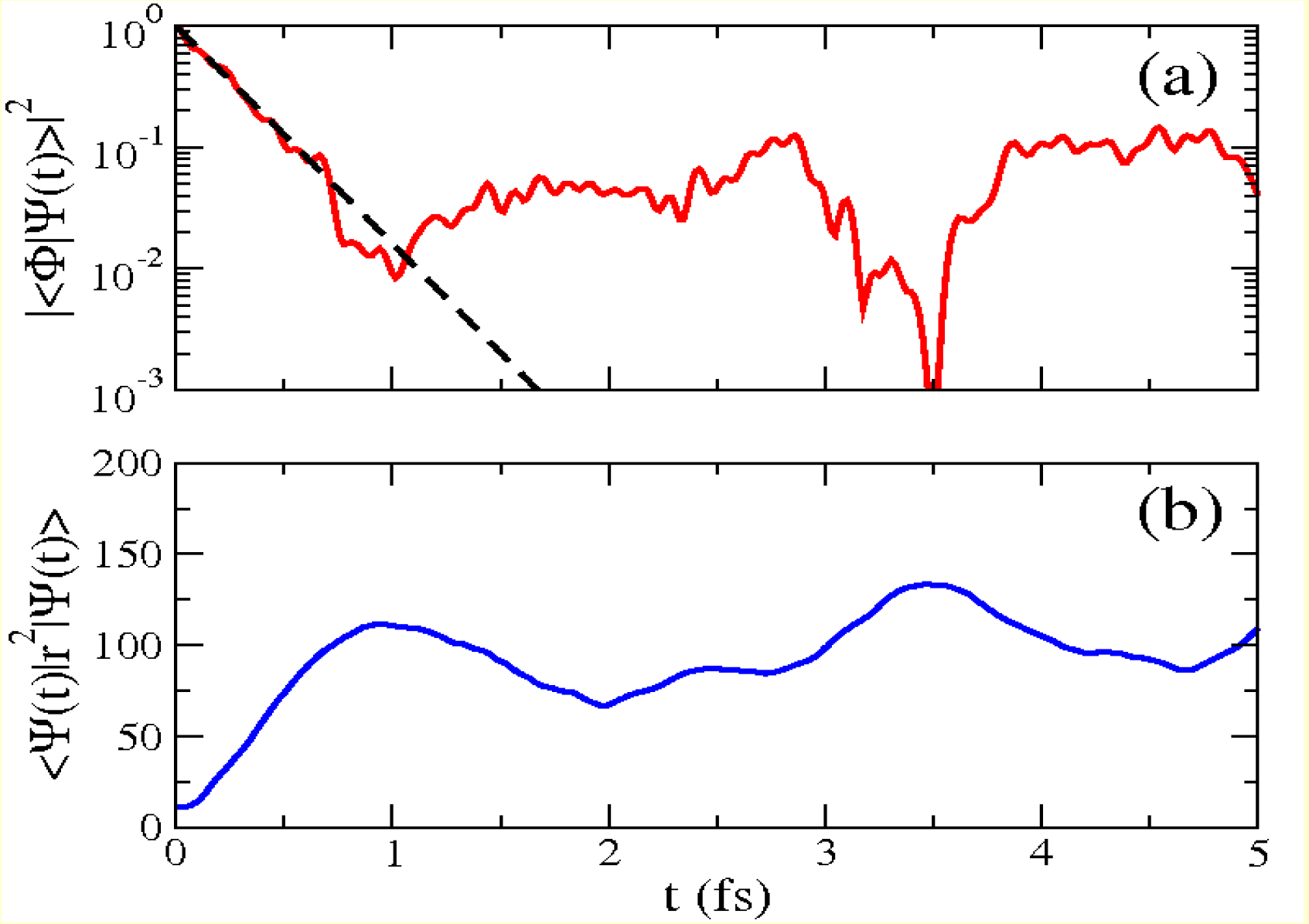
$$E_i = E_s - \alpha + i\epsilon, \qquad i = 0, \pm 1, \pm 2, \cdots.$$

Equidistant, E_{i+1}-E_i=ε, "quasicontinuum" levels

Uniform bound-quasicontinuum coupling, v

Exponential decay takes place for $t<\hbar/\varepsilon$

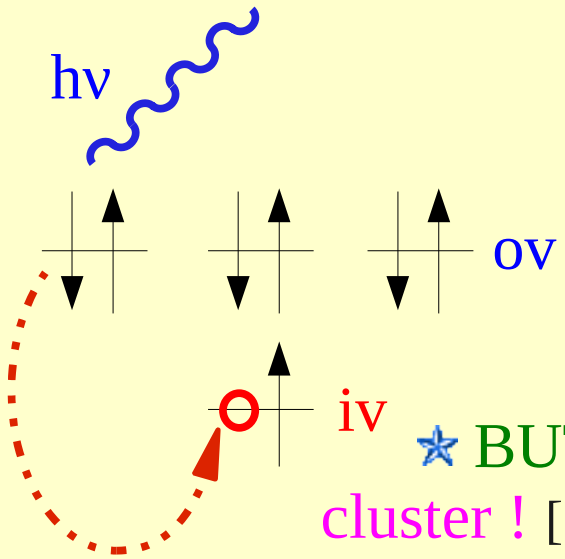
Results for a model $(2s^{-1})Ar^{+}(H^{+})_{12}$ cluster



Quasi-bound state Φ_0 is propagated under Fano-type Hamiltonian

[Averbukh, Saalmann & Rost, PRL **104**, 233002 (2010)]

From core to inner valence holes: ICD

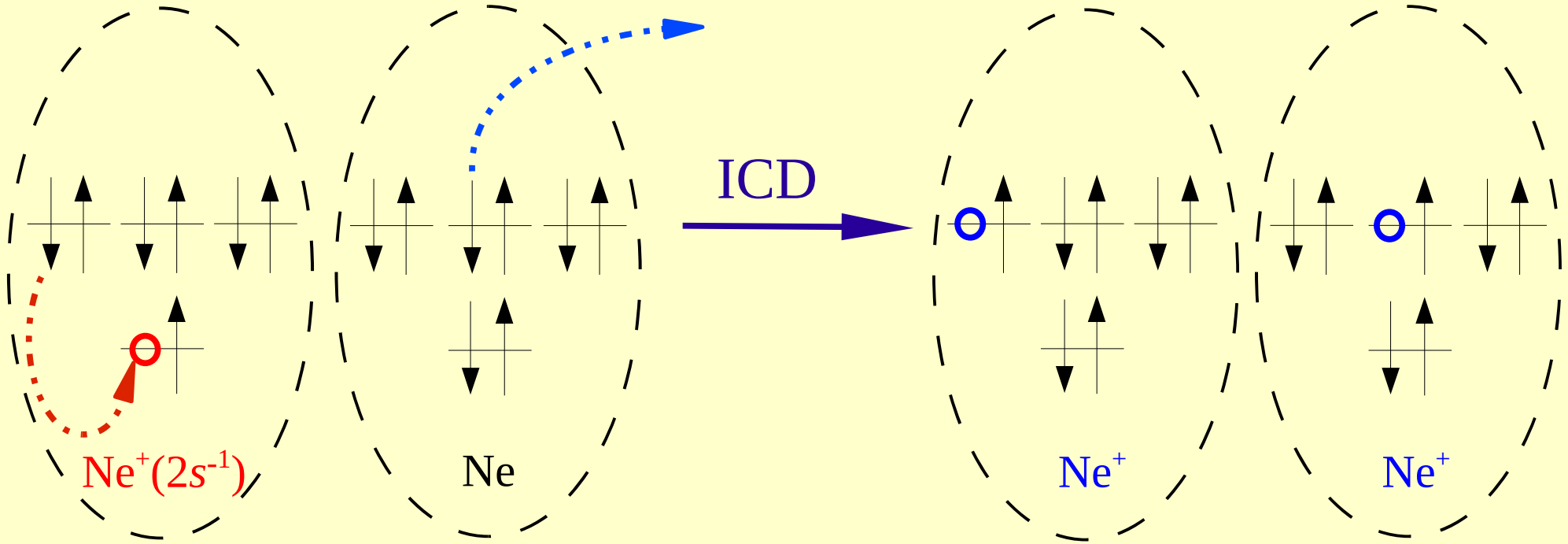


★ Inner valence ionization of isolated species leads to the slow (ns) radiative decay

$$E[Ne^{+}(2s^{-1})] < E[Ne^{2+}]$$

★ BUT... the situation is dramatically different in a cluster ! [Cederbaum, Zobeley & Tarantelli, PRL **79**, 4778 (1997)]

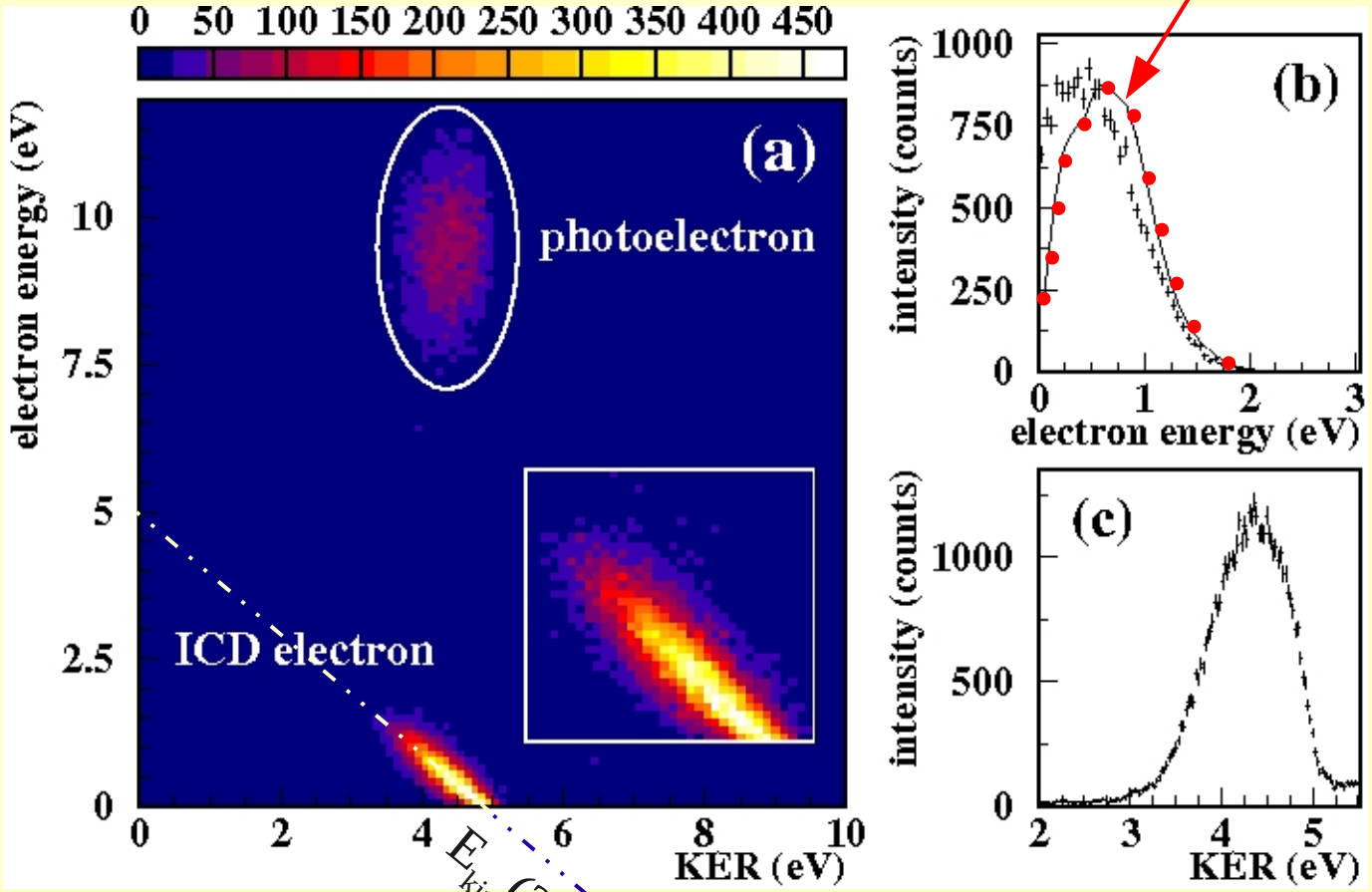
$E[Ne^{+}(2s^{-1})] > E[Ne_2^{2+}]$ leads to: $NeNe^{+}(2s^{-1}) \rightarrow Ne^{+}(E_{kin}) + Ne^{+}(E_{kin}) + e^{-}(E_{kin})$



ICD in Ne_2: The experiment

Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) experiment of Dörner's group, PRL **93**, 163401 (2004)

Theoretical calculation of Scheit, Averbukh *et al.*, JCP **121**, 8393 (2004)

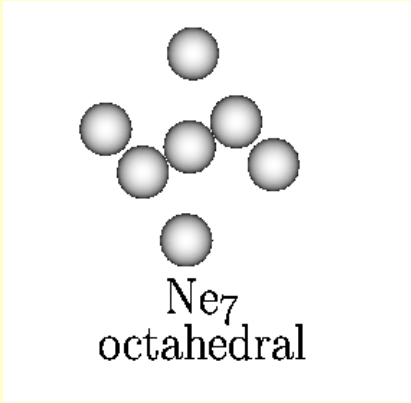


ICD: A general phenomenon

★ Van der Waals clusters

$MgNe$, $CaNe$, Ne_n^*, $Ne_nAr_m^*$, ...

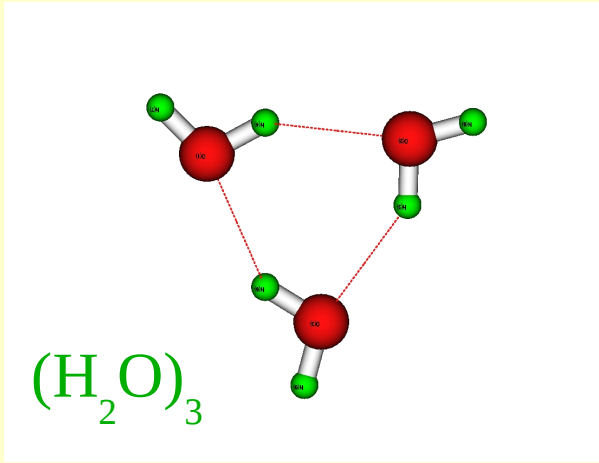
* - confirmed experimentally: Hergenhahn and coworkers, PRL **90**, 203401 (2003); Björneholm, Svensson and coworkers, PRL **93**, 173401 (2004); Dörner and coworkers, PRL **93**, 163401 (2004).



★ Hydrogen bonded clusters

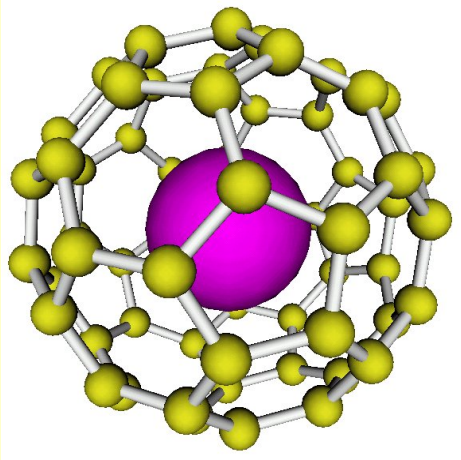
$(H_2O)_n^*$, $(HF)_n$, ...

* - confirmed experimentally: Dörner and co-workers, Nature Physics **6**, 139 (2010), Hergenhahn and co-workers, Nature Physics **6**, 143 (2010)

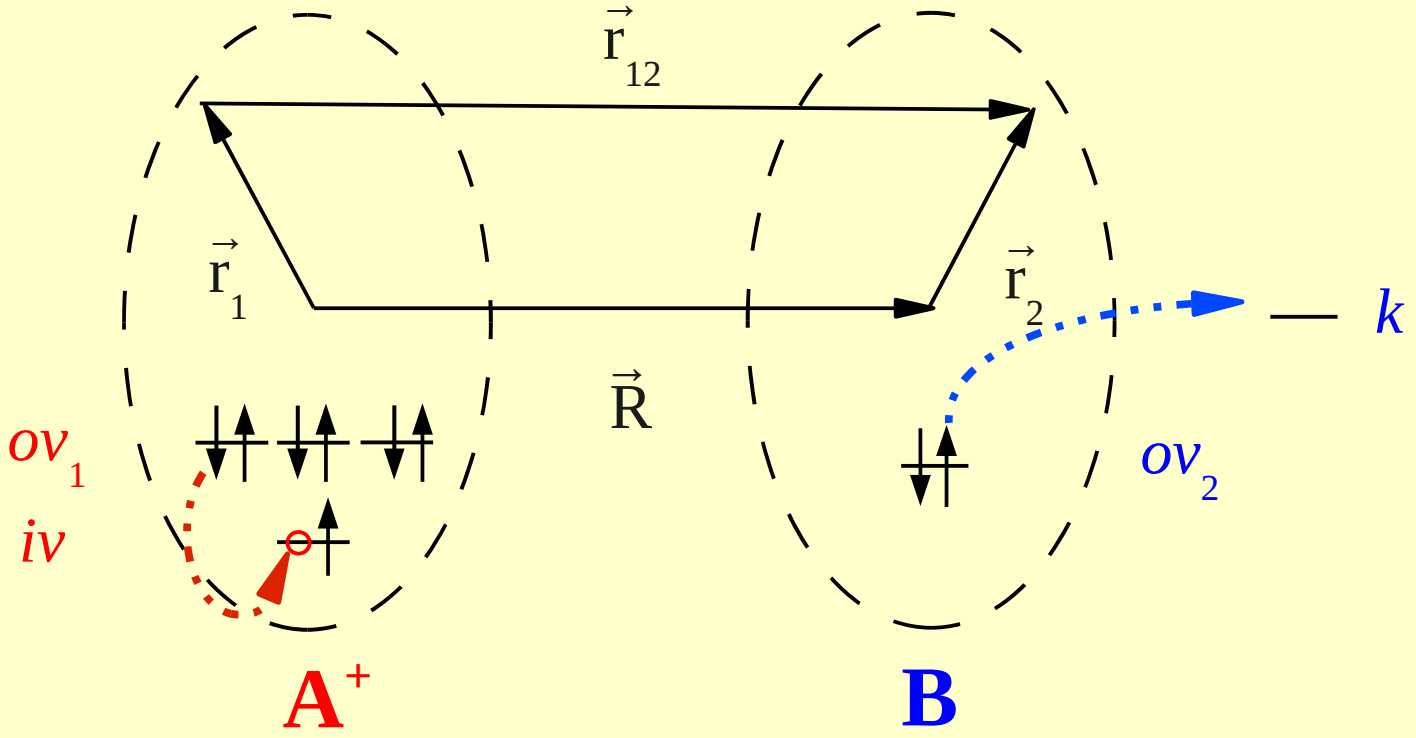


★ Endohedral fullerenes

$Ne@C_{60}$, $Ar@C_{60}$, ...



ICD: Virtual photon transfer mechanism



The dipole-dipole contribution to:

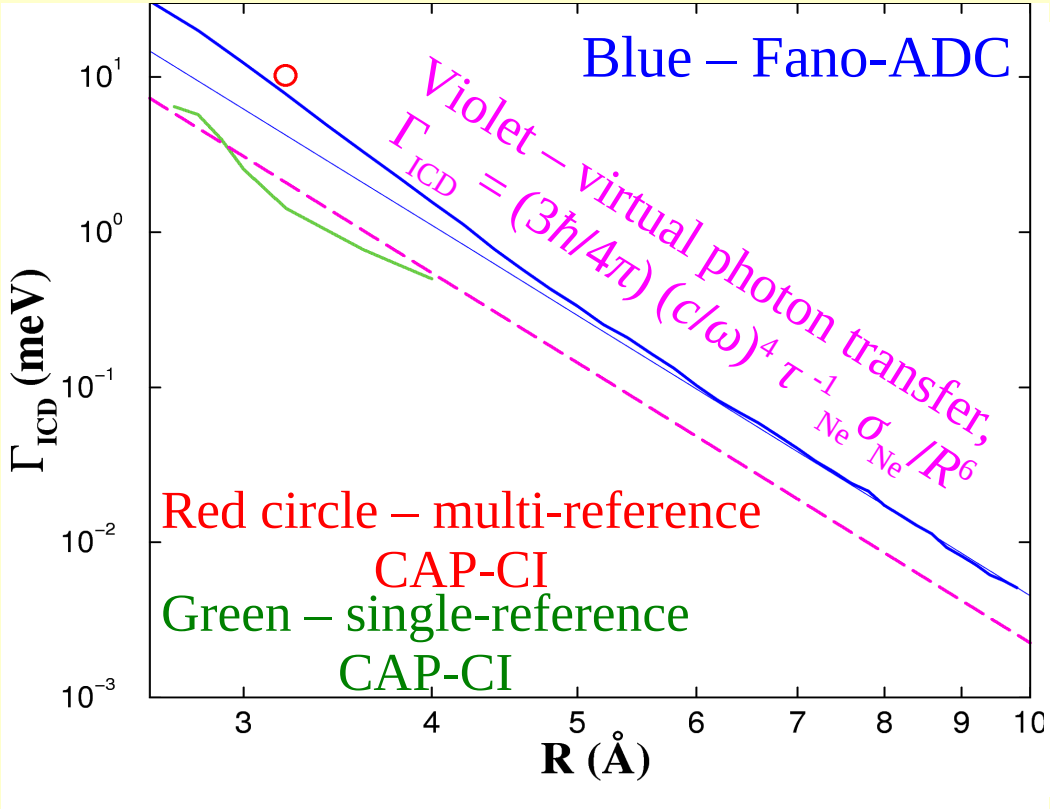
$$\Gamma_{\text{Auger}} = 2\pi \left| \left\langle ov_1(r_1)\, ov_2(r_2) \left| e^2/r_{12} \right| iv(r_1)\, k(r_2) \right\rangle \right|^2$$

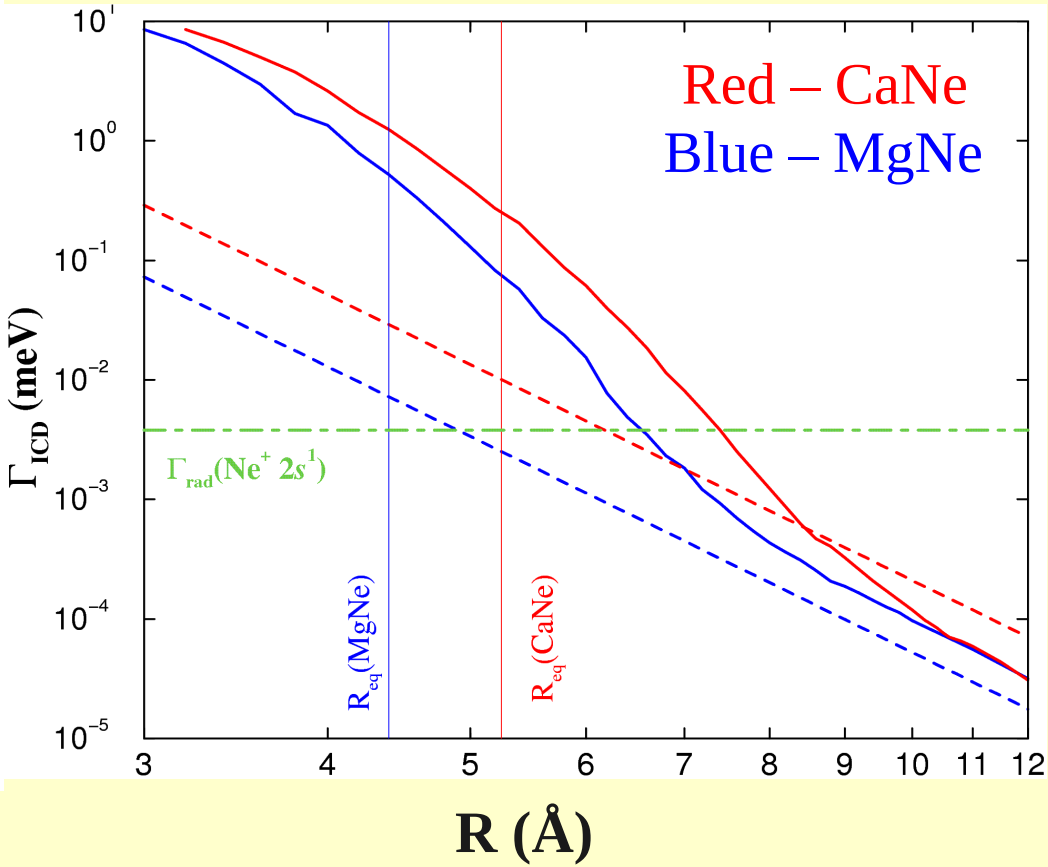
gives: $\Gamma=(3\hbar/4\pi)\,(c/\omega)^4\,\tau_{A+}^{-1}\,\sigma_B/R^6$ τ_A^{-1} is the radiative lifetime of A^+

σ_B is the total ionization cross-section of B

[Matthew & Komninos, Surf. Sci. **53**, 716 (1975)]

ICD: The overlap enhancement effect



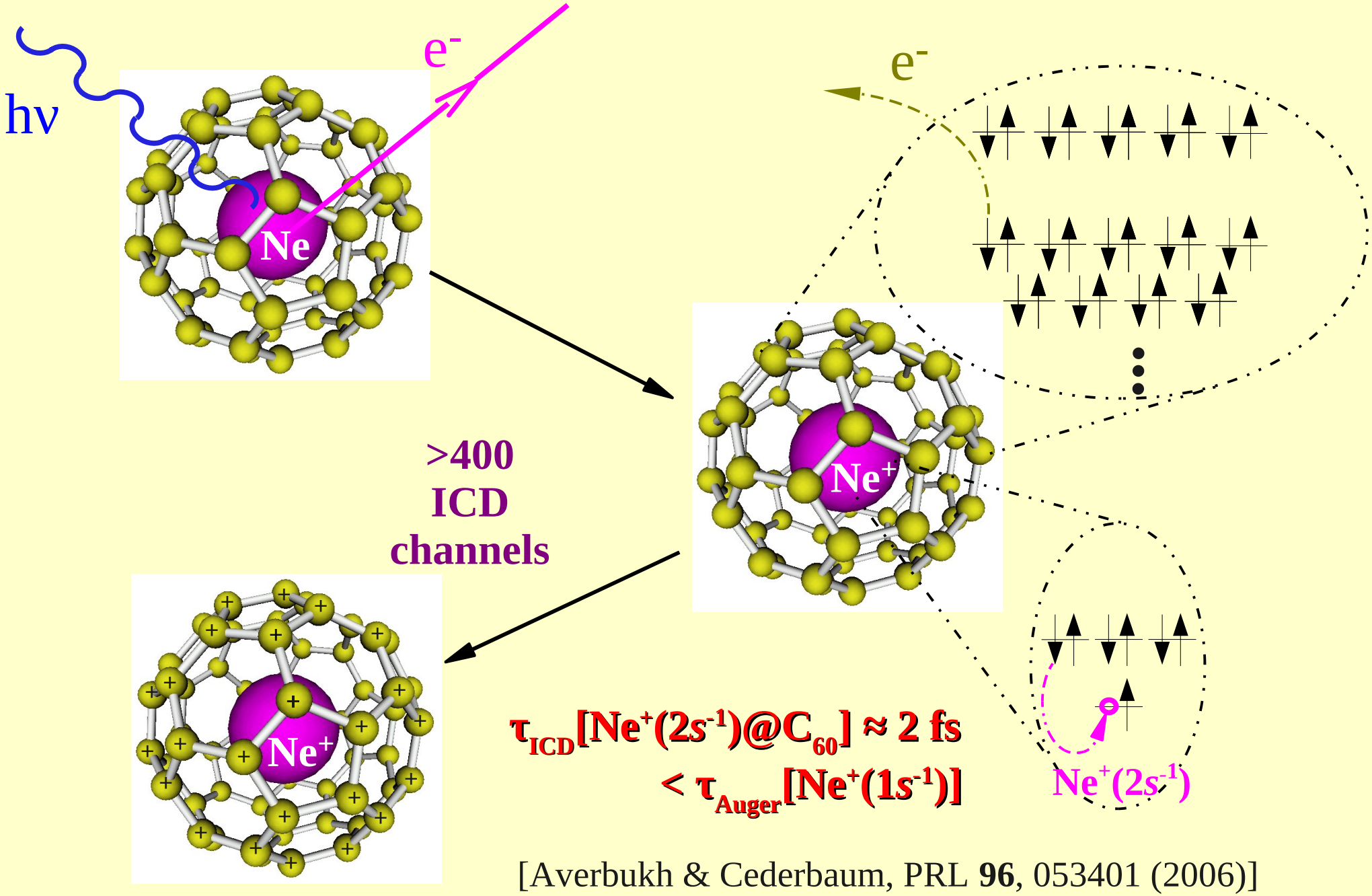


★ While the virtual photon transfer model is qualitatively correct for rare gas clusters, it can fail badly for other systems. Overlap enhancement in MgNe, CaNe diatoms reaches two orders of magnitude!

[Averbukh, Müller & Cederbaum, PRL **93**, 263002 (2004)]

[Averbukh & Cederbaum, JCP **123**, 204107 (2005)]

ICD in Endohedral Fullerene Complexes

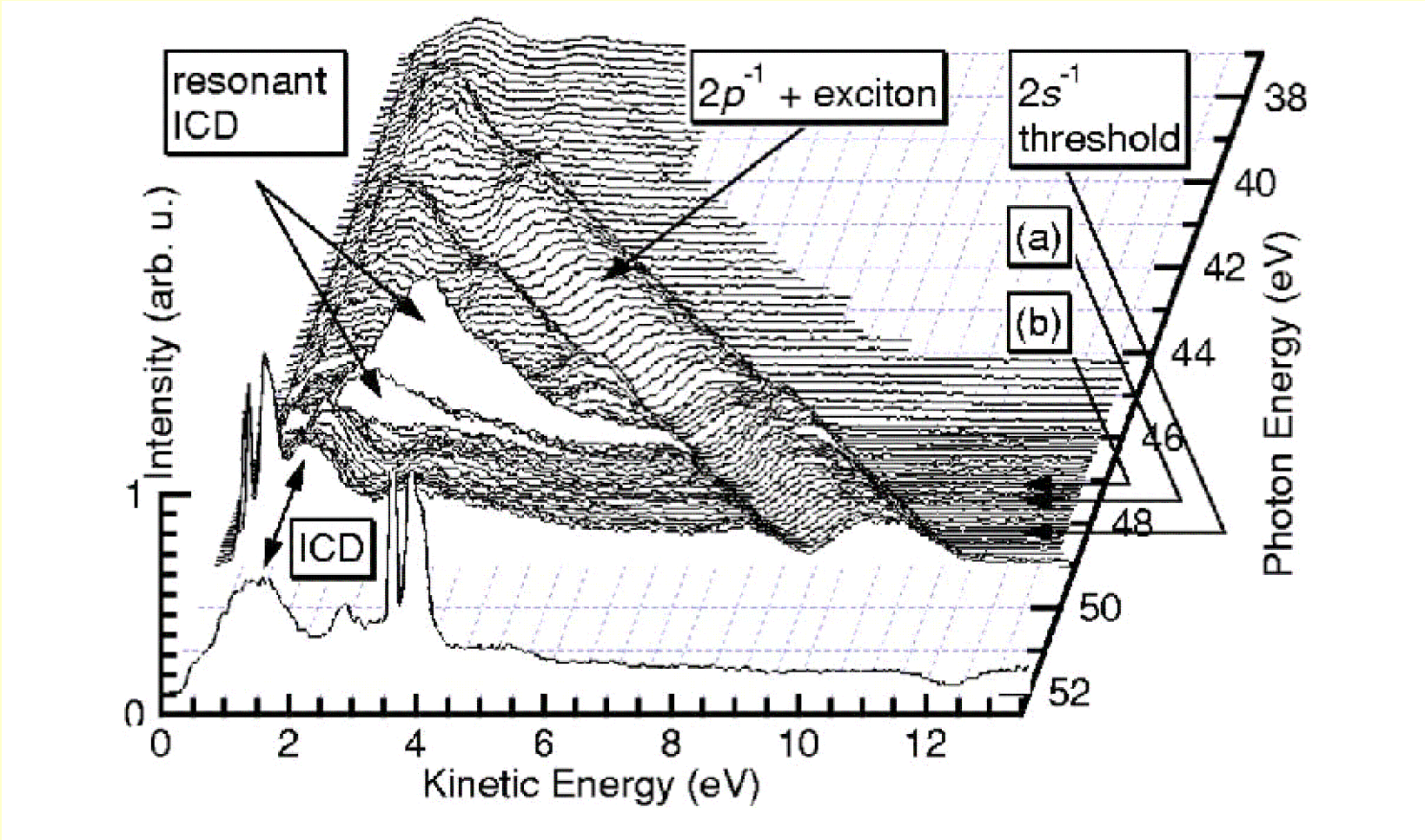


$\tau_{ICD}[Ne^{+}(2s^{-1})@C_{60}] \approx 2$ fs

$< \tau_{Auger}[Ne^{+}(1s^{-1})]$

[Averbukh & Cederbaum, PRL **96**, 053401 (2006)]

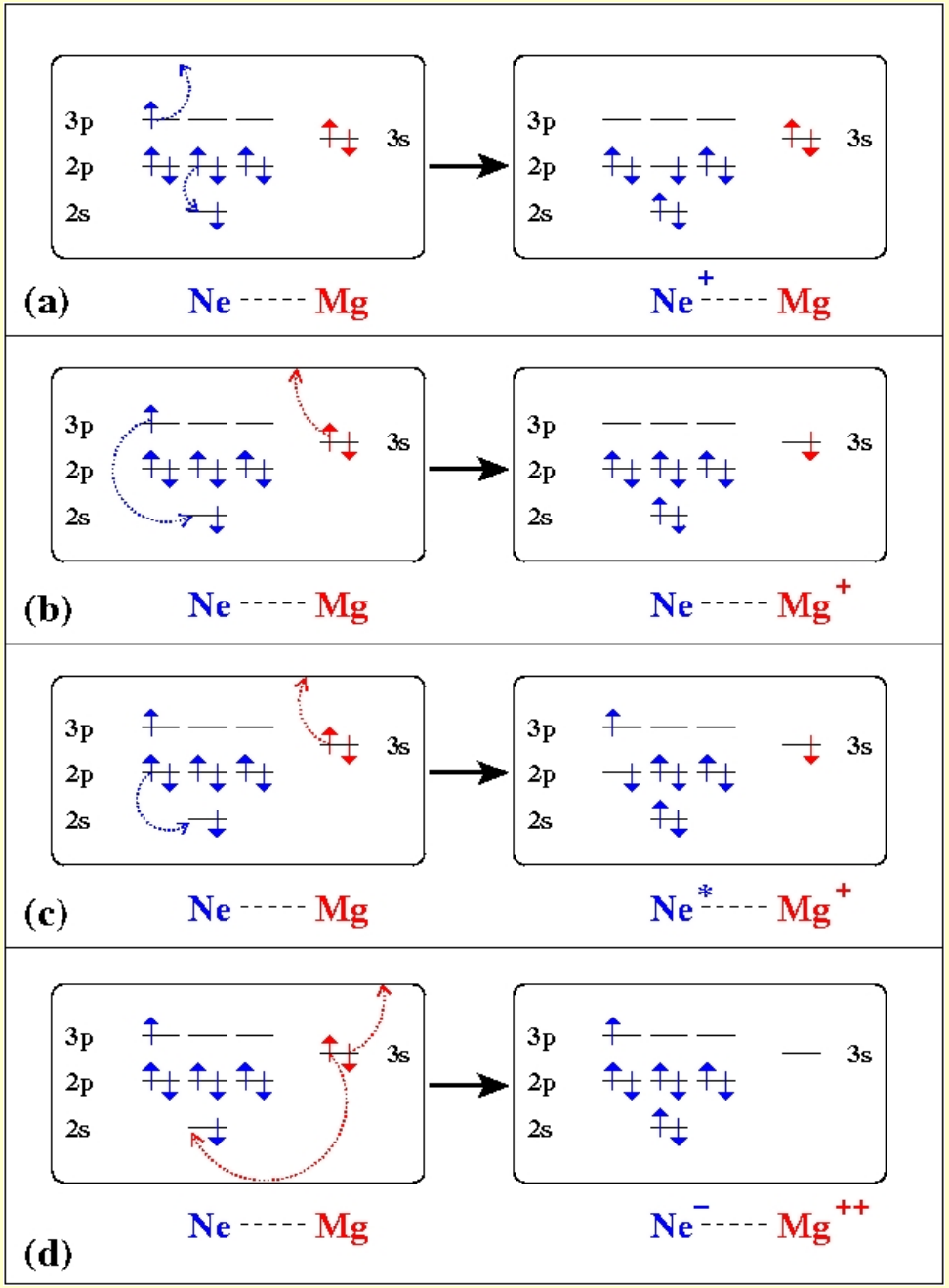
Interatomic decay of *excited* clusters: RICD



Photon energy independent feature below Ne 2s threshold
→ *spectator* resonant ICD (*s*RICD) –
interatomic analog of spectator resonant Auger decay

[Barth *et al.*, JCP **122**, 241102 (2005)]

Resonant ICD in MgNe: possible decay pathways



Autoionization (AI)

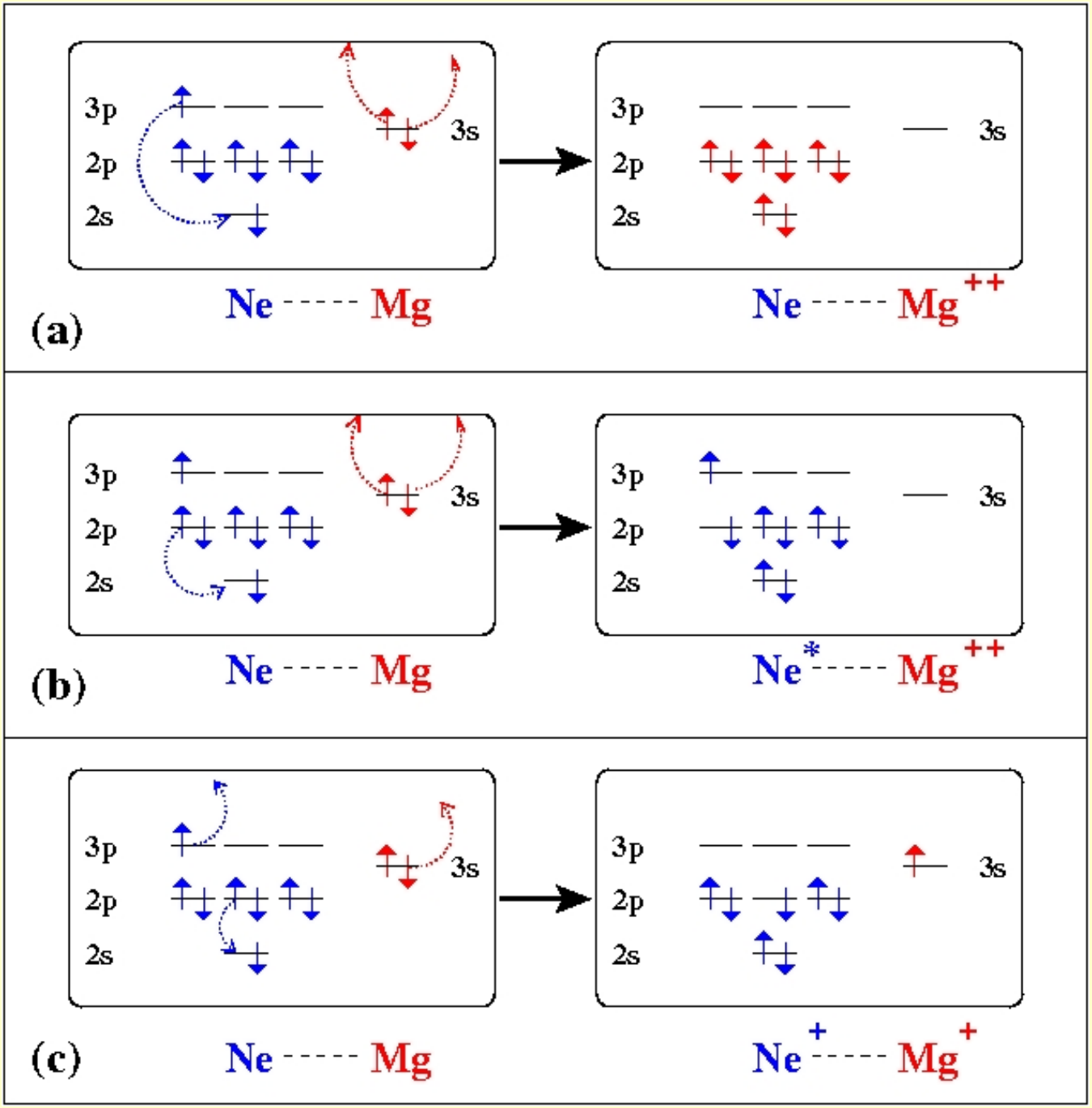
Participator resonant ICD (*p*RICD)

Spectator resonant ICD (*s*RICD)

ETMD? - Not feasible!

[Gokhberg, Averbukh & Cederbaum, JCP **124**, 144315 (2006)]

Resonant ICD in MgNe: still more decay pathways

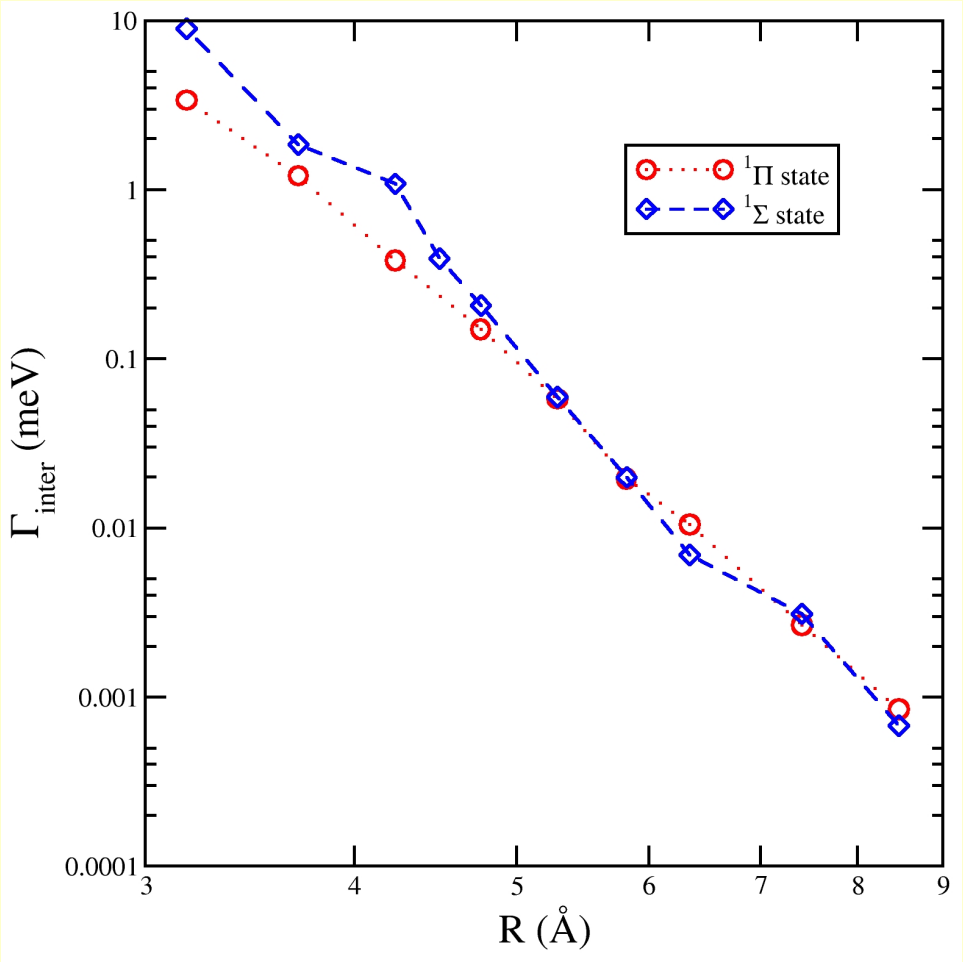


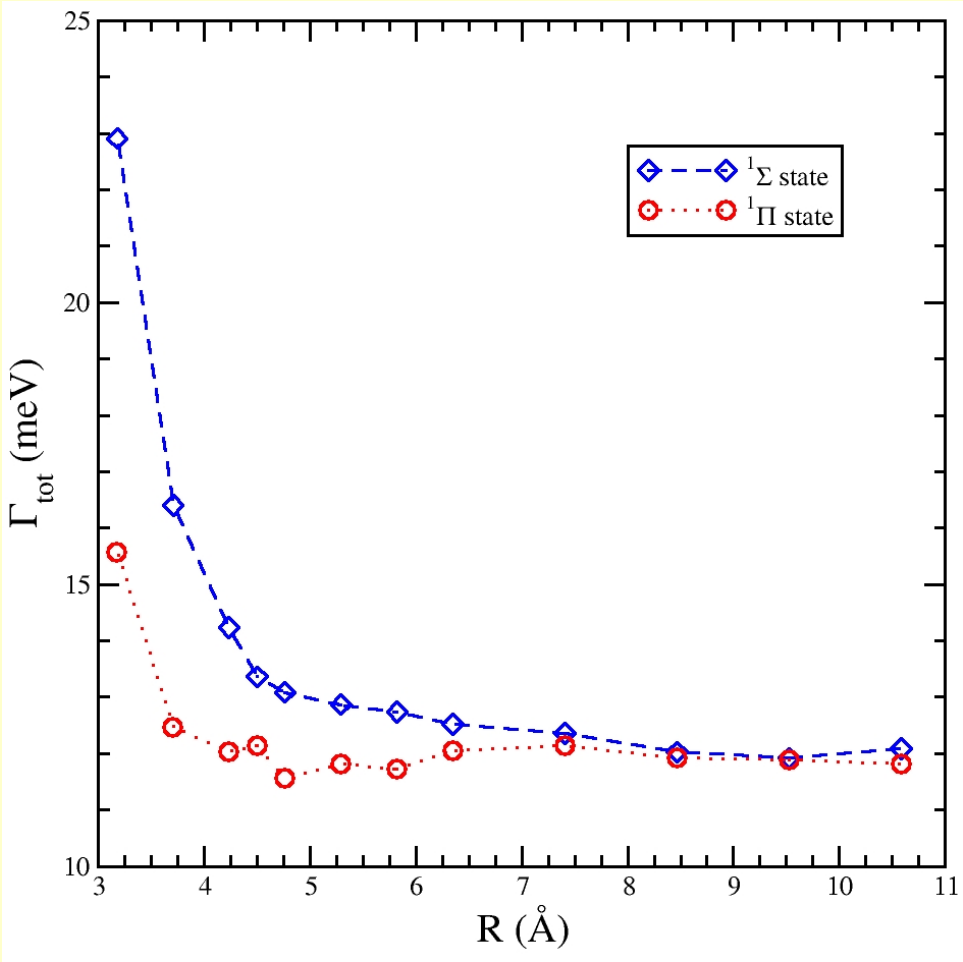
Participator double resonant ICD (*p*DRICD)

Spectator double resonant ICD (*s*DRICD)

AI – RICD hybrid

Resonant ICD in MgNe: the Fano-ADC rates



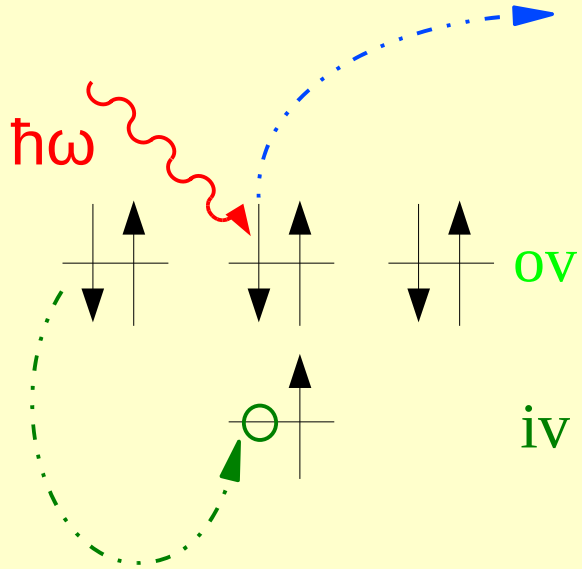


- The spectator RICD process is much stronger than the participator decay
- At small R's, RICD and AI are comparably fast

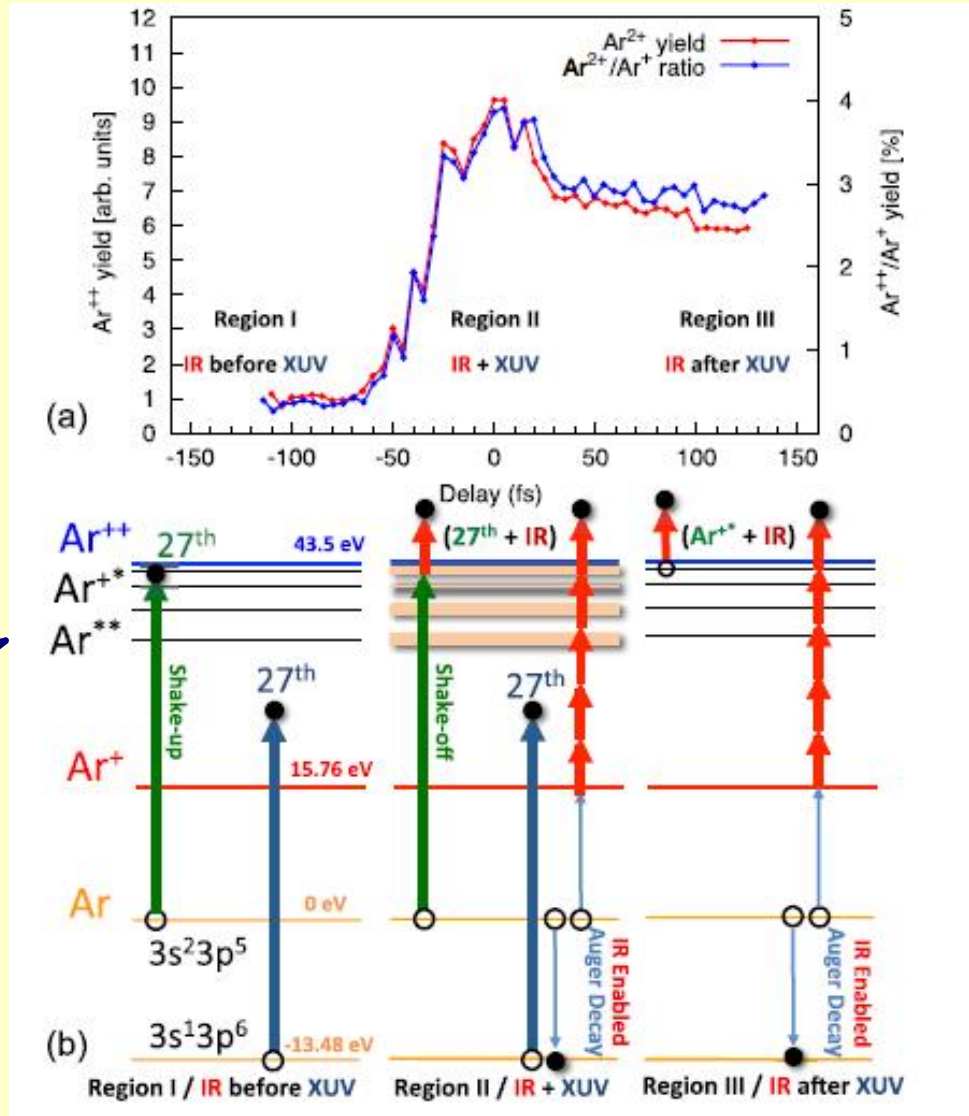
[Kopelke, Gokhberg, Averbukh, Tarantelli and Cederbaum, J. Chem. Phys. **134**, 094107 (2011)]

More on the inner valence holes: Laser-enabled Auger decay

An idea inspired by radiative Auger:

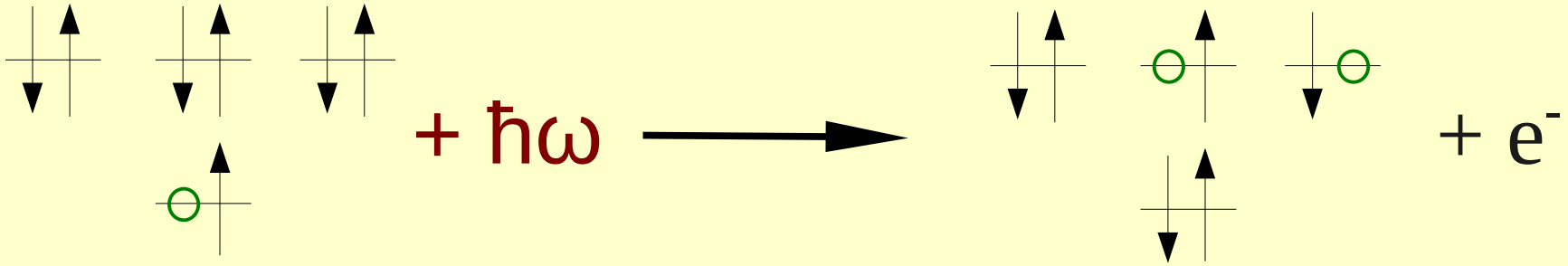


Very recent experimental realization in the multiphoton regime

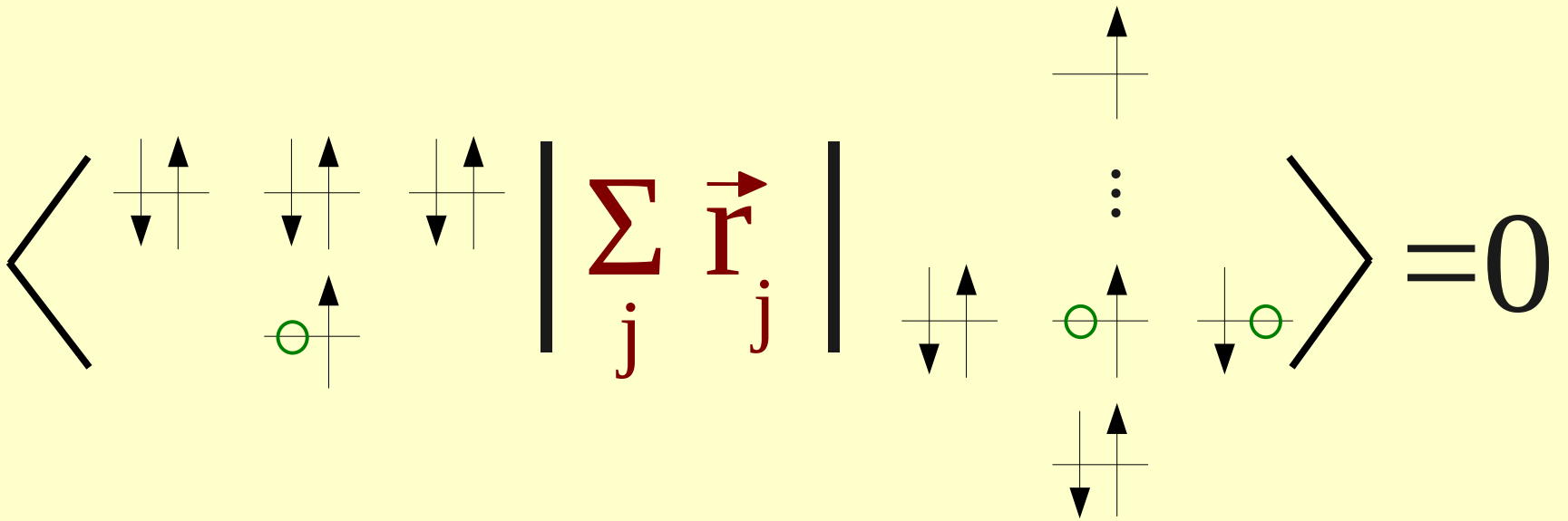


[Ranitovic *et al.*, PRL **106**, 053002 (2011)]

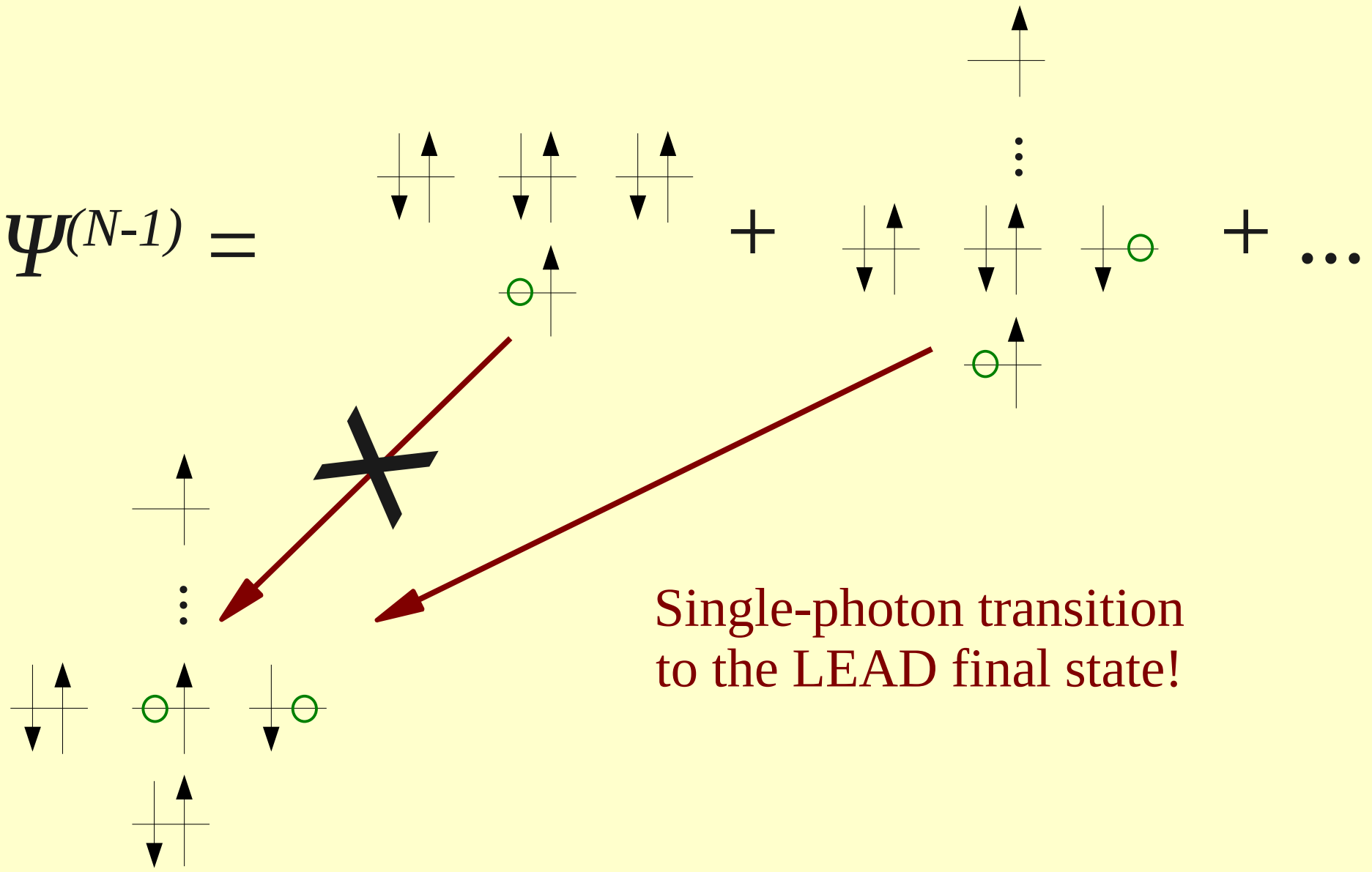
Single-photon laser-enabled Auger decay...



… is forbidden in the single Slater determinant approximation!

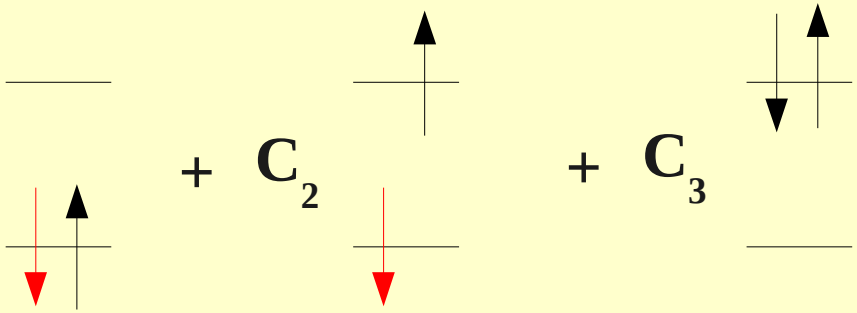


Single-photon LEAD: Measure of CI in the inner-valence-ionized states

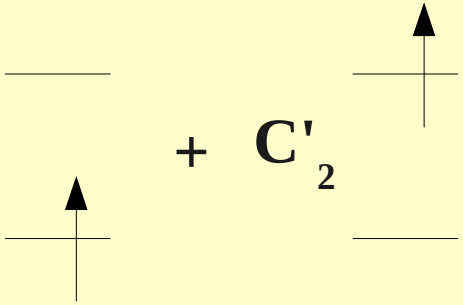


The initial state of LEAD: Sudden ionization?

$$\Psi_0^{(N)} = C_1 \; + \; C_2 \; + \; C_3$$



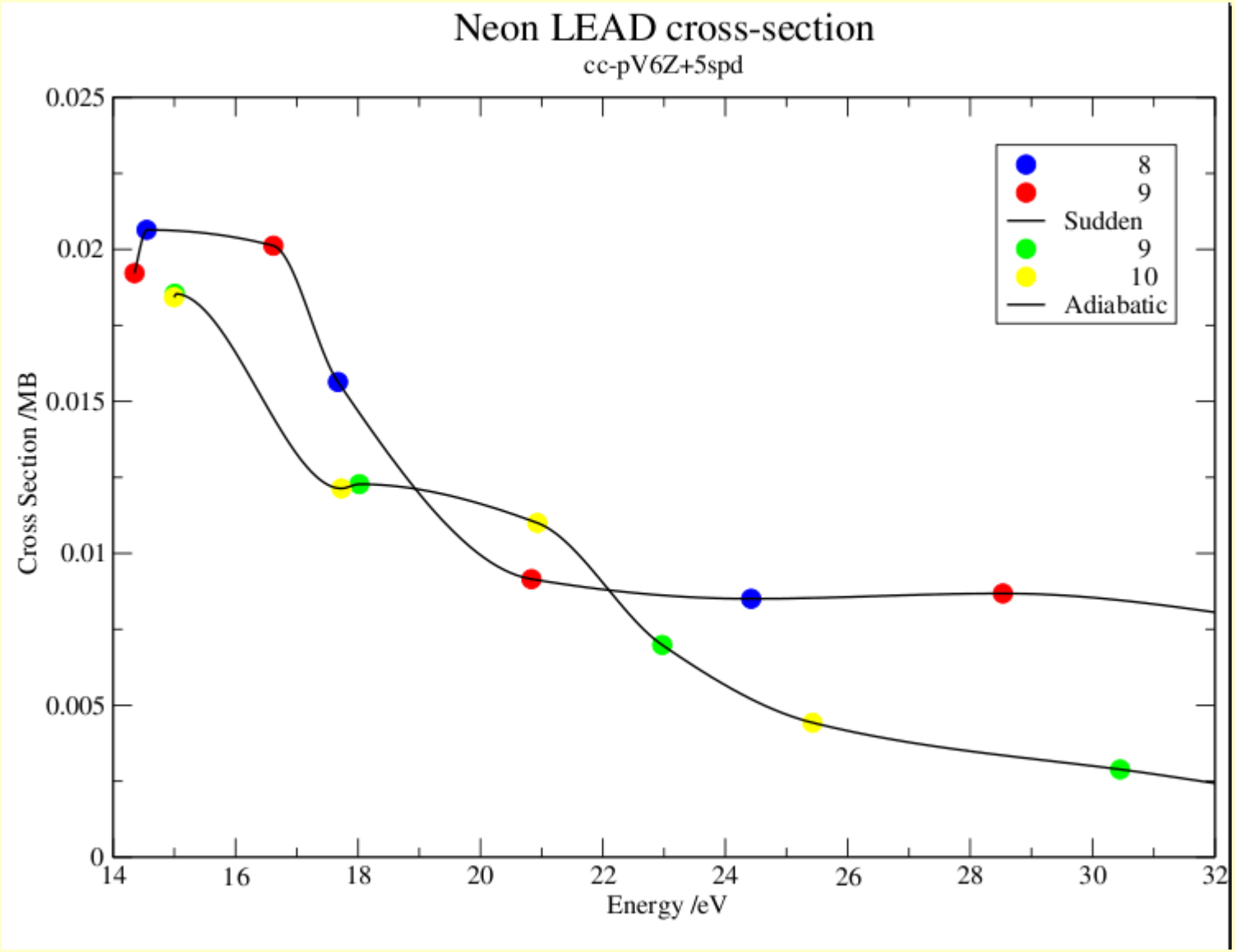
$$\hat{a}_{1\beta}\Psi_0^{(N)} = C'_1 \; + \; C'_2 \neq \Psi_j^{(N-1)}$$



Sudden annihilation of an electron produces a non-stationary state of the ion!

Single-photon LEAD: ADC(2)x-Stieltjes results

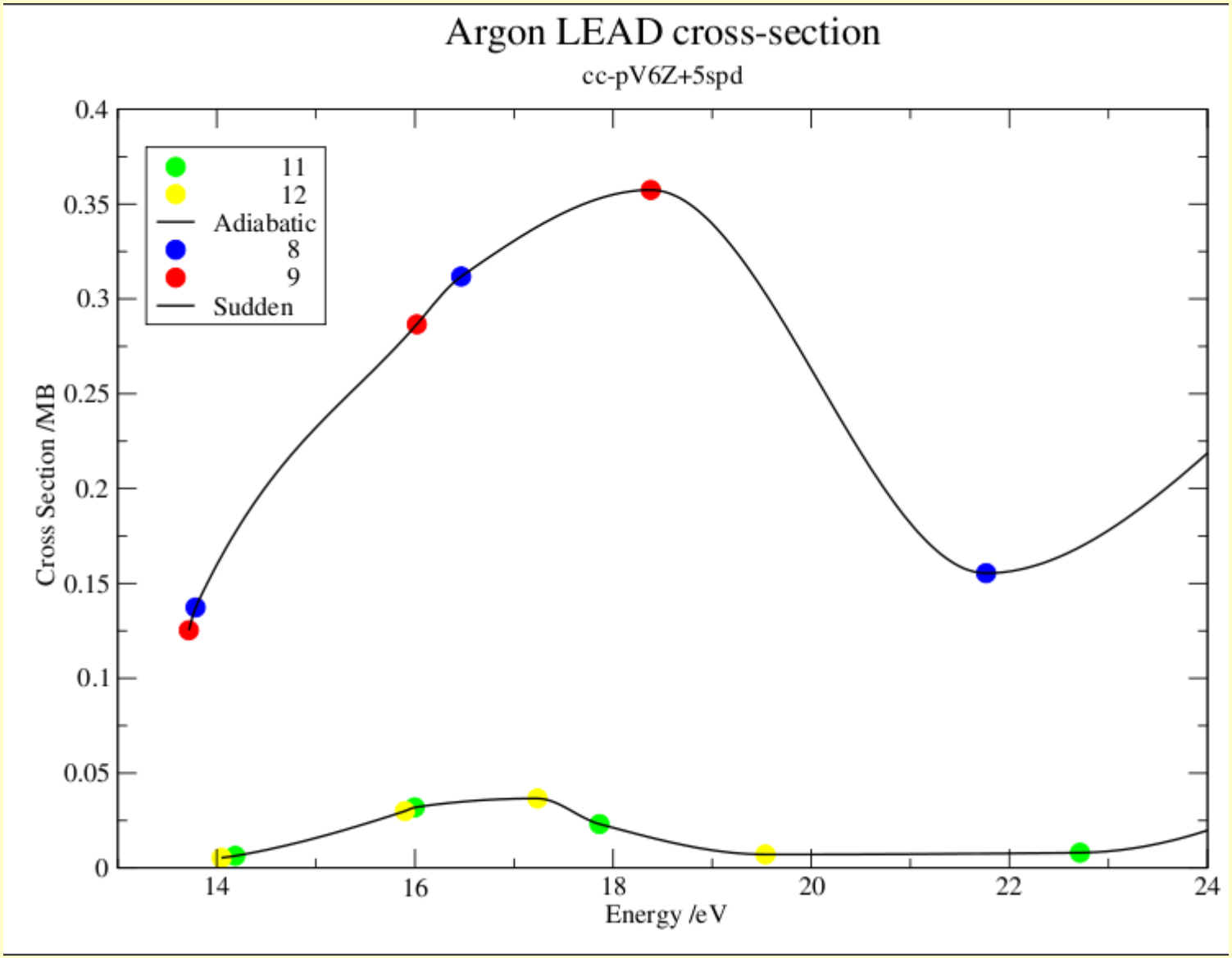
$$(2s^{-1})Ne^{+} + \hbar\omega \rightarrow (2p^{-2})Ne^{++} + e^{-}$$



Cooper & Averbukh, 2012

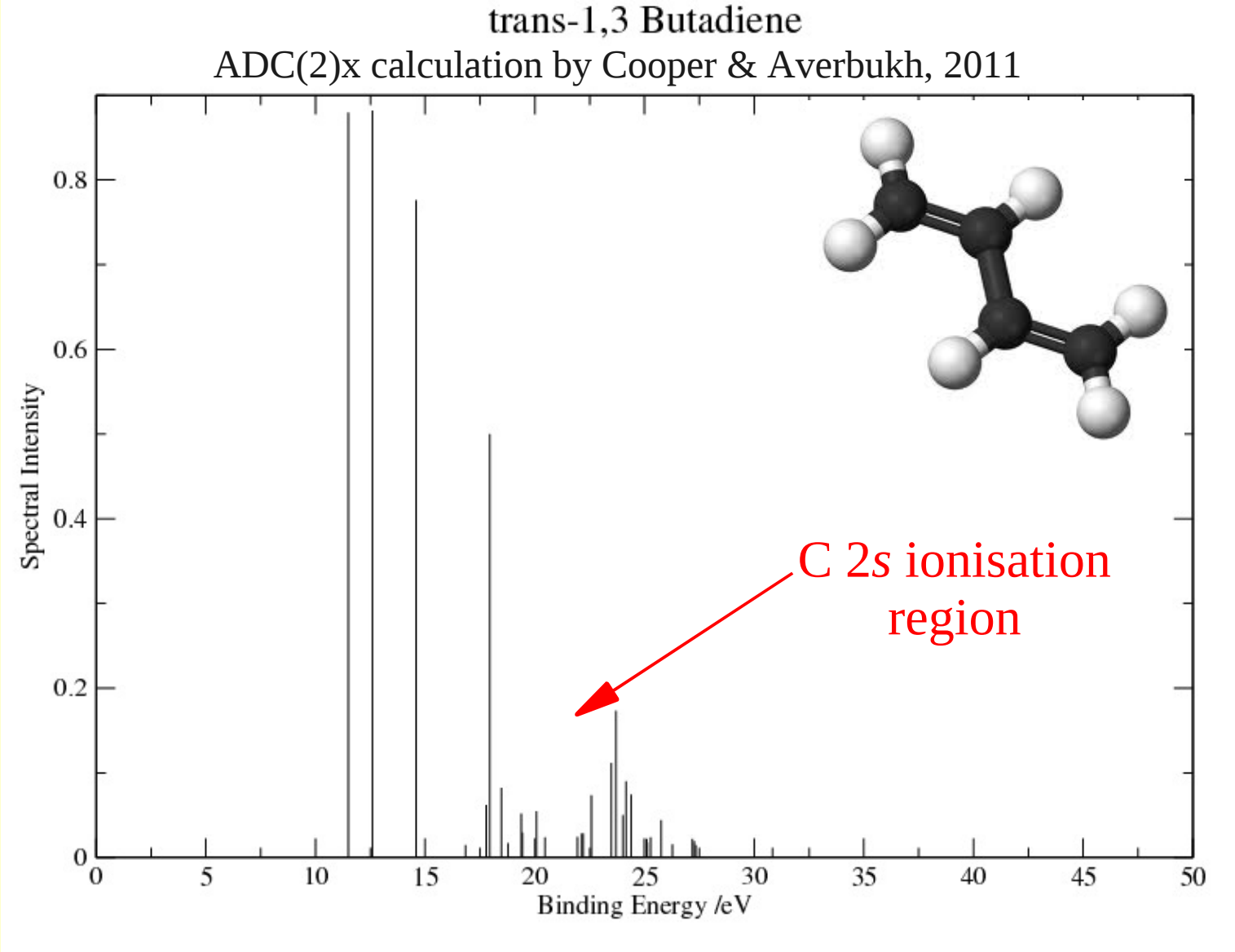
Single-photon LEAD: ADC(2)x-Stieltjes results

$$(3s^{-1})Ar^{+} + \hbar\omega \rightarrow (3p^{-2})Ar^{++} + e^{-}$$



Cooper & Averbukh, 2012

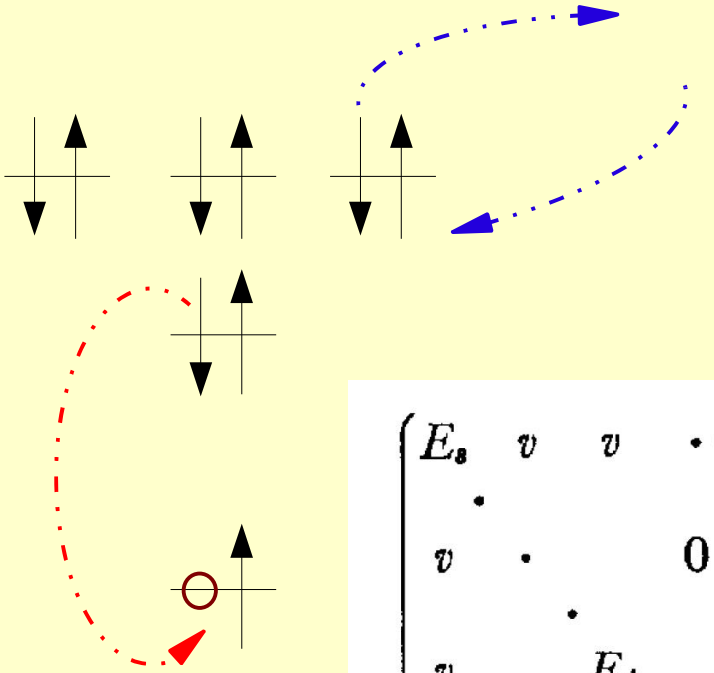
Inner valence ionisation in molecules: Breakdown of MO picture



[Cederbaum, Domcke, Schirmer & von Niessen, Adv. Quantum Chem. **65**, 115 (1986)]

Breakdown of MO picture: an Auger transition that did not happen...

Bixon-Jortner type instead of Fano-Feshbach type situation



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 48, NUMBER 2 15 JANUARY 1968

Intramolecular Radiationless Transitions

MORDECHAI BIXON AND JOSHUA JORTNER
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(Received 7 August 1967)

$$\begin{pmatrix} E_s & v & v & \cdots \\ & \cdot & & \\ v & \cdot & & 0 \\ & & \cdot & \\ v & & E_i & \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & 0 & & \cdot \end{pmatrix} \begin{pmatrix} a_n \\ \cdot \\ \cdot \\ \cdot \\ b_i{}^n \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} = E_n \begin{pmatrix} a_n \\ \cdot \\ \cdot \\ \cdot \\ b_i{}^n \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}$$

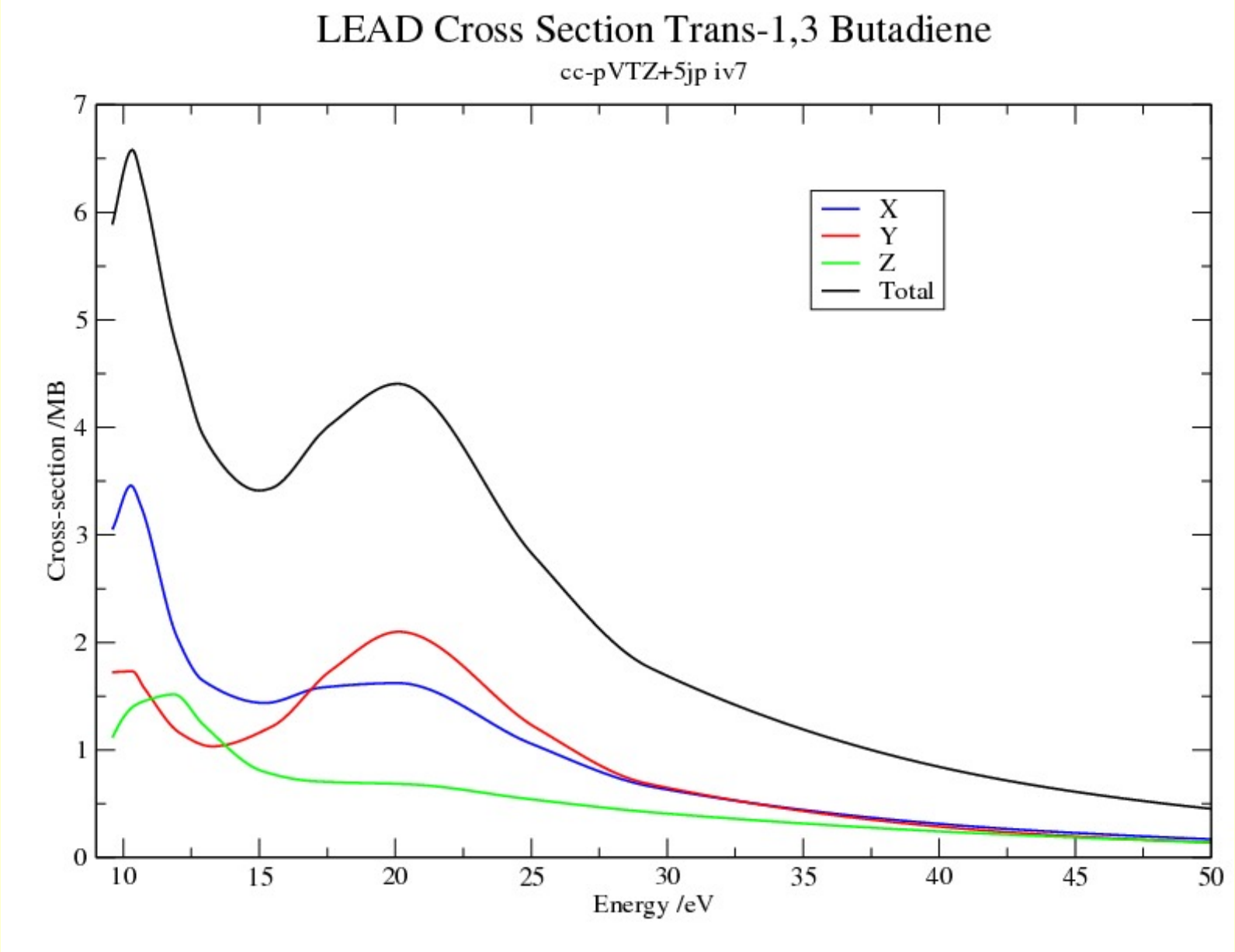
Equidistant, E_{i+1}-E_i=ε, "quasicontinuum" levels

Uniform bound-quasicontinuum coupling, v

Exponential decay takes place for $t<\hbar/\varepsilon$

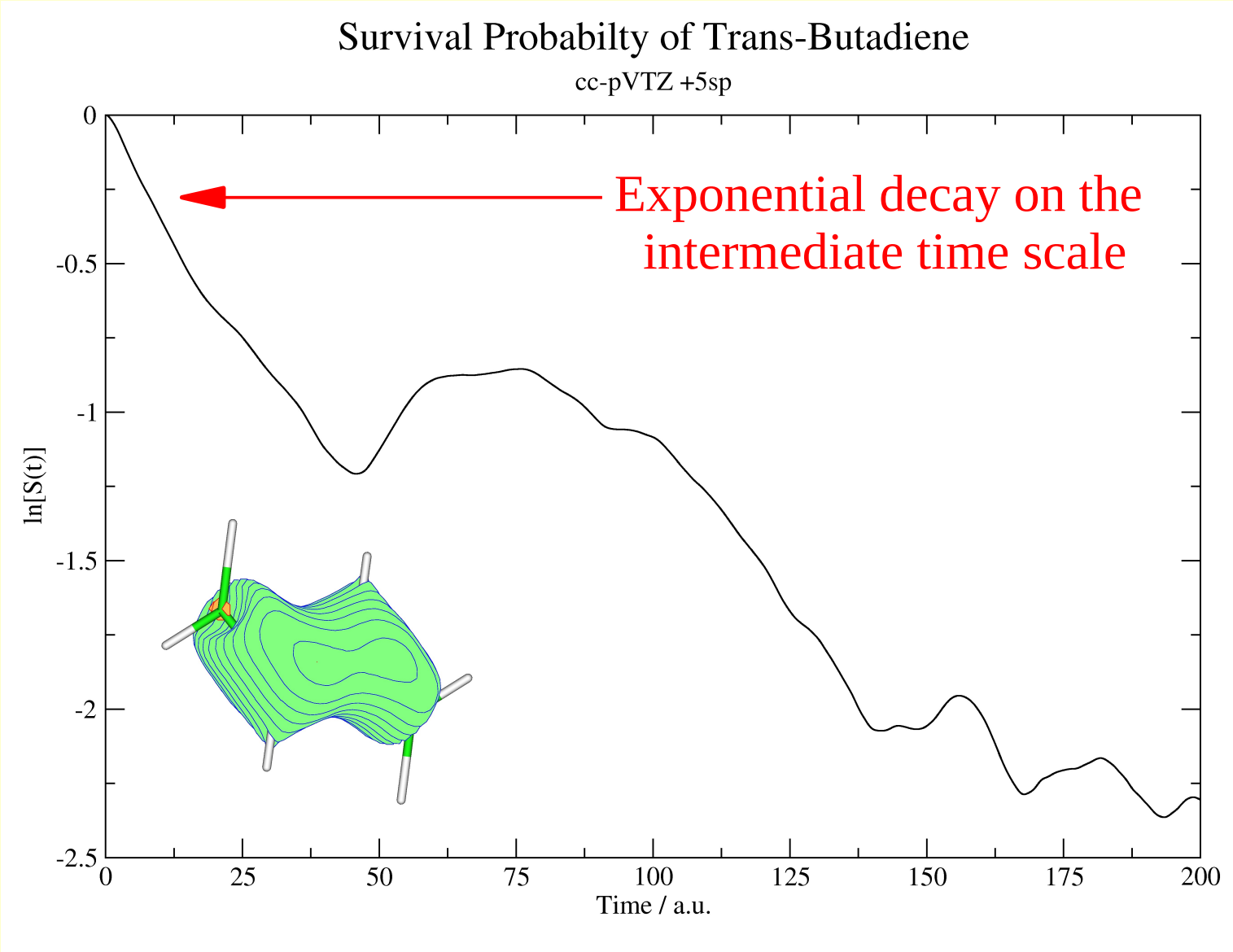
$$E_i = E_s - \alpha + i\epsilon, \qquad i = 0, \pm 1, \pm 2, \cdots.$$

Single-photon LEAD & MO picture breakdown: Strong enhancement relative to atomic case



Cooper & Averbukh, 2012

Breakdown of MO picture: The time-dependent picture



Cooper & Averbukh, 2012

Rate of quasi-exponential decay without time propagation

True exponential decay widths: $\Gamma = 2\pi \left| \langle \Phi \mid \hat{H} - E_r \mid \chi_{E_r} \rangle \right|^2$

can be obtained using discretized continuum and Stieltjes imaging.

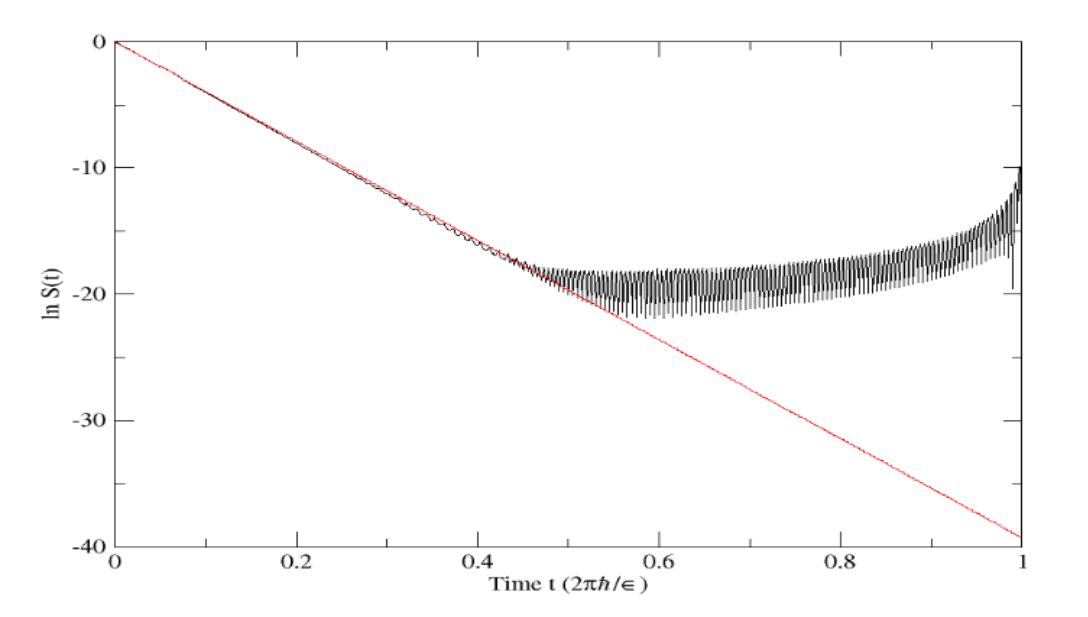
Why not to apply the Stieltjes imaging procedure to truly discrete final states?

This is a mapping of the real discrete-level system onto imaginary system with a discrete state coupled to a continuum.

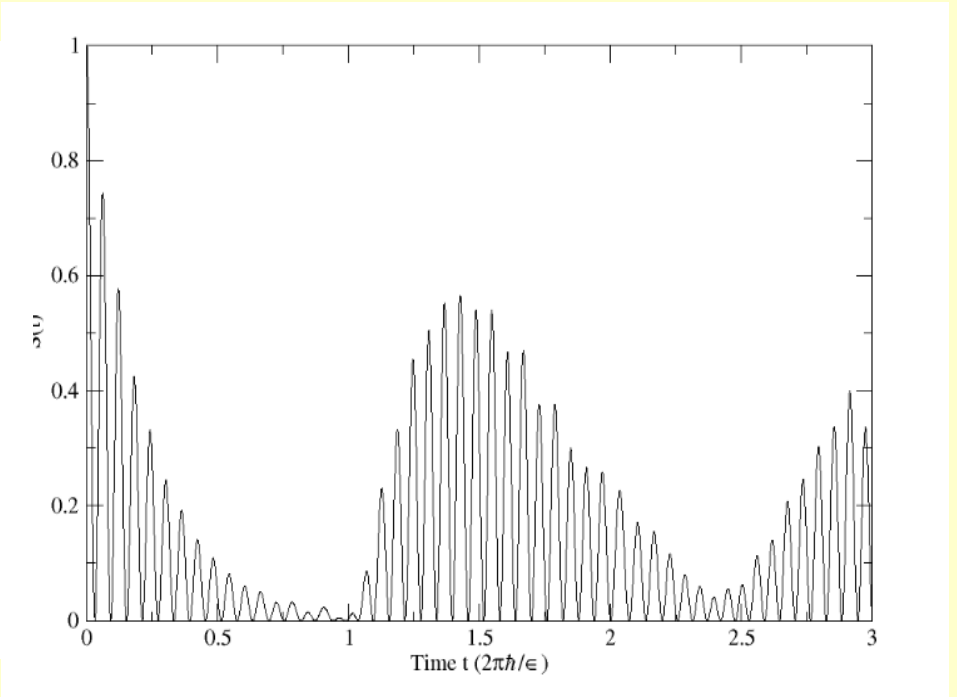
Will it work...?

Rate of quasi-exponential decay without time propagation

... it will!



... it won't!

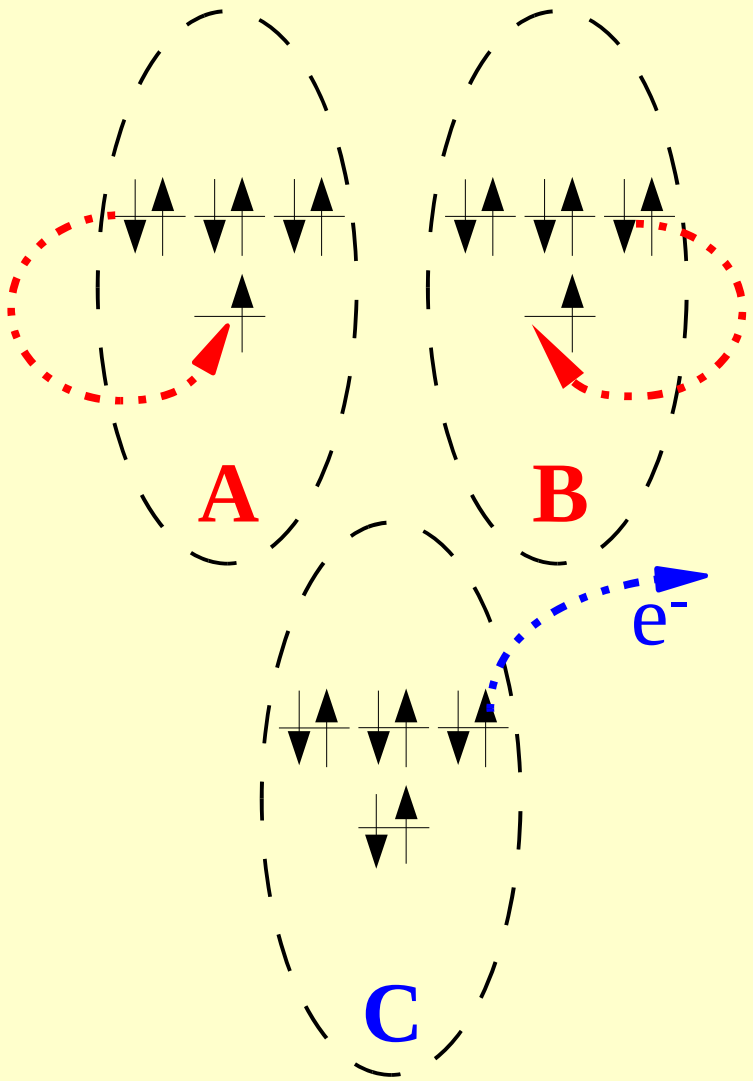


if there IS exponential decay (Bixon-Jortner model).

if there IS NO exponential decay (Morokuma-Freed model).

Craigie, Hammad & Averbukh, BSc project, 2011

Three-electron transitions: Collective decay



Example:

$(3s^{-1})Ar^{+}Ar \not\rightarrow$

but

$[(3s^{-1})Ar^{+}]_2Ar \rightarrow 3\,(3p^{-1})Ar^{+}$

Two-virtual-photon transfer, an equivalent of a two-photon ionization process

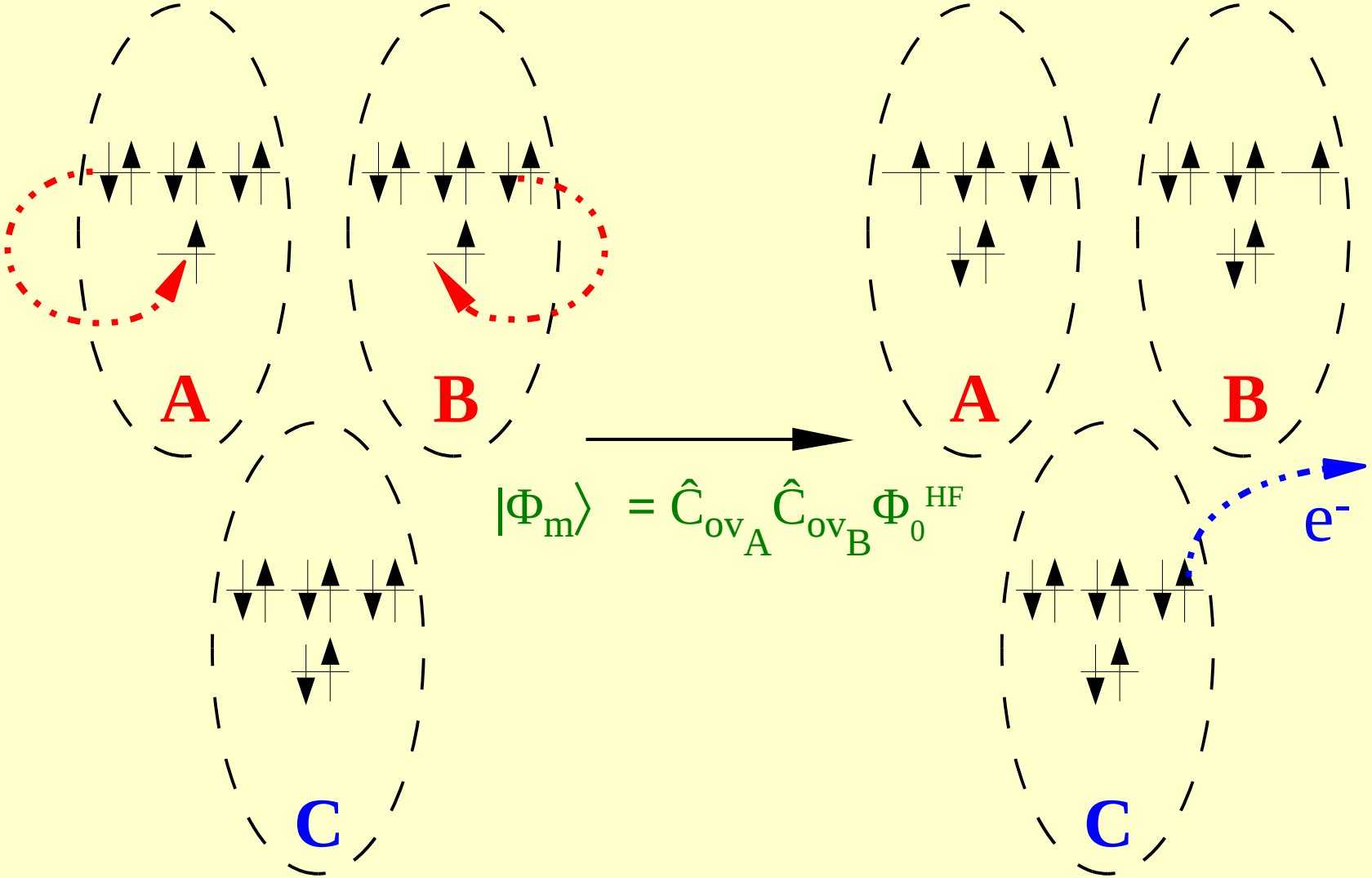
Description of the collective decay requires second-order perturbation theory:

$$\Gamma = 2\pi \left| \sum_m \frac{\langle \Phi_{fin}|V|\Phi_m\rangle\langle \Phi_m|V|\Phi_{in}\rangle}{E_{in} - E_m} \right|^2 \delta(E_{fin}-E_{in})$$

an intermediate state $|\Phi_m\rangle$ defines a two-step decay pathway contributing to Γ

[Averbukh and Kolorenč, PRL **103**, 183001 (2009)]

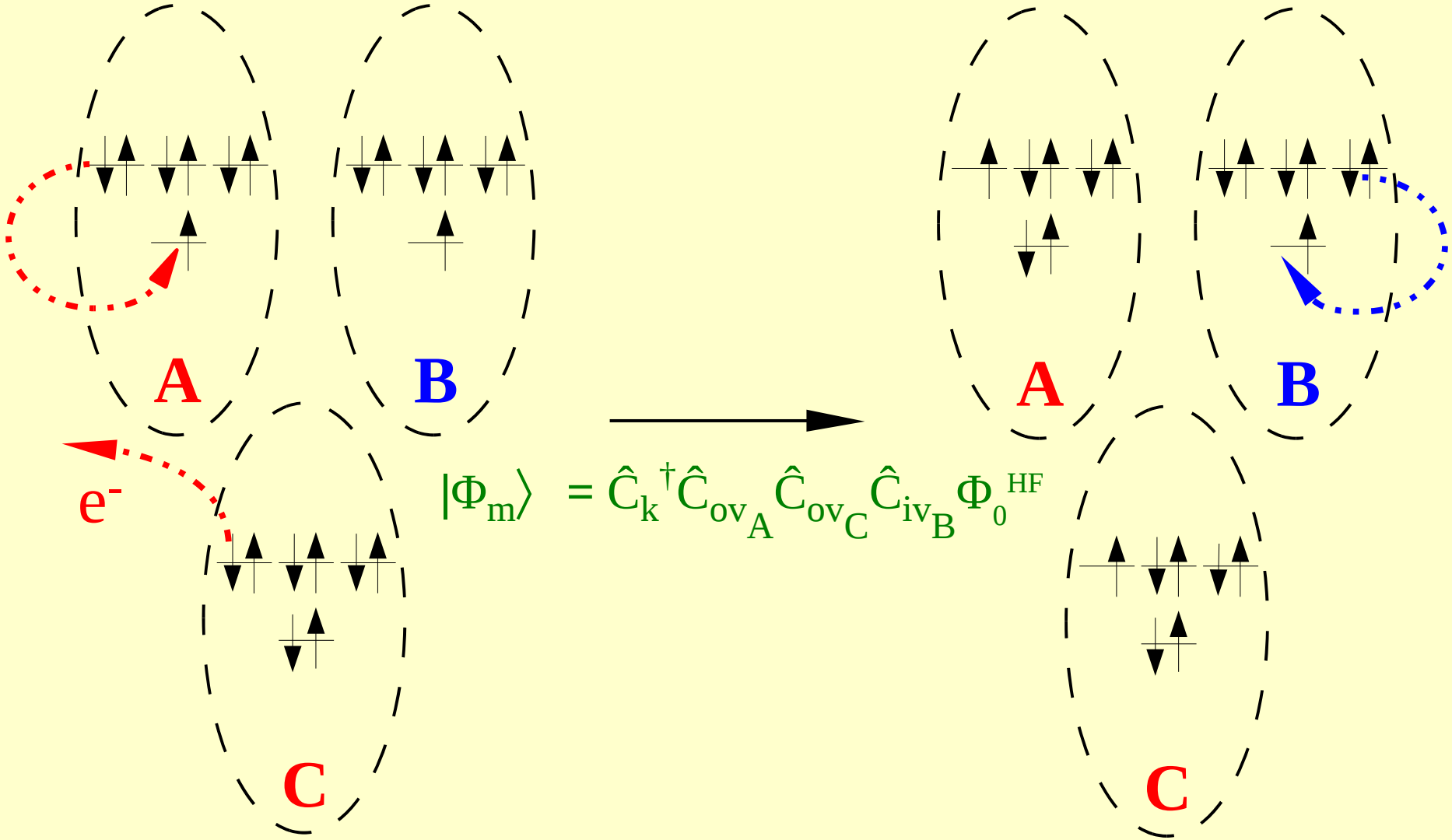
Examples of collective decay pathways



virtual recombination, $1/R^6_{AB}$

ionization, $1/R^4_{AC}$, $1/R^4_{BC}$

Examples of collective decay pathways

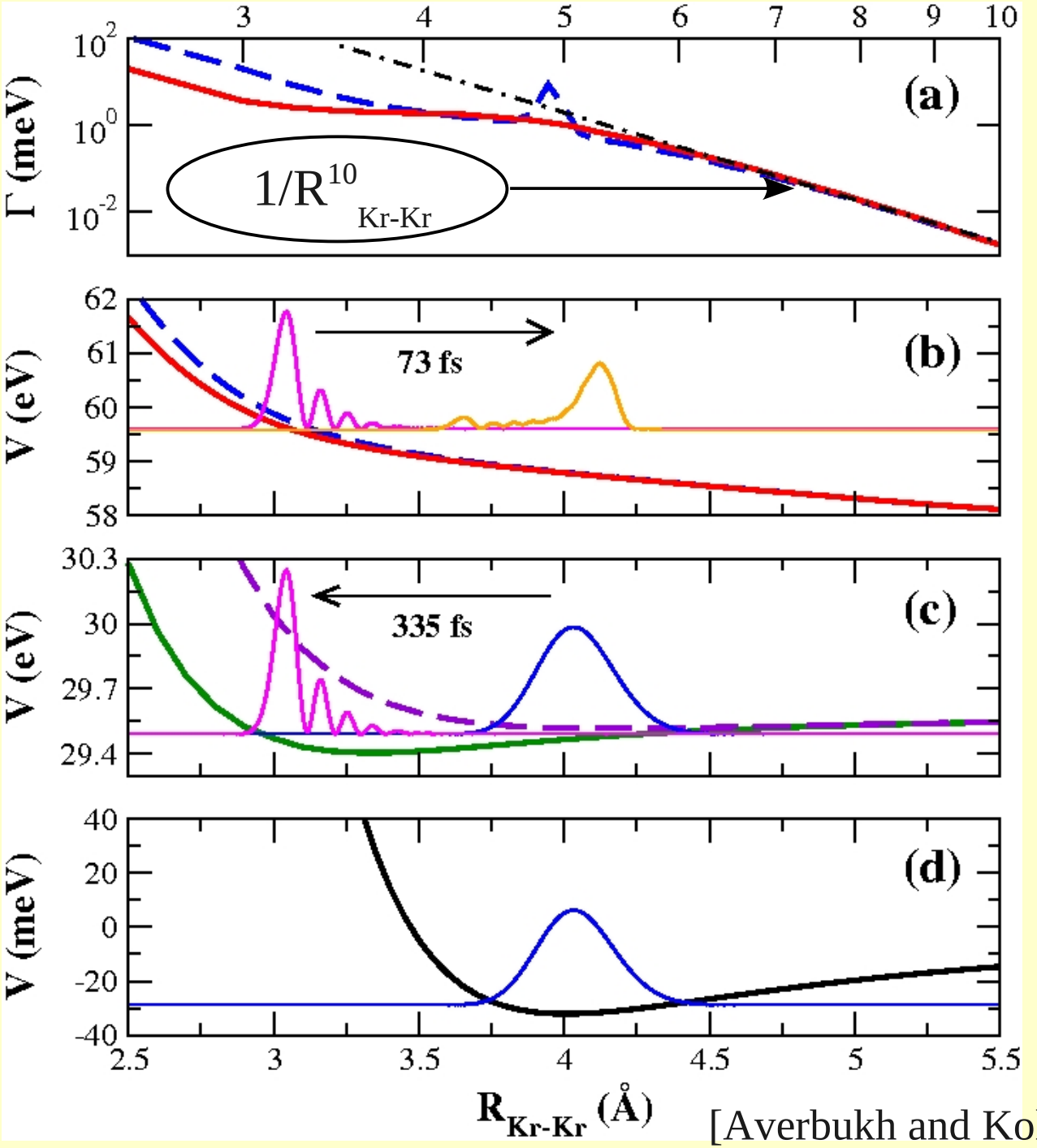


$$|\Phi_m\rangle = \hat{C}_k^{\dagger}\hat{C}_{ov_A}\hat{C}_{ov_C}\hat{C}_{iv_B}\Phi_0^{HF}$$

virtual ICD, $1/R^6_{AC}$

recombination, $1/R^4_{AB}$, $1/R^4_{BC}$

Collective decay in $[(4s^{-1})\ Kr^{+}]_2Ar$



$\tau(4Å) \approx 300$ fs

30%-65% yields for the collective decay

$(4s^{-1})\ Kr^{+}$ $(4s^{-1})\ Kr^{+}$

Ar

$(4s^{-1})\ Kr^{+}$ Kr

Ar

Kr Kr

Ar

[Averbukh and Kolorenč, PRL **103**, 183001 (2009)]

Summary

- Quantum chemistry is not only for bound state energies and properties – with some tricks, it can be used for bound-continuum transitions.

- But there is no magic, of course, and using $\mathscr{L}^2$ functions does impose very strict limits on what you can do, that is not much beyond total cross-sections and decay width...

- So, future belongs to hybrid computational approaches, where quantum chemistry machinery is used for bound states and some kind of one- or (better!) two-electron true continuum states are constructed.

The team

Imperial College:

Ms. N. Bahmanpour – inter-atomic decay in endohedral fullerenes

Dr. B. Cooper – laser-enabled Auger decay

Mr. J. Leeuwenburgh – streaking and HHG spectroscopy of Auger decay

Mr. M. Ruberti – photoionization by B-spline ADC

Perugia:

Prof. F. Tarantelli

MPI PKS, Dresden:

Prof. J.-M. Rost

Dr. U. Saalmann

TC Heidelberg:

Prof. L. S. Cederbaum

Prof. J. Schirmer

Dr. K. Gokhberg

Dr. S. Kopelke

Prague:

Dr. P. Kolorenč

Soon also: P. Decleva, Trieste

Funding:

EPSRC Career Acceleration Fellowship

Imperial College London

CORINF ITN, EPSRC Programme Grant