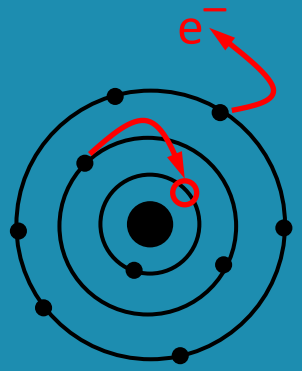
KU LEUVEN

Complex-scaled coupled-cluster methods for decaying electronic states



$$E_{\mathrm{res}} = E - \mathrm{i}\,\Gamma/2$$

Thomas Jagau

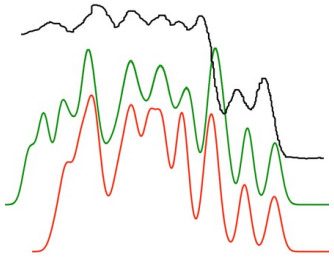
Department of Chemistry, KU Leuven, Belgium

https://chem.kuleuven.be/en/research/qcpc/tue/

Many-Body Theory: Nuclear Physics Meets Quantum Chemistry

Mainz, September 1, 2026

Unbound electrons & loosely bound electrons

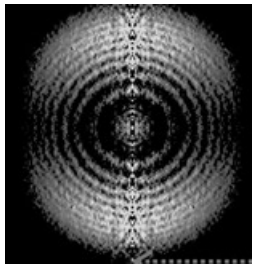


X-ray & Auger spectroscopies

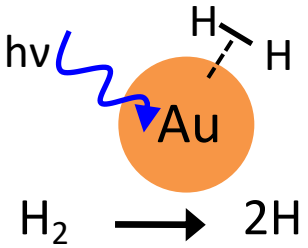
Nuclear chemistry

Laser physics

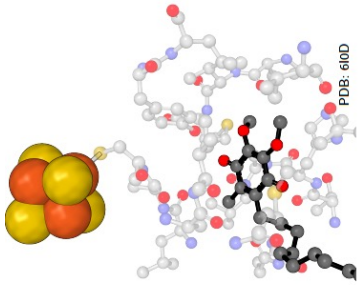
Atmospheric chemistry



Photodetachment spectroscopy

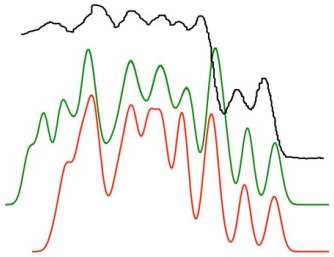


Plasmonic catalysis



Biological electron transfer

Unbound electrons & loosely bound electrons



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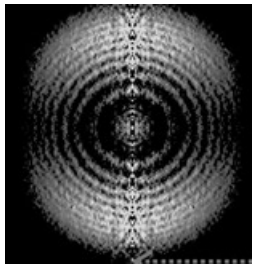

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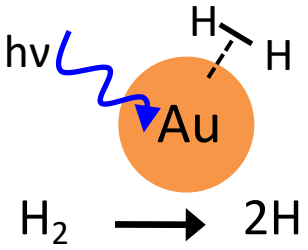

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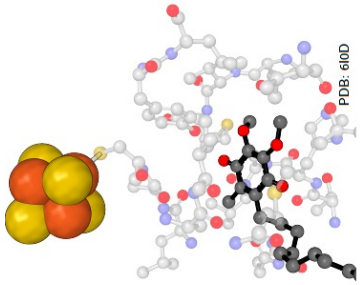
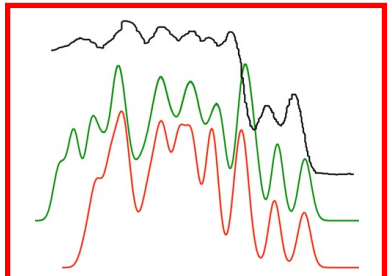


Biological electron transfer

- Superexcited electronic states
  - Small energy differences
  - Open shells
  - Multiconfigurational character
  - Decaying character

Relevant from meVs to keVs

Unbound electrons & loosely bound electrons



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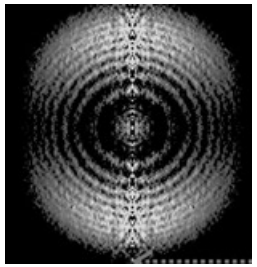

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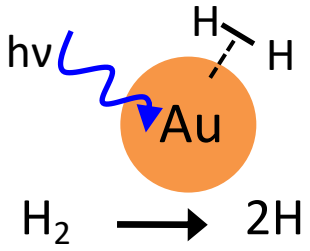

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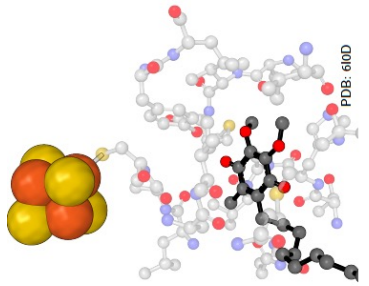

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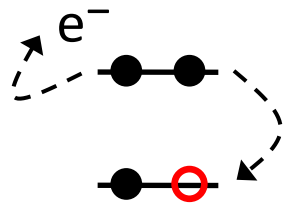
Relevant from meVs to keVs

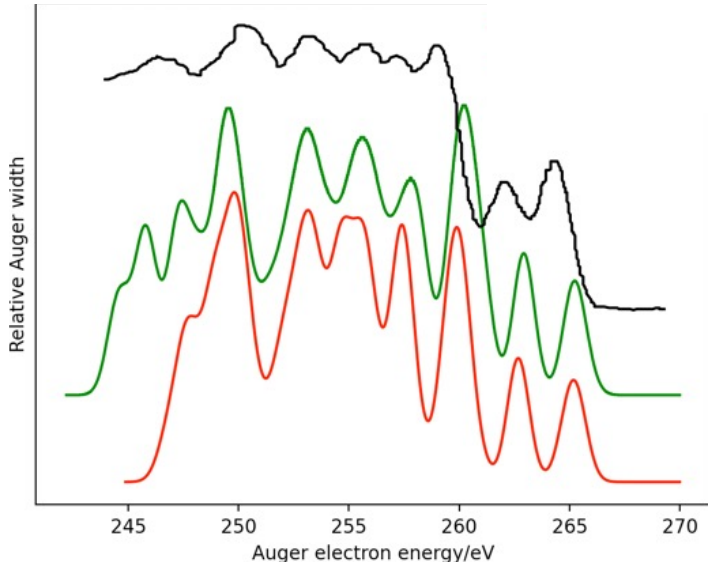
- Auger decay



Example:

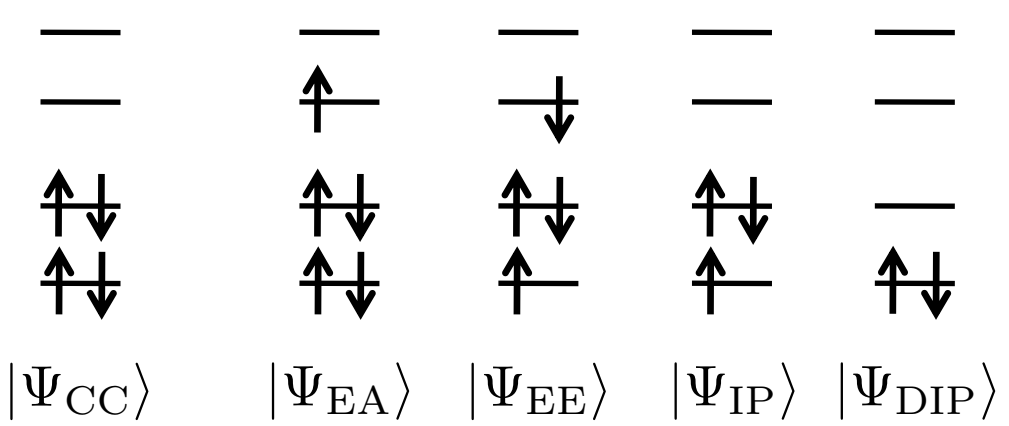
$C_6H_6^+ (1s^{-1}) \longrightarrow C_6H_6^{2+} + e^-$

  - 6 initial states of $C_6H_6^+ (1s^{-1})$
  - 166 final states of $C_6H_6^{2+}$
  - >1000 transitions



Electronic-structure methods for excited states

- Equation-of-motion coupled-cluster theory (EOM-CC)
  - Reference state $|\Psi_{\mathrm{CC}}\rangle = e^{T}|\Psi_{\mathrm{HF}}\rangle$
  - Target states $|\Psi_k\rangle = R_k\,|\Psi_{\mathrm{CC}}\rangle$
  - Common truncation: EOM-CCSD $T = T_1 + T_2$, $R = R_1 + R_2$



- Second-order approximate coupled-cluster theory (CC2)
  - Perturbative approximation to EOM-CCSD, applicable to larger molecules

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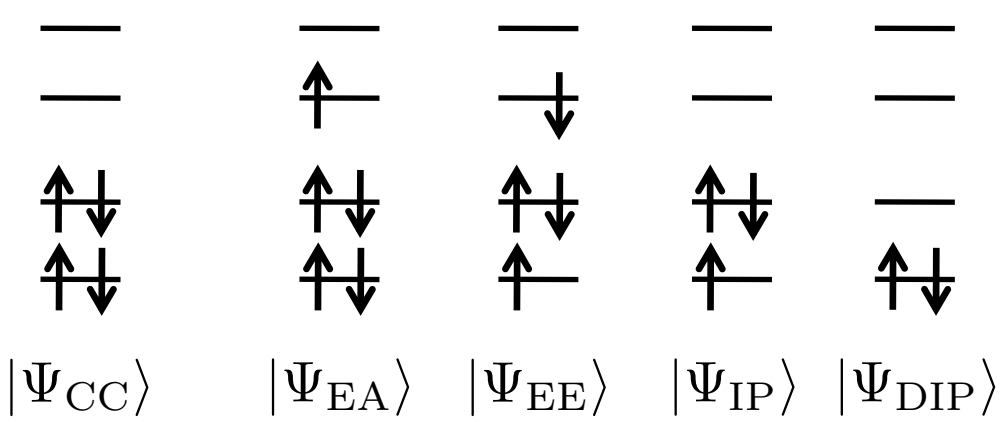
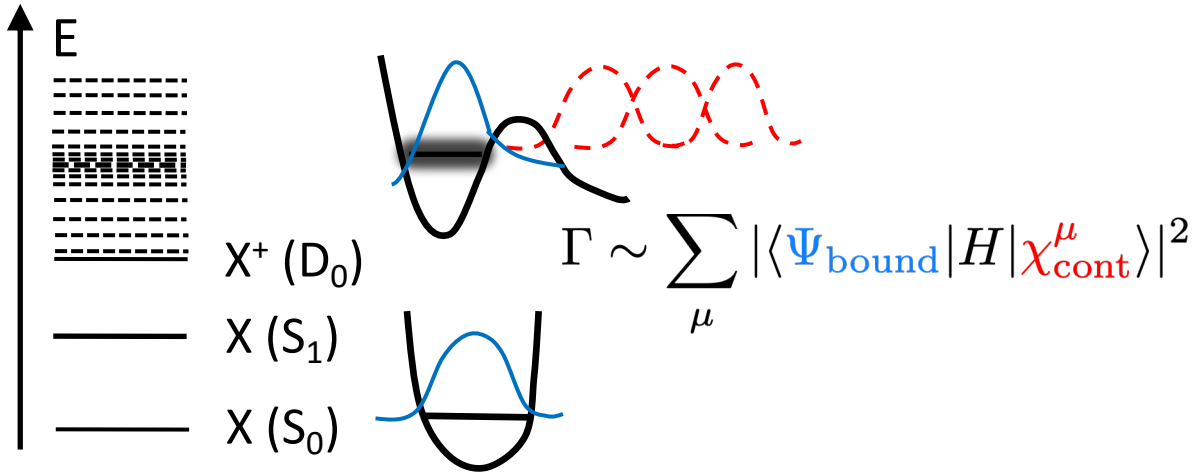


- Second-order approximate coupled-cluster theory (CC2)
  - Perturbative approximation to EOM-CCSD, applicable to larger molecules
- Our implementation Q-CHEM
  - Excitation energies (EE), ionization potentials (IP), double ionization potential (DIP), electron affinities (EA), spin flip (SF)
  - Resolution-of-the-identity approximation, Cholesky decomposition
  - Dyson orbitals, natural Auger orbitals
  - Complex scaling, complex basis functions, complex absorbing potentials for decaying states

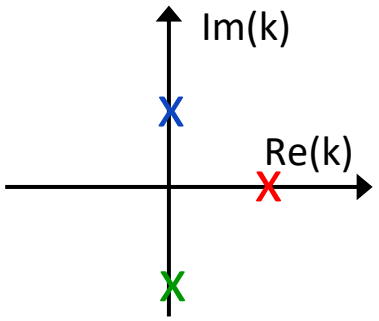
Theory of unbound electrons

- Hermitian quantum mechanics



$$\Gamma \sim \sum_{\mu} |\langle \Psi_{\text{bound}} | H | \chi^{\mu}_{\text{cont}} \rangle|^2$$

- Complex momentum plane $\Psi(x) \sim \exp(ikx)$



  - bound states $\Psi(x) \sim \exp(-k_I x)$
    $E = -k_I^2/2 \in \mathbb{R}^-$
  - continuum states $\Psi(x) \sim \exp(i\, k_R\, x)$
    $E = +k_R^2/2 \in \mathbb{R}^+$
  - virtual states $\Psi(x) \sim \exp(+k_I x)$
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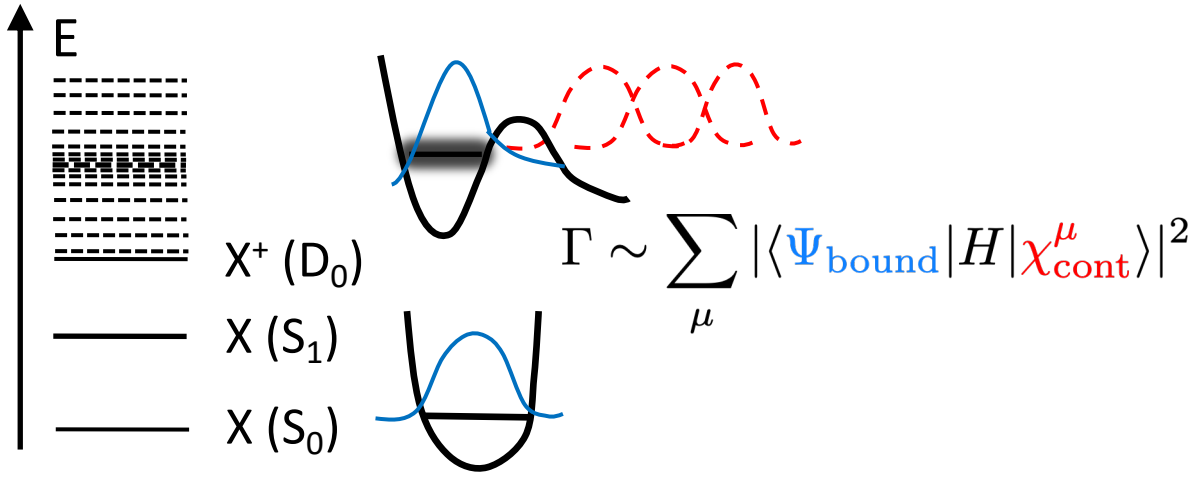

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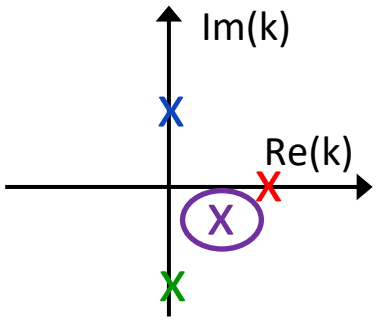

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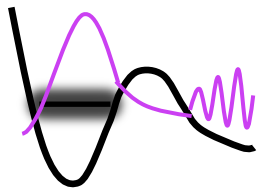
- Non-Hermitian quantum mechanics



$$\Psi(x) \sim \exp(+k_I x)\exp(i\,k_R\,x)$$
$$E_{\text{res}} = 1/2\,[k_R^2 - k_I^2 - 2i\,k_R k_I] \in \mathbb{C}$$
$$= E - i\,\Gamma/2$$

  - Resonances are discrete states
  - No need for explicit continuum treatment

$$E_{\text{res}} = E - i\,\Gamma/2 \;\in\; \mathbb{C}$$

  - Realization via
    - complex absorbing potentials
    - complex scaling
    - complex basis functions

Complex scaling and complex basis functions

- Resonance wave function requires regularization $\Psi(x) \sim \exp(+k_I x) \exp(i\, k_R\, x)$

Aguilar, Balslev, Combes, Commun. Math. Phys. 22, 269 (1971)
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McCurdy, Rescigno, Phys. Rev. Lett. 41, 1364 (1978)
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Matz, Jagau, J. Chem. Phys. 156, 114117 (2022)

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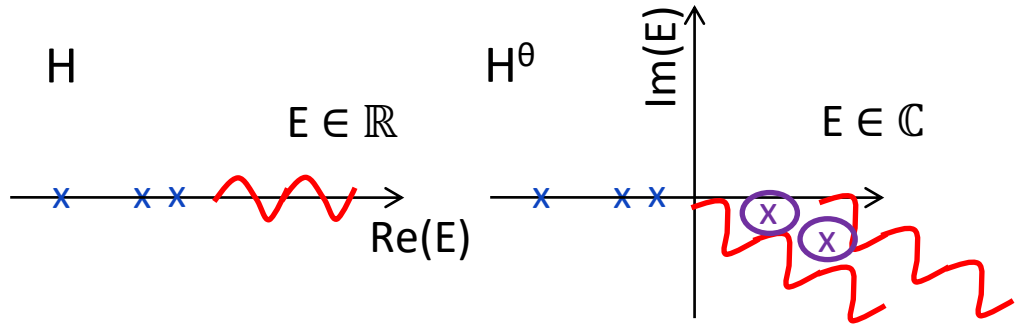
- Complex scaling: $H(x) \rightarrow H^\theta(x\,e^{i\theta})$ $0 < \theta < \pi/4$ $H^\theta = SHS^{-1}$ $S = \exp(\mathrm{i}\,\theta\,x\,\mathrm{d}/\mathrm{d}x)$
  - Exact representation of Ψ: dE/dθ = 0
  - Finite basis sets: dE/dθ ≠ 0

    ⟶ min[dE/dθ] ; computational overhead

Complex energy plane:



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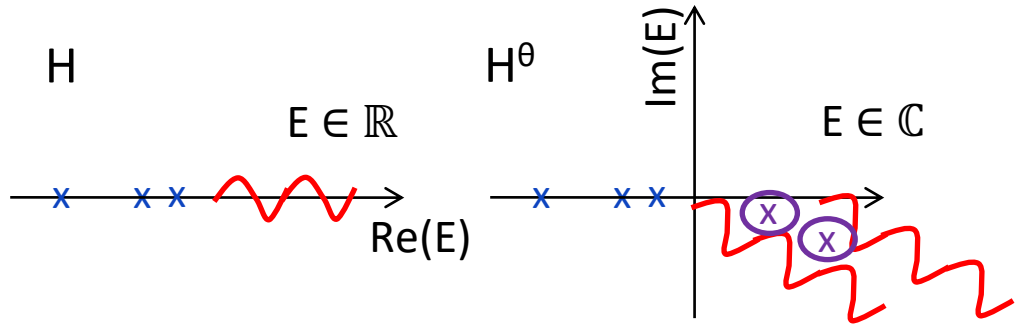

$E_{\mathrm{res}} = E - \mathrm{i}\Gamma/2$

- Method of complex basis functions:
  - Born-Oppenheimer Hamiltonian is not analytic in θ
  - Solution: scale exponents of basis functions $\chi^\theta(x) \sim \exp\left(-\alpha\,e^{-2i\theta}(x-A)^2\right)$

$$E = \frac{\langle\Psi(x)|H(x\,e^{i\theta})|\Psi(x)\rangle}{\langle\Psi(x)|\Psi(x)\rangle} = \frac{\langle\Psi(x\,e^{-i\theta})|H(x)|\Psi(x\,e^{-i\theta})\rangle}{\langle\Psi(x\,e^{-i\theta})|\Psi(x\,e^{-i\theta})\rangle}$$

  - Available for RI-CC2, CCSD, EOM-EE/EA/IP/SF-CCSD, EOM-EE-CCSDT
  - *Not all basis functions need to be scaled*

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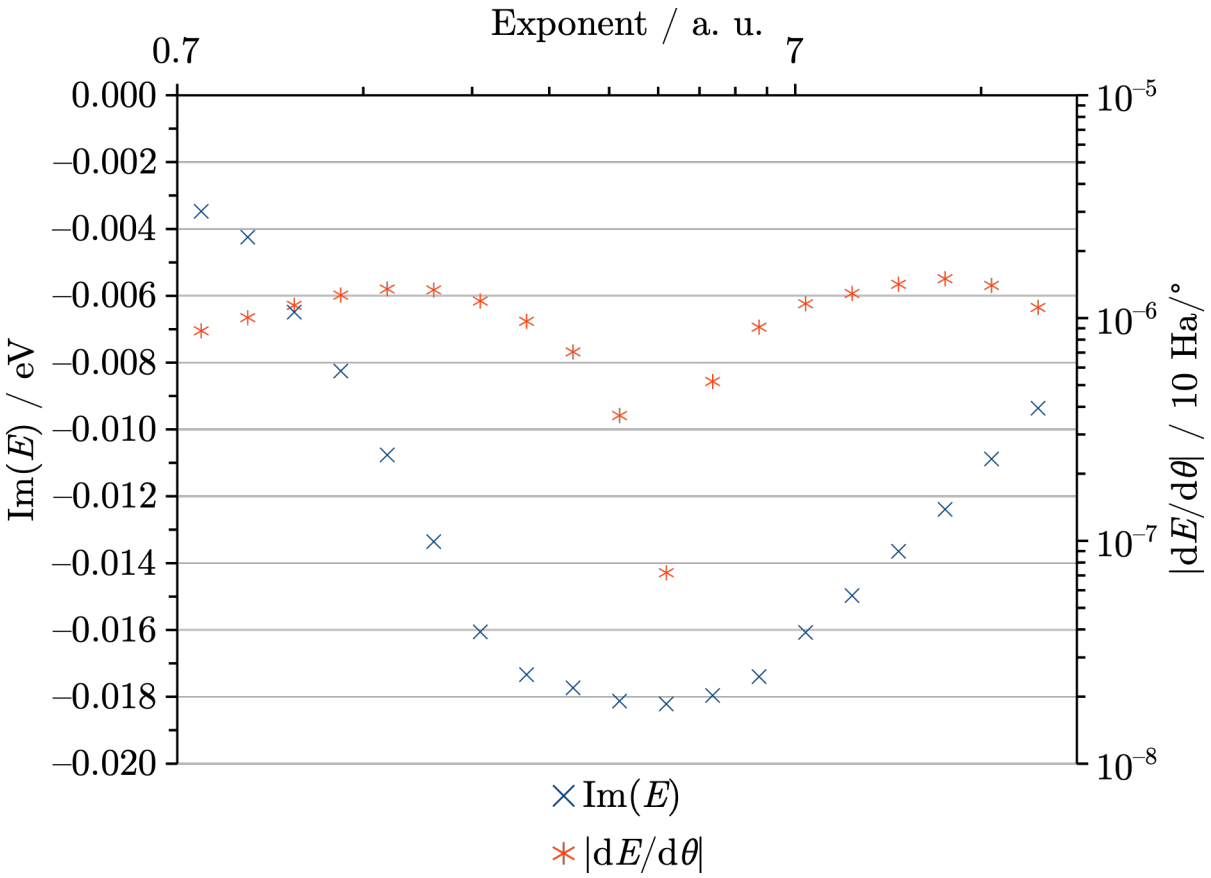
Choice of complex basis functions

- Example: Ne^+ ($1s^{-1}$)

CBF-EOMIP-CCSD / aug-cc-pV5Z + 1 *complex s function*



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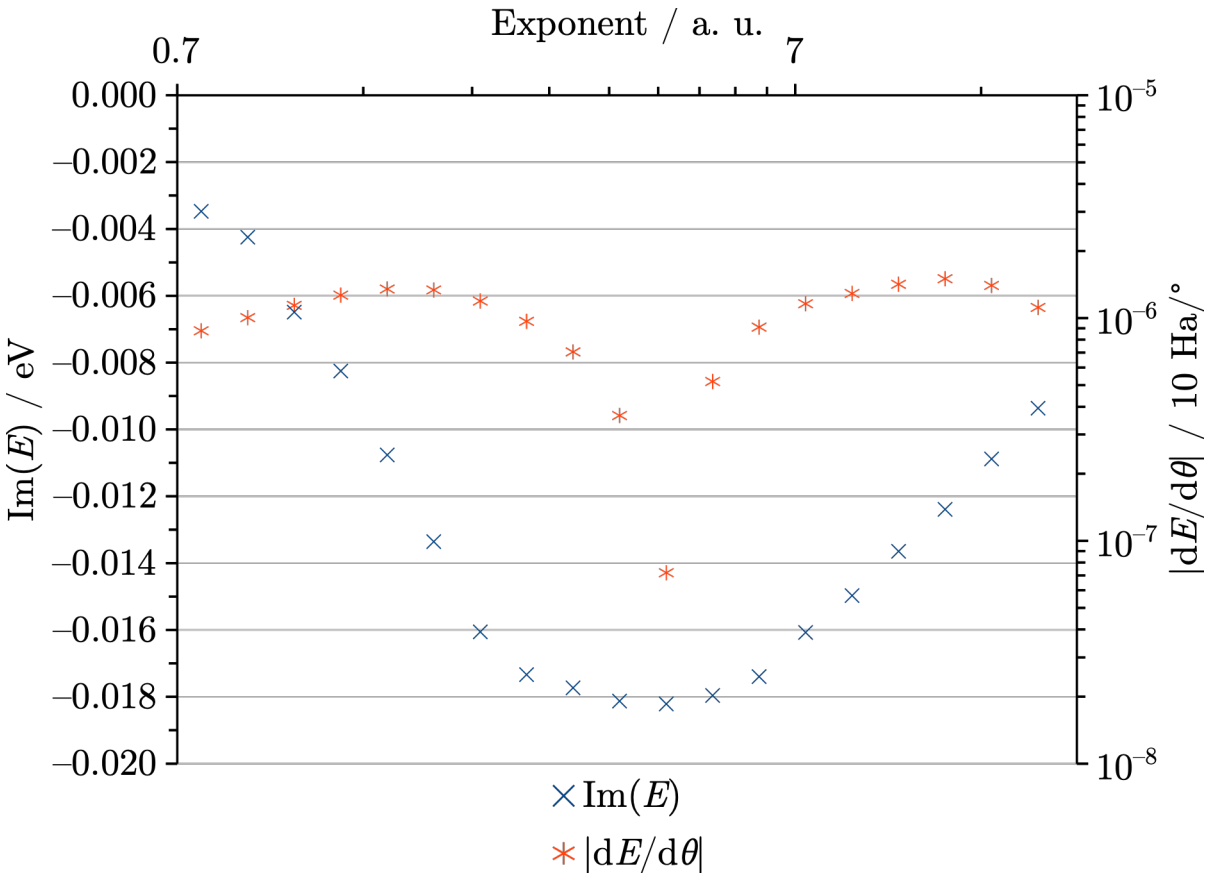

- Estimate for α for Ne^+ ($1s^{-1}$)

$$\chi^{\theta}(x) \sim \exp\left(-\alpha\, e^{-2i\theta}(x-A)^2\right)$$

E_{kin} ≈ 750–820 eV
→ α ≈ k ≈ 7.4–7.7 au

- Optimized total width of Ne^+ ($1s^{-1}$) / meV

Experiment		260
EOM-CCSD	Fano	218
EOM-CCSD	CS	226
EOM-CCSD	CBF	228

Basis: aug-cc-pCV5Z, for CBF: + *2s2p2d*

fast e^- ↓ steep slow e^- ↓ diffuse
CBFs

Matz, Jagau, J. Chem. Phys. 156, 114117 (2022)

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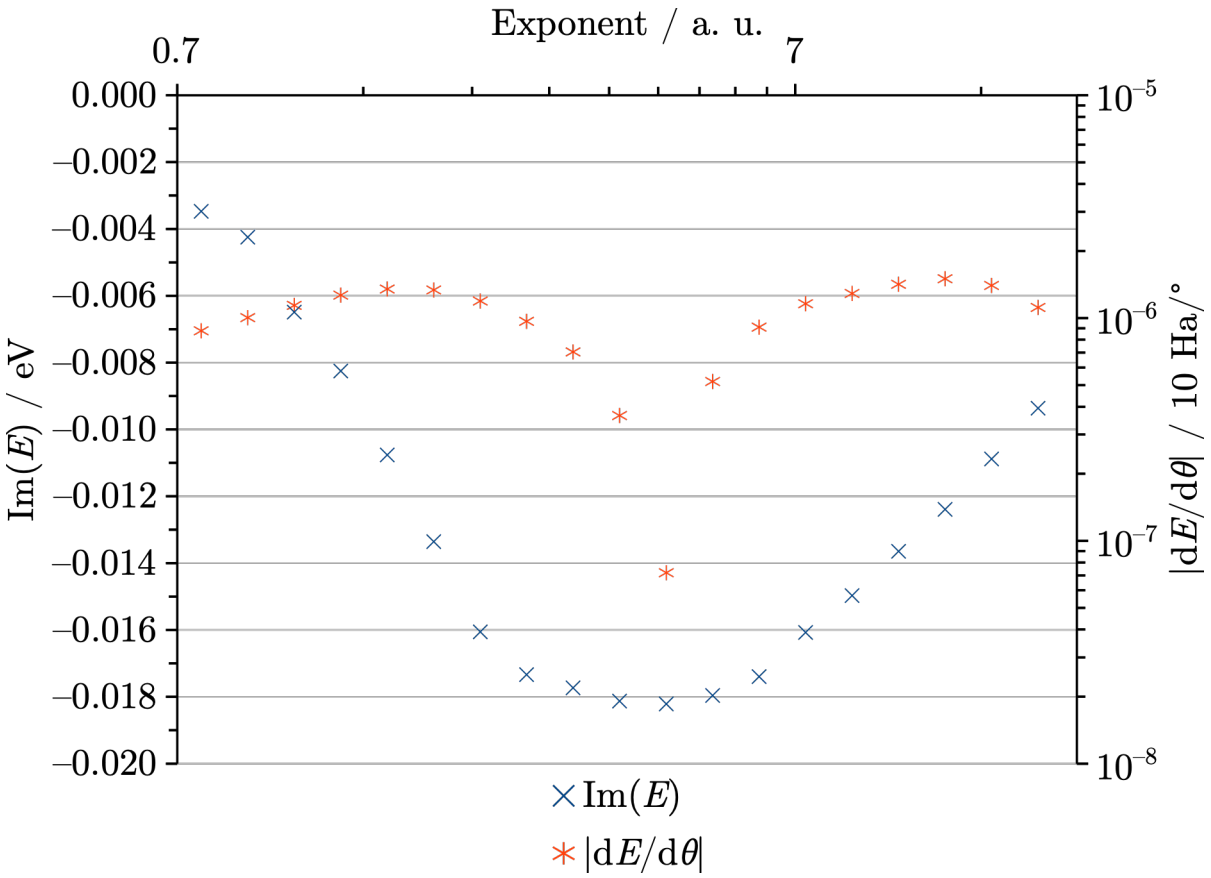

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CBFs

- Partial widths / meV

CBF-EOMIP-CCSD		Expt
aug-cc-pCV5Z + *2s*	38	40
aug-cc-pCV5Z + *2p*	62	68
aug-cc-pCV5Z + *2d*	128	150

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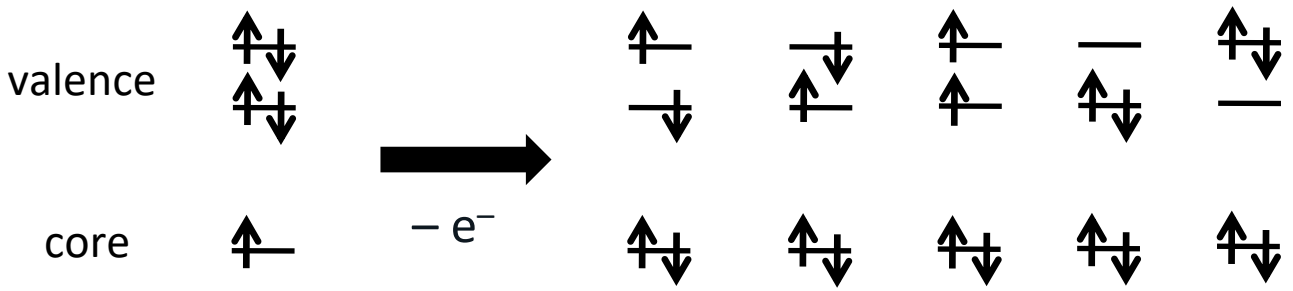
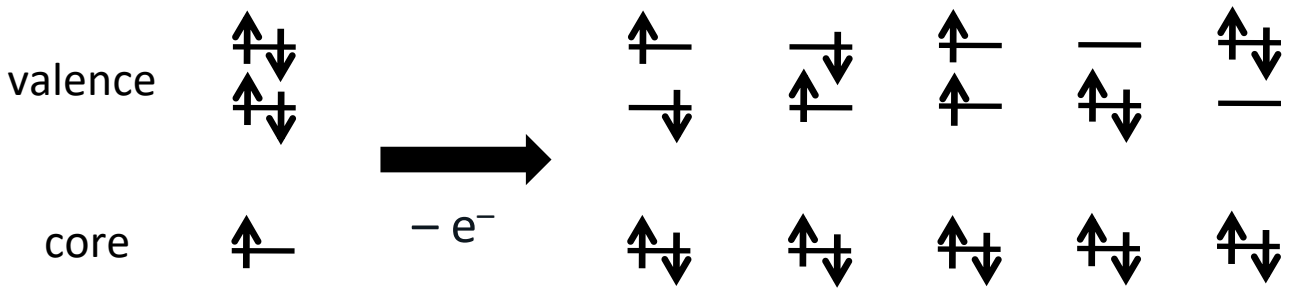
Modeling Auger spectra



- Total decay width $E_{\mathrm{res}} = E - i\,\Gamma/2 \;\in\; \mathbb{C}$
- Partial decay widths ?

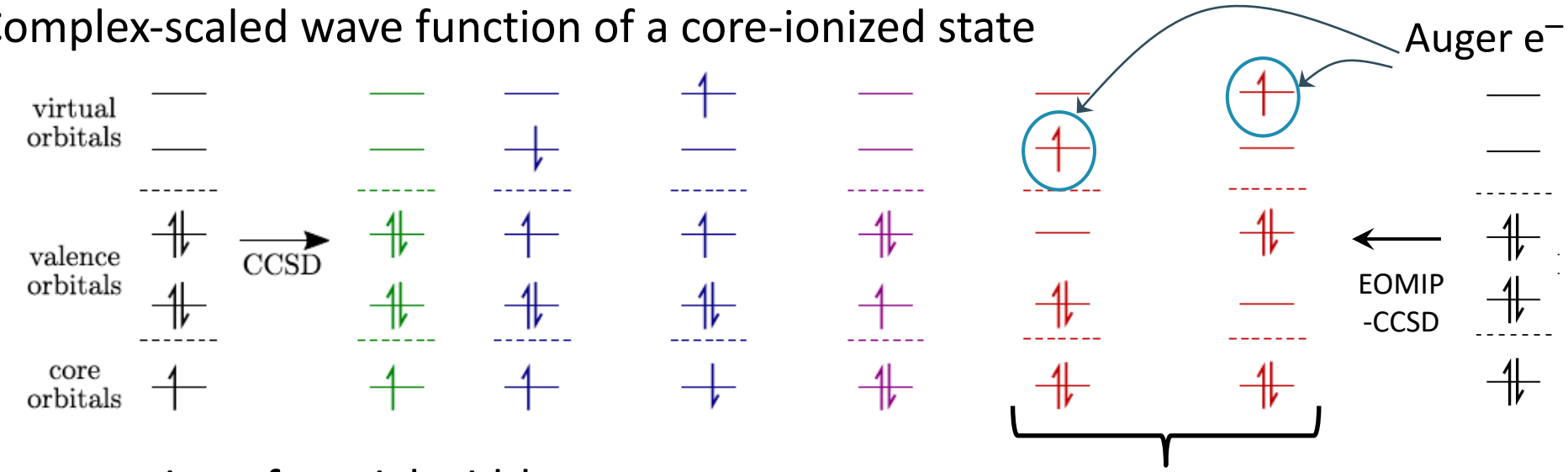
Matz, Jagau, J. Chem. Phys. 156, 114117 (2022)
Matz, Jagau, Mol. Phys. 121, e2105270 (2022)
Matz, Nijssen, Jagau, J. Phys. Chem. A 127, 6147 (2023)
Matz, Gkogkos, Jagau, J. Phys. Chem. A 130, 2252 (2026)

Modeling Auger spectra



- Total decay width $E_{\mathrm{res}} = E - i\,\Gamma/2 \in \mathbb{C}$
- Partial decay widths

- Complex-scaled wave function of a core-ionized state



- Computation of partial widths
  - Auger channel projector (ACP)
  - Decomposition of Im(*E*)

Matz, Jagau, J. Chem. Phys. 156, 114117 (2022)
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Modeling Auger spectra

- Analysis of core-ionized wave function yields partial widths Γ_{ij} in terms of orbital pairs i,j of $|\Psi_{\mathrm{coreIP}}\rangle$
- Separate calculation of peak positions $E_{\mathrm{Auger}} = E_{\mathrm{coreIP}} - E_{\mathrm{DIP}}$
- Mapping of partial widths Γ_{ij} onto $|\Psi_{\mathrm{DIP}}\rangle = \left(\sum_{ij} r_{ij} a_i a_j + \frac{1}{6}\sum_{ijka} r^a_{ijk} a^\dagger_a a_i a_j a_k\right)|\Psi_{\mathrm{CC}}\rangle$
  - ⟶ Use r^2_{ij} as weighting factor
  - ⟶ Accounts for orbital relaxation
  - ⟶ Results are invariant w.r.t. orbital rotations

Jayadev, Ferino-Perez, Matz, Krylov, Jagau, J. Chem. Phys. 158, 064109 (2023)
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- Peak width
  - Option 1: Uniform fwhm
  - Option 2: Explicit consideration of vibrational effects

$$\mathrm{fwhm}_I = \sqrt{8\ln 2 \cdot \beta_I^2 (1 + 2\kappa^2/\omega^2)}$$

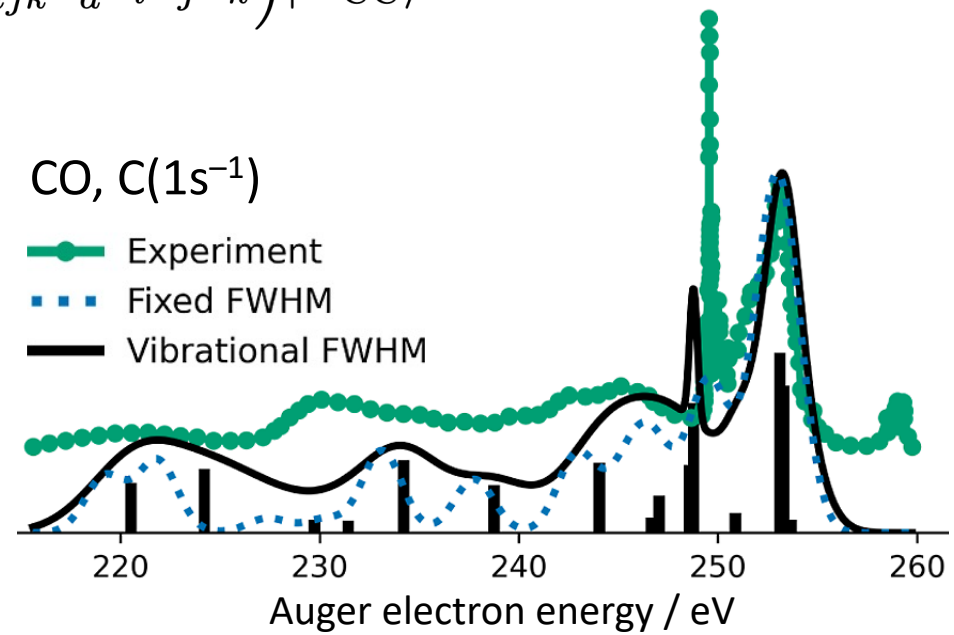
$$\beta_I = \frac{1}{\sqrt{2\mu\omega}} \frac{\mathrm{d}(E_{\mathrm{coreIP}} - E^I_{\mathrm{DIP}})}{\mathrm{d}R} \qquad \kappa = \frac{1}{2\mu\omega} \frac{\mathrm{d}E_{\mathrm{coreIP}}}{\mathrm{d}R} \qquad \omega = \frac{\mathrm{d}^2 E_0}{\mathrm{d}R^2}$$

Cederbaum et al., J. Chem. Phys. 95, 6634 (1991)
Camps, Jagau, et al., J. Phys. Chem. A 129, 4798 (2025)
Matz, Gkogkos, Jagau, J. Phys. Chem. A 130, 2252 (2026)

Modeling Auger spectra

- Analysis of core-ionized wave function yields partial widths Γ_{ij} in terms of orbital pairs i,j of $|\Psi_{\mathrm{coreIP}}\rangle$
- Separate calculation of peak positions $E_{\mathrm{Auger}} = E_{\mathrm{coreIP}} - E_{\mathrm{DIP}}$
- Mapping of partial widths Γ_{ij} onto $|\Psi_{\mathrm{DIP}}\rangle = \left(\sum_{ij} r_{ij} a_i a_j + \frac{1}{6}\sum_{ijka} r^a_{ijk} a^\dagger_a a_i a_j a_k\right)|\Psi_{\mathrm{CC}}\rangle$
  - ⟶ Use r^2_{ij} as weighting factor
  - ⟶ Accounts for orbital relaxation
  - ⟶ Results are invariant w.r.t. orbital rotations
- Peak width
  - Option 1: Uniform fwhm
  - Option 2: Explicit consideration of vibrational effects

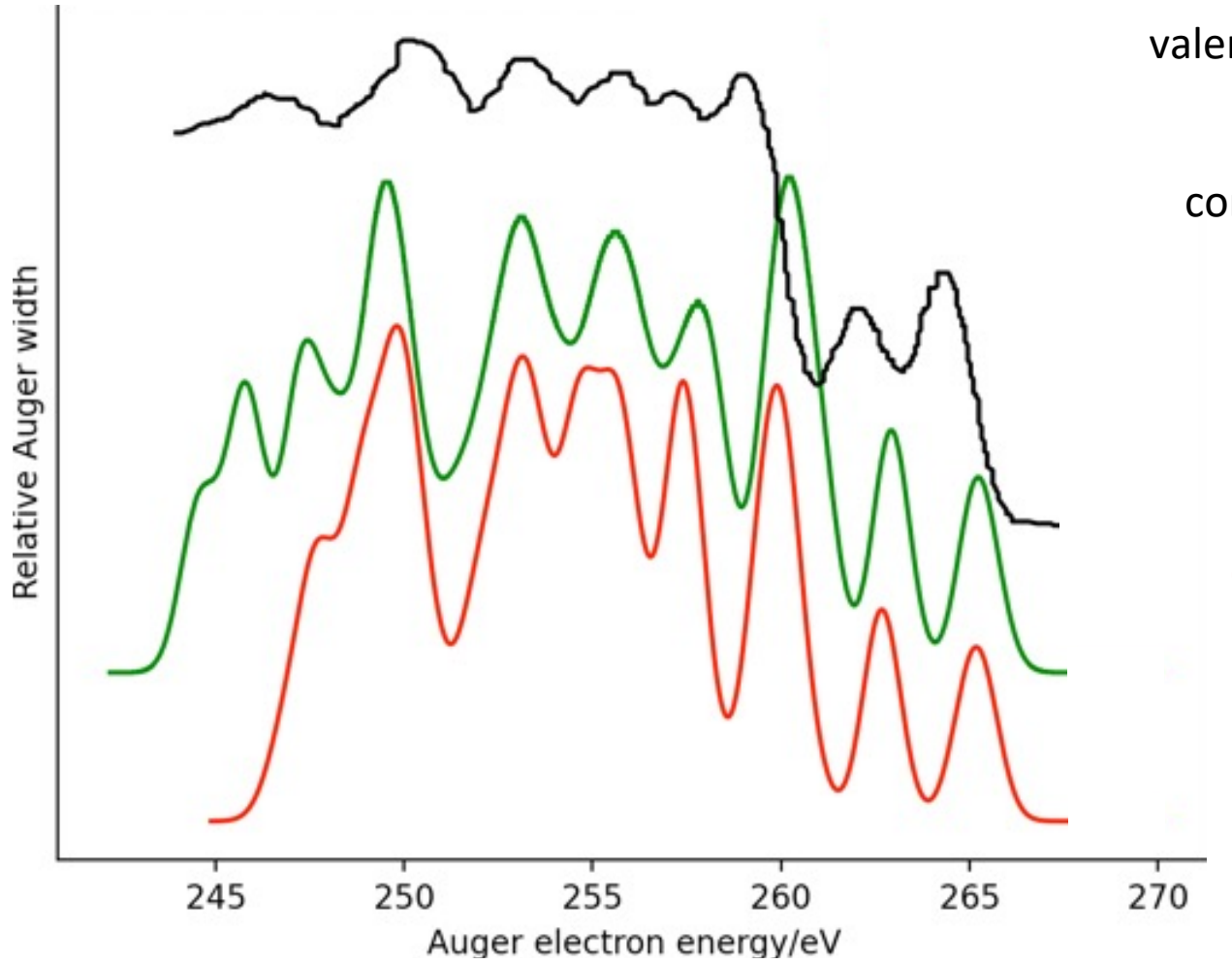
$$\mathrm{fwhm}_I = \sqrt{8\ln 2 \cdot \beta_I^2 (1 + 2\kappa^2/\omega^2)}$$

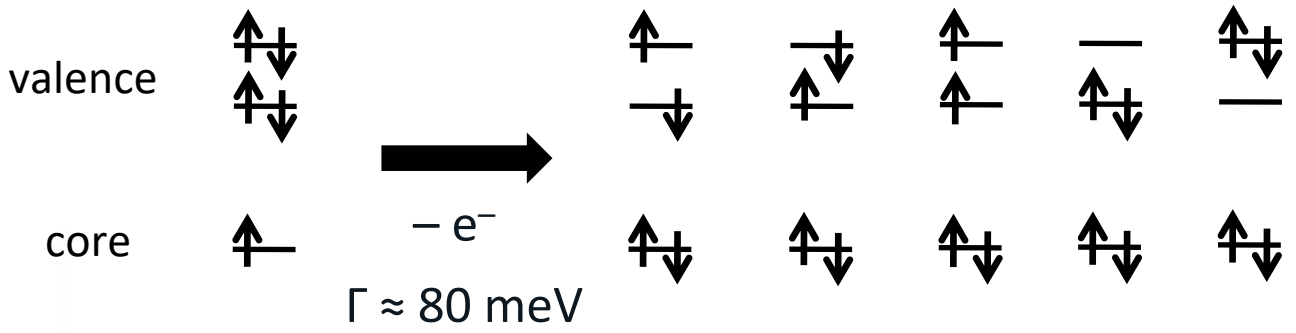


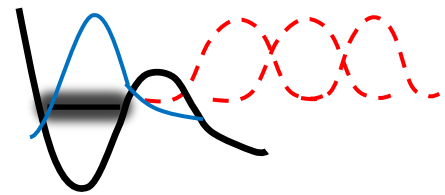
$$\beta_I = \frac{1}{\sqrt{2\mu\omega}} \frac{\mathrm{d}(E_{\mathrm{coreIP}} - E^I_{\mathrm{DIP}})}{\mathrm{d}R} \qquad \kappa = \frac{1}{2\mu\omega} \frac{\mathrm{d}E_{\mathrm{coreIP}}}{\mathrm{d}R} \qquad \omega = \frac{\mathrm{d}^2 E_0}{\mathrm{d}R^2}$$

Moddeman et al., J. Chem. Phys. 55, 2317 (1971)
Cederbaum et al., J. Chem. Phys. 95, 6634 (1991)
Camps, Jagau, et al., J. Phys. Chem. A 129, 4798 (2025)

Auger spectrum of benzene





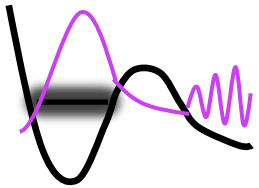


Experiment

CVS-EOMIP-CCSD / EOM-DIP-CCSD, unc. 6-311(2+,+)G**
Explicit continuum treatment via Feshbach projection & plane wave

Γ: CBF-CCSD / cc-pCVTZ(5sp)+*2s2p2d,* E: EOMDIP-CCSD / cc-pCVTZ
No explicit continuum treatment

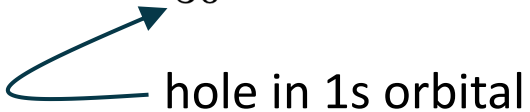
FWHM fixed to 1.15 eV



Carniato et al., J Phys B 53, 244010 (2020)
Jayadev, Ferino-Perez, Matz, Krylov, Jagau, J. Chem. Phys. 158, 064109 (2023)

K–LL Auger spectrum of zinc

- Motivation: Auger therapy $^{67}_{31}\mathrm{Ga} + \mathrm{e}^- \longrightarrow {}^{67}_{30}\mathrm{Zn} + \nu_e$



hole in 1s orbital

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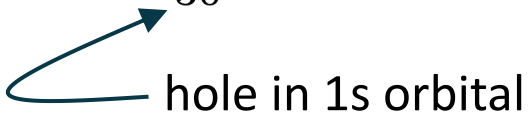

hole in 1s orbital

- 1s core ionization energy / eV

Experiment	9655–9668
EOMIP-CCSD/non-relativistic	9568.6
EOMIP-CCSD/SFX2c-1e	9681.8

- Auger electron energies

Transitions	E / eV
LL	7000–7500
LM/LN	8300–8700
MM/MN/NN	9350–9650

- No substantial changes for $[Zn(H_2O)_6]^{2+}$

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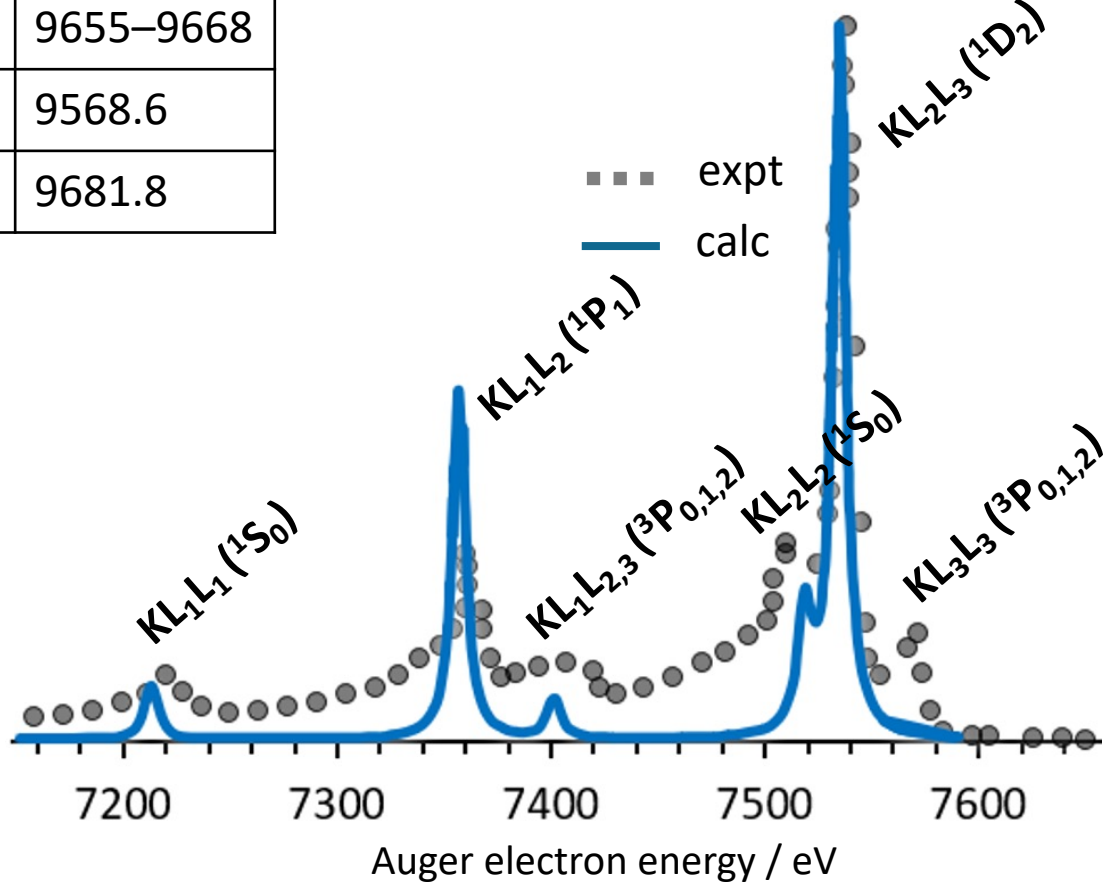

- Auger decay widths

	# of channels	Γ / meV	
LL	16	623	630
LM/LN	80	145	166
MM/MN/NN	100	8	11
total	196	776	807

Kovalik et al., J. Electron. Spectrosc. 134, 67 (2004)
Martins et al., X-Ray Spectrom. 49, 192 (2020)
Ferino-Perez, Jagau, JPCA 128, 3957 (2024)

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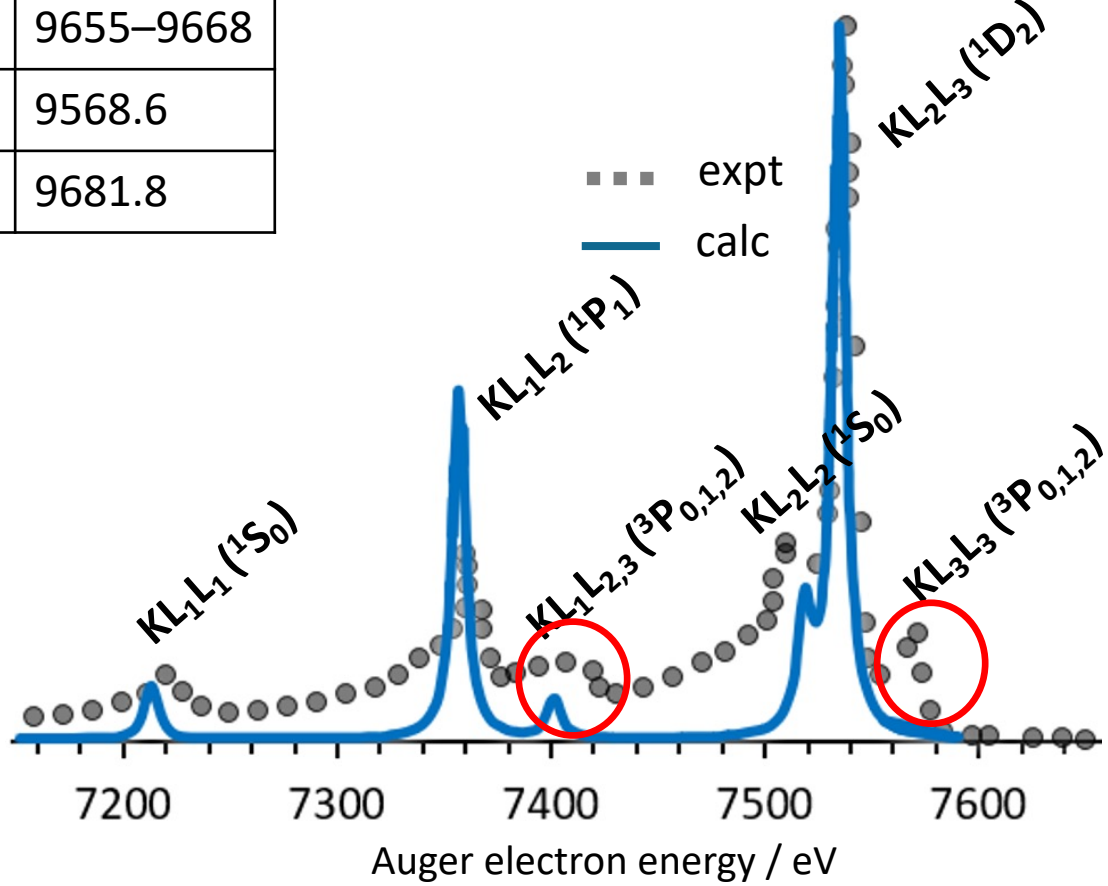

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	# of channels	Γ / meV	
LL	16	623	630
LM/LN	80	145	166
MM/MN/NN	100	8	11
total	196	776	807

- Spin-orbit splitting in E

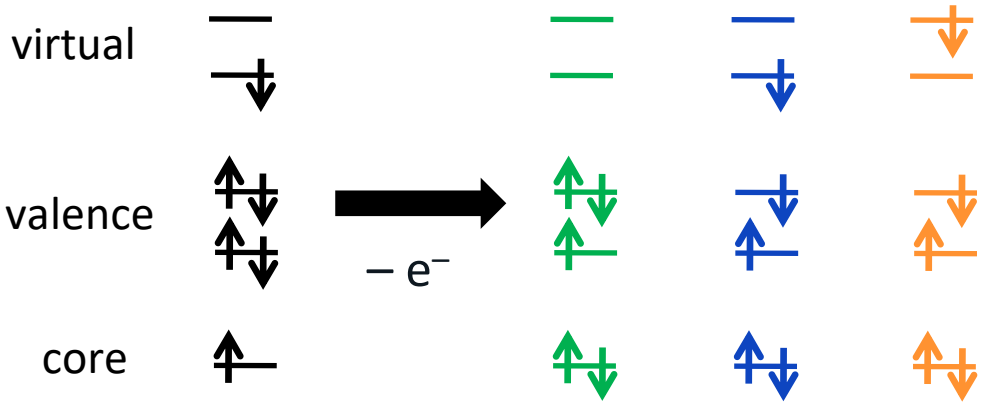
	$L_1L_{2,3}$	L_3L_3
Expt.	10.8–12.2	13.4
Theory	11.41	11.42

EOMDIP-CCSD/SFX2c-1e/ANO-RCC

Kovalik et al., J. Electron. Spectrosc. 134, 67 (2004)
Martins et al., X-Ray Spectrom. 49, 192 (2020)
Ferino-Perez, Jagau, JPCA 128, 3957 (2024)

Resonant Auger decay

- Decay of core-excited states:



  - Initial state: 1h1p
  - Participator channels: 1h
  - Spectator channels: 2h1p
  - Shake-up channels: 2h1p

Chemical reactivity is different !

- Complex-scaled description:
  - No need to treat 2h1p states explicitly
  - Balanced description of participator and spectator channels

Rye et al., J. Chem. Phys. 73, 4867 (1980)
Liu et al., J. Phys. Chem. B 115, 5103 (2011)
Matz, Jagau, unpublished (2025)

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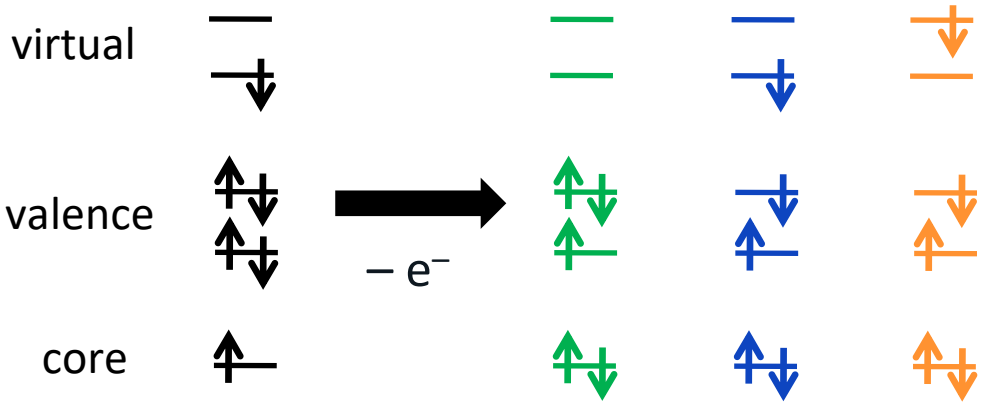
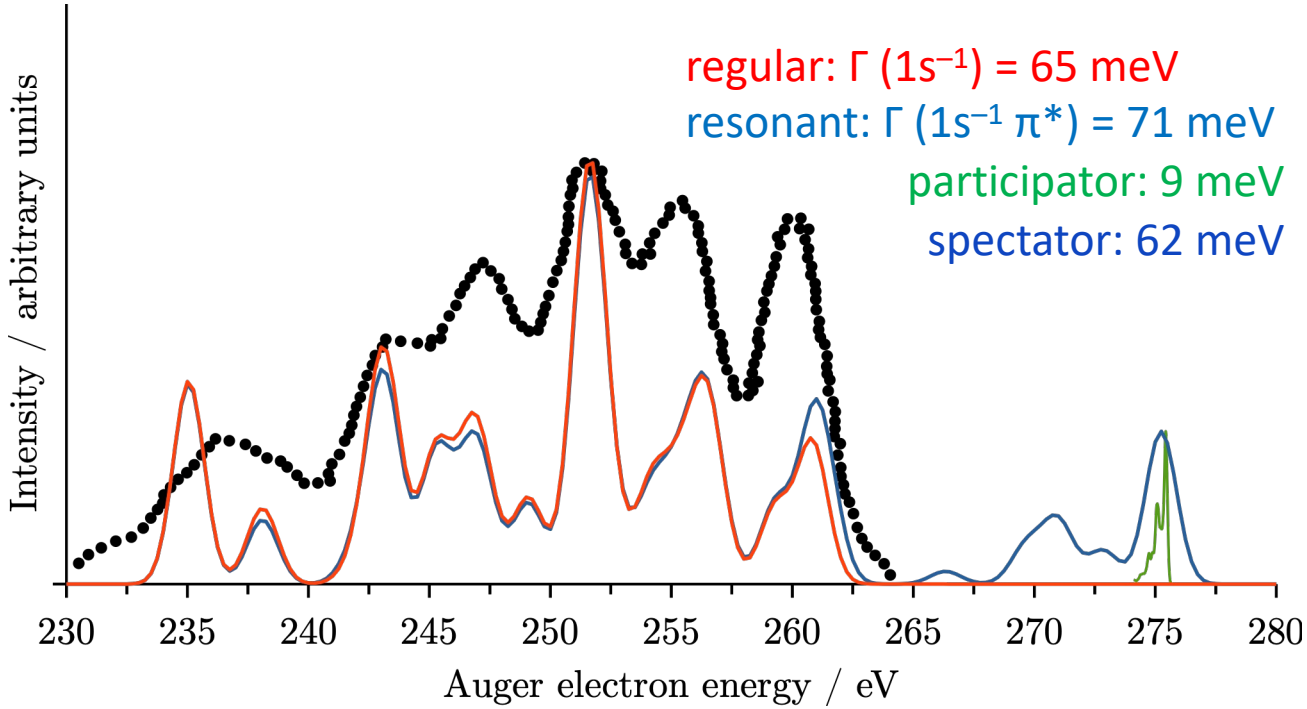


  - Initial state: 1h1p
  - Participator channels: 1h
  - Spectator channels: 2h1p
  - Shake-up channels: 2h1p

Chemical reactivity is different !

- Example: C_2H_4 ($1s^{-1}\,\pi^*$)

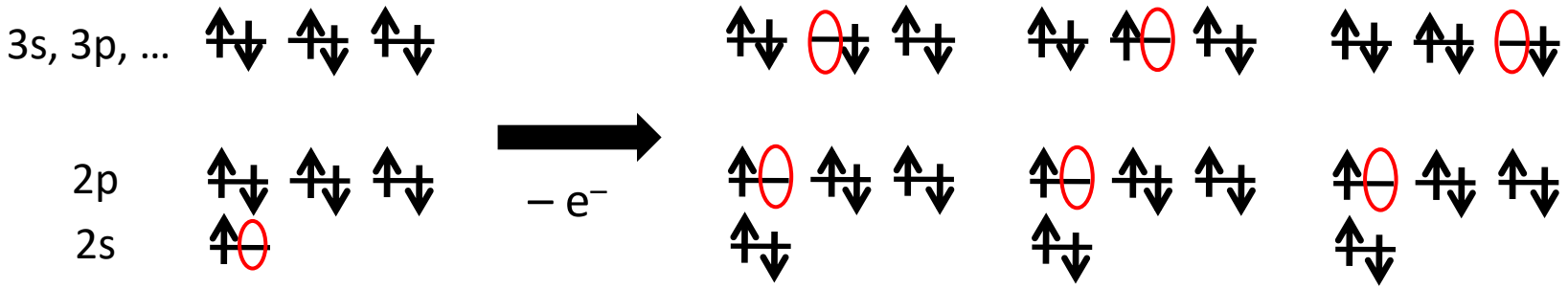


Experiment: regular / resonant
Theory: regular / resonant (CBF-EOM-CCSD / cc-pCVTZ(5sp)+*2s2p2d)*

- Complex-scaled description:
  - No need to treat 2h1p states explicitly
  - Balanced description of participator and spectator channels

Rye et al., J. Chem. Phys. 73, 4867 (1980)
Liu et al., J. Phys. Chem. B 115, 5103 (2011)
Matz, Jagau, unpublished (2025)

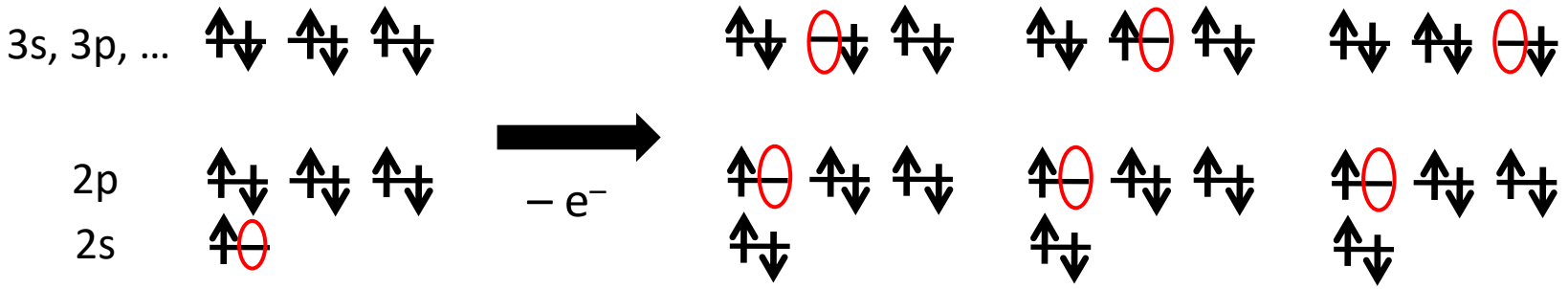
L–LM Coster–Kronig decay



- CK electrons are slow (20–100 eV)
- CK decay widths are large

Coster, de Laer Kronig, Physica, 2, 13 (1935)

L–LM Coster–Kronig spectrum of H_2S



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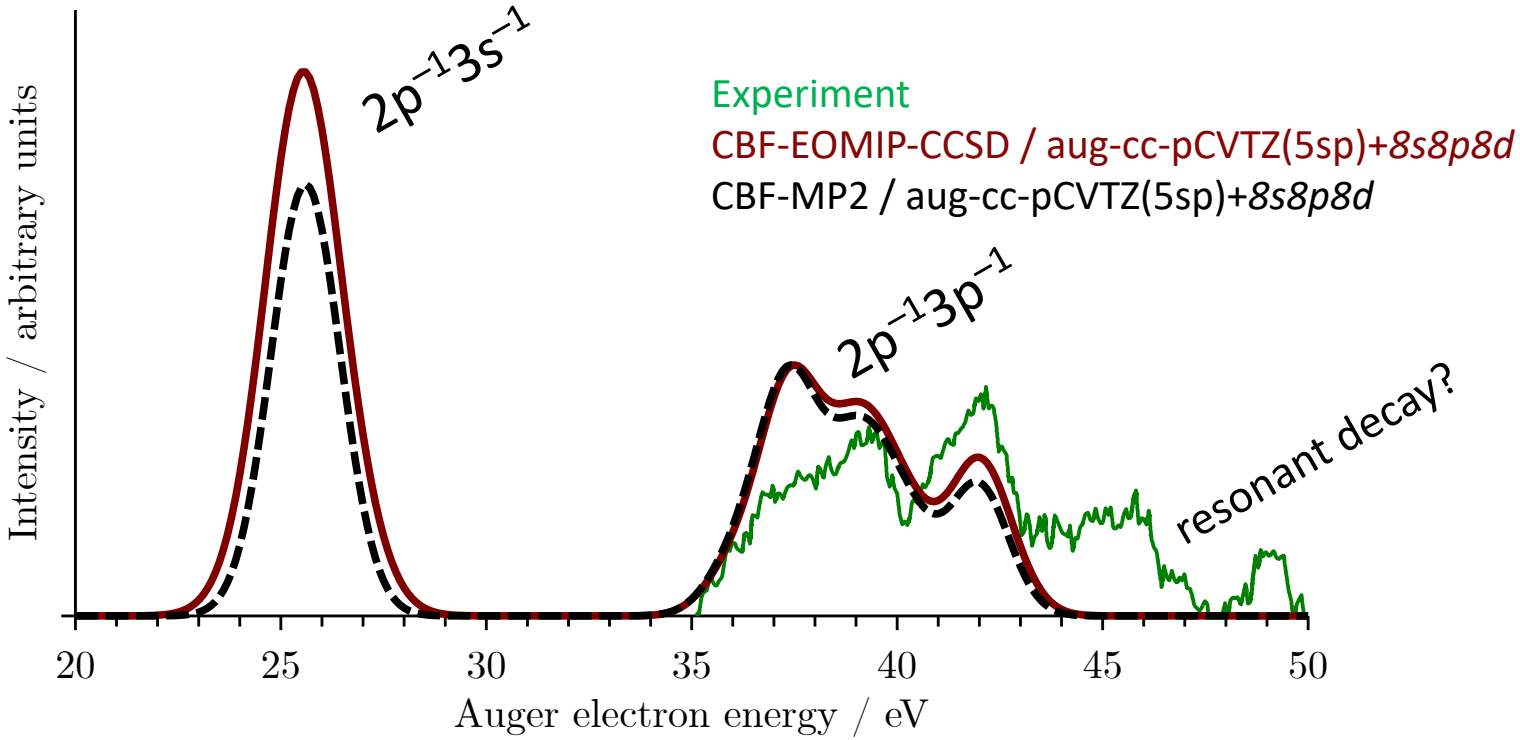
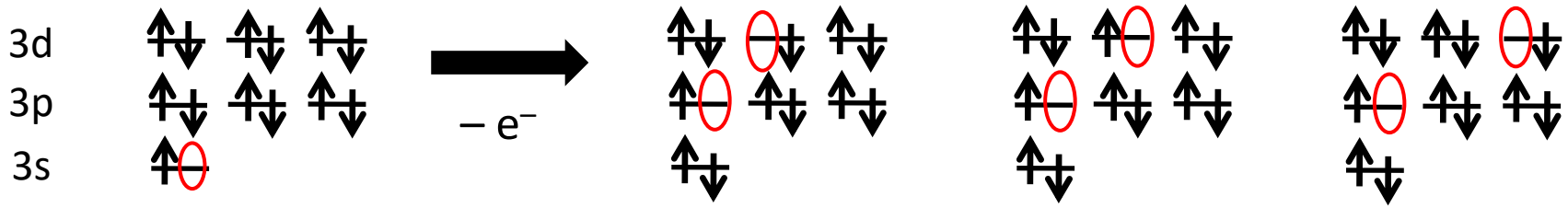


	Transitions	Γ / meV (theory)	Γ / meV (expt)
Ar ($2s^{-1}$)	L_1-$L_{23}M$	2259	2250±50
	L_1-MM	75	
H_2S ($2s^{-1}$)	L_1-$L_{23}M$	1396	1800±100
	L_1-MM	44	
H_2S ($1s^{-1}$)	K-LL	431	500±100
H_2O ($1s^{-1}$)	K-LL	150	160±10

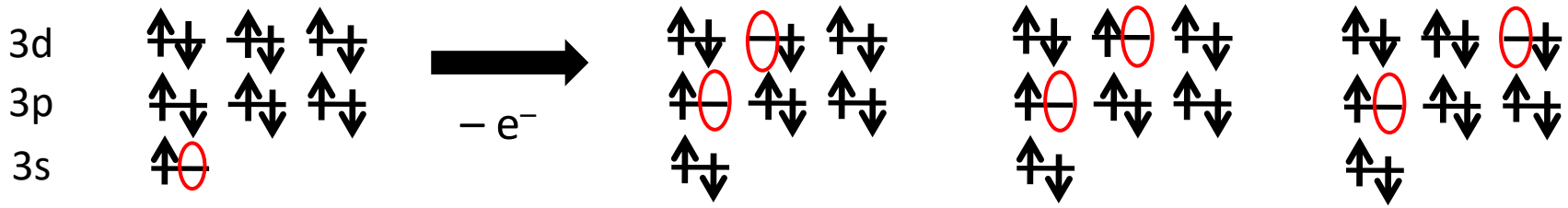
Hikosaka et al., J. Electron Spectr. 137, 287 (2004)
Drennhaus, Ferino Perez, Matz, Jagau, PCCP 26, 23846 (2024)
Matz, Drennhaus, Ferino-Pérez, Jagau, JCP 163, 104113 (2025)

M–MM Super–Coster–Kronig decay



Guillot et al., Phys. Rev. Lett. 39, 1632 (1977)
Bruhn et al., Phys. Lett. 69A, 9 (1978)

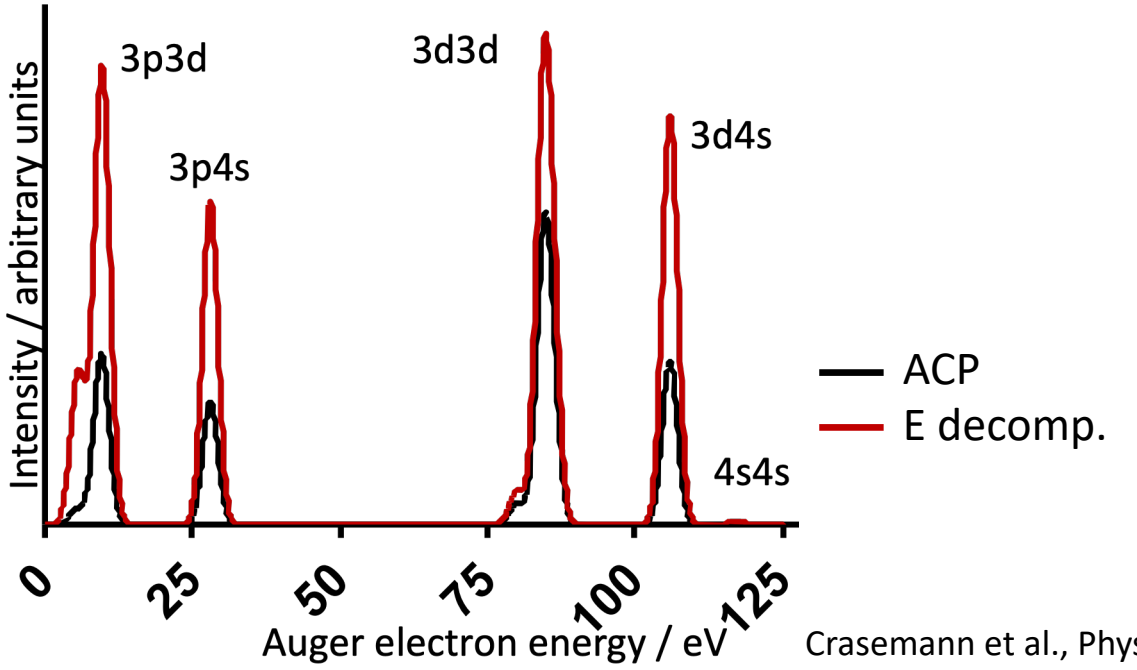
M–MM Super–Coster–Kronig decay



Example: Zn	Γ / meV (theory)	Γ / meV (expt)
Zn ($3s^{-1}$)	790	1700
Zn ($3p^{-1}$)	1450	2100
Zn^{2+} ($3s^{-1}$)	310	
Zn^{2+} ($3p^{-1}$)	1200	
$Zn(CH_3)_2$ ($3s^{-1}$)	1250	
$Zn(CH_3)_2$ ($3p^{-1}$)	4400	
Zn ($1s^{-1}$)	870	900±50
$Zn(H_2O)_6^{2+}$ ($1s^{-1}$)	920	

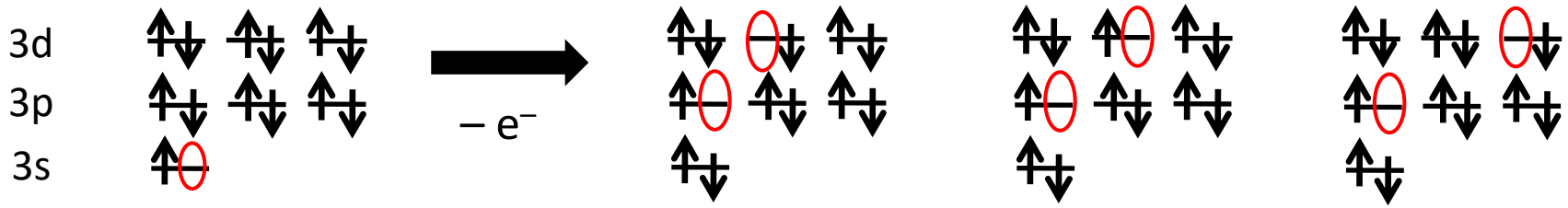
CBF-EOMIP-CCSD/ aug-cc-pCVTZ(5sp)+*4s4p4d4f2g*

- sCK spectrum of Zn ($3s^{-1}$)



Crasemann et al., Phys. Rev. A, 9, 1070 (1974)
Ferino-Pérez, Jagau, J. Phys. Chem. A 128, 3957 (2024)
Wittemann, Matz, Jagau, unpublished (2025)

M–MM Super–Coster–Kronig decay



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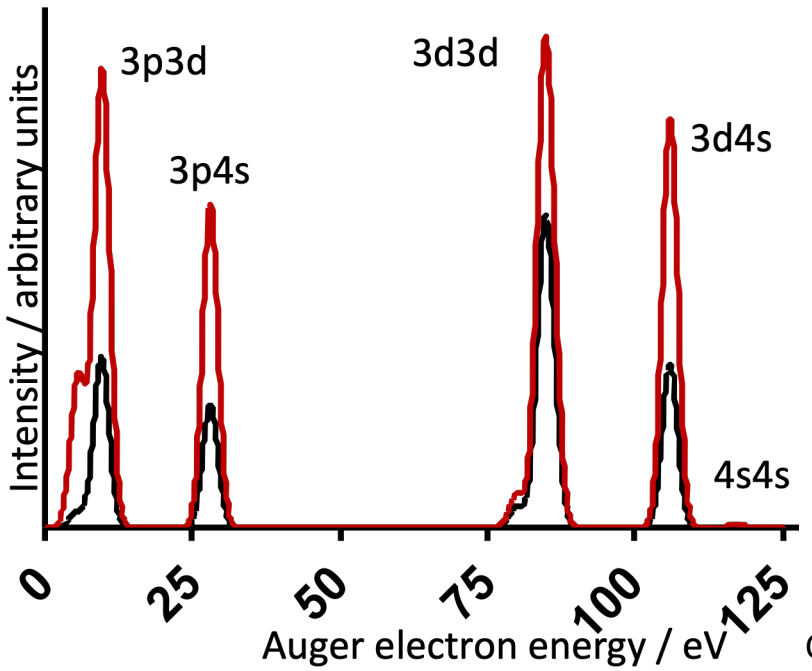

- Deviation theory / expt

  Double sCK decay?

  Cascade process?

$$Zn(1s^{-1}) \longrightarrow Zn^{3+} + 2e^-$$
$$\hookrightarrow Zn^{2+} + e^- \nearrow$$

Crasemann et al., Phys. Rev. A, 9, 1070 (1974)
Ferino-Pérez, Jagau, J. Phys. Chem. A 128, 3957 (2024)
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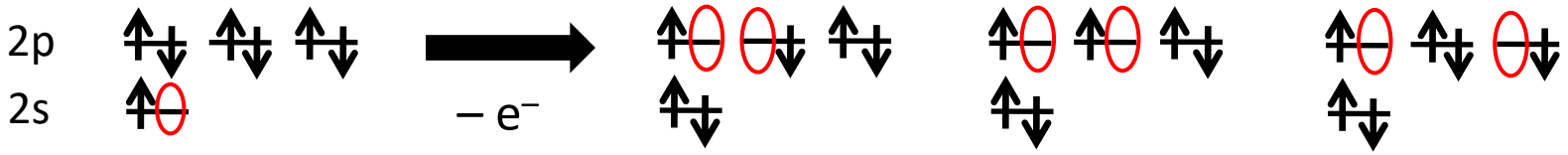
L–LL Super–Coster–Kronig decay



- forbidden for light atoms (C, N, O, …)
- allowed for loosely bound clusters ⟶ Interatomic Coulombic Decay

Molloy, Eland, Chem. Phys. Lett. 421, 31 (2006)
Eland, Chem. Phys. 345, 82 (2008)
Schepens, Camps, Ferino-Pérez, Jagau, to be submitted (2026)

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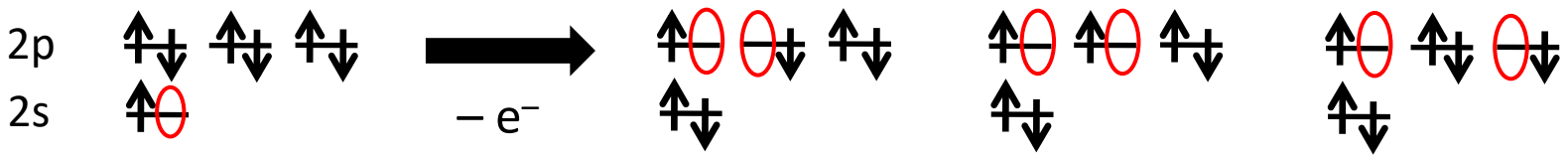

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- forbidden for some molecules: H_2O, NH_3, CH_4, C_2H_6, C_2H_4, C_2H_2, …
- allowed for some other molecules: C_6H_6, H_2O_2, N_2H_4, NH_2CHO, adamantane, triethylenediamine, … ⟶ Stability of dication is crucial !

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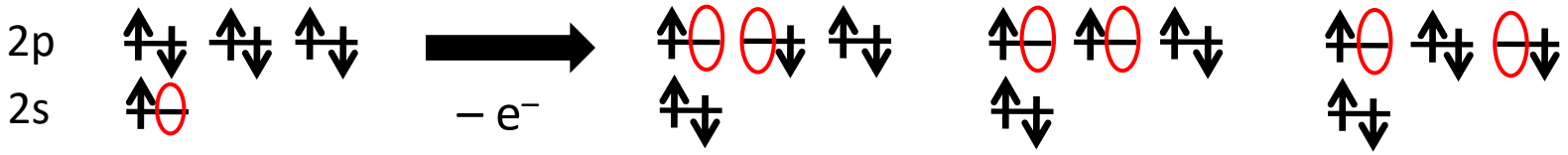

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- Decay widths $1s^{-1}$ vs $2s^{-1}$

	Γ / meV (theory)	Γ / meV (expt)
C_6H_6 ($1s^{-1}$)	79	80±10
NH_3 ($1s^{-1}$)	112	~100
H_2O ($1s^{-1}$)	142	160±20
C_6H_6 ($2s^{-1}$)	21	?
N_2H_4 ($2s^{-1}$)	34	?
H_2O_2 ($2s^{-1}$)	36	?

CBF-EOMIP-CCSD
basis for $1s^{-1}$: aug-cc-pCVTZ(5sp)+*2s2p2d*
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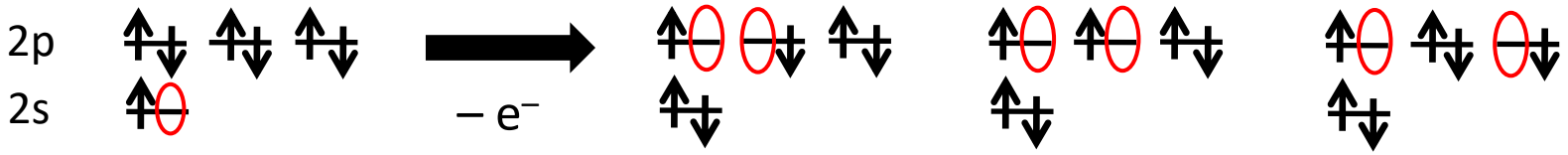

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- Comparison K–LL / L–LL decay

	K–LL ($1s^{-1}$)	L–LL ($2s^{-1}$)
Kinetic energy	100–1000 eV	0–9 eV
Lifetime	2.5–10 fs	15–50 fs
Final states	dissociative	stable
Nature	atomic	molecular

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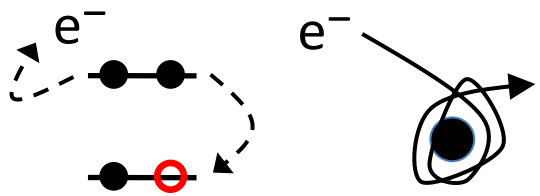
Molloy, Eland, Chem. Phys. Lett. 421, 31 (2006)
Eland, Chem. Phys. 345, 82 (2008)
Schepens, Camps, Ferino-Pérez, Jagau, to be submitted (2026)

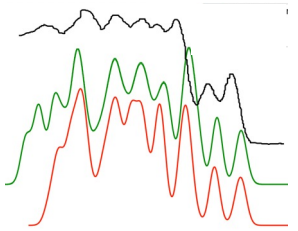
Summary & Conclusions

- Chemistry of core-ionized and core-excited states
  - (Resonant) Auger decay
  - (super-) Coster-Kronig decay



- Decaying states can be modeled in terms of complex energies

$$E_{\mathrm{res}} = E - \mathrm{i}\,\Gamma/2$$



  - No need for explicit treatment of the continuum
  - Instead use complex-scaled basis functions
  - EOM-CCSD suite of methods

- Further method development is needed
  - Resonant Auger decay: participator ⟷ spectator channels
  - Double Auger decay and Auger cascades
  - Vibrational effects

New chemistry ⟷ Opportunity to extend quantum chemistry

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Dr. Garrette Paran
Dr. Valentina Parravicini
Dr. Koushik Chatterjee
Dr. Joel Creutzberg
Dr. Jerryman Gyamfi
Dr. Mario Hernandez
Dr. Axel Molle
Jan Drennhaus
Stef Eversdijk
Tianyi Gao
Mauro Gascón
Jesse Stalmans
Angelos Gkogkos
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