Insights to the Auger Decay in Benzene

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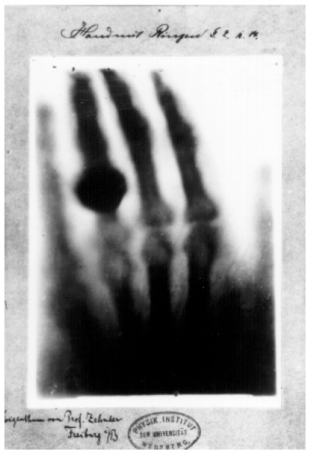
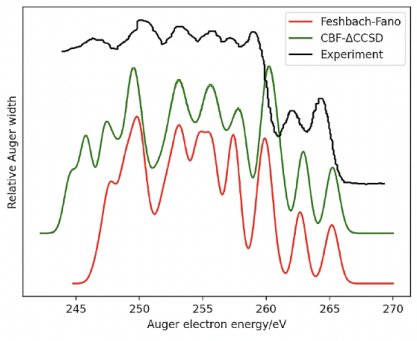
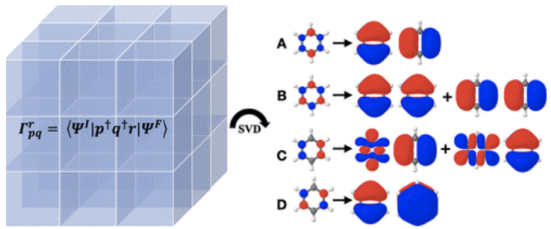
June 19, 2024

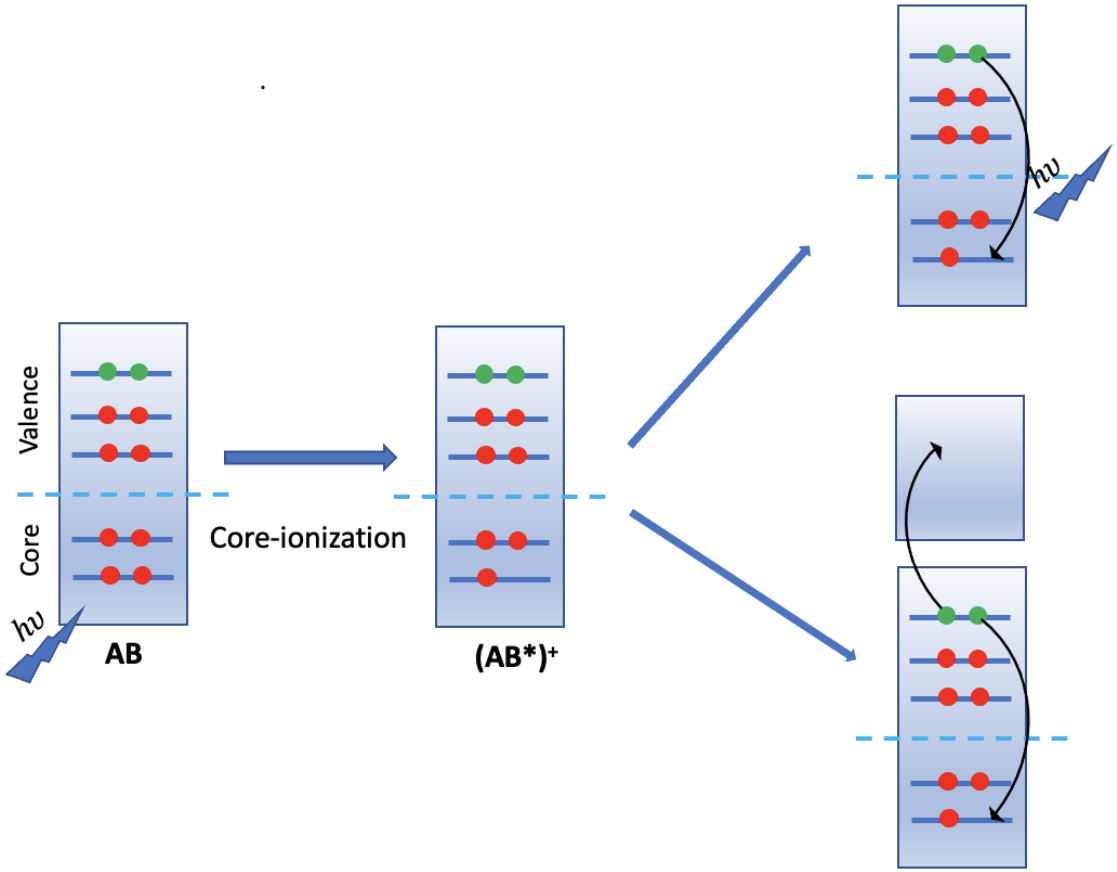






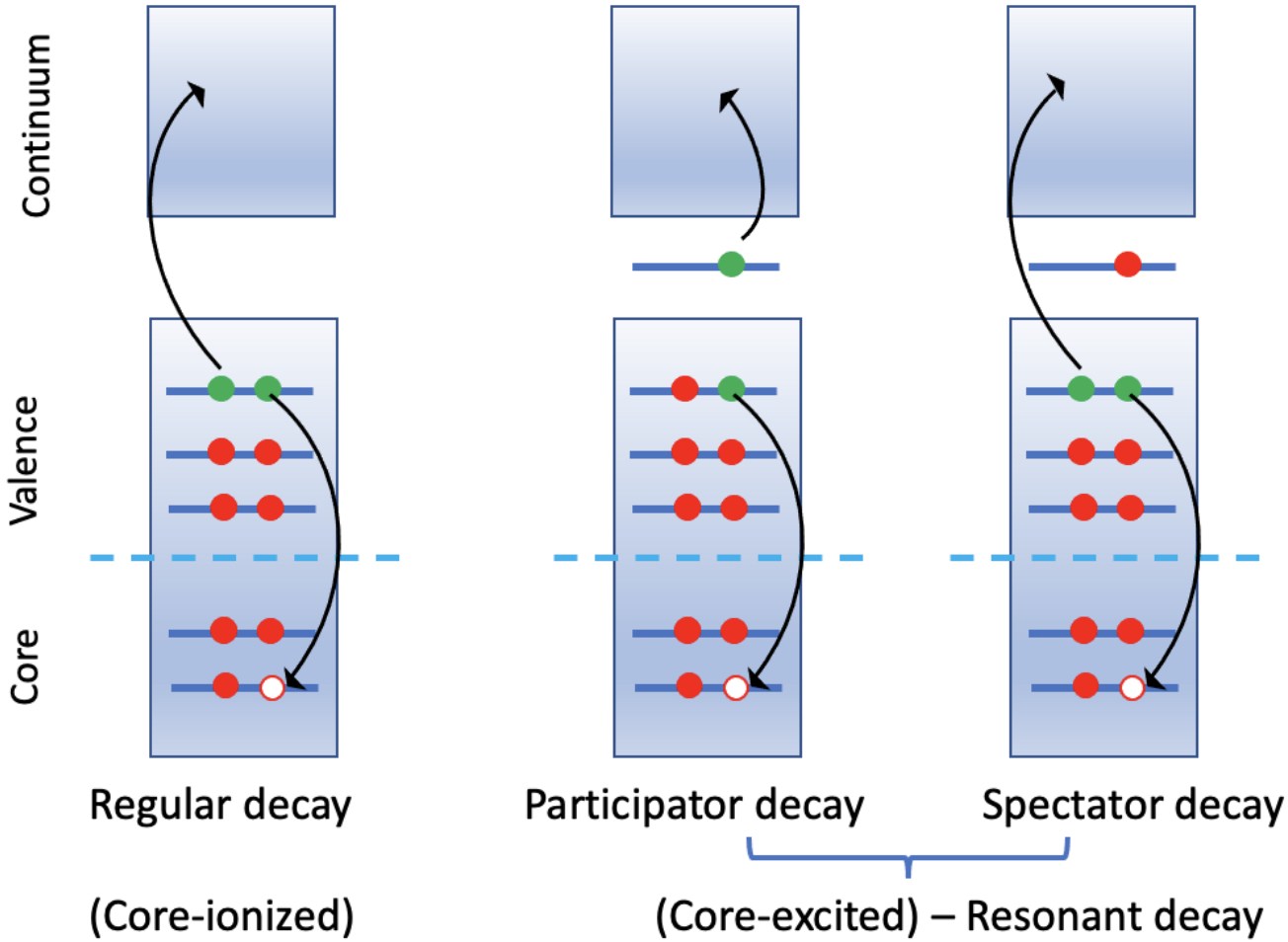
Core-ionization

- X-ray absorption creates vacancies in the core-shell



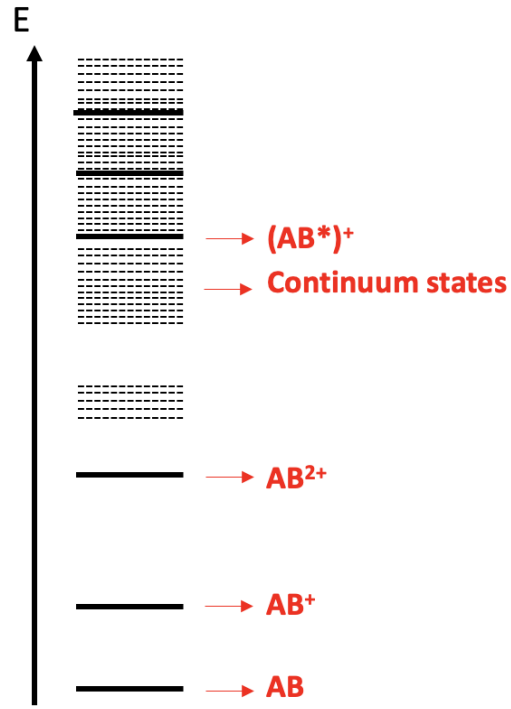
- Decay via non-radiative auto-ionization - **Auger decay**

Auger decay - different types



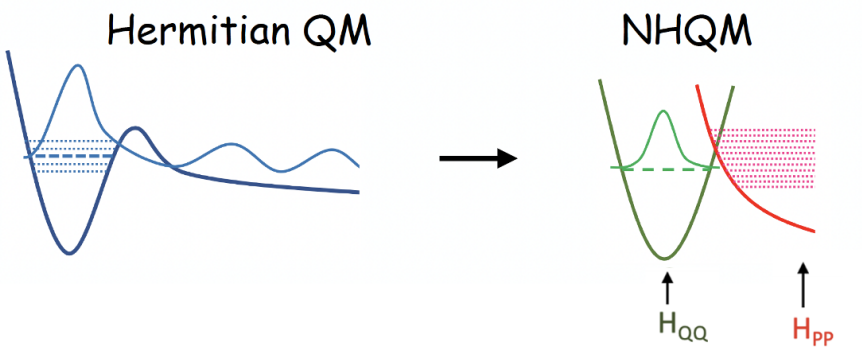
Challenges

- Resonant nature of initial core-ionized or core-excited states



- Continuum nature of the Auger electron

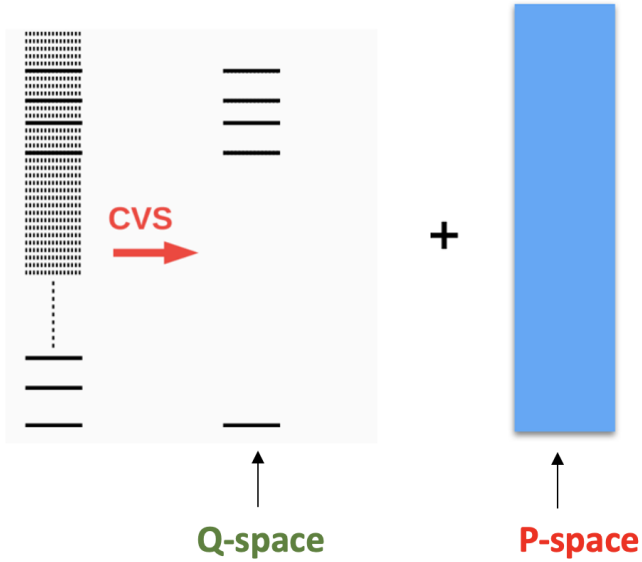
Feshbach-Fano framework



$$\begin{bmatrix} H_{QQ} & H_{QP} \\ H_{PQ} & H_{PP} \end{bmatrix} \begin{bmatrix} Q\Psi \\ P\Psi \end{bmatrix} = E \begin{bmatrix} Q\Psi \\ P\Psi \end{bmatrix}$$

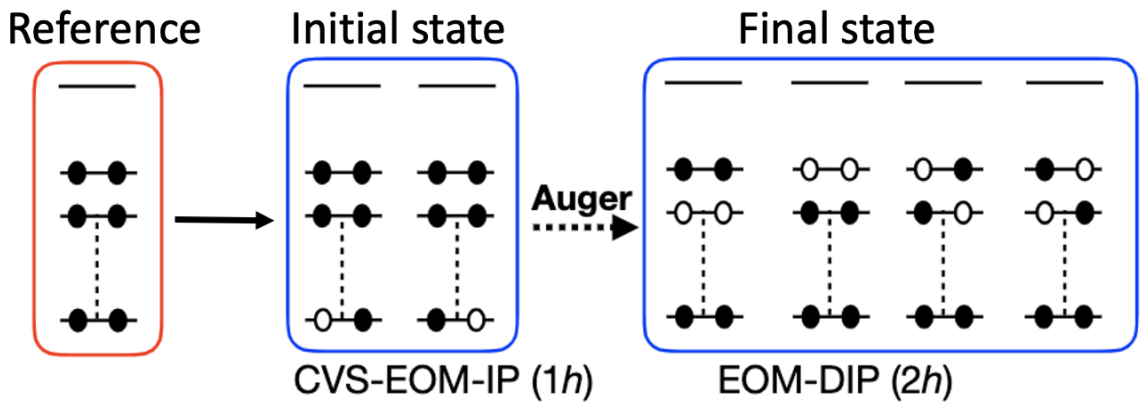
$$\mathscr{H}_{QQ}\tilde{\psi}_n = \tilde{\mathscr{E}}_n \tilde{\psi}_n$$
$$\tilde{\mathscr{E}}_n = \mathscr{E}_n - i\frac{\Gamma_n}{2}$$

- Interaction between bound and continuum states



- Project out the continuum by core-valence separation (CVS)
- Describe the continuum explicitly

Initial and final states from EOM-CC theory



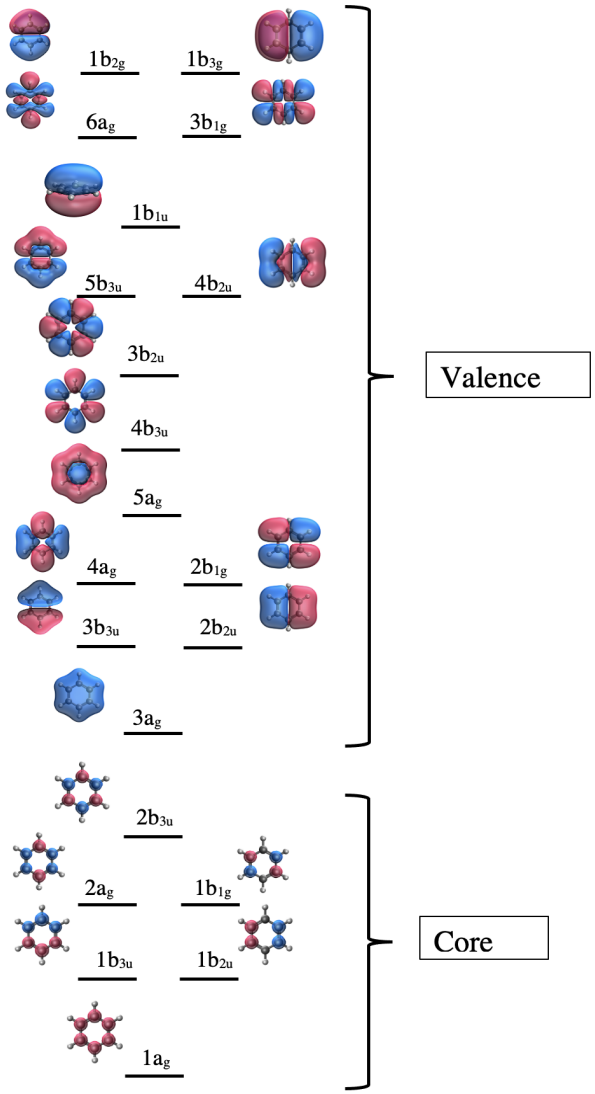
Decay width: $\tilde{\Gamma} = 2\pi \langle \Psi^I | H | \Psi^F \times \Psi_{el} \rangle \langle \Psi^F \times \Psi_{el} | H | \Psi^I \rangle$

$$\tilde{\Gamma} = \frac{\pi}{2} \int d\Omega_{\mathbf{k}} \left(\sum_{pqr} \langle pq || \mathbf{k}r \rangle \Gamma_r^{pq} \right) \left(\sum_{pqr} \langle \mathbf{k}r || pq \rangle \Gamma_{pq}^r \right)$$

Two-body Dyson orbital: $\Gamma_r^{pq} = \langle \Psi^I | p^\dagger q^\dagger r | \Psi^F \rangle$

Skomorowski, W. and Krylov, A. I., J. Chem. Phys., 154, 84 (2021)

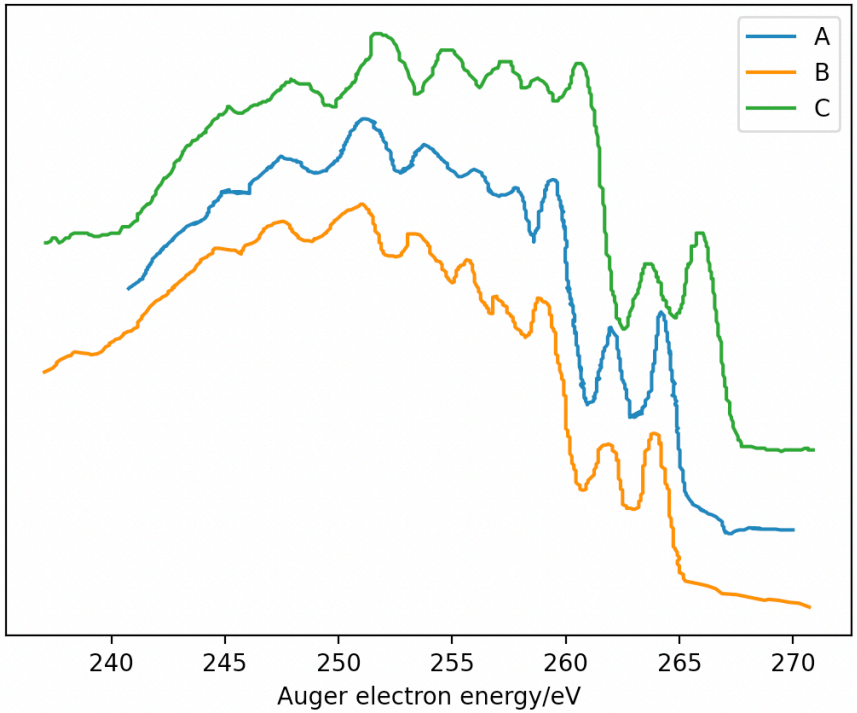
Benzene: Molecular orbital framework



RI-MP2 cc-pVTZ optimized structure of benzene.

- The carbon 1s orbitals have similar core-ionization energies.
- DIP states are final states in Auger decay - major 2 hole contribution
- Different doubly ionized states correspond to different decay channels - Auger electrons with specific energies.

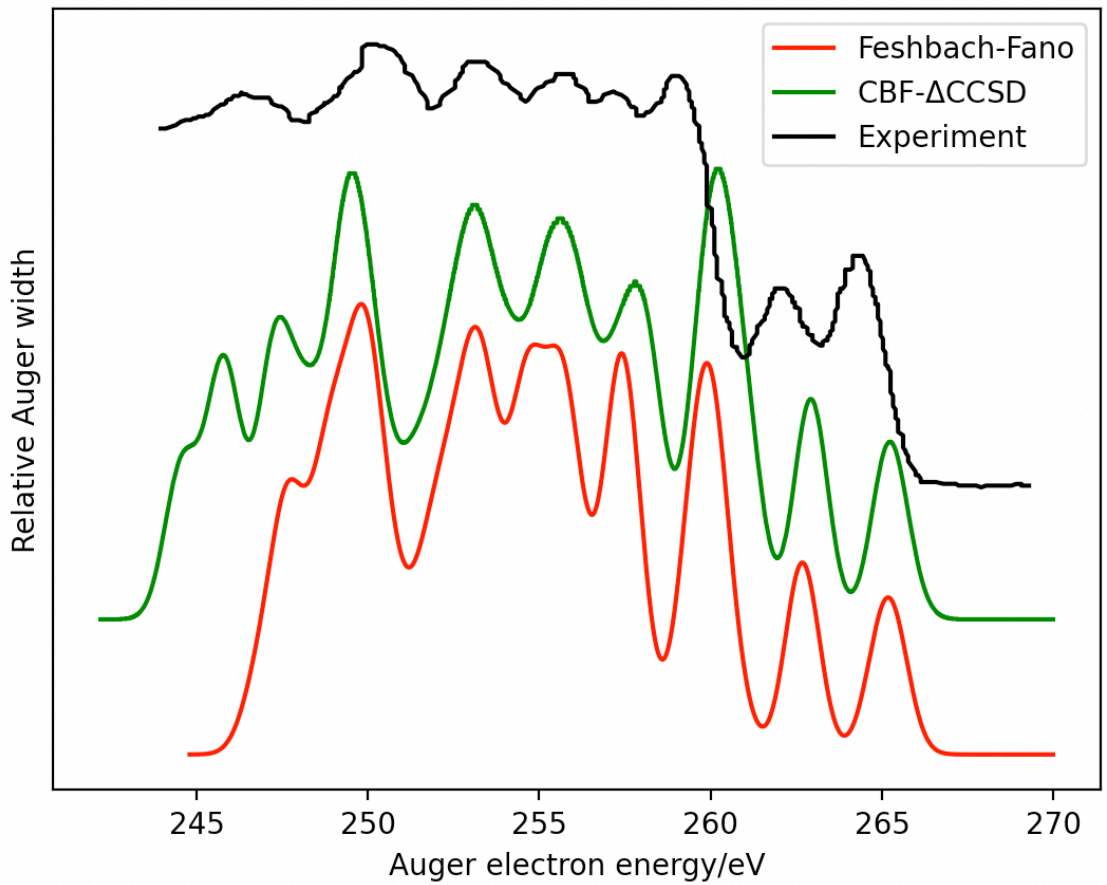
Previous experiments: Auger decay of benzene



- Auger decay spectrum from three experiments: (a) Spohr et al., (b) Rennie et al., and (c) Carniato et al.
- The overall shape of the spectra is similar but not identical

Spohr, R. et al., Phys. Scrp., 2, 31, (1970)
Rennie, E. E. et al., J. Chem. Phys., 113, 7362 (2000)
Carniato, S. et al., J. Phys. B, 53, 244010 (2020)

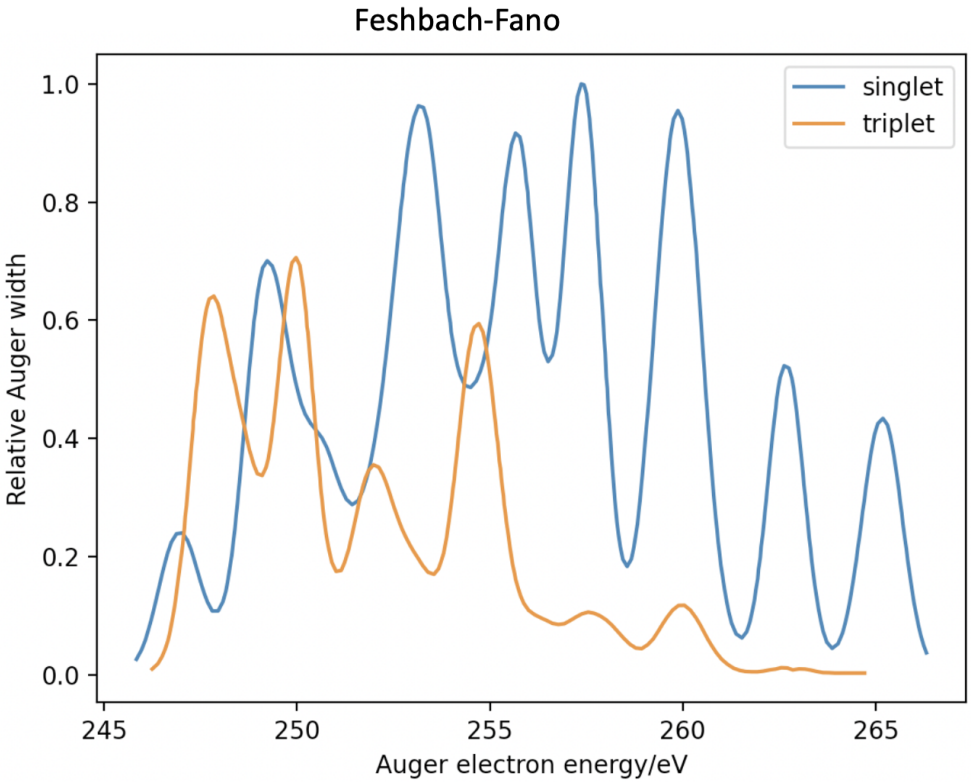
Regular Auger spectrum : theory vs experiment

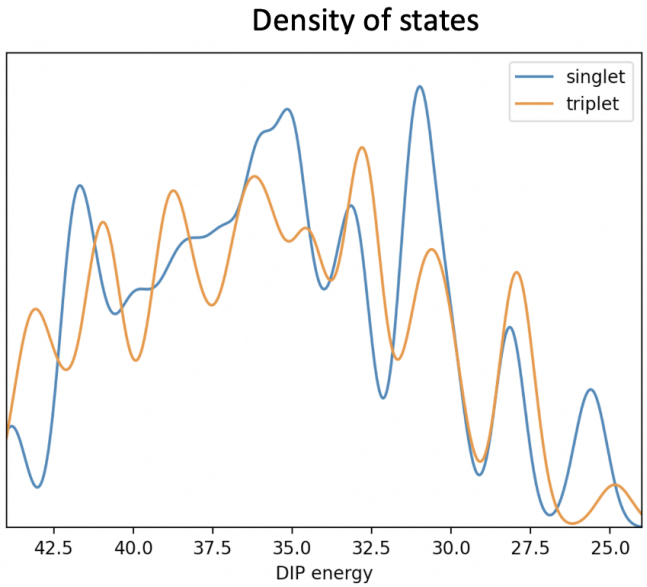


- DIP states: 143 states between 24-43 eV
- Feshbach-Fano and CBF calculations agrere well with each other

Jayadev, N. K. et al., J. Chem. Phys., 158, 064109, (2023)

Regular Auger spectrum





- The spectra from Feshbach-Fano approach calculated widths gives clearer picture
- Mere calculation of density of states is not sufficient

Orbitals

"Just as a small child, without understanding its grammar and rules learns to speak his native language with great effectiveness, chemists learn how to speak orbitals before they learn quantum mechanics."

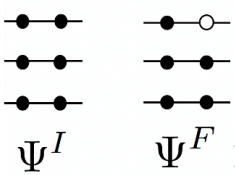
- Prof. Anna. I. Krylov

From orbitals to observables and back

Cite as: J. Chem. Phys. **153**, 080901 (2020); https://doi.org/10.1063/5.0018597
Submitted: 16 June 2020 . Accepted: 31 July 2020 . Published Online: 24 August 2020

Anna I. Krylov

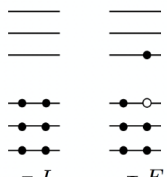
Dyson orbitals



$\Psi^I \qquad \Psi^F \times \Psi_{el}$

$\gamma_p = \langle \Psi^F | p | \Psi^I \rangle$

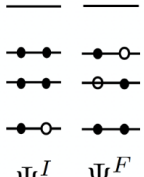
Natural transition orbitals



$\Psi^I \qquad \Psi^F$

$\gamma_{pq}^{f \leftarrow i} = \langle \Psi^F | p^\dagger q | \Psi^I \rangle$

Natural Auger orbitals



$\Psi^I \qquad \Psi^F \times \Psi_{el}$

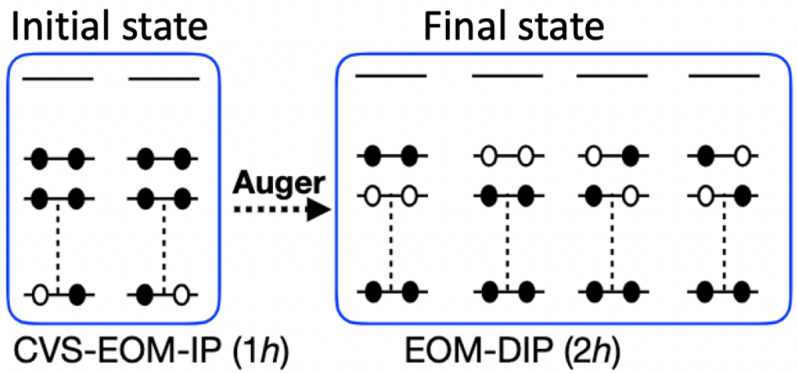
$\Gamma_r^{pq} = \langle \Psi^I | p^\dagger q^\dagger r | \Psi^F \rangle$

Natural Auger orbitals

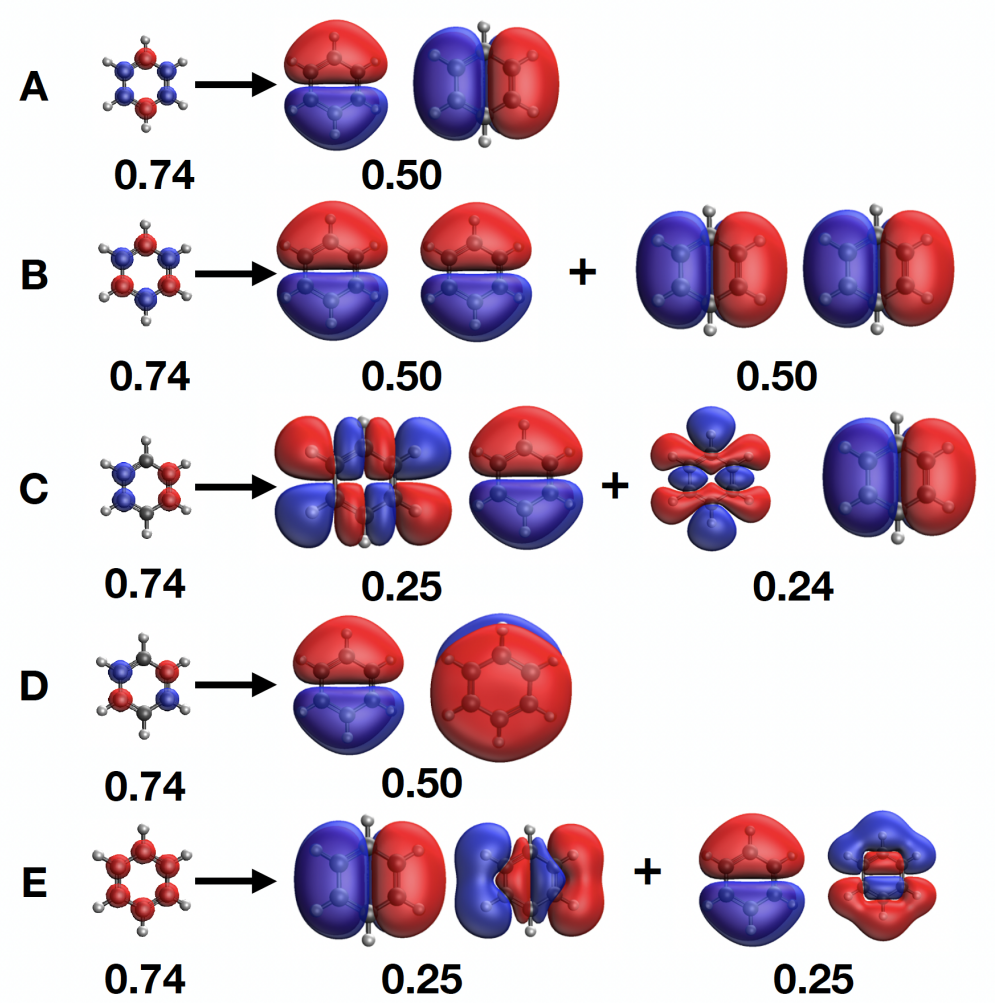
- The two-electron part of Auger decay width contains two-body Dyson function amplitudes

$$ {}^{R}\Gamma_r^{pq} = < \Psi_n^{(N)} | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r | \Psi_\mu^{N-1} > $$

- Γ_r^{pq} contains information about decay from the bound domain
- Two step singular value decomposition of Γ_r^{pq} - Natural Auger orbitals

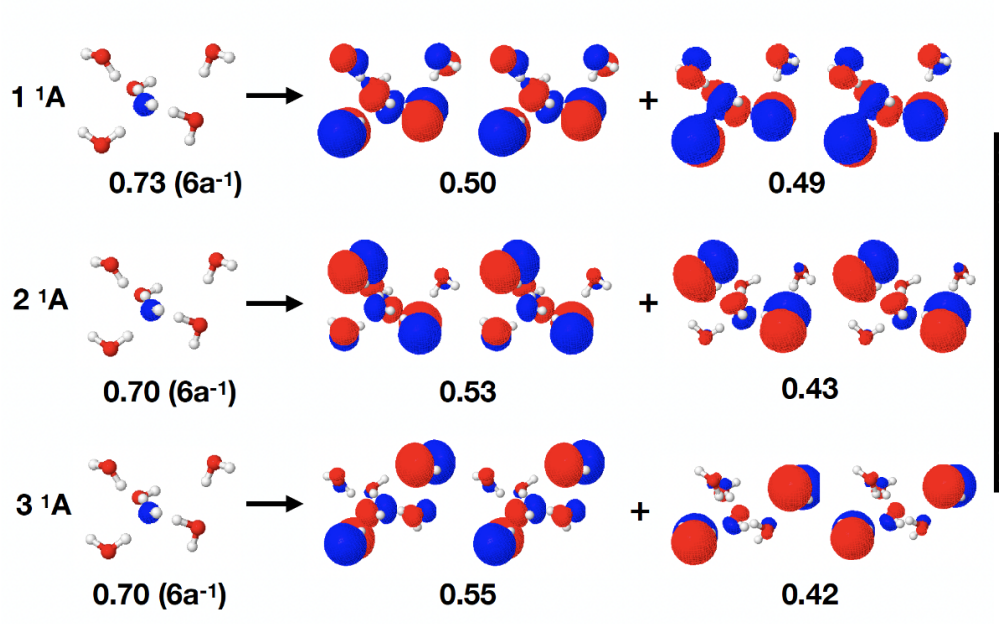


Natural Auger orbitals: Benzene



Jayadev, N. K., Skomorowski, W., Krylov, A. I.,J. Phys. Chem. Lett.,14,8612(2023)

Natural Auger orbitals- OH^--$(H_2O)_5$



Amplitude	Transitions between orbitals	
-0.3834	28 (A) A	30 (A) B
-0.3834	30 (A) A	28 (A) B
0.3834	30 (A) B	28 (A) A
0.3834	28 (A) B	30 (A) A
0.2836	26 (A) A	28 (A) B
0.2836	28 (A) A	26 (A) B
-0.2836	28 (A) B	26 (A) A
-0.2836	26 (A) B	28 (A) A
0.2380	25 (A) A	28 (A) B
0.2380	28 (A) A	25 (A) B
-0.2380	28 (A) B	25 (A) A
-0.2380	25 (A) B	28 (A) A

- Decay channels can be described by a small set of NAOs
- Decay channels show local and non-local character of varied proportion
- Decay channels reflect mixed Auger-ICD character

Jayadev, N. K., Skomorowski, W., Krylov, A. I.,J. Phys. Chem. Lett.,14,8612(2023)

Conclusion

- Feshbach-Fano approach enables calculations of Auger decay rates
- Theoretical Auger spectrum of benzene comparable with experiments
- Natural Auger orbitals provide rigorous orbital picture of 2-electron relaxation processes (Auger, ICD, EMTD, etc)

Acknowledgements

- Prof. Anna. I. Krylov
- Prof. Wojciech Skomorowski (University of Warsaw)
- Prof. Thomas. C. Jagau (KU Leuven)
- Anthuan Perez, Florian Matz (KU Leuven)