

*Relativistic ADC:  
A Powerful Tool for Quantum Chemistry*

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## Outline of the talk

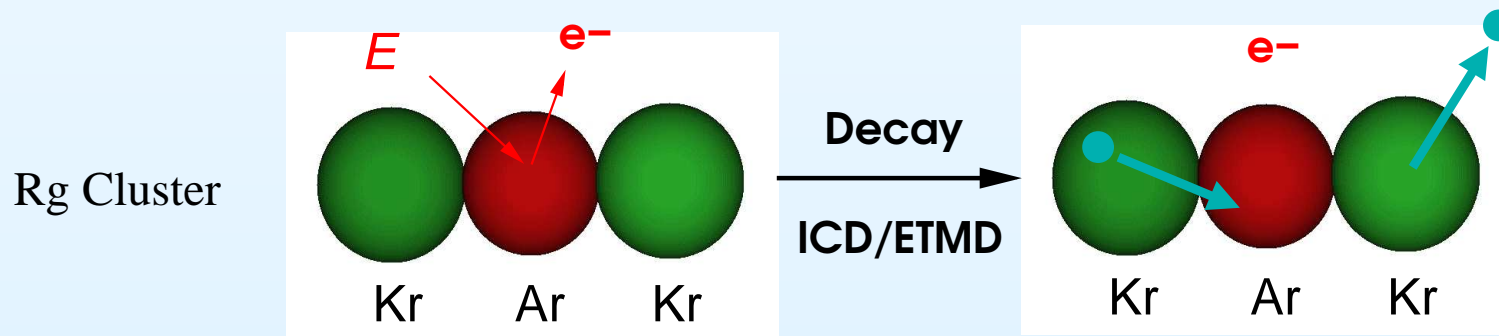
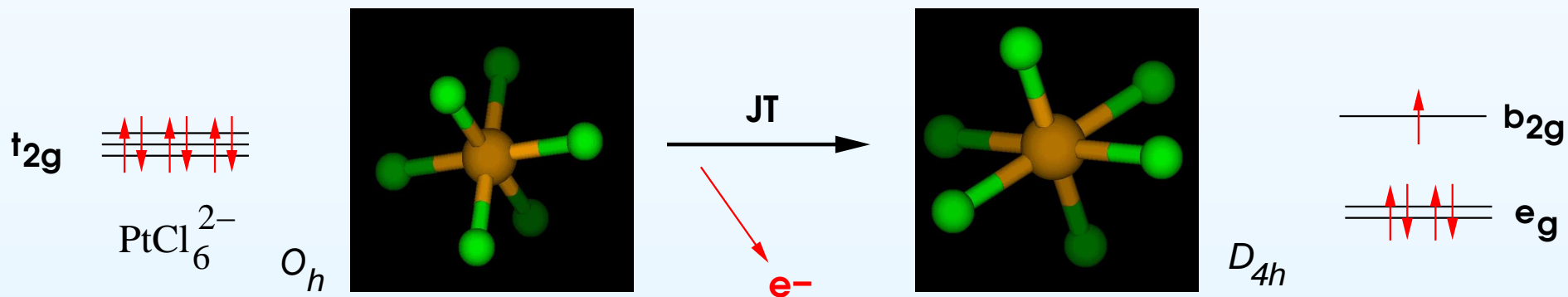
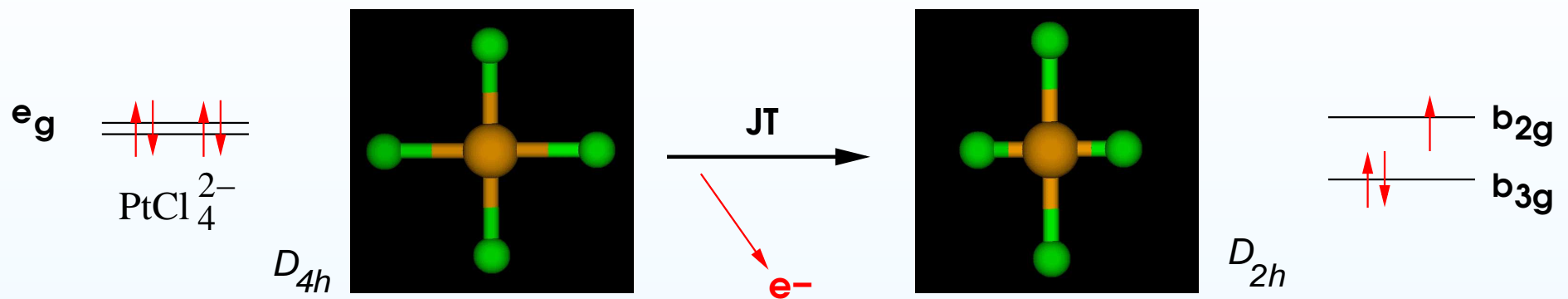
- Photoionization processes and electronic decay in

heavy dianionic systems  
and  
noble gas clusters

- Method of description
- Results:

Jahn-Teller vs. Spin-Orbit coupling  
ICD vs. ETMD

# Systems of Interest



## Requirements of the method

### A Relativistic

- Strong focus on heavy systems
- Nonadditivity of relativistic and electron correlation effects
- Spin-orbit contributions included from the start

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- Spectral intensities and hole populations
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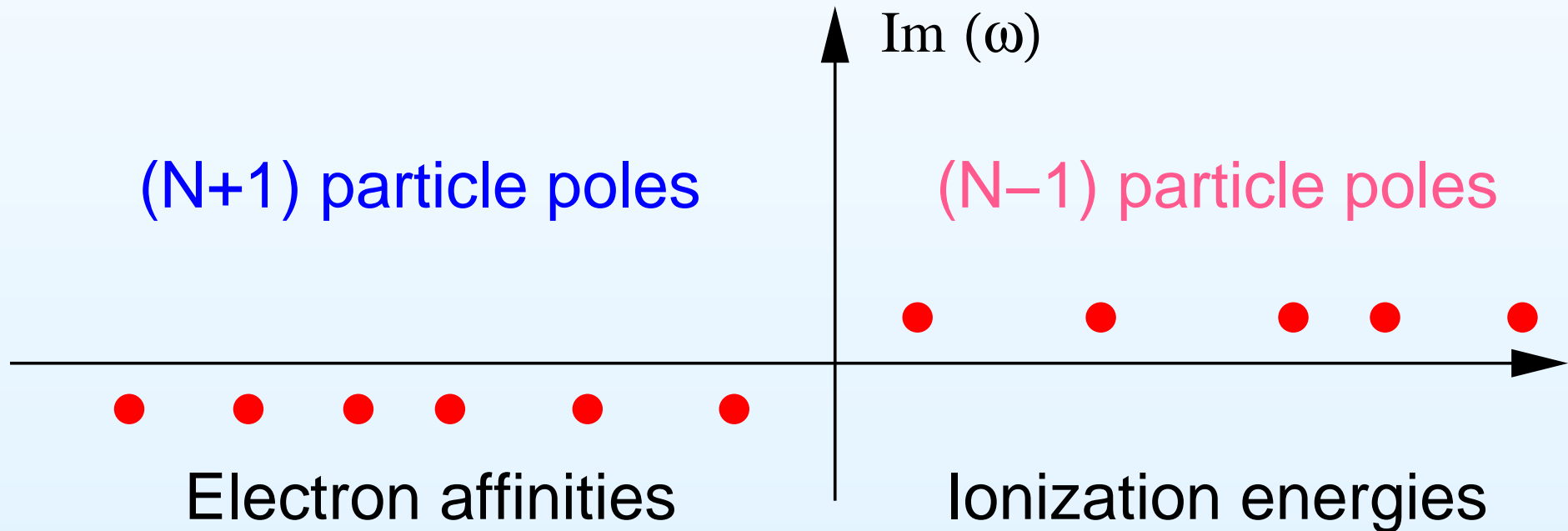
### B Access to excited states

- Energy distribution of excited states in the ionized species
- Spectral intensities and hole populations
- Size-consistency

⇒ Relativistic propagator methods very suitable

## Lehmann representation of the one-particle propagator

$$G_{pq}(\omega) = \sum_n \frac{\langle \Psi_0^N | \hat{c}_p | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | \hat{c}_q^\dagger | \Psi_0^N \rangle}{\omega + E_0^N - E_n^{N+1} + i\eta} + \sum_n \frac{\langle \Psi_0^N | \hat{c}_q^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \hat{c}_p | \Psi_0^N \rangle}{\omega + E_n^{N-1} - E_0^N - i\eta}$$



# The Algebraic Diagrammatic Construction (ADC)<sup>[1]</sup>

$$\mathbf{G}^{-}(\omega) = \mathbf{x}^{\dagger}(\omega\mathbf{1} - \Omega)^{-1}\mathbf{x} \quad \begin{array}{c} |\tilde{\Psi}_I^{N-1}\rangle\langle\tilde{\Psi}_I^{N-1}| \\ \longrightarrow \end{array} \quad \mathbf{f}^{\dagger}(\omega - \mathbf{K} - \mathbf{C})^{-1}\mathbf{f}$$

diagonal matrix nondiagonal (ADC) matrix

- Matrix entries by comparison of diagrams/perturbation expansion

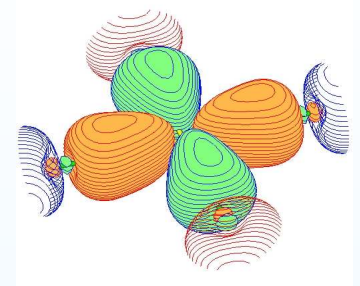
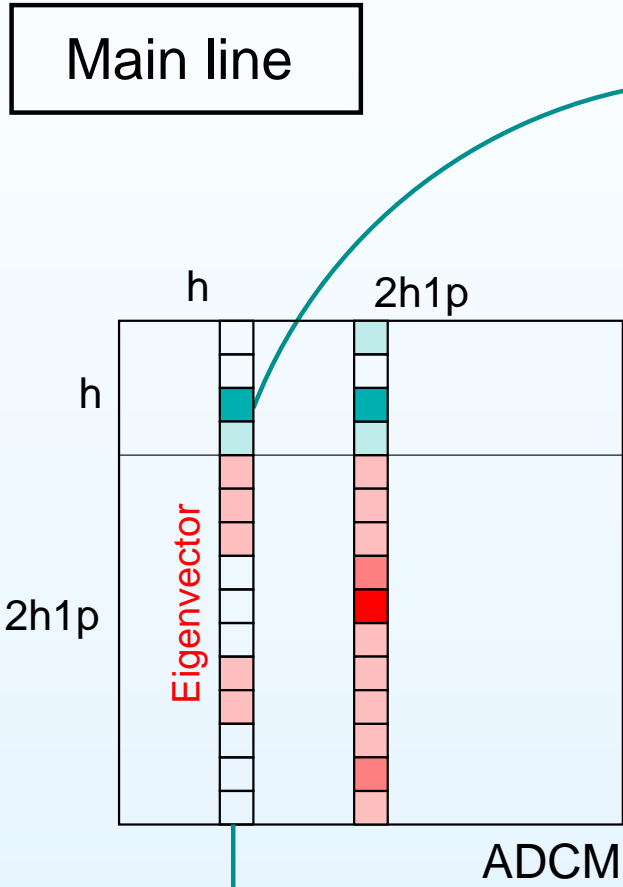
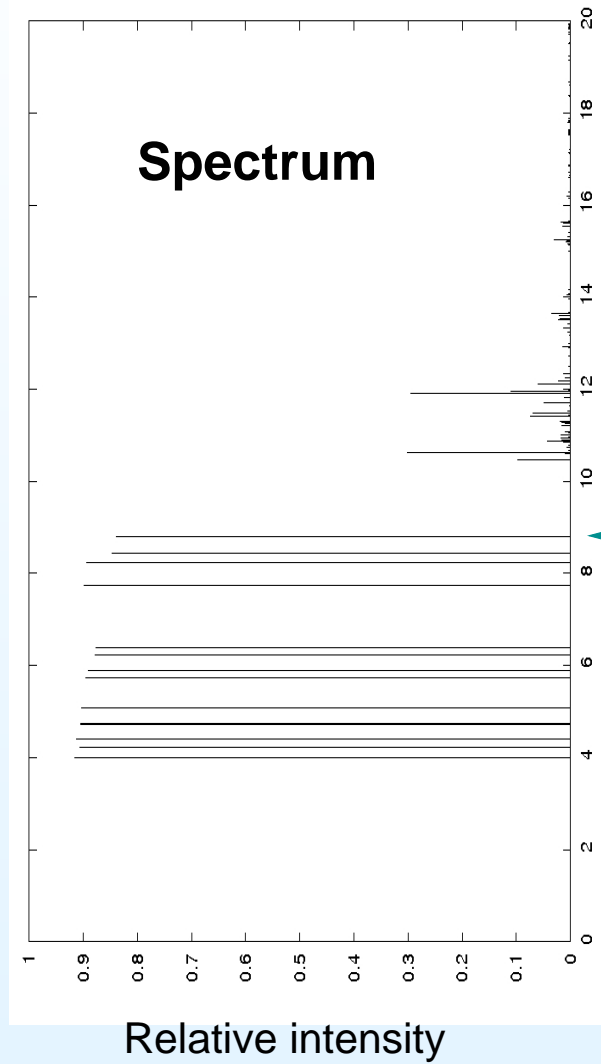
**Non-Dyson ADC-matrix**

h/h Block	Coupling block
Coupling block	Satellite block

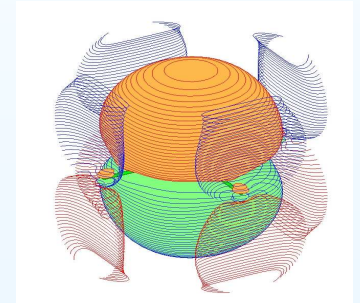
[1] J. Schirmer, L. S. Cederbaum, O. Walter, Phys. Rev. A **28**, 1237 (1983);  
M. Pernpointner, J. Chem. Phys. **121**, 8782 (2004).



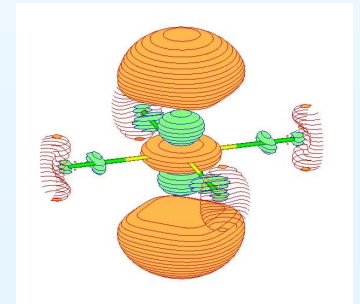
# Interpreting the results



occ(3)

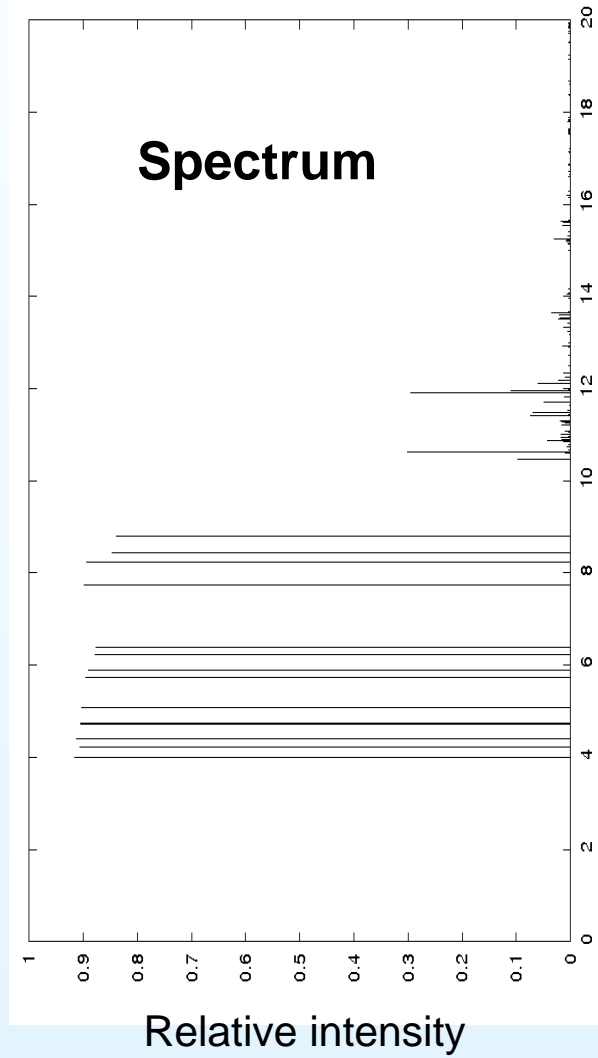


occ(4)

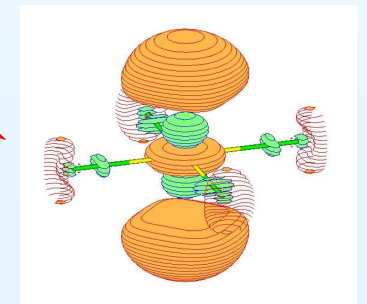
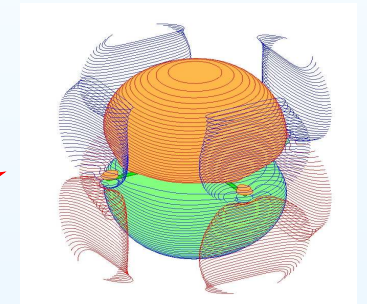
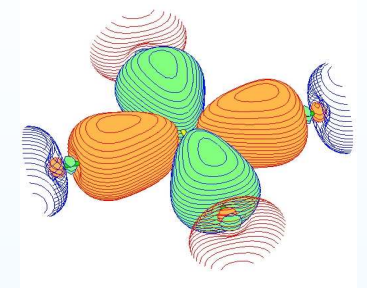
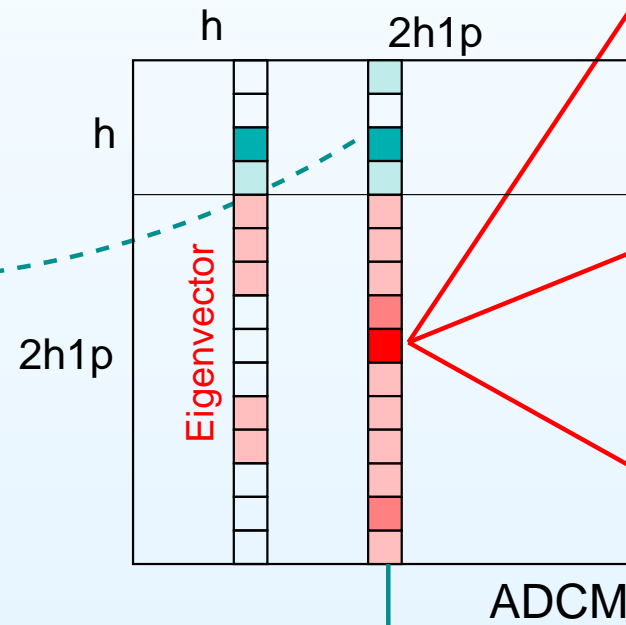


virt(5)

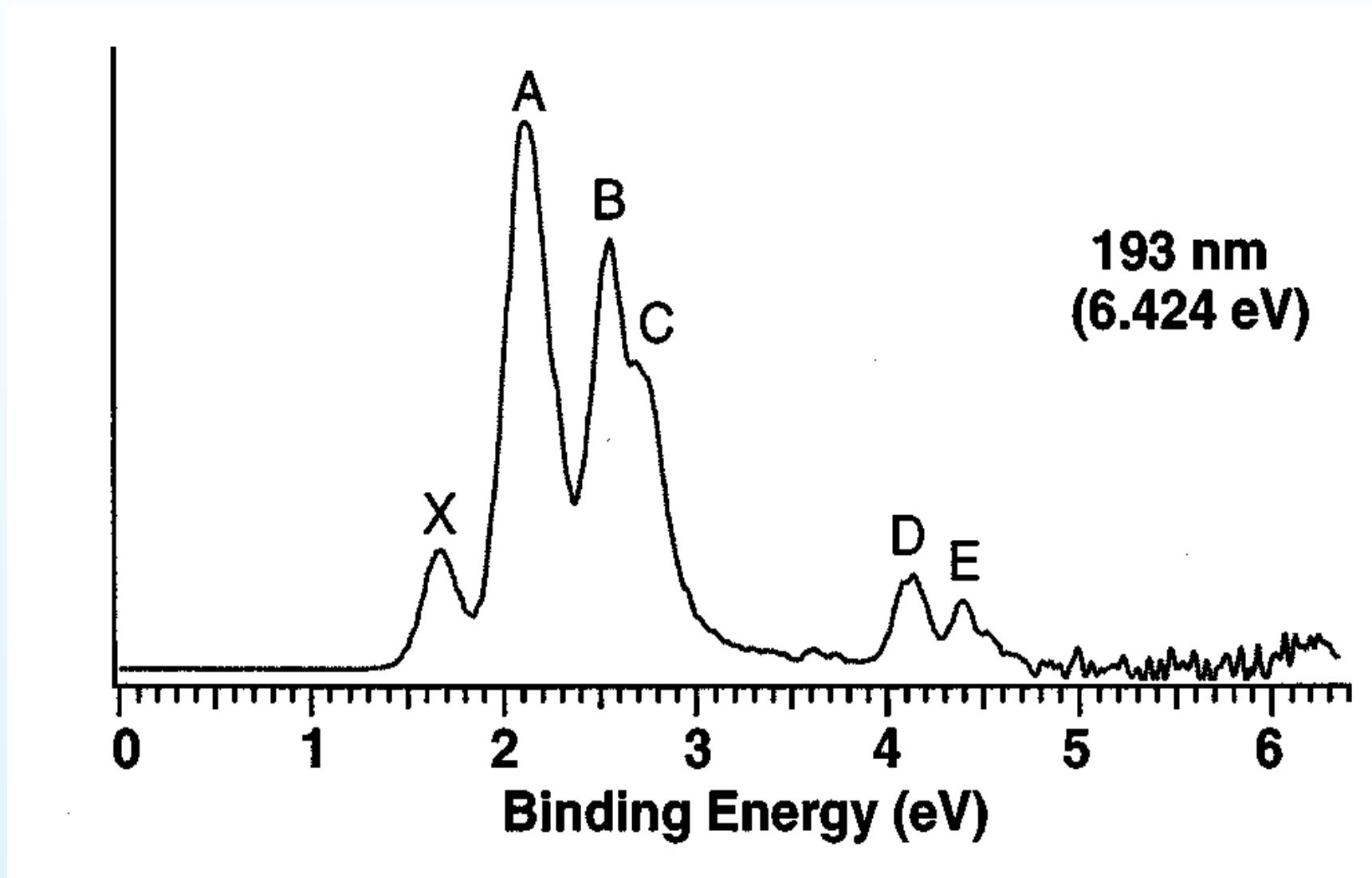
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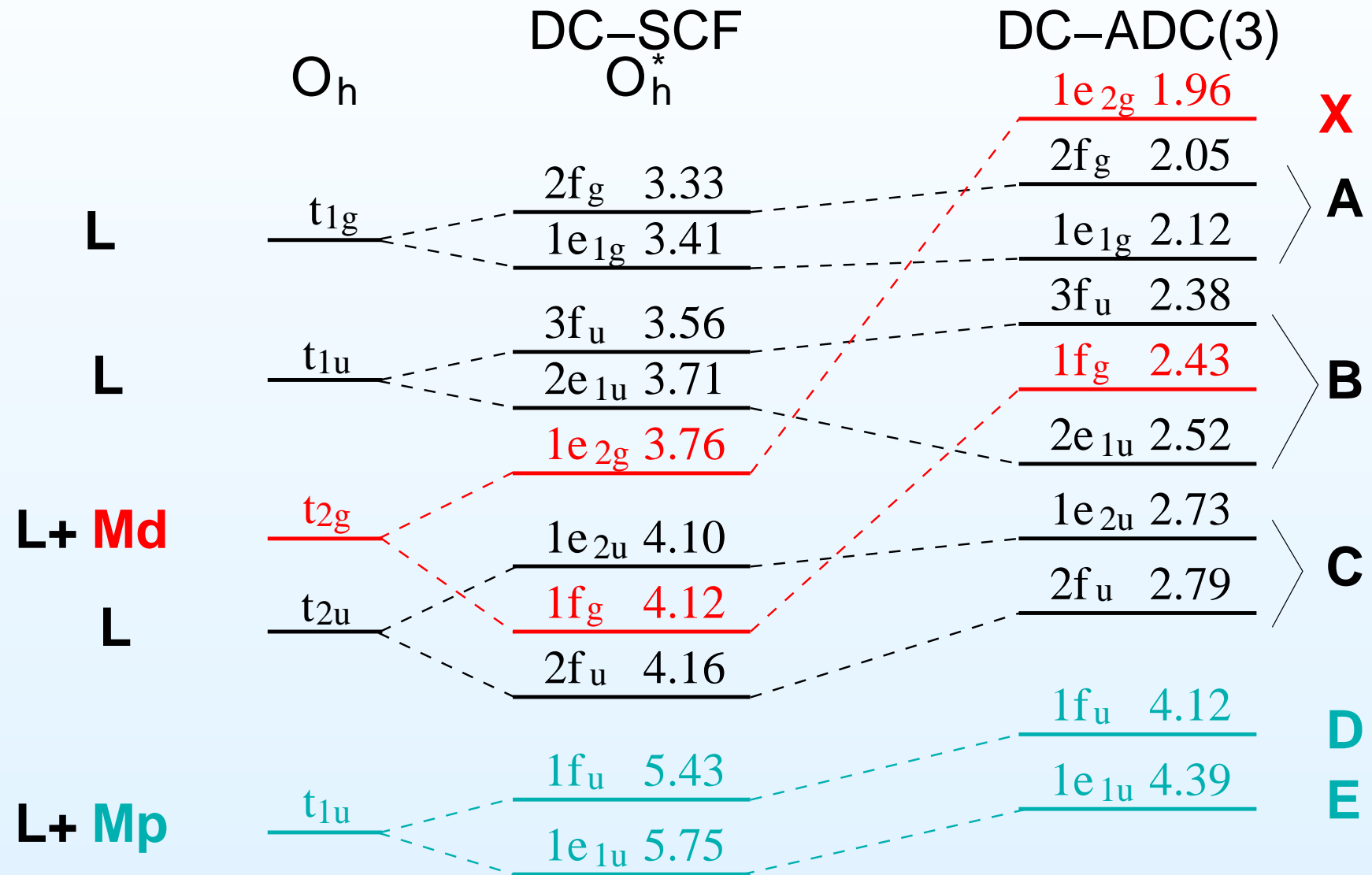
Satellite line



# Jahn-Teller and Spin-orbit effects for the $\text{PtCl}_6^{2-}$ ionization spectrum

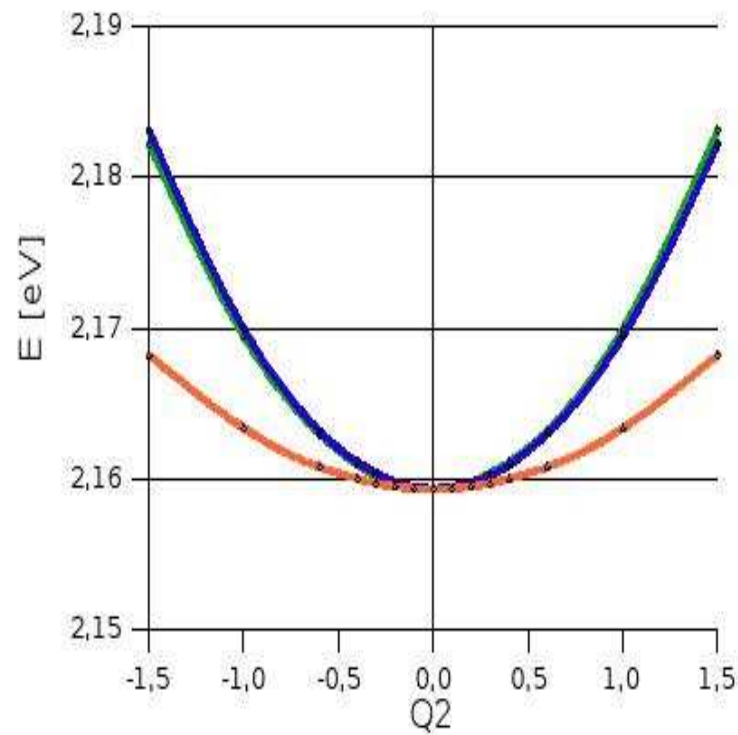
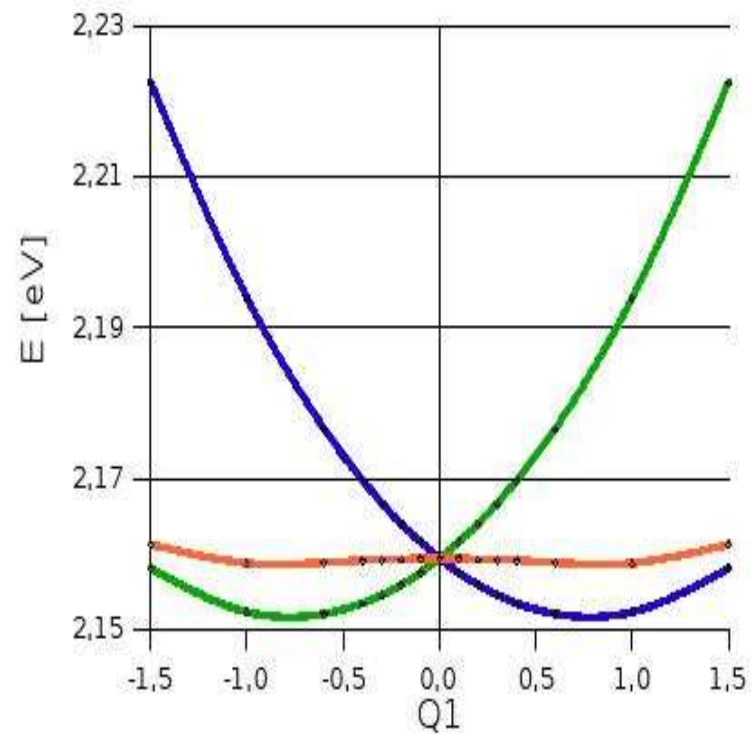


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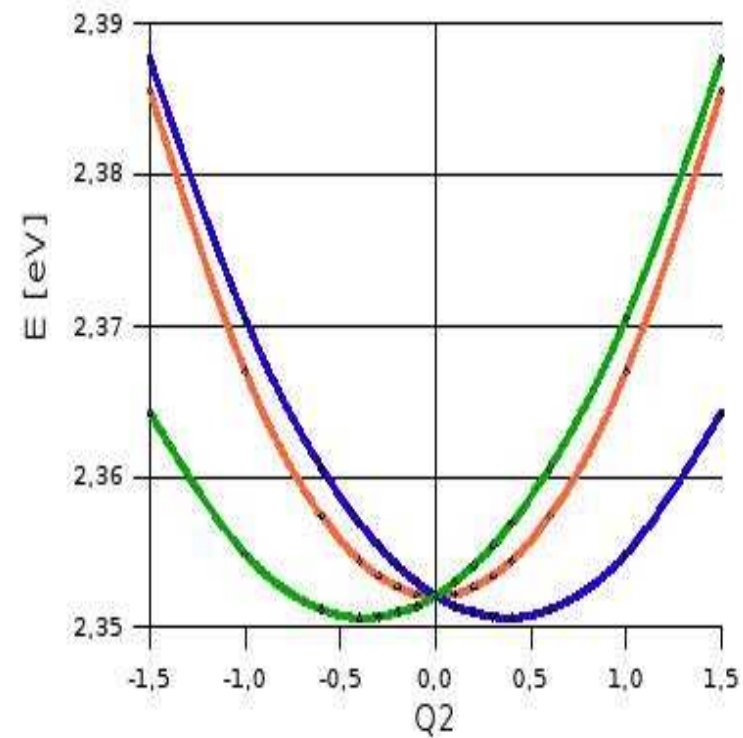
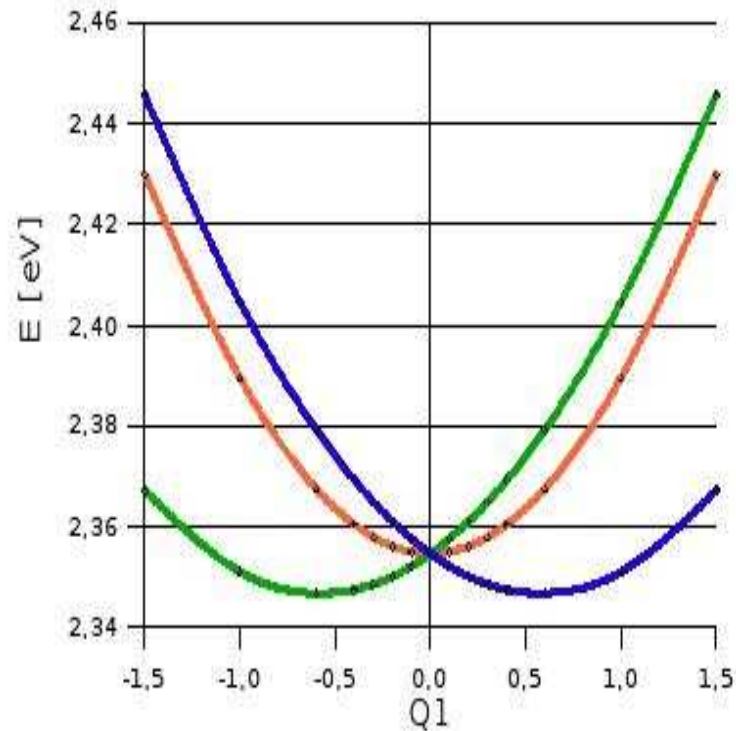
# Jahn-Teller stabilizations for the scalar relativistic calculation

**1t1g**



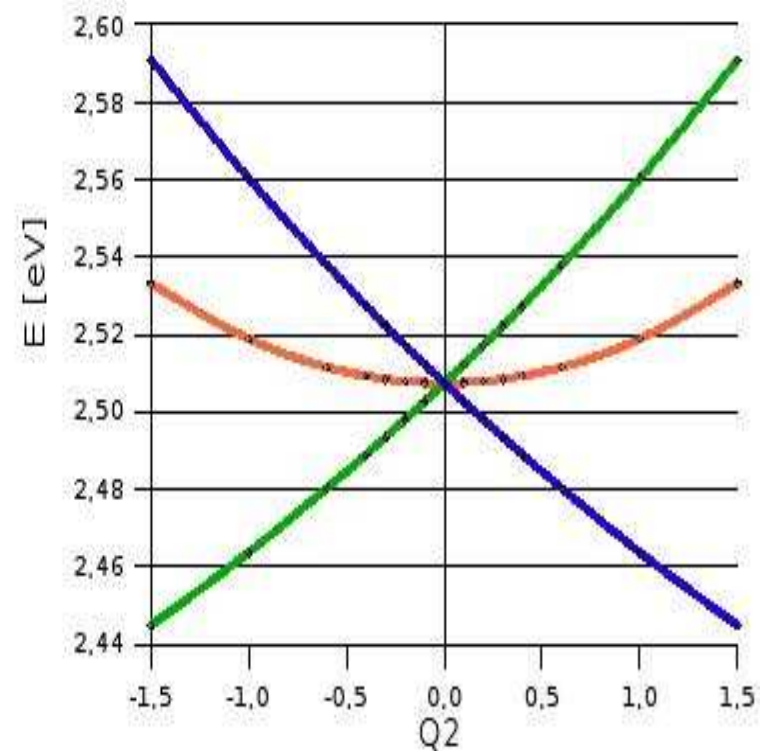
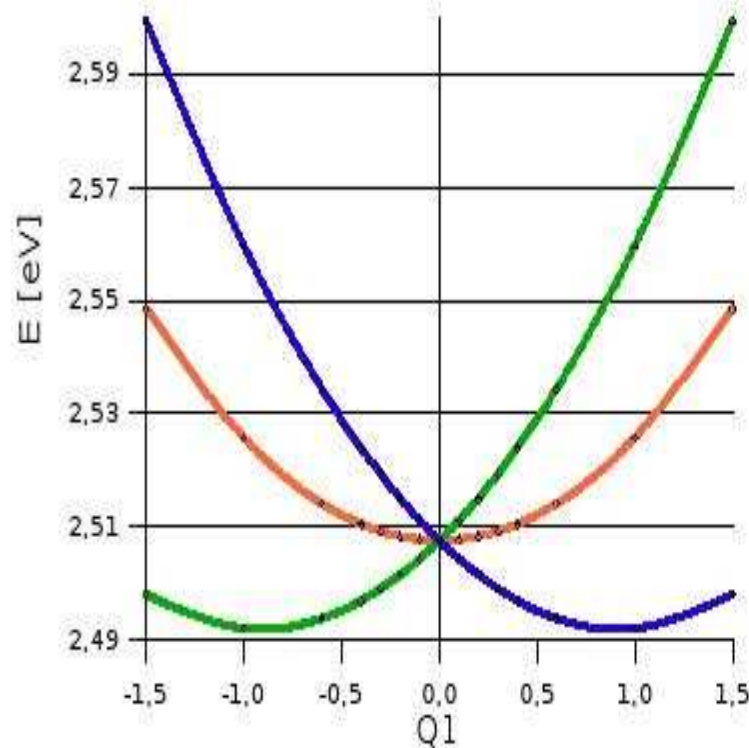
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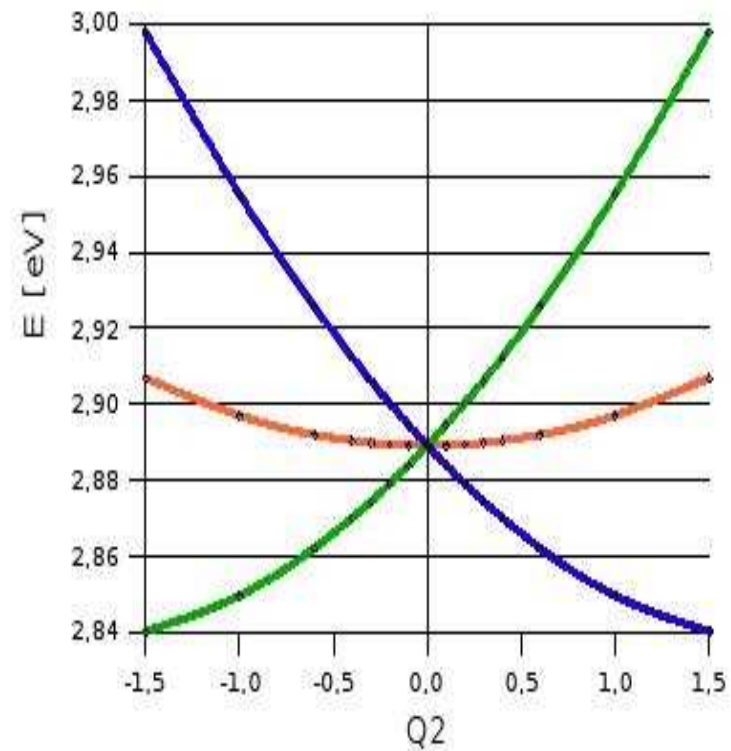
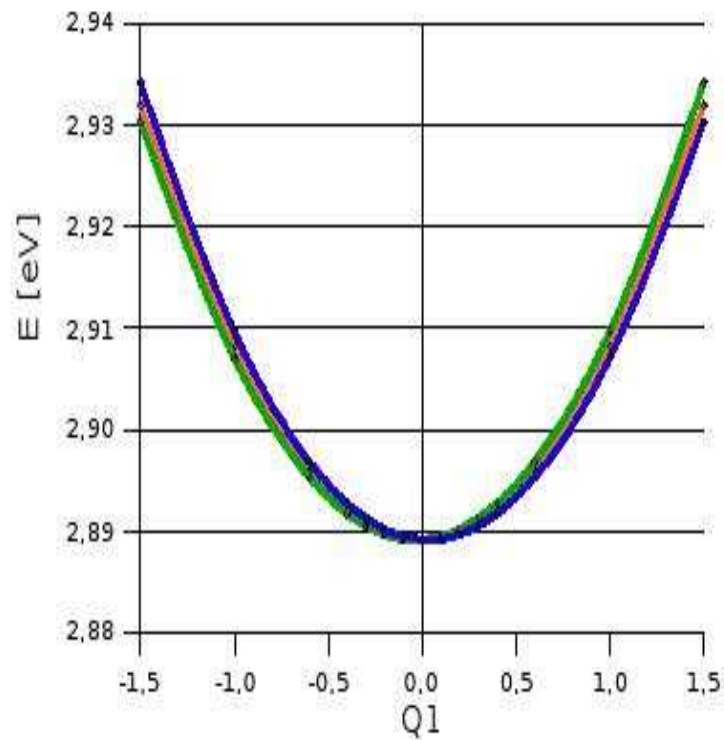
# Jahn-Teller stabilizations for the scalar relativistic calculation

**2t1u**



# Jahn-Teller stabilizations for the scalar relativistic calculation

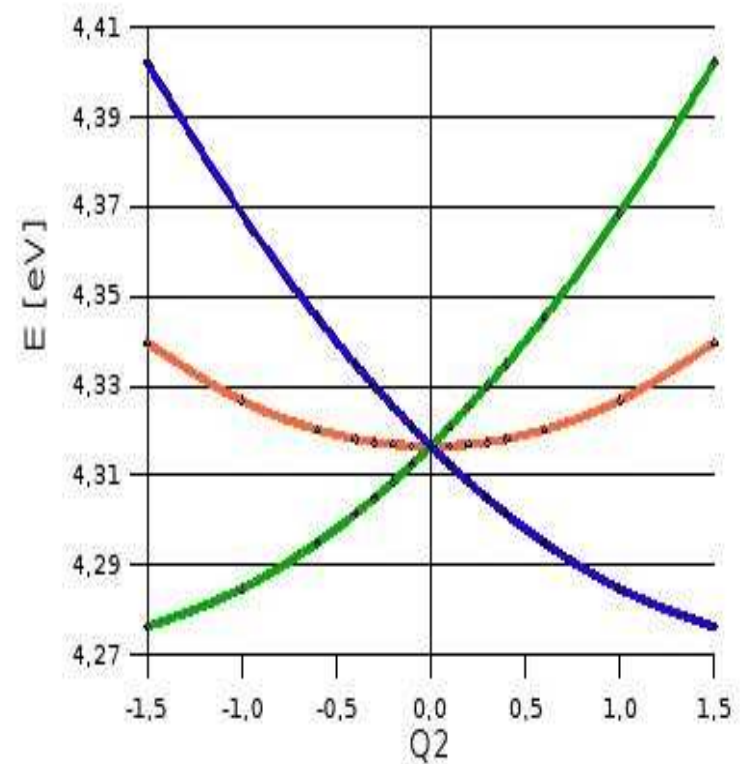
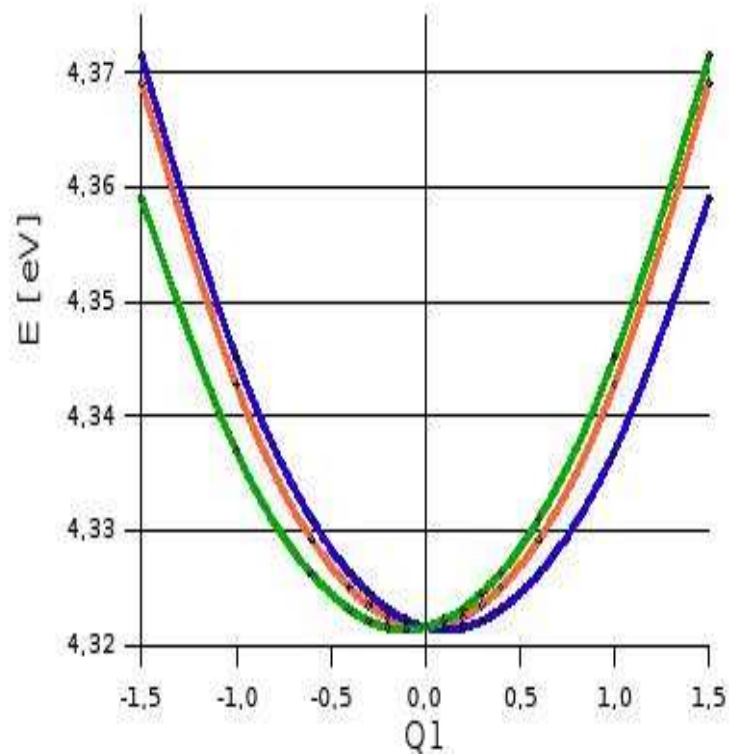
**1t2u**





# Jahn-Teller stabilizations for the scalar relativistic calculation

**1t1u**



## The JT stabilization energies in the scalar relativistic case

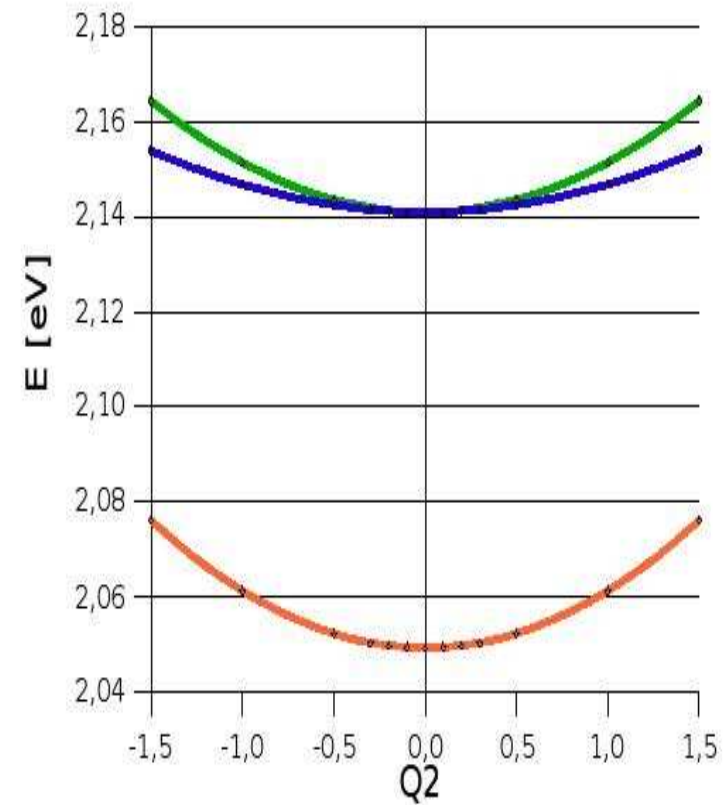
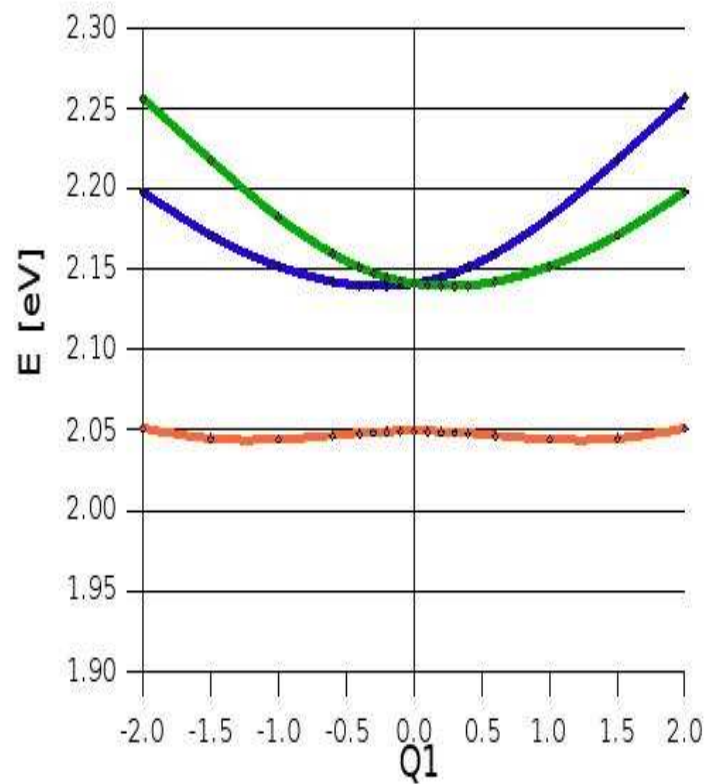
State/mode	$\Delta E_{JT}$	State/mode	$\Delta E_{JT}$
$1T_{1g}/Q1$	0.009	$1T_{1g}/Q2$	—
$1T_{2g}/Q1$	0.01	$1T_{2g}/Q2$	0.001
$2T_{1u}/Q1$	0.014	$2T_{1u}/Q2$	0.06*
$1T_{2u}/Q1$	—	$1T_{2u}/Q2$	0.05*
$1T_{1u}/Q1$	—	$1T_{1u}/Q2$	0.04*

⇒ JT stabilization not very pronounced

# Jahn-Teller stabilizations for the four-component calculation

A features (L)

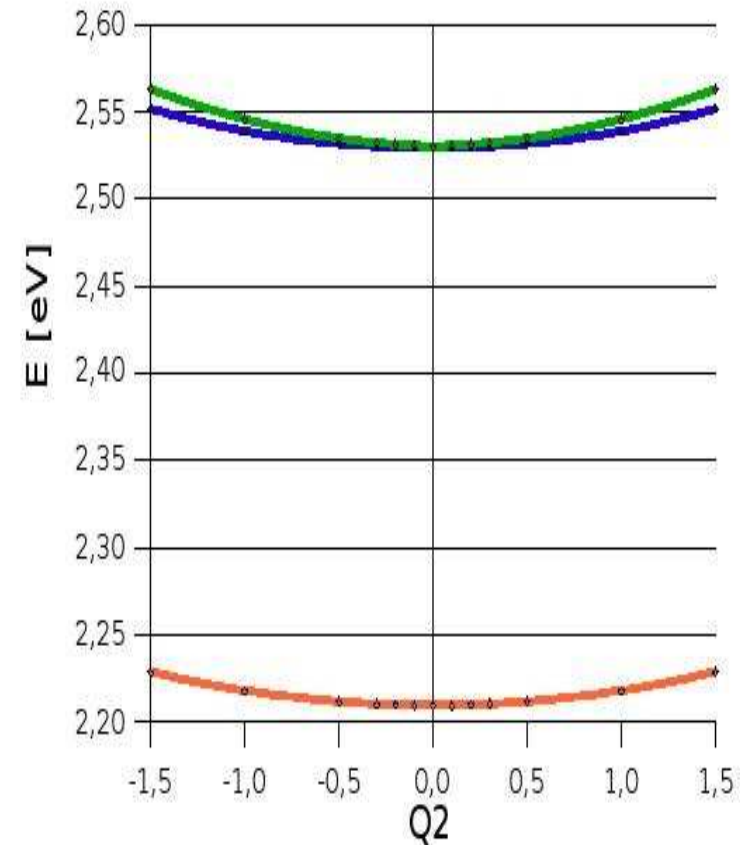
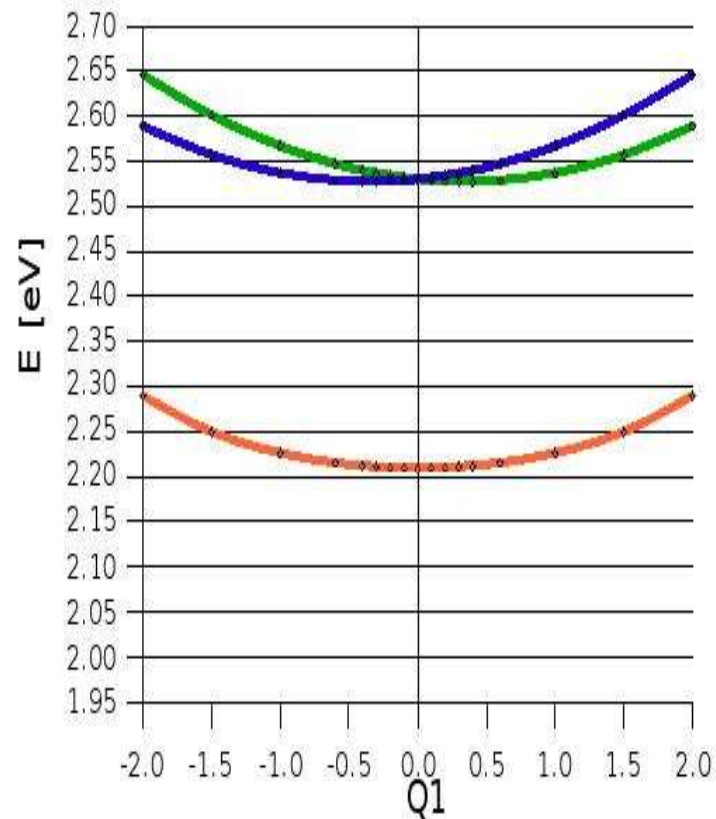
Fg + E1g



# Jahn-Teller stabilizations for the four-component calculation

B feature (L +  $Md$ ), X feature (L +  $Md$ )

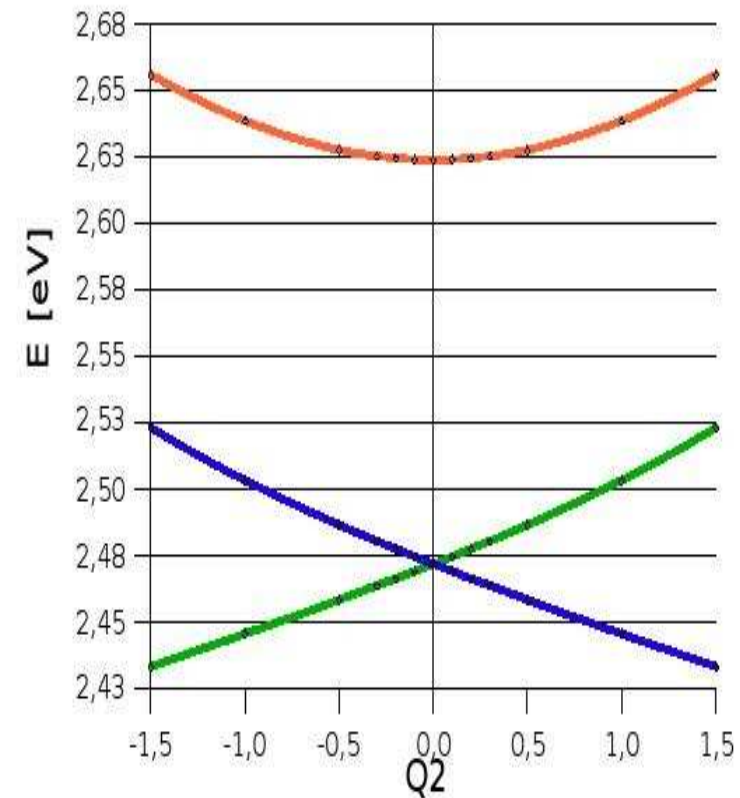
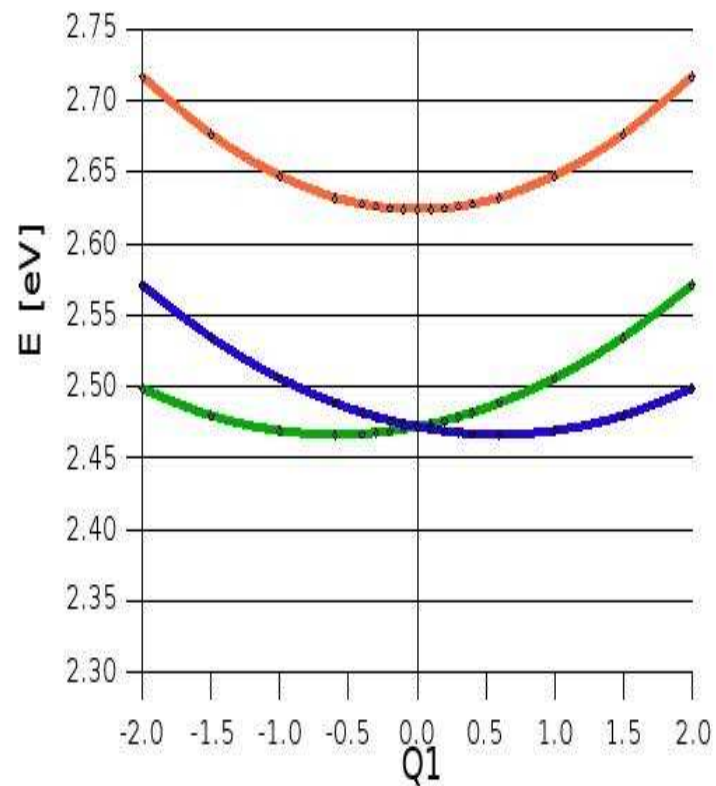
Fg + E2g



# Jahn-Teller stabilizations for the four-component calculation

## B features (L)

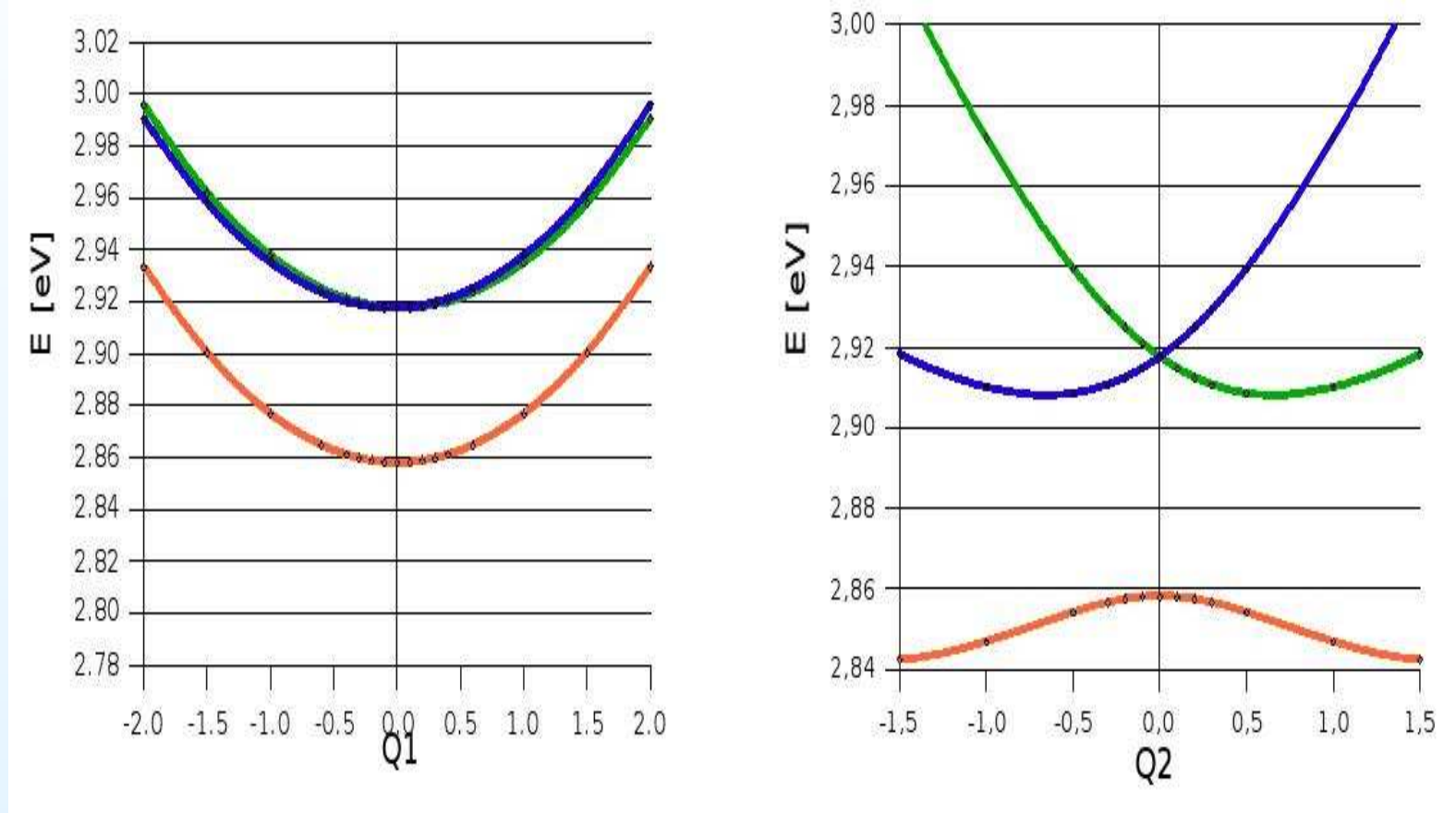
Fu + E1u



# Jahn-Teller stabilizations for the four-component calculation

## C features (L)

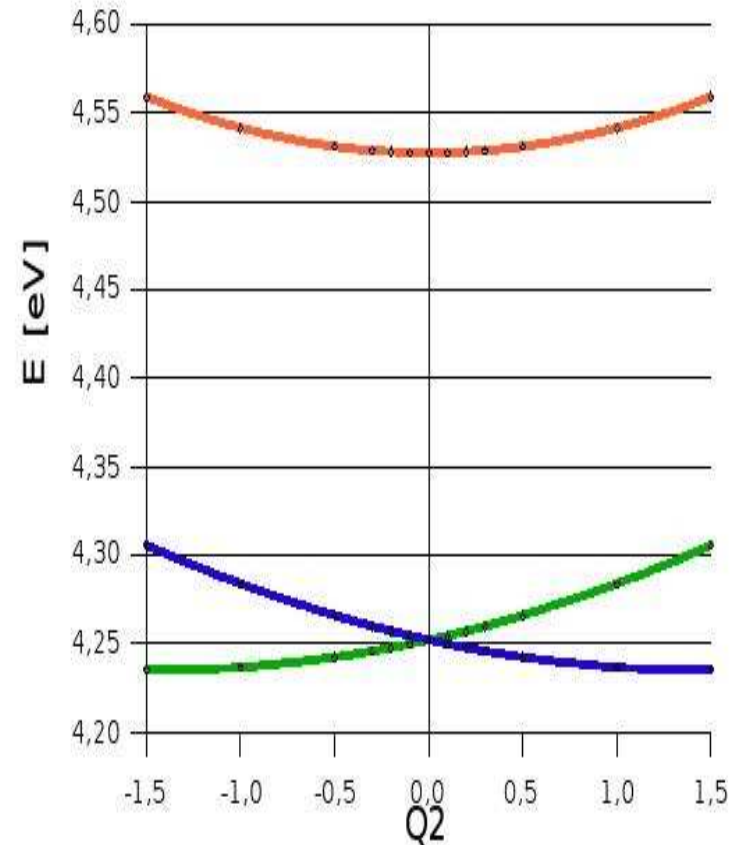
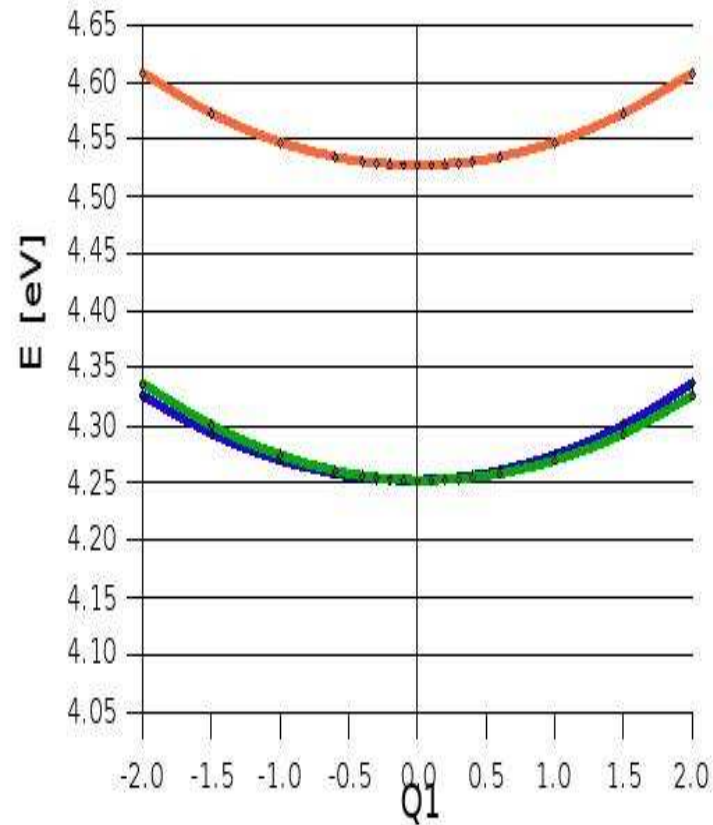
Fu + E2u



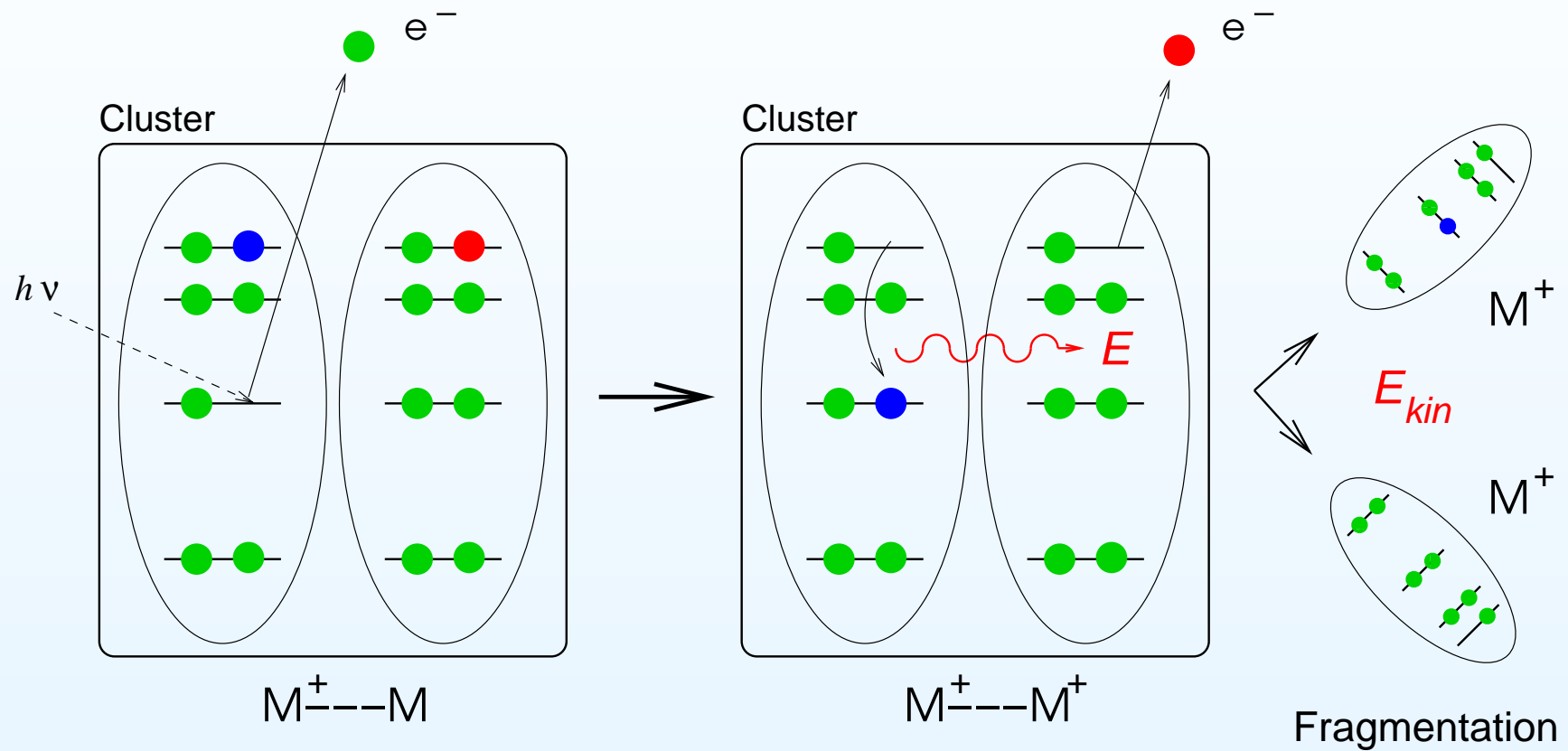
# Jahn-Teller stabilizations for the four-component calculation

D/E features (L+M<sub>p</sub>)

Fu + E1u

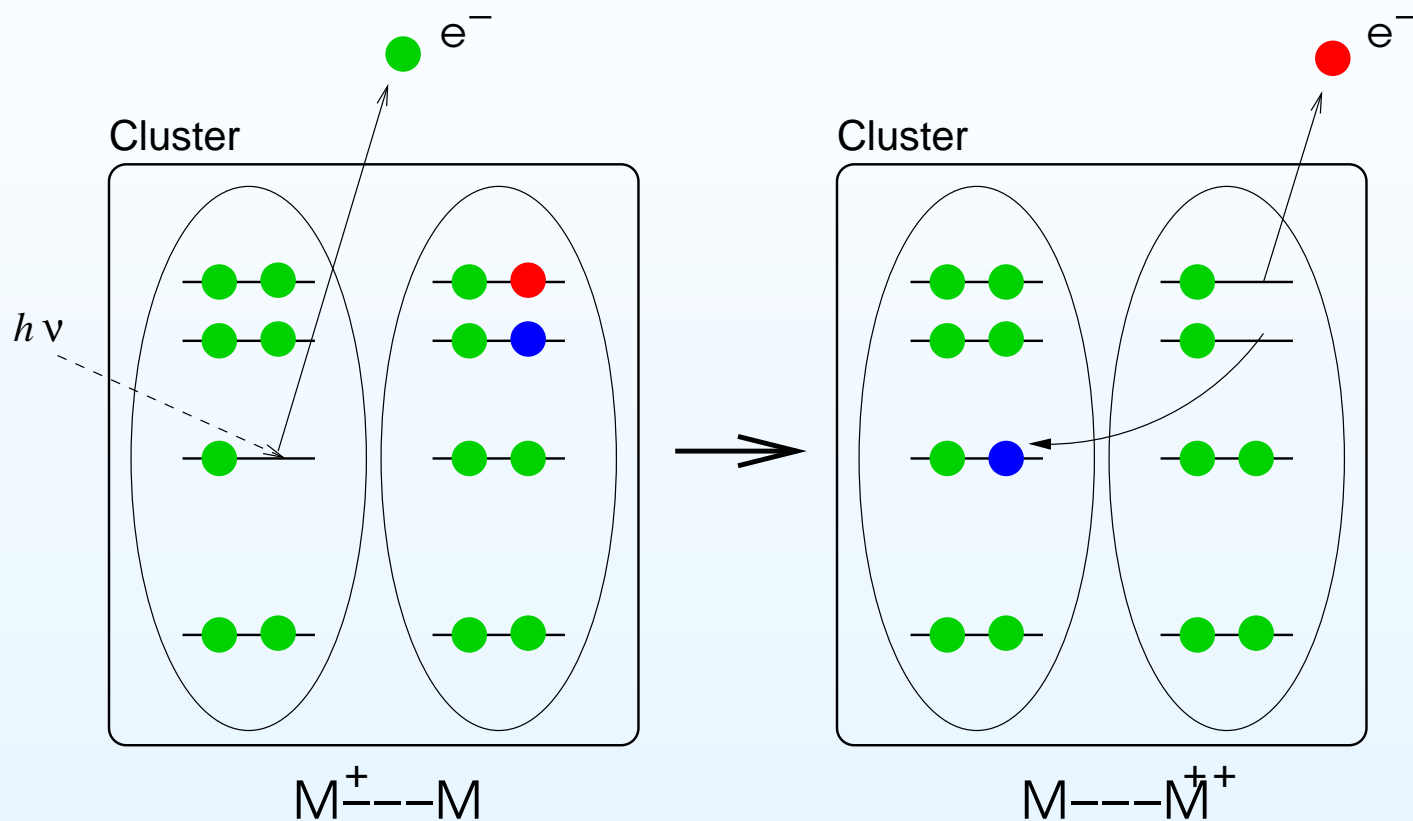


# The Intermolecular Coulombic Decay ICD



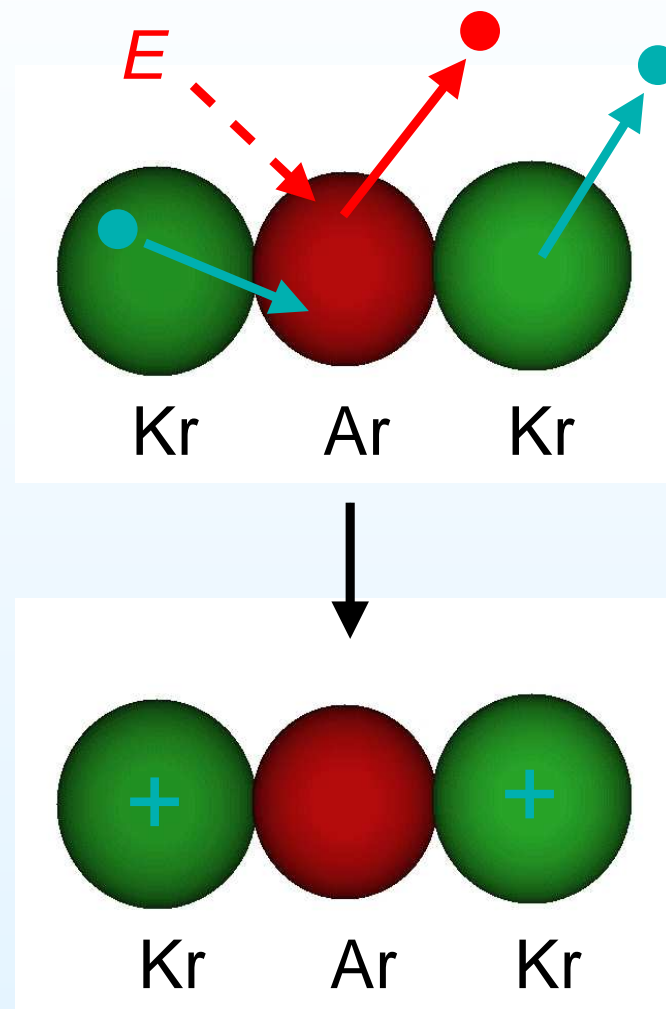
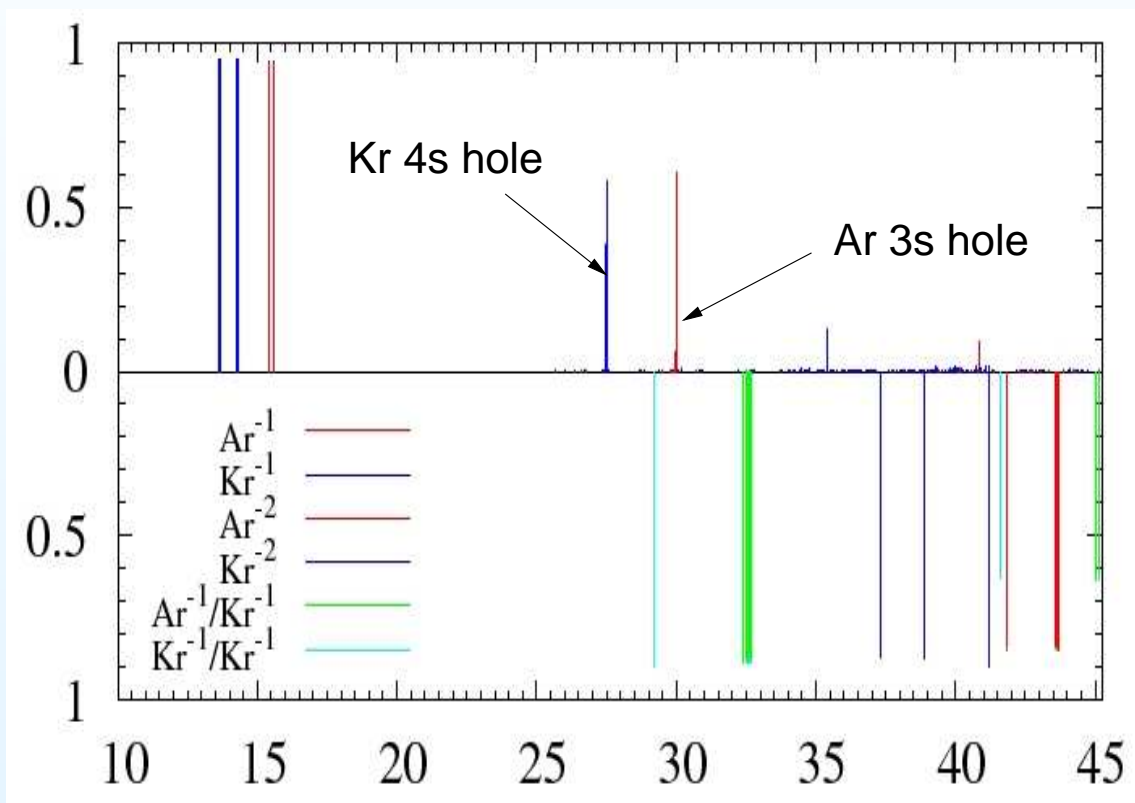


# The two-monomer **E**lectron-**T**ransfer **M**ediated **D**ecay (ETMD)

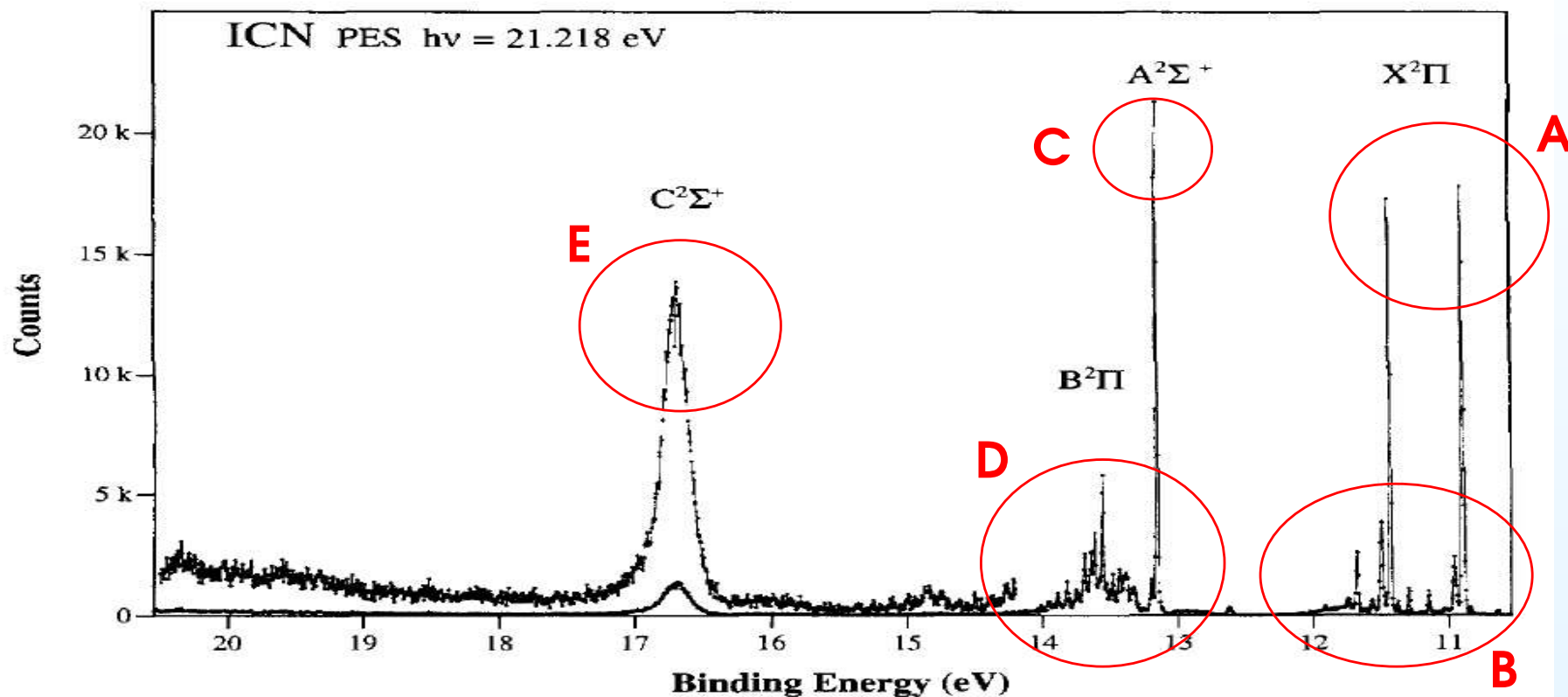


Characteristics: Much slower than ICD, concurrent process

# ETMD in the ArKr<sub>2</sub> trimer



## Current work: Ionization spectrum of ICN



A: Strong spin-orbit Coupling      B: Vibronic/satellite structure

C: Unsplit main state

D: Breakdown of MO picture/ possibly strong vibronics

E: Satellite state, no corresponding Koopmans energy

## Coworkers

- The DIRAC developers group
- Nikolai Kryzhevoi
- Horst Köppel

## Acknowledgments

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