Electronic states in atoms, molecules, and crystals

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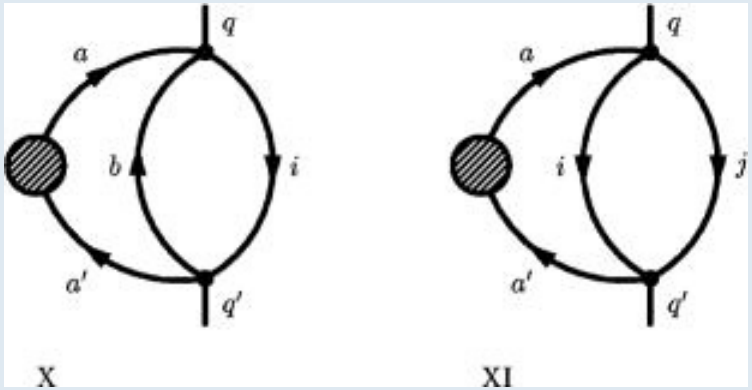
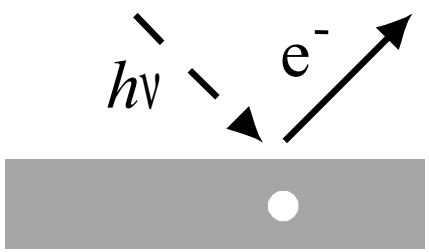


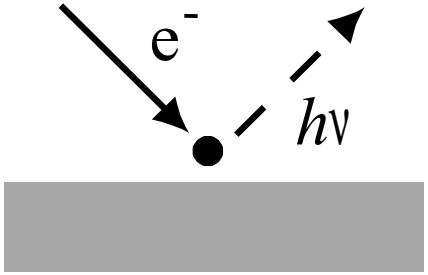
1.0 Contents

1.1 (Inverse) photoelectron spectroscopy

- Probe excited states of atoms, molecules and crystals



Ionization potentials
Valence bands



Electron affinities
Conduction bands

1.2 Many-body Green's functions

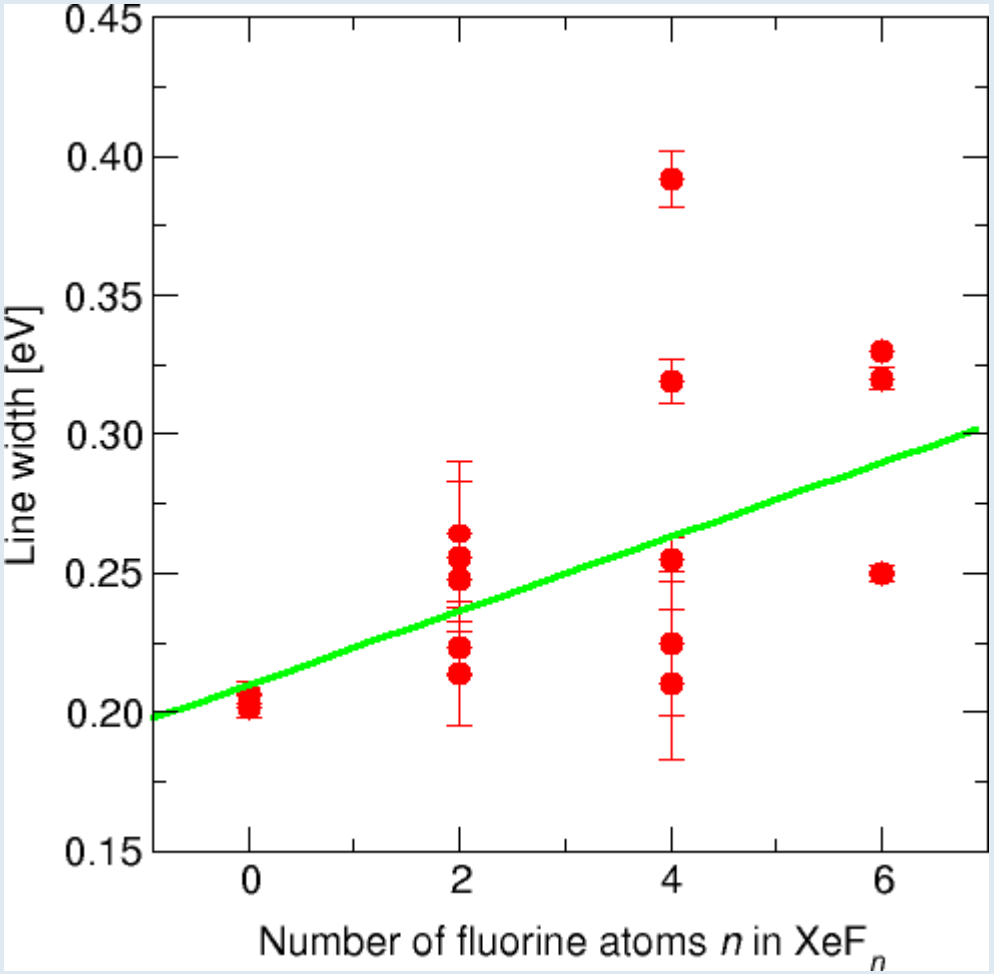
- QED description of one-photon processes in photoelectron spectra
- Many-body Green's function

$$i\,G_{pq}(t-t') = \langle \Psi_0^N \,|\, \hat{T}\,[\,\hat{c}_p(t)\,\hat{c}_q^{+}(t')\,]\,|\,\Psi_0^N \rangle$$

- Pole positions in energy representation yield ionization potentials (IP) and electron affinities (EA)
- IP/EA to study electronic decay processes

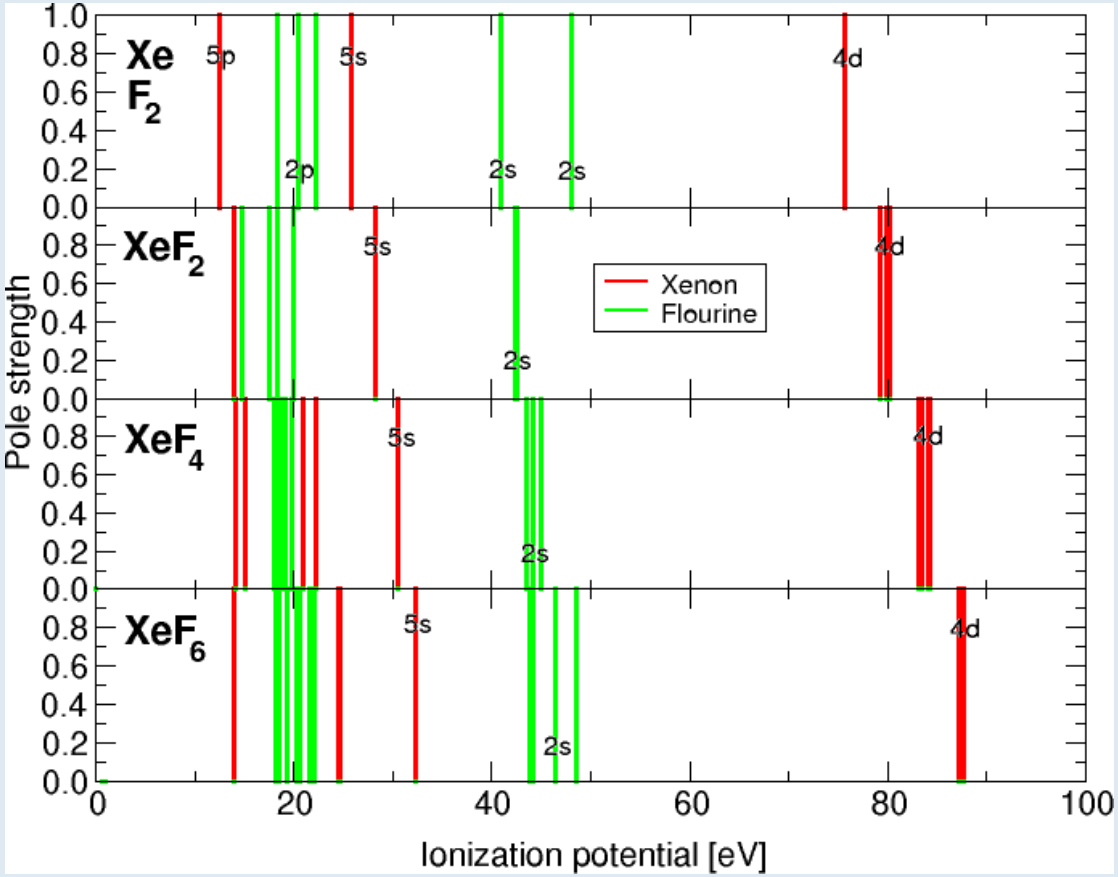
1.3 Width of the Xe 4*d* core lines in XeF_n

- Xe 4*d* line width in the xenon fluorides
- Width increases with the number of ligands



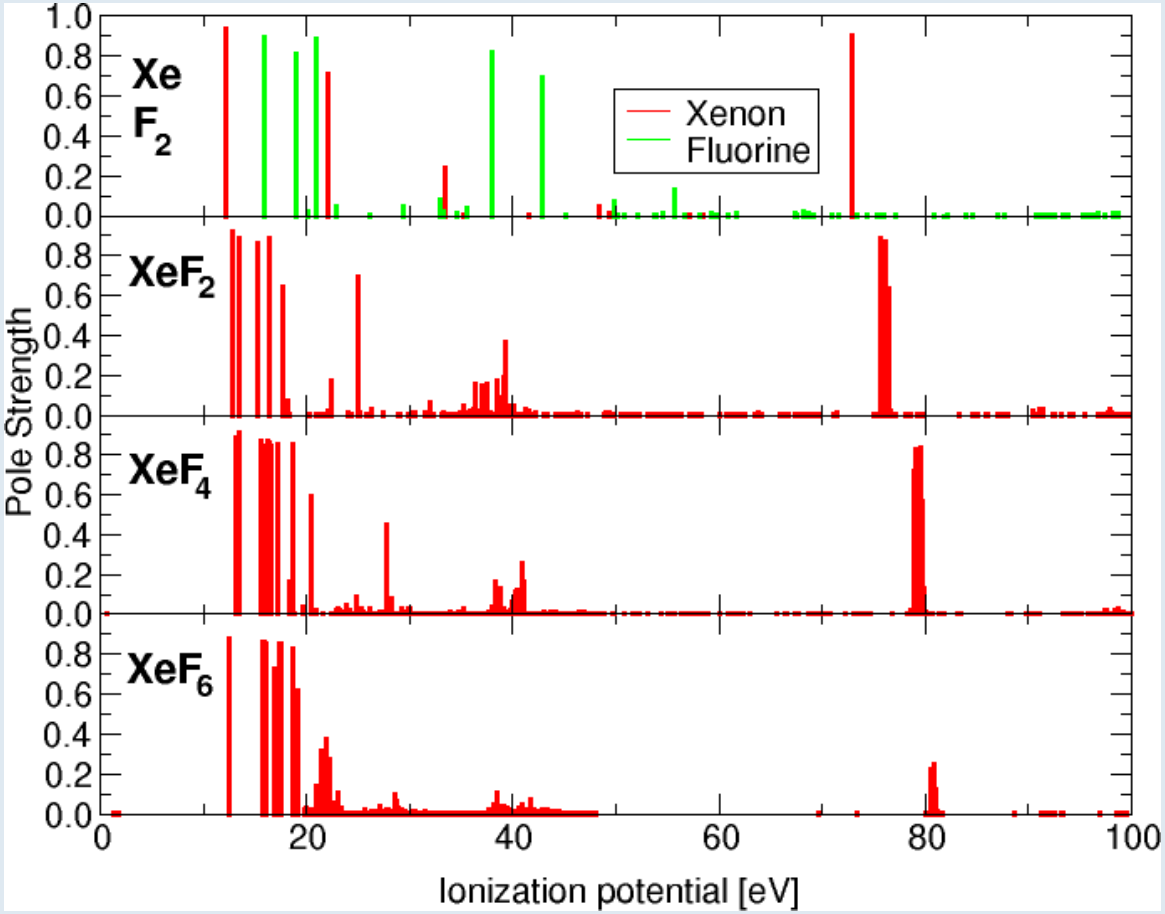
1.4 Hartree-Fock ionization potentials

- Ligand field removes degeneracies
- Charge transfer to fluorine atoms causes increasing IPs



1.5 ADC(3) ionization potentials

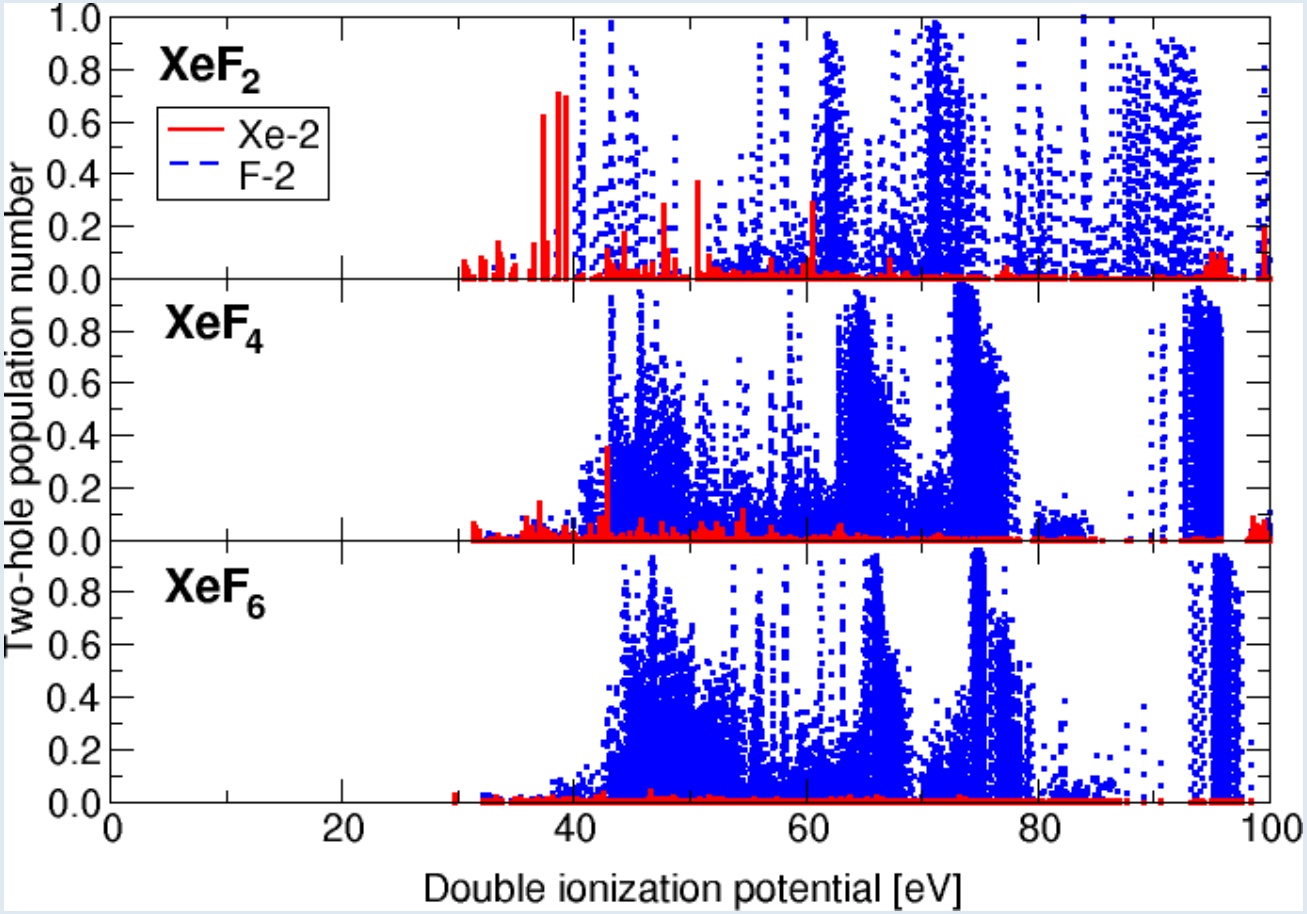
- Improvement of Hartree-Fock results
- Strong correlation
- Decay profiles



[Buth, Santra, Cederbaum, J. Chem. Phys. **119** 7763 (2003)]

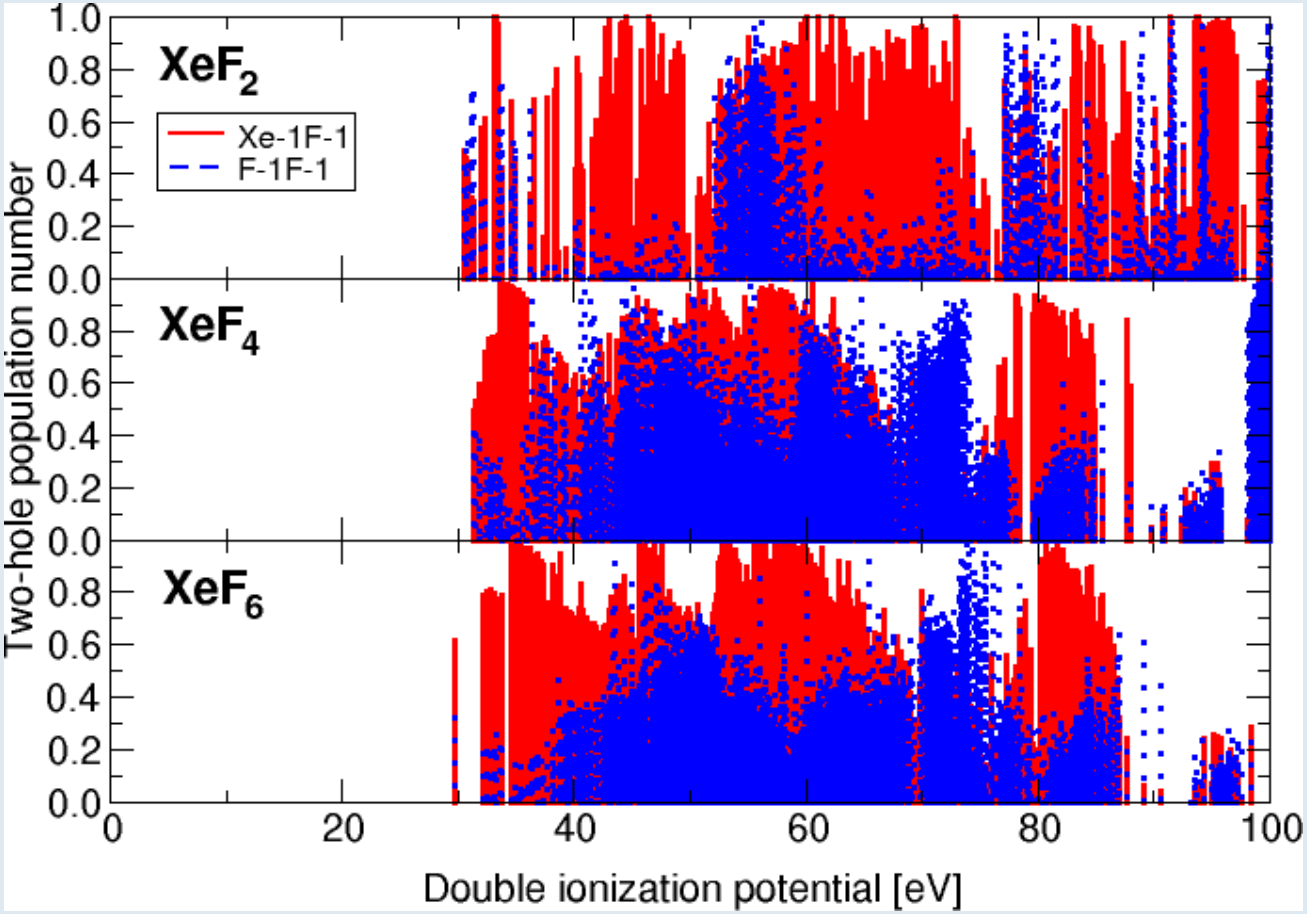
1.6 One-site final states of XeF_n^{++}

- One-site decay into Xe^{-2} holes suppressed
- F 2*s* holes decay predominantly into two-site states



1.7 Two-site Final States of XeF_n^{++}

- $F^{-1}F^{-1}$ states in XeF_2 less important, in XeF_4 strongest
- $Xe^{-1}F^{-1}$ states are dominant



2.0 Contents

2.1 Decay width and population analysis

- Analysis of the localization of the two final-state-holes yields population numbers
- Total decay width of Xe 4*d* holes decomposes

$$\Gamma = \Gamma_{\mathrm{IAED}} + \Gamma_{\mathrm{ICD}} + \Gamma_{\mathrm{ETMD2}} + \Gamma_{\mathrm{ETMD3}}$$

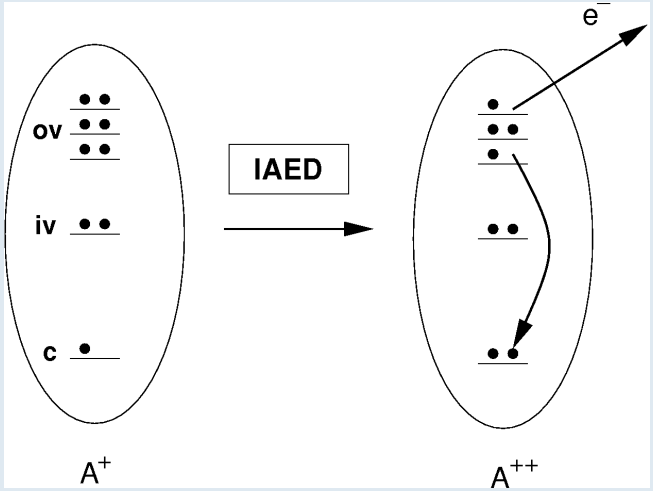
- Connection of two-hole population number $Q_{process}$ and decay width $\Gamma_{process}$

$$\Gamma_{\mathrm{process}} = |T_{\mathrm{process}}|^2 Q_{\mathrm{process}}$$

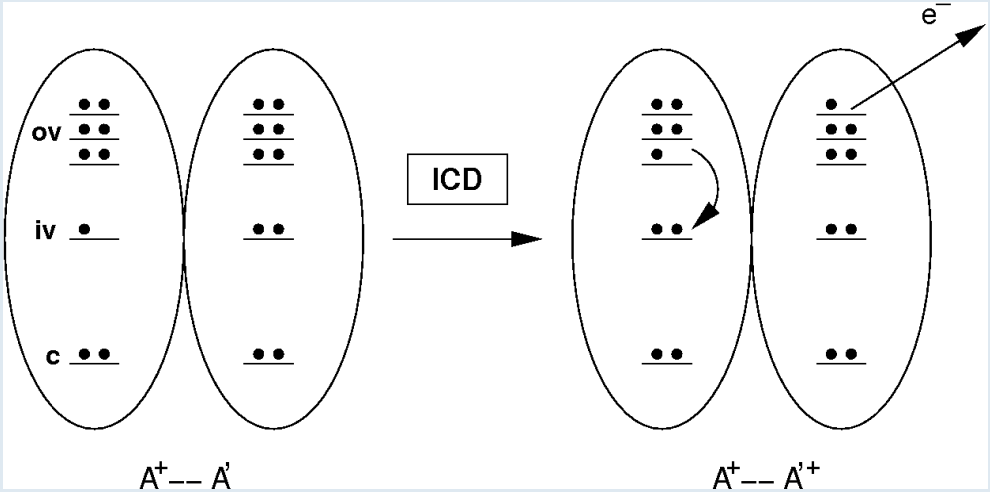
[Buth, Santra, Cederbaum, J. Chem. Phys. **119** 10575 (2003)]

2.2 Intraatomic and interatomic decay

- Intraatomic electronic decay
- Core ionized
- No neighbor involved

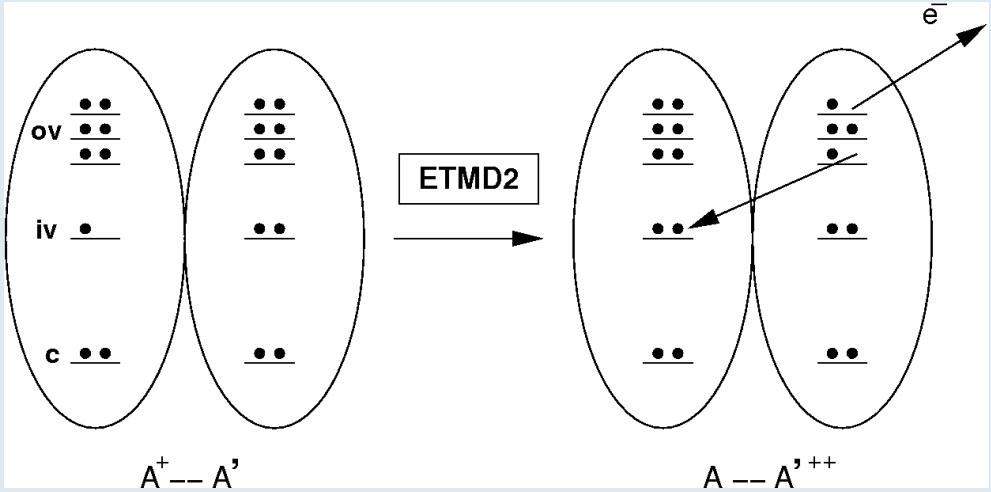


- Interatomic Coulombic decay
- Energy transfer to neighbor atom

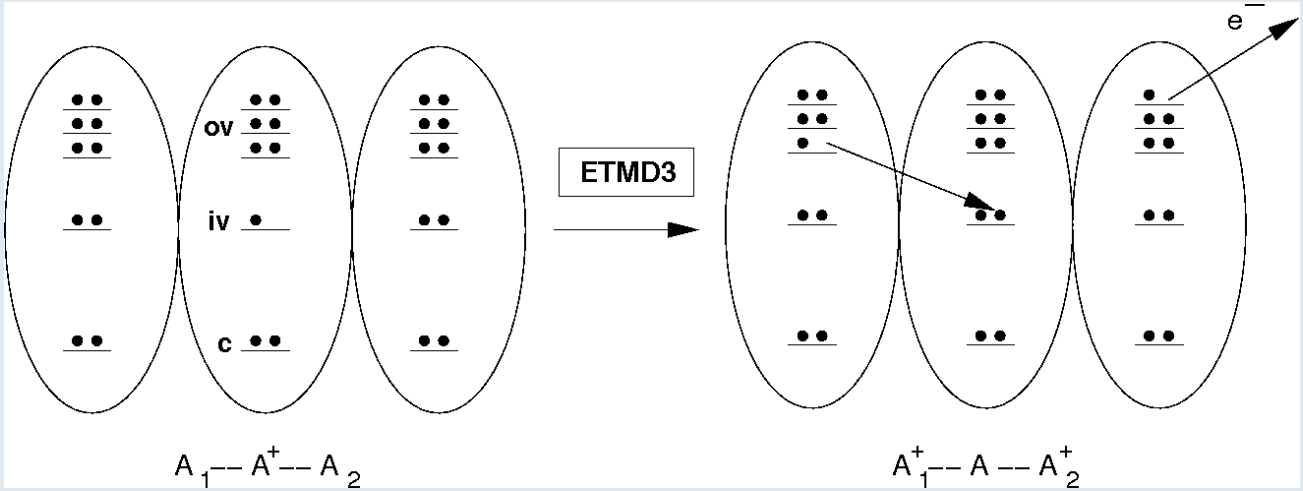


2.3 Electron transfer mediated decay

- Less important than ICD
- Electron transferred to neighbor atom

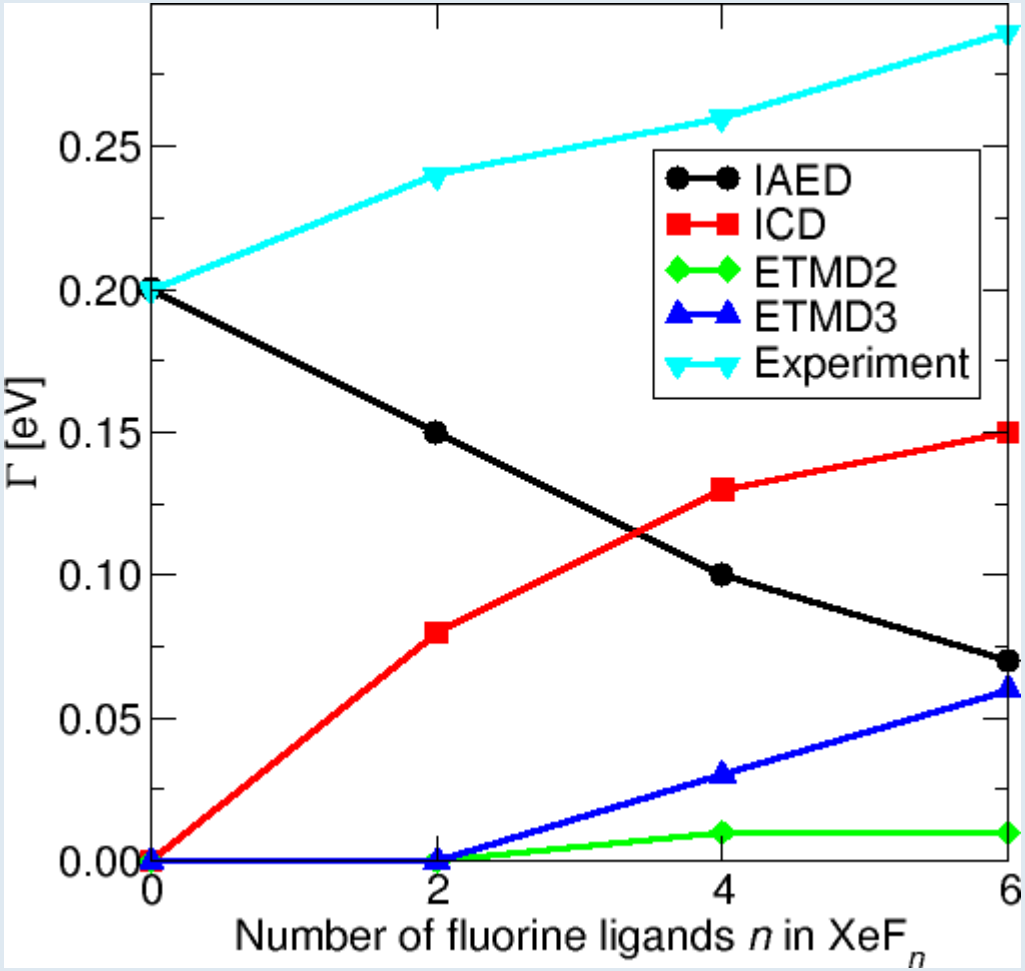


- Electron transferred to one neighbor
- Energy trans-ferred to other neighbor



2.4 Partial decay widths

- Two opposite effects
- Drop of intraatomic rate
- Contribution of interatomic processes

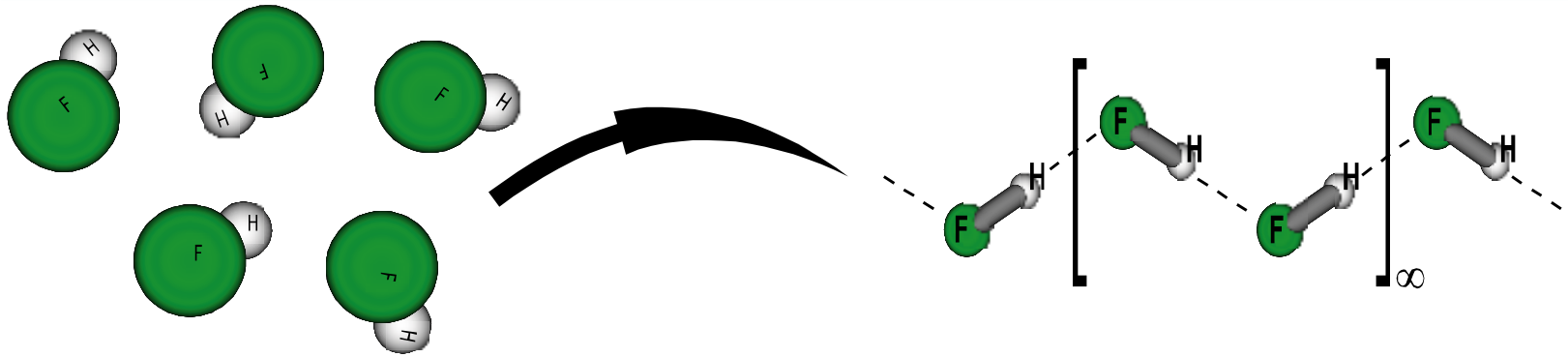


3.0 Contents

1. Xe 4d core holes of XeF_n
2. Electronic decay processes
3. **Transition to crystals**
4. HF and LiF
5. Conclusion

3.1 From molecules to crystals

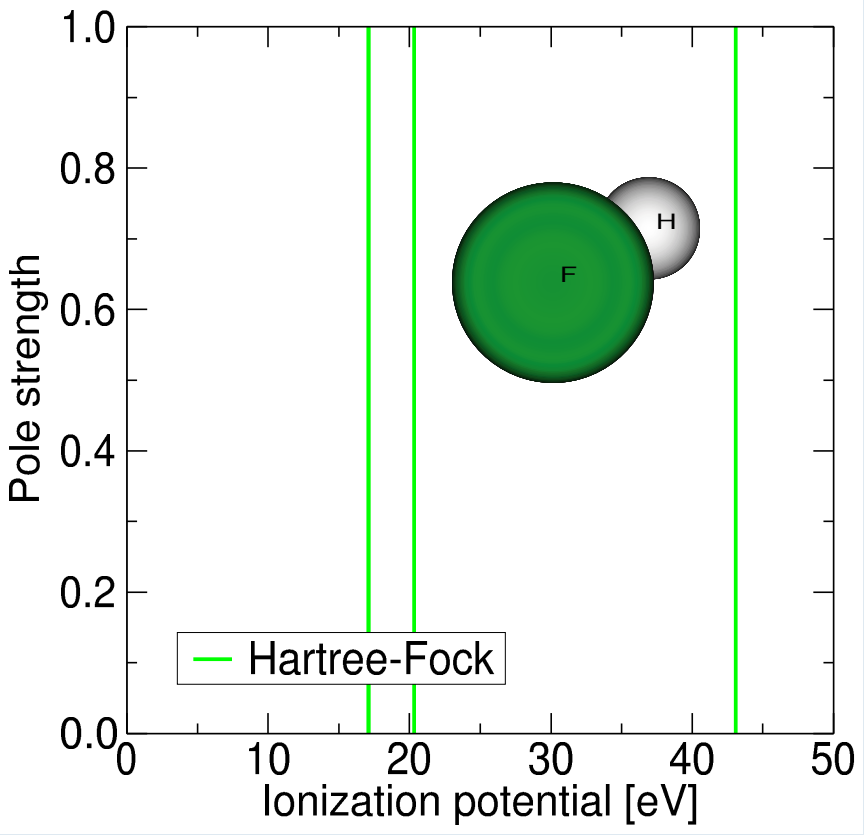
- Crystallization



- Crystals are huge molecules
- Periodic repetition (translational symmetry)
- **Usual model:** crystals extend to infinity

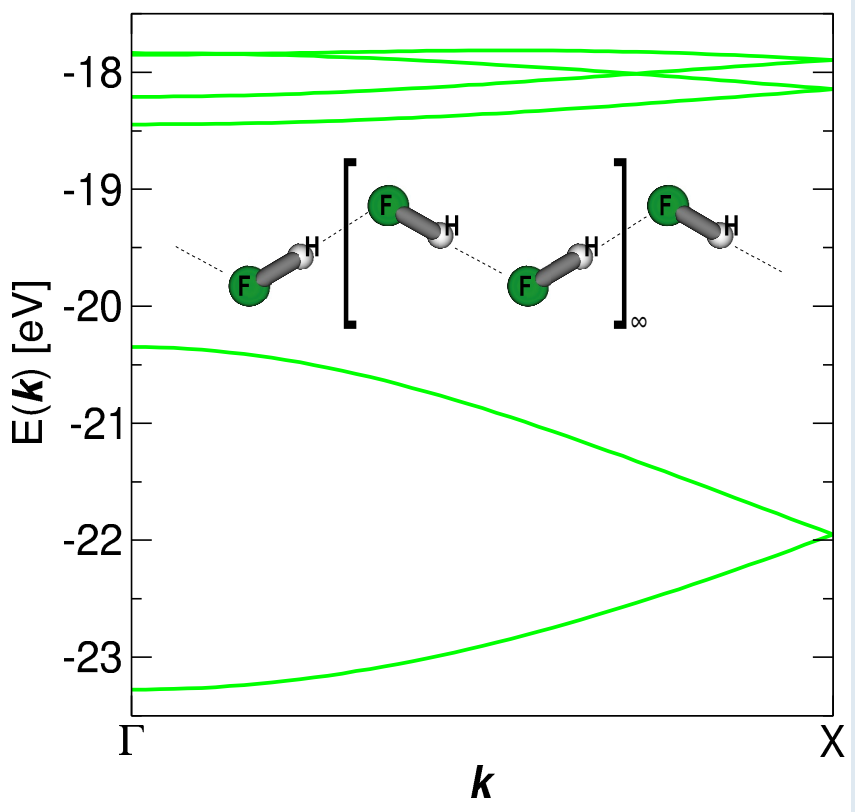
3.2 Hydrogen fluoride molecule

- HF molecule
- Hartree-Fock approximation
- IPs and EAs via Koopmans' theorem
- Basis set cc-pVDZ



3.3 Hydrogen fluoride chain

- $(HF)_\infty$ chain
- Hartree-Fock approximation
- Energy levels
- Translational symmetry classified
- Calculations are routine
- Basis set cc-pVDZ



3.4 A full treatment of correlations

- The algebraic diagrammatic construction (ADC) scheme has proven very accurate for atoms and molecules
- Devise a crystal orbital ADC (CO-ADC) scheme
- Systematically improvable correlation method CO-ADC(2,2), CO-ADC(3,2), …
- Full treatment of many-body effects
- Semiconducting and insulating crystals

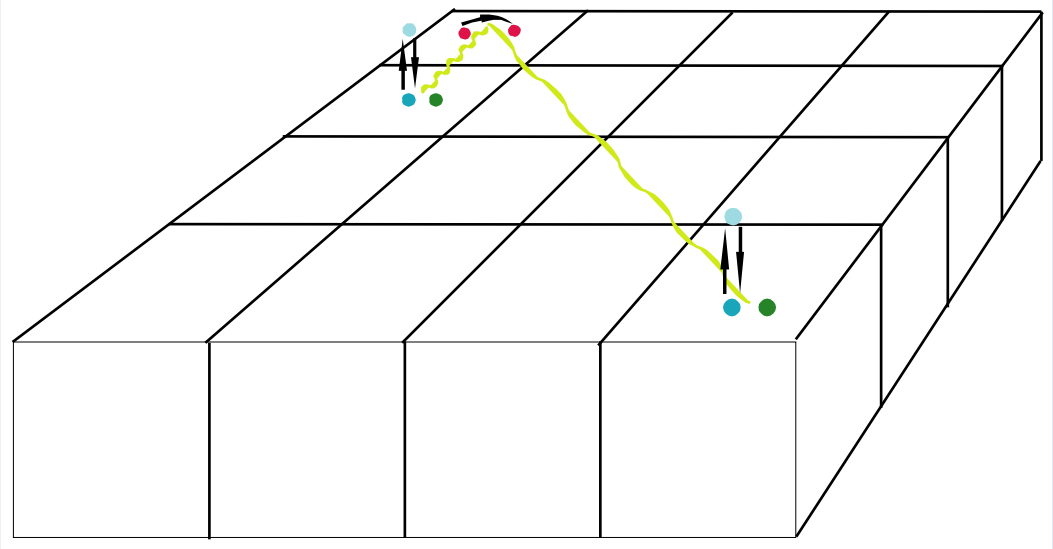
[Buth, Birkenheuer, Albrecht, Fulde, Phys. Rev B **72** 195107 (2005)]

3.5 Views on independent electrons

- Orbitals are a view on independent electrons in crystals
- Canonical orbitals are delocalized
- Unitary transformation
- Hartree-Fock wave function unchanged
- Other orbitals can be defined which are localized
- Periodically repeated in crystals (Wannier orbitals)

3.6 Electron configuration selection

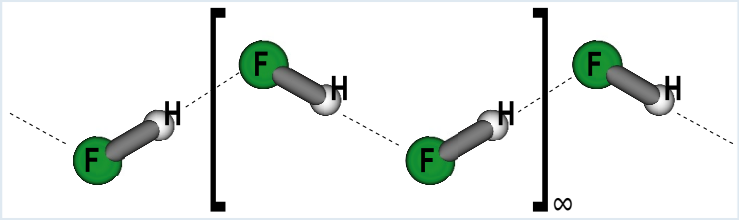
- Crystals are infinite
  ⇒ select excited configurations
- Dynamical selection for each crystal anew



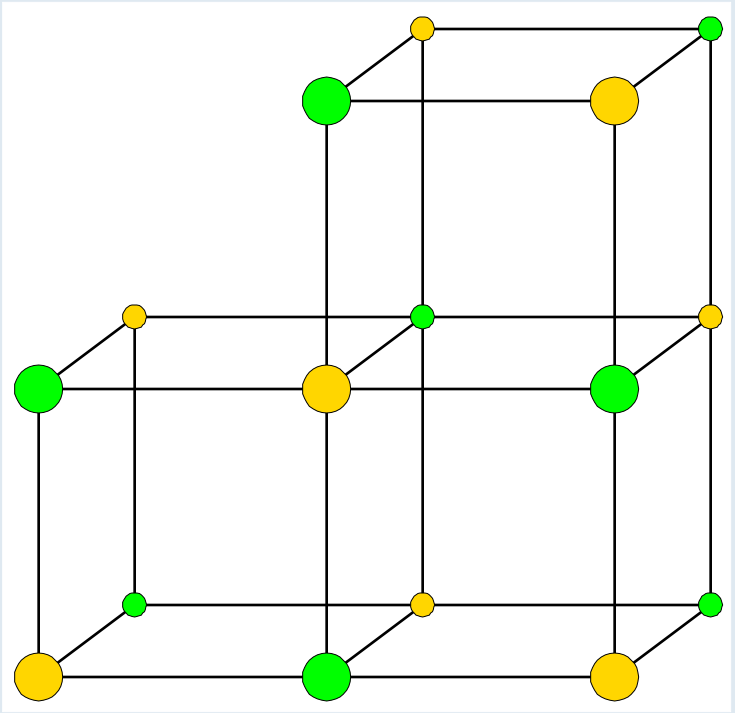
- Neglect of couplings
- Selection criterion

4.1 Exemplary applications

- $(HF)_\infty$ simple model for HF crystal
- Hydrogen-bonded



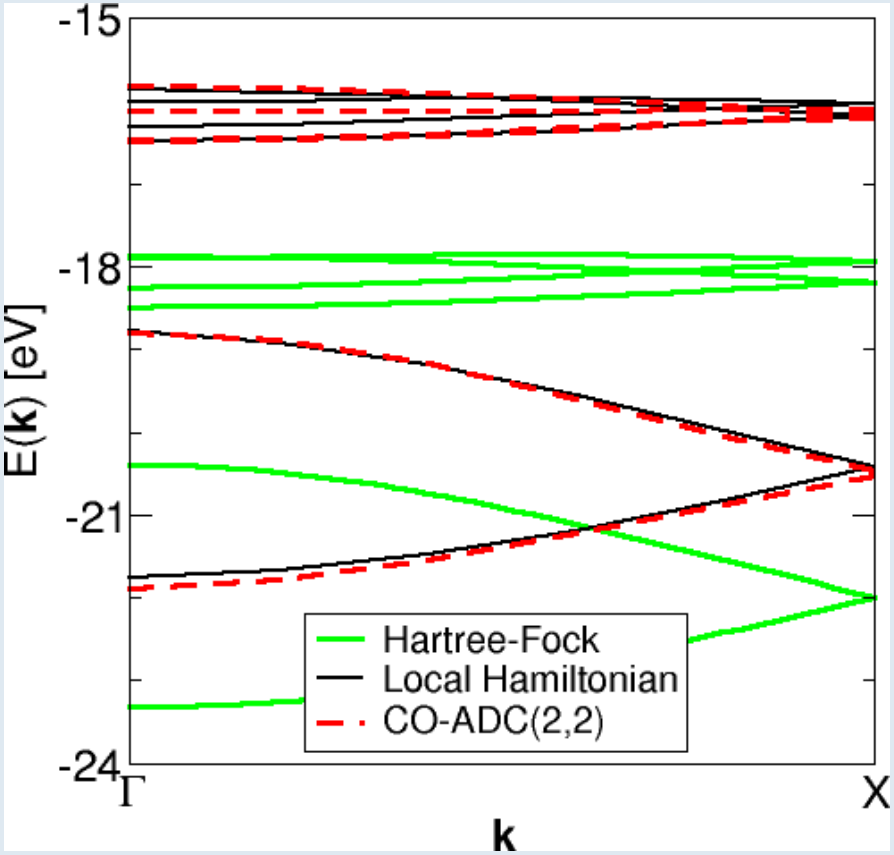
- LiF crystal
- Rock salt structure (fcc)
- Ionic



[Buth, http://planet.pks.mpg.de/trac/co-adc]

4.2 Quasi-particle band structure of $(HF)_\infty$

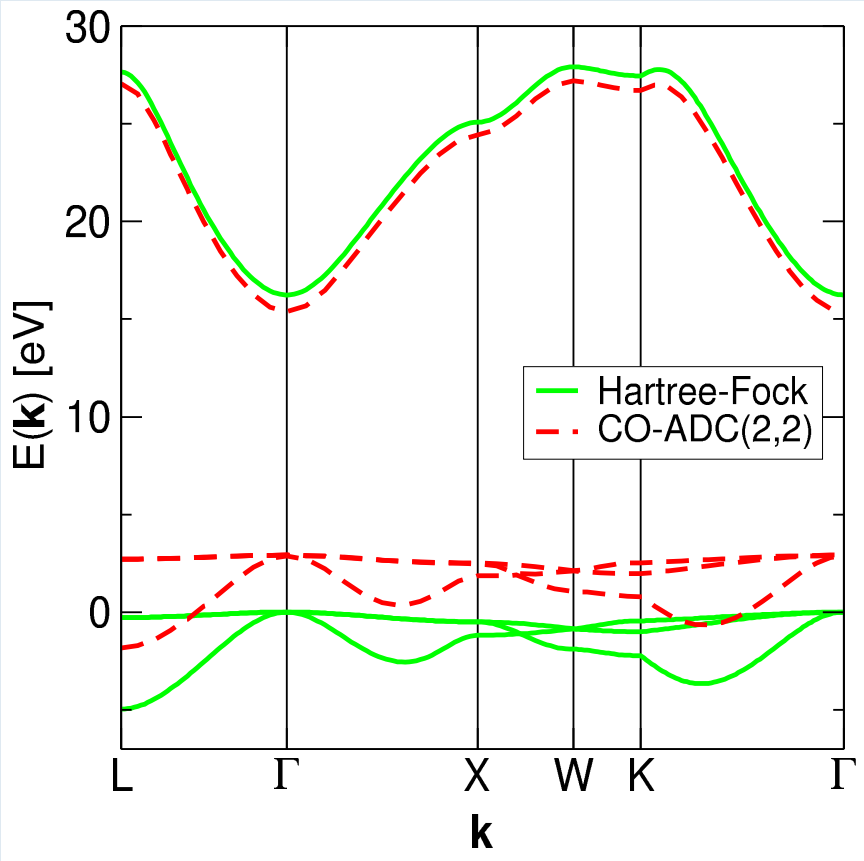
- Excitations from origin cell only
- Band widths are slightly increased by electron correlation
- Basis set cc-pVDZ



Local Hamiltonian calculation by **Viktor Bezugly**
[Theory: Bezugly, Birkenheuer: Chem. Phys. Lett. **399** 57 (2004)]

4.3 Quasi-particle band structure of LiF

- Minimal basis set STO-6G
- Excitations from 19 unit cells (up to 2nd nearest neighbors)
- Shift of conduction and valence bands
- Band widths are hardly influenced
- Good agreement with experiments



[Buth, Birkenheuer, Albrecht, Fulde, Phys. Rev B **72** 195107 (2005)]

5.1 Conclusion

- Xe 4*d* core holes in XeF_n can decay by electron emission
- Many dicationic final states are on two sites
- Observed increase in line width explained in terms of four electronic decay processes
- Electron correlation methods for local orbitals
- Translational symmetry exploited
- Configuration selection employed
- Clusters can be treated similarly

5.2 Acknowledgment

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