The Decay of Electronic Resonances in Molecules

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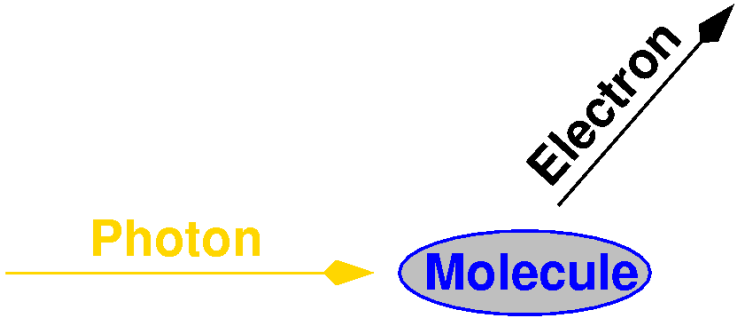
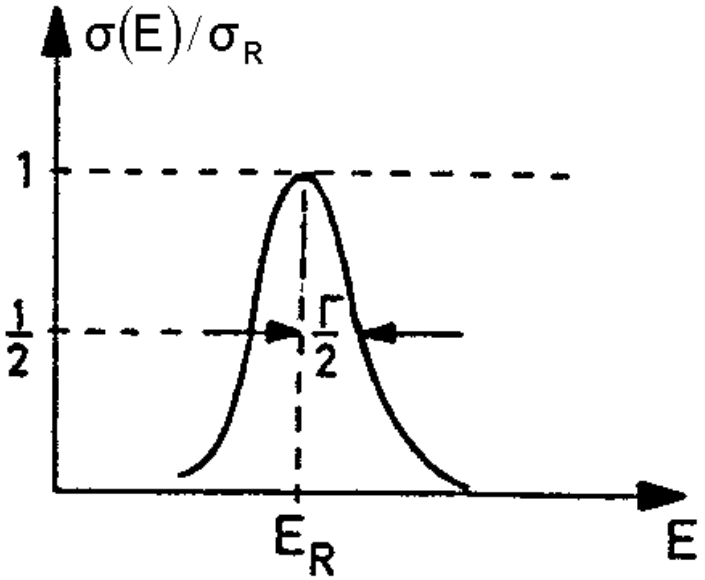
Electronic Resonances

- Features
  - Definite quantum numbers
  - Siegert energy

$$E_{\mathrm{Res}} = E_{\mathrm{R}} - \mathrm{i}\,\Gamma / 2$$



- Calculation
  - Decay electron is in the continuum
    - Not in Hilbert space
    - *Ab initio* methods fail
  - Many-body effects

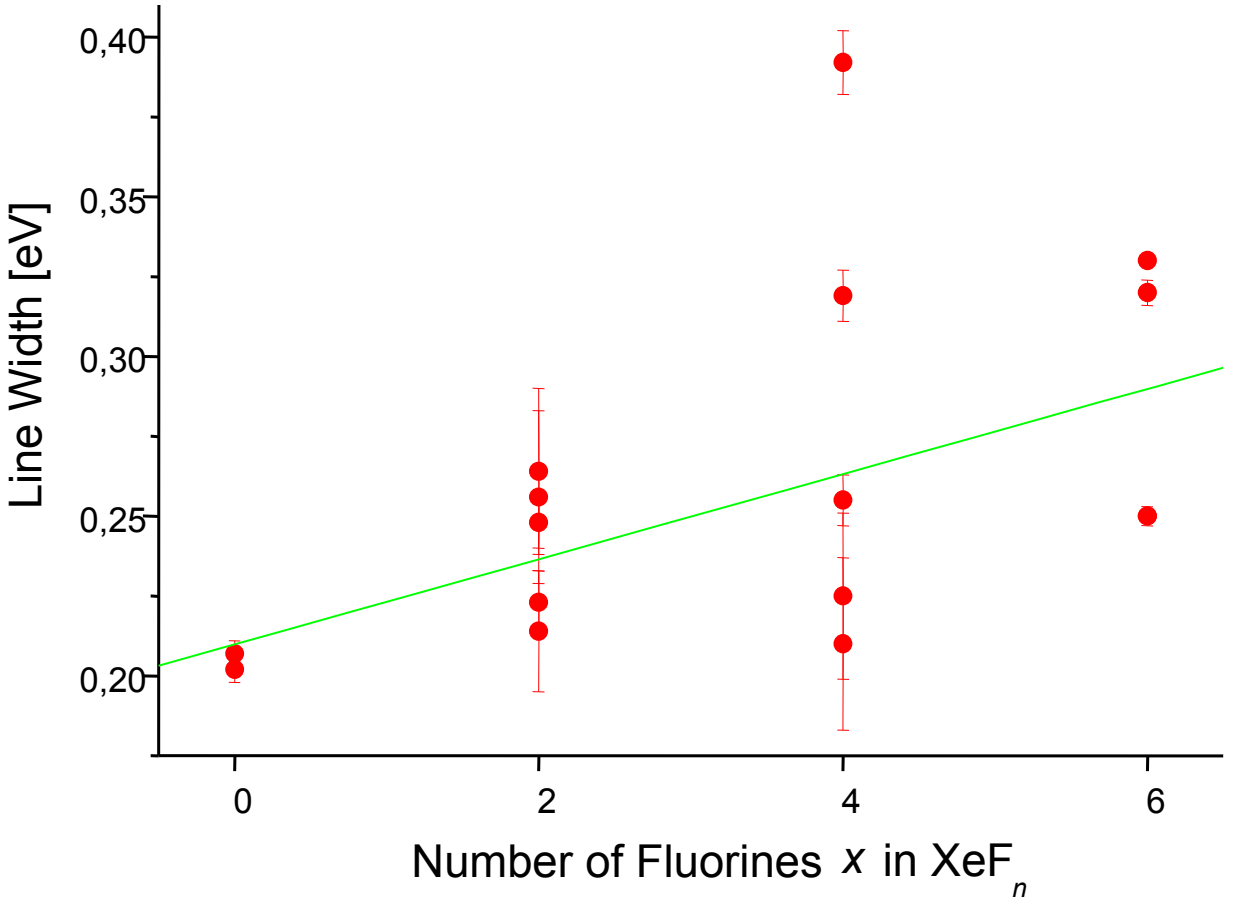


Electronic Decay in Clusters

- Inner valence ionised weakly bound clusters.
  - Ne_n, NeAr, $(HF)_n$, …
  - New electronic decay processes.
  - Very fast (femtoseconds).
  - Electronic decay is induced by neighbouring atoms/molecules.
- In this work the electronic decay in molecules is examined.

Width of the Xenon 4*d* Core Lines in the Xenon Fluorides

- Line width of the Xe 4*d* core lines increases with the number of fluorine atoms.
- Ligands seem to influence the width.
- J. Am. Chem. Soc. **113** 9125 (1991)



The Hartree-Fock Method

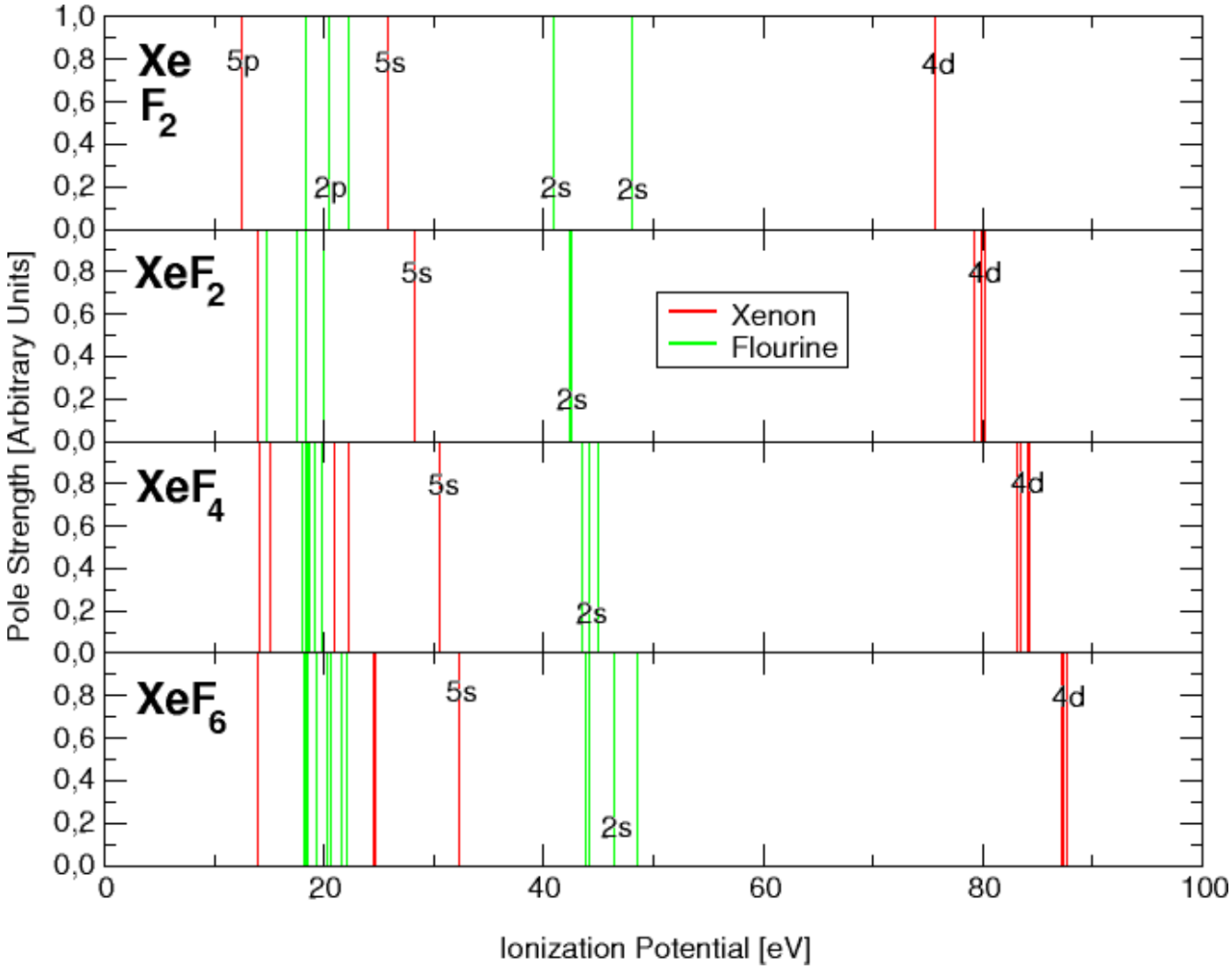
- The Hamiltonian for a molecule depends on the nuclear and electronic coordinates.
  - Nuclei are fixed (Born-Oppenheimer approximation).
  - The mutual repulsion of the electrons leads to correlated movement.
- Hartree-Fock describes one electron in the field of fixed nuclei and fixed other electrons.
  - One-particle picture.
  - Ground state at minimum energy (Ritz variation principle).
  - Ionisation energy is given by the negative of the Hartree-Fock orbitals (Koopmans´ theorem).

Relativistic Effects in XeF_n

- Relativistic effects occur in heavy atoms $\propto Z^2$.
  - Radial contraction of the *s*, *p* shells and energetic stabilisation.
  - Spin-orbit splitting.
  - Radial expansion and the energetic destabilisation of the *d*, *f* shells.
- A rule of thumb to correct for these effects.
  - Numerical Hartree-Fock and Dirac-Fock calculation for xenon.
  - Comparison of the orbital energies yields the relativistic shift. Spin-orbit coupling is not considered.

Hartree-Fock Ionisation Potentials

- Koopmans´ theorem.
- Ligand field removes degeneracies.
- Charge transfer to fluorines, potentials shift to higher energy.



Green´s Function Methods 1

- The one-particle Green´s function (GF) is well suited to calculate ionisation potentials (IP).
  - IP are pole positions of the GF.
  - There is a perturbation expansion of the GF that can be evaluated using Goldstone diagrams (time-ordered Feynman graphs) to arbitrary order.
- Algebraic Diagrammatic Construction (ADC) is a scheme to transform the search for the poles of the GF into a Hermitian eigenvalue problem.
  - Geometric series expansion reproduces analytic structure of the diagrammatic equations.

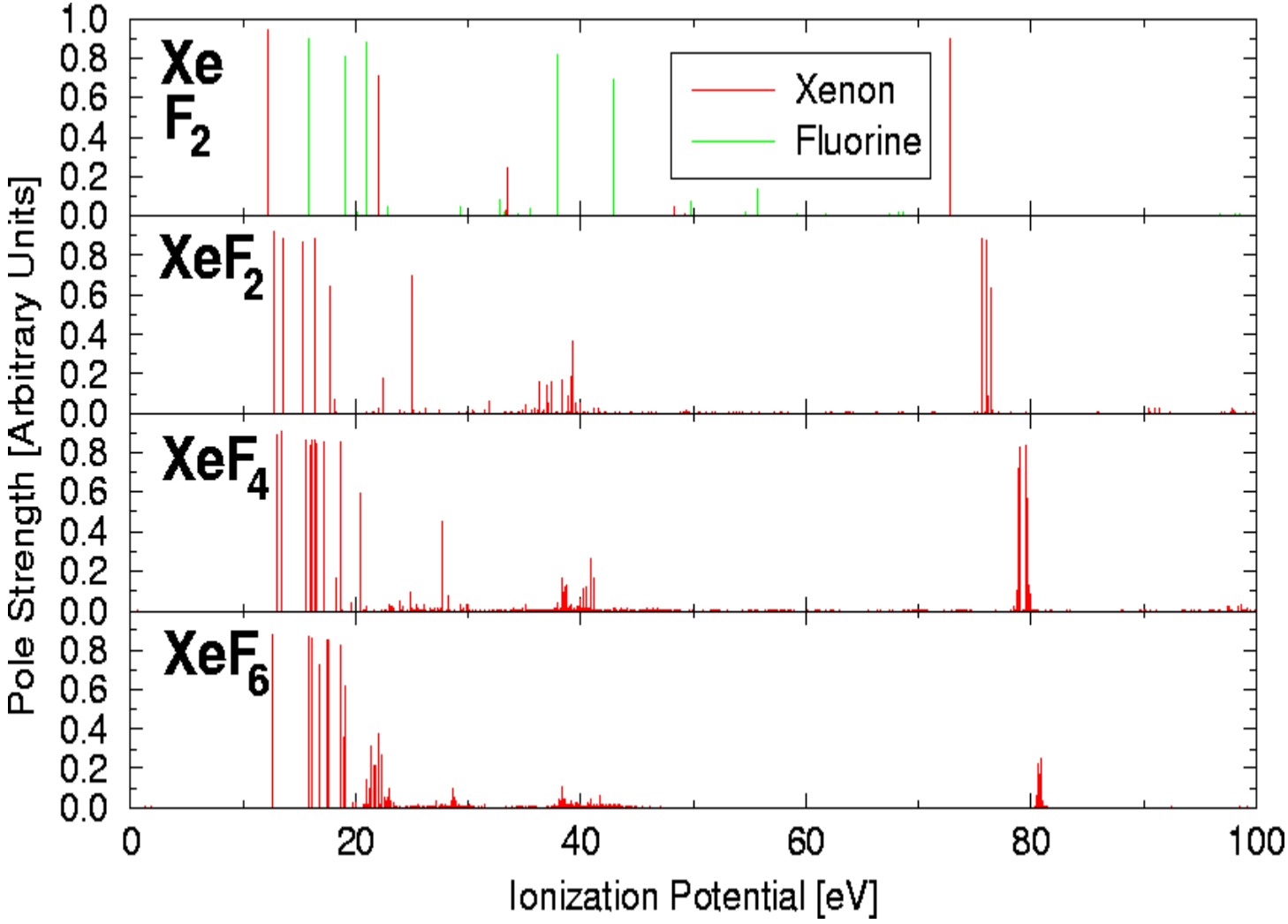
Green´s Function Methods 2

- The order in the geometric series expansion defines the order of ADC and is identical with the order of the respective diagrams.
- Summation of infinitely many diagrams of certain classes by the sum formula of the geometric series (and the Dyson equation).
- Eigenvalues of the ADC matrix are the poles of the GF.

- The particle-particle propagator derived from the two-particle GF yields similar results for double IP.

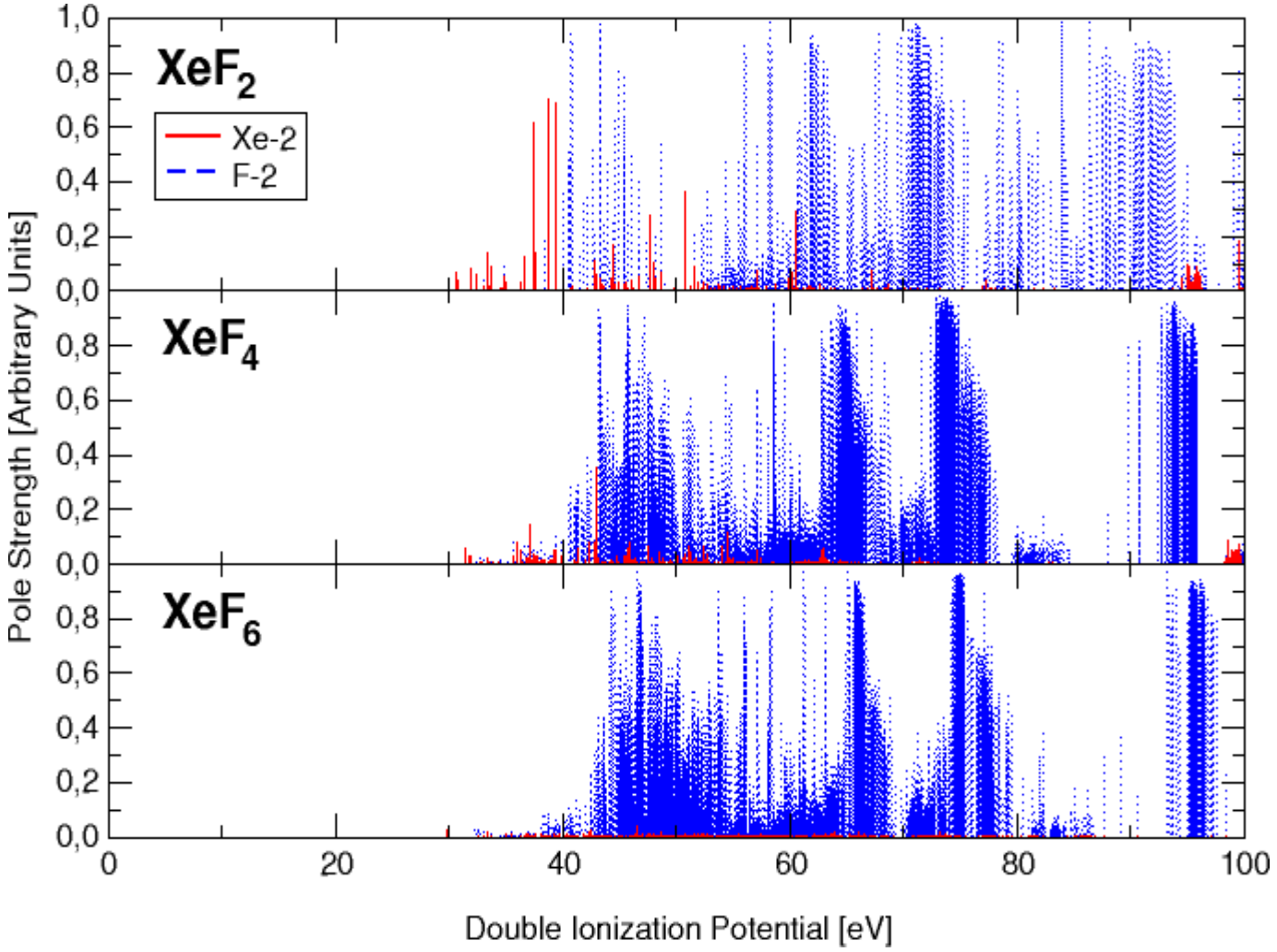
ADC(3) Ionisation Potentials

- Improvement of Hartree-Fock results by correlated electrons.
- Breakdown
- Lorentz profiles.
- Less pronounced energy shift.



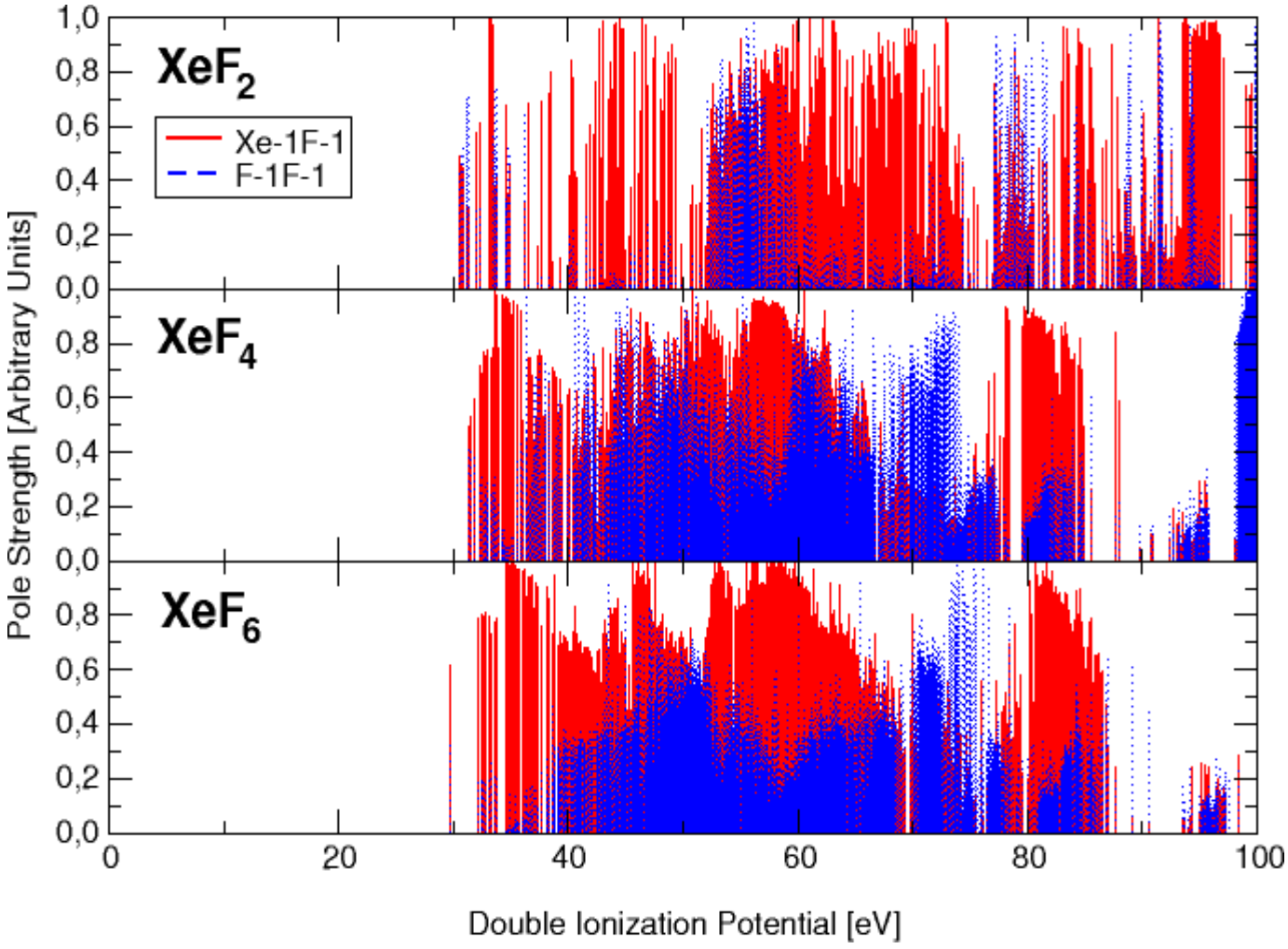
One-site Final States

- Charge transferred to F´s.
- One-site decay into Xe^{-2} holes suppressed.
- F 2*s* holes decay predominantly into two-site states.



Two-site Final States

- First double ionisation potentials are nearly the same.
- $F^{-1}F^{-1}$ states in XeF_2 less important, in XeF_4 strongest.
- $Xe^{-1}F^{-1}$ states are always the dominant states.



Decay Width and Population Analysis

- Decay width depends on the matrix element $V_{\vec{k}\,\mathrm{ch}\,n}$.
- Connection to population analysis is given by the expansion

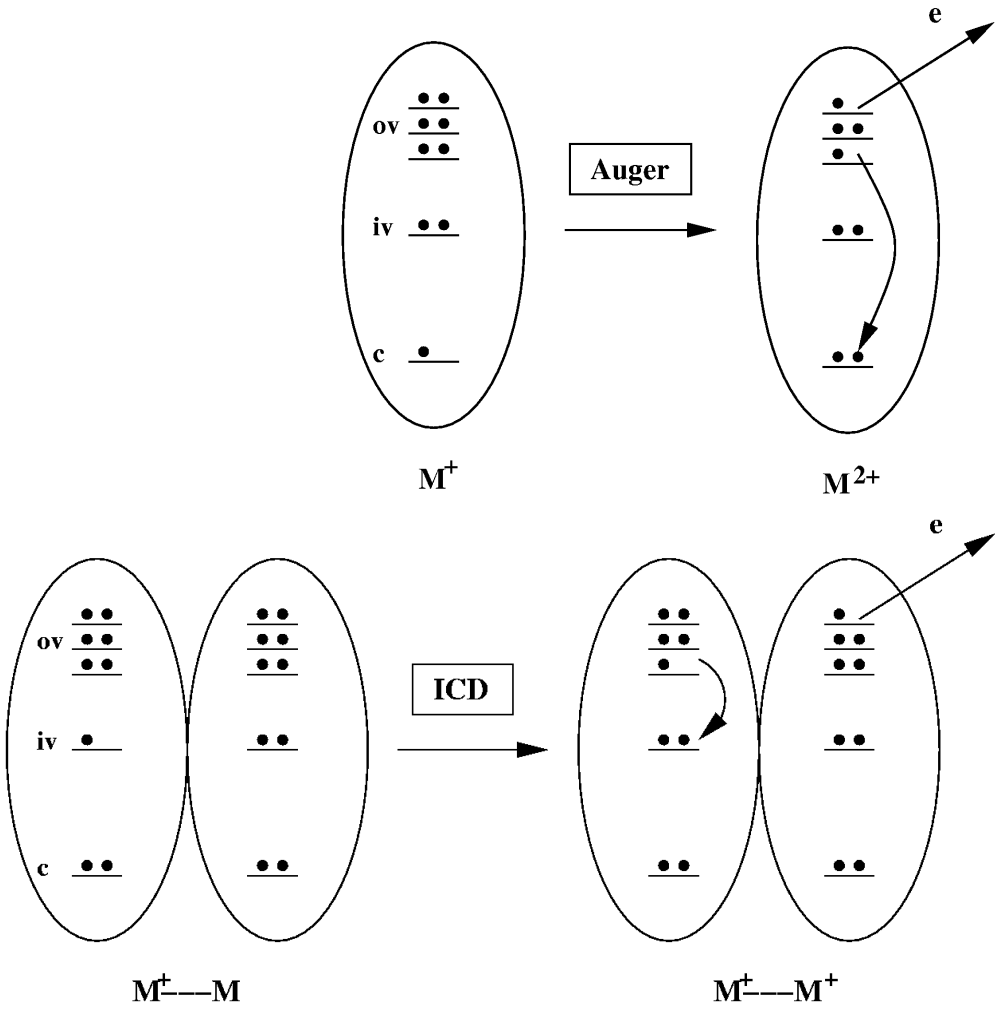
$$|V_{\vec{k}\,\mathrm{ch}\,n}|^2 = \sum_{ij,lm} (X_n^+)_{ij} (X_n)_{lm} V^*_{\vec{k}\,\mathrm{ch}\,ij} V_{\vec{k}\,\mathrm{ch}\,lm} \approx \sum_{ij} (X_n^+)_{ij} (X_n)_{ij} |V_{\vec{k}\,\mathrm{ch}\,ij}|^2.$$

- The total decay width of the Xe 4*d* ionised states decomposes into the partial decay widths of inter- and intramolecular processes.
- One type of matrix elements (e.g. ICD) varies less pronounced for several dicationic configurations.

$$|V_{\vec{k}\,\mathrm{ch}\,[n]}|^2 = |V_{\mathrm{ICD}}|^2 \sum_{[pq]} Q_{pq,n}$$

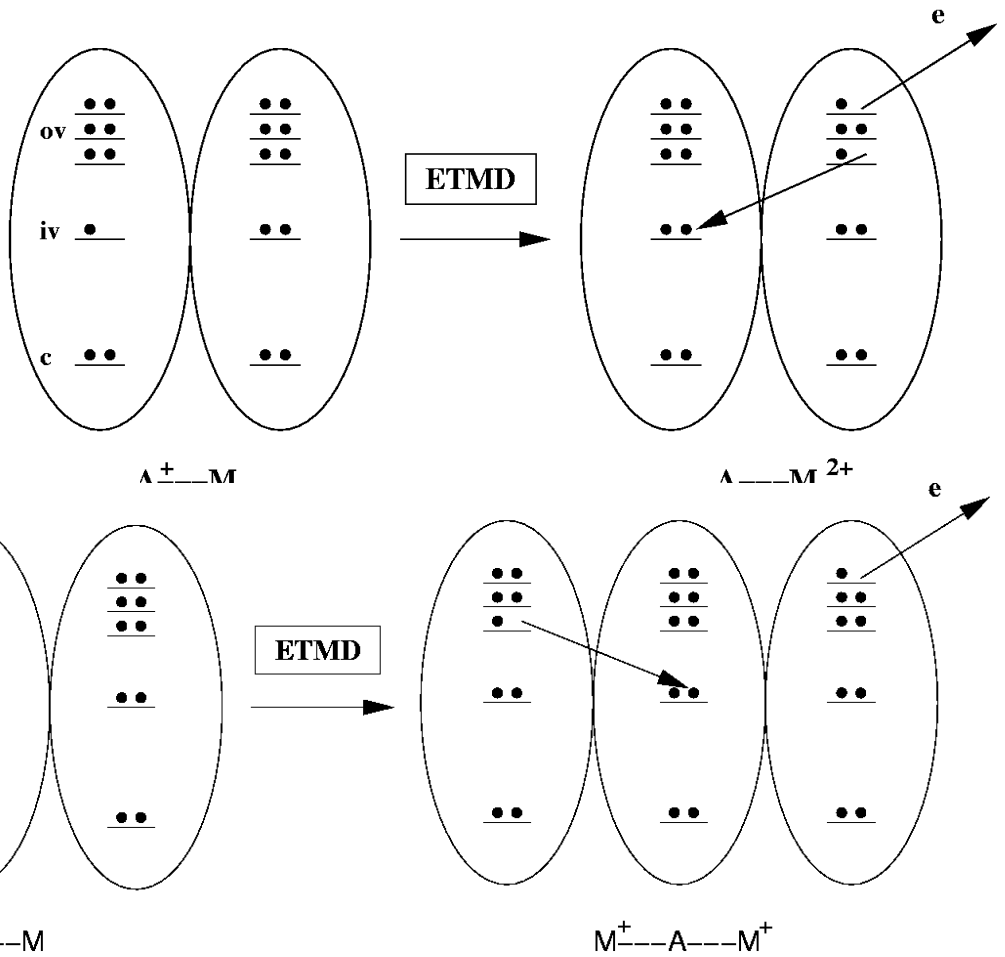
Auger Decay and ICD

- Auger decay.
  - Atoms or molecules.
  - Core ionised.
- Interatomic/intermolecular Coulombic decay.
  - Weakly bound clusters.
  - Inner valence ionised.
  - Monomer cannot decay electronically.
  - Phys. Rev. Lett. **79** 4778 (1997)



Electron Transfer Mediated Decay

- Two ETMD processes.
  - Weakly bound hetero-clusters (NeAr).
  - Two-atomic/ three-atomic
  - Less important than ICD in weakly bound clusters.
- Three-atomic ETMD has not been studied so far.



Self and Foreign Imaging

- Auger decay in core ionised molecules.
- Self imaging in SiH_4 (Si 2*p* holes).
  - Final dicationic valence states have the atomic character of silicon p^{-2}, $p^{-1}s^{-1}$, s^{-2} valence holes.
- Foreign imaging in SiF_4 (Si 2*p* holes).
  - Final valence states have atomic character of neighbouring atoms.
  - Eight distinct groups of final dicationic valence states on xenon, one and two fluorine atoms.
  - Phys. Rev. Lett. **71** 649 (1993)
- Two extreme positions.

Wigner-Weisskopf Theory 1

- Time-dependent perturbation theory for decaying states (Fermi's golden rule).
- Take a single excited determinant as reference Φ_i^a.
- Siegert energy

$$E_R = \langle \Phi_I | \hat{H} | \Phi_I \rangle + \Delta_I - i\,\Gamma_I / 2$$

- Decay width

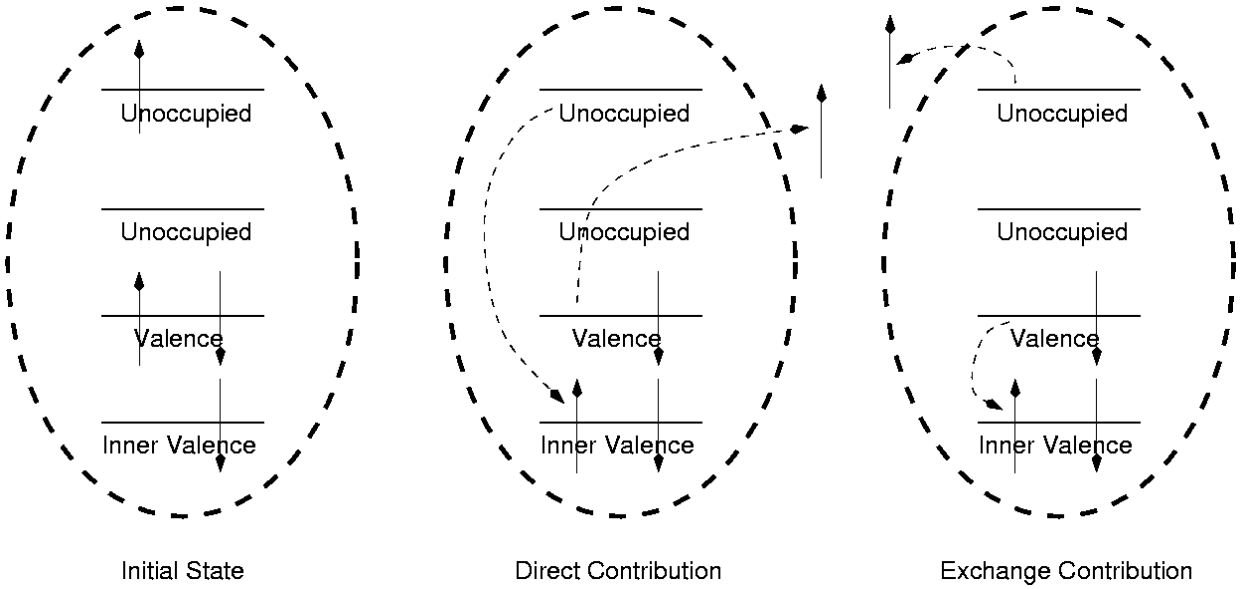
$$\Gamma_I = 2\pi \sum_{F \neq I} \left| \langle \Phi_F | \hat{H} | \Phi_I \rangle \right|^2 \delta \left(\langle \Phi_F | \hat{H} | \Phi_F \rangle - \langle \Phi_I | \hat{H} | \Phi_I \rangle \right)$$

Wigner-Weisskopf Theory 2

- Transition matrix element $\langle \Phi_F | \hat{H} | \Phi_I \rangle$.
  - Initial configuration Φ_i^a couples to singly, doubly and triply excited determinants (Slater-Condon rules).

- Decay into singly excited final states.

$$\left\langle \Phi_j^{\bar{k}} \middle| \hat{H} \middle| \Phi_i^a \right\rangle = V_{\bar{k}i[ja]}$$



Wigner-Weisskopf Theory 3

- Decay into doubly excited final states
  - Initial inner valence vacancy is unchanged.

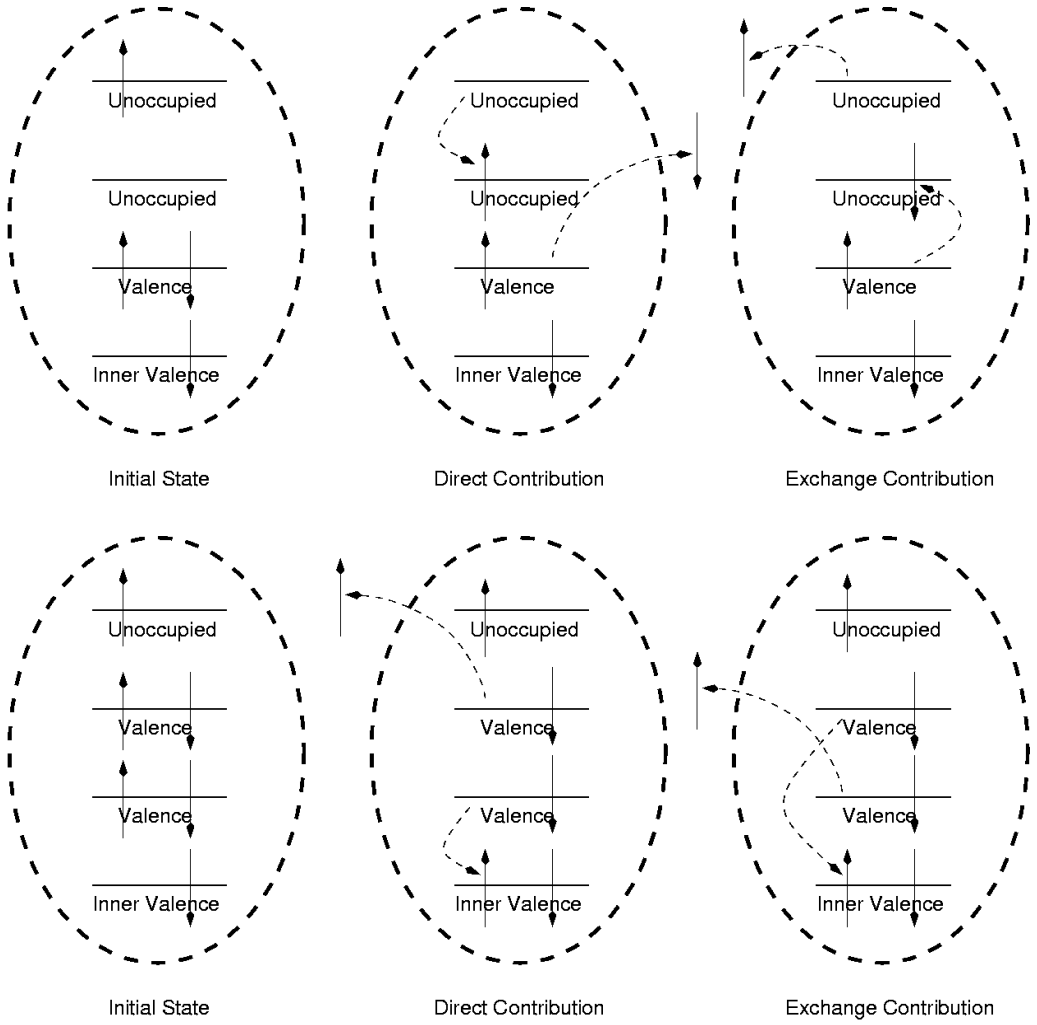
$$\left\langle \Phi \begin{matrix} b\bar{k} \\ ji \end{matrix} \middle| \hat{H} \middle| \Phi \begin{matrix} a \\ i \end{matrix} \right\rangle = V_{b\bar{k}[aj]}$$

  - Initially excited electron is unchanged.

$$\left\langle \Phi \begin{matrix} \bar{k}a \\ jl \end{matrix} \middle| \hat{H} \middle| \Phi \begin{matrix} a \\ i \end{matrix} \right\rangle = V_{i\bar{k}[jl]}$$

  - Initially excited electron and initial vacancy are unchanged.

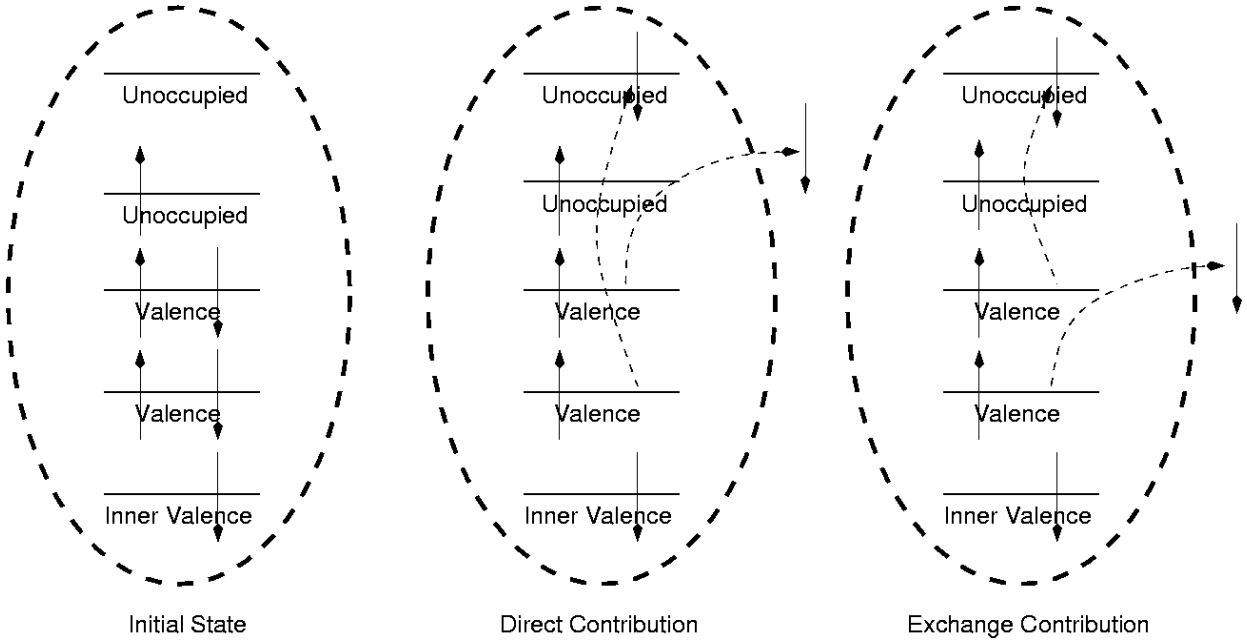
$$\left\langle \Phi \begin{matrix} \bar{k}a \\ ji \end{matrix} \middle| \hat{H} \middle| \Phi \begin{matrix} a \\ i \end{matrix} \right\rangle = V_{\bar{k}a[ja]} - V_{\bar{k}i[ji]}$$



Wigner-Weisskopf Theory 4

- Decay into triply excited final states
  - Initial vacancy and electron are unchanged.

$$\left\langle \Phi \begin{matrix} b\bar{k}a \\ jli \end{matrix} \middle| \hat{H} \middle| \Phi \begin{matrix} a \\ i \end{matrix} \right\rangle = V_{b\bar{k}[jl]}$$



Wigner-Weisskopf Theory 5

- Frequently states are not very good described by a single reference (breakdown in the inner valence).
- Transition matrix elements involve continuum electrons.
  - Wave function of decay electron are not square integrable.
  - Stieltjes-Chebyshev moment theory must be used with finite basis sets.

Complex Absorbing Potentials (CAP)

- System is modified

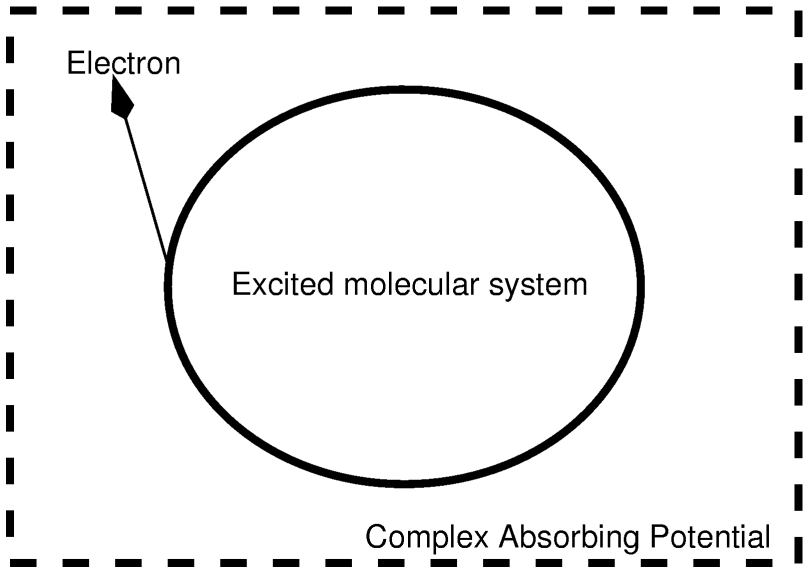
$$\hat{H}(\eta) = \hat{H} - i\eta\,\hat{W}$$

- Complex-symmetric bilinear form

$$(\varphi\,|\psi) := \int \varphi(\vec{x})\,\psi(\vec{x})\,\mathrm{d}^3x$$

- Schrödinger equation

$$\hat{H}(\eta)\,|\psi(\eta)\rangle = E(\eta)\,|\psi(\eta)\rangle$$



- Optimisation problem for finite basis sets in η .

Practical Challenges

- System is described using configuration interaction (CI) $\Rightarrow$ $10^5 \times 10^5$ matrices.
- Many *complex* eigenvalue problems have to be solved for varying η .
- The computation of resonances of the neon dimer took *two* month on *seven* PCs.
- To apply CAPs routinely calculations should be sped up.

Single Reference Perturbation Theory

- CAPs renders the decay problem time-independent. Hence non-degenerate time-independent perturbation theory with a CAP can be used.
- Epstein-Nesbet partition $\hat{H}(\eta) = \hat{H}_0(\eta) + \hat{H}_1(\eta)$.
- Perturbation theory with a single reference

$$E_n = (\Phi_n^{(0)} | \hat{H}_0(\eta) | \Phi_n^{(0)}) + \lambda^2 \sum_{i \neq n} \frac{(\Phi_n^{(0)} | \hat{H}_1(\eta) | \Phi_i^{(0)})^2}{E_n^{(0)} - E_i^{(0)}} + O(\lambda^3).$$

- Analogue to Wigner-Weisskopf theory.

Multireference Perturbation Theory 1

- Resonances in the inner valence can be approximated by particle-hole configurations, a subspace of these serving as references.
- Projection operators

$$\hat{P} = \sum_{j=1}^{n} |\Phi_j)(\Phi_j|, \quad \hat{Q} = \hat{1} - \hat{P}$$

- Application to the CAP-Hamilton operator

$$H(\eta) = \begin{pmatrix} PH(\eta)P & PH(\eta)Q \\ QH(\eta)P & QH(\eta)Q \end{pmatrix}$$

Multireference Perturbation Theory 2

- Diagonalize $PH(\eta)P, \quad \Phi_j \rightarrow \breve{\Phi}_j, \quad \hat{P} \rightarrow \breve{\hat{P}}$
- Problem to solve

$$\hat{H}_{\text{eff}}(\eta) = \breve{\hat{P}}^T \hat{H}(\eta) \breve{\hat{P}} + \breve{\hat{P}}^T \hat{H}(\eta) \hat{Q} \cdot \hat{G}(\eta) \cdot \hat{Q} \hat{H}(\eta) \breve{\hat{P}}$$

$$E_j(\eta) = (\breve{\Phi}_j \mid \hat{H}_{\text{eff}}(\eta) \mid \breve{\Phi}_j), \qquad \hat{G}(\eta) := [E_j(\eta) \cdot \hat{1} - \hat{Q} \hat{H}(\eta) \hat{Q}]^{-1}$$

- Second partition for perturbation theory

$$H^{(\lambda)}(\eta) = \begin{pmatrix} * & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & * \end{pmatrix} + \lambda \cdot \begin{pmatrix} 0 & 0 & * \\ 0 & \ddots & * \\ * & * & 0 \end{pmatrix}$$

Multireference Perturbation Theory 3

- Expansion

$$\breve{\Phi}_j = \breve{\Phi}_j^{(0)} + \lambda \cdot \breve{\Phi}_j^{(1)} + \ldots, \quad E_j = E_j^{(0)} + \lambda \cdot E_j^{(1)} + \ldots, \quad \hat{G} = \hat{G}^{(0)} + \lambda \cdot \hat{G}^{(1)} + \ldots$$

- Complex energies up to second order

$$E_j^{(0)} = (\breve{\Phi}_j^{(0)} | \breve{\hat{P}}^T \hat{H}(\eta) \breve{\hat{P}} | \breve{\Phi}_j^{(0)}), \qquad E_j^{(1)} = 0$$

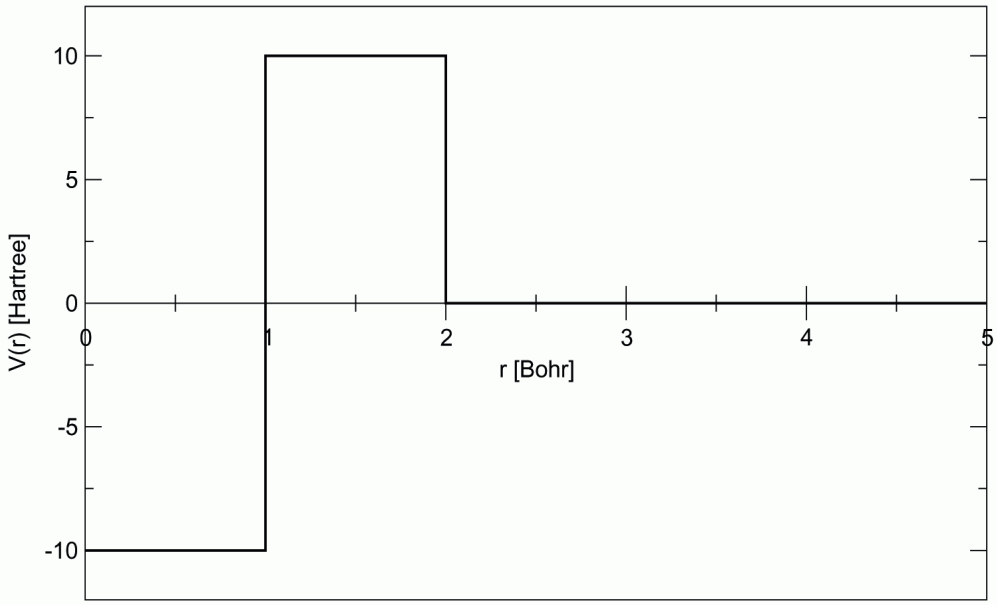
$$E_j^{(2)} = (\breve{\Phi}_j^{(0)} | \breve{\hat{P}}^T \hat{H}(\eta) \hat{Q} \cdot \hat{G}^{(0)} \cdot \hat{Q} \hat{H}(\eta) \breve{\hat{P}} | \breve{\Phi}_j^{(0)})$$

- Inserting the definition of the projection operators

$$E_j = E_j^{(0)} + \lambda^2 \sum_{k=n+1}^{N} \frac{(\breve{\Phi}_j^{(0)} | \hat{H}(\eta) | \Phi_k)^2}{E_j^{(0)}(\eta) - (QH(\eta)Q)_{k-n\,k-n}} + \mathrm{O}(\lambda^3)$$

Model Problem 1

- Spherical symmetric Potential

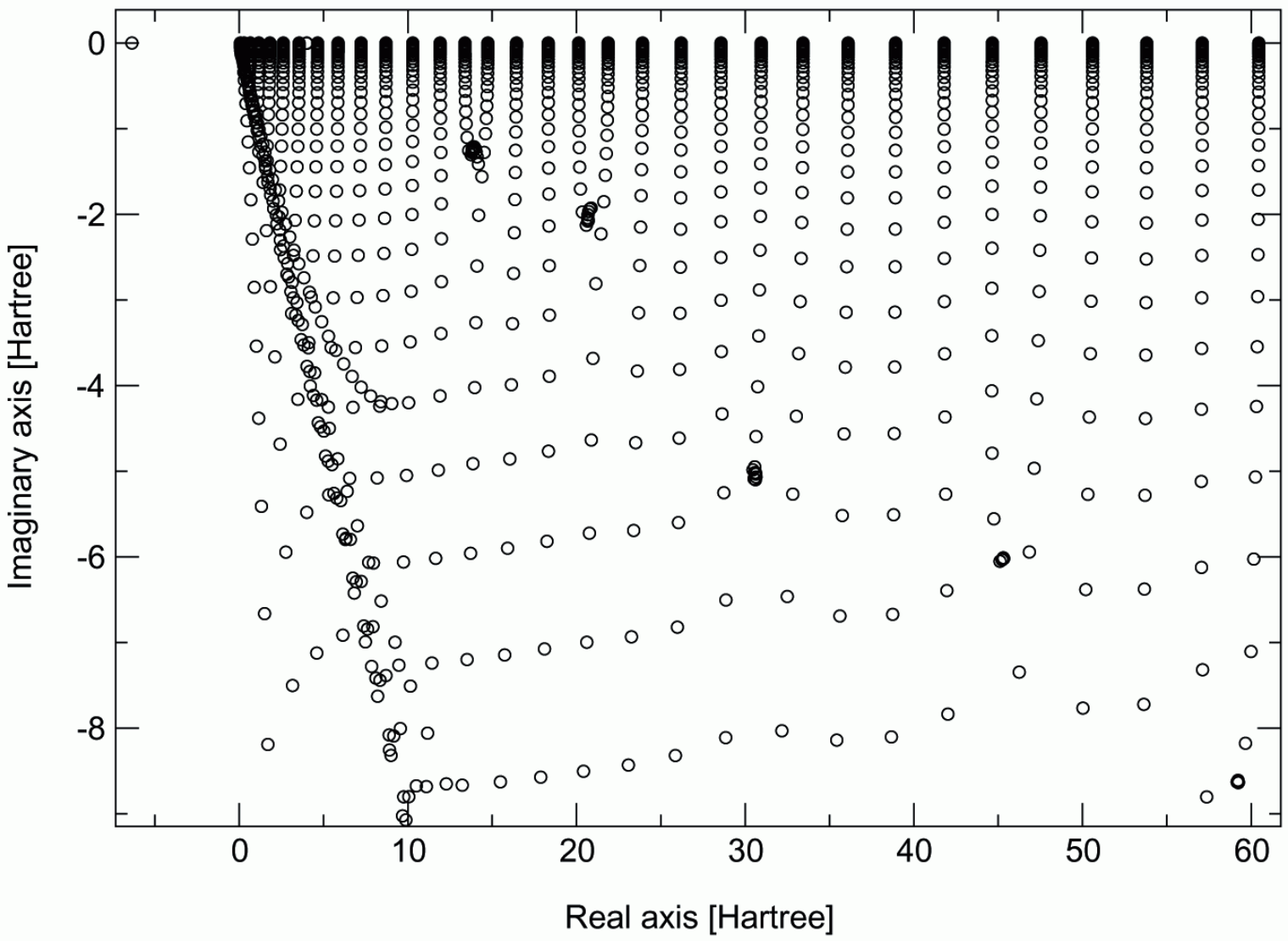


- Analytic solution
  - Bound state
    - 6.353803650 Hartree
  - First resonance

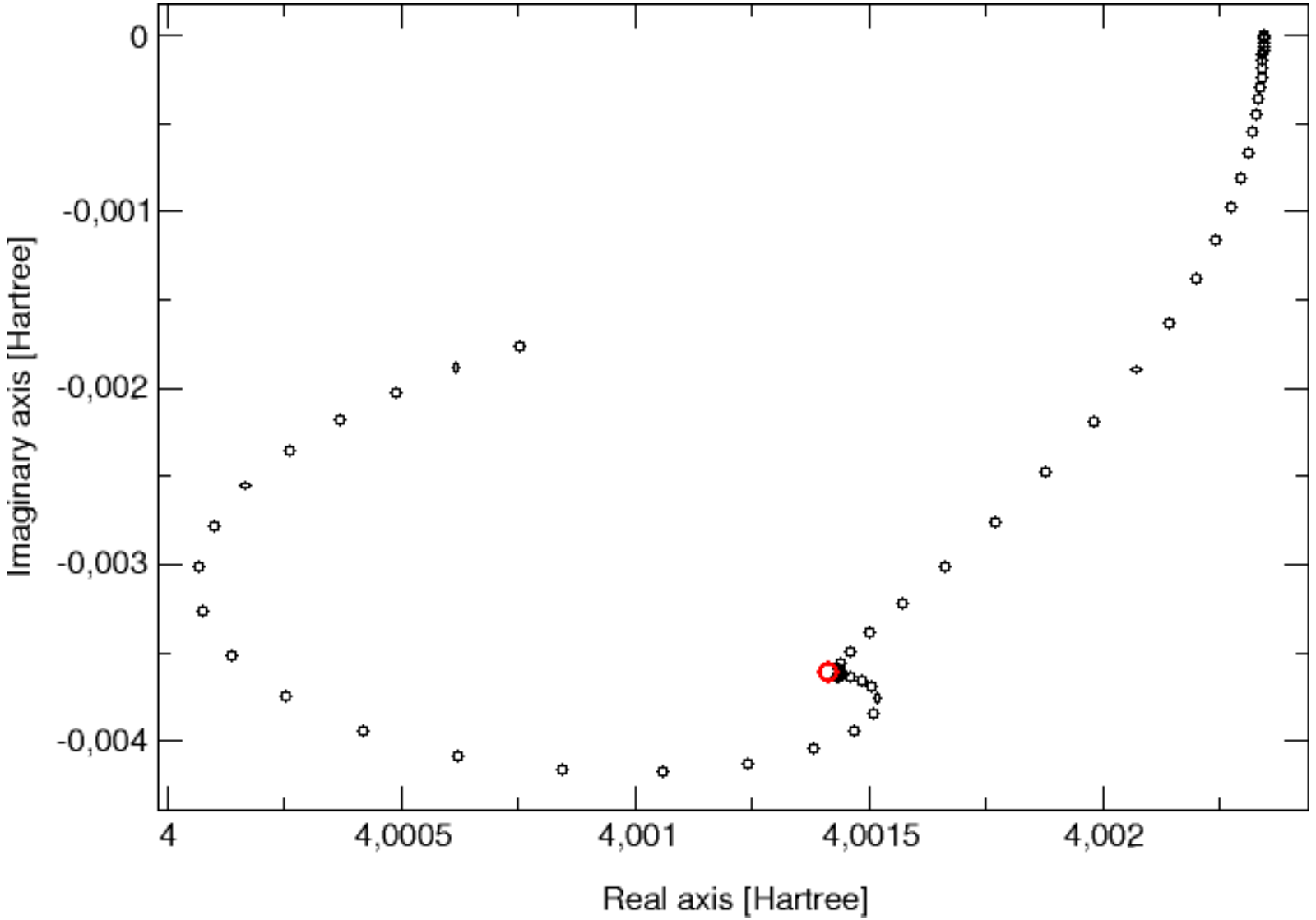
$$4.001414397 - 0.003616371 \cdot i \text{ Hartree}$$

Model Problem 2

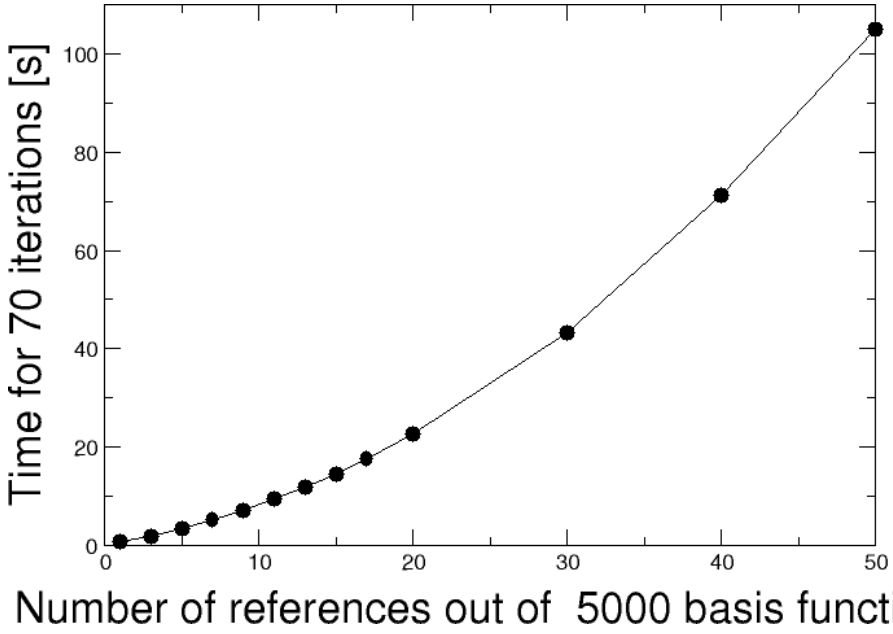
- Bound state
- Stabilisation point of the trajectory at resonances.
- Indifferent states.

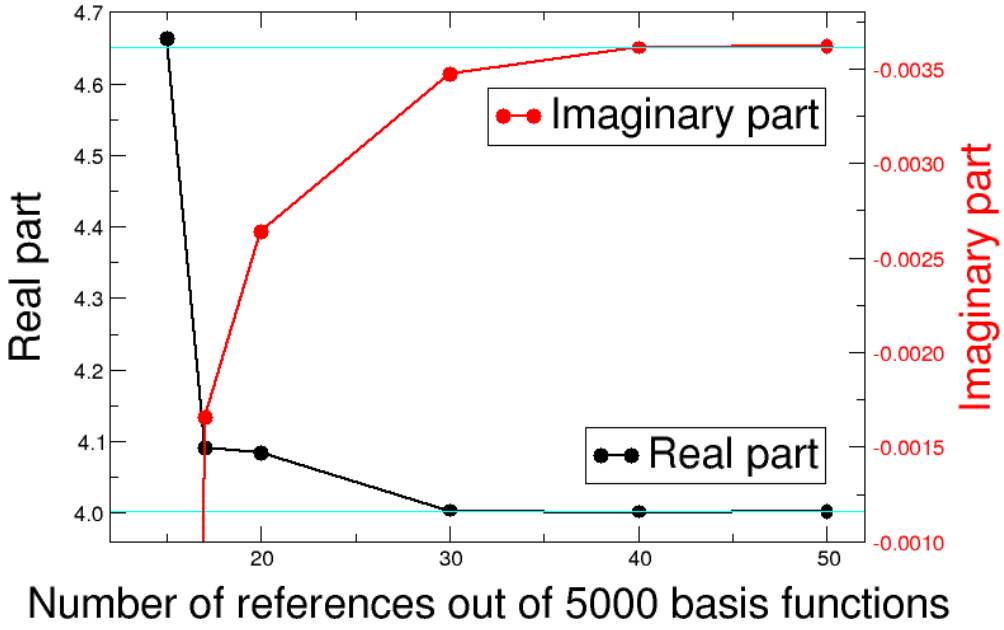


Model Problem 3



Performance of the Theory





- 20 references yield an accuracy of 5% after 21s time for a 5000×5000 matrix.
- Time for a full diagonalization: 20 days.

Conclusion 1

- The xenon fluorides show breakdown effects (Xe 5*s*, F 2*s*) which become stronger for an increasing number of fluorine atoms.
- Many dicationic states are located on two sites.
  - Two-site decay channels are accessible for the decay of the Xe 4*d* lines.
  - This suggests new decay processes: *intra*molecular *inter*atomic Coulombic decay (IICD) and *intra*molecular electron transfer mediated decay (IETMD).
  - This may explain the increase of the width of the Xe 4*d* lines.

Conclusion 2

- Resonances can be described with *ab initio* methods by enclosing the system by a CAP.
- Calculations are very expensive. Speed up with multireference perturbation theory.
- Perturbation theory is very fast and gives good results for the model problem.
- DIESEL MRCI shall be used to calculate a resonance of the neon dimer with this theory.