ICD - The Decay Widths II

Beyond Wigner-Weisskopf

Přemysl Kolorenč

Institute of Theoretical Physics, Charles University in Prague

ICD Summer School

Bad Honnef
September 1^{st} – 5^{th}

Decay widths – Beyond 1^{st} order

- Complex absorbing potential
  - *tame the divergent Siegert state* to fit into the L^2 space

- Fano-ADC
  - *discrete state revisited* – time independent, non-perturbative approach

Outline

1. Complex absorbing potential
2. Fano-Feshbach theory
3. ADC – Algebraic Diagrammatic Construction
4. ADC & Fano partitioning
5. Stieltejs-Chebychev moment theory
6. Comparison with CAP methods
7. Appendix – partial decay widths, computational details

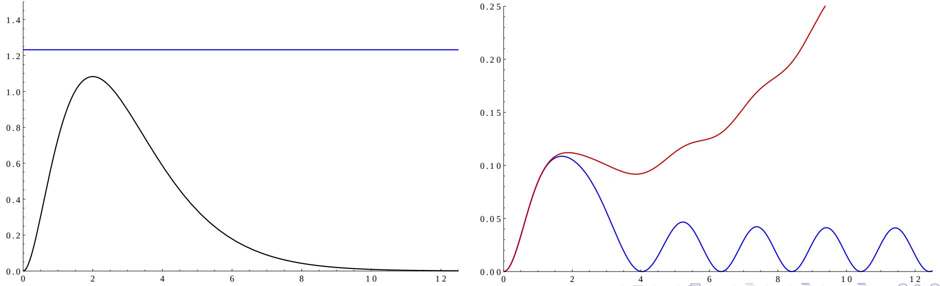
CAP – Example

$$V(r) = 2r^2 e^{-r} \qquad E_{\text{res}} = 1.2318 - \frac{i}{2} 0.3299$$

- Solution of SE at real and complex energy

$$(H - E)|\Psi_E\rangle = 0 \qquad E \in \mathbb{R}/\mathbb{C}$$

- Introduce CAP $W = -i\eta(r - r_{\mathrm{C}})^2$
  - exponential damping on a length scale $1/\sqrt[4]{\eta}$



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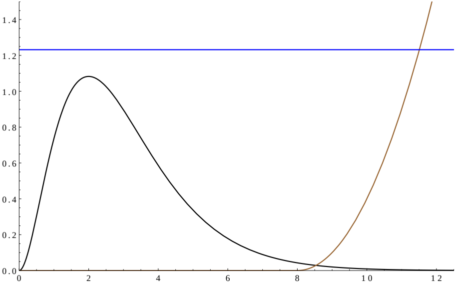
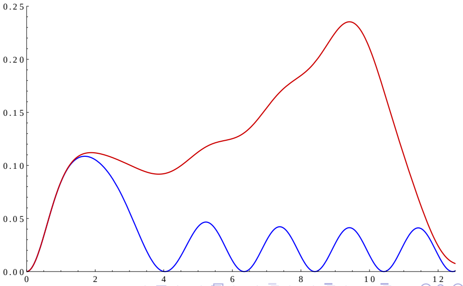


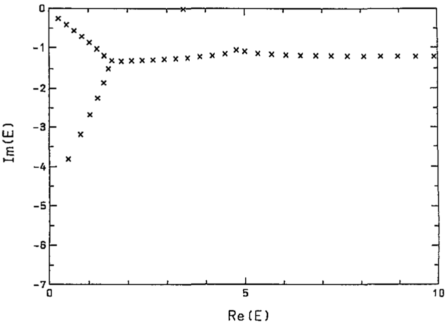


CAP – Eigenvalues of $\hat{H}(\eta)$

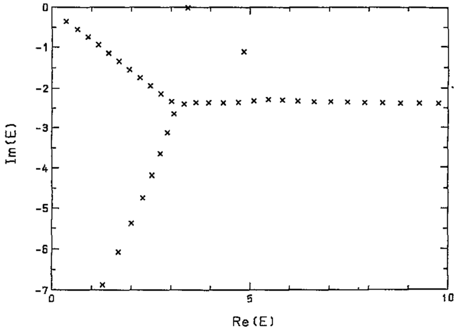
$$V(r) = 7.5r^2 e^{-r} + i\eta(r - r_c)^2$$

$E_{\mathrm{res1}} = 3.426 - 0.013i$ $E_{\mathrm{res2}} = 4.835 - 1.117i$

$\eta = 7.6 \times 10^{-3}$

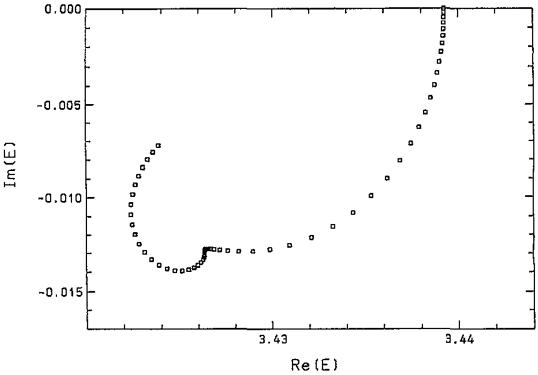


$\eta = 1.5 \times 10^{-2}$



Riss and Meyer, J. Phys. B **26**, 4503 (1993)

η-trajectory of the resonance pole



- Best approximation $E(\eta)$ to Siegert energy $E(\eta = 0)$ – minimization of

$$|E(\eta) - E(0)| = \left|\eta \frac{dE(\eta)}{d\eta}\right| + O(\eta^2)$$

- Reflection properties of CAP: Riss and Meyer, J. Chem. Phys. **105**, 1409 (1996)

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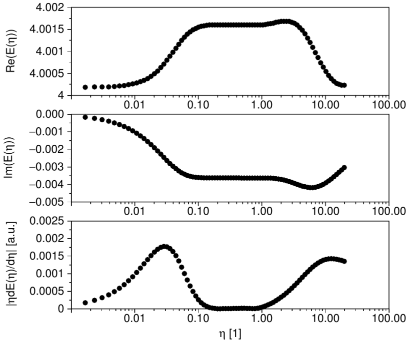
R. Santra, L.S. Cederbaum / Physics Reports 368 (2002) 1–117



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Complex symmetric eigenvalue problem

- Symmetric bilinear form instead of usual scalar product

$$(\phi|\psi) \equiv \int \phi(\mathbf{x})\psi(\mathbf{x})\, d^3x$$

- Possible incompleteness of the spectrum of nonhermitian operator

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

  - occurs only for **isolated points** of η – not a real issue for numerical calculations

- Diagonalization techniques and search for the stabilization points
  - complex Lanczos algorithm
  - parallel filter diagonalization

Santra and Cederbaum, Phys. Rep. **368**, 1 (2002)

Moiseyev, Non-Hermitian Quantum Mechanics, Cambridge, 2011

CAP in *ab initio* many-body methods

- Simple choice $W(\mathbf{x}, \mathbf{c}, n) = \sum_{i=1}^{3} (|x_i| - c_i)^n, \quad |x_i| > c_i$
  - **efficient matrix elements evaluation** in Guassian basis sets
  - minimum reflection considerations irrelevant due to **low basis quality**
  - elimination of $|\Phi_0^N\rangle$ perturbation: $(\varphi_p|W|\varphi_q) = 0$ for p or q occupied
- CAP/CI

$W =$

	1h	**2h1p**
1h	0	0
2h1p	0	$W_{aa'}\delta_{ii'}\delta_{jj'}$

- CAP/ADC(3)
  - Santra and Cederbaum, Phys. Rep. **368** (2002)
  - Vaval and Cederbaum, J. Chem. Phys. **126**, 164110 (2007)
- CAP/EOM-CC
  - Ghosh, Pal and Vaval, J. Chem. Phys. **139**, 064112 (2013); Mol. Phys. **112**, 669 (2014)

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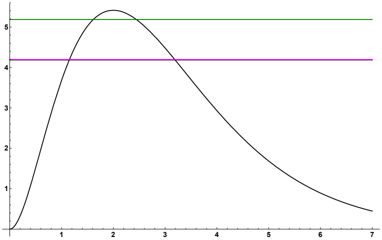
Discrete state in continuum – example

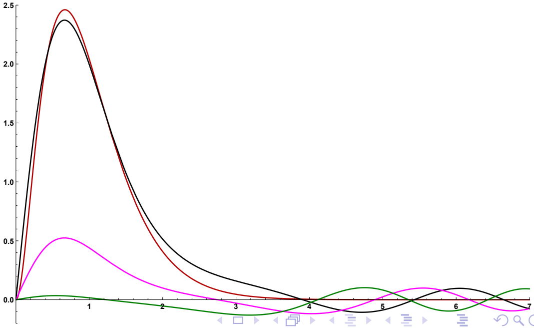
- Potential scattering

$$V(r) = 10r^2 e^{-r} \qquad E_{\mathrm{res}} = 4.1856 - \frac{i}{2}0.0045$$

- Discrete state in continuum character of exact wave function ($E \in \mathbb{R}$)

$$|\Psi_E\rangle = a(E)|\phi_d\rangle + \int b(E,\epsilon)|\chi_\epsilon\rangle \, d\epsilon$$





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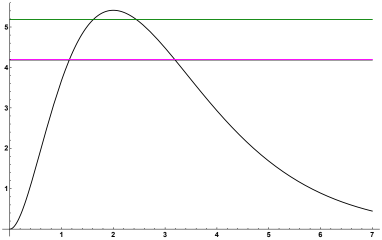

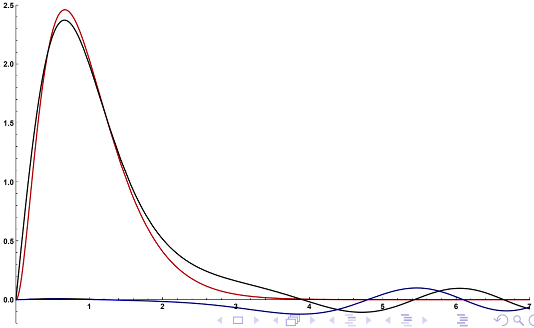

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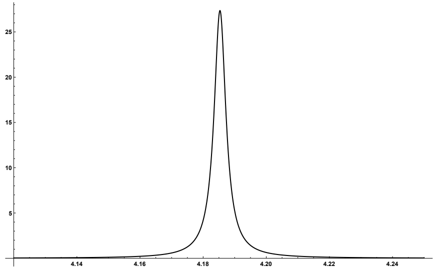
$a^2(E)$:



$$a^2(E) \propto \frac{\Gamma(E)}{(E - E_d - \Delta(E))^2 + \Gamma^2(E)/4}$$

Projection operator approach

- Separation of the Hilbert space – resonance and background continuum

$$\mathcal{H} = \mathcal{Q} \oplus \mathcal{P}$$

$$Q = |\phi_d\rangle\langle\phi_d| \qquad P = \int |\chi_\epsilon\rangle\langle\chi_\epsilon|\, d\epsilon \qquad PQ = 0$$

- Key requirement – $\mathcal{P}$ asymptotically complete

$$\lim_{r\to\infty} P\Psi_E(r) = \lim_{r\to\infty} \Psi_E(r) \Longleftarrow \phi_d(r) \in L^2$$

- Hamiltonian

$$H = H_{QQ} + H_{PP} + H_{QP} + H_{PQ}, \qquad H_{QP} = QHP, \ \ldots$$

- Schrödinger equation

$$(E - H)|\Psi_E\rangle = 0 \quad (E \in \mathbb{R})$$

Feshbach, Ann. Phys. **19**, 287 (1962); Domcke, Phys. Rep. **208**, 97 (1991)

Čížek, Ph.D. thesis, Charles University in Prague (1999)

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Solution in the $\mathcal{Q}$-space

- Projected Schrödinger equation

$$(E - H_{PP})P|\Psi_E\rangle = H_{PQ}Q|\Psi_E\rangle \quad (1)$$
$$(E - H_{QQ})Q|\Psi_E\rangle = H_{QP}P|\Psi_E\rangle \quad (2)$$

- (1) together with $(E - H_{PP})|\chi_E\rangle = 0$ gives

$$P|\Psi_E\rangle = |\chi_E\rangle + (E - H_{PP} + i\eta)^{-1}H_{PQ}Q|\Psi_E\rangle \quad (3)$$

- (3) + (2) yields equation for the Q-projection of $|\Psi_E\rangle$

$$(E - H_{QQ})Q|\Psi_E\rangle = H_{QP}|\chi_E\rangle + H_{QP}(E - H_{PP} + i\eta)^{-1}H_{PQ}Q|\Psi_E\rangle \quad (4)$$

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$$Q|\Psi_E\rangle = [E - H_{QQ} - H_{QP}(E - H_{PP} + i\eta)^{-1}H_{PQ}]^{-1}H_{QP}|\chi_E\rangle$$

Solution in the $\mathcal{Q}$-space

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Complex level shift function

$$F(E) \equiv QHP(E - PHP + i\eta)^{-1}PHQ$$

- evaluation of the operator $P(E - PHP + i\eta)^{-1}P =$

$$\iint d\epsilon' d\epsilon |\chi_{\epsilon'}\rangle\langle\chi_{\epsilon'}|(E - PHP + i\eta)^{-1}|\chi_\epsilon\rangle\langle\chi_\epsilon|$$

$$= \iint d\epsilon' d\epsilon |\chi_{\epsilon'}\rangle\langle\chi_{\epsilon'}|\chi_\epsilon\rangle(E - \epsilon + i\eta)^{-1}\langle\chi_\epsilon|$$

$$= \iint d\epsilon' d\epsilon |\chi_{\epsilon'}\rangle(E - \epsilon + i\eta)^{-1}\delta(\epsilon - \epsilon')\langle\chi_\epsilon|$$

- applying the usual $\lim_{\eta\to 0^+} \frac{1}{x+i\eta} = \mathcal{P}\frac{1}{x} - i\pi\delta(x)$

$$= \mathcal{P}_\epsilon \iint d\epsilon' d\epsilon \frac{|\chi_{\epsilon'}\rangle\langle\chi_\epsilon|}{E - \epsilon}\delta(\epsilon - \epsilon') - i\pi \iint d\epsilon' d\epsilon |\chi_{\epsilon'}\rangle\langle\chi_\epsilon|\delta(\epsilon - \epsilon')\delta(E - \epsilon)$$

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Complex level shift function

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- The only nonzero element of $F(E)$ is

$$\langle \phi_d | F(E) | \phi_d \rangle = \mathcal{P} \int d\epsilon \frac{\langle \phi_d | QHP | \chi_\epsilon \rangle \langle \chi_\epsilon | PHQ | \phi_d \rangle}{E - \epsilon} - i\pi \langle \phi_d | QHP | \chi_E \rangle \langle \chi_E | PHQ | \phi_d \rangle$$

- Energy dependent level shift and decay width

$$\langle \phi_d | F(E) | \phi_d \rangle = \Delta(E) - \frac{i}{2} \Gamma(E)$$

$$\Gamma(E) \equiv 2\pi |V_{dE}|^2 \qquad V_{d\epsilon} = \langle \phi_d | H | \chi_\epsilon \rangle$$

$$\Delta(E) \equiv \mathcal{P} \int \frac{|V_{d\epsilon}|^2}{E - \epsilon} d\epsilon = \frac{1}{2\pi} \mathcal{P} \int \frac{\Gamma(\epsilon)}{E - \epsilon} d\epsilon$$

Interpretation as decay width

$$|\Psi_E\rangle = a(E)|\phi_d\rangle + \int b(E,\epsilon)|\chi_\epsilon\rangle \, d\epsilon$$

- $\langle\phi_d|\chi_\epsilon\rangle = 0$ gives

$$Q|\Psi_E\rangle = a(E)|\phi_d\rangle = [E - QHQ - F(E)]^{-1} QHP|\chi_E\rangle$$

- Resonance profile of $a(E)$

$$\langle\phi_d|Q|\Psi_E\rangle = a(E) = \frac{V_{dE}}{E - E_d - \Delta(E) + \frac{i}{2}\Gamma(E)}$$

$$\Longrightarrow \quad |a(E)|^2 = \frac{1}{2\pi} \frac{\Gamma(E)}{(E - E_d - \Delta(E))^2 + \Gamma^2(E)/4}$$

Fano, PRA **124**, 1866 (1961)

Howat, Åberg and Goscinski, J. Phys. B **9**, 1575 (1978)

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Two-potential formula for the T-matrix

$$S_{fi} = \delta_{fi} - 2\pi i \delta(E_f - E_i) T_{fi}$$

- T-matrix

$$T_{fi} = \langle i|V|f\rangle$$

- background scattering and resonance T-matrix

$$T(E', E) = T_{\mathrm{bg}}(E', E) + T_{\mathrm{res}}(E', E) = \langle k'|H_{PP} - K|\chi_\epsilon\rangle + \langle \chi_{\epsilon'}|H_{PQ}|\Psi_E\rangle$$

- resonance term

$$T_{\mathrm{res}}(E', E) = \langle \chi_{E'}|H_{PQ}(E - H_{QQ} - F(E))^{-1} H_{QP}|\chi_E\rangle$$

- **Siegert energy** – poles of the resonance term of T-matrix

$$z_{\mathrm{res}} = E_d + \Delta(z_{\mathrm{res}}) - \frac{i}{2}\Gamma(z_{\mathrm{res}}) = E_{\mathrm{res}} - \frac{i}{2}\Gamma \qquad \approx \mathbf{E_d} - \frac{\mathbf{i}}{\mathbf{2}}\Gamma(\mathbf{E_d})$$

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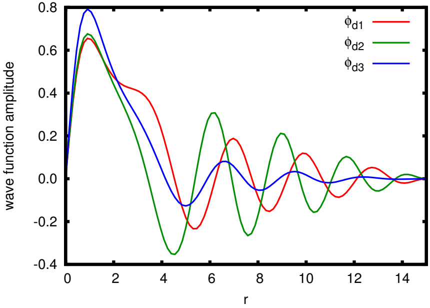
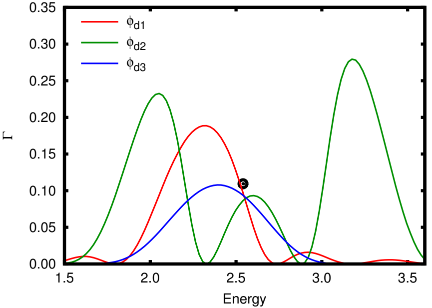
Discrete state and $\Gamma(E)$ – example

$$V(r) = 5r^2 e^{-r}$$





Kolorenč, Ph.D. thesis, Charles University in Prague (2005)

Fano-ADC-Stieltejs method – overview

- Fano-Feshbach theory of resonances
  - exact continuum wave function – discrete state in continuum character

$$|\Psi_E\rangle = a(E)|\phi_d\rangle + \sum_{\beta=1}^{N_c} \int b_\beta(E,\epsilon)|\chi_{\beta,\epsilon}\rangle\, d\epsilon$$

  - $|\phi_d\rangle \in L^2$ – discrete state (not a Hamiltonian eigenstate)
  - $|\chi_{\beta,\epsilon}\rangle$ – background continuum $\langle\chi_{\beta',\epsilon'}|\chi_{\beta,\epsilon}\rangle = \delta_{\beta'\beta}\delta(\epsilon-\epsilon')$
  - decay width of the resonance represented by $|\phi_d\rangle$

$$\Gamma(\epsilon) = 2\pi \sum_\beta |\langle\phi_d|H|\chi_{\beta,\epsilon}\rangle|^2$$

- ADC – representation of the many-body wave functions
  - background continuum discretized

$$|\chi_{\beta,\epsilon}\rangle,\ \epsilon\in\mathbb{R} \ \rightarrow\ |\chi_i\rangle,\ i\in\mathbb{N},\ \langle\chi_i|\chi_j\rangle = \delta_{ij}$$

- Stieltjes imaging
  - spectral moments μ_k of $\Gamma(\epsilon)$ correctly reproduced by $\{\epsilon_i, |\chi_i\rangle\}$

$$\mu_k = \int \epsilon^k \Gamma(\epsilon)\, d\epsilon = 2\pi \sum_\beta \int \epsilon^k |\langle\phi_d|H|\chi_{\beta,\epsilon}\rangle|^2\, d\epsilon \approx 2\pi \sum_i \epsilon_i^k |\langle\phi_d|H|\chi_i\rangle|^2$$

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$$\mu_k = \int \epsilon^k \Gamma(\epsilon)\, d\epsilon = 2\pi \sum_\beta \int \epsilon^k |\langle\phi_d|H|\chi_{\beta,\epsilon}\rangle|^2 \, d\epsilon \approx 2\pi \sum_i \epsilon_i^k |\langle\phi_d|H|\chi_i\rangle|^2$$

Fano-ADC-Stieltejs method – overview

- Fano-Feshbach theory of resonances
  - exact continuum wave function – discrete state in continuum character

$$|\Psi_E\rangle = a(E)|\phi_d\rangle + \sum_{\beta=1}^{N_c} \int b_\beta(E,\epsilon)|\chi_{\beta,\epsilon}\rangle \, d\epsilon$$

  - $|\phi_d\rangle \in L^2$ – discrete state (not a Hamiltonian eigenstate)
  - $|\chi_{\beta,\epsilon}\rangle$ – background continuum $\quad \langle\chi_{\beta',\epsilon'}|\chi_{\beta,\epsilon}\rangle = \delta_{\beta'\beta}\delta(\epsilon-\epsilon')$
  - decay width of the resonance represented by $|\phi_d\rangle$

$$\Gamma(\epsilon) = 2\pi \sum_\beta |\langle\phi_d|H|\chi_{\beta,\epsilon}\rangle|^2$$

- ADC – representation of the many-body wave functions
  - background continuum discretized

$$|\chi_{\beta,\epsilon}\rangle, \ \epsilon \in \mathbb{R} \ \rightarrow \ |\chi_i\rangle, \ i \in \mathbb{N}, \ \langle\chi_i|\chi_j\rangle = \delta_{ij}$$

- Stieltjes imaging
  - spectral moments μ_k of $\Gamma(\epsilon)$ correctly reproduced by $\{\epsilon_i, |\chi_i\rangle\}$

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ADC – Intermediate state representation of GF

$$G(\omega) = \mathbf{f}^\dagger(\omega\mathbf{1} - \mathbf{K} - \mathbf{C})^{-1}\mathbf{f}$$

1. perturbation theoretically corrected ("correlated") ground state $|\Phi_0^N\rangle$
2. correlated excited states (not orthogonal!)

$$|\Psi_J^0\rangle = \hat{C}_J|\Phi_0^N\rangle \qquad \{\hat{C}_J\} = \{\hat{c}_i,\ \hat{c}_a^\dagger\hat{c}_i\hat{c}_j,\ \ldots\}$$
$$[J] = 1\ \text{(one-hole)},\ 2\ \text{(two-hole one-particle)},\ \ldots$$

3. precursor states – Gramm-Schmidt orthogonalization to lower exc. classes

$$|\Psi_J^\#\rangle = |\Psi_J^0\rangle - \sum_{\substack{K \\ [K]<[J]}} |\tilde{\Psi}_K\rangle\langle\tilde{\Psi}_K|\Psi_J^0\rangle$$

4. intermediate states – symmetric orthogonalization within the exc. class

$$|\tilde{\Psi}_J\rangle = \sum_{\substack{J' \\ [J']=[J]}} |\Psi_{J'}^\#\rangle(\boldsymbol{\rho}^{\#-1/2})_{J'J} \qquad \rho_{IJ}^\# = \langle\Psi_I^\#|\Psi_J^\#\rangle$$

- can be still classified as $1h$, $2h1p$, ...

Schirmer, PRA **43**, 4647 (1991); Mertins, Schirmer, PRA **53**, 2140 (1996)

ADC(2)x for the 1p-Green's Function

$$H_{ADC} = K + C = \begin{array}{c|c|c} & 1h & 2h1p \\ \hline 1h & -\epsilon_i\delta_{ii'} + C^{(1)}_{i,i'} + C^{(2)}_{i,i'} & C^{(1)}_{i,a'i'j'} \\ \hline 2h1p & C^{(1)}_{aij,i'} & \begin{array}{c}(-\epsilon_i - \epsilon_j + \epsilon_a)\delta_{ii'}\delta_{jj'}\delta_{aa'} \\ +C^{(1)}_{aij,a'i'j}\end{array} \end{array}$$

- representation of $|\phi_d\rangle$, $|\chi_\epsilon\rangle$ in the basis of intermediate states
  - initial state – **selected eigenstate** of $QH_{ADC}Q$ of $1h$ character
  - final states – **all eigenstates** of $PH_{ADC}P$ of $2h1p$ character
- Decay of doubly ionized systems (ICD after Auger, . . .)
  - ADC(2)x for 2p-Green's function
  - $2h$ and $3h1p$ excitation classes, . . .

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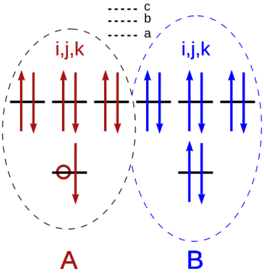
Fano partitioning – scheme I (heteronuclear clusters)

- molecular orbitals (MOs) **localized** either on atom A or atom B
- discrete state $|\phi_d\rangle$

$$|\phi_d\rangle = \sum_i Y_i\, \hat{c}_i |\Phi_0^N\rangle + \sum_{aij} Y_{ij}^a\, \hat{c}_a^\dagger \hat{c}_i \hat{c}_j |\Phi_0^N\rangle$$

$$i, j \in A$$



- final ("continuum") states $|\chi_\epsilon\rangle$

$$|\chi_\epsilon\rangle = \sum_i Y_i\, \hat{c}_i |\Phi_0^N\rangle + \sum_{aij} Y_{ij}^a\, \hat{c}_a^\dagger \hat{c}_i \hat{c}_j |\Phi_0^N\rangle$$

$$i, j \in A, B \qquad \sum_i |Y_i|^2 \ll 1$$

- **no interatomic correlation** in initial state

Averbukh and Cederbaum, JCP **123**, 204107 (2005)

Kolorenč *et al.*, JCP **129**, 244102 (2008)

Fano partitioning – scheme II (homonuclear clusters)

- scheme I not applicable – MOs **delocalized due to inversion symmetry**
- solution – **localization**
- example: $2h1p$ intermediate states derived from $2h$ singlet:

$$|^1\Phi_{i,j,a}\rangle = \frac{1}{\sqrt{2}}(\hat{c}^\dagger_{a\uparrow}\hat{c}_{i\downarrow}\hat{c}_{j\uparrow} - \hat{c}^\dagger_{a\uparrow}\hat{c}_{i\uparrow}\hat{c}_{j\downarrow})|\Phi_0\rangle$$

1. diagonalize 2×2 Hamiltonian submatrix for $\{^1|\Phi_{i,j,a}\rangle,\ |^1\Phi_{i',j',a}\rangle\}$
   - a is selected particle orbital
   - $\{i,i'\}$, $\{j,j'\}$ are gerade-ungerade pairs
   - higher-energy eigenstate: "one-site" character (both holes on a single atom)
   - lower-energy eigenstate: "two-site" character (each hole on a different atom)
2. "one-site" states contribute to the discrete state expansion ($\mathcal{Q}$-space), "two-site"" to the continuum of final states ($\mathcal{P}$-space)

- generalization to **2p-GF** possible, but **not straightforward**

Averbukh and Cederbaum, JCP **125**, 094107 (2006)

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Averbukh and Cederbaum, JCP **125**, 094107 (2006)

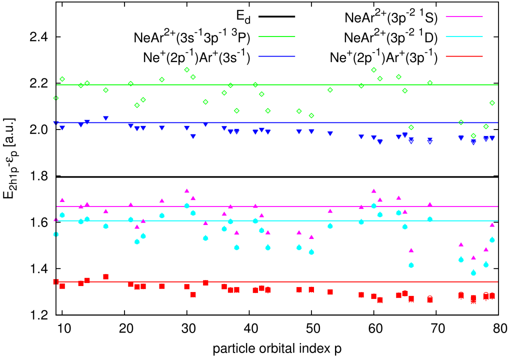
Fano partitioning – scheme III (universal)

- **generalization of scheme II:**

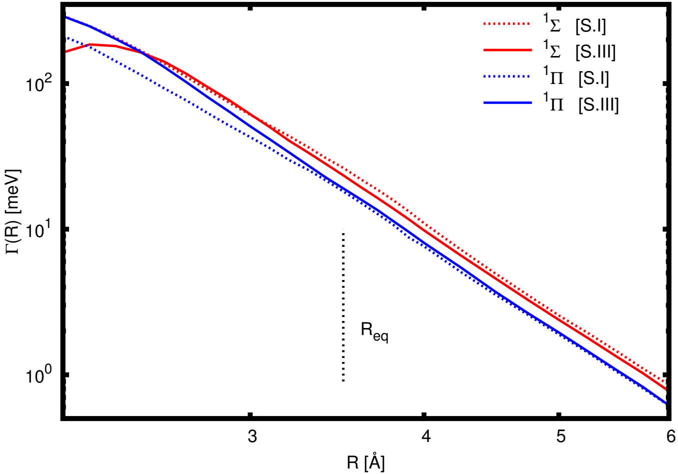
  diagonalization of the whole $2h1p$ ADC blocks characterized by the particle orbital p

- resulting eigenvalues **reflect the structure of DI spectrum**

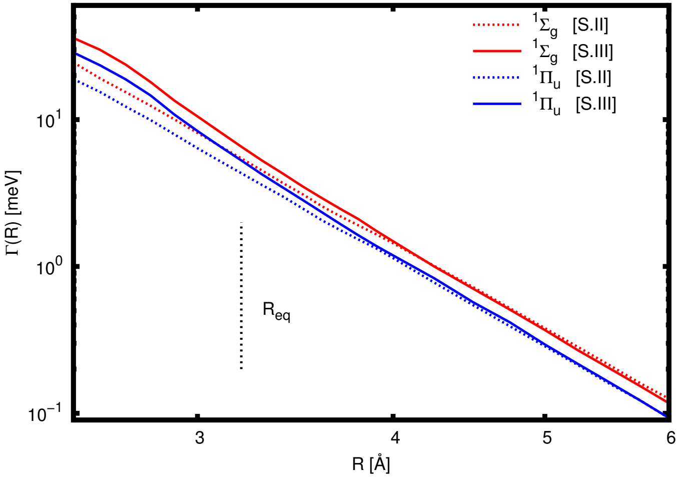
  ⇒ allows association of the eigenstates with open or closed channels



Heteronuclear dimers – $Ne^{2+}(2s^{-1}2p^{-1})Ar$



Homonuclear dimers – ICD after Auger in Ne_2



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Stieltjes imaging – motivation

- description of continuum in L^2 basis – no direct use of the formula

$$\Gamma(\epsilon) = 2\pi \sum_{\beta} |\langle \phi_d | H | \chi_{\beta,\epsilon} \rangle|^2$$

  - spectrum discretized

$$\{\epsilon, |\chi_\epsilon\rangle\} \longrightarrow \{\epsilon_i, |\chi_i\rangle\}$$

  - incorrect boundary condition, normalization to unity

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \neq \delta(\epsilon_i - \epsilon_j)$$

- completness

$$\sum_{\beta} \int |\chi_{\beta,\epsilon}\rangle\langle\chi_{\beta,\epsilon}| \, d\epsilon \approx \sum_i |\chi_i\rangle\langle\chi_i|$$

- spectral moments – $k \leq 0$ used for convergence reasons

$$\mu_k = \int \epsilon^k \Gamma(\epsilon) \, d\epsilon = 2\pi \sum_{\beta} \int \epsilon^k \langle \phi_d | H | \chi_{\beta,\epsilon}\rangle\langle\chi_{\beta,\epsilon} | H | \phi_d \rangle \, d\epsilon$$

$$\approx 2\pi \sum_i \epsilon_i^k \langle \phi_d | H | \chi_i \rangle\langle \chi_i | H | \phi_d \rangle = 2\pi \sum_i \epsilon_i^k |\langle \phi_d | H | \chi_i \rangle|^2 = \sum_i \epsilon_i^k \gamma_i$$

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Stieltjes imaging

Goal: find Gaussian quadrature associated with unknown weight function $\Gamma(\epsilon)$

$$\mu_{-k} = \int \epsilon^{-k}\Gamma(\epsilon)\,d\epsilon = \sum_{j}^{n_S}(\epsilon_j^{(n_S)})^{-k} w_j^{(n_S)}, \quad k = 0, \ldots 2n_S - 1$$

1. recurence formula for polynomials orthogonal with respect to $\Gamma(\epsilon)$

$$\int \Gamma(\epsilon) Q_n(1/\epsilon) Q_m(1/\epsilon)\,d\epsilon = N_n \delta_{nm}$$

   can be expressed in terms of $\{\epsilon_i, \gamma_i\}$

2. abscissas $1/\epsilon_j^{(n_S)}$ – roots of $Q_{n_S}(1/\epsilon)$ (diagonalization of tridiagonal matrix)
3. weights $w_j^{(n_S)}$

$$w_j^{(n_S)} = \frac{N_m}{\sum_{m=0}^{n_S-1} Q_m^2(1/\epsilon_j^{(n_S)})}$$

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Stieltjes imaging

4. Stieltejs distribution

$$F(\epsilon) = \int_{\epsilon_{\min}}^{\epsilon} \Gamma(\epsilon')\, d\epsilon' \approx F^{(n_S)}(\epsilon)$$

$$F^{(n_S)}(\epsilon) = \sum_{j=1}^{q} w_j^{(n_S)} \qquad \epsilon_q^{(n_S)} < \epsilon < \epsilon_{q+1}^{(n_S)}$$

$$F^{(n_S)}(\epsilon_i^{(n_S)}) = \frac{1}{2}[F^{(n_S)}(\epsilon_i^{(n_S)} - 0) + F^{(n_S)}(\epsilon_i^{(n_S)} + 0)]$$

5. desired approximation to the width function – Stieltjes derivative

$$\Gamma^{(n_S)}(\epsilon) = \frac{1}{2}\frac{w_{q+1}^{(n_S)} + w_q^{(n_S)}}{\epsilon_{q+1}^{(n_S)} - \epsilon_q^{(n_S)}} \qquad \epsilon_q^{(n_S)} < \epsilon < \epsilon_{q+1}^{(n_S)}$$

6. **effectively yields $\Gamma(\epsilon)$ at $n_S - 1$ discrete points using $2n_S$ lowest μ_k**

Müller-Plathe and Diercksen, PRA **40**, 696 (1989), . . .

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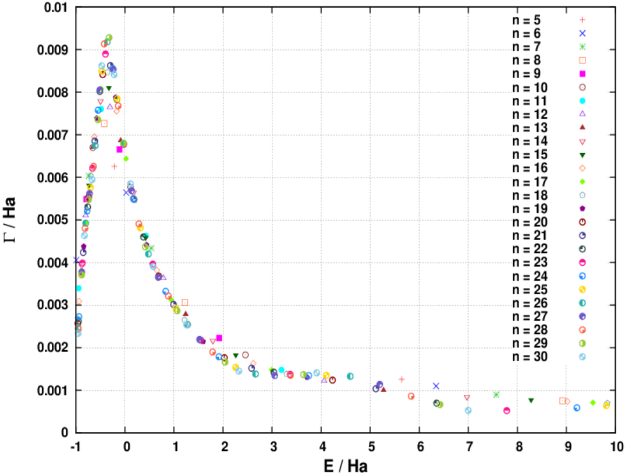
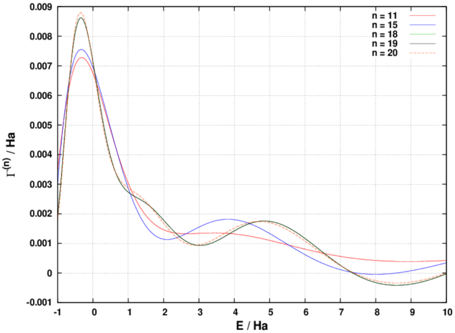
Stieltejs imaging output – example

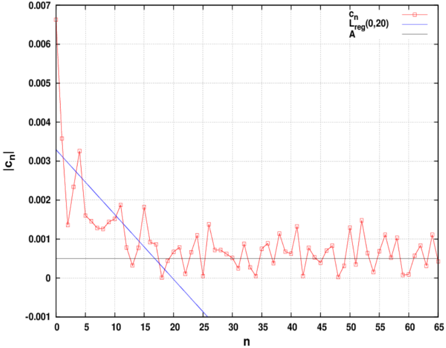


$$\epsilon_q^{(n_S+1)} < \epsilon_q^{(n_S)} < \epsilon_{q+1}^{(n_S+1)}$$

Direct expansion approach

- basis of known orthogonal polynomials $L_n(1/x)$





Votavová, Bc. thesis, Charles University in Prague (2014)

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ICD widths – Fano-ADC vs. CAP

- van der Waals clusters – Ne_2 ($^2\Sigma_u^+$, $R = 3.2$ Å)

CAP/CI	(d-aug-cc-pVDZ + 3s3p3d)	10.3 meV	JCP **115**, 6853 (2001)
CAP/ADC	(d-aug-cc-pVQZ)	7.0 meV	JCP **126**, 164110 (2007)
Fano-ADC	(d-aug-cc-pVQZ + 5s5p5d)	7.0 ± 0.3 meV	

- Hydrogen-bonded systems – $(HF)_2$

	donor		acceptor	
	E_R (eV)	Γ (meV)	E_R (eV)	Γ (meV)
CAP/CI (aug-cc-pVQZ)	38.6	18	40.5	30
CAP/EOM-CC (aug-cc-pVTZ)	39.1	21	40.8	33
Fano-ADC (d-aug-cc-pVQZ)	37.3	17-18	39.0	19-21

Santra *et al.*, Chem. Phys. Lett. **303**, 413 (1999)

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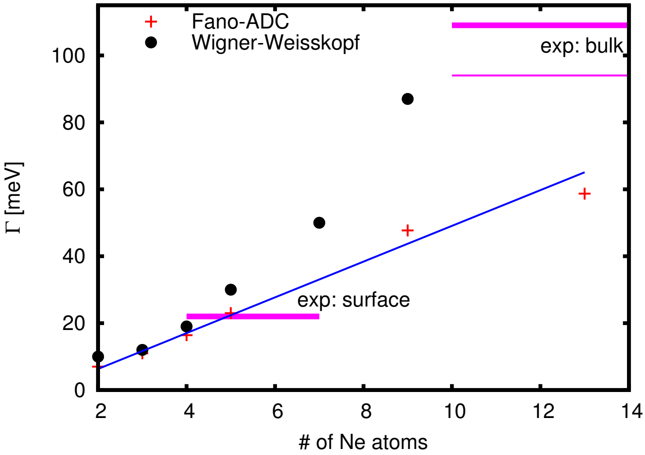
Ne clusters – Fano-ADC vs. Wigner-Weisskopf



exp: Öhrwall *et al.*, PRL **93**, 173401 (2004)

WW: Santra *et al.*, Phys. Rev. B **64**, 245104 (2001)

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Partial decay widths in Fano-ADC

- rigorously unattainable in L^2 theory
  - channels only defined **asymptotically**
- estimation possible using suitable L^2 channel projectors P_β
  1. evaluate channel-specific couplings
     $$\gamma_{\beta,i} = 2\pi |\langle \phi_d | H P_\beta | \chi_i \rangle|^2$$
  2. apply Stieltjes imaging procedure on the sets $\{\epsilon_i, \gamma_{\beta,i}\} \rightarrow \tilde{\Gamma}_\beta$
  3. normalize by independently evaluated total width Γ
     $$\Gamma_\beta \approx \frac{\tilde{\Gamma}_\beta}{\sum_\alpha \tilde{\Gamma}_\alpha} \Gamma$$
- reliability depends on how well the channel projectors can be defined in terms of localized wave functions

Cacelli, Caravetta and Moccia, Mol. Phys. **59**, 385 (1986)
Averbukh and Cederbaum, J. Chem. Phys. **123**, 204107 (2005)

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Diagonalization procedures

- Initial state – selected eigenstate of QHQ
  - **Davidson** diagonalization – convergence of individual eigenvectors
  - J. Comp. Phys. **17**, 87 (1975); SIAM Rev. **42**, 267 (2000)
  - JADAMILU library – Comp. Phys. Commun. **177**, 951 (2007)
- Final states – all eigenstates of PHP
  - full diagonalization
  - band **Lanczos** diagonalization possible
    - representation of the matrix in **Krylov space** $\{q_i, Hq_i, H^2q_i, \ldots\}$
    - diagonalization of **comparatively small band matrix** T
    - **conserves spectral moments** of the matrix [Gokhberg, Ph.D. thesis (2008)]
    - starting block **must contain** $PHQ|\phi_d\rangle$ – vital for convergence
    - $\langle\chi_i|H|\phi_d\rangle$ **couplings** available as **elements of (short) eigenvectors** of T
    - **Stieltjes-Lanczos**: J. Chem. Phys. **134**, 094107 (2011); **139**, 144107 (2013); **140**, 184107 (2014)

Parlett, The Symmetric Eigenvalue Problem, SIAM (1998)

Summary

- Fano-ADC-Stieltjes
  - computationally **efficient** tool for calculating decay widths
  - **stable** over many orders of magnitude
  - **applicable when** $\mathcal{Q} - \mathcal{P}$ **separation possible** in terms of L^2 basis
    - van der Waals clusters (orbital localization achievable)
    - Auger decay (large energetic gap)
    - problems in hydrogen-bonded clusters?
  - results may be **sensitive to the discrete state definition**
  - estimation of partial rates available
- Complex absorbing potential
  - applicable to wider range of problems
  - usable with **different *ab initio* methods**
  - non-hermitian eigenvalue problem, **questionable with Gaussian basis**
- **NO BLACK BOX METHODS!**