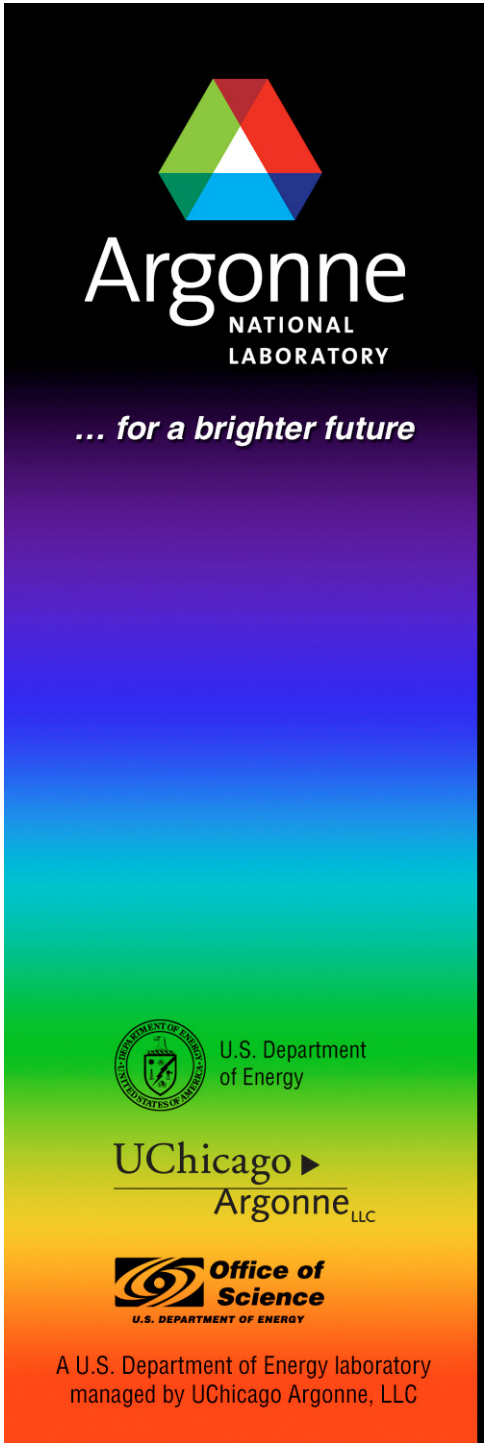

Calculating resonances using a complex absorbing potential

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Acknowledgment

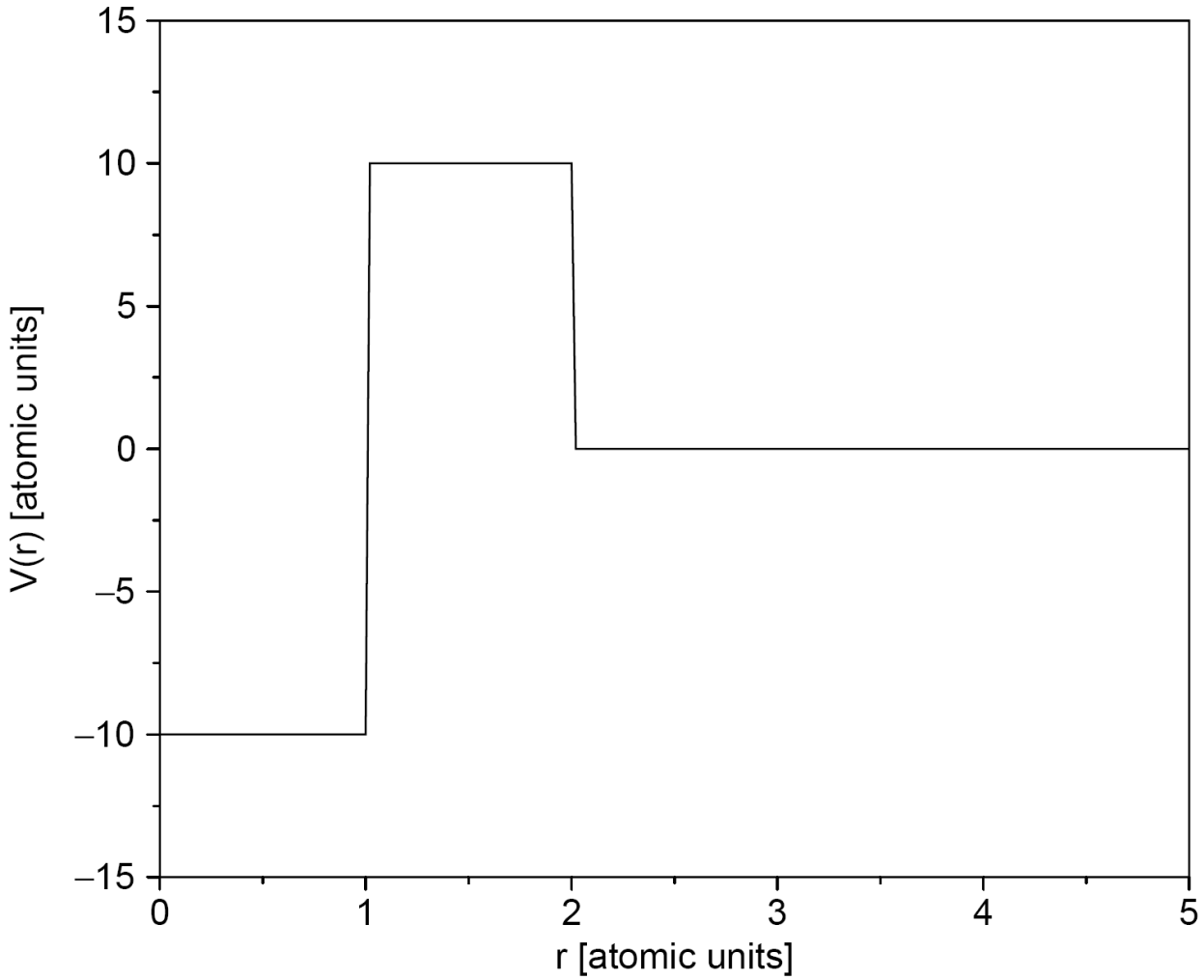
- Lorenz Cederbaum (University of Heidelberg, Germany)

- Hans-Dieter Meyer (University of Heidelberg, Germany)

Overview

- Pragmatic introduction to complex absorbing potentials
- Complex absorbing potentials and many-body theory
- Applications:
  - Electronic decay of valence holes in clusters
  - Elastic electron–molecule scattering
  - Isolated atoms exposed to intense free-electron laser radiation

Example: s-wave scattering from spherically symmetric one-particle model potential



Let $$\psi(\boldsymbol{x}) = \frac{u(r)}{r} Y_{00}(\vartheta, \varphi)$$

Radial Schrödinger equation: $$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + V(r)\right] u(r) = E u(r)$$

Impose boundary conditions $$u(0) = 0$$

$$\lim_{r\to\infty} \frac{\mathrm{d}\ln u(r)}{\mathrm{d}r} = \mathrm{i}k \qquad E = k^2/2$$

A. J. F. Siegert, Phys. Rev. **56**, 750 (1939).

Therefore, outside potential, $$u(r) = A\exp(\mathrm{i}kr)$$

Calculate poles of scattering amplitude using complex version of Newton's algorithm

	E (a.u.)
Bound state	$-$ 6.353803650
1st resonance	4.001414397 $-$ i0.003616371
2nd resonance	13.80434250 $-$ i1.269152015
3rd resonance	20.67730611 $-$ i2.065452506

- Resonance states (Siegert or Gamow states) are *discrete* solutions of the Schrödinger equation satisfying Siegert boundary conditions
- The energy of a resonance state is complex

  → *Siegert energy* $\boxed{E_{\text{res}} = E_R - \mathrm{i}\Gamma/2}$

- Siegert states are not elements of Hilbert space → exponentially divergent wave function

Complex Absorbing Potential (CAP)

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

Rigorous justification: U. V. Riss and H.-D. Meyer, J. Phys. B **26**, 4503 (1993).

Connection to complex scaling: N. Moiseyev, J. Phys. B **31**, 1431 (1998).

U. V. Riss and H.-D. Meyer, J. Phys. B **31**, 2279 (1998).

Reviews: R. Santra and L. S. Cederbaum, Phys. Rep. **368**, 1 (2002).

J. G. Muga, J. P. Palao, B. Navarro, and I. L. Egusquiza, Phys. Rep. **395**, 357 (2004).

Suitable CAP in spherically symmetric case:

$$-\mathrm{i}\eta W(r) = \begin{cases} 0, & 0 \leqslant r < c \\ -\mathrm{i}\eta(r-c)^2, & r \geqslant c \end{cases},$$

Solve eigenvalue problem in square-integrable basis

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}\,r^2} + V(r) - \mathrm{i}\eta W(r)\right] u_\eta(r) = E(\eta) u_\eta(r)$$

using particle-in-box basis set

→

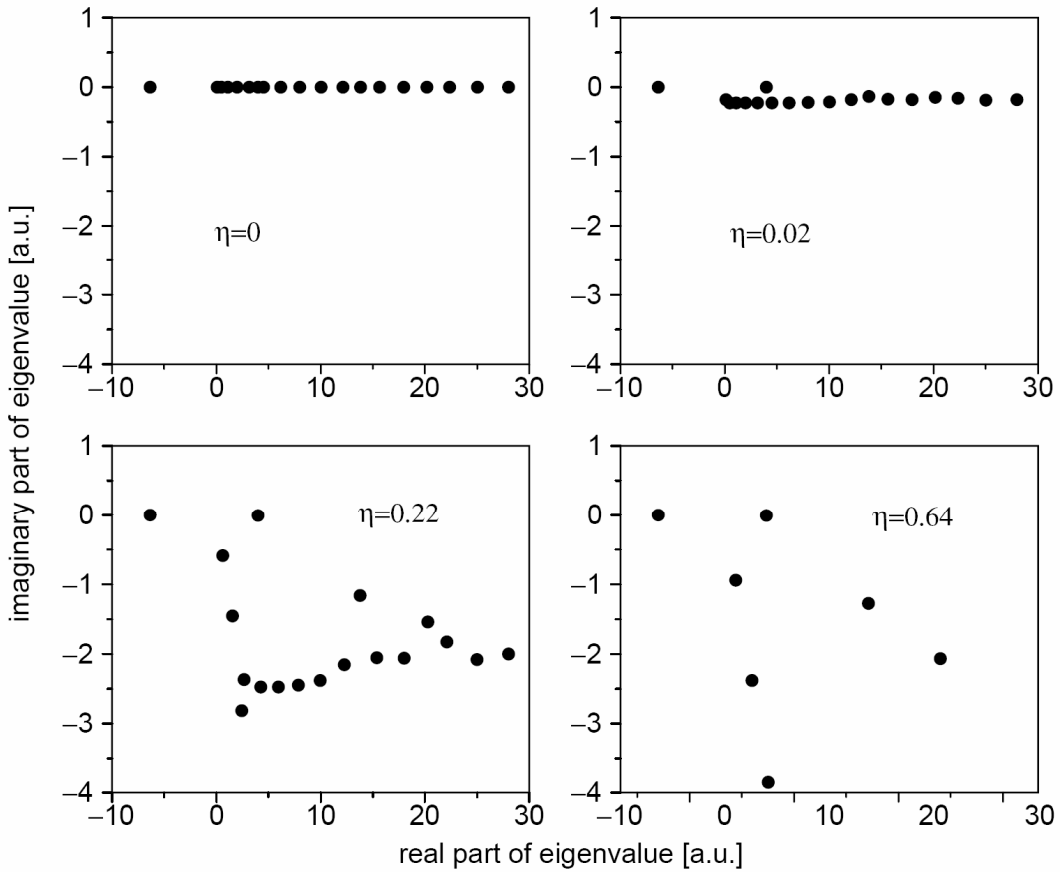


Fig. 10. Spectra of the complex symmetric matrix $\boldsymbol{H}(\eta) \in \mathbb{C}^{N\times N}$ (Eqs. (120) and (125)–(129)) for four different η, where $N = 200$. The basis-set wall is located at $L = 8.0$ and the CAP acts at radial distances r larger than $c = 2.0$. For the physical potential, $V_0 = 10$ and $a = 1$ are used.

Resonance wave function: with and without CAP

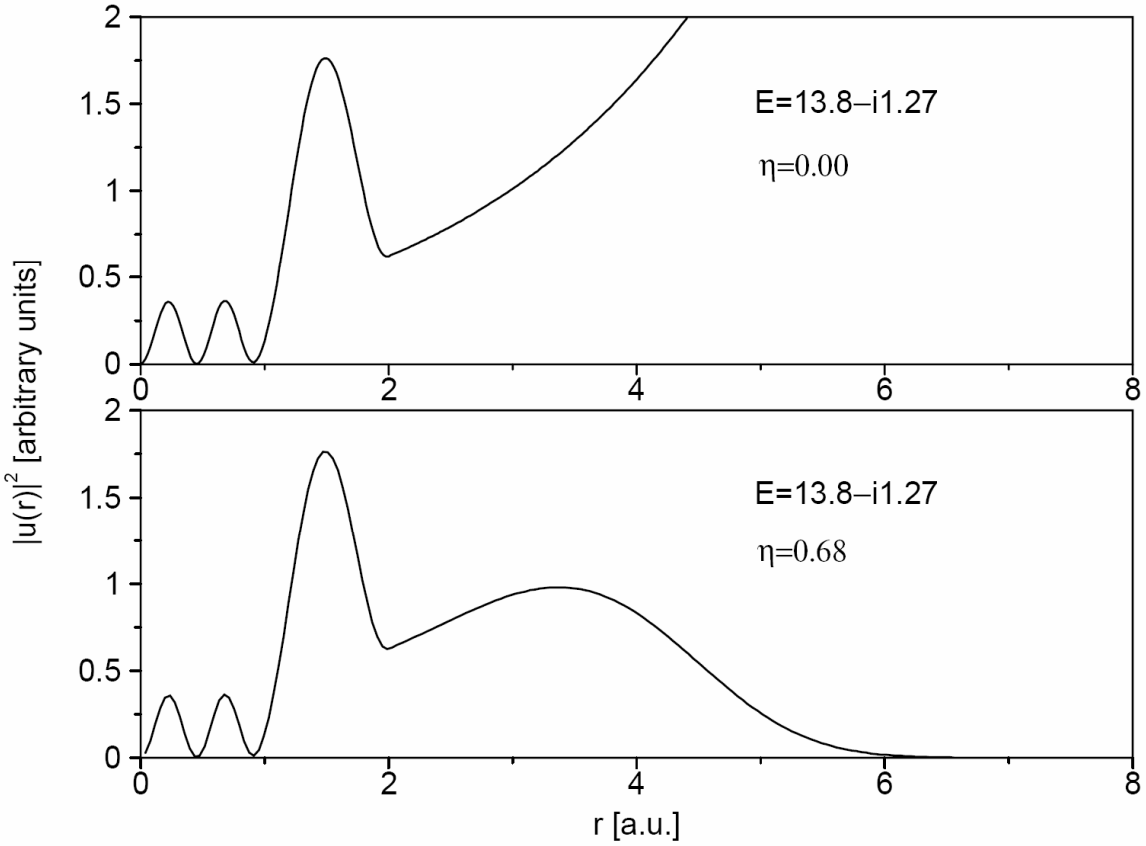


Fig. 11. The radial density $|u(r)|^2$ of the wave function corresponding to the second resonance state ($E = 13.8 - i1.27$). In the upper frame no absorbing potential is applied. The Siegert wave function diverges exponentially. The lower frame demonstrates that with the CAP turned on ($\eta = 0.68$ in this example), the resonance wave function is bound and well representable in the finite basis set used ($L = 8.0$, $N = 200$).

Optimization of CAP strength η

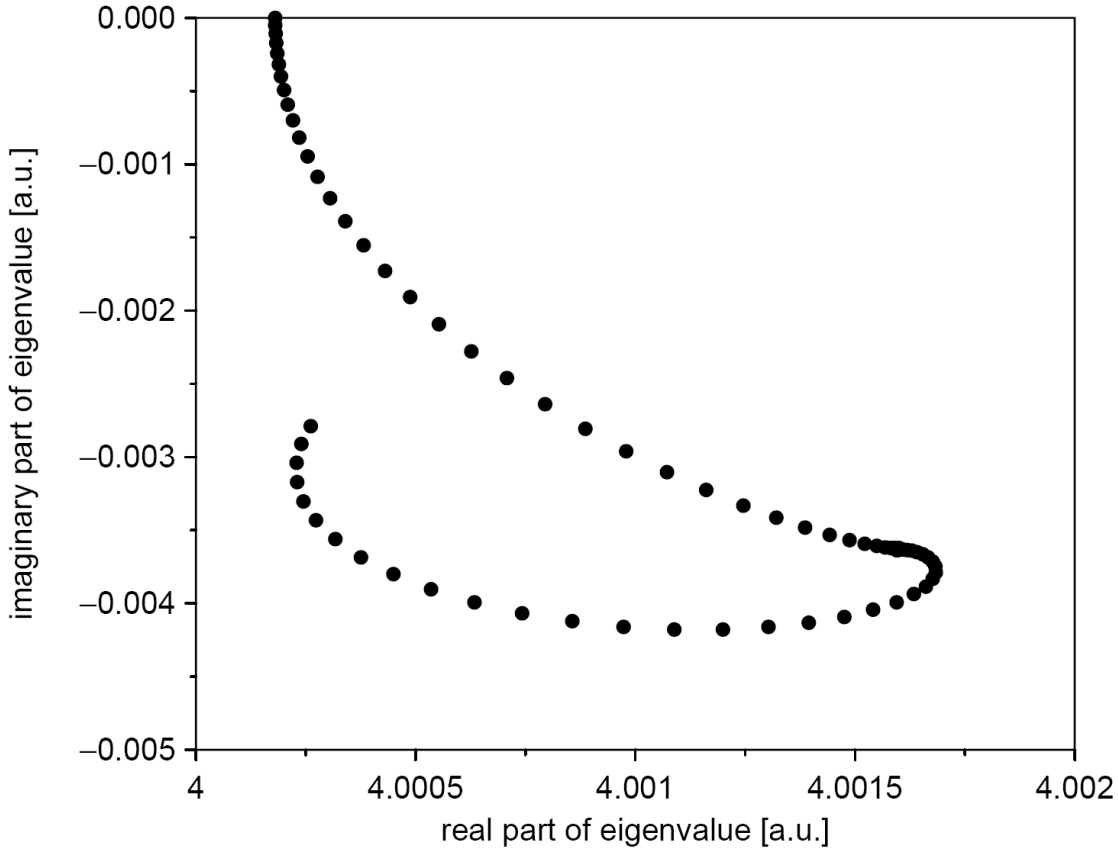


Fig. 12. η-trajectory in the vicinity of the first resonance ($E = 4.001 - i0.004$). One specific eigenvalue $E(\eta)$ of the complex symmetric matrix $\boldsymbol{H}(\eta)$ is plotted as a function of η. Note the accumulation of data points at $E = 4.0016 - i0.0036$. This is the best approximation of the complex Siegert energy of the first resonance within the basis set employed ($L = 8.0,\ N = 200$).

Resonance energies calculated using CAP

$$4.0014 - i0.0036164, \quad 13.80434 - i1.26915, \quad 20.6773 - i2.06545$$

All digits shown are converged and agree with numerically exact results.

Combining CAP with electronic many-body theory

- Multireference configuration interaction (MRCI)

  T. Sommerfeld, U. V. Riss, H.-D. Meyer, L. S. Cederbaum, B. Engels, and H. U. Suter, J. Phys. B **31**, 4107 (1998).
  R. Santra and L. S. Cederbaum, J. Chem. Phys. **115**, 6853 (2001).

- One-particle Green's function/algebraic diagrammatic construction (ADC)

  R. Santra and L. S. Cederbaum, J. Chem. Phys. **117**, 5511 (2002).
  S. Feuerbacher, T. Sommerfeld, R. Santra, and L. S. Cederbaum, J. Chem. Phys. **118**, 6188 (2003).

- Fock space multireference coupled cluster (FSMRCC)

  Y. Sajeev, R. Santra, and S. Pal, J. Chem. Phys. **122**, 234320 (2005).

  Y. Sajeev, R. Santra, and S. Pal, J. Chem. Phys. **123**, 204110 (2005).

Matrix elements with respect to Gaussian basis set

Symmetric inner product

$$(\phi|\psi) := \int \phi(\boldsymbol{x})\,\psi(\boldsymbol{x})\,d^3x$$

Gaussian basis function

$$\chi_\mu(\boldsymbol{x}) = N_\mu \exp(-\alpha_\mu(\boldsymbol{x}-\boldsymbol{R}_\mu)^2)\prod_{j=1}^{3}(x_j-(\boldsymbol{R}_\mu)_j)^{k_{\mu,j}}.$$

Box-CAP for molecules

$$W(\boldsymbol{x};\boldsymbol{c};n) := \sum_{i=1}^{3} W_i(x_i;c_i;n),$$

$$W_i(x_i;c_i;n) := \begin{cases} 0, & |x_i| \leqslant c_i \\ (|x_i|-c_i)^n, & |x_i| > c_i \end{cases}.$$

3d integrals can be expressed in terms of incomplete gamma function

$$\gamma(\alpha,\beta) := \int_0^\beta t^{\alpha-1}e^{-t}dt, \quad \mathrm{Re}\,\alpha > 0,$$

Example: CAP + MRCI

- Calculate Hartree-Fock orbitals for target molecule: $\varphi_p(\boldsymbol{x}) = \sum_\mu C_{\mu p}\chi_\mu(\boldsymbol{x})$
- Transform from Gaussian to HF orbitals: $(\varphi_p|\hat{W}|\varphi_q) = \sum_{\mu,\nu} C_{\mu p}(\chi_\mu|\hat{W}|\chi_\nu)C_{\nu q}$
- Select configuration space, e.g. $\{|\Phi_I)\} := \{c_i|\Phi_0^N), c_a^\mathrm{T}c_k c_l|\Phi_0^N)\ (k<l), \ldots\}$
- Real part of many-electron Hamiltonian calculated using standard code $\hat{H}(\eta) = \hat{H} - \mathrm{i}\eta\hat{W}$
- CAP is one-body operator; its matrix elements are easily calculated:

$$\boldsymbol{W} = \left[\begin{array}{c|c|c} 1h/1h & 1h/2h1p & \ldots \\ \hline 2h1p/1h & 2h1p/2h1p & \ldots \\ \hline \vdots & \vdots & \ddots \end{array}\right] = \left[\begin{array}{c|c|c} \mathbf{0} & \mathbf{0} & \ldots \\ \hline \mathbf{0} & W_{aa'}\delta_{kk'}\delta_{ll'} & \ldots \\ \hline \vdots & \vdots & \ddots \end{array}\right]$$

we have to solve complex symmetric eigenvalue problem (CAP/CI, CAP/ADC)

Reminder:

A matrix $\boldsymbol{A} \in \mathbb{C}^{N \times N}$ is called *symmetric* if

$$\boldsymbol{A}^{\mathrm{T}} = \boldsymbol{A} \ ,$$

where $\boldsymbol{A}^{\mathrm{T}}$ is the transpose of $\boldsymbol{A}$ $((\boldsymbol{A}^{\mathrm{T}})_{ij} = (\boldsymbol{A})_{ji})$.

Properties of complex symmetric matrices

Theorem 3. *Let $\boldsymbol{A} \in \mathbb{C}^{N\times N}$ be an arbitrary complex matrix. There exists a complex symmetric matrix $\boldsymbol{S} \in \mathbb{C}^{N\times N}$ that is similar to $\boldsymbol{A}$.*

Theorem 4. *If $\boldsymbol{A} \in \mathbb{C}^{N\times N}$, then there exists a unitary matrix $\boldsymbol{Q} \in \mathbb{C}^{N\times N}$ such that*

$$\boldsymbol{Q}^{\dagger}\boldsymbol{A}\boldsymbol{Q} = \begin{bmatrix} \lambda_1 & * & \dots & * \\ & \ddots & & \vdots \\ & & \ddots & * \\ & & & \lambda_N \end{bmatrix} =: \boldsymbol{T} \ . \tag{255}$$

$\boldsymbol{T}$ is upper triangular and its diagonal elements λ_i $(i=1,\dots,N)$ are the eigenvalues of $\boldsymbol{A}$. $\boldsymbol{T}=\boldsymbol{Q}^{\dagger}\boldsymbol{A}\boldsymbol{Q}$ is the Schur decomposition of $\boldsymbol{A}$.

Theorem 5. *Let $\boldsymbol{A} \in \mathbb{C}^{N\times N}$ be complex symmetric and non-defective. There exists a complex orthogonal matrix $\boldsymbol{Q} \in \mathbb{C}^{N\times N}$, $\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{Q} = \mathbf{1}$, such that*

$$\boldsymbol{Q}^{\mathrm{T}}\boldsymbol{A}\boldsymbol{Q} = \mathrm{diag}(\lambda_1,\dots,\lambda_N) \ . \tag{303}$$

The set $\{\lambda_1,\dots,\lambda_N\}$ is the spectrum of $\boldsymbol{A}$.

Numerical techniques optimized for complex symmetric eigenvalue problem → preserve symmetry!

- Full diagonalization:
  - Complex symmetric variant of Householder algorithm
  - Complex symmetric QR algorithm
- Large, sparse matrices:
  - Complex symmetric Davidson algorithm
  - Complex symmetric Lanczos algorithm

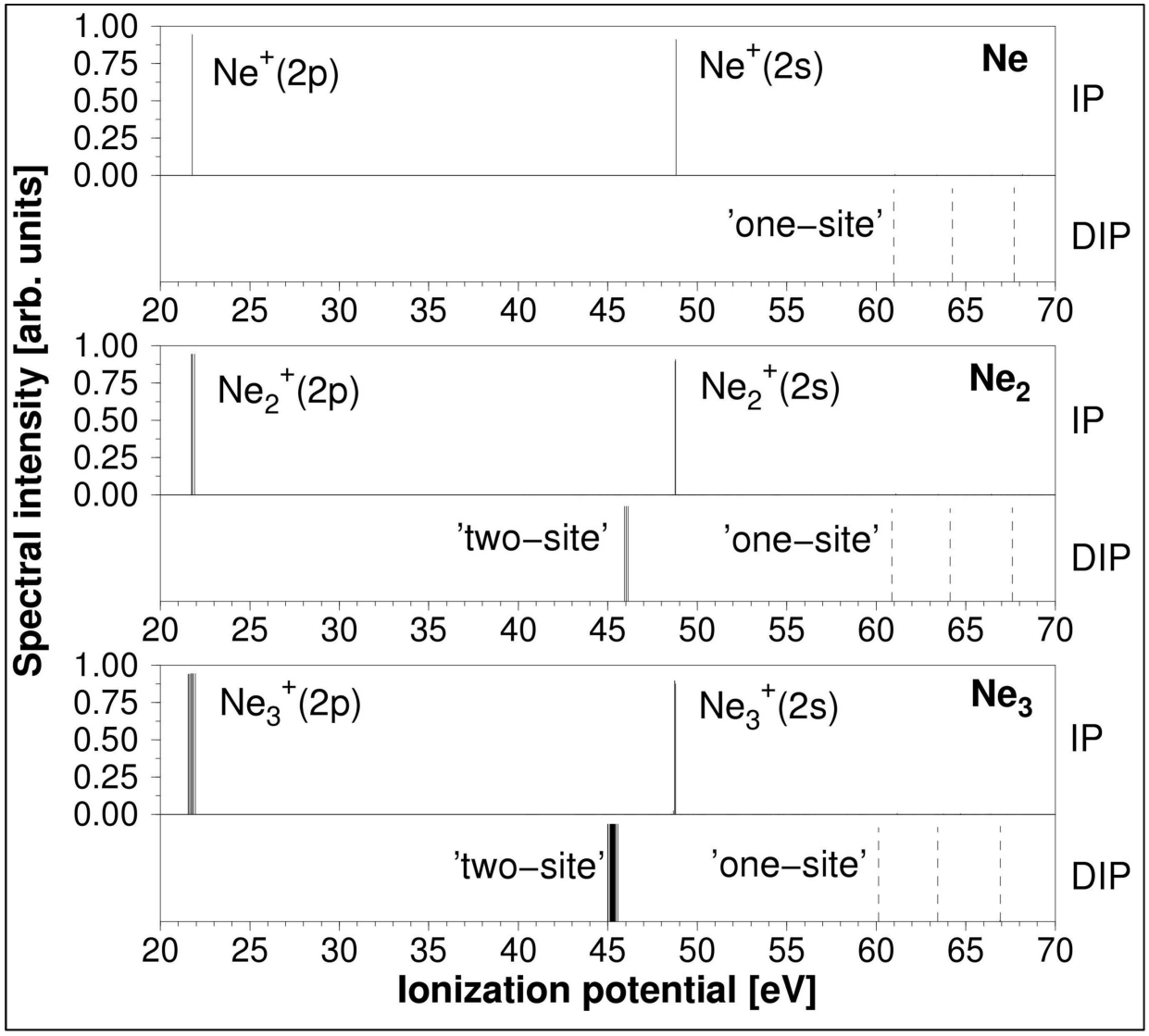
Recall that eigenvalue problem has to be solved several times in order to optimize η

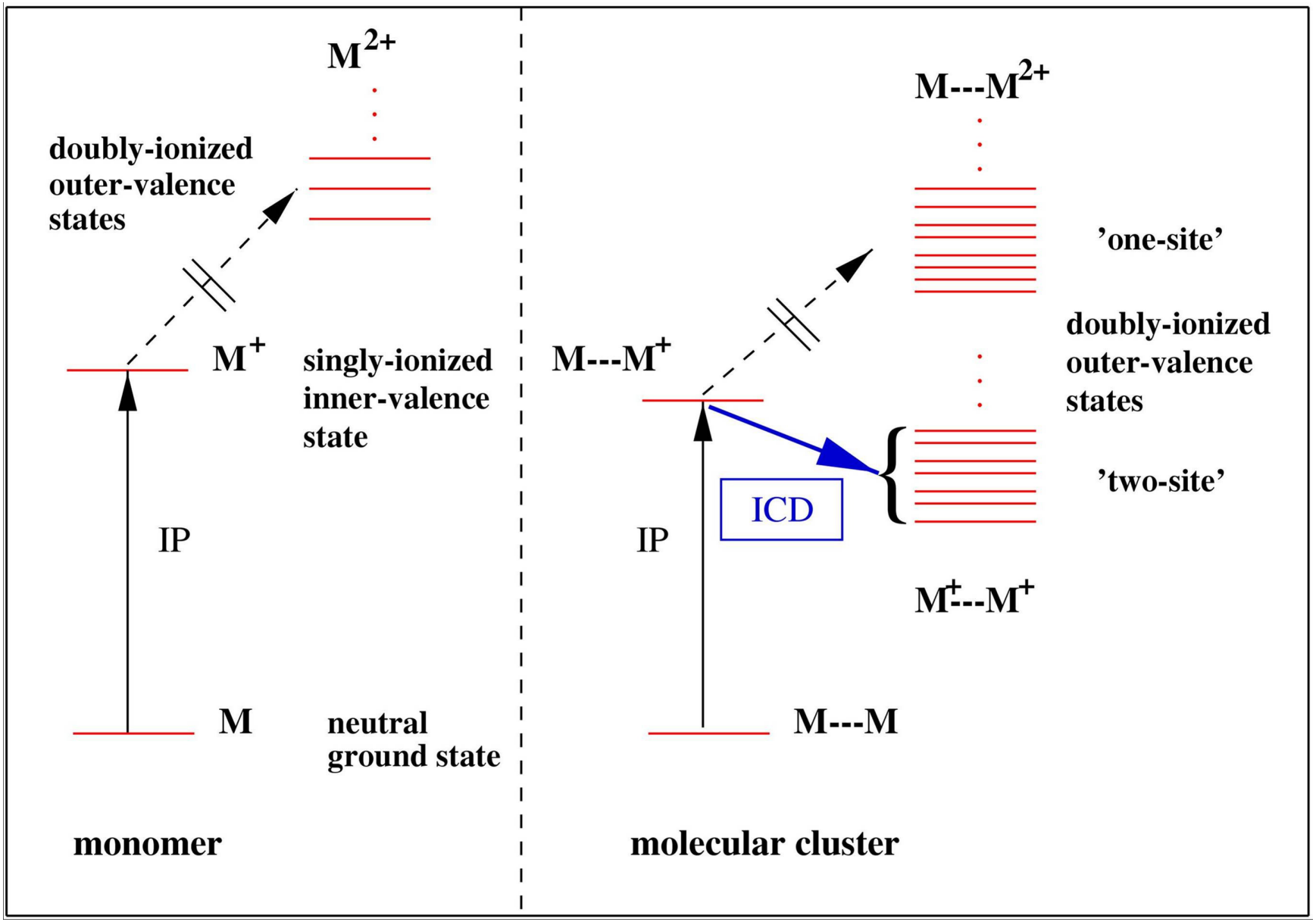
Strategy that works well:

- First calculate subset of eigenvectors of H (real part of Hamiltonian)
- Represent H - iηW in small subspace
- Perform optimization of η by diagonalizing small complex symmetric matrix

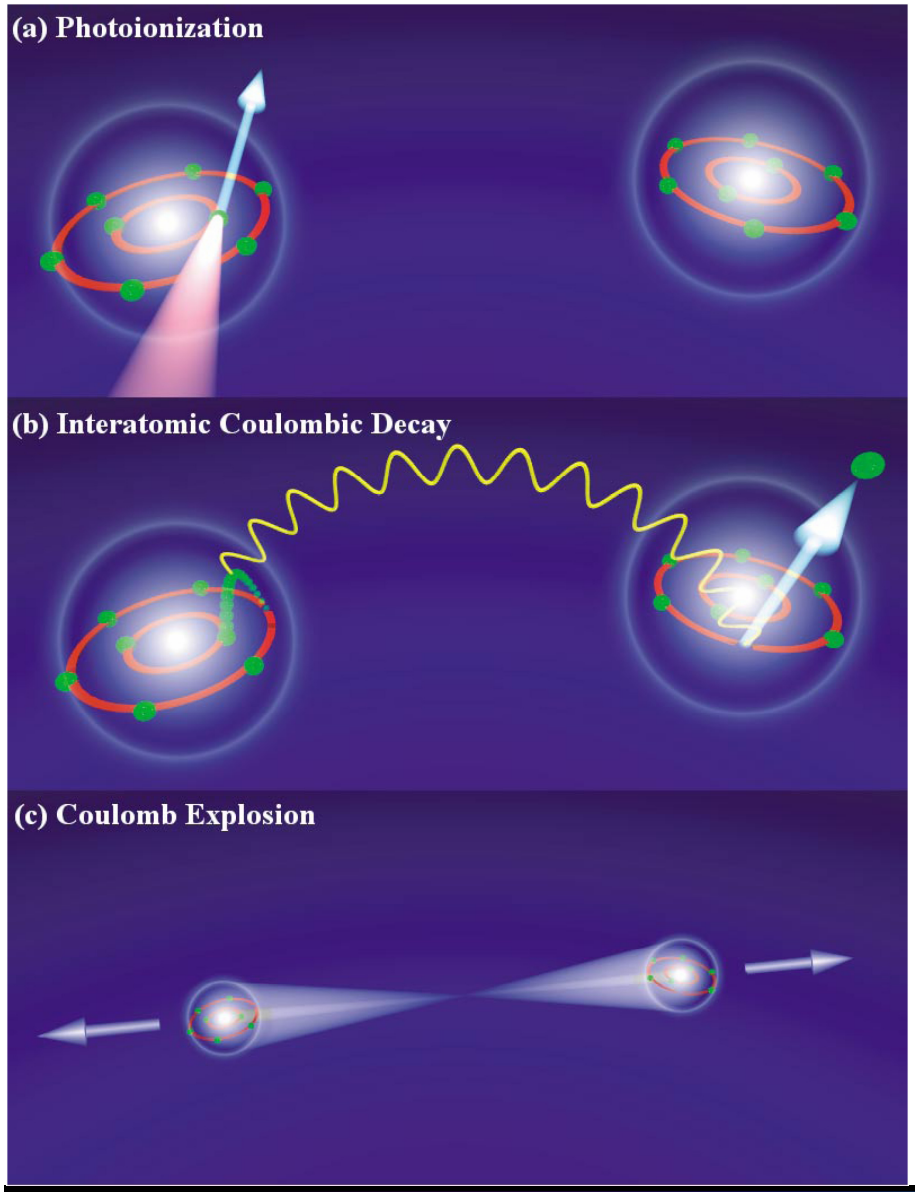
Application of a CAP to the computational treatment of Interatomic Coulombic Decay (ICD) in clusters

One- and two-particle Green's function spectra of Ne_n



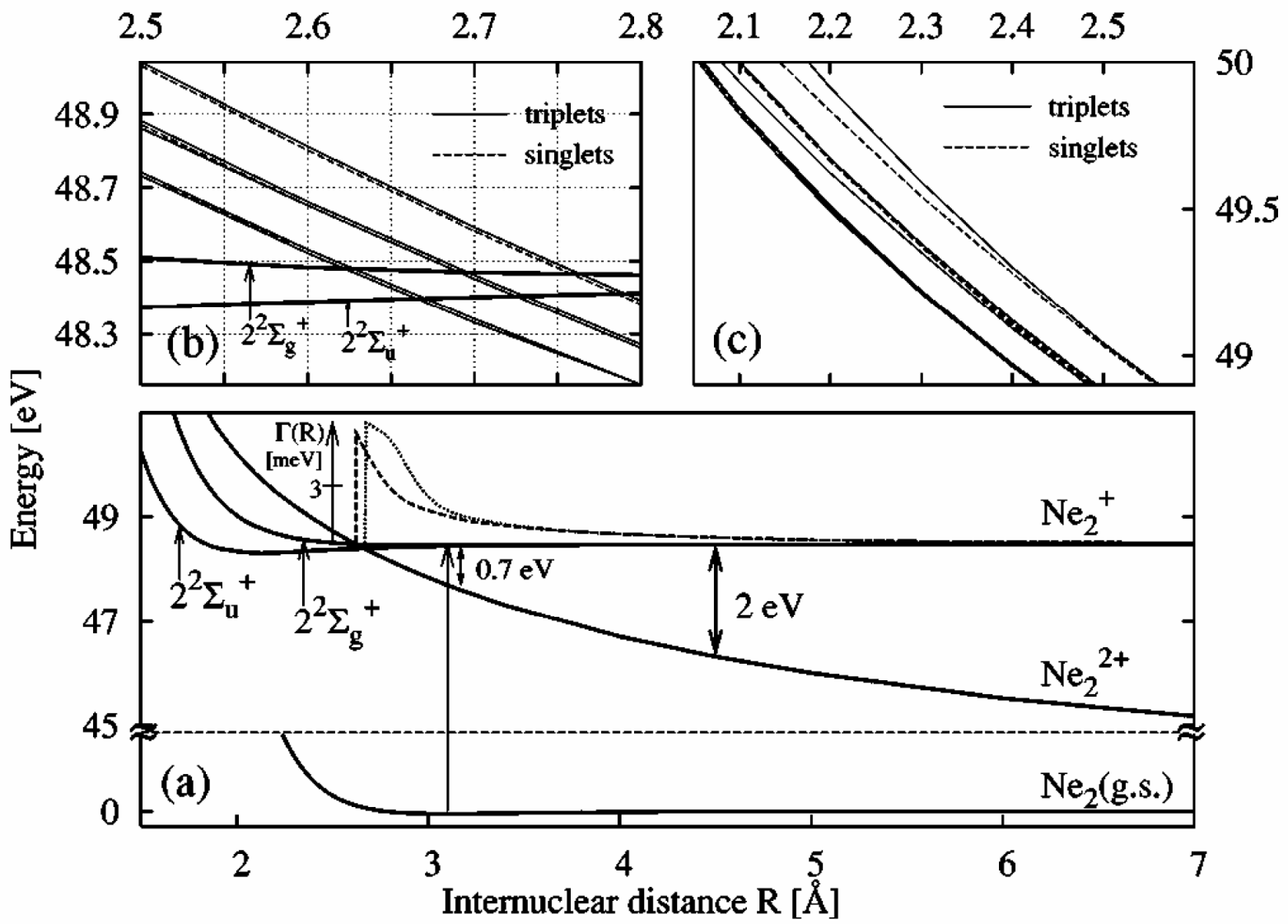

M2+
doubly-ionized
outer-valence
states
M+
singly-ionized
inner-valence
state
IP
M
neutral
ground state
monomer
M---M2+
'one-site'
doubly-ionized
outer-valence
states
'two-site'
M---M+
ICD
IP
M+---M+
M---M
molecular cluster

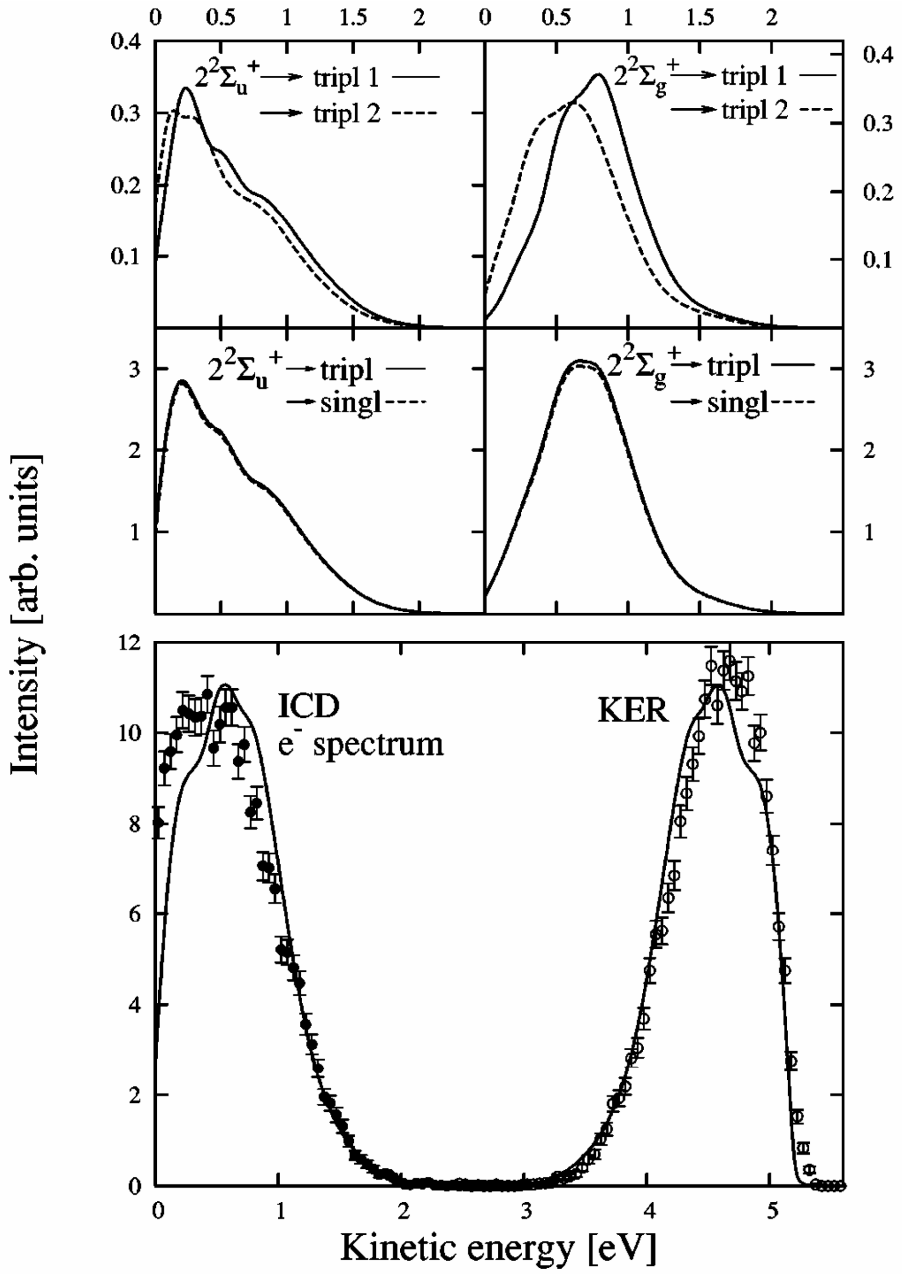
Interatomic Coulombic Decay (ICD) in neon dimer



- Theory:
  - Santra *et al.*, Phys. Rev. Lett. **85**, 4490 (2000).
  - Scheit *et al.*, J. Chem. Phys. **121**, 8393 (2004).
- Experiment:
  - Jahnke *et al.*, Phys. Rev. Lett. **93**, 163401 (2004).

Potential energy curves and decay rates





Kinetic energy distribution of ICD electrons: theory and experiment

- Distribution is a manifestation of vibrational wave-packet dynamics
- It is rather insensitive with respect to the magnitude of the ICD rate

Application of a CAP to the description of shape resonances in elastic electron–molecule scattering

- Interesting because of dissociative attachment reaction

- Important mechanism underlying radiation damage in biological samples

B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Science **287**, 1658 (2000).

Construct optical potential:

$$\hat{V}_{\mathrm{opt}}(\omega) = \hat{V}_{\mathrm{SE}} + \hat{\Sigma}(\omega).$$

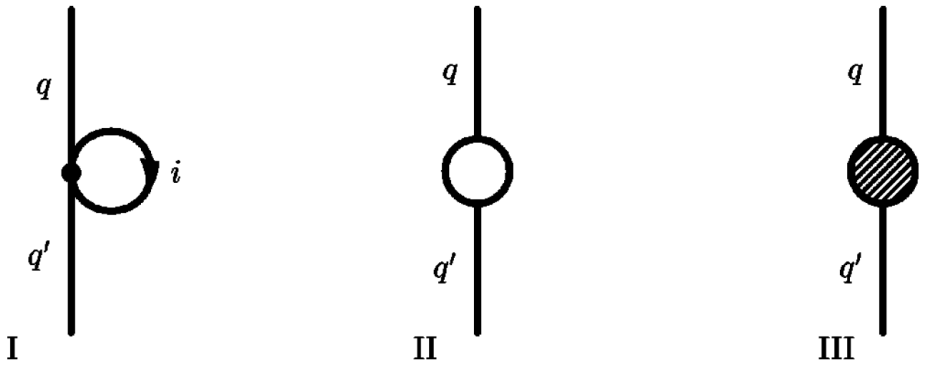
$\hat{V}_{\mathrm{SE}}$ Hartree-Fock mean field generated by electrons in occupied orbitals PLUS Coulomb attraction to nuclei

$\hat{\Sigma}(\omega)$ Self-energy with CAP and electron–electron interactions

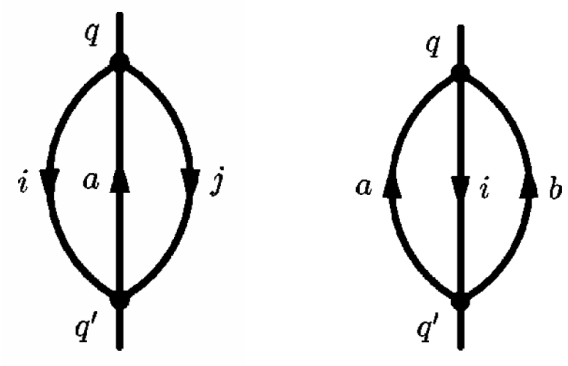
- Solve discrete eigenvalue of effective one-electron Hamiltonian
- Very efficient at second-order level

Self-energy diagrams:

- Noninteracting particles are Hartree-Fock particles
- Treat CAP as perturbation in many-body Green's function



First-order diagrams



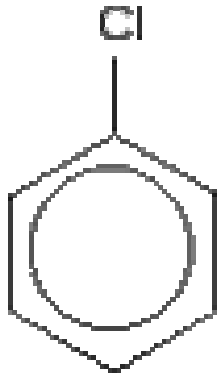
Second-order diagrams

TABLE IV. Selected results for energy and width of the $^2\Pi_g$ resonance of N_2^- computed with different methods. If not indicated otherwise, CAP always means a box-CAP.

Method	Energy (eV)	Width (eV)
"Experimental" value (see text)	2.32	0.41
Linear algebraic method[a]	2.13	0.31
Schwinger multichannel method[b]	2.26	0.39
R-matrix method[c]		
-without	2.27	0.35
-with inclusion of polarized pseudostates	1.90	0.26
MRDCI extrapolation method[d]	2.62	0.45
QBSCCI[e]	1.8	0.39
Quadratic CAP/static-exchange[f]	3.90	1.39
CAP/SEP[g]	1.76	0.20
CAP/CI[g]	2.97	0.65
Schwinger variational principle		
combined with $\Sigma^{(2)h}$	2.609	0.583
combined with $\Sigma^{(3)h}$	2.534	0.536
CAP/$\Sigma^{(2)i}$	2.58 ± 0.13[j]	0.55 ± 0.14[j]

TABLE V. Energies and widths of resonances in elastic electron scattering from chlorobenzene. Theoretical values obtained in this work by CAP/SE (static exchange) and CAP/$\Sigma^{(2)}$ are compared with experimental values. We rely on the values of Burrow *et al.* (Ref. 59) because their spectra are well resolved and show both the $^2\Pi$ and $^2\Sigma$ resonances. Note the error of about 5% for the energy and about 25% for the width estimated for the values of CAP/$\Sigma^{(2)}$ due to the incomplete basis set.

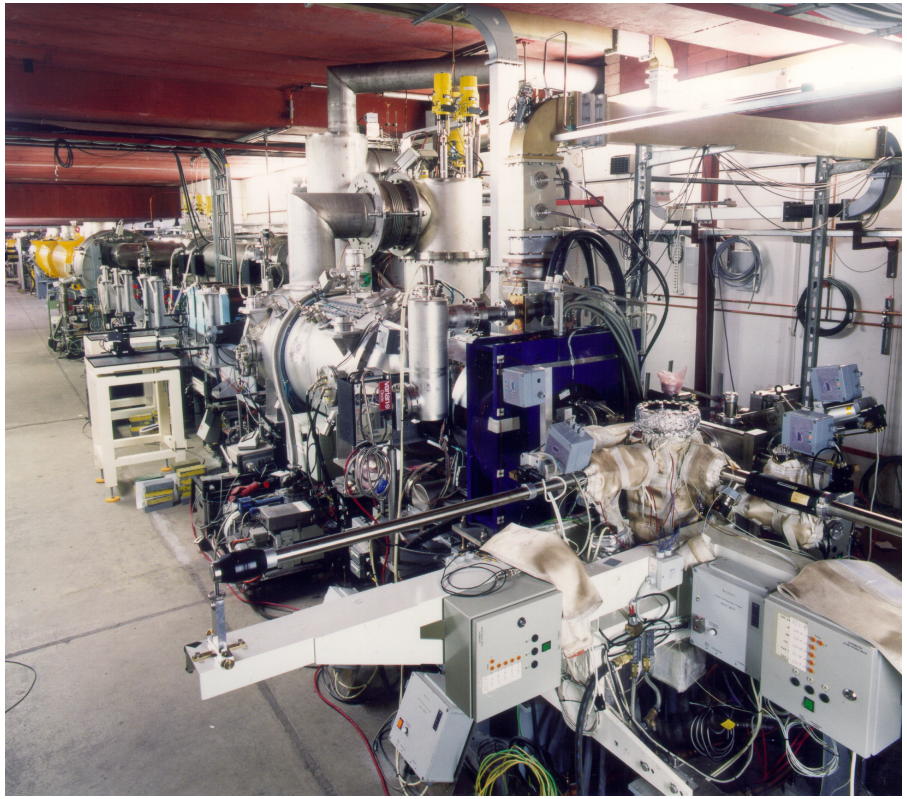
	Energy (eV)			Width (eV)	
Symmetry	Experiment	CAP/SE	CAP/$\Sigma^{(2)}$	CAP/SE	CAP/$\Sigma^{(2)}$
A_1	2.42	5.41	2.92	1.84	1.01
B_1	0.75	2.83	1.27	0.52	0.17
A_2	0.75	2.73	1.29	0.45	0.05



R. Santra and L. S. Cederbaum, J. Chem. Phys. **117**, 5511 (2002).
S. Feuerbacher, T. Sommerfeld, R. Santra, and L. S. Cederbaum, J. Chem. Phys. **118**, 6188 (2003).

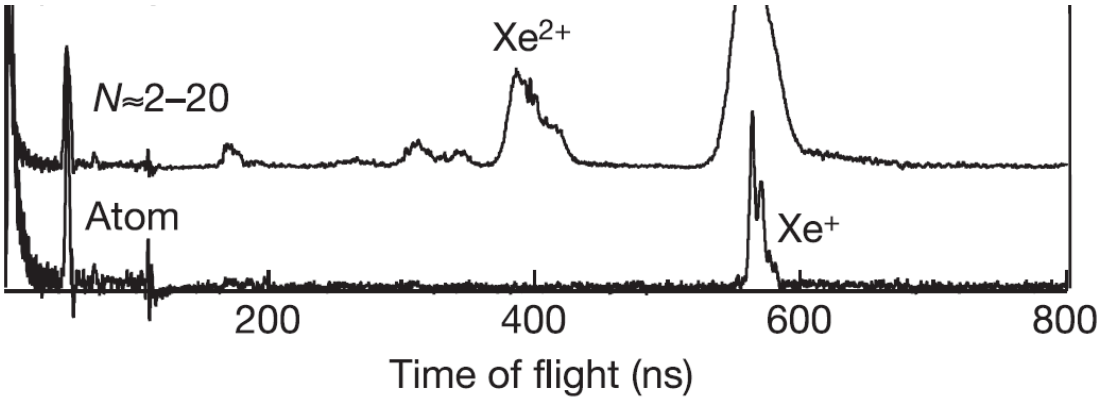
Application of a CAP to the problem of multiphoton ionization of a noble-gas atom

TTF-FEL at DESY (Hamburg)
→ most intense VUV laser



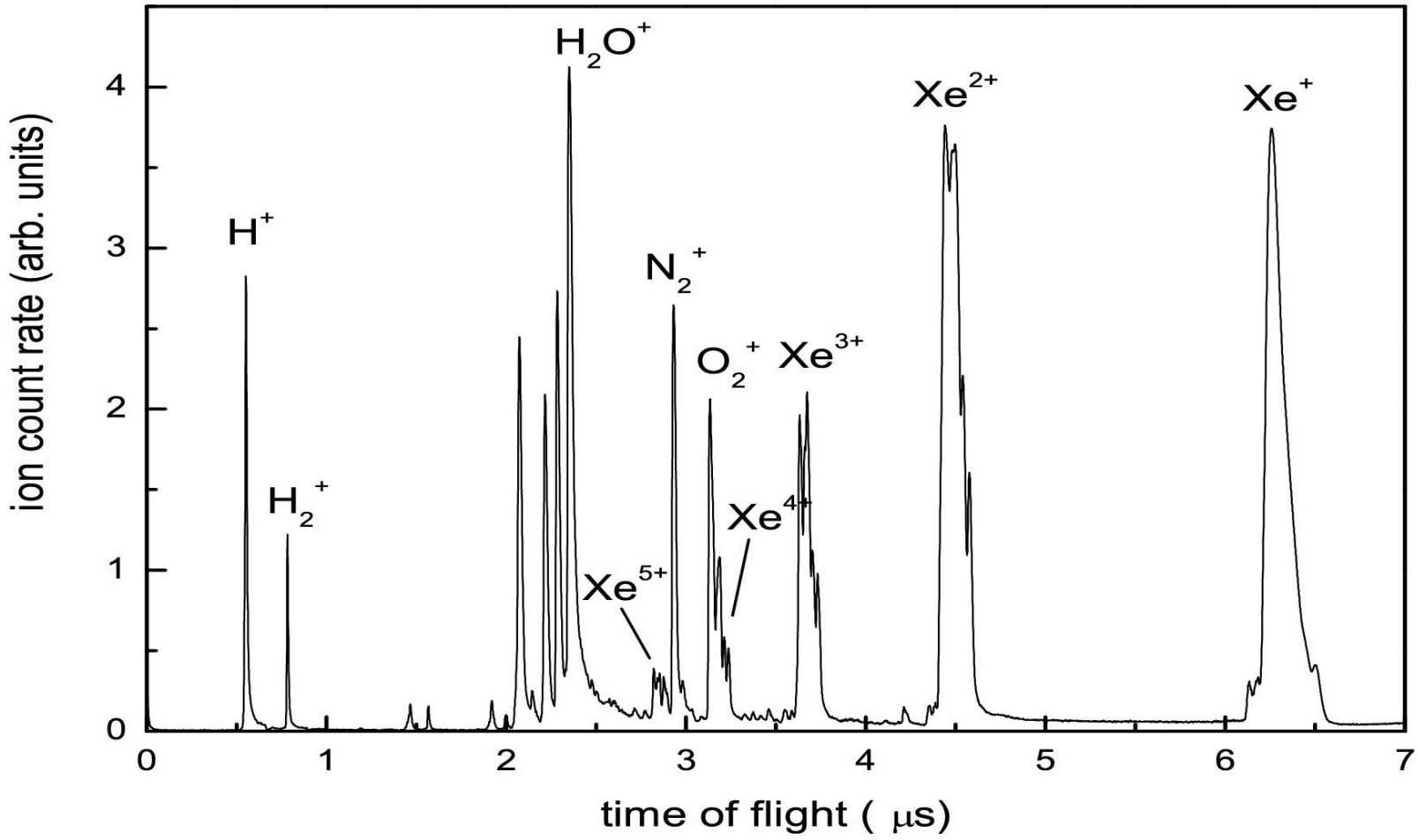
Experiments on atomic xenon (I will not talk about clusters)

- Photon energy = 12.7 eV
- Pulse duration ~ 100 femtoseconds
- Peak intensity ~ 10^{13} W/cm^2
- Following initial measurements, it was believed that TTF-FEL produced only Xe^+ ions (ionization potential of Xe is 12.1 eV)
  [Wabnitz *et al.*, Nature **420**, 482 (2002)]



Experimental mass spectrum (free atoms)

Wabnitz *et al.,* Phys. Rev. Lett. **94**, 023001 (2005)



Hamiltonian

$$H = H_{\mathrm{AT}} + H_{\mathrm{EM}} + H_{\mathrm{I}} - \mathrm{i}\eta W$$

$$H_{\mathrm{AT}} = -\frac{1}{2}\nabla^2 + V_{\mathrm{HS}}(r)$$

$$H_{\mathrm{EM}} = \sum_{\boldsymbol{k},\lambda} \omega a^{\dagger}_{\boldsymbol{k},\lambda} a_{\boldsymbol{k},\lambda}$$

$$H_{\mathrm{I}} = \boldsymbol{x} \cdot \sum_{\boldsymbol{k},\lambda} \mathrm{i}\sqrt{\frac{2\pi}{V}\omega} \left\{ \boldsymbol{e}_{\boldsymbol{k},\lambda} a_{\boldsymbol{k},\lambda} - \boldsymbol{e}^{*}_{\boldsymbol{k},\lambda} a^{\dagger}_{\boldsymbol{k},\lambda} \right\}$$

$$W(r) = \begin{cases} 0, & 0 \le r < c \\ (r-c)^2, & r \ge c \end{cases}$$

Basis vectors: $\left|\Phi_{n,l,m,\mu}\right\rangle = \left|\psi_{n,l,m}\right\rangle \left|N-\mu\right\rangle$

$\left|\psi_{n,l,m}\right\rangle$: atomic eigenstate

$\left|N-\mu\right\rangle$: Fock state of laser mode

Linear polarization, strong-field limit →

$$\begin{aligned}
\left\langle\Phi_{n,l,m,\mu}\right| H_{\mathrm{AT}} + H_{\mathrm{EM}} \left|\Phi_{n,l,m,\mu}\right\rangle &= \varepsilon_{n,l} - \mu\omega \ , \\
\left\langle\Phi_{n,l,m,\mu}\right| H_{\mathrm{I}} \left|\Phi_{n',l',m,\mu+1}\right\rangle &= \sqrt{2\pi\alpha I}\left\langle\psi_{n,l,m}\right| z \left|\psi_{n',l',m}\right\rangle \\
\left\langle\Phi_{n,l,m,\mu+1}\right| H_{\mathrm{I}} \left|\Phi_{n',l',m,\mu}\right\rangle &= \sqrt{2\pi\alpha I}\left\langle\psi_{n,l,m}\right| z \left|\psi_{n',l',m}\right\rangle \\
\left\langle\Phi_{n,l,m,\mu}\right| W \left|\Phi_{n',l,m,\mu}\right\rangle &= \left\langle\psi_{n,l,m}\right| W \left|\psi_{n',l,m}\right\rangle \ .
\end{aligned}$$

$$I = \frac{N}{V}\frac{\omega}{\alpha} \qquad I_0 = E_{\mathrm{h}}/(t_0 a_0^2) = 6.43641 \times 10^{15}\ \mathrm{W/cm^2}$$

Calculated multiphoton ionization cross sections at a photon energy of 12.7 eV

$$\sigma_2\left(\mathrm{Xe}^{+}\right) = 4.6\times10^{-49}\,\mathrm{cm}^4\,\mathrm{s}\,,$$

$$\sigma_3\left(\mathrm{Xe}^{++}\right) = 2.0\times10^{-82}\,\mathrm{cm}^6\,\mathrm{s}^2\,,$$

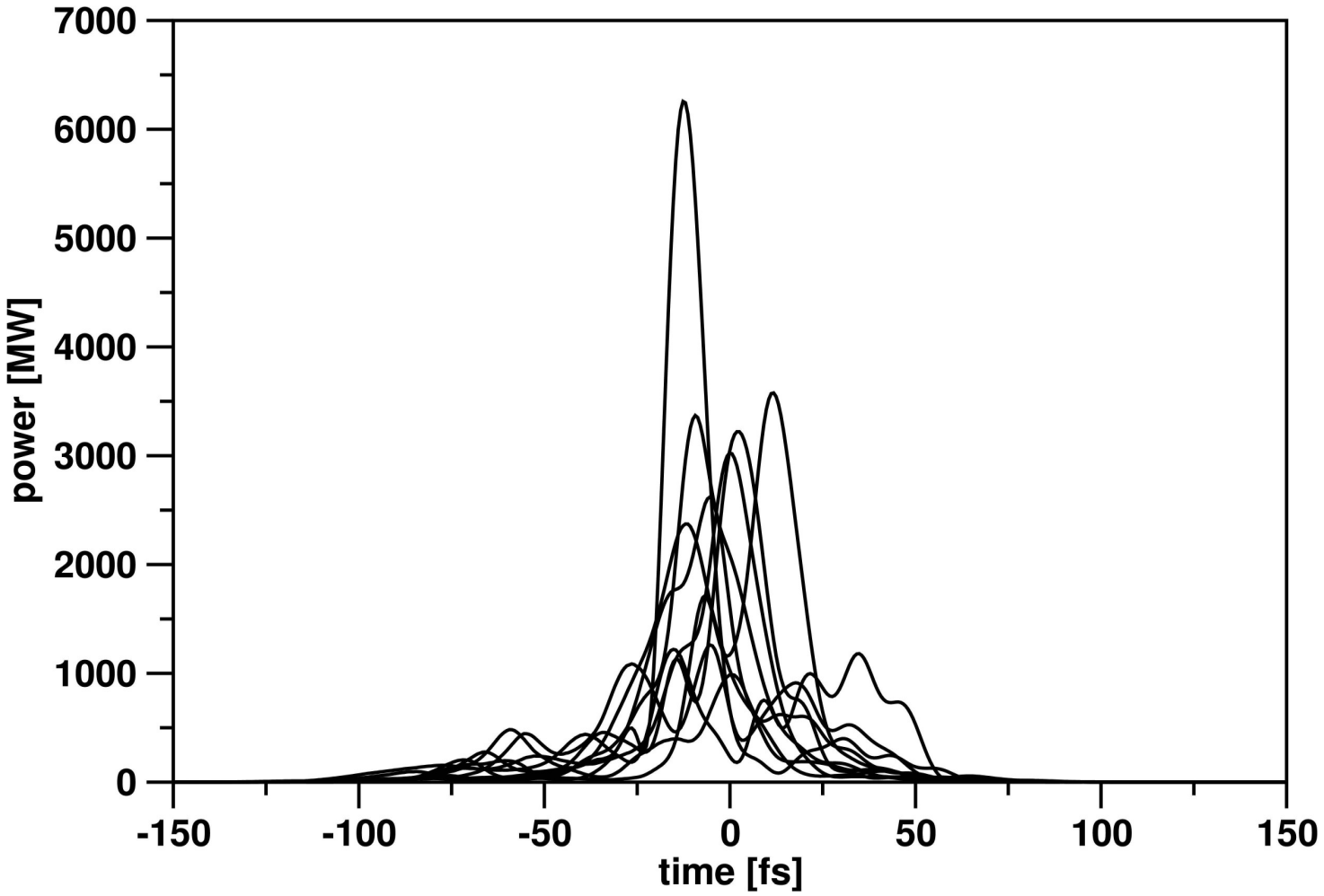
$$\sigma_4\left(\mathrm{Xe}^{3+}\right) = 3.3\times10^{-115}\,\mathrm{cm}^8\,\mathrm{s}^3\,,$$

$$\sigma_5\left(\mathrm{Xe}^{4+}\right) = 3.7\times10^{-147}\,\mathrm{cm}^{10}\,\mathrm{s}^4\,,$$

$$\sigma_6\left(\mathrm{Xe}^{5+}\right) = 6.4\times10^{-179}\,\mathrm{cm}^{12}\,\mathrm{s}^5\,.$$

Santra, Greene, Phys. Rev. A **70**, 053401 (2004)

Simulated VUV-FEL pulses (Mikhail Yurkov et al., *DESY)*



Calculation of expected ionic distribution

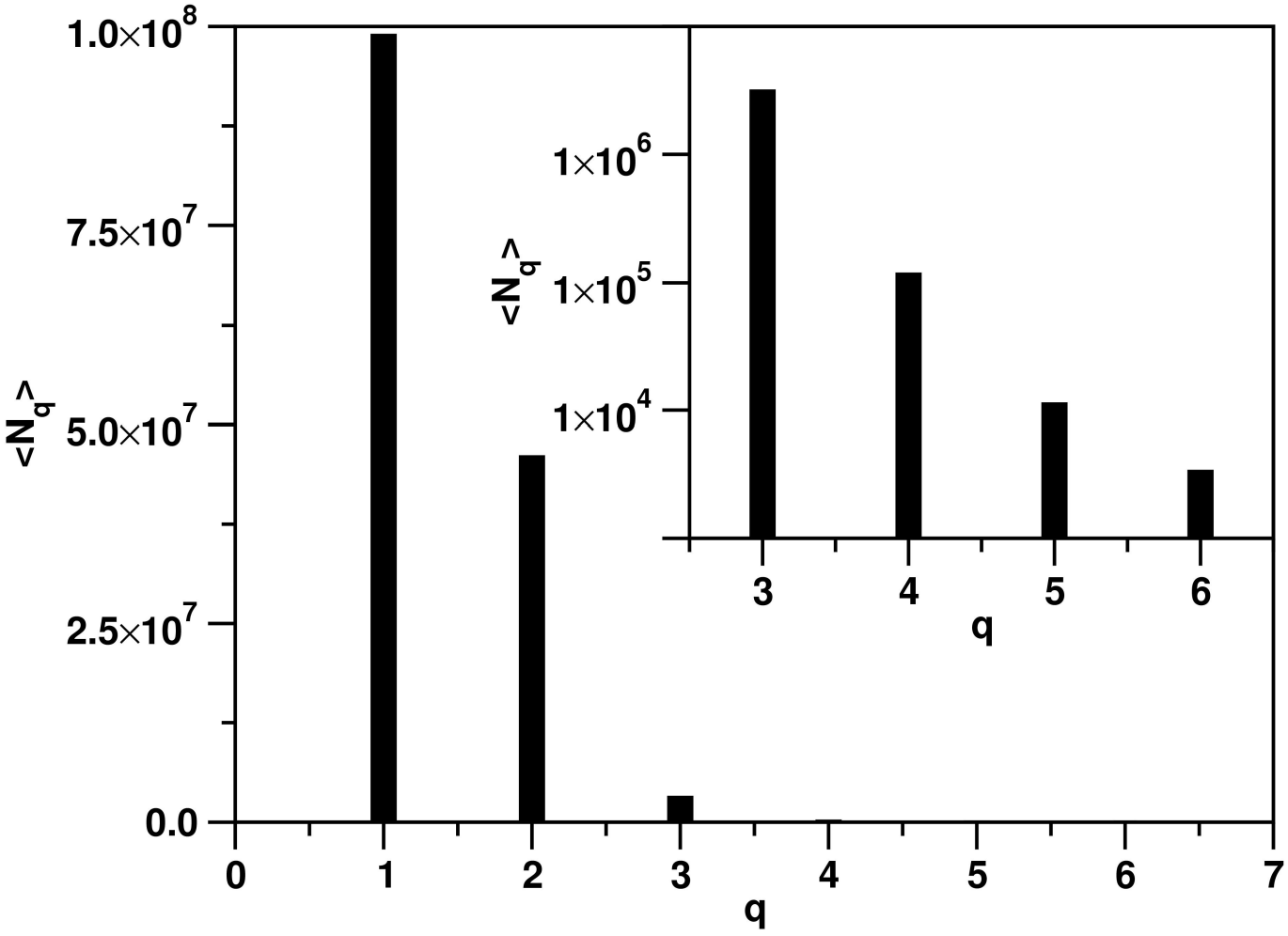
$$I(\rho, z, t) = \frac{4 \ln 2}{\pi \Delta^2(z)} \exp\left(-\frac{4 \ln 2}{\Delta^2(z)} \rho^2\right) P(t)$$

$$\Delta(z) = \Delta \sqrt{1 + (z/z_0)^2}$$

$$\begin{aligned}
\dot{n}_0(\rho, z, t) &= -\sigma_1 \frac{I(\rho, z, t)}{\omega} n_0(\rho, z, t) \ , \\
\dot{n}_1(\rho, z, t) &= \sigma_1 \frac{I(\rho, z, t)}{\omega} n_0(\rho, z, t) - \sigma_2 \left(\frac{I(\rho, z, t)}{\omega}\right)^2 n_1(\rho, z, t) \ , \\
\dot{n}_2(\rho, z, t) &= \sigma_2 \left(\frac{I(\rho, z, t)}{\omega}\right)^2 n_1(\rho, z, t) - \sigma_3 \left(\frac{I(\rho, z, t)}{\omega}\right)^3 n_2(\rho, z, t) \\
&\vdots
\end{aligned}$$

$$N_q = 2\pi\kappa \int_{z_{\min}}^{z_{\max}} \mathrm{d}z \int_0^{\infty} \mathrm{d}\rho \, \rho \, n_q(\rho, z, t \to +\infty)$$

Calculated ionic distribution



Santra, Greene, Phys. Rev. A **70**, 053401 (2004)

Conclusion

- A complex absorbing potential provides a simple and practical approach to the treatment of resonances in quantum mechanics.
- A CAP can be used in conjunction with virtually any computational bound-state method.
- A number of applications of topical interest in atomic, molecular, and optical physics have been treated using a CAP-based approach.