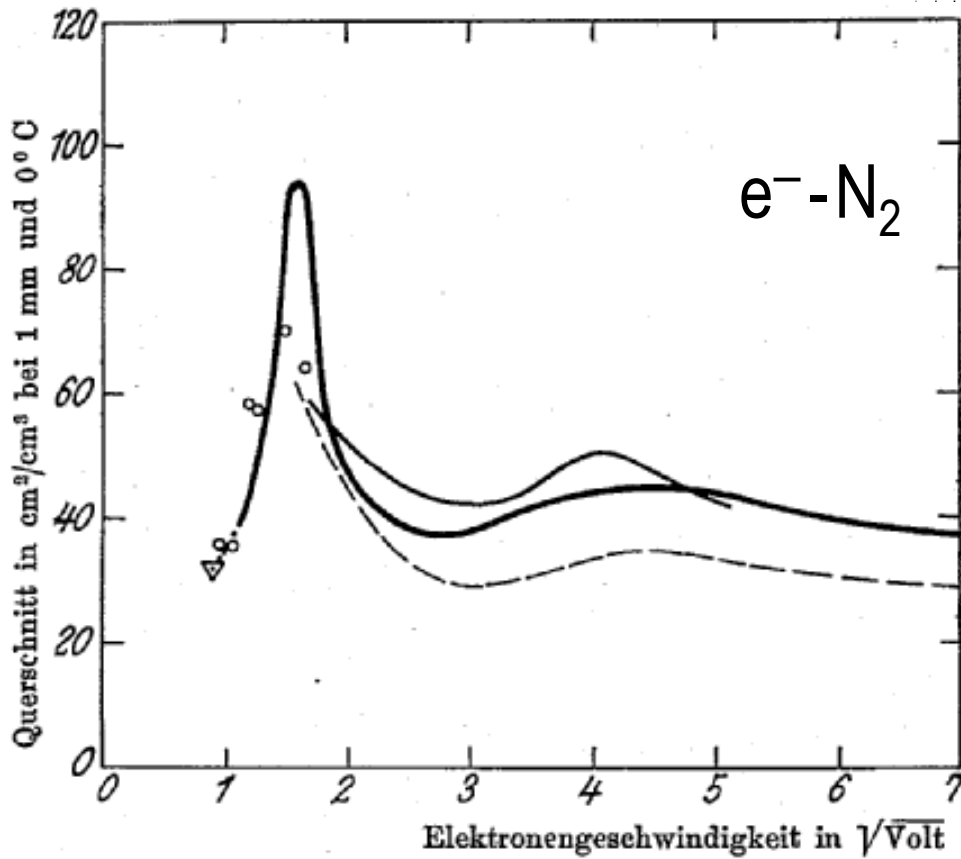# Resonances in Atomic and Molecular Continuum Processes

Isao Shimamura, RIKEN

Peak-shaped resonance in e^--N_2 scattering measured by Brüche (1927)

e^--N_2

electronic resonance

N_2^-

Not exactly Lorentzian due to coupling betw. electronic & internuclear motion

Querschnitt in cm²/cm³ bei 1 mm und 0° C

Elektronengeschwindigkeit in $\sqrt{\text{Volt}}$

Neuere Querschnittsmessungen an Stickstoff

Eigene Messungen { „Ann. I" mit Lenard-Methode . . . ∘ ∘——
{ Diese Arbeit mit Ramsauer-Methode ——

Kurve Hrn. Brodes (vereinfachte Ramsauer-Methode) . —·—·—

Punkt Hrn. Ramsauers . . . . ▽

Fine structure in the resonance profile due to the coupling betw. electronic & internuclear N-N motion
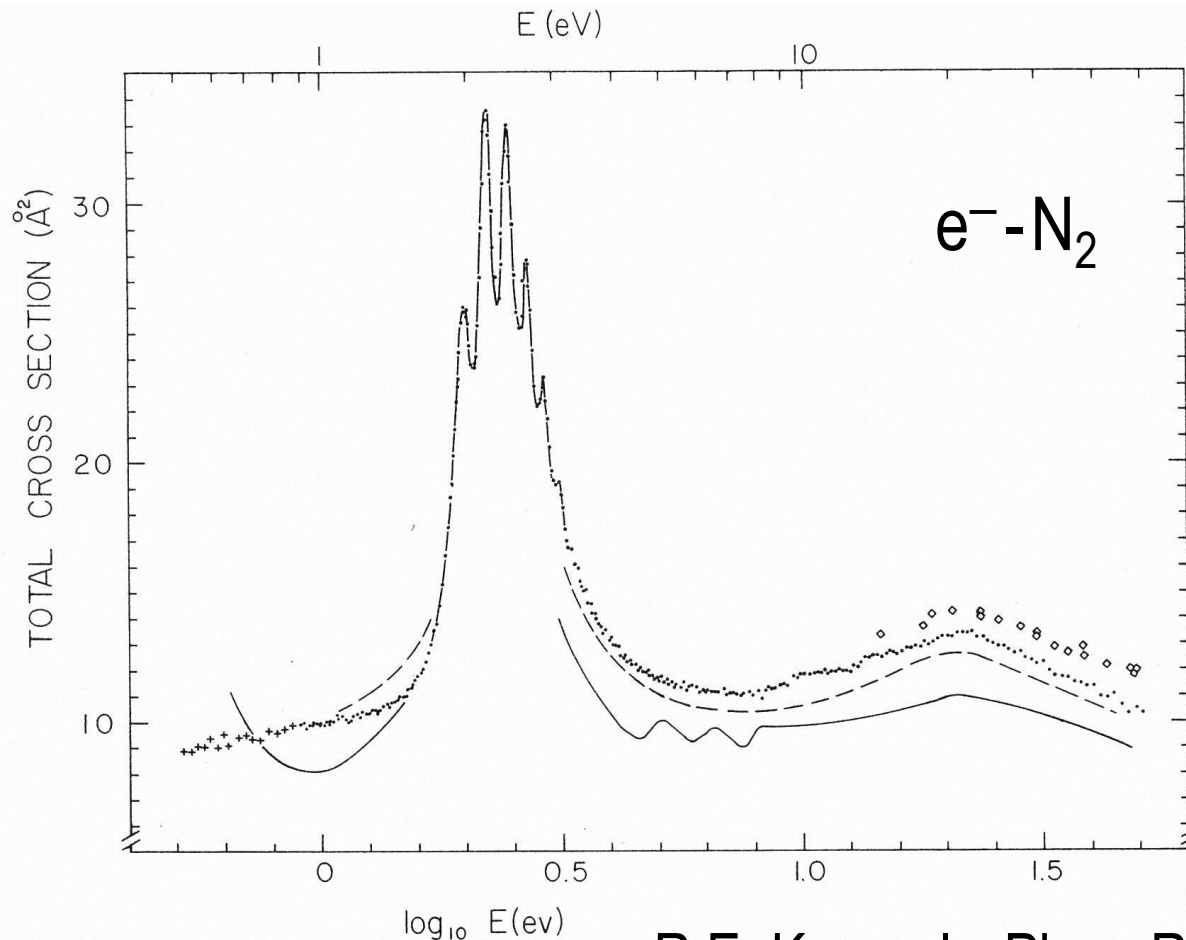
$e^- \text{-} N_2$

FIG. 3. The total cross section for N_2 between 0.5 and 50 eV. The solid circles, ●, and crosses + , depict the present results. The solid curve, ——, represent the results of Normand (Ref. 36) and the dashed curve, -----, those of Brüche (Ref. 37). The open diamonds represent the results of Blaauw *et al.*, but note that de Heer (Ref. 39) has advised that these results should be decreased by 5%.

R.E. Kennerly, Phys. Rev. A **21,** 1876 (1980)

Asymmetrically shaped photoabsorption spectra measured and theory formulated: Beutler-Fano profile

Measurement: H. Beutler, Zeit. f. Phys. **93**, 177 (1935)
Theory: U. Fano, Nuovo Cim. **12**, 154 (1935), directed by E. Fermi
J. Res. Natl Inst. Stand. Tech. **110,** 583 (2005) (Engl. transl.)

Reformulated and generalized: U. Fano, Phys. Rev. **124,** 1866 (1961)

Xe spectrum betw. $Xe^+(^2P_{3/2})$ and $Xe^+(^2P_{1/2})$ thresholds
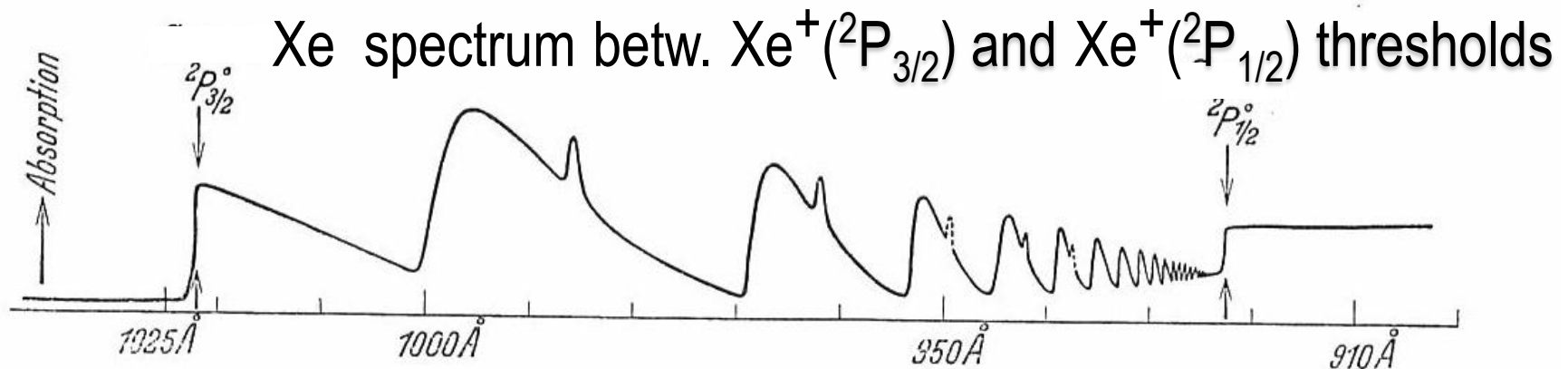

Fig. 2.   Absorption des Xe im Gebiet der Seriengrenzen 1022—922 Å des Bogenspektrums. In Richtung der Ordinate steigt die Absorption an; die Wellenlängen sind an der Abszisse verzeichnet. — Die Figur wurde so gewonnen, daß Aufnahmen bei verschiedenen Xe-Drucken ausgemessen und die Breiten der Absorptionslinien auf Parallelen zur Abszisse abgetragen wurden.

SULLO SPETTRO DI ASSORBIMENTO
DEI GAS NOBILI
PRESSO IL LIMITE DELLO SPETTRO D'ARCO

Nota di Ugo Fano

Sunto. - *Termini spettrali Rydbergiani di un atomo sono talvolta sovrapposti allo spettro continuo di una diversa configurazione. Si studiano teoricamente gli effetti dell'interazione fra le diverse configurazioni in un caso di questo tipo, ottenendo una formula che rappresenta l'andamento dell'intensità dello spettro d'assorbimento. Si giustificano qualitativamente alcuni risultati sperimentali ottenuti da Beutler studiando in assorbimento gli spettri d'arco dei gas nobili e gli spettri I^b di alcuni vapori metallici.*

È noto sperimentalmente che le serie dello spettro d'arco dei gas nobili non convergono verso un unico limite, ma verso due limiti distinti. Ciò si spiega col fatto che, allontanando l'elettrone ottico da un atomo di gas nobile, si ottiene uno ione che non ha come stato fonda-
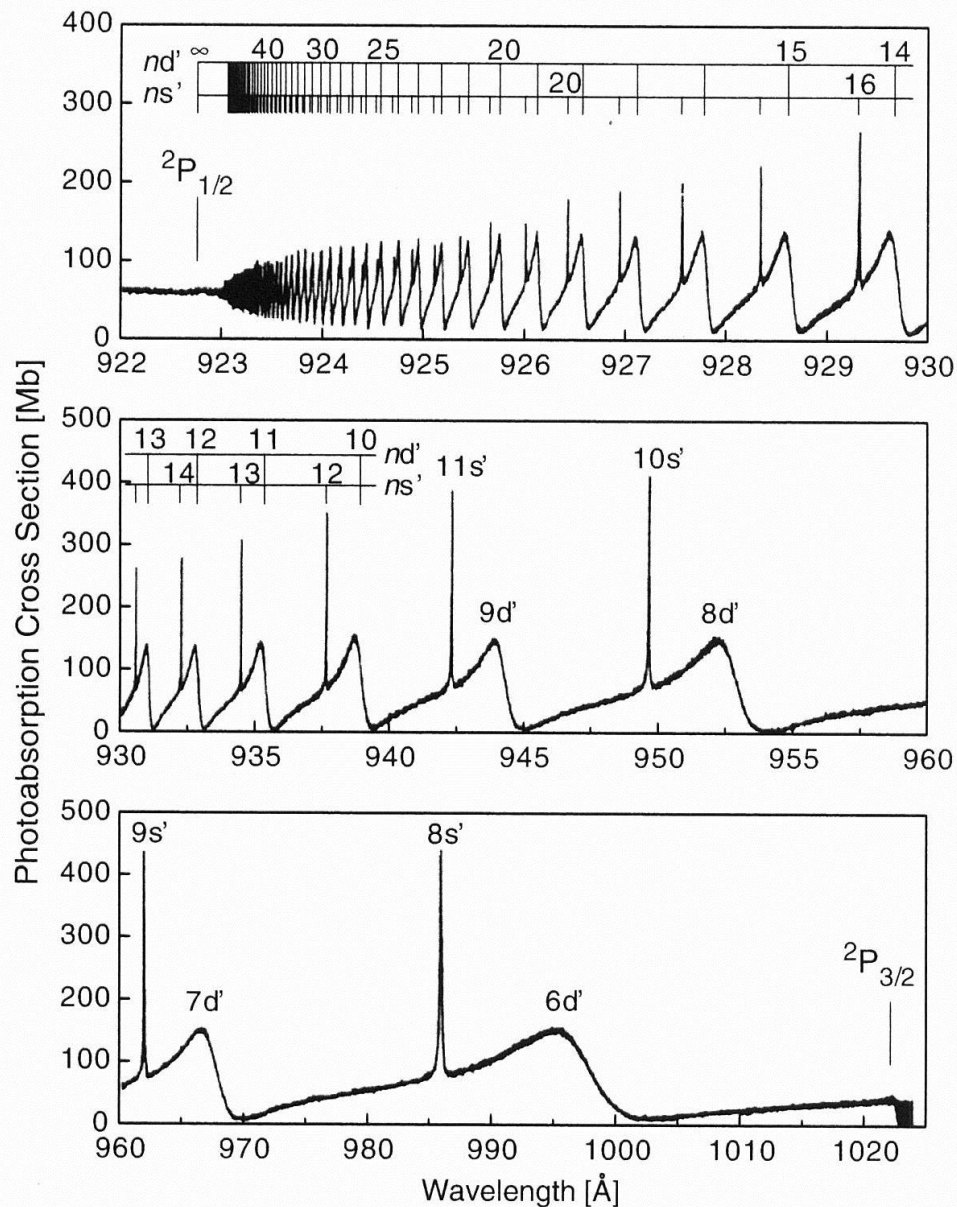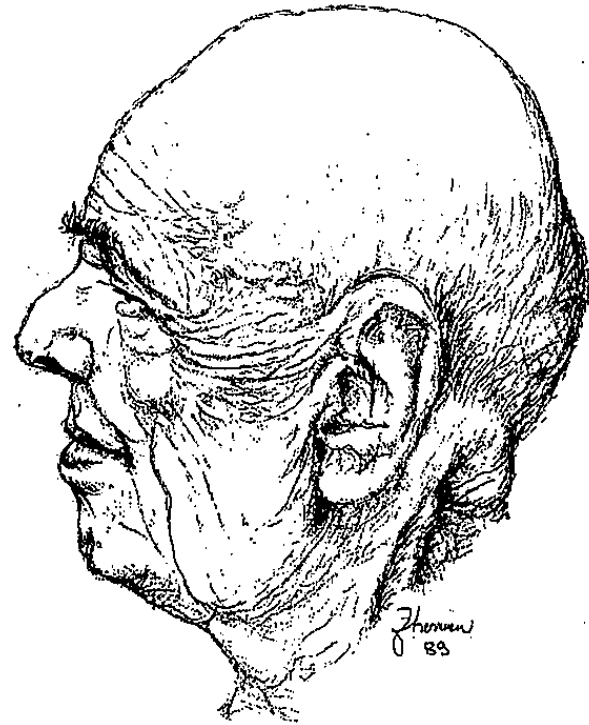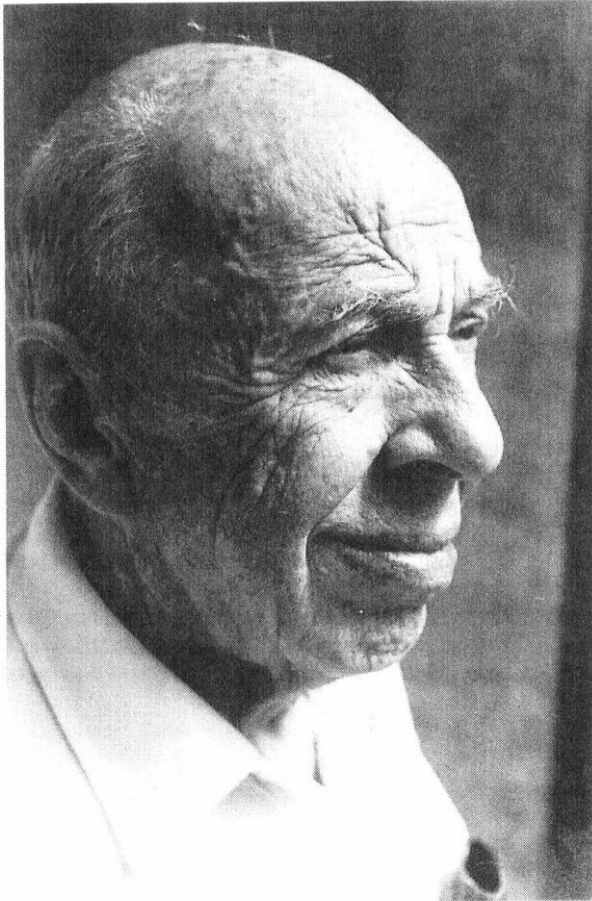
Figure 6. Photoabsorption cross section of ground state Xe atoms between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds measured with a bandwidth (FWHM) of 0.0074 Å (1 Å = 0.1 nm). (Adapted from [15] with permission.)

review:
V L Sukhorukov et al.,
J. Phys. B **45**, 092001 (2012)

Fano's profile（プロフィール，横顔）

Ugo Fano (1912－2001)

Beutler-Fano profile from Breit-Wigner one-level formula for the phase shift: High-school mathematics

Breit-Wigner one-level formula for resonance at $E=E_r-i\Gamma/2$

$$\delta(E) = \delta_b + \delta_r(E) \qquad -\cot\delta_r(E) = \varepsilon \equiv (E - E_r)/(\Gamma/2)$$

reduced energy

$$[4\pi(2l+1)]^{-1}\sigma_l(E) = k^{-2}\sin^2(\delta_b + \delta_r)$$

$$= \frac{(\cot\delta_r + \cot\delta_b)^2}{k^2(1 + \cot^2\delta_b)(1 + \cot^2\delta_r)}$$

$q \equiv -\cot\delta_b(E)$
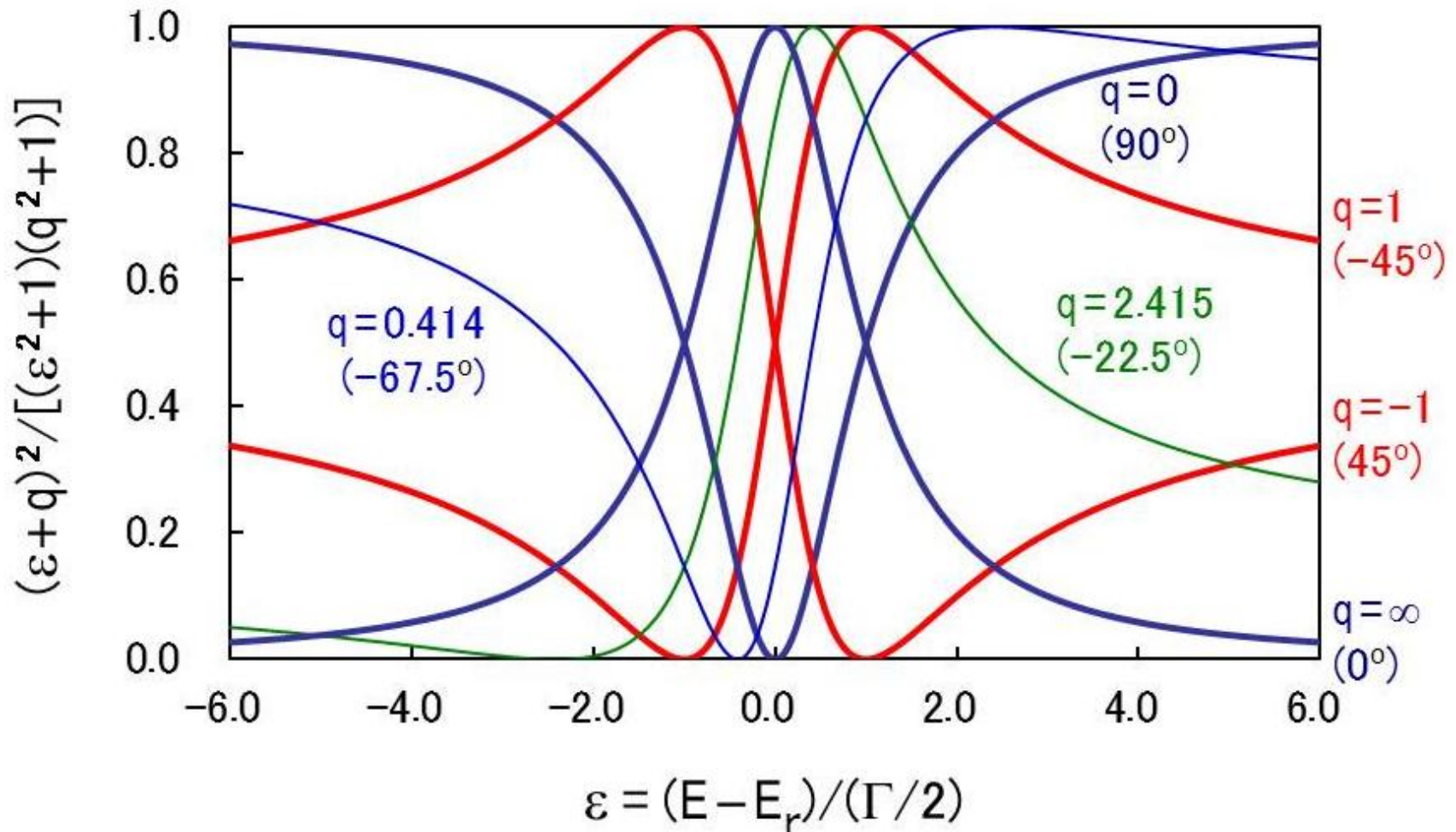shape parameter

$$= \frac{(\varepsilon + q)^2}{k^2(1 + q^2)(1 + \varepsilon^2)} = \frac{(1 + \varepsilon/q)^2}{k^2(1 + q^{-2})(1 + \varepsilon^2)}$$
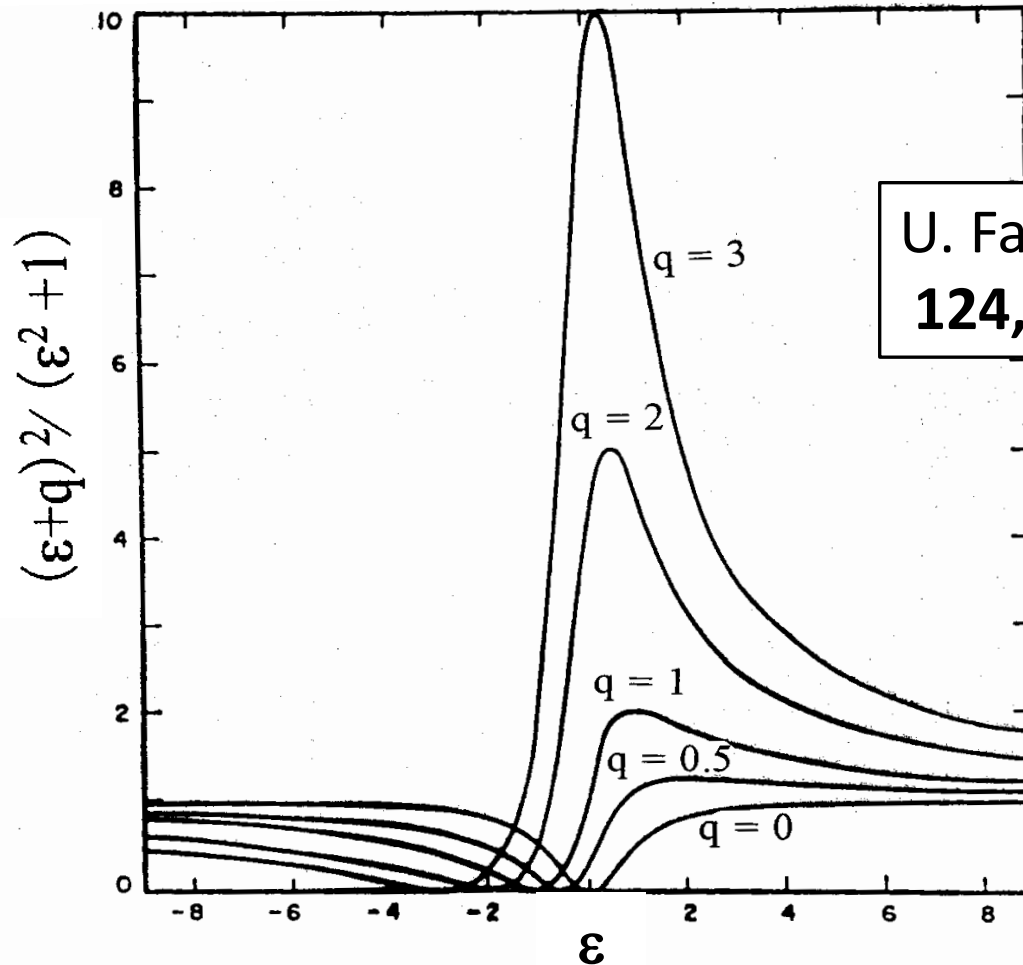
Beutler-Fano profile

The variety of profiles stems from the interference between the resonance and the background.

Beutler-Fano profile for a resonance at $E=E_r-i\Gamma/2$

$$\delta(E) = \delta_r(E) + \delta_b, \quad \varepsilon = -\cot\delta_r, \quad q = -\cot\delta_b$$

Vertical axis: $(\varepsilon+q)^2/[(\varepsilon^2+1)(q^2+1)]$

Horizontal axis: $\varepsilon = (E-E_r)/(\Gamma/2)$

Curve labels:
- $q=0$ (90°)
- $q=1$ (-45°)
- $q=2.415$ (-22.5°)
- $q=-1$ (45°)
- $q=\infty$ (0°)
- $q=0.414$ (-67.5°)

Original figure in U. Fano (1961)

U. Fano, Phys. Rev. **124,** 1866 (1961)

Ugo Fano's theory

Mixing betw. bound (Φ) and continuum (ψ) configurations

for any transition operator

May be re-interpreted (similarly to Feshbach) as:

$$Q = |\Phi\rangle\langle\Phi|, \quad Q\Phi = \Phi, \quad H_Q \equiv QHQ = \langle\Phi|H|\Phi\rangle Q = E_Q Q$$
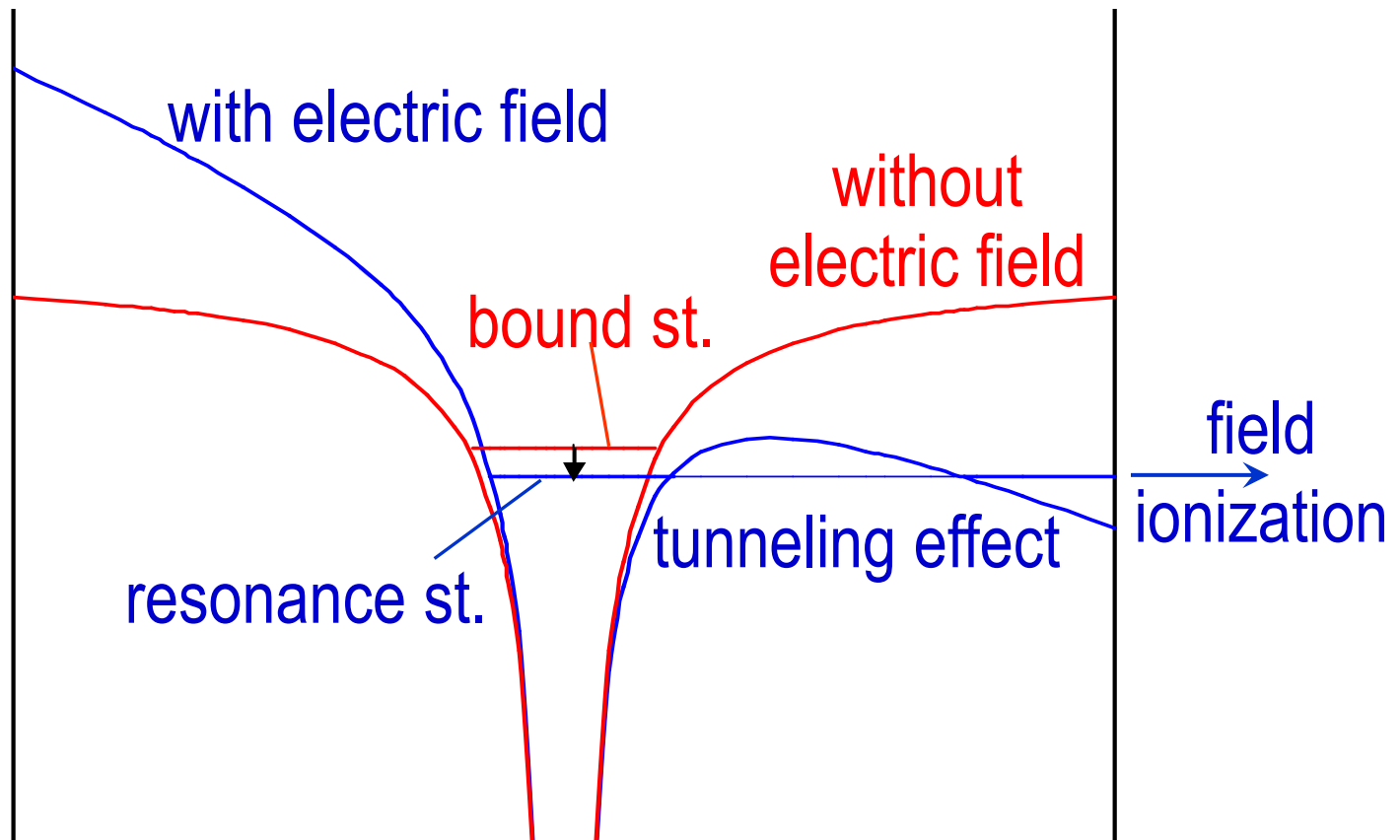
$$\therefore E_Q(Q\Phi) = H_Q(Q\Phi), \quad H = H_Q + H' \rightarrow E_r = E_Q + \Delta E \text{ and } \Gamma$$

- isolated resonance for one open channel
- isolated resonance for more than one open channel
- overlapping resonances for one open channel
- NOT for overlapping resonances for more than one open channel

Stark effect: Perturbation by static electric field

$$Q = |\Phi\rangle\langle\Phi|, \quad Q\Phi = \Phi, \quad H_Q \equiv QHQ = \langle\Phi|H|\Phi\rangle Q = E_Q Q$$

$$\therefore E_Q(Q\Phi) = H_Q(Q\Phi), \quad H = H_Q + H' \rightarrow E_r = E_Q + \Delta E \text{ and } \Gamma$$

$$Q = |\Phi\rangle\langle\Phi|, \quad Q\Phi = \Phi, \quad H_Q \equiv QHQ = \langle\Phi|H|\Phi\rangle Q = E_Q Q$$

$$\therefore E_Q(Q\Phi) = H_Q(Q\Phi), \quad H = H_Q + H' \rightarrow E_r = E_Q + \Delta E \text{ and } \Gamma$$

Atomic/molecular physics is rich in resonances.

For example,

an infinite series of eigenstates of QHQ

coupled to continuum produces

an infinite series of Feshbach resonances.

Asymptotic Coulomb potential $\propto -\alpha/r$

Neutral atom A:

electron-ion interaction $\mathrm{e}^- - \mathrm{A}^+(E_+)$
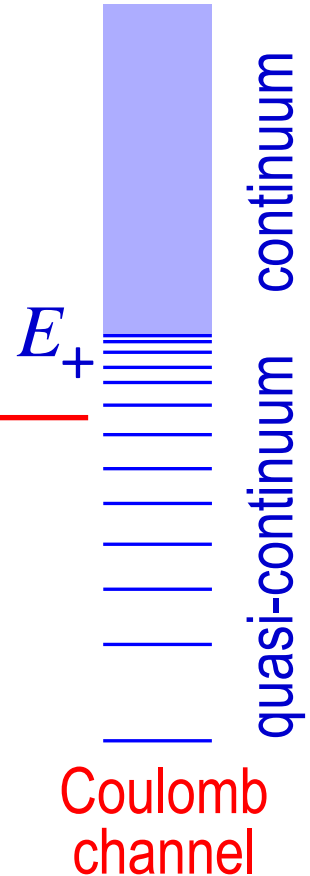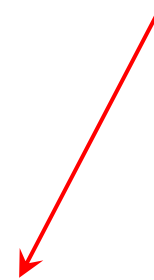
Infinite series of bound Rydberg states

$$E_{nl} = E_+ - [2(n-\mu_{nl})^2]^{-1} \text{ a.u.}$$

μ_{nl} quantum defect:

slowly varying with n (or E_{nl})

intruder

sudden increase of μ_{nl} by 1

resonance-like behavior

E_+

continuum

quasi-continuum

Coulomb channel
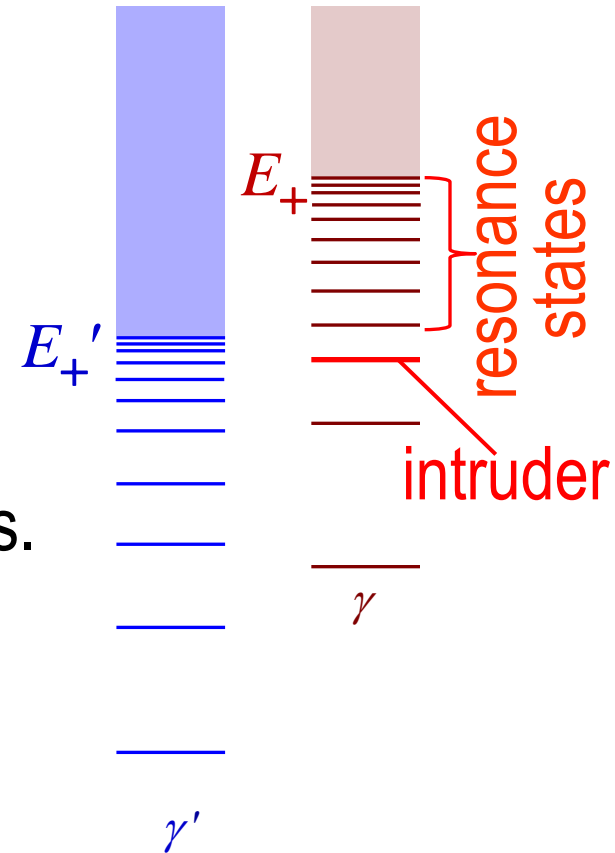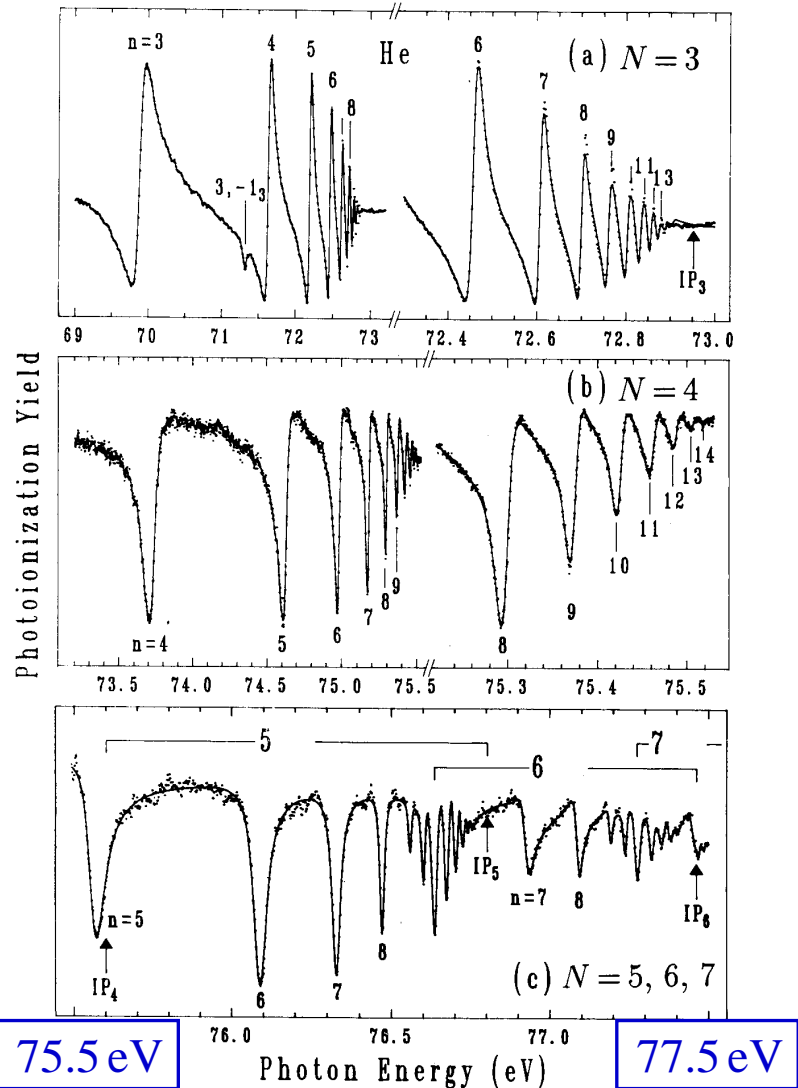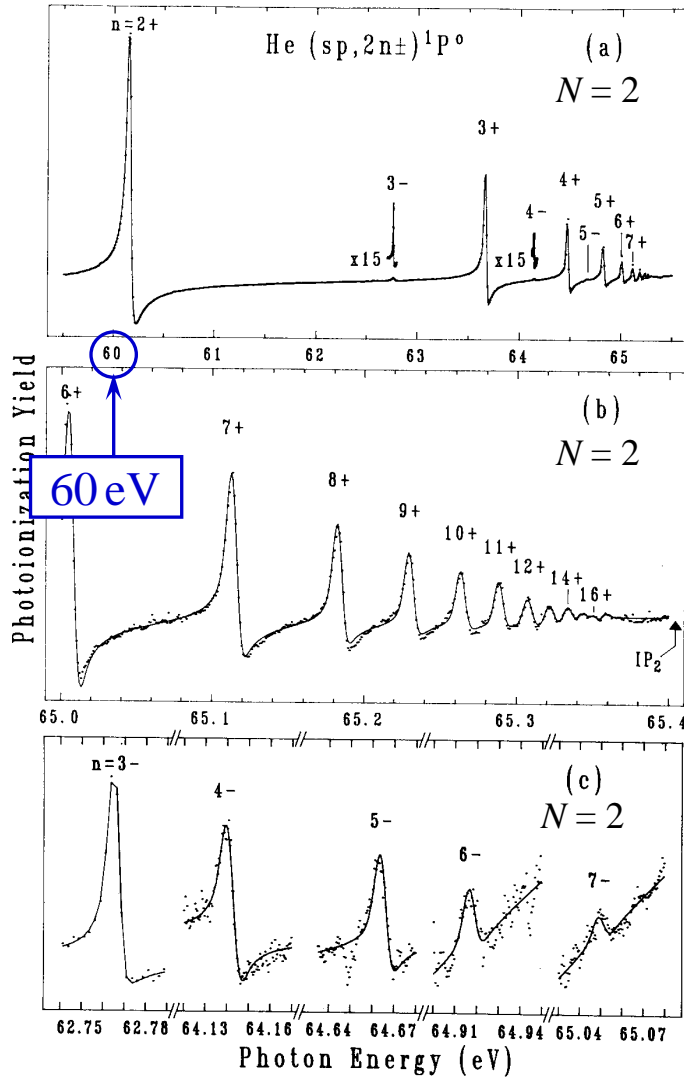
Coupled Coulomb channels

Multichannel Quantum Defect Theory:

Theory similar to multichannel scattering
theory leads to elucidation of the regularity
in the bound and resonance Rydberg series.

E_+

$E_+{'}$

resonance states

intruder

γ

$\gamma{'}$

Photoabsorption spectra of He atom
$(60\,\text{eV} < h\nu < 78\,\text{eV})$

He $(sp, 2n\pm)^1 P^o$ (a) $N = 2$

(b) $N = 2$

60 eV

(c) $N = 2$

(a) $N = 3$ He

(b) $N = 4$

(c) $N = 5, 6, 7$

75.5 eV   77.5 eV

Photon Energy (eV)

Photoionization Yield

M. Domke et al., Phys. Rev. Lett. **66**, 1306 (1991)

Energy diagram of helium
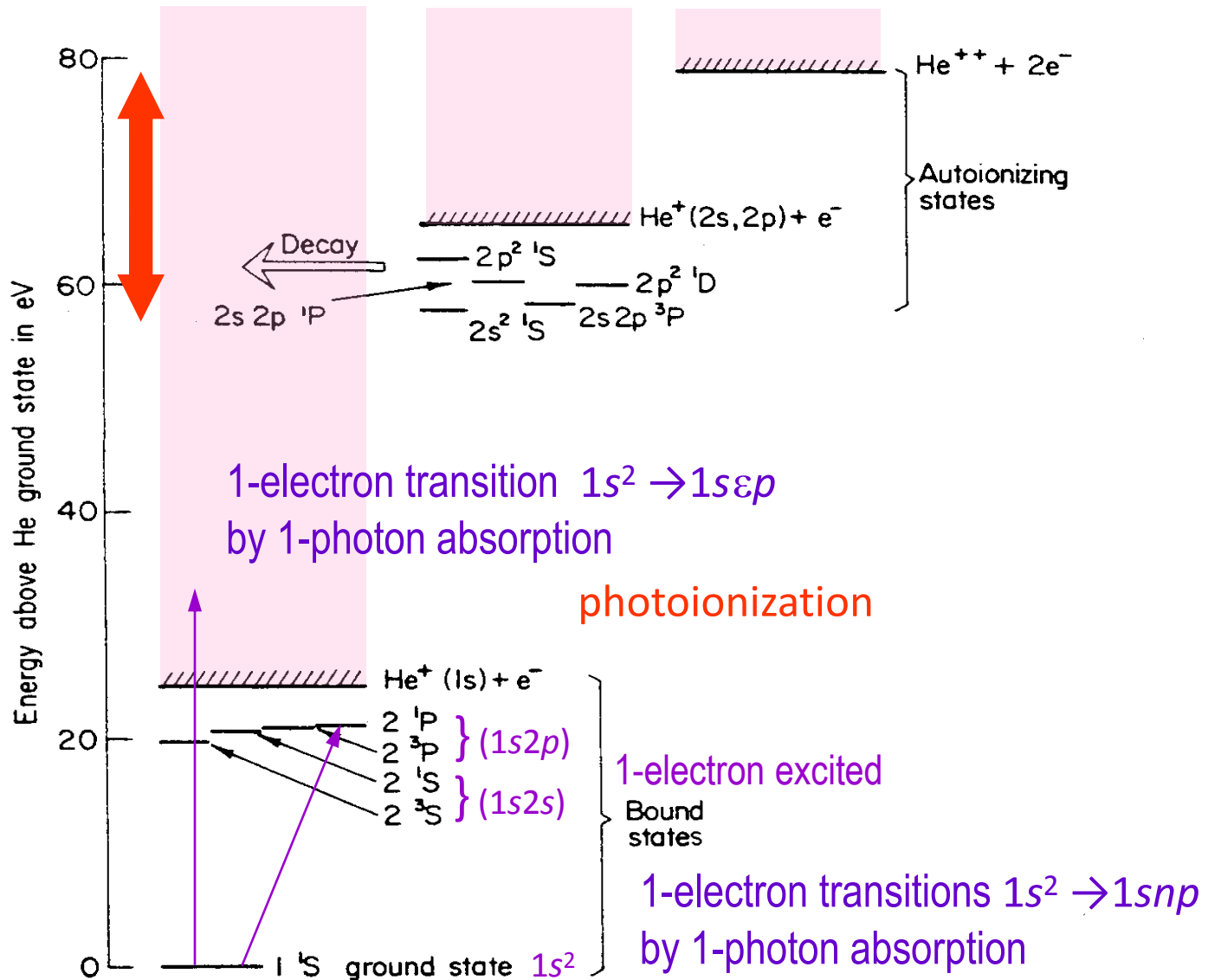
Bound states and autoionizing states of helium.

Atomic/molecular physics is rich in resonances.

infinite series of eigenstates of QHQ

 due to the long-range Coulomb potential $\propto -\alpha/r$

 due to over-critical attractive dipole potential $\propto -\beta/r^2$

$\rightarrow$ infinite series of resonances by coupling with continuum
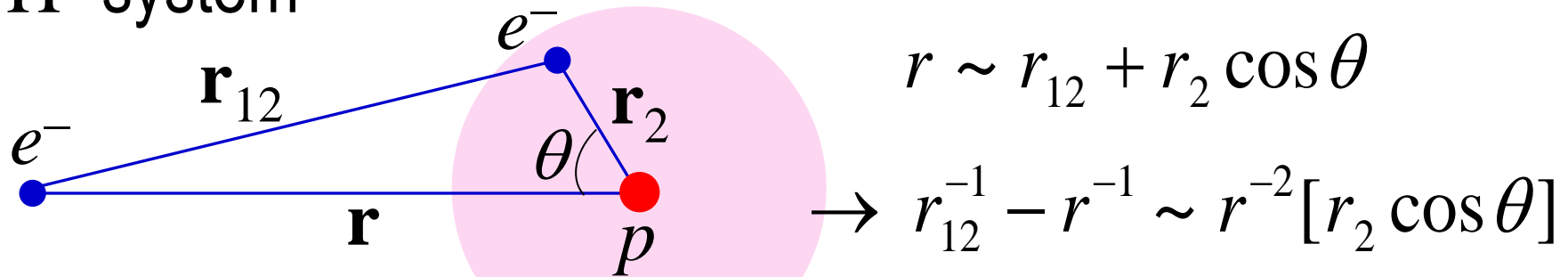
Infinite series of bound states are supported by a potential
 with an asymptotic form $\sim -\beta/r^2$ for $\beta > \beta_l$
 for an angular-momentum-dependent critical value β_l

e⁻ + H(nl) channels

H⁻ system

$$r \sim r_{12} + r_2 \cos\theta$$

$$\rightarrow r_{12}^{-1} - r^{-1} \sim r^{-2}[r_2 \cos\theta]$$

Asymptotic dipole potential couples nl and nl' channels
with $l' = l \pm 1$ with a common channel energy k_n^2
(common because of the sublevel degeneracy).
$\rightarrow$ Diagonalization of the asymptotic potential matrix $\propto r^{-2}$
results in diagonal dipole potentials $\propto r^{-2}$,
i.e., in decoupled single-channel dipole potentials.
If overcritical, they support infinite series of bound states.

Other dipole-supported series of states

- Electron (or positron) bound by a polar molecule having a dipole moment μ $\qquad V(r) \propto \mu \cos \chi / r^2$
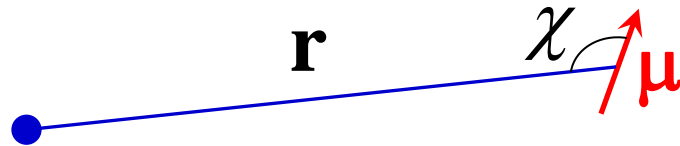

- Efimov states bound by a dipole potential in terms of the hyperradius

Types of resonance states
in atomic/molecular systems

- autoionizing Rydberg states: series coupling
- two or more electrons excited
- inner-shell electron(s) excited
- Feshbach resonances with respect to vibrational excitation
- electronically & vibrationally excited molecules
- predissociating states

Vibrationally excited Rydberg states
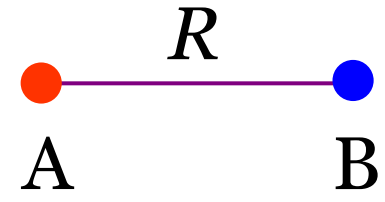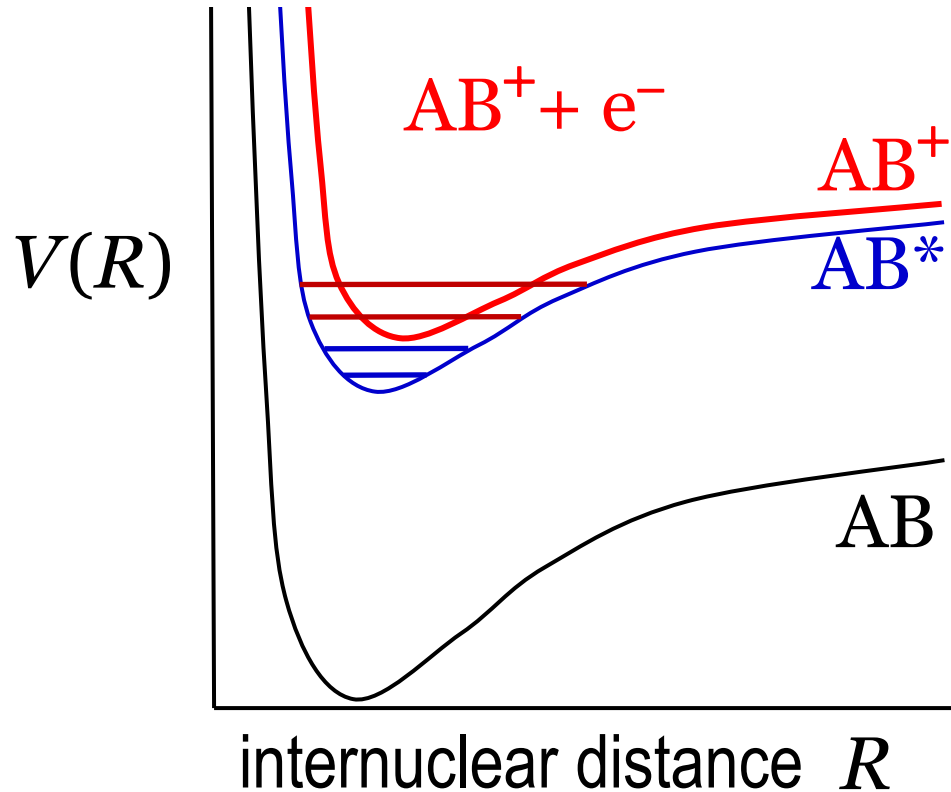
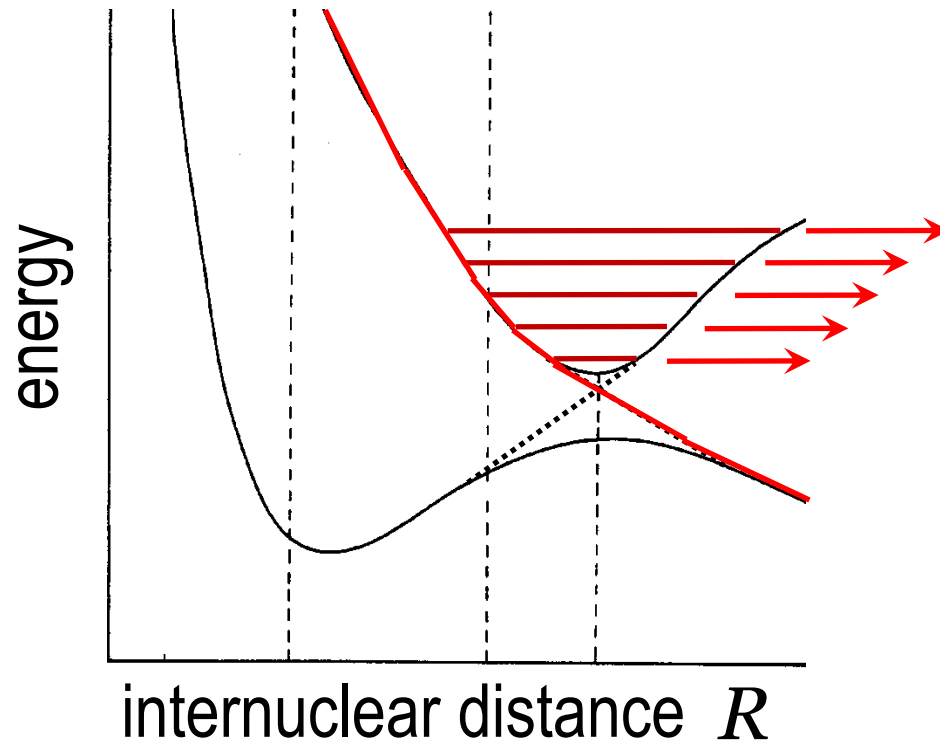# Vibrational predissociation

Nonadiabatic coupling of a bonding adiabatic state with a repulsive adiabatic state turns vibrational states into dissociative states.
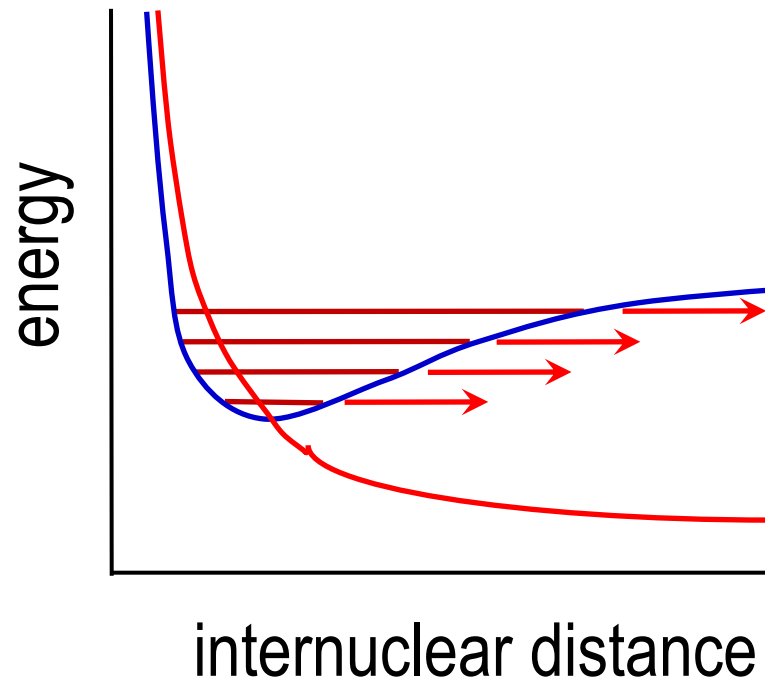
Vibrational predissociation

An adiabatic electronic state turns into a replusive diabatic state by nonadiabatic coupling with a lower adiabatic electronic state.

Atomic and molecular processes

- low-E electron impact on atoms
    compound-state resonances
- low-E electron impact on molecules
    compound-state resonances decaying into
    different arrangement channels
- high-E electron impact on atoms/molecules
    excitation of the target into resonance states
- low E ion-atom, atom-atom collisions
- atom-molecule, molecule-molecule collisions
    direct and reactive processes
- high-E ion-atom collisions
- single-photon absorption
    two(or more)-electron excited states
    Auger processes (inner-shell excitation)
- multiphoton absorption

Standard computational methods for resonances

- Direct calculation of $E_{\mathrm{r}} - i\Gamma/2$

  $\rightarrow$ No observable physical quantities

  e.g.: complex coordinate scaling $r \rightarrow re^{i\theta}$

  For molecules, exterior complex scaling, or scaling
  only outside of a sphere enclosing the molecule

- S- or K-matrix calculation $\rightarrow$ resonance information

  Coupled-channel equations

  defined in terms of the target and/or projectile states
  or of the adiabatic states of the whole system

  R-matrix method

  Kohn or Schwinger variational method

R-matrix method: Concept

Example: electron-molecule collision $e^- $ - M

external region

internal region

a

molecule M
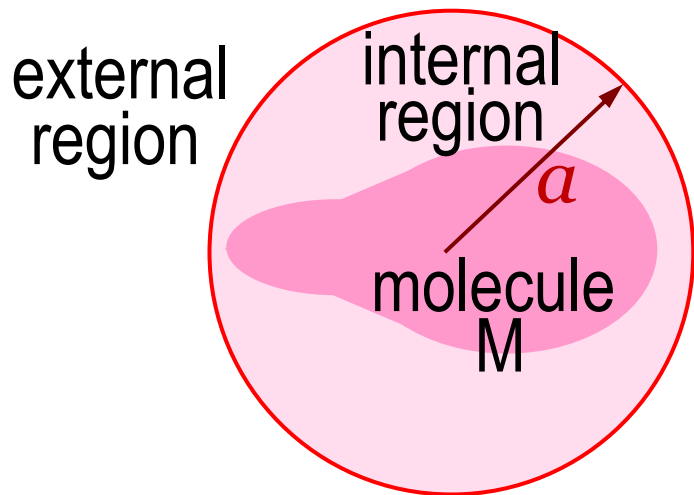
Internal $(r<a)$

quantum-chemistry-like calculation
of the total system M^-

$\rightarrow \psi' \psi^{-1}$ of channel wave func. at $r=a$

External $(r>a)$

coupled-channel calculation with
local potentials (multipole explansion)

channel wave funcs. connected smoothly at $r=a$

R-matrix method: General computer codes

- Electron-atom (ion) and positron-atom (ion) collisions
  automatic search/fitting of resonances
- Electron-molecule and positron-molecule collisions
- Atomic and molecular bound-state calculations
- Photoionization of atoms and molecules
- Multiphoton processes:
  time-independent and time-dependent approaches

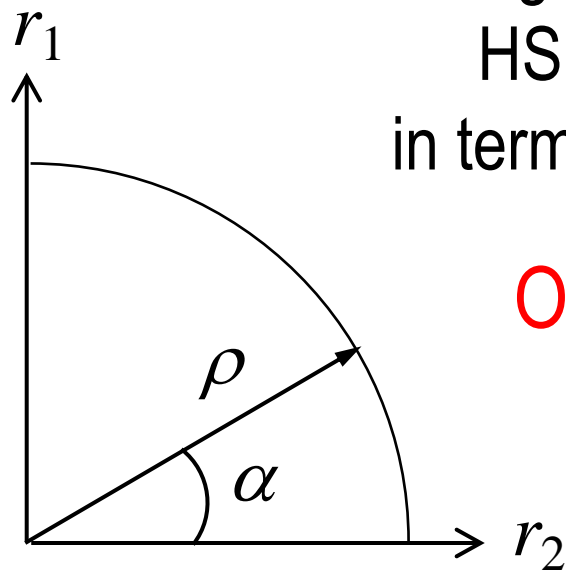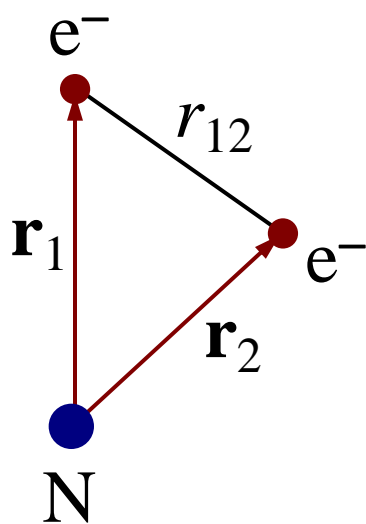P. G. Burke, R-matrix theory of atomic collisions,
(Springer, Heidelberg, 2011)

Coordinate system

- independent-particle coordinates

    $\rightarrow$ Jacobi coordinates

- complex coordinates

- hyperspherical (HS) coordinates

    for few-body systems

Hyperspherical coordinates: Two-electron systems

$(\mathbf{r}_1, \mathbf{r}_2) \rightarrow (\rho, \alpha)$ polar coordinates

hyperradius ρ, hyperangle α $(\mathbf{r}_1, \mathbf{r}_2) \rightarrow (\rho, \Omega) = (\rho, \alpha, \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$
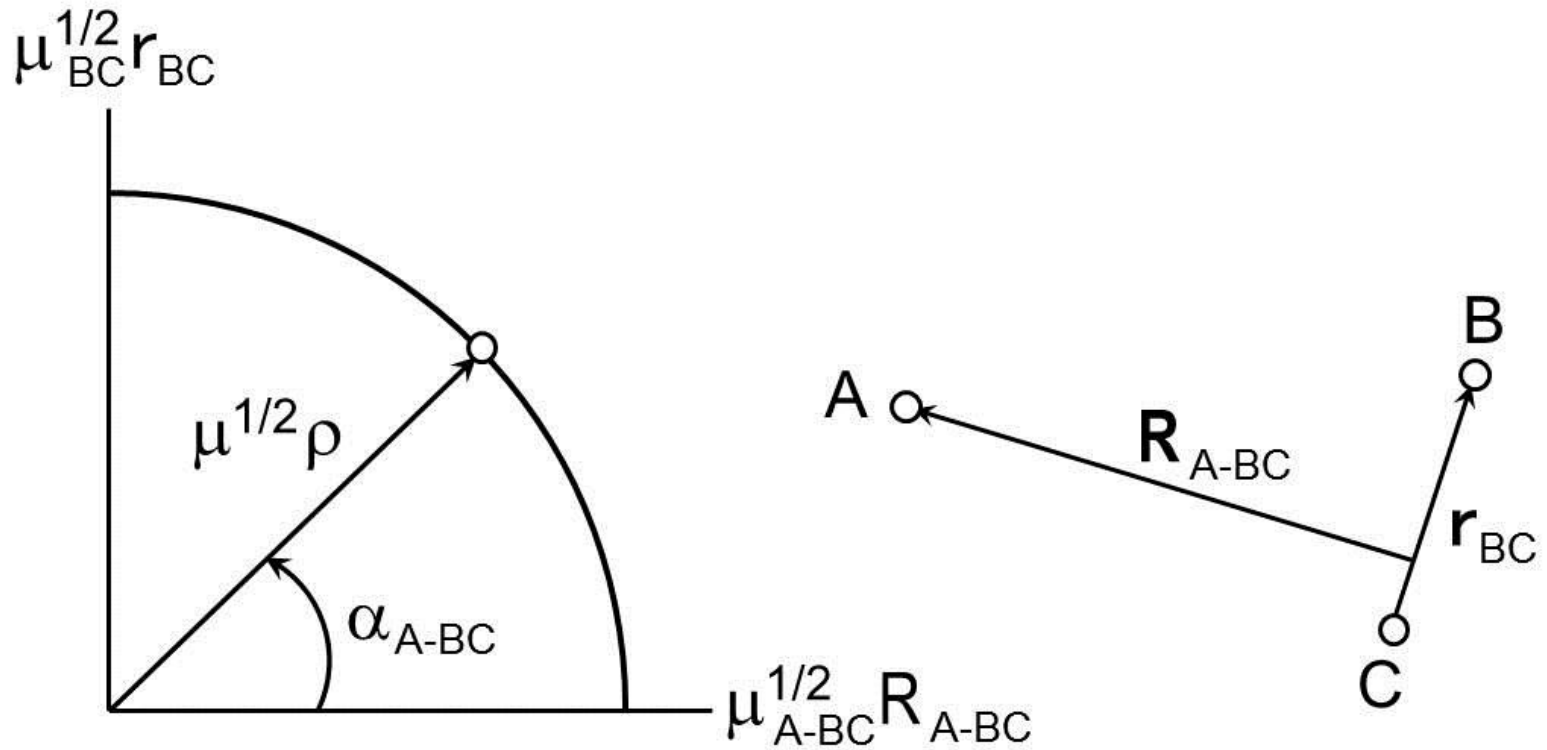

For general three-body systems:
HS coordinates are defined
in terms of the Jacobi coordinates.

Only a single coordinate
extends to infinity.

Extension for N-body systems:
$0 \leq \rho < \infty$, others: angular coord.

Hyperspherical coordinates: General 3-body systems

Applications of hyperspherical coordinates

- Efimov states

  dipole-supported states in terms of ρ

- Coulomb three-body systems

  complete breakup expressible by $\rho \rightarrow \infty$

  asymptotic form for 3-body breakup known

- HS coupled-channel equations in ρ

- Concept of new correlation quantum numbers

Coulomb three-body breakup

For scattering by $V(r)$ with asymptotic form $\sim (\hbar^2/2m)\,\zeta/r$

$$\psi(\mathbf{r}) \xrightarrow[r\to\infty]{} \exp\left[\,ikz + i\,(\zeta/2k)\ln\{2kr\sin^2(\theta/2)\}\,\right]$$

$$+ f(\theta)\,r^{-1}\exp\left[\,ikr - i\,(\zeta/2k)\ln 2kr\,\right]$$

For breakup $\qquad \mathrm{e}^- + \mathrm{H} \to \mathrm{e}^- + \mathrm{p} + \mathrm{e}^-$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) \xrightarrow[r_1,r_2,r_{12}\to\infty]{} [\text{initial channel}]$$

$$- f(\Omega)(i\kappa^3/\rho^5)^{1/2}\exp[i\kappa\rho + i\{\zeta(\Omega)/\kappa\}\ln 2\kappa\rho]$$

$$\zeta(\Omega)/\rho = \zeta(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\alpha)/\rho \equiv -[V_1 + V_2 + V_{12}] = r_1^{-1} + r_2^{-1} - r_{12}^{-1}$$

$$\text{total energy} \quad E = (\hbar^2/2m)\kappa^2$$

R.K. Peterkop, Opt. Spectrosc. **13,** 87 (1962)
M.R.H. Rudge and M.J. Seaton, Proc. R. Phys. Soc. **283,** 262 (1965)
M.R.H. Rudge, Rev. Mod. Phys. **40,** 564 (1968)
Review: McCurdy et al., J. Phys. B **37**, R137 (2004)

Hyperspherical coupled-channel equations

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (\rho^{5/2} \sin 2\alpha)^{-1} \psi(\rho, \Omega)$$

$$H\psi = E\psi, \quad H = H(\rho, \Omega) = T_\rho + \Lambda^2(\Omega)/2\rho^2 + V$$

$$\psi(\rho, \Omega) = \sum u_n(\rho)\, \Phi_n(\Omega) \rightarrow \quad \text{coupled-channel eqs.}$$

I. Expansion in terms of hyperspherical harmonics

$$\Lambda^2(\Omega)\Phi_n(\Omega) = \varepsilon_n \Phi_n(\Omega)$$

II. Expansion in terms of adiabatic states $\rightarrow$ converges rapidly

$$[\Lambda^2(\Omega)/\rho^2 + V]\,\Phi_n(\Omega; \rho) = U_n(\rho)\Phi_n(\Omega; \rho)$$

$U_n(\rho)$: similar to molecular potential energy curves
$\rightarrow$ visual understanding of the dynamics

- single-channel (adiabatic) approximation already reasonable
- concept of new electron-correlation quantum numbers

The success of
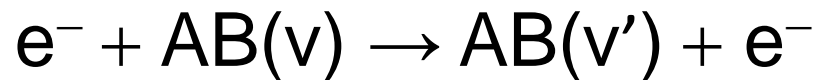the hyperspheical coordinate method
owes much
to the adiabatic expansion.

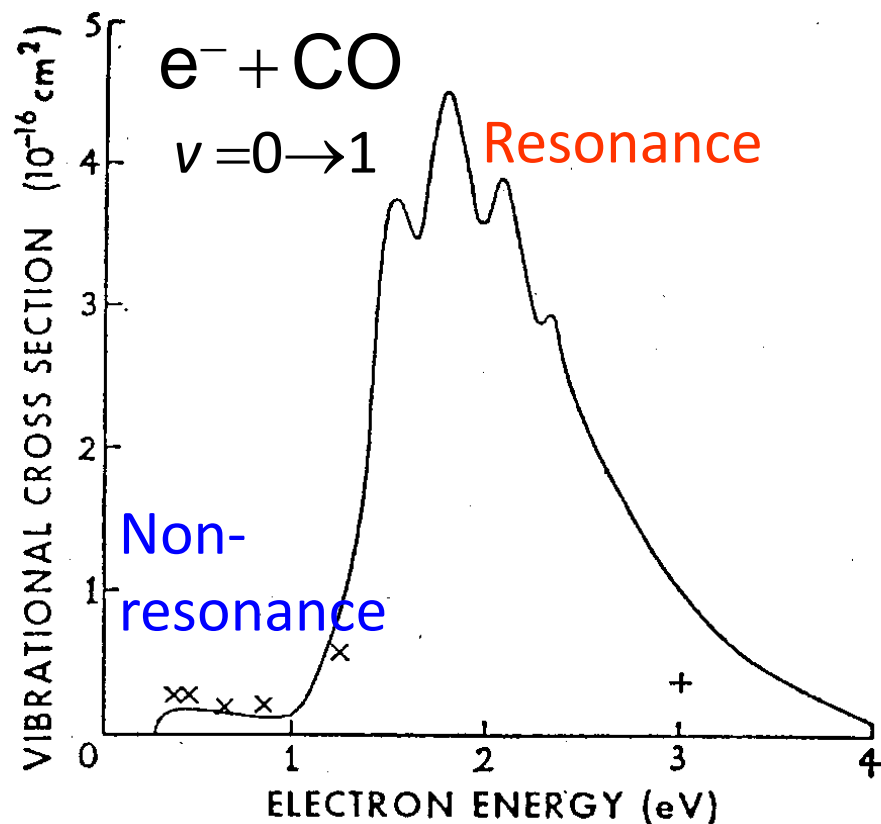# Vibrational excitation in electron-molecule collisions

Vibrational motion (nuclear motion) normally
hard to excite by the light e^- impact.

$e^- + AB(v) \rightarrow$ AB^- $\rightarrow AB(v') + e^-$

Resonances greatly enhance the cross section.

Vibrational excitation in electron-molecule collisions
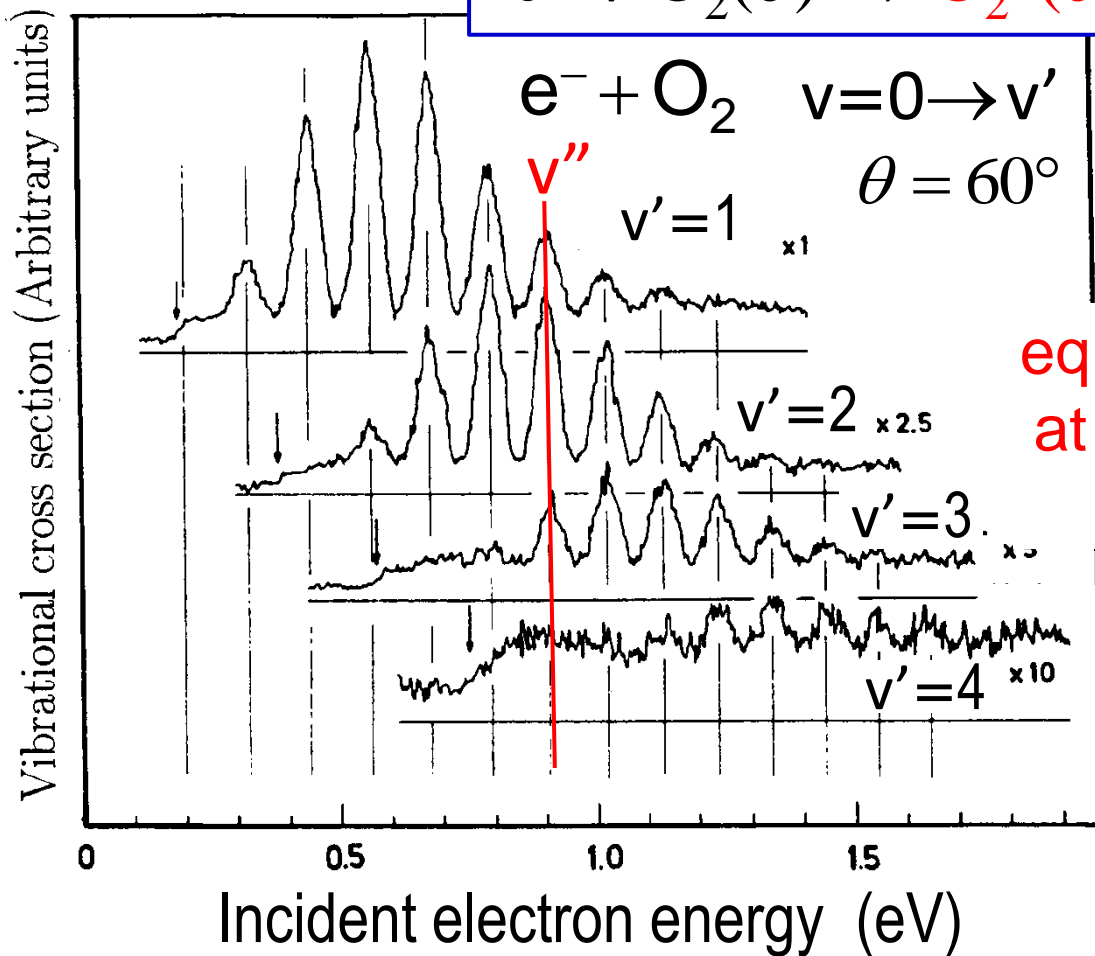
$$e^- + AB(v) \rightarrow AB(v') + e^-$$

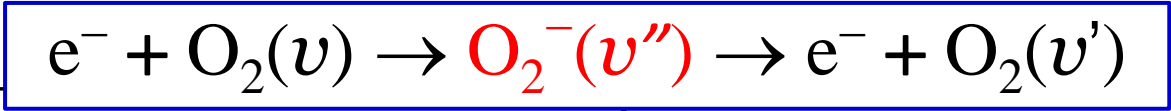Vibrational motion (nuclear motion) normally hard to excite by the light e^- impact.

If the interaction time is long, however, the energy transfer from e^- to vibration motion can be efficient.

$\rightarrow$ Resonance enhancement of vibrational excitation by temporary electron capture

$e^- + CO$

$v = 0 \rightarrow 1$

Resonance

Non-resonance

VIBRATIONAL CROSS SECTION (10^{-16} cm^2)

ELECTRON ENERGY (eV)

e⁻ - O₂ collisions (compound-state limit)

$$e^- + O_2(v) \rightarrow O_2^-(v'') \rightarrow e^- + O_2(v')$$

$e^- + O_2 \quad v=0 \rightarrow v'$

$\theta = 60°$

v''

v'=1 ×1

v'=2 ×2.5

v'=3 ×5

v'=4 ×10

Vibrational cross section (Arbitrary units)

Incident electron energy (eV)

0   0.5   1.0   1.5
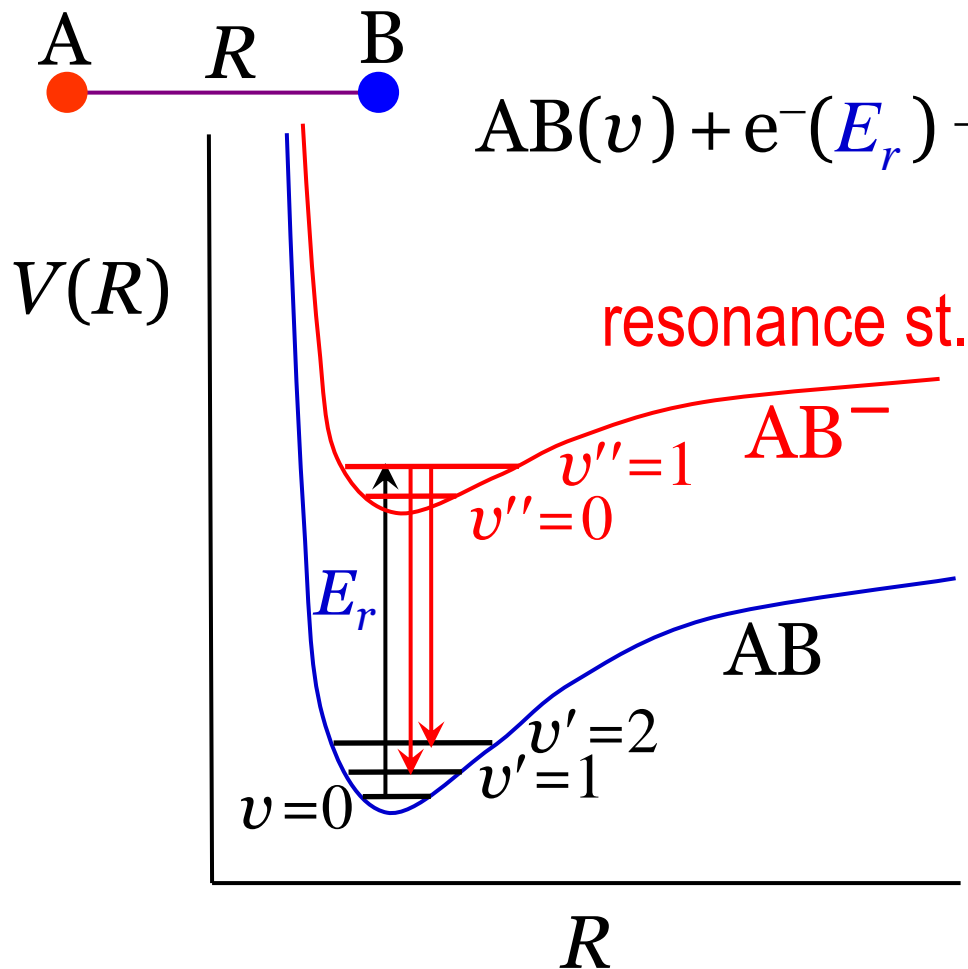
temporary
O₂⁻(v'')

equally spaced peaks
at common positions
irrespective of v'

fine structure due
to different v''

F. Linder and H. Schmidt, Z. Naturforsch. A **26**a, 1617 (1971)

Vibrational excitation via compound-state resonance

$$\mathrm{AB}(v) + \mathrm{e}^-(E_r) \to \mathrm{AB}^-(v'') \to \mathrm{AB}(v') + \mathrm{e}^-$$

equally spaced vibrational levels v''

Resonance energy E_r of the incident electron is common to all v'.

e⁻-H₂ collisions (impulse limit)
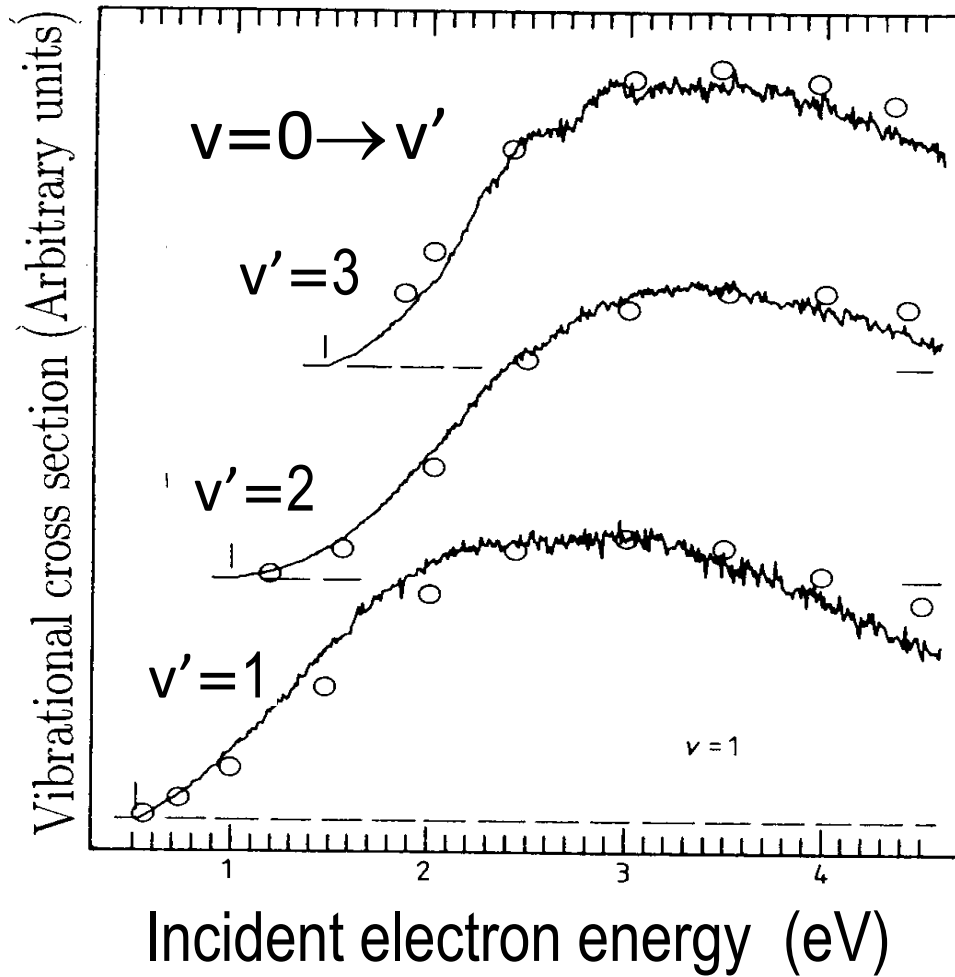
M. Allan, J. Phys. B **18**, L451 (1985)

Resonance lifetime vs. vibrational period

τ_{vib} : vibrational period (time for one vibration) $\cong 10^{-14}\,\text{s}$

τ_{res} : resonance lifetime ($\cong$ collision time)

$\tau_{\text{res}} \gg \tau_{\text{vib}}$ enough time for the resonance state to develop
well-defined vibrational levels

$\tau_{\text{res}} \ll \tau_{\text{vib}}$ little time for developing resonance vib. levels,
i.e., almost no nuclear motion during the collision
$\rightarrow$ adiabatic approximation for scatt. amplitude

$$f(\theta) = \left\langle \upsilon_f(R) \middle| F(\theta; R) \middle| \upsilon_i(R) \right\rangle$$

superposition of resonances with varying $E_r(R), \Gamma(R)$

Boomerang model

τ_{res} $\cong$ τ_{vib}

A   B

Only one or a few vibrations before the resonance decays.
Not enough time for developing vibrational states of AB^-.

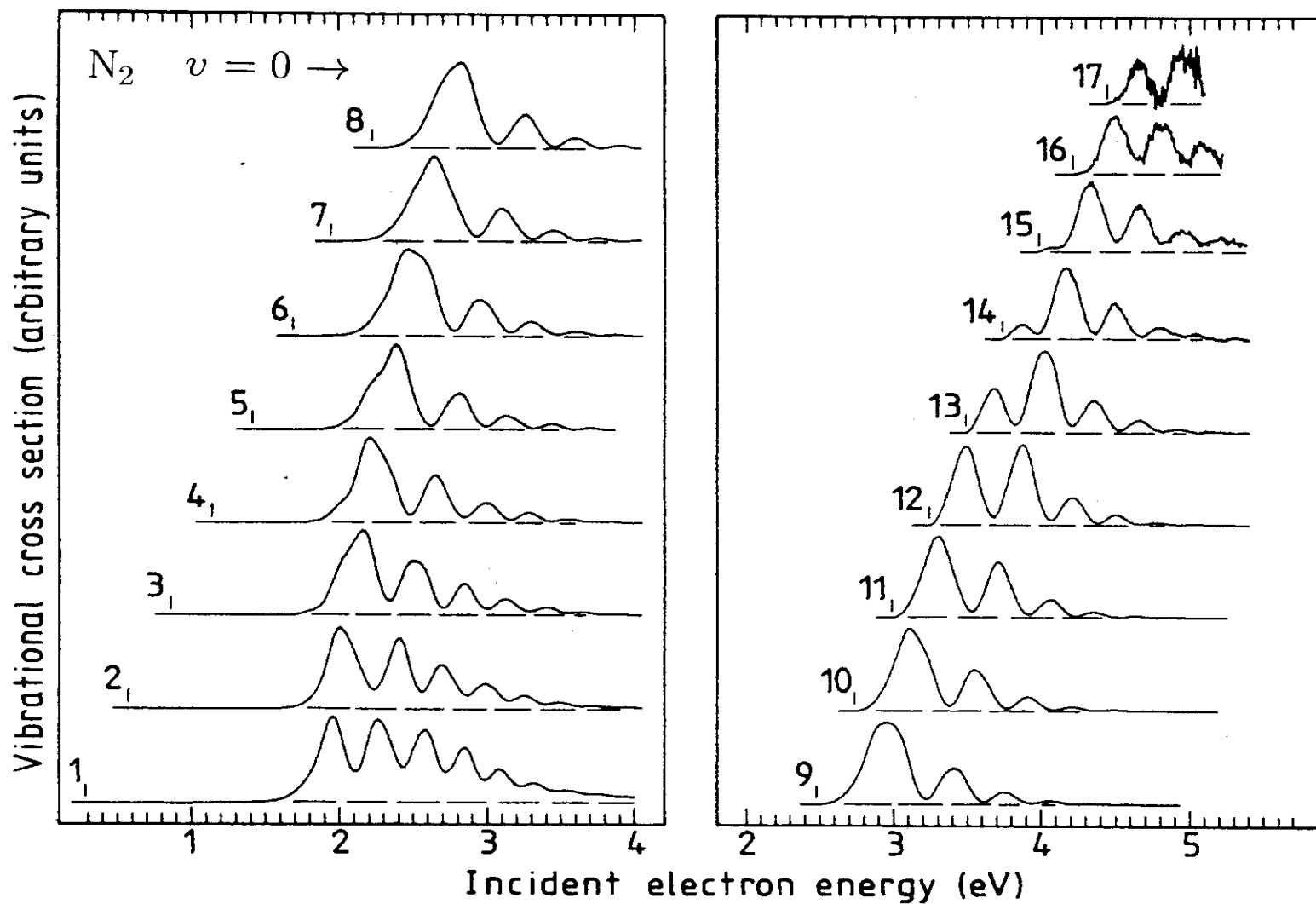Time enough only for forming a standing wave: wave number k_{AB}

$$\mathrm{e}^-(E) + \mathrm{AB}(v) \rightarrow \mathrm{AB}^-(k_{\mathrm{AB}}) \rightarrow \mathrm{e}^- + \mathrm{AB}(v')$$

Scattering amplitude essentially determined by the overlap
$\left\langle \Psi_{\mathrm{AB}}(v'),\ \Psi_{\mathrm{AB}^-}(k_{\mathrm{AB}}) \right\rangle$, which oscillates with $k_{\mathrm{AB}} = k_{\mathrm{AB}}(E)$.

$\rightarrow$ irregular oscillations with E

$e^- - N_2$ collisions （boomerang resonance）

Competition with dissociative channels

$$e^- + AB(v) \rightarrow \textcolor{red}{AB^-} \rightarrow AB(v') + e^-$$

$$\rightarrow A + B^- \qquad \text{dissociative attachment}$$
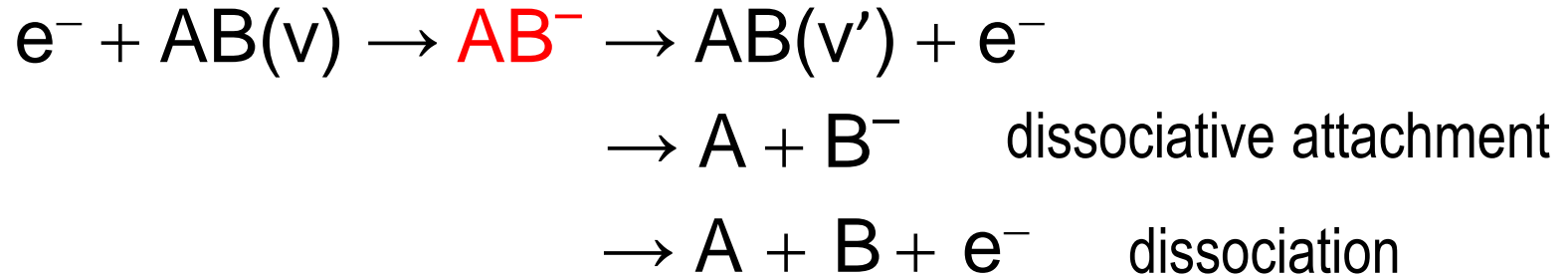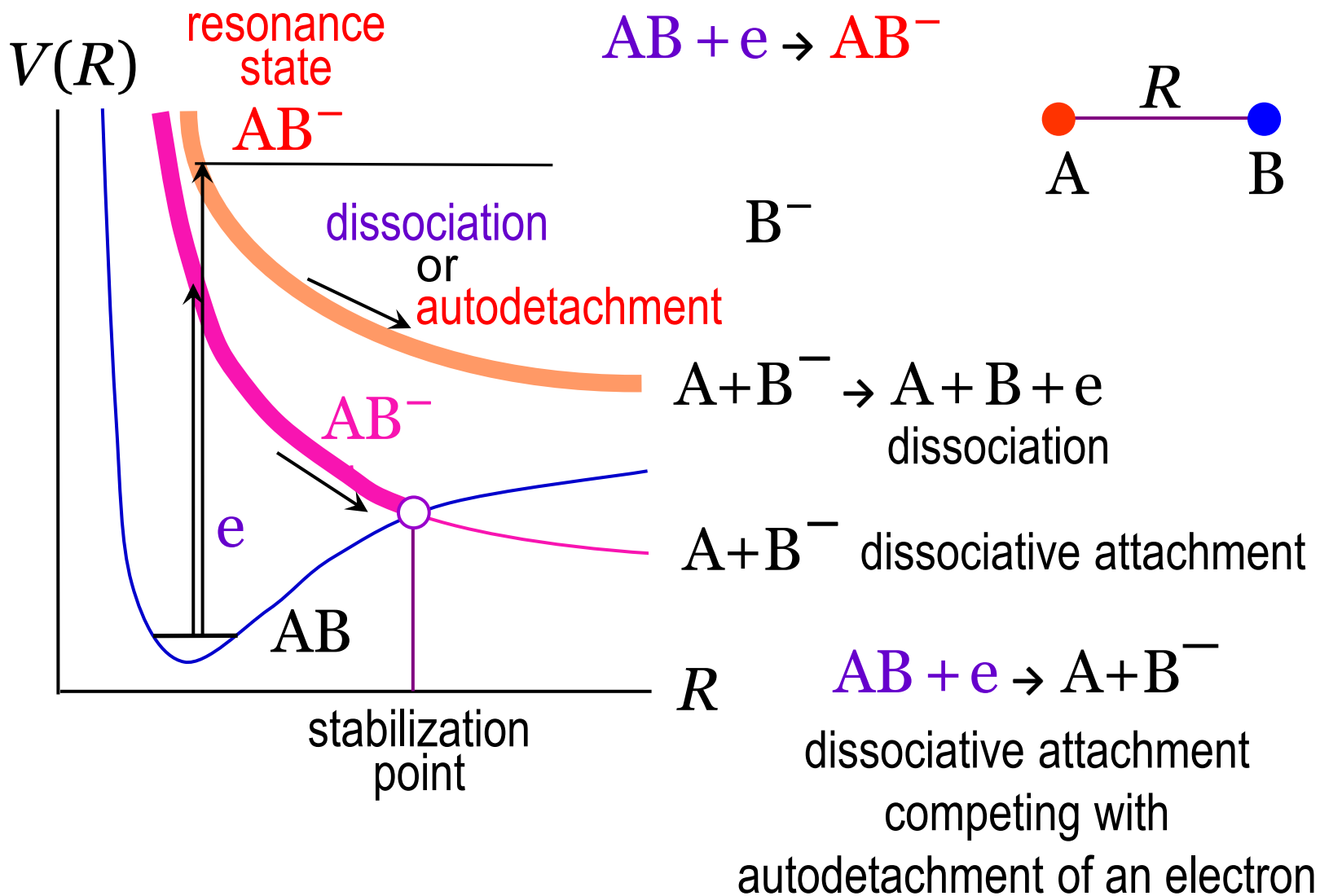
$$\rightarrow A + B + e^- \qquad \text{dissociation}$$

Dissociative electron attachment occurs
almost only via resonances.

Coupling with the dissociative mode

$V(R)$

resonance state

AB^-

$AB + e \rightarrow AB^-$

AB^-

dissociation
or
autodetachment

B^-

$A + B^- \rightarrow A + B + e$
dissociation

AB^-

e

$A + B^-$ dissociative attachment

AB

stabilization point

R

$AB + e \rightarrow A + B^-$

dissociative attachment
competing with
autodetachment of an electron

R

A   B

Resonance state may change its geometry.

CO_2

O C O

$CO_2{}^{-}$

θ

Linear molecule may be excited in the bending mode
or in the asymmetric stretching mode.

Geometry dependence of the resonance parameters

CO_2
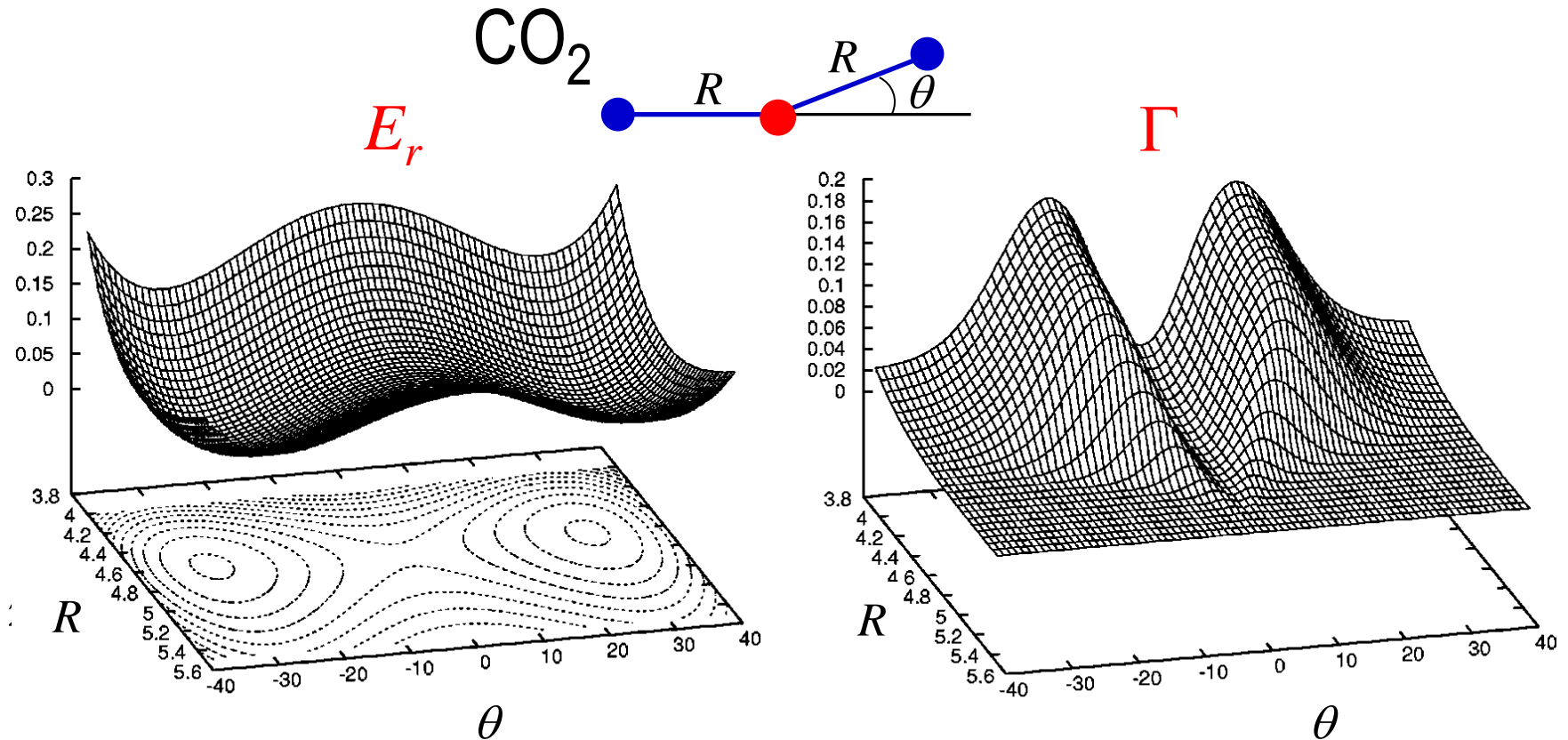
Complex $^2A_1$ resonance energy of CO_2^-, in units of hartrees, as a function of symmetric-stretch distance, in units of bohrs, and bend angle, in degrees. Left panel shows the real part of the energy surface and the right panel shows the corresponding width.

RESCIGNO, ISAACS, OREL, MEYER, AND McCURDY, PHYS. REV. A **65** 032716 (2002)

Resonance information

from the S matrix

Breit-Wigner one-level formula for the phase shift

$$\delta = \delta_r + \delta_b, \quad \delta_r = -\cot^{-1}\frac{E - E_r}{\Gamma/2}, \quad \frac{d\delta_r}{dE} = \frac{\Gamma/2}{(E - E_r)^2 + (\Gamma/2)^2}$$

convenient for locating resonances and for resonance fitting, but more convenient is $d\delta(E)/dE$
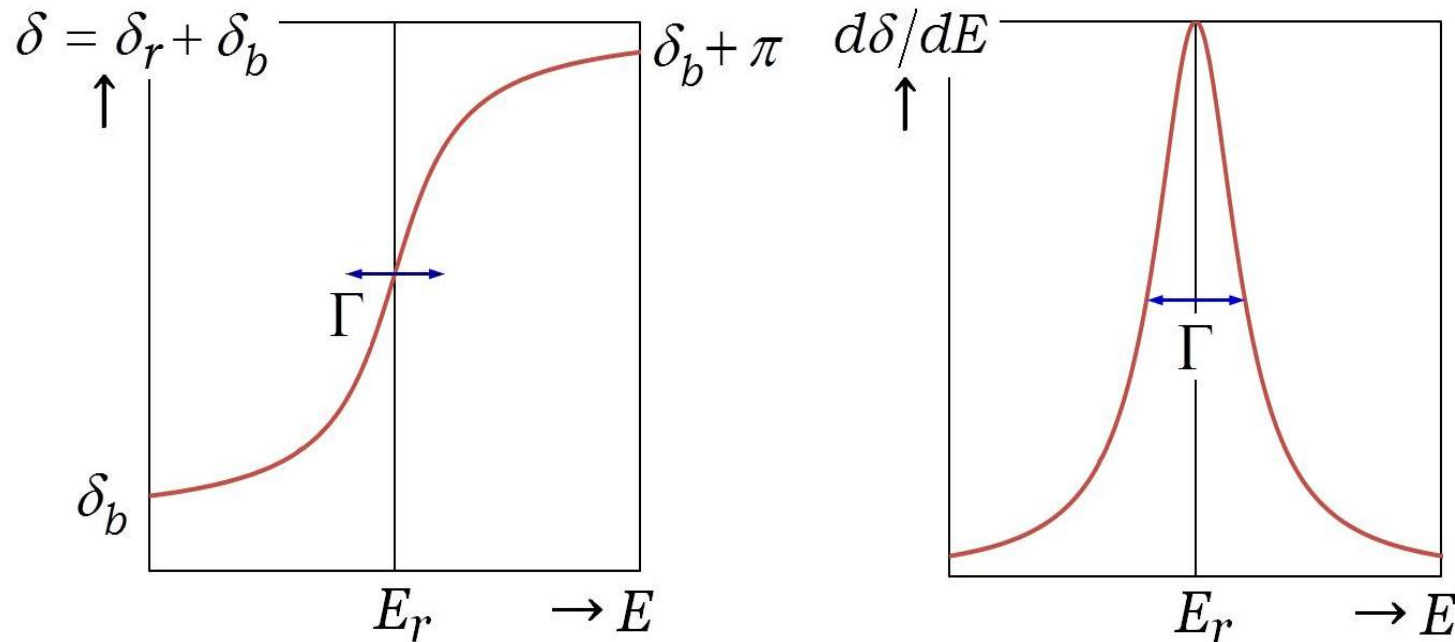
Single-channel N overlapping resonances

$$\delta = \delta_r + \delta_b \, ,$$

$$\delta_r = -\sum_{v=1}^{N} \cot^{-1} \frac{E - E_v}{\Gamma_v/2}, \quad \frac{d\delta_r}{dE} = \sum_{v=1}^{N} \frac{\Gamma_v/2}{(E - E_v)^2 + (\Gamma_v/2)^2} \equiv \sum_{v=1}^{N} L_v(E)$$

Breit-Wigner one-level formula: Single channel

For the phase shift δ

$$\delta = \delta_r + \delta_b, \qquad \delta_r : \text{resonance} \qquad \delta_b : \text{background}$$

$$\delta_r = -\cot^{-1}\frac{E - E_r}{\Gamma/2}, \quad \frac{d\delta_r}{dE} = \frac{\Gamma/2}{(E - E_r)^2 + (\Gamma/2)^2} \equiv L(E)$$
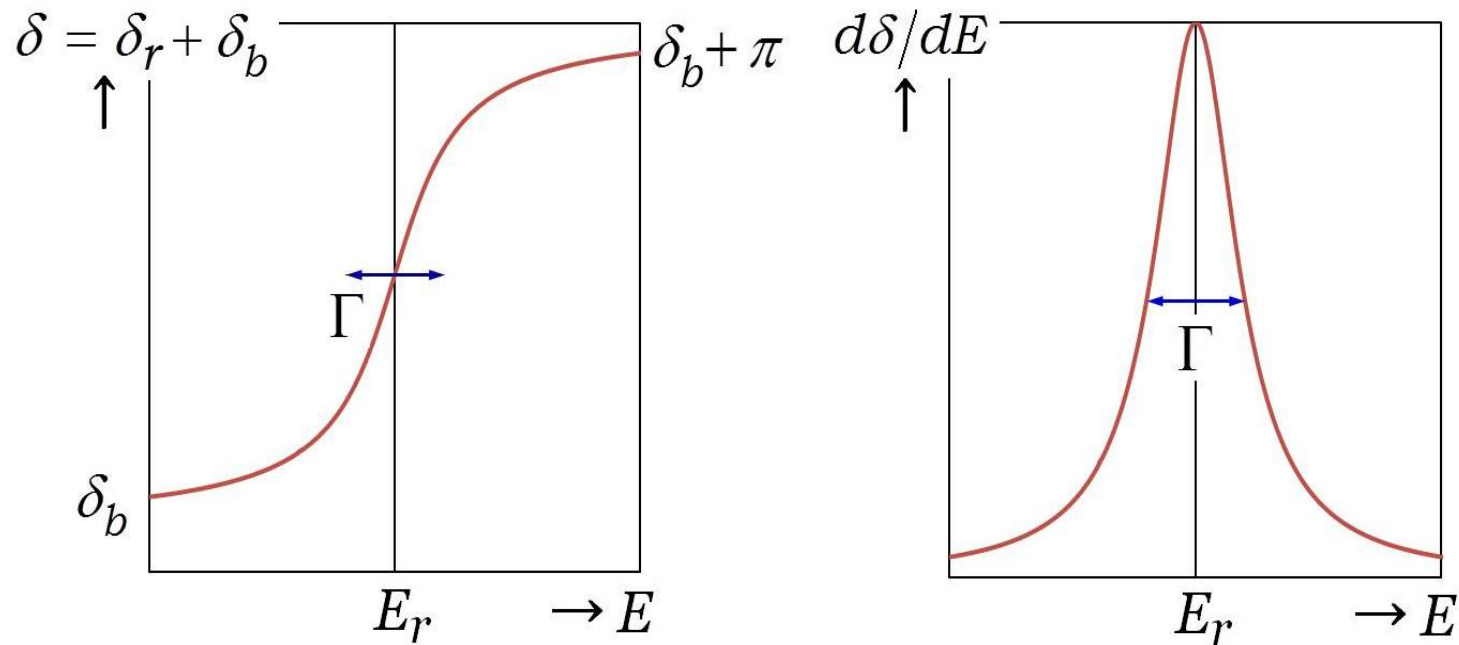
For the S matrix

$$S = e^{2i\delta} = e^{i\delta_b}\frac{E - (E_r + i\,\Gamma/2)}{E - (E_r - i\,\Gamma/2)}e^{i\delta_b} = e^{i\delta_b}\left[1 - \frac{i\,\Gamma}{E - (E_r - i\,\Gamma/2)}\right]e^{i\delta_b}$$

pole at $E = E_r - i\Gamma/2, \quad S^*S = SS^* = 1$ for real $E > 0$

Parameter fitting

Breit-Wigner one-level formula for $\delta(E)$:
convenient for locating resonances and for resonance fitting
but more convenient is $d\delta(E)/dE$

Single-channel overlapping resonances

For the phase shift δ

$$\delta = \delta_r + \delta_b, \qquad \delta_r : \text{resonance} \qquad \delta_b : \text{background}$$

$$\delta_r = -\sum_{\nu} \cot^{-1} \frac{E - E_\nu}{\Gamma_\nu/2}, \quad \frac{d\delta_r}{dE} = \sum_{\nu} \frac{\Gamma_\nu/2}{(E - E_\nu)^2 + (\Gamma_\nu/2)^2} = \sum_{\nu} L_\nu(E)$$

For the S matrix

$$S = e^{i\delta_b} \prod_{\nu} \frac{E - (E_\nu + i\,\Gamma_\nu/2)}{E - (E_\nu - i\,\Gamma_\nu/2)}\, e^{i\delta_b} = e^{i\delta_b} \prod_{\nu} \left[1 - \frac{i\,\Gamma_\nu}{E - (E_\nu - i\,\Gamma_\nu/2)} \right] e^{i\delta_b}$$

poles at $E = E_\nu - i\Gamma_\nu/2$, $\quad S^*S = SS^* = 1$ for real $E > 0$

Breit-Wigner one-level formula: Multichannel

$\Gamma_i/\hbar$ decay rate to each channel

$$S = U \left(I - \frac{i\mathbf{g}\mathbf{g}^\dagger}{E - E_r + i\Gamma/2} \right) U^{\mathrm{T}}, \quad (g_i = \Gamma_i^{1/2})$$

U unitary matrix, I unit matrix

$S_b = UU^T$ background S matrix (unitary & symmetric)

$\Gamma = \sum \Gamma_i$ total width

pole at $E = E_r - i\Gamma/2$
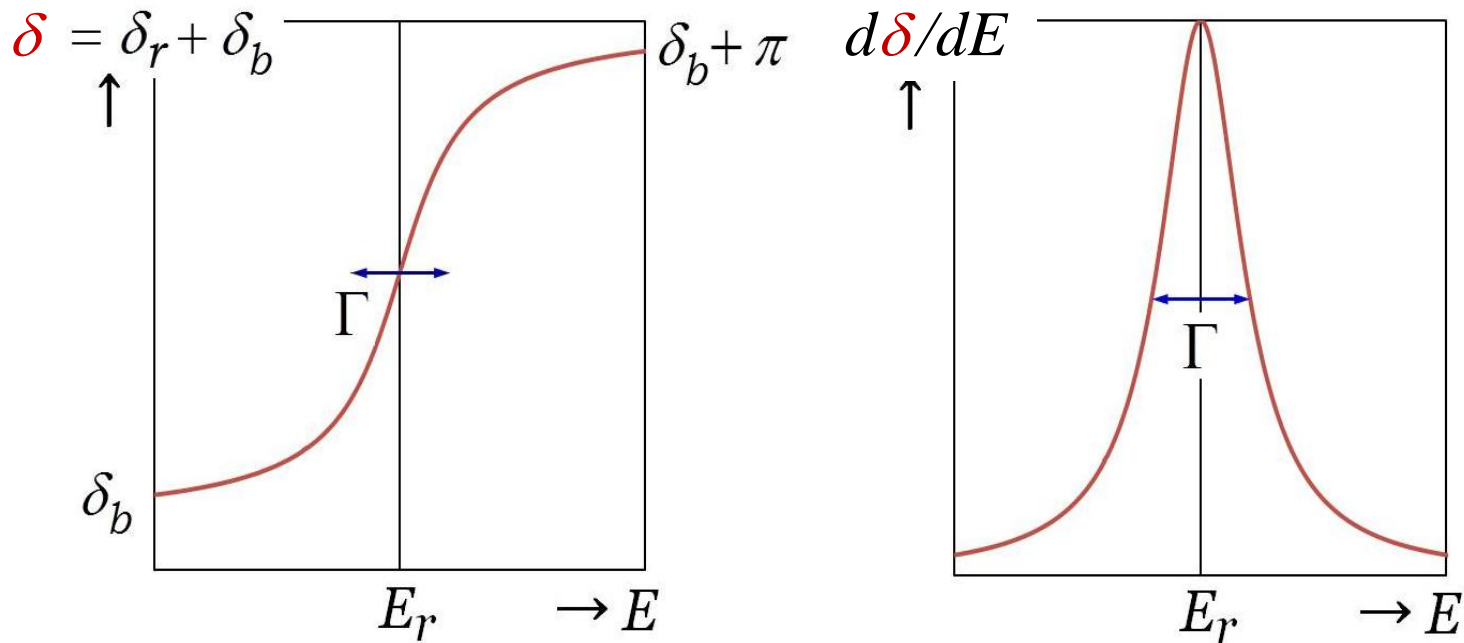unitary for real $E > 0 \rightarrow$ flux conservation
symmetric $\rightarrow$ time reversal

Breit-Wigner formula for multichannel scattering

Diagonalize S as $OSO^T = \Lambda,\ \ \Lambda_{ij} = \delta_{ij}\exp(2i\eta_i).$

Define eigenphase sum $\delta = \Sigma_i\,\eta_i$.

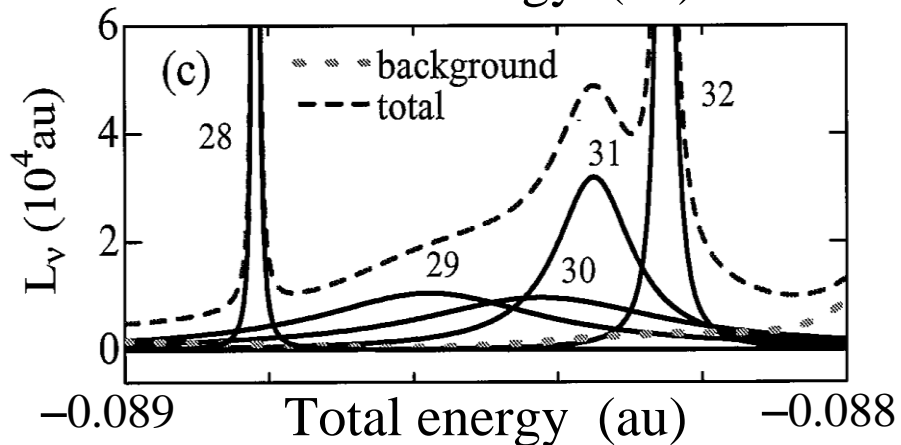Then, this δ satisfies the same Breit-Wigner formula as the single-channel phase shift (Weidenmüller 1967).
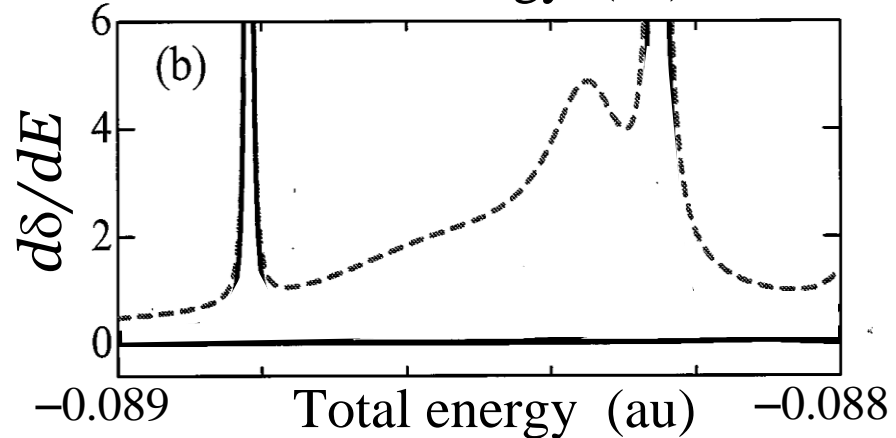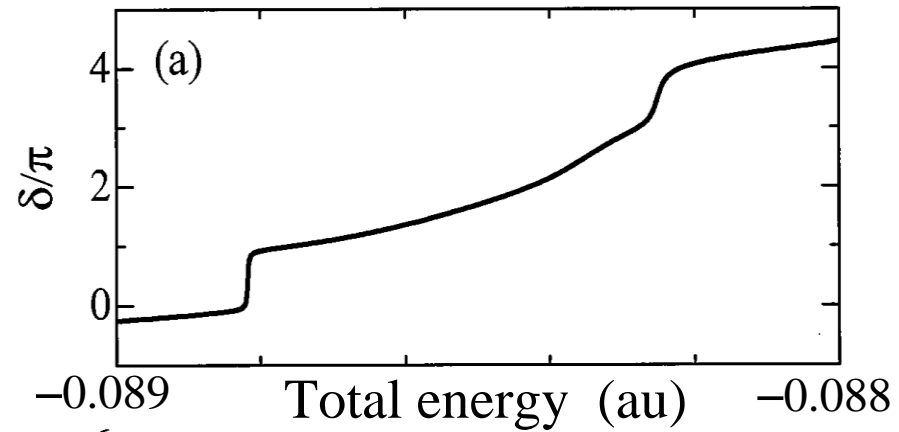
He(^{1}P^o)
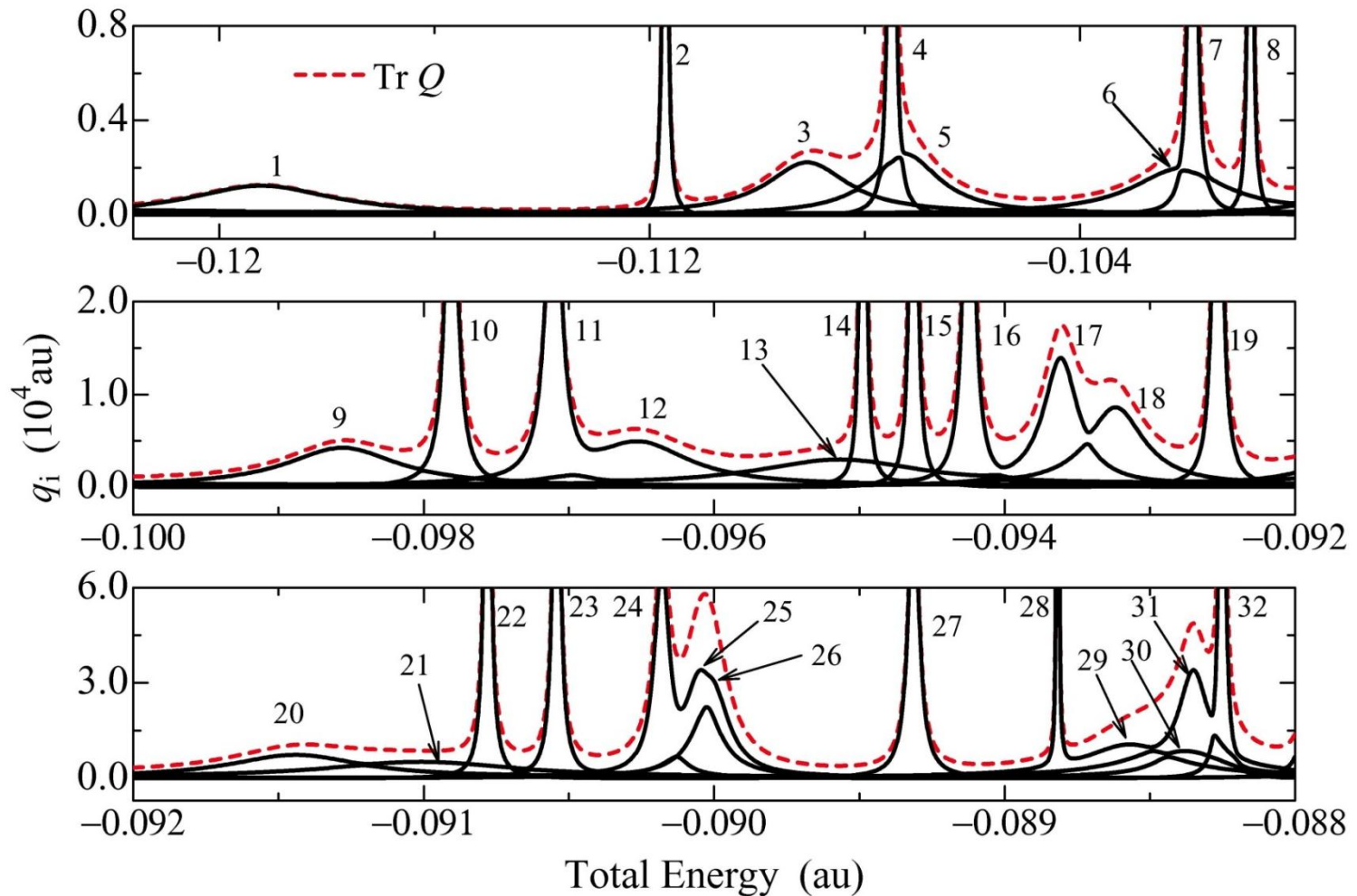
eigenphase sum δ

twice sudden increase

$d\delta/dE$
3 Lorentzians

In fact,

5 Lorentzians were
extracted by
another technique!

Aiba, Igarashi & Shimamura,
J. Phys. B **40**, F9 (2007)

Eigenvalues of the time-delay matrix for He($^1P^o$)

Aiba, Igarashi & Shimamura,
  J. Phys. B **40**, F9 (2007)

Time delay due to scattering

Single-channel time delay:

Wave packet of outgoing spherical wave is delayed by the time

$$\Delta t = 2\hbar \frac{d\delta}{dE} = -i\hbar \frac{dS}{dE} S^* \equiv Q, \qquad S = \exp(2i\delta)$$

compared with no scattering. For a Breit-Wigner resonance

$$Q(E) = \frac{\hbar \Gamma}{(E - E_r)^2 + (\Gamma/2)^2} + 2\hbar \frac{d\delta_{\mathrm{b}}}{dE}$$

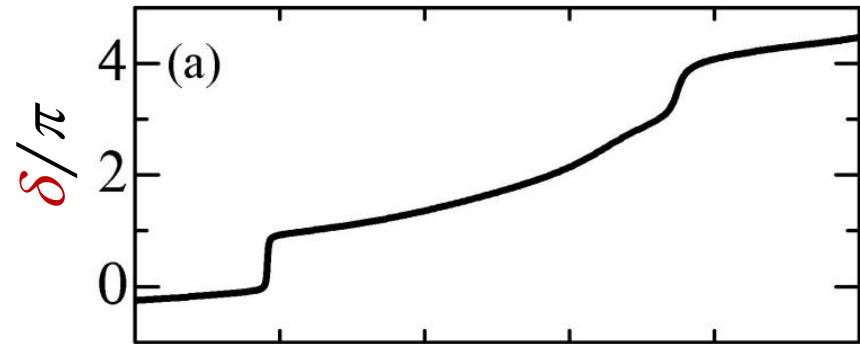**Multichannel time-delay matrix** (proposed by F.T. Smith, 1960)

$$Q = -i\hbar \frac{dS}{dE} S^\dagger$$

being related to eigenphase sum

$$\mathrm{Tr}\, Q(E) = 2\hbar \frac{d\delta}{dE} = \frac{\hbar \Gamma}{(E - E_r)^2 + (\Gamma/2)^2} + 2\hbar \frac{d\delta_{\mathrm{b}}}{dE}$$
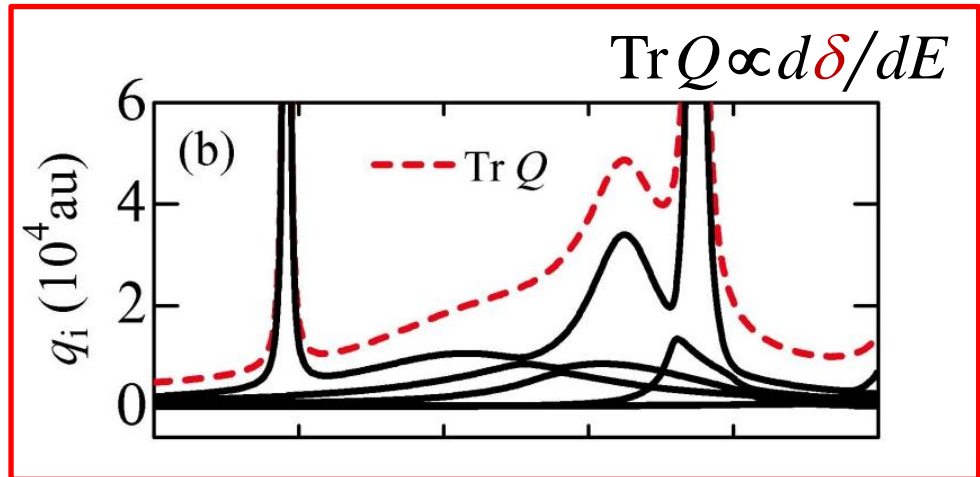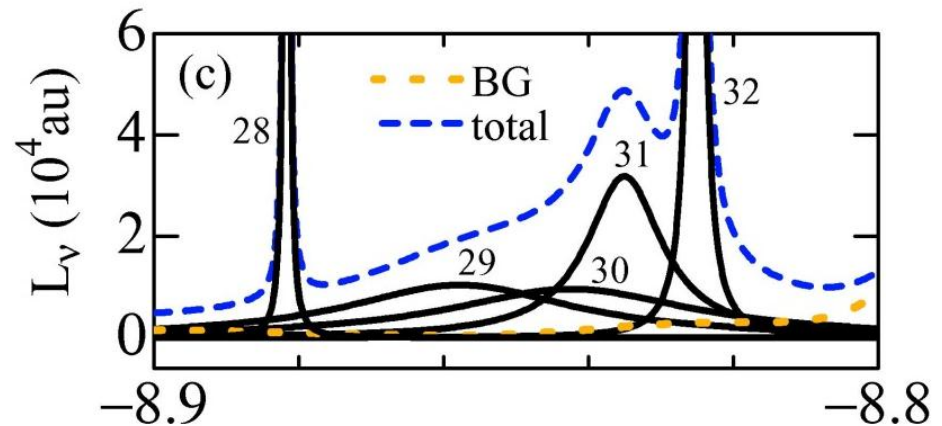
He(^{1}P^o)

eigenphase sum δ

Q-matrix eigenvalues q_i

5 Lorentzians $L_\nu(E)$ avoiding each other

Other eigenvalues $\cong 0$

Tr Q fitted to $\Sigma_\nu L_\nu$ with 5 Lorentzians and background

Complicated overlapping resonances resolved

Aiba, Igarashi & Shimamura, J. Phys. B **40**, F9 (2007)

$\mathrm{Tr}\,Q \propto d\delta/dE$

Multichannel overlapping resonances

No S-matrix representation is known
that is explicitly unitary and symmetric
and that has poles at
$$E = E_\nu - i\Gamma_\nu/2, \quad \nu = 1, \cdots, N.$$

Simonius (1974) proposed a representation
that has resonance poles and is unitary,
but not explicitly symmetric.

Simonius representation of the S matrix

$$S_{\text{Sim}} = U \left[\prod_{\nu=1}^{N} S_\nu \right] U^T, \quad S_\nu = 1 - \frac{i\, \Gamma_\nu\, \mathbf{g}_\nu\, \mathbf{g}_\nu^{\dagger}}{E - (E_\nu - i\, \Gamma_\nu/2)}$$

elements of the vector $\mathbf{g}_\nu$: resonance parameters

resonance-order dependent
not explicitly symmetric

Can be made symmetric, in principle, by choosing $\mathbf{g}_\nu$.

not wrong, just inconvenient for application purposes,
but convenient for theoretical formulation purpose

Separation theorem for N overlapping resonances

Proof using the Simonius representation of resonance S matrix

N eigenvalues $q_i(E)$ of the Q matrix form
N Lorentzian peaks avoiding each other at the crossing points,
the other eigenvalules being quite small.

Also, $\quad \mathrm{Tr}Q(E) = \sum_i q_i(E) = \sum_\nu L_\nu(E) +$ small background

N eigenvectors corresponding to the resonance eigenvalues
define the N-dimensional resonance eigenchannel space.
Resonances decay only into this N-dimensional channel space,
whereas they decay into all the physical channels
and into all the eigenchannels of the S matrix.

Importance of the time-delay matrix eigenvalues

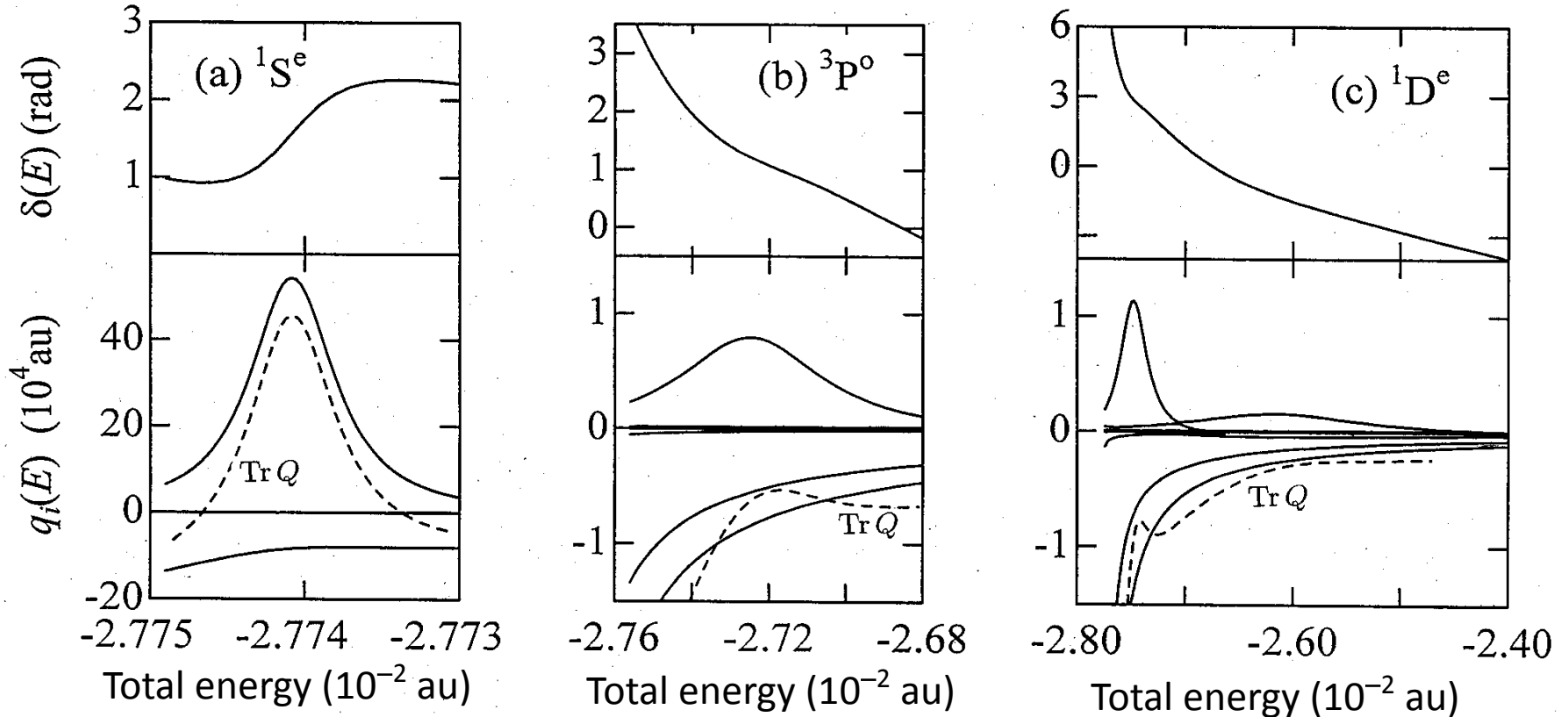Resonances clearly stand out against background.

Overlapping resonances can be easily resolved.

Useful for
- Spotting resonances otherwise hidden
- Resonance fitting
- Resolving overlapping resonances
- Separating out the resonance channel space from the whole channel space

Strong background cancelling time dealy : $e^- + Ps$

$$Ps^- = (e^+e^-)\,e^-$$ above Ps(n=3) threshold

Igarashi and Shimamura, J. Phys. B **37**, 4221 (2004)

Strong dipole background

Dipole potential due to linear Stark effect

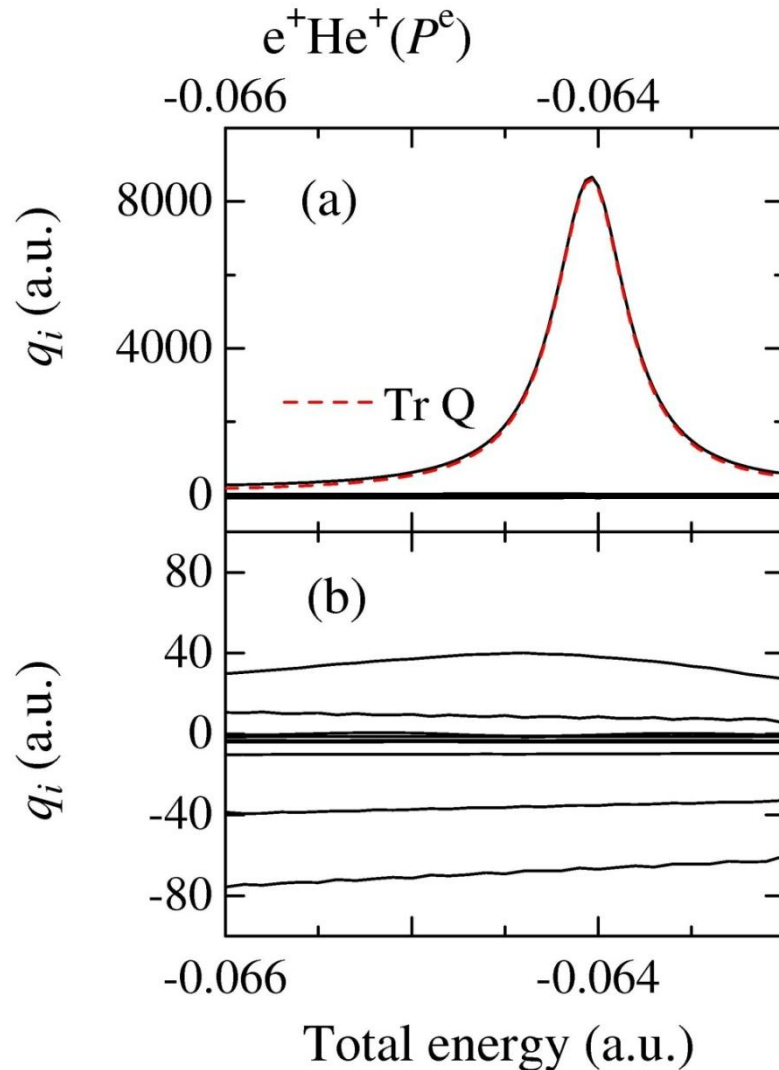$$\text{Tr}\, Q(E) = 2\hbar \frac{d\delta}{dE} = \frac{\hbar\Gamma}{(E - E_r)^2 + (\Gamma/2)^2} + 2\hbar \frac{d\delta_{\text{b}}}{dE}$$

The background δ_{b} diverges toward the threshold.

Parametrization: $\delta_{\text{b}} = -C_{-1} \ln(E - E_{\text{thresh}}) + C_0 + C_1 E$

$$\longrightarrow d\delta_{\text{b}}/dE = -C_{-1}/(E - E_{\text{thresh}}) + C_1$$

Negative time delay due to the dipole background

Weak resonance hidden behind a stronger one

Shimamura, Wakimoto & Igarashi, Phys. Rev. A **80**, 032708 (2009)