I. **Shape Resonances**

These are the simplest of several types of continuum and scattering resonances we will encounter later. They are often just quasi-bound levels behind a centrifugal barrier, but sometimes they are just "reflections" from an oddly shaped potential curve.

A few examples appear on the following pages. Obviously, these do not occur in a pure Coulomb potential.

"Condensation oscillations"

The vibrational equivalent of a Cooper minimum is the beating of the initial and final vibrational wave functions.

On a large energy scale, the cross sections roughly map our peaks or nodes of the initial vibrational wave function. Here we show a calculated example for \( \text{H}_2 \).

J. Tellinghause has experimentally studied this phenomenon in \( \text{F}_2 \), quite extensively.
H$_2$ states near the second dissociation limit
to H(1s) + H (2s or 2p)
$C^1\Pi_u, \nu=13, N=3$ Shape Resonance in $H_2$

Measured Width: $3.6 \pm 0.3$ cm$^{-1}$

Theory (crude WKB): $0.09$ cm$^{-1}$

Theory (non-adiabatic): $0.10$ cm$^{-1}$

$N''=1$ threshold of $\text{H}_2$ (Low resolution)

- **C, $v=13$, $N=2$**
  - "quasi-bound" shape resonance
- **$B'$, $v=9$, $N=2$**
  - (shape resonance)

![Graph showing H$^+$ Signal vs. Offset in scan (cm$^{-1}$)]

- Threshold at 14771 cm$^{-1}$

(From my group's work, 1997)
Calculated cross-sections using ab-initio potentials, for $B'$ state

From Zucker & Eyler, 1986.
C <-> EF (dotted)
B' <-> EF (solid)
adiabatic cross sections (calc.)

From Zucker & Exler, 1986
Feshbach Resonances (2-channel case)

We will follow closely the treatment in Friedrich, Section 1.4.2. Assume two "channels" converge to different limits: an internal excitation state of product atom or ion

\[ \Phi_0 \leftrightarrow V_{12} \rightarrow \Phi_2 \]

Look at the resonance caused by the effect of the coupling \( V_{12} \) on the bound state \( \Phi_0 \) in the uncoupled channel 2.

(Ch. 1 open, Ch. 2 closed)

In general,

\[
\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_1 (r) \right) \Phi_1 (r) + V_{12} \Phi_2 (r) = E \Phi_1 (r) \tag{21}
\]

\[
\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_2 (r) \right) \Phi_2 (r) + V_{21} \Phi_1 (r) = E \Phi_2 (r) \tag{22}
\]

and if \( V \) is real, need \( V_{12} = V_{21} \) for the Hamiltonian to be Hermitian.

The bound level \( \Phi_0 \) in the uncoupled problem satisfies

\[
\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_2 (r) \right) \Phi_0 (r) = E_0 \Phi_0 (r) \tag{22}
\]

Near \( E_0 \), assume the wave function \( \Phi_2 \) in channel 2 of the coupled system is a multiple of \( \Phi_0 \),

\[ \Phi_2 = A \Phi_0 \]. Then (21) becomes, (22)

\[
\begin{align*}
\left\{ \begin{array}{ll}
(E + \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - V_1) \Phi_1 = A V_{12} \Phi_0 \\
A (E - E_0) \Phi_0 = V_{21} \Phi_1
\end{array} \right.
\tag{24}
\]

Formally solve using a Green's function,

\[
(E + \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - V_1) G (r, r') = \delta (r - r') \tag{25}
\]

We can solve the top equation in (24) with

\[ \Phi_1 = \Phi_{reg} + A \int G (r, r') V_{12} (r') \Phi_0 (r') dr' \].

\[ \Phi_0 \rightarrow \Phi_{reg} \]
where \( \Phi_{\text{reg}} \) solves the homogeneous equation,

\[
(E + \frac{k^2}{2m} \frac{d^2}{dr^2} - V_i) \Phi_{\text{reg}} = 0 \tag{27}
\]

"regular" solution \( \to 0 \) as \( r \to 0 \).

Asymptotically, energy normalized \( \Phi_{\text{reg}} \) can be written as

\[
\Phi_{\text{reg}} (r) \to \sqrt{\frac{2m}{\pi \hbar^2 k}} \sin (kr + \phi_y) \tag{28}
\]

"background phase shift" mostly from \( V_i (r) \); varies only slowly with \( E \).

Inserting (27) in the bottom equation of (24) and multiplying by \( \langle \Phi_o | \) we obtain

\[
A = \frac{\langle \Phi_o | V_{21} | \Phi_{\text{reg}} \rangle}{E - E_0 - \langle \Phi_o | V_{21} \hat{G} V_{12} | \Phi_o \rangle} \tag{29}
\]

\[\equiv \int \! dr \int \! dr' \Phi_o (r) V_{21} (r) \hat{G} (r, r') V_{12} (r') \Phi_o (r')\]

Now find the asymptotic form of \( \Phi_1 \), and interpret it.

The Green's function for \( V_i (r) \) in channel 1 can be expressed as (see problem 1.4 in Friedrich),

\[
G (r, r') = - \pi \begin{cases} 
\Phi_{\text{reg}} (r) \Phi_{\text{irr}} (r') & r \leq r' \\
\Phi_{\text{reg}} (r') \Phi_{\text{irr}} (r) & r' \leq r
\end{cases} \tag{30}
\]

Same as (28), with \( \sin \to \cos \).

At large \( r \), \( \Phi_o (r) \) will vanish (it's bound), so in (26) we can assume \( r' < r \) and integrate.

Using (29) for \( A \), we get

\[
\Phi_1 (r) \to \Phi_{\text{reg}} + \tan \phi_{\text{irr}} \tan \phi_{\text{irr}} \tag{31}
\]

\[\equiv \frac{1}{r \to 0} \sqrt{\frac{2m}{\pi \hbar^2 k}} \sin (kr + \phi_y + \phi) (\chi \text{ constant})\]

must be \( 2 \pi \cos \phi \) to energy

(since \( \Phi_o \) is tied to \( \Phi_1 \), \( A \Phi_o \) must also be multiplied by \( \cos \phi \))
Bottom line: coupling leads to additional phase shift $\phi$ in open channel 1.

The result (31) is often written as

$$\phi = -\tan^{-1}\left(\frac{\hbar \Gamma/2}{E-E_R}\right)$$  \hspace{1cm} (32)$$

Where $$\Gamma \equiv \frac{2\pi}{\hbar} \left| \langle \Phi_0 | V_{21} | \Phi_{0\gamma} \rangle \right|^2$$, and the resonance position is shifted slightly,

$$E_R \equiv E_0 + \langle \Phi_0 | V_{21} \hat{G} V_{12} | \Phi_0 \rangle$$

If $\Gamma$, $d$, and $E$ are constants near the resonance, the phase $\phi$ changes by $\pi$ at the resonance position, with a width of $\Gamma$ between the $\frac{\pi}{4}$ and $\frac{3\pi}{4}$ points:

The derivative $\frac{d\phi}{dE}$ is max. at the resonance, and is Lorentzian,

$$\frac{d\phi}{dE} = \frac{\hbar \Gamma/2}{(E-E_R)^2 + (\hbar \Gamma/2)^2}$$

This type of isolated resonance is called \underline{Breit-Wigner} resonance, and corresponds to the isolated-resonance limit of an MWT treatment. There we employ not the phase, but the amplitude. These are connected:

the admixture of the closed channel in the total wave function is, from (31) with the correct normalization,

$$|A_{\text{cos}}|^2 = \frac{1}{\pi} \frac{\hbar \Gamma/2}{(E-E_R)^2 + (\hbar \Gamma/2)^2} = \frac{1}{\pi} \frac{d\phi}{dE}$$
III. A. Ionizing Resonances

Here we loosely follow Friedrich, §2.2.2.

Look at this region

Electronic states
or molecular rot. or vib. series
(Can simplify if $V \sim$ Coulomb)

After normalizing $\Phi_1$, as indicated in Eq. (51),

$$\Phi_1(r) = \cos \theta \Phi_{reg} + \sin \theta \Phi_{irr}, \text{ and also,}$$

$$\Phi_2(r) = \cos \theta \frac{\langle \Phi_0 | V_{12} | \Phi_{reg} \rangle}{E - E_2} \Phi_0(r)$$

$$= -\frac{\sin \theta}{\pi \langle \Phi_{reg} | V_{12} | \Phi_0 \rangle} \Phi_0(r)$$

The decay of $\Phi(r)$ is described by the
Lorentzian, (35).

But photoionization can be much richer:

Assume a reasonably isolated resonance exists,
but allow both $d_1, d_2$ to be non-zero.

$\Phi_{initial}$
Including the core or internal wave function, the total wave function near the resonance is, after antisymmetrizing and recalling \( \psi_{\text{int}} = \Phi \),

\[
\Phi = \cos \delta \hat{A} \left( \psi_{\text{int}} (1) \Phi_{\text{reg}} (r) \right)
\]

\[
= \cos \delta \hat{A} \psi_{\text{int}} (1) - \frac{\sin \delta}{\pi \langle \Phi_{\text{reg}} | V_{12} | \Phi_{0} \rangle} \hat{A} \psi_{\text{int}} (2)
\]

For photoionization, generalize the equation for \( \frac{dF}{dE} \) at the bottom of p. C-5.

Writing

\[
d_1 = \langle \psi_{\text{int}} (1) | E \hat{A} | \Phi_{\text{init}} \rangle \quad (39)
\]

\[
d_2 = \langle \psi_{\text{int}} (2) | E \hat{A} | \Phi_{\text{init}} \rangle
\]

\[
\frac{dF_{E_i}}{dE} = \frac{2 \mu}{\kappa} w d_i^2 \cos^2 \delta \left( 1 - \frac{d_2}{d_1} \frac{\tan \delta}{\pi \langle \Phi_{\text{reg}} | V_{12} | \Phi_{0} \rangle} \right)^2
\]

\[
\frac{dF_{E_i}}{dE} = \frac{2 \mu}{\kappa} w d_i^2 \frac{(\varepsilon + \varepsilon_i)^2}{1 + \varepsilon^2}
\]

\[
\varepsilon = \frac{E - E_{Fr}}{\Gamma/2}, \quad \varepsilon_i = \frac{d_2}{d_1} \frac{\tan \delta}{\pi \langle \Phi_{\text{reg}} | V_{12} | \Phi_{0} \rangle}
\]

Butler-Fano profile, \( \beta \) = shape parameter

\( \varepsilon \) = reduced energy

(in units of \( V_2 \)-width)
These lineshapes are asymmetric except for 
\[ q = \infty \] (Lorentzian, from exciting ch. 2 only) 
and \[ q = 0 \] (Lorentzian dip, ch. 1 only)

(See p. 143 of Friedrich for better plots.)

\[ \frac{d\sigma}{dE} \] 
or \[ \sigma \]

\[ q = 1 \] (mirror image for \(-1\))
\[ q = 0 \]
\[ q = \infty \]

"Window resonance"

Note that \( q \propto \frac{d^2\sigma}{d\Omega} \), so lineshape depends on method of excitation!

These asymmetric resonances are ubiquitous in photoionization and photodissociation spectroscopy.

**III. Complex Resonances**

Note that if \( R \) is large, the adjacent resonances will overlap. An elegant way to deal with this situation, especially for the Coulomb potential, is to use

Multichannel quantum defect theory (see Friedrich, or \( E^3 \) notes available upon request.)

Idea: Extend \( R \)-matrix scattering theory to \( E < 0 \) by treating \( n \) as a continuous variable; scale every thing per unit energy. Works beautifully for strongly interacting Rydberg series.
The Stark spectra -- Nussenzweig, Pollock & Eyler 1958

ION SIGNAL
(from autoionization)

"Field induced narrowing" -- an interference effect.

Beutler-Fano and overlapping complex resonances

THEORY
(Bergeman)
USES MQDT in parabolic coordinates
Interference at the Upper \((H + D^*)\) Dissociation Limit of HD

See Cheng, Kim, Eyler, and Melikechi,


D\((2s)\) at High Resolution, with fit to two ground-state hyperfine thresholds