Introduction to Two BIG IDEAS of theoretical physics

— The COMPLEX resonance

— The LOW Energy PSEUDOPOTENTIAL

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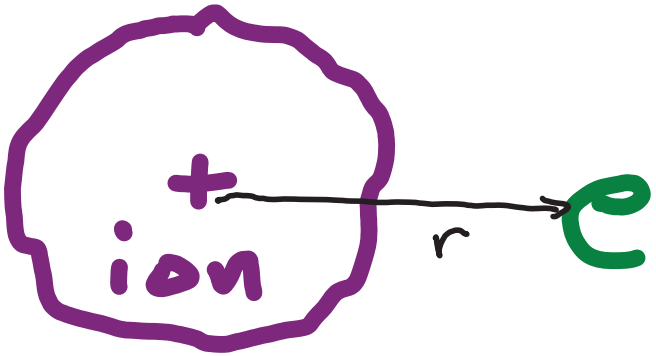
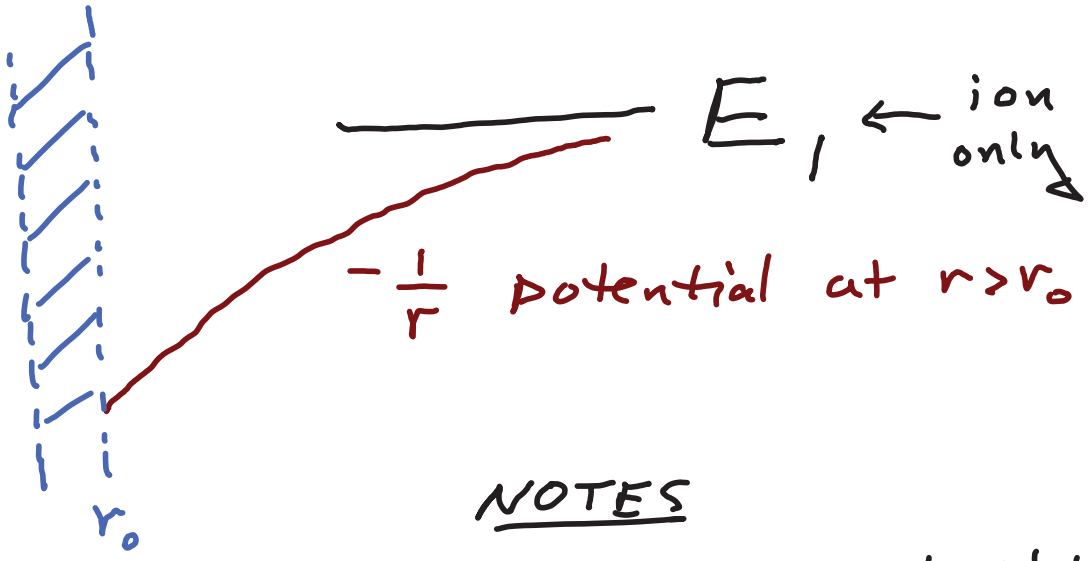
http://www.physics.purdue.edu/fermion/ICPEAC2017/

COMPLEX RESONANCE (first consider 1-channel)

~ Consider an electron interacting with a positive ion with energy levels E_i





The Hamiltonian for this system can be written as

$$H = H_{ion} + h_e + V^{sr}(r)$$

with $H_{ion} = |1\rangle E_1 \langle 1|$

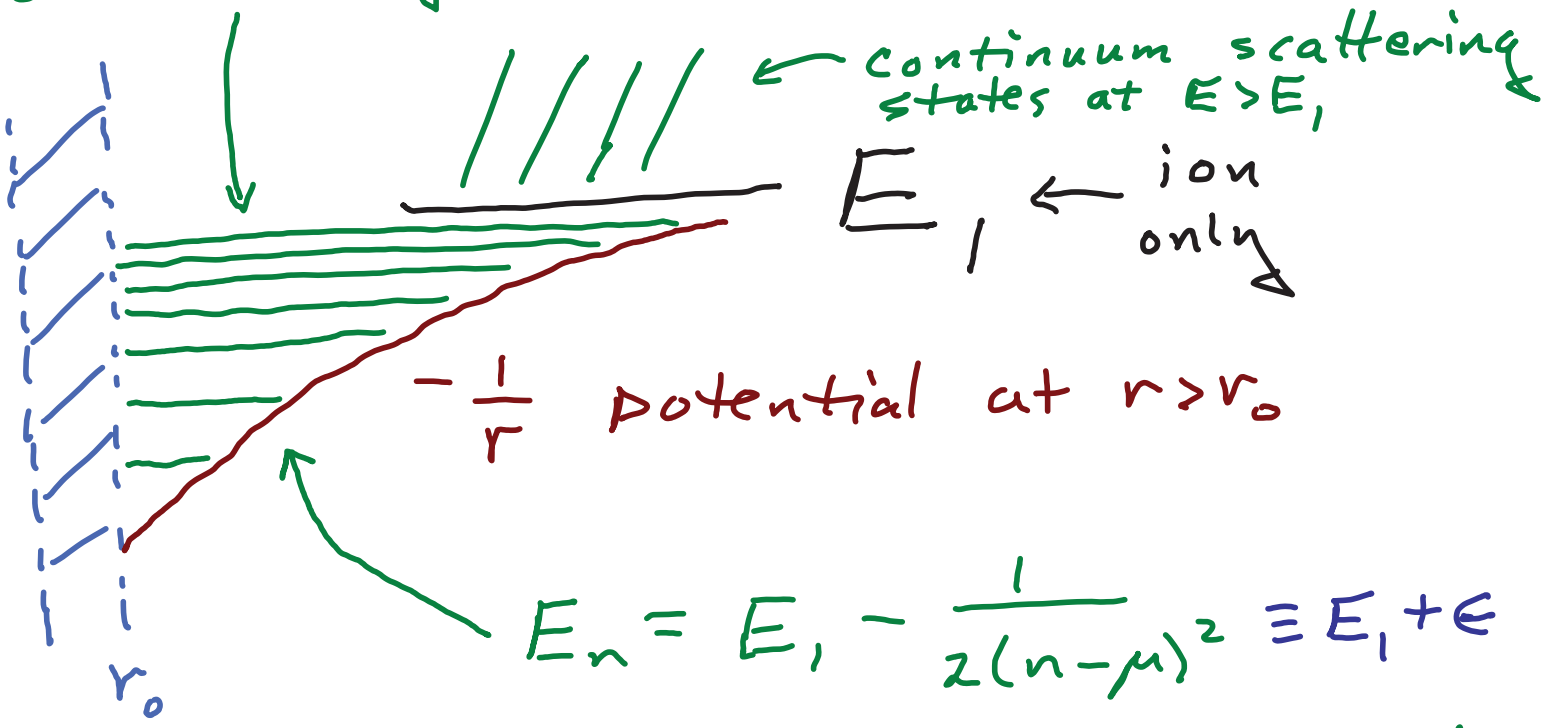
$h_e = T_e - \frac{1}{r}$

$V^{sr}(r)$ = nonzero only at $r<r_0$

NOTES

- The long-range potential need not be Coulomb, as these effects occur also, e.g. in ultracold collisions
- This scenario here is referred to as "QUANTUM DEFECT THEORY"

single channel Rydberg levels at $E<E_1$



$$E_n = E_1 - \frac{1}{2(n-\mu)^2} \equiv E_1 + \epsilon$$

μ = quantum defect, would vanish if $V^{sr} \to 0$

$\mu \simeq$ energy-independent

Unnormalized solution $(r>r_0)$

If $V^{sr}=0 \longrightarrow f_\epsilon(r)$

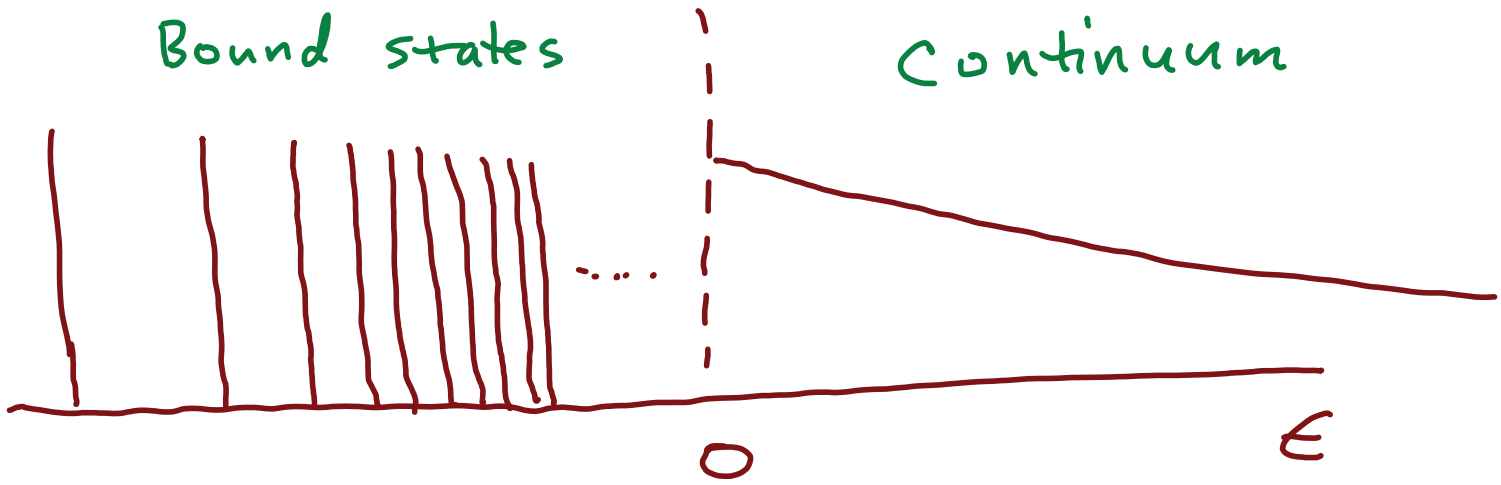
If $V^{sr}\neq 0 \longrightarrow f_\epsilon(r) - g_\epsilon(r)\tan\delta$

Note: call $\nu \equiv (-2\epsilon)^{-1/2}$ = effective quantum number

Seaton, others: $\delta \equiv \pi\mu$

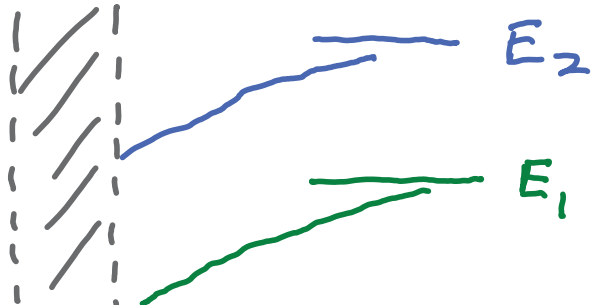
scattering phaseshift δ gives bound quantum defects!

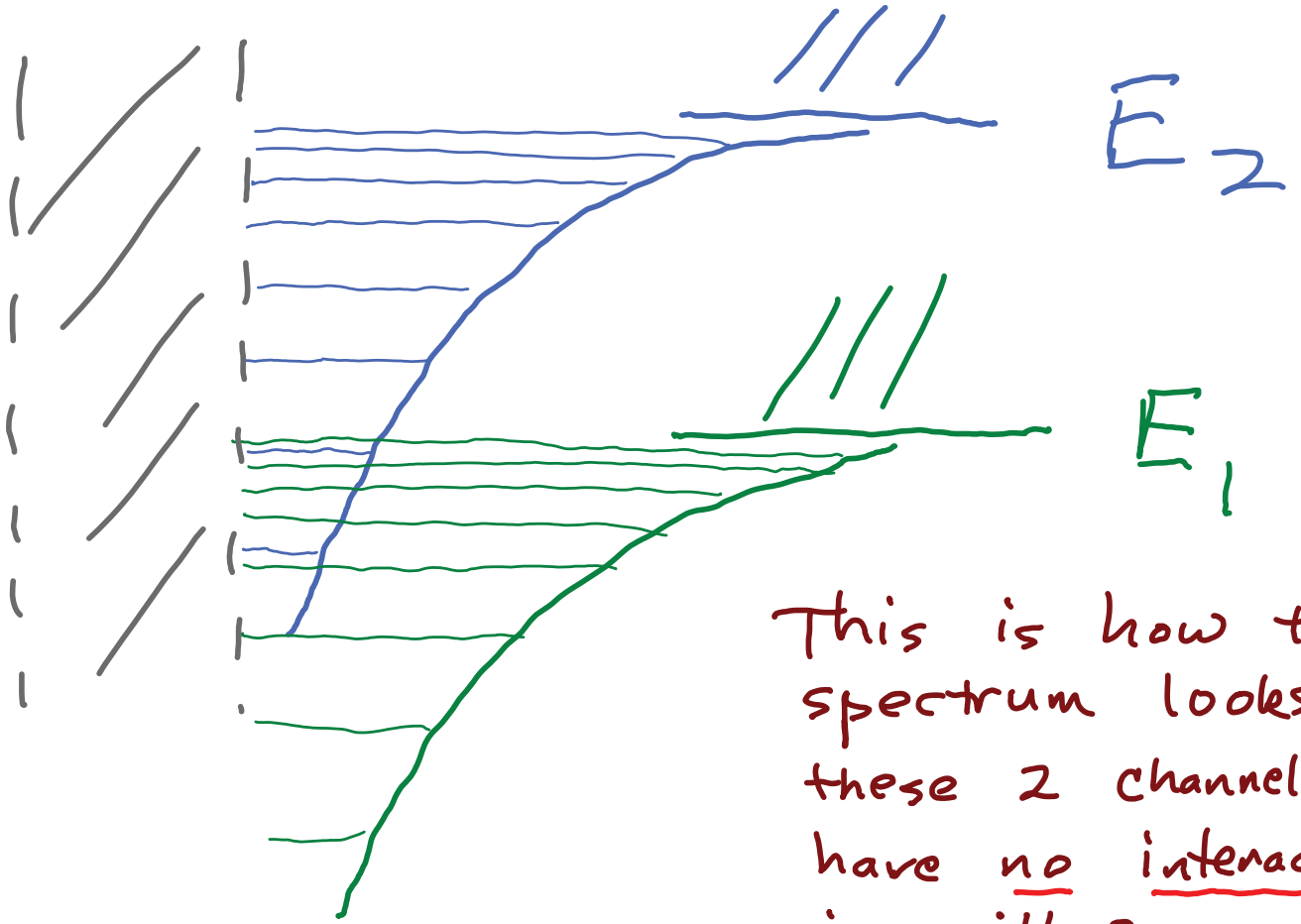
Single channel photoabsorption oscillator strengths



Multichannel generalization

Of course an atomic or molecular ion often has 2 or more energy eigenstates E_i in the range of interest, e.g. with 2 channels this looks like





This is how the atom spectrum looks if these 2 channels have no interaction, i.e. with 2 separate regular Rydberg series "unperturbed"

⇒ If no interaction, each eigenstate belongs to either channel 1 or channel 2

IN practice there will always be some interaction unless the channels have different symmetries

Effects of interactions between 2 channels

- bound state energy level perturbations at $E < E_1$
- autoionization of levels in region $E_1 < E < E_2$
- elastic and inelastic collisions at $E > E_2$

We're used to this situation in ordinary collision theory $\Rightarrow$ we need a scattering matrix $\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$

The i'-th independent solution at energy E at $r > r_0$ is:

$$\Psi^S_{i'} = \mathcal{A} \sum_i |i\rangle \left(f_i^-(r)\, \delta_{ii'} - f_i^+(r)\, S_{ii'} \right)$$

$f_i^-(r)$: incoming radial wave

$f_i^+(r)$: outgoing radial wave

or we often like to work with real representations of scattering amplitudes and information, i.e. the $\underline{K}$-matrix, related to $\underline{S}$ by

$$\underline{S} = \frac{\underline{1} + i\underline{K}}{\underline{1} - i\underline{K}} \quad , \underline{K} = \text{real, symmetric}$$

$$\Psi^k_{i'} = \mathcal{A} \sum_i |i\rangle \left(f_i(r)\,\delta_{ii'} - g_i(r)\,K_{ii'} \right)$$

where $K_{ii'}(E)$ depends only weakly on E and for our analysis can be assumed constant

The most interesting spectral region for a 2-channel problem is the autoionization region $E_1 < E < E_2$

Remarkably, the same constant $\underline{K}$ matrix at $E > E_2$ applies at $E < E_2$, but we need one extra step, the famous MQDT closed channel elimination:

Why "eliminate" channel 2?

- Because at $E < E_2$, (f_2, g_2) both grow exponentially, i.e.

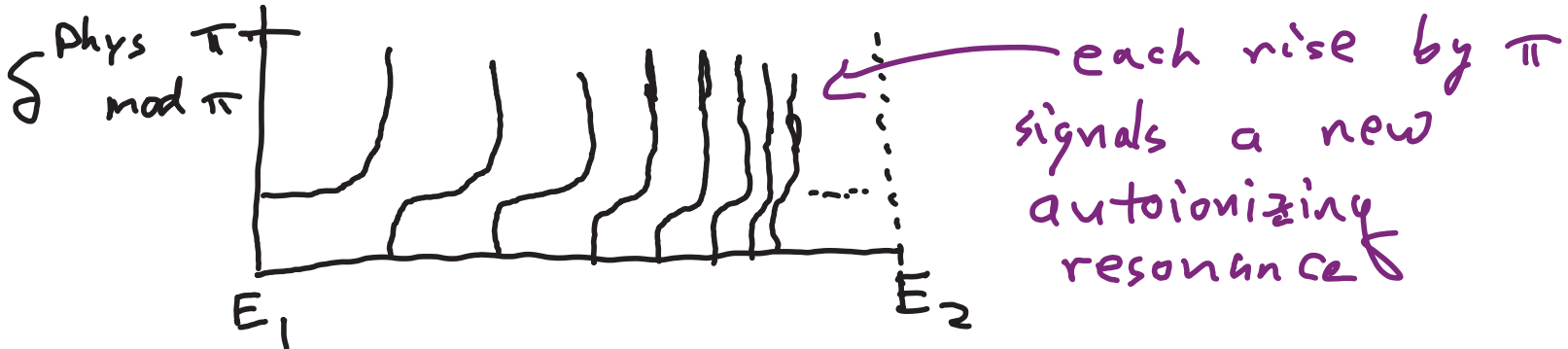
$$f_i(r) \longrightarrow \sin \pi\nu_i \, e^{Kir}(\cdots) + e^{-Kir}(\cdots)$$

$$g_i(r) \longrightarrow -\cos \pi\nu_i \, e^{Kir}(\cdots) - e^{-Kir}(\cdots)$$

and we must form a linear combination of Ψ_1^K and Ψ_2^K that kills the exponential growth,

giving the physical phaseshift at $E_1 < E < E_2$ as:

$$\tan \delta^{phys}(E) = K_{11} - K_{12}\,(K_{22} + \tan \pi\nu_2)^{-1} K_{21}$$



or in photoabsorption, we see a simple Rydberg series of autoionizing Fano resonances

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

each Fano lineshape looks like $\sigma_n = \sigma_{BG} \dfrac{\left(q + \frac{E-E_n}{\frac{1}{2}\Gamma_n}\right)^2}{1 + \left(\frac{E-E_n}{\frac{1}{2}\Gamma_n}\right)^2}$

and $\Gamma_n = \dfrac{\vec{\mu}^2}{\nu_n^3}$

Other observations

→ If only one continuum, then each Fano resonance has a point where $\sigma = 0$

→ The phaseshift rises by π across each Fano resonance

→ TIME DOMAIN IMPLICATIONS: see Ott et al. Science 340, 716 (2013)

Now, the preceding discussion involved "simple" resonances. Now we discuss the COMPLEX RESONANCE, and we need to consider at least 3 channels

Most of the mathematical details are worked out in the following article by Q. Wang & CHG, Phys. Rev. A 44, 1874 (1991). For earlier relevant work, see Giusti-Suzor and Fano, JPB 17, 215 (1984) and Friedrich & Wintgen, PRA 32, 3231 (1985)

We are mainly interested in the energy range $E_1<E<E_2$ between thresholds 1 and 2

$$\nu_i = [-2(E-E_i)]^{-1/2}$$

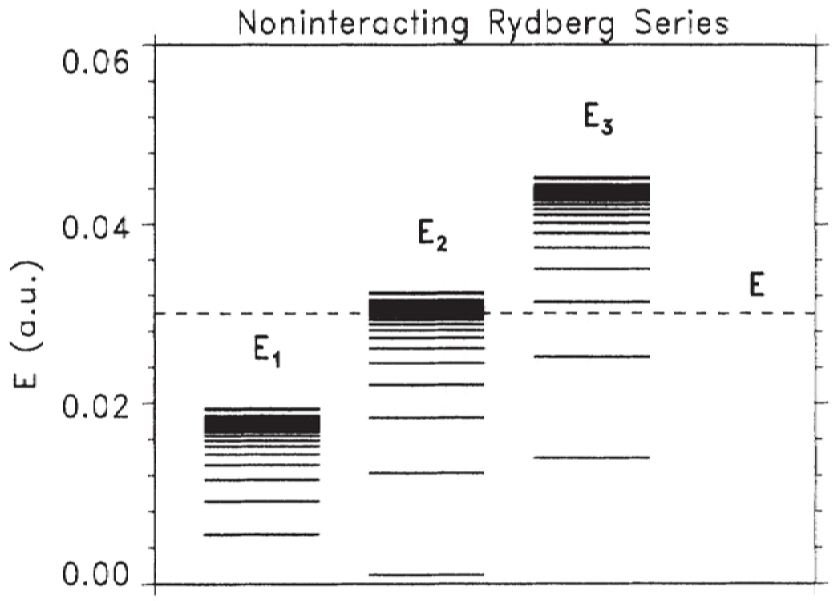


FIG. 1. Zeroth-order picture of a Rydberg series converging to three ionization thresholds $E_1 < E_2 < E_3$.

In fact we can first "eliminate" channel 3 to obtain energy-dependent 2-channel parameters, and then use our 2-channel math

$$\tilde{K} = \begin{bmatrix} K_{11} - \frac{K_{13}K_{31}}{T_3} & K_{12} - \frac{K_{13}K_{32}}{T_3} \\ K_{21} - \frac{K_{23}K_{31}}{T_3} & K_{22} - \frac{K_{23}K_{32}}{T_3} \end{bmatrix}$$

where $T_i \equiv \tan\pi\nu_i + K_{ii}$

And for photoabsorption processes that probe these states, we need to introduce three constant dipole amplitudes d1, d2, d3, and the channel elimination gives two energy dependent dipole amplitudes with a

$$\tilde{d} = \begin{bmatrix} d_1 - \frac{K_{13}d_3}{T_3} \\ d_2 - \frac{K_{23}d_3}{T_3} \end{bmatrix}$$

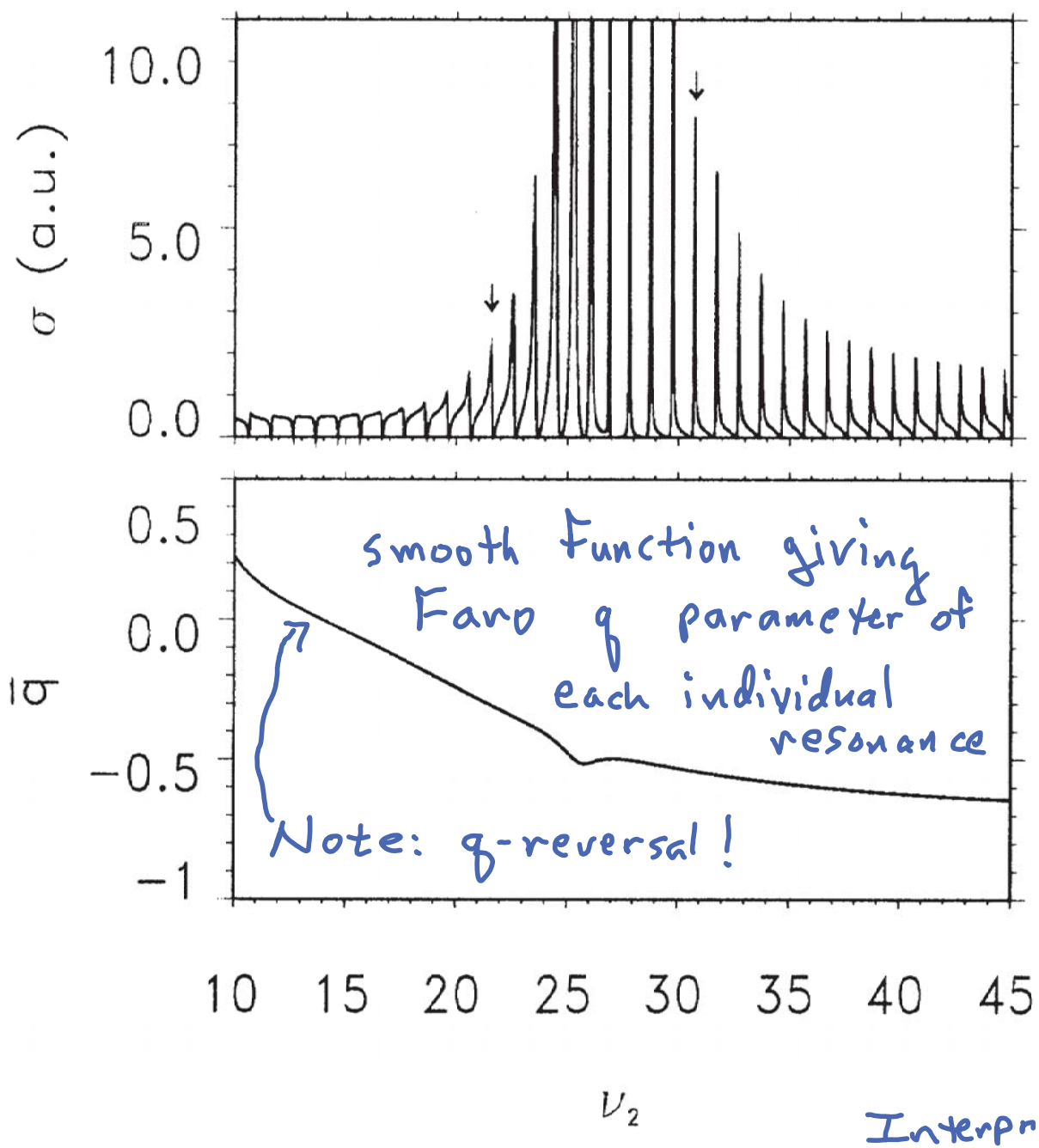
The energy-dependent photoabsorption cross section is given by

$$\sigma = I_0 \cos^2\Delta \left[\tilde{d}_1 - \frac{\tilde{K}_{12}\tilde{d}_2}{\tan\pi\nu_2 + \tilde{K}_{22}} \right]^2$$

where $\tan\Delta = \tilde{K}_{11} - \frac{\tilde{K}_{12}^2}{\tan\pi\nu_2 + \tilde{K}_{22}}$

So the cross section and physical phaseshift formulas are the same as for 2-channel QDT, except that now the $\tilde{K}$, $\tilde{d}$ are themselves energy-dependent in a resonant way.

Here is an example spectrum across a single "complex resonance"



Effects to note

1) The individual resonance widths vary across the complex resonance

2) One resonance has nearly zero width

3) The individual q-parameters change sign, called a "q-reversal" effect

Interpretation of multiple time scales...

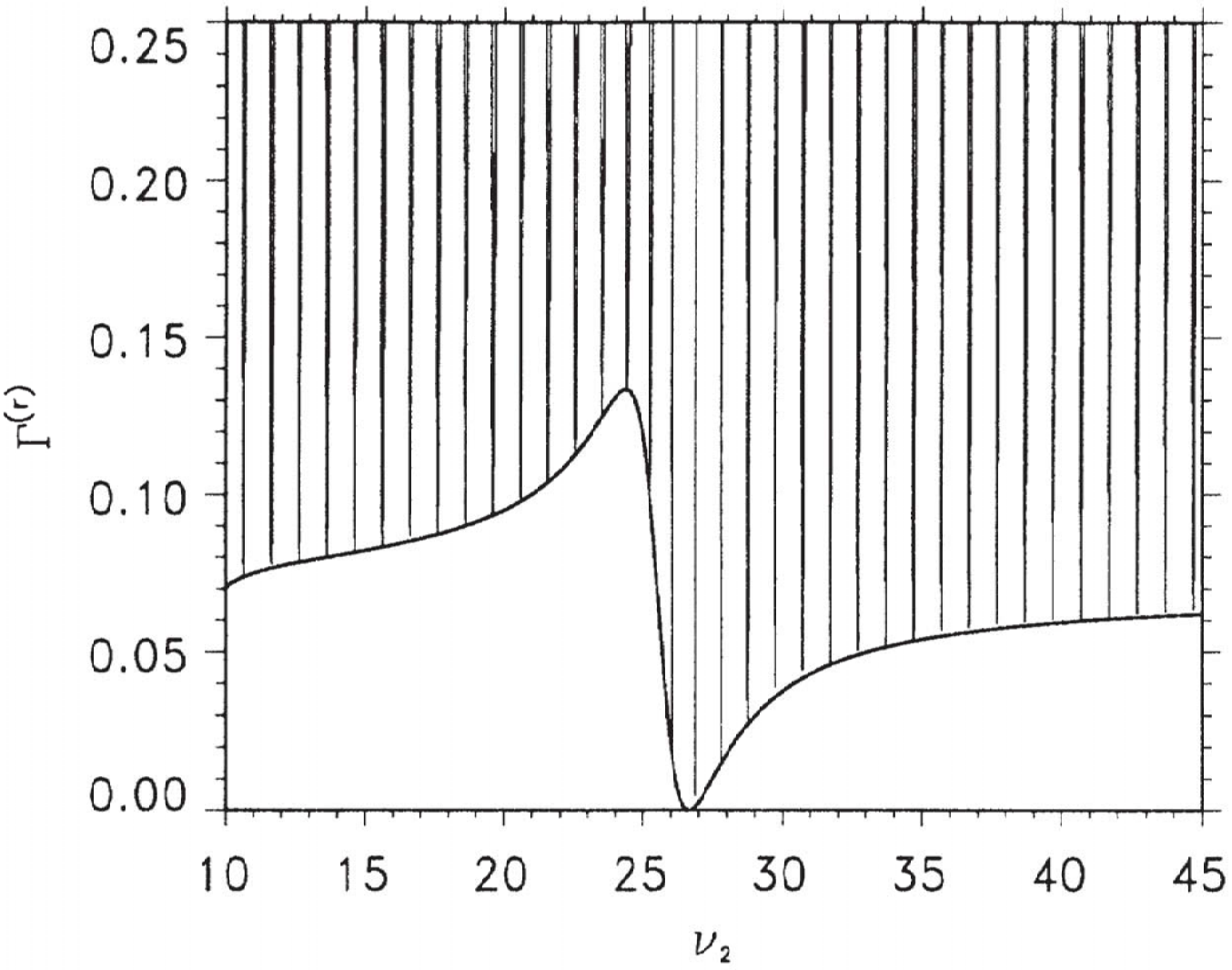
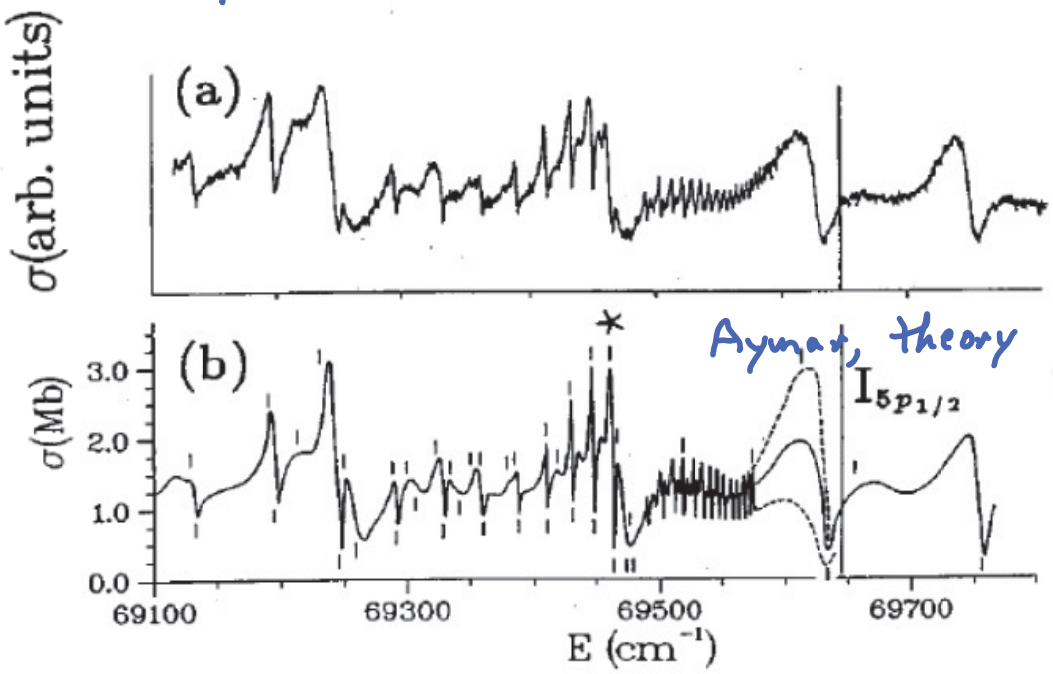


FIG. 5. The rapidly oscillating function is the reduced width function calculated from Eq. (9a). The solid curve is the smooth reduced width function, whose analytical form is given in Eq.

Sr photoionization example

Brown + Ginter, expt



Ayuso, theory

H2 photoionization

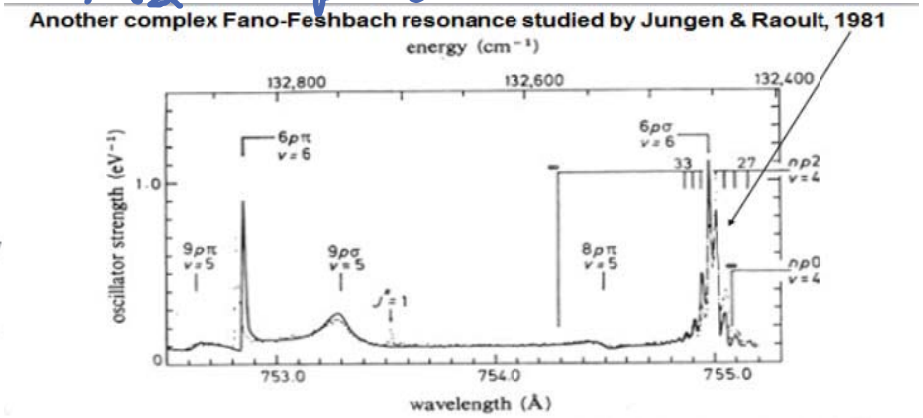
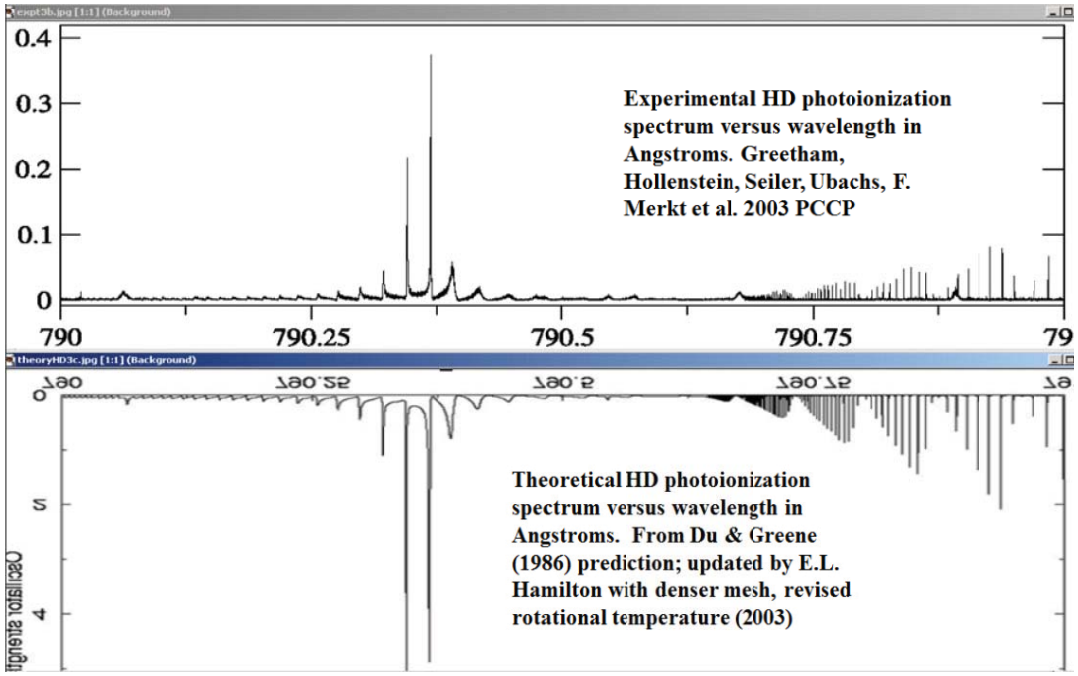


FIG. 10. Preionization near the $v^+ = 4$, $N^+ = 0$ and 2 thresholds in H_2 ($J = 1, J'' = 0$). The observed and calculated total oscillator strengths are shown as functions of photon wavelength. The experimental points from Dehmer and Chupka (1976) have been shifted by −0.068 Å so as to bring the observed and calculated $9p\sigma$, $v = 5$ peaks into coincidence. The calculated spectrum is broadened to a resolution of 0.016 Å to correspond to the experimental measurements. (After Jungen and Raoult, 1981.)

HD photoionization example



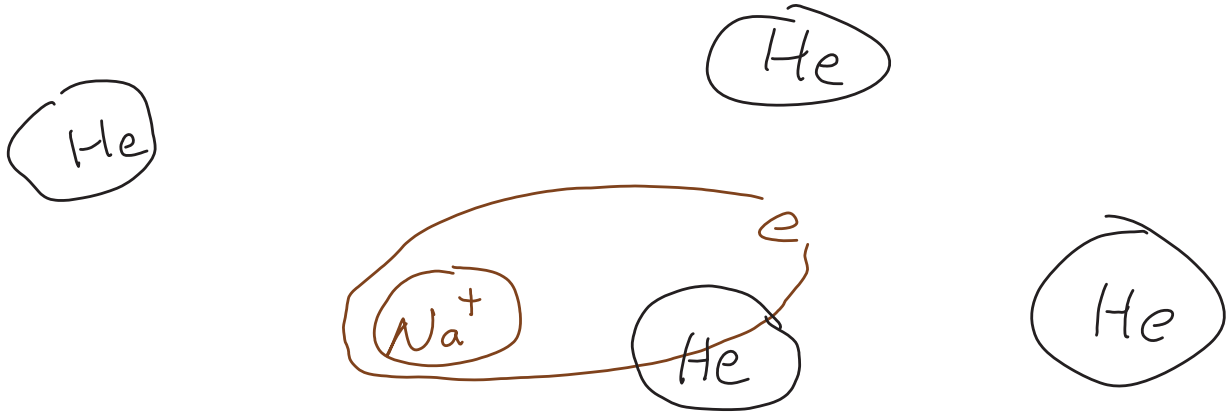
Topic #2

The Fermi pseudopotential

= a powerful idea that emerges from simple one-channel scattering theory

Reference: E. Fermi, Nuovo Cimento 11, 157 ('34)

Context: Fermi considered the spectrum of a highly-excited (Rydberg) atom like sodium that is embedded in a gas of ground state (helium) atoms which are also called PERTURBERS.



Notice that a high-n Rydberg e^- has a very slow average velocity, namely $v \propto \frac{1}{n}$ which implies a long de Broglie wavelength.

$\Rightarrow$ This implies that electron collisions with perturbing atoms occur essentially at zero energy $\Rightarrow$ s-wave only

Consider the time-independent Schrödinger equation for an electron-ion system having reduced mass m:

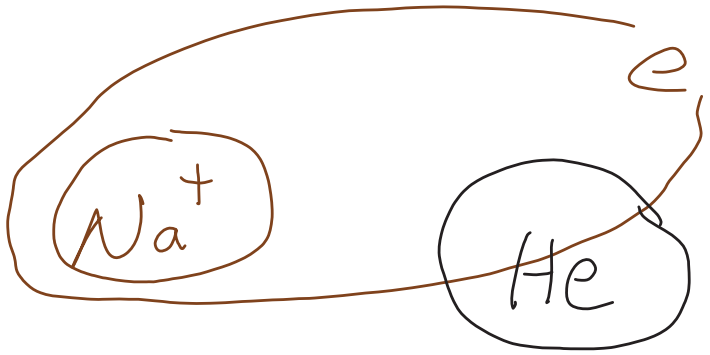
$$\nabla^2\Psi + \frac{2m}{\hbar^2}\left(E - U - \sum_i V_i\right)\Psi = 0$$

U: electron-ion potential

V_i: electron-perturber interactions

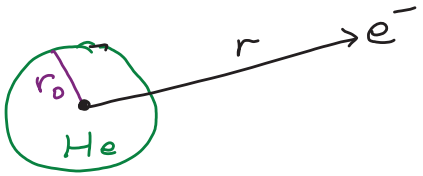
$\Rightarrow$ We can use the fact that the de Broglie wavelength is very long to compute the AVERAGE effect of all perturbers.

$\Rightarrow$ Denote this average wavefunction $\overline{\Psi}$ and call the average of $V\Psi \longrightarrow \overline{V\Psi}$



$$\Rightarrow \nabla^2\bar{\psi} + \frac{2m}{\hbar^2}(E-U)\bar{\psi} - \frac{2m}{\hbar^2}\sum_i \overline{V_i\psi} = 0$$

Now, to go farther, consider the wavefunction for an e^- very close to a perturbing He atom, in a coordinate system centered on the He atom:



The Wigner threshold law implies that since the scattering is at very low E where

$$\delta_\ell \propto k^{2\ell+1}$$

$\Rightarrow$ S-wave scattering dominates!

Therefore consider just the $\ell = 0$ radial Schrödinger equation,

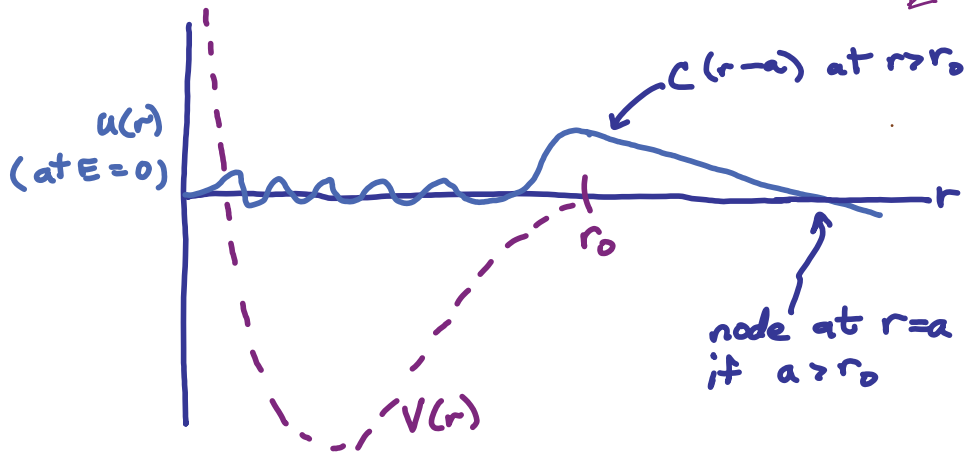
$$\Rightarrow \text{Set } \psi = \frac{u(r)}{r} Y_{00}(\theta,\phi)$$

so that $u(r)$ obeys

$$u''(r) = \frac{2m}{\hbar^2}\left(V(r)u(r) - \cancel{E}u(r)\right)$$

neglect since $E \simeq 0$

Fermi recognized that the solution for $r > r_0$, where $V(r) \to 0$, is simply a straight line, since $u''(r) = 0$ in that region. As we saw earlier



$\Rightarrow$ The next step in Fermi's derivation is to find the average $\overline{V\Psi}$, accomplished as follows:

Step 1 observe that

$$\frac{2m}{\hbar^2}\int V\Psi\, d^3r = 4\pi Y_{00} C\, a$$

Proof Start from $\frac{\hbar^2}{2m}\nabla^2\psi = V\Psi$ ($\overset{\text{at}}{E=0}$)

$$\frac{2m}{\hbar^2}\int V\Psi\, d^3r = \frac{2m}{\hbar^2} 4\pi Y_{00}\int_0^{r_0} V(r)\frac{u(r)}{r} r^2 dr$$

$$= 4\pi Y_{00} \int_0^{r_0} u''(r)\, r\, dr ,$$

using $\frac{2m}{\hbar^2} V u = u''$ from the radial Schrödinger eqn.

now integrate by parts,

$$= 4\pi Y_{00} \left[-\int_0^{r_0} u'(r)\, dr + r u'(r) \Big|_0^{r_0} \right]$$

$$= 4\pi Y_{00} \left(-u(r_0) + r_0 u'(r_0) \right)$$

(where we have used $u(0) = 0$)

or since $u(r) = (r-a)C$ at $r \geq r_0$

$$\Rightarrow \frac{2m}{\hbar^2} \int V \psi \, d^3r = 4\pi Y_{00} \left[-C(r_0 - a) + r_0 C \right]$$

$$= 4\pi Y_{00} C a ,$$

as was asserted above

Step 2 define the average $\psi \to \bar{\psi}$ near the perturber as

$$\bar{\psi} = \frac{\int d^3r \, Y_{00} \frac{u(r)}{r}}{\int d^3r} \simeq \frac{\int d^3r \, Y_{00} \frac{C(r-a)}{r}}{\int d^3r}$$

$\Rightarrow \bar{\Psi} \simeq C\, Y_{00}$ provided the averaging volume $\mathcal{V} \simeq \frac{1}{\text{density}}$ is large compared with a^3, i.e. if $(\text{density}) \times a^3 \ll 1$

Step 3 Now, putting steps 1 and 2 together $\Rightarrow \frac{2m}{\hbar^2} \int V\Psi\, d^3r = 4\pi a \bar{\Psi}$

$\Rightarrow$ This key relationship is often expressed in a different but equivalent form that can be used as an effective interaction V^{eff}, in the limit of LOW DENSITY and LOW ENERGY, i.e. For a perturber located at $\vec{R}$, the effective potential energy is

$$V^{\text{eff}}(\vec{r}) = \frac{2\pi a \hbar^2}{m} \delta(\vec{r} - \vec{R})$$

where again, m = reduced mass.

This last expression is known as the ZERO-RANGE FERMI PSEUDOPOTENTIAL

$\Rightarrow$ It can be used in place of the "true potential" $V(\vec{r})$, because it ensures that certain properties will come out correctly, such as energies, scattering phaseshifts, etc.

Note: While the Fermi pseudopotential is too singular to be used in an exact solution of the 3D Schrödinger equation, it can be extremely convenient and accurate in perturbative theories, or in mean-field theories (Hartree or Hartree-Fock)

Application 1 Rydberg molecule potential curves

Treat the effective interaction between a Rydberg electron and a neutral perturbing atom located at $\vec{R}$, using first-order perturbation theory.

$\Rightarrow$ The Hamiltonian is approximated as

$$H = H_0 + V$$

where H_0 is the unperturbed atomic Hamiltonian, whose eigenvalues are the energies of the isolated Rydberg atom, obeying

$$H_0 \, \psi_{n\ell m}(\vec{r}) = E_{n\ell}^{(0)} \, \psi_{n\ell m}(\vec{r})$$

If the Rydberg atom is an alkali atom, or if the principal quantum number is very high, its unperturbed energy levels are given by

$$E_{n\ell}^{(0)} \simeq \frac{-1}{2(n-\mu_\ell)^2} \quad \text{in atomic units.}$$

And the 1^{st}-order perturbative energy correction is just

$$\Delta E_{n\ell m}^{(1)} = \langle \psi_{n\ell m} | \frac{2\pi a_0 \hbar^2}{m_e} \delta(\vec{r}-\vec{R}) | \psi_{n\ell m} \rangle$$

$$= \frac{2\pi a_0 \hbar^2}{m_e} |\psi_{n\ell m}(\vec{R})|^2$$

Or, plugging in $\Psi_{nlm}(\vec{R}) = \frac{u_{nl}(R)}{R} Y_{lm}(\hat{R})$

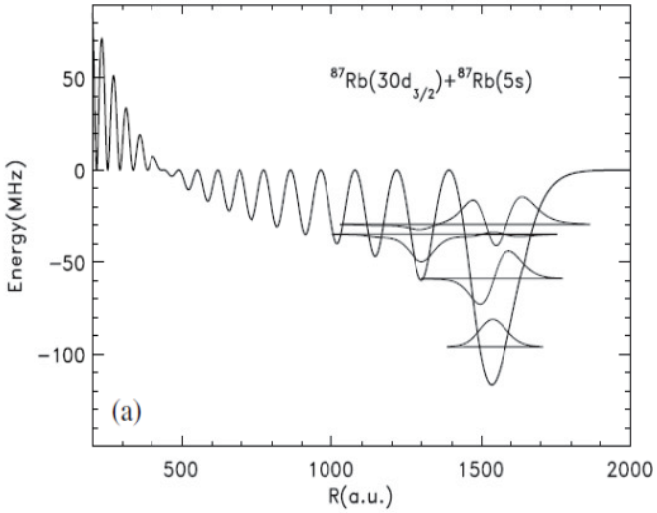
where $Y_{lm}(\hat{R}) = Y_{lm}(0,0) = \sqrt{\frac{2l+1}{4\pi}}\,\delta_{m,0}$

we find the Born-Oppenheimer potential curve for this Na^*He or analogous molecule is

Born-Oppenheimer

$$U(R) \simeq E_{nl} + \frac{2\pi a \hbar^2}{m_e}\left(\frac{2l+1}{4\pi}\right)\frac{u_{nl}^2(R)}{R^2}$$

this is an oscillatory potential curve that tracks the Rydberg electron wavefunction oscillations.



These ideas, predicted in Phys. Rev. Lett. 85, 2458 (2000) have been confirmed and extended experimentally by V. Bendkowsky et al. Nature 458, 1005 (2009)

Rydberg molecules, case (ii)

A second scenario in Rydberg molecule systems is the possibility that the unperturbed atomic levels are degenerate or nearly so..

$\Rightarrow$ must use degenerate perturbation theory

$\Rightarrow$ Let's denote by l_0 the largest Rydberg partial wave with an appreciable, non-negligible quantum defect.

Then to a good approximation, the energies of all states with $l > l_0$ are

$$E_{nl} = \frac{-1}{2n^2}, \quad l = l_0+1, l_0+2, \ldots n-1$$

Since these levels are degenerate, we must use degenerate perturbation theory

e.g. if we neglect all spin-orbit interactions then $\vec{l} \cdot \hat{R} = \lambda$ = conserved

Again, for a δ-function interaction, only $\lambda = 0$ states contribute

And the Hamiltonian matrix elements are

$$\langle n\ell\lambda | H | n\ell'\lambda\rangle = \frac{-1}{2n^2} + \frac{\delta_{\lambda 0}}{4\pi}(2\ell+1)^{1/2}(2\ell'+1)^{1/2}\,2\pi a\,\frac{u_{n\ell}(R)\,u_{n\ell'}(R)}{R^2}$$

Now, aside from the constant $\frac{-1}{2n^2}$, this is a separable matrix which is simple to diagonalize.

e.g., define $C_\ell \equiv a^{1/2}\left(\frac{2\ell+1}{2}\right)^{1/2}\frac{u_{n\ell}(R)}{R}$

$$\Rightarrow \quad \underline{C} = \begin{pmatrix} C_{\ell_0+1} \\ C_{\ell_0+2} \\ \vdots \\ C_{\ell=n-1} \end{pmatrix} \Rightarrow \underline{V} = \underline{C}\,\underline{C}^T$$

$\underline{C}^T$: transpose of $\underline{C}$

The eigenvalue problem reads

$$\underline{V}\vec{z} = v\vec{z} \quad \text{or} \quad \underline{C}\left(\underline{C}^T\vec{z}\right) = v\vec{z}$$

or after multiplying by $\underline{C}^T$ from the left,

$$\Rightarrow \left(\underline{C}^T\underline{C}\right)\left(\underline{C}^T\vec{z}\right) = v\left(\underline{C}^T\vec{z}\right)$$

Now dividing both sides by the NUMBER $\underline{C}^T\vec{z}$ gives the lone nonzero eigenvalue to be:

$$v = \underline{C}^T\underline{C} \quad \text{or} \quad v = \sum_{\ell=\ell_0+1}^{n-1} C_\ell^2 = a\sum_\ell \left(\frac{2\ell+1}{2}\right)\frac{u_{n\ell}^2(R)}{R^2}$$

$\Rightarrow$ the degeneracy is lifted, but only

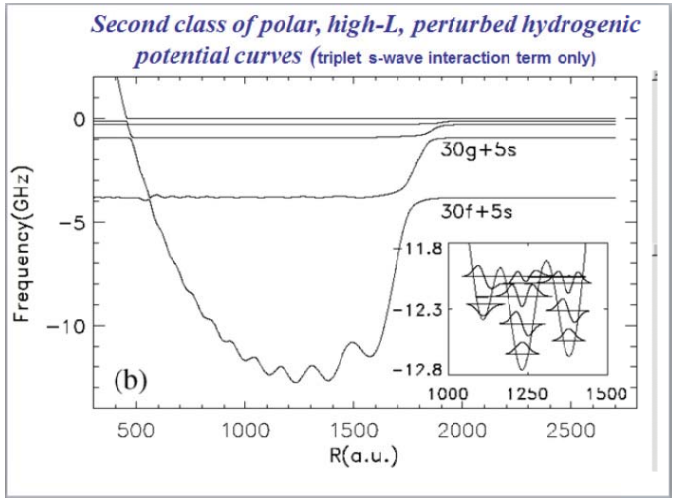
for one energy level,

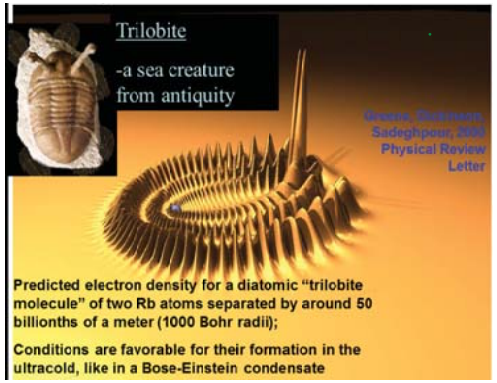
e.g

↓ v

↓ a.s.o

electronic wavefunction ?





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Observation of pendular butterfly Rydberg molecules

Thomas Niederprüm[1], Oliver Thomas[1,2], Tanita Eichert[1], Carsten Lippe[1], Jesús Pérez-Ríos[3], Chris H. Greene[3] & Herwig Ott[1]

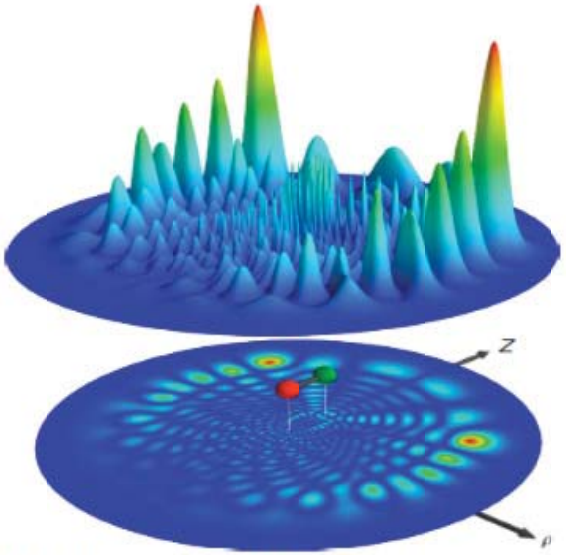
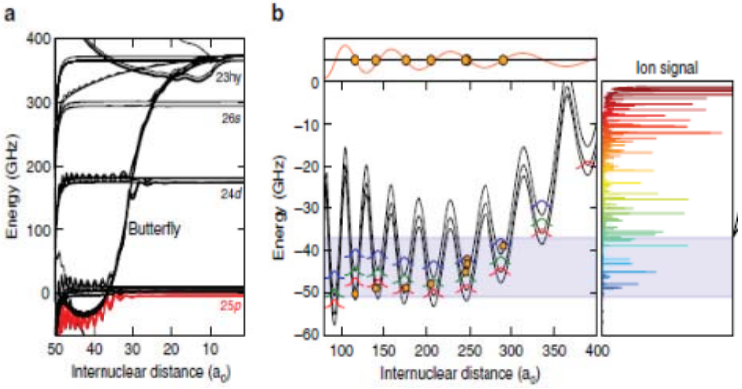
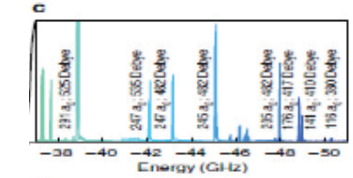


Figure 1 | Radial electron density of a butterfly molecule. The upper plane shows a surface plot of the radial electron density $\rho|\Psi(z,\rho)|^2$ for a butterfly molecule near the 25p-state of rubidium. The lower plane shows the





The Rb*-Rb molecule seen in 2009 by Vera Bendkowsky, Tilman Pfau, and collaborators, with size around 100 nm

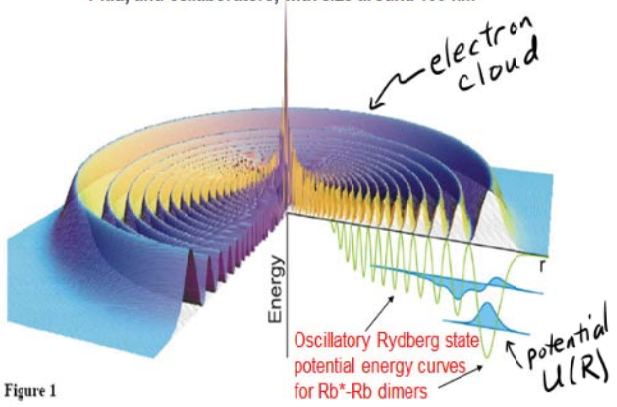
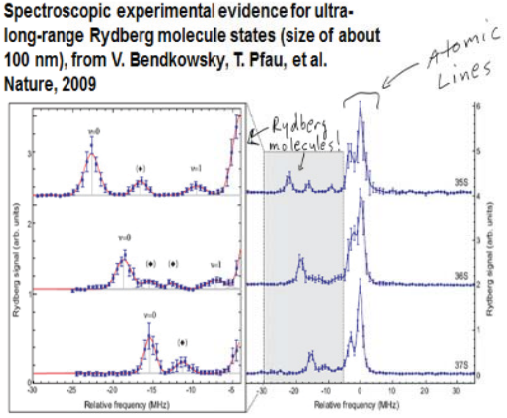


Figure 1

Electron probability density in the (r,φ) plane $\frac{r}{2\pi}|\psi(r)|^2$ of the ^{87}Rb 35S state. The surface plot shows the spherically symmetric density distribution of the Rydberg electron and the attractive potential for a 5S ground state atom (green line).The repulsive part of the potential at short distances is not shown. Around the potential minimum at a distance of 1897 Bohr radii from the core there exist two vibrational states with a binding energy $E_B(v=0)$ = -23.4 MHz and $E_B(v=1)$ = -10.6 MHz.

Spectroscopic experimental evidence for ultra-long-range Rydberg molecule states (size of about 100 nm), from V. Bendkowsky, T. Pfau, et al. Nature, 2009



experimental verification by Tilman Pfau's group, - spectroscopic signatures

↑ Nature 2009

See also recent papers: Eiles & CHG, PRA 2017;

Theory of a dilute Bose-Einstein condensate with interactions

Application #2

↑ this is an application of the Fermi pseudopotential in mean-field theory

Consider N identical ultracold atoms in an atom trap, that interact through the Fermi pseudopotential,

$$V = \frac{4\pi a \hbar^2}{M} \delta(\vec{r}_1 - \vec{r}_2)$$

Note that if these are interacting atoms with unequal mass, you should replace

$$M \longrightarrow 2m_{\text{reduced}}$$

A variational "Hartree" or "Hartree-Fock" trial function that is consistent with the concept of a "mean-field" is

$$\Psi = \psi(\vec{r}_1)\,\psi(\vec{r}_2)\,\cdots\,\psi(\vec{r}_N)$$

and this is expected to give a reasonable description of the ground state.

i.e. each atom is placed into one orbital $\psi(\vec{r}_i)$, and that orbital is optimized variationally to minimize the energy functional $E[\psi] = \dfrac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

Derivation Next sketch the logic, step by step, starting with the Hamiltonian for N particles:

$$H = \sum_{i=1}^{N} h(\vec{r}_i) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} V(\vec{r}_i - \vec{r}_j)$$

where the one-atom Hamiltonian is

$$h(\vec{r}_i) = -\frac{\hbar^2}{2m}\nabla_i^2 + V_{ext}(\vec{r}_i)$$

Typically the external trapping potential can be approximated as a 3D harmonic oscillator, $\frac{1}{2}m\omega^2 r_i^2$, where r_i is the distance of the i^{th} atom from the center of the trap.

The atom-atom interaction will be replaced in this derivation by the Fermi pseudopotential

$$V(\vec{r}_i - \vec{r}_j) = \frac{4\pi a \hbar^2}{m}\delta(\vec{r}_i - \vec{r}_j)$$

which turns out to give MUCH better results in mean field theory than the "true" atom-atom potential which has a very repulsive short-range core and a long range van der Waals interaction

We can require the first variation with respect to Ψ^* to vanish,

i.e.

$$\frac{\delta E}{\delta \Psi^*} = N\langle \delta\Psi | h | \Psi\rangle + \frac{N(N-1)}{2}\,\delta\langle\Psi\Psi|V|\Psi\Psi\rangle - \epsilon N\langle\delta\Psi|\Psi\rangle = 0 \qquad (*)$$

and

$$\frac{\delta E}{\delta \epsilon} = 0 = N\left(\langle\Psi|\Psi\rangle - 1\right) \qquad (**)$$

and observe that

$$\delta\langle\Psi\Psi|\, g\,\delta(\vec{r}-\vec{r}_2)\,|\Psi\Psi\rangle$$

$$= \delta \int d^3r \int d^3r_2\, \Psi^*(\vec{r})\Psi^*(\vec{r}_2)\,\delta(\vec{r}-\vec{r}_2)\Psi(\vec{r})\Psi(\vec{r}_2)\, g$$

$$= \delta \int d^3r\, \Psi^*(\vec{r})\Psi^*(\vec{r})\Psi(\vec{r})\Psi(\vec{r})\, g$$

$$= 2\int d^3r\, \delta\Psi^*\,\Psi^*(\vec{r})\Psi(\vec{r})\Psi(\vec{r})\, g$$

$$V(\vec{r}_i - \vec{r}_j) = \frac{4\pi a\hbar^2}{m}\,\delta(\vec{r}_i - \vec{r}_j), \qquad g$$

$\Rightarrow$ So plugging this into $(*)$, dividing $(*)$ by N, and setting the sum of integrands to vanish at all $\vec{r}$ gives

$$h|\Psi\rangle + (N-1)\,g|\Psi|^2|\Psi\rangle = \epsilon|\Psi\rangle \qquad \text{GP}$$

with the auxiliary normalization constraint,

$$\langle\Psi|\Psi\rangle = 1 \quad \text{and} \quad g = \frac{4\pi a\hbar^2}{m}$$