Begin Many-e⁻ Atoms: Quantum Defect Theory

See MQDT Primer by Stephen Ross, pages 73-110 in Half Collision Resonance Phenomena in Molecules (AIP Conf. Proc. #225, M. Garciá-Sucre, G. Raseev, and S.C. Ross) 1991.

Last Time:

$$\text{turning points of } V_\ell(r) = -\frac{e^2}{r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}$$

* $$r_\pm(n,\ell) = a_0 n^2 \left[1 \pm \left(1 - \frac{\ell(\ell+1)}{n^2}\right)^{1/2}\right] \approx a_0 n^2 \left[1 \pm 1 \mp \frac{\ell(\ell+1)}{2n^2}\right] \text{ for } \ell << n$$

* $u_{n\ell}(r) \equiv rR_{n\ell}(r)$ is dominated by a small lobe (n-independent nodal position) near the inner turning point, amplitude scales as $n^{-3/2}$, and a large lobe at the outer turning point (containing essentially all of the probability).

envelope
$u_{n\ell}(r) \propto p_{n\ell}(r)^{-1/2}$

* $$E_{n\ell} = IP - \frac{\Re}{n^2}$$

* nodes: $n - \ell - 1$ radial nodes
  ℓ angular nodes
  $n - 1$ total nodes
  $\bar{\lambda}/2$ gives spacing between radial nodes, $\lambda(x) = \dfrac{h}{p(x)}$

* expectation value scaling of $\langle r^\sigma \rangle$

$\sigma < -1$	$\propto n^{-3}$
$\sigma \geq +1$	$\propto n^{2\sigma}$ (see below)
$\sigma = -1$	$\propto n^{-2}$ (H-atom energy levels)

Geometric mean of expectation values of r for off-diagonal matrix elements:

$$\langle r \rangle_{n\ell} \propto n^2$$

$$\langle n\ell | r^\sigma | n'\ell' \rangle \propto \left[\left(r_{+n\ell}\right)^{1/2}\left(r_{+n'\ell'}\right)^{1/2}\right]^\sigma \approx \left[\left(n^2\right)^{1/2}\left(n'^2\right)^{1/2}\right]^\sigma$$

$$= \left(nn'\right)^\sigma \approx n^{2\sigma}$$

(when is $\langle r^n \rangle \approx \langle r \rangle^n$?)

TODAY

1. Many-e⁻ atom treated as a core plus an outer e⁻ that sees a partly shielded core as having a charge distribution Z(r).
2. ℓ-dependent energy shifts → n-independent quantum defects $E_{n\ell} = IP - \dfrac{\Re}{\left(n - \mu_{n\ell}\right)^2}$ ($n \to \nu$)
3. energy shifts are actually phase shifts of $u_{n\ell}$(r) relative to $u_{n\ell}$(r) for H-atom
4. Rigorous QDT
   A. regular and irregular Coulomb functions *f,g* satisfy Hydrogen-like Schrödinger Equation <u>OUTSIDE</u> the core

   B. Boundary conditions at $r \to \infty$

   Noninteger values of $\nu = \left[-\dfrac{\Re}{E_{n\ell}}\right]^{1/2}$ require a sum of f and g Coulomb functions.

   Find the value of $\nu = n - \mu_\ell$ that satisfies the $r \to \infty$ boundary condition

   ∞ number of members in the series of ν's (effective principal quantum number) spaced by 1.000, $\therefore$ constant quantum defect

   C. $\pi\mu_\ell$ is a phase shift
   repeated patterns in each $\nu \to \nu + 1$ integer region of ν

   D. Multi-channel QDT
   $\boldsymbol{\mu}$ matrices. The matrix $\boldsymbol{\mu}$ is a generalization of the quantum defect.

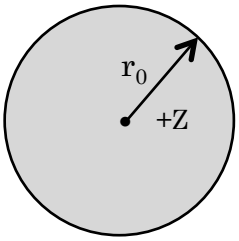
e⁻ colliding with core can also transfer energy and angular momentum to the core-e⁻

* "channels" rather than individual eigenstates

* focus on dynamics, but in a "black box" way. Dynamics happens within a restricted region of space. This region of space is *always* sampled, regardless of E, in the same way for every member of a Rydberg series. Everything is determined by the boundary conditions for the outgoing wave. SCATTERING THEORY rather than an EFFECTIVE HAMILTONIAN MODEL.

The goal here is to extract from a complicated many-body problem some regular features that will help in assigning, understanding, and modeling experimental data.

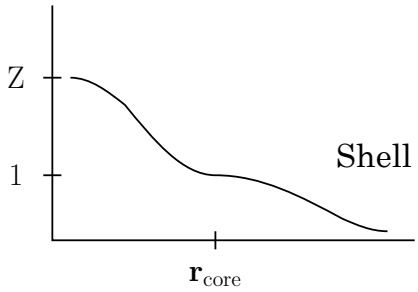
1. Many-e⁻ Atom



outside core e⁻ sees Z = +1
inside core e⁻ sees Z(r)

e^-

outer electron
(valence, Rydberg)



Shell Structure

ensures n^{-3} rather than n^{-2}

as $r \to 0$, $\mathbf{H}^{(1)}$ diverges faster than $-e^2/r$ because Z(0) > 1.

2. ℓ-dependent sampling of core
   high ℓ : see $\langle Z(r) \rangle \sim +1$
   low ℓ : see $\langle Z(r) \rangle = Z_\ell^{eff} >> 1$
   energy stabilization

$$\therefore E_{n\ell}^{(1)} = \langle n\ell | \mathrm{H}^{(1)} | n\ell \rangle \propto -\frac{|c_\ell|}{n^3}$$

$$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}$$

$$\mathbf{H}^{(1)} \approx -\frac{[Z(r)-1]e^2}{r}$$

$$\therefore E_{n\ell} = -\frac{\Re}{n^2} - \frac{|c_\ell|}{n^3} \approx \frac{-\Re}{(n-\mu_\ell)^2} \quad \therefore \quad \mu_\ell = \frac{|c_\ell|}{2\Re} << n$$

expand in Taylor series

call this ν, "effective principal quantum number*"

so far we have focussed on $E_{n\ell}$

3. What does Z(r) do to $u_{n\ell}$(r)?

* outside core e^- sees same $V_\ell(r)$ as Hydrogen atom
* must be same as $u_{n\ell}(r)$ for H except for phase shift inward (why inward?)
* all the unique stuff occurs inside the core — causes the phase shift.
  - nodal structure inside core is invariant with respect to n or E (the locations of the nodes are not dependent on ν, but the amplitudes between nodes scale as $\nu^{-3/2}$)

Mulliken: "ontogeny recapitulates phylogeny"
intra-core nodal structure is n-independent
nodal structure encodes *all* $e^- \leftrightarrow$ nucleus dynamics!

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4. Do all of this more rigorously: Quantum Defect Theory

* regular Rydberg series, one series for each value of ℓ
* n-scaling of inner lobe amplitude and of all matrix elements
* large quantum defects for small ℓ
* entire Rydberg series and the associated ionization continuum (e^- ejected in a specified ℓ-partial wave) is a single entity

These are what we will obtain.

follow treatment by Ross, but not using atomic units:

redefine 0 of E $E_n = -\frac{\Re}{n^2}$ $\quad n = 1,2,\ldots$ for H, $E = 0$ at $n = \infty$

$$n = \left[-\frac{E_n}{\Re}\right]^{-1/2}$$

generalize to noninteger-n for non-hydrogen: $\nu \equiv \left[-\frac{E_\nu}{\Re}\right]^{-1/2}$

use ν (effective principal quantum number, ν) rather than E as a label for $u_{n\ell}(r)$

Schrödinger Equation for H (the "Coulomb Equation")

as a continuous variable rather than as an integer quantum number

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2}\right] - \frac{e^2}{r} - \underbrace{E}_{E = -\frac{\Re}{\nu^2}}\right\} u_\ell(\nu, r) = 0$$

well known solutions:

2nd-order differential equation - two linearly independent solutions (at each ℓ, ν)

$$f_\ell(\nu, r) \to 0 \text{ as } r \to 0 \qquad \text{"regular"}$$

$$g_\ell(\nu, r) \to \infty \text{ as } r \to 0 \qquad \text{"irregular"}$$

of no use for Hydrogen, but it turns out that we need both f and g to satisfy $r \to \infty$ boundary condition when ν is non-integer

(We do not use f or g all the way in to $r \to 0$. We use them only outside some critical radius. So we are not concerned by the divergence of g_ℓ as $r \to 0$)

For the H atom, we have no use for $g_\ell(\nu, r)$ because it cannot satisfy the boundary condition as $r \to 0$

A. For many-e⁻ atoms, <u>beyond some critical</u> r_0, Schrödinger Equation is identical to that of H. The only difference is that we must treat the $r \to 0$ boundary condition differently.

Universal boundary conditions are $r \to \infty, u_\ell(\nu, r) \to 0$

for $E < 0, r \to \infty$, *asymptotic* forms for f and g are

$$f_\ell(\nu, r \to \infty) \to C(r)\sin[\pi(\nu - \ell)]e^{r/\nu}$$

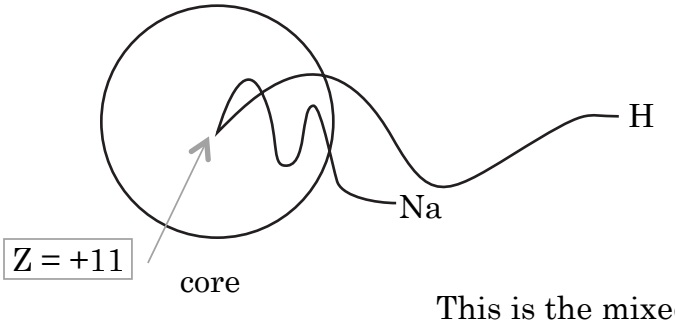
$$g_\ell(\nu, r \to \infty) \to -C(r)\cos[\pi(\nu - \ell)]e^{r/\nu}$$

$C(r) \to 0$ as $r \to \infty$

but $C(r)e^{r/\nu} \to \infty$ as $r \to \infty$, so the only way to satisfy the $r \to \infty$ boundary condition <u>for a pure</u> $u_\ell(\nu, r) = f_\ell(\nu, r)$ is for $(\nu - \ell)$=integer

└ regular Coulomb function

B. But we might want to use a mixture of f_ℓ and g_ℓ to deal with non-integer $(\nu - \ell)$, which we will need to deal with many-electron atoms.



For an Na atom, $u_\ell(\nu, r)$ emerges from the core with extra phase accumulation relative to the H atom. This corresponds to a "sucking in" of a hydrogenic function.

This is the mixed f, g form of $u_\ell(\nu_s r)$ when $\nu - \ell$ is non-integer.

$$u_\ell(\nu, r) = \alpha f_\ell(\nu, r) - (1 - \alpha^2)^{1/2} g_\ell(\nu, r) \quad **$$

* invariance of intra-core nodal structure – amount of phase shift along a Rydberg series should be independent of ν. [We expect this to be true.]

* mixing of 2 types of Coulomb functions is required in order to have noninteger ν, yet still satisfy the $u_\ell(\nu, r) \to 0$ as the $r \to \infty$ boundary condition.

TRICK: $\left.\begin{aligned}\alpha &\equiv \cos(\pi\mu_\ell)\\ -(1-\alpha^2)^{1/2} &= -\sin(\pi\mu_\ell)\end{aligned}\right]$ plug this into the ** equation on page 29-5

$$\psi = u_\ell(v,r)\Phi_\ell(\text{CORE}) = \left[f_\ell(v,r)\cos(\pi\mu_\ell) - g_\ell(v,r)\sin(\pi\mu_\ell)\right]\Phi_\ell$$

plug in the asymptoptic forms for f and g

$$\psi \Rightarrow \Big\{\underbrace{\sin[\pi(v-\ell)]}_{f_\ell(\nu,r)}\cos(\pi\mu_\ell) + \underbrace{\cos[\pi(v-\ell)]}_{-g_\ell(\nu,r)}\sin(\pi\mu_\ell)\Big\}C(r)e^{r/v}\Phi_\ell$$

the factor $\{\ \} \to 0$ as $r \to \infty$ is required. How?

$\{\ \} = 0$: $\sin\left[\pi(\nu-\ell)\right]\cos(\pi\mu_\ell) = -\cos\left[\pi(\nu-\ell)\right]\sin(\pi\mu_\ell)$

This requires that $\dfrac{\sin\left[\pi(\nu-\ell)\right]}{\cos\left[\pi(\nu-\ell)\right]} = -\dfrac{\sin(\pi\mu_\ell)}{\cos(\pi\mu_\ell)}$

constraint on ν. What are <u>all</u> of the values of ν which are consistent with this constraint?

$\tan\left[\pi(\nu-\ell)\right] = -\tan(\pi\mu_\ell)$

$\tan\theta = -\tan(-\theta) = -\tan(-\theta + n'\pi)$ n' integer ordinary trigonometry

let $\theta = \pi\mu_\ell$

$\therefore \tan[\pi(\nu-\ell)] = \tan(-\theta + n'\pi)$

thus $-\theta + n'\pi = \pi(\nu-\ell) \Rightarrow \theta = n'\pi - \pi(\nu-\ell)$

$\theta = \pi\mu_\ell$

$\downarrow$

but $\pi\mu_\ell = \pi(\underbrace{n' - \nu + \ell}_{n'+\ell=n})$

$\uparrow$

integer

$$\theta = \pi(n' - \nu + \ell)$$

$$n = n' + \ell,\ \mu_\ell = n - \nu$$

$$\boxed{\nu = n - \mu_\ell}$$

ν is smaller than integer-n by constant term μ_ℓ.

This implies the existence of an infinite series of ψ with values of integer n for which $\psi \to 0$ as $r \to \infty$.

Get this infinite series of ν's, increasing in steps of 1, simply by specifying <u>one</u> ν-independent value of μ_ℓ!

All of the ν-dependence (E-dependence) of $\psi_\ell(\nu,r)$ is explicitly built into $f_\ell(\nu,r)$ and $g_\ell(\nu,r)$. μ_ℓ describes the relative amounts of f_ℓ and g_ℓ in ψ. This amount of *f,g* mixing is determined when the e^- leaves the core with the precise phase shift ensures that $\psi \to 0$ at $r \to \infty$.

C. How can we show that $\pi\mu_\ell$ is a phase shift?

The asymptotic form of ψ is

$$\psi \to \left\{\sin\left[\pi\left(\nu-\ell\right)\right]\cos\left(\pi\mu_\ell\right)+\cos\left[\pi\left(\nu-\ell\right)\right]\sin\left(\pi\mu_\ell\right)\right\}C(r)e^{r/\nu}$$

use the double angle formula: $\sin A\cos B+\sin B\cos A=\sin(A+B)$

$$\psi \to \left\{\sin\left[\pi\left(\nu-\ell\right)+\underline{\underline{\pi\mu_\ell}}\right]\right\}C(r)e^{r/\nu}$$

but $f_\ell\left(\nu,r\right)\to \sin\left[\pi\left(\nu-\ell\right)\right]C\left(r\right)e^{r/\nu}$

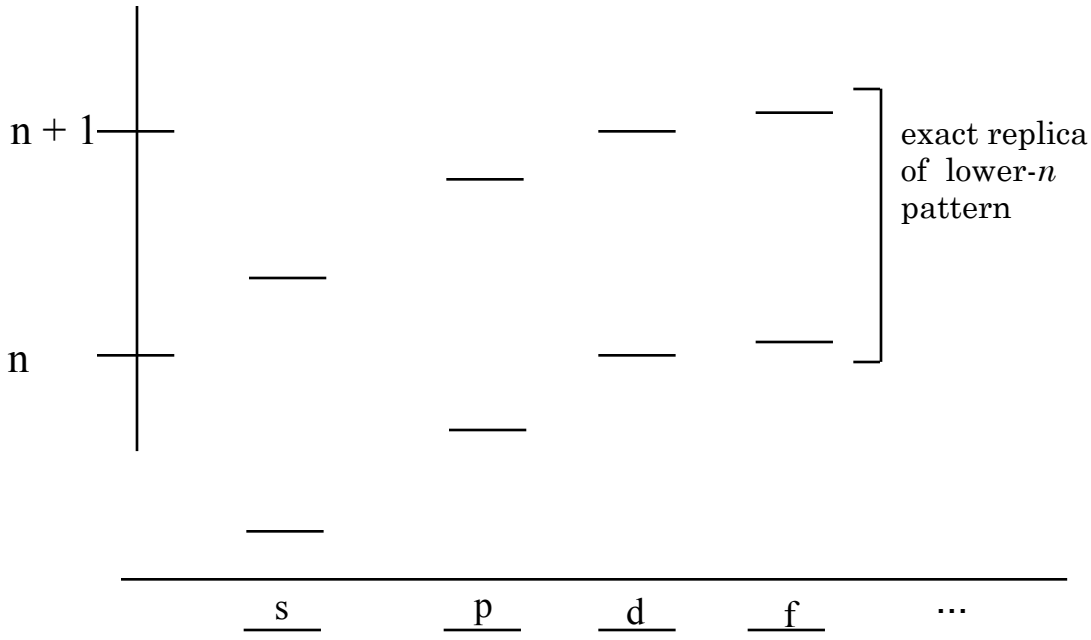
so this modified function is identical to the <u>regular</u> [i.e. $f_\ell(\nu,r)$] Coulomb function but with a $\pi\mu_\ell$ phase shift.

If $\mu_\ell > 0$, this corresponds to an <u>advance</u> of the phase of $u_\ell(\nu,r)$ relative to that for H. As expected, Ψ is sucked into the core by an amount $\pi\mu_\ell$ [+ an arbitrary number of 2π's] by the radial charge distribution Z(r) of the core.

$\pi\mu_\ell$ is the phase shift that occurs inside the core. It is the boundary condition at r = 0 shifted out to $r = r_0$. On the other hand, the $r \to \infty$ boundary conditions is satisfied by $\nu = n - \mu_\ell$ where *n* is an integer.

the quantum defect!

Small (replicated) region of the n-scaled energy level diagram:



$$\mu_s >> \mu_p > \mu_d > \mu_f \ldots \approx 0$$

<u>everything</u> is exactly repeated in each to + 1 region of

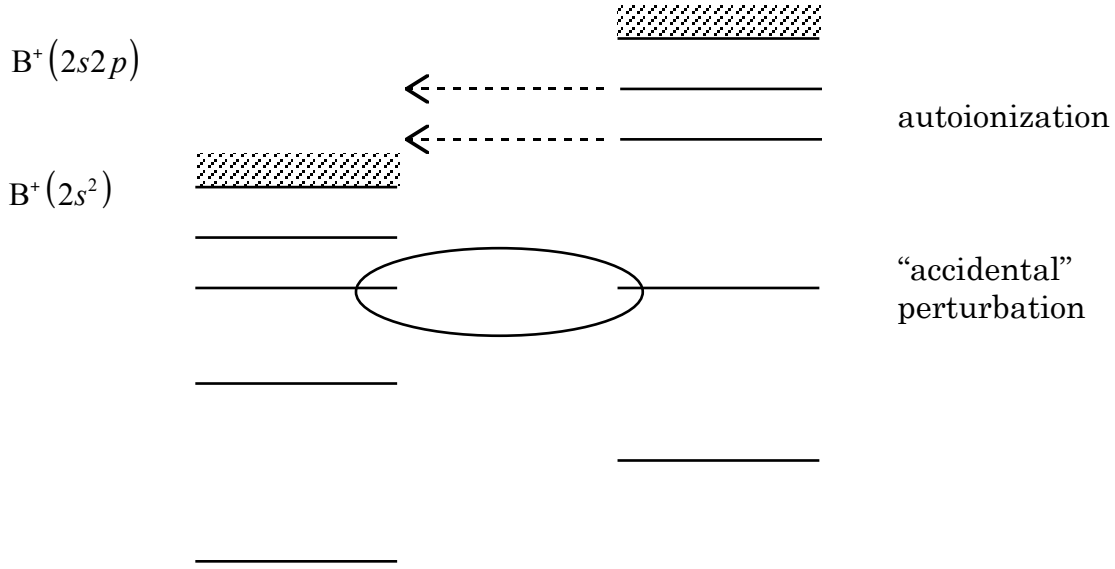
ν ν, not E, is the way to look at Rydberg "patterns"

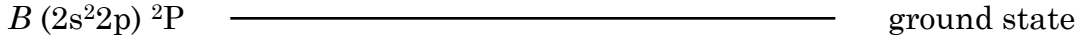
Finding the way to see a pattern is ALWAYS the route to both "assignment" and "insight".
THIS COULD BE THE MOTTO FOR 5.73!

μ_ℓ decreases as ℓ increases because of the expected behavior of $Z^{\text{eff}}(r)$ as sampled in the presence of a centrifugal barrier $\propto \frac{\ell(\ell+1)}{2\mu r^2}$, which reduces the penetration of the electron inside the core.

As ℓ increases, the electron feels progressively less and less of the inside-core region in which $Z^{\text{eff}}(r) > 1$.

D. Inter-series interactions? Suppose you have B $2s^2 2p^1$ (B = Boron).





Separate series converging to two series limits: B^+ $2s^2$ and B^+ $2s2p$.
perturbations (accidental)
autoionization (systematic)

But there is a relationship between perturbation and auto-ionization matrix elements.

These inter-series interactions are all described by Multichannel Quantum Defect Theory

Replace μ_s, μ_p, μ_d etc.

by $3 \times 3\,\mu$ matrices, one for each symmetry of the ion:

$$\left[2s^2\left({}^1S\right) \otimes n_1\ell\right] \quad {}^2\ell$$

$$\left[2s2p\left({}^3P\right) \otimes n_2\ell \pm 1\right] \quad {}^2\ell$$

$$\left[2s2p\left({}^1P\right) \otimes n_3\ell \pm 1\right] \quad {}^2\ell$$

more complicated many-electron coupling problem

subject of the next few lectures.

Overall symmetry: **H** is totally symmetric.

Off-diagonal elements describe inter-channel interactions (exchange of angular momentum between Rydberg e^- and core e^-s).

They describe what happens in a collision of the Rydberg e^- with the ion-core. Does it change the state of the ion? Does it change the kinetic energy and/or angular momentum of the e^-? Unified picture of scattering at both negative E (bound states) and positive E.

Next few lectures:

states of many-electron atoms

How to calculate matrix elements of many-electron (many Fermion) systems.

5.73 Quantum Mechanics I
Fall 2018