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:

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

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

* $\mu_{n\ell}(r) \equiv rR_{n\ell}(r)$ dominated by small lobe (n-independent nodal position) at inner turning point, amplitude scales as n–3/2, and large lobe at outer turnin point (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

* expectation value scaling

$$\begin{array}{llll} r^\sigma & \sigma < -1 & \propto n^{-3} & \\ & \sigma \geq +1 & \propto n^{2\sigma} & \text{(see below)} \\ & \sigma = -1 & \propto n^{-2} & \text{(H - atom energy levels)} \end{array}$$

geometric mean of expectation values of r for off - diagonal matrix elements

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

$$\propto \left[(r_{+nl})^{1/2}(r_{+n'l'})^{1/2}\right]^\sigma \approx \left[(n^2)^{1/2}(n'^2)^{1/2}\right]^\sigma$$

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

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

TODAY

1. Many-e^- atom treated as core plus outer e^- that sees shielded core as Z(r).
2. ℓ-dependent energy shifts $\rightarrow$ n-independent quantum defects $E_{nl} = IP - \frac{\Re}{\underbrace{(n-\mu_{nl})^2}_{\nu}}$
3. energy shifts are actually phase shifts in $u_{n\ell}(r)$ relative to $u_{n\ell}(r)$ for H-atom
4. Rigorous QDT

   A. regular and irregular Coulomb functions *f,g* satisfy Hydrogen-like Schr. Eq. <u>OUTSIDE</u> core

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

   noninteger values of $\nu = \left[-\frac{\Re}{E_{nl}}\right]^{1/2}$ require mixture of *f* and *g*

   find $\nu = n - \mu_l$ satisfies $r \rightarrow \infty$ boundary condition

   ∞ number of members in series of ν⊚ with integer spacings, $\therefore$ constant quantum defect

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

   D. Multi-channel QDT
   μ matrices

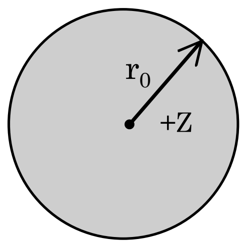
e^- colliding with core can also transfer energy and angular momentum to core-e^-

* channels rather than 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. Everything is determined by the boundary conditions for the outgoing wave.
  SCATTERING THEORYrather than EFFECTIVE HAMILTONIAN MODEL.

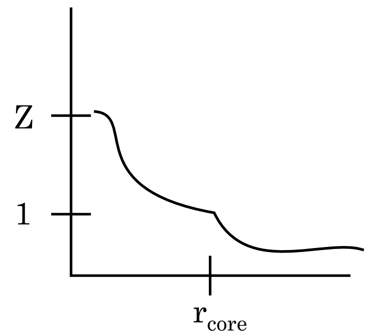
The goal here is to extract from a complicated many-body problem some regular features that will help in assigning and modeling experimental data.

1. Many-e⁻ Atom



e^-

outer electron
(valence, Rydberg)



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

Shell Structure

2. ℓ-dependent sampling of core

high ℓ : see $\langle Z(r)\rangle \sim +1$

low ℓ : see $\langle Z(r)\rangle = \underbrace{Z_\ell^{eff}} >> 1$

energy stabilization

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

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

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

$$\boxed{-\frac{e^2}{r}}$$

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

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

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

expand in Taylor series

call this ν, effective principal qn

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

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

* outside core sees same $V_l(r)$ as H
* must be same as $u_{nl}(r)$ for H except for phase shift inward (why inward?)
* all the unique stuff is inside core – causes the phase shift.
  - nodal structure inside core is invariant wrt n or E

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

4. Do all of this more rigorously: QDT

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

These are what we will obtain.

follow Ross but not using atomic units

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

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

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

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

Schrödinger Equation for H (the "Coulomb Equation")

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

as variable rather than as q.n.

$$E = -\frac{\Re}{\nu^2}$$

well known solutions:

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

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

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

of no use for Hydrogen, but it turns out that we need both *f* and *g* to satisfy r → ∞ boundary condition.

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

A. For many-e^- atoms, beyond some critical r_0, Schr. Eq. 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

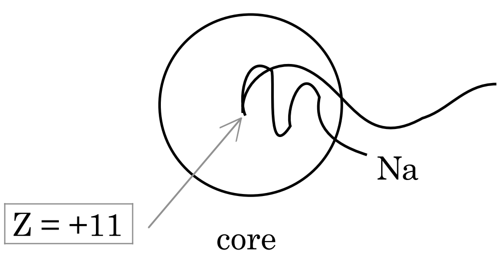
$$f_\ell(\nu, r \to \infty) \to C(r)\sin[\pi(\nu - \ell)]e^{r/\nu}$$

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

$C(r) \to 0$ 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 for a pure $u_\ell(\nu,r) = f_\ell(\nu,r)$ is for $(\nu - \ell) =$ integer

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



Na $u_\ell(\nu,r)$ emerges from core with extra phase – sucking in of hydrogenic function

* invariance of intra-core nodal structure – amount of phase shift should be independent of n. [We expect this to be true.]

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

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

TRICK: $\alpha \equiv \cos(\pi\mu_1)$

$-(1-\alpha^2)^{1/2} = -\sin(\pi\mu_1)$ plug this into ** equation on page 29 - 5

$$\psi = u_\ell(\nu,r)\underbrace{\Phi_\ell(\text{CORE})}_{\text{other } e^-} = \left[f_\ell(\nu,r)\cos(\pi\mu_\ell) - g_\ell(\nu,r)\sin(\pi\mu_\ell)\right]\Phi_\ell$$

plug in asymptoptic forms for f,g

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

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

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

$$\frac{\sin[\pi(\nu-\ell)]}{\cos[\pi(\nu-\ell)]} = -\frac{\sin(\pi\mu_\ell)}{\cos(\pi\mu_\ell)}$$

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

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

$$\tan\theta = -\tan(-\theta) = -\tan(-\theta + \underset{\substack{\uparrow \\ \text{integer}}}{n'}\pi)$$

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

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

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

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

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

but $\pi\mu_\ell = \pi(\underbrace{n' - \nu + \ell}_{n'+\ell \equiv n \;\uparrow\; \text{integer}})$

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

ν is smaller than integer n by constant term μ_ℓ.

Implies existence of infinite series of values of ν 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 *f,g* mixing is determined when the e^- leaves the core with the precise phase shift so 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

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

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

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

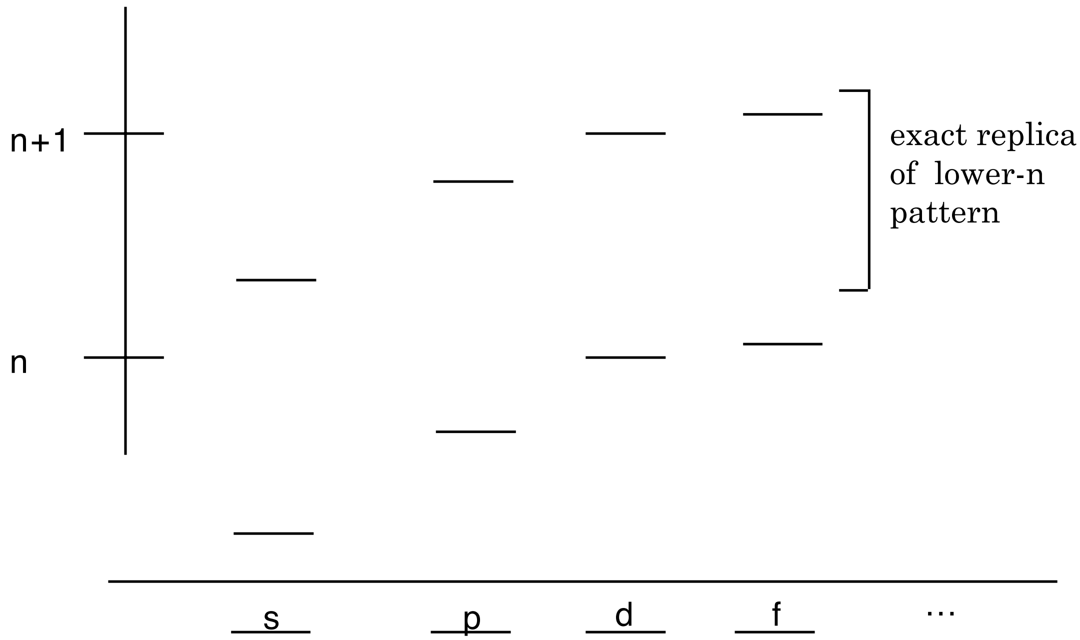
but $f_\ell(\nu,r) \to \sin[\pi(\nu-\ell)]C(r)e^{r/\nu}$

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 core by an amount $\pi\mu_\ell$ [+ an arbitrary number of 2π's] by the Z(r) 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 $r \to \infty$ b.c. is satisfied by $\nu = n - \mu_\ell$ where n is integer.

the quantum defect!



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

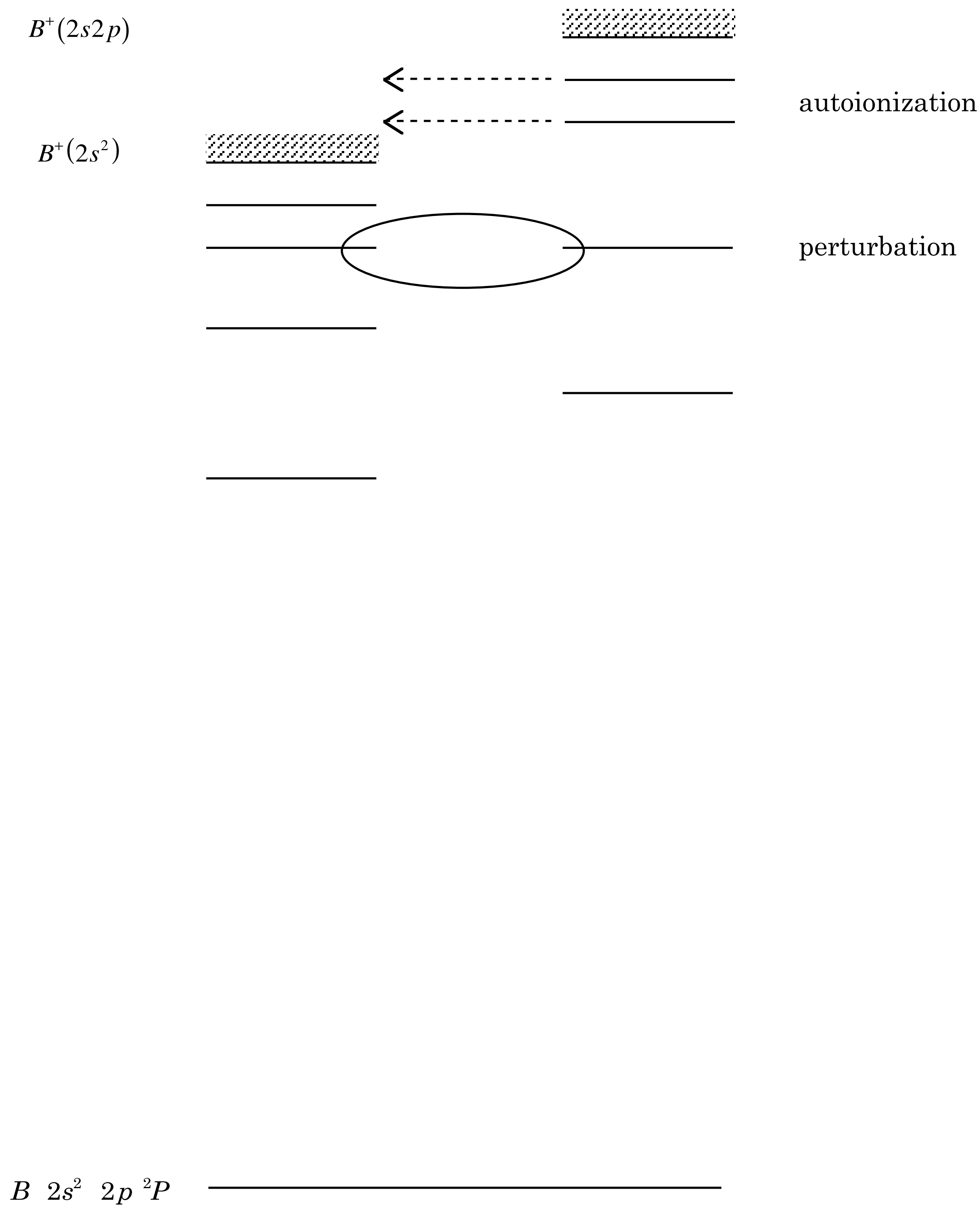
<u>everything</u> is repeated in each integer region of ν

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"

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 $\propto \dfrac{\ell(\ell+1)}{2\mu r^2}$

D. inter-series interactions? Suppose you have B $2s^2 2p^1$



Separate series converging to 2 series limits

perturbations

autoionization

Described by a Multichannel Quantum Defect Theory

Replace $\mu_s,\ \mu_p,\ \mu_d$ etc.

by 3×3 $\boldsymbol{\mu}$ matrices, one for each symmetry

$$\left.\begin{array}{ll}
\left[2s^2\left({}^1S\right) \otimes \nu_1 \ell\right] & {}^2\ell \\
\left[2s2p\left({}^3P\right) \otimes \nu_2 \ell \pm 1\right] & {}^2\ell \\
\left[2s2p\left({}^1P\right) \otimes \nu_3 \ell \pm 1\right] & {}^2\ell
\end{array}\right\}$$

more complicated many-electron coupling problem

subject of 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.)

describe what happens in a collision of e^- with 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 negative E (bound states) and at positive E.

Next few lectures:

states of many-electron atoms

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