5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #5: Alkali and Many e⁻ Atomic Spectra

What am I doing spending all of this time on ATOMS?

One of the goals of spectroscopy is to recover what is unique about the system by using what is universal and general as a road map.

Form and flavor of electronic structure models.

> * patterns for assignment of spectra
> * predictions of unobserved states and properties
> * ways to estimate size and shape of orbitals
> * quantitative reconstruction of $V_\ell(r)$ from spectrum
> * zero-order pictures for describing dynamics.

$$\Psi(Q,t) = \sum_i a_i(t)\psi_i^0(\underset{\sim}{Q})$$

time evolving non-eigenstate expressed in terms of basis states, ψ_i^o

$$\psi_i \leftrightarrow \sum \alpha_i \psi_i^0$$

eigenstate expressed in terms of basis states, ψ_i^o

Construct interesting $\Psi(Q, 0)$ and predict its time evolution.

How do we know n, ℓ, and Z for 1e⁻ spectrum?

pattern
  * convergence $\Re Z^2/n^2$
  * fine structure $Z^4/[n^3 (\ell + 1)(\ell + 1/2)\ell]$
  * hyperfine?
  * selection rules for electric dipole transition
redundancy * exactly repeated intervals in two series

Alkalis SCF → mathematical definition of 1e⁻ orbitals
  Scaling generalized

  $Z \to Z_{n\ell}^{eff}$ interpretive
                  intuitive
  $n \to n^* = n - \delta_\ell$ diagnostic
                  systematic probe

  core, valence, Rydberg
  core-penetrating, non-penetrating

  Ontogeny recapitulates phylogeny [Mulliken]

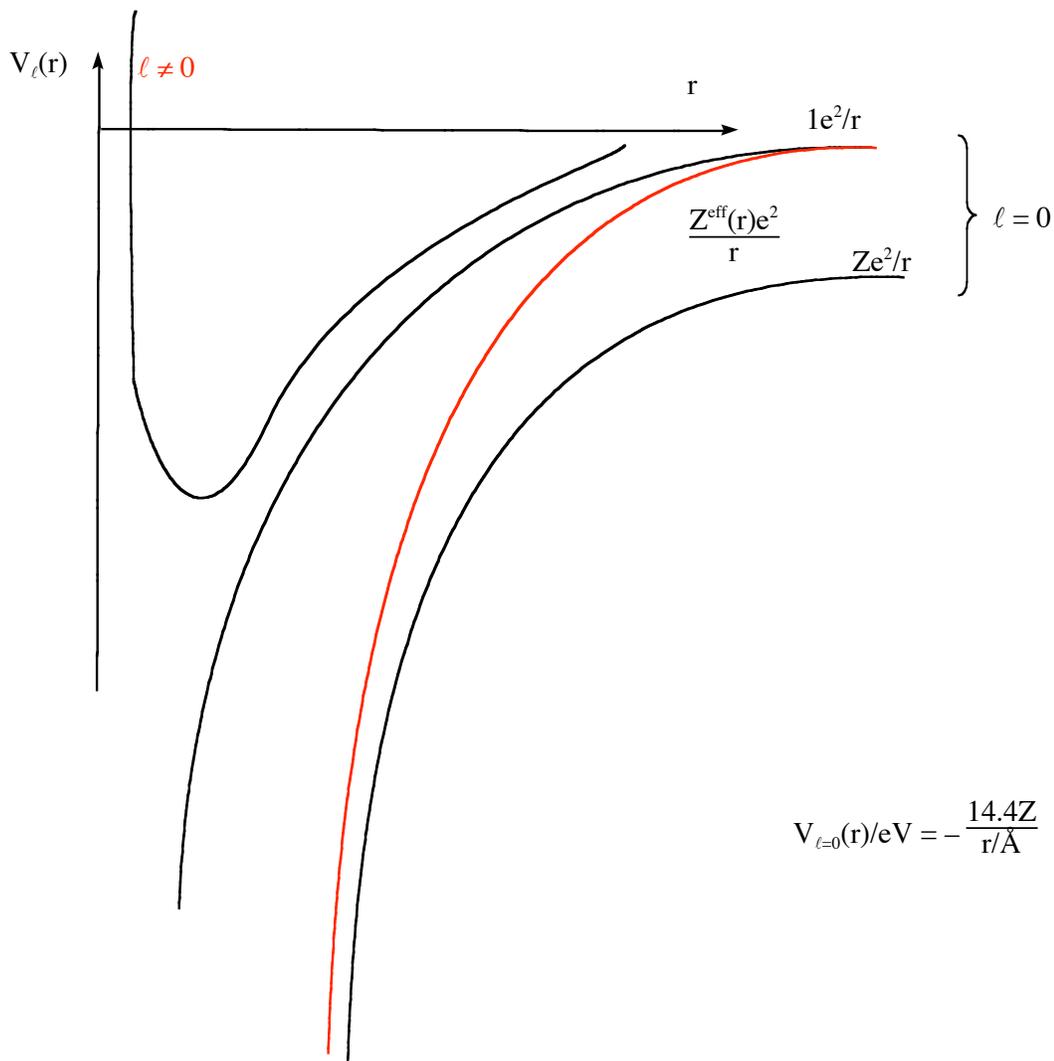 What happens when you throw an e⁻ at a closed shell ion?
        - intuition
        - Quantum mechanical wavepacket calculation.

$$V_\ell(r) = -\frac{Z_{eff}(r)e^2}{r} + \frac{\hbar^2 \ell(\ell+1)}{r^2} \qquad \ell\text{-dependent effective potential}$$

# of radial nodes   ?   2s vs 2p?

spacing of radial nodes? $\lambda = h/p$ $p_\ell(r) = [(E - V_\ell(r))2\mu]^{1/2}$

effect of $\dfrac{\ell(\ell+1)}{r^2}$ on $E_{n\ell}$, on $r_{n\ell}$?
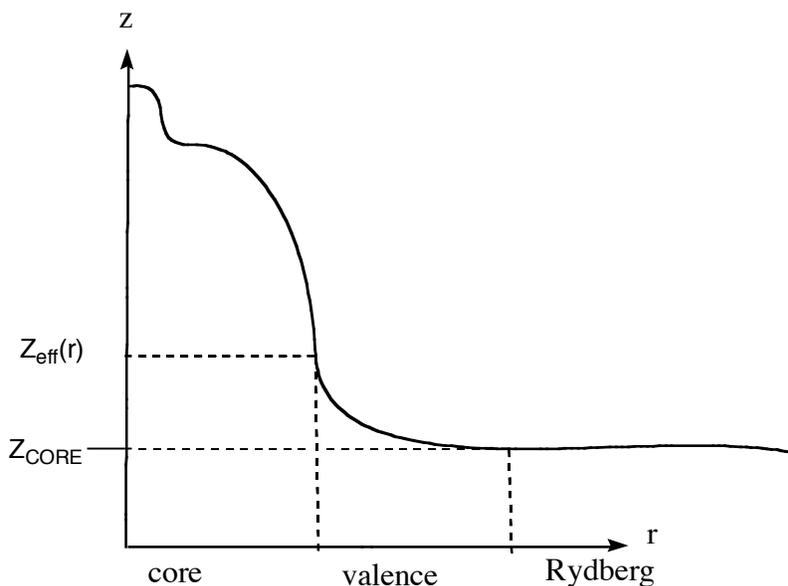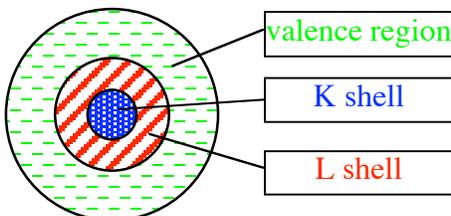

Real curve is more attractive than Z = 1 curve

ask for these and other effects. Why?
$\Big\{$
$E_{n\ell}$'s are lowered $\qquad$ $\boxed{\text{for n? for n*?}}$
nodes are closer together (same node count?)
$\qquad$ inner part of $R_{n\ell}$ becomes more compact
break 1e⁻ atom degeneracy

3s	3p	3d
2s	2p	
1s		

$\boxed{\begin{array}{l}\text{not a simple}\\ \text{r/Z scaling of } \psi\end{array}}$

outer part of $R_{n\ell}$ same as $Z = 1$ at that value of E that corresponds to n*

Shell model

valence region

K shell

L shell

$Z_{eff}(r)$

Z_{CORE}

z

core $\qquad$ valence $\qquad$ Rydberg $\qquad$ r

(filled) low-n* orbitals are exclusively inside core

$\qquad$ valence orbital penetrates inside core $\rightarrow$ HOAO $\rightarrow n_0^*$

Rydberg orbitals $\Big\langle$
penetrating $\qquad$ low-ℓ $\qquad$ $\delta_\ell > 0$

non-penetrating $\qquad$ high-ℓ $\leftarrow$ $\boxed{\text{see } Z_{CORE} = \text{integer}}$

$\qquad\qquad\qquad\qquad\qquad\uparrow$

$\qquad\qquad\qquad\qquad \delta_\ell = 0$

$\delta_{\ell=0} > \delta_p > \delta_d > \delta_f \approx 0$

$Z_{n\ell}^{eff}$ core orbitals - XPS spectrum
core part of valence orbitals $\left.\rule{0pt}{28pt}\right\}$ properties like spin-orbit
core part of penetrating Rydberg orbitals $\,$ and hyperfine

$$Z^{eff} > Z_{CORE}$$
and $\delta_\ell \neq 0$ and independent of n

$n^* = n - \delta_\ell$ * outer part of valence orbitals $\left.\rule{0pt}{28pt}\right\}$ $Z = Z_{CORE}$
                     * outer part of penetrating orbitals $\,$ OR
                     * all of non-penetrating orbitals $\,$ Z_{ION}
                                                                     (integer)

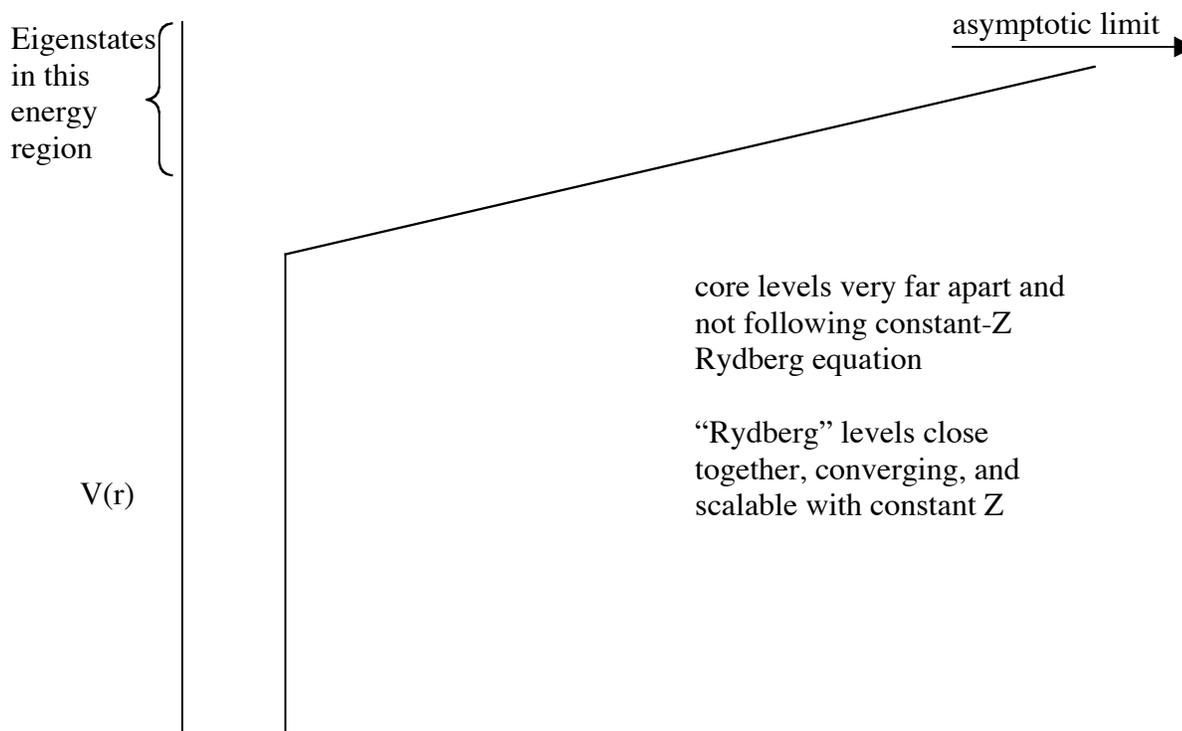ontogeny recapitulates phylogeny
   ↪ Rydberg Series   * Replicated inner lobes
                         * $n^{*-3/2}$ amplitude scale factor
                                  $e^- \leftrightarrow$ core energy exchange

e^- scattered off core
       $\pi\delta_\ell$ phase shift (with respect to $H^+ + e^-$)
       inter-channel interactions, due to $1/r_{ij}$, with core excited states

simple picture follows in order to understand δ_ℓ systematics and $\psi_{n^*\ell}$ recapitulation.

Eigenstates in this energy region

asymptotic limit

V(r)

core levels very far apart and not following constant-Z Rydberg equation

"Rydberg" levels close together, converging, and scalable with constant Z
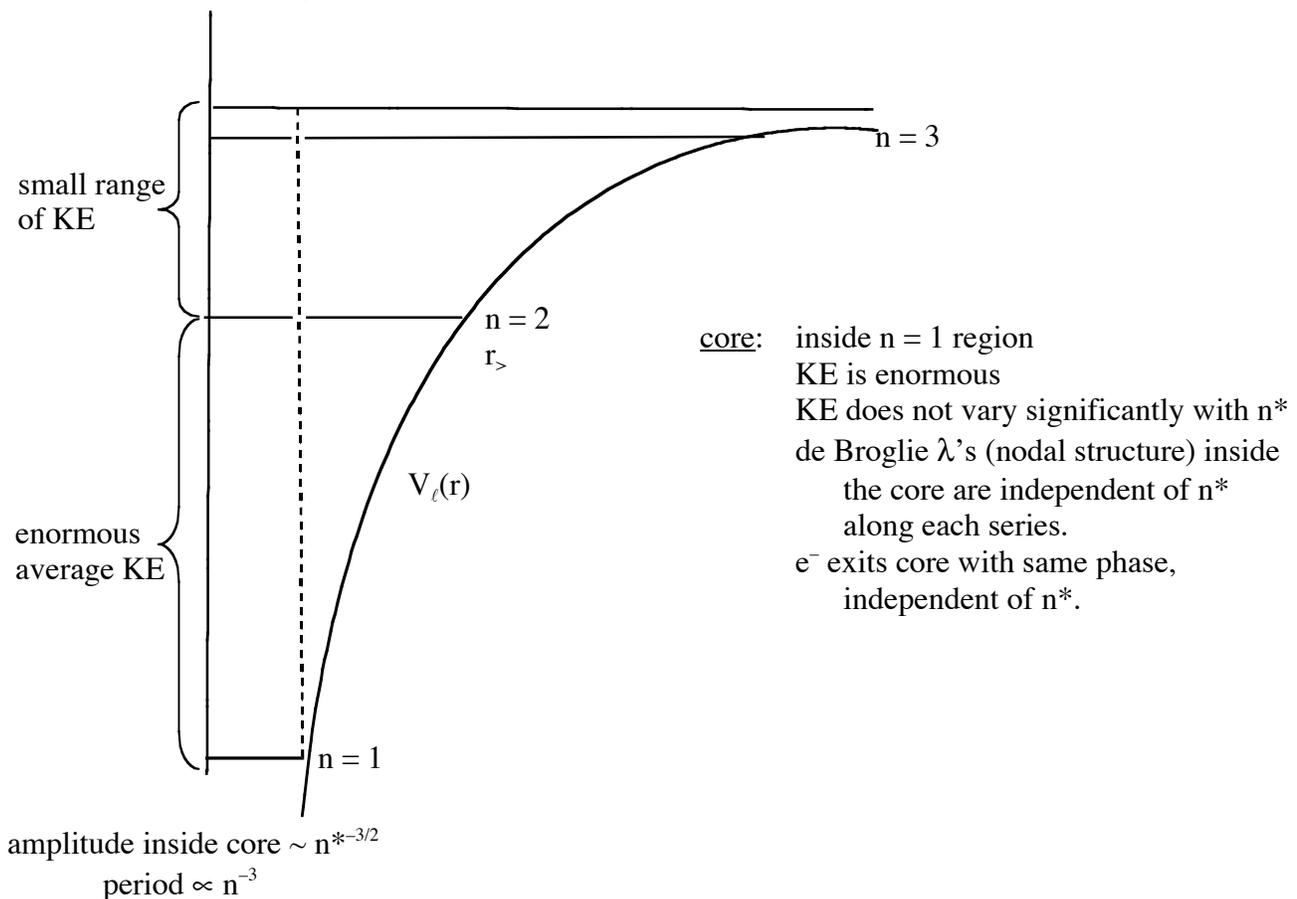
What do we know about this kind of potential?

Are all eigenfunctions pictorially related?
How do E levels tell us about form of V(r)?

Why is δ_ℓ n-independent?

Boundary condition: $R_{n\ell}(r) \to 0$ at $r \to \infty$ (so phase at outer turning point, $r_>$, must be just right to
          prevent blow-up at $r \to \infty$)
Outside "core", $Z_{n\ell}^{eff}(r) \to Z_{CORE}$ (integer) thus all $R_{n\ell}(r)$ have identical asymptotic form (except for the
possibility of a phase shift), because the $V_\ell(r) \to -Z_{CORE}/r$.

Inside "core" — all of the extra phase accumulates because $Z_{n\ell}^{eff}(r) > Z_{CORE}$. All $\psi_{n*\ell}$ in a specific
Rydberg series (channel) exit core with same phase. Must splice (universal) Coulomb long range
wavefunction onto (ℓ-specific) core wavefunction.

small range
of KE

enormous
average KE

$V_\ell(r)$

$r_>$

n = 3

n = 2

n = 1

core: inside n = 1 region
          KE is enormous
          KE does not vary significantly with n*
          de Broglie λ's (nodal structure) inside
               the core are independent of n*
               along each series.
          e⁻ exits core with same phase,
               independent of n*.

amplitude inside core $\sim n*^{-3/2}$
          period $\propto n^{-3}$

SEMI-CLASSICAL

          Harmonic oscillator period is $T = \dfrac{1}{\nu} = \dfrac{2\pi}{\omega}$

          Quantum Mechanical period is $\left[\dfrac{E_{n+1} - E_{n-1}}{2h}\right]^{-1} \to n*^{-3}$

          Δt inside core independent of n*

          $\dfrac{\Delta t}{T} \propto n^{-3}$ probability inside core (amplitude inside core $\propto n^{-3/2}$)

Quantum Defect Theory

throw e^- at M^+ ion
set of δ_ℓ's tells us about $Z^{eff}(r)$ from extra phase accumulated inside core region.
different ℓ's tell us different depths of penetration — partial wave analysis.
[complementary inside-core information from spin-orbit and hfs $\leftrightarrow Z^{eff}$]

What if e^- hits a core e^- and scatters it out?

Perturbation of Rydberg series member n^2L by a core excited state? Usually it costs too much to promote a core e^-. Except for $3d^{10}4s^1$ (Cu, Ag, Au) (but not for a Rydberg series converging to an electronically excited state of the ion.)

Doubly excited states — Rydberg series built on a core hole.
e.g.   Na $[1s^2\ 2s^2\ 2p^5]3s\ n^*\ell$

$$\boxed{\begin{matrix} {}^{2,4}\ell + 1 \\ \ell \\ \ell - 1 \end{matrix}}$$ are the possible states

^{2}P CORE

Spectrum gets very complicated at high E!

Autoionization: eject e^-
        matrix elements of $1/r_{ij}$ between ionization continuation and doubly excited state.

Crucial differences between hydrogenic and alkali-like spectra

*   loss of degeneracy between $n^2L_{j=\ell+1/2}$ and $n^2(L + 1)_j$
     (different shielding/core-penetration of s,p, d, f...)

*   loss of simple analytic f(quantum numbers) for all radial properties. Retain empirically corrected scaling relationships. Retain ability to estimate sizes.
     (n-independence of δ's means that a quantitative theory exists)

*   possibility of core-excited states (core no longer ^{1}S closed shell)
     possibility of core $e^- \leftrightarrow$ valence e^- energy transfer "autoionization", "superexcited" states, "resonances"

*   retain one doublet state for each closed-shell core plus single-electron $n\ell$ electronic configuration.

What happens when there is more than one e^- outside of closed shells — amazing complexity!