5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #4: Atoms: $1e^-$ and Alkali

1e– Atoms: H, He^+, Li^{2+}, etc.
coupled and uncoupled basis sets: $|j\ell s\, m_j\rangle$ or $|\ell\lambda s\sigma\rangle$

radial Schrödinger Equation
- centrifugal term $\dfrac{\hat{\ell}^2}{2\mu r^2} \to \dfrac{\ell(\ell+1)}{2\mu r^2} \to V_\ell(r)$ effective potential
- spin-orbit $\dfrac{\hat{\ell}\cdot\hat{s}}{r^3}$

n-scaling (also μ and Z) exact, integer n and integer Z
inter-relationships
notation

Self Consistent Field to define $1e^-$ orbitals: Alkali atoms (one e^- outside closed shells) extension of scaling

semi-empirical, non-integer n* and Z^{eff}

$$IP - E_{n\ell} = \Re \frac{\left(Z_\ell^{eff}\right)^2}{\left(n-\delta_\ell\right)^2}$$

seems like we have 2 different kinds of corrections for the same thing. Effective core potential.

Quantum defect theory — a scattering based model
- constant phase shifts along Rydberg series
- properties that probe inner vs. outer parts of orbital
- penetrating vs. non-penetrating orbitals

Qualitative differences between $1e^-$ and alkali-like electronic structures

Patterns: Assignment
Prediction and Extrapolation
Information about complicated part of ψ from "fudge factors"

$1\text{-}e^-$ Atoms "Hydrogenic"

$$\widehat{\mathbf{H}}(r,\theta,\phi,s) = \widehat{\mathbf{H}} = \underbrace{-\frac{\hbar^2}{2\mu}\widehat{\nabla}^2}_{\text{kinetic energy}} \underbrace{-\frac{Ze^2}{r}}_{\text{potential energy}} + \underbrace{\frac{Ze^2}{2\mu^2c^2}\frac{1}{r^3}\hat{\ell}\cdot}_{\widehat{\mathbf{H}}\text{ spin-orbit}}\hat{s}$$

central force **H**

heavily weighted at nucleus

kinetic energy includes

$$\underbrace{+\hbar^2\frac{\ell(\ell+1)}{2\mu r^2} \to V_\ell(r)}_{\text{"centrifugal barrier"}\ \widehat{\mathbf{H}}^{\text{nucleus-electron}}} \text{ effective radial potential}$$

integrate over θ,ϕ
$\psi(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$

ψ reduces to universal angular part $Y_{\ell m}(\theta,\phi)$
and atom-specific radial part $R_{n\ell}(r)$ (still universal for 1 e^- atoms)

Z is charge on nucleus

$\mu = \dfrac{m_N m_e}{m_N + m_e}$ is "reduced mass" $\mu \approx m_e$ because $m_N \gg m_e$

$$\left.\begin{array}{l} m_N = 1 \text{ amu} \rightarrow \mu = 5.4828 \times 10^{-4} \\ m_N = 200 \text{ amu} \rightarrow \mu = 5.4858 \times 10^{-4} \end{array}\right\rangle \sim 1 \text{ part in } 10^3 -$$

seems small but electronic spectra are typically measured to 1 part in 10^6

Basis sets: sets of mutually commuting operators that also commute with **H°**

* uncoupled $|n\ell m_\ell s m_s\rangle$

  $\vec{j} \equiv \vec{\ell} + \vec{s}$

* coupled $|n\ell s j m_j\rangle$

complete basis only if we include continuum $|\varepsilon \ell s j m_j\rangle$ $\varepsilon > 0$

$\boldsymbol{\ell}\cdot\mathbf{s} = \boldsymbol{\ell}_z \mathbf{s}_z + 1/2(\boldsymbol{\ell}^+\mathbf{s}^- + \boldsymbol{\ell}^-\mathbf{s}^+)$

$\ell^+|\ell m_\ell\rangle = [\ell(\ell + 1) - m_\ell(m_\ell + 1)]^{1/2}\, |\ell\ m_\ell + 1\rangle$

$\widehat{\mathbf{H}}^{SO}$ not diagonal in uncoupled basis because of $\frac{1}{2}(\ell^+ s^- + \ell^- s^+)$ $[\ell^{\pm} = \ell_x \pm i\ell_y]$

$\mathbf{j}^2 = (\boldsymbol{\ell} + \mathbf{s})^2 \Rightarrow \boldsymbol{\ell}\cdot\mathbf{s} = 1/2[\mathbf{j}^2 - \boldsymbol{\ell}^2 - \mathbf{s}^2]$

$\widehat{\mathbf{H}}^{SO}$ is diagonal in coupled basis $[-\boldsymbol{\ell}\cdot\mathbf{s} = 1/2(\boldsymbol{\ell}^2 + \mathbf{s}^2 - \mathbf{j}^2)]$

[I use **bold** or $\widehat{\text{hat}}$ to denote an operator]

A rigorously good Quantum Number is an eigenvalue of an operator that commutes with exact $\widehat{\mathbf{H}}$.

$j \rightarrow \hat{j}^2 \quad m_j \rightarrow \hat{j}_z$

$\ell \rightarrow \hat{\ell}^2 \quad m_\ell \rightarrow \hat{\ell}_z$

$s \rightarrow \hat{s}^2 \quad m_s \rightarrow \hat{s}_z$

note that $[\hat{\ell}_Z, \hat{\ell}\cdot\hat{s}] \neq 0$, $[\hat{s}_Z, \hat{\ell}\cdot\hat{s}] \neq 0$, but $[\hat{j}_Z, \hat{\ell}\cdot\hat{s}] = 0$

Since $|n\ell s j m_j\rangle$ maximally factorizes the one-electron $\widehat{\mathbf{H}}$ into 1×1 matrices, it is useful to examine the eigenvalues.

cm^{-1} units

$$\left\langle n\ell' s' j' m_j' \left| \frac{\widehat{\mathbf{H}}}{hc} \right| n\ell s j m_j \right\rangle = -\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\times \left(\frac{\mu}{m_e}\right)\left[\overbrace{109737.318}^{\text{Rydberg constant}} \frac{Z^2}{n^2} + 5.844\frac{Z^4}{n^4}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right] = E_{n\ell_j}(Z, j$$

in cm^{-1}

13.61eV orbital energies E→0 as n→∞ (E≡0 at IP)

spin-orbit $j=\ell+1/2$ above $j=\ell-1/2$ "normal multiplet" fine structure splitting — decreases as n^{-3}, increases as Z^4

small isotope shifts

≈ 1
$= 1$ for $m \to \infty$
< 1 for $m = 1$

"doublet" $\boxed{2s+1}$ $\boxed{\ell}$

notation e.g. $2\ ^2p_{3/2}$

$\boxed{n}$ $\boxed{j}$

$\ell =$	0,	1,	2,	3,	4,	5,	6,	7
	s	p	d	f	g	h	i	k

$2\ ^2P_{3/2} - 2\ ^2P_{1/2}$ Splitting (spin-orbit)

I denotes "1st spectrum" of **H** (1st spectrum is of neutral atom)

obey Z^4 scaling relationship very accurately

	ΔE
H I	0.366 cm^{-1}
Li III	30 cm^{-1}
Na XI	5400 cm^{-1}

This notation disagrees with standard chemist's notation. e.g. Sc II ⇔ Sc^{2+} but an atomic spectroscopist expects Sc II means Sc^{1+}

Above equation predicts exact degeneracy between $n^2P_{3/2}$ and $n^2D_{3/2}$. There is actually a small splitting — "LAMB SHIFT" ~ 0.035 cm^{-1} for H n = 2, j = 1/2, due to "higher order radiative corrections" — a new basis set that combines atom and radiation field. Beyond the scope of 5.80.

In the $|n\ell s j m_j\rangle$ or $|n\ell m_\ell s m_s\rangle$ basis sets, we can derive simple analytic expressions for matrix elements of many f(r) and f(p). These analytic expressions are explicitly expressed in terms of the quantum numbers

$n,n',\ \ell,\ell',\ s,s',\ j,j'$, etc.

For example, electronic transitions (i = initial, f = final) have relative intensities

$$P_{if} \propto \left|\langle i|e\vec{r}|f\rangle\right|^2$$

$\vec{r}$:

1. operates only on spatial, not spin coordinates **Very Important**
2. is a "vector" with respect to ℓ and j [like an angular momentum] (spherical tensors)
3. has odd parity.

we can immediately deduce selection rules

$\Delta\ell = \pm 1$	(parity $(-1)^{\ell}$)
$\Delta s = 0$	(but 1 e^- can only have s = 1/2)
$\Delta j = \boxed{0,} \pm 1$	$\Delta j = 0$ is possible because $\vec{j} = \vec{\ell} + \vec{s}$
$\Delta m_s = 0$	
$\Delta m_j = 0, \pm 1$	
Δn = any	(Δn = 0,1 strong because of best spatial overlap)

example of formula [Condon and Shortley, page 133]

$$\text{Hydrogenic matrix element } |\langle 1s \,|\, er \,|\, np\rangle|^2 \propto n^7(n-1)^{2n-5}(n+1)^{-2n-5} \approx n^{-3}$$

k	$a^{-k}\int_0^\infty r^k R^2(n\ell)dr$ (expectation value of powers of r)
1	$\frac{1}{2Z}\left[3n^2 - \ell(\ell+1)\right]$
2	$\frac{n^2}{2Z^2}\left[5n^2 + 1 - 3\ell(\ell+1)\right]$
3	$\frac{n^2}{8Z^3}\left[35n^2(n^2-1) - 30n^2(\ell+2)(\ell-1) + 3(\ell+2)(\ell+1)\ell(\ell-1)\right]$
4	$\frac{n^4}{8Z^4}\left[63n^4 - 35n^2(2\ell^2+2\ell-3) + 5\ell(\ell+1)(3\ell^2+3\ell-10) + 12\right]$
-1	$\frac{Z}{n^2}$ (Coulomb)
-2	$\frac{Z^2}{n^2(\ell+\frac{1}{2})}$ (centrifugal barrier, core dipole)
-3	$\frac{Z^3}{n^3(\ell+1)(\ell+\frac{1}{2})\ell}$ (spin-orbit)
-4	$\frac{Z^4\frac{1}{2}[3n^2-\ell(\ell+1)]}{n^5(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}$ (all k < –3 have $\langle r^k\rangle$ scale as $\sim n^{-3}$)

* note n and Z scaling for each r^k.

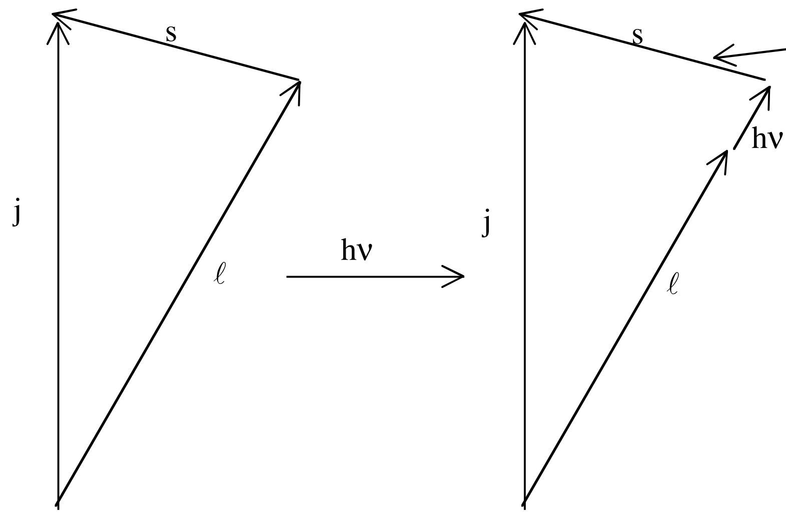
** In this table r is measured in atomic units. The general eigenfunctions for any Z and arbitrary length unit are obtained by multiplying the functions of this table by $\sqrt{Z/a}$ and replacing r by Zr/a.

† The average values of r^{-5} and r^{-6} may be found in Van Vleck, *Proc. Roy. Soc.* **A143**, 679 (1934).

example of usefulness of simple geometric pictures — vector models in spectroscopy.

Explain $\Delta\ell = \Delta j$ propensity rule for transitions.

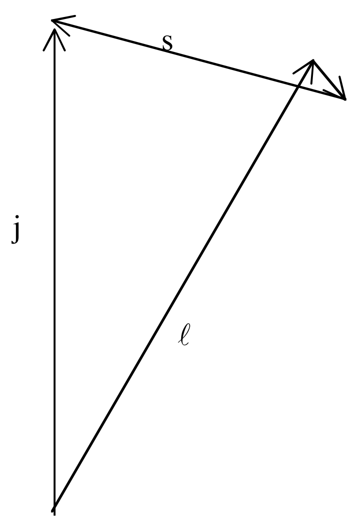
initial　　　　　　add a photon parallel to $\vec{\ell}$ $(\Delta\ell = +1)$



try for drawing with no change in length of s vector or angle between $\vec{\ell}$ and $\vec{s}$

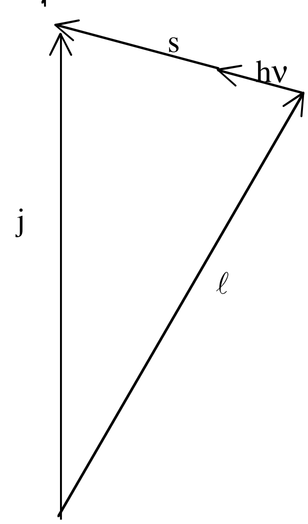
$\ell \to \ell + 1$
j tends to be lengthened

alternatively, **add hν ⊥ to** ℓ $(\Delta\ell = 0)$



$\ell = \ell$

both pictures have j not significantly different length than initially



OR

$\Delta j = \Delta\ell$ propensity rule

Crucial points

each electron orbital $\leftrightarrow$ a single (doublet) electronic state

all properties expressible as explicit f(quantum numbers) with explicit Z,μ scaling

establishes typical magnitudes for all observable properties of any atom

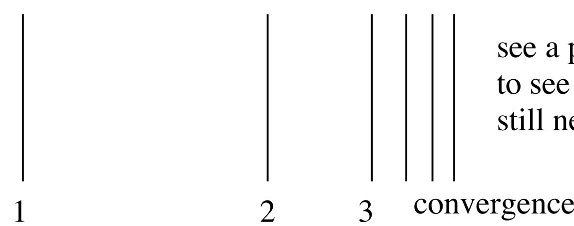
E_n, IP, s–o, hyperfine, transition moment, Stark effect

*** KEY IDEA *** | Measurement of one property of a given state identifies which state it is and implies specific predictable values for all other observable properties of that state.

This is what we would like electronic "structure" to mean. The value of one thing is related (predictably) many others.

What do we need to know about a $1e^-$ atom to know everything? Z and μ

How to find out values of Z and μ? Rydberg Series



see a pattern that we expect to see in spectrum, but we still need to "assign" it.

plot a vs. $\dfrac{\Re^{1/2}}{[\bar{\nu}_c - \bar{\nu}_a]^{1/2}}$ (from Rydberg equation)

convergence limit ($\bar{\nu}_c$)

arbitrary integer principal quantum number (a)

a is arbitrary integer: consecutive numbering of members of series

$a = n + b$ (unknown offset b)

$n = a - b$

straight line: slope 1/Z, y intercept is –b/Z

Alkali-like atoms

$1\ e^-$ outside of closed shells

$$\hat{\mathbf{H}} = \underbrace{\hat{\mathbf{H}}^\circ}_{\text{separable}} + \sum_{i>j} e^2/r_{ij}$$

destroys *all* one-e^- orbital angular momentum quantum numbers but preserves total angular momenta

$$\vec{L} = \sum_i \vec{\ell}_i$$

$$\vec{S} = \sum_i \vec{s}_i$$

$$\vec{J} = \sum_i \vec{j}_i$$

$\boxed{\text{can't really treat } 1/r_{ij} \text{ as a perturbation because its contribution to the energy of an electronic state is comparable in magnitude to all other terms in } \hat{\mathbf{H}}\text{!}}$

Commutation rules:

Bernath shows that $\begin{bmatrix} \widehat{\mathbf{H}}, & L^2 \\ & S^2 \\ & J^2 \end{bmatrix} = 0$ but $\begin{bmatrix} \widehat{\mathbf{H}}, & \ell_i^2 \\ & j_i^2 \end{bmatrix} \neq 0$

$\boxed{\text{replace } V_\ell(r) + \sum e^2/r_{ij} \text{ by } V_{n\ell}^{SCF}(r)}$

Self Consistent Field to define 1e$^-$ orbitals — not 1e$^-$ Schrödinger Equation. [Orbitals depend on occupancy of all other orbitals.] (Best possible single product of N 1e$^-$ orbitals.)

e$^-$ moves in field defined by nucleus plus average charge distribution produced by all other e$^-$. This is like replacing Z in 1e$^-$ Schrödinger Equation by $Z^{eff}(r)$. "Shielding."

$$Z^{eff}(r) \begin{cases} Z \text{ at } r = 0 \\ 1 \text{ at } r = \infty \end{cases}$$

Represent spherical, non-point core by two modifications of scaling formulas.

$$Z \rightarrow Z_{n\ell}^{eff} = Z - \sum_{\substack{n'\ell' \\ \text{all other } e^-}} S_{n\ell}^{n'\ell'}$$

sum of shielding contributions from all other e$^-$

$$n \rightarrow n_{eff} \equiv n^* = n - \delta_\ell$$

$\boxed{\text{quantum defect, core penetration}}$

qualitative interpretation of δ_ℓ

- * when $\delta_\ell > 0$ $n^* < n$ — net stabilization relative to hydrogenic orbital with $n\ell$ quantum numbers
- * when e$^-$ in $n\ell$ orbital penetrates inside other orbitals, it sees larger $Z^{eff}(r)$ and is therefore stabilized.

  $\ell = 0$ penetrates best $\therefore$ has largest δ

  1 less

  2 hardly at all

<u>non-penetrating</u> orbitals have $Z_{n\ell}^{eff} = 1$ and $\delta_\ell = 0$

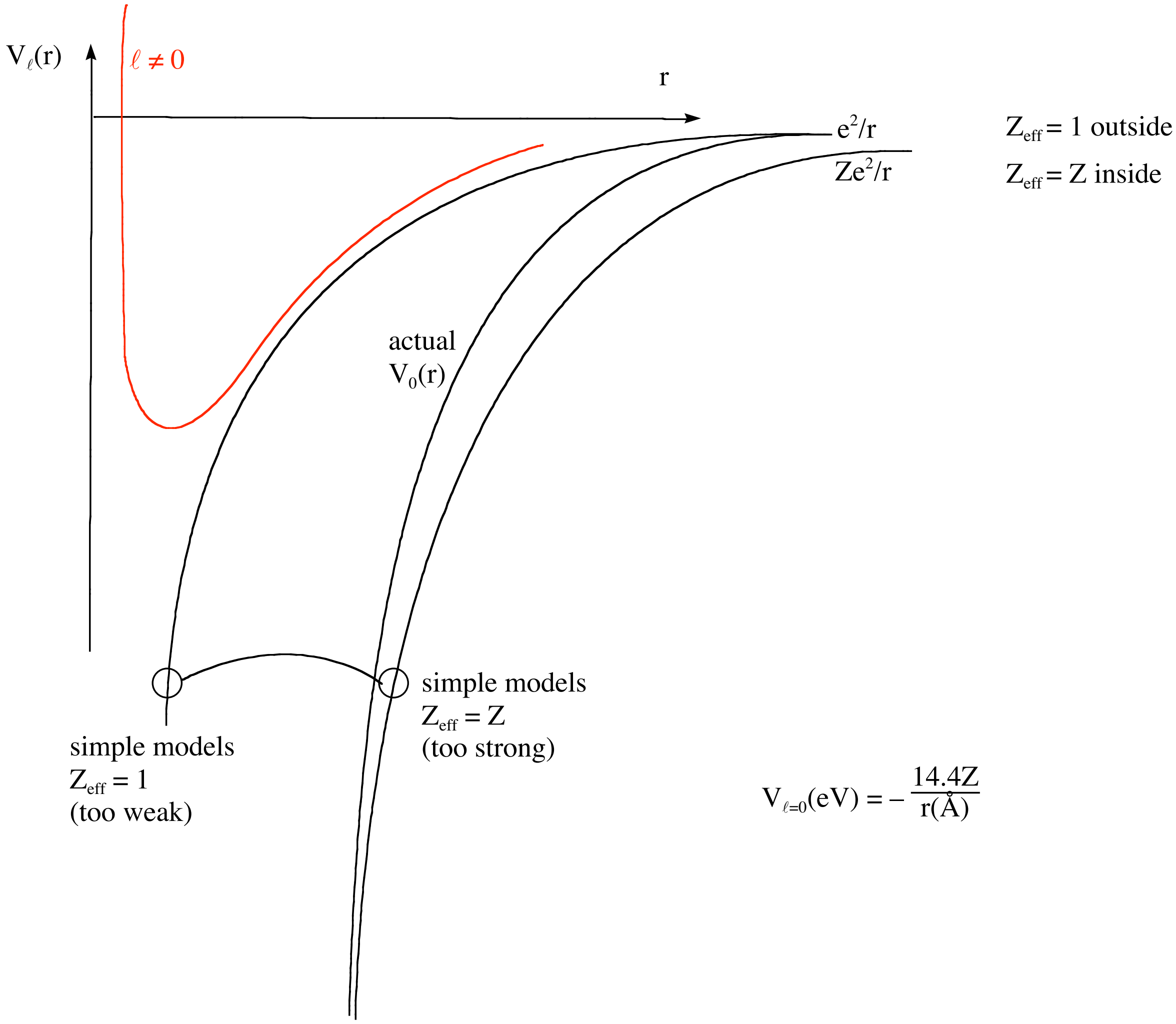
spin-orbit, hyperfine

Some properties are sensitive to amplitude in the intra-core part of an orbital — so we need Z^{eff} to get their values correct.

Rydberg E_n's, transition probabilities, Stark effect

Other properties are sensitive to the long-range (extra-core) part of an orbital — so we need δ_ℓ.

Quantum Defect Theory $\delta_\ell \pi$ is a phase shift — describes the phase of the outside-the-core part of the $n\ell$ orbital relative to that for $n\ell$ on a bare Z = 1 nucleus.



$$V_{\ell=0}(\text{eV}) = -\frac{14.4Z}{r(\text{Å})}$$

Form of $V_\ell(r)$ depends on ℓ because ℓ determines how deeply the valence e^- penetrates into core.

repulsive barrier to core penetration:

$$+\frac{\ell(\ell+1)}{r^2} \text{ term}$$

(centrifugal barrier)

$$E_{n\ell} \approx -\frac{\Re Z^2_{CORE}}{n^{*2}} \qquad n^{*2} = \boxed{(n-\delta_\ell)^2}$$

(Z_{CORE} = 1 for alkali atoms)

$$\langle r \rangle_{n\ell} \approx \langle n\ell | r | n\ell \rangle = \frac{a_0}{2Z_{CORE}}[3n^{*2} - \ell(\ell+1)]$$

This is much more than an empirical correction scheme. The quantum defect is n-independent.

Typical values for alkalis $1.5 \approx \delta_{ns} > \delta_{np} > \delta_{nd} > \delta_{nf} \approx 0.$