Lecture #4: Atoms: 1e⁻ and Alkali

1e⁻ Atoms: H, He⁺, Li²⁺, etc.
coupled and uncoupled basis sets: |j ls m_l⟩ or |ℓsσ⟩

radial Schrödinger Equation

\[ \frac{\hat{L}^2}{2\mu r^2} \rightarrow \frac{\ell(\ell+1)}{2\mu r^2} \rightarrow V_e(r) \text{ effective potential} \]

spin-orbit \[ \hat{\ell} \cdot \hat{s} \]

n-scaling (also \( \mu \) 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 \( Z_{eff} \)

\[ \text{IP} - E_n = \Re \left( \frac{(Z_{eff})^2}{(n - \delta_i)^2} \right) \]

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 \( \psi \) from “fudge factors”

1-e⁻ Atoms “Hydrogenic”

\[ \hat{H}(r, \theta, \phi, s) = \hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{r} + \frac{Ze^2}{2\mu^2 c^2} \frac{1}{r^3} \ell \cdot \hat{s} \]

central force \( \hat{H} \)

heavily weighted at nucleus

integrate over \( \theta, \phi \)
\[ \psi(r, \theta, \phi) = R_n(r)Y_{\ell m}(\theta, \phi) \]

“centrifugal barrier”

\[ \hat{H}_{nucleus-electron} \]

\( \psi \) reduces to universal angular part \( Y_{\ell m}(\theta, \phi) \)
and atom-specific radial part \( R_n(r) \) (still universal for 1 e⁻ atoms)
Z is charge on nucleus
\[ \mu = \frac{m_N m_e}{m_N + m_e} \] is “reduced mass” \( \mu \approx m_e \) because \( m_N \gg m_e \)

\[ m_N = 1 \text{ amu} \Rightarrow \mu = 5.4828 \times 10^{-4} \]
\[ m_N = 200 \text{ amu} \Rightarrow \mu = 5.4858 \times 10^{-4} \]

\[ \sim 1 \text{ part in } 10^3 \] 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 \( H^0 \)
- uncoupled \( |n/m,s,m\rangle \)
  \[ \hat{j} = \hat{l} + \hat{s} \]
- coupled \( |\ell/sjm\rangle \)

complete basis only if we include continuum \( |\ell/sjm\rangle \)

\[ \ell \cdot s = \ell \cdot \hat{s} + 1/2(\ell \cdot \hat{s} + \ell \cdot s^+) \]

\[ \ell^\ast |\ell m\rangle = [\ell(\ell + 1) - m(m + 1)]^{1/2} |\ell m + 1\rangle \]

\( \hat{H}^\text{SO} \) not diagonal in uncoupled basis because of

\[ \ell_x = \ell_x \pm i \ell_y \]

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

\( \hat{H}^\text{SO} \) is diagonal in coupled basis

\( I \) use \textbf{bold} or \( \hat{\text{hat}} \) to denote an operator

A rigorously good Quantum Number is an eigenvalue of an operator that commutes with exact \( \hat{H} \).

\[ j \rightarrow \hat{j}^2 \quad m_j \rightarrow \hat{j}_z \]

\[ \ell \rightarrow \hat{\ell}^2 \quad m_\ell \rightarrow \hat{\ell}_z \]

\[ s \rightarrow \hat{s}^2 \quad m_s \rightarrow \hat{s}_z \]

note that \( [\hat{\ell}_z, \hat{\ell} \cdot \hat{s}] \neq 0, [\hat{s}_z, \hat{\ell} \cdot \hat{s}] \neq 0, \text{ but } [\hat{j}_z, \hat{\ell} \cdot \hat{s}] = 0 \)

Since \( |n/sjm\rangle \) maximally factorizes the one-electron \( \hat{H} \) into \( 1 \times 1 \) matrices, it is useful to examine the eigenvalues.
\[ \left\langle n \ell' s' j' m'_j \middle| \hat{H} \middle| n \ell s j m_j \right\rangle = -\delta_{\ell \ell'} \delta_{ss'} \delta_{jj'} \delta_{m_j m'_j} \]

\[
\times \left( \frac{\mu}{m_e} \right) \left[ \frac{109737.318 Z^2}{n^2} + 5.844 \frac{Z^4}{n^4} \left( \frac{n}{j + 1/2} - \frac{3}{4} \right) \right] = E_{n \ell j} (Z, \lambda)
\]

- Rydberg constant
- Orbital energies:
  - E\(\rightarrow 0\) as \(n\rightarrow\infty\)
  - (E=0 at IP)
  - small isotope shifts
  - \(\approx 1\)
  - \(= 1\) for \(m \rightarrow \infty\)
  - \(< 1\) for \(m = 1\)

“Doublet” notation e.g. \(2^2p_{3/2}^3\)

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

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

I denotes “1st spectrum” of \(H\) (1st spectrum is of neutral atom)

- 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 \(\leftrightarrow\) 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” \( \sim 0.035 \) 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 \( |n\ell sjm\rangle \) or \( |n\ell m,sm\rangle \) basis sets, we can derive simple analytic expressions for matrix elements of many \( f(\mathbf{r}) \) and \( f(p) \). These analytic expressions are explicitly expressed in terms of the quantum numbers

\[ n,n', \ell,\ell', s,s', j,j', \text{ etc.} \]

For example, electronic transitions (\( i = \text{initial} \), \( f = \text{final} \)) have relative intensities

\[ P_{if} \propto |\langle i|\mathbf{\bar{r}}|f\rangle|^2 \]

\( \mathbf{\bar{r}} \) :  
1. operates only on spatial, not spin coordinates
2. is a “vector” with respect to \( \ell \) and \( j \) [like an angular momentum] (spherical tensors)
3. has odd parity.
we can immediately deduce selection rules

\[ \Delta \ell = \pm 1 \quad (\text{parity } -1^\ell) \]
\[ \Delta s = 0 \quad (\text{but } 1^0 \text{ can only have } s = 1/2) \]
\[ \Delta j = \frac{1}{3}\Delta \ell \]  
\[ \Delta j = 0 \text{ is possible because } j = \ell + s \]
\[ \Delta m_s = 0 \]
\[ \Delta m_j = 0, \pm 1 \]
\[ \Delta n = \text{any} \quad (\Delta n = 0, 1 \text{ strong because of best spatial overlap}) \]

example of formula [Condon and Shortley, page 133]

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

\[
\begin{array}{c|c}
 k & a^{-k} \int_0^\infty r^k H_2(n\ell) dr \\
\hline
 1 & \frac{1}{2\pi} \left[ 3n^2 - \ell(\ell + 1) \right] \\
 2 & \frac{n^2}{\pi^2} \left[ 5n^2 + 1 - 3\ell(\ell + 1) \right] \\
 3 & \frac{n^4}{\pi^4} \left[ 35n^2(n^2 - 1) - 30n^2(\ell + 2)(\ell - 1) + 3(\ell + 2)(\ell + 1)\ell(\ell - 1) \right] \\
 4 & \frac{n^4}{\pi^4} \left[ 63n^4 - 35n^2(2\ell^2 + 2\ell - 3) + 5\ell(\ell + 1)(3\ell^2 + 3\ell - 10) + 12 \right] \\
 -1 & \frac{Z^2}{n^2} \quad (\text{Coulomb}) \\
 -2 & \frac{Z^2}{n^2(\ell + \frac{1}{2})^2} \quad (\text{centrifugal barrier, core dipole}) \\
 3 & \frac{Z^2}{n^2(\ell + \frac{1}{2})^2} (\text{spin-orbit}) \\
 -4 & \frac{Z^2}{n^2(\ell + \frac{1}{2})(\ell + \frac{3}{2})(\ell - \frac{1}{2})} (\text{all } k < -3 \text{ have } \langle r^k \rangle \text{ scale as } n^{-3})
\end{array}
\]

* 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 \( r^{-6} \) and \( r^{-10} \) 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 \( \ell \) (\( \Delta \ell = +1 \))

\[ \ell \rightarrow \ell + 1 \]

\( j \) tends to be lengthened

alternatively, **add \( \mathbf{hv} \perp \ell \) (\( \Delta \ell = 0 \))**

\( \ell = \ell \)

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 $Z, \mu$ 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 $\mu$

How to find out values of $Z$ and $\mu$? Rydberg Series

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

Alkali-like atoms

1 e$^-$ outside of closed shells

$\hat{H} = \hat{H}^0 + \sum_{i>j} e^2/r_{ij}$

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

$\hat{L} = \sum_i \hat{l}_i$

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

$\hat{J} = \sum_i \hat{j}$

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

Bernath shows that

\[
\begin{bmatrix}
\hat{H}, L^2 \\
S^2 \\
J^2
\end{bmatrix} = 0 \text{ but } \begin{bmatrix}
\hat{H}, f_i^2 \\
f_i^2 \\
f_i^2
\end{bmatrix} \neq 0
\]

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

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 \( Z^{\text{eff}}(r) \). “Shielding.”

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

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

\[
Z \rightarrow Z^{\text{eff}}_{n\ell} = Z - \sum_{n'\ell'} S_{n\ell}^{n'\ell'} \text{ sum of shielding contributions from all other } e^- \\
n \rightarrow n^{\text{eff}} \equiv n^* = n - \delta_{\ell} \quad \text{quantum defect, core penetration}
\]

qualitative interpretation of \( \delta_{\ell} \)

* 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 \( Z^{\text{eff}}(r) \) and is therefore stabilized.

\[\ell = 0 \quad \text{penetrates best} \quad . \quad \text{has largest } \delta\]

\[1 \quad \text{less}\]

\[2 \quad \text{hardly at all}\]

non-penetrating orbitals have \( Z^{\text{eff}}_{n\ell'} = 1 \) and \( \delta_{\ell} = 0 \)

Some properties are sensitive to amplitude in the intra-core part of an orbital — so we need \( Z^{\text{eff}} \) 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 \( \delta_{\ell} \).
Quantum Defect Theory \( \delta \pi \) 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.

\[
V_{\text{eff}}(r) = -\frac{14.4Z}{r(\text{Å})}
\]

Form of \( V_{\text{eff}}(r) \) depends on \( \ell \) because \( \ell \) determines how deeply the valence \( e^- \) penetrates into core.

\[
E_{n\ell} \approx -\frac{\mathcal{R}Z_{\text{CORE}}^2}{n^2} (n - \delta_{\ell})^2
\]

\[
\langle r \rangle_{n\ell} \approx \frac{a_0}{2Z_{\text{CORE}}} [3n^2 - \ell(\ell + 1)]
\]

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

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