5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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Lecture #6: Many e⁻ Atoms

Outline of approach:

Configuration → which L–S–J states?
→ \( H^{\text{eff}} [\varepsilon, \zeta, F^k, G^k] \) → energy levels
→ eigenstates
→ transition intensities

alternative Limiting Case Coupling Schemes
L–S–J vs. \( j_1 - j_2 - J \)
off-diagonal \( \zeta \) vs. \( F^2 \)

1. list of orbital occupancies e.g. 1s² 2s² 2p² “configuration”

2. Which L–S terms result?
   * list all spin-orbitals p: 1 \( \bar{1} \) 0 \( \bar{0} \) –1 –\( \bar{1} \) (overbar means \( m_s = -1/2 \) or “\( \beta \)”)
   * list all Slater determinants (anti-symmetrized microstates) consistent with Exclusion Principle
     e.g. \( |\bar{1} \bar{1}| M_L = 2 \ M_S = 0 \)
     standard order of spin-orbitals (needed to get correct signs of matrix elements)
   * Classify Slatters according to \( M_L \) and \( M_S \)
   * Method of crossing out of microstates: \( M_L, M_S \) ranges for each L–S term (\( p^3 \rightarrow ^2S, ^2D, ^2P \))
   * Total degeneracy of a configuration \( \left( p^3: \frac{6 \cdot 5 \cdot 4}{3 \cdot 2 \cdot 1} = 20 \right) \)

3. Find the linear combinations of Slaters that are eigenstates in either representation:
   \[ |LM_LM_{S}\rangle \text{ OR } |LSJM_J\rangle \]
   These cause \( H^{\text{eff}} \) to be block diagonalized.

4. Compute matrix elements of \( \hat{H} \) in selected basis set.
   * \( \hat{H}^{\text{SO}} = \sum \xi(r)_\ell s_\ell \) ME of 1e⁻ operator \( \rightarrow \sum n\ell \xi(n\ell) \)
   * \( \hat{H}^{\text{ee}} = \sum e^2 / r_{ij} \) ME of 2e⁻ operator \( \rightarrow \sum k,n,n' \left[ f_k F_k(n\ell, n'\ell') + g_k G_k(n\ell, n'\ell') \right] \)

\( H^{\text{eff}} \) expressed in terms of fit parameters:
   orbital energy \( \varepsilon \)
   spin-orbit \( \zeta \)
   direct \( F^k \)
   exchange \( G^k \)

\( \varepsilon, \zeta, F^k, G^k \) orbital radial integrals \( \leftrightarrow \) fit parameters
   \( z_n, f_k, g_k \) are exactly calculable ANGULAR INTEGRALS

Would take 2 or 3 lectures to explain how to compute:
   * 1e⁻ and 2e⁻ operator matrix elements of Slater determinants
* how to work out $z_n$, $f_k$, $g_k$ factors
(see Group Theory and Quantum Mechanics, M. Tinkham, pp. 154-188)

My goal here is to expose you to the atomic $H_{\text{eff}}$ models.

Often the relevant $1/r_{ij}$ and spin-orbit matrices can be found in a book like Condon and Shortley. Read Tinkham pages 154-188 for methods of evaluating these matrix elements yourselves.

Examine the $n = 3$ and $n = 2$ levels of H atom explicitly and compare against the observed spectrum.

$n = 2$ can have $\ell = 0$ and 1

$n = 3$ has $l = 0, 1, 2$

\[
\begin{array}{cccccc}
\text{n} & \ell & j & s & E^0/\hbar c & H_{\text{SO}}/\hbar c \\
2 & 0 & 1/2 & 1/2 & -27419.396 & -0.457 \\
2 & 1 & 1/2 & 1/2 & -27419.396 & -0.457 \\
2 & 1 & 3/2 & 1/2 & -27419.396 & -0.091 & 0.366 \\
3 & 0 & 1/2 & 1/2 & -12186.398 & -0.162 \\
3 & 1 & 1/2 & 1/2 & -12186.398 & -0.162 \\
3 & 1 & 3/2 & 1/2 & -12186.398 & -0.054 & 0.108 \\
3 & 2 & 3/2 & 1/2 & -12186.398 & -0.054 \\
3 & 2 & 5/2 & 1/2 & -12186.398 & -0.018 & 0.036 \\
\end{array}
\]

See Figures Energy Level Diagram
Spectrum (Theoretical from C & S)

Compare $2^2P_{3/2} - 2^2P_{1/2}$ energy level splitting for hydrogenic systems vs. $Z$

\[
\begin{array}{ll}
\text{H I} & 0.366 \text{ cm}^{-1} \\
\text{Li III} & 30 \text{ cm}^{-1} \\
\text{Na XI} & 5400 \text{ cm}^{-1} \\
\end{array}
\]
Energy level Diagram for $\text{H}_\text{i}$ $n=3$ and $n=2$

**Transition Label**

<table>
<thead>
<tr>
<th>Transition</th>
<th>CALC</th>
<th>OBS</th>
<th>energy order of transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>15233.3071</td>
<td>3.070</td>
<td>3</td>
</tr>
<tr>
<td>$b$</td>
<td>15233.3035</td>
<td>3.034</td>
<td>2</td>
</tr>
<tr>
<td>$c$</td>
<td>15233.401</td>
<td>3.399</td>
<td>5 - highest</td>
</tr>
<tr>
<td>$d$</td>
<td>15233.401</td>
<td>3.364</td>
<td>5 -</td>
</tr>
<tr>
<td>$e$</td>
<td>15233.293</td>
<td>3.356</td>
<td>4</td>
</tr>
<tr>
<td>$f$</td>
<td>15233.293</td>
<td>3.301</td>
<td>4</td>
</tr>
<tr>
<td>$g$</td>
<td>15233.297</td>
<td>2.936</td>
<td>1</td>
</tr>
</tbody>
</table>

parity selection rule $\rightarrow \Delta \ell = \pm 1$

vector coupling $\Delta \ell = \Delta j$ favored (propensity rule, solid lines a, c, d, g)
This illustrates the spin-orbit fine structure of the H atom $n = 3 \leftarrow n = 2$ spectrum. Transitions are labeled $(a)\rightarrow(g)$ following the table on the previous page. The lengths of the lines represent the calculated relative intensities (assuming equal populations in all $m_j$ components of the $n = 2$ levels).

Orbital-Based Periodic Correlations: what do we look at to see the correlations?  
Lowest L–S–J state?  Center of gravity of entire configuration?

\[
\begin{align*}
\text{Degeneracy} & \quad \text{2D} & \quad \text{d}^9 \quad (2L + 1)(2S + 1) = 10 \\
\text{d}^1 & \quad 10 & \\
\text{d}^2 & \quad \frac{10\cdot9}{2} = 45 & \quad 1^1\text{G}, 3^3\text{F}, 1^1\text{D}, 3^3\text{P}, 1^3\text{S} \\
\text{d}^3 & \quad \frac{10\cdot9\cdot8\cdot7}{2\cdot3} = 120 & \quad 2^2\text{H}, 2^2\text{G}, 4^4\text{F}, 2^2\text{F}, 2^2\text{D}, 2^2\text{D}, 4^4\text{P}, 2^4\text{P} \\
\text{d}^4 & \quad \frac{10\cdot9\cdot8\cdot7\cdot6}{2\cdot3\cdot4\cdot5} = 210 & \quad \text{incredible} \\
\text{d}^5 & \quad \frac{10\cdot9\cdot8\cdot7\cdot6}{2\cdot3\cdot4\cdot5} = 224 & \quad \text{unbelievable}
\end{align*}
\]

Yet all is given by $\zeta(\text{nd})$, $F^0$, $F^2$, $F^4$ (no $G^k$'s for $p^2$ or any set of identical $n\ell$ orbitals) Massively complicated spectra for 3d series.

No corresponding states for $3d^n \rightarrow 3d^{n+1}$

Magic decoder is $\zeta$, $F^0$, $F^2$, $F^4$ in effective Hamiltonian.

We know how each of these parameters should scale

vs. Z for isoelectronic series or across row as $Z \rightarrow Z +1$, or as $N \rightarrow N + 1$

vs. n for Rydberg series

Example $\zeta(3d)$ for $3d^n4s^2$ of Sc $\rightarrow$ Cu

Goes as $Z_{\text{eff}}^4$ (imperfect shielding of one 3d by others) as Z increases.

The plot of $\zeta(\text{LS})$ is for the lowest L–S term (MAX S, MAX L) (Hund’s rules)
Look at Figure 6-2 from Tinkham:

Figure removed due to copyright restrictions.
Please see: Figure 6-2 in Moore, C. E. "Atomic Energy Levels." *Natl Bur Standards, Circ 467.* [Vols. I (1949) ; Vol II. (1951)].

\[ p^2 \text{ Example } \quad \text{LS} \rightarrow jj \text{ Coupling} \]

\[ p^2 \text{ configuration } \rightarrow ^1D_2, \ 3P_{2,1,0}, \ 1S_0 \]

See Condon and Shortley, pages 198, 268, 274-5, 294
The Russell-Saunders Case: Energy Levels removed due to copyright restrictions.
$$\begin{align*}
{^1S}_0 & \begin{pmatrix} F_0 + 10F_2 & 0 & 0 & 0 & 0 \\ 0 & F_0 + F_2 & 0 & 0 & 0 \\ 0 & 0 & F_0 - 5F_2 & 0 & 0 \\ 0 & 0 & 0 & F_0 - 5F_2 & 0 \\ 0 & 0 & 0 & 0 & F_0 - 5F_2 \end{pmatrix} \\
{^1D}_2 & \begin{pmatrix} 0 & -2^{1/2} & 0 & 0 & 0 \\ -2^{1/2} & -1 & 0 & 0 & 0 \\ 0 & 0 & -1/2 & 0 & 0 \\ 0 & 0 & 0 & 2^{-1/2} & \frac{1}{2} \\
\end{pmatrix} \\
{^3P}_0 & \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \end{pmatrix} \end{align*}$$

5 × 5 is fully diagonal

$$\begin{align*}
{^1S}_0 & \begin{pmatrix} 0 & -2^{1/2} & 0 & 0 & 0 \\ -2^{1/2} & -1 & 0 & 0 & 0 \\ 0 & 0 & -1/2 & 0 & 0 \\ 0 & 0 & 0 & 2^{-1/2} & \frac{1}{2} \\
\end{pmatrix} \\
{^1D}_2 & \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \end{pmatrix} \\
{^3P}_0 & \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \end{pmatrix} \end{align*}$$

5 × 5, in different order than above $H^e$, factors into $2 \times 2$, $1 \times 1$, and $2 \times 2$

Add $H^e + H^S$ to get secular equations for $J = 2, 1, 0$. These matrices were evaluated in L–S–J basis set. Could have used $L M_L$, $S M_S$. More work, same results.

To get secular equations into most convenient form

* subtract out center of gravity (C of G)

* put $2 \times 2$ into form

$$\begin{pmatrix}
\frac{\Delta}{2} - E & V \\
V & \frac{-\Delta}{2} - E
\end{pmatrix} = 0$$

Eigenvalues $E_\pm = \pm(\Delta/4 + V^2)^{1/2}$

$$J = 0 \begin{align*}
{^1S}_0 & \begin{pmatrix} F_0 + 10F_2 & -2^{1/2} \zeta \\ -2^{1/2} \zeta & F_0 - 5F_2 - \zeta \end{pmatrix} = \begin{pmatrix} F_0 + 5/2F_2 - 1/2 \zeta \\ \end{pmatrix} + \begin{pmatrix} 15/2 \zeta^2 + 1/2 \zeta \\ \end{pmatrix} \\
{^3P}_0 & \begin{pmatrix} 0 & -2^{1/2} \zeta \\ -2^{1/2} \zeta & F_0 - 5F_2 - \zeta \end{pmatrix} = \begin{pmatrix} -15/2 \zeta^2 - 1/2 \zeta \\ \end{pmatrix} \\
\end{align*}$$

So $E_\pm(J = \pm) = F_0 + 5/2F_2 - 1/2 \zeta \pm \left[ \begin{align*}
225/4 & F_2^2 + 15/2 F_2 \zeta + 1/4 \zeta^2 + 2 \zeta^2 \\
\end{align*} \right]^{1/2}$

$J = 1 \ \ E(J = 1) = F_0 - 5F_2 - \zeta/2$

$$J = 2 \begin{align*}
{^1D}_2 & \begin{pmatrix} F_0 + F_2 & 2^{-1/2} \zeta \\ 2^{-1/2} \zeta & F_0 - 5F_2 + 1/2 \zeta \end{pmatrix} = \begin{pmatrix} F_0 - 2F_2 + 1/4 \zeta \\ \end{pmatrix} + \begin{pmatrix} 3F_2 - 1/4 \zeta \\ \end{pmatrix} \\
{^3P}_2 & \begin{pmatrix} 0 & 2^{-1/2} \zeta \\ 2^{-1/2} \zeta & F_0 - 5F_2 + 1/2 \zeta \end{pmatrix} = \begin{pmatrix} -3F_2 + 1/4 \zeta \\ \end{pmatrix} \\
\end{align*}$$

$E_\pm(J = \pm) = F_0 - 2F_2 + 1/4 \zeta \pm \left[ \begin{align*}
9F_2^2 - 3/2 F_2 \zeta + 1/16 \zeta^2 + 1/2 \zeta^2 \\
\end{align*} \right]^{1/2}$
Note that these matrices have $\zeta$ off-diagonal and $\Delta E^e$ differences that are dominated by $F_2$.

There are two convenient limits for intraconfigurational energy level patterns. For $p^2$:

$$\zeta = 0$$

L–S coupling

$$\tilde{J} = \tilde{L} + \tilde{S}$$

- $10F_2$ → $^1S$
- $9F_2$
- $F_2$ → $^1D$
- $6F_2$
- $-5F_2$ → $^3P_{0,1,2}$

$$\zeta = 0$$

j–j coupling

$$\tilde{J} = \tilde{j}_1 + \tilde{j}_2$$

- $\zeta = (3/2, 3/2)$ → fine
- $3/2\zeta$
- $-1/2\zeta = (3/2, 1/2)_0$ → fine
- $3/2\zeta$
- $-2\zeta = (1/2, 1/2)_0$

Be sure that total degeneracy of all states is the same in both limits.

possible values for $j_1$ and $j_2$ for $p \rightarrow \ell = 1, s = 1/2$ are $3/2$ and $1/2$

<table>
<thead>
<tr>
<th>total degeneracy</th>
<th>$(j_1, j_2)$</th>
<th>possible values of J</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 3$</td>
<td>$(3/2, 3/2)$</td>
<td>❌ exclusion principle</td>
</tr>
<tr>
<td>$4 \times 2$</td>
<td>$(3/2, 1/2)$</td>
<td>2</td>
</tr>
<tr>
<td>$2 \times 1$</td>
<td>$(1/2, 1/2)$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{2}$</td>
<td>❌ exclusion</td>
</tr>
</tbody>
</table>
LS → (j, j')ₗ Coupling Patterns

<table>
<thead>
<tr>
<th>LS states</th>
<th>Ge(4p)²</th>
<th>Pb(6p)²</th>
<th>jj states</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹S₀</td>
<td>³P₀</td>
<td>³P₀(¹S₀)</td>
<td>¹S₀-³P₀</td>
</tr>
<tr>
<td>³P₀</td>
<td>¹D₂</td>
<td>³P₁(¹D₂)</td>
<td>¹D₂-³P₂</td>
</tr>
<tr>
<td>³P₂</td>
<td>³P₁</td>
<td>³P₂</td>
<td>(3/2, 3/2)₀</td>
</tr>
<tr>
<td>³P₁</td>
<td>³P₁</td>
<td>³P₀(³P₀)</td>
<td>(3/2, 3/2)₂</td>
</tr>
<tr>
<td>³P₀, 1/2, 2</td>
<td>³P₀</td>
<td>(1/2, 1/2)₀</td>
<td></td>
</tr>
</tbody>
</table>

| Electrostatic | F₂ = 1017 cm⁻¹ |
| Spin-orbit | ζ = 880 cm⁻¹ |

See Condon and Shortley, pages 274-5, plotted on scale to keep E_{MAX} - E_{MIN} = constant.

p³ Matrix in L–S–J BASIS SET

\[
\begin{pmatrix}
1S₀ \left( F₀ + 10F₂ \right) & -2^{1/2} \zeta \\
3P₀ & -2^{1/2} \zeta & F₀ - 5F₂ - \zeta \\
³P₁ & F₀ - 5F₂ - \zeta / 2 \\
³P₂ & F₀ + F₂ & 2^{-1/2} \zeta \\
³P₂ & 2^{-1/2} \zeta & F₀ - 5F₂ + \zeta / 2
\end{pmatrix}
\]
Perturbation Theory in $\zeta/F_2 \ll 1$ limit

\[ {^1S_0} = E_{iS}^0 + \frac{2\zeta^2}{15F_2 + \zeta} \]
\[ {^3P_0} = E_{ip}^0 - \zeta = \frac{2\zeta^2}{15F_2 + \zeta} \]
\[ {^3P_1} = E_{ip}^0 - \zeta/2 \]
\[ {^3P_2} = E_{ip}^0 + \zeta/2 + \frac{\zeta^2/2}{6F_2 - \zeta/2} \]

Landé Interval Rule

Perturbation Theory works when \( \left| \frac{H'_{ij}}{E_i^0 - E_j^0} \right| \). Thus, our L–S–J basis set matrix for \( \mathbf{H} \) is suitable for perturbation theory if

\[ \left| \frac{2^{1/2} \zeta}{15F_2 + \zeta} \right| \quad \text{and} \quad \left| \frac{2^{-1/2} \zeta}{6F_2 - \zeta/2} \right| \quad \text{are} \ll 1 \]

\[ J = 0 \quad J = 2 \quad (\text{i.e.} \: \zeta \ll F_2) \]

Alternatively, we can transform to the \( jj \) basis set using the transformation given on page 294 of Condon and Shortley.

\[
(3/2, 3/2)_2 = \left( \frac{2}{3} \right) ^{3/2} P_2 + \left( \frac{1}{3} \right) ^{1/2} D_2 \\
(3/2, 1/2)_2 = \left( \frac{1}{3} \right) ^{1/2} P_2 - \left( \frac{2}{3} \right) ^{1/2} D_2 \\
(3/2, 1/2)_1 = \quad P_1 \\
(3/2, 3/2)_0 = \left( \frac{2}{3} \right) ^{3/2} S_0 - \left( \frac{1}{3} \right) ^{1/2} P_0 \\
(1/2, 1/2)_0 = \left( \frac{1}{3} \right) ^{1/2} S_0 + \left( \frac{2}{3} \right) ^{1/2} P_0
\]
And the matrices are given by

\[
H_{(3/2,3/2)_2,(3/2,3/2)_2} = \frac{2}{3} H^{1p_2^3p_2} + \frac{1}{3} H^{1d_2^1d_2} + \frac{2 \cdot 2^{1/2}}{3} H^{1p_2^1d_2}
\]

\[
H_{(3/2,1/2)_2,(3/2,1/2)_2} = \frac{1}{3} H^{1p_2^3p_2} + \frac{2}{3} H^{1d_2^1d_2} - \frac{2 \cdot 2^{1/2}}{3} H^{1p_2^1d_2}
\]

\[
H_{(3/2,3/2)_2,(3/2,1/2)_2} = \frac{\sqrt{2}}{3} H^{1p_2^3p_2} - \frac{\sqrt{2}}{3} H^{1d_2^1d_2} - \frac{1}{3} H^{1p_2^1d_2}
\]

**MATRICES TRANSFORMED TO j_1−j_2−J BASIS SET**

\[
H(J = 2) = \begin{pmatrix}
-3F_2 + \zeta & -2^{3/2}F_2 \\
-2^{3/2}F_2 & -F_2 - \frac{1}{2}\zeta
\end{pmatrix} (3/2, 3/2)_2
\]

\[
H(J = 1) = \begin{pmatrix}
-5F_2 - \zeta/2 \\
5F_2 + \zeta & 5\sqrt{2}F_2
\end{pmatrix} (3/2, 1/2)_2
\]

\[
H(J = 0) = \begin{pmatrix}
5\sqrt{2}F_2 & -2\zeta
\end{pmatrix} (3/2, 1/2)_0
\]

Goes to limiting j–j pattern when \(F_2 \to 0\).

Note: \(\zeta\) is off-diagonal in L–S–J basis

\(F_2\) is off-diagonal in \(j–j–J\) basis

This is an example of the battle between two terms in \(H^{\text{eff}}\).

Suggested homework problem: repeat all of the steps in pages 5-11 for the \(d^2\) configuration. Use tables in Condon and Shortley.
Transitions $p^2 \leftrightarrow sp$

also other weak $^3P_1 - ^3P_2$ lines

$^1S_0$

$^1D_2$

$^3P_2$

$^3P_1$

$^3P_0$

$^1P_1$

propensity rules

$\Delta \ell = \pm 1$

$\Delta J = \Delta L$ strong

$\Delta S = 0$

$\Delta J_1 = \Delta J$

or

$\Delta J_2 = \Delta J$

$\Delta J = 0, \pm 1$

but

$J = 0 \not\Rightarrow J = 0$

same $\zeta$ as for sp

$^3P_2$

$^3P_1$

$^3P_0$

sp (lower states)

other “forbidden” transition strengths predictable from mixing coefficients

$\Delta \ell = \pm 1$

$\Delta J = \Delta L$ strong

$\Delta S = 0$

$\Delta j_1 = 0$ (inactive $e^-$)

$\Delta j_2 = 0, \pm 1$

$\Delta J = 0, \pm 1$

$J = 0 \Rightarrow J = 0$

$\Delta J = \Delta j_2$ strong
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Table of matrices of spin-orbit interaction removed due to copyright restrictions.
Transformations in the theory of complex spectra text removed due to copyright restrictions.