5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #6: Many e^- Atoms

Outline of approach:

Configuration $\rightarrow$ which L–S–J states?
$\rightarrow \mathbf{H}^{\text{eff}}\,[\varepsilon, \zeta, F^k, G^k]$ $\rightarrow$ energy levels
$\rightarrow$ eigenstates
$\rightarrow$ transition intensities
alternative Limiting Case Coupling Schemes
L–S–J vs. $j_1 - j_2 - J$
off-diagonal ζ vs. F^2

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1. list of orbital occupancies e.g. $1s^2\,2s^2\,2p^2$ "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 "β")
   - * list all Slater determinants (anti-symmetrized microstates) consistent with Exclusion Principle
     e.g. $|1\bar{1}|$ $M_L = 2$ $M_S = 0$
     standard order of spin-orbitals (needed to get correct signs of matrix elements)
   - * Classify Slaters according to M_L and M_S
   - * Method of crossing out of microstates: M_L, M_S ranges for each L–S term ($p^3 \rightarrow {}^4S, {}^2D, {}^2P$)
   - * Total degeneracy of a configuration $\left(p^3: \quad \dfrac{6\cdot5\cdot4}{3\cdot2\cdot1} = 20\right)$

3. Find the linear combinations of Slaters that are eigenstates in either representation:
   $|LM_LSM_S\rangle$ OR $|LSJM_J\rangle$
   These cause $\mathbf{H}^{\text{eff}}$ to be block diagonalized.

4. Compute matrix elements of $\widehat{\mathbf{H}}$ in selected basis set.
   - * $\widehat{\mathbf{H}}^{\text{SO}} = \sum \xi(r_i)\ell_i\cdot s_i$ ME of $1e^-$ operator $\rightarrow \sum\limits_{n\ell} z_{n\ell}\zeta(n\ell)$
   - * $\widehat{\mathbf{H}}^{\text{ee}} = \sum\limits_{i>j} e^2/r_{ij}$ ME of $2e^-$ operator $\rightarrow \sum\limits_{k,n\ell,n'\ell'}\left[f_k F^k(n\ell,n'\ell') + g_k G^k(n\ell,n'\ell')\right]$

$\mathbf{H}^{\text{eff}}$ expressed in terms of fit parameters:

orbital energy	ε
spin-orbit	ζ
direct	F^k
exchange	G^k

$\varepsilon, \zeta, F^k, G^k$ orbital radial integrals $\leftrightarrow$ fit parameters
$z_{n\ell}$, 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 $z_{n\ell}$, 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 $\mathbf{H}^{\text{eff}}$ 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 ℓ = 0 and 1 $\quad$ $\swarrow$ $\boxed{j = 1/2}$ $\quad$ $\searrow$ $\boxed{j = 1/2 \text{ and } 3/2}$

n = 3 has l = 0, 1, 2 $\quad$ $\downarrow$ $\boxed{j = 5/2, 3/2}$

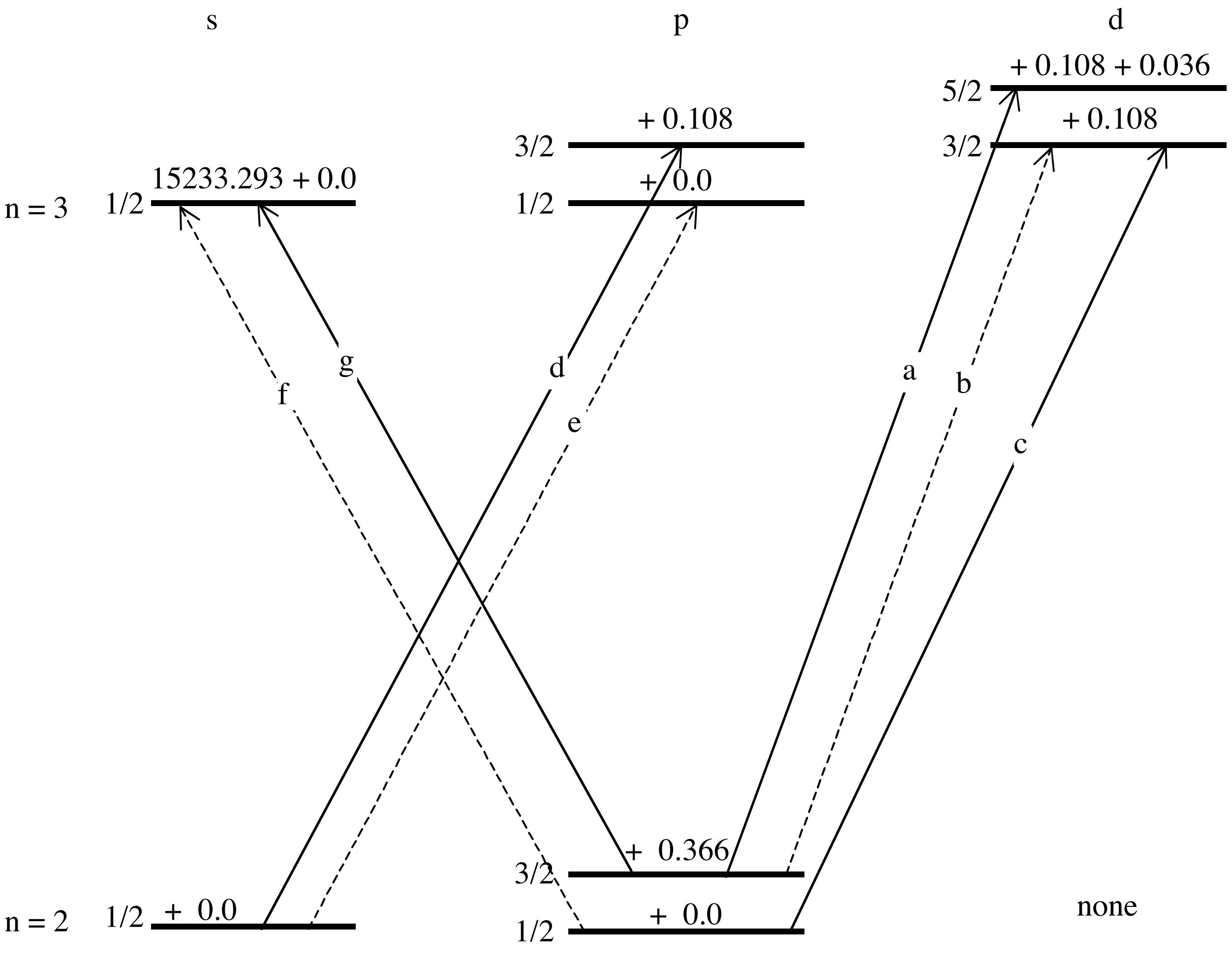
n	ℓ	j	s	E°/hc	$\mathbf{H}^{SO}$/hc		
2	0	1/2	1/2	–27419.396	–0.457		–27419.853
2	1	1/2	1/2	–27419.396	–0.457	0.366	–27419.853
2	1	3/2	1/2	–27419.396	–0.091		–27419.487
3	0	1/2	1/2	–12186.398	–0.162		–12186.560
3	1	1/2	1/2	–12186.398	–0.162	0.108	–12186.560
3	1	3/2	1/2	–12186.398	–0.054		–12186.452
3	2	3/2	1/2	–12186.398	–0.054	0.036	–12186.452
3	2	5/2	1/2	–12186.398	–0.018		–12186.416

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

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

Energy level Diagram for H_I n=3 and n = 2



Transition Label	**CALC**	**OBS**	**energy order of transition**
a = 15233.293 – 0.366 + 0.108 + 0.036	= 152333.071	3.070	3
b = 15233.293 – 0.366 + 0.108	= 152333.035	3.034	2
c = 15233.293 – 0.366 + 0.108	= 152333.401	3.399	5 - highest
d = 15233.293 – 0.366 + 0.108	= 152333.401	3.364	5 - "
e = 15233.293 – 0.366 + 0.000	= 152333.293	3.356	4
f = 15233.293 – 0.366 + 0.000	= 152333.293	3.301	4
g = 15233.293 – 0.366 + 0.108	= 152332.927	2.936	1
			↓
			lowest

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

vector coupling $\Delta\ell = \Delta j$ favored (propensity rule, solid lines a, c, d, g)

Image of *The Theory of Atomic Spectra* by E. U. Condonand G. H. Shortley removed due to copyright restrictions.

Figure removed due to copyright restrictions.
Please see: Fig. 35 in Condon, E. E., and G. H. Shortley. *The Theory of Atomic Spectra*. Cambridge, UK. Cambridge University Press, 1951.

This illustrates the spin-orbit fine structure of the H atom n = 3 ← n = 2 spectrum. Transitions are labeled (*a*)–(*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?

	Degeneracy			
d^1	10	^2D	d^9	$(2L + 1)(2S + 1) = 10$
d^2	$\frac{10\cdot9}{2} = 45$	$^1G, {}^3F, {}^1D, {}^3P, {}^1S$	d^8	
d^3	$\frac{10\cdot9\cdot8}{2\cdot3} = 120$	$^2H, {}^2G, {}^4F, {}^2F, {}^2D, {}^2D, {}^4P, {}^2P$	d^7	
d^4	$\frac{10\cdot9\cdot8\cdot7}{2\cdot3\cdot4} = 210$	incredible	d^6	
d^5	$\frac{10\cdot9\cdot8\cdot7\cdot6}{2\cdot3\cdot4\cdot5} = 224$	unbelievable	d^5	

Yet all is given by $\zeta(nd)$, 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 ζ, 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 → Cu
Goes as Z_{eff}^4 (imperfect shielding of one 3d by others) as Z increases.
The plot of $\zeta(LS)$ is for the lowest L–S term (MAX S, MAX L) (Hund's rules)

Look at Figure 6-2 from Tinkham:

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

← property of 3d orbital $\left(Z_{3d}^{\text{eff}}\right)^4$ scaling. Z^{eff} increases in steps of 0.8.

← property of lowest L–S term of $(3d)^{x}(4s)_2$ configuration. No scaling. Hund's 3rd Rule.

p^2 Example LS → jj Coupling

p^2 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.

$$\mathbf{H}^{ee}\left(p^2\right) = \begin{array}{c} {}^1S_0 \\ {}^1D_2 \\ {}^3P_2 \\ {}^3P_1 \\ {}^3P_0 \end{array}\begin{pmatrix} F_0+10F_2 & 0 & 0 & 0 & 0 \\ 0 & F_0+F_2 & 0 & 0 & 0 \\ 0 & 0 & F_0-5F_2 & 0 & 0 \\ 0 & 0 & 0 & F_0-5F_2 & 0 \\ 0 & 0 & 0 & 0 & F_0-5F_2 \end{pmatrix}$$

5 × 5 is fully diagonal

$$\mathbf{H}^{SO}\left(p^2\right) = \begin{array}{c} {}^1S_0 \\ {}^3P_0^{J=0} \\ {}^3P_1^{J=1} \\ {}^1D_2 \\ {}^3P_2^{J=2} \end{array}\left(\begin{array}{cc|c|cc} 0 & -2^{1/2} & 0 & 0 & 0 \\ -2^{1/2} & -1 & 0 & 0 & 0 \\ \hline 0 & 0 & -1/2 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 2^{-1/2} \\ 0 & 0 & 0 & 2^{-1/2} & 1/2 \end{array}\right)\zeta(np)$$

5 × 5, in different order than above $\mathbf{H}^{ee}$, factors into 2 × 2, 1 × 1, and 2 × 2

Add $\mathbf{H}^{ee} + \mathbf{H}^{SO}$ to get secular equations for J = 2, 1, 0. These matrices were evaluated in L–S–J basis set. Could have used LM_LSM_S. More work, same results.

To get secular equations into most convenient form

* subtract out center of gravity (C of G)

* put 2 × 2 into form $\begin{vmatrix} \frac{\Delta}{2}-E & V \\ V & \frac{-\Delta}{2}-E \end{vmatrix} = 0$

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

$$J = 0 \quad \begin{array}{c} {}^1S_0 \\ {}^3P_0 \end{array}\begin{pmatrix} F_o+10F_2 & -2^{1/2}\zeta \\ -2^{1/2}\zeta & F_o-5F_2-\zeta \end{pmatrix} = \left[F_o+\frac{5}{2}F_2-\frac{1}{2}\zeta\right] + \begin{pmatrix} \frac{15}{2}F_2+\frac{1}{2}\zeta & -2^{1/2}\zeta \\ \text{sym} & \frac{-15}{2}F_2-\frac{1}{2}\zeta \end{pmatrix}$$

$$\text{So } E_\pm(J=0) = F_0+\frac{5}{2}F_2-\frac{1}{2}\zeta \pm \left[\frac{225}{4}F_2^2+\frac{15}{2}F_2\zeta+\frac{1}{4}\zeta^2+2\zeta^2\right]^{1/2}$$

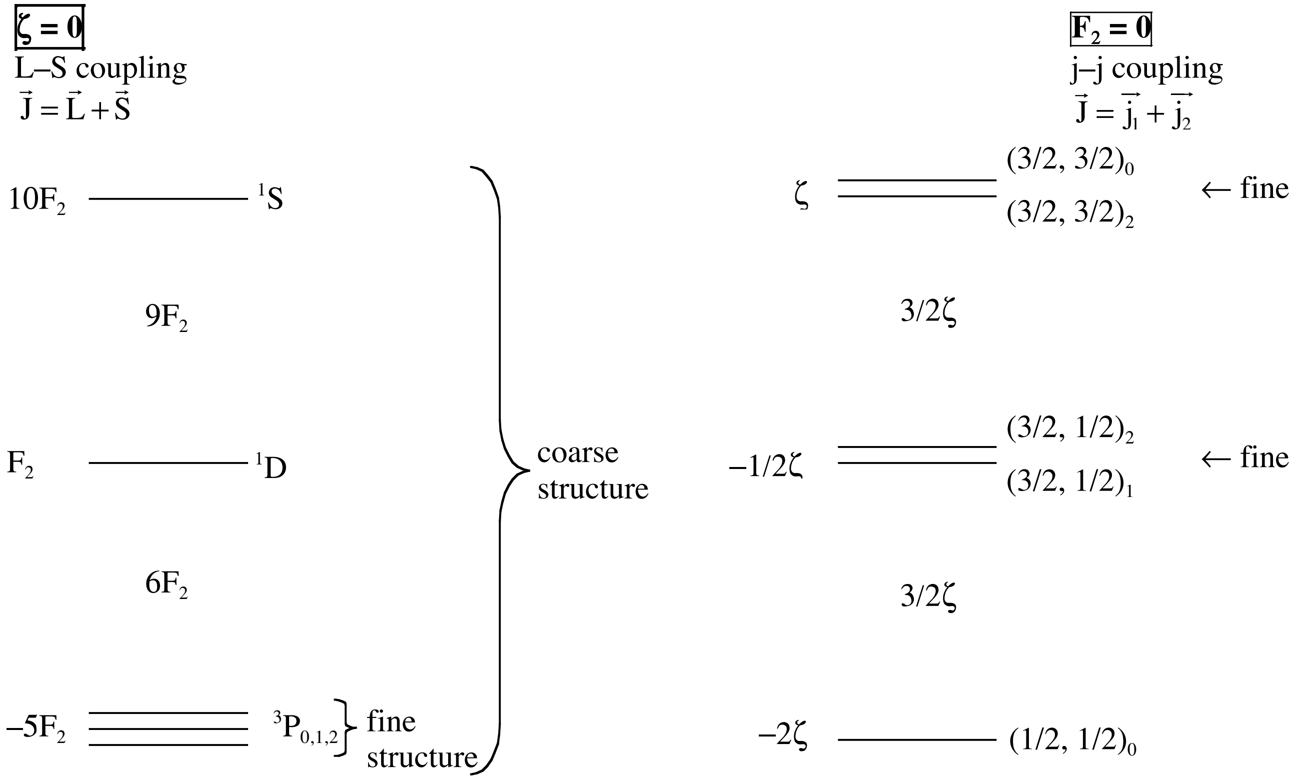
$J = 1 \quad E(J = 1) = F_0 - 5F_2 - \zeta/2$

$$J = 2 \quad \begin{array}{c} {}^1D_2 \\ {}^3P_2 \end{array}\begin{pmatrix} F_0+F_2 & 2^{-1/2}\zeta \\ 2^{-1/2}\zeta & F_0-5F_2+\frac{1}{2}\zeta \end{pmatrix} = F_0-2F_2+\frac{1}{4}\zeta + \begin{pmatrix} 3F_2-\frac{1}{4}\zeta & 2^{-1/2}\zeta \\ 2^{-1/2}\zeta & -3F_2+\frac{1}{4}\zeta \end{pmatrix}$$

$$E_\pm(J=2) = F_0-2F_2+\frac{1}{4}\zeta \pm \left[9F_2^2-\frac{3}{2}F_2\zeta+\frac{1}{16}\zeta^2+\frac{1}{2}\zeta^2\right]^{1/2}$$

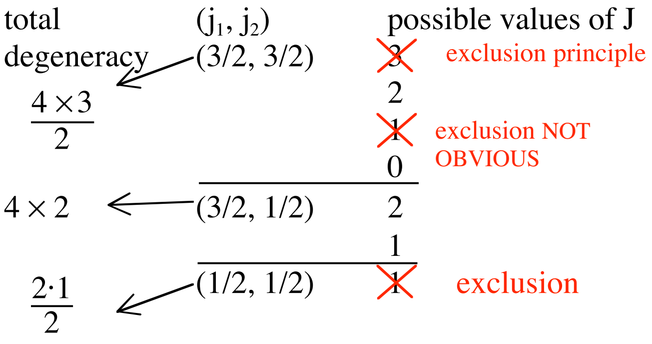
Note that these matrices have ζ off-diagonal and ΔE° differences that are dominated by F_2.

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

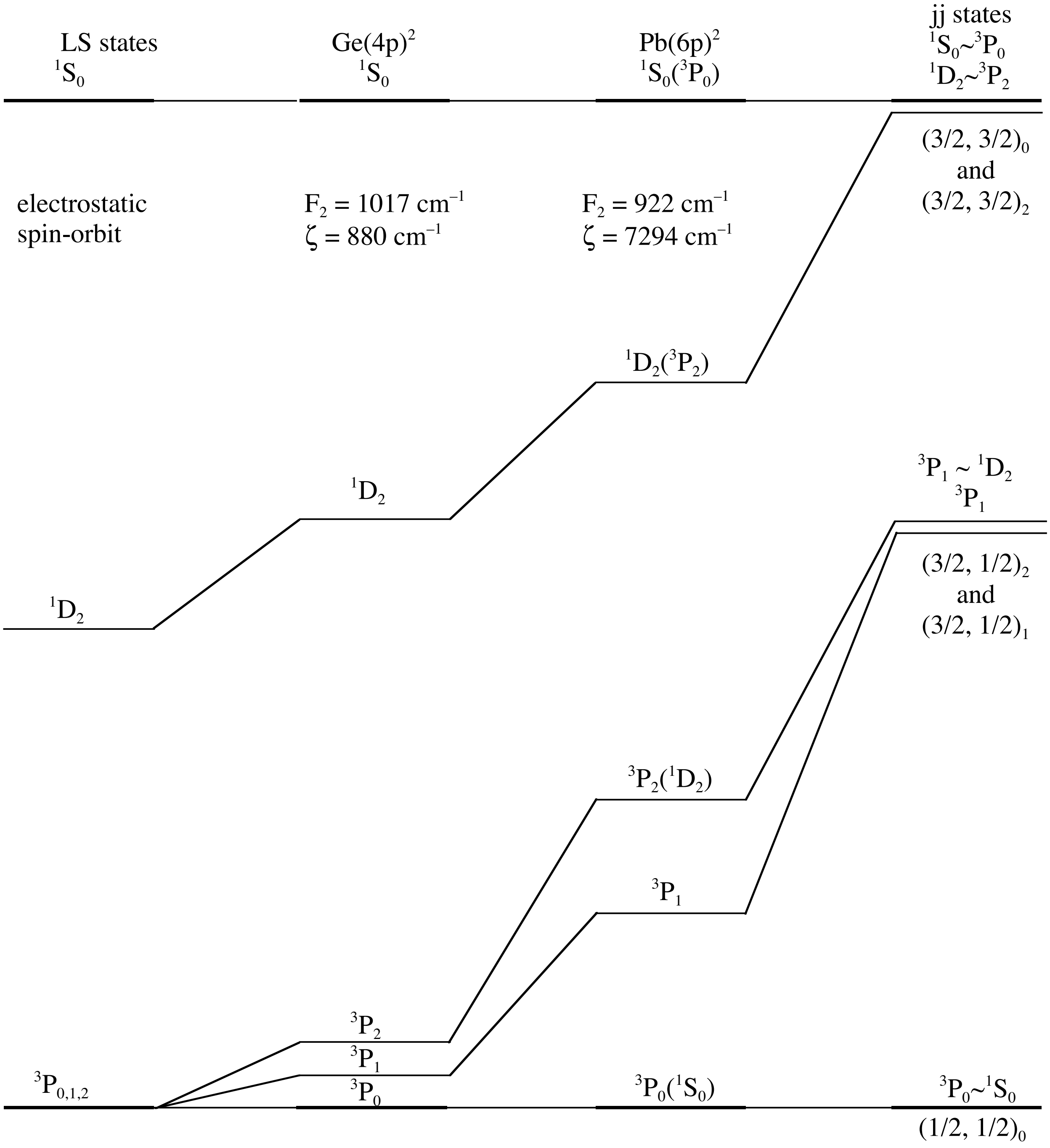


Be sure that total degeneracy of all states is the same in both limits.

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



LS → (j, j′)$_J$ Coupling Patterns



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

p^2 Matrix in L–S–J BASIS SET

$$
\begin{array}{c}
{}^1S_0 \\ {}^3P_0 \\ {}^3P_1 \\ {}^1D_2 \\ {}^3P_2
\end{array}
\begin{pmatrix}
F_0 + 10F_2 & -2^{1/2}\zeta & & & \\
-2^{1/2}\zeta & F_0 - 5F_2 - \zeta & & & \\
 & & F_0 - 5F_2 - \zeta/2 & & \\
 & & & F_0 + F_2 & 2^{-1/2}\zeta \\
 & & & 2^{-1/2}\zeta & F_0 - 5F_2 + \zeta/2
\end{pmatrix}
$$

Perturbation Theory in $\zeta/F_2 \ll 1$ limit

$$
\begin{aligned}
{}^1S_0 &= E^o_{{}^1S} + \frac{2\zeta^2}{15F_2+\zeta} \\
{}^3P_0 &= E^o_{{}^3P} - \zeta \quad - \frac{2\zeta^2}{15F_2+\zeta} \\
{}^3P_1 &= E^o_{{}^3P} - \zeta/2 \\
{}^3P_2 &= E^o_{{}^3P} + \zeta/2 + \frac{\zeta^2/2}{6F_2-\zeta/2}
\end{aligned}
$$

negligible

Landé
Interval Rule

Perturbation Theory works when $\left|\dfrac{\mathbf{H}'_{ij}}{E^o_i - E^o_j}\right|$. Thus, our L–S–J basis set matrix for **H** is suitable for perturbation theory if

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

$$J = 0 \qquad\qquad J = 2 \qquad\qquad (\text{i.e. } \zeta \ll F_2)$$

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

$$
\begin{aligned}
(3/2,3/2)_2 &= \left(\frac{2}{3}\right)^{1/2} {}^3P_2 + \left(\frac{1}{3}\right)^{1/2} {}^1D_2 \\
(3/2,1/2)_2 &= \left(\frac{1}{3}\right)^{1/2} {}^3P_2 - \left(\frac{2}{3}\right)^{1/2} {}^1D_2 \\
(3/2,1/2)_1 &= {}^3P_1 \\
(3/2,3/2)_0 &= \left(\frac{2}{3}\right)^{1/2} {}^1S_0 - \left(\frac{1}{3}\right)^{1/2} {}^3P_0 \\
(1/2,1/2)_0 &= \left(\frac{1}{3}\right)^{1/2} {}^1S_0 + \left(\frac{2}{3}\right)^{1/2} {}^3P_0
\end{aligned}
$$

And the matrices are given by

$$\mathbf{H}_{(3/2,3/2)_2,(3/2,3/2)_2} = \frac{2}{3}\mathbf{H}_{{}^3\mathrm{P}_2{}^3\mathrm{P}_2} + \frac{1}{3}\mathbf{H}_{{}^1\mathrm{D}_2{}^1\mathrm{D}_2} + \frac{2\cdot 2^{1/2}}{3}\mathbf{H}_{{}^3\mathrm{P}_2{}^1\mathrm{D}_2}$$

$$\mathbf{H}_{(3/2,1/2)_2,(3/2,1/2)_2} = \frac{1}{3}\mathbf{H}_{{}^3\mathrm{P}_2{}^3\mathrm{P}_2} + \frac{2}{3}\mathbf{H}_{{}^1\mathrm{D}_2{}^1\mathrm{D}_2} - \frac{2\cdot 2^{1/2}}{3}\mathbf{H}_{{}^3\mathrm{P}_2{}^1\mathrm{D}_2}$$

$$\mathbf{H}_{(3/2,3/2)_2,(3/2,1/2)_2} = \frac{\sqrt{2}}{3}\mathbf{H}_{{}^3\mathrm{P}_2{}^3\mathrm{P}_2} - \frac{\sqrt{2}}{3}\mathbf{H}_{{}^1\mathrm{D}_2{}^1\mathrm{D}_2} - \frac{1}{3}\mathbf{H}_{{}^3\mathrm{P}_2{}^1\mathrm{D}_2}$$

MATRICES TRANSFORMED TO $j_1 - j_2 - J$ BASIS SET

$$\mathbf{H}\,(J = 2) = \begin{array}{cc} \begin{pmatrix} -3F_2 + \zeta & -2^{3/2}F_2 \\ -2^{3/2}F_2 & -F_2 - \frac{1}{2}\zeta \end{pmatrix} & \begin{array}{l} (3/2,\,3/2)_2 \\ (3/2,\,1/2)_2 \end{array} \end{array}$$

$$\mathbf{H}\,(J = 1) = \begin{array}{cc} -5F_2 - \zeta/2 & (3/2,\,1/2)_1 \end{array}$$

$$\mathbf{H}\,(J = 0) = \begin{array}{cc} \begin{pmatrix} 5F_2 + \zeta & 5\sqrt{2}F_2 \\ 5\sqrt{2}F_2 & -2\zeta \end{pmatrix} & \begin{array}{l} (3/2,\,3/2)_0 \\ (3/2,\,1/2)_0 \end{array} \end{array}$$

Goes to limiting j–j pattern when $F_2 \to 0$.

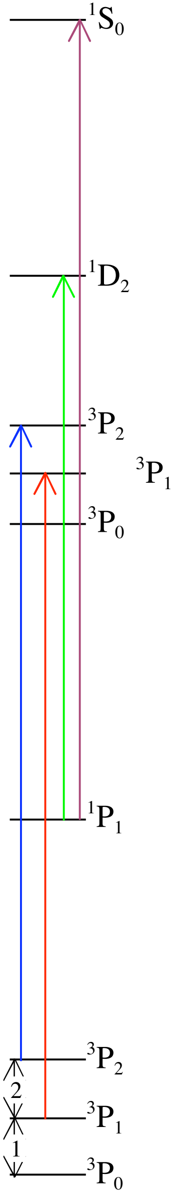
Note: ζ is off-diagonal in L–S–J basis
F_2 is off-diagonal in j–j–J basis

This is an example of the battle between two terms in $\mathbf{H}^{\mathrm{eff}}$.

Suggested homework problem: repeat all of the steps in pages 5-11 for the d^2 configuration. Use tables in Condon and Shortley.

Transitions $p^2 \leftarrow sp$

also other weak $^3P_J - {}^3P_{J'}$ lines



p^2 (upper states)

propensity rules

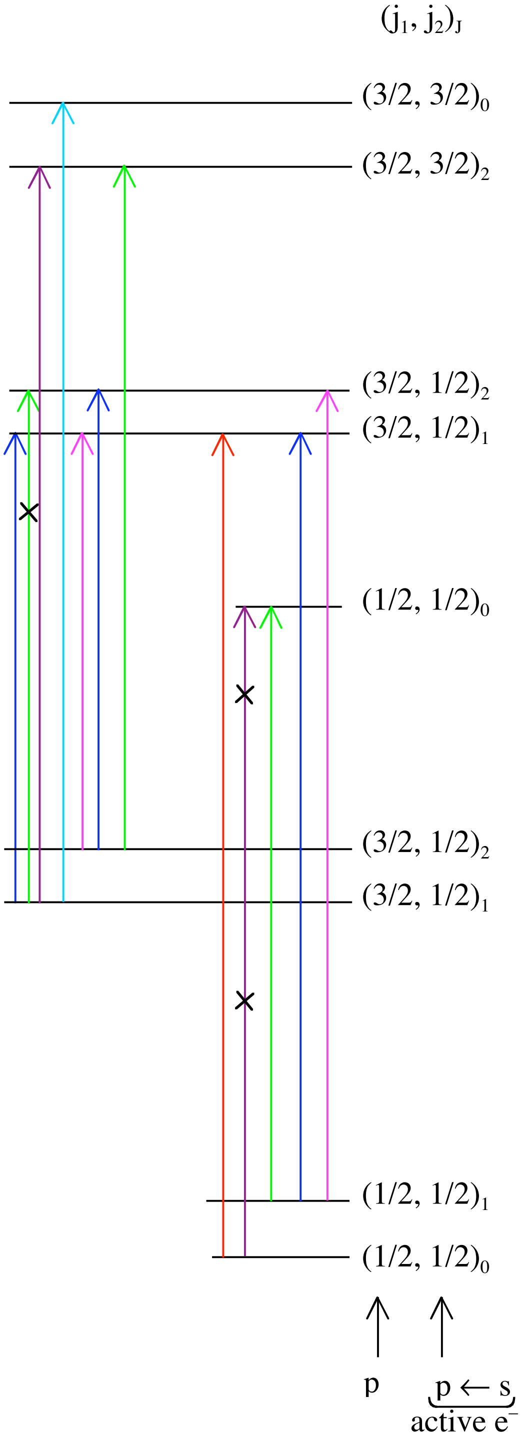
$\Delta\ell = \pm1$
$\Delta J = \Delta L$ strong
$\Delta S = 0$

$\Delta j_1 = \Delta J$
or
$\Delta j_2 = \Delta J$

$\Delta J = 0, \pm1$
but
$J = 0 \not\to J = 0$

same ζ as for sp

sp (lower states)



other "forbidden" transition strengths
predictable from mixing coefficients

$\Delta\ell = \pm1$
$\Delta J = \Delta L$ strong
$\Delta S = 0$

$\Delta j_1 = 0$ (inactive e^-)
$\Delta j_2 = 0, \pm1$
$\Delta J = 0, \pm1$
$J = 0 \not\to J = 0$
$\Delta J = \Delta j_2$ strong

Figure removed due to copyright restrictions.
Please see: Pages 274-275 in Condon, E. E., and
G. H. Shortley. *The Theory of Atomic Spectra*.
Cambridge, UK: Cambridge University Press, 1951.