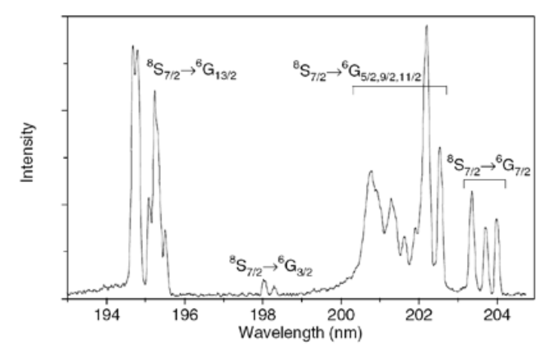
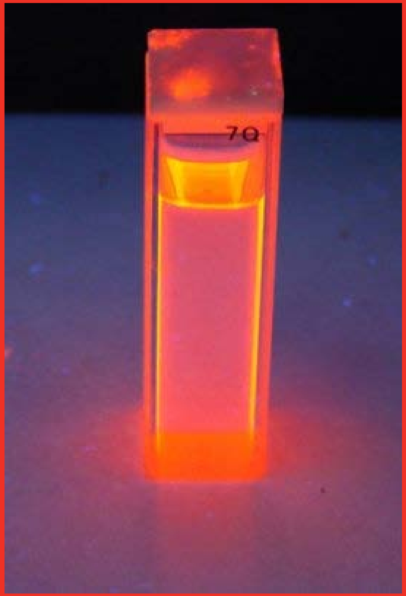
Electronic Structure and Transition Intensities in Rare-Earth Materials





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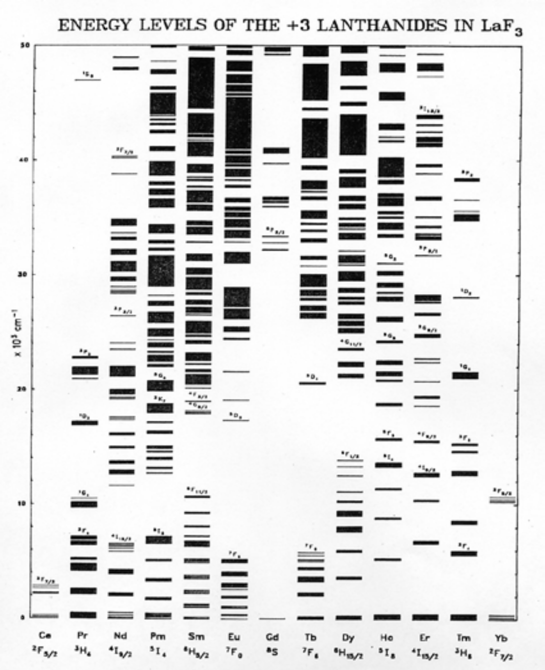
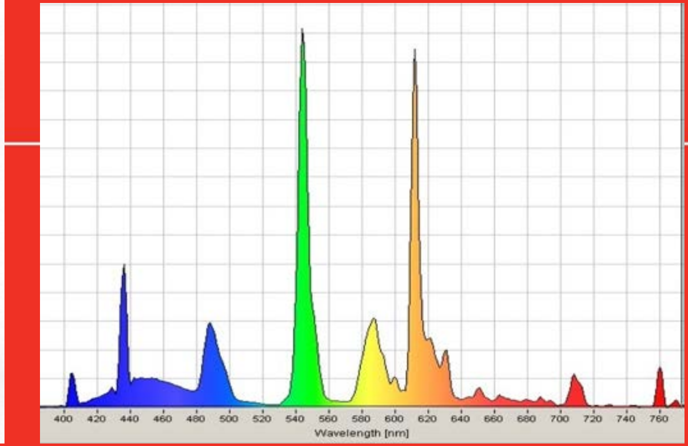


Fig. 23. Energy Level Structure of Ln^{3+}:LaF_3 Based on Computed Crystal-field Energies in the Range 0-50000 cm^{-1}.



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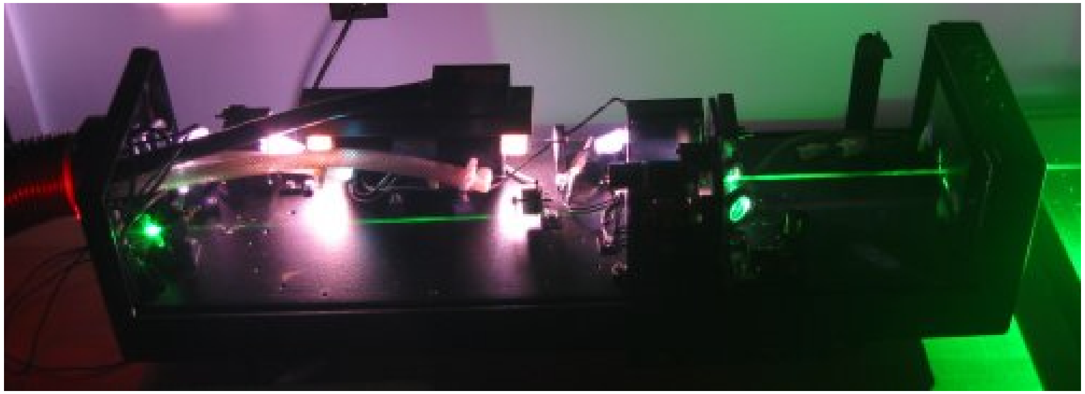
Outline

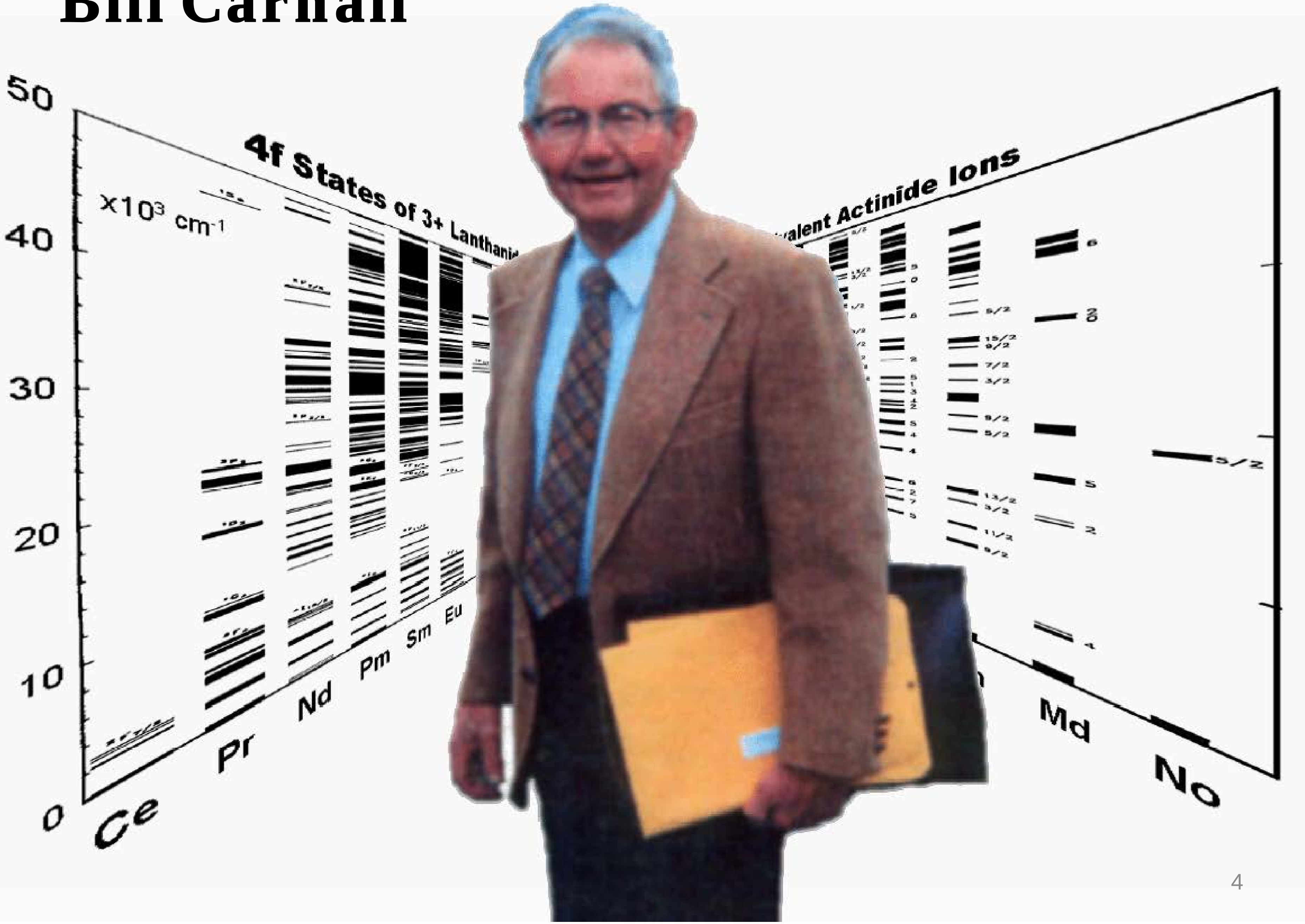
- Background on rare-earth (lanthanide) ions.
- States and transitions
- Effective Hamiltonian for $4f^N$
- Some simple calculations of energy levels
- Transition intensities
- $4f^{N-1}5d$
- Ab-initio calculations



Gerhard Dieke

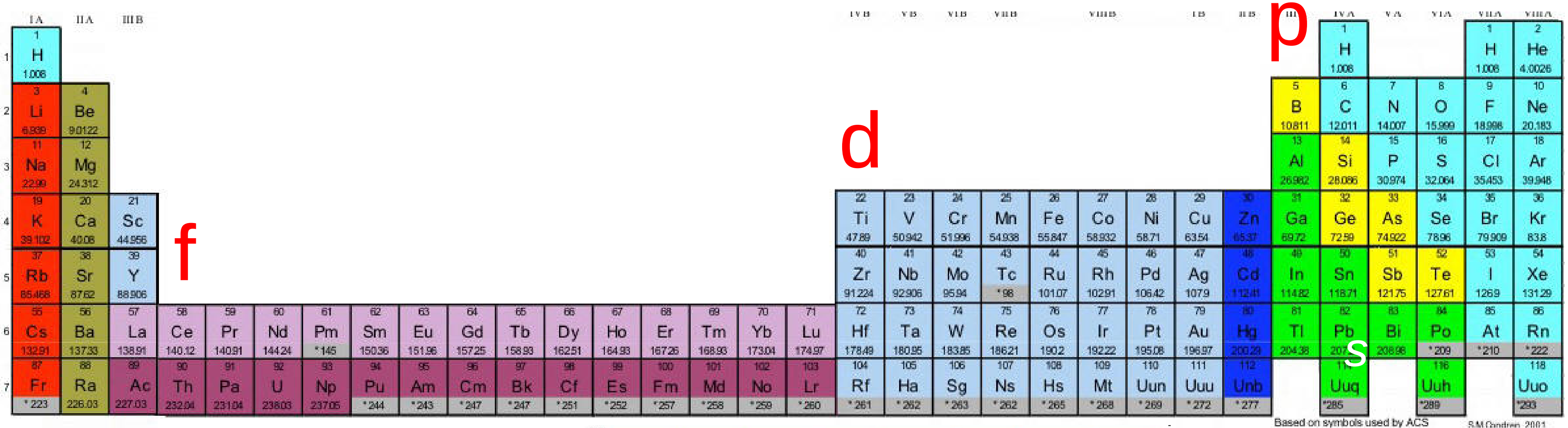
Johns Hopkins 1950-1965

Bill Carnall



1960’s Theory: Judd, Ofelt, Wybourne

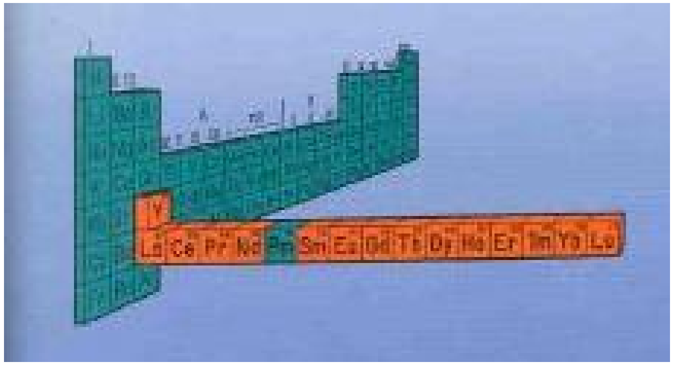
Filling of orbitals

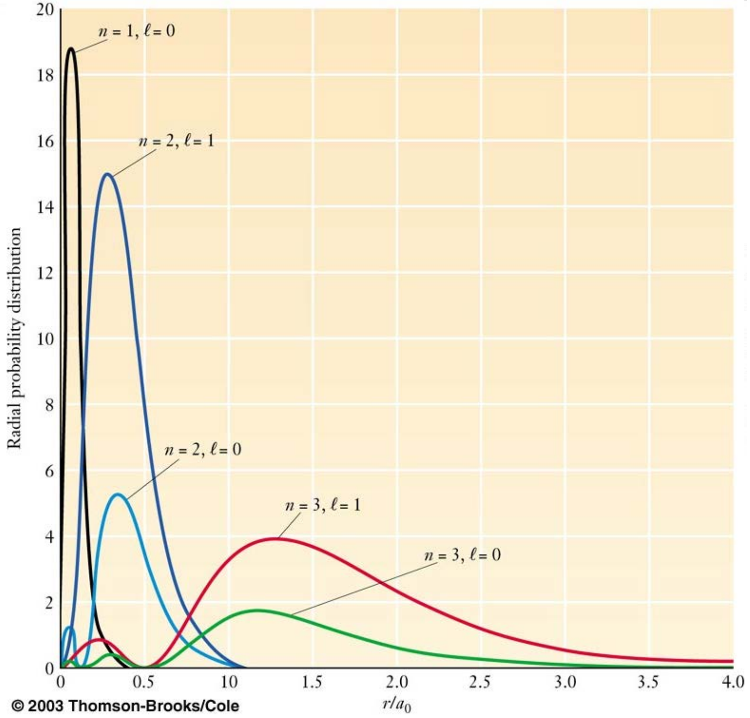


	IA	IIA	IIIB															IVB	VB	VIB	VIIB	VIIIB			IB	IIB	III	IVA	VA	VIA	VIIA	VIIIA
1	1 H 1.008																											1 H 1.008			1 H 1.008	2 He 4.0026
2	3 Li 6.939	4 Be 9.0122																									5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
3	11 Na 22.99	12 Mg 24.312																									13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
4	19 K 39.102	20 Ca 40.08	21 Sc 44.956															22 Ti 47.89	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.932	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.909	36 Kr 83.8
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906															40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc *98	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.9	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.61	53 I 126.9	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm *145	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.51	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.29	81 Tl 204.38	82 Pb 207	83 Bi 208.98	84 Po *209	85 At *210	86 Rn *222
7	87 Fr *223	88 Ra 226.03	89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu *244	95 Am *243	96 Cm *247	97 Bk *247	98 Cf *251	99 Es *252	100 Fm *257	101 Md *258	102 No *259	103 Lr *260	104 Rf *261	105 Ha *262	106 Sg *263	107 Ns *262	108 Hs *265	109 Mt *268	110 Uun *269	111 Uuu *272	112 Unb *277		11 Uuq *285		116 Uuh *289		118 Uuo *293

Based on symbols used by ACS

S.M.Condren 2001





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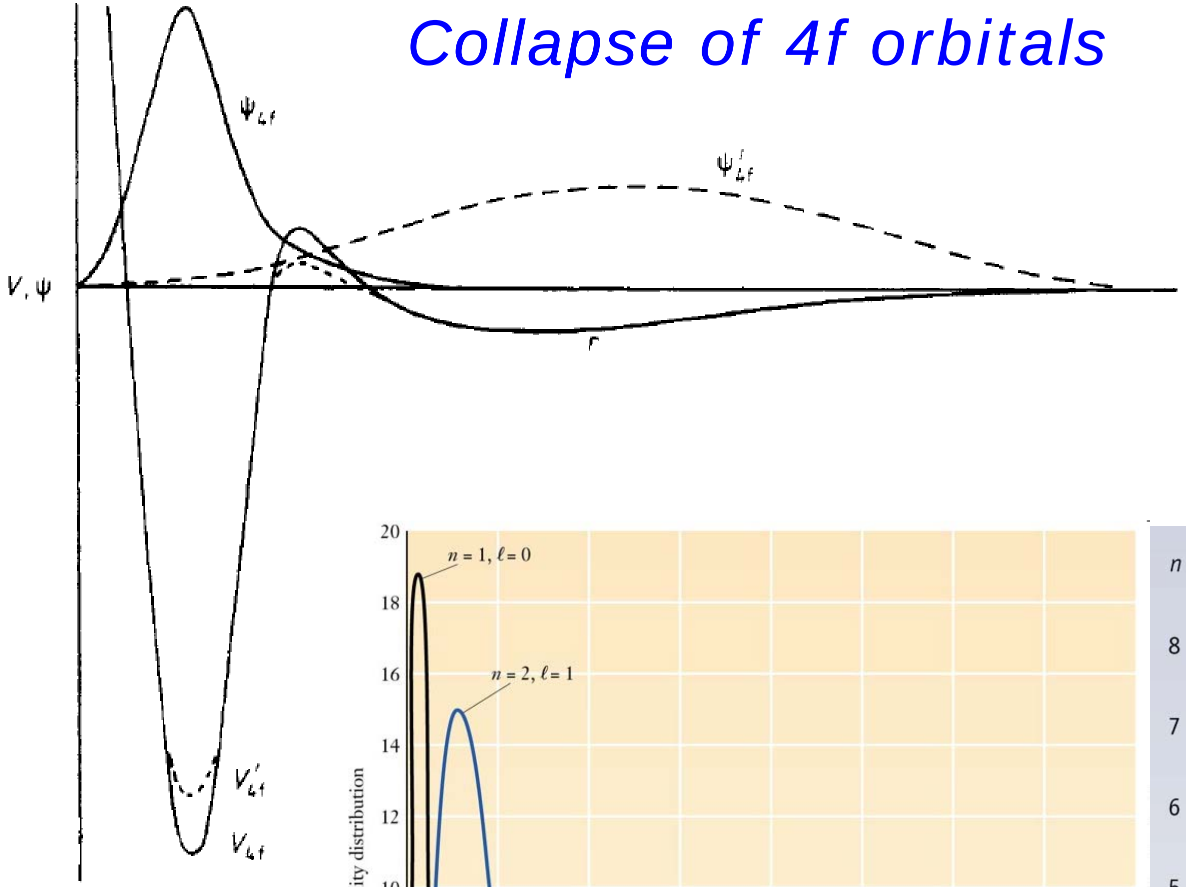
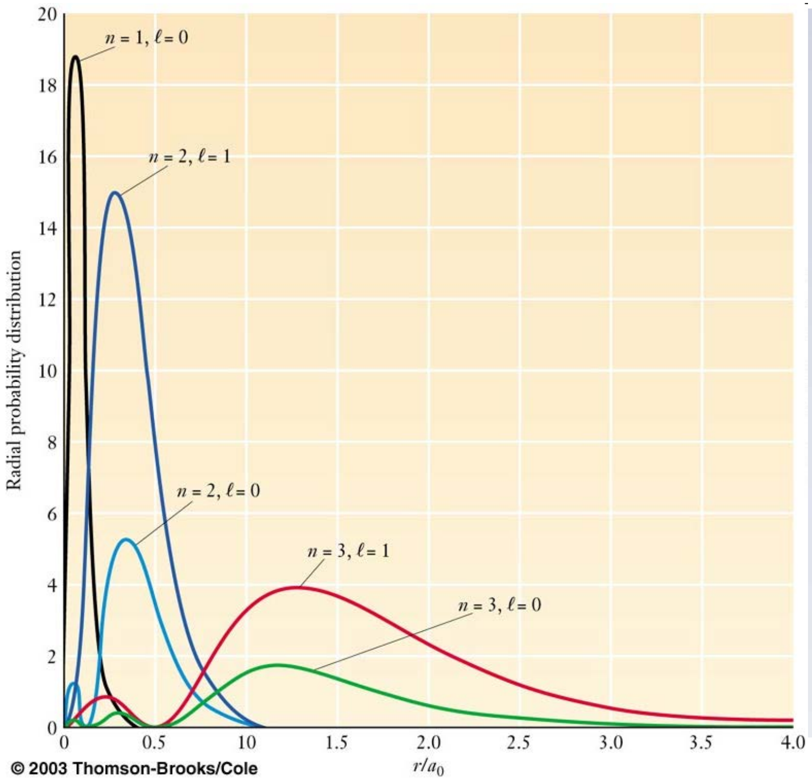
Collapse of 4f orbitals *JP Connerade, 1982*





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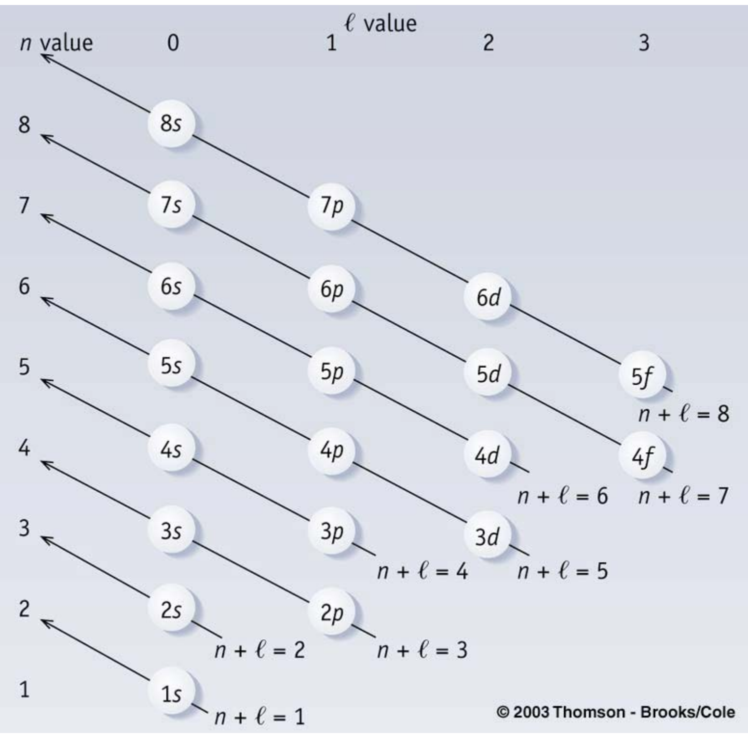

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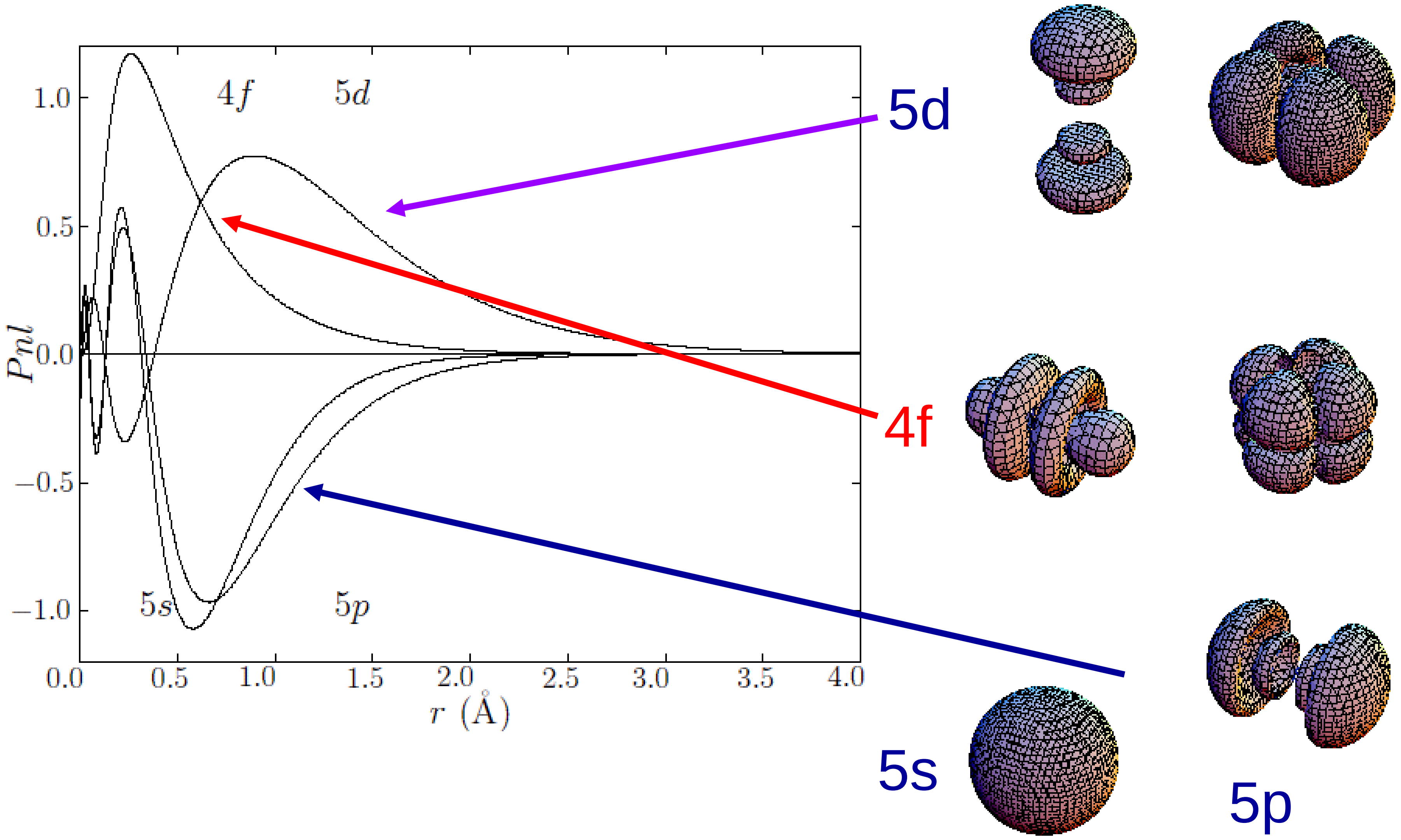
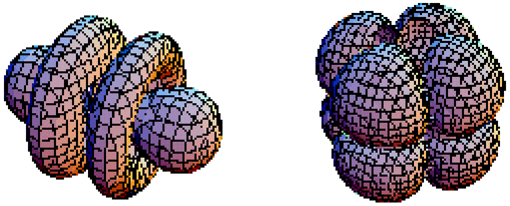
Lanthanide 3+ ground state: $5s^2\ 5p^6\ 4f^N\ 5d^0$

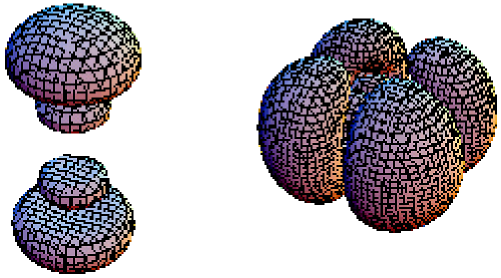


Lanthanides: $4f^N$, $4f^{N-1}5d$, Excitons

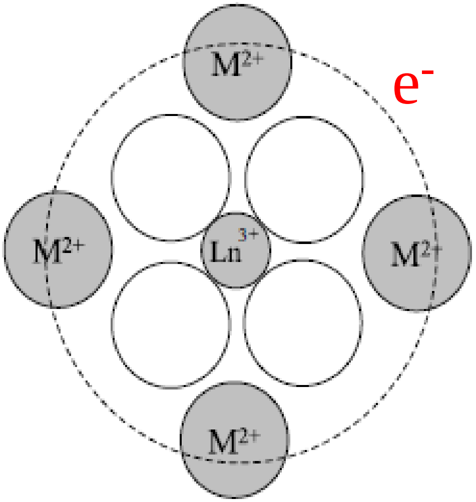
- **$4f^N$**
  - Sharp lines
  - Long lifetimes
  - So ideal for laser and phosphor applications



- **$4f^{N-1}5d$**
  - Broad absorption bands from $4f^N$
  - Useful for absorbing energy
  - Short lifetimes useful in some applications, such as scintillators

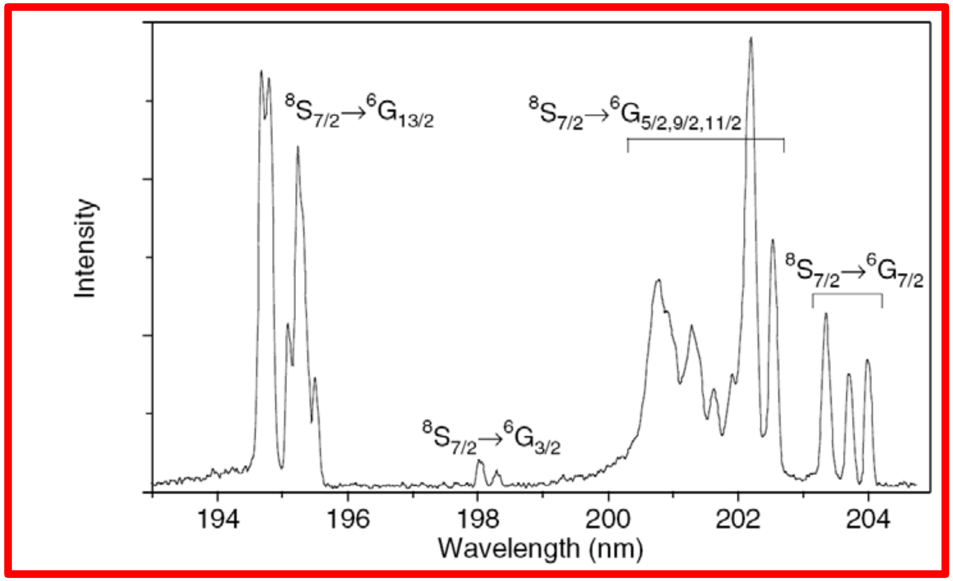


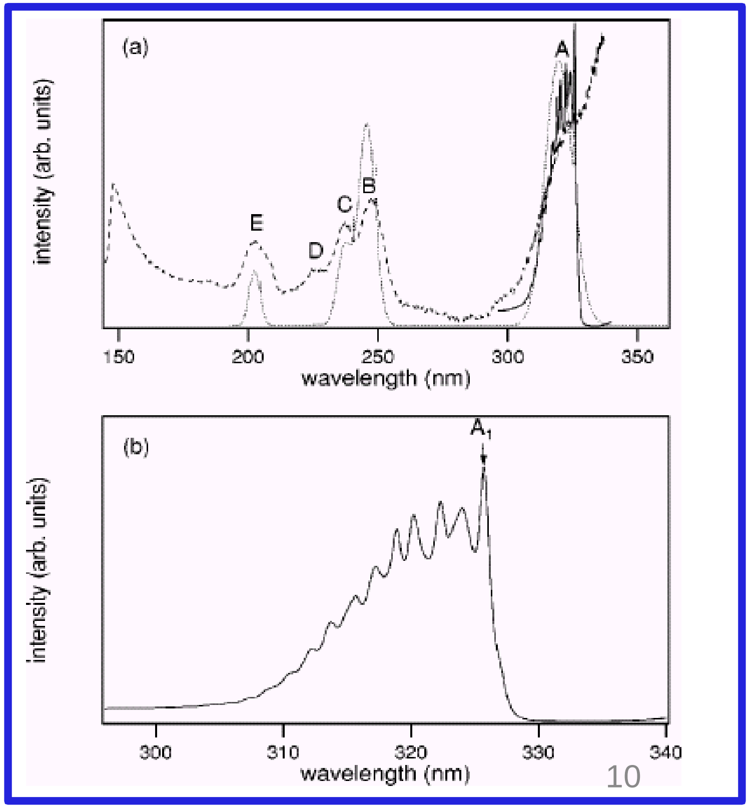
- **Excitons**
  - Excited electron can become delocalized, giving an excitonic state.
- **Charge Transfer Transitions**
  - Ligand to lanthanide electron transfer

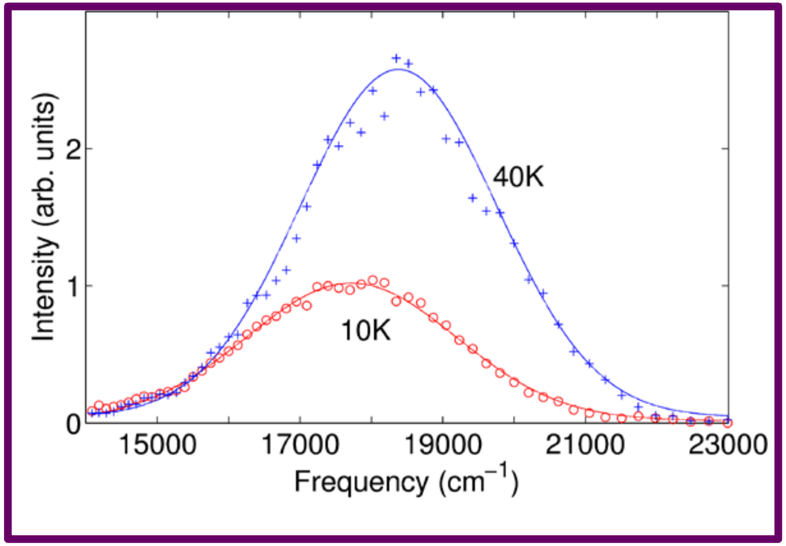


Transitions

- $4f^N – 4f^N$
  - No configuration shift
  - Sharp lines
- $4f^N – 4f^N5d$
  - Configuration shift
  - Broad bands
- Excitonic states $\rightarrow 4f^N$
  - Large configuration shift
  - Very broad bands





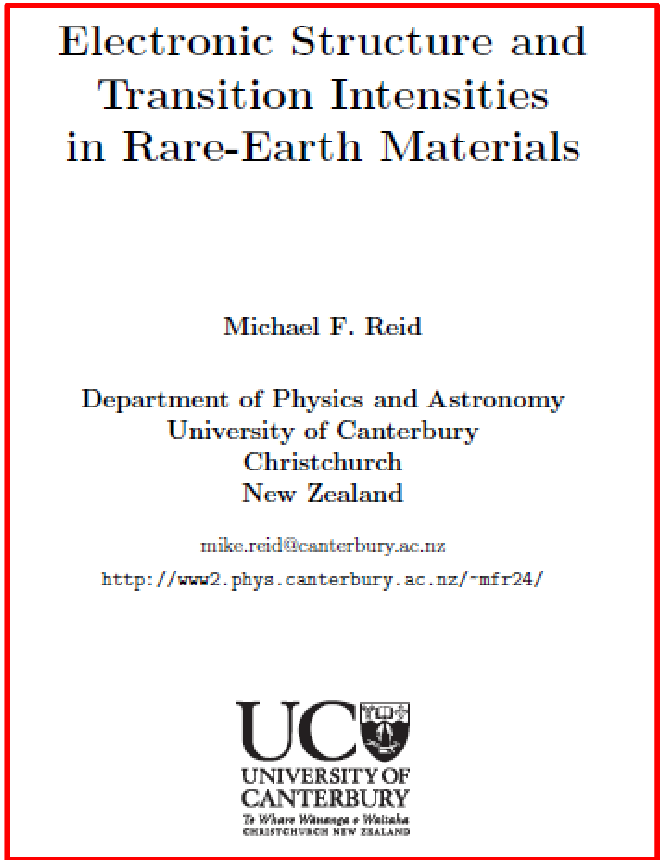


How do we proceed?

- Ab-initio (first principles) calculations
  - Well established in atoms
  - Hartree-Fock + perturbations
  - Now viable for lanthanide complexes but slow
- Effective Hamiltonians (“crystal field”)
  - Requires parameter fitting
  - Relatively quick and easy, allowing rapid interpretation of spectra.
  - Can be related to ab-initio calculations.

Tutorial

- Mike Reid, Personal Home Page
- http://www2.phys.canterbury.ac.nz/~mfr24/
- Electronic Structure Calculations Handout.
- Tutorial Presentation (Asia, January 2018).



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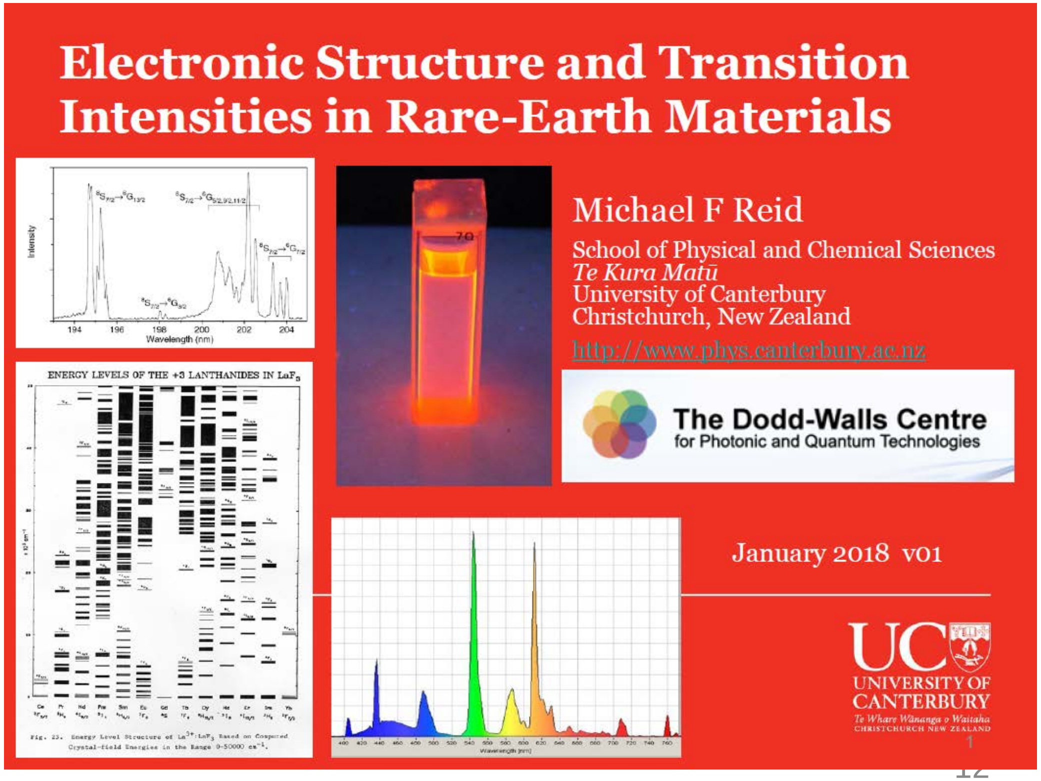

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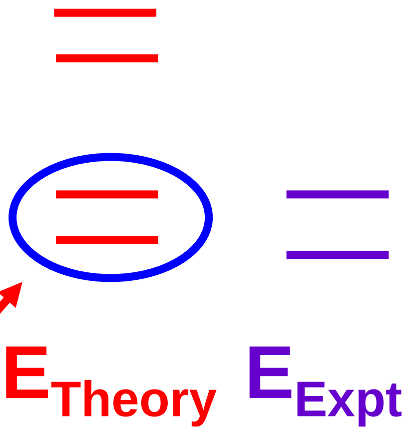
Effective Hamiltonian Calculations

- $H \; |\Psi_i\rangle = E_i \, |\Psi_i\rangle$ (H is Hamiltonian)
- $H_{eff} \, |\phi_i\rangle = E_i \; |\phi_i\rangle$ (H_{eff} is Effective Hamiltonian)

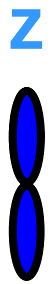


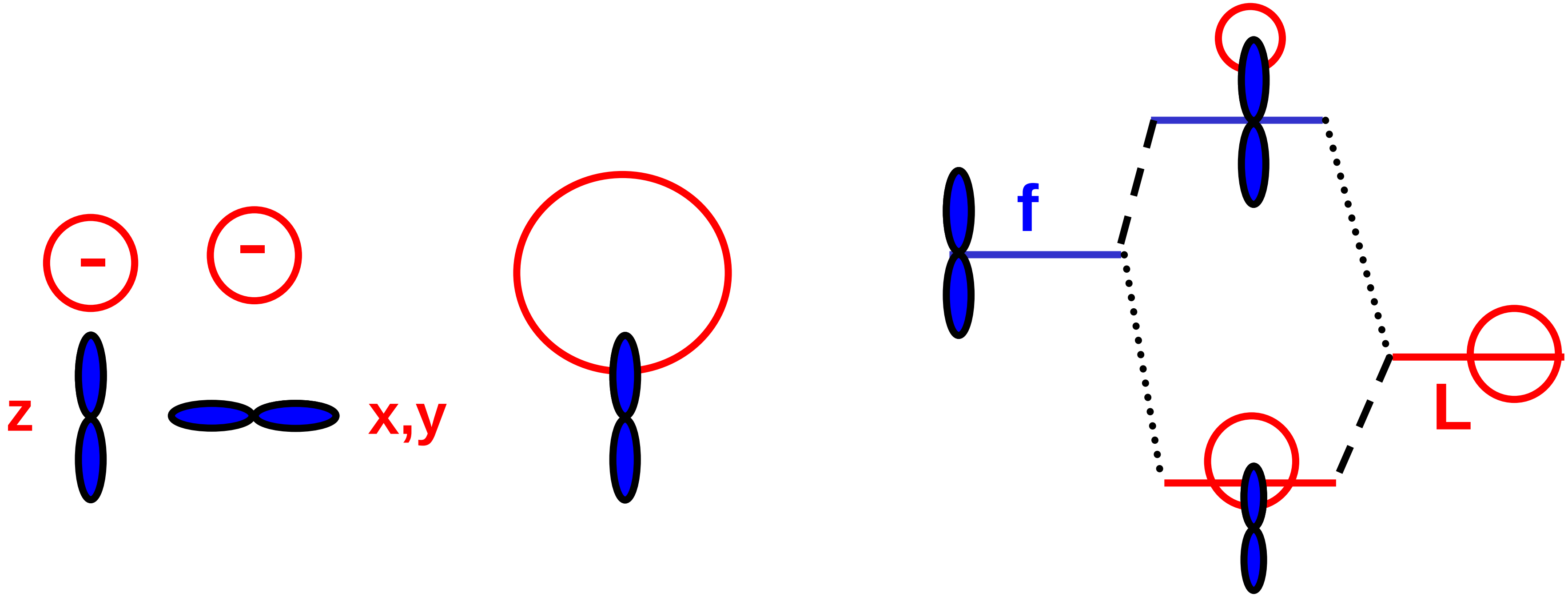
$$\left(H \right) \rightarrow \left(H_{eff} \right)$$

$$\left(H_{eff} \right) \rightarrow \sum_\alpha P_\alpha \left(M_\alpha \right)$$

"Crystal Field"

$$\left(\sum_{k,q} B_q^k C_q^{(k)} \right)$$



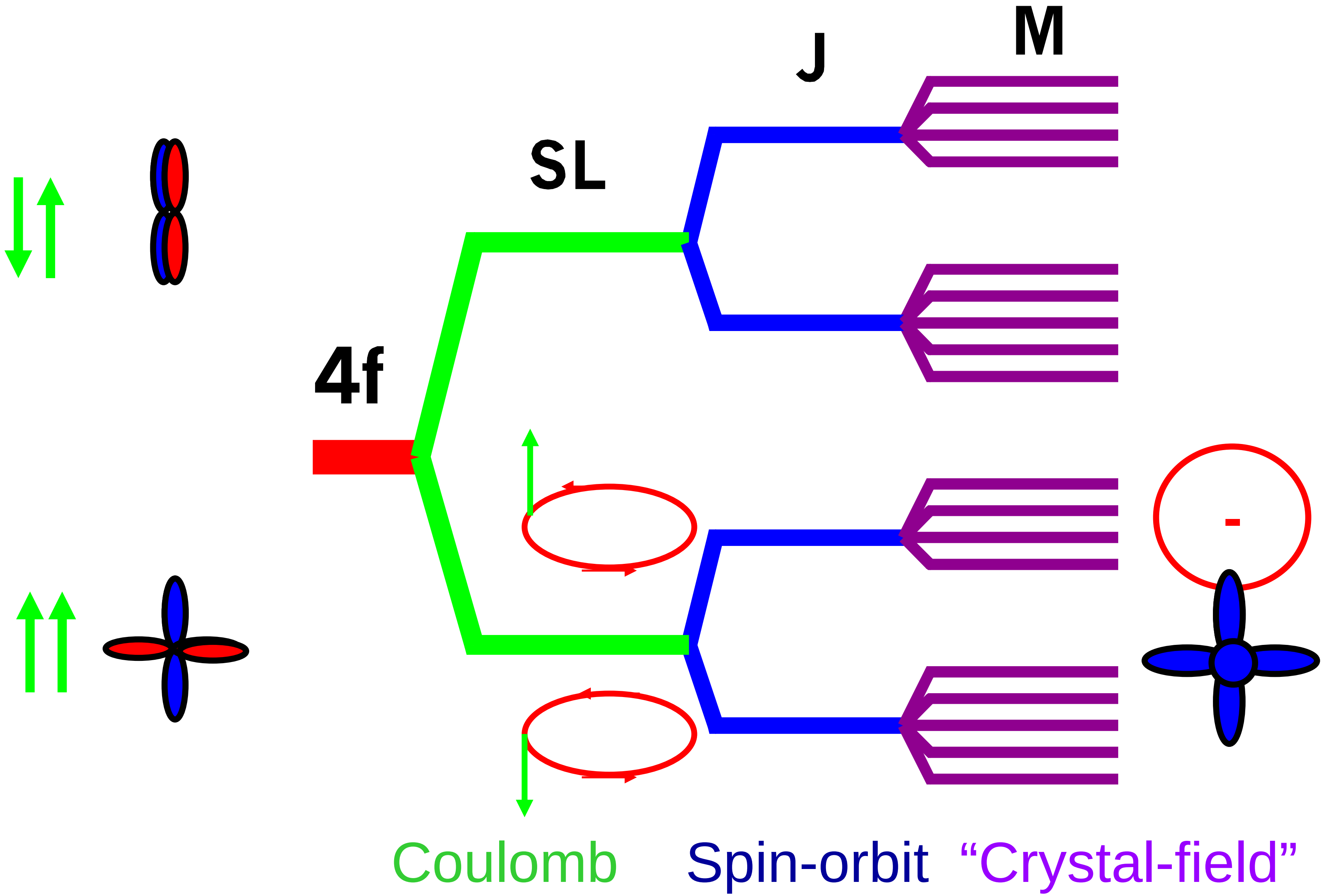


Electrostatic Overlap Covalency

All increase energy of z orbital more than x,y

Orbital energies ↔ crystal-field parameters

Understanding the energy levels: $4f^N$



Effective Hamiltonian for 4f^N

$$H=E_{avg}+\sum_{k=2,4,6}F^k f_k+\zeta_f A_{so}+\sum_{k,q}B_q^k C_q^{(k)}$$

Coulomb **Spin-Orbit** **Crystal Field**

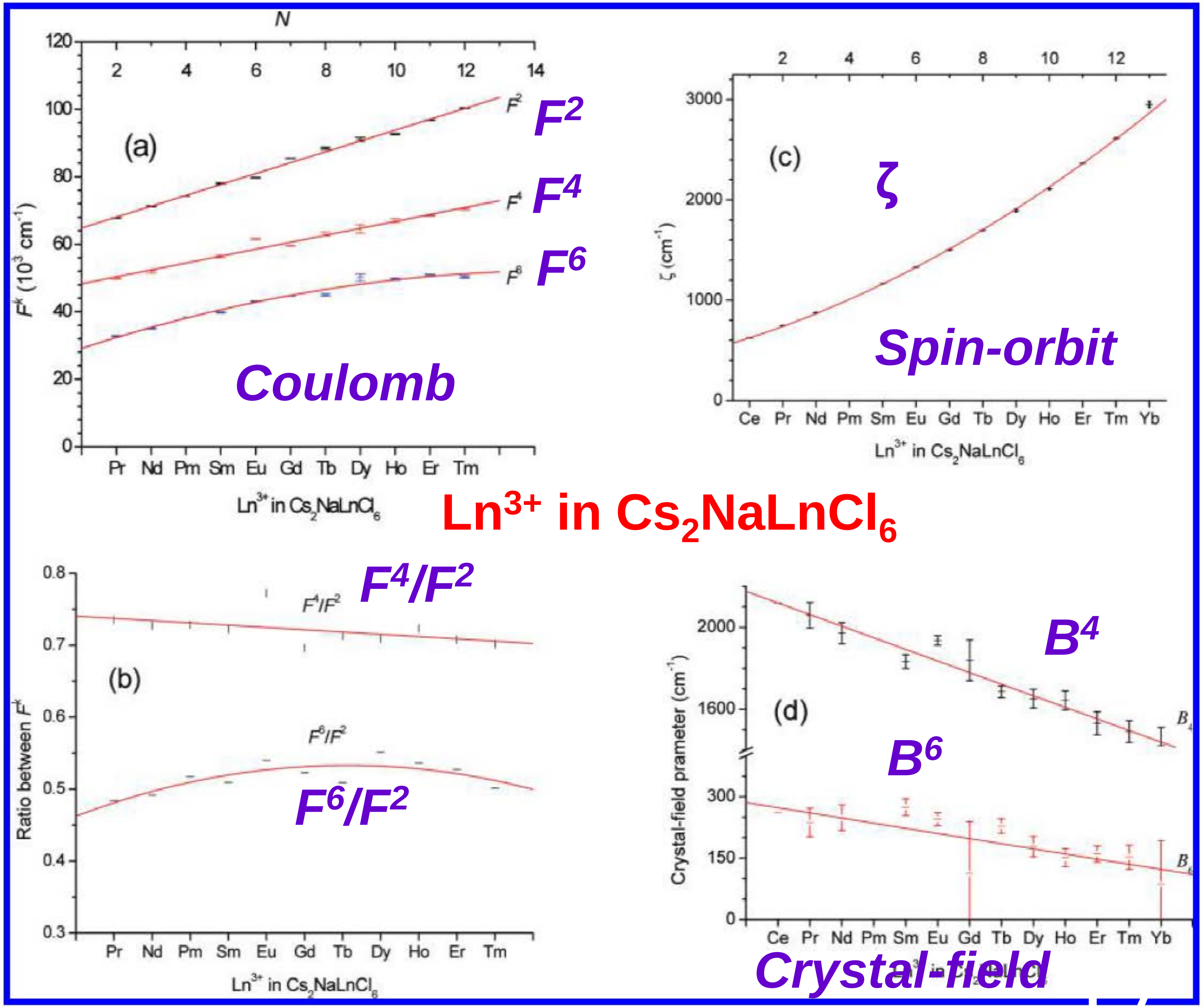
Correlation and other corrections

$$+\alpha L(L+1)+\beta G(G_2)+\gamma G(R_7)+\sum_{i=2,3,4,6,7,8}T^i t_i$$

$$+\sum_{h=0,2,4}M^h m_h+\sum_{k=2,4,6}P^k p_k$$

Parameter trends across the lanthanide series.

C-K Duan and P A Tanner, J. Phys. Chem. A, **2010**, 114, pp 6055–6062



F^2

F^4

F^6

Coulomb

ζ

Spin-orbit

Ln^{3+} in $Cs_2NaLnCl_6$

F^4/F^2

F^6/F^2

B^4

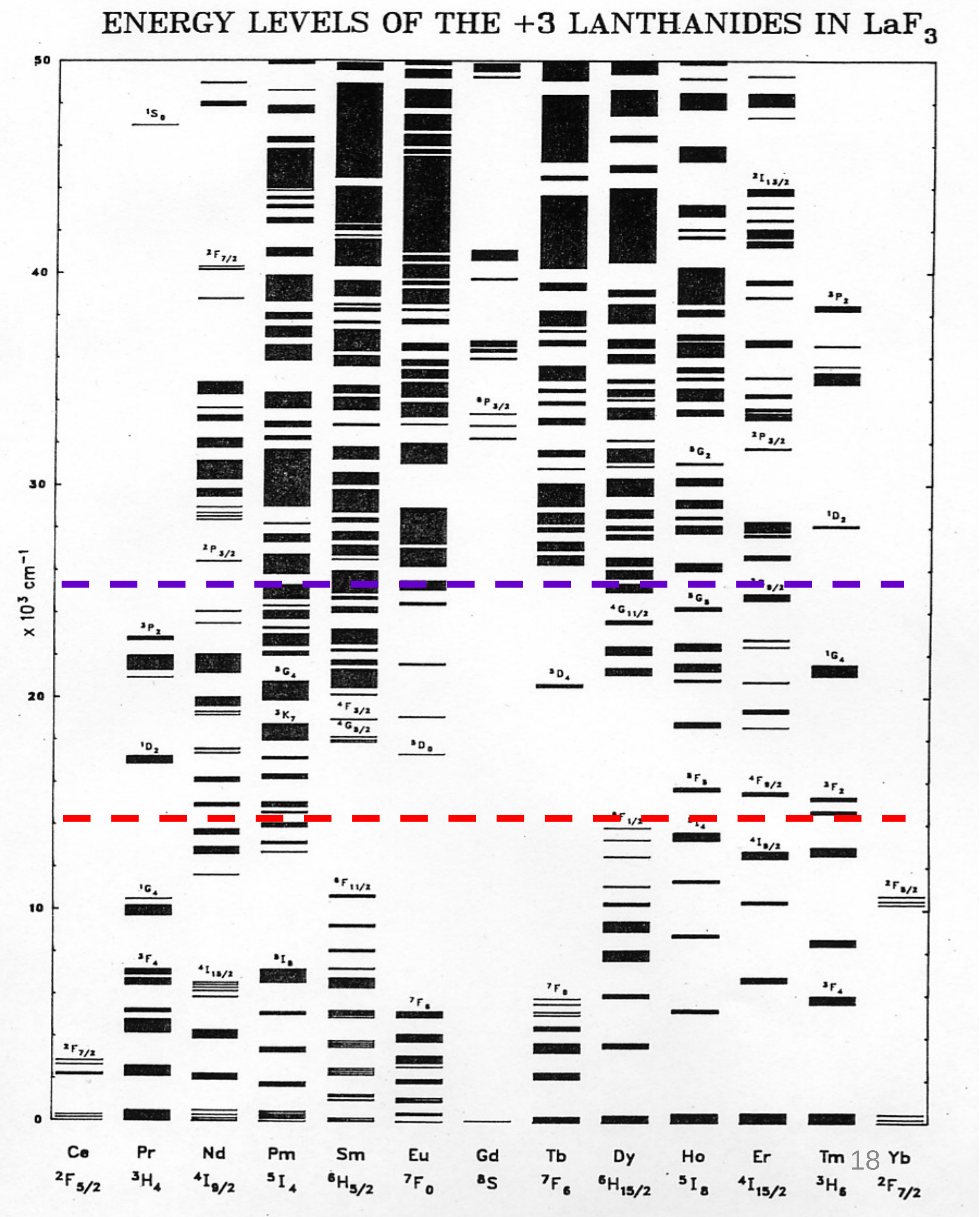
B^6

Crystal-field

“Dieke Diagram”
1960s

Carnall, Goodman, Rajnak, Rana, **1988**

20,000 cm^{-1}
500 nm
2.5 eV



Calulating Matrix elements

- Wigner-Eckart Theorem

$$\langle \alpha J M | T_q^{(k)} | \alpha' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \alpha J || T^{(k)} || \alpha' J' \rangle$$

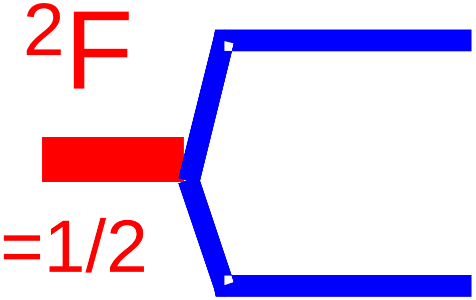
matrix element

"geometrical" factors
3j symbol or
Clebsh-Gordan Coeffieient

"reduced"
matrix element

- Selection Rules
  - M'+q = M
  - J k J' form a triangle: |J-J'| ≤ k ≤ J+J'
- |SLJM> states
  - More complex versions of WET.
  - Triangle rules for S S' L L' J J' and operator labels.

Ce^{3+}: $4f^1\ 5d^1$



^2F

S=1/2

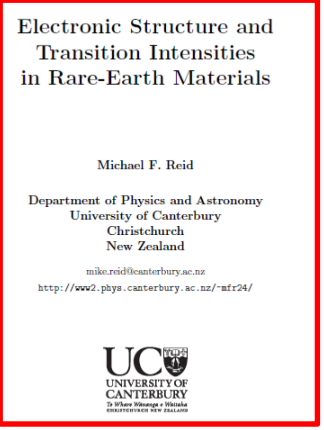
L=3

J=7/2 $E_{avg} + 1.5\,\zeta = 2253\ cm^{-1}$

J=5/2 $E_{avg} - 2.0\,\zeta = \quad 0\ cm^{-1}$

Free-ion splitting is 2253 cm^{-1} so $\zeta = 644\ cm^{-1}$

Similarly for $5d^1$



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Chapter 3

Energy level examples

3.1.2 Atomic (free-ion) energies

The atomic energies for Ce^{3+} (Ce IV in Atomic Spectroscopy Notation) are available at NIST (`http://physics.nist.gov`) and [20]. The energies are given in Table 3.1.

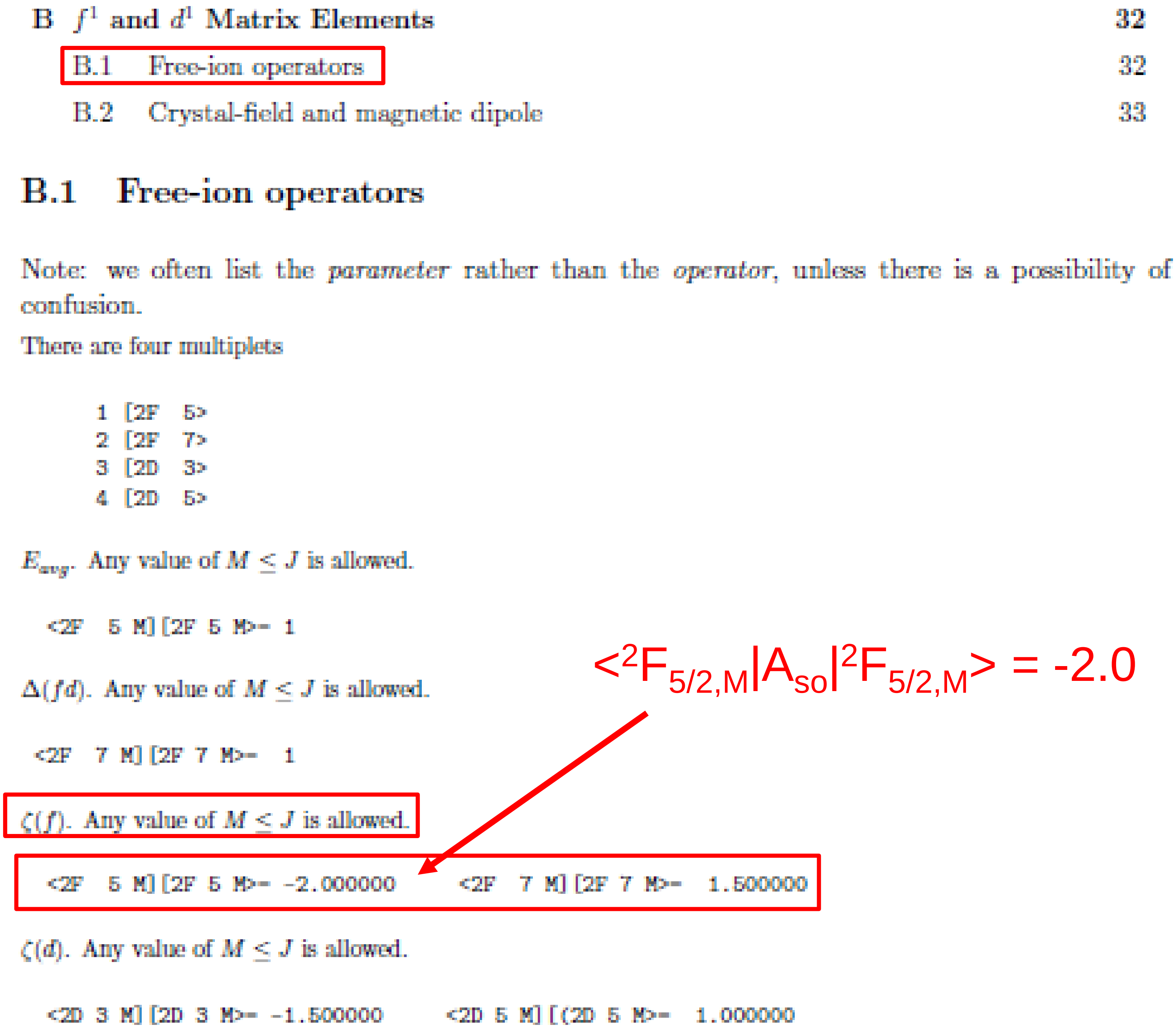
Use the matrix elements of the `ZETAFF` and `ZETADD` operators to work out the ζ_f and ζ_d parameters and the difference between the average energies of the two configurations.

Partial solution

From Section B.1 the matrix elements of the spin-orbit interaction for ${}^2F_{5/2}$ and ${}^2F_{7/2}$ are -2 and $+1.5$ respectively, so the splitting of 2253 cm^{-1} is $3.5\zeta_f$ and therefore $\zeta_f = 644\ \mathrm{cm}^{-1}$.

Table 3.1: Energies for $4f^1 + 5d^1$ configurations of gaseous Ce^{3+}.

Multiplet	Energy (cm^{-1})
${}^2F_{5/2}$	0
${}^2F_{7/2}$	2253
${}^2D_{3/2}$	49737
${}^2D_{5/2}$	52226



B.1 Free-ion operators

Note: we often list the *parameter* rather than the *operator*, unless there is a possibility of confusion.

There are four multiplets

```
1 [2F  5>
2 [2F  7>
3 [2D  3>
4 [2D  5>
```

E_{avg}. Any value of $M \le J$ is allowed.

```
<2F  5 M][2F 5 M>= 1
```

$\Delta(fd)$. Any value of $M \le J$ is allowed.

```
<2F  7 M][2F 7 M>=  1
```

$\zeta(f)$. Any value of $M \le J$ is allowed.

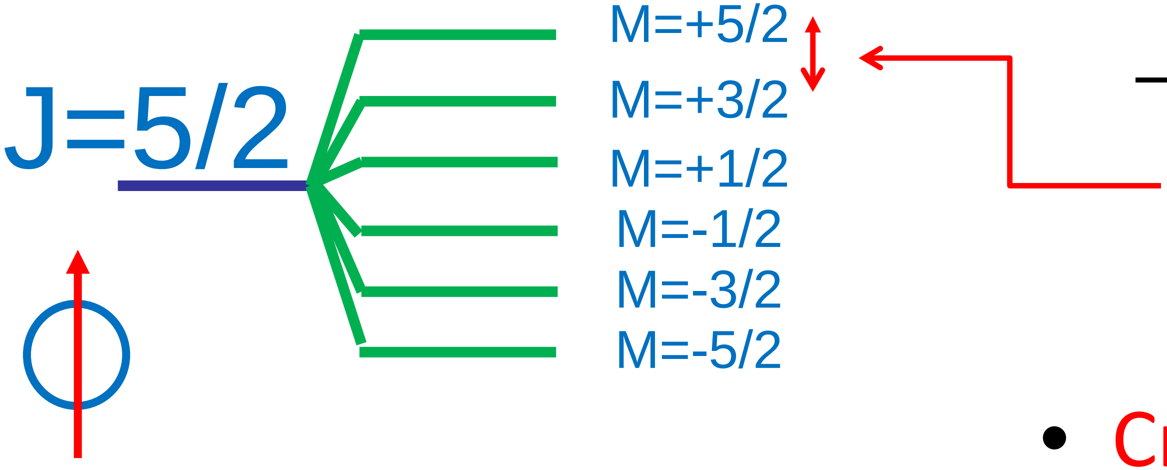
```
<2F  5 M][2F 5 M>= -2.000000     <2F  7 M][2F 7 M>=  1.500000
```

$<{}^2F_{5/2,M}|A_{so}|{}^2F_{5/2,M}> = -2.0$

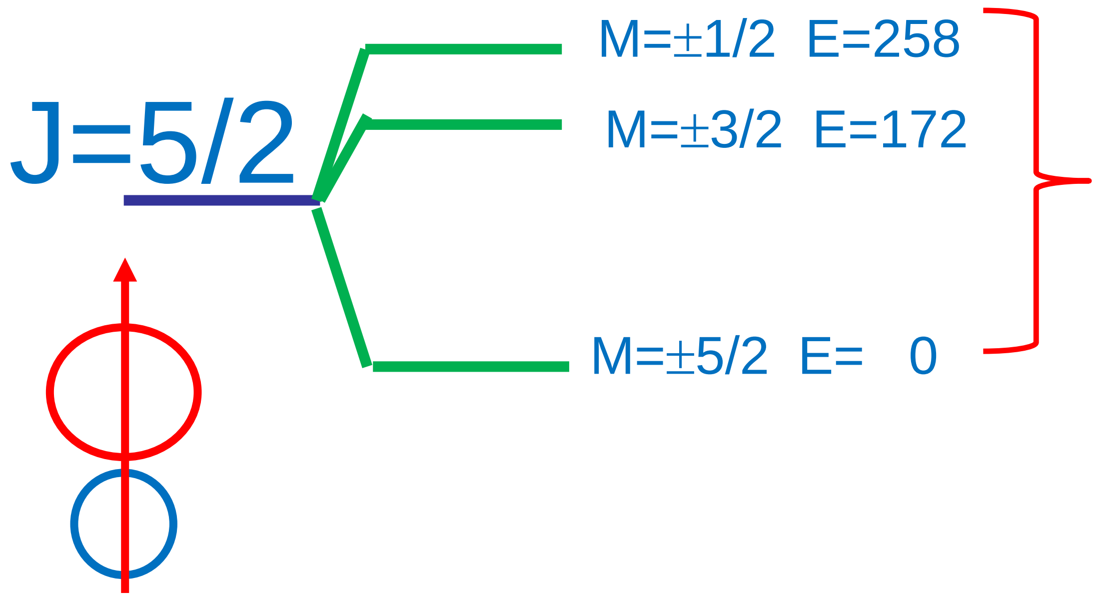
$\zeta(d)$. Any value of $M \le J$ is allowed.

```
<2D 3 M][2D 3 M>= -1.500000     <2D 5 M][(2D 5 M>=  1.000000
```

Splitting of J=5/2 multiplet



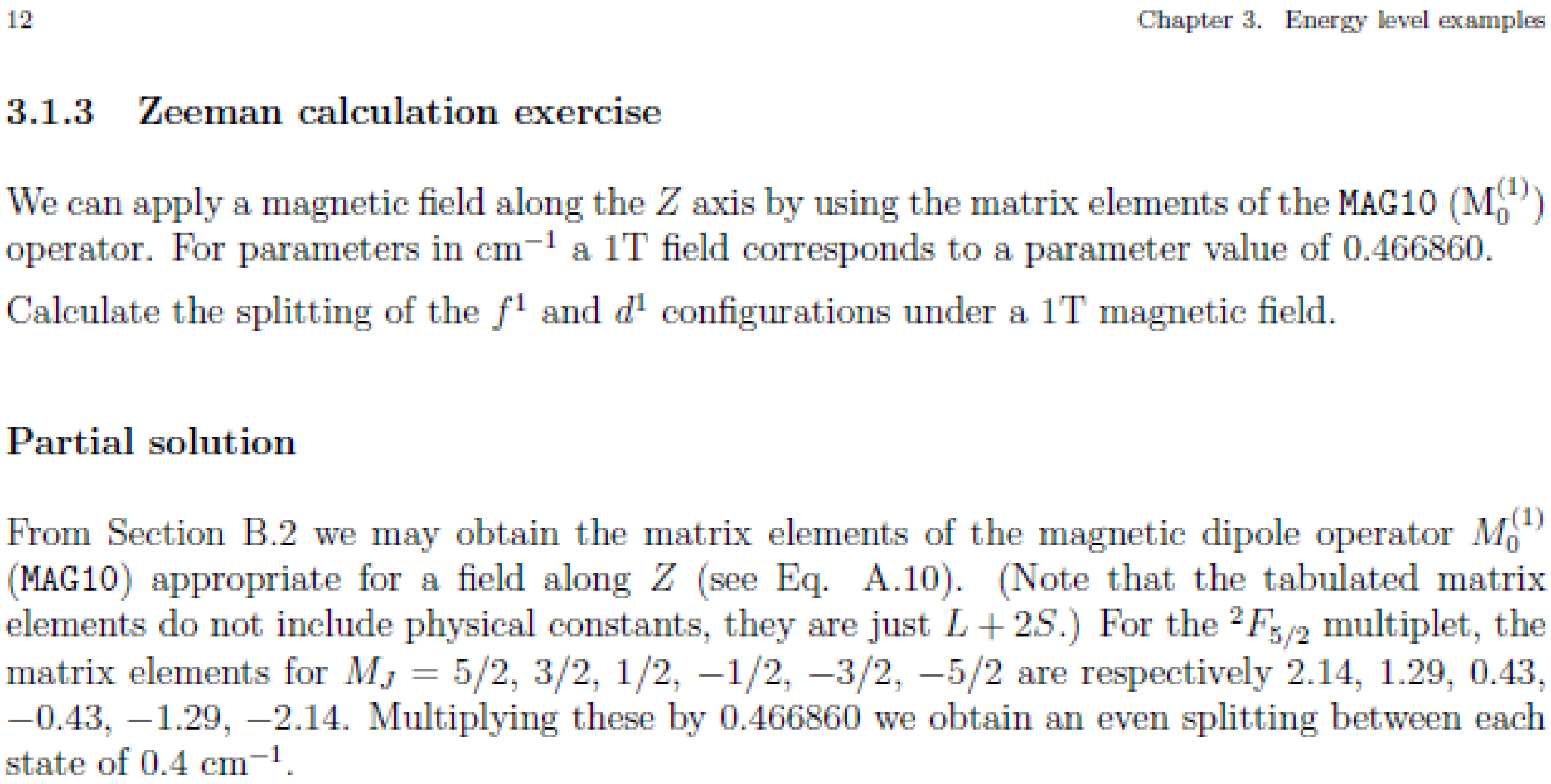
- Magnetic field
  - Even spacing:
    - 0.4 cm^{-1} for 1T field



- Crystal Field

$$H_{\mathrm{cf}} = \sum_{k,q} B^k_q C^{(k)}_q$$

  - Uneven spacing
  - Example:
    - $B^2{}_0 = 500\ \mathrm{cm}^{-1}$
  - More complex cases mix up M labels.


12 Chapter 3. Energy level examples

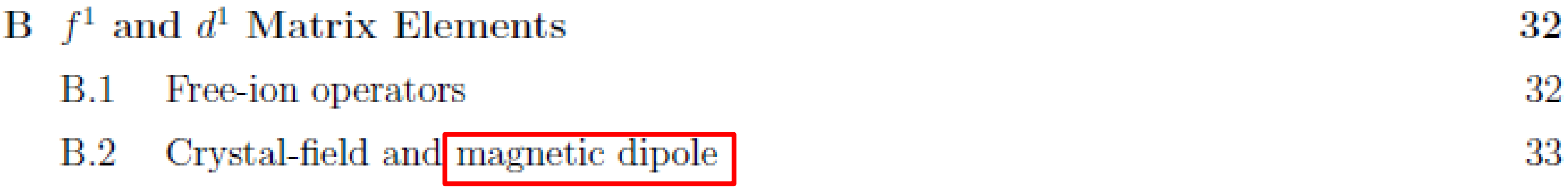
3.1.3 Zeeman calculation exercise

We can apply a magnetic field along the Z axis by using the matrix elements of the `MAG10` ($\mathrm{M}_0^{(1)}$) operator. For parameters in cm^{-1} a 1T field corresponds to a parameter value of 0.466860.

Calculate the splitting of the f^1 and d^1 configurations under a 1T magnetic field.

Partial solution

From Section B.2 we may obtain the matrix elements of the magnetic dipole operator $M_0^{(1)}$ (`MAG10`) appropriate for a field along Z (see Eq. A.10). (Note that the tabulated matrix elements do not include physical constants, they are just $L+2S$.) For the ${}^2F_{5/2}$ multiplet, the matrix elements for $M_J = 5/2,\ 3/2,\ 1/2,\ -1/2,\ -3/2,\ -5/2$ are respectively 2.14, 1.29, 0.43, −0.43, −1.29, −2.14. Multiplying these by 0.466860 we obtain an even splitting between each state of 0.4 cm^{-1}.



Magnetic dipole matrix elements

Note that these are matrix elements of $L_q + 2S_q$, and must be multiplied by the constants in Eq. (4.2) to obtain matrix elements of $M_q^{(1)}$.

```
MAG10   S= 0   L= 0   K= 1     Q= 0
```

```
<2F 7  7][2F 7  7>=  4.00116000   <2F 5  5][2F 5  5>=  2.14202857   <2F 5  5][2F 7  5>=  0.35073894
<2F 7  5][2F 7  5>=  2.85797143   <2D 5  5][2D 5  5>=  3.00116000   <2F 5  3][2F 5  3>=  1.28521714
<2F 5  3][2F 7  3>=  0.45280202   <2F 7  3][2F 7  3>=  1.71478286   <2D 3  3][2D 3  3>=  1.19930400
<2D 3  3][2D 5  3>=  0.40092800   <2D 5  3][2D 5  3>=  1.80069600   <2F 5  1][2F 5  1>=  0.42840571
<2F 5  1][2F 7  1>=  0.49601976   <2F 7  1][2F 7  1>=  0.57159429   <2D 3  1][2D 3  1>=  0.39976800


<2D 3  1][2D 5  1>=  0.49103451   <2D 5  1][2D 5  1>=  0.60023200   <2F 5 -1][2F 5 -1>= -0.42840571
<2F 5 -1][2F 7 -1>=  0.49601976   <2F 7 -1][2F 7 -1>= -0.57159429   <2D 3 -1][2D 3 -1>= -0.39976800
<2D 3 -1][2D 5 -1>=  0.49103451   <2D 5 -1][2D 5 -1>= -0.60023200   <2F 5 -3][2F 5 -3>= -1.28521714
<2F 5 -3][2F 7 -3>=  0.45280202   <2F 7 -3][2F 7 -3>= -1.71478286   <2D 3 -3][2D 3 -3>= -1.19930400
<2D 3 -3][2D 5 -3>=  0.40092800   <2D 5 -3][2D 5 -3>= -1.80069600   <2F 5 -5][2F 5 -5>= -2.14202857
<2F 5 -5][2F 7 -5>=  0.35073894   <2F 7 -5][2F 7 -5>= -2.85797143   <2D 5 -5][2D 5 -5>= -3.00116000
<2F 7 -7][2F 7 -7>= -4.00116000
```

$$C_0^{(1)} = z/r$$

$$C_{\pm1}^{(1)} = \mp\sqrt{\frac{1}{2}}(x \pm iy)/r$$

Splitting:

$(2.142 - 1.285) * 0.46680 = 0.4\ \mathrm{cm}^{-1}$

3.2.1 Axial crystal-field exercise

1. Use the spin-orbit parameters calculated above and add a crystal-field with $B_0^4(f) = 500\text{cm}^{-1}$ for the $4f^1$ configuration and $B_0^4(d) = 20000\text{cm}^{-1}$ for the $5d^1$ configuration.

2. Use the spin-orbit parameters calculated above and add a crystal-field with $B_0^2(f) = 500\text{cm}^{-1}$ for the $4f^1$ configuration and $B_0^2(d) = 20000\text{cm}^{-1}$ for the $5d^1$ configuration.

Partial solution

The matrix elements of $C_0^{(2)}$ are diagonal in M. For the $J = 5/2$ multiplet the matrix elements are:

$$0.2286, \qquad 0.0571, \qquad -0.2857$$

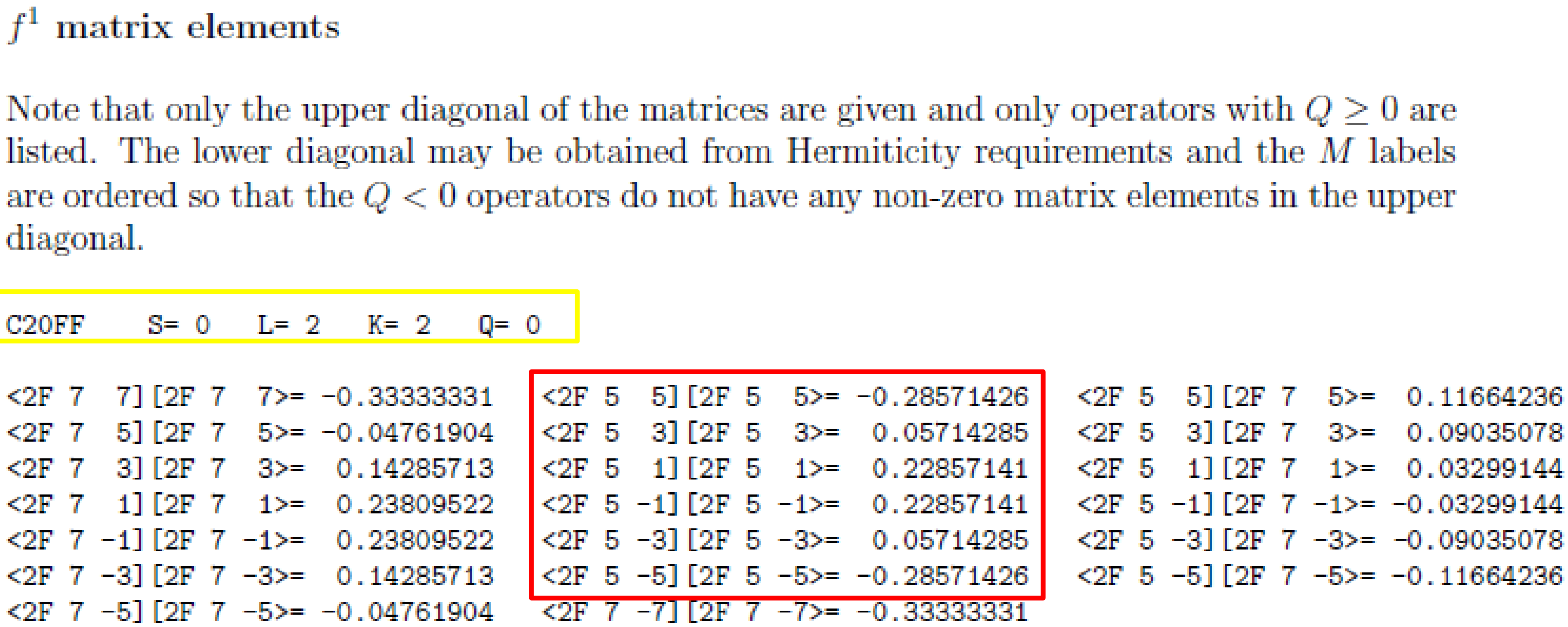
for

$$M = \pm 1/2, \qquad \pm 3/2, \qquad \pm 5/2,$$

repectively. Multiplying by $B_0^2(f) = 500\text{cm}^{-1}$ and setting the lowest energy to zero gives:

$$257, \qquad 171, \qquad 0\ \text{cm}^{-1}.$$

Note that these axial fields do not give an even splitting of the multiplets (in contrast to a magnetic field). The $B_0^{(2)}$ parameters represent a quadrupolar potential, as opposed to the magnetic dipole.



f^1 matrix elements

Note that only the upper diagonal of the matrices are given and only operators with $Q \geq 0$ are listed. The lower diagonal may be obtained from Hermiticity requirements and the M labels are ordered so that the $Q < 0$ operators do not have any non-zero matrix elements in the upper diagonal.

```
C20FF     S= 0    L= 2    K= 2    Q= 0

<2F 7  7][2F 7  7>= -0.33333331   <2F 5  5][2F 5  5>= -0.28571426   <2F 5  5][2F 7  5>=  0.11664236
<2F 7  5][2F 7  5>= -0.04761904   <2F 5  3][2F 5  3>=  0.05714285   <2F 5  3][2F 7  3>=  0.09035078
<2F 7  3][2F 7  3>=  0.14285713   <2F 5  1][2F 5  1>=  0.22857141   <2F 5  1][2F 7  1>=  0.03299144
<2F 7  1][2F 7  1>=  0.23809522   <2F 5 -1][2F 5 -1>=  0.22857141   <2F 5 -1][2F 7 -1>= -0.03299144
<2F 7 -1][2F 7 -1>=  0.23809522   <2F 5 -3][2F 5 -3>=  0.05714285   <2F 5 -3][2F 7 -3>= -0.09035078
<2F 7 -3][2F 7 -3>=  0.14285713   <2F 5 -5][2F 5 -5>= -0.28571426   <2F 5 -5][2F 7 -5>= -0.11664236
<2F 7 -5][2F 7 -5>= -0.04761904   <2F 7 -7][2F 7 -7>= -0.33333331
```

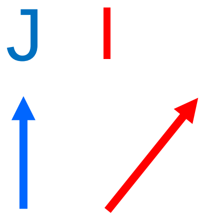
$$C_0^{(2)} = \sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2$$

$$C_{\pm 1}^{(2)} = \mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2$$

$$C_{\pm 2}^{(2)} = \sqrt{\frac{3}{8}}(x \pm iy)^2/r^2.$$

±1/2	0.229*500 =	114	257
±3/2	0.057*500 =	29	171
±5/2	-0.285*500 =	-143	0

Hyperfine Interactions



$$H_{\mathrm{MD}} = A_{\|} J_z I_z + A_{\perp}(J_x I_x + J_y I_y)$$

$$H_{\mathrm{MD}} = A_{\|} J_0^{(1)} I_0 + A_{\perp}(-J_{+1}^{(1)} I_{-1}^{(1)} - J_{-1}^{(1)} I_{+1}^{(1)})$$

Or, in terms of ladder operators:

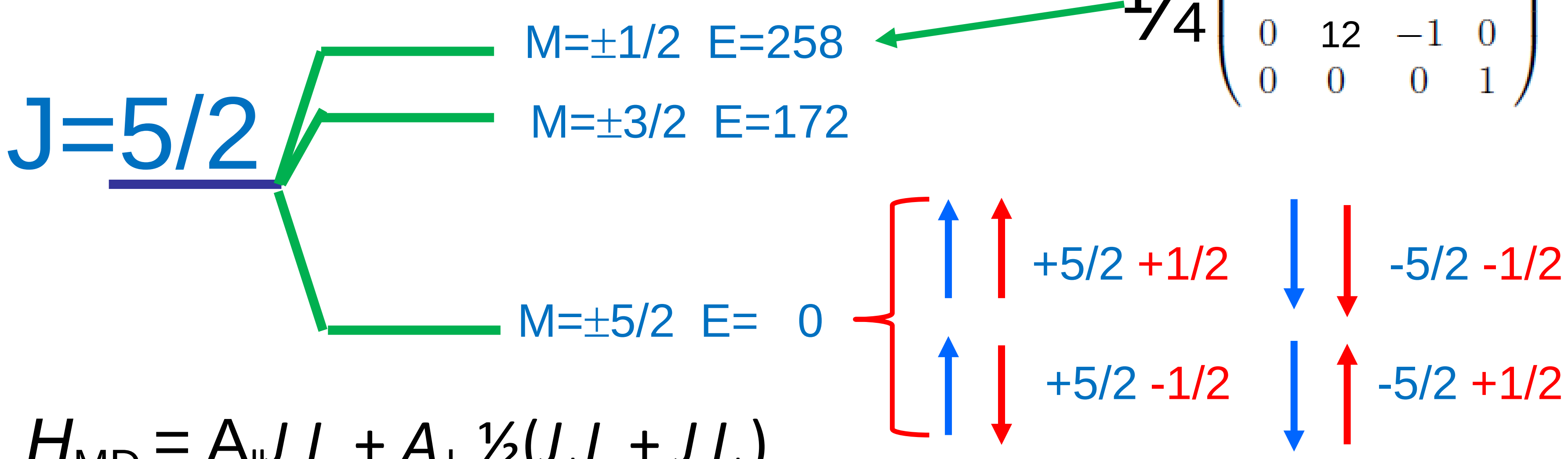
$$H_{\mathrm{MD}} = A_{\|} J_z I_z + A_{\perp}\, ½(J_+ I_- + J_- I_+)$$

Write in terms of tensor operators (see Wiessbluth, etc):

$$H_{\mathrm{MD}} = 2\beta\left[\frac{\boldsymbol{\mu}\cdot(\mathbf{L}-\mathbf{S})}{r^3} + \frac{(\boldsymbol{\mu}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})}{r^5} + \frac{8\pi}{3}\delta(\mathbf{r})\boldsymbol{\mu}\cdot\mathbf{S}\right]$$

Ce^{3+} Example with (fictitious) I=1/2

(this is relevant for Yb^{3+})



$$\tfrac{1}{4}\begin{pmatrix}1&0&0&0\\0&-1&12&0\\0&12&-1&0\\0&0&0&1\end{pmatrix}$$

J=5/2

M=±1/2 E=258

M=±3/2 E=172

M=±5/2 E= 0

+5/2 +1/2

-5/2 -1/2

+5/2 -1/2

-5/2 +1/2

$$H_{MD} = A_{\|} J_z I_z + A_{\perp}\, \tfrac{1}{2}(J_+ I_- + J_- I_+)$$

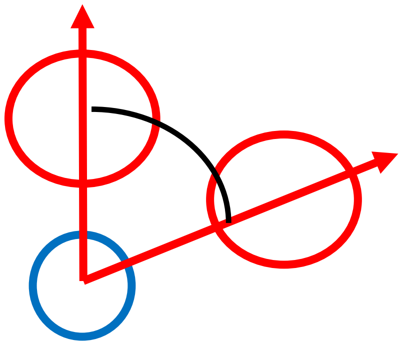
J_z |5/2 ±1/2> = ±1/2|5/2 ±1/2>,

J_+ |5/2 -1/2> = +3|5/2 +1/2>, J_- |5/2 +1/2> = +3|5/2 -1/2>.

I_z |1/2 ±1/2> = ±1/2|1/2 ±1/2>,

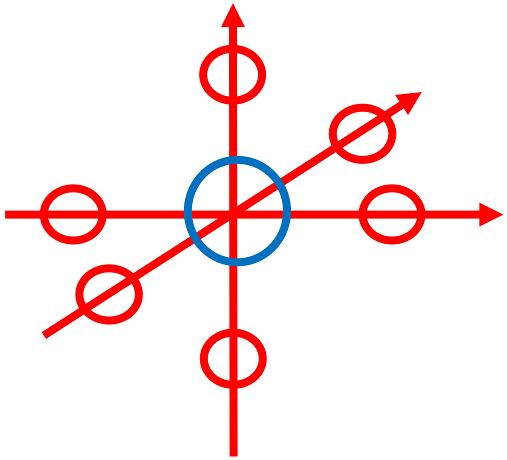
I_+ |1/2 -1/2> = +1|1/2 +1/2>, I_- |1/2 +1/2> = +1|1/2 -1/2>.

Superposition Model



$$B_q^k = \sum_L \bar{B}_k(R_0)(-1)^q C_{-q}^{(k)}(\theta_L, \phi_L) \left(\frac{R_0}{R_L}\right)^{t_k}$$

$$C_0^{(2)}(x,y,z) \quad = \quad \frac{1}{r^2}\sqrt{\frac{1}{4}}(3z^2 - r^2)$$



3.4 Superposition-model exercise

Cubic sites in $\mathrm{CaF_2}$ have 8 equidistant ligands on the corners of a cube. Use the superposition model (Eq. 2.10) to show that the B^4 parameter in Eq. (3.2) should be *negative* in this case and that the B_0^2 parameters are zero.

Now consider the case of a six-fold octahedral coordination, with the ligands on the X, Y, and Z axes. Show that in this case B^4 should be *positive.*

Recall that in Cartesian form we have (Weissbluth [4] Table 1.1):

$$C_0^{(2)}(x,y,z) = \frac{1}{r^2}\sqrt{\frac{1}{4}}(3z^2 - r^2), \tag{3.4}$$

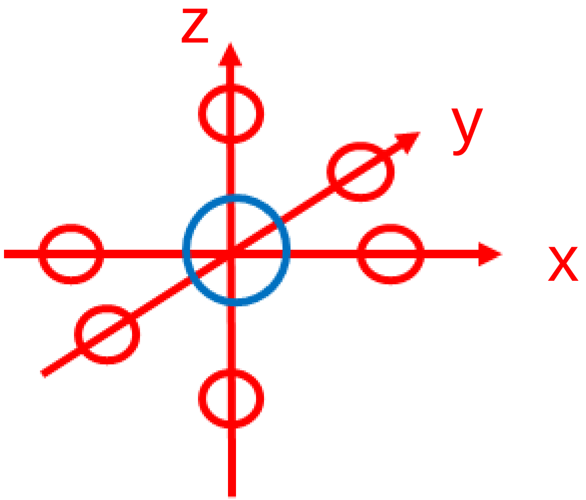
$$C_0^{(4)}(x,y,z) = \frac{1}{r^4}\sqrt{\frac{1}{64}}(35z^4 - 30z^2r^2 + 3r^4), \tag{3.5}$$

$$C_{\pm 4}^{(4)}(x,y,z) = \frac{1}{r^4}\sqrt{\frac{35}{128}}(x \pm iy)^4. \tag{3.6}$$

$$B_q^k = \sum_L \bar{B}_k(R_0)(-1)^q C_{-q}^{(k)}(\theta_L, \phi_L)\left(\frac{R_0}{R_L}\right)^{t_k} . \tag{2.10}$$

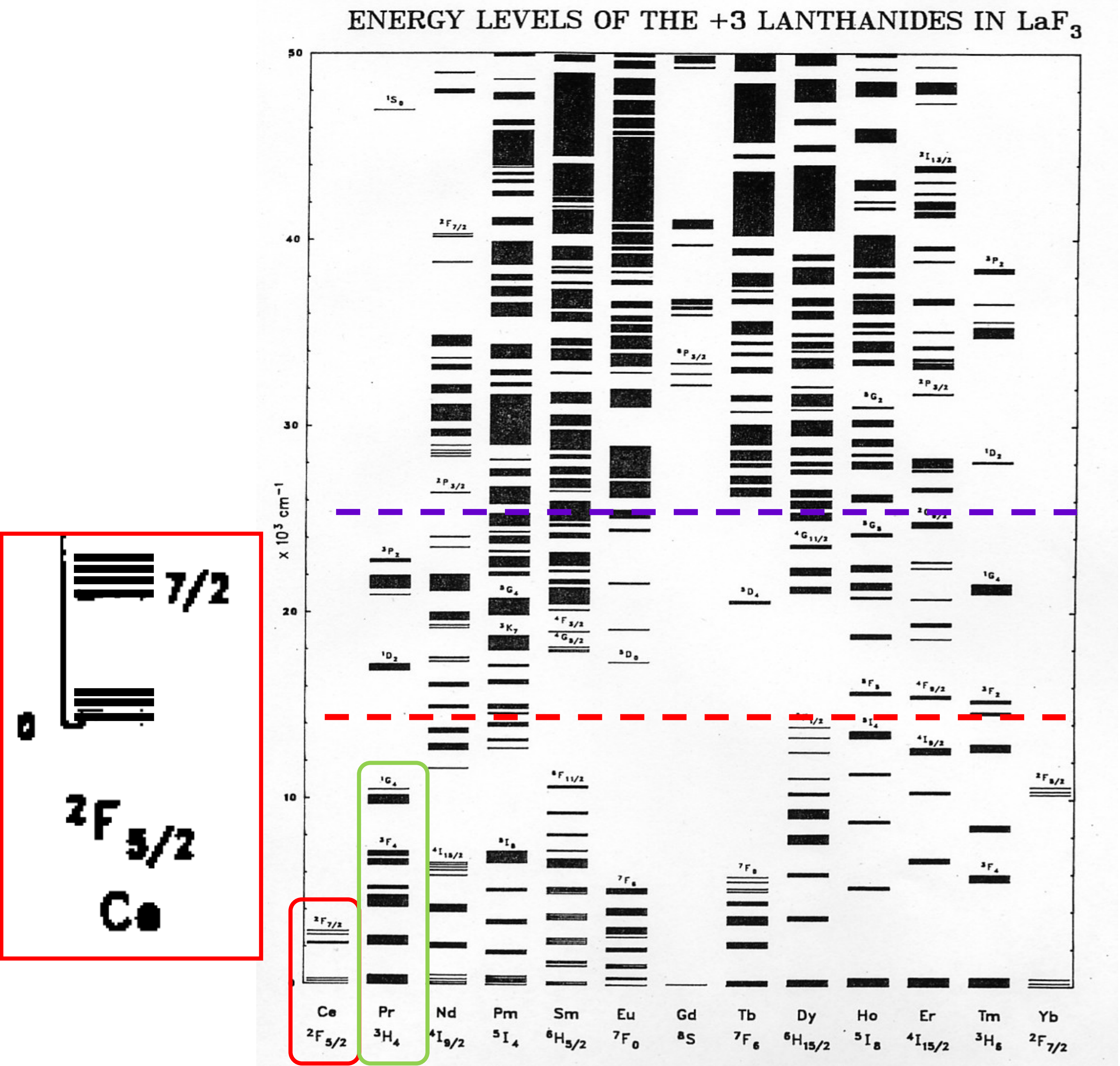
$$H_{\mathrm{CF}}(d) = B^4\left[C_0^{(4)} + \sqrt{\frac{5}{14}}\left(C_4^{(4)} + C_{-4}^{(4)}\right)\right] . \tag{3.2}$$

$$C_0^{(2)}(x,y,z) = \frac{1}{r^2}\sqrt{\frac{1}{4}}(3z^2 - r^2)$$



x: $3*0^2 - 1^2 = -1$
y: $3*0^2 - 1^2 = -1$
z: $3*1^2 - 1^2 = +2$

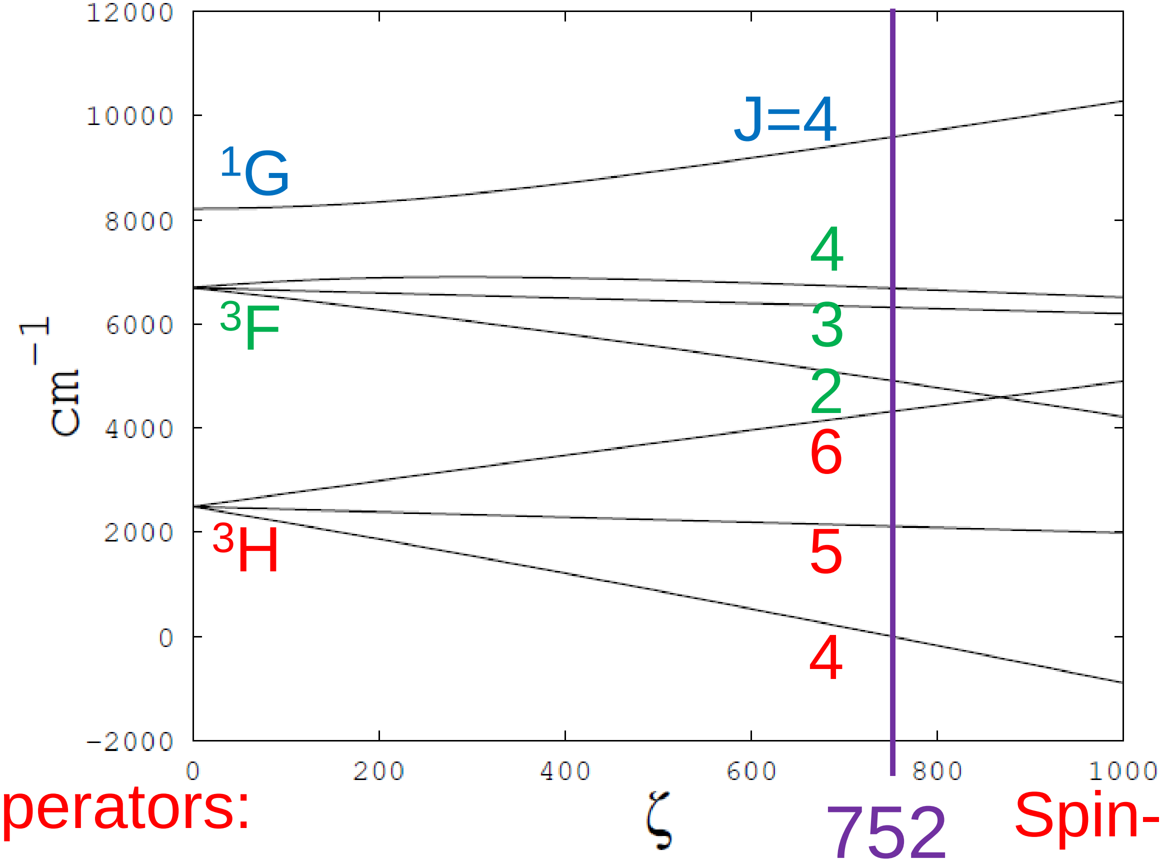
Sum = 0.



ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF_3

Pr^{3+} : $4f^2$ Coulomb + Spin-orbit

$$
\begin{aligned}
E(^3H_J) &= -0.0906F^2 - 0.0328F^4 + 0.0162F^6 = -7359\ \mathrm{cm}^{-1}, \\
E(^3F_J) &= -0.0239F^2 - 0.0163F^4 - 0.0209F^6 = -3155\ \mathrm{cm}^{-1}, \\
E(^1G_4) &= -0.1128F^2 + 0.1031F^4 + 0.0285F^6 = -1641\ \mathrm{cm}^{-1}.
\end{aligned}
$$



Coulomb operators:
S=0, L=0, J=0

Spin-orbit operator:
S=1, L=1, J=0

3.5.2 Pr^{3+}

Pr^{3+} has a $4f^2$ configuration.

1. First calculate the energies using these parameters:

$$F^2 = 68878, \qquad F^4 = 50347, \qquad F^6 = 32901. \tag{3.8}$$

2. Now use perturbation theory to add

$$\zeta = 751.7. \tag{3.9}$$

3. Now diagonalize the matrices explicitly.

Check your calculations against published energy levels, e.g. the Dieke-Carnall diagram, Fig. 2.1.

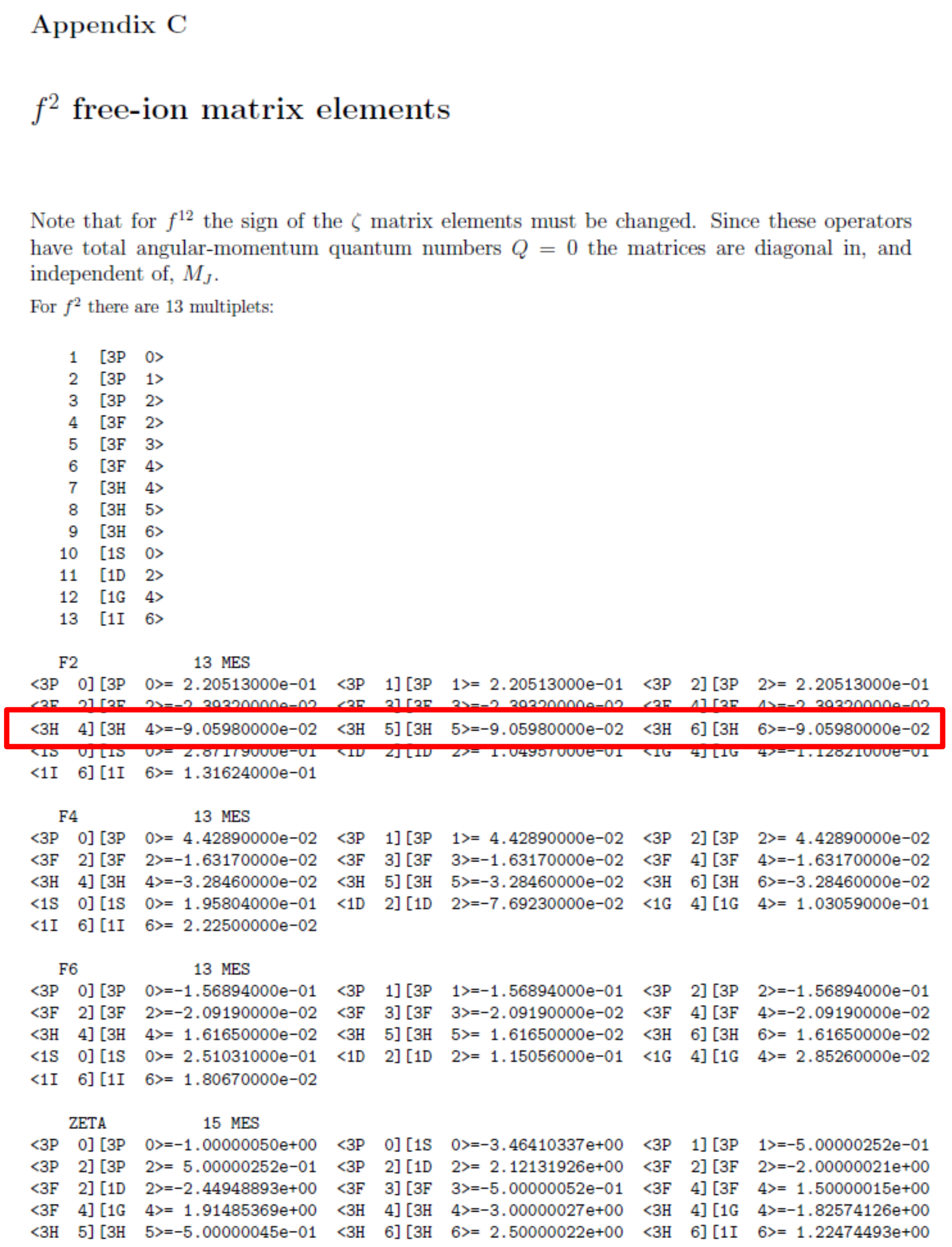
Partial solution

If we ignore the spin-orbit interaction, all states with the same S and L have the same energy. The lowest three are:

$$\boxed{E(^3H_J) = -0.0906F^2} - 0.0328F^4 + 0.0162F^6 = -7359\ \mathrm{cm}^{-1}, \tag{3.10}$$

$$E(^3F_J) = -0.0239F^2 - 0.0163F^4 - 0.0209F^6 = -3155\ \mathrm{cm}^{-1}, \tag{3.11}$$

$$E(^1G_4) = -0.1128F^2 + 0.1031F^4 + 0.0285F^6 = -1641\ \mathrm{cm}^{-1}. \tag{3.12}$$



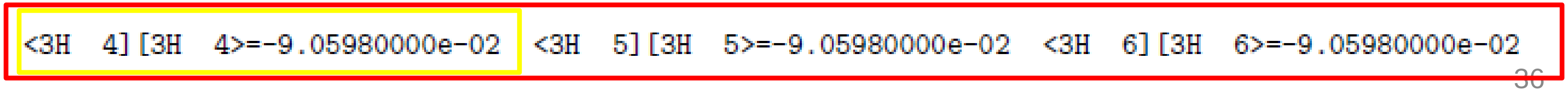
Appendix C

f^2 free-ion matrix elements

Note that for f^{12} the sign of the ζ matrix elements must be changed. Since these operators have total angular-momentum quantum numbers $Q = 0$ the matrices are diagonal in, and independent of, M_J.

For f^2 there are 13 multiplets:

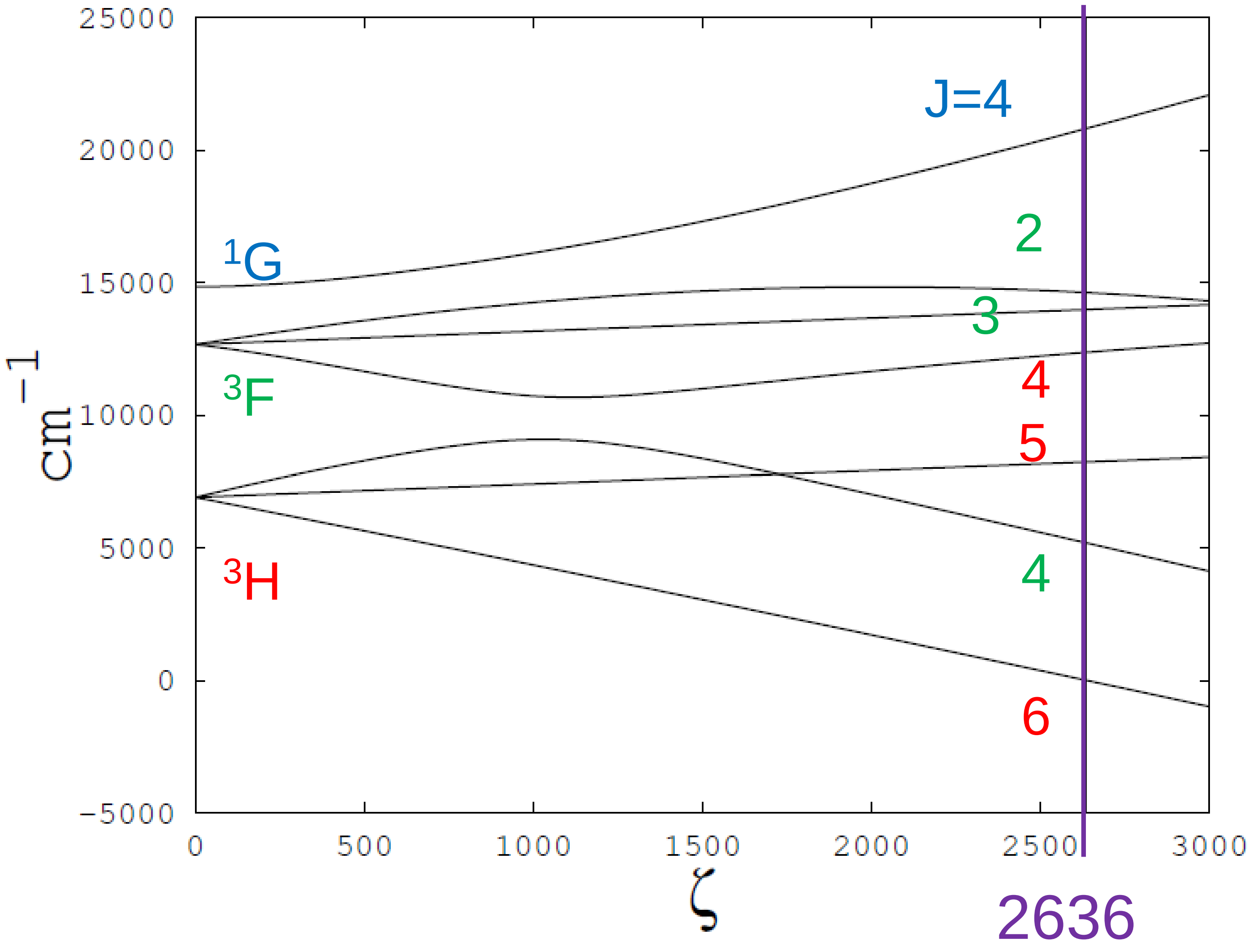
```
    1  [3P  0>
    2  [3P  1>
    3  [3P  2>
    4  [3F  2>
    5  [3F  3>
    6  [3F  4>
    7  [3H  4>
    8  [3H  5>
    9  [3H  6>
   10  [1S  0>
   11  [1D  2>
   12  [1G  4>
   13  [1I  6>

   F2            13 MES
<3P  0][3P  0>= 2.20513000e-01  <3P  1][3P  1>= 2.20513000e-01  <3P  2][3P  2>= 2.20513000e-01
<3F  2][3F  2>=-2.39320000e-02  <3F  3][3F  3>=-2.39320000e-02  <3F  4][3F  4>=-2.39320000e-02
<3H  4][3H  4>=-9.05980000e-02  <3H  5][3H  5>=-9.05980000e-02  <3H  6][3H  6>=-9.05980000e-02
<1S  0][1S  0>= 2.87179000e-01  <1D  2][1D  2>= 1.04957000e-01  <1G  4][1G  4>=-1.12821000e-01
<1I  6][1I  6>= 1.31624000e-01

   F4            13 MES
<3P  0][3P  0>= 4.42890000e-02  <3P  1][3P  1>= 4.42890000e-02  <3P  2][3P  2>= 4.42890000e-02
<3F  2][3F  2>=-1.63170000e-02  <3F  3][3F  3>=-1.63170000e-02  <3F  4][3F  4>=-1.63170000e-02
<3H  4][3H  4>=-3.28460000e-02  <3H  5][3H  5>=-3.28460000e-02  <3H  6][3H  6>=-3.28460000e-02
<1S  0][1S  0>= 1.95804000e-01  <1D  2][1D  2>=-7.69230000e-02  <1G  4][1G  4>= 1.03059000e-01
<1I  6][1I  6>= 2.22500000e-02

   F6            13 MES
<3P  0][3P  0>=-1.56894000e-01  <3P  1][3P  1>=-1.56894000e-01  <3P  2][3P  2>=-1.56894000e-01
<3F  2][3F  2>=-2.09190000e-02  <3F  3][3F  3>=-2.09190000e-02  <3F  4][3F  4>=-2.09190000e-02
<3H  4][3H  4>= 1.61650000e-02  <3H  5][3H  5>= 1.61650000e-02  <3H  6][3H  6>= 1.61650000e-02
<1S  0][1S  0>= 2.51031000e-01  <1D  2][1D  2>= 1.15056000e-01  <1G  4][1G  4>= 2.85260000e-02
<1I  6][1I  6>= 1.80670000e-02

    ZETA          15 MES
<3P  0][3P  0>=-1.00000050e+00  <3P  0][1S  0>=-3.46410337e+00  <3P  1][3P  1>=-5.00000252e-01
<3P  2][3P  2>= 5.00000252e-01  <3P  2][1D  2>= 2.12131926e+00  <3F  2][3F  2>=-2.00000021e+00
<3F  2][1D  2>=-2.44948893e+00  <3F  3][3F  3>=-5.00000052e-01  <3F  4][3F  4>= 1.50000015e+00
<3F  4][1G  4>= 1.91485369e+00  <3H  4][3H  4>=-3.00000027e+00  <3H  4][1G  4>=-1.82574126e+00
<3H  5][3H  5>=-5.00000045e-01  <3H  6][3H  6>= 2.50000022e+00  <3H  6][1I  6>= 1.22474493e+00
```



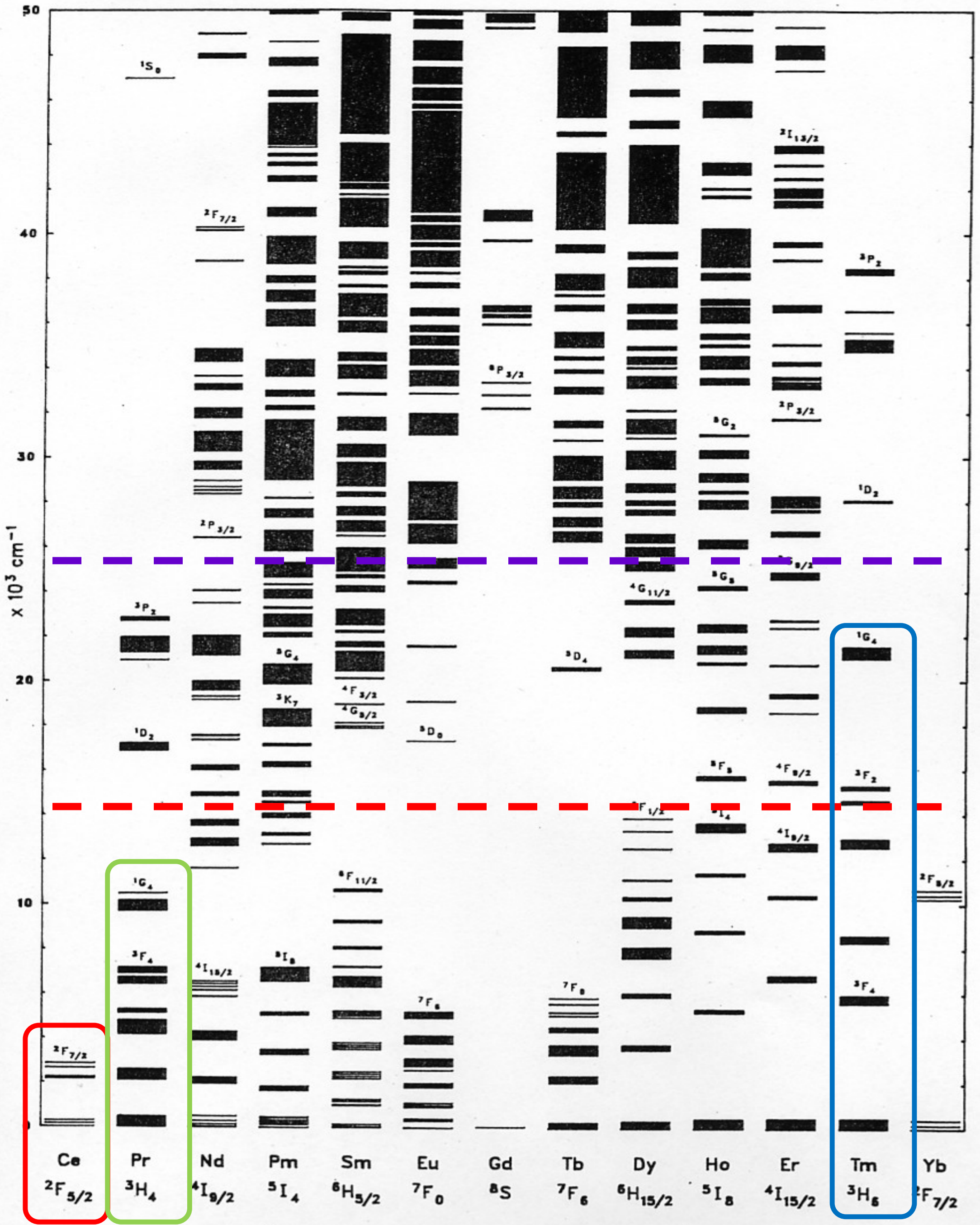
```
<3H  4][3H  4>=-9.05980000e-02  <3H  5][3H  5>=-9.05980000e-02  <3H  6][3H  6>=-9.05980000e-02
```

Tm^{3+}: 4f^{12}

Spin-orbit much larger and matrix elements change sign.



ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF_3



Transition Intensities

- Electric Dipole, Magnetic Dipole, …
- ED between $4f^{N}$ and $4f^{N-1}5d$ can be calculated directly
  - But require modelling of vibronic bands.
- ED within $4f^{N}$ are parity forbidden.
  - Construct Effective ED operator that accounts for mixing of configurations of opposite parity on ion or ligand.
  - First detailed treatment: Judd, Ofelt, 1962.

Effective Electric Dipole Operator

$$D_{\mathrm{eff},q} = D_q^{(1)} + D_q^{(1)} \sum_{\beta \notin \mathrm{M}} \frac{|\beta\rangle\langle\beta| V}{E_0 - E_\beta^{(0)}} + \sum_{\beta \notin \mathrm{M}} \frac{V|\beta\rangle\langle\beta|}{E_0 - E_\beta^{(0)}} D_q^{(1)} + \ldots$$

Can derive a parametrization. λ=2,4,6, t=λ±1, λ

$$D_{\mathrm{eff},q} = \sum_{\lambda,t,p} A_{tp}^{\lambda} U_{p+q}^{(\lambda)} (-1)^q \langle \lambda (p+q), 1 - q | tp \rangle$$

Dipole strength

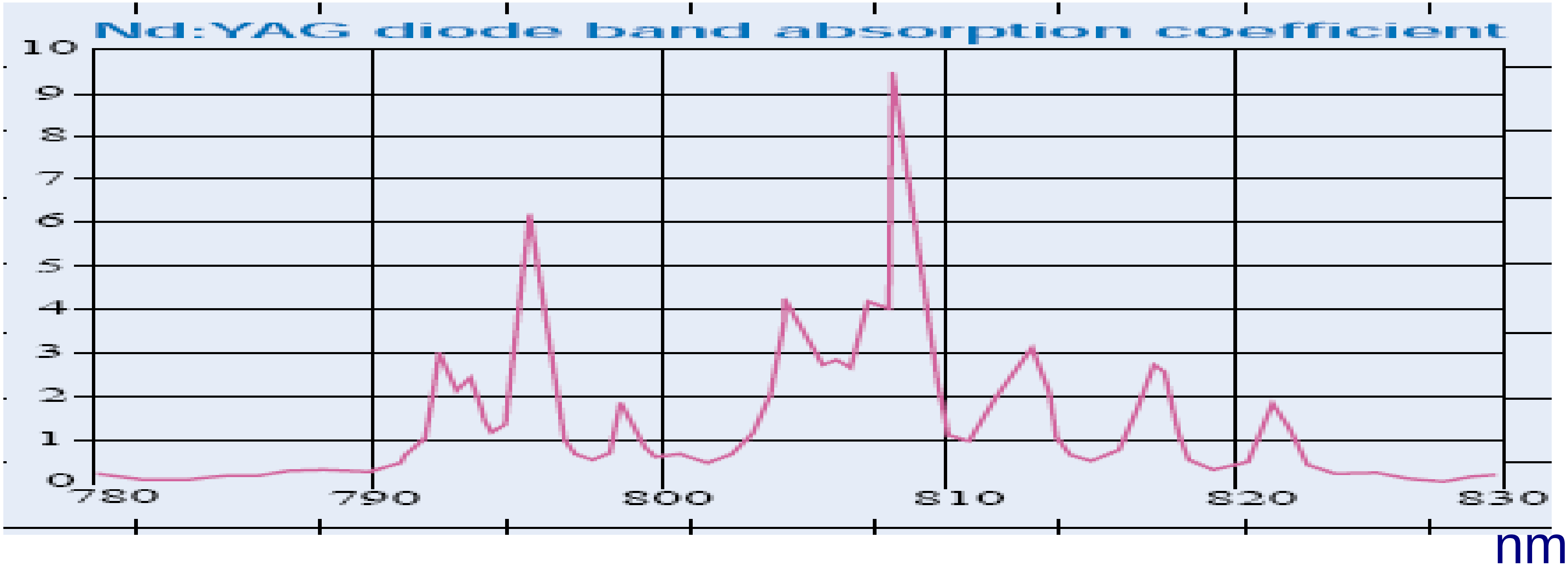
$$S_{FI,q}^{\mathrm{ED}} = \sum_i \sum_f e^2 \left| \langle F f | D_q^{(1)} | I i \rangle \right|^2$$

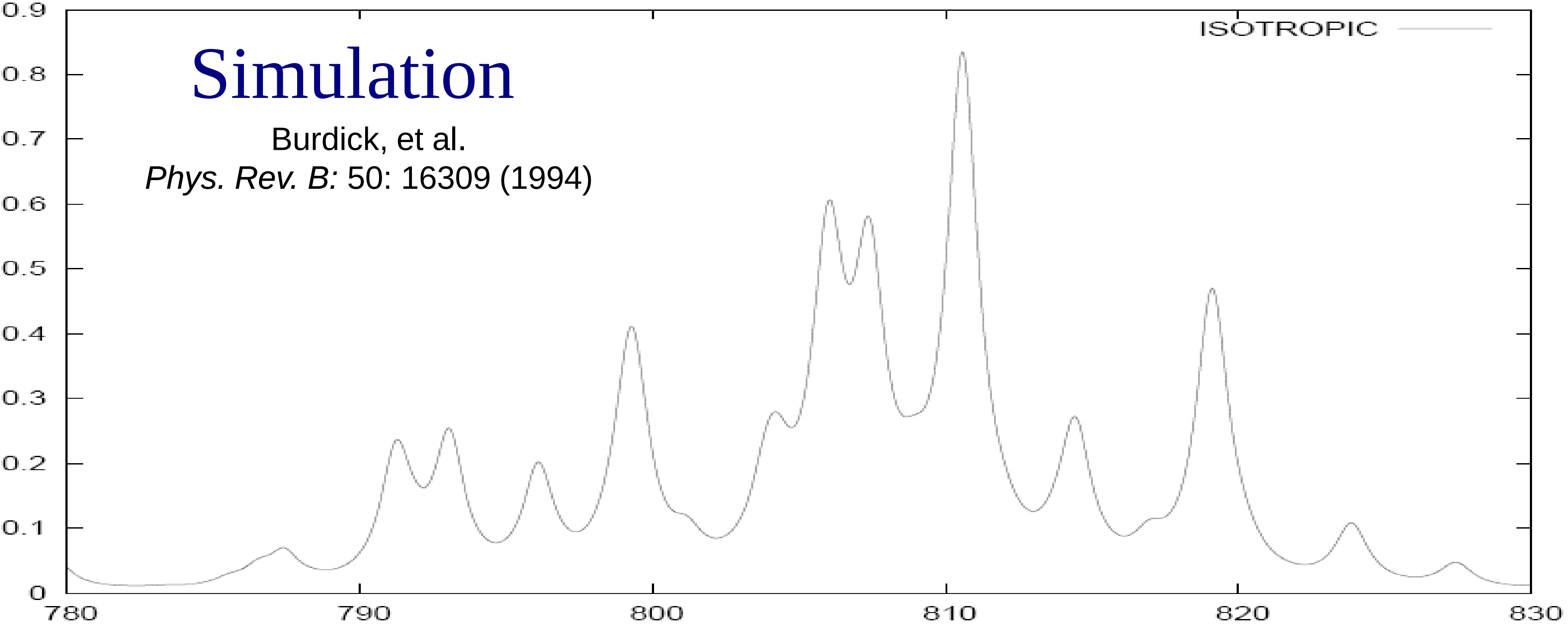
Oscillator strength

$$f_{FI,q}^{\mathrm{ED}} = \frac{2m\omega}{\hbar e^2} \frac{\chi_{\mathrm{L}}}{n} \frac{1}{g_I} S_{FI,q}^{\mathrm{ED}}$$

Einstein A coefficients (1/τ)

$$A_{FI,q}^{\mathrm{ED}} = \frac{1}{4\pi\epsilon_0} \frac{4\omega^3}{\hbar c^3} n \chi_{\mathrm{L}} \frac{1}{g_I} S_{FI,q}^{\mathrm{ED}}$$





Simulation

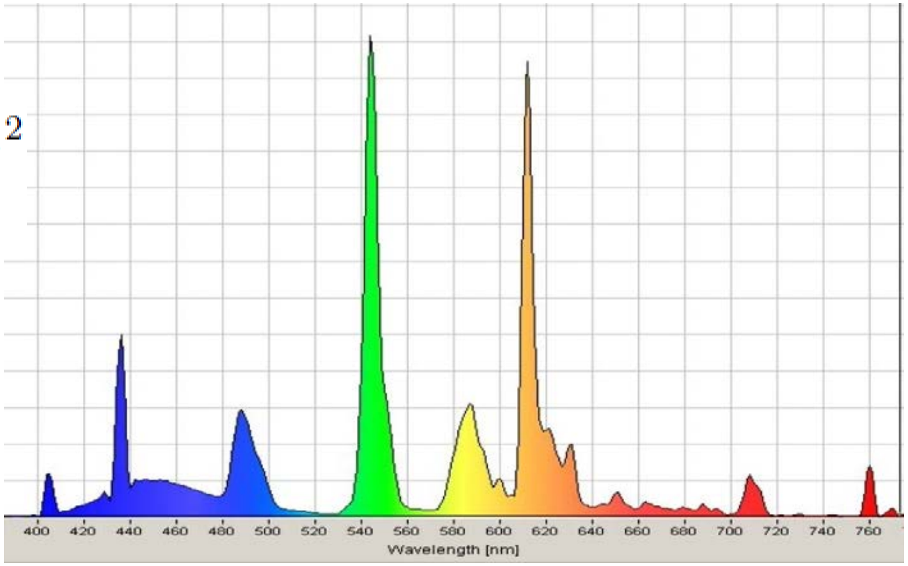
Burdick, et al.
Phys. Rev. B: 50: 16309 (1994)

Multiplet-Multiplet transitions

- Judd 1962
  - For solutions and glasses at room temperature.
  - Sum over all states in a multiplet and all polarizations.
  - Reduces to three-parameter *linear* fit.
  - Ω_λ parameters with λ=2,4,6
  - Over 3000 citations!

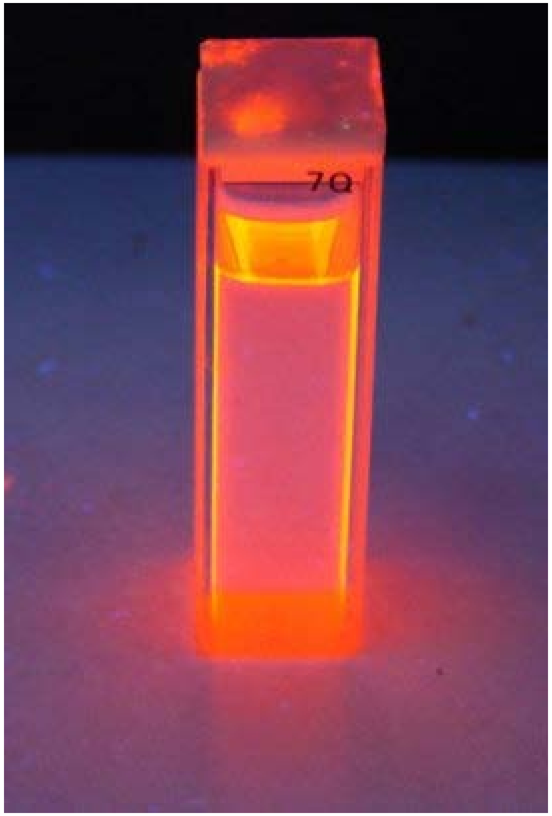
$$\bar{S}^{\mathrm{ED}}_{\alpha_F J_F, \alpha_I J_I} = \frac{1}{3} e^2 \sum_\lambda \Omega_\lambda \langle \alpha_F J_F \| \mathrm{U}^{(\lambda)} \| \alpha_I J_I \rangle^2$$

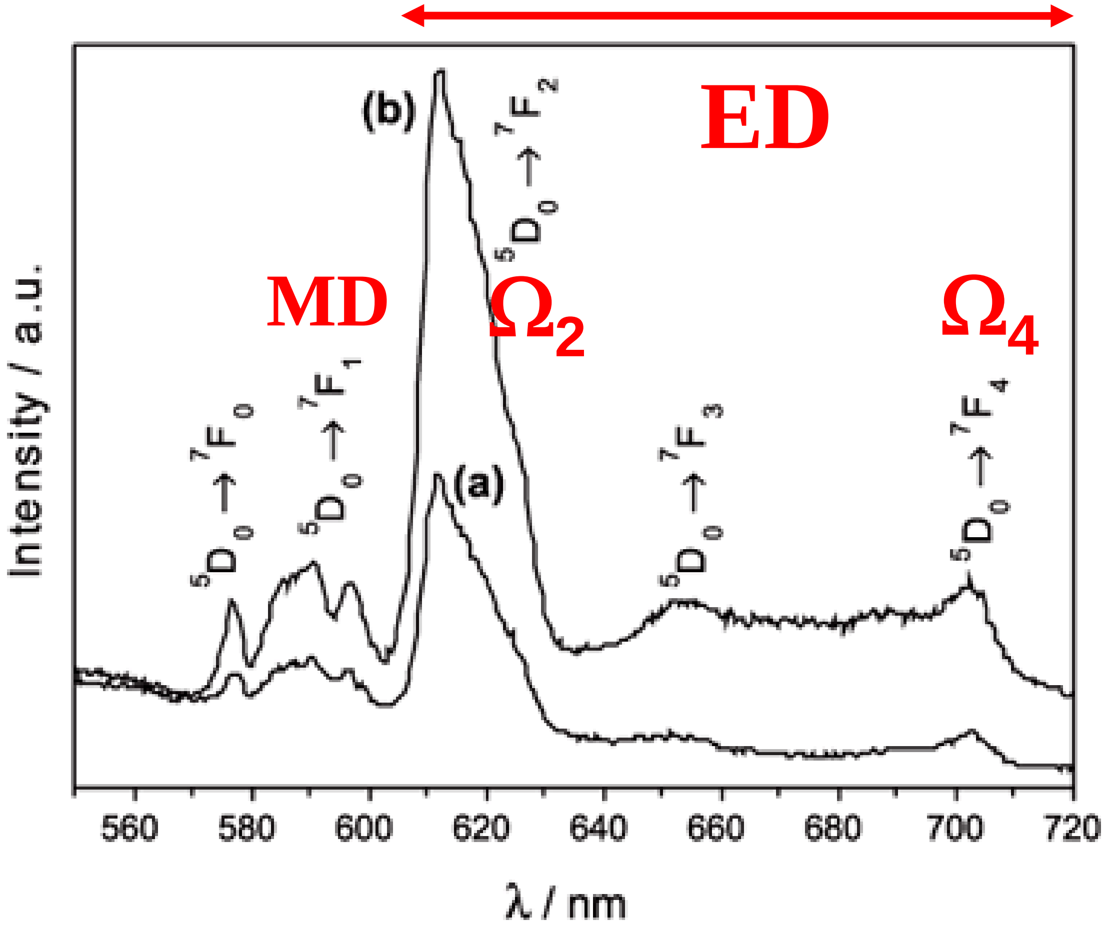
$$\Omega_\lambda = \sum_{t,p} \frac{1}{2\lambda + 1} \left| A^\lambda_{tp} \right|^2$$



Eu^{3+}: $^5D_0 \rightarrow {}^7F_J$ Emission

$$\frac{1}{3}e^2 \sum_{\lambda} \Omega_\lambda \langle \alpha_F J_F \| \mathrm{U}^{(\lambda)} \| \alpha_I J_I \rangle^2$$





ED

MD

Ω_2

Ω_4

5.2 Multiplet-multiplet Judd-Ofelt calculations

I have provided you with the relevant matrix elements for Eu^{3+} and Nd^{3+} in Appendix C.

5.3 Eu^{3+} in oxyfluoride glass

B. Klimesz et al. [47] have measured absorption and emission spectra of several ions in an oxyfluoride glass. We start by considering their measurements on Eu^{3+}.

1. Use the Ω_λ parametrization given in Section 3.5 of the paper to calculate the Ω_λ parameters from the absorption oscillator strengths from the ground state ${}^7F_0$ to the excited ${}^5D_0$, ${}^5D_1$, ${}^5D_2$, ${}^5D_3$, ${}^5L_6$ multiplets. These are given in Table 5.1. Assume a refractive index $n = 1.65$

2. Use the Ω_λ parameters to calculate the A coefficients for emission from ${}^5D_0$ and ${}^5D_1$ multiplets to the ${}^7F_J$ multiplets and hence calculate the radiative lifetimes. The measured lifetime of ${}^5D_0$ is 1.7 ms.

Table 5.1: Oscillator strengths for transitions from the ground state ${}^7F_0$ in Eu^{3+} in oxyfluoride glass[47].

Final state	Energy (cm^{-1})	$f \times 10^{-6}$
${}^5D_0$	17270	0.01
${}^5D_1$	21500	0.07*
${}^5D_2$	21500	0.15
${}^5D_3$	24080	0.03
${}^5L_6$	25350	0.91

* This value is not tabulated. I have estimated it from Figure 12 of [47].

5.3.1 Questions

1. For some transitions your calculations give zero intensity. Why do you think this is?
2. Why is the calculated lifetime different from the measured lifetime?

Partial solutions

This calculation is very simple. Since we start from states with $J = 0$, electric-dipole transitions are only allowed to states with $J' = 2, 4, 6$, via matrix elements of $U^{(2)}$, $U^{(4)}$, and $U^{(6)}$ respectively. Therefore, calculating the Ω_λ is very simple. Magnetic-dipole transitions to states with $J' = 1$ are also allowed. Transitions to $J' = 0$ and $J' = 3$ are calculated to be zero in this approximation, and are very small. They arise due to crystal-field mixing between the J-multiplets.

Intensity Matrix Elements

Note that for the magnetic dipole case we give reduced matrix elements of $L + 2S$, and must be multiplied by the constants in Eq. (4.2) to obtain reduce matrix elements of $M^{(1)}$.

D.1 Eu^{3+} matrix elements for Judd-Ofelt Intensity Calculations

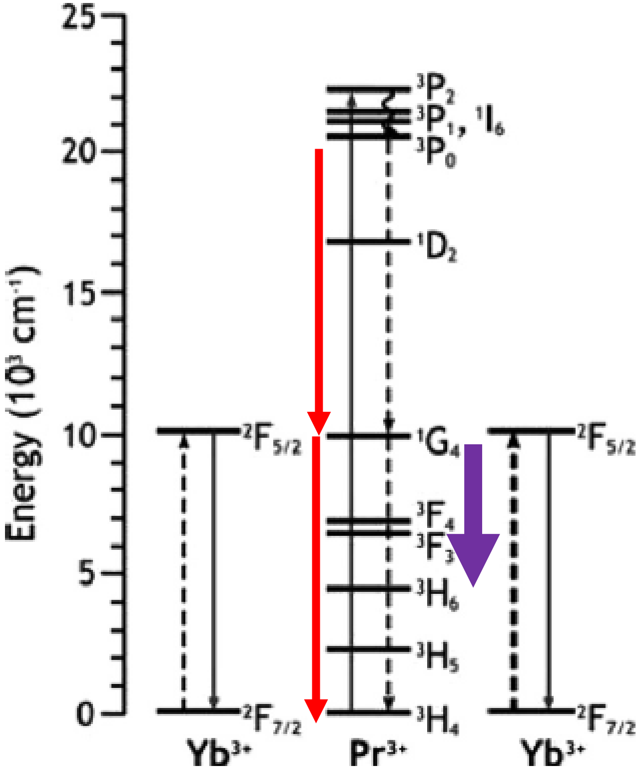
We give only the lowest 12 free-ion energy levels. Note that in states like `5D1 0` or `5D3 0` the labels `1` and `3` distinguish states with the same S and L. The reduced matrix elements below are calculated between the free-ion eigenvectors.

```
PARAMETERS

    F2          =   83125.0000
    F4          =   59268.0000
    F6          =   42560.0000
    ALPHA       =      20.1600
    BETA        =    -566.0000
    GAMMA       =    1500.0000
    T2          =     300.0000
    T3          =      40.0000
    T4          =      60.0000
    T6          =    -300.0000
    T7          =     370.0000
    T8          =     320.0000
    ZETA        =    1338.0000
    M0          =       2.1000
    P2          =     360.0000

ENERGIES and EIGENVECTORS

       Largest two components                 Energy
   1  -0.97 [7F  0>  + 0.19 [5D1 0>        0.000000
   2  -0.97 [7F  1>  + 0.17 [5D1 1>      382.280778
   3  -0.98 [7F  2>  + 0.14 [5D1 2>     1051.745175
   4   0.99 [7F  3>  - 0.10 [5D1 3>     1913.683906
   5  -0.99 [7F  4>  - 0.08 [5F2 4>     2898.069679
   6  -0.99 [7F  5>  - 0.09 [5G1 5>     3956.481323
   7   0.98 [7F  6>  + 0.13 [5G1 6>     5055.294405
   8  -0.68 [5D3 0>  + 0.54 [5D1 0>    17303.939101
   9   0.71 [5D3 1>  - 0.57 [5D1 1>    19062.381439
  10  -0.74 [5D3 2>  + 0.59 [5D1 2>    21552.658483
  11  -0.74 [5D3 3>  + 0.60 [5D1 3>    24465.310601
  12   0.94 [5L  6>  + 0.17 [3K5 6>    25289.533334
```

```
REDUCED MATRIX ELEMENTS

  U2

  (7F  0][7F  2)= -0.37071251     (7F  0][5D3 2)=  0.02863683     (7F  1][7F  1)=  0.39247451
  (7F  1][7F  2)= -0.22763455     (7F  1][7F  3)=  0.45744059     (7F  1][5D3 1)=  0.05139697
  (7F  1][5D3 2)=  0.01209694     (7F  1][5D3 3)=  0.02100905     (7F  2][7F  2)=  0.31624714
  (7F  2][7F  3)=  0.43165963     (7F  2][7F  4)= -0.47188391     (7F  2][5D3 0)=  0.05734750
  (7F  2][5D3 1)=  0.02800057     (7F  2][5D3 2)= -0.04296343     (7F  2][5D3 3)=  0.01495244
  (7F  3][7F  3)=  0.16619088     (7F  3][7F  4)=  0.62292816     (7F  3][7F  5)=  0.41895169
  (7F  3][5D3 1)=  0.06234619     (7F  3][5D3 2)=  0.04891052     (7F  3][5D3 3)=  0.03328467
  (7F  4][7F  4)= -0.10845512     (7F  4][7F  5)= -0.75402011     (7F  4][7F  6)=  0.29274168
  (7F  4][5D3 2)=  0.04542062     (7F  4][5D3 3)= -0.06292137     (7F  4][5L  6)=  0.00209655
  (7F  5][7F  5)= -0.52537734     (7F  5][7F  6)=  0.73568597     (7F  5][5D3 3)=  0.01199047
  (7F  5][5L  6)=  0.00051674     (7F  6][7F  6)= -1.09663378     (7F  6][5L  6)= -0.01494471
  (5D3 0][5D3 2)= -0.11855803     (5D3 1][5D3 1)=  0.11449795     (5D3 1][5D3 2)=  0.11009838
  (5D3 1][5D3 3)=  0.13407535     (5D3 2][5D3 2)=  0.03344036     (5D3 2][5D3 3)= -0.18573543
  (5D3 3][5D3 3)= -0.12237537     (5L  6][5L  6)=  0.07283253

  U4

  (7F  0][7F  4)= -0.37441512     (7F  1][7F  3)= -0.35801908     (7F  1][7F  4)= -0.41730018
  (7F  1][7F  5)= -0.34535052     (7F  1][5D3 3)= -0.03501958     (7F  2][7F  2)= -0.34926575
  (7F  2][7F  3)= -0.46089269     (7F  2][7F  4)= -0.07907540     (7F  2][7F  5)= -0.56157621
  (7F  2][7F  6)=  0.21857838     (7F  2][5D3 2)=  0.03894144     (7F  2][5D3 3)= -0.04483753
  (7F  2][5L  6)= -0.00165383     (7F  3][7F  3)=  0.16126061     (7F  3][7F  4)= -0.36775763
```

Eliminate options: Pr-Yb downconversion

Linda Aarts ,
Spectroscopy Letters, 43:373–381, 2010



$$\frac{1}{3}e^2\sum_{\lambda}\Omega_\lambda\langle\alpha_F J_F\|\mathrm{U}^{(\lambda)}\|\alpha_I J_I\rangle^2$$

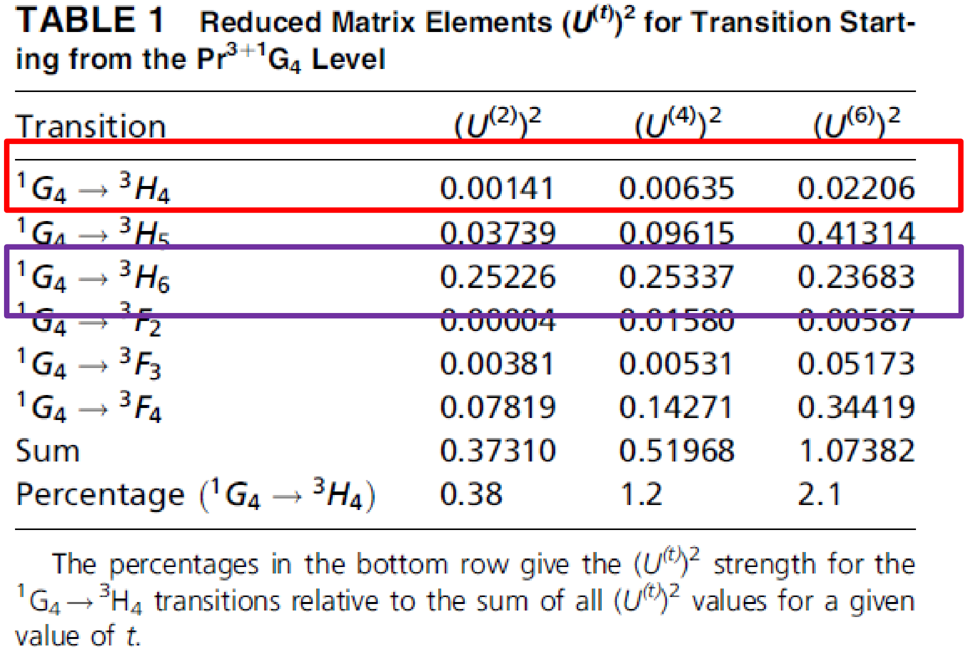


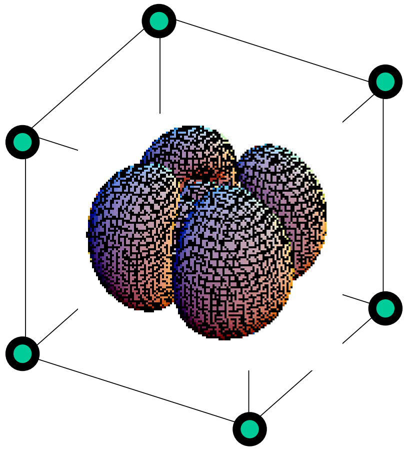
TABLE 1 **Reduced Matrix Elements $(U^{(t)})^2$ for Transition Starting from the Pr^{3+} $^1G_4$ Level**

Transition	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$
$^1G_4 \rightarrow {}^3H_4$	0.00141	0.00635	0.02206
$^1G_4 \rightarrow {}^3H_5$	0.03739	0.09615	0.41314
$^1G_4 \rightarrow {}^3H_6$	0.25226	0.25337	0.23683
$^1G_4 \rightarrow {}^3F_2$	0.00004	0.01580	0.00587
$^1G_4 \rightarrow {}^3F_3$	0.00381	0.00531	0.05173
$^1G_4 \rightarrow {}^3F_4$	0.07819	0.14271	0.34419
Sum	0.37310	0.51968	1.07382
Percentage ($^1G_4 \rightarrow {}^3H_4$)	0.38	1.2	2.1

The percentages in the bottom row give the $(U^{(t)})^2$ strength for the $^1G_4 \rightarrow {}^3H_4$ transitions relative to the sum of all $(U^{(t)})^2$ values for a given value of *t*.

$^1G_4 \rightarrow {}^3H_4$ can never be strong…

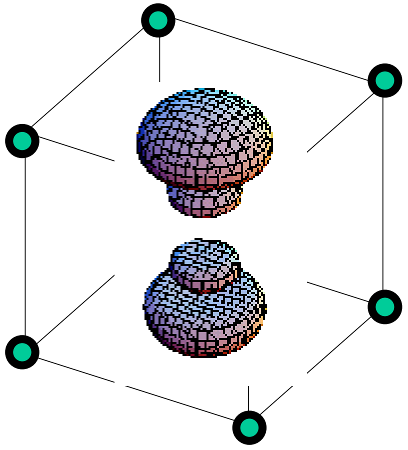
Understanding the energy levels: $4f^{N-1}5d$



T_2

Cubic:

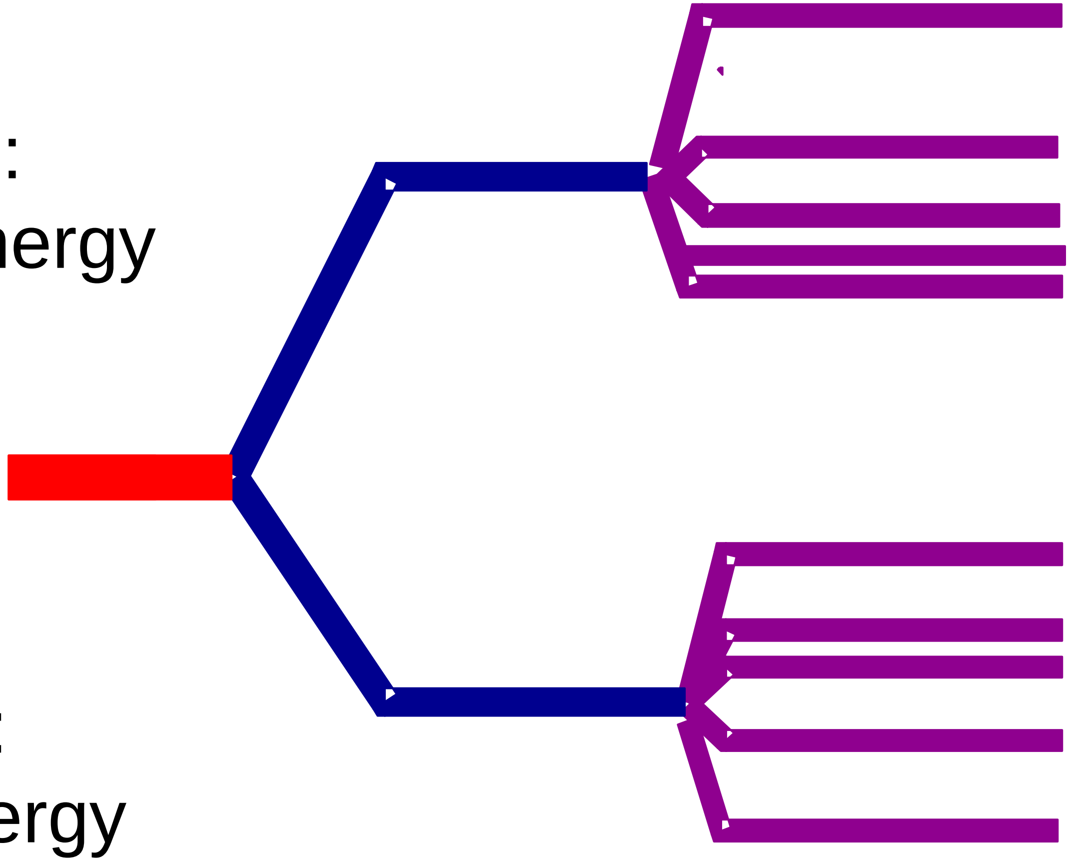
higher energy



E

Cubic:

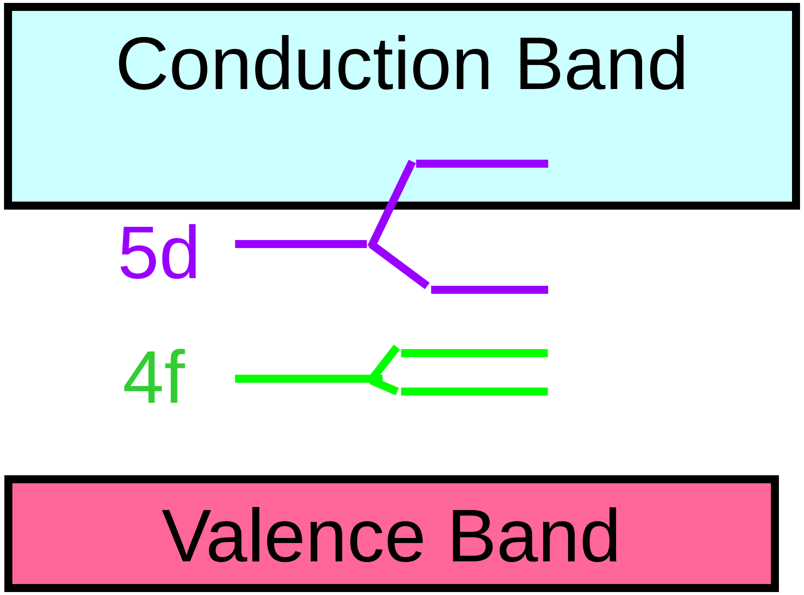
lower energy



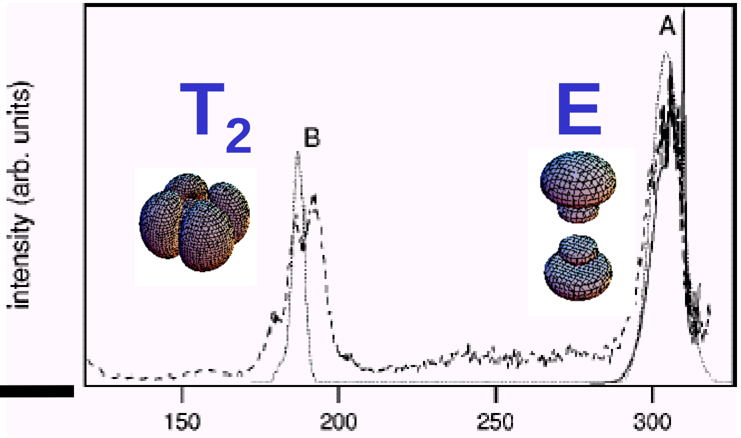
Crystal field Coulomb, etc

40 x 4f (20,000 vs 500)

Conduction Band, Free Electrons, Excitons

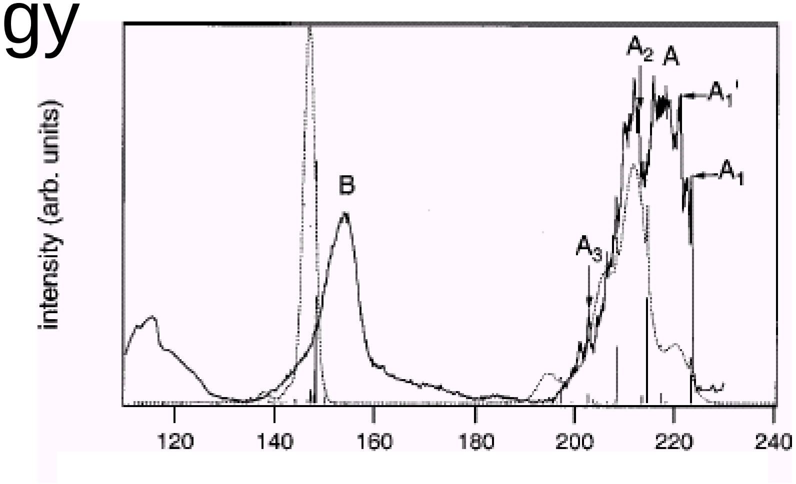


CaF_2 (cubic sites)

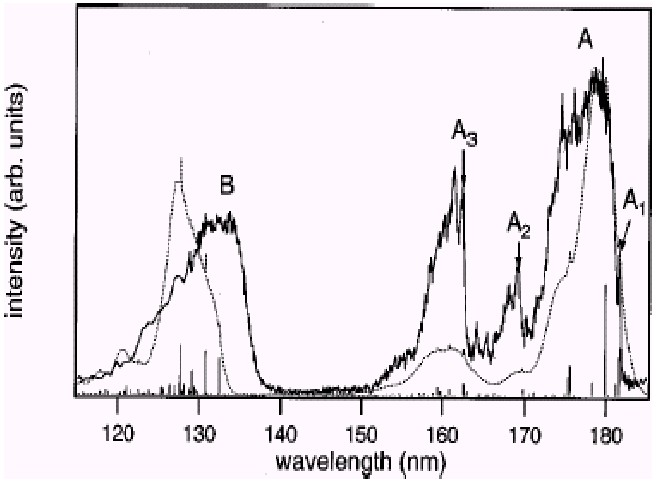


Ce^{3+} : $4f^1 \rightarrow 5d^1$

← Energy



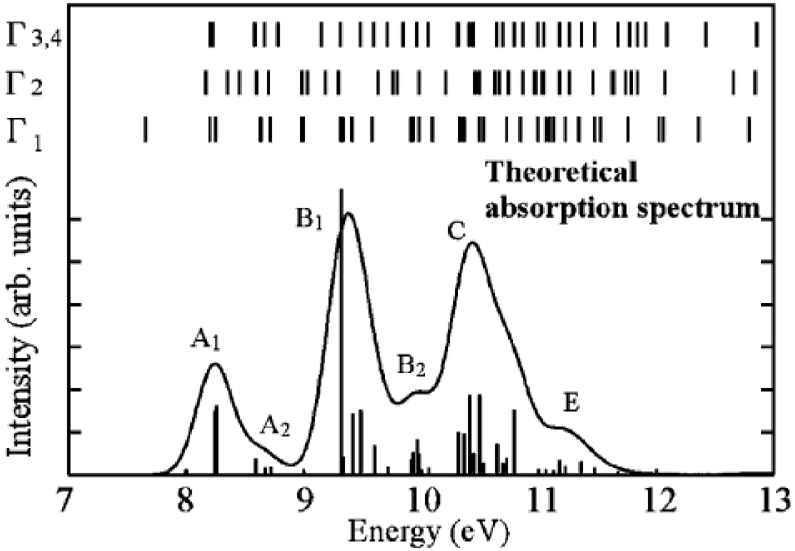
Pr^{3+} : $4f^2 \rightarrow 4f^15d^1$

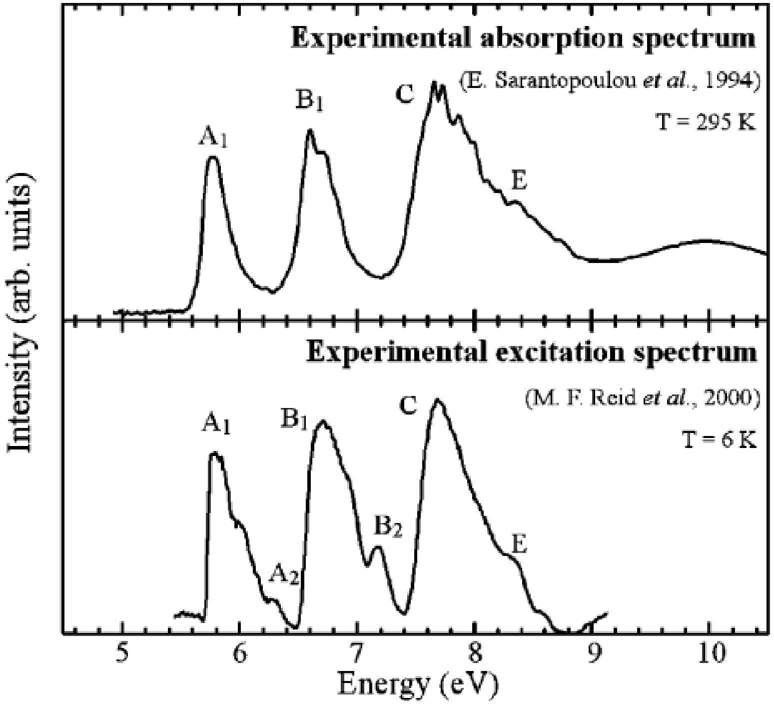


Nd^{3+} : $4f^3 \rightarrow 4f^25d^1$

First-Principles Calculations

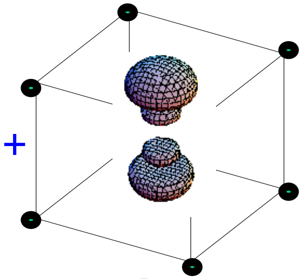
- Relativistic ab-initio calculations are now possible for these systems.
- Ogasawara et al.
  J. Solid State Chem. 178, 412 (2005).
  - Calculations for entire series. Some inaccuracies.
- Seijo et al.
  J. Chem. Phys. 125, 074511 (2006)
  - Very accurate and detailed calculations for particular ions, including potential surfaces.





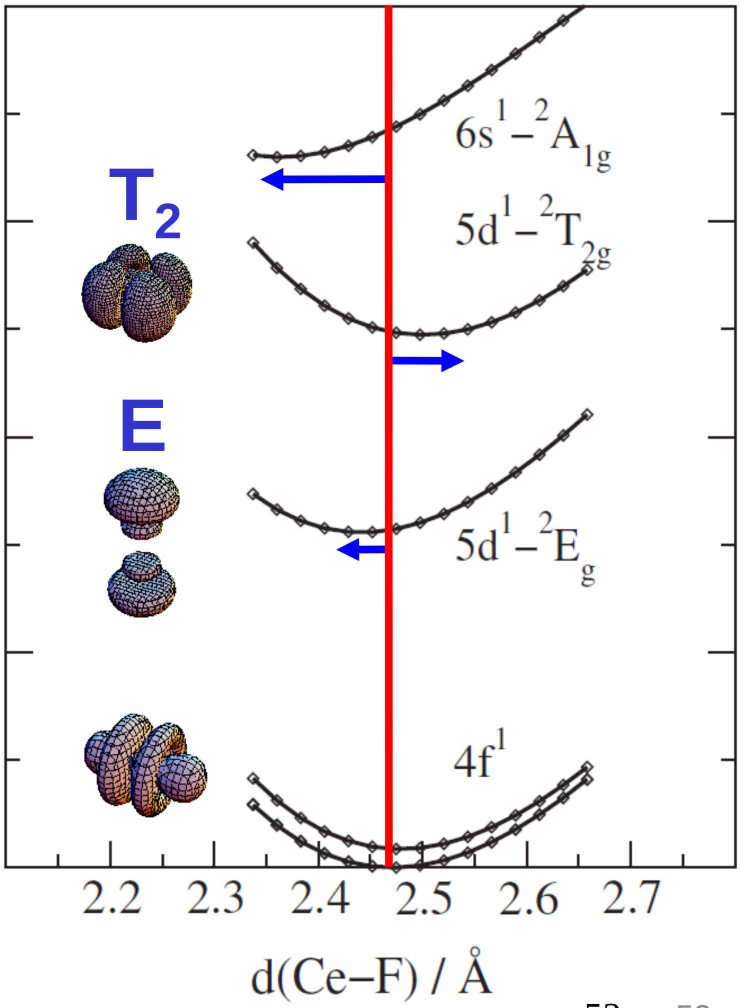
Pr^{3+}:$LiYF_4$

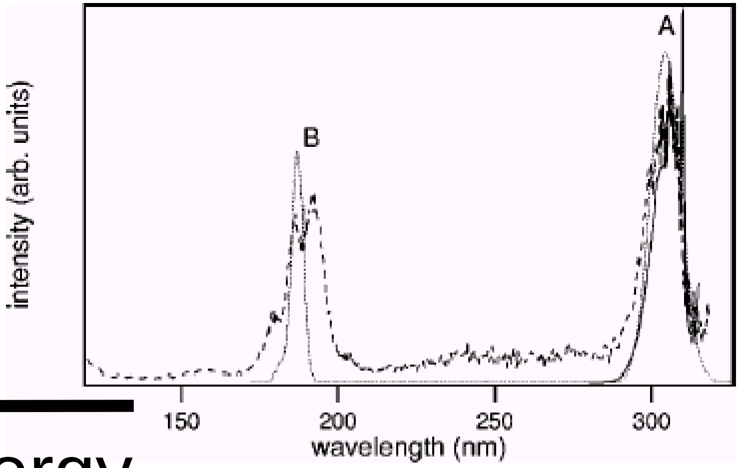
Excited-state geometry: CaF$_2$:Ce^{3+}



- Pascual, Schamps, Barandiaran, Seijo, PRB 74, 104105 (2006)
  BaF$_2$:Ce^{3+} cubic sites.
- Potential surfaces:
  - 5d E is contracted
  - 5d T$_2$ is expanded
  - As bond length contracts 6s orbital becomes delocalized.

Ce^{3+} : 4f^1 → 5d^1



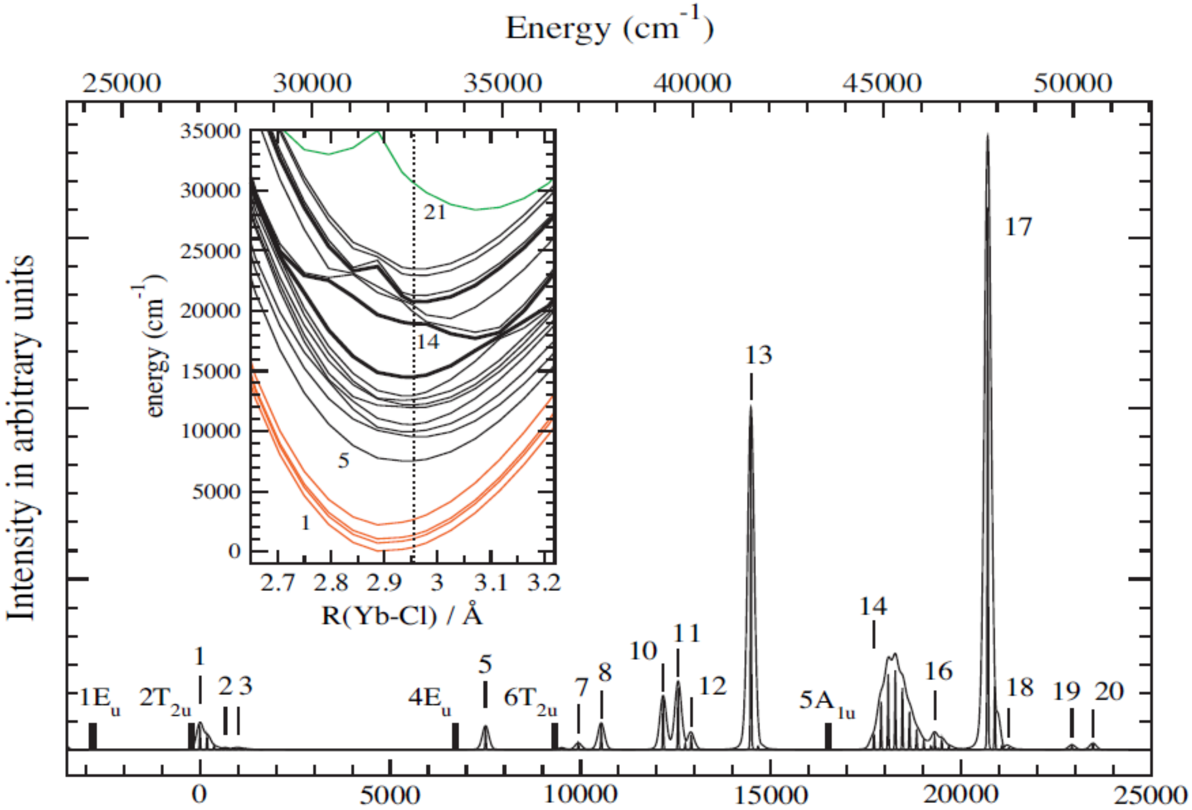


←
Energy

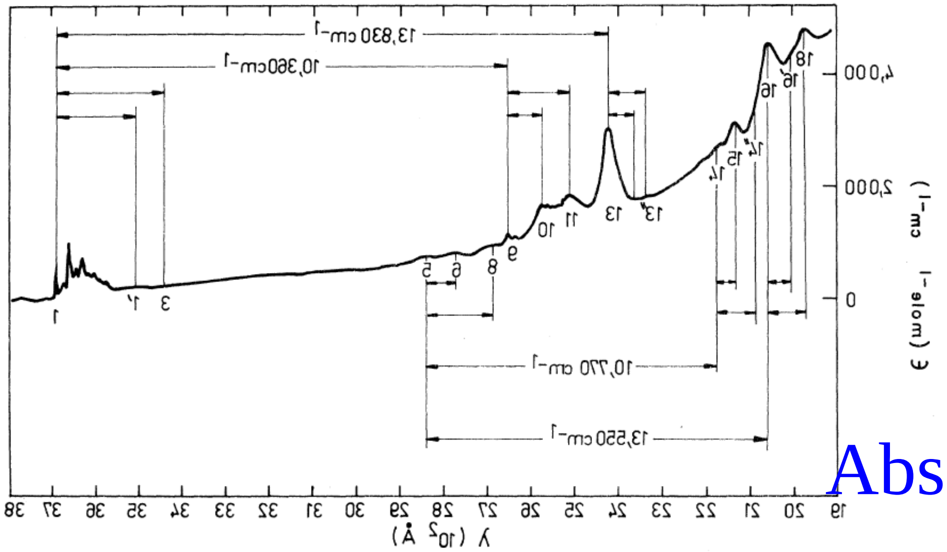
Ce^{3+}:CaF$_2$ 4f^1 →5d^1

SrCl$_2$:Yb^{2+}

Sánchez-Sanz et al.
J. Chem. Phys.
133, 114509 2010



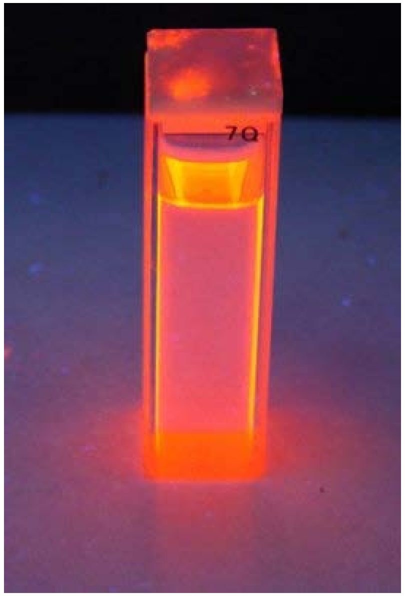
Some of our recent work is on extracting parameters from these calculations.



Absorption

Conclusion

- Effective Hamiltonian for $4f^N$
- Examples of energy level calculations
- Transition intensities
- $4f^{N-1}5d$
- Ab-initio calculations



- Further information and *exercises*:

  http://www2.phys.canterbury.ac.nz/~mfr24/

  http://www.phys.canterbury.ac.nz/people/reid.shtml

  Email: mike.reid@canterbury.ac.nz

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