

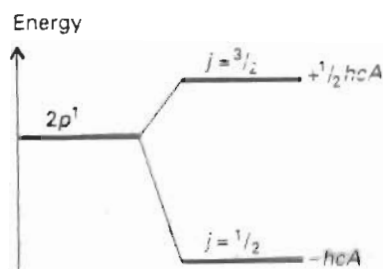
efore, we can

eqn 21.

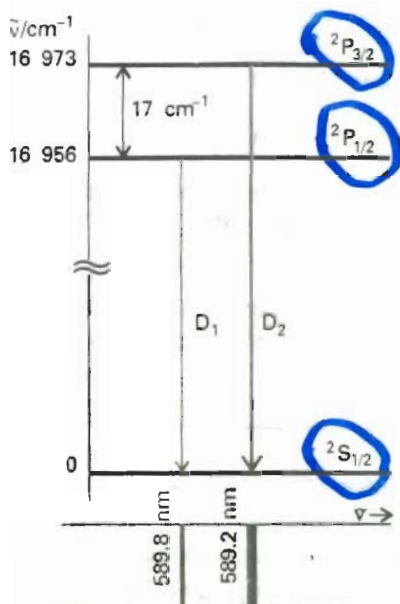
re states of any  
an alkali metal  
electron has  $l = 0$ ,  
in this state, the  
setting  $j = s$  and  
with  $l = 1$ , it has  
magnetic field that  
can have  $j = \frac{3}{2}$  or

nuclear charge.  
riding on the  
cently orbiting  
result we find  
the nuclear  
the magnetic  
electron interacts  
charge, the  
es sharply with  
(giving rise to  
a heavy atoms  
ds of  $\text{cm}^{-1}$ ).

es a transition  
pectral lines are  
[ $l$ ] $p^1$  configura-  
ample of **fine**  
ly seen in the  
electric discharge  
line at 589 nm  
e at 589.76 nm  
The transitions  
configuration  
the spin-orbit



13.29 The levels of a  $^2P$  term arising from spin-orbit coupling. Note that the low- $j$  level lies below the high- $j$  level.



13.30 The energy-level diagram for the formation of the sodium D lines. The splitting of the spectral lines (by  $17 \text{ cm}^{-1}$ ) reflects the splitting of the levels of the  $^2P$  term.

### Example 13.7 Analysing a spectrum for the spin-orbit coupling constant

The origin of the D lines in the spectrum of atomic sodium is shown in Fig. 13.30. They lie at  $16\,956.2 \text{ cm}^{-1}$  and  $16\,973.4 \text{ cm}^{-1}$ . Calculate the spin-orbit coupling constant for the upper configuration of the Na atom.

**Method.** We see from Fig. 13.30 that the splitting of the lines is equal to the energy separation of the  $j = \frac{3}{2}$  and  $\frac{1}{2}$  levels of the excited configuration, which can be expressed in terms of  $A$  by using eqn 21. Therefore, we set the observed splitting equal to the energy separation calculated from eqn 21 and solve for  $A$ .

**Answer.** The two levels are split by

$$\Delta \bar{\nu} = \frac{1}{2}A\left\{\frac{3}{2}\left(\frac{3}{2} + 1\right) - \frac{1}{2}\left(\frac{1}{2} + 1\right)\right\} = \frac{3}{2}A$$

The experimental value is  $17.2 \text{ cm}^{-1}$ ; therefore

$$A = \frac{2}{3} \times 17.2 \text{ cm}^{-1} = 11.5 \text{ cm}^{-1}$$

**Comment.** The same calculation repeated for the other alkali metal atoms gives Li:  $0.23 \text{ cm}^{-1}$ ; K:  $38.5 \text{ cm}^{-1}$ ; Rb:  $158 \text{ cm}^{-1}$ ; Cs:  $370 \text{ cm}^{-1}$ .

**Exercise E13.7.** The configuration  $\dots 4p^6 5d^1$  of rubidium has two levels at  $25\,700.56 \text{ cm}^{-1}$  and  $25\,703.52 \text{ cm}^{-1}$  above the ground configuration. What is the spin-orbit coupling constant in this excited state?

[ $1.18 \text{ cm}^{-1}$ ]

## 13.8 Term symbols and selection rules

We have used expressions such as 'the  $j = \frac{3}{2}$  level of a configuration'. A **term symbol**, which is a symbol looking like  $^2P_{3/2}$  or  $^3D_2$ , conveys this information much more succinctly. The convention of using lower-case letters to label orbitals and upper-case letters to label overall states applies throughout spectroscopy, not just to atoms.

A term symbol gives three pieces of information:

- (1) The letter (e.g. P or D in the examples) indicates the **total orbital angular momentum quantum number  $L$** .
- (2) The left superscript in the term symbol (e.g. the 2 in  $^2P_{3/2}$ ) gives the **multiplicity** of the term.
- (3) The right subscript on the term symbol (e.g. the  $\frac{3}{2}$  in  $^2P_{3/2}$ ) is the value of the **total angular momentum quantum number  $J$** .

We shall now say what each of these statements means; the contributions to the energies which we are about to discuss are summarized in Fig. 13.31.

### The total orbital angular momentum

When several electrons are present, it is necessary to judge how their individual orbital angular momenta add together or oppose each other.