

doublet state ($^2S_{1/2}$) for reasons which should become clear during the discussion of multiplicity in Section 4.3.

We can now consider the relevance of this discussion to atomic spectroscopy.

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 [2.4. The Fine Structure of the Hydrogen Atom Spectrum. The hydrogen atom contains but one electron and so the coupling of orbital and spin momenta and consequent splitting of energy levels will be exactly as described above. We summarize the essential details of the energy levels in Fig. 5.6. Each level is labelled with its n quantum number on the extreme left, and its j -value on the right;

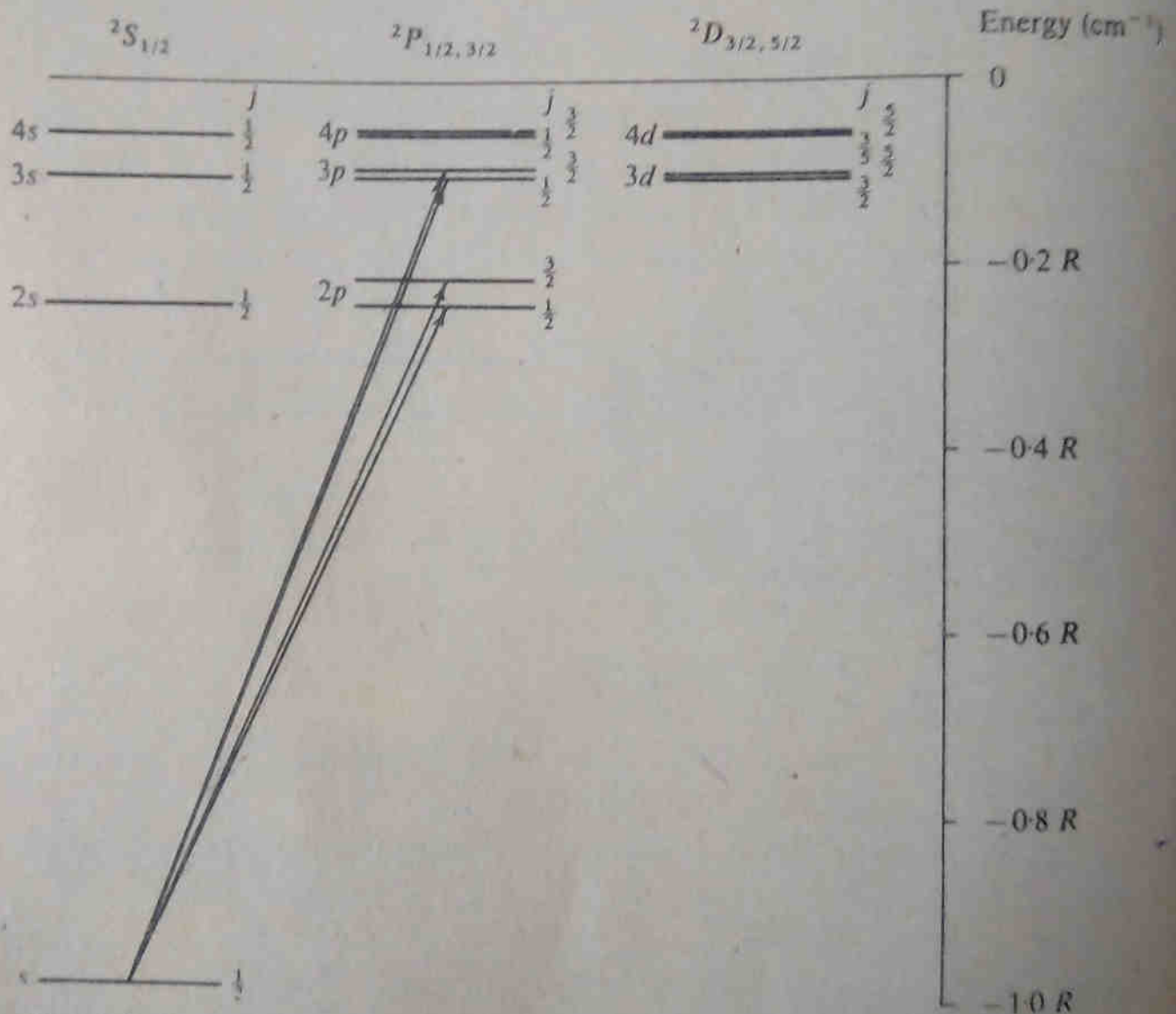


Fig. 5.6: Some of the lower energy levels of the hydrogen atom showing the inclusion of j -splitting; the splitting is greatly exaggerated for clarity.

the l -value is indicated by the state symbols S, P, D, \dots at the top of each column. There is no attempt to show the energy level splitting of the P and D states to scale in this diagram—the separation between levels differing only in j is many thousands of times smaller than the separation between levels of different n . However, we do indicate that the j -splitting *decreases* with increasing n and with increasing l . The F, G, \dots states, not shown on the diagram, follow the same pattern.

The selection rules for n and l are the same as before:

$$\Delta n = \text{anything}, \quad \Delta l = \pm 1 \text{ only} \quad (5.14)$$

but now there is a selection rule for j :

$$\Delta j = 0, \pm 1. \quad (5.15)$$

These selection rules indicate that transitions are allowed between any S level and any P level:

$$\begin{aligned} {}^2S_{1/2} &\rightarrow {}^2P_{1/2} & (\Delta j = 0) \\ {}^2S_{1/2} &\rightarrow {}^2P_{3/2} & (\Delta j = +1). \end{aligned}$$

Thus the spectrum to be expected from the ground ($1s$) state will be identical with the Lyman series (cf. Section 1.3) except that *every line will be a doublet*. In fact the separation between the lines is too small to be readily resolved but we shall shortly consider the spectrum of sodium in which this splitting is easily observed.

Transitions between the 2P and 2D states are rather more complex; Fig. 5.7 shows four of the energy levels involved. Plainly the transition at lowest frequency will be that between the closest pair of levels, the ${}^2P_{3/2}$ and ${}^2D_{3/2}$. This, corresponding to $\Delta j = 0$ is allowed. The next transition, ${}^2P_{3/2} \rightarrow {}^2D_{5/2}$ ($\Delta j = +1$), is also allowed and will occur close to the first because the separation between the doublet D states is very small. Thirdly, and more widely spaced, will be ${}^2P_{1/2} \rightarrow {}^2D_{3/2}$ ($\Delta j = +1$), but the fourth transition (shown dotted) ${}^2P_{1/2} \rightarrow {}^2D_{5/2}$, is not allowed since for this $\Delta j = +2$.

Thus the spectrum will consist of the three lines shown at the foot of the figure. This, arising from transitions between doublet levels, is usually referred to as a "compound doublet" spectrum.

We see, then, that the inclusion of coupling between orbital and

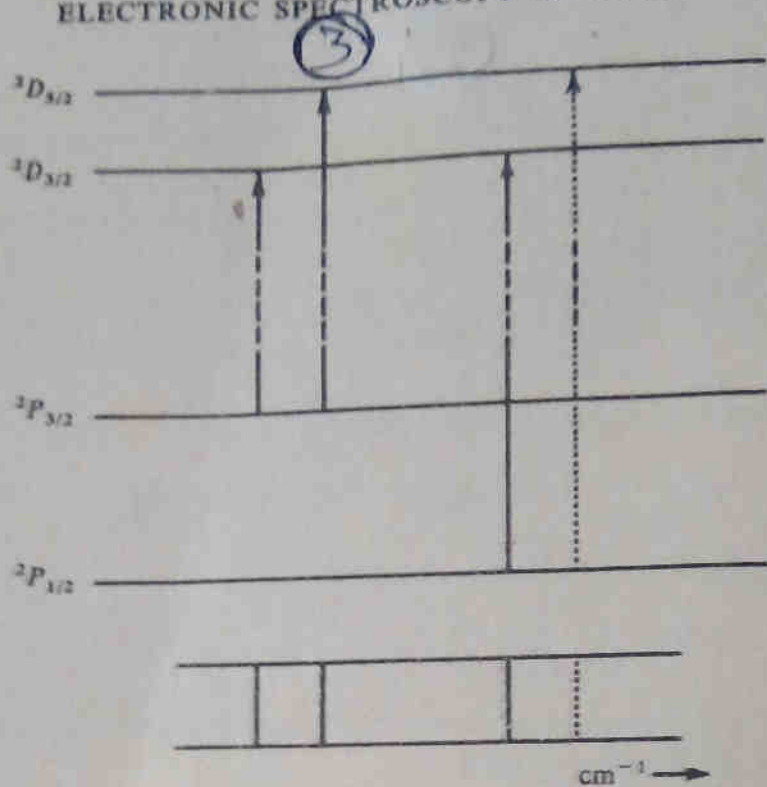


Fig. 5.7: The "compound doublet" spectrum arising as the result of transitions between $2P$ and $2D$ levels in the hydrogen atom.

spin momenta has led to a slight increase in the complexity of the hydrogen spectrum. In practice, the complexity will be observed only in the spectra of heavier atoms, since for them the j -splitting is larger than for hydrogen. In principle, however, all the lines in the hydrogen spectrum should be close doublets, if the transitions involve s levels, or "compound doublets" if s electrons are not involved.] upto this for fine structure.

3. Many-Electron Atoms

3.1. The Building-up Principle. The Schrödinger equation shows that electrons in atoms occupy orbitals of the same type and shape as the s , p , d , . . . orbitals discussed for the hydrogen atom, but that the energies of these electrons differ markedly from atom to atom. There is no general expression for the energy levels of a many-electron atom comparable to equation (5.3) for hydrogen; each atom must be treated as a special case and its energy levels either tabulated or shown on a diagram similar to Fig. 5.2 or Fig. 5.6.

There are three basic rules, known as the building-up rules, which