

is decomposed according to

$$\mathcal{H}(R) = \begin{pmatrix} E_{1s\sigma}^{AD}(R) & H(R) \\ H(R) & E_{2p\sigma}^{AD}(R) \end{pmatrix} + \begin{pmatrix} 0 & A(R) \\ -A(R) & 0 \end{pmatrix}, \quad (6.141)$$

where

$$\begin{aligned} H(R) &= \frac{1}{2} \left\{ \int \phi_{1s\sigma}^* \mathcal{H} \phi_{2p\sigma} \, d\mathbf{r}_g + \int \phi_{2p\sigma}^* \mathcal{H} \phi_{1s\sigma} \, d\mathbf{r}_g \right\}, \\ A(R) &= \frac{1}{2} \left\{ \int \phi_{1s\sigma}^* \mathcal{H} \phi_{2p\sigma} \, d\mathbf{r}_g - \int \phi_{2p\sigma}^* \mathcal{H} \phi_{1s\sigma} \, d\mathbf{r}_g \right\}. \end{aligned} \quad (6.142)$$

$\mathcal{H}$  is the complete non-relativistic Hamiltonian given in (6.130). The Hermitian matrix in (6.141) is diagonalised to obtain the coefficients in the wave functions (6.140) and effective potential curves for the coupled states using these wave functions as a function of  $R$ .

Other methods of treating the  $\text{HD}^+$  ion have been developed by Moss and Sadler [51] and relativistic [52] and radiative [53] corrections have also been calculated. These are small, but still significant in comparison with the accuracy of the experimental data. We should also note that the other one-electron molecule to have been studied theoretically [54] is  $\text{HeH}^{2+}$ ; although the ground state is predicted to be repulsive, some excited states are calculated to have potential minima. No spectroscopic studies of this molecular ion have been described.

Adiabatic corrections for  $\text{H}_2$  were first calculated by Kolos and Wolniewicz [27], and much later confirmed by Bishop and Cheung [55]. The best potential curves for  $\text{H}_2$  and  $\text{D}_2$ , incorporating both adiabatic and relativistic corrections, have been tabulated by Bishop and Shih [56]. Bishop and Cheung [55] have also carried out non-adiabatic calculations for  $\text{H}_2$ , the energy of the lowest level being lowered by  $0.42 \text{ cm}^{-1}$  compared with the adiabatic value. A small number of calculations for excited states have also been reported.

Formidable problems arise for many-electron molecules, and the non-adiabatic effects will, in general, be smaller for molecules with heavier atoms.

## 6.7. Coupling of electronic and rotational motion: Hund's coupling cases

### 6.7.1. Introduction

We have already seen in chapter 5 the importance of angular momenta in diatomic molecules. We now consider the various ways in which these angular momenta can be coupled in diatomic molecules, giving rise to Hund's coupling cases [57]. As we will see many times elsewhere in this book, Hund's coupling cases are idealised situations which help us to understand the pattern of rotational levels and the resulting spectra. They are also central to the theory underlying the quantitative analysis of spectra and the consequent definition and determination of molecular parameters.

The angular momenta which are involved are as follows:

$L$  – the electronic orbital angular momentum,

$S$  – the electronic spin angular momentum,

$J$  – the total angular momentum,

$N$  – the total angular momentum excluding electron spin, so that  $N = J - S$ ,

$R$  – the rotational angular momentum of the nuclei, so that  $R = N - L$ .

In addition there will often be nuclear spin angular momentum ( $I$ ), which is coupled to the electronic orbital and spin angular momenta; these coupling cases are described in section 6.7.8.

### 6.7.2. Hund's coupling case (a)

In Hund's case (a), illustrated in the vector diagram shown in figure 6.13, the orbital angular momentum  $L$  is strongly coupled to the internuclear axis by electrostatic forces; the electron spin angular momentum in turn is strongly coupled to  $L$  through spin-orbit coupling. The axial components of  $L$  and  $S$  are well defined and are denoted  $\Lambda$  and  $\Sigma$ ; their sum is denoted  $\Omega$ , i.e.  $\Omega = \Lambda + \Sigma$ . The angular momentum of the rotating nuclei is  $R$ ; this is coupled to a vector  $\Omega$  pointing along the axis to form the resulting total angular momentum  $J$ . The precession of  $L$  and  $S$  about the internuclear axis is presumed to be much faster than the nutation of  $\Omega$  and  $R$  about  $J$ .

The precessions of  $L$  and  $S$  about the internuclear axis have two equal and opposite senses, so that the projections also have magnitudes  $\pm\Lambda$ ,  $\pm\Sigma$ . Consequently the total

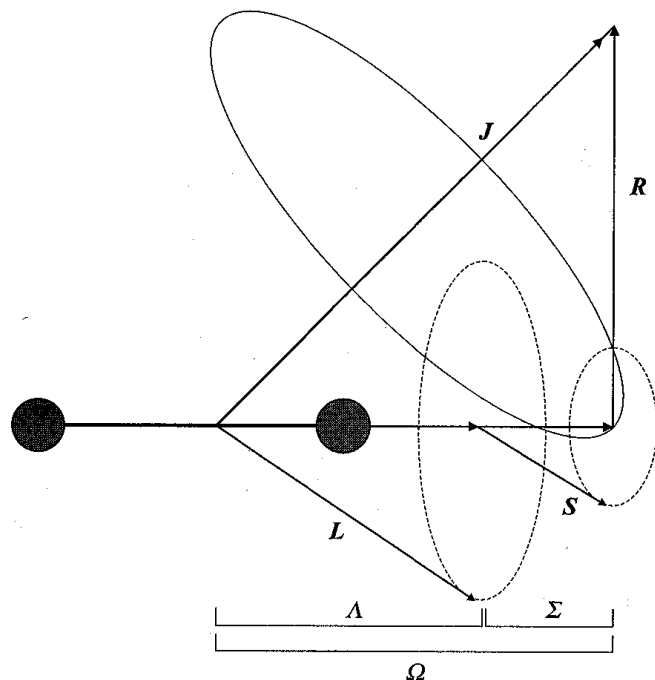


Figure 6.13. Vector coupling diagram for Hund's case (a).

Table 6.7. *Hund's coupling cases*

Coupling case	Good quantum numbers	Requirements
(a)	$\eta, \Lambda, S, \Sigma, J, \Omega$	$A\Lambda \gg BJ$
(b)	$\eta, \Lambda, N, S, J$	$A\Lambda \ll BJ$
(c)	$\eta, (J_a), \Omega, J$	$A\Lambda \gg \Delta E_{el}$
(d)	$\eta, L, R, N, S, J$	$BJ \gg \Delta E_{el}$
(e)	$\eta, J_a, R, J$	$A\Lambda \gg BJ \gg \Delta E_{el}$

projection of electronic angular momentum also has two senses,  $\pm\Omega$ . The two-fold degeneracy in  $\Lambda$  is called  $\Lambda$ -doubling, and that in  $\Omega$  is called  $\Omega$ -doubling; we will see elsewhere how the molecular rotation can remove this degeneracy.

The various Hund's coupling cases can be defined more rigorously in terms of their good quantum numbers (see table 6.7). Thus case (a) wave functions may be written in ket notation as  $|\eta, \Lambda; S, \Sigma; J, \Omega, M_J\rangle$ . The symbol  $\eta$  here denotes all other quantum numbers not expressed explicitly, for example, electronic and vibrational.  $M_J$  is the component of  $J$  in a space-fixed  $Z$  direction, and is important when we discuss the effects of external magnetic or electric fields. It should be appreciated that Hund's case (a) is a *decoupled* basis set, that is,  $L$  and  $S$  are decoupled along the internuclear axis. The operator describing the rotational energy in Hund's case (a) notation is given by

$$\mathcal{H}_{\text{rot}} = BR^2 = B[\mathbf{J} - \mathbf{L} - \mathbf{S}]^2. \quad (6.143)$$

$B$  is called the rotational constant, and will be discussed in detail later; the operator form of the rotational energy in (6.143) has profound consequences, as we shall see.

Case (a) is a good representation whenever  $A\Lambda$  is much greater than  $BJ$ ,  $A$  being the spin-orbit coupling constant. In a good case (a) system there are  $2S + 1$  fine-structure states, characterised by their  $\Omega$  values, with spin-orbit energies  $A\Lambda\Sigma$ . Each fine-structure state has a pattern of rotational levels, with relative energies  $BJ(J + 1)$ , the lowest rotational level having  $J = \Omega$ . As  $J$  increases, case (a) becomes less appropriate; we will see why in due course.

### 6.7.3. Hund's coupling case (b)

When  $\Lambda = 0$  and  $S \neq 0$  the spin vector  $S$  is no longer coupled to the internuclear axis because spin-orbit coupling vanishes in this case. Consequently  $\Omega$  is not defined. Even in some very light molecules with  $\Lambda \neq 0$ , the coupling of the spin to the internuclear axis is so weak that case (a) coupling does not apply. Hund's case (b) may then be appropriate, and the corresponding vector coupling diagram is shown in figure 6.14. Once again,  $L$  precesses very rapidly about the internuclear axis with a well-defined component,  $\Lambda$ .  $\Lambda$  is coupled to  $R$  to form  $N$ ;  $N$  is then coupled with  $S$  to form the total angular momentum  $J$ . Basis functions in this coupling scheme are written  $|\eta, \Lambda; N, S, J, M_J\rangle$

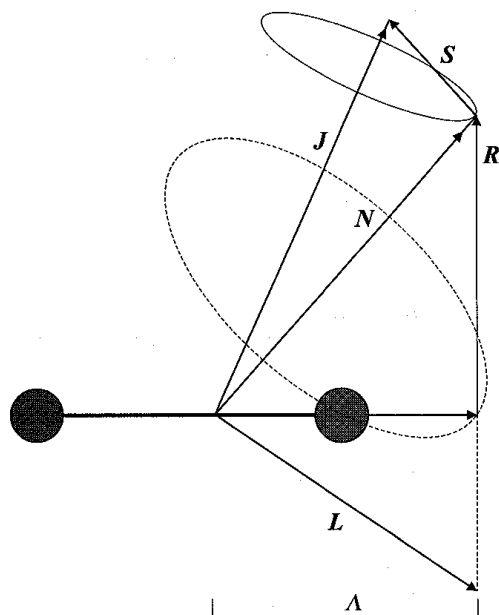


Figure 6.14. Vector coupling diagram for Hund's case (b).

(see table 6.7). The projection of  $N$  on the internuclear axis is  $A$ . In the older literature, the symbol  $K$  is used rather than  $N$ .

The operator which describes the rotational kinetic energy in Hund's case (b) notation is

$$\mathcal{H}_{\text{rot}} = BR^2 = B[N - L]^2, \quad (6.144)$$

so that the rotational levels have energies  $BN(N + 1)$ , with the lowest  $N$  level having  $N = A$ . If  $S = 1/2$ , each  $N$  level for  $N \geq 1$  is then split into a doublet by the spin-rotation interaction, represented in the effective Hamiltonian by a term  $\gamma N \cdot S$ ; the resulting levels are characterised by values of the total angular momentum  $J$ . The series which has  $J = N + 1/2$  is called the  $F_1(J)$  series, whilst that with  $J = N - 1/2$  is the  $F_2(J)$  series. If  $S \geq 1$  there is still a spin-rotation splitting but the pattern of levels is more complicated, as we will see elsewhere.

The operator form for the rotational kinetic energy, given in (6.144), can be expanded to give

$$\mathcal{H}_{\text{rot}} = B[N - L]^2 = B[N^2 + L^2 - 2N \cdot L] = B[N(N + 1) + L^2 - 2N \cdot L]. \quad (6.145)$$

The second and third terms in (6.145) have no effect *within* a case (b) state, but do have non-zero matrix elements between different electronic states.

Cases (a) and (b) are the most widely observed for diatomic molecules; most molecules, indeed, conform to coupling which is intermediate between cases (a) and (b). We will discuss the nature and origin of this intermediate coupling in due course, but first deal with three other limiting coupling cases which can be important in certain specific situations.

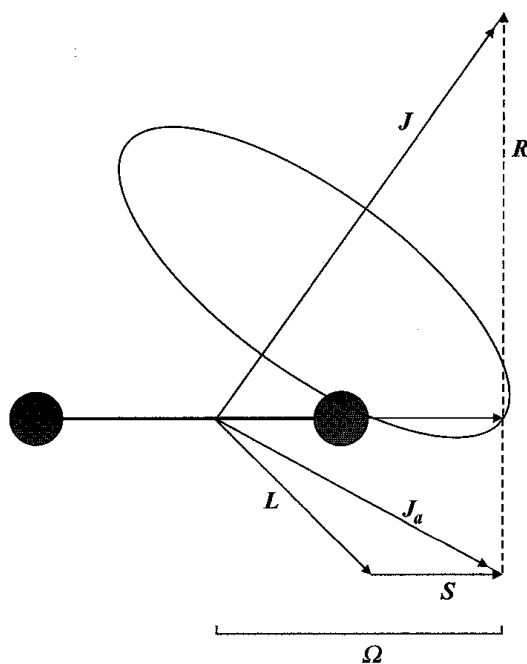


Figure 6.15. Vector coupling diagram for Hund's case (c).

#### 6.7.4. Hund's coupling case (c)

In some cases the coupling between  $L$  and  $S$  may be stronger than the interaction with the internuclear axis; this situation can arise in heavy molecules. In this case the projections  $\Lambda$  and  $\Sigma$  are not defined; instead  $L$  and  $S$  first couple to form a resultant  $J_a$ , which then precesses rapidly about the internuclear axis with a component  $\Omega$ . The nuclear rotational angular momentum now adds vectorially to  $\Omega$  to form the total angular momentum  $J$ . The vector diagram illustrating case (c) coupling is given in figure 6.15. Case (c) basis functions are specified in the form  $|\eta, J_a, J, \Omega, M_J\rangle$ ; different electronic states are characterised by different values of  $\Omega$ . The component of total angular momentum along the internuclear axis is also  $\Omega$ . If  $\Omega = 0$  the states are non-degenerate, but for  $\Omega \neq 0$  we have states which would be degenerate for a non-rotating molecule. This degeneracy is removed by rotation, and is called  $\Omega$ -doubling. The rotational levels have relative energies  $BJ(J+1)$ , just as in case (a).

A particularly clear example of Hund's case (c) coupling has been observed for the  $\text{HeAr}^+$  ion in its near-dissociation vibration-rotation levels [58]; it also occurs for the  $\text{I}_2$  molecule [59].

#### 6.7.5. Hund's coupling case (d)

In Hund's case (d) the coupling between  $L$  and the nuclear rotation  $R$  is much stronger than that between  $L$  and the internuclear axis. As shown in figure 6.16, the result of the coupling between  $L$  and  $R$  is  $N$ , which can be further coupled with  $S$  in suitable open

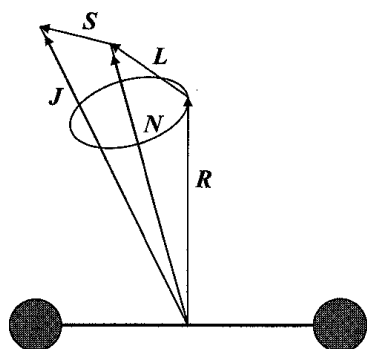


Figure 6.16. Vector coupling diagram for Hund's case (d).

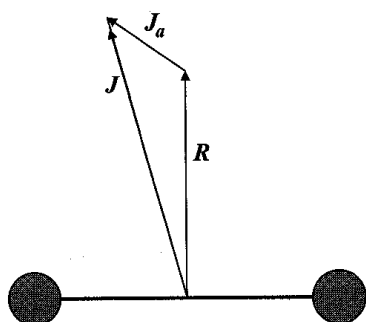


Figure 6.17. Vector coupling diagram for Hund's case (e).

shell systems. The value of  $N$  is given by

$$N = (R + L), (R + L - 1), (R + L - 2), \dots, |R - L|, \quad (6.146)$$

so that there are  $2L + 1$  different  $N$  values for each  $R$ , except when  $R < L$ . The rotational energy in case (d) is given by

$$E_{\text{rot}} = BR(R + 1), \quad (6.147)$$

each level being then further split into  $2L + 1$  components. Hund's case (d) coupling is an appropriate description for the electronic states of many Rydberg molecules, where the Rydberg electron interacts only very weakly with the molecular core. We will discuss the transition from case (b) to case (d) coupling in section 6.7.7.

### 6.7.6. Hund's coupling case (e)

Although not identified by Hund, a fifth vector coupling case is possible, which we will call Hund's case (e); it is described in the vector coupling diagram shown in figure 6.17.  $L$  and  $S$  are strongly coupled to each other, to form a resultant  $J_a$ . However, the interaction of  $L$  and  $S$  with the internuclear axis is very weak; their resultant  $J_a$  is combined with the nuclear rotation  $R$  to form the total angular momentum  $J$ . Different  $J$  components of the rotational levels arise, since for given values of  $J_a$  and  $R$ ,

$$J = R + J_a, R + J_a - 1, R + J_a - 2, \dots, |R - J_a|. \quad (6.148)$$

Notice that in both case (d) and case (e) there is no molecular projection quantum number. An example of case (e) coupling, probably the first, has been observed [60] for vibration-rotation levels of the  $\text{HeKr}^+$  ion which lie very close to the dissociation limit. The  $\text{Kr}^+$  atomic ion has  $L = 1$  and  $S = 1/2$ , so that  $J_a$  is  $3/2$  or  $1/2$ , and the spin-orbit interaction is strong. When a very weak bond is formed with a He atom,  $J_a$  remains a good quantum number, at least for the most weakly bound levels, but there are nevertheless series of rotation levels, with rotational energy  $BR(R + 1)$ . The details are described in chapter 10, where we show that case (e) coupling is identified, both by the observed pattern of the rotational levels, and by the measured Zeeman effects and effective  $g$  factors for individual rotational levels.

### 6.7.7. Intermediate coupling

As Lefebvre-Brion and Field [61] point out, the only coupling cases for which the electronic and nuclear motions can be separated are cases (a) and (c); consequently only in these cases can potential curves be defined unambiguously and accurately. However, as we have already pointed out, Hund's coupling cases are idealised descriptions and for most molecules the actual coupling corresponds to an intermediate situation. Moreover, the best description of the vector coupling often changes as the molecular rotation increases. In this section we consider the nature of the intermediate coupling schemes in more detail; some of these will appear elsewhere in this book in connection with the observed spectra of specific molecules.

The general procedure for analysing a spectrum, particularly one which involves the fine and hyperfine structure of rotational levels, is to choose a convenient Hund's case basis set for defining the effective Hamiltonian, and for calculating its matrix elements and eigenvalues. Whilst, in a sense, the choice of basis may be irrelevant, it always makes both physical and analytical sense to choose, if possible, the basis which most nearly diagonalises the effective Hamiltonian. Amongst other things, this points to the most appropriate quantum numbers to use to label the eigenstates. It is, however, always possible to express the basis functions of one Hund's coupling case in terms of those of another. For example, case (b) basis functions can be expressed as linear combinations of case (a) functions, by using Wigner 3- $j$  symbols:

$$|\eta, \Lambda; N, S, J\rangle = \sum_{\Sigma=-S}^{+S} (-1)^{J-S+\Lambda} (2N+1)^{1/2} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} |\eta, \Lambda; S, \Sigma; J, \Omega\rangle. \quad (6.149)$$

In many instances in this book we shall discuss the transition from one Hund's coupling case to another, in connection with the spectra of specific molecules. We now summarise a particularly common example, the transition from case (a) to case (b). This is probably the most frequently encountered example; it is discussed in considerable detail in chapter 9 so we will confine ourselves to a brief outline here. Figure 6.18, which reappears in chapter 9 in our description of the NO molecule, shows the correlation between case (a) levels on the left-hand side, and case (b) on the right-hand side.

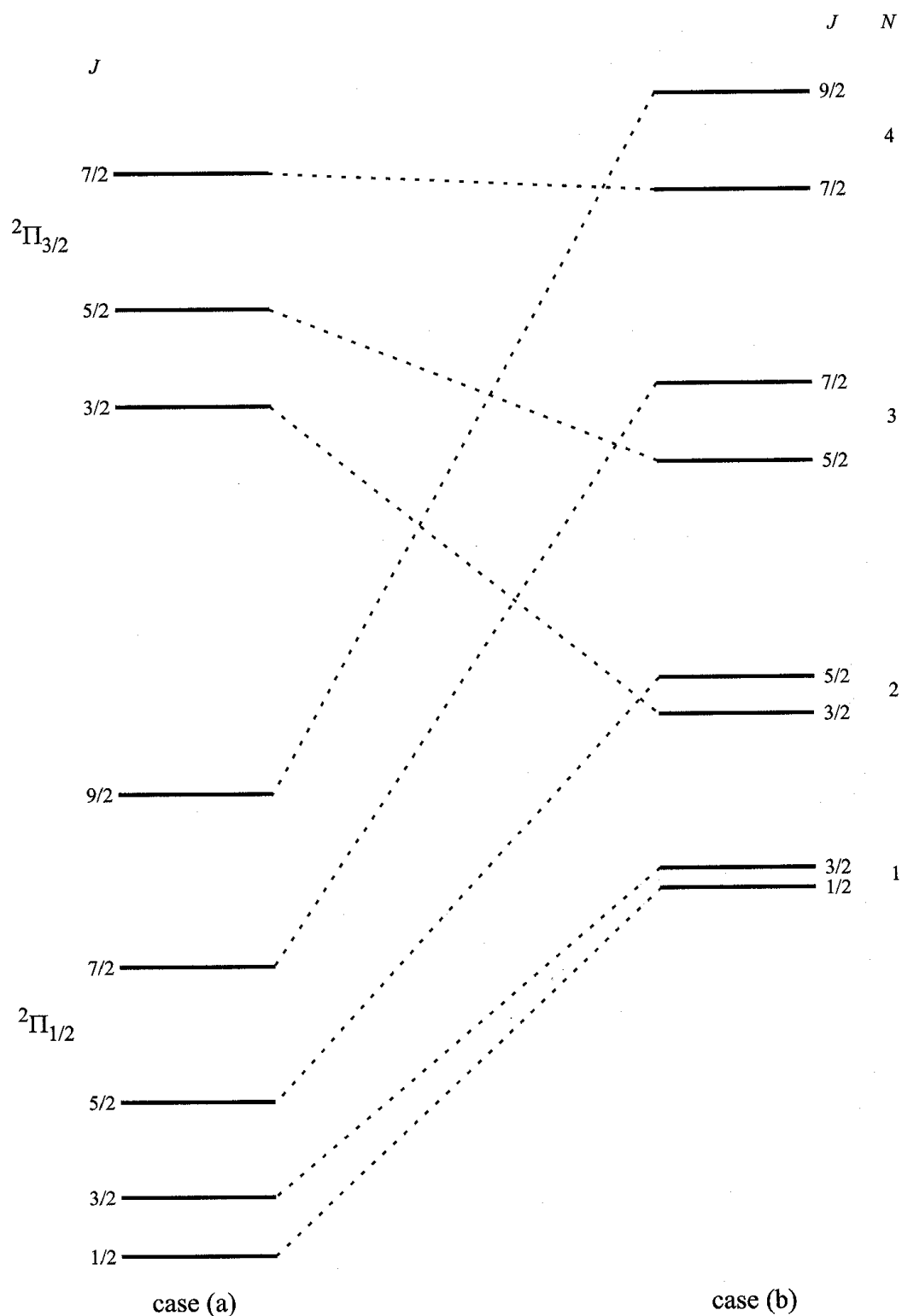


Figure 6.18. Transition from case (a) to case (b) for the rotational levels of a regular  ${}^2\Pi$  state.

For NO the  ${}^2\Pi_{1/2}$  fine structure component lies lower than the  ${}^2\Pi_{3/2}$ ; this is called a 'regular'  ${}^2\Pi$  state. Each level in figure 6.18 is actually doubly-degenerate, because of the  $\Lambda$ -doubling, which is indeed resolved in the rotational spectrum of NO. The transition from case (a) to case (b) coupling, which is also called spin-decoupling,