

the $NS_{1z}I_{2z}$ and B_z terms (which do not allow spin flips) can connect the z case $\pm MmS$ and $\pm MmT$ levels to each other via the matrix elements

$$\begin{aligned}
& \langle \pm MmS | NS_{1z}I_{2z} + \mu_B B_z (g_{1z}S_{1z} + g_{2z}S_{2z}) / h | \pm MmT \rangle \\
&= \langle \pm MmT | NS_{1z}I_{2z} + \mu_B B_z (g_{1z}S_{1z} + g_{2z}S_{2z}) / h | \pm MmS \rangle \quad (6.20) \\
&= \mp \frac{1}{2} [Nm + \mu_B B_z (g_{1z} - g_{2z}) / h] \sin 2\theta_M.
\end{aligned}$$

All of the above terms, although giving zero for their expectation values for z case eigenvectors, contribute more subtly to eigenvalues by providing connections between z case levels that allow the z case levels to mix. This mixing becomes quite important when the z case levels are degenerate or attempt to cross each other and shows itself via level repulsions; that is, if the levels strongly mix, they cannot cross and instead repel each other. Fig. 6.2 shows some repulsions due to the terms A_1 , A_2 , and B_x (A_2 is nonzero only in the rhombic case) while Fig. 6.1f shows some repulsions due to N (evident at several crossings involving the $\pm \frac{1}{2}S$, $\pm \frac{3}{2}S$, or $\pm \frac{3}{2}T$ levels). The simplest system showing level repulsions is a 2×2 Hamiltonian, the topic of the next section.

6.2.5 2×2 Systems

In order to describe the B_{12} results it is useful to first consider a 2×2 system. [111, p.408] shows that for a two-level system in the $|n\rangle$, $|m\rangle$ basis:

$$V = \begin{pmatrix} V_{nn} & V_{nm} \\ V_{mn} & V_{mm} \end{pmatrix} \quad (6.21)$$

when all four elements of V are real (which lets $V_{nm} = V_{mn}$), one gets the eigenvectors

$$|a\rangle = \cos \Omega |n\rangle + \sin \Omega |m\rangle \quad \text{and} \quad |b\rangle = -\sin \Omega |n\rangle + \cos \Omega |m\rangle \quad (6.22)$$

and the corresponding eigenvalues

$$W_a, W_b = \frac{V_{nn} + V_{mm}}{2} \pm \left[\frac{V_{nn} - V_{mm}}{2} \cos 2\Omega + V_{nm} \sin 2\Omega \right] \quad (6.23)$$

where

$$\left| \frac{V_{nn} - V_{mm}}{2} \cos 2\Omega + V_{nm} \sin 2\Omega \right| = \frac{1}{2} \sqrt{(V_{nn} - V_{mm})^2 + 4V_{nm}^2}. \quad (6.24)$$

In the above, Ω is determined by

$$\tan 2\Omega = \frac{2V_{nm}}{V_{nn} - V_{mm}} \quad (6.25)$$

where $\Omega = 0$ to $\pi/2$ for $V_{nm} > 0$ and $\Omega = 0$ to $-\pi/2$ for $V_{nm} < 0$. These let $|a\rangle$ have higher energy than $|b\rangle$ no matter what sign V_{nm} is.

Note that when $|V_{nn} - V_{mm}| \gg |2V_{nm}|$ (Ω near 0 or $\pm\pi/2$), the eigenvectors become nearly pure states $|n\rangle$ or $|m\rangle$ with energies V_{nn} or V_{mm} , while when $|V_{nn} - V_{mm}| \ll |2V_{nm}|$ (Ω near $\pm\pi/4$), the eigenvalues approach $V_{nn} \pm V_{nm}$ and the eigenvectors approach $\frac{1}{\sqrt{2}}(|m\rangle \pm |n\rangle)$, an equal mixture of the two basis states. Thus, instead of crossing, the energy levels approach each other and exchange character, and, at the point closest to a crossing, the upper and lower levels contain equal amounts of the states $|n\rangle$ and $|m\rangle$. This mixing occurs no matter how small $|V_{nm}|$ is, but one should note that tiny $|V_{nm}|$ also has a tiny range of $V_{nn} - V_{mm}$ values that allow such large mixing to occur. Thus, V_{nm} sets the minimum energy separation of W_a and W_b as well as the range of $V_{nn} - V_{mm}$ in which there can be large mixing of states. The importance of these phenomena will become more clear when this chapter treats effects of steady and oscillating fields on the yields Φ_{ST} .

In many cases, however, mixing is more subtle and occurs via higher order terms.

6.2.6 Finding Effective 2×2 Systems

For the B_{12} system, most repulsions occur via higher order terms involving multiple elements like V_{nm} and a number of intermediate energy levels. Nevertheless, such systems behave as in the 2×2 case, giving level repulsions instead of crossing and giving equal mixing at the point nearest degeneracy. One should note, however, that higher order repulsions tend to be weaker and have narrower ranges of equal mixing than do lower order repulsions.

To treat such mixing near a crossing of two levels $|n\rangle$ and $|m\rangle$, one can often treat part of a large Hamiltonian H_o as an effective 2×2 system, as described in [146]. For an eigenvector $|W\rangle$ and steady Hamiltonian H_o , one has, in terms of the basis states $|i\rangle$ (that are eigenvectors of the diagonal part of H_o),

$$H_o|W\rangle = W|W\rangle \quad \text{and} \quad \langle i|H_o|W\rangle = W\langle i|W\rangle \quad (6.26)$$

but, using $H_{ij} = \langle i|H_o|j\rangle$,

$$W\langle i|W\rangle = \langle i|H_o|W\rangle = \sum_j \langle i|H_o|j\rangle \langle j|W\rangle = \sum_j H_{ij} \langle j|W\rangle = H_{ii} \langle i|W\rangle + \sum_{j \neq i} H_{ij} \langle j|W\rangle \quad (6.27)$$

thus

$$(W - H_{ii})\langle i|W\rangle = \sum_{j \neq i} H_{ij} \langle j|W\rangle \quad \text{and so} \quad \langle i|W\rangle = \sum_{j \neq i} \frac{H_{ij} \langle j|W\rangle}{W - H_{ii}}. \quad (6.28)$$

Now, if H_o is diagonal, each of the basis states $|i\rangle$ is an eigenvector with eigenvalue H_{ii} . Likewise, if all the H_{ij} terms are very small compared to the differences between

the H_{ii} elements, the basis states $|i\rangle$ are very close to the eigenvectors of H_o and have eigenvalues near H_{ii} .

Next, if two of the basis states $|n\rangle$ and $|m\rangle$ approach degeneracy so that $H_{nn} \simeq H_{mm}$ while all other differences between H_{ii} values are large compared to the off-diagonal elements H_{ij} , two of the eigenvectors come out composed almost exclusively of the states $|n\rangle$ and $|m\rangle$. Thus it is useful to write an effective 2×2 Hamiltonian V (as in eq. (6.21)) that treats $|n\rangle$ and $|m\rangle$ as a complete basis (so that the completeness relation $\sum_{j=n,m} |j\rangle\langle j| = I$ holds). In this new basis one has the new eigenvectors $|W'\rangle$ with eigenvalues W' such that $W' \simeq W$ and $|W'\rangle \simeq |W\rangle$. In this basis one has, where $V_{ij} = \langle i|V|j\rangle$,

$$V|W'\rangle = W'|W'\rangle \quad \text{and} \quad \langle i|V|W'\rangle = W'\langle i|W'\rangle \quad (6.29)$$

and so

$$\begin{aligned} W'\langle n|W'\rangle &= \langle n|V|W'\rangle = \sum_{j=n,m} \langle n|V|j\rangle\langle j|W'\rangle & (6.30) \\ &= \langle n|V|n\rangle\langle n|W'\rangle + \langle n|V|m\rangle\langle m|W'\rangle \\ &= V_{nn}\langle n|W'\rangle + V_{nm}\langle m|W'\rangle \\ W'\langle m|W'\rangle &= V_{mn}\langle n|W'\rangle + V_{mm}\langle m|W'\rangle \end{aligned}$$

Combining eqs. (6.27) and (6.30), one obtains

$$\begin{aligned} W'\langle n|W'\rangle &= V_{nn}\langle n|W'\rangle + V_{nm}\langle m|W'\rangle \\ \simeq W\langle n|W\rangle &= H_{nn}\langle n|W\rangle + H_{nm}\langle m|W\rangle + \sum_{j \neq n,m} H_{nj}\langle j|W\rangle \end{aligned} \quad (6.31)$$

which, when $\langle j|W\rangle$ is expanded using eq. (6.28) so that all terms end in $\langle n|W\rangle$ or $\langle m|W\rangle$, gives to 4th order in off-diagonal elements of H_o

$$\begin{aligned} V_{nn} \simeq H_{nn} &+ \sum_{j \neq n,m} \frac{H_{nj}H_{jn}}{W - H_{jj}} + \sum_{j \neq n,m} \sum_{k \neq j,n,m} \frac{H_{nj}H_{jk}H_{kn}}{(W - H_{jj})(W - H_{kk})} & (6.32) \\ &+ \sum_{j \neq n,m} \sum_{k \neq j,n,m} \sum_{l \neq k,n,m} \frac{H_{nj}H_{jk}H_{kl}H_{ln}}{(W - H_{jj})(W - H_{kk})(W - H_{ll})} \end{aligned}$$

$$\begin{aligned} V_{nm} \simeq H_{nm} &+ \sum_{j \neq n,m} \frac{H_{nj}H_{jm}}{W - H_{jj}} + \sum_{j \neq n,m} \sum_{k \neq j,n,m} \frac{H_{nj}H_{jk}H_{km}}{(W - H_{jj})(W - H_{kk})} & (6.33) \\ &+ \sum_{j \neq n,m} \sum_{k \neq j,n,m} \sum_{l \neq k,n,m} \frac{H_{nj}H_{jk}H_{kl}H_{lm}}{(W - H_{jj})(W - H_{kk})(W - H_{ll})}. \end{aligned}$$

Using $W'\langle m|W'\rangle \simeq W\langle m|W\rangle$ instead of $W'\langle n|W'\rangle \simeq W\langle n|W\rangle$ gives similar expressions for V_{mn} and V_{mm} . The pattern is rather straightforward. One simply connects the two basis states $|n\rangle$ and $|m\rangle$ using elements of H_o as links. Each link connects one basis state (or node) to another. The nodes $|n\rangle$ and $|m\rangle$ can be used a total of

two times, once at the beginning, and once at the end. The remaining nodes can only be connected by off-diagonal elements of H_o and the links are given by terms $H_{ij}/(W - H_{ii})$, which multiply together to give the total product, part of one of the four elements of V . Also, since H_o is Hermitian, V can be shown to be Hermitian using $H_{ij} = H_{ji}^*$, replacing $\sum_{k \neq j, n, m}$ by $\sum_{k \neq n, m} (1 - \delta_{jk})$, swapping indices, and rearranging terms.

Now, when the two states $|n\rangle$ and $|m\rangle$ are nearly degenerate, their eigenvalues W can be found approximately by diagonalizing the 2×2 V in eq. (6.21). The only problem is that V is given in terms of W . This is not a big problem when $W \simeq W'$ is very close to $H_{nn} \simeq H_{mm}$ and the off-diagonal elements H_{ij} of H_o are tiny compared to the differences $W - H_{ii}$. For such cases one can replace W in the expressions for V by H_{nn} , H_{mm} , or their average. This then gives when V is diagonalized approximately correct eigenvalues $W' = W_a, W_b$ and eigenvectors $|W'\rangle = |a\rangle, |b\rangle$, as in section 6.2.5.

Using the above method, near $J = 0$ in the rhombic case with $N = 0$, one obtains, using 6 intermediate levels, minimum energy differences as low as 0.8 and 2 Hz for the repulsions $\frac{7}{2}T_+$, $-\frac{7}{2}T$ (scaling roughly as $A_1^3 A_2^4$) and $\frac{7}{2}T_-$, $-\frac{7}{2}S$ (scaling roughly as $A_1^4 A_2^3$), respectively. Similarly, near $J = -500$ MHz in the $H_d \neq 0$, $\epsilon = 10^\circ$ case with $N = 0$, the levels $\frac{7}{2}T_+$ and $\frac{1}{2}T$ repel via 4 intermediate levels by about 2 Hz (scaling roughly as $A_1^3 \sin^4 \epsilon$). These compare favorably to results calculated via numerical diagonalization of the full Hamiltonian. It is also interesting that such small splittings can occur when they are determined by much larger spin Hamiltonian terms. Note, however, that the above method is rather unwieldy compared to numerical diagonalization methods for doing such calculations and that its accuracy tends to decrease for larger repulsions. Its chief value is the qualitative insight it gives about magnitudes and causes of level repulsions.

One insight the above method gives is that level repulsions are smaller for larger numbers of intermediate states. Thus, in Fig. 6.2a, the largest repulsions occur near $J = 0$ for the levels closest to energy zero because these levels can connect more directly via a smaller number of intermediate states. Similarly, the repulsions at larger J tend to decrease, in part because the crossing levels require more spin flips, and so larger numbers of intermediate states, in order to repel.

6.3 Yields

Having discussed the B_{12} system energy levels, this chapter moves on to singlet-to-triplet yields Φ_{ST} . To this end, eq. (3.24) is useful and gives for $l_{max} = 0$ (cases with