If we add eqs. (4.44) and (4.46) we form a new angular momentum operator, the total angular momentum

$$\hbar\mathbf{j} = \hbar(\mathbf{l} + \mathbf{s}) \tag{4.47}$$

whose equation of motion is

$$\frac{\mathrm{d}}{\mathrm{d}t}(\hbar\mathbf{j}) = \xi\mathbf{s} \times \mathbf{l} + \xi\mathbf{l} \times \mathbf{s} = 0. \tag{4.48}$$

In other words, $\mathbf{j}$ is a constant of the motion for the problem and it commutes with the Hamiltonian $\mathscr{H}_0 + \xi\mathbf{s} \cdot \mathbf{l}$. This constant of the motion is just what we have set out to find.

It can be verified that $\mathbf{j}$, introduced here through eq. (4.47), obeys the commutation rules

$$[j_x, j_y] = \mathrm{i}j_z \quad \text{(and cyclically)} \tag{4.49}$$

and so, like $\mathbf{l}$ and $\mathbf{s}$, it satisfies the rule for a quantum-mechanical angular momentum operator.

The mechanics of the vector model are as follows: since $\mathbf{l} \times \mathbf{l} = 0$ we can rewrite eq. (4.38) as

$$\frac{\mathrm{d}}{\mathrm{d}t}(\hbar\mathbf{l}) = \xi(\mathbf{s} + \mathbf{l}) \times \mathbf{l} = \xi\mathbf{j} \times \mathbf{l}. \tag{4.50}$$

Similarly

$$\frac{\mathrm{d}}{\mathrm{d}t}(\hbar\mathbf{s}) = \xi\mathbf{j} \times \mathbf{s}. \tag{4.51}$$

These two equations represent a classical *precession* of $\mathbf{l}$ and $\mathbf{s}$ about $\mathbf{j}$ with a precession frequency $\omega = |\xi\mathbf{j}|/\hbar$, i.e.,

$$\frac{\mathrm{d}\mathbf{l}}{\mathrm{d}t} = \boldsymbol{\omega} \times \mathbf{l}. \tag{4.52}$$

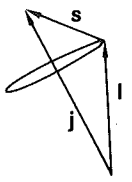

Fig. 4.2. The vector model representing $\mathbf{l} + \mathbf{s} = \mathbf{j}$, with precession.

The vector addition $\mathbf{l} + \mathbf{s} = \mathbf{j}$ and the precession are represented in Fig. 4.2. The larger the magnitude of ξ, which determines the energy of interaction in the perturbation term $\xi\mathbf{s} \cdot \mathbf{l}$, the faster the rate of precession

The time average of $\mathbf{l}_1 \cdot \mathbf{s}_1$, indicated by a bar, with respect to the rapid precessional motion is

$$\overline{\mathbf{l}_1 \cdot \mathbf{s}_1} = \overline{\left(\frac{(\mathbf{l}_1 \cdot \mathbf{L})}{L^2}\mathbf{L}\right) \cdot \left(\frac{(\mathbf{s}_1 \cdot \mathbf{S})}{S^2}\mathbf{S}\right)}. \tag{7.39}$$

But $\mathbf{L} \cdot \mathbf{S}$ is constant under this averaging process, hence

$$\overline{\sum_i \xi_i \mathbf{l}_i \cdot \mathbf{s}_i} = \zeta(L, S)\mathbf{L} \cdot \mathbf{S} \tag{7.40}$$

where

$$\zeta(L, S) = \overline{\sum_i \xi_i \frac{(\mathbf{l}_i \cdot \mathbf{L})(\mathbf{s}_i \cdot \mathbf{S})}{L^2 S^2}}. \tag{7.41}$$

The rule is therefore: consider the most rapid precessional motion first, and project each of the individual vectors partaking in that motion on to their resultant. In transferring to quantum mechanics, the quantities L^2 and S^2 in eq. (7.41) are replaced by expectation values $L(L + 1)$ and $S(S + 1)$.

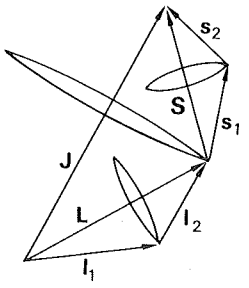

Fig. 7.3. Vector model for the angular momenta of two electrons in *LS* coupling.

This rule is a good one because quantum mechanics makes an equivalent statement in terms of matrix elements rather than time averages. To illustrate the projection procedure we refer to operators in orbit space. In taking matrix elements *diagonal in* L the dependence on M_L of *any vector operator in orbit space*, in particular $\mathbf{l}_i$, is just that of the operator $\mathbf{L}$ itself. The reason for this is that all vector operators in orbit space transform in the same way under a rotation of the co-ordinate system so that the dependence on the orientation of the co-ordinate system (the M_L dependence) is the same for all. Thus for matrix elements diagonal in L we can write the direct proportionality:

$$\langle LM_L|\, \mathbf{l}_i \,|LM'_L\rangle = c\langle LM_L|\, \mathbf{L} \,|LM'_L\rangle \tag{7.42}$$

where the constant of proportionality c is independent of M_L and M'_L.