

## Direct Products of Irreps

- When we have products of functions (say, angular momentum or spin eigenfunctions), their symmetry properties involve direct products of irreps of  $SU(2)$  or  $SO(3)$ .
- These can be obtained from the Clebsch-Gordan series, namely

$$D^{j_1} \otimes D^{j_2} = \sum_{j=|j_1-j_2|}^{j_1+j_2} D^j.$$

- For example,  $D^{\frac{3}{2}} \otimes D^{\frac{5}{2}}$  gives  $D^1 \oplus D^2 \oplus D^3 \oplus D^4$ .
- Total degeneracy is a useful check:  $(2j_1 + 1) * (2j_2 + 1)$ .



## Eigenfunctions of Spin

- We have already encountered the two basic spinors

$$\alpha = \left| \begin{array}{cc} 1 & 1 \\ 2 & 2 \end{array} \right\rangle \quad \beta = \left| \begin{array}{cc} 1 & 1 \\ 2 & -2 \end{array} \right\rangle.$$

- These are eigenfunctions of the spin operators associated with one electron. We denote the latter by  $\hat{s}^2$  and  $\hat{s}_z$ , with eigenvalues  $s(s + 1)$  and  $m_s$  respectively.
- If we have more than one electron we use the labels

$$\hat{S}^2 = \sum_i \hat{s}^2(i) \quad \hat{S}_z = \sum_i \hat{s}_z(i),$$

with eigenvalues  $S(S + 1)$  and  $M_S$ , and where  $i$  runs over all electrons.

- What does this mean for two electrons?



## Two-electron Spin Eigenfunctions

- We can build four combinations of  $\alpha$  and  $\beta$  for two electrons:  $\alpha(1)\alpha(2)$ ,  $\alpha(1)\beta(2)$ ,  $\beta(1)\alpha(2)$ , and  $\beta(1)\beta(2)$ .
- The direct product of the irrep  $D^{\frac{1}{2}}$  of  $SU(2)$  with itself is  $D^0 \oplus D^1$  (singlet and triplet).
- Since the combination  $\alpha(1)\alpha(2)$  has  $M_S = 1$ , it must be the  $|1\ 1\rangle$  component of the triplet. We can apply the shift operator to get the other  $M_S$  components.



## Two-electron Spin Eigenfunctions

- We obtain

$$\begin{aligned} |1\ 0\rangle &= \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\ |1\ -1\rangle &= \beta(1)\beta(2) \end{aligned}$$

- Then the singlet will be

$$|0\ 0\rangle = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

where we adopt the convention that the particle label is indicated by its position.



## Three Electrons

- We have

$$\begin{aligned}
 D^{\frac{1}{2}} \otimes D^{\frac{1}{2}} \otimes D^{\frac{1}{2}} &= D^{\frac{1}{2}} \otimes \{D^0 \oplus D^1\} \\
 &= 2D^{\frac{1}{2}} \oplus D^{\frac{3}{2}}.
 \end{aligned}$$

- The quartet ( $S = \frac{3}{2}$ ) case is straightforward. We can begin with the  $M_S = \frac{3}{2}$  component  $\alpha\alpha\alpha$ , and apply shift operators to get the other components.
- But how do we handle the two doublets? And what we do if we have more electrons??



## Permutational Symmetry

- Recall(!) that the Born-Oppenheimer Hamiltonian is not only independent of spin, it is invariant to permutations of identical particles (electrons).
- That is, the Hamiltonian operator commutes with all permutations of the electrons. This is of course the symmetric group of  $N$  objects.
- $\mathcal{A}(N)$  has many irreps. Which of these are valid for a system of electrons? Electrons have spin  $\frac{1}{2}$ : they obey *Fermi-Dirac statistics*. The total wave function must be *antisymmetric* with respect to exchange of two electrons:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N) = -\Psi(\mathbf{x}_2, \mathbf{x}_1 \dots \mathbf{x}_N).$$

This is the Pauli principle.



## Permutational Symmetry

- Each electron coordinate  $\mathbf{x}_i$  comprises a *space* part, denoted  $\vec{r}_i$ , and a spin part  $\sigma_i$ . We can restate the Pauli principle as

$$\Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2 \dots \vec{r}_N\sigma_N) = -\Psi(\vec{r}_2\sigma_2, \vec{r}_1\sigma_1 \dots \vec{r}_N\sigma_N).$$

$\Psi$  transforms as a basis function for the *totally antisymmetric* irrep of  $\mathcal{A}(N)$ .

- Suppose now we want to write our wave function as a product of two functions that depend respectively on space coordinates alone and spin coordinates alone:

$$\Psi(\vec{r}_1\sigma_1 \dots \vec{r}_N\sigma_N) = \Xi(\vec{r}_1 \dots \vec{r}_N) \Theta(\sigma_1 \dots \sigma_N).$$

- What does the Pauli principle imply about the permutational symmetry of  $\Xi$  and  $\Theta$ ?



## Permutational Symmetry

- If we denote the totally antisymmetric irrep of  $\mathcal{A}(N)$  by  $D^{-1}$ , then for the Pauli principle to be satisfied, at least one irrep  $D^i$  in

$$D^{\Xi} \otimes D^{\Theta} = \sum_i c_i D^i$$

must be  $D^{-1}$ .

- This corresponds to only three possible cases. The first two are obvious:

$$\begin{array}{ll} D^{\Xi} = D^{-1} & D^{\Theta} = D^1 \\ D^{\Xi} = D^1 & D^{\Theta} = D^{-1} \end{array}$$

where  $D^1$  is the totally symmetric irrep.

- We will return to what the third case is later.



## Spin Part is Totally Symmetric

- This is easily arranged: the spin part is  $\alpha\alpha\alpha\dots$  for the highest  $M_S$  case ( $S = \frac{N}{2}$ ).
- All other  $M_S$  cases for this  $S$  can be obtained from shift operators.
- Then the space part has to be totally antisymmetric.



## Spin Part is Totally Antisymmetric

- We have only two basic spin functions! How do we construct spin functions of more than two electrons that are totally antisymmetric?
- We cannot. The only case in which the spin part is totally antisymmetric is the two-electron singlet  $\alpha\beta - \beta\alpha$ , for which the space part must be totally symmetric.
- Sidebar: projection operator for the totally antisymmetric irrep.



## Spin Part is a Degenerate Irrep of $\mathcal{A}(N)$

- This is the third case referred to above. It requires that  $D^{\Xi}$  and  $D^{\ominus}$  are *conjugate* irreps of  $\mathcal{A}(N)$ . These are defined as irreps whose direct product, on reduction, contains the totally antisymmetric irrep.
- Sidebar: Conjugate irreps via Young shapes.
- Obtain appropriate spin functions by applying projection operators for  $\mathcal{A}(N)$ .
- This becomes quite difficult in practice: use a sequential or *genealogical* coupling scheme. Use spin eigenfunctions for  $N$  electrons to get spin eigenfunctions for  $N + 1$ .



## Genealogical Spin-Coupling Scheme

- Start with an  $N$  electron spin eigenfunction denoted  $\Theta_S^N$  (with  $M_S = S$ ) and construct

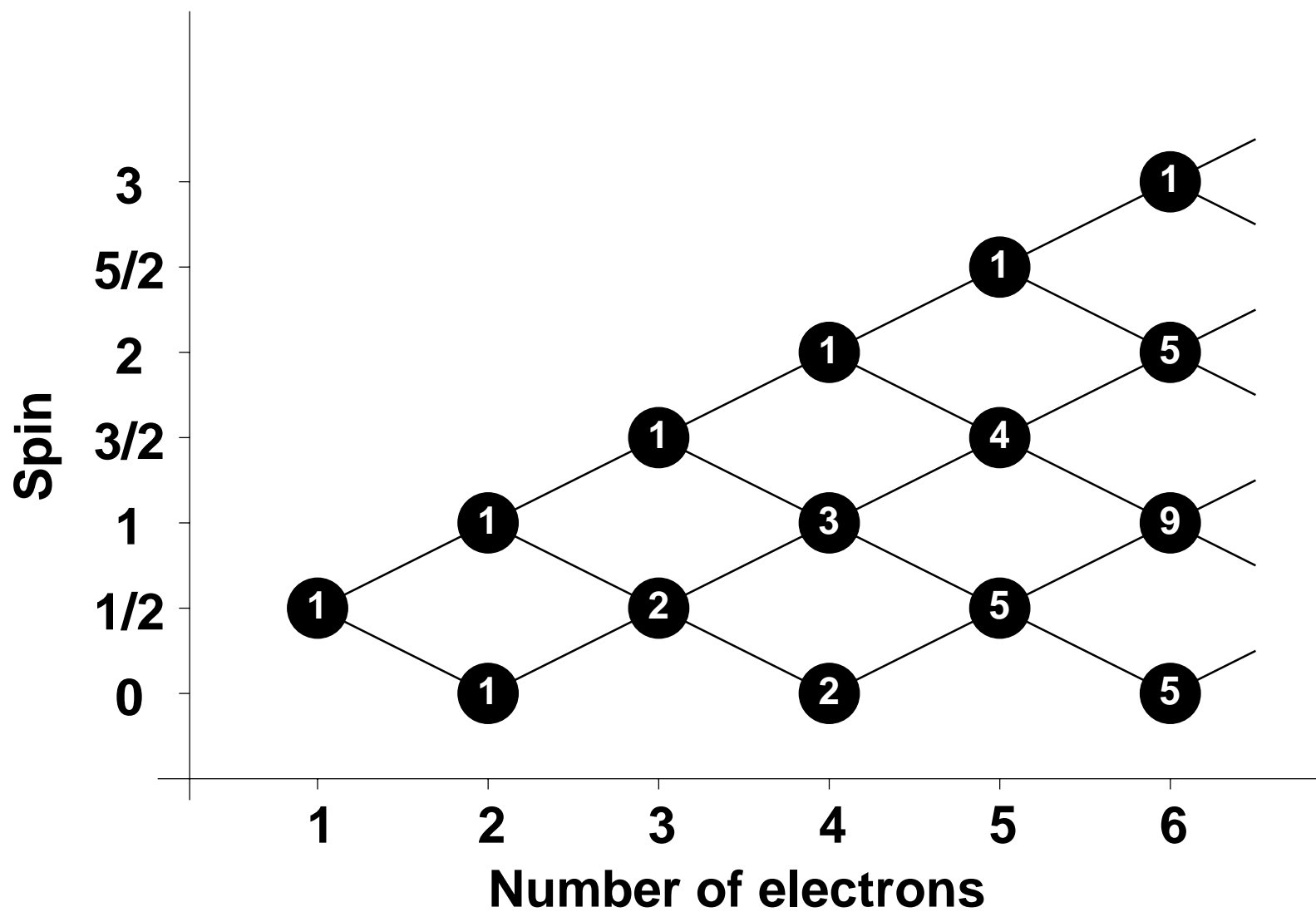
$$\Theta_{S+\frac{1}{2}}^{N+1} = \Theta_S^N \alpha$$

$$\Theta_{S-\frac{1}{2}}^{N+1} = -\left(\hat{S}_- \Theta_S^N\right) \alpha + 2S\Theta_S^N \beta.$$

- These are the two possible spin eigenfunctions that can be constructed from  $\Theta_S^N$  (unless  $S = 0$ , in which case only the first construction is possible).
- We couple “up” and “down” from  $\Theta_S^N$ , which can be shown diagrammatically.



## Branching Diagram



## Genealogical Spin-Coupling Scheme

- The number of spin eigenfunctions  $f(N, S)$  with spin  $S$  for  $N$  electrons is

$$f(N, S) = \frac{(2S + 1)N!}{(N/2 + S + 1)!(N/2 - S)!}.$$

- For 30 electrons this gives us ten million singlet spin couplings. . .
- In practice there are substantial simplifications possible. In an orbital model, for example, any orbital that is fully occupied contributes nothing to the overall spin. Thus only electrons in partially occupied orbitals must be considered (“open shells”).

