An Engineer's Guide to Quantized Angular Momentum

The magnitude of an angular momentum vector **j** with quantum number j is given by:

$$|\mathbf{j}| = \frac{h}{2\pi}\sqrt{j(j+1)} = \hbar\sqrt{j(j+1)}$$; j can take integer or half-integer values only.

Orbital angular momentum vectors are restricted to integer quantum numbers but spin angular momenta may have either integer or half-integer quantum numbers. An angular momentum state is not completely specified by the single quantum number j. The projection of the vector **j** on any space-fixed axis (traditionally one uses the z-axis) is also quantized. The magnitude j_z is thus an additional quantum number.

$$j_z = m\hbar$$; where $m = j, j\text{-}1,...,\text{-}j$; $(2j+1)$ possible values.

If space is isotropic (no electric or magnetic fields) then angular momentum states with the same j, but different j_z have the same energy, i.e. **j** is $(2j+1)$-fold degenerate.

When two angular momenta couple with each other the resultant depends on the orientation of the vectors. Since specifying the quantum number j, does not specify the direction, one can get several different results when angular momenta of magnitudes j_1 and j_2 are added. The discussion below uses spin as an example of an angular momentum, but the rules are the same for any type of angular momentum coupling, i.e. spin-spin, spin-orbit, orbit-orbit, … I use s for spin quantum number designation, which is a mnemonic for spin. This is the conventional symbol for individual electron spins, nuclear spin quantum numbers are usually designated by I.

If there are two spins characterized by spin quantum numbers s_1 and s_2, then the quantum rules for adding angular momentum say that the resultant vector has a spin quantum number that obeys the following sum rule:

$\mathbf{s} = \mathbf{s}_1 + \mathbf{s}_2 \Rightarrow s$ can have any one of the following values: (s_1+s_2), $(s_1+s_2\text{-}1)$, $(s_1+s_2\text{-}2)$,...$|s_1\text{-}s_2|$

For example, if $s_1{=}1$, $s_2{=}2$, then $s = 3,2$, or 1. Similarly, if $s_1{=}\frac{1}{2}$, $s_2{=}\frac{1}{2}$, then the resultant $s = 1$ or 0. In general, the energies of the states with different resultant angular momentum are different, although differences may be small.

When angular momenta with quantum numbers s_1 and s_2 couple, then there are $(2s_1+1)(2s_2+1)$ possible combinations, corresponding to the different possible orientations of the original two vectors (i.e. different values of s_z) and remembering that one is doing a vector addition. If you compare the $(2s+1)$ fold degeneracy of the angular momenta generated by the sum rule given above you find that it matches.

Specifically, for the example above where $s_1{=}1$, $s_2{=}2$, we have $(2s_1+1){=} 3$, $(2s_2+1) = 5$, so there should be 3×5=15 possible vector combinations. If you use the results of the sum rule for the possible results you get:

s	$(2s+1)$-*fold degeneracy*
3	$2 \times 3 + 1 = 7$
2	$2 \times 2 + 1 = 5$
1	$2 \times 1 + 1 = 3$
Total	15

Similarly, if $s_1 = s_2 = \dfrac{1}{2}$ then $(2s+1) = 2$ (corresponding to $s_z = \pm\dfrac{1}{2}$ spin "up" or "down") there should be $2 \times 2 = 4$ combinations. Again:

s	$(2s+1)$-*fold degeneracy*
1	$2 \times 1 + 1 = 3$
0	$0 \times 2 + 1 = 1$
Total	4

Finally, if the particles are identical, and the angular momentum quantum numbers are the same, then the vector combinations can also be examined for their symmetry with respect to exchange of these identical particles. If $s_1 = s_2 = s$ then there are:

$(s+1)(2s+1)$ combinations that are symmetric, and

$s(2s+1)$ combinations that are anti-symmetric

with respect to exchange of identical particles. Returning to the $s_1 = s_2 = \frac{1}{2}$ example,

there are $(\dfrac{1}{2} + 1) \times (2 \times \dfrac{1}{2} + 1) = 3$ symmetric combinations, and (you do the math) 1 anti-symmetric combination. Incidentally, don't be fooled by the coincidence of 3 and 1 with the values in the table above. The $(s_1 + s_2) = 0$ combination is symmetric; two other symmetric states and one anti-symmetric state are obtained from the three $(s_1 + s_2) = 1$ states.

One final example, you work out the details: $s_1 = s_2 = 1$. The resultant $(s_1 + s_2) = 2$, 1, or 0. There are $3 \times 3 = 9$ individual spin quantum states possible, distributed 5, 3, and 1 between $(s_1 + s_2) = 2$, 1, and 0 respectively. If these are identical bosons, e.g. ^{14}N nuclei, then we must distinguish symmetry of the combinations. There are 6 symmetric and 3 anti-symmetric spin quantum states that can be formed.

The symmetric and anti-symmetric spin combinations are associated with symmetric and anti-symmetric rotational, vibrational, and electronic state descriptions so that the **overall** description is symmetric (for identical bosons) or anti-symmetric (for identical fermions).

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Rotational states and nuclear spin

Heteronuclear molecules

For heteronuclear molecules, e.g. CO, HD, DT, $^{16}O^{17}O$, etc. the effects of nuclear spin can be safely neglected. They are only needed if one needs to enumerate the total number of microstates precisely. For a generic molecule AB with nuclear spins I_a and I_b respectively, the nuclear spin degeneracy $g_{ns} = (2I_a+1)(2I_b+1)$ appears as a constant multiplier for the degeneracy of each rotational (actually angular momentum) state (it is temperature- and J-independent). Thus the rotational partition function can be computed as follows:

$$Q_{rot} = \sum_J (2I_a + 1)(2I_b + 1)(2J + 1)e^{-\frac{\varepsilon(J)}{kT}} = \sum_J g_{ns}(2J + 1)e^{-\frac{\varepsilon(J)}{kT}} = g_{ns}\sum_J (2J + 1)e^{-\frac{\varepsilon(J)}{kT}}.$$

The spin degeneracy terms can be factored out of the sum because they are the same for all states. Here $\varepsilon(J)$ is the energy of rotational state with quantum number J. If one uses a rigid rotor approximation for the rotational energy, $\varepsilon(J) = k\theta_r J(J+1)$, then:

$$g_{ns}\sum_{J=0,1,2,3,...}(2J + 1)e^{-\frac{J(J+1)\theta_r}{T}} \approx g_{ns}\frac{T}{\theta_r}.$$

in the usual limit $T \gg \theta_r$. When calculating population fractions in a particular rotational state described by quantum number J, we have

$$\frac{n_J}{n} = \frac{g_{ns}(2J + 1)e^{-\frac{\varepsilon(J)}{kT}}}{g_{ns}\sum_J (2J + 1)e^{-\frac{\varepsilon(J)}{kT}}} = \frac{(2J + 1)e^{-\frac{\varepsilon(J)}{kT}}}{\sum_J (2J + 1)e^{-\frac{\varepsilon(J)}{kT}}}.$$

Thus the fraction can be computed correctly neglecting the spin degeneracy completely and computing the rotational partition function from

$$Q_{rot} = \sum_J (2J + 1)e^{-\frac{\varepsilon(J)}{kT}} \approx \frac{T}{\theta_r}.$$

The rotational partition function so computed is too small by the constant factor g_{ns}. However, since thermodynamic properties depend on $\partial \ell n Q_{rot}/\partial T$ no error is induced by neglecting it. It is true that there is an error in absolute entropy associated with enumerating microstates because Ω will be undercounted by a factor g_{ns} i.e.

$$\Omega_{true} = g_{ns}\, \Omega_{neglecting\ spin}$$

However:

$$S = k\,\ell n\Omega_{true} = k\left[\ell n\,\Omega_{neglecting\ spin} + \ell n\, g_{ns}\right]$$

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Because $\ell n\ \Omega_{neglecting\ spin}$ is so large (typically ~10^{20}) the factor $\ell n\ g_{ns}$ which is invariably ~1 is negligible unless one is dealing with systems at temperatures close to absolute zero. In any case changes in entropy are correctly calculated because $\ell n\ g_{ns}$ is a constant.

Homonuclear molecules

For homonuclear molecules, e.g. H_2, D_2, O_2($^{16}O^{16}O$), etc. the effects of nuclear spin must be considered when computing both the rotational partition function and the fractional populations. The overall wave function describing the system must be symmetric with respect to exchange of identical bosons and anti-symmetric with respect to exchange of identical fermions. Rotational motion of the nuclear framework exchanges the nuclei in space and hence spin-symmetry effects affect the rotational states. For the simplest case of a linear diatomic molecule a rotation through 180° exchanges the nuclear positions.[1] The wave function describing the nuclear rotational motion must have the correct symmetry for fermions or bosons (or both, e.g. acetylene which is H-C≡C-H). For a rotation through 180° the rotational wavefunctions are anti-symmetric (i.e. change sign, –) for odd J, and symmetric (i.e. do not change sign, +) for even J. Now the overall wavefunction must be symmetric for bosons or anti-symmetric for fermions with respect to the exchange of the nuclei (and only the nuclei). However, when the nuclei rotate they carry the electrons with them. To bring the electrons back to where they started from, leaving the nuclei where they were carried by the rotation (say about the z-axis) one needs two successive operations: (i) reflect electrons in xy-plane $[(x,y,z) \rightarrow (x,y,-z)]$; (ii) invert all electrons through the origin $[(x,y,z) \rightarrow (-x,-y,-z)]$. Explicitly, if the electron coordinates were (x_e,y_e,z_e) initially, then the first rotation through 180° about the z-axis gives $(x_e,y_e,z_e) \rightarrow (-x_e,-y_e,z_e)$. Now $(-x_e,-y_e,z_e)$ $\xrightarrow{(i)} (-x_e,-y_e,-z_e) \xrightarrow{(ii)} (x_e,y_e,z_e)$, and the electron is back where it started. The electron wave function designations tell us how the wave function behaves under operations (i) and (ii).

Usually the electronic ground state has zero resultant electronic orbital angular momentum (denoted as a Σ state). In this case the state is designated Σ^+ or Σ^- depending on whether reflection operation (i) leaves the wave function sign unchanged or changed respectively. If the charge distribution has a center of symmetry (as it must for homonuclear molecules) then a subscript g or u is added to indicate the result of the inversion operation (ii), g for symmetric, and u for anti-symmetric.

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[1] The same general principle applies to more complicated molecules, e.g. in NH_3 at equilibrium the three H atoms form an equilateral triangle in a plane with the N atom above or below. Hence a rotation through 120° or 240° exchanges H atom positions. We will not consider these more complicated cases, but restrict ourselves to homonuclear diatomics.

	Symmetry differentiator	Degeneracy contribution	Effect on wave function
Nuclear spin, I I fixed	*Ortho* (symmetric) *Para* (anti-symmetric)	$(I+1)(2I+1)$ $I(2I+1)$	+ –
Rotation, J J varies	Even J Odd J	$(2J+1)$ $(2J+1)$	+ –
Electronic reflection	+ –	n a	+ –
Electronic inversion	g u	n a	+ –

Example 1:

Ground state (X) of N_2: $^1\Sigma_g^+$, nuclei are bosons with $I = 1$. Because nuclei are bosons the overall wavefunction must be symmetric (+) with respect to exchange.

Electronic	Nuclear spin	Rotation	Overall	Nuclear spin degeneracy
(+)×(+)=(+) + g	*ortho* (+) *para* (–)	Even J (+) Odd J (–)	(+) (+)	$(I+1)(2I+1) = 6$ (g_{even}) $I(2I+1) = 3$ (g_{odd})

Example 2:

Excited (A) state of N_2: $^3\Sigma_u^+$, nuclei are bosons with $I=1$. Because nuclei are bosons the overall wavefunction must be symmetric (+) with respect to exchange.

Electronic	Nuclear spin	Rotation	Overall	Nuclear spin degeneracy
(+)×(–)=(–) + u	*ortho* (+) *para* (–)	Odd J (–) Even J (+)	(+) (+)	$(I+1)(2I+1) = 6$ (g_{odd}) $I(2I+1) = 3$ (g_{even})

Note: In the A excited state of N_2 it is the odd J states that have greater degeneracy.

Example 3:

Ground (*X*) state of O_2: $^1\Sigma_g^-$, nuclei are bosons with *I*=0. Because nuclei are bosons the overall wavefunction must be symmetric (+) with respect to exchange.

Electronic	Nuclear spin	Rotation	Overall	Nuclear spin degeneracy
(–)×(+)=(–)	*ortho* (+)	Odd *J* (–)	(+)	(*I*+1)(2*I*+1) = 1 (g_{odd})
– *g*	*para* (–)	Even J (+)	(+)	*I*(2*I*+1) = 0 (g_{even})

Example 4:

Ground (*X*) state of H_2: $^1\Sigma_g^+$, nuclei are fermions with $I={}^1/_2$. Because nuclei are fermions the overall wavefunction must be anti-symmetric (–) with respect to exchange.

Electronic	Nuclear spin	Rotation	Overall	Nuclear spin degeneracy
(+)×(+)=(+)	*ortho* (+)	Odd *J* (–)	(–)	(*I*+1)(2*I*+1) = 3 (g_{odd})
+ *g*	*para* (–)	Even J (+)	(–)	*I*(2*I*+1) = 1 (g_{even})

Partition function calculation

We assume that only the ground electronic state is significantly populated, so only sums over rotational states in the ground electronic state need to be considered. Hence even if excited states have different statistics than the ground state, e.g. the *A*-state of N_2, the error in the calculation of partition function is insignificant. When computing the rotational partition function one has to sum over even and odd *J* separately because they are multiplied by different nuclear spin degeneracies.

$$Q_{rot} = \sum_{all\,J} g_{spin}(2J+1)e^{-\frac{\varepsilon(J)}{kT}} = g_{even}\sum_{\substack{even\,J \\ J=0,2,4,..}}(2J+1)e^{-\frac{\varepsilon(J)}{kT}} + g_{odd}\sum_{\substack{odd\,J \\ J=1,3,5,..}}(2J+1)e^{-\frac{\varepsilon(J)}{kT}}$$

If one uses a rigid rotor approximation for the rotational energy, $\varepsilon(J) = k\theta_r\, J(J+1)$, and in the usual limit $T \gg \theta_r$, then:

$$\sum_{J=0,2,4,...}(2J+1)e^{-\frac{J(J+1)\theta_r}{T}} = \sum_{J=1,3,5,...}(2J+1)e^{-\frac{J(J+1)\theta_r}{T}} = \frac{T}{2\theta_r}.$$

Hence, in this limit

$$Q_{rot} = (g_{even} + g_{odd})\frac{T}{2\theta_r} = \left((I+1)(2I+1) + I(2I+1)\right)\frac{T}{2\theta_r} = (2I+1)^2\frac{T}{2\theta_r}$$

The fractional population in any rotational state is then given by:

$$\frac{n_J}{n} = \frac{g_{even/odd}(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{(g_{even} + g_{odd})\frac{T}{2\theta_r}} = \left[\frac{g_{even/odd}}{(g_{even} + g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right]$$

The numerical value of the fraction $\frac{g_{even/odd}}{(g_{even} + g_{odd})} = \frac{I+1}{2I+1} \text{ or } \frac{I}{2I+1}$ arising from nuclear spin statistics depends on the type of the nucleus (fermion or boson), the nuclear spin quantum number, and the electronic state symmetries as discussed above.

Example 1b: N_2 (see Example 1 above)

$$\frac{n_{J\,even}}{n_{total}} == \left[\frac{g_{even}}{(g_{even} + g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = \frac{6}{9}\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right];$$

$$\frac{n_{J\,odd}}{n_{total}} == \left[\frac{g_{odd}}{(g_{even} + g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = \frac{3}{9}\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right].$$

Hence the envelopes of the rotational distribution functions for even- and odd-J are in the ratio 6:3 i.e., 2:1. The figure below shows a rotational Raman spectrum of N_2 measured in our laboratory. The relative intensities of individual lines within a branch show the 2:1 intensity alteration predicted by the theory. (The strong elastic light scattering at $\Delta v=0$ is suppressed with an atomic filter).

Rotational Raman Spectrum of $^{14}N_2$ ($I_N=1$)
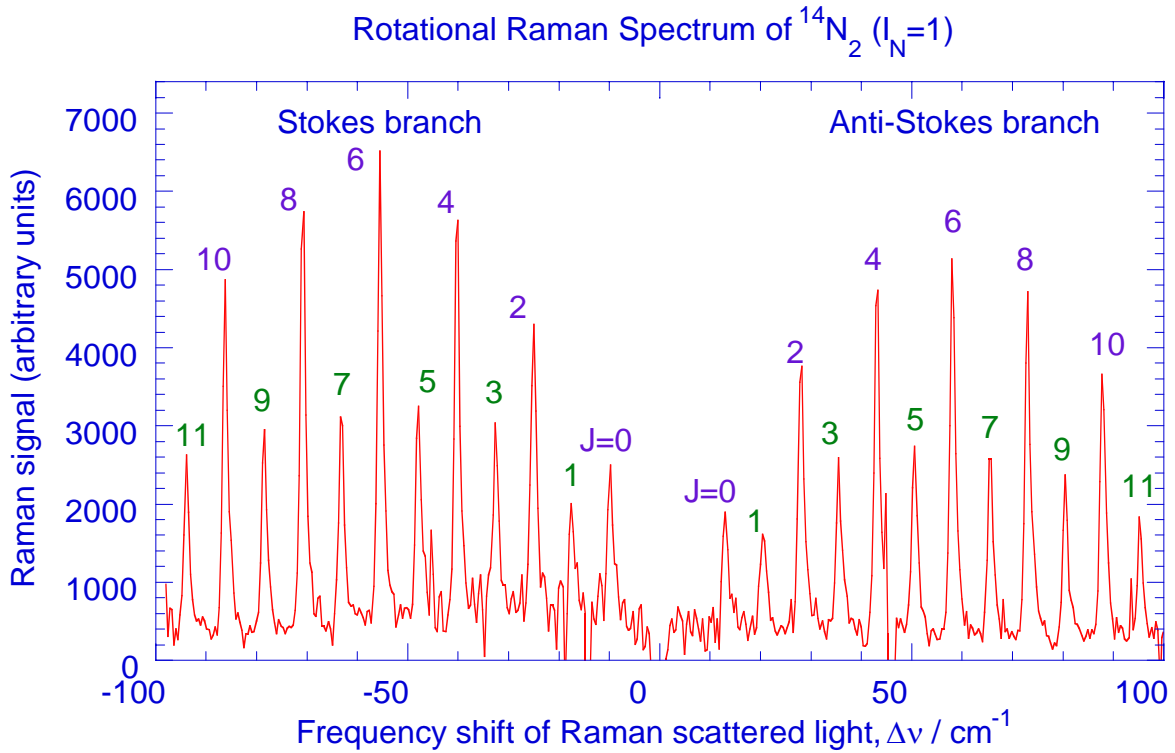
Example 3b: O_2 (see Example 3 above)

$$\frac{n_{J\,even}}{n_{total}} == \left[\frac{g_{even}}{(g_{even}+g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = \frac{0}{1}\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = 0;$$

$$\frac{n_{J\,odd}}{n_{total}} == \left[\frac{g_{odd}}{(g_{even}+g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = \frac{1}{1}\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right].$$

In this case the even-*J* states are missing entirely because $g_{even}=0$.

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Example 4b: H_2 (see Example 4 above)

$$\frac{n_{J\,even}}{n_{total}} == \left[\frac{g_{even}}{(g_{even}+g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = \frac{1}{4}\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right];$$

$$\frac{n_{J\,odd}}{n_{total}} == \left[\frac{g_{odd}}{(g_{even}+g_{odd})}\right]\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right] = \frac{3}{4}\left[\frac{(2J+1)e^{-\frac{J(J+1)\theta_r}{T}}}{\frac{T}{2\theta_r}}\right].$$

Hence the envelopes of the rotational distribution functions for even and odd-*J* are in the ratio 1:3.

States with different nuclear spin symmetry (*ortho-* and *para-*) are not easily inter-converted, i.e. they do not reach thermodynamic equilibrium with each other, but rather behave as different chemical species. Hence if homonuclear diatomic gases are cooled they maintain the ratio of *ortho-* to *para-* that prevails at high ($T>>\theta_r$) temperature. This is most obvious for H_2 which has a large θ_r (~85 K) and condenses at 20 K at atmospheric pressure. Most other gases have much smaller θ_r (~2 K typically) and are not commonly used in the vapor phase at temperatures where $T\sim\theta_r$.

The nuclear spin degeneracy g_{ns} must be treated consistently when computing equilibrium constants. Suppose, for example, that we are computing K_p for the reaction:

$$N_2 + O_2 \rightarrow 2\,NO\,,$$
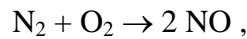
with the common isotopes ^{14}N ($I=1$) and ^{16}O($I=0$). If the three-fold nuclear spin degeneracy of the NO is neglected, one must only use a factor of $\frac{1}{2}$ in the rotational partition functions of N_2 and O_2. Conversely, if one uses $g_{ns}=3\times1=3$ when calculating $Q_{rot}^{NO} = g_{ns}^{NO}\frac{T}{\theta_r^{NO}} = 3\frac{T}{\theta_r^{NO}}$, then the corresponding rotational partition functions of N_2 and O_2 are

$$Q_{rot}^{N_2} = (2I_N+1)^2\frac{T}{2\theta_r^{N_2}} = 9\frac{T}{2\theta_r^{N_2}} \qquad Q_{rot}^{O_2} = (2I_O+1)^2\frac{T}{2\theta_r^{O_2}} = \frac{T}{2\theta_r^{O_2}}.$$

When calculating the equilibrium constant the spin factors cancel and we get the same result as before:

$$\frac{\left(Q_{rot}^{NO}\right)^2}{Q_{rot}^{N_2}Q_{rot}^{O_2}} = \frac{3^2\left(\frac{T}{\theta_r^{NO}}\right)^2}{9\frac{T}{2\theta_r^{N_2}}\frac{T}{2\theta_r^{O_2}}} = \frac{\left(\frac{T}{\theta_r^{NO}}\right)^2}{\frac{T}{2\theta_r^{N_2}}\frac{T}{2\theta_r^{O_2}}}.$$