Nuclear Spin Statistics

The following discussion is largely taken from Atkins' MQM, 1st Edition, p.335.

Any heteronuclear diatomic will show a pure rotational spectrum (as there is a dipole moment, albeit possibly weak, for any heteronuclear diatomic), with all expected lines present in the spectrum. However, for the rotational spectra of homonuclear diatomics[1], there is a complication due to the **nuclear spin statistics**.

Rotating a diatomic molecule is an operation which interchanges the nuclei, and therefore affects the total wavefunction. If the atoms are the same, then this must affect the total wavefunction in accordance with the Pauli principle[2]. With this in mind, consider the expression for the total wavefunction:

$$\Psi_{tot} = \psi_{el}\psi_{vib}\psi_{rot}\psi_{nuc} \tag{1}$$

This should hopefully be familiar to you - decomposing the total wavefunction into a product of a wavefunction for the electrons, nuclear vibrations, nuclear rotations, and nuclear spins respectively. Rotation is essentially relabelling, or permuting, the two nuclei. Permuting the two nuclei, which we will represent with an operator $\hat{P}_{nuc}$, will have the following effects on the various parts of the total wavefunction (we decompose it in this way to analyse the effect it has on various parts of the decomposed wavefunction).

- We rotate the spatial coordinates of the molecule by 180 degrees - the operation $\hat{C}_2$.
- We then invert the coordinates of the electrons ($\hat{i}_{el}$), and then reflect them in a plane orthogonal to the rotation axis ($\hat{\sigma}_{el}$).
- We finally swap, or permute, the nuclear spins - $\hat{p}_n$.

So we can write:

$$\hat{P}_{nuc} = \hat{p}_n\hat{\sigma}_{el}\hat{i}_{el}\hat{C}_2 \tag{2}$$

Operating with this bad boy on the total wavefunction does the following:

$$\hat{P}_{nuc}\Psi_{tot} = \hat{\sigma}_{el}\hat{i}_{el}\psi_{el} \times \psi_{vib} \times \hat{C}_2\psi_{rot} \times \hat{p}_n\psi_{nuc} \tag{3}$$

The vibrational part is unaffected because this only depends on the magnitude of the separation of the nuclei. The overall effect of $\hat{P}_{nuc}$ must be to produce Ψ_{tot} (if the particles are bosons), or to produce $-\Psi_{tot}$ (if they are fermions). So consider now how the sign of each part of the wavefunction changes under it's relevant symmetry operation:

- ψ_{rot} changes by $(-1)^J$ under a C_2 rotation.[3]
- If ψ_{el} is of u or g symmetry then the wavefunction sign changes by 1 or -1 under $\hat{i}_{el}$.
- For a Σ state, we also consider $\Sigma^{\pm}$ - $+$ states and $-$ change by 1 or -1 under $\hat{\sigma}_{el}$. If it's not in a Σ state, both $+$ and $-$ occur, so the wavefunction changes by $1 \times -1 = -1$ if there is one of each state.

---

[1] These are, by definiton, *Raman* transitions - as a rotational electric dipole transition is not allowed for a non-polar molecule, which all homonuclear diatomics are by definiton.

[2] Remember that the Pauli Principle is just a small part of the wider **Spin-Statistics Theorem**, which states that the wavefunction of of a system of *identical* integer-spin particles must have the same value when the positions of any two particles are swapped, and must change sign if the particles have half-integer spin. The point here is that it only matters if the particles are **identical** - if the diatomic was heteronuclear then this argument doesn't apply/isn't necessary. Still another way of looking at it is to say that the Pauli principle ensures that two fermions cannot have the same set of quantum numbers - if the particles are different then they don't have the same set of quantum numbers by definition.

[3] This is only true for a singlet spin state - otherwise we have to couple J to the total spin S, to give $G = J + S$ and therefore $(-1)^G$. This is the case for molecular oxygen, but doesn't actually turn out to affect things very much so the examples we did where we ignored this are still correct - try it and see. You're welcome!

To illustrate how we can use this, consider a ${}^1\Sigma_g^+$ state. We operate with our $\hat{P}_{nuc}$ operator and see what effect it has:

$$\hat{P}_{nuc}\Psi_{tot} = \hat{\sigma}_{el}\hat{i}(\psi_{el}({}^1\Sigma_g^+)) \times \psi_{vib} \times \hat{C}_2\psi_{rot} \times \hat{p}_n\psi_{nuc} \tag{4}$$

$$\hat{P}_{nuc}\Psi_{tot} = (+1)(+1)(\psi_{el}({}^1\Sigma_g^+)) \times \psi_{vib} \times (-1)^J\psi_{rot} \times \hat{p}_n\psi_{nuc} \tag{5}$$

$$\hat{P}_{nuc}\Psi_{tot} = (-1)^J\psi_{el} \times \psi_{vib} \times \psi_{rot} \times \hat{p}_n\psi_{nuc} \tag{6}$$

Which leads to the following expressions for the total wavefunction, depending on whether the nuclear spin wavefunction is symmetric or antisymmetric.

$$\hat{P}_{nuc}\Psi_{tot} = (-1)^J\Psi_{tot} \quad \text{If the nuclear part is symmetric.} \tag{7}$$

$$\hat{P}_{nuc}\Psi_{tot} = (-1)^{J+1}\Psi_{tot} \quad \text{If the nuclear part is antisymmetric - an extra factor of (-1).} \tag{8}$$

So, if we assume the particles are fermions, then the overall wavefunction has to be antisymmetric. Which means that any symmetric spin states will produce lines with **odd** values of J, and vice versa. If the particles are bosons, then the opposite is true - symmetric spin states produce even values of J.

So, the obvious question is then - how do I know if there are symmetric or asymmetric spin states? For this, we have to consider the nuclear spin angular momentum I, and it's projection onto a space-fixed axis m_I. Any value of I will have $2I+1$ values of m_I associated with it, as we are familiar with, so if there are two nuclei, there are $(2I+1)^2$ possible spin states (where each state is labelled with by both $m_{I(1)}$ and $m_{I(2)}$ for nuclei 1 and 2 respectively). Out of the $(2I+1)^2$ total possible states, there are $2I+1$ states where $m_{I(1)} = m_{I(2)}$, as follows logically from the two nuclei having the same nuclear spin (homonuclear diatomic), and these states are clearly symmetric under exchange. Of the other $(2I+1)^2 - (2I+1) = 2I(2I+1)$ states, half of them are symmetric and half are antisymmetric (as we can take antisymmetric or symmetric linear combinations of the two initial projections). Therefore:

$$N_{sym} = 2I+1+I(2I+1) = 2I^2+3I+1 = (2I+1)(I+1) \tag{9}$$

$$N_{asym} = I(2I+1) \tag{10}$$

Therefore the ratio of symmetric to antisymmetric spin states is:

$$\frac{N_{sym}}{N_{asym}} = \frac{(2I+1)(I+1)}{I(2I+1)} = \frac{I+1}{I} \tag{11}$$

Which is a familiar formula from the lecture notes. Then it is possible to work out the number of possible symmetric and antisymmetric spin states, and therefore if there missing lines a spectrum, or what the ratio of the odd/even lines will be.

You can also do this for non-diatomic molecules, to quote Atkins: *"The principles are the same but it is substantially more difficult"* - so I think we can safely leave it here for now...