

Indistinguishable Particle Effects in Rotational Raman Scattering
An Example of Quantum Statistics

The purpose of this example is to

- Work a concrete problem using a wavefunction involving more than one particle,
- Demonstrate how to deal with issues involving identical particles, in particular symmetric and antisymmetric wavefunctions,
- Increase your understanding of the concepts of spin and composite particles,
- Point out that identical particle effects can have a profound influence on the results of simple experiments such as Raman scattering,
- Show that early experiments of this sort helped clarify our understanding of the composition of the nucleus.

Earlier in the course we studied the rotational motion of diatomic molecules. We used the canonical ensemble to determine the probability that a molecule would be in a particular rotational energy level in thermal equilibrium. The new feature of that example was the influence of the degeneracy of the energy levels. Recall that the rotational energy levels are indexed by the “magnitude”¹ of the rotational angular momentum, l , such that $\epsilon_l = k\Theta_R l(l+1)$ where $\Theta_R \equiv \hbar^2/2I_{\perp}k$ is the “rotational temperature” of the molecule. If there were only one quantum state associated with each energy (no degeneracy) the probability that a given energy level was occupied would fall off monotonically with increasing energy. But these states are degenerate: there are $2l+1$ different rotational states which have the same energy ϵ_l . When this is taken into account an interesting effect occurs when $T \gg \Theta_R$. The occupation of the energy levels first increases with increasing energy before it finally begins to fall off at high energies. One can see this clearly in the Raman spectrum of the molecule. Each line in the spectrum corresponds to the molecule being excited from an l to an $l+2$ rotational state with a corresponding decrease in the frequency of the scattered photon. The intensity of the line is proportional to the probability that the l th energy level is occupied. Figure 1 shows the Raman spectrum to be expected under these circumstances.

¹Why the quotes? Recall that the eigenvalues of the operator representing the square of the angular momentum, $\vec{L} \cdot \vec{L}$, are $l(l+1)\hbar^2$. Thus the true magnitude of the angular momentum is $\sqrt{l(l+1)}\hbar$. l is more properly an index used to identify the total angular momentum state. However it has become commonplace to refer to l as the magnitude of the angular momentum.

ROTATIONAL RAMAN SPECTRUM OF A DIATOMIC MOLECULE

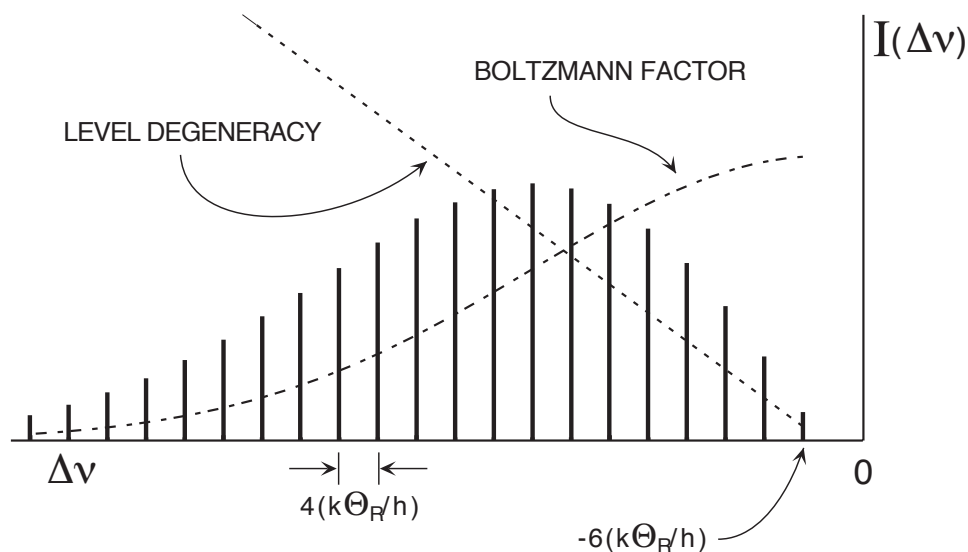


Figure 1

In this part of the course we have discussed the concept of spin, an intrinsic angular momentum associated with elementary particles and, as long as one does not change their internal degrees of freedom, composite particles as well. The spin adds another independent variable to the wavefunction of the particle in addition to those necessary to specify the particle's spatial state. If there are no cross terms between the spatial and spin variables in the Hamiltonian, the energy eigenfunctions can be written as a product of a spatial and a spin part: $\psi_{\text{total}}(\vec{r}, \vec{s}) = \psi_{\text{space}}(\vec{r})\psi_{\text{spin}}(\vec{s})$. The spin most often enters the Hamiltonian through the interaction of its associated magnetic moment with an externally applied magnetic field. In such a case if there were no applied magnetic field the Hamiltonian would not have any spin contribution and the factorization indicated above would be appropriate.

For a given value of the “magnitude” of the spin angular momentum, s , there are $2s + 1$ possible values for the component of the spin along any particular direction. In the absence of a magnetic field this gives rise to a $2s + 1$ fold contribution to the degeneracy of the single particle energy eigenstates. If the degeneracy of the spatial states alone is d , the total degeneracy of the energy level would be $(2s + 1)d$ since any one of the spatial states can be paired with any one of the spin states to form a distinct quantum state of the particle. The simplest example is the two-fold spin degeneracy of the single particle states we use to describe a non-interacting electron gas.

Now let us go back to the problem of the rotational motion of diatomic molecules. For simplicity we are going to restrict ourselves to homonuclear diatomic molecules. Homonuclear refers to the fact that not only are the two atoms in the molecule the same, but they are the same isotope of that atom. Using as an example the two stable isotopes of hydrogen, H and D, H-H and D-D are homonuclear diatomic molecules, H-D is not.

The atomic nucleus is a composite particle and, as such, it has a spin with some magnitude which we will designate as I . I will be an integer if the sum of the number of protons and neutrons in the nucleus is even, a half-integer if the nuclear mass number is odd. Fortunately, to a high degree of accuracy the nuclear spins interact neither with themselves nor with the electrons in the atoms. This has two important consequences. First, the nuclear state of the molecule is not changed as it rotates, and second, the energy eigenfunctions of the molecule can be factored into spatial and spin parts.

How many different spin states can the molecule have? Although the I for each of the two nuclei is the same, each nucleus could be in any one of its $2I + 1$ states of m_I . Thus there are $(2I + 1)^2$ possible nuclear spin states for the molecule.

“So what’s the big deal?” you may ask. “There is a spin degeneracy and you have shown us how to calculate it. The energy eigenfunctions factor so the degeneracy is just the product of that due the spatial part, $2l + 1$, times that due to the spin part $2I + 1$. The scattering of a photon does not change the spin state, so the intensities of all the lines in Figure 1 are multiplied by the same factor and the resulting spectrum looks identical to what we had before. Why all the fuss?”

The added complication in the case of homonuclear diatomic molecules — the origin of the “fuss” — is that we are dealing with a system containing two identical particles, the nuclei. The total wavefunction² must be symmetric or antisymmetric with respect to their interchange: symmetric if I is integer, antisymmetric if I is half-integer. We will see below that this requirement causes a correlation between the rotational and spin states of the nuclei. The rotational states do not have a common spin degeneracy as assumed in the argument in the previous paragraph.

² $\psi_{total} = \psi_{total}(\vec{r}_{n_1}, \vec{I}_{n_1}; \vec{r}_{n_2}, \vec{I}_{n_2}; \vec{r}_{e_1}, \vec{s}_1; \dots; \vec{r}_{e_{2N}}, \vec{s}_{2N})$. Here n_1 and n_2 refer to the two nuclei. \vec{r}_{e_i} and \vec{s}_i refer to the position and spin of the i^{th} electron. N is the number of electrons in each atom. The 2 nuclei are identical. The $2N$ electrons are identical. We are focusing on the 2 nuclei.

The spatial location of the nuclei is given by the rotational part of the wavefunction $\psi_{l,m_l}(\vec{r})$ where \vec{r} is a vector from the position of one nucleus to that of the other. We will indicate the spin contribution to the total nuclear wave function as $\psi_{\text{spin}}(\vec{I}_1, \vec{I}_2)$. Thus

$$\psi_{\text{nuclei}}(\vec{r}, \vec{I}_1, \vec{I}_2) = \psi_{l,m_l}(\vec{r})\psi_{\text{spin}}(\vec{I}_1, \vec{I}_2)$$

Note that the energy of the state depends only on l , so there may be a substantial degeneracy of the energy levels, and $\psi_{\text{nuclei}}(\vec{r}, \vec{I}_1, \vec{I}_2)$ must be symmetric or antisymmetric with respect to the interchange of the two nuclei. Note that exchanging the positions of the two nuclei causes \vec{r} to be replaced by $-\vec{r}$. Now it happens that all angular momentum eigenfunctions with even l are even under such a replacement (they are said to have even “parity”) but the angular momentum eigenfunctions with odd l change sign under such a replacement (odd parity). Therefore the $\psi_{l,m_l}(\vec{r})$ we are using already exhibit by themselves the sought after symmetric or antisymmetric behavior.

Note that the product of two symmetric or two antisymmetric functions will be symmetric, and the product of a symmetric and antisymmetric function will be antisymmetric. Thus to obtain the proper statistics for the nuclear wavefunction we must find spin wavefunctions which are themselves either symmetric or antisymmetric. One way of doing this is as follows. First take one of the single spin eigenfunctions of nucleus 1. It will be indexed by some value for the z component of the spin m_{I_1} . Now multiply it by a single spin eigenfunction of nucleus 2 with the same value of m . The product has the form $\alpha(1)\alpha(2)$ and is symmetric with respect to the exchange of nuclei 1 and 2. One can find $2I + 1$ symmetric two particle spin wavefunctions $\psi_{\text{spin}}(\vec{I}_1, \vec{I}_2)$ in this way. Now make a product of single particle spin states using different values of m for each of the two particles. There will be $(2I + 1)2I/2$ possible ways of doing this since the order of choice does not matter. The resulting simple product wavefunction would look like $\alpha(1)\beta(2)$ and would not have the required symmetry. However, by forming the linear combinations $(\alpha(1)\beta(2) \pm \alpha(2)\beta(1))/\sqrt{2}$ we can generate another $(2I + 1)I$ symmetric two particle spin wavefunctions and $(2I + 1)I$ antisymmetric two particle spin wavefunctions. Note that we now have a total of $(2I + 1)^2$ different choices for $\psi_{\text{spin}}(\vec{I}_1, \vec{I}_2)$, all of which have exchange symmetry. The ratio of the number of antisymmetric spin states to the number of symmetric spin states is given by the function $f(I) = I/(I + 1)$.

Finally we can determine the actual degeneracy of the rotational energy states of our homonuclear diatomic molecule.

If I is half integer, $\psi_{\text{nuclei}} = \psi_{l,m_l}\psi_{\text{spin}}$ must be antisymmetric.

- If l is even, ψ_{spin} must be antisymmetric. There are $(2l + 1)(2I + 1)I$ states
- If l is odd, ψ_{spin} must be symmetric. There are $(2l + 1)(2I + 1)(I + 1)$ states

If I is an integer, $\psi_{\text{nuclei}} = \psi_{l,m_l}\psi_{\text{spin}}$ must be symmetric.

- If l is even, ψ_{spin} must be symmetric. There are $(2l + 1)(2I + 1)(I + 1)$ states
- If l is odd, ψ_{spin} must be antisymmetric. There are $(2l + 1)(2I + 1)I$ states

Note that in either case, integer or half integer I , as one moves from one energy level to the next, incrementing l by one each time, the spin contribution to the degeneracy alternates between two values whose ratio is given by $f(I) = I/(I + 1)$. Thus in the rotational Raman spectrum of homonuclear diatomic molecules there will be two interlaced sets of lines. One set will be weaker than the other by the factor $I/(I + 1)$.

Consider the special case where $I = 0$. The spin part of the nuclear wavefunction can only be symmetric. On the other hand, the entire nuclear wavefunction must also be symmetric under the exchange of these two Bosons. Thus the rotational part of the nuclear wavefunction must also be symmetric. The rotational states with odd l can never be excited. Half of the lines in the Raman spectrum will disappear. The spectrum will *look* like that in Figure 1; however, if one measured the spacing between the observed lines it would be $8k\Theta_R/h$ rather than $4k\Theta_R/h$. This is actually the case in O_2 since the nuclear spin of ^{16}O is zero.

The most famous case is that of N_2 where $I = 1$ for ^{14}N . Since I is integer the nuclei are Bosons and the entire nuclear wave function must be symmetric with respect to their exchange. For $I = 1$ there are 6 symmetric spin states for the two nuclei and 3 antisymmetric spin states. The rotational ground state (and all other even l states) will have a 6 fold spin degeneracy; the next highest energy state (and all others with odd l) will be have a 3 fold spin degeneracy. In this case $f(I) = I/(I + 1) = 1/2$ and the line with the smallest shift, which arises from transitions out of the ground state, will belong to the set of lines with the greater of the two spin degeneracies. The resulting rotational Raman spectrum looks like that in Figure 2.

ROTATIONAL RAMAN SPECTRUM OF N₂

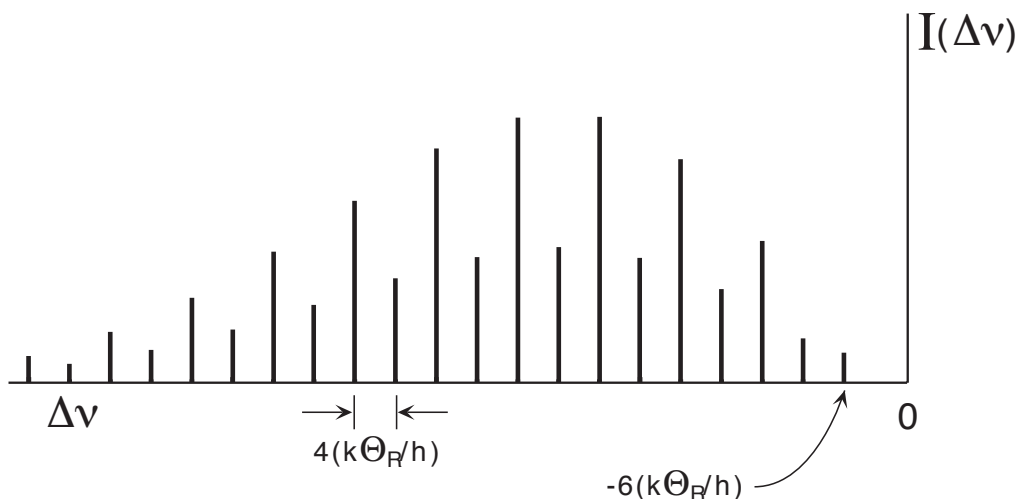


Figure 2

The alternation in the intensities of the rotational Raman lines in N₂ was first observed experimentally by Rasetti [F. Rasetti, Proc. Nat. Acad. Am. **15**, 411 (1929)]. The spectrum was obtained using a mercury arc lamp as a source, a modest spectrometer for dispersion, and was recorded on a photographic plate. It had no where near the resolution or signal to noise ratio that can be obtained today with laser sources, double grating spectrographs, and phototube detectors. None the less, he determined that the lines alternated in intensity by a factor of 2. It was Walter Heitler and Gerhard Herzberg [W. Heitler, G. Herzberg, Naturwiss. **17**, 673 (1929)] who recognized that this implied that $I = 1$ and thus required that the nuclei of nitrogen obey Bose statistics. This was puzzling, since it was thought at the time that the nucleus of ¹⁴N contained an odd number of spin 1/2 particles: 14 protons and 7 electrons. The problem was only resolved after the discovery of the neutron three years later.