Internal degrees of freedom - rotational partition function

Rotational energies & degeneracies

\[ \varepsilon_{rot} (J) = J(J+1) \frac{\hbar^2}{8\pi^2 I} = J(J+1) \frac{\hbar^2}{8\pi^2 \mu r_e^2} = J(J+1) h c B_e \]

\[ I = \mu r_e^2 \quad \text{moment of inertia} \quad B_e = \frac{\hbar}{8\pi^2 c l} = \frac{\hbar}{8\pi^2 c \mu r_e^2} \quad \text{rotational constant (cm}^{-1}) \]

\[ g_{rot} (J) = 2J + 1 \]

Rotational partition function

\[ q_{rot} = \sum_{\varepsilon_J} g(\varepsilon_J) e^{-\varepsilon_J/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-h c B_e J(J+1)/kT} \]

High-\( T \) limit \( \varepsilon_{rot} \ll kT \) or \( h c B_e / kT \ll 1 \)

In this case we can consider \( \varepsilon_{rot} \) continuous - classical or high-\( T \) limit

Can do the sum using the Euler-Maclaurin summation formula

\[ \sum_{J=m}^{n} f(J) = \int_{m}^{n} f(J)dJ + \frac{1}{2} [f(m) + f(n)] + \text{residue} \]

\[ q_{rot} = \int_{0}^{\infty} (2J+1) e^{-h c B_e J(J+1)/kT} dJ + \frac{1}{2} (1+0) + \cdots \]

Do integral by substitution \( \omega = J(J+1) \)

\[ d\omega = (2J+1) dJ \]

\[ q_{rot} = \int_{0}^{\infty} e^{-h c B_e \omega/kT} d\omega + \frac{1}{2} + \cdots = -\frac{kT}{h c B_e} e^{-h c B_e \omega/kT} \bigg|_{\omega=0} + \frac{1}{2} + \cdots = 0 - \left( -\frac{kT}{h c B_e} \right) + \frac{1}{2} + \cdots \]

\[ q_{rot} = \frac{kT}{h c B_e} \quad \text{High-}\ T \text{rotational partition function - almost!} \]

Important correction to \( q_{rot} \):
\[ \sigma \equiv \text{symmetry number} \equiv \# \text{ equivalent orientations in space that leave the appearance of the molecule unchanged} \]

\[ q_{\text{rot}} = \frac{kT}{\sigma \hbar c B_e} \equiv \frac{T}{\sigma \theta_{\text{rot}}} \]

with \[ \theta_{\text{rot}} = \frac{\hbar B_e}{k} \]

Rotational partition function, diatomic molecule, high-\( T \) limit

Note we can rewrite \[ \varepsilon_{\text{rot}}(J) = J(J+1)\hbar c B_e = J(J+1)k\theta_{\text{rot}} \]

Recall \[ q_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}} + \frac{1}{2} + \cdots \]

\[ \text{good approximation to drop } \frac{1}{2} ? \]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( B_e (\text{cm}^{-1}) )</th>
<th>( \sigma )</th>
<th>( \theta_{\text{rot}} ) (K)</th>
<th>( q_{\text{rot}} ) (300 K)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>10.59</td>
<td>1</td>
<td>15.24</td>
<td>19.688 + ( \frac{1}{2} )</td>
<td>2.5</td>
</tr>
<tr>
<td>CO</td>
<td>1.93</td>
<td>1</td>
<td>2.77</td>
<td>108.30 + ( \frac{1}{2} )</td>
<td>0.4</td>
</tr>
<tr>
<td>I(_2)</td>
<td>0.037</td>
<td>2</td>
<td>0.1065</td>
<td>1408.5 + ( \frac{1}{2} )</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Larger molecules have higher moment of inertia \( I \), more closely spaced rotational levels, higher \( q_{\text{rot}}(T) \).

Rotational contributions to thermodynamic functions in high-\( T \) limit

\[ q_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}} \quad Q_{\text{rot}} = q_{\text{rot}}^N = \left( \frac{T}{\sigma \theta_{\text{rot}}} \right)^N \]

\[ A_{\text{rot}} = -kT \ln Q_{\text{rot}} = -NkT \ln \left( \frac{T}{\sigma \theta_{\text{rot}}} \right) \]

\[ E_{\text{rot}} = kT^2 \left( \frac{\partial \ln Q_{\text{rot}}}{\partial T} \right)_{N,V} = NkT^2 \left( \frac{\partial \ln q_{\text{rot}}}{\partial T} \right)_{N,V} \]

\[ E_{\text{rot}} = NkT \quad C_{\text{rot}} = \left( \frac{\partial E_{\text{rot}}}{\partial T} \right)_{N,V} = Nk \]

Classical equipartition theorem result!

Two rotational degrees of freedom, \( \frac{1}{2} kT \) energy per degree of freedom

As in the case of translation, we calculated \( q_{\text{rot}} \) quantum mechanically but ended up with a classical result. Why? For most molecules at room \( T \), the rotational
levels are closely spaced compared to $kT$. Once this limit is reached it doesn’t matter what the molecule is! The rotational energy is the same. Consider molecules A, B, C, and D with different densities of states.

In the sparse limit, in order to establish a Boltzmann distribution of populations in the levels, we just need a few of the $N$ molecules to be in states 1 or 2. Almost all are in state 0. But as soon as any levels are within $kT$ of the lowest level, the population of that level starts to decrease significantly. The partition function $q$ starts to increase significantly. That’s already near the high- $T$ limit.

**Origin of $\sigma$ - nuclear spin statistics**

For identical nuclei, total wavefunction $\psi_{\text{tot}}$ must be symmetric or antisymmetric with respect to interchange of nuclei.

$$\psi_{\text{tot}}(x) \xrightarrow{\text{exchange}} \pm \psi_{\text{tot}}(-x)$$
\( \psi_{\text{tot}} \) is **symmetric** for nuclei with integral spins (bosons)

\( \psi_{\text{tot}} \) is **antisymmetric** for nuclei with half-integral spins (fermions)

e.g. \( O_2 \) with \( ^{16}O \) nuclei - \( I = 0 \) \( \Rightarrow \) bosons

\( H_2 \) with \( ^1H \) nuclei - \( I = \frac{1}{2} \) \( \Rightarrow \) fermions

\( D_2 \) with \( ^2D \) nuclei - \( I = 1 \) \( \Rightarrow \) bosons

\[
\psi_{\text{tot}} = \psi_{\text{trans}} \psi_{\text{elec}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{spn}}
\]

look at each part

\( \psi_{\text{trans}} \) - only depends on C.O.M. coordinates, cannot interchange identical nuclei on the same molecule. We've already accounted for interchange of identical nuclei through translation.

\( \psi_{\text{elec}} \) - have to look at MO symmetries.

e.g.

![Diagram of MO symmetries](image)

\( \psi_{\text{vib}} \) - HO wavefunctions are all symmetric w.r.t. interchange of the nuclei. So no don't need to consider \( \psi_{\text{vib}} \).

\( \psi_{\text{rot}} \) - angular momentum wavefunctions are the spherical harmonics \( s, p, d, f, \ldots \)

\[
J = 0, 2, 4, \ldots \text{ even } J \quad \Rightarrow \quad \text{even } \psi_{\text{rot}}(J)
\]

\[
J = 1, 3, 5, \ldots \text{ odd } J \quad \Rightarrow \quad \text{odd } \psi_{\text{rot}}(J)
\]

with respect to particle interchange
\( \psi_{\text{nuc}} \) \text{ example: } ^{16}\text{O}^{16}\text{O} \text{ each nucleus has } I = 0 \Rightarrow \text{ boson} \\
\Rightarrow \psi_{\text{tot}} \text{ must be even} \\

The \( \text{O}_2 \) linear combination spin states also have 0 spin \Rightarrow \text{ all } \psi_{\text{nuc}} \text{ even.} \\

So for \( \text{O}_2 \):

\[
\psi_{\text{tot}} \text{ even} = \psi_{\text{elec odd}} \psi_{\text{rot even}} \psi_{\text{nuc even}} \\
\Rightarrow \psi_{\text{rot even}} \text{ must be odd! Only } J = 1, 3, 5, \ldots \text{ allowed!} \\
\Rightarrow \text{O}_2 \text{ never has zero rotational energy, when in the ground electronic state.} \\

\( \text{O}_2 \):

\[
q_{\text{rot}} = \sum_{J=1,3,5,\ldots} (2J + 1)e^{-J(J+1)\theta_{\text{rot}}/T} \approx \frac{1}{2} \int_0^\infty (2J + 1)e^{-J(J+1)\theta_{\text{rot}}/T} dJ = \frac{T}{2\theta_{\text{rot}}} = \frac{T}{\sigma \theta_{\text{rot}}} \\
\]

Symmetry number \( \sigma = 2 \)

\( \text{O}_2 \) is a simple case, with \( I = 0 \). For \( I > 0 \), need to look at linear combination spin states and their symmetries.

General result for homonuclear diatomics

Degeracies of even and odd nuclear spin states:

\[
g_{\text{even}}(I) = (2I + 1)(I + 1) = \# \text{ even nuclear spin states} \\
g_{\text{odd}}(I) = (2I + 1)I = \# \text{ odd nuclear spin states} \\
\]

e.g. \( ^1\text{H}^1\text{H} \) \( I = \frac{1}{2} \) \( I_z = \pm \frac{1}{2} \) \text{ label the two spin states } \alpha, \beta \\

Properly symmetrized spin wavefunctions:

\[
\alpha(1)\alpha(2) \quad \beta(1)\beta(2) \quad \alpha(1)\beta(2) + \alpha(2)\beta(1) \quad \alpha(1)\beta(2) - \alpha(2)\beta(1) \\
\]

\( g_{\text{even}}(1/2) = 3 \quad g_{\text{odd}}(1/2) = 1 \quad \text{as predicted above} \]}
Also can see this from vector addition of the z-components, giving total nuclear spin \( I = 0 \) or 1 and total nuclear spin z-component \( I_z = 0 \) for \( I = 0 \) and \( I_z = -1, 0, \) or +1 for \( I = 1 \).

\[
\begin{align*}
I &= \hbar \sqrt{I(I+1)} = \hbar \sqrt{2} \\
I_z &= \hbar (−1, 0, \text{ or } 1)
\end{align*}
\]

e.g. \( ^2\text{H}-^2\text{H} \quad I = 1 \quad I_z = -1, 0, +1 \)

Adding the z-components shows that we could have \( I = 0, 1, \) or 2, and these have 1, 3, and 5 different \( I_z \) states, giving 9 states in all.

\[ g_{\text{even}} (1) = 6 \quad g_{\text{odd}} (1) = 3 \quad \text{as predicted above} \]

\( \sigma = \frac{2}{2} \) for all homonuclear diatomics. For any spin state, only half the rotational states are allowed. \( \sigma \) is given by rotational symmetry - how many equivalent configurations can be reached through rotation.

**Ortho-para hydrogen example**

\( ^1\text{H}-^1\text{H} \quad \text{spin } I = \frac{1}{2} \quad \text{fermions} \)

\[ \Rightarrow \quad \psi_{\text{tot}} \text{ must be odd w.r.t. } ^1\text{H} \text{ interchange} \]

Electronic ground state \( \psi_{\text{elec}} \) of \( \text{H}_2 \) is even

\[
\psi_{\text{tot}} \text{ odd} = \psi_{\text{elec}} \psi_{\text{rot}} \psi_{\text{nuc}} \text{ even}
\]

so product \( \psi_{\text{rot}} \psi_{\text{nuc}} \) must be odd. We already saw

\[ g_{\text{even}} (1/2) = 3 \quad g_{\text{odd}} (1/2) = 1 \]

so our possibilities are
\[ \psi_{\text{tot}} = \psi_{\text{elec}} \psi_{\text{rot}} \psi_{\text{nuc}} \]

- para-hydrogen

\[ \psi_{\text{tot}} = \psi_{\text{elec}} \psi_{\text{rot}} \psi_{\text{nuc}} \]

- ortho-hydrogen

When \( \psi_{\text{nuc \, ODD}} \) state is occupied, only even \( J \) states allowed.

When any of the 3 \( \psi_{\text{nuc \, EVEN}} \) states are occupied, only odd \( J \) states allowed.

Degeneracy \( g(J_{\text{odd}}) = 3g(J_{\text{even}}) \) since 3x more \( \psi_{\text{nuc \, EVEN}} \) states than \( \psi_{\text{nuc \, ODD}} \).

Sometimes degeneracy written explicitly as \( g(I)g(J) \) or \( g_I(J) \)

\[ g(J) = 2J + 1 \text{ and } g(I) = 1 \text{ or } 3. \]

At high \( T \), equilibrium \( \text{H}_2 \) gas is 25%-75% para:ortho.

At \( T = 0 \text{ K} \), at equilibrium, it's all para! - since only para can have \( J = 0 \).

**Rotational partition function at low \( T \)**

At low or intermediate \( T \), we can't replace the sum with an integral and arrive at our simple results \( q_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}} \), \( E_{\text{rot}} = NkT \), \( C_{\text{rot}} = Nk \).

Then we have to take the terms in the sum one by one.

\[ q_{\text{rot}} = \sum_J (2J + 1)e^{-J(J+1)\theta_{\text{rot}}/T} = 1 + 3e^{-2\theta_{\text{rot}}/T} + 5e^{-6\theta_{\text{rot}}/T} + \ldots \]

Usually converges quickly since Boltzmann factors become very small.

**\( E_{\text{rot}} \cdot C_{\text{rot}} \) in low- \( T \) limit**

\[ E_{\text{rot}} = kT^2 \left( \frac{\partial \ln Q_{\text{rot}}}{\partial T} \right)_{N,V} = NkT^2 \left( \frac{\partial \ln q_{\text{rot}}}{\partial T} \right)_{N,V} \]
\[
\ln q_{\text{rot}} = \ln \left( 1 + 3e^{-2\theta_{\text{rot}}/T} + 5e^{-6\theta_{\text{rot}}/T} + \cdots \right) \approx \ln \left( 1 + 3e^{-2\theta_{\text{rot}}/T} \right)
\]

\[
\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \cdots \quad \text{for} \quad -1 < x \leq 1 \quad \approx x \quad \text{for} \quad |x| \ll 1
\]

\[
\ln q_{\text{rot}} \approx 3e^{-2\theta_{\text{rot}}/T} \quad \text{for low} \quad T \ll \theta_{\text{rot}}
\]

\[
E_{\text{rot}} \approx NkT^2 \left( \frac{\partial \left( 3e^{-2\theta_{\text{rot}}/T} \right) }{\partial T} \right)_{N,V} = NkT^2 \frac{6\theta_{\text{rot}}}{T^2} e^{-2\theta_{\text{rot}}/T} = 6Nk\theta_{\text{rot}} e^{-2\theta_{\text{rot}}/T}
\]

\[
C_{v,\text{rot}} = \left( \frac{\partial E_{\text{rot}}}{\partial T} \right)_{N,V} = 6Nk\theta_{\text{rot}} \frac{2\theta_{\text{rot}}}{T^2} e^{-2\theta_{\text{rot}}/T} = \frac{12Nk\theta_{\text{rot}}^2}{T^2} e^{-2\theta_{\text{rot}}/T}
\]

\[E_{\text{rot}}, C_{v,\text{rot}} \text{ both } \rightarrow 0 \text{ as } T \rightarrow 0.\]

In this limit, there’s not enough thermal energy to reach even \( J = 1 \). So there’s essentially no rotational energy. And if some heat is put into the system, it still isn’t enough to reach \( J = 1 \), so the rotational heat capacity is zero also.

\[J = 1 \quad \square \quad J = 0 \quad \uparrow \quad kT\]

\[E_{\text{rot}}, C_{v,\text{rot}} - \text{ full } T \text{ dependence}\]

No simple analytical expressions for intermediate \( T \) regime. Can calculate the results numerically and display them to see when the transitions from low- \( T \) limit to intermediate \( T \) to high- \( T \) limit occur.

To connect to thermodynamics, substitute \( Nk = nR \) in our expressions for \( E_{\text{rot}}, C_{v,\text{rot}} \) and show the results per mole.
Note high-T limit is reached when $\frac{T}{\theta_{rot}} \approx 2$ - not very high! $\frac{\epsilon_{rot}}{k} = J(J+1)\theta_{rot}$, so this is when $kT \approx 2\theta_{rot} = \epsilon_{rot}(J = 1)$, just the first level above $J = 0$!

Levels are not very "continuous" yet - but $J = 0$ state is significantly depleted as soon as $J = 1$ level is within $kT$. At this point high-T limit is near.