

This series of problems will focus on the statistical mechanics of hydrogen. While the semiclassical treatment of hydrogen is essentially equivalent to that for a classical rigid rotor, we will see that quantum-mechanical effects permeate our treatment. The physics of statistical mechanics lies in identifying the density of states in our model. The rest is mathematics.

1. Consider a rigid rotor consisting of two particles with masses m_A and m_B linked by a rigid rod with length R . From classical mechanics, the motion of the two masses can instead be described by the motion of the center of mass of the rotor and the motion of a single particle with mass

$$\mu := m_A m_B / (m_A + m_B)$$

located a distance R from the center of mass. Semiclassically, we will soon learn that each microstate occupies a hypercube of side length λ in position space, where λ is the thermal wavelength

$$\lambda := \frac{h}{\sqrt{2\pi\mu k_B T}}.$$

- (i) Argue that the semiclassical rotational partition function for the rigid rotor should be given by

$$z_{\text{rot}} = \frac{4\pi R^2}{\lambda^2} = \frac{8\pi^2 I k_B T}{h^2}, \quad I := \mu R^2.$$

- (ii) In fact, this result holds true only for heteronuclear diatomic molecules. For homonuclear diatomic molecules, the partition function must be divided by a factor of two. Explain why.

Solving the Schrödinger equation for a quantum-mechanical rigid rotor leads to the energy levels

$$\epsilon_J = \frac{h^2 J(J+1)}{8\pi^2 I}, \quad J \in \mathbb{Z}^+ = \{0, 1, 2, \dots\},$$

where each energy level ϵ_J , indexed by the total angular momentum J of the system, is $(2J+1)$ -fold degenerate.

- (iii) Hence write out the quantum-mechanical rotational partition function for the rigid rotor as an infinite series, neglecting the effect described in (ii). You may, but need not, attempt to sum the series.
- (iv) You should be able to identify a characteristic temperature for rotation

$$\theta_{\text{rot}} := \frac{h^2}{8\pi^2 I k_B}$$

in your rotational partition function. θ_{rot} is a temperature close to and below which quantum effects are important. Calculate θ_{rot} for H_2 and for F_2 , and compare your results.

- (v) In the high-temperature limit $T \gg \theta_{\text{rot}}$, the quantum-mechanical partition function calculated in (iii) should reduce to the semiclassical partition function of (i). Show this explicitly by first arguing that the sum in (iii) may be well approximated by an integral in this limit.

What is the quantum-mechanical analogue of the effect described in (ii)? When the two nuclei are identical, it turns out that only half the angular momentum states—either those of even J or those of odd J —are acceptable quantum states of the molecule. If these nuclei are bosons, the total wavefunction must be symmetric under exchange. If these nuclei are fermions, the total wavefunction must be antisymmetric under exchange. The relevant contributions to the total wavefunction are the rotational and nuclear wavefunctions,

$$\Psi_{\text{tot}} \propto \Psi_{\text{rot}} \Psi_{\text{nuc}}.$$

(The electronic ground state wavefunction ψ_{elec} of H_2 is symmetric and may thus be neglected.) The rotational wavefunctions are simply the eigenfunctions of the quantum-mechanical rigid rotor, the spherical harmonics. Spherical harmonics associated with even J are symmetric, and those associated with odd J are antisymmetric. With regards to nuclear wavefunctions, the combination of two fermionic hydrogen nuclei produces four nuclear

spin states: $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$, and $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$. Of these, the former three are in symmetric triplet states, and the latter in an antisymmetric singlet state. Hydrogen that exists in a symmetric triplet state is known as *ortho*-hydrogen, and hydrogen that exists in an antisymmetric singlet state is known as *para*-hydrogen.

(vi) Argue that *ortho*-hydrogen can only access rotational states of odd J and that *para*-hydrogen can only access rotational states of even J . In the high- T limit, show that the rotational partition functions of *ortho*- and *para*-hydrogen are both divided by a factor of two upon taking this symmetry restriction into account, recovering the semiclassical result.

At high temperatures, thermal fluctuations are strong enough to overcome the activation energy barrier between *ortho*- and *para*-hydrogen, and the two species can interconvert.

(vii) Identify the equilibrium ratio of *ortho*- to *para*-hydrogen at high temperatures.

(vii)* (Optional, ungraded.) Deuterium is a rare form of hydrogen with one neutron. A deuterium nucleus is bosonic with nuclear spin 1, so that each nucleus has three spin states. Identify the equilibrium ratio of *ortho*- to *para*-deuterium at high temperatures.

Magnetic interactions between hydrogen molecules that may cause interconversion between the *ortho* and *para* forms are weak enough that a hot equilibrium mixture of hydrogen may be cooled to low temperatures *while maintaining a constant ratio of the two forms of hydrogen*. This mixture is metastable. In the presence of a catalyst, such as paramagnetic impurities like O_2 or the presence of metal surfaces on which H_2 molecules can dissociate and recombine, the two forms of hydrogen are able to interconvert and equilibrate at any temperature.

(viii) Calculate, to leading order, the equilibrium ratio of *ortho*- to *para*-hydrogen at low temperatures.

(ix) Calculate the heat capacity of an equilibrium mixture of hydrogen at high temperatures. How much of this heat capacity is contributed by *ortho*-hydrogen? Calculate, to leading order, the heat capacity of an equilibrium mixture of hydrogen at low temperatures. How much of this heat capacity is contributed by *ortho*-hydrogen?

(x) Write out the rotational partition function for (a) *ortho*-hydrogen, (b) *para*-hydrogen, (c) a metastable mixture of hydrogen, and (d) an equilibrium mixture of hydrogen as infinite series.

(xi) Plot the rotational energy of (x.a)-(x.d) on the same graph as a function of temperature. Plot the rotational heat capacity of (x.a)-(x.d) on the same graph as a function of temperature. You will need to evaluate the rotational partition functions numerically.

(xi)* (Optional, ungraded.) Sketch the rotational heat capacity of HD.

The specific heat of a metastable mixture of hydrogen is of historical significance. Eucken (1912) was the first to measure the heat capacity of such a mixture of hydrogen as a function of temperature. The theoretical explanation for the resulting data remained an open problem, attempted by such luminaries as Einstein, Planck, Lorentz, Nernst, Ehrenfest, Bohr, and Schrödinger, and no satisfactory answer was found until the development of quantum theory proper in the 1920s. The modern understanding of the shape of this heat capacity curve was first elucidated by Dennison (1927), after the concepts of spin and symmetry had been firmly established. As you have shown, statistical mechanics thus provides a concrete link between these abstract concepts and experimentally measurable quantities like the heat capacity.