1. Problem 18–2 from McQuarrie & Simon:

   Show that the difference between the successive terms in the summation in Equation 18.4 is very small for $m = 10^{-26}$kg, $a = 1\,\text{dm}$, and $T = 300\,\text{K}$. Recall from Problem 18–1 that typical values of n are $O\left(10^9\right)$.

2. Problem 18–10 from McQuarrie & Simon:

   Plot the fraction of HCl(g) molecules in the first few vibrational states at 300K and 1000K.

3. Problem 18–11 from McQuarrie & Simon:

   Calculate the fraction of molecules in the ground vibrational state and in all excited states at 300K for each of the molecules in Table 18.2.

4. Problem 18–12 from McQuarrie & Simon:

   Calculate the value of the characteristic rotational temperature Θ_{rot} for H_2(g) and D_2(g). (The bond lengths of H_2 and D_2 are 76.14pm.) The atomic mass of deuterium is 2.014.

5. Problem 18–13 from McQuarrie & Simon:

   The average molar rotational energy of a diatomic molecule is RT. Show that typical values of J are given by $J(J+1) = {}^{T}/_{\Theta_{\text{rot}}}$. What are typical values of J for N_2(g) at 300K?

6. Problem 18–14 from McQuarrie & Simon:

   There is a mathematical procedure to calculate the error in replacing a summation by an integral as we do for the translational and rotational partition functions. The formula is called the Euler-Maclaurin summation formula and goes as follows:

$$\sum_{n=a}^{b} f(n) = \int_a^b f(n)\,dn + \frac{1}{2}\{f(b)+f(a)\} - \frac{1}{12}\left\{\left.\frac{df}{dn}\right|_{n=a} - \left.\frac{df}{dn}\right|_{n=b}\right\} + \frac{1}{720}\left\{\left.\frac{d^3f}{dn^3}\right|_{n=a} - \left.\frac{d^3f}{dn^3}\right|_{n=b}\right\} + \cdots$$

   Apply this formula to Equation 18.33 to obtain

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}}\left\{1 + \frac{1}{3}\left(\frac{\Theta_{\text{rot}}}{T}\right) + \frac{1}{15}\left(\frac{\Theta_{\text{rot}}}{T}\right)^2 + O\left[\left(\frac{\Theta_{\text{rot}}}{T}\right)^3\right]\right\}$$

   Calculate the correction to replacing Equation 18.33 by an integral for N_2(g) at 300K; H_2(g) at 300K (being so light, H_2 is an extreme example).

7. 10 points Extra Credit: Problem 18–40 from McQuarrie & Simon:

   In Chapter 13, we learned that the harmonic-oscillator model can be corrected to include anharmonicity. The energy of an anharmonic oscillator was given as (Equation 13.21)

$$\tilde{\varepsilon}_v = \left(v + \frac{1}{2}\right)\tilde{\nu}_e - \tilde{x}_e\tilde{\nu}_e\left(v + \frac{1}{2}\right)^2 + \cdots$$

where the frequency $\tilde{\nu}_e$ is expressed in cm^{-1}. Substitute this expression for $\tilde{\varepsilon}_v$ into the summation for the vibrational partition function to obtain

$$q_{\mathrm{vib}}(T) = \sum_{v=0}^{\infty} e^{-\beta\tilde{\nu}_e\left(v+\frac{1}{2}\right)} e^{\beta\tilde{x}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}$$

Now expand the second factor in the summand, keeping only the linear term in $\tilde{x}_e\tilde{\nu}_e$, to obtain

$$q_{\mathrm{vib}}(T) = \frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1-e^{-\Theta_{\mathrm{vib}}/T}} + \beta\tilde{x}_e\tilde{\nu}_e e^{-\Theta_{\mathrm{vib}}/2T} \sum_{v=0}^{\infty} \left(v+\frac{1}{2}\right)^2 e^{-\Theta_{\mathrm{vib}}v/T} + \cdots$$

where $\Theta_{\mathrm{vib}}/T = \beta\tilde{\nu}_e$. Given that (Problem I-15)

$$\sum_{v=0}^{\infty} v x^v = \frac{x}{(1-x)^2}$$

and

$$\sum_{v=0}^{\infty} v^2 x^v = \frac{x^2+x}{(1-x)^3}$$

show that

$$q_{\mathrm{vib}}(T) = q_{\mathrm{vib,ho}}(T)\left[1+\beta\tilde{x}_e\tilde{\nu}_e\left(\frac{1}{4}+2q^2_{\mathrm{vib,ho}}(T)\right)+\cdots\right]$$

where $q_{\mathrm{vib,ho}}$ is the harmonic-oscillator partition function. Estimate the magnitude of the correction for Cl_2(g) at 300K, for which $\Theta_{\mathrm{vib}} = 805\mathrm{K}$ and $\tilde{x}_e\tilde{\nu}_e = 2.675\mathrm{cm}^{-1}$.

Numbered equations:

$$q_{\text{trans}}(V,T) = \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right]^3 \tag{18.4}$$

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)\, e^{-\Theta_{\text{rot}} J(J+1)/T} \tag{18.33}$$

Table 18.2: Molecular constants for several diatomic molecules. These parameters were obtained from a variety of sources and do not represent the most accurate values because they were obtained under the rigid rotator-harmonic oscillator approximation

Molecule	Electronic state	Θ_{vib}/K	Θ_{rot}/K	D_0/kJ mol^{-1}	D_e/kJ mol^{-1}
H_2	$^1\Sigma_g^+$	6215	85.3	432.1	457.6
D_2	$^1\Sigma_g^+$	4394	42.7	435.6	453.9
Cl_2	$^1\Sigma_g^+$	805	0.351	239.2	242.3
Br_2	$^1\Sigma_g^+$	463	0.116	190.1	191.9
I_2	$^1\Sigma_g^+$	308	0.0537	148.8	150.3
O_2	$^3\Sigma_g^-$	2256	2.07	493.6	503.0
N_2	$^1\Sigma_g^+$	3374	2.88	941.6	953.0
CO	$^1\Sigma^+$	3103	2.77	1070	1085
NO	$^2\Pi_{1/2}$	2719	2.39	626.8	638.1
HCl	$^1\Sigma^+$	4227	15.02	427.8	445.2
HBr	$^1\Sigma^+$	3787	12.02	362.6	377.7
HI	$^1\Sigma^+$	3226	9.25	294.7	308.6
Na_2	$^1\Sigma_g^+$	229	0.221	71.1	72.1
K_2	$^1\Sigma_g^+$	133	0.081	53.5	54.1