Chemistry 4000/5000/7000 Fall 2021
Assignment 2 solutions

1. I'm going to do the sodium dimer (Na_2) as an illustration. I chose the aug-cc-pVTZ basis set. It's the largest basis set for which I can get answers in reasonable time. It has polarization functions built in. Moreover, it has diffuse functions, which improves the quality of calculations when we're going to look at interactions between distant atoms (as we will when getting a potential energy curve).

   Note: There are many other acceptable answers here. The point is to pick something reasonable, preferably with diffuse functions.

2. I carried out a geometry optimization with the ωB97X-D density functional, spin-restricted wavefunctions, and the aug-cc-pVTZ basis set. The optimized bond length was 3.0496 Å, and the energy was -324.5646 hartree.

3. My plot is in figure 1. In order to get a reasonably smooth curve without computing a ridiculous number of points, I carried out two scans, one starting at 1.5 Å taking 48 steps of size 1 Å, and the other starting at 1.6 Å taking 14 steps of 0.2 Å each. I then merged the two data sets (using a text editor) before plotting them. They could also have been imported into a spreadsheet and handled there.

4. I set up a frequency calculation with the parameters set as above: aug-cc-pVTZ basis set, ωB97X-D density functional, restricted spin.

   The ideal gas law is $pV = Nk_BT$, thus $V/N = k_BT/p$. At the standard pressure $p = p^\circ$, Gaussian's "volume" is in fact a volume per molecule. It's not the volume of any real system, so the "translational partition function" calculated using this volume has no physical meaning.

   We can start with the translational partition function

$$q_{\text{tr}} = \frac{V}{h^3}(2\pi m k_B T)^{3/2} = \frac{k_B T}{p^\circ h^3}(2\pi m k_B T)^{3/2}.$$

   The last equality uses Gaussian's volume.

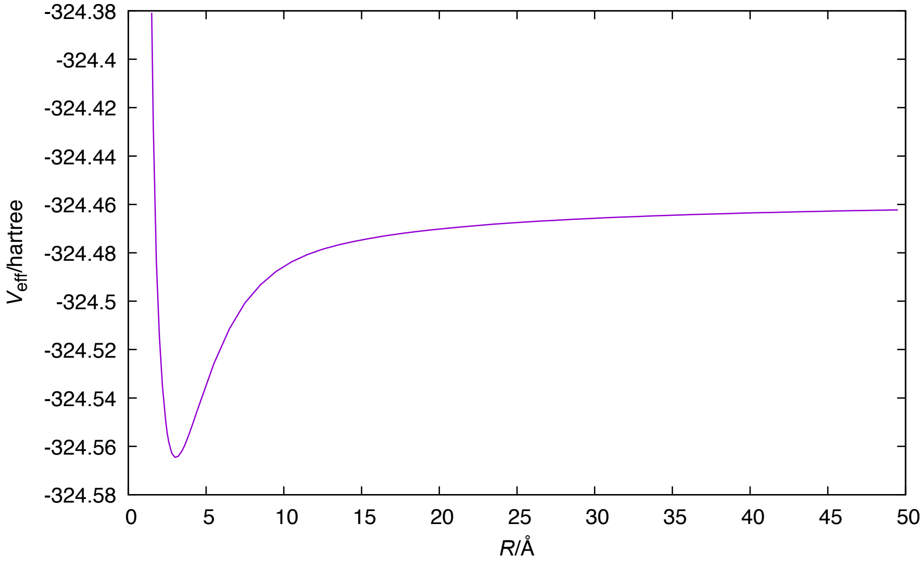

Figure 1: Sodium dimer potential energy curve computed with the ωB97X-D density functional, spin-restricted wavefunctions, and the aug-cc-pVTZ basis set.

The Gaussian output file gives a molar mass of $45.979\,54\,\mathrm{g\,mol^{-1}}$, which is $7.635\,0822 \times 10^{-26}\,\mathrm{kg}$. The standard pressure is $10^5\,\mathrm{Pa}$. This gives, at 25 °C,

$$\begin{aligned} q_{\mathrm{tr}} &= \frac{(1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}{10^5\,\mathrm{Pa}} \\ &\quad \times \left(\frac{\sqrt{2\pi(7.635\,0822 \times 10^{-26}\,\mathrm{kg})(1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}}{6.626\,070 \times 10^{-34}\,\mathrm{J\,Hz^{-1}}} \right)^3 \\ &= 1.241 \times 10^8. \end{aligned}$$

Gaussian's value is slightly smaller due to the slightly larger pressure used by the program by default.

The ideal-gas law is $pV = Nk_BT$, so $V = k_BT/p$ represents the volume of an ideal gas per molecule. This doesn't in general make much sense since the partition function depends on the volume truly available to the molecule.

The rotational partition function is

$$q_{\mathrm{rot}} = \frac{2Ik_BT}{\sigma\hbar^2}.$$

For a homonuclear diatomic molecule, $\sigma = 2$. (The Gaussian output file agrees. Look for '`Rotational symmetry number`' in the output file.) For a diatomic molecule, $I = \mu R^2$, and for a homonuclear diatomic, $\mu = m_{\mathrm{Na}}/2 = 22.98977\,\mathrm{g\,mol^{-1}}/2 = 11.49489\,\mathrm{g\,mol^{-1}} \equiv 1.90877 \times 10^{-26}\,\mathrm{kg}$. Given a bond length of 3.0496 Å, the moment of inertia works out to

$$\begin{aligned} I &= (1.90877 \times 10^{-26}\,\mathrm{kg})(3.0496 \times 10^{-10}\,\mathrm{m})^2 \\ &= 1.7752 \times 10^{-45}\,\mathrm{kg\,m^2}. \end{aligned}$$

The value of the rotational partition function is therefore

$$\begin{aligned} q_{\mathrm{rot}} &= \frac{2(1.7752 \times 10^{-45}\,\mathrm{kg\,m^2})(1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}{2(1.054\,572 \times 10^{-34}\,\mathrm{J\,s})^2} \\ &= 657. \end{aligned}$$

Gaussian's value agrees exactly with this one.

The vibrational frequency was calculated as $176.2\,\mathrm{cm^{-1}}$. Therefore,

$$\begin{aligned}
\hbar\omega_0 &= hc\tilde{\nu}_0 \\
&= (6.626\,070 \times 10^{-34}\,\mathrm{J\,Hz^{-1}})(2.997\,924\,58 \times 10^{10}\,\mathrm{cm\,s^{-1}})(176.2\,\mathrm{cm^{-1}}) \\
&= 3.5001 \times 10^{-21}\,\mathrm{J}.
\end{aligned}$$

Using the lowest vibrational level as out energy reference, the vibrational partition function is

$$\begin{aligned}
q_{\mathrm{vib}}(v=0) &= \left[1 - \exp\left(-\frac{\hbar\omega_0}{k_B T}\right)\right]^{-1} \\
&= \left[1 - \exp\left(-\frac{3.5001 \times 10^{-21}\,\mathrm{J}}{(1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15,\mathrm{K})}\right)\right]^{-1} \\
&= 1.746.
\end{aligned}$$

The wavefunction use the bottom of the potential well as the reference is corrected by a multiplicative term:

$$\begin{aligned}
q_{\mathrm{vib}}(\mathrm{bot}) &= q_{\mathrm{vib}}(v=0)\exp\left(-\frac{\hbar\omega_0}{2k_B T}\right) \\
&= 1.141.
\end{aligned}$$

Gaussian agrees with both versions of the vibrational partition function I calculated.

Finally, the electronic wavefunction is just the spin multiplicity, which is 1 for a closed-shell molecule. Again, Gaussian agrees.

5. See textbook pp. 76–77, where the Gaussian-style partition functions are denote $\hat{q}$.

6. Table 1 gives all of the relevant data from calculations done with the ωB97X-D density functional and the aug-cc-pVTZ basis set. Restricted wavefunctions were used in both cases.

   We previously saw the formula

$$q_{\mathrm{tr}} = \frac{k_B T}{p^\circ h^3}(2\pi m k_B T)^{3/2}.$$

Table 1: Calculation results from Gaussian, as well as manual calculations described in the text.

	ϵ_0/hartree	q_{tr}	q_{vib}	q_{rot}	q_{elec}
Na_2	-324.5646	1.225×10^7	1.746	657	1
Na	-162.2689	4.390×10^6			2

Applying it to the Na atom ($m = 3.817\,541 \times 10^{-26}\,\text{kg}$), we get

$$\begin{aligned}
q_{\text{tr}} &= \frac{(1.380\,649 \times 10^{-23}\,\text{J}\,\text{K}^{-1})(298.15\,\text{K})}{10^5\,\text{Pa}} \\
&\quad \times \left(\frac{\sqrt{2\pi(3.817\,541 \times 10^{-26}\,\text{kg})(1.380\,649 \times 10^{-23}\,\text{J}\,\text{K}^{-1})(298.15\,\text{K})}}{6.626\,070 \times 10^{-34}\,\text{J}\,\text{Hz}^{-1}} \right)^3 \\
&= 4.390 \times 10^6.
\end{aligned}$$

For Na_2, the overall partition function is

$$q_{\text{Na}_2} = (1.241 \times 10^8)(1.141)(657)(1) = 9.30 \times 10^{10}.$$

For Na, we have

$$q_{\text{Na}} = (4.390 \times 10^6)(2) = 8.780 \times 10^6.$$

Also,

$$\begin{aligned}
\Delta\epsilon_0 &= 2\epsilon_0(\text{Na}) - \epsilon_0(\text{Na}_2) \\
&= 2(-162.2689) - (-324.5646)\,\text{hartree} \\
&= 0.0268\,\text{hartree} \equiv 70.4\,\text{kJ}\,\text{mol}^{-1}
\end{aligned}$$

Using the formula from the previous question, we get

$$\begin{aligned}
K &= \frac{q_{\text{Na}}^2}{q_{\text{Na}_2}} e^{-\Delta\epsilon_0/k_B T} \\
&= \frac{(8.780 \times 10^6)^2}{9.30 \times 10^{10}} \exp\left(\frac{-70.4 \times 10^3\,\text{J}\,\text{mol}^{-1}}{(8.314\,463\,\text{J}\,\text{K}^{-1}\text{mol}^{1})(298.15\,\text{K})} \right) \\
&= 3.85 \times 10^{-10}.
\end{aligned}$$