Problem 1. Born-Openheimer potential for $H_2^+$

1.1

[Plot of $V_1(x)$ against $x$]

1.2

[Plot of $V(d)$ against $d$]

1.3
One of you astutely pointed out that the probability density of the two eigenfunctions look identical, so why would one be bonding and the other be antibonding? The reason is that we are plotting the wavefunctions at \( d = 3 \), which is much further than the equilibrium value of \( d \sim 0.5 \). Had you plotted the wavefunctions at the equilibrium value, the difference in probability density becomes more pronounced.

**Problem 2. Semiclassical Molecule.**

2.1

The bond lengths of \( H_2 \) and \( CO \) are 0.74 Å and 1.128 Å respectively.

2.2

Using \( L = 1 \) Å, the ground state energy for a particle trapped in a cube of sides \( L \) is

\[
3 \times \frac{\hbar^2 \pi^2}{2mL^2} = 3 \times \frac{(6.62606957 \times 10^{-34})^2}{2 \times 9.10938291 \times 10^{-31} \times (10^{-10})^2} \times \frac{\pi^2}{12} \times \pi^2 = 1.8 \times 10^{-17} \text{ J} \sim 100 \text{ eV}
\]  

(1)

2.3

\[
[k] = \frac{M}{T^2}
\]  

(2)

2.4

Some considerations:

- We expect Planck constant \( \hbar \) to be involved.
- Since the actual interactions are electrostatic, we also expect \( \frac{e^2}{4\pi\epsilon_0} \) to be involved.
Part of the interactions is the electrostatic attraction of the nuclei to the electron cloud. Since the size of the electron cloud is important in this case, we expect the electron mass $m_e$ to be involved.

As $m_p$ appears in the kinetic terms of the nuclei, it might affect the separation of the nuclei and hence the potential seen by the electron, and hence the size of the electron cloud, but it is clear from this long chain of argument that the effects are very indirect. Since it has the same dimensions as $m_e$, it seems more reasonable to consider $m_e$ in place of $m_p$.

Let us now construct a unique $k$ out of $\hbar$, $\frac{e^2}{4\pi\epsilon_0}$, and $m_e$. Keeping in mind that

$$[\hbar] = \frac{ML^2}{T}, \quad \left[ \frac{e^2}{4\pi\epsilon_0} \right] = \frac{ML^3}{T^2}, \quad [m_e] = M$$

We find that

$$k = m_e^3 \left( \frac{e^2}{4\pi\epsilon_0} \right)^4 \hbar^{-6} = 1557 \text{ J m}^2$$

2.5

$$\hbar \omega = \sqrt{\frac{k}{m_p}} = 0.6 \text{ eV}$$

2.6

Quantum-mechanically, $L^2 = \hbar^2 l(l + 1)$, where $l$ is a nonnegative integer.

2.7

Treating it as a dumb-bell shaped molecule,

$$I = 2 \times m_p \times \left( \frac{L}{2} \right)^2 = 8.4 \times 10^{-48} \text{ kgm}^2$$

2.8

Taking $l = 1$, we have

$$\frac{L^2}{2I} = \frac{\hbar^2}{I} = 0.008 \text{ eV}$$

Problem 3. Equipartition

3.1

$$E = \frac{1}{2m} p^2 + \frac{1}{2} m \omega^2 x^2$$
3.2

Since

$$\int P(x,p)dx dp = \frac{1}{Z}\int e^{-E(x,p)/k_B T} dx dp = 1,$$

this implies that

$$Z = \int e^{-\beta (\frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2)} dx dp$$

$$= \int e^{-\beta \frac{1}{2m}p^2} dp \int e^{-\beta \frac{1}{2}m\omega^2 x^2} dx$$

$$= \left( \sqrt{\frac{2m\pi}{\beta}} \right) \left( \frac{1}{\omega} \sqrt{\frac{2\pi}{m\beta}} \right)$$

$$= \frac{2\pi}{\omega \beta}$$

3.3

Using the Gaussian integral formula you found in Homework 1,

$$\langle E \rangle = \frac{1}{Z} \int e^{-\beta (\frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2)} \left( \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2 \right) dx dp$$

$$= \frac{1}{Z} \int \frac{1}{2m}p^2 e^{-\beta \frac{1}{2m}p^2} dp \int e^{-\beta \frac{1}{2}m\omega^2 x^2} dx + \frac{1}{Z} \int e^{-\beta \frac{1}{2m}p^2} dp \int \frac{1}{2}m\omega^2 x^2 e^{-\beta \frac{1}{2}m\omega^2 x^2} dx$$

$$= \frac{\omega \beta}{2\pi} \left( \frac{1}{2m} \cdot \frac{1}{2} \sqrt{\frac{2m\pi}{\beta}} \right) \left( \frac{1}{\omega} \sqrt{\frac{2\pi}{m\beta}} \right) + \frac{\omega \beta}{2\pi} \left( \sqrt{\frac{2m\pi}{\beta}} \right) \left( \frac{1}{2}m\omega^2 \cdot \frac{1}{2}m\omega^2 \beta \omega \sqrt{\frac{2\pi}{m\beta}} \right)$$

$$= \frac{1}{2\beta} + \frac{1}{2\beta}$$

$$= k_B T$$

Problem 4. Rayleigh-Jeans Law

4.1

Periodicity implies

$$e^{ik_x x} = e^{ik_x (x+L)}$$

(12)

and so $$k_x = \frac{2\pi}{L} n_x$$ for $$n_x \in \mathbb{Z}$$. Similar conditions hold for $$k_y$$ and $$k_z$$.

4.2

Since $$\omega = c|\vec{k}|$$, if we want modes with $$\omega$$ less than $$\nu$$, this is equivalent to finding the 3-tuples $$(n_x, n_y, n_z)$$ such that

$$\frac{2\pi c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} < \nu$$

(13)
Ignoring photon polarisation, we just sum over all such 3-tuples that satisfy the inequality above to get the total number of modes.

\[
N(\nu) = \sum_{n_x, n_y, n_z \in \mathbb{Z}, \sqrt{n_x^2 + n_y^2 + n_z^2} < \frac{L \nu}{2 \pi c}} 1
\]  

(14)

4.3

Just as we did in Homework 7, we can approximate this sum as an integral. Define \( R = \frac{L \nu}{2 \pi c} \).

\[
N(\nu) = \int_{n_x^2 + n_y^2 + n_z^2 < R^2} dn_x dn_y dn_z = \frac{4}{3} \pi R^3 = \frac{L^3 \nu^3}{6 \pi^2 c^3}
\]  

(15)

4.4

\[
\rho(\nu) = \frac{\partial N(\nu)}{\partial \nu} = \frac{L^3 \nu^2}{2 \pi^2 c^3}
\]  

(16)

4.5

Since \( \Gamma(\nu) \propto I(\nu) \propto k_B T \rho(\nu) \), we expect \( \Gamma(\nu) \propto \nu^2 \). So \( \Gamma(\nu) \) should scale quadratically with \( \nu \).

Problem 5. Energy in a Thermal Quantum Harmonic Oscillator

5.1

Ignoring ground state energy,

\[
Z = \sum_{n=0}^{\infty} e^{-\hbar \omega n \beta}
\]

\[
= \sum_{n=0}^{\infty} e^{-\hbar \omega n \beta}
\]

\[
= \frac{1}{1 - e^{-\hbar \omega \beta}}
\]  

(17)

where in the last step we have evaluated the sum by recognising that it is a geometric series.

\[
\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \left[ \frac{-(-\hbar \omega)(-e^{-\hbar \omega \beta})}{(1 - e^{-\hbar \omega \beta})^2} \right]
\]

\[
= \frac{\hbar \omega e^{-\hbar \omega \beta}}{1 - e^{-\hbar \omega \beta}}
\]

\[
= \frac{\hbar \omega}{e^{\hbar \omega \beta} - 1}
\]  

(18)

The relation used in the first line can be deduced from the given definitions of \( \langle E \rangle \) and \( Z \).

5.2 We get the classical equipartition result if \( \frac{\hbar \omega \beta}{2} \ll 1 \), or \( k_B T \gg \frac{\hbar \omega}{2} \).
Problem 6. Planck

6.1

Since the equipartition theorem no longer holds, we should replace the $k_B T$ factor in

$$I(\nu)d\nu = k_B T \rho(\nu)d\nu$$  \hspace{1cm} (19)

by our results for $\langle E \rangle$:

$$I(\nu)d\nu = \frac{\hbar \nu}{e^{\hbar \nu / \beta} - 1} \rho(\nu)d\nu$$  \hspace{1cm} (20)

6.2

Recalling our results for $\rho(\nu)$ earlier on,

$$\Gamma(\nu) \propto I(\nu)$$

$$= \frac{\hbar \nu}{e^{\hbar \nu / \beta} - 1} \rho(\nu)$$

$$= \frac{\hbar \nu}{e^{\hbar \nu / \beta} - 1} L^3 \nu^2$$

$$= \frac{\hbar L^3}{2\pi^2 c^3} \frac{\nu^3}{e^{\hbar \nu / \beta} - 1}$$  \hspace{1cm} (21)

6.3

As $\nu \rightarrow \infty$, $\frac{1}{e^{\hbar \nu / \beta} - 1} \sim e^{-\hbar \nu / \beta}$, which overwhelms the $\nu^3$ factor. Therefore, $\Gamma(\nu)$ exponentially decays to zero.

Note that had you included the vacuum energy in Problem 5, you would have obtained the wrong result, because you will find that $\langle E \rangle$ has an extra contribution of $\frac{1}{2}\hbar \nu$, so your $I(\nu)$ will contain an extra term that is just proportional to $\nu^3$, which diverges for large $\nu$. The key point is that vacuum energy cannot be radiated out of the aperture.

6.4
Plot of $\Gamma(\nu)$ against $\nu$