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

The $H_2^+$ ion consists of two protons, and one electron. Within the Born Oppenheimer approximation, we “integrate out” the electron to produce an effective potential felt by the protons. The Born-Oppenheimer potential is

$$V(R_1 - R_2) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|R_1 - R_2|} + \mathcal{E}(R_1 - R_2)$$

where the first term is the direct interaction between the protons, and the electronic contribution is the eigenvalue of an electronic problem. In the case of $H_2^+$, this is a single electron problem,

$$\mathcal{E}\psi(r) = -\frac{\hbar^2}{2m_e} \nabla^2 \psi(r) - \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{|R_1 - r|} + \frac{1}{|R_2 - r|} \right] \psi(r).$$

Adimensionalized, this equation reads

$$\mathcal{E}\psi(r) = \frac{1}{2} \nabla^2 \psi(r) - \left[ \frac{1}{|R_1 - r|} + \frac{1}{|R_2 - r|} \right] \psi(r).$$

We will work with this adimensionalized form – so our energies are in Rydbergs, and our lengths in Bohr’s, and $V = 1/|R_1 - R_2| + \mathcal{E}$.

If you are interested in an analytic variational solution to this – you can look at Griffiths Chapter 7.3. It is kind of ugly though, because it is a 3D problem without spherical symmetry. Last year I walked students through that as a homework problem, but many students found it dissatisfying and mathematical. Instead we will numerically consider the 1D analog

$$\mathcal{E}\psi(x) = -\frac{1}{2} \frac{d^2}{dx^2} \psi(x) - \left[ W(x - X_1) + W(x - X_2) \right] \psi(x),$$

where $W(x)$ is the Coulomb interaction between the nucleus and the electron. It turns out that the $1/x$ potential is not that well behaved in 1D, so we will use a truncated version

$$W(x) = \frac{1}{\sqrt{x^2 + \delta^2}}.$$

We will take $\delta$ to be a small number, so that this is similar to a $1/x$ potential. For your numerics take $\delta = 0.1$.

1.1. Plot the function $V_e(x) = -W(x - X_1) - W(x - X_2)$ for $x$ running from $-5$ to $5$ with $X_1 = -3/2$ and $X_2 = 3/2$. Choose a scale for your axes so that the main features can be seen. Label your axes. Do not submit a program which plots this, just submit this graph.
1.2. Write a program which will numerically solve Eq. (4), finding the 5 eigenvalues closest to \(-8\), for fixed \(d = X_1 - X_2\). [These will be the 5 lowest eigenvalues.] Take \(\delta = 0.1\), and a real space grid running from \(x = -10\) to 10 with a grid spacing of 0.1. Place the two “protons” symmetrically, \(X_1 = d/2\) and \(X_2 = -d/2\).

To make `eigsh` return eigenvalues close to \(-8\), make one of its arguments `sigme=-8`.

Tabulate the function \(E(d)\), for these 5 states, with \(d\) running from 0 to 5 in steps of 0.1. *Do not hand this in – this is just so that you can plot \(V\).*

Make a properly labeled plot of the Born-Oppenheimer potential \(V(d) = E(d) + W(d)\) as a function of \(d\) for these 5 orbitals. [We add \(W(d)\), as this is the direct interaction between the protons.] *Do not submit your program, just submit this graph with your homework.* Annotate your graph (either by hand or with the computer) to point out the potential coming from the bonding orbital and from the lowest antibonding orbital.

1.3. Plot the electronic wavefunction for the lowest bonding and antibonding orbitals when the nuclei are separated by a distance \(d = 3\). Label your graph, and mark which is bonding, and which is antibonding. *Do not submit your program, just submit the graph.*

**Problem 2. Semiclassical Molecule** I want you to model the excitation spectrum of a neutral diatomic molecule. Generically there are three types of excitations:

- electronic – an electron is promoted to a higher level
- vibrational – the distance between the two atoms oscillates
- rotational – the atoms rotate around one-another

Here you will estimate the energy scale of each of these excitations.

2.1. What is the typical bond length in a diatomic molecule (such as CO, or \(H_2\))? Feel free to look this up in a textbook or on the web. You could also figure it out with dimensional analysis. We just need an order of magnitude.

2.2. One can roughly model the electronic states by considering the electrons to be trapped in a square box of size given by your solution to 2.1. If so, what is the energy scale of electronic excitations (in eV)?

One can estimate the vibrational energy by approximating the Born-Openheimer potential as a harmonic oscillator \(V(r) \sim \frac{1}{2}k(r - r_0)^2\), where \(r_0\) is the equilibrium size of the molecule, and \(r\) is the separation between the nuclei. We will use dimensional analysis to estimate the constant \(k\).
2.3. What units does $k$ have?

2.4. The Born Oppenheimer potential comes from the solution of an electronic problem in the presence of the nuclei. List the dimensional quantities that it seems reasonable for $k$ to depend on. Can you construct a unique $k$ from these? If you have too many dimensional quantities, check to see if any of them are similar in size. Since we are looking for a numerical answer, these all are equivalent for us. If you still have too many, critically evaluate them and discard ones which are less likely to play a role in this physics. If you have too few dimensional quantities, look at Eq. (2). This is the equation for the Born-Oppenheimer potential, so they should all be there. Maybe you missed a fundamental constant like $\hbar$?

Use these numbers to estimate $k$ (in physical units).

2.5. The energy of these vibrations should be $\hbar \omega = \hbar \sqrt{k/m}$, where $m$ should be a the nuclear mass. Estimate the energy of vibrational excitations (in eV).

2.6. For the rotational energy scales, we can use the classical expression, $E = L^2/2I$. Quantum mechanically, what are the allowed values of $L$?

2.7. From the geometry of the diatomic molecule, estimate the moment of inertia $I$.

2.8. Estimate the energy (in eV) of the rotational excitations.

Problem 3. Equipartition Note: This is a problem from classical statistical mechanics. We will need the answer for the next few problems, and it will reveal a failing of classical mechanics. We will then show how quantum mechanics fixes the problem. If I wanted to challenge you I would just ask: Find the average energy of a classical harmonic oscillator attached to a heat bath at temperature $T$. I am however nice, so I’ve laid out the required modeling below. If you want the extra challenge, feel free to try it without looking at these hints – in that case you don’t need to do all of the subparts to the problem, just come up with an answer (and give a sound argument).

3.1. The first modeling step is to think of a concrete realization of a harmonic oscillator. Lets take a particle of mass $m$ attached to a spring with spring constant $k = \omega^2$. Write the energy $E$ of this particle as a function of its position $x$ and momentum $p$.

3.2. According to classical statistical mechanics, the probability of the particle being within $dx$ of position $x$ and with have momentum within $dp$ of $p$ is

$$P(x, p) \, dx \, dp = \frac{e^{-E(x,p)/k_B T}}{Z} \, dx \, dp \quad (6)$$

where the partition function $Z$ is a normalization constant, defined to make

$$\int P(x, p) \, dx \, dp = 1. \quad (7)$$

Write $Z$ as an integral. You don’t need to evaluate it (yet).
3.3. The average energy is then

\[ \langle E \rangle = \int P(x,p)E(x,p) \, dx \, dp. \quad (8) \]

Calculate \( \langle E \rangle \). Hint: its easiest if you write this as a ratio of two integrals, and make a change of variables to scale out all dimensional quantities.

You have just proved the equipartition function, which says that a classical harmonic oscillator in thermal equilibrium has energy \( k_B T \), regardless of its frequency.

**Problem 4. Rayleigh-Jeans Law** We will use the equipartition function to estimate the spectrum of a “black body”. A black body is a model for a furnace. The idea is that inside a furnace the electromagnetic field is in thermal equilibrium with the walls. Imagine we drill a small hole in our furnace, and put a filter in the hole so that it only lets photons with an angular frequency within \( d\nu \) of \( \nu \) out of the hole, then the power emerging from the hole is \( \Gamma(\nu) \, d\nu \). The function \( \Gamma(\nu) \) is the black body spectrum.

The way we will estimate \( \Gamma(\nu) \) is we will first calculate \( \mathcal{I}(\nu) \), the amount of energy stored in the furnace in modes with angular frequency between \( \nu \) and \( \nu + d\nu \). Since all light moves at the same speed, we should have \( \Gamma(\nu) \propto \mathcal{I}(\nu) \).

Recall from PHYS 2214/2218 that each mode of the electromagnetic field is just a harmonic oscillator. If we let \( \rho(\nu) \, d\nu \) be the number of modes in the cavity with angular frequency within \( d\nu \) of \( \nu \), then equipartition tells us that the energy contained in those modes will be

\[ \mathcal{I}(\nu) \, d\nu = k_B T \rho(\nu) \, d\nu. \quad (9) \]

The function \( \rho(\nu) \) is known as the density of states.

4.1. To find the electromagnetic modes in the furnace, we would in principle need to know all sorts of details about its shape and the material properties. (For example, conducting walls will give different boundary conditions for Maxwell’s equations than insulating walls.) We just need an estimate though, so we will treat the furnace as a cubic box of length \( L \), with periodic boundary conditions. You can also use ”hard wall” boundary conditions if you prefer. The result is the same in the end.

What are the allowed wavevectors for electromagnetic waves in a box of length \( L \)?

4.2. Write a sum which expresses how many modes have angular frequency less than \( \nu \). Call this quantity \( \mathcal{N}(\nu) \). [This is similar to the calculation you did in HW 7, except the dispersion is different.] Ignore polarization.

4.3. Approximate the sum as an integral, and perform the integral to estimate \( \mathcal{N}(\nu) \).
4.4. The number of modes is just the integral of the density of states:

\[ \mathcal{N}(\nu) = \int_{0}^{\nu} \rho(\tilde{\nu}) \, d\tilde{\nu}. \]  

(10)

Take a derivative to calculate \( \rho(\nu) \).

4.5. How does \( \Gamma(\nu) \) scale with \( \nu \) for larger \( \nu \). This is known as the Rayleigh-Jeans law.

If you actually do the experiment, you will see that \( \Gamma(\nu) \to 0 \) as \( \nu \to \infty \). Thus the classical theory gives a qualitatively incorrect result.

Problem 5. Energy in a Thermal Quantum Harmonic Oscillator

The error in Rayleigh and Jeans’ argument is that equipartition does not hold in a quantum world. The eigenstates of the harmonic oscillator are labeled by an integer \( n \). The average energy at temperature \( T \) should be

\[ \langle E \rangle = \frac{\sum_n E_n e^{-E_n/k_B T}}{Z}, \]  

(11)

where

\[ Z = \sum_n e^{-E_n/k_B T}. \]  

(12)

5.1. Calculate Eq. (11), using the spectrum of a harmonic oscillator. Do not include the zero-point energy, as it will not contribute to the power emerging from the furnace. That is take \( E_n = \hbar \omega n \) for integer \( n \).

5.2. Under what circumstances does this reduce to the classical equipartition result?

Problem 6. Planck

6.1. How should equation (9) be corrected to account for the quantum mechanical result you found in problem 5?

6.2. What is the quantum result for \( \Gamma(\nu) \) – this is known as the Planck black body spectrum. Don’t worry about multiplicative constants, I just want to know how it scales with \( \nu \).

6.3. How does \( \Gamma(\nu) \) behave as \( \nu \to \infty \)?

6.4. Plot \( \Gamma(\nu) \).

Problem 7. Feedback

7.1. How long did this homework take?

7.2. Which of the following words come to mind when you think about this homework (feel free to add your own words if you have something better): frustrating, fun, tedious, insightful, hard, easy, useful, useless, fair, unfair