Homework 11

Due: 11:59 PM MST, December 1. Submit your homework via Canvas.

Grading: 40 points required for full credit. 50 points are possible. You can score over 100%.

Problem 1: Consider a quantum system with an "exactly solvable" Hamiltonian H_0, which is diagonal in the basis $|n^{(0)}\rangle$: $H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$. For simplicity assume H_0 is not degenerate. Now, imagine that we have a time-dependent Hamiltonian

$$H(t) = H_0 + \epsilon(t)V \tag{1}$$

with V a generic operator with only off-diagonal elements in the H_0 eigenbasis, and

$$\epsilon(t) = \epsilon \times \begin{cases} 1 & 0 \le t \le T \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

with ϵ a perturbatively small parameter. Suppose that for times $t < 0$, we have a quantum system in an eigenstate of H_0: $|\psi(t)\rangle = \mathrm{e}^{-\mathrm{i}E_m^{(0)}t/\hbar}|m^{(0)}\rangle$.

5 points (a) Find a formula for $\langle n^{(0)}|\psi(t)\rangle$ for every n, valid to first order in ϵ, for all $0 < t < T$. Write the answer in terms of $\langle m^{(0)}|V|n^{(0)}\rangle$, $E_n^{(0)}$; evaluate all integrals in your answer.

5 points (b) Use the fact that $\langle\psi|\psi\rangle = 1$ to determine the probability that the state stays in $|m^{(0)}\rangle$, valid to second order in ϵ. Namely, using only the result of part (a), find $|\langle m^{(0)}|\psi(t)\rangle|^2$ to second order in ϵ. Hence, some things in second order time-dependent perturbation theory are "easy" to calculate!

5 points (c) Calculate $\langle\psi(t)|H(t)|\psi(t)\rangle$ to $\mathrm{O}(\epsilon^2)$, for all times $0 < t < T$. Show that

$$\langle\psi(t)|H(t)|\psi(t)\rangle = E_m^{(0)}. \tag{3}$$

Why is energy conserved?

(d) Now calculate $\langle\psi(t)|H(t)|\psi(t)\rangle$ for $t > T$, after the perturbation has been switched off, to second order in ϵ. Show that

$$\langle\psi(t)|H(t)|\psi(t)\rangle = E_m^{(0)} + 2\epsilon^2 \sum_{n\neq m} \frac{|\langle m^{(0)}|V|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \left(1 - \cos\frac{(E_n^{(0)} - E_m^{(0)})T}{\hbar}\right) + \cdots. \tag{4}$$

Why is energy no longer conserved?

10 points **Problem 2:** What is the lifetime of an electron in the $n = 2$, $l = 1$, $m = 0$ state of the hydrogen atom, due to the spontaneous emission of photons? Ignore spin and fine structure.

10 points **Problem 3 (21 cm radiation):** Recall that there is a hyperfine interaction between the electron and proton spin, and in the 1s state of the hydrogen atom, the effective spin Hamiltonian is

$$H_0 = A\mathbf{S}\cdot\mathbf{I} \tag{5}$$

where $\mathbf{S}$ denotes the electron spin, and $\mathbf{I}$ denotes the proton spin.

In the presence of a background electromagnetic wave, we can approximate that the spin of the electron (as it is much lighter) dominates the coupling to the electromagnetic wave. The coupling of the electron spin to classical radiation is governed by the Hamiltonian

$$H'(t) = gB_0S_z\cos(\omega t), \tag{6}$$

for a certain polarization of photon. Show explicitly that this perturbation couples (some of) the singlet and triplet states when ω is chosen correctly. What is the required value of ω? As a consequence, we can expect that the hyperfine levels in hydrogen couple to electromagnetic radiation. This coupling is to light with wavelength 21 cm, and is responsible for the ubiquitous "21 cm radiation" that is used in astronomy.

Problem 4 (Greenhouse gases): The primary concern with greenhouse gas emissions – such as CO_2, carbon dioxide – is that they can lead to global warming via the greenhouse effect. A cartoon of this is as follows. Imagine that you have a CO_2 molecule in the atmosphere, and a photon comes up from the Earth's surface, carrying away energy. If the molecule can absorb this photon, it will re-emit it towards space half the time, but half the time emit it back down to Earth, where it gets reabsorbed. This process repeats many times until the photon escapes, but more energy is trapped on Earth while this process occurs, and this leads to a rise in temperature. Is this process is likely to occur?

First, let us analyze the CO_2 molecule itself; the molecule is linear, as shown in Figure 1. For the purposes of this problem, we can indeed assume that the atoms move along a one dimensional line. Let x_0 denote the displacement of the central carbon atom, and x_+ and x_- denote the displacements of the right/left oxygen atoms respectively. We define p_0, p_+ and p_- as the corresponding momenta. The Hamiltonian of the CO_2 molecule is then

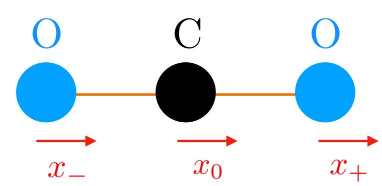

Figure 1: The CO_2 molecule, together with the displacements of the 3 atoms.

$$H = \frac{p_0^2}{2m_\mathrm{C}} + \frac{p_+^2+p_-^2}{2m_\mathrm{O}} + \frac{k}{2}(x_0-x_-)^2 + \frac{k}{2}(x_0-x_+)^2 \tag{7}$$

where m_C and m_O denote the masses of carbon and oxygen respectively, and k is a spring constant arising due to the covalent bonding energy between C and O.

5 points **(a)** Doing as little linear algebra as possible, argue that the three normal modes of the coupled oscillators above must correspond to[1]

$$\begin{pmatrix} x_- \\ x_0 \\ x_+ \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \quad \begin{pmatrix} 1 \\ -2m_\mathrm{O}/m_\mathrm{C} \\ 1 \end{pmatrix}. \tag{8}$$

(b) Show that the vibrational frequencies of the corresponding normal modes are

$$\omega = 0, \quad \sqrt{\frac{k}{m_\mathrm{O}}}, \quad \sqrt{\frac{k}{m_\mathrm{O}}\left(1+\frac{2m_\mathrm{O}}{m_\mathrm{C}}\right)}. \tag{9}$$

[1] *Hint:* This is a rather symmetric problem. What do those symmetries imply? The third mode is the only one that should require a modest amount of algebra.

5 points (c) Let us now determine how a simple harmonic oscillator couples to electromagnetic radiation. You may now for simplicity study a single harmonic oscillator of frequency ω, with Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2. \tag{10}$$

If the dipole moment operator is

$$\mathfrak{p} = \alpha x, \tag{11}$$

show that the frequency of electromagnetic radiation that can be emitted or absorbed by this oscillator is (within the dipole approximation) *only* ω. Why can we not absorb efficiently at 2ω, 3ω, etc.?

(d) Due to the asymmetry of the electronic wave functions around C vs. O atoms, the dipole moment of the CO_2 molecule can be approximated to be

$$\mathfrak{p} = a(x_+ + x_-) - 2ax_0. \tag{12}$$

Use the results of part (a) to show that only the third normal mode of the CO_2 molecule might effectively absorb and emit electromagetic radiation. Use part (b) to then determine what the frequency of this radiation is.

5 points (e) Now, let us plug in numbers. Give a heuristic explanation for why the energy scale associated with a chemical bond is about 2×10^{-18} J, and the length of a chemical bond is about 10^{-10} m.[2] Then, combine these estimates with dimensional analysis to estimate what the spring constant k should be for a typical chemical bond.

(f) Given the mass of hydrogen at $m \approx 2 \times 10^{-27}$ kg, estimate the masses of carbon and oxygen atoms, and then the angular frequency of the normal mode which couples to electromagnetic radiation.

(g) What is the wavelength of light λ that this oscillator mode couples to?

(h) A thermal body emits electromagnetic radiation at all wavelengths. However, the *typical* wavelength λ_* of radiation by a thermal body at temperature T is

$$\lambda_* T \approx 3 \times 10^{-3}\ \mathrm{m \cdot K}. \tag{13}$$

Compare the typical wavelength of radiation emitted by the Earth to the wavelength absorbed by CO_2. Do you conclude based on this simple analysis that the greenhouse effect is possible?

(i) Without doing any calculations, explain why N_2 is not a greenhouse gas, while H_2O is.

[2] *Hint:* A useful starting point would be to think about the exact solution of the quantum hydrogen atom.