Homework 8

Due: April 6 at 11:59 PM. Submit on Canvas.

Problem 1 (Clock transitions): Identifying good "qubits" in atomic or solid-state platforms is a problem of current research interest. A toy model for how we can try to find such a good qubit is as follows. Consider a single nuclear spin $\mathbf{I}$, interacting with a single electron spin $\mathbf{S}$, through the hyperfine interaction. (These spins could either be in an isolated atom, or in a defect atom in a solid.) The total nuclear spin and total electron spin are both $\frac{1}{2}$. In the presence of a background magnetic field of strength B, pointing in the z-direction, we model the Hamiltonian for the two spins as

$$H = H_0 + V, \quad H_0 = A\mathbf{S} \cdot \mathbf{I} + Bg_0(S_z + I_z), \quad V = B\delta S_z. \tag{1}$$

Here, for convenience, set $\delta \ll g_0$ to be a small perturbation, with $A, B, g_0 > 0$ all constants.

10   **A:** Show that the eigenstates of H_0 are the coupled basis states (Lecture 17), while the eigenvalues are

$$E^{(0)} = -\frac{3}{4}A\hbar^2, \frac{1}{4}A\hbar^2 - Bg_0\hbar, \frac{1}{4}A\hbar^2, \frac{1}{4}A\hbar^2 + Bg_0\hbar. \tag{2}$$

20   **B:** Assume that H_0 is non-degenerate (which is true for generic magnetic field strengths B). Now consider $\delta \neq 0$, and for V to be a small perturbation.

     B1. Write down the matrix elements of V in the coupled basis.

     B2. Calculate the eigenvalues of H, E_n, up to second order in δ:

$$E \approx -\frac{3}{4}A\hbar^2 - \frac{B^2\delta^2}{4A}, \frac{1}{4}A\hbar^2 - Bg_0\hbar - \frac{B\delta\hbar}{2}, \frac{1}{4}A\hbar^2 + \frac{B^2\delta^2}{4A}, \frac{1}{4}A\hbar^2 + Bg_0\hbar + \frac{B\delta\hbar}{2}. \tag{3}$$

5   **C:** If there is magnetic field noise in nature (so B fluctuations), we would like to be able to accurately address our qubit, meaning that we should store the qubit in two energy levels a and b such that $\Delta E = E_a - E_b$ is approximately independent of B. Find ω_0 (and the states a and b) such that for small b, ΔE depends on B as weakly as possible (when B is small). Such a transition is called a **clock transition**, since its frequency is more stable than the other possible transitions.

Problem 2 (Fine structure of hydrogen): Small relativistic corrections to the hydrogen atom's spectrum are called **fine structure**. Ignoring spin, the relativistic Hamiltonian for the hydrogen atom is given by

$$H = \sqrt{m^2c^4 + \mathbf{p}^2c^2} - mc^2 - \frac{e^2}{4\pi\epsilon_0 r}. \tag{4}$$

The speed of light c is very large, and so we can think of $1/c$ as a small parameter.

5   **A:** Perform a Taylor series in $1/c$, and show that

$$H \approx \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} - \frac{\left(\mathbf{p}^2\right)^2}{8m^2c^2} + \cdots. \tag{5}$$

20 **B:** The $1/c^2$ term in (5) can be treated as a small perturbation. Although the hydrogen atom spectrum is degenerate in general, if all we care about is the correction to the ground state energy, since the ground state is non-degenerate we can go ahead and use non-degenerate perturbation theory. Let H_0 denote the non-relativistic hydrogen atom Hamiltonian, namely (5) with $c = \infty$.

B1. Write $\mathbf{p}^2$ in terms of H_0 and $1/r$, together with any constants of nature (m, c, ϵ_0, e).

B2. Let $E_0^{(0)}$ denote the ground state energy of hydrogen. Show that at first order in perturbation theory,

$$E_0^{(1)} = -\frac{1}{2mc^2}\left(\left(E_0^{(0)}\right)^2 + \frac{e^2}{2\pi\epsilon_0}E_0^{(0)}\left\langle\frac{1}{r}\right\rangle + \frac{e^4}{(4\pi\epsilon_0)^2}\left\langle\frac{1}{r^2}\right\rangle\right), \tag{6}$$

where $\langle\cdots\rangle$ are expectation values in the unperturbed ground state of the hydrogen atom.

B3. Show how to evaluate out these integrals, using the ground state wave function in spherical coordinates,

$$\psi_0(r) = \frac{e^{-r/a}}{\sqrt{\pi a^3}}, \quad a = \frac{4\pi\epsilon_0\hbar^2}{me^2}. \tag{7}$$

B4. Defining the **fine structure constant**

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}, \tag{8}$$

conclude that

$$E_0^{(0)} + E_0^{(1)} \approx -\frac{1}{2}mc^2\alpha^2 - \frac{5}{8}mc^2\alpha^4 + \cdots. \tag{9}$$

(9) tells us that the ground state energy of hydrogen is smaller than its rest mass by a factor of α^2. The same factor describes the strength of relativistic corrections to the hydrogen atom spectrum, which are evidently rather small (but detectable in experiment nonetheless!).

Problem 3 (Dissociation of the hydrogen molecule): We saw on Homework 1 that the harmonic oscillator could be a good approximation for a chemical bond in a diatomic molecule, such as H_2. Consider the following oscillator model for such a bond:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - \gamma x^3 + \cdots \tag{10}$$

We solved this problem exactly when $\gamma = 0$. Now, let us solve this problem with perturbation theory when γ is "small".

10 **A:** Let us begin with dimensional analysis.

A1. What are the SI units of the parameter γ?

A2. Build a quantity with the same units as γ out of m, $\hbar$ and ω: i.e. $m^a\hbar^b\omega^c$ (what are a, b, c?).

A3. Explain why γ must be small relative to this quantity you have built for perturbation theory to be a sensible approximation method.

20 **B:** Go up to second order in perturbation theory in the "small parameter" γ.

B1. Show that the nth energy level of H is approximately[1]

$$E_n \approx \hbar\omega\left(n + \frac{1}{2}\right) - \frac{\hbar^2\gamma^2}{8m^3\omega^4}\left(11 + 30n + 30n^2\right) + \cdots \tag{11}$$

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[1]*Hint:* First express x in terms of raising and lowering operators.

Is your argument from part reasonable?

C: The result of part **B** suggests that for large enough n, the values E_n start to decrease! At this point, we should expect the covalent bond will break, since this downturn is signaling that the particle is beginning to escape to $x = +\infty$ (where the potential energy is arbitrarily negative). We can *estimate* the energy scale at which H_2 would break apart (the **dissociation energy**) by fitting the discrete energy levels E_n measured in the actual H_2 molecular bond to a quadratic function of the parameter n (treat it as continuous for this part), and looking for the maximum value of this fitting function. The energy levels of the H_2 bond are

$$\Delta E = 0.52, 1.00, 1.46, 1.89, 2.29, 2.67, 3.01, 3.33, 3.61, 3.86, 4.08, 4.25, 4.38, 4.46 \text{ eV}. \tag{12}$$

(The first entry in this list is $E_1 - E_0$, the second is $E_2 - E_0$, and so on.) Estimate the dissociation energy of this bond, and compare to the experimental value of 4.52 eV.

Problem 4 (Perturbation theory from block matrix inversion): Consider a non-degenerate Hamiltonian H_0 on a finite dimensional Hilbert space. Assume H_0 has eigenvectors $|n^{(0)}\rangle$ with eigenvalues $E_n^{(0)}$. Let λ be perturbatively small, and consider the new Hamiltonian $H = H_0 + \lambda V$.

In this problem, we will think about the perturbation theory for the eigenvalues of H by using the following block matrix inversion formula: let A be an $m \times m$ matrix, B be an $m \times n$ matrix, C be an $n \times m$ matrix and D be an $n \times n$ matrix. Then

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{pmatrix} (A - BD^{-1}C)^{-1} & -(A - BD^{-1}C)^{-1}BD^{-1} \\ -D^{-1}C(A - BD^{-1}C)^{-1} & D^{-1} + DC^{-1}(A - BD^{-1}C)^{-1}BD^{-1} \end{pmatrix}. \tag{13}$$

You may also find the following formula useful: for "small" matrix N compared to invertible matrix M:

$$(M - N)^{-1} = M^{-1} \sum_{k=0}^{\infty} \left(NM^{-1} \right)^k. \tag{14}$$

1. Define the **resolvent** operator $R(z) = (z - H)^{-1}$. Argue that if we are perturbatively calculating E_n, we are looking for the value of z (close to $E_n^{(0)}$) at which $\langle n^{(0)}|R(z)|n^{(0)}\rangle = \infty$.

2. Show that this condition is satisfied when

$$z = E_n^{(0)} + \lambda \langle n^{(0)}|V|n^{(0)}\rangle + \lambda^2 \sum_{m,k \neq n} \langle n^{(0)}|V|m^{(0)}\rangle \left\langle m^{(0)} \left| \left(z - H_0^\perp - \lambda V^\perp \right)^{-1} \right| k^{(0)} \right\rangle \langle k^{(0)}|V|n^{(0)}\rangle. \tag{15}$$

   where $H_0^\perp$ and $V^\perp$ are the matrices H_0 and V with the $|n^{(0)}\rangle$ row/column deleted.

3. Describe qualitatively how to solve this equation to find the expression for the perturbed E_n to *any order* in λ. Concretely show how the method works by giving the *analytical expressions* for the perturbed E_n up to *fourth order* in λ. As a partial answer:

$$E_n^{(3)} = \sum_{m,k \neq n} \frac{\langle n^{(0)}|V|m^{(0)}\rangle\langle m^{(0)}|V|k^{(0)}\rangle\langle k^{(0)}|V|n^{(0)}\rangle}{(E_m^{(0)} - E_n^{(0)})(E_k^{(0)} - E_n^{(0)})} - \langle n^{(0)}|V|n^{(0)}\rangle \sum_{m \neq n} \frac{|\langle m^{(0)}|V|n^{(0)}\rangle|^2}{(E_m^{(0)} - E_n^{(0)})^2}. \tag{16}$$

This "strange" method for evaluating higher order corrections to $E_n(\lambda)$ should, at a minimum, help explain why the higher order corrections in perturbation theory involve the peculiar sums over $m \neq n$.

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