Week 9 Worksheet Solutions
More Perturbation Theory

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Exercise 1. ***Griffiths 7.54.*** Last week, you derived the first order correction to the expectation value of an observable A in the n^{th} energy eigenstate of a system perturbed by H'. You found

$$\langle A\rangle^1 = 2\sum_{m\neq n}\frac{\left\langle\psi_n^0\middle|A\middle|\psi_m^0\right\rangle\left\langle\psi_m^0\middle|H'\middle|\psi_n^0\right\rangle}{E_n^0-E_m^0}.$$

Suppose we have a particle of charge q in a weak electric field $\mathbf{E} = E_{\text{ext}}\hat{x}$, so that $H' = -qE_{\text{ext}}x$. This induces a dipole moment $p_e = qx$ in the "atom." The expectation value of p_e is proportional to the applied field, and the proportionality factor is called the **polarizability**, α. Show that

$$\alpha = -2q^2\sum_{m\neq n}\frac{\left|\left\langle\psi_n^0\middle|x\middle|\psi_m^0\right\rangle\right|^2}{E_n^0-E_m^0}.$$

Find α for the ground state of a 1-D harmonic oscillator, and compare the classical answer.

Hint: Recall that x can be written in terms of creation and annihilation operators. Given

$$H^0 = \frac{1}{2m}\left[p^2+(m\omega x)^2\right],$$

you can derive what a and $a^\dagger$ should be in terms of x and p by using the sum of squares formula. To get the "usual" form, rescale each of them by $a\to\frac{1}{\sqrt{\hbar\omega}}a$ (so that the hamiltonian can be written $H^0 = a^\dagger a+1/2$).

Just plug in $A = qx$ into the formula for $\langle A\rangle^1$. Since $H' = -qE_{\text{ext}}x$, we get exactly the formula for α shown. Now, we want to find α for the ground state of the harmonic oscillator. In fact, we can find it for any energy eigenstate. Denote the n^{th} energy eigenstate by $|n\rangle$, so that

$$\alpha = -2q^2\sum_{m\neq n}\frac{|\langle n|x|m\rangle|^2}{(n-m)\hbar\omega}.$$

Following the derivation suggested in the hint, we get

$$\begin{aligned}a^\dagger =& \frac{1}{\sqrt{2m}}(m\omega x + ip)\\ a =& \frac{1}{\sqrt{2m}}(m\omega x - ip),\end{aligned}$$

where we can obtain the relative minus sign by remembering that $[a, a^\dagger] = 1$ (this in turn follows from the form of H^0 in terms of a and $a^\dagger$ given in the hint). Now, rescale a and $a^\dagger$ as indicated, so that

$$\begin{aligned}a^\dagger =& \frac{1}{\sqrt{2m\hbar\omega}}(m\omega x + ip)\\ a =& \frac{1}{\sqrt{2m\hbar\omega}}(m\omega x - ip).\end{aligned}$$

Thus,

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger).$$

Plugging this in to the form for α above, we get

$$\begin{aligned}\alpha =& -\frac{\hbar q^2}{m\omega}\sum_{m\neq n}\frac{|\langle n|(a+a^\dagger)|m\rangle|^2}{(n-m)\hbar\omega}\\ =& -\frac{q^2}{m\omega^2}\big(n-(n+1)\big)\\ =& -\frac{q^2}{m\omega^2}.\end{aligned}$$

Classically, a charged particle in a harmonic oscillator potential with an electric field has equation of motion given by Newton's second law:

$$m\ddot{x} = -kx + qE_{\text{ext}}.$$

The solution of this equation is just

$$x(t) = A\sin(\omega t) + B\cos(\omega t) - \frac{1}{k}qE_{\text{ext}},$$

where $\omega = \sqrt{\frac{k}{m}}$. Since the average value of a sinusoid is 0, we get $\langle x\rangle = -\frac{q^2}{m\omega^2}$, *which is exactly the same as the perturbation theory calculation*! This is something that commonly occurs in perturbation theory calculations (especially in quantum field theory), where the first order correction just gives back the classical result. This necessitates going to second or higher order to get any truly quantum effects due to the perturbation!

Exercise 2. ***Griffiths 7.45*. Stark Effect in Hydrogen.** When an atom is placed in a uniform electric field $\mathbf{E}_{\text{ext}}$, the energy levels are shifted. This is known as the **Stark effect**. You'll analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Suppose $\mathbf{E}_{\text{ext}} = E_{\text{ext}}\hat{z}$, so that

$$H' = eE_{\text{ext}} r\cos\theta$$

is the perturbation of the hamiltonian for the electron, where $H^0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$.

a) Show that the ground state energy is unchanged at first order.

b) How much degeneracy does the first excited state have? List the degenerate states.

c) Determine the first-order corrections to the energy. Into how many levels does E_2 split?

Hint: All W_{ij} are 0 except for two, and you can avoid doing all of the zero integrals in this problem by using symmetry and selection rules. You'll need the following

$$\begin{aligned}\psi_{210} =& \frac{1}{2\sqrt{6}} a^{-3/2} \frac{r}{a} e^{-r/2a} \sqrt{\frac{3}{4\pi}} \cos\theta \\ \psi_{200} =& \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{r}{2a}\right) e^{-r/2a} \frac{1}{2\sqrt{\pi}}.\end{aligned}$$

d) What are the "good" wavefunctions for (b)? Find the expectation value of the electric dipole moment in each of these states.

a) The ground state is spherically symmetric, so clearly $\langle H' \rangle = 0$. (Also, you can recall that Y_{00} is a constant).

b) There are 4 degenerate states, ψ_{200}, ψ_{21m}, where $m \in \{-1, 0, 1\}$.

c) First, note that all diagonal elements are 0. This is because a diagonal element will have an even angular part, cosine is even, and the measure will have a sine, which is odd. Since the integral is over an even interval, it will integrate to 0. The integral of ψ_{200} with any of the $m \neq 0$ states will be 0, since the integral of $e^{\pm i\varphi}$ will be 0. Likewise, this kills the integrals of ψ_{210} with any of the $m \neq 0$ states. Finally, we're left with the integral of ψ_{211} with ψ_{21-1}. But this will be 0 by the selection rule that $\ell + \ell'$ must be odd for the matrix element of an operator with odd parity (like $z = r\cos\theta$). We are thus left with one integral, that between the two states given in the hint. Let's do this integral. It will equal

$$\begin{aligned}&\frac{eE_{\text{ext}}}{16a^4\pi} \cdot 2\pi \int_0^\pi \mathrm{d}\theta \int_0^\infty \mathrm{d}r r^4 \left(1 - \frac{r}{2a}\right) e^{-r/a} \cos^2\theta \sin\theta = \\ =& \frac{eE_{\text{ext}}}{8a^4} \cdot \frac{2}{3} \int_0^\infty \mathrm{d}r r^4 \left(1 - \frac{r}{2a}\right) e^{-r/a}.\end{aligned}$$

The integral over r can be done by noticing the following.

$$\int_0^\infty \mathrm{d}r r^n e^{-r/a} = -ar^n e^{-r/a}\Big|_0^\infty + an \int_0^\infty \mathrm{d}r r^{n-1} e^{-r/a}.$$

Notice that the boundary term vanishes, and we get the same integral multiplied by an with the exponent of r reduced by 1. Repeating this process, we'll be left with

$$a^n n! \int_0^\infty e^{-r/a} = a^{n+1} n!.$$

Thus, our original integral is equal to

$$\frac{eE_{\text{ext}}}{12a^4}(4!a^4 - 60a^4) = -3aeE_{\text{ext}}.$$

Denoting $\xi \equiv -3aeE_{\text{ext}}$, we want to find the eigenvalues of a 4×4 matrix all of whose terms are 0 except for a 2×2 minor which is of the form

$$\begin{bmatrix} 0 & \xi \\ \xi & 0 \end{bmatrix}. \tag{1}$$

The eigenvalues of this matrix are $\pm\xi$, and its eigenvectors are

$$\begin{bmatrix} 1 \\ 1 \end{bmatrix} \leftrightarrow \xi$$
$$\begin{bmatrix} 1 \\ -1 \end{bmatrix} \leftrightarrow -\xi.$$

Thus, the energy E_2 splits into *three* energies. One corresponds to the states ψ_{2lm} which aren't ψ_{210} or ψ_{200}. These states have the same energy as for unshifted hydrogen. $\psi_{210} + \psi_{200}$ has energy which is shifted up by ξ, while $\psi_{210} - \psi_{200}$ has energy shifted down by ξ (so up by $3aeE_{\text{ext}}$).

d) The good wavefunctions are given in the previous paragraph. To find $\langle ez \rangle$, the expectation value of the electric dipole, we again have to compute some integrals. But since $z = r\cos\theta$, we have already done them in (c)! Consider first

$$\frac{1}{\sqrt{2}}(\psi_{210} + \psi_{200}).$$

Then, since $H' = ezE_{\text{ext}}$, we have

$$\begin{aligned} \langle ez \rangle &= \frac{1}{E_{\text{ext}}}\langle \psi_{210}|H'|\psi_{200}\rangle \\ &= -3ae. \end{aligned}$$

On the other hand, if we instead consider the state

$$\frac{1}{\sqrt{2}}(\psi_{210} - \psi_{200}),$$

we get $\langle ez \rangle = 3ae$.