Lecture 9 Highlights

In perturbation theory we start with a Hamiltonian H^0 for which we can find the exact eigenvalues E_n^0 and eigenfunctions ψ_n^0:

$$\mathrm{H}^0\psi_n^0 = E_n^0\psi_n^0 \tag{1}$$

We are interested in solving another problem with a very similar Hamiltonian $\mathrm{H} = \mathrm{H}^0 + \lambda\mathrm{H}'$, where H' is called the perturbing Hamiltonian, and $\lambda << 1$ is a small parameter to remind us that the perturbation should be "small." (Later we will take $\lambda = 1$ and replace it with a "smallness" condition on the perturbing Hamiltonian H'.) The exact solution to this problem involves new eigenvalues and eigenfunctions:

$$\mathrm{H}\psi_n = E_n\psi_n \tag{2}$$

To (approximately) solve this new problem we do a perturbation series expansion in powers of the small parameter λ:

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + ... \tag{3}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + ... \tag{4}$$

The terms on the RHS represent zeroth-order, first-order, and second-order corrections to the eigenfunctions and eigenvalues. Note that the superscripts on the ψ's and E's are NOT powers, but labels that keep track of the order of the correction. Remember also that n represents a list of quantum numbers, in general. The expectation is that the new eigenvalues and eigenfunctions will be close to those of the unperturbed problem.

Substituting (3) and (4) into (2) and gathering like powers of the bookkeeping parameter λ yields:

$$\lambda^0: \quad \mathrm{H}^0\psi_n^0 = E_n^0\psi_n^0$$

$$\lambda^1: \quad \mathrm{H}^0\psi_n^1 + \mathrm{H}'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0 \tag{5}$$

$$\lambda^2: \quad \mathrm{H}^0\psi_n^2 + \mathrm{H}'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0 \tag{6}$$

The zeroth-order equation reproduces Eq. (1) for the unperturbed problem. The first-order equation can be solved using the fact that ψ_n^1 can be expressed as a linear combination of all the eigenfunctions of H^0 (a postulate of QM) as,

$$\psi_n^1 = \sum_\ell a_{nl}\ \psi_\ell^0\ , \tag{7}$$

where the $a_{n\ell}$ are unknown at this point. Putting (7) into (5) and exploiting orthonormality of the unperturbed eigenfunctions ψ_n^0 yields two equations:

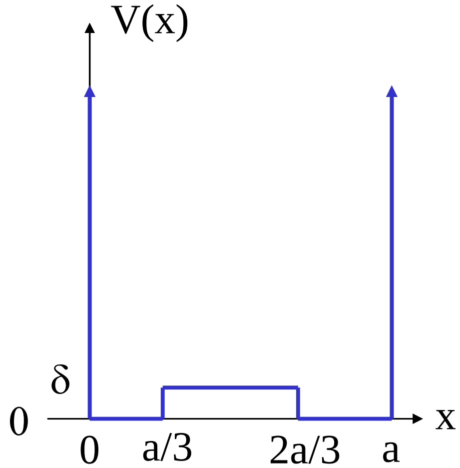
$$E_n^1 = \int \psi_n^{0*}\ \mathrm{H}'\,\psi_n^0\ d^3r \tag{8}$$

$$\psi_n^1 = \sum_{\ell\neq n}\left(\frac{\int \psi_\ell^{0*}\ \mathrm{H}'\,\psi_n^0\ d^3r}{E_n^0 - E_\ell^0}\right)\psi_\ell^0 \tag{9}$$

These are the first-order corrections to the n[th] eigenvalue and eigenfunction, respectively. Note that the sum in Eq. (9) excludes the case $\ell = n$, and assumes that the energy levels are non-degenerate. We expect that $\left|E_n^1\right| << \left|E_n^0\right|$ and $\left|\int \psi_\ell^{0*}\ \mathrm{H}'\,\psi_n^0\ d^3r\right| << \left|E_n^0 - E_\ell^0\right|$ for the perturbation expansion to be valid (this is the "smallness" condition on the perturbing

Hamiltonian). The first order change in energy is the expectation value of the perturbing Hamiltonian in the un-perturbed basis. As seen from Eq. (9), the perturbation has the effect of mixing together all of the eigenfunctions of the unperturbed case, in general. From the denominator of Eq. (9) one sees that states that are nearby in energy tend to be mixed in the most.

Now an example is in order. Consider the infinite square well of width a with a small rectangular bump in the bottom of the potential well. How does this bump change the ground state energy and ground state eigenfunction? It is not possible to solve the Schrödinger equation for this problem exactly. However we can achieve an approximate solution through perturbation theory. We write the unperturbed case as follows.



$$\mathrm{H}^0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \text{ where } V(x) = \begin{cases} 0 \text{ for } 0 < \mathrm{x} < \mathrm{a} \\ \infty \text{ for } x < 0, \mathrm{x} > \mathrm{a} \end{cases}$$

The unperturbed eigenvalues and eigenfunctions are:

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$\psi_n^0(x) = \begin{cases} \sqrt{\frac{2}{\mathrm{a}}} sin\left(\frac{\mathrm{n}\pi\mathrm{x}}{\mathrm{a}}\right) \text{ for } 0 < \mathrm{x} < \mathrm{a} \\ 0 \text{ for } x < 0, \mathrm{x} > \mathrm{a} \end{cases}$$

Here n is a positive integer.

The perturbing Hamiltonian is this:

$$\mathrm{H}'(x) = \begin{cases} \delta \text{ for } a/3 < \mathrm{x} < 2\mathrm{a}/3 \\ 0 \text{ for } x < \mathrm{a}/3, \mathrm{x} > 2\mathrm{a}/3 \end{cases}$$

where δ could be a positive or negative energy. This represents a small "brick" placed in the bottom of the infinite square well.

Examine the effects of this perturbation on just the ground state (n =1) of the system. The un-perturbed ground state is characterized by:

$$E_1^0 = \frac{\pi^2\hbar^2}{2ma^2} \text{ and } \psi_1^0(x) = \sqrt{\frac{2}{\mathrm{a}}} \sin\left(\frac{\pi\mathrm{x}}{\mathrm{a}}\right)$$

The first order correction to the ground state energy is:

$$E_1^1 = \int_{-\infty}^{\infty} \psi_1^{0*}\ \mathrm{H}'\,\psi_1^0\ dx = \int_{a/3}^{2a/3} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \delta \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) dx = \delta\left\{\frac{1}{3} + \frac{\sqrt{3}}{2\pi}\right\} \cong 0.61\,\delta$$

If δ is positive (upward bump on the bottom of the well), the energy of the ground state shifts up. A small well on the bottom ($\delta < 0$) will decrease the energy. The new ground state energy to first order is given by:

$$E_1 \cong E_1^0 + E_1^1 = \frac{\pi^2\hbar^2}{2ma^2} + 0.61\,\delta$$

The first order correction to the ground state wavefunction is:

$$\psi_1^1 = \sum_{\ell \neq 1} \left(\frac{\int \psi_\ell^{0*}\ \mathrm{H}'\,\psi_1^0\ d^3r}{E_1^0 - E_\ell^0} \right) \psi_\ell^0$$

The first term in the sum is $\ell = 2$, but the integral in that case is zero (check it!). The first non-zero term is $\ell = 3$, and this yields for the coefficient a_{13}:

$$a_{13} = \frac{\int_{-\infty}^{\infty} \psi_3^{0*}\ \mathrm{H}'\psi_1^0\ dx}{E_1^0 - E_3^0} = \frac{\int_{a/3}^{2a/3} \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right) \delta \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) dx}{E_1^0 - E_3^0}$$

The integral can be done by standard methods and yields:

$$a_{13} = \frac{\delta m a^2}{4\pi^2\hbar^2} \frac{3\sqrt{3}}{4\pi}$$

The new ground state wavefunction now is to (part of) first order:

$$\psi_1 \cong \psi_1^0 + \psi_1^1 = \psi_1^0 + a_{13}\psi_3^0 + \ldots$$

or

$$\psi_1 \cong \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) + \frac{\delta m a^2}{4\pi^2\hbar^2} \frac{3\sqrt{3}}{4\pi} \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right) + \ldots$$

If we assume $\delta > 0$, note that the correction decreases the wavefunction amplitude in the middle of the well (near x = a/2) and increases it in the “wings”, away from the bump, as we might expect. The unperturbed ground state wavefunction (red) and corrected ground state wavefunction (blue) are sketched in the figure below. The perturbing potential is also shown in green.