Lecture 3 Highlights
Phys 402

Whenever we change the Hamiltonian operator (for example by considering new physical effects in the Hydrogen atom), we have to go back and re-solve the TISE and TDSE from scratch, and find the new eigenvalues and eigenfunctions. This can be very tedious and time-consuming. It would be nice to find a shortcut that relies on the exact solutions to the 'un-perturbed' Hydrogen atom, and determines the new eigenvalues and eigenfunctions as minor corrections to the original versions. This will work as long as the new terms in the Hamiltonian are sufficiently "small." This handy shortcut method is called *perturbation theory*.

Perturbation Theory

The point of perturbation theory is to form an approximate solution for the eigenvalues and eigenfunctions of a complicated problem that is closely related to an exactly solved problem. In perturbation theory we start with an 'unperturbed' 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:

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

We want to solve this Schrodinger equation for the new eigenvalues E_n and eigenfunctions ψ_n. The purpose of perturbation theory is to find approximate expressions for the new eigenvalues E_n and eigenfunctions ψ_n in terms of the eigenvalues and eigenfunctions of the unperturbed problem, and the perturbing Hamiltonian. To (approximately) solve this new problem we do a **perturbation series expansion** in powers of the small parameter λ:

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

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

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.

For now we will be considering systems with non-degenerate spectra, meaning that each eigenstate of the system has a unique eigen-energy. In addition we will consider time-independent problems for now. Both of these restrictions will be lifted later.

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,

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

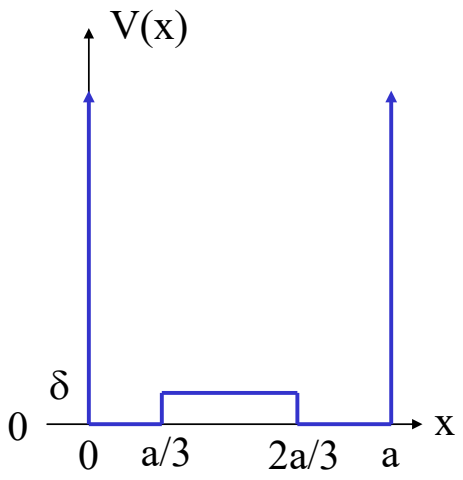
where the $a_{n\ell}$ are unknown at this point. Putting (7) into (5) and exploiting orthonormality (sum-busting!) of the unperturbed eigenfunctions ψ_n^0 yields two equations:

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

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

These are the first-order corrections to the n$^{\text{th}}$ eigenvalue and eigenfunction, respectively. After we evaluate them, these expressions will go back into Eqs. (3) and (4) to get a first-order approximation to the perturbed Schrodinger equation. Note that the sum in Eq. (9) excludes the case $\ell = n$, and assumes that the energy levels of the un-perturbed Hamiltonian are non-degenerate (i.e. $E_n^0 \neq E_l^0$ for all l). 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. We expect the infinite series in Eq. (9) to converge quickly because i) the numerator will likely get small as ℓ increases (due to the integration of a rapidly "wiggling" function ψ_ℓ^{0*} multiplying two – in general - relatively slowly-varying functions H' and ψ_n^0), and ii) the denominator will grow in magnitude as ℓ increases beyond n.

Now an example is in order. Consider a particle of mass *m* in 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. In this case the perturbation is made to the potential function $V(x)$. This represents a small "brick" placed in the bottom of the infinite square well. Note that we expect δ to be "small" in the sense that it should not change completely the character of the problem, such as creating two smaller finite-square wells with many levels in each sub-well. We will state the "smallness" criterion on δ below.

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:

$E_1 \cong E_1^0 + E_1^1 = \dfrac{\pi^2\hbar^2}{2ma^2} + 0.61\,\delta$. The "smallness" requirement for perturbation theory to be valid can be stated as $\left|E_1^1\right| << E_1^0$, or in other words $0.61\left|\delta\right| << \dfrac{\pi^2\hbar^2}{2ma^2}$.

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:

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

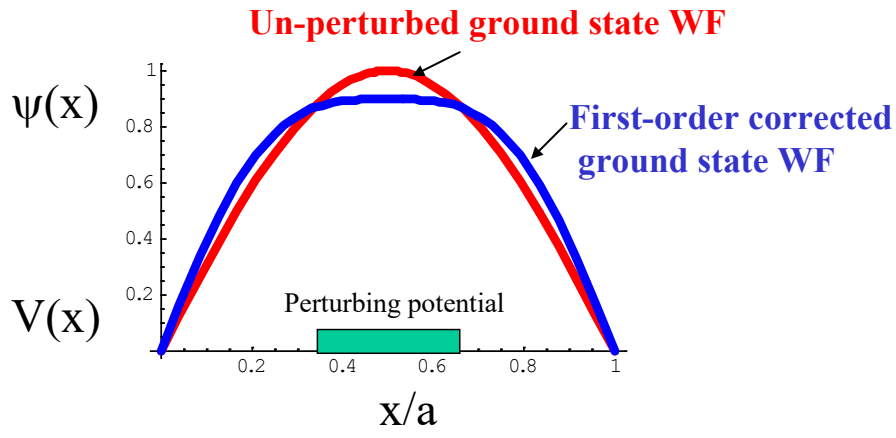
The new ground state wavefunction now is to (part of) first order:

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

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.



Note that the next term in the series expansion for ψ_1 will be proportional to $\sin\left(\frac{5\pi x}{a}\right)$ due to the symmetry of the problem.