

Perturbation Theory

The set of potentials for which the time-independent Schrödinger equation can be exactly solved is very limited and typically these solvable potential will be stylized approximations (the infinite square well) that do not really correspond to physically realistic potentials. This unfortunately means that, more often than not, quantum particles in experimentally accessible potentials can not be described exactly by stationary states than can be expressed as closed form functions. Luckily it is generally possible to use approximation techniques to develop stationary states that are quite close to accurate. The first of these techniques is perturbation theory.

Suppose that we have already exactly solved the set of stationary states and energies of some simplified potential (the infinite square well of simple harmonic oscillator will be obvious examples): $\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0$. Now we wish to *perturb* the Hamiltonian by changing it slightly. We would now like to determine the real set of stationary states and energies: $\hat{H} \psi_n = E_n \psi_n$. But often we can't actually solve this eigenvalue problem exactly. We will then write the Hamiltonian as $\hat{H} = \hat{H}^0 + \lambda \hat{H}'$ where λ is a number that we will crank between 0 (giving the simplified Hamiltonian) and 1 (giving the real Hamiltonian). ψ_n and E_n can be written as power series in λ :

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad \text{and} \quad E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

where E_n^1 is the first-order correction to the energy, etc. Writing out the energy eigenvalue equation gives us

$$(\hat{H}^0 + \lambda \hat{H}')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots]$$

If we rewrite this collecting like powers of λ together it becomes

$$\begin{aligned}\hat{H}^0\psi_n^0 + \lambda(\hat{H}^0\psi_n^1 + \hat{H}'\psi_n^0) + \lambda^2(\hat{H}^0\psi_n^2 + \hat{H}'\psi_n^1) + \dots \\ = E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \dots\end{aligned}$$

and, equating like powers of λ

$$\hat{H}^0\psi_n^1 + \hat{H}'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

and so on.

Now we take the previous equation and inner product ψ_n^0 with it:

$$\langle\psi_n^0|\hat{H}^0\psi_n^1\rangle + \langle\psi_n^0|\hat{H}'\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\langle\psi_n^0|\psi_n^0\rangle$$

but $\hat{H}^0$ is hermitian which implies that $\langle\psi_n^0|\hat{H}^0\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle$ which means that $\boxed{E_n^1 = \langle\psi_n^0|\hat{H}'|\psi_n^0\rangle}$: the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state.

In order to determine the perturbation to the stationary state, we re-write the equation that came from equating the terms that were first-order in λ as $(\hat{H}^0 - E_n^0)\psi_n^1 = -(\hat{H}' - E_n^1)\psi_n^0$. We then re-write

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0$$

First, this equation takes advantage of the fact that the unperturbed stationary states form a complete basis, so that the first-order correction can clearly be written as a superposition of them. We have excluded $m = n$ from the sum. Given that this is the change from the unperturbed state ψ_n^0 it seems like we don't need it there. Further, we can add or subtract any multiple of ψ_n^0 to ψ_n^1 and not change the value of $(\hat{H}^0 - E_n^0)\psi_n^1$ at all, so we are clearly free to exclude this term. From this we have

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(\hat{H}' - E_n^1) \psi_n^0$$

Then we inner product $\langle \psi_l^0 |$ with both sides:

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | \hat{H}' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle$$

The inner product on the left hand side will be zero except when $m = l$, and we assume that $l \neq n$ so that the inner product on the right side is zero, which implies that $(E_l^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | \hat{H}' | \psi_n^0 \rangle$ or

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$$

Note that the $(E_n^0 - E_m^0)$ in the denominator means that this is valid only for non-degenerate problems.

Example

Consider an infinite square well in which the left half of the well has been shifted up by the amount V_0 :

$$V(x) = \begin{cases} V_0 & 0 < x < \frac{a}{2} \\ 0 & \frac{a}{2} < x < a \\ \infty & x < 0 \text{ or } x > a \end{cases}$$

The unperturbed ground state is of course $\psi_1^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right)$ with energy $E_1^0 = \frac{\pi^2 \hbar^2}{2ma^2}$.

The first-order correction to the energy is $E_1^1 = \langle \psi_1^0 | \hat{H}' | \psi_1^0 \rangle = \int_0^{a/2} (\psi_1^0)^* V_0 \psi_1^0 dx = \frac{V_0}{2}$. This integral is quite easy, and in fact this is the first-order shift in all stationary state energies: $E_n^1 = \frac{V_0}{2}$ for all n .

Now we move to the perturbation in the state itself:

$$\langle \psi_2^0 | \hat{H}' | \psi_1^0 \rangle = \int_0^{a/2} \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}x\right) V_0 \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) dx = \frac{4V_0}{3\pi}$$

$$\langle \psi_3^0 | \hat{H}' | \psi_1^0 \rangle = \int_0^{a/2} \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}x\right) V_0 \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) dx = 0$$

$$\langle \psi_4^0 | \hat{H}' | \psi_1^0 \rangle = \int_0^{a/2} \sqrt{\frac{2}{a}} \sin\left(\frac{4\pi}{a}x\right) V_0 \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) dx = \frac{-8V_0}{15\pi}$$

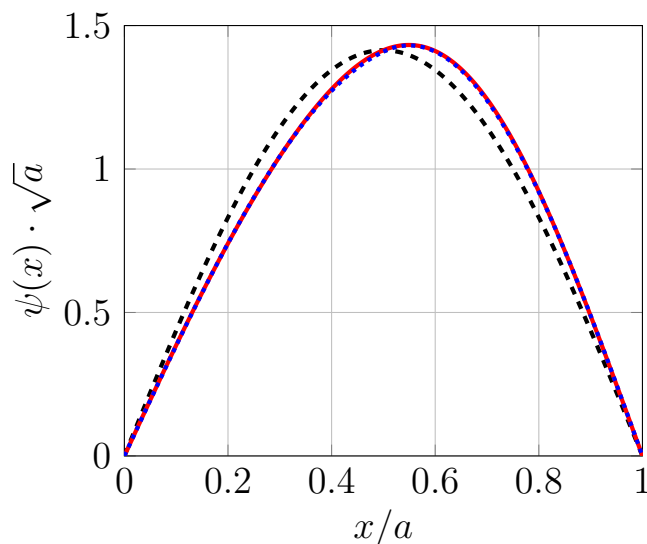
Therefore, expanding out to keep the first two nonzero terms:

$$\psi_1^1 \approx \frac{4V_0}{3\pi \cdot (-3E_1^0)} \sqrt{\frac{a}{2}} \sin\left(\frac{2\pi}{a}x\right) - \frac{8V_0}{15\pi \cdot (-15E_1^0)} \sqrt{\frac{a}{2}} \sin\left(\frac{4\pi}{a}x\right)$$

If we set $V_0 = \frac{1}{2}E_1^0 = \frac{\hbar^2\pi^2}{4ma^2}$ we have an approximate ground state of

$$\psi_1^0(x) + \psi_1^1(x) \approx \sqrt{\frac{2}{a}} \left[\sin\left(\frac{\pi}{a}x\right) - \frac{2}{9\pi} \sin\left(\frac{2\pi}{a}x\right) + \frac{4}{225\pi} \sin\left(\frac{4\pi}{a}x\right) \right]$$

This is not exactly normalized, but it is pretty close and we could of course normalize it if we wished.



I have plotted the unperturbed ground state, the actual ground state (this problem can be solved exactly), and this estimate (keeping the first two nonzero terms) of the perturbed ground state in the

figure above. The unperturbed state is the dashed black line while the estimate of the perturbed state is the solid red line. Notably, the perturbation pushes probability density to the right, meaning that the particle is more likely to be found on the side of the well without the perturbation. The actual ground state is the dashed blue line, showing that our perturbation theory estimate is remarkably close even though we only kept a two terms in the first-order expansion.

Second-order energies

As before, we can determine the second-order correction to the energy as

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$$

Using the same example as before, keeping the first two nonzero terms in this gives

$$E_1^2 \approx \frac{|4V_0/(3\pi)|^2}{-3E_1^0} + \frac{|-8V_0/(15\pi)|^2}{-15E_1^0} = -\frac{|V_0|^2}{E_1^0} \frac{688}{1125\pi^2}$$

So, our estimate on the ground state energy, up to the first two nonzero terms in second-order perturbation theory, is: $E_1 \approx E_1^0 + E_1^1 + E_1^2 \approx E_0 + \frac{V_0}{2} - \frac{|V_0|^2}{E_1^0} \frac{688}{1125\pi^2}$ keeping a perturbation of strength $V_0 = \frac{1}{2}E_1^0$ this gives us $E_1 \approx E_1^0 + 0.469V_0 \approx 1.235E_1^0$. This is almost exactly equal to the actual energy, which is $E_1 \approx 1.234E_1^0$.

Degenerate Perturbation Theory

Several of the equations we have developed had $(E_n^0 - E_m^0)$ in their denominator. This causes an infinity for degenerate states, and this is no small problem as degeneracies are common. It might seem that we can still use the equation for the first-order perturbation to the energy, $E_n^1 = \langle \psi_n^0 | \hat{H}' | \psi_n^0 \rangle$, because it does not contain the problematic denomi-

nator. But even that runs into a problem: in the case of a degeneracy, there will always be an infinite number of ways of constructing the stationary states. Different choices will give different results here, and we won't always know a priori which linear combination of stationary states is good to use.

We will start with a simple example where we would not need perturbation theory: a spin-1/2 particle in a magnetic field. We consider a spin-1/2 particle, which can of course be either spin-up ($\uparrow$) or spin-down ($\downarrow$). Let's start with no magnetic field. This basically means that $\hat{H}^0 = 0$ both states are degenerate with zero energy. This energy level is two-fold degenerate, so we can choose orthogonal stationary states. One possible choice would be to choose spin-up ($\uparrow$) and spin-down ($\downarrow$) as the two stationary states. But we could just as easily choose $|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(\uparrow \pm \downarrow)$ as our two stationary states. But now we turn on a magnetic field along the z -axis. This adds the perturbation $\hat{H}' = g\mu_B B_z \hat{S}_z$ where g is the electron g -factor and μ_B is the Bohr magneton.

What is the first order perturbation to the energy? If we choose $\uparrow$ and $\downarrow$ as the two basis states we would have first-order energy perturbations of $\langle \uparrow | \hat{H}' | \uparrow \rangle = g\mu_B \frac{1}{2} B_z$ and $\langle \downarrow | \hat{H}' | \downarrow \rangle = -g\mu_B \frac{1}{2} B_z$, which are the correct energies (not just the correct first-order perturbations, but really the correct energies). However, if we had chosen $|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(\uparrow \pm \downarrow)$ as our two basis states we would have $\langle \psi_{\pm} | \hat{H}' | \psi_{\pm} \rangle = 0$ as the first-order perturbation. This is clearly incorrect.

The main insight from this example is that degeneracies are caused by symmetries, and when a perturbation breaks that symmetry the degeneracy is lifted. We can use typically first-order perturbation theory to determine the energy correction, but only if we choose the “good” linear combination of states as our basis. The “good” choice of degenerate basis states is the limit of the split (non-degenerate) stationary states after the perturbation is applied in the limit of $\lambda \rightarrow 0$. But in

general we won't know what the stationary states are after the perturbation has been applied: if we knew then we wouldn't need to do the perturbation theory at all. This is the difference from nondegenerate perturbation theory. In nondegenerate perturbation theory we assume that the perturbation changes the stationary states. In degenerate perturbation theory we assume that the perturbation does not actually change the stationary states, it just lifts a degeneracy between them so long as we choose the right definition for the states.

Let's say that ψ_a^0 and ψ_b^0 are orthonormal unperturbed degenerate states (such as $\uparrow$ and $\downarrow$ in our example). Therefore $\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$ will also be an eigenstate of the unperturbed Hamiltonian. Let us assume that this ψ^0 is a "good" state that is an eigenstate of the perturbed Hamiltonian. The first order equation gives us $\hat{H}^0\psi^1 + \hat{H}'\psi^0 = E^0\psi^1 + E^1\psi^0$. We inner product $\langle\psi_a^0|$ with both sides as obtain

$$\langle\psi_a^0|\hat{H}^0\psi^1\rangle + \langle\psi_a^0|\hat{H}'\psi^0\rangle = E^0\langle\psi_a^0|\psi^1\rangle + E^1\langle\psi_a^0|\psi^0\rangle$$

Because $\hat{H}^0$ is hermitian the first terms on each side cancel. We are then left with

$$\alpha\langle\psi_a^0|\hat{H}'|\psi_a^0\rangle + \beta\langle\psi_a^0|\hat{H}'|\psi_b^0\rangle = \alpha E^1$$

This can be written more compactly as $\alpha W_{aa} + \beta W_{ab} = \alpha E^1$ where $W_{ij} \equiv \langle\psi_i^0|\hat{H}'|\psi_j^0\rangle$. Similarly, inner producting $\langle\psi_b^0|$ with both sides yields $\alpha W_{ba} + \beta W_{bb} = \beta E^1$. These two equations can be combined into a matrix equation:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

This equation is equivalent to saying that the vector $\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ is an eigenstate of the matrix with eigenvalue E^1 . Therefore we solve for

the eigenvalues and eigenstates of this matrix. Solving for the eigenvalues is easy, and tells us that the first-order corrections to the energy

are $E_{\pm}^1 = \frac{1}{2}[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}]$ where the "good"

linear combinations are determined by solving for the eigenvectors of the matrix to get values of α and β . Now, suppose you guess correctly, and your original states ψ_a^0 and ψ_b^0 are the "good" states. Then $W_{ab} = W_{ba} = 0$ and you will find that the two eigenvectors are $\alpha = 1, \beta = 0$ with $E_+^1 = W_{aa} = \langle \psi_a^0 | \hat{H}' | \psi_a^0 \rangle$ and $\alpha = 0, \beta = 1$ with $E_-^1 = W_{bb} = \langle \psi_b^0 | \hat{H}' | \psi_b^0 \rangle$. This means that if you can correctly guess the "good" linear combination you can just calculate the energy perturbation directly this way. There is a theorem that can help:

Theorem: Suppose you can find a hermitian operator $\hat{A}$ that commutes with both $\hat{H}^0$ and $\hat{H}'$. If ψ_a^0 and ψ_b^0 (the degenerate eigenfunctions of $\hat{H}^0$) are both also eigenstates of $\hat{A}$ with distinct (different) eigenvalues, then ψ_a^0 and ψ_b^0 are good eigenstates to use in perturbation theory.

The Variational Principle

The basics of the variational principle is quite simple. Suppose you have a Hamiltonian $\hat{H}$. Then pick any normalized wave function ψ . The expectation value of the energy for that wave function must be greater than or equal to the ground state energy for that Hamiltonian:

$$\langle H \rangle = \langle \psi | \hat{H} | \psi \rangle \geq E_{\text{ground state}}$$

So for a given Hamiltonian you pick a test wave function, ideally with one or more adjustable parameters. Then you optimize those parameters and eventually achieve a fairly close estimate of the ground state energy.

Example: Suppose we wish to determine the ground state energy of a delta function well: $V(x) = -\alpha \delta(x)$. We will pick a normalized Gaussian function as our trial wave function: $\psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2}$.

The expectation value of the kinetic energy is

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^* \frac{\partial^2}{\partial x^2} \psi dx = -\frac{\hbar^2}{2m} \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} e^{-bx^2} (4b^2 x^2 - 2b) e^{-bx^2} dx$$

So

$$\langle T \rangle = -\frac{\hbar^2}{2m} \sqrt{\frac{2b}{\pi}} \left[4b^2 \cdot \frac{1}{4} \sqrt{\frac{\pi}{2b^3}} - 2b \cdot \sqrt{\frac{\pi}{2b}} \right] = \frac{\hbar^2 b}{2m}$$

The expectation value of the potential energy is

$$\langle V \rangle = -\alpha \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} \delta(x) e^{-2bx^2} dx = -\alpha \sqrt{\frac{2b}{\pi}}$$

Therefore $\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}}$ which will be greater than or equal to the ground state energy for any b . Therefore we choose the value of b that minimizes the energy.

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0$$

which gives

$$b = \frac{2m^2\alpha^2}{\hbar^4\pi}$$

Plugging this value into our energy expectation value we get

$$\langle H \rangle_{min} = -\frac{m\alpha^2}{\pi\hbar^2} \geq E_{\text{ground state}}$$

This potential is exactly solvable, so we already knew that $E_{\text{ground state}} = -\frac{m\alpha^2}{2\hbar^2}$ so we see that our minimum bound was in fact larger than the actual ground state.

The helium ground state

The variational principle can be used to estimate the ground state of helium. Helium features two electrons in orbit around a nucleus with two protons. Therefore the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$

where $\vec{r}_1$ and $\vec{r}_2$ are the locations of the two electrons.

We would start by assuming a test function that is just the product of two hydrogen-like ground states:

$$\psi_0(\vec{r}_1, \vec{r}_2) \equiv \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0}$$

Determining $\langle H \rangle$ for this state will give us an upper bound for the ground state energy. This is also a convenient place to start because it is an exact eigenstate of *almost* the entire Hamiltonian: it is an

eigenstate of the Hamiltonian if we were to ignore the electron-electron repulsion term. This gives us

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle \quad \text{with} \quad \langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a_0^3} \right) \int \frac{e^{-4(r_1+r_2)/2}}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2$$

where $E_1 \approx -13.6$ eV is the hydrogen binding energy. The integral for $\langle V_{ee} \rangle$ evaluate to

$$\langle V_{ee} \rangle = \frac{5}{4a_0} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5}{2}E_1 \approx +34.0 \text{ eV}$$

Putting these together, we have $\langle H \rangle \approx -74.8$ eV. This is the same estimate we obtained using first-order perturbation theory and forms an initial upper bound on the ground state energy. It's about 6% away from the real ground state energy; we can do better because we haven't done any variational optimization yet. So we will assume that each electron forms a cloud of negative charge that partially screens the nucleus from the other electron. Therefore we pretend that the nucleus has an effective charge of Z where Z will end up being a bit smaller than 2. We use a variational trial wave function

$$\psi = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$$

We then calculate $\langle H \rangle = [-2Z^2 + (27/4)Z]E_1$. This is minimized when $Z = \frac{27}{16} \approx 1.69$. We have lowered our upper bound on the ground state energy to $\langle H \rangle = -77.5$ eV, which is now within 2% of the experimental measured value. Further subtle variations with more complicated test wave functions can keep on improving this.