

Time Independent Perturbation Theory

Not all QM techniques are solvable analytically. which is why tools like perturbation theory were developed.

Perturbation theory can be applied to any problem for which a closely related problem can be solved analytically. The difference between the two problems is written as a small additional term added to the Hamiltonian of the analytically solvable problem. This additional term will not change the solution that much, but will need a small correction to existing eigenvalues and eigenfn's.

We will start with a situation where all eigenvalues are non degenerate.

Non-degenerate

Consider a QM system described by Hamiltonian \hat{H}_0 and non-degenerate eigenvalues E_i , and eigenfunctions ψ_i :

$$\hat{H}_0 \psi_i = E_i \psi_i$$

Now let there be a small change in the system, a perturbation, that does not change boundary conditions. We will represent it by a small change to the Hamiltonian and we will control its "strength" with a factor λ .

Let the new eigenvalues and eigenfunctions be ψ'_j , E'_j

$$[\hat{H}_0 + \lambda \hat{H}_p] \psi'_j = E'_j \psi'_j$$

If $\lambda \rightarrow 0$, then the solutions should tend to those we had earlier.

If λ is small, we should be able to represent the new eigenvalues and eigenfunctions as a power series in λ :

$$E_j' = E_j + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + \lambda^3 E_j^{(3)} + \dots$$

The first term E_j is the eigenvalue of the unperturbed hamiltonian. $E_j^{(1)}$ and $E_j^{(2)}$ etc. are the first and second etc. order corrections. Similarly:

$$\psi_j' = \psi_j + \lambda \psi_j^{(1)} + \lambda^2 \psi_j^{(2)} + \lambda^3 \psi_j^{(3)} + \dots \quad (*)$$

We need to calculate the correction terms. To do this, we make use of the expansion theorem:

$$\psi_j^{(1)} = \sum_i a_{i,j}^{(1)} \psi_i \quad \psi_j^{(2)} = \sum_i a_{i,j}^{(2)} \psi_i$$

The subscript j is the index of the perturbed wavefunction and i is the index of the unperturbed wavefunction.

Instead of demanding our wavefunctions be normalised to 1, we will pick a different normalisation that will be useful to us. We will see why soon.

In (*) we see that ψ_j has no coefficient. So we choose a normalisation of ψ_j' that retains no coefficient for ψ_j for all λ .

Let's substitute our sums into the eigenvalue equation.

$$[\hat{H}_0 + \lambda \hat{H}_p](\psi_j + \lambda \sum_i a_{ij}^{(1)} \psi_i + \lambda^2 \sum_i a_{ij}^{(2)} \psi_i + \dots)$$

$$= (E_j + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + \dots)(\psi_j + \lambda \sum_i a_{ij}^{(1)} \psi_i + \lambda^2 \sum_i a_{ij}^{(2)} \psi_i + \dots)$$

We then group terms by power of λ :

$$0 = \underbrace{[\hat{H}_0 - E_j] \psi_j}_{(1)} + \lambda \left\{ \underbrace{\hat{H}_0 \sum_i a_{ij}^{(1)} \psi_i + \hat{H}_p \psi_j - E_j^{(1)} \psi_j - E_j \sum_i a_{ij}^{(1)} \psi_i}_{(2)} \right.$$

$$+ \lambda^2 \left\{ \hat{H}_0 \sum_i a_{ij}^{(2)} \psi_i + \hat{H}_p \sum_i a_{ij}^{(1)} \psi_i - E_j^{(2)} \psi_j - E_j^{(1)} \sum_i a_{ij}^{(1)} \psi_i - E_j \sum_i a_{ij}^{(2)} \psi_i \right\}_{(3)}$$

$$+ \lambda^3 \{ \dots \} + \dots \left. \right\}_{(4)}$$

In order for this to be true, we require each (1) (2) (3) (4) to be equal to 0.

$$[\hat{H}_0 - E_j] \psi_j = \hat{H}_0 \psi_j - E_j \psi_j = 0 \quad \text{since we know } \hat{H}_0 \psi_j = E_j \psi_j$$

(2) tells us:

$$\hat{H}_0 \sum_i a_{ij}^{(1)} \psi_i + \hat{H}_p \psi_j - E_j^{(1)} \psi_j - E_j \sum_i a_{ij}^{(1)} \psi_i = 0$$

If we pre-multiply each term by the complex conjugate of the unperturbed eigenfunction ψ_k^* , and integrate over all space:

$$\sum_i a_{ij}^{(1)} \int \psi_k^* \hat{H}_0 \psi_i dV + \int \psi_k^* \hat{H}_p \psi_j dV - E_j^{(1)} \int \psi_k^* \psi_j dV - E_j \sum_i a_{ij}^{(1)} \int \psi_k^* \psi_i dV = 0$$

$$\Rightarrow \sum_i a_{ij}^{(1)} E_i \delta_{k,i} + \int \psi_k^* \hat{H}_p \psi_j dV - E_j^{(1)} \delta_{k,j} - E_j \sum_i a_{ij}^{(1)} \delta_{k,i} = 0$$

In the case that $k=j$, the first and last terms cancel and we have:

$$\int \psi_j^* \hat{H}_p \psi_j dV - E_j^{(1)} \int \psi_j^* \psi_j dV = 0$$

$$\Rightarrow \boxed{E_j^{(1)} = \int \psi_j^* \hat{H}_p \psi_j dV}$$

This is the first order correction to Energy.

In the case that $k \neq j$:

we know $a_{j,j}^{(1)} = 0$ from our normalisation condition, since we need no coefficient on ψ_j for all λ

So we are left with

$$a_{k,j}^{(1)}(E_j - E_k) = \int \psi_k^* \hat{H}_P \psi_j dV \quad \text{note we set } i=k$$

$$\text{so: } \boxed{\psi_j^{(1)} = \sum_{k \neq j} \frac{\int \psi_k^* \hat{H}_P \psi_j dV}{E_j - E_k} \psi_k}$$

Repeating all this for (3) tells us:

$$\boxed{E_j^{(2)} = \sum_{k \neq j} \frac{|\int \psi_k^* \hat{H}_P \psi_j dV|^2}{E_j - E_k}}$$

This might all be a little overwhelming but we will do some examples to see how this is done in practice.

1D Infinite Potential Well

Consider an infinite square well of width $2a$ from $x=0$ to $x=2a$.

We know from quantum physics last year that

$$E_n = \frac{\pi^2 \hbar^2 n^2}{8ma^2}$$

These are the unperturbed eigenvalues.

The associated unperturbed eigenfunction is:

$$\psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)$$

Right now, in a region $x=a-b$ to $x=a+b$

for $b \ll a$, we expect 0 potential.

This is what we will perturb, making the potential into some small V

There is 0 energy otherwise in this region, so the perturbation hamiltonian will simply be $\hat{H}_p = V$

$$\begin{aligned} \text{so } E_n^{(1)} &= \int_{-\infty}^{+\infty} \psi_n^* \hat{H}_p \psi_n dV \\ &= \int_{a-b}^{a+b} \psi_n^* V \psi_n dx = \frac{1}{a} \int_{a-b}^{a+b} \sin^2\left(\frac{n\pi x}{2a}\right) V dx \\ E_n^{(1)} &= V \left\{ \frac{b}{a} - (-1)^n \frac{1}{n\pi} \sin\left(\frac{n\pi b}{a}\right) \right\} \end{aligned}$$

Now let's work out the first order correction to eigenfunction.

$$\psi_j^{(1)} = \sum_{k \neq j} \frac{\int \psi_k^* \hat{H}_p \psi_j dV}{E_j - E_k} \psi_k$$

Let's first work out $\int \psi_k^* \hat{H}_p \psi_j dV$. We will call k n_1 and j n_2 for consistency:

$$\int \psi_k^* \hat{H}_p \psi_j dV = \frac{V}{a} \int_{a-b}^{a+b} \sin\left(\frac{n_1 \pi x}{2a}\right) \sin\left(\frac{n_2 \pi x}{2a}\right) dx$$

= 0 if $n_1 + n_2$ is odd

if $n_1 + n_2$ is even:

$$= -\frac{2V}{\pi} \left[\frac{(-1)^{\frac{n_1+n_2}{2}}}{n_1+n_2} \sin\left(\frac{(n_1+n_2)\pi b}{2a}\right) - \frac{(-1)^{\frac{n_1-n_2}{2}}}{n_1-n_2} \sin\left(\frac{(n_1-n_2)\pi b}{2a}\right) \right]$$

The first one is 0 because both our original system and the perturbation we made are symmetric about a . So the perturbation has to contain all symmetric eigenfunctions or all anti-symmetric. It cannot be an admixture of the two.

We can now use this to work out $\psi_n^{(1)}$. Left as an exercise to the reader.

2D Infinite Potential Well

Now let's consider a case in which the eigenvalues are degenerate. This is a 2D infinite potential well example.

There is 0 potential in a region $0 \leq x \leq 2a$ and $0 \leq y \leq 2a$ and an infinite potential outside this.

The eigenfunctions for this problem are:

$$\psi_{\lambda_x, \lambda_y}(x, y) = \frac{1}{a} \sin\left(\frac{\lambda_x \pi x}{2a}\right) \sin\left(\frac{\lambda_y \pi y}{2a}\right)$$

which we will refer to as $|\lambda_x, \lambda_y\rangle$ in short hand.

The eigenvalues are

$$E_{\lambda_x, \lambda_y} = \frac{\hbar^2 \pi^2}{8ma^2} (\lambda_x^2 + \lambda_y^2)$$

Our perturbation will be a small spike at $(\frac{a}{2}, \frac{a}{2})$, represented by a dirac delta function:

$$\hat{H}_p = Va^2 \delta(x - \frac{a}{2}) \delta(y - \frac{a}{2})$$

We have chosen this form with a^2 to make later integrations simpler.

It is important to know that for first order energy

perturbation $E_{\lambda_x, \lambda_y}^{(1)} : E_{1,2}^{(1)} \neq E_{2,1}^{(1)}$

Let's begin by working out $E_{1,1}^{(1)}$:

$$\begin{aligned} E_{1,1}^{(1)} &= \iint \psi_{1,1}^* \hat{H}_p \psi_{1,1} dx dy = Va^2 \frac{1}{a^2} \iint \sin\left(\frac{\pi y}{2a}\right) \sin\left(\frac{\pi x}{2a}\right) dy dx \\ &= Va^2 \frac{1}{a^2} \frac{1}{4} = \underline{\underline{\frac{V}{4}}} \end{aligned}$$

Now we can perhaps work out $E_{1,2}^{(1)}$:

Since $E_{1,2}^{(1)} \neq E_{2,1}^{(1)}$, matrix elements mixing these two states are expected to be 0.

$$\text{so } \langle \Psi_{1,2} | \hat{H}_p | \Psi_{2,1} \rangle$$

$$= \iint \frac{1}{a} \sin\left(\frac{\pi x}{2a}\right) \sin\left(\frac{\pi y}{a}\right) V a^2 \delta(x - \frac{a}{2}) \delta(y - \frac{a}{2}) \frac{1}{a} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{2a}\right) dx dy$$

$$= \frac{V}{2} \quad \text{so it is non-zero! This seems to be a problem.}$$

Now let's think about the first order wavefunction correction:

$$\Psi_j^{(1)} = \sum_{k \neq j} \frac{\int \Psi_k^* \hat{H}_p \Psi_j dV}{E_j - E_k} \Psi_k$$

this term for $j = 2, 1$ is given below:

$$\frac{\int \Psi_{1,2}^* \hat{H}_p \Psi_{2,1} dV}{E_{1,2} - E_{2,1}} \quad \leftarrow \quad \text{but } E_{1,2} = E_{2,1} \quad \left(\begin{array}{l} \text{even though} \\ E_{1,2}^{(1)} \neq E_{2,1}^{(1)} \end{array} \right)$$

so this would be infinite.

The same problem exists also for all higher order terms.
Everything is breaking! How do we proceed?

Well, we know that any linear combination of wavefunctions we write down is also an eigenfunction with the same eigenvalue. So, to fix the perturbation calculation, we have to choose the correct sets of degenerate eigenfunctions so that all matrix elements involving the perturbation and two different eigenfunctions from the degenerate set are always 0.

We mentioned this briefly in our definition of orthogonality in page 1 of the Quantum Mechanics revision section of these notes.

so let's try to generate two linear combinations of the eigenfunctions $|1, 2\rangle$ and $|2, 1\rangle$ which are orthogonal to each other, and so give a 0 matrix element when combined with the perturbation Hamiltonian.

We will write these as:

$$\tilde{\Psi}_1 = \alpha \Psi_{1,2} + \beta \Psi_{2,1}$$

$$\tilde{\Psi}_2 = \gamma \Psi_{1,2} + \delta \Psi_{2,1}$$

These should be orthogonal to each other.
we also require $\int \tilde{\Psi}_1^* \hat{H}_p \tilde{\Psi}_2 dV = 0$

$$\int \tilde{\Psi}_1^* \hat{H}_p \tilde{\Psi}_2 dV = (\alpha^* \beta^*) \begin{pmatrix} \frac{\sqrt{V}}{2} & \frac{\sqrt{V}}{2} \\ \frac{\sqrt{V}}{2} & \frac{\sqrt{V}}{2} \end{pmatrix} \begin{pmatrix} \gamma \\ \delta \end{pmatrix}$$

in integral form:

$$\begin{aligned} \int \tilde{\Psi}_1^* \hat{H}_p \tilde{\Psi}_2 dV &= \int (\alpha^* \Psi_{1,2}^* + \beta^* \Psi_{2,1}^*) \hat{H}_p (\gamma \Psi_{1,2} + \delta \Psi_{2,1}) dV \\ &= \int \alpha^* \Psi_{1,2}^* \hat{H}_p \gamma \Psi_{1,2} + \beta^* \Psi_{2,1}^* \hat{H}_p \delta \Psi_{2,1} \\ &\quad + \alpha^* \Psi_{1,2}^* \hat{H}_p \delta \Psi_{2,1} + \beta^* \Psi_{2,1}^* \hat{H}_p \gamma \Psi_{1,2} dV \\ &= \alpha^* \gamma \int \Psi_{1,2}^* \hat{H}_p \Psi_{1,2} dx + \beta^* \delta \int \Psi_{2,1}^* \hat{H}_p \Psi_{2,1} dx \\ &\quad + \alpha^* \delta \int \Psi_{1,2}^* \hat{H}_p \Psi_{2,1} dx + \beta^* \gamma \int \Psi_{2,1}^* \hat{H}_p \Psi_{1,2} dx \\ &= (\alpha^* \gamma + \beta^* \delta + \alpha^* \delta + \beta^* \gamma) \frac{\sqrt{V}}{2} = 0 \end{aligned}$$

$$\text{so } \alpha^* \gamma + \beta^* \delta + \alpha^* \delta + \beta^* \gamma = 0$$

$$\alpha^* (\gamma + \delta) + \beta^* (\delta + \gamma) = 0 \Rightarrow \alpha^* + \beta^* = 0 \quad \alpha^* = -\beta^*$$

$$\text{we choose } \alpha = \frac{1}{\sqrt{2}} \text{ and } \gamma = \frac{1}{\sqrt{2}} \text{ so:}$$

$$\left[\text{and } \begin{aligned} \text{so } \alpha &= \beta \\ \gamma &= -\delta \end{aligned} \right.$$

$$\tilde{\Psi}_1 = \frac{1}{\sqrt{2}} (\Psi_{1,2} + \Psi_{2,1})$$

$$\tilde{\Psi}_2 = \frac{1}{\sqrt{2}} (\Psi_{1,2} - \Psi_{2,1})$$

we can now use these to work out energy perturbations

so: $E_{1,1}^{(1)} = \frac{V}{4}$ as calculated earlier

$$E_{(1,2)+(2,1)}^{(1)} = V$$

$$E_{(1,2)-(2,1)}^{(1)} = 0$$

So the perturbation breaks the degeneracy of the first two excited states. i.e the perturbation correction terms are different so the corrected energies will also be different. This is why we encountered a problem before. For the unperturbed system, any linear combination of two degenerate wavefunctions are eigenstates. But this isn't true if there is a perturbation. In that case, there is only one combination of wavefunctions that is an eigenstate.

This is why we have to choose the correct combination in a degenerate system. Otherwise, the perturbation causes a sudden shift to the corrected wavefunctions which doesn't agree with the small changes needed for perturbation theory.

We can also think about this in terms of symmetry. In the unperturbed system, we have 4 axis of symmetry on the square well. So we can convert $\psi_{1,2}$ into $\psi_{2,1}$ and leave the system unchanged, implying degeneracy. But if we introduce the potential spike (perturbation), the rotational symmetry no longer exists. This is called symmetry breaking.

So there is no reason why new eigenfunctions have to be degenerate so they won't be. In general, if degeneracy is not needed by symmetry, it does not happen.

Note: When I was writing these notes, I thought the potential spike was in the centre of the square so I was confused that we were saying it wasn't symmetric. But the spike is at $(\frac{a}{2}, \frac{a}{2})$ on a $2a \times 2a$ square, so it isn't symmetric.

The Stark Effect

Now let's try and use time-independent perturbation theory in an atomic physics problem. Our perturbation will be a small electric field applied to a hydrogen atom.

Quantum Mechanically, we have already previously solved our unperturbed system. [The whole $R(r)Y(\theta, \phi)$ thing!]

The perturbation is an electric field pointing in a specific direction, say \hat{z} . The field will cause the average position of the proton and electron to not coincide, creating a dipole which acts to lower the energy of the atom. $\Delta \text{Energy} = -\underline{d} \cdot \underline{E} \propto E^2$

If you didn't know this from classical EM, that's ok! You know it now.

\underline{d} here will be $-ze$ so our perturbation hamiltonian is:

$$\hat{H}_p = -eEz = -eE r \cos \theta$$

E here is the magnitude of the electric field

Consider the ground state wavefunction:

$$\psi_{1,0,0} = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$$

The first order energy correction is:

$$\begin{aligned} E_{1,0,0}^{(1)} &= \int \psi_{1,0,0}^* \hat{H}_p \psi_{1,0,0} dV \\ &= \pi a_0^3 \int \exp(-2r/a_0) \times -eE r \cos \theta dV \\ &= 0 \end{aligned}$$

You can work this out very easily using $dV = r^2 \sin \theta dr d\theta d\phi$ with r between $0 \rightarrow \infty$ θ between $0 \rightarrow \pi$ and ϕ between $0 \rightarrow 2\pi$

The second order correction to the energy of the ground state is:

$$E_{1,0,0}^{(2)} = \sum_{k \neq (1,0,0)} \frac{|\int \Psi_k^* \hat{H}_p \Psi_{1,0,0} dV|^2}{(E_{1,0,0} - E_k)}$$

We would thus construct a matrix for this. But it turns out most of the elements are 0.

However, the matrix elements with $k=1,1,0$ are non-zero. (This is due to some sines and cosines $\Rightarrow 0$ when integrated).

Note that the E in the \hat{H}_p becomes E^2 after the norm squared, so we show $\Delta \text{Energy} \propto E^2$ as expected.

Let's now consider the effect of $l=2$ states. These are degenerate so we will need to decide on the correct basis wave functions.

The conventional wavefunctions are $\Psi_{200}, \Psi_{210}, \Psi_{21-1}, \Psi_{211}$ so we will need 4 linear combinations of these to use.

It turns out the only non-zero matrix elements are given by:

$$\int \Psi_{2,1,0}^* \hat{H}_p \Psi_{2,0,0} dV = \int \Psi_{2,0,0}^* \hat{H}_p \Psi_{2,1,0} dV = 3ea_0 E$$

we will call this Δ . So our matrix looks like:

$$= \begin{bmatrix} \langle 200 | \hat{H}_p | 200 \rangle & \langle 200 | \hat{H}_p | 210 \rangle & \langle 200 | \hat{H}_p | 211 \rangle & \langle 200 | \hat{H}_p | 21-1 \rangle \\ \langle 210 | \hat{H}_p | 200 \rangle & \langle 210 | \hat{H}_p | 210 \rangle & \langle 210 | \hat{H}_p | 211 \rangle & \langle 210 | \hat{H}_p | 21-1 \rangle \\ \langle 211 | \hat{H}_p | 200 \rangle & \langle 211 | \hat{H}_p | 210 \rangle & \langle 211 | \hat{H}_p | 211 \rangle & \langle 211 | \hat{H}_p | 21-1 \rangle \\ \langle 21-1 | \hat{H}_p | 200 \rangle & \langle 21-1 | \hat{H}_p | 210 \rangle & \langle 21-1 | \hat{H}_p | 211 \rangle & \langle 21-1 | \hat{H}_p | 21-1 \rangle \end{bmatrix}$$

$$= \begin{bmatrix} 0 & \Delta & 0 & 0 \\ \Delta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

So the set of unperturbed states we require are:

$$\frac{1}{\sqrt{2}}(\Psi_{200} + \Psi_{210}), \frac{1}{\sqrt{2}}(\Psi_{200} - \Psi_{210}), \Psi_{211} \text{ and } \Psi_{21-1}$$

In this case the first order corrections to the energy of the states are: $3ea_0 E, -3ea_0 E, 0, 0$. These are observed in experiments and are called Stark shifts.