Perturbation Theory

Perturbation theory is a diverse set of methods used to construct solutions to non-exactly solvable problems that are closely related to exactly solvable problems. These methods exist in all fields of physics and are often highly specialized.

We will consider two approximate methods:

I. Variation Principle

II. Non-degenerate perturbation theory.

Variational Principle - Pure Black Magic.

Suppose we are given a Hamiltonian, H, an wish to determine to ground state energy E_g.

Variational Principle $\quad \langle \psi | H | \psi \rangle \geq E_g$

for all $|\psi\rangle$.

This means we can guess a function $\psi(x)$ and we are guaranteed that

$$\int \psi^* H \psi \, dx \geq E_g$$

If ψ depends on some parameters, we can minimized E_g with respect to the parameters to get the best estimate of the ground state.

For example, we could investigate the ground state of an oscillator that was not purely harmonic.

$$V(x) = \frac{1}{2}kx^2 + \gamma x^4$$

We still use the $\gamma = 0$ ground state wave function, but now

$$\psi = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}$$

and a is a parameter that can be varied.

$$\langle \psi | H | \psi \rangle =$$

$$= \frac{\hbar^2 a}{m} + \frac{3}{16}\frac{\gamma}{a^2} - \frac{4\hbar^2 a^2 - km}{8am}$$

$$= E_g(a) = E_g(a)$$

Minimize with respect to a

$$\frac{\partial E}{\partial a} = 0 = -\frac{3}{8}\frac{\gamma}{a^3} + \frac{1}{8}\frac{4\hbar^2 a^2 - km}{a^2 m}$$

Quick check, $\gamma = 0$

$$4\hbar^2 a^2 = km$$

$$a = \sqrt{\frac{km}{4\hbar^2}}$$

$$\omega^2 = \frac{k}{m}$$

$$E_g = \frac{\hbar^2}{m}\sqrt{\frac{km}{4\hbar^2}}$$

$$= \frac{1}{2}\hbar \frac{\sqrt{\omega^2 m^2}}{m}$$

$$= \frac{1}{2}\hbar\omega \checkmark$$

If $\gamma \neq 0$,

$$-\frac{3}{8}\gamma m + \frac{1}{8}\cdot\left(4\hbar^2 a^3 - kma\right) = 0$$

$$4\hbar^2 a^3 - kma - 3\gamma m = 0$$

Solution is a cubic, one real root.

The Maple calculation is included on the next page.

- A key point: My trial wave function remained normalized as I varied a.
- There are a couple of simpler examples in text.
- Obviously, a very powerful method if coupled with a numeric solver.

$> psi := \left(\frac{2\ a}{Pi}\right)^{\left(\frac{1}{4}\right)} exp\left(-a \cdot x^2\right)$

$$\psi := 2^{(1/4)} \left(\frac{a}{\pi}\right)^{(1/4)} e^{\left(-a x^2\right)} \tag{1}$$

$> assume(a :: real)$

$> assume(a :: positive)$

$> int(psi \cdot psi,\ x = -infinity..infinity)$

$$1 \tag{2}$$

$> V := \frac{k\ x^2}{2} + gamma \cdot x^4$

$$V := \frac{1}{2} k x^2 + \gamma x^4 \tag{3}$$

$> Hpsi := \frac{-hbar^2}{2\ m} diff(psi,\ x,\ x) + V \cdot psi$

$$Hpsi := -\frac{1}{2} \frac{hbar^2 \left(-2\, 2^{(1/4)} \left(\frac{a\sim}{\pi}\right)^{(1/4)} a\sim e^{\left(-a\sim x^2\right)} + 4\, 2^{(1/4)} \left(\frac{a\sim}{\pi}\right)^{(1/4)} a\sim^2 x^2 e^{\left(-a\sim x^2\right)}\right)}{m} + \left(\frac{1}{2} k x^2 + \gamma x^4\right) 2^{(1/4)} \left(\frac{a\sim}{\pi}\right)^{(1/4)} e^{\left(-a\sim x^2\right)} \tag{4}$$

$> int(psi \cdot Hpsi,\ x = -infinity..infinity)$

$$\frac{a\sim hbar^2}{m} + \frac{3}{16} \frac{\gamma}{a\sim^2} - \frac{1}{8} \frac{4\, hbar^2 a\sim^2 - k m}{a\sim m} \tag{5}$$

$> diff(\%,\ a)$

$$-\frac{3}{8} \frac{\gamma}{a\sim^3} + \frac{1}{8} \frac{4\, hbar^2 a\sim^2 - k m}{a\sim^2 m} \tag{6}$$

$> solve\left(4 \cdot hbar^2 \cdot a^3 - k\ \ m\ \ a\ -\ 3\ \ gamma\ \ m\ =\ 0, a\right)$

$$\frac{1}{6} \frac{3^{(1/3)} \left(m \left(27 \gamma\, hbar + \sqrt{3} \sqrt{-k^3 m + 243 \gamma^2 hbar^2}\right)\right)^{(1/3)}}{hbar} + \frac{1}{6} \frac{k m 3^{(2/3)}}{hbar \left(m \left(27 \gamma\, hbar + \sqrt{3} \sqrt{-k^3 m + 243 \gamma^2 hbar^2}\right)\right)^{(1/3)}}, \tag{7}$$

real root

$$-\frac{1}{12} \frac{3^{(1/3)} \left(m \left(27 \gamma\, hbar + \sqrt{3} \sqrt{-k^3 m + 243 \gamma^2 hbar^2}\right)\right)^{(1/3)}}{hbar} - \frac{1}{12} \frac{k m 3^{(2/3)}}{hbar \left(m \left(27 \gamma\, hbar + \sqrt{3} \sqrt{-k^3 m + 243 \gamma^2 hbar^2}\right)\right)^{(1/3)}}$$

$$+ \frac{1}{2} I \sqrt{3} \left(\frac{1}{6} \frac{3^{(1/3)} \left(m \left(27 \gamma\, hbar + \sqrt{3} \sqrt{-k^3 m + 243 \gamma^2 hbar^2}\right)\right)^{(1/3)}}{hbar}\right.$$

$$-\frac{1}{6}\,\frac{k\,m\,3^{(2/3)}}{hbar\left(m\left(27\,\gamma\,hbar+\sqrt{3}\,\sqrt{-k^3\,m+243\,\gamma^2\,hbar^2}\right)\right)^{(1/3)}}\Bigg),$$

$$-\frac{1}{12}\,\frac{3^{(1/3)}\left(m\left(27\,\gamma\,hbar+\sqrt{3}\,\sqrt{-k^3\,m+243\,\gamma^2\,hbar^2}\right)\right)^{(1/3)}}{hbar}$$

$$-\frac{1}{12}\,\frac{k\,m\,3^{(2/3)}}{hbar\left(m\left(27\,\gamma\,hbar+\sqrt{3}\,\sqrt{-k^3\,m+243\,\gamma^2\,hbar^2}\right)\right)^{(1/3)}}$$

$$-\frac{1}{2}\,\mathrm{I}\sqrt{3}\,\Bigg(\frac{1}{6}\,\frac{3^{(1/3)}\left(m\left(27\,\gamma\,hbar+\sqrt{3}\,\sqrt{-k^3\,m+243\,\gamma^2\,hbar^2}\right)\right)^{(1/3)}}{hbar}$$

$$-\frac{1}{6}\,\frac{k\,m\,3^{(2/3)}}{hbar\left(m\left(27\,\gamma\,hbar+\sqrt{3}\,\sqrt{-k^3\,m+243\,\gamma^2\,hbar^2}\right)\right)^{(1/3)}}\Bigg)$$

>

Non-degenerate Perturbation Theory

Suppose we have a hamiltonian H_0^0 with a non-degenerate spectrum E_n^0 with eigenfunctions ψ_n

$$H_0^0 |\psi_n\rangle = E_n^0 |\psi_n\rangle$$

and $E_n^0 \neq E_m^0$ if $m \neq n$.

This hamiltonian is slightly perturbed by a <u>small</u> modification H' such that the real hamiltonian of the system is

$$H = H_0^0 + H'$$

Our task is to construct approximations to the energies and eigenfunctions of H from ψ_n^0 and E_n^0.

Introduce a ~~[illegible]~~ parameter to keep track of smallness.

$$H = H^0 + \lambda H'$$

Since H' is small, H'^2 is smaller etc. We can count the <u>smallness</u> by the powers of λ. At the end, we set $\lambda = 1$ and recover the real hamiltonian.

Expand E_n and ψ_n in terms of λ

$$H\psi_n = E_n \psi_n \quad \text{(real solution)}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 \cdots\cdots$$

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 \cdots\cdots$$

TISE

$$H \psi_n = E_n \psi_n$$

Substitute expansions

$$(H^0 + \lambda H')(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 \cdots)$$

$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 \cdots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 \cdots)$$

Collect terms in λ

λ^0: $\quad H^0 \psi_n^0 = E_n^0 \psi_n^0$ $\qquad$ unperturbed system

λ^1: $\quad H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

λ^2: $\quad H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

First-order

$$H^0|\psi_n^1\rangle + H^1|\psi_n^0\rangle = E_n^0|\psi_n^1\rangle + E_n^1|\psi_n^0\rangle$$

$$\langle\psi_n^0|H^0|\psi_n^1\rangle + \langle\psi_n^0|H^1|\psi_n^0\rangle =$$

$$E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\underbrace{\langle\psi_n^0|\psi_n^0\rangle}_{1}$$

$$\langle\psi_n^0|H^0|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle$$

$$E_n^1 = \langle\psi_n^0|H^1|\psi_n^0\rangle$$

<u>Ex</u> Find the correction to the ground state energy for a delta function perturbation $V(x) = \gamma\delta(x - a/2)$ in the middle of an infinite square well.

$$H' = \gamma \delta(x - a/2)$$

Unperturbed ground state $\quad \psi_1^0 = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$

$$E_1' = \langle \psi_1^0 | H' | \psi_1^0 \rangle$$

$$= \frac{2\gamma}{a} \int_0^a dx \, \sin^2 \frac{\pi x}{a} \, \delta\left(x - \frac{a}{2}\right)$$

$$= \frac{2\gamma}{a} \sin^2 \frac{\pi}{2} = \frac{2\gamma}{a}$$

$$E_1 = E_1^0 + E_1' = \frac{\hbar^2 \pi^2}{2ma^2} + \frac{2\gamma}{a}$$ to first order.

First-order correction for wave function

$$H^0 \psi_n^1 + H^1 \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$$

$$(H^0 - E_n^0)\,\psi_n^1 = -(H^1 - E_n^1)\,\psi_n^0$$

Expand

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

complete set

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

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

Dot with $|\psi_l^0\rangle$

$$\sum_{m \neq n} (E_m^0 - E_n^0)\, c_m^n \langle \psi_l^0 | \psi_m^0 \rangle$$

$$= -\langle \psi_l^0 | H^1 | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle$$

If $l = n$, the right side is zero.

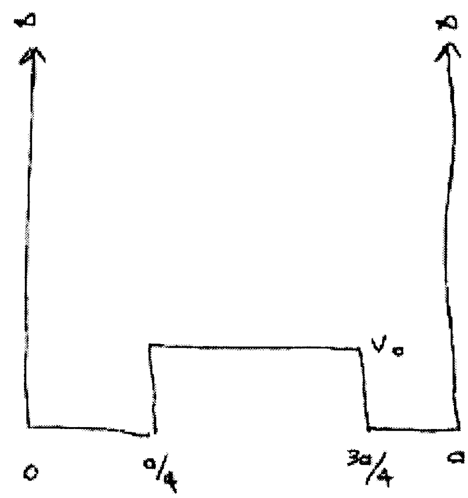
If $l \neq n$, $\langle \psi_l^0 | \psi_n^0 \rangle = 0$

$$(E_l^0 - E_n^0)\, c_l^n = -\langle \psi_l^0 | H' | \psi_n^0 \rangle$$

$$c_l^n = \frac{\langle \psi_l^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_l^0}$$

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

Example - Square Well with Barrier



Unperturbed System

$$E_n = \frac{\hbar^2 k_n^2}{2m} \qquad k_n = \frac{n\pi}{a} \qquad n = 1, \dots$$

$$\psi_n = \sqrt{\frac{2}{a}} \sin k_n x$$

$$H' = \begin{cases} V_0 & \frac{a}{4} \le x \le 3a/4 \\ 0 & \text{otherwise} \end{cases}$$

$$H^0 = \frac{-\hbar^2 d^2}{2m\, dx^2} + \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

First order correction to ground state energy E_1

$$E_1 = E_1^0 + E_1^1 + E_1^2 \cdots$$

$$E_1^1 = \langle \psi_1^0 | H' | \psi_1^0 \rangle$$

$$= V_0 \int_{a/4}^{3a/4} \left(\frac{2}{a}\right)^2 \sin^2 k_1 x \, dx$$

$$= \frac{V_0}{2\pi}(2+\pi) = 0.81 V_0$$

Shifts the energy substantially. This makes sense most of the ground state weight in center of well.

$$E_2^1 = V_0 \int_{a/4}^{3a/4} \left(\frac{2}{a}\right)^2 \sin^2 k_2 x \, dx = \frac{V_0}{2}$$

$$E_3^1 = V_0 \int_{a/4}^{3a/4} \left(\frac{2}{a}\right)^2 \sin^2 k_3 x \, dx = \frac{V_0}{6\pi}(3\pi - 2)$$

$$= 0.4 V_0$$

Correct the Wave Function

$$\psi_1 = \psi_1^0 + \sum_{j \neq i} c_j^1 \, \psi_j^0$$

Find $c_1^2 = \dfrac{\langle \psi_2^0 | H' | \psi_1^0 \rangle}{E_1^0 - E_2^0} =$

$$\frac{1}{E_1^0 - E_2^0} \, V_0 \int_{a/4}^{3a/4} \left(\frac{2}{a}\right) \sin k_2 x \, \sin k_1 x \, dx$$

$$= \cancel{\frac{1}{2} \frac{a V_0}{\pi^2} \quad \frac{1}{4} \frac{a^2 V_0 m}{\pi^3 \hbar^2}}$$

$$= 0$$

$$c_1^3 = \frac{\langle \psi_3^0 | H' | \psi_1^0 \rangle}{E_1^0 - E_3^0} = \frac{1}{4} \, \frac{a^2 V_0 \, m}{\pi^3 \hbar^2}$$

Ground State

```
> k:= Pi/a;
```

$$k := \frac{\pi}{a}$$

```
> integrate(v*(2/a)*sin(k*x)^2, x=a/4..3*a/4);
```

$$\frac{1}{2}\frac{v(2+\pi)}{\pi}$$

First Excited State

```
> k:= 2*Pi/a;
```

$$k := 2\frac{\pi}{a}$$

```
> integrate(v*(2/a)*sin(k*x)^2, x=a/4..3*a/4);
```

$$\frac{1}{2}v$$

Second Excited State

```
> k:= 3*Pi/a;
```

$$k := 3\frac{\pi}{a}$$

```
> integrate(v*(2/a)*sin(k*x)^2, x=a/4..3*a/4);
```

$$\frac{1}{6}\frac{v(-2+3\pi)}{\pi}$$

Wave Function Corrections

```
> ka := Pi/a;
```

$$ka := \frac{\pi}{a}$$

```
> kb:= 3*Pi/a;
```

$$kb := 3\frac{\pi}{a}$$

```
> Ea:=h^2 *ka^2/(2*m);
```

$$Ea := \frac{1}{2}\frac{h^2\pi^2}{a^2 m}$$

```
> Eb:=h^2 *kb^2/(2*m);
```

$$Eb := \frac{9}{2}\frac{h^2\pi^2}{a^2 m}$$

```
> cab:=integrate(v*(2/a)*sin(ka*x)*sin(kb*x)/(Ea-Eb), x=a/4..3*a/4);
```

$$cab := \frac{1}{4}\frac{a^2 v m}{\pi^3 h^2}$$

Second Cofficient

```
> ka := Pi/a;
```

$$ka := \frac{\pi}{a}$$

```
> kb:= 2*Pi/a;
```

$$kb := 2\,\frac{\pi}{a}$$

```
> Ea:=h^2 *ka^2/(2*m);
```

$$Ea := \frac{1}{2}\,\frac{h^2\,\pi^2}{a^2\,m}$$

```
> Eb:=h^2 *kb^2/(2*m);
```

$$Eb := 2\,\frac{h^2\,\pi^2}{a^2\,m}$$

```
> cab:=integrate(v*(2/a)*sin(ka*x)*sin(kb*x)/(Ea-Eb), x=a/4..3*a/4);
```

$$cab := 0$$

```
>
>
```