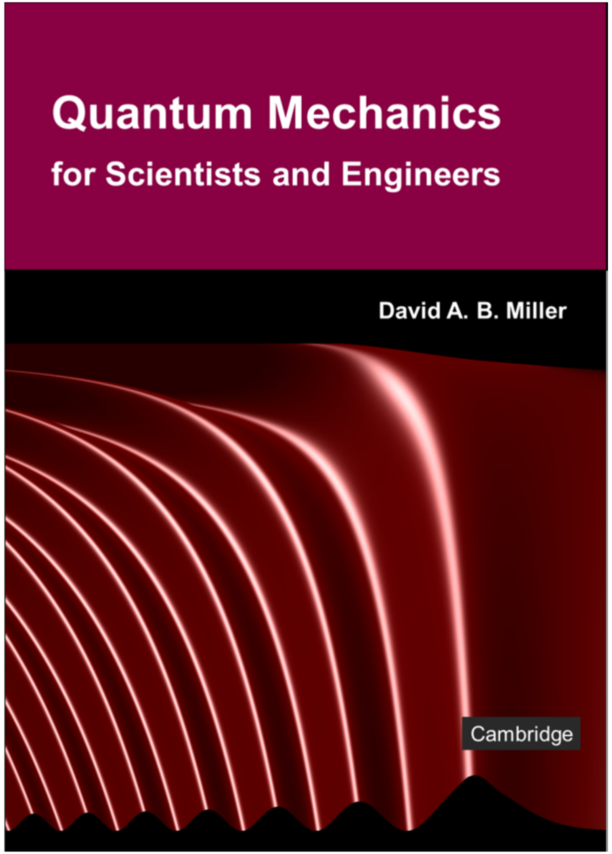
8.3 Perturbation theory

Slides: Video 8.3.2 First and second order theories

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.3 (starting at "First order perturbation theory" up to "Example of well with field")



Perturbation theory

First and second order theories

Quantum mechanics for scientists and engineers

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First order perturbation theory

Now we can calculate the various perturbation terms

Starting with $\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_m\right\rangle$

and premultiplying by $\left\langle\psi_m\right|$ gives

$$\left\langle\psi_m\left|\hat{H}_o - E_m\right|\phi^{(1)}\right\rangle = \left(\left\langle\psi_m\right|\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left\langle\psi_m\right|\left(E_m - E_m\right)\left|\phi^{(1)}\right\rangle = 0$$

$$= \left\langle\psi_m\left|E^{(1)} - \hat{H}_p\right|\psi_m\right\rangle = E^{(1)} - \left\langle\psi_m\left|\hat{H}_p\right|\psi_m\right\rangle$$

i.e.,

$$\boxed{E^{(1)} = \left\langle\psi_m\left|\hat{H}_p\right|\psi_m\right\rangle}$$

a formula for the first-order energy correction $E^{(1)}$

in the presence of our perturbation $\hat{H}_p$

First order perturbation theory

For the first order correction to the wavefunction $\left|\phi^{(1)}\right\rangle$

we expand that correction in the basis set $\left|\psi_n\right\rangle$

$$\left|\phi^{(1)}\right\rangle = \sum_n a_n^{(1)}\left|\psi_n\right\rangle$$

Substituting this is in

$$\left(\hat{H}_o - E_m\right)\left|\phi^{(1)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\psi_m\right\rangle$$

and premultiplying by $\left\langle\psi_i\right|$ gives

$$\left\langle\psi_i\left|\hat{H}_o - E_m\right|\phi^{(1)}\right\rangle = \left(E_i - E_m\right)\left\langle\psi_i\middle|\phi^{(1)}\right\rangle = \left(E_i - E_m\right)a_i^{(1)}$$

$$= \left\langle\psi_i\left|E^{(1)} - \hat{H}_p\right|\psi_m\right\rangle = E^{(1)}\left\langle\psi_i\middle|\psi_m\right\rangle - \left\langle\psi_i\left|\hat{H}_p\right|\psi_m\right\rangle$$

First order perturbation theory

So we have $\left(E_i - E_m\right) a_i^{(1)} = E^{(1)} \langle \psi_i | \psi_m \rangle - \langle \psi_i | \hat{H}_p | \psi_m \rangle$

We presume the energy eigenvalue E_m is not degenerate

i.e., only one eigenfunction for this eigenvalue

With no degeneracy, we still need to distinguish two cases

First, for $i \neq m$, from above $\left(E_i - E_m\right) a_i^{(1)} = -\langle \psi_i | \hat{H}_p | \psi_m \rangle$

So $\quad a_i^{(1)} = \dfrac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_i}$

Second, for $i = m$

$$\left(E_m - E_m\right) a_m^{(1)} = 0 a_m^{(1)} = E^{(1)} - \langle \psi_m | \hat{H}_p | \psi_m \rangle = E^{(1)} - E^{(1)} = 0$$

which gives no constraints on $a_m^{(1)}$

First order perturbation theory

We are therefore free to choose $a_m^{(1)}$

The choice that makes the algebra simplest

- is to set $a_m^{(1)} = 0$
  - which is the same as saying
    - we choose to make $\left|\phi^{(1)}\right\rangle$ orthogonal to $\left|\psi_m\right\rangle$

The same happens for the higher order equations

- Hence, quite generally
  - we make the convenient choice

$$\left\langle \psi_m \middle| \phi^{(j)} \right\rangle = 0$$

First order perturbation theory

Hence with $a_i^{(1)} = \dfrac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_i}$ and $a_m^{(1)} = 0$

the first order correction to the wavefunction is

$$\boxed{\left| \phi^{(1)} \right\rangle = \sum_{n \neq m} \frac{\langle \psi_n | \hat{H}_p | \psi_m \rangle}{E_m - E_n} \left| \psi_n \right\rangle}$$

and we have the first order correction to the energy

$$\boxed{E^{(1)} = \langle \psi_m | \hat{H}_p | \psi_m \rangle}$$

Second order perturbation theory

We continue similarly to find the higher order terms

Premultiplying $\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + E^{(2)}\left|\psi_m\right\rangle$

on both sides by $\left\langle\psi_m\right|$ gives

$$= 0$$

$$= \left\langle\psi_m\right|\left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + \left\langle\psi_m\right|E^{(2)}\left|\psi_m\right\rangle = E^{(1)}\left\langle\psi_m\middle|\phi^{(1)}\right\rangle - \left\langle\psi_m\right|\hat{H}_p\left|\phi^{(1)}\right\rangle + E^{(2)}$$

so $E^{(2)} = \left\langle\psi_m\right|\hat{H}_p\left|\phi^{(1)}\right\rangle - E^{(1)}\left\langle\psi_m\middle|\phi^{(1)}\right\rangle$

Since we chose $\left|\phi^{(j)}\right\rangle$ orthogonal to $\left|\psi_m\right\rangle$

$$\boxed{E^{(2)} = \left\langle\psi_m\right|\hat{H}_p\left|\phi^{(1)}\right\rangle}$$

Second order perturbation theory

Using our result for the first-order wavefunction correction

$$\left|\phi^{(1)}\right\rangle = \sum_{n\neq m} \frac{\left\langle \psi_n \middle| \hat{H}_p \middle| \psi_m \right\rangle}{E_m - E_n} \left|\psi_n\right\rangle$$

then from

$$E^{(2)} = \left\langle \psi_m \middle| \hat{H}_p \middle| \phi^{(1)} \right\rangle$$

we obtain

$$E^{(2)} = \left\langle \psi_m \right| \hat{H}_p \left(\sum_{n\neq m} \frac{\left\langle \psi_n \middle| \hat{H}_p \middle| \psi_m \right\rangle}{E_m - E_n} \left|\psi_n\right\rangle \right)$$

Equivalently

$$\boxed{E^{(2)} = \sum_{n\neq m} \frac{\left|\left\langle \psi_n \middle| \hat{H}_p \middle| \psi_m \right\rangle\right|^2}{E_m - E_n}}$$

Second order perturbation theory

For the second order wavefunction correction

we expand $\left|\phi^{(2)}\right\rangle$

noting now that $\left|\phi^{(2)}\right\rangle$ is chosen orthogonal to $\left|\psi_m\right\rangle$

$$\left|\phi^{(2)}\right\rangle = \sum_{n \neq m} a_n^{(2)} \left|\psi_n\right\rangle$$

We premultiply $\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + E^{(2)}\left|\psi_m\right\rangle$

by $\left\langle\psi_i\right|$ to obtain

$$\left\langle\psi_i\right|\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E_i - E_m\right)a_i^{(2)}$$

$$= \left\langle\psi_i\right|\left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + \left\langle\psi_i\right|E^{(2)}\left|\psi_m\right\rangle = E^{(1)}a_i^{(1)} - \sum_{n \neq m} a_n^{(1)}\left\langle\psi_i\right|\hat{H}_p\left|\psi_n\right\rangle$$

Second order perturbation theory

So, we have $\left(E_i - E_m\right) a_i^{(2)} = E^{(1)} a_i^{(1)} - \sum_{n \neq m} a_n^{(1)} \langle \psi_i | \hat{H}_p | \psi_n \rangle$

Note this summation excludes the term $n = m$

because we chose $\left|\phi^{(1)}\right\rangle$ to be orthogonal to $\left|\psi_m\right\rangle$

i.e., we have chosen $a_m^{(1)} = 0$

Hence, for $i \neq m$ we have

$$a_i^{(2)} = \left(\sum_{n \neq m} \frac{a_n^{(1)} \langle \psi_i | \hat{H}_p | \psi_n \rangle}{E_m - E_i} \right) - \frac{E^{(1)} a_i^{(1)}}{E_m - E_i}$$

Note that the second order wavefunction depends only

on the first order energy and wavefunction

First and second order perturbation results

$$E^{(1)} = \langle \psi_m | \hat{H}_p | \psi_m \rangle$$

First order

$$\left| \phi^{(1)} \right\rangle = \sum_{n \neq m} a_n^{(1)} | \psi_n \rangle$$

$$a_i^{(1)} = \frac{\langle \psi_i | \hat{H}_p | \psi_m \rangle}{E_m - E_i}, \quad a_m^{(1)} = 0$$

$$E^{(2)} = \left\langle \psi_m \middle| \hat{H}_p \middle| \phi^{(1)} \right\rangle$$

Second order

$$\left| \phi^{(2)} \right\rangle = \sum_{n \neq m} a_n^{(2)} | \psi_n \rangle$$

$$a_i^{(2)} = \left(\sum_{n \neq m} \frac{a_n^{(1)} \langle \psi_i | \hat{H}_p | \psi_n \rangle}{E_m - E_i} \right) - \frac{E^{(1)} a_i^{(1)}}{E_m - E_i}, \quad a_m^{(2)} = 0$$