8.3 Perturbation theory

Slides: Video 8.3.1 Constructing perturbation theory

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.3 (up to "First order perturbation theory")

Perturbation theory

Constructing perturbation theory

Quantum mechanics for scientists and engineers

David Miller

Time-independent perturbation theory

Presume some unperturbed Hamiltonian $\hat{H}_o$

    that has known normalized eigen solutions

      i.e., $\qquad \hat{H}_0 \left| \psi_n \right\rangle = E_n \left| \psi_n \right\rangle$

We can imagine that our perturbation

    could be progressively "turned on"

      at least in a mathematical sense

For example

    we could be progressively increasing applied field E
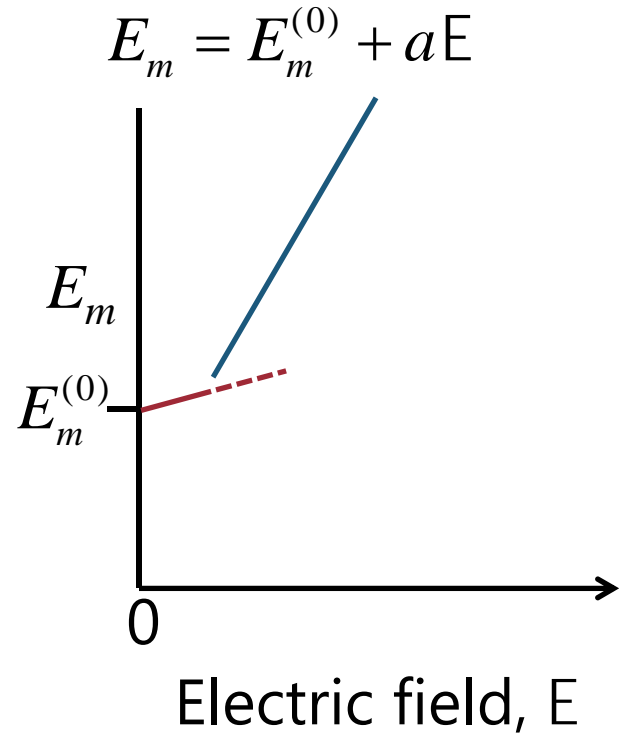
      from zero to some specific value

Time-independent perturbation theory

We look successively
　　for the changes in the solutions
　　　for example, for the mth energy
　　　　eigenvalue E_m
　　proportional first to electric field E
　　　"first-order corrections"

$$E_m = E_m^{(0)} + a\mathrm{E}$$

E_m

$E_m^{(0)}$

0

Electric field, E

Time-independent perturbation theory

We look successively

for the changes in the solutions
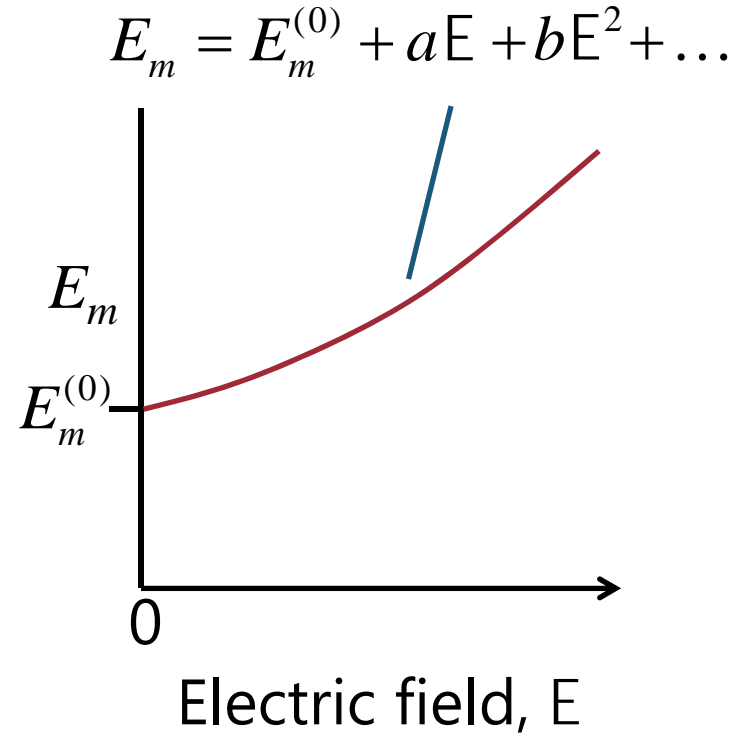
for example, for the mth energy eigenvalue E_m

proportional first to electric field E

"first-order corrections"

proportional to E²

"second-order corrections"

and so on

$$E_m = E_m^{(0)} + a\text{E} + b\text{E}^2 + \ldots$$

E_m
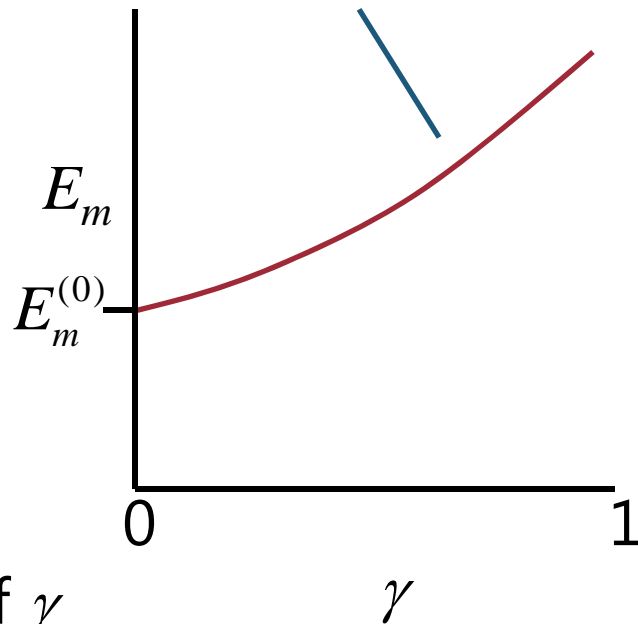
$E_m^{(0)}$

0

Electric field, E

Time-independent perturbation theory

It is more convenient and general
if we imagine a specific fixed
perturbation (e.g., a field E)
and we mathematically increase a
"house-keeping" parameter γ
from 0 to 1
so our perturbation is γE
with E fixed
Now we express changes as orders of γ
rather than of the field itself

$$E_m = E_m^{(0)} + \gamma E_m^{(1)} + \gamma^2 E_m^{(2)} + \ldots$$

The "house-keeping" parameter γ

So, instead of writing $E_m = E_m^{(0)} + a\mathrm{E} + b\mathrm{E}^2 + \dots$

we are writing $E_m = E_m^{(0)} + \gamma E_m^{(1)} + \gamma^2 E_m^{(2)} + \dots$

and instead of working out a and b

we are going to work out parameters

$E_m^{(1)}$ and $E_m^{(2)}$ and so on

These have dimensions of energy

and reflect the "first order" and "second order"

corrections to the energy

as a result of the specific perturbation

e.g., a *specific* field E

The "house-keeping" parameter γ

In general, then, we imagine that our perturbed system has some additional term in the Hamiltonian

the "perturbing Hamiltonian" $\hat{H}_p$

In our example case of an infinitely deep potential well

with an applied field

that perturbing Hamiltonian would be $\hat{H}_p = e\mathsf{E}\left(z - L_z/2\right)$

In the theory, we write the perturbing Hamiltonian as $\gamma\hat{H}_p$

using γ to keep track of the order of the corrections

through the powers of γ in the expressions

We can set $\gamma = 1$ at the end if we like

The "house-keeping" parameter γ

So, we could set up the theory using $E_m = E_m^{(0)} + a\mathrm{E} + b\mathrm{E}^2 + \ldots$

    in which case we would work out a and b

      and some other parameters

But, to make it more general we use

$$E_m = E_m^{(0)} + \gamma E_m^{(1)} + \gamma^2 E_m^{(2)} + \ldots$$

    and work out the parameters

      $E_m^{(1)}$ and $E_m^{(2)}$ and some other parameters

If this is confusing at first

    then just think of γ as the strength of the electric field
      in our specific problem

With this way of thinking about the problem mathematically

we can write the perturbed Schrödinger equation as

$$\left(\hat{H}_o + \gamma \hat{H}_p \right) \left| \phi \right\rangle = E \left| \phi \right\rangle$$

We now presume that we can express

the resulting perturbed eigenfunction and eigenvalue

as power series in this parameter, i.e.,

$$\left| \phi \right\rangle = \left| \phi^{(0)} \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \gamma^3 \left| \phi^{(3)} \right\rangle + \cdots$$

$$E = E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \gamma^3 E^{(3)} + \cdots$$

Construction of the orders of perturbation theory

We now substitute these power series

$$\left|\phi\right\rangle = \left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \gamma^3\left|\phi^{(3)}\right\rangle + \cdots$$

$$E = E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \gamma^3 E^{(3)} + \cdots$$

into the perturbed Schrödinger equation

$$\left(\hat{H}_o + \gamma\hat{H}_p\right)\left|\phi\right\rangle = E\left|\phi\right\rangle$$

to get

$$\left(\hat{H}_0 + \gamma\hat{H}_p\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)$$

$$= \left(E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)$$

Now, at any specific point in space, each function $\left|\phi^{(n)}\right\rangle$
and each function $\left(\hat{H}_0 + \gamma\hat{H}_p\right)\left|\phi^{(n)}\right\rangle$
is just some number

So, at any specific point in space, the left hand side of

$$\left(\hat{H}_0 + \gamma\hat{H}_p\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)$$

$$= \left(E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots\right)\left(\left|\phi^{(0)}\right\rangle + \gamma\left|\phi^{(1)}\right\rangle + \gamma^2\left|\phi^{(2)}\right\rangle + \cdots\right)$$

is just a power series in γ, e.g., $a_0 + a_1\gamma + a_2\gamma^2 + a_3\gamma^3 + \cdots$

and so is the right hand side, e.g., $b_0 + b_1\gamma + b_2\gamma^2 + b_3\gamma^3 + \cdots$

Construction of the orders of perturbation theory

Because a power series expansion is unique

the only way the equality of two power series can work

$$a_0 + a_1\gamma + a_2\gamma^2 + a_3\gamma^3 + \cdots = b_0 + b_1\gamma + b_2\gamma^2 + b_3\gamma^3 + \cdots$$

for every value of γ within some convergence range

e.g., 0 to 1

is if the terms are equal, one by one, i.e.,

$$a_0 = b_0 \quad a_1 = b_1 \quad a_2 = b_2 \quad a_3 = b_3$$

and so on

Hence, in

$$\left(\hat{H}_0 + \gamma \hat{H}_p \right)\left(\left| \phi^{(0)} \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \cdots \right)$$

$$= \left(E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots \right)\left(\left| \phi^{(0)} \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \cdots \right)$$

we can equate each term with a specific power of γ

and hence obtain

a progressive set of equations

which we can solve to evaluate corrections

to whatever order we wish

Progressive set of perturbation theory equations

In $\left(\hat{H}_0 + \gamma \hat{H}_p \right)\left(\left| \phi^{(0)} \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \cdots \right)$

$$= \left(E^{(0)} + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots \right)\left(\left| \phi^{(0)} \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \cdots \right)$$

equating terms in γ^0, i.e., terms without γ

gives the "zeroth" order equation $\hat{H}_o \left| \phi^{(0)} \right\rangle = E^{(0)} \left| \phi^{(0)} \right\rangle$

i.e., the unperturbed Hamiltonian equation

with eigenfunctions $\left| \psi_n \right\rangle$ and eigenvalues E_n

So if we now presume we start in a specific eigenstate $\left| \psi_m \right\rangle$

we write $\left| \psi_m \right\rangle$ and E_m

instead of $\left| \phi^{(0)} \right\rangle$ and $E^{(0)}$

Progressive set of perturbation theory equations

So, with $\left(\hat{H}_0 + \gamma \hat{H}_p \right)\left(\left| \psi_m \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \cdots \right)$

$$= \left(E_m + \gamma E^{(1)} + \gamma^2 E^{(2)} + \cdots \right)\left(\left| \psi_m \right\rangle + \gamma \left| \phi^{(1)} \right\rangle + \gamma^2 \left| \phi^{(2)} \right\rangle + \cdots \right)$$

we get a progressive set of equations

each equating a different power of γ

$$\hat{H}_o \left| \psi_m \right\rangle = E_m \left| \psi_m \right\rangle$$

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

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

and so on

Progressive set of perturbation theory equations

We can rewrite these equations as

$$\hat{H}_o\left|\psi_m\right\rangle = E_m\left|\psi_m\right\rangle \quad \rightarrow \quad \boxed{\left(\hat{H}_o - E_m\right)\left|\psi_m\right\rangle = 0}$$

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

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

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

$$\rightarrow \quad \boxed{\left(\hat{H}_o - E_m\right)\left|\phi^{(2)}\right\rangle = \left(E^{(1)} - \hat{H}_p\right)\left|\phi^{(1)}\right\rangle + E^{(2)}\left|\psi_m\right\rangle}$$
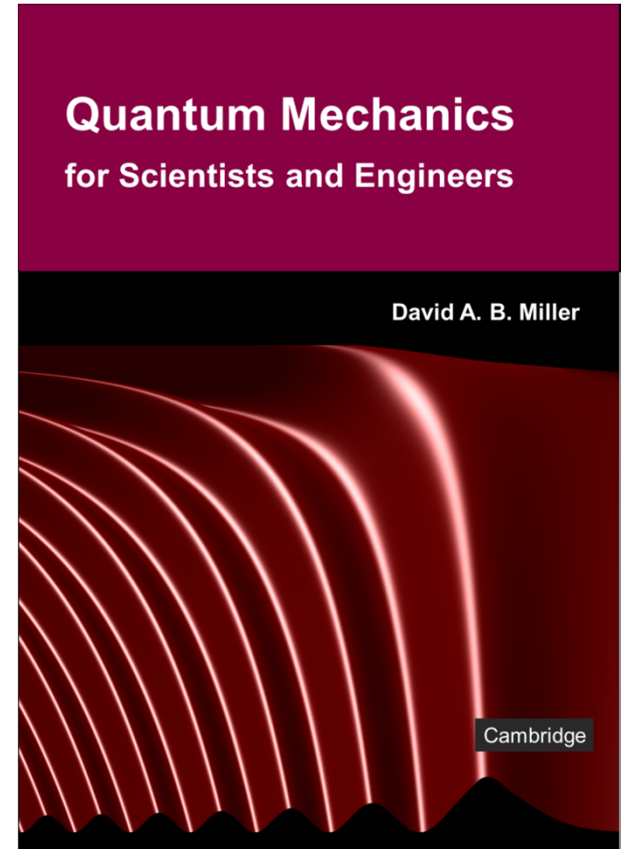
and so on
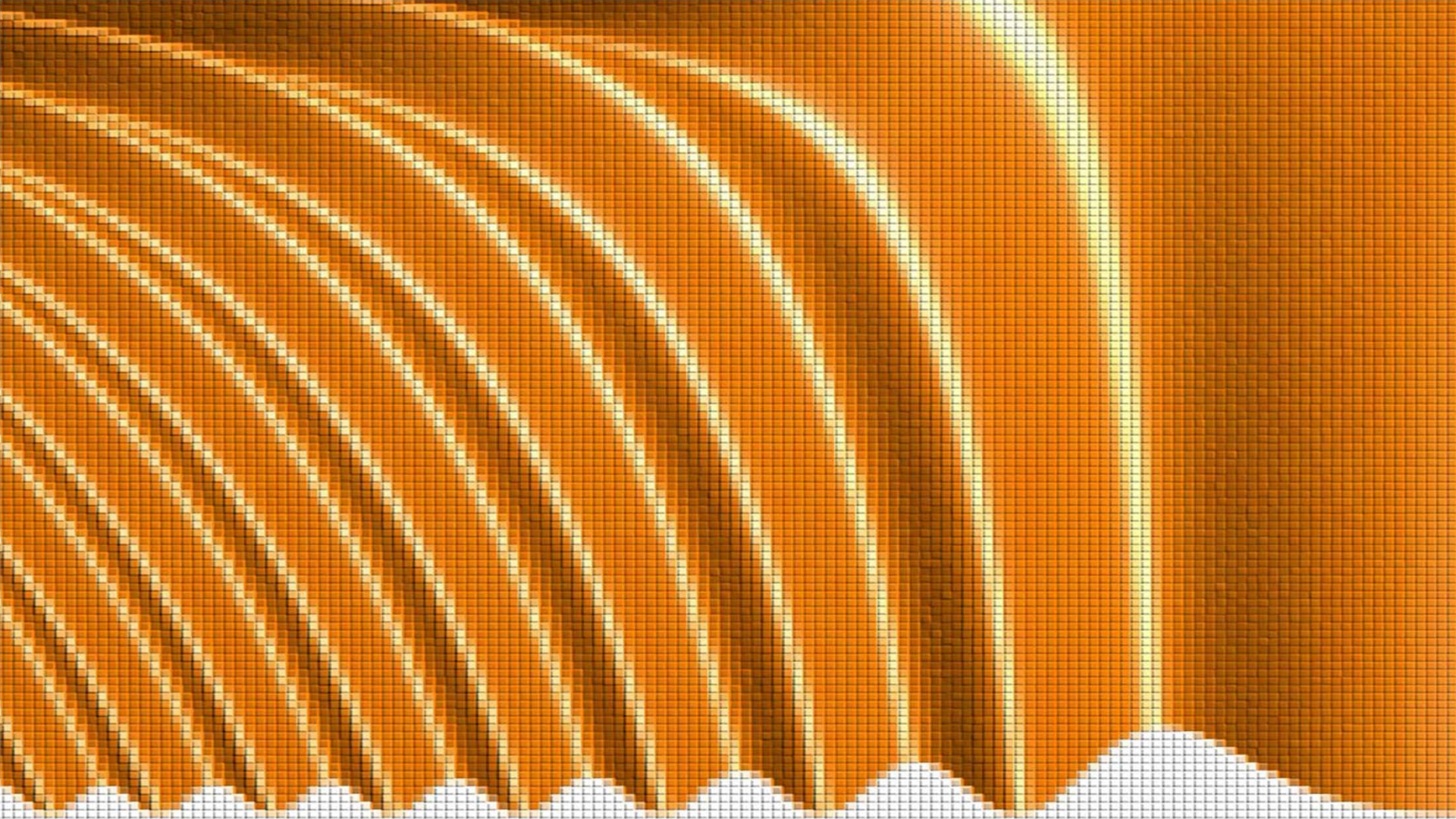
8.3 Perturbation theory

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")

Quantum Mechanics
for Scientists and Engineers

David A. B. Miller

Cambridge

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

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

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

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

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

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

   Second, for $i = m$

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

   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

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

and we have the first order correction to the energy

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

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

$$= 0$$

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

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

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

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

Second order perturbation theory

Using our result for the first-order wavefunction correction

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

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

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

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

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

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

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

Second order perturbation theory

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

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

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

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

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

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

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

Second order

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

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

8.3 Perturbation theory

Slides: Video 8.3.4 Applying perturbation theory

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.3 (starting at "Example of well with field")
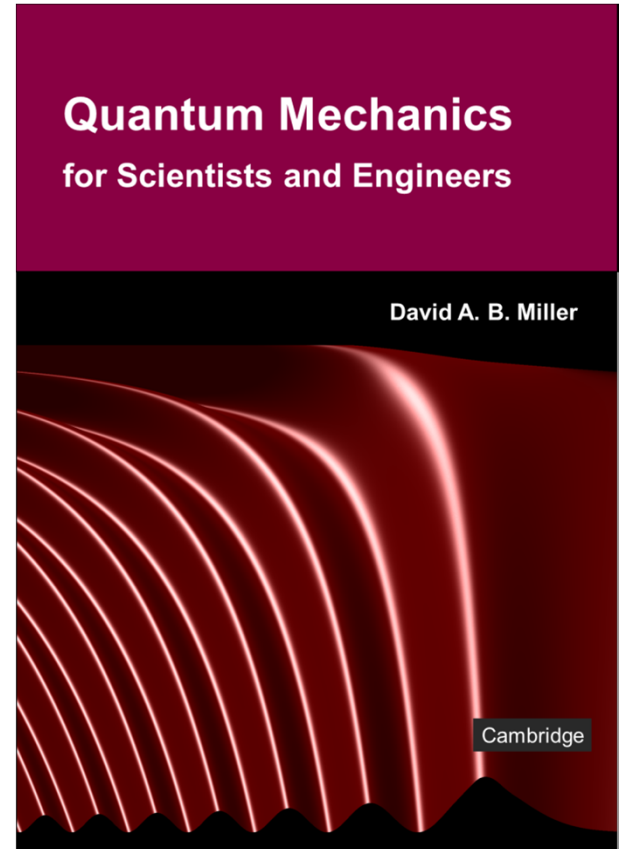
Perturbation theory

Applying perturbation theory

Quantum mechanics for scientists and engineers

David Miller

Example of a well with field

We write the Hamiltonian as the sum of

the unperturbed Hamiltonian

which is, in the well, in our dimensionless units

$$\hat{H}_o = -\frac{1}{\pi^2}\frac{d^2}{d\xi^2}$$

and the perturbing Hamiltonian

$$\hat{H}_p = \mathrm{f}\left(\xi - 1/2\right)$$

where again we take $\mathrm{f} = 3$ for an explicit calculation

First order energy correction

In first order, the energy shift with applied field is

$$E^{(1)} = \left\langle \psi_m \middle| \hat{H}_p \middle| \psi_m \right\rangle = f \int_0^1 \sqrt{2} \sin\left(m\pi\xi\right)\left(\xi - 1/2\right)\sqrt{2}\sin\left(m\pi\xi\right)d\xi$$

$$= 2f \int_0^1 \left(\xi - 1/2\right)\sin^2\left(m\pi\xi\right)d\xi = 0$$

The integrals here are zero for all m

because the sine squared function is even with
respect to the center of the well

whereas $\left(\xi - 1/2\right)$ is odd

Hence, for this particular problem there is no first order
energy correction

First order energy correction

There no first order energy correction
  because of symmetry
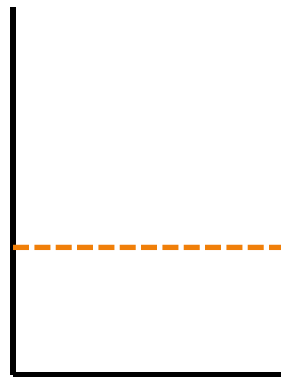
First order energy correction

There no first order energy correction
because of symmetry
If the energy changed
proportionately with applied field

?
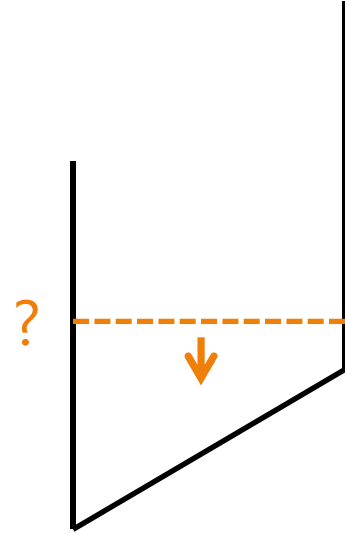
First order energy correction

There no first order energy correction
  because of symmetry
If the energy changed
  proportionately with applied field
  changing field direction (or sign)
    would change the energy
      correction sign
But, by symmetry here
  the energy change cannot depend
    field direction

?
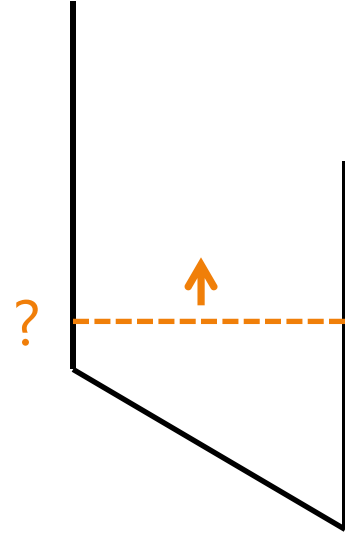
Matrix elements for perturbation calculations

The general matrix elements that we will need for further perturbation calculations are

$$H_{puv} = \left\langle \psi_u \left| \hat{H}_p \right| \psi_v \right\rangle = f \int_0^1 \sqrt{2} \sin\left(u\pi\xi\right)\left(\xi - 1/2\right)\sqrt{2}\sin\left(v\pi\xi\right)d\xi$$

In general we need u and v to have opposite parity

i.e., if one is odd, the other must be even

for these matrix elements to be non-zero

since otherwise

the overall integrand is odd about $\xi = 1/2$

First order correction to the wavefunction

We calculate the first order wavefunction correction

for the first state, i.e., for $m = 1$

$$\left|\phi^{(1)}\right\rangle = \sum_{n=2}^{q} a_n^{(1)} \left|\psi_n\right\rangle \qquad a_i^{(1)} = \frac{\left\langle\psi_i\left|\hat{H}_p\right|\psi_1\right\rangle}{\varepsilon_{o1} - \varepsilon_{oi}}$$

where $\varepsilon_{on} = n^2$ are the energies of the unperturbed states, and

q is a finite number we must choose in practice

Here, we chose $q = 6$

though a smaller number would likely be quite accurate

First order correction to the wavefunction

Explicitly, for the expansion coefficients

$$a_i^{(1)} = \langle \psi_i | \hat{H}_p | \psi_1 \rangle / \left(\varepsilon_{o1} - \varepsilon_{oi} \right)$$

for 3 units of field

we have numerically

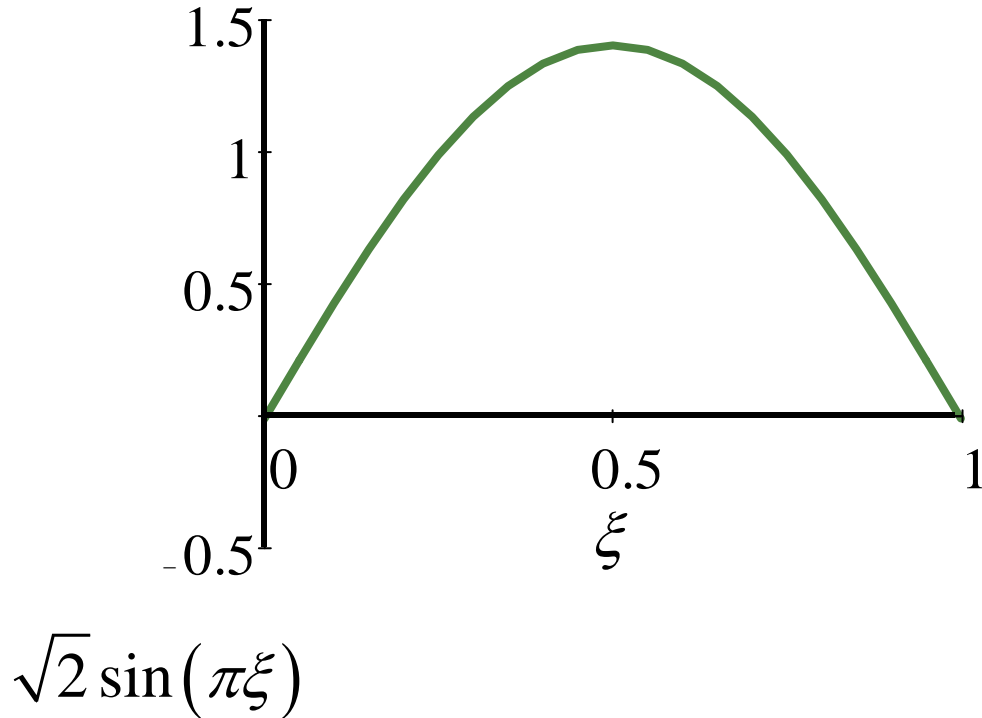$$a_2^{(1)} \simeq 0.180 \qquad a_3^{(1)} = 0 \qquad a_4^{(1)} \simeq 0.003$$

Here

the value of 0.180 for $a_2^{(1)}$

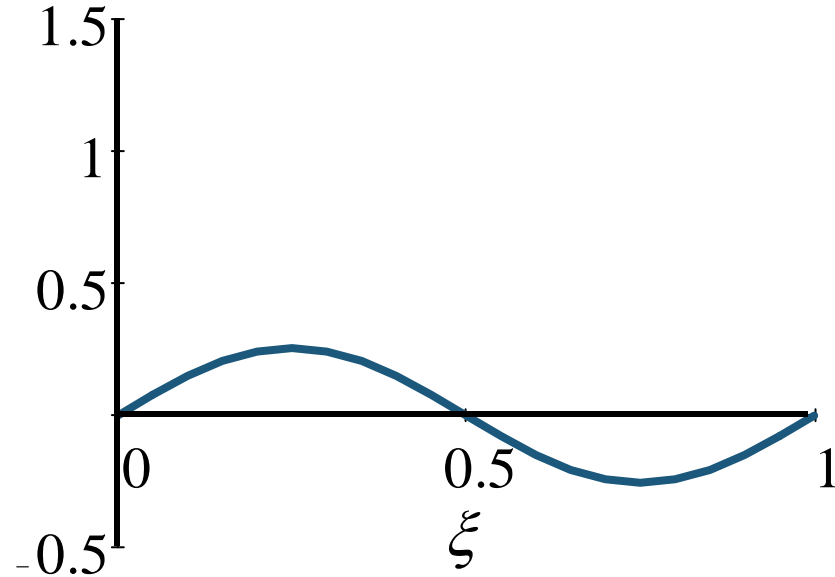compares closely with the value of 0.174 obtained above in the finite basis subset method

First order correction to the wavefunction

We sum the zero-order (unperturbed) wavefunction

$$\sqrt{2}\sin\left(\pi\xi\right)$$

First order correction to the wavefunction
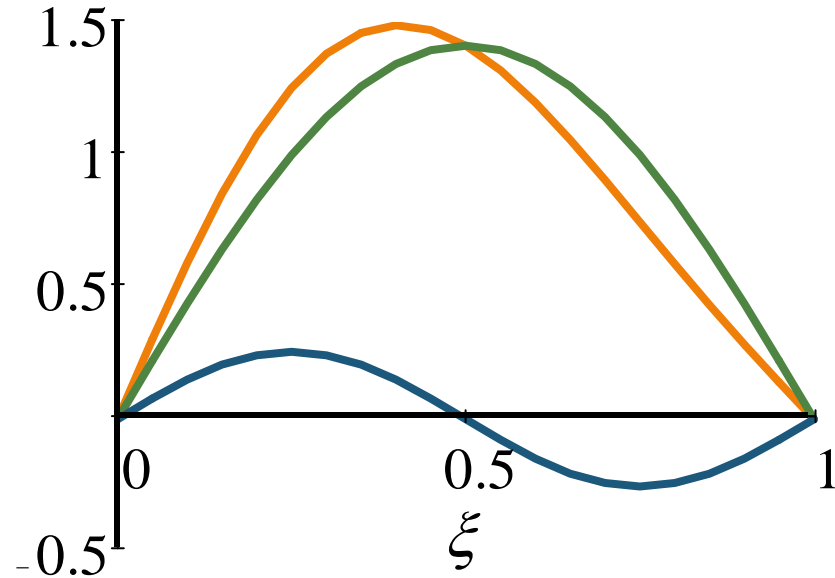
and the first order correction part from the second basis
  function

$$0.180\sqrt{2}\sin(2\pi\xi)$$

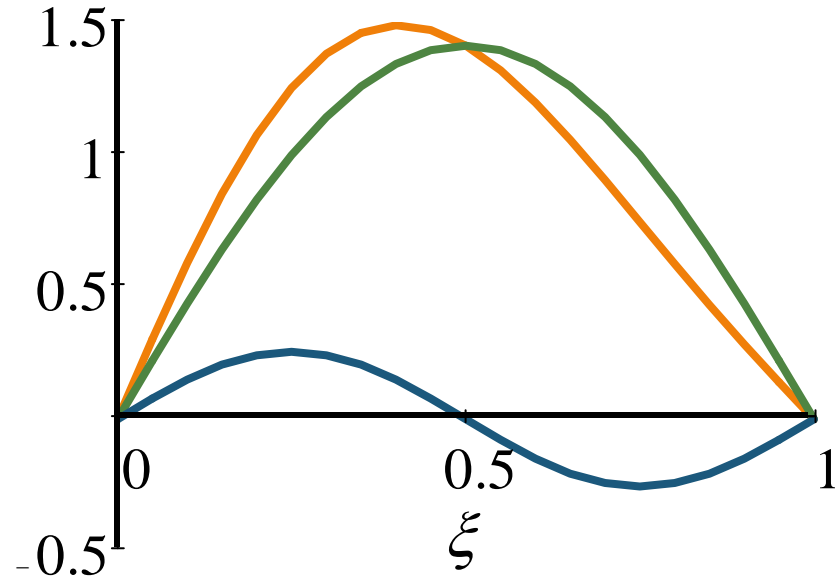# First order correction to the wavefunction

To get our approximate wavefunction solution

$$\psi(\zeta) \simeq \sqrt{2}\sin(\pi\xi) + 0.180\sqrt{2}\sin(2\pi\xi)$$

First order correction to the wavefunction

Adding the next correction makes negligible difference

$$\psi(\zeta) \simeq \sqrt{2}\sin(\pi\xi) + 0.180\sqrt{2}\sin(2\pi\xi) + 0.003\sqrt{2}\sin(4\pi\xi)$$

Second order energy correction

Since the first order correction to the energy was zero
to get a perturbation correction to the energy
we go to second order

Explicitly, we have $E^{(2)} = \left\langle \psi_1 \left| \hat{H}_p \right| \phi^{(1)} \right\rangle = \sum_{n=2}^{q} \dfrac{\left| \left\langle \psi_n \left| \hat{H}_p \right| \psi_1 \right\rangle \right|^2}{E_1 - E_n}$

which numerically here gives $E^{(2)} = -0.0975$

or a total energy of $\eta_1 \simeq \varepsilon_1 + E^{(1)} + E^{(2)} = 0.9025$
which compares with the result of

$\eta_1 = 0.904$ from the finite basis subset method

Approximate analytic formulas

Note that $E^{(2)}$

is analytically proportional to the square of the field f²

$$E^{(2)} = \sum_{n=2}^{q} \frac{\left|\left\langle \psi_n \left| \hat{H}_p \right| \psi_1 \right\rangle\right|^2}{E_1 - E_n} = \sum_{n=2}^{q} \frac{\left|\left\langle \psi_n \left| f(\xi - 1/2) \right| \psi_1 \right\rangle\right|^2}{E_1 - E_n}$$

$$= f^2 \sum_{n=2}^{q} \frac{\left|\left\langle \psi_n \left| (\xi - 1/2) \right| \psi_1 \right\rangle\right|^2}{E_1 - E_n}$$

Approximate analytic formulas

Hence perturbation theory
gives an approximate analytic result for the energy
which we can now use for any field
Explicitly, we can write for the energy of the first state
in dimensionless units

$$\eta_1 \cong \varepsilon_1 - 0.0108 \mathrm{f}^2$$

This typical kind of result from perturbation theory
gives us an approximate analytic formula
valid for small perturbations

Approximate analytic formulas

Similarly, for the wavefunction

the correction is approximately proportional to field

for example with expansion coefficient

$$a_i^{(1)} = \frac{\left\langle \psi_i \middle| \hat{H}_p \middle| \psi_m \right\rangle}{E_m - E_i} = f \frac{\left\langle \psi_i \middle| (\xi - 1/2) \middle| \psi_m \right\rangle}{E_m - E_i}$$

So, keeping only the dominant contribution from the second-state wavefunction in our example

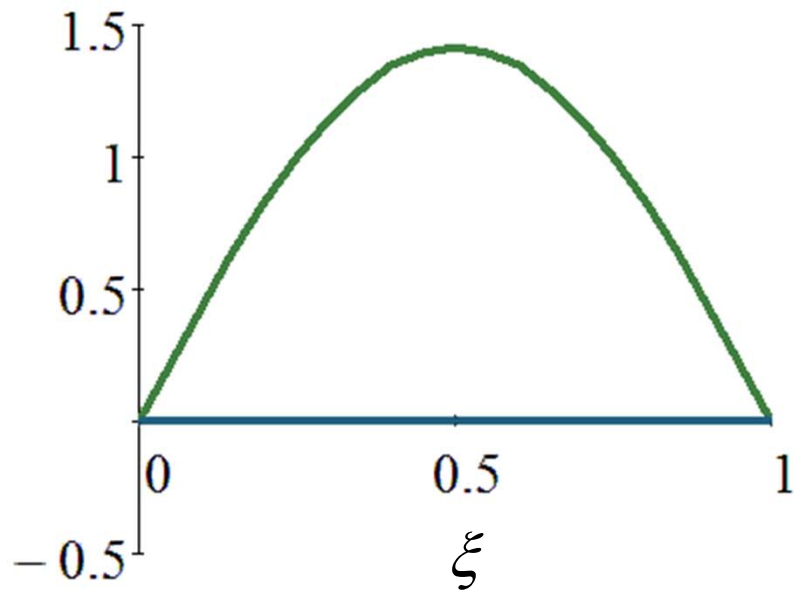we would have the approximate formula for small f

$$\phi(\xi) \cong \sqrt{2} \sin(\pi\xi) + 0.06f\sqrt{2} \sin(2\pi\xi)$$

(This is not quite normalized, though that could be done)

Approximate analytic results

Wavefunction   Field = 0   Energy