

The Variational Method and Perturbation Theory

We have concentrated on problems that were analytically solvable so far, such as the simple harmonic oscillator, the hydrogen atom, and square well type potentials. In fact, we shall soon be confronted with situations where an exact analytic solution is unknown: more general potentials, or atoms with *more than one electron*. To make progress in these cases, we need approximation methods. The best known method is perturbation theory, which has proved highly successful over a wide range of problems (but by no means all). Here, though, we shall first review another approximation method – the variational method, which works best for the ground state, and in some circumstances (to be described below) for some other low lying states.

1. Variational Method for Finding the Ground State Energy

1.1 Nonlinear variation

The idea is to guess the ground state wave function, but the guess must have an adjustable parameter, which can then be varied (hence the name) to minimize the expectation value of the energy, and thereby find the best approximation to the true ground state wave function.

We'll begin with a single particle in a potential, $\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r})$. If the particle is restricted to one dimension, and we're looking for the ground state in any fairly localized potential well, we can start with the family of normalized Gaussians $\phi(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$: just find $\int \phi^* H \phi d\tau$, differentiate the result with respect to α , setting this to zero.

$$\frac{\partial \int \phi^* H \phi d\tau}{\partial \alpha} = 0 \quad (1)$$

Here, $\phi(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ is called a *trial function*.

Not surprisingly, this gives the exact ground state for the simple harmonic oscillator potential, and for nothing else. What is perhaps surprising is that the result is only off by 30% or so for the attractive delta-function potential, even though the wave function looks a lot different. Obviously, the Gaussian family cannot be used if there is an infinite wall anywhere: one must find a family of wave functions vanishing at the wall.

The variational principle can be proved by expanding the function ϕ in terms of orthonormal set of functions ψ_i , assumed to be complete.

$$\phi = \sum_i a_i \psi_i \quad (2)$$

The a_i are fixed constants.

Owing to the normalization of ϕ and the orthonormality of the ψ_i

$$\int \phi^* \phi d\tau = \sum_i \sum_j a_j^* a_i \int \psi_j^* \psi_i d\tau = 1 \quad (3)$$

or

Substituting equation (2) to $E = \int \phi^* \hat{H} \phi d\tau$

$$\begin{aligned} E &= \sum_i \sum_j a_j^* a_i \int \psi_j^* H \psi_i d\tau \\ &= \sum_i \sum_j a_j^* a_i E_i \int \psi_j^* \psi_i d\tau \\ &= \sum_i a_i^* a_i E_i \end{aligned} \quad (4)$$

If subtracting the ground state energy E_1 from equation (4), we obtain

$$E - E_1 = \sum_i |a_i|^2 (E_i - E_1) \geq 0 \quad (5)$$

E is equal to E_1 only if $a_i = 0$ except a_1 - in other words, only if ϕ is the function ψ_1 .

If the function ϕ is not normalized, the variational principles applies to the integral

$$E = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau} \quad (6)$$

The trial function is chosen to be of an analytical form which is likely to be close to that of the true ground state wavefunction ψ_1 , but containing several undetermined parameters.

For example, if the chosen form of ϕ is

$$\phi = e^{-\alpha r} (1 + \beta r + \gamma r^2) \quad (7)$$

for a one-particle system, and E is expressed as a function of the parameters α, β, γ . E is now minimized with respect to these parameters $\frac{\partial E}{\partial \alpha} = \frac{\partial E}{\partial \beta} = \frac{\partial E}{\partial \gamma} = 0$.

We apply the method to the ground state of the hydrogen atom. We know it's going to be spherically symmetric, so it amounts to a one-dimensional problem: just the radial wave function. Using standard notation

$$a_0 = \frac{\hbar^2}{me^2}, E_0 = \frac{me^4}{2\hbar^2}, \rho = \frac{r}{a_0} \quad (8)$$

and for a trial wave function u

$$E(u) = \frac{-\int u \left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} \right) u d\rho}{\int u^2 d\rho} \quad (9)$$

(we're going to take u real).

we try three families:

$$\begin{aligned} u_1 &= \rho e^{-\alpha\rho} \\ u_2 &= \frac{\rho}{\alpha^2 + \rho^2} \\ u_3 &= \rho^2 e^{-\alpha\rho} \end{aligned} \quad (10)$$

and find $\alpha_{min} = 1, \pi/4, 3/2$ respectively for the three families.

For the first family u_1

$$E = -E_0 \frac{\int \rho e^{-\alpha\rho} \left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} \right) (\rho e^{-\alpha\rho}) d\rho}{\int \rho^2 e^{-2\alpha\rho} d\rho} \quad (11)$$

(useful integrals: $\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$, $\int_{-\infty}^\infty e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$)

Equation (11) becomes

$$E = E_0 \frac{\int (2\alpha\rho e^{-2\alpha\rho} - \alpha^2 \rho^2 e^{-2\alpha\rho} - 2\rho e^{-2\alpha\rho}) d\rho}{\frac{1}{4\alpha^3}} = 4\alpha^3 \left(\frac{1}{2\alpha} - \frac{1}{4\alpha} - \frac{1}{2\alpha^2} \right) E_0 = (\alpha^2 - 2\alpha) E_0 \quad (12)$$

The first family, u_1 , includes the exact result, and the minimization procedure finds it. For the three families, then the energy of the best state is off by 0, 25%, 21% respectively.

How about wavefunctions? The wavefunction error is defined as how far the square of the overlap with the true ground state wave function falls short of unity. For the three families,

$$\epsilon = 1 - \int \psi_0^* \phi_{var} d\tau : 0, 0.21, 0.05.$$

The third family has far better wave function overlap than the second, but only a slightly better energy estimate. Why? A key point is that the potential is singular at the origin, there is a big contribution to potential energy from a rather small region, and the third family wave function is the least accurate of the three there. The second family functions are very inaccurate at large distances: the expectation value $\langle r \rangle = 1.5 a_0, \infty, 1.66 a_0$ for the three families. But at large distances, both kinetic and potential energies are small, so the result can still look reasonable. T

These example reinforces the point that *the variational method should be used cautiously.*

1.2. Variational Method for Higher States

In some cases, the approach can be used easily for higher states: specifically, in problems having some symmetry. For example, if the one dimensional attractive potential is symmetric about the origin, and

has more than one bound state, the ground state will be even, the first excited state odd. Therefore, we can estimate the energy of the first excited state by minimizing a family of odd functions, such as

$$\psi(x, \alpha) = (\sqrt{\pi}/2\alpha^{3/2}) x e^{-\alpha x^2/2}.$$

1.3. Ground State Energy of the Helium Atom by the Variational Method

The Hamiltonian operator for the Helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \quad (13)$$

Using atomic units $1 \text{ Rydberg} = \frac{me^4}{2\hbar^2}$, $1 \text{ Bohr unit} = \frac{\hbar^2}{me^2}$, we have

$$\frac{me^4}{2\hbar^2} \hat{H} = -\left(\frac{me^2}{\hbar^2}\right)^2 \frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \left(\frac{me^2}{\hbar^2}\right) \left(\frac{2e^2}{r_1} + \frac{2e^2}{r_2} - \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\right) \quad (14)$$

Or

$$\hat{H} = -\nabla_1^2 - \nabla_2^2 - \frac{4}{r_1} - \frac{4}{r_2} + \frac{2}{r_{12}} \quad (15)$$

If neglecting the Coulomb interaction between the electrons, the Schrödinger equation can be separated into two hydrogenic equations. The ground state wavefunction is then in atomic units

$$\psi = e^{-2(\vec{r}_1 + \vec{r}_2)} \quad (16)$$

Let's improve this by including the Coulomb interaction and using the variational method, with trial function suggested by

$$\phi = e^{-\alpha(\vec{r}_1 + \vec{r}_2)} \quad (17)$$

Here, α is a parameter, assumed to be real and positive, whose value shall be obtained by minimizing the integral

$$E = \frac{\int \int \phi^* H \phi d\vec{r}_1 d\vec{r}_2}{\int \int \phi^* \phi d\vec{r}_1 d\vec{r}_2} \quad (18)$$

Both ϕ and ϕ^* are real functions. Now,

$$\begin{aligned} \int \int \phi^* \phi d\vec{r}_1 d\vec{r}_2 &= \int e^{-2\alpha r_1} d\vec{r}_1 \int e^{-2\alpha r_2} d\vec{r}_2 = \int_0^\infty e^{-2\alpha r_1} 4\pi r_1^2 dr_1 \int_0^\infty e^{-2\alpha r_2} 4\pi r_2^2 dr_2 \\ &= 16\pi^2 \frac{2}{(2\alpha)^3} \frac{2}{(2\alpha)^3} = \frac{\pi^2}{\alpha^6} \end{aligned} \quad (19)$$

For a spherically symmetrical function $f(r)$ we may write

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{df}{dr} \right) \quad (20)$$

from which it follows that

$$\nabla^2 e^{-\alpha r} = \left(\alpha^2 - \frac{2\alpha}{r} \right) e^{-\alpha r} \quad (21)$$

Hence,

$$\begin{aligned} H\phi &= -\left(\alpha^2 - \frac{2\alpha}{r_1} \right) e^{-\alpha(r_1+r_2)} - \left(\alpha^2 - \frac{2\alpha}{r_2} \right) e^{-\alpha(r_1+r_2)} - \left(\frac{4}{r_1} + \frac{4}{r_2} - \frac{2}{r_{12}} \right) e^{-\alpha(r_1+r_2)} \\ &= \left[-2\alpha^2 + \frac{2\alpha-4}{r_1} + \frac{2\alpha-4}{r_2} + \frac{2}{r_{12}} \right] e^{-\alpha(r_1+r_2)} \end{aligned} \quad (22)$$

And

$$\int \int \phi^* H\phi = \int \int \left[-2\alpha^2 + \frac{2\alpha-4}{r_1} + \frac{2\alpha-4}{r_2} + \frac{2}{r_{12}} \right] e^{-2\alpha(r_1+r_2)} d\vec{r}_1 d\vec{r}_2 \quad (23)$$

We have

$$\int \int \frac{1}{r_1} e^{-2\alpha(r_1+r_2)} d\vec{r}_1 d\vec{r}_2 = \int_0^\infty \frac{1}{r_1} e^{-2\alpha r_1} 4\pi r_1^2 dr_1 \int_0^\infty e^{-2\alpha r_2} 4\pi r_2^2 dr_2 = 16\pi^2 \frac{1}{(2\alpha)^2} \frac{2}{(2\alpha)^3} = \frac{\pi^2}{\alpha^5} \quad (24)$$

With trivial mathematic work, we also have

$$\int \int \frac{1}{r_{12}} e^{-2\alpha(r_1+r_2)} d\vec{r}_1 d\vec{r}_2 = \frac{5\pi}{8\alpha^5} \quad (25)$$

Using these integrals, we have

$$\int \phi^* H\phi d\tau = 2\alpha^2 \frac{\pi^2}{\alpha^6} + 2(2\alpha-4) \frac{\pi^2}{\alpha^5} + 2 \frac{5\pi}{8\alpha^5} \quad (26)$$

Hence

$$E(\alpha) = 2\alpha^2 - \frac{27}{4}\alpha \quad (27)$$

Minimizing this, we have $\alpha = \frac{27}{16}$ and the minimum energy of E for the chose form of ϕ is

$$E\left(\frac{27}{16}\right) = 5.76 \text{ Ryd.}$$

The observed value of the ground state energy is -5.81 Ryd, so that the calculated value is in error by only 0.12 Ryd, or about 2%. With more complicated form of ϕ involving several parameters, the value of the ground state energy of helium calculated by the variational method, has been brought into almost perfect agreement with the experimental value.

The effective charge of the proton is $\frac{27}{16} < 2$ is caused by the screening effect. According to this, Slater constructed rules to form Slater-type orbitals (STO), which will be discussed in the future.

1.4. Linear Variation Functions

A frequent useful form of trial function ϕ is one which consists of a linear combination of definite functions with coefficients which are treated as variational parameters

$$\phi = \sum_i a_i \phi_i \quad (28)$$

Let us consider just to such functions

$$\phi = a_1 \phi_1 + a_2 \phi_2 \quad (29)$$

For simplicity, we assume a_1, a_2, ϕ_1, ϕ_2 are all real. It should be noted that here ϕ_1 and ϕ_2 need not to be orthogonal or normalized.

According to the variational method, we wish to choose a_1 and a_2 so as to minimize the function

$$E(a_1, a_2) = \frac{\int \phi H \phi d\tau}{\int \phi \phi d\tau} \quad (30)$$

Define the following symbols

$$H_{ij} = \int \phi_i^* H \phi_j d\tau, S_{ij} = \int \phi_i^* \phi_j d\tau \quad (31)$$

(H_{ij} is called **matrix elements**; S_{ij} is called **overlap integrals**)

Owing to the Hermiticity of the Laplace operator, it is obvious $H_{ij} = H_{ji}^*$ and $S_{ij} = S_{ji}^*$

Equation (30) becomes

$$a_1^2 S_{11} + a_1 a_2 S_{12} + a_2 a_1 S_{21} + a_2^2 S_{22} = a_1^2 H_{11} + a_1 a_2 H_{12} + a_2 a_1 H_{21} + a_2^2 H_{22} \quad (32)$$

Differentiating equation (32) with respect to a_1 and a_2 yields

$$(a_1 S_{11} + a_2 S_{12})E = a_1 H_{11} + a_2 H_{12} \quad (33)$$

and

$$(a_1 S_{21} + a_2 S_{22})E = a_1 H_{21} + a_2 H_{22} \quad (34)$$

Equations (33) and (34) may be rearranged as follows

$$\begin{aligned} a_1(H_{11} - E S_{11}) + a_2(H_{12} - E S_{12}) &= 0 \\ a_1(H_{21} - E S_{21}) + a_2(H_{22} - E S_{22}) &= 0 \end{aligned} \quad (35)$$

A determinantal equation is derived

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{21} - E S_{21} & H_{22} - E S_{22} \end{vmatrix} = 0 \quad (36)$$

Equation (36) is referred to as the **secular equation**, and the left side is called the **secular determinant**. The general form is

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \cdots & H_{1N} - E S_{1N} \\ H_{21} - E S_{21} & H_{22} - E S_{22} & \cdots & H_{2N} - E S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - E S_{N1} & H_{N2} - E S_{N2} & \cdots & H_{NN} - E S_{NN} \end{vmatrix} = 0 \quad (37)$$

Example: A Hydrogen atom in a uniform electric field

1.5 Matrix formulation the linear variational method

A matrix equivalent to equation (35) is

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1N} \\ c_{21} & c_{22} & \cdots & c_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ c_{N1} & c_{N2} & \cdots & c_{NN} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1N} \\ c_{21} & c_{22} & \cdots & c_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ c_{N1} & c_{N2} & \cdots & c_{NN} \end{pmatrix} \begin{pmatrix} E_{11} & 0 & \cdots & 0 \\ 0 & E_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_{NN} \end{pmatrix} \quad (38)$$

Or

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E} \quad (39)$$

Matrix elements:

matrix of coefficients (matrix of eigenvectors):

matrix of eigenvalues:

Q: How to solve the matrix equation?

Fact 1: \mathbf{S} can be a unit matrix (identity matrix).

Fact 2: \mathbf{C} is unitary (meaning $\mathbf{C}^+ \mathbf{C} = \mathbf{I}$)

The problem becomes: Given \mathbf{H} , find a unitary matrix \mathbf{C} such that $\mathbf{C}^+ \mathbf{H} \mathbf{C}$ is diagonal – matrix diagonalization.

2. Time-Independent Perturbation Theory

If an atom (not necessarily in its ground state) is placed in an external electric field, the energy levels shift, and the wave functions are distorted. This is called the Stark effect. The new energy levels and wave functions could in principle be found by writing down a complete Hamiltonian, including the external field, and finding the eigenstates. This actually can be done in one case: the hydrogen atom, but even there, if the external field is small compared with the electric field inside the atom (which is billions of volts per meter) it is easier to compute the changes in the energy levels and wave functions with a scheme of successive corrections to the zero-field values. This method, termed perturbation theory, is the single most important method of solving problems in quantum mechanics, and is widely used in atomic physics, condensed matter and particle physics.

2.1 First-order Perturbation Theory for a Non-Degenerate State

We begin with a Hamiltonian having known eigenstates and eigenenergies:

$$H \psi = E \psi \quad (40)$$

The task is to find how these eigenstates and eigenenergies change if a small term (an external field, for example) is added to the Hamiltonian, so

$$H = H^0 + H' \quad (41)$$

H^0 is the Hamiltonian of the unperturbed system, H' is the perturbation term.

If the perturbation is truly small, then the wavefunctions after perturbation will not differ very much from ψ . Thus, approximately,

$$E = \frac{\int \psi^* (H^0 + H') \psi d\tau}{\int \psi^* \psi d\tau} = E_0 + \frac{\int \psi^* H' \psi d\tau}{\int \psi^* \psi d\tau} \quad (42)$$

The ground state of the Helium Atom

$$H^0 = -\nabla_1^2 - \nabla_2^2 - \frac{4}{r_1} - \frac{4}{r_2} \quad (43)$$

$$H' = \frac{2}{r_{12}} \quad (44)$$

The unperturbed states corresponding to equation (40) are two hydrogenic wave functions

$$\psi = e^{-2(r_1 + r_2)} \quad (45)$$

The unperturbed ground state energy is $E^0 = -8 \text{ Ryd}$

The ground state energy of the perturbed state, according to the first-order perturbation theory, is

$$E = E_0 + \frac{\int \int \psi^* H' \psi d\vec{r}_1 d\vec{r}_2}{\int \int \psi^* \psi d\vec{r}_1 d\vec{r}_2} = E_0 - \frac{27}{4} (\alpha) = -5.5 \text{ Ryd} \quad (46)$$

This is quite a good approximation to the observed value, -5.81 Ryd ; the error being about 5%. It is not so good as the result of the variational method, however; which was to be expected, for ψ has

the same form as ϕ but not with the optimum value of α . The first-order energy correction in this case is 2.5 Ryd, which is by no means small – in other words, the Coulomb interaction is not a small perturbation.

2.2 First-order Perturbation Theory for a Degenerate State

Suppose the unperturbed state is doubly degenerated with two orthonormalized wavefunctions ψ_1 and ψ_2 .

Now, any function of the form

$$\psi = a_1 \psi_1 + a_2 \psi_2 \quad (47)$$

is also a wave function of the unperturbed system corresponding to the energy E^0 .

Under a first-order perturbation, we can write (assuming a_1 and a_2 are not perturbed):

$$(H^0 + H') (a_1 \psi_1 + a_2 \psi_2) = (E_0 + E') (a_1 \psi_1 + a_2 \psi_2) \quad (48)$$

This reduces to

$$(H' - E') (a_1 \psi_1 + a_2 \psi_2) = 0 \quad (49)$$

Multiplying both sides by ψ_1^* and ψ_2^* respectively, we obtain

$$\begin{aligned} a_1 (H_{11}' - E') + a_2 H_{12}' &= 0 \\ a_1 H_{21}' + a_2 (H_{22}' - E') &= 0 \end{aligned} \quad (50)$$

The secular determinant for the perturbation becomes

$$\begin{vmatrix} H_{11}' - E' & H_{12}' \\ H_{21}' & H_{22}' - E' \end{vmatrix} = 0 \quad (51)$$

which can also be written (why?)

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \quad (52)$$

In this case, the perturbation has split the doubly degenerate unperturbed level into two different levels, and we say that it has *removed the degeneracy*. On the other hand, the secular equation might have two equal roots, in which case, we say *the degeneracy is not removed to the first order by the perturbation*.

This method is valid for N-fold degenerate level. In this case we take the wavefunction to be

$$\psi = \sum_1^N a_i \phi_i \quad (53)$$

If written in terms of H and E, the secular equation for the perturbed state becomes

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22}-E & \cdots & H_{2N} \\ \vdots & \vdots & \cdots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN}-E \end{vmatrix} = 0 \quad (54)$$

Now, let us comment on the similarity between the secular equations for the variational method and the perturbation method.

The differences between the two methods:

- ψ is not arbitrarily chosen for the perturbation method..
- the variational method only applies to the lower level energies, whereas perturbation theories applies to all states of the system.

2.3 Generalized Time-independent Perturbation Theory

We will now show how second-order and higher-order perturbation corrections to the system may be obtained.

If we assume that all the energy levels E_i^0 of the unperturbed system are discrete, and the at the wavefunctions ψ_i form a complete orthonormal set, then we may express a wavefunction ψ of the perturbed system exactly in the form

$$\psi = \sum_i a_i \psi_i \quad (55)$$

The secular equation becomes

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22}-E & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33}-E & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} = 0 \quad (56)$$

There will be mathematical difficulties associated with the convergence of the infinite determinant. (But this will be ignored in this lecture).

If the perturbation term is exactly zero, the off-diagonal elements in equation (54) would vanish. The equation reduces to

$$\begin{vmatrix} H_{11}-E & 0 & 0 & \cdots \\ 0 & H_{22}-E & 0 & \cdots \\ 0 & 0 & H_{33}-E & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} = 0 \quad (57)$$

If fact, for non-degenerate states, we simply ignore all off-diagonal elements! This agrees with equation (40).

If we have a degenerate unperturbed state (e.g., $E_1^0 = E_2^0$), the off-diagonal elements CANNOT be

ignored (why?) Therefore, we keep the off-diagonal elements of those degenerate states

$$\begin{vmatrix} H_{11}-E & H_{12} & 0 & \cdots \\ H_{21} & H_{22}-E & 0 & \cdots \\ 0 & 0 & H_{33}-E & \cdots \\ \vdots & \vdots & & \vdots \end{vmatrix} = 0 \quad (58)$$

This agrees with equation (50). Here, we are not implying that the degenerate state(s) correspond to low energy levels. They can be blocks anywhere in the matrix!

Let us go back to the non-degenerate state, and talk about the second-order perturbation correction to the energy.

Suppose E_1^0 is non-degenerate, and we wish to find the perturbed level E_1 corresponding to it. Based on the result of the first-order approximation E_1 is H_{11} , so let us substitute every diagonal element of the determinant in equation (56) except the first, which we write $H_{11}-E_1$. We also want to remain all matrix elements involving ψ_1 (because ψ_1 is greatly perturbed now). Putting other off-diagonal elements zero, we have

$$\begin{vmatrix} H_{11}-E_1 & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22}-H_{11} & 0 & \cdots \\ H_{31} & 0 & H_{33}-H_{11} & \cdots \\ \vdots & \vdots & & \vdots \end{vmatrix} = 0 \quad (59)$$

After mathematical treatment, the non-diagonal element is gone, and the first element of the first row becomes

$$H_{11}-E_1 - \sum_{j=2}^{\infty} \frac{H_{1j}H_{j1}}{H_{jj}-H_{11}} \quad (60)$$

Expanding the determinant in terms of the first row gives

$$\left(H_{11}-E_1 - \sum_{j=2}^{\infty} \frac{H_{1j}H_{j1}}{H_{jj}-H_{11}} \right) (H_{22}-H_{11})(H_{33}-H_{11}) = 0 \quad (61)$$

Only the first factor can be zero. We therefore find

$$E_1 = H_{11} - \sum_{j=2}^{\infty} \frac{H_{1j}H_{j1}}{H_{jj}-H_{11}} \quad (62)$$

Also,

$$H_{jj}-H_{11} = E_j^0 - E_1^0 + H_{jj}' - H_{11}' \approx E_j^0 - E_1^0 \quad (63)$$

Hence,

$$E_1 = H_{11} - \sum_{j=2}^{\infty} \frac{H_{1j}H_{j1}}{E_j^0 - E_1^0} \quad (64)$$

The same formula holds for any other non-degenerate states

$$E_i = H_{ii} - \sum_{j \neq i} \frac{H_{ij} H_{ji}}{E_j^0 - E_i^0} \quad (65)$$

Due to the Hermiticity of H , equation (63) is equivalent to

$$E_i = H_{ii} - \sum_{j \neq i} \frac{|H_{ij}|^2}{E_j^0 - E_i^0} \quad (66)$$

Or

$$E_i = E_i^0 + H_{ii}' - \sum_{j \neq i} \frac{H_{ij} H_{ji}}{E_j^0 - E_i^0} \quad (67)$$

Q: What if the second-order perturbation method still fails?

PROBLEMS: (due Feb. 26, 2008)

1. Consider a particle of mass m moving in one-dimension under the influence of an attractive delta function potential located at the origin. $H = \frac{p^2}{2m} + \alpha \delta(x)$ (a) Use the variational principle

with the trial wave function $\psi = A e^{-b^2 x^2/2}$ to estimate the ground state energy for the particle.

(b) The exact solution of this problem yields the wave function $\psi = A' e^{-k|x|}$. Insert this expression into the Sch equation to determine the exact ground state energy and compare with the variational result. [Hint: You will need to integrate the Schrödinger equation about the origin to treat

the discontinuity in the derivative of ψ : $\lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} (H - E)\psi dx = 0$].

2. A particle of mass m is bound in a 3D radially symmetric potential well which is weakly anharmonic, $V(r) = k \frac{r^2}{2} + \epsilon r^4$.

(a) The ground state energy can be written as a power series $E_0 = \frac{3}{2} \hbar \omega + O(\epsilon) + O(\epsilon^2) + \dots$. Use first order perturbation theory to determine the $O(\epsilon)$ term exactly.

(b) The first order correction to the ground state wavefunction will mix the unperturbed $\psi_o^{(0)}(r)$ with a limited set of $\psi_n^{(0)}(r)$ unperturbed basis states. Which basis states are mixed at $O(\epsilon)$ in the perturbed $\psi_o^{(0)}(r)$ (Specify these using both the Cartesian (n_x, n_y, n_z) and the spherical (N, L, M) labels for the harmonic oscillator.)

(c) Now suppose we set $k=0$, so we have a pure ϵr^4 potential. Without attempting an explicit solution, show using a scaling argument that all the eigenenergies are proportional to ϵ^ν and find ν .