

PERTURBATION THEORY

Skip Degenerate Perturbation Theory, Sect. 9.5, 9.6, 9.7; Time-Dependent Perturbation Theory 9.9 & Interaction of Radiation with Matter, 9.10

Perturbation Theory is a method of approximation not limited to the ground state of a system. It is useful when we know a solution to a similar problem which we can use as a first approximation to the problem that must be solved. Let's say we want to solve the Schrödinger Eq.

$$H \psi_N = E_N \psi_N,$$

where N =state of the system; $N=0$, ground state; $N=1$, first excited state, etc.

Let's say we know the solution to a similar problem

$$H^0 \psi_N^0 = E_N^0 \psi_N^0,$$

where H^0 is very similar to H such that

$$H = H^0 + H^1,$$

where H^1 is small. Assume that:

H^0 is Hermitian

Its eigenfunctions, ψ_N^0 , are orthonormal.

We can use the ψ_N^0 to find the ψ_N .

Example: Harmonic Oscillator

One-dimensional *Anharmonic Oscillator* has

$$H = -\frac{\hbar^2}{2m} \{d^2/dx^2\} + k x^2/2 + c x^3 + d x^4$$

One-dimensional *Harmonic Oscillator* has

$$H^0 = -\frac{\hbar^2}{2m} \{d^2/dx^2\} + k x^2/2$$

If c & d are small, then the eigenfunctions & eigenvalues of the anharmonic oscillator must be closely related to those of the harmonic oscillator--which we know. But how can we use this information? We can expand the wavefunction & energy of the anharmonic oscillator in a Taylor series around the wavefunction & energy that we know.

Define the system with H^0 as the *unperturbed* system & the with H as the *perturbed* system.

$$H = H^0 + H^1$$

$$H^1 = H - H^0 = c x^3 + d x^4 \text{ for the anharmonic oscillator}$$

Introduce the parameter λ , the perturbation parameter. Essentially, λ is used for “bookkeeping”. The following is the use of perturbation theory for nondegenerate energy levels (degenerate levels will not be covered due to lack of time).

Let

ψ_N^0 = wavefunction of the unperturbed nondegenerate level N

E_N^0 = energy of the unperturbed nondegenerate level N

$\psi_N^0 \rightarrow \psi_N$ & $E_N^0 \rightarrow E_N$ when the perturbation is applied.

We want to solve

$$H \psi_N = (H^0 + \lambda H^1) \psi_N = E_N \psi_N$$

Since H depends on λ , E_N & ψ_N will too.

Expand ψ_N in a Taylor Series around ψ_N^0 (i.e. ψ_N evaluated at $\lambda = 0$, or $\psi_N |_{\lambda=0}$):

$$\begin{aligned} \psi_N &= \psi_N |_{\lambda=0} + (\partial \psi_N / \partial \lambda) |_{\lambda=0} \cdot \lambda + (\partial^2 \psi_N / \partial \lambda^2) |_{\lambda=0} \cdot \lambda^2 / 2! + \\ &\quad (\partial^3 \psi_N / \partial \lambda^3) |_{\lambda=0} \cdot \lambda^3 / 3! + \dots \\ &= \psi_N^0 + (\partial \psi_N / \partial \lambda) |_{\lambda=0} \cdot \lambda + (\partial^2 \psi_N / \partial \lambda^2) |_{\lambda=0} \cdot \lambda^2 / 2! + \\ &\quad (\partial^3 \psi_N / \partial \lambda^3) |_{\lambda=0} \cdot \lambda^3 / 3! + \dots \end{aligned}$$

Also expand E_N in a Taylor Series around E_N^0

$$\begin{aligned} E_N &= E_N |_{\lambda=0} + (\partial E_N / \partial \lambda) |_{\lambda=0} \cdot \lambda + (\partial^2 E_N / \partial \lambda^2) |_{\lambda=0} \cdot \lambda^2 / 2! + \\ &\quad (\partial^3 E_N / \partial \lambda^3) |_{\lambda=0} \cdot \lambda^3 / 3! + \dots \\ &= E_N^0 + (\partial E_N / \partial \lambda) |_{\lambda=0} \cdot \lambda + (\partial^2 E_N / \partial \lambda^2) |_{\lambda=0} \cdot \lambda^2 / 2! + \\ &\quad (\partial^3 E_N / \partial \lambda^3) |_{\lambda=0} \cdot \lambda^3 / 3! + \dots \end{aligned}$$

Define $\psi_N^k = (\partial^k \psi_N / \partial \lambda^k) |_{\lambda=0} / k!$

$$E_N^k = (\partial^k E_N / \partial \lambda^k) |_{\lambda=0} / k!$$

Then

$$\psi_N = \psi_N^0 + \lambda \psi_N^1 + \lambda^2 \psi_N^2 + \lambda^3 \psi_N^3 + \dots$$

$$E_N = E_N^0 + \lambda E_N^1 + \lambda^2 E_N^2 + \lambda^3 E_N^3 + \dots$$

Substitute these expansions into

$$H \psi_N = (H^0 + \lambda H^1) \psi_N = E_N \psi_N \rightarrow$$

$$(H^0 + \lambda H^1) (\psi_N^0 + \lambda \psi_N^1 + \lambda^2 \psi_N^2 + \lambda^3 \psi_N^3 + \dots)$$

$$= (E_N^0 + \lambda E_N^1 + \lambda^2 E_N^2 + \dots) (\psi_N^0 + \lambda \psi_N^1 + \lambda^2 \psi_N^2 + \dots)$$

Collect terms in λ :

$$H^0 \psi_N^0 + \lambda (H^0 \psi_N^1 + H^1 \psi_N^0) + \lambda^2 (H^0 \psi_N^2 + H^1 \psi_N^1) + \dots$$

$$= E_N^0 \psi_N^0 + \lambda (E_N^1 \psi_N^0 + E_N^0 \psi_N^1)$$

$$+ \lambda^2 (E_N^0 \psi_N^2 + E_N^1 \psi_N^1 + E_N^2 \psi_N^0) + \dots$$

If the left side equals the right side, then the left & right sides must be equal *for each power of λ* . This gives the Perturbation Eq.:

$$\lambda^0: \quad H^0 \psi_N^0 = E_N^0 \psi_N^0 \quad (1)$$

$$\lambda^1: \quad H^0 \psi_N^1 + H^1 \psi_N^0 = E_N^1 \psi_N^0 + E_N^0 \psi_N^1$$

$$(H^0 - E_N^0) \psi_N^1 = (E_N^1 - H^1) \psi_N^0 \quad (2)$$

$$\lambda^2: \quad H^0 \psi_N^2 + H^1 \psi_N^1 = E_N^0 \psi_N^2 + E_N^1 \psi_N^1 + E_N^2 \psi_N^0$$

$$(H^0 - E_N^0) \psi_N^2 = E_N^2 \psi_N^0 + (E_N^1 - H^1) \psi_N^1 \quad (3)$$

etc.

Eq. (1) is the Schrödinger Eq. for the unperturbed problem. We already know the solutions ψ_N^0 & E_N^0 . We can use these to

solve Eq. (2) for E_N^1 , the first order correction to the energy, & ψ_N^1 , the first order correction to the wavefunction. At this point, we will have improved our approximation to E_N :

$$E_N \approx E_N^0 + E_N^1, \lambda=1$$

$$\psi_N \approx \psi_N^0 + \psi_N^1, \lambda=1$$

Solve Eq. (2):

$$(H^0 - E_N^0) \psi_N^1 = (E_N^1 - H^1) \psi_N^0$$

Solve for E_N^1

Since H^0 is Hermitian, then the ψ_N^0 are a complete set. So we can expand the unknown ψ_N^1 in terms of the ψ_N^0 . Let

$$\psi_N^1 = \sum_j a_j \psi_j^0$$

$$\text{Then } (H^0 - E_N^0) \sum_j a_j \psi_j^0 = (E_N^1 - H^1) \psi_N^0$$

$$= \sum_j a_j (H^0 - E_N^0) \psi_j^0$$

$$= \sum_j a_j H^0 \psi_j^0 - \sum_j a_j E_N^0 \psi_j^0$$

$$\begin{aligned}
&= \sum_j a_j E_j^0 \psi_j^0 - \sum_j a_j E_N^0 \psi_j^0 \\
&= \sum_j a_j (E_j^0 - E_N^0) \psi_j^0 = (E_N^1 - H^1) \psi_N^0
\end{aligned}$$

We want to calculate E_N^1 . Multiply both sides by $(\psi_m^0)^*$ & integrate over the spatial coordinates:

$$\begin{aligned}
&\int (\psi_m^0)^* \sum_j a_j (E_j^0 - E_N^0) \psi_j^0 d\tau \\
&= \int (\psi_m^0)^* (E_N^1 - H^1) \psi_N^0 d\tau \\
&\sum_j a_j (E_j^0 - E_N^0) \int (\psi_m^0)^* \psi_j^0 d\tau \\
&= \int (\psi_m^0)^* E_N^1 \psi_N^0 d\tau - \int (\psi_m^0)^* H^1 \psi_N^0 d\tau \\
&\sum_j a_j (E_j^0 - E_N^0) \delta_{mj} = E_N^1 \delta_{mN} - \int (\psi_m^0)^* H^1 \psi_N^0 d\tau \\
&a_m (E_m^0 - E_N^0) = E_N^1 \delta_{mN} - H_{mN}^1
\end{aligned}$$

If $m=N$, we can calculate E_N^1 :

$$\begin{aligned}
0 &= E_N^1 - H_{NN}^1 \\
E_N^1 &= H_{NN}^1 \text{ (Note: Don't need } \psi_N^1 \text{ to get } E_N^1)
\end{aligned}$$

If m is not equal to N , we can calculate ψ_N^1 :

$$\begin{aligned}
a_m (E_m^0 - E_N^0) &= -H_{mN}^1 \\
a_m &= -H_{mN}^1 / (E_m^0 - E_N^0) = H_{mN}^1 / (E_N^0 - E_m^0)
\end{aligned}$$

Since $\psi_N^1 = \sum_j a_j \psi_j^0$

j

from the above we know the form of all the a_j 's except a_N . We can set $a_N = 0$. So

$$\psi_N^1 = \sum_{j \text{ not } = N} [H_{jN}^1 / (E_N^0 - E_j^0)] \psi_j^0$$

And

$$\begin{aligned} \psi_N &\approx \psi_N^0 + \psi_N^1, \lambda=1 \\ &\approx \psi_N^0 + \sum_{j \text{ not } = N} [H_{jN}^1 / (E_N^0 - E_j^0)] \psi_j^0 \end{aligned}$$

Solve for E_N^2

Expand ψ_N^2 in terms of the ψ_N^0

$$\psi_N^2 = \sum_j b_j \psi_j^0$$

Then $(H^0 - E_N^0) \psi_N^2 = E_N^2 \psi_N^0 + (E_N^1 - H^1) \psi_N^1$

becomes

$$\begin{aligned} (H^0 - E_N^0) \sum b_j \psi_j^0 &= E_N^2 \psi_N^0 + (E_N^1 - H^1) \psi_N^1 \\ &= \sum b_j (H^0 \psi_j^0 - E_N^0 \psi_j^0) \\ &= \sum b_j (E_j^0 \psi_j^0 - E_N^0 \psi_j^0) \\ &= \sum b_j (E_j^0 - E_N^0) \psi_j^0 \end{aligned}$$

Multiply both sides by $(\psi_m^0)^*$ & integrate over the spatial coordinates:

$$\int (\psi_m^0)^* \sum b_j (E_j^0 - E_N^0) \psi_j^0 d\tau$$

$$= E_N^2 \int (\psi_m^0)^* \psi_N^0 d\tau + \int (\psi_m^0)^* (E_N^1 - H^1) \psi_N^1 d\tau$$

The Σ below stands for the sum over j:

$$\begin{aligned} \Sigma b_j (E_j^0 - E_N^0) \int (\psi_m^0)^* \psi_j^0 d\tau \\ = E_N^2 \int (\psi_m^0)^* \psi_N^0 d\tau + E_N^1 \int (\psi_m^0)^* \psi_N^1 d\tau \\ - \int (\psi_m^0)^* H^1 \psi_N^1 d\tau \end{aligned}$$

$$\begin{aligned} \Sigma b_j (E_j^0 - E_N^0) \delta_{mj} \\ = E_N^2 \delta_{mN} + E_N^1 \int (\psi_m^0)^* \psi_N^1 d\tau - \int (\psi_m^0)^* H^1 \psi_N^1 d\tau \end{aligned}$$

$$\begin{aligned} b_m (E_m^0 - E_N^0) \\ = E_N^2 \delta_{mN} + E_N^1 \int (\psi_m^0)^* \psi_N^1 d\tau - \int (\psi_m^0)^* H^1 \psi_N^1 d\tau \end{aligned}$$

If $m=N$, we can calculate E_N^2 :

$$E_N^2 = E_N^1 \int (\psi_N^0)^* \psi_N^1 d\tau + \int (\psi_N^0)^* H^1 \psi_N^1 d\tau$$

Note: to get the second order correction to the energy we only need to know the first order correction to the wavefunction. In general, we can calculate E_N^{2k+1} from knowing ψ_N^k

Can we simplify E_N^2 ? We must evaluate $\int (\psi_N^0)^* \psi_N^1 d\tau$. But

$$\psi_N^1 = \sum_{j \text{ not equal to } N} a_j \psi_j^0$$

and $a_j = H_{jN}^1 / (E_N^0 - E_j^0)$, $a_N = 0$.

The Σ below stands for the sum over j not equal to N:

$$\begin{aligned}
\text{So } \int (\psi_N^0)^* \psi_N^1 d\tau &= \int (\psi_N^0)^* \sum a_j \psi_j^0 d\tau \\
&= \sum a_j \int (\psi_N^0)^* \psi_j^0 d\tau \\
&= \sum a_j \delta_{Nj} \\
&= 0 \text{ since } j \text{ cannot be equal to } N.
\end{aligned}$$

Therefore

$$E_N^2 = \int (\psi_N^0)^* H^1 \psi_N^1 d\tau$$

Using the definition of ψ_N^1

$$E_N^2 = \int (\psi_N^0)^* H^1 \sum a_j \psi_j^0 d\tau$$

$$E_N = E_N^0 + H_{NN}^1 + \sum_{j \text{ not equal to } N} |H_{jN}^1|^2 / (E_N^0 - E_j^0)$$

We could continue in the same method as above (Rayleigh-Schrödinger Perturbation Theory) to higher order of perturbation. But how do you know when to stop? Does the perturbation series converge? Expect $|E_N^0| > |E_N^1| > |E_N^2| > \dots$

What does the perturbation procedure actually do?

Since ψ_N^1 is expanded in terms of ψ_j^0 for k not equal to N , the effect of the procedure is to add into first order those states from the complete set that were left out of zeroth order. But they aren't added in with equal weight to that of ψ_N^0 (i.e. 1), but rather with weight a_j . Since

$$a_j \propto 1/(E_N^0 - E_j^0)$$

the terms which have E_j^0 close to E_N^0 will cause $1/(E_N^0 - E_j^0)$ to be large & therefore result in a larger contribution from the states close to N .

Practical Considerations:

(1) E_N^1 is easy to evaluate since only ψ_N^0 is used in

$$H_{NN}^1 = \int (\psi_N^0)^* H^1 \psi_N^0 d\tau$$

(2) E_N^2 is difficult to evaluate because you would need the complete set of ψ_j^0 (except $j=N$). This is an infinite number of terms! If you have a Hamiltonian that supports both discrete & continuous states, as with the hydrogen atom, then you must include not only the sum over all discrete states, but the integral over all the continuous states, as well. This is impossible to do

exactly. Instead you could use a combination variation-perturbation treatment.

Perturbation Treatment of the Ground State of He (we will also do a Variation treatment)

He has 2 protons & 2 electrons. The nucleus has a charge of +2e & each electron has a charge of -e. Electrons are indistinguishable particles, but we will number them to keep track of them. Electron #1 is at distance r_1 from the nucleus; Electron #2 is at distance r_2 from the nucleus. The distance between the two electrons is r_{12} . Let us set up the problem to treat a general two-electron ion by using a nuclear charge of +Ze. Then

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z(e')}{r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z(e')}{r_2} + \frac{(e')}{r_{12}}$$

In spherical polar coordinates

$$\psi = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

$$r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$$

Let H_1^0 be the hydrogen-like Hamiltonian for electron #1; Let H_2^0 be the hydrogen-like Hamiltonian for electron #2:

$$H_1^0 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z(e')}{r_1}; E_1 = -(Z^2/N_1^2)(e')^2/(2a_0)$$

$$H_2^0 = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z(e')}{r_2}; E_2 = -(Z^2/N_2^2)(e')^2/(2a_0)$$

where

$$H_1^0 F_1(r_1, \theta_1, \phi_1) = E_1 F_1(r_1, \theta_1, \phi_1)$$

$$H_2^0 F_2(r_2, \theta_2, \phi_2) = E_2 F_2(r_2, \theta_2, \phi_2)$$

and F_1 & F_2 are the hydrogen-like wavefunctions & E_1 & E_2 are the hydrogen-like energies.

Define $H^0 = H_1^0 + H_2^0$.

If the Hamiltonian is a sum of two Hamiltonians, then the wavefunction is a product of their eigenfunctions:

$$\psi^0(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = F_1(r_1, \theta_1, \phi_1) F_2(r_2, \theta_2, \phi_2)$$

Then

$$\begin{aligned} H^0 \psi^0 &= (H_1^0 + H_2^0) F_1 F_2 \\ &= F_2 H_1^0 F_1 + F_1 H_2^0 F_2 \\ &= F_2 E_1 F_1 + F_1 E_2 F_2 \\ &= (E_1 + E_2) F_1 F_2 \\ &= E^0 \psi^0, E^0 = E_1 + E_2 = -(Ze')^2 / (2a_0) (1/N_1^2 + 1/N_2^2) \end{aligned}$$

The assumption in this choice of H^0 is that the two electrons exert no repulsive force on each other (i.e. they operate as independent particles). This is not physically correct, but can be used as a first approximation.

In the ground state of helium, both electrons are in the 1s orbit, but have opposite spins. Indicate the electronic configuration by $1s^2$. So the zeroth-order approximation to the ground state wavefunction can be given

$$\psi_{1s^2}^0 = F_1 F_2$$

$$F_1 = 1/\sqrt{\pi} (Z/a_0)^{3/2} e^{-Zr_1/a_0}$$

$$F_2 = 1/\sqrt{\pi} (Z/a_0)^{3/2} e^{-Zr_2/a_0}$$

$$E_{1s^2}^0 = -(Ze')^2 / (2a_0)(1/r_1^2 + 1/r_2^2)$$

$$= -[(Ze')^2 / (2a_0)](2); \quad (e')^2 / (2a_0) = 13.6 \text{ eV}$$

$$= - (4) (2) (13.6\text{eV}) \text{ for He}$$

$$= -108.8\text{eV} \quad \text{for He.}$$

How does this compare to the actual ground state energy of He?

He has $E = 0$ when both electrons have been ionized, So

$$E_{\text{true}} = -(\text{IP}^1 + \text{IP}^2); \text{ IP} = \text{ionization potential}$$

$$= - (24.6 \text{ eV} + 54.4 \text{ eV}) = -79.0 \text{ eV}$$

So -108.8 eV is off by 38%! This is not unexpected because the perturbation

$$H^1 = H - H^0 = (e')^2 / r_{12}$$

is not necessarily small. When r_1 is close to r_2 , $(e')^2 / r_{12}$ is large.

Let's see what improvement we can get by calculating E^1 :

$$E^1 = \langle \psi^0 | H^1 | \psi^0 \rangle$$

$$= Z^6 (e')^2 / (\pi^2 a_0^6) \int_0^\infty \int_0^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} r_1^2 r_2^2 e^{-Zr_1/a_0} e^{-Zr_2/a_0} (1/r_{12})$$

$$\cdot \sin \theta_1 \sin \theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2$$

$1/r_{12}$ can be expanded in terms of r_1 & r_2 & the Spherical Harmonics, $Y_l^m(\theta, \phi)$:

$$1/r_{12} = \sum_l \sum_m [4\pi/(2l+1)] (r_{<}^l / r_{>}^{l+1}) [Y_l^m(\theta_1, \phi_1)]^* [Y_l^m(\theta_2, \phi_2)],$$

where $r_{<}$ is the smaller of r_1 & r_2 & $r_{>}$ is the larger of r_1 & r_2 . Skim through the details of how the integral is done (p. 230-231). The result is

$$\begin{aligned} E^1 &= (5Z/8) (e')^2/a_0 \\ &= (5Z/4) (e')^2/(2a_0) \\ &= (5 \times 2/4) (13.6 \text{ eV}) \\ &= 34.0 \text{ eV} \end{aligned}$$

$$\text{So } E^0 + E^1 = -108.8 \text{ eV} + 34.0 \text{ eV} = -74.8 \text{ eV}$$

Compared to -79.0 eV, this is in error by only 5.3%.

It is impossible to calculate all the contributions to E^2 from the discrete & continuum states. Other combinations of F_1 & F_2 are $F_1 = 1s, F_2 = 2s, 2p, 3s, 3p, \dots$; $F_1 = 2s, F_2 = 2s, 2p, 3s, 3p, \dots$, etc. ψ^1 is a sum over all these discrete states, as well as the integral over all the continuum states. Since ψ^1 contains configurations other than $1s^2$, this is called *Configuration Interaction*.

However, we can get an accurate E^2 by the Variation Method. Hylleraas has shown that

$$I \geq E^2$$

for I defined as

$$I = \int (\phi^1)^* (H^0 - E^0) \phi^1 d\tau + \int (\phi^1)^* (H^1 - E^1) \psi^0 d\tau \\ + \int (\psi^0)^* (H^1 - E^1) \phi^1 d\tau$$

where ϕ^1 is a trial function for ψ^1 . (Note: If $\phi^1 = \psi^1$, then the first two terms cancel since

$$(H^0 - E^0) \psi^1 = -(H^1 - E^1) \psi^0.$$

$$\text{If } \phi^1 = \psi^1, \text{ then } I = \int (\psi^0)^* (H^1 - E^1) \psi^1 d\tau \\ = \int (\psi^0)^* [E^2 \psi^0 - (H^0 - E^0) \psi^2] d\tau \\ = E^2 \int (\psi^0)^* \psi^0 d\tau = E^2$$

So choose a trial function ϕ^1 with several variable parameters & minimize I with respect to these parameters so as to approximate E^2 .

Scherr & Knight used 100 variables in their trial function & calculated

$$E^2 = -4.3 \text{ eV} \quad \& \quad E^3 = 0.1 \text{ eV}$$

$$\text{Then } E \approx (-108.8 + 34.0 - 4.3 + 0.1) \text{ eV} = -79.0 \text{ eV}$$

The series is converging because $|E^n|$ decreases as n increases.

To 13th order in perturbation, $E \approx -2.903\,724\,33 (e')^2/a_0$;

From a variational calculation, $E \approx -2.903\,724\,38 (e')^2/a_0$.

Comparison of Variation & Perturbation Methods:

Let's compare the variation & perturbation methods: Actually we would get the same energy correct through first order if we

used the ground state wavefunction as the trial function. Show that this is true:

Perturbation Method:

Let $H = H^0 + H^1$ & $H^0 \psi_g^0 = E_g^0 \psi_g^0$; $g =$ ground state

Define $E_g = E_g^0 + E_g^1$ (truncate energy at first order)

$$E_g^1 = \langle \psi_g^0 | H^1 | \psi_g^0 \rangle$$

Variation Method:

$$I = \langle \phi | H | \phi \rangle \geq E_g$$

$$\text{If } \phi = \psi_g^0, \text{ then } I = \langle \psi_g^0 | H | \psi_g^0 \rangle$$

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

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

$$= \langle \psi_g^0 | E_g^0 | \psi_g^0 \rangle + \langle \psi_g^0 | H^1 | \psi_g^0 \rangle$$

$$= E_g^0 \langle \psi_g^0 | \psi_g^0 \rangle + \langle \psi_g^0 | H^1 | \psi_g^0 \rangle$$

$$= E_g^0 + E_g^1$$

So the perturbation & variation methods give the same result through first order if the true ground state wavefunction happens to be used as the trial function.

Variation Treatment of the Ground State of Helium

Let's compare results (energy) for different choices of trial function.

Choice (I): We saw above that if $\psi_g^0 = \psi_{1s^2}$

$$= 1/\sqrt{\pi} (Z/a_0)^{3/2} e^{-Zr_1/a_0} \quad 1/\sqrt{\pi} (Z/a_0)^{3/2} e^{-Zr_2/a_0}$$

then the energy is -74.8 eV

Choice (II): Try making the trial function more flexible by replacing the atomic number, Z , by a variational parameter, ρ . This allows for the screening of the nuclear charge by the other

electrons. (Full nuclear charge corresponds to $\rho=2$; full screening, $\rho=2-1=1$)

Optimize I with respect to ρ , the effective nuclear charge.

$$I = \langle \phi | H | \phi \rangle$$

Choose $\phi = f_1 f_2$

where $f_1 = 1/\sqrt{\pi} (\rho/a_0)^{3/2} e^{-\rho r_1/a_0}$

$$f_2 = 1/\sqrt{\pi} (\rho/a_0)^{3/2} e^{-\rho r_2/a_0}$$

and $[-\hbar^2/(2m) \nabla_1^2 - \rho (e')^2/r_1]f_1 = -\rho^2(e')^2/(2a_0) f_1$

$$[-\hbar^2/(2m) \nabla_2^2 - \rho (e')^2/r_2]f_2 = -\rho^2(e')^2/(2a_0) f_2$$

We can simplify the calculation if we write H to contain the Hamiltonians for these eigenfunctions. We must add & subtract terms in ρ so that we still have the He atom Hamiltonian.

$$\begin{aligned} H &= -\hbar^2/(2m) \nabla_1^2 - Z(e')^2/r_1 - \hbar^2/(2m) \nabla_2^2 - Z(e')^2/r_2 + (e')^2/r_{12} \\ &= [-\hbar^2/(2m) \nabla_1^2 - \rho (e')^2/r_1] + [-\hbar^2/(2m) \nabla_2^2 - \rho (e')^2/r_2] \\ &\quad + (\rho - Z) (e')^2/r_1 + (\rho - Z) (e')^2/r_2 + (e')^2/r_{12} \end{aligned}$$

Then $H \phi = H f_1 f_2$

$$\begin{aligned} &= f_2 [-\hbar^2/(2m) \nabla_1^2 - \rho (e')^2/r_1] f_1 + f_1 [-\hbar^2/(2m) \nabla_2^2 - \rho (e')^2/r_2] f_2 \\ &\quad + \{(\rho - Z) (e')^2/r_1 + (\rho - Z) (e')^2/r_2 + (e')^2/r_{12}\} f_1 f_2 \end{aligned}$$

Skim through the details of the integration, which shows that

$$I = \langle \phi | H | \phi \rangle = (\rho^2 - 2Z\rho + 5\rho/8) (e')^2/a_0$$

$$\partial I/\partial \rho = 0 \rightarrow 2\rho - 2Z + 5/8 = 0 \rightarrow \rho = Z - 5/16$$

Since $Z \geq \rho \geq Z-1$, ρ is a screening parameter.

Evaluate I with this value of ρ to get the energy:

$$I = [(Z - 5/16)^2 - 2Z(Z - 5/16) + 5(Z - 5/16)/8] (e')^2/a_0$$

$$= -77.7 \text{ eV for } Z=2 \text{ (1.9\% error)}$$

(Remember (I) with $Z-2$ was in error by 5.3% when no ρ was used.)

Choice (III): Let $\phi = g(1) g(2)$. No matter what the choice of g is, we can't get the energy to be closer than 1.4% from the exact energy because ϕ has the wrong functional form. In He, the electrons are not truly independent because of the $1/r_{12}$ term. Therefore, the Schrödinger Eq. is not really separable.

Choice IV: Use a function that depends on r_{12} ; allows electron motion to be correlated.

$$\text{Hylleraas: } \phi = N[e^{-\rho r_1/a_0} e^{-\rho r_2/a_0} (1 + b r_{12})]$$

Vary ρ, b to get $\rho = 1.849$, $b = 0.364$, $I = -78.7 \text{ eV}$ (off by 0.3 eV)

Choice V: Allow even more flexibility; Hylleraas:

$$\phi = e^{-\rho r_1/a_0} e^{-\rho r_2/a_0} \sum_{i,j,k} c_{ijk} (r_1 + r_2)^i (r_1 - r_2)^j r_{12}^k$$

Results in I off by only 0.01 eV

Choice VI: Same as V, but more terms (1,078 terms- Pekeris)

$$I = -2.903\ 724\ 375 (e')^2/a_0 \rightarrow$$

$$\text{Ionization energy} = 198\ 310.69\ \text{cm}^{-1}$$

$$\text{Experimental ionization energy} = 198\ 310.82\ \text{cm}^{-1}$$

Very good agreement.

SUMMARY OF METHODS:

<u>Variation Method</u>	<u>Perturbation Theory</u>
Applicable to ground & first few excited states	Applicable to all states
Easy to evaluate integrals because have chosen the form of the trial function	Hard to evaluate infinite sums over discrete states & integrals over continuum states necessary to the evaluation of second & higher-order corrections
A poor trial function can give an accurate energy	$\psi^k \rightarrow E^{2k+1}$
Other properties are not calculated with the same accuracy as the energy	Other properties are not calculated with the same accuracy as the energy