Lecture 11

Variational Method

Theorem 1

$\langle \psi | H | \psi \rangle \geq E_0$

$\langle \psi | H | \psi \rangle = E_0 \Rightarrow H|\psi\rangle = E_0|\psi\rangle$

Theorem 2

$P = P^+ = P^2$

Solve $PHP|\chi_n\rangle = \tilde{E}_n|\chi_n\rangle \Rightarrow$

$\tilde{E}_n \geq E_n \quad n = 1 \cdots \dim(P)$

$\tilde{E}_n = E_n \quad H|\chi_n\rangle = E_n|\chi_n\rangle$

Application: Hydrogen atom ground state

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right) - \frac{Ze^2}{r}$$

(radial equation)

Step 1 - choose a variational wave function

$$\tilde{\psi}(r) = N e^{-\alpha r} Y_0^0(\theta\phi)$$

where in this example α is the variational parameter. The normalization constant is a function of α chosen so

$$1 = N^2 \int_0^\infty r^2 \left(e^{-\alpha r}\right)^2 dr$$

$$= N^2 \int_0^\infty r^2 e^{-2\alpha r} dr$$

For this problem it will be necessary to compute integrals of the general form

$$\int_0^\infty r^n e^{-2\alpha r}\, dr = \qquad \left(\text{let } u = 2\alpha r \quad r = \frac{u}{2\alpha} \quad dr = \frac{du}{2\alpha}\right.$$

$$\frac{1}{(2\alpha)^{n+1}} \int_0^\infty u^n du = \frac{1}{(2\alpha)^{n+1}} \Gamma(n+1)$$

where $\Gamma(z+1) = z\,\Gamma(z)$ $\quad \Gamma(n+1) = n!$

$$\therefore \int_0^\infty r^n e^{-2\alpha r}\, dr = \frac{n!}{(2\alpha)^{n+1}}$$

($\Gamma(z)$ is called the Gamma function of factorial function)

We use this to compute the normalization constant

$$1 = N^2 \int_0^\infty r^2 e^{-2\alpha r}\, dr = \frac{1}{(2\alpha)^3}\, 2!$$

$$N = \frac{(2\alpha)^{3/2}}{\sqrt{2}} = 2\alpha^{3/2}$$

$$\psi(r) = 2\alpha^{3/2} e^{-\alpha r}$$

This ensures that the correct normalization is maintained for different values of α.

Step 2 Compute

$$\langle \psi(\alpha) | H | \psi(\alpha) \rangle =$$

$$N^2 \int_0^\infty r^2 e^{-\alpha r} \left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} \right) - \frac{Ze^2}{r} \right] e^{-\alpha r}$$

* $\frac{d^2}{dr^2} e^{-\alpha r} = \alpha^2 e^{-\alpha r}$

* $\frac{2}{r}\frac{d}{dr} e^{-\alpha r} = -2\alpha \frac{1}{r} e^{-\alpha r}$

* $N^2 = 4\alpha^3$

This gives $\langle \psi(\alpha) | H | \psi(\alpha) \rangle =$

$$4\alpha^3 \int_0^\infty e^{-2\alpha r} \left\{ -\frac{\hbar^2 \alpha^2}{2\mu} r^2 + \frac{\hbar^2}{2\mu} 2\alpha r + \frac{\hbar^2}{2\mu} \ell(\ell+1) - Ze^2 r \right\} dr =$$

using the gamma function

$$= 4\alpha^3\left(-\frac{\hbar^2\alpha^2}{2\mu}\frac{2!}{(2\alpha)^3} + \frac{\hbar^2\alpha}{\mu}\frac{1}{(2\alpha)^2} + \frac{\hbar^2}{2\mu}\ell(\ell+1)\frac{1}{2\alpha} - \frac{Ze^2}{(2\alpha)^2}\right)$$

$$= -\frac{1}{2}\frac{\hbar^2}{\mu}\alpha^2 + \frac{\hbar^2}{\mu}\alpha^2 + \frac{\hbar^2}{\mu}\alpha^2\ell(\ell+1) - Ze^2\alpha$$

$$= \frac{\hbar^2\alpha^2}{\mu}\left(\frac{1}{2} + \ell(\ell+1)\right) - Ze^2\alpha$$

step 3 - determine which values of α minimize

$\langle\psi(\alpha)|H|\psi(\alpha)\rangle$

$$0 = \frac{d}{d\alpha}\left[\frac{\hbar^2\alpha^2}{\mu}\left(\frac{1}{2} + \ell(\ell+1)\right) - Ze^2\alpha\right]$$

$$= \frac{2\hbar^2\alpha}{\mu}\left(\frac{1}{2} + \ell(\ell+1)\right) - Ze^2$$

solving for $\alpha_{min} \equiv \alpha^*$ gives

$$\alpha^* = \frac{Ze^2\mu}{2\hbar^2}\left(\frac{1}{\frac{1}{2} + \ell(\ell+1)}\right)$$

* check that α^* minimizes the function

$$\frac{d^2}{d\alpha^2}\langle\psi(\alpha)|H|\psi(\alpha)\rangle = \frac{2\hbar^2\alpha^*}{\mu}\left(\frac{1}{2} + \ell(\ell+1)\right)$$

$$= \frac{2\hbar^2}{\mu}\left(\frac{1}{2}+\ell(\ell+1)\right)\frac{Ze^2\mu}{2\hbar^2}\frac{1}{\left(\frac{1}{2}+\ell(\ell+1)\right)}$$

$$= Ze^2 > 0$$

so $\langle\psi(\alpha)|H|\psi(\alpha)\rangle$ is minimized when $\alpha=\alpha^*$.

step 3 : Substitute α^* in the variational wave function and $\langle\psi(\alpha)|H|\psi(\alpha)\rangle$ to get the approximate wave function and ground state energy

$$\langle\psi(\alpha)|H|\psi(\alpha)\rangle =$$

$$\frac{\hbar^2\alpha^2}{\mu}\left(\frac{1}{2}+\ell(\ell+1)\right) - Ze^2\alpha =$$

$$\frac{\hbar^2}{\mu}\frac{Z^2e^4\mu^2}{4\hbar^4}\frac{1}{\left(\frac{1}{2}+\ell(\ell+1)\right)} - \frac{(Ze^2)^2}{2\hbar^2}\frac{\mu}{\left(\frac{1}{2}+\ell(\ell+1)\right)} =$$

$$\frac{Z^2e^4\mu}{\hbar^2}\left(\frac{1}{4}-\frac{1}{2}\right)\frac{1}{\frac{1}{2}+\ell(\ell+1)} =$$

$$= -\frac{Z^2 e^4 \mu}{4\hbar^2}\frac{1}{\left(\frac{1}{2}+\ell(\ell+1)\right)} =$$

$$= -\frac{Z^2 e^4 \mu}{2\hbar^2}\frac{1}{(1+2\ell(\ell+1)}$$

Note that this is exact Hydrogen ($Z=1$ $\ell=0$) binding energy for $\ell=0$

When $\ell \neq 0$ this is just an upper bound on the exact binding energy

Since the $\ell=0$ case gives the exact binding energy the exact wave function is

$$\psi(\vec{r}) = 2\alpha^{*3/2} e^{-\alpha^* r} Y_0^0(\theta\phi) =$$

$$\frac{2}{\sqrt{4\pi}}\left(\frac{Ze^2\mu}{\hbar^2}\right)^{3/2} e^{-\frac{Ze^2\mu}{\hbar^2}r}$$

Application 2:

Multielectron atoms - the central field approximation

Assume that the kinetic energy of the nucleus can be ignored. Then the Hamiltonian has the form

$$H = \sum_{n=1}^{N} \left(-\frac{\hbar^2}{2m_e} \nabla_n^2 - \frac{Ze^2}{r_n} \right) + \sum_{m<n} \frac{e^2}{|r_m - r_n|}$$

This is a complex N particle problem because of the interactions between the electrons.

We will treat this using the variational principle

We use a trial wave function that is a product of N single electron wave functions (for a realistic calculation this should be an antisymmetrized product, but in this illustration I will treat the electrons as distinguishable

$$\Psi(\vec{r}_1 \cdots \vec{r}_N) = \phi_1(\vec{r}_1) \cdots \phi_N(\vec{r}_N)$$

The variational problem is to find the best choice of single particle wave functions that minimize the binding energy

In this case the variations parameters are functions

* assume $\phi_k^0(\vec{r}_k)$ is the single particle wave function that minimizes the binding energy

* consider $\phi_k(r_k) = \phi_k^0(r_k) + \delta\phi_k(\vec{r}_k)$

  It is useful to introduce a parameter η

$$\phi_k(r_k) = \phi_k^0(r_k) + \eta\,\delta\phi_k(r_k)$$

We define

$$F[\eta] = \sum_{n=1}^{N} \int \phi_n^*(\vec{r}_n)\left(-\frac{\hbar^2}{2m}\nabla_n^2\right)\phi_n(\vec{r}_n)\,d^3r_n$$

$$+ \sum_{n=1}^{N} \int \phi_n^*(\vec{r}_n)\,\frac{Ze^2}{r_n}\,\phi_n(\vec{r}_n)\,d^3r_n$$

$$- \frac{1}{2}\sum_{m\neq n} \int \phi_n^*(\vec{r}_n)\,\phi_m^*(\vec{r}_m)\,\frac{e^2}{|\vec{r}_m - \vec{r}_n|}\,\phi_m(\vec{r}_m)\,\phi_n(\vec{r}_n)$$

$$- \lambda \sum_n \left(\int \phi_n^*(\vec{r}_n)\,\phi_n(\vec{r}_n)\,d^3r_n - 1\right) d^3r_m\,d^3r_n$$

here λ is a Lagrange multiplier like we use in mechanics. It will be chosen so the single particle wavefunctions are normalized to 1.

* use $\phi = \phi_0 + \lambda \delta\phi - \delta\phi$ represents a displacement in an ∞ dimensional space. — $\lambda = 0$ represents the critical value of ϕ in the $\delta\phi$ direction ⇒ Local minimum ⇒

$$\frac{d}{d\lambda} F[\,]\Big|_{\lambda=0} = 0$$

$$\frac{d^2F}{d\lambda^2}[\,]\Big|_{\lambda=0} \geq \text{positive quadratic form}$$

The first equation will give an equation for ϕ_0 - unfortunately it is non linear. To derive the desired equation

$$\frac{d}{d\lambda} F = 0 =$$

$$\frac{d}{d\lambda} \Bigg\{ \int \sum_{m=1}^{N} \left(\phi_m^{0*}(r_m) + \lambda \delta \phi^{*}(r_m) \right) \left(-\frac{\hbar^2}{2m} \nabla_m^2 \right)^{*} \left(\phi_m^{0}(r_m) + \lambda \delta \phi_m(r_m) \right) d^3 r_m +$$

$$- \int \sum_{n} \left(\phi_m^{0*}(r_m) + \lambda \delta \phi_m^{*}(r_m) \right) \frac{Ze^2}{r_m} \left(\phi_m^{0}(r_m) + \lambda \delta \phi_m(r_m) \right) d^3 r_n +$$

$$+ \frac{1}{2} \int \sum_{m \neq n} \left(\phi_{m}^{0}(r_m) + \lambda \delta \phi_m(r_m) \right) \left(\phi_n^{0}(r_n) + \lambda \delta \phi_n(r_n) \right) \frac{e^2}{|r_m - r_n|} \left(\phi_m(r_m) + \lambda \delta \phi_m(r_m) \right) \left(\phi_n(r_n) + \lambda \delta \phi_n(r_n) \right)$$

$$- \lambda \sum \int \left(\phi_m^{*}(r_m) + \lambda \delta \phi_m^{*}(r_m) \right) \left(\phi_m(r_m) + \lambda \delta \phi_m(r_m) \right) \Bigg\}$$

$$\lambda = 0$$

rather that treat λ as complex we get 2 equations - one treating λ as real and one treating λ as pure imaginary. We use the chain rule to calculate the derivatives

$$0 = \sum_{m=1}^{n} \int \pm \delta\phi_m^*(r_m)\left(-\frac{\hbar^2}{2m}\nabla_m^2 - \frac{e^2}{r_m}\right)\phi_m^0(r_m)\,dr$$

$$\sum_{m=1}^{n} \int \phi_m^{0*}(r_m)\left(-\frac{\hbar^2}{2m}\nabla_m^2 - \frac{e^2}{r_m}\right)\delta\phi_m(r_m)\,dr$$

$$\frac{1}{2}\sum_{m\neq n}\int\left(\pm\,\delta\phi_m^*(r_m)\phi_n^0(r_n) \pm \phi_m^{0*}(r_m)\,\delta\phi_n^*(r_n)\right)$$

$$\frac{e^2}{r_m - r_n}\left(\phi_m^0(r_m)\phi_n^0(r_n)\right)d^3r_m\,d^3r_n +$$

$$\frac{1}{2}\sum_{m\in n}\int\left[\phi_m^{0*}(r_m)\,\phi_n^{0*}(r_n)\,\frac{e^2}{|r_m - r_n|}\right.$$

$$\left.\left(\delta\phi_m(r_m)\phi_n^0(r_n) + \phi_m^0(r_m)\,\delta\phi_n(r_n)\right)\right]d^3r_m d^3r_n$$

$$-\lambda\sum_m\int\left(\phi_m^{0*}(r_m)\,\delta\phi_m(r_m) \pm \phi_m^*(r_m)\,\phi_m^0(r_m)\right)$$

$$\times\, d^3r_m = 0$$

adding and subtracting the equations and assuming the $\delta\phi(r)$ terms are arbitrary give the following equation

$$-\frac{\hbar^2}{2m}\nabla^2\phi_m^{\cdot}(r_m) - \frac{Ze^2}{r_m}\phi_m^{\cdot}(r_m) + e^2 2\sum_{n\neq m}\phi_m^{\circ}(r_m)\int \phi_n^{\cdot *}(r_n)\frac{d^3r_n}{|r_m - r_n|}\phi_n^{\circ}(r_n) - \lambda\phi_m^{\circ}(r_m)$$

with a similar equation for the complex conj $\phi_m^{\cdot *}(r_m)$ which is just the complex conjugate of this equation

This is a set of coupled non linear equations in the ϕ_m

To determine the lagrange multiplier multiply by $\phi_m^*(r)$, integrate and set the integral to 1. Then

$$\langle \phi_m | \hat{Q}_m | \phi_m \rangle = \lambda (\phi_m, \phi_m) = \lambda$$

This means that λ

$$\hat{Q}_m | \phi_m \rangle = \lambda | \phi_m \rangle$$

In order to proceed we try to solve this by iteration.

step 1 Ignore the interactions between the individual electrons

⇒ In this case the possible solutions are the solutions for single electron atoms

(in the symmetric case they are all in the ground state — for fermions we use the solutions $(\phi_m^1(r_n))$ with the N lowest eigenvalues)

<u>The next approximation</u> is to use Hydrogen atom solutions to construct

$$V(r) = \sum_{m \neq n} \int \frac{e^2}{|r_m - r_1|} \phi_m^{i*}(r_m)\, \phi_m^i(r_m)\, d^3 r_m$$

with the approximation

the equations for $\phi_n^0(r)$

$$\left(-\frac{\hbar^2}{2m} - \frac{Ze^2}{r} + V(r)\right)\phi_n^0(r) = \lambda\phi_n^0(r)$$

This is just a one electron Schrodinger equation interacting with the nucleus and the average field due to the other electrons

<u>step 2</u> These solutions can be used to construct an improved mean field calculation and the process can be repeated as needed.

Galerkin Method

Consider the eigenvalue problem

$$H|\Psi\rangle = E|\Psi\rangle$$

Let $\{|\phi_m\rangle\}_{m=1}^{\infty}$ be a orthonormal basis

$$\langle\phi_m|\phi_n\rangle = \delta_{mn}$$

$$|\Psi\rangle = \sum_n |\phi_n\rangle\langle\phi_n|\Psi\rangle$$

combining gives

$$\sum_n H|\phi_n\rangle\langle\phi_n|\Psi\rangle = E\sum_n |\phi_n\rangle\langle\phi_n|\Psi\rangle$$

multiply by $\langle\phi_m|$

$$\sum_n \underbrace{\langle\phi_m|H|\phi_n\rangle}_{H_{mn}}\underbrace{\langle\phi_n|\Psi\rangle}_{c_n} = E\langle\phi_m|\Psi\rangle$$

In matrix form this equation becomes

$$\sum_n H_{mn} C_n = E C_m$$

This equation is exact, however the matrix and vectors are infinite dimensional.

To use this with a computer - if $\langle \Psi | \Psi \rangle = 1$ $\sum_n |\langle \Psi | \Phi_n \rangle|^2 = 1$ for this to converge we expect for any $\epsilon > 0$ there is an $N(\epsilon)$ such that

$$\sum_{n=N(\epsilon)}^{\infty} |\langle \Psi | \Phi_n \rangle|^2 < \epsilon$$

Then it makes sense

to consider $N \in \mathbb{N}$

$$P = \sum_{m=1} |\phi_m\rangle\langle\phi_m|$$

Then we solve

$$PHP\,|\psi_n\rangle = \tilde{E}_n\,|\psi_n\rangle$$

Then the second variational

theorem means that

$\tilde{E}_n \geq E_n$ are rigorous

bounds on the exact

eigenvalues.