Lecture 12

many electron atom

$$H = -\sum_n \frac{\hbar^2}{2m_e}\nabla_n^2 - \sum_n \frac{Ze^2}{r_n} + \frac{1}{2}\sum_{m\neq n}\frac{e^2}{|r_n - r_m|}$$

This expression ignores the kinetic energy of the nucleus

If we ignore the interaction between the electrons the solution is a product of one electron atoms

$$\psi(\vec{r}_1 \cdots \vec{r}_N) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\cdots\phi_N(\vec{r}_N)$$

$$E = E_1 + E_2 + \cdots + E_N$$

In order to account for the electrons, we assume a product wave function, except we

choose them so they minimize the energy

$$\Psi_{TRIAL}(\bar{r}_1 \cdots \bar{r}_N) = \prod_{n=1}^{N} \phi_n(\bar{r}_n) \qquad (1)$$

(for real electrons which are fermions the actual wave function should be antisymmetric — we treat that later

<u>step 1</u> Choose $\Psi_{TRIAL}(\bar{r}_1 \cdots \bar{r}_N)$ of the form (1)

Let $\phi_n(\bar{r}_n) = \phi_n^0(\bar{r}_n) + \lambda \delta\phi_n(\bar{r}_N)$

where $\prod_{n=1}^{N} \phi_n^0(r_n)$ minimize the energy.

step 2 calculate

$$\langle \psi_{TRIAL} | H | \psi_{TRIAL} \rangle =$$

$$F(\lambda)$$

we choose the ϕ_n° so

$$\left.\begin{aligned} &* \quad \frac{dF}{d\lambda}\Big|_{\lambda=0} = 0 \\ &* \quad \frac{d^2F}{d\lambda^2}\Big|_{\lambda=0} > 0 \end{aligned}\right\} \text{independent of } \delta\phi_n(r_n)$$

here we only consider the first equation

$$F(\lambda) = \sum_{n=1}^{N} \int \left(\phi_n^\circ(r_n) + \lambda \delta\phi_n(r_n)\right)^* \left(-\frac{\hbar^2}{2m}\nabla_n^2 - \frac{e^2}{r_n}\right) \times$$

$$\left(\phi_n(r_n) + \lambda \delta\phi_n(r_n)\right) d^3r_n$$

$$+ \frac{1}{2} \sum_{m \neq n} \int \left(\phi_n^\circ(r_n) + \lambda \delta\phi_n(r_n)\right)^* \left(\phi_m^\circ(r_m) + \lambda \delta\phi_m(r_m)\right)^* \times$$

$$\frac{e^2}{|r_m - r_n|} \left(\phi_n^\circ(r_n) + \lambda \delta\phi_n(r_n)\right)\left(\phi_m^\circ(r_m) + \lambda \delta\phi_m(r_m)\right)$$

$$d^3r_m\, d^3r_n$$

we also add a Lagrange multiplier to treat the normalization

$$0 = \sum \eta_n \left(1 - \int \phi_n^*(r_n)\, \phi_n(r_n)\, d^3 r_n \right)$$

differentiating $\left.\frac{dF}{d\lambda}\right|_{\lambda=0}$ gives

only terms like in $\delta\phi_n(r)$ or $\delta\phi_n^*(r)$

$$0 = \sum_{n=1}^{N} \int \delta\phi_n^*(\vec{r}_n) \left(-\frac{\hbar^2}{2m}\nabla_n^2 - \frac{Ze^2}{r_n} \right) \phi_n^0(\vec{r}_n)\, d^3 r_n +$$

$$\sum_{n=1}^{N} \int \phi_n^{0*}(\vec{r}_n) \left(-\frac{\hbar^2}{2m}\nabla_n^2 - \frac{Ze^2}{r_n} \right) \delta\phi_n(\vec{r}_n)\, d^3 r_n$$

$$- \sum_{n=1}^{\infty} \int \delta\phi_n^*(r_n) \sum_{m \neq n} \phi_m^{*0}(r_m) \frac{e^2}{|r_n - r_m|} \phi_n^0(\vec{r}_n)\, \phi_m^0(r_m)\, d^3 r_m\, d^3 r_n$$

$$- \sum_{n=1}^{\infty} \int \phi_n^{*0}(r_n) \sum_{m \neq n} \phi_m^{*0}(r_m) \frac{e^2}{|r_n - r_m|} \phi_m^0(\vec{r}_m)\, \delta\phi_n(\vec{r}_n)\, d^3 r_m\, d^3 r_n$$

$$- \sum_n \eta_n \int \left(\delta\phi_n^*(r_n)\, \phi_n^0(r_n) + \phi_n^{*0}(r_n)\, \delta\phi(r_n) \right) d^3 r_n$$

the factor $\frac{1}{2}$ does not appear because we let $\delta\phi_m \to \delta\phi_n$ and $\frac{1}{|r_n - r_m|} \to 1$

Letting $\delta\phi_n \to i\delta\phi_n$ gives identical results with the opposite sign on the conjugated quantities.

This means that the coefficients of $\delta\phi_n$ and $\delta\phi_n^*$ can be separately set to 0

This gives the following equations

$$-\frac{\hbar^2}{2m}\nabla_n^2\phi_n^0(r_n) - \frac{2e^2}{r_n}\phi_n^0(r_n) + \sum_{m\neq n}\int \phi_m^{0*}(r_m)\frac{d^3r_m}{|r_n - r_m|}\phi_m^0(r_m)\phi_n^0(r_n) = \eta_n\phi_n^0(r_n)$$

and the complex conjugate of this equation

this is a set of non linear coupled equations — If we require $\int \phi_n^*(r_n)\,\phi_n^*(r_n) = 1$ and sum over n this becomes

$$\langle \psi | H | \psi \rangle = \sum \eta_n = \eta$$

where $\langle \psi | \psi \rangle = 1$

* To approximate this start by ignoring the electron-electron interaction — denote the normalized solutions by $\phi_n^{-1}(r_n)$

* Use the $\phi_n^1(r_n)$ to construct

$$V^1(r_n) = \sum_{m \neq n} \int \phi_m^{*1}(r_m) \frac{-e^2 d^3 r_m}{|r_m - r_n|} \phi_m^1(r_n)\, d^3 r_m$$

use this to construct an equation for $\phi_n^2(r_n)$

$$-\frac{\hbar^2}{2m}\nabla_n^2\phi_n^2(r_n) - \frac{Ze^2}{r_n}\phi_n^2(r_n) + V^1(r_n)\phi_n^2(r_n) = E_n^2\phi_n^1(r_n)$$

this is a linear schrodinger equation for an electron in the field of the nucleus and an average field of the other electrons

* Next use $\phi_n^2(r_n)$ to construct $V^2(r_n)$ and use that to compute $\phi_n^3(r_n)$ — in general

$$V_n^{k-1}(r_n) \simeq \sum_{m \neq n} \int \phi_m^{k-1\,*}(r_m)\frac{d^3r_m}{|r_m - r_n|}\phi_m^{k-1}(r_m)$$

$$-\frac{\hbar^2}{2m}\nabla_n\phi_n^k(r_n) - \frac{Ze^2}{r_n}\phi_n^k(r_n) + V^{k-1}(r_n)\phi_n^k(r_n) = E_n^k\phi_n^k(r_n)$$

this repeated until it converges (which is not automatic)

The final solutions are

$$E \simeq \sum_{n=1}^{N} E_n^{IF}$$

$$\psi(r_1 \cdots r_N) \simeq \prod_{n=1}^{N} \phi_n^{K}(r_n)$$

For fermions the single particle states have to be antisymmetrized - this will be discussed later

This reduces the calculation to solving the one body problem in a potential a number of times

Another useful exact method is called the Hellmann Feynman Theorem

Let $H(\alpha_1 \ldots \alpha_K)$ depend on some parameters $\alpha_1 \ldots \alpha_K$

example

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

The eigenvalues all will depend on the parameters

$$H(\alpha_1 \ldots \alpha_K)\,\psi(\alpha_1 \ldots \alpha_K) = E(\alpha_1 \ldots \alpha_K)\,\psi(\alpha_1 \ldots \alpha_K)$$

$$E_n(m, \hbar, e, Z) = -\frac{Z^2 m e^4}{2\hbar^2} \frac{1}{(n+e+1)^2}$$

The statement of the theorem is

$$\frac{\partial E}{\partial \alpha_i}(\alpha_1 \ldots \alpha_n) = \langle \psi(\alpha_1 \ldots \alpha_n) | \frac{\partial H}{\partial \alpha_i} | \psi(\alpha_1 \ldots \alpha_n) \rangle$$

To use this consider expectation value of $\frac{1}{r}$

$$\frac{\partial H}{\partial Z} = -\frac{e^2}{r} \quad \text{(1)}$$

$$\langle \psi | \frac{1}{r} | \psi \rangle = -\frac{1}{e^2} \langle \psi | \left(-\frac{e^2}{r}\right) | \psi \rangle$$

$$= -\frac{1}{e^2} \langle \psi | \frac{\partial H}{\partial Z} | \psi \rangle = -\frac{1}{e^2} \frac{\partial E}{\partial Z}$$

$$= -\frac{1}{e^2} \left(-\frac{2Zme^4}{2\hbar^2}\right) \frac{1}{(n+e+1)^2}$$

$$= \frac{Zme^2}{\hbar^2} \frac{1}{(n+e+1)^2}$$

In this example this method can be use to calculate the expectation value of r^2 $\frac{1}{r}$ $\frac{1}{r^2}$

Proof

$$\frac{\partial}{\partial \alpha} \langle \psi(\alpha) | (H(\alpha) - E(\alpha)) | \psi(\alpha) \rangle = 0$$

$$= \langle \frac{\partial \psi}{\partial \alpha} | (H(\alpha) - E(\alpha)) | \psi(\alpha) \rangle + \langle \psi(\alpha) | (H(\alpha) - E(\alpha)) | \frac{\partial \psi}{\partial \alpha} \rangle$$

$$\langle \psi(\alpha) | \left(\frac{\partial H(\alpha)}{\partial \alpha} - \frac{\partial E(\alpha)}{\partial \alpha} \right) | \psi(\alpha) \rangle =$$

$$\langle \psi(\alpha) | \frac{\partial H(\alpha)}{\partial \alpha} | \psi(\alpha) \rangle - \frac{\partial E(\alpha)}{\partial \alpha}$$

$$\therefore \quad \frac{\partial E}{\partial \alpha} = \langle \psi(\alpha) | \frac{\partial H}{\partial \alpha}(\alpha) | \psi(\alpha) \rangle$$

This is useful when you know how how the eigenvalues depend on parameters. Note that this can also be applied numerically

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The virial theorem is a related result

Assume $H|\psi\rangle = E|\psi\rangle$

and consider

$$\langle\psi|[H, \vec{x}\cdot\vec{p}]|\psi\rangle =$$

$$(E-E)\langle\psi|\vec{x}\cdot\vec{p}|\psi\rangle = 0 =$$

$$\langle\psi|[H,\vec{x}]\cdot\vec{p}|\psi\rangle +$$

$$\langle\psi|\vec{x}\cdot[H\vec{p}]|\psi\rangle$$

For $H = \frac{p^2}{2m} + V(r)$

$$[H, \vec{x}] = \left[\frac{p^2}{2m}, \vec{x}\right] = -\frac{2i}{2m}\vec{p}\hbar$$

$$[H, \vec{p}] = \frac{i}{\hbar}\vec{\nabla}V$$

If we put everything together we get

$$0 = [H\vec{x}]\cdot\vec{p} + \vec{x}\cdot[H\vec{p}] =$$

$$-\frac{2i\hbar}{2m}p^2 + i\hbar\,\vec{x}\cdot\nabla V$$

canceling the $i\hbar$ gives

$$-2(\text{Kinetic energy}) + r\frac{\partial V}{\partial r} = 0$$

For $V = ar^n$ $\quad r\cdot\frac{\partial V}{\partial r} = nV$

$$\boxed{-2(KE) + nV}$$

we also have energy conservation

$$\boxed{KE + V = E}$$

This means for power law potentials

$$T = K\bar{E} = \frac{n}{2} V$$

$$T + V = E = T + \frac{2}{n} T$$

$$= \left(1 + \frac{2}{n}\right) T$$

$$\left(1 + \frac{n}{2}\right) V$$

For a Coulomb potential

$$V = e^2 Z / r \qquad n = -1$$

$$\boxed{\bar{E} = -T = \frac{V}{2}}$$

Rayleigh Schrödinger perturbation theory

Assume

$$H = H_0 + V$$

where

$$H_0 |\phi_n^\circ\rangle = E_n^\circ |\phi_n^\circ\rangle$$

is known and V is "small"

we assume that the exact eigenvectors and eigenvalues can be expanded in powers of V. For the purpose of bookkeeping we write

$$H = H_0 + \lambda V$$

where we use powers of λ to keep track of powers of V $\Rightarrow$

$$|\psi_n\rangle = |\psi_n^0\rangle + \sum_{m=1}^{\infty} \lambda^m |\psi_n^m\rangle$$

$$E_n = E_n^0 + \sum_{m=1}^{\infty} \lambda^m E_n^m$$

In order to find all of the corrections we substitute into the

the schrodinger equation and equate power of λ

$$(H_0 + \lambda V)\left(|\psi_n^0\rangle + \sum_{m=1}^{\infty} \lambda^m |\psi_n^m\rangle\right) =$$

$$\left(E_n^0 + \sum_{m=1}^{\infty} \lambda^m E_n^m\right)\left(|\psi_n^0\rangle + \sum_{k=1}^{\infty} \lambda^k |\psi_n^k\rangle\right) =$$

$$H_0 \sum_{m=0}^{\infty} \lambda^m |\psi_n^m\rangle + V \sum_{m=0}^{\infty} \lambda^{m+1} |\psi_n^m\rangle =$$

$$\sum_{m=0}^{\infty} \sum_{k=0}^{\infty} \lambda^{m+k} E_n^m |\psi_n^k\rangle$$

next express these in terms of common power of λ

$$H_0 \sum_{m=0}^{\infty} \lambda^m |\psi_n^m\rangle + V \sum_{k=1}^{\infty} \lambda^k |\psi_n^{k-1}\rangle =$$

$$\sum_{\ell=0}^{\infty} \lambda^\ell \sum_{m=0}^{\ell} E_n^m |\psi_n^{\ell-m}\rangle$$

For $m = 0$ we get

$$H_0 |\psi_n^0\rangle = E_0^n |\psi_n^0\rangle$$

which is the unperturbed solution

for $m=1$

$$H_0 |\psi_n^1\rangle + V|\psi_n^0\rangle = E_n^0 |\psi_n^1\rangle + E_n^1 |\psi_n^0\rangle$$

and in general

$$H_0 |\psi_n^m\rangle + V|\psi_n^{m-1}\rangle = \sum_{k=0}^{m} E_n^k |\psi_n^{m-k}\rangle$$

This can be put in the form

$$(H_0 - E_n^0)|\psi_n^m\rangle = -V|\psi_n^{m-1}\rangle + \sum_{k=0}^{m-1} E_n^{m-k} |\psi_n^k\rangle$$

Note that if we add $|\psi_n^0\rangle$ to $|\psi_n^k\rangle$ the left side of this equation does not change — to fix this we assume that

$$\langle \psi_n^0 | \psi_n^k \rangle = 0 \quad k > 0$$

the second thing to note is is

$$|\psi_n\rangle = |\psi_n^0\rangle + \sum \lambda^k |\psi_n^k\rangle$$

and all of the $|\psi_n^k\rangle$ are $\perp$ to $|\psi_n^0\rangle$ then $|\psi_n^0\rangle$ and $|\psi_n\rangle$ cannot both be normalized to unity

choose $\langle \psi_n^0 | \psi_n^0 \rangle = 1$

using these 2 assumptions it is possible to solve for $|\psi_n^m\rangle$ and E_n^m in terms of $|\psi_n^k\rangle$ and E_n^k for $k<m$

case 1 $m=1$

$$H_0|\psi_n^1\rangle + V|\psi_n^0\rangle = E_n^1|\psi_n^0\rangle$$

multiply by $\langle\psi_n^0|$

$$\langle\psi_n^0|H_0|\psi_n^1\rangle = E_n^0\underbrace{\langle\psi_n^0|\psi_n^1\rangle}_{0} = 0$$

this gives

$$\langle\psi_n^0|V|\psi_n^0\rangle = E_n^1\underbrace{\langle\psi_n^0|\psi_n^0\rangle}_{1} = E_n^1$$

$$\therefore E_n^1 = \langle\psi_n^0|V|\psi_n^0\rangle$$

$$H_0|\psi_n'\rangle + V|\psi_n^0\rangle = E_n'|\psi_n^0\rangle + E_n^0|\psi_n'\rangle$$

multiply by $\langle\psi_m^0|$ $\boxed{m \neq n}$

then

$$\langle\psi_m^0|(H_0 - E_n^0)|\psi_n'\rangle = \boxed{E_n'\langle\psi_m^0|\psi_n^0\rangle = 0} - \langle\psi_m^0|V|\psi_n^0\rangle$$

($H_0 \to E_m^0$)

$$\langle\psi_m^0|\psi_n'\rangle = \frac{\langle\psi_m^0|V|\psi_n^0\rangle}{E_n^0 - E_m^0}$$

using completeness of $|\psi_m^0\rangle$ and $\langle\psi_m^0|\psi_n'\rangle = 0$ $m \neq n$ $\Rightarrow$

$$|\psi_n'\rangle = \sum_{m\neq n} |\psi_m^0\rangle\langle\psi_m^0|\psi_n'\rangle$$

$$\boxed{|\psi_n'\rangle = \sum_{m\neq n} \frac{\langle\psi_m^0|V|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle}$$

In some cases $\langle \psi_n^0 | V | \psi_n^0 \rangle = E_n^1$ is 0; then the leading correction will be the second order term

$$H_0 |\psi_n^2\rangle + V |\psi_n^1\rangle = E_n^0 |\psi_n^2\rangle + E_n^1 |\psi_n^1\rangle + E_n^2 |\psi_n^0\rangle$$

Taking matrix elements with $\langle \psi_n^0 |$ gives

$$\langle \psi_n^0 | V | \psi_n^1 \rangle = E_n^2$$

since

$$0 = \langle \psi_n^0 | (H_0 - E_n^0) | \psi_n^1 \rangle$$

$$0 = E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle$$

using the result for $|\psi_n^1\rangle$ gives

$$E_n^2 = \langle \psi_n^0 | V | \left(\sum_{m \neq n} |\psi_m^0\rangle \frac{\langle \psi_m^0 | V | \psi_n^0 \rangle}{E_n - E_m} \right)$$

$$= \sum_{m \neq n} \frac{|\langle \psi_n^0 | V | \psi_m^0 \rangle|^2}{E_n - E_m}$$

The second order wave function can be constructed using

$$\langle \psi_n^k | \psi_n^0 \rangle = 0 \qquad k > 0$$

In general the recursive relations give

$$E_n^k = \langle \psi_n^0 | V | \psi_n^{k-1} \rangle$$

$$\langle \psi_\ell^0 | \psi_n^m \rangle = \frac{\langle \psi_\ell^0 | V | \psi_n^{m-1} \rangle - \sum_{k=1}^{m-1} E_n^{m-k} \langle \psi_\ell^0 | \psi_n^k \rangle}{E_n^0 - E_\ell^0}$$

This can be used to go to arbitrarily high order - however this method works best when the corrections are small