$$= \langle ab|V|a'b'\rangle - \langle ab|V|b'a'\rangle$$

if $a' \neq a$
$b \neq b'$

but $c = c'$, etc.

2/22 Hartree-Fock Method.

Basic (variational) approximation for many-fermion systems. Provides basis in which to do perturbation theory.

Surprisingly accurate for many atomic properties. Lousy for nuclei.

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} -\frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

$$\equiv \sum_{i=1}^{N} (t_i + u_i) + \frac{1}{2}\sum_{i \neq j} v_{ij}$$

Variational principle

$$E \leq \frac{\langle E|H|E\rangle}{\langle E|E\rangle}$$ for any Ψ

Want to pick convenient Ψ

$$\Psi(r_1, \ldots r_n) = \frac{1}{\sqrt{N!}} \det(\psi_1, \psi_2, \ldots \psi_N)$$

N single-particle wave functions $\{\psi_i\}$

(where $\langle \psi_i|\psi_j\rangle = \int d^3r\, \psi_i \psi_j = \delta_{ij}$)

$\det \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) \\ \psi_1(r_2) & \psi_2(r_2) \end{vmatrix}$ (the Slater determinant

Try to pick best possible $\{\psi_i\}$ to minimize.

$\langle\Psi|H|\Psi\rangle$ wrote down $\langle$ one-body part $\rangle$ in last lecture

$$= \sum_{i=1}^{N} \langle \psi_i | t + u | \psi_i \rangle$$

$$+ \frac{1}{2} \langle ij | v | ij - ji \rangle$$

$$= \sum_{i=1}^{N} \int d^3r\, \psi_i^*(\vec{r}) \left(-\frac{\hbar^2 \nabla^2}{2m} + u(\vec{r}) \right) \psi_i(\vec{r})$$

$$+ \frac{1}{2} \sum_{i \neq j} \int d^3r\, d^3r'\, \psi_i^*(\vec{r})\, \psi_j^*(\vec{r}')\, v[\vec{r} - \vec{r}'] \, \underbrace{[\psi_i(\vec{r})\psi_j(\vec{r}')}_{\text{direct}} \underbrace{- \psi_i(\vec{r}')\psi_j(\vec{r})]}_{\text{exchange}}$$

($i=j$ just given zero)

$\to \sum_{i,j}$

Require that

$$\frac{\delta}{\delta \psi_\ell^*(\vec{s})} \left[\langle \Psi | H | \Psi \rangle - \sum_{ij} \lambda_{ij} \langle \psi_i | \psi_j \rangle \right] = 0$$

all values ℓ all positions s

set of Lagrange multipliers

to keep ψ's orthogonal.

chosen at end so $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ (a constraint, this is)

ψ^* doesn't matter.

$$\frac{\delta}{\delta \psi_\ell^*(\vec{s})} \langle \Psi | H | \Psi \rangle$$

Run on term first. Picks out $i = \ell$, $\vec{r} = \vec{s}$.

$$= \left(-\frac{\hbar^2}{2m}\nabla^2 + u(\vec{s})\right)\psi_\ell(\vec{s})$$

$$\left(\frac{\delta \psi_i^*(\vec{r})}{\delta \psi_\ell(\vec{s})} = \delta(\vec{r}-\vec{s})\,\delta_{i\ell}\right.$$

More detail

Imagine making a small variation $\delta\psi_\ell^*(s)$

δ 1st term

$$\sum_{i=1}^{N}\int d^3r\ \delta\psi_i^*(\vec{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_i(\vec{r})$$

but $\delta\psi_i^*(\vec{r}) = 0$ unless $r = s$, $i = \ell$.

(are varying wrt. $\underline{\underline{\psi^*}}$, so ψ not affected.)

$$= \cancel{\sum \int} d^3r\ \delta\psi_\ell^*(\vec{s})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_\ell(\vec{s})$$

$$\frac{\delta}{\delta\psi_\ell^*(\vec{s})} = \left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_\ell(\vec{s})$$

2 body part.

$$\frac{1}{2} \sum \underbrace{\psi_i^*(\vec{r})\, \psi_j^*(\vec{r}')}$$

give equal contribution

$$\delta\psi_i \qquad \psi_j$$

$$\psi_i \qquad \delta\psi_j$$

j, i = l (one at a time)

$r, r' = s$

$\frac{1}{2}$ goes.

$$\sum_j \int d^3r'\, \psi_j^*(\vec{r}')\, v(s-\vec{r}') \left(\psi_l(\vec{s})\, \psi_j(\vec{r}') - \psi_l(\vec{r}')\, \psi_j(\vec{s}) \right)$$

(have set our dummy index j, $\vec{r}'$)

$$\frac{\delta}{\delta\psi_l^*(s)} \sum_{ij} \lambda_{ij} \int d^3r\, \psi_i^*(\vec{r})\, \psi_j(\vec{r})$$

$$= \sum_j \lambda_{lj}\, \psi_j(\vec{s})$$

so

$$\frac{\delta}{\delta\psi_l^*(\vec{s})} \langle\psi|H|\psi\rangle = \left(-\frac{\hbar^2}{2m}\nabla^2 + u(\vec{s})\right)\psi_l(\vec{s})$$

$$+ \sum_j \int$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2+u\right]\psi_e(\vec{s}) + \left(\int d^3r' \sum_j |\psi_j(\vec{r}')|^2 v(\vec{s}-\vec{r}')\right)\psi_e(\vec{s})$$

$$-\int d^3r'\, v(\vec{s}-\vec{r}')\left(\sum_j \psi_j(s)\psi_j(\vec{r}')\right)\psi_e(r')$$

$$-\sum_j \lambda_{ej}\psi_j(s) = 0$$

$$\equiv \left(-\frac{\hbar^2\nabla^2}{2m}+u\right)\psi_e(s) + W_H(s)\,\psi_e(s)$$

$$\cancel{\int d^3r'\, v(\vec{s}-\vec{r}')\left(\sum_j \psi_j(\vec{s})\psi_j^*(\vec{r}')\right)}$$

$$-\int d^3r'\, W_F(\vec{s},\vec{r}')\,\psi_e(\vec{r}') = \sum_j \lambda_{ej}\psi_j(\vec{s})$$

$$W_H(\vec{s}) = \int d^3r'\,\rho(r')\,v(s-r')$$ Hartree potential.

$$\rho(\vec{r}') = \sum_j |\psi_e(\vec{r}')|^2 = \text{density}$$

$W_F(\vec{s},\vec{r}')$ = Fock potential = $v(\vec{s}-\vec{r}')\sum_j \psi_j(\vec{s})\psi_j^*(\vec{r}')$

<u>nonlocal</u> acting on $\psi_e(\vec{r}')$

("picks up at r', moves to s'")

$$h\psi_l = \sum_j \lambda_{lj}\psi_j$$

h is Hartree-Fock hamiltonian

$$= -\frac{\hbar^2}{2m}\nabla^2 + U + W_H - \underbrace{W_F}$$

interpreted as the integral operator.

choose: $\lambda_{lj} = 0$ if $l \neq j$

$\lambda_{ll} = e_l$ $\quad$ e_l is eigenvalue of h.

then, $\quad$ this fulfills orthogonal.

$$h\psi_l = e_l\psi_l \qquad \langle l|j\rangle = \delta_{lj}$$

guaranteed orthogonal ψ_j's (guaranteed since eigenfunctions of same h)

Summary: The "best" determinant Ψ is built from N single-part wf's ψ_j which solve a S.E-like equation

$h\psi_j = e_j\psi_j$, but $\underline{h}$ itself depends on the ψ's (self-consistency) will see that

e_j's are roughly the energy to add or remove an electron from orbital j.

Total energy

assume have found ψ's.

$$\langle H \rangle = \sum_i \langle i | t+u | i \rangle + \frac{1}{2} \sum_{i,j} \langle ij | v | ij - ji \rangle$$

What is

$$\langle h \rangle = \sum_i \langle i | h | i \rangle$$

(not full Ham, but Hartree-Fock ham.

h is 1-body operator

$|i\rangle$ was chosen ~~such~~ so $h|i\rangle = e_i|i\rangle$

$$= \sum_{i=1}^{N} e_i$$

(sum of energies to remove electrons)

Not manifestly equal to $\langle H \rangle$. Should have some relation

$$= \sum_i \langle i | t+u | i \rangle + \underbrace{\sum_i \langle i | W_H | i \rangle - \sum_i \langle i | W_F | i \rangle}_{\text{want}\,=\,2\text{body}}$$

$$\sum_i \langle i | W_H | i \rangle = \sum_i \int d^3r \; \psi_i^*(r) \, W_H \, \psi_i(r)$$

$$= \sum_{i,j} \int d^3r \, d^3r' \, |\psi_i|^2 \, |\psi_j(\vec{r}')|^2 \, v(\vec{r} - \vec{r}')$$

$$= (2) \tfrac{1}{2} \sum_{i,j} \langle ij | v | ij \rangle$$

when work out

$$\sum_i \langle i | W_F | i \rangle = 2 \cdot \tfrac{1}{2} \sum_{i,j} \langle ij | v | ji \rangle$$

$$\sum_i e_i = \sum_i \langle i | t + u | i \rangle + 2 \cdot \tfrac{1}{2} \sum_{i,j} \langle ij | v | ij - ji \rangle$$

$$= \langle \Psi | t + u | \Psi \rangle + 2 \langle \Psi | v | \Psi \rangle$$

$\sum$ ind part energies overcount pairwise intera by factor of 2.

$$\langle H \rangle = \sum_i e_i - \tfrac{1}{2} \sum_{i,j} \langle ij | v | ij - ji \rangle$$

$$= \tfrac{1}{2} \left(\sum_i e_i + \langle i | t + u | i \rangle \right)$$

2/24

$$\Psi = \frac{1}{\sqrt{N!}} \det(\psi_1, \dots \psi_N)$$

$h\psi_i = e_i \psi_i \qquad h = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + W_H(r) - W_F$

$\rho(r) = \sum_j |\psi_j(r)|^2 \qquad W_H(r) = e^2 \int d^3r' \frac{\rho(r')}{|r-r'|}$

$$W_F(r,r') = \frac{e^2}{|r-r'|} \sum_j \psi_j(r)\psi_j^*(r')$$

$$E = \langle H \rangle = \sum_i \langle i | -\frac{\nabla^2}{2m} + \underset{\uparrow \atop -Ze^2/r}{u} | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \frac{e^2}{|r-r'|} | ij \rangle$$

ψ_i's satisfy 1-body equation.

W_F non-local, ordinarily is very small correction.

$H\Psi = E\Psi$ 3N dimensional

$\rightarrow$ n coupled 3-d equation through H-F.

Simplifications:

Drop W_F (no exchange term in $\langle H \rangle$)

(W_F sort of a self-interaction)

(W_H sums over everything.

$$W_F \approx \frac{1}{N} W_H$$

assume $W_H(\vec{r}) = W_H(r)$ is spherically symmetric

tantamount to assuming $\rho(r)$ symmetrically
same as symmetric

(good for calculating energies of deep electrons,
not good for chemical properties.

good for total energies. good for noble gases

Steps:

① Guess $W_H(r)$ (eg $= 0$)

② Solve $h\psi = e\psi$ for e's, ψ's.

$$\left(-\frac{\nabla^2}{2m} + U(r) + W_H(r)\right)\psi_j = e_j \psi_j$$

in general, many e's, ψ's.

③ Select from set of solutions, N orbitals to be occupied.
(generally those with lowest e's)

④ Calculate $\rho(r) = \sum_{i \text{ occupied}} |\psi_i(\vec{r})|^2$ (may not be spherically symmetric;

so average ...

(5) Calculate $W_H(r) = \int \frac{e^2}{|r-r'|} \rho(r') d^3r'$

(6) Return to (2), iterate to convergence.

---

(2) Solve $h\psi = e\psi$ on a mesh in R space

$$\psi = \frac{R_i(r)}{r} Y_{em}(\hat{r})$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2mr^2} + u + W_H\right) R = e R$$

French + Taylor form numerical solutions.

(3) Given (2), how to occupy them.

Do Ne, $Z=10$, $N=10$ electrons

3s ———

2p ——— 6 here

2s ——— 2 here

unambiguous.

——— 2e's here

1s

Suppose Ne + 4e's (Si)

3d ——— 10

3p ——— 6

3s ——— 2

close in energy, not obvious

trial and error.

④ Suppose a level with l is completely filled.

$$\rho(\vec{r}) = \sum_{spin} \sum_{m} \left(\frac{R(r)}{r}\right)^2 |Y_{lm}(\hat{r})|^2$$

$$= 2\left(\frac{2l+1}{4\pi}\right)\left(\frac{R(r)}{r}\right)^2 \qquad \sum_m |Y_{lm}(\hat{r})|^2 = \frac{2l+1}{4\pi}$$

~~each electron~~

if orbital only partly occupied.

do as if shell filled, take appropriate fraction.

⑤ $W_H(r)$ simplest to compute as

$$\nabla^2 W_H = -4\pi e^2 \rho(r)$$

(solving the diff eq. rather than convoluting)

$$W_H \equiv \frac{u(r)}{r}$$

$$\frac{d^2u}{dr^2} = -4\pi e^2 \rho r$$

W vanish large distance

W constant at some point inside

Electron gas: (at zero temperature)

1) need to do Thomas-Fermi.
2) would like to estimate contribution of W_F
3) zeroth-order description of electrons in a metal.

Model:

large volume Ω. filled with uniform background + charge density $\rho(\vec{r}) = \rho$

(say, the nuclei in a metal)

N electrons moving in volume, interact with each other through coulomb force (interact with positive charge)

Take N so that $\frac{N}{\Omega} = \rho$ as $N, \Omega \to \infty$

(same as background charge density, guarantees neutral charge system)

Calculate energy of ground state, as function of ρ.

continuous momenta of e^-'s (big box)

Expect $E = \Omega\, \varepsilon(\rho)$

total energy — energy density,

Hartree-Fock valid at "low" ρ.

Hamiltonian: $$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|r_i - r_j|}$$

$$-\sum_i \int \frac{e^2 \rho(r')\, d^3r'}{|r_i - r'|}$$

ρ constant, so $\int$ is ∞, but ~~[illegible]~~ ρ's will cancel

self-energy of density background

$$+\frac{1}{2}\int d^3r\, d^3r' \frac{\rho(r)\rho(r')}{|r - r'|}$$

(this is extreme low-energy limit (low Temperature))

(could replace $\frac{1}{r}$ by $\frac{e^{-\lambda r}}{r}$ (slightly screened,

won't do this $\longrightarrow$ avoids infinities,
then take $\lambda \to 0$.)

Need trial state for H-F

single-particle wave functions

False:

$$\Psi = \frac{\det}{\sqrt{N!}} (\psi_1\ \psi_2 \ldots \psi_N)$$

This turns out to be H-F solution

2 labels for each

$$\psi_{\vec{k},m} = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} \chi_m$$

(plane waves, spinor)

$$\boxed{\langle km | km\rangle = \int d^3r \left|\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}}\right|^2 = 1} \equiv |km\rangle$$

$m = \pm 1/2$.
$\vec{k}$ arbitrary

$\langle \Psi | H | \Psi \rangle$

$$\langle H\rangle = \sum_{\substack{k,m \\ \text{occupied}}} \langle km | \frac{p^2}{2m} | km\rangle - e^2 \sum_{km} \langle km | \int \frac{d^3r' \rho(r')}{(r-r')} | km\rangle$$

(mass, not label)

from $\frac{1}{2}\frac{e^2}{|r_i - r_j|} \to$ $$+\frac{e^2}{2} \sum_{\substack{km \\ k'm'}} \langle km k'm' | \frac{1}{r} | km k'm' - k'm' km \rangle$$

$$+\frac{e^2}{2} \int d^3r\, d^3r' \frac{\rho(r)\,\rho(r')}{|r-r'|} \Leftarrow \text{constant}$$

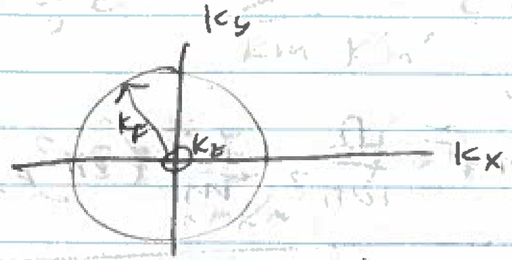
(equivalent to before, $|i\rangle = |km\rangle$)

3/1

Which states are occupied

occupy all states with $|k| < k_F$ = Fermi momentum

will determine k_F from density.



choose k_F so $N = \Omega \rho$, as required

$$N = \sum_{\substack{k,m \\ \text{occupied}}} 1 = \underset{\uparrow \text{ spin}}{2} \sum_{k<k_F} 1$$

$$\boxed{\sum_k = \Omega \int \frac{d^3k}{(2\pi)^3}}$$

$$= 2\,\Omega \int_0^{k_F} \frac{d^3k}{(2\pi)^3}$$

$$= \frac{2}{8\pi^3}\,\Omega \left(\frac{4\pi}{3} k_F^3\right)$$ volume of momentum sphere

$$N = \frac{\Omega k_F^3}{3\pi^2} \Rightarrow \rho = \frac{k_F^3}{3\pi^2}$$

$(p = \hbar k)$
$(p_F = \hbar k_F)$

$k_F \sim$ Å in metal.

$$E_{kin} = \sum_{\substack{km \\ \text{occupied}}} \langle km | \frac{p^2}{2m} | km \rangle$$

$\frac{p^2}{2m} |km\rangle$ (plane wave)

$= \frac{\hbar^2 k^2}{2m} |km\rangle$

$$= \sum_{\substack{km \\ occ}} \frac{\hbar^2 k^2}{2m}$$

$$= \frac{\hbar^2}{2m} \underset{\uparrow \text{ spin}}{(2)} \sum_{k\ occ} k^2 = \frac{\hbar^2}{m} \Omega \int_0^{k_F} \frac{d^3k}{(2\pi)^3} k^2$$

$$E_{kin} = \frac{\hbar^2}{m} \Omega \frac{4\pi}{(2\pi)^3} \int_0^{k_F} k^2 (k^2 dk)$$

$$= \Omega \frac{k_F^5}{10\pi^2} \frac{\hbar^2}{m} = \frac{\Omega}{10\pi^2} \frac{\hbar^2}{m} (3\pi^2 \rho)^{5/3}$$

$$e^2 \sum_{km} \langle km | \left(\int d^3r' \frac{\rho(r')}{|\underset{\sim}{r} - \underset{\sim}{r}'|} \right) | km \rangle$$

$$= -e^2 \sum_{km} \int \psi_{km}^*(\vec{r}) \int \frac{d^3r' \rho(r')}{|r-r'|} \psi_{km}(\vec{r}) d^3r$$

$$|\psi_{km}(\vec{r})|^2 = \frac{1}{\Omega}$$

$$\sum_{km} |\psi_{km}(\vec{r})|^2 = \frac{1}{\Omega} \sum_{km} 1 = \frac{N}{\Omega} = \rho$$

$$= -e^2 \int d^3r' d^3r \frac{1}{|r-r'|} \rho(r') \rho(\vec{r})$$

cancels part of last term.

Direct $e^- e^-$ interaction

$$\frac{1}{2} e^2 \sum_{km\ k'm'} \langle km\ k'm' | \frac{1}{|r-r'|} | km\ k'm' \rangle$$

$$= \frac{1}{2} e^2 \sum_{kmk'm'} \int d^3r\, d^3r' \, \frac{e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}} \frac{e^{-i\vec{k}'\cdot\vec{r}'}}{\sqrt{\Omega}} \frac{1}{|r-r'|} \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}} \frac{e^{ik}}{\sqrt{\Omega}}$$

$$\sum_{km} 1 \sum_{k'm'} 1 = N^2$$

$$= \frac{1}{2} e^2 \int d^3r\, d^3r' \, \frac{\rho(r)\rho(r')}{|r-r'|}$$

cancels with rest of last term.

No direct interaction, (charge neutral overall)

Have just kinetic energy, and exchange

Exchange:

$$-\frac{e^2}{2} \sum_{km\ k'm'} \langle km\ k'm' | \frac{1}{|r-r'|} | k'm'\ km \rangle$$

yields 2 instead of 4 for spin

yields 2 instead of 4 for spin $\leftarrow \delta_{mm'}$ exchange only important if exchange e^-'s of same spin

$$= -\frac{e^2}{2}(2) \sum_{k,k'<k_F} \int d^3r\, d^3r' \, \frac{e^{-ikr} e^{-ik'r'}}{\Omega} \frac{1}{|r-r'|} \frac{e^{ik'r} e^{ik\cdot r'}}{\Omega}$$

$$E_{exch} = -e^2 \int d^3r\, d^3r' \left(\sum_{k<k_F} \frac{e^{-ik\cdot(r-r')}}{\Omega} \right) \left(\sum_{k'<k_F} \frac{e^{ik'\cdot(r-r')}}{\Omega} \right) \frac{1}{|r-r'|}$$

everything depends on $\vec{r} - \vec{r}\,'$

center-of-mass coordinates:

$$\vec{R} = \frac{\vec{r} + \vec{r}\,'}{2} \qquad s = r - r' \qquad d^3R\, d^3s = d^3r\, d^3r'$$

$$= -e^2 \underbrace{\int d^3R}_{\Omega} \int d^3s \left(\sum_{k<k_F} \frac{e^{-ik\cdot\vec{s}}}{\Omega} \right) \left(\sum_{k'<k_F} \frac{e^{+ik'\cdot\vec{s}}}{\Omega} \right) \frac{1}{|S|}$$

~~Slater~~ $\rho_{slater}(\vec{s}) = \sum_{k<k_F} \frac{e^{-i\vec{k}\cdot\vec{s}}}{\Omega}$ = Slater density

no preferred direction

$= \rho_{SL}(|s|)$

$\rho_{SL} = \rho_{SL}^{*}$ as turns out

$$= -e^2 \Omega \int d^3s\, \rho_{SL}^2(s) \frac{1}{s}$$

$$\rho_{SL} = \sum_{k<k_F} \frac{e^{-i\vec{k}\cdot\vec{s}}}{\Omega} = \int_0^{k_F} \frac{d^3k}{(2\pi)^3} e^{-i\vec{k}\cdot\vec{s}}$$

$$\int d(\cos\theta)\, d\varphi \; e^{-iks\cos\theta}$$

$\cos\theta \equiv x$

$$2\pi \int_{-1}^{1} dx \, \cancel{d\varphi} \; e^{-iksx} = 2\pi \frac{1}{-iks} \underbrace{\left(e^{-iks} - e^{iks}\right)}_{-2i \sin ks}$$

$$= 4\pi \frac{\sin ks}{ks} = 4\pi j_0(ks)$$

not surprising

$$e^{ikr\cos\theta} = \sum_l i^l j_l(kr) P_l(\cos\theta)(2l+1)$$

$\int_{\text{angles}}$, $l=0$ survives

$$= \frac{4\pi}{(2\pi)^3} \int_0^{k_F} k^2 dk \; j_0(ks)$$

$$\rho_{SL}(s) = \frac{1}{2\pi^2} \int_0^{k_F} k^2 dk \, \frac{\sin ks}{ks}$$

$ks = x$

$$= \frac{1}{2\pi^2 s^3} \int_0^{k_F s} x^2 dx \, \frac{\sin x}{x}$$

$$= \frac{1}{2\pi^2 s^3} \int_0^{k_F s} x \sin x \, dx$$

real, depends on $|s|$ only.

units $\sim \frac{1}{s^3}$

$$= \frac{1}{2\pi^2 s^3} \left(\sin k_F s - k_F s \cos k_F s\right)$$

Spherical Bessel function

$$j_1(x) = \frac{1}{x^2}\left(\sin x - x\cos x\right)$$

$\rho = \frac{k_F^3}{3\pi^2}$

$$= \frac{(k_F)^3}{2\pi^2} \left(\frac{j_1(k_F s)}{k_F s} \right)$$

$$= \frac{1}{2}\rho \left(\frac{3 j_1(k_F s)}{k_F s} \right.$$

$$E_{exchange} = -e^2\Omega \int d^3s \left(\frac{1}{2}\rho\right)^2 \left(\frac{3 j_1(k_F s)}{k_F s}\right)^2 \left(\frac{1}{s}\right)$$

$$= \frac{-e^2\Omega}{k_F^2} 4\pi \int_0^\infty \cancel{x}^2 dx \, \frac{1}{4} \underset{\text{constant}}{\rho^2} \left(\frac{3 j_1(x)}{x}\right)^2 \left(\frac{1}{x}\right)$$

will go $\sim \rho^{4/3}$

$\boxed{3/3}$

<u>Exchange contribution</u>

remember $\frac{1}{\Omega} \sum_{k<k_0} e^{-i\vec{k}\cdot\vec{s}} = \left(\frac{1}{2}\rho\right) \left(\frac{3 j_1(k_F s)}{k_F s}\right)$

$j_1(x) = \frac{1}{x^2}(\sin x - x\cos x)$

$\simeq \frac{1}{3}x$ x small.

~~E_{exch}~~

$$E_{exch,} = -e^2\Omega\pi \frac{\rho^2}{k_F^2} \underbrace{\int_0^\infty x\,dx \left(\frac{3 j_1(x)}{x}\right)^2}_{3\pi/2}$$

negative definite

Coulomb positive exchange attractive

$k_{F_0} \sim \rho^{1/3}$

$\propto \Omega$.

$\rho = \frac{k_F^3}{3\pi^2}$

$\approx \Omega\rho^{4/3}$

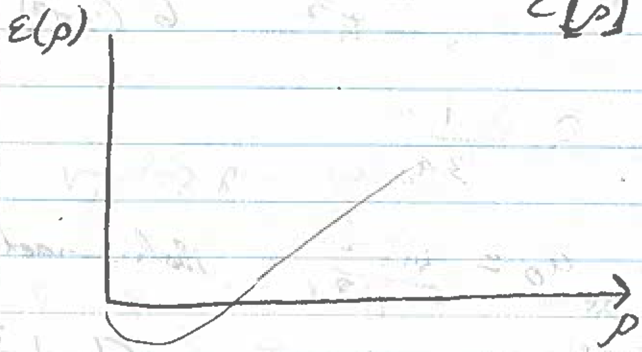
$$E_{exchange} = -e^2 \Omega \rho^{4/3} \left(\frac{3\pi^2}{8}\right)^{1/3}$$

Total energy:

$$E_{kin} + E_{exch} = \Omega\left(\frac{\hbar^2}{m}\frac{1}{10\pi^2}\left(3\pi^2\rho\right)^{5/3} - e^2\left(\frac{3\pi^2}{8}\right)^{1/3}\rho^{4/3}\right)$$

$$= \Omega\big(\underbrace{A\rho^{5/3} - B\rho^{4/3}}_{\mathcal{E}[\rho] \text{ energy density}}\big)$$

dominates ρ small



density

Pressure: $$P = -\frac{\partial E}{\partial \Omega}\Big)_N = -\frac{\partial}{\partial \Omega}\,\Omega\,\mathcal{E}[\rho]\Big)_N$$

$$= -\frac{\partial}{\partial \Omega}\left(\Omega\, \mathcal{E}\left[\frac{N}{\Omega}\right]\right)$$

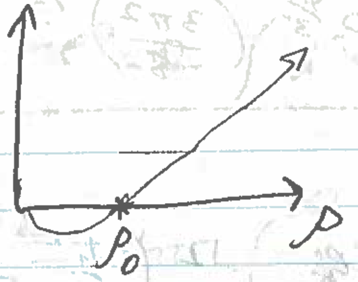
$$\boxed{P = -\mathcal{E}[\rho] + \frac{d\mathcal{E}[\rho]}{d\rho}\rho}$$

$$P = \rho^2 \frac{d}{d\rho}\left(\frac{\mathcal{E}}{\rho}\right) = \rho^2 \frac{d}{d\rho}\left[A\rho^{2/3} - B\rho^{1/3}\right]$$

$$= \rho^2\left(\tfrac{2}{3}A\rho^{-1/3} - \frac{B}{3}\rho^{-2/3}\right)$$

$$= \tfrac{2}{3}A\rho^{5/3} - \frac{B}{3}\rho^{4/3}$$

$P(\rho)$



densities $> \rho_0$, pressure positive, $< \rho_0$, pressure negative

stable equilibrium

$$P=0 \text{ at } \rho^{1/3} = \rho_0^{1/3} = \frac{e^2 m}{\hbar^2} \frac{5}{6(3\pi^2)^{1/3}}$$

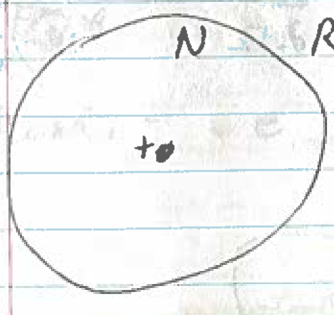
$$\approx \frac{1}{3a_0}$$

$$a_0 = \frac{me^2}{\hbar^2} - \text{Bohr radius},$$

electron gas stable at density $\sim \left(\frac{1}{Å}\right)^3$

---

eg



N electrons around central + charge.

$$E_{direct} \simeq \frac{N^2 e^2}{R}$$

$$E_{exchange} \approx -R^3 e^2 \left(\frac{N}{R^3}\right)^{4/3}$$

$$\approx \frac{-e^2 N^{4/3}}{R}$$

$$\frac{E_{exchange}}{E_{direct}} \approx N^{-2/3} << 1$$

when $N >> 1$

(exchange not as important at higher density

Physical interpretation for exchange

assume not e^2/r, but arbitrary $v(r)$

$$\langle V \rangle = \frac{1}{2} \sum_{\substack{km \\ k'm'}} \langle km\, k'm' | v | km\, k'm' - k'm'\, km \rangle$$

$$= \frac{1}{2} \sum_{\substack{km \\ k'm'}} \int d r^3 d r'^3 \frac{e^{-ik\cdot r}}{\sqrt{\Omega}} \frac{e^{-ik'\cdot r'}}{\sqrt{\Omega}} v(r-r')$$

$$\left[\frac{e^{ik\cdot r} e^{ik'\cdot r'}}{\sqrt{\Omega}} - \delta_{mm'} \frac{e^{ik\cdot r'} e^{ik' \cdot r}}{\Omega} \right]$$

$r, r' \Rightarrow R = \frac{r+r'}{2}$

$S = r - r'$

$d^3R\, d^3S = d^3r\, d^3r'$

$$= \frac{1}{2\Omega^2} \sum_{\substack{km \\ k'm' \\ \text{occupied}}} \int \underbrace{d^3S\, d^3R}_{\Omega}\, v(S) \underbrace{\left[1 - \delta_{mm'} e^{ik\cdot s} e^{-ik'\cdot s} \right]}_{}$$

Σ gives total # of particles twice

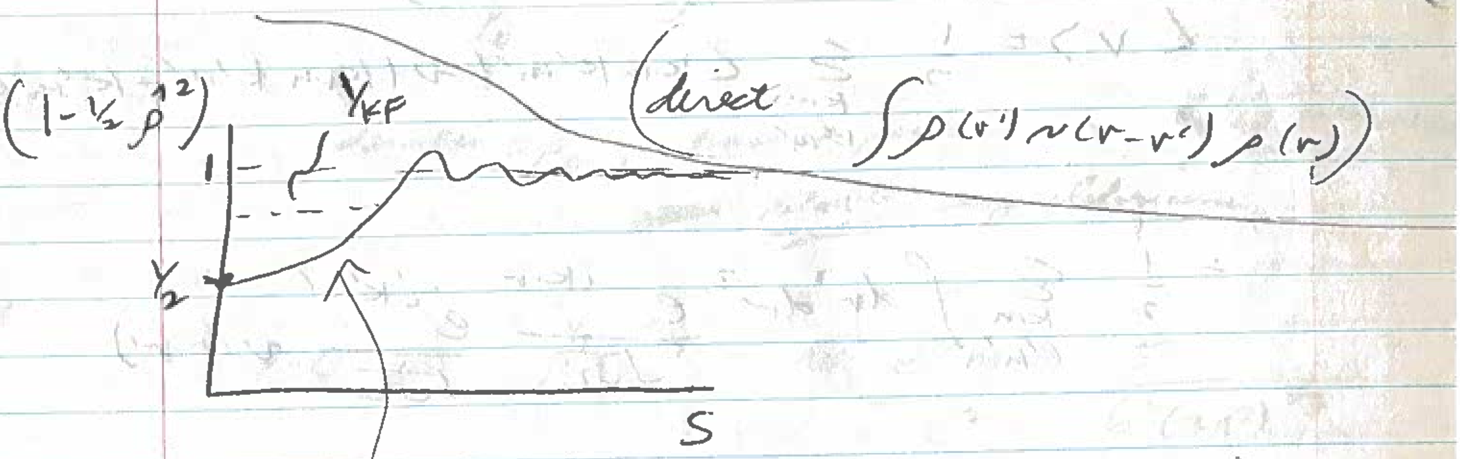
$$\langle V \rangle = \frac{\Omega}{2} \left[\frac{N^2}{\Omega^2} \int (d^3 s) v(s) - 2 \int (d^3 s) \left(\frac{1}{\Omega} \sum_k e^{ik\cdot s} \right) \left(\frac{1}{\Omega} \sum e^{ik'\cdot s} \right) \right]$$

$\frac{1}{2} \rho\, \rho^1(k_F s)$

$\rho^1(k_F s)$

$= \frac{3 j_1(x)}{x}$

$$\langle V \rangle = \frac{\Omega}{2}\int d^3s\, \rho^2 v(s)\left[1 - \frac{1}{2}\hat{\rho}^2(ks)\right]$$



Pauli hole. e^-'s cannot get arbitrarily close to each other.

e^-'s of same spin can't get on top of each other.

range is $\sim 1/k_F$

Thomas - Fermi. (Dirac - von Weizsacker)

(can write stuff in terms of 1 function; has broad mediocre applicability) late 1920's.

In H-F, must deal with all of individual ψ_i's.

T-F, "macroscopic" description, only the density $\rho(r) = \sum_i |\psi_i|^2$ is available

In H-F,

$$E = \frac{\hbar^2}{2m} \int d^3r \sum_i^N |\nabla \psi_i|^2 \quad \text{kinetic}$$

$$- \int d^3r \, \rho(r) \frac{Ze^2}{r} \quad \text{nuclear-electrons.}$$

$$+ \frac{e^2}{2} \int d^3r \, d^3r' \, \rho(r) \frac{1}{|r-r'|} \rho(r')$$

$$+ E_{exchange}.$$

demanded E to be min. w.r.t. 1-particle wave functions

involves ρ, but also $\nabla\psi$,

and $E_{exchange}$ involves ψ's explicitly

T-F, replace kinetic energy density, and exchange energy density, by the ~~density~~ energy of an electron gas. at density $\rho(r)$

$$E = \int d^3r \left[A\rho^{5/3} - \frac{Ze^2}{r}\rho(r) \right]$$

kinetic — nucleon attraction

$$+\frac{e^2}{2}\int d^3r\, d^3r' \frac{\rho(r)\rho(r')}{|r-r'|} - \int B\rho^{4/3} d^3r$$

T-F — exchange. Dirac

drop this for now. it is small.

Find best density, so that E is minimized,

subject to $\int \rho(r)\, d^3r = Z$, total # e's (neutral atom)

$E[\rho]$

Suppose make small change $\delta\rho(r)$ demand

$$\delta\left[E - \lambda \int d^3r\, \rho(r)\right] = 0$$

Lagrange multiplier

equal integrals

$$= \int d^3r \left(\frac{5}{3} A\rho^{2/3} - \frac{Ze^2}{r} + \Phi(r) - \lambda \right)\delta\rho(r) -$$

$$\Phi(r) = e^2 \int \frac{d^3r'\, \rho(r')}{|r-r'|}$$

(potential generated by electrons

$$\frac{5}{3} A \rho^{2/3} - \frac{Ze^2}{r} + \Phi(r) - \lambda = 0$$

$\boxed{3/5}$ Remember

H-F:

$$E = K + U + V$$

$$= \int d^3r \sum_{i=1}^{N} \frac{\hbar^2}{2m} (\nabla \psi_i)^2$$

$$+ \int d^3r \left(-\frac{Ze^2}{r} \rho(r) \right)$$

$$+ \frac{1}{2} \int d^3r \, d^3r' \, \frac{\rho(r) \, e^2 \rho(r')}{|r - r'|} \quad + \text{Exchange}$$

$$\left(\rho = \sum_{i=1}^{N} |\psi_i|^2 \right)$$

Thomas-Fermi : $K \to K_{\text{free electron gas}}$

$$= \int d^3r \, A \rho^{5/3}(r) + \int d^3r \left(-\frac{Ze^2}{r} \rho(r) \right)$$

$$+ \frac{1}{2} \int d^3r \, d^3r' \, \frac{\rho(r) \, e^2 \rho(r')}{|r - r'|} = E[\rho]$$

remember $A = \frac{\hbar^2}{m} \frac{1}{10\pi^2} (3\pi^2)^{5/3}$

find ρ to minimize energy

with constraint $\int \rho(\underset{\sim}{r}) \, d^3r = Z$

$$\delta \left[E - \lambda \int d^3r \, \rho(\underset{\sim}{r}) \right] = 0$$

Result is:

$$\frac{5}{3} A \rho^{2/3} - \frac{Ze^2}{r} + \varphi(r) - \lambda = 0$$

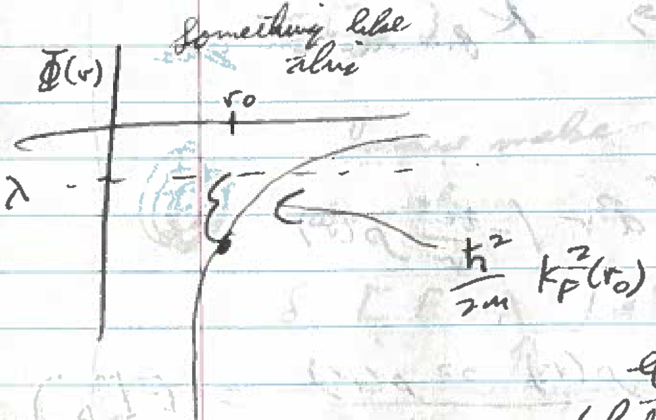
$$\left(\begin{array}{l} \varphi(r) = \displaystyle\int \frac{e^2}{|r-r'|} \rho(r')\, d^3r' \\ \\ \text{equivalently} \quad \nabla^2 \varphi = -4\pi e^2 \rho(r) \end{array} \right)$$

$$\frac{5}{3} A \rho^{2/3} \equiv \frac{\hbar^2}{2m} k_F^2(r) \quad \text{where} \quad \frac{k_F^3(r)}{3\pi^2} = \rho(r)$$

K.E. $\rightarrow$ $$\frac{\hbar^2 k_F^2}{2m} = \lambda - \varphi + \frac{Ze^2}{r} = \lambda - \Phi$$

$$\Phi = \underbrace{-\frac{Ze^2}{r}}_{\text{nuclear part}} + \underbrace{\varphi}_{\text{electron part}}$$

of potential.



effectively
(fill up all states up to the λ)

(λ is the chemical potential)

~~MAX energy of~~

ρ big when $\lambda - \Phi$ big (i.e. potential deep)

ρ small when $\lambda - \Phi$ small density in terms of potential

$$\rho = \left(\frac{3}{5A} (\lambda - \Phi) \right)^{3/2}$$

know $\nabla^2 \Phi = \nabla^2 \left(-\frac{Ze^2}{r} + \varphi \right) = -Ze^2 \nabla^2 \left(\frac{1}{r}\right) + \nabla^2 \varphi$

$$= -Ze^2 4\pi \delta^3(\vec{r}) - 4\pi e^2 \rho(r)$$

so $\boxed{\nabla^2 \Phi} = -Ze^2 4\pi \delta^3(r) - 4\pi e^2 \left(\frac{3}{5A} (\lambda - \Phi) \right)^{3/2}$

dif eq.

finished have Φ in terms of λ

$$= \boxed{-4\pi e^3 \left(\frac{3}{5A} (\lambda - \Phi) \right)^{3/2}} \quad \text{at } r \neq 0$$

$$\chi \equiv \lambda - \Phi$$

$$\boxed{\nabla^2 \chi = \beta \chi^{3/2}} \qquad \beta = \frac{4}{3\pi} e^2 \left(\frac{2m}{\hbar^2} \right)^{3/2}$$

choose $\lambda = 0$

$\chi = -\Phi$ find solution which $\to 0$ as $r \to \infty$ faster than $1/r$

(nucleus totally screened)

B.C. on χ

$\chi \underset{r \to \infty}{\to} 0$ faster than $\frac{1}{r}$

$$\chi \underset{r \to 0}{\to} \frac{Ze^2}{r}$$

for $\lambda = 0$

$$-\Phi = \chi \equiv \frac{Ze^2}{r}\psi(r)$$

(gets rid of $\frac{1}{r}\frac{d}{dr}$)

$$\psi(r) \xrightarrow[r\to 0]{} 1$$

$$\psi(r) \xrightarrow[r\to\infty]{} 0$$

$$\nabla^2 \chi = \beta \chi^{3/2} \Rightarrow \frac{Ze^2}{r}\frac{d^2}{dr^2}\psi(r) = \beta\left(\frac{Ze^2}{r}\right)^{3/2}\psi^{3/2}$$

(assuming spherically symmetric potential)

$$\frac{d^2\psi}{dr^2} = \beta\,(Ze^2)^{1/2}\,\frac{\psi^{3/2}}{r^{1/2}}$$

scale out dimensions $r = \alpha x$

$$\frac{1}{\alpha^2}\frac{d^2\psi}{dx^2} = \frac{\beta(Ze^2)^{1/2}}{\alpha^{1/2}}\frac{\psi^{3/2}}{x^{1/2}}$$

$$\psi'' = \alpha^{3/2}\beta(Ze^2)^{1/2}\frac{\psi^{3/2}}{x^{1/2}}$$ define α so

$$\psi'' = \frac{\psi^{3/2}}{x^{1/2}}$$

$$\alpha = \frac{1}{Z^{1/3}}\left(\frac{a_0}{4}\right)\left(\frac{9\pi^2}{2}\right)^{1/3}$$

$a_0 = \frac{\hbar^2}{me^2}$

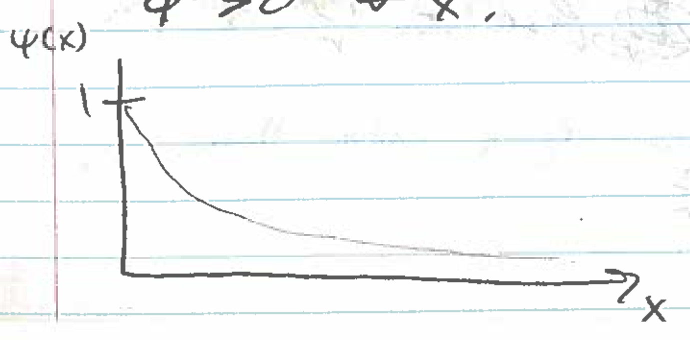
$\psi(x=0) = 1$ $\psi(x=\infty) = 0$

notice size of atom $\sim \frac{1}{Z^{1/3}}$

cannot do analytically

but have 1 function that describes all atoms

$\psi'' > 0 \;\forall x$.



Tables exist

$$\psi'(0) = -1.59\ldots$$

$$\psi(x) \xrightarrow{x\to\infty} \frac{144}{x^3}$$

$$E = K + U + V$$

$$= \int A\rho^{5/3} + \int \frac{-Ze^2}{r}\rho + \frac{1}{2}\int d^3r\, d^3r' \frac{\rho(r)\, e^2 \rho(r')}{|r-r'|}$$

Simplify expression.

Original T-F:

$$\frac{5}{3} A\rho^{2/3} - \frac{Ze^2}{r} + \varphi = 0$$

multiply by $\rho(r)$, integrate d^3r

$$\Rightarrow \boxed{\frac{5}{3}K + U + 2V = 0} \quad (1)$$

Suppose $\rho_0(r)$ is the T-F solution.

consider a density $\rho_\lambda(r) = \lambda^3 \rho_0(\lambda r)$

(not the old λ) (scale transformation)

$$\int d^3r\, \rho_\lambda(r) = \int d^3r\, \lambda^3 \rho_0(\lambda r) = \int d^3 \rho_0(x) = Z$$

if compute $E(\lambda) = E[\rho_\lambda(r)]$

$$\frac{\partial E}{\partial \lambda} = 0 \quad \text{at } \lambda = 1$$ (since then have the solution)

$$E(\lambda) = \int A\lambda^5 \rho_0^{5/3}(\lambda r)\, d^3r$$

$$- \int \frac{Ze^2}{r} \lambda^3 \rho_0(\lambda r)\, d^3r$$

$$+ \frac{1}{2} \int d^3r\, d^3r' \, \frac{\lambda^3 \rho_0(\lambda r)\, \lambda^3 \rho_0(\lambda r)}{|r-r'|}$$

$$= \lambda^2 K\Big)_{\rho=\rho_0} + \lambda U + \lambda V$$

$$\frac{\partial}{\partial\lambda} E(\lambda)\Big)_{\lambda=1} = 0 \qquad ② \ \boxed{K = -\frac{1}{2}(U+V)}$$

(virial theorem)

①, ② $\quad \frac{5}{3}K + U + 2V = 0$

$$2K + U + V = 0$$

$$\Rightarrow \quad K = -\frac{3U}{7} \qquad V = -\frac{U}{7}$$

$$\boxed{E} = K + U + V = -\frac{3U}{7} + U - \frac{U}{7} = \boxed{\frac{3U}{7}}$$

interac between nucle electron

$$U = -Ze^2 \int d^3r \, \frac{\rho(r)}{r} \qquad \varphi(r=0) = e^2 \int d^3r' \, \frac{\rho(r')}{r'}$$

$$= -Z\,\varphi(0)$$

$$\boxed{E = -\frac{3}{7} Z\,\varphi(0)}$$

$$\varphi(r) = \Phi + \frac{Ze^2}{r} = -X + \frac{Ze^2}{r}$$

X is negative of total potential =

$$\varphi(r) = (1-\psi)\left(\frac{Ze^2}{r}\right)$$

but $\psi(r) = 1 + \left.\frac{\partial\psi}{\partial r}\right)_{r=0} r + \ldots\ldots$ Taylor

$$\varphi(0) \approx -Z\, e^2 \left.\frac{\partial\psi}{\partial r}\right)_{r=0}$$

$$= -\frac{Ze^2}{\alpha}\,\psi'(0)$$ 1.59 . . .

$$E = -\tfrac{3}{7} Z \varphi(0)$$

(from definition of α

$$E = Z^{7/3}\,\frac{e^2}{a_0}\,\frac{12}{7}\left(\frac{2}{9\pi^2}\right)^{1/3}\psi'(0)$$

$$= -.770\, Z^{7/3}$$ (in Hartrees $= e^2/a_0$ $= 27\,\mathrm{ev}$)

Notice ($Z=1$, $-.77 \neq -.5$)

This is exact as $Z \to \infty$. (from H-F calculation)

Can take $\Phi(r)$ compare to H-F potential, works well.

$Z = 18$

$$E_{TF} = -651$$

$$E_{HF} = -527$$

3/8

$E = -.77 \; Z^{7/3}$ hartrees

Intuitive justification for $Z^{7/3}$

consider an atom in which electrons <u>don't</u> interact with each other

all are in hydrogenic orbitals

$n=3$ ——— $g = 18$ $\qquad E_n = -\frac{Z^2}{n^2}\, Ry$

$n=2$ ——— $g = 8$

$\qquad g_n = 2n^2$

1s ——— $g = 2$

degeneracy

Imagine $\exists$ Z electrons, Z very large

Build this non-interacting atom by filling shells up to $n = N$

$$Z = \sum_{n=1}^{N} g_n = \sum_{n=1}^{N} 2n^2 \approx \tfrac{2}{3} N^3$$

$$N = \left(\frac{3Z}{2}\right)^{1/3}$$

$$E = \sum_{n=1}^{N} g_n E_n = \sum_{n=1}^{N} (2n^2)\left(-\frac{Z^2}{n^2}\right) Ry$$

$$= -2 Z^2 Ry \left(\sum_{n=1}^{N} 1\right)$$

$$= -2 N Z^2 Ry$$

$$= - N Z^2 \text{ Hart} \qquad N = \left(\frac{3Z}{2}\right)^{1/3}$$

$$= -\left(\frac{3}{2}\right)^{1/3} \boxed{Z^{7/3}} \text{ Hartree}$$

$\sim Z^{7/3}$ intuitively

$$= -1.15 \; Z^{7/3}$$

close to Thomas-Fermi $\quad = -.770 \; Z^{7/3}$

Decay of Atoms: