6 Atoms & Molecules & Solids

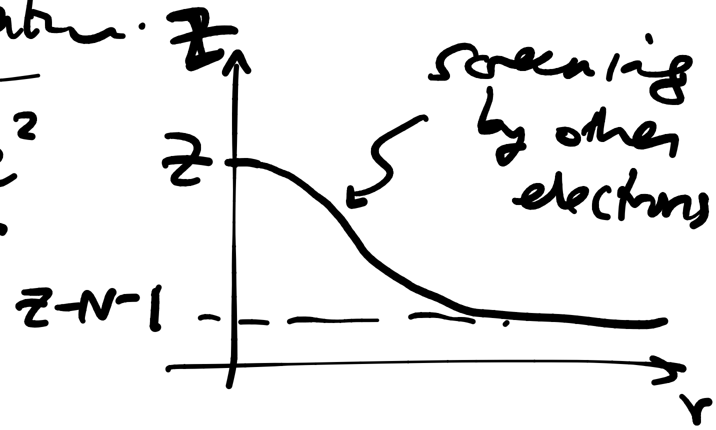
$$H = \sum_{i=1}^{N} \frac{p_i^2}{2\cancel{m}} + \sum_{i}^{N} V_{nucl}(r_i) + \sum_{ij} V_{int}(r_{ij})$$

$$V_{nucl}(r) = \frac{-Z}{|r|} \qquad V_{int}(r) = \frac{1}{|r|}.$$

atomic units: $e = m = 0.$

Central Force Approximation.

$$V_{eff}(|r|) = -\frac{Z(r)e^2}{r}$$



Hydrogen reminder:

$$H = \frac{p^2}{2} - \frac{Z}{r}.$$

(n, l, m) $\quad n = 1, 2, 3 \ldots$

$$\begin{cases} l = 0 \ldots n \\ m = -l, -l+1 \ldots l-1, l \end{cases}$$

	s	p	d	f
l	0	1	2	3

$$E = E_n = -\frac{Z^2}{2n^2}$$

huge degeneracy.

$$H_{atom} = H_0 + \underbrace{\sum_{ij} V_{int}(r_{ij})}_{\text{perturbation.}}$$

$\longrightarrow$ large degeneracy

eg between 2s & 2p

3s 3p 3d

. . . . .

1s

2s 2p

3s 3p 3d

4s 4p 4d 4d

Helium groundstate ($Z=2$)

H_0 : $\Psi(r_1\sigma_1\, r_2\sigma_2) = \psi_{100}(r_1)\,\psi_{100}(r_2)$ $\times\left(\dfrac{\delta_{\sigma_1\uparrow}\delta_{\sigma_2\downarrow} - \delta_{\sigma_1\downarrow}\delta_{\sigma_2\uparrow}}{\sqrt{2}}\right)$

$$\begin{cases} E_0^{(0)} = 2\left(-\dfrac{Z^2}{2}\right) = -4. \\ E_0^{expt} = -2.903. \end{cases}$$

$$\Delta E_0^{(1)} = \langle 100|\langle 100|\frac{1}{|r_{12}|}|100\rangle|100\rangle = \frac{5}{8}Z = \frac{5}{4}.$$

$$= \int d^3r_1 \int d^3r_2 \frac{\psi_{100}^2(r_1)\,\psi_{100}^2(r_2)}{|r_1 - r_2|}$$

$$\frac{1}{|r_{12}|} = \frac{1}{r_>}\sum_{\ell=0}^{\infty}\left(\frac{r_<}{r_>}\right)^{\ell} P_\ell(\cos\theta)$$

Incorporate screening:

$$\psi_{100}(r) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr/a_0} \rightsquigarrow \psi(r) \propto e^{-\lambda r/a_0}$$

$$= \sqrt{\frac{Z^3}{\pi}}\, e^{-Zr}$$

vary λ.

$$\langle H \rangle_\lambda = Z^2 - 2Z\lambda + \frac{5}{8}\lambda$$

min at $\lambda = Z - \frac{5}{16}$

$$\geq -\left(Z - \frac{5}{16}\right)^2 = -2.85.$$

lesson: screening!

Helium excited states:

one $e^- \to 1s$ $\quad \alpha \to 2$

other $\to \underbrace{2s}_{\substack{l=0 \\ 2}}$ or $\underbrace{2p}_{\substack{l=1 \\ 3\cdot 2=6}}$. $\quad \beta$ $\quad \to 8$

16 states!

$$\Psi_{S/A}(r_1, r_2) = \frac{1}{\sqrt{2}}\left(\psi_\alpha(r_1)\,\psi_\beta(r_2) \pm \psi_\beta(r_1)\,\psi_\alpha(r_2)\right) \otimes \text{spin}$$

ie $\psi_S \otimes (\text{singlet})$ $\quad \psi_A \otimes (\text{triplet})$

$$E_{S/A} = \epsilon_\alpha + \epsilon_\beta + I \pm J$$

$$J = \iint \frac{\psi_\alpha(r_1)\psi_\beta(r_2)\,\psi_\beta(r_1)\psi_\alpha(r_2)}{|r_1 - r_2|}$$

$$= \iint \underbrace{\psi_\alpha(r_1)\psi_\beta(r_1)}_{4\pi\rho(r_1)} \frac{1}{|r_1 - r_2|} \underbrace{\psi_\alpha(r_2)\psi_\beta(r_2)}_{4\pi\rho(r_2)}$$

<u>claim</u>: <u>$J \geq 0$</u>.

<u>Pf</u>: $\nabla^2\phi = -4\pi\rho$ is solved by

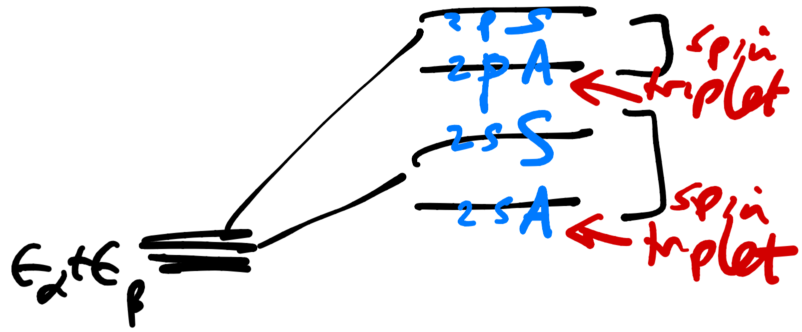
$$\phi(r) = \int \frac{\rho(r')\,d^3r'}{|r - r'|}$$

$$J = \int d^3r\, \phi(r)\, 4\pi\rho(r) = -\int \phi \nabla^2 \phi$$

$$\overset{\text{IBP}}{=} \int (\vec{\nabla}\phi)^2 \geq 0.$$

$\Rightarrow$ AS (triplet) has lower energy

$\psi_A(r_1 = r_2) = 0$. avoids the region where $\frac{1}{|r_1 - r_2|}$ is large.



$$(I \pm J)_{2s} < (I \pm J)_{2p}$$

large l have less support near $r=0$.

screening $\Rightarrow$ aufbau. (sees smaller Z.)

6.1 Self-consistent Mean-field Theories

Hartree: $\Psi(r_1 .. r_N) \overset{?}{=} \psi_{\alpha_1}(r_1) \dots \psi_{\alpha_N}(r_N)$

$(\alpha = (n, l, m, \sigma))$

Treat the whole $\{\psi_\alpha(r)\}$ as variational param.

$$\langle H \rangle = \sum_{i=1}^{N} \int d^3r \left(\frac{\hbar^2}{2m} |\vec\nabla \psi_{\alpha_i}|^2 - \frac{Z}{r} |\psi_\alpha(r)|^2 \right)$$

$$+ \sum_{i<j} \int dr \int dr' \, \frac{\psi^*_{\alpha_i}(r) \psi^*_{\alpha_j}(r') \psi_{\alpha_j}(r) \psi_{\alpha_i}(r)}{|r - r'|}$$

minimize wrt $\{\psi_\alpha\}$:

$$F[\psi] = \langle H \rangle - \sum_i \epsilon_i \left(\int |\psi_{\alpha_i}|^2 - 1 \right)$$

$$0 = \frac{\delta F}{\delta \psi^*_{\alpha_i}} = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Z}{r} + U_{\alpha_i}(r)\right)\psi_{\alpha_i}(r) - \epsilon_i \psi_{\alpha_i}(r) \quad (1)$$

$$U_{\alpha_i}(r) = \sum_{j\neq i}\int d^3r' \, \frac{|\psi_{\alpha_i}(r')|^2}{|r-r'|}. \quad (2)$$

$$V_{eff} = -\frac{Z}{r} + U_\alpha(r).$$

Solve by iteration:

(1) guess U. eg $U=0$ or from hydrogen

(2) solve (1) for $\{\psi_{\alpha_i}\}$ w/ lowest ϵ_i

(3) use (2) to make $U_{\alpha_i}(\vec{r})$

CFA: $U_{\alpha_i}(|r|) \longleftarrow \int \frac{d\Omega}{4\pi} U_{\alpha_i}(\vec{r})$

(4) GOTO step (2).

(**Hint:** $U_{new} = x\, U_{old} + (1-x)\, U_{new}$)

$$E_0 \le \langle H \rangle \underset{\text{plug } ①}{=} \sum_i \epsilon_i - \sum_{j\neq i} \iint \frac{|\psi_{\alpha_i}(r_1)|^2 |\psi_{\alpha_j}(r_2)|^2}{|r_1 - r_2|}$$

actual g.s.

Hartree-Fock (Slater): $|\Psi\rangle \overset{?}{=} a^\dagger_{\alpha_1} \cdots a^\dagger_{\alpha_N} |0\rangle$

$$\Psi(r_1\sigma_1 \dots r_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_{\alpha_1}(r_1) & \cdots & \psi_{\alpha_1}(r_N) \\ \vdots & & \\ \psi_{\alpha_N}(r_1) & \cdots & \psi_{\alpha_N}(r_N) \end{pmatrix}$$

Wick:

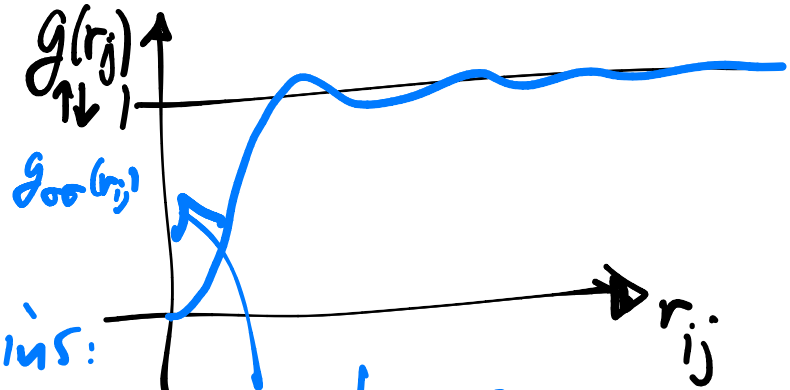
$$\langle a_1^\dagger a_2^\dagger a_3 a_4 \rangle_\Psi$$

$$= \quad - \quad +$$

$$= \underbrace{\langle a_1^\dagger a_4 \rangle \langle a_2^\dagger a_3 \rangle}_{\text{Hartree}} - \underbrace{\langle a_1^\dagger a_3 \rangle \langle a_2^\dagger a_4 \rangle}_{\text{Fock}} + \cancel{\langle a_1^\dagger a_2^\dagger \rangle \langle a_3 a_4 \rangle} \to 0$$

$$\langle H \rangle = \langle H \rangle_{\text{Hartree}} - \sum_{ij} \underbrace{J_{\alpha_i \alpha_j}}_{\geq 0} \delta_{\sigma_i \sigma_j}$$

why fermi state has lower energy?



for like spins:

exchange hole lowers the Coulomb energy $\left(+ \frac{1}{|r_{ij}|} \right)$

$\Rightarrow$ having aligned spins lowers energy.

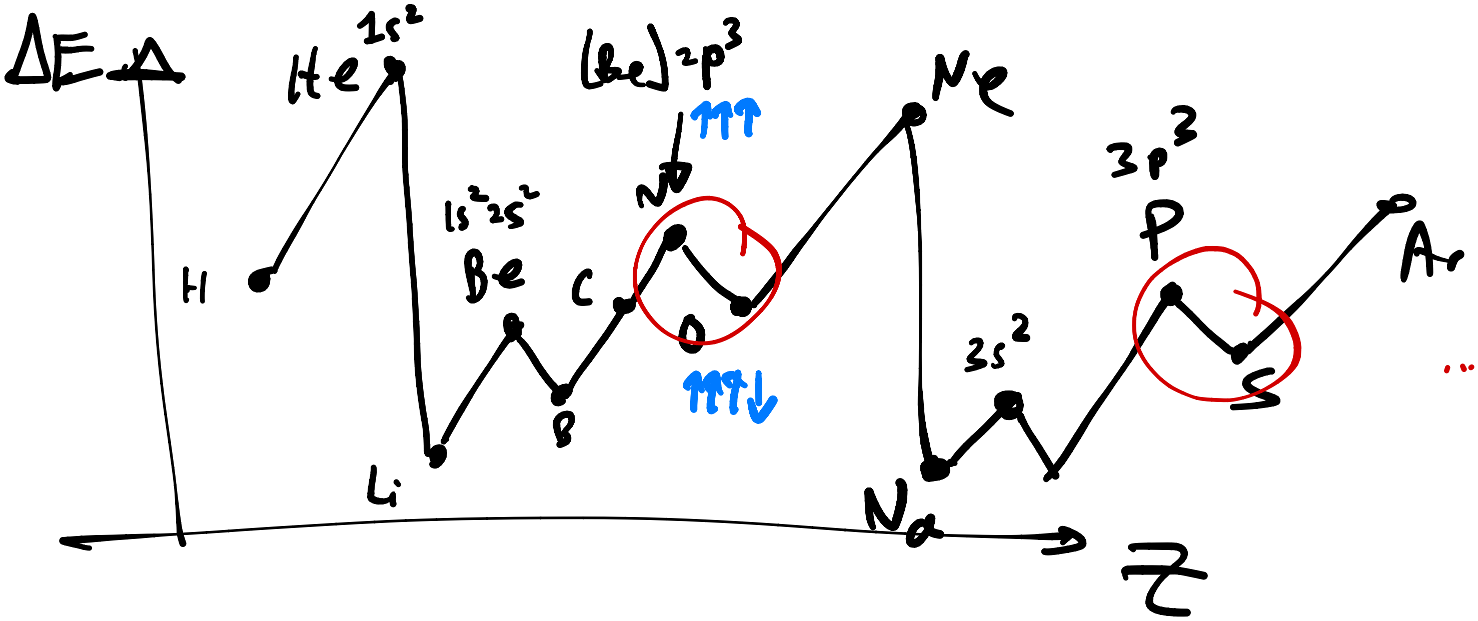
solids $\Longrightarrow$ (Slater) ferromagnetism

chemistry $\Longrightarrow$ Hund's Rules $\Longrightarrow$ half-filled shell is stable

e^- binding energy (Z) : $= \Delta E(Z)$

p-shell: $\uparrow\uparrow\uparrow$ $m_z = -1, 0, 1$ $\Longrightarrow$ gain exchange energy $-J_{ij}$

vs: add one more: $\uparrow\uparrow\uparrow\downarrow$ $-1\ 0\ 1\ \uparrow$ $m_z = 0$. $\Longrightarrow$ don't.



$$H_{atom} = \sum_{r\sigma} a^\dagger_{r\sigma} \left(-\frac{\nabla^2}{2m} + V_{ext}(r) \right) a_{r\sigma}$$

$$+ \sum_{\substack{r r' \\ \sigma \sigma'}} a^\dagger_{r\sigma} a^\dagger_{r'\sigma'} V(r-r') a_{r'\sigma'} a_{r\sigma}$$

$$\equiv \hat{T} + \hat{V}_{ext} + \hat{V}$$

approx gs by $|\psi\rangle = a^\dagger_{\alpha_1} \cdots a^\dagger_{\alpha_N} |0\rangle$

is the gs. of some quadratic hamiltonian

$$H_{MF} = \hat{T} + \hat{V}_{ext} + \sum_r a^\dagger_r U(r) a_r$$

$$+ \sum_{rr'} a^\dagger_r \Gamma_{rr'} a_{r'}$$

let $|MF\rangle$ be the g.s. of H_{MF}

$$\langle MF|\hat{H}_{atom}|MF\rangle \overset{\text{Wick}}{=} \langle T\rangle + \langle V_{ext}\rangle + \sum_{r<r'} V(r-r')\Big(\langle a_r^\dagger a_r\rangle\langle a_{r'}^\dagger a_{r'}\rangle - \langle a_r^\dagger a_{r'}\rangle\langle a_{r'}^\dagger a_r\rangle \cancel{+ \langle a^\dagger a^\dagger\rangle\langle a a\rangle}\Big)$$

vary the state

$$0 \overset{!}{=} \delta\langle H_{atom}\rangle$$

$$= \delta\langle T\rangle + \delta\langle V_{ext}\rangle + 2\sum_{rr'} V_{rr'}\Big(\delta\langle a_r^\dagger a_r\rangle\langle a_{r'}^\dagger a_{r'}\rangle - \delta\langle a_r^\dagger a_{r'}\rangle\langle a_{r'}^\dagger a_r\rangle\Big)$$

automatic

$$0 = \delta\langle H_{MF}\rangle = \delta\langle T\rangle + \delta\langle V_{ext}\rangle + \sum_r U(r)\,\delta\langle a_r^\dagger a_r\rangle + \sum_{r'r} \Gamma_{rr'}\,\delta\langle a_r^\dagger a_{r'}\rangle$$

$$\begin{cases} U(r) = \sum_{r'} V_{rr'}\langle a_{r'}^\dagger a_{r'}\rangle \\ \Gamma(rr') = V_{rr'}\langle a_{r'}^\dagger a_r\rangle \end{cases}$$

$$0 = \frac{\delta}{\delta \psi^*_{\alpha_i}} \left(\langle H \rangle - \sum_i \epsilon_i \left(\int |\psi_\alpha|^2 - 1 \right) \right)$$

$$= \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Z}{r} + V_{\alpha_i}(r) \right) \psi_{\alpha_i}(r)$$

$$- \sum_j \delta_{\sigma_i \sigma_j} \int d^3 r' \frac{\psi^*_{\alpha_j}(r') \psi_{\alpha_i}(r')}{|r - r'|} \psi_{\alpha_j}(r)$$

$$- \epsilon_i \psi_{\alpha_i}(r)$$

extra Fock term acts as an attractive potential for same-spin electrons.

Thomas-Fermi ($Z > 10$): idea is: treat e^- as a fluid. determine $n(r)$.

recall free e^- gas: $dn = 2 \dfrac{d^3 p}{e^{\frac{\epsilon_p - \mu}{T}} + 1} \equiv 2 f(p) d^3 p$

$$f(p) \xrightarrow{T \to 0} \begin{cases} 0 & |p| > p_F \\ 1 & |p| < p_F. \end{cases} \rightarrow n = 2 \int d^3 p \, f(p) \overset{T=0}{=} p_F^3 / 3\pi^2.$$

$$u = 2\int d^3p\, \frac{p^2}{2m} f(p) \overset{T=0}{=} \cdots n^{5/3}.$$

Subject to slowly-varying $\Phi(r)$.

$$V(r) = -e\,\Phi(r).$$

only $\mu + V(r)$ appears in H.

$$\mu \to \mu + V(r)$$

local eqbm $\Rightarrow$ μ is const

$$\mu = \epsilon_F = \frac{p_F^2}{2m} \rightsquigarrow \mu = \underline{\underline{\frac{p_F^2(r)}{2m} - e\Phi(r)}}$$

$$\Rightarrow p_F = p_F(r).$$

given Φ

$$\Rightarrow n(r) = 2\int_0^{p_F(r) = 2m\sqrt{e\Phi + \mu}} \frac{p^2\, dp \cdot 4\pi}{(2\pi)^3}$$

$$= \frac{(2m)^{3/2}}{3\pi^2} \left(e\,\Phi(r) + \mu\right)^{3/2}.$$

also: $\nabla^2 \Phi = \underbrace{e\,n(r)}_{e^-} - \underbrace{Ze\,\delta^3(r)}_{\text{nucleus.}}$

let $e\Phi_0 \equiv -e\Phi + \mu$

$$\boxed{\nabla^2 \Phi_0 = e\alpha\, \Phi_0^{3/2}}$$

w/ bc: $\Phi_0(r) \xrightarrow{r\to 0} \frac{Ze}{4\pi r}$

$\Phi_0(r) \xrightarrow{r\to\infty} \ldots$ depends on $\underline{Z-N}$.

$\overset{\text{scaling}}{\Longrightarrow}$ size of an atom $\propto Z^{-1/3}$.

TF Screening: apply small $\delta\phi(r)$.

$$-\nabla^2 \delta\phi = -4\pi e\, \underline{n_{ind}(r)}$$ ← induced change in $n(r)$.

linear response: $n_{ind}(q,\omega) = -\chi(q,\omega)\, e\,\delta\phi(q\omega)$

↑ charge compressibility

TF: $n(r) = \alpha\left(\mu + e(\Phi + \delta\phi)\right)^{3/2}$

$$= n_0 + \underbrace{\frac{\partial n}{\partial \mu}}\, e\delta\phi + O(\delta\phi^2)$$

$\rightarrow n_{ind} = -\chi_0\, e\,\delta\phi$ $\qquad \chi_0 = -\partial_\mu \int^\mu d\epsilon\, g(\epsilon)$

$= -g(\epsilon)$.

$\Rightarrow -\nabla^2 \delta\phi = 4\pi e^2 \chi_0 \delta\phi$

solve for $\delta\phi$ $\Longrightarrow$ $\delta\phi(r) \sim \dfrac{e^{-q_{TF} r}}{r}$

$$q_{TF}^2 = 4\pi e^2 |\chi_0| .$$

<u>Warnings</u>: ① In a real metal

$$\delta\phi \sim \frac{\cos 2k_F r}{r^3} .$$

② true g.s. is not a gaussian state.
(entanglement !)

③ e^- are not at origin!

④ spin-orbit coupling $\sim Z^2$ along columns.