

Atomi

generalità

$$H = \sum_{i=1}^Z \left(\frac{p_i^2}{2m} - \frac{e^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{|r_i - r_j|}$$

Simmetrie e i # quantici generali.

$$[L_i, H] = [S, H] = 0, \quad [P, H] = 0$$

$$[L^2, H] = [S^2, H] = 0, \dots$$

$\Rightarrow$ Stato di un atomo $\sim (L, S)$
con $\# = (2L+1)(2S+1)$

Spin? Statistica di F-D $\Rightarrow$ Non tutte le combinazioni ammesse $\Rightarrow (L, S)$ Multipletti (degen!)

Correzioni relativistiche (e.g. per H):

$$\Delta H = \underbrace{-\frac{p^4}{8m^3c^2}}_{\propto \sqrt{p^2 + m^2c^2}} + \underbrace{\frac{\alpha \hbar}{2m^2c} \frac{(\mathbf{L} \cdot \mathbf{S})}{r^3}}_{\propto \text{Spin-orbita}} + \underbrace{\frac{\pi \alpha \hbar^3}{2m^2c} \delta^3(r)}_{\propto \text{Darwin}}$$

$$\alpha \equiv \frac{e^2}{\hbar c} \sim \frac{1}{137} : \text{cost. di struttura fine.}$$

$$H^{\text{tot}} = H + \Delta H \Rightarrow$$

$$\Rightarrow [L_i, H] \neq 0, [S_i, H] \neq 0.$$

$$\text{Ma } [L^2, H] = [S^2, H] = 0, \quad e$$

$$[J, H] = 0, \quad J = L + S.$$

$$[J^2, H] = 0. \quad \Rightarrow \text{i numeri totali.}$$

$$\text{Sono } \{L, S; J, J_z\}$$

$$(2L+1)(2S+1) \begin{array}{l} \nearrow J=L+S \\ \vdots \\ \searrow J=|L-S| \end{array}$$

Tabelle: l'energia di ionizzazione.
(potenziale)

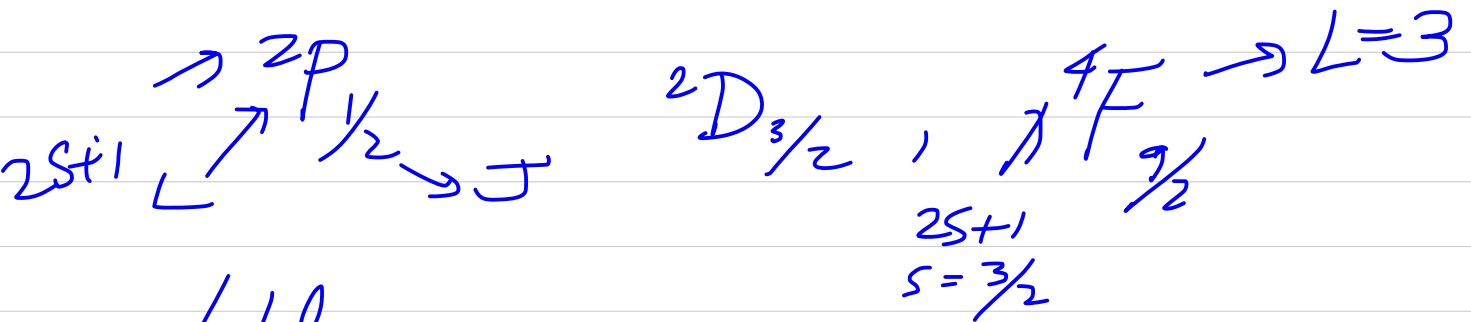
$\Rightarrow$

Preambolo.

- (a) Sforzo per comprendere lo spettro di atomi.
 $\Rightarrow$ MQ. Livelli discreti; emissione, assorbimento di luce, raggi X, tabelle periodiche.
- (b) 1° terreno di prova della MQ.
Calcolo dettagliato e preciso dei livelli.
- (c) Tecniche/metodi di approssimazione.
Sviluppati.
- (d) Dall'atomo, ai nuclei, alle particelle elementari.
Una rivoluzione scientifica senza precedenti.
 $\Rightarrow$ Conoscenza, tecnologie, controllo di sistemi: microscopici $\Rightarrow$ macroscopici.
- (e) Tecnologie contemporanee (smartphone e...)
- (f) Tutto oggi in continua evoluzione
- tecnologico
- in gravità, cosmologia, fisica
- Nuovo paradigma?

Livelli atomici, da:

1) # quatici f.b.l. (termini spettrali)



orbitali:

$$L = 0, 1, 2, 3, 4 \dots$$

S P D F, G. --

(2) Configurazione elettronica
stato d. Z elettroni

Programma.

(1) App. di elettroni indipendenti.

$$H \approx H_0 = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right)$$

+ Principio
Pauli

(2) Campo efficace $\Rightarrow$ Campo eff. a simmetria
autocompatibile

(3) Raggi X

(4) Approssimazione di Hartree

(5) Hartree-Fock e le interaz. di scambio.

(6) Elettroni equivalenti, Conf. di termine
e multipletti.

(7) Correz. relativistiche / struttura
fine

(8) Atomi in campo magnetico

(9) Teo. semiclassica della radiazione

(10) Coeff. di Einstein

Appr. elettroni indipendenti.

$$H \rightarrow H_0 = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right)$$

$$\Rightarrow \Psi = \frac{1}{N} \sum_{\text{antis.}} (-)^P \prod_i \psi_{n_i, l_i, m_i}(r_i)$$

$$E = \sum E_{n_i, l_i, s_i} = - \frac{Ze^2}{2r_B} \sum_i \frac{1}{n_i^2}$$

$$\text{es. } H_0: E_{(1)}^{\text{He}} = - \frac{2Ze^2}{2r_B} = -4 \left(\frac{e^2}{r_B} \right)$$

$$\begin{aligned} &= -2.75 \quad \text{pert.} \\ &\searrow \quad = -2.85 \quad \text{var.} \\ &\quad \quad = -2.904 \quad \text{Spur.} \end{aligned}$$

L'olletto di schermaggio

3L_1

$$\Psi_{\frac{3}{2}, 1, 1}^{l, m, \uparrow} = \frac{1}{\sqrt{6}} \sum (-)^P \psi_{100}(r_1) \psi_{100}(r_2) \psi_{21m}(r_3) \frac{\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow}{\sqrt{2}} \cdot \frac{2lm}{100}$$

$$\begin{aligned} &= \frac{1}{\sqrt{6}} \left[\psi_{100}(r_1) \psi_{100}(r_2) \psi_{21m}(r_3) (\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow) \right. \\ &\quad - \psi_{100}(r_1) \psi_{21m}(r_2) \psi_{100}(r_3) (\uparrow\uparrow\downarrow - \downarrow\uparrow\uparrow) \\ &\quad \left. - \psi_{21m}(r_1) \psi_{100}(r_2) \psi_{100}(r_3) (\uparrow\downarrow\uparrow - \uparrow\uparrow\downarrow) \right] \end{aligned}$$

In questo appr. Li e' $2^2 \cdot 2 = 8$ volte
degenera.

Energia di ionizzazione

= energia minima necessario per
liberare un elettrone.

$$= \frac{Z^2 e^2}{8\epsilon_B} \stackrel{(Z=3)}{=} \frac{9}{4} E_H \sim 30.6 \text{ eV} \quad \left(\begin{array}{l} \text{app.} \\ \text{el. indip} \end{array} \right)$$

$$cfr = 5.4 \text{ eV} \quad (\text{val. speriment.})$$

$$cfr. = 3.4 \text{ eV} \quad \left(\begin{array}{l} \text{schermaggio totale} \\ \text{"} \\ \text{H} \end{array} \right)$$



Osservazioni:

- (i) App. elettr. indipendenti $\Rightarrow$
Degenerazioni di st. non osservate
- ii) Interaz. tra elettr. importanti,
effetto di schermaggio e carica effettiva
(He)
- (ii') Per Li (atomi alcali),
effetto di schermaggio è dominante

(ii'), (ii'') $\Rightarrow$

Campo efficace, a simmetria
centrale.

- idee elementari
- campo autoconsistente.

Comp efficacia : idea

$$V_{\text{eff}} \quad H + e$$



e^-

$$V_{\text{eff}}(r) = -\frac{e^2}{R} + e^2 \int \frac{3}{4\pi} \frac{|\psi_{100}(r)|^2}{|r-R|}$$

$$\psi_{100} = \frac{1}{\sqrt{\pi}} e^{-r} \left(= \frac{2\sqrt{b}^{-3/2}}{\sqrt{4\pi}} e^{-r/b} \right)$$

$$\frac{1}{|r-R|} = \begin{cases} \frac{1}{R} \sum_{\ell} \left(\frac{r}{R}\right)^{\ell} P_{\ell}(\cos\theta) & r < R \\ \frac{1}{r} \sum_{\ell} \left(\frac{R}{r}\right)^{\ell} P_{\ell}(\cos\theta) & r > R \end{cases}$$

$$e^2 \int \frac{3}{4\pi} \frac{|\psi|^2}{|r-R|} = \int_{r < R} + \int_{r > R} \quad \begin{matrix} \int d\Omega P_{\ell}(\cos\theta) \\ 4\pi \delta_{\ell,0} \end{matrix}$$

$$= e^2 \frac{4\pi}{R} \int_0^R dr r^2 |\psi_{100}|^2 + 4\pi \int_R^{\infty} dr r |\psi_{100}|^2$$

$$= \frac{4e^2}{R} \int_0^R dr r^2 e^{-2r} + 4 \int_R^{\infty} dr r e^{-2r}$$

$$= \frac{4e^2}{R} \left(\left. -\frac{1}{2} e^{-2r} r^2 \right|_0^R + \left. \int_0^R dr r e^{-2r} \right) + \right.$$

$$4 \left(\left. -\frac{1}{2} e^{-2r} r \right|_R^{\infty} + \frac{1}{2} \int_R^{\infty} dr e^{-2r} \right)$$

$$= e^2 \left[-e^{-2R} - \frac{1}{R} (e^{-2R} - 1) \right] = e^2 \left[\frac{1}{R} - \left(\frac{1}{R_B} + \frac{1}{R} \right) e^{-2R/R_B} \right]$$

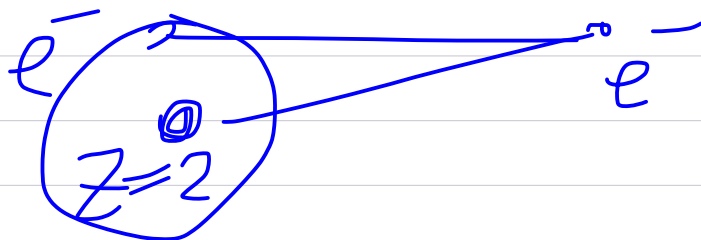
$$V_{eff} = -\frac{e^2}{R} + e^2 \int_0^3 dr \frac{14_{100}^2}{|r-R|}$$

$$= -e^2 \left(\frac{1}{R} + \frac{1}{R_B} \right) e^{-2R/R_B} \rightarrow 0, R \rightarrow \infty$$

$$\rightarrow -\frac{e^2}{R}, R \rightarrow 0$$

OK.

ex. 2 He, V_{eff}



$$V_{eff} = -\frac{2e^2}{R} + e^2 \int_0^3 dr \frac{14_{100}^{(Z=2)^2}}{|r-R|}$$

$$= -\frac{2e^2}{R} + e^2 \left[\left(\frac{1}{R} + \frac{1}{R_B'} \right) e^{-2R/R_B'} + \frac{1}{R} \right]$$

$$= -\frac{e^2}{R} - e^2 \left[\left(\frac{1}{R} + \frac{1}{R_B'} \right) e^{-2R/R_B'} \right]$$

$$\begin{matrix} R \rightarrow \infty & \rightarrow & -\frac{e^2}{R} \\ R \rightarrow 0 & \rightarrow & -\frac{2e^2}{R} \end{matrix} !$$



Li: l'elettrone di valenza

$$H \approx \frac{p^2}{2m} + V_{\text{eff}}(r)$$

$$V_{\text{eff}} = -\frac{3e^2}{r} + 2e^2 \int \frac{dr' |\psi_{100}^{Z=3}(r')|^2}{|r-r'|}$$

$$= -\frac{e^2}{r} - \underbrace{2e^2 \left(\frac{1}{r} + \frac{1}{r_B} \right) e^{-2r/r_B}}_{V_{\text{pert.}}} \quad \left(r_B' = \frac{r_B}{3} \right)$$

$\begin{matrix} \leq \\ \text{Carica} \\ \text{schermata} \end{matrix}$

$$\Rightarrow E^{(\text{val})} = -\frac{e^2}{2.4 r_B} + \langle \psi_{200} | V^{\text{pert}} | \psi_{200} \rangle$$

$$= -\frac{e^2}{8r_B} - 2e^2 \int dr \psi_{200}^* \left(\frac{1}{r} + \frac{3}{r_B} \right) e^{-6r/r_B} \psi_{200}$$

$$\hookrightarrow 2e^2 \frac{1}{8r_B^3} \int dr r^2 \left(2 - \frac{r}{r_B} \right)^2 e^{-r/r_B} \left(\frac{1}{r} + \frac{3}{r_B} \right) e^{-6r/r_B}$$

$$= \frac{e^2}{4} \int dr r^2 (2r)^2 \left(\frac{1}{r} + 3 \right) e^{-7r} = \frac{e^2}{4} \frac{1766}{16807}$$

$$\therefore E^{(\text{val})} \approx \left(\frac{1}{4} + \frac{883}{16807} \right) \frac{e^2}{2r_B} \approx 4.18 \text{ eV}$$

(fr 5.4 spet.
 3.4 scherm. tot
 30.6 el. indip.

Ricapitolando: l'energia (potenziale) di ionizzazione

$$H: + \frac{e^2}{2a_B} \sim \underline{13.8 \text{ eV}} \text{ (esatto.)}$$

$$He: \sim 25 \text{ eV} \text{ (spec.)}$$

$$\text{cfr. } \frac{4e^2}{2a_B} \text{ (app. elett. ind.)} \sim 4 \cdot 14 \sim 56 \text{ eV}$$
$$\frac{e^2}{2a_B} \text{ (total screening)} \sim 14 \text{ eV}$$

$$Li: \sim 5.4 \text{ eV. (spec.)}$$

$$\text{cfr. } \frac{Z^2 e^2}{8a_B} \sim \frac{9}{4} E_H \sim 30.6 \text{ eV} \text{ (elett. ind.)}$$
$$\frac{e^2}{8a_B} \sim \frac{1}{4} E_H \sim 3.4 \text{ eV} \text{ (screen. completo)}$$

Campo eff. e autoconsistente.

$$U_{\text{eff}}(r_i) = -\frac{Ze^2}{r_i} + \sum_{j \neq i} \int d\mathbf{r}_j \frac{e^2 |\psi_j(r_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\begin{aligned} &\rightarrow -e^2/r \quad r \rightarrow \infty \\ &\rightarrow -Ze^2/r \quad r \rightarrow 0 \end{aligned}$$

Degeneraz. Coulombiana eliminata $\Rightarrow$

$$E_{n,l} > E_{n,l'} \quad (l > l')$$



Approccio iterativo

$$(i) \quad \psi_j^{(0)}(r_j) = \psi_{\text{el. indp.}}(r_j) \Rightarrow$$

$$(ii) \quad U_j^{(1)}(r_j)$$

$$(iii) \quad \{\psi_j^{(1)}(r_j)\} \Rightarrow$$

$$(iv) \quad U_j^{(2)}(r_j) \Rightarrow \dots$$

Campo autoconsistente

$$\left\{ \begin{aligned} \psi_k^{(i+1)}(r_k) &= \psi_k^{(i)}(r_k) \\ U_k^{(i+1)}(r_k) &= U_k^{(i)}(r_k) \end{aligned} \right\} \quad k=1, 2, \dots, Z$$

(i) Ogni elettrone si muove nel campo efficace generato da tutti gli altri elettroni e del nucleo.

(ii) Ciascun el. è nello stato

$$(n, l, m; s_z)$$

es. $3p, 4d, etc \Rightarrow$ strato ;
guscio ;
orbita .

Lo strato (n, l) Max $2(2l+1)$ elettroni
nel pot. $V_{eff}^{(n,l)}(r) \Downarrow$ elettroni equivalenti

N elettroni in (n, l) occupano

$N \leq 2(2l+1)$ stati, diversi

$$P_1 = |n, l, m_1; s_{z1}\rangle, P_2 = |n, l, m_2; s_{z2}\rangle, \dots$$

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum (-1)^P |P_1^{(1)}\rangle \dots |P_N^{(N)}\rangle$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} |P_1^{(1)}\rangle & \dots & |P_N^{(N)}\rangle \\ \vdots & & \vdots \end{vmatrix}$$

antisimmetria

dove $|p_i\rangle \equiv \underbrace{|n_i, l_i, m_i\rangle}_{\text{orbitale}} ; \underbrace{s_{z i}}_{\text{spin}}$

N.B. $p_i = p_j \ (i \neq j) \Rightarrow \Psi = 0$

Principio di esclusione di Pauli.
 $\nwarrow$ FD

Nella rapp. delle coordinate

$$\Psi(\underbrace{\xi_1}_{(r_1, \xi_1)}, \underbrace{\xi_2}_{(r_2, \xi_2)}, \dots, \xi_N) \quad \xi_i = \pm (\cdot)$$

$$= \frac{1}{\sqrt{N!}} \sum (-)^P \begin{vmatrix} \psi_{p_1}(\xi_1) & \psi_{p_1}(\xi_2) & \dots & \psi_{p_1}(\xi_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{p_N}(\xi_1) & \psi_{p_N}(\xi_2) & \dots & \psi_{p_N}(\xi_N) \end{vmatrix}$$

ψ

$$\begin{pmatrix} \psi(r_1, 1) \\ \vdots \\ \psi(r_2, 2) \end{pmatrix}$$

Teo: Uno stato chiuso porta $S=L=0$.

$(n, l) \Rightarrow 2(2l+1)$ stati, $N=2(2l+1)$

e.g. p-shell ($l=1$) $\Rightarrow 6$ stati

$|p_1\rangle = |m=1, \uparrow\rangle$; $|p_2\rangle = |m=1, \downarrow\rangle$

$|p_0\rangle = |m=0, \uparrow\rangle$; etc.

Determinante di Slater

$|\Phi\rangle = \text{tot. antisim.}$

$$= \frac{1}{\sqrt{N!}} \det \begin{vmatrix} |p_1^{(1)}\rangle & |p_1^{(2)}\rangle & \dots & |p_1^{(N)}\rangle \\ |p_2^{(1)}\rangle & \dots & \dots & |p_2^{(N)}\rangle \end{vmatrix}$$

$$\text{Def } S_+ = \sum s_{i+}; \quad L_+ = \sum L_{i+}$$

$$S_- = \sum s_{i-}; \quad L_- = \sum L_{i-}$$

$$(L_{i+} \equiv L_{ix} + iL_{iy})$$

$$S_+|\Phi\rangle = S_-|\Phi\rangle = 0 \quad \therefore S=0$$

$$L_+|\Phi\rangle = L_-|\Phi\rangle = 0 \quad \therefore L=0$$

Configurazione elettronica.

Atomo con # atomico Z

$$\sim (1s)^2 (2s)^2 (2p)^6 \dots (nl)^N$$

$$2 + 2 + 6 + \dots + N = Z$$

Il termine spettrale $\rightarrow {}^{2S+1}L$ è determinato
(L, S)

da N elettroni di valenza, noti
elettroni equivalenti.

Problema, dati $N (\leq 2(2l+1))$
elettroni, trovare i possibili valori
(L, S) (multipletti)
compatibili con la statistica di F-D?

$\leadsto$ Dg!

En. ^1H $1s^1$

^2He $(1s)^2$

^3Li $(1s)^2(2s)^1$, etc.

^{10}Ne $(1s)^2(2s)^2(2p)^6 / ^1S_0$ gusci completi
 $L = S = 0$

^{11}Na $(1s)^2(2s)^2(2p)^6(3s)^1$ $^2S_{1/2}$

^{26}Fe $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^6$
 $\underbrace{\hspace{10em}}_{10}$ $\underbrace{\hspace{10em}}_{18 \text{ Ar}}$ $S=2$ $L=2$ 5D_4 (?)

Nomi per vari orbitali.

$n = 1, 2, 3, 4, 5, 6, 7, \dots$

Nome K L M N O P Q ...

"strato K" etc.

L'ordine di energia $\neq$ orbitale d. Bohr.

$(1s)^2$ $(2s)$ $(2p)$ $(3s)$ $(3p)$ $(4s)$ $(3d)$ $(4p)$ $(5s)$ $(4d)$ $(5p)$ $(6s)$ $(4f)$ $(5d)$ $(6p)$ $(7s)$ $(5f)$ $(6d)$ $(7p)$ $(8s)$ $(6f)$ $(7d)$ $(8p)$ $(9s)$ $(7f)$ $(8d)$ $(9p)$ $(10s)$ $(8f)$ $(9d)$ $(10p)$ $(11s)$ $(9f)$ $(10d)$ $(11p)$ $(12s)$ $(10f)$ $(11d)$ $(12p)$ $(13s)$ $(11f)$ $(12d)$ $(13p)$ $(14s)$ $(12f)$ $(13d)$ $(14p)$ $(15s)$ $(13f)$ $(14d)$ $(15p)$ $(16s)$ $(14f)$ $(15d)$ $(16p)$ $(17s)$ $(15f)$ $(16d)$ $(17p)$ $(18s)$ $(16f)$ $(17d)$ $(18p)$ $(19s)$ $(17f)$ $(18d)$ $(19p)$ $(20s)$ $(18f)$ $(19d)$ $(20p)$ $(21s)$ $(19f)$ $(20d)$ $(21p)$ $(22s)$ $(20f)$ $(21d)$ $(22p)$ $(23s)$ $(21f)$ $(22d)$ $(23p)$ $(24s)$ $(22f)$ $(23d)$ $(24p)$ $(25s)$ $(23f)$ $(24d)$ $(25p)$ $(26s)$ $(24f)$ $(25d)$ $(26p)$ $(27s)$ $(25f)$ $(26d)$ $(27p)$ $(28s)$ $(26f)$ $(27d)$ $(28p)$ $(29s)$ $(27f)$ $(28d)$ $(29p)$ $(30s)$ $(28f)$ $(29d)$ $(30p)$ $(31s)$ $(29f)$ $(30d)$ $(31p)$ $(32s)$ $(30f)$ $(31d)$ $(32p)$ $(33s)$ $(31f)$ $(32d)$ $(33p)$ $(34s)$ $(32f)$ $(33d)$ $(34p)$ $(35s)$ 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Raggi X.

Raggi EM L. $10^{-2} - 10^2 \text{ \AA}$

(fr $10^3 \text{ \AA}$ x luce visibl.)

9. vari el. bent. sono colpiti da fasci di elettroni energetici

Raggi X caratteristici. (spettro discreto)

Serie K, L, M, ...

in analogia con le serie di Lyman, Balmer-Paschen ---

Raggi X da $Z \gtrsim 11$

L " $Z \gtrsim 30$ --

Caratteristiche

(1) $\sqrt{\nu}$ di una serie (K, L, ...) $\propto Z$

(2) Raggi X nello spettro di emissione
ma non nello spettro di assorbimento.

--> Meccanismo diverso?

Kossel: sempre assumendo

$$\nu = \frac{E_i - E_f}{h}$$

i raggi X vengono emessi quando
un elettrone nelle orbite più interne
vengono rimossi

1s elettrone rimosso

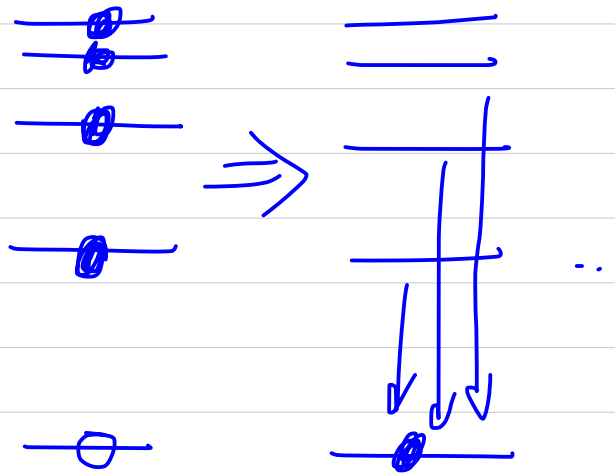
$\left. \begin{array}{l} 2p \rightarrow 1s \\ 3p \rightarrow 1s \\ \dots \end{array} \right\} \text{serie K.}$

Elettrone 1s vede

$$V \sim -\frac{Ze^2}{r}$$

$$E_K \sim \frac{Ze^2}{2r_D} \left(1 - \frac{1}{n^2}\right) \quad n=2, 3, 4, \dots$$

$$\rightarrow \sqrt{h\nu} \propto Z \left(1 - \frac{1}{n^2}\right)^{1/2}$$



Analogante $\rightarrow$ Schroedinger.

$$E_L \sim \frac{(Z-s')^2}{2r_0^2} \left(\frac{1}{4} - \frac{1}{n^2} \right) \quad n=3, 4, \dots$$

Per Na ($Z=11$)

$$Z_{\text{eff}}(1s) \sim 8.91$$

$$Z_{\text{eff}}(2s) \sim 4.56, \text{ etc.},$$

*) La frequenza limite ($n \rightarrow \infty$)
di serie K $\simeq$ l'energia richiesta
per estrarre l'elettrone K $\simeq$
l'energia dell'elettrone K !

$\Rightarrow$ Metodo di misurare l'energia
d'elettroni in vari stati.

$\Rightarrow$ Tabelle

Approssimazione di Hartree

L'i-esimo elettrone:

$$-\hbar^2 \frac{\nabla_i^2}{2m} \psi_i - \frac{Ze^2}{r_i} \psi_i(r) + e^2 \int d^3r' \frac{\rho(r')}{|r-r'|} \psi_i(r) = \epsilon_i \psi_i(r) \quad (A)$$

dove

$$\rho_i(r) = \sum_{j \neq i} |\psi_j(r)|^2$$

• Appr. di potenziale eff. a simmetria centrale

$$\frac{\rho(r')}{|r-r'|} \Rightarrow \frac{\overline{\rho(r')}}{|r-r'|} \rightarrow \text{media sulle direzioni}$$

$$\Rightarrow \psi_j(r) = R_{n,l}(r) Y_{lm}(\theta) \chi_s$$

Un elettrone ψ_j contribuisce nell'eq. (*)

$$\int d^3r' \rho_{nl}^2(r') |Y_{lm}(\hat{r}')|^2 \frac{1}{|r-r'|}$$

$$\text{App. } |Y_{lm}(\hat{r}')|^2 \Rightarrow \overline{|Y_{lm}(\hat{r}')|^2}$$

$$= \frac{1}{2l+1} \sum_m |Y_{lm}(\hat{r}')|^2 = \frac{1}{4\pi} \quad (8.)$$

$$(8.) \quad P_l(\cos \theta) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}(\theta_1) Y_{lm}^*(\theta_2) \quad \begin{matrix} \nearrow \theta_1 \\ \searrow \theta_2 \end{matrix}$$

$$r=0 \quad 1 = \frac{4\pi}{2l+1} \sum_m |Y_{lm}|^2 \therefore \rightarrow (8.)$$

Oppure, semplificando,

$$|Y_{\ell, m}(\hat{r})|^2 = c \quad (\text{cost.})$$

$$\int d\Omega |Y_{\ell, m}(\hat{r})|^2 = 1 \quad \left(\because c = \frac{1}{4\pi} \right)$$

Ricapitolando, la media direzionale $\Rightarrow$

$$|Y_{\ell, m}(\hat{r}')|^2 \rightarrow \frac{1}{4\pi}$$

Il contributo di un elettrone ad (n, ℓ)

$$\simeq \frac{1}{4\pi} \int d^3r' R_{n\ell}^2(r') \frac{1}{|r - r'|}$$

$$\frac{1}{|r - r'|} \rightarrow \begin{cases} \frac{1}{r} \sum_{\ell} \left(\frac{r'}{r}\right)^{\ell} P_{\ell}(\cos\theta) & (r > r') \\ \frac{1}{r'} \sum_{\ell} \left(\frac{r}{r'}\right)^{\ell} P_{\ell} & (r < r') \end{cases}$$

$$\begin{aligned} V_{n,\ell} &= \frac{1}{r} \int_0^r dr' P_{n,\ell}^2(r') + \int_r^{\infty} \frac{dr'}{r'} P_{n,\ell}^2(r') \\ &\equiv V_a \end{aligned}$$

dove $R_{n,\ell}(r) \equiv \frac{P_{n,\ell}(r)}{r} \rightsquigarrow \left(\frac{\chi_{n,\ell}(r)}{r} \right)$

Teo Gauss.

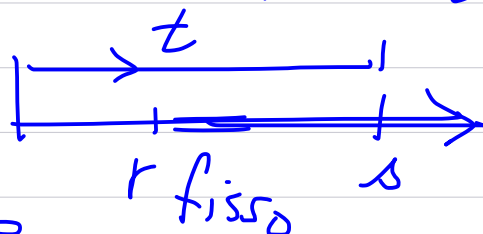
$$Q(r) = \int_0^r dr' P_{nl}^2(r') \quad \text{la "carica" intorno alla sfera con raggio } r.$$

campo el.

$$E_r = \frac{Q(r)}{r^2} = -\frac{\partial V}{\partial r} \quad (*)$$

$$\Rightarrow V(r) = \int_r^\infty ds \frac{Q(s)}{s^2} \quad (OK \text{ con } (*) \text{ e } V \rightarrow 0, r \rightarrow \infty)$$

$$= \int_r^\infty \frac{ds}{s^2} \int_0^s dt P_{nl}^2(t)$$



$$= \int_r^\infty \frac{ds}{s^2} \left\{ \int_0^r dt P_{nl}^2(t) + \int_r^s dt P_{nl}^2(t) \right\}$$

$$= \frac{1}{r} \int_0^r dt P_{nl}^2(t) + \int_r^\infty \int_t^\infty \frac{ds}{s^2} dt P_{nl}^2(t)$$

$$= \frac{1}{r} \int_0^r dt P_{nl}^2(t) + \int_r^\infty \frac{dt}{t} P_{nl}^2(t)$$

OK.

radiale
Equazione per un elettrone nello strato $a \equiv (n, l)$
($m = l = k = 1$)

$$-\frac{1}{2} P_a''(r) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) P_a(r)$$

$$+ \left[\sum_{b \neq a} q_b V_b(r) + (P_a - 1) V_a(r) \right] P_a(r) = \epsilon_a P_a(r) \quad (*)$$

dove $V_c(r) = \frac{1}{r} \int_0^r dt P_c^2(t) + \int_r^\infty \frac{dt}{t} P_c^2(t)$

(*) è un'equazione integra-differenziale per $P_a(r) = r R_{n,l}(r)$

(**) $P_c = \#$ di elettroni nel guscio $c \equiv (n, l)$.

e.g. $Z=6$ C $1s^2 2s^2 2p^2$

$a, b, c = (n, l) = (1s), (2s), (2p)$

$$\Rightarrow -\frac{1}{2} P_{1s}'' - \frac{Z}{r} P_{1s} + (V_{1s} + 2V_{2s} + 2V_{2p}) P_{1s} = \epsilon_{1s} P_{1s}$$

$$-\frac{1}{2} P_{2s}'' - \frac{Z}{r} P_{2s} + (V_{2s} + 2V_{1s} + 2V_{2p}) P_{2s} = \epsilon_{2s} P_{2s}$$

$$-\frac{1}{2} P_{2p}'' + \left(\frac{2}{2r^2} - \frac{Z}{r} \right) P_{2p} + (2V_{1s} + 2V_{2s} + V_{2p}) P_{2p} = \epsilon_{2p} P_{2p}$$

dove $V_{n,l}(r) = \frac{1}{r} \int_0^r dr' P_{n,l}^2(r') + \int_r^\infty \frac{dr'}{r'} P_{n,l}^2(r')$

⌋

Soluzioni iterative

$$P_{n,l}^{(0)}(r) = r \cdot R_{n,l}^{\text{Bohr}}(Z) \Rightarrow \{V_{n,l}^{(0)}\} \Rightarrow$$

$$P_{n,l}^{(1)}(r) \Rightarrow \{V_{n,l}^{(1)}\} \Rightarrow \dots$$

Interpretazione.

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i}\right) \psi_i + e^2 \sum_{j \neq i} \int d\mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$\sum_i \int d^3r \psi_i^*(\mathbf{r}) \times$$

$$\sum_i \left\langle \psi_i \left| \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right| \psi_i \right\rangle + \frac{e^2}{2} \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \frac{|\psi_i|^2 |\psi_j|^2}{|\mathbf{r} - \mathbf{r}'|} = \sum_i \epsilon_i$$

of r. can

$$H = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i > j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\text{tra } \Psi = \prod_i \psi_i$$

$$\langle \Psi | H | \Psi \rangle = \sum_i \left\langle \psi_i \left| \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right| \psi_i \right\rangle + \frac{e^2}{2} \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \frac{|\psi_i|^2 |\psi_j|^2}{|\mathbf{r}_i - \mathbf{r}_j|} !$$

$$\text{i.e., } \sum_i \epsilon_i = E + \frac{e^2}{2} \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \frac{|\psi_i|^2 |\psi_j|^2}{|\mathbf{r}_i - \mathbf{r}_j|} !$$

Principio variazionale e l'eq. di Hartree

$$|\Psi\rangle = \prod |\varphi_i\rangle \quad e$$

$$\Rightarrow \langle \Psi | H | \Psi \rangle = \sum_i \int \varphi_i^* \left(\frac{p^2}{2m} - \frac{Ze^2}{r_i} \right) \varphi_i \\ + \frac{e^2}{2} \sum_{i \neq j} \int |\varphi_i|^2 |\varphi_j|^2 \frac{1}{|r_i - r_j|}$$

Calcolo variazionale,

$$\frac{\delta}{\delta \varphi^*} [\langle \Psi | H | \Psi \rangle - \sum_i \epsilon_i (\langle \varphi_i | \varphi_i \rangle - 1)] = 0$$

$$\Rightarrow -\frac{1}{2} \nabla^2 \varphi_i - \frac{Z}{r_i} \varphi_i + \sum_{j \neq i} \int d\mathbf{r}' \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r}_i - \mathbf{r}'|} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}_i)$$

∴ Equazioni di Hartree !!

Tabl. s.

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(fr. $\underline{F} = -\frac{\alpha}{2} E^2$ (dipolo indotto))

dove $d = \alpha E$

$$\Leftrightarrow E = -d \cdot E \quad \left(\begin{array}{l} \text{dipolo} \\ \text{permanente} \end{array} \right)$$

Deviazione da un potenziale efficace a simm. centrale

$$H = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + e^2 \sum_{i>j} \frac{1}{|r_i - r_j|} + H_{rel}.$$

$$= \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + V_i(r_i) \right) + H_{ee} + H_{rel}.$$

dove

$$H_{ee} \equiv \sum_{i>j} \frac{e^2}{|r_i - r_j|} - \sum_i V_i(r_i)$$

risulta che per atomi relativamente leggeri,

$$H_{ee} \gg H_{rel}.$$

$\Rightarrow$ Tenere conto prima di H_{ee} , poi H_{rel} .

Poniamo prima $H_{rel} = 0$.

$$H = H^{sim. cent} + H_{ee} \quad \left(\begin{array}{l} \text{Accoppiamento } L-S \\ \text{" Russell-Saunders"} \end{array} \right)$$

(cf. $H_{rel} \approx H_{ee}$: $j-j$ coupling).

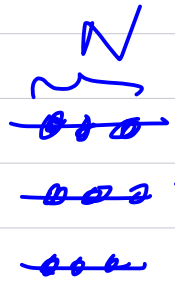
$\Rightarrow$ Multipletti.

app. Hartree $\Rightarrow$

Tipicamente un atomo ha

(i) $N \leq 2(2l+1)$ elettroni nello strato (n, l) più esterno (valenza), not: elettroni equivalenti

(ii) Simmetria centrale $\Rightarrow$ ogni stato (L, L_z, S, S_z) (quarto q con H_{ee}) ma la simmetria è più grande.

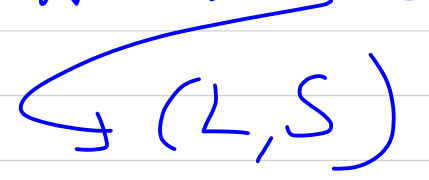
(iii) $\# = \binom{2(2l+1)}{N}$ possibil. stati [p.] :  } stati chiusi

occupati da elettroni $\Rightarrow \binom{2(2l+1)}{N}$

possibili. Determinanti di Slater (stati totalmente antisimmetrici).

(iv) Quest: sono tutte degeneri ($\#$) i
Questa degenerazione è parziale, rimossa

$$\binom{2(2l+1)}{N} = \sum_{L, S} (2L+1)(2S+1)$$

$\hookrightarrow (L, S)$ multipl. $\Rightarrow$ Anal? 

esempio 1. 2 elettroni in $(n, p) \rightarrow l=1$.

$$\Rightarrow \binom{6}{2} = 15 \text{ stati possib.}$$

$$S: \frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0 \Rightarrow S=1 \text{ o } S=0$$

$$S=1 \text{ (spin tot. simm.)} \Rightarrow \text{orbital antisim.}$$

$$\Rightarrow \sum (-)^{l_1} \psi_{1m_1} \psi_{1m_2} \Rightarrow \binom{3}{2} = 3 \text{ stati}$$

$$L=1 \quad \begin{matrix} \downarrow \\ \text{S} \end{matrix} \quad \begin{matrix} \downarrow \\ \text{A} \end{matrix} \quad \begin{matrix} \downarrow \\ \text{S} \end{matrix} \quad \left(\begin{matrix} l_1 \otimes l_2 = 1 \otimes 1 \\ = 2 \oplus 1 \oplus 0 \end{matrix} \right)$$

$$\therefore (L, S) = (1, 1) \Rightarrow 3 \cdot 3 = 9 \text{ stati}$$

$$S=0 \text{ (spin antis.)} \Rightarrow \text{orbital simmetric}$$

$$\begin{matrix} L=2 & (5 \text{ stati}) \\ L=0 & (1) \end{matrix} \} 6 \text{ stati}$$

$$\therefore \Rightarrow (L, S) = (1, 1) + (2, 0) + (0, 0)$$

$$9 \quad 5 \quad 1 = 15 \text{ OK.}$$

$$^3P \quad ^1D \quad ^1S$$

$$3 \text{ elettroni } \hookrightarrow (n, l) = (n, 1) \quad ?$$

Tabelle di Young $\leftrightarrow$ rappresentazione del gruppo di permutazione.
 Tableaux

N oggetti che possono prendere ciascuno uno dei possibili valori, $a_i = 1, 2, \dots, p$ e si considera il prodotto

$$\psi = \psi_{a_1}^{(1)} \psi_{a_2}^{(2)} \dots \psi_{a_N}^{(N)} \quad (*)$$

per es. $a_i = 1, 2 \quad (S_2 = \pm 1/2)$
 $a_i = 1, 2, 3 \quad (S_{S_z} = \pm 1, 0; L_z = \pm 1, 0)$

Forme comb. lineari di termini (*) che hanno proprietà particolare $\times$ scambi di oggetti:

$\Leftrightarrow$ tabelle di Young

(i) Un oggetto $\square \sim \psi_a, a = 1 \dots p$

(ii) 2 .. $\square\square = \frac{1}{\sqrt{2}} (\psi_{a_i}^{(1)} \psi_{a_j}^{(2)} + \psi_{a_j}^{(1)} \psi_{a_i}^{(2)})$

$\Rightarrow \frac{p(p+1)}{2}$ membri.

$\square\square = \frac{1}{\sqrt{2}} (\quad - \quad)$

$\Rightarrow \frac{p(p-1)}{2}$

Gruppo di permutazioni S_N

per n. S_3

Elementi

Permuta.

e	$ABC \rightarrow ABC$
(12)	$ABC \rightarrow BAC$
(23)	$ABC \rightarrow ACB$
(13)	$ABC \rightarrow CBA$
(123)	$ABC \rightarrow CAB$
(321)	$ABC \rightarrow BCA$

Prodotti: $(12) \cdot (23) = (123)$

$(23) \cdot (123) = (13)$, etc

$(12) \cdot (12) = e$.

Rappresentazione ($g \rightarrow M(g)$, $g_1, g_2 \rightarrow M(g_1)M(g_2) = M(g_1 g_2)$)

$$e = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix}, (12) = \begin{pmatrix} & 1 & \\ 1 & & \\ & & 1 \end{pmatrix} (23) = \begin{pmatrix} 1 & & \\ & & 1 \\ & 1 & \end{pmatrix}$$

$$(123) = \begin{pmatrix} & & 1 \\ & 1 & \\ 1 & & \end{pmatrix}; (321) = \begin{pmatrix} & 1 & \\ & & 1 \\ 1 & & \end{pmatrix}$$

(iii) $N=3$.

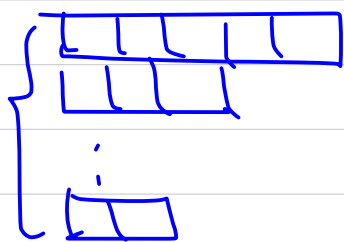
 $\sim$ tot. simm.

 $\sim$ tot. antisim.

 $\sim$ simmetrica mista.

(iv) In generale, $N = N_1 + N_2 + \dots + N_r$

N_1 ~~oggetti~~ simmetrici,
 N_2 " " " " " " " " " " " "



 $r=0$ $\sup$ $r > p$

(v) Spin $\frac{1}{2}$ ($SU(2)$) $a=1, 2$.



$S=1$



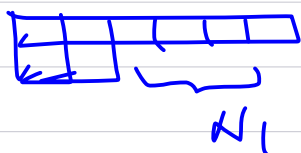
$S=0$



$S=3/2$



$S = N/2$



$S = N_1/2$

$\left(r \left\{ \begin{array}{c} \text{box with cross} \\ \text{box with cross} \\ \text{box with cross} \end{array} \right\} = 0 \right)$
 $r > 2$

(vi) $p=3$ $SU(3)$ vs $SO(3)$

$$\square \sim \psi_i \sim \underline{3}, \quad i=1,2,3$$

$$SO(3)(L, L_z) / SU(3) \quad q = \begin{pmatrix} u \\ d \\ s \end{pmatrix}$$

$$\square \sim \underline{3}, \quad l=1 \quad \square \sim \underline{3}$$

$$\begin{array}{l} \square \square \sim \underline{5} \oplus \underline{1} \quad (l=2,0) \quad \square \square \sim \underline{6} \\ \square \sim \underline{3} \quad (l=1); \quad \square \sim \underline{3}^* \end{array} \left. \begin{array}{l} \text{rapp} \\ \text{irriduc.} \end{array} \right\}$$

Maeh: per $SO(3)$ Υ . tab. $\neq$ rapp. irrid.

per $SU(3)$, tab. $\text{irrid.} \Leftrightarrow$ rapp. irriduc.
 $SU(N)$,

$SU(3)$ e il modello dei quarks.

$$q = \begin{pmatrix} u \\ d \\ s \end{pmatrix} \sim \underline{3}; \quad \bar{q} = \begin{pmatrix} \bar{u} \\ \bar{d} \\ \bar{s} \end{pmatrix} \sim \underline{3}^*$$

$$\pi^\pm, K, \dots \text{ (mesoni) } \sim |q \bar{q}\rangle$$

$$\text{in } \underline{3} \otimes \underline{3}^* = \square \times \square = \square + \square$$

8 1

$$\{ \pi^\pm, \pi^0, K^+, K^0, \bar{K}^0, K^-, \eta \} \rightarrow \eta'$$

Barioni (p, n, Σ , Λ ...)

$$\sim |qqq\rangle$$

$$\square \times \square \times \square = \square \times (\square + \square)$$

$$\text{in } \underline{3} \otimes \underline{3} \otimes \underline{3} = \underline{3} \otimes (\underline{6} \oplus \underline{3}^*) = \square + \square + \square + \square$$

10 8 8 1

$$p, n, \Sigma^\pm, \Sigma^0, \Xi^0, \Xi^\pm, \Lambda$$

Costruire multipletti: (L, S) da
 N elettroni equivalenti: (n, l)

N spin $\begin{array}{|c|c|c|c|} \hline \hline \hline \hline \hline \hline \end{array} = \frac{N}{2}, \begin{array}{|c|c|c|c|} \hline \hline \hline \hline \hline \hline \end{array} = \frac{N}{2} - 1, \text{ etc}$

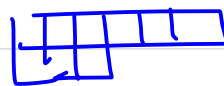
$$\frac{1}{2} \otimes \frac{1}{2} \otimes \dots = \frac{N}{2} \oplus \frac{N}{2} - 1 \oplus \dots$$

Orbitale deve avere la tabella di Young
 "complementare"

Orbitale $\otimes$ Spin



$\times$



r_1
 r_2

Torniamo a $N=3$ elettroni in $(n, 1)^{\rightarrow p}$

Ci sono $\binom{6}{3} = \frac{6 \cdot 5 \cdot 4}{3!} = 20$ stati (Det. Slater)

$$L: \underline{1} \otimes \underline{1} \otimes \underline{1} = \underline{1} \otimes (\underline{2} \oplus \underline{1} \oplus \underline{0}) \\ = \underline{3} \oplus \underline{2} \oplus \underline{1} \oplus \underline{2} \oplus \underline{1} \oplus \underline{0} \oplus \underline{1}$$

$$S: \underline{1/2} \otimes \underline{1/2} \otimes \underline{1/2} = \underline{1/2} \otimes (\underline{1} \oplus \underline{0}) = \underline{3/2} \oplus \underline{1/2} \oplus \underline{1/2}$$

Classifichiamo S :

$S=3/2$: $\square \square \square \Rightarrow$ Orbital. $\square \left. \begin{array}{l} 3 \text{ stat.} \\ \rightarrow \text{differenti} \end{array} \right\}$

$$l=1, l_2=\pm 1, 0 \Rightarrow \psi = \sum_{\text{anti}} \psi_{1,1}^{(r_1)} \psi_{1,0}^{(r_2)} \psi_{1,-1}^{(r_3)}$$

$$\therefore L=0. \quad (L, S) = (0, 3/2) \quad 4 \text{ stat.}$$

$S=1/2$ $\square \square \Rightarrow$ Orbital. $\square$

Escluso $L=3$, $\leftarrow \square \square \square$

Torniamo $L=2$ e sceglio $L_z=2$

$$\psi_{\text{orb.}} \sim \psi_{1,1} \psi_{1,1} \psi_{1,0}$$

$$\therefore \psi \sim \left(\psi_1^{\uparrow} \psi_1^{\downarrow} \psi_0^{\uparrow} \right) \left(\begin{array}{c} \text{scelgo} \\ S_z = 1/2 \end{array} \right)$$

$$= \text{Det Slater. di } \underline{L+S=0},$$

$$(L, S) = (2, 1/2) \text{ OK } \Rightarrow 10 \text{ stat.}$$

$$\text{Gra } L_- \psi = (L_{1-} + L_{2-} + L_{3-}) \psi$$

$$= L_- \frac{1}{\sqrt{3}} D_2 \left(|1\uparrow\rangle |1\downarrow\rangle |0\uparrow\rangle \right)$$

$$= \frac{\sqrt{2}}{\sqrt{6}} \left\{ D_2 \left(|1\uparrow\rangle |1\downarrow\rangle |-1, \uparrow\rangle \right) + D_2 \left(|1\uparrow\rangle |0\downarrow\rangle |0\uparrow\rangle \right) \right\} \left(\begin{array}{l} L_- |l, m\rangle \\ = \sqrt{(l+m)(l-m+1)} |l, m-1\rangle \end{array} \right)$$

$$= 2 \cdot \psi^{(L=2, L_z=1)}$$

$\exists$ Un altro stato d. $L_z = 1$

$$\tilde{\psi} = \frac{1}{\sqrt{12}} \left[D_2 \left(|1\uparrow\rangle |1\downarrow\rangle |-1, \uparrow\rangle \right) - D_2 \left(|1\uparrow\rangle |0\downarrow\rangle |0\uparrow\rangle \right) \right]$$

$$\bullet \quad \langle \tilde{\psi} | \psi \rangle = 0$$

$$\text{Gra } L_+ \tilde{\psi} = 0$$

$$\therefore \tilde{\psi} = \tilde{\psi}^{(L=1, L_z=1)}$$

$$\therefore (L, S) = (1, 1/2) \quad \text{OK}$$

$$\text{Tot } (L, S) = (0, 3/2), (2, 1/2), (1, 3/2)$$

$$4 + 10 + 6 = 20 \text{ OK.}$$

$$^4S, \quad ^2D, \quad ^2P$$

Stato fondamentale ?

Regole di Hund. (Empirica. OK.)

Tra i possibili multipletti, lo stato fond.

$$\Leftrightarrow S = S_{\text{Max.}}$$

Se questo criterio non dà (L,S) univoco,
Lo st. fond $\sim L_{\text{Max.}}$.

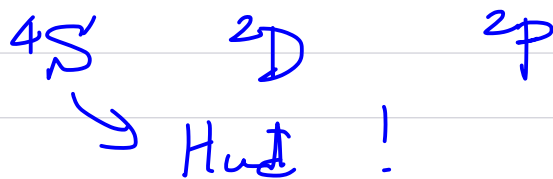
es. 1. $(\dots)(np)^2$: C, Si, Ge, Sn, Pb ...

$$(L,S) = (1,1) \quad (2,0) \quad (0,0)$$



es. 2. $(\dots)(np)^3$: N, P, As, Sb, Bi

$$(L,S) = (0, \frac{3}{2}), (2, \frac{1}{2}), (1, \frac{1}{2})$$



Teoremi at.l.

Teo. Due elettroni equivalenti: $\Rightarrow$
 $L + S = \text{pari}$.

$$\begin{array}{l} \because S=1 \Rightarrow \psi_{\text{orb}} \text{ disp.} = 2l-1, 2l-3, \dots \\ S=0 \Rightarrow \psi_{\text{orb}} \text{ sim.} = 2l, 2l-2, \dots \end{array} \quad \left. \vphantom{\begin{array}{l} \because S=1 \\ S=0 \end{array}} \right\} \text{sk}$$

Teo. $L=S=0$ $N_{\text{el. eq}} = 2(2l+1)$.

$$\Psi = \frac{1}{\sqrt{N!}} \text{Det } \psi_{p_i} \quad p_i = 1, \dots, 2(2l+1)$$

Teo. L'esistenza di multipletti $(L, S)^N \xrightarrow{\text{Coulomb}} \text{per } \# = N \text{ elettroni equivalenti.}$
 $\Rightarrow \quad \quad \quad (L, S)^{2(2l+1)-N}$

$\therefore$ Per determinare (L, S) , si può considerare le lacune, anziché gli elettroni !

Hartree-Fock e le interazioni di scambio.

Appr di campo efficace autocompatibile
ma con i determinanti di Slater.

Eq. di Schrödinger.
 $H \rightarrow \psi$.

$$\frac{\delta}{\delta \psi^*} [\langle \psi | H | \psi \rangle - \lambda (\langle \psi | \psi \rangle - 1)] = 0$$

$$\Rightarrow H|\psi\rangle = \lambda |\psi\rangle; \quad \langle \psi | \psi \rangle = 1.$$

$$\bullet H = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{|r_i - r_j|}$$

$$\Psi = \prod_i \psi_i \Rightarrow \text{Eq. L. Hartree}$$

• Ma ora uso

$$\Psi = \frac{1}{\sqrt{N!}} \text{Det} \begin{vmatrix} \psi_{p_1}(q_1) & \dots & \psi_{p_1}(q_N) \\ \vdots & & \vdots \end{vmatrix}$$

$$(q_i \equiv (r_i, \sigma_i))$$

$\underbrace{\text{in } E_g}_{\text{variabili}}$

$$H = \sum_i f_i + \sum_{i<j} g_{ij}, \quad f_i \equiv -\frac{1}{2} \nabla_i^2 - \frac{Ze^2}{r_i}$$

Ora

$$g_{ij} = \frac{e^2}{|r_i - r_j|}$$

$$\langle \Psi | H | \Psi \rangle = \sum_i \langle i | f | i \rangle + \sum_{i<j} (\langle ij | g | ij \rangle - \langle ij | g | ji \rangle)$$

$$\begin{aligned} \text{dove } \langle i | f | i \rangle &= \int d^3r \psi_i^*(\vec{r}) \left(-\frac{\nabla^2}{2} - \frac{Ze^2}{r} \right) \psi_i(\vec{r}) \\ &\quad \downarrow \\ &= \sum_{\sigma} \chi_{j,i}^*(\sigma) \chi_{j,i}(\sigma) \int dr \psi_i^*(r) \left(-\frac{\nabla^2}{2} - \frac{Ze^2}{r} \right) \psi_i(r) \end{aligned}$$

$i = (n, l, m, j_z)$

$$\langle ij | g | ij \rangle - \langle ij | g | ji \rangle$$

$$= \int_{r_1, r_2} \left[\psi_i^*(r_1) \psi_j^*(r_2) \frac{1}{|r_1 - r_2|} \psi_i(r_1) \psi_j(r_2) \right. \\ \left. - \psi_i^*(r_1) \psi_j^*(r_2) \frac{1}{|r_1 - r_2|} \psi_j(r_1) \psi_i(r_2) \right]$$

$$I^0 = \int d^3r_1 d^3r_2 \sum_{n_1, l_1, m_1} |\psi_{n_1, l_1, m_1}(r_1)|^2 \sum_{n_2, l_2, m_2} |\psi_{n_2, l_2, m_2}(r_2)|^2 \frac{1}{|r_1 - r_2|}$$

$$2^0 = \langle \chi_{1,i} | \chi_{1,j} \rangle \cdot \langle \chi_{1,j} | \chi_{1,i} \rangle \times$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{n,l,m}^*(\mathbf{r}_1) \psi_{n',l',m'}^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n,l,m}(\mathbf{r}_1) \psi_{n',l',m'}(\mathbf{r}_2)$$

N.B. Il termine di scambio è presente
solo se $\delta_{iz} = \delta_{jz}$.

$\Rightarrow$ Eq. di Hartree-Fock

El₁₀: stato fond e il primo stato eccitato.
Lo stato fondamentale. $1s^2$ $S=0$ (para El₁₀)

1° st. to ecc. 1s 2s

$S=0$ Parallel $\bar{S}=1$ Ortho el.

$E_{1s2s} < E_{1s2p}$
 $\leftarrow$ Hartree

Interact. scambio $\Rightarrow E_{123}^{orb} < E_{123}^{para}$.

$$1s^2 \quad \Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(r_1) \chi_+(s_1) & \psi_{1s}(r_2) \chi_+(s_2) \\ \psi_{1s}(r_1) \chi_-(s_1) & \psi_{1s}(r_2) \chi_-(s_2) \end{vmatrix}$$

$$= \psi_{1s}(r_1) \psi_{1s}(r_2) (\underline{x}_+ \underline{x}_- - \underline{x}_- \underline{x}_+) / \sqrt{2}$$

$\Rightarrow$ Eg. Hartree

1s 2s

$P_1 = |1s 2s \uparrow \uparrow\rangle, |1s 2s \downarrow \downarrow\rangle, |1s 2s \uparrow \downarrow\rangle, |1s 2s \downarrow \uparrow\rangle$

Ψ_1	Ψ_2	Ψ_3	Ψ_4
$S_z = 1$	$S_z = -1$	$S_z = 0$	$S_z = 0$
$S = 1$	$S = 1$	$S = 1, 0$	

Le eq. x ψ_{1s}, ψ_{2s} :

$$E_{1s} \psi_{1s} = \left(-\frac{\nabla^2}{2} - \frac{2e^2}{r} \right) \psi_{1s} + \int_{r'} \frac{1}{|r-r'|} \left(|\psi_{2s}(r')|^2 \psi_{1s}(r) - \psi_{2s}^*(r') \psi_{1s}(r') \psi_{2s}(r) \right)$$

$$E_{2s} \psi_{2s} = \left(-\frac{\nabla^2}{2} - \frac{2e^2}{r} \right) \psi_{2s} + \int_{r'} \frac{1}{|r-r'|} \left(|\psi_{1s}(r')|^2 \psi_{2s}(r) - \psi_{1s}^*(r') \psi_{2s}(r') \psi_{1s}(r) \right)$$

Dati queste soluzioni $\Rightarrow$

$$\langle \Psi_1 | H | \Psi_1 \rangle = I_{1s} + I_{2s} + J - K$$

$$\langle \Psi_2 | H | \Psi_2 \rangle = I_{1s} + I_{2s} + J - K$$

dove $I_a = \int \psi_a^*(r) \left(-\frac{\nabla^2}{2} - \frac{2e^2}{r} \right) \psi_a(r)$

$$J = \int_{r, r'} |\psi_{1s}(r)|^2 |\psi_{2s}(r')|^2 \frac{1}{|r-r'|}$$

$$K = \int_{r, r'} \psi_{1s}^*(r) \psi_{2s}(r') \frac{1}{|r-r'|} \psi_{2s}(r) \psi_{1s}(r')$$

$\Psi_3, \Psi_4 \Rightarrow$ NO termine di scambio

$$\langle \Psi_3 | H | \Psi_3 \rangle = \langle \Psi_4 | H | \Psi_4 \rangle = I_{1s} + I_{2s} + J$$

ma $\langle \Psi_3 | H | \Psi_4 \rangle = -K$!

∴ Nel settore di due stati $S_z = 0$,

(teo. perturbaz. degenera !)

$$H = \begin{pmatrix} I_{1s} + I_{2s} + J & -K \\ -K & I_{1s} + I_{2s} + J \end{pmatrix}$$

$\Rightarrow$ Gli autostati (autovetori) sono

$$\rightarrow \frac{|\Psi_3\rangle + |\Psi_4\rangle}{\sqrt{2}} = \psi_{1s} \psi_{2s} \frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}} \quad \begin{matrix} S=1 \\ S_z=0 \end{matrix}$$

con $E = I_{1s} + I_{2s} + J - K$

$$\rightarrow \frac{|\Psi_3\rangle - |\Psi_4\rangle}{\sqrt{2}} = \psi_{1s} \psi_{2s} \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}} ; S=0$$

con $E = I_{1s} + I_{2s} + J + K$.

$$K > 0 \Rightarrow \underbrace{E_{S=1}^{\text{ort}} < E_{S=0}^{\text{par.}}}_{\text{reg. Hund}}$$

(cf. reg. Hund)

Correzioni relativistiche e la struttura fine.

Interazioni L-S.

Eq. di Dirac in campo esterno (ϕ, A) $A_\mu =$

$\Rightarrow$ Sviluppo in $1/c$ e la riduzione all'eq. per il componente dominante (L.L.V. 4, p. 33)

$O(1/c)$

$$\Rightarrow i\hbar \frac{\partial \psi}{\partial t} = H \psi$$

$$S = \frac{\hbar}{2} \sigma$$

$$H = \frac{1}{2m} \left(p - \frac{e}{c} A \right)^2 - e\phi - g \frac{e}{2mc} S \cdot B$$

Eq. di Pauli.

con $g = 2$. $\Leftarrow$ predizione Eq. Dirac.

cf. $g_{sp.} = 2.0023193043617 \dots$

Osservazioni

- (i) Non tutte le particelle di $sp \frac{1}{2}$ ha $g \approx 2$
- (ii) Nucleoni (protoni, neutroni)

$$\frac{\mu_N}{\mu_{\text{Bohr}(N)}} = g_N g \begin{cases} g_n \approx -3.8 \\ g_p \approx 5.6 \end{cases} !$$

(iii) $g_n \approx 2.0023 \dots$ OK

(iv) $g_n^{\text{th}} \approx 2.00233183716 \pm \dots$
 $g_n^{\text{exp}} \approx 2.00233184160 \dots$

1/2) Trasformazione di Lorentz:

$$B' = \frac{1}{c} v \times E \quad \left(\begin{array}{l} \text{Campo magnetico} \\ \text{visto da un corpo} \\ \text{in moto} \end{array} \right)$$

$$= \frac{1}{mc} (p \times E) \quad \Rightarrow$$

$$H = \left(p - \frac{e}{c} A \right)^2 / 2m - e\phi - \frac{g e \hbar}{2mc} S \cdot B$$

$$- \frac{p^4}{8m^3 c^2} - \frac{e \hbar}{4m^2 c^2} \nabla \cdot (E \times p) - \frac{e \hbar^2}{8m^2 c^2} \nabla \cdot E$$

$$ma \quad E = -\nabla \Phi$$

$$= -\frac{1}{r} \frac{d\Phi(r)}{dr}$$

$$V_{eff}(r) = e\Phi(r)$$

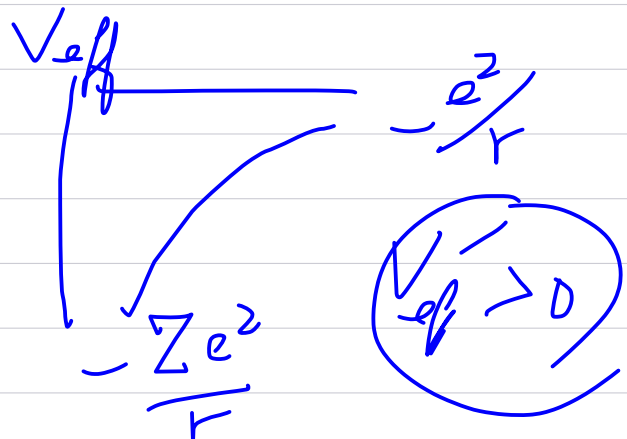
$$\therefore 5^a \text{ termine} = \frac{\hbar}{4m^2 c^2 r} \nabla \cdot (r \times p) \frac{dV_{eff}}{dr}$$

$$= \frac{\hbar^2}{2m^2 c^2 r} \frac{dV_{eff}(r)}{dr} (S \cdot L)$$

> 0 !

$$\Rightarrow H_{LS} = \sum_k \alpha(r_k) L_k \cdot S_k$$

$$con \quad \alpha(r_k) = \frac{\hbar^2}{2m^2 c^2 r_k} \frac{dV_{eff}(r)}{dr_k} > 0$$



H_{LS} dovuto alle interazioni tra lo spin dell'elettrone e il campo elettrico generato dal nucleo e da altri elettroni.



Per H, $V_{eff} = V_{Coul.} = -\frac{e^2}{r}$, $\vec{E} = \frac{e^2}{r^2} \vec{r}$

$$\nabla \cdot \vec{E} = -\nabla^2 V = 4\pi e^2 \delta^3(r)$$

$$V_{rel} = -\frac{p^4}{8m^3c^2} + \frac{e^2}{2m^2c^2r^3} \vec{L} \cdot \vec{S} + \frac{\pi e^2 \hbar^2}{2m^2c^2} \delta^3(r)$$

$$O(\delta E)^{LS} \sim \frac{e^2}{m^2c^2} \hbar^2 \left(\frac{me^2}{\hbar^2} \right)^2 \frac{1}{r_B} \sim \alpha^2 \frac{e^2}{r_B} \quad \checkmark \text{ OK.}$$

$$O(\delta E)^{Dar} \sim \frac{e^2 \hbar^2}{m^2c^2} |\psi(0)|^2 \sim \frac{e^2 \hbar^2}{m^2c^2} \frac{1}{r_B} \left(\frac{me^2}{\hbar^2} \right)^2 \sim \alpha^2 \frac{e^2}{r_B} \quad \checkmark$$

$$O(\delta E)^{p^4} \sim \left(\frac{\hbar^2}{2m} \cdot 2m \right)^2 \cdot \frac{1}{m^3c^2} \left(\frac{e^2}{r_B} \right) \cdot \frac{1}{m^2c^2} \frac{e^2}{r_B} \left(\frac{me^2}{\hbar^2} \right) \frac{\hbar^2}{m^2c^2} \sim \alpha^2 \frac{e^2}{r_B}$$

$\Rightarrow n=2$

$$\Delta E_{2p_{1/2}} = \frac{11}{384} \alpha^2 \frac{e^2}{r_B}, \quad \Delta E_{2p_{1/2}} = \Delta E_{2s_{1/2}} = -\frac{5}{128} \alpha^2 \frac{e^2}{r_B}$$

$\rightarrow$ Lamb shift.

Interazioni Spin-orbita come perturbazioni
negli stat. d. mult. pletto: segue d. A

$$H_{LS} = \sum_k \alpha_k(r_k) \mathbf{L}_k \cdot \mathbf{S}_k$$



dove $\alpha_k(r_k) = \frac{\hbar^2}{2m^2 c^2 r_k} \frac{1}{dr_k} \frac{dV_{eff}(r_k)}{dr_k}$

$$(L, S) \Rightarrow \text{?}$$

$$\Delta E = \langle \psi_{(L,S)} | H_{LS} | \psi_{(L,S)} \rangle$$

$$= \langle \psi_{(L,S)} | A \mathbf{L} \cdot \mathbf{S} | \psi_{(L,S)} \rangle \quad \begin{matrix} \text{Wigner-} \\ \text{Eckart} \end{matrix}$$

$$\mathbf{L} = \sum_k \mathbf{L}_k ; \quad \mathbf{S} = \sum_k \mathbf{S}_k$$

Segue d. A per lo stato fondamentale.

(i) multipletto normale ($N \leq \frac{1}{2} \cdot 2(2l+1)$)

$$\chi_{sp} = \boxed{\uparrow \uparrow \uparrow \uparrow \uparrow}$$

$$S = N/2$$

$$\mathbf{S}_k = \frac{1}{N} \mathbf{S}$$

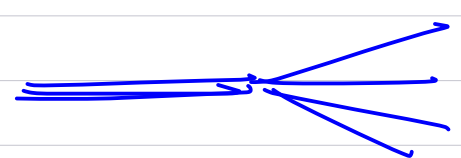
$$\begin{aligned}
& \langle \psi(L, S) | \sum_k \alpha(r_k) \mathbf{p}_k \cdot \mathbf{S}_k | \psi(L, S) \rangle \\
&= \frac{1}{N} \langle | \sum_k \alpha(r_k) \mathbf{p}_k \cdot \mathbf{S} | \psi(L, S) \rangle \\
&= \frac{\alpha}{N} \langle \psi(L, S) | \mathbf{L} \cdot \mathbf{S} | \psi(L, S) \rangle \\
&= \langle \psi(L, S) | A \mathbf{L} \cdot \mathbf{S} | \psi(L, S) \rangle
\end{aligned}$$

con $A = \frac{\alpha}{N} = \frac{1}{N} \int dr \vec{P}(r)^2 \alpha(r) > 0.$

$$= \langle \frac{A}{2} (J^2 - L^2 - S^2) \rangle$$

$$= \frac{A}{2} (J(J+1) - L(L+1) - S(S+1))$$

$$\therefore \Delta E_J = E_J - E_{J-1} = A \cdot J \quad \left(\begin{array}{l} \text{regola di} \\ \text{Landé} \end{array} \right)$$

$(L, S) \Rightarrow$

 $\begin{array}{l} L+S \\ L+S-1 \\ \vdots \\ |L-S| \end{array}$
 per un
~~mult. piatto~~
normale.

Per un mult. piatto invertito ($N > 2L+1$)

$$A < 0.$$

Per i multipletti invertiti:

$$(L, S) \longrightarrow \begin{cases} J = |L - S| \\ J = |L - S| + 1 \\ \vdots \\ J = L + S \end{cases}$$

• Per $N = \frac{1}{2} \cdot 2(2l+1) = 2l+1$? ?

Esempio: il termi-gatto (lo stato fond.)

1. $np \Rightarrow {}^2P \Rightarrow J = 3/2, 1/2 \rightarrow {}^2P_{1/2}$
(B, Al, Ga ...)

2. $np^2 \Rightarrow (L, S) = (1, 1) \Rightarrow J = 2, 1, 0 \xrightarrow{A > 0} {}^3P_0$
($\begin{matrix} 2p^2 & 3p^2 & 4p^2 \\ C & Si & Ge \end{matrix}$...)

3. $(np)^3 \Rightarrow (L, S) = (0, 3/2) \Rightarrow J = 3/2$
($\begin{matrix} 2p^3 & 3p^3 & 4p^3 \\ N & P & As \end{matrix}$...)

4. $(np)^4 \Rightarrow (L, S)_{comp} \Rightarrow (L, S) = (1, 1) \Rightarrow J = 2, 1, 0$
 $(2p)^2 \Rightarrow (L, S) = (1, 1) \Rightarrow J = 2, 1, 0$
 $A < 0 \rightarrow {}^3P_2$
 $\begin{matrix} 2p^4 & 3p^4 & 4p^4 \\ O & S (Zolfo) & Se (Selenio) \end{matrix}$

5. $(np)^5 (L, S) \rightarrow (L, S) \Rightarrow 2P \rightarrow J = \frac{3}{2}, \frac{1}{2}$
 core $(np) = (1, \frac{1}{2}) \Rightarrow A < 0 \hookrightarrow 2P_{3/2}$
 $2p^5 \quad 3p^5 \quad 4p^5$
 F Cl Br (bromine)

6. $(np)^6 \rightarrow (L, S) = (0, 0) \Rightarrow 1S_0$
 Ne, Ar, Kr --

7. $(nd)^1 (L, S) = (2, \frac{1}{2}) \Rightarrow 2D \Rightarrow J = \frac{5}{2}, \frac{3}{2}$
 $3d \quad 4d \quad 5d$
 $S_0 \quad Y, La$
 $A > 0 \hookrightarrow 2D_{3/2}$

8. $(nd)^2 \rightarrow (L, S) = (3, 1) \Rightarrow 3F \Rightarrow J = 1, 3, 5$
 $\uparrow$
 Hund
 $A > 0 \Rightarrow 3F_2$
 ex. $(3d)^2 \quad (4d)^2$
 Ti Zr --

Teoria quantistica della radiazione e
transizioni di dipolo.

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + V - e \cdot \mathbf{B}$$

Campo di radiazione

$$\phi = 0; \quad \nabla \cdot \mathbf{A} = 0 \quad (\text{gauge radiating})$$

Eq. di Maxwell

$$\Rightarrow (\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}) \mathbf{A} = 0;$$

$$\Rightarrow \mathbf{A} = \mathbf{A}_0 \epsilon \cdot e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + c.c.$$

$$(\mathbf{k}c = \omega)$$

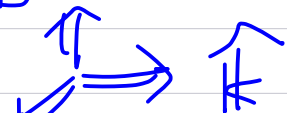
$$\mathbf{k} \cdot \epsilon = 0, \quad \mathbf{k} = (0, 0, k) \rightarrow \begin{cases} \epsilon_x = (1, 0, 0) \\ \epsilon_y = (0, 1, 0) \end{cases}$$

$$\text{O } \begin{cases} \epsilon^{(1)} = \epsilon_x \\ \epsilon^{(2)} = \epsilon_y \end{cases} \quad |\epsilon^{(1)}|^2 + |\epsilon^{(2)}|^2 = 1$$

$$\mathbf{E} = -\frac{1}{c} \dot{\mathbf{A}} = \frac{i\omega}{c} \mathbf{A}_0 \epsilon e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + c.c.$$

$$\mathbf{B} = \nabla \times \mathbf{A} = i\mathbf{k} \times (\mathbf{A}_0 \epsilon) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + c.c.$$

$$\epsilon \quad \mathcal{S} = \frac{c}{4\pi} (\mathbf{E} \times \mathbf{B}) = \frac{c}{2\pi} A_0^2 \left(\frac{\omega}{c} \right)^2 \hat{\mathbf{k}}$$



Normal-radiation flux.

$I = |S| =$ intensity of radiation
(flux energy)

$$= \frac{\omega^2}{2\pi c} A_0^2 = \omega \hbar n_\gamma$$

interpreto

$$A_0^2 = \underbrace{\frac{2\pi c}{\omega^2} I(\omega)}$$

Transizioni di dipolo (elettrico).

$$\frac{1}{2m}(\mathbf{p} - \frac{e}{c}\mathbf{A})^2 = \frac{\mathbf{p}^2}{2m} - \frac{e}{mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \dots$$

$$= \frac{\mathbf{p}^2}{2m} - \frac{e}{mc}(\mathbf{A} \cdot \mathbf{p}) + \dots \quad (\nabla \cdot \mathbf{A} = 0)$$

$$\Rightarrow \Delta H = -\frac{e}{mc} \sum_k \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k \rightarrow \text{elettroni}$$

$$\mathbf{A}(\mathbf{r}_k) = \mathbf{A}_0 \cdot e^{i\mathbf{k} \cdot \mathbf{r}_k - i\omega t} + \text{c.c.}$$

$$\Delta H = \hat{\mathbf{F}} \cdot e^{-i\omega t} + \text{h.c.} \Rightarrow \text{Fermi!}$$

$$\rightarrow W = \frac{2\pi}{h} |\hat{\mathbf{F}}|^2 \delta(E_f - E_i - \omega \hbar) d\Phi \quad !$$

$$\hat{\mathbf{F}} = -\frac{e}{mc} \sum_k (\mathbf{E} \cdot \hat{\mathbf{p}}_k) e^{i\mathbf{k} \cdot \mathbf{r}_k}$$

App. di dipolo:

$$e^{i\mathbf{k} \cdot \mathbf{r}_k} \sim 1.$$

$$\therefore k = \frac{\omega}{c} = \frac{\omega \hbar}{c \hbar} = \frac{E_f - E_i}{c \hbar} \propto \left(\frac{e^2}{r_B \cdot c \hbar} \right)$$

$$\sim \frac{\alpha}{r_B} \therefore |k \cdot \mathbf{r}_k| \sim k r_B \sim \alpha \sim O\left(\frac{1}{137}\right)!$$

$$< 1.$$

$$\Rightarrow F_{fi} = -\frac{eA_0}{mc} \langle f | \mathbf{E} \cdot \hat{\mathbf{p}} | i \rangle$$

$$\text{ora } [r_k, H] = \left[r_k, \sum_{k'} \frac{p_{k'}^2}{2m} + \dots \right] \\ = i\hbar \cdot \frac{p_k}{m}$$

$$\Rightarrow F_{fi} = -\frac{ieA_0}{\hbar c} \mathbf{E} \cdot \langle f | [H, r_k] | i \rangle$$

$$= -\frac{ieA_0}{\hbar c} (\mathbf{E}_f - \mathbf{E}_i) \langle f | (\mathbf{E} \cdot r_k) | i \rangle$$

$$= -i \frac{eA_0}{\hbar c} \langle f | \mathbf{E} \cdot d_k | i \rangle$$

$$d_k = e r_k : \text{dipolo dell' } k\text{-esimo elettrone!}$$

$\Rightarrow$ Regole di selezione (appr. d. dipolo)

E.g. Pd. circolare:

$$\mathbf{E} = \mathbf{E}_+ = -\frac{1}{\sqrt{2}}(1, i, 0) \Rightarrow \mathbf{E}_+ \cdot \mathbf{r} \sim T_+$$

$$\mathbf{E}_- = \frac{1}{\sqrt{2}}(1, -i, 0) \Rightarrow \mathbf{E}_- \cdot \mathbf{r} \sim T_-$$

Pd. lineare:

$$\mathbf{E}_1 = (1, 0, 0) \Rightarrow \mathbf{E}_1 \cdot \mathbf{r} \propto x = -\frac{T_+ - T_-}{\sqrt{2}}$$

$$\mathbf{E}_2 = (0, 1, 0) \Rightarrow \mathbf{E}_2 \cdot \mathbf{r} = y = \frac{T_+ + T_-}{\sqrt{2}}$$

$\Rightarrow$

Regole di selezione (trans. z.d. diplo)

$$\Pi = \leftrightarrow \sum_k l_k \quad (\neq (-)^L \text{ è generale})$$

(i) $\Pi_f = -\Pi_i$

(ii) $J_f - J_i = \pm 1, 0$ ma $0 \nrightarrow 0$

(iii) $L_f - L_i = \pm 1, 0; \quad 0 \nrightarrow 0$

(iv) $S_f - S_i = 0$.

(v) Conf. elettronica ψ_i / ψ_f differiscono per un elettrone.

(vi) $E \cdot R \propto T_0, T_{\pm 1},$

$J_z: M_f - M_i = \pm 1, 0 \quad (\neq 0 \text{ se } l_k \neq 0 \text{ o } k)$

$L_z: L_{zf} - L_{zi} = \pm 1, 0 \quad (\neq 0 \quad " \quad)$

Esempio: con $k=(0,0,k)$ e l'assorbimento di luce con $\epsilon_+ = -\frac{1}{\sqrt{2}}(1,i,0)$, $\epsilon_+ r = -\frac{1}{\sqrt{2}}(x+iy) = T'$, $\langle f | T' | i \rangle \rightarrow$

$$J_{fz} - J_{iz} = +1 \quad \Delta J = \begin{cases} +1 \\ 0 \end{cases}, 0 \leftrightarrow 0$$

$$L_{fz} - L_{iz} = +1, \quad \Delta L = \begin{cases} +1 \\ 0 \end{cases} \quad 0 \leftrightarrow 0$$

Luce (il fotone) "porta" il num. ang. $\overset{S}{1}, \overset{S_z}{1} \rangle$

Il fotone (con $m_y = 0$) porta l'elicità

$$\hat{S} \cdot \hat{k} = \pm 1 \rightarrow \text{No stati di } S_k = 0.$$

$$\equiv \hbar = \pm 1.$$

Una particella con $m=0$ ha soltanto
"di spin S "

gli stati $\hbar = \pm S$. (No sistema di
riposa. w/f c.)

Esempio transizioni tra gli stati del carbonio
 $(1s)^2 \{ \dots \}$ (st. fin. $3P$)

- (1) $(2s)(2p)(3d)^3 D \rightarrow (2s)^2(2p)^2 3P$ ✓
- (2) $(2s)^2(3s) 3P \rightarrow (2s)^2(2p)^2 1S$ ΔS
- (3) $(2s)^2(2p)(3d) 1D \rightarrow (2s)^2(2p) 3s 1P$ ΔT
- (4) $(2s)(2p)^3 3D \rightarrow (2s)^2(2p)^2 3P$ ✓
- (5) $(2s)^2(2p)(3p) 3P \rightarrow (2s)^2(2p)^2 3P$ ΔT
- (6) $(2s)(2p)^3 5S \rightarrow (2s)^2(2p)^2 3P$ ΔS
- (7) $(2s)^2(2p)(3d) 1D \rightarrow (2s)^2(2p)^2 1S$ ΔL
- (8) $(2s)^2(2p)(3s) 1P \rightarrow (2s)^2(2p)^2 1S$ ✓
- (9) $(2s)^2 2p 3s 1P \rightarrow (2s)^2(2p)^2 3P$ ΔS
- (10) $(2s)(2p)(3d)^2 3P \rightarrow (2s)^2(2p)^2 3P$ due elettroni

Radiazione non monocromatica e incoerente

Teo. pert. periodica.

$$A = \underbrace{A_0}_{A_0 \in} e^{i(k \cdot r - \omega t)} + \underbrace{A_0^*}_{A_0^* \in^*} e^{-i(k \cdot r - \omega t)}$$

(A)
assorbimento

(B)
emissione indotta

$$e^{i k \cdot r} \approx 1. \Rightarrow V = -\frac{e}{2m c} A \cdot \hat{p} \Rightarrow$$

$$= \hat{F} e^{-i \omega t} + h.c.$$

$$\Rightarrow W_{fi} = \frac{2\pi}{\hbar} |\bar{F}_{fi}|^2 \delta(E_f - E_i - \omega \hbar) d\Omega.$$

$$\hat{F} = -\frac{e}{2m c} A_0 \hat{E} \cdot \hat{p}$$

$$[H, r] = -i \frac{\hbar}{m}$$

$$(A) \quad \bar{F}_{fi} = \frac{-e}{2m c} A_0 \langle f | \hat{p} | i \rangle =$$

$$= -i \frac{e}{2 \hbar c} \langle f | [H, r]_k | i \rangle$$

$$= -i \frac{A_0 \cdot \omega_{fi}}{c} \underbrace{\langle f | \hat{E} \cdot d | i \rangle}_b \underbrace{\quad}_a$$

$$= -i A_0 \frac{\omega_{ba}}{c} \hat{E} \cdot d_{ba}$$

(B)



$$F_{fi} = -i A_0 \frac{\omega_{fi}}{c} \langle f | \hat{E} \cdot \hat{d} | i \rangle$$
$$= -i A_0 \frac{\omega_{ab}}{c} \langle f | \hat{E} \cdot \hat{d} | i \rangle$$

$\Rightarrow$ (A)

$$W_{ba} = \frac{\omega_{ba}^2}{\hbar^2 c^2} |d_{ba}|^2 \sum_{\omega} A(\omega) 2\pi \delta(\omega_{ba} - \omega)$$

$$\Rightarrow \int d\omega I(\omega) \frac{2\pi c}{\omega^2} \frac{\omega_{ba}^2}{\hbar^2 c^2} |d_{ba}|^2 \delta(\omega_{ba} - \omega)$$

$$= \frac{4\pi^2}{\hbar^2 c} |d_{ba}|^2 I(\omega_{ba})$$

(B) $\leadsto W_{ab} = \frac{4\pi^2}{\hbar^2 c} |d_{ab}|^2 I(\omega_{ba})$

Atomi in campo magnetico / Effetto Zeeman
(unif. cost.) Paschen-Back.

$$H = \frac{1}{2m} \left(p - \frac{e}{c} A \right)^2 + e\phi - \mu \cdot B.$$

$$A = \frac{1}{2} B \times r \quad (\Leftrightarrow B = \nabla \times A)$$

$$H = \frac{p^2}{2m} - \frac{e}{2mc} (B \times r) \cdot p + \dots$$

$$= \frac{p^2}{2m} - \frac{e}{2mc} B \cdot (r \times p) + \dots \quad \mu$$

$$= \dots - \frac{e\hbar}{2mc} B \cdot L - g \frac{e\hbar}{2mc} S \cdot B$$

$$= \dots - \frac{e\hbar}{2mc} (L + gS) \cdot B$$

$$B = (0, 0, B)$$

$$\Delta H = \frac{|e|\hbar}{2mc} (L_z + 2S_z) B = \hbar \omega_L (J_z + S_z)$$

dove $\omega_L = \frac{|\mu_B| B}{\hbar} = \text{frequenza di Larmor.}$

$\Rightarrow$ Or Line di grandezza.

$$|\mu_B| \sim 5.78 \cdot 10^{-5} \text{ eV} \cdot T^{-1} \quad \left(T = \text{Tesla} = 10^4 \text{ Gauss} \right)$$

$$|\mu_B| B \Leftrightarrow$$

$$\Delta E_{\text{struttura fine}} \sim \alpha^2 \cdot \frac{e^2}{r_B} \sim 10^{-4} \text{ eV}$$

$$B \gg 1 \text{ T} \Rightarrow \Delta E^{\text{Zeeman}} \gg \Delta E^{\text{str. fine}}$$

$$B \lesssim 1 \text{ T} \quad \text{struttura fine importante.}$$

$$\omega_{FS} \equiv \Delta E_{FS} / \hbar$$

$$\omega_L \gg \omega_{FS} \quad \text{eff. Paschen-Back.}$$

$$\omega_L \lesssim \omega_{FS} \quad \text{eff. Zeeman}$$

$$(LS) \quad \begin{array}{c} \text{---} \leftarrow \text{---} \quad J=L+S \\ \text{---} \quad \vdots \\ \text{---} \rightarrow \text{---} \quad J=|L-S| \end{array} \quad \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \quad \begin{array}{c} B=0 \\ B \neq 0 \end{array}$$

$$10^{-3} \text{ T} \leq B \leq 1 \text{ T}$$

N.B. $\mu B < 10^{-3} \text{ T} \Rightarrow$ struttura iperfine
va tenuto conto

Esercizio: Effetto Zeeman e la splitting delle
linee gialle di Na.

$$\begin{array}{c} 3P_{1/2} \rightarrow 3S \\ 3P_{3/2} \nearrow \end{array}$$

Teo perturbazione

$$H_B = \hbar \omega_L (L_z + 2S_z)$$

$$\langle J, J_z' | H_B | J, J_z \rangle \Rightarrow \Delta E_J$$

$$W-E \Rightarrow \langle \alpha; J, J_z' | L_z | \alpha; J, J_z \rangle \propto \langle J_z \rangle$$

$$\langle S_z \rangle \propto \langle J_z \rangle$$

$$\therefore \langle \alpha J J_z' | H_B | \alpha J, J_z \rangle = \delta_{J_z' J_z} \cdot \hbar \omega_L g_L J_z$$

$g_L \equiv$ fattore di Landé.

Calcolo di g_L :

$$\text{Set } L = c J$$

$$c J^2 = L \cdot J = - \frac{(J-L)^2 - J^2 - L^2}{2}$$

$$= + \frac{1}{2} (J^2 + L^2 - S^2)$$

$$\therefore c J(J+1) = \frac{1}{2} (J(J+1) + L(L+1) - S(S+1))$$

$$c = \frac{1}{2J(J+1)} \left\{ \begin{array}{c} \text{ } \end{array} \right\}$$

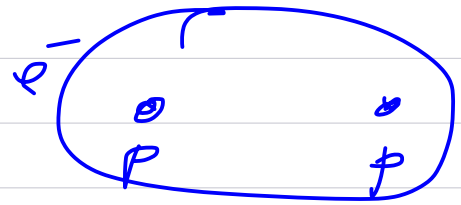
$$\langle H_B \rangle = \hbar \omega_L (2-c) J_z \quad \leftarrow \begin{array}{l} L_z + 2S_z = J_z + S_z \\ = 2J_z - L_z \end{array}$$

$$= \hbar \omega_L \cdot \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} J_z$$

$$g_L = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

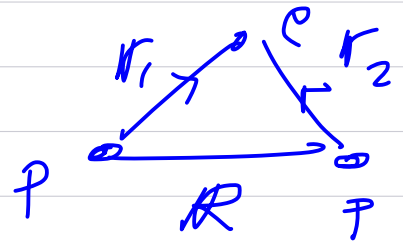
Legame molecolare.

molecola H_2^+



$$H = \frac{p^2}{2\mu} + \frac{e^2}{R} - \frac{p^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

$$\mu = \frac{m}{2} \gg m$$



⇒ Quantizzare il moto dell'elettrone
prima (Bohr-Oppenheimer).

N.B. $R \gg r_B \Rightarrow$ doppia
dega



$|1\rangle$

$|1\rangle$: $H' = \frac{e^2}{R} - \frac{e^2}{|R-r|}$
con perturb.



$|2\rangle$

$$H' = -\frac{e^2}{R} \sum_{l=1}^{\infty} \left(\frac{r}{R}\right)^l P_l(\cos\theta) \approx -e^2 \frac{r}{R^2} \cos\theta$$

$$\Delta E \approx \sum_{n,l,m} \frac{|\langle nlm | z | 100 \rangle|^2}{E_{100} - E_{nlm}} = -\frac{9e^4}{4R^4}$$

$|1\rangle$ $|2\rangle$ = doppio buco

Effetto tunnel.

$$E \approx c e^{-\frac{1}{\hbar} \int dr \sqrt{2m(V-E)}} = c e^{-R/r_B}$$
$$c \approx 1.47 R e^2 / r_B^3$$

$$\Rightarrow H = \begin{pmatrix} E_0 & -c \\ -c & E_0 \end{pmatrix}$$

$$|\psi_0\rangle \approx -\frac{1}{\sqrt{2}} (|\psi_1\rangle + |\psi_2\rangle)$$

$$\rightarrow E_0 \approx -\frac{e^2}{2r_B} - \frac{9e^4}{4R^4} - \frac{c}{2} e^{-R/r_B}$$

forze attrattive

MA NON SUFFICIENTE

$\rightarrow$ regione $R \sim r_B$ fondamentale.

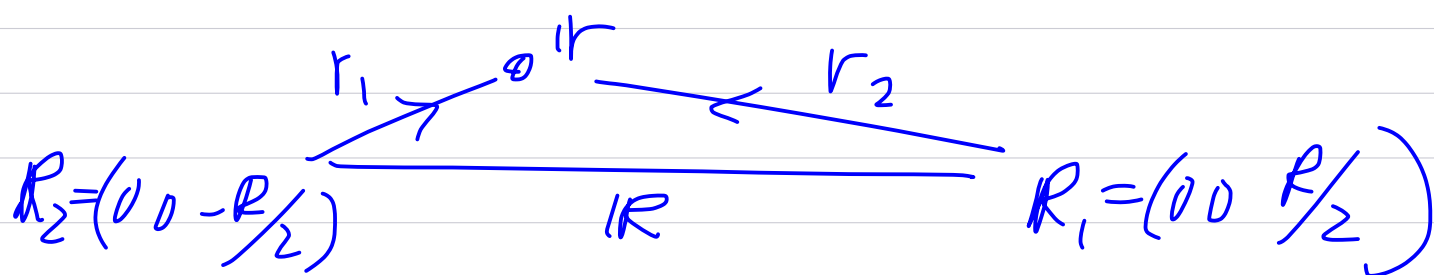
$\Rightarrow$ Approccio variazionale

Funz. d. prova.

$$\psi = c_1 \psi_1 + c_2 \psi_2$$

$$\psi_1 = \psi_{100}(r_1) \quad ; \quad \psi_2 = \psi_{200}(r_2)$$

con $c_1, c_2, \in \mathbb{R}$ come parametri variabili.



At fixed R :

$$H\psi = E\psi$$

$$H = \frac{p^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R}$$

$$\langle \psi_1 | \Rightarrow (H_{11} - E S_{11}) c_1 + (H_{12} - E S_{12}) c_2 = 0$$

$$\langle \psi_2 | \quad (H_{21} - E S_{21}) c_1 + (H_{22} - E S_{22}) c_2 = 0$$

dove $S_{ij} = \langle \psi_i | \psi_j \rangle$! $S_{12} \neq 0$!

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle$$

Cambio var. obl. $R_1 = (00 - \frac{R}{2})$; $R_2 = (00 \frac{R}{2})$

$$r_1 \equiv |r - R_1| = \sqrt{x^2 + y^2 + (z - R/2)^2}$$

$$r_2 \equiv |r - R_2| = \sqrt{\text{" " } (z + R/2)^2}$$

$$d^3r = \frac{1}{R} dr_1 r_1 dr_2 r_2 d\phi$$

$$\tan \phi = y/x$$

$$|R - r_1| \leq r_2 \leq |R + r_1|, \quad 0 < r_1 < \infty$$

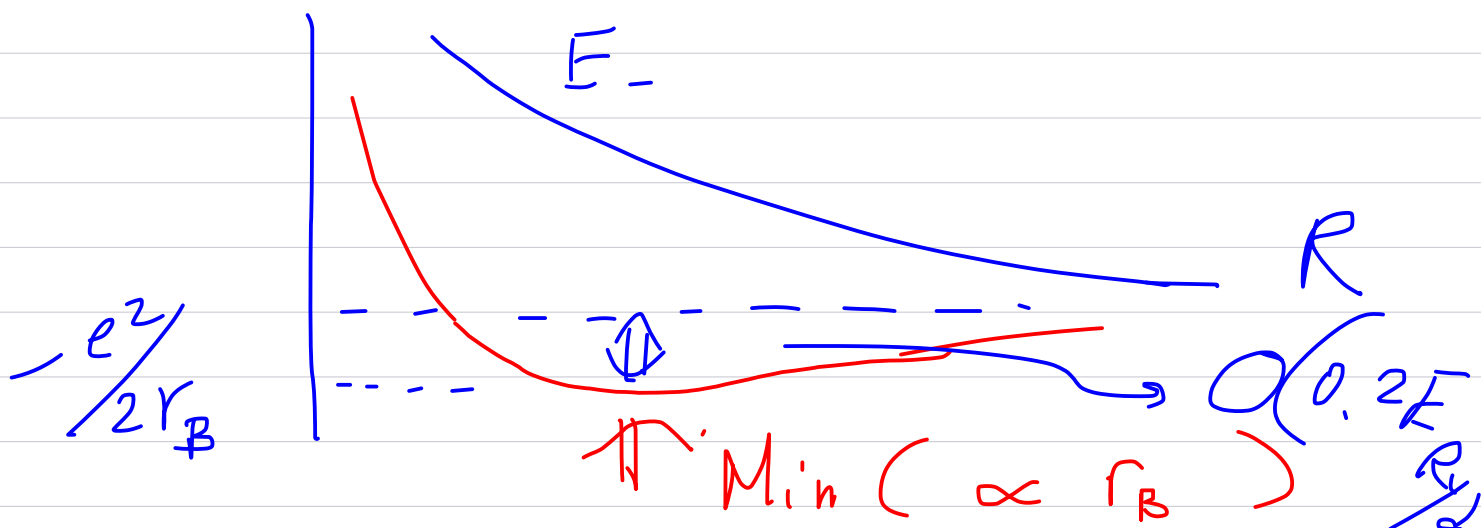
$$S = S_{12} \equiv \langle \psi_2 | \psi_1 \rangle = e^{-R} (1 + R + R^2/3)$$

Diagonalizz.

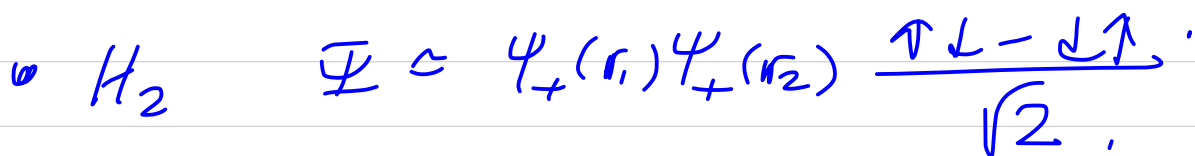
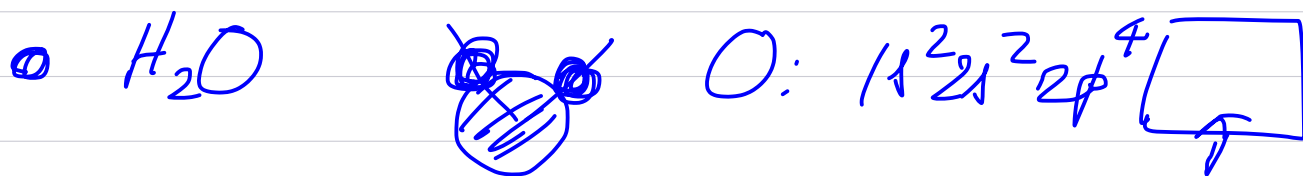
$$|H_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (|\psi_1\rangle \pm |\psi_2\rangle) \quad (r_B = 1)$$

con

$$E_{\pm}(R) = \frac{1}{2} \left[-1 + \frac{2}{R} \mp \frac{2e^{-R}(1+R) \pm \frac{2}{R} [1 - e^{-2R}(1+R)]}{1 \pm e^{-R}(1+R+R^2/3)} \right]$$



- Soltanto $|\psi_+$ $\propto |\psi_1\rangle + |\psi_2\rangle$ ha uno stato legato.
- Attrazione dovuta alla condivisione dell'orbita più bassa dei due nuclei dall'elettrone
- Stato legato a $R \approx 2r_B$.
- Il legame è debole.
- $V(R) = E_+(R) = E_{\min} + \frac{\Omega^2}{2} (R - R_{\min})^2 + \dots$
 $\Downarrow$
 Eccitazione radiale (vibraz.)



Orbitali ibridi

$$\text{"sp ibridi"} \quad \text{--- } (ns)^2 np \Rightarrow (ns)(\text{ibrido})$$

$$\text{con } \psi_1 = \cos \alpha \psi_{ns} + \sin \alpha \psi_{np_z} \rightarrow Y_{1,0}(\theta, \varphi) \propto \cos \theta$$
$$\psi_2 = \sin \alpha \psi_{ns} - \cos \alpha \psi_{np_z}$$

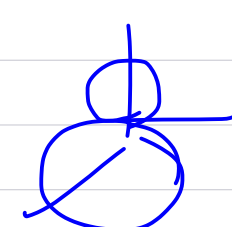
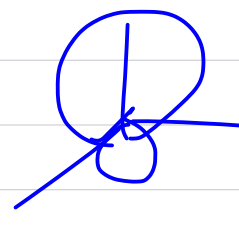
Richiedendo che i due orbitali abbiano la stessa forma geometrica, si ha

$$\cos \alpha = \sin \alpha \quad (\alpha = \pi/4)$$

$$\rightarrow \psi_{n,1p_z} = \frac{1}{\sqrt{2}} (\psi_{ns} + \psi_{np_z})$$

$$\psi'_{n,1p_z} = \frac{1}{\sqrt{2}} (\psi_{ns} - \psi_{np_z})$$

$$\lambda = \sqrt{\frac{1}{4\pi}} R_{n,0}(r) \neq \mu = \sqrt{\frac{3}{4\pi}} R_{n,1}(r)$$

$$\therefore \psi \sim \text{diagramma 1} \quad \psi' \sim \text{diagramma 2}$$


Orbitali ibridi (Cohen-Tannoudji e com.) Vol I

$$\psi_{nlm} = R_{n,l}(r) Y_{lm}(\theta, \varphi)$$

(i) Orbitali s $l, m = 0$ $\psi = R_{n,0}(r)$

(ii) Orbitali p. $l=1$ $m = \pm 1, 0$

$$\psi_{n,1,1} = -\sqrt{\frac{3}{8\pi}} R_{n,1}(r) \sin\theta e^{-i\varphi} \rightarrow (Y_{1,1})$$

$$\psi_{n,1,-1} = \sqrt{\frac{3}{8\pi}} R_{n,1}(r) \sin\theta e^{i\varphi} \rightarrow (Y_{1,-1})$$

$$\psi_{n,1,0} = \sqrt{\frac{3}{4\pi}} R_{n,1}(r) \cos\theta$$

ma $Y_{1,1} = -\frac{x+iy}{\sqrt{2}r}$,

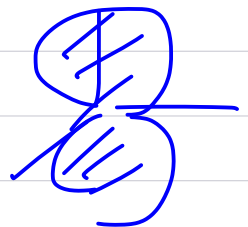
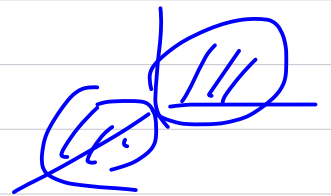
$$Y_{1,-1} = \frac{x-iy}{\sqrt{2}r}; \quad Y_{1,0} = \frac{z}{r}$$

$\Rightarrow$ Orbitali p. reali:

$$\psi_{n,1,x} = \sqrt{\frac{3}{4\pi}} R_{n,1} \frac{x}{r} \rightarrow$$

$$\psi_{n,1,y} = \frac{y}{r}$$

$$\psi_{n,1,z} = \frac{z}{r} \rightarrow$$



Orbitale p è direz. generico in

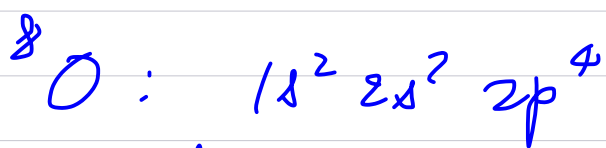
$$n.\hat{x} = \cos\alpha \quad n.\hat{y} = \cos\beta, \quad n.\hat{z} = \cos\gamma$$

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

$$|\psi_n\rangle = \cos\alpha |n p_x\rangle + \cos\beta |n p_y\rangle + \cos\gamma |n p_z\rangle$$

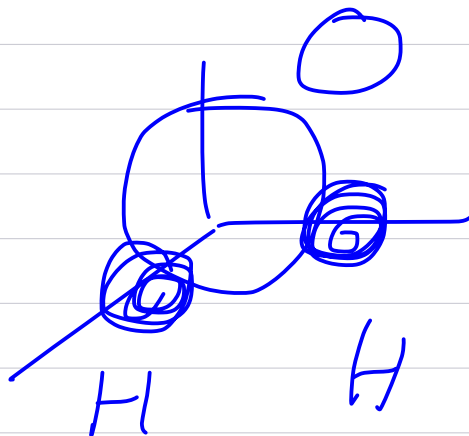
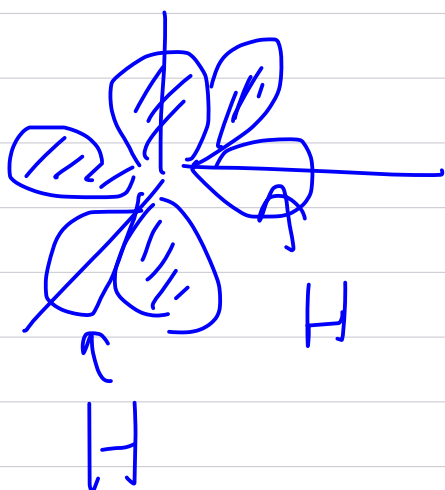
$$= \sqrt{\frac{3}{4\pi}} R_{n,1} \times \frac{\cos\alpha + y \cos\beta + z \cos\gamma}{r} = \sqrt{\frac{3}{4\pi}} R_{n,1} \frac{u}{r}$$

Struttura d. H_2O



Supp. che $(2p_z)^2 (2p_x)(2p_y)$ siano occupati.
→ gli orbitali vacanti sono $(2p_x)(2p_y)$

Se questi sono occupati (condivisi) dagli
elettroni di due H.



attualmente l'angolo $\sim 104^\circ$

← ripulsione tra i due protoni.

metano CH_4 e ibridi sp^3

Orbitali ibridi sp^3 sono comp. lineari

$$\psi = c_1 \psi_{ns} + c_2 \psi_{np_x} + c_3 \psi_{np_y} + c_4 \psi_{np_z}$$

$$\text{con } c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$$

$$\psi' = c_1' \psi_{ns} + \dots$$

$$\psi'' = c_1'' \psi_{ns} + \dots$$

$$\psi''' = c_1''' \psi_{ns} + \dots$$

Richiedendo che le quattro distribuz. abbiano
le stesse forme geometriche $\Rightarrow$

$$c_1 = c_1' = c_1'' = c_1'''$$

Richiediamo l'ortogonalità tra loro

$$(c_1, c_2, c_3, c_4) = \frac{1}{2} (1, 1, 1, 1)$$

$$(c_1', c_2', c_3', c_4') = \frac{1}{2} (1, -1, -1, 1)$$

$$(c_1'', c_2'', c_3'', c_4'') = \frac{1}{2} (1, -1, 1, -1)$$

$$(c_1''', c_2''', c_3''', c_4''') = \frac{1}{2} (1, 1, -1, -1)$$

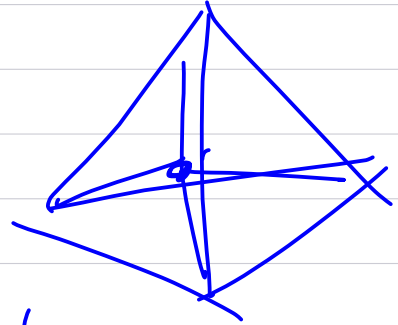
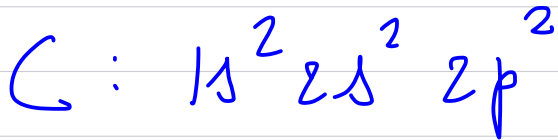
Sono orientati in

$$n_1 = (1, 1, 1), \quad n_2 = (-1, -1, 1),$$

$$n_3 = (-1, 1, -1) \quad n_4 = (1, -1, -1)$$

⇒ 4 dir. dal centro ai quattro vertici
i un tetraedro regolare !

e.g. CH_4



Ma è presente di 4 H's ⇒ conviene

$2s^2 2p^2 \rightarrow 2s 2p^3$ e formare

i quattro orbitali ibridi sp^3 !

e condividere quest. orbitali con un
elettrone ciascuno di H

