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

$[L_i, H] = [S_i, H] = 0$, $[P, H] = 0$

$[L^2, H] = [S^2, H] = 0$, ...

$\Rightarrow$ 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 (dopo!)

Correzioni relativistiche (e.g. per H):

$$\Delta H = -\frac{p^4}{8m^3c^2} + \frac{\alpha\hbar}{2m^2 c\, r^3}(L \cdot S) + \frac{\pi\alpha\hbar^3}{2m^2c}\delta^3(r)$$

$\uparrow$ $c\sqrt{p^2+m^2c^2}$ $\quad$ $\uparrow$ spin-orbita $\quad$ $\uparrow$ Darwin

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

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

$\Rightarrow [\mathbb{L}_i, H] \neq 0, \ [\mathbb{S}_i, H] \neq 0$.

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

$[\mathbb{J}, H] = 0$, $\quad \mathbb{J} \equiv \mathbb{L} + \mathbb{S}$.

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

sono $\{L, S; J, J_z\}$

$$(2L+1)(2S+1) \longrightarrow \begin{cases} J = L+S \\ \vdots \\ J = |L-S| \end{cases}$$

Tabella: l'energia di ionizzazione (potenziale)

$\Rightarrow$

Preambolo.

(a) Sforzo per comprendere lo spettro di atomi
⇒ MQ. Livelli discreti; emissione assorbimento di luce, raggi X, tabella periodica

(b) 1° terreno di prova della MQ.
Calcolo dettagliato e preciso dei livelli

(c) Tecniche/metodi di approssimaz. sviluppati

(d) Dall'atomo, a nuclei, a particelle elem.
Una rivoluzione scientifica senza precedente
⇒ Conoscenze, tecnologie, controllo di sistemi microscopici ⇒ macroscopici.

(e) Tecnologie contemporanee (smartphone...)

(f) Tutto oggi in continua evoluzione
- tecnologiche
- in gravità, cosmologia, fisica particelle...
- Nuovo paradigma ?

Livelli atomici, dati:

(1) # quantici globali (termini spettrali)

$^{2S+1}L_J$: $^{2}P_{1/2}$, $^{2}D_{3/2}$, $^{4}F_{9/2}$ → $L=3$

$2S+1$

$S=3/2$

orbitali

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

S P D F, G. ...

(2) Configurazione elettronica

stato di Z elettroni

Programma.

(1) App. di elettroni indipendenti + Principio Pauli

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

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

(3) Raggi X

(4) Approssimaz. di Hartree

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

(6) Elettroni equivalenti, Conf. elettroniche e multipletti.

(7) Correz. relativistiche / struttura fine

(8) Atomi in campo magnetico

(9) Teo. semiclassica della radiazione

(10) Coeff. di Einstein

Appr. elettroni indipendenti:

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

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

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

es. He: $E^{He}_{(0)} = -\frac{2 Z^2 e^2}{2 r_B} = -4 \left(\frac{e^2}{r_B}\right)$

$= -2.75$ pert.

$= -2.85$ var.

$= -2.904$ sper.

L'effetto di schermaggio

^3L_i

$$\Psi^{l,m,\uparrow} = \frac{1}{N} \sum (-)^P \psi_{100}(r_1)\psi_{100}(r_2)\psi_{2lm}(r_3) \frac{\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow}{\sqrt{2}}.$$

$N \leftarrow \sqrt{3!}$

$2lm$ —

100 —

$$= \frac{1}{\sqrt{6}} \Big\{ \psi_{100}(r_1)\psi_{100}(r_2)\psi_{2lm}(r_3)(\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow)$$

$$- \psi_{100}(r_1)\psi_{2lm}(r_2)\psi_{100}(r_3)(\uparrow\uparrow\downarrow - \downarrow\uparrow\uparrow)$$

$$- \psi_{2lm}(r_1)\psi_{100}(r_2)\psi_{100}(r_3)(\uparrow\downarrow\uparrow - \uparrow\uparrow\downarrow) \Big\}$$

$2 \; 3$

$1 \; 3$

In questa appr. Li è $2^2 \cdot 2 = 8$ volte degenere.

<u>Energia di ionizzazione</u>

$\equiv$ energia minima necessaria per liberare un elettrone.

$$= \frac{Z^2 e^2}{8 r_B} \overset{Z=3}{=} \frac{9}{4} E_H \sim 30.6 \text{ eV}$$ (appr. el. indip.)

cfr $= 5.4$ eV (val. sperim.)

cfr. $= 3.4$ eV (schermaggio totale $\overset{\shortparallel}{H}$)

Osservazioni

(i) App. elettroni indipendenti $\Longrightarrow$ Degenerazioni di stati non osservate

(ii) Interaz. tra elettroni importanti, l'effetto di schermaggio e carica effettiva (He)

(iii) Per Li (atomi alkali), l'effetto di schermaggio è dominante

(ii), (iii) $\Longrightarrow$

Campo efficace, a simmetria centrale.

- idee elementari
- campo autoconsistente.

Campo efficace : idea

V_{eff},   H + e

$\cdot e^-$

$$V_{eff}(r) = -\frac{e^2}{R} + e^2 \int d^3r \, \frac{|\psi_{1s}(r)|^2}{|r - R|}$$

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

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

$$e^2 \int \frac{d^3r \, |\psi|^2}{|r-R|} = \int_{r<R} + \int_{r>R}$$

$\int d\Omega \, P_\ell(\cos\theta) = 4\pi \, \delta_{\ell,0}$

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

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

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

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

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

$$V_{eff} = -\frac{e^2}{R} + e^2\int d^3r\,\frac{|\psi_{100}|^2}{|r-R|}$$

$$= -e^2\left(\frac{1}{R}+\frac{1}{r_B}\right)e^{-2R/r_B} \;\begin{cases}\to 0, & R\to\infty\\ \to -\dfrac{e^2}{R}, & R\to 0\end{cases}$$

OK.

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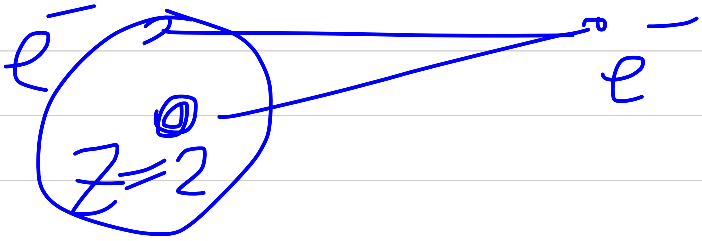
ex. 2 He, V_{eff}



$$V_{eff} = -\frac{2e^2}{R} + e^2\int d^3r\,\frac{|\psi^{(Z=2)}_{100}|^2}{|r-R|}$$

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

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

$$\begin{cases}\xrightarrow{R\to\infty} -e^2/R \; ! \\ \xrightarrow{R\to 0} -2e^2/R\end{cases}$$

Li : l'elettrone di valenza

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

$$V_{eff} = -\frac{3e^2}{r} + 2e^2 \int d^3r' \frac{|\psi^{Z=3}_{100}(r')|^2}{|r-r'|}$$

$$= \underbrace{-\frac{e^2}{r}}_{\text{carica schermata}} \underbrace{- 2e^2\left(\frac{1}{r}+\frac{1}{r_B'}\right)e^{-2r/r_B'}}_{V^{pert.}} \qquad \boxed{r_B' = \frac{r_B}{3}}$$

$$\Rightarrow E^{(val)} = -\frac{e^2}{2 \cdot 4\, r_B} + \langle \psi_{200} | V^{pert} | \psi_{200} \rangle$$

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

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

$$= \frac{e^2}{4}\int_0^\infty dr\, r^2(2-r)^2\left(\frac{1}{r}+3\right)e^{-7r} = \frac{e^2}{4}\frac{1766}{16807}$$

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

cfr 5.4 sper.

3.4 scherm. tot

30.6 el. indip.

Ricapitolando: l'energia (potenziale) di ionizzazione

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

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

cfr. $\quad 4\frac{e^2}{2r_B}$ (app. elett. indip) $\sim 4 \cdot 14 \sim 56\ \text{eV}$

$\frac{e^2}{2r_B}$ (total screening) $\sim 14\ \text{eV}$

Li $\quad \sim 5.4\ \text{eV}$. (sperim.)

cfr. $\quad \frac{Z^2 e^2}{8 r_B} \sim \frac{9}{4} E_H \sim 30.6\ \text{eV}$ (elett. indip.)

$\frac{e^2}{8 r_B} \sim \frac{1}{4} E_H \sim \underline{3.4\ \text{eV}}$ (schermo completo)

Campo eff. e autoconsistente.

$$U_{eff}(r_i) = -\frac{Ze^2}{r_i} + \sum_{j\neq i}\int d^3 r_j \, \frac{e^2|\psi_j(r_j)|^2}{|r_i - r_j|}$$

$$\Rightarrow -e^2/r \qquad r\to\infty$$

$$\Rightarrow -Ze^2/r \qquad r\to 0$$

Degeneraz. Coulombiana eliminata $\Rightarrow$

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

Approccio iterativo

(i) $\psi^{(0)}_{p_j}(r_j) = \psi^{el.\,idr.}(r_j) \Rightarrow$

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

(iii) $\{\psi^{(1)}(r_j)\} \Rightarrow$

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

Campo autocompatibile

$$\left\{\begin{array}{l} \psi^{(i+1)}(r_k) = \psi^{(i)}(r_k) \\ U^{(i+1)}(r_k) = U^{(i)}(r_k) \end{array}\right\} \quad k = 1, 2 \ldots Z$$

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

(ii) Ciascun el. è nello stato

$(n, \ell, m; s_z)$

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

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

N elettroni in (n, ℓ) occupano $N \leq 2(2\ell+1)$ stati diversi

$P_1 = |n, \ell, m_1; s_{1z}\rangle$, $P_2 = |n; \ell_2\, m_2, s_{2z}\rangle$, ...

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

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

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

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

Principio di esclusione di Pauli.

$\leftarrow$ FD

Nella rapp. delle coordinate

$$\Psi(\underbrace{r_1, \zeta_1}_{\xi_1}, \underbrace{r_2\, \zeta_2}_{\xi_2}, \dots\, r_N, \zeta_N) \qquad \zeta_i = \pm \;, \; \binom{\cdot}{\cdot}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-)^P \begin{vmatrix} \psi_{p_1}(\xi_1) & \psi_{p_1}(\xi_2) \; \dots & \psi_{p_1}(\xi_N) \\ & - \; - & \\ \psi & & \end{vmatrix}$$

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

$\boxed{\text{Teo:}}$ Uno strato chiuso porta $S = L = 0$.

$(n, \ell) \Rightarrow 2(2\ell+1)$ stati, $\boxed{N = 2(2\ell+1)}$

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

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

$|p_3\rangle = |m=0, \uparrow\rangle$; etc.

Determinante di Slater

$|\Psi\rangle =$ tot. antisim.

$$= \frac{1}{\sqrt{6!}} \det \begin{vmatrix} |p_1\rangle^{(1)} & |p_1\rangle^{(2)} & \cdots & |p_1\rangle^{(6)} \\ \cdots & & & \\ |p_6\rangle^{(1)} & \cdots & & |p_6\rangle^{(6)} \end{vmatrix}$$

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

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

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

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

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

Configurazione elettronica.

Atomo con # atomico Z

$$\sim (1s)^2 (2s)^2 (2p)^6 \cdots (n\ell)^N$$

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

Il termine spettrale ^{2S+1}L è determinato

(L, S)

da N elettroni di valenza, noti elettroni equivalenti.

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

$\rightsquigarrow$ Dopo!

Es. ${}^1H$ $1s^1$

${}^2He$ $(1s)^2$

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

- - -

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

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

- -

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

Nomi per vari orbitali.

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

Nome K L M N O P Q ...

"strato K" etc.

L'ordine di energia ≠ orbite di Bohr.

$\underbrace{(1s)^2}_{} \ \underbrace{(2s)(2p)}_{10}(3s\ 3p) \underbrace{(4s\ 3d\ 4p)}_{36}$ ...

(18)

$H\to He$ $Li\to Ne$ $Ne\to Ar$ $K\to Kr$ elementi di transizione

Raggi X.

Raggi EM di $\lambda \sim 10^{-2} - 10^{2}$ Å

(cfr $\lambda \sim 10^{3}$ Å x luce visibile.)

g. vari element. 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 K da $Z \gtrsim 11$
L " $Z \gtrsim 30$ ...

Caratteristiche

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

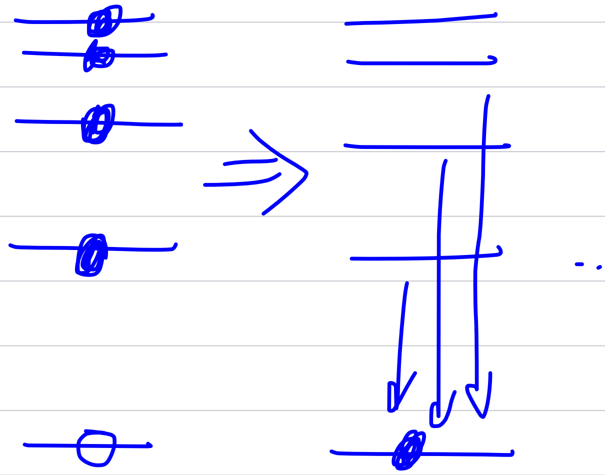
(2) Raggi X nello spettro di emissione ma non nello spettro di assorbimento.

--> 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

$2p \to 1s$ } serie
$3p \to 1s$ } K.

--

Elettrone 1s vede

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

$$E_K \sim \frac{Z^2 e^2}{2 r_B}\left(1 - \frac{1}{n^2}\right) \quad n = 2, 3, 4 \ldots$$

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

analogamente $\rightarrow$ schermaggio

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

Per Na $(Z=11)$

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

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

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

$\Longrightarrow$ Metodo di misurare l'energia di elettroni in vari strati.

$\Rightarrow$ Tabella

Approssimazione di Hartree

L'i-simo elettrone:

$$-\frac{\hbar^2\nabla_i^2}{2m}\psi_i - \frac{Ze^2}{r_i}\psi_i(r) + e^2\int d^3r' \frac{\rho_i(r')}{|r-r'|}\psi_i(r) = \varepsilon_i\psi_i(r) \qquad (*)$$

dove

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

• Appr. di potenziale eff. a simmetria centrale

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

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

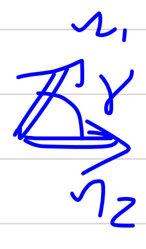
Un elettrone ψ_j contribuisce nell'eq. (*)

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

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

$$= \frac{1}{2l+1}\sum_m |Y_{l,m}(\hat{r}')|^2 = \frac{1}{4\pi}. \qquad (S.)$$

(S.) $$P_l(\cos\gamma) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{l,m}(\Omega_1)\, Y^*_{lm}(\Omega_2)$$



$\gamma=0$ $$1 = \frac{4\pi}{2l+1}\sum_m |Y_{lm}|^2 \;\therefore\; \rightarrow (S.)$$

Oppure, semplicemente,

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

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

Ricapitolando, la media direzionale $\Rightarrow$

$$|Y_{lm}(\hat{r}')|^2 \longrightarrow \frac{1}{4\pi}$$

Il contributo di un elettrone nel (n,l)

$$\simeq \frac{1}{4\pi}\int d^3r'\, R^2_{nl}(r')\, \frac{1}{|r'-r|}$$

$$\frac{1}{|r'-r|} \Rightarrow \begin{cases} \frac{1}{r}\sum_l \left(\frac{r'}{r}\right)^l P_l(\cos\theta) & (r > r') \\ \frac{1}{r'}\sum \left(\frac{r}{r'}\right)^l P_l & (r < r') \end{cases}$$

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

$$\equiv V_a$$

dove $R_{n,l}(r) \equiv \dfrac{P_{n,l}(r)}{r} \rightarrow \left(\dfrac{\chi_{nl}(r)}{r}\right.$

Teo Gauss.

$$Q(r) = \int_0^r dr' \, P_{n\ell}^2(r')$$

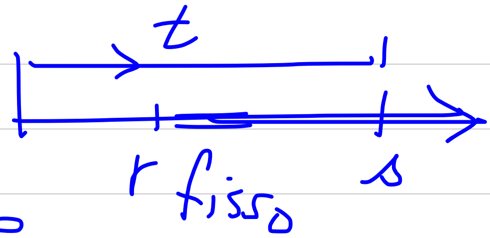
la "carica" interno alla sfera con raggio r.

campo el.

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

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

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



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

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

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

! OK.

$\overbrace{\text{Equazione}}^{\text{radiale}}$ per un elettrone nello strato $a \equiv (n, \ell)$
$(m = e = \hbar = 1)$

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

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

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 integro-differenziale per $\underbrace{P_a(r) = r R_{n\ell}(r)}$

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

e.g. $Z = 6$ C $\underbrace{1s^2 2s^2 2p^2}$.

$a, b, c = (n, \ell) = (1s), (2s), (2p)$.

$Z = 6$

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

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

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

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

Soluzione iterativa

$$P^{(0)}_{n\ell}(r) = r \cdot R^{Bohr(Z)}_{n,\ell}(r) \Rightarrow \{V^{(0)}_{n,\ell}\} \Rightarrow$$

$$P^{(1)}_{n,\ell}(r) \Rightarrow \{V^{(1)}_{n,\ell}\} \Rightarrow \cdots$$

Interpretazione.

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Ze^2}{r_i}\right)\psi_i+e^2\sum_{j\neq i}\int d^3r'\,\frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r})$$

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

$$\sum_i\langle\psi_i|\frac{p_i^2}{2m}-\frac{Ze^2}{r_i}|\psi_i\rangle+e^2\sum_{j\neq i}\int d^3r\,d^3r'\,\frac{|\psi_j|^2|\psi_i|^2}{|\mathbf{r}-\mathbf{r}'|}=\sum_i\epsilon_i$$

cfr. con

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

tra $\Psi=\prod_i\psi_i$:

$$\langle\Psi|H|\Psi\rangle=\sum_i\langle\psi_i|\frac{p_i^2}{2m}-\frac{Ze^2}{r_i}|\psi_i\rangle+\frac{e^2}{2}\sum_{i\neq j}\int d^3r\,d^3r'\,\frac{|\psi_i|^2|\psi_j|^2}{|\mathbf{r}_i-\mathbf{r}_j|}\ !$$

i.e.,

$$\sum_i\epsilon_i=E+\frac{e^2}{2}\sum_{i\neq j}\iint d^3r_i\,d^3r_j\,\frac{|\psi_i|^2|\psi_j|^2}{|\mathbf{r}_i-\mathbf{r}_j|}\quad !$$

Principio variazionale e l'eq. di Hartree

$|\Psi\rangle = \prod |\psi_i\rangle$ e

$$\Rightarrow \langle\Psi|H|\Psi\rangle = \sum_i \int \psi_i^* \left(\frac{p^2}{2m} - \frac{Ze^2}{r_i}\right)\psi_i$$

$$+ \frac{e^2}{2}\sum_{i \neq j}\int |\psi_i|^2 |\psi_j|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Calcolo variazionale,

$$\frac{\delta}{\delta\psi^*}\left[\langle\Psi|H|\Psi\rangle - \sum_i \epsilon_i\left(\langle\psi_i|\psi_i\rangle - 1\right)\right] = 0$$

$$\Rightarrow -\frac{1}{2}\nabla^2\psi_i - \frac{Z}{r_i}\psi_i + \sum_{j \neq i}\int d^3r' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r}_i - \mathbf{r}_j|}\psi_i(\mathbf{r}_i) = \epsilon_i \psi_i(\mathbf{r}_i)$$

: Equazione di Hartree !!

Tables. p. 429 - <u>QM</u>

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

dove $d = \alpha E$

$\Leftrightarrow$ $E = -d \cdot E$ (dipolo permanente)

Derivazione da un potenziale efficace a simm. centrale

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

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

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 $H_{rel} = 0$.

$$H = H^{sim.cent} + H_{ee}$$ (Accoppiamento L-S o " Russel-Sanders)

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

$\Rightarrow$ Multipletti.

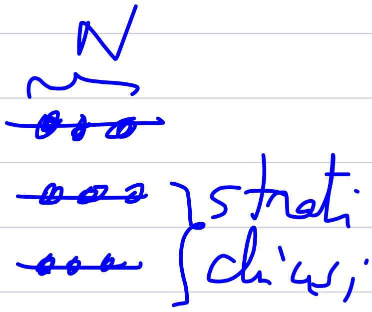
app. Hartree $\Rightarrow$

Tipicamente un atomo ha

(i) $N \le 2(2l+1)$ elettroni nello strato (n,l) più esterno (valenza), noti: elettroni equivalenti

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

(iii) $\# = \binom{2(2l+1)}{N}$ possibili stati $\{P_i\}$:



occupati da elettroni $\Rightarrow \binom{2(2l+1)}{N}$ possibili Determinanti di Slater (stati totalmente antisimmetrici).

(iv) Questi sono tutte degeneri $(\#)$ i

Questa degenerazione è parzialmente rimossa

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

$\hookrightarrow$ (L,S) multipletti $\Rightarrow$ Quali?

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

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

$S: \ \frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0 \Rightarrow S = 1 \ , \ S = 0$.

$S = 1$ (spin tot. simm.) $\Rightarrow$ orbitali antisimm.

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

$L = 1$! $\quad \left(l_1 \otimes l_1 = 1 \otimes 1 = \underset{S}{2} \oplus \underset{A}{1} \oplus \underset{S}{0} \right)$

$\therefore$

$(L, S) = (1, 1) \Rightarrow 3 \cdot 3 = 9$ stati

$S = 0$ (spin antis.) $\Rightarrow$ orbitali simmetrici.

$\left.\begin{array}{ll} L = 2 & (5 \text{ stati}) \\ L = 0 & (1 \quad) \end{array}\right\} 6$ stati.

$\therefore \Rightarrow (L, S) = \underset{9}{(1, 1)} + \underset{5}{(2, 0)} + \underset{1}{(0, 0)} = 15$ ok.

$\qquad {}^3P \qquad {}^1D \qquad {}^1S$

3 elettroni in $(n\, l) = (n, 1)$?

Tabelle di Young $\Leftrightarrow$ rappresentazioni 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

$$\psi = \psi_{a_1}(1)\, \psi_{a_2}(2) \cdots \psi_{a_N}(N) \qquad (*)$$

per es. $a_i = 1, 2 \quad (S_z = \pm 1/2)$

$a_i = 1, 2, 3 \quad (S=1,\ S_z = \pm 1, 0\ ;\ L=1,\ L_z = \pm 1, 0)$

Possibili comb. lineari di termini $(*)$ che hanno proprietà particolare x scambi di oggetti

$\Longleftrightarrow$ tabelle di Young

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

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

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

$\begin{smallmatrix}\square\\\square\end{smallmatrix} = \frac{1}{\sqrt{2}}\left(\quad - \quad \right)$

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

Gruppo di permutazioni S_N

per es. S_3

Elementi	Permutaz.
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

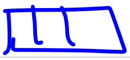
$(12)\cdot(12) = e$.

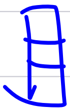
Rappresentazione $\left(g \to M(g),\ g_1 g_2 \Rightarrow M(g_1)M(g_2) = M(g_1 g_2) \right)$

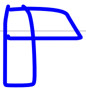
$$e = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix}, \quad (12) = \begin{pmatrix} & 1 & \\ 1 & & \\ & & 1 \end{pmatrix} \quad (23) = \begin{pmatrix} 1 & & \\ & & 1 \\ & 1 & \end{pmatrix}$$

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

(iii) $N=3$.

 ~ tot. simm.

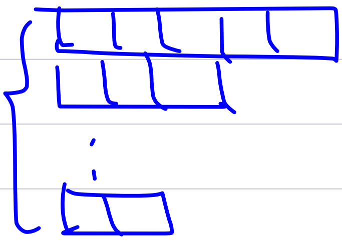
 ~ tot. antisimm.

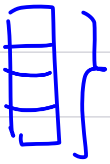
 ~ simmetria mista.

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

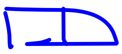
N_1 oggetti simmetrici,

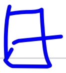
N_2 " ...

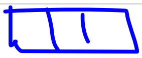


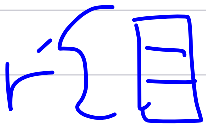
 $r = 0$ se $r > p$

(v) Spin 1/2 (SU(2)) $a = 1, 2$.

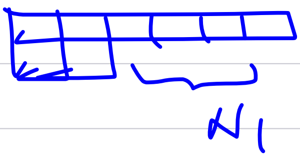
 $S = 1$

 $S = 0$

 $S = 3/2$

 $= 0$, $r > 2$

 $S = N/2$

 $S = N_1/2$.

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

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

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

$\square \sim \underline{3} \;, \; \ell = 1 \qquad \square \sim \underline{3}$

$\square\!\square \sim \underline{5} \oplus \underline{1} \;\; (\ell = 2, 0) \qquad \square\!\square \sim \underline{6}$ } rappr irriduc.

$\begin{smallmatrix}\square\\ \square\end{smallmatrix} \sim 3 \;\; (\ell = 1) \;; \qquad \begin{smallmatrix}\square\\ \square\end{smallmatrix} \sim \underline{3}^*$

Morale: per $SO(3)$ Y. Tab $\neq$ rapp. irrid.

per $SU(3)$, tab. Young $\Leftrightarrow$ rappr. irriduc.

$SU(N)$,

SU(3) e il modello dei quarks.

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

$\pi^\pm, K \ldots$ (mesoni) $\sim |q\bar{q}>$

in $$\underline{3} \otimes \underline{3}^* = \Box \times \begin{smallmatrix}\Box \\ \Box\end{smallmatrix} = \underbrace{\begin{smallmatrix}\Box\Box \\ \Box\end{smallmatrix}}_{\underline{8}} + \underbrace{\begin{smallmatrix}\Box \\ \Box \\ \Box\end{smallmatrix}}_{\underline{1}}$$

$\underline{8} \to \pi^\pm, \pi^0, K^+, K^0, \bar{K}^0, K^-, \eta$; $\underline{1} \to \eta'$

Barioni ($p, n, \Sigma, \Lambda \ldots$)

$\sim |q q q>$

$$\Box \times \Box \times \Box = \Box \times \left(\Box\Box + \begin{smallmatrix}\Box \\ \Box\end{smallmatrix} \right)$$

in $$\underline{3} \otimes \underline{3} \otimes \underline{3} = \underline{3} \otimes (6 \oplus 3^*) = \underbrace{\Box\Box\Box}_{10} + \underbrace{\begin{smallmatrix}\Box\Box \\ \Box\end{smallmatrix}}_{8} + \underbrace{\begin{smallmatrix}\Box\Box \\ \Box\end{smallmatrix}}_{8} + \underbrace{\begin{smallmatrix}\Box \\ \Box \\ \Box\end{smallmatrix}}_{1}$$

$8 \to p, n, \Sigma^\pm, \Sigma^0, \Xi^0, \Xi^-, \Lambda$

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

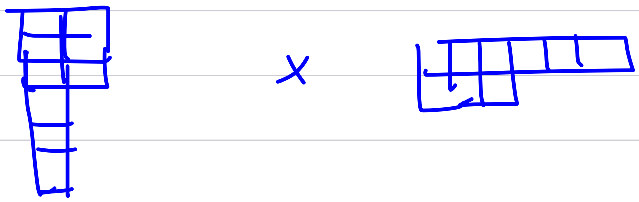
N spin $= \frac{N}{2}$, $= \frac{N}{2} - 1$, etc

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

Orbitale deve avere la tabella di Young "complementare"

Orbitali $\otimes$ Spin

r_1 r_2



r_1

r_2

Torniamo a $N=3$ elettroni in $(n,1) \to p$

Ci sono $\binom{6}{3} = \frac{6\cdot5\cdot4}{3!} = 20$ stati (Det. Slater)

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

$$S: \quad \underline{\tfrac12\otimes\tfrac12\otimes\tfrac12} = \tfrac12\otimes(\underline{1}\oplus\underline{0}) = \tfrac32\oplus\tfrac12+\tfrac12$$

Classifica di S:

$S=3/2$: $\square\square\square \Rightarrow$ Orbitale $\begin{array}{c}\square\\\square\\\square\end{array}$ } 3 stati differenti

$l=1,\ l_z=\pm1,\ 0 \Rightarrow \psi = \sum_{ant.} \psi_{1,1}(r_1)\,\psi_{1,0}(r_2)\,\psi_{1,-1}(r_3)$

$\therefore\ L=0$. $\quad (L,S)=(0,3/2)$ 4 stati.

$S=1/2$ $\begin{array}{cc}\square&\square\\\square&\end{array} \Rightarrow$ Orbitale $\begin{array}{cc}\square&\square\\\square&\end{array}$

Escludo $L=3$, $\Leftarrow \square\square\square$

Troviamo $\underline{\underline{L=2}}$. Scelgo $L_z=2$

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

$\therefore\ \psi \sim \mathcal{A}\left(\psi_1^{\uparrow}\,\psi_1^{\downarrow}\,\psi_0^{\uparrow}\right)$ (scelgo $S_z=1/2$)

$=$ Det Slater. OK. $L_+\psi = 0$,

$\therefore\ (L,S) = (2,1/2)$ OK $\Rightarrow$ 10 stati.

Ora $L_- \psi = (L_{1-} + L_{2-} + L_{3-})\, \Psi$

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

$= \frac{\sqrt{2}}{\sqrt{6}} \left\{ \mathrm{Det}\left(|1\uparrow\rangle|1\downarrow\rangle|-1,\uparrow\rangle\right) \right.$

$\left. + \mathrm{Det}\left(|1\uparrow\rangle|0\downarrow\rangle|0\uparrow\rangle\right) \right\}$

$\left(L_-|\ell\, m\rangle = \sqrt{(\ell+m)(\ell-m+1)}\,|\ell, m-1\rangle \right)$

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

$\exists$ Un altro stato di $L_z = 1$

$\tilde{\Psi} = \frac{1}{\sqrt{12}} \left[\mathrm{Det}\left(|1\uparrow\rangle|1\downarrow\rangle|-1\uparrow\rangle\right) - \mathrm{Det}\left(|1\uparrow\rangle|0\downarrow\rangle|0\uparrow\rangle\right) \right]$

! $\langle \tilde{\psi} | \psi \rangle = 0$

Ora $L_+ \tilde{\psi} = 0$

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

$\therefore (L, S) = (1, 1/2)$ OK

Tot $(L, S) = (0, 3/2), (2, 1/2), (1, 1/2)$

$4 + 10 + 6 = 20$ OK!

^4S, ^2D, ^2P

Stato fondamentale ?

Regola di Hund. (Empirica. OK.)

Tra i possibili multipletti, lo stato fond.

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

Se questo criterio non dà (L,S) univoco,

Lo st. fond $\sim L_{Max}$.

---

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

$$(L,S) = \underbrace{\underset{^3P}{(1,1)}\ \underset{^1D}{(2,0)}\ \underset{^1S}{(0,0)}}_{\text{Hund}\ \longrightarrow\ ^3P}.$$

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

$$(L,S) = \underset{^4S}{(0, 3/2)},\ \underset{^2D}{(2, 1/2)}\ \underset{^2P}{(1, 1/2)}$$

$^4S \rightarrow$ Hund !

Teoremi utili

Teo. Due elettroni equivalenti, $\Rightarrow$

$L + S =$ pari.

$\because$ $S = 1$ $\boxed{}$ $\rightarrow$ ψ_{orb} disp. $= 2l-1, 2l-3, \dots$)

$S = 0$ $\boxed{}$ $\rightarrow$ ψ_{orb} simm. $= 2l, 2l-2, \dots$) OK

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

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

Teo. L'insieme di multipletti $(L, S)^N$ ~~Compl~~.

per $\# = N$ elettroni equivalenti

$=$ " " $(L, S)^{2(2l+1)-N}$

$\therefore$ 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 determinante di Slater.

Eq. di Schrödinger.

$H \to \psi$.

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

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

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

$\Psi = \prod_i \psi_i \Rightarrow$ Eq. di Hartree

- Ma ora uso

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

$(q_i \equiv (\mathbf{r}_i, \sigma_i))$

ψ_i Eq variaz.

$$H = \sum_i f_i + \sum_{i<j} g_{ij} ,$$

$f_i = -\frac{1}{2}\nabla_i^2 - \frac{Ze^2}{r_i}$

$g_{ij} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$

Ora

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

dove $\langle i|f|i\rangle = \int dq\, \psi_i^*(q)\left(-\frac{\nabla^2}{2}-\frac{Ze^2}{r}\right)\psi_i(q)$ $\qquad i = (n\, l\, m,\, s_z)$

$\Downarrow$

$\int d\mathbf{r} \sum_\sigma$

$$= \underbrace{\left(\sum_{\sigma'} \chi^*_{s_i}(\sigma')\, \chi_{s_i}(\sigma')\right)}_{=1} \int d^3r\, \psi_i^*(\mathbf{r})\left(-\frac{\nabla^2}{2}-\frac{Ze^2}{r}\right)\psi_i(\mathbf{r})$$

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

$$= \int_{q_1,q_2} \Big[\psi_i^*(q_1)\psi_j^*(q_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_i(q_1)\psi_j(q_2)$$

$$- \psi_i^*(q_1)\psi_j^*(q_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_j(q_1)\psi_i(q_2) \Big]$$

$$1^\circ = \int d^3r_1\, d^3r_2\, |\psi_{n_i l_i m_i}(\mathbf{r}_1)|^2\, |\psi_{n_j l_j m_j}(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$$2^\circ = \underbrace{\langle \chi_{s_i}|\chi_{s_j}\rangle}_{\delta_{s_{z_i} s_{z_j}}} \cdot \underbrace{\langle \chi_{s_j}|\chi_{s_i}\rangle}_{\delta} \times$$

$$\int d^3r_1\, d^3r_2\, \underset{a}{\psi^*_{n_i l_i m_i}(\mathbf{r}_1)}\, \underset{b}{\psi^*_{n_j l_j m_j}(\mathbf{r}_2)} \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \underset{b}{\psi_{n_j l_j m_j}(\mathbf{r}_1)}\, \underset{a}{\psi_{n_i l_i m_i}(\mathbf{r}_2)}$$

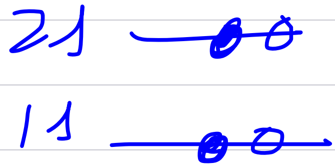
N.B. Il termine di scambio è presente solo se $s_{iz} = s_{jz}$.

$\Rightarrow$ Eq. di Hartree-Fock

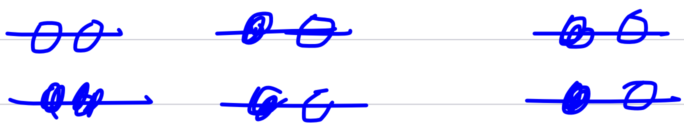
Elio: stato fond e il primo stato eccitato.

Lo stato fond. $1s^2$ $S=0$ (para elio)

1° stato ecc. $1s\,2s$



$S=0$ Paraelio $\quad\quad$ $S=1$ Orto elio



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

Interaz. scambio $\Longrightarrow$ $E^{orto}_{1s2s} < E^{para}_{1s2s}$.

$1s^2$
$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\chi_+(\sigma_1) & \psi_{1s}(\mathbf{r}_2)\chi_+(\sigma_2) \\ \psi_{1s}(\mathbf{r}_1)\chi_-(\sigma_1) & \psi_{1s}(\mathbf{r}_2)\chi_-(\sigma_2) \end{vmatrix}$$

$$= \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)\left(\chi_+\chi_- - \chi_-\chi_+\right)/\sqrt{2}$$

$\Longrightarrow$ Eq. Hartree

1s 2s

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

$\Phi_1 \quad \Phi_2 \quad \Phi_3 \quad \Phi_4$

$S_z = 1 \quad S_z = -1 \quad S_z = 0 \quad S_z = 0$

$S = 1 \quad S = 1 \quad S = 1, 0.$

Le eq. x ψ_{1s}, ψ_{2s}:

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

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

Date queste soluzioni $\Rightarrow$

$$\langle\Phi_1|H|\Phi_1\rangle = I_{1s} + I_{2s} + J - K$$

$$\langle\Phi_2|H|\Phi_2\rangle = I_{1s} + I_{2s} + J - K$$

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

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

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

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

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

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

$\therefore$ Nel settore di due stati $S_z = 0$,

(Teo. perturbaz. degenere !)

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

$\Rightarrow$ gli autostati (autovalori) sono

$$\rightarrow \frac{|\Psi_3\rangle + |\Psi_4\rangle}{\sqrt{2}} = \psi_{1s}\psi_{2s} \frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}} \qquad S = 1,\ S_z = 0$$

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

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

con $E = I_{1s} + I_2 + J + K$.

$$K > 0 \Rightarrow \underbrace{E^{ort}_{S=1} < E^{par.}_{S=0}}.$$

(cfr regola di 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. Vol 4, §33).

$O(1/c)$

$$\Rightarrow \quad i\hbar \frac{\partial \psi}{\partial t} = H\psi \qquad \qquad S = \frac{\hbar}{2}\sigma$$

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

Eq. di Pauli

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

cf. $g_{sp.} \simeq 2.00231930436\,17\ldots$

Osservazioni

(i) Non tutte le particelle di spin $1/2$ ha $g \simeq 2$

(ii) Nucleoni (protone, neutrone)

$$\mu_N / \mu_{Bohr(N)} = g_N S \quad \begin{cases} g_n \simeq -3.8 \\ g_p \simeq 5.6 \end{cases} \quad !$$

(iii) $g_\mu \simeq 2.0023\ldots$ OK

(iv) $g_\mu^{th} \simeq 2.0023318371\,6\,1\ldots$

$g_\mu^{sp} \simeq 2.0023318416\,0\ldots$

1/2) Trasformazione di Lorentz:

$$B' = \frac{1}{c}\, v \times E$$ (Campo magnetico visto da un corpo in moto)

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

$$H = \left(p - \frac{e}{c}A\right)^2\!/2m - e\phi - g\frac{e\hbar}{2mc}\, s \cdot B - \frac{p^4}{8m^3c^2} - \frac{e\hbar}{4m^2c^2}\,\sigma\cdot(E \times p) - \frac{e\hbar^2}{8m^2c^2}\,\nabla\cdot E$$

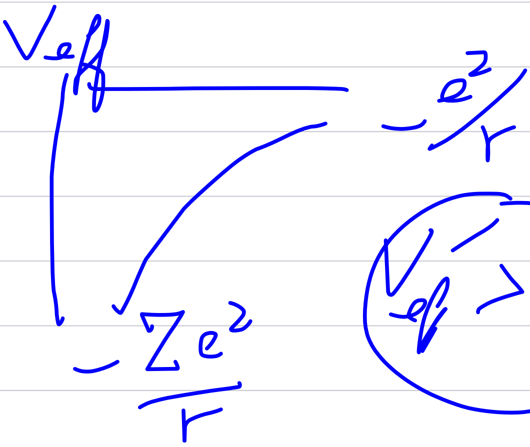
Ma $E = -\nabla\Phi$

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

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

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

$$= \frac{\hbar^2}{2m^2c^2 r}\underbrace{\frac{dV_{eff}(r)}{dr}}_{>0\ !}(s \cdot L)$$



$V_{eff}' > 0$

$$\Rightarrow H_{LS} = \sum_k \alpha_k(r_k)\, L_k \cdot s_k$$

con $$\alpha_k(r_k) = \frac{\hbar^2}{2m^2c^2}\,\frac{1}{r_k}\,\frac{dV_{eff}(r_k)}{dr_k} > 0.$$

∴ H_{L-S} dovuto alle interazione tra lo spin dell'elettrone e il campo elettrico generato dal nucleo e da altri elettroni.

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

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

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

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

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

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

$\Rightarrow$ $n=2$: $2p$, $2s$ $\longrightarrow$ $j=3/2$: $2P_{3/2}$; $j=1/2$: $2P_{1/2}$, $2S_{1/2}$

$$\Delta E_{2P_{3/2}} = \frac{11}{384}\alpha^2\frac{e^2}{r_B}, \quad \Delta E_{2P_{1/2}} = \Delta E_{2S_{1/2}} = -\frac{5}{128}\alpha^2\frac{e^2}{r_B}$$

→ Lamb shift.

Interazioni Spin-orbita come perturbazioni negli stati di multipletto: segno di A

$$H_{LS} = \sum_k \alpha_k(r_k)\, \mathbf{l}_k \cdot \mathbf{s}_k$$

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

(L,S) ?

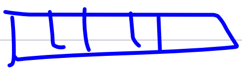
$$\Delta E = \langle \psi_{(L,S)} | H_{LS} | \psi_{(L,S)} \rangle$$

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

$\mathbf{L} = \sum_k \mathbf{l}_k$; $\mathbf{S} = \sum_k \mathbf{s}_k$.

Segno di A per lo stato fondamentale.

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

$\chi_{spin} =$  $S = N/2$.

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

$$\langle \psi(L,S)| \sum_k \alpha(r_k)\, \ell_k \cdot s_k\, |\psi(L,S)\rangle$$

$$= \frac{1}{N} \langle \;|\; \sum_k \underbrace{\alpha(r_k)}\, \ell_k \cdot S\, |\psi(L,S)\rangle$$

$$= \frac{\alpha}{N} \langle \psi(L,S)|\, L \cdot S\, |\psi(L,S)\rangle$$

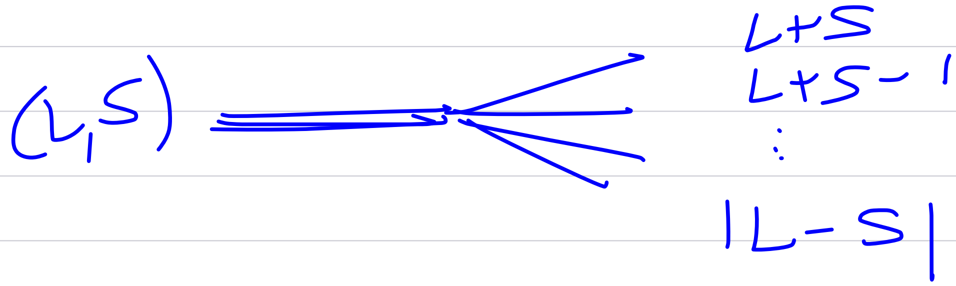
$$= \langle \psi(L,S)|\, A\, L \cdot S\, |\psi(L,S)\rangle$$

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

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

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

$\therefore \Delta E_J = E_J - E_{J-1} = A \cdot J$ (Regola di Landé)



per un multipletto normale.

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

?

Esempi: il termine gettato (lo stato fond.)

1. $np \Rightarrow {}^2P \Longrightarrow J = 3/2, 1/2 \hookrightarrow {}^2P_{1/2}$

(B, Al, Ga ---)

2. $np^2 \underset{Hund}{\Rightarrow} (L,S) = (1,1) \Rightarrow J = 2, 1, 0$
$A>0 \hookrightarrow {}^3P_0$

$2p^2$	$3p^2$	$4p^2$	
C	Si	Ge	...

3. $(np)^3 \underset{Hund}{\Longrightarrow} (L,S) = (0, 3/2) \Rightarrow J = 3/2$
${}^4S_{3/2}$

$2p^3$	$3p^3$	$4p^3$	
N	P	As	...

4. $(np)^4 \Rightarrow (L,S)$ comp $(2p)^2 \Rightarrow (L,S) = (1,1) \Rightarrow J = 2, 1, 0$
$A<0 \hookrightarrow {}^3P_2$

$2p^4$	$3p^4$	$4p^4$
O	S (Zolfo)	Se (Selenio)

5. $(np)^5$ $(L,S) \rightsquigarrow (L,S)$
Same $(np)^1 = (1, \frac{1}{2}) \Rightarrow {}^2P \to J = \frac{3}{2}, \frac{1}{2}$

$A<0 \hookrightarrow {}^2P_{3/2}$

$2p^5$ $3p^5$ $4p^5$

F Cl Br (bromide)

6. $(np)^6 \rightsquigarrow (L,S) = (0,0) \Rightarrow {}^1S_0$

Ne, Ar, Kr ---

7. $(nd)^1$ $(L,S) = (2, \frac{1}{2}) \Rightarrow {}^2D \Rightarrow J = \frac{5}{2}, \frac{3}{2}$

$A>0 \hookrightarrow {}^2D_{3/2}$

3d 4d 5d

Sc Y, La

8 $(nd)^2 \to (L,S) = (3,1) \Rightarrow {}^3F \Rightarrow J = 1 \oplus 3 = 4+3+2$

Hund

$A>0 \Rightarrow {}^3F_2$

ex. $(3d)^2$ $(4d)^2$

Ti Zr ---

Teoria semi-classica della radiazione e transizioni di dipolo.

$$H = \frac{1}{2m}\left(p_i - \frac{e}{c}A_i\right)^2 + V - \mu\cdot B$$

Campo di radiazione

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

Eq. di Maxwell

$$\Rightarrow \left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right) A = 0 \; ; \qquad \boxed{kc = \omega}$$

$$\Rightarrow A = A_0\, \varepsilon \cdot e^{i k\cdot r - i\omega t} + c.c.$$

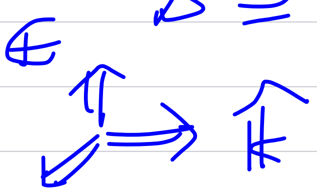
$$k\cdot \varepsilon = 0, \quad k = (0\,0\,k) \Rightarrow \begin{cases} \varepsilon_x = (1,0,0) \\ \varepsilon_y = (0,1,0) \end{cases}$$

$$\text{o} \quad \begin{cases} \varepsilon^{(1)} = c_1 \varepsilon_x + c_2 \varepsilon_y & |c_1|^2 + |c_2|^2 = 1 \\ \varepsilon^{(2)} = \ldots \end{cases}$$

$$E = -\frac{1}{c}\dot{A} = \frac{i\omega}{c} A_0\, \varepsilon\, e^{i(k\cdot r - \omega t)} + c.c.$$

$$B = \nabla\times A = i k \times (A_0 \varepsilon)\, e^{i(\;)} + c.c.$$

$$S = \frac{c}{4\pi}(E\times B) = \underbrace{\frac{c}{2\pi} A_0^2 \left(\frac{\omega}{c}\right)^2}\, \hat{k}$$



Normalizzazione flusso.

$I = |S| =$ intensità di radiazione
(flusso energia)

$$= \frac{\omega^2}{2\pi c} A_0^2 \underset{\text{interpreto}}{=} \underbrace{\omega \hbar\, n_\gamma}$$

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

Transizioni di dipolo (elettrico).

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

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

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

$$\mathbf{A}(\mathbf{r}_k) = A_0\,\boldsymbol{\epsilon}\cdot e^{i\mathbf{k}\cdot\mathbf{r}_k - i\omega t} + c.c.$$

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

$$\rightarrow w = \frac{2\pi}{\hbar}|F_{fi}|^2\,\delta(E_f-E_i-\omega\hbar)\,d\Phi \qquad !$$

$$\hat{F} = -\frac{eA_0}{mc}\sum_k(\boldsymbol{\epsilon}\cdot\hat{\mathbf{p}}_k)\,e^{i\mathbf{k}\cdot\mathbf{r}_k}$$

app. di dipolo: $e^{i\mathbf{k}\cdot\mathbf{r}_k} \sim 1.$

$$\because\ k = \frac{\omega}{c} = \frac{\omega\hbar}{c\hbar} = \frac{E_f-E_i}{c\hbar} \approx \mathcal{O}\left(\frac{e^2}{r_B\cdot c\,\hbar}\right)$$

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

$$\ll 1.$$

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

Ora $$[\mathbf{r}_k, H] = \left[\mathbf{r}_k, \sum_{k'} \frac{\mathbf{p}_{k'}^2}{2m} + \ \ldots \right]$$

$$= i\hbar \cdot \frac{\mathbf{p}_k}{m}$$

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

$$= -\frac{ieA_0}{\hbar c} (E_f - E_i) \langle f | (\boldsymbol{\epsilon} \cdot \mathbf{r}_k) | i \rangle$$

$$= -i \frac{\omega_{fi} A_0}{c} \langle f | \boldsymbol{\epsilon} \cdot \mathbf{d}_k | i \rangle$$

$\mathbf{d}_k = e\mathbf{r}_k$: dipolo dell'k-simo elettrone!

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

E.g. Pol. circolare:

$$\boldsymbol{\epsilon} = \boldsymbol{\epsilon}_+ = -\frac{1}{\sqrt{2}}(1, i, 0) \Rightarrow \boldsymbol{\epsilon}_+ \cdot \mathbf{r} \sim T^1_1$$

$$\boldsymbol{\epsilon}_- = \frac{1}{\sqrt{2}}(1, -i, 0) \Rightarrow \boldsymbol{\epsilon}_- \cdot \mathbf{r} \sim T^1_{-1}$$

Pol. lineare:

$$\boldsymbol{\epsilon}_1 = (1, 0\, 0) \Rightarrow \boldsymbol{\epsilon}_+ \cdot \mathbf{r} \propto x = -\frac{T^1_1 - T^1_{-1}}{\sqrt{2}}$$

$$\boldsymbol{\epsilon}_2 = (0, 1, 0) \Rightarrow \boldsymbol{\epsilon}_- \cdot \mathbf{r} = y = \frac{T^1_1 + T^1_{-1}}{\sqrt{2}}$$

$\Rightarrow$

Regole di selezione (transiz. di dipolo)

$\Pi = (-)^{\sum_k l_k}$ ($\neq (-)^L$ in generale)

(i) $\Pi_f = - \Pi_i$

(ii) $J_f - J_i = \pm 1, 0$ ma $0 \not\to 0$

(iii) $L_f - L_i = \pm 1, 0$; $0 \not\to 0$

(iv) $S_f - S_i = 0$.

(v) Conf. elettronica Ψ_i / Ψ_f differiscono per un elettrone.

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

J_z : $M_f - M_i = \pm 1, 0$ ($\neq 0$ se $|k\rangle = |0 \, k\rangle$)

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

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

$\langle f | T' | i \rangle \rightarrow$

$J_{fz} - J_{iz} = +1 \qquad \Delta J = \begin{cases} +1 \\ 0 \end{cases}, \quad 0 \not\to 0$

$L_{fz} - L_{iz} = +1, \qquad \Delta L = \begin{cases} +1 \\ 0 \end{cases} \quad 0 \not\to 0$

Luce (il fotone) "porta" il mom. ang. $\underbrace{|1,1\rangle}_{}$ (S S_z)

Il fotone (con $m_\gamma = 0$) porta l'elicità

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

$\equiv h = \pm 1$.

Una particella con $m=0$ ha soltanto "di spin S" gli stati $h = \pm S$. (No sistema di riposo. $v<c$.)

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

(1) $(2s)^2(2p)(3d)\ ^3D \to (2s)^2(2p)^2\ ^3P$ ✓

(2) $(2s)^2(2p)(3s)\ ^3P \to (2s)^2(2p)^2\ ^1S$ ΔS

(3) $(2s)^2(2p)(3d)\ ^1D \to (2s)^2(2p)(3s)\ ^1P$ $\Delta\Pi$

(4) $(2s)(2p)^3\ ^3D \to (2s)^2(2p)^2\ ^3P$ ✓

(5) $(2s)^2(2p)(3p)\ ^3P \to (2s)^2(2p)^2\ ^3P$ $\Delta\Pi$

(6) $(2s)(2p)^3\ ^5S \to (2s)^2(2p)^2\ ^3P$ ΔS

(7) $(2s)^2(2p)(3d)\ ^1D \to (2s)^2(2p)^2\ ^1S$ ΔL

(8) $(2s)^2(2p)(3s)\ ^1P \to (2s)^2(2p)^2\ ^1S$ ✓

(9) $(2s)^2\,2p\,2s\ ^1P \to (2s)^2(2p)^2\ ^3P$ ΔS

(10) $(2s)(2p)(3s)^2\ ^3P \to (2s)^2(2p)^2\ ^3P$ due elettroni

Emissione indotta

$$\omega \; \overline{\underline{\;\Psi\;}} \rightsquigarrow f$$

$$\langle f|\delta H|i\rangle = -\langle f|\frac{e}{mc}A_0^* \cdot p|i\rangle$$

$$= -\frac{ie}{c}\omega_{fi}\langle f|A_0^* \cdot r|i\rangle$$

$$= -\frac{ie}{c}\omega_{fi}A_0 \cdot \langle f|\epsilon^* \cdot r|i\rangle$$

$$\Longleftrightarrow \quad E_f - E_i < 0$$

Per $\epsilon = \frac{-1}{\sqrt{2}}(1, i, 0)$

$$\left.\begin{array}{l} J_{zf} - J_{zi} = -1 \\ L_{zf} - L_{zi} = -1 \end{array}\right)$$ il ~~fotone~~ porta via mom. ang. $(1,1)$

$$|\langle f|\delta H|i\rangle|^2 \propto A_0^2 = I$$

Prob. di emissione indotta $\propto I$.

Il processo $\Rightarrow$ amplificazione della luce. ($\to$ Laser)

Einstein.

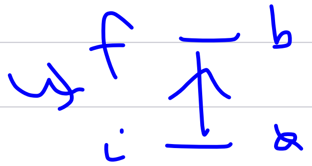
Radiazione non monocromatica e incoerente

Teo. pert. periodica.

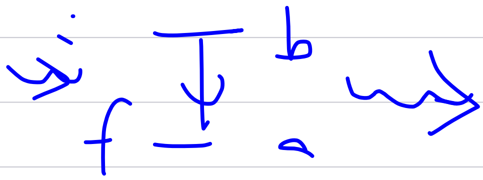
$$A = A_0 e^{i(k\cdot r - \omega t)} + A_0^* e^{-i(k\cdot r - \omega t)}$$

$$A_0 = A_0 \epsilon \qquad A_0^* = A_0^* \epsilon^*$$

(A) assorbimento



(B) emissione indotta



$$e^{ik\cdot r} \simeq 1 \Rightarrow V = -\frac{e}{2mc} A \cdot p \Rightarrow$$

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

$$\Rightarrow W_{fi} = \frac{2\pi}{\hbar} |F_{fi}|^2 \delta(E_f - E_i - \omega\hbar) \, d\Phi .$$

$$\hat{F} = -\frac{e}{2mc} A_0 \epsilon \cdot \hat{p} \qquad [H, r] = -i \frac{p}{m} \hbar$$

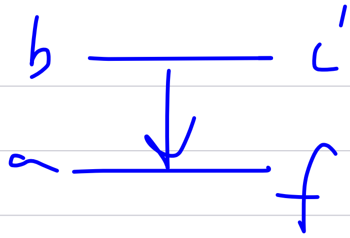
(A) $$F_{fi} = -\frac{e}{2mc} A_0 \epsilon \langle f | \hat{p} | i \rangle =$$

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

$$= -i \frac{A_0 \cdot \omega_{fi}}{c} \underbrace{\langle f | \epsilon \cdot d | i \rangle}_{b \qquad a}$$

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

(B)



$$F_{fi} = -i \frac{A_0^* \cdot \omega_{fi}}{c} \langle \underbrace{f}_{a} | \underbrace{\epsilon^* \cdot d\, | i}_{b} \rangle$$

$$= -i \frac{A_0 \, \omega_{ab}}{c} \epsilon^* \cdot d_{ab}$$

$\Rightarrow$ (A)

$$W_{ba} = \frac{\omega_{ba}^2}{\hbar^2 c^2} |d_{ba}|^2 \sum_{\omega} A_0^2(\omega)\, 2\pi \delta(\omega_{ba} - \omega)$$

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

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

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

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

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

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

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

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

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

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

$$B = (0 \; 0 \; B)$$

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

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

$\Rightarrow$ Ordine di grandezza.

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

$|\mu_B| B \Longleftrightarrow$

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

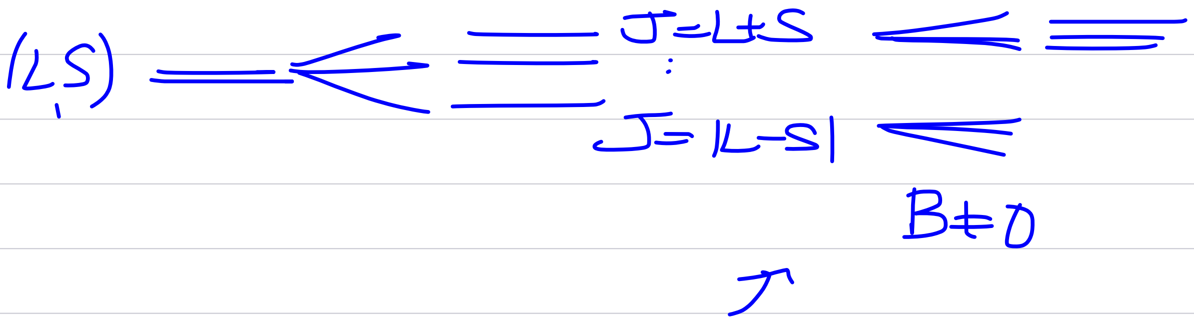
$B \gg 1\,T \Rightarrow \Delta E^{\text{Zeeman}} \gg \Delta E^{\text{str. fine}}$

$B \lesssim 1\,T$ struttura fine importante.

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

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

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



$10^{-3}\,T \le B \le 1\,T$

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

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

$3P_{1/2} \longrightarrow 3s$

$3P_{3/2} \longrightarrow 3s$

Teo perturbazione

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

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

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

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

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

$g_L \equiv$ fattore di Landé.

Calcolo di g_L :

Set $\mathbb{L} = c\,\mathbb{J}$

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

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

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

$$c = \frac{1}{2J(J+1)}\left\{ \quad " \quad \right\}$$

$$\langle H_B \rangle = \hbar\omega_L (2-c) J_z$$

$$L_z + 2S_z = J_z + S_z$$

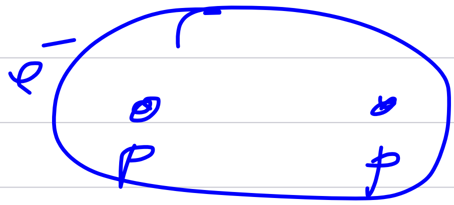
$$= 2J_z - L_z$$

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

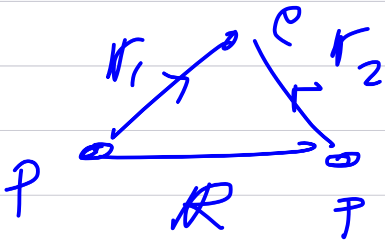
$$g_L = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

Legame molecolare.

molecola H_2^+



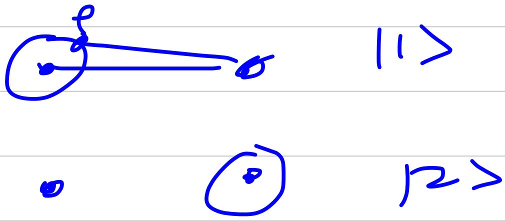
$$H = \frac{P_R^2}{2\mu} + \frac{e^2}{R} - \frac{p^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$



$$\mu = m_p/2 \gg m$$

$\Rightarrow$ Quantizziamo il moto dell'elettrone prima (Born-Oppenheimer).

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

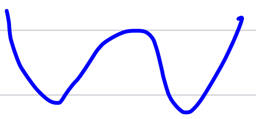


$|1\rangle$: $H' = \frac{e^2}{R} - \frac{e^2}{|R-r|}$

come perturb.

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

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



$\simeq$ doppia buca

Effetto tunnel:

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

$$c \simeq 1.47\, R\, e^2/r_B^3$$

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

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

$$\dashrightarrow E_0 \simeq -\frac{e^2}{2r_B} \underbrace{- \frac{9e^4}{4R^4} - \frac{c}{2}e^{-R/r_B}}_{\text{forze attrattive}}$$

MA NON SUFFICIENTE

$\dashrightarrow$ Regione $R \sim r_B$ fondamentale.

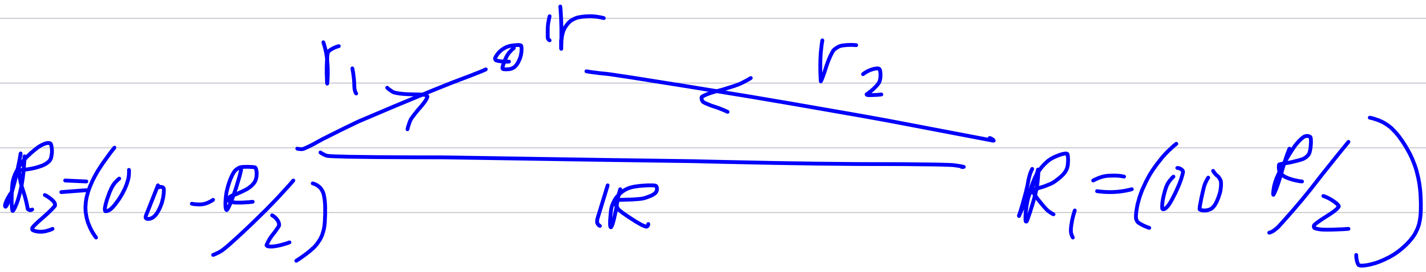
$\Rightarrow$ Approccio variazionale

Funz. di prova.

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

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

con c_1, c_2, e R come parametri variaz.



At fixed R: $\qquad r_1 = |r - R_2|$ etc.

$$H\psi = E\psi$$

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

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

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

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

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

Cambio variable: $\mathbb{R}_1 = (0\,0\,-\tfrac{R}{2})$; $\mathbb{R}_2 = (0\,0\,R/2)$

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

$$r_2 \equiv |\mathbb{r} - \mathbb{R}_2| = \sqrt{\;''\quad '' \quad (z + R/2)^2}$$

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

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

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

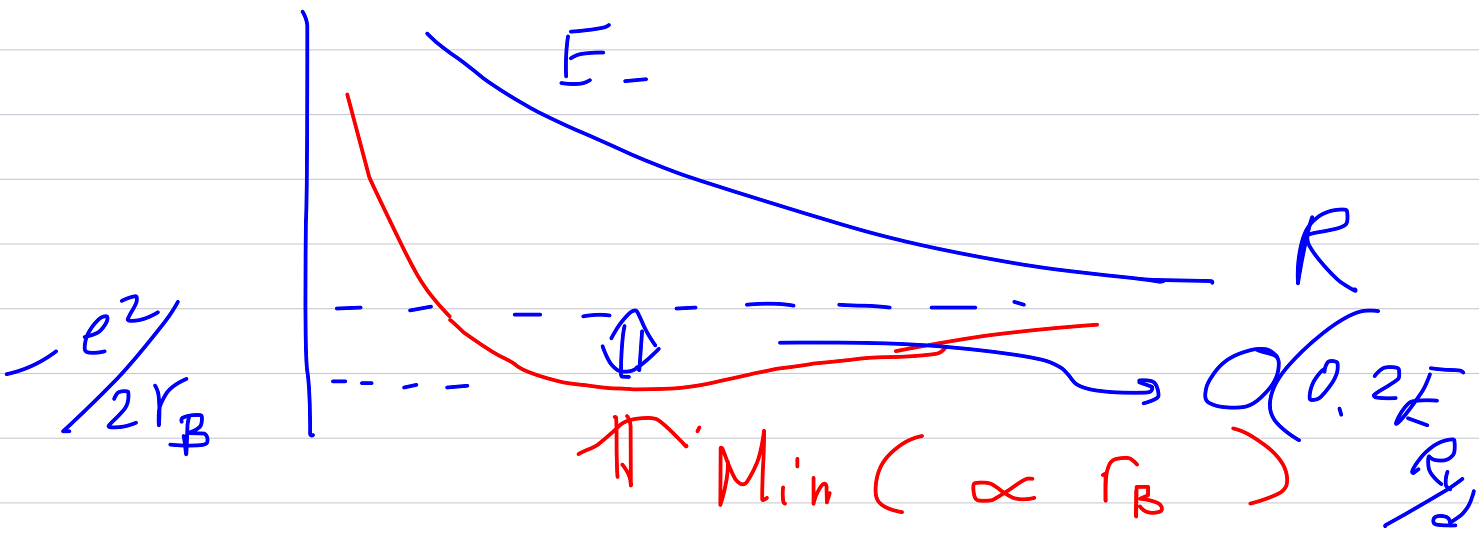
$$S = S_{12} \equiv \langle \psi_2 | \psi_1 \rangle = e^{-R}\left(1 + R + R^2/3\right)$$

Diagonalizz.

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2(1 \pm S)}}\left(|\psi_1\rangle \pm |\psi_2\rangle\right) \qquad (r_B = 1)$$

con

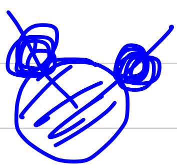
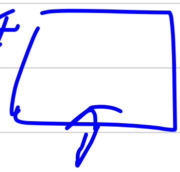
$$E_\pm(R) = \frac{1}{2}\left[-1 + \frac{2}{R} \mp \frac{2e^{-R}(1+R) \pm \frac{2}{R}\{1 - e^{-2R}(1+R)\}}{1 \pm e^{-R}(1 + R + R^2/3)}\right]$$



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

  ⇙

  Eccitazione radiale. (vibraz.)

- H_2O  O: $1s^2 2s^2 2p^4$ 
- H_2 $\Psi \simeq \psi_+(r_1)\psi_+(r_2) \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}$.

Orbitali ibridi

"sp ibridi" $\quad -- (ns)^2 np$

$$\Longrightarrow (ns)(\text{ibrido})$$

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

$\psi_2 = \sin\alpha\, \psi_{ns} - \cos\alpha\, \psi_{np_z}$

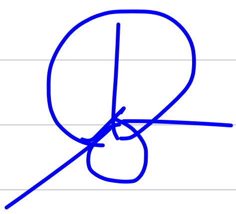
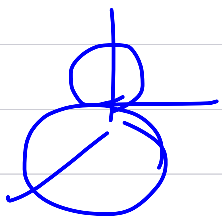
Richiedendo che i due orbitali abbiano la stessa forma geometrica, si ha

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

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

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

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

$\therefore \quad \psi \sim$  $\quad \psi'$ 

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

$$\psi_{n\ell m} = R_{n,\ell}(r)\, Y_{\ell m}(\theta,\varphi)$$

(i) orbitali s $\quad \ell, m = 0 \quad \psi = R_{n0}(r)$

(ii) orbitali p. $\quad \ell = 1 \quad m = \pm 1, 0$

$$\psi_{n,1,1} = -\sqrt{\frac{3}{8\pi}}\, R_{n1}(r) \sin\theta\, e^{-i\varphi} \to (Y_{11})$$

$$\psi_{n1-1} = \sqrt{\frac{3}{8\pi}}\, R_{n1} \sin\theta\, e^{-i\varphi} \to (Y_{1-1})$$

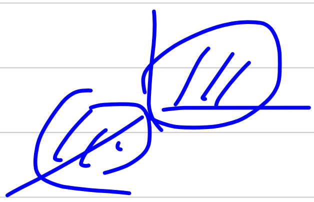
$$\psi_{n10} = \sqrt{\frac{3}{4\pi}}\, R_{n1} \cos\theta$$

ma $\quad Y_{11} = -\frac{x+iy}{\sqrt{2}\,r},$

$\quad Y_{1-1} = \frac{x-iy}{\sqrt{2}\,r} \quad ; \quad Y_{10} = \frac{z}{r}$

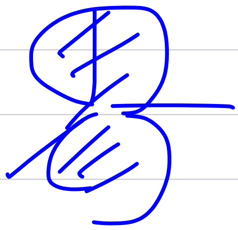
$\Rightarrow$ orbitali p reali

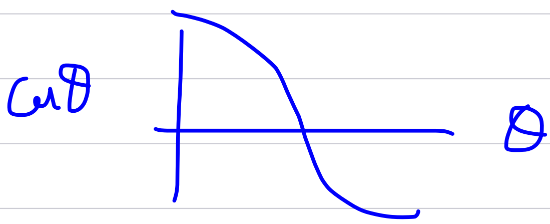
$$\psi_{n,1,x} = \sqrt{\frac{3}{4\pi}}\, R_{n,1}\, \frac{x}{r} \to$$



$$\psi_{n1y} = \qquad y/r$$

$$\psi_{n1z} \qquad z/r \to$$





Orbitale p in direz. generico n

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

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

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

$$= \sqrt{\frac{3}{4\pi}}\,R_{n1} \quad \frac{x\cos\alpha + y\cos\beta + z\cos\gamma}{r} = \sqrt{\frac{3}{4\pi}}\,R_{n,1}\,\frac{u}{r}$$

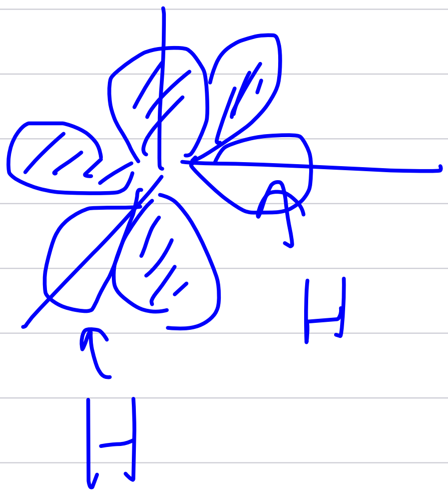
Struttura di H_2O

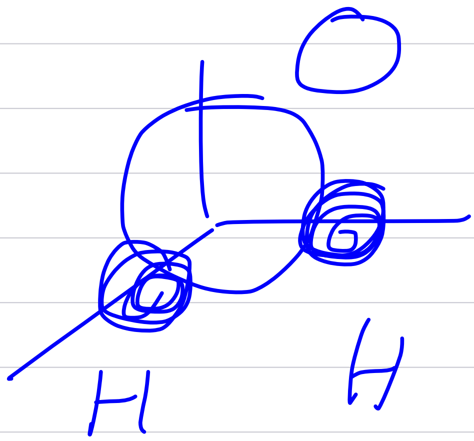
^8O : $1s^2\, 2s^2\, 2p^4$

Supp. che $(2p_z)^2 (2p_x)(2p_y)$ siano occupati

$\rightarrow$ gli orbitali vacanti sono $(2p_x)(2p_y)$

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





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

$\Leftarrow$ repulsione tra i due protoni.

<u>metano</u> CH_3 e ibridi sp^3

Orbitali ibridi sp^3 sono comb. lineare

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

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 $\Rightarrow$

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

Richiedendo l'ortogonalità tra loro

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

$$(c_1' \qquad c_4') = \frac{1}{2}(1\ -1\ -1\ 1)$$

$$(c_1'' \qquad c_4'') = \frac{1}{2}(1\ -1\ 1\ -1)$$

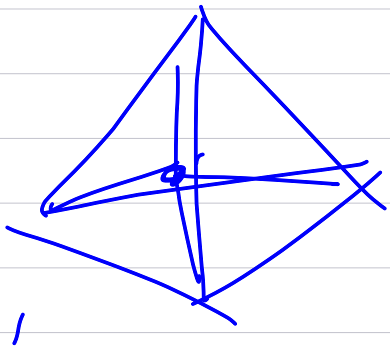
$$(c_1''' \qquad) = \frac{1}{2}(1\ 1\ -1\ -1)$$

Sono orientati

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

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

$\Rightarrow$ 4 dir. dal centro ai quattro vertici di un tetraedro regolare !



e.g. CH_4

$C : 1s^2 2s^2 2p^2$

ma in presenza di 4 H's $\Rightarrow$ conviene

$2s^2 2p^2 \longrightarrow 2s\, 2p^3$ e formare i quattro orbitali ibridi sp^3 !

e condividere questi orbitali con un elettrone ciascuno di H