Teoria delle perturbazioni indip. del tempo

Problema: Supp. che $H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$ soluz. sia nota

Risolvere $H|\psi_n\rangle = E_n |\psi_n\rangle$, $H = H_0 + \lambda V$

(V = il potenziale/l'Hamilt. di perturbazione)

di modo che

$$E_n(\lambda) \xrightarrow[\lambda\to 0]{} E_n^{(0)}; \quad |\psi_n(\lambda)\rangle \xrightarrow[\lambda\to 0]{} |\psi_n^{(0)}\rangle$$

Lasciamo implicito "n"

$n+1$ ——— ⟷ ———

n ——— ⟷ ———

$n-1$ ——— ⟷ ———

$\vdots$

$\lambda = 0 \qquad \lambda \neq 0$

$$|\psi\rangle = |\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + \dots$$

$$E = E^{(0)} + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + \dots$$

ordine x ordine in λ

NORMALIZZAZIONE

Opz. 1 Imporre $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$

Opz 2. Imporre $\langle\psi^{(0)}|\psi(\lambda)\rangle = 0$ (*)

e imporre $\langle\psi|\psi\rangle = 1$ alla fine del calcolo

(*) $\langle\psi^{(0)}|\psi^{(L)}\rangle = 0$, $(L = 1, 2, \dots)$

- assumiamo, inoltre, che i livelli non perturbati $E_n^{(0)}$ siano non-degeneri.
- gli stati non perturbati:

$|\psi_n^{(0)}\rangle \equiv |n\rangle$, (*)

$|\psi_k^{0}\rangle \equiv |k\rangle$, ...

$$(H_0+V)\left(|\psi^{(0)}\rangle+|\psi^{(1)}\rangle+|\psi^{(2)}\rangle+\cdots\right)$$

$$=\left(E^{(0)}+\epsilon^{(1)}+\epsilon^{(2)}+\cdots\right)\left(|\psi^{(0)}\rangle+|\psi^{(1)}\rangle+|\psi^{(2)}\rangle+\cdots\right)$$

$\Rightarrow$ λ^0: $\quad H_0|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle \qquad$ OK, x def.

λ^1: $\quad (H_0-E^{(0)})|\psi^{(1)}\rangle + (V-\epsilon^{(1)})|\psi^{(0)}\rangle = 0,$

λ^2: $\quad (H_0-E^{(0)})|\psi^{(2)}\rangle + (V-\epsilon^{(1)})|\psi^{(1)}\rangle - \epsilon^{(2)}|\psi^{(0)}\rangle = 0$

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λ^L: $\quad (H_0-E^{(0)})|\psi^{(L)}\rangle + V|\psi^{(L-1)}\rangle - \sum_{k=1}^{L}\epsilon^{(k)}|\psi^{(L-k)}\rangle = 0.$

(S.)

$\Rightarrow$ Soluzioni

λ^1: Proietto Eq. (λ^1) su $\langle\psi^{(0)}| \equiv \langle\psi_n^{(0)}| \equiv \langle n|$

$\Rightarrow \quad 0 + \langle\psi^{(0)}|V-\epsilon^{(1)}|\psi^{(0)}\rangle = 0$

$\therefore \quad \epsilon_n^{(1)} = \langle n|V|n\rangle = V_{nn}$ &

Proiettando Eq(λ^1) su $\langle\psi_k^{(0)}| = \langle k|$ $(k\neq n)$

$$(E_k^{(0)}-E_n^{(0)})\langle k|\psi^{(1)}\rangle + \langle k|V|n\rangle = 0$$

$$\therefore \quad \langle k|\psi^{(1)}\rangle = -\frac{V_{kn}}{E_k^{(0)}-E_n^{(0)}} \qquad (k\neq n).$$

e NON degenerazione

$$\therefore \quad |\psi^{(1)}\rangle = \sum_k{}' \frac{V_{kn}}{E_n^{(0)}-E_k^{(0)}}|k\rangle \; \underbrace{+\; c_n^{(1)}|n\rangle}_{=0 \text{ per la scelta (2)}} \; ?$$

$$\equiv \sum_k c_k^{(1)}|k\rangle,$$

$$c_k^{(1)} = V_{kn}/(E_n^{(0)}-E_k^{(0)})$$

λ^2: $\langle n| : Eq(\lambda^2) \Rightarrow$

$$\langle n|V|\psi^{(1)}\rangle - \epsilon^{(2)} = 0 . \quad \left(\langle n|\psi^{(1)}\rangle = 0\right)$$

$$\therefore \quad \epsilon_n^{(2)} = \langle n|V \sum_k{}' \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}|k\rangle$$

$$= \sum_k{}' \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$$

(Correz. al 2° ordine all'energia ($\epsilon_0^{(2)} < 0$).)

$(k \neq n)$ $\langle k| Eq(\lambda^2) \Rightarrow$

$$(E_k^{(0)} - E_n^{(0)})|\psi^{(2)}\rangle + \langle k|V - \epsilon^{(1)}|\psi^{(1)}\rangle = 0$$

$$\langle k|\psi^{(2)}\rangle = \frac{1}{E_n^{(0)} - E_k^{(0)}}\left\{ \sum_l{}' \frac{V_{kl}V_{ln}}{E_n^{(0)} - E_l^{(0)}} - \frac{V_{nn}V_{kn}}{E_n^{(0)} - E_k^{(0)}} \right\}$$

$$|\psi^{(2)}\rangle = \sum_k c_k^{(2)} |k\rangle$$

$$c_k^{(2)} = \sum_l{}' \frac{V_{kl}V_{ln}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \frac{V_{kn}V_{nn}}{(E_n^{(0)} - E_k^{(0)})^2}$$

N.B. di nuovo, $c_n^{(2)}$ rimane indeterminato.

$c_n^{(2)} = 0 \Leftarrow$ opz. 2 .

La struttura iterativa.

$$\lambda^L : (H_0 - E^{(0)})|\psi^{(L)}\rangle + V|\psi^{(L-1)}\rangle - \sum_{k=1}^{L} \epsilon^{(k)}|\psi^{(L-k)}\rangle = 0 .$$

$$\langle\psi^{(0)}|\; Eq(\lambda^{(L)}) \quad \Rightarrow$$

$$\langle\psi^{(0)}|V|\psi^{(L-1)}\rangle - \epsilon^{(L)} = 0 .$$

! (Nota se lo è nota $|\psi^{(L-1)}\rangle$)

1 $\therefore \quad \epsilon^{(L)} = \langle\psi^{(0)}|V|\psi^{(L-1)}\rangle$

$$\langle\psi_k^{(0)}|\psi^{(L)}\rangle = \frac{1}{E_k^{(0)} - E_\psi^{(0)}}\left\{\langle k|V|\psi^{(L-1)}\rangle - \sum_{k=1}^{L-1}\epsilon^{(k)}\langle k|\psi^{(L-k)}\rangle\right\}$$

2 $\therefore \quad \psi^{(L)}$ nota se $\begin{cases} \psi^{(k)} \text{ nota } & k = 1, 2, \dots, L-1 \\ \epsilon^{(k)} \text{ nota per } & k = 1 \dots L-1 . \end{cases}$

(struttura iterativa)

abbiamo visto che

$$|\psi^{(1)}\rangle = -\sum_k{}' \frac{V_{kn}}{E_k^{(0)}-E_n^{(0)}}|k\rangle + \underbrace{c_n^{(1)}}_{\text{indeterminato}}|n\rangle$$

Le equazioni (.8) sono omogenee. $\Rightarrow$

Non determinano la norma.

La normalizzazione: Supp. di avere calcolato.

$$|\psi\rangle = \underset{|n\rangle}{|\psi^{(0)}\rangle} + |\psi^{(1)}\rangle + \cdots |\psi^{(L)}\rangle.$$

$$\equiv Z_\psi^{-1/2} |\psi\rangle_N \longrightarrow \text{normalizzato}$$

$$1 = {}_N\langle\psi|\psi\rangle_N = Z_\psi \langle\psi|\psi\rangle$$

$$\therefore Z_\psi = \frac{1}{\langle\psi|\psi\rangle}.$$

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al 1°

$$|\psi\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle$$

$$\langle\psi|\psi\rangle = 1 + \langle\psi^{(1)}|\psi^{(1)}\rangle + \cdots = 1 + O(\lambda^2).$$

$\therefore$ al primo ordine $|\psi\rangle$ è normalizzata.

$$Z_\psi = \frac{1}{\langle\psi|\psi\rangle} \simeq 1 - \langle\psi^{(1)}|\psi^{(1)}\rangle + \cdots$$

$$Z_\psi^{1/2} = 1 - \underbrace{\frac{1}{2}\langle\psi^{(1)}|\psi^{(1)}\rangle + \cdots}_{O(\lambda^2)}.$$

Al λ^2:

$$|\psi\rangle_n = Z_\psi^{1/2}\left(|\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle\right)$$

$$= \left(1 - \frac{1}{2}\langle\psi^{(1)}|\psi^{(1)}\rangle\right)\left(|\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle\right)$$

$$= \underbrace{|\psi^{(0)}\rangle}_{O(\lambda^0)} + \underbrace{|\psi^{(1)}\rangle}_{O(\lambda)} + \underbrace{|\psi^{(2)}\rangle - \frac{1}{2}\langle\psi^{(1)}|\psi^{(1)}\rangle \cdot |\psi^{(0)}\rangle}_{O(\lambda^2)}$$

Vediamo che $\quad c_n^{(2)} = -\frac{1}{2}\langle\psi^{(1)}|\psi^{(1)}\rangle$

Illustrazioni e esempi.

(1) $H = H_0 + V$; $H_0 = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$; $V = gx$

g^1: $\Delta E_n^{(1)} = \epsilon_n^{(1)} = \langle n|V|n\rangle = 0$.

g^2: $\Delta E_n^{(2)} = \epsilon_n^{(2)} = \sum_k{}' \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$

$V_{kn} = \langle k|V|n\rangle = g\, x_{kn} \neq 0$, $k = n \pm 1$

$$\left.\begin{aligned} V_{n+1,n} &= g\, x_{n+1,n} = g \sqrt{\frac{\hbar}{m\omega}} \sqrt{\frac{n+1}{2}} \\ V_{n-1,n} &= g\, x_{n-1,n} = g \sqrt{\frac{\hbar}{m\omega}} \sqrt{\frac{n}{2}} \end{aligned}\right\} \Longrightarrow$$

$\Delta E_n^{(2)} = \epsilon_n^{(2)} = \frac{1}{\omega\hbar} g^2 \frac{\hbar}{m\omega} \left(\frac{n}{2} - \frac{n+1}{2} \right) = - \frac{g^2}{2m\omega^2}$ (indip. da n!)

$E_n = \omega\hbar\left(n + \frac{1}{2}\right) - \frac{g^2}{2m\omega^2} + O(g^4)$

NB. $H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} + gx = \frac{p^2}{2m} + \frac{m\omega^2}{2}\left(x + \frac{g}{m\omega^2}\right)^2 - \frac{g^2}{2m\omega^2}$

$\Rightarrow E_n = \omega\hbar\left(n + \frac{1}{2}\right) - \frac{g^2}{2m\omega^2}$: esatto!

In questo esempio la serie perturbativa è convergente ed è finita. !

(2) $H = H_0^{H.O.} + V \quad ; \quad V = \frac{g_2}{2} x^2 .$

$$\Delta E_n^{(1)} = \epsilon_n^{(1)} = \langle n | V | n \rangle = \frac{g_2}{2} x^2_{nn} ,$$

ma $(x^2)_{nn} = \frac{\hbar}{m\omega} \frac{2n+1}{2} \Longrightarrow$

$$\Delta E_n^{(1)} = \epsilon_n^{(1)} = \frac{g_2}{2} \frac{\hbar}{m\omega} \frac{2n+1}{2} = \frac{g_2 \hbar}{2m\omega}(n+1/2) \quad \text{(dipende da } n)$$

$$E_n = \omega\hbar(n+1/2) + \frac{g_2 \hbar}{2m\omega}(n+1/2) + O(g_2^2) \Longrightarrow ?$$

Anche questo sistema è esattamente solubile.

$$H = \frac{p^2}{2m} + \left(\frac{m\omega^2}{2} + \frac{g_2}{2}\right) x^2 ,$$
$$= p^2/2m + \frac{m\tilde{\omega}^2}{2} x^2 , \qquad \tilde{\omega} = \sqrt{\omega^2 + g_2/m} .$$

$$\Rightarrow E_n^{esatto} = \tilde{\omega}\hbar(n+1/2)$$

ma $\tilde{\omega} = \omega(1 + g_2/m\omega^2)^{1/2}$

$$\simeq \omega + \frac{g_2}{2m\omega} - \frac{g_2^2}{8m\omega^3} + \cdots$$

$\therefore \epsilon_n^{(1)} = \frac{g_2 \hbar}{2m\omega}(n+\frac{1}{2})$ OK. con la teo. perturb. al 1° ord.

$$\epsilon_n^{(2)} = -\frac{g_2^2 \hbar}{8m\omega^3}(n+1/2) , \text{ etc.}$$

La serie perturb. in questo caso ha il raggio di convergenza $|g_2/m\omega^2| < 1$

- $g_2 < -m\omega^2$ il sistema è instabile!
- $g_2 > m\omega^2$ il sistema è stabile (H.O.)!
- $g_2 = -m\omega^2 \Rightarrow H = p^2/2m$. (particella libera)

Preparazione, $(x^2)_{m,n}$, $(x^4)_{m,n}$, ...

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2} x^2 = \omega\hbar\left(a^\dagger a + \frac{1}{2}\right),$$

$$\left.\begin{aligned} x &= \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^\dagger) \\ p &= i\sqrt{\frac{m\omega\hbar}{2}}\,(a - a^\dagger) \end{aligned}\right\} \circlearrowleft$$

$$[a, a^\dagger] = 1 \iff [x, p] = i\hbar$$

$$|n\rangle = \frac{a^{\dagger n}}{\sqrt{n!}}|0\rangle; \qquad a|0\rangle = 0,$$

$$a^\dagger a|n\rangle = n|n\rangle; \quad a|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$a a^\dagger|n\rangle = (n+1)|n\rangle;$$

$$\Rightarrow \quad (x^2)_{nn} = \frac{\hbar}{2m\omega}\langle n|(a+a^\dagger)(a+a^\dagger)|n\rangle$$

$$= \frac{\hbar}{2m\omega}\left(\langle n|a a^\dagger|n\rangle + \langle n|a^\dagger a|n\rangle\right)$$

$$= \frac{\hbar}{2m\omega}(2n+1) = \frac{\hbar}{m\omega}\left(n + 1/2\right)$$

$$(x^2)_{n+2,2} = \frac{\hbar}{2m\omega}\langle n+2|(a+a^\dagger)(a+a^\dagger)|n\rangle$$

$$= \frac{\hbar}{2m\omega}\langle n+2|a^{\dagger 2}|n\rangle = \frac{\hbar}{2m\omega}\sqrt{(n+2)(n+1)}$$

$$(x^2)_{n-2,2} = \frac{\hbar}{2m\omega}\langle n-2|a^2|n\rangle = \frac{\hbar}{2m\omega}\sqrt{n(n-1)}$$

$$(x^4)_{nn} = (x^2)_{n,n+2}(x^2)_{n+2,n} + (x^2)_{nn}(x^2)_{nn} + (x^2)_{n,n-2}(x^2)_{n-2,n}$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \left\{(n+1)(n+2) + (2n+1)^2 + n(n-1)\right\}$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \left[6n^2+6n+3\right] = 3\left(\frac{\hbar}{2m\omega}\right)^2 \left(2n^2+2n+1\right)$$

alter$_n$.

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \langle n|(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)|n\rangle$$

$$= \text{〃} \left\{\langle n|\left(a^2+aa^\dagger+a^\dagger a+a^{\dagger 2}\right)\left(a^2+aa^\dagger+a^\dagger a+a^{\dagger 2}\right)|n\rangle\right\}$$

$$= \text{〃} \left\{\langle n|\, a^2 a^{\dagger 2} + aa^\dagger aa^\dagger + aa^\dagger a^\dagger a + a^\dagger a a a^\dagger + a^\dagger a a^\dagger a + a^{\dagger 2} a^2 \,|n\rangle\right\}$$

$$= \text{〃} \left\{(n+1)(n+2) + (n+1)^2 + n(n+1) + (n+1)n + n^2 + n(n-1)\right\}$$

$$= \text{〃} \left\{6n^2+6n+3\right\}$$

ok.

$$(x^4)_{n+4,n} = \left(\frac{\hbar}{2m\omega}\right)^2 \cdot \langle n+4|\, a^{\dagger 4} \,|n\rangle$$

$$= \text{〃} \sqrt{(n+1)(n+2)(n+3)(n+4)}$$

$$(x^4)_{n+2,n} = \left(\frac{\hbar}{2m\omega}\right)^2 \langle n+2|\left(a^2+aa^\dagger+a^\dagger a+a^{\dagger 2}\right)\left(a^2+aa^\dagger+a^\dagger a+a^{\dagger 2}\right)|n\rangle$$

$$= \text{〃} \langle n|\, aa^\dagger a^{\dagger 2} + a^\dagger a a^{\dagger 2} + a^{\dagger 2} a a^\dagger + a^{\dagger 2} a^\dagger a \,|n\rangle$$

$$= \text{〃} \left\{\sqrt{n+3}\sqrt{(n+3)(n+2)(n+1)} + (n+2)\sqrt{(n+2)(n+1)} + (n+1)\sqrt{(n+2)(n+1)} + n\sqrt{(n+2)(n+1)}\right\}$$

$$= \text{〃} \sqrt{(n+2)(n+1)}\left\{n+3+n+2+n+1+n\right\} = \text{〃}\sqrt{(n+2)(n+1)}\,(4n+6) = \left(\frac{\hbar}{2m\omega}\right)^2 \cdot 2(2n+3)\sqrt{(n+1)(n+2)}$$

Analogamente,

$$\left(x^4\right)_{n-2,n} = \left(\frac{\hbar}{2m\omega}\right)^2 \cdot 2(2n-1)\sqrt{n(n-1)}\ .$$

Per cui:

$$\left(x^4\right)_{n+2,n} = \left(\frac{\hbar}{2m\omega}\right)^2 2(2n+3)\sqrt{(n+1)(n+2)}$$

$$\left(x^4\right)_{nn} = -3\left(\frac{\hbar}{2m\omega}\right)^2 \left(2n^2+2n+1\right.$$

$$\left(x^4\right)_{n+4,n} = \left(\frac{\hbar}{2m\omega}\right)^2 \sqrt{(n+1)(n+2)(n+3)(n+4)}$$

$$\left(x^4\right)_{n-4,n} = \left(\frac{\hbar}{2m\omega}\right)^2 \sqrt{n(n-1)(n-2)(n-3)}$$

(3) $H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} + \frac{g_4}{2} x^4$ Oscillatore anarmonico

$V = \frac{g_4}{2} x^4$

$\epsilon_n^{(1)} = \Delta E_n^{(1)} = \langle n | V | n \rangle = \frac{g_4}{2} \langle n | x^4 | n \rangle$.

$= \frac{g_4}{2} (x^4)_{nn} = \frac{3 g_4}{8} \left(\frac{\hbar}{m\omega} \right)^2 (2n^2 + 2n + 1)$,

dove $(x^4)_{nn} = \frac{3}{4} \left(\frac{\hbar}{m\omega} \right)^2 \cdot (2n^2 + 2n + 1)$.

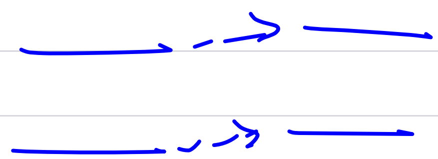
$\epsilon_n^{(2)} = \sum_k' \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$, $\left(k = n, n \pm 2, n \pm 4 \right)$

- Criterio di validità.

(i) $|\psi^{(1)}| \ll |\psi^{(0)}|$, $|\psi^{(1)}| = \left| \sum_k' \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} |k\rangle \right|$

$|c_k^{(1)}| \ll 1$. $= \sum_k c_k^{(1)} |k\rangle$

(ii) $|\Delta E_n^{(1)}| \ll |E_{n\pm 1}^{(0)} - E_n^{(0)}|$



$g_4 = 0$ $g_4 \neq 0$

(i) $$\left|\frac{V_{n+4,n}}{E_n^0 - E_{n+4}}\right| \sim \frac{g_4}{2}\left|\frac{(x^4)_{n+4,n}}{4\omega\hbar}\right|$$

$$\sim \frac{g_4}{2}\left(\frac{\hbar}{2m\omega}\right)^2 \frac{\sqrt{(n+1)(n+2)(n+3)(n+4)}}{4\omega\hbar} \sim \frac{g}{4}\cdot\frac{\hbar}{m^2\omega^3}\cdot n^2$$

$$\therefore \underbrace{\frac{g\hbar}{m^2\omega^3} n^2 \ll 1}$$ (dipende da n, g_4, m, ω ..)

(ii) $$|\delta E^{(1)}| \ll |E^{(0)}_{n\pm 1} - E^{(0)}_n|$$

$$\delta E^{(1)}_n = \frac{3g_4}{8}\left(\frac{\hbar}{m\omega}\right)^2 (2n^2 + 2n + 1),$$

$$\Rightarrow \frac{g}{4}\left(\frac{\hbar}{m\omega}\right)^2 n^2 \ll \omega\hbar$$

$$\therefore \frac{g_4 \cdot \hbar}{m^2\omega^3} n^2 \ll 1$$

ok.

Calcolo di $\epsilon_n^{(2)}$

$$\epsilon_n^{(2)} = -\sum_k{}' \frac{|V_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} \qquad (k \neq n)$$

$$= -\frac{|V_{n+4,n}|^2}{4\omega\hbar} - \frac{|V_{n+2,n}|^2}{2\omega\hbar} + \frac{|V_{n-2,n}|^2}{2\omega\hbar} + \frac{|V_{n-4,n}|^2}{4\omega\hbar}$$

$$= \frac{g_4^2}{4}\left(\frac{1}{4\omega\hbar}\right)\left[-|x^4_{n+4,n}|^2 - 2|x^4_{n+2,n}|^2 + 2|x^4_{n-2,n}|^2 + |x^4_{n-4,n}|^2\right]$$

$$= -\frac{g^2}{32}\frac{\hbar^3}{m^4\omega^5}\left(34n^3 + 51n^2 + 59n + 21\right).$$

Teo. delle perturbazioni degenere.

La procedura nel caso non degenere $\dashrightarrow$

$$n \;\equiv\; \Rightarrow ?$$

$$\langle k|\psi^{(1)}\rangle = -\frac{V_{kn}}{E_k^{(0)} - E_n^{(0)}} \Rightarrow \text{Problema se } E_k^0 = E_n^0 \,,\; k \neq n$$

Torniamo indietro di un passo:

$$(H - E^{(0)})|\psi^{(1)}\rangle + (V - \epsilon^{(1)})|\psi^{(0)}\rangle = 0 \quad (*)$$

$$|\psi^{(0)}\rangle = |n\rangle \quad ? \qquad |n\rangle \longrightarrow |n,i\rangle \quad i=1\ldots s$$

$$E_{n,i} = E_n \quad \text{in presenza della degenerazione}$$

Poniamo

$$|\psi^{(0)}\rangle = \sum c_i |n,i\rangle \equiv \sum c_i |\varphi_i\rangle$$

$$\langle\varphi_j|(*) \qquad 0 + \langle\varphi_j|V\sum_i c_i|\varphi_i\rangle - \epsilon^{(1)} c_j = 0$$

$$\sum_i \underbrace{\langle\varphi_j|V|\varphi_i\rangle}\, c_i - \epsilon^{(1)} c_j = 0$$

$$\sum_i V_{ji}\, c_i = \epsilon^{(1)} c_j$$

$$\mathbb{V} \cdot \begin{pmatrix} c \end{pmatrix} = \epsilon^{(1)} \begin{pmatrix} c \end{pmatrix}$$

$\epsilon^{(1)}$ da $\det|\mathbb{V} - \epsilon^{(1)}\mathbb{1}| = 0$ (Equazione secolare).

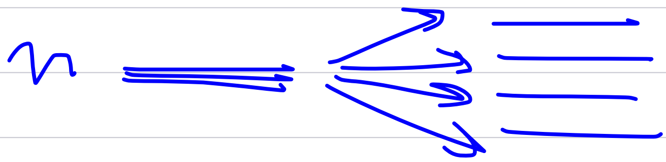
È equazione agli autovalori di

$$\mathbb{V}_{ij} = \langle\varphi_i|V|\varphi_j\rangle = \langle n,i|V|n,j\rangle$$

$\hookrightarrow$ Elementi di matrice di V tra gli stati degeneri del n-simo livello. $\Rightarrow$ Le correz. $\epsilon^{(1)}$ sono autovalori di $\mathbb{V}$.

Se $\epsilon_k^{(1)}$ $(k=1,2 \ldots s)$ sono distinti, la degenerazione del livello n (con $E_n^{(0)}$) viene eliminata al primo ordine in V:

N.B.



$$\epsilon_i^{(1)} \Leftrightarrow |\psi_i^{(0)}\rangle = \underbrace{\sum_j c_j^{(i)} |\varphi_j^{(0)}\rangle}_{\text{i-simo autovettore di } V.}$$

$V=0$ $\qquad$ $V\neq 0$

"La correzione" alla funzione d'onda sopra è dell'ordine zero !

- In presenza di degenerazione nel sistema H_0, lo stato "nonperturbato" $|n\rangle$ non era univocamente determinato. $c_j^{(i)}|\varphi_j\rangle$

$$|n,i\rangle = \varphi_{n,i} \Rightarrow \psi_n^i = \underbrace{\sum_j c_{ij} |\varphi_{n,j}\rangle}$$

$$= U_{ij} |\varphi_j\rangle \qquad U = \text{trasformazione unitaria}$$

Cambio base :

$$\langle \psi_i^{(0)} | V | \psi_j^{(0)} \rangle =$$

$$= \sum_{k,l} c_k^{(i)*} c_l^{(j)} \langle \varphi_k | V | \varphi_l \rangle$$

$$= \sum_{k,l} c_k^{(i)*} (V)_{kl} (c^{(j)})_l = \sum$$

$$= \sum_k c_k^{(i)*} \epsilon^{(1,j)} c_k^{(j)} =$$

$$= \epsilon^{(1,j)} \delta_{ij} \quad \dashrightarrow$$

V è diagonale nella nuova base

$$V = \begin{pmatrix} \epsilon^1 & & 0 \\ & \epsilon^2 & \\ 0 & \ddots & \epsilon^g \end{pmatrix}$$

Tornando all'espressione "sbagliata"

$$|\psi^{(1)}\rangle = -\sum_k \frac{V_{kn}}{E_k^{(0)} - E_n^{(0)}} \quad ;$$

L'idea è preparare (ridefinire) gli stati non perturbati, di modo che

se $\quad E_{n_j}^{(0)} = E_{n_i}^{(0)} \longrightarrow V_{ji} = \delta_{(j \neq i)}$

di modo che l'effetto della perturbazione sia continuo

- In presenza di stati degeneri nonperturbati, le perturbazioni, anche se sono infinitesime, "orientano" gli stati nonperturbati $|\varphi_{ni}\rangle$ di modo che le correzioni siano piccole all'energia.

N.B. $c_{j,i} \sim O(1)$ anche con $V \simeq 0$

- Se alcuni autovalori di V sono uguali, la degenerazione sarà eliminata solo parzialmente.

Esempio. $\boxed{\text{Effetto Stark-Lo-Surdo.}}$ al primo ordine

$n=2$ Atomo di idrogeno $n^2=4$ stati

$|2s\rangle$, $|2p\rangle$, $m=1,0,-1$.

in campo (esterno) elettrico

$$V = -ezE. \qquad z \sim T^1_0$$

Gli stati non perturbati sono

$$\underset{n\ l\ m}{|2s\rangle = |2,0\ 0\rangle}, \quad \underset{n\ l\ m}{|2p,0\rangle = |2,1,0\rangle} \quad \underset{n\ l\ m.}{|2p\pm1\rangle = |2,1,\pm1\rangle}$$

⇒ Elementi di matrice di V tra questi:

parità ≠ W-E

$$V = \begin{pmatrix} 0 & * & \\ * & 0 & \\ & & 0 \end{pmatrix} \begin{array}{l} |2\,0\,0\rangle \\ |2\,1\,0\rangle \\ |2\,1\,1\rangle \\ |2\,1\,-1\rangle \end{array}$$

Basta calcolare $\langle 2,1,0|V|2,0,0\rangle$

$$= -eE \int dr\, r^2 \cdot R_{2,1} \cdot r \cdot R_{2,0}$$

$$\int d\theta \sin\theta\, d\varphi\; Y^*_{1,0} \cdot \cos\theta \cdot Y_{0,0}$$

$$= 3eE r_B$$

$$R_{2,1} = \frac{r}{2\sqrt{6}} e^{-r/2}$$

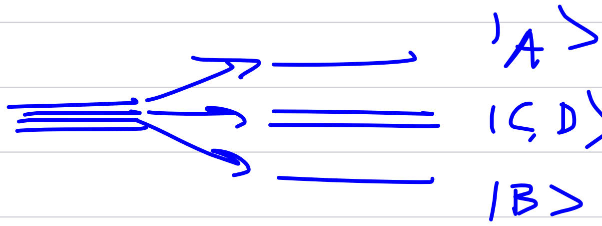
$$R_{20} = \frac{2-r}{2\sqrt{2}} e^{-r/2}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_{00} = 1/\sqrt{4\pi}$$

$$V = \begin{pmatrix} 0 & 3eEr_B & \\ 3eEr_B & 0 & \\ & & 0 \end{pmatrix}$$

$\Rightarrow \quad \epsilon^{(1)} = \pm 3 e \mathcal{E} r_B$



$$|A\rangle = \frac{1}{\sqrt{2}}\left(|2s\rangle - |2p\ 0\rangle\right)$$

$$|B\rangle = \frac{1}{\sqrt{2}}\left(|2s\rangle + |2p, 0\rangle\right)$$

$$|C\rangle, |D\rangle \sim |2p, \pm 1\rangle$$

$$3 e \mathcal{E} r_B \sim 1.5 \cdot 10^{-8}\, \mathcal{E}\ \mathrm{eV} \qquad \left(\mathcal{E} \text{ in } \mathrm{V/cm}\right)$$

$$\Rightarrow \quad \mathcal{E} \ll 10^{9}\ \mathrm{V/cm} \qquad \delta E \ll 14\ \mathrm{eV}$$

Correzioni relativistiche (dopo!)

$$2p,\,2s \longrightarrow \begin{cases} j=3/2 \;\; (2p_{3/2}) \\ j=1/2 \;\; (2p_{1/2}),\ (2s_{1/2}) \end{cases}$$

ΔE struttura fine $\sim O(\alpha^2)\ \frac{e^2}{r_B}$

$10^{-4} \sim 10^{-5}$

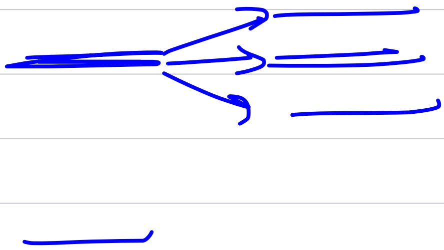
(Stark)

$$|\Delta E| \simeq e\mathcal{E} r_B \sim 10^{-9}\,\mathcal{E} \cdot 10\ eV$$

$$|\Delta E^{str.\,fine}| \sim 10^{-5} \cdot 10\ eV$$

$\mathcal{E} \gg 10^4$ ok trascuro la struttura fine.

$$\Delta E \simeq \pm 3 e\mathcal{E} r_B$$

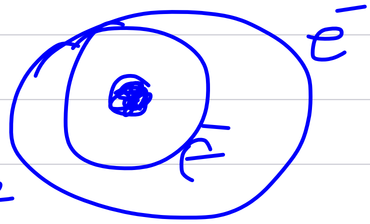


buono per

$$10^4 \ll \mathcal{E}\left(\frac{V}{cm}\right) \ll 10^9$$

Per $\mathcal{E} \ll 10^4\ V/cm$ la struttura fine importante.

Atomo di Elio



$$H = \underbrace{\frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}}_{H_0} + \underbrace{\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}}_{V}$$

2lm ——

100 ——

$$H_0 \Psi = E^{(0)} \Psi$$

$$\Psi = \psi_{100}^{Z=2}(\mathbf{r}_1)\, \psi_{100}^{Z=2}(\mathbf{r}_2)\, \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}.$$

Statistica di FD $\Longrightarrow$

$$E^{(0)} = -2 \cdot \frac{2e^2}{2 r_B'} = -\frac{4e^2}{r_B} = 8 \cdot E_H^{(0)}$$

$$r_B^{(2)} = \frac{\hbar^2}{2me^2}$$

$$-\frac{Z^2 e^2}{r_B}$$

$\Rightarrow$

$$\Delta E = \langle \Psi^{(0)} | \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} | \Psi^{(0)} \rangle$$

$$= \int d^3r_1\, d^3r_2\, \psi_{100}^{Z=2\,*}(\mathbf{r}_1)\, \psi_{100}^{Z=2\,*}(\mathbf{r}_2)\, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\, \psi_{100}^{Z=2}(\mathbf{r}_1)\, \psi_{100}^{Z=2}(\mathbf{r}_2).$$

$$\psi_{100}(r) = \frac{2}{\sqrt{4\pi}} e^{-r} \underset{Z=2}{\Longrightarrow} \frac{2 Z^{3/2}}{\sqrt{4\pi}} e^{-Zr} \qquad \left(\psi_{100} = \frac{2}{\sqrt{4\pi}} r_B^{-3/2} e^{-r/r_B}\right)$$

$$r_B^Z = r_B / Z$$

$Z = 2$ ma lasciamo Z generico (dopo!).

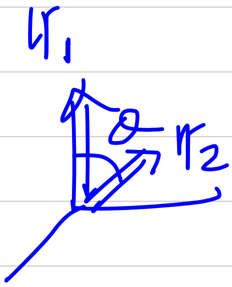
$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \frac{1}{\sqrt{\mathbf{r}_1^2+\mathbf{r}_2^2-2\mathbf{r}_1\cdot\mathbf{r}_2}} = \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}}$$

$$\begin{cases} = \frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l P_l(\cos\theta) & r_2<r_1 \\ = \frac{1}{r_2}\sum\left(\frac{r_1}{r_2}\right)^l P_l(\cos\theta) & r_1<r_2. \end{cases}$$

$$\langle\Psi|\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}|\Psi\rangle$$

$$= \int d^3\mathbf{r}_1\, d^3\mathbf{r}_2 (\cdots) = \iint_{r_1>r_2}\cdots + \iint_{r_1<r_2}\cdots$$

$$= 2\int_{r_1>r_2} d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, \psi^*(\mathbf{r}_1)\,\psi^*(\mathbf{r}_2)\,\frac{e^2}{r_1}\sum_l\left(\frac{r_2}{r_1}\right)^l P_l(\cos\theta)\,\psi_\cdot(\mathbf{r}_1)\psi(\mathbf{r}_2)$$



$$d^3\mathbf{r}_2 = dr_2\, r_2^2\, d\cos\theta_2\, d\varphi_2 \quad \text{prima}.$$

$$\int d\cos\theta\, d\varphi\, P_l(\cos\theta) = 4\pi\,\delta_{l,0}$$

$$\Rightarrow 2\cdot 4\pi e^2\int_0^\infty dr_1\, r_1^2 \overbrace{d\cos\theta_1\, d\varphi_1}^{4\pi}\cdot\left(\frac{2}{\sqrt{4\pi}}\right)^4\cdot \cancel{Z^6} \qquad \left(\int d\cos\theta\, P_l(\cos\theta)\, P_0(\cos\theta) = 2\delta_{l,0}\right.$$

$$\underbrace{e^{-2Zr_1}\cdot\frac{1}{r_1}}\cdot\int_0^{r_1} dr_2\, r_2^2\cdot e^{-2Zr_2}$$

Integral radial: $(r_B=1)$

$$\int_0^\infty dr_1\, r_1\, e^{-2Zr_1}\int_0^{r_1} dr_2\, r_2^2\, e^{-2Zr_2}$$

$$\int_0^\infty dr_1\, r_1\, e^{-2Zr_1} \int_0^{r_1} dr_2\, r_2^2\, e^{-2Zr_2} \qquad \begin{pmatrix} 2Zr_1 = x_1 \\ 2Zr_2 = x_2 \end{pmatrix}$$

$$= (2Z)^{-5} \int_0^\infty dx_1\, x_1\, e^{-x_1} \int_0^{x_1} dx_2\, x_2^2\, e^{-x_2}$$

$$= (2Z)^{-5} \int_0^\infty dx_2\, x_2^2\, e^{-x_2} \int_{x_2} dx_1\, x_1\, e^{-x_1}$$

$$= \text{''} \int dx_2\, x_2^2 e^{-x_2} \left(-x_1 e^{-x_1} \Big|_{x_2} + \int_{x_2} dx_1\, e^{-x_1} \right)$$

$$= \text{''} \int dx_2\, x_2^2 e^{-x_2} \left(x_2 e^{-x_2} + e^{-x_2} \right)$$

$$= \text{''} \left(\int dx_2\, x_2^3 e^{-2x_2} + \int dx_2\, x_2^2 e^{-2x_2} \right)$$

$$= \text{''} \left(2^{-4} \cdot \Gamma(4) + 2^{-3} \Gamma(3) \right)$$

$$= \text{''} \left(2^{-4}\, 3! + 2^{-3} \cdot 2! \right)$$

$$= \text{''} \left(\frac{3}{8} + \frac{1}{4} \right) = \frac{5}{8} \cdot (2Z)^{-5}$$

$$= 2^5 e^2 \cdot Z^6 \cdot (2Z)^{-5} \cdot \frac{5}{8}$$

$$= \underbrace{e^2 \frac{5}{8} Z} = \frac{e^2}{r_B} \frac{5}{8} Z \quad \checkmark$$

$$\xrightarrow[Z=2]{} \frac{5}{4} \frac{e^2}{r_B}$$

$$\left(= -4 \frac{e^2}{r_B} \right.$$ NON pert. oltre il precedente)

$$\therefore E = -Z^2 + \frac{5Z}{8} \underset{Z=2}{=} -2.75 \left(\frac{e^2}{r_B}\right)$$

$$\text{cfr} \quad E^{sp.} \simeq -2.90 \left(\frac{e^2}{r_B}\right)$$

OK entro 5 %