Metodo variazionale

$$H|\psi_0\rangle = E_0|\psi_0\rangle \quad :$$

$H = H_0 + V$
solubile piccolo

? E_0, ψ_0 → parametri variazionali:

$\psi^{\{\beta\}}$ (funz. d'onda di prova; funz. d'onda variazionale)

$$\Rightarrow \quad E^{\{\beta\}} \equiv \langle\psi^\beta|H|\psi^{(\beta)}\rangle / \langle\psi^\beta|\psi^\beta\rangle$$

$$\frac{\partial E^{\{\beta\}}}{\partial\beta} = 0 \Rightarrow \beta = \beta_*$$

$$E^{(var)} \equiv E^{\{\beta\}}\Big|_{\beta=\beta^*} \; ; \quad \psi^{(var)} = \psi^{\{\beta\}}\Big|_{\beta=\beta^*}$$

Principio variazionale.

$$E^{(var)} \geq E_0 \quad \leftarrow \text{esatto.}$$

$$|\psi^{(\beta)}\rangle = \sum_n c_n|\psi_n\rangle \qquad \{\beta\} \Leftrightarrow \{c_n\}$$

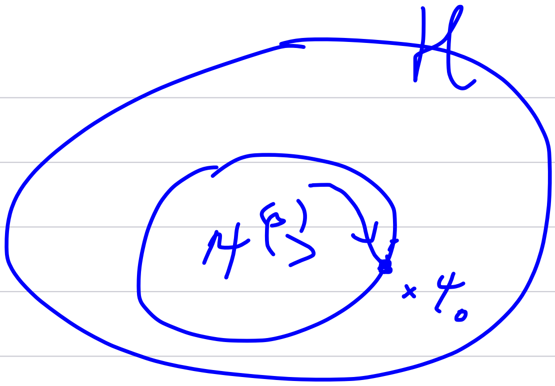
$$\hookrightarrow H\psi_n = E_n|\psi_n\rangle$$

$$\sum_n |c_n|^2 = 1$$

$$E^{(\beta)} = \langle\psi^\beta|H|\psi^\beta\rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum |c_n|^2 = E_0 .$$

$\therefore$ Minimizzazione $\dfrac{\partial E^\beta}{\partial\beta} = 0 \Rightarrow E^{(\beta)} \simeq E_0$.

- Se per fortuna $\{|\psi^{(\beta)}\rangle\} \supset |\psi_0\rangle$ il metodo è destinato a dare il risultato esatto.



- In generale, $E^{(var)} \geq E_0$.
- In generale, il metodo funziona bene.

$\because$

$$\psi^{(var.)} = \frac{1}{\sqrt{1+\epsilon^2}}\left(\psi_0 + \epsilon\psi_\perp\right); \quad \psi_\perp = \sum_{n\neq 0} c_n \psi_n, \quad \sum_{n\neq 0}|c_n|^2 = 1$$

$$E^{(var)} = \langle\psi^{var}|H|\psi^{var}\rangle = \frac{1}{1+\epsilon^2}\left(E_0 + \epsilon^2 \sum_n c_n E_n\right) = E_0 + O(\epsilon^2) \, . \, !$$

- $Q = \langle\psi|H|\psi\rangle / \langle\psi|\psi\rangle$ (SEGRETO!)

$$\frac{\delta Q}{\delta(\langle\psi|)} = 0 \qquad \frac{\langle\psi|\psi\rangle\cdot H|\psi\rangle - \langle\psi|H|\psi\rangle\cdot|\psi\rangle}{(\langle\psi|\psi\rangle)^2} = 0$$

$\forall \psi$

$$\therefore \quad H|\psi\rangle = \left(\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\right)\cdot|\psi\rangle$$

Eq. di Schr. con $E_0 = \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ ok.

- $Q = \langle\psi|H|\psi\rangle - \lambda\langle\psi|\psi\rangle$.

$$\left.\begin{array}{ll} \dfrac{\delta Q}{\delta\langle\psi|} = 0 & H|\psi\rangle = \lambda|\psi\rangle \\ \dfrac{\delta Q}{\delta\lambda} = 0 & \langle\psi|\psi\rangle = 0 \end{array}\right\} \text{Eq. di Schr.}$$

- Fisica atomica, Molecole, Chimica-fisica, (molti gradi di libertà; $H \neq H_0 + V$

- Versatilità.

$\Leftrightarrow$ Ottimizzazione tra

$\begin{cases} \#\text{ di parametri } \{\beta\} ; \\ \text{Calcolabilità di } \langle\beta|H|\beta\rangle,\ \partial_\beta\langle\beta|H|\beta\rangle = 0. \end{cases}$

- Bontà del metodo dipende da
  - una buona intuizione su ψ_0 $\left(\psi^{(\beta)} \sim \psi_0\right)$
  - esperienza ?
  - comprensione fisica.

cfr. Teo perturbaz.

- Per uno stato eccitato, $|\psi^{(\beta)}\rangle \perp |\psi^{(0)}\rangle$

$$\frac{\partial}{\partial\beta}\langle\beta|H|\beta\rangle = 0, \qquad \begin{array}{l}\langle\beta|0\rangle = 0 \\ \langle\beta|\beta\rangle = 1\end{array}$$

$$\rightarrow \beta = \beta^* \qquad E_1^{var} = \langle\beta|H|\beta\rangle\Big|_{\beta=\beta^*} \gtrsim E_1, \quad \text{etc.}$$

Esempi.

Es. 1. $H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$ (Supponiamo che non si conoscano $\{E_n, \psi_n\}$)

La funz. di prova

$$\varphi = \sqrt{\alpha}\, e^{-\alpha|x|}.$$

$$E(\alpha) = \frac{2\alpha}{2}\int_0^\infty dx \left\{\left(\frac{d}{dx}e^{-\alpha x}\right)^2 + \omega^2 x^2 e^{-2\alpha x}\right\} \qquad m=1$$

$$= \alpha\left\{\alpha^2 \frac{1}{2\alpha} + \omega^2 \cdot \frac{2}{(2\alpha)^3}\right\} = \frac{1}{2}\left(\alpha^2 + \frac{\omega^2}{2\alpha^2}\right)$$

$$\frac{\partial E}{\partial \alpha^2} = 1 - \frac{\omega^2}{2(\alpha^2)^2} = 0 \quad \therefore \quad \alpha^2 = \omega/\sqrt{2}$$

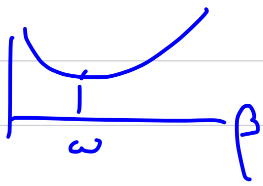
$$\therefore E^{var} = \frac{1}{2}\left(\frac{\omega}{\sqrt{2}} + \frac{\omega^2\sqrt{2}}{2\omega}\right) = \frac{\omega}{\sqrt{2}} \simeq 0.707\,\omega$$! (Non è granché)

cfr. $E_0 = 0.5\,\omega$

Con $\varphi^{(\beta,\alpha)} = (1+\beta x^2)\,e^{-\alpha|x|}$

$$\Rightarrow \left.\begin{aligned}\alpha^* &\simeq -0.0523\\ \beta^* &= 0.73\end{aligned}\right\} \Rightarrow E^{var} \simeq 0.64\,\omega$$

$$\varphi^{(\beta)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}}$$



$$H = \frac{p^2}{2} + \frac{\beta^2 x^2}{2} + \frac{(\omega^2-\beta^2)}{2}x^2$$

$$\langle\beta|H|\beta\rangle = \frac{\beta}{2} + \frac{\omega^2-\beta^2}{2}\underbrace{\langle x^2\rangle_\beta}_{1/2\beta} = \frac{1}{4}\left(\beta + \frac{\omega^2}{\beta}\right) \Rightarrow$$

$$\frac{\partial}{\partial\beta}E(\beta) = 1 - \frac{\omega^2}{\beta^2} = 0 \quad \therefore \quad \beta = \omega \quad \therefore \quad E^* = \frac{\omega}{2} \checkmark$$

$$\left.\begin{aligned} H &= \frac{p^2}{2m} - \frac{e^2}{r}, \\ \psi^{\beta} &= C \cdot e^{-\beta r} \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} E_0 &= -\frac{e^2}{2 r_B} \\ \psi_0 &= C\, e^{-r/r_B} \end{aligned}\right.$$

$$H = \frac{p^2}{2m} + \frac{m \omega_0^2 x^2}{2} + \frac{g}{2} x^4 \qquad (m = \omega_0 = 1, \text{ in seguito}$$

$$\psi^{(\omega)} = C_\omega\, e^{-\frac{\omega}{2\hbar} x^2} = \left(\frac{\omega}{\pi \hbar}\right)^{1/4} e^{-\frac{\omega}{2\hbar} x^2} \qquad (\omega = \text{il parametro variazionale})$$

$$\langle \omega | H | \omega \rangle = \frac{1}{2} \langle p^2 \rangle_\omega + \frac{1}{2} \langle x^2 \rangle_\omega + \frac{g}{2} \langle x^4 \rangle_\omega$$

$$= \langle \omega | \frac{p^2}{2} + \frac{\omega^2 x^2}{2} | \omega \rangle + \langle \omega | \frac{1 - \omega^2}{2} x^2 | \omega \rangle + \frac{g}{2} \underbrace{\langle \omega | x^4 | \omega \rangle}_{\frac{3\hbar^2}{4\omega^2}}$$

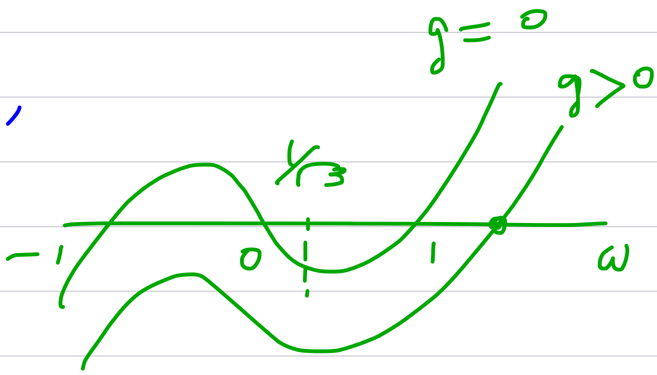
$$= \frac{\omega \hbar}{2} + \frac{1 - \omega^2}{2} \cdot \frac{\hbar}{2\omega} + \frac{g}{2} \cdot \frac{3\hbar^2}{4\omega^2},$$

$$= \frac{\omega \hbar}{4} + \frac{\hbar}{4\omega} + \frac{3g}{8} \frac{\hbar^2}{\omega^2} \underset{\hbar = 1}{=} \frac{\omega}{4} + \frac{1}{4\omega} + \frac{3g}{8\omega^2}$$

$$\frac{\partial}{\partial \omega} \langle \omega | H | \omega \rangle = 0$$

$$\Rightarrow \frac{1}{4} - \frac{1}{4\omega^2} - \frac{3g}{4\omega^3} = 0,$$

$$\omega^3 - \omega - 3g = 0$$



e.g. $g = 0 \Rightarrow \omega \simeq 3.21447$

$\Rightarrow E^{var.}(g = 10) \simeq 1.24431\ldots$

cfr. $E^{pert.} = \frac{1}{2} + \frac{3g}{8} + \ldots \underset{g=10}{=} 4.25$!

cfr. $E^{exact}(g = 10) \simeq 1.22459\ldots$

Elio

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|r_1 - r_2|}$$

- Il calcolo perturbativo con $V = \frac{e^2}{|r_1 - r_2|} \Rightarrow$

$$E_0 = 2 \cdot \left(-\frac{2e^2}{2\, r_B^{(2)}}\right) = -\frac{4e^2}{r_B} = 8 \cdot E_0^{Bohr}$$

$$\delta E_0^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle \quad \text{dove} \quad \Psi_0 = \psi_{100}^{(Z=2)}(r_1)\, \psi_{100}^{(Z=2)}(r_2)\, \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}$$

$$= \frac{5}{8} \cdot Z \frac{e^2}{r_B} \underset{(Z=2)}{=} \frac{5}{4} \frac{e^2}{r_B} \quad \therefore \quad E^{(0)} + E^{(1)} = -\left(4 + \frac{5}{4}\right) \frac{e^2}{r_B} = -2.75\, \frac{e^2}{r_B}$$

cfr $E^{(exp)} = -2.90$.

- Metodo variazionale:

Funz. prova $\psi_{100}^{(Z)}(r_1)$ $\psi_{100}^{(Z)}(r_2)$

$$\Psi^{(Z)} = \left(\frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Z r_1}\right)\left(\frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Z r_2}\right) \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}.$$

Z = carica efficace (param. variazionale)

$$E^{var.} = \langle \Psi^Z | H | \Psi^Z \rangle$$

$$= \langle \Psi^Z | \underbrace{\frac{p_1^2}{2m} - \frac{Ze^2}{r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_2}}_{(A)} + \underbrace{\frac{(Z-2)e^2}{r_1} + \frac{(Z-2)e^2}{r_2}}_{(B)} + \underbrace{\frac{e^2}{|r_1 - r_2|}}_{(C)} | \psi^{(Z)} \rangle$$

$$(A) + (C) = \left(-Z^2 + \frac{5Z}{8}\right) \frac{e^2}{r_B} \leftarrow \text{Teo. perturbaz. con } V = \frac{e^2}{|r_1 - r_2|}$$

Basta calcolare (B)!

$$(B) = 2(Z-2)e^2 \langle \psi^{(Z)} | \frac{1}{r_1} | \psi^{(Z)} \rangle$$

$$= 2(Z-2)e^2 \cdot \langle \psi^{Z}_{100} | \frac{1}{r_1} | \psi^{Z}_{100} \rangle$$

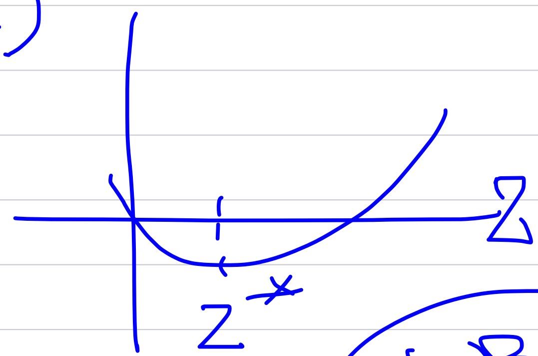
$$= 2(Z-2)e^2 \frac{1}{\pi} Z^3 \cdot \int_0^\infty dr_1 \, r_1 \, e^{-2Zr_1} \cdot \overset{d\Omega}{4\pi} .$$

$$= 2(Z-2)e^2 \cdot 4Z^3 \cdot \frac{1}{(2Z)^2} \Gamma(2)$$

$$= 2Z(Z-2)\frac{e^2}{r_B} .$$

$$E^{var} = -Z^2 + \frac{5}{8}Z + 2Z(Z-2)$$

$$= Z^2 - \frac{27}{8}Z$$



$$\frac{\partial E^{var}}{\partial Z} = 2Z - \frac{27}{8} = 0$$

$$Z^* = \frac{27}{16} \simeq 1.6875$$

N.B. $1 < Z^* < 2$

$$E^{var} = \left(\frac{27}{16}\right)^2 - \frac{27}{8} \cdot \frac{27}{16} = -\left(\frac{27}{16}\right)^2 \simeq -2.8477$$

(OK. ∼2%)

cfr. $E^{(pert)} \simeq -2.75$ (∼5%).

$E^{(exp.)} \simeq -2.90357$

N.B. $E^{var.} > E^{(exp.)}$

Calcolo variazionale di Hylleraas. (1929)

$$s = r_1 + r_2 \; ; \quad t = r_1 - r_2 \; , \quad u = r_{12}$$

$$0 \le t \le u \le s < \infty$$

$$\varphi_{lmn}(s,t,u) = s^l t^{2m} u^n e^{-s/2}$$

$$i \begin{cases} l = 0,1,2,\cdots d_s \\ m = 0,1,2,\cdots d_t \\ n = 0,1,2,\cdots d_u \end{cases}$$

$$d^3 r_1 d^3 r_2 = 2\pi^2 u (s^2 - t^2) \, ds \, dt \, du$$

$$\psi = \Sigma c_i \tilde{\varphi}_i(\lambda s, \lambda t, \lambda u) \qquad (\lambda \sim Z)$$

$$\tilde{\varphi}_i = \lambda^6 \varphi_i(\lambda s, \lambda t, \lambda u)$$

$$i = l + (d_s+1) m + (d_s+1)(d_t+1) n + 1$$

$$i = 0, 1, 2, \cdots N, \qquad N = (d_s+1)(d_t+1)(d_u+1)$$

$N = 1$ ($l = m = n = 0$, Calcolo elementare, $\lambda = Z$)

$$\Rightarrow E^{var} \simeq -2.84766$$

$N = 120$

$$\Rightarrow E^{var} \simeq -2.9037241\,3$$

cfr $E^{sper.} \simeq -2.90357\cdots$

$$\Delta E / E \sim 10^{-4} .$$

cfr. Correz. massa, $M_{nucleo} < \infty$, correz. relativistiche.

N.B. Storicamente: una verifica inconfutabile della nuova meccanica.