Teoria del funzionale densità.

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Hohenberg e Kohn

$$\Psi \underset{?}{\rightleftharpoons} \rho$$

$$\Psi_0 \rightleftharpoons \rho_0$$

Dipende dalla forma dell'hamiltoniana.

$$H = \underbrace{-\sum_i \frac{\nabla_i^2}{2} + \sum_{i<j} \frac{1}{|r_i - r_j|}}_{U^N} + \sum_i V(r_i) \tag{1}$$

per assurdo

$$H^1 = U^N + \sum_i V^1(r_i) \quad H^1\Psi_0^1 = \epsilon_1\Psi_0^1 \quad \langle\Psi_0^1|\hat{d}(r)|\Psi_0^1\rangle = \rho(r)$$

$$H^2 = U^N + \sum_i V^2(r_i) \quad H^2\Psi_0^2 = \epsilon_2\Psi_0^2 \quad \langle\Psi_0^2|\hat{d}(r)|\Psi_0^2\rangle = \rho(r)$$

per ipotesi, o principio variazionale

$$\langle\Psi_0^1|H^1|\Psi_0^1\rangle \leq \langle\Psi_0^2|H^1|\Psi_0^2\rangle$$

$$\langle\Psi_0^2|U^N|\Psi_0^2\rangle + \cancel{\int \rho V^1 dr} > \langle\Psi_0^1|U^N|\Psi_0^1\rangle + \cancel{\int \rho V^1 dr}$$

$$\langle\Psi_0^1|U^N|\Psi_0^1\rangle + \cancel{\int \rho V^2 dr} > \langle\Psi_0^2|U^N|\Psi_0^2\rangle + \cancel{\int \rho V^2 dr}$$

che assurdo!

applicazione?

$$E[\rho] = F[\rho] + \int V(x)\rho(x)dx$$

$$F[\rho] = \min_{\rho} E_v[\rho]$$

Levy-Lieb

$$\langle\psi|U_N + V|\psi\rangle \geq \langle\psi_0|U_N + V|\psi_0\rangle \qquad \text{(ancora)}$$

$$E = \min_{\rho}\left[\min_{\psi\to\rho}\langle\psi|U|\psi\rangle + \int V\rho\right]$$

$$F[\rho] = \min_{\psi\to\rho}\langle\psi|U|\psi\rangle$$

Kohn-Sham

$$F[\rho] = T_S[\rho] + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + E_{XC}[\rho]$$

$$T_S[\rho] = \langle \psi_{\rho,\text{non interagente}} | T | \psi \rangle$$

tassonomia

$F_L[\rho] = \int f(\rho(x))dx$	LDA, es. B97
$F_G[\rho] = \int g(\nabla\rho(x))dx$	GGA, es. PBE
$F_H[\phi_k] = w_{HF} Xc_{HF}(\phi_k) + w_{DF} Xc(\rho[\phi_k])$	ibrido: Hybrid, es. B3LYP
$F_M[\rho] = \int g(\nabla^2\rho(x))dx$	meta, es. M05
$F_N[\rho] = \iint L(\rho(x_1), \rho(x_2))dx_1 dx_2$	non locale, es. CAM-B3LYP