QUANTUM CHEMISTRY-10

DENSITY FUNCTIONAL THEORY: FUNDAMENTALS

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ROMÂNIA 1918-2018 | SĂRBĂTORIM ÎMPREUNĂ

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Hohenberg-Kohn theorems & Effective Kohn-Sham Equation

- overcome from a single shoot both the *exchange and correlation* terms to the total electronic energy (THAT FUNCTIONAL the title of theory is referring at)
- Observable Quantum Chemistry (as based on electronic DENSITY; at its turn it can be experimentally expressed, e.g. X-Ray studies, etc.)
- **The Nobel Prize in Chemistry 1998 (Walter Kohn, John Pople)/Kohn Nobel Lecture: https://www.nobelprize.org/prizes/chemistry/1998/kohn/lecture/**

$$N[\rho] = \int \rho(r)dr = \sum_i n_i$$

$$\rho(\mathbf{r}) = N\int \Psi^*(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)d\mathbf{r}_2...d\mathbf{r}_N$$

(N-1) integrals

Electrons

V-representability…"insurance for OBSERVABILITY

$$\rho(\mathbf{r}) \geq 0 \;,\; \forall|\mathbf{r}| \in \Re \qquad \int_{\Re} \left|\nabla \rho(\mathbf{r})^{1/2}\right|^2 d\mathbf{r} < \infty$$

"N-orbital uni-occupancy"

---> Effective uni-electronic chem-reactivity

$$\overline{\rho}(\mathbf{r}) = N\varphi^*(\mathbf{r})\varphi(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]\varphi(\mathbf{r}) = \mu\varphi(\mathbf{r})$$

$$V_{eff}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2 + V_{xc}(\mathbf{r})$$

$$E[\rho] = F_{HK}[\rho] + C_A[\rho]$$

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \qquad C_A[\rho] = \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

Approx.

$$E[\overline{\rho}] \geq E[\rho] \Leftrightarrow \delta E[\rho] = 0$$

$$\delta\{E[\rho] - \mu N[\rho]\} = 0$$

Approx.

"Comput-Chem"

$$\overline{\rho}(\mathbf{r}) = \sum_i^N n_i|\varphi_i(\mathbf{r})|^2$$

$$0 \leq n_i \leq 1 \;\; vs. \;\; 0 \leq n_i \leq 2$$

$$\sum_i n_i \sim N \;\; vs. \;\; \sum_i n_i = N$$

$$\mu = -\chi = \left(\frac{\delta E[\rho]}{\delta \rho}\right)_{\rho=\rho(V)}$$

"Chem-Reactivity"