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① Density-functional theory (DFT)

made in Canada

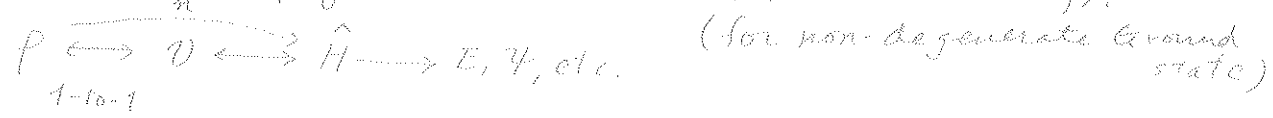
$$\hat{H} = \sum_{i=1}^n \left(-\frac{1}{2} \nabla_i^2 + \sum_{I=1}^N \frac{-Z_I}{|R_i - R_I|} \right) + \sum_{(i,j)} \frac{1}{|R_i - R_j|}$$

Note --- only n (electrons) and "external potential" $V(R_i)$ are system-dependent.

Specify n and $V \rightarrow$ specify $\hat{H} \rightarrow \psi, E, \text{etc.}$

Hohenberg-Kohn theorem I : 1964

There's a one-to-one mapping between V and ρ (electron density).



So, E is a functional of $\rho : E[\rho]$

* On this basis, it is often stated that one can obtain exact E of Schrödinger equation bypassing wave functions (3 n dimensional) but with ρ (3 dimensional) as a basic variable. Is this true??

Hohenberg-Kohn theorem II

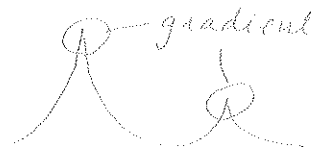
$$E[\rho_{\text{trial}}] \geq E[\rho_{\text{exact}}] \quad (\text{equal sign when } \rho_{\text{trial}} = \rho_{\text{exact}})$$

So, one can vary ρ and minimize $E[\rho]$ to reach the exact solution.

$$\frac{\delta}{\delta \rho} (E[\rho] - \lambda (\int \rho d\tau - n)) = 0$$

E. B. Wilson's remark

If one has exact ρ for non-degenerate ground state, $\int \rho d\tau = n$ gives the total number of electrons, the cusps of ρ give the positions and charges of nuclei (V). Then one knows \hat{H}



gradients $\propto Z_I$

and can in principle solve $\hat{H}\psi = E\psi$ to obtain exact E .

$$\frac{\partial \bar{\rho}(r)}{\partial r} = -Z \bar{\rho}(r) \text{ at } r=0 \quad (\bar{\rho} \text{ is angle-averaged})$$

② Density functionals

$$E = \underbrace{\langle \psi | \hat{T} | \psi \rangle}_{\text{kinetic}} + \underbrace{\int \rho(r) v(r) dr}_{\text{external or nuclear attraction}} + \underbrace{\frac{1}{2} \iint \frac{\rho(r) \rho(r')}{|r-r'|} dr dr'}_{J \text{ (including self interaction)}} + \underbrace{E_{xc}}_{\text{exchange + correlation}} \quad \text{see below}$$

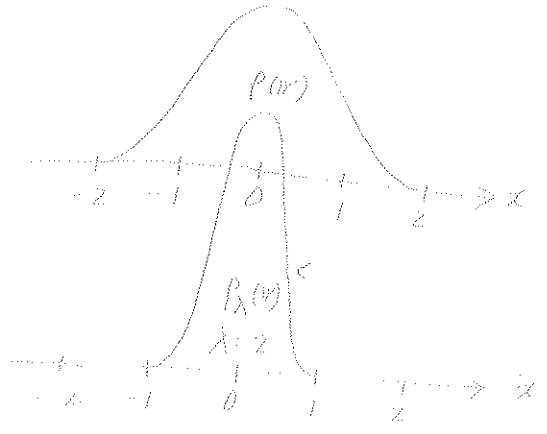
$\langle \psi | \hat{T} - \frac{1}{2} \nabla^2 | \psi \rangle$
 E_T

already density functional

i) Thomas-Fermi functional (kinetic) 19'4, 19'8

$$E_T = C_{TF} \int \rho^{5/3} dr$$

How do they come up with this approximation? — scaling + homogeneous electron gas ($\rho = \text{const.}$)



To maintain normalization

$$\rho_\lambda(r) = \lambda^3 \rho(\lambda r)$$

$$E_T[\rho_\lambda] = \lambda^2 E_T[\rho] \quad \left[\frac{1}{\lambda^2} \nabla^2 = \frac{1}{\lambda^2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \right]$$

increased curvature by λ^2

$$E_T[\rho_\lambda] = C_{TF} \int (\lambda^3 \rho(\lambda r))^{5/3} dr = C_{TF} \lambda^5 \int [\rho(\lambda r)]^{5/3} \frac{1}{\lambda^3} d(\lambda r) = \lambda^2 E_T[\rho]$$

Weakness: TF kinetic energy functional cannot describe chemical bond!!

ii) Dirac-Slater functional (exchange)

1930, 1931

$$E_x = C_{DS} \int \rho^{4/3} d\mathbf{r}$$

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda\mathbf{r})$$

$$E_x[\rho_\lambda] = \lambda E_x[\rho] \quad \frac{1}{r_{12}} = \frac{1}{\sqrt{(\lambda r_1 - \lambda r_2)^2 + (\lambda y_1 - \lambda y_2)^2 + (\lambda z_1 - \lambda z_2)^2}}$$

$$E_x[\rho_\lambda] = C_{DS} \int (\lambda^3 \rho(\lambda\mathbf{r}))^{4/3} d\mathbf{r} = C_{DS} \lambda^4 \int [\rho(\lambda\mathbf{r})]^{4/3} \frac{1}{\lambda^3} d(\lambda\mathbf{r}) = \lambda E_x[\rho]$$

Strength: DS exchange energy functional strikes a nice balance between accuracy and cost.

③ Kohn-Sham scheme (kinetic) 1965

TF-DS would be a "true" DFT which involves no orbitals or wave function. However, TF turns out to be rather useless in chemistry as it cannot account for chemical bonds.

In Kohn-Sham scheme, we concede a little bit and use orbitals to evaluate T_1 much more accurately:

$$E_1 = \langle \psi | \hat{T} | \psi \rangle \approx \langle \Phi_0 | \hat{T} | \Phi_0 \rangle$$

↑
True many-det. wavefn

↓
KS determinant

$$E_1 = \langle \Phi_0 | \hat{T} | \Phi_0 \rangle + \int \rho v d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}$$

This is just formality as DFT in practice can not reach exactness even in H atom.

exchange + correlation + kinetic
 $\langle \psi | \hat{T} | \psi \rangle - \langle \Phi_0 | \hat{T} | \Phi_0 \rangle$

$$0 = \frac{\delta}{\delta \varphi_i^*} \left\{ E - \sum_{k,l} \lambda_{kl} (\langle \varphi_k | \varphi_l \rangle - 1) \right\}$$

$$= \frac{\delta}{\delta \varphi_i^*} \left\{ \sum_i \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle + \int \rho V d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc} - \sum_{k,l} \lambda_{kl} \langle \varphi_k | \varphi_l \rangle \right\}$$

$$\left(\frac{\delta P}{\delta \varphi_i^*} \frac{\delta}{\delta P} = \varphi_i \frac{\delta}{\delta P} \quad ; \quad P = \sum_i \varphi_i^* \varphi_i \right)$$

$$= \left(-\frac{1}{2} \nabla^2 + V + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \underbrace{\frac{\delta E_{xc}}{\delta P}}_{V_{xc}} \right) \varphi_i - \sum_l \lambda_{li} \varphi_l$$

Kohn-Sham eq.

exchange
correlation
potential
 V_{xc}

orbital rotation
to
canonical form

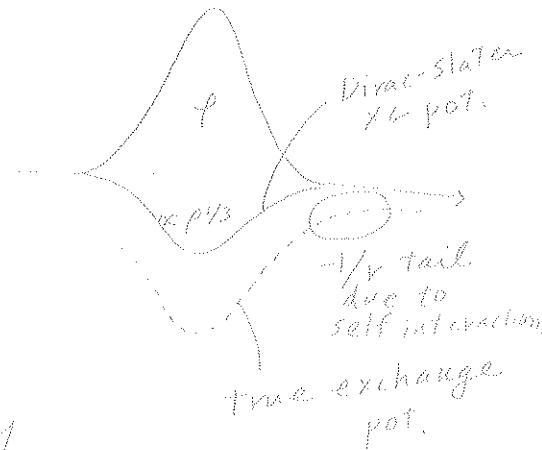
$$\left\{ -\frac{1}{2} \nabla^2 + V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right\} \varphi_i = \epsilon_i \varphi_i$$

identical to HF

KS orbital
KS orbital energy

Note the similarity to HF. DFT is usually implemented in the same framework as HF.

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta P} \propto \rho^{4/3} \text{ dir} = \frac{4}{3} C_{xc} \rho^{1/3}$$



Weakness: DFT's exchange potentials, being local functions of density which decays exponentially, are almost always too rapidly decaying and too shallow everywhere. This leads to

- incomplete cancellation of self interaction (This can be viewed a cause)
- too low ionization potential
- too low Rydberg states
- too high polarizabilities, etc.

(4) Basis set expansion

HF Roothaan-Hall (closed shell)

Fock

$$\mathbb{H}C = SC\epsilon$$

$$\rightarrow S_{\mu\nu} = (\mu|\nu)$$

$$\rightarrow F_{\mu\nu} = (\mu|\hat{f}|\nu)$$

$$= \underbrace{(\mu|\hat{h}|\nu)}_{\substack{\text{core} \\ H_{\mu\nu} \\ (\text{kin.} + \text{nucl.})}} + \underbrace{\sum_{\kappa\lambda} P_{\lambda\kappa} (\mu\nu|\kappa\lambda)}_{\text{Coulomb, } J} - \underbrace{\sum_{\kappa\lambda} \frac{1}{2} P_{\lambda\kappa} (\mu\lambda|\kappa\nu)}_{\text{exchange, } K}$$

$$E_{\text{HF}} = \sum_{\mu\nu} (\mu|\hat{h}|\nu) P_{\nu\mu}$$

$$+ \frac{1}{2} \sum_{\substack{\mu,\nu \\ \kappa,\lambda}} (\mu\nu|\kappa\lambda) P_{\nu\mu} P_{\lambda\kappa} - \frac{1}{4} \sum_{\substack{\mu,\nu \\ \kappa,\lambda}} (\mu\lambda|\kappa\nu) P_{\nu\mu} P_{\lambda\kappa}$$

KS (closed shell)

KS Hamiltonian

$$\mathbb{H}C = SC\epsilon$$

$$\rightarrow S_{\mu\nu} = (\mu|\nu)$$

$$\rightarrow H_{\mu\nu} = (\mu|\hat{h}|\nu) + \sum_{\kappa\lambda} P_{\lambda\kappa} (\mu\nu|\kappa\lambda) + (\mu|V_{\text{xc}}|\nu)$$

3D numerical
integration using
Becke's Furry-all quadrature

$$E_{\text{DF-T}} = \sum_{\mu,\nu} (\mu|\hat{h}|\nu) P_{\nu\mu}$$

$$+ \frac{1}{2} \sum_{\substack{\mu,\nu \\ \kappa,\lambda}} (\mu\nu|\kappa\lambda) P_{\nu\mu} P_{\lambda\kappa} + \int \text{Exc}[P] d\tau$$

3D integration
w/ quadrature