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Introduction to Density Functional Theory (DFT)

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DFT = Subset of "Electronic Structure Theory"

- Hartree-Fock
- DFT
- MBPn (MPn)
- GW
- CCSD(T)
- MCSCF, CASSCF, CASPT2, etc
- ...
- . . .

We will see why ELECTRONic soon



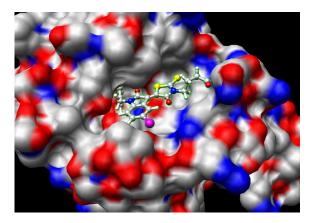
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Applications of DFT (Correct)

Drug Docking in Protein



$$E_{
m binding} = E_{
m PD} - (E_{
m P} + E_{
m D})$$

 $E_{
m binding} > 0 \Rightarrow$ No binding

 $\frac{E_{\rm binding}}{\rm Binding} < 0 \Rightarrow$

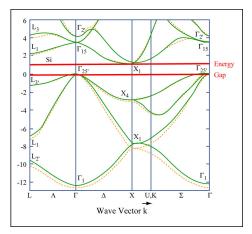
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Applications of DFT (Wrong)

Band Structure



... but we do it (why?) and can be corrected ...



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Calculating Energies

- E = KE[electrons]
 - + KE[ions]
 - + *PE*[electrons]
 - + PE[ions]
 - + PE[el ions]





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Calculating Energies

$$E = KE[\text{electrons}] \leftarrow \sum_{j} \frac{p_{j}^{2}}{2m}$$

$$+ KE[\text{ions}] \leftarrow \sum_{l} \frac{P_{l}^{2}}{2M_{l}} \quad \text{BO}$$

$$+ PE[\text{electrons}] \leftarrow \frac{1}{2} \sum_{i,j} \frac{(-e)(-e)}{|r_{i} - r_{j}|}$$

$$+ PE[\text{ions}] \leftarrow \frac{1}{2} \sum_{l,j} \frac{(Z_{l}e)(Z_{j}e)}{|R_{l} - R_{j}|}$$

$$+ PE[\text{el} - \text{ions}] \leftarrow \sum_{i} V(r_{i}, R_{\text{all}})$$



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Some QM

$$egin{array}{rcl} p_j &\longrightarrow& \hat{p}_j \longrightarrow rac{\hbar}{i}
abla_i \ E_{
m el} &\longrightarrow& \hat{H}_{
m el} \end{array}$$

(1)

Introduce $\Psi(r_{all})$, where $r_{all} = (r_1, r_2, \dots, r_N)$. Solve:

$$\hat{H}_{\mathrm{el}}\Psi = \mathcal{E}\Psi(r_1, r_2, \ldots, r_N)$$

Get different energy states, the lowest energy state Ψ_0 is called the ground state (GS). Its energy is the GS Energy \mathcal{E}_0 .



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Function vs. Functional

Also,

$$\mathcal{E}_0 = \frac{\int \Psi_0^* \hat{H}_{\rm el} \Psi_0 dr_1 dr_2 \dots dr_N}{\int \Psi_0^* \Psi_0 dr_1 dr_2 \dots dr_N}$$

Infact, instead of $\Psi_0,$ I can put any $\Psi_{\rm trial}$ in the RHS to get:

$$E[\Psi_{\text{trial}}] = \frac{\int \Psi_{\text{trial}}^* \hat{H}_{\text{el}} \Psi_{\text{trial}} dr_1 dr_2 \dots dr_N}{\int \Psi_{\text{trial}}^* \Psi_{\text{trial}} dr_1 dr_2 \dots dr_N}$$

And there is a theorem that, if Ψ_{trial} has the correct (permutational) symmetry then:

 $\textit{E}[\Psi_{\rm trial}] \geq \mathcal{E}_0$



Function vs. Functional

Functional: Not just "function of a function" but: Functional: Eats functions and spits out numbers

$$E[\Psi_0] = E[\rho_0] = KE[\Psi_0] \longleftarrow KE[\rho_0]??$$

$$+ KE[\text{ions}] \longleftarrow \approx 0$$

$$+ PE[\text{electrons}] \longleftarrow = E_H[\rho_0] + \tilde{E}_{\text{xc}}[\rho_0]$$

$$+ PE[\text{ions}] \longleftarrow \text{Constant for fixed Ions}$$

$$+ PE[\text{el-ions}] \longleftarrow = \int V(r, R_{\text{all}})\rho_0 dr$$

where,

$$ho_0(r) = \langle \Psi_0 | \sum_j \delta^3(r-r_j) | \Psi_0
angle$$





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Original DFT

 $\mathit{KE}[\rho_0] \approx c_0 \int \rho_0^{5/3} dr$

$$E[
ho] pprox c_0 \int
ho^{5/3} dr + \int V(r, R_{
m all})
ho dr + E_H[
ho] + ilde{E}_{
m xc}[
ho]$$

and when $\rho = \rho_0$ we get the GS energy.

We get ρ_0 by minimizing the functional above wrt ρ .

There is a theorem (H-K theorem) that tells us that $V(r, R_{all})$ corresponds to one and only one ρ_0 which minimizes the energy.



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Kohn-Sham DFT

Assume we have fictitious independent electrons which have the same density as the true density. In this case ρ and the "independent" electron wavefunctions φ_i are related by:

$$ho(r) = \sum_{i}^{occ} arphi_i(r)^* arphi_i(r)$$

 $\mathsf{KE}[\rho] \approx \sum_{i} \int \varphi_{i}^{*} [-\frac{\hbar^{2}}{2m} \nabla_{i}^{2}] \varphi_{i} dr$

$$E[\rho] \approx \sum_{i} \int \varphi_{i}^{*} \left[-\frac{\hbar^{2}}{2m} \nabla_{i}^{2}\right] \varphi_{i} dr + \int V(r, R_{\rm all}) \rho dr + E_{H}[\rho] + E_{\rm xc}[\rho]$$



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DFT:Ground State Theory or ...?

We get ρ_0 by minimizing the functional above wrt φ_j^* . This gives:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r, R_{\rm all}) + V_H[\rho] + V_{\rm xc}[\rho]\right]\varphi_j = \epsilon_j\varphi_j$$
(3)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\rm eff}\right]\varphi_j = \epsilon_j\varphi_j$$

(4)

... like a 1-particle equation. Hence, the use for



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