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Introduction to Density Functional Theory (DFT)

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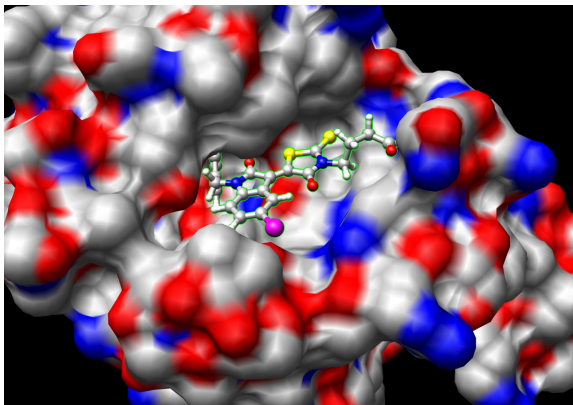
DFT = Subset of "Electronic Structure Theory"

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

We will see why ELECTRONic soon

Applications of DFT (Correct)

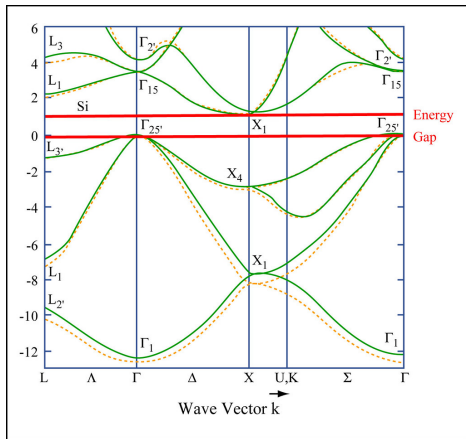**Drug Docking in Protein**

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

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

$E_{\text{binding}} < 0 \Rightarrow$
Binding

Applications of DFT (Wrong)

Band Structure

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

Calculating Energies

$$
\begin{aligned}
E \quad = \quad & KE[\text{electrons}] \\
+ \quad & KE[\text{ions}] \\
+ \quad & PE[\text{electrons}] \\
+ \quad & PE[\text{ions}] \\
+ \quad & PE[\text{el} - \text{ions}]
\end{aligned}
$$

Calculating Energies

$$
\begin{aligned}
E \;=\; & KE[\text{electrons}] \quad \leftarrow \sum_j \frac{p_j^2}{2m} \\[2mm]
+\; & KE[\text{ions}] \quad \longleftarrow \sum_I \frac{P_I^2}{2M_I} \qquad \text{BO} \\[2mm]
+\; & PE[\text{electrons}] \quad \longleftarrow \frac{1}{2}\sum_{i,j} \frac{(-e)(-e)}{|r_i - r_j|} \\[2mm]
+\; & PE[\text{ions}] \quad \longleftarrow \frac{1}{2}\sum_{I,J} \frac{(Z_I e)(Z_J e)}{|R_I - R_J|} \\[2mm]
+\; & PE[\text{el} - \text{ions}] \quad \longleftarrow \sum_i V(r_i, R_{\text{all}})
\end{aligned}
$$

Some QM

$$p_j \longrightarrow \hat{p}_j \longrightarrow \frac{\hbar}{i}\nabla_i$$

$$E_{\mathrm{el}} \longrightarrow \hat{H}_{\mathrm{el}}$$

$$\tag{1}$$

Introduce $\Psi(r_{\mathrm{all}})$, where $r_{\mathrm{all}} = (r_1, r_2, \ldots, r_N)$.
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 $\mathcal{E}_0$.

Function vs. Functional

Also,

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

Infact, instead of Ψ_0, I can put any Ψ_{trial} in the RHS to get:

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

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

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

Function vs. Functional

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

$$
\begin{aligned}
E[\Psi_0] = E[\rho_0] \;=\; & KE[\Psi_0] \quad \longleftarrow KE[\rho_0]?? \\
+\; & KE[\text{ions}] \quad \longleftarrow \approx 0 \\
+\; & PE[\text{electrons}] \quad \longleftarrow = E_H[\rho_0] + \tilde{E}_{\text{xc}}[\rho_0] \\
+\; & PE[\text{ions}] \quad \longleftarrow \text{Constant for fixed Ions} \\
+\; & PE[\text{el} - \text{ions}] \quad \longleftarrow = \int V(r, R_{\text{all}})\rho_0 \, dr
\end{aligned}
$$

where,

$$
\rho_0(r) = \langle \Psi_0 | \sum_j \delta^3(r - r_j) | \Psi_0 \rangle
$$

Original DFT

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

$$E[\rho] \approx c_0 \int \rho^{5/3} dr + \int V(r, R_{\mathrm{all}})\rho dr + E_H[\rho] + \tilde{E}_{\mathrm{xc}}[\rho]$$

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 $V(r, R_{\mathrm{all}})$ corresponds to one and only one ρ_0 which minimizes the energy.

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:

$$\rho(r) = \sum_i^{occ} \varphi_i(r)^* \varphi_i(r)$$

(2)

$$KE[\rho] \approx \sum_i \int \varphi_i^* [-\frac{\hbar^2}{2m}\nabla_i^2]\varphi_i dr$$

$$E[\rho] \approx \sum_i \int \varphi_i^* [-\frac{\hbar^2}{2m}\nabla_i^2]\varphi_i dr + \int V(r, R_{\mathrm{all}})\rho dr + E_H[\rho] + E_{\mathrm{xc}}[\rho]$$

DFT:Ground State Theory or ...?

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

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

(3)

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

(4)

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