



# Introduction to Density Functional Theory (DFT)

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# The Problem:

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i,j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I,J \neq I} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}\end{aligned}$$



# What's the big deal?

- Materials we are often interested in contain a macroscopically large number of particles ( $\sim 10^{23}$ )
- Motion of electrons and ions is correlated
- Quantum nature of the problem – the solution to the entire problem must obey the Pauli exclusion principle

# The Born–Oppenheimer approx. (making it less terrible)

The ions are much heavier and SLOWER than the electrons  
(mass ratio of 1:1836 *at worst*)



The electrons then can be taken to instantaneously adjust to the ionic positions as the ions move





And this means what exactly?

$$\Phi(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = \sum_n \Theta_n(\mathbf{R}_I) \Psi_n(\mathbf{r}, \mathbf{R}_{fixed})$$

It means the full wavefunction can be written as a product of an ionic part, and an electronic part for which the ionic positions come in as *only parameters* and not variables



$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i,j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{ion}(\mathbf{r}_i) + \frac{1}{2} \sum_{i,j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Purely electronic Hamiltonian



still **HARD** to solve...why?

Consider a system of 10 electrons with wavefunction solution:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_6, \mathbf{r}_7, \mathbf{r}_8, \mathbf{r}_9, \mathbf{r}_{10})$$

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– Assume a 10x10x10 real-space grid, then  
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With single-precision floats at 4 bytes each, this is  $4 \times 10^{18}$  TB. Even if we could get a bulk discount and get 1 TB of space for \$1, that's still 4 million *trillion* dollars.



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Thus we have a STRONG incentive to consider approaches which might allow us to get around the full determination of the wavefunction..



# What about the electronic density?

In the previous example the density would only take  $10 \times 10 \times 10$  numbers, which is the equivalent of about 28 text messages on your phone.

But can the problem even be formulated  
in terms of the density?

Hmm...dunno

...I want to say 'yes'



Thomas



Fermi



Their work led to the Thomas–Fermi model (1927), later added to by Dirac (1930)

They tried to write each contribution to the total energy in the form:

$$E_{\alpha}[\rho] = \int \rho(\mathbf{r}) \epsilon_{\alpha}[\rho(\mathbf{r})] d^3 \mathbf{r}$$



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This leads to a total energy expression:

$$E_{TFD}[\rho] = C_1 \int \rho(\mathbf{r})^{5/3} d^3 \mathbf{r} + \int \rho(\mathbf{r}) V_{ext} d^3 \mathbf{r} \\ + C_2 \int \rho(\mathbf{r})^{4/3} d^3 \mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}'$$



## Thomas–Fermi doesn't work so well though

- × Total energies poor
- × Density does not decay exponentially at long distances
- × Shell structure of the atoms is not present

Major difficulty in writing the kinetic energy contribution in terms of the density





# The Hohenberg-Kohn Theorems



Hohenberg



Kohn



## HK Theorem #1

Within the TF model, we had the result that the interacting density could be uniquely related to the external potential, but is this actually true?



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Yes, it is, and the proof is quite simple!



## Proof of HK #1, via proof-by-contradiction

Assume that the external potential is NOT determined by the density; thus assume that we have two potentials  $V_{ext}^1(\mathbf{r})$  and  $V_{ext}^2(\mathbf{r})$ , which differ by more than a trivial constant but give rise to the same ground state density  $\rho_0(\mathbf{r})$

Associated with these two potentials are two Hamiltonians,  $\hat{H}^1$  and  $\hat{H}^2$ , which differ only by these two external potentials. The lowest energy solutions (e.g., the ground state) for these Hamiltonians is  $\Psi^1$  and  $\Psi^2$ , respectively, both assumed to give rise to the same ground state density  $\rho_0(\mathbf{r})$ . These ground state energies are given simply as:

$$E_0^1 = \langle \Psi^1 | \hat{H}^1 | \Psi^1 \rangle \quad \text{and} \quad E_0^2 = \langle \Psi^2 | \hat{H}^2 | \Psi^2 \rangle$$



By the variational principle we know that:

$$\begin{aligned} E_0^1 &< \langle \Psi^2 | \hat{H}^1 | \Psi^2 \rangle = \langle \Psi^2 | \hat{H}^2 + \hat{H}^1 - \hat{H}^2 | \Psi^2 \rangle \\ &= E_0^2 + \int \rho_0(\mathbf{r}) (V_{ext}^1(\mathbf{r}) - V_{ext}^2(\mathbf{r})) d^3 \mathbf{r} \end{aligned}$$

We can make the same argument for the second energy

$$E_0^2 < E_0^1 + \int \rho_0(\mathbf{r}) (V_{ext}^2(\mathbf{r}) - V_{ext}^1(\mathbf{r})) d^3 \mathbf{r}$$

We can add these two equations together and obtain:

$$E_0^1 + E_0^2 < E_0^1 + E_0^2$$

which can never be true, and thus we take it that our initial assumption was incorrect



Therefore there is a direct one-to-one correspondence between the interacting ground state charge density and the external potential

Corollary: Since the integral of the charge density gives the number of electrons and determines the external potential, it determines the full Hamiltonian. Since it specifies the Hamiltonian, it also specifies the solutions of that Hamiltonian (i.e., all many-body wavefunctions, excited state.....ANY property determined by the Hamiltonian).



## HK Theorem #2

The total energy of the system can be written as an explicit functional  
Of the density:

$$\begin{aligned} E_{HK}[\rho] &= T[\rho] + E_{int}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} \\ &\equiv F_{HK}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} \end{aligned}$$

where  $F_{HK}$  is a universal functional of the density (i.e., is the same for all systems of electrons). The minimum of this energy functional with respect to the density is the true, ground state energy of the interacting system and the density that minimizes it is the true, interacting ground state density.



## Proof of HK Theorem #2

Consider the ground state of the system described by Hamiltonian  $\hat{H}$  with ground-state density  $\rho_0$ . This ground state has an energy:

$$E_0 = E_{HK}[\rho_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

If we now consider a different density,  $\rho'$ , constructed from a different many-body wavefunction  $\Psi'$ , the variational principle tells us that

$$E' = E_{HK}[\rho'] = \langle \Psi' | \hat{H} | \Psi' \rangle > \langle \Psi | \hat{H} | \Psi \rangle = E_{HK}[\rho_0] = E_0$$

Therefore the energy given by the HK energy functional for the true, interacting ground state density minimizes that function.





Thus we have shown that the complicated many-body problem can be formulated in terms of the density being the fundamental variable, and we have shown that by minimizing that functional we can find the true ground state density!



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...but we don't have any idea what the HK functional looks like...

In 1965 Kohn and his postdoc Sham introduce a practical scheme in which to proceed, by mapping the interacting problem to an auxiliary non-interacting problem



Kohn

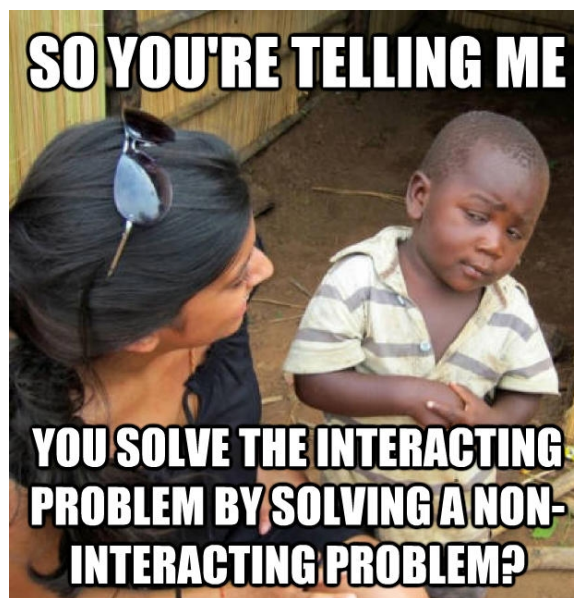


Sham

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Kohn



Sham



In Kohn's 1998 Nobel Prize lecture, he said his aim as to extract Hartree-like equations for the HK functional for the energy.

Why?

Because for a system of non-interacting particles the kinetic energy expression is easily computed (oh, and exact) as:

$$T = -\frac{\hbar^2}{2m} \sum_i f_i \langle \phi_i | \nabla^2 | \phi_i \rangle$$



Kohn and Sham rewrote the HK total energy functional as:

$$\begin{aligned} F_{HK}[\rho] &= F_{KS}[\rho] = T_s[\rho] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{xc}[\rho] \\ &= T_s[\rho] + E_{Hartree}[\rho] + E_{xc}[\rho] \end{aligned}$$

where  $T_s$  is the kinetic energy of the particles in the non-interacting Kohn-Sham system.  $E_{xc}$  is then defined by this equation (thus transferring what we don't know from  $F_{HK}$  to  $E_{xc}$ )



But we can write  $E_{xc}$  in a more illuminating way –

$$E_{xc}[\rho] = \langle T \rangle - T_s[\rho] + \langle E_{int} \rangle - E_{Hartree}[\rho]$$

So  $E_{xc}$  is the electron–electron interaction energy not accounted for by the Hartree term PLUS the interacting kinetic energy not accounted for by the kinetic energy of the non–interacting particles. These two differences we will hope to approximate somehow (with the safety net that if we do a terrible job at this these terms should still hopefully be relatively small!)



If we have the exact  $E_{xc}$ , then  $F_{KS}$  equals  $F_{HK}$ , and we obtain the ground state energy and density by minimizing the Kohn–Sham expression

Taking the functional derivative of the KS expression with respect to either the density or the orbitals leads to the Kohn–Sham equations:





Taking the functional derivative of the KS expression with respect to either the density or the orbitals leads to the Kohn–Sham equations:

$$\left[ -\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

where the Kohn–Sham potential is given as:

$$V_{ks}[\rho](\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r})$$

$$V_{Hartree}[\rho](\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}'$$

$$V_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$



The Kohn-Sham equations require a self-consistent solution

$$\left[ -\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

but the density is constructed from the wavefunctions via:

$$\rho(\mathbf{r}) = \sum_i^{occ} |\phi_i(\mathbf{r})|^2$$



El fin