Introduction to Density Functional Theory

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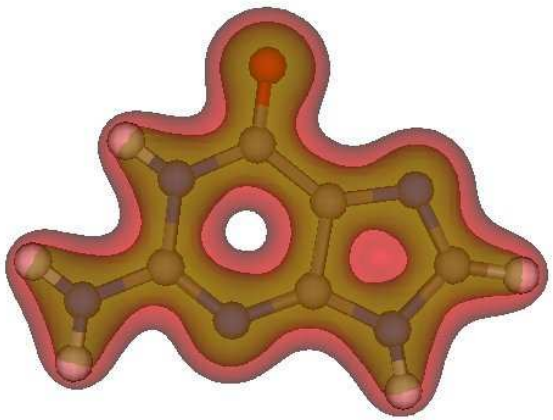
Outline

Outline for section 1

Introduction

- would like to understand the electrical properties of a material
- need its electron ground state
  - ground state energy E_0
  - ground state electron wavefunction Ψ_0
- can get useful expectation values $\langle Q \rangle = \langle \Psi_0 | \hat{Q} | \Psi_0 \rangle$

- Density Functional Theory (DFT) is a method that can find this ground state



Gaunine

Introduction

- very popular – physics, chemistry, material science, etc
- used since 1970's, made more accurate in 1990's
- Walter Kohn – Nobel Prize in Chemistry 1999

How Do We Deal With Many Particles?

- need many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$
- a function of $3N$ variables $\rightarrow$ a lot of memory needed to store
- our electron Schrödinger equation will be complicated

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \quad (1)$$

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i=1}^{N} V^{\text{ext}}(\mathbf{r}_i) + \sum_{i<j}^{N} V^{\text{e-e}}(\mathbf{r}_i, \mathbf{r}_j) \quad (2)$$

- kinetic
- external potential (like from any nuclei)
- electron - electron Coulomb repulsion
- also Ψ must follow Pauli principle

Solving SE Is Too Difficult

$$H\Psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\right) = E\Psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\right)$$

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- would like to solve the SE for lowest state
- working with $\Psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\right)$ is too difficult
- can we instead work with just the electron density $\rho(\mathbf{r})$?

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 d\mathbf{r}_2, ..., d\mathbf{r}_N \tag{3}$$

- theorem: knowing $\rho\left(\mathbf{r}\right)$ let's you know all expectation values
- $\rho(\mathbf{r})$ is a function of only 3 variables $\rightarrow$ much easier

Density Functional Theory (DFT)

- with DFT we describe ficticious **noninteracting** particles
- they will have the same density $\rho(\mathbf{r})$ as electrons
- so same expectation values

- we'll have to find new potentials that can make these new particles feel like electrons
- we'll have to artificially manufacture the Pauli principle!

Outline for section 2

Designing the Hamiltonian for These Particles

- needs to mimic real interacting electrons
- kinetic term
- Coulomb repulsion between electrons $\rightarrow$ Hartree Potential + "correlation"
- Pauli effects $\rightarrow$ "exchange potential"
- external potential

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \left\{ V^{\mathsf{H}}[\rho](\mathbf{r}) + V^{\mathsf{C}}[\rho](\mathbf{r}) \right\} + V^{\mathsf{X}}[\rho](\mathbf{r})$$

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$$H^{KS} = -\frac{\hbar^2}{2m}\nabla^2 + V^{H}[\rho](\mathbf{r}) + V^{XC}[\rho](\mathbf{r})$$

$$\rightarrow H^{KS} + V^{ext}(\mathbf{r})$$

Potentials which are density-dependent

- notation $V^{H}[\rho](\mathbf{r})$ means it's a potential that is determined by the density
- example:

$$V^{H}(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{4}$$

- the exchange-correlation potential similarly is calculated by plugging in the density

NOTE: The form for $V^{XC}[\rho]$ is only known approximately. Improving it is a major research subject

Kohn-Sham (KS) Equation

- we will describe our new particles as Kohn-Sham orbitals $\phi_k(\mathbf{r})$
- they are the eigenfunctions of our new Hamiltonian
- we have the new Schrödinger-like equation

$$\left[H^{KS} + V^{ext}(\mathbf{r})\right]\phi_k(\mathbf{r}) = \epsilon_k\phi_k(\mathbf{r}) \tag{5}$$

$$H^{KS} = -\frac{\hbar^2}{2m}\nabla^2 + V^{H}[\rho](\mathbf{r}) + V^{XC}[\rho](\mathbf{r}) \tag{6}$$

- if we can solve this for the orbitals $\phi_k(\mathbf{r})$, we can get our density

$$\rho(\mathbf{r}) = \sum_k 2|\phi_k(\mathbf{r})|^2 \tag{7}$$

Solving the Kohn-Sham Equation Self-Consistently

$$\left[H^{\mathrm{KS}} + V^{\mathrm{ext}}(\mathbf{r})\right]\phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{r})$$

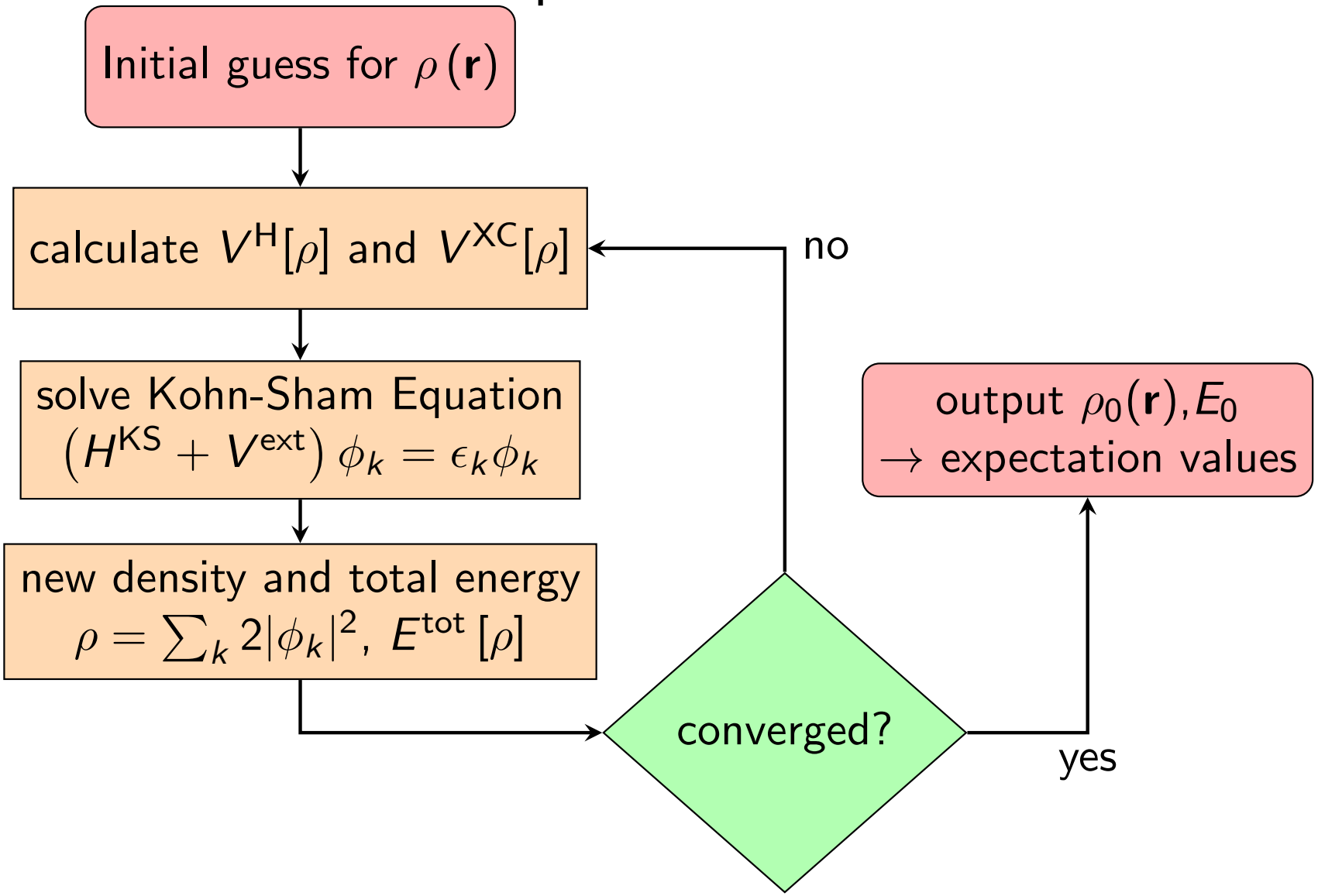
$$H^{\mathrm{KS}} = -\frac{\hbar^2}{2m}\nabla^2 + V^{\mathrm{H}}[\rho](\mathbf{r}) + V^{\mathrm{XC}}[\rho](\mathbf{r})$$

- we can also define the energy of the system by using "functionals"

$$E^{\mathrm{tot}}[\rho] = T^{\mathrm{KS}}[\rho] + E^{\mathrm{H}}[\rho] + E^{\mathrm{XC}}[\rho] + E^{\mathrm{ext}}[\rho] \tag{8}$$

- How can we solve if ρ depends on ϕ_k and H^{KS} depends on ρ, but we need H^{KS} to solve for ϕ_k in the first place?
- solve self-consistently

How To Solve the KS Equation



Conclusion

- DFT calculates the ground state electron density of atoms, molecules, materials
- does so by representing fictitious noninteracting particles that have the same density
- must approximate the exchange and correlation effects
- the Kohn Sham equation is solved self-consistently