

8 Density Functional Theory

8.1 Theoretical Motivation

↳ 8.1.1 Philosophy

- Instead of working w/ a wave function, we want to work w/ a physical observable in determining the energy of a molecule

↳ Observables # e^-

can obtain
 e^- density, ρ

Atomic # of nuclei
positions of nuclei

$$N = \int \rho(r) dr$$

↓
e^-

↓
electron density

• the positions of the nuclei correspond to local maxima in e^- density (these maxima are also cusps)

- ① We have a known density
- ② Use it to form Hamiltonian operator
- ③ solve Schrödinger equation
- ④ Determine ψ and energy eigenvalues
↓
wavefunctions

8.1.2 Early approximations

DFT → energy computed w/ no wave function

Functional → a function whose argument is also a function

'Slater exchange'

$$E_x[\rho(r)] = -\frac{9\alpha}{8} \left(\frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(r) dr$$

exchange energy

within Slater's derivation, the value for α is 1

In HF theory,
exchange corrections >>>
correlation corrections

Slater ignored
correlation
corrections +
kept exchange
corrections

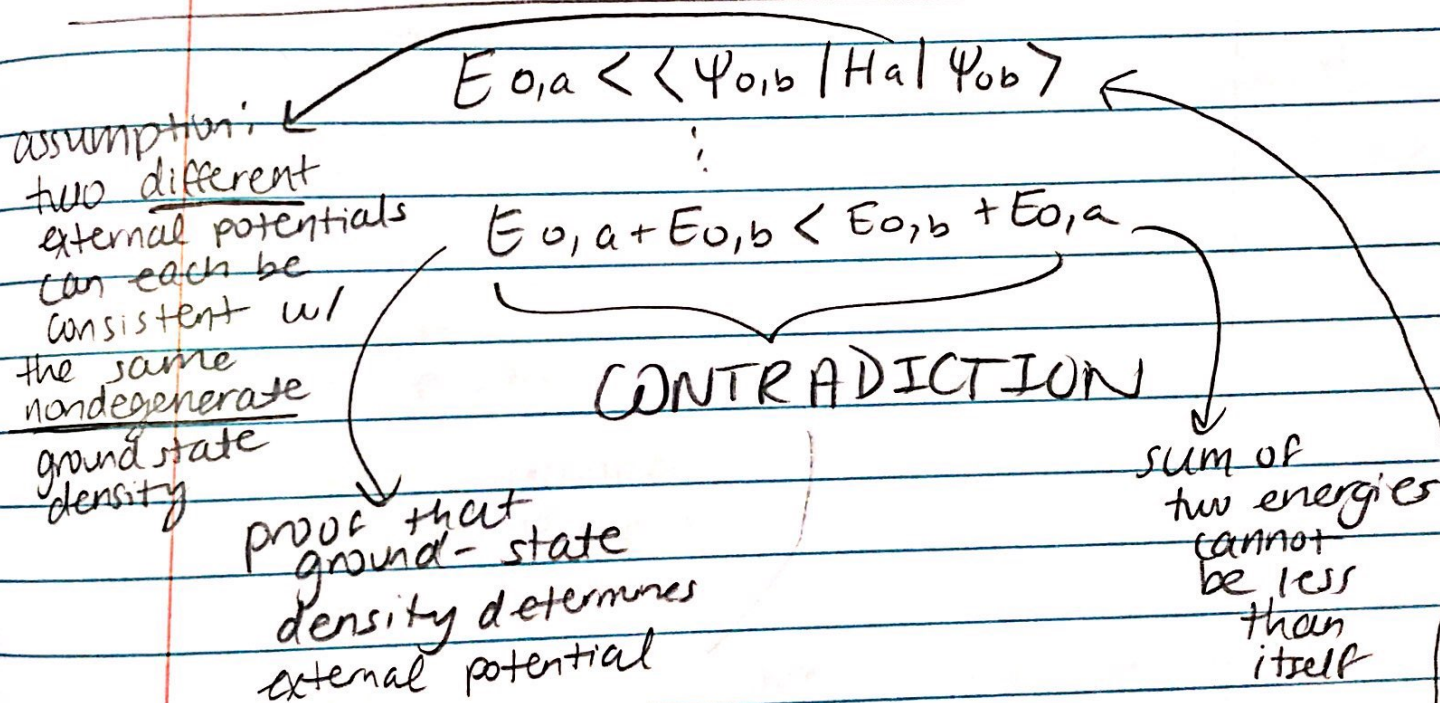
The exchange hole about any position could be approximated as a sphere of constant potential with a radius depending on the magnitude of the density at that position

8.2 Rigorous Foundation

↳ early DFT models failed b/c of their lack of variational principle

8.2.1 The Hohenberg-Kohn Existence Theorem

- DFT states that e^- interact w/ one another and w/ an 'external potential'
charges + positions of nuclei



Conclusion - Hamiltonian determines ground-state wave function and all excited-state wave functions as well

Variational theorem of MO theory dictates that the expectation value of the Hamiltonian 'a' over the wave function 'b' must be higher than the ground state energy of a

8.2.2 The Hohenberg-Kohn Variational Theorem

- We need now to predict the density of a system

Conclusion : Density obeys a variational principle (like MO theory)

★ candidate density

$$\langle \Psi_{\text{cand}} | H_{\text{cand}} | \Psi_{\text{cand}} \rangle = E_{\text{cand}} \geq E_0$$

① Assume we have a well-behaved candidate density that integrates to the proper number of e^- , N

energy
expectation
value

↓
true
ground-
state
energy

② Density determines candidate Ψ and H

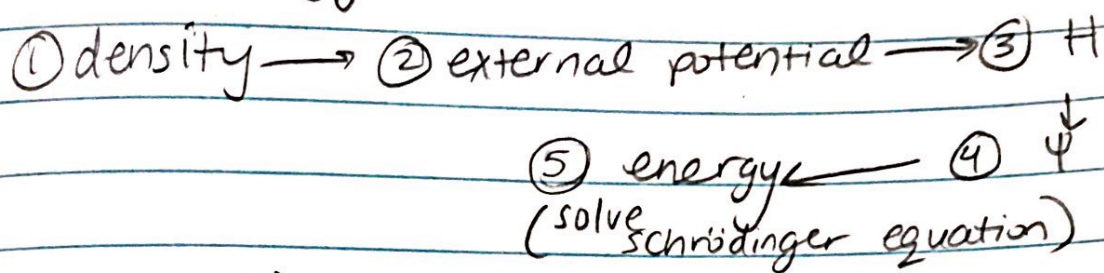
Problem : we don't want to keep guessing densities and solve the schrodinger equation to get an energy

Q : How can we use density as a general argument / in an equation w/o recourse to the wave function?

★ DFT provides no approximations - it is exact!!

8.3 Kohn-Sham self-consistent Field Methodology

To find energy:



\rightarrow Things would be simpler if only the Hamiltonian operator were on for a non-interacting system of e^-

$\hookrightarrow H \equiv$ sum of one e^- operators

\hookrightarrow has eigenfunctions that are Slater determinants of the individual one e^- eigenfunctions

\hookrightarrow has eigenvalues that are the sum of the one e^- eigenvalues

$$E[p(r)] = \sum_i^N \left(\langle \chi_i | -\frac{1}{2} \nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k^{\text{nuclei}} \frac{Z_k}{|r_i - r_k|} | \chi_i \rangle \right) + \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{p(r')}{|r_i - r'|} dr' | \chi_i \rangle + E_{xc}[p(r)]$$

N = number of e^-

E_{xc} = exchange-correlation energy (ΔT and ΔV_{ee})

χ = orbitals

\downarrow
kinetic energy

\downarrow
potential energy

p = density

needs to be approximated

$$\rho = \sum_{i=1}^N \langle \chi_i | \chi_i \rangle$$

includes effects of quantum mechanical exchange + correlation, correction for classical self-interaction energy, + diff. in kinetic E. b/w fictitious non-interacting system + real one