

Electronic Structure of Matter — Wave Functions and Density Functionals [1]

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Schrödinger's Equation

$$E\Psi = \hat{H}\Psi \quad (1)$$

Shortly after Schrödinger's equation had been validated for simple small systems like He and H₂, Dirac declared that chemistry had come to an end.

- ▶ Chemistry's content was entirely contained in this powerful equation
- ▶ But he added: in almost all cases, this equation is far too complex to solve

Problems with Schrödinger's Equation

- ▶ Comprehension becomes difficult: When high accuracy is required, so many Slater determinants are required.
 - ▶ In some calculations up to $\sim 10^9$ Slater determinants
- ▶ Practical problems: Multiparticle wavefunction methods when applied to systems of N particles encounter an exponential wall
 - ▶ Critical value at $N_0 \approx 10$

Contributions of Density Functional Theory (DFT)

- ▶ Improved comprehension: Focuses on quantities in the real, 3-dimensional coordinate space, i.e., density $n(r)$ of the ground state
- ▶ Practical contribution: computing time T rises much more moderately with increasing N ($T \sim N^\alpha$, $\alpha = 2, 3$)
 - ▶ DFT can handle systems with up to $N = \mathcal{O}(10^2) - \mathcal{O}(10^3)$ atoms

DFT Theory Background

- ▶ Kohn had been interested in disordered metallic alloys
- ▶ In a Cu – Zn alloy there is transfer of charge between Cu and Zn
- ▶ Electrostatic interaction energy of these charges are important part of the total energy
- ▶ Natural emphasis on the electron density distribution $n(r)$ due to given energetics of the system

Thomas Fermi (TF) Theory

- ▶ Crude theory of electronic energy in terms of $n(r)$
 - ▶ Existed since the 1920s
- ▶ Good for describing total energies of atoms
- ▶ Bad for questions of chemistry and materials science
 - ▶ Example: did not lead to any chemical binding
- ▶ Interesting feature: considered interacting electrons moving in an external potential $v(r)$

Thomas Fermi (TF) Theory

- ▶ Rough representation of the exact solution of the many-electron Schrödinger equation
- ▶ TF theory: expressed in terms of $n(r)$
- ▶ Schrödinger theory: expressed in terms of $\Psi(r_1, \dots, r_N)$

Question:

1. How does one establish a connection between the two theories?
2. Is a *complete*, exact description of the groundstate in terms of $n(r)$ possible in principle?
 - ▶ Requirement: $n(r)$ has to completely characterize the system

The Hohenberg-Kohn (HK) Formulation of DFT

Hypothesis: Knowledge of groundstate density of $n(r)$ for any electronic system uniquely determines the system.

Basic Lemma of Hohenberg-Kohn: The groundstate density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines this potential uniquely.

- ▶ *Uniquely* means up to an uninteresting additive constant
- ▶ Lemma is mathematically rigorous

The Hohenberg-Kohn Variational Principle

- ▶ Most important property of electronic groundstate is energy E
- ▶ Rayleigh-Ritz minimal principle:

$$E = \min_{\tilde{\Psi}} \langle \tilde{\Psi}, H \tilde{\Psi} \rangle \quad (2)$$

- ▶ Constrained energy minimum:

$$E_v[\tilde{n}(r)] = \int v(r)\tilde{n}(r) + F[\tilde{n}(r)] \quad (3)$$

Result: Seemingly trivial problem of finding minimum of $E_v[\tilde{n}(r)]$ with respect to 3-dimensional trial function $\tilde{n}(r)$ ($\tilde{\Psi}$ is $3N$ -dimensional)

The Universal Functional $F[\tilde{n}(r)]$

$$F[\tilde{n}(r)] = T_s[\tilde{n}(r)] + \frac{1}{2} \int \frac{\tilde{n}(r)\tilde{n}(r')}{|r - r'|} dr dr' + E_{xc}[\tilde{n}(r)] \quad (4)$$

- ▶ $E_{xc}[\tilde{n}(r)]$ is the exchange-correlation energy functional and is unknown

The Self Consistent Kohn-Sham Equations

- ▶ Hartree proposed a set of self consistent single particle equations for the approx. description of electronic structure of atoms
- ▶ Hartree equations describe atomic groundstates much better than TF theory
- ▶ Kohn extracted Hartree equations from the HK variational principle for the energy (with the help of Lu Sham)

The Self Consistent Kohn-Sham Equations

The groundstate energy is given by

$$E = \sum_j \epsilon_j + E_{xc}[\tilde{n}(r)] - \int v_{xc}(r)n(r)dv - \frac{1}{2} \int \frac{\tilde{n}(r)\tilde{n}(r')}{|r - r'|} drdr' \quad (5)$$

- ▶ $v_{xc}(r)$ is the exchange-correlation potential (derived from E_{xc})
- ▶ With exact E_{xc} and v_{xc} all many body effects are included

Approximation for $E_{xc}[\tilde{n}(r)]$

- ▶ DFT has been presented as a formal mathematical framework for viewing electronic structure from the perspective of $n(r)$
- ▶ Requires approximations for $F[n(r)]$ (HK) and for $E_{xc}[n(r)]$ (KS)
- ▶ Approximations reflect the physics of the electronic structure and come from outside of DFT

The Local Density Approximation (LDA)

$$E_{xc}^{LDA} = \int e_{xc}(n(r))n(r)dr \quad (6)$$

- ▶ Exchange-correlation energy of a uniform electron gas of density n
- ▶ Exact for uniform electron gas
- ▶ Fails for heavy fermion systems

Conclusion

- ▶ DFT referred to as standard model for periodic solids
- ▶ DFT complements traditional wave-function based methods in chemistry
- ▶ DFT works rather poorly for long range polarization energies, partially filled electronic shells and reaction barriers
- ▶ Accuracy of E_{xc} approximations dominates DFT



Walter Kohn.

Nobel lecture: Electronic structure of matter—wave functions and density functionals.

[Reviews of Modern Physics, 71\(5\):1253, 1999.](#)