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

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by Walter Kohn

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by Giuseppe Accaputo
Schrödinger’s Equation

\[ E\Psi = \hat{H}\Psi \]  \hspace{1cm} (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 $\Psi(r_1, \ldots, r_N)$

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:
  
  $$ E = \min_{\Psi} (\tilde{\Psi}, H\tilde{\Psi}) $$

- Constrained energy minimum:
  
  $$ E_v[\tilde{n}(r)] = \int v(r)\tilde{n}(r) + F[\tilde{n}(r)] $$

**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 $F[\tilde{n}(r)]$

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

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

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

(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)

\[ E_{xc}^{LDA} = \int e_{xc}(n(r))n(r)\,dr \]  

- 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.