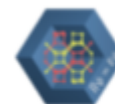




САМАРСКИЙ УНИВЕРСИТЕТ
SAMARA UNIVERSITY



Samara Center
for Theoretical Materials Science

Density Functional Theory: Foundations and Possibilities

Alexander F. Krutov

Samara Center for Theoretical Material Science
Samara University, Samara State Technical University,
Samara, Russia

Particle in the field of force

Nonrelativistic Schrodinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

$$\psi(\vec{r}, t)$$

is wave function of particle;

$$\hat{H}$$

is full energy operator of particle in field (Hamiltonian);

$$\hbar = h/2\pi \quad h$$

is Planck's constant.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}, t)$$

$V(\vec{r}, t)$ is interaction operator for the particle in field;

m is mass of particle.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Detection probability of particle in the volume dV :

$$dP = |\psi(\vec{r}, t)|^2 dV$$

**The average value of physical observable \hat{A}
in the state $\psi(\vec{r}, t)$:**

$$\langle A \rangle = \int \psi^*(\vec{r}, t) \hat{A} \psi(\vec{r}, t) dV$$

The average value of energy:

$$\langle E \rangle = \int \psi^*(\vec{r}, t) \hat{H} \psi(\vec{r}, t) dV$$

In the case when $V(\vec{r}, t) \equiv V(\vec{r})$:

$$\psi(\vec{r}, t) = e^{-\frac{i}{\hbar} E t} \psi(\vec{r})$$

Stationary Schrodinger equation:

$$\hat{H} \psi(\vec{r}) = E \psi(\vec{r})$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})$$

E

is eigenvalue of Hamiltonian in the state $\psi(\vec{r})$

Methods of solution of the Schrodinger equation

1. Methods of theory of the differential equations in partial derivatives.

$$V(\vec{r}) = \frac{e^2}{|\vec{r}|}, \quad V(\vec{r}) = \frac{\omega r^2}{2}, \dots$$

2. Perturbation theory.

$$V(\vec{r}) = V_0(\vec{r}) + \varepsilon v(\vec{r}), \quad \varepsilon \ll 1$$

The solution for $V_0(\vec{r})$ is known.

$$\psi(\vec{r}) = \sum_n \varepsilon^n \psi_n(\vec{r}), \quad E = \sum_n \varepsilon^n E_n$$

Methods of solution of the Schrodinger equation

3. Variational method.

$$E[\psi] = \int \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) dV$$

$$\int \psi^*(\vec{r}) \psi(\vec{r}) dV = 1$$

Variational principle.

$$\delta E[\psi] = 0 \quad \Rightarrow \quad \text{stationary Schrodinger equation}$$

$E[\psi]$ has minimum at the true solution of the Schrodinger equation.

$$\tilde{\psi}(\vec{r}, \alpha_i)$$

is test function;

$$\frac{\partial E[\tilde{\psi}]}{\partial \alpha_i} = 0, \quad i = 1, 2, \dots$$

Systems of many electrons

The Born-Oppenheimer approximation

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i,j} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\vec{R}_j, \quad Z_j$$

are positions and atom numbers of nuclei $j = 1, 2, \dots, N_A$

$$\Psi = \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_A})$$

Systems of many electrons

The Pauli principle:

$$\hat{P}_{ij}\Psi = -\Psi$$

Hartree-Fock approximation

The Slater determinant:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N) =$$

$$= \frac{1}{\sqrt{N!}} \det[\psi_j(\vec{r}_i, \sigma_i)]$$

The functional of energy for the electron system

$$E[\Psi] = \sum_{i,\sigma_i} \int d^3r \psi_{i\sigma_i}^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(\vec{r}) \right) \psi_{i\sigma_i}(\vec{r}) +$$
$$+\frac{1}{2} \sum_{i,j,\sigma_i,\sigma_j} \int d^3r d^3r' \psi_{i\sigma_i}^*(\vec{r}) \psi_{j\sigma_j}^*(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \psi_{j\sigma_j}(\vec{r}') \psi_{i\sigma_i}(\vec{r}) -$$
$$-\frac{1}{2} \sum_{i,j,\sigma_i} \int d^3r d^3r' \psi_{i\sigma_i}^*(\vec{r}) \psi_{j\sigma_i}^*(\vec{r}') \frac{e^2}{|\vec{r} - \vec{r}'|} \psi_{i\sigma_i}(\vec{r}') \psi_{j\sigma_i}(\vec{r})$$

Variational principle:

$$\delta E[\Psi] = 0 \Rightarrow$$

One-particle Schrodinger equation for

$$\psi_{i\sigma_i}(\vec{r})$$

Principal difficulties of the theory of the many-electron systems

Exponential wall (without spin and symmetries)

p is number of parameters per one of degrees of freedom;

M is number of parameters in wave function for desired accuracy;

$$3 \leq p \leq 10$$

$$M = p^{3N}, \quad N_{max} = \frac{1}{3} \cdot \frac{\ln M_{max}}{\ln p}$$

$$M \approx 10^9, \quad p = 3 \quad N_{max} \approx 6$$

$$N = 100 \quad p = 3, \quad M \approx 10^{150}$$

Van Fleck catastrophe

N_M is number of weak interacting molecules;

n is number of electrons per molecule with
 $\Psi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$

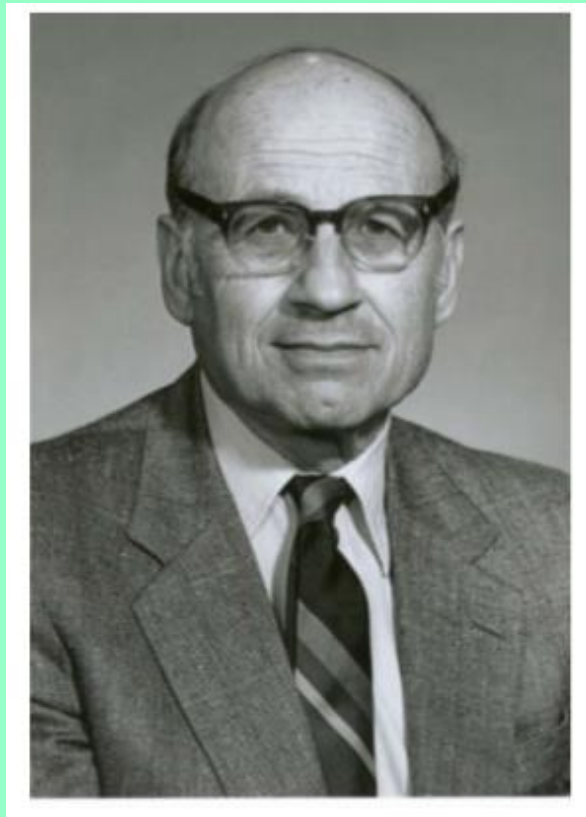
$\tilde{\Psi}_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$ is test function;

$$\langle \Psi_i, \tilde{\Psi}_i \rangle = 1 - \varepsilon, \quad \varepsilon = 10^{-2}$$

$$N_M = 100, \quad n = 1000 \quad \langle \Psi, \tilde{\Psi} \rangle = (1 - \varepsilon)^{N_M} \approx e^{-\varepsilon N_M} \approx 0.37$$

$$N_M = 1000, \quad n = 10^4 \quad \langle \Psi, \tilde{\Psi} \rangle \approx e^{-\varepsilon N_M} \approx 5 \cdot 10^{-5}$$

Density Functional Theory



Walter Kohn
Nobel Prize in Chemistry 1998

$$\Psi = \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N) \Rightarrow n(\vec{r})$$

The electron density:

$$n(\vec{r}) = N \sum_{\sigma} \int d^3r_2 \dots d^3r_N \times \\ \times \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N) \times \\ \times \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N)$$

The Hohenberg-Kohn Theorems

1. The ground-state density $n(\vec{r})$ of system of interaction electron in some external potential $V_{ext}(\vec{r})$ determines this potential unique (up to unessential constant).
2. For any external potential $V_{ext}(\vec{r})$ there exist the universal functional $E_{HK}[n]$ and minimum of this functional take place at electron density of ground state.

$$E_{HK}[n] = T[n] + E_{int}[n] + \int d^3r V_{ext}(\vec{r})n(\vec{r})$$

$T[n]$ is functional of kinetic energy;

$E_{int}[n]$ is functional of interaction energy of electrons.

The Kohn-Sham Approach

1. Original system of interacting with each other electrons with ground state density $n(\vec{r})$ is replaced by system of noninteracting electrons moving in effective potential with the same electron density $n(\vec{r})$.
2. Effective local potential contains the external potential and electron interaction taking into account exchange and correlation energies.

$$E_{KS}[n] = T_S[n] + V_H[n] + V_{ext}[n] + V_{XC}[n]$$

The Kohn-Sham equation

$$\delta E_{KS}[n] = 0$$

$$\begin{aligned} & -\frac{1}{2}\nabla^2\psi_{i\sigma}(\vec{r}) + \\ & + (V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r}))\psi_{i\sigma}(\vec{r}) = \\ & = \varepsilon_{i\sigma}\psi_{i\sigma}(\vec{r}) \end{aligned}$$

$$V_H(\vec{r}) = \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$n(\vec{r}) = \sum_{i\sigma} |\psi_{i\sigma}(\vec{r})|^2$$

Exchange-correlation potential for uniform electron gas

Local-density approximation

$$V_{XC}[n] = \int d^3r \tilde{V}_{xc}(n(\vec{r}))n(\vec{r})$$

Exchange potential:

$$\tilde{V}_x(n(\vec{r})) = -0.458 \left(\frac{3}{4\pi n(\vec{r})} \right)^{-1/3}$$

Correlation potential:

$$\tilde{V}_c(n(\vec{r})) = -\frac{0.44}{7.8 + \left(\frac{3}{4\pi n(\vec{r})} \right)^{1/3}}$$

Exchange-correlation potential for uniform electron gas

Interpolation for exchange-correlation potential:

$$\tilde{V}_{xc}(n(\vec{r})) = -1.272 \left(\frac{3}{4\pi n(\vec{r})} \right)^{-1/3} - 0.066 \ln \left(1 + 11.4 \left(\frac{3}{4\pi n(\vec{r})} \right)^{-1/3} \right)$$

The Kohn-Shame scheme

1. Selection of initial guess for $n(\vec{r})$;

2. Calculation of

$$\tilde{V}_H(\vec{r}) , \quad \tilde{V}_{xc}(\vec{r}) , \quad V_{ext}(\vec{r})$$

3. Solution of Kohn-Shame equation

$$\psi_{i\sigma}(\vec{r}) \quad \epsilon_{i\sigma}$$

4. Calculation of new electron density

$$n(\vec{r}) = \sum_{i\sigma} |\psi_{i\sigma}(\vec{r})|^2$$

5. Iterations up to desired accuracy.

Development of the Density Functional Theory

1. More accurate calculations of the exchange-correlation potential
2. Generalized gradient approximation;

$$V_{XC}[n] = V_{XC}^{LDA}[n] + \int d^3r f\left(n(\vec{r}), \vec{\nabla}n(\vec{r})\right) n(\vec{r})$$

3. Generalization on spin-density $n_{\uparrow}(\vec{r})$, $n_{\downarrow}(\vec{r})$

4. Generalization on time-dependent interaction (TDDFT);

Development of the Density Functional Theory

5. Generalization on region $T > 0$;

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{kT}\right) + 1}$$

6. Consideration of thermodynamics of ion subsystem;

7. Calculations of thermodynamics potentials: free energy, grand potential, entropy and so on.

Calculations of physical values in DFT

1. Calculations of systems with small number of electrons
e.g. ionization potential for *He*, *Li*, *Be* ;
2. Heat conductivity;
3. Electron-phonon coupling;
4. Complex dielectric constant;
5. Thermal expansion coefficient;
6. Electrical conductivity;
- ...

Thanks for attention !