

# *Ab initio* methods in solid state physics

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February 25, 2021

# *Ab initio* methods

*Ab initio* is a Latin term meaning "from the beginning".

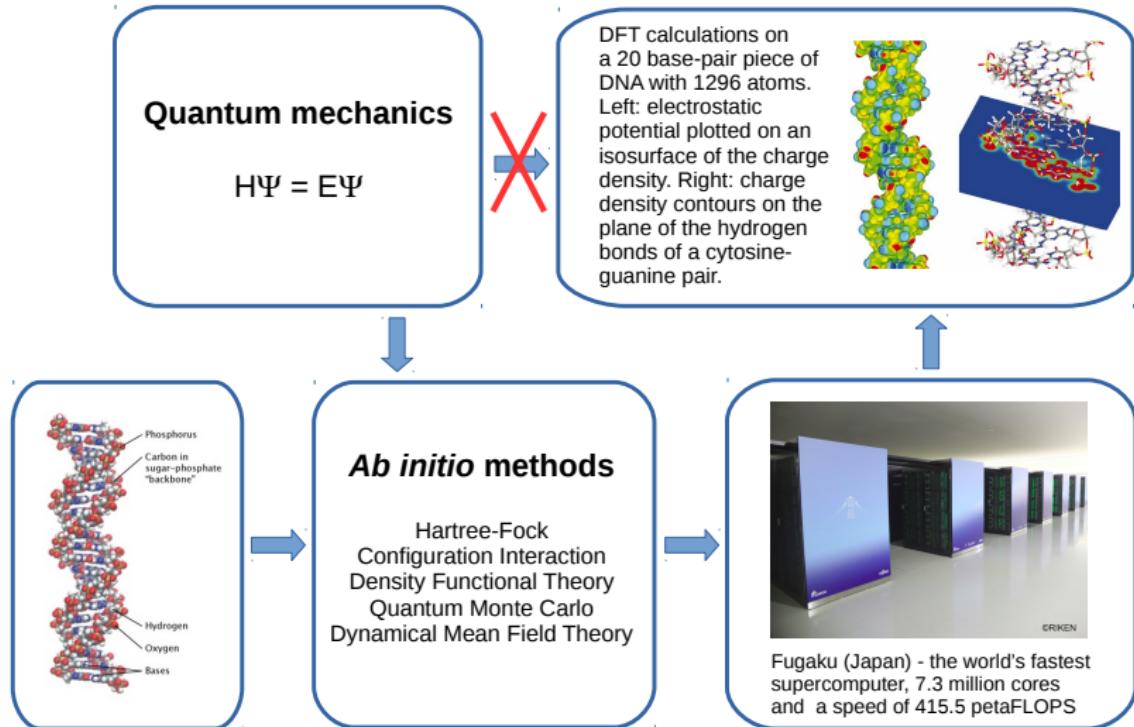
*Ab initio* or first-principles methods are the computational techniques based on the fundamental laws of quantum mechanics and statistical physics.



P. A. M. Dirac, Proc. Roy. Soc. A 123, 714 (1929)

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. **It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed**, which can lead to an explanation of the main features of complex atomic systems without too much computation.

# *Ab initio* methods



# Historical overview

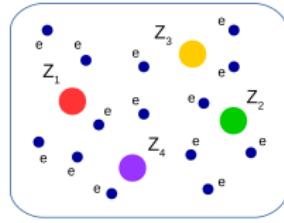
- 1925 – Pauli exclusion principle
- 1926 – Schrödinger equation
- 1926 – Fermi-Dirac statistics
- 1927 – Thomas-Fermi model
- 1928 – Dirac equation
- 1928 – Bloch states in crystals
- 1928,1930 – Hartree-Fock (HF) approximation
- 1937 – Augmented plane wave (APW) method
- 1937,1939 – Hellmann-Feynman theorem
- 1940 – Orthogonalized plane wave (OPW) method
- 1947,1954 – Korringa-Kohn-Rostocker (KKR) method
- 1954,1959 – Pseudopotential method
- 1950 – Configuration interaction (CI) method
- 1964,1965 – Density functional theory (DFT)
- 1975 – Linearized augmented plane wave (LAPW) method
- 1991 – LDA+U method
- 1993 – Hybrid functionals
- 1994 – Projector augmented-wave (PAW) method

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- 1 Electron interactions – theoretical background
- 2 Density functional theory
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# Basic Hamiltonian for interacting electrons and nuclei

Any system of electrons and nuclei such as a molecule or a solid can be described by the Hamiltonian



$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,j} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 - \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|}, \quad (1)$$

where  $\mathbf{r}_i$  define positions of electrons,  $\mathbf{R}_j$  are positions of nuclei,  $Z_j$  are atomic numbers,  $M_j$  are masses of nuclei, and  $m_e$  is the mass of electron.

The wave functions of the whole system  $\Psi(\mathbf{r}_i, \mathbf{R}_j)$  is the solution of the Schrödinger equation

$$H\Psi(\mathbf{r}_i, \sigma_i; \mathbf{R}_j) = E\Psi(\mathbf{r}_i, \sigma_i; \mathbf{R}_j), \quad (2)$$

where  $\sigma_i = \uparrow, \downarrow$  is the direction of spin and  $E$  is the total energy of the system.

# Born-Oppenheimer (adiabatic) approximation

M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927)

Nucleus mass is much larger than electron mass ( $m_p/m_e = 1836$ ). Since nuclei move much slower than electrons, we can assume that electronic states change adiabatically with the movement of atoms. In the Born-Oppenheimer (BO) approximation, the wave function is written as the product of an electronic and a nuclear part

$$\Psi(\mathbf{r}_i, \sigma_i; \mathbf{R}_j) = \Phi(\mathbf{r}_i, \sigma_i) \xi(\mathbf{R}_j), \quad (3)$$

and the Schrödinger equation can be separated into two equations

$$(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i,j} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}) \Phi(\mathbf{r}_i, \sigma_i) = E_n(\mathbf{R}_j) \Phi(\mathbf{r}_i, \sigma_i) \quad (4)$$

$$(-\sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 - \sum_{i,j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} + E_n(\mathbf{R}_j)) \xi(\mathbf{R}_j) = \varepsilon_n \xi(\mathbf{R}_j). \quad (5)$$

# Wave function

$\Phi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N)$  -  $N$ -electron wave function.

The electron wave function is **antisymmetric** – the exchange of two electrons  $\mathbf{r}_i\sigma_i \leftrightarrow \mathbf{r}_j\sigma_j$  changes its sign

$$\Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_i\sigma_i, \dots, \mathbf{r}_j\sigma_j, \dots, \mathbf{r}_N\sigma_N) = -\Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_j\sigma_j, \dots, \mathbf{r}_i\sigma_i, \dots, \mathbf{r}_N\sigma_N). \quad (6)$$

It is a consequence of the Pauli principle, which says that two fermions with the same quantum numbers cannot be placed in the same quantum state.

The electron density at point  $\mathbf{r}$  is given by the formula

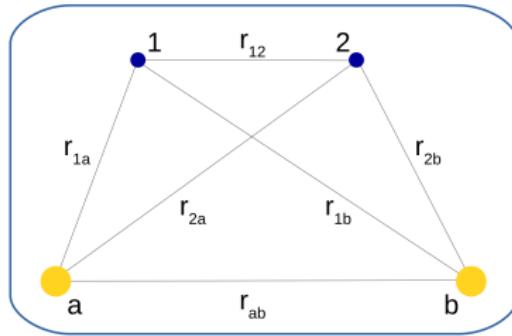
$$n(\mathbf{r}) = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N |\Phi^*(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N)|^2. \quad (7)$$

# Hydrogen molecule H<sub>2</sub>

Accurate numerical solutions of the Schrödinger equation can be obtained only for atoms and small molecules. As an example we can consider the hydrogen molecule H<sub>2</sub> described by the Hamiltonian in the BO approximation

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{2b}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{ab}}, \quad (8)$$

where  $r_{1a}$ ,  $r_{1b}$ ,  $r_{2a}$ ,  $r_{1b}$  are distances between electrons (1 i 2) and protons (a i b),  $r_{12}$  is the distance between electrons, and  $r_{ab}$  is the distance between protons.



# Hydrogen molecule H<sub>2</sub>

W. Heitler and F. London, Zeitschrift für Physik **44**, 455 (1927)

Heitler and London proposed the wave function in the form

$$\Phi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \Psi_{S,A}(\mathbf{r}_1, \mathbf{r}_2)\chi_\sigma, \quad (9)$$

$$\Psi_S(\mathbf{r}_1, \mathbf{r}_2) = N[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)], \quad (10)$$

$$\Psi_A(\mathbf{r}_1, \mathbf{r}_2) = N[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)], \quad (11)$$

where  $N$  is normalization factor,  $\chi_\sigma$  is the spin part of the wave function, and  $\psi_\alpha(\mathbf{r})$  are the 1s orbitals of the hydrogen atom

$$\psi_\alpha(\mathbf{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{|\mathbf{r}-\mathbf{R}_\alpha|}{a_0}}, \quad (12)$$

where  $a_0$  is Bohr radius and  $\mathbf{R}_\alpha$  are positions of protons  $\alpha = a$  or  $b$ .

# Hydrogen molecule H<sub>2</sub>

Singlet state ( $S = 0$ )  $\Phi_S(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \Psi_S(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$  (13)



Triplet state ( $S = 1$ )  $\Phi_T(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \Psi_A(\mathbf{r}_1, \mathbf{r}_2) \begin{cases} |\uparrow\uparrow\rangle & (S_z = 1) \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & (S_z = 0) \\ |\downarrow\downarrow\rangle & (S_z = -1) \end{cases}$  (14)



# Hydrogen molecule H<sub>2</sub>

Ground state energy

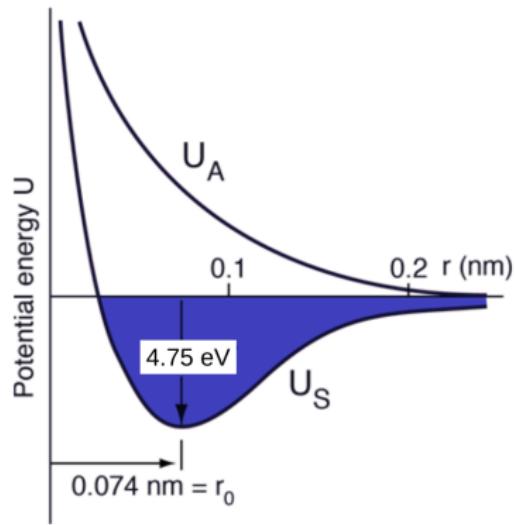
$$E_S(r_{ab}) = \langle \Phi_S | H | \Phi_S \rangle = \min$$

$$r_{ab} = 0.87 \text{ \AA} = 0.087 \text{ nm}$$

Binding energy

$$E_{\text{bind}} = 2E(\text{H}) - E(\text{H}_2) = 3.14 \text{ eV}$$

$$U = -E_{\text{bind}}$$



This is the **covalent bond**, in which the hydrogen atoms share two electrons in the single state (bonding state), thus lowering the total energy in comparison to the energy of two separate atoms. In contrast, the electrons in the triplet state do not create the bound state of hydrogen atoms (anti-bonding state).

## Hydrogen molecule H<sub>2</sub>

The best results were obtained within the variational method, in which the space part of the wave function is written in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^M c_i \psi_i(\mathbf{r}_1, \mathbf{r}_2) \quad (15)$$

where the coefficients  $c_i$  are determined by the minimization of the total energy.

W. Kołos and L. Wolniewicz, J. Phys. Chem. **41**, 3663 (1964)

Using the wave function expanded into 54 terms they obtained:

$$r_{ab} = 0.74141 \text{ \AA} \text{ (exp. } 0.74158 \text{ \AA)}$$

$$E_{\text{bind}} = 4.7482375 \text{ eV} \text{ (exp. } 4.7477168 \text{ eV)}$$

# Hartree approximation

D. Hartree, Proc. Cambridge Philos. Soc. **24**, 89 (1928)

The electronic Hamiltonian of  $N$ -electron system ( $e = 1$ )

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i,j} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (16)$$

The  $N$ -electron wave function is written as the product of one-electron orbitals

$$\Phi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N) = \psi_1^{\sigma_1}(\mathbf{r}_1)\psi_2^{\sigma_2}(\mathbf{r}_2)\dots\psi_N^{\sigma_N}(\mathbf{r}_N), \quad (17)$$

and electron density is given by the formula

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) = \sum_{i,\sigma} |\psi_i^{\sigma}(\mathbf{r})|^2. \quad (18)$$

# Hartree approximation

The total energy is calculated as the expectation value of the Hamiltonian

$$E = \langle \Phi | H | \Phi \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \Phi^* H \Phi = E_k + E_Z + E_H, \quad (19)$$

where kinetic energy is given as

$$E_k = - \sum_{i,\sigma} \int d\mathbf{r} \psi_i^{\sigma*}(\mathbf{r}) \frac{\hbar^2}{2m_e} \nabla_i^2 \psi_i^{\sigma}(\mathbf{r}). \quad (20)$$

Interaction between electrons and nuclei

$$E_Z = \sum_j \int d\mathbf{r} \frac{Z_j n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_j|}. \quad (21)$$

Hartree interaction – direct Coulomb interaction

$$E_H = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (22)$$

# Hartree equation

From the variational principle

$$\frac{\delta}{\delta \psi^{\sigma*}} [\langle \Phi | H | \Phi \rangle - \sum_i \varepsilon_i \sum_{\sigma} \int d\mathbf{r} |\psi_i^{\sigma}(\mathbf{r})|^2] = 0, \quad (23)$$

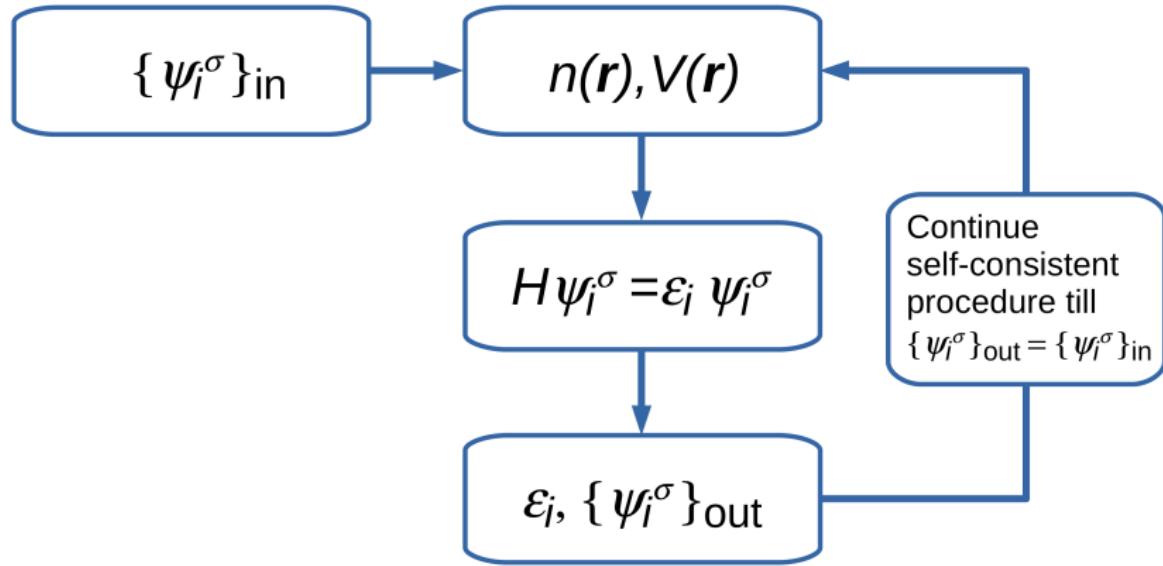
we obtain the Hartree equation

$$[-\frac{\hbar^2 \nabla_i^2}{2m_e} + V(\mathbf{r})] \psi_i^{\sigma}(\mathbf{r}) = \varepsilon_i \psi_i^{\sigma}(\mathbf{r}), \quad (24)$$

with the effective potential

$$V(\mathbf{r}) = V_Z(\mathbf{r}) + V_H(\mathbf{r}) = \sum_j \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (25)$$

# Self-consistent field method



# Hartree-Fock approximation

V. Fock, Z. Physik **61**, 126 (1930)

J. C. Slater, Phys. Rev. **35**, 210 (1930)

P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930)

In the Hartree-Fock (HF) approach, the  $N$ -electron wave function is written in the form of the Slater determinant

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \phi_2(\mathbf{r}_1, \sigma_1) & \dots & \phi_N(\mathbf{r}_1, \sigma_1) \\ \phi_1(\mathbf{r}_2, \sigma_2) & \phi_2(\mathbf{r}_2, \sigma_2) & \dots & \phi_N(\mathbf{r}_2, \sigma_2) \\ \dots & \dots & \dots & \dots \\ \phi_1(\mathbf{r}_N, \sigma_N) & \phi_2(\mathbf{r}_N, \sigma_N) & \dots & \phi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix}, \quad (26)$$

where

$$\phi_i(\mathbf{r}_i, \sigma_i) = \psi_i^\sigma(\mathbf{r}_i) \chi_i(\sigma). \quad (27)$$

The total energy in the HF approximation is

$$E = \langle \Phi | H | \Phi \rangle = E_k + E_Z + E_H + E_x. \quad (28)$$

# Exchange interaction

Exchange interaction is a quantum phenomenon that only occurs between identical particles and with the same direction of spins

$$E_x = -\frac{1}{2} \sum_{i,j,\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\psi_i^{\sigma*}(\mathbf{r}_1) \psi_j^{\sigma*}(\mathbf{r}_2) \psi_i^{\sigma}(\mathbf{r}_2) \psi_j^{\sigma}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (29)$$

This interaction is directly related to the Pauli exclusion principle – it increases the average distance between electrons and reduces the Coulomb repulsion energy.

Using the spin density matrix

$$\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \psi_i^{\sigma*}(\mathbf{r}_1) \psi_i^{\sigma}(\mathbf{r}_2), \quad (30)$$

the exchange energy can be written in the form

$$E_x = -\frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{|\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (31)$$

# Hartree-Fock equation

From the variational principle

$$\frac{\delta}{\delta \psi^{\sigma*}} [\langle \Phi | H | \Phi \rangle - \sum_i \varepsilon_i \sum_{\sigma} \int d\mathbf{r} |\psi_i^{\sigma}(\mathbf{r})|^2] = 0, \quad (32)$$

we obtain the Hartree-Focka equation

$$\boxed{[-\frac{\hbar^2 \nabla_i^2}{2m_e} + V(\mathbf{r})]\psi_i^{\sigma}(\mathbf{r}) - \frac{1}{2} \sum_{j,\sigma} \int d\mathbf{r}' \frac{\psi_j^{\sigma*}(\mathbf{r}') \psi_i^{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_j^{\sigma}(\mathbf{r}) = \varepsilon_i \psi_i^{\sigma}(\mathbf{r})} \quad (33)$$

where

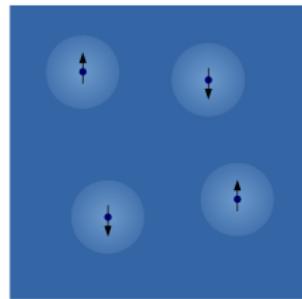
$$V(\mathbf{r}) = \sum_j \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (34)$$

# Exchange hole

Slater proposed [Phys. Rev. **81**, 385 (1951)] to transform the HF equation to one-electron form

$$[-\frac{\hbar^2}{2m}\nabla_i^2 + V_i(\mathbf{r})]\psi_i^\sigma(\mathbf{r}) = \varepsilon_i\psi_i^\sigma(\mathbf{r}), \quad (35)$$

with the effective potential



$$V_i(\mathbf{r}) = V_Z(\mathbf{r}) + V_H(\mathbf{r}) - \frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (36)$$

where  $n(\mathbf{r}, \mathbf{r}')$  is called the exchange charge

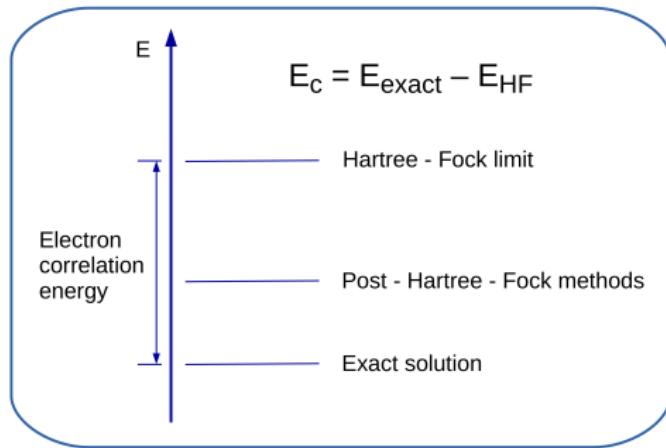
$$n(\mathbf{r}, \mathbf{r}') = \sum_{j,\sigma} \frac{\psi_j^{\sigma*}(\mathbf{r}')\psi_i^\sigma(\mathbf{r}')\psi_j^\sigma(\mathbf{r})}{\psi_i^\sigma(\mathbf{r})}. \quad (37)$$

Effectively, each electron interacts with the exchange hole of the positive charge, which equals to elementary charge, as can be seen by integration  $n(\mathbf{r}, \mathbf{r}')$  over  $\mathbf{r}'$

$$q = \sum_{j,\sigma} \left[ \int d\mathbf{r}' \psi_j^{\sigma*}(\mathbf{r}')\psi_i^\sigma(\mathbf{r}') \right] \frac{\psi_j^\sigma(\mathbf{r})}{\psi_i^\sigma(\mathbf{r})} = \sum_{j,\sigma} \delta_{ij} \frac{\psi_j^\sigma(\mathbf{r})}{\psi_i^\sigma(\mathbf{r})} = 1. \quad (38)$$

# Electron correlations

Electron correlations result from the Coulomb repulsion between electrons. The HF approximation replaces this instantaneous electron-electron interaction with the repulsion of each electron with an average electron charge cloud. HF partially includes correlations between electrons with the same directions of spins, but electrons with the opposite directions of spins are uncorrelated. The difference between the exact ground state energy and the lowest energy obtained in the HF appoximation is called correlation energy.



# Post-Hartree-Fock methods

The wave function of the  $N$ -electron system can be written in the form of expansion into Slater determinants

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = c_0 \Phi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) + \sum_{i=1}^{N_{\text{det}}} c_i \Phi_i(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (39)$$

where  $\Phi_0$  is the ground state wave function in the HF approximation, and  $\Phi_i$  are the determinants corresponding to excited states. The larger number of determinants  $N_{\text{det}}$  the more accurate electron correlations are described.  $\Phi_i$  are constructed with the one-electron orbitals, which are empty in the HF ground state, and can be occupied by excited electrons.

Determinants can describe the single electron transitions to empty states ( $\Phi_i^S$ ), double excitations ( $\Phi_i^D$ ), triple excitations ( $\Phi_i^T$ ), etc.

The total number of all excited configurations grows rapidly with the number of electrons  $N$  and orbitals  $M$  (empty and occupied), according the formula

$$N_{\text{det}} = \frac{(M+1)!}{N!(M+1-N)!}. \quad (40)$$

# Configuration interaction

In the configuration interaction (CI) method, determinants are constructed from the occupied and empty orbitals obtained within the HF approximation.

The wave functions is written as expansion of determinants with the increasing number of excited electrons

$$\Phi_{\text{CI}} = c_0 \Phi_0 + \sum_{i=1}^{N_s} c_i^S \Phi_i^S + \sum_{i=1}^{N_D} c_i^D \Phi_i^D + \sum_{i=1}^{N_T} c_i^T \Phi_i^T + \dots \quad (41)$$

The ground state is found by the minimization of the total energy

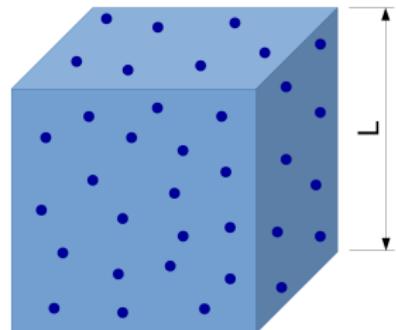
$$E_{\text{CI}} = \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \Phi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) H \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \min, \quad (42)$$

with respect to coefficients  $c_i$ , which fulfill the constrain  $\sum_i c_i^2 = 1$ .

In the limit of infinite number of determinants, we can obtain the exact wave function. In practice, only the largest terms are included in the expansion.

The computation time scales exponentially with  $N$ , therefore the CI and other post-HF methods are used mainly for molecules.

# Free-electron gas



$N$  noninteracting electrons in the box  $V = L^3$ .

By imposing the period boundary conditions  $\psi_k(0) = \psi_k(L)$  and wavelengths must fulfil the condition  $n\lambda = L$ , which leads to quantization of wave vectors along the  $x$ ,  $y$ , and  $z$  directions

$$\mathbf{k} = \left( \frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right). \quad (43)$$

Energies and wave functions are obtained by solving the Schrödinger equation

$$-\frac{\hbar^2}{2m_e} \nabla_i^2(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}), \quad (44)$$

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m_e}, \quad (45)$$

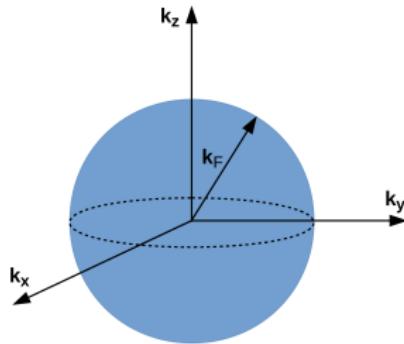
$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (46)$$

# Free-electron gas

We consider unpolarized magnetically electron gas with  $N_{\uparrow} = N_{\downarrow} = \frac{1}{2}N$ . At  $T = 0$  K electrons occupy the energy levels up to Fermi energy  $E_F$  and the total energy is equal to

$$E = 2 \sum_{k < k_F} \varepsilon_k = \frac{2V}{(2\pi)^3} \int d\mathbf{k} \frac{\hbar^2 k^2}{2m_e} = \frac{V}{(2\pi)^3} \frac{4\pi\hbar^2}{5m_e} k_F^5, \quad (47)$$

where  $(2\pi)^3/V$  is the volume corresponding to one quantum state in the  $\mathbf{k}$ -space.



$k_F$  is the Fermi wave vector – the radius of the sphere in the reciprocal space, which contains the states occupied by  $N$  electrons

$$N = \frac{2V}{(2\pi)^3} \int d\mathbf{k} = \frac{2V}{(2\pi)^3} \frac{4\pi}{3} k_F^3. \quad (48)$$

# Free-electron gas

Dividing (47) by (48) we get the average energy of one electron

$$\frac{E}{N} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} = \frac{3}{5} \varepsilon_F. \quad (49)$$

The electron density is given by

$$n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}, \quad (50)$$

and the volume of a sphere per one electron

$$V_s = \frac{4\pi}{3} r_s^3 = \frac{1}{n}, \quad (51)$$

where  $r_s$  is its radius

$$r_s = \left( \frac{3}{4\pi n} \right)^{1/3} \quad (52)$$

$$r_s \rightarrow 0 \quad \text{high-density gas} \quad (53)$$

$$r_s \rightarrow \infty \quad \text{low-density gas}$$

# Density of states

The number of states in the range  $[0, k]$

$$N_k = \frac{V}{3\pi^2} k^3, \quad (54)$$

and the number of state in the range  $[k, k + dk]$

$$dN_k = \frac{V}{\pi^2} k^2 dk. \quad (55)$$

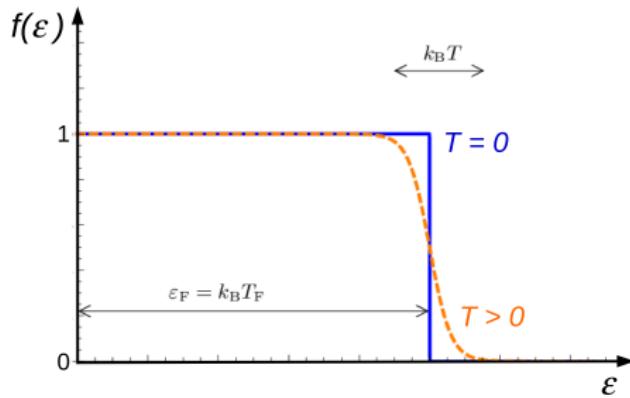
From  $\varepsilon = \frac{\hbar^2 k^2}{2m_e}$  we get

$$dk = \frac{1}{2} \sqrt{\frac{2m_e}{\hbar^2 \varepsilon}} d\varepsilon. \quad (56)$$

Using (55) and (56), we obtain the electron density of states

$$\rho(\varepsilon) = \frac{dN_k}{d\varepsilon} = \frac{V}{2\pi^2} \sqrt{\frac{2m_e \varepsilon}{\hbar^2}}. \quad (57)$$

# Fermi-Dirac statistics



$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \quad (58)$$

The internal energy of the electron gas can be calculated from the formula

$$U(T) = 2 \int_0^{\mu} d\varepsilon \rho(\varepsilon) \varepsilon f(\varepsilon), \quad (59)$$

from which the heat capacity at low temperatures can be obtained

$$C_V = \frac{\partial U}{\partial T} = \frac{2\pi^2}{3} k_B^2 \rho(\varepsilon_F) T = \gamma T. \quad (60)$$

# Electron gas – Hartree-Fock approximation

We assume that the positive charge is distributed homogeneously in the whole space and its density is the same as density of electron  $n$ . The interaction of electrons with such field cancels with the Hartree energy, therefore the total energy consists only of kinetic and exchange energy.

The exchange energy can be calculated using the Fourier transform of the Coulomb potential

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = 4\pi \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{q^2}, \quad (61)$$

Using the plane waves, after integration over  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , we get

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} - \int_{k' < k_F} \frac{d\mathbf{k}'}{(2\pi)^3} \frac{4\pi}{|\mathbf{k} - \mathbf{k}'|^2} = \frac{\hbar^2 k^2}{2m} - \frac{k_F}{\pi} \left(1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right). \quad (62)$$

The total energy is obtained by summation over  $\mathbf{k}$  vectors

$$E = \sum_{k < k_F} \left[ \frac{\hbar^2 k^2}{2m} - \frac{k_F}{\pi} \left(1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right) \right]. \quad (63)$$

# Electron gas – Hartree-Fock approximation

Replacing summation in second term by integration, we get

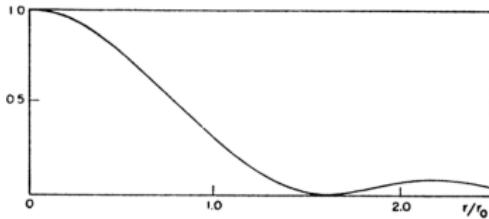
$$E = N \left( \frac{3}{5} E_F - \frac{3k_F}{4\pi} \right) = N \left[ \frac{3}{5} E_F - \frac{3(3\pi^2 n)^{\frac{1}{3}}}{4\pi} \right]. \quad (64)$$

The exchange energy per one electron is equal

$$\varepsilon_x = \frac{E_x}{N} = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{1}{3}}. \quad (65)$$

This formula is used in the local density approximation (LDA).

Exchange charge density as a function of  $r/r_0$  ( $\frac{4}{3}\pi r_0^3 n_\sigma = 1$ )



$$g_x^\sigma(r) = 1 - \left[ 3 \frac{\sin(rk_F) - rk_F \cos(rk_F)}{(rk_F)^3} \right]^2. \quad (66)$$

## Electron gas – electron correlations

It is not possible to obtain the exact analytical formula for the correlation energy of the electron gas.

Wigner proposed the approximate equation [Phys. Rev. **46**, 1002 (1934)]

$$\varepsilon_c(r_s) = -\frac{0.44}{r_s + 7.8}. \quad (67)$$

In the limit of low density ( $r_s \rightarrow \infty$ ), electrons may create the Wigner crystal.

In the limit of high density ( $r_s \rightarrow 0$ ), Gellmann and Breuckner obtained the correlation energy of the unpolarized electron gas [Phys. Rev. **106**, 364 (1957)]

$$\varepsilon_c(r_s) = 0.311 \ln(r_s) + r_s(A \ln(r_s) + C) - 0.048 + \dots \quad (68)$$

The most accurate values of correlation energy were obtained numerically using the Quantum Monte Carlo method:

D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).