

Lecture on First-principles Computation (2): The Hartree-Fock theory and the homogeneous electron gas

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Recall: the Hartree approximation

$$E = \sum_{n=1}^N \left\langle \varphi_n \left| -\frac{\nabla^2}{2m} \right| \varphi_n \right\rangle + \frac{1}{2} \sum_{m \neq n}^N \iint d\mathbf{r} d\mathbf{r}' \frac{|\varphi_n(\mathbf{r})|^2 |\varphi_m(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

$$n(\mathbf{r}) = \sum_{n=1}^N |\varphi_n(\mathbf{r})|^2 = \sum_{n=1}^N \varphi_n^*(\mathbf{r}) \varphi_n(\mathbf{r})$$

Minimizing $E = E[\varphi_n]$ with respect to $\varphi_n^*(\mathbf{r})$ under the constraint that $\langle \varphi_n | \varphi_n \rangle = 1$,

$$\frac{\delta}{\delta \varphi_n^*} \{E[\varphi_n] - \epsilon_n [\langle \varphi_n | \varphi_n \rangle - 1]\} = 0$$

one obtains the Hartree equation:

$$\left[-\frac{\nabla^2}{2m} + \sum_{m \neq n}^N \int d\mathbf{r}' \frac{|\varphi_m(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + v_{ext}(\mathbf{r}) \right] \varphi_n(\mathbf{r}) = \epsilon_n \varphi_n(\mathbf{r})$$

The Hartree equation

$$\left[-\frac{\nabla^2}{2m} + \sum_{m \neq n}^N \int d\mathbf{r}' \frac{|\varphi_m(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + v_{ext}(\mathbf{r}) \right] \varphi_n(\mathbf{r}) = \epsilon_n \varphi_n(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{n=1}^N |\varphi_n(\mathbf{r})|^2$$

Thus the Hartree equation can also be expressed as:

$$\left[-\frac{\nabla^2}{2m} + \int d\mathbf{r}' \frac{n(\mathbf{r}') - |\varphi_n(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + v_{ext}(\mathbf{r}) \right] \varphi_n(\mathbf{r}) = \epsilon_n \varphi_n(\mathbf{r})$$

The original Hartree approximation excludes **the self-interaction term**

Nowadays, the Hartree approximation is understood as

$$\left[-\frac{\nabla^2}{2m} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{ext}(\mathbf{r}) \right] \varphi_n(\mathbf{r}) = \epsilon_n \varphi_n(\mathbf{r})$$

The anti-symmetrized wave function

The Hartree approximation ignores the Fermi-Dirac statistics of the electrons, and hence is intrinsically problematic.

The Hartree-Fock approximation, instead, assumes a single-Slater determinant form of the wave function,

$$\Phi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \cdots & \varphi_N(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \cdots & \varphi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(x_N) & \varphi_2(x_N) & \cdots & \varphi_N(x_N) \end{pmatrix} \quad x_i = (\mathbf{r}_i, \sigma_i)$$

Electrons are fermions with spin $\frac{1}{2}$. The full electron coordinate x contains a spatial coordinate \mathbf{r} and a spin coordinate σ . The complete specification of an single-electron state is called spin orbital:

$$\varphi_n(\mathbf{r}_i, \sigma_i) = \varphi_{n,\sigma_i}(\mathbf{r}_i) \alpha_{\sigma_i}(i) \quad \sigma_i = \begin{cases} \uparrow & \text{Spin up} \\ \downarrow & \text{Spin down} \end{cases} \quad \alpha_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \alpha_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The Hartree-Fock approximation

With the single Slater determinant trial wavefunction, the total energy $E = \langle \Phi | \hat{H}^e | \Phi \rangle$ is given by

$$E[\{\varphi_l(\mathbf{r})\}] = \sum_{n,\sigma}^{occ.} \left\langle \varphi_{n,\sigma} \left| -\frac{\nabla^2}{2m} \right| \varphi_{n,\sigma} \right\rangle + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \sum_{m,n,\sigma,\sigma'}^{occ.} \iint d\mathbf{r} d\mathbf{r}' \frac{|\varphi_{n,\sigma}(\mathbf{r})|^2 |\varphi_{m,\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

The Hartree term

$$- \frac{1}{2} \sum_{m,n,\sigma}^{occ.} \iint d\mathbf{r} d\mathbf{r}' \frac{\varphi_{n,\sigma}^*(\mathbf{r}) \varphi_{n,\sigma}(\mathbf{r}') \varphi_{m,\sigma}(\mathbf{r}) \varphi_{m,\sigma}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The exchange term

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) = \sum_{n,\sigma}^{occ.} |\varphi_{n,\sigma}(\mathbf{r})|^2$$

Please note that $m = n, \sigma = \sigma'$ term is included in both the Hartree and the exchange terms, and hence cancel each other out.

The Hartree-Fock approximation

Again minimizing $E = E[\varphi_n]$ with respect to φ_n^* under the constrain that $\langle \varphi_n | \varphi_n \rangle = 1$,

$$\frac{\delta}{\delta \varphi_n^*} \{E[\varphi_n] - \epsilon_n [\langle \varphi_n | \varphi_n \rangle - 1]\} = 0$$

one obtains the Hartree-Fock equation:

$$\left[-\frac{\nabla^2}{2m} + v_{ext}(\mathbf{r}) + \sum_{m,\sigma'}^{occ.} \int d\mathbf{r}' \frac{\varphi_{m,\sigma'}^*(\mathbf{r}') \varphi_{m,\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \varphi_{n,\sigma}(\mathbf{r}) - \sum_m^{occ.} \int d\mathbf{r}' \frac{\varphi_{m,\sigma}^*(\mathbf{r}') \varphi_{n,\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_{m,\sigma}(\mathbf{r}) = \epsilon_n \varphi_{n,\sigma}(\mathbf{r})$$

The Hartree-Fock approximation

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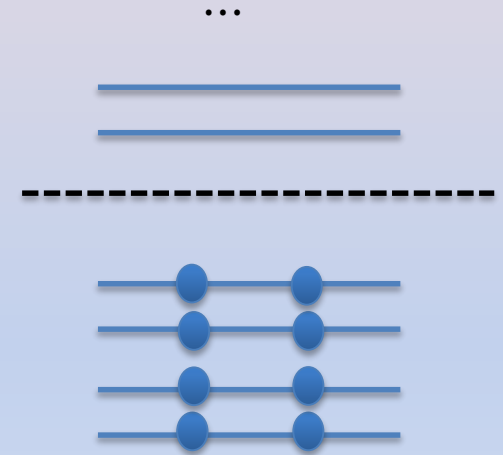
The second term can be seen as obtained by exchanging the orbital index m and n of the first term.

The Hartree-Fock equation

The Hartree-Fock equation can also be written as

$$\left[-\frac{\nabla^2}{2m} + v_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \varphi_{n,\sigma}(\mathbf{r}) + \sum_m^{occ.} \int d\mathbf{r}' \frac{\varphi_{n,\sigma}(\mathbf{r}') \varphi_{m,\sigma}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_{m,\sigma}(\mathbf{r}) = \epsilon_n \varphi_{n,\sigma}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{n,\sigma}^{occ.} |\varphi_{n,\sigma}(\mathbf{r})|^2$$



The Hartree-Fock equations are a set of non-linear equations that need to be solved self-consistently. The resultant set of eigenstates are called Hartree-Fock orbitals.

The Koopman's theorem

The Hartree-Fock orbital energy ϵ_n can be interpreted as the energy cost to remove an electron from occupied orbitals, or the energy gain to add an electron to unoccupied orbitals.



Tjalling Koopman
Nobel Laureate in
economics (1975)

- The **relaxation effect** of orbitals upon adding/removing electrons is neglected.
- The electron correlation effect is neglected.

The Hartree-Fock ground-state energy

$$|\Phi_{\text{HF}}\rangle = \det\{\varphi_{l,\sigma}\}$$

$$E[\{\varphi_l(\mathbf{r})\}] = \langle \Phi_{\text{HF}} | \hat{H}^e | \Phi_{\text{HF}} \rangle = T[\varphi_l] + V_{\text{ext}}[n] + J[n] + K[\varphi_l]$$

$$T = \sum_{n,\sigma}^{\text{occ.}} \left\langle \varphi_{n,\sigma} \left| -\frac{\nabla^2}{2m} \right| \varphi_{n,\sigma} \right\rangle$$

The kinetic energy

$$V_{\text{ext}} = \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

The external potential energy

$$J = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The Hartree energy

$$K = -\frac{1}{2} \sum_{m,n,\sigma}^{\text{occ.}} \iint d\mathbf{r} d\mathbf{r}' \frac{\varphi_{n,\sigma}^*(\mathbf{r}) \varphi_{n,\sigma}(\mathbf{r}') \varphi_{m,\sigma}(\mathbf{r}) \varphi_{m,\sigma}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The exchange energy

The correlation energy

The correlation energy of an electronic system is defined as the difference between the exact ground-state energy and the Hartree-Fock ground-state energy.

$$E_c = \langle \Psi_0 | \hat{H}^e | \Psi_0 \rangle - \langle \Phi_{\text{HF}} | \hat{H}^e | \Phi_{\text{HF}} \rangle$$

$|\Psi_0\rangle$: the exact ground state

$|\Phi_{\text{HF}}\rangle$: The Hartree-Fock ground state

By definition, the correlation energy is negative $E_c < 0$, and the Hartree-Fock approximation does not include the correlation effect.

Summary of the Hartree-Fock theory

- Variational: the Hartree-Fock total energy is above the exact ground-state energy.
- The Hartree-Fock approximation neglects the electron correlation effect.
- No single-particle self-interaction error.
- The Hartree-Fock single-particle energies have physical meanings.
- The Hartree-Fock theory is still important today. It is an important ingredient of hybrid density functional approximations.

The homogeneous electron gas model

The homogeneous electron gas (HES) model is also called **the “jellium” model**, where the contribution of nuclear ions is treated as an uniform positive charge background.

As a first approximation, the $q = 0$ component of the electron-electron interaction cancels the attraction between electrons and the positive charge background, and the residual ($q \neq 0$) components are neglected. This is called the non-interacting HES model.

The Hamiltonian of **the non-interacting HES** is given by

$$\hat{H}_{HEG} = \sum_{i=1}^N \hat{h}(i) = \sum_{i=1}^N [-\nabla_i^2/2]$$

Particles moving in a cubic box

The eigenvalue problem:

$$\hat{h}\varphi_n(\mathbf{r}) = -\frac{1}{2m}\nabla^2\varphi_n(\mathbf{r}) = \epsilon_n\varphi_n(\mathbf{r})$$

It is convenient to choose **Born von-Karmen (BvK) periodic boundary condition**:

$$\varphi(x, y, z) = \varphi(x + L, y, z)$$

$$\varphi(x, y, z) = \varphi(x, y + L, z)$$

$$\varphi(x, y, z) = \varphi(x, y, z + L)$$

Volume of the box: $V = L^3$

$$\varphi(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\mathbf{r}} = \varphi_k(\mathbf{r})$$

$$\epsilon = \frac{k^2}{2m} = \epsilon_k \quad \left(\frac{\hbar^2 k^2}{2m}, \text{ here } \hbar = 1 \right)$$



Torus: periodic in two dimensions

The plane wave vector \mathbf{k} is the quantum number here

Consequence of the BvK boundary condition

$$\varphi(x, y, z) = \varphi(x + L, y, z)$$

$$\varphi(x, y, z) = \varphi(x, y + L, z)$$

$$\varphi(x, y, z) = \varphi(x, y, z + L)$$

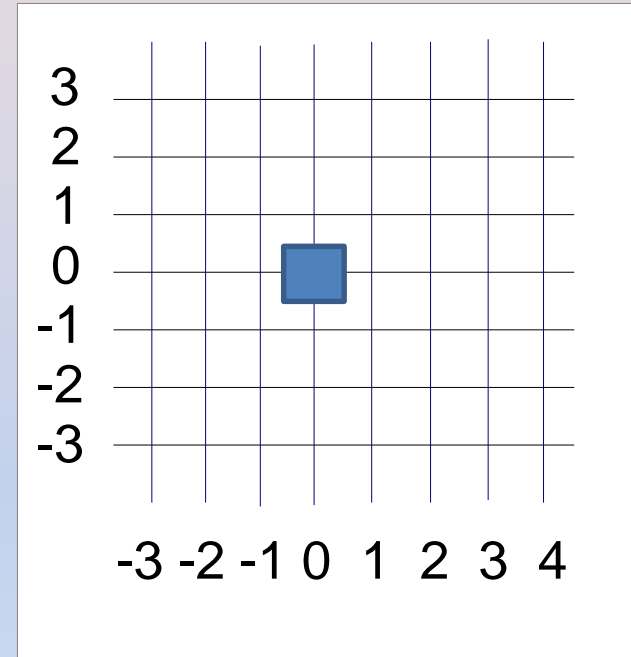
The BvK boundary condition implies:

$$e^{ik_x L} = 1, e^{ik_y L} = 1, e^{ik_z L} = 1$$

Therefore

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L},$$

where n_x, n_y, n_z are integer numbers.



The wave vectors of plane waves are quantized, and the allowed wave vectors (states) are uniformly distributed in the reciprocal space. Each state occupies a volume of $(2\pi/L)^3 = (2\pi)^3/V$.

The *ab-initio* electronic many-body Hamiltonian

$$\begin{aligned}\hat{H}^e &= - \sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i^{N_e} V_{\{\mathbf{R}_i, Z_i\}}^{ext}(\mathbf{r}_i) \\ &= \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}\end{aligned}$$

The ground state and excited states of the electronic Hamiltonian determine most properties of materials. The solution of the electronic Hamiltonian is often called the “*electronic structure*”.

Despite the considerable simplification that the Born-Oppenheimer approximation brings, the computational challenge remains. **The exact solution of the interacting many-body Hamiltonian is not accessible even numerically for $O(N) > 10$.**

Further simplification/approximation is a must!

The Fermi vector and Fermi energy

The electronic states are occupied according to the “aufbau principle”, i.e., the energy levels are filled from low to high, until certain highest energy, called **the Fermi energy**.

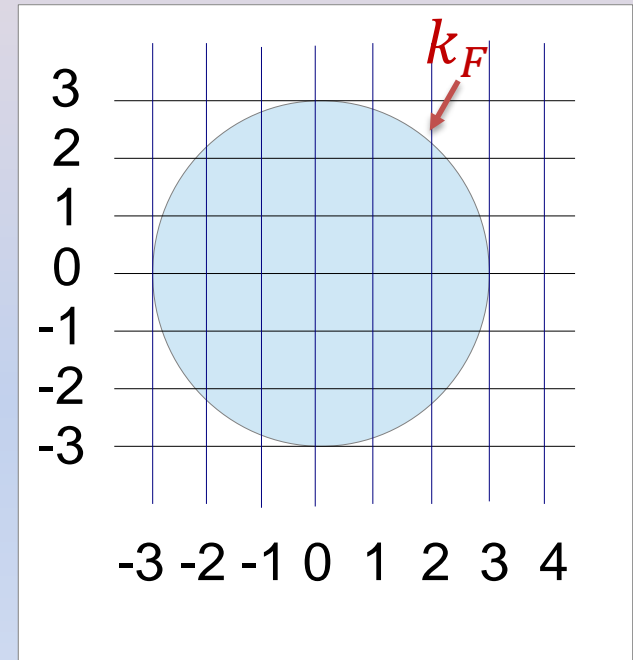
Suppose there are N electrons in system, we have

$$\begin{aligned} N &= 2 \sum_{|\mathbf{k}| < k_F} (1) = 2 \left(\frac{V}{8\pi^3} \right) \int_0^{k_F} d^3 k \quad (1) \\ &= 2 \left(\frac{V}{8\pi^3} \right) \frac{4\pi}{3} k_F^3 = V \frac{k_F^3}{3\pi^2} \end{aligned}$$

Thus we obtain an important relation:

The Fermi vector: $k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3} = (3\pi^2 n)^{1/3}$

The Fermi energy: $E_F = k_F^2 / 2m = (3\pi^2 n)^{2/3} / 2m$



Taking $N, V \rightarrow \infty$, while keeping the density $n = \frac{N}{V}$ fixed.

The Fermi temperature and Fermi surface

Fermi vector: $k_F = (3\pi^2 n)^{1/3}$

Fermi energy: $\epsilon_F = \frac{k_F^2}{2m} = \frac{(3\pi^2 n)^{2/3}}{2m}$

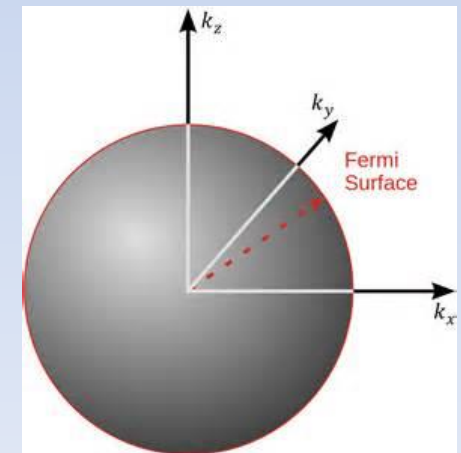
Fermi temperature: $T_F = \epsilon_F / \kappa_B$

The Fermi temperatures of alkali metals are of $O(10^4)$ kelvin.

The solution of equation $\epsilon(k) = E_F$ defines sections in the \mathbf{k} space; this is called the Fermi surface. The Fermi surface of a 3D HES is a sphere surface.

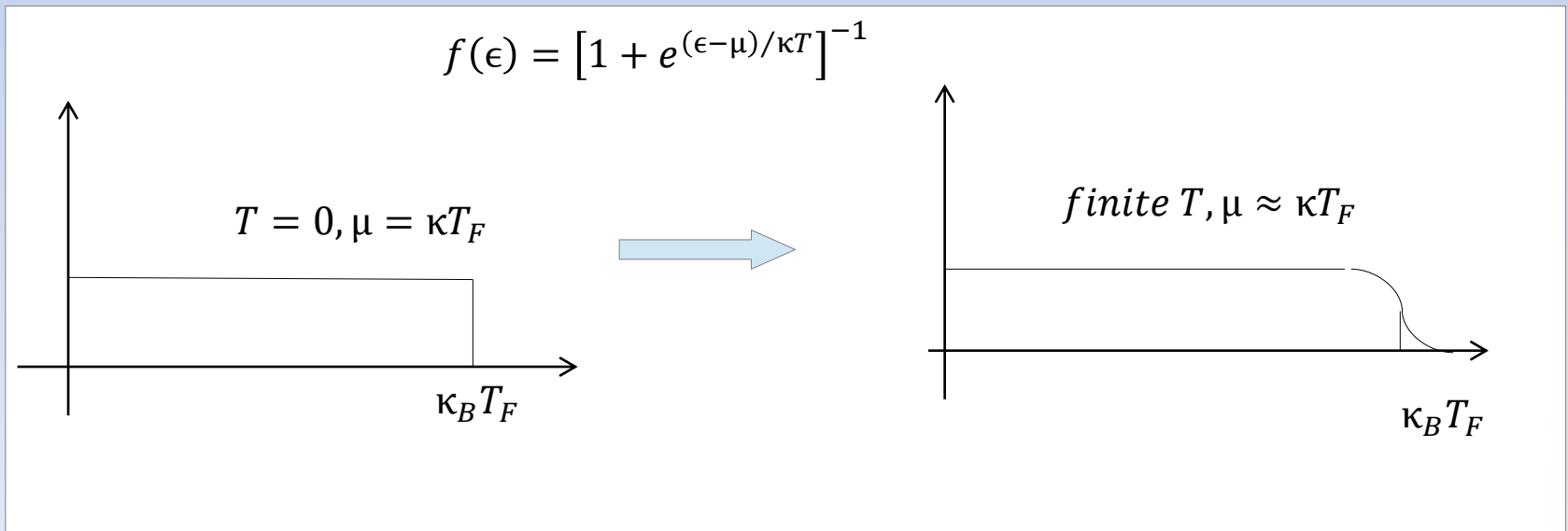


Enrico Fermi

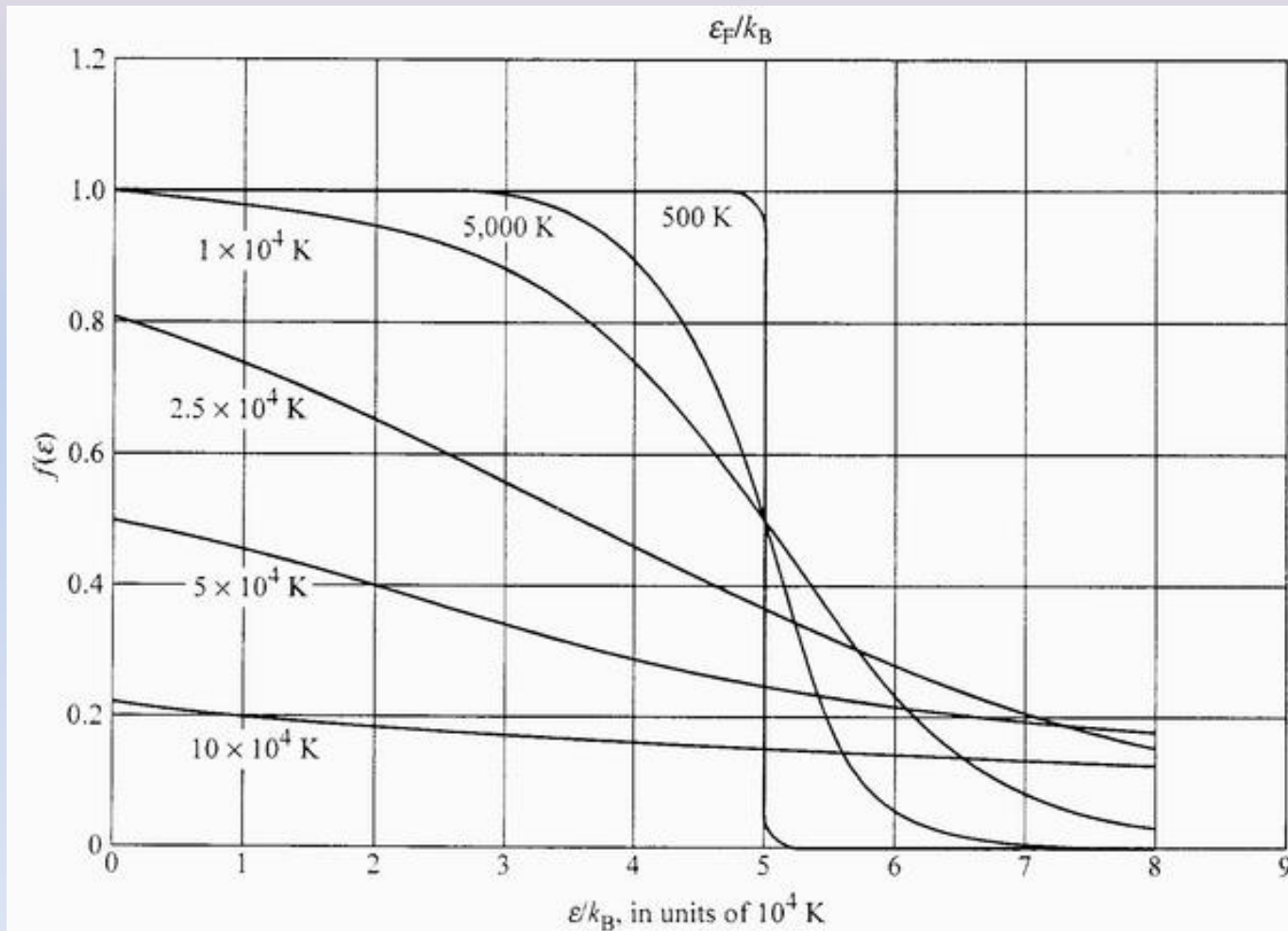


Basic properties of HES

- The characteristic energy scale of HES is its Fermi energy E_F or Fermi temperature k_F , and this is uniquely determined by its electron density (or valence electron density for real metals).
- The Fermi temperature of normal metals is $\sim 10^4$ kelvin or higher; this is much higher than the room temperature (273 kelvin). Therefore, under the room temperature, only electrons in the neighborhood of the Fermi surface will become active, and contribute to the thermodynamics of the system.



Fermi-Dirac distribution function under different temperatures



Density of states (DOS)

- Suppose we want to get the energy of HES:

$$\begin{aligned} E &= \sum_{\mathbf{k}} f(\epsilon(\mathbf{k}))\epsilon(\mathbf{k}) = \frac{2V}{8\pi^3} \int_0^\infty d^3 k f(\epsilon(\mathbf{k}))\epsilon(\mathbf{k}) \\ &= \frac{V}{\pi^2} \int_0^\infty dk k^2 f(\epsilon(\mathbf{k}))\epsilon(\mathbf{k}) = \int_0^\infty d\epsilon D(\epsilon) f(\epsilon)\epsilon \end{aligned}$$

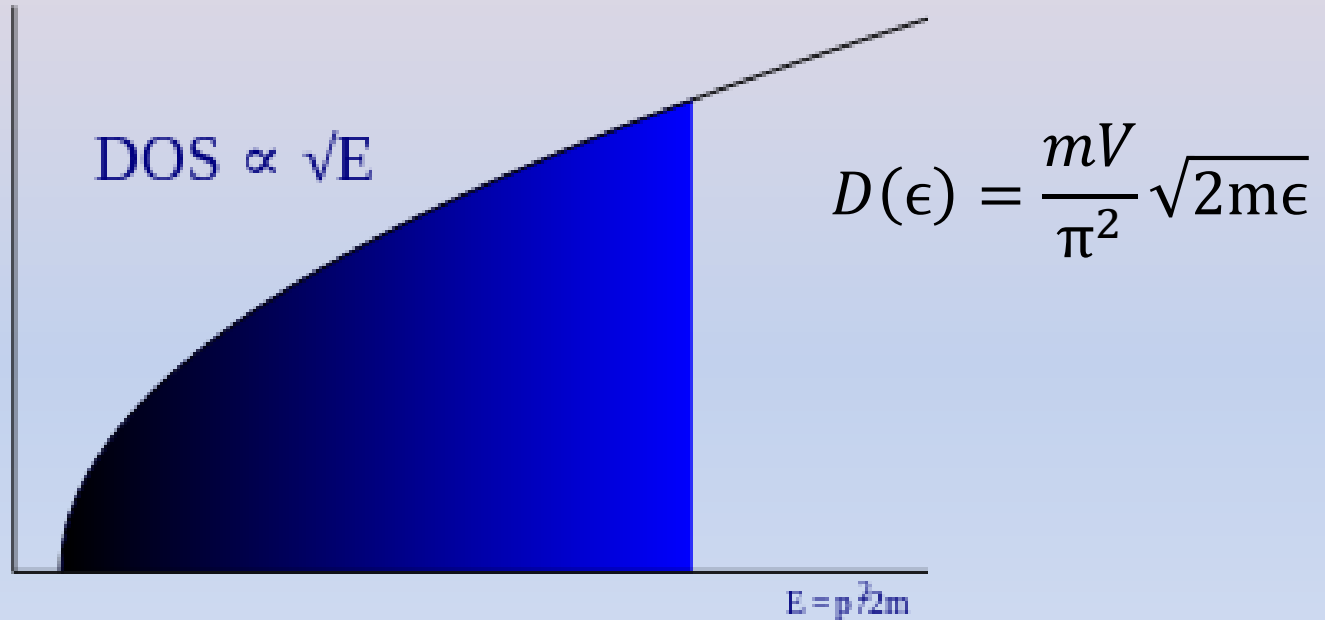
Density of states:

$D(\epsilon)d\epsilon$: the number of states between the energy interval ϵ and $d\epsilon$.

$$D(\epsilon) = \frac{mV}{\pi^2} \sqrt{2m\epsilon}, \quad \text{with } \epsilon \geq 0 \quad dk = \frac{k}{m} d\epsilon = \sqrt{\frac{m}{2\epsilon}} d\epsilon$$

$$\text{In general, } D(\epsilon) = \frac{(2\pi)^3}{V} \int d\mathbf{k} \frac{1}{|\nabla_{\mathbf{k}}\epsilon(\mathbf{k})|} \delta(\epsilon - \epsilon(\mathbf{k}))$$

DOS of 3-dimensional HES



The DOS around the Fermi level determines many properties of the electronic system.

Homework I

Please try to derive the Hartree-Fock equations from the single Slater determinant assumption and the variational principle.