THE HARTREE-FOCK AND THOMAS-FERMI APPROXIMATIONS, AND THE ELECTRON GAS

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Introduction

Since the early times of quantum mechanics, the ground state properties of many interacting particles were studied by variational methods. In the Hartree-Fock approximation the minimum of the total energy is found in the subset of Slater determinants. In the Thomas-Fermi approximation the total energy is written as a functional of the unknown particle density, and minimized. The application to the electron gas is presented. The two approximations are still used and useful. They found completion in the Density Functional Theory, by which most of the progress in the study of electronic properties of solids molecules or atoms was made.

1. The Hartree-Fock approximation

The Hartree-Fock equations provide an approximate evaluation of the ground state of the Hamiltonian for a system of N interacting particles

$$H = \sum_{i=1..N} h(i) + \tfrac{1}{2} \sum_{i \neq j} v(i,j) \tag{1}$$

$h(i)$ is a single particle operator, and $v(i,j) = v(j,i)$ is the two-particle interaction. The Hartree equation was studied first [3]; it is a single-particle equation where the interaction with other particles enters as mean field (Hartree potential):

$$(hu_i)(\mathbf{x},\sigma) + U_H(\mathbf{x}) u_i(\mathbf{x},\sigma) = \epsilon_i u_i(\mathbf{x},\sigma), \quad i = 1 \dots N. \tag{2}$$

The Hartree potential is evaluated with the ground state density, to be calculated self-consistently:

$$U_H(\mathbf{x}) = \int d\mathbf{x}'\, v(\mathbf{x},\, \mathbf{x}')\, n(\mathbf{x}'), \qquad n(\mathbf{x}) = \sum_{j=1..N} \sum_{\sigma} |u_j(\mathbf{x},\sigma)|^2. \tag{3}$$

and has the problem of including a self-interaction of the particle.
A radical improvement was done by Fock, who added the important *exchange* interaction, as a consequence of the antisymmetry of the wave-function of two identical fermions. The term cancels the self-interaction in the Hartree potential [2].

There are several ways to deduce the HF equations. An elegant one is variational: instead of minimizing $\langle \Psi | H | \Psi \rangle$ among all normalized antisymmetric vectors for N particles, the viable search is restricted to Slater[1] determinants of orthonormal one-particle trial states. As such, the HF ground state energy E_{HF} is the best (lowest) upper bound to the exact ground state energy E_{GS}, in a description

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[1]John Slater, Oak Park (Illinois) 1900 - Sanibel Isl. (Florida) 1976.

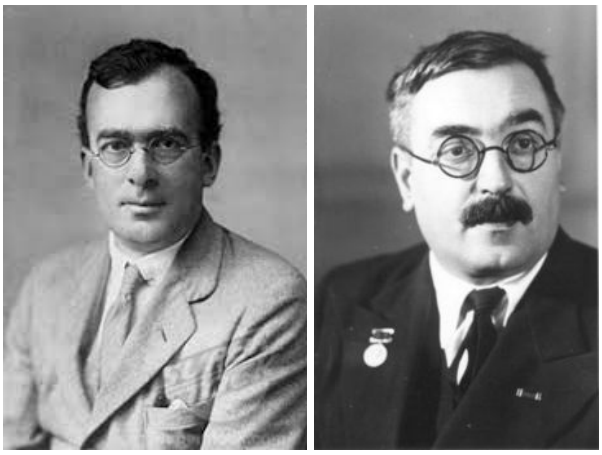

FIGURE 1. Douglas Hartree (Cambridge 1897 - Cambridge 1958) obtained his PhD in 1926 with numerical studies of Bohr's model of the atom. His advisor was Ernest Rutherford. In the same year Schrödinger's equation appeared, and in 1927 Hartree derived the Hartree equations for multi-electron atoms. He was a pioneer in mechanical solvers for differential equations (he built one with his student A. Porter, with Meccano parts) and then in computer numerical applications to physics (from Wikipedia).
Vladimir A. Fock (St. Petersburg 1898, Leningrad 1974) contributed to theoretical physics and geophysics. He introduced occupation number states and the Fock space, and developed the HF method in 1930. He independently obtained the Klein-Gordon equation, described the degeneracy of H-atom as a SO(4) symmetry (1935), studied Dirac's equation in an external gravitational field (1929). He was arrested in 1937 during Stalinian terror and freed a week later, thanks to Kapitza's letter to Stalin.

with independent particles. The error is the *correlation energy*, and is negative by definition: $E_C = E_{GS} - E_{HF} \leq 0$

1.1. **The HF equations.** In the variational approach one starts from N orthonormal one-particle trial states $|u_i\rangle$. The antisymmetrized product state

$$|HF\rangle = \sqrt{N!}\, A(N)|u_1, \ldots, u_N\rangle \tag{4}$$

is normalized (Slater state). The transformation $|u_i'\rangle = \sum_j U_{ij}|u_j\rangle$ with a SU(N) matrix preserves orthonormality and does not change the Slater state $|HF\rangle$ (appendix 1).
The expectation value of the Hamiltonian (appendix 2)

$$\boxed{\langle HF|H|HF\rangle = \sum\nolimits_i \langle u_i|h|u_i\rangle + \frac{1}{2}\sum\nolimits_{i,j}\langle u_i u_j|v|u_i u_j - u_j u_i\rangle} \tag{5}$$

is then unchanged. It involves one or two particles at a time, the others being spectators. The interaction contains a *direct* term and an *exchange* term. The

negative sign results from Fermi statistics (particles are exhanged) and cancels the self-term $i = j$.

Minimization of the energy as a functional of u_i is done while enforcing orthogonality and normalization, that are required for eq.(6) to hold. The functional to minimize is

$$E_{HF}[u_1, ..., u_N] = \langle HF|H|HF\rangle - \sum_{ij} \epsilon_{ij} \left(\langle u_i|u_j\rangle - \delta_{ij}\right) \tag{6}$$

with Lagrange parameters ϵ_{ij} that are the entries of a Hermitian matrix (reality of E_{HF}). The N first variations for infinitesimal variations $u_i + \eta_i$ are:[2]

$$\begin{aligned}\delta_i E_{HF} =& E_{HF}[u_1, ..., u_i + \eta_i, .., u_N] - E_{HF}[u_1, .., u_i, .., u_N] \\ =& \langle \eta_i|h|u_i\rangle + \sum\nolimits_j \langle \eta_i u_j|v|u_i u_j - u_j u_i\rangle - \epsilon_{ij}\langle \eta_i|u_j\rangle + \text{c.c.}\end{aligned}$$

They must vanish for all variations $|\eta_i\rangle$. In a Hilbert space, if $\langle\eta|w\rangle + \langle w|\eta\rangle = 0$ for all η, then $w = 0$. Since the $N-$particle Slater state is left unchanged by a unitary transformation, there is a degeneracy in the solutions u_i. We may always pick the set that diagonalizes the Hermitian matrix ϵ_{ij}: $\sum_j \epsilon_{ij}|u_j\rangle = \epsilon_i|u_i\rangle$. Then we obtain the system of Hartree-Fock equations:

$$\boxed{h|u_i\rangle + \sum_{j=1}^{N} \langle \cdot\, u_j|v|u_i u_j - u_j u_i\rangle = \epsilon_i|u_i\rangle, \quad i = 1 \dots N} \tag{7}$$

Projection of the equation on the solution $|u_i\rangle$ gives:

$$\epsilon_i = \langle u_i|h|u_i\rangle + \sum\nolimits_j \langle\, u_i\, u_j|v|u_i u_j - u_j u_i\rangle \tag{8}$$

The identity simplifies the evaluation of the ground state energy (6):

$$E_{HF}(N) = \sum\nolimits_i \epsilon_i - \tfrac{1}{2}\sum\nolimits_{i,j} \langle u_i u_j|v|u_i u_j - u_j u_i\rangle = \tfrac{1}{2}\sum_i \left[\langle u_i|h|u_i\rangle + \epsilon_i\right] \tag{9}$$

The chemical potential in the Hartree-Fock approximation is

$$\mu_{HF} \equiv E_{HF}(N) - E_{HF}(N-1)$$

Proposition 1.1 (Koopman's lemma, 1934)**.** *For $N \gg 1$ particles, $\mu_{HF} = \epsilon_N$.*

Proof. Let $|u_1\rangle, \dots, |u_N\rangle$ be the solutions of HF equations for N particles. The Hartree Fock energy is

$$\begin{aligned}E_{HF}(N) =& \sum_{j=1..N} \langle u_j|h|u_j\rangle + \frac{1}{2}\sum_{i\neq j}^{N} \langle u_i u_j|v|u_i u_j - u_j u_i\rangle \\ =& \langle u_N|h|u_N\rangle + \sum_{j<N} \langle u_N u_j|v|u_N u_j - u_j u_N\rangle + \\ &+ \sum_{j<N} \langle u_j|h|u_j\rangle + \frac{1}{2}\sum_{i\neq j}^{N-1} \langle u_i u_j|v|u_i u_j - u_j u_i\rangle \\ =& \epsilon_N + E_{HF}[u_1 \dots u_{N-1}]\end{aligned}$$

[2]the term $\langle u_i\eta_j|v|u_i u_j - u_j u_i\rangle$ is identical to $\langle \eta_j u_i|v|u_j u_i - u_i u_j\rangle$ because of the exchange symmetry of the potential $\langle 12|v|34\rangle = \langle 21|v|43\rangle$. The dummy indices ij are then redifined.

For $N-1$ particles, the solution of HF equations is a different set $|u'_1\rangle \dots |u'_{N-1}\rangle$ that give the total energy $E_{HF}(N-1)$. Therefore

$$\mu_{HF} = E_{HF}(N) - E_{HF}(N-1) = \epsilon_N + E_{HF}[u_1 \dots u_{N-1}] - E_{HF}(N-1) \geq \epsilon_N$$

because $E_{HF}(N-1)$ is a stationary point. Let $|u'_N\rangle$ be an arbitrary but normalized state orthogonal to the solution $|u'_1\rangle, \dots, |u'_{N-1}\rangle$, then:

$$E_{HF}(N) \leq E_{HF}[u'_1, \dots, u'_N] = \epsilon'_N + E_{HF}(N-1)$$

where ϵ'_N is the expression (9) evaluated with primed states. Therefore

$$\epsilon_N \leq \mu_{HF} \leq \epsilon'_N.$$

While the total energy is $\mathcal{O}(N)$, single particle energies are $\mathcal{O}(1)$. If we assume that, for large N, the difference of two energies evaluated with HF states for N and $N-1$ particles (plus another which is arbitrary and can be adjusted to lower the gap) is $\mathcal{O}(1/N)$ then $\mu_{HF} = \epsilon_N$. □

In the representation of position and spin, the equations gain the familiar form

$$\boxed{(h + U_H)u_i(\mathbf{x},\sigma) - \sum\nolimits_{\sigma'} \int d\mathbf{x}' J_{\sigma,\sigma'}(\mathbf{x},\mathbf{x}')u_i(\mathbf{x}',\sigma') = \epsilon_i u_i(\mathbf{x},\sigma)} \tag{10}$$

where h is the local 1-particle Hamiltonian, U_H is the self-consistent Hartree potential (3) and the *exchange integral* is a bi-local potential with the kernel

$$J_{\sigma\sigma'}(\mathbf{x},\mathbf{x}') = \sum_{j=1..N} u_j(\mathbf{x},\sigma)v(\mathbf{x},\mathbf{x}')u_j^*(\mathbf{x}',\sigma')$$

The single Hartree equation that only requires an initial guess for the density, is now replaced with N coupled equations, which require a start of N vectors to improve by iteration towards self-consistency.

If the Hamiltonian does not depend on spin, the solutions factorize as $u_i(\mathbf{x})v_{m_i}(\sigma)$, where v_m is an eigenstate of S_z. The completeness relation $\sum_\sigma v_m(\sigma)v_{m'}(\sigma) = \delta_{mm'}$ simplifies the HF equations:

$$(h + U_H)u_i(\mathbf{x}) - \int d\mathbf{x}'\, v(\mathbf{x},\mathbf{x}')u_i(\mathbf{x}')\sum\nolimits_j \delta_{m_i,m_j} u_j(\mathbf{x})u_j(\mathbf{x}')^* = \epsilon_i u_i(\mathbf{x}) \tag{11}$$

Slater [6] (1951) suggested to restore locality by approximating the exchange term with the exchange term of the homogeneous electron gas (plane waves), adapted to the local density. This anticipated the progress of Density Functional Theory.

1.2. **Homogeneous systems.** The HF equations can be analytically solved if the system is translation invariant, i.e. the two particle interaction is a function $v(\mathbf{x}-\mathbf{y})$ (for simplicity we avoid spin dependence) and there is no external potential. We consider $h = p^2/2m$.

Proposition 1.2. *The Hartree-Fock equations for N particles in a box with periodic b.c. are solved by an arbitrary set of N eigenvectors $|\mathbf{k}_i, m_i\rangle$ of $\mathbf{p}$ and S_z.*

Proof. Let's show that

$$\frac{\hbar k_i^2}{2m}|\mathbf{k}_i, m_i\rangle + \sum_j \langle\, \cdot\, , \mathbf{k}_j m_j | v | \mathbf{k}_i m_i, \mathbf{k}_j m_j - \mathbf{k}_j m_j, \mathbf{k}_i m_i\rangle = \epsilon_i |\mathbf{k}_i m_i\rangle$$

A resolution of identity is inserted in the matrix element: $\langle \cdot\,, \mathbf{k}_j m_j|v|\ldots\rangle = \sum_{\mathbf{k},m} |\mathbf{k}m\rangle\langle \mathbf{k}m, \mathbf{k}_j m_j|v|\ldots\rangle$. Translation invariance enforces conservation of total momentum, $\mathbf{k}+\mathbf{k}_j = \mathbf{k}_i + \mathbf{k}_j$ and spin conservation requires $m = m_i$. Therefore the sum reduces to the single term $(\mathbf{k}, m) = (\mathbf{k}_i, m_i)$, and the vectors $|\mathbf{k}_i m_i\rangle$ solve the HF equations. □

The matrix element is evaluated:

$$\langle \mathbf{k}_i m_i, \mathbf{k}_j m_j|v|\mathbf{k}_i m_i, \mathbf{k}_j m_j - \mathbf{k}_j m_j, \mathbf{k}_i m_i\rangle = \frac{1}{V}\left[\tilde{v}(0) - \delta_{m_i,m_j}\tilde{v}(\mathbf{k}_i - \mathbf{k}_j)\right]$$

where $\tilde{v}(\mathbf{k}) = \int d^3x\, v(\mathbf{x}) e^{-i\mathbf{k}\cdot\mathbf{x}}$. Note that $\tilde{v}(\mathbf{k})$ is real and even.
The eigenvalues and the total energy per particle are obtained:

$$\epsilon_i = \frac{\hbar^2 k_i^2}{2m} + n\,\tilde{v}(0) - \frac{1}{V}\sum_j \delta_{m_i m_j}\,\tilde{v}(\mathbf{k}_i - \mathbf{k}_j) \tag{12}$$

$$\boxed{\frac{E_{HF}}{N} = \frac{1}{N}\sum_{i=1}^{N}\frac{\hbar^2 k_i^2}{2m} + \tfrac{1}{2}n\,\tilde{v}(0) - \frac{n}{2N^2}\sum_{ij}\delta_{m_i m_j}\,\tilde{v}(\mathbf{k}_i - \mathbf{k}_j)} \tag{13}$$

If $\tilde{v}(\mathbf{k}) \geq 0$, the set $\{(\mathbf{k}_i, m_i)\}$ that actually minimizes E_{HF} is not obvious, because of two contrasting terms:
• The kinetic energy is minimized by choosing the vectors $\mathbf{k}_i$ in the Fermi sphere $|\mathbf{k}| \leq k_F$, with both values of m_s. This choice gives:

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} + n\tilde{v}(\mathbf{0}) - \frac{1}{V}\sum_{\mathbf{k}'}\theta(k_F - k')\tilde{v}(\mathbf{k} - \mathbf{k}') \tag{14}$$

$$\frac{E_{HF}}{N} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} + \tfrac{1}{2}n\tilde{v}(\mathbf{0}) - \frac{n}{2N^2}\sum_{\mathbf{k}\mathbf{k}'}\theta(k_F - k)\theta(k_F - k')\tilde{v}(\mathbf{k} - \mathbf{k}'). \tag{15}$$

This total HF energy coincides with the energy evaluated in first order perturbation theory: $E_{HF} = \langle F|H|F\rangle$, where $|F\rangle$ is the Slater state with filled Fermi sphere.
• If $\tilde{v}(\mathbf{k}) > 0$ the negative exchange term in (14) is lowered by requiring $m_i = m_j$ for all particles. This increases the kinetic energy, but may be advantageous at low density. The HF ground state would then be *spin polarized*.

Exercise. Consider a homogeneous system of N particles in a volume V, with total energy E, density $n = N/V$, mean energy per particle $\epsilon = E/N$. If ϵ only depends on n, show that the chemical potential, the pressure and the bulk modulus are given by:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_V = \frac{d}{dn}[n\epsilon(n)], \quad p = -\left(\frac{\partial E}{\partial V}\right)_N = n[\mu - \epsilon(n)] = n^2\frac{d\epsilon}{dn}, \tag{16}$$

$$B = -V\left(\frac{\partial p}{\partial V}\right)_N = n^2\frac{\partial \mu}{\partial n} \tag{17}$$

The bulk modulus measures the volume response of a solid to pressure, and is always positive. At the equilibrium density n^* the pressure is zero, and $\mu = \epsilon(n^*)$.

2. The electron gas

An important model is the gas of N electrons in presence of a static charge distribution $\rho(\mathbf{x})$, with Coulomb interactions:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_j|} - \sum_{i=1}^{N} \int d\mathbf{y} \frac{e\rho(\mathbf{y})}{|\mathbf{y}-\mathbf{x}_i|} + \frac{1}{2}\iint d\mathbf{x}d\mathbf{y} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \tag{18}$$

The terms in $H = T + U_{ee} + U_{eb} + U_{bb}$ are the kinetic and potential energy of the electrons, the electron - static charge interaction energy, and the potential energy of the static charge. Depending on the charge distribution, we are describing atoms, molecules, crystals.
To express the operators with creation and destruction operators for the discrete basis of spin and momentum, the system is enclosed in a box of volume $L^3 = V$, with periodic b.c. Since the Coulomb potential $1/r$ is long-range, it is temporarily replaced by a Yukawa potential $U(r) = e^{-\mu r}/r$ with $L\mu \gg 1$, so that it decays well within the box (up to a region near the walls, that contributes negligibly in the large volume limit). When taking the limit of infinite box, the limit $\mu \to 0$ restores the Coulomb potential. The operators are:

$$\begin{aligned}
T &= \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} \\
U_{ee} &= \frac{e^2}{2V} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} \frac{4\pi}{q^2+\mu^2} a^\dagger_{\mathbf{k}+\mathbf{q},\sigma} a^\dagger_{\mathbf{k}'-\mathbf{q},\sigma'} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}\sigma} \\
U_{eb} &= -\frac{e}{V} \sum_{\sigma} \sum_{\mathbf{k}\mathbf{q}} \frac{4\pi}{q^2+\mu^2} a^\dagger_{\mathbf{k},\sigma} a_{\mathbf{k}-\mathbf{q}\sigma} \rho(\mathbf{q}) \\
U_{bb} &= \frac{1}{2V} \sum_{\mathbf{q}} \rho(\mathbf{q})\rho(-\mathbf{q}) \frac{4\pi}{q^2+\mu^2}
\end{aligned}$$

where $\rho(\mathbf{q}) = \int_V d\mathbf{x}\, \rho(\mathbf{x}) \exp(-i\mathbf{q}\cdot\mathbf{x})$. In particular $\rho(\mathbf{0}) = Q$ (total charge). The operator H does not change the number of electrons, which is fixed to be N.
Being $\mathbf{q} = (2\pi/L)\mathbf{n}$, $\mathbf{n} \in \mathbb{Z}^{\mathbf{3}}$, the only terms that diverge for $\mu = 0$ are those with $\mathbf{q} = \mathbf{0}$ (otherwise $q \gg \mu$ in the limit):

$$\begin{aligned}
H_{\mathbf{q}=\mathbf{0}} &= \frac{4\pi}{V\mu^2} \left[\frac{e^2}{2} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}\sigma} a^\dagger_{\mathbf{k}'\sigma'} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}\sigma} - eQ \sum_{\mathbf{k}\sigma} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \frac{Q^2}{2} \right] \\
&= \frac{4\pi}{V\mu^2} \left[\frac{e^2}{2} N(N-1) + (-eN)Q + \frac{Q^2}{2} \right] = \frac{2\pi}{L(L\mu)^2} (Q-eN)^2 - \frac{2\pi N}{V\mu^2} e^2
\end{aligned}$$

The limit $\mu \to 0$ can be taken with the conditions:
- If N and Q are finite, and $L \to \infty$, $\mu \to 0$ with $L\mu \gg 1$ then $H_{\mathbf{q}=\mathbf{0}} = 0$.
- If N and Q scale as the volume, we require neutrality ($Q - Ne = 0$) and a finite energy per unit volume. Then the ratio $H_{\mathbf{q}=\mathbf{0}}/V$ becomes zero in the limit.
Therefore, in the infinite box limit, H no longer contains the terms with $\mathbf{q} = \mathbf{0}$, and in the other terms one may set $\mu = 0$ to restore the Coulomb potential.

2.1. **HEG: the homogeneous electron gas.**

The simplest situation occurs when the charge density is uniform: the N electrons are immersed in a cloud with charge

density eN/V. This model is the 'homogeneous electron gas' (HEG) or 'jellium'. Now $\rho(\mathbf{q})$ is non-zero only for $\mathbf{q} = \mathbf{0}$, and the Hamiltonian simplifies:

$$H_{HEG} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \frac{e^2}{2V} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} \frac{4\pi}{q^2} a^\dagger_{\mathbf{k}+\mathbf{q}\sigma} a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}\sigma} \tag{19}$$

The HEG is neutral and translation invariant. It is a simple model for the conduction of electrons in metals, with the crystal structure being smoothed to a uniform background.

2.2. **Total energy in first order perturbation.** If we consider the interaction U as a perturbation to T, we can evaluate the total energy as $\langle F|T+U|F\rangle$ where $|F\rangle$ is the ground state for free electrons in the box: all and only the states in the Fermi sphere are occupied. The total number of particles and the kinetic energy are

$$N = \sum_{\mathbf{k}\sigma} \langle F|a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}|F\rangle = 2\sum_{\mathbf{k}} \theta(k_F - k)$$
$$T = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} \langle F|a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}|F\rangle = 2\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} \theta(k_F - k)$$

In the thermodynamic limit the first equation gives $k_F^3 = 3\pi^2 n$, where $n = N/V$ and the second one gives $T = \frac{3}{5} N E_F$ where the Fermi energy is $E_F = \hbar^2 k_F^2/(2m)$. The first order correction is:

$$U = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} \frac{4\pi e^2}{q^2} \langle F|a^\dagger_{\mathbf{k}+\mathbf{q}\sigma} a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}\sigma}|F\rangle \tag{20}$$

The matrix element is zero if k and k' are greater than k_F. The two holes must be compensated by particles. Since $\mathbf{q} \neq \mathbf{0}$ this is only possible if $\mathbf{k} = \mathbf{k}' - \mathbf{q}$ and $\sigma = \sigma'$. Then, after spin summation:

$$\begin{aligned} U &= \frac{1}{V} \sum_{\mathbf{k}\neq\mathbf{k}'} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2} \langle F|a^\dagger_{\mathbf{k}'\sigma} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma} a_{\mathbf{k}\sigma}|F\rangle \theta(k_F - k)\theta(k_F - k') \\ &= -\frac{1}{V} \sum_{\mathbf{k}\neq\mathbf{k}'} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2} \theta(k_F - k)\theta(k_F - k') \\ &= -V \iint \frac{d\mathbf{k}}{(2\pi)^3} \frac{d\mathbf{k}'}{(2\pi)^3} \frac{4\pi e^2}{k^2 + k'^2 - 2\mathbf{k}\cdot\mathbf{k}'} \theta(k_F - k)\theta(k_F - k') \end{aligned}$$

The result for the average energy per particle is:

$$\boxed{\epsilon(n) = \frac{E}{N} = \frac{3}{10}\frac{\hbar^2}{m}(3\pi^2 n)^{2/3} - \frac{3^{4/3}}{4\pi^{1/3}} e^2 n^{1/3}} \tag{21}$$

$$\mu = \partial_n(n\epsilon(n)) = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} - \frac{3^{1/3}}{\pi^{1/3}} e^2 n^{1/3} = E_F - \frac{1}{\pi} e^2 k_F \tag{22}$$

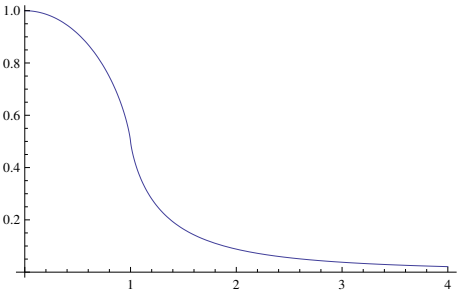

FIGURE 2. The function F(x).

2.3. **HEG in Hartree-Fock.** The same total energy is obtained in the HF approximation if we choose to fill the Fermi sphere. The single particle energy is

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m} - \int \frac{d\mathbf{k}'}{(2\pi)^3}\theta(k_F - k')\frac{4\pi e^2}{|\mathbf{k}' - \mathbf{k}|^2} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right), \tag{23}$$

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x}\log\frac{1+x}{|1-x|}$$

The function F is continuous but with singular derivative in $x = 1$: this result is bad because $d\epsilon/dk$ diverges at $k = k_F$. It implies that, in this approximation, the density of states (per unit volume and spin component)

$$\rho(\epsilon) = \frac{1}{V}\sum_{\mathbf{k}} \delta(\epsilon - \epsilon(k)) = \frac{4\pi}{(2\pi)^3}\frac{k^2}{|\epsilon'(k)|}\Big|_{\epsilon(k)=\epsilon} \tag{24}$$

vanishes at the Fermi energy $\epsilon(k_F)$, in sharp disagreement with experimental data for several physical quantities at low temperature, such as the specific heat[3], the conductivity of metals, or the critical temperature for the superconducting transition[4]. Nevertheless, the total energy (that coincides with (22)) is of interest and reliable at high density:

$$\frac{E_{HF}}{N} = \frac{e^2}{2a_0}\left[\frac{3}{5}(k_F a_0)^2 - \frac{3}{2\pi}(k_F a_0)\right] \tag{25}$$

The energy scale is fixed by the ionization energy of the H-atom, $e^2/2a_0 = 13.61$ eV (the Hartree energy unit is 1 Ha $= e^2/a_0$). If Seitz's parameter r_s is used[5]:

$$\frac{E_{HF}}{N} = \frac{e^2}{2a_0}\left[\frac{3}{5}\left(\frac{9\pi}{4}\right)^{\frac{2}{3}}\frac{1}{r_s^2} - \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{1}{r_s}\right]$$

$$\approx 13.61\,\text{eV}\left[\frac{2.210}{r_s^2} - \frac{0.916}{r_s}\right].$$

[3]For the electron gas $c_V = \frac{2}{3}\pi^2 k_B^2 \rho(\epsilon_F)T$.

[4]In the BCS model it is $T_C \approx T_D \exp(1/\rho(\epsilon_F)g)$, where T_D is Debye's temperature and g is the coupling of electrons to phonons

[5]r_s measures the radius available per particle in units of Bohr's radius: $(4/3)\pi(r_s a_0)^3 = V/N$. For spin 1/2: $k_F = (3\pi^2 N/V)^{1/3}$, then: $(a_0 k_F) = (9\pi/4)^{1/3}(1/r_s)$

The negative *exchange energy* explains the cohesion of conduction electrons in metals: it balances the kinetic energy and stabilizes the electron gas at finite densities. The minimum is achieved at $r_{min} = (4\pi/5)(9\pi/4)^{1/3} \approx 4.83$, with an energy per particle equal to -1.29 eV. The value r_{min} is within the range of r_s-values of metals: r_s(Li)= 3.25, r_s(Na)= 3.93, r_s(K)= 4.86, r_s(Rb)= 5.20, r_s(Cs)= 5.62, r_s(Al)= 2.07, r_s(Au)= 3.01.
The HF energy per particle at the value r_s(Na) is -1.23 eV, which compares with the experimental value -1.13 eV of the binding energy measured as heat of vaporization of the metal.

The HF expression (27) is an upper bound for the exact ground-state energy per particle. A lower bound was found by Lieb and Narnhofer, by minimisinig T and V separately [4]:

$$\frac{E_{GS}}{N} > \frac{e^2}{2a_0}\left[\frac{3}{5}\left(\frac{9\pi}{4}\right)^{\frac{2}{3}}\frac{1}{r_s^2} - \frac{9}{5}\frac{1}{r_s}\right]$$

The minimum value for kinetic energy is that of the ideal gas; the Coulomb minimum corresponds to delta-localized electrons.

The relation $dE = -pdV + \mu dN$ gives the pressure[6] and the chemical potential in HF approximation at $T = 0$, as functions of the density:

$$p = -\frac{\partial E}{\partial V}\Big|_N = -\frac{dE}{dr_s}\frac{dr_s}{dV}\Big|_N = \frac{e^2}{2a_0^4}\left[\frac{0.352}{r_s^5} - \frac{0.073}{r_s^4}\right] \tag{26}$$

$$\mu = \frac{\partial E}{\partial N}\Big|_V = \frac{e^2}{2a_0}\left[\frac{3.683}{r_s^2} - \frac{1.222}{r_s}\right] \tag{27}$$

It is $\mu = \epsilon(k_F)$. At r_{min} the pressure vanishes, and the value $\mu = 1.29$ eV coincides with the average energy per particle.

Exercise. Evaluate the bulk modulus for the HEG. Show that at $r_{min} = 4.83$ it is $B = 2.1 \times 10^{10}$ erg/cm^3; for Potassium ($r_s = 4.86$) the experimental value is $B = 2.81 \times 10^{10}$ erg/cm^3. Other values are: Al) $B = 76.0 \times 10^{10}$ erg/cm^3, Na) $B = 6.42 \times 10^{10}$ erg/cm^3 (from Ashcroft-Mermin, Solid State Physics, Holt Saunders 1976). Show that $B < 0$ for $r_s > 6.03$, where HF badly fails.

What is the HF ground state as r_s increases? Bloch (1929) conjectured that the gas prefers to polarize, because parallel spins lower the Coulomb energy. However, Overhauser showed that neither the para or ferro-magnetic HF ground states are stable against the formation of spin density waves (particle density is uniform, but with spatial modulation of spin density) [7]. The subject was reconsidered by Ceperley et al. [1], with numerical simulations.

2.4. **The Wigner Crystal.** At very low densities ($r_s > 100$), the total energy is minimized by a state with the electrons localized in lattice sites (*Wigner crystal*), where they perform zero point motion.
A 2D Wigner crystal was first observed in 1979 by Grimes and Adams [10]. The electrons were bound to the surface of liquid He by the induced image charges and the crystal structure was detected through the resonant coupling of a surface wave in He to collective excitations of the electrons.

[6] $e^2 a_0^{-4} = 2.94 \times 10^{13}$ Pa.

In 3D the energy per particle for large r_s is

$$\frac{E}{N} = \frac{e^2}{2a_0}\left[-\frac{1.79}{r_s} + \frac{2.66}{r_s^{3/2}} + \dots\right] \tag{28}$$

The formula refers to the optimal Wigner crystal structure (body centred cubic), with 1 electron per cell. The first term is the electrostatic potential per cell (Madelung's constant).
We give a simple evaluation where the unit cell is approximated by a sphere of radius $R = r_s a_0$. The sphere has charge $-e$ at the center and charge e uniformly distributed in its volume. At the surface, the forces are null (Gauss theorem). The electrostatic energy per cell is

$$\epsilon = \frac{\rho_0^2}{2}\int \frac{d\mathbf{x}d\mathbf{y}}{|\mathbf{x}-\mathbf{y}|} - e\rho_0 \int \frac{d\mathbf{x}}{|\mathbf{x}|} = \frac{3}{5}\frac{e^2}{R} - \frac{3}{2}\frac{e^2}{R}$$

The electron is subject to a harmonic potential, with energy $p^2/(2m) + \frac{1}{2}(e^2/R^3)r^2$. The lowest eigenvalue is $\frac{3}{2}\hbar\omega$. The approximate formula is obtained:

$$\frac{E}{N} = \frac{e^2}{2a_0}\left[-\frac{1.8}{r_s} + \frac{3}{r_s^{3/2}}\right].$$

It is conjectured that the Wigner crystal provides the equation of state for "metallic Hydrogen" (where protons form a lattice and electrons are spread in the volume). Such crystal state may be present in the center of Jupiter.

3. The Thomas-Fermi approximation

Thomas [11] and Fermi [12] introduced an approximate method, variational in character. The method aims at expressing the total energy as a functional of the density. The ground state energy and density are obtained by minimization.
A main difficulty is to construct an effective functional for the kinetic energy. The Thomas-Fermi functional is based on the total energy of the ideal Fermi gas, adjusted to allow for a position-dependent density:

$$\boxed{T^{TF}[n] = \frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2)^{\frac{2}{3}}\int d\mathbf{x}\, n(\mathbf{x})^{\frac{5}{3}}} \tag{29}$$

For a uniform density N/V, the total energy of free electrons is recovered.
The Thomas-Fermi energy functional for an atom with Z electrons is:

$$E^{TF}[n] = T^{TF}[n] - Ze^2\int d\mathbf{x}\frac{n(\mathbf{x})}{|\mathbf{x}|} + \frac{e^2}{2}\int d\mathbf{x}d\mathbf{y}\frac{n(\mathbf{x})n(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} \tag{30}$$

The electrostatic terms are classical. The functional is minimized with the additional Lagrange multiplier $\mu\left[Z - \int d^3x\, n(\mathbf{x})\right]$, to fix the number of electrons. The density at minimum solves:

$$0 = \frac{\delta E^{TF}}{\delta n(\mathbf{x})} = \frac{\hbar^2}{2m}(3\pi^2)^{\frac{2}{3}}n(\mathbf{x})^{\frac{2}{3}} - \frac{Ze^2}{|\mathbf{x}|} + e^2\int d\mathbf{y}\frac{n(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} - \mu$$

and $\mu = \partial E_{TF}/\partial Z$. The equation can be rewritten with the aid of Poisson's formula:

$$\mu = \frac{\hbar^2}{2m}(3\pi^2)^{\frac{2}{3}}n(\mathbf{x})^{\frac{2}{3}} - e\varphi(\mathbf{x})$$
$$\nabla^2\varphi(\mathbf{x}) = -4\pi e^2\left[Z\,\delta(\mathbf{x}) - n(\mathbf{x})\right]$$

A solution is found with the assumption of spherical symmetry, but the result is not good: the atom is too large. Dirac (1930) [13] introduced an extra term, the exchange energy functional, given by the expression for HEG, i.e. the second term in eq.(26), but with local density:

$$E_x[n] = -e^2 \frac{3^{\frac{4}{3}}}{4\pi^{\frac{1}{3}}} \int d\mathbf{x}\, n(\mathbf{x})^{\frac{4}{3}}. \tag{31}$$

A term dependent on the gradient of the density was introduced by von Weizsacker (1935) [14], to improve the kinetic functional:

$$T^{vW}[n] = \frac{\hbar^2}{8m} \int d\mathbf{x}\, \frac{|\nabla n(\mathbf{x})|^2}{n(\mathbf{x})}.$$

This form can be justified on the basis of HF approximation: the kinetic energy is $\langle T\rangle = \frac{\hbar^2}{2m}\sum_{i=1}^N \sum_m \int d\mathbf{x} |\mathrm{grad}\, u_i(\mathbf{x},m)|^2$. Put $u_i(\mathbf{x},m) = \sqrt{n(\mathbf{x})} f_i(\mathbf{x},m)$ where $n(\mathbf{x})$ is the total density; then $\sum_{i=1}^N \sum_m |f_i(\mathbf{x},m)|^2 = 1$. One evaluates: $\langle T\rangle = T^{vW}[n] + \frac{\hbar^2}{2m}\int d\mathbf{x}\, n(\mathbf{x}) \sum_m \sum_{i=1}^N |\nabla f_i(\mathbf{x},m)|^2$. The second term is the "exchange kinetic energy".

Making approximations exact. DFT originated in 1964 from a theorem by Hohenberg and Kohn [8] who established that for of a quantum system of particles with given interaction, there is a one-to-one correspondence among the external potential (up to a constant) and the ground state density. This implies that the total energy is a sum of the potential energy and a universal (unknown) functional of the density, that makes the Thomas-Fermi approach exact.
Soon after, Kohn and Sham wrote a Schrödinger equation which made DFT usable. The many particle problem is associated to a single particle problem with an appropriate exchange-correlation local potential

$$(h + U_H)u_i(\mathbf{x}) + v_{xc}(\mathbf{x})u_i(\mathbf{x}) = \epsilon_i u_i(\mathbf{x}), \quad i = 1 \dots N \tag{32}$$

In Kohn's words [9], the equation is the *exactification* of the Hartree equation. The potential v_{xc} is unknown, but useful approximations to it were obtained from the theory of the homogeneous electron gas, that has been studied in depth by perturbative methods and Montecarlo simulations.

Appendix 1. Let $|u_1\rangle \dots |u_N\rangle$ be orthonormal single particle states. Define the new orthonormal states $|u'_i\rangle = \sum_j U_{ij}|u_j\rangle$, where U is a SU(N) matrix. The two sets produce the same N-particle fermionic Slater state.
Proof. Let us evaluate the new state, $|\Psi'\rangle = \sqrt{N!}\, S(N)_-|u'_1, \dots, u'_N\rangle = \sqrt{N!}\, U_{1j_1} \dots U_{Nj_N} S(N)_-|u_{j_1} \dots u_{j_N}\rangle$. The operator $S(N)_-$ produces a non zero state only if $\{j_1 \dots j_N\}$ is a permutation σ of $\{1 \dots N\}$. Therefore, the summation on $\{j_1 \dots j_N\}$ is a sum over permutations P_σ on N-particle states

$$\begin{aligned} |\Psi'\rangle =& \sqrt{N!} \sum\nolimits_\sigma U_{1\sigma_1} \dots U_{N\sigma_N} S(N)_- P_\sigma |u_1 \dots u_N\rangle \\ =& \sum\nolimits_\sigma (-1)^\sigma U_{1\sigma_1} \dots U_{N\sigma_N}\, \sqrt{N!} S(N)_- |u_1 \dots u_N\rangle = \det U\, |\Psi\rangle \end{aligned}$$

Appendix 2. Let $|u_1\rangle \dots |u_N\rangle$ be orthonormal one-particle states, and construct the N-particle fermionic state $|\Psi\rangle = \sqrt{N!}S(N)_-|u_1,\dots,u_N\rangle$. For one and two-particle operators $O_1 = \sum_{i=1}^N o(i)$ and $O_2 = \frac{1}{2}\sum_{i\neq j} o(i,j)$, with $o(i,j) = o(j,i)$, it is:

$$\boxed{\langle\Psi|O_1|\Psi\rangle = \sum_{i=1..N}\langle u_i|o|u_i\rangle, \quad \langle\Psi|O_2|\Psi\rangle = \sum_{ij}\langle u_iu_j|o|u_iu_j - u_ju_i\rangle} \tag{33}$$

Proof: Since O_1 commutes with $S(N)_-$ and $S(N)_-^2 = S(N)_-$:

$$\begin{aligned}\langle\Psi|O_1|\Psi\rangle =& N!\sum\nolimits_i \langle u_1\dots u_N|O_1S(N)_-|u_1,\dots,u_N\rangle \\ =& \sum\nolimits_i\sum\nolimits_\sigma (-1)^\sigma \langle u_1|u_{\sigma_1}\rangle\dots\langle u_i|o|u_{\sigma_i}\rangle\dots\langle u_N|u_{\sigma_N}\rangle\end{aligned}$$

The inner products are zero unless $\sigma_k = k$ for all $k\neq i$. Then necessarily $\sigma_i = i$, and only the identity permutation contributes to the sum. Similarly:

$$\begin{aligned}\langle\Psi|O_2|\Psi\rangle =& N!\sum\nolimits_{ij}\langle u_1\dots u_N|o(i,j)S(N)_-|u_1\dots u_i\dots u_j\dots u_N\rangle \\ =& \sum\nolimits_{ij}\sum\nolimits_\sigma (-1)^\sigma \delta_{1\sigma_1}\dots\langle u_iu_j|o|u_{\sigma_i}u_{\sigma_j}\rangle\dots\delta_{N\sigma_N}\end{aligned}$$

the inner products are non-zero if $\sigma_k = k$ for $k\neq i,j$. Then, the only permutations that contribute are the identity and the exchange $\sigma_i = j$, $\sigma_j = i$. The last one has a factor $(-1)^\sigma = -1$.

Helium atom

Neglecting spin, the Hamiltonian of the Helium atom with fixed nucleus is:

$$H = \sum_{i=1,2}\left(\frac{p_i^2}{2m} - \frac{2e^2}{|\mathbf{x}_i|}\right) + \frac{e^2}{|\mathbf{x}_1-\mathbf{x}_2|} \tag{34}$$

The ground state is spherically symmetric: $\psi(r_1,r_2,\xi)v_{0,0}(\sigma_1,\sigma_2)$ where $\psi(r_1,r_2,\xi) = \psi(r_2,r_1,\xi)$, $\xi = \cos\theta$ (θ is the angle formed by the vectors $\vec{r}_1$ and $\vec{r}_2$) and $v_{0,0}(\sigma_1,\sigma_2) = \frac{1}{\sqrt{2}}[v_\uparrow(\sigma_1)v_\downarrow(\sigma_2) - v_\uparrow(\sigma_2)v_\downarrow(\sigma_1)]$ is the singlet state of total spin, antisymmetric in σ_1, σ_2. The eigenvalue equation for the ground state

$$\begin{aligned}-\frac{\hbar^2}{2m}\left[\frac{1}{r_1^2}\frac{\partial}{\partial r_1}r_1^2\frac{\partial}{\partial r_1} + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}r_2^2\frac{\partial}{\partial r_2} + \frac{r_1^2+r_2^2}{r_1^2r_2^2}\frac{\partial}{\partial\xi}(1-\xi^2)\frac{\partial}{\partial\xi}\right]\psi \\ -\left[\frac{2e^2}{r_1} + \frac{2e^2}{r_2} - \frac{e^2}{\sqrt{r_1^2+r_2^2-2r_1r_2\xi}}\right]\psi = E_{GS}\psi\end{aligned} \tag{35}$$

cannot be solved analytically. In the HF approximation one employs trial functions $u(r)v_\uparrow(\sigma)$ and $u(r)v_\downarrow(\sigma)$, which give the state $u(r_1)u(r_2)v_{00}(\sigma_1,\sigma_2)$. The single particle function $u(r)$ solves the HF equation

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}r^2\frac{du}{dr} - e^2\frac{Z(r)}{r} = \epsilon\, u(r) \tag{36}$$

The equation describes an electron in the potential of an effective charge

$$Z(r) = 2 - r\int d^3r'\frac{u(r')^2}{|\vec{r}-\vec{r}'|} = 2 - 4\pi\int_0^r r'^2dr'\,u(r')^2 - 4\pi r\int_r^\infty r'dr'\,u(r')^2$$

Two terms measure the total charge (in units of e) in the sphere of radius r. For large r the screened nucleus charge is $Z(\infty) = 1$, while for $r \to 0$ it is $Z(0) = 2$. The total Hartree-Fock energy is:

$$E_{HF}[u] = 8\pi \int_0^\infty r^2 dr \left[\frac{\hbar^2}{2m} u'^2 - \frac{2e^2}{r} u^2\right] - 32\pi^2 e^2 \int_0^\infty r\, dr\, u^2 \int_0^r r'^2 dr' u^2$$

The HF equation is non-linear and is not solved analytically. A viable approximation (the standard calculation found in textbooks) is to impose a Hydrogen-like solution with a variational parameter Z:

$$u(r) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0},$$

and minimize $E_{HF}(Z) = (e^2/a_0)(Z^2 - 4Z + \frac{5}{8}Z)$. The minimum is at $Z = \frac{27}{16}$, which gives the ground state estimate (an upper bound) $E_{HF} = -77.5$ eV.

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