II. My first density functional: Thomas-Fermi Theory

A. Uniform electronic density of the large atom

We develop here a qualitative theory for the electronic structure of the atom. The atom is composed of a nucleus of charge +Ze and Z electrons. We want the large Z limit. Let us assume the electrons are of uniform density, packed into the volume R. Since we have to account for Pauli's principle, we assume that each electron occupies a volume in its own small sphere a so that the spheres are non-overlapping. Neglecting the volume between the spheres, and since there are Z small spheres fit into the large sphere $Za^3 = R^3$. The kinetic energy of each electron is $\frac{\hbar^2 \pi^2}{2m_e a^2}$ and so the total kinetic energy is:

$$T = \frac{\hbar^2 \pi^2}{2m_e a^2} Z = \frac{\hbar^2 \pi^2}{2m_e R^2} Z^{5/3}.$$

Exercise 1: Calculate the energy of a uniform sphere of charge, having radius R and total charge Ze .

Solution: First build a uniform density R-sphere of smeared uniform charge having Z electrons and then bringing the positive nucleus to the center. The negative charge density is $\rho = \frac{3Z}{4\pi R^3}$. The energy of the uniform sphere is

$$U_e = \int_0^R \rho 4\pi r^2 dr \left(\rho \frac{4\pi}{3} r^3 \right) \frac{\kappa}{r} = \frac{3}{5} \frac{\kappa Z^2}{R}, \text{ where } \kappa = \frac{e^2}{4\pi \epsilon_0}.$$

Exercise 2: Calculate the Coulomb energy of a neutral charge distribution composed of a positive point charge $+Ze$ in the center of a sphere of radius R containing uniform negative charge.

Solution: We first build the electron sphere, as in the above exercise, then bring the positive nucleus to its center. The nucleus is brought to the center in

2 stages. First to the rim, this takes energy $U_1 = -\kappa \frac{Z^2}{R}$. Then, inside the

negatively charge the Electric field is $\kappa \frac{Z}{r^2} \frac{\rho 4\pi}{3} r^3 = \kappa Z \frac{\rho 4\pi}{3} r$ so the potential is:

$U_2 = \frac{1}{2} \kappa Z \frac{\rho 4\pi}{3} r^2 = \frac{1}{2} \kappa \frac{Z^2}{R^3} r^2$. Thus the total energy gained in bringing the

nucleus into the center is: $U_1 + U_2 = -\frac{3\kappa Z^2}{2R}$ and the total Coulomb energy is

$U = U_e + U_1 + U_2 = -\frac{9}{10} \frac{\kappa Z^2}{R}$.

The Coulomb energy is calculated classically, as shown in the above exercises

yielding $U = -\frac{9}{10} \frac{\kappa Z^2}{R}$. From this, we subtract the self-interaction energy $\frac{3}{5} \frac{\kappa}{a}$ of

each small sphere, since there are Z spheres we obtain: $U - U_{self} = -\frac{9}{10} \frac{\kappa Z^2}{R} -$

$\frac{3}{5} \frac{\kappa Z^{4/3}}{R}$. In the large Z limit the self-interaction energy term is negligible, since

it is this limit we want, we neglect it henceforth. The energy of the atom is

then:

$$E = \frac{A}{R^2} - \frac{B}{R} \tag{2.1.1}$$

With

$$A = \frac{\hbar^2 \pi^2}{2m_e} Z^{5/3} \qquad B = \frac{9\kappa Z^2}{10} \tag{2.1.2}$$

The minimum is obtained by $E'(R_*) = 0$:

$$-2\frac{A}{R_*^3} + \frac{B}{R_*^2} = 0 \quad \rightarrow \quad R_* = \frac{2A}{B}, \qquad E_{min}(Z) = -\frac{B^2}{4A} \tag{2.1.3}$$

Substituting everything we have:

$$R_* = \frac{10\pi^2 a_0}{9} Z^{-1/3}, \qquad E_{min}(Z) = -\frac{81 E_h}{200\pi^2} Z^{7/3} \tag{2.1.4}$$

It is interesting that in this model, as Z grows, the radius of the atom R_* shrinks as $Z^{-1/3}$, so the density grows as Z^2, while the energy of the atom drops in proportion to $Z^{7/3}$.

Our model is exceedingly simplistic, assuming a constant density, neglecting correlation, taking a very crude approach for the kinetic energy – these are indeed great "sins". For the hydrogen atom it give the much too high and very large radius:

Note for "hydrogen atom" in our treatment yields a much too large sphere is obtained and the energy much too high:

$$R_*(1) = 10.9a_0 \qquad E_{min}(1) = -0.04E_h$$

Part of the reason for the high energy is the self-interaction energy which we neglected. But we already discussed above how to remove self-interaction: we would only have to increase B_1 by the self interaction $\frac{5\kappa}{3}$, giving $B_1 = \frac{3\kappa}{2}$. In this case, the radius is reduced and energy drops:

$$R_*(1) = 6.6a_0 \qquad E_{min}(1) = -0.11E_h$$

But the values are still not quantitative. But for high Z it was proved by Lieb and Simon that the scaling of the energy (but not our multiplicative constant) is indeed what one finds for an exact solution of the non-relativistic many-electron Schrödinger equation.

Our crude approach above is an example of a "statistical" electronic structure theory, where many electrons are present at high densities. We describe in the rest of this chapter the Thomas Fermi theory, which is a different, more orderly approach to the statistical theory of electrons, developed by Thomas and Fermi shortly after the advent of quantum mechanics. The idea behind this theory is to enable theoretical work on many-body systems, especially

atoms. We do this in a way that stresses that this theory can also be viewed as an approximation to density functional theory.

B. Basic concepts in the electron gas and the Thomas-Fermi Theory

In the early days of quantum mechanics there was no practical way of using the Schrödinger equation to determine the electronic structure of many-electron systems such as heavy atoms. A simple, albeit approximate method was in need and supplied separately by Thomas[1] and Fermi[2]. Their theory can be thought of as a density functional approach. One writes an expression for the energy of an atom or a molecule which is a functional of the 1-particle density as follows:

$$E_{TF}[n] = T_{TF}[n] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d^3r + \frac{\kappa}{2}\iint \frac{n(r)n(r')}{|r-r'|}d^3rd^3r' \qquad (2.2.1)$$

Thomas and Fermi assumed that the density that characterizes the ground-state minimizes this functional under the constraint:

$$\int n(\mathbf{r})d^3r = N_e \qquad (2.2.2)$$

The first question, beyond the rigor of this approach is, what is the kinetic energy functional? In order to take into account the Fermi nature and the quantum nature of the electrons, this functional must include both these considerations. The Thomas Fermi solution is to assume:

$$T_{TF}[n] = \int t_S(n(\mathbf{r}))n(\mathbf{r})d^3r \qquad (2.2.3)$$

What shall we take for $t_S(n)$? Consider first a simple case: a homogeneous gas of density n (i.e. $n(\mathbf{r})$ is independent of $\mathbf{r}$). Furthermore, let us assume that the electrons are non-interacting. This is a simple enough system to enable the analytic calculation of the kinetic energy functional. From the form of (2.2.3)

we see that the total kinetic energy is the sum of contributions of various infinitesimal cells in space. Each cell contains $n(\boldsymbol{r})d^3r$ electrons and so, if we interpret $t(n)$ as the kinetic energy <u>per electron</u> of a homogeneous gas of non-interacting electrons then this sum is yields exactly the total kinetic energy for this homogeneous gas. The Thomas-Fermi approximation then uses this same $t(n)$ also for the inhomogeneous interacting case.

Let us now compute $t(n)$. Consider a *homogeneous gas of N uncharged electrons. They are non-interacting*. These electrons are put in a cubic cell of length L. The electron density is everywhere the same $n = \frac{N_e}{V} = \frac{N_e}{L^3}$.

We assume the wave functions are periodic in the box. According to Fourier's theorem, we can write any periodic wave function as a linear combination of plane-waves, as follows:

$$\psi(\boldsymbol{r}) = \sum_{\mathbf{n}} \frac{a_{\mathbf{n}} e^{i\frac{2\pi}{L}\mathbf{n}\cdot\mathbf{r}}}{\sqrt{V}} \tag{2.2.4}$$

Where:

$$\mathbf{n} = \left(l_x, l_y, l_z\right). \tag{2.2.5}$$

and $l_{x/y/z}$ are integers. Fourier's theorem is based on the orthonormality of the plane waves

$$\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}'}\rangle = \frac{1}{V}\iiint_V e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}d^3r = \delta_{\mathbf{k},\mathbf{k}'} \tag{2.2.6}$$

Where we defined

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\,\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \qquad \mathbf{k} = \frac{2\pi}{L}\mathbf{n} \tag{2.2.7}$$

We imagine 3-dimensional k-space divided into an array of small compartments, indexed by a set of integers $\mathbf{n} = \left(l_x, l_y, l_z\right)$ or by the vector $\boldsymbol{k}$.

Each compartment is of k-length $\Delta k = \frac{2\pi}{L}$ and its k-volume is $\Delta k^3 = \frac{(2\pi)^3}{V}$. For large r-space boxes the k-space compartment is extremely small since Δk^3 is proportional to the inverse box volume. Since we are interested eventually in the limit $L \to \infty$, we may assume approximate sums of any function $f(\mathbf{k})$ over the discrete values of $\mathbf{k} = \frac{2\pi}{L}\mathbf{n}$ by integrals:

$$\sum_{\mathbf{k}} f(\mathbf{k}) \to \frac{V}{(2\pi)^3}\int f(\mathbf{k})d^3k \quad (V \to \infty) \tag{2.2.8}$$

Let's show that plane-waves are eigenstates of kinetic energy operator $\hat{T}_1$:

$$\hat{T}_1\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\frac{1}{\sqrt{V}}\nabla^2 e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{\hbar^2 k^2}{2m_e}\psi_{\mathbf{k}}(\mathbf{r}) \tag{2.2.9}$$

Now, consider the wavefunction of the N_e non-interacting electrons in their ground-state. Since they are non-interacting, this wave-function is a product of single-electron wave-functions:

$$\Psi = \psi_{\mathbf{k}_1}(\mathbf{r}_1)\bar{\psi}_{\mathbf{k}_1}(\mathbf{r}_2)\cdots\psi_{\mathbf{k}_{N_e/2}}(\mathbf{r}_{N_e-1})\bar{\psi}_{\mathbf{k}_{N_e/2}}(\mathbf{r}_{N_e}) \tag{2.2.10}$$

Here $\psi_{\mathbf{k}}(\mathbf{r})$ is the state of a spin-up electron with wave vector $\mathbf{k}$. while $\bar{\psi}_{\mathbf{k}}(\mathbf{r})$ is the state of a spin down electron with wave vector $\mathbf{k}$. Anticipating the antisymmetry, we build this wave function by placing 2 electrons in the same spatial orbital (once with spin up and the other with spin down). Since non-interacting electrons have only one type of energy, i.e. kinetic energy: $\hat{H} = \sum_{n=1}^{N_e}\left(-\frac{\hbar^2}{2m_e}\nabla_n^2\right)$, we can easily show that (2.2.10) is an eigenstate of the Hamiltonian:

$$\hat{H}\Psi = \sum_{n=1}^{N_e} \left(-\frac{\hbar^2}{2m_e}\nabla_n^2\right) \psi_{\mathbf{k}_1}(\mathbf{r}_1)\bar{\psi}_{\mathbf{k}_1}(\mathbf{r}_2)\cdots\psi_{\mathbf{k}_{N_e/2}}(\mathbf{r}_{N_e-1})\bar{\psi}_{\mathbf{k}_{N_e/2}}(\mathbf{r}_{N_e})$$

$$= \sum_{n=1}^{N_e/2} 2\left(\frac{\hbar^2 \mathbf{k}_n^2}{2m_e}\right) \psi_{\mathbf{k}_1}(\mathbf{r}_1)\bar{\psi}_{\mathbf{k}_1}(\mathbf{r}_2)\cdots\psi_{\mathbf{k}_{N_e/2}}(\mathbf{r}_{N_e-1})\bar{\psi}_{\mathbf{k}_{N_e/2}}(\mathbf{r}_{N_e}) \qquad (2.2.11)$$

$$= \sum_{n=1}^{N_e/2} 2\left(\frac{\hbar^2 \mathbf{k}_n^2}{2m_e}\right)\Psi$$

One sees that the energy is just the sum of kinetic energy $\sum_{n=1}^{N_e/2} 2\left(\frac{\hbar^2 \mathbf{k}_n^2}{2m_e}\right)$ in each spin-orbital of the product wave function. Let us now anti-symmetrize this product wave function. We do this by adding all products resulting from even permutations of the electrons and subtracting all odd permutation products. One convenient way to represent such a sum is using a determinant, called a Slater wave function:

$$\Psi = \frac{1}{\sqrt{N!}}\det\begin{bmatrix} \psi_{\mathbf{k}_1}(\mathbf{r}_1) & \cdots & \bar{\psi}_{\mathbf{k}_{N_e}}(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_{\mathbf{k}_1}\left(\mathbf{r}_{\frac{N_e}{2}}\right) & \cdots & \bar{\psi}_{\mathbf{k}_{N_e}}\left(\mathbf{r}_{\frac{N_e}{2}}\right) \end{bmatrix}. \qquad (2.2.12)$$

For this wave function to be minimal energy must fill 2 electrons per level starting from the lowest kinetic energy and going up until electrons are exhausted. Denote the highest filled level by $\mathbf{k}_F$. Then:

$$N_{filled} = \frac{V}{(2\pi)^3}\iiint \theta(k_F - k)d^3k. \qquad (2.2.13)$$

Where $\theta(x)$ is 0 if x is negative and 1 otherwise. This is called the Heaviside function. We now perform the integral using spherical coordinates:

$$N_{filled} = \frac{V}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 dk = \frac{Vk_F^3}{6\pi^2}. \qquad (2.2.14)$$

The number of filled orbitals is the product of the real-sapce volum V and the k-space occupied state volume, divided by $(2\pi)^3$. Since $N_e = 2N_{filled}$ and the density is $n = \frac{N_e}{V}$ we have:

$$n = \frac{2N_{filled}}{V} = \frac{k_F^3}{3\pi^2}. \tag{2.2.15}$$

The electron density determined directly the highest filled momentum state:

$$T_{TF}[n] = \frac{2V}{(2\pi)^3} \int_0^{k_F} \left(\frac{\hbar^2 k^2}{2m_e}\right) 4\pi k^2 dk = \frac{V\hbar^2}{10\pi^2 m_e} k_F^5$$

$$= \frac{\hbar^2}{10\pi^2 m_e} (3\pi^2)^{5/3} n^{5/3} V. \tag{2.2.16}$$

Define A by:

$$C = \frac{1}{2}(3\pi^2)^{2/3} E_h a_0^2 \tag{2.2.17}$$

Then:

$$T_{TF}[n] = \frac{3}{5} C n^{5/3} V. \tag{2.2.18}$$

Using $\frac{V}{N} = n$, the energy per particle is:

$$t_{TF}(n) = \frac{T_{TF}}{N} = \frac{3}{5} C n^{2/3}, \tag{2.2.19}$$

Plugging into Eq. (2.2.3), the Thomas-Fermi kinetic energy functional is obtained to be used in Eq. (2.2.1):

$$T_{TF}[n] = \frac{3}{5} C \int n(\boldsymbol{r})^{5/3} d^3 r. \tag{2.2.20}$$

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Exercise: The Thomas Fermi functional for the hydrogen atom.

   a. Repeat the calculation above but now for a "spin-polarized HEG". That is, do not assume that there are 2 electrons in each k-state (the "spin-unpolarized" case) but instead, that all spins are up and so there is only one electron per k-state.
   b. Since the electron in a hydrogen-like atom is spin-polarized, use the Thomas-Fermi KE functional derived in (a) and compare its estimation of the kinetic energy of the electron in a hydrogen-like atom to the exact value. Using the exact kinetic energy in the hydrogen atom (you can find it using the virial theorem), assess the quality of the result as a function of the nucleus charge Z.

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We thus find the Thomas-Fermi energy as:

$$E_{TF}[n] = T_{TF}[n] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d^3r + \frac{\kappa}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r' \qquad (2.2.21)$$

If we consider that $v_{ext}(\mathbf{r}) = -\kappa \int n_+(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d^3r'$ is the Coulomb potential from a given positive charge distribution $n_+(\mathbf{r})$ we have:

$$E_{TF}[n] = T_{TF}[n] - \kappa\iint \frac{n(\mathbf{r})n_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r' + \frac{\kappa}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r' \qquad (2.2.22)$$

It will be of value, when we consider atoms and molecules, to add the "repulsive" positive charge energy $\frac{\kappa}{2}\iint \frac{n_+(r)n_+(r')}{|r-r'|}d^3rd^3r'$. In this case, we will obtain a "total" energy functional (which still neglects the kinetic energy of the nuclei though):

$$E_{tot}[n; n_+] = T_{TF}[n] + \frac{\kappa}{2}\iint \frac{(n_+(\mathbf{r}) - n(\mathbf{r}))(n_+(\mathbf{r}') - n(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r' \qquad (2.2.23)$$

To obtain energies of atoms and molecules this energy functional must be minimized with respect to the electronic density (subject to a given electron number). We will do this in the next subsection. One thing we have to admit in this expression is that it treats the particles as smeared charges, which is not the correct physics. Also, the energy is manifestly positive, which is not what we think about when we consider stable materials. This is mainly because the expression in (2.2.23) includes the self repulsion energy of both positive and negative charge distributions. In real atoms and molecules each electron does not repel itself; also, nuclei do not repel themselves. Removing the nuclear self energy is not a big problem, if we think of $n_+(\mathbf{r}) = \sum_{i=1}^{M} n_{+i}(\mathbf{r})$ as composed of M non overlapping components $n_{+i}(\mathbf{r})n_{+j}(\mathbf{r}') = 0$ whenever $i \neq j$. In this case we can write:

$$E_{tot}[n; n_+] = T_{TF}[n] + U[n; n_+] \qquad (2.2.24)$$

Where

$$
\begin{aligned}
U[n; n_+] = {} & \frac{\kappa}{2} \iint \frac{\big(n_+(\mathbf{r}) - n(\mathbf{r})\big)\big(n_+(\mathbf{r}') - n(\mathbf{r}')\big)}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' \\
& - \sum_{i=1}^{M} \frac{\kappa}{2} \iint \frac{n_{+i}(\mathbf{r}) n_{+i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'
\end{aligned}
\qquad (2.2.25)
$$

Note that the last correction is just a constant and will not affect the minimizing electron density.

C. The virial Theorem for the Thomas−Fermi atom

The Thomas-Fermi theory enjoys some interesting scaling laws. Some of them, like the one we study here turn out to be valid in the exact Schrödinger equation. Others are unique to the theory and are correct only for infinitely heavy atoms.

The virial theorem in quantum mechanics is studied in detail in chapter XXX. Here we give only the details pertinent to TF theory. We consider the TF functional for an atom:

$$E_{TF}[n] = T_{TF}[n] + U[n] \qquad (2.3.1)$$

Where

$$U[n] = -\kappa \int \frac{Z}{r} n(\mathbf{r}) d^3 r + \frac{\kappa}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' \qquad (2.3.2)$$

Let us assume that $n(\mathbf{r}) \geq 0$ is the electron density which minimized the above functional, subject to $\int n(\mathbf{r}) d^3 r = N$ for some $N > 0$. Let us now scale this electronic density in the following way, using the scaling parameyter $\lambda > 0$:

$$n_\lambda(\boldsymbol{r}) = \lambda^3 n(\lambda \boldsymbol{r}) \tag{2.3.3}$$

Clearly, $\int n(\boldsymbol{r})d^3r = \int n_\lambda(\boldsymbol{r})d^3r$, so both charge distributions ascribe to the same number of electrons. Similarly it is straightforward to check that:

$$T_{TF}[n_\lambda] = \lambda^2 T_{TF}[n]$$

$$U[n_\lambda] = \lambda U[n] \tag{2.3.4}$$

Thus the TF energy changes as:

$$E_{TF}[n_\lambda] = \lambda^2 T_{TF}[n] + \lambda U[n] \tag{2.3.5}$$

Considering this as a function of λ we can take the derivative:

$$\frac{d}{d\lambda} E_{TF}[n_\lambda] = 2\lambda T_{TF}[n] + U[n]$$

Since $n_{\lambda=1}(\boldsymbol{r}) = n(\boldsymbol{r})$ minimizes E_{TF}, this derivative, evaluated at $\lambda = 1$ must be zero and so $-2T_{TF}[n] = U[n]$. Since, $E_{TF} = T_{TF} + U$ we find:

$$-T_{TF}[n] = \frac{1}{2}U[n] = E_{TF}[n] \quad (for\ atoms) \tag{2.3.6}$$

This relation is called the Virial Theorem for the TF atom. Interestingly, despite the fact that the TF theory for an atom is an gross approximation it obeys this virial relation which is identical in form to the exact quantum mechanical virial theorem, to be discussed later.

D. Minimization of the Thomas-Fermi energy: the Thomas Fermi equation

The TF philosophy is that the ground-state electron density should be determined by *minimizing $E_{TF}[n]$*, among all densities having the required number of electrons of N_e, so this is a constraint for the minimization:

$$\int n(\boldsymbol{r})d^3r = N_e \tag{2.4.1}$$

Thus, we must build a Lagrangian to be minimized as:

$$L[n, \lambda] = E_{TF}[n] - \mu \left[\int n(\mathbf{r}) d^3r - N_e \right] \qquad (2.4.2)$$

Minimizing this Lagrangian gives the Thomas-Fermi equation:

$$0 = \frac{\delta L}{\delta n(\mathbf{r})} = \frac{\delta E_{TF}}{\delta n(\mathbf{r})} - \mu \qquad (2.4.3)$$

We see that the Lagrange constant μ is the chemical potential, since it is equal to the change in energy when we perturb the density and this change is everywhere constant. The functional derivatives of (2.2.22) can be easily computed, and after plugging them into Eq.(2.4.3), the following equation is obtained:

$$\mu = Cn(\mathbf{r})^{2/3} + v_{ext}(\mathbf{r}) + \kappa \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r'. \qquad (2.4.4)$$

This is an integral equation for $n(\mathbf{r})$. It is called the integral Thomas-Fermi equation. The potential $v_{ext}(\mathbf{r})$ is due to the positive charge, hence we can write: $v_{ext}(\mathbf{r}) = -\kappa \int \frac{n_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'$, so we can define a *potential energy*

$$\phi(\mathbf{r}) = \mu + \kappa \int \frac{n_+(\mathbf{r}') - n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r', \qquad (2.4.5)$$

as the sum of the total electrostatic potential and the chemical potential. Since $\nabla^2 \frac{1}{r} = -4\pi\delta(\mathbf{r})$, this potential is the electrostatic potential obtained from the Poisson equation:

$$\nabla^2 \phi(\mathbf{r}) = 4\pi\kappa \big(n(\mathbf{r}) - n_+(\mathbf{r}) \big). \qquad (2.4.6)$$

On the other hand, plugging Eq. (2.4.5) in (2.4.4) gives:

$$\phi(\mathbf{r}) = Cn(\mathbf{r})^{2/3}. \qquad (2.4.7)$$

Thus, the potential energy ϕ obeys the equation:

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$$\nabla^2 \phi(\boldsymbol{r}) = 4\pi\kappa \left[\left(\frac{\phi(\boldsymbol{r})}{C} \right)^{3/2} - n_+(\boldsymbol{r}) \right] \qquad (2.4.8)$$

which is called the "differential **Thomas Fermi equation**". Once we solve for the potential we can reconstruct the density and the TF energy.

E. Physical meaning of the potential energy $\phi(r)$

We have introduced the TF potential energy $\phi(\boldsymbol{r})$ mainly as a device for obtaining an equation. However, as we show now it does indeed has a meaning of a potential, namely the potential governing the change in total energy when a change in the nuclear potential is made. Consider the total energy defined in (2.2.23) and consider a change in the positive charge $\delta n_+(\boldsymbol{r})$ such that the total charge is unchanged (that is we add or subtract electrons as needed). Thus we assume that $\int \delta n(\boldsymbol{r}) d^3 r = \int \delta n_+(\boldsymbol{r}) d^3 r$. The change in the total energy is:

$$\delta E_{tot}[n, n_+] = \int \left(\frac{\delta E_{TF}}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r}) + \frac{\delta E_{TF}}{\delta n_+(\boldsymbol{r})} \delta n_+(\boldsymbol{r}) \right) d^3 r$$

$$+ \kappa \iint \frac{n_+(\boldsymbol{r}) \delta n_+(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r d^3 r' \qquad (2.5.1)$$

Using Eq. (2.4.3), and $\frac{\delta E_{TF}}{\delta n_+(\boldsymbol{r})} = -\kappa \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3 r'$ and the fact that $\int \delta n(\boldsymbol{r}) d^3 r = \int \delta n_+(\boldsymbol{r}) d^3 r$ we have:

$$\delta E_{tot}[n, n_+] = \int \left(\mu + \kappa \int \frac{n_+(\boldsymbol{r}') - n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r' \right) \delta n_+(\boldsymbol{r}) d^3 r \qquad (2.5.2)$$

and thus from Eq. (2.4.5):

$$\delta E_{tot}[n, n_+] = \int \phi(\boldsymbol{r}) \delta n_+(\boldsymbol{r}) d^3 r \qquad (2.5.3)$$

We find that the potential energy $\phi(\boldsymbol{r})$ is that which determines the change in the total energy when the positive energy is changed, while the system

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remains neutral. Remember that $\phi(r)$ is non-negative for all r, so adding positive charge always increases the total energy.

F. Neutral systems under spherical symmetry

If n_+ is localized within a small radius R and spherical symmetric and contains total positive charge Z then for $r > R$

$$\phi(r) = \mu + \kappa \int \frac{n_+(r') - n(r')}{|r - r'|} d^3r' = \mu + \kappa \frac{Z}{r} - \kappa \int \frac{n(r')}{|r - r'|} d^3r' \qquad (2.6.1)$$

we expect $\phi(r)$ to be spherical symmetric and for $r > R$ there is no positive density so it must obey (see Eq. (2.4.8)):

$$\nabla^2 \phi(r) = 4\pi\kappa \left(\frac{\phi(r)}{C}\right)^{3/2} \qquad (2.6.2)$$

We consider only the neutral case, as for ions the solution must be cut off and requires additional technical issues. For a system with total electronic charge Z we assume the following asymptotic behavior:

$$\int \frac{n(r')}{|r - r'|} d^3r' \to \frac{Z}{r} + \frac{\alpha}{r^k} \qquad r \to \infty \qquad (2.6.3)$$

The term $\frac{\alpha}{r^k}$ is the first correction term after the monopole Coulomb potential. In order to determine α and k we plug in Eq. (2.6.1) and obtain the asymptotics of the potential:

$$\phi(r) = \mu + \kappa \frac{\alpha}{r^k} \qquad r \to \infty \qquad (2.6.4)$$

Finally, plugging into Eq. (2.6.2) we find the condition:

$$\nabla^2 \frac{\alpha}{r^k} = 4\pi \left(\frac{1}{C}\left(\mu + \kappa \frac{\alpha}{r^k}\right)\right)^{3/2} \qquad r \to \infty \qquad (2.6.5)$$

Using $\nabla^2 \psi(r) = \frac{1}{r}\left(r\psi(r)\right)''$ we find:

$$\frac{\alpha k(k-1)}{r^{k+2}} = 4\pi \left(\frac{1}{C}\right)^{3/2} \left(\mu + \kappa \frac{\alpha}{r^k}\right)^{3/2} \quad r \to \infty \tag{2.6.6}$$

Clearly, for this to be valid we must have $\mu = 0$ and by solving for k we find $k = 4$ and $\alpha = \frac{9}{\pi^2}\left(\frac{C}{\kappa}\right)^3$. Thus:

$$\phi(r) = \kappa \left(\frac{3}{\pi}\right)^2 \left(\frac{C}{\kappa}\right)^3 \frac{1}{r^4} \quad r \to \infty$$

$$n(r) = \left(\frac{3}{\pi}\frac{C}{\kappa}\right)^3 \frac{1}{r^6} \quad r \to \infty \tag{2.6.7}$$

We should note that a real system of electrons (in an atom for example) does not exhibit this density dependence. In fact the decay of the density is exponential and not polynomial. Thus, the TF theory exhibits spurious density decay. Note also that the density decay is unrelated to any details of the system since A is a universal constant. We note that for non-neutral systems the TF theory becomes more complicated. One then changes the chemical potential so as to make the potential ϕ negative in certain regions. The density usually determined from Eq. (2.4.7) is set to zero in those regions. μ is changed until the integral of the density is the required electron number N. It can be shown that this process can be done when $N < Z$ (cations) but not for $N > Z$ (anions). We will not treat the TF theory of ions further.

We will show in the next section that in order to describe a neutral atom in TF theory, we only need to solve the H atom. So, let us do this now. The nucleus is a point charge so $R \to 0$ and from Eq. (2.4.8) we simply need to solve

$$\nabla^2 \phi(r) = 4\pi\kappa \left[\left(\frac{\phi(r)}{C}\right)^{3/2} - \delta(r) \right] \tag{2.6.8}$$

In spherical coordinates we have:

$$\frac{1}{r}(r\phi(r))'' = 4\pi\kappa \left[\left(\frac{\phi(r)}{C} \right)^{3/2} - \delta(r) \right] \tag{2.6.9}$$

Multiplying by r^2 and integrating over r from 0 to a small ρ gives:

$$\rho^2 \phi'(\rho) = 4\pi\kappa \left(\frac{1}{C} \right)^{3/2} \int_0^\rho r^2 dr \phi(r)^{3/2} - \kappa \tag{2.6.10}$$

By plugging, it is evident that for $r \leq \rho$: $\phi(r) = \frac{\kappa}{r}$ or $\lim_{r \to 0} r\phi(r) = \kappa$ Thus, what we need to solve is:

$$\frac{1}{r}(r\phi(r))'' = 4\pi\kappa \left(\frac{\phi(r)}{C} \right)^{3/2}, \quad \lim_{r \to 0} r\phi(r) = \kappa \tag{2.6.11}$$

Exercise: By defining: $\frac{1}{\kappa} r\phi(r) = \psi(\alpha r)$ show that the following equation for $\psi(x)$ needs to be solved:

$$\psi''(x) = \frac{\psi(x)^{3/2}}{\sqrt{x}}, \quad \psi(0) = 1, \psi(x \to \infty) \to \frac{12^2}{x^3} \tag{2.6.12}$$

where

$$\alpha = (4\pi)^{2/3} \frac{\kappa}{C} \tag{2.6.13}$$

Exercise: The short range behavior of $\psi(x)$. Assume for small x $\psi(x) = 1 + ax^{1/2} + bx + cx^{3/2} + dx^2 + ex^{5/2}$ .... By inserting into the equation, show that:

$$\psi(x) = 1 + bx + \frac{4}{3}x^{3/2} + \frac{2}{5}bx^{5/2} + \cdots$$

The potential is $\phi(r) = (4\pi)^{2/3} \frac{\kappa^2}{C} \frac{\psi(x)}{x}$ thus the density is $n(r) = \frac{1}{4\pi} \alpha^3 \left(\frac{\psi(x)}{x} \right)^{3/2}$. The kinetic energy for the H atom in the TF approximation then becomes:

$$T_{TF}^H = \frac{3}{5}(4\pi)^{2/3} \frac{\kappa^2}{C} \int_0^\infty \frac{\psi(x)^{5/2}}{\sqrt{x}} dx \tag{2.6.14}$$

Exercise: Prove that:

$$\int_0^\infty \frac{\psi(x)^{5/2}}{\sqrt{x}} dx = -\frac{5}{7}\psi'(0) = -\frac{5}{7}b \qquad (2.6.15)$$

Solution: Prove by two processes of integration by parts that

$$\int_0^\infty \frac{\psi(x)^{5/2}}{\sqrt{x}} dx = -\psi'(0) - \int_0^\infty \psi'(x)^2 dx$$

Also prove by alternative integration by parts that:

$$\int_0^\infty \frac{\psi(x)^{5/2}}{\sqrt{x}} dx = \frac{5}{2}\int_0^\infty \psi'(x)^2 dx$$

Combine the two results to show that

$$\psi'(0) = \frac{7}{2}\int_0^\infty \psi'(x)^2 dx$$

From Eqs. (2.2.17), (2.6.14) and (2.6.15) we find:

$$T_{TF}^H = -\frac{6}{7}\left(\frac{4}{3\pi}\right)^{2/3} E_h b \qquad (2.6.16)$$

Since the left-hand side is positive we see that b must be negative. Taking the

virial theorem into account the H atom TF energy is $E^H = -T_{TF}^H = \frac{6}{7}\left(\frac{4}{3\pi}\right)^{2/3} E_h b$.

This expression depends on the single constant b which must be obtained

from an exact global solution of Eq. (2.6.12). Such a solution has been obtained

(Tal-Levy), giving $b = -1.5881$, from which

$$E^H = -0.7688 E_h$$

G. More scaling relations for TF theory

We have discussed the Virial theorem for the TF theory for the atom. Now we

will obtain more relations with some interesting consequences. Suppose the

potential $\phi(r)$ is the solution of the Thomas Fermi equation Eq. (2.4.8). Consider the family of potentials obtained by scaling this solution:

$$\phi_{\lambda,\alpha}(r) = \alpha\phi(\lambda r) \tag{2.7.1}$$

for some $\lambda, \alpha > 0$. The density of the positive charge can be reconstructed from this potential is also obtained from the Thomas-Fermi equation:

$$n_{+\lambda,\alpha}(r) \equiv \left[\frac{3}{5C_{TF}}\phi_{\lambda,\alpha}(r)\right]^{3/2} - \frac{1}{4\pi}\nabla^2\phi_{\lambda,\alpha}(r)$$

Now, since $\nabla^2\phi_{\lambda,\alpha}(r) = \alpha\lambda^2(\nabla^2\phi)(\lambda r)$ we can write:

$$n_{+\lambda,\alpha}(r) = \left[\frac{3}{5C_{TF}}\alpha\phi(\lambda r)\right]^{3/2} - \frac{1}{4\pi}\alpha\lambda^2(\nabla^2\phi)(\lambda r)$$

Using Eq. (2.4.8) once more gives the following expression:

$$n_{+\lambda,\alpha}(r) = \left[\frac{3}{5C_{TF}}\phi(\lambda r)\right]^{3/2}\alpha\left(\alpha^{1/2} - \lambda^2\right) + \alpha\lambda^2 n_+(\lambda r).$$

Choosing $\alpha = \lambda^4$ eliminates the first term and we are left with:

$$n_{\lambda+}(r) = \lambda^6 n_+(\lambda r) \tag{2.7.2}$$

And this density creates the potential of (2.7.1):

$$\phi_\lambda(r) = \lambda^4 \phi(\lambda r) \tag{2.7.3}$$

Since $\lambda^3 n_+(\lambda r)$ has the same charge as $n_+(r)$ we see that the family of TF systems thus generated involves

1) Multiplication of the total positive charge by λ^3 and
2) Simultaneously scaling the distances by λ.
3) The result is a potential which is the scaled potential but multiplied by λ^4

It is straightforward to check that the negative charge density which solves the TF equations behaves similarly to the positive charge, i.e. from Eq. (2.4.7): $n_\lambda(r) = \lambda^6 n(\lambda r)$. From this one can check that the TF kinetic energy scales as

$T_{TF}[n_\lambda] = \lambda^7 T_{TF}[n]$ and a similarly relation holds for the potential energy. Thus, the total energy, minimizing the TF functional scales as:

$$E_{tot}[n_\lambda, n_{+\lambda}] = \lambda^7 E_{tot}[n, n_+] \qquad (2.7.4)$$

Suppose our system is an atom of total positive charge $n_+(\boldsymbol{r}) = Z\delta(\boldsymbol{r})$. We can now transform to the Hydrogen atom, by taking $\lambda = Z^{-1/3}$ system, $n_+^H(\boldsymbol{r}) = \delta(\boldsymbol{r})$. The energy will be denoted by E^H. Then for charge Z one has:

$$n^Z(\boldsymbol{r}) = Z^2 n^H(Z^{1/3}\boldsymbol{r})$$

$$n_+^Z(\boldsymbol{r}) = Z^2 n_+^H(Z^{1/3}\boldsymbol{r}) \qquad (2.7.5)$$

$$E^Z = E^H Z^{7/3} = -0.7688 Z^{7/3}$$

Thus, in TF theory, determining E^H for the H atom, as we did in the previous subsection, allows to determine of all the energies of any other atom. Interestingly, the dependence of the energy on Z, as $Z^{7/3}$ was also found from our crude statistical model in subsection A. The main difference is in the value of E^H which was very small in the crude limit. When the Hartree-Fock method is used to estimate the total energy $E(Z)$ of rare gas atoms with Z electrons, the results of $Z^{-7/3}E(Z)$ is plotted in the following graph.
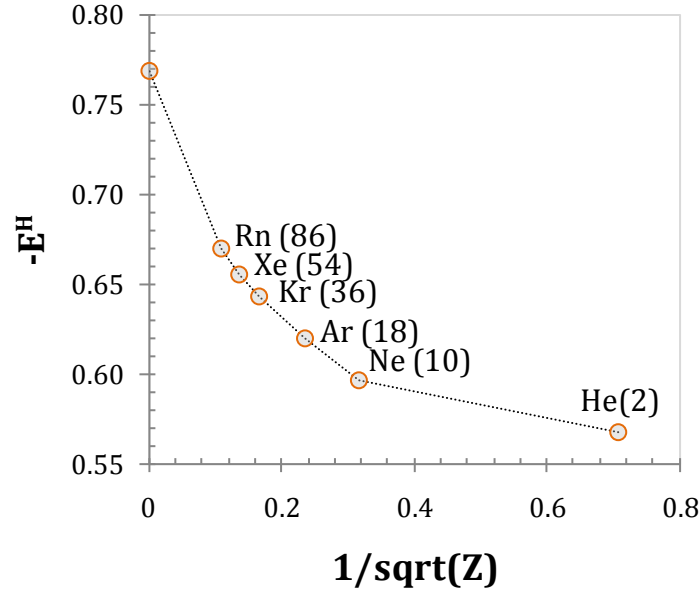
Figure 1: The Hartree-Fock $-E^H \equiv -E_{HF}(Z)Z^{-7/3}$ as a function of Z for rare gas atoms. The horizontal axis depicts $1/\sqrt{Z}$ for convenience. The $1/\sqrt{Z} = 0$ is the Thomas Fermi $-E^H = 0.7688$.

The energy of the TF atom has a consequence for exact energies of real atoms, which is supposed to be determined by the exact solutions of the Schrödinger equation. This was first discussed by by Lieb and Simon[3]. They considered the Schrödinger equation for Z electrons in the presence of M static nuclei located at $Z_i^{-1/3} \boldsymbol{R}_i$ ($i = 1, .., M$) each having a charge $Z_i = Z f_i$ where $f_i > 0$ and $\sum_i f_i = 1$. If $n_{SE}^Z(\boldsymbol{r})$ is the exact electronic density of ground state and E_{SE}^Z its exact total energy (including the nuclei) then in the limit that $Z \to \infty$ they find:

$$\frac{1}{Z^2} n_{SE}^Z\big(Z^{-1/3}r\big) \to n^1(r) \quad r < fixed\ R$$

$$Z^{-7/3} E_{SE}^Z \to E^1$$

(2.7.6)

Thus, for large Z the Schrödinger atom and the TF atom have the same energy and the "same" density. The last sentence has to be qualified since we must keep R fixed. Essentially, this means that the TF theory describes the core and mantle of the infinite Z atom, while the valence electrons are not described.

Since the majority of electrons are core and mantle we do get the correct energy. What we do not get is chemistry. We do not get binding…

H. Teller's Lemma and the instability of molecules in TF theory

Teller [4] proved the following Lemma:

If one makes a positive change $\delta n_+(\boldsymbol{r}_0) > 0$ in the positive density at some point $\boldsymbol{r}_0$, keeping the system neutral by adding the corresponding amount of electrons, then the change $\delta\phi(\boldsymbol{r})$ in the potential is positive *everywhere*.

Proof: This relies on the fact that $\delta\phi(\boldsymbol{r})$ always has the <u>same sign</u> as $\delta n(\boldsymbol{r})$. (This is immediate from the relation $\delta\phi(\boldsymbol{r}) = \left(\frac{10}{9}\frac{C_{TF}}{n(r)^{\frac{1}{3}}}\right)\delta n(\boldsymbol{r})$).

Now consider the point $\boldsymbol{r}_0$. Since we added some positive charge there and also added some electronic charge the electron density there must have increased there, i.e $\delta n(\boldsymbol{r}_0) > 0$. Hence $\delta\phi(\boldsymbol{r}_0) > 0$. Now we show a contradiction arises if we suppose the theorem is violated. Indeed, if there is a volume V away from $\boldsymbol{r}_0$ inside which $\delta\phi(\boldsymbol{r}) < 0$. This volume can be encircled by a surface S on which $\delta\phi(\boldsymbol{r}) = 0$. Inside V we have:

1) Since $\delta n(\boldsymbol{r})$ and $\delta\phi(\boldsymbol{r})$ have same sign it too is negative.
2) From Eq. (2.4.6) $\nabla^2\delta\phi = 4\pi\delta n(\boldsymbol{r})$, integrating over V and using Gauss' theorem yields: $\oiint_S \nabla\delta\phi(\boldsymbol{r})\cdot\hat{s}d^2r = \iiint_V \delta n(\boldsymbol{r})d^3r$
3) Because $\delta\phi$ is negative inside V and zero on its boundary S the gradient $\nabla\delta\phi$ must point outward, i.e. $\nabla\delta\phi\cdot\hat{s} > 0$ on S.

Now from 1) and 2) $\oiint_S \nabla\delta\phi(\boldsymbol{r})\cdot\hat{s}d^2r < 0$ in contradiction to 3). QED.

Based on this lemma Teller discovered that TF theory cannot stabilize molecules. Remember that the work to build an atom by adding δn_+ to the positive core (and simultaneously compensating by electronic charge δq) involves investment of energy $\int \phi\delta n_+$ (Eq. (2.5.3)). Now, when the atom is

built in the presence of another atom, Teller's Lemma shows that $\phi(r)$ is always larger than when it is built in solitude. Thus the energy invested in building the atom in the presence of another atom is larger than the energy invested in building the atom in solitude. This shows that the energy of distant atoms is smaller than the energy of nearby atoms.

I. Absence of shell structure in TF description of atomic densities

TF theory gives a smoothed value for the atomic density, not showing the shell structure. This is exemplified in the following figure, where the radial density of HF theory and TFD (Thomas-Fermi-Dirac) theory.
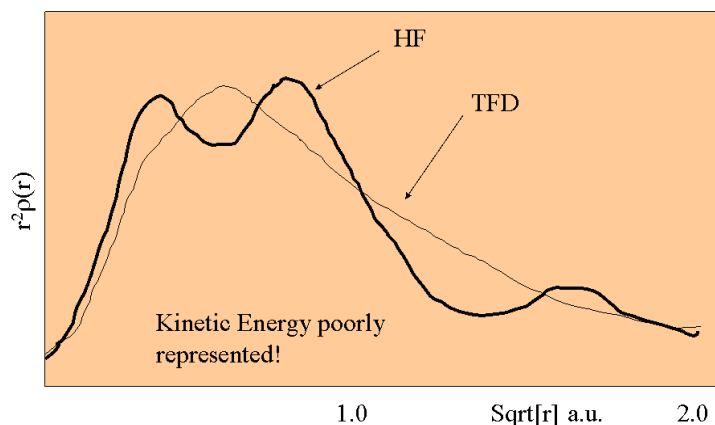
There is a question of how does the minimal energy of the Thomas Fermi functional compare with the accurate quantum mechanical energy. This question has been examined. It was found that for atoms with $Z \to \infty$ we have:

$$\lim_{z \to \infty} \frac{E_{TF}(N = \lambda Z)}{E_{exact}(N = \lambda Z)} = 1 \tag{2.9.1}$$

For $0 < \lambda < 1$ (i.e. the number of electrons is smaller than that of the protons and $\frac{N}{Z}$ is held while $Z \to \infty$). Note that the Thomas Fermi energy for an atom has the property that:

$$E_{atom}^{TF}(\lambda, Z) = Z^{7/3} E_{atom}^{TF}(\lambda, 1) \tag{2.9.2}$$

J. Some relations between the various energies

If we multiply Eq. (2.4.4) by $n(\boldsymbol{r})$ and integrate we obtain $N\mu = \frac{5}{3}T + V_{ext} + 2E_H$ and so:

$$E_{TF} = N\mu - \frac{2}{3}T - E_H \tag{2.10.1}$$

Using $T = E_{TF} - V - E_H$ we have:

$$E_{TF} = \frac{3}{5}N\mu + \frac{2}{5}V - \frac{1}{5}E_H \tag{2.10.2}$$

K. Thomas-Fermi Screening

When a point impurity Ze is inserted into an electronic system, it pulls (Z positive) or repels (Z negative) electrons towards it. This has an effect that the impurity is partially screened by opposite charge and so it has a smaller effect on distant charges. Let us study this phenomenon in the electron gas, using Thomas-Fermi theory. The homogeneous gas of electrons is a model for ideal metals, so the screening effect we address here is relevant for many metallic systems. Macroscopically, the "free" metal electrons completely screen the charged impurity. However microscopically, perfect screening is not possible because electrons have kinetic energy – even at zero temperature – and a short ranged electric field develops around the impurity. Thomas Fermi theory takes kinetic energy effects into account and can be used to estimate the form of the local electric field, specifically its size or length scale.

Let us study an unperturbed homogeneous electron gas using Thomas-Fermi theory. Such a "gas" has no structure and it is characterized by only one parameter: its density n_0. In order to neutralize it and support the electron

homogeneity, we add positive smeared homogeneous charge density $+en_0$. All the Coulomb energies (e-e, e-N and N-N) cancel exactly so the only energy left is the electronic kinetic energy:

$$E_{TF}[n_0] = \int C_{TF} n_0(\boldsymbol{r})^{5/3} d^3 r \qquad (2.11.1)$$

The constraint minimization of this functional yields the following condition, relating the density to the chemical potential:

$$\mu = \frac{\delta E_{TF}}{\delta n_0(\boldsymbol{r})} = \frac{5}{3} C_{TF} n_0(\boldsymbol{r})^{2/3} \qquad (2.11.2)$$

Comparing with Eq. (2.2.15), and using Eq. (2.2.18) we find for the chemical potential:

$$\mu = \frac{\delta E_{TF}}{\delta n_0(\boldsymbol{r})} = \frac{5}{3} C_{TF} \left(\frac{k_F^3}{3\pi^2} \right)^{2/3} = \frac{\hbar^2 k_F^2}{2m_e} \qquad (2.11.3)$$

Thus we see that indeed the electron density is constant and the chemical potential is equal to the kinetic energy corresponding to the maximal occupied momentum $\hbar k_F$.

Now we introduce a positive charge Ze. The density of electrons is changed:

$$n(\boldsymbol{r}) = n_0 + n_1(\boldsymbol{r}) \qquad (2.11.4)$$

It is physically clear that $n_1(\boldsymbol{r})$ is localized around the impurity (assumed at the origin). We therefore have for the total energy of the system in terms of n_1:

$$E_{TF}[n_1] = \int C_{TF} \big(n_0 + n_1(\boldsymbol{r}) \big)^{5/3} d^3 r - \int \frac{Ze^2 n_1(\boldsymbol{r})}{r} d^3 r$$
$$+ \frac{e^2}{2} \iint \frac{n_1(\boldsymbol{r}) n_1(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r d^3 r' \qquad (2.11.5)$$

The corresponding TF equation comes from minimizing:

$$\mu = \frac{\delta E_{TF}}{\delta n_1(\boldsymbol{r})} = \frac{5}{3} C_{TF} \big(n_0 + n_1(\boldsymbol{r})\big)^{2/3} - \frac{Ze^2}{r} + e^2 \int \frac{n_1(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r' \qquad (2.11.6)$$

We write: $\phi(\boldsymbol{r}) = e \int \frac{n_1(\boldsymbol{r}')}{|r-r'|} d^3 r'$ and so:

$$\mu = \frac{\delta E_{TF}}{\delta n_1(\boldsymbol{r})} = \frac{5}{3} C_{TF} \big(n_0 + n_1(\boldsymbol{r})\big)^{\frac{2}{3}} - \frac{Ze^2}{r} + e\phi(\boldsymbol{r}) \qquad (2.11.7)$$

Upon linearizing, assuming $n_1 \ll n_0$:

$$\frac{5}{3} C_{TF} n_0^{2/3} \left(1 + \frac{2}{3} \frac{n_1}{n_0}\right) - \frac{Ze^2}{r} + e\phi(\boldsymbol{r}) = \mu \qquad (2.11.8)$$

We can write: $\frac{5}{3} C_{TF} n_0^{2/3} = \mu_0$ and so:

$$\frac{10}{9} C_{TF} n_0^{-1/3} n_1 - \frac{Ze^2}{r} + e\phi(\boldsymbol{r}) = \mu - \mu_0 \qquad (2.11.9)$$

Finally since $\nabla^2 \phi = -4\pi e n_1$ we have:

$$-\frac{10}{9} \frac{1}{4\pi e^2} n_0^{-1/3} C_{TF} \nabla^2 \phi - \frac{Ze}{r} + \phi(\boldsymbol{r}) = \frac{\mu - \mu_0}{e} \qquad (2.11.10)$$

We have from Eq. (2.2.15) $k_F = (3\pi^2 n_0)^{\frac{1}{3}}$ and we use the definition of the Bohr radius $a_0 = -\frac{\hbar^2}{m_e e^2}$, defining the Thomas Fermi screening parameter k_{TF}:

$$\frac{10}{9} \frac{1}{4\pi e^2} n_0^{-1/3} C_{TF} = \frac{\pi a_0}{4 k_F} \equiv \frac{1}{k_{TF}^2} \qquad (2.11.11)$$

With this we have the equation:

$$\nabla^2 \phi = k_{TF}^2 \left(\phi(\boldsymbol{r}) - \frac{Ze}{r} - \frac{\mu - \mu_0}{e}\right) \qquad (2.11.12)$$

Passing to spherical coordinates we find:

$$\frac{1}{r} \big(r\phi(\boldsymbol{r})\big)'' = k_{TF}^2 \left(\phi(\boldsymbol{r}) - \frac{Ze}{r} - \Delta\mu\right). \qquad (2.11.13)$$

Defining $\chi = r\phi$ we find:

$$\chi'' = k_{TF}^2(\chi - Ze - \Delta\mu r) \tag{2.11.14}$$

The homogeneous equation is $\chi'' = k_{TF}^2\chi$ which has the solution $\chi_H = Ae^{-k_{TF}r} + Be^{k_{TF}r}$. Clearly, for a localized potential solution we must take $B = 0$. To this we need add *any* solution of the inhomogeneous equation which clearly is $\chi_{IH} = Ze + \Delta\mu r$. Thus:

$$\chi = Ae^{-k_{TF}r} + Ze + \Delta\mu r \tag{2.11.15}$$

This leads to:

$$\phi = \frac{Ae^{-k_{TF}r}}{r} + \frac{Ze}{r} + \Delta\mu \tag{2.11.16}$$

In the limit that $r \to 0$ we must have $r\phi(r) \to 0$ since the electronic charge n_1 has no cusps. Thus $A = -Ze$. The total electrostatic potential is

$$\phi_{tot}(r) = \phi(r) - \frac{Ze}{r} = \frac{-Ze}{r}e^{-k_{TF}r} + \Delta\mu \tag{2.11.17}$$

Aside from the constant $\Delta\mu$, far from the impurity the surface integral of $\nabla\phi_{tot}$ evaluates to zero and by Gauss's theorem a large sphere around the impurity includes zero charge in it, meaning that the total amount of electronic charge pulled into the sphere is exactly equal to that of the impurity (Z).

It is interesting that the screening length is proportional to $k_F^{-1/2}$ or to $n_0^{-1/6}$. The higher the density the smaller the length, i.e. the more efficient is the screening, however, the dependence on n_0 is mild because of the small exponent. It is also interesting to note that k_{TF} is independent of Z. However, this latter results holds only in so far as our linearization is valid. For strong impurities the non-linear equation will give a different result and the screening will depend on Z.

L. Von Weizsäcker kinetic energy

The Thomas Fermi kinetic energy density functional is exact in the limit of non-interacting homogeneous gas of electrons in an infinite box. We would like to mention here another density functional which is exact in a certain limit, i.e the limit of a single electron. In this case the kinetic energy is: $T = \int \psi(\boldsymbol{r}) \left(-\frac{\hbar^2}{2\mu_e} \nabla^2 \right) \psi(\boldsymbol{r}) d^3r$. For wave functions that decay to zero at $r \to \infty$, one can integrate by parts and obtain $T = \frac{\hbar^2}{2\mu_e} \int \left(\nabla \psi(\boldsymbol{r}) \right)^2 d^3r$, stressing the absolute positivity of kinetic energy (it cannot be zero). Finally, if $\psi(\boldsymbol{r})$ is a non-degenerate ground-state it can be written as $\psi(\boldsymbol{r}) = \sqrt{n(\boldsymbol{r})}$ and so we obtain the kinetic energy functional of von Weizsäcker:

$$T_{vW}[n] = \frac{\hbar^2}{2\mu_e} \int \left(\nabla \sqrt{n(\boldsymbol{r})} \right)^2 d^3r \tag{2.12.1}$$

Which can be written as follows, using local wave vector:

$$\boldsymbol{k}(\boldsymbol{r}) \equiv \frac{1}{2} \frac{\nabla n(\boldsymbol{r})}{n(\boldsymbol{r})} \tag{2.12.2}$$

So:

$$T_{vW}[n] = \int \frac{\hbar^2 \boldsymbol{k}(\boldsymbol{r})^2}{2\mu_e} n(\boldsymbol{r}) d^3r \tag{2.12.3}$$

This functional is now used for any density, even a many electron one. The variation is:

$$\delta T_{vW} = \frac{\hbar^2}{8\mu_e} \int \left(\frac{\left(\nabla \big(n(\boldsymbol{r}') + \epsilon \Phi(\boldsymbol{r}') \big) \right)^2}{n(\boldsymbol{r}') + \epsilon \Phi(\boldsymbol{r}')} - \frac{\left(\nabla \big(n(\boldsymbol{r}') \big) \right)^2}{n(\boldsymbol{r}')} \right) d^3r' \tag{2.12.4}$$

Working this out to linear terms in ϵ, using: $\left(n(\boldsymbol{r}') + \epsilon \Phi(\boldsymbol{r}') \right)^{-1} \approx n(\boldsymbol{r}')^{-1} \left(1 - \epsilon \Phi\boldsymbol{r}' n\boldsymbol{r}' \right)$ we obtain:

$$\delta T_{vW} = \frac{\hbar^2}{8\mu_e} \epsilon \int \left(\frac{2\nabla n(\mathbf{r}') \cdot \nabla \Phi(\mathbf{r}')}{n(\mathbf{r}')} - \left(\nabla(n(\mathbf{r}')) \right)^2 \frac{\Phi(\mathbf{r}')}{n(\mathbf{r}')^2} \right) d^3 r' \qquad (2.12.5)$$

Which after integration by parts of the first term finally gives:

$$\delta T_{vW} = \frac{\hbar^2}{8\mu_e} \epsilon \int \left(-2\nabla \cdot \left(\frac{\nabla n(\mathbf{r}')}{n(\mathbf{r}')} \right) - \left(\frac{\nabla(n(\mathbf{r}'))}{n(\mathbf{r}')} \right)^2 \right) \Phi(\mathbf{r}') d^3 r' \qquad (2.12.6)$$

Thus the von-Weizsäcker potential is:

$$v_{vW}(\mathbf{r}) = -\frac{\hbar^2}{8\mu_e} \left(2\nabla \cdot \left(\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} \right) + \left(\frac{\nabla(n(\mathbf{r}))}{n(\mathbf{r})} \right)^2 \right) \qquad (2.12.7)$$

Which can be written more compactly as:

$$v_{vW}(\mathbf{r}) = -\frac{\hbar^2}{2\mu_e} [\nabla \cdot \mathbf{k}(\mathbf{r}) + k(\mathbf{r})^2] \qquad (2.12.8)$$

Exercise: For 1-electron system, discuss the claims: 1) The wave vector $\mathbf{k}(\mathbf{r})$ is the gradient of the log of the of the wavefunction: $\mathbf{k}(\mathbf{r}) = \nabla \log \psi(\mathbf{r})$ (2) the von Weizsäcker potential is the potential for which $n(\mathbf{r})$ is the ground state density.

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