

Thomas Fermi Atoms

If a many electron atom has many (more than a few) electrons, it might seem reasonable to treat them with statistical methods. Such a method has indeed been developed by Thomas and Fermi and allows for the calculation of some simple properties of many electron atoms and ions, e.g. the ionization energy and the polarizability.

It is based on the assumption that the electrons in a many electron atom feel a constant potential over their wavelength and, thus, may be approximated by a local plane wave. Their density and Fermi energy, however, will depend on the coordinate \mathbf{r} .

Let $n(\mathbf{r})$ be the density of the electron gas in the field of a nucleus with nuclear charge Z . The approximate energy of this gas is:

$$E[n] = \frac{3\gamma}{5} \int d^3\mathbf{r} n^{\frac{5}{3}}(\mathbf{r}) - Z\alpha \int d^3\mathbf{r} \frac{n(\mathbf{r})}{r} + \frac{\alpha}{2} \iint d^3\mathbf{r} d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where $\gamma = (3\pi^2)^{\frac{2}{3}} \frac{1}{2m_e}$. Now we want to find the electron density that minimizes the energy of the electron gas with the side condition

$$\int d^3\mathbf{r} n(\mathbf{r}) = N, \quad (2)$$

where N is the number of electrons. This gives us the following Lagrange functional to be minimized:

$$\mathcal{L}[n, \mu] = E[n] - \mu \left(\int d^3\mathbf{r} n(\mathbf{r}) - N \right) \quad (3)$$

and thus

$$\frac{\delta}{\delta n} \mathcal{L}[n, \mu] = \int d^3\mathbf{r} \delta n(\mathbf{r}) \left[\gamma n^{\frac{2}{3}}(\mathbf{r}) - \frac{Z\alpha}{r} + \alpha \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \mu \right] = 0. \quad (4)$$

Since this has to be fulfilled for all variations $\delta n(\mathbf{r})$, we get the Thomas-Fermi-Equation for the electron density $n(\mathbf{r})$ that minimizes the energy

$$\gamma n^{\frac{2}{3}}(\mathbf{r}) - \frac{Z\alpha}{r} + \alpha \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \mu. \quad (5)$$

The first term in this equation is the Fermi energy of the electron, the second one is the Coulomb energy and the last term is the Coulomb interaction with the mean field

of the other electrons. Thus $\mu = -e\phi_0$ is the total energy of one electron. With the Thomas-Fermi-Potential

$$\phi(\mathbf{r}) = \frac{Z\sqrt{\alpha}}{r} - \sqrt{\alpha} \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

we get the simple form of Eq. (5):

$$\gamma n^{\frac{2}{3}}(\mathbf{r}) = \sqrt{\alpha}(\phi(\mathbf{r}) - \phi_0). \quad (7)$$

We see that the electron density vanishes for $\phi(\mathbf{r}) = \phi_0$, thus, this defines the border of the atom. Moreover we set $n(\mathbf{r}) = 0$ for $\phi_0 > \phi(\mathbf{r})$. Neutral atoms have no potential outside, i.e. $\phi_0 = 0$, while for Ions $\phi_0 \neq 0$. The Thomas-Fermi-Potential (6) fullfills the Poisson equation

$$\Delta\phi(\mathbf{r}) = -4\pi\sqrt{\alpha} (Z\delta^{(3)}(\mathbf{r}) - n(\mathbf{r})) \stackrel{\mathbf{r} \neq \mathbf{0}}{=} 4\pi\sqrt{\alpha}n(\mathbf{r}). \quad (8)$$

Using Eq. (7) we obtain:

$$\Delta\phi(\mathbf{r}) = 4\pi\sqrt{\alpha} \left(\frac{\sqrt{\alpha}(\phi(\mathbf{r}) - \phi_0)}{\gamma} \right)^{\frac{3}{2}}. \quad (9)$$

We seek now radially symmetric solutions of this equation of the form

$$\phi(r) = \frac{Z\sqrt{\alpha}}{r} \chi(r), \quad (10)$$

where $\chi(r)$ is the screening of the nuclear potential by the electron cloud. For a neutral atom we immediately obtain

$$\frac{Z\sqrt{\alpha}}{r} \chi''(r) = 4\pi\sqrt{\alpha} \left(\frac{Z\sqrt{\alpha}}{\gamma r} \chi(r) \right)^{\frac{3}{2}}. \quad (11)$$

By rescaling the radial coordinate $r = \frac{1}{2m_e\alpha} \left(\frac{3\pi}{4}\right)^{\frac{2}{3}} Z^{-\frac{1}{3}} s$, we get the universal equation for $\chi(r)$:

$$\frac{d^2}{ds^2} \chi(s) = s^{-\frac{1}{2}} \chi^{\frac{3}{2}}(s). \quad (12)$$

For small radii the nucleus is not screened and therefore $\chi(0) = 1$, while for large radii χ has to vanish. Eq. (12) has to be solved numerically; we can only give an asymptotiv behaviour:

$$\chi(s) \approx \frac{144}{s^3} \quad \text{for} \quad s \rightarrow \infty \quad (13a)$$

$$\chi(s) \approx 1 - 1.59s + \frac{4}{3}s^{\frac{3}{2}} \quad \text{for} \quad s \rightarrow 0. \quad (13b)$$

With this we can obtain $\chi(s)$ once, all the atomic properties are contained in the variable s . The solutions of the Dirac-Equation with this potential will have the hydrogenic degeneracy in l lifted, because the potential is not coulombic anymore.

We make, however a very obvious mistake here. The electron-electron interaction is written as

$$V_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{\alpha}{r_{ij}} \quad (14)$$

or for the case of charge densities

$$V_{ee} = \frac{1}{2} \sum_{i \neq j} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\alpha n_i(\mathbf{r}) n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (15)$$

However we only consider a mean charge density $n(\mathbf{r})$ instead of a charge density for each electron. Therefore we also account for the interaction of the electrons with themselves. One possibility to circumvent this problem has been developed by Fock and is discussed in the next chapter.

Hartree-Fock-Approximation

The Hartree-Fock method is an approximation technique to determine the ground state of a many-body quantum system. It is based on the Rayleigh-Ritz variational principle. Let us recall this method by considering the expectation value of the Hamilton operator \hat{H} with respect to a normalized state $|\psi\rangle$ as a functional of $|\psi\rangle$:

$$E[\psi] = \langle \psi | \hat{H} | \psi \rangle. \quad (16)$$

The wavefunction ψ_{min} that minimizes the energy functional, per definition, is the ground state of the system. The difficulty with the variational principle is to find a proper set of trial states. The Hartree-Fock method is based on the assumption that the ground state of a many-body system can be sufficiently approximated by a product state of single-particle states. In general this assumption is not valid. For the Th^+ ion, for example, it is still disputed wih single-electron configuration assembles the ground state. For other systems, however, the Hartree-Fock method can work pretty well.

For a fermionic many-body system, the trial state is a Slater determinant

$$\psi_{SD}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, m_1, m_2, \dots, m_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, m_1) & \phi_1(\mathbf{r}_2, m_2) & \dots & \phi_1(\mathbf{r}_N, m_N) \\ \phi_2(\mathbf{r}_1, m_1) & \phi_2(\mathbf{r}_2, m_2) & \dots & \phi_2(\mathbf{r}_N, m_N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_n(\mathbf{r}_1, m_1) & \phi_n(\mathbf{r}_2, m_2) & \dots & \phi_n(\mathbf{r}_N, m_N) \end{vmatrix}, \quad (17)$$

where the functions $\phi_i(\mathbf{r}_j)$ are the orthonormal single-particle wavefunctions.

Hartree-Fock method for a many-electron atom

The Hamiltonian for a many-electron atom is

$$\hat{H} = \sum_{i=1}^N \frac{\hat{\mathbf{p}}^2}{2m_e} - \sum_{i=1}^N \frac{Z\alpha}{r} + \frac{\alpha}{2} \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (18)$$

It is easily seen that the expectation value of a one-particle operator, such as the kinetic and Coulomb energies with respect to the Slater determinant reduce to the sum of expectation values of each one-electron wavefunction

$$\langle \psi_{SD} | \sum_{i=1}^N \frac{\hat{\mathbf{p}}^2}{2m_e} | \psi_{SD} \rangle = \frac{1}{2m_e} \sum_{i=1}^N \sum_m \int d^3\mathbf{r} |\nabla \phi_i(\mathbf{r}, m)|^2 \quad (19)$$

and

$$\langle \psi_{SD} | - \sum_{i=1}^N \frac{Z\alpha}{r} | \psi_{SD} \rangle = - \frac{Z\alpha}{2m_e} \sum_{i=1}^N \sum_m \int d^3\mathbf{r} \frac{|\phi_i(\mathbf{r}, m)|^2}{r}. \quad (20)$$

In order to get the expectation value of the electron-electron interaction, let us rewrite the Slater determinant

$$\begin{aligned} \psi_{SD}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, m_1, m_2, \dots, m_N) = \\ \frac{1}{\sqrt{N!}} \sum_{\Pi} \text{sign}(\Pi) \phi_{\Pi(1)}(\mathbf{r}_1, m_1) \phi_{\Pi(2)}(\mathbf{r}_2, m_2) \dots \phi_{\Pi(N)}(\mathbf{r}_N, m_N). \end{aligned} \quad (21)$$

The two-particle operator r_{ij} in Eq. (18) now acts on the single-electron wavefunctions that depend on either \mathbf{r}_i or \mathbf{r}_j , i.e.

$$\begin{aligned} \langle \psi_{SD} | \frac{\alpha}{2} \sum_{i \neq j} \frac{1}{r_{ij}} | \psi_{SD} \rangle = \frac{\alpha}{2} \frac{(N-2)!}{N!} \sum_{p \neq q} \sum_{mm'} \sum_{i \neq j} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\ \times \left[\phi_q^\dagger(\mathbf{r}', m') \phi_p^\dagger(\mathbf{r}, m) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_p(\mathbf{r}, m) \phi_q(\mathbf{r}', m') \right. \\ \left. - \phi_p^\dagger(\mathbf{r}', m') \phi_q^\dagger(\mathbf{r}, m) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_q(\mathbf{r}, m) \phi_p(\mathbf{r}', m') \right]. \end{aligned} \quad (22)$$

Since all terms depend trivially on the spin state m , we define a mean kinetic energy and charge density of the i 'th single-electron state:

$$t_i(\mathbf{r}) = \frac{1}{2m} \sum_m |\nabla \phi_i(\mathbf{r}, m)|^2 \quad (23a)$$

$$n_i(\mathbf{r}) = \sum_m |\phi_i(\mathbf{r}, m)|^2. \quad (23b)$$

With these abbreviations we can write the expectation value of the Hamiltonian (18):

$$\langle \psi | \hat{H} | \psi \rangle = \sum_i \int d^3\mathbf{r} \left[t_i(\mathbf{r}) - Z\alpha \frac{n_i(\mathbf{r})}{r} \right] + \frac{\alpha}{2} \sum_{i \neq j} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n_i(\mathbf{r}) n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - A, \quad (24)$$

where A is the exchange energy

$$A = \frac{\alpha}{2} \sum_{i \neq j} \sum_{mm'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\phi_j^\dagger(\mathbf{r}, m) \phi_j(\mathbf{r}', m') \phi_i^\dagger(\mathbf{r}', m') \phi_j(\mathbf{r}, m)}{|\mathbf{r} - \mathbf{r}'|}. \quad (25)$$

While the first three terms are easily interpreted classically, the last term solely comes from the quantum nature of the system and the indistinguishability of identical particles. Finally $E[\psi_{SD}]$ has to be minimized under the constraint that the ψ_{SD} are orthonormal. The variation yields

$$\delta \langle \psi_{SD} | \hat{H} | \psi_{SD} \rangle = 2(\delta \langle \psi_{SD} |) \hat{H} | \psi_{SD} \rangle \quad (26)$$

and thus

$$\begin{aligned} \delta \langle \psi_{SD} | \hat{H} | \psi_{SD} \rangle = \sum_{i,m} \int d^3\mathbf{r} \delta \phi^\dagger(\mathbf{r}, m) & \left[\left(-\frac{1}{2m_e} \nabla^2 - \frac{Z\alpha}{r} + \alpha \sum_{i \neq j} \int d^3\mathbf{r}' \frac{n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \phi_i(\mathbf{r}, m) \right. \\ & \left. - \alpha \sum_{i \neq j, m'} \int d^3\mathbf{r}' \frac{\phi_i(\mathbf{r}', m') \phi_j^\dagger(\mathbf{r}', m')}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}, m) \right]. \end{aligned} \quad (27)$$

By implementing the orthogonality condition by means of lagrange multipliers ε_i for each single electron component ϕ_i , we obtain the Hartree-Fock equations for each single-electron wavefunction $\phi_i(\mathbf{r}, m)$:

$$\begin{aligned} & \left(-\frac{1}{2m_e} \nabla^2 - \frac{Z\alpha}{r} + \alpha \sum_{i \neq j} \int d^3\mathbf{r}' \frac{n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \varepsilon_i \right) \phi_i(\mathbf{r}, m) \\ & = \alpha \sum_{i \neq j, m'} \int d^3\mathbf{r}' \frac{\phi_i(\mathbf{r}', m') \phi_j^\dagger(\mathbf{r}', m')}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}, m). \end{aligned} \quad (28)$$

These equations are coupled non-linear integro-differential equations which are difficult and numerically expensive to solve. Practically one solves these equations iteratively. For the first iteration typically the well known solutions for a hydrogen atom are taken. A more advanced approach is to start with Thomas-Fermi wavefunctions. Then one computes the integrals over \mathbf{r}' and then solves the Hartree-Fock equations (28) numerically and uses these results to solve the \mathbf{r}' integrals, and so on hoping for convergence.