LECTURE 12.  

Prof. R. Parthasarathy

Thomas-Fermi Statistical Model

The method of determining the equivalent potential \( V(r) \) due to Thomas and Fermi (1927-28) assumes that \( V(r) \) varies slowly in an electron wavelength so that many electrons can be localized within a volume over which \( V(r) \) changes by a small fraction of itself. Then, the electrons can be treated by statistical mechanics obeying Fermi-Dirac statistics. At normal temperatures, the thermal energy \( kT \) is very small compared with \( V(r) \) everywhere except at the edge of the atom, where the chances of finding the electron is small. FD statistics requires that the electron states fill in order of increasing energy.

The number of electron states in a cube of edge length \( L \) is \( \left( \frac{L}{2\pi} \right)^3 dk_x dk_y dk_z \) times 2 (possible spin states). Then, the number of states for which the momentum \( \vec{p} = \hbar \vec{k} \) is \( < \vec{p}_0 \) is

\[
2 \left( \frac{L}{2\pi} \right)^3 \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} k^2 d\kappa \sin \theta d\theta d\phi = \frac{p_0^3 L^3}{3\pi^2 \hbar^3}.
\]

If all the states are occupied, then the number of electrons per unit volume is \( \frac{p_0^3}{3\pi^2 \hbar^3} \) and the kinetic energy does not exceed \( \frac{p_0^2}{2m} \). The maximum kinetic energy at any distance \( r \) from the nucleus is \( -V(r) \) and so \( p_0^2 = -2mV(r) \). Then, the number of electrons depends on \( r \) as

\[
n(r) = \frac{p_0^3}{3\pi^2 \hbar^3},
\]

\[
= \left( \frac{-2mV(r)}{3\pi^2 \hbar^3} \right)^\frac{3}{2}.
\]

The charge density is \( en(r) \) and so the Poisson equation for the electrostatic is

\[
\frac{1}{e} \nabla^2 V(r) = -4\pi en(r),
\]

\[
\frac{1}{e} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dV(r)}{dr} \right) = -4\pi en(r).
\]
Equations 2 and 3 are the two simultaneous equations for \( n(r) \) and \( V(r) \). The idea is to solve them! We recall that for neutral atoms of atomic number \( Z \), we realize that when \( r \to 0 \), the leading term in \( V(r) \) should be \(-\frac{Ze^2}{r}\), the potential due to the nucleus. This is written as

\[
\text{Limit}(r \to 0)(rV(r)) = -Ze^2. \tag{4}
\]

As \( r \to \infty \), there must be no net charge inside the sphere of radius \( r \). So, \( \text{Limit}(r \to \infty)V(r) = 0 \). These are the boundary conditions necessary. Substituting (2) in (3) for \( n(r) \), we have

\[
\frac{1}{r^2} \frac{d}{dr}(r^2 \frac{dV(r)}{dr}) = -\frac{4e^2}{3\pi \hbar^3} \left( -2mV(r) \right)^{\frac{3}{2}}. \tag{5}
\]

In (5), let us put \( V(r) = -\frac{Ze^2}{r} \chi \) and note \( \frac{dV(r)}{dr} = -Ze^2\left\{ -\frac{1}{r^2} \chi + \frac{d\chi}{dr} \right\} \). Then it follows that: \( \frac{d}{dx}(r^2 \frac{dV(r)}{dr}) = -Ze^2r \frac{d^2\chi}{dr^2} \). Let us set \( r = bx \) where \( b \) is a constant to be fixed shortly. Then, (5) becomes

\[
\frac{d^2\chi}{dx^2} = \frac{8e^2m\sqrt{2mZe^2}}{3\pi \hbar^3} \frac{b\sqrt{b}}{\sqrt{x}} \chi^{\frac{3}{2}}. \tag{6}
\]

The constant \( b \) is fixed now as

\[
b\sqrt{b} = \frac{3\pi \hbar^3}{8me^2\sqrt{2mZe^2}},
\]

\[
b = \frac{1}{2} \left( \frac{3\pi}{4} \right)^{\frac{3}{2}} \frac{\hbar^2}{me^2Z^\frac{3}{2}}. \tag{7}
\]

The above result for \( b \) can be further simplified upon using the Bohr radius \( a_0 \) since \( a_0 = \frac{\hbar^2}{me^2} \) as

\[
b = \frac{1}{2} \left( \frac{3\pi}{4} \right)^{\frac{3}{2}} \frac{a_0}{Z^\frac{3}{2}},
\]

\[
b = \frac{1}{Z^\frac{3}{2}} 0.885a_0. \tag{8}
\]

This shows that \( b \) has the dimension of length and so in \( r = bx \), \( x \) is dimensionless. Now let us look at the boundary conditions for \( \chi \). As \( r \to 0 \), we
have \((rV(r)) = -Ze^2\) and as \(V(r) = -\frac{Ze^2}{r}\chi\), it reads as: \(\text{limit}(x \to 0) \chi = 1\). Similarly, we have \(\text{limit}(x \to \infty) \chi = 0\). Thus, equation 6 upon using (7), becomes,
\[
\frac{d^2\chi(x)}{dx^2} = \frac{1}{\sqrt{x}} \chi(x)^\frac{3}{2}, \quad \text{with}
\chi(x) = 1, \quad \text{at} \quad x = 0; \quad \chi(x) = 0, \quad \text{at} \quad x = \infty,
\]
which is known as the Thomas-Fermi equation. In here \(\chi(x) > 0\). We know that the there is a maximum for the kinetic energy and from (2), it follows that when \(\chi(x) < 0\), \(n(r)\) must vanish. From (3) and (5), we have \(\frac{d^2\chi}{dx^2} = 0\) when \(\chi < 0\). So, the Thomas-Fermi equations become:
\[
\frac{d^2\chi(x)}{dx^2} = \frac{1}{\sqrt{x}} \chi(x)^\frac{3}{2}, \quad \text{for} \quad \chi > 0,
\]
\[
\frac{d^2\chi(x)}{dx^2} = 0, \quad \text{for} \quad \chi < 0,
\]
with the same boundary conditions as in (9). The second equation in (10) is easy to solve and the solution is \(\chi(x) = A(x - x_0)\) with \(A\) negative. So \(\chi(x)\) has at most one zero in the interval \((0, \infty)\) such that \(\chi\) will be positive in the interval \((0, x_0)\) and negative in the interval \((x_0, \infty)\). Where is \(x_0\)? The number of electrons given in (2) should satisfy the normalization
\[
4\pi \int_0^\infty n(r)r^2dr = Z.
\]
This expression using (2) and (7) reads as
\[
\int_0^{x_0} \sqrt{x}\chi(x)^\frac{3}{2}dx = 1.
\]
The upper limit is taken to be \(x_0\) since after this, \(n(r)\) is taken to be zero as in here \(\chi\) is negative. From (10), this becomes
\[
1 = \int_0^{x_0} \frac{d^2\chi}{dx^2}dx,
\]
\[
= \left\{x \frac{d\chi}{dx} - \chi\right\}_0^{x_0},
\]
\[
= x_0\chi'(x_0) + 1,
\]
using the boundary conditions. This condition requires the derivative $\chi'$ to vanish at the same point as does $\chi$ itself. This means that the point in question must be at infinity. The Thomas-Fermi function $\chi(x)$ satisfying (10) is independent of $Z$. It is an universal function, valid for large $Z$. The differential equation (10) is numerically solved by V.Bush and S.H.Caldwell, Phys.Rev. 38 (1931) 1898. We give the graph of the solutions below.

![Graph of the Thomas-Fermi $\chi(x)$ function for any value of $Z$.](image)

The Thomas-Fermi $\chi(x)$ function for any value of $Z$. 
The notion of atomic radius now needs to be defined. Why? The electronic density given in (2) and expresses in terms of $\chi$ becomes zero only at infinity (as the point $x_0$ is at infinity) and so the atom is not occupying a well defined region in space! This is unphysical. By atomic radius, we mean the radius $R(\alpha)$ of the sphere centered at the origin and containing a given fraction $(1 - \alpha)Z$ of the $Z$-atomic electrons. Then, it follows that

$$
(1 - \alpha)Z = 4\pi \int_0^{R(\alpha)} n(r) r^2 dr.
$$

From (2) and following the steps in (12), we find,

$$
(1 - \alpha)Z = Z \int_0^{X(\alpha)} x \frac{d^2 \chi}{dx^2} dx, \quad R(\alpha) = bX(\alpha),
$$

$$
= Z \{X(\alpha)\chi'(X(\alpha)) - \chi(X(\alpha)) + \chi(0)\}.
$$

Using the boundary condition $\chi(0) = 1$, we have

$$
\alpha = \chi(X(\alpha)) - X(\alpha)\chi'(X(\alpha)).
$$

This equation must be solved numerically. If we use the same value of $\alpha$ for all atoms, $X$ will be the same for them. So $R(\alpha) \propto Z^{-\frac{1}{3}}$ since $R(\alpha) = bX(\alpha)$ and $b = Z^{-\frac{1}{3}} \times 0.885a_0$. For $\alpha = \frac{1}{Z}$, we have $R\left(\frac{1}{Z}\right) = \bar{R} = Z^{-\frac{1}{3}} \times 0.885a_0 \times \frac{1}{Z}$ is the radius of the sphere containing all but one of the electrons. The figure below gives the $Z$ dependence of $\bar{R}$. 

Applications

Atomic Radius

The notion of atomic radius now needs to be defined. Why? The electronic density given in (2) and expresses in terms of $\chi$ becomes zero only at infinity (as the point $x_0$ is at infinity) and so the atom is not occupying a well defined region in space! This is unphysical. By atomic radius, we mean the radius $R(\alpha)$ of the sphere centered at the origin and containing a given fraction $(1 - \alpha)Z$ of the $Z$-atomic electrons. Then, it follows that

$$
(1 - \alpha)Z = 4\pi \int_0^{R(\alpha)} n(r) r^2 dr.
$$

From (2) and following the steps in (12), we find,

$$
(1 - \alpha)Z = Z \int_0^{X(\alpha)} x \frac{d^2 \chi}{dx^2} dx, \quad R(\alpha) = bX(\alpha),
$$

$$
= Z \{X(\alpha)\chi'(X(\alpha)) - \chi(X(\alpha)) + \chi(0)\}.
$$

Using the boundary condition $\chi(0) = 1$, we have

$$
\alpha = \chi(X(\alpha)) - X(\alpha)\chi'(X(\alpha)).
$$

This equation must be solved numerically. If we use the same value of $\alpha$ for all atoms, $X$ will be the same for them. So $R(\alpha) \propto Z^{-\frac{1}{3}}$ since $R(\alpha) = bX(\alpha)$ and $b = Z^{-\frac{1}{3}} \times 0.885a_0$. For $\alpha = \frac{1}{Z}$, we have $R\left(\frac{1}{Z}\right) = \bar{R} = Z^{-\frac{1}{3}} \times 0.885a_0 \times \frac{1}{Z}$ is the radius of the sphere containing all but one of the electrons. The figure below gives the $Z$ dependence of $\bar{R}$. 

Applications

Atomic Radius

The notion of atomic radius now needs to be defined. Why? The electronic density given in (2) and expresses in terms of $\chi$ becomes zero only at infinity (as the point $x_0$ is at infinity) and so the atom is not occupying a well defined region in space! This is unphysical. By atomic radius, we mean the radius $R(\alpha)$ of the sphere centered at the origin and containing a given fraction $(1 - \alpha)Z$ of the $Z$-atomic electrons. Then, it follows that

$$
(1 - \alpha)Z = 4\pi \int_0^{R(\alpha)} n(r) r^2 dr.
$$

From (2) and following the steps in (12), we find,

$$
(1 - \alpha)Z = Z \int_0^{X(\alpha)} x \frac{d^2 \chi}{dx^2} dx, \quad R(\alpha) = bX(\alpha),
$$

$$
= Z \{X(\alpha)\chi'(X(\alpha)) - \chi(X(\alpha)) + \chi(0)\}.
$$

Using the boundary condition $\chi(0) = 1$, we have

$$
\alpha = \chi(X(\alpha)) - X(\alpha)\chi'(X(\alpha)).
$$

This equation must be solved numerically. If we use the same value of $\alpha$ for all atoms, $X$ will be the same for them. So $R(\alpha) \propto Z^{-\frac{1}{3}}$ since $R(\alpha) = bX(\alpha)$ and $b = Z^{-\frac{1}{3}} \times 0.885a_0$. For $\alpha = \frac{1}{Z}$, we have $R\left(\frac{1}{Z}\right) = \bar{R} = Z^{-\frac{1}{3}} \times 0.885a_0 \times \frac{1}{Z}$ is the radius of the sphere containing all but one of the electrons. The figure below gives the $Z$ dependence of $\bar{R}$. 

Applications

Atomic Radius

The notion of atomic radius now needs to be defined. Why? The electronic density given in (2) and expresses in terms of $\chi$ becomes zero only at infinity (as the point $x_0$ is at infinity) and so the atom is not occupying a well defined region in space! This is unphysical. By atomic radius, we mean the radius $R(\alpha)$ of the sphere centered at the origin and containing a given fraction $(1 - \alpha)Z$ of the $Z$-atomic electrons. Then, it follows that

$$
(1 - \alpha)Z = 4\pi \int_0^{R(\alpha)} n(r) r^2 dr.
$$

From (2) and following the steps in (12), we find,

$$
(1 - \alpha)Z = Z \int_0^{X(\alpha)} x \frac{d^2 \chi}{dx^2} dx, \quad R(\alpha) = bX(\alpha),
$$

$$
= Z \{X(\alpha)\chi'(X(\alpha)) - \chi(X(\alpha)) + \chi(0)\}.
$$

Using the boundary condition $\chi(0) = 1$, we have

$$
\alpha = \chi(X(\alpha)) - X(\alpha)\chi'(X(\alpha)).
$$

This equation must be solved numerically. If we use the same value of $\alpha$ for all atoms, $X$ will be the same for them. So $R(\alpha) \propto Z^{-\frac{1}{3}}$ since $R(\alpha) = bX(\alpha)$ and $b = Z^{-\frac{1}{3}} \times 0.885a_0$. For $\alpha = \frac{1}{Z}$, we have $R\left(\frac{1}{Z}\right) = \bar{R} = Z^{-\frac{1}{3}} \times 0.885a_0 \times \frac{1}{Z}$ is the radius of the sphere containing all but one of the electrons. The figure below gives the $Z$ dependence of $\bar{R}$. 

Applications

Atomic Radius

The notion of atomic radius now needs to be defined. Why? The electronic density given in (2) and expresses in terms of $\chi$ becomes zero only at infinity (as the point $x_0$ is at infinity) and so the atom is not occupying a well defined region in space! This is unphysical. By atomic radius, we mean the radius $R(\alpha)$ of the sphere centered at the origin and containing a given fraction $(1 - \alpha)Z$ of the $Z$-atomic electrons. Then, it follows that

$$
(1 - \alpha)Z = 4\pi \int_0^{R(\alpha)} n(r) r^2 dr.
$$

From (2) and following the steps in (12), we find,

$$
(1 - \alpha)Z = Z \int_0^{X(\alpha)} x \frac{d^2 \chi}{dx^2} dx, \quad R(\alpha) = bX(\alpha),
$$

$$
= Z \{X(\alpha)\chi'(X(\alpha)) - \chi(X(\alpha)) + \chi(0)\}.
$$

Using the boundary condition $\chi(0) = 1$, we have

$$
\alpha = \chi(X(\alpha)) - X(\alpha)\chi'(X(\alpha)).
$$

This equation must be solved numerically. If we use the same value of $\alpha$ for all atoms, $X$ will be the same for them. So $R(\alpha) \propto Z^{-\frac{1}{3}}$ since $R(\alpha) = bX(\alpha)$ and $b = Z^{-\frac{1}{3}} \times 0.885a_0$. For $\alpha = \frac{1}{Z}$, we have $R\left(\frac{1}{Z}\right) = \bar{R} = Z^{-\frac{1}{3}} \times 0.885a_0 \times \frac{1}{Z}$ is the radius of the sphere containing all but one of the electrons. The figure below gives the $Z$ dependence of $\bar{R}$.
It is seen that $\bar{R}$ is practically independent of $Z$. $\bar{R} \simeq (2 - 3) \times 10^{-8} \text{cm}$.

**Charge Form Factor**

In the Thomas-Fermi model, all atoms are identical in shape and the scale of the length is proportional to $Z^{-\frac{1}{3}}$ since $r = bx$ and $b = 0.885a_0 \times Z^{-\frac{1}{3}}$. Thus the charge form factor will be an universal function for all heavy atoms. The electron density in Thomas-Fermi model can be written as

$$n(r) = \frac{Z^2}{4\pi (0.885a_0)^3} \left( \frac{x}{X} \right)^{\frac{3}{2}}. \quad (17)$$
\( \chi \) is the universal Thomas-Fermi function. The form factor is

\[
F(q) = \int n(r)e^{iq\vec{r}}d\vec{r},
\]

\[
= \frac{4\pi}{q} \int_0^\infty n(r)\sin(qr)rdr,
\]

\[
= \frac{4\pi b^2}{q} \int_0^\infty n(x)\sin(qbx)x\,dx,
\]

\[
= \frac{4\pi b^2}{q} \frac{Z^2}{4\pi(0.885a_0)^3} \int_0^\infty (\chi(x))^{3/2} \sin(qbx)x^{-1/2}dx,
\]

\[
= \frac{Z^{3/2}}{q(0.885a_0)} \int_0^\infty (\chi(y))^{3/2} \sin((q\cdot 0.885a_0)y)\,y^{-1/2}dy,
\]

where \( y = Z^{-1/3}x \). The quantity \( G(Q) = \frac{1}{Q} \int_0^\infty [\chi(y)]^{3/2} y^{-1/2} \sin(Qy)dy \) is tabulated in the literature. Here \( Q = 0.885a_0q \). From the table, the charge form factor can be read.