Physics of atoms and molecules

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As we already showed in Section 4.2, the allowed components of the wave vector $\mathbf{k}$ are then given by (see (4.57))

$$k_x = \frac{2\pi}{L} n_x, \qquad k_y = \frac{2\pi}{L} n_y, \qquad k_z = \frac{2\pi}{L} n_z \tag{8.46}$$

where n_x, n_y and n_z are positive or negative integers, or zero. The number of spatial orbitals in the range $d\mathbf{k} = dk_x\, dk_y\, dk_z$ is $(L/2\pi)^3\, dk_x\, dk_y\, dk_z$ and this number must be multiplied by 2 to take into account the two possible spin states. A unit volume of $\mathbf{k}$-space will therefore accommodate $V/(4\pi^3)$ electrons (with $V = L^3$). Thus, the individual electron states having energies up to $E = \hbar^2k^2/(2m)$ will be contained within a sphere in $\mathbf{k}$-space, of radius k, the number N_s of these states being given by

$$N_s = \frac{V}{4\pi^3}\frac{4}{3}\pi k^3 = \frac{1}{3\pi^2} V k^3$$

$$= \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V E^{3/2} \tag{8.47}$$

in agreement with (8.36).

We have seen above that in the ground state of the Fermi electron gas the N electrons fill all the states up to the Fermi energy E_F. Thus in $\mathbf{k}$-space all states up to a maximum value of k equal to k_F are then filled, while the states for which $k > k_F$ are empty. In other words all occupied spin-orbitals of a Fermi electron gas at 0 K fill a sphere in $\mathbf{k}$-space having radius k_F. This sphere, which is called the *Fermi sphere*, obviously contains

$$\frac{1}{3\pi^2} V k_F^3 = N \tag{8.48}$$

spin-orbitals, so that

$$k_F = (3\pi^2\rho)^{1/3} \tag{8.49}$$

At the surface of the Fermi sphere, known as the *Fermi surface*, the energy is the Fermi energy

$$E_F = \frac{\hbar^2}{2m} k_F^2 \tag{8.50}$$

and we note that the result (8.41) follows upon substitution of (8.49) in (8.50). It is also convenient to introduce the Fermi momentum $\mathbf{p}_F$, velocity $\mathbf{v}_F$ and temperature T_F such that

$$E_F = \frac{p_F^2}{2m} = \frac{1}{2} m v_F^2 = k_B T_F \tag{8.51}$$

where k_B is Boltzmann's constant.

The Thomas–Fermi theory for multielectron atoms and ions

The theory developed independently by L.H. Thomas and E. Fermi for the ground state of complex atoms (or ions) having a large number of electrons is based on *statistical* and *semi-classical* considerations. The N electrons of the system are treated as a Fermi electron gas in the ground state, confined to a region of space by a central potential $V(r)$ which vanishes at infinity. It is assumed that this potential is slowly varying over a distance which is large compared with the de Broglie wavelengths of the electrons, so that enough electrons are present in a volume where $V(r)$ is nearly constant, and therefore the statistical approach used in studying the Fermi electron gas can be applied. In addition, since the number of electrons is large, many of them have high principal quantum numbers, so that semi-classical methods should be useful.

The aim of the Thomas–Fermi model is to provide a method of calculating the potential $V(r)$ and the electron density $\rho(r)$. These two quantities can first be related by using the following arguments. The total energy of an electron is written as $p^2/(2m) + V(r)$, and this energy cannot be positive, otherwise the electron would escape to infinity. Since the maximum kinetic energy of an electron in a Fermi electron gas at 0 K is the Fermi energy E_F, we write for the total energy of the most energetic electrons of the system the classical equation

$$E_{max} = E_F + V(r) \tag{8.52}$$

It is clear that E_{max} must be independent of r, because if this were not the case electrons would migrate to that region of space where E_{max} is smallest, in order to lower the total energy of the system. Furthermore, we must have $E_{max} \leq 0$. We note from (8.50) and (8.52) that the quantity k_F is now a function of r. That is,

$$k_F^2(r) = \frac{2m}{\hbar^2}[E_{max} - V(r)] \tag{8.53}$$

Using (8.41) and (8.52) we then have

$$\rho(r) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} [E_{max} - V(r)]^{3/2} \tag{8.54}$$

and we see that ρ vanishes when $V = E_{max}$. In the classically forbidden region $V > E_{max}$ we must set $\rho = 0$, since otherwise (8.52) would yield a negative value of the maximum kinetic energy E_F. Let us denote by

$$\phi(r) = -\frac{1}{e} V(r) \tag{8.55}$$

the electrostatic potential and by $\phi_0 = -E_{max}/e$ a non-negative constant. Setting

$$\Phi(r) = \phi(r) - \phi_0 \tag{8.56}$$

we see that $\rho(r)$ and $\Phi(r)$ are related by

$$\rho(r) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}[e\Phi(r)]^{3/2}, \qquad \Phi \geqslant 0 \tag{8.57a}$$

$$= 0, \qquad \Phi < 0 \tag{8.57b}$$

The equation $\Phi = 0$ (that is, $\phi = \phi_0$ or $V = E_{\max}$) may be thought of as determining the 'boundary' $r = r_0$ of the atom (ion) in this model. Now, for a neutral atom ($N = Z$) the electrostatic potential $\phi(r)$ vanishes at the boundary, so that we shall set $\phi_0 = 0$ in that case. On the other hand $\phi_0 > 0$ for an ion.

A second relation between $\rho(r)$ and $\Phi(r)$ may be obtained as follows. The sources of the electrostatic potential $\phi(r)$ are:

(i) the point charge Ze of the nucleus, located at the origin;
(ii) the distribution of electricity due to the N electrons.

Treating the charge density $-e\rho(r)$ of the electrons as continuous, we may use Poisson's equation of electrostatics to write

$$\nabla^2\Phi(r) = \frac{1}{r}\frac{d^2}{dr^2}[r\Phi(r)] = \frac{e}{\varepsilon_0}\rho(r) \tag{8.58}$$

The equations (8.57a) and (8.58) are two simultaneous equations for $\rho(r)$ and $\Phi(r)$. Eliminating $\rho(r)$ from these equations, we find that for $\Phi \geqslant 0$

$$\frac{1}{r}\frac{d^2}{dr^2}[r\Phi(r)] = \frac{e}{3\pi^2\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}[e\Phi(r)]^{3/2}, \qquad \Phi \geqslant 0 \tag{8.59}$$

On the other hand, when $\Phi < 0$ we see from (8.57b) and (8.58) that

$$\frac{d^2}{dr^2}[r\Phi(r)] = 0, \qquad \Phi < 0 \tag{8.60}$$

For $r \to 0$ the leading term of the electrostatic potential must be due to the nucleus, so that the boundary condition at $r = 0$ reads

$$\lim_{r\to 0} r\Phi(r) = \frac{Ze}{4\pi\varepsilon_0} \tag{8.61}$$

On the other hand, since the N electrons of the system are assumed to be confined to a sphere of radius r_0, we must have the 'normalisation' condition

$$4\pi\int_0^{r_0}\rho(r)r^2\,dr = N \tag{8.62}$$

In order to simplify the above equations, it is convenient to introduce the new dimensionless variable x and the function $\chi(x)$ such that

$$r = bx, \qquad r\Phi(r) = \frac{Ze}{4\pi\varepsilon_0}\chi(x) \tag{8.63}$$

where

$$b = \frac{(3\pi)^{2/3}}{2^{7/3}}a_0 Z^{-1/3} \simeq 0.8853\, a_0 Z^{-1/3} \tag{8.64}$$

and $a_0 = (4\pi\varepsilon_0)\hbar^2/(me^2)$ is the first Bohr radius. The relation (8.57) then becomes

$$\rho = \frac{Z}{4\pi b^3}\left(\frac{\chi}{x}\right)^{3/2}, \qquad \chi \geqslant 0 \tag{8.65a}$$

$$= 0, \qquad \chi < 0 \tag{8.65b}$$

and the important equation (8.59) may be written in dimensionless form as

$$\frac{d^2\chi}{dx^2} = x^{-1/2}\chi^{3/2}, \qquad \chi \geqslant 0 \tag{8.66}$$

This is known as the *Thomas–Fermi equation*. For negative χ we see from (8.60) and (8.63) that

$$\frac{d^2\chi}{dx^2} = 0, \qquad \chi < 0 \tag{8.67}$$

In addition, the boundary condition at $r = 0$, expressed by (8.61), now reads

$$\chi(0) = 1 \tag{8.68}$$

It is clear from (8.66) and (8.67) that $\chi(x)$ has at most one zero in the interval $(0, +\infty)$. Let x_0 be the position of this zero. From our above discussion we have $x_0 = r_0/b$, where r_0 is the 'boundary' of the system. We also note that $\chi > 0$ for $x < x_0$ and $\chi < 0$ for $x > x_0$. Moreover, the equation (8.67) has the solution $\chi = C(x - x_0)$, where C is a negative constant, which must be equal to $\chi'(x_0)$. As a result, the solution $\chi(x)$ is entirely determined if we know it for $\chi \geqslant 0$. We also remark that for any finite x_0 the quantity $\chi'(x_0)$ must be different from zero, since otherwise both χ and χ' would vanish at $x = x_0$, and the equation (8.66) would yield the unacceptable trivial solution $\chi = 0$.

The Thomas–Fermi equation (8.66) is a 'universal' equation, which does not depend on Z, nor on physical constants such as $\hbar$, m or e which have been 'scaled out' by performing the change of variables (8.63). We also note that it is a second-order, non-linear differential equation. Since the boundary condition at the origin (8.68) only specifies one constraint, there exist a whole family of solutions $\chi(x)$ satisfying the Thomas–Fermi equation (8.66) and the condition (8.68), which differ by their initial slope $\chi'(0)$. It is also clear from (8.66) that all these solutions must be concave upwards. As illustrated in Fig. 8.4, we can classify them into three categories:

1. a solution which is asymptotic to the x axis;
2. solutions which vanish for a finite value $x = x_0$;
3. solutions which never vanish and diverge for large x.

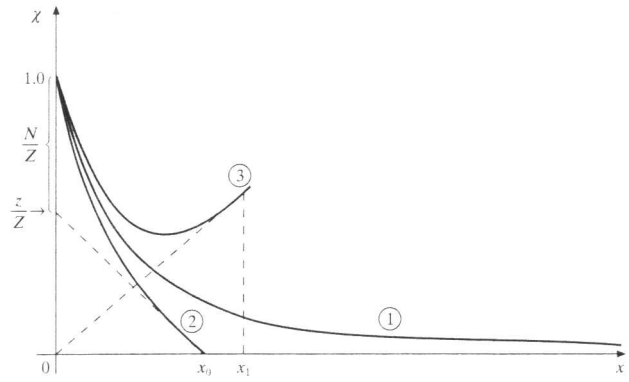

Figure 8.4 The three categories of solutions of the Thomas–Fermi equation: (1) neutral atom solution; (2) solution corresponding to a positive ion ($N < Z$); (3) solution corresponding to a neutral atom under pressure.

The physical meaning of the solutions belonging to the first two categories may be obtained by looking at the 'normalisation' condition (8.62). Taking into account (8.63), (8.65) and (8.66), this condition reads

$$\begin{aligned} N &= Z\int_0^{x_0} x^{1/2}\chi^{3/2}\,\mathrm{d}x \\ &= Z\int_0^{x_0} x\chi''\,\mathrm{d}x \\ &= Z[x\chi' - \chi]_0^{x_0} \end{aligned} \qquad \textbf{(8.69)}$$

Using the boundary condition (8.68) and the fact that $\chi(x_0) = 0$, we then have

$$x_0\chi'(x_0) = \frac{N-Z}{Z} \qquad \textbf{(8.70)}$$

Let us first consider *neutral atoms* for which $N = Z$. The condition (8.70) then requires that $\chi'(x_0) = 0$, so that χ' should vanish at the same point as χ. Since this condition cannot be satisfied for a finite value x_0 by non-trivial solutions, the point x_0 must be at infinity. As a consequence, the solution $\chi(x)$ corresponding to a neutral atom must be asymptotic to the x axis, namely

$$\chi(\infty) = 0 \qquad \textbf{(8.71)}$$

and is therefore the (unique) solution classified above in the first category. We remark that since $\chi(x)$ vanishes only at infinity, there is no 'boundary' to the neutral atom in the Thomas–Fermi model.

Table 8.5 Values of the function $\chi(x)$ for neutral atoms.

x	$\chi(x)$	x	$\chi(x)$	x	$\chi(x)$	x	$\chi(x)$
0.00	1.000	0.9	0.453	3.4	0.135	9.0	0.029 5
0.02	0.972	1.0	0.425	3.6	0.125	9.5	0.026 8
0.04	0.947	1.2	0.375	3.8	0.116	10	0.024 4
0.06	0.924	1.4	0.333	4.0	0.108	11	0.020 4
0.08	0.902	1.6	0.298	4.5	0.0918	12	0.017 2
0.1	0.882	1.8	0.268	5.0	0.0787	13	0.014 7
0.2	0.793	2.0	0.242	5.5	0.0679	14	0.012 6
0.3	0.721	2.2	0.220	6.0	0.0592	15	0.010 9
0.4	0.660	2.4	0.201	6.5	0.0521	20	0.005 8
0.5	0.607	2.6	0.185	7.0	0.0461	25	0.003 5
0.6	0.561	2.8	0.171	7.5	0.0409	30	0.002 3
0.7	0.521	3.0	0.158	8.0	0.0365	40	0.001 1
0.8	0.485	3.2	0.146	8.5	0.0327	50	0.000 63

The Thomas–Fermi equation (8.66) and the boundary conditions (8.68) and (8.71) define a *universal function* $\chi(x)$ for all neutral atoms. Values of this function, obtained by numerical integration, are given in Table 8.5. We remark from this table that $\chi(x)$ is monotonically decreasing. It can be shown that the asymptotic form of $\chi(x)$ for large x is given by the function $144x^{-3}$. At $x = 0$ one has $\chi'(0) = -1.588$ so that in the vicinity of the origin

$$\chi(x) \simeq 1 - 1.588x + \ldots \qquad \textbf{(8.72)}$$

Knowing the universal function $\chi(x)$, we can obtain the function $\Phi(r)$, and hence the electrostatic potential $\phi(r)$, the potential energy $V(r)$ and the density $\rho(r)$. Using (8.55), (8.56), (8.63), and remembering that $\phi_0 = 0$ for a neutral atom, we see that in the Thomas–Fermi model the central potential $V(r)$ is given for neutral atoms by

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r}\chi \qquad \textbf{(8.73)}$$

As $r \to 0$, we have $V(r) \to -Ze^2/(4\pi\varepsilon_0 r)$. More precisely, we deduce from (8.63), (8.72) and (8.73) that for small r

$$V(r) \simeq \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r} + 1.794\frac{Z^{4/3}}{a_0}\right) \qquad \textbf{(8.74)}$$

or, using atomic units,

$$V(r) \simeq -\frac{Z}{r} + 1.794Z^{4/3} + \ldots \qquad \textbf{(8.75)}$$

The first term is the nuclear attraction while the second one, which is repulsive, arises from the contribution of the electrons. When $r \to \infty$, we see from (8.71) and (8.73) that $rV(r) \to 0$, so that the Thomas–Fermi potential (8.73) falls off more rapidly than $1/r$ for large r. This behaviour is at variance with the result (8.8c) which we obtained in our discussion of the central field approximation. The reason is that the potential V discussed in Section 8.1 is the one felt by an atomic electron, while the Thomas–Fermi potential (8.73) is that experienced by an infinitesimal negative test charge. The difference between the two potentials is due to the statistical and semi-classical approximations made in the Thomas–Fermi model, the Thomas–Fermi result becoming exact in the limit when $\hbar$ and e tend to zero, while the number $N (= Z)$ of electrons becomes infinite.

Turning now to the electron density $\rho(r)$, we see from (8.65a) that it is similar for all atoms, except for a different length scale, which is determined by the quantity b (see (8.64)) and is proportional to $Z^{-1/3}$. As a result, the radial scale of $\rho(r)$ contracts according to $Z^{-1/3}$ when Z increases. We remark that for fixed Z the Thomas–Fermi method is inaccurate at both small r ($r < a_0/Z$) and large r ($r \gg a_0$), where it overestimates the electron density. Indeed, the Thomas–Fermi electron density (8.65a) diverges at the origin (as $r^{-3/2}$) and falls off like r^{-6} as $r \to \infty$, while the correct electron density should remain finite at $r = 0$, and decrease exponentially for large r. Thus the application of the Thomas–Fermi method is limited to 'intermediate' distances r between a_0/Z and a few times a_0. It is worth noting, however, that in complex atoms most of the electrons are to be found precisely in this spatial region. Thus we expect the Thomas–Fermi method to be useful in calculating quantities which depend on the 'average electron', such as the total energy of the atom. On the other hand, quantities which rely on the properties of the 'outer' electrons (such as the ionisation potential) are poorly given in the Thomas–Fermi model.

We have shown above that a neutral atom has no 'boundary' in the Thomas–Fermi model. Nevertheless, it is possible to define in this case an atomic 'radius' $R(\alpha)$ as the radius of a sphere centred at the origin and containing a given fraction $(1 - \alpha)$ of the Z electrons. We then have (see (8.62))

$$4\pi \int_0^{R(\alpha)} \rho(r) r^2 \, dr = (1 - \alpha) Z \tag{8.76}$$

Making the change of variable

$$R(\alpha) = bX(\alpha) \tag{8.77}$$

and taking into account (8.63), (8.65) and (8.66), we find for X the equation

$$\chi(X) - X\chi'(X) = \alpha \tag{8.78}$$

which must be solved numerically. If the same value of α is adopted for all atoms, (8.78) becomes a 'universal' equation and X is the same for all atoms. Using (8.64) and (8.77) we see that the atomic radius $R(\alpha)$ is then proportional to $Z^{-1/3}$. On the other hand, if we set $\alpha = Z^{-1}$, then $R(Z^{-1}) = bX(Z^{-1})$ is the radius of a sphere containing all the atomic electrons except one. The quantity $R(Z^{-1})$ is found to be a slowly increasing function of Z, such that $4a_0 < R(Z^{-1}) < 6a_0$. Thus in both cases the atomic radius is nearly independent of Z. Similarly, the energy of the 'outer' electrons – and hence the ionisation potential of the atom – is almost independent of Z. As a consequence, the Thomas–Fermi model cannot account for the periodic properties of atoms as a function of Z, discussed in Section 8.2.

Let us now briefly discuss the two other categories of solutions (see Fig. 8.4) mentioned in our discussion of the Thomas–Fermi equation (8.66). Returning to (8.69)–(8.70) we remark that solutions $\chi(x)$ which vanish at a finite value $x = x_0$ (that is, which belong to the second category) are such that $N \neq Z$, and hence correspond to *ions* of radius $r_0 = bx_0$. Moreover, since the slope of χ is negative at x_0 (see Fig. 8.4) the equation (8.70) implies that these ions must be *positive ions*, such that $Z > N$ [7]. Setting $z = Z - N$, so that ze is the net charge of the ion, we note from (8.70) that the quantity z/Z is readily obtained from the tangent to the curve χ at $x = x_0$, as shown in Fig. 8.4. Since $\chi(x_0) = 0$, the electron density $\rho(r)$ vanishes at $r = r_0 = bx_0$, as seen from (8.65). On the other hand, looking at (8.55), (8.56) and (8.63), and remembering that $\phi_0 > 0$ for an ion, we see that the potential $V(r)$ remains finite at $r = r_0$.

The solutions of the Thomas–Fermi equation belonging to the third category (that is, those which have no zero and diverge for large x) are more difficult to interpret. First of all, the electron density $\rho(r)$ does not vanish in this case, and one may consider that these solutions correspond to negative values of ϕ_0. As seen from Fig. 8.4, such solutions lie above the 'universal' curve of the neutral atom. Now the total charge inside a sphere of radius $r = bx$ is just

$$Ze - 4\pi e \int_0^r \rho(r') r'^2 \, dr' = Ze[\chi(x) - x\chi'(x)] \tag{8.79}$$

Thus, at the point $r_1 = bx_1$, where

$$\chi(x_1) - x_1\chi'(x_1) = 0 \tag{8.80}$$

the total charge inside the sphere $r = r_1$ vanishes, and we note that the tangent to $\chi(x)$ at $x = x_1$ passes through the origin (see Fig. 8.4). For $x \leqslant x_1$, the curve $\chi(x)$ therefore corresponds to a neutral atom having a finite boundary at $r = r_1$, where the density $\rho(r)$ does not vanish. This may be interpreted as a representation of a *neutral atom under pressure* [8]. Further developments of the Thomas–Fermi method can be found in the monograph of Englert (1988).

[7] Negative ions cannot be handled by the Thomas–Fermi theory.

[8] We are not considering ions under pressure, since in dealing with an ensemble of such ions, difficulties due to the presence of the Coulomb forces between ions would arise.