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Thomas-Fermi Atom

We develop a self-consistent treatment of many-electron atoms by using the WKB method to treat single electrons moving in an unknown electrostatic potential $\Phi(r)$ which is itself determined be the density of electrons computed from those single particle states filled up to a Fermi energy E_f chosen so that a total of Z electron states are occupied.

Overview

Let $\rho(r)$ be the density of orbital electrons in an atom with atomic number Z. Then the potential $\Phi(r)$ should obey

$$\vec{\nabla}\Phi(r) = +4\pi e\rho(r), \tag{1}$$

where $-e$ is the charge carried by a single electron. Instead of including a delta function in $\rho(r)$ corresponding to the positive charge for the nucleus, we will require that

$$\lim_{r\to 0} r\Phi(r) = eZ. \tag{2}$$

The same potential Φ will enter the Schrödinger equation obeyed by the electronic wave function $\psi_{n,l,m}(r)$:

$$\left\{-\frac{\hbar^2\vec{\nabla}^2}{2m} - e\Phi(r)\right\}\psi_{n,l,m}(r) = E_{n,l}\psi_{n,l,m}(r). \tag{3}$$

We will show that if the WKB approximation is used to describe the single-particle energy eigenstates $\psi_{n,l,m}(r)$, we can compute the density of electrons per unit volume at a radial position r:

$$\rho(r) = \sum_{\substack{n,l,m \\ E_{n,l}<E_f}} |\psi_{n,l,m}(r)|^2 = \frac{(p_f(r))^3}{3\pi^2\hbar^3}. \tag{4}$$

Here the position-dependent "Fermi momentum",

$$p_f(r) = \sqrt{2m\left(E_f + e\Phi(r)\right)}, \tag{5}$$

is the largest spatial momentum that a classical electron located at the position r with energy $\leq E_F$ could have. The right-most expression in Eq. (4) can be recognized as the particle density per unit volume of a free-fermion gas with Fermi momentum $p_f(r)$. Combining Eqs. (1,4,5), we obtain the self-consistent Thomas-Fermi equation for Φ:

$$\vec{\nabla}\Phi(r) = +4\pi e\frac{\left(2m\left(E_f + e\Phi(r)\right)\right)^{\frac{3}{2}}}{3\pi^2\hbar^3}. \tag{6}$$

Before studying this non-linear equation for $\Phi(r)$ we will first derive the Eq. (4).

WKB derivation of density of states

We first use the WKB approximation to derive the density of states per unit volume for a one-dimensional problem in which many independent particles are bound in a potential $V(x)$. As above, we start with the equation obeyed by the single particle eigenstates $\psi_n(x)$:

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right\}\psi_n(x)=E_n\psi_n(x). \tag{7}$$

In the WKB approximation a bound state of $V(x)$ with energy E_n has the wave function:

$$\psi_n(x)=\frac{N_E}{\sqrt{v_E(x)}}\sin\left(\frac{1}{\hbar}\int_{x_1}^{x}p(x')dx'\right), \tag{8}$$

where x_1 is the turning point on the left where $E=V(x_1)$ and $p(x)=\sqrt{2m\left(E-V(x)\right)}$ and E_n is determined by the quantization condition

$$\oint p(x)dx=2\pi\hbar(n+\frac{1}{2}). \tag{9}$$

The normalization factor N_E is determined by the equation:

$$1=N_E^2\int_{x_1}^{x_2}dx\frac{1}{v_E(x)}\sin^2\left(\frac{1}{\hbar}\int_{x_1}^{x}p(x')dx'\right)=N_E^2\int_{x_1}^{x_2}\frac{dx}{v_E(x)}\frac{1}{2}=N_E^2\frac{\tau}{4} \tag{10}$$

which implies $N_E=2/\sqrt{\tau}$ where τ is the classical period of oscillation for classical motion with the energy E.

The number of integers n per unit energy, dn/dE can be obtained by differentiating Eq. (9) with respect to E:

$$\frac{dn}{dE}=\frac{1}{2\pi\hbar}\oint\frac{dp(x)}{dE}dx=\frac{1}{2\pi\hbar}\oint\frac{dx}{v_E}=\frac{\tau}{2\pi\hbar}. \tag{11}$$

These results can now be combined to determine the number of electrons per unit distance for the case that all states are filled up to $E=E_f$:

$$\rho(x) = \sum_{\substack{n\\ E_n\le E_f}}|\psi_n(x)|^2=\int_0^{E_f}dE\frac{dn(x)}{dE}\frac{1}{2v_E(x)}\frac{4}{\tau} \tag{12}$$

$$= \int_0^{E_f}dE\frac{\tau}{2\pi\hbar}\frac{1}{2v_E(x)}\frac{4}{\tau} \tag{13}$$

$$= \int_0^{p_f(x)}dp\frac{1}{\pi\hbar}=2\,\frac{p_f(x)}{2\pi\hbar}, \tag{14}$$

where the extra factor of two multiplying the familiar $p_f(x)/(2\pi\hbar)$ result comes because both $\pm p$ are being counted. Note, in both Eqs. (10) and (12)

we are assuming that for small $\hbar$ we can approximate $\sin^2\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x')dx'\right) \approx \frac{1}{2}$.

We can now use this one-dimensional result to derive the three-dimensional relation we need. For three dimensions write $\psi_{n,l,m}(r) = \frac{1}{r}u_{n,l}(r)Y_{l,m}$ so that $u_{n,l}(r)$ obeys the one-dimensional equation:

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - e\Phi(r) + \frac{l(l+1)\hbar^2}{2m}\right\}u_{n,l}(r) = E_{n,l}u_{n,l}(r). \tag{15}$$

Using our one-dimensional result to find the density of particle per unit volume with energy less than E_f and orbital angular momentum l and then summing this over l, we arrive at the total density of particles per unit volume with energy less than E_f:

$$\begin{aligned}
\rho(r) &= 2\sum_{0}^{l_{\max}}\sum_{m=-l}^{l}\left|\frac{u_{n,l}(r)}{r}\right|^2|Y_{l,m}|^2 &(16)\\
&= 2\sum_{0}^{l_{\max}}(2l+1)\frac{1}{r^2}2\frac{\sqrt{2m\left(E_f + e\Phi(r)\right) - \frac{l(l+1)\hbar^2}{r^2}}}{2\pi\hbar}\frac{1}{4\pi} &(17)\\
&= \int_0^{2m(E_F+e\Phi(r))} dx\frac{\sqrt{2m\left(E_f + e\Phi(r)\right) - x}}{2\pi^2\hbar^3} &(18)\\
&= \frac{\left\{2m\left(E_f + e\Phi(r)\right)\right\}^{\frac{3}{2}}}{3\pi^2\hbar^3}. &(19)
\end{aligned}$$

Here we have introduced an overall factor of 2 to count both spins, the integration variable $x = l(l+1)\hbar^2/r^2$ and assumed that on average $|Y_{l,m}|^2 \approx 1/(4\pi)$. The final result can be recognized as our usual free particle density per unit volume $p_f^3/(3\pi^2\hbar^3)$. (Note, in all of these equations E_f is negative.)

Properties of Thomas-Fermi equation

We can simplify Eq. (6) if we define two new quantities:

$$e^2Z\frac{1}{r}\varphi(r) = E_f + e\Phi(r) \quad \text{and} \quad x = r/\lambda. \tag{20}$$

Note, with this definition of $\varphi(x)$ the condition that $\Phi(r)$ satisfies as $r \to 0$ becomes simply $\lim_{x\to 0}\varphi(x) = 1$. Then Eq. (6) becomes:

$$\frac{eZ}{r}\frac{d^2}{dr^2}\varphi(r) = 4\pi e\frac{\left(2me^2Z\frac{\varphi(r)}{r}\right)^{\frac{3}{2}}}{3\pi^2\hbar^3} \tag{21}$$

or

$$\frac{d^2}{dx^2}\varphi(r) = \lambda^{\frac{3}{2}}\frac{4\pi e^3Z^{\frac{1}{2}}(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3}\frac{\left(\varphi(r)\right)^{\frac{3}{2}}}{x^{\frac{1}{2}}} \tag{22}$$

or

$$\frac{d^2}{dx^2}\varphi(r) = \frac{\left(\varphi(r)\right)^{\frac{3}{2}}}{x^{\frac{1}{2}}}, \tag{23}$$

if we choose:

$$\lambda = \left(\frac{3\pi}{4}\frac{\hbar^3}{(2m)^{\frac{3}{2}}e^3 Z^{\frac{1}{2}}}\right)^{\frac{2}{3}} = a_0 \frac{1}{2Z^{\frac{1}{3}}}\left(\frac{3\pi}{4}\right)^{\frac{2}{3}}. \tag{24}$$

Consider what large x behavior of $\varphi(x)$ might be consistent with Eq. (23). An important constraint comes from the integral of $\rho(r)$ which determines the number of electrons, $N(R)$, which are enclosed inside a sphere of radius R:

$$\begin{aligned} N(R) &= \int_{|\vec{r}|\leq R} d^3r\rho(r) = \frac{1}{4\pi e}\int_{|\vec{r}|\leq R} d^3r\vec{\nabla}^2\Phi(r) && (25)\\ &= \frac{Z}{4\pi}\int_{|\vec{r}|\leq R} d^3r\vec{\nabla}^2\left(\frac{\varphi(r)}{r}\right) && (26)\\ &= Z\int_0^R rdr\frac{d^2}{dr^2}\varphi(r) && (27)\\ &= Z\left(R\frac{d}{dr}\varphi(R) - \varphi(R) + 1\right). && (28) \end{aligned}$$

One possible behavior that we might find for φ is that the entire cloud of electrons is enclosed within a radius R_0 so that φ, which is proportional to the electron density, vanishes at R_0. However, this behavior is inconsistent with Eq. (28) since if that equation is evaluated at R_0 we obtain:

$$Z = Z\left(R_0\frac{d}{dr}\varphi(R_0) - \varphi(R_0) + 1\right), \tag{29}$$

which implies that if $\varphi(R_0) = 0$ then $\frac{d}{dr}\varphi(R_0) = 0$ which would in turn imply that $\varphi(r) = 0$ everywhere.

A consistent behavior of $\varphi(x)$ for large x can be determined by substituting a power law ansatz: $\varphi(x) \sim cx^n$ for large x in Eq. (23). We find both a specific value for n and, because of the non-linearity, for c as well:

$$\lim_{x\to\infty}\varphi(x) = 144\frac{1}{x^3}. \tag{30}$$

We can use this asymptotic form and Eq. (28) to determine the radius which encloses all but one of the electrons, $R_{(Z-1)}$:

$$Z - 1 = Z\left(144(-x\frac{3}{x^4} - \frac{1}{x^3} + 1\right) \tag{31}$$

which can be easily solved for x:

$$x = \left(Z\cdot 4\cdot 144\right)^{\frac{1}{3}}, \tag{32}$$

which can then be used to determine $R_{(Z-1)}$:

$$R_{(Z-1)} = \lambda x = a_0\frac{1}{2Z^{\frac{1}{3}}}\left(\frac{3\pi}{4}\right)^{\frac{2}{3}}\left(Z\cdot 4\cdot 144\right)^{\frac{1}{3}} = 7.3a_0. \tag{33}$$

l	$1.252(l_{\max}+\frac{1}{2})^3$	Z(experiment)
0	0.156	1
1	4.22	4
2	19.55	19
3	53.6	57
4	113.9	>118?

Table 1: The left-most column lists values of the largest orbital angular momentum found in the atomic ground state. The second column lists the smallest value of Z for which the Thomas-Fermi model predicts the presence of that value of l in the atomic ground state. The third column lists the smallest value of Z for which an atom found in nature contains that value of l in its ground state.

This is an interesting result saying that for large Z the radius of the atom does not grow with Z but is substantially larger than the Bohr radius a_0.

Finally we can use this Thomas-Fermi treatment to determine the smallest value of Z that will support a multi-electron wave function with contains a largest orbital angular momentum $l_{\max}$. Recall that for a given E_f, the position-dependent Fermi momentum is given by:

$$p_f(r) = \sqrt{2m(E_f + e\Phi(r)) - \frac{l(l+1)\hbar^2}{r^2}}. \tag{34}$$

Thus,

$$\begin{aligned} l(l+1) &\leq 2m\frac{r^2}{\hbar^2}\left(E + e\Phi(r)\right) = 2m\frac{r^2}{\hbar^2}\frac{e^2 Z\varphi(r)}{r} && (35)\\ &\leq 2m\frac{e^2 Z}{\hbar^2}\left[a_0\left(\frac{3\pi}{4}\right)^{\frac{3}{2}}\frac{1}{2Z^{\frac{1}{3}}}\right]x\varphi(x) && (36)\\ &\leq Z^{\frac{2}{3}}\left(\frac{3\pi}{4}\right)^{\frac{3}{2}}x\varphi(x) && (37)\\ &\leq 0.861 Z^{\frac{2}{3}}, && (38) \end{aligned}$$

where in the final equation we have used the numerical result that $x\varphi(x) \leq 0.486$. This equation can be rewritten as

$$1.252(l+\frac{1}{2})^3 \leq Z, \tag{39}$$

where we have replaced the quantity $l(l+1)$ by $(l+\frac{1}{2})^2$ which is what appears if a more careful WKB treatment of the $l(l+1)\hbar^2/r^2$ term at $r=0$ is attempted (see the Appendix below). We compare this result with experiment in Table 1.

1 Appendix

The replacement of $l(l+1)$ in WKB formula by $(l+\frac{1}{2})^2$ is suggested by studying the behavior of the WKB approximation to the radial wavefunction $u(r)$ as $r \to 0$. Define $p(r)$ in the usual way and examine its behavior for small r

$$p(r) = \sqrt{2m\left(E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right)} \tag{40}$$

$$\sim i\hbar\frac{\sqrt{l(l+1)}}{r}. \tag{41}$$

This behaivor can be substituted into the usual WKB wave function:

$$u(r) = \frac{1}{\sqrt{p_l(r)}} e^{\pm\frac{1}{\hbar}i\int_r^{r_0} dr' p_l(r)} \tag{42}$$

$$\propto r^{\frac{1}{2}} e^{\pm\sqrt{l(l+1)}\ln(r)} \tag{43}$$

$$= r^{\frac{1}{2}\pm\sqrt{l(l+1)}} \tag{44}$$

which does not agree with the r^{l+1} or r^{-1} behavior found for the exact solutions when $r \to 0$. However if we replace $l(l+1) \to (l+\frac{1}{2})^2$ then we do find the correct $r \to 0$ behavior:

$$u(r) = r^{\frac{1}{2}\pm\sqrt{(l+\frac{1}{2})^2}} = r^{\frac{1}{2}\pm(l+\frac{1}{2})}. \tag{45}$$

A more complete discussion of the correct WKB treatment of the $1/r^2$ singularity in the radial wave function can be found in Part 2 of R. Langer, *On the Connection Formulas and the Solutions of the Wave Equation*, Phys. Rev. 51, p669, 1937.

A useful reference for the numerical solution of the Thomas-Fermi equation can be found in Harry Krutter, *Numerical Integration of the Thomas-Fermi Equation from Zero to Infinity*, Journal of Computational Physics **47**, 308-312 (1982).