

On the atomic binding energy in the Thomas-Fermi model

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Abstract

The "empirical" binding energy $-16Z^{7/3}$ eV of heavy atoms is computed by a Hartree-type correction to a linearized version of the Thomas-Fermi model; the computations are carried out by means of a variational approach. Corrections to the exchange energy are also estimated.

As it is well-known,[1] the Thomas-Fermi model is based on the quasi-classical description and the statistical character of the electronic single-particle states in heavy atoms, *i.e.* in atoms with large atomic numbers Z ($Z \gg 1$). The electrons are assumed to form an inhomogeneous gas of fermions, and the Fermi wavevector k_F is determined by a self-consistent field potential φ , according to

$$\hbar^2 k_F^2 / 2m - e\varphi = 0 ; \quad (1)$$

(\hbar is Planck's constant, m is the electron mass, and $-e$ is the electron charge). The electric potential φ is determined by Poisson's equation

$$\Delta\varphi = -4\pi Ze\delta(\mathbf{r}) + 4\pi ne \quad , \quad (2)$$

where the electron density is given by $n = k_F^3 / 3\pi^2$, as for a Fermi gas. The atomic binding energy as computed by means of this theory[1],[2] is given by $E \simeq -20.8Z^{7/3}$ eV, which is the exact result in the limit $Z \rightarrow \infty$. [3] Actually, the atomic binding energy may be represented as an asymptotic series in powers of $Z^{-1/3}$, including, beside the leading term $-20.8Z^{7/3}$ eV, the so-called "boundary correction" $13.6Z^2$ eV, [4],[5] the exchange contribution $-5.98Z^{5/3}$ eV (or $-7.3Z^{5/3}$ eV), [6] etc; in addition, the relativistic effects must also be considered for large Z . Such an asymptotic series reproduces satisfactorily the experimental atomic binding energies, which, as it is widely agreed, may be represented approximately as $E \simeq -16Z^{7/3}$ eV (at least for not very large values of Z). [7] Various other computations have also been worked out, including higher-order corrections to the quasi-classical approximation, self-consistent Hartree, or Hartree-Fock, equations, as well as density-functional models. [8] In this Note we present a different approach to the problem, which provides a more direct access to the $E \simeq -16Z^{7/3}$ eV-representation of the "empirical" binding energies of the atoms, and may throw additional light upon the nature of the Thomas-Fermi model and the quasi-classical description. The method employed here is a variational treatment of a linearized version of the Thomas-Fermi model, as based on the quasi-classical description. It is worth noting that such linearized schemes of approaching the Thomas-Fermi model have recently been suggested by various authors, especially in connection with the atomic clusters. [9]

According to the prescriptions of the quasi-classical approximation eq. (1) is valid as long as the potential φ varies slowly in space; consequently, the Fermi wavevector k_F has also a slow spatial variation, so that one may linearize eq. (1) by substituting $\bar{k}_F k_F$ for k_F^2 , where \bar{k}_F is viewed as a variational parameter, assumed to be constant in space, and the whole spatial dependence is transferred upon the new variable k_F ; this substitution is justified for those spatial regions where \bar{k}_F and k_F are comparable in magnitude, and one can see easily that this is so for a moderate range of intermediate distances; it is precisely this range over which the most part of the electrons are localized in heavy atoms, so that one may expect to get a reasonable description by employing this linearization procedure. Therefore, we obtain

$$k_F = (2me/\hbar^2 \bar{k}_F) \varphi \quad (3)$$

for the linearized version of eq.(1), while a similar linearization for the electron density $n = k_F^3/3\pi^2 \rightarrow n = \bar{k}_F^2 k_F/3\pi^2$ leads to

$$n = (2m\bar{k}_F/3\pi^2 \hbar^2) \varphi = (q^2/4\pi e) \varphi \quad , \quad (4)$$

where the Thomas-Fermi screening wavevector q has been introduced through

$$q^2 = 8me^2 \bar{k}_F / 3\pi \hbar^2 \quad ; \quad (5)$$

now, Poisson's equation (2) has the well-known solution $\varphi = (Ze/r)e^{-qr}$, *i.e.* the screened Coulomb potential, as expected. One can see that this potential falls abruptly to zero at large distance, where the quasi-classical description does not apply (as the wavelengths increase indefinitely there), varies slowly over intermediate distances, as needed (and expected), and has an abrupt variation over short distances, *i.e.* near the atomic nucleus; in the small region around the nucleus the computations will be corrected, as required by the quantum behaviour of the electrons in this region. For the moment, however, we proceed further on, by computing the total energy.

By using the same linearization procedure the kinetic energy $E_{kin} = V\hbar^2 k_F^5 / 10\pi^2 m$ of the electron gas enclosed in a volume V is replaced by

$$E_{kin} = (\hbar^2 \bar{k}_F^4 / 10\pi^2 m) \int d\mathbf{r} \cdot k_F = \frac{e}{5\pi^2} (3\pi \hbar^2 / 8me^2)^3 q^6 \int d\mathbf{r} \cdot \varphi \quad , \quad (6)$$

which yields

$$E_{kin} = \frac{4}{5\pi} Ze^2 (3\pi \hbar^2 / 8me^2)^3 q^4 \quad . \quad (7)$$

The potential energy is given by

$$\begin{aligned} E_{pot} &= \int d\mathbf{r} \cdot (\rho_e \varphi - \frac{1}{2} \rho_e \varphi_e) = \frac{1}{2} \int d\mathbf{r} \cdot (\rho_e \varphi + \rho_e \varphi_c) = \\ &= -\frac{e}{2} \int d\mathbf{r} \cdot n(\varphi + \varphi_c) = -\frac{q^2}{8\pi} \int d\mathbf{r} \cdot (\varphi^2 + \varphi \varphi_c) \quad , \end{aligned}$$

where $\rho_e = -en$ is the density of the electronic charge, $\varphi_e = \varphi - \varphi_c$ is the electric potential produced by the electrons, and $\varphi_c = Ze/r$ is the Coulomb potential of the atomic nucleus. The computations are straightforward, and one obtains

$$E_{pot} = -\frac{3}{4} Z^2 e^2 q \quad . \quad (8)$$

The total energy reads therefore

$$E = E_{kin} + E_{pot} = \frac{4}{5\pi} Z e^2 (3\pi\hbar^2/8me^2)^3 q^4 - \frac{3}{4} Z^2 e^2 q \quad , \quad (9)$$

and it reaches the minimum value

$$E = -\frac{9}{16} Z^2 e^2 q = -11.78 Z^{7/3} eV \quad (10)$$

for the optimal value

$$q = (2me^2/3\pi\hbar^2)(15\pi)^{1/3} Z^{1/3} = \frac{2}{3\pi} (15\pi)^{1/3} Z^{1/3} a_H^{-1} \simeq 0.77 Z^{1/3} a_H^{-1} \quad (11)$$

of the variational parameter q ; the Bohr radius $a_H = \hbar^2/me^2 \simeq 0.53\text{\AA}$ is introduced here, and the atomic unit for energy $e^2/a_H \simeq 27.2\text{eV}$ will also be used. One can see that the radial density of electrons $\sim r^2 n$, as given by (4), has a maximum value at $R \sim 1/q \sim Z^{-1/3} a_H$, which may be taken as the "radius" of the electronic charge (while the "radius" of the atom is of the order of a_H); thus, one can see again that the quasi-classical description for large Z is justified; indeed, the quasi-classical description holds for distances longer than the radius a_H/Z of the first Bohr orbit and shorter than the Bohr radius a_H , and the electronic "radius" $R \sim Z^{-1/3} a_H$ is such that the inequalities $a_H/Z \ll R \sim a_H/Z^{1/3} \ll a_H$ are satisfied for large Z ; the most part of the electrons are localized around R , which justifies the statistical character of the Thomas-Fermi model for large Z . However, the linearization of the basic equations of the quasi-classical description, together with the variational approach, as well as the approximate character of the quasi-classical description in general, which alters the distinction between the exact kinetic and potential energies, lead to the breakdown of the virial theorem; indeed, one can check easily that $E_{kin} = -(1/4)E_{pot}$, instead of $E_{kin} = -(1/2)E_{pot}$, as required by the virial theorem; however, this is not a major drawback, as it is well-known that approximate calculations may give wrong values for both the "kinetic" and "potential" energies and still the total energy be quite close to the exact one;[10] this is due to the variational treatment, as employed here.

According to eq.(1) and the Thomas-Fermi model, the electronic states are described by quasi-plane waves everywhere in space, whose wavevector depends weakly on position; they correspond to the electrons motion in a slowly-varying potential, vanishing at large distances; the screened Coulomb potential φ is consistent with this assumption, except for short distances where it has a sudden variation; the electron single-particle energies must therefore be corrected for this additional potential energy, corresponding to the electrons motion close to the atomic nucleus; the correction is carried out to the first order of the perturbation theory, by estimating the average of the potential energy $-e\varphi$ over plane waves confined to a small spherical region of radius R around the nucleus; the radius R must be regarded as a variational parameter, and the correction to the energy will be minimized with respect to R ; doing so, we obtain an additional energy

$$-\frac{e}{v} \int_v d\mathbf{r} \cdot \varphi = -3Ze^2 q \cdot \frac{1}{x^3} (1 - e^{-x} - xe^{-x}) \quad , \quad (12)$$

to each electron state, where $v = 4\pi R^3/3$ and $x = qR$; the total change in energy ΔE is obtained by multiplying the above result by the total number of electrons in the volume v , which is given by $\int_v d\mathbf{r} \cdot n$;[11] one obtains

$$\Delta E = -3Z^2 e^2 q \cdot \frac{1}{x^3} (1 - e^{-x} - xe^{-x})^2 = \frac{16}{3} E \cdot \frac{1}{x^3} (1 - e^{-x} - xe^{-x})^2 \quad ; \quad (13)$$

this is a contribution to the total energy of the electrons, and it must be minimized with respect to the parameter R , or, equivalently, x , as noted above; the function of x in eq. (13) has a maximum value 0.073 for $x \simeq 0.75$, which corresponds to $R \simeq Z^{-1/3}a_H$, *i.e.* close to the electronic "radius", and yields

$$\Delta E = 0.39E = -4.56Z^{7/3}\text{eV} ; \quad (14)$$

therefore, the total energy is obtained as

$$E = -11.78Z^{7/3}\text{eV} - 4.56Z^{7/3}\text{eV} = -16.34Z^{7/3}\text{eV} , \quad (15)$$

which agrees well with the "empirical" binding energy $E \simeq -16Z^{7/3}\text{eV}$. Since the values derived here for the variational and the electronic "radii" are close to each other one may say that the computations are consistent; one can see also that ΔE amounts to cca 25% of the binding energy E , so that one may indeed regard ΔE as a correction to this energy; higher-order perturbation theory calculations modify the electronic (quasi-) plane waves, and the single-particle energies, according to the quantum behaviour; however, according to the perturbation theory, the main contribution to the total energy given above is not affected significantly. It is worth noting that the quantum correction given above vanishes in the limit $Z \rightarrow \infty$, as the electrons approach the quasi-classical limit; in addition, the main contribution $-11.78Z^{7/3}\text{eV}$ to the total energy derived above is in error in the limit $Z \rightarrow \infty$, as the linearization procedure is not valid anymore in this limit; indeed, the linearization holds as long as the Fermi wavevector k_F varies slowly in space; a measure of the departure from this behaviour is given by the extent to which the variational parameter $q = 0.77Z^{1/3}$ given by (11) differs from the parameter $q = (64Z/9\pi^2)^{1/3} \equiv 0.9Z^{1/3}$ given by (5), where the average \bar{k}_F is computed by using the electron density $n(\mathbf{r}) = (q^2/4\pi)\varphi(r) = (q^2Z/4\pi)e^{-qr}/r$ derived here; as one can see, the difference in the q -values is $\sim 15\%$, which implies a similar decrease in the total energy from $-16.34Z^{7/3}\text{eV}$ to $-18.8Z^{7/3}\text{eV}$; this value is closer to the exact value $-20.8Z^{7/3}\text{eV}$ for very large Z , as it ought to be. For finite values of Z the error in energy produced by the linearization procedure is nearly compensated by the error in the quantum correction ΔE noted in Ref.11. This may explain the rather surprising proximity of the energy E given by (15) to the experimental atomic binding energy. In this regard, one may say that the present linearized Thomas-Fermi approach is more appropriate for an intermediate range of Z -values, as corresponding to the "actual" atoms. The exchange energy must be added to the result given above by (15), and one can check that it brings a $\sim 4\%$ -correction at most, for $Z = 20$. As it can be seen easily, the ΔE -correction computed here in (14) corresponds to the Hartree contribution to the linearized Thomas-Fermi model; a similar correction to the exchange energy can also be obtained; though very small, we give it here since such corrections have previously been discussed to a rather large extent, in the framework of the atomic theory;[6][12] on the other hand, the computation of such exchange corrections helps to further enlighten the virtues of the linearized Thomas-Fermi model.

As it is well known the exchange energy of a homogeneous gas of electrons is given by $E_{ex} = -(e^2/4\pi^3)Vk_F^4$; according to the linearization procedure this energy is written as

$$E_{ex} = -\frac{e^2}{4\pi^3}\bar{k}_F^3 \int d\mathbf{r} \cdot k_F , \quad (16)$$

and making use of the results obtained above, in particular of eq. (3) and of the variational parameter q derived in (11), one obtains $E_{ex} = -4.53Z^{5/3}\text{eV}$. The correction to this exchange energy originates in the abrupt variation of the electronic density near the atomic nucleus; to the first-order of the perturbation theory it may be written as

$$\Delta E_{ex} = -\frac{e^2}{(2\pi)^6} \int_v d\mathbf{r} \int d\mathbf{r}' \int_F d\mathbf{k}d\mathbf{k}' \cdot e^{-i\mathbf{Q}\rho} \frac{1}{\rho} , \quad (17)$$

where $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$, $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}'$, v is the spherical volume of radius R around the nucleus, and F denotes the Fermi sea; in contrast to the Hartree correction given by (13) the integration over \mathbf{r}' is extended over the whole space, as a consequence of the non-local character of the exchange energy. The calculations in (17) proceed in the usual manner; first, we pass from the integration over \mathbf{r}' to the integration over $\boldsymbol{\rho}$; the result of this integration is $4\pi/Q^2 - (4\pi/3)r(3R + 2r) + \dots$; one may neglect the small contribution of the second term, and retain the main term $4\pi/Q^2$; next, we perform the \mathbf{k}, \mathbf{k}' -integrations, which lead to

$$\Delta E_{ex} = -\frac{e^2}{4\pi^3} \int_v d\mathbf{r} \cdot k_F^4 ; \quad (18)$$

according to the linearization procedure eq. (18) may also be written as

$$\Delta E_{ex} = -\frac{e^2}{4\pi^3} \bar{k}_F^3 \int_v d\mathbf{r} \cdot k_F ; \quad (19)$$

one gets straightforwardly

$$\Delta E_{ex} = (1 - e^{-x} - xe^{-x})E_{ex} ; \quad (20)$$

where E_{ex} is given by (16) and $x = qR$; for the electronic "radius" $x \simeq 1$ one obtains $\Delta E_{ex} \simeq 0.27E_{ex}$, while for the variational "radius" $x \simeq 0.75$ derived above one obtains $\Delta E_{ex} \simeq 0.18E_{ex}$; it follows that the exchange energy changes by a factor which lies somewhere between 1.18 and 1.27; it agrees well with similar exchange corrections derived in Ref.6 (which indicates a factor 1.22). It is customary to refer such a factor in the exchange energy, denoted by α , to the value $2/3$, which corresponds to the homogenous electron gas, *i.e.* to E_{ex} in the present calculations (and which is known as the Kohn-Sham value[13]); this is the α -factor in Slater's $X\alpha$ -method (and in density-functional calculations);[12] according to the present results the value of the α -factor runs between $\alpha \simeq (2/3) \cdot 1.18 \simeq 0.78$ and $\alpha \simeq (2/3) \cdot 1.27 \simeq 0.85$; more accurate density-functional computations[12],[14] of atomic and molecular orbitals recommend $\alpha \simeq 0.69 - 0.75$, which are in good agreement with the present results (the terms neglected in the above $\boldsymbol{\rho}$ -integration diminish to some extent the value of the α -factor); while Slater's original value[15] is $\alpha = 1$.

In conclusion, one may say that the variational treatment of the linearized Thomas-Fermi model provides a consistent quasi-classical description for the atomic binding energies in the range of realistic values of atomic numbers Z (heavy atoms), providing the quantum corrections (Hartree-type contributions) are properly included.[16] Therefore, to "the principle of unreasonable utility of asymptotic estimates"[17] one may add the principle of "expected utility of a consistent physical picture".

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