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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 herein 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.

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 ($Z \gg 1$).[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

$$\hbar^2 k_F^2/2m - e\varphi = 0 \ ; \tag{1}$$

here, the notations are the usual ones, *i.e.* $\hbar$ 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

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

where the electron density is given by $n = k_F^3/3\pi^2$, as for a Fermi gas. As it is well known, the atomic binding energy as computed by means of this theory[1],[2] is given by $E \simeq -20.8Z^{7/3}$eV, a value which differs, to some extent, from the empirical value[3] $E \simeq -16Z^{7/3}$eV. The main source of errors resides, of course, in the substitution of a classical problem for the quantum one, the Thomas-Fermi model being only the leading approximation to the exact result. Higher-order corrections to the quasi-classical approximation, or the self-consistent Hartree, or Hartree-Fock equations, as well as the density-functional approach, may be employed in order to improve upon the result.[4],[5] However, such computation schemes are usually iterative, and they may converge slowly, so that a higher accuracy is often difficult to be attained this way for a generic atom. In this Note we present a variational approach to the Thomas-Fermi model which leads to better numerical results; this is peformed by a linearized version of the quasi-classical approximation.

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, and 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

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

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

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

where the Thomas-Fermi wavevector q has been introduced through

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

now, Poisson's equation (2) has the well known solution $\varphi = (Ze/r)e^{-qr}$, *i.e.* the screened Coulomb potential. One can see that this potential falls abruptly to zero at large distances, where the quasi-classical description does not appply (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; over small regions around the nucleus the computations will be corrected, as required by the quantum behaviour of the electrons in such regions. For the moment, however, we proceed further with 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

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

which yields

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

The potential energy is given by

$$E_{pot} = \int d\mathbf{r} \cdot (\rho_e\varphi - \frac{1}{2}\rho_e\varphi_e) = \frac{1}{2}\int d\mathbf{r} \cdot (\rho_e\varphi + \rho_e\varphi_c) =$$

$$= -\frac{e}{2}\int d\mathbf{r} \cdot n(\varphi + \varphi_c) = -\frac{q^2}{8\pi}\int d\mathbf{r} \cdot (\varphi^2 + \varphi\varphi_c) \quad ,$$

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

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

The total energy reads therefore

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

and it reaches the minimum value

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

for the optimal value

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

of the variational parameter q; the Bohr radius $a_H = \hbar^2/me^2 \simeq 0.53$Å is introduced here (the atomic unit $e^2/a_H \simeq 27.2$eV is also used often in such type of computations). One can see that the radial density of electrons $\sim r^2 n$ 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, and the electronic "radius" $R \sim Z^{-1/3}a_H$ is such that the inequailities $a_H/Z \ll R \sim a_H/Z^{1/3} \ll a_H$ are satisfied for large Z; and 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 to computations, 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, by compensating errors;[6] one may expect such a possibility due to the variational treatment employed here.

According to eq.(1) and the Thomas-Fermi model, the electronic states are quasi-plane waves everywhere in space, whose wavevector depends weakly on position; they correspond to the electrons motion in a weak 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; since the actual quasi-plane waves are approximated this way by exact plane waves, we regard the radius R as a variational parameter, and the correction to the energy will be minimized with respect to R; doing so, we obtain an additional energy

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

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 $\int_v d\mathbf{r} \cdot n$; one obtains

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

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

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

the total energy is therefore

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

which is in good agreement with the empirical value $E \simeq -16Z^{7/3}\text{eV}$. 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 exact value of the binding energy E, so that one may regard indeed 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, the Thomas-Fermi leading term to the total energy will not be affected much, for large Z, according to the present calculations; in particular, the quantum corrections account for the electronic shell effects, and for the small, irregular behaviour of the atomic binding energy, as seen in the ionization potentials. In this respect, we recall that the next-order correction to the binding energy comes, as it is known, from the exchange energy, and it goes like $Z^{5/3}$, *i.e.* it is smaller by a $Z^{-2/3}$-factor than the leading $Z^{7/3}$-contribution given here; as one can see easily, the ΔE-correction computed here in (14) corresponds to the Hartree contribution to the usual Thomas-Fermi model; a similar correction to the exchange energy can also be obtained.

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

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

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 quantum behaviour of the electrons near the atomic nucleus; to the first-order of the perturbation theory it may be written as

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

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, due to the non-local character of the exhange 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 $4\pi/Q^2 - (4\pi/3)r(3R+2r)+...$; 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

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

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

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

one gets straightforwardly

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

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 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[5]); this is the α-factor in Slater's $X\alpha$-method (and in density-functional calculations);[7] 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[7],[8] of atomic and molecular orbitals recommend $\alpha \simeq 0.69 - 0.75$, which are in good agreement with the present results (the correcting terms neglected in the above $\boldsymbol{\rho}$-integration diminish to some extent the value of the α-factor); while Slater's original value[9] is $\alpha = 1$. A comparison with more accurate computations of the binding energy would not be appropriate yet, as such type of calculations are not available for heavy atoms.

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