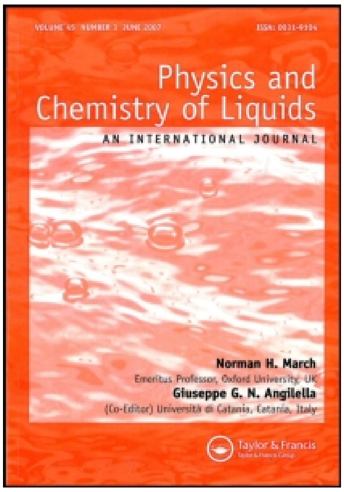

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# Relativistic theory of an inhomogeneous electron liquid in relation to atomic binding energies

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# RELATIVISTIC THEORY OF AN INHOMOGENEOUS ELECTRON LIQUID IN RELATION TO ATOMIC BINDING ENERGIES

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Experimentally determined ionization potentials in the literature are used to plot the binding energies for neutral atoms as a function of atomic number $Z$ for $Z=2$–30, 32, 36, 42. From this pretty smooth plot we have subtracted non-relativistic Hartree–Fock binding energies, using both available numerical values and the almost analytical result, based on the non-relativistic Thomas–Fermi statistical theory valid for large $Z$. The difference is still relatively smooth. For Mo, with $Z=42$, the difference is about 70 atomic units. This difference is then analyzed using first relativistic theory of an inhomogeneous electron liquid and then the Local Density Approximation (LDA), and for Mo their results yield approximately 88 and 67 atomic units respectively. We infer that a highly accurate relativistic many-electron theory will therefore be needed before reliable electron correlation energies can be extracted from the experimental binding energies for atoms heavier than Argon. This fact has prompted us to use available LDA calculations to confront three theoretical predictions of the $Z$ dependence of non-relativistic electron correlation energies at large $Z$.

*Keywords:* Relativistic electron liquid; Atomic binding energies; Correlation

## 1. INTRODUCTION

The electron correlation energies in atoms ranging from helium to argon are by now reasonably well known, a recent contribution being that of Alonso *et al.* [1], where contact is made with the density functional studies of Perdew *et al.* [2]. Our interest in this work is in heavier atoms.

The experimental way of determining the total binding energy of an atom is by adding all its ionization potentials. The two most complete data sets of ionization energies are those in the CRC Handbook of Chemistry and Physics [3] and in the NIST Atomic Spectra Database [4]. The former lists all ionization energies for the first 30 elements of the periodic table, and the latter adds another four, namely $Z = 32, 34, 36, 42$, and gives in some cases, the uncertainty of the measured values.

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The difference between the total binding energy and the Hartree–Fock energy of an atom is due to Coulomb correlation and relativistic effects. In order to determine the importance of each of them we study in Section 2 the relativistic contribution calculated within both the Thomas–Fermi model and the Local Density Approximation (LDA) to the Density Functional Theory (DFT), and compare the results to various estimates of the Coulomb correlation energy.

Finally, in Section 3 we analyze the asymptotic behavior of the Coulomb correlation energy for large atomic number. Since there are no experimental data for the total binding energies of heavy atoms, we use LDA results for testing three theoretical predictions of the $Z$ dependence of non-relativistic electron correlation energies at large $Z$.

## 2. MEDIUM-WEIGHT ATOMS

If we denote the ground-state neutral atom energies by $E(Z)$, we have used experimental ionization potentials given in Refs. [3,4] to plot in Fig. 1 the binding energies $|E(Z)|$ as a function of $Z$, for all the atoms for which the complete set of ionization potentials is known, that is for $Z \leq 30$ and $Z = 32, 34, 36, 42$. The corresponding data are presented in the third and fourth columns of Table I. The total binding energies have been calculated as the sum of ionization energies and, when possible, an estimation of the uncertainty is given. The differences between both sources are not very large and can be taken as lower limits of the uncertainty in those cases where the uncertainty of all the ionization energies is not known.

Figure 1 shows that binding energies depend on atomic number in a smooth way. Therefore, in Fig. 2, we present the results of subtracting from the experimental curve in Fig. 1 the non-relativistic Hartree–Fock ground state energies given by Clementi and Roetti [5]. The numerical values are listed in the sixth column of Table I. We note that for Mo, as the heaviest atom considered in Figs. 1 and 2, the difference shown in Fig. 2 is approximately two orders of magnitude smaller than the binding energy given in Fig. 1.

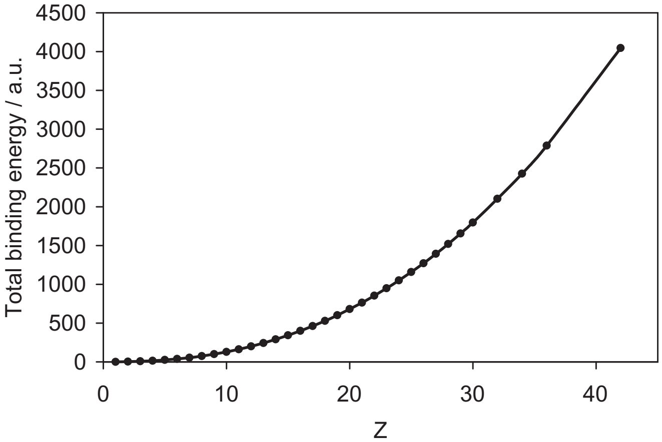

FIGURE 1 Experimental atomic binding energies, in atomic units, calculated as the sum of the successive ionization potentials given in [3,4]. The line is merely a guide for the eye.

TABLE I Experimental atomic binding energies (CRC from Ref. [3], and ASD from Ref. [4]), non-relativistic Hartree–Fock energies from Ref. [5], relativistic Thomas–Fermi corrections from Eq. (2), and relativistic LDA corrections calculated from Ref. [6], in atomic units

| $Z$ | *Atom* | $-E_{\mathrm{exp}}$(CRC) | $-E_{\mathrm{exp}}$(ASD) | $-E_{\mathrm{HF}}$ | $E_{\mathrm{HF}} - E_{\mathrm{exp}}$ | $-E_{\mathrm{rel}}$(TF) | $-E_{\mathrm{rel}}$(LDA) |
|---|---|---|---|---|---|---|---|
| 1 | H | 0.4997335 | 0.4997335 | — | — | — | — |
| 2 | He | 2.903388 | 2.9033 | 2.861680 | 0.04171 | 0.0005 | -0.000051 |
| 3 | Li | 7.477980 | 7.4779 | 7.432726 | 0.04526 | 0.0022 | 0.000036 |
| 4 | Be | 14.66846 | 14.66838 | 14.57302 | 0.0954 | 0.0065 | 0.000788 |
| 5 | B | 24.65823 | 24.65824 | 24.52906 | 0.1292 | 0.0153 | 0.003133 |
| 6 | C | 37.85569 | 37.85570 | 37.68861 | 0.1671 | 0.0310 | 0.008422 |
| 7 | N | 54.61193 | 54.61194 | 54.40092 | 0.2110 | 0.0566 | 0.018468 |
| 8 | O | 75.1084 | 75.1086 | 74.8094 | 0.299 | 0.0959 | 0.035576 |
| 9 | F | 99.8062 | 99.8060 | 99.4093 | 0.397 | 0.1532 | 0.062591 |
| 10 | Ne | 129.0504 | 129.0505 | 128.5470 | 0.503 | 0.2336 | 0.102922 |
| 11 | Na | 162.4310 | 162.4315 | 161.8589 | 0.572 | 0.3428 | 0.161631 |
| 12 | Mg | 200.3254 | 200.3252 | 199.6146 | 0.711 | 0.4874 | 0.243559 |
| 13 | Al | 242.7289 | 242.7282 | 241.8767 | 0.852 | 0.6747 | 0.353750 |
| 14 | Si | 289.8894 | 289.8888 | 288.8543 | 1.035 | 0.9126 | 0.498528 |
| 15 | P | 341.9819 | 341.9818 | 340.7187 | 1.263 | 1.2100 | 0.684798 |
| 16 | S | 399.080 | 399.076 | 397.505 | 1.58 | 1.5765 | 0.920204 |
| 17 | Cl | 461.381 | 461.384 | 459.482 | 1.90 | 2.0225 | 1.213157 |
| 18 | Ar | 529.1 | 529.2 | 526.817 | 2.4 | 2.5594 | 1.572854 |
| 19 | K | 601.9 | 602.0 ± 0.4 | 599.165 | 2.8 ± 0.4 | 3.1992 | 2.010603 |
| 20 | Ca | 680.2 | 680.2 ± 0.5 | 676.758 | 3.4 ± 0.5 | 3.9550 | 2.537063 |
| 21 | Sc | 763.9 | 763.8 ± 0.5 | 759.735 | 4.1 ± 0.5 | 4.8406 | 3.157198 |
| 22 | Ti | 853.4 | 853.4 ± 0.4 | 848.406 | 5.0 ± 0.4 | 5.8707 | 3.885247 |
| 23 | V | 948.8 | 948.9 ± 0.7 | 942.884 | 6.0 ± 0.7 | 7.0612 | 4.733680 |
| 24 | Cr | 1050.49 | 1050.54 | 1043.355 | 7.1 | 8.4286 | 5.708051 |
| 25 | Mn | 1158.3 | 1158.2 ± 1.0 | 1149.866 | 8.3 ± 1.0 | 9.9906 | 6.844840 |
| 26 | Fe | 1271.7 | 1273.1 ± 1.1 | 1262.443 | 10.7 ± 1.1 | 11.7655 | 8.136024 |
| 27 | Co | 1393.4 | 1393.3 ± 1.2 | 1381.414 | 11.9 ± 1.2 | 13.7731 | 9.604559 |
| 28 | Ni | 1520.7 | 1521 ± 2 | 1506.870 | 14 ± 2 | 16.0337 | 11.266670 |
| 29 | Cu | 1655.1 | 1655 ± 7 | 1638.963 | 16 ± 7 | 18.5690 | 13.124536 |
| 30 | Zn | — | 1796 ± 6 | 1777.848 | 18 ± 6 | 21.4016 | 15.240735 |
| 32 | Ge | — | 2102 ± 8 | 2075.359 | 26 ± 8 | 28.0543 | 20.250263 |
| 34 | Se | — | 2426 | 2399.866 | 26 | 36.1940 | 26.456690 |
| 36 | Kr | — | 2789 | 2752.055 | 36 | 46.0409 | 34.051298 |
| 42 | Mo | — | 4050 ± 30 | 3975.534 | 70 ± 30 | 88.3089 | 67.248699 |

For comparison with the use of numerical Hartree–Fock data, we record the analytic form of the electron density theory (see, e.g. Ref. [7])

$$\left|E_{\mathrm{TF}}(Z)\right| \approx 0.7687\, Z^{7/3} - \frac{1}{2} Z^2 + 0.26\, Z^{5/3}\ . \tag{1}$$

In Eq. (1), the first term is the self-consistent energy of the Thomas–Fermi non-relativistic atom; going back to Milne [8], the $Z^2$ term is dominantly accounting for the large electron density gradient in the $K$ shell and was first given by Scott [9], and the final $Z^{5/3}$ term is mainly exchange energy corrected for differences between WBK-like discrete atomic eigenvalues and the Thomas–Fermi semiclassical distribution of eigenvalues (see Refs. [10–12]). The use of Eq. (1) instead of Hartree–Fock results [13] does not change Fig. 2.

The difference between experimental binding energies and non-relativistic Hartree–Fock values arises from two sources: correlation and relativistic corrections. In order to estimate the relative importance of each of them, and motivated by the usefulness

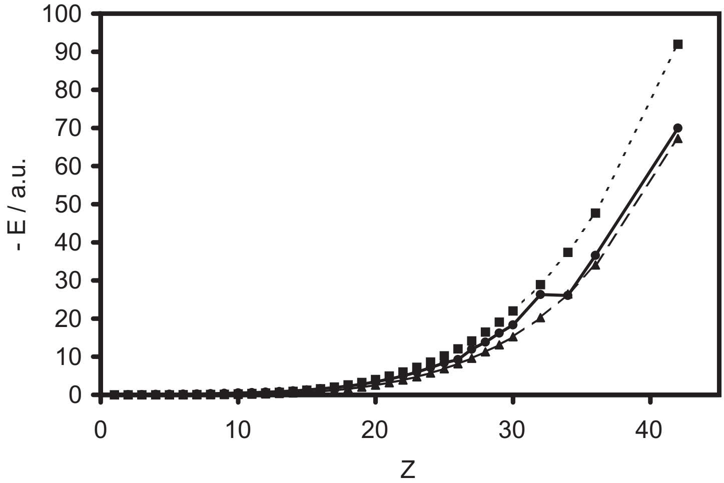

FIGURE 2 Energy differences between experimental and Hartree–Fock atomic binding energies (●), compared to relativistic Thomas–Fermi corrections to atomic binding energies (■) and relativistic LDA corrections to atomic binding energies (▲). See text for details.

of Eq. (1) in the analysis of experimental data, we proceed to bring Fig. 2 into direct contact with the self-consistent relativistic Thomas–Fermi calculations for neutral atoms carried out by Hill *et al.* [14]. These workers write the relativistic correction $E_{\text{rel}}(\text{TF})$ to atomic binding energies of neutral atoms, with large $Z$ since the Thomas–Fermi model has statistical origins and therefore comes into its own for large $Z$, as

$$E_{\text{rel}}(\text{TF}) = E_{\text{rel}}^{(1)} + E_{\text{rel}}^{(2)} \tag{2}$$

where

$$\begin{aligned} E_{\text{rel}}^{(1)} = -(\alpha Z)^2 Z^2 \big(&0.94435 - 2.07506\, Z^{-1/3} + 1.46232\, Z^{-2/3} \\ &+ 2.47358\, Z^{-1} - 2.28582\, Z^{-4/3}\big) \end{aligned} \tag{3}$$

and

$$E_{\text{rel}}^{(2)} = -(\alpha Z)^4 Z^2 \big(0.238715 + 4.97877\, Z^{-2/3} - 0.07781 Z^{-1} - 4.74528 Z^{-1} \log Z\big) \tag{4}$$

In Fig. 2, we have therefore, also plotted the result $E_{\text{rel}}(\text{TF})$ from Eqs. (2)–(4) given in the seventh column of Table I. As expected from such an electron gas theory (including also electron gas approximation for kinetic energy) the $Z$ dependence is entirely smooth. Besides, it is evident that this simple approximation overestimates the relativistic contribution to the total binding energy, since $-E_{\text{rel}}(\text{TF})$ is greater than the sum of Coulomb correlation and relativistic effects ($E_{\text{HF}} - E_{\text{exp}}$) for $Z > 15$. A better approximation to the relativistic contribution can be obtained from the Density Functional Theory. In the last column of Table I we present the difference between

TABLE II Nonrelativistic second-order Møller-Plesset (MP2) atomic binding energies from Ref. [16], the corresponding relativistic contribution to total energies calculated using the experimental energies in Table I, and several estimations of the Coulomb correlation energies: MP2 from Ref. [16], "soft" Coulomb-hole approach (SCH) from Refs. [17,18], and the virial constrained effective Hamiltonian method (VCEH) from Ref. [19]. All of them in atomic units

| $Z$ | *Atom* | $-E_{\mathrm{tot}}$(MP2) | $-E_{\mathrm{rel}}$ | $-E_{\mathrm{c}}$(MP2) | $-E_{\mathrm{c}}$(SCH) | $-E_{\mathrm{c}}$(VCEH) |
|---|---|---|---|---|---|---|
| 10 | Ne | 128.938298 | 0.112 | 0.38811 | 0.347 | 0.4080 |
| 12 | Mg | 200.054066 | 0.27 | 0.42793 | 0.442 | 0.4656 |
| 18 | Ar | 527.543613 | 1.5 | 0.70945 | 0.736 | 0.7817 |
| 30 | Zn | 1779.5456 | $16\pm6$ | 1.69746 | 1.740 | 1.6860 |
| 36 | Kr | 2753.9457 | 35 | 1.8907 | 2.262 | 2.0671 |

the very accurate non-relativistic and the relativistic total energies calculated within the LDA approximation by Kotochigova *et al.* [6]. This difference is also plotted in Fig. 2. Using this local approximation the relativistic contribution to the total binding energy is also smooth on $Z$, but $-E_{\mathrm{rel}}$(LDA) is always smaller than $E_{\mathrm{HF}} - E_{\mathrm{exp}}$.

Summarizing, this plot shows that, save for the lightest elements, the main contribution to the difference between experimental and Hartree–Fock atomic binding energies comes from relativistic effects rather than from correlation. So, while the problem of electron correlation in medium-weight atoms remains, of course highly interesting, it is clear that the dominant correction to, say the electron gas theory embodied in Eq. (1) for non-relativistic quantum mechanics, comes from relativistic effects. We stress here, that for internal consistency, we have restricted our comparisons entirely to the results of the original relativistic Thomas–Fermi theory going back to Vallarta and Rosen [15].

It is possible in some cases to compare in a numerical way semiempirical correlation energies with relativistic corrections. We present in Table II, the non-relativistic total energies of several atoms calculated within the accurate second order Møller–Plesset (MP2) approximation calculated by Flores *et al.* [16]. The relativistic contribution to the total binding energies can be obtained by subtracting these energies from the experimental ones given in Table I, $E_{\mathrm{rel}} = E_{\mathrm{exp}} - E_{\mathrm{MP2}}$. It is interesting to note that the comparison with the last column of Table I shows that LDA estimations of this contribution are indeed rather accurate, in spite of LDA being quite a simple approximation. The table also presents the results of three calculations of the Coulomb correlation energies: MP2 [16], the "soft" Coulomb hole approach [17,18], and the virial constrained effective Hamiltonian method [19]. From this table it is easy to see that even for a relatively light element like Ar, the relativistic contribution to the total binding energy is twice as large as the correlation energy and, as $Z$ increases the difference gets bigger, reaching for Zn one order of magnitude.

## 3. HEAVY ATOMS

Three proposals have been made on the behaviour of the Coulomb correlation energy for $Z \to \infty$, namely $E_{\mathrm{c}} \propto Z$ [20], $E_{\mathrm{c}} \propto Z^{4/3}$ [21] and $E_{\mathrm{c}} \propto Z \log Z$ [22]. There are no complete series of experimental ionization potentials for heavy atoms and even for medium-weight ones the uncertainties in their sum, as shown in Table I, are greater than the correlation energies. Thus, the different proposals for the asymptotic

TABLE III Nonrelativistic LDA atomic binding energies for heavy atoms, with (xc) and without (xo) Coulomb correlation from Ref. [23], and the corresponding correlation energy calculated as the difference of them, in atomic units

| $Z$ | *Atom* | $-E_{xo}$(LDA) | $-E_{xc}$(LDA) | $-E_c$(LDA) |
|---|---|---|---|---|
| 54 | Xe | 7223.6572 | 7228.8068 | 5.150 |
| 56 | Ba | 7874.7341 | 7880.0616 | 5.328 |
| 70 | Yb | 13380.9107 | 13387.9732 | 7.062 |
| 78 | Pt | 17318.5338 | 17326.5715 | 8.038 |
| 80 | Hg | 18395.9201 | 18404.1822 | 8.262 |
| 86 | Rn | 21852.3214 | 21861.2472 | 8.926 |
| 88 | Ra | 23079.4706 | 23088.5875 | 9.117 |
| 102 | No | 32772.2698 | 32783.1575 | 10.888 |
| 110 | Uun | 39206.0988 | 39217.9791 | 11.880 |
| 112 | Uub | 40918.1951 | 40930.3013 | 12.106 |
| 118 | | 46303.5053 | 46316.2867 | 12.781 |
| 120 | | 48181.7155 | 48194.6929 | 12.977 |

$Z$ dependence of non-relativistic electron correlation energies, have to be tested via appeal to Schrödinger many-electron theory rather than by direct extraction from experimental binding energies.

As a first step in this direction we have calculated LDA atomic correlation energies for closed-shell heavy atoms up to $Z=120$ from the exchange-only and exchange +correlation calculations of Andrae *et al.* [23]. The results are presented in Table III. The fitting of these data to the three proposed asymptotic behaviors gives the following regression coefficients: $Z$, $R^2 \approx 0.9998$; $Z^{4/3}$, $R^2 \approx 0.9983$; $Z\log Z$, $R^2 \approx 0.9993$. Thus, the first proposal seems to fit in slightly better than the other two, at least within a local density framework. Nevertheless, further calculations for heavier atoms and with more accurate models have to be carried out before the dispute among the three proposals can be settled.

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