Improved Upper Bounds for the Atomic Ionization Potential

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ABSTRACT: Two sets of rigorous upper bounds on the atomic ionization potential are derived from some known inequalities of the classical analysis. The first set of bounds are expressed in terms of radial expectation values of the electron density; they improve previously found bounds of the same kind and converge to the exact ionization potential. The other bounds depend on various atomic density functionals which describe global physical quantities such as the Thomas–Fermi and exchange energies and the Boltzmann–Shannon information entropy. The accuracy of some of the bounds is numerically analyzed within a Hartree–Fock framework.
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Introduction

The first ionization potential in atoms ϵ, an experimentally measurable quantity, plays a very important role in the description of many physical and chemical properties of the atomic systems [1]. In this sense, it is worthy to remark that the long-range behavior of the one-particle density $\rho(r)$ is strongly related to the value of ϵ as [2, 3]

$$\rho(r) \sim r^{2(\gamma-1)} e^{-2\sqrt{2\epsilon}\, r}, \tag{1}$$

where $\gamma = Z - N + 1/\sqrt{2\epsilon}$, N is the number of electrons, and Z is the nuclear charge. This is one of the reasons why much effort has been devoted to obtaining rigorous bounds to the ionization potential in terms of physically meaningful quantities. Among these quantities, especially relevant are the radial expectation values

$$\langle r^{\alpha} \rangle \equiv \int r^{\alpha} \rho(\mathbf{r})\, d\mathbf{r} = 4\pi \int_0^{\infty} r^{\alpha+2} \rho(r)\, dr \tag{2}$$

as well as some *local* values such as the density and its first derivatives at the nucleus.

In [4], several upper bounds to the atomic ionization potential ϵ, within the infinite nuclear mass

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approximation, were given in terms of radial expectation values. Their obtainment is based on the differential in equation [5]

$$\rho''(r) + \frac{2}{r}[\rho'(r) + 2Z\rho(r)] - 4\epsilon\rho(r) - \frac{1}{2}\frac{[\rho'(r)]^2}{\rho(r)} \geq 0, \quad (3)$$

which is valid for the exact spinless electron density. In the first step, the bounds are expressed in the form

$$\epsilon \leq \frac{1}{4\langle r^{\alpha-1}\rangle}\left\{\alpha(\alpha-1)\langle r^{\alpha-3}\rangle + 4Z\langle r^{\alpha-2}\rangle - 2\pi\int_0^\infty r^{\alpha+1}\frac{[\rho'(r)]^2}{\rho(r)}\,dr\right\} \quad (4)$$

for any $\alpha > 0$. Let us write here the particular case corresponding to $\alpha = 1$:

$$\epsilon \leq \frac{1}{N}\left\{Z\langle r^{-1}\rangle - \frac{\pi}{2}\int_0^\infty r^2\frac{[\rho'(r)]^2}{\rho(r)}\,dr\right\}, \quad (5)$$

that is, an upper bound to ϵ which involves the electron–nucleus attraction energy $E_{eN} \equiv -Z\langle r^{-1}\rangle$, and the number of electrons of the atom $N = \langle r^0\rangle$. The integral term is related to the Weizsäcker functional T_W [1] as well as to the so-called *Fisher information entropy* [6].

In [4], the contribution of the integral term in Eq. (4) is bounded in terms of two radial expectation values, giving rise to upper bounds on ϵ which only depend on quantities of the type $\langle r^n\rangle$. In this derivation, the generalized Hölder's inequality is used assuming that the charge density $\rho(r)$ is a monotonically decreasing function.

In the present work, two different techniques are used in order to extend and to improve the accuracy of the bounds on the integral term in Eqs. (4) and (5). First, the Redheffer's inequality [7, 8] is used to improve the accuracy of the bounds to the integral term, involving the same radial expectation values and avoiding the assumption of monotonically decreasing $\rho(r)$. Second, new bounds in terms of density-functionals, such as the frequency moments

$$\omega_n \equiv \int \rho^n(\mathbf{r})\,d\mathbf{r} \quad (6)$$

and the Boltzmann–Shannon entropy [9]

$$S_\rho \equiv -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r})\,d\mathbf{r} \quad (7)$$

are obtained by means of a Sobolev-type inequality [10, 11].

A numerical analysis of the accuracy of the bounds is carried out in a Hartree–Fock framework. Finally, some concluding remarks are given.

Bounds in Terms of Radial Expectation Values

The Redheffer's inequality [7, 8],

$$\int_0^\infty r^{m+n-1}u^2(r)\,dr \leq \frac{2}{m+n}\left\{\int_0^\infty r^{2n}[u'(r)]^2\,dr\int_0^\infty r^{2m}u^2(r)\,dr\right\}^{1/2}, \quad (8)$$

is valid for any absolutely continuous function $u(r)$ and where $-m < n \leq m+1$. Let us replace the parameters $\{m, n\}$ by $\{\delta \equiv 1-2n,\ \beta \equiv m-n\}$ and choose $u(r) \equiv r^k\rho^{1/2}(r)$ with $k = (\alpha+\delta)/2$. Then, $u(r)$ is absolutely continuous and Eq. (8) becomes

$$2\pi\int_0^\infty r^{\alpha+1}\frac{[\rho'(r)]^2}{\rho(r)}\,dr \geq \frac{(\beta-\delta+1)^2}{2}\frac{\langle r^{\alpha+\beta-2}\rangle^2}{\langle r^{\alpha+2\beta-1}\rangle} + \frac{\alpha^2-\delta^2}{2}\langle r^{\alpha-3}\rangle, \quad (9)$$

with $\alpha > 0$, $\beta > \delta - 1$, and $\beta \geq -1$. Now, we optimize the above lower bound on the parameter δ, giving rise to

$$2\pi\int_0^\infty r^{\alpha+1}\frac{[\rho'(r)]^2}{\rho(r)}\,dr \geq \frac{\langle r^{\alpha-3}\rangle}{2}\left[\alpha^2 + (\beta+1)^2 \times \frac{\langle r^{\alpha+\beta-2}\rangle^2}{\langle r^{\alpha+2\beta-1}\rangle\langle r^{\alpha-3}\rangle - \langle r^{\alpha+\beta-2}\rangle^2}\right], \quad (10)$$

with $\alpha > 0$ and $\beta \geq -1$. Joining this expression with Eq. (4), we obtain the upper bound to the ionization potential ϵ in terms of radial expectation values:

$$\epsilon \leq \frac{Z\langle r^{\alpha-2}\rangle}{\langle r^{\alpha-1}\rangle} - \frac{\langle r^{\alpha-3}\rangle}{8\langle r^{\alpha-1}\rangle} B_{\alpha\beta} \equiv \epsilon^{R}_{\alpha\beta}, \quad (11)$$

where the factor $B_{\alpha\beta}$ is given by

$$B_{\alpha\beta} \equiv \alpha(2-\alpha) + \frac{(\beta+1)^2\langle r^{\alpha+\beta-2}\rangle^2}{\langle r^{\alpha-3}\rangle\langle r^{\alpha+2\beta-1}\rangle - \langle r^{\alpha+\beta-2}\rangle^2}. \quad (12)$$

It is interesting to write the particular case corresponding to the choice $\alpha = 3$ and $\beta = -1$, namely:

$$\epsilon \leq \frac{1}{\langle r^2\rangle}\left[Z\langle r\rangle + \frac{N}{8}\left(3 - \frac{1}{\Delta^2(\ln r)}\right)\right], \quad (13)$$

which involves the logarithmic uncertainty

$$\Delta(\ln r) \equiv \left[\frac{N\langle(\ln r)^2\rangle - \langle \ln r\rangle^2}{N^2}\right]^{\frac{1}{2}}, \quad (14)$$

a quantity which has been shown to be very useful in the study of the internal disorder of atomic systems [12–14].

In [4], similar upper bounds on ϵ were obtained by using Hölder's inequality (instead of Redheffer's inequality) to bound the contribution of the integral term. It was assumed there that the charge density $\rho(r)$ is monotonically decreasing. However, the same result is valid even for nonmonotonic densities, as can be shown by using Redheffer's inequality for two moments. Such a bound is given by

$$\epsilon \leq \frac{Z\langle r^{\alpha-2}\rangle}{\langle r^{\alpha-1}\rangle} - \frac{\langle r^{\alpha-3}\rangle}{8\langle r^{\alpha-1}\rangle} A_{\alpha\beta} \equiv \epsilon^{H}_{\alpha\beta}, \quad (15)$$

where the factor $A_{\alpha,\beta}$ is

$$A_{\alpha\beta} \equiv 2\alpha(1-\alpha) + \frac{(\alpha+\beta+1)^2\langle r^{\alpha+\beta-2}\rangle^2}{\langle r^{\alpha-3}\rangle\langle r^{\alpha+2\beta-1}\rangle}, \quad (16)$$

with $\alpha > 0$, $\beta \geq -1$.

First, we observe that both bounds (11) and (15) are expressed in terms of the same quantities [except for $\alpha = 1$, for which the factor $\langle r^{\alpha-3}\rangle$ cancels out in Eq. (15)]. Second, $B_{\alpha\beta} \geq A_{\alpha\beta}$ for any $\alpha > 0$, $\beta \geq -1$. This means that the upper bounds given by Eq. (11) are more accurate than are those given by Eq. (15). Moreover, in both cases, the bounds (i) converge to the exact value of the ionization potential ϵ when $\alpha, \beta \to \infty$, due to the asymptotic behavior [15]

$$\frac{\langle r^{\alpha}\rangle}{\langle r^{\alpha+1}\rangle} \sim \frac{\sqrt{8\epsilon}}{\alpha}$$

for $\alpha \to \infty$, and (ii) the bounds are saturated (i.e., they reach the exact value of ϵ) for $\beta = 0$ and any $\alpha > 0$ in hydrogenic atoms.

Let us write explicitly the expressions for some particular cases:

$\alpha = 1,\ \beta = 0$:

$$\epsilon^{H}_{\alpha\beta} = \frac{16\langle r^{-1}\rangle^2}{N\langle r^{-2}\rangle},\ \epsilon^{R}_{\alpha\beta} = 4 + \frac{4\langle r^{-1}\rangle^2}{N\langle r^{-2}\rangle - \langle r^{-1}\rangle^2}$$

$\alpha = 1,\ \beta = 2$:

$$\epsilon^{H}_{\alpha\beta} = \frac{36N^2}{\langle r^{-2}\rangle\langle r^2\rangle},\ \epsilon^{R}_{\alpha\beta} = 4 + \frac{16N^2}{\langle r^{-2}\rangle\langle r^2\rangle - N^2}$$

$\alpha = 2,\ \beta = 0$:

$$\epsilon^{H}_{\alpha\beta} = \frac{36N^2}{\langle r^{-1}\rangle\langle r\rangle} - 16,\ \epsilon^{R}_{\alpha\beta} = \frac{4N^2}{\langle r^{-1}\rangle\langle r\rangle - N^2}$$

$\alpha = 3,\ \beta = 0$:

$$\epsilon^{H}_{\alpha\beta} = \frac{64\langle r\rangle^2}{N\langle r^2\rangle} - 48,\ \epsilon^{R}_{\alpha\beta} = \frac{4\langle r\rangle^2}{N\langle r^2\rangle - \langle r\rangle^2} - 12.$$

To have an idea of the accuracy of the bounds $\epsilon^{H}_{\alpha\beta}$ and $\epsilon^{R}_{\alpha\beta}$, we computed their values in a Hartree–Fock framework using the atomic wave functions of Clementi–Roetti [16] and McLean–McLean [17]) for all neutral atoms (i.e., with $N = Z$) within the range $1 \leq N \leq 92$. Such calculation reveals that the values of the bounds strongly depend on the parameter α, while for fixed α, those values are almost independent of β. For this reason, and for simplicity, we will restrict the discussion on the accuracy to the case $\beta = 0$, for which we consider the notation

$$\epsilon^{H}_{\alpha} = \epsilon^{H}_{\alpha 0} = \frac{Z\langle r^{\alpha-2}\rangle}{\langle r^{\alpha-1}\rangle} - \frac{\langle r^{\alpha-3}\rangle}{8\langle r^{\alpha-1}\rangle} \times \left[2\alpha(1-\alpha) + \frac{(\alpha+1)^2\langle r^{\alpha-2}\rangle^2}{\langle r^{\alpha-3}\rangle\langle r^{\alpha-1}\rangle}\right] \quad (17)$$

$$\epsilon_\alpha^R \equiv \epsilon_{\alpha 0}^R = \frac{Z\langle r^{\alpha-2}\rangle}{\langle r^{\alpha-1}\rangle} - \frac{\langle r^{\alpha-3}\rangle}{8\langle r^{\alpha-1}\rangle} \times \left[\alpha(2-\alpha) + \frac{\langle r^{\alpha-2}\rangle^2}{\langle r^{\alpha-3}\rangle\langle r^{\alpha-1}\rangle - \langle r^{\alpha-2}\rangle^2}\right]. \quad (18)$$

In Table I, a quantitative analysis of the above-mentioned two sets of bounds is carried out for $\alpha = 1, 2, 5, 6$ in some atoms, and the experimental values of the atomic ionization potential are also shown. We see that (i) the accuracy of the bounds greatly increases when increasing the value of the parameter α, that is, when involving radial expectation values of higher order (as could be expected from the property of convergence of the bounds to the exact value of the ionization potential); this fact is especially apparent for medium and heavy atoms; (ii) Redheffer's inequality does not produce a significant improvement in accuracy relative to that of the generalized Hölder's inequality except for very low values of α, in which case both bounds are inaccurate; and (iii) both upper bounds to ϵ are reasonably accurate only for very light atoms. These comments suggest that the improvement of the bounds should be based on obtaining a more accurate differential inequation on $\rho(r)$ than Eq. (3), rather than on the evaluation of the integral term appearing in Eq. (4). In fact, the dominant contribution to the upper bounds on ϵ is due to the term which depends on the nuclear charge Z. Then, more effort should be done in decreasing such a contribution.

Bounds in Terms of Density Functionals

In this section, upper bounds to the atomic ionization potential ϵ in terms of some density functionals, namely, frequency moments and Boltzmann–Shannon entropy, are shown. These bounds are not very accurate, but they are the only ones known depending on such measures of information of the system.

The bounds in terms of frequency moments ω_n, defined by

$$\omega_n \equiv \int [\rho(\mathbf{r})]^n \, d\mathbf{r}, \quad (19)$$

are given by

$$\epsilon \leq \frac{Z\langle r^{-1}\rangle}{N} - \frac{3}{2N}\left(\frac{\pi}{2}\right)^{4/3}\left(\frac{\omega_c^{3-b}}{\omega_b^{3-c}}\right)^{\frac{1}{3(c-b)}} \quad (20)$$

for any $3 \leq b < c$ or $0 < b < c \leq 3$. Some of these frequency moments are related to physically relevant quantities, such as the Thomas–Fermi kinetic energy $(n = 5/3)$ and the Dirac–Slater exchange energy $(n = 4/3)$, T_0 and K_0, respectively, within a density functional theory context [1]. The particular case $(b = 4/3,\ c = 5/3)$ gives

$$\epsilon \leq \frac{1}{N}\left[-E_{eN} - \frac{1}{8}\left(\frac{45\pi^2 T_0}{2K_0^2}\right)^{1/3}\right], \quad (21)$$

TABLE I
Comparison between the upper bounds ϵ_α^H and ϵ_α^R to the ionization potential ϵ for several atoms.

N	ϵ_1^H	ϵ_1^R	ϵ_2^H	ϵ_2^R	ϵ_5^H	ϵ_5^R	ϵ_6^H	ϵ_6^R	ϵ (exp.)
2	1.95	1.95	1.76	1.75	1.40	1.40	.133	1.33	0.904
6	11.7	10.8	5.27	4.90	2.20	2.20	1.95	1.95	0.414
10	26.3	24.3	12.8	12.3	5.74	5.73	4.94	4.93	0.793
14	43.1	39.7	14.2	13.4	3.64	3.64	3.15	3.15	0.300
18	62.2	57.3	20.9	19.9	7.17	7.17	6.23	6.23	0.579
27	112.	103.	34.3	33.0	6.44	6.43	5.27	5.27	0.289
36	170.	157.	50.8	49.1	13.1	13.1	11.3	11.3	0.515
45	233.	216.	63.9	61.9	11.2	11.2	8.60	8.59	0.274
54	301.	279.	76.6	74.3	17.7	17.7	15.0	15.0	0.446
63	373.	347.	89.6	87.1	10.5	10.5	8.70	8.70	0.208
72	452.	421.	115.	112.	14.6	14.6	11.9	11.9	0.202
81	534.	498.	135.	132.	19.0	19.0	15.1	15.1	0.225

Atomic units are used throughout.

which is an upper bound to the ionization potential in terms of three energies: exchange, kinetic, and electron–nucleus attraction.

The bounds in terms of the Boltzmann–Shannon entropy [9] $S_\rho \equiv -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r}$ (which measures the degree of delocalization of the charge distribution) are given by

$$\epsilon \leq \frac{Z\langle r^{-1}\rangle}{N} + \frac{\pi}{2N}(S_\rho + N \ln N) \qquad (22)$$

$$\epsilon \leq \frac{Z\langle r^{-1}\rangle}{N} - \frac{3}{2}\left(\frac{\pi}{2}\right)^{4/3} N^{-1/2} e^{-\frac{2}{3}S_\rho/N}. \qquad (23)$$

Equations (20)–(23) follow straightforwardly from consideration of Eq. (5) together with the lower bounds given in [18] for the Weizsäcker functional T_W of any many-particle system in terms of the above-mentioned density functionals. Such lower bounds were obtained by use of the three-dimensional Sobolev inequality [10, 11].

Conclusions

It has been shown that a strong relationship exists between the first ionization potential and various fundamental quantities in atoms, such as radial expectation values, frequency moments, and Boltzmann–Shannon entropy. The bounds which involve radial expectation values improve the previously known bounds in terms of the same quantities and are convergent to the exact value of the ionization potential in a limiting case. Some bounds have been expressed in terms of density functionals (e.g., the Thomas–Fermi kinetic and exchange energies).

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