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LETTER TO THE EDITOR

# Rigorous bounds to the atomic ionization potential

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**Abstract.** Several rigorous upper bounds to the atomic ionization potential $\epsilon$ are obtained from the Schrödinger equation for atomic systems. They are expressed in terms of radial expectation values $\langle r^{\alpha}\rangle$ and/or the electron density and its second derivative at the nucleus, $\rho(0)$ and $\rho''(0)$ respectively. A numerical study in a non-relativistic Hartree–Fock framework is carried out for some atoms. It is shown that the accuracy of the relationship among $\epsilon$, $\rho(0)$ and $\rho''(0)$ is higher than 80% for all atoms studied. An interesting property of the bounds in terms of various $\langle r^{\alpha}\rangle$ is that they reach the exact value of the ionization potential in a limiting case.

The first ionization potential in atoms, $\epsilon$, plays an important role in the study of the atomic structure (Parr and Yang 1989), not only because it describes the long-range behaviour of the spherically-averaged atomic charge density $\rho(r)$ (Hoffmann-Ostenhof and Hoffmann-Ostenhof 1977, Tal 1978) but also because it is an experimentally measurable quantity of paramount importance (Parr and Yang 1989).

In Hoffmann-Ostenhof and Hoffmann-Ostenhof (1977) it is shown that the value $\epsilon$ determines a region for which $\rho(r)$ presents some structural properties. The argument is based on their equation (2.24), i.e.

$$-\tfrac{1}{2}u'' + (\epsilon - Z/r)u \leqslant 0 \tag{1}$$

which is valid for any atom of nuclear charge $Z$ for which $\rho(r)$ is derived from the Schrödinger equation in the infinite nuclear mass approximation. Here, $u(r) \equiv r[\rho(r)]^{1/2}$. Atomic units are used throughout this paper.

In the present work, we use this expresion to obtain several rigorous bounds to $\epsilon$ in terms of some radial expectation values as well as a rigorous relationship among $\epsilon$ and the charge density and its second derivative at the nucleus, $\rho(0)$ and $\rho''(0)$ respectively.

First of all, we write (1) in terms of $\rho(r)$:

$$\rho''(r) + \frac{2}{r}[\rho'(r) + 2Z\rho(r)] - 4\epsilon\rho(r) - \frac{1}{2}\frac{[\rho'(r)]^2}{\rho(r)} \geqslant 0. \tag{2}$$

For $r = 0$, and taking into account the so-called *cusp condition* (Kato 1957, Steiner 1963, Hoffmann-Ostenhof *et al* 1978), which gives that $\rho'(0) = -2Z\rho(0)$, this equation transforms into

$$\frac{\rho''(0)}{4Z^2\rho(0)} \geqslant \frac{5}{6} + \frac{\epsilon}{3Z^2} \tag{3}$$

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**Table 1.** The ratio $\rho''(0)/4Z^2\rho(0)$ and the lower bound given by (3) for several atoms. Atomic units are used throughout.

| $Z$ | $\frac{\rho''(0)}{4Z^2\rho(0)}$ | $\frac{5}{6}+\frac{\epsilon}{3Z^2}$ | % |
|---|---|---|---|
| 2 | 1.0642 | 0.909 | 85.4 |
| 6 | 1.0326 | 0.837 | 81.1 |
| 10 | 1.0199 | 0.836 | 82.0 |
| 14 | 1.0134 | 0.834 | 82.3 |
| 18 | 1.0111 | 0.834 | 82.5 |
| 27 | 1.0084 | 0.833 | 82.7 |
| 36 | 1.0032 | 0.833 | 83.1 |
| 45 | 0.9999 | 0.833 | 83.3 |
| 54 | 1.0003 | 0.833 | 83.3 |

which is the only rigorous bound to $\rho''(0)$ known up to now, to the best of our knowledge. Other bounds to $\rho''(0)$ have been found recently (Angulo and Dehesa 1991), although (i) they do not depend on the ionization potential $\epsilon$ and (ii) they are non-rigorous since they are based on some realistic, but not yet proved, properties of $\rho(r)$. This result has to be compared with the well known behaviour (Angulo and Dehesa 1991)

$$\frac{\rho''(0)}{4Z^2\rho(0)} \approx 1.$$

In table 1 is shown the goodness of (3). It is easy to see that, as $Z$ increases, the bound to $\rho''(0)$ improves. Its accuracy is always higher than 80%; for $Z \to \infty$, it is $\sim 83\%$.

Another way to obtain relationships involving $\epsilon$ is by multiplying (2) by $r^{\alpha+1}$. Now, we can write

$$r^{\alpha+1}\rho''(r) + 2r^{\alpha}\rho'(r) + 4Zr^{\alpha}\rho(r) - 4\epsilon r^{\alpha+1}\rho(r) - \tfrac{1}{2}r^{\alpha+1}\frac{[\rho'(r)]^2}{\rho(r)} \geqslant 0. \quad (4)$$

It is worthwhile to point out that this expression transforms into an equality in the case of the ground-state hydrogen atom, i.e. when $\rho(r) = \pi^{-1}e^{-2r}$ and $\epsilon = \frac{1}{2}$.

Now we can follow two different methods.

(i) To take into account the negativity of the last term, i.e.

$$\tfrac{1}{2}r^{\alpha+1}\frac{[\rho'(r)]^2}{\rho(r)} \geqslant 0$$

to remove it from (4).

(ii) To use the *generalized Hölder's inequality* (Marshall and Olkin 1979) in order to bound the contribution of this term. When $\rho(r)$ is monotonically decreasing, which is actually the case for ground-state atoms (Sperber 1971, Weinstein *et al* 1975, Simas *et al* 1988), the following inequality holds:

$$\frac{1}{2}\int_0^\infty r^{\alpha+1}\frac{[\rho'(r)]^2}{\rho(r)}\mathrm{d}r \geqslant \frac{1}{32\pi}\frac{(\alpha+\beta)^2\langle r^{(\alpha+\beta)/2-3}\rangle^2}{\langle r^{\beta-3}\rangle} \quad (5)$$

for any $\alpha, \beta \geqslant 0$.

The results obtained in the first method coincide with those obtained in the second method when such a term is not considered. Because of that, we will restrict ourselves to the study of the second method, which provides results valid for $\rho'(r) \leqslant 0$. When the term with $\beta$ is neglected, the results are valid even if $\rho(r)$ is not monotonic.

Now, by integrating (4) from $r = 0$ to $+\infty$ (which is only possible for $\alpha > -1$) and taking into account (5), we obtain a set of rigorous relationships involving the quantities $\epsilon$, $\rho(0)$ and various radial expectation values.

For $\alpha = 0$ $$\epsilon \leqslant \frac{Z\langle r^{-2}\rangle - \pi\rho(0)}{\langle r^{-1}\rangle} - \frac{\beta^2\langle r^{\beta/2-3}\rangle^2}{32\langle r^{-1}\rangle\langle r^{\beta-3}\rangle} \equiv \epsilon_{0,\beta}(z).$$

For $\alpha > 0$ $$\epsilon \leqslant \frac{\alpha(\alpha-1)\langle r^{\alpha-3}\rangle + 4Z\langle r^{\alpha-2}\rangle}{4\langle r^{\alpha-1}\rangle} - \frac{(\alpha+\beta)^2\langle r^{(\alpha+\beta)/2-3}\rangle^2}{32\langle r^{\alpha-1}\rangle\langle r^{\beta-3}\rangle} \equiv \epsilon_{\alpha,\beta}(Z).$$

As a particular subcase we have that for $\beta = \alpha > 0$

$$\epsilon \leqslant \frac{\alpha(\alpha-2)\langle r^{\alpha-3}\rangle + 8Z\langle r^{\alpha-2}\rangle}{8\langle r^{\alpha-1}\rangle} \equiv \epsilon_{\alpha,\alpha}(Z).$$

It is interesting to show the inequalities for some of the lowest integer values of $\alpha$ and $\beta$.

For $\alpha = 0$ and $\beta = 0$ $$\epsilon \leqslant \frac{Z\langle r^{-2}\rangle - \pi\rho(0)}{\langle r^{-1}\rangle} = \epsilon_{0,0}(Z).$$

For $\alpha = 0$ and $\beta = 4$ $$\epsilon \leqslant \frac{Z\langle r^{-2}\rangle - \pi\rho(0)}{\langle r^{-1}\rangle} - \frac{\langle r^{-1}\rangle^2}{2\langle r^{-1}\rangle\langle r\rangle} = \epsilon_{0,4}(Z).$$

For $\alpha = 1$ and $\beta = 0$ $$\epsilon \leqslant \frac{Z\langle r^{-1}\rangle}{N} = \epsilon_{1,0}(Z).$$

This bound is specially interesting, because, apart from $Z$, it only involves $N$ (the number of electrons) and $\langle r^{-1}\rangle$ (basically the energy of attraction electron–nucleus).

For $\alpha = 1$ and $\beta = 3$ $$\epsilon \leqslant \frac{Z\langle r^{-1}\rangle}{N} - \frac{\langle r^{-1}\rangle^2}{2N^2} = \epsilon_{1,3}(Z).$$

As well as for $\alpha = 1$, $\beta = 0$, here only $N$, $Z$ and $\langle r^{-1}\rangle$ appear.

For $\alpha = 1$ and $\beta = 5$ $$\epsilon \leqslant \frac{Z\langle r^{-1}\rangle}{N} - \frac{9N}{8\langle r^2\rangle} = \epsilon_{1,5}(Z).$$

Here, also the diamagnetic susceptibility, proportional to $\langle r^2\rangle$, contributes to the bound to the ionization potential.

For $\alpha = 2$ and $\beta = 0$ $$\epsilon \leqslant \frac{\langle r^{-1}\rangle + 2ZN}{2\langle r\rangle} = \epsilon_{2,0}(Z).$$

For $\alpha = 2$ and $\beta = 2$ $$\epsilon \leqslant \frac{Zn}{\langle r\rangle} = \epsilon_{2,2}(Z).$$

For $\alpha = 3$ and $\beta = 0$ $$\epsilon \leqslant \frac{3N + 2Z\langle r\rangle}{2\langle r^2\rangle} = \epsilon_{3,0}(Z).$$

For $\alpha = 3$ and $\beta = 3$ $$\epsilon \leqslant \frac{3N + 8Z\langle r\rangle}{8\langle r^2\rangle} = \epsilon_{3,3}(Z).$$

**Table 2.** Some upper bounds $\epsilon_{\alpha,\beta}$ to the ionization potential $\epsilon$ for several atoms. Remember that those with $\beta = 0$ do not make use of the property of monotonic decreasing for $\rho(r)$. Atomic units are used throughout.

| | $\alpha = 0$ | | $\alpha = 1$ | | $\alpha = 2$ | | $\alpha = 3$ | | $\epsilon$ |
|---|---|---|---|---|---|---|---|---|---|
| Z | $\beta = 0$ | $\beta = 4$ | $\beta = 0$ | $\beta = 5$ | $\beta = 0$ | $\beta = 4$ | $\beta = 0$ | $\beta = 5$ | (Expt.) |
| 2 | 3.76 | 2.46 | 3.37 | 2.42 | 3.07 | 1.76 | 2.83 | 1.60 | 0.9037 |
| 6 | 29.40 | 28.37 | 14.69 | 14.20 | 6.07 | 5.28 | 3.76 | 3.22 | 0.4140 |
| 10 | 70.73 | 68.76 | 31.11 | 29.91 | 14.64 | 12.83 | 10.02 | 8.60 | 0.7926 |
| 14 | 130.78 | 129.08 | 49.24 | 48.75 | 15.24 | 14.19 | 6.94 | 6.54 | 0.2996 |
| 18 | 205.17 | 203.00 | 69.73 | 68.95 | 22.33 | 20.92 | 12.15 | 11.39 | 0.5794 |
| 27 | 420.37 | 417.58 | 122.05 | 121.28 | 36.06 | 34.35 | 16.04 | 15.42 | 0.2890 |
| 36 | 692.65 | 689.17 | 182.85 | 181.83 | 52.88 | 50.76 | 25.27 | 24.39 | 0.5147 |
| 45 | 1027.86 | 1024.05 | 248.05 | 247.09 | 66.01 | 63.86 | 29.10 | 28.34 | 0.2743 |
| 54 | 1418.67 | 1414.60 | 317.87 | 316.90 | 78.72 | 76.57 | 34.97 | 34.19 | 0.4460 |

$N = \langle r^0 \rangle$ is the number of electrons of the atom.

In table 2, the values of some of these upper bounds to $\epsilon$ are shown for several atoms with $Z \leqslant 54$. We have taken experimental values of $\epsilon$, while $\rho(0)$ and the expectation values $\langle r^\alpha \rangle$ have been calculated by means of the near-Hartree–Fock wavefunctions of Clementi and Roetti (1974).

A few comments are in order. First, the quality of the upper bounds to $\epsilon$ quickly worsens with increasing Z. So, these bounds are only reasonably good for very light atoms. Secondly, the quality of the bounds $\epsilon_{\alpha,\beta}(Z)$ increases appreciably for increasing $\alpha$, while the effect of considering $\beta > 0$ for fixed $\alpha$ (which implies to take into account the property of monotonicity of $\rho(r)$) is almost unappreciable except for very light atoms. A deeper study of the left-hand side of (5) is required in order to improve the results. Finally, it is remarkable that these bounds reach the exact value of the ionization potential for the limiting case $\alpha = \beta \to \infty$ for all atoms, due to the behaviour for high $\alpha$

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

which is a consequence of the asymptotic behaviour of $\rho(r)$ as (Hoffmann-Ostenhof and Hoffmann-Ostenhof 1977, Tal 1978)

$$\rho(r) \rightsquigarrow \mathrm{e}^{-\sqrt{8\epsilon} r}$$

Summarizing, we have shown that (i) there is a strong relationship among $\rho(0)$, $\rho''(0)$ and $\epsilon$, especially interesting for heavy atoms, and (ii) high order moments are useful quantities to bound from above the atomic first ionization potential, especially for light atoms.

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