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Do atomic electrons fall to the center of multi-electron atoms?

E. B. Manoukian

The Institute for Fundamental Study, Naresuan University,
Phitsanulok 65000, Thailand
anoukian_eb@hotmail.com

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This communication is involved in providing, via a modern approach, a *direct* derivation that, with 100% probability, none of the atomic electrons falls to the center of multi-electron atoms — a problem which has been around historically in the quantum mechanics of atoms since the birth of the former and has, undoubtedly, come across every learner of the subject since then. No need arises for explicit eigenfunctions.

Keywords: Atomic physics; atomic electrons of multi-electron atoms; fall or not the fall of atomic electrons to the center of multi-electron atoms; problem of historical importance.

1. Introduction

Undoubtedly, we have all come across the problem of the "fall" of atomic electrons to the center of atoms since the birth of quantum mechanics as applied to atoms. Arguments are often used based on the uncertainty relation or by constructing approximate solutions for the system, to formally infer that their fall is not possible. Although such arguments are interesting and often illuminating they cannot be considered as conclusive and firmly established. Interesting formal, easy to follow and recommended treatments may be found, e.g., Refs. 1–3.

In the present note, we use a rather modern approach developed in Refs. 4 and 5, to provide a clear-cut *direct* derivation with probability one, i.e. with 100%, where none of the atomic electrons falls to the center of multi-electron atoms. No explicit eigenfunctions need to be obtained to establish this. The problem addressed here is to bound neutral multi-electron atoms. It is not involved, however, with scattering states such as in the capture of an electron by an atom or by other processes such as of the ionization of atoms.

The multi-electron neutral atom Hamiltonian considered is taken as

$$H = \sum_{j=1}^{Z} \frac{\mathbf{p}_j^2}{2m} + V \,, \tag{1}$$

$$V = -\sum_{j=1}^{Z} \frac{Ze^2}{|\mathbf{x}_j|} + \sum_{1\leq i<j\leq Z} \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_j|} \,. \tag{2}$$

For atoms, the number Z of electrons is finite and bounded. We have to start somewhere from the theory, and the strategy of attack of the problem is based on two bounds established many years ago, which for our purposes in applications are spelled out as follows:

1. A Schwinger bound,[6] based on a publication by Schwinger in (1961), which amounts to the following. Given a Hamiltonian

$$h_0 = \frac{-\hbar^2 \boldsymbol{\nabla}^2}{2m} - v(\mathbf{x}), \quad v(\mathbf{x}) > 0 \,. \tag{3}$$

Then, for any normalized state φ,

$$\langle \varphi | h_0 | \varphi \rangle > -\frac{1}{3\pi} \left(\frac{m}{2\hbar^2} \right)^3 \left(\int d^3\mathbf{x}\, v^2(\mathbf{x}) \right)^2 . \tag{4}$$

That is, if E_0 denotes the lower end of the spectrum of h_0, then

$$E_0 > -\frac{1}{3\pi} \left(\frac{m}{2\hbar^2} \right)^3 \left(\int d^3\mathbf{x} v^2(\mathbf{x}) \right)^2 . \tag{5}$$

2. Cauchy–Schwarz inequality for integrals: For two real positive functions $f_1(\mathbf{x})$, $f_2(\mathbf{x})$,

$$\int d^3\mathbf{x} f_1(\mathbf{x}) f_2(\mathbf{x}) \leq \left(\int d^3\mathbf{x} f_1^2(\mathbf{x}) \right)^{1/2} \left(\int d^3\mathbf{x} f_2^2(\mathbf{x}) \right)^{1/2} . \tag{6}$$

In Sec. 2, a simple lower bound to the spectrum of the Hamiltonian H of multi-electron atoms in (1) is derived which is *sufficient* to establish the main result being sought. Section 3 combines this bound with upper and lower bounds derived for the expectation value of the kinetic energy of electrons in multi-electron atoms to obtain an upper bound for the probability that any one or more or all the electrons are confined within a radius R from the center of the atom, to finally establish the result sought in this communication, that with 100%, no atomic electrons fall to the center of multi-electron atoms, as the resulting probabilities vanish. Due to the technical nature of the derivations of the upper and lower bounds to the expectation value of the kinetic energy of electrons in multi-electron atoms, they are relegated to Secs. 4 and 5, respectively.

The above treatment is involved with the problem of falling or not falling of electrons to the center of an atom. In the problem of stability of matter, again consisting of a finite of electrons per atom, but involving several nuclei and correspondingly a large number of electrons N, the stability of neutral matter, based on the Pauli exclusion principle, or instability of so-called "bosonic matter", in which the exclusion principle is abolished, rests rather on the following. For "bosonic matter", the ground state $E_N \sim -N^{\alpha}$, with $\alpha > 1$, where $(N+N)$ denotes the number of the negatively charged particles plus an equal number of positively charged particles. This behavior for "bosonic matter" is unlike that of matter, with the exclusion principle, for which $\alpha = 1$. A power-law behavior with $\alpha > 1$ implies instability as the formation of a single system consisting of $(2N + 2N)$ particles is favored over two separate systems brought together each consisting of $(N + N)$ particles, and the energy released upon collapse of the two systems into one, being proportional to $[(2N)^{\alpha} - 2(N)^{\alpha}]$, will be overwhelmingly large for realistic large N, e.g., $N \sim 10^{23}$.[7–10] For the underlying details, we refer the interested reader to the monumental work in Ref. 9, containing a wealth of information, which has been very useful in formulating the present problem, as well as the ones in Refs. 7–13. It is interesting to quote Dyson[7] regarding "bosonic matter": "[Bosonic] matter in bulk would collapse into a condensed high-density phase. The assembly of any two macroscopic objects would release energy comparable to that of an atomic bomb . . . ". The fact that matter occupies so large a volume and its connection to the exclusion principle was emphasized clearly as addressed by Ehrenfest to Pauli in 1931 on the occasion of the Lorentz medal[14] to this effect:

"We take a piece of metal, or a stone. When we think about it, we are astonished that this quantity of matter should occupy so large a volume". He went on by stating that the exclusion principle is the reason: "Answer: only the Pauli principle, no two electrons in the same state". In this regard, a rigorous treatment[4,5] shows that the extension of matter radially grows not any slower than $N^{1/3}$ for large N. No wonder why matter occupies so large a volume.

2. A Lower Bound to the Spectrum of Multi-Electron Atoms

Let

$$\mathbf{F}_j = -\frac{Ze^2}{2}\frac{\mathbf{x}_j}{|\mathbf{x}_j|}\,, \tag{7}$$

then

$$\boldsymbol{\nabla}_j \cdot \mathbf{F}_j = -\frac{Ze^2}{|\mathbf{x}_j|}, \quad \sum_{j=1}^{Z}\langle\psi|\mathbf{F}_j \cdot \mathbf{F}_j|\psi\rangle = \frac{Z^3 e^4}{4} \tag{8}$$

for a normalized state ψ. We use the above in the following inequality:

$$\sum_{j=1}^{Z}\left\|\left(-\frac{\hbar\boldsymbol{\nabla}_j}{\sqrt{2m}} + \frac{\sqrt{2m}}{\hbar}\mathbf{F}_j\right)\psi\right\|^2 \geq 0\,, \tag{9}$$

to obtain

$$\langle\psi|H|\psi\rangle \geq \langle\psi|\sum_{j=1}^{Z}\left(\frac{\mathbf{p}_j^2}{2m} - \frac{Ze^2}{|\mathbf{x}_j|}\right)|\psi\rangle \geq -\frac{2m}{\hbar^2}\sum_{j=1}^{Z}\langle\psi|\mathbf{F}_j\cdot\mathbf{F}_j|\psi\rangle = -\frac{Z^3 me^4}{2\hbar^2}\,. \tag{10}$$

Since *a priori* it is not ruled out that the state ψ is the ground-state of the atom, the above shows that the ground-state energy cannot be smaller than the bound $-Z^3e^4m/2\hbar^2$.

3. Fall or not the Fall of Electrons to the Center of Multi-Electron Atoms

We introduce the electron density $\varrho(\mathbf{x})$ in the bound atom by

$$\varrho(\mathbf{x}) = Z\sum_{\sigma_1,\dots,\sigma_Z}\int d^3\mathbf{x}_2\dots d^3\mathbf{x}_Z|\psi(\mathbf{x}\sigma_1,\mathbf{x}_2\sigma_2,\dots,\mathbf{x}_Z\sigma_Z)|^2\,, \qquad (11)$$

involving a normalized antisymmetric wave function ψ, with $\sigma_1,\dots,\sigma_Z$ denoting electron spin projections, and where

$$\int d^3\mathbf{x}\,\varrho(\mathbf{x}) = Z\,. \qquad (12)$$

From the upper bound of the expectation value of the kinetic energy of electrons in multi-electron atoms that will be derived later in (24) of Sec. 4, and the lower bound one to be derived later in (32) of Sec. 5, we obtain the following simple bound

$$\frac{2\hbar^2}{m}\left(\frac{3\pi}{16Z}\right)^{1/3}\left(\int d^3\mathbf{x}\varrho^2(\mathbf{x})\right)^{2/3} < \frac{2Z^3me^4}{\hbar^2} \qquad (13)$$

or

$$\int d^3\mathbf{x}\varrho^2(\mathbf{x}) < \left(\frac{16}{3\pi}\right)^{1/2}\left(\frac{me^2}{\hbar^2}\right)^3 Z^5\,. \qquad (14)$$

Now let $\chi_R(\mathbf{x}) = 1$, if $\mathbf{x}$ lies within a sphere of radius R and $= 0$ otherwise. Then clearly for the probability of, say, k of the electrons to lie within such a sphere, for $k = 1, 2, \dots, Z$, we have from the definition of a probability

$$\mathrm{Prob}[|\mathbf{x}_1| \le R, \dots, |\mathbf{x}_k| \le R] \le \mathrm{Prob}[|\mathbf{x}_1| \le R] = \frac{1}{Z}\int d^3\mathbf{x}\chi_R(\mathbf{x})\varrho(\mathbf{x})\,. \qquad (15)$$

From the Cauchy–Schwarz inequality (6)

$$\int d^3\mathbf{x}\chi_R(\mathbf{x})\,\varrho(\mathbf{x}) \le \left(\frac{4\pi R^3}{3}\right)^{1/2}\left(\int d^3\mathbf{x}\varrho^2(\mathbf{x})\right)^{1/2}, \qquad (16)$$

where we have used the fact that $\chi_R^2(\mathbf{x}) = \chi_R(\mathbf{x})$, and $\int d^3\mathbf{x}\chi_R(\mathbf{x}) = 4\pi R^3/3$.

Therefore, from (14)–(16)

$$\mathrm{Prob}\big[|\mathbf{x}_1| \le R, \dots, |\mathbf{x}_k| \le R\big] < \left(\frac{16}{3\pi}\right)^{1/4}\left(\frac{me^2}{\hbar^2}\right)^{3/2} Z^{3/2}\left(\frac{4\pi R^3}{3}\right)^{1/2} \qquad (17)$$

or

$$\mathrm{Prob}[|\mathbf{x}_1| \le R, \dots, |\mathbf{x}_k| \le R] < 2.34 Z^{3/2}\left(\frac{R}{a_0}\right)^{3/2} \qquad (18)$$

for $k = 1, 2, \ldots, Z$, and where $a_0 = \hbar^2/me^2$ is the Bohr radius. We may infer from (18) that the probability of any of the electron's fall to the center is zero, since the right-hand side of the above upper bound to the probability in question vanishes for $R \to 0$. That is, with 100% probability, none of the electrons fall ($R \to 0$) to the center of multi-electron atoms. The demonstration obviously holds for the hydrogen atom as well, although a simpler one for it may be given (see Ref. 15, pp. 360–363).

It must be stressed that any sharper estimates such as obtaining a larger value than 3/2 for the power of (R/a_0), or any smaller value than the coefficient 2.34 in the above inequality, changes in no way the established result. It is also worth indicating that a nonvanishing probability density of finding an electron at the origin does not necessarily imply that the probability of finding it there is nonzero, as the probability is obtained by multiplying the probability density by the volume element.

In the subsequent two sections, an upper and a lower bound to the expectation value of the kinetic energy of electrons in multi-electrons are derived thus completing the analysis of the problem.

4. Upper Bound to the Expectation Value of the Kinetic Energy of the Electrons in Multi-Electron Atoms

Let $\psi(m)$ denote the normalized state in (11), which may, in general, depend on m, corresponding to a bound atom, such as the ground-state, giving a strictly negative expectation value for the Hamiltonian H, in (1), i.e.

$$-\frac{Z^3 me^4}{2\hbar^2} \leq \langle\psi(m)|H|\psi(m)\rangle < 0\,, \tag{19}$$

By definition of the ground-state energy, the state $\psi(m/2)$, equally, cannot lead a numerical value for $\langle\psi(m/2)|H|\psi(m/2)\rangle$ lower than $-Z^3e^4m/2\hbar^2$, for the Hamiltonian H in (1), otherwise this would *contradict* that $-Z^3me^4/2\hbar^2$ is a lower bound to the ground-state energy. That is, we must also have

$$-\frac{Z^3 me^4}{2\hbar^2} \leq \langle\psi(m/2)|H|\psi(m/2)\rangle \tag{20}$$

with no additional factor of two on the right-hand side of the inequality. Accordingly, if replace m by $2m$ in the above equation, we have

$$-\frac{Z^3 me^4}{\hbar^2} \leq \langle\psi(m)|\left(\sum_{j=1}^{Z}\frac{\mathbf{p}_j^2}{4m} + V\right)|\psi(m)\rangle \leq \langle\psi(m)|H|\psi(m)\rangle < 0\,, \tag{21}$$

where, in writing the second inequality, we have used, in the process, that $\mathbf{p}_j^2/4m \leq \mathbf{p}_j^2/2m$, and finally (19). Upon writing $\mathbf{p}_j^2/2m$ as $(\mathbf{p}_j^2/4m + \mathbf{p}_j^2/4m)$, the inequality on the extreme right-hand side of the above equation leads to

$$\langle\psi(m)|\sum_{j=1}^{Z}\frac{\mathbf{p}_j^2}{4m}|\psi(m)\rangle\langle-\langle\psi(m)|\left(\sum_{j=1}^{Z}\frac{\mathbf{p}_j^2}{4m} + V\right)|\psi(m)\rangle\,. \tag{22}$$

On the other hand, the inequality on the extreme left-hand side of (21) gives

$$-\langle\psi(m)|\left(\sum_{j=1}^{Z}\frac{\mathbf{p}_j^2}{4m}+V\right)|\psi(m)\rangle \leq \frac{Z^3me^4}{\hbar^2}\,. \tag{23}$$

From the above two inequalities, the following bound emerges for the expectation value of the kinetic energy of the electrons in multi-electron atoms upon multiplying by 2:

$$T \equiv \langle\psi(m)|\sum_{j=1}^{Z}\frac{\mathbf{p}_j^2}{2m}|\psi(m)\rangle < \frac{2Z^3me^4}{\hbar^2}\,, \tag{24}$$

giving the upper bound to the expectation value of the kinetic energy of the electrons in multi-electron atoms we were seeking.

5. Lieb–Thirring Bound and a Lower Bound to the Expectation Value of the Kinetic Energy of the Electrons in Multi-Electron Atoms

For the convenience of the reader, we here derive a well known bound due to Lieb and Thirring[10] which consists of a lower bound to the expectation value of the kinetic energy of electrons with the lower bound involving the integral of some power of the electron density ϱ. To this end, consider now a different problem with a hypothetical Hamiltonian of Z non-interacting electrons,[10] with each electron, however, interacting with a potential $-u(\mathbf{x})$, given by

$$h = \sum_{i=1}^{Z}\left[\frac{\mathbf{p}_i^2}{2m} - u(\mathbf{x}_i)\right]. \tag{25}$$

This hypothetical Hamiltonian is introduced just to *obtain* a lower bound to the expectation value of the kinetic energy of electrons of a multi-electron atom.

Let

$$u(\mathbf{x}) = 2\frac{\varrho(\mathbf{x})}{\int d^3\mathbf{x}'\varrho^2(\mathbf{x}')}T\,, \tag{26}$$

where, as before, the expectation value of the kinetic energy, in general, for a multi-electron atom is given by

$$\int\sum_{\sigma_1,\dots,\sigma_Z} d^3\mathbf{x}_1\cdots d^3\mathbf{x}_Z\psi^*(\mathbf{x}_1\sigma_1,\dots,\mathbf{x}_Z\sigma_Z)\sum_{i=1}^{Z}\left(\frac{-\hbar^2\nabla_i^2}{2m}\right)\psi(\mathbf{x}_1\sigma_1,\dots,\mathbf{x}_Z\sigma_Z) = T. \tag{27}$$

Then

$$\int \sum_{\sigma_1,\ldots,\sigma_Z} d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_Z \psi^*(\mathbf{x}_1\sigma_1,\ldots,\mathbf{x}_Z\sigma_Z)\left(\sum_{i=1}^{Z} u(\mathbf{x}_i)\right)\psi(\mathbf{x}_1\sigma_1,\ldots,\mathbf{x}_Z\sigma_Z)$$

$$= \frac{1}{Z}\int \sum_{i=1}^{Z} d^3\mathbf{x}_i\,\varrho(\mathbf{x}_i)u(\mathbf{x}_i) = \int d^3\mathbf{x}\,\varrho(\mathbf{x})u(\mathbf{x}) = 2T\,, \tag{28}$$

and

$$\int \sum_{\sigma_1,\ldots,\sigma_Z} d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_Z \psi^*(\mathbf{x}_1\sigma_1,\ldots,\mathbf{x}_Z\sigma_Z)\sum_{i=1}^{Z}\left(\frac{-\hbar^2\nabla_i^2}{2m} - u(\mathbf{x}_i)\right)$$

$$\times\, \psi(\mathbf{x}_1\sigma_1,\ldots,\mathbf{x}_Z\sigma_Z) = -T\,. \tag{29}$$

The Pauli exclusion principle states that we can allow only two electrons in each energy level of such a "Hamiltonian", due to the spin multiplicity consisting of two possible spin states per electron. We may thus start by putting two electrons in the lowest energy level of the operator in (3), which is denoted by E_0 in (5), and then consecutively two in each of the higher energy states to obtain the lowest energy possible.[?] Clearly, the ground-state energy of the above "Hamiltonian" then cannot be smaller than ZE_0. But according to the Schwinger bound in (5),

$$ZE_0 > Z\left[-\frac{1}{3\pi}\left(\frac{m}{2\hbar^2}\right)^3\left(\int d^3\mathbf{x}u^2(\mathbf{x})\right)^2\right], \tag{30}$$

or from (26) and (29), this leads to

$$-T \geq ZE_0 > -\frac{16Z}{3\pi}\left(\frac{m}{2\hbar^2}\right)^3 T^4 \frac{1}{(\int d^3\mathbf{x}\varrho^2(\mathbf{x}))^2}\,, \tag{31}$$

which gives a Lieb–Thirring bound

$$\frac{2\hbar^2}{m}\left(\frac{3\pi}{16Z}\right)^{1/3}\left(\int d^3\mathbf{x}\varrho^2(\mathbf{x})\right)^{2/3} < T\,, \tag{32}$$

giving a lower bound to the expectation value of the kinetic energy of the electrons in multi-electron we were seeking.

We hope that this problem which has been around historically in the quantum mechanics of atoms since the birth of the former and has, undoubtedly, come across every learner of the subject since then, and has been considered at different levels of sophistication, justifies the present derivation addressed *directly* to the "fall or not the fall of atomic electrons to the center of multi-electron atoms".

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