Commentary on "Probing the Orbital Energy of an Electron in an Atom"

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We wish to comment on a recent article by Bills, "Probing the Orbital Energy of an Electron in an Atom" (*1*). Bills' thesis is that the behavior of electrons in atoms can be successfully analyzed using classical concepts. For example, he writes

> A theoretical snapshot of an atom, showing the screened nuclear charge and the electron to be ionized at its radius of zero kinetic energy, enables anyone to approximate its ionization energy.
>
> Each eigenvalue is the constant sum of classical values of potential and kinetic energy.
>
> The classical potential energy, V(R), is independent of n, but the classical kinetic energy, $T_n(R)$, depends on n.
>
> When He electron *i* reaches r_0, much of the charge of electron *j* is distributed within r_0.

From these statements we infer that the electron is executing a classical trajectory; that it has well-defined classical values for position, momentum, and kinetic and potential energy. Unfortunately, this classical picture violates accepted and validated quantum mechanical principles.

To support his model Bills draws on the authority of John C. Slater by referencing Slater's classic monograph on the quantum theory of atomic structure (*2*). We acknowledge that Slater strove to provide an intuitive meaning to quantum theory by exploiting classical ideas. He was one of the early users of quantum theory in the search for an understanding of atomic and molecular structure, and so we should not be surprised that he attempted to use the classical concepts of kinetic and potential energy as guides for interpretive purposes. However, today we know that this program is not viable; classical concepts cannot provide an acceptable model for the stability and structure of atoms and molecules, nor their interaction with electromagnetic radiation.

We live in a macroscopic, classical world and are therefore challenged by the non-classical model of the nanoscopic world of atoms and molecules that quantum mechanics requires. Peter Atkins said it well recently in his forward to Jim Baggott's most recent book. (*3*)

> No other theory of the physical world has caused such consternation as quantum theory, for no other theory has so completely overthrown the previously cherished concepts of classical physics and our everyday interpretation of reality.

Along the same lines Niels Bohr once said that if you are not shocked by quantum mechanics, you do not understand what it is saying.

We now articulate in detail our objections to the classical model that Bills proposes.

By assigning classical meaning to $T(r)$ and $V(r)$, and identifying a special electron position, r_0, where its kinetic energy is zero, Bills contradicts accepted quantum mechanical ideas regarding the behavior of electrons in atoms. The wave functions of atomic electrons are not eigenfunctions of the position, momentum, kinetic energy or potential energy operators. Consequently, according to quantum mechanics, the physical properties represented by these operators do not have well-defined values. Therefore, it is impossible to attach any physical significance to the values of $T(r)$ or $V(r)$ shown in Figure 1 of Bills' paper because they are neither eigenvalues nor expectation values of their respective operators.

The only physically meaningful entries in Table 1 of Bills' paper are the calculated orbital energies and the experimental ionization energies. As Figure 1 shows a good Hartree-Fock wave function gives a constant orbital energy and therefore a reliable estimate, according to Koopmans' theorem, for the ionization energy.

What is the real meaning of r_0? It is simply the inflection point of the wave function, nothing more and nothing less. Initially defining r_0 as the electron's radius of zero kinetic energy, Bills goes on to identify r_0 with atomic size in two places – one explicitly and one implicitly.

> Each r_0 measures the orbital size of the weakest-held electron…
>
> This r_0 is analogous to the classical turning point of the harmonic oscillator.

The latter statement implies that the electron has reached its apogee and is turning back in the direction of the nucleus, again suggesting a classical trajectory. However, a serious difficulty emerges if one associates the calculated r_0 values with atomic size. The r_0 values in Table 1 of Bills' paper are significantly larger than the literature values for the atomic radii for the chemically active elements, while for the inert gases they are significantly smaller than the literature values for the atomic radii. (*4*) This doesn't make physical sense.

Bills' r_0 is physically meaningless because his model violates the basic quantum mechanical principles that govern the nanoscopic world of atoms and molecules. This is easily seen by looking at the ionization process in terms of two fundamental physical principles which hold both classically and quantum mechanically: They are energy conservation ($\Delta E = \Delta T + \Delta V$) and the virial theorem ($\Delta E = \Delta V / 2 = -\Delta T$). Under Bills' model with $\Delta T = 0$ the first equation says that $\Delta E = \Delta V$, while the second equation says $\Delta E = \Delta V / 2 = -\Delta T = 0$!

Bills' model also violates the uncertainty principle. If the position of the electron is precisely known, the uncertainty in momentum and therefore kinetic energy must be

infinitely large. In other words, an electron cannot have a well-defined position (r_0) at the same time it has a precise value for kinetic energy (zero). In addition, since he takes a classical view of electronic behavior in the atom Bills is left with the challenging problem of assigning meaning to the negative kinetic energies that result for values of r greater than r_0 (see Bills' Figure 1).

A quantum mechanically correct description of the behavior of electrons in atoms and molecules has been provided by Harris (*5*):

> Electrons are characterized by their entire distributions (called *wave functions* or *orbitals*) rather than by instantaneous positions and velocities: an electron may be considered always to be (with appropriate probability) at all points of its distribution (which does not vary with time).

"There is no space-time inside the atom," is Heisenberg's succinct summary of the electron's behavior in the atom. Pascal Jordan provided further insight by stating that we measure the position of the electron, not to find out where it is, but to cause it to be somewhere.

In exploring the message of quantum theory Anton Zeilinger recently wrote (*6*):

> It is not just that we are unable to measure two complementary quantities of a particle, such as position and momentum, at the same time. Rather the assumption that a particle possesses both position and momentum, before the measurement is made, is wrong.

Thus it is impossible, within the quantum mechanical view, to assign a classical trajectory to an electron confined in an atom or molecule. In fact, assigning such a trajectory to an electron calls into question the stability of matter because an orbiting electron would continuously radiate energy and (according to classical physics) collapse into the nucleus. Bohr famously remarked that the stability of matter is "a pure miracle when considered from the standpoint of classical physics."

In summary, classical concepts fail at the atomic and molecular level because they cannot account for the stability and internal electronic structure of atoms and molecules, nor the interaction of matter with electromagnetic radiation. This has been known for more than a century. It is well beyond time to abandon classical models of the nano-world and teach our students atomic and molecular structure from the quantum mechanical perspective. Richard Feynman made this point forcibly in his inimitable colloquial style when he said, (*7*)

> And I'm not happy with all the analyses that go with just the classical theory, because nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical…

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