Letters

Potential Energy Sufficient for Atoms

In their commentary "The Crucial Role of Kinetic Energy in Interpreting Ionization Energies", Frank Rioux and Roger L. DeKock (*J. Chem. Educ.* **1998,** *75,* 537–539) criticize an analysis of atomic ionization energies by Gillespie, Spencer, and Moog (*1*). One of the criticisms (not addressed in the response [*2*] by Gillespie, Moog, and Spencer) was that the analysis should have considered kinetic energy, not just potential energy.

The quantum mechanical virial theorem shows this criticism to be invalid. The average electronic kinetic energy of any atom equals the negative of half its average potential energy (*3, 4*). Therefore the total energy of any electronic state of an atom equals precisely half its potential energy, and consideration of kinetic energy would be redundant.

These virial relationships among energies are exact for states of actual atoms but may be merely approximate for energies associated with approximate wave functions. However, the simple expedient of optimally scaling the approximate wave function satisfies virial relationships exactly (*3, 4*).

These virial relationships do not apply to molecules except at equilibrium geometries or other special situations in which forces on nuclei may be ignored (*5*). Since ionization of a molecule involves a vertical transition (*6*), nuclei of the resulting ion may be subject to strong net forces. For molecules, therefore, Rioux and DeKock are correct in warning that analyses of ionization energies should consider kinetic energies.

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The authors reply:

Misapplication of the Virial Theorem

When asked what motivated the creation of his model of the atom Bohr replied "The stability of matter, a pure miracle when considered from the standpoint of classical physics." Kinetic energy is not, as Carlton claims, redundant at the atomic level. It is essential for an understanding of atomic stability and electronic structure. The virial theorem does not say kinetic energy is redundant any more than it says that potential energy is redundant.

For example, the misapplication of the virial theorem has stood in the way of a clear understanding of the nature of the chemical bond. More than 35 years ago Ruedenberg demonstrated, "the virial theorem notwithstanding" (*1*), that kinetic energy plays an essential role in chemical bond formation. In other words, chemical bonding is not simply an electrostatic phenomenon as many have been led to believe on the basis of the virial theorem. Twenty-five years ago in a review of Ruedenberg's model of the chemical bond, Kutzelnigg (*2*) commented incisively on the misuse of the virial theorem in interpreting the chemical bond (see following letter by DeKock).

The jurisdiction of the virial theorem is not such as to prohibit the partitioning of a process (bond formation or ionization, for example) into a sequence of steps for interpretive purposes. Two recent publications (*3, 4*) show that using Ruedenberg's approach, chemical bond formation can be interpreted simply as a two-step process consisting of charge delocalization followed by orbital contraction. Our quantum mechanical analysis of the H/He ionization energy trend (*5*) runs parallel to this analysis of the chemical bond. In our approach we factor ionization into two steps: frozen ionization followed by relaxation. Our wave function and our calculation satisfy the virial theorem. Just as Ruedenberg's goal was to develop a mechanism for chemical bond formation, our goal was to develop a quantum mechanical mechanism that would reveal the essential features of the ionization process.

In summary, the uncritical adherence to the virial theorem has prevented generations of chemists from recognizing the importance of kinetic energy at the atomic and molecular level. It is because of this potential to mislead, rather than inform, that we chose not to explicitly invoke the virial theorem in our analysis. The virial theorem serves as a criterion for acceptable wave functions and calculations, but one has to go beyond it to interpret phenomena such as chemical bond formation and atomic ionization.

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An Instructive Analogy for the Virial Theorem in the H Atom

In his letter, Carlton stated that the quantum mechanical virial theorem shows that one need consider only potential energy for the "analysis" of the ionization energy of the H atom and the He atom. In his response, Rioux addressed this question directly. My approach is to use an analogy first put forward by Kutzelnigg about 25 years ago (*1*). Kutzelnigg developed his analogy in a discussion of the physical mecha-

nism of the chemical bond. I have modified his analogy to make it appropriate for discussion of the ionization process of the H atom. I think the crux of the matter comes down to whether we want only to obtain the right answer (number), or whether we want also to provide "understanding" or "interpretation" of that number.

Recall that in quantum mechanics the total energy $E = <V> + <T>$, where $<V>$ is the expectation value of the potential energy and $<T>$ the expectation value of the kinetic energy. The virial theorem states that $<V> = -2<T>$, so that one could write

$$E = -<T> = <V>/2$$

or

$$-E = <T> = -<V>/2$$

In the analogy given below we will examine the physical nature of combining a proton with an electron to form an H atom. The reverse of the process described here is the ionization of the H atom. This analogy will help us to understand the nature of the virial theorem in atoms.

Once upon a time the electron and the proton were separate entities; they merged to become Hatom, Inc. The financial formula for all corporations is very simple:

profit = income − expenditures

We could rewrite this as

− profit = − income + expenditures

We could also write this financial formula using symbols as

$$E = <V> + <T>$$

The symbols correspond to the words as follows: profit ($-E$), income ($-<V>$), and expenditures ($<T>$).

Before merging, electron and proton were not part of the financial world and therefore had no expenditures ($<T>$), no income ($-<V>$), and no profit ($-E$). After the merger, Hatom, Inc. entered the financial world of all atomic corporations.

Suppose that all atomic corporations operate so that the ratio of expenditures $<T>$, income ($-<V>$), and profit ($-E$) has a certain value, and assume for simplicity that the optimum ratio is such that

profit ($-E$) = expenditures ($<T>$) = 0.5 × income ($-<V>$)

A certain outside accountant examined the financial books and was asked to rationalize the profit of the corporation. He argued that one could ignore expenditures entirely, since the profit can be obtained by taking only the income and dividing by two. A second accountant argued that the profit could be determined by ignoring the income and he simply equated the profit to the expenditures. A third accountant arrives and she wants to more fully understand the true corporate financial dynamics. She sees, correctly, that although there are shortcuts to obtaining the profit of the corporation, the real *process* (as opposed to mere bookkeeping) involves looking at income minus expenditures.

Moral of the story: Although we might obtain the correct answer for profit by ignoring expenditures or income and simply applying a tried and true formula, such an approach does not give us insight into the *interpretation* of the corporate finances. We side with the third accountant.

Added notes:

1. The analogy takes on additional interest with students if the instructor replaces the word merger with marriage, atom with family, and profit with savings.

2. With slight modification, the analogy also holds for understanding the changes that occur upon ionization of He or any other atom, as long as one works with *total* energy, *total* potential energy, and *total* kinetic energy. That is, the virial theorem does not hold for orbital energies.

We now apply the virial theorem to the ionization energy of the hydrogen atom. In the following we use "atomic units" (*2*). The experimental ionization energy is $IE = 0.5$ hartree. Hence $E = -IE = -0.5$ hartree. Using the formula displayed above, $E = <V>/2$. Since $<V> = -<1/R>$, we obtain an empirical value for R of 1 bohr. This is exactly the value for R that we tell students is "most probable" for the ground state of the hydrogen atom, so everything is going fine. A student could look at the formula $E = <V>/2$ and conclude that kinetic energy is unneeded. However, this is a sleight of hand. We have merely "buried" the kinetic energy term by dividing the potential energy by 2.

The origin of this discussion dealt with how to use experimental ionization energies to deduce the shell structure of atoms. Patterns among these energies do provide evidence for shell structure (*3, 4*), particularly when we also include the results of photoelectron spectra (*5*). The virial theorem is no doubt helpful to understand these patterns. However, this hardly fits under the original rubric of "demystifying" introductory chemistry (*5*)!

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2. Mills, I., et al. *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell: Oxford, 1993; p 76. One hartree is 4.359×10^{-18} J or 2625.5 kJ/mol. One bohr is 5.29×10^{-11} m.
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Response to Letters by Rioux and DeKock:

I regret having stated that "consideration of kinetic energy would be redundant" for electronic states of atoms. Judging from the preceding responses of Rioux (*1*) and DeKock (*2*), my statement appears to have suggested that kinetic energy cannot play a useful interpretive role for atoms. That is not my view. My intention was to stress that for atoms, explanations that refer solely to potential energy can be legitimate in a way that is impossible for molecules. Rioux and DeKock appear to disagree even with this assertion.

This disagreement is a matter of some importance. Many general chemistry textbooks provide qualitative explanations of trends in atomic ionization energies. These explanations discuss variations in orbital sizes and effective nuclear charges, usually in the context of electrostatic potential energy alone. Can these explanations be legitimate if they do not discuss kinetic energy? Rioux and DeKock say no. I say yes, not only because potential energy changes dominate, but also because changes in total energy of atoms are exactly proportional to changes in potential energy.

What is to be done? I propose that we provide a preamble to explanations of these trends. First, discuss kinetic energy T and potential energy V as such. Then point out that an electron's kinetic energy increases if its orbital gets smaller. Finally, point out that as a practical matter for atoms, we need consider changes in potential energy alone because

$$T = -(1/2) V = -E.$$

for electronic states of atoms (but not molecules).

This preamble would alert students to the importance of kinetic energy. It also would validate explanations that are based on (i) the effects of changes in effective nuclear charge on subshell radii and (ii) the effects of changes in charge and radii jointly on electrostatic energy and hence ionization energy. This minimal set of causal relationships is already moderately complicated, since it involves two interrelated causal variables: charge and radius. Why complicate the causal relationships further with kinetic energy, a variable that is redundant for treating these trends?

Rioux and DeKock say that the importance of kinetic energy should be stressed. The proposed preamble makes this importance clear—kinetic energy is as large in magnitude as total energy. One could also remind students repeatedly that each decrease of a radius increases kinetic energy.

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2. DeKock, R. L. *J. Chem. Educ.* **1999**, *76*, 605–606.

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About Letters to the Editor

Chemical Supplies

I've just received my latest issue of the *Journal of Chemical Education.* There has been a hiatus in my subscription and reading of many, many years. I received my B.A. from Columbia College in 1964 with a major in chemistry, and then I went on to receive a Ph.D. in Chemical Physics, also from Columbia University. Once I entered the field of medicine, I simply couldn't keep up with my chemistry interest, so all my subscriptions lapsed. Now that I have children I am rediscovering the world of chemistry in an effort to teach my kids. Unfortunately, it is almost impossible for an ordinary person (even one with advanced degrees in chemistry) to teach hands-on chemistry in the home nowadays. I can still remember with delight my first Chem Craft set and laboratory with supplies from Gilbert Scientific. But it seems that there is no repeating those marvelous days of discovery today—everyone is terrified of liability suits, safety hazards, and who knows what else. Apparently, the only way to order scientific supplies and chemicals from most companies is through your school, with a school purchase order. What about ordinary men and women who simply want to share the delight of chemistry with their children and neighbors, or simply want to experiment on their own? Having exhausted most of the catalogs that I found in the library, I thought that I would subscribe to the *Journal of Chemical Education* and surely there would be advertisements from chemical companies. No luck. If I want to get software, CD-ROMs, or more books and periodicals, then I am set. But if I want to mix some chemicals in a test tube, heat some material in a flask, I'm out of luck.

How did this happen? Has the fear of liability and bomb making, and who knows what other fears the lawyers and the media have concocted, really put and end to non-school exploration, experimentation, and just having fun with chemistry? Has anyone stopped to realize the implications for future generations of chemists who have not been allowed to experiment or tinker in their homes or garages or basements and whose first experiences with chemistry begin in high school in a supervised laboratory? Isn't anyone interested in nurturing curiosity with the actual touch and smell of chemicals—even if some of them are dangerous when improperly handled? Software and print material are obviously essential, but so is real-time, real-life experimenting.

Please share with me your thoughts on the historical reasons for the present state of affairs, as well as on the implications for society in the future. Also, if you have any names of chemical companies who are more responsive than the usual lot to home tinkerers and experimenters, I'd be very appreciative.

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Letters

In Defense of Quantum Numbers

I write in response to Richman's recent article "In Defense of Quantum Numbers" (*1*). Richman feels compelled to defend the use of quantum numbers and atomic orbitals in teaching chemistry in opposition to Gillespie et al. who prefer a presentation based on observables such as ionization energies (*2*).

However, this is only one form of attack which has been leveled against the use of quantum mechanical approximations in teaching chemistry. The reason why Gillespie rejects these theoretical approaches is because he regards them as being too complicated for beginning students. But in recent years an altogether different and perhaps deeper objection has been leveled against the use of quantum numbers as a way of teaching chemistry. Some philosophers of chemistry have emphasized the fact that quantum numbers are not strictly defined in many-electron atoms and conclude that atomic orbitals and configurations are ontologically redundant, or in other words, they simply do not exist (*3*). Granted that the use of orbitals provides an extremely powerful approximation but it also promotes a view of the misplaced concreteness of these theoretical entities. In addition, the increasing use of computer animation and other aids to visualization all reinforce the incorrect realistic view of atomic orbitals. It is for this entirely theoretical, or perhaps philosophical reason, that one might be inclined to ground chemistry in observable facts. As somebody once said, the tragedy of modern chemical education is that students frequently know the electronic configuration of chlorine, for example, but do not have the slightest idea that it is a green poisonous gas. It would have been interesting if Richman had also attempted a defense of quantum numbers in the light of this deeper objection alluded to above.

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2. Gillespie, R. J.; Spencer, J. N.; Moog, R. S. *J. Chem. Educ.* **1996**, *73*, 617–622.
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The author replies:

Scerri makes the excellent point that wavefunctions and quantum numbers derived from one-electron Hamiltonians are not eigenfunctions and good quantum numbers of many-electron Hamiltonians. Thus it is not strictly correct to teach, for example, that the two electrons in the ground state of helium have $n = 1$, $l = 0$, $m_l = 0$, and $m_s = \pm 1/2$. However, the angular wavefunctions are still correct (any error residing exclusively in the radial wavefunctions), and the widespread acceptance of the orbital approximation seems to indicate that its value outweighs any theoretical problems. Indeed, a direct extension of Scerri's reasoning to polyatomic systems would preclude us from using molecular orbital diagrams in teaching or doing chemistry at *any* level.

Chemistry is filled with examples of widely used theories that are correct only in zero-order approximations. In introductory chemistry courses, I would argue that we should teach chemistry as it is done by practicing chemists. We should be *descriptive*, not *prescriptive*.

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Correction to Fifty-Year Trends in the Chemical Industry

We are grateful to the sharp-eyed reader who picked out the mistake in our article, "Fifty-Year Trends in the Chemical Industry" (*J. Chem. Educ.* **1999,** *76*, 177–189). The correct caption for Figure 2 on page 179 of the February 1999 issue is shown below.

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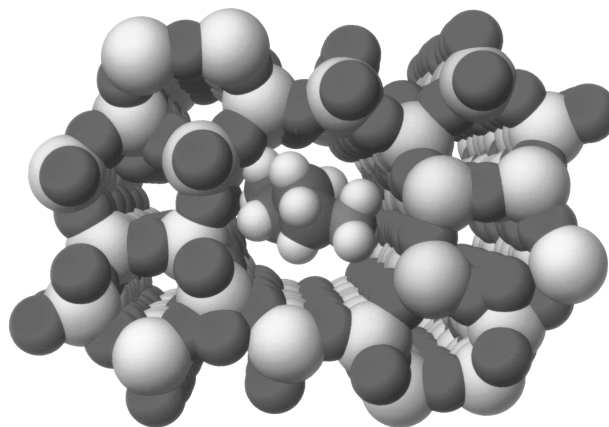2504 Delaware Ave.
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Figure 2. Schematic representation showing the snug fit of an *n*-butylammonium ion in a channel of a ZSM-5 zeolite. The zeolite crystal is made up of Si and Al ions (both shown in silver) linked together by oxygens (red). The nitrogen atom (blue) of the organic molecule is ionically bound to an anionic site in the channel wall.

Correction to The Art and Science of Organic and Natural Products Synthesis

My chemistry students and I discovered several mistakes in the Lewis structures of the "selected medications of the 20th century," Figure 45, page 1250 of the October 1998 issue. We wish to identify those mistakes to you. It was a learning experience for my students and me, especially at a time when we were just discussing a chapter on chemical bonding.

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The author replies:

Figure 45 of our article (Nicolaou, K. C.; Sorensen, E. J.; Winssinger, N. *J. Chem. Educ.* **1998**, *75*, 1225–1258) contains a number of errors and should be replaced by the corrected figure below.

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Figure 45. Selected medications of the 20th century (only the active ingredients are shown in their neutral form).