

Letters

Response to Potential-Energy-Only Models

In his recent commentary Lowe (*1*) does not challenge our quantum mechanical explanation of the H/He ionization energy ratio (*2*), but argues that our claim that consideration of kinetic energy is essential at the atomic level is too restrictive. To prove this he offers a potential-energy-only (PEO) model for the successive ionization energies of sulfur that he claims is “extremely simple”, works well, and is suitable for introductory students. We suggest that this PEO model is not a suitable pedagogical model for two reasons. First, it is built (incorrectly) on the virial theorem, and therefore an added piece of theory needs to be explained to introductory students. Second, it is built on the incorrect assumption that atomic size does not change with ionization from a given subshell, or at least that such changes can be ignored. Lowe acknowledges both of these features, but we feel the second item deserves more attention as we show below.

Lowe uses the virial theorem to establish a mathematical relationship between the ionization energy and electron potential energy as shown below in atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$),

$$I_i = \Delta E_i = \frac{\Delta V_i}{2} = \frac{i}{2r_i}$$

where i is the index for the ionization potential and the charge on the “ion left behind”, and r_i is the distance of the ionized electron from the nucleus. Lowe says of the model he proposes that “It is theoretically supported by the virial theorem.” However the virial theorem is valid only when the initial and final states are stable, equilibrium states. The product ion, under the model used in this calculation, is not in an equilibrium state, since the radius is assumed fixed, and therefore the application of the virial theorem will be compromised.

The next step is to write the ratio of i th and j th ionization energies based on the previous equation.

$$\frac{I_j}{I_i} = \left(\frac{j}{i}\right)\left(\frac{r_i}{r_j}\right)$$

If we again assume that within a subshell $r_i = r_j$ and then choose one of the ionization energies as a reference, we can proceed to calculate the other ionization energies within the subshell. Unfortunately this assumption is not consistent with experimental data available for atomic and ionic radii. For example, sulfur has an atomic radius of 104 pm, whereas S^{4+} , S^{6+} , and S^{2-} have ionic radii of 37, 29, and 170 pm, respectively (*3*). These data indicate that adding or removing electrons has a significant effect on the radius of an element, and therefore presumably on the radii of the shells.

As noted above, this model as used by Lowe requires a reference point (and re-referencing for each new subshell), and it is very sensitive to the reference point chosen. For example, Lowe uses the second ionization energy of sulfur as

the reference point, because using the first ionization energy does not give good results. Looking at the first four ionization energies and choosing I_2 as the reference yields a cumulative error of 14% (*1*). Using I_1 as the reference yields a cumulative error of 34% (I_1 [1000, ref]; I_2 [2000, 11.2%]; I_3 [3000, 10.6%]; I_4 [4000, 12.2%]), where the ionization energies are given in kJ/mol.

To explain this difference, Lowe invokes the special stability of the half-filled shell (we assume he means half-filled subshell). This argument is not convincing, since both ionization processes involve a half-filled subshell— I_1 on the product side ($3p^4 \rightarrow 3p^3$) and I_2 on the reactant side ($3p^3 \rightarrow 3p^2$). In any case, it seems his simple model requires guidance from a more advanced model, the orbital approximation of modern quantum theory, just to get started. In addition, the re-referencing required for each subshell in order to achieve modest quantitative success is tedious and challenges the pedagogical utility of this PEO model.

This PEO model gives noticeably worse predictions for oxygen than it does for sulfur. Again, using the cumulative error as a criterion of goodness of fit, oxygen yields a cumulative error of 42% compared to 14% for sulfur. We might expect an atom with fewer electrons to yield better results, but this is not the case.

We would also like to stress that we do not criticize the use of the shell model to teach the basic elements of atomic structure. The most important characteristic of electronic shells and subshells is their capacity for electrons. This can be seen clearly by a *direct* examination of graphs of the first ionization energies of the elements or tables of successive ionization energies, which can be found in any general chemistry text (*4*). Or one can follow Gillespie, Spencer, and Moog (*5*) and use the orbital ionization energies obtained from photoelectron spectroscopy. All these approaches clearly reveal the *existence* of electronic shells; one does not need to construct a classical PEO model with questionable foundations to demonstrate the validity and utility of the atomic shell model. In his article Lowe made reference to the fact that DeKock and Gray used an electrostatic-only model in their textbook (*6*). For the reasons described above, DeKock now wishes to distance himself from this model as a pedagogical tool.

Shells, subshells, quantized energy levels, and atomic stability have their origin in the wave nature of the electron, which we all recognize is manifested in the electron's kinetic energy. That is why we think consideration of kinetic energy is essential.

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Letters

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The author replies:

Despite the arguments of Rioux and DeKock (1), I continue to maintain (2) that their statement that “interpreting the ionization of any atom or molecule requires quantum chemical tools and a consideration of both kinetic and potential energies” (3) is too restrictive. Carlton has also criticized this statement (4). Authors of general chemistry texts often interpret ionization energies as evidence for the shell structure of atoms. First ionization energies across a series of atoms are most often used for this purpose (which Rioux and DeKock appear to find acceptable), and successive ionization energies for a single atom are sometimes used also (5–7).

The point raised independently by Carlton and by me is that the virial theorem guarantees that the change in total energy for such a process involving atoms is equal to twice the change in potential energy and also to the negative of the change in kinetic energy. Thus, if we know the ionization energy, we also know the potential energy change accompanying the ionizing process as well as the kinetic energy change. We can use our knowledge of potential energy changes, inferred from measured ionization energies, to draw conclusions about the electronic structure of atoms. When we do this, the shell structure is revealed. However, for this approach to work, we must have some sort of relationship in mind that connects the data (ionization energies) and the structure. That relationship, which I have referred to as a “model”, is the *mediator* between the data and the structure. As mediator, a model should work in both directions: It should allow one to infer the structure from the data, and it should allow one to predict the data from the structure. If a model is acceptable for use in one direction, it ought to be acceptable for use in the other direction.

The model I have been discussing is referred to in my paper as a potential-energy-only (PEO) model. One could also seek to focus on the kinetic energy changes, creating a kinetic-energy-only model (not yet done successfully, to my knowledge), or one could seek a model that deals directly

with the total energy change. According to their statement quoted above, Rioux and DeKock are of the opinion that a PEO model is inappropriate. However, according to certain other statements they make, they seem to think it is appropriate. In their penultimate paragraph they make the comment, “Evidence for electronic shells and subshells is easily seen in a graph of the first ionization energies of the elements found in any general chemistry text.” This statement, along with the subsequent sentences, indicates to me that Rioux and DeKock are themselves using a PEO model, perhaps without realizing it. How else does any of us get from a graph of ionization energies to a shell structure than by supposing that there is a relationship between the energy needed to extract an electron and the distance from the nucleus from which it starts its journey? Isn't that a potential energy model?

Rioux and DeKock raise a number of criticisms of the PEO model and, in the process, often refer to it as “Lowe's model”. This is misleading. I certainly cannot lay claim to having discovered this model, and I am far from the first person to use it to infer shell structure from ionization energies. In my paper I cite related approaches going back to 1973. Interestingly, one of the earlier users of this model is DeKock himself, who coauthored a textbook (7) that uses a similar PEO model. Using the symbols defined above in Rioux and DeKock's response (1), the formula given by DeKock (7) for the i th ionization energy is $I_i = i/r_i$. Comparing this with the formula given above by Rioux and DeKock, we see that it is in error by a factor of two. Apparently the distinction between potential and total energy changes was overlooked when DeKock's textbook was written. Despite Rioux and DeKock's attacks on PEO models, I have so far not seen an attack on, or retraction of, the model used by DeKock himself, which is the only one I have seen in print that explicitly posits the relationship confusing total with potential energy that they find so objectionable. Because of this history, it would be more appropriate for them to label the model they are criticizing as “the corrected version of DeKock's PEO model” rather than “Lowe's model”.

Of course, the factor of two doesn't lead to errors if one uses the PEO model only for purposes of comparison, as I did in my paper (2), and as DeKock himself does in his textbook. In his Problem 8 of Chapter 2, for example, he asks the student to calculate I_i/i for the 12 ionization energies of Mg (8). Thus, DeKock uses observed successive ionization energies to demonstrate patterns in r_i values that suggest shell structure. I described the alternative of estimating ionization energies from assumed shell structure. If one of these approaches is suitable for use in an introductory course, then so is the other. They both rely on the PEO model, but they simply use it in opposite directions.

Rioux and DeKock imply in their first paragraph that I have misled readers by not being *up front* in my discussion. I leave it to readers to examine my paper and draw their own conclusions. I put considerable effort into making the discussion clear, and I believe that I pointed out the approximate nature of the model and certain pedagogical advantages that accompany such approximate and (yes) simple models.

Turning to specific criticisms:

Rioux and DeKock claim that the model “considers only electron–nuclear potential energy and ignores electron–electron potential energy.” This simply isn’t true. If only electron–nuclear potential energy were included, then every electron would “see” the full nuclear charge, and the model would become $I_i = Z/2r_i$, where Z is the atomic number. This would be an absurd model, and would not even come close to reproducing trends in observed ionization energies.

Rioux and DeKock claim that known ionic radii are incompatible with the PEO model, but their data are not relevant for the claims they make. They claim that the radius of S^{4+} tells us something about the size of the 3p subshell, but this ion doesn’t have any 3p electrons, and S^{6+} has no 3p or 3s electrons. Their comparisons of the radii of S^{4+} and S^{6+} come from data on coordinate complexes having different coordination numbers. Inspection of the table from which these data are taken (9) reveals that even the *same* ion (same charge) in complexes having different coordination numbers is tabulated with rather different radii.

Finally, Rioux and DeKock question why anyone would use I_2 instead of I_1 to predict I_3 , or I_4 of sulfur. The answer, which I alluded to in my paper, is that I_3 and I_4 are processes where an electron is being removed from a half-filled p orbital. I_2 is similar in this regard, hence makes a good basis for comparison. But I_1 is different, since, in that case, an

electron is being removed from a filled orbital. My students seem to get it.

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