Accounting for electron spin in user-friendly simulations of chemical reaction pathways

The electrons that swarm around the nuclei in atoms and molecules, not only carry electricity to our homes and offices, but also control how bonds are made and broken in chemical reactions. The challenge in describing this behavior comes from the fact that electrons are so light (more than 2,000-fold lighter than even the lightest nucleus) that their trajectories are not as well defined as those of more familiar objects like baseballs and rockets. Moreover, electrons exist in two possible "spin" states, often referred to as "up" and "down". Nevertheless, as Gilbert N. Lewis pointed out a century ago, we can understand much of what electrons do by regarding them as particles that obey some peculiar rules and, to this day, chemists rely on these "Lewis dot" pictures to think and communicate about molecular structure and reactivity.

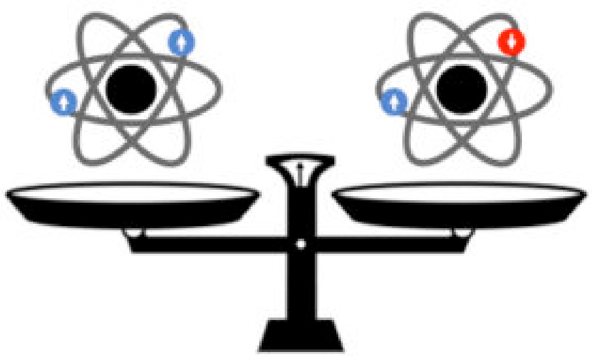

Fig. 1.

Our goal is to translate Lewis' rules for electrons into equations that can predict and explain the details of chemical reaction pathways in a fashion that is more efficient and user-friendly than current approaches. An important rule is that electrons of like spin interact differently from electrons of unlike spin. The difference between the two is called "the exchange energy" and getting this right has been difficult for all approaches to describing electron behavior.

In this paper, we have analyzed each of the three contributions to the exchange energy. As expected, the kinetic contribution, which is related to the motion of the electrons, always favors unlike spins. On the other hand, we find that the contribution associated with repulsions between the negative charges of the electrons always favors like spins. Meanwhile, the effect of the third contribution, based on the attractions of the negative charges of the electrons to the positive charges of the atomic nuclei, depends on the location of the nucleus with respect to the electrons: when the nucleus is between the two electrons, this contribution favors unlike spins; otherwise it favors like spins.

With this study we show that in order for equations to render Lewis' rules effectively, they need to include the effects of all three contributions to the exchange energy. Moreover, whereas two contributions depend only on the distance between the two electrons, the third also depends on the locations and charges of near-by nuclei.

Judith Herzfeld, Solen Ekesan
Department of Chemistry, Brandeis University, Waltham, MA, USA

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