

# Where Should the Nuclei Be Located?

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In the scientific literature and particularly in textbooks, atom nuclei are often placed in misleading positions in orbital representations. Several common representations taken from well-known textbooks for the positions of nuclei in molecular orbitals (1, 2) and hybrid orbitals (3–5) are shown in Figure 1. The orbital representations in Figure 1 can readily cause misunderstandings in the nature of the electron wave function for these systems. While this can be shown quantitatively via numerical calculations (6–10), it is also possible to explain the inadequacies of these diagrams qualitatively. This approach is demonstrated in this article.

The wave function for an atomic system consists of two parts, the radial part and the angular part:

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

The angular parts of the wave function are shown in Figure 2 for a diatomic molecule and in Figure 3 for a hybrid orbital. These provide a more suitable representation of the positions of the nuclei than the examples in Figure 1.

The angular representation of a wave function is not the shape of the function though its contour map may have a similar shape. For an atomic orbital, the angular part of the wave function represents the variation of values for the wave

function along different directions for a fixed distance of an electron from the nucleus. When the nuclei are at an infinite distance apart the values of the wave function will be zero at the positions of the nuclei 1 and 2. However as the atoms approach each other the  $\sigma$  bonding and  $\sigma^*$  antibonding orbitals begin to be formed from the two p atomic orbitals of atoms 1 and 2 as shown in Figure 2B and then as the distance decreases further the diatomic molecule is formed in Figure 2C. It can readily be demonstrated that the value of the wave function at the nuclei in Figures 2B and 2C will not be zero. Thus for the nucleus of atom 1 of the  $\sigma$  bonding orbital, the wave function will be positive rather than zero, because although its value at this point is zero for the atomic orbital of atom 1, its value will be positive for the atomic orbital of atom 2. The equivalent effect will be found at the nucleus of atom 2. For the same reason, the summed value of the sp hybrid orbital at the nucleus is not zero as shown in Figure 3. So, the representations in Figure 1, particularly 1A and 1C are misleading. The convention of representing nuclei as chemical symbols as shown in Figure 1B and 1D is acceptable, provided that it is understood that these diagrams represent only approximate pictures, simplified for convenience, and are not intended to indicate the exact positions of the nuclei.

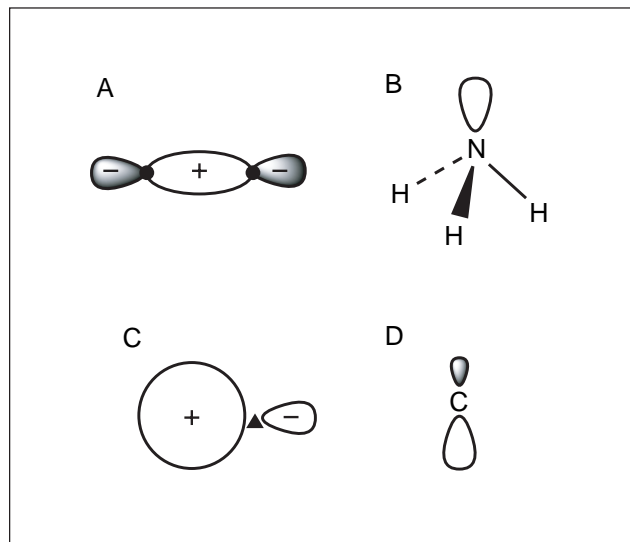


Figure 1. Common representations for the positions of nuclei in orbital diagrams:

- (A) Overlap of two p orbitals,
- (B) Orbital containing a lone pair
- (C) Hybrid of s and p orbitals
- (D) Hybrid p orbital

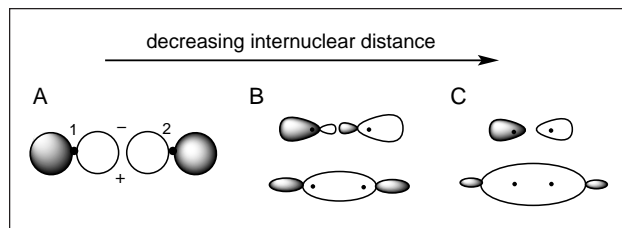


Figure 2. Combination of two p atomic orbitals at different internuclear distances:

- (A) At infinity with no overlap
- (B) Bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals at a long bonding distance
- (C) The bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals at a short bonding distance.

These figures provide more suitable representations for the positions of nuclei in molecular orbitals.

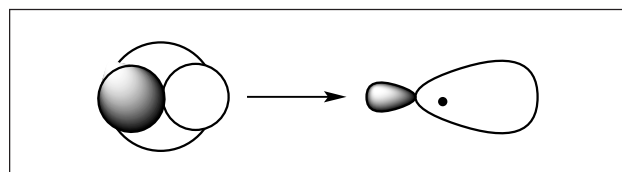


Figure 3. More suitable representation for the positions of the nucleus in an sp hybrid orbital.

A further problem in dot representations is illustrated by the different diagrams of the antibonding  $\sigma^*$  orbital shown in Figures 2B and 2C. In Figure 2B where the atoms are separated by a long distance, the orbital contains small tails pointing inward toward each other, whereas these disappear at short bonding distance represented by Figure 2C. The change in the shape of the orbital with distance can easily be demonstrated quantitatively.

If the atomic 2p orbital at each nucleus is given by,

$$\Psi(x)_{2p_x} = \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Z(x+c)}{a_0} e^{-Z \frac{\sqrt{(x+c)^2}}{2a_0}}$$

where  $Z$  is the atomic number (here equal to 1),  $a_0$  is the Bohr radius,  $x$  is the coordinate of the electron in the orbital measured from the center of the bond,  $|x+c|$  is either  $r_1$  or

$r_2$ , the distance of the electron from nucleus 1 or 2 in the  $p_x$  orbital,  $c$  is the negative of the coordinate of nucleus 1 or 2 along the  $x$  axis, and  $\psi$  is the radial part of  $2p_x$  for nucleus 1 or 2. Then the wave function for the  $\sigma$  bonding and  $\sigma^*$  antibonding orbitals can be calculated with the result shown in Figure 4. At short bonding distance for the antibonding orbital, Figure 4C, the wave function shows only negative areas at negative  $x$  and positive areas at positive  $x$ , consistent with the representation in Figure 2C. As the internuclear distance increases from  $2 a_0$  (Bohr units) in Figure 4C to  $5 a_0$  in Figure 4B the small tail areas with different signs begin to appear, consistent with the representation in Figure 2B, and as the distance increases further to  $50 a_0$  Figure 4A, then the atoms are separated and the inward tails increase in size to form the separate p orbitals. At the united atom limit, the inward tails of the antibonding orbital and the outward tails of the bonding orbital will disappear.

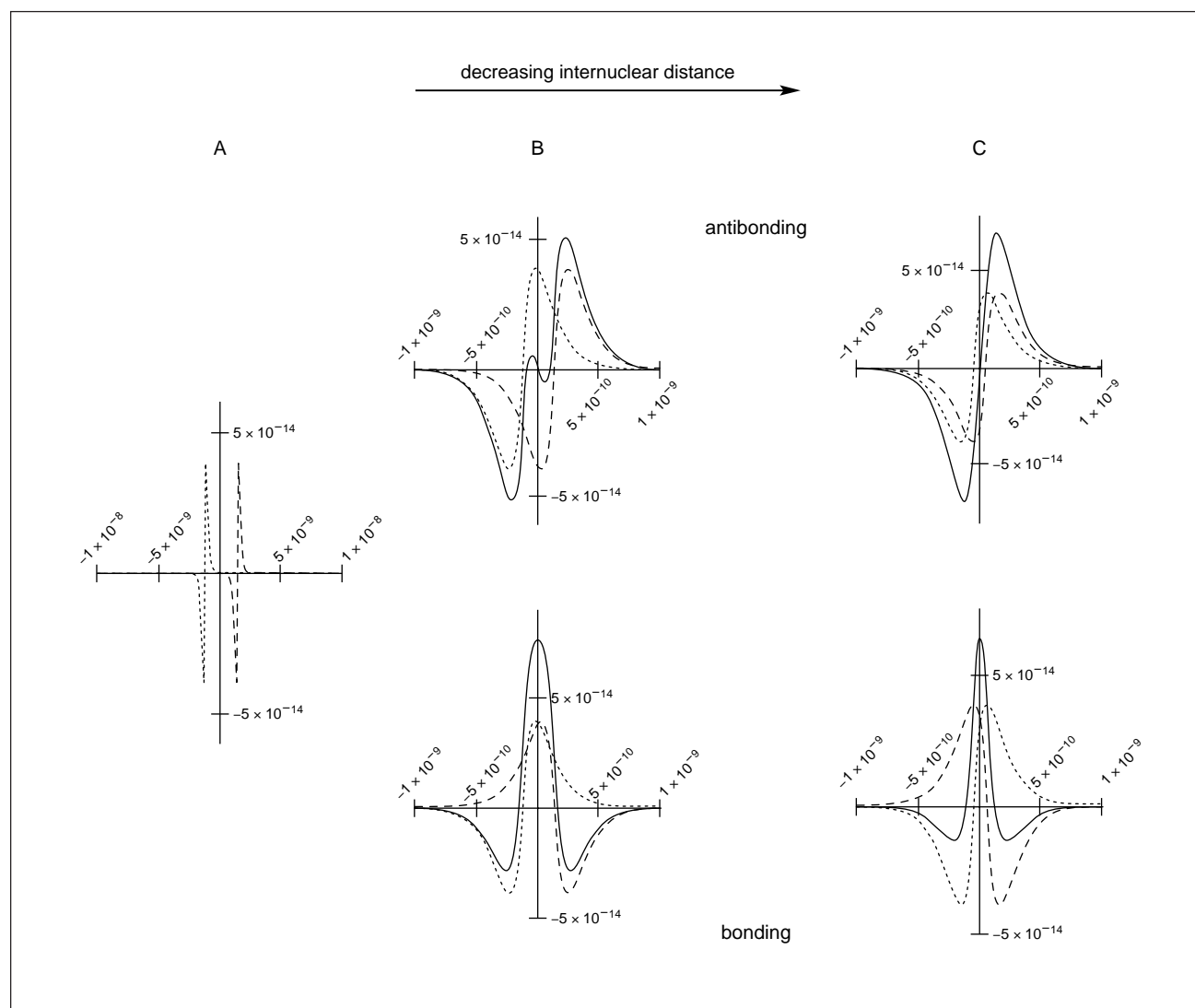


Figure 4. The value of wave function  $\psi/m^{-3/2}$  for atomic, bonding, and antibonding orbitals plotted against distance from the center of the bond in units of meters. The distance between the two nuclei is: (A)  $50 a_0$ , (B)  $5 a_0$ , and (C)  $2 a_0$ . The dotted and dashed lines represent the atomic  $p_x$  orbitals and the solid lines represent the resulting bonding and antibonding  $\sigma$  orbitals.

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## Literature Cited

1. Whittaker, A. G.; Mount, A. R.; Heal, M. R. *Instant Notes in Physical Chemistry*; Bios Scientific Limited: Abingdon, United Kingdom, 2000; p 210.
2. Cox, P. A. *Instant Notes in Inorganic Chemistry*; Scientific Limited: Abingdon, United Kingdom, 2000; pp 46, 58.
3. Patrick, G. L. *Instant Notes in Organic Chemistry*; Scientific Limited: Abingdon, United Kingdom, 2000; p 10.
4. Verkade, J. G. *A Pictorial Approach to Molecular Bonding and Vibrations*, 2nd ed.; Springer-Verlag: New York, 1997; p 107.
5. Lowe, J. P. *Quantum Chemistry*; Academic Press, Inc.: New York, 1978; p 479.
6. Liu, Y.; Wang, Q.; Liu, Y.; Yang, X. Z. *Chem. Phys. Letters* **2003**, *373*, 338–343.
7. Che, C. B.; Zhang, H.; Zhang, X.; Liu, Y.; Liu, B. *J. Phys. Chem. A* **2003**, *107*, 2929–2933.
8. Liu, Ying; Liu, Yue. *Higher Education for Teachers Towards 21st Century*; Wang, Yuzhuo, Zhang, Zhijun, Eds.; Heilongjiang Education Press: Harbin, P. R. China, 2001; pp 339–342.
9. Liu, Ying; Liu, Yue; Drew, M. G. B. *Chinese J. Chem.* **2003**, *21*, 481–484.
10. Liu, Yue; Yang, Zhaodi; Liu, Ying. *Acta Chimica Sinica* **2003**, *61*, 1528–1532.