THE JOURNAL OF PHYSICAL CHEMISTRY A

ADDITION/CORRECTION

pubs.acs.org/JPCA

Correction to "Atoms and Bonds in Molecules from Radial Densities"

Peter L. Warburton,* Raymond A. Poirier, and Devin Nippard

The Journal of Physical Chemistry A **2011**, *115*, 852–867. DOI: 10.1021/jp1093417

The figure presented as both the Graphical Abstract and Figure 3 on page 854 is in error due to a minor software issue that has been recently discovered. In the original figure, the total radial density (TRD) of CO is seen to be zero at the distances associated with nuclear positions along the bond axis for every axis parallel to the bond axis. As the radial density depends on both the calculated electron density at a point, as well as the distance from the nucleus of interest to that point, a zero value for the radial density should not be possible except at a distance of zero from the nucleus, or at points where there is no electron density, likely very far from the atoms of the molecule. Therefore, points of zero total radial density on the axes parallel to the bond should not be possible for the distances from the nuclei considered in the figure. Because the software issue only affected the calculation of total radial density for lines offset from the bond axis, all other figures in the original work are correct.

Figure 1 shows the CO total radial density after the software correction. This figure includes more lines offset from the bond axis (every 0.25 bohr from the bond axis to a maximum offset of 2.00 bohr) to give a much clearer picture of the total radial density of CO.

In the original work, starting with the last paragraph on page 861 and ending with the first paragraph on page 863, we discussed some of the features of the TRD of CO off the bond axis, including the distances to the maxima in the total radial density in both the bonding and nonbonding regions of the C and O atoms. The following text replaces the discussion of the CO TRD of the original work with similar discussion of the corrected figure presented here.

To visualize the TRD away from the CO bond axis, we plotted axes parallel to the bond at incremental distances of 0.25 bohr (see Figure 1). The distances from a nucleus to the maxima in the TRD were calculated. For the carbon of CO, the distance to the maximum of the TRD in the bonding region occurs at 1.198 bohr on the internuclear axis (Table 3 of the original work) but increases steadily to 1.232, 1.327, and 1.471 bohr as we consider each shifted axis up to an offset of 0.75 bohr. The behavior of oxygen in the bonding region of CO mirrors this increase, with the distance to the TRD maxima increasing from 0.907 (Table 3 of original work) to 0.932, 1.008, and 1.125 bohr, respectively.

In the nonbonding region the carbon TRD maxima occur at distances of 1.187, 1.199, 1.238, and 1.303 bohr, respectively. When compared to the bonding region maxima for the same axes, it can be seen that the nonbonding maximum occurs at a shorter distance than the bonding region maximum along all the considered axes. This behavior indicates distortion of the carbon AIMRD from the spherical free carbon radial density due to the presence of the O. For oxygen, the TRD nonbonding maxima occur at 0.835, 0.841, 0.859, and 0.894 bohr, respectively. Whereas the nonbonding region maxima once again occur at a shorter distance from the nucleus compared to the bonding maxima along the same axis, here the change in distance is much less pronounced then for carbon in the nonbonding region. Therefore, the oxygen AIMRD is also distorted by the C atom, but not to as great an extent as the distortion of the C atom by oxygen. These observations are also consistent with Parr's description of AIM undergoing change in shape relative to free atoms.[1]

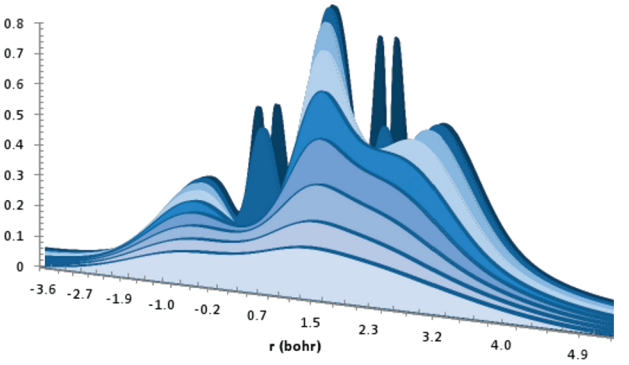

Figure 1. Total radial density along lines parallel to the CO bond in CO. Each line is offset by 0.25 bohr. The darkest region corresponds to the bond axis, and the lightest is 2.00 bohr from the bond axis.

REFERENCES

(1) Reference 21 in the original work:Parr, R. G.; Ayers, P. W.; Nalewajski, R. F. *J. Phys. Chem. A* **2005**, *109*, 3957–3959.

Published: October 05, 2011