Written Qualifying Examination – Inorganic Chemistry I

June 17, 2008

Questions related to J. Reinhold, O. Kluge, and C. Mealli, *Inorg. Chem.*, **2007**, *46*, 7142.

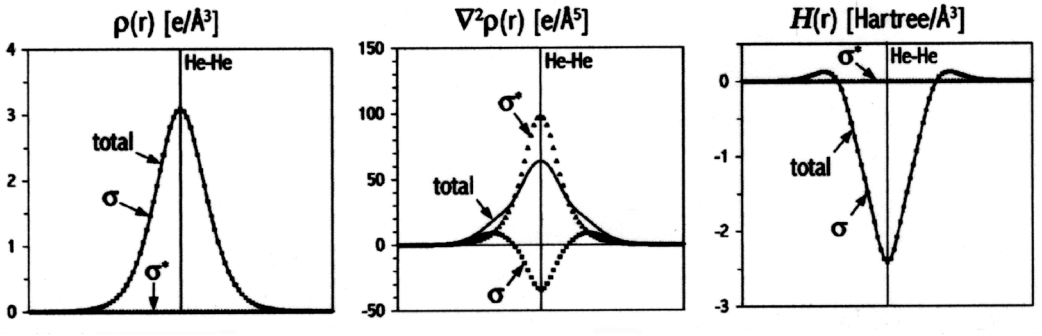
Questions Related to the Assigned Paper (10.0 points)

Give essay answers to each of the following four questions, whose individual point values are indicated. Your answer in each case should throughly address the issues raised by the question, without unnecessary restatement of given information. Your responses must be written in standard English with appropriate chemical notation, where appropriate.

1. (2.0 points) The authors describe AIM and MO as very different approaches to understanding chemical bonding, drawing an analogy (which you may want to use in your response) with X-ray crystallography to underscore the distinctions. Carefully describe the differences in these two approaches to bonding anaysis, paying particular attention to the fundamental starting points in each case. How does the authors' electron density orbital partitioning approach (EDOP) combine these two methods?

2. (2.0 points) The arguments in this paper use some key concepts of AIM theory: the bond critical point (bcp), $\boldsymbol{r}_b$; the electron density, $\rho(\boldsymbol{r})$; the Laplacian, $\nabla^2\rho(\boldsymbol{r})$; and the energy density, $H(\boldsymbol{r})$. Define each of these terms and explain its significance for analysis of bonding. For shared-shell interactions between bonded light atoms, what are the expected relative magnitudes and signs at the bcp for $\rho(\boldsymbol{r}_c)$, $\nabla^2\rho(\boldsymbol{r}_c)$, and $H(\boldsymbol{r}_c)$? How do these concepts apply to individual bonding or antibonding MOs in EDOP analysis?

3. (2.0 points) By way of explaining their analysis of $Fe_2(CO)_9$, the authors discuss the variation of $\rho(\boldsymbol{r})$, $\nabla^2\rho(\boldsymbol{r})$, and $H(\boldsymbol{r})$ along a C_2 axis (perpendicular to the internuclear axis) of the model system He_2 at a fixed separation of 75 pm. Their Figure 4, showing the variations of these parameters, is shown below.



Although He_2 has a net repulsion (no bond), there is a bcp, positive $\nabla^2\rho(\boldsymbol{r}_b)$, and negative $H(\boldsymbol{r}_b)$. Explain these seemingly contrary results in terms of $\rho(\boldsymbol{r})$, $\nabla^2\rho(\boldsymbol{r})$, and $H(\boldsymbol{r})$ of the two MOs (σ and σ*) and their nodal structures.

4. (4.0 points) The goal of this paper is to demonstrate the utility of EDOP to verify the existence of Fe–Fe bonding in $Fe_2(CO)_9$. Based on their calculations, the authors find a positive Fe–Fe delocalization index, $\delta_{Fe-Fe} = +0.4$, which they say "underlines the presence of an intermetallic bond and encourages us to look for its origin." To that end, they present the detailed plots shown in Figure 2, which are reproduced on page 3 of this test packet. They interpret the results from these plots in terms of the MOs, shown in their Figure 3, reproduced on page 4 of this test packet. In addressing the problem and with reference to Figure 2, the authors write the following:

   > The total energy density (bottom-left box) reaches a negative minimum at the Fe–Fe intersection ($H(\boldsymbol{r}_c)$= –0.09 au/Å^3), where there is also a positive minimum of the total Laplacian ($\nabla^2\rho(\boldsymbol{r}_c)$ = 2.1 e/Å^5). Altogether, the quantitative information emerging from classical AIM tools and based on the total densities appears contradictory because the depletion of the charge density (positive Laplacian) points to a closed-shell interaction. However, an improvement of the basis set with the detection of the bcp seems to change the interaction from repulsive to attractive and leaves the existence of the Fe–Fe bond uncertain.

   With specific reference to the plots of Figure 2 and the MOs shown in Figure 3, describe in detail how the authors' orbital partitioning analysis provides a reasonable explanation for such a global response of the AIM method that is nonetheless consistent with the existence of Fe–Fe direct bonding in $Fe_2(CO)_9$.

Green Chemistry Question (2.0 points)

Much of the argument for Fe–Fe bonding in $Fe_2(CO)_9$ in this paper rests on an analysis of the bonding and antibonding characteristics of frontier orbitals. In light of this, discuss how AIM, MO, and EDOP methodologies might be applied to green chemistry. Your answer should include a description of what is meant by the term "frontier orbital" and how such MOs are related to chemical reactivity.

Figure 2. Variation of $\rho(\boldsymbol{r})$, $\nabla^2\rho(\boldsymbol{r})$, and $H(\boldsymbol{r})$ along a C_2 axis of $Fe_2(CO)_9$.

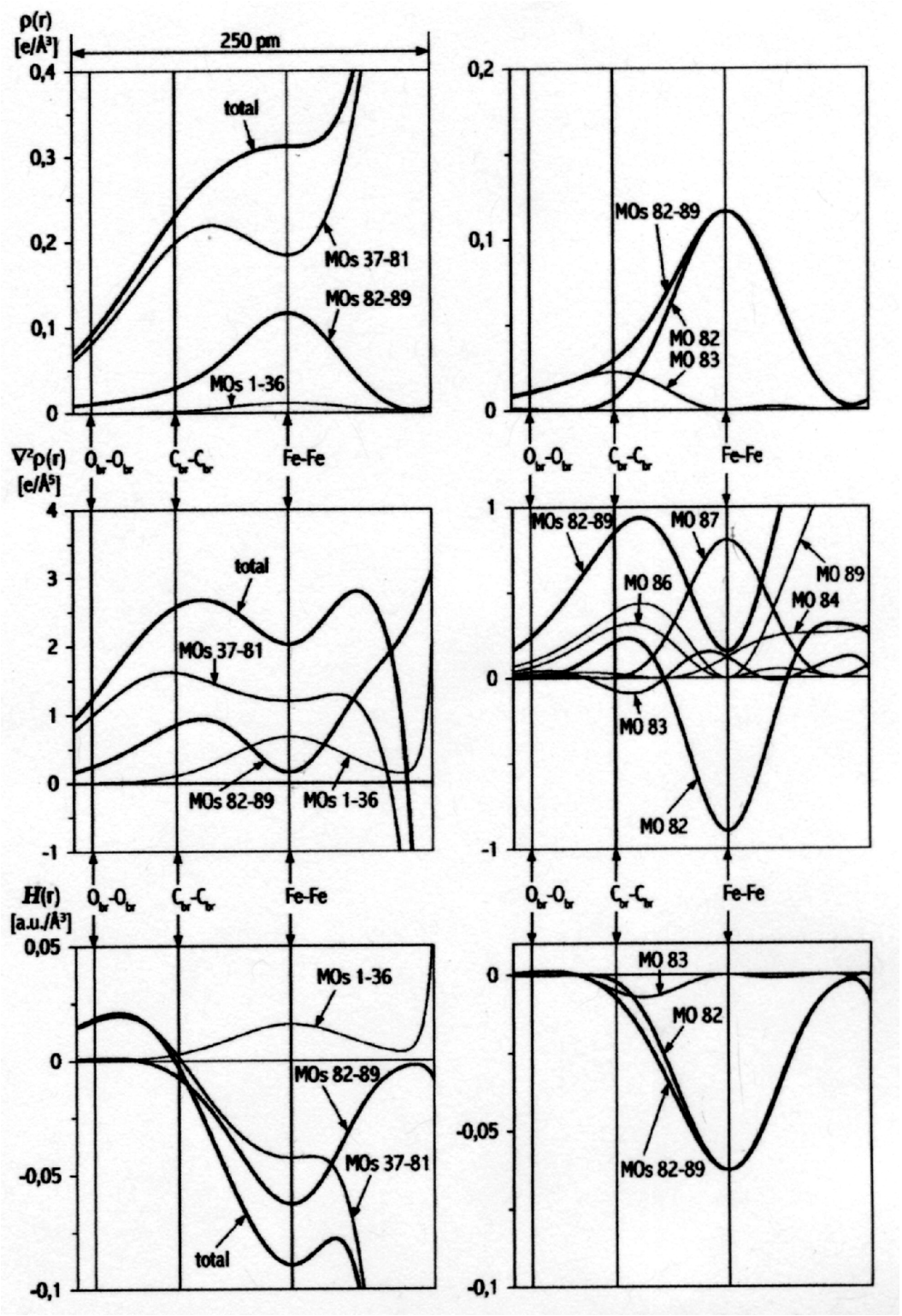


Fig. 3 Relative energies of the eighty-nine occupied levels of $Fe_2(CO)_9$ (left side) and sketches of the eight highest frontier MOs (right side).