

CHEMISTRY IN A SPIN

SIDNEY F. A. KETTLE*

Institute of Inorganic and Analytical Chemistry,

Attila József University

Dóm tér 7., H-6720 Szeged, Hungary

(Received December 13, 1990)

THE IMPORTANCE OF CONSIDERING RELATIVISTIC EFFECTS, BEING IN CLOSE CONNECTIONS WITH THE ELECTRON SPIN, IN UNDERSTANDING OF BONDING PROPERTIES IN MOLECULES IS EMPHASIZED, ILLUSTRATED BY CHEMICAL EXAMPLES AND SHOWN HOW THESE EFFECTS CAN BE TREATED QUALITATIVELY BY GROUP THEORETICAL TOOLS, ESPECIALLY THOSE CALLED DOUBLE GROUPS.

The theory of relativity is essential to our understanding of bonding in molecules. Electron spin is a relativistic phenomenon and is relevant to the simplest system. Elementary lectures refer to the fact, sooner or later, we must use the quantum number $j (=l+s)$ rather than l and s separately. We are aware that the (relativistic) phenomenon of spin-orbit coupling exists and that the use of j is linked to the importance of spin-orbit coupling. Yet it is usual to assume that all this can be forgotten even when discussing the bonding in compounds of the heavier elements. Of course, relativity is a "difficult" topic but this does not make its neglect a valid approximation. Indeed, it does not take much of a literature survey to point out the need to take relativistic phenomena on board. For instance, down the series Co, Rh and Ir the spin-orbit coupling constants for the $4+$ ions (ions for which data are

* Permanent address: School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, ENGLAND, U.K.

available for all three elements) are 650, 1570 and 5000 cm^{-1} respectively — an order of-magnitude change, moving from an energy typical of a vibration to one typical of a low-energy electronic excitation. Perhaps more obvious is a comparison of the relative energies of the Pb—Pb single bond (1.0eV) and the corresponding spin-orbit coupling energy -1.32eV . How can one hope to correctly describe the Pb—Pb bond unless the importance of spin-orbit coupling is considered, even if it is subsequently dismissed? Similarly, a recent approximate study of the bonding in an equilateral triangular array of Pt atoms concluded that the bonding energy is $7.12 \text{ kJ}\cdot\text{mol}^{-1}$ on a non-relativistic basis but is $36.43 \text{ kJ}\cdot\text{mol}^{-1}$ on a relativistic basis [1]. Therefore, we must surely conclude that we must make a serious attempt to include relativistic phenomena in our qualitative description of heavy-metal clusters. Of course, relativistic calculations are much more difficult to do than non-relativistic ones and, in particular, it becomes much more difficult to include the effects of electron-electron repulsion. So, detailed calculations are limited to simple systems but still we can learn a great deal from them. So, as one relevant example, it seems clear that although Ag—H and Au—H are very similar at the non-relativistic level, they become very different when relativistic effects are included (see the energy level diagram in Fig.1). This not only accounts for the different colours of silver and gold (a transition in metallic silver moves to much lower energy in gold) but, almost certainly, for the very different chemistries of the two elements. Further manifestations of relativistic phenomena are the low melting point of mercury, the inert pair effect (both manifestations is from the fact that a pair of s electrons have become a bit similar to those in He) and a contribution to the lanthanide contraction.

Relativistic atomic orbitals differ in one major way from their non-relativistic

counterparts. They are a superposition of four "bits". Each "bit" is quite like one of the familiar atomic orbitals but the fact the orbitals are superpositions means that the

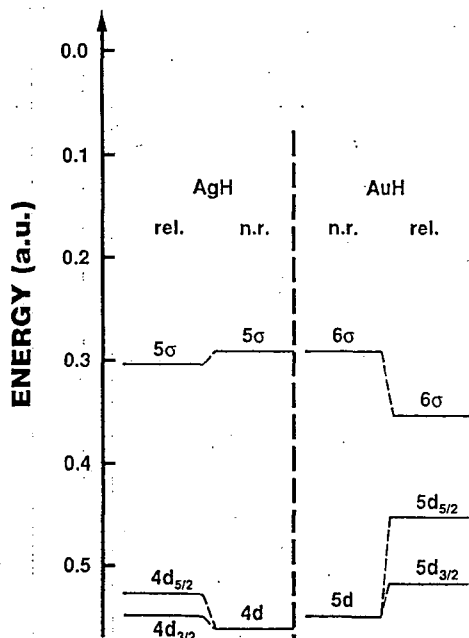


Figure 1: Energy level diagrams of AgH and AuH

nodal pattern inherent in one "bit" will not normally coincide with those of the other "bits". So, overall, there are no nodes. All of this makes it difficult to draw relativistic orbitals and they tend to be pictured as electron densities. Even this is not really satisfactory because relativistic orbitals have intrinsic angular momentum which cannot be "cancelled-out" (such cancelling-out is the way that the standing waves p_x and p_y are obtained from the angular momentum containing functions p_1 and p_{-1}). The result is that the subject is made yet more difficult by half-true statements,

intended to help saying: "both the functions $s_{1/2}$ and $p_{1/2}$ are spherically symmetrical" or " $p_{1/2}$ consists of a σ bonding component and a π antibonding component".

Although a proper description of bonding in heavy-element compounds must surely use such orbitals there is a half-way house. This is to use functions appropriate to j , to use spin-orbit functions. Again, however, these functions are shrouded in mystery and no-one seems to attempt to draw them. Yet the group-theory associated with them is well-developed – it is the theory of the so-called "double groups". These are usually introduced as a mathematical trick but, in fact, a reality can be attached to them. In Fig. 2 is given the character table of the C_{2v}^* double group, usually denoted C_{2v}^* , together with the nodal patterns associated with each of its irreducible representations.

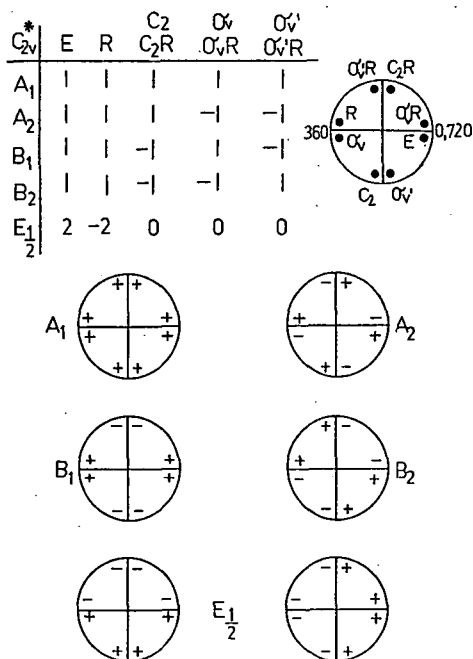


Figure 2. Character table and nodal patterns of the C_{2v}^* (double) group

It will be noticed that it is possible to give standing-wave pictures of the (two) spin $= \pm 1/2$ functions (these are the components of the $E_{1/2}$ basis).

As an example I now give a double-group description of the metal-metal bonding in the $\text{Pt}_3(\text{CO})_6$ cluster. It will help to take a result from the reference cited earlier, that in a Pt_3 cluster there is a "hole" of 0.768 electrons in the d-shell [1]. This hole is a result of an enhanced occupation of the 6s-shell (relativistic effects lower the energies of s-electrons, a phenomenon which is manifest in mercury being a liquid and in the inert-pair effect). For the moment, for simplicity, we take the d-electron hole as unity. Regarding the Pt as square-planar (three CO groups and the Pt_2 unit forming the square plane) then simple crystal field theory places the hole in the $d_{x^2-y^2}$ orbital. The electron is therefore in an $E_{1/2}$ orbital of the C_{2v}^* group, that shown earlier. Now, because electrons in Pt-CO bonding orbitals spend part of their time on the CO ligands, where relativistic effects are small, the consequences of relativistic effects will be most important for the Pt-Pt bonding. The symmetry of the $\text{Pt}_3(\text{CO})_6$ unit is D_{3h} and so we work in the D_{3h}^* (double) group. It is a simple matter to show that the $E_{1/2}$ functions of C_{2v}^* form a basis for the $E_{1/2} + E_{3/2} + E_{5/2}$ irreducible representations of D_{3h}^* . We do not know the relative ordering of these levels; it depends on the relative importance of spin-orbit coupling and bonding (although, in the event, our conclusions will depend only on the relative position of $E_{3/2}$ and this probably does not depend on the winner). Let us take bonding to be the winner, so that the (node-dependent) energy sequence is that given above. If the first two spin-orbitals are filled then the d-orbital hole is 0.667 electrons, not too far from the result of calculations [1] on Pt_3 . A double-group picture of the $E_{3/2}$ functions is given in Fig. 3. To get the electron density associated with these functions we simply have to square them, whereupon the phase pattern which forced the use of a rotation of

720° as the identity changes to one compatible with the real-world identification of 360° as identity. Occupancy of $E_{3/2}$ as the HOMO corresponds to bumps of high electron density by every 60°, so that we would expect that if two $Pt_3(CO)_6$ units stack together, free from crystal environment constraints, that they would be rotated 30° relative to each other.

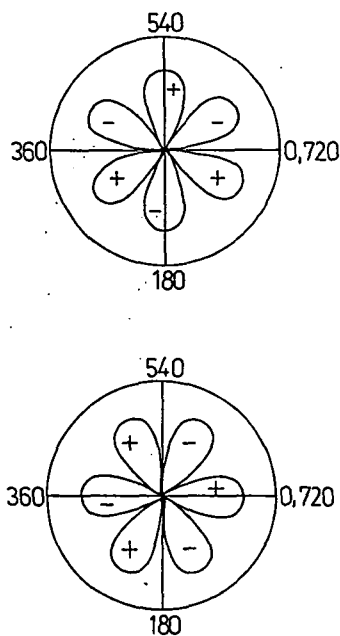


Figure 9: Double-group picture of the $E_{3/2}$ functions

It is therefore interesting to note [2] that the central $Pt_3(CO)_6$ unit in $[Pt_3(CO)_6]_2^{2-}$ is rotated relative to the adjacent units by 27.2° and 28.6°. Of course, this argument requires that the Pt-Pt bonding between adjacent layers is rather insensitive to the angle of rotation between them. The variability of this angle offers some evidence in support of such a speculation, as does the generally lower geometry-sensitivity of

relativistic orbitals: " $p_{1/2}$ is spherically symmetrical".

References

- [1] *Gavezzotti A., G. F. Tantardini, H. Miessner: J. Phys. Chem. 92, 872 (1988).*
- [2] *Calabrese, J. C., L. F. Dahl, P. Chini, G. Longoni, S. Martinengo: J. Am. Chem. Soc. 96, 2616 (1974).*