Theor Chim Acta (1988) 74: 165–166

Theoretica Chimica Acta

Book review

Verkade J. G.: A pictorial approach to molecular bonding. Berlin Heidelberg New York Tokyo: Springer 1986. ix+282 pp., (ISBN 3-540-96271-9) DM 125.00

This nicely produced book is the fruit of a thorough pedagogic experiment started 1968, how to give undergraduate chemistry students a working base for understanding chemical bonding both in terms of localized and strongly delocalized orbitals. The major characteristics are the introduction of GO (generator orbitals) and the replacement of abstract group-theory by more obvious arguments. The emphasis on images fits well the revival of the frescos and stained-glass windows of medieval time in the modern trend of television and computer games.

The reader (born in a more reading society) may start with the Socratic question what orbitals are. They are certainly far more useful than one would have expected. The squared amplitude of the Hartree-Fock function in the groundstate Schrödinger wave-function is 0.99 for helium, 0.89 for beryllium and 0.93 for neon atoms, and is almost certainly varying between 0.7 and 0.3 for Z between 30(zinc) and 70(ytterbium). Nevertheless, the (S, L)-terms and J-levels of monatomic entities are exceedingly well described by classificatory electron configurations, using some (but not all) of the properties of Hartree-Fock nl-functions. As far as pictorial aspects go, the l angular nodes (cones counting for two nodes) of the one-electron functions written on real form are pleasantly underlined. In many-electron atoms, n is certainly not "principal" and hardly a "quantum number" except for $(n-l-1)$ radial nodes at positive, finite r. The repeated smallprint discriminating against the radial node at infinite r suggests that it is not a node at all, but rather guaranteeing the normalizability.

Coming to approximate orbitals in systems with two or more nuclei, there is a pervading sentiment that chemical bonding is determined by electrostatic nucleus–electron attraction, neglecting what the éminence grise Klaus Ruedenberg wrote on modified kinetic energy (e.g. in Reviews of Modern Physics 1962). In the book, "kinetic energy" mainly refers to the nuclei (p. 51) and electrons are only mentioned p.6 (standing waves) and p. 32 (the virial theorem preventing the implosion of atoms). The corollary is that orbitals containing two electrons mainly play the rôle of prefiguring a chemical bond rather than (as any remaining atomic spectroscopist would believe) constituting some kind of a niche able to accommodate at most 2 electrons, and in high symmetries forming collective manifolds of k orbitals (in spherical symmetry $k=2l+1$) having the same one-electron energy, and coexisting (in our three-dimensional space) to a large extent, in spite of their mutual orthogonality.

A great virtue of the book is that it does not make appeal to the variational principle (which almost exclusively is concerned with the 10 inner-most electrons for Z above 20). Comparing with the total binding energy E in atoms, the closed-shell effects (passing a noble gas) decreases from 0.002 E for $Z=18$ (argon) to a few times $10^{-5}E$ for $Z=86$ (radon). The typical dissociation energies (of a compound to gaseous atoms) are ten times smaller (per atom) than these closed-shell effects. This means that even the intra-atomic correlation energy for $Z=10$ to 80 increases from roughly 3 to 50 times the average atomization energies per atom. Hence, we *have* to construct a clear picture of the valence-shells (as also done in pseudo-potential theories) if quantum chemistry has any relevance to trans-neon chemists, and the book presents indeed a plausible and viable set of ideas.

The subject is almost exclusively diamagnetic molecules (not typical inorganic solids) having two electrons firmly paired in each orbital (whatever an orbital is). The intermezzo p. 178 on d-group octahedral complexes is, obviously, not expected to include the rattling of the skeletons recently found by Katriel, Vanquickenborne et al. in the cupboard of parameters of interelectronic repulsion (messed up by the virial theorem) but the ingenue student should be warned that the statement p. 184 that "the more ionic the interaction [between d-group ions and ligands] is, the more the two Δ values [calculated from "ligand field" theory and from "crystal field" theory] will tend to agree" does not remove the surprising result that the major part of the energy difference Δ is connected with increasing kinetic energy of the anti-bonding d-like electrons, and that the contribution from the tiny non-spherical component of the (frequency quite strong) Madelung potential is numerically negligible.

The book might have concentrated on the valence shells and the atomization energies of molecules involving $N = 2$ through 14 nuclei. but it has one further laudable ambition: to rationalize the equilibrium geometries connected with energy differences, at least 10 times smaller than the closed-shell effects in atoms, which are again two or more orders of magnitude smaller than the total binding energies of Z electrons in atoms with two-digit Z values. Chemistry, in the strongest sense, is the variation of the $(3N-6)$ mutually independent internuclear distances for N at least 3 (accepting the Born-Oppenheimer factorization) on a $(3N-5)$ dimensional potential surface having absolute and relative minima corresponding to differing equilibrium geometries and different redistribution of the nuclei on the various species. One might fear that quantum chemistry is as hopeless as emptying the ocean with a spoon. However, there may be a paradoxical side of chemistry (due to its ancient history of fluctuating paradigms, and its inductive approach, as opposed to deductive physics) that it is much more able to treat the minor effects using correlative concepts, than the much larger energy differences fundamentally connected with the electric-field quasi-singularities established by the nuclei. As also pointed out by the book, the photo-electron spectra have provided reliable evidence for penultimate, delocalized molecular orbitals, and identified all orbitals of benzene, ethane, CF_4 and SF_6. A comprehensive treatment of normal modes of vibrations of the polyatomic molecules is also given. The present book contributes significantly to this enterprise of presenting the multifarious chemical bonding effects to the science undergraduate students as rationalized by valence-shell orbitals, and can certainly be recommended for this purpose.

C. K. Jørgensen, Geneva