Ab Initio Computation of the Ground-state Electronic Wavefunction for Bis-(π-allyl)nickel: a Revision

By A. VEILLARD

(*Institut de Chimie B.P.*296*R*8, 67-*Strasbourg, France*)

Summary The *ab initio* wavefunction previously reported for bis-(π-allyl)nickel has been revised.

IN my previous communication,[1] an *ab initio* wavefunction was reported for bis-(π-allyl)nickel. I subsequently found that a poor SCF process had led to an incorrect wavefunction. I now report a preliminary analysis from the revised wavefunction.

The computed total energy is $-1723{\cdot}396$ a.u. with the $4p$ functions included, lower than the value previously reported. The corresponding electronic configuration is $(11b_u)^2(13a_g)^2(7a_u)^2(6b_g)^2$. The energies of these four orbitals are (in a.u.) $-0{\cdot}52$ ($11b_u$), $-0{\cdot}50$($13a_g$), $-0{\cdot}36$ ($7a_u$), and $-0{\cdot}35$ ($6b_g$). The $13a_g$ orbital is a mixing of some σ-allyl orbitals with some $3d$ orbitals of the nickel atom. The $6b_g$, $7a_u$, and $11b_u$ orbitals are nearly pure π-orbitals of the allyl group. In this respect, our previous conclusion that orbitals built mainly from the $3d$ orbitals of the nickel atom are lower in energy than some ligand orbitals, is left unchanged. The value predicted for the ionization potential is 0·35 a.u., or 9·61 ev.

The Mulliken population analysis gives a total population of 26·08 for the nickel atom, 6·64 and 6·34 for the carbon atoms and varying from 0·78 to 0·92 for the hydrogen atoms, with the $4p$ functions deleted. The population of the $3d$ orbitals of the nickel atom is 8·20, the population of the $2p_z$ orbitals is 0·94 for C-2 and C-5 and 1·43 for the other carbon atoms. The overlap population is $-0{\cdot}06$ between the nickel atom and C-2 (or C-5) and $-0{\cdot}07$ between the nickel atom and the other carbon atoms. Not too much significance should be attached to these small negative values.

(*Received, October 20th*, 1969; *Com.* 1596.)

---

[1] A. Veillard, *Chem. Comm.*, 1969, 1022.