Ab-initio Computation of the Ground-state Electronic Wavefunction for Bis-(π-allyl)nickel

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Summary Calculation of an *ab-initio* wavefunction for the ground state of bis-(π-allyl)nickel indicates that most of the bonding between the nickel atom and the ligands involves the 4*s*- and 4*p*-orbitals of the metal.

INNUMERABLE studies have been devoted in the last ten years to the electronic structure of transition metal complexes. They resort to semi-empirical methods like for instance the Wolfsberg–Helmholz method[1] or the Extended Hückel method.[2] Several of the approximations involved in this kind of calculations for large electronic systems can be questioned.

I report here a preliminary analysis on a computation for the ground state wavefunction of bis-(π-allyl)nickel, $Ni(C_3H_5)_2$. The customary set of approximations in computing wavefunctions for this kind of molecule has been abandoned; all the electrons are explicitly considered and the standard assumptions or use of empirical parameters or approximations in computing many-centre integrals have been rejected. The basis set consists of 166 Gaussian functions, with orbital exponents optimized for the ground states of the nickel, carbon, and hydrogen atoms. The procedure used for this optimization has been previously described.[3] This Gaussian basis set is built from a 10*s*, 6*p*, 3*d* atomic set for the Ni atoms, from a 6*s*, 3*p* atomic set for the C atoms and from a 3*s* for the H atoms. These 166 Gaussian functions are then reduced to 69 contracted Gaussians,[4] namely a 5*s*, 4*p*, 2*d* set for the Ni atom (minimal basis set except for the 3*d*, 4*s* and 4*p* orbitals which use split functions), a 2*s*, 1*p* set for the C atoms and a 1*s* set for the H atoms. These are then combined in symmetry-adapted functions of the C_{2h} symmetry group.

The computation used the general program IBMOL.[4,5] Two calculations were carried out, without and with $4p$ functions on the Ni atom.

TABLE. *Orbital energies for bis-(π-allyl)nickel (in a.u.)*

A_g	B_g	A_u	B_u
− 0·08	− 0·56	− 0·35	− 0·49
− 0·52	− 0·66	− 0·59	− 0·56
− 0·55	− 0·72	− 0·65	− 0·71
− 0·67	− 0·99	− 0·99	− 0·80
− 0·72	−11·36	− 3·30	− 1·15
− 0·77		−11·36	− 3·28
− 0·83		−30·86	− 3·30
− 0·85			−11·25
− 1·17			−11·36
− 4·81			−30·83
− 11·25			−30·86
− 11·36			
− 36·63			
−302·94			

The geometry used is the experimental one.[7] The z-axis was taken perpendicular to the planes of the allyl groups.

The computed total energy is −1722·888 a.u. with the $4p$ functions included. The orbital energies (in a.u.) for the occupied orbitals are reported in the Table, together with their irreductible representation. I shall analyse briefly the main features of the wavefunction. Orbitals $1a_g$, $2a_g$, $1a_u$, $1b_u$, $2b_u$, $5a_g$, $3a_u$, $5b_u$, and $6b_u$ are inner-shell orbitals of the Ni atom. Orbitals $3a_g$, $4a_g$, $1b_g$, $2a_u$, $3b_u$, and $4b_u$ are inner-shell orbitals of the C atoms. Orbitals $6a_g$, $7b_u$, $4a_u$, $2b_g$, $8b_u$, $9b_u$, $4b_g$, $5a_u$, $6a_u$, $5b_g$, $10b_u$, $12a_g$, $13a_g$, $11b_u$, and $7a_u$ are ligand orbitals nearly unchanged (I performed a separate calculation for the allyl radical). Orbitals $7a_g$, $8a_g$, $9a_g$, $10a_g$, and $3b_g$ are mainly $3d$-orbitals of the Ni atom with some mixing of ligand orbitals. Similarly, the $11a_g$ orbital is mainly an allyl orbital with some participation of the $3d$-orbitals. Last, the $14a_g$ orbital is built from the π-orbitals of the allyl group, with some admixture of the $4s$-orbital of the Ni atom. One noticeable feature in this picture of the molecular orbitals is that orbitals built mainly from the $3d$-orbitals of the Ni atom are deeply embedded in the ligand orbitals. One will also notice the low value predicted by Koopman's theorem[6] for the ionization potential of $Ni(C_3H_5)_2$, 0·080 a.u. = 2·18 ev. Although the Hartree–Fock method in conjunction with Koopman's theorem gives relatively accurate values of the ionization potential,[8] it is hard to tell how reliable is the above value, because of the limitations in the basis set.

A Mulliken population analysis[7] was carried out. The total population is found to be 25·97 for the Ni atom, 6·51 for each carbon atom and varies from 0·84 to 0·95 for the various hydrogen atoms. The formal charge for the Ni atom is then +2·03, very close to the one for the ion Ni^{2+}. According to this charge distribution, the complex seems better viewed as an association between a Ni^{II} ion and two allyl anions. The orbital populations are 0·44 for the $4s$-orbital of the Ni atom and 7·81 for the $3d$-orbitals. The population of the $2p_z$-orbitals of the C-2 and C-5 atoms (middle carbon atoms of each allyl group) is 1·46. This accumulation can be traced to the orbital $14a_g$. The population analysis indicates for this orbital a distribution of 0·48 e on the $4s$ orbital of the Ni atom and 0·55 e on the $2p_z$ orbitals of the C-2 and C-5 atoms. Most of the bonding between the metal and the ligands involves this $14a_g$ orbital. The total overlap population between the Ni atom and the C-2 (or C-5) atoms is 0·866, out of which the $14a_g$ orbital contributes an overlap population of 0·660 (for comparison the total overlap population for a C–C bond is found equal to 0·898). When the $4p$-orbitals on the Ni atom are deleted from the calculation, the corresponding values are 0·678 for the total overlap population and 0·638 for the contribution of the $14a_g$ orbital. Since the $4s$ orbital is the only orbital of the Ni atom which participates to the $14a_g$ orbital, most of the bonding between the metal and the ligand is ensured through the $4s$-orbital. Moreover, the next important contribution to this bonding does not come from the $3d$-orbitals but from the $4p$-orbitals of the metal.

Finally, a separate atomic calculation was carried out for the Ni atom. Examination of the $3d$-orbitals in the free atom and in the molecular complex shows no significant contraction or expansion for these orbitals.

Calculations were performed on the IBM 360/75 computer at the Centre de Calcul du CRNS, Orsay. I thank the staff of the Computation Centre.

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