# Broken Symmetry in an Organometallic: the Ground State of Bis($\eta^3$-allyl)nickel

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The first SCFMO calculation which shows the ground-state singlet electronic structure of a molecule at its equilibrium molecular geometry to exhibit 'broken spin symmetry' is reported; the molecule has different orbitals for different spins.

The electronic structure of the bis($\eta^3$-allyl)nickel molecule has been the subject of considerable theoretical and computational interest over the past few years with claims and counter-claims that its SCFMO orbital energies do or do not obey Koopmans' theorem. (Is it a 'non-Koopmans' molecule?)[1]

The molecule is nominally a closed-shell singlet and all the SCFMO calculations reported have been carried out using the appropriate SCF approximation to the restricted Hartree–Fock (RHF) scheme: closed shell for the molecule to obtain 'Koopmans ionisation energies' and open shell for the daughter ions to obtain ΔSCF energies. Now the nickel *atom* is what one might term a 'non-Koopmans atom,' in that the ground state ($3d^84s^2$) ionises to an ion with configuration $3d^9$. The excited states from the configuration $3d^74s^2$ are not observed so that the experimental 3d ionisation potential is not known. Thus, an RHF calculation on the electronic structure of the atom yields orbital energies not relevant to the atom's observed ionisation potentials; the orbitals may be stationary for the ion but very far from optimum. The allyl radical is a well-known case of the breakdown of the RHF model.[2] The equilibrium geometry of the radical is predicted to be asymmetrical by the RHF method but the UHF method generates a qualitatively and quantitatively correct symmetrical structure.

Since the RHF model gives an inadequate description of the electronic structure of both components of the bis($\eta^3$-allyl)-nickel molecule it is not *a priori* unreasonable to assume that the SCF approximation to the RHF model of the electronic structure of the molecule itself may be at least suspect. In the context of the calculation of orbital energies it is noteworthy that, if the constrained SCF calculations do not reach a minimum in the energy surface (and they may not even reach a turning point), then the 'orbital energies' produced by such a calculation are quite useless in any comparison with experiment; in particular, Koopmans' theorem does not apply to them.

**Table 1.** Highest orbital energies.[a]

| RHF | UHF $\alpha$ | UHF $\beta$ |
|---|---|---|
| $-0.300443$ $a_u$ $\sigma(L)$ | $-0.240694$ $a_u$ $\sigma(L)$ | $-0.322283$ $b_g$ $\pi(L)$ |
| $-0.340315$ $b_g$ $\pi(L)$; 3d | $-0.406395$ $b_u$ $\sigma(L)$ | $-0.341544$ $a_u$ $\sigma(L)$; 3d |
| $-0.417405$ $b_u$ $\sigma(L)$ | $-0.436154$ $a_g$ 4s, 3d | $-0.418929$ $a_g$ 3d,4s |
| $-0.461472$ $a_g$ L; 3d,4s | $-0.448546$ $b_g$ $\pi(L)$; 3d | $-0.425327$ $b_u$ $\sigma(L)$ |
| $-0.481751$ $a_g$ L; 3d | $-0.474397$ $a_g$ $\sigma(L)$; 3d | $-0.436192$ $a_g$ 3d |
| $-0.509465$ $a_g$ 3d | $-0.477275$ $a_g$ 3d | $-0.460877$ $b_g$ 3d |

[a] The ordering of the RHF orbital energies follows that of ref. 1 closely; the main differences being some changes in the ligand σ and π contributions as might be expected from the different geometry used here.

We carried out UHF (*i.e.* completely unconstrained SCFMO) calculations on the lowest state of the electronic structure of the molecule and closed shell RHF calculations for comparison. The geometry of the molecule was taken from the crystallographic database (CSSR) held on-line at the S.E.R.C. Daresbury Laboratory and 'idealised' by making the molecule have strict $C_{2h}$ symmetry. This molecular geometry is different from that described in ref. 1 in that it is taken from the neutron diffraction study[7] of bis($\eta^3$-allyl) nickel itself, not the methyl derivative, and has slightly non-planar allyl fragments which will blur the $\sigma/\pi$ classification of the allyl M.O.s. The Gaussian basis functions were taken from a standard compilation.[3] The calculations were carried out using CADPAC[4] on the ULCC Cray and ATMOL[5] using the UMRCC Cyber 205.

By utilising different level shifters for $\alpha$ and $\beta$ molecular orbitals we have been able to obtain a solution of the UHF equations of the DODS type with an energy lower than the lowest RHF solution of closed shell type. The total energy of the DODS solution is $-1737.98652245$ while that of the closed shell RHF solution is $-1737.98102282$. The highest few orbital energies for each solution are given in Table 1. For the moment we simply report these results as the first example of the calculation of the electronic structure of a *closed shell singlet molecule at its equilibrium nuclear configuration* to show a spontaneous spin disproportionation of the type familiar in the dissociation of closed shell molecules to radical fragments ($H_2$ at large R is the classic case).

There are just two possible explanations: (i) that the SCFMO approximation or the Hartree–Fock method itself has broken down and the DODS result is an artifact of this breakdown; or (ii) that the result is a meaningful one and the electronic structure generated by the UHF method contains new insights into the electronic structure of bis($\eta^3$-allyl)nickel and (presumably) molecules of similar electronic structure.

It has been our experience over the past several years that in all cases of spontaneous symmetry-breaking in the HF model (spatial or spin) there are genuine physical reasons for the phenomenon; none of the results are artifacts of the model.[6] It must also be said that if the SCFMO approximation has broken down, *i.e.* (i) pertains, then this has catastrophic consequences for theories of the electronic structure of organometallic compounds; for, if there are no UHF solutions, then there certainly are no RHF solutions to the SCFMO equations.

We are therefore about to perform a detailed analysis of this and similar DODS solutions, their orbital energies, orbitals, spin densities, *etc.* It is of some initial interest to report that the spatial symmetry of the orbitals is that of the molecule. The mean value of $\hat{S}^2$ is 0.523 (the function is an eigenfunction of $\hat{S}_z$ with eigenvalue zero). We have not yet analysed the wavefunction into pure spin states but if we make the usual assumption that the principal components are singlet and triplet then the function is *ca.* 0.85 singlet plus 0.5 triplet, presumably indicating the existence of a low-lying triplet state.

With hindsight, it is perhaps not so surprising that the molecule shows some of the features of an organic molecule undergoing dissociation: it is a very large molecule in the sense that bonded atoms are a large distance apart by the standards of organic chemistry and the field of force holding the electrons in these regions is rather weak. The distance between some next-nearest neighbours are huge by the same standard, *e.g.* the C–Ni–C distance is *ca.* 4 Å.

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## References

1 D. Moncrieff, I. H. Hillier, V. R. Saunders, and W. von Niessen, *J. Chem. Soc., Chem. Commun.*, 1985, 300, and references cited therein.

2 D. B. Cook, *J. Chem. Soc., Faraday Trans.*, 1986, **82**, 187, and references cited therein.

3 R. Poirier, R. Kari, and I. G. Csizmadia, 'Handbook of Gaussian Basis Sets,' Elsevier, 1985, Ni Table 28.9.3 (12/6/5 contracted to 8/4/3); C and H, 321G.

4 R. D. Amos, 'Cambridge Analytical Derivatives Package,' Issue 3.0.

5 D. Moncrieff and V. R. Saunders, ATMOL, UMRCC NAT 648.

6 See ref. (2) and D. B. Cook, *Int. J. Theoret. Chem.*, 1987, XXXI, 251.

7 R. Goddard, C. Krüger, F. Mark, R. Stansfield, and X. Zhang, *Organometallics*, 1985, **4**, 285.