On the Bonding to Transition Metal Atoms in Low Oxidation States

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Ab initio spin-coupled calculations have been carried out on MH and MH$^+$ species to investigate the electronic structure of systems containing transition metal atoms in low oxidation states; results are presented for VH, where the bonding can be understood in terms of the overlap between a 'bonding hybrid' on vanadium and a distorted 1s function on hydrogen.

Progress in characterizing and understanding the bonding to transition metal atoms in low oxidation states has been very slow. This is true even for small molecules containing just one or two transition metal atoms. Such systems present problems for any theoretical method because of subtle electron correlation effects. In addition there is competition between the strong d–d coupling in the separated atoms, and the process of bond formation, which necessitates the breakdown of at least some of this coupling.

We are in the process of applying spin-coupled theory to this general problem, and present here our preliminary findings for the ground state of VH. Although this diatomic molecule is very small by the usual standards of inorganic chemistry, it is already sufficiently complex to exhibit a number of the general features which we have observed so far. The spin-coupled wavefunction[1] is based on an orbital picture with one orbital for each *correlated* electron, and it has no double-occupancy or orthogonality requirements of any kind. The orbitals $\phi_\mu(r_\mu)$ are fully optimized in the form of linear combinations of basis functions on all of the atomic centres, so that they are not constrained to be localized around particular nuclei. Their form is a unique outcome of the variational procedure.

An important consequence of the fact that all the non-orthogonal orbitals are singly occupied is that there are almost always several modes of spin coupling. It is particularly important in transition metal systems to utilize a complete set of spin functions, $\Theta^N_{SM;k}$, especially if we wish to describe correctly the dissociation limits. The spin-coupled wavefunction for a system of N electrons with total spin S takes the form in equation (1). As the internuclear separation increases, a complicated reorganization of the electron spin coupling takes place, in which pairings characteristic of the molecule give way to couplings associated with the alignment of the d electrons in the isolated transition metal atom. This can only be described properly by a linear combination of a full set of N-electron spin functions, as in this wavefunction. The wavefunction can be improved subsequently in a non-orthogonal CI ('spin-coupled valence bond' calculation) but this does not change the essential physical picture.

$$\Psi_{SM} = \sum_k c_{Sk} \mathcal{A} [\phi_1(r_1)\phi_2(r_2) \ldots \phi_N(r_N)\, \Theta^N_{SM;k}] \qquad (1)$$

Calculations on transition metal systems such as VH ($^5\Delta$) have been carried out with basis sets of approximately triple-zeta quality.[2] Spin-coupled theory has been used explicitly for the six valence electrons, with the 'core' electrons described by the natural orbitals from a suitable multiconfiguration SCF wavefunction. More sophisticated calculations will need to take into account the effects of core-valence correlation.

The spin-coupled orbitals for VH ($^5\Delta$) are presented in Figure 1 for (a) large R (8 bohr), (b) intermediate R (5 bohr), and (c) $R \approx R_e$ (3.263 bohr). At large R we observe a $4s^23d^3$ configuration on vanadium and a 1s orbital on hydrogen. As the atoms are brought together, the H(1s) orbital (ϕ_2) distorts slightly towards vanadium. More marked changes occur in the two essentially 4s orbitals on the transition metal centre. One of them, ϕ_1, distorts towards hydrogen and appears to take on substantial d_{z^2} character. The other, ϕ_6, remains essentially the same shape but starts to point away from hydrogen. The remaining orbitals on vanadium change remarkably little. At still shorter R, ϕ_1 and ϕ_6 take on characteristic forms to which we refer as 'the bonding hybrid' and 'the non-bonding hybrid', respectively. The bonding is linked to the high overlap of orbitals ϕ_1 and ϕ_2, which is a distorted H(1s) orbital, and to the singlet coupling of the associated spins. The remaining electrons on vanadium have their spins coupled to the highest possible value.

As the atoms are brought together there is a rapid change in the spin-coupling coefficients c_{Sk} from values characteristic of separated atoms to values characteristic of the formation of a new covalent bond. The most dramatic changes occur between

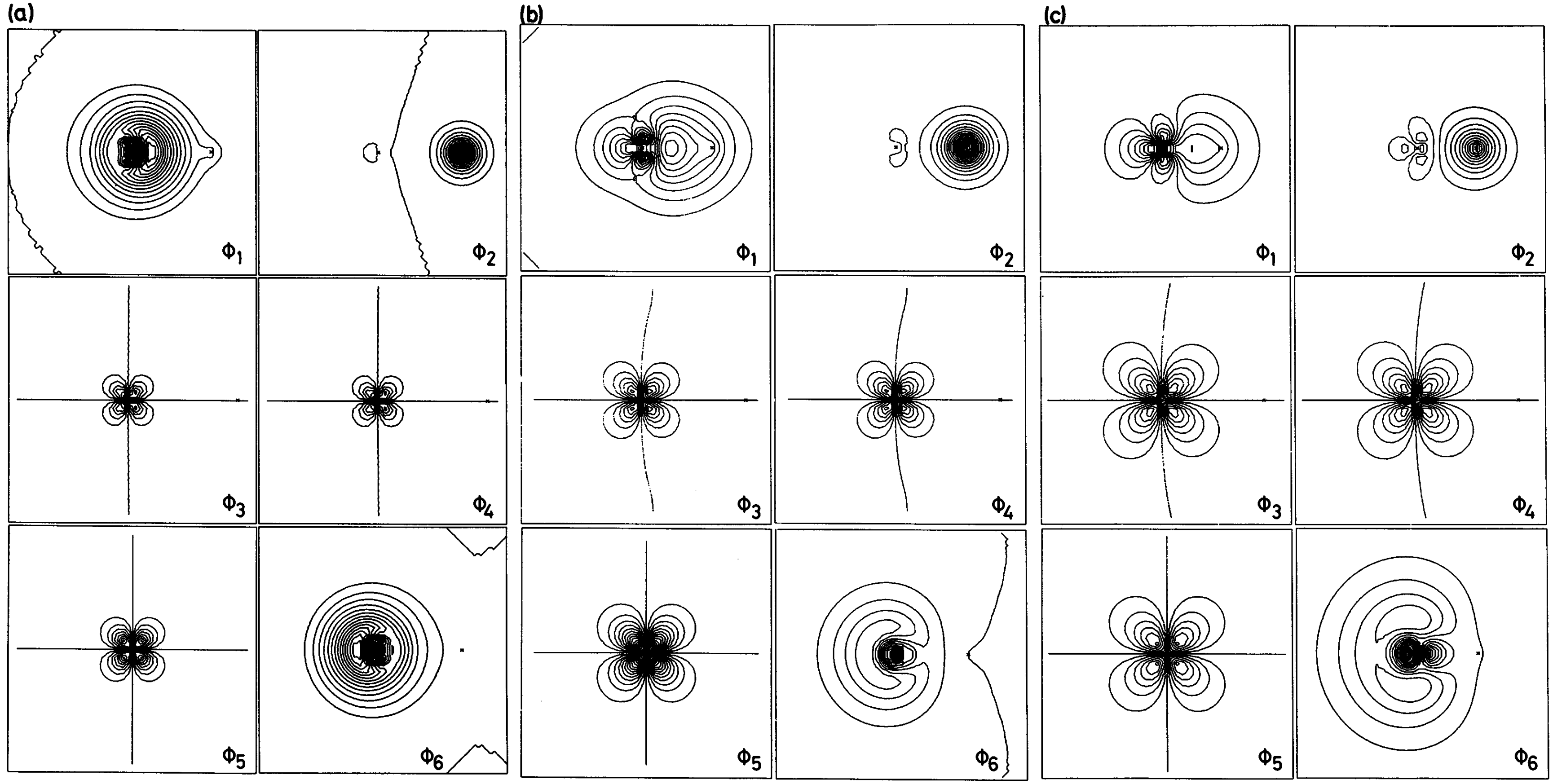

Figure 1. Contour plots of the spin-coupled orbitals $\phi_\mu(r)$ for VH ($^5\Delta$); (a) large R, (b) intermediate R, and (c) $R \approx R_e$. The co-ordinates of the nuclei are $z = 0$ for V and $z = R$ for H, with the z axis pointing from left to right across the page except for ϕ_5, which is plotted in the plane $z = 0$.

8 and 6 bohr, so that the mode of spin coupling at 5 bohr already corresponds to the molecular regime.

We have found that the spin-coupled description of the ground state of the VH^+ ion ($^4\Delta$) closely resembles that for the neutral VH ($^5\Delta$) system, except for the absence of the non-bonding hybrid. Analogous calculations have been carried out for the ground and low-lying excited states of MH and MH^+ for M=Sc–Cr and Y–Mo over the complete range of R from less than R_e to dissociation. Pictures similar to those for VH (and VH^+) emerge in each case. We have found that it is possible to formulate simple rules, based on the availability of empty d_{z^2} orbitals at large R, to rationalize the ordering of electronic states in these systems. Our results so far for the MH and MH^+ diatomics compare favourably with the sophisticated MCPF-based calculations of Langhoff and co-workers.[3] In each case, our calculated states dissociate correctly, give good values of R_e, and are ordered correctly. We are in the process of comparing the MCPF-based[3a] and spin-coupled dipole moments.

The spin-coupled description of the behaviour of correlated electrons in these systems is a unique outcome of the energy minimization process. The orbital pictures for high- and low-spin transition metal systems turns out to be very similar, and this gives us confidence that analogous descriptions will apply to a wide range of more complex molecules with metal–metal bonding, and with carbonyl, alkene, and phosphine ligands. Calculations are now in progress for such systems. From preliminary results, we have reason to believe that the mode of spin-coupling for M–M systems will be particularly novel.

More detailed accounts of all this work will appear in due course. We believe that the orbital picture provided by spin-coupled theory represents significant progress towards understanding the nature of the bonding to transition metal atoms in low oxidation states.

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References

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