AB INITIO CALCULATION OF ELECTRONIC TRANSITIONS IN TRANSITION METAL COMPLEXES

Helge Johansen
Chemical Physics, Chemistry Department B
The Technical University of Denmark, DTH 301
DK-2800 Lyngby
Denmark

ABSTRACT. d-d transitions and charge transfer transitions in transition metal complexes are discussed in terms of selected examples. The theoretical methods comprise restricted Hartree-Fock, configuration interaction, and multiconfigurational self-consistent-field calculations. Their results are compared with experimental spectra. The systems considered are NiF$_6^{2-}$, CoO$_6^{10-}$, CuF$_6^{2-}$, CoC$_4^{2-}$, VO(H$_2$O)$_5^{2+}$ and MnO$_4^{-}$. A great deal of attention is paid to the influence of the Madelung potential from the crystals in which the ions are imbedded. The significance of this potential turns out to be less important than expected. The calculated transition energies are mostly in good agreement with the experimental values, but configuration interaction has to be invoked in order to give reliable results, and the configuration space has to be large enough to accommodate both electron correlation and relaxation.

1. INTRODUCTION

The present contribution is discussing electronic transitions in transition metal complexes on the basis of a selection of theoretical studies, each of which considers one particular molecular ion. The main part of the work has been done in our laboratory, and the selection of methods and systems is, therefore, far from arbitrary and unbiased. MS Xa calculations, Hartree-Fock-Slater calculations and pseudo-potential methods will thus not be discussed, even though much work of high quality exists.

The "ab initio" label by no means ensures the quality of a calculation, but only that for a particular all electron Hamiltonian, the energy of a system has been minimized with respect to a particular all electron type wave function in a mathematically correct way. The procedure is, therefore, just as dependent on the selection of Hamiltonian and the representation of the wave function as most other methods. In particular the choice of atomic basis functions and the choice of configuration space are critical. Since the transition metal atoms invariably have many electrons and usually require four to six ligands to
saturate their coordination sphere, calculations on these systems tend to be very large. The basis set selection is therefore usually a compromise which involves computer availability and funding more than accuracy. History has in this respect reduced once mighty calculations to desk top exercises.

Another choice which has to be made is the extent of the system to be considered. How small a unit may be treated without losing accuracy? This is a particularly crucial question when studying surfaces and solids.

It should be mentioned that a good outline of ab initio calculations before 1977 on transition metal compounds has been given by Veillard and Demuynck [1]. The present paper will consist of four main sections: The calculational framework, the external field, d-d transitions and charge transfer transitions.

2. CALCULATIONAL FRAMEWORK

The aim of the calculations is to solve the stationary Schrödinger equation in an orbital based formalism. The building blocks are usually cartesian Gaussians of the form

$$\chi = A \times y^m e^{-\zeta r^2}$$  \hspace{1cm} (1)

where $A$ is a normalization constant, $\zeta$ an orbital exponent, and $k$, $\lambda$ and $m$ small integers, which control the form of the angular part. From these, the molecular orbitals are constructed as linear combinations

$$\phi_i = \sum_{p=1}^{L} C_{i p} \chi_p , \hspace{1cm} i = 1, 2, \ldots L$$  \hspace{1cm} (2)

where the matrix $C$ contains the expansion coefficients and $L$ is the length of the expansions. Between expressions (1) and (2) there will usually be two further layers. In the first one the primitive Gaussians $\chi$ will be "contracted", which is a process where from two to six functions are grouped together with fixed coefficients (thereby reducing $L$), and in the second the functions are symmetry adapted according to the space group of the system. Spin orbitals, $\psi$, are formed by supplying the $\phi$'s with $\alpha$ or $\beta$ spin, and from these again determinantal N electron functions are built.

$$\Xi = |\psi_1 \psi_2 \ldots \psi_N|$$  \hspace{1cm} (3)

From the determinants we construct configuration state functions, $\Psi$, which have the proper space and spin symmetry for the state under consideration. Finally, we may construct total N electron wave functions as linear combinations of these so-called CSFs,

$$\Psi = \sum_{p=1}^{M} D_{i p} \phi_p$$  \hspace{1cm} (4)