

Molecular Orbital Studies of the Series $[M^{II}(H_2O)_6]^{2+}$ ($M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu$) by the Iterative Extended Hückel Method

N. J. FITZPATRICK and M. A. MCGINN

Department of Chemistry, University College, Belfield, Dublin 4, Ireland

Received March 15, 1984

*Self-Consistent Charge and Configuration (SCCC) calculations are reported for $[M(H_2O)_6]^{2+}$ ($M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu$). The computed energy levels agree with those reported in *ab initio* studies. Trends in the calculated orbital and overlap populations and charges agree with experimental data.*

Introduction

The aquo complexes of the transition metals are important species in coordination chemistry. Any transition metal ion dissolved in water exists as a complex of this type. Therefore, the process of forming a coordination complex is actually one of replacing the bound water molecules by other ligands. It is thus desirable to understand the structures and stabilities of such systems.

Several theoretical investigations of the electronic structures of metal cation–water complexes have been published, spanning a range of sophistication from the semi-empirical [1–7] and semi-quantitative [8, 9], to the *ab initio* [10–23]. Most of these studies consider complexes of the alkali and alkaline-earth metal cations, and attempt to explain experimentally observed solvation energies, solvent-shell radii, etc. [4–7, 10–20].

Originally, *ab initio* calculations on such systems were confined to consideration of hypothetical complexes containing only one or two solvent molecules. Semi-empirical techniques were able to consider more realistic numbers of ligands, but with a corresponding decrease in accuracy. Recently, however, the increased availability of very powerful digital computers has made *ab initio* work on larger systems feasible.

By comparison, studies of transition metal hydrates are far less numerous [1–3, 8, 9, 21–23]. Such calculations were originally confined exclusively to the semi-empirical level, but recently several *ab initio* investigations have appeared. These latter should be viewed with caution, however, as no Madelung potential correction (to account for the interaction of the electrons in the complex with the electrostatic field set up by the highly charged metal

atom) was included. Unfortunately, no *ab initio* study of a series of the complexes has been published, and inconsistencies in the choice of basis sets, core potentials and convergence procedures make comparison of the existing calculations difficult. In addition, previous extended Hückel calculations on the complexes were not iterative, and hence no self consistent charges or configurations were obtained, neither was a Madelung correction term used.

We have therefore performed extended Hückel calculations of the Self-Consistent Charge and Configuration (SCCC) type on the series $[M^{II}(H_2O)_6]^{2+}$ where M is a first row transition metal. The results are compared with those previously published, and with experimental trends. We have not carried out calculations for a range of complex geometries or coordination numbers, as the simple approach employed is probably unable to describe accurately the delicate balance which exists between the various possible structures. It should be remembered that all of the systems under investigation are of the open shell type (all are found experimentally to be high-spin) and consequently will not be wholly accurately represented by the single-configuration type wave function used by the SCCC method.

Computational and Structural Details

Very little structural information is available for the complexes, either in solution or in the solid state [24]. In the calculations reported here, the metal–oxygen framework corresponds to strict O_h symmetry, reduced to T_h by the arrangement of the hydrogen atoms of the ligands (T_d symmetry could also have been adopted, and may be obtained from the T_h arrangement by the appropriate 45° rotations of the water molecules about the axes of the $M-O$ bonds) (see Fig. 1). The metal oxygen bond length was fixed in all cases at 2.14 Å, the $O-H$ distance at 0.96 Å, and the $H-O-H$ angle at 104.5° . The water molecules are dipole rather than lone-pair directed. This geometry was adopted because it has been observed for several of the ions, trapped in crystal lattices [25–30]. In addition, comparison

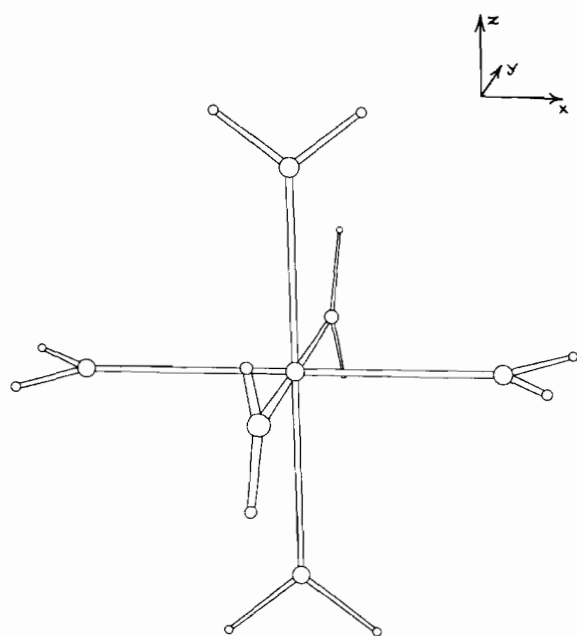


Fig. 1. Geometry of the $[M(H_2O)_6]^{2+}$ system.

with previous work is facilitated by this choice of geometry.

The calculations were performed using the FORTICON 8 program of Hoffmann *et al.* [31]. A Madelung potential correction term was included. A 'weighted' Wolfsberg-Helmholz parameterisation was used to calculate the off-diagonal elements [31]

of the coulomb matrix. Details of the basis set and semi-empirical parameters used are given in the next section. Calculations typically required 20–30 minutes of computing time, using an IBM 4331 computer with a VM/CMS operating system. Convergence of the total energy was achieved to thresholds from 0.01 to 0.00001 eV.

Choice of Basis Set and Semi-Empirical Parameters

The basis set for the metal consists of valence Slater-type 3d, 4s and 4p atomic orbitals. The radial functions calculated by Richardson *et al.* [32, 33] were chosen (double-zeta orbitals were used to represent the d-functions). For the ligand oxygen 2s and 2p orbitals the single-zeta Slater-type functions of Clementi and Raimondi were chosen [34]. A value of 1.300 [31] was used as the exponent for the hydrogen atom 1s orbitals.

Valence orbital ionization potentials (V.O.I.P.s) for nine configurations of the metal atom and two configurations of the oxygen atom were taken from the work of Basch, Viste and Gray [35] as approximations to the diagonal terms of the Coulomb matrix.

Results

Energy Levels and Molecular Orbitals

The computed energy levels and corresponding symmetry labels for each complex are given in Table I. The correlated free metal atomic orbitals

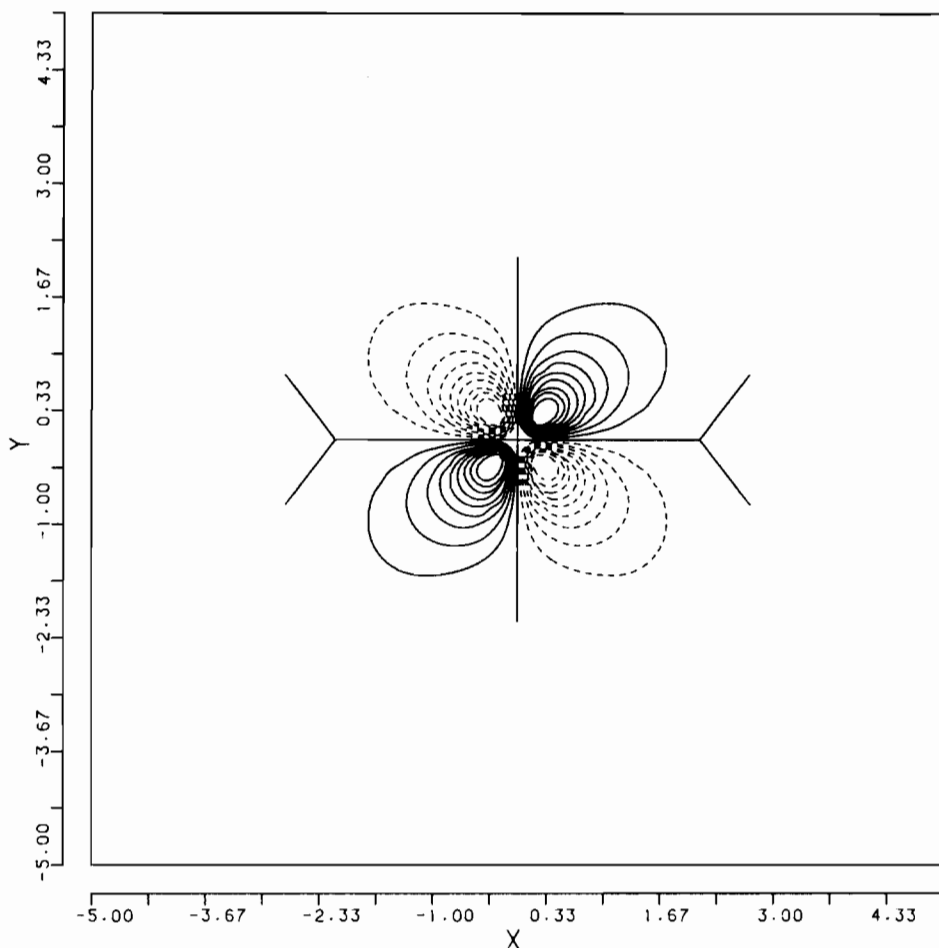
TABLE I. Computed Energy Levels of $[M^{II}(H_2O)_6]^{2+}$ (eV).

Level	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
7t _u (4p - 2a ₁)	5.29	4.62	4.68	4.66	4.60	4.47	4.30	3.91
4a _g (4s - 3a ₁)	3.75	4.18	3.94	3.58	3.22	2.74	2.28	1.72
4e _g (3d _{z², x²-y² - 3a₁)}	0.45	0.40	0.28	0.21	0.17	0.14	0.11	-0.01
6t _u (4p - 3a ₁)	-0.91	-0.94	-1.43	-1.75	-2.19	-2.76	-3.20	-3.83
3a _g (4s - 3a ₁)	-1.56	-1.83	-2.48	-3.24	-4.06	-5.01	-6.03	-7.34
4t _g (3d _{xy, xz, yz} - 2b ₂)	-9.75	-9.75	-9.76	-9.77	-9.78	-9.79	-9.79	-9.77
5t _u (4p - 2b ₂)	-9.89	-9.91	-9.89	-9.88	-9.86	-9.85	-9.83	-9.80
3e _g (3d _{z², x²-y² - 1a₁)}	-14.92	-16.61	-18.13	-19.41	-20.50	-21.72	-22.81	-23.57
3t _g (3d _{xy, xz, yz} - b ₁)	-18.19	-19.28	-20.29	-21.17	-21.97	-23.02	-23.92	-23.79
4t _u (4p - b ₁)	-22.96	-23.70	-23.89	-24.00	-24.11	-24.19	-24.34	-23.87
2t _g (3d _{xy, xz, yz} - b ₁)	-23.01	-23.76	-23.95	-24.07	-24.17	-24.29	-24.54	-25.09
3t _u (4p - 2a ₁)	-23.96	-24.87	-25.08	-25.21	-25.32	-25.41	-25.48	-25.53
2e _g (3d _{z², x²-y² - 2a₁)}	-24.42	-25.18	-25.38	-25.50	-25.61	-25.78	-26.00	-26.26
2a _g (4s - 2a ₁)	-24.40	-25.24	-25.48	-25.65	-25.81	-25.97	-26.11	-25.82
2t _u (4p - 1b ₂)	-26.30	-27.17	-27.38	-27.51	-27.63	-27.73	-27.81	-27.41
1t _g (3d _{xy, xz, yz} - 1b ₂)	-26.31	-27.18	-27.39	-27.52	-27.64	-27.74	-27.82	-27.43

(continued on facing page)

TABLE I. (continued)

Level	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$1e_g$ ($3d_{x^2-y^2, z^2} - 1a_1$)	-40.03	-41.04	-41.30	-41.47	-41.62	-41.73	-41.81	-41.42
$1t_u$ ($4p - 1a_1$)	-40.26	-41.23	-41.47	-41.63	-41.78	-41.88	-41.95	-41.54
$1a_g$ ($4s - 1a_1$)	-40.67	-41.28	-41.54	-41.72	-41.88	-42.00	-42.09	-41.72

Fig. 2. $3t_g$ Molecular Orbital of $[Fe(H_2O)_6]^{2+}$, showing predominantly metal contributions.

and ligand molecular orbitals are shown in brackets. The sequence of energy levels is similar for each complex, with only two changes in order.

The importance of the octahedral 'heavy atom' framework is clear. Descending in symmetry from O_h to the subgroup T_h , the following correlation between the irreducible representations exists: $A_{1g} \rightarrow A_g$, $A_{2g} \rightarrow A_g$, $E_g \rightarrow E_g$, $T_{1g} \rightarrow T_g$, $T_{2g} \rightarrow T_g$, $A_{1u} \rightarrow A_u$, $A_{2u} \rightarrow A_u$, $E_u \rightarrow E_u$, $T_{1u} \rightarrow T_u$ and $T_{2u} \rightarrow T_u$. The highest occupied molecular orbital (HOMO) of the complexes is therefore seen to be of a symmetry correlating with t_{2g} , while the lowest unoccupied MO (LUMO) correlates with e_g . Both

of these levels are predominantly metal in character (Figs. 2, 3), a result which agrees well with the Ligand Field and Crystal Field theories of octahedral complexes.

A complete energy level diagram for the iron complex is given in Fig. 4.

Comparison with the results of Jafri, Logan and Newton [23], who published a set of levels for this complex calculated by the *ab initio* method, shows exact agreement in the ordering, with the exception of the HOMO, which was found by the rigorous study (surprisingly) to be ligand dominated.

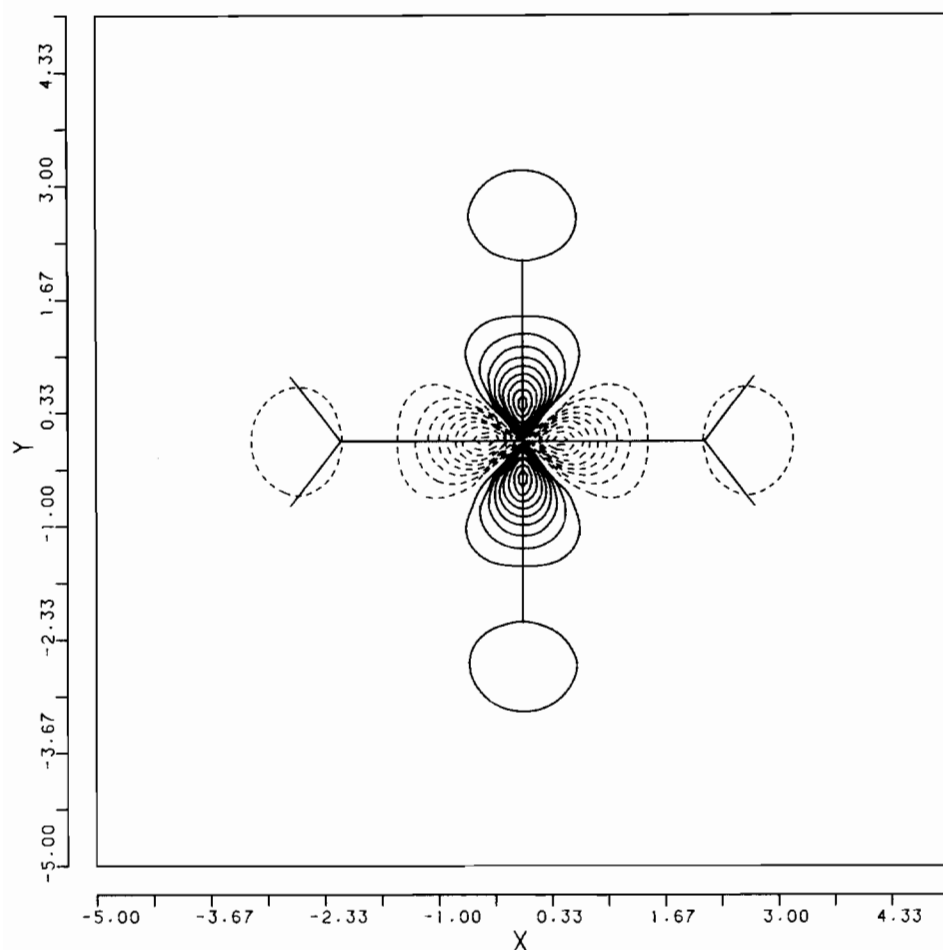


Fig. 3. $3e_g$ Molecular Orbital of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, showing predominantly metal contributions.

Several trends in the results are apparent. Firstly, the total energy of the complex becomes more negative across the series from titanium to copper, indicating an overall stabilisation of the ions. This mirrors a drop in energy of the HOMO along the row relative to the energy of the metal 3d level, which experimentally should render removal of an electron less favourable, and improve the stability of the complexes towards oxidation. This behaviour is in fact observed. Titanium(II) is not known in aqueous solution, spontaneous oxidation to titanium(III) being postulated. Chromium(II) aqueous solutions must be protected from air, iron(II) solutions decompose slowly, while nickel(II) and copper(II) solutions are stable [36].

Secondly, as the HOMO drops in energy relative to the metal d orbitals, it changes from slightly antibonding character to slightly bonding.

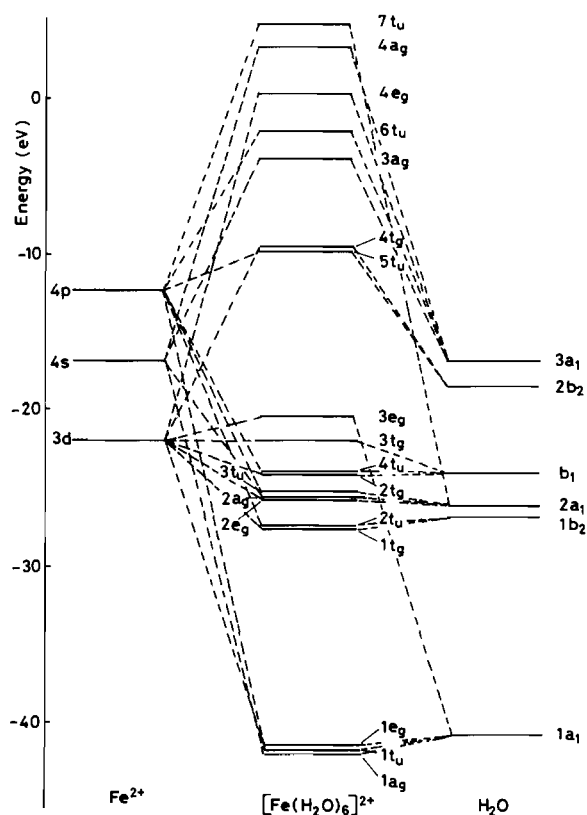
Finally, the ΔE (LUMO-HOMO) values decrease along the series, following the trend in the experimentally observed values [36, 37]. Contour diagrams of the MOs of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ cation are available on request to the authors.

Orbital Populations, Charges and Configurations

The calculated atomic orbital electronic populations of the metal and the free and coordinated ligand are summarised for each complex in Table II. The following points may be made concerning patterns of charge transfer within the complexes:

(1) Sigma-type donation occurs from the 2s orbitals of the oxygen atoms into the 4p and 3d metal orbitals.

(2) The principal charge transfer occurs within the ligands – that is the metal enhances the polarization. In fact, the total population on the oxygen atom is greater in the coordinated than in the uncoordinated ligand. The hydrogen atom 1s orbital populations decrease on complexation, indicating that the metal is drawing charge from the outer regions of the complex. The charges and configurations reflect this trend. Across the series from titanium to copper, the metal withdraws more charge from the ligands, paralleling the increase in electronegativity. However, this extra charge comes from the hydrogen atoms (Table III).

Fig. 4. Energy Level Diagram for $[Fe(H_2O)_6]^{2+}$.

The increase in positive charge on the hydrogen atoms is in fact experimentally observable by measurements of the equilibrium $[M(H_2O)_6]^{2+} \rightleftharpoons [M(H_2O)_5(OH)]^+ + H^+$ [36].

TABLE II. $[M^{II}(H_2O)_6]^{2+}$ Orbital Populations.

		Free Water	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
<i>Metal</i>										
4p			-0.39	-0.06	0.00	0.03	0.06	0.06	0.08	0.15
3d	e_g		0.56	0.56	0.60	0.66	0.72	1.70	2.67	3.62
	t_g		2.12	3.08	4.06	5.03	6.00	6.00	6.00	6.00
4s			0.09	0.11	0.13	0.16	0.18	0.21	0.24	0.29
			2.38	3.69	4.79	5.88	0.96	7.97	8.99	10.06
<i>Total Water</i>										
<i>Oxygen</i>										
σ	2s	1.810	1.61	1.59	1.58	1.58	1.58	1.58	1.58	1.58
	2p _x	1.235	1.59	1.58	1.57	1.56	1.54	1.54	1.50	1.51
π	2p _y	1.105	1.12	1.13	1.13	1.13	1.14	1.13	1.13	1.12
	2p _z	2.000	1.98	2.00	2.00	2.00	2.00	2.00	2.00	2.00
<i>Hydrogen</i>										
	1s	0.925	0.81	0.80	0.80	0.80	0.79	0.79	0.79	0.79
Total		8.000	7.92	7.90	7.88	7.87	7.84	7.83	7.79	7.79

It is found that the acidity of the water molecules increases on complexation.

Overlap Populations

The electron density in the M–O bonds may be estimated from the Mulliken overlap populations. These are decomposed into sigma and pi contributions in Table IV.

Ideally, the overlap populations should be correlated with the M–O bond stretching force constants, but these have not been measured. Nevertheless, several general points may be made.

The sigma populations undergo a net increase from one end of the series to the other. The principal contributors to this are the metal 4s-oxygen and metal 4p-oxygen sigma populations. Up to and including the iron complex, the largest single contributor is the M(3d)–O(σ) population.

The π contribution is always small, and is in fact negative, indicating that a π interaction is unfavourable. This unfavourable contribution decreases in magnitude across the series, which probably accounts for the drop in HOMO energy with respect to the metal 3d level.

Discussion and Conclusions

The calculations presented indicate the value of a semi-empirical approach in providing rationalisations of trends in the properties of closely related series of compounds.

The increase in stability of the complexes from titanium to copper, together with a decrease in the susceptibility to oxidation may be attributed to a

TABLE III. Calculated Atomic Charges.

	Free Ligand	$[M^{II}(H_2O)_6]^{2+}$							
		Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Metal		1.62	1.30	1.21	1.13	1.05	1.00	0.98	0.94
Oxygen	-0.20	-0.31	-0.28	-0.27	-0.26	-0.25	-0.25	-0.25	-0.24
Hydrogen	0.10	0.19	0.20	0.20	0.20	0.21	0.21	0.21	0.21

TABLE IV. $[M^{II}(H_2O)_6]^{2+}$ Overlap Populations.

Metal	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Metal 4s-O $_{\sigma}$	0.189	0.208	0.239	0.272	0.300	0.334	0.365	0.409
4p-O $_{\sigma}$	-0.565	0.025	0.095	0.130	0.162	0.212	0.245	0.296
4p-O $_{\pi}$	-0.079	-0.002	0.000	0.001	0.001	0.001	0.002	0.002
3d-O $_{\sigma}$	0.592	0.541	0.510	0.478	0.448	0.097	0.259	0.044
3d-O $_{\pi}$	0.082	-0.103	-0.090	-0.062	-0.043	-0.030	-0.021	-0.016
Total σ	0.216	0.774	0.844	0.880	0.910	0.643	0.869	0.749
Total π	0.003	-0.105	-0.090	-0.061	-0.042	-0.029	-0.019	-0.014
Total	0.219	0.669	0.794	0.819	0.868	0.614	0.850	0.735

drop in energy of the HOMO relative to the 3d orbitals of the uncomplexed metal. This in turn is caused by an improved bonding σ overlap between the metal and oxygen orbitals across the series, and a decrease in magnitude of the unfavourable π overlap population.

The metal atom increases the polarisation of the water molecules – pulling electrons from the hydrogen atoms in parallel with an increase in electronegativity in the metal, thus enhancing the ligand acidity.

The additional electrons entering the system, across the series, almost exclusively enter MOs dominated by d-orbital contributions, implying that there is no tendency for the metal to attempt to obtain a more stable half-filled d-configuration by directing electrons into other orbitals.

References

- 1 D. A. Zhogolev, B. Kh. Bunyatyan, V. B. Volkov and K. B. Yatsimirskii, *Chem. Phys. Lett.*, **29**, 506 (1974).
- 2 B. Roos, *Acta. Chem. Scand.*, **20**, 1673 (1966).
- 3 A. M. Chmelnick and D. Fiat, *J. Magnet. Res.*, **7**, 418 (1972).
- 4 D. A. Zhogolev, B. Kh. Bunyatyan and Y. A. Krugylak, *Chem. Phys. Lett.*, **18**, 135 (1973).
- 5 H. Lischka, T. Plessner and P. Schuster, *Theor. Chim. Acta*, **16**, 263 (1970).
- 6 P. Russeger, H. Lischka and P. Schuster, *Theor. Chim. Acta*, **24**, 191 (1972).
- 7 D. W. Clack and M. S. Farrimond, *J. Chem. Soc., Dalton Trans.*, **1**, 29 (1972).
- 8 D. W. Clack and M. S. Farrimond, *J. Chem. Soc., A*, 299 (1971).
- 9 E. Kai and K. Nishimoto, *Int. J. Quant. Chem.*, **18**, 403 (1980).
- 10 G. H. F. Diercksen and W. P. Kraemer, *Theor. Chim. Acta*, **23**, 387 (1971).
- 11 G. H. F. Diercksen and W. P. Kraemer, *Theor. Chim. Acta*, **23**, 393 (1971).
- 12 E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 1077 (1972).
- 13 H. Kistenmacher, H. Popkie and E. Clementi, *J. Chem. Phys.*, **58**, 1689 (1973).
- 14 P. Schuster and H. W. Preuss, *Chem. Phys. Lett.*, **11**, 35 (1971).
- 15 P. Russeger and P. Schuster, *Chem. Phys. Lett.*, **19**, 254 (1973).
- 16 B. Rode, *Chem. Phys. Lett.*, **26**, 350 (1974).
- 17 A. Pullman and P. Schuster, *Chem. Phys. Lett.*, **24**, 472 (1974).
- 18 M. Perricaudet and A. Pullman, *FEBS Letters*, **34**, 222 (1973).
- 19 P. A. Kollman and I. D. Kuntz, *J. Am. Chem. Soc.*, **94**, 9236 (1972).
- 20 P. A. Kollman and I. D. Kuntz, *J. Am. Chem. Soc.*, **96**, 4766 (1974).
- 21 J. Andriessen, *Mol. Phys.*, **23**, 1103 (1972).
- 22 H. Veillard, J. Demuyneck and A. Veillard, *Chem. Phys. Lett.*, **33**, 221 (1975).
- 23 J. A. Jafri, J. Logan and M. D. Newton, *Isr. J. Chem.*, **19**, 340 (1980).
- 24 A great contribution to our knowledge of the properties and solution structures of transition metal aquo ions has been made by H. Taube and coworkers. For a review of work on aquo ions of the first transition series, see *Progr. Inorg. Chem.*, **30**, 359 (1983). This work has been extended by Taube and others to ele-

- ments for the second and third transition series. See, for example, H. Taube, *Coord. Chem. Revs.*, **26**, 33 (1978) and references therein.
- 25 D. Getz and B. L. Silver, *J. Chem. Phys.*, **61**, 630 (1974).
 - 26 R. Poupko and Z. Luz, *J. Chem. Phys.*, **57**, 3311 (1972).
 - 27 D. Van Ormondt, R. De Beer, M. Brouha and F. De Groot, *Z. Naturforsch (A)*, **24**, 1746 (1969).
 - 28 A. Zalkin, J. D. Forrester and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963).
 - 29 N. J. Hair and J. K. Beattie, *Inorg. Chem.*, **16**, 245 (1977).
 - 30 H. L. Friedman and L. Lewis, *J. Soln. Chem.*, **5**, 445 (1976).
 - 31 J. Howell, A. Rossi, D. Wallace, K. Haraki and R. Hoffman, QCPE, Program manual for program No. 344, ICON 8 and FORTICON 8.
 - 32 J. W. Richardson, R. R. Powell and W. C. Nieuwpoort, *J. Chem. Phys.*, **38**, 796 (1963).
 - 33 J. W. Richardson, R. R. Powell, W. C. Nieuwpoort and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).
 - 34 E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
 - 35 H. Basch, A. Viste and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).
 - 36 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley, London and New York, 1980.
 - 37 O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).