

## Perspective

# Perspective on “The spectra and electronic structure of the tetrahedral ions $\text{MnO}_4^-$ , $\text{CrO}_4^-$ , and $\text{ClO}_4^-$ ”

Wolfsberg M, Helmholz L (1952) *J Chem Phys* 20:837–843

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**Abstract.** The paper by Wolfsberg and Helmholz represents the first molecular orbital calculation on a transition-metal complex. Published in the heyday of ligand-field theory, the paper was 10 years ahead of its time. Here, the present author provides an overview of the title paper: a brief description of the results, his perspective on the historical context of the work and its influence on subsequent developments, personal reminiscences about the paper by Max Wolfsberg, and biographical sketches of the authors.

**Key words:** Transition metal – Molecular orbital – Extended Hückel – Metal oxides – Tetrahedral ions

## 1 Introduction

The title paper by Wolfsberg and Helmholz represents the beginning of a paradigm shift in the way chemists approached the electronic structure of transition-metal complexes. Prior to this work the main emphasis by chemists had been on the development of valence bond methods to explain the bonding and magnetic behavior, while physicists, less concerned about the bonding, preferred crystal-field theory to explain the magnetic and spectroscopic properties of the complexes. The paper by Wolfsberg and Helmholz represents the first molecular orbital calculation on a transition-metal complex. Published in the heyday of ligand-field theory, the paper was 10 years ahead of its time.

## 2 Summary of the work

After mentioning previous successes of both valence bond and molecular orbital methods in organic chemistry [1], the authors set two principal goals. First, the nature of the  $\text{X}=\text{O}$  bonds needed clarification; their relatively, short length had been attributed to resonance

of double-bonded Lewis structures [2] and, alternatively, to a change in the hybridization on oxygen [3]. Second, while ions such as  $\text{ClO}_4^-$  show no absorption in the visible or near ultraviolet (only a single band in the ultraviolet), the valence isoelectronic transition-metal species such as  $\text{MnO}_4^-$  and  $\text{CrO}_4^{2-}$  show two strong characteristic bands in this region. Permanganate, in particular, had been thoroughly studied in dilute single crystals [4].

The authors built a linear combination of atomic orbitals model of the ions  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{ClO}_4^-$  by using only the valence orbitals of the central atom ( $3d$ ,  $4s$ ,  $4p$  for Mn and Cr;  $3s$  and  $3p$  for Cl) and the  $2p$  orbitals of O; thus, all complexes had 24 valence electrons. The inner-shell electrons were treated as part of the core. Using group theory [5], the authors determined the irreducible representations of the valence orbitals, the corresponding normalized linear combination of the oxygen orbitals (oxygen–oxygen overlap was neglected), and the group overlaps,  $G$ . The authors then set-up and solved the secular equation

$$|H_{ij} - G_{ij}\epsilon| = 0$$

to obtain the eigenvalues. The  $H_{ii}$  terms were taken as parameters whose range was restricted by known valence-shell ionization energies [6]. For O the authors gave  $H_{\sigma\sigma}$  a more stable value than  $H_{\pi\pi}$  in accord with earlier calculations [7]. The authors found that calculating the overlap integrals [8] with the usual Slater functions [9] gave values too small to yield reasonable interactions. To remedy the problem the authors created their own set of analytic atomic functions that more closely approximated known atomic self-consistent field functions [10].

The off-diagonal terms in the secular equation were approximated by the now famous “Wolfsberg–Helmholz formula”.

$$H_{ij} = F_x G_{ij} (H_{ii} + H_{jj}) / 2 .$$

The adjustable parameter  $F_x$  was given different values for the  $\sigma$  and  $\pi$  interactions.

Solution of the secular equation yielded a set of occupied orbitals  $(1e)^4 (1t_2)^6 (1a_1)^2 (2t_2)^6 (t_1)^6$  for the 24 valence electrons. The authors used the bonding nature of the occupied orbitals to provide a qualitative description of the multiple-bond character of the X=O bonds. The calculation also gave the  $3t_2$  orbital as the lowest-lying virtual orbital. Using the orbital energy differences, the authors assigned the lowest energy band in all the spectra to the allowed  ${}^1A_1 \rightarrow {}^1T_2$  transition, arising from exciting an electron from the nonbonding oxygen  $t_1$  molecular orbital to this  $3t_2$  orbital. The second band, which was observed only for Cr and Mn, was assigned to the allowed  ${}^1A_1 \rightarrow {}^1T_2$  transition arising from the  $2t_2$  to  $3t_2$  excitation. The calculations provided qualitative agreement with the experimentally observed band positions, given that more than qualitative comparison would require knowledge of several two-electron integrals, as described in the paper's appendix.

The authors also obtained qualitative agreement with the observed intensities and with the spectra of  $MnO_4^-$  diluted into  $KClO_4$  and  $NaClO_4$  single crystals. The authors were able to account for many of the weaker transitions which were now allowed by the lower site symmetry.

### 3 Perspectives on subsequent developments

The importance of this work was not the accuracy of the assignments, but the fact that it was the first molecular orbital treatment of a transition-metal complex. Until then bonding had usually been described with Pauling's valence bond approach [2]. The explanation of magnetic properties had proponents in the valence bond school [2] and the crystal-field school [11], while spectral analysis tended to be the province of physics and was treated by the crystal-field approach. Earlier, Van Vleck [12] had argued that both valence bond and crystal-field theory were subsets of molecular orbital theory [12]. The paper by Wolfsberg and Helmholtz was the first to apply quantitative molecular orbital theory to inorganic complexes. An early review states that "Modern quantum chemistry of coordination compounds started actually in 1952 when Wolfsberg and Helmholtz carried out calculations for  $MnO_4^-$  and  $CrO_4^{2-}$ ..." [13].

The timing of this paper was also important. Inorganic chemists were just beginning to take a serious interest in spectroscopy, which had been the realm of physicists and chemical physicists, and they needed a method that would give a unified explanation of the bonding, magnetic properties, and spectra. Inorganic chemistry was also about to undergo a renaissance with the discovery of ferrocene in 1951 [14]. The subsequent development of the entire field of organometallic chemistry needed a robust molecular orbital approach; the Wolfsberg-Helmholtz paper presaged this need.

Some early applications of the method were made by Japanese workers [15], but the 1950s were the "heyday" of crystal- and ligand-field theory [16]. It was not until the early 1960s that the molecular orbital approach for transition-metal complexes gained momentum. This interest was driven by a combination of spectroscopists'

interest in charge-transfer (non-ligand-field) transitions, as found in  $MnO_4^-$  and  $CrO_4^{2-}$ , and chemists' desire to understand the bonding in organometallic complexes. The early 1960s found Harry Gray on a postdoctoral assignment with Carl Ballhausen. Together they developed the self-consistent charge and configuration method, an iterative Wolfsberg-Helmholtz approach [17]. The method was exploited by Gray and his coworkers to study the spectral properties of a wide variety of complexes [18].

Richard Fenske arrived as Assistant Professor at the University of Wisconsin in 1961 after having completed his PhD, with Donald Martin at Iowa State University on applying crystal-field theory to square-planar platinum complexes [19]. Fenske was interested in developing a method more closely tied to the ab initio molecular orbital method described so beautifully by Roothaan [20]. Building on some previous suggestions [21], he and his first students, especially Ken Caulton and Doug Radtke, developed an approximate self-consistent field method that had no empirical or adjustable parameters. With some later refinements by this author, the method became widely known as the Fenske-Hall method [22], and in this form it is still being used today [23].

Approximate molecular orbital theory continues to play an important role, especially as an adjunct to experimental work. However, by the late 1960s, as computers became faster and computer codes improved, theoreticians began applying ab initio methods to metal complexes [24].

### 4 Reminiscences by Max Wolfsberg

As a freshman at Washington University, I asked my instructor why the color of permanganate ion is purple. He answered "because God made it so". I remember saying to one of my friends that I would still like to find out "why". I started graduate study at Washington University in 1948 although the department did not think that this was very wise because (1) one should change universities between undergraduate school and graduate school and (2) I had declared an interest in theoretical chemistry and there was no one in the department who was considered to be a theoretical chemist. During my first year, Lindsay Helmholtz consented to be my PhD mentor. I had already told him, when I was doing undergraduate study with him, of my interest in permanganate ion. He shared this interest and indeed he showed me notes on permanganate ion that Linus Pauling had written when he visited St. Louis. Lindsay's interest in permanganate had been fired by two beautiful papers by the German physicist J. Teltow on low temperature absorption spectroscopy of single crystals of dilute solutions of permanganate ion imbedded in perchlorate ion lattices with different site symmetries.

Since I had difficulties writing down mathematical expressions for the various Lewis multi-bonded resonance structures in Pauling's notes, I decided to try the molecular orbital approach, which in 1949 was not popular among chemists. I consequently spent the summer of 1949 studying papers on molecular orbital theory, especially those of R.S. Mulliken in *The Journal of Chemical Physics*. I then proceeded to set up the symmetry molecular orbital combinations for  $RX_n$  compounds of various symmetries (tetrahedral, square-planar, etc.). Lindsay and I then started discussing permanganate ion spectroscopy in terms of molecular orbital theory. S.I. Weissman participated in many of these discussions. Central to these discussions was our "understanding" that the interactions between the orbitals on the manganese atom and the orbitals on the oxygen atoms are proportional to the overlap

integral between these orbitals. While I deified Mulliken, who also emphasized the importance of overlap considerations, I must state that my own feeling about the importance of overlap came from Pauling's classic "The nature of the chemical bond". In the fall of 1949, I opened a new issue of *The Journal of Chemical Physics* and found the paper on the calculation of overlap integrals by Mulliken, Rieke, Orloff, and Orloff (*J Chem Phys* (1949) 17: 1248). We then realized that we could make quantitative statements about spectroscopy (rather than waving our arms) if we combined calculated overlap integrals and observed ionization potential data in a Hückel type of molecular orbital theory. I proceeded to calculate overlap integrals for Slater type *d* orbitals with Slater type *p* and *s* orbitals using the methodology of Mulliken et al. (see above). After comparing the single exponential Slater orbitals (using the Slater recipes for the screening constants) with Hartree Fock orbitals in the literature, I concluded that single exponential atomic orbitals were inadequate and fitted all (most) known theoretical data on Hartree Fock atomic orbitals in terms of linear combinations of single Slater functions with exponents which included the nuclear charges and appropriate new screening terms. This material is in my thesis, but we never wrote it up for publication. Other parts of the calculations are also given in more detail in my thesis than they are in the 1952 paper by Wolfsberg and Helmholz.

In the Spring of 1951, Lindsay wrote his PhD mentor Joe Mayer about our calculations, hoping he would show this communication to his wife Maria Goepfert Mayer. If I remember correctly, Maria wrote back a very encouraging letter and somehow she communicated with Mulliken. Mulliken invited Lindsay to give a seminar to his group, and Lindsay took me along to Chicago. It is typical of Lindsay that he paid for this trip for me out of his own pocket, as well as the cost of a trip to the Ohio State Symposium a couple of months later, where I presented our calculations at a session chaired by G. Herzberg. At the time when we visited Chicago, C. Roothaan was a postdoc of Mulliken; before the seminar, Mulliken warned that Roothaan would be unhappy about what we had done but not to be discouraged by that.

### 5 Biographical sketch of Max Wolfsberg

Max Wolfsberg was born on May 28, 1928 in Hamburg, Germany, and came to the US with his parents and brother, arriving via Sweden on September 22, 1939. He attended Washington University on an Honor Scholarship and graduated with an A.B. degree in 1948. He remained at Washington University for graduate work and obtained his Ph.D. degree under Prof. Lindsay Helmholz in 1951. He was an AEC predoctoral fellow during his final year at Washington.

Following graduation, he joined the staff of Brookhaven National Laboratory where he rose through the ranks to Senior Chemist. While at Brookhaven, he was awarded a National Science Foundation Senior Postdoctoral Fellowship (with R.P. Bell at Oxford, with C. Ballhausen at Copenhagen, and with P.O. Loewdin at Uppsala), and was visiting Professor of Chemistry at Cornell University in the spring of 1963 and at Indiana University in spring 1965. He was also Professor of Chemistry at the State University of New York at Stony Brook from 1966 to 1969.

Following a winter semester at the University of California, Irvine, as Regents' Lecturer, he joined the faculty as Professor of Chemistry in 1969. While at Irvine, Wolfsberg was awarded Alexander von Humboldt Awards in 1977, 1984, and 1993. He was Lecturer, Troisième Cycle, at EPF Lausanne and the University of Berne in 1978, Deutsche Forschungs Gemeinschaft Guest Professor at the University of Ulm in 1986,

National Academy Exchange Scholar at Leipzig in 1989, and Forchheimer Visiting Professor at Hebrew University in 1993. He also served as Chair of the Department of Chemistry from 1974 to 1980.

Wolfsberg's theoretical researches have focused on a variety of topics including quantum chemistry, isotope effects on thermodynamic properties and on chemical reaction rates, mass-spectrometric fragmentation patterns, translational-vibrational energy transfer, molecular dynamics calculations on condensed phases, and rotational-vibrational spectroscopy.

### 6 Biographical sketch of Lindsay Helmholz

Lindsay Helmholz was born in Chicago on November 11, 1909. From 1926 until 1928 he attended Cornell University and in 1933 received his Ph.D. degree from John Hopkins University, where he was an early student of Joseph E. Mayer. He was one of the few Mayer students to do experimental work and he worked on the Born-(Mayer)-Haber cycle to determine the electron affinities of F. Helmholz came to the California Institute of Technology first as a National Research Fellow (1934-1936) then as an Instructor in Chemistry (1936-1941). At the Institute Helmholz worked with Linus Pauling and became a crystallographer. In 1941 he moved to Dartmouth College as an Assistant Professor and set up his own X-ray diffraction apparatus.

During the Second World War, Helmholz was a chemist on the Manhattan Project in Los Alamos. In 1946 he received a Guggenheim Fellowship and later that year joined the Department of Chemistry at Washington University in St. Louis as an Assistant Professor. Helmholz and several others from the Manhattan Project joined the faculty of Washington University because Joseph W. Kennedy, previously Head of Chemistry at Los Alamos, moved there after the war and became Chairman of the Department in 1945. At Washington University Helmholz embarked on research programs in X-ray diffraction and spectroscopy; the diffractometer that he had set up at Dartmouth was moved to Washington University. He was promoted to Associate Professor in 1948 and to Professor in 1957. While at Washington University, he served two terms as Acting Chair (1963-1964 and 1976-1978). He retired in 1978 and died on March 17, 1993.

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