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CLUSTER MODEL FOR THE ELECTRONIC STRUCTURES OF COMPLEX MOLECULES AND SOLIDS (*)

K. H. JOHNSON

Department of Metallurgy and Materials Science
Center for Materials Science and Engineering, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139, USA

Résumé. — Un modèle « d'agglomérat » a été développé pour le calcul *a priori* de la structure électronique des molécules complexes et des solides. Dans ce modèle, l'intérêt est concentré sur un groupe particulier d'atomes qui peut être une molécule complète, une fraction de molécule plus grande ou de cristal ordonné ou désordonné. Le groupe est découpé en régions adjacentes : atomique, interatomique et extramoléculaire. L'équation de Schrödinger, contenant un modèle de potentiel Hartree-Fock avec approximation statistique $X\alpha$ de Slater pour l'échange et la corrélation, est résolue de manière self-consistante dans chaque région par le formalisme des ondes diffusées quelque peu semblable à celui développé originellement par Korringa. Les effets de l'environnement particulier sont pris en compte par des conditions aux limites de l'agglomérat : on impose la continuité des solutions dans la région extramoléculaire aux solutions dans les régions atomique et interatomique sur une sphère enfermant l'ensemble du groupe d'atomes. Aucune référence explicite n'est faite au théorème de Bloch, si ce n'est par l'introduction de conditions de périodicité aux limites de l'agglomérat. Les exemples suivants illustrent les applications du modèle : calcul auto-cohérent sans restriction sur le spin dans les complexes de métaux de transition, calcul dans un grand agglomérat des niveaux d'impuretés profondes dans les semi-conducteurs et calcul de la liaison chimique de groupes de certaines métallo-enzymes et protéines biologiquement actifs. Les fonctions d'onde et des courbes de densité de charge illustrant la liaison chimique sont présentées pour divers agglomérats.

Abstract. — A cluster model has been developed for calculating from first principles the electronic structures of complex molecules and solids. In this model, attention is focused on a particular cluster of atoms which may be an entire molecule, part of a larger molecule, or part of an ordered or disordered crystal. The cluster is geometrically partitioned into contiguous *atomic*, *interatomic*, and *extramolecular* regions. The self-consistent-field Schrödinger equation is set up in each region for a model Hartree-Fock potential including Slater's $X\alpha$ statistical approximation to exchange correlation, and the problem is solved via scattered-wave formalism somewhat similar to that developed originally by Korringa. The effects of the particular environment are described by boundary conditions on the cluster, e. g. the matching of the solutions of Schrödinger's equation in the extramolecular region to the solutions in the atomic and interatomic regions at an artificial spherical boundary surrounding the entire cluster. No explicit use is made of Bloch's theorem, unless through the introduction of periodic boundary conditions on the cluster. Illustrative applications of the model to be described include : (1) self-consistent-field spin-unrestricted calculations on transition-metal complexes ; (2) large-cluster calculations of deep impurity levels in semiconductors ; and (3) calculations of the chemical bonding of the biologically active prosthetic groups of certain metallo-enzymes and proteins. Computer generated contour maps of the electronic wavefunctions and charge densities illustrating the chemical bonds in various clusters are also presented.

The SCF- $X\alpha$ cluster model. — The nature of the electronic structures of complex molecules and solids is central to a wide class of problems in chemistry, solid-state physics, biology, and materials technology. Illustrative, although not exclusive, examples include : polyatomic molecules in the gaseous or liquid phase, in crystalline environments, or in aqueous solution ; ordered crystals with many atoms per unit cell ;

impurities and defects in an otherwise perfect crystal ; disordered and amorphous materials ; biological macromolecules, and polymers. There is much current interest in developing quantitative theories for the chemical bonding and related properties of such systems.

The application of quantum theory to these problems depends, to a large degree, on one's understanding of the electronic structures of component polyatomic clusters which are often arranged in complex stereochemical configurations. Traditional *ab initio* Hartree-Fock self-consistent-field methods of quantum chemistry, based on representing molecular orbitals as linear combinations of atomic orbitals (SCF-LCAO

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methods) [1], are difficult and costly in computer time to implement on many-electron polyatomic systems, because of the necessity of having to compute many multicenter integrals or equivalent Hartree-Fock matrix elements. Simpler semiempirical LCAO-type molecular-orbital methods, such as those based on the «complete neglect of differential overlap» (CNDO methods) [2], depend on the *ad hoc* (often not physically justified) parametrization of matrix elements and yield only semiquantitative results for complex molecules and crystals. Conventional band theory [3] is likewise difficult to apply to crystals with more than a few atoms per unit cell and suffers from its dependence on the assumption of lattice periodicity and on a reciprocal-space representation. Theories of deep impurity levels [4], such as those associated with substitutional transition-metal atoms and vacancies in semiconductors, require, in principle, the knowledge of a complete set of Wannier or Bloch wavefunctions for the otherwise perfect host lattice.

Following a suggestion made originally by Slater [5], we have developed and applied [6]-[18] a new theoretical technique for calculating, from first principles, the electronic structures of complex molecules and solids. This technique eliminates many of the aforementioned difficulties associated with more conventional methods of quantum chemistry and solid-state theory. It leads to an accurate description of the chemical bonding of molecules and solids of considerable stereochemical complexity without undue computational effort or cost. We refer the reader of references [6]-[8] for details of the theoretical formalism.

It is sufficient to summarize here that the method is based, first of all, on the division of matter into component polyatomic clusters. Each cluster, which may be an isolated polyatomic molecule, part of a macromolecule, or a polyatomic complex in an ordered or disordered solid, is geometrically partitioned into contiguous I. *atomic*, II. *interatomic*, and III. *extramolecular* regions (see Fig. 1). The one-electron Schrödinger equation is numerically integrated within each region in the partial-wave representation for spherically averaged and volume averaged potentials which include Slater's [19]-[25] $X\alpha$ statistical approximation to exchange correlation. The wavefunctions and their first derivatives are joined continuously throughout the various regions of the cluster via multiple-scattered-wave theory (see ref. [6]-[18]) somewhat similar to that developed originally by Korringa [26]. The effects of a particular environment on the cluster are described by boundary conditions, e. g. in the case of an isolated polyatomic molecule the matching of the solutions of Schrödinger's equation in the extramolecular region to those within the cluster at an artificial spherical boundary surrounding the cluster (see Fig. 1). This procedure leads to a set of rapidly convergent secular equations which are solved numerically for the molecular-orbital energies and wavefunctions. The matrix elements of these equations

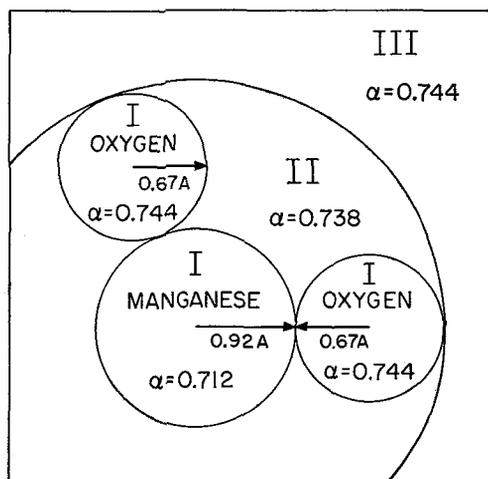


FIG. 1. — Division of the MnO_4^- cluster (in an O-Mn-O plane) into I. atomic, II. interatomic, and III. extramolecular regions. The $X\alpha$ exchange-correlation parameters, optimized by the first-principles method suggested by Slater, are shown.

are simple to evaluate in comparison with those characteristic of LCAO methods. In particular, there are no multicenter integrals. This entire numerical procedure is repeated, using the wavefunctions obtained at each iteration to generate a charge density and new potential, until self consistency is attained.

The scattered-wave technique requires only a small fraction of the computer time required by *ab initio* LCAO methods. Furthermore, it yields results which are in significantly better quantitative agreement with experiment than do either *ab initio* or semiempirical LCAO methods. For example, in conjunction with Slater's [22]-[25] «transition-state» theory of optical excitations, the scattered-wave model leads to an accurate description of the optical properties of molecules and crystals, including the effects of orbital relaxation. The method is practicable, moreover, on polyatomic systems of considerable stereochemical complexity, where *ab initio* LCAO methods are too difficult and costly to implement. The total energy and energy as a function of stereochemical geometry are also within the scope of the scattered-wave approach, using the $X\alpha$ statistical total Hamiltonian as the starting point [21]-[25]. For the electronic structure of an ordered complex crystal, i. e. one with several or more atoms per unit cell (e. g. a «molecular crystal»), we can assume the periodic cell to be our unit polyatomic cluster. The boundary condition on the cluster orbitals is then just the Bloch condition, and the theoretical model reduces exactly to band theory (see ref. [10] and [12]). Because of the flexibility of boundary conditions and the practicality of dealing with reasonably large clusters of atoms, the theoretical formalism is readily extended to various problems in the electronic structure of complex materials. For example, since we are concentrating on the electronic structures of finite polyatomic clusters and are therefore not dependent on the assumption of long-range

order, we are able to consider problems such as the bonding of impurities and defects in crystals and the electronic structures of disordered or amorphous materials.

Electronic structure of a transition-metal complex in a crystalline environment. — As an illustrative application of this model to transition-metal bonding, we consider the electronic structure of the tetrahedrally coordinated permanganate ion (MnO_4^-) in a typical crystalline environment. The nature of the chemical bonding and related properties of MnO_4^- and similar complex transition-metal ions have been discussed by inorganic chemists for many years [27]. MnO_4^- does not exist in the gaseous phase, but is stable as an anion in crystals such as KMnO_4 , as an impurity cluster in crystals like KClO_4 , and in aqueous solution. The characteristic purple color of KMnO_4 is associated with a strong optical absorption peak at 2.3 eV in the complementary green part of the spectrum [28]. Permanganate crystals exhibit only a weak temperature-independent paramagnetism of the van Vleck [29] type, suggesting a « closed-shell » ground-state electronic structure. The similarities of the chemical, magnetic, and optical properties of permanganate crystals suggest that the neighboring cations have little effect on the chemical bonding of an MnO_4^- cluster, other than providing a stabilizing electrostatic field. The unit cell of the orthorhombic KMnO_4 crystal, for example, can clearly be divided into four distinct tetrahedrally coordinated MnO_4^- molecules and four K^+ ions [30]. In our calculations the stabilizing field was approximated by surrounding the cluster with a spherical shell of charge + 1 e which does not overlap the nearest K^+ ions and neighboring MnO_4^- molecules in the KMnO_4 unit cell.

The spherical boundaries of the MnO_4^- cluster are illustrated schematically in an O-Mn-O plane in figure 1, including the value of the exchange-correlation scaling parameter α in each region. This parameter is optimized for each component atom by the first-principles method suggested by Slater [22]-[25], namely satisfying the virial theorem and matching the statistical total energy of the atom to the Hartree-Fock total energy. Using this procedure, Schwarz [31] has calculated values of $\alpha = 0.712$ and $\alpha = 0.744$ for the Mn and O atoms, respectively. We then use these values in the corresponding atomic region I of the MnO_4^- cluster. For the interatomic region II, a weighted average $\alpha = 0.738$ is chosen (four parts O to one part Mn). In the extramolecular region III, we choose $\alpha = 0.744$, the value appropriate for O. In the SCF calculation the $X\alpha$ potentials are spherically averaged in regions I and III and volume averaged in region II. Spherical averaging can also be carried out in region II.

To investigate the observed non-spin-polarized ground state of permanganate crystals, we have

carried out both a spin-unrestricted calculation (i. e. different orbitals for different spins) and a spin-restricted calculation. In constructing the superposed-atom potential used to initiate the spin-unrestricted SCF- $X\alpha$ procedure, we assumed that all five Mn 3 d electrons have their spins unpaired. The spin-unrestricted calculation converged in 15 iterations to the same non-spin-polarized « closed-shell » limit determined in the spin-restricted calculation (± 0.001 Ry). The latter procedure required only 8 minutes of CPU time on an IBM 360/65 computer.

The fully occupied and first few unoccupied orbital energies of MnO_4^- , determined by the SCF- $X\alpha$ cluster method are listed in Table I. The deepest orbitals $(1 a_1)^2 (2 a_1)^2 (1 t_2)^6 (3 a_1)^2 (2 t_2)^6 (4 a_1)^2 (3 t_2)^6 (5 a_1)^2 (4 t_2)^6$ are Mn $1 s^2 2 s^2 2 p^6 3 s^2 3 p^6$ and O $1 s^2 2 s^2$ levels « chemically shifted » from the SCF- $X\alpha$ free-atom limits shown in parentheses in Table I. The principal bonding valence orbitals $(5 t_2)^6 (1 e)^4$ are combinations of O 2 p- and Mn 3 d-like partial waves. The $(6 a_1)^2 (6 t_2)^6$ orbitals are O 2 p-like, except for some hybridization with Mn 3 d- and 4 s-like partial waves. The highest occupied level $(1 t_1)^6$ is a nonbonding O 2 p orbital. The valence- and highest core-electron energy levels are also shown in figure 2, along with the first few unoccupied orbital energies $(2 e)^0 (7 t_2)^0 (8 t_2)^0 (7 a_1)^0$, and are compared with the SCF- $X\alpha$ Mn and O atomic energy levels.

One of the major accomplishments during the past year has been the development of a computer program which accurately and efficiently generates con-

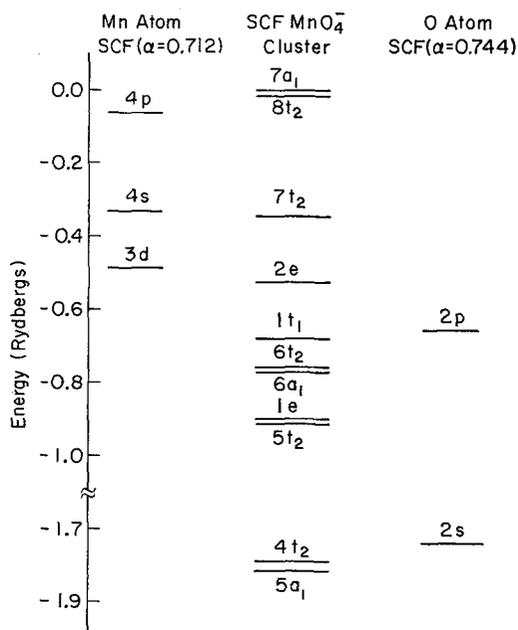


FIG. 2. — SCF electronic energy levels of an MnO_4^- cluster in the stabilizing field of a crystalline environment. The energies are labeled according to the various irreducible representations of the tetrahedral (T_d) symmetry group. The highest occupied level in the ground state is $(1 t_1)^6$. Also shown, for comparison, are the corresponding SCF- $X\alpha$ energy levels of the free atoms.

four maps of the electronic wavefunctions and charge densities determined by the SCF- $X\alpha$ cluster method. This makes practical for the first time (such maps are very expensive to generate via LCAO methods) the «real-space» representation of theoretical chemical bonds in complex molecules and crystals. Several such contour maps are shown for the O-Mn-O plane of the MnO_4^- cluster in figures 3-5. The $5 t_2$ and $1 e$ orbital wavefunctions of MnO_4^- are mapped in figures 3 and 4, respectively, illustrating O 2 $p\sigma$ -Mn 3 d and O 2 $p\pi$ -Mn 3 d bonding. The total valence charge density of MnO_4^- is mapped in figure 5. It should be emphasized

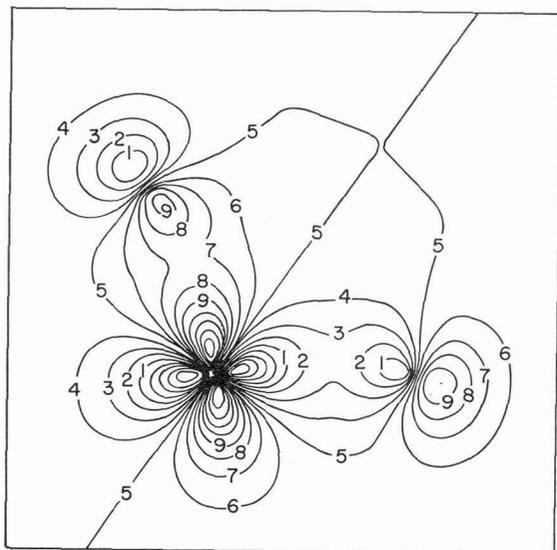


FIG. 3. — Contour map of a normalized $5 t_2$ « σ -bonding» orbital wavefunction in an O-Mn-O plane of the MnO_4^- cluster. Value of contour No. 1 = -0.2 ; value of contour No. 9 = $+0.2$; contour interval = 0.05.

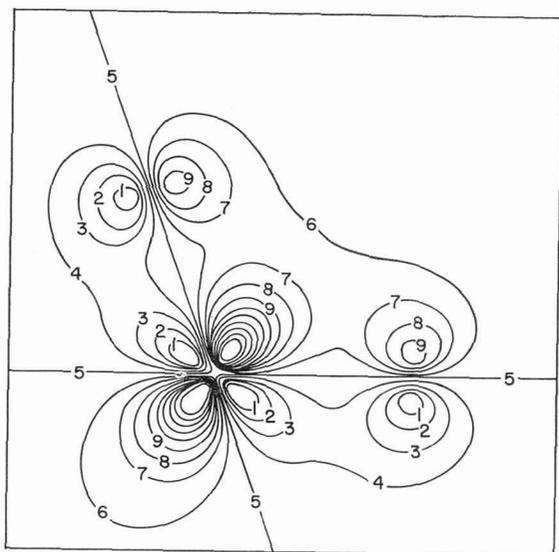


FIG. 4. — Contour map of a normalized $1 e$ « π -bonding» orbital wavefunction in an O-Mn-O plane of the MnO_4^- cluster. Value of contour No. 1 = -0.2 ; value of contour No. 9 = $+0.2$; contour interval = 0.05.

that these maps have not been generated from wavefunctions based on linear combinations of atomic orbitals of the type traditionally used in Hartree-Fock molecular-orbital theory. They have been generated simply from the exact numerical partial-wave solutions of Schrödinger's equation for an SCF- $X\alpha$ model potential, the solutions being joined throughout the various regions of the MnO_4^- cluster by multiple-scattering theory.

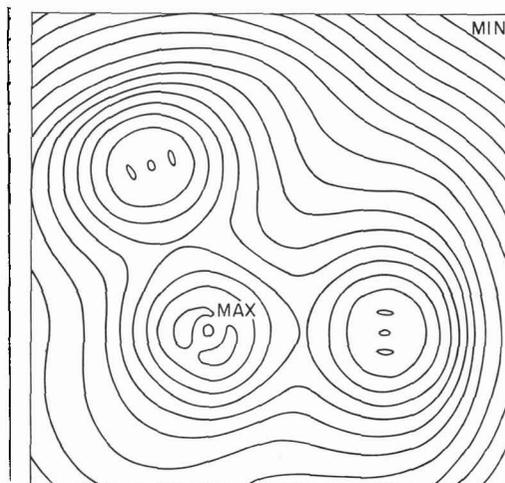


FIG. 5. — Contour map of the total valence electronic charge density in an O-Mn-O plane of the MnO_4^- cluster. Value of maximum contour = 1.23. The values of succeeding contours decrease by a factor of two to a minimum value of 7.1×10^{-6} (in units of electrons per cubic Bohr radius).

The first two unoccupied levels $2 e$ and $7 t_2$ listed in Table I and illustrated in figure 2 are principally Mn 3 d -like orbitals. The ordering of these levels is consistent with that expected for tetrahedral geometry on the basis of ligand-field theory. The positions of these levels with respect to the occupied valence levels are critical for the interpretation of the measured optical properties. The optical absorption spectrum of MnO_4^- , measured for a solid solution of KMnO_4 , consists of three intense bands with maxima at 2.3 eV, 4.0 eV, and 5.5 eV, and a «shoulder» at 3.5 eV [28]. A complete theoretical analysis of the optical properties cannot, of course, be carried out without a quantitative treatment of orbital relaxation and configuration interaction. Nevertheless, it has recently been shown by Slater [22]-[25] that the difference between the $X\alpha$ statistical total energies of the initial and final states of an optical transition is equal, to good approximation, to the difference between the $X\alpha$ one-electron energies of orbitals whose occupation numbers are half way between those of the initial and final states. To determine these orbitals, called «transition states», it is necessary for one to carry out a complete SCF- $X\alpha$ cluster calculation for each pair of levels involved in an optical transition, removing one half a unit of electronic charge from the initial orbital and adding one half

TABLE I

SCF- $X\alpha$ electronic energy levels (in Rydbergs) of an MnO_4^- cluster in a crystalline environment. Levels below the solid line are fully occupied in the ground state; those above the line are empty. Corresponding « free-atom » energy levels are shown in parenthesis.

Symmetry	Energy Levels
7 a_1	— 0.006
8 t_2	— 0.020
7 t_2	— 0.350
2 e	— 0.526
1 t_1	— 0.682
6 t_2	— 0.761
6 a_1	— 0.775
1 e	— 0.901
5 t_2	— 0.915
4 t_2 (O 2 s)	— 1.785 (— 1.732)
5 a_1 (O 2 s)	— 1.813 (— 1.732)
3 t_2 (Mn 3 p)	— 4.259 (— 3.952)
4 a_1 (Mn 3 s)	— 6.435 (— 6.126)
2 t_2 (O 1 s)	— 37.738 (— 37.822)
3 a_1 (O 1 s)	— 37.738 (— 37.822)
1 t_2 (Mn 2 p)	— 46.513 (— 46.274)
2 a_1 (Mn 2 s)	— 54.105 (— 53.829)
1 a_1 (Mn 1 s)	— 468.584 (— 468.203)

a unit of charge to the final orbital. This procedure automatically includes the effects of orbital relaxation.

In Table II we list the calculated energy differences between the initial and final SCF transition-state orbitals for each orbitally-allowed optical transition of MnO_4^- . Included, for comparison, are the energy differences between the corresponding « unrelaxed » virtual orbitals and valence orbitals for the ground-state SCF results shown in Table I. Also included are the assigned experimental absorption energies. The two sets of theoretical transition energies are in close agreement. This result is consistent with Slater's prediction [22]-[25] that the relaxation of $X\alpha$ orbitals should be relatively small for optical transitions between occupied valence-type levels and unoccupied levels lying immediately above. This argument also explains the well known success of the $X\alpha$ statistical

TABLE II

Theoretical and experimental optical transition energies (in eV) for the MnO_4^- cluster

Transition	Unrelaxed SCF Calculation	Transition-state Calculation	Experiment ^(a)
1 $t_1 \rightarrow 2 e$	2.1	2.3	2.3
6 $t_2 \rightarrow 2 e$	3.2	3.3	3.5
1 $t_1 \rightarrow 7 t_2$	4.5	4.7	4.0
5 $t_2 \rightarrow 2 e$	5.3	5.3	5.5

(^a) See reference [28].

exchange-correlation potential in accounting for the optical properties of crystals via band theory. The visible and near-ultraviolet optical properties of many crystals have been quantitatively described in terms of the difference between the $X\alpha$ one-electron energies of bands just below and bands just above the Fermi level. The theoretical optical transition energies listed in Table II are in better quantitative agreement with experiment than are the results of semiempirical [32] and *ab initio* [33] LCAO calculations on MnO_4^- . The transition-state calculation brings the 1 $t_1 \rightarrow 2 e$ theoretical transition energy into « exact » agreement with the measured 2.3 eV absorption energy, although this accuracy may be fortuitous. Thus we interpret this absorption peak as due predominantly to electronic « charge transfer » between the 1 t_1 nonbonding 2 p-like orbital localized on the O ligands and the empty 2 e 3 d-like orbital localized on the Mn atom.

It is perhaps surprising that the scattered-wave model, in conjunction with Slater's $X\alpha$ method and transition-state theory, can lead to a reasonably accurate description of the chemical bonding and optical properties of a complex molecular cluster like MnO_4^- with the expenditure of only a few minutes of computer time. In contrast, the *ab initio* calculations reported in reference [33], using both minimal and « better-than-minimal » atomic-orbital basis sets, required over 10 hours of computer time on a comparable machine.

Electronic structure of « luminescent » impurities in II-VI compounds. — The luminescent properties of II-VI compounds (e. g. ZnS and CdS) have been and continue to be a very active area for scientific and technological investigation [34]. Of importance to luminescence in these materials is the presence of small amounts of substitutional metallic impurities (called « activators »), such as Cu, Ag, Au, and Mn. Specific impurities in specific compounds produce characteristic luminescent emission bands, e. g. the « blue » and « green » emission lines associated with Cu in ZnS.

Although some progress has been made toward developing a quantitative theory of impurity-activated luminescence, many questions remain to be answered. For example, it is believed that impurity-activated luminescence involves electronic transitions between the energy bands of the host crystal and impurity levels lying deep within the band gap [35]. However the exact nature of these levels and their positions with respect to the valence- and conduction-band edges are not thoroughly understood from first principles.

To describe how the SCF- $X\alpha$ cluster model can be extended to this impurity problem, we consider a Mn atom substitutionally replacing a Zn atom in the tetrahedrally coordinated II-VI compound ZnS. Following a suggestion originally made by Birman [36], we then focus our attention on a 17-atom cluster $\text{MnS}_4\text{Zn}_{12}$ consisting of a Mn atom tetrahedrally coordinated by four S atoms, each of which completes its tetrahedral

(carboxypeptidase), copper (ceruloplasmin), and magnesium (chlorophyll) are also recognized to be biocatalysts of important metabolic processes occurring in the living cells of animals and plants.

The biological functions of these systems cover a wide spectrum, varying with the particular metal and organic ligands with which it interacts (see ref. [37]). Nevertheless, there are gross similarities in the stereochemical geometries of the active centers of these macromolecules, e. g. approximate octahedral, tetrahedral, or square-planar coordination of a central metal atom with the organic ligands of a porphyrin-like prosthetic group or other molecular sub-unit (e. g. see Fig. 8). A quantitative theoretical analysis of the electronic structures and chemical bonding of these metals in their local molecular environments should lead to a better understanding of the nature of their biocatalytic and transport functions. Since complex «charge-transfer» and spin-polarization effects between the metal atom and ligands are undoubtedly important in these systems, conventional ligand-field and semiempirical molecular-orbital theories are not appropriate. *Ab initio* Hartree-Fock LCAO theory is also inappropriate because of the vast computational effort which would be required to obtain a reliable description of the electronic structure.

To illustrate how the more practical SCF- $X\alpha$ cluster technique is applied to this problem we consider in greater detail the structure of the hemoglobin protein macromolecule (see Fig. 8), whose biological function is well known to be the transport of oxygen between the lungs and tissues. Protein molecules are long-chain polymers consisting of amino-acid residues called polypeptides, each protein being characterized by a specific sequence of amino acids along the polypeptide chains. The hemoglobin molecule consists of 574 amino acids ($\sim 10,000$ atoms) organized into four intricately wound chains [38]. A prosthetic heme group is tucked into each of the four chains. The heme complex consists of an iron atom coordinated by four nitrogen-atom ligands which are part of a planar molecule known as protoporphyrin (see Fig. 8 a). A fifth nitrogen ligand «below» the plane of the porphyrin attaches the heme complex to the protein chain via the amino acid histidine (see Fig. 8 b). The corresponding position «above» the plane of the porphyrin is of major importance to the biological function of hemoglobin, for it is here that an oxygen molecule (or other ligands such as carbon monoxide) can be attached to the iron atom for transport between the lungs and tissues. If an oxygen molecule attaches itself by only one of the oxygen atoms, then this atom together with the five nitrogen ligands are in six-fold coordination with respect to the central Fe atom [39]. It has also been suggested that the O_2 molecule may be joined symmetrically to the heme by both O atoms, leading to a seven-fold geometry [40]. From steric considerations, some conformational changes of the heme complex during deoxygenation can be expected,

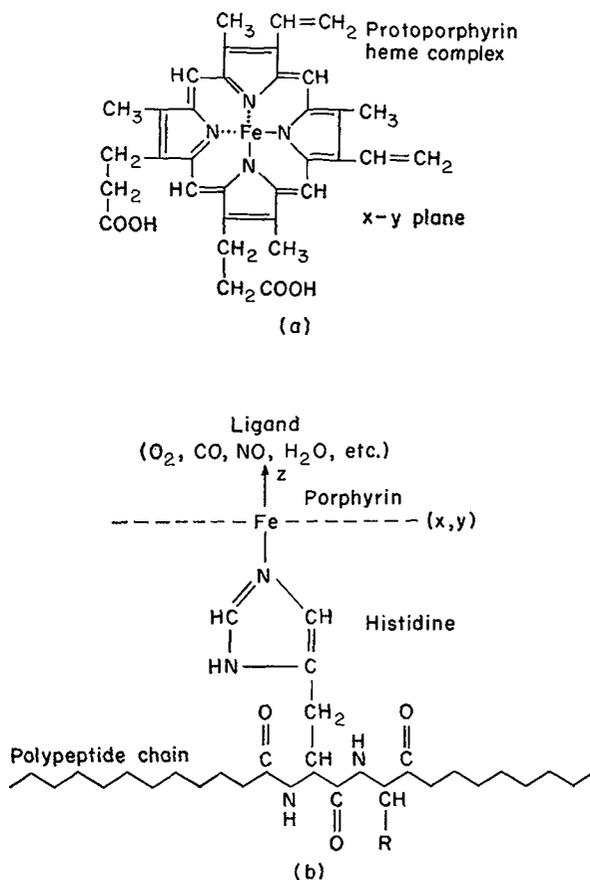


FIG. 8. — a) Protoporphyrin heme complex in hemoglobin; b) attachment of the heme complex to the polypeptide chain of the hemoglobin protein via the amino acid histidine.

including a small displacement of the Fe atom out of the plane of the porphyrin [41].

Although the nature of the electronic structure of the heme complex before and after oxygenation and as a function of conformation is a more difficult problem than the non-biological examples described earlier, it is well within the scope of the SCF- $X\alpha$ cluster method. For our initial model of the heme complex we have chosen a 18-atom cluster consisting of the central Fe atom, five N atoms (four in the porphyrin plane and one «below» the plane), and the ring of twelve nearest porphyrin C atoms centered on the Fe atom (see Fig. 8). In oxyhemoglobin the 19th position «above» the porphyrin plane is occupied, symmetrically or asymmetrically, by the O_2 molecule. In deoxyhemoglobin this position is vacant. The SCF- $X\alpha$ potentials are constructed and the Schrödinger solved self-consistently for the atomic, interatomic, and extramolecular regions of the cluster in essentially the same fashion described earlier. We model the O_2 vacancy in deoxyhemoglobin in terms of «empty» diatomic regions in which only the contributions of the $X\alpha$ potentials of neighboring atoms are superposed. For oxyhemoglobin the contributions of the O atomic potentials are included in these regions. Thus we can

directly compare the electronic energy levels and charge densities of the heme cluster before and after oxygenation and as a function of geometry within the same theoretical framework.

A variety of experimental techniques, leading to information about the magnetic state of the heme complex, have been applied to hemoglobin and myoglobin, including magnetic susceptibility, electron paramagnetic resonance, Mössbauer absorption, and nuclear magnetic resonance. It has been established that the heme group is paramagnetic in deoxyhemoglobin and diamagnetic in oxyhemoglobin, suggesting spin pairing upon oxygenation [42]. One can therefore carry out SCF- $X\alpha$ calculations on the heme cluster in spin-unrestricted form, as we described earlier for the example of the MnO_4^- cluster. Magnetic hyperfine parameters can be calculated and contour maps of the charge and spin densities throughout the cluster can be generated for comparison with experiment.

Discussion. — It is well known that the limitations of applying LCAO methods to complex molecules and solids are the size of the basis sets and the number of multicenter integrals or equivalent Hartree-Fock matrix elements. In the SCF- $X\alpha$ cluster model, which is also a first-principles technique, there is no basis-set problem because we are numerically integrating Schrödinger's equation for an $X\alpha$ potential. There are no multicenter integrals, and the model is practicable in both spin-restricted and spin-unrestricted forms for polyatomic systems of considerable stereochemical complexity. Applications of the SCF- $X\alpha$ cluster technique to free polyatomic molecules, molecules and impurities in crystals, and biological macromolecules

are continuing at M.I.T. and the University of Florida.

Thus far, our applications of the SCF- $X\alpha$ cluster method to polyatomic molecules and solids have been concerned with the generation of one-electron energies and wavefunctions. While a one-electron analysis leads to a quantitative description of many important chemical and physical properties (e. g. charge densities, chemical shifts, magnetic and optical properties), it is also very useful to attempt to determine the total many-electron energy. In particular, a knowledge of the ground-state total energy as a function of stereochemical geometry is essential to developing a quantitative understanding of molecular or crystal stability (e. g. the binding energy, force constants, etc.) and the nature of chemical reactions. Therefore, we have recently extended our cluster computer programs to permit the calculation of the total energies within the framework of the $X\alpha$ statistical total Hamiltonian (see ref. [21]-[25]). Calculations of the total energies of polyatomic molecules and clusters as a function of interatomic distance and bond angle are in progress. Since a rapidly convergent set of spin-orbitals is obtained, perturbation theory can be systematically used, when necessary, to improve the accuracy of the theoretical model.

Acknowledgments. — I am greatly indebted to Professor J. C. Slater for originally suggesting this theoretical approach to molecules and solids and for many helpful discussions. I am also very grateful to my colleague, Dr. Franklin C. Smith, Jr, for writing most of the computer programs used in this work and for assistance in many of the applications.

References

- [1] SLATER (J. C.), *Quantum Theory of Molecules and Solids*, 1963, **1**, McGraw-Hill Book Company, New York.
- [2] POPLÉ (J. A.) and BEVERIDGE (D. L.), *Approximate Molecular Orbital Theory*, 1970, McGraw-Hill Book Company, New York.
- [3] SLATER (J. C.), *Quantum Theory of Molecules and Solids*, 1965, **2**, McGraw-Hill Book Company, New York.
- [4] KOSTER (G. F.) and SLATER (J. C.), *Phys. Rev.*, 1954, **94**, 1392; 1954, **95**, 1167.
- [5] SLATER (J. C.), *J. Chem. Phys.*, 1965, **43**, S 228.
- [6] JOHNSON (K. H.), *J. Chem. Phys.*, 1966, **45**, 3085.
- [7] JOHNSON (K. H.), *Inter. J. Quantum Chem.*, 1967, **1S**, 361.
- [8] JOHNSON (K. H.), *Inter. J. Quantum Chem.*, 1968, **2S**, 233.
- [9] SMITH (F. C., Jr) and JOHNSON (K. H.), *Phys. Rev. Letters*, 1969, **22**, 1168.
- [10] JOHNSON (K. H.) and SMITH (F. C., Jr), *Phys. Rev. Letters*, 1970, **24**, 139.
- [11] JOHNSON (K. H.) and SMITH (F. C., Jr), *Chem. Phys. Letters*, 1970, **7**, 541.
- [12] JOHNSON (K. H.) and SMITH (F. C., Jr), *Computational Methods in Band Theory*, edited by Marcus (P. M.), Janak (J. F.) and Williams (A. R.), 1971, Plenum Press, New York, p. 377.
- [13] JOHNSON (K. H.), *Inter. J. Quantum Chem.*, 1971, **4S**, 153.
- [14] JOHNSON (K. H.) and SMITH (F. C., Jr), *Chem. Phys. Letters*, 1971, **10**, 219.
- [15] JOHNSON (K. H.) and SMITH (F. C., Jr), *Inter. J. Quantum Chem.*, 1971, **5S**, 429.
- [16] JOHNSON (K. H.), *Advances in Quantum Chemistry*, in press, Vol. 7, edited by Löwdin (P.-O.), Academic Press, New York.
- [17] JOHNSON (K. H.) and SMITH (F. C., Jr), *Phys. Rev.*, 1972, **B 5**, 831.
- [18] CONNOLLY (J. W. D.) and JOHNSON (K. H.), *Chem. Phys. Letters*, 1971, **10**, 616.
- [19] SLATER (J. C.), WILSON (T. M.), and WOOD (J. H.), *Phys. Rev.*, 1969, **179**, 28.
- [20] SLATER (J. C.), MANN (J. B.), WILSON (T. M.) and WOOD (J. H.), *Phys. Rev.*, 1969, **184**, 672.
- [21] SLATER (J. C.) and WOOD (J. H.), *Inter. J. Quantum Chem.*, 1971, **4S**, 3.
- [22] SLATER (J. C.), *Computational Methods in Band Theory*, 1971, edited by Marcus (P. M.), Janak (J. F.) and Williams (A. R.), Plenum Press, New York, p. 447.
- [23] SLATER (J. C.), *Advances in Quantum Chemistry*, in press, Vol. 6, edited by Löwdin (P.-O.), Academic Press, New York.
- [24] SLATER (J. C.), this volume.

- [25] SLATER (J. C.) and JOHNSON (K. H.), *Phys. Rev.*, 1972, **B 5**, 844.
- [26] KORRINGA (J.), *Physica*, 1947, **13**, 392.
- [27] COTTON (F. A.) and WILKINSON (G.), *Advanced Inorganic Chemistry*, 1966, Second Edition, Interscience Publishers, New York.
- [28] HOLT (S.) and BALLHAUSEN (C. J.), *Theoret. Chim. Acta*, 1967, **7**, 313.
- [29] VAN VLECK (J. H.) and FRANK (A.), *Proc. Natl. Acad. Sci. U. S.*, 1929, **15**, 539.
- [30] MOONEY (R. C. L.), *Phys. Rev.*, 1931, **37**, 1306.
- [31] SCHWARZ (K.), *Phys. Rev.*, 1972, **B 5**, 2466.
- [32] DAHL (J. P.) and BALLHAUSEN (C. J.), *Advances in Quantum Chemistry*, 1968, edited by Löwdin. (P.-O.), Academic Press, New York, p. 170.
- [33] HILLIER (I. H.) and SAUNDERS (V. R.), *Proc. Roy. Soc., London*, 1970, **A 320**, 161; *Chem. Phys. Letters*, 1971, **9**, 219.
- [34] CURIE (D.) and PRENER (J. S.), *Physics and Chemistry of II-VI Compounds*. 1967, North-Holland Publishing Company, Amsterdam, p. 433.
- [35] BIRMAN (J. L.), *Phys. Rev.*, 1961, **121**, 144.
- [36] BIRMAN (J. L.), *Proceedings of the International Conference on Luminescence*, 1968, edited by Szigeti (G.), Akadémiai Kiadó, Budapest, p. 919.
- [37] JOHNSON (K. H.), *Biomedical Physics and Biomaterials Science*, in press, MIT Press, Cambridge, Massachusetts.
- [38] KENDREW (J. C.), DICKERSON (R. E.), STRANDBERG (B. E.), HART (R. G.), DAVIES (D. R.), PHILLIPS (D. C.) and SHORE (V. C.), *Nature*, 1960, **185**, 422; PERUTZ (M. F.), *J. Mol. Biol.*, 1965, **13**, 646.
- [39] PAULING (L.), *Nature*, 1964, **203**, 182.
- [40] GRIFFITH (J. S.), *Proc. Roy. Soc., London*, 1956, **A 235**, 23.
- [41] PERUTZ (M. F.), *Nature*, 1970, **228**, 726.
- [42] BENNETT (J. E.), GIBSON (J. F.) and INGRAM (D. J. E.), *Proc. Roy. Soc., London*, 1957, **A 240**, 67.