Quantum chemistry and catalysis

Powerful theoretical techniques are revealing similarities—particularly the role of the d-electrons—in the electronic structure of molecules, complexes and clusters important in many diverse catalytic processes.

John C. Slater and Keith H. Johnson

Why do platinum, palladium, nickel and iron, as well as other Group-VIII transition metals, continually turn up as the active sites in catalysts? Why do certain enzymes and proteins—substances such as hemoglobin and ferredoxin that catalyze metabolic processes in living organisms—also appear to rely on transition metals for their action? How do catalysts work anyway, and could we design better ones? We are much nearer answering these questions and other related ones now that new methods, both theoretical and experimental, are available to investigate the electronic structure of complex molecules and materials of the type important to catalysis.

One of the more promising theoretical developments, the Self-Consistent-Field X-alpha scattered-wave approach to quantum chemistry, is already far enough advanced for the quantitative investigation of catalytic and biocatalytic systems. We are still far from a complete working-out of the theory and the computational procedure—we cannot yet, for example, predict the complete reaction path of a catalytic process as a function of temperature and pressure. However, we can already recognize certain electronic factors crucial to catalytic activity, specificity and stability that show up in the nature of the stationary ground and excited states, energies and charge distributions of catalyst–absorbate complexes and reaction intermediates.

One fundamental point that emerges is the important role played by the d-electrons in catalytic action by the transition metals. Figure 1 shows, as an example, contour maps of two orbital wavefunctions of the cubic cluster Cu_8; d-like contours are clearly evident here, and the directed d lobes at the cube corners may be significant for the catalytic activity of small transition-metal particles. We will show later how this d-electron significance is repeated in other catalytic materials; particularly interesting is the strong similarity we observe between the electronic structures of two very different systems, ferredoxin and Ni_8—one biological and the other nonbiological.

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Catalysts

The authors of two recent PHYSICS TODAY articles, John C. Fisher[1] ("Energy crises in perspective") and Traugott E. Fischer[2] ("A new look at catalysis"), have emphasized that a significant part of our present and future energy needs can be supplied by fossil fuels if those fuels can be converted into more usable and pollution-free forms. The gasification of coal to methane by the reactions

$$C + H_2O \rightarrow CO + H_2$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

is one of several processes discussed by Fischer[2] that can be best achieved through the design of a catalyst capable of permitting both reactions to occur in the same vessel. In discussing such examples, Fischer also emphasized that by making catalysis and the development of catalytic materials more of a science than an art, physical scientists can help to solve the current high-priority energy problem. Indeed, the applications of surface physics and chemistry to catalysis have received much attention at several recent workshops and conferences on catalysis.[3–5]

Catalysts for the hydrogenation of unsaturated hydrocarbons, reforming catalysts used in the refining of petroleum, and catalysts for the oxidation of carbon monoxide and reduction of nitrogen oxides in automobile exhaust emissions—these are all examples of systems that surface physicists and chemical physicists must begin to study if catalytic activity, specificity and stability are to be understood on a more fundamental level. Such reactions are typically catalyzed by highly dispersed particles (≈10 Å to 100 Å in size) of platinum, palladium, nickel, or other Group-VIII elements supported on a porous refractory material such as silica or alumina.[6] Highly dispersed bimetallic and multimetallic "alloy" clusters, typically based on Group-VIII and Group-IB elements (for example, Pt–Ni, Ni–Cu, and Pd–Au systems), have also become increasingly important as the active centers of commercial catalysts.[7] Some chemical reactions can be catalyzed by semiconductors and insulators, for example metal oxides and so-called "solid-acids."[2]

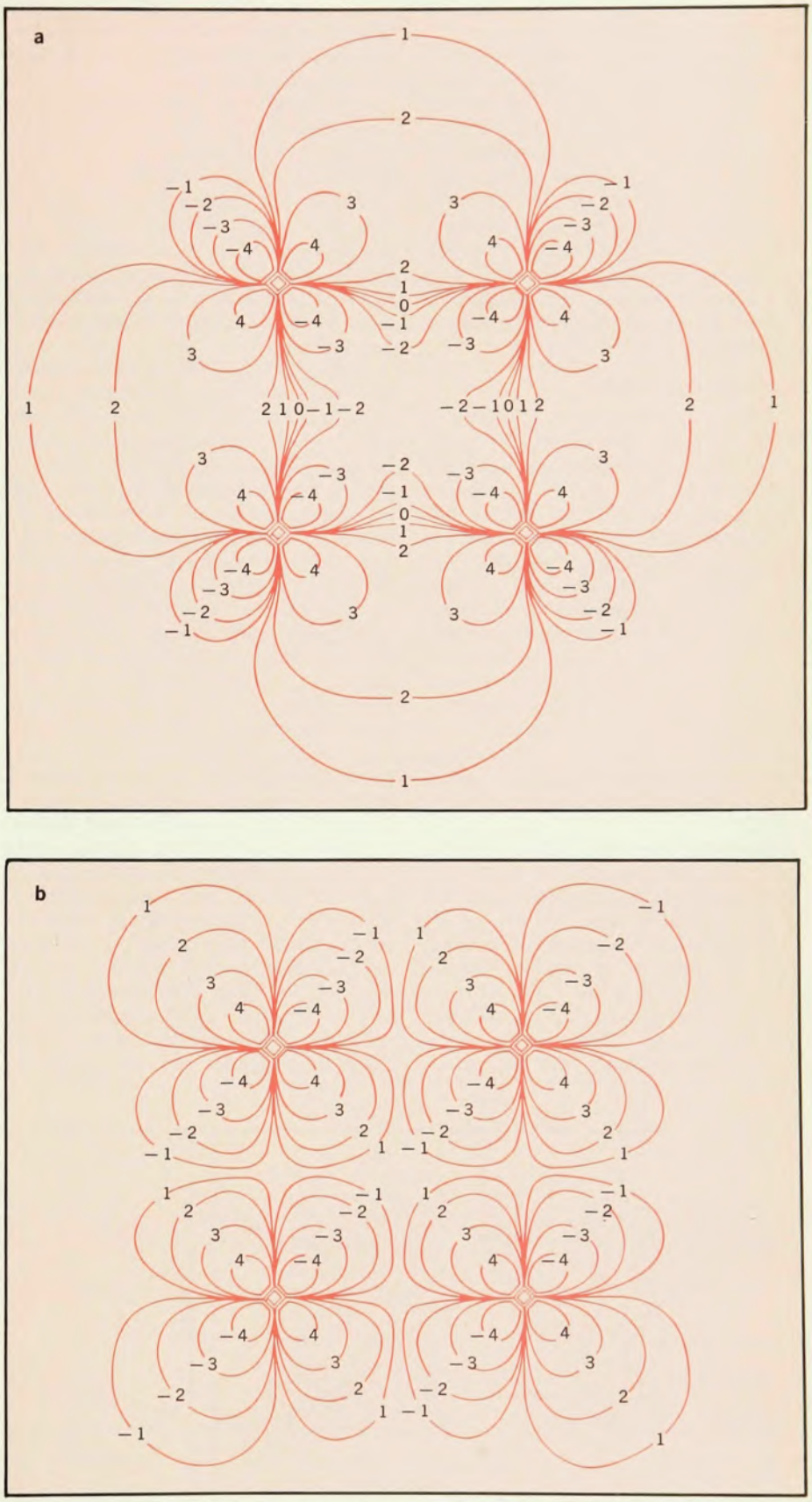
Olefin hydrogenation by Group-VIII transition metals is a good example of a reaction that can be catalyzed *heterogeneously* and *homogeneously*, that is, from the gas or liquid phase respectively on dispersed transition-metal surfaces, and by transition-metal salts or complexes in aqueous solution.[8] Heterogeneous olefin hydrogenation can occur by transfer of hydrogen atoms to ethylene molecules chemisorbed on the surface of a small, supported transition-metal aggregate, as schematically represented in figure 2a. Homogeneous olefin hydrogenation can occur through ligand exchange and transfer of hydrogen atoms to an ethylene ligand at the periphery of an isolated transition-metal complex, as represented in figure 2b. (A "ligand" is any atom or molecule that is directly bonded to a particular metal atom.)

Transition metals are also found in relatively small amounts in living cells as the biocatalytically active centers of certain enzymes and proteins. For example, hemoglobin, found in the red blood cells, is responsible for the transport of oxygen between the lungs and tissues. Oxygen transport occurs through the reversible binding of an oxygen molecule to an iron atom strategically located at the center of a porphyrin ring (as illustrated in figure 3a), which is attached to the protein poly-

peptide chain.[9] The approximately cubic ferredoxin cluster shown in figure 3b is typical of the active centers of iron–sulfur proteins, which catalyze electron transport processes in the metabolism of bacteria, plants, and animals.[10]

It is a well known property of the Group-VIII transition metals that these d-electron elements can form coordination complexes. These complexes can involve two or three metal-ligand bonds, but four bonds (with square-planar or tetrahedral symmetry) and six bonds (with octahedral symmetry) are more common. Coordination to eight or twelve nearest-neighbor atoms is largely characteristic of the bonding between transition-metal atoms in bulk crystals, small aggregates and clusters.

Catalytic activity is generally thought to be a surface phenomenon in which reactive atoms or molecules are chemisorbed onto a small part of the catalyst surface through the formation of a "surface molecule" or "complex" that in some way lessens the amount of energy (the activation energy) needed for a given chemical reaction to begin, thereby allowing it to proceed more rapidly. In heterogeneous catalysis, there is chemisorption, motion and reaction of the absorbates from the gas or liquid phase directly on the surface of a solid catalyst, as represented in figure 2a. In homogeneous catalysis, the reacting atoms or molecules are present as ligands in individual molecular complexes in solution, and the ligands are labile enough (that is, they undergo chemical change sufficiently easily) to move around and be exchanged at the periphery of the complex, as represented in figure 2b. To explain the fundamental nature of catalytic activity and specificity, we must therefore begin to understand the physics underlying the coordination chemistry of inorganic and organic transition-metal complexes and the surface chemistry of highly dispersed transition-metal particles. It is also important to investigate the phys-



Contour maps for two of the d-orbital wavefunctions of cubic Cu_8, plotted in the plane of a cube face. **Part a** is the a_{1g} orbital corresponding to the energy level −0.533 Ry shown in figure 4a, and **part b** is the a_{2u} orbital corresponding to the energy level −0.467 Ry shown in figure 4a. The contour values decrease in absolute magnitude with decreasing absolute values of the contour labels, the zero contour indicating a node in the wavefunction. The sign of the contour label gives the sign of the wavefunction.

Figure 1

ics of ideal, single-crystal metal surfaces and the nature of chemisorption thereon, even though such surfaces are usually poor catalysts from the point of view of commercial significance.

Progress in the experimental study of surfaces, chemisorption and catalysis was reviewed by Fischer,[2] and we will not discuss this further. We will instead concentrate on the new developments in quantum chemistry represented by the self-consistent-field X-alpha scattered-wave method; after saying a little about the ideas behind this approach—whose history goes back more than forty years—we will describe its applications to several prototype catalytic systems.

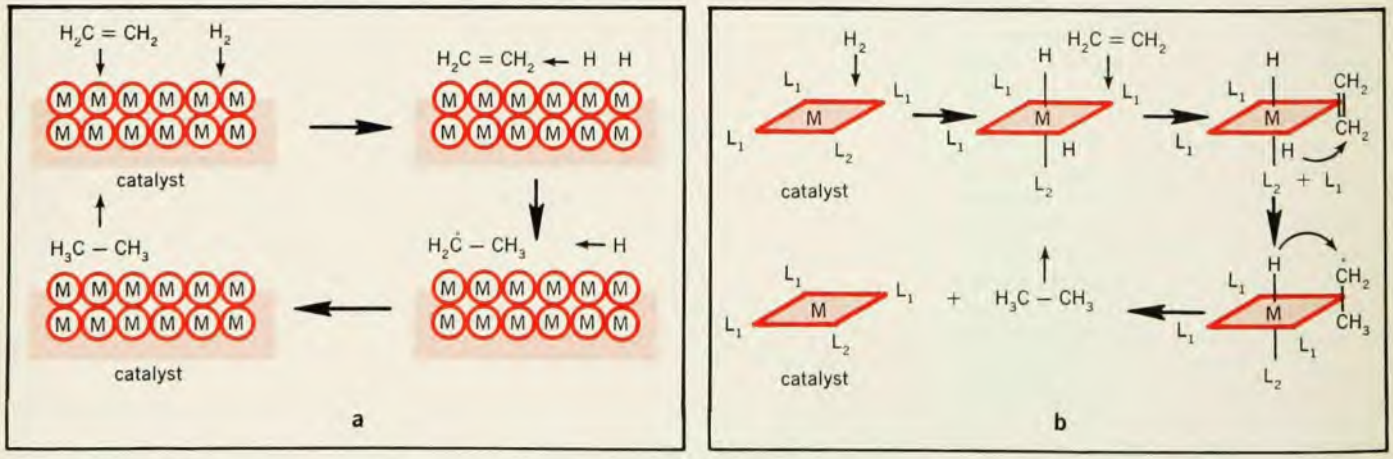
Historical perspective

In 1926, the discoveries of Louis de Broglie, Werner Heisenberg, P. A. M. Dirac, and Erwin Schrödinger led to the development of wave mechanics. Within two years, Douglas Hartree had devised his self-consistent-field method of solving Schrödinger's equation for the electronic structure of isolated atoms. Hartree replaced the Coulomb interactions between all the electrons of an atom and one of these electrons by an average potential arising from the averaged charge of all of these electrons. The resulting atomic potential is approximately spherically symmetrical, making Schrödinger's equation separable and straightforward to solve numerically.

About the same time, Walter Heitler and Fritz London applied wave mechanics to the hydrogen molecule, introducing the valence-bond concept. Robert Mulliken and Friedrich Hund developed the idea of molecular orbitals, based on essentially the same self-consistent-field approach that Hartree had used for atoms. Hans Bethe, Felix Bloch, Léon Brillouin and others applied similar methods to crystals. By about 1932, one knew how to proceed, in principle, with molecular and solid-state theory. Erich Hückel extended molecular-orbital theory, in semiempirical form, to molecules as complicated as ethylene and benzene. The valence-bond concept was further developed by Linus Pauling and others and furnished the basis of the molecular theory that has been taught to chemists ever since. Unfortunately, Schrödinger's equation was much more difficult to solve for molecules than for atoms, and the feeling developed that semiempirical methods were the best that chemists could do in applying wave mechanics to their problems.

The theory of solids in their crystalline form, however, developed much more rapidly. In 1933, Eugene Wigner and Frederick Seitz noticed they could build up a simple crystal like sodium by joining polyhedral cells together, each containing one atom. They solved the one-electron Schrödinger equation for a spherically symmetrical potential within each atomic cell, as in Hartree's self-consistent-field treatment of an isolated atom, but imposed the boundary condition that the wavefunctions and potential join smoothly from one cell to the next. It was found that the energy levels of the system, which are sharp, discrete levels for an isolated atom, broadened into bands, as had been predicted earlier by Bethe, Bloch, and Brillouin. It was out of this energy-band theory, worked out in the 1930's, that physicists learned the differences among metals and insulators and semiconductors. This particular type of study, interrupted by the war, was revived in the later 1940's. During this postwar period, William Shockley, John Bardeen, and Walter Brattain at Bell Laboratories made use of the band theory of solids in their development of the transistor. Indeed, the rapid growth of solid-state electronics technology and the expansion of basic research in solid-state physics during the 1950's and 1960's would not have been possible without the basic principles of band theory formulated during the 1930's.

However, no corresponding advances had come about in quantum chemistry. The development of the digital computer during the 1950's made it possible to carry through much more elaborate calculations on molecules than had been possible in prewar days, and the theoretical chemists began to apply the methods of Heitler and London, Mulliken and Hund, Hückel and Pauling more accurately than had been possible before the war. However, even with the advent of large-scale computers, these theories were inherently difficult and costly to implement on polyatomic molecules, especially those containing heavier atoms. In the Solid State and Molecular Theory Group at MIT, which the senior author organized in 1951, calculations were being carried out simultaneously on both the energy-band theory of crystals and the electronic structure of molecules. One thing was very clear: The methods we had used for energy bands, since the first work of Wigner and Seitz in 1933, resulted in a far more practical approach to calculating band structures than the methods that the chemists were applying to molecules. The chemists' approach was based on the LCAO (Linear Combination of Atomic Orbitals) technique, which when applied to energy bands in crystals is called the "tight-binding" method. We had given up the tight-binding approach as not being nearly as computationally convenient as the Augmented-Plane-Wave and Korringa–Kohn–Rostoker methods, which are sophisticated "muffin-tin" variants of the Wigner–Seitz cellular technique that we



Heterogeneous and homogeneous catalysis. **Part a** shows the heterogeneous catalysis of olefin hydrogenation on the surface of a supported transition-metal aggregate. The major steps of the reaction are: chemisorption of ethylene and hydrogen; hydrogenation of ethylene, and desorption of ethane. **Part b** shows a schematic representation of the homogeneous catalysis of olefin hydrogenation by an isolated "square-planar" transition-metal complex. L_1 and L_2 represent ligands. The major steps of the reaction are: the addition of hydrogen and ethylene as ligands; hydrogenation of ethylene, and dissociation of ethane from the complex. Figure 2

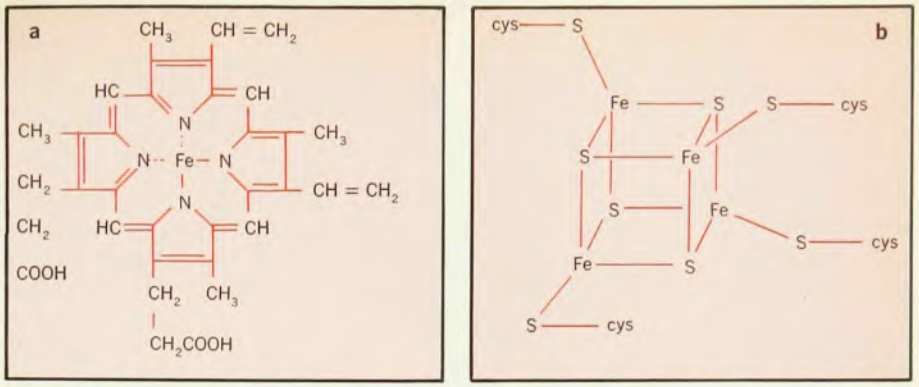
noted above had been used for crystals.

In 1965 and 1966, respectively, we published two papers[11,12] that showed how a molecular-orbital theory of polyatomic molecules might be developed by methods similar to those successfully used in crystals. Our technique, which we call the "self-consistent-field X-alpha scattered-wave" method, consists of two initial stages—the "X-alpha" part and the "scattered-wave" part—to obtain first an initial approximation to the molecular potential and then to solve Schrödinger's equation for the molecule; the second stage leads to an improved molecular potential, and the cycle is repeated until the entire process is self-consistent.

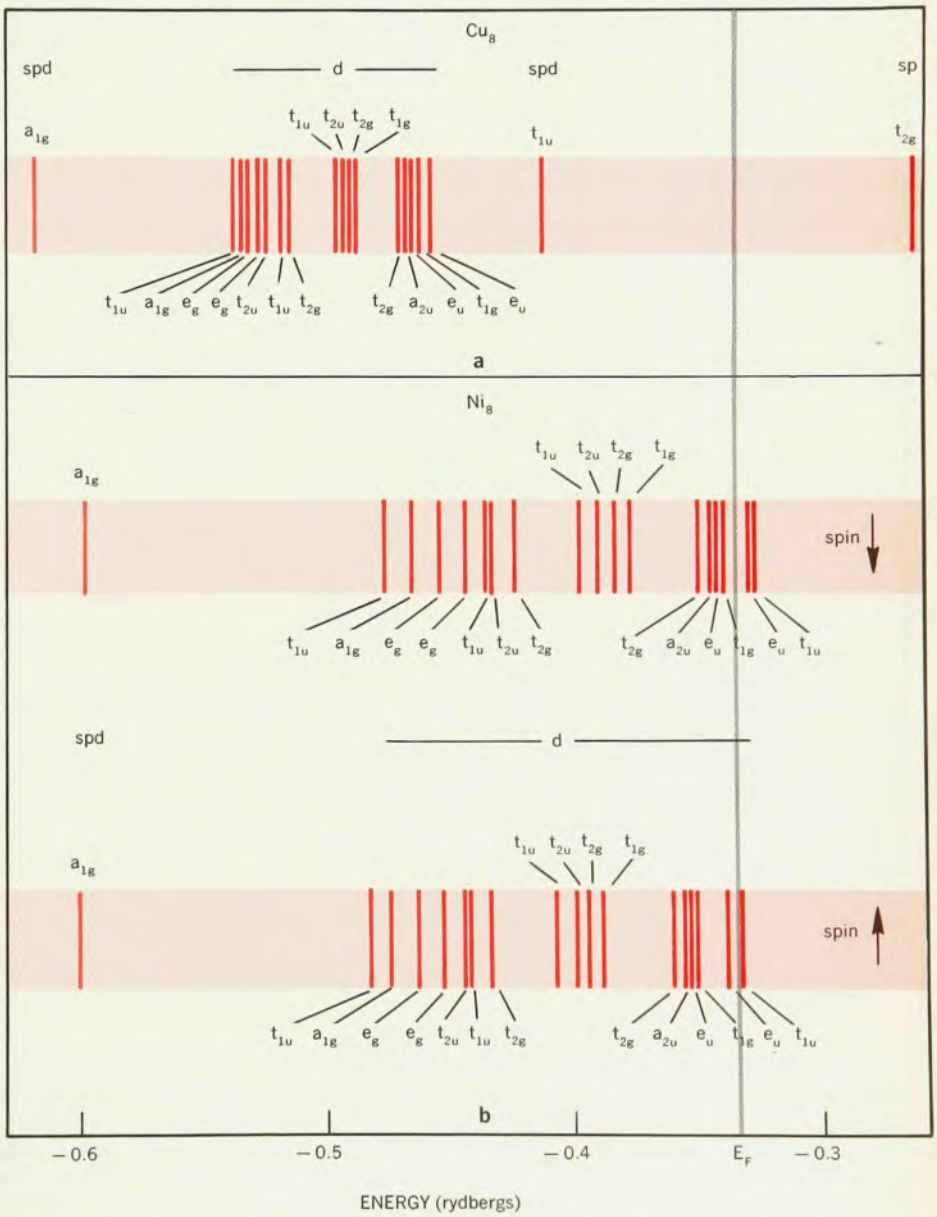
First, in place of the Hartree–Fock approximation to exchange (which theoretical chemists have traditionally used for atoms and molecules) we use the statistical approximation to exchange correlation, proportional to the one-third power of the electronic charge density. This approximation, the X-alpha method,[13] was introduced originally by the senior author in 1951; by 1965 it was being widely used in band-structure calculations for crystals and in atomic-structure calculations. The X-alpha potential, together with the solutions of Poisson's equation of classical electrostatics for a superposition of atomic charge densities, provides the initial approximation to the molecular potential.

Then we have the problem of solving Schrödinger's equation, but without the multicenter-integral difficulty associated with the LCAO approach. We partition the molecule into contiguous atomic, interatomic, and extramolecular regions of spherically averaged and volume-averaged potential, much as in the cellular or "muffin-tin" treatments of solids. Schrödinger's equation is solved in each region, and the wavefunctions, represented in appropriate partial-wave expansions, are joined continuously and with continuous first derivatives across the boundaries separating neighboring regions. We find it convenient to accomplish this wavefunction matching by a "multiple-scattered-wave" procedure analogous to that introduced by Jan Korringa for crystals, instead of by the original cellular method of Wigner and Seitz. This procedure leads to rapidly convergent secular equations that can be solved for the molecular spin orbitals and energies. With the occupied spin orbitals we can then construct the electronic charge density throughout the space of the molecule.

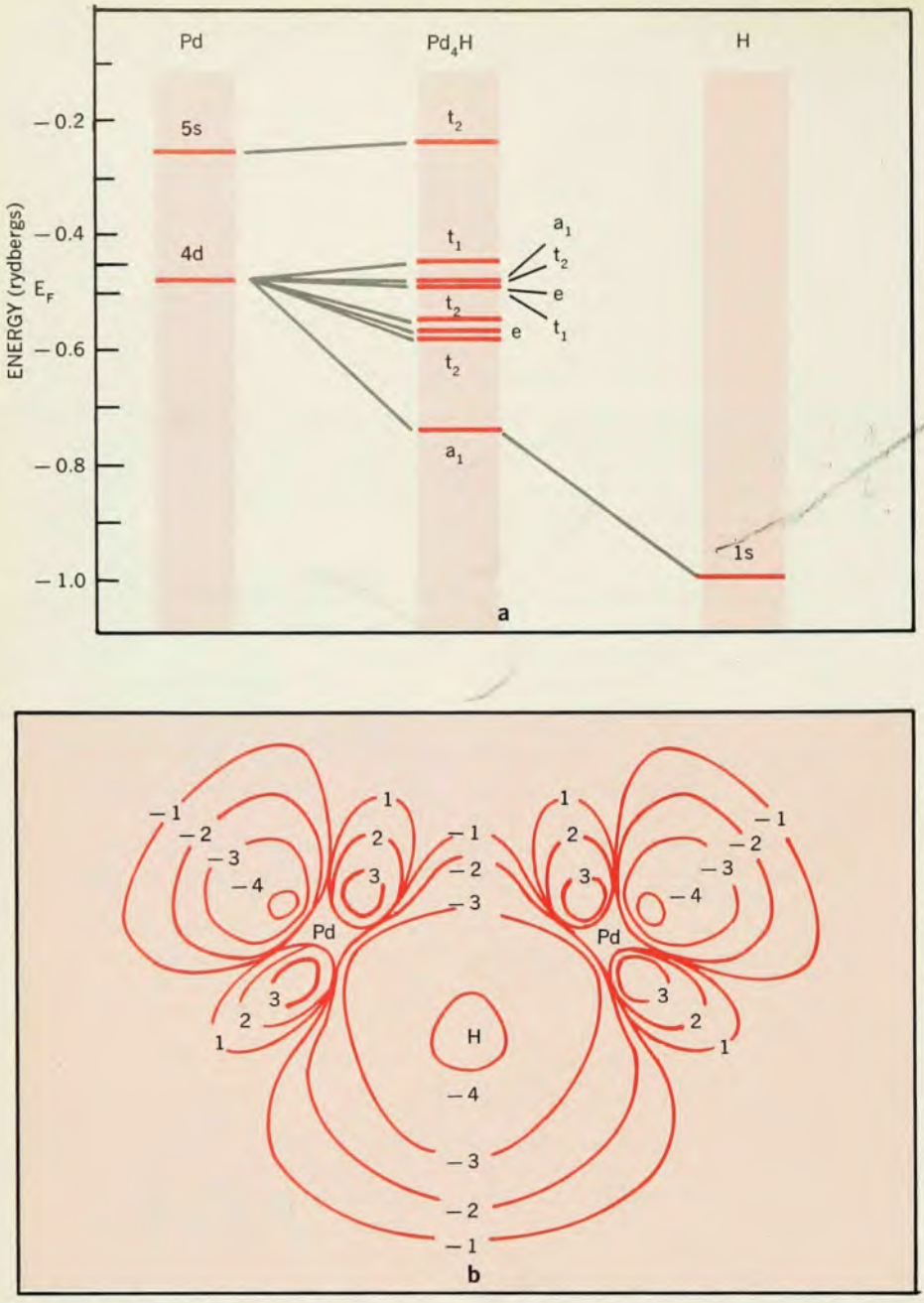
This charge density, in conjunction with Poisson's equation and the X-alpha exchange-correlation expression, leads to a new molecular potential for which Schrödinger's equation can be solved for a new set of spin orbitals. The entire computational procedure is



Hemoglobin and ferredoxin. Part a: The approximately planar iron–porphyrin complex that constitutes the active center of hemoglobin. This complex is normally attached to the polypeptide chain of the hemoprotein via the amino acid histidine. **Part b:** The approximately cubic cluster of iron and sulfur atoms that is the active center of bacterial ferredoxin. The four cysteine molecules attach the cluster to the polypeptide chain of the protein. Figure 3



Copper and nickel-cluster energy levels. Part a shows the SCF-Xα electronic energy levels for a cubic Cu_8 cluster; **part b,** the spin-polarized SCF-Xα electronic energy levels of a cubic Ni_8 cluster. For each cluster, the results are shown for a nearest-neighbor internuclear distance equal to that in the corresponding bulk crystal. The levels are labeled according to the irreducible representations of the cubic (O_h) symmetry group. The "Fermi level" E_F separates the occupied levels from the unoccupied ones. Figure 4



Hydrogen in palladium. Part a: The SCF-Xα electronic energy levels for a tetrahedral cluster of four palladium atoms containing an interstitial hydrogen atom. The levels are labeled according to the irreducible representations of the tetrahedral (T_d) symmetry group, and the top of the d-band is marked by the "Fermi level" E_F. Also shown are the energy levels for a palladium atom (in the $4d^9$ 5s configuration) and a free hydrogen atom. **Part b:** Contour map of the a_1 orbital wavefunction of Pd_4H for the energy level −0.746 Ry shown in part a and plotted in a plane containing two palladium atoms and the hydrogen atom. The contour values decrease in absolute magnitude with decreasing absolute values of the contour labels. The sign of the contour label gives the sign of the wavefunction. To ensure clarity of presentation, the interior nodes of the wavefunction near each palladium nucleus are not shown. Figure 5

iterated until self-consistency is attained.

Between 1967 and 1970, this Self-Consistent-Field X-alpha (SCF-Xα) scattered-wave method was programmed for digital computer with the expert assistance of Franklin C. Smith, Jr. The method was also extended to clusters of atoms in solids, providing a localized description of electronic structure and chemical bonding.[14] It was clear by 1972 that the technique has many advantages over other theoretical approaches to molecules and solids. For example, relatively little computer time is required, even for polyatomic systems containing heavy atoms. The X-alpha statistical total energy satisfies the virial and Hellmann–Feynman theorems.[13,14] The theory also satisfies Fermi statistics, and the total energy goes to the proper separated-atom limit.[13,14] In conjunction with the "transition-state" concept, this approach leads to an accurate description of excited spin orbitals, including relaxation effects.[13,14]

The SCF-Xα scattered-wave method and transition-state procedure have been applied successfully to a wide range of molecules and solids over the past few years, and the computer programs are now in wide use at many other institutions. We have no space here to summarize all these applications or to cite all the recent references to this work. However, several articles and a textbook have been published that review the theory, computational procedure, and range of applications up to 1973.[13–17] Since then the theory and computational procedure have been generalized to overlapping atomic spheres and true cellular representations of the potential, permitting one to go beyond the original muffin-tin approximation. Let us now focus on a few recent applications of this technique to systems of catalytic importance.

Heterogeneous catalysis

An important electronic factor in heterogeneous catalysis by transition metals and their alloys is the fundamental role of the d-electrons, especially their behavior at the catalyst surface. Let us first consider Cu_8 and Ni_8 clusters with cubic geometry, the simplest structure that has been used to characterize the surfaces and dispersion of small catalytic particles.

The SCF-Xα electronic energy levels for these clusters, calculated in collaboration with Richard P. Messmer's group at GE,[18] are shown in figure 4. We may characterize the complete set of Cu_8 energies shown in figure 4a as a dense band of d-levels bounded above and below, respectively, by the t_{1u} level at −0.411 rydbergs and the a_{1g} level at −0.617 Ry, both of which are predominantly s- and p-like in character, but with some d admixture. ("a_{1g}", "t_{1u}", etc. are the conventional symmetry labels for the orbitals of a cubic molecule.) Thus if we regard this $a_{1g} - t_{1u}$ energy interval as the precursor of the sp-band in bulk, crystalline copper, then the Cu_8 d-band is totally overlapped by the sp-band, as in the solid, although the band width is smaller in the cluster. Even the onset of electronic excitations from the highest fully occupied orbitals t_{1u} and e_u to the first empty orbital t_{2g}, computed by the transition-state procedure,[13,14] occurs in the same energy range (2.0–2.6 eV) as the interband transitions that are responsible for the characteristic color of solid copper.

Contour maps for two of the orbital wavefunctions of Cu_8, plotted in the plane of the cube face, have been shown in figure 1. In figure 1a, we have the normalized a_{1g} orbital corresponding to the energy level −0.533 Ry shown in fig-

ure 4a. The d-like nature of the a_{1g} orbital is clearly evident in the "four-lobe" contours spreading out around each copper nucleus. This orbital is strongly bonding in the plane of the cube face, as is indicated in figure 1a, by the large amount of net wavefunction overlap. The a_{2u} d-orbital with energy −0.467 Ry is mapped in figure 1b. In contrast to the a_{1g} bonding d-orbital, a_{2u} is antibonding in the plane of the cube face because there is a net cancellation of positive and negative regions of the wave function, leading to effectively zero net overlap.

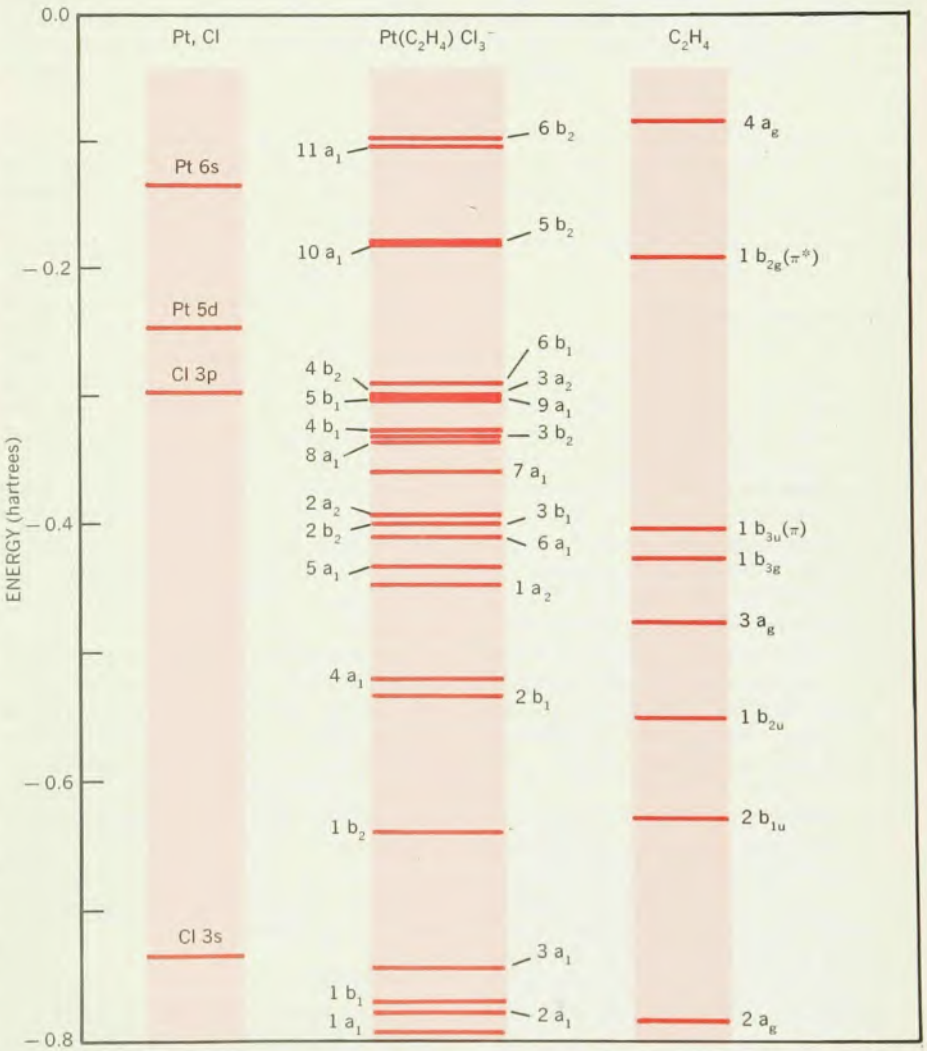
Calculations by the spin-unrestricted SCF-Xα scattered-wave technique have also been carried out in collaboration with Messmer's group[18] for the simple-cubic Ni_8 aggregate, and the resulting electronic energy levels are shown in figure 4b. In comparison with the Cu_8 results, the Ni_8 d-band is shifted to higher energies, significantly widened and split in energy by the paramagnetic spin polarization, which arises because the highest occupied d-orbital e_u is only half filled. The electronic structure of the Ni_8 cluster is similar to the spin-polarized band structure for ferromagnetic crystalline nickel, especially with respect to the high density of d-states around the Fermi level, a condition that appears to be correlated with the generally high catalytic activity of nickel, as compared with copper. Moreover, the spin magneton number per atom (0.25) in paramagnetic Ni_8 is considerably less than the value (0.54) for ferromagnetic crystalline nickel. This decrease is consistent with the results of paramagnetic susceptibility measurements for small catalytic nickel particles.[19]

All of the atoms of Cu_8 and Ni_8 are "surface" atoms, so that figure 4 is a measure of the respective "surface densities of states." The orbitals mapped in figure 1 illustrate the types of "surface chemical bonds" (for example, the directed d-lobes at the cube corners) that may be responsible for the capacities of highly dispersed transition-metal particles[6] (or stepped surfaces of crystalline transition metals[20]) to act as centers of chemisorption and catalysis. SCF-Xα calculations for 13-atom lithium clusters, carried out with Michel Boudart's group at Stanford[21] suggest the icosahedral geometry to be more stable than the cubo-octahedral one, a result of possible general significance to the structure of small particles. A unique characteristic of an icosahedral particle is that it exposes only close-packed (111)-type surfaces. Preliminary SCF-Xα studies of the chemisorption of ethylene (C_2H_4) on the surfaces of small metal clusters suggest increasing metal–C_2H_4 bond strength from nickel to platinum.[18,22] Of the three metals, nickel, palladium and platinum, palladium is well known to be the most active catalyst for ethylene hydrogenation, a property that appears to be correlated with the moderate (not "too strong," not "too weak") Pd–C_2H_4 chemisorption.

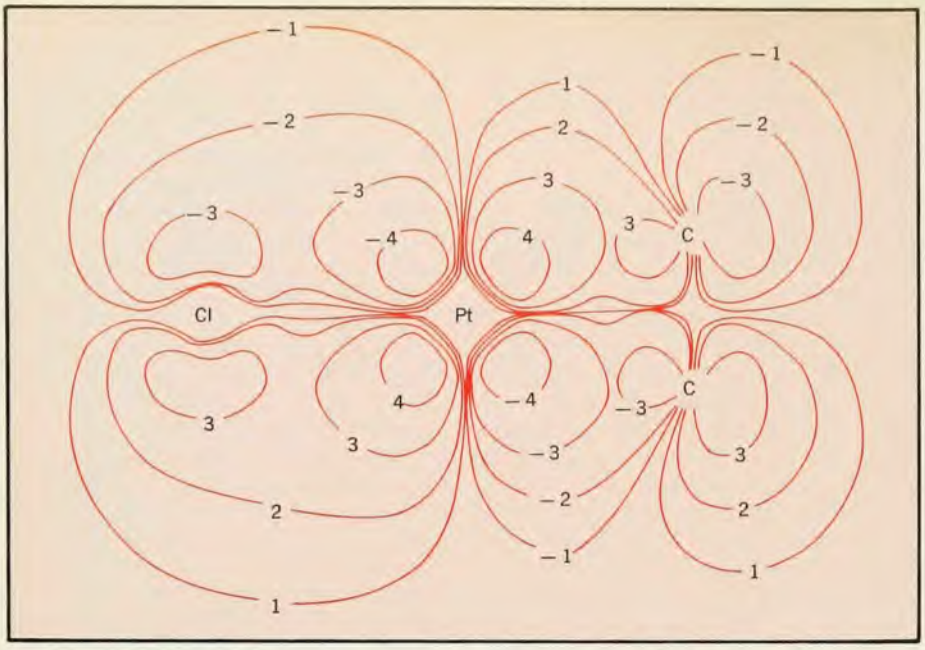
Hydrogen in metals

Molecular hydrogen is dissociatively chemisorbed, and the resulting hydrogen atoms absorbed, by the small metallic particles that constitute the active centers of hydrogenation catalysts—for example, palladium-based catalysts. Of fundamental importance, therefore, is the nature of the interaction of interstitial hydrogen in catalytic palladium aggregates as a function of cluster size and geometry. In figure 5a, we show the SCF-Xα electronic energy levels for the simplest palladium–hydrogen system investigated at MIT, a single hydrogen atom at the center of a tetrahedral Pd_4 cluster. Of special significance is the "splitting off" of a hydrogen-bonding a_1 level from the bottom of the Pd_4 d-band. This splitting occurs at approximately the same relative energies as determined by Dean Eastman's group[23] in photoemission measurements for a two-phase mixture of β-PdH with Pd. The Pd(4d)–H(1s) hybridization in the a_1 orbital, responsible for proton screening, is shown in the orbital contour map, figure 5b. A comparison of the electronic structures and binding energies for hydrogen in palladium, platinum and nickel aggregates as functions of cluster size and geometry should lead to a better understanding of observed differences in hydrogen solubility in these metals and the possible effects on catalytic behavior.

For bimetallic cluster catalysts,[7] one can study the effects of "alloying" on the electronic structure of metal aggregates by systematically substituting "impurity" atoms in the cluster (for example, Cu in Ni_8 or Ni_{13}) and then carrying out the SCF-Xα cluster calculations to self-consistency. It is also possible to study the effects of supporting materials, such as silica (SiO_2), on



Zeise's anion. The SCF-Xα electronic energy levels for this platinum–olefin complex, $[Pt(C_2H_4)Cl_3]^-$, which is similar in geometry to the reaction intermediate illustrated in figure 2b, are shown here labeled according to the irreducible representations of the C_{2v} symmetry group. The highest occupied level is $6b_1$, and the lowest unoccupied level is $10a_1$. Also shown are the SCF-Xα energy levels of an isolated ethylene molecule, together with those of the platinum (in the $5d^96s$ configuration) and chlorine atoms. Figure 6



Contour map of Zeise's anion. This is the $2b_2$ π-bonding orbital wavefunction of the complex $[Pt(C_2H_4)Cl_3]^-$ plotted in a plane containing the central platinum atom, the trans-chlorine ligand, and the ethylene ligand (see figure 2b). The hydrogen atoms lie out of this plane, so their contribution to the chemical bonding is not visible. The contour values decrease in absolute magnitude with decreasing absolute values of the contour labels, and the sign of the contour label gives the sign of the wavefunction. The interior nodes of the wavefunction near each atomic nucleus are not shown, to ensure clarity of presentation. Figure 7

the electronic structures and surface properties of the metal clusters—embed the metal cluster in the local molecular environment of an SiO_2 lattice, and then carry out SCF-Xα calculations on the composite system.

Homogeneous catalysis

Let us now consider Zeise's anion $[Pt(C_2H_4)Cl_3]^-$, which is an important prototype example of transition-metal olefin π-electron complexes thought to be reaction intermediates in homogeneous olefin catalysis.[8] The geometry of Zeise's anion is similar to that of the metal–olefin complex shown in figure 2b. The SCF-Xα electronic energy levels calculated in collaboration with Notker Rösch and Messmer[24] are shown in figure 6. In figure 7 is a contour map of the $2b_2$ orbital, the orbital responsible for the π-bonding of ethylene to platinum via the "back-donation" of Pt-5d electrons into the empty C_2H_4-π^* orbital.

The optical and photochemical properties of Zeise's anion are particularly important because their analysis provides insight into observed photocatalytic effects in olefin hydrogenation by platinum catalysts.[25] Using the transition-state procedure,[13,14] we have determined all the important optical excitations in Zeise's anion; they are compared with experiment in tables II and III of reference 24.

The unoccupied ethylene-like $5b_2$ orbital of Zeise's anion is antibonding with respect to platinum. Thus the $^3B_1$ and $^1B_1$ multiplets at calculated energies[24] of 3.5 eV and 4.3 eV, respectively, arising from the $3a_2 \rightarrow 5b_2$ platinum-to-ethylene charge-transfer excitation, would be expected to weaken the platinum–ethylene bond. In fact, Zeise's anion in solution undergoes a photoaquation reaction in which ethylene is replaced by a water molecule.[24] The onset of this reaction is at about 3.6 eV and reaches a maximum quantum yield at about 4.2 eV. Thus it is possible that these transitions to the $5b_2$ orbital weaken the Pt–C_2H_4 bond and allow the aquation to take place. It has been observed that the rate of catalytic hydrogenation of ethylene on a metallic platinum surface is significantly reduced when the surface is illuminated with light of photon energy 4.2 eV.[25] It is possible that platinum-to-ethylene charge-transfer excitations occurring at this energy (analogous to those occurring in Zeise's anion) weaken the Pt–C_2H_4 bonds and lead to photodesorption of C_2H_4 from the platinum surface, with the concomitant reduction in catalytic activity. SCF-Xα transition-state calculations for C_2H_4 chemisorbed on platinum aggregates are in progress to test this hypothesis.

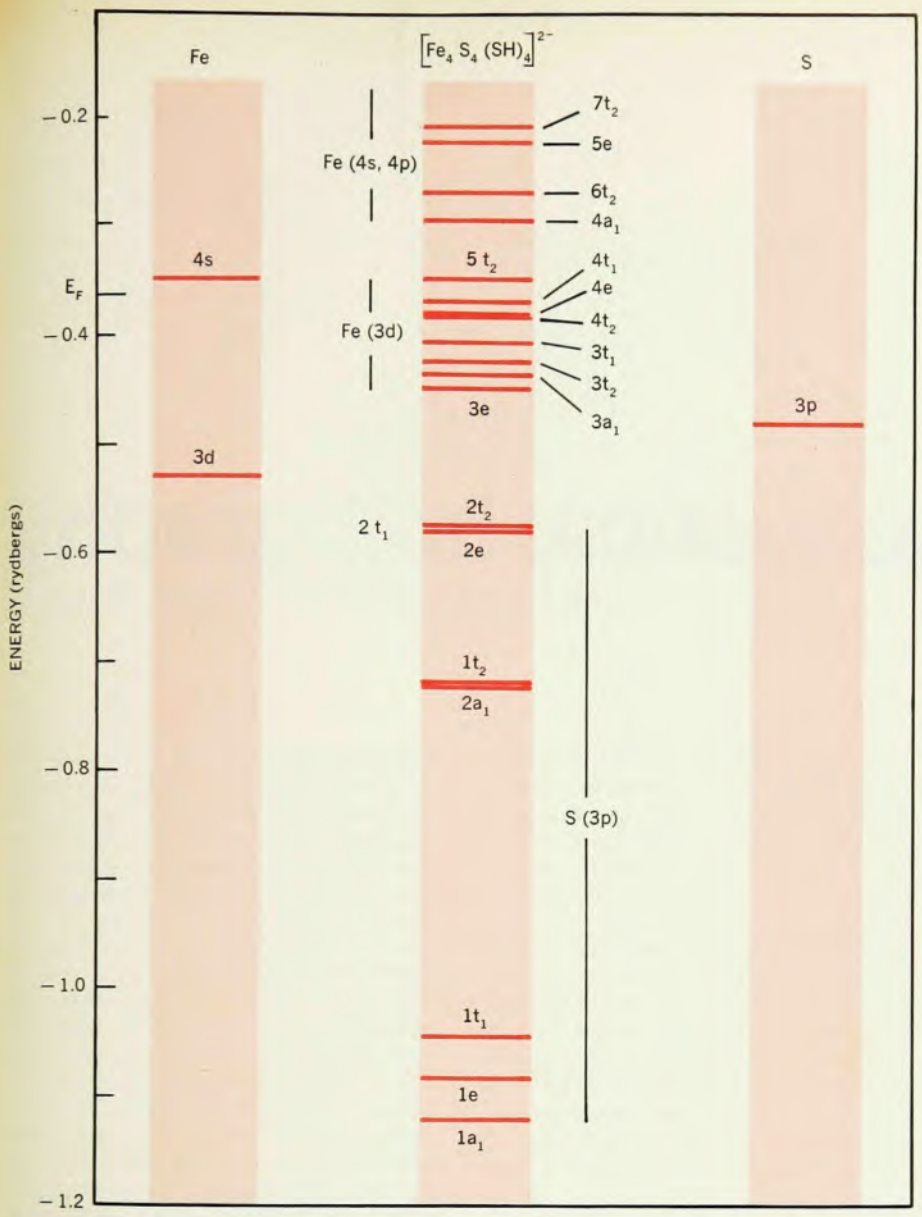
Biocatalysis

Intermolecular charge transfer or charge polarization appears to be crucial to the biocatalytic activities and specifities of some enzymes and proteins. For example, ferredoxin $[Fe_4S_4(S\text{-}cys)_4]^{2-}$, with the cube-like structure of alternating iron and sulfur atoms shown in figure 3b,[10] is the active center of a protein believed to catalyze electron transfer in nitrogen fixation (the conversion of nitrogen to ammonia) by soil bacteria, a process of key importance in the nitrogen cycle. In figure 8 we display the SCF-Xα electronic energy levels recently calculated at MIT for $[Fe_4S_4(SH)_4]^{2-}$, a preliminary model of ferredoxin—one in which the cysteine-containing polypeptide moieties have been replaced by four hydrogen atoms. The most important feature of the electronic structure is the band of predominantly iron d-orbitals occupied up to the $4t_1$ level and including the low-lying empty $5t_2$ d-orbital. The $5t_2$ orbital, localized with respect to each iron atom and directed away from each cube corner (compare figure 3b), can readily accept electrons from an occupied orbital of proper symmetry, overlap and energy, localized on a neighboring molecule.

It is interesting to compare the high density of d-levels and presence of low-lying unoccupied states around the Fermi level in our model for ferredoxin with the calculated density of states around the Fermi level in Ni_8 (see figure 4b). This is a striking similarity between the electronic structures of two quite different prototype catalytic systems, one biological and the other nonbiological. The occurrence of a relatively wide sulfur p-band just below the band of localized d-levels in figure 8 also suggests some similarity between the electronic structure of ferredoxin and the band structure of crystalline iron disulfide.[26]

The array of iron and sulfur atoms in ferredoxin is actually somewhat distorted from the ideal cubic geometry shown in figure 3b.[10] SCF-Xα scattered-wave calculations for this lower symmetry structure show a lifting of certain orbital degeneracies and a significantly lower total energy, like the effects of a Jahn–Teller distortion. Melvin Calvin has recently suggested[27] that ferredoxin could function as an ideal electron acceptor and center of electron–proton recombination in a synthetic enzyme system designed to catalyze the photosynthesis of hydrogen, in sufficient quantities, to serve as a possible source of energy.

We hope that these examples demonstrate that, even in its present approximate form, our approach offers real hope of eventually developing truly predictive theories of catalytic behavior, whose importance to the energy problem, pollution control, and biology have already been pointed out. This is what happened to solid-state physics when the fundamental band-theoretical developments of the 1930's led to the advances in solid-state electronics technology during the 1950's. One may hope with a good deal of justification that similar advances will be made in



Ferredoxin-model energy levels. These are the SCF-Xα electronic energy levels for the complex $[Fe_4S_4(SH)_4]^{2-}$, a prototype model of the ferredoxin cluster shown in figure 3b. The levels are labeled according to the irreducible representations of the T_d symmetry group. The highest occupied level is $4t_1$ and the lowest unoccupied level is $5t_2$. Also shown for comparison are the energy levels for an iron atom (in the $3d^64s^2$ configuration) and a sulfur atom. Figure 8

the fundamental understanding of complex catalytic molecules and solids, and in their technological applications, in the next twenty years.

* * *

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