Paul S. Bagus
Arthur R. Williams

Electronic Structure Theory

This paper reviews the history of IBM contributions over the last quarter century to electronic structure theory. The two main sections of the paper deal with large-scale computations in quantum chemistry and the study of the electronic structure of solids. The paper briefly discusses the methods of ab initio quantum chemistry, a field in which IBMers have devoted major effort and made substantial innovative, scientific contributions. Partly as a result of these contributions, it is now possible to use these methods to address theoretically problems of practical importance in chemistry. Major contributions toward understanding the electronic structure of solids, particularly with regard to metallic bonding, surface electronic structure, the nature of magnetism, and semiconductor defects, are discussed as well as pioneering efforts in the analysis of photoemission and low-energy electron diffraction data.

A. Large-scale computations in quantum chemistry

I. Introduction

This section of the paper deals primarily with the determination of the electronic structure of molecules by rigorous *ab initio* methods. Work in this field belongs to a discipline of theoretical chemistry called quantum chemistry, and this section deals with a subset of possible applications of quantum mechanics to chemistry; the subset is primarily concerned with the motion and energetics of electrons bound to nuclei and to the motion and interaction energies of atoms composing molecules. The first applications of quantum mechanics to chemical problems (atomic and molecular spectroscopy) were made in the 1920s shortly after the formulation of the basic principles of quantum mechanics. Today, *ab initio* methods in quantum chemistry can successfully address problems in a variety of disciplines ranging from free radical spectroscopy to surface chemistry [1, 2]. IBM has been heavily involved in the development and application of these methods and has contributed in many significant ways to progress in this field over the past two decades.

The fundamental quantum-mechanical equation of motion is given by Schrödinger's equation [3]. A knowledge of the solutions of this equation can lead to theoretical predictions of many of the observable properties of atoms, molecules, and extended condensed-phase systems (solids and liquids). However, because of the inherent complexity of this equation, even for atoms and molecules with only a few electrons, it is essential to use approximate methods. In fact, as late as the mid-1930s there were accurate solutions for only two two-electron systems: He [4] and H_2 [5]. More complex systems required the use of crude and often uncertain approximations [6]; consequently the results were of limited reliability. In addition, different approximation methods often led to contradictory results. Thus, the objective of *ab initio* quantum chemistry was (and is) to obtain accurate, albeit approximate, solutions to the Schrödinger equation for atoms and molecules.

The data processing power of modern digital computers is one of the essential requirements for accurate molecular electronic structure calculations. There must also be theoretical and mathematical methods which, when implemented in suitable computer programs, will lead to solutions of the desired accuracy. In the mid-1950s computers with reasonable, although by present standards very modest, power were constructed and became available to quantum chemists. This availability spurred interest in the development of methods that would have practical computational value [7–9]. The two parallel

developments in computational power and theoretical and numerical methods have brought us today to the point where it is possible to obtain accurate, reliable theoretical predictions relating directly to problems of *current* chemical interest. First, the application of *ab initio* methods can provide sound, detailed, and reliable theoretical bases for understanding observed results. This has always been a prime objective of quantum chemistry. Now that accurate results are generally possible, they can be used to guide and complement experimental efforts. A particularly significant aspect of this is the prediction of new, as yet unobserved, properties. Another valuable aspect is the ability to have an independent assessment of the accuracy of experimental results. Finally, accurate theoretical results are valuable for situations where experiments are either impossible or very difficult, *e.g.*, in identification of short-lived intermediates in chemical reactions [2(e)] or properties of interstellar molecules [10]. In a sense, *ab initio* quantum chemistry has become another of the "spectroscopic" methods of modern chemistry; however, it is unique in its ability to construct and evaluate theoretical models.

Work in *ab initio* quantum chemistry was begun at the IBM San Jose Research laboratory by E. Clementi, who came there in 1961. He was joined shortly afterwards by R. K. Nesbet, A. D. McLean, and M. Yoshimine. The current members of the group actively working in bound-state molecular electronic structure theory are P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine. Their activities have been enhanced by close contacts and collaboration with research groups outside IBM. There has been major effort devoted by IBM to the development of new theoretical methods and computer programs to implement these methods. The activity in quantum chemistry is concentrated on large-scale scientific computations in a variety of scientific disciplines. For example, in 1967 Clementi [11] reported an extensive *ab initio* study of the interaction of the NH_3 and HCl molecules to form NH_4Cl. He made significant contributions to the understanding of hydrogen bonding [12], a rather general chemical mechanism for the formation of molecules; in NH_4Cl the bond involves both charge-transfer ($NH_4^+Cl^-$) and covalent interaction processes. Clementi analyzed the nature of the bonding and carefully considered the consequences of neglecting correlation effects. For the first time, an extensive region of the potential energy surface of a chemically interesting molecule was mapped out. When the work was performed, and for some time afterward, this was the largest molecule for which such a potential surface was available [13, 14].

It is interesting to note that although NH_4Cl was well known to exist as a molecular solid, at the time Clementi carried out his work it was universally believed [15, 16] that gaseous NH_4Cl was not stable toward dissociation into NH_3 and HCl. Clementi's work predicted that gaseous NH_4Cl was indeed stable by ≈ 76 kJ/mole ($\approx$19 kcal/mole) and that there was no activation barrier hindering formation of the molecule. These conclusions were completely contrary to the accepted ideas about this relatively simple system, yet because of the care taken in his theoretical work, and because he knew the reliabilities and uncertainties of the *ab initio* method used, Clementi argued that his prediction was correct. Less than two years later, Goldfinger and Verhaegen [17] reported an experimental study that confirmed Clementi's theoretical prediction. The error of the theoretical value was about 25%; however, it was sufficiently accurate to guide the experimental search in the proper direction.

Once a substantial base of methods and programs had been developed at the IBM San Jose laboratory, closer interactions between theorists and experimentalists were encouraged. This interaction led to several important contributions toward understanding practical chemical problems of interest. As examples, we cite the work of Liu and Siegbahn [18-20] on the calculation of an accurate potential energy surface for H_3 in the hydrogen exchange reaction $H + H_2 \rightarrow H_2 + H$ and the prediction of features of the $H + H_2$ scattering. This reaction has long been considered a first and important testing ground for fundamental theories of chemical kinetics [21]. This work marked a major landmark in chemical reaction theory. For the first time, a potential surface was available of high enough quality that unambiguous tests of various theories and approaches to the treatment of reaction dynamics could be made [22].

Another example of the close collaboration of theorists and experimentalists was work by Bagus *et al.* [23-25] related to the theory of x-ray photoemission in ionic solids. In this study the ideas and methods of quantum chemistry were applied to the analysis of properties of condensed materials rather than molecules. It was also an application concerned with highly excited electronic states created when x-rays are used to ionize the core levels of a system. Such x-rays can provide very useful information about the nature of the chemical bonding in a system [26]. The theoretical idea that atoms, particularly metal atoms, retain much of their individual free-ion character in ionic solids is widely used to explain various electronic properties of these solids [27, 28]. This notion is incorporated in the theoretical formalisms described as crystal field theory and liquid field theory. Bagus and his collaborators were able to show that the atomic character of Mn^{2+} was able to account for observed features in the x-ray photoemission spectra of MnF_2 and MnO. Most

importantly, they also showed that correlation effects in the free ion led to new features that could not be predicted from independent-particle (one-electron) theory. In fact, they were able to show when one-electron theory should be expected to work well and when it should break down badly [25]. Their predictions of the new features were verified by experimental work [29] only a few weeks later, nicely illustrating the ability of current *ab initio* quantum chemistry to conduct both theoretical and experimental studies on a comparative time scale.

We will now briefly review the basic theoretical foundations and relate them to computational capabilities needed to perform accurate *ab initio* calculations. Interestingly, the ability to perform sophisticated manipulation of a large data base is easily as important as the ability to rapidly perform arithmetic operations ("number crunching"). Important methodological contributions are identified. With the background thus established, we review some scientific studies carried out at IBM and demonstrate their scope and relevance to chemistry. Finally, some perspective for the future is given.

II. Theoretical foundations and computational requirements

The quantum-mechanical Hamiltonian operator $\mathcal{H}$ for the motion of the electrons in the field of nuclei at fixed positions is the starting point for virtually all work on molecular electronic structure [30]. Schrödinger's equation relates $\mathcal{H}$ to the quantized energy values (eigenvalues) E_I by use of wave functions Ψ_I. In order to understand much of the chemistry, and in particular, the way in which a reaction proceeds, it is necessary to know the interaction energies between atoms and molecules for many different sets of nuclear coordinates. In principle, these E_I must be determined in a $(3N - 6)$-dimensional space, where N is the number of nuclei involved. In practice, chemical considerations can be used to substantially reduce the dimension of the "interesting" nuclear coordinate space; however, it is still often necessary to know the E_I and Ψ_I for a large number of nuclear coordinates [2(e)].

The greatest difficulty in obtaining solutions to Schrödinger's equation arises from the electron-electron repulsion term, which makes it impossible to separate the motions of individual electrons. Thus, Ψ_I is a general function of the coordinates of all n electrons. Except for one-electron systems, it has not been possible to obtain closed-form solutions for the Schrödinger equation. Two systems that are of only modest size by normal chemical standards are the zinc atom, with $N = 30$ electrons, and benzene, with 42. In the first, Ψ is a function of 90 coordinates (neglecting electron spin); thus the requirements for tabulating, let alone evaluating, a numerical solution for Schrödinger's equation are staggering; at least 10^{90} values would be required to specify Ψ at a rather coarse grid. It can readily be seen that the n-electron problem cannot be solved "exactly" except for truly *small* systems. The problem thus becomes one of obtaining "accurate" approximate solutions through the use of good, reliable approximate methods.

The usual approach with a function like Ψ, where the general form is too complicated, is to replace it with an approximate functional form Φ that is tractable and to examine the consequences of that approximation. Thus, it is assumed that the wave function can be written as a product of functions of the coordinates of one electron. These one-electron functions φ_i are called orbitals or molecular orbitals (MOs). The electrons are, in a sense, independent of one another; thus, the approximation is often referred to as the *independent-particle model*. Since it is only necessary to specify the φ_i to define Φ, this function is a vastly simpler quantity to deal with than the exact Ψ.

Although Φ is a much simpler function to handle than Ψ, it is necessary to understand the nature of the approximations introduced when Φ is used. Note that Φ is an exact solution for a Hamiltonian $\mathcal{H}_0$ of the form

$$\mathcal{H}_0 = -\hbar^2/2m\,\Sigma_i\nabla_i^2 + \Sigma_i\overline{V}(\mathbf{x}_i) + \Sigma_{a<b}Z_aZ_b\,e^2/R_{ab}\,;$$
$$V' = \Sigma_i\overline{V}(\mathbf{x}_i)\,. \qquad (1)$$

Here, the potential V', representing the electrostatic interactions of the electrons with themselves and with the nuclei, is expressed as a sum of one-electron terms. In this case, $\mathcal{H}_0\Phi = E^0\Phi$ can be factored into separate, one-electron equations for each MO. However, the exact electron-electron interaction, $V = \Sigma_{i\leq j}e^2/r_{ij}$, cannot be expressed in the form of V'. At best, a $\overline{V}$ is found such that the difference $\Delta V = V - V'$ is reasonably small. Thus, $\mathcal{H} = \mathcal{H}_0 + \Delta V$. If ΔV is sufficiently small, E^0 and Φ will be good approximations to the exact solutions Ψ and E. Furthermore, ΔV can be treated as a perturbation and E^0 and Φ can be improved by relatively straightforward techniques.

The Hartree-Fock (HF) method is a variational procedure for determining a V' or $\overline{V} = V_{\widehat{\text{HF}}}$ that has the desirable characteristics. In fact, HF wave functions and energies are quite useful both in themselves and as starting points for improved wave functions. Hartree-Fock theory is the first or lowest level in a hierarchy of accurate *ab initio* methods, which can be applied today with relative ease to a wide variety of molecules [30(a), 13].

[A more sophisticated but closely related multi-configuration HF theory (MCHF or MCSCF) is increasingly being applied to molecular problems [31].] The HF method is an independent-particle model where the potential and orbitals are obtained by a self-consistent-field (SCF) method.

Although the HF equations are vastly simpler than the original Schrödinger equation, coupled three-dimensional integro-differential equations arise for molecules of general geometry. These equations present formidable problems for direct numerical treatment and are normally cast in matrix form [9, 32, 33]. The MOs are expanded in terms of fixed elementary functions χ. An expansion SCF procedure is satisfactory provided the basis set χ is sufficiently flexible to provide a good representation of the HF MOs and at the same time sufficiently compact to result in Fock matrices F of reasonable order. The basis sets used to represent molecular wave functions are normally based on functions carefully chosen to accurately represent the HF orbitals of the atoms that compose the molecule and may be supplemented with extra functions chosen to represent certain changes in the atomic charge distribution after formation of the molecule. The determination of suitable basis sets is an essential prerequisite for the calculation of molecular wave functions. As a very rough guide, the number m of basis functions required for a reasonably accurate representation of a molecular wave function ranges between $2n$ and $3n$, where n is the number of electrons. There have been extensive efforts at San Jose to develop a suitable program [33] to determine accurate basis sets for atoms and to compile such sets [34–39]. These efforts have contributed in an important way to the current ability to compute molecular wave functions. It is worth noting that the compendium of atomic HF basis sets and wave functions by Clementi [34] is one of the most cited works in the quantum chemistry literature.

It is now possible to characterize some of the sources of computational complexity and to describe methods adapted by IBM scientists to make the problems tractable. The first concern is with the integrals needed to determine the elements of the Fock matrix **F**. These integrals are particularly difficult when the various χ are centered about different nuclei, and the time required to evaluate them was once considered the major problem in *ab initio* quantum chemistry [7]. On a computer with the speed of an IBM 3033 and with current algorithms, the time required to evaluate an individual integral is trivial. For χ with a Gaussian $\exp(-\alpha r^2)$ radial dependence, Clementi and his collaborators [40] and others [41, 42] have developed programs that require representative times of $\approx$0.1 ms to compute an individual integral. For χ with an exponential $\exp(-\zeta r)$ radial dependence, the numerical problems of integral evaluation are more formidable. However, for diatomic and linear molecules, Liu, McLean, and Yoshimine [43] have developed algorithms and computer programs that can compute integrals in times comparable to those required for Gaussian type χ. Their program is an estimated order of magnitude faster than similar programs developed by others. This is quite important because an exponential basis set appears to offer significant advantages for very accurate wave functions [44] and because it is useful to benchmark Gaussian with exponential basis sets [20].

However, there are a large number of integrals of order $m^4/8$ where there are m basis functions. For a relatively simple system such as benzene ($m = 100$), there would be $\approx 10^7$ two-electron integrals (neglecting any savings due to molecular point-group symmetry). Although such a calculation would take under one hour to compute, it would require approximately half of a 2400-foot tape written at 6250 bits per inch to store the results. Thus, it would seem that the m^4 dependence would make work on *large* systems very difficult indeed. When one considers the cytosine-guanine ($C_4N_3OH_5$—$C_5N_5OH_5$) base pair studied by Clementi [45], where $m \approx 250$ would be required for reasonable accuracy, it is seen that $\approx 5 \times 10^8$ integrals, well over ten hours of computing time, and approximately eleven tapes would be required to store the results. Work on still larger systems would appear essentially impossible.

One consideration useful in vastly reducing the apparently huge requirements for computational time and data storage is the strong exponential dependence of the magnitude of a multicenter two-electron integral on the distance between the nuclei where the basis functions are centered. Thus, in large molecules many nuclei are sufficiently distant from one another that the great majority of integrals are effectively zero. Although this fact had been known for some time, Clementi [46] was the first to point out how it could be used to reduce the ultimate m^4 dependence of the integral calculation. He did this by ordering the calculation of integrals first over centers and then over basis functions belonging to a center. Thus, if two centers were sufficiently far apart, all integrals involving the product of their basis functions could be neglected. When Clementi's algorithm is used, the dependence of the number of nonzero integrals (and hence the computational requirement) on m becomes complex [46]; it can be roughly approximated as $N(m/N)^4$. Thus, for the cytosine-guanine example, the number of integrals that must now be computed represents a two-order-of-magnitude decrease in computing time and data storage requirements. In addition, these requirements for large molecules grow much less rapidly than appeared to be the

case. Clementi and his collaborators [45, 47, 48] have extensively exploited his algorithm in their studies of the electronic structure of proteins and amino acids.

For the same reasons just discussed, many of the nonzero integrals are also small. Thus, it is only necessary to know the values to a number of decimal places; it is not necessary to retain the same number of significant figures for each integral. The largest integrals are of order one, and if these large integrals are stored to eight decimal places, fewer decimals are required for the smaller integrals without any loss of accuracy. For example, for an integral in the range of 10^{-5} to 10^{-6} only three decimal places need to be retained. Bagus and Viinikka [49] and McLean [50] were among the first to develop packing and unpacking algorithms so that only the required number of decimal places needed to be stored on magnetic disk or tape. McLean's algorithms are extremely efficient. He was able to show that even for small molecules, the data storage requirements could be reduced by almost an order of magnitude below that required if all nonzero integrals were stored in a standard floating-point representation. Given these two developments, it can be said fairly that the integral "bottleneck" has been broken.

The remaining computational burdens in an SCF-HF procedure involve the construction of the Fock matrix **F** and its diagonalization at each of the iterations required to achieve self-consistency. This requires [32, 51] of order only a multiplication and an addition for each nonzero integral. Thus, there is low computing weight, although there may be considerable data processing (I/O) activity involved. This is one reason why McLean's contribution [50] is so valuable. Diagonalization of **F** is rather efficient [52], *e.g.* by a Householder-Wilkinson procedure, provided there is sufficient real memory available to store both the **F** matrix and the required eigenvectors. Assuming that the matrix and eigenvectors are stored in IBM System/370 double-precision floating-point representation, a matrix of order 400 and 200 eigenvectors requires $\approx$1 megabyte of real memory. For molecules of reasonable point-group symmetry, the basis set could be considerably larger [32, 51], since the dimension of any block may be considerably less than the full size of the basis set. However, in the treatment of excited states of molecules or, in general, of open-shell states, it may be difficult to obtain convergence of the SCF procedure. For this reason, Bagus and his collaborators [52–54] and others [55] have developed and implemented algorithms to improve the convergence of the iterative process. As a general rule, approximately twenty iterations are required to obtain convergence, even in difficult cases.

In summary, calculating good HF-SCF wave functions for large molecules requires 1) computational capability in terms of the central processor performance and real memory (such as that available with an IBM 3033 computer) and the data-storage capacity and transfer speed available with 6250-bpi tapes (or with IBM 3350 disk devices); and 2) suitable algorithms for the calculation [40–43, 46] and compact storage [49, 50] of the two-electron multicenter integrals, and for obtaining convergence [52–55] in the SCF iterative process.

Current state-of-the-art hardware and software make it possible to perform calculations on systems with a few hundred electrons with basis sets of order $\approx$500 (depending on the molecular symmetry). Rather few calculations of this size have been undertaken; the work of Bagus and Seel [56] on $Cu_5(CO)$ using 221 basis functions is one of the largest. This is, at least in large part, probably due to the only-recent availability of high-density storage devices for scientific computation in quantum chemistry. Recently, there has been a great deal of rather successful work in the development of *ab initio* pseudo- or effective potentials for avoiding explicit treatment of the core electrons of atoms [57] in the determination of the molecular wave functions. The use of pseudo-potentials serves to reduce the number m of basis functions needed for a given molecular problem.

The SCF-HF method represents a standard level of approximation within *ab initio* quantum chemistry. It involves some of the same or similar computational problems that arise when more accurate methods are used, and the HF approximation is rather well defined from a mathematical point of view. More accurate methods are, in general, closely linked to the chemical problem being studied; hence, a brief discussion of these methods must be somewhat abstract. A major reason that quantum chemistry has become such an important and valuable approach is precisely because it is possible to obtain results considerably superior to HF results. Because of this, a discussion of more accurate methods is essential.

The difference between the HF and exact energy levels is called the *correlation energy* [58], since account is taken of the correlation of the motion of the electrons due to their instantaneous electrostatic repulsion. This correlated motion is neglected in the HF treatment. Differences (errors) obtained between properties derived from Φ_{HF} and from Ψ_{exact} are also referred to as *correlation differences* (errors). There are a variety of approaches for the treatment of the molecular correlation problem used in quantum chemistry [2]. They are, however, fairly closely related to one another and have many of the same computational problems. The discussion of correlation focuses on the approach used by the San Jose group: the

configuration interaction (CI) method. In this method an expansion is made of the exact Ψ_K of the Schrödinger equation into a sum of antisymmetrized functions (ASFs) (or more properly configuration state functions, CSFs), $\Psi_K = \Sigma_L C_{KL}\Phi_L$. The different Φ_L are constructed by using sets of MOs that differ by one or more MOs for different quantum numbers L. Hartree-Fock theory is a special case of CI in which the summation over L is restricted to a single term. For HF theory, n MOs were required for an n-electron system. If a set of $M > n$ MOs is used, then

$$\binom{M}{n} = M!/(M-n)!n!$$

different ASFs, Φ_L, may be constructed from this set. If the set of MOs forms a complete set of one-electron functions and if all the ASFs that may be constructed from this set are used, an exact solution of the Schrödinger equation is represented. Obviously, such complete sets cannot be used in practice and truncations must be made in both the one-particle (MO or φ) and n-particle (Φ) spaces.

The truncation of the n-particle space is normally associated with the construction of hierarchies or classes of configurations [30(b)]. The development of physically meaningful hierarchal classifications of the Φ_L is essential if the CI approach is to give accurate results. Nesbet [59] has used a rather straightforward classification scheme with substantial success in treating the correlation problem in atoms. McLean and Liu [30(b), 60] have developed a sophisticated general classification scheme. The utility of this scheme for molecular problems has been successfully tested in a variety of applications (see, *e.g.*, Refs. [44] and [61]). Unfortunately, a description of their schemes or others is outside the scope of this paper.

Another problem relates to the choice of MOs to be used to construct the n-particle Φ_L. For both CI and SCF calculations, these MOs are expanded in basis sets. One way of constructing the one-particle space is to use the HF-SCF orbitals and a set of virtual orbitals orthogonal to the HF orbitals. The virtual space may be truncated by using, *e.g.*, natural-orbital-based methods [30(b), 62]. In general, however, a more complicated choice is necessary, one involving the use of multiconfiguration MCHF or MCSCF orbitals [31]. The computational complexity of the MCSCF approach combines the problems discussed above for HF with many of those to be discussed next for CI. There is a distinction between more important orbitals (SCF, MCSCF, or internal orbitals in general) and less important orbitals (virtual or external), and this distinction is an important feature in the classification of configurations into hierarchies [30(b), 60].

One important computational step in the CI procedure involves transformation of integrals over basis functions into integrals over MOs. This step is required in all methods used in quantum chemistry for treating the correlation problem. If all integrals can be kept in the real memory of a computer, the transformation is trivial. However, for even a rather modest size basis, say $m = 50$, the number of integrals is quite large, of order 10^6, and the space required to store them exceeds the memory available on any existing computer. Yoshimine [63] has developed the most efficient existing algorithm to treat this problem and it, or variants of it, are used for most treatments of the correlation problem when other than rather small basis sets are used. The novel aspect of Yoshimine's algorithm is that it depends on sorting or reordering the partially transformed integrals into the most convenient order for transformation of further indices. This means that large direct-access disk space roughly equal to the number of nonzero two-electron integrals is required. Only a fixed number of passes are made over the data stored on the direct-access device. The virtue of this approach is that the number of arithmetic operations required is the same as if all quantities had been kept in real memory.

A second computation step involves construction of the Hamiltonian matrix elements, which requires the merging of two long lists of data. Yoshimine has developed sorting algorithms [64] to make this merging efficient, and here again large amounts of direct access storage are required. The final step in the CI procedure is diagonalization of the CI Hamiltonian, which often requires eigenvalues and eigenvectors for several, say $\approx$10–50, of the lowest roots of the Hamiltonian $\mathcal{H}$. Since the order of $\mathcal{H}$ is large, this often cannot be done in real memory. The order of $\mathcal{H}$ is commonly $1\text{–}2 \times 10^4$ [61, 65] and orders of about 10^5 are used in large calculations [66]. Efficient, iterative algorithms [67, 68] exist that are tailored to the structure of the matrices encountered; however, they require the matrix elements to be read from auxiliary (tape or disk) storage at each iteration.

An important feature of the computations for both SCF and CI calculations is that they require extensive data-handling capability as well as central processor speed. As long as the calculation of two-electron integrals over basis functions was the limiting step in *ab initio* quantum chemical computation, the primary need was for greater central processor speed. Now that this is no longer the critical rate-limiting step [40–43, 46], the need for data handling has clearly emerged. In fact, whether the effective and accurate treatment of electron correlation can be made for large systems depends on the availability of large ($\geq$1 megabyte) direct-access disk-storage devices.

It is much more difficult for the correlation problem than for the SCF-HF problem to describe the size of molecules that can be considered. The magnitude of the problem depends critically on the selection of one- and n-particle basis sets and on the accuracy desired, factors which affect the computational complexity in a way that is difficult to relate simply to n. When considering a chemical process, certain approximations can also be made based on chemical aspects of the particular system. Thus, certain electrons can be described by HF (or MCSCF) orbitals and the correlated behavior considered only for those electrons that, by some measure, participate in the processes of interest. For example, H_2, as well as Li_2, Na_2, and K_2, can be considered as two-electron problems since only their outer open-shell electrons are involved in chemical reactions. As a result, the CI calculations for the latter three are essentially no more difficult than for H_2. With somewhat similar arguments, the study of the low-lying excited states of benzene can be restricted to a CI treatment of only six electrons [69] instead of the full 42 electrons that comprise the molecule. Thus, if it is possible to distinguish a small number of "chemically active" electrons from a large remainder that are chemically "inert," CI or other correlation treatments of quite large systems can become feasible. Unfortunately, it is not often easy to make such a distinction. McLean and Ellinger [70] have investigated the possibility of using localized orbitals for this purpose and their results have been quite encouraging. A general but conservative statement describing the state-of-the-art possibilities for CI is that the interactions between atoms (or the potential surfaces) for molecules containing three or at most four "heavy" atoms (C, N, O, etc.) can be determined with accuracy sufficient to provide new insight into the behavior of important chemical reactions [2(e)]. The *ab initio* study by Tanaka and Yoshimine [2(e), 71] analyzing the Wolff rearrangement (WR) reaction of C_2H_2O is an excellent example.

The WR is an important mechanism that has both great synthetic utility [72, 73] and considerable current technological relevance for photoresist materials used in the fabrication of high-density electronic circuits [74]. Although extensively studied both experimentally and theoretically, the details of the reaction mechanism and the role of various reaction intermediates have not been clearly or unequivocably established. The principal objectives of the Tanaka/Yoshimine study were to determine theoretically the geometric structures of various isomers of C_2H_2O, their relative stabilities, the nature and/or existence of activation barriers along the reaction paths for isomerization, and the energetics for reaction to various dissociation products. Their conclusions (not discussed here) had also been suggested from experimental observations and from less rigorous and less accurate theoretical work; however, for the first time, the work of Tanaka and Yoshimine was sufficiently accurate to provide definitive and unambiguous support for them. In fact, the "computer" experiments, which formed the basis of the theoretical work, make it possible to examine the Wolff rearrangement in more detail than in real "test tube" experiments.

Because of space limitations it has not been possible to discuss a large body of work in other areas where quantum chemistry has made a major impact or to present a complete survey of work related to potential surfaces. Areas where IBMers have made substantial contributions include spectroscopic properties of small molecules and transient species, the nature of weak van der Waals interactions, chemical bonding in molecules containing transition metal atoms, and the interaction of atoms and molecules with solid surfaces (chemisorption). Some of this work has been discussed in a recent review article [2(d)].

Special mention should also be given to the innovative, pioneering, and ambitious work of Clementi and his collaborators on systems of relevance to biological processes. His work on the determination of a microscopic description of the electronic structure of biomolecules [45, 47, 48] formed only the first part of this project. His objective of obtaining a macroscopic description of biological processes made it necessary to develop pair interaction potentials from the electronic wave functions and to use these potentials together with methods of statistical mechanics and thermodynamics. An important component of this project has been the understanding of the interaction of water with biomolecules and related atomic ions (Li^+, Na^+, K^+, F^-, and Cl^-). A large part of this work has been reviewed by Clementi [75].

Another area not discussed here but closely related to problems of electronic structure relates to free (continuum or unbound) states. Nesbet [76, 77] has made major contributions to problems involving the scattering of electrons from atoms and molecules, and the closely related areas of molecular photoionization and photodissociation [78]. Another area involving continuum states of a different kind is that of atom-molecule scattering, where Lester and his collaborators [79–81] and Nesbet [82] have been deeply involved. An important aspect of this area is that it forms a crucial bridge between the *ab initio* determination of potential surfaces and a large amount of experimental data bearing on the detailed mechanisms of chemical reactions. The work of Lester *et al.* [81] on the $O + H_2 \rightarrow OH + H$ reaction is a case where both quantum chemistry and scattering theory and ex-

periment were carried out in the same laboratory. This sort of collaboration greatly enhances the value of the efforts in the separate disciplines.

III. Program systems: IBMOL and ALCHEMY

It seems worthwhile to now give a brief description of the two major *ab initio* quantum chemistry program systems developed at IBM. These are IBMOL, developed by Clementi and his collaborators [40], and ALCHEMY, developed by P. S. Bagus, B. Liu, A. D. McLean, M. Yoshimine, and their collaborators [43, 83]. These programs have evolved over a period of years as their authors' knowledge of numerical methods and their relation to chemical problems increased and as available computational resources increased. IBMOL developed over roughly a ten-year period from 1965 to 1975. Work on ALCHEMY was begun in 1969 and to some degree continues. However, fairly major changes and improvements are now needed and work has begun on an entirely new program system, ALCHEMY2 [84], which will be similar in function but greatly superior in performance to ALCHEMY.

The different capabilities of these programs reflect the different emphasis in the scientific interests of their authors. Clementi and collaborators emphasized the study of large molecules, particularly those of biological importance [45, 47, 48], which in general lacked any simplifications arising from point-group symmetry; they focused on the HF method. The latest versions of IBMOL incorporate features designed to optimize integral evaluation for very large systems [46] and to carry out efficient SCF-HF calculations for ground states. The authors of ALCHEMY were concerned with resolving spectroscopic problems generally involving smaller systems and systems where an understanding of electron-correlation effects was generally essential. In order to treat these systems efficiently, advantage was taken of the molecular point-group symmetry. For electronically excited states, efficient techniques for dealing with open-shell systems were developed. The features contained in ALCHEMY include the capabilities to perform SCF-HF calculations for rather arbitrary open-shell configurations, MCSCF calculations using a fairly large number of terms, and large CI calculations with an unrestricted ("open-ended") way to select the classes or hierarchies of configurations to be used. Another feature is the capability to directly calculate many chemical observables from the molecular SCF and CI wave functions.

IV. Summary and perspective

The ability to perform complex computations in *ab initio* quantum chemistry requires not only access to high-performance computers but also the development of new algorithms and numerical methods, since these computations involve not only "number crunching" but also the sophisticated manipulation of large data bases. There have been, over the years, major and continuing efforts at IBM directed toward the development and implementation of new methods to enhance the power and versatility of computation in quantum chemistry. These efforts have led to two program systems, IBMOL and ALCHEMY, which are among the most efficient and flexible systems that exist. They have also made it possible to realize major strides in the application of quantum chemistry to scientific problems.

Work in *ab initio* quantum chemistry can, in a timely fashion, be related directly to problems of substantial and current interest in chemistry. Such timeliness can lead to close interactions and collaboration between theoreticians and experimentalists. Current developments in computational methods may make it possible in the very near future to considerably extend the range of applicability of *ab initio* quantum chemistry. At IBM, these developments are taking the form of construction of a new program system called ALCHEMY2 [84, 85]. This program will incorporate a new CI method to greatly improve the computing and data handling aspects of the calculation, making it possible to obtain correlated wave functions for more complex systems. It will further include the capability to perform automated determinations of reaction paths and related quantities such as minimum energy structures and transition states. The improved capabilities of ALCHEMY2 will not only permit more efficient treatments of the kind of problems described, but they will also make possible an accuracy which will lead to much more meaningful chemical results in new areas of applications.

B. The electronic structure of solids

I. Metal surfaces

Important early work on this problem was done by Bardeen in 1936 at Princeton University. He studied the uniform-background (jellium) model of a metal surface, in which the positive ion cores of a semi-infinite metal are smeared out into a semi-infinite uniform background of positive charge. Treatment of the electron distribution in this model using an approximate numerical solution of the Hartree-Fock equations permitted Bardeen to give an account of the surface charge distribution and work function of sodium metal.

In the period 1968–1971, extensive work was done on this model of a surface using the newly developed density-functional formalism [86] for treating inhomogeneous electron distributions. An analysis of the charge distribution and surface energy was carried out jointly by N. D.

Lang and W. Kohn [87] at the University of California; this study was continued by N. D. Lang at IBM (jointly with Kohn) in an analysis of the work function [87]. Parallel work (using a Thomas-Fermi-like version of the formalism, rather than the wave-mechanical version used by Lang and Kohn) was done by J. R. Smith at Ohio State University. These studies gave a good account of the work functions of all of the simple metals (*e.g.*, Al, Mg, the alkalies) and permitted discussion of their surface electron distributions. The treatment of Lang and Kohn, which re-introduced the discrete lattice into the uniform-background model using perturbation theory, also explained the behavior of the surface energies of these metals. A simple extension of this work gave a quite complete explanation of the changes in work function due to adsorption of a layer of alkali atoms on a metal surface [88], a phenomenon studied experimentally since the 1920s. The Davisson-Germer prize of the American Physical Society was later given to Lang and Kohn for their work on surfaces (1977).

The topic of chemisorption—the bonding of atoms (or molecules) to a surface—is one of the most basic problems in the physics of surfaces. Lang and A. R. Williams [89] developed at IBM a treatment of a single atom adsorbed on a metal surface, with the surface represented using the uniform-background model, in the period 1974–78. This work provided a clear, detailed picture of the nature of this bond. Figure 1, which has been reproduced in many texts and review articles [90], shows the way in which electronic charge is redistributed upon formation of a cationic, a covalent, and an anionic atom-surface bond.

This analysis was also used (1977) to study the screening of a core hole in a chemisorbed atom [91]. Such a core hole is usually produced with an x-ray or a fast electron in an experiment designed to determine the energy of a core-electron level; the screening by other electrons in the system shifts the observed energy of the level. This study settled a controversy concerning whether the screening charge distribution has an image-like or an atomic-like form. (It is found to be the latter, except in cases where there is no unfilled or partially filled atomic resonance in the vicinity of the Fermi level, such as in rare-gas adsorption.) The model of this screening charge distribution that was used in this study (excited-atom model) was employed to analyze core-hole screening in other systems such as bulk transition metals, and gave a successful account of the experimental data [92].

Beginning in 1972–75 [93], several groups at different laboratories developed programs to calculate (using the density-functional formalism) the properties of a bare

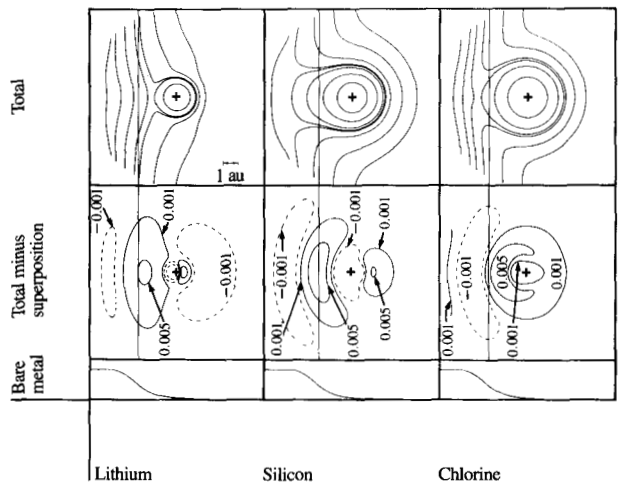


Figure 1 Electron-density contours for chemisorption of a single atom on a metal surface (uniform-background model). Upper row: contours of constant total density in a plane normal to the surface and containing a d atom nucleus (+). Metal is to left; positive background edge is indicated by vertical line. Contours shown only within inscribed circle. Center row: total density minus superposition of atomic and bare-metal densities. Solid line represents an accumulation, dashed line, a depletion. Bottom row: bare-metal electron density profile, from Ref [89(b)].

metal surface including the full effects of the discrete lattice structure. The first studies were again carried out for simple metals, but the general approach made possible the study of noble- and transition-metal and semiconductor surfaces (where lattice effects are more important).

Early studies of chemisorption using this approach were carried out by Appelbaum and Hamann (H adsorbed on Si), Smith *et al.* (N adsorbed on Cu), and S. G. Louie at IBM (H on Pd). Louie's work [94], for example, gives a quite complete account of the changes in the surface states and in charge density distribution that occur when adsorption takes place. Its results for the surface state density are in good agreement with the data of photoemission experiments for hydrogen adsorbed on palladium.

Batra *et al.* at IBM have extensively investigated the electronic structure of clean and adsorbate-covered surfaces. They have utilized finite clusters to model transition metals [95] and semiconductor surfaces [96]. The theoretical approach used has its basis in the SCF-X_α-SW method. With this approach they successfully investigated the effect of surface relaxation and hydrogen chemisorption on the electronic structure of Si(111) and Si(100) surfaces. Their cluster calculations for CO on Ni(001) [95] proved to be quite useful in identifying the adsorbate-induced levels observed in the photoemission spectra. In particular, the calculation predicted that the

gas phase levels 5σ and 1π may well be inverted upon chemisorption on Ni(001). This was subsequently borne out by angular resolved photoemission experiments.

Batra *et al.* have also made significant contributions in the area of adsorbate-adsorbate interactions. They have developed a general-purpose Extended Tight Binding computer program based on the LCAO-local density scheme which is capable of treating slabs with two-dimensional periodicity (to model a surface) as well as bulk solids. With this technique Batra *et al.* [97] have investigated bulk semiconductors (Si), insulators (SiO_2), metals (Al and Cu), polymers [$(SN)_x$ and $(CH)_x$], chlorine, fluorine, and oxygen chemisorption on Si. They have very nicely demonstrated [98] that the dispersion observed on the 4σ level of CO adsorbed on Pd can be accounted for by direct adsorbate-adsorbate interaction. For the dispersion of the 2p level of oxygen chemisorbed on Al, their calculation shows [99] that the indirect O-O interaction (through substrate) plays an important role. Their versatile computer programs represent a service to the scientific community at large, since several laboratories besides IBM are starting to use this resource.

II. Photoemission: establishment of the direct-transition model

In the photoemission experiment, an electron near the surface of a solid absorbs a photon from incident monochromatic radiation, acquiring both its momentum and its energy. Because of the small momentum of an optical or ultraviolet photon, the photoexcitation process is represented by a vertical or "direct" transition (no electron-momentum change) between an occupied and an unoccupied energy band, with the energy difference exactly equal to the energy of the absorbed photon. The excited electron can then move to the surface and escape from the crystal. The energy distribution of electrons excited by photons of a given energy is then studied. If direct transitions dominate, this photoemission distribution directly reflects the energy bands in the solid. That this is the case in semiconductors was demonstrated by Gobeli and Allen and Kane.

In the direct-transition model for free-electron bands, the photoemission distributions should show a series of peaks whose positions depend linearly on the photon energy. In the first photoemission observation of noble-metal d bands by Berglund and Spicer, the photoemission distributions instead showed stationary peaks whose amplitudes changed only gradually with the photon energy. This result, so uncharacteristic of what was expected from the direct-transition model, led Berglund and Spicer to propose the existence of "nondirect" transitions, in which some unspecified mechanism destroyed electron momentum conservation, but not energy conservation, during the photoexcitation process. The photoemission distributions predicted by this model are simple images of the electronic density of states, close to what is observed.

The mechanism responsible for nondirect transitions remained a theoretical puzzle until early direct-transition calculations by Smith and Spicer for Cu and by Janak, Eastman, and Williams [100] for Pd demonstrated that the direct-transition model *was* capable of explaining the experimental results. This is because of the flatness of the d bands: The rate at which a contribution to photoemission shifts its position with changes in photon energy is fixed by the momentum dependence of the energy of the initial state. The d-band energies are very nearly momentum-independent, so the photoemission distributions will appear to be nearly stationary as the photon energy is changed.

In any photoexcitation process, the strength of a particular transition is determined by the magnitude of the matrix elements of the momentum operator. These early photoemission calculations assumed constant matrix elements; a subsequent calculation by Williams, Janak, and Moruzzi [101] took full account of the effects of these matrix elements on both photoemission and optical absorption in Cu. This calculation showed that it was possible to explain the experimental results in strictly one-electron terms; many-body effects ("vertex corrections," etc.) are not important in Cu. Moruzzi, Williams, and Janak [102] then interpreted photoemission experiments in Cu to determine the location and extent in momentum space of the optical transitions in this material.

All these calculations were performed using one-electron potentials that were obtained by superposing atomic potentials. Janak, Williams, and Moruzzi [103] constructed a self-consistent potential which fit the Fermi surface and optical properties of Cu to a high degree of accuracy; this potential was later used by Moruzzi, Marcus, and Knapp [104] in a study of angle-resolved photoemission in this material.

The success of the above calculations depends on having fast and accurate algorithms for computing the energy bands, and also algorithms for computing observables such as optical absorption and photoemission from these energy bands. Janak [105] developed algorithms (based on the Gilat-Raubenheimer method) for computing Fermi-surface, optical-absorption, and photoemission properties, and Williams, Janak, and Moruzzi [106] developed an interpolation method which greatly increased the speed of the energy-band calculation.

III. Metallic bonding in elements and compounds

The understanding of the microscopic mechanisms responsible for metallic bonding and cohesion has increased markedly in the 1970s. Work at IBM has played a leading role in this advance. Prior to this period the understanding of metallic cohesion consisted of approximate but incisive theories designed to elucidate specific chemical trends, or cohesion in certain classes of materials. For example, Wigner and Seitz in 1933 correctly identified the factors responsible for cohesion in simple metals, but their analysis was clearly inappropriate for the majority of metals whose valence shells contain relatively localized d and f electrons. Friedel in 1969 correctly identified covalent bonding among the d electrons as the source of the approximately parabolic dependence of cohesive properties (lattice constant, cohesive energy, and compressibility) on the number of d electrons within each transition series. Numerical values for the parameters entering the Friedel theory could not be theoretically justified. Furthermore, the bonding mechanism of the theory increases without limit as the atoms are brought closer together, so that the theory provided no insight into the repulsive mechanism which balances the attractive forces in establishing the equilibrium volume.

The modern theory of metallic cohesion supports the conjectures of the earlier analyses and provides a detailed description of both the attractive and repulsive forces in both simple and transition metals. The modern theory accurately describes cohesive properties using calculations which require as input only the atomic number of the material. The first such calculations, some of which were performed at IBM, considered individual systems. In 1970, Moruzzi *et al.* [107] of IBM published a set of calculations describing the cohesive properties of twenty-six metals of diverse types. The results of these calculations are compared with experiment in Fig. 2. The details of these calculations were later published in book form [108]. These calculations served several roles: Their parameter-free character established that the theory, based on the density-functional formalism of Hohenberg, Kohn, and Sham [86], contained all the essential aspects of metallic bonding. The occasional departure of the calculated results from measured values indicated the existence of interesting anomalous behavior. For example, the experimental bulk moduli for some of the 3d transition metals are anomalously small. Janak and Williams [109] of IBM later showed that the anomalous behavior is due to the presence of magnetic order in these materials. Subsequent work by Andersen and collaborators has shown that the same mechanism is fundamental to the understanding of the transition-metal oxides, the actinides and even the rare-earth metals. Knowing that the theory contained all the important ingredients of

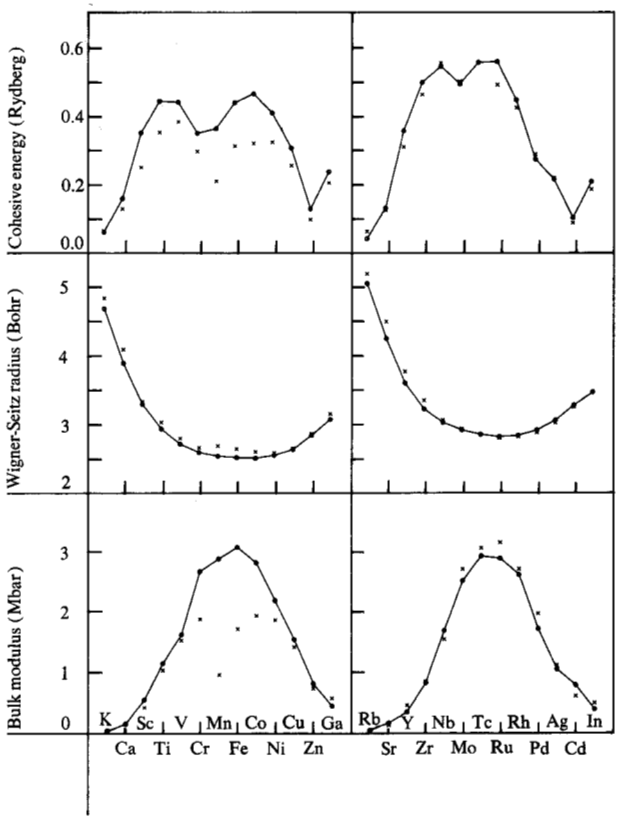


Figure 2 Comparison of measured and calculated cohesive properties. The left- and right-hand sides of the figure present results for the 3d and 4d transition series, respectively. The upper row gives equilibrium atomic volumes or lattice constants in terms of the corresponding Wigner-Seitz radii. The middle row gives cohesive energies, and the bottom row gives bulk moduli. References to the experimental work can be found in [108]. The calculated results were obtained using self-consistent energy-band calculations to which the only input is the atomic number.

metallic bonding, subsequent work at IBM and elsewhere, based on the use of the equation of state as an interpretive tool [110], has made the conceptual content of the elaborate numerical calculations both clear and consistent with earlier interpretive theories.

The extension of this type of analysis to problems of metallic compound formation has proved to be interesting and controversial. A dominant fact in this context is the success of an empirical theory due to Miedema in describing a variety of compound-bonding properties. Two very different microscopic models had been proposed to explain or justify the empirical theory, one emphasizing the role of delocalized electrons and the other emphasizing the localized d electrons. Using a very efficient procedure developed at IBM [111] for the application of density-functional theory to such problems, Williams, Gelatt, and

Moruzzi [112] of IBM conducted a careful study of the 28 simplest compounds to which the empirical theory applies. The study indicated that only one of the two previously proposed models (that emphasizing d electrons) was correct and that, furthermore, the empirical theory is wrong in the particular constituent properties it emphasizes. The IBM work argues that the bonding properties represent sufficiently little independent information that an empirical theory, although based on incorrect constituent properties, can be fit to the observed results. This conclusion remains controversial. It is noteworthy that no other group has succeeded in calculating the heat of formation of compounds involving transition metals.

IV. Itinerant *versus* localized magnetism

One of the earliest applications of the quantum theory to the physics of solids was to the problem of magnetism in such elements as iron and nickel. Efforts to develop a comprehensive theory of ferromagnetic materials began in the late 1920s, and, somewhat surprisingly, these efforts continue today. As of this writing, no single computationally feasible theory has been able to account successfully for all of the observed properties of ferromagnets.

Over the last fifty years many schools of thought on magnetism have developed [113]; among these schools of thought, the two simplest, most clearly defined, and in many ways most successful are the localized and itinerant pictures of magnetism. Each accounts very successfully for some features of the magnetic behavior of iron, nickel, and many other magnetic transition-metal elements and compounds. But each also fails to explain other properties of the same magnetic materials. Interestingly enough, the domains of success of these two views of magnetism have almost no overlap whatsoever.

The localized picture of magnetism, first proposed by Heisenberg in 1928 [114], views magnetism as arising from the spin magnetic moment of electrons which are tightly bound to individual atoms in the solid. Each atom is assigned a magnetic-moment vector given by the spin-magnetic-moment vector of a single electron multiplied by the (integer) number of tightly bound electrons contributing to the atomic moment. The size of this atomic (or local) moment is constant; only its direction can vary. The magnetic moment of a bulk sample is nonzero only if the individual atomic moments tend to point in the same direction. At high temperatures, the atomic moments are directed randomly, and the average magnetization vanishes. At absolute zero, all of the atomic moments are perfectly aligned, and the average magnetization is some *integer* multiple of the magnetic moment per electron.

The localized picture gives reasonable estimates of the Curie temperature T_c, below which the system exhibits a non-zero magnetization. In addition, the localized picture correctly predicts that (above T_c) the magnetic susceptibility (the change in magnetization of the sample in response to an applied magnetic field) varies inversely with temperature (Curie-law susceptibility). The most notable failure of the localized picture is its inability to account for a zero-temperature magnetization that is a non-integral multiple of the moment per electron (for iron the multiple is observed to be 2.2, for nickel it is 0.6).

The itinerant picture of magnetism, first proposed by Bloch [115] in 1929 and by Stoner [116] in 1936, takes a very different point of view. In the itinerant picture, magnetism is assumed to arise from the spin magnetic moment of conduction electrons (that is, electrons that are free to travel throughout the sample as opposed to being bound to any individual atom). The magnetization of an itinerant ferromagnet is everywhere the same in magnitude and direction; the magnitude of the magnetization is proportional to the fraction of spin-up electrons minus the fraction of spin-down electrons. The itinerant model successfully accounts for the non-integral values of the zero-temperature magnetization (as measured in units of the moment per electron), giving the correct multiplicative factors of 2.2 and 0.6 for iron and nickel, respectively. The itinerant picture is further supported by experimental evidence that the same d electrons responsible for transition-metal magnetism also participate in the process of electrical conduction; *i.e.*, the "magnetic" electrons are also induction electrons.

One notable failure of the itinerant model is that it predicts a Curie temperature some ten to twenty times higher than that observed experimentally. A second failure is that above the Curie temperature the itinerant model demands that the magnetization is everywhere zero, in disagreement with the observation that even above T_c there exist small patches of non-zero magnetization (the direction of magnetization varies randomly from patch to patch, resulting in a vanishing average magnetization). A third failure is that the itinerant picture does not yield the observed Curie-law temperature dependence of the high-temperature magnetic susceptibility.

Much effort has been expended over the last decade in an attempt to marry these two opposing views of magnetism. Among the many ideas recently put forward, one of the most promising is the idea of a local "exchange-field," due to John Hubbard [117] of IBM Research, San Jose. Hubbard's theory is itinerant in that the electrons responsible for the magnetism are free to move throughout the solid. Features reminiscent of the localized pic-

ture are incorporated through the observation that the forces responsible for the alignment of magnetic moments operate most effectively in regions of high electron density—that is, near the individual atoms. Hubbard proposed the use of a local "exchange-field," defined for each atom, which acts to align the moments of nearby electrons and is proportional to the total magnetic moment of all the electrons in the vicinity of that atom. Since itinerant electrons are distributed over a large volume containing many atoms, each itinerant electron contributes a fraction of its magnetic moment to any individual atom. The result is a local "exchange-field" associated with each atom, that is a multiple (not necessarily integral) of the moment per electron.

Though Hubbard's theory is computationally unwieldy, several simple calculations performed within the local "exchange-field" framework have yielded encouraging results. First, Hubbard's theory reduces to the successful itinerant description of the zero-temperature properties of transition-metal ferromagnets, giving the correct zero-temperature magnetization. Second, it improves upon the itinerant description of low-temperature magnetic excitations by including not only the two-particle excitations of Stoner but also the spin waves characteristic of a localized viewpoint. Third, Hubbard's calculations show that it costs far less energy to rotate the atomic magnetic moment (or "exchange-field") than it does to alter the length of the moment vector, a result strongly suggestive of localized behavior, although the moment in Hubbard's theory arises from itinerant electrons. This result continues to hold for temperatures well above T_c, indicating that one would expect patches of non-zero magnetization to appear above T_c in Hubbard's framework. Fourth, Hubbard found a Curie-law temperature dependence of the magnetic susceptibility for temperatures above T_c. Finally, on the basis of the "local-exchange-field" concept, Hubbard estimated the Curie temperature for iron to be $\approx$1800 K, far closer to the actual value of 1044 K than the 20 000 K value predicted by the itinerant model.

Though many questions remain about the ultimate success and utility of the local "exchange-field" model, the results so far seem to indicate that Hubbard made great progress towards the development of a comprehensive theory of transition-metal magnetism.

V. Semiconductors (point defects, surfaces, and interfaces)

A very important set of electronic structure calculations for semiconductors and insulators is due to S. T. Pantelides and his collaborators at IBM. This work can be viewed as an outgrowth of Pantelides' early application of tight-binding models to problems of x-ray emission, x-ray absorption, and optical absorption in SiO_2 [118] and of K. C. Pandey's tight-binding studies of semiconductor surfaces [119].

Recently, in a collaborative effort initiated by Pantelides, general Green's-function methods for a quantitative description of the electronic structure of point defects, surfaces, and interfaces have been developed. Though the basic idea of the method has existed for more than twenty-five years [120], its potential had not been appreciated because applications were either carried out on model systems or were hampered by inappropriate technical choices. An efficient version of the Green's-function method was first developed at IBM by J. Bernholc and Pantelides [121] for the vacancy in tetrahedral semiconductors. In parallel, the method was developed by J. Pollmann and Pantelides [122] for surfaces, and subsequently for interfaces and overlayers. Both of these developments made use of semiempirical tight-binding Hamiltonians. Soon after, Bernholc, N. O. Lipari, and Pantelides [123] developed the Green's-function method for point defects using self-consistent pseudo-potentials. For the first time, a crystal containing a point defect, specifically the isolated vacancy, was treated with the same accuracy as is currently possible for perfect crystals.

The Green's-function method has substantial conceptual and computational advantages over other methods because it exploits the fact that $\mathcal{H}$, the Hamiltonian of the defect-containing crystal, can be written as $\mathcal{H}^0 + U$, where $\mathcal{H}^0$ is infinite and periodic and U is localized. These aspects of the problem are illustrated in Fig. 3. The contour plots are the results of calculations [123] illustrating that the change in the charge density produced by the vacancy is indeed quite localized. The calculations also give detailed information about individual states (wave functions, energy levels, ionization energies, etc.) [123, 124]. The method has also been used to describe the reconstructed vacancy (*i.e.*, by allowing the neighboring atoms to move from their bulk-crystalline positions to the "relaxed" positions indicated by experiment) [125], substitutional impurities in Si [126], and defects in GaP [127].

VI. Low-energy-electron diffraction

Low-energy-electron diffraction (LEED) at IBM Research and its application to analysis of surface structure was a natural outgrowth of interest in surfaces. The Surface Studies group acquired the newly available Varian LEED instrument in 1964 and F. Jona immediately applied it to a series of studies of semiconductor and metal surfaces [128]. Particularly noteworthy was the work on Al, which produced a set of intensity curves

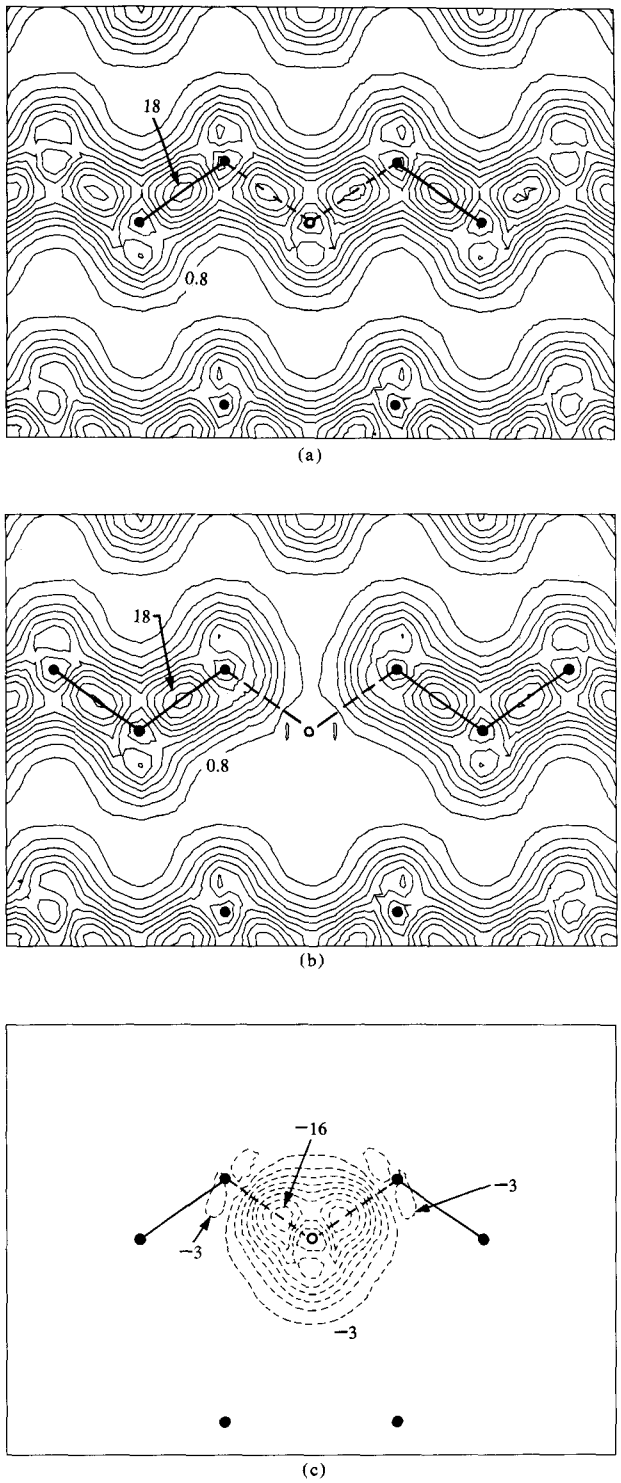


Figure 3 Contours of constant electron density showing the rearrangement of charge in the vicinity of a vacancy in Si. (a) The unbroken chain of covalent bonds in bulk Si. (b) The dangling-bond character of the electron density near a vacancy. (c) The electron-density change associated with the removal of a Si atom. The SCF calculations which produced these electron densities were based on a Green's-function formulation of the imperfection problem developed at IBM by Bernholc and Pantelides.

suitable for structural analysis. This pioneering work, made before Auger electron spectroscopy was available to test the impurity content of the surface, required close study of conditions of preparation and cleaning. In 1968, at the urging of Jona and A. Nowick, two theorists, P. Marcus and D. Jepsen, starting from a background in band theory, attempted to interpret the Al data. The first studies [129] were revealing but not quantitatively successful, since they used oversimplified models of the potential and solved matrix differential equations based on plane wave (beam) representations that could not adequately handle strong coulomb singularities. Real structure determination was achieved only when the layer-scattering problem was treated in spherical waves using the application by Kambé to layers of the Korringa-Kohn-Rostoker (KKR) method for energy bands [130]. The detailed application to Al(001) and other face-centered cubic (fcc) metals [131] showed remarkable quantitative agreement of a kind not previously achieved.

Success with the chemically more interesting surface structures of ordered adsorbed atoms on a substrate came with analysis of LEED intensity measurements on Ni and various adsorbates on Ni made by J. Demuth as a thesis student of T. Rhodin at Cornell University. The application of the layer-KKR LEED programs to analysis of these data was very successful, leading to a remarkably good fit of the clean Ni data [132] that gave not only convincing evidence of interlayer contraction on Ni(110) but also permitted estimates of the energy dependence of the correlation potential and of the attenuation potential. The application to adsorbate data gave detailed structures for O, S, Se, and Te on various Ni surfaces [133], which firmly established the suitability of both the LEED model and the scattering computation for analysis of adsorbate structures.

Successful analysis of the structure of additional adsorbate systems continued under a joint studies contract with Jona and his associates and students at the State University of New York at Stony Brook, where Jona moved in 1969. Studies of Fe, Ti, Ag, Mo, and Co with various adsorbates were carried out. In each case the clean substrate surface was analyzed first, and the values of the fitting parameters were then used and supplemented in the analysis of the adsorbate structure. Basic information on the nature of surface bonding accumulated as studies continued.

Work on Fe was started early and still continues in view of its technological importance. It is found that the surface contraction of clean Fe(001) is reversed when O is added (and slips into the fourfold hollow), but not when the larger S atom is adsorbed. Adsorption of CO on

Fe(001) was shown to be dissociated into random C and O atoms, but the LEED spectrum is still analyzable because C and O atoms scatter electrons similarly. Analyses of Fe(001) and Fe(111) have been successfully carried out, the latter very open surface showing the largest known contraction of a metal surface (15%) [134]. Studies of clean Ti(0001) determined the first hexagonal close-packed surface structure, and required mixing domains with the two possible surface terminations. Analysis of N adsorbed on Ti(0001) led to the unusual situation of underlayer formation; deposition of successive Cd layers on Ti(0001) and study of each layer led to analysis of epitaxial growth and discovery of a stacking fault at the interface. The Cd layer work showed that LEED analysis can see through three layers of atoms, and thus that LEED can successfully study interfaces [135]. The first correct study (with collaborators from the University of Houston) of a molecule adsorbed on a metal surface was carried out for CO on Ni(001). This work showed that the CO was in a top-atom position and perpendicular to the surface, thereby correcting an error in a previous LEED analysis by another group (which had given a different orientation) and bringing LEED into agreement with angle-resolved photoemission measurements on this system [136].

A long-time interest has been the study of Si surfaces. The complex reconstructions make these problems difficult, but in view of the interest in and importance of these surfaces, considerable effort has been made and continues, especially when a new model is suggested or an improvement in the technique is made. An encouraging development was the production and analysis of an impurity-stabilized Si(111) surface [137], which avoided the complications of reconstruction and was well fitted by a truncated bulk model with 21% contraction of the first interlayer distance. This work showed that LEED analysis could be successfully applied to a covalently bonded material, provided the intensity curves were analyzed above some minimum energy of order 40 eV.

VII. Summary

As this report indicates, electronic-structure calculations have established both their credibility and their utility. Bulk solids, because of their great symmetry, were the first to be studied and remain the context of greatest sophistication. The concepts and analytical methods developed for bulk solids are now being applied with great success to systems possessing less symmetry, such as solid surfaces and imperfections in solids. Work at IBM is very much at the forefront of these developments.

VIII. Acknowledgments

The assistance of I. P. Batra, J. F. Janak, N. D. Lang, D. Ling, P. M. Marcus, and S. T. Pantelides in preparing the condensed-matter portion of this manuscript is gratefully acknowledged.

References and notes

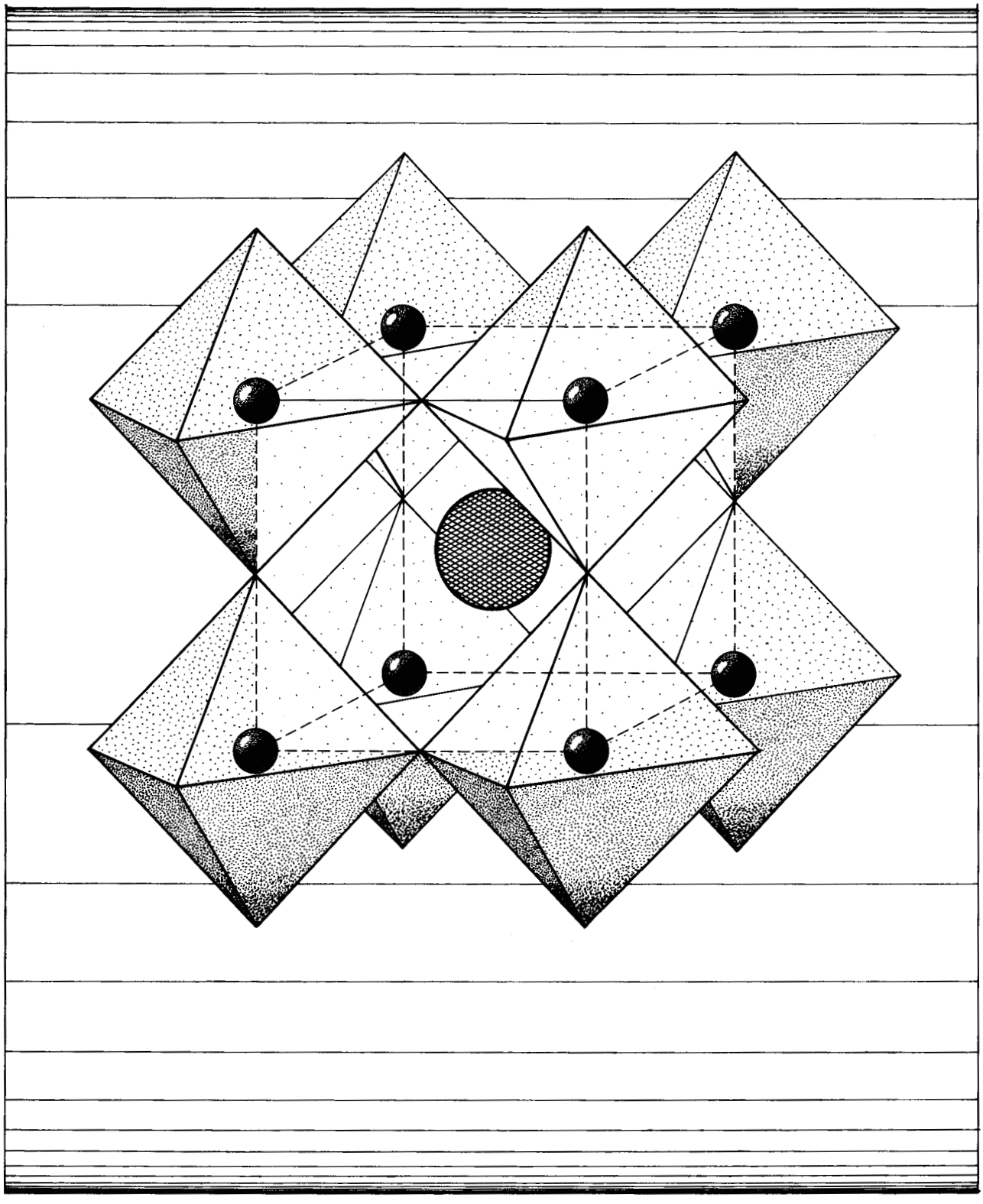
1. Graham Richards, *Nature* **278,** 507 (1979).
2. *Computational Methods in Chemistry*, Joachim Bargon, Ed., IBM Research Symposia Series, Plenum Publishing Co., New York, 1980. See in particular the articles by (a) W. von Niessen, L. S. Cederbaum, W. Domcke, and J. Schirmer, p. 65; (b) Wilfried Meyer, Peter Botschywina, Pavel Rosmus, and Hans-Joachim Werner, p. 157; (c) S. D. Peyerimhoff and R. J. Buenker, p. 175; (d) P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, p. 203; and (e) Joachim Bargon, Kiyoshi Tanaka, and Megumu Yoshimine, p. 239.
3. See any standard quantum mechanics text. L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co., Inc., New York, 1935, is particularly useful since it presents a good review of some of the early work in quantum chemistry.
4. Egil A. Hylleraas, *Z. F. Phys.* **65,** 209 (1930).
5. Hubert M. James and Albert Sprague Coolidge, *J. Chem. Phys.* **1,** 825 (1933); **3,** 129 (1935).
6. R. G. Parr, *The Quantum Theory of Molecular Electronic Structure; A Lecture-note and Reprint Volume*, Pergamon Press, Inc., Elmsford, NY, 1963.
7. R. G. Parr and B. L. Crawford, Jr., *Proc. Nat. Acad. Sci.* **38,** 547 (1952).
8. C. C. J. Roothaan, *J. Chem. Phys.* **19,** 1445 (1951); Klaus Rüdenberg, *J. Chem. Phys.* **19,** 1459 (1951).
9. C. C. J. Roothaan, *Rev. Mod. Phys.* **23,** 69 (1951).
10. K. Kirby-Docken and B. Liu, *J. Chem. Phys.* **66,** 4309 (1977).
11. Enrico Clementi, *J. Chem. Phys.* **46,** 3851 (1967).
12. Robert S. Mulliken, *Science* **157,** 13 (1967).
13. W. G. Richards, T. E. H. Walker, and R. K. Hinkley, *A Bibliography of Ab Initio Molecular Functions*, Clarendon Press, Oxford, England, 1971; W. G. Richards, T. E. H. Walker, L. Farnell, and P. R. Scott, *Bibliography of Ab Initio Molecular Wave Functions. Supplement for 1970–1973*, Clarendon Press, Oxford, England, 1974.
14. Christoph Schlier, *Ann. Rev. Phys. Chem.* **20,** 191 (1969).
15. J. W. Mellor, *Comprehensive Treatise of Inorganic and Theoretical Chemistry*, John Wiley & Sons, Inc., New York, 1951, Vol. 8, Suppl. I.
16. Robert S. Mulliken, *J. Phys. Chem.* **56,** 801 (1952).
17. P. Goldfinger and G. Verhaegen, *J. Chem. Phys.* **50,** 1467 (1969).
18. B. Liu, *Intl. J. Quantum Chem.* **55,** 123 (1971).
19. B. Liu, *J. Chem. Phys.* **58,** 1925 (1973).
20. P. Siegbahn and B. Liu, *J. Chem. Phys.* **68,** 2457 (1978).
21. (a) Donald G. Truhlar and Robert E. Wyatt, *Ann. Rev. Phys. Chem.* **27,** 1 (1976); (b) *Adv. Chem. Phys.* **36,** 141 (1977).
22. Donald G. Truhlar and Charles J. Horowitz, *J. Chem. Phys.* **68,** 2466 (1978).
23. C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Lett.* **23,** 1397 (1969).
24. P. S. Bagus, A. J. Freeman, and F. Sasaki, *Phys. Rev. Lett.* **30,** 850 (1973); *Intl. J. Quantum Chem.* **57,** 83 (1973).
25. A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Intl. J. Magnetism* **4,** 35 (1973).
26. See for example K. Siegbahn *et al.*, *ESCA—Atomic, Molecular, and Solid State Structure Studies by Means of Electron Spectroscopy*, Almquist and Wiksells, Uppsala, Sweden, 1967; *ESCA Applied to Free Molecules*, North-Holland Publishing Co., Amsterdam, 1969; *Proceedings of the International Conference on Electron Spectroscopy*, D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972.
27. See for example J. S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University Press, Cambridge, England, 1961.

28. C. K. Jorgensen, *Modern Aspects of Ligand Field Theory*, North-Holland Publishing Co., Amsterdam, 1971.
29. S. P. Kowalczyk, L. Ley, R. A. Pollak, F. R. McFeely, and D. A. Shirley, *Phys. Rev. B* **7,** 4009 (1973).
30. For more detailed discussions of $\mathcal{H}$ and other theoretical aspects, see Ref. 3 and (a) H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules*, Addison-Wesley Publishing Co., Inc., Reading, MA, 1972; (b) P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, *Wave Mechanics: The First Fifty Years*, W. C. Price, S. S. Chissick, and T. Ravensdale, Eds., Butterworths, London, 1973, p. 99.
31. Representative theoretical treatments of multiconfiguration Hartree-Fock can be found in A. C. Wahl and G. Das, *Modern Theoretical Chemistry*, H. F. Schaefer III, Ed., Plenum Publishing Co., New York, 1976, Vol. 3, and in J. Hinze, *J. Chem. Phys.* **59,** 6424 (1973). See also Per Siegbahn, Anders Heilberg, B. Roos, and B. Levy, *Physica Scripta* **21,** 323 (1980) and Byron H. Lengsfield III, *J. Chem. Phys.* **73,** 382 (1980).
32. C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics*, Vol. II, Academic Press, Inc., New York, 1963, pp. 47–94.
33. B. Roos, C. Salez, A. Veillard, and E. Clementi, *Technical Report RJ518*, IBM Research Division Laboratory, San Jose, CA, 1968.
34. (a) E. Clementi, *Tables of Atomic Functions* [Supplement to *IBM J. Res. Develop.* **9,** 2 (1965)]; (b) E. Clementi and C. Roetti, *Atomic Data and Nuclear Data Tables*, Academic Press, Inc., New York, 1974.
35. A. D. McLean and M. Yoshimine, *IBM J. Res. Develop.* **12,** 206 (1968).
36. Sigeru Huzinaga, *J. Chem. Phys.* **42,** 1293 (1965).
37. F. B. van Duijneveldt, *Technical Report RJ945*, IBM Research Division Laboratory, San Jose, CA, 1971.
38. A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72,** 5639 (1980). A. D. McLean, *Technical Reports RJ2295* and *RJ2296*, IBM Research Division Laboratory, San Jose, CA, 1978.
39. A. J. H. Wachters, *J. Chem. Phys.* **52,** 1033 (1970).
40. E. Clementi and J. W. Mehl, *Technical Reports RJ853, RJ883*, and *RJ889*, IBM Research Division Laboratory, San Jose, CA, 1971.
41. J. Almlof, *Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry*, Strassborg, 1972, Max-Planck-Institut, München, 1973, p. 14.
42. Harry F. King and Michel Dupuis, *J. Comp. Phys.* **21,** 144 (1976); Michel Dupuis, John Rys, and Harry F. King, *J. Chem. Phys.* **65,** 111 (1976).
43. A. D. McLean, *Proceedings of the Conference on Potential Energy Surfaces in Chemistry*, University of California, Santa Cruz, August 1970; *Technical Publication RA18*, IBM Research Division Laboratory, San Jose, CA, 1971.
44. B. Liu and A. D. McLean, *J. Chem. Phys.* **59,** 4557 (1973); **72,** 3418 (1980).
45. E. Clementi, J. Mehl, and W. von Niessen, *J. Chem. Phys.* **54,** 508 (1971).
46. Enrico Clementi, *Proc. Nat. Acad. Sci.* **69,** 2942 (1972).
47. E. Clementi and H. Popkie, *Chem. Phys. Lett.* **20,** 1 (1973).
48. George C. Lie and Enrico Clementi, *J. Chem. Phys.* **60,** 3005 (1977).
49. P. S. Bagus and E.-K. Viinikka, IBM Research Division Laboratory, San Jose, CA, unpublished results.
50. A. D. McLean, *Proceedings of the 1978 IBM Symposium on Mathematics and Computation*, San Jose, CA, 1978, K. L. Deckert, Ed., p. 133; *Technical Report RJ2215*, IBM Research Division Laboratory, San Jose, CA, 1978.
51. C. C. J. Roothaan, *Rev. Mod. Phys.* **32,** 179 (1960).
52. P. S. Bagus, B. Liu, and G. Schwenzer, *Documentation for ALCHEMY: SCF Programs*, unpublished paper, IBM Research Division Laboratory, San Jose, CA.
53. P. S. Bagus, I. P. Batra, and E. Clementi, *Chem. Phys. Lett.* **23,** 305 (1973).
54. C. W. Bauschlicher, Jr., P. S. Bagus, D. R. Yarkony, and B. H. Lengsfield III, *J. Chem. Phys.* **74,** 3965 (1981).
55. V. R. Saunders and I. H. Hillier, *Intl. J. Quantum Chem.* **7,** 699 (1973).
56. Paul S. Bagus and M. Seel, *Phys. Rev. B*, in press.
57. See for example V. Bonifacic and S. Huzinaga, *J. Chem. Phys.* **60,** 2779 (1974) and **62,** 1507, 1509 (1975); C. F. Melius, B. D. Olafson, and W. A. Goddard III, *Chem. Phys. Lett.* **28,** 457 (1974).
58. P. O. Löwdin, *Adv. Chem. Phys.* **2,** 207 (1959).
59. R. K. Nesbet, *Adv. Chem. Phys.* **14,** 1 (1969).
60. A. D. McLean and B. Liu, *J. Chem. Phys.* **58,** 1066 (1973).
61. B. Liu, K. M. Sando, C. S. North, H. B. Friedrich, and D. M. Chipman, *J. Chem. Phys.* **69,** 1425 (1978).
62. Ernest R. Davidson, *Adv. Quantum Chem.* **6,** 235 (1972); Per-Olov Löwdin, *Phys. Rev.* **97,** 1474 (1955).
63. M. Yoshimine, *Technical Report RJ555*, IBM Research Division Laboratory, San Jose, CA, 1969; see also Ref. 43.
64. M. Yoshimine, *J. Comp. Phys.* **11,** 449 (1973).
65. See for example R. P. Saxon, K. Kirby, and B. Liu, *J. Chem. Phys.* **73,** 1873 (1980).
66. Björn O. Roos and Per E. M. Siegbahn, *Intl. J. Quantum Chem.* **17,** 485 (1980).
67. Ernest R. Davidson, *J. Comp. Phys.* **17,** 87 (1975).
68. B. Liu, *Report LBL-8158, UC-32, Conf-780878*, Lawrence Berkeley Laboratory, Berkeley, CA, 1978.
69. P. Jeffrey Hay and Isaiah Shavitt, *J. Chem. Phys.* **60,** 2865 (1975).
70. A. D. McLean and Y. Ellinger, *Technical Report RJ2827*, IBM Research Division Laboratory, San Jose, CA, 1980 and *J. Chem. Phys.*, in press.
71. Kiyoshi Tanaka and M. Yoshimine, *J. Amer. Chem. Soc.* **102,** 7655 (1980).
72. Bernd Eistert, *Neuere Methoden der Praparativen Organischen Chemie*, W. Foerst, Ed., Verlag Chemie, Weinheim, Germany, 1949, Vol. I, p. 359.
73. Bernd Eistert, *Angew. Chem.* **54,** 124 (1941) and **55,** 118 (1942).
74. J. Pacansky and J. R. Lyerla, *IBM J. Res. Develop.* **23,** 42 (1979).
75. E. Clementi, *Determination of Liquid Water Structure. Coordination Numbers for Ions and Solvation for Biological Molecules*, Springer-Verlag, Berlin, 1976.
76. R. K. Nesbet, *Variational Methods in Electron-Atom Scattering Theory*, Plenum Publishing Co., New York, 1980.
77. R. K. Nesbet, *Phys. Rev. A* **19,** 551 (1979).
78. J. Barsuhn and R. K. Nesbet, *J. Chem. Phys.* **68,** 2783 (1978).
79. W. A. Lester, Jr., *Adv. Quantum Chem.* **9,** 199 (1975).
80. B. J. Garrison, W. A. Lester, Jr., W. H. Miller, and S. Green, *Astrophys. J.* **200,** 9075 (1975).
81. (a) R. E. Howard, A. D. McLean, and W. A. Lester, Jr., *J. Chem. Phys.* **71,** 2412 (1979); (b) R. Schinke and W. A. Lester, Jr., *J. Chem. Phys.* **70,** 4893 (1979); **72,** 3754 (1980); (c) A. C. Luntz, R. Schinke, W. A. Lester, Jr., and Hs. H. Günthard, *J. Chem. Phys.* **70,** 5908 (1979).
82. R. K. Nesbet, *Theoretical Chemistry: Advances in Perspectives*, H. Eyring and D. J. Henderson, Eds., Academic Press, Inc., New York, 1981, Vol. 6B.
83. Paul S. Bagus, in *Selected Topics in Molecular Physics, Proceedings of the 1970 International Symposium*, at Ludwigsburg, Germany, Verlag Chemie GmbH, Weinheim, Germany, 1972.
84. B. Liu, A. D. McLean, and M. Yoshimine, IBM Research Division Laboratory, San Jose, CA, unpublished work.
85. B. Liu and M. Yoshimine, *J. Chem. Phys.* **74,** 612 (1981).
86. P. Hohenberg and W. Kohn, *Phys. Rev.* **136,** B864 (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140,** A1133 (1965).
87. N. D. Lang, *Solid State Commun.* **7,** 1047 (1969); N. D. Lang and W. Kohn, *Phys. Rev. B* **1,** 4555 (1970) and **3,** 1215 (1971).
88. N. D. Lang, *Phys. Rev. B* **4,** 4234 (1971).
89. (a) N. D. Lang and A. R. Williams, *Phys. Rev. Lett.* **34,** 531

(1975) and (b) **37,** 212 (1976); (c) *Phys. Rev. B* **18,** 616 (1978).
90. See for example W. A. Harrison, *Electronic Structure and the Properties of Solids*, W. H. Freeman, San Francisco, 1980, p. 404; N. H. March, in *Physics and Contemporary Needs*, Plenum Publishing Co., New York, 1977, p. 71.
91. N. D. Lang and A. R. Williams, *Phys. Rev. B* **16,** 2408 (1977).
92. A. R. Williams and N. D. Lang, *Phys. Rev. Lett.* **40,** 954 (1978).
93. J. A. Appelbaum and D. R. Hamann, *Phys. Rev. B* **6,** 2166 (1972); G. P. Alldredge and L. Kleinman, *Phys. Rev. B* **10,** 559 (1974); J. R. Chelikowsky, M. Schluter, S. G. Louie, and M. L. Cohen, *Solid State Commun.* **17,** 1103 (1975).
94. S. G. Louie, *Phys. Rev. Lett.* **42,** 476 (1979).
95. I. P. Batra and O. Robaux, *J. Vac. Sci. Technol.* **12,** 242 (1975); *Surface Sci.* **49,** 653 (1975); I. P. Batra and P. S. Bagus, *Solid State Commun.* **16,** 1097 (1975); I. P. Batra and C. R. Brundle, *Surface Sci.* **57,** 12 (1976).
96. I. P. Batra and S. Ciraci, *Phys. Rev. Lett.* **34,** 1337 (1975) and **36,** 170 (1976); I. P. Batra, S. Ciraci, and I. B. Ortenburger, *Solid State Commun.* **18,** 563 (1976).
97. I. P. Batra, *J. Vac. Sci. Technol.* **16,** 1359 (1979); S. Ciraci and I. P. Batra, *Phys. Rev. B* **15,** 4923 (1977); A. Ajmani, I. P. Batra, E. E. Lafon, and C. S. Fadley, *J. Phys. C* **13,** 2807 (1980); I. P. Batra, S. Ciraci, and W. E. Rudge, *Phys. Rev. B* **15,** 5858 (1977); P. M. Grant and I. P. Batra, *Solid State Commun.* **29,** 225 (1979); M. Chen and I. P. Batra, *J. Vac. Sci. Technol.* **16,** 570 (1979); M. Chen, I. P. Batra, and C. R. Brundle, *J. Vac. Sci. Technol.* **16,** 1216 (1979).
98. I. P. Batra, K. Hermann, A. M. Bradshaw, and K. Horn, *Phys. Rev. B* **20,** 801 (1979).
99. I. P. Batra and S. Ciraci, *Phys. Rev. Lett.* **39,** 774 (1977).
100. J. F. Janak, D. E. Eastman, and A. R. Williams, in *NBS Special Publication* **323,** 181 (1969); J. F. Janak, D. E. Eastman, and A. R. Williams, *Solid State Commun.* **8,** 271 (1970).
101. A. R. Williams, J. F. Janak, and V. L. Moruzzi, *Phys. Rev. Lett.* **28,** 671 (1972).
102. V. L. Moruzzi, A. R. Williams, and J. F. Janak, *Phys. Rev. B* **8,** 2546 (1973).
103. J. F. Janak, A. R. Williams, and V. L. Moruzzi, *Phys. Rev. B* **6,** 4367 (1972) and **11,** 1522 (1975).
104. V. L. Moruzzi, P. M. Marcus, and J. A. Knapp, *Institute of Physics Conference Series*, No. 39, p. 234 (1978).
105. J. F. Janak, in *Computational Methods in Band Theory*, Plenum Publishing Co., New York, 1971, p. 323; *Solid State Commun.* **10,** 833 (1972).
106. A. R. Williams, J. F. Janak, and V. L. Moruzzi, *Phys. Rev. B* **6,** 4509 (1972).
107. V. L. Moruzzi, A. R. Williams, and J. F. Janak, *Phys. Rev. B* **15,** 2854 (1977).
108. V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals*, Pergamon Press, Inc., Elmsford, NY, 1978.
109. J. F. Janak and A. R. Williams, *Phys. Rev. B* **14,** 4199 (1976).
110. A. R. Williams, C. D. Gelatt, Jr., and J. F. Janak, *Proceedings of the Symposium on Theory of Alloy Phase Formation*, New Orleans, LA, 1979, L. H. Bennett, Ed., American Society for Metals, New York.
111. A. R. Williams, J. Kubler, and C. D. Gelatt, Jr., *Phys. Rev. B* **19,** 6094 (1979).
112. A. R. Williams, C. D. Gelatt, Jr., and V. L. Moruzzi, *Phys. Rev. Lett.* **44,** 429 (1980).
113. C. Herring, in *Magnetism IV*, G. T. Rado and H. Suhl, Eds., Academic Press, Inc., New York, 1966.
114. W. Heisenberg, *Z. Physik* **49,** 619 (1928).
115. F. Bloch, *Z. Physik* **57,** 545 (1929).
116. E. C. Stoner, *Proc. Roy. Soc. A* **154,** 656 (1936).
117. J. Hubbard, *Phys. Rev. B* **19,** 2626 (1979) and **20,** 4584 (1979).
118. Representative references are S. T. Pantelides and W. A. Harrison, *Phys. Rev. B* **13,** 2667 (1976); S. T. Pantelides, B. Fischer, R. A. Pollak, and T. H. DiStefano, *Solid State Commun.* **21,** 1003 (1977); S. T. Pantelides, *J. Vac. Sci. Technol.* **14,** 965 (1977) and in *The Physics of SiO_2 and Its Interfaces*, Pergamon Press, Inc., Elmsford, NY, 1978, p. 80.
119. J. A. Knapp, D. E. Eastman, K. C. Pandey, and F. Patella, *J. Vac. Sci. Technol.* **15,** 1252 (1978); D. E. Eastman, F. J. Himpsel, J. A. Knapp, and K. C. Pandey, *Institute of Physics Conference Series*, No. 43, Ch. 28, p. 1059 (1979).
120. G. F. Foster and J. C. Slater, *Phys. Rev.* **95,** 1167 (1954).
121. J. Bernholc and S. T. Pantelides, *Phys. Rev. B* **18,** 1780 (1978).
122. J. Pollmann and S. T. Pantelides, *Phys. Rev. B* **18,** 5524 (1978) and **21,** 709 (1980); *J. Vac. Sci. Technol.* **16,** 1503 (1979).
123. J. Bernholc, N. O. Lipari, and S. T. Pantelides, *Phys. Rev. Lett.* **41,** 895 (1978); *Phys. Rev. B* **21,** 3545 (1980).
124. S. T. Pantelides, N. O. Lipari, and J. Bernholc, *Solid State Commun.* **33,** 1045 (1980).
125. N. O. Lipari, J. Bernholc, and S. T. Pantelides, *Phys. Rev. Lett.* **43,** 1354 (1979).
126. J. Bernholc, S. T. Pantelides, N. O. Lipari, and A. Baldereschi, *Solid State Commun.*, in press.
127. M. Scheffler, S. T. Pantelides, N. O. Lipari, and J. Bernholc, IBM Thomas J. Watson Research Center, Yorktown Heights, NY, unpublished results.
128. F. Jona, *IBM J. Res. Develop.* **9,** 375 (1968) and **14,** 444 (1970); *Surface Sci.* **8,** 57 (1967); *Appl. Phys. Lett.* **9,** 235 (1966).
129. P. M. Marcus and D. W. Jepsen, *Phys. Rev. Lett.* **20,** 925 (1968); P. M. Marcus, D. W. Jepsen, and F. Jona, *Surface Sci.* **17,** 442 (1969).
130. D. W. Jepsen and P. M. Marcus, in *Computational Methods in Band Theory*, Plenum Publishing Co., New York, 1971, pp. 416–443.
131. D. W. Jepsen, P. M. Marcus, and F. Jona, *Phys Rev. Lett.* **26,** 1365 (1971); *Phys. Rev. B* **5,** 3933 (1972) and **6,** 3684 (1972).
132. J. E. Demuth, P. M. Marcus, and D. W. Jepsen, *Phys. Rev. B* **11,** 1460 (1975).
133. J. E. Demuth, D. W. Jepsen, and P. M. Marcus, *Phys. Rev. Lett.* **31,** 540 (1973) and **32,** 1182 (1974); *J. Phys. C* **6,** 9207 (1973); *Solid State Commun.* **13,** 1311 (1973); *J. Vac. Sci. Technol.* **11,** 190 (1974); *Surface Sci.* **45,** 733 (1974).
134. K. O. Legg, F. Jona, D. W. Jepsen, and P. M. Marcus, *J. Phys. C* **10,** 937 (1977) and **8,** 9392 (1975); *Phys. Rev. B* **16,** 5271 (1977); F. Jona, K. O. Legg, H. D. Shih, D. W. Jepsen, and P. M. Marcus, *Phys. Rev. Lett.* **40,** 1466 (1978).
135. H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, *J. Phys. C* **9,** 1405 (1976); *Phys. Rev. Lett.* **36,** 798 (1976); *Surface Sci.* **60,** 445 (1976); *Commun. Phys.* **1,** 25 (1976); *Phys. Rev. B* **15,** 5550, 5561 (1977).
136. M. Passler, A. Ignatiev, F. Jona, D. W. Jepsen, and P. M. Marcus, *Phys. Rev. Lett.* **43,** 360 (1979).
137. H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, *Phys. Rev. Lett.* **37,** 1622 (1976); *Phys. Rev. B* **22,** 814 (1980).

Received July 31, 1980; revised February 20, 1981

Paul S. Bagus is located at the IBM Research Division Laboratory, 5600 Cottle Road, San Jose, California 95193. Arthur R. Williams is located at the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.



Perovskite structure