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Publication Date
1976

To be published in the Annual Review
of Physical Chemistry

LBL-4589 c.1
Preprint

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January 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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To be published in the 1976
Annual Review of Physical Chemistry

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Molecular Electronic Structure Theory: 1972-1975

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Introduction

Four years ago, in writing the preface to my book (1), I noted that "although the quantum mechanical principles required for an understanding of electronic structure have been recognized for forty years, it is only during the past five years that rigorous quantum mechanical investigations have begun to make real contributions to chemistry." Although the advances reported in that five year period appeared monumental at the time, they pale in comparison with the tremendous body of chemical research carried out using ab initio methods during the past four years.

Theoretical studies that were truly state-of-the-art in January of 1972 may now be considered relatively routine. The final example in my book was Clementi's study of hydrogen bonding in the guanine-cytosine base pair (2), a system of 136 electrons. While each point (after the first) on the potential energy surface required ∿ 5 hours of machine time, this same calculation may now be carried out in less than thirty minutes on the same computer, the IBM 360/195. As a second example, consider the XeF_2 molecule, for which a self-consistent-field (SCF) study using a limited gaussian basis was reported (3) in late 1971. In contrast, a paper (4) appearing in the December, 1975 issue of the Journal of the American Chemical Society reports a nearly quantitative treatment of electron correlation in terms of a very large (near Hartree-Fock) basis set of Slater functions. These two examples illustrate rather clearly the leaps and bounds which have occurred in the development of ab initio theoretical methods over the past four years.

More important in a broader perspective is the fact that theory has now become accepted by organic, inorganic, and physical chemists as a legitimate tool for the study of significant chemical problems. One of the most striking confirmations of this trend is the recent reorientation of a distinguished organic chemist, Professor Paul Schleyer, from a laboratory research program to one making extensive use of *ab initio* electronic structure theory. Although *ab initio* procedures are still neither as routine nor reliable as taking an NMR spectrum, that day is coming, thanks in large part to the systematic and authoritative studies (5) of Pople and co-workers at Carnegie-Mellon.

Given the vast number of papers appearing each year on electronic structure theory, it would be hopeless for me to attempt to be encyclopedic in this review. Therefore, the emphasis here will be on the most important and innovative contributions since Frank Harris's 1972 review (6). Fortunately, Richards and co-worker have compiled an excellent update (7) (for the period 1970 through 1973) of their earlier bibliography (8) of *ab initio* calculations. This compendium is highly recommended and should greatly help to reduce possible duplication of scientific research.

For reasons of space I will not be able to cover recent progress using semi-empirical methods, e.g., extended Hückel theory and methods involving varying degrees of neglect of differential overlap (NDO). Also unfortunately omitted is the beautiful work on qualitative molecular orbital theory by the Hoffmann school (9). My personal feeling, however, is that a fundamental goal of careful *ab initio* calculations is to provide guidelines for the use of the simpler and more broadly applicable methods. The recent volume edited by Segal (10) may be referred to by readers seeking a balanced discussion of semi-empirical methods.

Several international meetings of electronic structure theorists were held during the review period. The Boulder (June, 1972) Summer Conference on Theoretical Chemistry, the Houston (November, 1972) Robert A. Welch Foundation Conference, the Menton (July, 1973) First International Congress of Quantum Chemistry, and the Oxford conference (April, 1974) Quantum Chemistry: The State of the Art are particularly noteworthy since the proceedings were published in book form (11-14). Per Löwdin's Sanible Symposia continue to be held each January and the proceedings are published in the International Journal of Quantum Chemistry. Five other volumes (15-19) of theoretical review articles were also published during the past four years.

Numerous review articles involving electronic structure theory have appeared since 1972. The best, in my opinion, and certainly the most influential was delivered by Robert Parr (20) in April, 1974 at the annual meeting of the members of the U.S. National Academy of Sciences. A somewhat related discussion of the growth of computational chemistry was published by Hall (21) in the Chemical Society Reviews. Another important review was that of Buenker and Peyerimhoff (22) concerning the origin of Walsh's rules.

Since worthwhile review articles sometimes appear in unexpected places, the documentation of a few of these is in order here. A comprehensive discussion of hydrogen bonding was given by Schaad (23) in a recent book of which he is co-author. Appropriately enough, two theoretical papers (24,25) appeared in the proceedings of a conference (Dartmouth College, June, 1973) on the Critical Evaluation of Chemical and Physical Structural Information. Lipscomb has recently surveyed (26) his group's *ab initio* studies of boron hydrides and carboranes. In June of this year an article (27) appeared in Chemistry in Britain concerning potential energy surfaces for methylene reactions. The proceedings (28) of the August, 1973 NATO Advanced Study Institute (held in Valmorin, Quebec) contains reviews by S. D. Peyerimhoff, V. McKoy, and O. Sinanoglu. Finally Kern and Karplus have reviewed the electronic structure of water (29), Davidson (30) has discussed the properties and uses of natural orbitals, Bagus (31) has evaluated the role of ab initio theory in the analysis and interpretation of X-ray photoelectron spectra, and Weiss (32) has given an analysis of the correlation problem for excited states of atoms.

Volumes 6, 7, 8 and 9 of Advances in Quantum Chemistry appeared during the review period and contain a number of interesting articles. Another fruitful source of theoretical articles is the series Advances in Chemical Physics. Noteworthy here are the papers by Browne and Matsen (33) on small molecules, Green (34) on the accuracy of ab initio dipole moment predictions, Hinze's overview (35) of computational techniques for large molecules, and the reviews of Kaufman (36) and Balint-Kurti (37) on potential energy surfaces.

Several brief but informative research perspectives have appeared in the Accounts of Chemical Research. In chronological order are those of Whitten (38) on concepts of molecular structure, Lipscomb (39) on three-center bonds in electron-deficient compounds, Goddard and co-workers (40) on the generalized valence bond method, Harrison (41) on the structure of methylene, Bader (42) on the role of molecular fragments in chemical bonding, and Hehre (43) on carbonium ions. A final source of helpful reviews is the serial Topics in Current Chemistry. Articles I was particularly attracted to were those of the Pople group (44) on three-membered rings, Kutzelnigg (45) on pair correlation methods, Scrocco and Tomasi (46) on electrostatic molecular potentials, Simonetta (47) on reaction pathways, and Devaquet (48) on organic triplet states.

A particularly important treatise (about eight volumes) entitled Modern Theoretical Chemistry will be published by Plenum in late 1976. Two volumes, edited by the present author, will appear on ab initio electronic structure theory. The first volume primarily concerns theoretical methods and includes articles by T. H. Dunning and P. J. Hay, A. A. Frost, A. C. Wahl, W. A. Goddard and F. B. Bobrowicz, I. Shavitt, W. Meyer, B. Roos and P. Siegbahn, C. F. Bender, W. Kutzelnigg, V. McKoy, and J. W. Moskowitz and L. C. Snyder. The second volume involves applications of theory, with articles by J. A. Pople, L. C. Allen, P. Kollmann, P. Pulay, A. Veillard and J. Demuynck, M. D. Newton, W. J. Hehre, L. Radom, K. Morokuma, M. E. Schwartz, and S. R. Langhoff and C. W. Kern. Although I can hardly rate as an impartial observer, it is nevertheless my opinion that these two volumes provide a rather accurate and comprehensive view of electronic structure theory in 1976.

In closing this introduction, I would like to mention a very unconventional piece of research by James Anderson. Anderson (49) has pointed out that the time-dependent Schrödinger Equation in one-dimension is similar in form to the diffusion equation. It became apparent to Anderson that rather than using the diffusion equation to simulate the random-walk dispersion process, one might use the random-walk process to simulate the diffusion equation. By including a first-order rate process, one may simulate the Schrödinger equation in the same way. The method has been applied to H_3^+ as well as a number of exactly soluble problems. Although it is not yet clear whether Anderson's approach will be competitive with existing ab initio methods, it certainly provides some very nice insights into the nature of electronic structure in many-electron systems.

Theoretical Developments

A. Hartree-Fock Problem.

The self-consistent-field (SCF) or Hartree-Fock approximation is the quantum mechanical embodiment of the chemist's notion of filling up molecular orbitals (in order of increasing energy) until the desired number of electrons is disposed of. As such the single-configuration SCF method will always play a key role in our understanding of electronic structure. In addition the SCF approximation is quite adequate for the qualitative prediction of several properties of chemical import, most notably molecular geometries or structures. Thus the extension of the Hartree-Fock method to larger and larger molecules is one of the critical challenges to the electronic structure theorist.

As mentioned in the introduction, important advances have been made in SCF methodology in recent years. Several of these advances date to the Pople group and their development of the program GAUSSIAN 70 (50). Particularly important was their recognition that by considering all two-electron integrals involving the three components (p_x, p_y, p_z) of a particular p function, great efficiencies could be introduced. It is obvious that the savings achieved are even greater when integrals involving d functions are treated in this manner. This innovation has also been incorporated in the other two most efficient programs available at present, Clementi and Popkie's IBMOL VI (51) and the MOLECULE program of Almlöf and Roos (52). Important features first introduced by Clementi in IBMOL are the so-called "MOVE" and "ADD" options. The MOLECULE program has the particularly useful feature of calculating two-electron integrals directly over symmetry orbitals (for nondegenerate point groups only, i.e., D_{2h} and any of its subgroups). Another widely used program POLYATOM (53) employs symmetry in a rather elegant manner, but becomes less effective for molecules having no elements of symmetry.

Several important articles have appeared recently concerning the computation of two-electron integrals, including two rather comprehensive discussions of integrals over contracted gaussian functions. Clementi (54) brings special attention to the importance of recognizing small integrals prior to their computation. This critical preprocessing of integrals is done with a level of effort proportional to n^2, as opposed to n^4, the approximate number of two-electron integrals. In the same article, Clementi advocates the use of an "adjoined" basis set. The basic idea here is that integrals of intermediate magnitude (say 10^{-5} to 10^{-7}) may be computed with a single primitive gaussian substituted for each contracted gaussian function appearing in the integrand. Clementi presents a number of demonstration calculations, the largest being the carbazole-trinitrofluorenone complex. The latter computation involved 618 primitive gaussians, 194 contracted functions, 232 electrons, and 6½ hours of IBM 360/195 machine time.

Ahlrichs (55) has given a carefully thought out discussion of the evaluation of two-electron integrals over gaussian lobe functions. For intermediate sized systems, (say, 60 contracted functions) the procedures advocated seem a bit faster than those of Clementi. Ahlrichs makes several interesting observations in his paper. These include the proof that for a large molecule A_n with an arbitrary but fixed basis set for the fragments A, the total number of two-electron integrals larger than a certain threshold T increases only like n^2. This certainly makes it clear that the n^4 "bottleneck" is valid only for small and moderate sized molecules, a point also emphasized by Clementi (54). Ahlrichs also points out that in using the notion of the "adjoined" basis set, not one but two primitive gaussians are needed in integral evaluations. Some interesting and related research concerning rigorous error bounds on the difference between exact two-electron integrals and proposed approximations has been reported by Jafri and Whitten (56).

A significant development in respect to both the computation of integrals and the facilitation of SCF procedures is Pitzer's work (57,58) on nonlinear polyatomic molecules of high symmetry. The conventional approach is to compute two-electron integrals over basis functions and use these integrals in the ensuing SCF procedures. As pointed out earlier, a key feature of the MOLECULE code (52) is the direct computation of integrals over symmetrized basis functions for Abelian point groups. Pitzer has developed analogous methods for the much more intricate non-Abelian groups, e.g., D_{6h}. In these high symmetry cases, the simplifications inherent in Pitzer's approach can be tremendous. As an example, consider Johansen's recent calculation (59) on tetrahedral MnO_4^- using a very large basis of 105 contracted gaussian functions. Pitzer and co-workers (60) were able to reduce the number of P supermatrix elements (61) from ca. 4,000,000 to 117,006. In addition to greatly reducing the integral computation time, the direct use of integrals over symmetry orbitals reduces the time per SCF iteration to 2 secs (IBM 370/165) or essentially no time at all! In the same paper, Pitzer et al. carried out comparable studies of both the hole states of MnO_4^- and the excited electronic states. Important additional studies making effective use of this approach have included benzene (62), and the series of transition metal compounds ScF_3 through CuF_3 (R. M. Pitzer, to be published). A very elegant generalization of Pitzer's method has been derived by Davidson (63) using double cosets. Davidson's method has recently been programmed by Dr. D. H. Liskow at Battelle Columbus.

The most important and innovative development since 1972 concerning the use of basis functions was Raffenetti's general contraction scheme (64) for gaussian functions. Prior to that time, essentially all contracted gaussian basis sets were of the segmented variety, with each primitive gaussian appearing in only one contracted function. When primitives were "duplicated" in different contracted functions, two-electron integrals involving the duplicated primitives had to be recomputed. In Raffenetti's scheme each primitive gaussian may be used in as many contracted functions as desired. The key to this method is the use of very rapid four-index transformations (of small dimension) involving the primitives that are repeated. As an example of the usefulness of this scheme consider the s function basis of a first-row transition metal, specifically the 14s set of Wachters (65). To obtain true double zeta flexibility, a segmented basis of 9 contracted functions must be employed. However, in Raffenetti's scheme, a single fully contracted function may be used for each of the 1s, 2s, and 3s orbitals, and two functions used for the 4s valence orbital. Thus a set of nine s functions is reduced to five with no loss in accuracy. Any reduction in number of contracted functions is of course extremely helpful at the SCF level and even more so if configuration interaction (CI) is to be performed. Raffenetti has written a general program BIGMOLLI to implement his method.

Another significant trend is the standardization of gaussian basis sets for the atoms hydrogen through neon. Most widespread are the STO-3G and 4-31 G basis sets of Pople and co-workers (66,67), followed by the Dunning-Huzinaga (68,69) double zeta sets, which are slightly more effective than the 4-31 G.

Some very carefully optimized primitive gaussian basis sets (for H-Ne) have been generated by van Duijneveldt (70) but unfortunately have not appeared in the open literature. For example, for the ^1S ground state of the neon atom, van Duijneveldt's (9s 5p) basis yielded a total energy -128.52822 hartrees, 0.00148 hartrees lower than the original Huzinaga set (69). In this context it is important to point out that Ruedenberg and Raffenetti's introduction of even-tempered basis functions (71) can be extremely helpful in the optimization of large gaussian basis sets. Finally an exhaustive and reoptimized (relative to Clementi's original Tables of Atomic Functions) set of analytical SCF wave functions and Slater function basis sets for the atoms He-Xe has been published by Clementi and Roetti (72).

As the computation of two-electron integrals becomes less of a bottleneck to ab initio calculations, the importance of efficient algorithms and computer programs for carrying out SCF procedures becomes more apparent. Two of the most efficient and general (in terms of applicability to open-shell states) methods available at present are those of Bagus (implemented in the ALCHEMY (73) linear molecule code) and Goddard (74) [developed with Bobrowicz in the GVBTWO program]. For open-shell states with Hartree-Fock energy expressions which cannot be written in terms only of coulomb and exchange integrals J_{ij} and K_{ij}, the above programs are not applicable. To treat such cases Yarkony (75) has proposed a general scheme for solving the SCF equations and applied this method to several excited states of CH_3CO^+, the acetyl cation. An interesting and lucid paper by Raffenetti (76) appeared on the subject of most effectively processing two-electron integrals during SCF iterations. Another frequent problem is convergence of the SCF procedure, and a very useful advance has been made in this regard by Saunders and Hillier (77). Their level-shifting technique represents a very simple but effective modification to existing SCF programs and has already gained relatively widespread acceptance.

In conventional methods for predictions of equilibrium geometries, transition states, force constants, and reaction pathways, it is often true that very many individual calculations at different geometries must be carried out. For example, a complete determination of the structure of the norbornyl cation $C_7H_{11}^+$ would require about 2500 calculations, even using the SIMPLEX method, a fairly effective search procedure (78). In striking contrast, by using the gradient method developed for ab initio SCF wave functions by Pulay (79-81), the $C_7H_{11}^+$ equilibrium geometry may be determined from ∿ 25 gradient evaluations. Most important, in Pulay's approach the gradient is obtained directly with a single calculation, requiring an amount of computation not much greater than a single point on the potential surface. Pulay's use of gaussian lobe functions means that the most complicated integrals arising involve p functions and hence can be computed rapidly using standard analytical techniques. Pulay and Meyer (82-84) have applied the gradient method to the calculation of equilibrium geometries and force constants of numerous polyatomic molecules. Their results, especially for force constants, are in surprisingly good agreement with experiment, even when relatively small basis sets (e.g. 7s 3p on C, N, or O) are used. For example, for the ethylene molecule Pulay and Meyer (82) were able to unambiguously resolve a conflict between two experimental force fields. An alternative approach to direct gradient evaluation, which does not restrict the basis to gaussian lobe functions, has recently been developed by Poppinger (85). Rather than analytically evaluating the required integral derivatives, Poppinger approximates them by finite differences. This method has been successfully used by Radom and Poppinger (to be published) to locate as many as nine distinct transition states on the HCNO potential surface.

Another innovative and novel development of the past two years is Newton's reformulation (86) of Hartree-Fock theory to include the case of a discrete molecular aggregate embedded in a continuum. The first problem to which this formalism was applied was the ground state hydrated electron. Specifically, Newton considered the electron and its first hydration shell of four water molecules, i.e., $(H_2O)_4^-$, surrounded by a continuous polarized dielectric. As expected on the basis of previous work by Naleway and Schwartz (87), the $(H_2O)_4^-$ entity is not predicted to be bound relative to the neutral water tetramer. More important, however, when the polarization is "turned on", the result is a strongly bound (by 1.1 eV) localized electron. Newton has also applied this new technique to the ammoniated electron in a paper (88) in which his formalism and general philosophy are spelled out in detail. The latter paper was presented as the plenary theoretical lecture at the Fourth International Colloque Weyl (June, 1975) on Electrons in Fluids.

Although we have of necessity deleted a discussion of semi-empirical methods, one such approach is quite closely related to *ab initio* methods using minimum basis sets. This is the partial retention of diatomic differential overlap (PRDDO) method of Halgren and Lipscomb (89). In the spirit of Pople's NDO methods (90), no experimental parameters are employed, but certain types of two-electron integrals are parameterized to reproduce ab initio results for a variety of small molecules. The method has been rather carefully tested and for molecular structures and force constants appears to reproduce quite closely (e.g., 0.01 Å agreement in bond distances) the results of full ab initio treatments. Lipscomb and co-workers also find (91) that PRDDO localized orbitals obtained by the Boys method (92) are generally in rather good agreement with ab initio localized orbitals derived from the theoretically sounder Edmiston-Ruedenberg (93) criteria. One of the most interesting applications of PRDDO is the full determination of the structure of the sandwich compound berylocene $Be(C_5H_5)_2$ by D. S. Marynick (to be published).

There seems to be a general feeling among electronic structure theorists that one of the most significant recent developments concerns the use of pseudopotentials in ab initio procedures. Certainly if one wants to carry out careful studies of molecules like UF_6, a pseudopotential approach will be required. Another tantalizing aspect of pseudopotentials is the hope that relativistic effects (corresponding to ∿ 1200 hartrees for the mercury atom) can somehow be embedded in an appropriate model potential. My own feeling is that pseudopotentials are close but have not quite reached the point of genuine reliability. The earliest (and continuing) important research on the use of effective potentials for molecular systems is that of Goddard, Kahn, and Melius (94-98). An interesting recent application (98) concerns the lowest $^5\Delta$ and $^5\Sigma^+$ states of the FeH^+ ion, for which a basis set of size (14s 9p 5d) on iron is reduced to (4s 5p) by using a pseudopotential to replace the fully-occupied 1s, 2s, 2p, 3s, and 3p orbitals. In this way the computation time is reduced by nearly an order of magnitude and reasonable agreement (1% for orbital energies, 0.04 eV and 0.14 eV for the two dissociation energies) is obtained with fully ab initio results. Additional important work on pseudopotentials has been carried out by the groups of Schwartz (99-101) and Huzinaga (102, 103). Specifically, Switalski and Schwartz (101) have studied a large number of polyatomic molecules using double zeta basis sets with core functions eliminated, courtesy of the pseudopotential. An interesting feature of their work was the correct energetic ordering, by comparison with Clementi's large scale ab initio predictions (104), of the isomers LiCN and LiNC. McWilliams and Huzinaga (103) have adapted Pople's 4-31 G basis to their pseudopotential approach and predicted the structures of a number of simple molecules. In most cases the results are quite impressive, e.g., the predicted bond distance and bond angle for NH_3 are 0.991 Å and 115.4°, compared to the fully ab initio results 0.991 Å and 115.9°. However, for the CN bond distance in HCN, the model potential yields a result 0.011 Å shorter than Pople's original finding. Although this may appear to some as nitpicking, it should be kept in mind that sophisticated semi-empirical methods (e.g., PRDDO) are also capable of reproducing ab initio bond distances to ∿ 0.01 Å. Finally we should note that there appears to be a particularly large amount of unpublished work on pseudopotentials, especially that reported by Luis Kahn at the June, 1975 Boulder Conference. In addition, G. Das and A. C. Wahl (to be published, J. Chem. Phys.) have developed a pseudopotential approach and applied it to several electronic states of the HgH molecule.

We conclude this section with a discussion of multiconfiguration self-consistent-field (MCSCF) methods. It seems clear that this discussion could just as appropriately have been placed in the following section on the correlation problem. The most exciting news about MCSCF methods is that they now work quite well--convergence problems are nicely under control and the choice of configurations is no longer limited, for example, to excitations of the type $a^2 \rightarrow b^2$. The thanks for this encouraging development goes to Das and Wahl (105) and Hinze (106). For diatomic molecules as large as $C\ell_2$, potential energy curves of semi-quantitative accuracy are now routinely obtained by Wahl and co-workers. Recent examples (107-109) include OH (14 configurations were included), the van der Waals molecule ArH (12 configurations), and CO (11 configurations), for which very good agreement with the experimental dipole moment and dissociation energy were obtained. Docken and Hinze (110) have reported a very comprehensive study of the ground and excited electronic states of LiH. An interesting feature of this work is that two states (X $^1\Sigma^+$ and A $^1\Sigma^+$) of the same symmetry were successfully investigated. Fifteen configurations were employed and the orbitals optimized in the averaged field of the two states, obtaining compromise orbitals which describe both states about equally well. The present practical limit of general MCSCF methods (105,106) is probably about 50 configurations, a number which is inadequate for a semi-quantitive description of electron correlation in even moderate sized organic molecules such as ketene CH_2CO. Therefore there is an increasing tendency (111-113) to use the MCSCF procedure to generate an optimum set of orbitals, and then use these orbitals in a configuration interaction (CI) calculation of some sort.

B. The Correlation Problem

In 1976 it certainly need not be emphasized that the theoretical resolution of many (perhaps most) problems of chemical significance necessitates going beyond the single-configuration Hartree-Fock approximation. Most obvious is the need for a consideration of electron correlation whenever a chemical bond is broken or formed. Unfortunately for even moderate sized molecules (e.g., ozone), existing reliable procedures for the theoretical description of electron correlation require typically an order of magnitude more computation than a simple SCF calculation with the same basis. Furthermore, since straight-forward CI (including all single and double excitations) is an N^6 procedure while ordinary SCF methods only increase as N^4, the situation promises to get worse as one goes to large systems. For these reasons, the correlation dilemma remains the outstanding problem facing electronic structure theory today. In my opinion the most exciting developments of the past four years are the unconventional CI methods of Meyer (114), Roos (115) and Bender (116). However, before going on to a discussion of the radically new approaches, we should review progress along the more conventional lines.

The acknowledged master of conventional CI calculations is I. Shavitt, and many of the techniques developed by Shavitt's group at Battelle-Ohio State were inspired by the late S. F. Boys. Other centers of excellence for the theoretical study of electron correlation in molecules are the IBM Research Laboratory, San Jose (Yoshimine and Liu), the Berkeley-Livermore group (Bender and Schaefer), and the Bonn group (Buenker and Peyerimhoff). The conventional CI techniques all involve three main steps after the completion of an SCF calculation of some kind: (1) transformation of two-electron integrals from basis functions to an orthogonal set of molecular orbitals, (2) generation of nonzero Hamiltonian matrix elements H_{ij} over configurations, (3) extraction of the lowest eigenvalue and corresponding eigenvector from the Hamiltonian matrix. Shavitt (117) has recently written an outstanding review of the status of general CI methods and considers in detail each of the above three steps. A very careful study of the water molecule using these techniques and a variety of basis sets, has recently been published by Rosenberg and Shavitt (118).

I have just recently received in preprint form an important paper that decidedly changes my opinions about the convergence (as a function of number of configurations) of the CI method. To put this new finding in the proper context, the reader should recall that the best existing conventional CI wave function for a 4-electron system is that of Bunge (119) for the Be atom. Using 180 configurations, he obtained a nonrelativistic energy of -14.664193 hartrees, or ∿ 96.7% of the correlation energy. Since CI convergence becomes slower and slower as one approaches the exact wave function, it seemed natural to assume that ∿ 99.5% of the correlation energy was the maximum attainable using less than ∿ 10,000 configurations. Sims and Hagstrom (120) obtained a lower energy (-14.666546 hartrees) than that of Bunge, but only by explicit use of interparticle coordinates. However, the entire complexion of the situation has been changed by Bunge's new paper (to be published). There he reports that a variational energy of -14.666902 hartrees (99.6% of the correlation energy) was obtained in a conventional CI calculation including only 650 configurations. The key features of Bunge's work include the exhaustive optimization of orbital exponents (a 10s 9p 8d 5f 4g 3h 1i basis of Slater orbitals was employed) and an intelligent use of natural orbitals (31). Bunge's attainment of all but 0.4% of the correlation energy of beryllium using such a modest sized CI is certainly an encouraging signal for the future of the CI technique.

An important method developed by Buenker and Peyerimhoff (121,122) over the past two years involves individualized configuration selection, followed by an energy extrapolation procedure. Actually the method of selecting configurations is related to one used for some time by Shavitt and co-workers. A group (usually of the order of 10) of reference or dominant configurations is chosen and the Hamiltonian diagonalized for this small CI to yield a wavefunction ψ_0. Then the importance of all single and double excitations is tested using ordinary first-order Rayleigh-Schrödinger perturbation theory with ψ_0 as the zeroth order wave function. By solving larger and larger secular equations (corresponding to tighter and tighter tolerances for the neglect of configurations), Buenker and Peyerimhoff are able to extrapolate their results to the full all singles and doubles result for the chosen set of reference configurations. If one simultaneously increases the number of reference configurations in ψ_0, it is possible to predict the full CI result for a given basis. Buenker and Peyerimhoff have tested the method rather thoroughly and applied it to the excited states of a variety of molecules (see their review in Reference 28, for example). A related paper (as regards configuration selection) by R. C. Raffenetti, K. Hsu, and I. Shavitt, with application to several excited states of the BH molecule, was presented at the June, 1973 Molecular Spectroscopy meeting in Columbus, Ohio, but has not yet been published. However, the concept of energy extrapolation is original with Buenker and Peyerimhoff and represents an important contribution to electronic structure theory.

A minor objection to the above procedures is that adjacent points on a potential energy surface will be described by wave functions made up of slightly different configurations. In addition, the use of a variable list of configurations eliminates the possibility of using the formula tape approach of Shavitt (117), which can result in very significant savings in computation when many points on a potential surface are required. The simplest CI method of qualitative reliability using a fixed list of configurations (specified only by basis set size and symmetry considerations) remains the first-order approach developed here at Berkeley (1). The effectiveness of this method has been significantly improved (112) by using MCSCF procedures to obtain an optimum set of valence molecular orbitals. In this way the use of the iterative natural orbital method (123), which requires the repeated four-index transformation of two-electron integrals, may be avoided.

As implied above, the four-index transformation of two-electron integrals is often a bottleneck in CI calculations. If the total number of integrals under consideration is relatively small and these can be stored in central memory, the algorithm of Bender (124) appears optimum. For larger basis sets the use of Yoshimine's efficient reordering algorithm (125), based on the use of large random access external storage, becomes necessary if economy is a consideration. Two other clear and helpful expositions of the four-index transformation, by Pendergast and Fink (126) and Diercksen (127), have appeared recently.

Four years ago, the most exciting development in molecular quantum mechanics was Meyer's PNO-CI method (114). The essence of Meyer's method, of course, is the use of a different set of pseudonatural orbitals (128), or pair natural orbitals (PNO's), to correlate each occupied pair of SCF orbitals. In this way, due to the unique properties of natural orbitals for two-electron systems, the CI expansion takes on a very rapidly convergent form. For example, Meyer (129) obtains ∿ 83% of the correlation energy of CH_4 using only 230 configurations. In the same paper, Meyer also gives a much more satisfactory discussion (which is applicable to both closed- and open-shell systems described qualitatively by a single-configuration Hartree-Fock wave function) of the PNO-CI formalism, than was presented in the original manuscript (114). One of the more interesting applications (130) is to proton transfer in $(H_5O_2)^+$, i.e., the H_2O-H_3O^+ system. In addition a very comprehensive study of the hydrides LiH through HCℓ has been reported recently (131,132). In the latter paper Meyer and Rosmus emphasize that the coupled electron pair approximation (CEPA), in which higher than double excitations are treated approximately, provides somewhat better agreement with experiment than the PNO-CI method. For example, for the SiH molecule ($^2\Pi$ ground state) the PNO-CI, CEPA, and experimental dissociation energies D_e are 2.99, 3.09, and 3.19 ± 0.05 eV. The general objection to the CEPA method, shared by the present author, is that it is a nonvariational procedure and can yield more than 100% of the correlation energy.

The research groups of Kutzelnigg (Bochum) and Ahlrichs (Karlsruhe) have made very extensive studies (133-139) using the PNO-CI and CEPA methods. Systems studied to date have included BeH_2, BH_3, CH_3^-, NH_3, H_3O^+, HF, and Ne(134), MgH_2, $A\ell H_3$, SiH_4, PH_3, H_2S, HCℓ, and Ar(135), N_2, F_2, C_2H_2, C_2H_4, and C_2H_6(136), B_2H_6 and $(LiH)_2$(137), H_5^+ (138), and BH_5(139). As a part of their work they have also given (133) an alternative presentation of Meyer's formalism. In fact their presentation is pedagogically superior to that of Meyer (114, 129), and includes a somewhat improved method for the computation of the PNO's. In any case these systematic studies of the PNO-CI method establish it clearly as one of the premier methods for the treatment of electron correlation in molecules. A particularly noteworthy example (137) is the dimerization energy of BH_3, for which experimental values range from 25 to 60 kcal/mole and a number of theoretical studies have been carried out (1, 140). Using a large basis (for calculations with an essentially complete description of electron correlation) of 68 contracted gaussian functions, Ahlrichs predicts 20.7 kcal (SCF), 34.2 kcal (PNO-CI), and 36.6 kcal (CEPA). The latter result is probably within 2 or 3 kcal of the exact (unknown) dimerization energy.

Just as Meyer's method was revolutionary in the use of nonorthogonal sets of pair natural orbitals, the new CI method of Roos (115) also differs abruptly from conventional methods. In his approach, Roos does not explicitly construct the Hamiltonian matrix elements H_{ij}, but instead works directly from the one- and two-electron integral list to the final eigenfunction (wave function) and eigenvalue (energy). In essence, the Roos method is a "look-ahead" scheme. That is, if one knows exactly how the H_{ij} are going to enter into the lowest solution of the secular equation and exactly how the H_{ij} are constructed from the integral list, one can omit the intermediate step of assembling the H_{ij}. The resulting method is extremely efficient if a rapidly convergent (say, four or five iterations) iterative scheme for obtaining the lowest eigenvalue is applicable. In fact the very largest CI calculations reported to date, including 56,268 configurations (all single and double excitations) for the water dimer, were carried out (141) with the Roos method. In the latter case about two hours of IBM 360/91 were required for a complete calculation, involving 66 contracted gaussian functions. The only obvious disadvantage of the Roos method is that the detailed programming of explicit formulas for the contributions of various H_{ij} is required. For this reason, only three versions of the method have been programmed: (a) a version including all singly- and doubly-excited configurations (i.e., spin eigenfunctions) with respect to a closed-shell single determinant SCF wave function (115); (b) a version including all singly- and doubly-excited Slater determinants with respect to a single determinant unrestricted SCF wave function (P. Siegbahn, unpublished); and (c) Siegbahn's full CI program (142) for systems with three valence electrons. Some of the interesting applications of the Roos-Siegbahn method will be described in the final section of this review.

The third important new method, which also capitalizes on the key feature of the Roos approach, is the Vector Method (VM) of Bender and colleagues (116,143). In both of these "direct" methods the lengthy computation of the Hamiltonian matrix is sidestepped. However, in other respects the two methods are quite different. The Vector Method is formulated within an occupation number representation of the Hamiltonian, i.e., in terms of the annihilation and creation operators familiar in many-body theory (144). More important in a practical sense is the fact that, unlike the methods of Meyer and Roos, the form of the VM wave function is very flexible. In the earlier stages of development, the VM worked strictly in terms of Slater determinants. More precisely, one specified any number of reference determinants (if only one reference determinant were chosen, it would of course be the SCF wave function) and then selected the level of excitations to be considered. For example one could choose all single, double, and triple spinorbital excitations with respect to a set of six reference determinants. This type of flexibility is particularly crucial for cases (e.g., the dissociation of most diatomic molecules [1]) where the wave function is not even qualitatively described by a single configuration. In such cases the Meyer and Roos methods as presently formulated cannot be intelligently applied. The more recent version (C. F. Bender, unpublished) of VM uses spin eigenfunctions rather than Slater determinants. Another strong point of Bender's method is its ability to routinely obtain several eigenvalues of the same symmetry. The use of Davidson's recent very efficient diagonalization procedure (145) is crucial in this regard. Although the current version of Bender's code does not appear as efficient as the Meyer and Roos methods, continuing development of this most recent method should shortly remove this disparity.

Although variational methods continue to dominate electronic structure theory, a significant trend over the past four years has been the development of useful many-body approaches. In particular the work of the McKoy group at Cal Tech on the Equations of Motion (EOM) method has had a significant impact on theoretical chemistry. The power of the EOM approach comes from the fact that both excitation energies and transition probabilities are obtained directly, i.e., without having to obtain wave functions for the two states involved. A key feature leading to the success (relative, for example, to the simpler RPA method) of the EOM is McKoy's use of perturbation theory to include the effects of double excitations (146). In this sense the EOM approximation goes well beyond ordinary Hartree-Fock theory. Applications of the EOM have ranged from diatomics such as N_2 and CO (147) all the way to the benzene molecule (148). In an important contribution to the formalism, Yeager and McKoy (149) have recently extended these techniques to systems with open-shell ground states. In their most recent work the McKoy group has applied some of these ideas to electron scattering and photoionization processes (150).

Related to EOM work is that of three theoretical groups primarily concerned with ionization potentials and electron affinities. Cederbaum (151) uses a form of many-body perturbation theory in which the ionization potentials are found from the negative real parts of the poles of the one-particle Green's function. Cederbaum's approach appears quite reliable and is applicable to rather large systems, as is apparent from a very impressive recent paper with von Niessen and Diercksen (152). Using flexible double zeta basis sets, they have studied the ionization potentials of pyridine and phosphoridine. Simons and co-workers (153) at the University of Utah have modified the EOM method to directly compute electron affinities as well as ionization potentials. Since electron affinities are notoriously (154) difficult to calculate with variational methods, Simons' research on systems such as OH^- (155) is very significant. Finally, Chong, Herring and McWilliams (156) have nicely illustrated that ordinary third-order Rayleigh-Schrödinger perturbation theory can provide a rather accurate accounting of the effect of electron correlation on ionization potentials. A number of polyatomic molecules (e.g., H_2O, H_2CO, and F_2O) have been studied using double zeta basis sets of Slater functions.

A significant research program designed to explore in a rigorous way the relationships between semi-empirical and ab initio methods is that of Karl Freed. For this purpose a formalism has been developed (157) and applied to the ethylene molecule (158), a simple π-electron system. The relation to Pariser-Parr-Pople theory was investigated in detail.

At this point we turn to some very promising, but not yet thoroughly tested, approaches to the correlation problem. The first is the group theoretical approach of Paldus (159) to CI calculations. Paldus uses as an N electron CI basis the Gelfand and Tsetlin canonical basis for the finite dimensional irreducible representations of the unitary groups. For certain types of calculations (e.g., full CI) it appears that the Paldus approach will allow the very rapid computation of Hamiltonian matrix elements H_{ij}. However, much experimentation and development remains to be done before we can form a final opinion of the effectiveness of this approach.

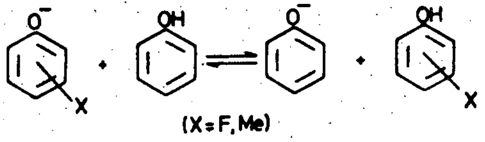
An important breakthrough appears in the making with Pople's adaption of Møller-Plesset perturbation theory. Although work published to date (160) includes only a second-order study of atomic correlation energies, a rather large amount of research on this method has been completed but not yet published. Specifically, Binkley and Pople find that the use of third-order Møller-Plesset theory provides consistently reasonable predictions for dissociation energies, a frequent source of error for SCF theory. As with the previous Pople group innovations (all at the SCF level) this new approach to the correlation problem promises to be applicable to a broad selection of chemical systems.

Perhaps the most promising of the very new methods is Meyer's Theory of Self-Consistent-Electron Pairs (TSCEP). Meyer's wave function (161) is given in terms of two-electron clusters represented by coefficients and density matrices referring directly to the basis functions. In the spirit of the direct methods of Roos and Bender, Meyer avoids the explicit construction of Hamiltonian matrix elements. But, in addition he avoids the four-index transformation of two-electrons. In fact the TSCEP is quite reminiscent of open-shell SCF theory, being an iterative procedure involving the construction of coulomb and exchange operators. One such generalized operator is required for each spin-adapted pair of occupied SCF orbitals. If as expected convergence can be achieved in $\sim$ 5 iterations, the method (which yields the equivalent of a CI wave function including all single and double excitations) should compare very favorably with existing techniques. A computer code for TSCEP has been developed by Clifford Dykstra and applied (162) to a number of simple systems, including LiH and H_4.

Applications of Theory

Any discussion limited to the size of the present one cannot possibly hope to cover even the more important contributions of ab initio theory to chemistry. In fact, with the invasion by all manner of experimentalists, this field has become so large that a review of the present scope may not be possible in the near future. In any case, I would like to apologize beforehand to the many authors whose work I have overlooked. Inevitably, my choice of topics in this section will reflect my own areas of special interest.

A good starting point is the exhaustive compendium of the Pople group (5) for molecules H_mABH_n, where A and B are first row atoms C, N, O, or F. Essentially all possible neutral and monopositively charged species of this general form were studied. The equilibrium geometry of each species was determined at the minimum basis set STO-3G level of theory, and a final calculation using the larger 4-31G basis was performed at the STO-3G optimum geometry. This paper represents an obvious jumping-off point for the future theoretical study of this broad class of molecules. A very important related study is that of Hehre and Pople (163) of the geometric structures, rotational potentials, relative isomer stabilities, and dipole moments of the neutral C_4 hydrocarbons for which simple valence structures may be drawn. Among the most fascinating of these molecules is cyclobutadiene C_4H_4, which Newton and co-workers (164) have also studied in order to ascertain whether the square planar (D_{4h}) triplet state or rectangular (D_{2h}) singlet state represents the true ground state. Although Hehre and Pople's most extensive SCF calculations (which include d functions on carbon) suggest the triplet state lies 6 kcal lower, they argue that correlation effects will shift this order and that a rectangular singlet ground state is probable. Since relatively little is known experimentally about other C_4H_4 isomers, Hehre and Pople's energetic order of these is particularly fascinating: but-1-yne-3-ene (the ground state, with a relative energy of 0 kcal), butatriene (11 kcal), methylenecyclopropene (24 kcal), 1,3-cyclobutadiene (${}^3A_{2g}$, 35 kcal), methylcyclopropenylidene (38 kcal), tetrahedrane (69 kcal), and 1,2-cyclobutadiene (73 kcal). Although the work of the Pople group (often in collaboration with Scheyer) on carbonium ions is well known (165), less research has been carried out on organic anions. However, at the Australian National University (Canberra), Radom has completed some very impressive work along just these lines. In a recent communication (166), for example, a number of gas phase acidities have been predicted and compared to available data from ion cyclotron resonance experiments. One of the cases considered was the abstraction of a proton from phenol by various substituted benzene anions, i.e., the reactions



(1)

For X being ortho-, meta-, and para-fluorine, the theoretical heats of reaction are +2.7 kcal, +5.0 kcal, and +1.7 kcal, compared to experiment (167), +2.8, +4.8, and +2.1 kcal. This agreement both with respect to the order and absolute difference is really remarkable, especially considering the use of minimum basis set SCF theory.

Although the focus of electronic structure theory has shifted away from diatomic molecules in the 70's, considerable research of a very high calibre continues in this area. For example, a potential energy curve of essentially quantitative reliability for He-He has recently been obtained at IBM San Jose by B. Liu and A. D. McLean (unpublished work). Their work builds upon the first qualitatively correct treatments of He_2, where a single configuration localized orbital representation was adopted and all interatomic correlation effects were accounted for (168,169). Liu and McLean propose a three-configuration description ($1s^2$, $2s^2$, $2p^2$) of each He atom and begin with a comparable MCSCF calculation for the He_2 molecule. On top of this are then added all configurations which vanish (relative to the three configuration description of both He atoms) as the two atoms are separated. A well depth of 10.7 °K is predicted, in essentially perfect agreement with the molecular beam results of Yuan Lee's group. A question on which theorists and experimentalists are still in disagreement concerns the diatomic radicals KrF and XeF, both of which are predicted to be only weakly bound by CI calculations (170,171) using respectable basis sets. In the most recent XeF theoretical study (B. Liu, unpublished), a basis set specifically designed to describe Xe^+F^- was used and the result remains a small attractive well of the order of 0.5 kcal/mole. Nevertheless, experimental papers continue to appear (172) in which a chemical well of the order of 20 kcal/mole is cited for XeF. Although the theoretical predictions to date are certainly not infallible, an XeF well depth of more than 5 kcal/mole seems very unlikely to the present reviewer. Other very important papers involving diatomics include the work of Lie, Hinze, and Liu (111) on the excited electronic states of CH, Julienne and Krauss's beautiful explanation (173) of the predissociation of the O_2 Schumann-Runge bands in terms of spin-orbit coupling, and the work of Kahn, Hay, and

Shavitt (174) on the avoided crossing of $^1\Sigma^+$ potential curves in LiF.

An area in which the interaction with experiment (primarily laser, chemiluminescence, and molecular beam workers) has been particularly fruitful is that of potential energy surfaces for simple reactions. One reflection of this is the fact that a Faraday Society meeting on this topic has been scheduled for September, 1976 in Sussex. A key contribution to this area was the paper (175) by Bender and co-workers on the $F + H_2$ reaction. More recent attention has been concentrated on the exchange reactions

$$F + HF \rightarrow FH + F \qquad (2)$$

$$H + FH \rightarrow HF + H \qquad (3)$$

both of which are important in the H_2-F_2 laser system. Contrary to some speculation that linear symmetric FHF might exist as a stable species, recent theoretical studies (176) show that reaction (2) has a barrier of 18 kcal or more. The collinear barrier for reaction (3) is even greater, ∿ 40 kcal/mole (177), and is in sharp disagreement with the values of ∿ 1 kcal/mole predicted by semi-empirical surfaces, e.g., LEPS and BEBO. Several very accurate potential energy surfaces have been obtained using the Roos-Siegbahn direct CI method. The first, the non-linear H_3 surface of Siegbahn and Liu, is not yet published, but in conjunction with Liu's collinear surface (178), appears to provide a definitive (1 kcal accuracy everywhere) result for this critically important prototype system. The other two surfaces, involving larger systems and inevitably less reliability, are for the $H + Li_2$ and HNC → HCN reactions (179,180). For the former system, a careful MCSCF study has also appeared very recently by England, Sabelli, and Wahl (181). For the HNC → HCN surface, the CI included 11,735 configurations in the non-linear region. Finally, an extremely ambitious undertaking has recently appeared (182), a study carried out in Lionel Salem's laboratory (using minimum and double zeta SCF and small CI methods) of the Diels-Alder condensation of ethylene and 1,3 butadiene.

A species of particular interest to both theoreticians and experimentalists is the methylene molecule. For a review of work leading to the resolution of the CH_2 structure, the reader is referred to Harrison's paper (41). A continuing problem concerning the isolated CH_2 radical is the separation between its lowest triplet ($^3B_1$) and single ($^1A_1$) electronic states. For some time now, the experimentalists have been split into two groups, those (183) favoring the "low" value (1-2 kcal) and those (184) favoring the "high" value (8-9 kcal). The most recent theoretical values are those of Hay, Hunt and Goddard (185) 11.5 kcal, Bender and co-workers (186), who calculated a separation of 14.0 kcal but estimated 11 ± 2 kcal for the exact result, and Staemmler (187) 9.2 kcal. Since all three theoretical values favor the high experimental result, it would appear that all we need do is sit back and wait for a definitive experiment to confirm the theoretical predictions. Unfortunately, an apparently definitive experiment (photodetachment of CH_2^-) has been carried out by W. C. Lineberger at Boulder (unpublished), with a resulting 18 kcal singlet-triplet separation, a value much higher than either the previous low or high experimental results. If Lineberger's result is correct it will undermine the simple qualitative model now rather widely accepted for the singlet-triplet separation: namely, that given an adequate basis set, a one-configuration description

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1 \tag{4}$$

of the triplet and two-configuration (or generalized valence bond)

$$\begin{gathered} 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2 \\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 1b_1^2 \end{gathered} \tag{5}$$

treatment of the singlet is all that is required. Recent calculations (188) of this type with a saturated (e.g., three sets of d functions on carbon) basis set yield a separation of 10.9 kcal/mole. Another important theoretical finding is that of Harrison and Wernette (189) concerning the Rydberg character of the bent $^3A_2$ and $^3B_2$ states of CH_2. Bound triplet states in this region (∿ 8.75 eV) of the spectrum are required by experiment and previous theoretical studies (excluding diffuse functions) had yielded only repulsive potential surfaces. In unpublished work, Harrison has also carried out detailed studies of the carbenes CLiH and CLi_2.

As a prototype for the reactions of CH_2 with saturated hydrocarbons, the Berkeley-Livermore group has carried out detailed CI calculations for the potential energy surfaces

$$CH_2(^3B_1) + H_2 \rightarrow CH_3 + H \tag{6}$$

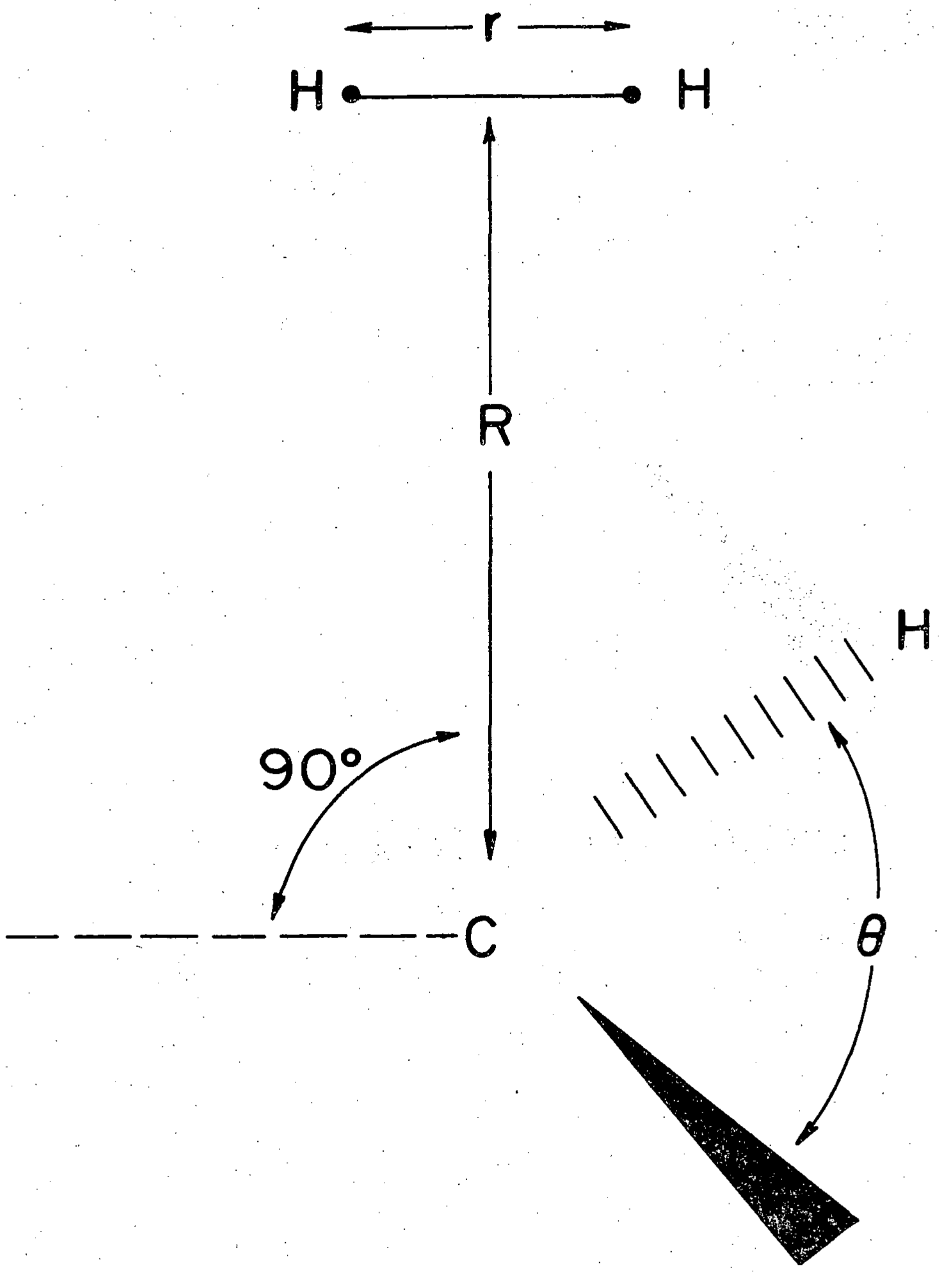
$$CH_2(^1A_1) + H_2 \rightarrow CH_4 \tag{7}$$

For reaction (6), the transition state occurs along the least motion path and a large barrier of ∿ 15 kcal is found (190). This agrees nicely with the BEBO prediction (19.7 kcal) of Carr (191), but contrasts strikingly with the prediction of Dewar's MINDO/3 method (192) that there is no barrier at all. The suggestion (27) of $CH_2 + H_2$ as a prototype has been verified for the case (193)

$$CH_2(^3B_1) + CH_4 \rightarrow CH_3 + CH_3$$

for which a large barrier (∿ 22 kcal) is also found, again in agreement with BEBO and in conflict with MINDO. For the singlet insertion reaction (194), the least motion approach (which is Woodward-Hoffmann forbidden) has a large barrier (27 kcal). However, by approaching in a manner which avoids the singlet methylene lone pair (see Figure) a pathway with no barrier at all has been found. In conclusion, theory predicts that while triplet methylene should not react with saturated hydrocarbons at thermal energies, the singlet insertion reactions should occur via non-least motion pathways.

A field upon which theoretical chemistry has had and will continue to have a significant impact is astrophysics. In particular, the identification of interstellar molecules and the study of molecular processes occurring under these unusual (by laboratory standards) conditions is well suited to theory. Perhaps the first two significant theoretical papers were those (195,196) identifying the interstellar microwave lines at 90.665 and 89.190 GHz as due to the HNC and HCO^+ species. In these studies large basis sets and sizeable CI treatments (6343 configurations, following the Roos approach) were used to provide a reliability of about 0.2 GHz, corresponding to an uncertainty of ± 0.003 Å in bond distances. Both of these ab initio identifications have now been verified by terrestrial experiments (197,198).



Geometry (0°, 90°)

XBL749-4316

A more recently discovered microwave line at 93.174 GHz has been theoretically identified as HN_2^+ from its hyperfine structure (199) and predicted geometry from CI calculations (200). Interstellar molecules may also be identified from observed spectra corresponding to transitions between the Λ-doubling components of the lower rotational levels. This requires a theoretical description of spin-orbit coupling and has been carried out very nicely by Richards and co-workers for CH (201) and SiH (202), the latter having not yet been observed. A potential energy surface of special interest to interstellar chemists is that for $C^+ + H_2$, which reaction Black and Dalgarno suggest (203) is crucial to the formation of hydrocarbons in the interstellar medium. The first ab initio study, by Liskow and co-workers (204), resulted in potential surface features consistent with laboratory molecular beam studies (205), but did not allow a very low energy pathway for the formation of CH_2^+. Specifically, the intersection of the $^2A_1$ and $^2B_2$ potential surfaces occurred at a minimum energy of 10 kcal. However, in an important recent communication, Pearson (206) has shown that the inclusion of polarization functions radically shifts the position of the "seam" between the two C_{2v} surfaces to an energy 15 kcal below the energy of separated C^+ plus H_2. Although Pearson's work clearly establishes the existence of the desired low-energy pathway, the problem of formation of CH_2^+ by radiative recombination must be carefully studed by dynamicists before the Black-Dalgarno hypothesis is accepted. Significant related research on the neutral $C + H_2$ system has been completed by Newton (207) and by J. F. Harrison (unpublished). The most ambitious and successful study to date of an interstellar process is that of Garrison on the cooling of the 6 cm and 2 cm doublets of formaldehyde by collisions. To test the Townes mechanism (208) for this nonthermal cooling, a very large scale (37,779 configurations were explicitly included for some geometries) CI study (209) of the He-H_2CO potential surface was undertaken. Fully quantum mechanical close-coupling calculations were then completed for the rotational excitation of H_2CO. The results (210) provide a very nice explanation of the observed interstellar cooling.

The attraction of the water molecule by a number of chemical species continues to be the topic of many quantum mechanical studies. Recently, Popkie, Kistenmacher, and Clementi (211) have demonstrated that the Hartree-Fock limit attraction between two rigid water molecules is ∿ 3.9 kcal, smaller than previously anticipated. In these calculations a very large gaussian basis set was used: O(13s 8p 2d 1f/8s 5p 2d 1f), H(6s 2p 1d/4s 2p 1d). The effect of electron correlation on the H_2O dimerization energy has been investigated quite thoroughly by Diercksen, Kraemer, and Roos (141). They find an increase of 0.9 kcal due to correlation, but estimate that zero-point vibrational corrections will lower the dimerization energy by about the same amount. Hence Clementi's Hartree-Fock result of 3.9 kcal may be quite close to the exact result, which has been determined experimentally (212) at a relatively low resolution as 5.2 ± 1.5 kcal. Diercksen <u>et al.</u> also studied Li^+-H_2O and F^--H_2O and found the correlation corrections to the binding energies to be small, -1.16 and + 1.94 kcal. In light of these results, it would certainly appear that theoretical studies of water interactions at the Hartree-Fock level of theory can be quite meaningful. With this in mind, Clementi and co-workers have carried out a systematic study of species of potential importance in ionic solutions. For example, using large basis sets they find the following binding energies (213): 35.2 kcal (Li^+-H_2O), 24.0 kcal (Na^+-H_2O), 16.6 kcal (K^+-H_2O), 23.7 kcal (F^--H_2O), and 11.9 kcal ($C\ell^-$-H_2O). In another interesting paper (214) the same authors have considered small clusters of water molecules surrounding a single Li^+, Na^+, K^+, F^-, and $C\ell^-$ ion. For example when 1, 2, 3, 4, 5, and 6 water molecules are added to an Li^+ ion, the respective incremental SCF energy lowerings are 34.3, 30.5, 23.9, 27.2, 6.8, and 11.9 kcal. These and other data have been used by Clementi in Monte Carlo dynamical studies of the structure of solutions. In a related but in some ways more thorough <u>ab initio</u> study, Kollman and Kuntz (215 and unpublished work) have shown that Li^+ prefers a tetrahedral (rather than octahedral)coordination sphere.

Excited electronic states have been the subject of an increasing number of first-rate papers. Especially noteworthy in this regard is the work of Hay, Dunning, and Goddard (112,216,217) on the ozone molecule. Using GVB-CI wave functions, they find several excited states lying close to the dissociation limit O_2 + O, which in turn is only 1.12 eV above equilibrium O_3. Goddard and co-workers also predict the "ring state" of ozone (an equilateral triangle closed shell singlet state) to lie 1.4 eV above the ground state. By the inclusion of polarization functions, Shih, Buenker, and Peyerimhoff (218) find the relative energy of the ozone cyclic conformer lowered to 0.7 eV. Other important excited state papers by the Goddard group include those on water (219), where a double zeta plus Rydberg basis set and large CI provided essentially quantitative agreement with experiment, and diazomethane (220), the dissociation of which leads to methylene. Comparable to the ozone research is a very impressive recent paper (113) by the Argonne and NBS groups on the NO_2 molecule. Using a flexible double zeta plus polarization basis in conjunction with a combined MCSCF-CI approach, they find the $\tilde{A}\ ^2B_2$, $\tilde{B}\ ^2B_1$ and $\tilde{C}\ ^2A_2$ excited states to lie 1.18, 1.66, and 1.84 eV above the $\tilde{X}\ ^2A_1$ ground state. This theoretical study should go a long way toward clarifying the murky electronic spectrum of NO_2. As mentioned above the selection and extrapolation scheme of Buenker and Peyerimhoff appears to be a very effective tool for the study of excited states. Among the more impressive studies reported to date are those on diimide (221), ethane (222), and diborane (223). The largest system studied by state-of-the-art methods is benzene, which Hay and Shavitt (224) have investigated with a double zeta plus Rydberg basis. Using ground state natural orbitals, they carried out π-electron CI calculations (up to 2636 configurations) which provide a standard of excellence for the evaluation of present and future semi-empirical π-electron theories. Finally, we note the excellent work of Elbert and Davidson (225) on the urea molecule. They predict the lowest singlet state to be the $n \rightarrow \pi^*$ state at 7.2 eV, but the $\pi \rightarrow \pi^*$ singlet to lie 1.9 eV higher, contrary to several previous assignments which assumed the lowest bond was a $\pi \rightarrow \pi^*$ amide resonance bond.

One essentially new area of research that has been opened up during the past four years is the ab initio study of the fine structure of polyatomic molecules. An excellent review of this area has been written by Langhoff and Kern (226) and will appear in late 1976. Perhaps the earliest research of this type was Harrison's study (227) of the spin-spin interaction in methylene. The theoretical treatment of the spin-orbit interaction is considerably more difficult, since matrix elements between different electronic states must be evaluated. However, recently both the spin-spin and spin-orbit contributions to the zero-field-splitting (ZFS) parameters of CH_2 have been evaluated using high-quality wave functions (228,229). Langhoff and Davidson find $D_{ss} = 0.78\ cm^{-1}$ and $D_{so} = 0.02\ cm^{-1}$, with the sum being in good agreement with experiment (230,231), $0.76 \pm 0.02\ cm^{-1}$. For the other ZFS parameter, E, the spin-spin contribution is predicted to be $0.050\ cm^{-1}$ and the spin-orbit zero to three significant figures. The experimental E value is $0.052 \pm 0.017\ cm^{-1}$ and one can conclude that theory accounts very satisfactorily for the observed ZFS parameters. Perhaps equally important, the theoretical techniques developed by Kern, Langhoff and Davidson are also applicable to much larger molecules. Very impressive studies of the fine structure of the lowest triplet states of formaldehyde (232 and unpublished work) and benzene (233) have been completed recently, and in the H_2CO case the phosphorescent lifetimes of the sublevels of the $^3A_2$ ($n \rightarrow \pi^*$) state have been predicted. In the near future, we can certainly expect exciting things from this type of theoretical research.

Theory continues to make significant contributions to inorganic chemistry concerning the electronic structure of transition metal complexes. The most important contributors here have been the research groups of Veillard (Strasbourg) and Hillier (Manchester). However, the most impressive single contribution is probably the ferrocene $Fe(C_5H_5)_2$ study of Bagus, Wahlgren, and Almlöf (234). They used a double zeta basis set, with the exception that three 3d functions were employed and a set of p functions added to each hydrogen atom, for a total of 188 contracted gaussians. Several ionization potentials were predicted from direct hole state calculations on the ferricinium ion, and symmetry assignments were made for the observed photoelectron spectra. The staggered and eclipsed forms of ferrocene were predicted to differ by less than 1 kcal, and the Mössbauer isomer shifts analyzed in detail. Even larger systems have been studied by the Veillard and Hillier groups using minimum basis sets, except that the 3d functions are given a double zeta representation. For example, Dedieu and Veillard (235) have explored the electronic aspects of dioxygen binding to cobalt-Schiff-base-complexes. Considering the *ab initio* model Co (acacen) LO_2 (acacen = N,N'-ethylenebis-(acetylacetoneiminato) and L = none, water, imidazole, CN^-, and CO), Veillard and co-workers conclude that a linear Co-0-0 structure is somewhat less stable than the bent one, with the perpendicular structure considerably less stable. The nickel tetracarbonyl molecule has been studied especially carefully by Hiller and co-workers, their most recent work (236) involving CI calculations of the satellite peaks in the X-ray photoelectron spectra. Other notable recent studies are a double zeta study of bis-(π-allyl) nickel (237) and a more modest investigation (238) of dibenzene chromium and benzene chromium tricarbonyl.

Currently one of the most exciting areas in experimental physical chemistry is surface chemistry, and it was inevitable that in time electronic structure theory would have an impact there. The most systematic and complete theoretical work reported to date is that of Bauschlicher and co-workers (239, 240) on the chemisorption of atomic hydrogen by the (0001) surface of metallic beryllium. The surface was modeled by finite metal clusters ranging in size from a single Be atom to a Be_{22} model. The effects of basis set and cluster size have been considered, and their most important results are summarized in

TABLE. Models of the chemisorption of atomic hydrogen by the (0001) surface of beryllium metal. The cluster notation $Be_{10}(7,3)$ denotes a model with seven atoms for the surface layer and three atoms for the second layer. Bond distances r_e are in Å and chemisorptive bond energies D_e in kcal/mole.

Open Site			Eclipsed Site			Bond Midpoint Site			Directly Overhead Site		
Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e
$Be_3(3,0)$	1.25	19.1	$Be_4(3.1)$	1.24	28.7	$Be_4(4,0)$	1.26	70.1	$Be_1(1,0)$	1.42	46.4
$Be_5(4,1)$	1.02	23.2	$Be_5(4,1)$	1.15	30.1	$Be_5(5,1)$	1.14	32.4	$Be_7(7,0)$	1.43	71.3
$Be_6(6,0)$	1.18	47.3	$Be_7(6,1)$	1.11	40.8	$Be_{10}(10,0)$	1.17	45.3	$Be_{10}(7,3)$	1.43	27.3
$Be_6(3,3)$	1.11	55.3	$Be_{13}(10,3)$[a]	0.90	57.2	$Be_{13}(10,3)$	1.05	44.8	$Be_{13}(10,3)$	1.41	31.1
$Be_9(6,3)$	1.13	50.2		0.94	58.3	$Be_{22}(14,8)$	1.04	53.4	$Be_{22}(14,8)$	1.39	31.4
$Be_{13}(10,3)$	0.99	39.0	$Be_{22}(14,8)$	0.97	51.9						
$Be_{22}(14,8)$	0.94	55.1									

Two distinct $Be_{13}(10,3)$ clusters were studied.

the Table. There we see that three sites for chemisorption are about equally favorable, with chemisorptive bond energies of ∿ 50 kcal/mole. However, the fourth site, the "traditional" site in earlier intuitive models, is decidedly less favorable. The chemisorption problem has also been pursued vigorously by Goddard and his students, who have proposed an ingenious chemical model for silicon surfaces (241) and studied the dissociative chemisorption of H_2 by nickel (242). The latter study was carried out using a nickel pseudopotential in collaboration with Moskowitz and Ratner at NYU. A general conclusion obtained in this work is that the Ni 3d orbitals have relatively little involvement in the chemisorptive bond. This result is for the most part consistent with semi-empirical theoretical studies (243) and was earlier found to be true for transition metal hydride diatomics (244-246). Certainly the study of catalysis, surface chemistry, and chemisorption will be tremendously enhanced by *ab initio* insights obtained over the next few years.

The number of applications of quantum mechanics to biological systems has grown exponentially over the past four years. Some of the most important recent research in this area has been carried out by Peter Kollman (UC San Francisco) and by the Pullmans (Paris). A topic of special importance is the role of the phosphate group in nucleic acid environments. For example, Marynick (247) has performed a careful study of model solvation complexes built up from $(RO)_2PO_2^-$ (R = CH_3 or H), H_2O, $C\ell^-$, and one of the metal ions Li^+, Na^+, K^+, Be^{++}, Mg^{++}, or Ca^{++}. By considering many molecular entities as large as $(HO)_2PO_2Ca\cdot(H_2O)C\ell$, he predicts that the energies of formation vary as $Be^{++} > Mg^{++} > Ca^{++} > Li^+ > Na^+ > K^+$. Hayes and Kollman have recently undertaken an even more ambitious investigation (unpublished) of the diphosphate anions $H_2P_2O_7^=$ and $H_3P_2O_7^-$. The Pullman group has made conformational studies of the phosphodiester linkage (248), investigated the role of phosphorous d functions (249) in dimethylphosphate, and studied the electrostatic potential (250) and hydration (251) of the same anion.

Some of the very largest ab initio calculations reported to date have dealt with systems of biological interest. For example, Almlöf (252) has carried out minimum basis (426 primitive gaussians, 136 contracted functions) of the free base porphin. He optimized the positions of the two central protons and found a linear NH·····HN arrangement to be most favorable. The NH vibrational frequencies were computed and direct calculations of several positive ion states carried out. The same molecule and several others, including ethyl chlorophyllide a (with 340 electrons!), have been computed by Christoffersen and co-workers (253) at Kansas using a very small gaussian basis. Clementi and Popkie (254) have investigated barriers to internal rotation in the sugar-phosphate-sugar complex $C_{10}H_{19}O_8P$.

Large scale computations have also been reported for the tetracyanoquinodimethane (TCNQ) molecule, which with tetrathiafulvene (TTF) forms the TTF-TCNQ charge transfer complex hailed as a possible organic superconductor. In the work of Nieuwpoort and co-workers (255), a medium sized [C(6s 3p), N(6s 3p), H(3s)] gaussian basis was flexibly contracted to the double zeta level (262 primitives, 168 contracted functions). The ground and excited states of the cation, neutral molecule, anion, and dianion were studied within the SCF approximation. An even larger scale TCNQ calculation has recently been reported by Johansen (256), who used the Dunning-Huzinaga double zeta basis, supplemented by p functions on each H atom, for a total of 412 primitive and 180 contracted gaussian functions. Johansen nicely illustrates the important features of the TCNQ electronic structure using contour maps of electron density differences. Finally Cavallone and Clementi (257) have carried out a minimum basis study of the entire TTF-TCNQ complex.

To conclude this review I would like to note Ermler and Kern's study (62) of a smaller molecule, benzene. By using a carefully designed double zeta plus polarization basis, they have obtained a benzene wave function fairly close to the Hartree-Fock limit. Although it is now well established that basis sets this large are unnecessary for the prediction of many properties, this type of calibration calculation is necessary to establish clearly the distinction between errors due to basis set and those due to the effects of electron correlation. For example, Ermler and Kern find that while the Hartree-Fock deuteron quadrupole coupling constants are in good agreement with experiment, the molecular quadrupole moment is nearly a factor of two larger than Flygare's experimental value (258). At this point however, it is unclear to the present author whether this quadrupole moment discrepancy is due to genuine correlation effects (they are usually small for this particular property) or experimental uncertainty. Thus, as is often the case, the way becomes clear for future studies of both the theoretical and experimental aspects of this problem.

I am especially grateful to Drs. E. R. Davidson, T. H. Dunning, K. F. Freed, J. F. Harrison, P. J. Hay, W. J. Hehre, I. Hillier, C. W. Kern, M. Krauss, W. N. Lipscomb, C. M. Moser, J. W. Moskowitz, M. D. Newton, S. D. Peyerimhoff, J. A. Pople, B. Roos, M. E. Schwartz, I. Shavitt, A. C. Wahl, J. L. Whitten, and N. W. Winter for helpful suggestions concerning the content of this review article. Finally, I thank Steven R. Ungemach, Clifford E. Dykstra, and William C. Swope.

Figure caption. Nonleast motion approach of singlet methylene to molecular hydrogen. There is no barrier at all associated with this initial reaction pathway for the formation of CH_4.

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* Supported in part by the U.S. Energy Research and Development Administration through the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California.

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