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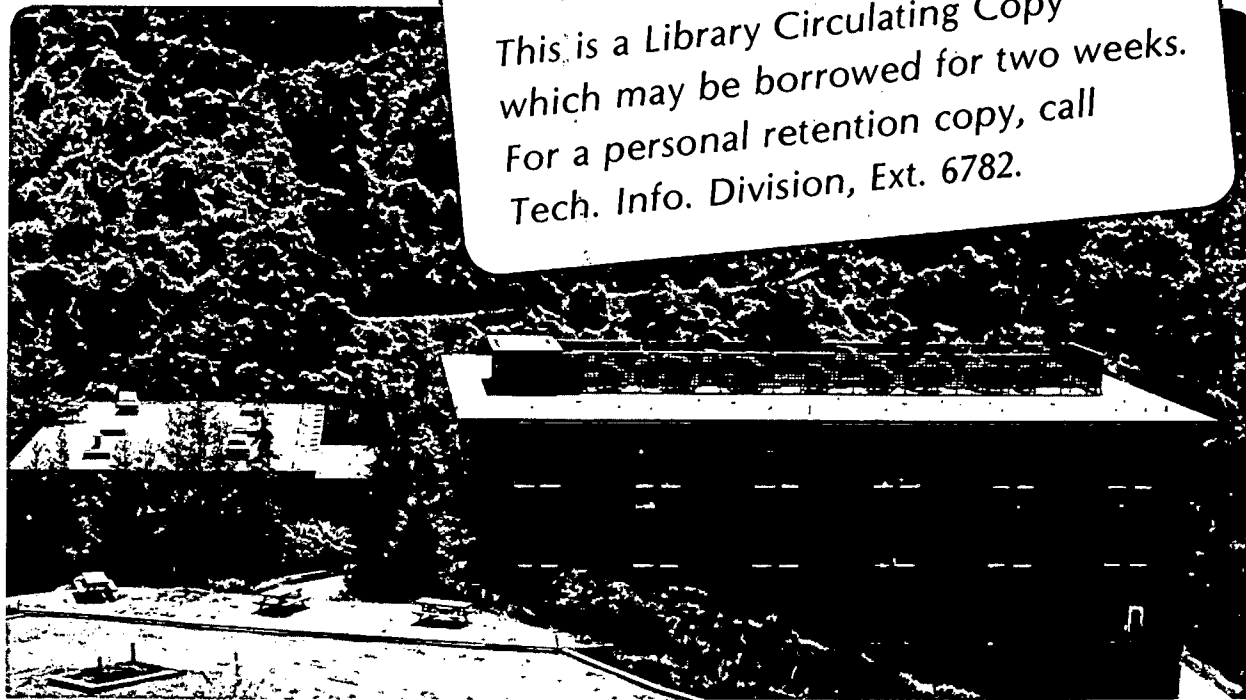
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APPLICATIONS OF MOLECULAR QUANTUM MECHANICS
TO PROBLEMS IN CHEMISTRY

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Abstract - The past decade has witnessed remarkable progress in the development of rigorous quantum mechanical methods for the study of molecular electronic structure. Key developments include the emergence of large scale configuration interaction methods (including more than one million variational parameters) and of analytic first and second energy derivative techniques. These advances have greatly increased the scope of current applications of quantum mechanics to chemistry. Present and anticipated future developments with respect to the fields of physical, organic, and inorganic chemistry are surveyed.

INTRODUCTION

The development of the fundamentals of quantum mechanics took place to a large degree during the years 1925-1927, with the principal figures being Heisenberg, Schrödinger, Born, and Dirac. Almost immediately these ideas began to be applied to atoms and molecules, the pioneers of theoretical chemistry being Hartree, Slater, Hylleraas, Fock, Mulliken, Heitler, London, Pauling, Brillouin, Koopmans, James, and Coolidge. Thus it may be stated that the foundations of molecular quantum mechanics were firmly in place by 1935. Nearly 50 years have elapsed (1) since that date and it is reasonable to ask what progress is being made today and what one can expect from quantum chemistry during the next decade.

THEORY AND METHODS

The (properly antisymmetrized) self-consistent-field (SCF), multiconfiguration (MC) SCF, and configuration interaction (CI) methods were developed in 1930, 1939, and 1928, respectively. These three techniques continue to be the mainstay of *a priori* quantum mechanical studies, although perturbation theory (2) and coupled cluster methods (3) have made very significant inroads during the past five years. The three workhorse methods will be discussed briefly in separate paragraphs here.

The first applications of *ab initio* SCF methods to polyatomic molecules began to appear in the early 1960's, the Pitzer-Lipscomb study (4) of the internal rotation barrier in ethane being of special import. In that study a minimum basis set (one basis function per occupied atomic orbital -- C 1s, 2s, 2p_x, 2p_y, 2p_z; H 1s) of 16 functions was employed. As an example of the current state-of-the-art, we point to the recent large basis set study of

decamethylferrocene by Almlöf and coworkers (5). The $\text{Fe}[\text{C}_5(\text{CH}_3)_5]_2$ study involved no less than 501 basis functions, formed as simple linear combinations of a larger set of 805 primitive gaussian functions. Since SCF studies require an amount of effort proportional to n^4 (n = number of basis functions), the decamethylferrocene calculation is seen to require $(501/16)^4$ or a factor of one million times more work. This increase in capabilities over the past 20 years is due in roughly equal measure to theoretical advances and to the decreasing cost of computation time/arithmetic operation.

The earliest molecular MCSCF studies were those of Das and Wahl (6) in 1966 on the H_2 , Li_2 , and F_2 molecules. For Li_2 as many as four configurations were included in that study, which was carried out using methods displaying first-order convergence. In contrast, by 1980 it was possible to report an MCSCF treatment (7) of the cyclopropyne molecule including 10,115 configurations. More important yet has been the recent development of quadratically convergent (QC) MCSCF methods, which typically reduce the number of cycles in such iterative procedures from 30 to 5. The largest problem to date to be treated by the QCMSCF method is the 2302 configuration ethyl radical study of Lengsfeld (8). New methods are continuing to develop very rapidly in this area and much larger problems are likely to be solved by the QCMSCF method in the near future.

One of the largest CI studies reported prior to 1969 was Bunge's 180 configuration wave function (9) for the beryllium atom. Since then enormous advances have been made in this the oldest of variational methods for the determination of correlated wave functions. It should be noted that electron correlation effects are due to the instantaneous correlations of the repulsive forces between electrons. SCF wavefunctions intrinsically neglect correlation, since each electron is constrained to move in the averaged field of the remaining electrons (and nuclei). With respect to theoretical advances in this area we should note specifically Shavitt's formulation (10) of the graphical unitary group approach. The latter template has been used for the development of several very powerful CI methods, the most recent of which allowed a fully variational description of the ethylene molecule involving 1,046,758 spin- and space-adapted configurations (11).

PHYSICAL CHEMISTRY

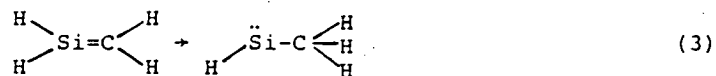
Since physical chemists tend to be especially interested in small molecules, the most powerful theoretical techniques are often applied first to problems in this general area. Thus, for example, we would expect the electronic spectrum of benzene to be largely understood by theorists one decade from now. By then techniques for the determination of correlated wave functions should have advanced to the point where predicting excitation energies to within 1000 cm^{-1} will be straightforward. In addition reliable ($\pm 5\%$) predictions of the vibrational frequencies of arbitrary electronic states of benzene should be quite possible.

To focus on the currently possible, consider the photochemistry of the

successfully, for example, for hydrocarbons, appear less suitable for transition metal systems. Nevertheless *ab initio* geometries have recently been determined (19, 20) for $\text{Ni}(\text{C}_4\text{H}_4)_2$ and $(\text{CO})_3\text{NiCH}_2$ using large basis sets, and studies of this sort will become routine during the next decade. This means, for example, that reliable predictions of the structure, energetics, and vibrational frequencies of fascinating species such as $\text{Fe}_2(\text{CO})_8\text{CH}_2$ will become possible. Should a completely satisfactory solution of the pseudo-potential problem (21) emerge, reliable *a priori* studies of much larger molecules will be regularly reported.

An interesting example of what is currently feasible in inorganic theoretical studies is seen in several controversies involving the silicon-carbon double bond, a subject of much recent interest. The first laboratory determination of the length of any Si=C bond was that of Mahaffy, Gutowsky, and Montgomery (22), who found the value 1.83 Å for the molecule dimethylsilaethylene $(\text{CH}_3)_2\text{Si}=\text{CH}_2$. They noted that their electron diffraction Si=C bond distance was more than 0.1 Å longer than predicted for the parent silaethylene from several *ab initio* studies, but held out the possibility that the methyl groups might explain at least part of the discrepancy. However, subsequent theoretical studies showed that $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ and $\text{H}_2\text{Si}=\text{CH}_2$ have essentially identical Si=C bond distances and confirmed at a much higher level of theory the earlier structural predictions for the parent (23). Support for these theoretical predictions has recently been provided by the preparation of the first room-temperature stable silaethylene and the determination of its crystal structure (24). The theoretical bond distance $r_e(\text{Si}=\text{C}) = 1.705 \pm 0.03$ Å for the parent silaethylene therefore now seems reasonably secure.

Two other theoretical predictions concerning the Si=C bond have been and continue to be hotly contested by experimentalists (25). These concern the simple isomerization reaction



which theory predicts to be slightly (~ 4 kcal) endothermic and to have a substantial barrier (> 25 kcal). Two completely independent sets of experiments (26,27) suggest that reaction (3) proceeds without a notable barrier and is necessarily exothermic. However, other experiments (28,29) may be interpreted in favor of theory and we are cautiously optimistic that the latter will eventually prevail.

ORGANIC CHEMISTRY

The present and anticipated future status of quantum organic chemistry may be viewed in light of the norbornyl cation, $\text{C}_7\text{H}_{11}^+$. The question of whether the norbornyl cation has a classical or nonclassical structure is of course the most vigorously disputed issue in the history of modern structural chemistry (30). Recently complete theoretical structures (31) for three $\text{C}_7\text{H}_{11}^+$ stationary points were reported at the SCF level of theory using a basis set slightly inferior to double zeta (DZ) in quality. There the nonclassical structure is found to lie 1.0 kcal above the classical form,

which might best be viewed as an unsymmetrically bridged species. Using these structures, the appendage of a set of d functions to each carbon atom places the nonclassical structure 0.2 kcal below the classical (31). It is apparent that higher levels of theory will be required for a definitive theoretical treatment. In fact this is already possible, with several groups working on higher level structural determinations, as well as perturbation theory and CI studies of correlation effects. A truly reliable theoretical prediction will require structures obtained from a DZ + P (basis set) CI including all singly- and doubly-excited configurations with respect to the SCF reference configuration. Such a theoretical study should be feasible 10 years from now.

The trimethylenemethane (TMM) molecule $C(CH_2)_3$ is one for which the predictions of theory were long considered to be highly dubious. This molecule is of historical interest, having been identified in 1948 by Moffitt and Coulson (32) as incorporating the greatest π bond order attainable by a carbon atom. TMM was eventually synthesized by Dowd (33) in 1966. The first *ab initio* theoretical study of TMM was the 1974 paper of Yarkony (34) and led to an energy difference of 18 kcal between the ground triplet ($^3A_2'$) and first excited singlet (1B_1) electronic states. The experimental studies of Berson (35) and of Dowd (36) cast grave doubt on the reliability of this prediction, suggesting instead a singlet-triplet separation less than 7 kcal. However, subsequent research (37) at a higher level of theory resulted in $\Delta E = 14$ kcal, qualitatively similar to the original prediction. And during the past year this result has been confirmed by experiment. The resolution of the apparent discrepancy came with the Yale group's realization (38) that the species thought to be the excited singlet TMM



1a was in fact the ring-closed methylenecyclopropane 1b. The true singlet-triplet separation in the substituted TMM was then found to be >13 kcal, in agreement with the earlier theoretical predictions.

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