

A FORECAST FOR THEORETICAL CHEMISTRY *

by

JOSEPH O. HIRSCHFELDER

**University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin**

**Peter Debye Award Speech at American Chemical Society Meeting,
Pittsburgh, March 28, 1966**

- - - - -
* This research was supported by the following grant:
National Aeronautics and Space Administration NsG-275-62.

I am thrilled that this award should carry the name of the great Peter Debye. The name, DEBYE, brings to mind a large number of brilliant achievements in electromagnetic theory, the scattering of light, the behaviour of strong electrolytes, the stability of colloidal suspensions, and the forces between biological molecules. His work is always thorough and his ideas are always clear and profound. Besides being a wonderful scientist, Debye is a wonderfully nice person and a great teacher. His tremendous enthusiasm has been a source of inspiration to three generations of scientists.

On occasions like this, one feels very humble and inadequate. I am in no sense brilliant, just a hard working guy with a great deal of tenacity. Whatever success I have had stems from the help which I have received from a great many wonderful people. Indeed, I am impressed with the deep debt of gratitude which I owe to my family, my friends, my colleagues, my teachers, and my students. It is upon their shoulders that I have tried to build.

Dick Bernstein told me that I should make this a very personal speech. Thus, I will take the occasion to do a bit of philosophizing. Let us start with some of the words of wisdom that have meant a great deal to me.

I owe a great debt to Henry Eyring for having given me a start on my scientific career. The Eyring philosophy I best remember is:

HENRY EYRING

"BE NICE TO THE GUYS ON THE WAY UP SO THAT THEY
WILL BE NICE TO YOU ON THE WAY DOWN".

In nature, or complicated systems, there is usually only ONE
slow step or bottleneck which determines its behaviour.

Always ask yourself, how might the phenomena occur. Make a
GEDENKS-model. It will suggest the proper groupings of variables -
a big help in semi-empiricizing.

"A SCIENTIST'S ACCOMPLISHMENTS ARE EQUAL TO THE
INTEGRAL OF HIS ABILITY INTEGRATED OVER THE HOURS
OF HIS EFFORT".

To Eyring, every problem in nature can be studied theoretically.

The first step is to ask yourself what might the solution look like.

I think that Einstein had much the same viewpoint:¹

- - - - -

1. I learned a great deal about Einstein from his research assistant, Nathan Rosen. Rosen collaborated with me in our calculations of the energy of H_3 and H_3^+ . He showed me that by properly systematizing the procedure and the format, I could reduce my computational effort by a factor of ten.

ALBERT EINSTEIN

"IT IS EASY, JUST HARD TO DO!"

Einstein seldom sought direct solutions to his equations. His first question was, "under what other conditions could these equations arise?" He learned a great deal from the way in which other people had solved these equations in other types of problems.

"NATURE IS SIMPLE, IT IS WE WHO ARE COMPLICATED!"

Surely it pays to spend a considerable amount of time looking at your problem from all different directions. Think before you leap! In this case, leaping corresponds to committing yourself to a particular research technique.

My first research as a graduate student was under the direction of Edward Condon. From him I learned that a theoretician should have a broad background.

EDWARD U. CONDON

A theoretician should be well-versed in a wide range of experimental techniques and facts. The three functions of a theoretician are:

- 1). Suggest new types of experiments.
- 2). Suggest new interpretations of existing data.
- 3). Further develop the theory so that it may become a more powerful tool in the understanding of nature.

At the Bikini Atom Bomb Tests in 1946, my title was Chief Phenomenologist. John Magee and I had the job of predicting all of the different effects of the bomb so that the experiments could be properly set up. Enrico Fermi felt very strongly that every scientist should be trained as a phenomenologist. He trained his students to get order of magnitude solutions to arbitrary questions. A typical Fermi question was "Estimate the number of railroad locomotives in the United States". It is interesting to note that Chemical Engineers are regarded as the most flexible and possessing the best background for Operational Research Analysis, where such ability is required.

I was, indeed, fortunate to be a graduate student at Princeton during the First Golden Age of Quantum Chemistry, 1931-6. This was a wonderful period of great discoveries and Princeton was the hub. It was a period during which many people had high hopes of explaining all of the physical and chemical properties of material and, indeed, all of natural phenomena in terms of the basic laws of physics. Even such erudite physicists as Dirac, Van Vleck, and London concocted simple approximation procedures which they hoped would help to explain molecular structure. It was a period of high hopes in which theoreticians took a fresh look at all sorts of natural phenomena and guessed at their mechanism. The methods which were used in those days were crude compared to our present techniques, but the men who used them were not afraid to stick their necks

out. Of course, the theoretical predictions served as challenges to the experimental scientists and were especially valuable when the theory suggested a critical experiment. Thus a very stimulating rivalry developed between the experimental and the theoretical men. The result was an era of exciting discoveries.

In a nutshell, the message which I want to convey today is that for the last 30 years theoretical chemists have been preoccupied with developing their mathematical techniques - that is, developing molecular quantum mechanics and statistical mechanics on a firm ab-initio basis resulting from accepted laws of physics. The importance of this theoretical development cannot be overemphasized. With the advent of giant high speed computing machines, new types of mathematical methods, and the renewed help of the theoretical physicists it appears that within five to ten years we will be able to make accurate theoretical predictions of most of the physical and chemical properties of matter. Then there will be a change of emphasis.

The theoretical chemists must start preparing themselves and their students right now for this change of emphasis. At present, theoretical chemists are concentrating on high power mathematics. They are also concentrating on very specific problems and only using a narrow range of techniques. The emphasis will shift from developing new methods to applying existing methods. Then the theoretical chemists must have a broad knowledge of experimental

physics and experimental chemistry as well as a broad knowledge of theoretical chemistry and theoretical physics.

In the development of basic ab-initio approaches to molecular quantum mechanics and statistical mechanics rigor is a virtue and absolutely essential in order to establish definitive results. But in the applications of theory to the world around us, the theory is most useful when it is stretched beyond those things which we know for sure. Thus, it will be important that the theoreticians of the future not be afraid to stick their necks out and make "guestimates" which can serve to guide experiments.

During the period 1931-6, thanks to the genius of Linus Pauling and Henry Eyring, theoretical chemists did try to apply their meager theoretical knowledge as far as they could stretch it. Out of this came many exciting discoveries. I predict that the period 1970-80 will resemble this first golden age of quantum chemistry. Therefore I will tell you a little bit about the good old days.

In 1931 quantum mechanics, in its present form, was only a few years old. No one knew its limitations and important discoveries were made every few months.

Quantum mechanics was first applied to problems of atomic energy. The explanation of the relative spacings or the "flags" corresponding to the splitting of multiplets was one of the first triumphs. The determination of the absolute values of the splittings required the evaluation of a set of radial integrals.

Ed Condon set a number of us young graduate students to work on these integrals, which subsequently became a part of Condon and Shortley's famous treatise.

Of course, modern quantum mechanics was designed to give the correct energy levels for atomic hydrogen. It was Egil Hylleraas who showed that it also worked for the two-electron helium atom. At one time or other, Hylleraas used or developed almost every basic technique which we use in quantum mechanics: different types of perturbation and variational principles, correlated orbitals, configurational interaction, etc. All of Hylleraas' calculations were made on a hand-cranked desk calculating machine. The next generation of quantum mechanicians had electric power to turn the crank.

The early treatment of many-electron atoms was very crude. Hartree expressed the wave function for an atom as the product of one-electron orbitals. These orbitals were supposed to be the solutions to a set of coupled differential equations which seemed hopelessly difficult to solve. Eventually Hartree was able to obtain approximate solutions on a mechanical differential analyzer which he built out of Mechano parts (You may remember having a Mechano toy when you were a child).

The early differential analyzers were very interesting.² Vannevar Bush' first model was completely electrical using a house-type watt-

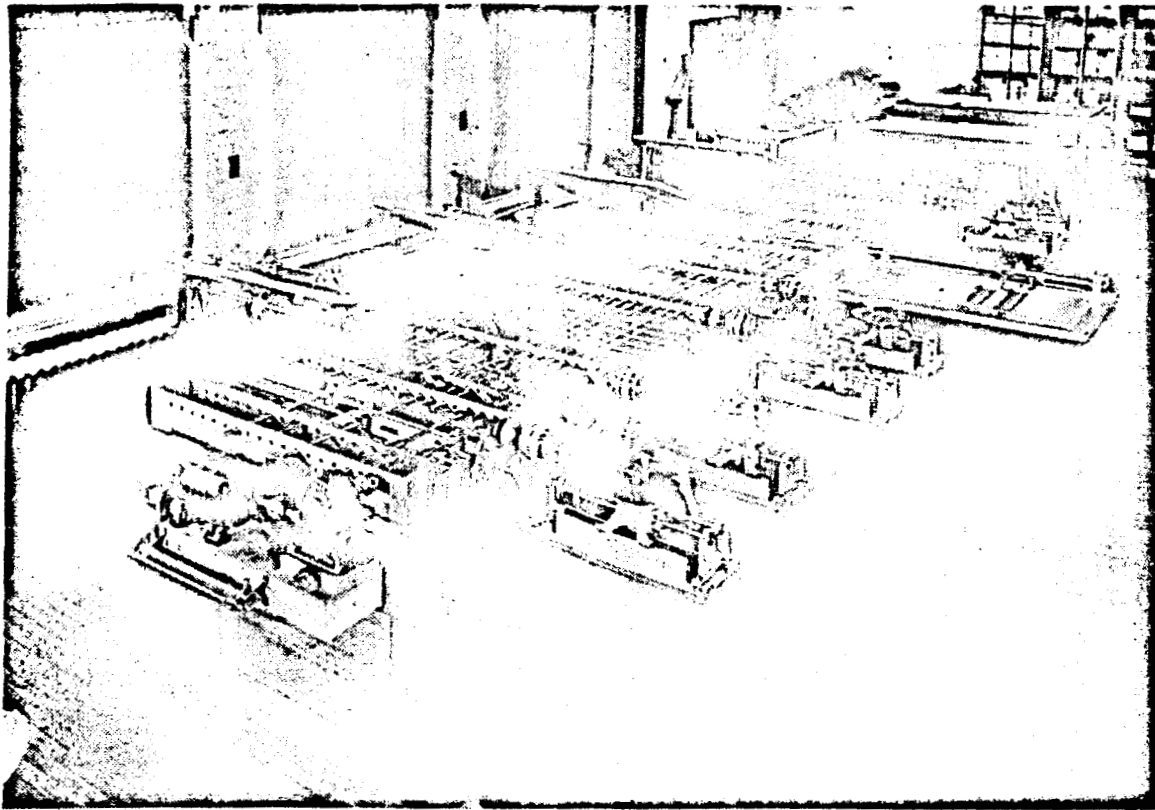
- - - - -

2. V. Bush, J. Franklin Inst. 212, 447 (1931).

hour meter for integration. However, he could not reduce the error in the watt-hour meter to less than two per cent (remember this when you pay your electric bill). Therefore he switched to an all-mechanical contrivance. I used the analyzer (see Fig. 1) at the Moore School of Electrical Engineering of the University of Pennsylvania³ during the winter of 1938-9. The independent variable was represented by the rotation of a rod forty feet long rotated by a three horsepower motor. Each of the dependent variables was represented by the rotation of another long rod which was rigidly connected to the independent variable rod by means of gear trains, "adders", "integraters", etc. in accordance with the constraints of the mathematical relations. Addition and subtraction was accomplished by an "adder" which embodied the principles of the differential gears of an automobile (see Fig. 2): the rotation of the drive shaft is proportional to the sum of the rotations of the two rear wheels. Multiplication by a constant factor was easily accomplished by two intermeshing gears of different numbers of teeth, but multiplication by a variable factor required integration by parts. The "integrater" looked like a phonograph turn-table with the pickup arm replaced by a steel disc perpendicular to the record (see Fig. 3). The rotation of the disc was equal to the integral of the distance of the disc from the center of the record integrated

- - - - -

3. I. Travis, Machine Design, 7, p. 15, July 1935.



The differential analyzer.

Fig. 1 The Differential Analyzer at the Moore School of Electrical Engineering, University of Pennsylvania, built in 1935. A similar machine was constructed for the Ballistics Research Laboratory at Aberdeen Proving Grounds for the U. S. Army. These differential analyzers were constructed by the Civil Works Administration as part of President Roosevelt's emergency relief program with the help of Professors Vannebar Bush, S. H. Caldwell, and L. S. Frost of Massachusetts Institute of Technology and Irven Travis of the Moore School of Electrical Engineering.

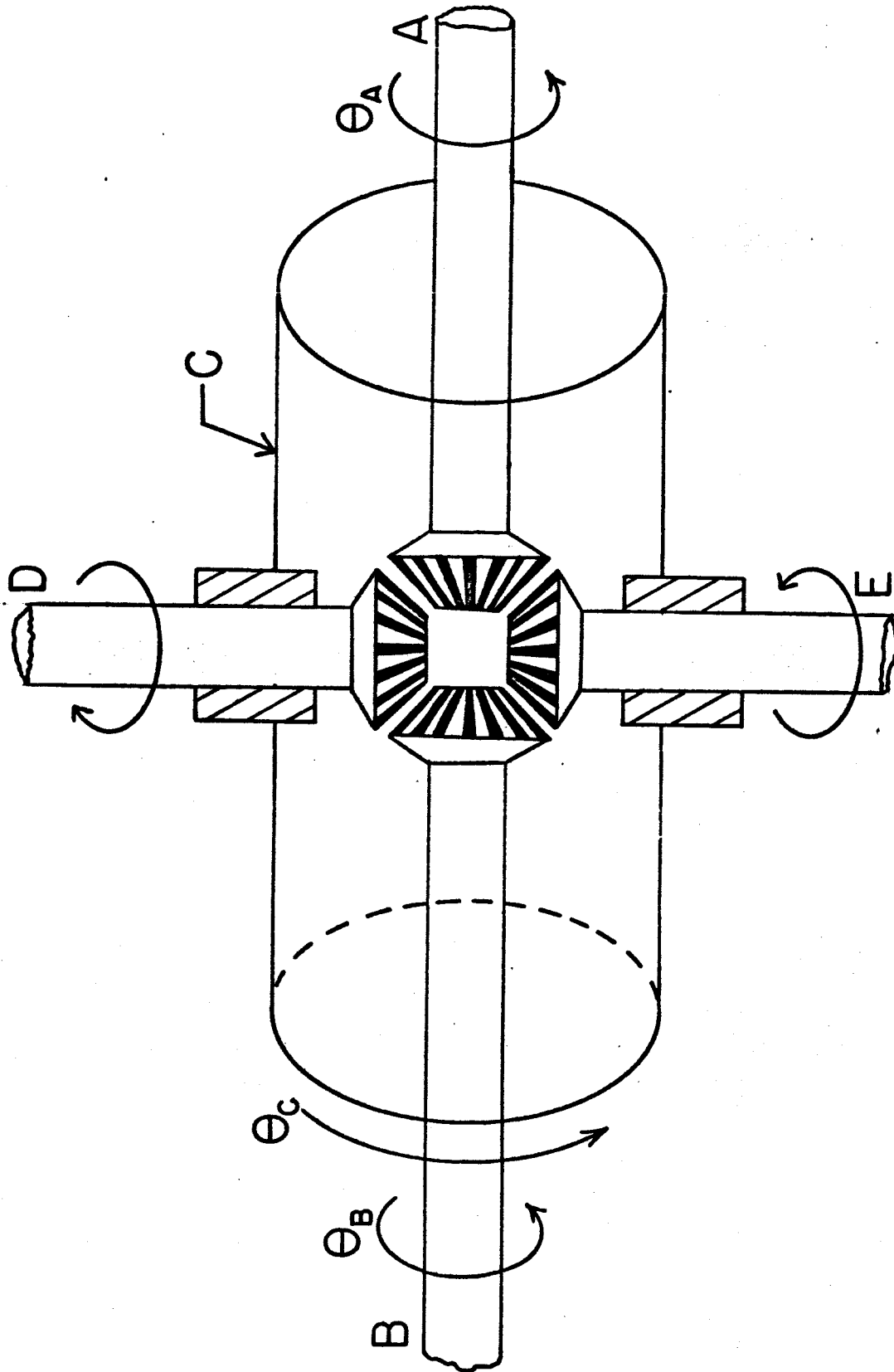


Fig. 2 Schematic diagram showing the principles of an "adder". Shafts D and E are "idlers" which are free to rotate and have no external connections. The four pinion gears in the center of the diagram are always engaged. Thus, when the two shafts A and B are rotated by θ_A and θ_B respectively, the housing C is constrained to rotate by $\theta_C = (\theta_A + \theta_B)/2$.

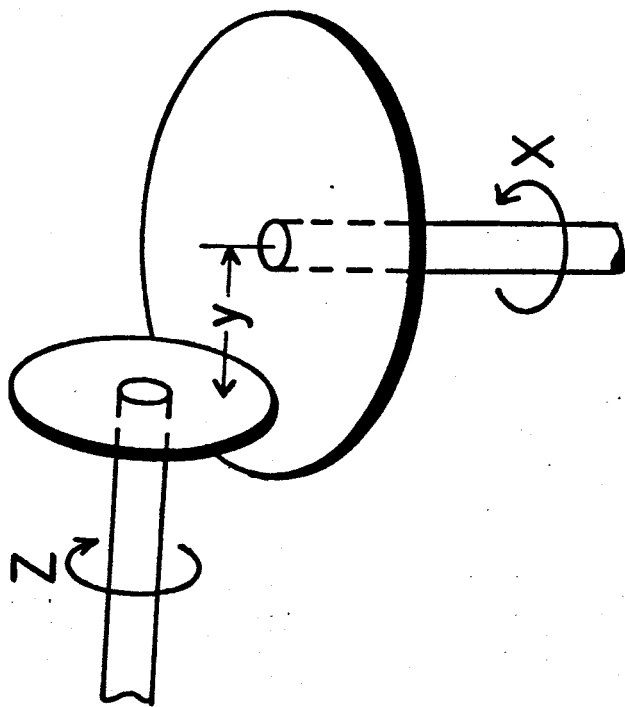


Fig. 3 Schematic diagram showing the principles of the "integrator". If the turntable is rotated through an angle x and the disk is moved in and out so that the point of contact of the disk is at the variable distance y from the center of the turntable, then the disk is constrained to rotate through an angle z where $z = a \int y dx$. Here a is the reciprocal of the radius of the disc, an instrumental constant.

over the number of rotations of the record. The difficulty was that the disc rested only lightly on the record and therefore could not supply much torque without slipping. The torque amplification was accomplished with two stages of mechanical amplification known as a double motorized winch (see Fig. 4). This involved a fish line in the first stage and a shoe string in the second state which had to be perfectly adjusted according to the humidity, etc.

Computing machines have come a long way during the past 30 years!

A big break-through in the applications of quantum mechanics to atomic problems resulted from the development of screening constants - first by Schrodinger in 1921, then by Pauling, in 1927, and finally by Slater in 1931. With the use of Slater screening constants it was possible to estimate the energy or almost any physical property of an atom. Of course, the accuracy of these predicted values was not always very good, but the predicted values were seldom wrong by as much as a factor of two and they were very useful.

Wigner deserves the credit for bringing order out of chaos in atomic physics by introducing Group Theory. Since the Hamiltonian for an atom or molecule is invariant with respect to the interchange of two electrons, the spatial parts of the wave functions are bases of irreducible representations of a finite permutation group. Then, too, the Hamiltonian for an atom is invariant with respect to rotations of the coordinate system.

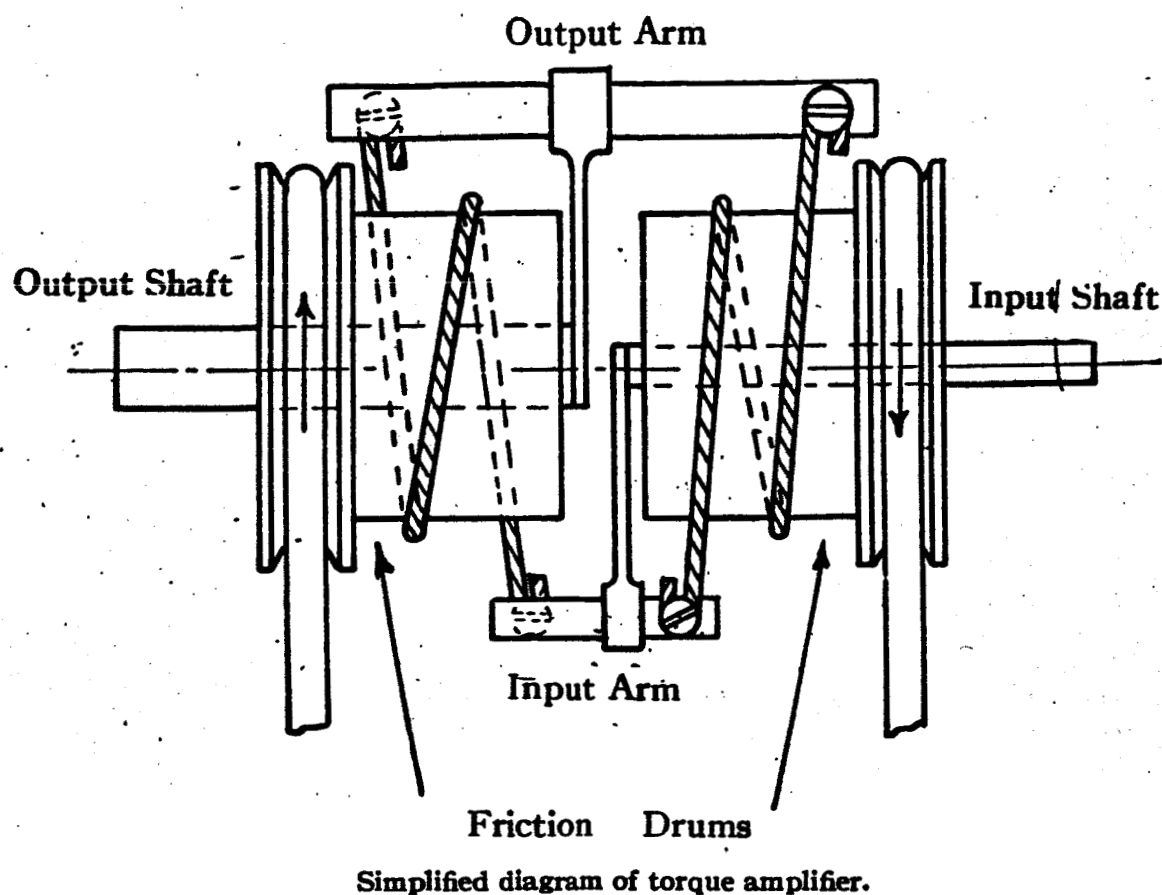


Fig. 4 Schematic diagram showing principles of the torque amplifier. The friction drums are attached by pulleys to an electric motor.

Thus, the wave functions must also be bases of irreducible representations of the infinite three-dimensional rotation group. As part of my doctor's thesis, I helped Wigner to separate off the rotational coordinates from the electronic, vibrational, and rotational motions of a molecular system. This is still unfinished business - Charles Curtiss, Felix Adler, and I are still trying to separate off these rotational coordinates without ending up with messy coupled equations. The introduction of group theory was very much resented by most of the physicists and referred to as "The group pest". The problem was that group theory required learning a new mathematical language. I remember frequently hearing the statement that there was nothing you could do with group theory that you could not do without it. However, the group theoreticist could derive in one page what would otherwise require fifteen pages. Thus, the poor physicists and now the poor chemists must all learn this elegant bit of mathematical formalism.

In 1927, Burrau calculated the energy of H_2^+ and Heitler and London treated the hydrogen molecule. In 1928, the Heitler-London or valence bond method was applied to many electron systems and simultaneously Hund and Mulliken started the development of the molecular orbital theory. In 1931, Slater expressed the wave functions of complex molecules in terms of Slater determinants made up of linear combinations of atomic orbitals. Thus, the Golden Age was born.

The Golden Age was marked by a feeling of great confidence in being able to solve any physical problem. The keynote was Dirac's often quoted statement in the preface of his 1930 book, "With the advent of quantum mechanics, all of the basic physical laws which are required for the solution of chemical problems are now known". The actual difficulty of solving the Schrodinger equation for many electron problems was not fully realized. Even the crudest approximations were extremely difficult to test when all the calculations had to be made by desk computers. Thus, naively, the young physicists and theoretical chemists felt that they had the world by its tail. It had the air of a Florida real estate boom get-rich-quick flamboyancy.

The physicists developed impressive equations which were supposed to represent the solutions to chemical problems and became discouraged because the chemists found it too difficult to test them numerically. In contrast, the chemists, such as Polanyi, Pauling, and Eyring, made whatever additional assumptions were required in order to get numerical solutions quickly and easily. The chemists' approach resembled engineering empiricism. They invented simple formulae which superficially agreed with the physicists' theoretical results on the one hand, and which possessed parameters which could be adjusted to agree with the known experimental data on the other hand. London told me that he was appalled at the way the chemists mangled his formulae and still

attached his name to the semi-empirical results. Whatever the justification of the semi-empiricism, it gave very reasonable results. Pauling's notions of hybrid orbitals explained the angles between chemical bonds and the resonance stability of aromatics. Eyring and Polanyi's 14 per cent coulombic approximation explained the activation energy for a large class of chemical reactions.

I should tell the following story about Eyring. In the spring of 1931 Eyring presented a paper at the Buffalo meeting of the ACS in which he claimed that the reaction $\text{H}_2 + \text{F}_2$ had a large activation energy since it required the breaking of two chemical bonds. Most people at the time thought that a homogeneous mixture of hydrogen and fluorine would explode instantaneously. Hugh S. Taylor, however, had been studying the reaction and found that the gas phase reaction was indeed slow, the fast reaction taking place on a surface. Thus, Hugh Taylor hired young Eyring to be an Assistant Professor of Princeton. And, to this day, Taylor has had the greatest confidence in Eyring's predictions.

After I passed my prelims in theoretical physics in 1933, I started to do my thesis work with Eyring. It was a tremendously stimulating experience. Eyring was young, vigorous, and even athletic. He prided himself on being able to beat his graduate students at the 100 yard dash. Eyring thought about his work from five or six o'clock in the morning, when he did his setting up exercises, until he went to sleep around midnight. He studied all

of the theoretical physics literature and new techniques. He tried to apply everything he learned to the behaviour of nature. Missing links in his arguments were temporarily filled by conjectures. Thus, he was prepared to attack any problem. In this sense he was the Compleat scientist. Each morning he would come to work bubbling over with new ideas. Most of his ideas were wrong and it was the responsibility of his graduate students to find the logical errors or the reasons why the ideas were not workable. However, there remained 5 to 10 per cent of the ideas which were inherently interesting and provided a useful concept of the gross way in which the phenomena occurred. Thus each day we had a very practical demonstration of winnowing and sifting of ideas. The ability to recognize which approaches were blind alleys was most important.

For a time, all of us graduate students were engaged in a potential energy surface factory. We mechanized the work in the following manner:⁴ I made up a set of scales giving the Morse curve energy of diatomic molecules as a function of the interatomic distance. These scales were glued onto steel rods. The steel rods were then fastened together so that their intersections corresponded to a configuration of the reacting atoms (see Fig. 5). The sum of the Morse curve energies on opposite sides of the quadrilateral were called α and β ; the sum of the energies of the diagonals was called γ . A second gadget (see Fig. 6) consisting of steel rulers (with two of them constrained to a sixty

4. J. O. Hirschfelder, J. Chem. Phys. 9, 645 (1941).

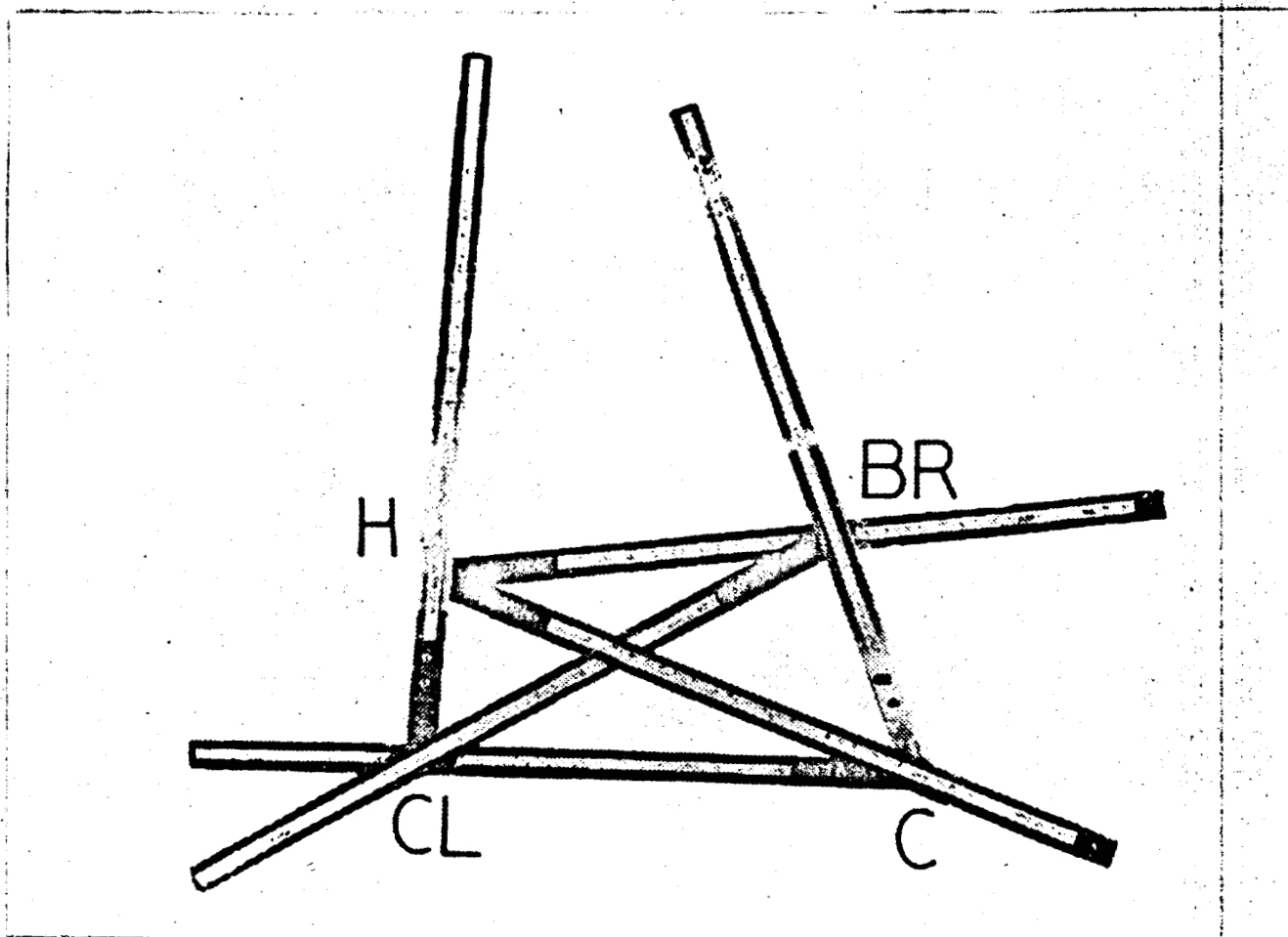


Fig. 5 Device used to simplify the calculation of potential energy surfaces. Here the steel rules correspond to a particular atomic configuration occurring in the reaction $\text{HCl} + \text{BrC} \rightarrow \text{HBr} + \text{ClC}$. The carbon atom is bonded to three other atoms which do not enter into the reaction. The scales on the rods give both the interatomic separations in Angstroms and the corresponding Morse curve energies for the "diatomic molecule" in kcal/mole.

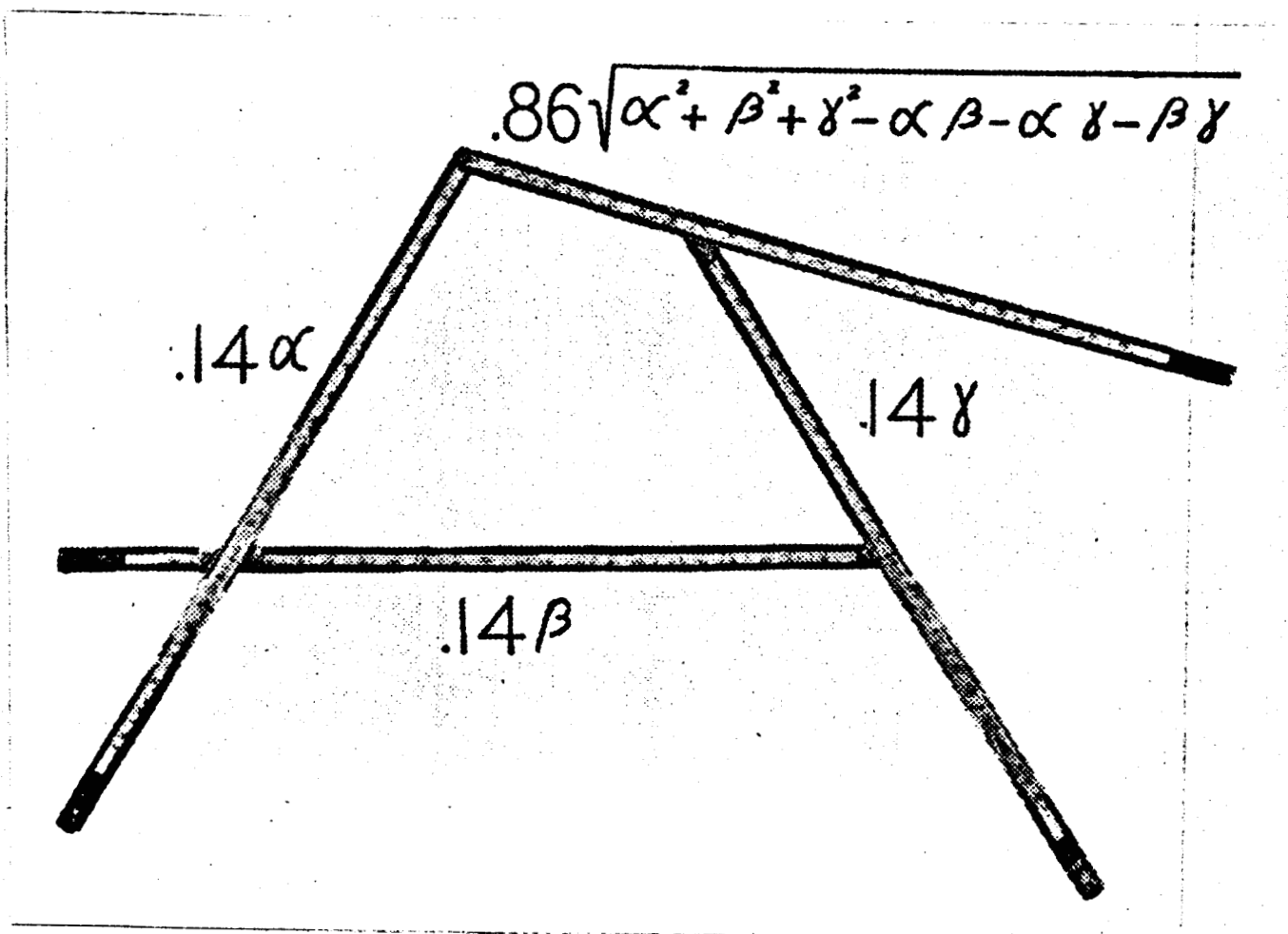


Fig. 6 Another device used in the calculation of the potential energy surfaces. Here, in accord with a suggestion of W. Altar, the angles between the α and the β , and between the β and the γ are restricted to 60° . Double scales are given on the rods so that one can read in α , β , and γ and read out the 0.14α , 0.14β , and 0.14γ . The distance between the ends of the α and γ scales is the required square root. The potential energy for a particular atomic configuration is then the sum of four numbers as shown on the rulers.

degree angle with respect to a third) made it possible to read in α , β , and γ and read out 0.14α , 0.14β , 0.14γ and $0.86 (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \alpha\gamma - \beta\gamma)^{1/2}$. With such devices it was easy for a graduate student to construct a potential energy surface for a four atom reaction with the expenditure of one afternoon's work. Fig. 7 is my favorite potential energy surface. This shows what a hydrogen molecule looks like to a hydrogen atom. The energy contours show that it is much easier for the hydrogen atom to penetrate deeply into the hydrogen molecule if it approaches along the internuclear axis rather than perpendicular to it.

A number of interesting principles emerged from these crude potential energy surface calculations:

1). At the activated state, the separations between the atoms is around fifteen per cent greater than their separations in normal molecules. This fact led Sherman and Eyring to explain why the atoms on the surface of an active catalyst should have unusually large separations.

2). The activation energy is generally very large for a reaction in which two chemical bonds are broken. Although this principle is usually true, there may be exceptions.

Many people, including myself, have tried to show errors in the Eyring theory of absolute reaction rate. The results have usually shown that the Eyring theory is surprisingly accurate.

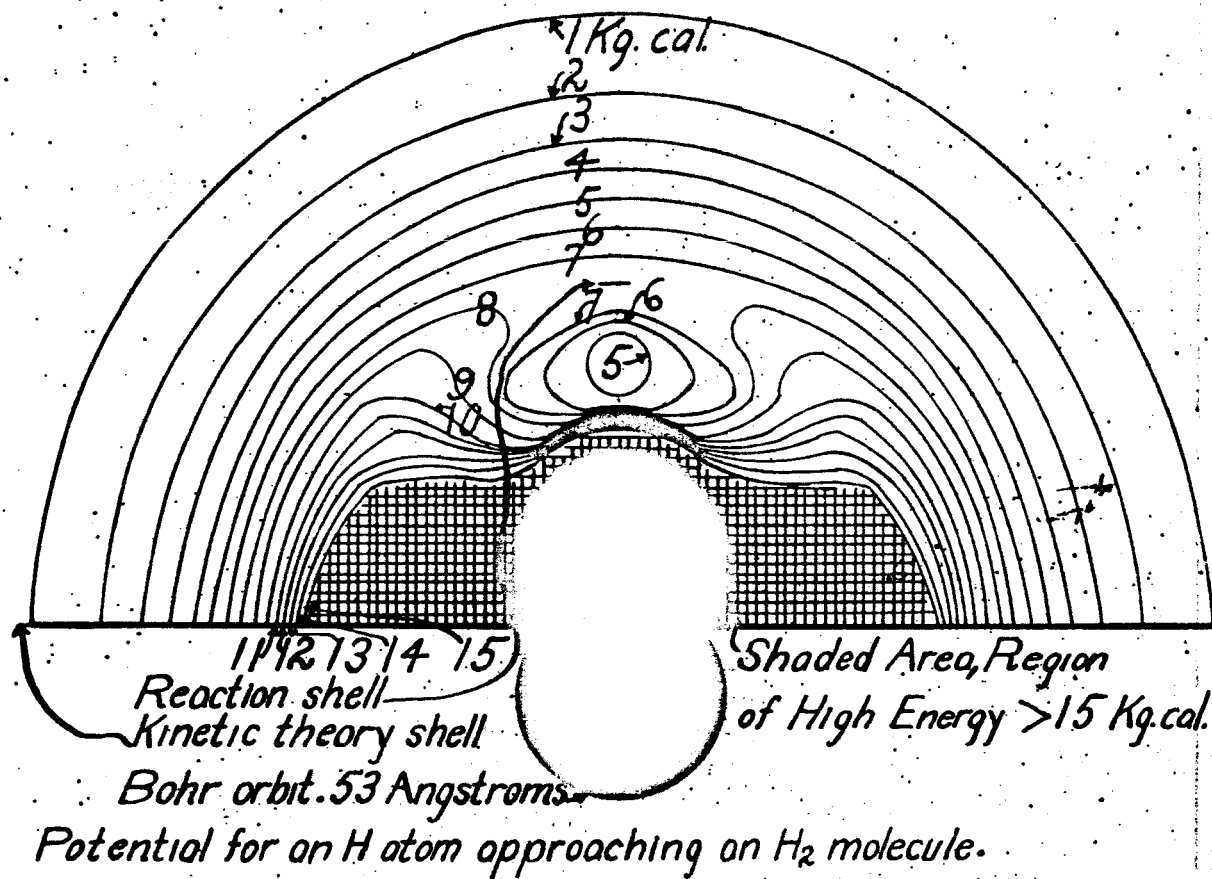


Fig. 7 Potential energy contours corresponding to a hydrogen atom approaching a hydrogen molecule.

I think that the most important feature of this theory is that it defines an entropy, as well as an enthalpy, of activation. Thus it provides two, instead of one, significant parameters which may be determined from the experimentally observed temperature dependence of the rate constant. In biological reactions, the entropy of activation may play a dominant role. For example, in the cooking of egg white the entropy of activation is extremely large and positive. This tends to compensate for the 140,000 calories per mole activation energy and make the boiling of eggs occur at a very sharp temperature.

So much for the philosophizing of an old man. The Golden Age ran out of steam because the theoretical predictions were far beyond the known experimental facts. You see, we were always ready and willing to add another adjustable constant to our equations so as to fit some new piece of experimental data. The theory of the Golden Age was an interesting mixture of engineering empiricism and basic physics. The Golden Age was sparked by the genius of two men: Henry Eyring and Linus Pauling.

Now let us jump to 1966 and take stock of our situation. What is the current status of quantum chemistry and where do we go from here?

- 1). With the use of high speed computing machines and many-configurational interactions, Chris Wahl and others are calculating the energy of a large number of diatomic molecules with a precision

comparable to or better than experiment. They are programmed to make similar calculations for triatomic molecules. Within two years they will be able to make precise calculations of the energy of simple organic molecules. These calculations are very, very expensive - roughly 10,000 to 20,000 dollars for each potential energy curve. We can afford sample calculations of every different kind. However, we should try to squeeze the most information from each calculation. Thus, every time a precise wave function is determined, the corresponding first and second order density matrices should also be calculated. These density matrices are easy to determine and they provide the essential features of the electron density and the electron correlations.

Perturbation theory provides another approach to molecular quantum mechanics. From perturbation theory we are learning how to start with an approximate wave function and estimate good values for the energy or other physical properties. The problem of calculating accurate first order properties, such as dipole moments, and accurate second order properties, such as polarizability, is very important. The dipole moment is very sensitive to the wave function. From perturbation theory, Peter Robinson was able to show that in order for the wave function to yield a good value for a dipole moment, it must satisfy a particular hypervirial theorem as a constraint. Thus we can provide a theoretical constraint that will insure that our wave function gives a good value for

the dipole moment. Similarly, we need to find theoretical constraints which will insure our calculation of accurate values for many different types of physical properties. Indeed, we shall not be content until we can calculate good upper and lower bounds so that we can bracket each of our theoretical estimates of physical properties.

Since the earliest days of quantum chemistry, it has been hoped that at least some parts of the molecular wave functions would be interchangeable as one goes from one molecule to another. It now appears that the inner orbitals are characteristic of the atomic species and the outer orbitals are characteristic of the valence state of the chemical bond. The basic significance of the chemical bonds is evident from the geminal calculations of Shull. Simple regularities in the electron densities in atoms and molecules have been observed by Clementi, Allen, Sinanoglu, and others. Thus we have reason to hope that it will be possible to use the precise mathematical calculations as our guide in developing a very sophisticated sort of semi-empiricism which will enable the high speed computing machines to quickly and easily obtain accurate solutions to the steady state Schrodinger equation for an arbitrary molecular aggregate.

2). One of the first applications of these molecular energies will be the large scale calculations of potential energy surfaces. Once we can construct potential energy surfaces, we can once more

predict chemical reaction rates - the bread-and-butter problem of chemistry. The problem of constructing accurate energy surfaces may not be so difficult as we might suppose. In 1964, Kenneth Cashion and Dudley Herschbach⁵ used the old Heitler-London first order perturbation formulae to calculate the potential energy surface for the $H + H_2$ reaction. Here, the coulombic energy of a diatomic hydrogen molecule at an interatomic separation R_{ab} is

$$J_{ab} = 1/2 \left[{}^1E(R_{ab}) + {}^3E(R_{ab}) \right]$$

and the exchange energy is

$$K_{ab} = 1/2 \left[{}^3E(R_{ab}) - {}^1E(R_{ab}) \right]$$

The energy of the three atom system is then

$$E_{abc} = J_{ab} + J_{bc} + J_{ac} + 2^{-1/2} \left[(K_{ab} - K_{bc})^2 + (K_{ab} - K_{ac})^2 + (K_{bc} - K_{ac})^2 \right]^{1/2}$$

You remember that Eyring and Polanyi used the same formulae in 1931.

The difference is that Cashion and Herschbach used the Kolos and Roothaan⁶ and Dalgarno and Lynn⁷ accurately calculated values of

- - - - -

5. J. K. Cashion and D. R. Herschbach, J. Chem. Phys. 40, 2358 and 41, 2199 (1964).

6. W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).

7. A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) A69, 821 (1956).

the singlet and triplet sigma diatomic molecular energies, $^1E(R_{ab})$ and $^3E(R_{ab})$, whereas Eyring and Polanyi used Morse curves for the singlet sigma energy and the fourteen per cent coulombic approximation. The Cashion and Herschbach energy surface leads to an energy of activation within one kcal/mole of the experimental value. Vanderslice and Mason have used the same sort of treatment to calculate the interactions between oxygen atoms and nitrogen molecules, etc. Apparently this type of approximation is good and should be explored further.

3). Molecular beams provide a much more precise way of studying molecular collision processes than do reaction rates. As you probably know, the collision cross-sections as a function of energy are essentially the Laplace transforms of the reaction rate constant as a function of temperature.⁸ Currently, Dick Bernstein and others are able to study collisions of molecules in specific electronic, vibrational, and rotational states and observe the quantum states of the product molecules as functions of scattering angles and translational energy. The precision of the experimental data is so great that quantum mechanical interference effects play an important role in the observed cross-sections. As a first step in explaining molecular beam behaviour, one might use the Born-Oppenheimer separation of electronic and nuclear motions and construct a potential energy surface. As a second step one might either calculate a manifold of classical

8. M. A. Eliason and J. O. Hirschfelder, J. Chem. Phys. 30, 1426 (1959).

trajectories a la Karplus or Marcus and determine the semi-classical collision cross-sections; or one might represent the molecular beam by a steady state wave packet moving across the potential energy surface, a technique which Eugene Wigner taught me in 1937. At the present time we have not estimated the magnitude of the errors which result from using the Born-Oppenheimer separation approximation. I think that the Born-Oppenheimer approximation is satisfactory if the collisions are truly adiabatic in the Ehrenfest sense. If, on the other hand, the collisions are frequently non-adiabatic in the sense of jumping from one potential energy surface to the other, then the Born-Oppenheimer approximation is not satisfactory. My guess is that most practical chemical reactions occur in the non-adiabatic fashion. Thus, it will be necessary for us to solve the full time-dependent Schrodinger equation including both the electronic and nuclear coordinates. This is an extremely difficult job. I doubt that this type of solution will be forthcoming for many-electron problems for another five to eight years. Solution of the full time-dependent Schrodinger equation is definitely required in considering electron-transfer reactions.

4) Much of the present experimental data being obtained by physical chemists is very precise and sophisticated: nuclear magnetic resonance, electron spin resonance, laser optics, microwave line shapes, etc. These experiments require a much higher degree of theoretical precision. Indeed, they require the solution

of quantum electrodynamic equations which are far more difficult than the Schrodinger equation. In considering nuclear magnetic resonance to the first approximation it suffices to use the Breit-Pauli Hamiltonian, which is the Schrodinger equation with a set of relativistic-magnetic correction terms tacked on. However, for second order effects such as fine structure or line intensities, using the Breit-Pauli Hamiltonian does not correspond to considering all of the pertinent Feynman diagrams. In laser optics, the light is so intense that as many as five quantum transitions occur practically simultaneously - this corresponds to the two quantum transitions which characterize the Raman spectra. To consider such Auger effects one needs quantum electrodynamics. Thus, as Bright Wilson said, "It is no longer sufficient to teach our students how to solve the Schrodinger equation, they must also know quantum electrodynamics".

5). During my little lecture I have concentrated on discussing quantum mechanics. However, it is clear that statistical mechanics and electricity and magnetism are equally important. From statistical mechanics we learn the behaviour of macroscopic systems: thermodynamics, equations of state, transport properties, etc. Except for dilute gases, the molecules which we consider in the laboratory are not isolated, they are surrounded by interacting neighbors. Thus, after we learn to cope with two-body intermolecular forces, we must consider three-body, four-body, etc. interactions.

In a plasma, strong electrolytes, or ionic crystals, long range forces between a very large number of ions is important. Thus, the quantum chemist is required to learn the techniques of solid state physics and the many-body problem.

Up to now quantum chemists have been pre-occupied with trying to explain the structure and properties of simple molecules. As soon as they have simple molecules under control, they will have to learn the tricks of their physicist friends. Three-body forces determine the face-centered cubic packing of noble gas crystals. They most likely determine the shapes of many high polymers. It is well-known that crystals of aromatic substances have very interesting optical and physical properties. Indeed, some of our chemist friends are already studying these "exciton" effects which form an important class of many-body interactions. Howard Reiss tells me that transistors, photoelectric cells, etc. offer a very interesting challenge to chemists and involve the same sort of considerations which occur in strong electrolytes - an interesting mixture of statistical mechanics, electricity and magnetism, and quantum mechanics. Solid state chemistry is needed to explain the physical and chemical properties of surfaces including surface catalysis. The activity of a catalyst depends strongly on traces of impurities and on the detailed history of its preparation which determines the metastable configuration of atoms on its surface. We are still puzzled over the strong correlation between paramagnetism

of a surface and its catalytic activity. The growth of crystals and the theory of nucleation are other avenues for theoretical research.

6). Perhaps the most important usage of quantum chemistry will be in predicting the behaviours of materials under extreme conditions of temperature, pressure, and electromagnetic fields. Chemical reactions in electrical discharges are extremely interesting and provide a real challenge to a theoretician. John Magee has shown that quantum chemistry is very useful in explaining radio-chemical phenomena. Bates and Dalgarno have applied quantum chemistry to the chemistry of the upper atmosphere. In partially ionized plasmas and in flames, the excited states of molecules occur in large numbers. Theoretical chemists are needed to predict the physical and chemical properties of excited state molecules since there is very little experimental data to serve as a guide. Then, there is the chemistry of extremely high pressures - making diamonds, polymerizing simple molecules, etc., where quantum mechanics should help in predicting the optimum conditions.

.

If time permitted I could keep rattling-off additional areas where quantum chemistry will be applied. The points which I have wanted to stress are:

1). Thanks to high speed computing machines and new techniques, quantum chemistry is making very, very rapid progress.

2). When quantum chemistry matures, it will be applicable to many types of experimental problems.

3). In order to prepare your students for this new Golden Age which is coming, give them a broad experimental and theoretical background.

4). And finally, let's stop being cynical conservatives afraid to stick our necks out. Let's have the fun of predicting useful and critical experiments, even if now and then we make a mistake.

FIGURE CAPTIONS

Fig. 1 The Differential Analyzer at the Moore School of Electrical Engineering, University of Pennsylvania, built in 1935. A similar machine was constructed for the Ballistics Research Laboratory at Aberdeen Proving Grounds for the U. S. Army. These differential analyzers were constructed by the Civil Works Administration as part of President Roosevelt's emergency relief program with the help of Professors Vannebar Bush, S. H. Caldwell, and L. S. Frost of Massachusetts Institute of Technology and Irven Travis of the Moore School of Electrical Engineering.

Fig. 2 Schematic diagram showing the principles of an "adder". Shafts D and E are "idlers" which are free to rotate and have no external connections. The four pinion gears in the center of the diagram are always engaged. Thus, when the two shafts A and B are rotated by θ_A and θ_B respectively, the housing C is constrained to rotate by $\theta_C = (\theta_A + \theta_B)/2$.

Fig. 3 Schematic diagram showing the principles of the "integrater". If the turntable is rotated through an angle x and the disk is moved in and out so that the point of contact of the disk is at the variable distance y from the center of the turntable, then the disk is constrained to rotate through an angle z where $z = a \int y \, dx$. Here a is the reciprocal of the radius of the disc, an instrumental constant.

FIGURE CAPTIONS (cont'd)

Fig. 4 Schematic diagram showing principles of the torque amplifier. The friction drums are attached by pulleys to an electric motor.

Fig. 5 Device used to simplify the calculation of potential energy surfaces. Here the steel rules correspond to a particular atomic configuration occurring in the reaction $\text{HCl} + \text{BrC} \rightarrow \text{HBr} + \text{ClC}$. The carbon atom is bonded to three other atoms which do not enter into the reaction. The scales on the rods give both the interatomic separations in Angstroms and the corresponding Morse curve energies for the "diatomic molecule" in kcal/mole.

Fig. 6 Another device used in the calculation of the potential energy surfaces. Here, in accord with a suggestion of W. Altar, the angles between the α and the β , and between the β and the γ are restricted to 60° . Double scales are given on the rods so that one can read in α , β , and γ and read out the 0.14α , 0.14β , and 0.14γ . The distance between the ends of the α and γ scales is the required square root. The potential energy for a particular atomic configuration is then the sum of four numbers as shown on the rulers.

Fig. 7 Potential energy contours corresponding to a hydrogen atom approaching a hydrogen molecule.