Self-Assessment of Scientific Contributions of Aron Kuppermann[†]

My early papers (refs 1−4, see List of Publications following) were published in Brazil before attending graduate school and reflect an early propensity toward accurate analysis of physical chemistry problems but are otherwise unimportant. The present assessment is aimed at the work done as an independent researcher at Illinois and Caltech.

1. Electronic Structure Calculations (refs 7, 8, 210, 211). The first two of these papers describe early pioneering applications of a programmable electronic digital computer (ILLIAC I) to the calculation of one-electron properties of molecules. Paper 210 describes a state of the art Exact Quantum Monte Carlo (EQMC) calculation of the PES of the ground state of H_3 having ab initio and fitting accuracies of 0.015 kcal/mol. Such high accuracy was needed in order to predict $H + D_2$ resonances within experimental accuracy. Paper 211 describes another state-of-the-art calculation of the PES s for the lowest $^3A'$ and $^3A''$ electronically adiabatic states of $O(^3P) + H_2$, having an absolute accuracy of about 0.3 kcal/mol over the entire range of geometrics of importance for its reaction dynamics. These surfaces are to be used in accurate quantum scattering calculations for this system. Both 210 and 211 stress the importance of accurate ab initio electronic structure calculations for reliable dynamics studies.

2. Diffusion Kinetics in Radiation Chemistry (refs 10, 11, 13, 14, 16, 17, 23, 25, 47, 74)**.** This body of work put the radiation chemistry of aqueous solutions on a firm theoretical basis. It explained quantitatively the yields of the molecular products H_2 and H_2O_2 obtained using γ-rays, X-rays and α-particles as radiation sources, and the effect of radical scavenger solutes on these yields. The initial effect of the energy deposition in the aqueous system (on a picosecond time scale) is to form spherical clusters (spurs) of H atoms and solvated electrons. These spurs are isolated from each other for low-density ionizing radiation (such as γ-rays and X-rays) and strongly overlap forming cylindrical tracks for high-density radiation (such as α-particles emitted by Po^{210} nuclei). These initial species either recombine with each other or diffuse away, reacting with free-radical solutes. The corresponding inhomogeneous kinetics is described by systems of partial differential equations containing diffusion as well as reaction terms. These equations were solved accurately for the first time on ILLIAC I and yielded results in close agreement with experiment, firmly establishing the validity of this diffusion-kinetic model. Although this work was done about forty years ago, this model is still the standard in Radiation Chemistry.

3. Unimolecular Decomposition Processes (refs 12, 107). Up to 1960 it was generally believed that when saturated gas-phase hydrocarbons are pyrolyzed in the presence of a sufficient amount of nitric oxide, which acts as an efficient free-radical scavenger, the reaction proceeds by a unimolecular decomposition mechanism not involving free-radical intermediates. The rates of such reactions represented a large fraction of the known unimolecular decomposition processes at the time, and their experimental rates were used to test unimolecular decomposition theories. In paper 12, we showed that these were not unimolecular processes at all. By pyrolyzing a mixture of the normal butanes C_4H_{10} and C_4D_{10} in the absence and presence of NO, it was shown that the methane products obtained were isotopically scrambled to the same extent in both cases, and according to a statistical distribution of the H and D atoms. This convincingly shows that the NO-inhibited process proceeds via a free radical mechanism, just as when NO is absent. As a result, NO-inhibited saturated hydrocarbon pyrolysis reaction rates could no longer be used to test unimolecular theories. In paper 107, using quasi-classical trajectory methods, we studied the intramolecular energy transfer processes occurring in an equilateral triangle model triatomic molecule and showed that neither of the assumptions underlying the Slater or RKR unimolecular theories, namely conservation of normal mode energies or bond energies respectively, was valid for such a small although highly coupled system. Nevertheless, the RKR assumptions were somewhat better than Slater's. The consequence of this work was that such simple theories should not be applied to very small systems without using great caution. Despite the limited scope of these two papers, I believe that they contributed in a significant way to the knowledge of unimolecular processes.

4. Low-Energy Electron Impact Spectroscopy (refs 19−22, 26, 30, 34−38, 40, 42, 46, 50, 54, 58, 59, 66, 69, 78, 79, 82−84, 91−94, 97, 109, 110, 113−117, 121−124, 129, 132, 133, 136, 138−140, 147, 159, 160, 164, 175, 178, 179, 180). Excited triplet states of molecules whose ground states are singlets play important roles in radiation chemistry, plasma chemistry and photochemistry. Nevertheless, until the development of laser-based optical techniques, their determination by optical absorption was very difficult, because of the spin-forbiddenness of photon-induced singlet → triplet transitions. The same is true for other spin-forbidden transitions, such as doublet → quartet ones. This situation prevailed up to about 10 years ago. On the other hand, low-energy electrons can easily induce such transitions by exchange with a molecular electron of opposite spin. This exchange proccess requires interaction times longer than the orbiting times of the molecular electrons, and as a result the angular distribution of the scattered electrons tends to be isotropic in the molecular frame and, therefore, sidewise peaked in the laboratory frame. On the other hand, electrons that are inelastically scattered after producing spin-allowed transitions, induced by long-range Coulombic forces not involving electron exchange, tend to be forward-peaked. This difference in the angular distributions of inelastically scattered electrons associated with spin-forbidden transitions and those associated with spin-allowed ones can be used to differentiate these two kinds of electronic excitation processes. On the basis of these principles, we pioneered the design and construction of several low energy, variable angle, electron impact spectrometers, and their use to study a large number of spin-forbidden and spin-allowed electronic transitions. For about 30 years this was the dominant technique for measuring spin-forbidden transition energies. The molecules studied included, among others, CO_2, CS_2, SO_2, ethylene and methylated ethylenes, alkynes, polyenes, benzene and the fluorobenzenes, five-membered heterocycles, NO, nitromethane, ketene, thiophosgene, norbornene, norbornadiene, acetonitrile and uranium hexafloride. Paper 129 is a review published in 1978 and contains a summary and individual references to some of these studies. Even today, the wide range of transition energies this technique can easily detect, from 1 eV or less to 20 eV or more,

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and corresponding to an optical wavelength of 1236 nm or greater to 62 nm or shorter, permits it to be used into the far vacuum ultraviolet region of molecular spectra. The body of knowledge accumulated using it has significantly contributed to our knowledge of spin-forbidden electronic states of molecules.

5. Variable Angle Photoelectron Spectroscopy (refs 56, 105, 118). The angular distributions of the photoelectrons ejected from atoms and molecules by vacuum-ultraviolet light, such as the 58.44 nm photons of a He discharge lamp, are characterized by an anisotropy parameter β. For a fixed incident wavelength β depends on the angular momentum of the electron before it is ejected. For atoms, s and p electrons have different values of β, and for molecules differences are found between σ and π electrons. We exploited this property by building a variable angle photoelectron spectrometer and used it to study a variety of molecules including ethylene, isobutylene, trimethylethylene, tetramethylethylene, benzene, halobenzenes, nitrogen, SF_6 and CO. The net conclusions of these studies was that at a fixed photon energy, the determination of β did not really give clear-cut information about the angular momentum properties of the photoelectron and that as a result the angular dependence of the photoionization cross sections was not nearly as informative as the corresponding electron ionization energies.

6. Multiphotoionization and Photoacoustic Spectroscopy (refs 148, 161−163). These studies were undertaken to extend the reach of optical spectroscopic techniques to the study of triplet states and of highly vibrationally excited states, using lasers. In one study (148), the $^3A_2$ state of CS_2 was investigated with optical resolution by resonance-enhanced multiphoton ionization. In another, a pulsed laser photoacoustic spectrometer was built and used to study high vibrational states of CHD_3, CH_2D_2, CH_3D and CH_4. They showed that CHD_3 does not undergo rapid intramolecular vibrational redistribution as it does in larger molecules such as benzene.

7. Reaction of Monoenergetic Deuterium Atoms of Variable Energy with H_2 Molecules (refs 24, 27, 28, 41). The photolysis of DI by monochromatic light in the 366−303 nm wavelength in a mixture of this gas with a large excess of H_2 produces essentially monoenergetic D atoms whose translational energy with respect to the H_2 is in the range of 0.14−0.48 eV, depending on the photolysis wavelength. These hot D atoms, if sufficiently energetic, react with H_2 to form DH and H. The D atoms that do not undergo this reaction react with DI to form D_2. Using this approach, we were able to determine the phenomenological energy threshold of the $D + H_2 \rightarrow DH + H$ reaction (24, 28) and the dependence of the integral cross section of this reaction on translational energy (41). The technique of producing monoenergetic H or D atoms by the photolysis of HX or DX ($X = Br, I$) in order to study the energy-dependence of the reactions of these atoms, used for the first time in these experiments, is now universally employed in such studies. Furthermore, these were the first experiments in which a threshold energy for a reaction involving the formation and breaking of covalent bonds was measured directly. Once more, although limited in scope, this work was very important, as it furnished much more detailed information about the dynamics of a reaction than that obtained from the temperature dependence of thermal rate constants.

8. Intermolecular Potentials from Crossed Molecular Beam Experiments (refs 44, 68, 70, 119, 120, 125, 134, 135, 157). We constructed a crossed molecular beam apparatus having a universal quadrupole mass spectrometer detector and used it to study intermolecular forces in the following systems: $H_2 + O_2$, $H_2 + SF_6$, $H_2 + NH_3$, $H_2 + CO$, $H_2 + CH_4$, $D_2 + N_2$, $D_2 + O_2$, $D_2 + SF_6$, $D_2 + NH_3$, He + Ar, He + CO_2, He + N_2, He + O_2, He + CO, He + NO, He + CO_2, He + N_2O and He + C_2N_2. All these systems display diffraction oscillations. Excluding the last three, central field potentials fitted the data quite well. Intermolecular potentials were obtained which were independent of isotopic composition and energy. For the last three, because of the linear nature of the CO_2, N_2O and C_2N_2 targets, the measured differential cross sections showed pronounced damping of the diffraction oscillations. A fit to these data using anisotropic potentials and the infinite order sudden approximation yielded physically reasonable potentials. The conclusion of this body of work is that in bimolecular collisions involving a variety of heavy molecules with the light species He, H_2 or D_2, diffraction oscillations in the observed differential cross sections occur from which reliable intermolecular potentials can be obtained without requiring a determination of the absolute magnitude of these cross sections. These were the first experiments involving molecules that showed that such oscillations existed and extended the usefulness of the crossed-beam technique for determining intermolecular potentials.

9. Studies of Metastable H_3 (refs 165, 174, 176, 204). In experiments designed to develop a high intensity-high energy beam of H atoms, a long-lived metastable state of H_3 was detected (165), and its properties were studied by total scattering, surface ionization and photoionization (176). It was concluded that the molecule was in a Rydberg excited state, and ab initio calculations of the corresponding potential energy surface and transition moments were made (204). This is a very interesting species and its reaction properties should be further investigated.

10. Collinear Quantum Reaction Dynamics (refs 45, 48, 49, 51−53, 55, 60, 62−65, 67, 72, 73, 85, 86, 102−104, 106, 145, 146, 149, 150, 151, 153, 155, 156, 158, 167, 168, 170, 172, 181, 186−189, 212). As a complement to our pioneering experiments in the reactions of monoenergetic D atoms with H_2 molecules (24), we decided to try to develop methods for doing accurate quantum mechanical calculations of the cross sections of the reactions of atoms with diatomic molecules. A first step in that direction was to consider collinear reactions. This was done for two reasons. One is that the corresponding number of degrees of freedom is two rather than the six involved in a three-dimensional reaction. The other is that the fundamental dynamical assumptions underlying absolute reaction rate theory were intended to be valid for such collinear conditions and could therefore be tested against the results of calculations of this kind, although this is an approximate model that ignores all angular momentum effects. After initial calculations using a boundary value method were performed (45), a significantly faster reaction coordinate propagation method was developed (47, 151) and, later, a more powerful and general hyperspherical coordinate method (149). The latter permitted calculations for heavy−light−heavy systems, which the reaction coordinate method did not. These methods were used to perform accurate calculations on $H + H_2$ and $F + H_2$ and their isotopic counterparts and reverses, I + HI, Br + HCl, Be + FH and C + NO. The methods were further extended to permit calculations on two coupled electronic states (103) and of collision-induced dissociation (153, 167). The results of these many calculations were used to test a variety of approximations including absolute reaction rate theory, the vibrationally adiabatic approximation, and the quasi-classical trajectory and semiclassical methods, and determine the conditions under which these approximations were valid. In addition, they led to the discovery of dynamic resonances in collinear reactions, their physical intrepretation (154), and a calculation of their delay times, lifetimes, and asymptotic state compositions. They also permitted a demonstration that significant tunneling can occur even under conditions of very straight Arrhenius plots (151). This large body of work on collinear reactions not only led to a fairly deep understanding of the quantum dynamics of these processes and the magnitude of the corresponding quantum effects but, as expected, set the groundwork for the development of accurate three-physical-dimension methods.

11. Three-Dimensional Quantum Reaction Dynamics of Triatomic Systems (refs 76, 81, 87, 90, 96, 98, 99, 100, 101, 108, 130, 151, 173, 177, 183, 190, 191, 192, 193, 194, 196, 198, 199, 200, 202, 203, 205, 206, 207). Papers 76, 98 and 99 describe methods and results for coplanar triatomic reactions. These were developed as a stepping stone in the transition from collinear to three-dimensional systems. Paper 87 describes for the first time a system of symmetrized internal hyperspherical coordinates in terms of which maps of three-dimensional potential energy surfaces depict the three asymptotic arrangement channels equivalently. These symmetrized maps have been enormously useful for the development of the quantum calculation methods for 3D triatomic systems and for helping in the interpretation of the results. The initial methods (100) involved integrating the three-atom Schrödinger equation separately in each arrangement channel region and matching the solutions on planes in the symmetrized space just mentioned. This approach produced excellent results for the H_3 system but was difficult to extend to more complicated triatomic systems because of numerical problems associated with the matching procedure. As a result, a method based on the symmetrized 3D hyperspherical coordinates was developed (96, 173, 191), which overcame these difficulties. The initial matching method permitted the accurate calculations, at relatively low energies, of the first state-to-state differential cross sections and constituted a bench-mark calculation for the testing of approximate methods. It also provided insight into the magnitude of the tunnelling in this 3D system. Furthermore, the H_3 potential energy surface is collinearly dominated and the calculations indicated that this resulted in a propensity rule favoring reagents and products whose rotation axes were perpendicular to the instantaneous triatomic plane. These calculations are a cornerstone in the evolution of quantum reaction dynamics. The symmetrized hyperspherical coordinate method permitted such calculations to be performed at higher energies and for more complex systems. The H_3 system and its isotopic counterparts DH_2 and HD_2 display a geometric phase (GP) effect and that hyperspherical method permitted this effect to be incorporated in a simple manner. This incorporation produced agreement with experimental results for $D + H_2$ which otherwise was absent. It also showed that for the $H + D_2$ reaction it produced dynamic resonances in certain state-to-state differential cross sections. The energy and lifetime of these resonances is very sensitive to the potential energy surface used. For an experimental prediction of these resonance properties, a very accurate surface is needed, and for this reason we have calculated one (210) that is accurate to 0.015 kcal/mol and is currently being used for such prediction. This predictive ability indicates the power of these new theoretical and computational methods.

12. The Use of Massively Parallel Computers in Reaction Dynamics (refs 183, 184, 195, 197). Massively parallel computers were partly developed at Caltech starting in the middle 1980s. Since they promised to become much faster than even the largest vector computers of the time, we developed efficient parallel algorithms for performing hyperspherical reactive scattering calculations on such machines and started using them about 10 years ago. Most of the three-dimensional scattering calculations we have performed since then have been done on machines of this kind, starting with the Intel Delta, then with the Intel Paragon and the HP/Exemplar. These codes are now being ported to the HP/V2500 and to an IBM teraflop machine, which are powerful enough for calculations of tetraatomic and perhaps pentaatomic systems.

13. Three-Dimensional Quantum Reaction Dynamics of Tetraatomic Systems (refs 201, 205, 208). We have recently developed a new system of row-orthonormal reactive coordinates (201) and derived the corresponding Hamiltonians for triatomic (205) and tetraatomic (208) systems. These coordinates and Hamiltonians have remarkable invariance properties under kinematic rotations. We are currently developing parallel computer codes for tetraatomic systems using these coordinates and aimed at producing state-to-state integral and differential cross sections of the same benchmark quality as those previously performed for triaatomic systems. Hopefully, these calculations can be generalized to three- and four-center reactions between large molecules, by treating the reaction centers with accurate quantum methods and the remaining atoms with perturbative, classical, or other approximate methods. This possibility indicates that theoretical reaction dynamics, although still in its infancy, is poised for rapid growth in the relatively near future. I hope to still be able to contribute to it.