

Special Issue Preface

Biography of Karl Freed

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Biography of Karl Freed

Karl Frederick Freed was born in Brooklyn, New York in 1942. He attended Stuyvesant High School, where he took his first formal class in chemistry from a teacher, Mr. Kerner, who exuded love for chemistry and for teaching the subject. However, Karl's training in chemistry started well before that when he was in grade school and his brother Jack Freed made several trips down town to Fisher Scientific to buy reagent grade chemicals, including concentrated acids and bases in order to set up a fully stocked chemistry laboratory in the basement of his home. High school provided a solid background in descriptive chemistry, as well as the other science and math courses that prepared Karl well for his studies in the School of Engineering at Columbia University, where he majored in chemical engineering. Since Karl was not permitted to take graduate engineering courses, he enrolled in several chemistry graduate courses. Karl had enjoyed the first semester of physical chemistry (on quantum mechanics and bonding, taught by Martin Karplus), so he gladly took George Frankel's course on introductory chemical physics and then the first semester of Karplus' course in quantum mechanics.

In 1963, Karl enrolled in the chemical physics program at Harvard rather than the chemistry graduate program because it would require courses to improve his education in physics and because he had already taken the equivalent of a number of Harvard's graduate chemistry courses. This choice, however,

meant that Karl had to take a full load of courses his first year as well as some courses into the second. At Harvard, Karl's education was further broadened by interaction with an outstanding group of theoreticians who taught each other their areas of expertise, as well as the excellent experimentalists who patiently explained their apparatus and experiments when Karl visited their laboratories, a habit he developed at Columbia when he visited his brother's laboratory.

At Harvard, Karl worked with Bill Klemperer on problems related to the extraction of hyperfine couplings from his molecular beam electric resonance spectroscopy data in order to provide checks on electronic structure calculations. E. Bright Wilson had suggested a project to Karl associated with the N-representability problem of reduced density matrices, again a problem that greatly influenced Karl's subsequent career. The latter influence began at a Theoretical Chemistry Gordon Conference that Karl attended as a graduate student. At the conference, Darwin Smith presented a solution to the 1-representability problem that was limited to nondegenerate states. Karl showed that this proof readily extends to degenerate systems by placing the system in an external field that lifts all degeneracies. The newly evolving many-body methods of perturbation theory yield energies that probably do not correspond to N-representable wave functions. Yet, these methods were being used to obtain highly accurate correlation energies

for small atoms. This led Karl, after a brief tutorial by Bill Reinhardt on the diagram rules, to sum analytically the diagrams Kelly evaluated and to show that this led to the pair theories that were being expounded at the time by Sinanoglu and Nesbet.

Karl also obtained exact solutions for a wide class of many-level multiresonance systems. This was important as double resonance experiments were often analyzed using two-level formulas with one strong field and the second treated perturbatively as weak. While at Harvard, Klemperer gave Karl complete freedom to work on anything he liked (under his watchful eye). Bill commented on strange vibronic effects in polyatomic molecules and suggested that Karl look at the problem. As Karl began reading about the theory of rotation–vibration energy levels, he was struck that the Hamiltonian was generally written in body-fixed coordinates under the assumption of small amplitude vibrations. Karl decided to derive the Hamiltonian by transforming the triatomic molecule vibration–rotation Hamiltonian from the space-fixed coordinates to a rotating frame defined in terms of the instantaneous moments of inertia for the vibrating molecule. The paper that resulted from this work provided insights into the treatment of large amplitude vibrations.

Stuart Rice offered Karl a faculty position at the University of Chicago. Stuart suggested that Karl consider working with Sam Edwards at Manchester, England. When Karl arrived in Manchester as a NATO postdoctoral fellow, he learned that Sam's interests had turned to polymers with his landmark work on excluded volume theory using a path integral formulation. Sam's idea was to consider the description of polymer networks and specifically the influence of multichain circuits. They developed the theory and found that loops enter as a random phase approximation. They discussed the problem of treating statistical mechanics with a macroscopic number of internal constraints. Karl's postdoctoral work with Sam Edwards provided insights that helped with the development of the lattice cluster theory much later on.

While still at Harvard, Karl was exposed to the vibronic problems Klemperer had in mind when Charlie Parmenter gave a seminar on his research with Kistiakowski on the fluorescence yield of benzene in the isolated molecule limit. The next encounter Karl had with the problem was when he was a postdoc in Manchester and Stuart Rice sent Karl a preprint of his paper concerning the problem of understanding radiationless transitions. After Karl's arrival at the University Chicago, he began working on radiationless transition theory using Mower's Greens function–projection operator methods to explain the then perplexing origin of the irreversibility observed by Kistiakowski and Parmenter. The initial two papers describing this work and the series of papers that followed considered how vibronic and spin orbit couplings between Born–Oppenheimer (BO) states of a molecule can profoundly affect the relaxation of an electronically excited molecule. The seminal analysis develops a general picture of the relaxation of excited polyatomic molecules that describes internal conversion, intersystem crossing, vibrational relaxation, and other processes. It provides criteria for the occurrence of irreversible intramolecular electronic relaxation and provides expressions for radiative decay and fluorescence quantum yields as functions of the initial vibronic state. An interesting application of the theory involves the explanation for the observation of a 3 orders of magnitude inverse H/D isotope effect in the thermally activated diffusion of hydrogen on the W(110) surface.

Karl's work also provided considerable insights into the photodissociation of small molecules. As diatomic molecules

dissociate into open shell atoms, several BO diatomic states approach the same separated atom limit. When the interatomic distance becomes large, the spin–orbit and hyperfine interactions are no longer small compared to the energy differences between those states converging to the same energy. Karl's work demonstrated that the branching ratios of the fine structure states arising from an atomic term are not statistical, and that anisotropy parameters and branching ratios into specific j states can be largely independent of the exact form of the bond length dependent potential for the dissociating diatomic. The product energy distributions from the dissociation of polyatomic molecules are predicted to be greatly affected by the change in natural coordinate systems (i.e., Frank–Condon factors) between the ground and dissociative states.

Two of Karl's early papers on the derivation of the exact π -electron Hamiltonian and the ab initio determination of the parameters that appear in empirical quantum chemical theories laid the groundwork for a research areas that would lead to new ideas in electronic structure theory for the next decades. These classic papers and ones to follow prove that semiempirical methods are approximations to exact ab initio configuration interaction (CI) calculations that have been transformed into the valence (P) space. The full space of configurations can be partitioned into a zero order or P space, which contains only valence shell configurations, and the rest of configurational space, referred to as the Q space. The exact CI calculation is then recast into a valence only form that has the dimensionality of the P space. The one and two valence electron integrals, which appear in the effective P-space Hamiltonian provided by these formulations of the ab initio problem, have the values that they would have in a P space only ab initio calculation, plus corrections due to the Q space. This formalism enabled Karl to test numerically the assumptions in semiempirical theories, such as a transferability of the parameters and the assumed dependence on interatomic distance, providing feedback that can be used in improving semiempirical theories.

This work also offered a new and different formalism for performing high level ab initio calculations. Karl developed multireference perturbative methods using the old idea of improved virtual orbitals that he has shown to provide highly accurate results, including yielding smooth potential energy curves, even for the cases in which the state-of-the-art coupled cluster calculations do not. Relativistic corrections have been added for calculations on heavy metals. Karl also has studied the use of many body Green's function and the equation of motion method in analyzing electron correlation contributions, and in the calculation of excitation energies, ionization potentials and electron affinities.

In early work, Freed developed second quantization methods for treating polymer networks. In groundbreaking work, Freed went on to develop what is arguably the most complete description yet of the self-consistent field theory of self-excluded volume interactions in polymer chains. His work also uses his knowledge of quantum theory to develop a powerful multiple-scattering method for calculating the dynamical properties of polymer solutions as a function of polymer concentration, and his theory led to the discovery of the important phenomenon of the screening of hydrodynamic interactions. Later the critical phenomena revolution in condensed matter physics attracted him to new many-body methods employing scaling theory ideas and subsequently to renormalization group techniques. His treatments of polymer science problems resulted in his well-known book "Renormalization Group Theory of Macromolecules". He applied renormalization group and other field theory techniques

to the properties of polymers in dilute and semidilute solutions and for polymers under confinement.

In the past decade, Freed's efforts have focused on how the particular geometrical structure and chemical interactions of polymers influence their phase behavior and the critical properties of polymer blends and solutions. Although his initial formulation of the lattice cluster theory involved the second quantization methods, he soon developed a more versatile and decisive formulation that involves a systematic Mayer cluster expansion that incorporates monomer structure and chain flexibility in his treatment of the thermodynamic properties of polymers. His first applications emphasized the influence of molecular monomer structure on the phase boundaries of polymer blends and ultimately resulted in a new classification scheme of blend classes that reduces to the classical Flory-Huggins theory in the special case of monomers having similar structure. The theory explained the previously enigmatic molecular origin for the entropic part of the Flory interaction parameter and made several bold predictions before their experimental verification, including the prediction of the pressure dependence of the Flory interaction parameter and its magnitude, the possibility that certain block copolymers could order on heating, the occurrence of closed loop phase diagrams in certain weakly interacting copolymer blends, and more.

Once chain semiflexibility was integrated into the lattice cluster theory, Freed went on to formulate and develop a molecular theory of glass formation in polymeric fluids. Incorporation of chain flexibility into the lattice cluster model shows Karl's considerable analytic skills and deep physical insight. This theory enables the direct computation of all the characteristic temperatures of glass formations, variations of fragility with polymer structure, and the explicit computation of the long wavelength structural relaxation time as a function of molecular parameters, such as monomer structure and differing flexibilities of different portions of the monomers. Of particular interest is the molecular explanation for glass fragility (i.e., temperature sensitivity of dynamical properties), the property governing the method by which a substance can be processed.

The pioneering work on glass-forming liquids has benefited from a series of studies on the thermodynamics and dynamics of equilibrium self-assembly, where the theory delineates a wide range of properties to enable distinguishing between various possible mechanisms. An application of the theory explains the unusual nonmonotonic temperature and pressure dependence of the polymerization of G-Actin to F-Actin. This body of work is starting to have a large impact in efforts to understand self-assembly for nonfabrication applications.

More recently, Karl has begun applying ideas from his theories of polymer dynamics to describe protein dynamics and protein folding. He has resolved a controversy between NMR and scattering experiments concerning the character of denatured proteins and has demonstrated the unfortunately great differences between common protein force fields when applied to proteins in non-native states. Karl has introduced rigorous criteria for the assessment of the wide range of qualitatively differing implicit solvent methods for describing protein dynamics. His method reproduces with 1 CPU the initial stages of folding of the villin headpiece that were studied in explicit solvent using a high level 256 CPU Cray computer. Current investigations of continuum electrostatic models are providing explanations for the huge discrepancies between the predictions of the widely popular Born model and experiment for transfer free energies and pK_a shifts on transfer of a charge between hydrophobic and hydrophilic media. Karl's very new theory of protein folding is the first to self-consistently determine secondary and tertiary structure.

Some other areas to which Karl has made landmark contributions are electron localization and electrical conductivity in disordered media, diffusion in random media, the dynamics of polymers and its transport coefficients in semidilute and dilute solutions, protein folding, equilibrium polymerization, and vibrational relaxation in condensed media, rigid media, collision-induced intersystem crossing, and collisionless intramolecular vibrational relaxation.

Karl is the recipient of many prestigious awards that include the A. P. Sloan Fellowship, Dreyfus Teacher-Scholar, Marlow Medal from the Faraday Division of the Chemical Society, John Simson Guggenheim Fellow, American Chemical Society Award in Pure Chemistry, Fellow of the American Physical Society, and Fellow of American Academy of Arts and Sciences.

Karl's interaction and association with his co-workers and students has extended greatly beyond than just scientific research. We have truly benefited from his rigorous and high standards for theoretical research, his unshakable support, and his friendship and kindness over the years.

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Guest Editors

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