

# A personal history of structural chemistry

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**Abstract** The title of the paper accurately reflects its contents.

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This is to honor Magdolna Hargittai in her special issue of structural chemistry on the occasion of her 70th birthday. I have known Magdi for a half-century and, as a former coauthor, I am keenly aware of her fierce determination to publish original ideas. As a 91 year-old I still regard Magdi as a rather young lady who might be interested in my personal review of a field she has contributed much to. In as much as I have worked in this field of structural chemistry for a lifetime, my review may sound far too self-centered. So be it. The references will show, however, that contributions from my laboratory owe much to my gifted students and postdoctoral associates. I will start at the beginning.

When I was discharged from the US Navy 2 months after WW II ended I enrolled in the Graduate School at the University of Michigan, well supported by the 100 % disability checks I received from the government (disability now down to 10 %). Of the research topics offered by the various faculty members, Brockway's gas-phase electron diffraction program seemed the most interesting I found quantum mechanics fascinating, imbuing electron particles with a wave nature. I could demonstrate this wave

nature every day as my electron waves gave interference patterns when they were diffracted by molecules in the vapor phase. Now it should be mentioned that this choice of research program was a bit of a gamble in view of statements made by Brockway's laboratory mate at the California Institute of Technology, the acerbic E. Bright Wilson. Wilson had begun to study gas-phase molecules by microwave spectroscopy with enormously greater precision (to about 0.0001 Å) than that claimed for electron diffraction (then only about 0.02 Å). So Wilson scathingly wrote the obituary of electron diffraction. He said he could measure the positions of atoms more accurately than the molecules, themselves, knew where they were (owing to quantum indeterminacy). That claim came back to haunt him later. In order to obtain enough different moments of inertia to derive structures of polyatomic molecules, he synthesized different isotopically substituted forms of his molecules. He then neglected the subtle changes in structure caused by the different isotopes and this degraded his structures.

I wasn't worried about Wilson's dismissal of electron diffraction because I was confident that I could design a diffraction unit and devise a means to measure diffraction patterns that would yield far greater accuracy in measurements. That turned out to be correct. As a matter of fact, our measurements of diffraction intensities were much more accurate than the theoretical expressions used to analyze them. Therefore, I worked out procedures [1] to analyze diffraction patterns of molecules vibrating anharmonically, in terms of mean internuclear distances and "equilibrium" distances. I compared these parameters with those corresponding to spectroscopic distances (in diatomic molecules) and X-ray diffraction interatomic distances. I sent a paper on this to the Journal of Chemical Physics, only to get back an insulting review asserting that

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Dedicated to Professor Magdolna Hargittai on the occasion of her 70th birthday.

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my paper was just a sterile exercise because electron diffraction patterns could not be measured with enough accuracy for my distinctions to matter. So I sent the editor evidence that our new unpublished experimental methods [2] could indeed obtain the accuracy involved. What happened next was quite upsetting, but my paper was eventually published and its content became adopted in the field.

After constructing my new electron diffraction unit, I thought it would be worthwhile to use its new capabilities and apply it to a problem I wanted to investigate, namely to determine the distribution of electrons around a nucleus. Brockway asked me how I could do that. I told him, never mind, let's just try it. So in 1953 I carried out the first experimental measurements via electron diffraction of the distribution of planetary electrons around an atomic nucleus [3]. X-ray diffraction measurements of electron distributions had been made before but, because the X-ray wavelength was about 20 times longer than the electron wavelength, the X-ray resolution was too crude, for example, to resolve the different electron shells in the argon atom. Electron diffraction data resolved the shells.

Many years ago Pauling demonstrated that linear combinations of atomic orbitals, known as hybrid orbitals, could exhibit different directional behaviors. Sets of four so-called  $sp^3$  combinations were directed toward vertices of a tetrahedron, making them suitable for bonds in methane, for example. Similarly  $sp^2$  and  $sp$  combinations would direct orbitals to  $120^\circ$  and  $180^\circ$ . Therefore many chemists believed that hybridization could “explain” bond angles in organic molecules, for example. To me this was nothing but a tautology, “explaining” something by naming it. But then, as I acquired more and more molecular structures, I noticed some remarkable regularities. Isobutene was the pivotal case. I lamented that the different geminal groups around the central carbon atom were not resolvable from each other. That was very disappointing because it meant that I could not distinguish between the geminal C–C distances between methyl groups and those between the methyl to the  $CH_2$  group. If only those geminal distances had been more distinct, I could have determined the bond angles much more accurately. It finally dawned on me that maybe nature was trying to tell me something. Maybe it was not hybridization that determined bond angles but the close packing of ligands. The carbons in the methyl and methylene groups were perhaps just touching each other. If this were true, then maybe carbon and hydrogen atoms in ethylene and other molecules could also be just touching each other. I found that a set of atomic radii could be constructed including atoms of H, C, N, O, F and Cl that gave quite decent structures of many molecules. So I included this idea in a paper on the structure of isobutene, only to have Verner Schomaker review the paper and

request that my idea of ligand close-packing be extracted from the isobutene paper and published on its own [4]. I was happy to comply. Clearly my idea was not accepted by many or most. A few years later, in a plenary lecture in a spectroscopy meeting in Columbus Ohio, the sharp-tongued E. Bright Wilson explicitly made fun of it. Finally Ron Gillespie, who had contributed much to the VSEPR model, a model which also explained structures of molecules, carried out extensive investigations and learned that ligand-close packing was superior to his VSEPR model, and he gave a more accurate version of it (For a complete list of references, see [5]) than I had originally published a half-century earlier [6]. What this example shows is that an experimental body of data is a much more reliable guide to structure than a theoretically intuitive hybridization approach.

If ligand close-packing were correct, that suggested interesting isotope effects. Hydrogen atoms, because of their light masses, execute substantially larger vibrational amplitudes than deuterium atoms, for example. This suggests that hydrogen atoms act as if they are larger than deuterium atoms. Therefore one might expect secondary isotope effects. Possibly the C–C bond length in  $H_3C-CH_3$  is larger than that in  $D_3C-CD_3$ . When I registered this prediction, a spectroscopist in Ottawa asserted that this was “impossible” [7]. My subsequent electron diffraction investigations of  $H_3C-CH_3$  and  $D_3C-CD_3$  verified the prediction.

In 1964 Bob Gavin and I were curious about effects of electron correlation on electronic structure. That is, the effect of the instantaneous mutual repulsions of electrons as they orbit nuclei. At the time, the theoretical treatment of electron correlation was the greatest obstacle to accurate quantum calculations of atomic and molecular structure. Except for this trouble, quantum chemistry would be quantum chemical engineering. So, we calculated the effects of electron correlation on X-ray and electron diffraction intensities [8]. This research constituted the first approach to direct experimental measurements of the spatial distribution of electrons as governed by their instantaneous mutual repulsions and led to continued studies by many laboratories.

Spurred on by the success of our model of ligand close-packing based on repulsions between geminal atoms, in the late 1960s Jean Jacob, Brad Thompson, and I introduced the first formulations of a “Molecular Mechanics” force field explicitly incorporating rational non-bonded interactions including geminal interactions [9]. It made far more accurate predictions of molecular structures than existing formulations of molecular mechanics incorporating a greater number of adjustable parameters. This was because our force field was a more faithful representation of the physics of force fields than those used by the (mainly)

organic chemists who had initiated Molecular Mechanics studies.

Jean Jacob was a meticulous experimenter, so when she studied rhenium fluorides and observed significant discrepancies between observed and calculated intensities of diffracted electrons [10], it was important to find the reason. Her calculated intensities had included the theory of effects of scattering by heavy atoms published by Schomaker and Glauber [11], a theory which had helped considerably. After a great deal of study of the problem I finally realized that Schomaker and Glauber only took care of intra-atomic dynamic effects and left out the interatomic effects. A heavy atom, as it were, casts a sort of shadow on downstream atoms. It took me a ridiculous amount of time to figure out how to include this. Tuck Wong wrote a program to incorporate the solution [12]. It nicely corrected the problem.

In the early 70's I was asked to speak about determinations of electron distributions around atomic nuclei. Since I hadn't done anything on the subject for some years, I cast around for fresh ideas, wondering if the new subject of holography might work with electrons. Even though Gabor, who won the Nobel Prize for inventing holography, had originally invented it for electron microscopy, hoping he could bypass the severe limitations of electron lenses at the time and get electron micrographs with the full resolution afforded by the short electron wavelength. Electron microscopes then had needed to use such small numerical apertures in their lenses to overcome their considerable spherical aberration, that resolving power was reduced 100-fold! But try as it might, the Metropolitan Vickers firm was unable to make holography work for electrons. It worked magnificently with laser light, however. The trouble was the difficulty in producing a "reference wave" that was coherent with the object wave, the wave carrying information about the desired image. I saw that electron diffraction patterns, of atoms, viewed suitably, were holograms with the reference wave scattered by the nucleus and the object wave scattered by the planetary electrons [13, 14]. So coherence was built in automatically. The method worked and I got holographic images of electron clouds. NSF, my source of support, was so pleased it put out a news story. I thought it would be a kindness to Gabor to write him that we got holograms with the full resolution he predicted was possible. He immediately wrote back, telling me he was thrilled but he asked "what is your idea that has escaped others?" I wrote him back but before he received my reply he wrote back, I have figured it out myself and I think your idea will revolutionize electron microscopy [15]! Later we got rotationally averaged images of molecules from which we could measure bond lengths with a ruler [16].

In analyzing electron diffraction patterns by least-squares, sometimes it turned out that a couple of

parameters were so closely correlated that accuracy in their determination was very poor. It dawned on me that maybe that correlation might be broken if we introduced "predicate observations" [17], that is, reasonable guesses of certain parameters, attaching to them a generous estimate of uncertainty. The method worked very nicely and soon was even adopted by spectroscopists who had the same problem of high correlations between parameters.

When we constructed holograms of atoms and molecules, the images were degraded by the Airy diffraction fringes of the sort one sees while looking at stars with a telescope on a very clear night. In our paper I "invented" a means of getting rid of the Airy diffraction rings [12, 14]. My "invention" turned out to be the well-known Mach-Zehnder interferometer. So I went over to our very accomplished specialist in optics, Emmet Leith, and asked if he had a Mach-Zehnder interferometer we might use. He said yes but told me it was a very tricky instrument to use. So he asked what we wanted it for and on the spot, came up with an alternative and MUCH simpler idea [18]. It worked beautifully. Leith was not only a very generous man but also an incredibly imaginative man. When I asked if there was an existing theory of the spatial domain filter he laid out, he said no, it was too complicated.

Challenged by this I worked out a quantitative theory of the optical spatial domain filter [17] and Angelo Gavezzotti, who was visiting my lab, programmed it. At the time I was too incompetent to program it myself. Angelo's results accounted very well for what we saw with and without Leith's filter [19]. When I published our result, of course I gave credit to Leith and Gavezzotti.

By a lucky accident in 1982, I found a way to study *extremely* hot molecules and Steve Goates carried out beautiful electron diffraction studies on such subjects [20, 21]. Mind you, the experiment was very tricky. It required an invisible infrared laser beam to be focused on an invisible jet of molecules issuing from a small nozzle, to be interrogated by an invisible electron beam. What happened was that as the molecules exited the small stainless steel nozzle, I accidentally focused the infrared laser beam on the nozzle, itself, instead of on the emerging molecules I intended to irradiate. This heated the nozzle almost to its melting point and, more astonishingly, it heated the molecules passing through it almost to the temperature of the hot nozzle, despite the very short residence time. Temperatures of the hot molecules could easily be inferred from the measured amplitudes of their molecular vibrations. What distinguished this study from many others on hot molecules was the extreme speed with which the heating and probing of the molecules was carried out. That meant that molecules could be probed while they were vibrating so violently that they were on the verge of flying apart. The methods used in previous studies of hot molecules disintegrated the molecules at *much* lower temperatures because

of the long residence times the hot molecules suffered. What was learned were details of the force fields of molecules that spectroscopy was blind to. This made it possible to test and verify the validity of a very simple model force field based on the ligand close-packing theory.

Anding Jin visited my laboratory in 1983. One project I assigned to him was to develop and test a quantitative theory of intermolecular multiple scattering of electrons. The more concentrated the molecules were, the more often electrons would be scattered more than once. Theory and experiment agreed [22].

We carried out the first quantitative electron diffraction study of the structure of a liquid in 1984 [23]. We started with small clusters of benzene, and our results turned out to be considerably more discriminating than prior X-ray and neutron diffraction studies of liquid benzene, partly because of the low temperature that was possible with the new technique, and partly because of the much shorter wavelength of the electrons.

A determination of the structure of a low-temperature phase of SF<sub>6</sub> from its neutron diffraction powder pattern was attempted in 1987 by a distinguished crystallographer. We were interested in the results because we had obtained small, very cold clusters of this material as SF<sub>6</sub> gas issued from a supersonic nozzle. The solution to this problem was frustrated by the inability of massive attempts of Rietveld analyses to avoid getting trapped in false minima. So when the crystallographer gave up, I asked him to send me his data. He replied that the problem was hopeless but he finally did send his data. At the time I had a very smart French postdoctoral associate in my group whose government gave him a choice. Either return to France immediately to join the army or stay in America in my laboratory. Since he was enjoying living with his beautiful blond girl friend then, the choice was easy for him to make. He was not a crystallographer but I asked him to write a program to analyze powder patterns, and suggested a strategy to avoid getting trapped in false minima. He disappeared for quite a while but eventually appeared with a fully written program [24]. It solved the neutron diffraction problem right away, and also gave the same structural result for our cluster patterns which were much blurrier, blurrier since the clusters were tiny compared with the bulk powder particles.

In 1991 we investigated the kinetics of freezing of liquids by pulsed electron diffraction studies [25]. This method was stated at the time to be the first new method in 50 years for studying freezing kinetics. The method made it possible to study the kinetics of extraordinarily fast phase changes (faster by a factor well over ten orders of magnitude than afforded by prior methods). This success prompted us to change our research field from structure to nucleation in phase changes, though a decade later we did study proto-snowflakes generated in supersonic flow of

water vapor [26]. Their development was followed by electron diffraction, and our results confirmed prior conjectures that that snowflakes start out in a metastable form of ice, not the stable form of fully grown snowflakes. These studies revealed the shape and crystalline orientation of newly formed flakes.

As mentioned in the preceding paragraph, our subsequent investigations of nucleation were so fruitful that we abandoned structural chemistry. This avoidance lasted until Magdi Hargittai noticed a very improbable structural result published by a Russian group [27]. This group asserted that the molecule LaI<sub>3</sub> exhibited absolutely no thermal expansion of its bonds. So Magdi invited me to explore what was wrong. I made myself a bit of a villain by objecting to her intuitive inferences, correct though they were, and I insisted on a fully rigorous analysis. The Russians had based their conclusion on deductions from a force field they constructed. When I studied their paper, I found no errors in their analysis but finally realized that they left out one symmetry-allowed interaction force constant. When Zoltan Varga calculated its value by a very nice quantum computation, it turned out that it indeed solved the problem by making bond lengths increase as the temperature increased, as expected. So Magdi's sharp eyes brought about a solution to a disturbing puzzle [28, 29].

In 2024 an issue in structural chemistry is planned to honor Magdolna Hargittai on the occasion of her 80th birthday. Sorry Magdi, I cannot promise to contribute because by then I'll be well over 100 and it seems very unlikely that I'll still be on this planet.

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