Reviews of Modern Quantum Chemistry

A Celebration of the
Contributions of Robert G. Parr

Volume I

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K. D. Sen

University of Hyderabad, India

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Personal Introduction

Walter Kohn

*Department of Physics,
University of California*

Santa Barbara, CA93106, U.S.A.

E-mail: kohn@physics.ucsb.edu

E-mail: hicks@physics.ucsb.edu

I am delighted to contribute some personal introductory remarks to this Festschrift, which celebrates the 80th birthday of Robert Parr, my dear friend and admired colleague for half a century.

Bob and I first met in 1950 at the Carnegie Institute of Technology (now Carnegie Mellon University) in Pittsburgh. He was in the Department of Chemistry and I had just joined the Department of Physics. At that time our interests did not strongly overlap but we did have a number of friends in common, including Per-Olov Löwdin and Fausto Fumi, as well as one of Bob's postdocs, Tadashi Arai, who regularly attended meetings of my little research and study group. During the remainder of the fifties, we had various kinds of interactions from time to time, including professional, social, and University-related. I remember Bob not only as a scientist with very original ideas, but also as a model of a good citizen of the University. In the early sixties, both Bob and I left Carnegie, he to Johns Hopkins and I to the University of California at San Diego. Then in 1964-65, Hohenberg, Sham, and I wrote our two initial papers on density functional theory (DFT). Rather soon thereafter, Bob Parr came as a visitor to the University of California, San Diego to give a colloquium on this theory. I had not been aware that he had caught the bug and was wondering what he was going to say. I remember Bob remarking in his introduction that he felt like "carrying coals to Newcastle," but of course, he wasn't doing that at all. As was typical of him, his work was totally original and none of us in San Diego would have ever dreamt of going in that direction. My other recollection from that colloquium is how much I enjoyed having the subject illuminated by a leading theoretical chemist whose perspective reflected that background and was very different from my own.

In those early years of DFT, the community of theoretical chemists felt, almost without exception, that this approach had nothing useful to offer

to them. Occasionally I was invited to give a paper at their meetings, but I had the feeling that most of the audience expected to confirm their conviction that it was full of irremediable defects, in particular, insufficient accuracy and the absence of guaranteed, systematic procedures to improve it. The most notable exception was Bob Parr. Secure in his prominent standing in his own community, based on earlier, excellent work in theoretical chemistry, he had convinced himself of the great promise of DFT, and probed for chemically interesting uses in several directions. Most physicists and a few quantum chemists were focusing on the new computational possibilities offered by the theory, but Bob also explored the possibilities of relating DFT, whose central concept is the total energy regarded as a functional of electron density $n(r)$, with known and developing chemical concepts expressed in terms of various changes of $n(r)$: e.g., the chemical potential/electronegativity, chemical hardness, and Fukui function. In this way he brought some very fruitful new ways of thinking about chemical reactions, which he sees as consisting of transfers of electron density from one place to another. His original contributions to this "conceptual density functional theory" continue to this day.

Finally, I would like to highlight two other tremendous contributions by Bob to DFT: through his excellent book with Weitao Yang which, more than any other, helped to train the current young activists in chemical DFT; and through his many students and postdoctoral fellows from all over the world, who absorbed his enthusiasm for the subject as well as his fearless way of striking out in new directions. Many of these young people, as they continued into independent careers, have become key figures in the next generation of leaders in DFT. I expect that most of them are among the authors in this volume. I can hardly imagine what the entire field would be like without them.

About 1990, after much excellent work, the accuracy of DFT had been greatly improved, and most theoretical chemists accepted the usefulness of DFT, especially for understanding systems consisting of many (about 100-1000) atoms. I felt then, and feel now, that Bob Parr was the principal figure of his generation responsible for this change of heart. When in 1998 the Chemistry Committee of the Nobel Foundation recommended me for a Nobel Prize, I was happy to invite my original collaborators, Pierre Hohenberg and Lu Sham, as well as Robert Parr, to accompany me to Stockholm.

For about two-thirds of my life, Bob Parr has been a wonderful friend and colleague to me, and I wish him the happiest of birthdays. May he enrich and enjoy our theory "till 120," as one says in the Jewish tradition.

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REMINISCENCE: ON THE DENSITY-FUNCTIONAL ROAD TO CHAPEL HILL WITH ROBERT G. PARR

Mel Levy

*Department of Chemistry and Quantum Theory Group, Tulane University
New Orleans, Louisiana 70118, U.S.A.*

E-mail: mlevy@tulane.edu

It is a joy for me to be given the opportunity to reminisce for this special volume in honor of Professor Parr. I feel that I have been fortunate in that I was a postdoctoral with him at the time that he commenced his research in density-functional theory (DFT), and that I have been privileged to have been able to follow closely his research in this area ever since, because I myself have been obsessed with DFT during this period.

Parr's entry into density-functional theory, twenty-eight years ago, coincided with a very special event in my life, my marriage. Michele and I were married (eloped) on November 10, 1973 in a civil ceremony in the magical village of Chapel Hill (in the basement of the police station). A party was kindly given later that month in Baltimore by the Bartlett's and Politzer's on behalf of the Group, and a small religious ceremony followed in Washington on December 23, 1973. Since I was a postdoctoral with Bob at Johns Hopkins, I spent most of the 1973-1974 academic year commuting between Baltimore, Maryland and Chapel Hill, North Carolina, a distance of about 300 miles, because Michele was taking the course work for her doctorate in comparative literature at The University of North Carolina (UNC) in Chapel Hill. I left Baltimore on Friday evenings and returned on Monday mornings. I did this almost every weekend. For obvious reasons, the trip down to Chapel Hill was much easier for me than the return, and it was this drive to Chapel Hill (at speeds, before the gasoline crisis, which I shall not mention here) that I recall with special fondness. I especially remember the warm feeling upon finally reaching route 15-501 which, for some reason, appears to be everywhere in the vicinity of Chapel Hill.

However, shortly after the beginning of the gasoline crisis, the speed limit was dropped considerably to 55 mph. As a result, I soon received 2 speeding tickets on the same trip to Chapel Hill, one in Virginia and one in North Carolina, even though I had reduced my speeds drastically!

At the same time that I was on this road to my new wife in Chapel Hill, Bob was on the road to his new mistress, density functional theory. It appeared to me then that he dropped everything else to court her; he made a conscious decision to concentrate solely on DFT, his new passion. Jane was, as always, an important and supportive companion, both to Bob on his latest new road, and to the Group. However, I must tell the following Bob and Jane road story, which reveals a certain spirit of adventure.

I had compiled enough speeding tickets and there was a severe shortage of gasoline. So in the winter of 1974 I decided to start taking the train or to ride with others who were going to Chapel Hill. On one trip, in either late winter or early spring, I actually accompanied the Parrs on their way to visit UNC to help them decide if Bob was going to accept an offer of a chaired professorship in theoretical chemistry. (This offer to him was clearly an amazing coincidence for me because, as everyone now knows, Bob finally took the position. Moreover, as a patriotic gesture on Bob's part, he "arranged" a two-year appointment for me as a lecturer at UNC, undoubtedly to help the country save gas. Or, did I "arrange" his chaired professorship....? In any case, the two years I spent at UNC were among the happiest of my life.) Well, somewhere in North Carolina we were down to less than 1/4 of a tank of fuel when we approached a gasoline station that actually had some gasoline and, as an added bonus, also had no line-up of cars for fuel. As a result, Jane strongly urged (insisted?) that Bob get fuel at this station, now! Bob refused to stop. He said no! "This is too easy to do. There is no excitement in it. Instead, let's see how close to empty we can get without running out." Bob drove on. Evidently, Bob had an idea of the density of open service stations and he conjectured that there probably would be another station open somewhere, on some road, before we hit Raleigh where I was to be dropped off. (My car was at the Raleigh train station which is about 30 miles from Chapel Hill). It is an understatement that the "arguments" which ensued between Jane and Bob were energetic. I was an amused observer who wondered quietly where we would sleep that night. By the miracle of '74, we and an empty tank made Raleigh. We all slept in Chapel Hill that night, but I arrived much earlier than they did. Ask the Parrs what happened after they dropped me off in Raleigh.

This brings me to another Parr story. (I have many more of them but, unfortunately, I am limited by library shelf space.) When I first arrived at John Hopkins, in December of 1971, RGP and I were having one of our

very first scientific discussions. I remember that the discussion had to do with localized orbitals and that it was late in the day. We started talking at the blackboard in RGP's inner office. This inner office connected to his outer office which connected to the Group's seminar room. As we were talking, I noticed that Professor Parr started to pace in a small ellipse as he was thinking. First he walked around the inner office several times. Then the ellipse became more elongated to include several trips involving the outer office as well as the inner office. Finally, his ellipse started to include even the seminar room,. After each one of his returns to me in the inner office, we resumed our discussions at the blackboard. But the length of time between each return kept growing. I was thus uncertain as to what to do and concerned that I do the right thing. After all, this was the famous author of the book entitled Quantum Theory of Molecular Electronic Structure. Should I follow him or should I just wait for him to return to the blackboard in his inner office? At first it appeared to be a good idea to wait because he kept returning. But eventually something strange happened. On his last trip, I waited for a return for about eight minutes or so. Then I finally decided to peek into the outer office. To my astonishment, I found that his overcoat was gone!

It is instructive for me to recall the way Bob started on his density-functional road twenty-eight years ago. For this indicates something about Bob and how he does science. If I remember correctly, it appeared to me that his early studies traced the history of the field. I recall his lectures at Hopkins in '74 on Thomas-Fermi theory which, of course, dates back to the late 1920's and is a precursor to modern DFT. The object was to start at the beginning, study the postulates, theorems, proofs, approximations, and conjectures, and carefully learn to distinguish which is which. (The reader might think that the distinctions between, say, postulate, theorem, and conjecture, are obvious, but a reading of what is sometimes asserted in the DFT literature reveals to me otherwise!). However, while I feel that he has handled the distinctions with care, as witness the acclaimed Parr-Yang book, what is so absolutely delightful about Bob is the fact that he approaches conjecture with complete abandon! Everyone knows this about him! One better take his questions, conjectures, and ideas seriously, even though they are often wild and even though there have been billions and billions of them, because every once in a while (often enough) he makes a major hit which lands miles ahead of the rest of the field.

A project that I was lucky enough to be involved in while on the road in '74 was one in collaboration with Marilyn Morrell and RGP. It concerned the asymptotic decay of the density, the ionization energy, and the extended Koopmans' theorem. Parr conjectured that since the Hartree-Fock equations yield a Koopmans' ionization energy, would not the analogous Löwdin equations, for the exact natural orbitals, yield, upon proper transformation, the exact ionization energy through an extension of Koopmans' theorem? Moreover, just as the exponential fall-off of the Hartree-Fock density yields the Koopmans' ionization energy, would not the exponential fall-off of the exact ground-state density yield the exact ionization energy? (My part in the proofs of the theorems took place, to a large extent, literally on interstates 85 and 95 in early 1974). I should add that there were some spirited arguments among the three of us at Hopkins that winter and spring, and there were debates with other research groups. For reasons which I shall not go into here, we actually discovered more than we published; it was the only time that I ever saw Bob hold back on something important. In any case, this research eventually led to some exact constraints used today for approximating density functionals and to the identification of the highest-occupied Kohn-Sham eigenvalue as the negative of the exact ionization energy.

Parr had the vision to begin his research in DFT long before it was as popular or as fashionable as it is today in the chemistry community. As a result of his contagious enthusiasm, Parr exposed many of his students and postdoctorals (myself included) to the basic ideas and principles during the relatively "early" stages in the development of the theory. Consequently, we were fortunate enough to be given the opportunity to make fundamental contributions of our own in a new field.

Shortly after I stopped commuting, and parked my car in Chapel Hill for the period 1974-1976, there were extensive discussions in Parr's group concerning the meanings of the various basic theorems in DFT. In line with what I stated earlier, there was careful thought given to the postulate-theorem connections. Accordingly, the v -representability question was included in the discussions of the Hohenberg-Kohn variational theorem; what happens if a trial density does not belong to some one-body attractive potential (some external potential)? What happens to the universal $F[\rho]$ for such a density? Can we generalize $F[\rho]$ to include such a density? Moreover, what happens to $F[\rho]$ if the density contains a fractional number of

electrons. Some of the answers did not come until 1979, while I was already at Tulane, and until later in 1982 in work co-authored with Perdew, Parr, and Balduz, Jr. on derivative discontinuities of the energy.

It was during the 1975-1976 academic year, just off campus at the Carolina Coffee Shop on Franklin Street, that Bob explained to a bunch of us his identification of electronegativity with the DFT chemical potential. He excitedly called me some years later after he asked himself "what is the meaning of the second derivative of the energy with respect to change in particle number?" Bob already knew the answer! I have since enjoyed following his work with collaborators, such as Weitao Yang and fellow faculty member Max Berkowitz, on seminal concepts such as local temperature, hardness, softness, and the reactivity index, etc., as well as his collaborative studies involving approximations to the exact kinetic, exchange, and correlation energy-density functionals, including conjointness and the Lee-Yang-Parr (LYP) functional, etc. I also await with keen interest further results involving density to wavefunction constructions.

Thanks greatly to Parr and associates, it is now second nature for so many of us to visualize the flow of electrons from a region of high chemical potential (low electronegativity) to a region of low chemical potential (high electronegativity) until electronegativity equalization takes place. Moreover, chemical systems at constant temperature and chemical potential evolve toward maximum hardness or minimum softness, and among potential partners of a given chemical potential, hard likes hard and soft likes soft.

I have quite recently had the pleasure of collaborating with Parr's group once again; Qingsheng Zhao, RGP, and I have utilized coordinate scaling within the coupling constant integration formula to generate an unorthodox local exchange-correlation functional. The LDA is the very best, of course, for a uniform density, but Bob asks "what is the best local exchange-correlation functional for molecular systems?" Parr is always asking questions.

This special tribute to Bob is indeed timely because the impact of his work appears to be accelerating, if this is possible! Observe, for instance, the intense and widespread interest in the LYP correlation functional, during the last few years, by *ab initio* quantum theorists. That is why I wish to include the following letter regarding Parr as a teacher. I feel that the letter is properly inserted here, as I wrote it just after arriving at Tulane in

November 1976, long before the present popularity of DFT in the chemistry community. In fact, one could say, perhaps, that it was written when Parr was just about to approach his first gasoline station on the DFT highway:

I am delighted to be able to write to you concerning Professor Robert G. Parr...I was a postdoctoral fellow with Professor Parr at John Hopkins. Subsequently, my association with him continued at North Carolina where I held a two-year faculty appointment.

It would be impossible to list all that I have gained from my association with Professor Parr. As far as I am concerned, his almost childlike contagious enthusiasm for science is his most important asset as a teacher. I find it amazing that he has been engaged in quantum chemistry for so long and yet he still appears to approach research problems as if the world were new to him. All of us who have worked with him smile when we think of his wild and crazy ideas.

Professor Parr has always emphasized that it is very easy for one to pursue routine research problems. It may on the other hand be more difficult and less comfortable to pioneer a new area of investigation, but it will be worth it in the end. For this reason, he has always granted his students and postdoctorals a great deal of freedom. Consequently, we all have gone through periods of struggle. We have emerged, however, as confident and independent thinkers. But most importantly, I feel that a little bit of his "madness" has rubbed off on all of us. In short, I often think how lucky and privileged I am to have known this remarkable man

I stand by what I wrote in the above 1976 letter. [Finally, I chose not to alter this manuscript, conceived some ten years ago for a very different purpose, in preparing it for publication here. For while, as everyone knows, Professor Parr has done a great deal of important work in the interim, I wanted to focus on precisely those years and those works covered in this piece.]

REMINISCENCE: THE DISCOVERY OF ZERO DIFFERENTIAL OVERLAP: AN EXAMPLE OF EXTRAORDINARY CREATIVITY

Rudolph Pariser

R. Pariser & Co., Inc. 851 Old Public Road, Hockessin, DE 19707-9631

E-mail: RudyPar@aol.com

1. INTRODUCTION

**"MAKING THE SIMPLE COMPLICATED IS COMMONPLACE:
MAKING THE COMPLICATED SIMPLE, AWESOMELY SIM-
PLE — THAT'S CREATIVITY".**

— Charles Mingus, American jazz composer and musician (1)

In my career as a scientist as well as manager of research at DuPont, I have had the unusual privilege of collaborating with Bob Parr in my early years with DuPont, that is during the nineteen fifties. I was able to observe first hand a fascinating display of creativity, namely the discovery of zero differential overlap (ZDO). In what follows, I will tell the story of this discovery from my personal perspective. Furthermore, since I am currently interested in the process of creativity in science and technology and have been fortunate to be in a position to observe and to be involved with many creative people and their contributions, I will conclude by discussing Bob's achievement in a somewhat analytical way from the perspective of the creative process (2).

2. ZERO DIFFERENTIAL OVERLAP (3)

The story of the discovery of zero differential overlap, or ZDO, by Bob Parr actually begins with my employment at Du Pont. The year was 1951. I had just completed my Ph.D. thesis in photochemistry at the University of Minnesota and started to work at Jackson Laboratory, located in the midst of the Chambers Works in New Jersey.

Jackson Laboratory was the R & D Laboratory of the Du Pont Organic Chemicals Department, a business organization which no longer exists under that name. This laboratory covered the range from basic research to pilot plant production. It was an old, crowded laboratory, without air conditioning, and the many odors from the Chambers Works were very preva-

lent. However, in retrospect, Jackson Lab can certainly claim an unusual record of creative achievement. It was where the fluoropolymers, neoprene and other elastomers, various dyes and pigments, and petroleum additives were invented. It was where Charlie Pedersen, the 1987 Nobel laureate in chemistry, and other creative people worked. At the time, Jackson Laboratory was heavily engaged in synthesizing dyes for Du Pont's new synthetic fibers. There must have been several dozen organic chemists busily engaged in this pursuit. It was my assignment to characterize these dyes. Besides me there were only two other physical chemists and one physicist amongst about 200 scientists and engineers. I began by measuring the spectra of dyes on a Beckman DU spectrophotometer, and as some of you may know, it took several hours to obtain just one spectrum. I soon decided that this was not a profitable occupation. Instead, I proposed that I might learn to provide guidance to this large synthetic effort through a better understanding of how chemical structure is related to color, light stability, and other important dye properties.

I remembered a quotation by Dirac about quantum mechanics which went something like this: "...and hereby most of the laws of physics and all of the laws of chemistry are completely understood, and what remains is their application..." Being at that time in my twenties, "all" that one needed to do was to apply quantum mechanics to answer most of our questions about dyes.

My background in quantum chemistry was only that which I had picked up in the graduate courses. My thesis at the University of Minnesota was experimental in the photochemistry of chlorophyll. But I remembered that my colleague Bob Parr at Minnesota had done his thesis on molecular orbital calculations. In July of 1951, I went to see Bob who had taken a position as an Assistant Professor at Carnegie Tech. I told Bob about my intentions.

It is to Bob's great credit that he took me very seriously and was generally encouraging and optimistic. What he did not tell me then was that it took a couple of Ph.D. theses to calculate ethylene and benzene, respectively, by a "non-empirical" p-electron molecular orbital method and that the results were quite far from agreement with experiment. What hope could there be for the calculation of the spectra of dyes!

We went to work. I succeeded in engaging Bob as a consultant for Du Pont. To Bob this also represented a new challenge and a new direction.

The molecular orbital method used at the time for large molecules was the so called Hückel p-electron method, which was quite empirical and did not explicitly consider the repulsion between electrons. This repulsion is large and it would certainly need to be included for the understanding of spectra, i.e., the color of dyes. However, to consider electronic repulsion involves very difficult calculations of many electron repulsion integrals. As already mentioned, in the pre-modern computer era it demanded a Ph.D. thesis to accomplish this for benzene alone.

The breakthrough came when Bob discovered a greatly simplified method for calculating these integrals. I quote from Bob's own delightful account "On the Genesis of a Theory" (4): "I had a wonderful flash of insight: the zero-differential-overlap approximation. I had earlier noticed that electron repulsion integrals over molecular orbitals for benzene p-electrons were tightly clustered in four groups and pointed out that one should try to find a theory to take advantage of that fact. I was also aware of the argument that in the Hückel theory neglect of overlap is not as bad as it seems there is a compensating cancellation of error...All one had to do is throw away all electron repulsion integrals involving (overlapping) charge distributions. A great simplification resulted. The slew of electron repulsion integrals over molecular orbitals reduced to just four. ...I instantly became cocksure that we now could calculate complex molecules in a better way than heretofore..". One must understand that it was extreme heresy at the time to suggest the neglect of overlap, since all chemical bonding was interpreted as resulting from such overlap.

I was inspired by Bob's discovery (5) and furiously began to apply it. One could now calculate the spectrum of benzene in just an hour on a mechanical desk calculator and get very similar results as were obtained in the complete "non-empirical" calculation. However, as was known, these results did not agree well with experiment. Why didn't they? To attack this problem, I borrowed from my previous experience in kinetics and photochemistry. What we often do there is to assume a mechanism for the reaction and to derive a rate equation containing unknown rate constants. These rate constants are then determined by fitting the experimental data to the rate equation.

With ZDO it was possible to do a similar calculation for benzene, that is, to calculate the values for the electron repulsion integrals which would give the known experimental spectrum. I fully expected to obtain some

nonsensical values for these integrals.

However, as it turned out, all of the experimentally determined integrals were not very different from their theoretical values, except for one such integral. This is the integral which measures the electrostatic repulsion between two p-electrons located on the same atom, or the "one center repulsion integral" (11/11). The theoretical value is about 17 ev, whereas the "experimentally" determined value was only about 11ev. A very large difference.

I realized that 11 ev was almost the same value as the ionization potential of carbon. It suddenly occurred to me that the experimental value of (11/11) should in fact be equal to the ionization potential, I , minus the electron affinity, A , which has a small value (6,7). That is, considered the reaction:

where, W_p is the energy of a π -electron on a carbon atom. (The so adjusted value for (11/11) compensates for the interaction with the inner electrons, the "sigma" electrons, which are formally ignored in the π electron approximation).

The elements of our new theory were now in place, and Bob and I published our work in two papers in 1953 (8,9). These papers became "citation classics" (ISI Current Contents) and were among the five most cited papers in chemistry or physics during the period 1961-77.

Not knowing of our work, John Pople at Trinity College, Cambridge, having previously received his degree in mathematics, had decided to switch his emphasis toward theoretical organic chemistry. He was attacking the same problem areas as we were and had neglected overlap involving three and four centers (10,11).

When Pople became aware of Parr's ZDO (including also two centers), he applied it to construct useful, simplified p-electron self-consistent field formulations . Soon after, our combined work acquired the name "Pariser-Parr-Pople method", or "PPP method".

Application of PPP to complex large molecules required the help of advancing technology, namely, the emergence of modern computers. I performed calculations for the polyacenes (naphthalene, anthracene, etc.) and

for azulene on the first fully transistorized computer at IBM, the IBM 701, during 1952-56 (12). The resulting agreement with the experimental spectra was quite remarkable; even electronic transitions were predicted which had not yet been previously observed. Since then, the theory has been used in the calculation of many complex molecules and extended, largely by Pople, to saturated molecules.

In 1990 Löwdin wrote (13): " The PPP method has, during the past 35 years, had an enormous impact on the development of the theory of conjugated systems and of quantum chemistry and solid state chemistry in general." ZDO is the essential foundation for this method as well as for its many subsequent extensions.

Throughout this work the management at the Jackson Laboratory and my colleagues there gave me their fullest, unconditional support. That is saying a lot for an enlightened management among a bunch of "hard nosed" industrial chemists. Without such support, ZDO, and subsequently, PPP, would not have happened when it did.

As to practical applications, the many theoretical methods based on ZDO have provided useful guidance to numerous developments, ranging from the design of organic phosphors to conductive polymers, and these methods continue to be used to this day, some fifty years later. This speaks well to these theories and to the ZDO foundation without which these theories and their multitudinous applications would not have been possible.

3. CONCLUSION: ABOUT CREATIVITY

Let me now discuss Bob Parr's discovery of ZDO from a perspective of the creative process. First, what is meant by "creativity"? It has been stated that "Creativity evades definition and even recognition" (14). For our purpose, let us accept the Random House dictionary definition for creativity: "The ability to transcend traditional ideas, rules, patterns, relationships, or the like, and to create meaningful new ideas, forms, methods, interpretations, originality, progressiveness, or imagination." This definition does convey that creativity is not merely novelty, but that it overcomes something of substance.

Can we draw some general conclusions regarding creativity? Dare one think about teaching creativity or even managing creativity? My very creative chemist/musician friend, Levon Ahranjian, who had been concert master for the Delaware Symphony for some thirty years as he was simulta-

neously a Ph.D. research chemist at DuPont, had this to say about creativity: "What's there to talk about? Either you have it or you don't". There is considerable truth in Levon's statement. Creative people have many traits in common: keen powers of observation, a restless curiosity, an ability to identify issues others miss, a talent for generating and exploring a large number of ideas, persistent questioning of the norm and a knack for seeing established structures in new ways (15). As will be discussed in what follows, these characteristics are most certainly applicable to Bob Parr. However, these traits alone may not be sufficient. What in addition brings on creativity?

Based on my studies of a number of examples of the creative process, I have proposed the following generalizations for enhancing creativity (2). These are enumerated below and presented in the light of Bob's discovery of ZDO:

- (1) *Find a supportive climate and infrastructure.* The research which Bob and I did was most certainly conducted in laboratories where a supportive, non-threatening climate prevailed, including an enlightened management at Du Pont, a management which was willing to take risks and the "long view", one which ensured both freedom and emotional security.

In addition, it should be stressed that an infrastructure supportive to creativity is also of essence. This includes not only the technical research facilities and financial support but also an environment conducive to intellectual stimulation and intercourse, such as was present at Carnegie Tech, where Bob worked, as well as at the Jackson Laboratory. In a related context, Virginia Woolf has so aptly stated (16):

"... a woman must have money and a room of her own if she is to write fiction..." I suggest the outlook, an openness to new experiences, a tolerance for ambiguity and for the shaping of unconventional hypotheses. It is interesting to note that Bob's creative insights occurred relatively soon after initiating this new research, namely, in just a few months, from initiation on July 18 to discovery on about November 2 (4).

- (2) *Set a well defined goal, but do not wear blinders, be alert for the unexpected.* Bob and I were sharply focussed towards a well defined, practical goal namely the understanding of the color and photochemical properties of organic dyes. Bob's unexpected discovery was that the electron repulsion integrals over molecular orbitals for benzene p-electrons were

tightly clustered in four groups. A lesser researcher might well have dismissed this observation as a trivial happenstance, and it would have been left to some future, more curious investigator to discover ZDO - the key that opened the doors to many, new useful, semi-empirical methods. Furthermore, Bob continued to be fully aware of potentially broader implications of our work, such as its extension to saturated molecules as manifest in CNDO and derivative methods (17).

- (3) *Be alert and don't forget what you once knew.* As is frequently quoted, "In the fields of observation, chance favors only the mind that is prepared" (18). In this example, the insightful breakthroughs came as a result of astute observations combined with the application of knowledge gained in previous fields of expertise. In other words, there was a borrowing or adaptation of knowledge from another field where Bob, as well as I, had worked previously, or which we knew intimately.

For example, after discovering ZDO, Bob found a useful shortcut to evaluating the needed two center integrals. In his own words (4): "Very quickly, I also noticed something else, that the remaining two-center repulsion integrals could be neatly calculated with an approximate representation of 2pp orbital densities: uniformly charged dumbbells just touching atom to atom. The heteroatom case could be readily included. This idea derives directly from the Kimball ideas I knew about (the Neumark thesis contained most of the formulas needed) (19). We could now proceed with calculations on the molecules we were interested in, using the full apparatus of the LCAO MO theory, with configuration interaction, but without being held up with the awful problem of integrals."

Indeed, creativity has been defined "as the insightful rearrangement of known information" (14), or "a new idea happens when someone discovers a new combination, arrangement, or adaptation of existing ideas" (20).

- (4) *Ask "WHY?" and ask "HOW?"*. Throughout the creative phase there is usually a continuing interplay or crossing between science and application. The "why" and the "how" are not distinctly separate functions. Basic research and applied research are often intermixed. The "borrowing" which is discussed above in 4.), was also very prevalent in exchanges between basic and applied concepts. In this instance, Bob was also concurrently involved in developing ab initio electronic structure

theory. He felt somewhat defensive about doing anything semiempirical without understanding the underlying science. However, this was soon clarified. In his own words: " By as early as December, 1952, when I received a letter from Per-Olov Löwdin about it, it was clear that the justification for zero differential overlap approximation lay in the transformation to symmetrically orthogonalized atomic orbitals." (4)

- (5) *Be strongly motivated, be persistent, don't give up.* Total concentration, immersion, optimism toward finding a solution, devotion to purpose, and tireless pursuit of the goal are necessary characteristics of the creative researcher.

Bob's new research direction centered around the discovery of useful semi-empirical theories was accompanied by his strong motivation to succeed. This is patently evident by his highly positive attitude expressed during our first meeting, as well as subsequently. He was not discouraged by his awareness and personal experience that available "non-empirical" methods would be far from satisfactory of meeting our goal. In fact, he conveyed persistent optimism and confidence that our goal was reachable.

- (6) *Associate with stimulating people.* The networking with knowledgeable and interested colleagues, the exchange and debating of ideas with ones peers and rivals, the building on other's experiences and knowledge are essential to the success of the creative individual. Although the "creative breakthrough" is normally an individual and very private act, it rests upon the foundations of knowledge and experiences as provided by others.

Bob was most certainly stimulated by many interactions with his peers and coworkers. This is well described in the opening paragraphs of his paper "On the Genesis of a Theory" (4). Below is reproduced just the first paragraph which conveys the richness of interactions which Bob was experiencing :

"The fall of 1951 was an exciting time for quantum chemistry. From September 8 to 10 there was the Shelter Island Conference on Quantum-Mechanical Methods in Valence Theory, organized by Robert Mulliken at the Ram's Head Inn, located on a small island off the end of Long Island. The experience was singularly important for me. Among the 25 attendees were Ted Berlin, Charles Coulson, Henry Eyring, Joe Hirschfelder, George Kimball, Masao Kotani, J. E. Lennard-Jones,

Henry Margenau, Joe Mayer, Kenneth Pitzer, John Slater, J. H. Van Vleck, and George Wheland. Mulliken asked Bryce Crawford and me to serve as secretaries, and we produced minutes of sorts. I was 29 years old”.

As I write this remembrance of my work with Bob and his extraordinary discovery, Bob is approaching his eightieth birthday, some 51 years later than the Shelter Island Conference mentioned above. It is indeed an honor as well as a great pleasure for me to be thus engaged.

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References

- (1) Quoted in Apple Computer Annual Report, 1996. Apple Computer, Cupertino, CA.
- (2) Pariser, R. CHEMTECH, **28**, 48 (1998).
- (3) The description of the discovery of ZDO is largely reproduced from Reference (2).
- (4) Parr, R.G. Int. J. of Quantum Chem., **37**, 327 (1990).
- (5) Parr, R.G. Int. J. of Quantum Chem., **20**, 1499 (1952).
- (6) Pariser, R. J. Chem. Phys., **21**, 568 (1953).
- (7) Pariser, R. Int. J. of Quantum Chem., **37**, 319 (1990).
- (8) Pariser, R., Parr, R.G. J. Chem. Phys., **21**, 466 (1953).
- (9) Pariser, R., Parr, R.G. J. Chem. Phys., **21**, 767 (1953).
- (10) Pople, J.A. Int. J. of Quantum Chem., **37**, 349 (1990).
- (11) Pople, J.A. Trans. Faraday Soc., **49**, 1375 (1953).
- (12) Pariser, J. Chem. Phys. 1956, **24**, 250 (1956) and **25**, 1112 (1956).
- (13) Löwdin, P.O., Int. J. of Quantum Chem., **37**, 317 (1990).
- (14) Council of Scholars, Inventory of Knowledge Series No. 1, Library of Congress, Washington, 1981.
- (15) Lancaster, H. The Wall Street Journal, 16 Sept., p. B1 (1997).
- (16) Woolf, V.A. A room of One's Own; Harcourt Brace Janovich: new York,

p.14 (1957).

- (17) Parr, R.G., Pariser, R. J. Chem. Phys., **23**, 711 (1955).
- (18) Vallery-Radot, R. The Life of Pasteur; Doubleday, Page & Co.: Garden City, N.Y. p.79 (1923).
- (19) For discussion, please see Reference 2 in current reference (4).
- (20) Clark, C.H. Idea Management: AMACOM. A division of the American Management Association: New York, p.14 (1980).

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