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Autobiography of Walter Thiel

I was born on March 7, 1949 in Treysa, a small town of less than 10000 inhabitants, situated in the central part of West Germany, about 80 miles north of Frankfurt. I grew up in an even smaller farming village (Rommershausen, pop. 500) close to Treysa. In postwar Germany, life was not affluent in the 1950s, but we did not suffer. My father was a federal employee in the National Railway System (Deutsche Bundesbahn), and we lived in a three-generation household, with my mother taking care of the aging parents of my father. Like my younger brother, I experienced in my childhood and youth the advantages and disadvantages of a small-village environment, being protective and healthy on one hand and rather restrictive and uneventful on the other hand. My family valued education highly, and I fulfilled their expectations at school, being allowed to skip one class in high school and passing the final exam (Abitur) with top grades at age 17.

Deciding on my field of study at university was not straightforward. While I had chosen languages as priority topics in the final years of high school, I felt also attracted to mathematics and the sciences. In hindsight, it was probably my chemistry teacher, Kurt Freytag, who made the difference. He was enthusiastic in the classroom, and I enjoyed the voluntary experimental courses very much that he offered. The good job prospects for chemists at that time also helped, and therefore, I left home in November 1966 to study chemistry at the University of Marburg.

Marburg (1966−1973). There are two dominant memories from the first semesters at Marburg, the joys of leading the free and independent life of a student and the challenges of the tough lab work and the steady exams in chemistry. Fortunately, everything worked out fine, including the tests of endurance in quantitative analysis and in organic chemistry. After the fourth-semester intermediate exam (Vordiplom), the chemistry curriculum became more relaxed, with more freedom to choose and less school-like exams. I became more interested in theory at this stage but also managed to carry out the required lab work swiftly. As a result, I had completed all course work by the end of the seventh semester and could spend the eighth semester at the University of Munich just for fun, attending lectures and enjoying life. Thereafter, I returned to Marburg for the final oral exams (Diplom), which I passed in December 1970.

During these years (1966−1970), students in Germany became more political, and this also applied to chemistry students like myself. We demonstrated in the streets against the war in Vietnam and against specific German issues (Notstandsgesetze, Federal Emergency Laws), and many of us got involved in initiatives for university reform and for greater participation of all groups in university affairs (Mitbestimmung). While our interest in politics was genuine and general, our activities were focused mostly on chemistry-specific issues, including an overdue modernization of the chemistry curriculum that was initiated by our actions and suggestions. I was elected as one of the speakers of the chemistry students and served as their representative in departmental councils for quite some time.

Back to chemistry: I had to decide at the end of 1970 on the field of research for my thesis. I had developed a keen interest in biochemistry, partly stimulated through an excellent summer school offered by the Studienstiftung, but my theoretical interests turned out to be stronger. I had listened to inspiring lectures in physical chemistry by Hans Kuhn, who had a special gift to explain theoretical concepts in a most lucid manner, but he had left Marburg to become a director at the Max Planck Institute for Biophysical Chemistry in Göttingen. Therefore, I joined the group of Armin Schweig, who had just then ventured into the new field of photoelectron spectroscopy, which I found exciting in view of its close connection to molecular orbital theory. My task was to develop theoretical methods for calculating photoelectron intensities, but I also had to measure these intensities to have experimental values for comparison. In hindsight, this subject was probably too difficult for a beginning research student, but since so little was known about photoelectron intensities, I could get by with a very simple plane wave treatment of the photoelectron. This allowed us to explain many intensity differences between HeI and HeII photoelectron spectra in a qualitative manner, as well as some effects depending on the type of ionized orbital. The results of this work gave rise to eight papers, and I received my Ph.D. degree in July 1973 at age 24 with summa cum laude. My oral Ph.D. exams were in Theoretical Chemistry, Organic Chemistry, and Political Science, the latter being the most serious one.

I enjoyed the Ph.D. time in the Schweig group very much, not only because of the exciting research but also for personal reasons. Led by an enthusiastic young professor, we were a team that got along very well on a personal level, and some of these friendships have lasted ever since, especially with Werner Schäfer, Hartmut Schmidt, and Karl-Wilhelm Schulte. Given all of this positive experience, it was clear to me that I wanted to stay in research, and this meant "going west" for a postdoc. After working on theoretical spectroscopy, I was curious about what theory could do for chemical reactivity. In the early 1970s, the Woodward−Hoffmann rules and related qualitative approaches were used all over chemistry, but I felt that theory should also be able to come up with quantitative calculations on chemical reactivity. I wanted to join a group that covered both aspects, and therefore, I was glad that Michael Dewar accepted my application.

Austin (1973−1975). I started my postdoc at the University of Texas at Austin in September 1973. I found out quickly that life in Texas is very different from life in Germany. While it was hard for me to adjust to the blistering heat outside, it did not take long to appreciate the laid-back Texan attitude, the pervasive feeling of individual freedom, the friendliness of the people, and the Austin country music. The Dewar group was also quite different from what I was used to before, a colorful bunch of roughly 20 individuals from approximately 10 countries, including both experimentalists and theoreticians. The closest associates in my first year were Andy Komornicki (of Polish origin) and Chuck Doubleday (U.S.), who were later joined by Henry Rzepa (U.K.) and Santiago Olivella (Spain). And then there was Michael Dewar himself, a towering figure with immense creativity who generated new ideas at a rapid pace and loved to argue about molecules and mechanisms. He championed semiempirical methods, of course, but he always viewed them as computational tools, and being an organic chemist at heart, his real interest was focused more on chemical reactions than on theoretical methods.

In the first year at Austin, I performed MINDO/3 calculations on the mechanism of singlet oxygen reactions with unsaturated

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hydrocarbons that explored different pathways for the ene reaction and for dioxetane formation. The surprising mechanistic conclusions from this work were documented in four papers. As an aside, with the help of Andy Komornicki, I extended the photoelectron work from my Ph.D. thesis to core electrons, which necessitated the use of all-electron wave functions; the resulting publication is the only one ever of Michael Dewar that has the term "ab initio" in its title.

After having learned how to apply MINDO/3 to study chemical reactivity, I felt ready to go for methodological developments in my second year at Austin. The obvious next step beyond MINDO/3 was to replace the INDO by the NDDO integral approximation. There had been some preliminary work on NDDO in the Dewar group before, but no full-fledged effort. It took me six months, from September 1974 to February 1975, to derive and implement the semiempirical formulation of the NDDO two-electron integrals, to produce a working NDDO SCF code, and to integrate it into the existing parametrization program. I spent the next five months, until July 1975, determining optimum parameters for the most important elements (H, C, N, and O), which was facilitated by the fact that the chosen formalism employed only atomic parameters (no bond parameters). While Michael Dewar had only been mildly interested in my initial progress report on methodological aspects, he was enthusiastic when he saw the results of the parametrization. The new treatment that was later called MNDO was superior to MINDO/3 for all properties considered, with mean absolute deviations from experiment reduced typically by a factor of 2.

Given this success, it might have been natural to continue with the MNDO development, but I had already made arrangements to return to Germany after two years, and therefore, I flew back in August 1975. It was clear that the detailed validation of MNDO and its parametrization for other elements were to be done by the Dewar group. My remaining tasks with regard to MNDO were two-fold. First, I had to draft three papers that described the basic method, the results obtained, and the semiempirical two-electron scheme. These drafts were completed by October 1975, and after extensive validation of MNDO at Austin, they were submitted essentially unchanged at the end of 1976 and were published in 1977. The basic MNDO paper has been cited heavily ever since, with a total of more than 6000 citations up to now. My second task was to release the MNDO program to the public for general use, via the Quantum Chemistry Program Exchange (QCPE). This was done in 1978, and program QCPE 353 became popular quickly, with more than 500 copies distributed. Maintaining the code and responding to user questions was cumbersome, however, and I was therefore grateful when Jimmy Stewart streamlined the codes from the Dewar group and took over program distribution by submitting MOPAC to QCPE in 1983.

In hindsight, the two postdoctoral years in Austin were among the best in my life. Scientifically, I ventured into a new field and learned a lot, and I managed to devise a method (MNDO) that, together with its later variants (AM1 and PM3), became one of the workhorses of computational chemistry, particularly in the 1980s and 1990s. On the personal side, I opened up by being exposed to life abroad, I made new friends coming from different countries, and I learned to appreciate the American way of life. Especially memorable was an eight week trip in a Volkswagen camping bus through the Western United States, together with three friends, that took us in the summer of 1974 from Austin to Los Angeles and then up the Pacific Coast to Portland before returning via Wyoming and Colorado to Texas.

Marburg (1975−1982). The next step in my scientific life was to go for the Habilitation, which was a prerequisite for obtaining a professorship in the traditional German system. Armin Schweig offered to be my mentor in this endeavor, which was supported by a Liebig fellowship from the Funds of the Chemical Industry. However, coming back to Marburg for the Habilitation turned out to be something of a letdown. First, it would perhaps have been better to go to another German university to experience yet another new environment rather than returning to a well-known one. Second, and more importantly, I felt a lack of independence which comes with the very concept of Habilitation, where the mentor provides the infrastructure but also has to consent to the general direction of research. This system has pros and cons, of course, but my overall recollection is that I would have preferred to be fully independent rather than protected.

Experimentally, the Schweig group had moved on to angle-resolved photoelectron spectroscopy, and hence, we agreed that I would develop methods for computing angle-resolved molecular photoionization cross sections. It was clear that realistic angular distributions could be obtained only by using wave functions that were much more sophisticated than the plane waves employed previously. I chose a multiple-scattering representation of the photoelectron and implemented this approach from scratch. The resulting treatment gave reasonable results for the photoelectron asymmetry parameters and their energy dependence and was applied successfully to a number of small molecules studied experimentally in the Schweig group. It allowed a detailed understanding of the angular distributions through partial-wave analysis, particularly also in the case of shape resonances and Cooper minima.

The second major project during the Habilitation period concerned the role of electron correlation in semiempirical methods. In MNDO-type models, dynamic electron correlation is implicitly incorporated in an average manner through the use of effective (damped) two-electron interactions and through the parametrization, but this does not account for specific correlation effects as encountered, for example, in reactive intermediates and electronically excited states. To enable the study of such effects at the semiempirical level, I extended my MNDO program by implementing second-order perturbation treatments and by adapting a flexible configuration interaction code developed in the Schweig group mainly by Karl-Wilhelm Schulte. Reparameterization of MNDO with explicitly included correlation led to a method called MNDOC, which performed as expected theoretically; it was superior to MNDO in systems with specific correlation effects (see above) and of similar quality for standard closed-shell molecules. The latter finding was rationalized by an analysis of the MNDOC correlation effects in such molecules, which turned out to be uniform, bond-specific, and transferable.

I turned 30 in 1979. In my twenties, I had not worried about my career. My basic attitude was to have fun with research, to do my best, and to assume that things would work out well enough to stay in academia. I then realized, however, that this might not be so easy. The German university system had expanded greatly in the late 1960s and the 1970s, most of the positions were filled with young people, and very few professorships would become available in the 1980s. Therefore, even before completing my Habilitation, I pursued my first application in 1979, for the position of an Associate Professor (C3) at the University of Bremen. To my surprise, I was short-listed and finished second, which was nice but did not really help. My Habilitation was approved in 1981, on the basis of a thesis that summarized my research on photoelectron angular distributions and on semiempirical electron correlation, and I became Privatdozent at the University of Marburg. Soon thereafter, I was awarded a Heisenberg fellowship by the Deutsche Forschungsgemeinschaft (DFG), which promised five years of independent research. All of this was reassuring, but professionally, I still felt in a state of limbo in the early 1980s.

In 1979, I met Elisabeth Dünweg, and we fell in love immediately. After studying German literature and history, she was on her way to become a teacher at high school (Gymnasium). We maintained a long-distance relationship because we worked in different places. She finished her training in 1982, and therefore, we were both looking for a permanent job at the same time. We were incredibly lucky in our search. Elisabeth got a civil-service job as a teacher (Studienrätin) at Ennepetal in 1982, and soon thereafter, I was offered a position as Associate Professor (C3) of Theoretical Chemistry and Spectroscopy at the University of Wuppertal. Elisabeth and I started our new jobs in September 1982 and January 1983, respectively. Since Ennepetal and Wuppertal are less than 20 miles apart, we bought a large flat in a Jugendstil villa in Wuppertal early in 1983, and after some major renovation, we moved into our new home in August 1983. We got married in July 1983, our son Thomas was born in June 1984, and our daughter Sonja followed four years later in September 1988. I remember the 1980s in Wuppertal as a happy time for the whole family.

Wuppertal (1983−1992). At the university, I had a senior colleague in Theoretical Chemistry, Bob Buenker, who was Full Professor (C4) and who specialized in multireference configuration interaction (MRCI) methods and their application to electronically excited states. My C3 position had been created by the university to strengthen the theoretical activities in the existing Collaborative Research Center (Sonderforschungsbereich, SFB), which received generous funding from the DFG to perform research on spectroscopy. One hallmark of this SFB 42 was the close cooperation between the experimental and theoretical groups. Bob Buenker was covering electronic spectroscopy, while the experimental groups in rovibrational spectroscopy had only little theoretical support. Therefore, I decided to phase out my research on photoelectron spectroscopy (there was no experimentalist in this field within the SFB) and to focus instead on rovibrational spectroscopy. This shift took some time to become effective, partly because of other obligations such as teaching. This was the first time in my life that I had to take on a full teaching load, and during the first few semesters at Wuppertal, I was busy assembling the usual portfolio of lectures and courses in Theoretical Chemistry. This was actually rewarding and also remained manageable since the teaching assignments were shared with Bob Buenker and his co-workers, of course.

My main experimental partner in the SFB was Hans Bürger, an inorganic chemist with special expertise in high-resolution rovibrational spectroscopy. He was interested in the synthesis and spectroscopic characterization of novel inorganic molecules, in particular, short-lived reactive intermediates and molecules with unusual bonding situations. It was evident that theory could be of great help in this regard by providing ab initio predictions for the rovibrational spectra and the associated spectroscopic constants. The cooperation with Hans Bürger was initiated in the 1980s on this basis. It lasted for two decades and proved to be very fruitful. Our combined experimental and theoretical studies allowed us to detect and characterize a number of reactive species, including difluorophosphorane, difluoroacetylene, difluorovinylidene, and bismuthine, and in many cases, the ab initio predictions guided the analysis of the high-resolution rovibrational spectra. This work has led to 32 joint publications overall.

Our initial theoretical approach in the 1980s involved harmonic force fields computed at the ab initio Hartree−Fock level and scaled in internal coordinates. As shown by Peter Pulay, the resulting scale factors tend to be transferable and thus allow realistic predictions for related molecules. In our work, we used the GRADSCF code written by Andy Komornicki to get analytic second derivatives, which were then processed further by our own evaluation programs. My first Ph.D. student, Winfried Schneider, went beyond the harmonic approximation and developed a numerical finite-difference procedure for computing anharmonic force fields that employed displacements along the normal coordinates and the calculation of analytic second derivatives at these displaced geometries. This yielded all cubic and semidiagonal quartic normal coordinate force constants that are required to calculate the anharmonic spectroscopic constants by second-order rovibrational perturbation theory. This theoretical treatment was applied throughout our long-standing cooperation with Hans Bürger because it enabled direct comparison with the corresponding experimental values determined in the same perturbational framework. My second Ph.D. student, Jürgen Breidung, derived and implemented analytic second derivatives for effective core potentials (ECPs) which may be used to replace the core electrons in heavy elements. This facilitated studies on the vibrational spectra of inorganic molecules such as those of interest to the Bürger group. While the developments outlined above were triggered by the needs of the cooperation within the SFB, they turned out to be generally useful and were thus adopted and implemented also by other groups.

In the context of these ab initio studies, I went to California for a sabbatical during the second half of 1987. Fritz Schaefer had agreed to be my host at the University of California at Berkeley but then decided to move to Georgia. Therefore, we had an overlap of only about two months at Berkeley, and hence, I interacted mostly with his senior co-workers, especially Wesley Allen and Gustavo Scuseria. Andy Komornicki and the theory group at NASA Ames Research Center were my second partner during the sabbatical, and in fact, I spent almost equal time at both locations. The collaborations were very fruitful. At Berkeley, I learned about their way of doing anharmonic calculations with the use of correlated ab initio methods, which gave rise to three joint publications. At NASA Ames, the focus was on the further development of the GRADSCF code, particularly with regard to the ECP functionality. On the personal side, it was fortunate that my family could accompany me since Elisabeth was granted an unpaid leave of absence from school and Thomas was still in the kindergarten age. We had a great time in the Bay Area and especially enjoyed the friendship with Andy Komornicki and Wilhelm Maier. As final family highlights, we spent Christmas in Mexico on the beaches of Puerto Vallarta and New Year's Eve in the Sierra Nevadas, skiing in the Lake Tahoe region, before flying back to Germany early in January 1988.

In the fall of 1988, I received a very generous award from the Alfried-Krupp foundation. This award was targeted at C3 professors under age 40 (one recipient per year nationwide) and carried a prize sum of then 850,000 DM (meanwhile upgraded to 1 million Euro). I could use this money over a period of five years for research purposes at my own discretion, with no strings attached. This exceeded my meager institutional budget by far and gave a great boost to my research. I am still most grateful to the Alfried-Krupp foundation and to its chairman, Berthold Beitz, for this crucial support at an early stage of my career. With this support and additional funding from the DFG, I managed to have a group of typically five co-workers in the period of 1988−1992.

Apart from the ongoing ab initio activities (see above), we had a fresh look at semiempirical methods during this time. Alexander Voityuk, an experienced researcher from Novosibirsk, joined us in 1990 and extended the MNDO formalism to d orbitals. The corresponding two-electron integral code was distributed freely and has since been incorporated into most other semiempirical packages which offer treatments with d orbitals (such as PM6). We also embarked on a parametrization of MNDO/d for selected elements, which showed it to be superior to MNDO in the expected areas, for example, in the case of hypervalent compounds. In a separate development, Matthias Kolb went beyond the MNDO model in his Ph.D. work by including explicit orthogonalization corrections into the one-center one-electron part of the Fock matrix to account for major exchange repulsion effects. The resulting OM1 treatment was parametrized for the elements H, C, N, and O, for which it performed better than MNDO-type methods. Finally, during his master thesis, Dirk Bakowies carried out systematic MNDO calculations on large fullerenes of different size and also on different isomers of a given size. This led to an improved understanding of the factors that govern the structure, stability, and reactivity of fullerenes and also demonstrated the usefulness and efficiency of MNDO in such studies.

As mentioned above, I was glad when MOPAC came out and relieved me of the obligation to maintain a standard semiempirical code for the community. However, we naturally continued to enhance our own semiempirical code with regard to functionality and speed. In 1990, we were asked by Cray Research to provide this code as a semiempirical engine for their UniChem package, which combined several state-of-the-art quantum chemical codes under a common graphical user interface, with the aim to achieve optimum performance on high-end machines. This concept appealed to me, and we thus joined this endeavor and optimized our code, particularly also with regard to shared-memory parallelization. In MNDO calculations on large fullerenes such as C_{540}, we reached 83% of the hardware performance limit on a Cray Y-MP8 machine, which won us second place in the 1990 Gigaflop contest of Cray Research. After the integration of our code into UniChem, it was widely distributed and used for large-scale semiempirical calculations in the 1990s. UniChem was later acquired by Oxford Molecular and then migrated to Accelrys, where it was discontinued. Our code is now distributed by Scienomics under a concept reminiscent of UniChem (www.scienomics.com).

Zurich (1992−1999). In 1992, I received the call to become Full Professor at the University of Zurich. Compared with the modest institutional resources at Wuppertal, this Swiss-style offer represented a quantum jump upward and was too good to refuse. Fortunately, my family was willing to trade our cozy situation in Wuppertal for an unknown future abroad, and Elisabeth took an extended leave of absence from her job. In October 1992, we moved to Zurich, or more precisely to Schwerzenbach, a village-like suburb located about 20 min from downtown Zurich near Lake Greifensee, where we rented a house with a large garden. Integrating into the Swiss society was not easy. Sonja adapted most quickly. She went to a private kindergarten where she picked up the Swiss dialect which helped her to make friends. It took longer for Thomas, then 8 years old, who, like his parents, did not switch to this dialect, but he also succeeded eventually. Elisabeth did not find a regular teaching job at a Swiss high school because her subjects (German and history) were oversubscribed by native teachers, and therefore, she engaged in numerous other activities including internships in the drama department of the famous Zurich theater (Schauspielhaus).

At the university, I joined the Institute of Organic Chemistry, which had traditionally been a stronghold of organic synthesis since the days of Paul Karrer. My predecessor had been a natural products chemist, but the faculty had considered it timely to change fields and to establish computational chemistry at the institute, as a complement to the five existing experimental groups. Despite the different research interests, I developed a very good relationship with my experimental colleagues, especially with John Robinson. I participated in the teaching program of the institute by giving a course on Qualitative Molecular Orbital Theory and Pericyclic Reactions, and I also contributed at the departmental level by offering a course on Introductory Computer Science for Chemists and by taking over the physical and theoretical chemistry part of the first-semester course on General Chemistry. As expected from my previous experience at Wuppertal, this expansion of my teaching portfolio demanded an appreciable fraction of my time during the first few semesters in Zurich.

Given the considerable increase in the available resources, I could continue my previous research activities and start a number of new projects. On the ab initio side, Jürgen Breidung carried on with the rovibrational studies. The collaboration with Hans Bürger continued to flourish in a long-distance mode, which posed no real problem in the era of electronic communication; the only disadvantage was that he could no longer explain to me personally how to interpret the thousands of grass-like lines in the high-resolution spectra. In the calculation of anharmonic force fields, we moved to correlated ab initio methods, first to MP2 using CADPAC and then to CCSD(T) using ACES. From a chemical point of view, one particular highlight was the detection and identification of difluorovinylidene and of its charge-transfer complex with xenon. Locally, we had many stimulating discussions on rovibrational spectroscopy with Martin Quack from ETH, but this did not lead to a joint project at that time.

In the semiempirical section of the group, Alexander Voityuk extended the parametrization of MNDO/d to cover all second-row elements and all halogens as well as zinc, cadmium, and mercury, achieving significant improvements over MNDO in all cases. He worked hard on several transition metals but could not reach a comparable overall accuracy. This indicated to me that minimal-basis-set semiempirical treatments may be overburdened by the task to describe the complicated electronic structure of transition metals like iron reliably enough. Therefore, we decided not to publish the transition-metal parameters for MNDO/d, even though the results were probably at least as accurate as those reported later by others in semiempirical work. Wolfgang Weber, a Ph.D. student, developed a second-generation orthogonalization model (OM2) in which the exchange repulsion corrections were included also in the two-center one-electron part of the Fock matrix (i.e., in the resonance integrals). He could show by careful analysis of simple model systems that these additional terms are responsible for many of the qualitative improvements in the OM2 results. Advances of OM2 over MNDO-type methods were found for conformational properties including rotational barriers, for hydrogen bonds, for species with repulsive four-electron interactions, and for electronically excited states. In addition, OM2 consistently outperformed the established semiempirical methods in the usual statistical evaluations of ground-state properties. Serguei Patchkovskii, another Ph.D. student, derived and implemented analytic first derivatives for all MNDO-type treatments then available in our code (closed-shell and open-shell SCF, minimal CI) as well as analytic second derivatives for the closed-shell SCF case. The code for the integral derivatives and for the solution of the coupled-perturbed Hartree−Fock (CPHF) equations added a major new section to our MNDO program. It allowed for more precise calculations in general and improved the efficiency for certain specific applications tremendously. Serguei Patchkovskii also derived and implemented a treatment for the calculation of NMR chemical shifts at the MNDO level, and he parametrized a corresponding MNDO variant for the elements H, C, N, and O, with results that were quite satisfactory, particularly for ^{13}C. Finally, in the context of the European PACC project, we developed a parallel version of our MNDO program for distributed-memory machines using message passing (on top of the existing parallel shared-memory code). This proved to be efficient for certain types of “embarrassingly parallel” applications but less convincing for the core task of performing an SCF calculation (especially for matrix diagonalization).

In the early 1990s, hybrid quantum mechanical/molecular mechanical (QM/MM) methods were recognized as promising tools for studying large molecules. After some initial attempts in Wuppertal, we moved into this emerging field early on in Zurich. Dirk Bakowies focused on the development of semiempirical QM/MM methods, combining MNDO with the MM3 force field. He defined a hierarchy of QM/MM coupling schemes, from mechanical via electronic to polarized embedding, and clarified the role of link atoms. His Ph.D. thesis also contained QM/MM reactivity studies. Somewhat later, Iris Antes investigated different QM/MM boundary treatments and came up with specially parametrized connection atoms that minimize adverse boundary effects. Tiziana Mordasini and Christoph Hanser performed molecular dynamics (MD) studies at the QM/MM level. Large-scale QM/MM code development was initiated in the European QUASI project which brought together three academic groups (apart from us, those of Paul Sherwood and Richard Catlow) as well as three industrial users. This was the origin of the ChemShell QM/MM package that provides a control module for all generic QM/MM tasks and interfaces to several popular QM and MM codes, thus allowing a flexible and tailor-made description of complex chemical systems. All in all, the QM/MM work during the 1990s in Zurich laid the foundation for our later large-scale applications by establishing methodology, developing software, and gaining experience in how to do QM/MM studies.

Density functional theory (DFT) was another new direction of research for us in Zurich. After the advent of gradient-corrected exchange-correlation functionals, DFT had become very popular in computational chemistry because of its favorable price/performance ratio. On the methodological side, Michael Filatov, another postdoc from Novosibirsk, tried to improve on the existing gradient-corrected functionals by a physically motivated modeling of the Coulomb and exchange holes, and he also went beyond the gradient approximation by including Laplacian terms into the exchange-correlation functional. Both approaches were theoretically appealing and gave reasonably accurate results which, however, were only slightly more accurate than those from other existing functionals and could thus not be regarded as a major improvement for practical purposes. On the application side, Volker Jonas employed standard functionals to compute the harmonic vibrational frequencies of many transition-metal compounds, including the prototypical transition-metal carbonyls and their cations. He found remarkable agreement with experiment and was able to explain the observed shifts in the CO stretching frequencies upon successive ionization. Sigmar Dressler established a numerical procedure for calculating DFT anharmonic frequencies, in analogy to the corresponding ab initio treatment (see above). This technique was later adopted and widely used by several other groups.

Michael Bühl joined our group in 1993 as Habilitand. He had obtained his Ph.D. degree with Paul Schleyer and had then been a postdoc with Fritz Schaefer. His interests were mainly computational, at that time with special focus on NMR chemical shifts and on fullerenes. Recalling my own experience during the Habilitation, I gave him as much freedom as possible for his projects, and he made fast progress so that his Habilitation was approved by the faculty in 1998. Being a team player, he spread his knowledge about ab initio and DFT computations in the group. These interactions were clearly beneficial for my co-workers and our own ab initio and DFT studies, for example, on the properties and reactions of fullerenes and transition-metal compounds.

A special highlight in Zurich was the collaboration with the colleagues from the ETH. I was invited to join the Competence Center for Computational Chemistry (C4) at ETH, led by Wilfred van Gunsteren, which united groups from the ETH, the University, and the IBM Research Laboratory at Rüschlikon. In the 1990s, other members included, for example, Michele Parrinello, Martin Quack, Ulrich Suter, Hans-Peter Lüthi, and Ursula Röthlisberger. The C4 research interests encompassed all branches of quantum chemistry and molecular simulation, and the interactions within the C4 community were truly inspiring. There were regular C4 seminars, a dedicated C4 compute cluster at the ETH that was open to all members, and joint research projects that involved the exchange of software and personnel. I cooperated mainly with Wilfred van Gunsteren in the QM/MM area where our expertise was complementary, and the co-workers that migrated between our groups included Iris Antes, Salomon Billeter, and Fred Hamprecht. I also participated in teaching at the ETH. Following a suggestion by Wilfred van Gunsteren, I gave one of the eight mandatory courses in their new graduate program in Computational Sciences, on Computational Quantum Mechanics, and it was fun to interact with the bright students that took this course.

In the late 1990s, I felt great about my professional situation in Zurich. The research environment was excellent, with secure funding to support a group of at least 10 people and with many exciting research projects. On the personal side, we enjoyed the cultural offers of Zurich and the natural beauty of Switzerland, especially in winter when we often went skiing in the Alps. There was one big sore point, however, namely, that Elisabeth had not found an adequate job around Zurich and thus felt unhappy in general. This was the situation when I received an attractive offer from the Max Planck Society to return to Germany and to become a director at the Max-Planck-Institut für Kohlenforschung. The University of Zurich made a very generous and competitive counteroffer, which included substantial additional research funding and a joint University−ETH professorship, with access to the ETH infrastructure and students. Both offers were excellent, and the choice was difficult. In the end, I decided in favor of the Max Planck Society for two reasons. First, Elisabeth wanted to return to Germany where she could go back to her teaching job (she was still on an extended leave of absence), and second, I felt motivated by the challenge at age 50 to start something new again in one of the top research institutes in Germany. Thus, after almost 7 years in Zurich, we moved to Mülheim in July 1999, into a beautiful house owned by the institute, in walking distance of the campus. I took up my new job in August 1999.

Mülheim (since 1999). The Max-Planck-Institut (MPI) für Kohlenforschung is one of the oldest institutes of the Max Planck Society, being founded in 1912. In the first 80 years, there were just three directors, namely Franz Fischer (1913−1943), Karl Ziegler (1943−1969), and Günther Wilke (1969−1993). Landmark discoveries included the Fischer−Tropsch process for coal liquefaction (1925), the Ziegler catalysts for olefin polymerization (1953), and the decaffeination process using supercritical carbon dioxide (1970). Manfred Reetz, the successor of Günther Wilke, decided to broaden the mission of the institute, from transition-metal chemistry in the Wilke era to catalysis in general. His basic idea was to bring together all branches of catalysis under one roof, and therefore, the institute was restructured into five departments, each headed by one director. I was appointed as head of the new theory department. The experimental departments are directed by Manfred Reetz, Ferdi Schüth, Alois Fürstner, and Ben List (since 2005). All of us get along very well because we share similar values and views, and it is therefore generally easy to reach consensus on all decisions concerning institute matters.

Given the mission of the institute, computational studies of catalysis were in high demand. Soon after our arrival, we thus started detailed investigations of the mechanisms of catalytic reactions, usually at the DFT level. As indicated by the following examples, many such projects were triggered by experimental work in the other departments. Klaus Angermund, Martin Graf, Anoop Ayyappan, and Jerome Gonthier studied the origin of enantioselectivity in asymmetric olefin hydrogenation by rhodium catalysts with BINOL-based monophosphite ligands that had been developed in the Reetz group. Sergei Vyboishchikov computed the catalytic cycles for ring-closing olefin metathesis catalyzed by ruthenium carbene complexes, using both model catalysts and real Grubbs-type catalysts, to explore the intricate stereochemistry observed in the Fürstner group. Aiping Fu explored the mechanism of an organocatalytic reaction discovered by the List group, the proline-catalyzed α-alkylation of aldehydes, and rationalized the different enantioselectivities with proline and 2-methylproline. Vidar Jensen, Klaus Angermund, Martin Graf, and Holger Herrmann carried out extensive DFT calculations on zirconocene-catalyzed olefin polymerizations that were experimentally investigated in the Fink group. They managed to explain the different stereochemistry observed during propene polymerization in terms of the microstructure of the catalysts and to support an unexpected σ-bond metathesis mechanism in the case of norbornene polymerization. In cooperation with the Goossen group, Debasis Koley and Holger Herrmann performed detailed DFT studies on palladium-catalyzed cross-coupling reactions. They clarified the mechanism of the oxidative addition of aryl halides to Pd(0) catalysts in the presence of anions and computed several complete, intertwined catalytic cycles for the cross-coupling of carboxylic anhydrides with arylboronic acids. These and related other investigations clearly demonstrated that the available DFT methods can provide a realistic picture of the mechanism of real-world catalytic reactions and that theory is thus capable to contribute to the understanding of the experimental work carried out at the institute. This is, of course, true in a more general sense and also applies to industrial work. This was confirmed in two collaborative projects with Wacker, in which M. N. Jagadeesh, Tell Tuttle, and Dongqi Wang employed DFT calculations to elucidate the mechanism of hydrosilylation with industrially relevant platinum and ruthenium catalysts.

It should be mentioned in this context that Michael Bühl had also moved from Zurich to Mülheim to become a group leader at the institute. Apart from his ongoing work on NMR chemical shifts of transition-metal compounds, he started his own DFT studies on homogeneous catalysis. He successfully cooperated with the MPI groups of Pörschke, Bönnemann, and Jonas, so that the theory department as a whole established joint projects with most of the experimental MPI groups. We also collaborated on a few occasional DFT projects, for example, on fullerenes (with Zhongfang Chen). Michael Bühl is no longer at the institute and now holds the Chair of Computational Chemistry at the University of St. Andrews (U.K.).

Biocatalysis is another important branch of catalysis. QM/MM methods are ideally suited for studying biocatalytic processes since the active site can be described by an appropriate QM method while the biomolecular and solvent environment can be handled by established MM force fields. Building on our previous work in Zurich (see above), we intensified our activities in this area. Several methodological advances were implemented in the ChemShell software. Salomon Billeter provided a linear scaling geometry optimizer and transition-state search in hybrid delocalized internal coordinates (based on a divide-and-conquer strategy). Johannes Kästner later improved the efficiency of this approach when using electrostatic embedding by tuning the microiterative algorithm. Hans Martin Senn and Johannes Kästner implemented at the QM/MM level a number of molecular dynamics and free-energy methods, including a novel analysis tool for umbrella sampling called umbrella integration. Stephan Thiel, together with Dan Geerke from the van Gunsteren group, extended the ChemShell code to allow for polarized embedding and polarized force fields based on the charge-on-spring model. Tobias Benighaus implemented the generalized solvent boundary potential originally proposed by Benoit Roux, which yielded a three-layer semiempirical QM/MM/continuum method, and more recently generalized this approach to handle any type of QM component. Finally, several co-workers including Frank Terstegen and Stephan Thiel enhanced the ChemShell code to make it more flexible and user-friendly. The ChemShell software is distributed by Daresbury Laboratory (www.chemshell.org) and is currently applied by quite a number of groups for QM/MM work.

Notwithstanding the need for continuous further improvements in QM/MM technology (see above), it was clear at the turn of the century that the available QM/MM methods were advanced enough to apply them in studies of enzymatic reactions. This became one focal point of our research activities at the MPI. Over the past decade, our most extensive work in this area was done on cytochrome P450cam, mostly at the DFT(B3LYP)/CHARMM level and in collaboration with Sason Shaik (Jerusalem). Jan Schöneboom showed in the initial stages of this project that the properties of Compound I, the crucial reactive intermediate in the catalytic cycle, are tuned by the protein environment, and he confirmed that the actual hydroxylation proceeds by a rebound mechanism, with involvement of the doublet and quartet states (two-state reactivity). In joint work with Frank Neese, he also predicted the spectroscopic properties of Compound I in P450cam to facilitate the identification of this experimentally not yet characterized species. Several other co-workers including Hai Lin, Ahmet Altun, Jingjing Zheng, Dongqi Wang, Devesh Kumar, Muhannad Altarsha, and Tobias

Benighaus participated in the later QM/MM studies on cytochrome P450cam and some of its mutants, which covered all intermediates and most of the reactions in the catalytic cycle. These calculations addressed, for example, the possible involvement of other reactive species and of low-lying excited states, the catalytic role of individual water molecules, an alternative mechanism for the conversion of Compound 0 to Compound I, and the effect of mutations on the ratio of coupling versus uncoupling. These and other results are summarized in two comprehensive articles in Chemical Reviews (with Sason Shaik).

We also performed QM/MM studies of several other biomolecular reactions. In collaboration with Hans-Joachim Werner (Stuttgart), we showed for *p*-hydroxybenzoate hydroxylase that highly accurate barriers can be obtained at the QM/MM level when using local coupled cluster methods as QM components. Hans Martin Senn examined the mechanism of enzymatic C−F bond formation in fluorinase and found the S_N2 pathway to be favored. Tell Tuttle explored different substrate orientations in 4-oxalocrotonate tautomerase to identify the most probable model for the reaction and also considered the effect of mutations on the active site. In addition, he studied the Bergman reaction of dynemicin A in the minor groove of DNA, in cooperation with Dieter Cremer and Elfi Kraka. Sebastian Metz investigated the reductive half-reaction in two Mo-containing enzymes, aldehyde oxidoreductase (AOR) and xanthine oxidase (XO). He established a Lewis-base-catalyzed stepwise mechanism in AOR (with Glu869 acting as an Lewis acid) and an even more elaborate multistep mechanism for XO (with essential roles of Glu1261 and Arg880 for first activating and then stabilizing the reactive xanthine species). Finally, in a cooperation within our institute, Marco Bocola and Nikolaj Otte performed classical MD simulations and QM/MM calculations on lipases to rationalize the highly enantioselective ester cleavage observed in certain mutants that were created by directed evolution in the group of Manfred Reetz. Their suggested cooperative mechanism was corroborated experimentally by confirming the theoretical prediction that a previously undetected two-fold mutant should show essentially the same enantioselectivity as the best available six-fold mutant.

Apart from the new research activities in computational catalysis outlined above, we continued to work in the other areas covered in Zurich, albeit with some change of direction. In ab initio rovibrational spectroscopy, we phased out the long-standing collaboration with Hans Bürger because of his retirement. One final noteworthy achievement was the detection and characterization of bismuthine, which was challenging theoretically due to the need to account for both inner-shell correlation and spin−orbit coupling in order to reach our usual target accuracy at the coupled cluster level. Over the past decade, we participated in two European spectroscopy networks named SPHERS and QUASAAR, which were both coordinated by Per Jensen. The theoretical focus of these projects was on accuracy and generality, and therefore, we moved away from rovibrational perturbation theory and into variational calculations. This work was carried out mainly by Sergei Yurchenko, with contributions from Hai Lin, Jingjing Zheng, and Andrey Yachmenev, in cooperation with Per Jensen. Sergei Yurchenko devised and implemented a general variational code called TROVE that employs a flexible finite basis set representation (with numerical basis functions for large-amplitude motion) and achieves generality through automated expansions in terms of linearized internal coordinates. TROVE was designed to allow for the treatment of rotational excitations up to high *J* values and the computation of rovibrational intensities. Using coupled cluster potential energy and dipole moment surfaces, TROVE calculations were performed for ammonia and its heavier group 15 homologues as well as for other small molecules like HSOH. The results turned out to be highly accurate, with excellent reproduction of experimental data (including inversion and torsion splittings) so that the computation of detailed line lists for astrophysical purposes became feasible (e.g., for ammonia). Rotational energy clustering was observed and analyzed in the case of the heavier XH_3 molecules.

Concerning semiempirical methods, Mirjam Scholten devised and parametrized a third-generation orthogonalization model (OM3) that differs from OM2 only by omitting a large number of small correction terms. Hence, OM3 is somewhat faster than OM2 and of similar accuracy overall. Tell Tuttle added empirical Grimme-type dispersion corrections to each OM*x* method, without any change in the OM*x* parameters, and noted great improvements in the treatment of noncovalent dispersion-dominated interactions. We found it reassuring that the DFT dispersion corrections seem to work equally well for the semiempirical OM*x* methods. Rouslan Kevorkiants produced a linear scaling version of our MNDO code using a conjugate gradient density matrix search which allows semiempirical calculations with many thousands of atoms. However, such linear scaling calculations on large biomolecules still consumed much more computation time than corresponding QM/MM calculations and were thus applied in our group only for validation purposes. Axel Koslowski wrote a new semiempirical MRCI program from scratch based on the graphical unitary group approach (GUGA), and together with Serguei Patchkovskii, he implemented analytic GUGACI gradients. Later, he extended the GUGACI code to generate also the nonadiabatic coupling matrix elements.

Electronically excited states have become another new focal point of our research. This was partly motivated by our participation in a Collaborative Research Center at the University of Düsseldorf (SFB 663: Molecular Response after Electronic Excitation), which started in 2005 with 14 experimental and 4 theoretical projects. Our task was the theoretical treatment of electronically excited states of large molecules at both the QM and QM/MM levels. In this context, Marko Schreiber, Mario Ramos da Silva, and Stephan Sauer carried out systematic ab initio benchmark studies (CASPT2, CC2, CCSD, CC3) for 28 medium-size molecules, covering the typical organic chromophores, to arrive at best theoretical estimates of vertical excitation energies. These were used to evaluate various DFT and semiempirical methods. It turned out that DFT/MRCI was the most accurate among the DFT treatments and that OM2/MRCI performed reasonably well given its low computational cost. Therefore, DFT/MRCI was chosen as the QM component in QM/MM calculations of electronic spectra in solution and in proteins, following protocols established by Maja Parac, Markus Doerr, and Elsa Sanchez (work in collaboration with Christel Marian). At the semiempirical level, OM2/MRCI was adopted as the method of choice for exploring excited-state surfaces. To extend our semiempirical program for such studies, Tom Keal added three different optimizers to locate conical intersections between excited states, and Eduardo Fabiano implemented surface hopping excited-state dynamics. Together with Zhenggang Lan, they used this new code to find conical intersections and to perform excited-state dynamics at the OM2/MRCI level for several small gas-phase molecules, in particular, for all DNA nucleobases where the surface hopping runs gave good agreement with the experimental decay times and detailed insight into the relaxation mechanisms. These developments were incorporated into ChemShell to enable corresponding QM/MM studies in the condensed phase.

Looking back on a decade of research at the MPI, it is obvious that we managed to maintain continuity with our previous work at Zurich while adding new activities in the areas of transition-metal catalysis, biocatalysis, and electronically excited states. This was made possible, of course, by the excellent research environment at the MPI. The generous funding from the MPI and from external sources always allowed us to have a large group of typically around 20 people who could fully concentrate on research, without intervening other duties. Moreover, we could always afford state-of-the-art equipment, and hence, all prerequisites for fast progress in our research activities were in place.

When coming to the MPI, I had expected to have more personal time for research than before. It is indeed true that my teaching obligations diminished. As Honorary Professor at the University of Düsseldorf (since 2001), I gave occasional courses, but the interactions with my Düsseldorf colleagues, especially with Christel Marian, were mainly at the research level (SFB 663, see above). However, the time gained by a lighter teaching load was normally overcompensated by other obligations that are hard to avoid after becoming MPI director. Over the past decade, I served as an elected DFG reviewer and panelist for 8 years and as Chairman of the German Theoretical Chemists for 4 years, and I became involved in a number of international and national advisory boards, editorial boards, evaluation and policy committees, academies, and the like. Perhaps most time-consuming was the task of being Managing Director of our institute for 3 years (2006−2008), which rotates among the five directors. Apart from everyday management duties, this involved the strategic planning for the Mülheim Chemistry Campus and the organization of special events like the Ziegler Lecture, the Open House for the public, and the evaluation by our own international advisory board. Pleasant surprises during these 3 years included the designation of our institute as Historic Site of Chemistry by the German Chemical Society and the outstanding marks in the nationwide research rating in chemistry conducted by the German Science Council (Wissenschaftsrat); among the 77 participating university departments and research institutes, we were the only institute that was rated “excellent” in all five possible categories (research quality, research impact, research efficiency, training of young scientists, and transfer).

On the personal side, the family enjoyed life in Mülheim from the very beginning. We felt at home quickly and made new friends. Thomas and Sonja breezed through high school smoothly. Last year, Thomas completed his studies at the University of Bonn with a masters degree in History, Political Science, and Public Law, while Sonja started at the University of Münster studying German and Biology. Elisabeth recently abandoned her teaching activities so that we could now, in principle, spend more time together (provided that I find a cure against my own chronic lack of time).

Closing Remarks. Writing down these recollections has taken me on a 40 year journey through my scientific life. In hindsight, it is amazing to see how well the field of theoretical and computational chemistry has developed during this time, from modest and esoteric beginnings to its present status as an essential companion to experiment. In my own career, the growing role of theory in chemistry is reflected by the fact that I have always been appointed to positions that were either newly created (Wuppertal) or converted to theory (Zurich and Mülheim). Clearly, the progress in our field remains rapid and permeates all branches of chemistry. When participating in these developments over the years, I have always enjoyed the diversity of our field, ranging from pure theory and programming to applications covering the whole of chemistry—there is always something new around the corner.

It was a privilege to have excellent co-workers at all stages of my career. I mentioned many of them by name, but I could not include everybody in the text. A full list is given in this issue (see also the list of publications). Needless to say, I am most grateful to all my co-workers for their scientific contributions, but also for many pleasant memories from everyday life and from special social events in our group. In a similar vein, I would also like to thank all scientific collaborators and friends—I feel fortunate that there are so many.

Finally, science is not everything. On my real-life journey, from a small German village through many parts of the world, I could always count on my family and friends. It was sometimes not easy, but we always managed. So, thank you for being around—and let us keep going.

Walter Thiel

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