

Philip J. Stephens: A scientific memoir

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I was extraordinarily moved when my ex-graduate students Gerard Jensen and Karl Jalkanen informed me of their plan to organize a special issue of *Theoretical Chemistry Accounts* to celebrate my scientific career. I am deeply grateful to all of the contributors to this issue, and, most of all, to Gerard and Karl for their work on this project.

Gerard and Karl asked me to contribute a summary of my scientific career. To do this I have had to read all of my papers again! The Memoir which follows attempts to describe how my career evolved.

King Edward (VI)'s School, Birmingham

I entered King Edward's School, Birmingham, a "Direct Grant" high school for boys, in 1950. All of the teachers were Oxford and Cambridge graduates and the primary aim of the school was to send as many students as possible to these elite Universities. For the first 5 years, the curriculum was very broad; I took Chemistry, Physics, Biology, and Maths each year, as well as English, French, German, Latin, History, Geography, Music, and Art. During the last 3 years, the curriculum narrowed in order to prepare for A-level exams and University entrance exams. My father encouraged me to specialize in Chemistry, undoubtedly because he had worked for a chemical company manufacturing plastics in the 1920s, which

unfortunately went out of business during the Depression. As a result, my last 3 years I took only Chemistry, Physics, and Maths classes. After A-levels, I applied to Christ Church College (Ch. Ch.), Oxford, to study Chemistry. After the famously challenging entrance exams, I was lucky enough to be offered an open scholarship at Ch. Ch., beginning in Autumn 1958.

Christ Church (Ch. Ch.) College, Oxford University

The Ch. Ch. Chemistry tutors in 1958 were Dr. A. David Buckingham (ADB) and Dr. Paul W. Kent (PWK). ADB was responsible for teaching me physical and inorganic chemistry, and PWK for organic chemistry. Since ADB was a theoretical chemist, I learned a lot of theoretical chemistry under his guidance, and this led to my choosing him as my Part II Thesis supervisor. The Oxford Chemistry B.A. degree was unique (in England) in requiring a year of research, leading to a thesis, after 3 years of normal undergraduate studies.

For my Part II Thesis, I worked on two projects: (1) the theory of the Stark effect in the microwave spectra of molecules containing atoms with nuclear quadrupoles; (2) the theory of the NMR shielding constants of H atoms directly bonded to transition-metal atoms. The purpose of the first project was to assess the impact of nuclear quadrupole coupling on the electric dipole moment of a molecule determined via microwave spectroscopy. While working on this project, I read Townes and Schawlow's famous monograph *Microwave spectroscopy*, which greatly boosted my knowledge of the quantum mechanics of molecules. The second project originated in a lecture at Oxford by Joseph Chatt on the subject of his newly synthesized transition-metal

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hydride complexes. Very large high-field proton chemical shifts are exhibited by H atoms bonded to transition metals. The question was: what is the mechanism of this phenomenon? In order to address this question, I studied the theory of NMR spectroscopy, elegantly covered in the famous monograph of Pople, Bernstein and Schneider, *High-resolution nuclear magnetic resonance*, and applied the concept of the neighbour-anisotropy effect on proton chemical shifts to the known transition-metal hydride complexes. The anisotropy of the magnetic susceptibility of transition-metal ions could be predicted using ligand-field theory and enabled the variation of proton chemical shift with transition-metal, oxidation state, and coordination geometry to be understood. These two projects eventually led to my first four papers, published in 1964–1965 [1–4].

In 1962, after receiving my B.A. degree, I began work on my D.Phil. thesis, under the continuing supervision of ADB. My D.Phil. research focused on the development of the theory of the Faraday effect, the optical rotation (OR) induced by an external longitudinal magnetic field, and of the closely related phenomenon of magnetic circular dichroism (MCD). At this time, studies of the anomalous dispersion of the OR of chiral molecules and the closely related phenomenon, circular dichroism (CD) (also known as the Cotton effect), were increasing rapidly, due to advances in instrumentation, permitting OR and CD measurements across the visible and near-UV spectral regions, and the development of the Octant Rule, relating the Cotton effect of organic molecules containing carbonyl groups to the molecular Absolute Configuration (AC) and conformation, and similar sector rules for other electronic chromophores. Djerassi's famous monograph, *Optical rotatory dispersion: application to organic chemistry*, had just been published. Achiral molecules do not exhibit OR but, as Faraday showed in 1846, OR is induced when an external magnetic field is applied, parallel to the light beam. To explore the theory of magneto-optical rotatory dispersion (MORD) and of MCD and to assess the potential applications of these phenomena to the elucidation of the geometrical and electronic structures of molecules was an exciting project, which enormously broadened my knowledge of the literature pertaining to the theories and applications of magneto-optical phenomena, as well as OR and CD. By the time my D.Phil. Thesis was submitted in 1964, the theories of anomalous MORD and of MCD were established. The contributions of an electronic transition to the two phenomena comprised three contributions, which I labeled A, B, and C terms. A terms originate in the Zeeman splitting of the transition, which occurs when either the ground state or excited state is degenerate, or when both are.

C terms originate in the population differences between the Zeeman levels of the ground state, when it is degenerate. B terms are due to mixing of the ground and excited states with other electronic states, due to the magnetic field perturbation. A terms exhibit a different frequency dependence from B and C terms; A and B terms are temperature independent, while C terms are temperature dependent. Simply put, anomalous MORD and MCD permit the Zeeman splittings of electronic transitions to be measured, despite their much smaller magnitudes than transition bandwidths, and the Zeeman splittings of degenerate ground states to be measured, providing an alternative to the phenomena of magnetic susceptibility and EPR.

Following this theoretical analysis, it became clear to me that the most productive area of application of MORD and MCD would be transition-metal chemistry. As a result, I applied for a post-doctoral fellowship to work in the group of Professor Carl Ballhausen at the University of Copenhagen, Denmark.

The Ørsted Institute, University of Copenhagen, Denmark

My first task in Copenhagen was to publish my D.Phil. thesis work. After discussion with ADB, it was decided that I should write a review of the field of magnetic optical activity. Doing this further enlarged my familiarity with the field and the contributions of many famous physicists including Becquerel, Van Vleck, Bethe, Serber, and Kramers. Eventually, the review appeared in the 1966 edition of the Annual Reviews of Physical Chemistry [11].

At the same time, I was working through such famous monographs as Wigner's *Group theory*, Condon and Shortley's *The theory of atomic spectra*, Griffith's *The theory of transition metal ions*, and Ballhausen's *Introduction to ligand field theory*, and beginning to analyze the existing MORD and MCD data on transition-metal complexes. The most exciting application was to the $\text{Fe}(\text{CN})_6^{3-}$ ion, whose visible-near-UV spectrum is dominated by charge-transfer transitions. The MORD of $\text{Fe}(\text{CN})_6^{3-}$ had been reported by Bernard Briat at the ESPCI in Paris. It was simple to show that the signs of the dominant C terms of the allowed charge-transfer transitions depend on the symmetry of the excited state and that the MORD allowed the UV spectrum to be assigned [5]. The application of MCD to the assignment of the charge-transfer spectra of transition-metal complexes subsequently became one of its major applications.

The University of Chicago

After a year in Copenhagen, I moved in 1965 to the University of Chicago to work in the group of Professor Don McClure, another of the leading figures in transition-metal spectroscopy. An added benefit of this move was that I was then much closer to the University of Virginia, where Professor Paul Schatz was setting up MORD and MCD instrumentation. Paul had been on sabbatical in Oxford with ADB during the year before I graduated and we had many discussions of my research on the Faraday effect. As a result, and also because Oxford Instruments was just beginning to market superconducting magnets, Paul decided to jump into the MORD/MCD field. I was lucky enough to be in Charlottesville on the occasion when the MORD/MCD instrument (consisting of a JASCO ORD/CD instrument and an Oxford Instruments superconducting magnet) was first turned on and the MORD and MCD spectra of inorganic complexes such as MnO_4^- and $\text{Fe}(\text{CN})_6^{3-}$ first appeared on the chart recorder. Following this, I collaborated with Paul and his group (which included Tony McCaffery, who had been in Copenhagen at the same time as me) on many MORD/MCD projects [7, 9, 10, 12–16, 19, 26, 45].

The main focus of the McClure group at that time was the spectroscopy of transition-metal ions in crystalline solids. Two topics were particularly hot: (1) effects, such as magnon sidebands, arising from inter-ionic magnetic interactions in magnetic solids; and (2) the Ham effect, arising from Jahn–Teller effects. Ham had recently shown that the Jahn–Teller effect could reduce the magnitude of spin–orbit coupling and Zeeman splittings of degenerate electronic states. I thought that it would be interesting to explore the Ham effect by measuring the Zeeman effects of zero-phonon bands of transition-metal ions in crystals. McClure was very receptive to this idea and promptly acquired a superconducting magnet. Together with Marian Lowe–Pariseau, a post-doc in the McClure group (who had been a post-doc with ADB during my D.Phil. studies), I then measured the Zeeman effect of the $^3\text{T}_{2g}$ excited state of V^{3+} , doped in Al_2O_3 . The results provided spectacular evidence of the Ham effect [17, 20].

The University of Southern California, USC

During my second year in Chicago, I accepted an offer of an Assistant Professorship from the Chemistry Department at USC. I knew the Department Chair, Professor David Dows, because he had spent a sabbatical year with ADB in Oxford while I was a student, and he had also

hired another ADB student, James Bridge, as a post-doc. I moved to Los Angeles in Fall 1967. My goal was to further develop the field of MCD spectroscopy. Initially, I focused on the application of moment analysis to the theory of MCD, a methodology well known in solid-state NMR spectroscopy, and recently applied to MCD by Slichter and coworkers [18, 23, 26, 29, 37, 46]. At the same time, of course, proposals for external funding had to be written and submitted. Fortunately, by September 1968 I had received an Alfred P. Sloan Fellowship and an NIH grant, and had been able to hire my first post-doc, Dr. George Osborne from Perth, Australia. George began the construction of an MCD instrument, designed to include the near-IR spectral region. Up till then, all CD instrumentation was based on KDP electro-optic phase modulators (Pockels cells), but they are not usable in the IR. Very fortunately, the photo-elastic modulator (PEM) had recently been invented, and commercialized by Jim Kemp and Morvue Instruments. By using a near-IR transmitting quartz PEM, we were able to extend the spectral range of CD/MCD instrumentation into the near-IR [32]. At the same time, I began to interact with Cary Instruments, who at that time were located in Monrovia, a suburb of LA, and were manufacturing visible-UV CD spectrometers. I was able to interest Jim Duffield and Ahmed Abu-Shumays at Cary in MCD and they acquired a superconducting magnet, interfaced it with their CD instrument and began measuring MCD spectra. This led to a paper on the MCD of the LiF F center [24] and an increase in sales of Cary 61 CD instruments. Another fortunate consequence of moving to USC was that Professor Otto Schnepf (who had obtained his Ph.D. with Don McClure at Berkeley) was simultaneously building a vacuum-UV CD spectrometer, to extend the application of CD spectroscopy to higher energies than previously possible. Being close to another group working on CD was an enormous benefit, and eventually led to collaborative vacuum-UV MCD measurements on a number of gases, the first MCD measurements in this spectral region [38–40].

After 3 years at USC, George Osborne moved on. Very fortunately, I was able to hire Dr. Jack Cheng, a graduate of the Jim Kemp group at the University of Oregon, one of the birthplaces of the PEM. One of Jack's Ph.D. projects had been the measurement of MCD–EPR double resonance, an exciting new development for the MCD field. Over the next 3 years, Jack vastly improved and extended our near-IR MCD spectrometer [32], especially by improving the electronics and by building new PEMs to extend the spectral range further into the IR.

Together with a newly acquired Cary CD spectrometer, our near-IR instrument allowed us to make MCD

measurements over a very wide spectral range. Much of this work involved transition-metal ions in crystalline solids and was carried out by graduate students Allen Mann and Joe LoMenzo and post-doc Dr. Barry Bird from Peter Day's group at Oxford [25,30,31,35,36].

In 1972, in collaboration with Bill Eaton at NIH, we carried out our first MCD experiments on metalloproteins, specifically met-hemoglobin and met-myoglobin, and their cyano-complexes. Ferric heme proteins exhibit near-IR electronic transitions. Their MCD is sensitive to the heme ligation and the ground state spin. The near-IR MCD of HbCN and MbCN confirmed the assignment of the near-IR transitions as ligand-to-metal charge-transfer transitions. The potential value of MCD in characterizing the ligation and spin states of heme proteins, demonstrated by this work, led us to publish it in *Nature* [33]. Further studies of heme proteins were carried out by post-doc Dr. John Sutherland [47,57]. This was the beginning of more than 20 years of work on the MCD of metalloproteins.

In 1973, I launched an exciting new project: the measurement of vibrational CD (VCD). While there had been speculation regarding the measurability of VCD, no measurements had been reported. Having a near-IR CD instrument, already capable of measurements down to $\sim 3,000$ nm, the limit of the InAs detector, extension of the spectral range to cover more of the fundamental IR seemed practical. To accomplish this, I hired two new post-docs to work with Jack Cheng, Dr. Larry Nafie (from U. Oregon) and Dr. Tim Keiderling (from Princeton). It was at this time, and for this reason, that Jack explored a range of new optical elements for the PEM having superior IR transmission to that of quartz. Many of the standard IR window materials turned out to be too fragile mechanically to permit sufficient phase modulation. However, serendipitously, an ex-student of Otto Schnepp's, Susan Allen, now working at the Hughes Research Labs in Malibu, asked me if Jack could build a PEM using ZnSe, to make possible infrared laser ellipsometry experiments. We immediately realized that ZnSe could be the solution to the VCD problem, since it is mechanically strong and transmits down to ~ 650 cm^{-1} . With ZnSe provided by Hughes, Jack built PEMs, and our first successful VCD measurements, published in 1975, followed soon thereafter [44]. Also critical to the measurement of VCD was a method which Jack invented to reduce the magnitude of pseudo-CD signals (termed artifacts) which originate in optical phenomena unrelated to the sample CD. The method involved placing a second PEM, with a different frequency than the first PEM, after the sample. We called this "Polarization Scrambling" [43]. Unfortunately, our VCD measurements were not the very first: George Holzwarth at the

University of Chicago had just published his first measurements, also made with a PEM-based IR CD instrument. However, our instrument had significantly higher sensitivity, and we were able in the next year to measure the VCD of a wide-range of chiral organic molecules [48,49,54,60]. [For a detailed account of the early VCD measurements by the Holzwarth group and at USC, see Publication 59.]

By 1976, Jack had moved on to the Lawrence Livermore Laboratory, and Larry and Tim had become Assistant Professors at Syracuse University and the University of Illinois at Chicago, respectively. Both Larry and Tim continued working on VCD, initially building dispersive instruments and subsequently extending the PEM-based modulation methodology to Fourier-transform IR spectrometers. Over the next 30 years, both have continued to develop the VCD field. I am extremely proud of their brilliant contributions.

In 1975, we began a collaboration with Harry Gray's group at Caltech, focusing on determining the structures of copper proteins. Ed Solomon, who had been a graduate student of Don McClure's at Princeton and a post-doc with Carl Ballhausen in Copenhagen, had recently come to Caltech and was working with Harry on blue copper proteins, such as stellacyanin, plastocyanin and azurin. In order to characterize the ligation of the Cu(II) in these proteins, Ed came over to USC and measured their CD and MCD. The near-IR $d \rightarrow d$ transitions of Cu(II) were particularly informative [50,53,64]. Subsequently, we studied laccase, ceruloplasmin and ascorbate oxidase copper proteins [62,63,65].

Another important bioinorganic collaboration began in 1976 when Andrew Thomson of the University of East Anglia in England brought a huge number of iron-sulfur proteins to USC in order to study their near-IR CD and MCD. I had known Andrew since my time in Oxford; he also did his D.Phil. research in the ICL, with R. J. P. Williams. Our experiments demonstrated that the MCD of Fe-S clusters is a sensitive function of their structure and oxidation state and, hence, that MCD is a useful technique for characterizing Fe-S proteins [56,58]. This work led to a later visit by Barry Smith of the Nitrogen Fixation Institute at the University of Sussex in England and a collaboration with Professor Charles McKenna at USC in which CD and MCD were used to study the iron-molybdenum and iron proteins of the nitrogenase enzyme [61,66–68,70,74,81].

In 1977, I hired a new post-doc, Dr. Frank Devlin, who had obtained his Ph.D. from University College, Dublin in Ireland. This was one of the smartest things I ever did. Frank is a brilliant instrumentalist and he has been responsible for all of the instrumental developments in my laboratories from his arrival to the present

time. I am deeply grateful to him for his work over the past three decades. Initially, Frank worked on enhancing our MCD instrumentation, so as to permit temperature-dependent measurements on metalloproteins down to pumped-liquid-helium temperatures (<4 K). Not only does decreasing the temperature increase the MCD magnitude when C terms are present, but it also permits the saturation behavior of the MCD as the magnetic field is increased to be measured, leading to electronic ground state parameters such as g values and zero-field splittings [71]. Critical to this development was the acquisition of an Oxford Instruments superconducting magnet with a split coil surrounding an optical cavity, permitting the protein sample to be inserted into the center of the magnetic field and cooled to liquid helium temperatures. This magnet was interfaced with a JASCO CD instrument, permitting liquid-helium temperature MCD measurements over the near IR–visible–near UV spectral range.

Inter alia, this new instrumentation made possible exciting studies of Ferredoxin I (FdI) of *Azotobacter vinelandii*, which were carried out by Dr. Vance Morgan, who had obtained his Ph.D. in Biochemistry at the University of Georgia and arrived to post-doc in 1980, in collaboration with Dave Stout at U. Pittsburgh and Barbara Burgess at Kettering Research Institute. FdI contains both 3Fe and 4Fe Fe–S clusters. We explored their chemistry, using CD, MCD and EPR spectroscopies to characterize cluster structures and oxidation states. A particularly interesting reaction of FdI was its oxidation by $\text{Fe}(\text{CN})_6^{3-}$, which leads to destruction of the 4Fe cluster. This permitted an EXAFS study on the 3Fe cluster of FdI in the absence of the 4Fe cluster, which conclusively demonstrated that the structure of this cluster determined by X-ray crystallography of native FdI was incorrect [72, 73, 76–78, 83].

Simultaneously with these bioinorganic studies, we continued to work on VCD. After we had successfully measured VCD spectra, it was clear that the productive utilization of VCD data required a theory permitting reliable calculations of VCD. In 1975, I was invited by Jim Ferguson to be a Visiting Professor at the Australian National University in Canberra, Australia. While in Canberra in Fall 1975, I worked on the theory of VCD. VCD intensities are determined by vibrational rotational strengths, which, in turn, depend on vibrational electric dipole and magnetic dipole transition moments. While the theory of vibrational electric dipole transition moments was well established, this was not the case for the magnetic dipole transition moments. In addition, it turns out that within the Born–Oppenheimer (BO) approximation, which is the basis for the standard theory of electric dipole transition moments, the

electronic contribution to magnetic dipole transition moments vanishes. Consequently, to correctly predict vibrational magnetic dipole transition moments, the vibronic wavefunctions must be more accurate than BO wavefunctions. Since the Jahn–Teller (JT) effect originates in the breakdown of the BO approximation, and I had become very familiar with the JT effect literature while in Chicago, it was easy for me to derive an equation for vibrational magnetic dipole transition moments, incorporating corrections to the BO wavefunctions. Simply put, the nuclear kinetic energy operator, which is not fully diagonalized in the BO approximation, mixes the vibrational levels of the electronic ground state with those of excited states and as a result ground state vibrational transitions are mixed with electronic transitions. Since electronic transitions can have non-zero magnetic dipole transition moments, non-zero vibrational magnetic dipole transition moments result. The equation I derived was formally correct, but involved both the ground and all excited electronic state wavefunctions, making it difficult to implement. Over the next few years, I frequently revisited my theory of vibrational magnetic dipole transition moments in the hopes of finding a way to simplify the equation, and make its implementation practical. Fortunately, lightning struck in 1980. After revisiting the theories of other magnetic phenomena, including paramagnetic susceptibilities and paramagnetic NMR shielding constants, I found that the “sum-over-states” equations for these properties had been contracted into equations involving only ground electronic state wavefunctions, and immediately understood how to contract my “sum-over-states” equation for vibrational magnetic dipole transition moments. The result for the magnetic dipole transition moment of a fundamental $\nu = 0 \rightarrow \nu = 1$ transition involving the i th normal mode was

$$\langle 0 | (\mu_{\text{mag}})_{\beta} | 1 \rangle_i = \left[4\pi \hbar^3 \nu_i \right]^{1/2} \sum_{\lambda, \alpha} S_{\lambda\alpha, i} M_{\alpha\beta}^{\lambda} \quad (1)$$

where ν_i is the frequency of the i th normal mode; $S_{\lambda\alpha, i}$ defines the i th normal coordinate, Q_i , via

$$X_{\lambda\alpha} = \sum_i S_{\lambda\alpha, i} Q_i \quad (2)$$

where $X_{\lambda\alpha}$ are the Cartesian nuclear displacement coordinates from the equilibrium geometry ($\lambda = \text{nucleus}$, $\alpha = x, y, z$); and the tensor $M_{\alpha\beta}^{\lambda}$ is the sum of electronic and nuclear contributions, $I_{\alpha\beta}^{\lambda}$ and $J_{\alpha\beta}^{\lambda}$, given by

$$I_{\alpha\beta}^{\lambda} = \langle (\partial \psi_G / \partial X_{\lambda\alpha})_0 | (\partial \psi_G / \partial H_{\beta})_0 \rangle \quad (3)$$

$$J_{\alpha\beta}^{\lambda} = \frac{i}{4\hbar c} \sum_{\gamma} (Z_{\lambda} e) R_{\lambda\gamma}^0 \varepsilon_{\alpha\beta\gamma} \quad (4)$$

$(\partial\psi_G/\partial X_{\lambda\alpha})_0$ are the derivatives of the ground electronic state wavefunction, ψ_G with respect to the Cartesian nuclear displacement coordinates, $X_{\lambda\alpha}$. $(\partial\psi_G/\partial H_\beta)_0$ is the derivative of the ground electronic state wavefunction of the molecule, to which the external magnetic field perturbation $-(\mu_{\text{mag}}^e)_\beta H_\beta$ ($\beta = x, y, z$) is applied, with respect to H_β . The corresponding electric dipole transition moment is given by

$$\langle 0 | (\mu_{\text{el}})_\beta | 1 \rangle_i = \left[\frac{\hbar}{4\pi v_i} \right]^{1/2} \sum_{\lambda,\alpha} S_{\lambda\alpha,i} P_{\alpha\beta}^\lambda \quad (5)$$

where the tensor $P_{\alpha\beta}^\lambda$ is the sum of electronic and nuclear contributions, $E_{\alpha\beta}^\lambda$ and $N_{\alpha\beta}^\lambda$, given by

$$E_{\alpha\beta}^\lambda = 2 \left\langle (\partial\psi_G/\partial X_{\lambda\alpha})_0 \left| (\mu_{\text{el}}^e)_\beta \right| \psi_G^0 \right\rangle \quad (6)$$

$$N_{\alpha\beta}^\lambda = (Z_\lambda e) \delta_{\alpha\beta} \quad (7)$$

The tensors $P_{\alpha\beta}^\lambda$ are termed the atomic polar tensors (APT). Since the magnetic dipole moment is an axial vector, in contrast to the electric dipole moment which is a polar vector, I named the tensors $M_{\alpha\beta}^\lambda$ atomic axial tensors (AATs). From Eqs. 3 and 6, it is clear that the electronic AATs, $I_{\alpha\beta}^\lambda$, involve the same derivatives $(\partial\psi_G/\partial X_{\lambda\alpha})_0$ as the electronic APTs, $E_{\alpha\beta}^\lambda$, but, in addition, involve the derivatives $(\partial\psi_G/\partial H_\beta)_0$. So the extra challenge in calculating vibrational magnetic dipole transition moments as well as electric dipole transition moments is to calculate $(\partial\psi_G/\partial H_\beta)_0$. Importantly, it turns out that these derivatives are also present in the contracted equations for paramagnetic susceptibilities and paramagnetic NMR shielding tensors, so they were not unheard of by quantum chemists. This fact led me to discuss the practicality of calculating the $(\partial\psi_G/\partial H_\beta)_0$ derivatives with Professor Gerry Segal at USC. Gerry was a quantum chemist, who had obtained his Ph.D. with John Pople at Carnegie–Mellon, and was well versed in ab initio methods. We arrived at the conclusion that the most practical option was to calculate $(\partial\psi_G/\partial H_\beta)_0$ at the ab initio Hartree–Fock (HF) level using the finite-difference method for calculating derivatives.

Incredibly, after this decision was made, I received a phone call from Professor Marian Lowe, my Chicago collaborator, now at Boston University, who was looking for a project on which to base an application to the new NSF Visiting Professorships for Women in Science and Engineering program. Marian was an expert in vibrational spectroscopy, having obtained her Ph.D. with John Overend at the University of Minnesota. After discussing my new theory of VCD and the planned ab initio calculations, we decided to put together a proposal to NSF. This was submitted in August 1982 and led to Marian's

arrival at USC in 1983. With Gerry Segal's assistance, the calculation of electronic AATs was implemented within the GAUSSIAN 80 program, and calculations of the VCD spectra of trans-1,2-dideuterio-cyclopropane, trans-1,2-dideuterio-cyclobutane and propylene oxide carried out. For the latter two molecules, experimental VCD spectra were already available and our calculations could be compared with experiment. The comparison was quite encouraging. My theory of VCD and our ab initio calculations were reported to the VCD community at a Symposium on VCD at the November 1983 APS meeting in San Francisco and at the Ohio State University Symposium on Molecular Spectroscopy in June 1984, and published in 1985–1986 [79, 80, 82, 84].

I spent the 1984–1985 academic year at the Nitrogen Fixation Institute at the University of Sussex in England, thanks to a Guggenheim Fellowship, working with Barry Smith on *Klebsiella pneumoniae* proteins, including nitrogenase and nif J. In May 1985, I went up to Cambridge, where ADB now occupied the Chair of Theoretical Chemistry, to give a seminar on VCD. After my talk, Nick Handy pointed out that the calculation of $(\partial\psi_G/\partial H_\beta)_0$ derivatives was carried out in his program CADPAC, using analytical derivative techniques based on the Coupled Hartree–Fock (HF) methodology, a much more efficient approach than our finite-difference technique. As a result, we agreed to incorporate the calculation of AATs, and thence vibrational rotational strengths, in the CADPAC program. This project was funded by a NATO UK–US collaborative research grant, which enabled Roger Amos to carry out the necessary code development and to bring the CADPAC program to USC, install it on the IBM computer at USC and the CRAY supercomputer at the San Diego Supercomputer Center, and teach my students how to use it. This was accomplished in 1986 [88]. At that time, Karl Jalkanen and Ron Kawiecki were Ph.D. students in my group, working on VCD. Karl had participated in the VCD experiments on matrix-isolated molecules carried out in 1981 by my post-doc Don Schlosser [69]. Subsequently, he moved to the Math Department to obtain an MS in Applied Mathematics. After that, he returned to my group to work on VCD theory. Initially, he continued finite-difference calculations using GAUSSIAN, but when CADPAC arrived he was able to carry out calculations more rapidly and accurately. Karl was amazingly hard working and very productive [88, 90, 91, 94, 95, 97–99, 106, 108–110, 112, 113, 117, 127, 131].

Several other important developments occurred during this period. On the experimental side, during my absence in 1984–1985 Frank Devlin carried out major improvements to our IR CD spectrometer. Most importantly, a closed-cycle refrigerator was installed, permit-

ting IR detectors to be cooled below liquid nitrogen temperatures, both increasing their sensitivities and enabling the low frequency limit to be extended. With a new As-doped Si detector operating at ~ 10 K, VCD measurement down to the ZnSe transmission limit of $\sim 650\text{ cm}^{-1}$ became possible for the first time [92]. On the theoretical side, the first advance was the introduction and implementation of the distributed origin gauge equation for AATs, which led for the first time to vibrational rotational strengths which were origin independent [89]. The second was the application of the RPA methodology to the calculation of electronic AATs, using the “sum-over-states” formalism. This was made possible by Professor Paolo Lazzeretti of the Università di Modena in Italy, who pointed out the formal connection between electronic AATs and the nuclear shielding tensors, $\xi_{\alpha\beta}^{\lambda}$, which determine the electric field at a nucleus when the molecule is subjected to an external magnetic field. Paolo, together with Riccardo Zanasi, had incorporated the calculation of these (and other) nuclear shielding tensors in their RPA program, SYSMO. I arranged for Paolo to bring the SYSMO program to USC, to permit us to use it in calculating VCD spectra. This led to a detailed comparison of APTs and AATs calculated using analytical derivative methods and the RPA method [86, 98, 99, 108, 110]. The collaboration with Paolo also led to Roberta Bursi’s arrival in 1987 to obtain her Ph.D. at USC, working on VCD [114, 118].

Around 1990, two important advances in the *ab initio* calculation of vibrational force fields occurred: the implementation of analytical derivative methods for calculating MP2 and density functional theory (DFT) Hessians. MP2 Hessians were incorporated in Gaussian 92 and DFT Hessians in Gaussian 92-DFT. Before these correlated methods were available our VCD calculations were based on Pulay-scaled-HF force fields [85, 96, 117, 119], which added considerable labor to the calculations. We therefore enthusiastically switched to using the more accurate force fields (without scaling) when they became available. Calculations using MP2 force fields gave significantly improved predictions, but were restricted to relatively small molecules [127, 130]. The most important development turned out to be the use of DFT force fields. Our initial calculations using DFT force fields were carried out in collaboration with Mike Frisch at Gaussian Inc., who was responsible for the DFT Hessian code in GAUSSIAN. We first compared the three classes of density functionals, local, gradient-corrected, and hybrid, the latter having very recently been introduced by Becke. Our results for a variety of molecules unambiguously demonstrated the inadequacy of local functionals and the superiority of hybrid functionals such as Becke’s B3PW91 functional and the

related functional B3LYP formulated by Mike Frisch [132, 136, 138, 139, 142, 144]. The hybrid force fields were shown to be at least as accurate as MP2 force fields. Given the much smaller computational labor involved in DFT calculations, DFT became the method of choice for calculating force fields. This has continued to be the case up to the present.

At that time, DFT force fields were coupled with DFT APTs and distributed origin gauge AATs combining DFT APTs and HF AATs. It was immediately clear that the next important advance in calculating VCD spectra would be to calculate AATs using DFT. As had been shown by Keld Bak and Poul Jørgensen in Denmark, the calculation of AATs is significantly enhanced by the use of the magnetic-field-dependent basis functions known as gauge-invariant atomic orbitals (GIAOs). The ideal DFT calculation of AATs would then incorporate GIAOs. Mike Frisch assigned the task of implementing the DFT/GIAO calculation of AATs to Jim Cheeseman at Gaussian Inc. One of the most exciting days in my life was the day Jim informed me that he had succeeded in doing this, and that we could now do VCD calculations simultaneously using DFT Hessians, APTs, and GIAO-based AATs. We immediately switched to this methodology [143, 145], which was eventually distributed in GAUSSIAN 98. Thorough studies of the two monoterpenes camphor and α -pinene fully documented the reliability of the new DFT methodology [146, 149, 150, 158].

The DFT implementation of my equation for vibrational rotational strengths revolutionized VCD spectroscopy, by making it possible to reliably predict VCD spectra and, as a result, to carry out the Configurational and Conformational Analysis of chiral molecules using their experimental VCD spectra. This development stimulated the commercialization of FT VCD instrumentation by several instrument companies, including Bomem, Bruker, Bio-Rad, and Jasco, making VCD spectroscopy much more accessible to Organic Chemists. The well-known advantages of FTIR instruments over dispersive IR spectrometers in turn led in 1997 to the installation of a FT VCD instrument in our laboratories and the closing down of our dispersive spectrometer. Since then, we have worked hard to expand the applications of VCD to the determination of the stereochemistries of chiral organic molecules. By far the most important application is to the determination of Absolute Configurations and this has been our primary focus [151, 152, 155, 159, 160, 163–165, 167, 169, 171, 174, 176, 180, 183, 184, 186, 187, 189–192]. As a result of our work, interest in the use of VCD by organic chemists has grown considerably, especially in the Pharmaceutical industry, where chiral drugs are increasingly important. For example, in 1999, the French pharmaceutical

company Sanofi sent Dr. Ahmed Aamouche to my lab to explore the potential of VCD spectroscopy.

Despite the boom in VCD originating in my development of the equation for vibrational rotational strengths, our work in the bioinorganic field continued, with emphasis on Fe–S proteins. After Barbara Burgess and Dave Stout moved to Southern California (U.C. Irvine and Scripps, La Jolla, respectively) we continued work on FdI of *Azotobacter vinelandii*, using site-directed mutagenesis to investigate the relationship of the structures and properties of its Fe–S clusters to the amino-acid sequence. Among the cluster properties of interest were their redox potentials, which brought the electrochemist Professor Fraser Armstrong, also at U.C. Irvine, into the collaboration. This project led Gerard Jensen, who transferred from UCLA to USC in 1986 after obtaining his BS in Biochemistry, to join my group. Gerard was responsible for the spectroscopic studies of FdI and its mutants, including liquid-helium temperature MCD and EPR studies [111, 115, 122, 128]. In addition, in collaboration with Professor Arieh Warshel at USC he initiated calculations of the redox potentials of Fe–S clusters, using Warshel's POLARIS program, which treated solvent effects using a Langevin dipoles methodology. The calculations led to a much more detailed understanding of Fe–S cluster redox potentials than had previously been possible [125, 133]. After Gerard's graduation, this work was continued by Dr. David Jollie [129, 147], who also continued studies of FdI mutants [134, 140, 148].

Our efforts in bioinorganic chemistry have diminished since Barbara Burgess' untimely death in 2001. At the same time, our work on the optical activity of chiral molecules has broadened in scope. The revolution in VCD spectroscopy due to the implementation of DFT calculations of VCD spectra led us to consider the application of DFT to the calculation of both electronic CD (ECD) spectra and OR. Discussions with Jim Cheeseman and Mike Frisch at Gaussian Inc. in August 1988 made it clear that the application of time-dependent density functional theory (TDDFT), recently implemented in GAUSSIAN, to the calculation of ECD and OR was feasible. By 1999, the code was in place in GAUSSIAN and calculations underway. The earliest results, reported at the 7th International CD Conference in Poland in August 1999 and the Chirality Symposium at the San Francisco ACS meeting in March 2000, demonstrated that the TDDFT methodology gives much more accurate results than the HF theory [157, 162, 166, 168]. Since then, TDDFT calculations of optical rotations and ECD spectra have expanded enormously, both at USC [173, 177–179, 181, 188] and, after the release of GAUSSIAN 03, elsewhere, driven by their application to deter-

mining Absolute Configurations (ACs). As of now, we are able, when determining the Absolute Configuration of a molecule, to utilize DFT calculations of its VCD, ECD, and OR simultaneously, considerably enhancing the certainty of the resulting AC. Very recent applications to the cytotoxic sesquiterpene natural product quadrone, to alkaloid and iridoid natural products, and to a novel calcium channel blocking molecule illustrate the power of this approach [187, 190–192].

Acknowledgments I am enormously fortunate to have had the opportunity to pursue a research career in Chemistry and to contribute to the development of the fields of quantum chemistry, molecular spectroscopy, optical activity and magneto-optical activity. I am profoundly grateful to all the graduate students, post-doctoral research associates, and collaborators who have been involved in our research projects, and without whom little would have been accomplished. Thank you again!

Appendix

Post-doctoral research associates

George Osborne	1968–1971
Barry Bird	1969–1971
Jack Cheng	1971–1974
John Sutherland	1972–1973
Larry Nafie	1973–1975
Tim Keiderling	1973–1976
Jill Rawlings	1974–1975
Roy Clark	1976–1979
John Dunn	1976–1978
Charles Connell	1976–1978
Frank Devlin	1977–Present
Don Schlosser	1978–1982
Richard Bowman	1978–1979
Vance Morgan	1980–1984
William Browett	1981–1982
Marie-Claire McKenna	1979–1989
David Jollie	1992–1996
Ahmed Aamouche	1999–2001

Graduate students

Allen Mann	1966–1973
Joseph LoMenzo	1968–1975
Karl Jalkanen	1980–1989
Ron Kawiecki	1981–1988
Gerard Jensen	1986–1993
Roberta Bursi	1987–1991

Bruno Reyntjens 1990–1996
 Claudine Ashvar 1992–1998
 J. J. Pan 2000–2007

Philip J. Stephens Publications: 1964–2006

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