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Schellman J A. Symmetry rules for optical rotation.
Account. Chem. Res. 1:144-51, 1968.

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This paper discusses the physical interactions of groups in molecules that lead to optical activity. Three types of interactions, electric dipole-electric dipole coupling, electric dipole-magnetic dipole coupling, and static perturbations, lead to three mechanisms for producing optical activity in an electron absorption band. [The *SCI*® indicates that this paper has been cited in over 350 publications.]

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In 1968 the primary activity of my laboratory was correlating measurements of optical rotatory dispersion (ORD) with theory. At that time, there was an almost total division between theoreticians and experimentalists, and it seemed likely that bridging that gap would take us into new areas of progress. Our main interest was in conformational problems in peptides and proteins and the use of spectroscopic methods to solve them. This was the dominant theme of our research from about 1964 to 1970 and recalls my associates, Patrick Oriel, Burt Litman, Steve Zimmerman, Eigil Nielsen, Peter Bayley, Dick Stigter, Vincent Madison, and Tom Hooker. The work started modestly with Litman and Zimmerman looking at simple models containing one peptide bond and progressed to a full discussion of proteins in Madison's thesis.

The theoretical method we developed for interpretation is called the matrix method, not, as most people suppose, because it uses matrices, which it does, but because the spirit of the calculation is that of the matrix representation of quantum mechanics. The Hamiltonian matrix for an oligomer or polymer is set

up in the monomer basis, mostly using experimentally determined quantities. At this point, it contains numerous off-diagonal elements because of the interactions of the monomeric units. When it is transformed to a diagonal basis, one has the correct polymer basis and can calculate such quantities as circular dichroism, band splitting, linear dichroism, hypochromicity, etc. A principal advantage of the procedure is that it is indifferent to whether bands are degenerate or not. This is important in polymers where degeneracy always arises and especially important with polypeptides and nucleic acids where there are overlapping bands.

As mentioned earlier, one of our purposes was to unite experiment with theory and we wrote two papers with experimentalists in mind.^{1,2} Instead of treating the equally easy general polymer case, we discussed dimers, where an excess of indices and summations could be avoided. Though the matrix method itself has been successful and is used in many laboratories besides our own, there is no sign that it was read by experimentalists with any enthusiasm. By contrast, the lectures and seminars I gave at that time emphasizing only the physical basis of the interactions seemed to appeal to experimental audiences.

At the time, I was on the editorial board of *Accounts of Chemical Research*. In its first year, this journal was distributed to all members of the American Chemical Society free of charge and had a circulation in excess of 100,000. Like all good journals to be, it had made a solid beginning and then ran into that dangerous period where the initial momentum has been used up but there has not been time for a backlog of submissions to accumulate. Unlike other starting journals, *Accounts* was in the limelight. I received a call from Joe Burnett, who is still chief editor of the journal: "We need a manuscript within a month; can you supply one?" I responded with a written version of my lectures on the physical basis of optical activity. The article has served me well. Because of it, I have found new collaborators and friends in the fields of inorganic and organic chemistry.

1. Schellman J & Nielsen B. Optical rotation and conformation studies on diamide models. (Ramachandran G N, ed.) *The conformation of biopolymers*. New York: Academic Press, 1967. p. 109-22.
2. Bayley P M, Nielsen E B & Schellman J A. The rotatory properties of molecules containing two peptide groups: theory. *J. Phys. Chem.* 73:228-43, 1969. (Cited 120 times.)