

1 Morse's Contributions to Atomic, Molecular, and Solid-State Physics

Philip Morse has made so many contributions to so many fields — mathematical physics, acoustics, operations research, computer technology, science administration, to name a few — that one may lose sight of the fundamental nature of his work in the field of the quantum theory of matter. In this note I should like to call attention to some of his papers, and to the main ideas which have underlain his work.

First of course was his collaboration on the Condon and Morse text on Quantum Mechanics, one of the very first texts in English on the subject and written in 1929 when he was still a very young man at Princeton. This established him at once as an authority in this new field, and his first applications were to the theory of diatomic molecules. His joint paper with Stueckelberg, in 1929, was one of the first successful attempts to apply Schrödinger's equation to the discussion of the electronic motion of the hydrogen molecular ion H_2^+ , which has proved to be the problem more than any other that has pointed the way to an understanding of the nature of electronic energy levels of diatomic molecules. This was carried out in the spirit of the Born-Oppenheimer approximation, which divides the discussion of a molecular problem into two parts, one the study of the electronic motion and the resulting energy levels as functions of the internuclear separation, the other the motion of the nuclei under the influence of the resulting potential.

The second paper in the series on diatomic molecules, by Morse alone, and also in 1929, dealt with the other half of the problem, the vibrational levels. It was in this paper that the famous Morse curve was introduced,

a simple analytic approximation to the energy of a diatomic molecule as function of internuclear distance, which allowed an exact analytic solution of the vibrational problem. The importance that this paper has had in the development of molecular theory can hardly be overestimated. Morse in this pioneering paper not only carried through the whole mathematical discussion of the problem but he correlated the experimental data then available, and gave the constants describing the potential curves for the molecular states of diatomic molecules for which numerical values existed.

This book, and two fundamental papers, in 1929 would have been enough to satisfy most new Ph.D.'s for several years, but with Morse it was different. He spent a summer working with Davisson at the Bell Telephone Laboratories and became interested in the theory of low-energy electron diffraction by crystals. He realized that neither the tight-binding nor the almost free-electron approximation for electrons in crystals was satisfactory and in 1930 he wrote a paper on the quantum mechanics of electrons in crystals, which formed one of the first proper treatments of the motion of electrons in a periodic potential. He analyzed the potential into a three-dimensional Fourier series, as Bethe had done shortly before, but went much farther than Bethe in analyzing the problem mathematically, showing its relation to Hill's equation, and working out in detail the soluble problem of the three-dimensional sinusoidal potential, which results in Mathieu's equation. This formed one of the very early contributions to the study of energy bands in crystals.

Next he went to Germany to work with Sommerfeld, who suggested that he work on the theory of the Ramsauer effect, the experimental phenomenon which had been discovered some years before, according to which the collision cross section of some atoms, such as the rare gases, for electrons, became very small for very slow electrons. Morse, and Allis, who was also working with Sommerfeld, realized the relation of this problem to the diffraction of light by spherical objects, which had been treated by Mie and Debye. They formulated the problem by wave mechanics, much along the lines that had been used shortly before by Faxen and Holtmark, but realized that to treat the problem realistically, they would have to approximate the self-consistent potential fairly accurately and carry out the problem by detailed analytic study of the actual cases. In their joint paper in the *Zeitschrift für Physik* in 1931, and in Morse's later review article in 1932, the whole theory of scattering of electrons by atoms is treated in a realistic manner, adapted to slow electrons rather than using the Born approximation which is only

suitable for fast electrons. This work forms a real landmark in scattering theory.

Here within a four-year period were papers on diatomic molecules, on the motion of electrons in crystals, and on the scattering of electrons by atoms, all of fundamental importance, and at the same time all showing some of the characteristics which have been striking in all of Morse's work. In all of them, he showed his mastery of mathematical methods — Laguerre functions, Hill's equation, Mathieu functions, and so on. But at the same time he showed his desire to carry out his calculations on the actual case of physical importance, getting physically applicable results, rather than to leave results in a vague state of mathematical generalities.

These same characteristics were shown in some of Morse's next pieces of work, on atomic wave functions. In collaboration with Vinti in 1933, he explored analytic approximations to atomic wave functions, and in the work with Young and Haurwitz in 1935, the authors set up an analytic approximation to atomic wave functions that had been shown to be useful and proceeded to determine the parameters in these wave functions by variational methods. so as to lead to numerically accurate and practically usable functions. This same type of work was carried further in Morse's work with Yilmaz, after the war in 1956. These calculations were the precursors of the more recent and more accurate analytical wave functions that have been worked out since 1956 by Roothaan, Clementi, and others. This work of Morse and Yilmaz, as well as the more recent work, was made possible by the use of the digital computer, and of course it was partly Morse's interest in computers that led him to continue with this atomic problem.

The last paper that I shall comment on was also written in 1956, dealing with waves in a lattice of spherical scatterers. This very interesting piece of work touched on many of Morse's areas of concern. It deals directly with the motion of electrons in crystals, and in particular with the approximation in which the potential is assumed to be spherically symmetrical in spheres representing the various atoms and constant between the spheres. The present author had proposed one method of solving this problem in 1937, a method which we now know as the augmented plane wave method. Other methods of handling the problem had been suggested in 1947 by Korringa and in 1954 by Kohn and Rostoker. Morse's work, however, was largely independent of this other work, and in fact he became aware of it only after he had arrived himself at a good many of the results of his 1956 paper.

He realized that one could build up the wave function of a scattered

electron in such a potential as a superposition of scattering problems such as he and Allis had treated in 1931 and 1932. He realized also that the problem was mathematically equivalent to one which he was meeting in acoustics, the scattering of sound waves by a collection of regularly spaced spherical scatterers. All of these facts, plus his thorough knowledge of Green's functions, and his recollection of his 1930 work on the quantum mechanics of electrons in crystals, combined to suggest the method which he did not actually publish until 1956, but which he had been turning over in his mind for a considerable period before. This paper has now taken its place as one of the important pieces of work which has led to our present understanding of methods of finding energy bands in crystals.

Here, then, we see contributions which Morse has made over a period of nearly 30 years to many different aspects of the theory of atoms, molecules, and solids, contributions which would have given him a secure place in the history of mathematical physics even if it had not been for his many other contributions in different, though related, fields.

General References

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