SOME APPLICATIONS OF THE RAYLEIGH-RITZ METHOD TO THE THEORY OF THE STRUCTURE OF MATTER[1]

HUBERT M. JAMES

I have been asked to discuss for you some applications of the Rayleigh-Ritz method in physics. Rather than attempt to survey the whole of a discouragingly large field I have preferred to restrict my attention to some few topics from the theory of atomic and molecular structure. The application of the Rayleigh-Ritz method in this field has been carried out with some care and persistence, and there are enough results available to make possible a critical discussion of the potentialities and limitations of the method. This field also presents good examples of how one's mathematical procedure is influenced by one's physical notions concerning the system to be studied, and, in turn, what sort of physical conclusions may be drawn from results yielded by the method.

First of all I shall indicate why recourse to the Ritz[2] method is necessary if one is to obtain a satisfactorily accurate treatment of some of the principal problems in atomic and molecular theory. I shall indicate, though not in as much detail as I should like, the nature of the considerations by which one chooses the set of coordinate functions employed in this method, and show how rapid a convergence one can hope for in the approach to the solution. After presentation of some of the very satisfactory results one can obtain, by the application of enough hard work, in not too unfavorable cases, I shall finally have to indicate the increasingly serious limitations of the method as one seeks to apply it to the treatment of more and more complicated physical systems.

The fundamental mathematical problem in the study of an atomic system by wave mechanics is usually the solution of the stationary state wave equation for that system. In the non-relativistic case this is a linear partial differential equation of the second order, which can be symbolized thus:

$$H\psi = E\psi.$$

Here H represents the Hamiltonian operator for the system obtained

---

[1] An address delivered before the meeting of the Society in Washington, D. C., on May 3, 1941, by invitation of the Program Committee.

[2] W. Ritz, Journal für die reine und angewandte Mathematik, vol. 135 (1909), p. 1.