Perturbation Theory Encyclopedia Article

Perturbation Theory

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Perturbation Theory

Perturbation theory is an approximation method useful in dealing with the Schrödinger equation as it relates to systems of interacting particles. In 1924, by using Albert Einstein's special theory of relativity, **Louis de Broglie** showed that particles have **waves** associated with them. It then became obvious that a specific type of partial differential equation should be able to describe their position and that their future behavior could be predicted. In 1926, **Erwin Schrödinger** used partial differential equations and the Hamiltonian function to develop a powerful equation that relates the **energy** of the **electron** to the energy of the electric field in which it is situated. This equation, the Schrödinger equation, relates the energy of a system to its wave properties and allows prediction of the energy of the electron and its future behavior, i.e. the probability of finding the electron in a particular region around the **nucleus**. Although the Schrödinger equation is a powerful equation it is not practical unto itself because it can rarely be solved. To overcome this problem scientists have developed two main methods that allow us to obtain approximations of the energy of a system without solving the Schrödinger equation. These two methods are the variation method and the perturbation theory.

The basic premise behind the perturbation theory is as follows. Assuming that the Hamiltonian of the perturbed system in which we are interested is only slightly different from the Hamiltonian of an unperturbed system for which we are able to solve the Schrödinger equation, the eigenfunctions and eigenvalues (solutions to the Schrödinger equation associated with special values of the electron's energy levels) of the perturbed system should be closely related to those of the unperturbed system. So we can determine the unknown, perturbed system's values from the known, unperturbed system's values. Basically perturbation theory is developed to deal with small corrections to problems which we know how to solve exactly.

The perturbation theory can be used for non-degenerate as well as degenerate systems. So, unlike the variation method that is restricted to the ground state of a system, the perturbation method applies to all the states of an **atom** or molecule. It can be used to predict the energies of electrons in excited atoms or molecules as well as ground state particles. The perturbation method allows one to calculate the energy much more accurately than it allows one to calculate the **wave function**.