

## perturbation theory

Along with variational method, the second major quantum-mechanical approximation method. The methods of perturbation theory are based on representation of the Hamiltonian of a system under study,  $H$ , through the Hamiltonian,  $H^0$ , of a system, whose Schroedinger equation is solvable, and its relatively small perturbation  $H'$ :  $H = H^0 + H'$ . Numerous techniques are derived allowing one to relate the unknown eigenvalues and eigenfunctions of the perturbed system to the known eigenvalues and eigenfunctions of the unperturbed system. As distinct from the variational method, the methods of perturbation theory are applicable to all the electronic states of an atom or molecule. When  $H'$  is time-dependent, the perturbed system does not have stationary states. In this case time-dependent perturbation theory, which is the method of approximate calculation of the expansion of wave-functions of the perturbed system over wave-functions of stationary states of the unperturbed system, must be employed. The applications of this method are associated mostly with studies of light emission and absorption by atoms and molecules.

**Source:**

PAC, 1999, 71, 1919 (*Glossary of terms used in theoretical organic chemistry*) on page 1957