

variational principle

The principle according to which for a molecular system an approximate wavefunction, when substituted into the Schroedinger equation, will always yield a higher energy than the actual energy of the system. The more precise the wavefunction that is chosen, the closer will the calculated energy be to the true energy. The computational method using this principle to obtain approximations to correct wavefunctions is called the variational method. The method is commonly restricted to the ground state, but can be extended to others provided they are orthogonalized to the (true) ground state.

1999, 71, 1968