

18.6: Wave Functions, Quantum States, Energy Levels, and Degeneracies

We approximate the wavefunction for a molecule by using a product of approximate wavefunctions, each of which models some subset of the motions that the molecule undergoes. In general, the wavefunctions that satisfy the molecule's Schrödinger equation are degenerate; that is, two or more of these wavefunctions have the same energy. (The one-dimensional particle in a box and the one-dimensional harmonic oscillator have non-degenerate solutions. The rigid-rotor in a plane has doubly degenerate solutions; two wavefunctions have the same energy. The J -th energy level of the three-dimensional rigid rotor is $(2J + 1)$ -fold degenerate; there are $(2J + 1)$ wavefunctions whose energy is E_J .) We use doubly subscripted symbols to represent the wavefunctions that satisfy the molecule's Schrödinger equation. We write $\psi_{i,j}$ to represent all of the molecular wavefunctions whose energy is ϵ_i . We let g_i be the number of wavefunctions whose energy is ϵ_i . We say that the energy level ϵ_i is g_i -fold degenerate. The wavefunctions

$$\psi_{i,1}, \psi_{i,2}, \dots, \psi_{i,j}, \dots, \psi_{i,g_i}$$

are all solution to the molecule's Schrödinger equation; we have

$$H_{\text{molecule}} \psi_{i,j} = \epsilon_i \psi_{i,j}$$

for $j = 1, 2, \dots, g_i$. Every energy level ϵ_i is associated with g_i quantum states. For simplicity, we can think of each of the g_i wavefunctions, $\psi_{i,j}$, as a quantum state; however, the molecule's Schrödinger equation is also satisfied by any set of g_i independent linear combinations of the $\psi_{i,j}$. For present purposes, all that matters is that there are g_i quantum-mechanical descriptions—quantum states—all of which have energy ϵ_i .

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