

The Chemical Bond and Quantum Mechanics*

The behavior of electrons in molecules and atoms is described by quantum mechanics; classical (Newtonian) mechanics cannot be used because the de Broglie wavelengths ($\lambda=h/mv$) of the electrons are comparable with molecular (and atomic) dimensions.

The relevant quantum-mechanical ideas are as follows:

- Electrons are characterized by their entire distributions (called wave functions or orbitals) rather than by instantaneous positions and velocities: an electron may be considered always to be (with appropriate probability) at all points of its distribution (which does not vary with time).
- Other things being equal, the kinetic energy of an electron decreases as the volume occupied by the bulk of its distribution increases, so delocalization lowers its kinetic energy.

$$KE = p^2/2m = h^2/2m\lambda^2 \approx A/D^2 \approx A/V^{2/3}$$

- The potential energy of interaction between an electron and other charges is as calculated by classical physics, using the appropriate distribution (wave function) for the electron: an electron distribution is therefore attracted by nuclei and its potential energy decreases as the average electron-nuclear distance decreases.

$$PE \approx -B/D \approx -B/V^{1/3}$$

- A minimum-energy electron distribution represents the best compromise between concentration near the nuclei (to reduce potential energy) and delocalization (to reduce kinetic energy).

$$E = KE + PE \approx A/V^{2/3} - B/V^{1/3}$$

A bond will form between two atoms when the electron distribution of the combined atoms (molecular orbital) yields a significantly lower energy than the separate-atom distributions (atomic orbitals). An example is a covalent bond, in which two electrons, one originally on each atom, change their distributions so that each extends over both atoms.

* Taken from "Molecules" in The Encyclopedia of Physics by Frank E. Harris (with some additions and modifications by Frank Rioux)