

Quantum Mechanics

Solving the Schrödinger Equation

All quantum chemistry methods involve finding a solution to the Schrödinger equation

$$\mathbf{H}\Psi = E\Psi$$

If we had the solution to the Schrödinger equation for a system we would have access to all the structure, properties and reactivity of the system. Unfortunately, it can only be solved directly for a limited number of (very) small systems. To solve for chemically interesting systems we must introduce a number of approximations. The following two approximations are common to most methods:

- **Born-Oppenheimer Approximation** – Electrons move much faster than nuclei and can adjust instantaneously to any change in nuclear geometry. Effectively means that the nuclear coordinates can be fixed decoupling electronic and nuclear motion.
- **Adiabatic Approximation** – Neglect coupling between different electronic states. Restricts calculation to one electronic state (usually the ground state).

Taking these two approximations means that we only have to solve the *electronic* Schrödinger equation which has the following form

$$\left(\sum_{i=1}^n -\frac{\hbar^2}{8\pi^2 m_e} \nabla_i^2 - \sum_{i=1}^n \sum_{a=1}^N \frac{Z_a e^2}{4\pi \epsilon_0 r_{ia}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{4\pi \epsilon_0 r_{ij}} \right) \Psi(\mathbf{R}, \mathbf{r}) = E(\mathbf{R}) \Psi(\mathbf{R}, \mathbf{r})$$

The first term represents the electronic kinetic energy; the second term the nuclear/electron potential energy and the third term the electron/electron potential energy. It is the third term, which couples the positions of all the electrons, that is the centre of most of the quantum mechanical calculations.