4.2.3. The Born-Oppenheimer Approximation

Hamiltonian:

$$H = \underbrace{-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k}\nabla_k^2}_{\text{KE terms}} \underbrace{- \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}}_{\text{PE terms}}$$

- Accurate wave functions are extremely difficult to express because of correlated motions of particles.
  ⇒ That's why Born-Oppenheimer approximation is useful.

- With typical physical conditions, nuclei of molecular systems move much slower, due to the heavier mass, than electrons

- For practicability, electronic "relaxation is done with respect to nuclear motion.
  ⇒ 2 motions are decoupled and compute electronic Es for fixed positions

nuclear ⇒ KE term is taken to be independent of electrons

⇒ Attractive electron-nuclear PE term is eliminated

⇒ repulsive nuclear-nuclear PE term becomes a simply evaluated constant for a given geometry

Electronic Schrodinger equation is:

$$(H_{el} + V_N)\Psi_{el}(q_i; q_k) = E_{el}\Psi_{el}(q_i; q_k)$$

- *el → invocation of the Born-Oppenheimer approximation
- H_{el} includes 1st, 3rd, 4th terms from the Hamiltonian equation above.
- V_N is the nuclear-nuclear repulsion E
- q_i = electronic coordinates (independent variable)
- q_k = nuclear coordinates (parameters)

• eigenvalue to the electronic Schrodinger equation is electronic E.

⇒ it is a constant for a given set of fixed nuclear coordinates, so usually it is ommited from electronic Schrodinger equation, and in that case eigenvalue would be called "pure electronic E".

⇒ Born-Oppenheimer approx. allows us to have the concept of potential energy surface (PES).
- • PES is the surface defined by electronic E over all possible nuclear coordinates.
- - concepts of equilibrium and transition state geometries

⇒ Some chemistry needs quantum mechanical character but we shouldn't give up advantages from this approximation