Chemical Bonding → Electrical Properties

Quantum Chemistry

- Particles have wave-like nature
  \[ \lambda = \frac{\hbar}{p} \] (wavelength \( \lambda \) \& momentum \( p \))
  \[ E = \hbar \nu \quad (= \epsilon \nu) \] (energy \( E \) \& Frequency \( \nu \))

Newtonian mechanics

\[ E_k = \frac{1}{2}mv^2 \quad \Rightarrow \quad E_k = \frac{1}{2} \frac{p^2}{m} \]

\[ E = E_k + E_p = \frac{p^2}{2m} + V \] (1)

Quantum mechanics

- Particle described by the wave \( \Psi(x,t) \)
- Energy operator: \( i\hbar \frac{\partial}{\partial t} \)
  \( \hbar = \frac{\hbar}{2\pi} \)
- Momentum operator: \( -i\hbar \frac{\partial}{\partial x} \)

Operator on \( \Psi(x,t) \) to get energy or momentum

QM form of Eq. (1)

\[ i\hbar \frac{\partial}{\partial t} \Psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x,t) + V(x,t) \Psi(x,t) \] (2)

Solve (2) to get \( \Psi(x,t) \) and get all properties of the particle within the limits of the Heisenberg uncertainty principle.
Important pieces of information from $\Psi(x,t)$

(i) average position, $\bar{x}$, of the particle

$$\bar{x} = \int_{-\infty}^{\infty} \Psi^*(x,t) \Psi(x,t) \, dx$$

$$\Psi(x,t) = R(x,t) + i I(x,t)$$

$$\Psi^*(x,t) = R(x,t) - i I(x,t)$$

(ii) probability of finding particle between $x \leq x_1 \leq dx$

$$P(x,t) \, dx = \Psi^*(x,t) \Psi(x,t) \, dx$$

Born Postulate

probability density function (prob per unit length)

probability of finding particle anywhere in space

$$\int_{-\infty}^{\infty} \Psi^*(x,t) \Psi(x,t) \, dx = 1$$

if $\Psi(x,t)$ is properly normalized

(iii) average value of the observable associated with operator $\hat{O}$

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \hat{O} \Psi(x,t) \, dx$$

Time independent situation

find $\Psi(x,t)$ when $V = V(x) \neq V(t)$

To solve 2) look for solutions of the form

$$\Psi(x,t) = \psi(x) \cdot T(t) \approx \text{separation of variables}$$

$$i\hbar \frac{\partial T(t)}{\partial t}, \psi(x) = -\frac{x^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \cdot T(t) + V(x) \cdot \psi(x) \cdot T(t)$$

next line

in the same
\[ i\hbar \frac{\partial T(t)}{\partial t} \cdot \psi(x) = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} T(t) + V(x) \psi(x) \cdot T(t) \]

\[ \text{by } T \cdot \psi \]
\[ \Rightarrow i\hbar \frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = \frac{-\hbar^2}{2m} \psi(x) \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \]

\[ \neq f(x) \quad \neq f(t) \]

for this to be true,

L.H.S. = R.H.S. = constant

L.H.S. \[ i\hbar \frac{1}{T} \frac{\partial T}{\partial t} \]

solution:
\[ T(t) = e^{-i\frac{G}{\hbar} t} = e^{-i\omega t} \quad \text{where } \omega = G/\hbar \]

\[ G = \hbar \omega \quad \text{so just } = E \]

insert back into (3) (i.e. by \( \psi(x) \))

\[ E \cdot \psi(x) = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \cdot \psi(x) \]

Schroedinger’s time independent equation

since \( V = V(x) \) only properties don’t change with time.

⇒ use \( \psi(x) \) rather than \( \overline{\psi(x,t)} \) in obtaining values of observables.
\[ E \cdot \Psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x) \cdot \Psi(x) \]  

in general, solutions are characterized by quantum \#'s

Electron about a charged nucleus. (positive)

Spherical Coulombic potential:

\[ V = V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r} \quad (sr = \frac{-Ze^2}{r}) \]

\[ \Psi(x) \rightarrow \Psi(r, \theta, \phi) \]

\[ z = \text{nuclear charge} \]
\[ e = \text{charge of an electron} \]
\[ \varepsilon_0 = \text{permittivity of free space} \]
\[ r = \text{e}^{-}\text{to nucleus distance} \]

rewrite 4 in terms of spherical co-ordinates

because \( V \neq f(\theta, \phi) \), separation of variables will work

\[ \Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \]

If there is just one electron, 4 has an analytical solution \( \Rightarrow \) the hydrogen atom.