Chemical Bonding → Electrical Properties

Quantum Chemistry

• particles have wave like nature

$\hbar = h/2\pi$

$\lambda = h/p$ ← momentum

wave-length, Planck's constant

$E = h\nu$ $(= \hbar\omega)$

energy, frequency

(photon: $\nu = c/\lambda$)

Newtonian mechanics

$$E_k = \tfrac{1}{2} m v^2 \qquad p = mv \Rightarrow E_k = \tfrac{1}{2} p^2/m$$

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

Quantum mechanics

• particle 'described' by the wave $\Psi(x,t)$

• Energy operator: $i\hbar \frac{\partial}{\partial t}$ $\quad i = \sqrt{-1} \quad \hbar = h/2\pi$

• Momentum operator: $-i\hbar \frac{\partial}{\partial x}$

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

QM form of Eq. ①

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

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

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

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

(ii) probability of finding particle between x & $x+dx$

$$P(x,t)\, dx = \Psi^*(x,t)\, \Psi(x,t)\, dx \qquad \text{Born Postulate}$$

probability density function (prob per unit length)

probability of finding particle anywhere in space

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\, \Psi(x,t)\, dx \equiv 1 \quad \text{if } \Psi(x,t) \text{ is properly normalized.}$$

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

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

Time independent situation

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

To solve ② look for solutions of the form

$\Psi(x,t) = \psi(x) \cdot T(t)$ ← separation of variables

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

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

$\div$ by $T \cdot \psi$

$$\Rightarrow \underbrace{i\hbar \frac{1}{T(t)} \frac{T(t)}{\partial t}}_{\neq f(x)} = \underbrace{\frac{-\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2}}_{\neq f(t)} + V(x) \qquad (3)$$

for this to be true,

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

L.H.S. $\quad i\hbar \frac{1}{T} \frac{\partial T}{\partial t} = G$

solution:

$$T(t) = e^{-iG/\hbar t} = e^{-i\omega t} \quad \text{where } \omega = G/\hbar$$

$G = \hbar\omega$ is just $= E$

insert back into (3) ($\div$ x by $\psi(x)$)

$$\boxed{E \cdot \psi(x) = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \cdot \psi(x)} \qquad (4)$$

Schroedinger's time independent equation

since $V = V(x)$ only, properties don't change with time.

$\Rightarrow$ use $\psi(x)$ rather than $\Psi(x,t)$ in obtaining values of observables.

$$E \cdot \psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\cdot\psi(x) \qquad (4)$$

in general, solutions are characterized by quantum #'s

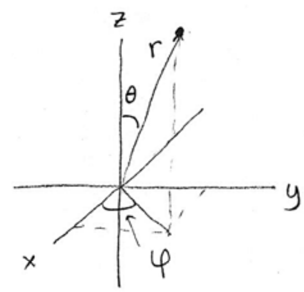
Electron about a charged nucleus. (positive)

Spherical Coulombic potential:

$$V = V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r} \qquad \left(\text{or } = \frac{-Ze^2}{r}\right)$$

Z = nuclear charge
e = charge of an electron
ϵ_0 = permittivity of free space
r = e^- to nucleus distance

$\psi(x) \rightarrow \psi(r, \theta, \varphi)$



rewrite (4) in terms of spherical co-ordinates

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

$$\psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

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