176(6): Applications of the Quantum Hamilton Equations Part 3.

The two quantum Hamilton equations are:

$$i\hbar \frac{d\hat{A}}{dq} \phi = [\hat{A}, \hat{p}] \phi \quad — (1)$$

and

$$i\hbar \frac{d\hat{A}}{dp} \phi = - [\hat{A}, \hat{q}] \phi \quad — (2)$$

in canonical representation. In the Cartesian representation they are:

$$\hat{p}(\hat{A}\phi) = [\hat{p}, \hat{A}] \phi \quad — (3)$$

and

$$\hat{p}\phi = -i\hbar \frac{\partial \phi}{\partial x} \quad — (4)$$

and

$$\hat{x}(\hat{A}\phi) = [\hat{x}, \hat{A}] \phi \quad — (5)$$

$$\hat{x}\phi = i\hbar \frac{\partial \phi}{\partial p} \quad — (6)$$

Therefore we find new equations of motion using:

$$[\hat{A}, \hat{H}] \phi = i\hbar \frac{d\hat{A}}{dt} \phi \quad — (7)$$

These are:

Quantum Hamilton	Classical Hamilton
$\frac{d\hat{p}}{dt}\phi = \frac{1}{i\hbar}\hat{p}(\hat{H}\phi)$	$\frac{dp}{dt} = -\frac{dH}{dq}$
$\frac{d\hat{q}}{dt}\phi = \frac{1}{i\hbar}\hat{q}(\hat{H}\phi)$	$\frac{dq}{dt} = \frac{dH}{dp}$

i.e. Now use the Schroedinger equation:

$$\hat{H}\phi = E\phi \quad -(8)$$

to find:

$$\frac{d\hat{p}}{dt}\phi = \frac{1}{i\hbar}\hat{p}\left(E\phi\right) \quad -(9)$$

$$\frac{d\hat{q}}{dt}\phi = \frac{1}{i\hbar}\hat{q}\left(E\phi\right) \quad -(10)$$

where

$$E = T + V \quad -(11)$$
$$= H$$

and where

$$H = T + V \quad -(12)$$

is the classical hamiltonian. Here T and V are the kinetic and potential energies respectively.

In the Cartesian position representation for example:

$$-i\hbar\frac{\partial}{\partial x}\left(E\phi\right) = i\hbar\left(\frac{d\hat{p}}{dt}\right)\phi \quad -(13)$$

so:

$$\boxed{\frac{\partial}{\partial x}\left(E\phi\right) = i\hbar\frac{d}{dt}\left(\frac{\partial\phi}{\partial x}\right)} \quad -(14)$$

This is a new equation of motion of quantum mechanics applicable to all of quantum chemistry, quantum optics and quantum field theory.

? If $\partial\phi/\partial x$ is independent of time then:

$$\boxed{\frac{\partial}{\partial x}\left(E\phi\right) = 0} \quad -(15)$$

or in the usual notation for the classical hamiltonian:

$$\frac{\partial}{\partial x}\left(H\phi\right) = 0 \quad -(16)$$

In canonical formulation:

$$\boxed{\frac{\partial}{\partial q}\left(H\phi\right) = 0} \quad -(17)$$

This is much easier to solve by computer than the Schroedinger equation, so has immediate applicability in computational quantum chemistry.

Harmonic Oscillator

In this case:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad -(18)$$

so

$$\frac{\partial H}{\partial x} = m\omega^2 x \quad -(19)$$

The zero point wave function is:

$$\phi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right) \quad -(20)$$

†) and is time independent, so:

$$\frac{\partial}{\partial x}\left(H\phi\right) = \left(\frac{\partial H}{\partial x}\right)\phi + \phi\left(\frac{\partial H}{\partial x}\right) = 0 \quad -(21)$$

where $H\frac{\partial \phi}{\partial x} = -Hx\alpha\phi \quad -(22)$

$$= -H\frac{xm\omega}{\hbar}\phi.$$

From (19) and (22):

$$E = H = \hbar\omega \quad -(23)$$

Q.E.D, which is the energy relation of Planck.

therefore:

$$\boxed{E = H = \hbar\omega = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2} \quad -(24)$$

which means that the total energy of the harmonic oscillator is quantized, giving a de Broglie type matter wave.

Note carefully that this is not the same result as quantized energy levels of the harmonic oscillator, namely

$$\hat{H}\phi = E\phi. \quad -(25)$$