THEORETICAL CHEMISTRY I
WINTER SEMESTER 2001/2002

1.Hamilton-operator Hamilton-operator for general case

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha=1}^{N}\frac{1}{M_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_i^2 + \sum_{\beta=\alpha+1}^{N}\sum_{\alpha=1}^{N-1}\frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - \sum_{\alpha=1}^{N}\sum_{i=1}^{n}\frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{j=i+1}^{n}\sum_{i=1}^{n-1}\frac{e^2}{r_{ij}}$$

where α and β refer to nuclei and i and j refers to the electrons.
The first term is the operator for the kinetic energy of the nuclei; the second term is the operator for the kinetic energy of the electrons; the third term represents the repulsions between the nuclei, $r_{\alpha\beta}$ being the distance between nuclei α and β of atomic number Z_α and Z_β; the fourth term represents the attraction between the electrons and the nuclei, $r_{\alpha\beta}$ being the distance between electron i and j. The nuclei are much heavier than electrons, hence the electrons move faster than the nuclei , and to a good approximation as far as electrons are concerned, we can regard the nuclei as fixed while the electrons carry out their motions.
Since nuclei are considered to be fixed, we can omit the kinetic-energy terms of the nuclei. So the *purely electronic hamiltonian* $\hat{H}_{el}$ is

$$\hat{H}_{el} = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_i^2 - \sum_{\alpha=1}^{N}\sum_{i=1}^{n}\frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{j=i+1}^{n}\sum_{i=1}^{n-1}\frac{e^2}{r_{ij}}$$

The *nuclear repulsion term* V_{NN} is

$$V_{NN} = \sum_{\beta=\alpha+1}^{N}\sum_{\alpha=1}^{N-1}\frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}$$

The electronic hamiltonian for CH_4 will include ;

The kinetic energy for electons ;

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{10}\nabla_i^2$$

Electron- nucleus attarction term ;

$$-\frac{6e^2}{r_{1,C}} - \frac{6e^2}{r_{2,C}} \dots - \frac{6e^2}{r_{10,C}} -$$

$$\frac{e^2}{r_{1,H_1}} \dots - \frac{e^2}{r_{10,H_1}} - \frac{e^2}{r_{1,H_2}} \dots - \frac{e^2}{r_{10,H_2}} - \frac{e^2}{r_{1,H_3}} \dots - \frac{e^2}{r_{10,H_3}} - \frac{e^2}{r_{1,H_4}} \dots - \frac{e^2}{r_{10,H_4}}$$

Electron-electron repulsion term ;

$$\sum_{j=i+1}^{10}\sum_{i=1}^{9}\frac{e^2}{r_{ij}}$$

The electronic hamiltonian for Ne will include ;
The kinetic energy for electons ;

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{10}\nabla_i^2$$

Electron- nucleus attarction term ;

$$-\frac{10e^2}{r_{1,Ne}} - \frac{10e^2}{r_{2,Ne}} \dots - \frac{10e^2}{r_{10,Ne}}$$

Electron-electron repulsion term ;

$$\sum_{j=i+1}^{10} \sum_{i=1}^{9} \frac{e^2}{r_{ij}}$$

It is seen that that the kinetic energy of electron and electron-electron repulsion is similar in the above two cases , since they are 10 electron system.

2. Harmonic Ocsillators a) Normalized wave-function

$$\Psi = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}}$$

b) The uncetainty in position

$$\triangle x = \sqrt{\frac{1}{2\alpha}}$$

The uncetainty in momentum

$$\triangle p = \hbar\sqrt{\frac{\alpha}{2}}$$

$$\triangle x \triangle p \approx \frac{\hbar}{2}$$

c) The energy of the ground state

$$E_0 = \frac{\hbar\omega}{2}$$

For the harmonic oscillator in classical physics framework the ground state energy is zero. This quantum mechanical ground state energy of harmonic oscillator is refered to as *zero point energy* and it is a direct consequence of *uncertainty principle* .