372(3): Lagrangian Method Applied to the Helium Atom

In this case the lagrangian is:

$$\mathcal{L} = \frac{1}{2m}\left(p_1^2 + p_2^2\right) - U \quad -(1)$$

and the Hamiltonian is:

$$H = \frac{1}{2m}\left(p_1^2 + p_2^2\right) + U \quad -(2)$$

where the subscripts 1 and 2 refer to the two electrons. The potential energy is:

$$U = -\frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad -(3)$$

and consists of two electron / proton terms and one repulsive electron / electron term. The nucleus has a charge of $2e$, because it contains two protons, and also neutrons. The lagrangian (1) can be written as:

$$\mathcal{L} = \frac{1}{2}\left(\dot{r}_1^2 + \dot{\beta}_1^2 r_1^2 + \dot{r}_2^2 + \dot{\beta}_2^2 r_2^2\right) - U \quad -(4)$$

and the proper Lagrange variables are: $r_1, \beta_1, r_2, \beta_2$, and r_{12}.

There are therefore five Euler Lagrange Equations in five unknowns:

$$\frac{\partial \mathcal{L}}{\partial r_1} = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{r}_1}\right) \quad -(5)$$

$$\frac{\partial \mathcal{L}}{\partial r_2} = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{r}_2}\right) \quad -(6)$$

2) $$\frac{\partial \mathcal{L}}{\partial r_{12}} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{r}_{12}} = 0 \quad -(7)$$

$$\frac{\partial \mathcal{L}}{\partial \beta_1} = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{\beta}_1}\right) \quad -(8)$$

and $$\frac{\partial \mathcal{L}}{\partial \beta_2} = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{\beta}_2}\right) \quad -(9)$$

These can be solved for $r_1, r_2, r_{12}, \beta_1, \beta_2,$ $\dot{r}_1, \dot{r}_2$ and $\dot{\beta}_1$ and $\dot{\beta}_2$. In general $\dot{r}_{12}$ is also non-zero.

Therefore the momentum can be computed as follows:

$$p^2 = m^2\left(\dot{r}_1^2 + \dot{r}_2^2 + \dot{\beta}_1^2 r_1^2 + \dot{\beta}_2^2 r_2^2\right) \quad -(10)$$

The wave function of the atom is found from:

$$-\hbar^2 \nabla^2 \psi = p^2 \psi \quad -(11)$$

where ψ is a function of the coordinates of both electrons.

The energy levels are found from:

$$\hat{H}\psi = E\psi \quad -(12)$$

The coordinate system used is (r, β), so the Laplacian is

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r}\frac{\partial \psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2 \psi}{\partial \beta^2} \quad -(13)$$

Therefore

$$-\hbar^2\nabla^2\psi = -\hbar^2\left(\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right) \quad -(14)$$

$$= m^2\left(\dot{r}_1^2 + \dot{r}_2^2 + \dot{\phi}_1^2 r_1^2 + \dot{\phi}_2^2 r_2^2\right)\psi$$

The energy levels are given by the expectation values:

$$\langle E \rangle = \int \psi^* \hat{H} \psi \, d\tau \quad -(15)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U \quad -(16)$$

This method has the advantage of giving the wave-function without the use of perturbation theory. It should be used with the Pauli exclusion principle and given the computer power, can be extended to any number of electrons in theory.