Non-relativistic hamiltonian for an Li^+ ion and an H_2 molecule (+ a demonstration of the Born-Oppenheimer approximation)

Hamiltonian, the total energy operator, is the sum of the kinetic energy operator $\hat{T}$ and potential energy operator $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V}$$

In general the Hamiltonian operator for an *N*-electron atom can be written as:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{ne}$$

Where $\hat{T}_e$ is the electron kinetic energy operator, $\hat{T}_n$ is the nuclear kinetic energy operator, $\hat{V}_{ee}$ operator is for electron-electron coulombic repulsion and $\hat{V}_{ne}$ is for nuclear-electron coulombic attraction. (For multiple atoms the Hamiltonian would contain nuclear repulsion $\hat{V}_{nn}$, which would be considered constant if utilizing the Born-Oppenheimer approximation which decouples nuclear and electronic motion)

In accordance with the Born-Oppenheimer approximation I will assume a „static" nucleus, thus $\hat{T}_n = 0$.

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne}$$

Lets write down the momentum operator for one particle:

$$\hat{T}_e = -\frac{\hbar^2}{2m}\Delta$$

where Δ is the Laplacian (nature of which is way beyond the scope of this excercise, yet we can see its related to the cartesian coordinates of our particle):

$$\Delta = \frac{\partial^2}{\partial x^2}\frac{\partial^2}{\partial y^2}\frac{\partial^2}{\partial z^2}$$

Should we assume that the force field includes only coulomb interactions of charged particles (electrons and protons), the kinetic energy operator is the expression for this electrostatic interaction. For example for an electron ($-e$) near a nucleus with a charge of $+Ze$:

$$\hat{V} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

Where r is the nucleus-electron distance, ε_0 is vacuum permitivity constant and the expression $4\pi\varepsilon_0$ is used due to usage of SI units. If atomic units are used the expression can be simplified.

So now we can finally write the Hamiltonian for Li^+:

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{3e^2}{4\pi\varepsilon_0 r_1} - \frac{3e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Where we can see the expressions for the kinetic energy of both electrons and the expressions for coulomb interactions between both electrons and nucleus and between the electrons themselves. This expression can be written in a more compact form:

$$\hat{H} = -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{3}{r_1} + \frac{3}{r_2} - \frac{1}{r_{12}}\right)$$

If I had included the kinetic energy of the nucleus, instead of using the Born-Oppenheimer approximation the expression would be:

$$\hat{H} = -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) - \frac{\hbar^2}{2M}\Delta - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{3}{r_1} + \frac{3}{r_2} - \frac{1}{r_{12}}\right)$$

Where M is the mass of the nucleus. (Note: The B-O approximation was not extremely useful right now, since an atom is a system with only one nucleus, but will come in handy when dealing with the H_2 molecule.)

The procedure for an H_2 molecule is similar, except we are now including nuclear repulsion $\hat{V}_{nn}$ in the Hamiltonian:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn}$$

The Born-Oppenheimer approximation lets us disregard nuclear motion again $\hat{T}_n$ and since we are assuming a stationary nucleus we can assume a constant nuclear repulsion energy $\hat{V}_{nn}$ thus:

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne}$$

So the Hamiltonian for electrons 1 and 2 around hydrogen nuclei A and B, using the Born-Oppenheimer approximation:

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2}{4\pi\varepsilon_0 r_{2A}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}} - \frac{e^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

And the total Hamiltonian for H_2 including nuclear motion:

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{\hbar^2}{2M}\Delta_A - \frac{\hbar^2}{2M}\Delta_B - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2}{4\pi\varepsilon_0 r_{2A}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}} - \frac{e^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}$$

(Sidenote: Lithium ion is a 3-body problem and the Hydrogen molecule is a 4-body problem. Thus making the wavefunction utilizing their total Hamiltonians impossible to solve analytically. See Many-body problem for more.)