Center of mass separation

A hydrogen-like atom consists of one nucleus of charge *Ze* and a single electron of charge −*e,* so in addition to H we have He^{+}, Li^{+2}, Be^{+3}, etc. Additionally we have the isotopes $^{2}H, ^{4}Li^{+2}$, etc. The time independent Schrodinger equation for these systems is given by

$$\left(-\frac{\hbar^2}{2m_e}\nabla_e^2 \;-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0\left|\vec{r}_e - \vec{r}_N\right|}\right)\Psi = E\Psi$$

Where the position vectors to the nucleus and electron are $\vec{r}_N$ & $\vec{r}_e$ while m_N & m_e are the respective masses. We can separate the center of mass motion from the relative internal motion by the transformation

$\vec{r}_{int} = \vec{r}_e - \vec{r}_N$ and $\vec{R}_{cm} = (m_e\vec{r}_e + m_N\vec{r}_N)/m_t$

where $m_t = m_e + m_n$. From these we get

$$\vec{r}_N = \vec{R}_{cm} - \frac{m_e}{m_t}\vec{r}_{int} \quad \& \quad \vec{r}_e = \vec{R}_{cm} + \frac{m_N}{m_t}\vec{r}_{int}$$

and

$$\frac{\partial}{\partial x_N} = \frac{\partial}{\partial X_{cm}}\frac{\partial X_{cm}}{\partial x_N} + \frac{\partial}{\partial x_{rel}}\frac{\partial x_{rel}}{\partial x_N} = \frac{m_N}{m_t}\frac{\partial}{\partial X_{cm}} - \frac{\partial}{\partial x_{rel}}$$

So

$$\nabla_n^2 = \left(\frac{m_n}{m_t}\right)^2\nabla_{cm}^2 + \nabla_{int}^2 - \frac{2m_n}{m_t}\nabla_{cm}\bullet\nabla_{int}$$

In a similar fashion

$$\nabla_e^2 = \left(\frac{m_e}{m_t}\right)^2\nabla_{cm}^2 + \nabla_{int}^2 + \frac{2m_e}{m_t}\nabla_{cm}\bullet\nabla_{int}$$

And because the cross terms cancel, the Schrodinger equation becomes

$$\left(-\frac{\hbar^2}{2m_t}\nabla_{cm}^2 \;-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\Psi = E\Psi$$

where $\mu = \dfrac{m_e m_N}{m_e + m_N}$ is the reduced mass and $\nabla^2 = \nabla_{int}^2$

Because the center of mass motion is independent of the internal motion we can write the wavefunction for the two particle system as a product $\Psi(\vec{R},\vec{r}) = \phi(\vec{R})\psi(\vec{r})$ and the total energy E can be written as the sum of the center of mass energy and the internal energy, $E = E_{cm} + E_{in}$ where

$$\hat{H}_{cm}\phi_{cm}(\vec{R}) = E_{cm}\phi_{cm}(\vec{R}) \quad \& \quad \hat{H}_{int}\psi_{int}(\vec{r}) = E_{int}\psi_{int}(\vec{r})$$

and

$$\hat{H}_{cm} = -\frac{\hbar^2}{2m_t}\nabla^2_{cm} \quad \& \quad \hat{H}_{int} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

In the absence of an external field, the center of mass motion is that of a neutral free particle and if the system is in free space (not bounded) the wave function is a plane wave and the energy a continuous function of the particles momentum.

$$\phi(\vec{R},\vec{k}) = Ce^{i\vec{k}\bullet\vec{R}} \quad \& \quad E_{cm} = \frac{\hbar^2 k^2}{2m_t} \text{ where } -\infty < k < +\infty$$

If however the system is in a one, two or three-dimensional box the eigenfunctions and eigenvalues are those appropriate for a particle of mass μ in the box.