Reduced mass in the Schrödinger equation

The Hamiltonian of the two-particle system in real space with coordinates ξ, η, ζ with index 1 for the proton (mass *M*) and index 2 for the electron (mass m) can be written as:

$$H = \frac{p_1^2}{2M} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0\rho}$$

with ρ the a between the two particles. Hence the Schrödinger equation reads:

$$- \quad \Delta_1\Psi - \frac{h_b^2}{2m}\Delta_2\Psi + \frac{Ze^2}{4\pi\varepsilon_0\rho} = E'$$

where the Laplacian with index 1 operates in the subspace of the electron:

$$\Delta_1 = \frac{\partial^2}{\partial\xi_1^2} + \frac{\partial^2}{\partial\eta_1^2} + \frac{\partial^2}{\partial\zeta_1^2}$$

and the wave function depends on the six coordinates of the two particles.
The coordinates of the centre-of-mass are:

$$= \frac{\xi_1 + m\xi_2}{M + m} \qquad x = \xi_2 - \xi_1$$

$$Y = \frac{M\eta_1 + m\eta_2}{M + m} \qquad y = \eta_2 - \eta_1$$

$$Z = \frac{M\zeta_1 + m\zeta_2}{M + m} \qquad z = \zeta_2 - \zeta_1$$

and:

$$\rho = \sqrt{x^2 + y^2 + z^2} = r$$

Insertion of the new parameters in the differential equation yields:

$$\frac{\partial^2}{\partial\xi_1^2}\Psi = \left(\frac{M}{M + m}\right)^2\frac{\partial^2}{\partial X^2}\Psi - 2\frac{M}{M + m}\frac{\partial^2}{\partial X\partial x}\Psi + \frac{\partial^2}{\partial x^2}$$

and it follows:

$$\Delta_1\Psi + \frac{1}{m}\Delta_2\Psi = \frac{1}{M + m}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right)\Psi + \frac{1}{\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi$$

With the reduced mass:

$$\mu = \frac{mM}{m + M}$$

This equation can be separated:

$$\Psi = \psi(x, y, z)\Phi(X, Y, Z) \qquad E' = E + E''$$

Giving two equations, one for the centre-of-mass motion:

$$- \qquad \Delta\Phi(X, Y, Z) = E''\Phi(X, Y, Z)$$

and for the relative electron motion:

$$-\frac{h_b^2}{2\mu}\Delta\psi(x, y, z) - \frac{Ze^2}{4\pi\varepsilon_0 r} = E\psi(X, Y, Z)$$

Thus the atomic units can be adopted to take into account the motion of the nucleus. μ can be taken as the new atomic unit of mass.