Schrödinger equation in parabolic coordinates

The Schrödinger equation for the relative electron motion is written as:

$$-\frac{1}{2}\Delta\psi(x, y, z) - \frac{Z}{r} = E\psi(X, Y, Z)$$

Where the system of atomic units is adopted. The solution for this equation is:

with energy given in Hartree. Note that the solutions should be scaled with μ/m_e. Usually it is solved in spherical coordinates because the problem can be separated in spherical polar coordinates. A problem of an *1/r* potential can also be sperated in parabolic coordinates, defined as:

$$\begin{aligned} &= \sqrt{\xi\eta}\cos\varphi & \xi &= r + z \\ y &= \sqrt{\xi\eta}\sin\varphi & \eta &= r - z \\ z &= \frac{1}{2}(\xi - \eta) & \varphi &= \operatorname{atan}\frac{y}{x} \end{aligned}$$

and:

$$= \sqrt{} = \quad (\xi + \eta)$$

This gives in matrix form:

$$\begin{bmatrix} \\ \\ \\ \end{bmatrix} = \begin{bmatrix} \sqrt{\frac{\eta}{\zeta}}\cos\varphi & \frac{1}{2}\sqrt{\frac{\xi}{\eta}}\cos\varphi & -\sqrt{\xi\eta}\sin\varphi \\ \frac{1}{2}\sqrt{\frac{\eta}{\zeta}}\sin\varphi & \frac{1}{2}\sqrt{\frac{\xi}{\eta}}\sin\varphi & \sqrt{\xi\eta}\cos\varphi \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{bmatrix} \begin{bmatrix} d\xi \\ d\eta \\ d\varphi \end{bmatrix}$$

Then:

$$= \qquad\qquad = \frac{\eta + \xi}{4\xi}d\xi^2 + \frac{\eta + \xi}{4\eta}d\eta^2 + \xi\eta\, d\varphi^2$$

and:

$$= \quad (\xi + \eta)\, d\xi\, d\eta\, d\varphi$$

It can be shown that the Laplace operator is equal to:

$$\Delta = \frac{4}{\xi + \eta}\frac{d}{d\xi}\left(\xi\frac{d}{d\xi}\right) + \frac{4}{\xi + \eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\right) + \frac{1}{\xi\eta}\frac{d^2}{d\varphi^2}$$

Then the Schrödinger equation becomes:

$$\left(\quad\right)\left[\frac{4}{\xi + \eta}\frac{d}{d\xi}\left(\xi\frac{d}{d\xi}\right) + \frac{4}{\xi + \eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\right) + \frac{1}{\xi\eta}\frac{d^2}{d\varphi^2}\right]\psi - \frac{2Z}{(\xi + \eta)}\psi = E\psi$$

Define now a solution of this equation as:

$$\psi(\xi,\eta,\varphi) \;=\; \psi_1(\xi)\psi_2(\eta)e^{\pm im\varphi}$$

with m ≥ 0.
Insertion and deviding by $4\psi_1\psi_2 e^{\pm im\varphi}$ yields:

$$(\quad)\left[\frac{4}{\xi+\eta}\frac{1}{\psi_1}\left(\frac{d}{d\xi}\;\xi\frac{d\psi_1}{d\xi}\right)+\frac{4}{\xi+\eta}\frac{1}{\psi_2}\left(\frac{d}{d\eta}\;\eta\frac{d\psi_2}{d\eta}\right)+\frac{1}{\xi\eta}m^2\right]-\frac{2Z}{(\xi+\eta)} \;=\; E$$

Multiply by $(\xi+\eta)$:

$$\left[\frac{}{\psi_1}\left(\frac{d}{d\xi}\;\xi\frac{d\psi_1}{d\xi}\right)+\frac{1}{\psi_2}\left(\frac{d}{d\eta}\;\eta\frac{d\psi_2}{d\eta}\right)+\frac{(\xi+\eta)}{4\xi\eta}m^2\right]+Z \;=\; -E\frac{1}{2}(\xi+\eta)$$

and separate the m^2 term as well as the Coulomb term in two parts with :

$$\left[\frac{}{\psi_1}\left(\frac{d}{d\xi}\;\xi\frac{d\psi_1}{d\xi}\right)\right]+\frac{1}{\psi_2}\left(\frac{d}{d\eta}\;\eta\frac{d\psi_2}{d\eta}\right)+Z_1+Z_2-\frac{1}{4\xi}m^2-\frac{1}{4\eta}m^2 \;=\; -\left(\frac{1}{2}\xi E+\frac{1}{2}\eta E\right)$$

These are in fact two identical differential equations, one for $\psi_1(\xi)$ and one for $\psi_2(\eta)$:

$$\left[\frac{d}{d\xi}\;\xi\frac{d\psi_1}{d\xi}\right]+Z_1\psi_1-\frac{1}{4\xi}m^2\psi_1 \;=\; -\frac{1}{2}\xi E\psi_1$$

The behaviour of the wave function ψ_1 in the limiting cases is:

for large $\xi \to e^{-\frac{1}{2}\varepsilon\xi}$

for small $\xi \to \xi^{\frac{1}{2}m}$

A solution is taken of the form:

$$\psi_1 \;=\; e^{-\frac{1}{2}\varepsilon\xi}\xi^{\frac{1}{2}m}f_1(\xi)$$

with $\;=\varepsilon\xi$ and $\varepsilon \;=\; \sqrt{-2E}$ this leads to an equation:

$$\frac{}{} + \qquad\qquad \frac{}{} + \left(\frac{}{\varepsilon}-\frac{m+1}{2}\right)f_1 \;=\; 0$$

Again a Laguerre-type equation with solutions:

with a quantisation condition, for each equation:

$$= \frac{}{\varepsilon}-\frac{1}{2}(m+1)$$

$$n_2 \;=\; \frac{Z_2}{\varepsilon}-\frac{1}{2}(m+1)$$

Also n_1 must be a non-negative integer if ε is to be real and ξ remains finite. So:

$$\frac{Z}{\varepsilon} = \frac{Z_1}{\varepsilon} + \frac{Z_2}{\varepsilon} = n_1 + n_2 + (m+1) = n$$

This gives the energy quantization:

$$= -\ \varepsilon^2 = -\frac{1}{2}\frac{Z^2}{n^2}$$

in hartree units. The normalized eiegenfunctions are:

$$\psi_{n_1 n_2 m} = \frac{e^{\pm im\varphi}}{\sqrt{n\pi}} \frac{(n_1!)^{1/2}(n_2!)^{1/2}}{(n_1+m)!^{3/2}(n_2+m)!^{3/2}} \xi^{m+3/2} e^{-\frac{1}{2}\varepsilon(\xi+\eta)} (\xi\eta)^{\frac{1}{2}m} L^m_{n_1+m}(\varepsilon\xi) L^m_{n_2+m}(\varepsilon\eta)$$

These eigenfunctions are symmetrical with respect to the plane z=0.
For the density is on the positive side of *z*, for at the negative side.