Mathematics 31: The Hydrogen Molecule: H_2^+

The hydrogen molecule H_2^+ involves two protons and a single electron and may be described, non-relativistically and in the limit that the proton mass is infinite, by:

$$H = \frac{|\,\hat{\mathbf{p}}\,|^2}{2m} - \frac{e^2}{|\,\mathbf{r}-\mathbf{R}_1\,|} - \frac{e^2}{|\,\mathbf{r}-\mathbf{R}_2\,|} + \frac{e^2}{|\,\mathbf{R}_1-\mathbf{R}_2\,|}$$

where $\mathbf{R}_\alpha$ are the positions, assumed fixed, of the two protons. This problem is the context of the current document.

Our initial task is to rescale the problem into an accessible form. We employ $\frac{1}{2}[\mathbf{R}_1+\mathbf{R}_2]$ as the origin and then choose our z-axis to be parallel to the line between the two protons: $\mathbf{R}_1 - \frac{1}{2}[\mathbf{R}_1+\mathbf{R}_2] = \frac{1}{2}[\mathbf{R}_1-\mathbf{R}_2] \mapsto R\hat{\mathbf{z}}$ and $\mathbf{R}_2 - \frac{1}{2}[\mathbf{R}_1+\mathbf{R}_2] = \frac{1}{2}[\mathbf{R}_2-\mathbf{R}_1] \mapsto -R\hat{\mathbf{z}}$. Rescaling space by $\mathbf{r}\mapsto R\mathbf{x}$ and energy by $E\mapsto \beta\epsilon$ we find:

$$H \mapsto -\frac{\hbar^2}{2mR^2\beta}\nabla^2_{\mathbf{x}} - \frac{e^2}{R\beta}\left[\frac{1}{|\,\mathbf{x}-\hat{\mathbf{z}}\,|} + \frac{1}{|\,\mathbf{x}+\hat{\mathbf{z}}\,|}\right] + \frac{e^2}{2R\beta} - \epsilon$$

and then if we choose:

$$\beta = \frac{\hbar^2}{2mR^2} \qquad\qquad \alpha = \frac{e^2}{R\beta} = \frac{me^2}{\hbar^2}2R$$

to achieve:

$$H - \epsilon \mapsto -\nabla^2_{\mathbf{x}} - \alpha\left[\frac{1}{|\,\mathbf{x}-\hat{\mathbf{z}}\,|} + \frac{1}{|\,\mathbf{x}+\hat{\mathbf{z}}\,|}\right] + \frac{\alpha}{2} - \epsilon$$

in terms of α which is the separation of the two nuclei measured in units of the Bohr radius. Although ϵ is the natural eigenvalue, in the natural units of Rydberg's, the corresponding eigenvalue is:

$$E = \beta\epsilon = \frac{me^4}{2\hbar^2} \times \frac{4\epsilon}{\alpha^2}$$

This problem can be greatly simplified by a cunning choice of orthogonal curvilinear coordinate system:

$$z = uv \qquad\qquad \rho^2 = [1-u^2][v^2-1] \qquad\qquad \phi$$

restricted to $u\in[-1,1]$ and $v\in[1,\infty)$. Firstly we verify the nature of the transformation:

$$\mathbf{dr} = d\rho\hat{\boldsymbol{\rho}} + dz\hat{\mathbf{z}} + \rho d\phi\hat{\boldsymbol{\phi}}$$

the differentials are elementary:

$$\rho d\rho = vdv[1-u^2] - udu[v^2-1] \qquad\qquad dz = vdu + udv$$

and consequently:

$$\mathbf{dr} = dv\left(v\left[\frac{1-u^2}{v^2-1}\right]^{\frac{1}{2}}\hat{\boldsymbol{\rho}} + u\hat{\mathbf{z}}\right) + du\left(v\hat{\mathbf{z}} - u\left[\frac{v^2-1}{1-u^2}\right]^{\frac{1}{2}}\hat{\boldsymbol{\rho}}\right) + d\phi\left[v^2-1\right]^{\frac{1}{2}}\left[1-u^2\right]^{\frac{1}{2}}\hat{\boldsymbol{\phi}}$$

which verifies the orthogonality of the coordinate system, combined with:

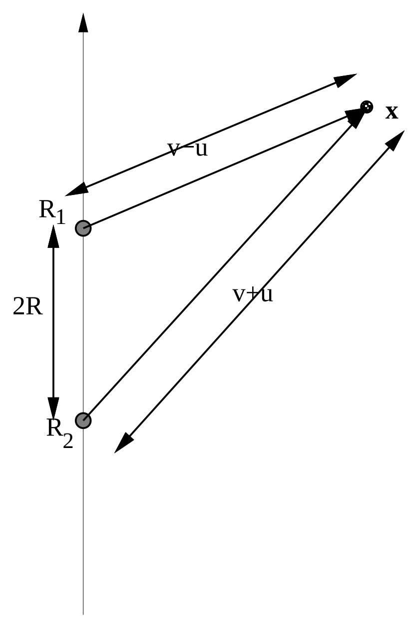
$$h_v = \left[\frac{v^2-u^2}{v^2-1}\right]^{\frac{1}{2}} \qquad h_u = \left[\frac{v^2-u^2}{1-u^2}\right]^{\frac{1}{2}} \qquad h_\phi = \left[v^2-1\right]^{\frac{1}{2}}\left[1-u^2\right]^{\frac{1}{2}}$$

to complete the description. The Laplacian in this coordinate system is:

$$\nabla^2 = \frac{1}{v^2-u^2}\left[\frac{\partial}{\partial v}(v^2-1)\frac{\partial}{\partial v} + \frac{\partial}{\partial u}(1-u^2)\frac{\partial}{\partial u} + \left(\frac{1}{v^2-1}+\frac{1}{1-u^2}\right)\frac{\partial^2}{\partial\phi^2}\right]$$

The main use of this coordinate system is the fact that:

$$\mid \mathbf{x} \pm \hat{\mathbf{z}} \mid^2 = \rho^2 + (z\pm 1)^2 = u^2+v^2-1-u^2v^2 \pm 2uv + 1 + u^2v^2 = (v\pm u)^2$$



and consequently that:

$$\frac{1}{\mid \mathbf{x}-\hat{\mathbf{z}}\mid} + \frac{1}{\mid \mathbf{x}+\hat{\mathbf{z}}\mid} = \frac{2v}{v^2-u^2}$$

and that in this coordinate system the current problem *separates:*

$$\psi(\mathbf{x}) = V(v)U(u)\Phi(\phi)$$

with:

$$\Phi(\phi) = \frac{1}{\sqrt(2\pi)}e^{im\phi}$$

and m an integer for the azimuthal motion about the z-axis and then:

$$(v^2-1)\frac{d^2V}{dv^2} + 2v\frac{dV}{dv} - \frac{m^2}{v^2-1}V + 2\alpha vV + \left(\epsilon - \frac{\alpha}{2}\right)(v^2-1)V = \lambda V$$

$$(1-u^2)\frac{d^2U}{du^2} - 2u\frac{dU}{du} - \frac{m^2}{1-u^2}U + \left(\epsilon - \frac{\alpha}{2}\right)(1-u^2)U = -\lambda U$$

where λ is a separation of variables constant.

The azimuthal asymptotics is extracted by:

$$V(v) \mapsto \left[v^2 - 1\right]^{\frac{m}{2}} V(v) \qquad\qquad U(u) \mapsto \left[1 - u^2\right]^{\frac{m}{2}} U(u)$$

and the renormalised equations are:

$$(v^2 - 1)\frac{d^2V}{dv^2} + 2(m+1)v\frac{dV}{dv} + \left[\left(\epsilon - \frac{\alpha}{2}\right)(v^2 - 1) + 2\alpha v + m(m+1) - \lambda\right] V = 0$$

$$(1 - u^2)\frac{d^2U}{du^2} - 2(m+1)u\frac{dU}{du} + \left[\left(\epsilon - \frac{\alpha}{2}\right)(1 - u^2) - m(m+1) + \lambda\right] U = 0$$