Solution of the Schrödinger equation for a hydrogen atom

Suppose Schrödinger, in his 1926 *annus mirabilis* which seem to have been initiated by a trip to Arosa with 'an old girlfriend from Vienna' (apparently it was neither his wife Anny who remained in Zurich, nor Lotte, Irene and Felicie [1]), came down from the mountains and handed you over his *Schrödinger equation* for the hydrogen atom – actually, by his own accounts [2], he handed it over this eigenwert equation to Hermann Klaus Hugo Weyl –

$$\begin{aligned}
&\frac{1}{2\mu}\left(\mathscr{P}_x^2+\mathscr{P}_y^2+\mathscr{P}_z^2\right)\psi=(E-V)\,\psi \text{ , or, with } V=-\frac{e^2}{4\pi\epsilon_0 r},\\
&-\left[\frac{\hbar^2}{2\mu}\Delta+\frac{e^2}{4\pi\epsilon_0 r}\right]\psi(\mathbf{x})=E\psi \text{ , or}\\
&\left[\Delta+\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)\right]\psi(\mathbf{x})=0,
\end{aligned} \tag{1}$$

and asked you if you could be so kind to please solve it for him. Here might also hint that μ, e, and ϵ_0 stand for some (reduced) mass, charge, and the permittivity of the vacuum, respectively, $\hbar$ is a constant of (the dimension of) action, and E is some eigenvalue which must be determined from the solution of (1).

So, what could you do? First, observe that the problem is spherical symmetric, as the potential just depends on the radius $r=\sqrt{\mathbf{x}\cdot\mathbf{x}}$, and also the Laplace operator $\Delta=\nabla\cdot\nabla$ allows spherical symmetry. Thus we could write the Schrödinger equation (1) in terms of spherical coordinates (r,θ,φ) with $x=r\sin\theta\cos\varphi$, $y=r\sin\theta\sin\varphi$, $z=r\cos\theta$, whereby θ is the polar angle in the x–z-plane measured from the z-axis, with $0\le\theta\le\pi$, and φ is the azimuthal angle in the x–y-plane, measured from the x-axis with $0\le\varphi<2\pi$ (cf page **??**). In terms of spherical coordinates the Laplace operator essentially "decays into" (i.e. consists addiditively of) a radial part and an angular part

$$\begin{aligned}
\Delta &= \left(\frac{\partial}{\partial x}\right)^2+\left(\frac{\partial}{\partial y}\right)^2+\left(\frac{\partial}{\partial z}\right)^2\\
&=\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right.\\
&\quad\left.+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right].
\end{aligned} \tag{2}$$

Separation of variables Ansatz

This can be exploited for a *separation ov variable Ansatz*, which, according to Schrödinger, should be well known (in German *sattsam bekannt*) by now (cf chapter **??**). We thus write the solution ψ as a product of functions of separate variables

$$\psi(r,\theta,\varphi)=R(r)Y_l^m(\theta,\varphi)=R(r)\Theta(\theta)\Phi(\varphi) \tag{3}$$

The spherical harmonics $Y_l^m(\theta,\varphi)$ has been written already as a reminder of what has been mentioned earlier on page **??**. We will come back to it later.

[1] Walter Moore. *Schrödinger life and thought*. Cambridge University Press, Cambridge, UK, 1989

[2] Erwin Schrödinger. Quantisierung als Eigenwertproblem. *Annalen der Physik*, 384(4):361–376, 1926. ISSN 1521-3889. DOI: 10.1002/andp.19263840404. URL http://dx.doi.org/10.1002/andp.19263840404

Separation of the radial part from the angular one

For the time being, let us first concentrate on the radial part $R(r)$. Let us first totally separate the variables of the Schrödinger equation (1) in radial coordinates

$$\begin{aligned}\Big\{\tfrac{1}{r^2}\Big[\tfrac{\partial}{\partial r}\Big(r^2\tfrac{\partial}{\partial r}\Big)\\ &+\tfrac{1}{\sin\theta}\tfrac{\partial}{\partial\theta}\sin\theta\tfrac{\partial}{\partial\theta}+\tfrac{1}{\sin^2\theta}\tfrac{\partial^2}{\partial\varphi^2}\Big]\\ &+\tfrac{2\mu}{\hbar^2}\Big(\tfrac{e^2}{4\pi\epsilon_0 r}+E\Big)\Big\}\psi(r,\theta,\varphi)=0,\end{aligned}\tag{4}$$

and multiplying it with r^2

$$\begin{aligned}\Big\{\tfrac{\partial}{\partial r}\Big(r^2\tfrac{\partial}{\partial r}\Big)+\tfrac{2\mu r^2}{\hbar^2}\Big(\tfrac{e^2}{4\pi\epsilon_0 r}+E\Big)\\ +\tfrac{1}{\sin\theta}\tfrac{\partial}{\partial\theta}\sin\theta\tfrac{\partial}{\partial\theta}+\tfrac{1}{\sin^2\theta}\tfrac{\partial^2}{\partial\varphi^2}\Big\}\psi(r,\theta,\varphi)=0,\end{aligned}\tag{5}$$

so that, after division by $\psi(r,\theta,\varphi) = Y_l^m(\theta,\varphi)$ and writing separate variables on separate sides of the equation,

$$\begin{aligned}\tfrac{1}{R(r)}\Big\{\tfrac{\partial}{\partial r}\Big(r^2\tfrac{\partial}{\partial r}\Big)+\tfrac{2\mu r^2}{\hbar^2}\Big(\tfrac{e^2}{4\pi\epsilon_0 r}+E\Big)\Big\}R(r)\\ =-\tfrac{1}{Y_l^m(\theta,\varphi)}\Big\{\tfrac{1}{\sin\theta}\tfrac{\partial}{\partial\theta}\sin\theta\tfrac{\partial}{\partial\theta}+\tfrac{1}{\sin^2\theta}\tfrac{\partial^2}{\partial\varphi^2}\Big\}Y_l^m(\theta,\varphi)\end{aligned}\tag{6}$$

Because the left hand side of this equation is independent of the angular variables θ and φ, and its right hand side is independent of the radius r, both sides have to be constant; say λ. Thus we obtain two differential equations for the radial and the angular part, respectively

$$\left\{\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)\right\}R(r)=\lambda R(r),\tag{7}$$

and

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_l^m(\theta,\varphi)=-\lambda Y_l^m(\theta,\varphi).\tag{8}$$

Separation of the polar angle θ from the azimuthal angle φ

As already hinted in Eq. (32) The angular portion can still be separated by the *Ansatz* $Y_l^m(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$, because, when multiplied by $\sin^2\theta/\Theta(\theta)\Phi(\varphi)$, Eq. (8) can be rewritten as

$$\left\{\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}+\lambda\sin^2\theta\right\}+\frac{1}{\Phi(\varphi)}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2}=0,\tag{9}$$

and hence

$$\tfrac{\sin\theta}{\Theta(\theta)}\tfrac{\partial}{\partial\theta}\sin\theta\tfrac{\partial\Theta(\theta)}{\partial\theta}+\lambda\sin^2\theta=-\tfrac{1}{\Phi(\varphi)}\tfrac{\partial^2\Phi(\varphi)}{\partial\varphi^2}=m^2,\tag{10}$$

where m is some constant.

Solution of the equation for the azimuthal angle factor $\Phi(\varphi)$

The resulting differential equation for $\Phi(\varphi)$

$$\frac{d^2\Phi(\varphi)}{d\varphi^2} = -m^2\Phi(\varphi), \tag{11}$$

has the general solution

$$\Phi(\varphi) = Ae^{im\varphi} + Be^{-im\varphi}. \tag{12}$$

As Φ must obey the periodic poundary conditions $\Phi(\varphi) = \Phi(\varphi + 2\pi)$, m must be an integer. The two constants A, B must be equal if we require the system of functions $\{e^{im\varphi} | m \in \mathbb{Z}\}$ to be orthonormalized. Indeed, if we define

$$\Phi_m(\varphi) = Ae^{im\varphi} \tag{13}$$

and require that it normalized, it follows that

$$\begin{aligned}
&\int_0^{2\pi} \overline{\Phi}_m(\varphi)\Phi_m(\varphi)d\varphi \\
&\quad = \int_0^{2\pi} \overline{A}e^{-im\varphi}Ae^{im\varphi}d\varphi \\
&\quad = \int_0^{2\pi} |A|^2 d\varphi \\
&\quad = 2\pi|A|^2 \\
&\quad = 1,
\end{aligned} \tag{14}$$

it is consistent to set

$$A = \frac{1}{\sqrt{2\pi}}; \tag{15}$$

and hence,

$$\Phi_m(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}} \tag{16}$$

Note that, for different $m \neq n$,

$$\begin{aligned}
&\int_0^{2\pi} \overline{\Phi}_n(\varphi)\Phi_m(\varphi)d\varphi \\
&\quad = \int_0^{2\pi} \frac{e^{-in\varphi}}{\sqrt{2\pi}}\frac{e^{im\varphi}}{\sqrt{2\pi}}d\varphi \\
&\quad = \int_0^{2\pi} \frac{e^{i(m-n)\varphi}}{2\pi}d\varphi \\
&\quad = -\left.\frac{ie^{i(m-n)\varphi}}{2(m-n)\pi}\right|_0^{2\pi} \\
&\quad = 0,
\end{aligned} \tag{17}$$

because $m - n \in \mathbb{Z}$.

Solution of the equation for the polar angle factor $\Theta(\theta)$

The left hand side of Eq. (10) contains only the polar coordinate. Upon division by $\sin^2\theta$ we obtain

$$\begin{aligned}
&\frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta(\theta)}{d\theta} + \lambda = \frac{m^2}{\sin^2\theta}, \text{ or} \\
&\frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta(\theta)}{d\theta} - \frac{m^2}{\sin^2\theta} = -\lambda,
\end{aligned} \tag{18}$$

Now, first, let us consider the case $m = 0$. With the variable substitution $x = \cos\theta$, and thus $\frac{dx}{d\theta} = -\sin\theta$ and $dx = -\sin\theta\, d\theta$, we obtain from (18)

$$\begin{array}{l} \frac{d}{dx}\sin^2\theta \frac{d\Theta(x)}{dx} = -\lambda\Theta(x), \\ \frac{d}{dx}(1-x^2)\frac{d\Theta(x)}{dx} + \lambda\Theta(x) = 0, \\ \left(x^2-1\right)\frac{d^2\Theta(x)}{dx^2} + 2x\frac{d\Theta(x)}{dx} = \lambda\Theta(x), \end{array} \tag{19}$$

which is of the same form as the *Legendre equation* (**??**) mentioned on page **??**.

The form $\lambda = l(1+1)$ is obtained from the requirement that Consider the series *Ansatz*

$$\Theta(x) = a_0 + a_1x + a_2x^2 + \cdots + a_kx^k + \cdots \tag{20}$$

for solving (19). Insertion into (19) and comparing the coefficients of x for equal degrees yields the recursion relation

This is actually a “shortcut” solution of the Fuchian Equation mentioned earlier.

$$\begin{array}{l} \left(x^2-1\right)\frac{d^2}{dx^2}[a_0 + a_1x + a_2x^2 + \cdots + a_kx^k + \cdots] \\ \quad +2x\frac{d}{dx}[a_0 + a_1x + a_2x^2 + \cdots + a_kx^k + \cdots] \\ \quad = \lambda[a_0 + a_1x + a_2x^2 + \cdots + a_kx^k + \cdots], \\ \left(x^2-1\right)[2a_2 + \cdots + k(k-1)a_kx^{k-2} + \cdots] \\ \quad +[2xa_1 + 2x2a_2x + \cdots + 2xka_kx^{k-1} + \cdots] \\ \quad = \lambda[a_0 + a_1x + a_2x^2 + \cdots + a_kx^k + \cdots], \\ \left(x^2-1\right)[2a_2 + \cdots + k(k-1)a_kx^{k-2} + \cdots] \\ \quad +[2a_1x + 4a_2x^2 + \cdots + 2ka_kx^k + \cdots] \\ \quad = \lambda[a_0 + a_1x + a_2x^2 + \cdots + a_kx^k + \cdots], \end{array} \tag{21}$$

and thus, by taking all polynomials of the order of k and proportional to x^k, so that, for $x^k \neq 0$ (and thus excluding the trivial solution),

$$\begin{array}{l} k(k-1)a_kx^k + (k+2)(k+1)a_{k+2}x^k + 2ka_kx^k - \lambda a_kx^k = 0, \\ k(k+1)a_k + (k+2)(k+1)a_{k+2} - \lambda a_k = 0, \\ a_{k+2} = a_k\frac{\lambda - k(k+1)}{(k+2)(k+1)}. \end{array} \tag{22}$$

In order to converge also for $x = \pm 1$, and hence for $\theta = 0$ and $\theta = \pi$, the sum in (20) has to have only *a finite number of terms.* That means that, in Eq. (22) for some $k = l \in \mathbb{N}$, the coefficient $a_{l+2} = 0$ has to vanish; thus

$$\lambda = l(l+1). \tag{23}$$

This results in *Legendre polynomials* $\Theta(x) \equiv P_l(x)$.

Let us now shortly mention the case $m \neq 0$. With the same variable substitution $x = \cos\theta$, and thus $\frac{dx}{d\theta} = -\sin\theta$ and $dx = -\sin\theta\, d\theta$ as before, the equation for the polar dependent factor (18) becomes

$$\left\{\frac{d}{dx}(1-x^2)\frac{d}{d\theta} + l(l+1) - \frac{m^2}{(1-x^2)}\right\}\Theta(x) = 0, \tag{24}$$

This is exactly the form of the general Legendre equation (**??**), whose solution is a multiple of the associated Legendre polynomial $\Theta_l^m(x) \equiv P_l^m(x)$, with $|m| \leq l$.

Solution of the equation for radial factor $R(r)$

The solution of the equation (7)

$$\begin{aligned}&\left\{\frac{d}{dr}r^2\frac{d}{dr}+\frac{2\mu r^2}{4\pi\epsilon_0\hbar^2}\left(\frac{e^2}{r}+E\right)\right\}R(r)=l(l+1)R(r)\text{ , or}\\&-\frac{1}{R(r)}\frac{d}{dr}r^2\frac{d}{dr}R(r)+l(l+1)-\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2}r=\frac{2\mu}{\hbar^2}r^2E\end{aligned} \tag{25}$$

for the radial factor $R(r)$ turned out to be the most difficult part for Schrödinger [3].

[3] Walter Moore. *Schrödinger life and thought*. Cambridge University Press, Cambridge, UK, 1989

Note that, since the additive term $l(l+1)$ in (25) is dimensionless, so must be the other terms. We can make this more explicit by the substitution of variables.

First, consider $y=\frac{r}{a_0}$ obtained by dividing r by the *Bohr radius*

$$a_0=\frac{4\pi\epsilon_0\hbar^2}{m_e e^2}\approx 5\,10^{-11}m, \tag{26}$$

thereby assuming that the reduced mass is equal to the electron mass $\mu\approx m_e$. More explicitly, $r=y\frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$. Second, define $\varepsilon=E\frac{2\mu a_0^2}{\hbar^2}$.

These substitutions yield

$$\begin{aligned}&-\frac{1}{R(y)}\frac{d}{dy}y^2\frac{d}{dy}R(y)+l(l+1)-2y=y^2\varepsilon,\text{ or}\\&-y^2\frac{d^2}{d^2y}R(y)-2y\frac{d}{dy}R(y)+\left[l(l+1)-2y-\varepsilon y^2\right]R(y)=0.\end{aligned} \tag{27}$$

Now we introduce a new function $\hat{R}$ *via*

$$R(x)=\eta^l e^{-\frac{1}{2}\eta}\hat{R}(\eta), \tag{28}$$

with $\eta=\frac{2y}{n}$ and by relacing the energy variable with a quantized one; that is, $\varepsilon=-\frac{1}{n^2}$, with $n\in\mathbb{N}-0$. We end up with an *associated Laguerre equation* of the form

$$\left\{\eta\frac{d^2}{d^2\eta}+[2(l+1)-\eta]\frac{d}{d\eta}+(n-l-1)\right\}\hat{R}(\eta)=0. \tag{29}$$

This is The polynomial solutions are the *Laguerre polynomials*, the solutions as the *associated Laguerre polynomials* L_{n+l}^{2l+1} which are the the $(2l+1)$-th derivatives of the Laguerre's polynomials L_{n+l}^{2l+1}; that is,

$$\begin{aligned}&L_n(x)=e^x\frac{d^n}{dx^n}\left(x^ne^{-x}\right),\\&L_n^m(x)=\frac{d^m}{dx^m}L_n(x).\end{aligned} \tag{30}$$

This yields a normalized wave function

$$\begin{aligned}&R_n(r)=\mathcal{N}\left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{a_0n}}L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)\text{, with}\\&\mathcal{N}=-\frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{[(n+l)!a_0]^3}},\end{aligned} \tag{31}$$

where $\mathcal{N}$ stands for the normalization factor.

Composition of the general solution of the Schrödinger Equation

Now we shall coagulate and combine the factorized solutions (32) into a complete solution of the Schrödinger equation

Always remember the alchemic principle of *solve et coagula*!

$$
\begin{aligned}
&\psi_{n,l,m}(r,\theta,\varphi) \\
&\quad = R_n(r)\,Y_l^m(\theta,\varphi) \\
&\quad = R_n(r)\Theta_l^m(\theta)\Phi_m(\varphi) \\
&\quad = -\frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{[(n+l)!a_0]^3}}\left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{a_0 n}}\,L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)P_l^m(x)\,\frac{e^{im\varphi}}{\sqrt{2\pi}}.
\end{aligned}
\tag{32}
$$

Bibliography

Walter Moore. *Schrödinger life and thought*. Cambridge University Press, Cambridge, UK, 1989.

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