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NOTE

Schrodinger Equation for the Hydrogen Atom - A Simplified Treatment

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Abstract: A simple method is presented here for solving the wave mechanical problem of the hydrogen atom. The normal method of converting the Cartesian coordinates into polar coordinates is tedious and also requires an understanding of the Legendre and Lagurre polynomials. In this paper we are using an alternative method, which requires only minimal familiarity with mathematical concepts and techniques.

Keywords: Schrödinger equation, Euler's theorem on homogeneous functions, Laplace equation.

The equation¹ $\nabla^2 \psi + \left(\frac{2\mu}{\hbar^2}\right) \left(E + \frac{e^2}{r}\right) \psi = 0$ is usually solved by expressing '∇²' in spherical polar coordinates²⁻⁴. The following is an alternative treatment of the same problem. Implicitly it is equivalent to the usual textbook treatment but explicitly it is easier to follow

The following assumptions are made. Their justification is a posteriori, since they yield the correct solution.

Assumption 1

Since the potential energy contains r explicitly, we choose ψ , a product function *i.e.*, $\psi = \psi_1 \psi_2$ where ψ_1 depends on r alone, while no restriction of a similar kind is placed on ψ_2 ; we have thus, a certain freedom regarding the choice of ψ_2 . We exercise this freedom in selecting a convenient form for ψ_2 .

Thus
$$\nabla^2 (\psi_1 \psi_2) + \left(\frac{2\mu}{\hbar^2}\right) \left(E + \frac{e^2}{r}\right) (\psi_1 \psi_2) = 0 \quad (1)$$

$$\Psi_2 (\nabla^2 \Psi_1) + \Psi_1 (\nabla^2 \Psi_2) + 2(\text{grad } \Psi_1) \cdot (\text{grad } \Psi_2) + \left(\frac{2\mu}{\hbar^2} \right) \left(E + \frac{e^2}{r} \right) (\Psi_1 \Psi_2) = 0 \quad (2)$$

Note: $\text{grad } \Psi_1$ = gradient vector of Ψ_1

$$= \hat{i} \frac{\partial \Psi_1}{\partial x} + \hat{j} \frac{\partial \Psi_1}{\partial y} + \hat{k} \frac{\partial \Psi_1}{\partial z}$$

$(\text{grad } \Psi_1) \cdot (\text{grad } \Psi_2)$ is the dot product of the gradient vectors *i.e.*,

$$\frac{\partial \Psi_1}{\partial x} \frac{\partial \Psi_2}{\partial x} + \frac{\partial \Psi_1}{\partial y} \frac{\partial \Psi_2}{\partial y} + \frac{\partial \Psi_1}{\partial z} \frac{\partial \Psi_2}{\partial z}$$

Assumption 2

We now choose Ψ_2 to be (i) a homogeneous function of degree ℓ in (x, y, z) , of such a nature that (ii) it is a solution of the equation “ $\nabla^2 \Psi = 0$ ” (Laplace equation⁵), such a function is called a spherical harmonic. The advantages of this choice are two. First, the term $\nabla^2 \Psi_2$ drops out in the equation (2) above. Further since Ψ_1 is a function of r alone,

$$\frac{\partial \Psi_1}{\partial x} = \frac{\partial \Psi_1}{\partial r} \times \frac{\partial r}{\partial x} = \frac{x}{r} \frac{\partial \Psi_1}{\partial r}$$

with similar expressions for y and z . Therefore, the term

$$2(\text{grad } \Psi_1) \cdot (\text{grad } \Psi_2) = \frac{2}{r} \frac{d\Psi_1}{dr} \left(x \frac{\partial \Psi_2}{\partial x} + y \frac{\partial \Psi_2}{\partial y} + z \frac{\partial \Psi_2}{\partial z} \right)$$

and this, by Euler’s theorem⁶, becomes $\left(\frac{2\ell \Psi_2}{r} \right) \frac{d\Psi_1}{dr}$

After cancellation of Ψ_2 equation (2) may now be written as

$$\nabla^2 \Psi_1 + \frac{2\ell}{r} \frac{d\Psi_1}{dr} + \left(\frac{2\mu}{\hbar^2} \right) \left(E + \frac{e^2}{r} \right) \Psi_1 = 0 \quad (3a)$$

It is now easy to show that $\Psi_1 = e^{-kr}$ is a solution of equation (3a) *viz*

$$\frac{d^2 \Psi_1}{dr^2} + \frac{2(\ell+1)}{r} \frac{d\Psi_1}{dr} + \left(\frac{2\mu}{\hbar^2} \right) \left(E + \frac{e^2}{r} \right) \Psi_1 = 0 \quad (3b)$$

Substitution of $\Psi_1 = e^{-kr}$ and simplification gives in this case

$$K^2 - \frac{2(\ell+1)}{r} K + \left(\frac{2\mu}{\hbar^2} \right) \left(E + \frac{e^2}{r} \right) = 0$$

Equating separately to zero, terms involving $\frac{1}{r}$ and terms independent of r , one gets

$$E = - \left(\frac{\hbar^2}{2\mu} \right) K^2 \text{ and } \left(\frac{\mu e^2}{\hbar^2} \right) = (\ell+1) K$$

$$\therefore E = - \left(\frac{2\pi^2 \mu e^4}{(\ell+1)^2 \hbar^2} \right)$$

It is further possible to select a function Ψ_2 for each value of ℓ .

ℓ	Ψ
0	Constant
1	x, y, z
2	xy, zx, yz, $(x^2 - y^2)$
..	$(x^2 - z^2), (y^2 - z^2)$

Note

The six functions chosen for Ψ_2 for $\ell = 2$ are not, all linearly independent. Thus one chooses xy, xz, yz, $(x^2 - y^2)$ and a linear combination of $(x^2 - z^2)$ and $(y^2 - z^2)$ as five linearly independent functions.

Assumption 3

The choice $\Psi_1 = e^{-kr}$ is too restrictive. One may therefore try $\Psi_1 = fe^{-kr}$, where $f = \sum_{p=0}^t a_p r^p$

is a polynomial in r of degree t. Equation (3) now gives.

$$(D - K)^2 f + \frac{2(\ell + 1)}{r} (D - K)f + \left(\frac{2\mu}{\hbar^2} \right) \left(E + \frac{e^2}{r} \right) f = 0 \quad (4)$$

$$\text{Where } D = \frac{d}{dr}.$$

The coefficient of r^t in this is $\left[K^2 + \left(\frac{2\mu E}{\hbar^2} \right) \right] a_t$.

Equating this to zero, we have recovered the relationship shown earlier between E and K.

Further the coefficient of r^{t-1} is $\left[-2Kt - 2(\ell + 1)K + \frac{2\mu e^2}{\hbar^2} \right] a_t$.

Equated to zero, this gives $K = \left(\frac{\mu e^2}{(\ell + t + 1) \hbar^2} \right)$

$$\text{Thus } E = - \left(\frac{2\pi^2 \mu e^4}{(\ell + t + 1)^2 \hbar^2} \right)$$

We may now identify $(\ell + t + 1)$ with the principal quantum number, n and ℓ with the (so called) azimuthal quantum number. The choice " $\ell = 0$ " gives the 's' orbitals, for which $t = (n - 1)$ is the degree of the polynomial 'f', for any given value of n. For $n = 1$, ($\ell = 0$, $t = 0$) is the only possible choice of ℓ and t, viz, the 1s orbital. For $n = 2$, ($\ell = 0$, $t = 1$) gives the '2s' orbital, which is accidentally degenerate with ($\ell = 1$, $t = 0$) viz. the three p orbitals (see table 1).

Their functional forms are (xe^{-kr}) , (ye^{-kr}) and (ze^{-kr}) . With $n = 3$, $\ell = 0$, $t = 2$, ($\ell = 1$, $t = 1$) and ($\ell = 2$, $t = 0$) yield the 3s, 3p and 3d orbitals. The functional forms of the orbitals present no difficulty. An examination of equation (4) shows that the coefficient of r^s equated to zero gives

$$a_{s+2} = \frac{-(t - s - 1)2K}{(s + 2)(2\ell + s + 3)} a_{s+1} \quad (5)$$

The largest and smallest values of $(s + 2)$ are t and 0 . Thus 's' varies from -2 to $(t - 2)$. The choice $s = -2$ gives the result that a_0 is indeterminate, since, in equation (5), a_{s+1} and $(S+2)$ are both zero for $s = -2$. For the other values of 's', equation (5) is the recurrence relation for the coefficients of powers of 'r' in f.

e.g., 1

2s orbital, $\ell = 0, t = 1$,

$$a_{s+2} = \left(\frac{Sx2K}{(S+2)(S+3)} \right) a_{s+1}. \text{ Put } S = -1 \quad a_1 = -\left(\frac{2K}{1 \times 2} \right) a_0.$$

Therefore f has the form $a_0(1 - kr)$ and ψ has the form, (constant) $(1 - kr)e^{-kr}$

e.g., 2

By a similar reasoning, we get the following results for $n = 3$

$$(\ell = 0, t = 2): \quad \psi = (\text{constant}) \left(1 - 2kr + \frac{2}{3} k^2 r^2 \right) e^{-kr}$$

$$(\ell = 1, t = 1): \quad \psi = (\text{constant}) \left(1 - \frac{kr}{2} \right) e^{-kr} \quad (x \text{ or } y \text{ or } z), \text{ three functions.}$$

($\ell = 2, t = 0$): $\psi = (\text{constant}) e^{-kr}$ (any of the five functions, $xz, xy, \dots$ (c.f Table). The constants in the above forms may be determined by normalization. Thus, the method outlined above yields the real forms of the orbitals of the hydrogen like atom, in a straightforward manner. Its merit is that there is no need here to struggle with the Legendre and Lagurre differential equations.

The method gives the real forms of orbitals directly. This has the advantage of visualizing the shapes of orbitals, including their nodes, and overlaps in chemical bonding. Further one may easily construct their linear combinations as eigen functions of L_z operator, if and when needed. For students and with no familiarity with the special functions of mathematical physics, the above method is mathematically transparent and demands no further knowledge than elementary calculus.

References

1. Schrödinger E, *Ann.Physik*, 1926, **79**, 361.
2. Schrödinger E, *Ann.Physik*, 1926, **80**, 437.
3. Epstein P S, *Phys.Rev.* 1926, **28**, 695.
4. Walter I, *Z.Physik*, 1926, **38**, 635.
5. Séroul R, *Programming for Mathematicians*, Springer-Verlag, 2000, p.15.
6. Shanks D, *Solved and Unsolved Problems in Number Theory*, 4th Ed., 1993, p.21, 23-25.