§11.1 The Schrödinger Equation in 3d

In three-dimensions, the $\mathcal{S}$ eq. is

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U(x,y,z)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

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Here, too, if we assume that

$$\Psi(x,y,z,t) = \psi(x,y,z)\phi(t)$$

then we get

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(x,y,z)\psi = E\psi$$

$$i\hbar\frac{\partial\phi}{\partial t} = E\phi$$

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§11.2 Spherical Symmetry

A convenient coordinate to use here is the usual radial coordinate r, given by

$$r^2 = x^2 + y^2 + z^2$$

(1) Find $\partial r/\partial x$.

$$2r\frac{\partial r}{\partial x} = 2x$$

So

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

The same holds for y and z.

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(2) If $f = f(r)$ is a function of r, what is $\partial f/\partial x$?

$$\frac{\partial f(r)}{\partial x} = \frac{df(r)}{dr}\frac{\partial r}{\partial x} = \frac{x}{r}\frac{df(r)}{dr}$$

Assuming that ψ is a function of r alone,

$$\frac{\partial\psi}{\partial x} = \frac{x}{r}\frac{d\psi}{dr}$$

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(3) Find $\partial^2\psi/\partial x^2$.

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{x}{r}\right)\frac{d\psi}{dr} + \frac{x}{r}\frac{\partial}{\partial x}\frac{d\psi}{dr}$$

$$= \left(\frac{1}{r} - \frac{x}{r^2}\cdot\frac{x}{r}\right)\frac{d\psi}{dr} + \frac{x^2}{r^2}\frac{d^2\psi}{dr^2}$$

$$= \frac{1}{r}\frac{d\psi}{dr} - \frac{x^2}{r^3}\frac{d\psi}{dr} + \frac{x^2}{r^2}\frac{d^2\psi}{dr^2}$$

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(4) Find $\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$.

$$\nabla^2\psi = \frac{3}{r}\frac{d\psi}{dr} - \frac{x^2+y^2+z^2}{r^3}\frac{d\psi}{dr} + \frac{x^2+y^2+z^2}{r^2}\frac{d^2\psi}{dr^2}$$

$$= \frac{2}{r}\frac{d\psi}{dr} + \frac{d^2\psi}{dr^2}$$

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ADDITIONAL NOTES

Let $f' \equiv df/dr$.

(5) What's $(r\psi)'$?

$$\psi + r\psi'$$

(6) What's $(r\psi)''$?

$$2\psi' + r\psi''$$

(7) Recognize this?

It's $r\nabla^2\psi$.

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Let $\hat{\psi}(r) = r\psi(r)$.

(8) Write the 3-d time-ind. $\mathcal{S}$ eq.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + U(x,y,z)\psi(r) = E\psi(r)$$

in terms of $\hat{\psi}(r)$. (Hint: Multiply the above by r.)

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$$r\left(-\frac{\hbar^2}{2m}\nabla^2\psi(r) + U(x,y,z)\psi(r)\right) = E\big(r\psi(r)\big) = E\hat{\psi}(r)$$

$$-\frac{\hbar^2}{2m}\hat{\psi}''(r) + U(r)\hat{\psi}(r) = E\hat{\psi}(r)$$

All this is true for any spherically symmetric case.

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§11.3 The Hydrogen Atom

Since the proton is around a thousand times as massive as the electron (similar to the sun-Jupiter system), we'll consider this as a problem of an electron moving in an electrostatic potential created by a fixed proton.

The potential is only a function of the distance between the electron and the proton.

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For the Hydrogen atom,

$$U(r) = -k\frac{e^2}{r}$$

The equation for $\hat{\psi}$ becomes

$$-\frac{\hbar^2}{2m_e}\hat{\psi}''(r) - k\frac{e^2}{r}\hat{\psi}(r) = E\hat{\psi}(r)$$

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Let's try $\hat{\psi}(r) = re^{-\alpha r}$.

(9) Find $\hat{\psi}'(r)$.

$$\hat{\psi}'(r) = e^{-\alpha r} - r\alpha e^{-\alpha r}$$

(10) Find $\hat{\psi}''(r)$.

$$\hat{\psi}''(r) = -2\alpha e^{-\alpha r} + r\alpha^2 e^{-\alpha r}$$

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ADDITIONAL NOTES

(11) Plug this into the $\mathcal{S}$ eq.

$$-\frac{\hbar^2}{2m_e}\left(-2\alpha e^{-\alpha r}+r\alpha^2 e^{-\alpha r}\right)-k\frac{e^2}{r}re^{-\alpha r}=Ere^{-\alpha r}$$

For this to be a respectable solution, it must work for all r.

(12) What's a good r to try?

$$r=0$$

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(13) So, what's α?

$$\frac{\hbar^2}{m_e}\alpha-ke^2=0$$

$$\alpha=\frac{km_e e^2}{\hbar^2}$$

(14) Does this look familiar? Yesssss!!!!!

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α^{-1} is the first Bohr radius.

The associated E is the ground state Bohr energy.

We get $\psi(x)=C\hat{\psi}(x)/r=Ce^{-r/r_1}$, where C is fixed by normalization.

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§11.4 Remarks on Helium

We model this, again, as a fixed nucleus with two electrons buzzing around it.

The potential energy is

$$-k\frac{2e^2}{r_1}-k\frac{2e^2}{r_2}+k\frac{e^2}{r_{12}}$$

(15) Can you interpret these terms? Yes.

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The problem can be treated exactly if we ignore the electron-electron interaction.

It can be treated approximately, with that term.

The analysis gives energy levels that agree with observation.

This may also be done with more complicated atoms.

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ADDITIONAL NOTES

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