Introduction to Nanoelectronics

Prof. Supriyo Datta
ECE 453
Purdue University

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Lecture 13: Atomic Energy Levels

Ref. Chapter 2.3 & 3.1

Network for Computational Nanotechnology

NCN
nanoHUB
online simulations and more

3D Schrödinger Equation

00:03

- 3D Schrödinger equation is:

$$E\Phi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) \right)\Phi$$

- Considering only one dimension:

$$E\Phi = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x) \right)\Phi$$

- We've learned how to turn this into a matrix equation using method of finite differences through which one can find the eigenvalues and eigenvectors.
- In 3D, we've discussed that the size of matrices can get very large if one tries to turn the whole 3D equation into a matrix equation. But under certain conditions we can use the idea of separation of variables which is very powerful in making the problem more tractable. (discussed last day)

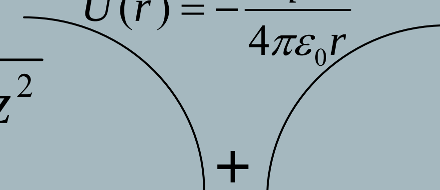
- We can use Separation of variables if the potential can be written as:

$$U(x,y,z) = U_x(x) + U_y(y) + U_z(z)$$

- If that is satisfied the one 3 dimensional problem can be written as 3 one dimensional problems which is easier to handle.
- What we want to talk about today is how the energy levels look like for atoms. We start with the simplest of all atoms: hydrogen atom.
- The potential that the electron sees in the hydrogen atom is:

$$U(\vec{r}) = -\frac{q^2}{4\pi\varepsilon_0 r}$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

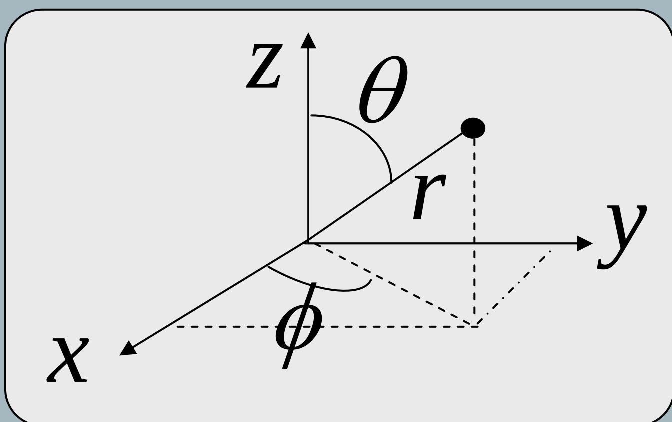


- The expression for "r" shows that this potential is not separable in Cartesian coordinates but it will be in spherical coordinates…

Spherical Coordinates

08:46

- In spherical coordinates the variables are:



- The potential in spherical coordinates depends only on “r” and it is separable. It can be written as 3 function of r, theta and phi where the function of and phi are basically zero.
- The hard thing about this coordinate system is that operators are much more complicate; hence more complicated to work with.

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

In Cartesian coordinates

$$\equiv \left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

In Spherical coordinates

Spherical Harmonics 1

• For potentials that are symmetric in "r" and do not depend on theta or phi one can write the solutions to the Schrödinger equation as:

$$\boxed{U(\vec{r}) = -\frac{q^2}{4\pi\varepsilon_0 r}}$$

$$\Phi(\mathrm{r},\theta,\varphi) = \underbrace{\frac{f(r)}{r}}_{Radial}\underbrace{Y_l^m(\theta,\varphi)}_{Angular}$$

• The function "f" can be found by solving a 1D equation: $Ef(r) = \left(\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} - U(\vec{r}) + \ldots\right)\mathrm{f(r)}$

• The angular part is already known for any atom whose potential does not depend on theta or phi. One only has to find the redial part. The Y(l,m) are called spherical harmonics. Let's discuss them more:

$$\nabla^2 \equiv \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\overbrace{\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)}^{\mathrm{L}}$$

• If we act operator "L" on Y(l,m)' s we get: $\mathrm{L}(\theta,\phi)\mathrm{Y}_l^m = -l(l+1)\mathrm{Y}_l^m$
We see that the operator acts on the function and generates the same function with a multiplicative constant. In such cases the functions are called to be the eigenfunctions of the operator. The property of Y(l,m) 's is that they are eigenfunctions of "L".

Spherical Harmonics 2

- The simplest Y(l,m) is Y(0,0) and is just a constant: Y(0,0)=1.
- The general rule is:

$$\text{If } l = n \text{ then}$$

$$m = -n, -n+1, \ldots, 0, \ldots, n-1, n$$

$$n = 0, 1, 2, \ldots$$

- So : if *l* = 1 then m = -1, 0, 1 and the Y(l,m)'s are:

$$Y_0^0 = 1$$

$$Y_1^0 = \cos(\theta)$$

$$Y_1^{\pm 1} = \sin(\theta) e^{\pm i\phi}$$

- Let's see if Y(1,0) is an eigenfunction of the operator "L"…

$$LY_1^0 = (\text{some constant}) \times Y_1^0 \quad ?$$

$$L = \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

- $$\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}(\cos\theta) = 0 \quad (1)$$
- $$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)(\cos\theta) =$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta \cdot -\sin\theta) =$$

$$\frac{1}{\sin\theta}(-2\sin\theta\cos\theta) = -2\cos\theta \quad (2)$$

- (1) & (2) => $LY_1^0 = -2 \times Y_1^0$

$$where \quad -l(l+1) = -1(1+1) = -2$$

Solution of Schrödinger Equation

26:03

- Back to the solution of Schrödinger equation. Consider the function:

$$\Phi(r,\theta,\varphi) = g(r)Y_l^{\,m}(\theta,\varphi) \qquad g(r) \equiv f(r)/r$$

- Putting this answer into the Schrödinger equation, $E\Phi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\Phi$ we get:

$$Eg\cancel{Y_l^m} = \left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)g - \frac{\hbar^2}{2mr^2}l(l+1)g + Ug\right]\cancel{Y_l^m}$$

$$\text{Note:}\quad \mathrm{L}(\theta,\phi)\mathrm{Y}_l^{\,m} = -l(l+1)\mathrm{Y}_l^{\,m} \;\text{ has been used.}$$

- Using g(r)=f(r)/r, we get the final result:

$$Ef(r) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + U(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right)f(r)$$

Hydrogen Energy Levels

36:00

$$Ef(r) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + U(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right) f(r)$$

- We can now talk about energy levels in H atom:
- Since the potential in Hydrogen atom has the form of 1/r, the levels 2s and 2p are at the same energy. This does not have to be the case for other atoms. Also note that for each value of “l”, there are 2l+1 values of “m” that have the same energy. So when l=1, m=-1,0,1 and the levels comes in triplets. When l=2, there will be 5 degenerate levels.
- One thing to remember is that anytime the Potential is spherically symmetric, the solutions to Schrödinger equation can be written as:

$$\Phi(\mathrm{r}, \theta, \varphi) = g(r) Y_l^{\,m}(\theta, \varphi)$$