

Module code - Lecture 21

Week 8

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Basic functions

Now, in the last series of videos, when we set up our general program, we talked about how we were going to create multiple matrices in each matrix element, would actually be a global integral space of some basis functions times to operator times another basis function.

One might ask why we choose one set of basis functions over another set of basis functions the way we do.

Our basis functions come down to how we can evaluate integrals on a computer.

If I have a function on a computer and we say it's $F(R)$, there are two ways to take an integral on that function.

1. The first is to create a finite grid and evaluate the function at each point on the grid, and then perform a Riemann sum by multiplying the value of a point by the width of the grid to get an estimate of the area. And if I move the points closer together, I can actually get the area under the curve.

$$M_{ij} = \int_{-\infty}^{+\infty} \phi_i^*(x, y, z) \widehat{M} \phi_j^*(x, y, z)$$

So to do this, I have to not only know what my function is, but I have to evaluate it on several different points and then some. All those points up there.

2. The second way to do an integral on a computer is to take a function whose anti-derivative I know and evaluate the anti-derivative at both ends.

INSERT FIGURE HERE

So here I only have to evaluate a function twice, but I need to know what the antiderivative of the function I'm trying to evaluate is.

$$f(r)r^2 dr = \sum f(r_i) * r_i^2 * \Delta r$$

INSERT FIGURE HERE

This is much easier and faster to implement. However, we need to have a function for which we know how to calculate it. We already need to know the response of the integral, and that's where Gaussian functions come in. All of the integrals we are going to study are an integral of the global space. If we look at a one-dimensional Gaussian, the interval over a one-dimensional Gaussian rate at some exponent α is equal to the root $\sqrt{\pi/\alpha}$. And our three-dimensional Gaussians, we will be able to separate into a Gaussian, an X , a Y and a Z .

INSERT FIGURE HERE

$$f(r)r^2 dr = F(r_b) - F(r_a)$$

And so the total interval for all of space would be equal to $\sqrt{\pi/a}$ or $\sqrt{\pi/\alpha^3}$ and we can do this really quite trivially. And our ability to evaluate these integrals, knowing this theorem is the reason why we use Gaussian functions for electronic structure theories. Just because we can do these calculations, we need these integrals and we need to evaluate the matrix elements as quickly as possible. So, if we use these functions as basis functions $\int f(r)r^2 dr = F(r_b) - F(r_a)$, it is quite reasonable to ask how close they are to real electronic wave functions.

And the answer $\int_{-\infty}^{\infty} e^{-\alpha x^2}$ is quite good.

So we know from the resolution of the hydrogen atom that a single electron orbital should not move away from the nucleus by a kind of exponential function. So here I have drawn the radial part of the carbon atom. The s orbital. And it has some functions. Normalize even the least λ_r where the electron would be some kind of decay. If we fit this to a simple Gaussian function. We have something that looks quite different. So Orange is the best Gaussian fit to this exponential. And we notice that it's rounded up here. It doesn't capture the electron wave, the electron wave function near the core. There's no peak as there should be in the case where the long part and the long-distance part are too fast. So, it doesn't really give us the right behavior. Using a Gaussian as an orbital might allow us to calculate things quickly, but maybe not as accurately. The way we do the calculations is: for a given basis function.

INSERT FIGURE HERE

We make it the sum of several Gaussians. So, in orange, this is the best fit to a single Gaussian. In yellow, if we take six Gaussians, add them up and call it a basis function, we get something a little bit closer to the real function. It's a bit sharper. It's still slightly rounded.

INSERT FIGURE HERE

We can make more peaks by adding more Gaussian functions, but at some point, we have to compromise between accuracy and speed. So we will use six Gaussian functions $\psi = N e^{-\alpha r^2}$ for the $1s$ orbital and the percentage of each Gaussian we add is fixed. So, whenever we talk about this particular basis function, we have a fixed value. The survival C that would be fixed for each of these individual Gaussians

INSERT FIGURE HERE

And we call the combined C the degree of contraction. The C is the exponent and the B_i is the normalization, so if we didn't have the C here and integrated it into each of the mine outliers by our global squared space, it would be one.

So this makes us normalize the system to a normalized Gaussian. And that was the type of basis function that we're going to use. We're going to have a number of these basis functions for each atom that we want to study.

So when you think about the set of basis functions that you're going to use, you're going to have a number of basis functions for each atom, and each basis function can include several Gaussian functions and represent them on a computer.

We're going to build an array, which technically will be an array structure of cells in N.B. MATLAB, which is the number of basis functions and the height, we're going to call it the base and the value of the base. And these contain a number of different pieces of information. We need to have the number of primitive Gaussians that we're going to use. And this can vary depending on the atom we have. For example, we're going to use more Gaussians to describe carbon than to describe hydrogen. It can vary depending on the range of the exponent. For example, we might need to use fewer Gaussian to describe the $3s$ orbital than the $1s$ orbital, which is tight.

We have reached a peak for this given basis function. We also need to have an array with some number of elements that we will call C in C , which will be the contraction coefficient of the Gaussian. We also need to give it an array of Gaussian functions and each Gaussian function will contain the location of the center, so its component X , Y and Z , its exponent α in its normalization constant and once we can construct an array. With all this information we will have our complete base set and the way we are going to get our CSA bands and our band suits is that we are going to search them.

Many groups have done research on how to calculate and create basis functions, and we are going to use in this program a basis set called the $6-31g$ basis.