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Fourier Series by Least Square Minimization

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I. SYNOPSIS

Our understanding of Hilbert spaces is illustrated using Fourier Series, where our ability to visualize what is going on is enhanced through imagining an oscilloscope.

II. DIRAC NOTATION

The notation employed in beginning discussions of quantum chemistry becomes cumbersome when the complexity of problems increase and the need to see structure in equations dominates. Dirac introduced a notation which eliminates the ever-redundant ψ from discourse. He defined a wave function as a ket.

The ket is defined as '$|index\rangle \equiv \psi$', where 'index' is some human chosen index or indicator whose purpose is to label the state (or the function) under discussion. For a particle in a box, a potential ket is

$$\psi_n(x) = |n\rangle \equiv N_n \sin\left(\frac{n\pi x}{L}\right) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (2.1)$$

where the domain is $0 \leq x \leq L$, N_n is a normalization constant, and 'n' is a quantum number, i.e., an index chosen by us.

For the hydrogen atom, an appropriate ket might be

$$\psi_{n=3,\ell=1,m_\ell=-1}(\rho,\theta,\phi) = |3,1,-1\rangle = N_{3,1,1}\rho(4-\rho)e^{-\rho}\sin\theta e^{-\imath\phi} \quad (2.2)$$

which is a 3p electron's state (ρ is a dimensionless radius).

A harmonic oscillator might have an appropriate ket of the form

$$\psi_3(x) = |3\rangle = N_3\left(8\beta^3x^3 - 12\beta x\right)e^{-\beta^2x^2/2} \quad (2.3)$$

i.e., the ket notation allows us to indicate inside the funny delimiters the essential characteristics of the involved wavefunction without extraneous elements which might distract attention from the overall viewpoint being propounded!

III. THE DOT PRODUCT

Returning to the hydrogen atom, the following 'vector'

$$\langle 3,1,-1| = N_{3,1,1}\rho(4-\rho)e^{-\rho}\sin\theta e^{+\imath\phi} \quad (3.1)$$

which is the complex conjugate of the original wave function [1] , is known as a 'bra' vector, and the notation

$$\langle 3,1,-1\,|\,3,1,-1\rangle = 1 \quad (3.2)$$

is a shorthand for

$$\int_{all\ space} \psi^*_{3,1,-1}\psi_{3,1,-1}d\tau = 1 \quad (3.3)$$

(i.e., the normalization equation, required so that the probability of finding the electron somewhere is 1, certain(!)), which itself is shorthand for the complicated three-dimensional integral, usually displayed in spherical polar coördinates.

One sees that constructing the 'bra''ket' [2] consists of two separate concepts, making the 'bra' from the 'ket' by using the complex conjugate, juxtaposing the two in the proper order, and integrating over the appropriate domain. The analogy of this process is the dot product of elementary vector calculus, and it is here where we get our mental images of the processes described.

In three space, x, y, and z, we have unit vectors $\hat{i},\hat{j},\hat{k}$, so that an arbitrary vector as:

$$\vec{R_1} = X\hat{i} + Y\hat{j} + Z\hat{k}$$

could be re-written as

$$|R_1\rangle = X\,|i\rangle + Y\,|j\rangle + Z\,|k\rangle$$

In this space, one doesn't integrate over all space, one adds up over all components, thus

$$\langle R_1\,|\,R_1\rangle = \vec{R_1}\cdot\vec{R_1} = X^2 + Y^2 + Z^2$$

since $|i\rangle$ is orthogonal (perpendicular) to $|j\rangle$ and $|k\rangle$, etc..

In the same sense,

$$|arb\rangle = \sum_n c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{3.4}$$

where $|arb\rangle$ is an arbitrary state. This is our normal entry point for Fourier[3] Series.

Before we go there, let us re-introduce orthogonality, i.e.,

$$\langle n|m\rangle = 0 = \int_{domain} \psi_n^* \psi_m d\tau \ ; \ \ m \neq n \tag{3.5}$$

where the domain is problem specific, as is the volume element $d\tau$. This orthogonality is the analog of the idea that

$$\hat{i} \cdot \hat{j} = 0$$

as an example in normal vector calculus.

IV. PARTICLE IN A BOX VIS-A-VIS FOURIER SERIES

The normal introduction to orthogonal functions is via Fourier Series, but in the context of quantum chemistry, we can re-phrase that into the Particle in a Box solution to the Schrödinger Equation, i.e.,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + 0\psi = E\psi \tag{4.1}$$

in the box (domain) $0 \leq x \leq L$. The solutions are known to be

$$\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{4.2}$$

where n is an integer greater than zero, and L remains the size of the box.

Now, a Fourier Series is an expansion of a function (periodic) over the same (repeated) domain as above, in the form

$$|function\rangle = \sum_i c_i |i> = \sum_i c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \tag{4.3}$$

(where we changed index for no particular reason, other than to remind you that the index is a dummy variable). The question is, what is the optimal, best, nicest, etc., etc., etc., value for each of the c_i in this expansion?

V. A MINIMUM ERROR APPROXIMATION

To answer this question, we look for a measure of error between the function and the expansion. To do this we define a truncated expansion:

$$S_m = \sum_{i=0}^{i=m} c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \tag{5.1}$$

where, contrary to the particle in a box, we have employed the i=0 particle in a box basis function. Now, we form an error at the point x:

$$|function\rangle - S_m(x) = err(x) \tag{5.2}$$

and notice that if we added up this error for every value of x in the domain $0 \leq x \leq L$ we would be approaching the concept we desire, a measure of the error, the difference between the function and its approximation, the truncated series.

But, you say, sometimes the error (err(x)) is positive, and sometimes its negative, depending on circumstances. We want a measure which counts either effect properly, and the answer is to define a new error

$$(|function\rangle - S_m(x))^2 = ERR(x) \equiv [err(x)]^2 \tag{5.3}$$

where clearly, the l.h.s. is positive definite, and therefore can not give rise to fortuitous cancelation.

So, adding up ERR(x) at each point x in the domain, we have

$$\int_0^L (|function\rangle - S_m(x))^2 \, dx = \int_0^L ERR(x)dx \equiv ERROR_m \tag{5.4}$$

$ERROR_m$ is now a postive definite number which measures the error committed in truncating the approximate series at m. We re-write this explicitly to show the summation:

$$\int_0^L \left(|function\rangle - \sum_{i=0}^{m} c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right)^2 dx = \int_0^L ERR(x) dx \equiv ERROR_m \tag{5.5}$$

and form the partial

$$\frac{\partial ERROR_m}{\partial c_j} \tag{5.6}$$

holding all other c_i constant, where $i = 0...j...m$, which is

$$\frac{\partial ERROR_m}{\partial j} = -2 \left\{ \int_0^L \left(|function\rangle - \sum_{i=0}^{m} c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right) \sqrt{\frac{2}{L}} \sin \frac{j\pi x}{L} dx \right\} \tag{5.7}$$

which we set equal to zero. This means that we are searching for that value of c_j which makes the ERROR an extremum (of course, we want a minimum). This leads to the equation

$$\int_0^L |function\rangle \left(sin \frac{j\pi x}{L} \right) dx = \int_0^L \left(\sum_{i=0}^{m} c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right) \sin \frac{j\pi x}{L} dx \tag{5.8}$$

and, since one can exchange summation and integration, one has

$$\int_0^L |function\rangle \left(sin \frac{j\pi x}{L} \right) dx = \sum_{i=0}^{m} \int_0^L \left(c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right) \sin \frac{j\pi x}{L} dx \tag{5.9}$$

But the right hand side of this equation simplifies because the sines are orthogonal to each other over this domain, so the r.h.s. becomes

$$\int_0^L |function\rangle \left(sin \frac{j\pi x}{L} \right) dx = c_j \int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{j\pi x}{L} \right) \sin \frac{j\pi x}{L} dx \tag{5.10}$$

since the only survivor on the r.h.s. is the i=j term.

$$c_j = \frac{\int_0^L |function\rangle \left(sin \frac{j\pi x}{L} \right) dx}{\int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{j\pi x}{L} \right) \sin \frac{j\pi x}{L} dx} \tag{5.11}$$

Multiplying top and bottom by $\sqrt{2/L}$ one has

$$c_j = \frac{\langle function|j\rangle}{\langle j|j\rangle} \tag{5.12}$$

which is fairly cute in its compactness. Of course, if $|j\rangle$ is normalized (as it is in our example) then

$$c_j = \langle function|j\rangle \tag{5.13}$$

which is even more compact!

VI. COMPLETENESS

What if we wanted to approximate a function of the form

$$\sin \frac{7\pi x}{L} \tag{6.1}$$

and i=7 were omitted from the summations (Equation 4.3), i.e., the summation ran past this particular harmonic. It would look like:

$$\cdots + c_6 \sin\frac{6\pi x}{L} + c_8 \sin\frac{8\pi x}{L} + \cdots = \sum_{i=0}^{6} c_i \sqrt{\frac{2}{L}} \sin\frac{i\pi x}{L} + \sum_{i=8}^{\infty} c_i \sqrt{\frac{2}{L}} \sin\frac{i\pi x}{L}$$

Clearly, since each sine is orthogonal to every other sine, the seventh sine would have no expansion in this series, i.e., each c_i would be zero! We can not leave out any term in the series, i.e., it must be complete, before one can assert that one can expand any function in terms of these sines (and cosines, if need be).

VII. ARBITRARY DOMAIN FOURIER SERIES

We chose to introduce Fourier Series using the Particle in a Box solution from standard elementary quantum mechanics, but, of course, the Fourier Series antedates Quantum Mechanics by quite a few years.

The normal discussion of Fourier Series starts with a domain for the independent variable (here x) from $-\pi \leq x \leq \pi$ and considers replicating functions (such as sine and cosine) which map partly on this domain, and yet really extend over the domain $-\infty \leq x \leq +\infty$, replicating themselves every 2π.

So, assume we have a function f(x) in the domain $-\pi \leq x \leq \pi$ which may be replicating itself as noted above.

The Fourier Series for f(x) is then given by

$$f(x) = \frac{A_0}{2} + \sum_{n=1}^{n=\infty} (A_n \sin nx + B_n \cos nx)$$

To repeat the derivation of the minimum error (above) here would require us to come to grips with the idea that $\sin x$ and $\cos x$ are orthogonal to each other. These integrals are trivial, over the domain in question, whether using 'x' or 'nx'. All one really needs is DeMoivre's Theorem and some expertise in using it.

The coefficients are determinable (using this orthogonality) via

$$A_n = \frac{\int_{-\pi}^{\pi} f(x) \sin nx dx}{\int_{-\pi}^{\pi} \sin^2 nx dx}$$

$$B_n = \frac{\int_{-\pi}^{\pi} f(x) \cos nx dx}{\int_{-\pi}^{\pi} \cos^2 nx dx}$$

and

$$A_0 = \frac{\int_{-\pi}^{\pi} \sin nx dx}{\int_{-\pi}^{\pi} \sin^2 nx dx}$$

Anyway, assuming that we accept the 2π domain Fourier Series, can be go on to any "even" domain Fourier Series? Yes. Consider the domain $-L \leq x \leq +L$, and write

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{n=\infty} \left(a_n \sin\frac{n\pi x}{L} + b_n \cos\frac{n\pi x}{L} \right)$$

where we use lower case letters in this case. The same argument that got us the coefficients before, works here, and we find

$$a_n = \frac{1}{2L} \int_{-L}^{L} f(x) \sin\frac{n\pi x}{L} dx$$

$$b_n = \frac{1}{2L} \int_{-L}^{L} f(x) \cos\frac{n\pi x}{L} dx$$

with

$$a_0 = \frac{1}{2L} \int_{-L}^{L} f(x) \cos\frac{0\pi x}{L} dx = \frac{1}{2L} \int_{-L}^{L} f(x) dx$$

VIII. FIGURES

[1] the only thing that happens in making the complex conjugate is that each $\imath$ is changed to $-\imath$ (and each $-\imath \rightarrow \imath$).

[2] the 'bracket', hah, hah.

[3] Jean Baptiste Fourier, 1768-1830

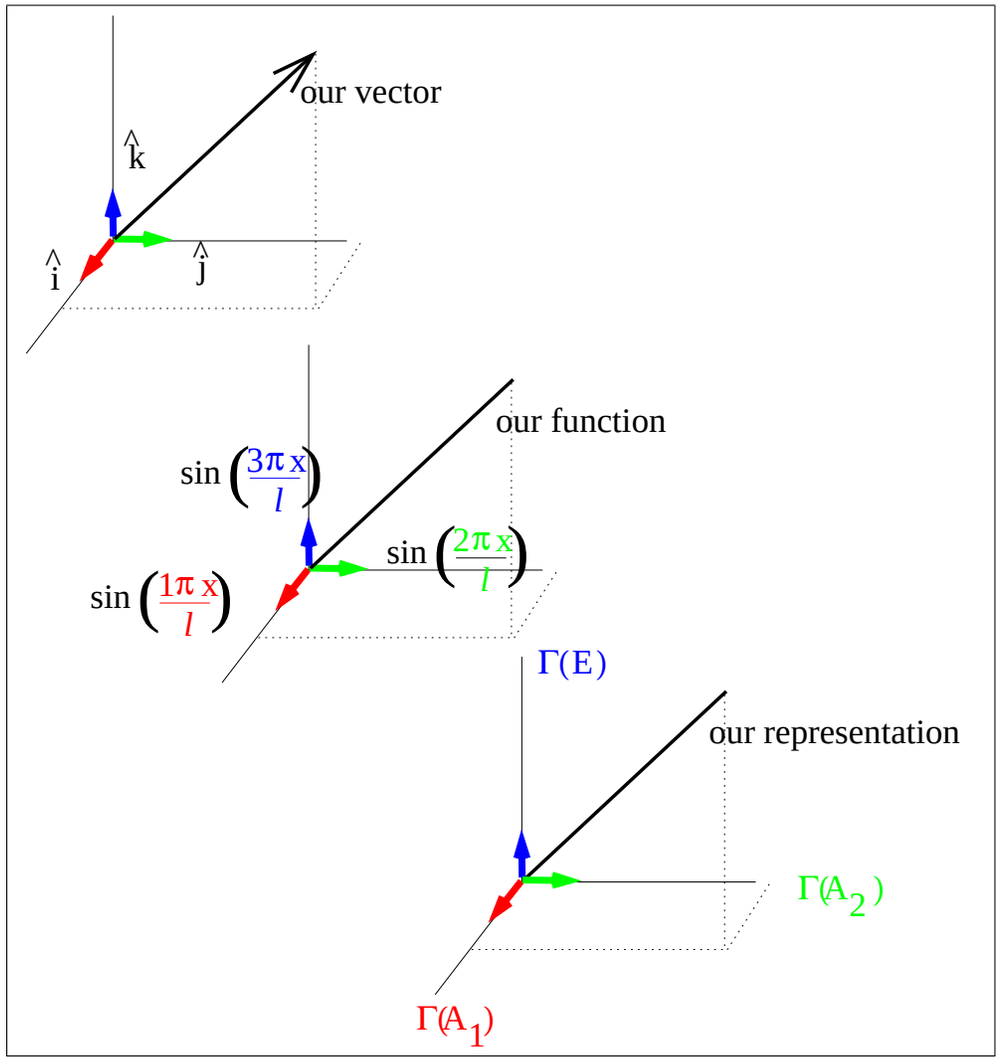

FIG. 1: Analogy between 3-D vectors and function spaces

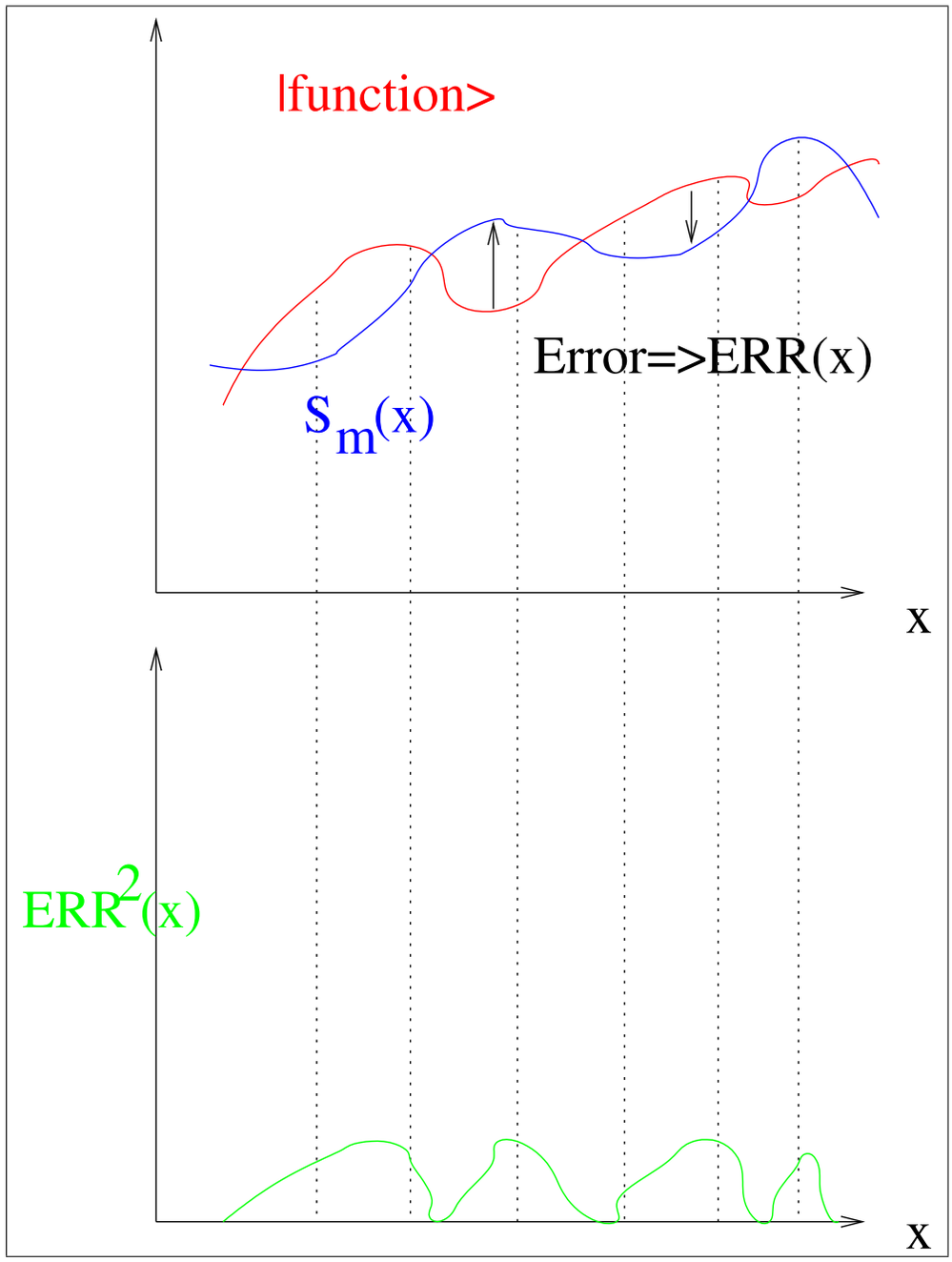

FIG. 2: Error involved in approximating a function.