Variable Separation in Quantum Chemistry*

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1 Introduction

The H-atom's Quantum Chemistry is treated usually via the method of separation of variables. Therefore, we need to see which functions are variable separable, and which aren't. What, then, is the difference between $f_1(x,y) = xy$ and $f_2(x,y) = e^{xy}$?

One can't answer this question until one specifies the operator involved, and we here choose, as an example, the operator

$$Op_1 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

and choose Laplace's equation in 2 dimensions, i.e., $Op_1 f_1(x,y) = 0$ as our example. Then for f_1 we have

$$y\frac{\partial^2 x}{\partial x^2} + x\frac{\partial^2 y}{\partial y^2} =?$$

Since $f_1 = x \times y$, and the second partial derivatives each vanish, their sum vanishes and Laplace's equation is truly satisfied. Thus $f_1(x,y)$ is separable and a solution of Laplace's Equation.

To paraphrase the standard argument, write (dividing through by f_1, i.e., by $x \times y$, i.e.,

$$\frac{y}{xy}\frac{\partial^2 x}{\partial x^2} + \frac{x}{xy}\frac{\partial^2 y}{\partial y^2} =?$$

*l2h2:var_sep.tex

which becomes, obviously

$$\frac{1}{x}\frac{\partial^2 x}{\partial x^2}+\frac{1}{y}\frac{\partial^2 y}{\partial y^2}=?$$

and here we see, eplicitly, that the first part is a function only of "x" while the second part is a function only of "y", and how their sum can equal anything is the nexus of the argument about variable separability.

What about $Op_1 f_2(x,y)$? We have

$$Op_1 f_2(x,y,)=\frac{\partial^2 e^{xy}}{\partial x^2}+\frac{\partial^2 e^{xy}}{\partial y^2}\to y^2e^{xy}+x^2e^{xy}=\left(x^2+y^2\right)e^{xy}$$

The r.h.s. of this equation bears little or no relation to the left hand side. Thus $Op_1 f_2(x,y)\neq 0$

2 So What?

Now consider the problem of finding a solution to the Laplace equation for a function $g(x,y)$,

$$Op_1 g(x,y)=\frac{\partial^2 g(x,y)}{\partial x^2}+\frac{\partial^2 g(x,y)}{\partial y^2}=0$$

Variable separation as an Ansatz (hypothesis) is what we assume, i.e.,

$$g(x,y,)\to X(x)Y(y)$$

where $X(x)$ is a function solely of x and $Y(y)$ is a function solely of y. Substituting, we have

$$\frac{\partial^2 X(x)Y(y)}{\partial x^2}+\frac{\partial^2 X(x)Y(y)}{\partial y^2}=0$$

which, following the rules of partial differential equations is

$$Y(y)\frac{\partial^2 X(x)}{\partial x^2}+X(x)\frac{\partial^2 Y(y)}{\partial y^2}=0$$

so that, dividing [1] both sides by $X(x)Y(y)$ we have

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}+\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=0$$

[1]Notice that if $X(x)Y(y)$ happens to be zero somewhere, this argument fails.

which says that a function of x plus a function of y *always* vanishes, i.e., if

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} = s(x)$$
$$\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} = t(y)$$

then both s(x) and t(y) must be constants (of opposite sign) so that their sum cancels everywhere, How is that possible. Can $\sin x + \cos y$ add up to zero for any x and any y; for all x and all y? What's going on here?

Clearly, only a special set of functions can work here. Thus, if

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} = constant$$

and

$$\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} = -constant$$

then their sum will be zero (irrespective of the values of x and y), as required and they will be solutions.

What else might be a solution? How about

$$X(x) = e^{\alpha x}$$

(α = a constant) and

$$Y(y) = e^{\alpha y}$$

so that

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{e^{\alpha x}}\frac{\partial^2 e^{\alpha x}}{\partial x^2} = constant = \alpha^2$$

and

$$\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} = \frac{1}{e^{\alpha y}}\frac{\partial^2 e^{\alpha y}}{\partial y^2} = constant = \alpha^2$$

Oh Oh. We have that

$$\frac{\partial^2 X(x)Y(y)}{\partial x^2} + \frac{\partial^2 X(x)Y(y)}{\partial y^2} = 2\alpha^2$$

which isn't zero, so this variable separation has failed.

3 One Last Try

How about

$$X(x) = e^{\alpha x}$$

and

$$Y(y) = e^{\imath \alpha y}$$

Then

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{e^{\alpha x}} \frac{\partial^2 e^{\alpha x}}{\partial x^2} = constant = \alpha^2$$

but

$$\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = \frac{1}{e^{\imath \alpha y}} \frac{\partial^2 e^{\imath \alpha y}}{\partial y^2} = constant = \imath^2 \alpha^2 = -\alpha^2$$

so

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = \alpha^2 - \alpha^2 = 0$$

so

$$e^{\alpha(x+\imath y)} = e^{\alpha x} e^{\alpha \imath y}$$

is variable separable (relative to the operator).

4

The most famous variable separable problem is that of the quantum mechanics of the hydrogen atom's electron. Suffice it to say that this problem involves the Laplacian in three dimensions, whose two forms are

$$\nabla^2_{x,y,z} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and

$$\nabla^2_{r,\vartheta,\phi} = \frac{1}{r^2} \frac{\partial \left(r^2 \frac{\partial}{\partial r} \right)}{\partial r} + \frac{1}{r^2 \sin^2 \vartheta} \left(\sin \vartheta \frac{\left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right)}{\partial \vartheta} + \frac{\partial^2}{\partial \phi^2} \right)$$

These two formulations are linked through the transformation equations between cartesian and spherical polar coördinates.

In any case, our example of Laplace's equation now becomes

$$\nabla^2 \chi = 0$$

where $\chi(x, y, z)$ or $\chi(r, \vartheta, \varphi)$ are applicable.

In the former case, the variable separation

$$\chi(x, y, z) = X(x)Y(y)Z(z)$$

works, while in the latter case the variable separation

$$\chi(r, \vartheta, \varphi) = R(r)\Theta(\vartheta)\Phi(\varphi)$$

works. Try it, you'll like it.