Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

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Answers to Homework Set 5

From lecture 18: On the interval 0 to 1, what is the square modulus (in terms of *a* and *b*) of the trial wave function in eq. 18-15?

Eq. 18-15 was

$$\xi(x;a,b) = x^a\left(1 - x^b\right) \qquad (18\text{-}15)$$

By analogy to eq. 18-5, we find the square modulus as

$$\begin{aligned}
\left\langle \xi(x;a,b) \middle| \xi(x;a,b) \right\rangle &= \int_0^1 x^a\left(1-x^b\right)x^a\left(1-x^b\right)dx \\
&= \int_0^1 x^{2a}dx - 2\int_0^1 x^{2a+b}dx + \int_0^1 x^{2a+2b}dx \\
&= \left.\frac{x^{2a+1}}{2a+1}\right|_0^1 - 2\left.\frac{x^{2a+b+1}}{2a+b+1}\right|_0^1 + \left.\frac{x^{2a+2b+1}}{2a+2b+1}\right|_0^1 \\
&= \frac{1}{2a+1} - \frac{2}{2a+b+1} + \frac{1}{2a+2b+1} \\
&= \frac{2b^2}{(2a+1)(2a+b+1)(2a+2b+1)}
\end{aligned}$$

From lecture 19: Today's in-class homework solution showed that the expectation value of the momentum operator for any real wave function must be zero. Why doesn't the same proof hold for any complex wave function?

Consider *any* complex wave function of one dimension *f*.

$$\begin{aligned}
\left\langle f(x) \middle| p_x \middle| f(x) \right\rangle &= \int_a^b f^*(x)\left(-i\hbar\frac{d}{dx}\right)f(x)dx \\
&= -i\hbar\int_a^b f^*(x)\left(\frac{df(x)}{dx}\right)dx
\end{aligned}$$

where we have assumed without loss of generality that f is normalized over the integration interval. We can *try* to solve the integral using integration by parts. If we use

$$\int_a^b u\,dv = uv\Big|_a^b - \int_a^b v\,du$$

$$u = f^*(x) \quad dv = \frac{df(x)}{dx}dx$$

$$du = \frac{df^*(x)}{dx}dx \quad v = f(x)$$

then we may write

$$\int_a^b f^*(x)\left(\frac{df(x)}{dx}\right)dx = \left|f(x)\right|^2\Big|_a^b - \int_a^b f(x)\left(\frac{df^*(x)}{dx}\right)dx$$

$$= -\int_a^b f(x)\left(\frac{df^*(x)}{dx}\right)dx$$

Again, the first term on the r.h.s. drops out because the square modulus of a well behaved wave function must be zero at its endpoints. However, this is of little help, since the remaining equation is nothing but a restatement of the relationship between a complex function and its complex conjugate, namely

$$\int_a^b f^*(x)\left(\frac{df(x)}{dx}\right)dx = -\int_a^b f(x)\left(\frac{df^*(x)}{dx}\right)dx = -\left[\int_a^b f^*(x)\left(\frac{df(x)}{dx}\right)dx\right]^*$$

This relationship is satisfied by all complex valued functions, so the integral certainly need not be zero, and indeed eigenfunctions of the momentum operator must be complex valued.

From lecture 20:

What are the normalized eigenfunctions and eigenvalues for S_x and S_y, respectively?

This problem may be done in at least two different ways. The intuitive way is to notice that both S_x and S_y operate on the spin functions α and β to give constants times the *opposite* spin function. That suggests that a linear combination of the 2 spin functions might work. So, to be specific, recall that

$$S_x\alpha = \frac{1}{2}\hbar\beta \quad S_x\beta = \frac{1}{2}\hbar\alpha \quad S_y\alpha = \frac{1}{2}i\hbar\beta \quad S_y\beta = -\frac{1}{2}i\hbar\alpha$$

Now, consider the spin function (α + β). If we operate on this function with S_x we have

$$\begin{aligned} S_x(\alpha+\beta) &= \frac{1}{2}\hbar\beta + \frac{1}{2}\hbar\alpha \\ &= \frac{1}{2}\hbar(\alpha+\beta) \end{aligned}$$

so, the function is indeed an eigenfunction of S_x with eigenvalue $\hbar/2$ (the same eigenvalue that α has for S_z). However, this spin function is not normalized—to check, note that

$$\begin{aligned} \langle\alpha+\beta|\alpha+\beta\rangle &= \langle\alpha|\alpha\rangle + \langle\alpha|\beta\rangle + \langle\beta|\alpha\rangle + \langle\beta|\beta\rangle \\ &= 1+0+0+1 \\ &= 2 \end{aligned}$$

So, to normalize our eigenfunction, we will need to multiply by $2^{-1/2}$, and the normalized eigenfunction (having the same eigenvalue as that determined above) is

$$\frac{1}{\sqrt{2}}(\alpha+\beta)$$

But, we expect, by analogy to S_z, that S_x will have another spin eigenfunction orthogonal to the first. The obvious choice is

$$\frac{1}{\sqrt{2}}(\alpha-\beta)$$

and inspection verifies that

$$\begin{aligned} S_x\left[\frac{1}{\sqrt{2}}(\alpha-\beta)\right] &= \frac{\hbar}{2\sqrt{2}}\beta - \frac{\hbar}{2\sqrt{2}}\alpha \\ &= -\frac{1}{2}\hbar\left[\frac{1}{\sqrt{2}}(\alpha-\beta)\right] \end{aligned}$$

where normalization is easily established too

$$\begin{aligned} \left\langle \frac{1}{\sqrt{2}}(\alpha-\beta) \middle| \frac{1}{\sqrt{2}}(\alpha-\beta) \right\rangle &= \frac{1}{2}\left(\langle\alpha|\alpha\rangle - \langle\alpha|\beta\rangle - \langle\beta|\alpha\rangle + \langle\beta|\beta\rangle\right) \\ &= \frac{1}{2}(1-0-0+1) \\ &= 1 \end{aligned}$$

Finally, if we were to express these spin functions in 2 x 2 matrix format, recalling that

$$\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{and} \quad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

we would have

$$\frac{1}{\sqrt{2}}(\alpha + \beta) = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}}(\alpha - \beta) = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$$

Some people may have started with the matrix formulation and seen this relationship, and that's fine too. Actually, the matrix picture is quite helpful, because noting that

$$S_x = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \text{and} \quad S_y = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

it seems logical that the eigenfunctions of S_y will be similar to those of S_x but with i involved somewhere. Some trial and error leads to

$$\frac{1}{\sqrt{2}}(\alpha + i\beta) = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{bmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}}(i\alpha + \beta) = \begin{bmatrix} \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$$

To check this, note

$$S_y\left[\frac{1}{\sqrt{2}}(\alpha + i\beta)\right] = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{bmatrix}$$

$$= \frac{\hbar}{2}\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{bmatrix}$$

and

$$S_y\left[\frac{1}{\sqrt{2}}(i\alpha+\beta)\right]=\frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\begin{bmatrix}\frac{i}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{bmatrix}$$

$$=-\frac{\hbar}{2}\begin{bmatrix}\frac{i}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{bmatrix}$$

So there is again a perfect analogy with S_z with respect to eigenvalues (and now you can see why for the spin 1/2 system $S^2=S_x^2+S_y^2+S_z^2=\frac{3\hbar^2}{4}$). Normalization is also easily proven, namely

$$\left\langle\frac{1}{\sqrt{2}}(i\alpha+\beta)\middle|\frac{1}{\sqrt{2}}(i\alpha+\beta)\right\rangle=\frac{1}{2}\left(\langle\alpha|\alpha\rangle-i\langle\alpha|\beta\rangle+i\langle\beta|\alpha\rangle+\langle\beta|\beta\rangle\right)$$

$$=\frac{1}{2}(1-0+0+1)$$

$$=1$$

and analogously for the other spin function (remember that a factor of *i* pulled out from a bra comes out as –*i* because the bra is a complex conjugate!)