Chem 542 Exam 2

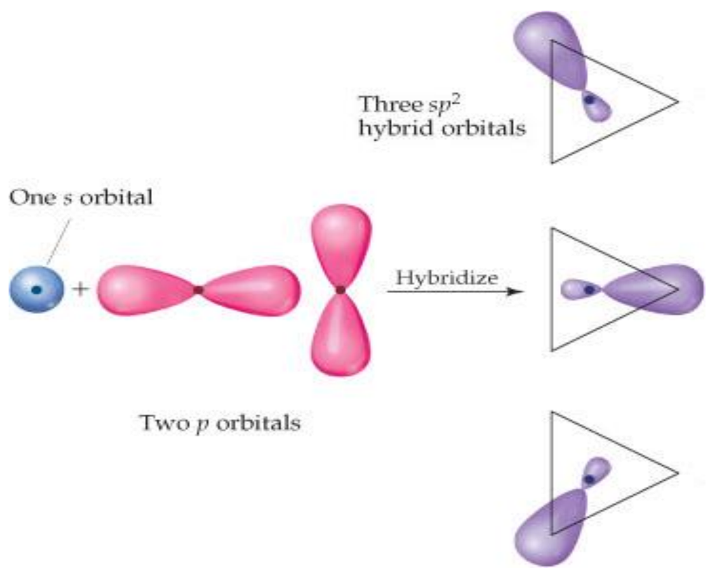
Creativity Question 1. If you were to use the translation operator: $\hat{\mathfrak{I}}(\Delta x) = e^{-i\frac{\hat{p}}{\hbar}\Delta x}$ on $|\psi\rangle$ in real space, you could end up with a bloody mess:

$$\left\langle x\left|e^{i\frac{\hat{p}}{\hbar}\Delta x}\right|\psi\right\rangle = \langle x|\left\{1 - i\frac{\Delta x}{\hbar}\hat{p} + \frac{\Delta x^2}{2\hbar^2}\hat{p}^2 + i\frac{\Delta x^3}{6\hbar^3}\hat{p}^3 \ldots \int |x'\rangle\langle x'|\psi\rangle\partial x'\right\}$$

This approach provides a huge number resolutions of the identity and $\hat{p}^n|x'\rangle$ terms to evaluate. Can you propose an alternative method for applying this momentum-based translation operator that saves a lot of trouble? Perhaps you can avoid expanding $e^{i\frac{\hat{p}}{\hbar}\Delta x}$? ***Hint:*** of course you know $\langle x|\psi\rangle \sim N \cdot e^{-x^2}$ or something like that.

Answer: Convert the real space wavefunction into the momentum representation $\int \partial p'|p'\rangle\langle p'|\psi\rangle$, in which case all the momentum operators work like: $\hat{p}^n|p'\rangle = p'^n|p'\rangle$.

Creativity Question 2. Sp^2 hybridized orbitals describe trigonal bonding as found in BF_3, a precursor for other boron compounds. Shown here is a model of the sp^2 hybridizes orbitals. Can you create a matrix $\hat{U}^t$ that describes the transformation from the "block" s, 3p system:



$$|block\rangle = \begin{bmatrix} \varepsilon_s \\ \varepsilon_{p_x} \\ \varepsilon_{p_y} \\ \varepsilon_{p_z} \end{bmatrix}$$

to sp^2 system? Here is a template for you to put in your final answer:

$$\hat{U}^t = \begin{bmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \\ m & n & o & p \end{bmatrix}$$

Answer:

$$\begin{matrix} s & p_x & p_y & p_z \end{matrix}$$

$$\begin{bmatrix} 1 & 1 & 1 & 0 \\ 1 & -1 & 1 & 0 \\ 1 & 1 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Dirac Notation Questions

3. On a homework question, I saw two approaches that resulting in the following:

(1) $$e^{-\lambda\hat{B}}\hat{A}\frac{\partial}{\partial\lambda}e^{\lambda\hat{B}} = e^{-\lambda\hat{B}}\hat{A}\hat{B}e^{\lambda\hat{B}} = e^{-\lambda\hat{B}}\hat{A}e^{\lambda\hat{B}}\hat{B}$$

(2) $$e^{-\lambda\hat{B}}\hat{A}\frac{\partial}{\partial\lambda}e^{\lambda\hat{B}} = e^{-\lambda\hat{B}}\hat{A}\hat{B}e^{\lambda\hat{B}} = \hat{B}e^{-\lambda\hat{B}}\hat{A}e^{\lambda\hat{B}}$$

One of these approaches is correct, and the other may, *or may not*, be correct. Which one is which and why?

Answer: The first is correct because an operator $\hat{B}$ and a function of an operator $e^{\lambda\hat{B}}$ commute, thus $\hat{B}e^{\lambda\hat{B}} = e^{\lambda\hat{B}}\hat{B}$. The second one has $\hat{A}$ and $\hat{B}$ switching places. This may nor may not be correct depending on whether $\hat{A}$ and $\hat{B}$ commute.

4. Let's examine the uncertainty principle for the case of the x-projection operator:

$$\hat{\Omega}_{Sx+} = |S_x,+\rangle\langle S_x,+| = \frac{1}{2}\begin{bmatrix}1 & 1\\1 & 1\end{bmatrix}$$

Is there an uncertainty principle in play with $\hat{S}_z$? Please use matrix multiplication to demonstrate yes or no!

Answer:

$$\hat{S}_z = \frac{\hbar}{2}|S_z,+\rangle\langle S_z,+| - \frac{\hbar}{2}|S_z,-\rangle\langle S_z,-| = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$$

You have to evaluate:

$$\hat{\Omega}_{Sx+}\hat{S}_z - \hat{S}_z\hat{\Omega}_{Sx+} = \frac{1}{2}\begin{bmatrix}1 & 1\\1 & 1\end{bmatrix}\frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} - \frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}\frac{1}{2}\begin{bmatrix}1 & 1\\1 & 1\end{bmatrix} =$$

$$\frac{\hbar}{4}\begin{bmatrix}1 & -1\\1 & -1\end{bmatrix} - \frac{\hbar}{4}\begin{bmatrix}1 & 1\\-1 & -1\end{bmatrix} = \frac{\hbar}{4}\begin{bmatrix}0 & -2\\2 & 0\end{bmatrix}$$

Not 0!

5. Let's take a closer look at the uncertainty principle. If a commutator $[\hat{\Omega}_1,\hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1 \neq 0$, then the order of the measurement matters. So, for spin systems:

$$\langle(\Delta\hat{S}_y)^2\rangle\langle(\Delta\hat{S}_z)^2\rangle \geq \frac{1}{4}|\langle[\hat{S}_y,\hat{S}_z]\rangle|^2 = \frac{\hbar^2}{4}|\langle\hat{S}_x\rangle|^2$$

is it true that $\langle(\Delta\hat{S}_y)^2\rangle\langle(\Delta\hat{S}_z)^2\rangle$ can never be 0?

a. To answer, use Dirac notation to evaluate: $\langle+|\hat{S}_x|+\rangle$.

b. The answer to pt. a was 0! I thought this wasn't possible; how do you interpret this? ***Hint:*** use the formula:

$$\langle(\Delta\hat{S}_y)^2\rangle\langle(\Delta\hat{S}_z)^2\rangle \geq \frac{1}{4}\left|\langle[\hat{S}_y,\hat{S}_z]\rangle\right|^2$$

Answer:

a. $\langle + | \hat{S}_x | + \rangle = \langle + | \left\{\frac{\hbar}{2} | -\rangle\langle + | + \frac{\hbar}{2} | +\rangle\langle - |\right\} | + \rangle = \frac{\hbar}{2}\langle + | - \rangle\langle + | + \rangle + \frac{\hbar}{2}\langle + | + \rangle\langle - | + \rangle = 0$

b. If you are evaluating $\langle(\Delta\hat{S}_z)^2\rangle = \left\langle S_z, + \middle| (\Delta\hat{S}_z)^2 \middle| S_z, + \right\rangle$, the result must be 0 because you clearly know exactly what the z-polarization is! As a result, we interpret the uncertainty principle as telling you that you the order of operations matters only for certain states but not others.

6. Let's put time evolution into matrix form. If silver atoms are in a magnetic field with a z-direction, then the effect of the Hamiltonian~$\hat{S}_z$ on $| \pm \rangle$ are:

$$\hat{H}| + \rangle = E_+ | + \rangle, \qquad \hat{H}| - \rangle = E_- | - \rangle$$

What would the matrix form of the time evolution operator:

$$e^{-i\hat{H}\Delta t/\hbar}$$

look like in the S_z representation? Do you think an initial spin up $| + \rangle$ state would mix with a spin down state over time? Hint: You can answer the question by:

$$\left\langle - \middle| e^{-i\hat{H}\Delta t/\hbar} \middle| + \right\rangle$$

Answer: The matrix should look like:

$$\begin{bmatrix} \left\langle + \middle| e^{-i\hat{H}\Delta t/\hbar} \middle| + \right\rangle & \left\langle + \middle| e^{-i\hat{H}\Delta t/\hbar} \middle| - \right\rangle \\ \left\langle - \middle| e^{-i\hat{H}\Delta t/\hbar} \middle| + \right\rangle & \left\langle - \middle| e^{-i\hat{H}\Delta t/\hbar} \middle| - \right\rangle \end{bmatrix}$$

Using the identities given, you should know that $e^{-i\hat{H}\Delta t/\hbar}| + \rangle = e^{-iE_+\Delta t/\hbar}| + \rangle$ etc thus the matrix is now:

$$\begin{bmatrix} e^{-iE_+\Delta t/\hbar}\langle + | + \rangle & e^{-iE_-\Delta t/\hbar}\langle + | - \rangle \\ e^{-iE_+\Delta t/\hbar}\langle - | + \rangle & e^{-iE_-\Delta t/\hbar}\langle - | - \rangle \end{bmatrix} = \begin{bmatrix} e^{-iE_+\Delta t/\hbar} & 0 \\ 0 & e^{-iE_-\Delta t/\hbar} \end{bmatrix}$$

There would be no mixing between states due to the lack of off-diagonal elements; you can show that via:

$$\begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} e^{-iE_+\Delta t/\hbar} & 0 \\ 0 & e^{-iE_-\Delta t/\hbar} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} e^{-iE_+\Delta t/\hbar} \\ 0 \end{bmatrix} = 0$$

Equations:

Uncertainty: $\langle(\Delta\hat{\Omega}_1)^2\rangle\langle(\Delta\hat{\Omega}_2)^2\rangle \geq \frac{1}{4}\left|\langle[\hat{\Omega}_1,\hat{\Omega}_2]\rangle\right|^2$ Commutator: $[\hat{\Omega}_1,\hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$

Anticommutator: $\{\hat{\Omega}_1,\hat{\Omega}_2\} = \hat{\Omega}_1\hat{\Omega}_2 + \hat{\Omega}_2\hat{\Omega}_1$ $\quad [\hat{\Omega}, f(\hat{\Omega})] = 0$

Dirac Notation: If: $\hat{\Omega}|a'\rangle = a'|a'\rangle$ then $f(\hat{\Omega})|a'\rangle = f(a')|a'\rangle$

Matrices: $\hat{\Omega} = \sum_{a''}\sum_{a'}|a''\rangle\langle a''|\hat{\Omega}|a'\rangle\langle a'|$

Real Space: $\hat{x}|x'\rangle = x'|x'\rangle$ $\quad \hat{p} = -i\hbar\frac{\partial}{\partial x}$ $\quad \langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ip'x/\hbar}$

Momentum Space: $\hat{p}|p'\rangle = p'|p'\rangle$ $\quad \hat{x} = i\hbar\frac{\partial}{\partial p}$ $\quad \langle p'|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-ip'x/\hbar}$

Translation: $\hat{\mathfrak{I}}(\partial x) = 1 - i\frac{\hat{p}}{\hbar}\partial x$ $\quad \hat{\mathfrak{I}}(\Delta x) = e^{-i\frac{\hat{p}}{\hbar}\Delta x}$

Time Evolution: $\hat{U}(\partial \mathrm{t}) = 1 - i\frac{\hat{H}}{\hbar}\partial t$ $\quad \hat{U}(\Delta \mathrm{t}) = e^{-i\hat{H}\Delta t/\hbar}$

Spin States:

$|S_z,+\rangle = |+\rangle$, $|S_z,-\rangle = |-\rangle$

$|S_x,+\rangle = \frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle$, $|S_x,-\rangle = \frac{1}{\sqrt{2}}|+\rangle - \frac{1}{\sqrt{2}}|-\rangle$,

$|S_y,+\rangle = \frac{1}{\sqrt{2}}|+\rangle + \frac{i}{\sqrt{2}}|-\rangle$, $|S_y,-\rangle = \frac{1}{\sqrt{2}}|+\rangle - \frac{i}{\sqrt{2}}|-\rangle$

Spin Operators:

$\hat{S}_z = \frac{\hbar}{2}|+\rangle\langle+| - \frac{\hbar}{2}|-\rangle\langle-|$ $\quad \hat{S}_x = \frac{\hbar}{2}|-\rangle\langle+| + \frac{\hbar}{2}|+\rangle\langle-|$ $\quad \hat{S}_y = \frac{\hbar}{2}i|-\rangle\langle+| - \frac{\hbar}{2}i|+\rangle\langle-|$

$\hat{S}_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$ $\quad \hat{S}_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$ $\quad \hat{S}_z = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$

Spin Uncertainty: $[\hat{S}_i,\hat{S}_j] = i\hbar\cdot\varepsilon_{i,j,k}\cdot\hat{S}_k$