Chem 542 Problem Set 6

1. Using the rules of Dirac notation algebra, prove or evaluate the following:

a) If $\hat{X}$ and $\hat{Y}$ are operators, then we can say that $\hat{X}\hat{Y}$ is also an operator. Can you show that the trace of $\hat{X}\hat{Y}$: $tr(\hat{X}\hat{Y})$ is equal to $tr(\hat{Y}\hat{X})$?

Hint: the trace of an operator $\hat{\Omega}$ is defined as: $\sum_{a'}\langle a'|\hat{\Omega}|a'\rangle$

b) Prove: $(\hat{X}\hat{Y})^{+} = \hat{Y}^{+}\hat{X}^{+}$, where $\hat{X}$ and $\hat{Y}$ are operators.

To start this derivation, first note that $\langle\psi|(\hat{X}\hat{Y})^{+}|\phi\rangle^{*} = \langle\phi|(\hat{X}\hat{Y})|\psi\rangle$; you will next want to resolve an identity ($1 = \sum_{a'}|a'\rangle\langle a'|$) and note that $\langle\phi|\hat{X}|a'\rangle = \langle a'|\hat{X}^{+}|\phi\rangle^{*}$

c) $\sum_{a'}\psi^{*}_{a'}(x')\psi_{a'}(x'') = \delta(x'' - x')$, where $\psi_{a'}(x') = \langle x'|a'\rangle$. Hint, the last step is:

$$\langle x''|x'\rangle = \delta(x'' - x')$$

Answers:

a) As the trace of the $\hat{X}\hat{Y}$ operator is defined as: $\sum_{a'}\langle a'|\hat{X}\hat{Y}|a'\rangle$, and for the first step we resolve an identity:

$$\sum_{a''}\sum_{a'}\langle a'|\hat{X}|a'\rangle\langle a'|\hat{Y}|a'\rangle$$

Now you can rearrange the interior because $\langle a'|\hat{X}|a'\rangle$ and $\langle a'|\hat{Y}|a'\rangle$ are just numbers:

$$\sum_{a''}\sum_{a'}\langle a'|\hat{X}|a'\rangle\langle a'|\hat{Y}|a'\rangle = \sum_{a''}\sum_{a'}\langle a'|\hat{Y}|a'\rangle\langle a'|\hat{X}|a'\rangle$$

Now you can remove a resolved identity: $\sum_{a''}\sum_{a'}\langle a'|\hat{Y}|a'\rangle\langle a'|\hat{X}|a'\rangle = \sum_{a''}\langle a''|\hat{Y}\hat{X}|a''\rangle$ which is the same as $tr(\hat{Y}\hat{X})$.

b) First we start with $\langle\psi|(\hat{X}\hat{Y})^{+}|\phi\rangle^{*}$. This is because we can immediately use this expression: $\langle\psi|(\hat{X}\hat{Y})^{+}|\phi\rangle^{*} = \langle\phi|(\hat{X}\hat{Y})|\psi\rangle$ and go further by inserting a resolution of the identity:

$$\langle\psi|(\hat{X}\hat{Y})^{+}|\phi\rangle^{*} = \langle\phi|\hat{X}\hat{Y}|\psi\rangle = \sum_{a'}\langle\phi|\hat{X}|a'\rangle\langle a'|\hat{Y}|\psi\rangle$$

Next, flip the order and remember those complex conjugates:

$$\sum_{a'}\langle\phi|\hat{X}|a'\rangle\langle a'|\hat{Y}|\psi\rangle = \sum_{a'}\langle a'|\hat{X}^{+}|\phi\rangle^{*}\langle\psi|\hat{Y}^{+}|a'\rangle^{*}$$

Since $\langle a'|\hat{X}^{+}|\phi\rangle^{*}$ and $\langle\psi|\hat{Y}^{+}|a'\rangle^{*}$ are just numbers you can rearrange them:

$$\sum_{a'}\langle a'|\hat{X}^{+}|\phi\rangle^{*}\langle\psi|\hat{Y}^{+}|a'\rangle^{*} = \sum_{a'}\langle\psi|\hat{Y}^{+}|a'\rangle^{*}\langle a'|\hat{X}^{+}|\phi\rangle^{*}$$

And you can remove the resolution of the identity:

$$\sum_{a'}\langle\psi|\hat{Y}^{+}|a'\rangle^{*}\langle a'|\hat{X}^{+}|\phi\rangle^{*} = \langle\psi|\hat{Y}^{+}\hat{X}^{+}|\phi\rangle^{*}$$

To summarize, $\langle\psi|(\hat{X}\hat{Y})^{+}|\phi\rangle^{*} = \langle\psi|\hat{Y}^{+}\hat{X}^{+}|\phi\rangle^{*}$, which must mean that $(\hat{X}\hat{Y})^{+} = \hat{Y}^{+}\hat{X}^{+}$.

There is another way to do the derivation without resolving an identity. First, we note that, by definition: $\langle\psi|\big(\hat{X}\hat{Y}\big)^{+}|\phi\rangle^{*} = \langle\phi|\big(\hat{X}\hat{Y}\big)|\psi\rangle$. Recall that: $\big(\hat{X}\hat{Y}\big)|\psi\rangle = \hat{X}\big(\hat{Y}|\psi\rangle\big)$ and that: $\langle\phi|\big(\hat{X}\hat{Y}\big) = \big(\langle\phi|\hat{X}\big)\hat{Y}$. Thus we can state:

$$\langle\phi|\big(\hat{X}\hat{Y}\big)|\psi\rangle = \big(\langle\phi|\hat{X}\big)\big(\hat{Y}|\psi\rangle\big)$$

We can insert the following equivalences: $\hat{Y}|\psi\rangle = \langle\psi|\hat{Y}^{+}$ and $\langle\phi|\hat{X} = \hat{X}^{+}|\phi\rangle$ to yield:

$$\big(\langle\phi|\hat{X}\big)\big(\hat{Y}|\psi\rangle\big) = \big(\hat{X}^{+}|\phi\rangle\big)\big(\langle\psi|\hat{Y}^{+}\big)$$

When you permute the order: $\big(\hat{X}^{+}|\phi\rangle\big)\big(\langle\psi|\hat{Y}^{+}\big) = \big\{\big(\langle\psi|\hat{Y}^{+}\big)\big(\hat{X}^{+}|\phi\rangle\big)\big\}^{*}$ you have to pick up a complex conjugate (because you're basically doing this: $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^{*}$). The expression $\big\{\big(\langle\psi|\hat{Y}^{+}\big)\big(\hat{X}^{+}|\phi\rangle\big)\big\}^{*}$ is of course equal to: $\langle\psi|\hat{Y}^{+}\hat{X}^{+}|\phi\rangle^{*}$. When you put the 1st step in with this last one you get:

$$\langle\psi|\big(\hat{X}\hat{Y}\big)^{+}|\phi\rangle^{*} = \langle\psi|\hat{Y}^{+}\hat{X}^{+}|\phi\rangle^{*}$$

which is the point of the proof.

c) First insert the bra-ket notation and make one simple rearrangement:

$$\sum_{a'}\langle a'|x'\rangle\langle x''|a'\rangle = \sum_{a'}\langle x''|a'\rangle\langle a'|x'\rangle$$

Now since $\sum_{a'}|a'\rangle\langle a'| = 1$ we are left with:

$$\langle x''|x'\rangle = \delta(x'' - x')$$

2. Let's say that an operator has the form: $\hat{X} = a_0 + \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{a}$. This isn't explained well, but what this means is that $\hat{\boldsymbol{\sigma}}$ are the spin matrices in x, y and z ($\sigma_x, \sigma_y, \sigma_z$) and a_0 is a weighted identity matrix. Likewise, $\boldsymbol{a}$ is a vector with components a_x in the x-direction, and the same for y and z. Thus: $\hat{X} = a_0 I + a_x\hat{\sigma}_x + a_y\hat{\sigma}_y + a_z\hat{\sigma}_z =$

$$\hat{X} = a_0\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + a_x\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} + a_y\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix} + a_z\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$$

a) Please sum these to show what the full matrix form of $\hat{X}$ is.

b) What is $tr(\hat{X})$? Hint: the trace of $\hat{X}$ is simply the sum of the diagonals

c) What are $tr(\hat{\boldsymbol{\sigma}} \cdot \hat{X})$? Hint, this is really three questions in one, which are $tr(\hat{\sigma}_{x,y,z}\hat{X})$

Answers: a) You literally just add up the matrices into one:

$$\hat{X} = \begin{bmatrix}a_0 & 0\\ 0 & a_0\end{bmatrix} + \begin{bmatrix}0 & a_x\\ a_x & 0\end{bmatrix} + \begin{bmatrix}0 & -ia_y\\ ia_y & 0\end{bmatrix} + \begin{bmatrix}a_z & 0\\ 0 & -a_z\end{bmatrix} = \begin{bmatrix}a_0 + a_z & a_x - ia_y\\ a_x + ia_y & a_0 - a_z\end{bmatrix}$$

b) The sum of the diagonals is: $2a_0$

c) The trace of: $tr(\hat{\sigma}_x\hat{X}) = tr\left(\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}a_0 + a_z & a_x - ia_y\\ a_x + ia_y & a_0 - a_z\end{bmatrix}\right) =$

$$tr\left(\begin{bmatrix}a_x + ia_y & a_0 - a_z\\ a_0 + a_z & a_x - ia_y\end{bmatrix}\right) = 2a_x$$

also: $tr(\hat{\sigma}_y\hat{X}) = tr\left(\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\begin{bmatrix}a_0 + a_z & a_x - ia_y\\ a_x + ia_y & a_0 - a_z\end{bmatrix}\right) = tr\left(\begin{bmatrix}-ia_x + a_y & -ia_0 + ia_z\\ ia_0 + ia_z & ia_x + a_y\end{bmatrix}\right) = 2a_y$

and:

$$tr(\hat{\sigma}_z\hat{X}) = tr\left(\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\begin{bmatrix}a_0 + a_z & a_x - ia_y\\ a_x + ia_y & a_0 - a_z\end{bmatrix}\right) = tr\left(\begin{bmatrix}a_0 + a_z & a_x - ia_y\\ -a_x - ia_y & -a_0 + a_z\end{bmatrix}\right) = 2a_z$$

3. a) Show that the determinant of the following 2×2 matrix $\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{a}$ is invariant under the similarity transformation:

$$\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{a} \rightarrow \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{a}' = exp\left(\frac{i\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{n}\phi}{2}\right)\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{a}\, exp\left(\frac{-i\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{n}\phi}{2}\right)$$

Hint: To state that a matrix is invariant after transformation means that the trace is the same before and after the transformation. Also, here are some properties of determinants: $det\{A \cdot B \cdot C\} = det\{C \cdot A \cdot B\} = det\{B \cdot C \cdot A\}$

b) Find $a'_{x,y,z}$ in terms of $a_{x,y,z}$ where $\boldsymbol{n}$ is a vector in the z direction. What this means is that $\boldsymbol{n}$ has component n_x in the x-direction, n_y in the y-direction, and n_z in the z-direction, and thus if $\boldsymbol{n}$ is in the z positive z direction then $n_x = n_y = 0$ and $n_z = 1$.

Please interpret your results.

Answer: a) The idea is to show that:

$$det\left\{exp\left(\frac{i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right)\cdot(\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a})\cdot exp\left(\frac{-i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right)\right\} =$$

$$det\left\{exp\left(\frac{-i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right)\cdot exp\left(\frac{i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right)\cdot\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a}\right\} =$$

$$det\left\{exp\left(\frac{-i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}+\frac{i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right)\cdot\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a}\right\} =$$

$$det\{\boldsymbol{I}\cdot\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a}\} = det\{\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a}\}$$

b) First, you should know that:

$$\frac{i}{2}\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi = \frac{i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2} = \frac{i}{2}\phi\cdot n_x\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix} + \frac{i}{2}\phi\cdot n_y\begin{bmatrix}0 & i\\ -i & 0\end{bmatrix} + \frac{i}{2}\phi\cdot n_z\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$$

Since we are in the z direction $n_x = n_y = 0$ and thus:

$$\frac{i}{2}\phi\cdot\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n} = \begin{bmatrix}\frac{i}{2}\phi & 0\\ 0 & -\frac{i}{2}\phi\end{bmatrix}$$

and taking the exponential means: $exp\left(\frac{i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right) = \begin{bmatrix}e^{\frac{i}{2}\phi} & 0\\ 0 & e^{-\frac{i}{2}\phi}\end{bmatrix}$.

Likewise: $exp\left(\frac{-i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right) = \begin{bmatrix}e^{-\frac{i}{2}\phi} & 0\\ 0 & e^{\frac{i}{2}\phi}\end{bmatrix}$, and: $\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a} = \begin{bmatrix}a_z & a_x - ia_y\\ a_x + ia_y & -a_z\end{bmatrix}$

Now we have to solve this:

$$exp\left(\frac{i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right)\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{a}\,exp\left(\frac{-i\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n}\phi}{2}\right) = \begin{bmatrix}e^{\frac{i}{2}\phi} & 0\\ 0 & e^{-\frac{i}{2}\phi}\end{bmatrix}\begin{bmatrix}a_z & a_x - ia_y\\ a_x + ia_y & -a_z\end{bmatrix}\begin{bmatrix}e^{-\frac{i}{2}\phi} & 0\\ 0 & e^{\frac{i}{2}\phi}\end{bmatrix}$$

$$= \begin{bmatrix}e^{\frac{i}{2}\phi} & 0\\ 0 & e^{-\frac{i}{2}\phi}\end{bmatrix}\begin{bmatrix}a_z\cdot e^{-\frac{i}{2}\phi} & (a_x - ia_y)\cdot e^{\frac{i}{2}\phi}\\ (a_x + ia_y)\cdot e^{-\frac{i}{2}\phi} & -a_z\cdot e^{\frac{i}{2}\phi}\end{bmatrix} =$$

$$\begin{bmatrix} e^{\frac{i}{2}\phi}\cdot a_z\cdot e^{-\frac{i}{2}\phi} & (a_x-ia_y)\cdot e^{i\phi} \\ (a_x+ia_y)\cdot e^{-i\phi} & e^{-\frac{i}{2}\phi}\cdot -a_z\cdot e^{\frac{i}{2}\phi} \end{bmatrix} = \begin{bmatrix} a_z & (a_x-ia_y)\cdot e^{i\phi} \\ (a_x+ia_y)\cdot e^{-i\phi} & -a_z \end{bmatrix}$$

Hence, we see that: $a'_z = a_z$ while the off-diagonal elements have to be evaluated as:

$$\begin{aligned}(a_x-ia_y)\cdot e^{i\phi} &= (a_x-ia_y)(\cos(\phi)+i\cdot sin(\phi)) \\ &= a_x\cdot\cos(\phi)+a_y\cdot sin(\phi)-i\{-a_x\cdot\sin(\phi)+a_y\cdot\cos(\phi)\}\end{aligned}$$

And $(a_x+ia_y)\cdot e^{-i\phi} = (a_x+ia_y)\cdot(\cos(\phi)-i\cdot\sin(\phi)) =$

$$a_x\cdot\cos(\phi)+a_y\cdot sin(\phi)+i\{-a_x\cdot\sin(\phi)+a_y\cdot\cos(\phi)\}$$

Since the real components of the off diagonal should be equal, thus:

$$a'_x = a_x\cdot\cos(\phi)+a_y\cdot sin(\phi)$$

Likewise the imaginary components switch signs but reveal:

$$a'_y = a_y\cdot\cos(\phi)-a_x\cdot\sin(\phi)$$

These are simple rotations.

4. Here you are going to practice with similarity transforms. **a.** Please construct the 2×2 transformation matrix $\hat{U}^+$ that connects the S_z diagonal basis to the S_x basis. You can figure it out using relationships derived from:

$$|S_X;+\rangle = \hat{U}^+|+\rangle$$

and

$$|S_X;-\rangle = \hat{U}^+|-\rangle$$

and the fact that: $|+\rangle = \begin{bmatrix}1\\0\end{bmatrix}$, $|-\rangle = \begin{bmatrix}0\\1\end{bmatrix}$, $|S_X;+\rangle = \begin{bmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{bmatrix}$, $|S_X;-\rangle = \begin{bmatrix}\frac{1}{\sqrt{2}}\\ \frac{-1}{\sqrt{2}}\end{bmatrix}$.

b. Now try to construct the 2×2 transformation matrix $\hat{U}$ using the general relation:

$$\hat{U} = \sum_r |b^{(r)}\rangle\langle a^{(r)}|$$

Hint: As it applies to this question, this means:

$$\hat{U} = |S_X;+\rangle\langle+| + |S_X;-\rangle\langle-|$$

c. Can you show that $\hat{U}^+\hat{U} = 1$?

Answer: a. First, we construct a 2×2 matrix with elements x_{ij} such that:

$$\begin{bmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$$

and

$$\begin{bmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} \end{bmatrix}$$

Multiply these out:

$$x_{11} \cdot 1 + x_{12} \cdot 0 = \frac{1}{\sqrt{2}};\ x_{21} \cdot 1 + x_{22} \cdot 0 = \frac{1}{\sqrt{2}};\ x_{11} \cdot 0 + x_{12} \cdot 1 = \frac{1}{\sqrt{2}};\ x_{21} \cdot 0 + x_{22} \cdot 1 = -\frac{1}{\sqrt{2}}$$

It is immediately clear that: $x_{11} = \frac{1}{\sqrt{2}};\ x_{21} = \frac{1}{\sqrt{2}};\ x_{12} = \frac{1}{\sqrt{2}};\ x_{22} = -\frac{1}{\sqrt{2}}$

And the transformation matrix is: $\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$.

b. First insert the definition of $|S_X; +\rangle = |+\rangle + \frac{1}{\sqrt{2}}|-\rangle$ and $|S_X; -\rangle = |-\rangle - \frac{1}{\sqrt{2}}|-\rangle$:

$$U = \left(\frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle\right)\langle +| + \left(\frac{1}{\sqrt{2}}|+\rangle + \frac{1}{\sqrt{2}}|-\rangle\right)\langle -| =$$

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

$$\frac{1}{\sqrt{2}}(|+\rangle\langle +| + |-\rangle\langle +|) + (|+\rangle\langle -| - |-\rangle\langle -|)$$

This is equivalent to $\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$

c. All you have to do is show:

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} = \begin{bmatrix} 1+1 & 1-1 \\ 1-1 & 1+1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

5. Let's say you are using quantum chemistry to model a solid-state material such as semiconducting CdSe. The electronic structure can be solved using the "tight binding" approximation, where you model the interaction of nearest neighbor atoms only. In

CdSe, we model the cadmium's 5s and 5p orbitals, and each orbital has a certain "self" energy $\varepsilon_{Cd,s}$ (for the 5s) and $\varepsilon_{Cd,px,y,z}$ (for the three 5p's). A Hamiltonian matrix that describes a cadmium atom by itself is:

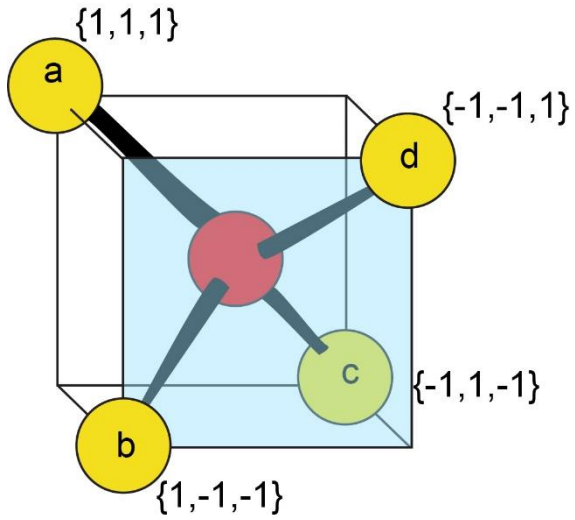
$$\begin{array}{c} \\ \langle s_{Cd}| \\ \langle p_{x,Cd}| \\ \langle p_{y,Cd}| \\ \langle p_{z,Cd}| \end{array} \begin{array}{c} \begin{array}{cccc} |s_{Cd}\rangle & |p_{x,Cd}\rangle & |p_{y,Cd}\rangle & |p_{z,Cd}\rangle \end{array} \\ \begin{bmatrix} \varepsilon_{Cd,s} & 0 & 0 & 0 \\ 0 & \varepsilon_{Cd,p} & 0 & 0 \\ 0 & 0 & \varepsilon_{Cd,p} & 0 \\ 0 & 0 & 0 & \varepsilon_{Cd,p} \end{bmatrix} \end{array}$$

The eigenvalues are $\varepsilon_{Cd,s}$ and three degenerate $\varepsilon_{Cd,p}$, which makes perfect sense. The trace is $\varepsilon_{Cd,s} + 3\varepsilon_{Cd,p}$.

When you throw in a single nearby Se atom (with its 4s and 4p orbitals) you get this Hamiltonian matrix:

$$\begin{array}{c} \\ s_{Cd} \\ p_{x,Cd} \\ p_{y,Cd} \\ p_{z,Cd} \\ s_{Se} \\ p_{x,Se} \\ p_{y,Se} \\ p_{z,Se} \end{array} \begin{array}{c} \begin{array}{cccccccc} \underline{s_{Cd}} & \underline{p_{x,Cd}} & \underline{p_{y,Cd}} & \underline{p_{z,Cd}} & \underline{s_{Se}} & \underline{p_{x,Se}} & \underline{p_{y,Se}} & \underline{p_{z,Se}} \end{array} \\ \begin{bmatrix} \varepsilon_{Cd,s} & 0 & 0 & 0 & V_{ss} & V_{sp} & V_{sp} & V_{sp} \\ 0 & \varepsilon_{Cd,p} & 0 & 0 & V_{ps} & V_{xx} & V_{xy} & V_{xy} \\ 0 & 0 & \varepsilon_{Cd,p} & 0 & V_{ps} & V_{xy} & V_{xx} & V_{xy} \\ 0 & 0 & 0 & \varepsilon_{Cd,p} & V_{ps} & V_{xy} & V_{xy} & V_{xx} \\ V_{ss} & V_{ps} & V_{ps} & V_{ps} & \varepsilon_{Se,s} & 0 & 0 & 0 \\ V_{ps} & V_{xx} & V_{xy} & V_{xy} & 0 & \varepsilon_{Se,p} & 0 & 0 \\ V_{ps} & V_{xy} & V_{xx} & V_{xy} & 0 & 0 & \varepsilon_{Se,p} & 0 \\ V_{ps} & V_{xy} & V_{xy} & V_{xx} & 0 & 0 & 0 & \varepsilon_{Se,p} \end{bmatrix} \end{array}$$

where all the $\varepsilon_{Se,s,p}$ matrix elements are the orbital energies for Se, and the coupling terms V represent the interaction of the Cd and Se atoms' atomic orbitals. Let's say you add "n" more Cd and Se atoms to the matrix and calculate the eigenvalues, you are able to determine the energies of the $(CdSe)_n$ cluster. If you then allow $n \rightarrow \infty$ then you are able to model the true solid state electronic structure. FYI the various energies and coupling terms can be derived from experiment or higher-level theories, which is why the tight binding method of quantum mechanics is called "semi-empirical".



None of this is the question- here is the real problem. It turns out that you can't model an infinite number of atoms, and thus you are going to have to have a surface with atoms that are missing one or more bonding partners. This results in "surface states"

appearing in the set of eigenvalues. This question seeks to understand surface states using the tight binding formalism. To begin, we first note that Cd has a tetrahedral environment as shown below, with four Se atoms that we label **a**, **b**, **c**, or **d** based on its coordinates within the cubic unit cell (CdSe may adopt a zinc blende structure which is in the cubic family). It makes more sense to think of the bonds as sp^3 hybridized orbitals rather than use the "block" s, p_x, p_y and p_z states. How do we transform the Cd matrix from the block to the sp^3 hybrid form? First, note that the four sp^3 bonding orbitals are:

Hybrid 1: $|sp_a^3\rangle \sim |s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle$

Hybrid 2: $|sp_b^3\rangle \sim |s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle$

Hybrid 3: $|sp_c^3\rangle \sim |s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle$

Hybrid 4: $|sp_d^3\rangle \sim |s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle$

Did you notice how the +'s and –'s track the location of the Se atoms in the unit cell?

a. Now your question is first to derive a matrix, $\hat{U}^+$, that transforms a vector that describes the cadmium block orbitals in the block form:

$$\begin{bmatrix} |s\rangle \\ |p_x\rangle \\ |p_y\rangle \\ |p_z\rangle \end{bmatrix}$$

into the hybrid form. Next, apply $\hat{U}^+$ to the cadmium Hamiltonian:

$$\hat{H} = \begin{bmatrix} \varepsilon_s & 0 & 0 & 0 \\ 0 & \varepsilon_p & 0 & 0 \\ 0 & 0 & \varepsilon_p & 0 \\ 0 & 0 & 0 & \varepsilon_p \end{bmatrix}$$

using the formula $\hat{U}^+\hat{H}\hat{U}$ to transform it into the sp^3 hybrid form. ***Hint***, you also need to know $\hat{U}$, which you can figure out using $\hat{U}^+\hat{U} = 1$.

b. When you calculate $\hat{U}^+\hat{H}\hat{U}$, its going to look something like this:

$$\begin{array}{c} \\ \langle sp_a^3| \\ \langle sp_b^3| \\ \langle sp_c^3| \\ \langle sp_d^3| \end{array} \begin{array}{c} \begin{array}{cccc} |sp_a^3\rangle & |sp_b^3\rangle & |sp_c^3\rangle & |sp_d^3\rangle \end{array} \\ \begin{bmatrix} a & b & b & b \\ b & a & b & b \\ b & b & a & b \\ b & b & b & a \end{bmatrix} \end{array}$$

where a and b are functions of $\varepsilon_{s,p}$.

What are the eigenvalues and trace of this matrix? Discuss whether the result makes sense.

c. If one or more of the Se atoms are missing for the surface bound Cd, then we are going to get undesirable surface states. Instead, what we can do is pretend to add a ligand that passivates the surface by raising the energy of the orbital. For example, if we are missing two Se atoms, at positions **a** and **c**, then we can add "δ" amount of energy to those diagonal elements as follows:

$$\begin{array}{c} \\ \langle sp_a^3| \\ \langle sp_b^3| \\ \langle sp_c^3| \\ \langle sp_d^3| \end{array} \begin{array}{c} \begin{array}{cccc} |sp_a^3\rangle & |sp_b^3\rangle & |sp_c^3\rangle & |sp_d^3\rangle \end{array} \\ \begin{bmatrix} a+\delta & b & b & b \\ b & a & b & b \\ b & b & a+\delta & b \\ b & b & b & a \end{bmatrix} \end{array}$$

This passivates the surface along these bond vectors and prevents surface states from forming. Now we ultimately need to transform the above back to the block form to use it. How do you do that? Please use Matlab to do so and show the results.

d. Let's say that the Cd atom was by itself and needs passivation along all four bond vectors. Can you represent:

$$\begin{array}{c} \\ \langle sp_a^3| \\ \langle sp_b^3| \\ \langle sp_c^3| \\ \langle sp_d^3| \end{array} \begin{array}{c} \begin{array}{cccc} |sp_a^3\rangle & |sp_b^3\rangle & |sp_c^3\rangle & |sp_d^3\rangle \end{array} \\ \begin{bmatrix} a+\delta & b & b & b \\ b & a+\delta & b & b \\ b & b & a+\delta & b \\ b & b & b & a+\delta \end{bmatrix} \end{array}$$

in the block form and discuss why the result makes sense?

Last Hint: I am basing this problem off of Lee et al. Phys Rev. B (2004), 69, 045316. You might want to look at it. There are also some Matlab codes in the appendix.

Answer: a. First define the matrices using Matlab:

```
syms es ep d;
cdH=[es, 0, 0, 0; 0, ep, 0, 0; 0, 0, ep, 0; 0 0 0 ep];
eig(cdH)
U=[1, 1, 1, 1; 1, 1, -1, -1; 1, -1, 1, -1; 1, -1, -1, 1];
transU=inv(U);
sp3cd=transU*cdH*U;
sp3cd
sp3cd =
[ (3*ep)/4 + es/4,     es/4 - ep/4,     es/4 - ep/4,     es/4 - ep/4]
[     es/4 - ep/4, (3*ep)/4 + es/4,     es/4 - ep/4,     es/4 - ep/4]
[     es/4 - ep/4,     es/4 - ep/4, (3*ep)/4 + es/4,     es/4 - ep/4]
```

```
[     es/4 - ep/4,     es/4 - ep/4,     es/4 - ep/4, (3*ep)/4 + es/4]
```

Let's make that look nicer:

$$\begin{array}{c} \\ \langle sp_a^3| \\ \langle sp_b^3| \\ \langle sp_c^3| \\ \langle sp_d^3| \end{array} \begin{array}{c} \begin{array}{cccc} |sp_a^3\rangle & |sp_b^3\rangle & |sp_c^3\rangle & |sp_d^3\rangle \end{array} \\ \begin{bmatrix} \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} \\ \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} \\ \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} \\ \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4} \end{bmatrix} \end{array}$$

b. First define a new matrix as:

```
delta=[d, 0, 0, 0; 0, 0, 0, 0; 0, 0, d, 0; 0, 0, 0, 0];
newsp3cd=sp3cd+delta;
newsp3cd =
```

[d + (3*ep)/4 + es/4, es/4 - ep/4, es/4 - ep/4, es/4 - ep/4]

[es/4 - ep/4, (3*ep)/4 + es/4, es/4 - ep/4, es/4 - ep/4]

[es/4 - ep/4, es/4 - ep/4, d + (3*ep)/4 + es/4, es/4 - ep/4]

[es/4 - ep/4, es/4 - ep/4, es/4 - ep/4, (3*ep)/4 + es/4]

Let's make that look nicer:

$$\begin{array}{c} \\ \langle sp_a^3| \\ \langle sp_b^3| \\ \langle sp_c^3| \\ \langle sp_d^3| \end{array} \begin{array}{c} \begin{array}{cccc} |sp_a^3\rangle & |sp_b^3\rangle & |sp_c^3\rangle & |sp_d^3\rangle \end{array} \\ \begin{bmatrix} \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4}+\delta & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} \\ \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} \\ \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4}+\delta & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} \\ \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}-\frac{\varepsilon_p}{4} & \frac{\varepsilon_s}{4}+\frac{3\cdot\varepsilon_p}{4} \end{bmatrix} \end{array}$$

Next we transform back to the block form:

```
newcdH=U*newsp3cd*transU
```

[d/2 + es, 0, d/2, 0]

[0, d/2 + ep, 0, d/2]

[d/2, 0, d/2 + ep, 0]

[0, d/2, 0, d/2 + ep]

Again let's make this more readable:

$$\begin{array}{cccc} |s_{Cd}\rangle & |p_{x,Cd}\rangle & |p_{y,Cd}\rangle & |p_{z,Cd}\rangle \end{array}$$

$$\begin{matrix}\langle s_{Cd}| \\ \langle p_{x,Cd}| \\ \langle p_{y,Cd}| \\ \langle p_{z,Cd}|\end{matrix}\begin{bmatrix}\varepsilon_s+\delta/2 & 0 & \delta/2 & 0 \\ 0 & \varepsilon_p+\delta/2 & 0 & \delta/2 \\ \delta/2 & 0 & \varepsilon_p+\delta/2 & 0 \\ 0 & \delta/2 & 0 & \varepsilon_p+\delta/2\end{bmatrix}$$

C. Likewise:

```
delta=[d, 0, 0, 0; 0, d, 0, 0; 0, 0, d, 0; 0, 0, 0, d];
newsp3cd=sp3cd+delta;
newcdH=U*newsp3cd*transU;
newcdH =
```

[d + es, 0, 0, 0]

[0, d + ep, 0, 0]

[0, 0, d + ep, 0]

[0, 0, 0, d + ep]

Which looks much better when using the word editor:

$$\begin{matrix}\langle s_{Cd}| \\ \langle p_{x,Cd}| \\ \langle p_{y,Cd}| \\ \langle p_{z,Cd}|\end{matrix}\begin{matrix}\begin{matrix}|s_{Cd}\rangle & |p_{x,Cd}\rangle & |p_{y,Cd}\rangle & |p_{z,Cd}\rangle\end{matrix} \\ \begin{bmatrix}\varepsilon_s+\delta & 0 & 0 & 0 \\ 0 & \varepsilon_p+\delta & 0 & 0 \\ 0 & 0 & \varepsilon_p+\delta & 0 \\ 0 & 0 & 0 & \varepsilon_p+\delta\end{bmatrix}\end{matrix}$$

You simply raise the energy of every diagonal element by δ.

Appendix

Matlab symbolic matrices, first define some symbolic variables, and put them in matrix form:

```
syms a b;
Hmatrix=[a, b; b, a];
```

We can ask the eigenvalues of this equation:

```
eig(Hmatrix)
```

ans =

a + b

a - b

Next, lets add off diagonal elements:

```
syms a b delta;
dm=[0 delta; delta, 0];
newHmatrix=Hmatrix+dm;
```

And now we can calculate the eigenvalues of this.

```
eig(newHmatrix)
```

ans =

a - b - delta

a + b + delta

Here is the inverse of the operator:

```
invHmatrix=inv(Hmatrix)
invHmatrix
```

ans =

[a^2/(a^2 - b^2) - b^2/(a^2 - b^2), 0]

[0, a^2/(a^2 - b^2) - b^2/(a^2 - b^2)]

Now normally I would expect the above to be the identity matrix. It is, its just not clear because there are no associated values. To demonstrate, you can assign values to a and b and then re-evaluate as follows:

```
a=5; b=9;
eval(Hmatrix)
ans =

     5     9
     9     5
eval(invHmatrix)
ans =
```

```
   -0.0893    0.1607
    0.1607   -0.0893
eval(invHmatrix*Hmatrix)
```
ans =

1 0

0 1

So, you have clearly ideintified the inverse. For similarity transforms, the inverse of a matrix is the definition of the transpose.