

## PHYS 10 CURE Lab Exercise

### From the square well model to real atomically thin materials and devices

Prof. David Strubbe, University of California, Merced, November 2023

**Objectives:** You will begin by understanding the concept of envelope functions via systems of square wells, and the concept of isosurfaces via the hydrogen atom. You will study the wavefunctions of a heterojunction of MoS<sub>2</sub> and MoSe<sub>2</sub> which are atomically thin 2D materials, and interpret them in terms of envelope functions. After this preparation, you will calculate the structure of a heterojunction of your own pair of 2D materials, and investigate whether the wavefunctions are confined (or not) in one of the materials in a way that resembles the square well model. This will be your own original research result!

I have noted in some particular places where you should be sure to take screenshots, make sketches, or save certain data. In general all the questions and things described for you to look at or think about are points that should be addressed in your lab report. My guest lecture on Tuesday will be a valuable reference.

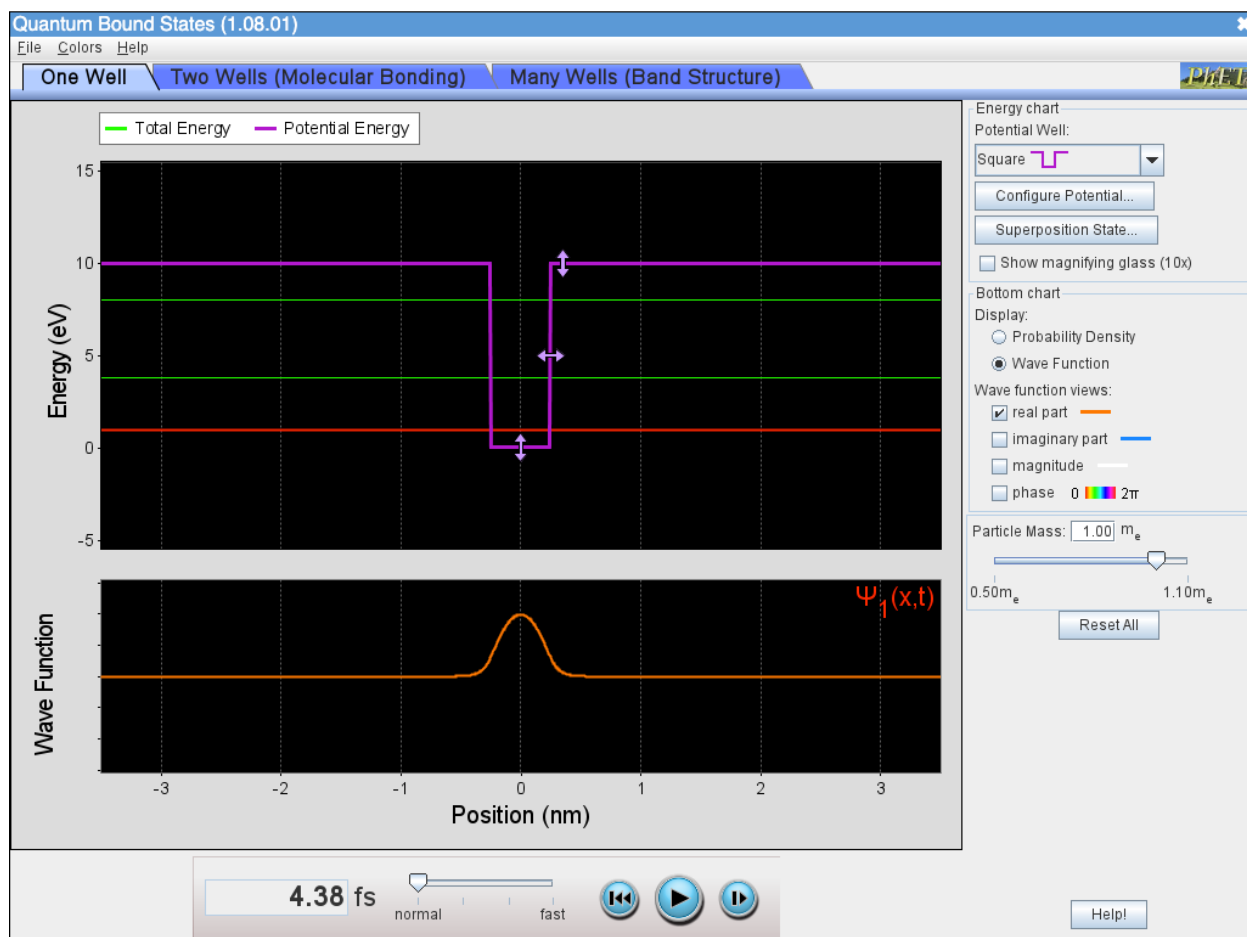
#### 1. PhET Simulation: quantum wells and envelope functions

We will get warmed up by exploring the concept of envelope functions in a system of square wells, like the GaAs/AlGaAs multilayers in a quantum well laser.

In a browser, go to the Quantum Bound States exercise at <https://phet.colorado.edu/sims/cheerpi/bound-states/latest/bound-states.html?simulation=bound-states>.

We will begin by looking at numerical solutions to the single square well, as you have seen before.

- Start in the tab “One Well”.
- Click “Configure Potential” in the upper right and set Width to 0.5 nm, equal to  $5 \times 10^{-10}$  m.
- In “Bottom chart” on the right, set “Display:” to “Wave Function”. You will see the wavefunction start to oscillate. At the bottom center, click the pause button at a moment when the wavefunction is positive and the amplitude looks large. We won’t be interested in the time-dependent behavior *per se*, which may otherwise be a bit distracting.
- The bottom chart should show the label  $\psi_1(x,t)$ , i.e. the lowest-energy state. The overall view should look like this:



- Make a sketch and/or save a screenshot of the wavefunction  $\psi_1$  (like the one above).
- In the upper chart, click on the green horizontal lines to select  $\psi_2$  and  $\psi_3$  [it may be helpful to click “Show magnifying glass (10x)” in the upper right], and again sketch or save the wavefunctions, making sure to include the horizontal axis scale. Compare each of these 3 lowest solutions of the wavefunction to what you have learned in class.
- Click “Configure Potential”, and set Width to 6.0 nm (the maximum), equal to  $6 \times 10^{-9}$  m.
- Again sketch/screenshot  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$ . What is similar and what is different between the results for 6.0 nm from the original 0.5 nm?

Next, we will investigate a system of many square wells and relate them to the single square well. We will set up a system of 10 wells of 0.5 nm width, with a total width close to 6.0 nm, so it has a connection to the two single square well systems we looked at.

- Select the tab “Many Wells (Band Structure)”.
- Set “Number of Wells” to 10 with the slider.
- Click “Configure Potential,” and set Height to 20.0 eV (the maximum) via slider or typing.
- In “Bottom chart” set “Display:” to “Wave Function”.
- As before, click the pause button at a moment when the amplitude looks large and the wavefunction is positive.

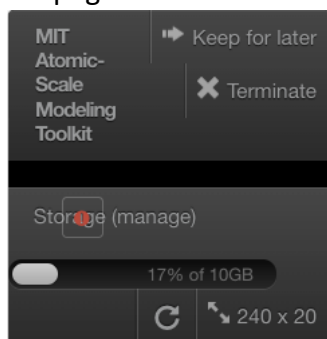
- Sketch  $\psi_1$  (you can screenshot too, but we'll want a sketch, to add more sketches to shortly).
- Take a look at the next states  $\psi_2$  and  $\psi_3$  by using the magnifying glass in the Energy diagram to select them. They will be all the way at the bottom. Sketch these too.
- Now consider  $\psi_1$  again. Looking at the wavefunction within a single one of the 10 wells, which wavefunction of the single 0.5 nm well does this wavefunction resemble most closely? Look back at your sketches/screenshots from the One Well. Sketch this corresponding wavefunction on your  $\psi_1$  sketch.
- Now looking at the entire wavefunction, which wavefunction of the 6.0 nm well solutions does it resemble most closely? This is the *envelope function*. Again, sketch this wavefunction on your  $\psi_1$  sketch and label it as the envelope function. The complete wavefunction should be equal to the 0.5 nm well solution *multiplied* by the envelope function.
- For  $\psi_2$  and  $\psi_3$ , identify their corresponding 0.5 nm well solutions and 6.0 nm well envelope functions, and add them to you. Be sure that in making the correspondence to the 0.5 nm well solutions you are looking at the right length scale, only at a *single* 0.5 nm well. If you look on a longer length scale, you will be getting this mixed up with the envelope function.
- You can see from the pattern of the green lines representing energy levels that they form several *bands* that are close in energy. Each band will correspond to one solution of the 0.5 nm well. Identify the solutions corresponding to the second band around 4 eV and the third band around 10 eV, supporting your interpretation with a sketch and/or screenshot.

## 2. nanoHUB: Wavefunctions and isosurfaces.

Go to <https://nanohub.org>. Click on "Menu" at the upper right, then Login, and Create Account. Use one of the methods offered such as Google or Login through your institution. In any case, you will need to enter a bit of info about yourself (for this academic project to keep track a bit about who is using it), and confirm your email. When you are logged in, go to the MIT Atomic-Scale Modeling Toolkit at the URL [https://nanohub.org/tools/ucb\\_compnano](https://nanohub.org/tools/ucb_compnano). This lab manual was prepared for version 5.9.2 of the tool. Click "Launch Tool." Select from the Applications dropdown menu at the upper right: "DFT for Solids, Nanostructures, and Molecules (SIESTA)."

A couple of points to note:

- nanoHUB will keep your sessions going unless you click "Terminate" or leave them for several days, and then can be accessed again from your account at <https://nanohub.org>.
- If the nanoHUB window shrinks down like below or doesn't respond, you can reload the page.



- If the simulation doesn't seem to run, or you don't have a Simulate button, click "Clear" or "Clear All" at the bottom.
- If you hover the mouse over an option in the graphical user interface (GUI), generally some text will appear to give you more information.

- Begin by setting the following parameters:

Basis: double zeta with polarization (DZP) (decent)

*[controls the number of atomic-like orbitals used to describe the wavefunctions]*

Plot wavefunctions in XCrySDen? yes

Wavefunction band index minimum: 1

Wavefunction band index maximum: 5

Type of System: Molecule

Coordinates (Cartesian): *[by typing, delete what is there and enter this:]*

1

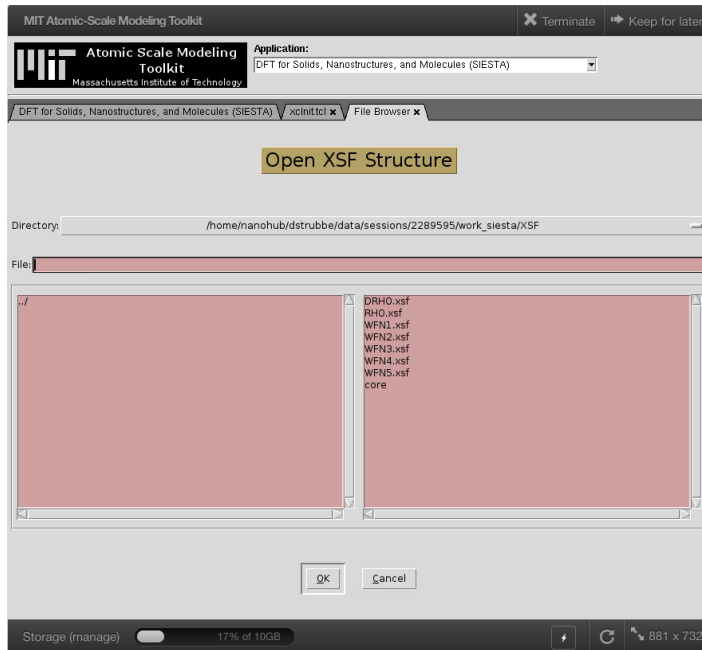
H 0.0 0.0 0.0

This input will give us a simulation of a single atom of hydrogen (H).

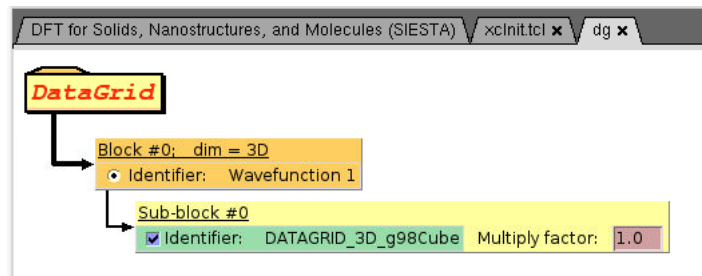
- Before running, resize the window by dragging the bottom right corner, where it says a size such as "780 x 600" – make it bigger, or else one of the windows later won't show some buttons. A size like 881 x 732, for example, worked.
- Now click Simulate.
- An XCrySDen tab will open. XCrySDen is a common program for visualizing structures and other outputs from density-functional theory (DFT) calculations.<sup>1</sup> You will see a big blue sphere, representing the H atom.
- Go to the File menu at the top, and click Close.
- Go to File again, and click Open Structure -> Open XSF (XCrySDen Structure File).
- A new tab "File Browser" will pop open listing the files available to view. RHO.xsf is the total electron density, and WFN1,2,3,4,5 are the wavefunctions. Click on WFN1.xsf to start with.

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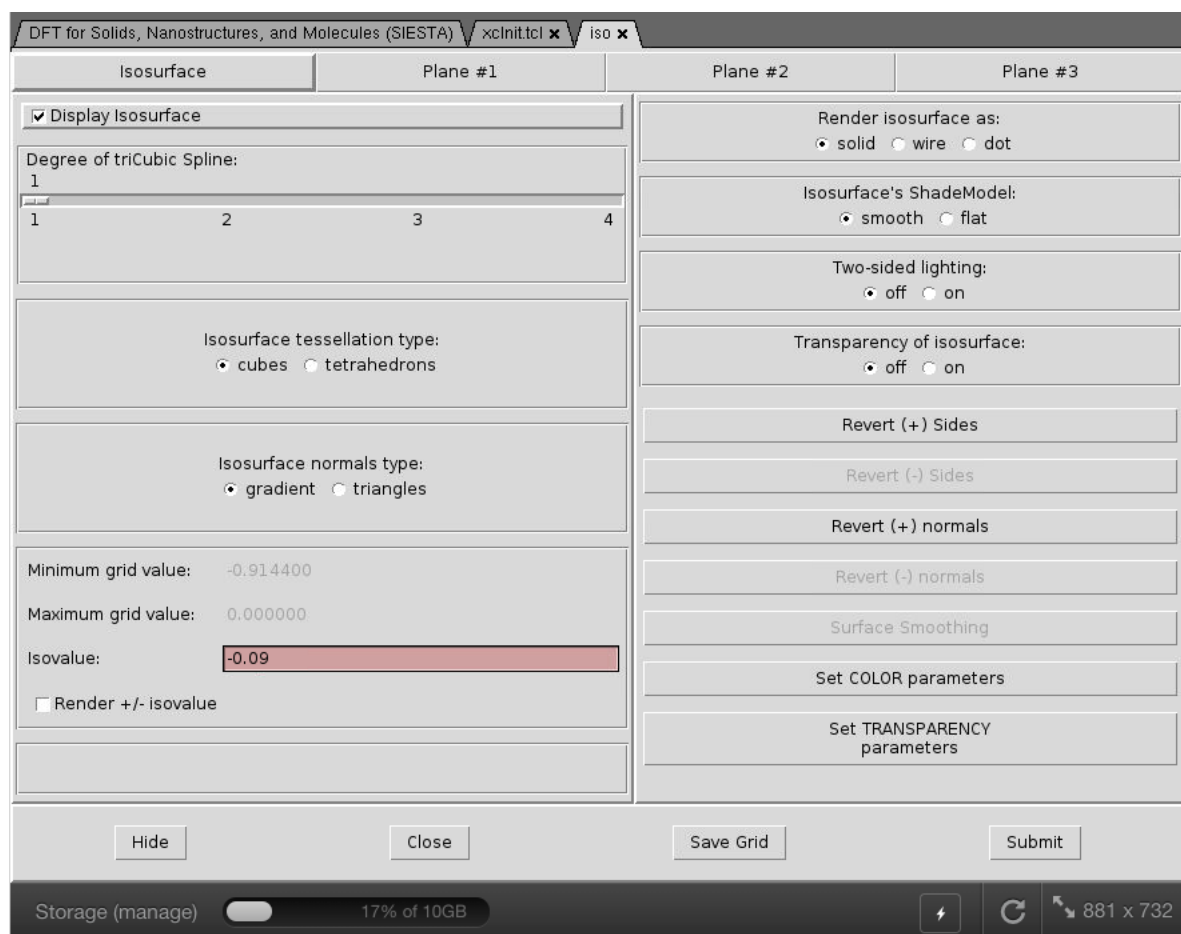
<sup>1</sup> You can resort if necessary to the documentation at <http://www.xcrysden.org/Documentation.html> for help.



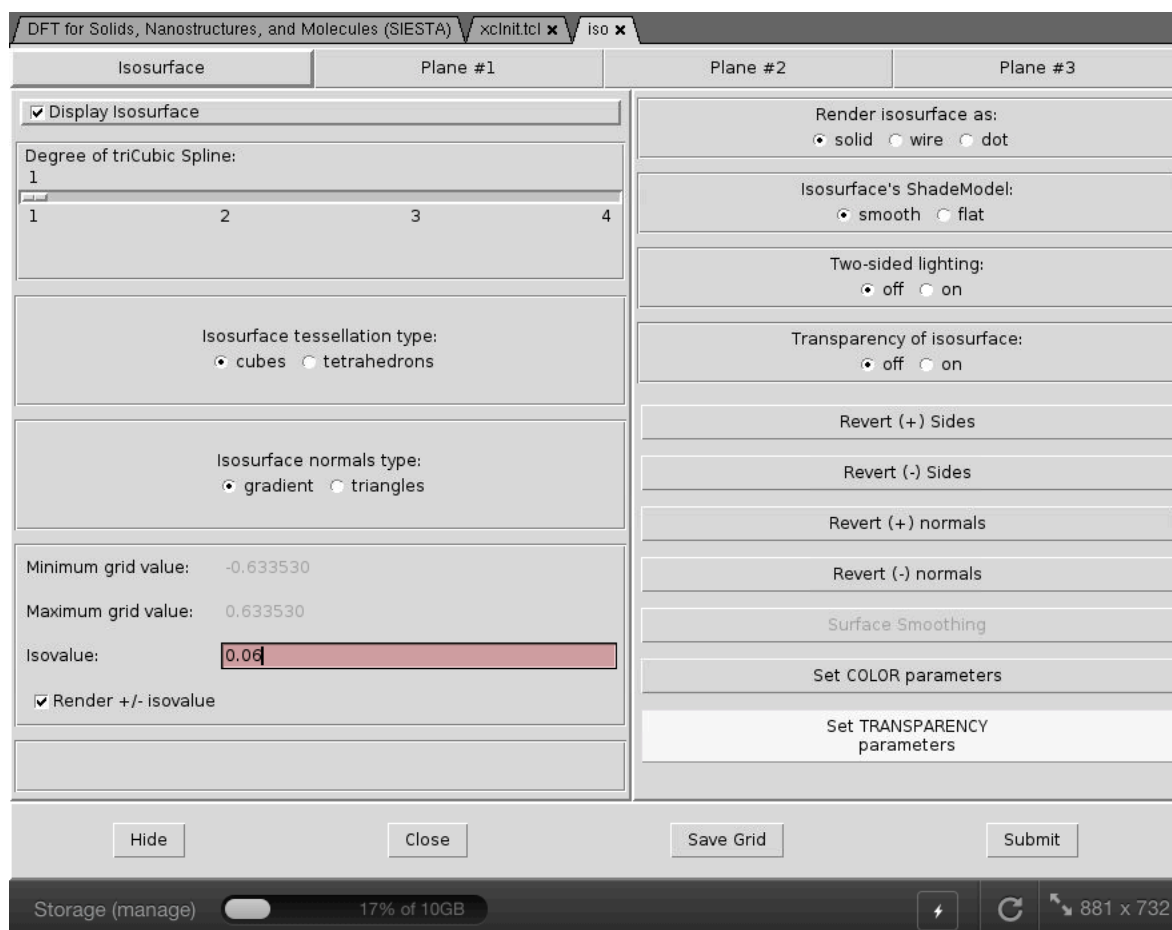
- Go to the Tool menu at the top, then select Data Grid. Another tab will pop open saying “DataGrid” and “Wavefunction 1” within it. Click Ok at the bottom right.



- A tab labeled “iso” will open up. Look for the “Minimum grid value” and “Maximum grid value” in the lower left. Choose whichever one is nonzero, and then enter as “Isovalue” about 10% of that value (including a negative sign if it is negative). Click Submit in the lower right. (If you don’t see the button, resize the window to make it bigger, close this tab, and reopen it by repeating the previous step.)



- Click on the XCrySDen tab to return to it. You will see just some yellow shades. Go to “Zoom–” in the upper right and click many times to zoom out, till you see a yellow sphere. You can also try scrolling via the mouse or touchscreen.
- This sphere is an isosurface, showing where the wavefunction is equal to the isovalue. We are looking at the lowest-energy 1s orbital of H. Save a screenshot. Click and drag to look from other angles to see that it is a sphere.
- Return to the “iso” tab and double the isovalue you used. Click Submit. How does the isosurfaces compare to the previous one in size and/or shape? Save a screenshot (don’t zoom in or out, to keep the same scale).
- Double the isovalue again, compare to the previous ones, and save a screenshot.
- Click File->Close, and File->Open Structure -> Open XSF (XCrySDen Structure File). This time, choose WFN3.xsf which will be a 2p orbital.
- Repeat the sequence of Tools->Data Grid, where it will say “Wavefunction 3”. Click Ok.
- This time you will find that the Minimum grid value and Maximum grid value are both nonzero and opposite to each other. Set the isovalue to 10% of the Maximum grid value, and select “Render +/- isovalue.” Click Submit.



- Zoom out again until you see the orbital, as a pair of blue (positive) and red (negative) lobes, with the light blue sphere representing the atom in the middle. The blue surface is where the wavefunction is equal to the positive isovalue and the red surface is where it has minus that value. Save a screenshot.
- Again, double the isovalue, see how the isosurfaces changes in size and/or shape, and save a screenshot.
- Double once more.
- Make a sketch of the 1s isosurfaces, centered on the same atom, labeling each with its isovalue. Do the same for the 2p isosurfaces.

### 3a. nanoHUB research calculation:

Now we will get started on a realistic material system, in particular the novel ones we are trying to study.

- Prof. Strubbe will assign you a material. We will work with a pair chosen from 8 options: MoO<sub>2</sub>, MoS<sub>2</sub>, MoSe<sub>2</sub>, MoTe<sub>2</sub>, WO<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, WTe<sub>2</sub>.
- Starting by setting the following parameters (and leaving others as they are by default):  
XC Functional: GGA/PBE

*[an approximation within DFT for how electrons interact with each other]*

Basis: double zeta with polarization (DZP) (decent)

*[controls the number of atomic-like orbitals used to describe the wavefunctions]*

Test calculation? yes

Plot total potential in XCrySDen? yes

Plot wavefunctions in XCrySDen? no

Type of System: Sheet/Slab

k-point sampling in x: 2

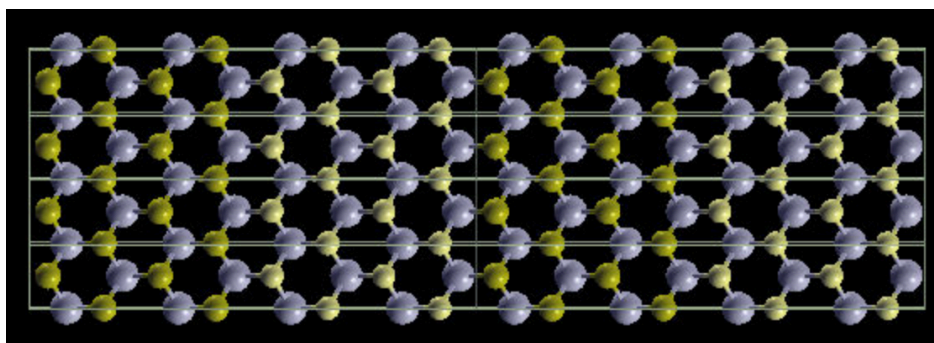
k-point sampling in y: 1

Sheet/surface slab structure: Molybdenum Disulfide (Supercell, 8x1)

Be sure to set “GGA/PBE” – with the default “LDA/CA,” any calculation with W will crash immediately because there is a problem with the LDA pseudopotential file for W.

- Next, set up the correct choice of atoms in your structure, in the Coordinates (Cartesian) section. The first two lines are the “lattice vectors” in Å which defines the repeat unit of the system. Then comes the number of atoms (24), and finally a list of all the atoms, one on each line, with the atomic symbol and then the x, y, and z coordinates in Å. The example structure is pure MoS<sub>2</sub>. Replace Mo and S in the first 12 lines with the appropriate atoms of your first material. Replace Mo and S in the last 12 lines with the appropriate atoms of your second material. This will give a quantum well structure with alternating strips of the two materials, each 4 units wide. Check your work carefully.
- Now click “Simulate”. You will see some text being written in the window as the SIESTA code runs, but it isn’t doing much with “test calculation mode.” When it finishes, you will have a tab with several panes of text information and plots (largely blank); and an XCrySDen tab which shows the atomic structure with only a single unit cell (the repeating unit).
- In XCrySDen, the balls of different colors are atoms, and each atom type has a different color (although they can be quite similar). Bonds are drawn as lines between them – this is just based on a somewhat arbitrary distance criterion and does not always correspond to chemical or physical intuition about covalent bonding. The box around the atoms indicates the repeating unit (the “unit cell”). You can click and drag to look at the structure from different angles. Note how it is atomically thin when viewed from the side. You can see the coordinate axes by pressing “y” or selecting Display->Coordinate System. You can click “Zoom +” or “Zoom –” to zoom in or out, or click the big red arrows in the upper right to move the structure in a given direction. You can return to viewing along a given axis by clicking one of the buttons in the lower right that has a red arrow in it.
- Use Display->Atomic Symbols to get atomic labels so you can be sure the elements are as intended. Use Modify->Number of Units Drawn [you may have to hold down the mouse button on Modify to keep it from selecting another option] to periodically repeat the structure: choose 4 in X-dir, 2 in Y-dir, and leave as 1 in Z-dir; then select Ok. The code is treating the structure as repeating infinitely in 2D (X and Y), but this setting visualizes the repetition. Verify that this structure is indeed what you meant it to be, in terms of your two materials. It should look similar to the image below (which I rotated by 90°). If you find there is any problem, fix it and repeat.





- Once you are satisfied you have the right structure, save your input coordinates by going back to the SIESTA tab. In the “XYZ Coordinates” pane, download them by clicking the green arrow to the right. Click “Input” at the bottom to return to the Input section, and set  
Run type: geometry optimization  
Test calculation? no  
Run in parallel? yes
- Save a screenshot of your input parameters.
- Click “Simulate.” This will take a little while. If it takes a very long time to get output (e.g. 25 minutes), or stops with some weird error, you can try doing it with “Run in parallel? No” instead, but in that case it will probably take around an hour. In the meantime, open [https://nanohub.org/tools/ucb\\_compnano](https://nanohub.org/tools/ucb_compnano) in another browser window or tab, for another run.

#### 4. nanoHUB benchmark calculations: MoS<sub>2</sub> / MoTe<sub>2</sub> system

While your lengthy geometry optimization is running, we will all do the same calculation as a benchmark, to get the hang of it. Continue with “DFT for Solids, Nanostructures, and Molecules (SIESTA).”

- Set parameters as follows:  
XC Functional: GGA/PBE  
Run type: total energy  
Basis: double zeta with polarization (DZP) (decent)  
Run Jmol viewer? no  
Plot total potential in XCrySDen? yes  
Plot wavefunctions in XCrySDen? yes  
Type of System: Sheet/Slab  
k-point sampling in x: 2  
k-point sampling in y: 1  
Sheet/surface slab structure: Molybdenum Disulfide (Supercell, 8x1)  
Run in parallel? no

- In Coordinates (Cartesian), again replace the first 12 lines with the first material (now, MoS<sub>2</sub> – well, that's what they are already) and the second 12 lines with the second material (now, MoTe<sub>2</sub>). This will give a quantum well structure with alternating strips of MoS<sub>2</sub> and MoTe<sub>2</sub>, each 4 atoms wide. So as not to have to wait too long, we are making the quite significant approximation of ignoring the structural changes due to substitution of atoms.

XC Functional: GGA/PBE  
 Run type: total energy  
 Basis: double zeta with polarization (DZP) (decent)

Test calculation?: ☐ no  
 Write FDF only?: ☐ no  
 Run Jmol viewer?: ☐ no  
 Plot total potential in XCrySDen?: ☒ yes  
 Plot wavefunctions in XCrySDen?: ☒ yes

Wavefunction band index minimum: 1  
 Wavefunction band index maximum: 5

Apply electric field?: ☐ no  
 Type of System: Sheet/Slab

Input for sheet/slab

k-point sampling in x: 2  
 k-point sampling in y: 1  
 Out-of-plane lattice constant (Angstroms): 20

Coordinate Data (Cartesian)

Sheet/surface slab structure: Molybdenum Disulfide (Supercell, 8x1)

Coordinates (Cartesian):

S	1.59516	-4.60484	1.46939
S	1.59516	-4.60484	4.67561
Mo	1.59516	-0.92096	3.07250
S	0.00000	-1.84195	1.46939
S	0.00000	-1.84195	4.67561
Mo	0.00000	1.84193	3.07250
Te	1.59516	0.92096	1.46939
Te	1.59516	0.92096	4.67561
Mo	1.59516	4.60484	3.07250
Te	0.00000	3.68385	1.46939

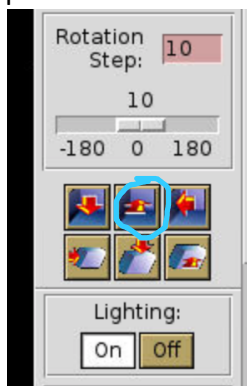
- To set the Wavefunction band index fields: we can calculate which is the highest occupied state, as follows. We have 8 Mo/W atoms (6 valence electrons each) and 16 S/Se/Te atoms (6 valence electrons each) in the structure. (You can try to see why we get these numbers of valence electrons based on the periodic table.) We only count valence electrons, i.e. those in the outermost shells which are key for bonding, electrical conductivity, and absorption of light, because we are able to treat the inner electrons as fixed through a computational scheme called a “pseudopotential.” This gives 144 electrons total. There are two electrons per state (up and down spins), so there are 72 occupied states. We will aim to see the two highest occupied states (71, 72) and two lowest unoccupied states (73, 74). In general, these

states are much more likely to fit the quantum well model than states that are much higher or lower in energy. So, set the parameters as follows:

Wavefunction band index minimum: 71

Wavefunction band index maximum: 74

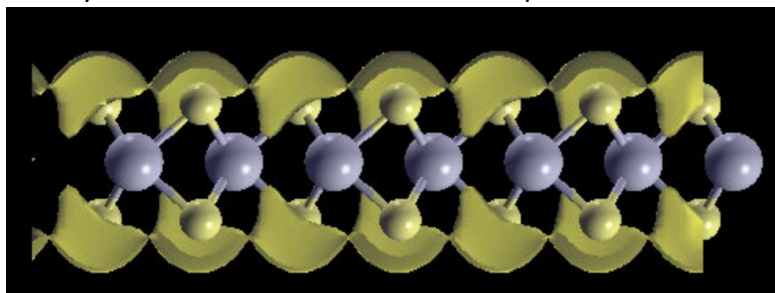
- Now click “Simulate”. You will see a lot of text being written in the window as the SIESTA code runs for a few minutes. Don’t worry about all the details. You will see it take a little while on a step about the charge density, which is expected.
- When it finishes, you will have a tab with several panes of text information and plots; and two XCrySDen tabs. Confirm from “Key Outputs” that the number of electrons is as expected by the reasoning above.
- Look at the structure in the first (leftmost) XCrySDen tab and confirm that it is the structure we were trying to set up, as in the previous section (or else fix it). Save a screenshot of the structure in different orientations.
- In XCrySDen, you can measure the distance between atoms by clicking on “Distance” at the bottom left. A new tab called “sel\_dist” will open up. Return to the XCrySDen tab where you had clicked “Distance,” and click on two atoms to select them; they should be shown in green. Return to the “sel\_dist” tab (you might need to increase the size of the window overall to see it, by clicking and dragging in the lower right corner), and you will see the coordinates of the selected atoms. Click “Done” to get the distance between the atoms.
- Let’s try it out, using a view in the yz plane. Display the coordinate system if needed to help you identify that plane. You can also use a button that directly orients the system in that plane.



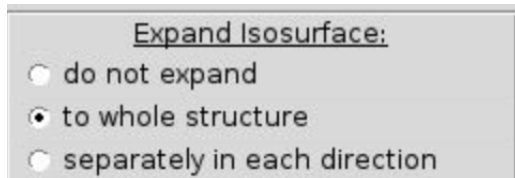
What is the bond distance between an Mo atom and one of its neighboring S atoms? What is the thickness of the layer, i.e. the distance between two S atoms on opposite sides?

- Now go to the rightmost XCrySDen tab (RHO.xsf) to visualize the density. This density is not just  $|\psi|^2$ , but the sum of this for each of the 72 occupied wavefunctions. Go to Tools -> Data Grid. Where it says “Identifier” you will see the text “Electronic Charge Density (RHO).” Click OK. [If you get Error: can’t read “DataGrid(launch\_command)”: no s...” then select OK, and in the XCrySDen window, use File->Close; File->Open Structure->Open XSF Structure to open RHO.xsf.] An isosurface tab will pop up. This is a way of visualizing a scalar function defined on a 3D grid: we will see a yellow surface that shows where the function has a specified value. It is like a 3D version of “contour lines” such as we can use to visualize a function defined in

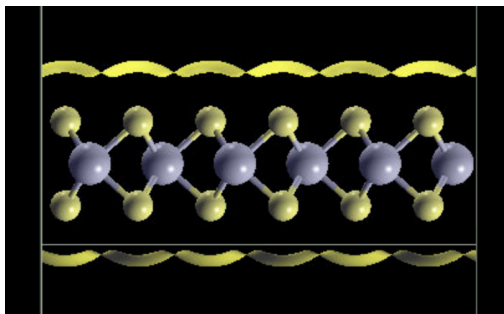
2D, like the elevation of mountains and valleys on a map for hiking. If you find that the isosurface tab that pops up lacks the buttons at the bottom, resize as described before. About 10% of the maximum magnitude (judging by the maximum and minimum values listed) is a good isosurface value to put in the red/purple box. The value chosen must be between the maximum and minimum or you will get an error, as there is nothing to show in that case. Once you have chosen your isovalue, click “Submit” to see the isosurfaces. You can play around with different values to get an idea of how the function varies in space. Note that due to some limitations of the codes that produce the files to visualize, the isosurfaces and the atoms may not cover exactly the same region; if needed for interpretation, remember that the atoms periodically repeat in plane. Annoyingly, you will not be able to use Modify->Number of Units Drawn in this pane.



- Is the density is concentrated in one material, or the other, or equally distributed over both? You will probably find that the view in the yz plane, *i.e.* where y is horizontal and z is vertical, is the most informative, not only for the density but also for the potential and wavefunctions.
- We don't need to look at it now, but there is also a related file DRHO.xsf available for viewing, which is the difference between the sum of the electron densities of isolated atoms and the electron density of the complete system.
- Next, let's look at the total potential,  $V(r)$ , which is in the second (rightmost) XCrySDen window. You will see the same atomic structure (though presented a bit differently), in the unit cell. Set Modify->Number of Units Drawn, In Z-Dir to 2, which will avoid the isosurface being split abruptly where it meet the edge of the unit cell.
- Go to Tools->Data Grid. If you get an error, close the file and load total\_potential.XSF in the method described above. In Data Grid, it should say “siesta.VT”, and the values should be mostly negative, as the potential is attractive so that electrons stay near the atoms rather than drifting out into the vacuum.
- In the isosurfaces tab, select the option to expand to whole structure, and then the “Number of Units Drawn” option will apply to the isosurfaces as well as the atoms.



You can zoom in on just one of the copies of the structure and its isosurface which may cross into the next unit cell.

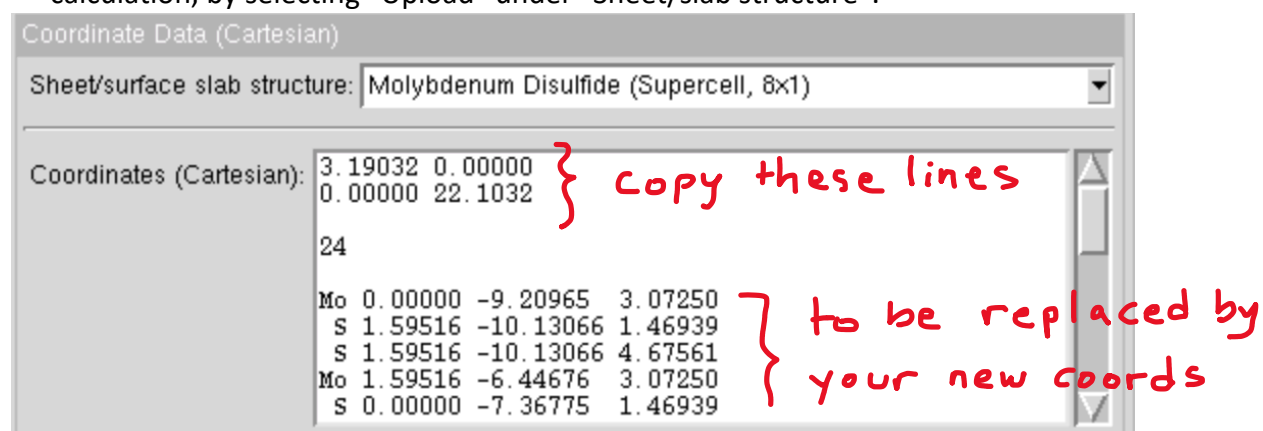


- Select a few isosurfaces to visualize the potential, starting with 10% of the minimum value (which is much larger in absolute value than the maximum value).
- Do you see a sign of the potential being different in one material than in the other? This has some relation to the chemistry concept of “electronegativity” of atoms.
- Finally, let’s check out the wavefunctions, using either of the XCrySDen tabs to load the files with names like WFN\*.xsf, as in the H atom example earlier. The number of the wavefunction will also be identified in the Data Grid screen. You will find typically that the minimum value is minus the maximum value. Again, around 10% of the maximum is a good isovalue. Select “Render +/- isovalue.” Now instead of the yellow surface you will get blue and red surfaces, which represent the positive and negative values. As recommended above, view in the yz plane which will be easiest to interpret.
- For each of the four wavefunctions, save screenshots that show whether the wavefunction is localized in one material or the other, or evenly distributed over both.
- Make a rough sketch of the “envelope function” of the wavefunction, along the y direction. Be sure to include axes in your plot, so that it is clear where your envelope function is positive, negative, or zero. Look back at the examples in lecture if needed to refresh your memory, recalling that the idea of the envelope function is to divide out the variation of the wavefunction on an atomic scale, and look at a larger scale pattern over several atoms.
- Note whether there is a node in this envelope function, i.e. whether it is like the  $n=1$  or  $n=2$  or higher solution of the square well. Don’t be distracted by atomic-scale variation or “wiggles” of the wavefunction, which are due to the nature of the atomic orbitals (e.g. like the  $p$  orbital of H) rather than to the envelope function. Also, don’t be distracted by the variation of the wavefunction in the  $z$  direction, since we are focusing on how the wavefunction varies in the  $y$  direction.

### 3b. nanoHUB research calculation:

- Check back on your geometry optimization. When it is finished, the simulation should have found the coordinates for the atoms to minimize the energy of the system, i.e. the equilibrium structure.
- Download the “Key Outputs” pane by clicking on the green arrow to the right, and the “SIESTA input file (FDF)” – you won’t necessarily understand the stuff in here, but it can be useful in diagnosing later if something went wrong.

- Download the final coordinates from the “XYZ Coordinates” pane. Include these in your lab report.
- You can then add to this file the first three lines shown in the coordinates for the “Molybdenum Disulfide (Supercell, 8x1)” example structure in the nanoHUB tool, which are defining the lattice vectors (dimensions of the unit cell), so that it looks like the example except for the details of the exact coordinates. Upload this file as coordinates for a new calculation, by selecting “Upload” under “Sheet/slab structure”.



- Then use “Run type” set to “total energy,” and turn back on both options for the XCrySDen visualization, including setting Wavefunction band index minimum to 71 and Wavefunction band index maximum to 74.
- Proceed as above in part 3, to study the density, potential, and wavefunctions of your heterostructure, and analyze to what extent the results resemble the quantum well model.
- Examine the structure in XCrySDen, and look for the effect we discussed in class in which bonds and layer thickness are lengthened as per the atomic radii,  $R_W > R_{Mo}$  and  $R_{Te} > R_{Se} > R_S$ .

## 5. Exploration of other aspects of your results.

- Finally, explore something else you find interesting within the outputs (the XCrySDen views or the text panes of output) of this simulation. You don’t need to carry out further simulations which would be more time-consuming. There is quite a lot of information there of which we have only scratched the surface, and the idea is for you to poke around a bit and see what else you find.
- Make note for your lab report of what you looked at and how, using screenshots to show it, and see if you can figure out the physical meaning or origin. It’s ok if you can’t figure out the meaning, as some things don’t have a simple explanation, require more advanced condensed matter physics knowledge to understand, or are artefacts of the numerical scheme used in these calculations. Feel free to discuss what you find with Prof. Strubbe, Kevin, Elsa, or Rafael.

## Special Halloween-themed activity, if you have time:

- Look for where the word “ghost” appears in the “SIESTA output” file.