Discussion: Covalent, ionic, and Van der Waals bonding in diatomic molecules

Exercises from Fall 2021
PHYS 141, PHYS 241, MBSE 245
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getting started

- Go to [https://nanoHUB.org](https://nanoHUB.org) and log in.
- Go to the MIT Atomic-Scale Modeling Toolkit at [https://nanohub.org/tools/ucb_compnano](https://nanohub.org/tools/ucb_compnano)
- Click the blue button “Launch Tool”
- In the “Application” menu in the upper right, select “Quantum Chemistry (GAMESS)”
define a diatomic molecule

• For “Coordinate File” select “New”.
• In the Coordinate Data section at the bottom, clear the text and enter:

2

H 0 0 -1
H 0 0 1

This means 2 H atoms, at coordinates (0, 0, -1 Å) and (0, 0, 1 Å).

This structure is a guess about what the bond length should be. What is the bond length in our guess?
find the equilibrium structure

- For “Basis Set” select “6-311G* (High)”
- For “Method” select “DFT-B3LYP”
- (The basis set and method are details of approximate ways of solving the Schrödinger equation which we don’t need to worry about.)
- For “Run Type” select “Optimize Structure”

- After run, check “Atomic Coordinates” panel, and look at coordinates of last step. What is the equilibrium bond length?
- Note the total energy (from “Key Outputs”, the last one listed which is for the last step, and choose the one in eV).
eigenvalues at equilibrium bond length

• For “Run Type” select “Energy Only”
• In Coordinate Data, change the coordinates to (0, 0, L/2) and (0, 0, L/2), where L is the equilibrium bond length you found.

• Note the total energy (from “Key Outputs”, in eV) and confirm it is the same as from your “optimize” run.
• Note the HOMO (high-occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies (from “Eigenvalues”). 3 decimal places will be sufficient. You can either copy these by hand, or if you prefer, copy and paste from the “Key Outputs” by clicking on the icon to the right of “Result:” with a green arrow.
molecular orbitals at equilibrium bond length

- Go to Jmol. Right-click in the window, and in the menu select Surfaces->Molecular Orbitals->#1. This is a list of the energy levels calculated, where #1 is the lowest. The energies are listed in Rydberg units here (27.2 eV). This orbital is the HOMO.
- Right-click again, select Zoom->50%. The blue surface is an isosurface of the orbital, showing its shape. Blue is for positive and red is for negative values.
- Look at the LUMO molecular orbitals (#2). You can determine which number this is in general from the occupations in the “Eigenvalue Log.”
- Take screenshots of HOMO and LUMO, and describe what they look like and how they differ from each other.
We are going to make two plots:
(1) total energy vs. bond length;
(2) HOMO and LUMO vs. bond length.
For “Run Type” select “Energy Only”
Turn off “Run Jmol?” for simplicity.

Choose 4 more bond lengths ($L=0.6d, 0.8d, 1.2d, 1.4d$), where $d=$equilibrium length found in previous step. *You can divide these up among your group and share your results.*
For each, in Coordinate Data, enter $(0, 0, -L/2)$ and $(0, 0, L/2)$.
Note the total energy, HOMO energy, and LUMO energy after each calculation.
Make these two plots (1: total energy; 2: HOMO and LUMO).
Think about how they relate to the shape of the bonding potential energy $V(r)$, and which kind of bond is in $H_2$. 
example $\text{H}_2$ results
Calculate molecular orbitals for LiF (select Coordinate File: “LiF – lithium fluoride”, which is equilibrium)
Note that Li is purple and F is green in Jmol.

If you have more time:
Calculate bonding curves for total energy, HOMO and LUMO energies.
Repeat for He₂ (guess 2 Å bond length)
Compare the equilibrium bond lengths for each.
Note any differences you find among H₂, He₂, and LiF in the molecular orbitals and the bonding curves
Connect these differences to the kind of bonding in these molecules.
Calculate each atom involved here individually, and use these total energies to determine the bonding energy ΔE for each molecule.
Try N₂.
Discussion: Types of matter, and the radial distribution function
noble gases

- Go to the MIT Atomic-Scale Modeling Toolkit at https://nanohub.org/tools/ucb_compnano
- Select “Molecular Dynamics (Lennard-Jones)”
- This subtool will simulate the motion of particles interacting via the Lennard-Jones potential, appropriate for a noble gas such as Ar.
- Start by running with defaults, and look at Jmol animation of motion, and the Radial Distribution Function. What is the starting state and the final state?
noble gases

Then do a more refined calculation with:

- Set Number of particles = 256
- Set Temperature = 0.0 [note: the temperature will be nonzero, this is just about how the velocities are initialized]
- Box Size = 7
- Timestep = 0.01
- Number of simulation steps = 10000
- Run Jmol viewer? No.

- Analyze the radial distribution function.

- Repeat with Number of simulation steps = 10, and Run Jmol viewer? Yes.
- Look at the Jmol animation. Then, what do you see in the radial distribution function. Why?
nanostructures and temperature

• Go to the MIT Atomic-Scale Modeling Toolkit at https://nanohub.org/tools/ucb_compnano
• Select “Molecular Dynamics (Carbon Nanostructures and More)”
• This tool uses a classical model of covalent bonding and Newton’s Laws to describe the motion of carbon atoms.

• Choose Simulation Type: Dynamics
• Thermostat: Yes (NVT)
• XYZ Coordinates: Graphene
• Number of simulation steps: 10000

• In Jmol, click and drag to rotate the sheet 90° so you can see what is happening better. This is an animation of the atoms’ motion.
• Look at Result: Radial Distribution Function.
nanostructures and temperature

- Default temperature was 300 K. Try 600 K, 1200 K, and 2400 K. What happens to the structure in Jmol, and the radial distribution function? Can you understand why you see this behavior?
CURE: Settings for pure MoS$_2$/MoSe$_2$ calculations

Use Quantum ESPRESSO tool
(This will take quite a long time)

Atomic positions
Mo 0.3333333 0.6666667 0.5
S 0.6666667 0.3333333 0.3701
S 0.6666667 0.3333333 0.6299

c = 12 Å
Calculation: scf
Bravais lattice: arbitrary (specify lengths/angles)
Lattice parameters: 1.0 1.0 c/a 90.0 90.0 120.0
Lattice constant: $a = 3.116$ Å
K-Grid: 4 4 1 1 1 0 [equivalent to 2 2 1 1 1 0 in the 2x2 alloy supercells]
Wavefunction kinetic energy cutoff: 75 Ry

Or to obtain $a$ and coordinates above:
Calculation: vc-relax
Lattice constraints: x and y free (2Dxy)
CURE: Settings for pure MoS$_2$/MoSe$_2$ calculations

- Phonons tab
  - Calculate only q=0? yes
  - Calculate Raman intensities? yes
  - Visualize q=0 modes in XCrySDen? yes
  - Visualize q=0 modes in MolDen? no
CURE: Settings for pure MoS$_2$/MoSe$_2$ calculations

Density of states
Energy resolution: 0.1 eV
Gaussian broadening [Ry]: 0.01
Number of bands to calculate: 23 [or 33 for MoSe2; choose e.g. 10 more bands than the number of occupied bands]
K-Grid: 32 32 1 0 0 0

Bandstructure
Same number of bands as above
Same k-path in the Brillouin zone as the q-path for phonons