

✓ Chem 30324, Spring 2025, Homework 7

Due March 29, 2025

✓ Many-electrons means many troubles

Helium (He) is only one electron larger than hydrogen, but that one more electron makes a big difference in difficulty in setting up and solving the Schrödinger equation.

- ✓ 1. Write down in as much detail as you can the Schrödinger equation for the electrons in a He atom. Can your differential equation be solved in closed form?

Schrödinger equation:

$$\begin{aligned}\hat{H}\Psi(r_1, r_2) &= E\Psi(r_1, r_2) \\ \hat{H} &= \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_1 - r_2|} \\ \hat{h}_1 &= -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{r_1} \\ \hat{h}_2 &= -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{r_2}\end{aligned}$$

- ✓ 2. "Density functional theory" offers an alternative strategy for describing this "many electron" system. What is the density in density functional theory? Provide an equation.

$$n(\mathbf{r}) = N \int d^3\mathbf{r}_2 \cdots \int d^3\mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N).$$

- ✓ 3. The DFT equation has five terms, or operators, on the left. Identify the physical meaning of each term and the sign of the expectation value when it is applied to one of the solutions.

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \hat{v}_{\text{Coul}}[\rho] + \hat{v}_{\text{ex}}[\rho] + \hat{v}_{\text{corr}}[\rho]\right)\psi = \epsilon\psi$$

$-\frac{1}{2}\nabla^2$: Kinetic energy. Always positive.

$-\frac{Z}{r}$: Due to the attraction between the electron and the nucleus. Negative.

\hat{v}_{Coul} : Classical repulsion between distinguishable electron “clouds”. Positive.

\hat{v}_{ex} : Accounts for electron indistinguishability (Pauli principle for fermions). Decreases Coulomb repulsion because electrons of like spin intrinsically avoid one another. Negative.

\hat{v}_{corr} : Decrease in Coulomb repulsion due to dynamic ability of electrons to avoid one another; “fixes” orbital approximation. Negative.

✓ 4. Briefly, what does it mean to solve this equation "self-consistently"?

All the potential terms \hat{v} depend on the ψ solved. The self-consistently means we get a ψ solution, then we use it to calculate new potential terms and solve for new ψ , and repeat until we get a ψ same with the last one.

Sophisticated computer programs that solve the DFT equation are now widely available and powerful tool for predicting the properties of atoms, molecules, solids, and interfaces. In this problem you'll do a DFT calculation using the *Orca* program (<https://www.its.hku.hk/services/research/hpc/software/orca>).

Now, let's set up your calculation (you may do this with a partner or two if you choose):

1. Log into the Webmo server <https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi> using "guest" as your username and password.
2. Select New Job-Creat New Job.
3. Use the available tools to draw an atom on the screen.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Choose Orca
6. Select “Molecular Orbitals” for the Calculation type, “PBE” for theory, “def2-SVP” for the basis set, “0” for the charge, an appropriate value for the "Multiplicity", and check “Unrestricted.”
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.
9. For fun, click on the Magnifying Glass icons to see the molecular orbitals in 3-D. You may have to play around with the Display Settings and Preferences to get good views.

- ✓ Make a table of energies of the occupied orbitals and identify them by their shell ($n = 1, 2, \dots$) and subshell (s, p, d, ...).

[illegible]

✓ wavelength of light necessary to remove each 1s electron. What range of the spectrum is this light in?

As seen in the spreadsheet, the wavelengths are in the X-Ray range.

- 7. Why, qualitatively, do the energies vary as they do?

The energies required to remove an 1s electron increase as you move across the periodic table. The largest factor is the addition of protons, adding additional positive charges to the nucleus increases the coulombic attraction between the nucleus and the electron thus increasing the energy required to remove an electron.

- ✓ Determine the wavelength of light necessary to remove each valence electron. What range of the spectrum is this light in?

As seen in the spreadsheet, the wavelengths required are in the UV range

✓ 9. Why, qualitatively, do the energies vary as they do?

Like with 7, the energies to remove the valence electron generally increase (with the exception of F→Ne) due to the increase in positive nuclear charge/coulombic factors. The two primary reasons that the magnitude is smaller than the 1s energies and that Ne ends up being lower than F are because of better shielding for the valence electrons by the other electrons and the valence electrons being further away on average from the nucleus lowers the impact of the additional coulombic attraction.

✓ Chemical bonding

The electron wavefunctions (molecular orbitals) in molecules can be thought of as coming from combinations of atomic orbitals on the constituent atoms. One of the factors that determines whether two atomic orbitals form a bond is their ability to overlap. Consider two atoms, A and B, aligned on the z axis and separated by a distance R .

10. The overlap between two 1s orbitals on A and B can be shown to be:

✓
$$S = \left\{ 1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right\} e^{-R/a_0}$$

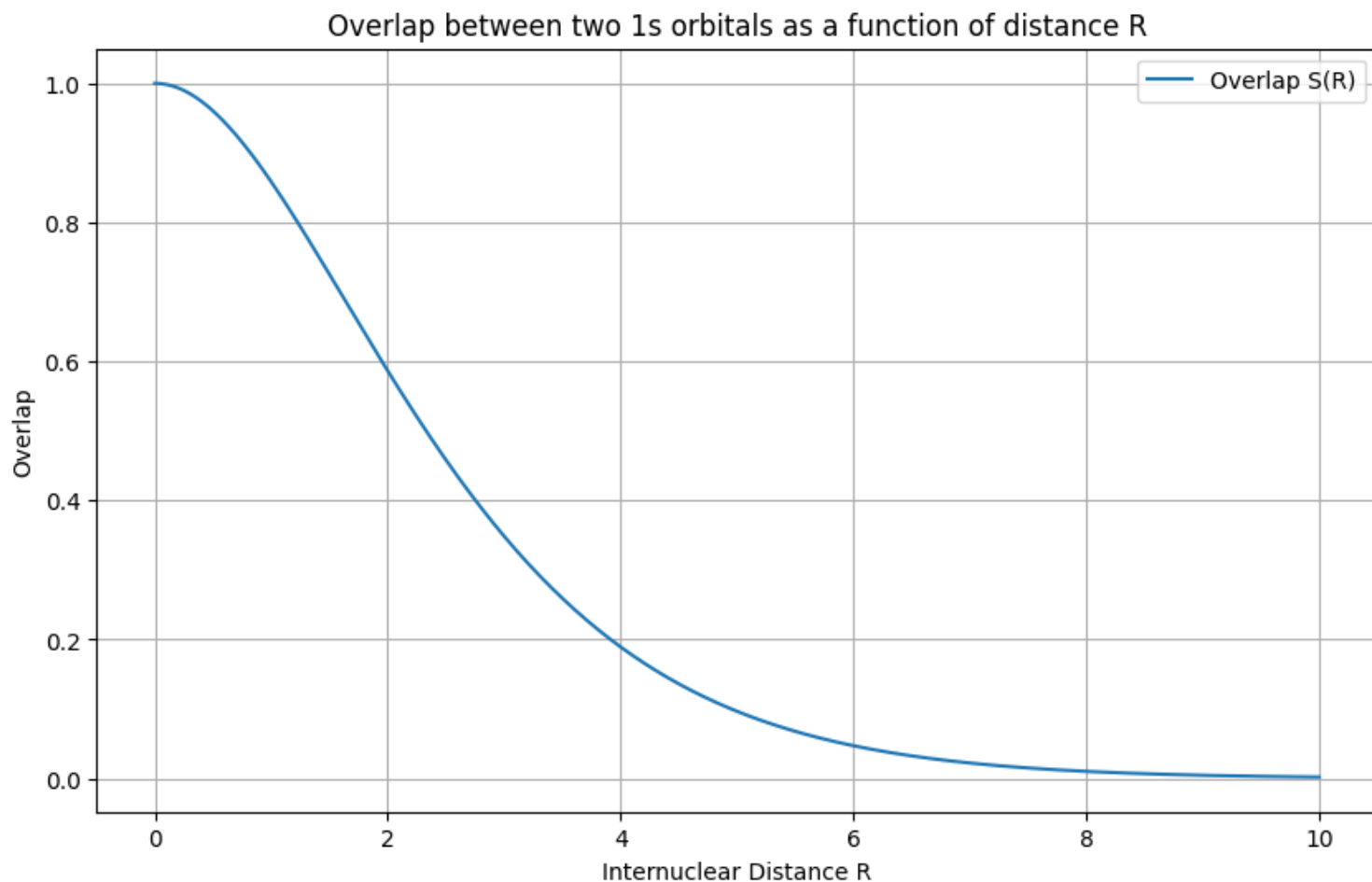
Plot out the overlap as a function of the internuclear distance R . Qualitatively explain why it has the shape it has.

```
import numpy as np
import matplotlib.pyplot as plt
```

```
def overlap(R, a0=1.0):
    return (1 + R/a0 + (1/3)*(R/a0)**2) * np.exp(-R/a0)
```

```
R = np.linspace(0, 10, 500)
S = overlap(R)
```

```
plt.figure(figsize=(10, 6))
plt.plot(R, S, label='Overlap S(R)')
plt.xlabel('Internuclear Distance R')
plt.ylabel('Overlap')
plt.title('Overlap between two 1s orbitals as a function of distance R')
plt.grid(True)
plt.legend()
plt.show()
```



At $R \rightarrow 0$, the overlap becomes large due to close proximity of the orbitals. As R increases, the overlap decreases exponentially because the wavefunctions decay with distance, making the interaction weaker.

11. The overlap functions for other pairs of orbitals are more complicated, but the general features are easily inferred. Neatly sketch the orbital overlap between a 1s orbital on A and $2p_z$ orbital on B as a function R . Carefully indicate the limiting values as $R \rightarrow 0$ and $R \rightarrow \infty$.

See pdf

12. Choose some other pair of atomic orbitals on A and B and sketch out their overlap as a function of R . Carefully indicate the limiting values as $R \rightarrow 0$ and $R \rightarrow \infty$.

See pdf

- ✓ 13. What property besides overlap determines whether two atomic orbitals will form a bond?

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- ✓ 14. For each pair, draw a Lewis dot structure. Indicate which bond is stronger in the pair, and give a very brief rationalization:

(a) H_2 vs LiH

(b) N_2 vs H_2

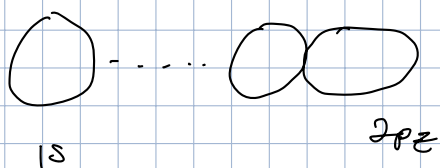
(c) N_2 vs CO

(d) H_2 vs He_2

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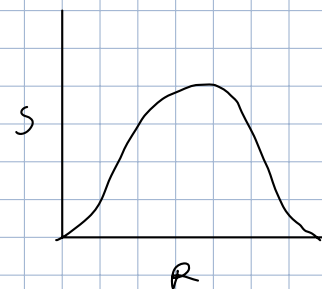
Start coding or [generate](#) with AI.

Problem #2

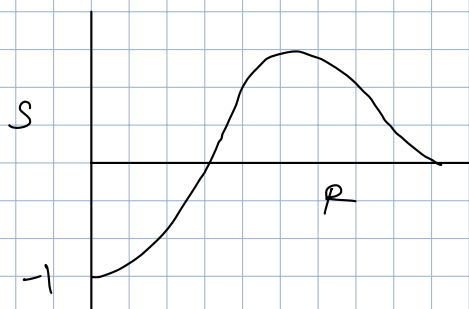


$$R \rightarrow 0 \quad S = 0$$

$$R \rightarrow \infty \quad S = 0$$



Problem #3



$$R \rightarrow 0 \quad S = -1$$

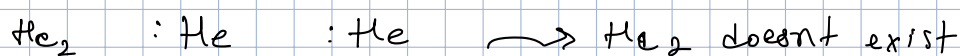
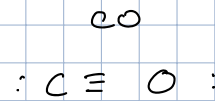
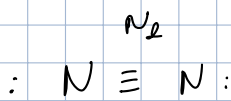
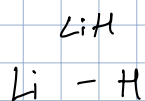
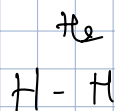
$$R \rightarrow \infty \quad S = 0$$



Problem #4

Energies of the two atoms should match

Problem #5



- H_2 is stronger because they have similar energies
- N_2 is stronger because it has a triple bond instead of a single bond
- Difficult to say N_2 is stronger because they are similar in energy
- H_2 is stronger because they have similar energies