<table>
<thead>
<tr>
<th>atom</th>
<th>$E^{\text{HF}}$</th>
<th>$E$</th>
<th>$E_x$</th>
<th>$E_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^-$</td>
<td>-0.486</td>
<td>-0.528</td>
<td>-0.381</td>
<td>-0.042</td>
</tr>
<tr>
<td>He</td>
<td>-2.862</td>
<td>-2.904</td>
<td>-1.025</td>
<td>-0.042</td>
</tr>
<tr>
<td>Be$^{++}$</td>
<td>-13.612</td>
<td>-13.656</td>
<td>-2.277</td>
<td>-0.044</td>
</tr>
</tbody>
</table>

TABLE II Energies for two-electron ions.

3. Calculate the one-electron energy of a single electron. Is the total energy equal to the sum of the one-electron energies? Explain your answer, including the sign of any difference.

4. Assume the ground-state energy of two-electron ions can be accurately approximated by a quadratic in $Z$. Estimate the coefficients using both your approximate results and the energies in Table 4 First apply to the HF energies, and then to the exact energies. Comment on the accuracy of your results from Problem Sec. 7.

5. Use your total energy expression to estimate the $Z$ value when the ionization potential vanishes, i.e., the theoretical, non-integer $Z$ below which the nucleus cannot bind two electrons. Comment on its sensitivity to correlation.

6. Bonus: Add a second exponential decay and repeat your calculation, now minimizing also with respect to the linear combination. Do you do any better than before?

22.8. Properties of real atoms

Using the chapter 5 handout of BRR, or Levine or Atkins or any other textbook, answer the following questions:

1. Electronic configurations:
   (a) Explain the Aufbau principle applied to atoms.
   (b) What is a configuration of an atom? What are the ordering of the orbital energies in atoms, and why are there exceptions?
   (c) State Koopmans’ theorem for HF atoms.

2. Atoms and ions:
   (a) Explain the trends in ionization potentials across a row and down a column.
   (b) Are there any atomic dianions? Explain your answer.

3. Chemistry:
   (a) Explain the difference between covalent and ionic radii, and the trends in covalent radii across and down the periodic table.
   (b) Why are transition metals different from main group elements? Justify in terms of electronic structure.

4. Terms
   (a) Explain what a term is and how it differs from a configuration. (See Fig 5.9 of BRR)
   (b) What are Hund’s rules?

5. Specific cases of terms:
   (a) For the He atom, why are triplets lower in energy than singlets? Why is the ground state then not a triplet?
   (b) Give the terms for the ground state configuration of the carbon atom, and say which is lowest in energy.

6. Bonus: Spin-orbit coupling:
   (a) What is spin-orbit interaction?
   (b) What are Russell-Saunders and jj coupling, and when does each apply?

22.9. Approximate calculations of ionization potentials

To answer some of these questions, use the table of energies (in hartrees) for atoms and ions in Table III.

You will also need the basis-set dependent results in the data files sent to you.

1. Staring at the HF data for the H atom, order the different basis sets listed by size.
2. Calculate the HF ionization energy of He in a sequence of increasingly large basis sets. If you can accept a 0.05 eV error, which basis set is large enough? Is the total energy converged to this accuracy in that basis set?

3. Plot the ionization potential \( I(Z) \), for the second and third rows. Explain all trends and features.

4. Plot \( I_{HF}(Z) \) on the same picture. What are the differences to the plot in the previous question? What are the trends?

5. Plot \( \Delta I_{HF}(Z) \), and explain it all.

6. Bonus: Repeat the He basis-set calculation for the correlation energy instead of the ionization energy using the CI calculation results.

2.2. Twisted logic of KS DFT

1. Suppose I give you (somehow) the exact \( E_{XC}[n] \) for two-electron densities, and I solve the He atom using the KS equations. Then, which is bigger, \( T \) or \( T_S \), the KS kinetic energy? And which expectation values would not be correct (i.e., not exact), if evaluated on exact KS wavefunctions? \( \langle r^2 \rangle, \langle r^4 \rangle, \langle p^2 \rangle, \langle p^4 \rangle \)? Justify all answers.