University of Caen Normandy

Density Functional Theory

Project 1–Koopman's theorem

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Chapter 1

Research of experimental values

Table 1.1: Experimental data taken from *Basic Atomic Spectroscopic Data* (n.d.). In the present study, we are interested in the atomic spin (S), the first ionization energy (IE_{exp}) determined experimentally in eV and, also the electronic configurations of the candidate atoms.

Atom	Z	2S+1	S	S(S+1)	IE_{exp}(eV)	Electronic configuration
He	2	2	1/2	3/4	24.587	$1s^2$
Li	3	4	3/2	15/4	5.391	$1s^2$ 2s
Be	4	4	3/2	15/4	9.323	$1s^2$ $2s^2$
Ne	10	1	0	0	21.564	$1s^2$ $2s^2$ $2p^6$
Na	11	4	3/2	15/4	5.139	[Ne] 3s
Mg	12	1	0	0	7.646	[Ne] $3s^2$
Ar	18	1	0	0	15.760	[Ne] $3s^2$ $3p^6$
K	19	4	3/2	15/4	4.340	[Ar] 4s
Ca	20	1	0	0	6.113	[Ar] $4s^2$

Chapter 2

Theoretical study

2.1 What does the BO approximation mean?

The Born-Oppenheimer approximation is based on the large mass difference between nuclei and electrons, rendering nuclei to have much shorter de-Broglie wavelength than the atoms themselves under ordinary conditions. Therefore, the quantum effects in the motion of nuclei can be neglected which allows treating them as inert point-like objects. In this approximation, the electronic wavefunction is calculated using Schrödinger equation while assuming fixed coordinates of the nuclei, and then the nuclear motion is treated separately using the resulting electronic potential energy surface.

The treatment eliminates the coordinates of nuclei in the Schrödinger equation altogether by substituting fixed positions in their place. Suitable values for the nuclear coordinates for an atomic ground state can be estimated by requiring a minimum expected value of the Hamiltonian. In adiabatic BO approximation, the nuclear repulsion is taken to be constant and their kinetic energy is neglected thus allowing electron wavefunctions to evolve independently from nuclei.

$$\hat{H} = -\sum_{i}^{N} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i}^{N} \sum_{j}^{M} \frac{Z_j e^2}{|\tilde{R}_j - \tilde{r}_i|} + \sum_{i,j}^{N} \frac{e^2}{|\tilde{r}_i - \tilde{r}_j|}$$

2.2 Explain briefly the principle of the Hartree-Fock method.

The Hartree-Fock's is based on the principle that each electron experiences a mean-field created by average density of all the other electrons. The method iteratively minimizes the total energy by solving the Fock equations, yielding self-consistent orbitals.

$$E_{\mathrm{HF}} = \sum_{i} \epsilon_i - \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij})$$

Where $\epsilon_i = \langle i|\hat{h}|i\rangle$ is the one electron operator including electronic kinetic operators and electron-nucleus Coulombic interaction, whereas $J_{i,j} = \langle ij|\hat{V}|ij\rangle$ and $K_{ij} = \langle ij|\hat{V}|ji\rangle$ are Coulomb and Exchange matrix elements, respectively. The problem seemingly has the form of an eigenvalue problem but $J_{i,j}$ and K_{ij} operators themselves depend on electron wavefunctions and the problem can be iteratively solved to convergence. Effectively, the interactions between the electrons are treated in an average way, not an instantaneous way.

2.3 Recall the expression of the Hartree-Fock energy for a system of $N = 2n$ electrons.

With the inclusion of spin degree of freedom, let us assume that a given spatial orbital can be used twice, once for spin up and once for spin down. If we assume all the electrons are paired so that wavefunction has $\frac{N}{2}$ spin-up electrons and $\frac{N}{2}$ spin-down electrons, then the reduced HF energy takes the expression,

$$E_{\text{HF}} = 2\sum_{a}^{N/2} \langle a|\hat{h}|a\rangle - \sum_{a,b} \Big(2\,\langle ab|\hat{V}|ab\rangle - \langle ab|\hat{V}|ba\rangle\Big)$$

2.4 Why is the Hartree-Fock theory a so-called self-consistent field (SCF) method?

HF theory is called so because its solution is consistent with the potential it generates. Initially, a guess is made for the electron orbitals, which are used to construct the Fock operator that defines the average potential each electron experiences. Solving the Fock equations provides updated orbitals, which are used to recalculate the Fock operator. This process is repeated until the input and output orbitals converge, so to speak the solution generates a potential which satisfies its own eigenproblem.

2.5 We want to study the Na^+ ion (composed of a nucleus of charge Z and 10 electrons) at the RHF level with a basis set of 10 Atomic Orbitals (AO).

2.5.1 Write the electronic Hamiltonian in atomic units.

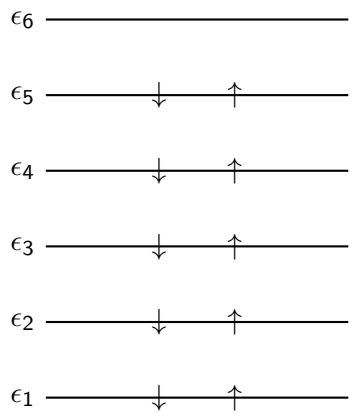
$$\hat{H} = -\sum_{i=1}^{10} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{10} \frac{11}{|\tilde{r}_i|} + \sum_{i,j=1}^{11} \frac{1}{|\tilde{r}_i - \tilde{r}_j|}$$

2.5.2 How many Molecular Orbitals (MO) can be generated with a SFC calculation?

We need only generate 5 molecular orbitals (spatial wavefunction) so that 10 electrons would pair up with their spins thereby completing the shell. The result would be an electronic configuration of Neon.

2.5.3 Draw the RHF scheme: energy of spin orbitals and their occupation numbers

Figure 2.1: RHF energy scheme for Na^+



2.5.4 Write the corresponding RHF wave function.

The RHF wavefunction written as a restricted determinant is,

$$|\Psi\rangle = |\psi_1\ \bar{\psi}_1\ \psi_2\ \bar{\psi}_2\ \psi_3\ \bar{\psi}_3\ \psi_4\ \bar{\psi}_4\ \psi_5\ \bar{\psi}_5\rangle$$

2.5.5 Apply the Koopman's theorem to express the ionization energy of Na^+.

According to Koopman's theorem, the ionization energy of a closed shell atom, as is the case with Na^+, is estimated by the highest occupied molecular orbital energy which in our case happens to be ϵ_5 so,

$$\text{IE} = \text{HOMO} = \epsilon_5$$

Chapter 3

Analysis and discussion of the numerical results

3.1 Presentation of the UHF results

Table 3.1: UHF calculations for the 3 basis sets: STO-3G, 3-21G, 6-31G. The approximations for highest occupied molecular orbital (HOMO) energy were compared with experimental values for the first ionization energy of each atom.

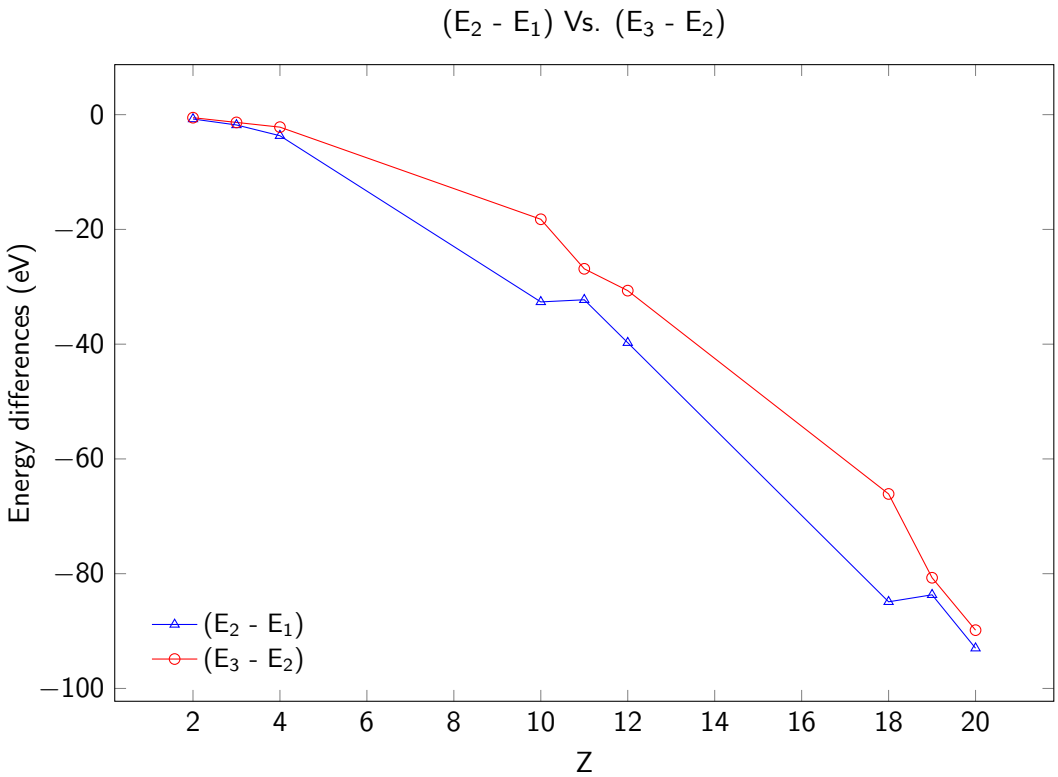
				S(S+1)			HOMO Energy (eV)		
Atom	Z	IE_{exp}(eV)	Electronic configuration	STO-3G	3-21G	6-31G	STO-3G	3-21G	6-31G
He	2	24.587	$1s^2$	0	0	0	23.8381	24.5874	24.8747
Li	3	5.391	$1s^2$ 2s	0.750000	0.750002	0.750001	4.9014	5.2908	5.327
Be	4	9.323	$1s^2$ $2s^2$	0	0	0	6.9127	8.317	8.1987
Ne	10	21.564	$1s^2$ $2s^2$ $2p^6$	0	0	0	14.7772	21.5063	22.6064
Na	11	5.139	[Ne] 3s	0.750348	0.750036	0.750050	-2.9421	4.9121	4.9608
Mg	12	7.646	[Ne] $3s^2$	0	0	0	1.2061	6.8544	6.8716
Ar	18	15.760	[Ne] $3s^2$ $3p^6$	0	0	0	13.4953	16.0182	16.0253
K	19	4.340	[Ar] 4s	0.751041	0.750145	0.750154	1.9709	3.9921	4.017
Ca	20	6.113	[Ar] $4s^2$	0	0	0	4.0561	5.3064	5.3201

Table 3.2: Estimations for total energy expressed in (au) and determined using UHF calculations for the 3 basis sets: STO-3G, 3-21G, 6-31G.

Atom	Z	Electronic configuration	Total Energy (au)		
			STO-3G	3-21G	6-31G
He	2	$1s^2$	-2.807	-2.835	-2.855
Li	3	$1s^2$ 2s	-7.315	-7.381	-7.431
Be	4	$1s^2$ $2s^2$	-14.352	-14.486	-14.566
Ne	10	$1s^2$ $2s^2$ $2p^6$	-126.604	-127.804	-128.473
Na	11	[Ne] 3s	-159.668	-160.854	-161.841
Mg	12	[Ne] $3s^2$	-197.007	-198.468	-199.595
Ar	18	[Ne] $3s^2$ $3p^6$	-521.223	-524.343	-526.772
K	19	[Ar] 4s	-593.078	-596.153	-599.119
Ca	20	[Ar] $4s^2$	-669.989	-673.406	-676.707

3.2 Calculate the energy differences (E_2 - E_1) and (E_3 - E_2) in eV and plot them according to Z. What is your conclusion?

Figure 3.1: Plotting the differences between total energies E_1, E_2, E_3 of atoms i.e., (E_2 - E_1) and (E_3 - E_2) in eV, obtained using the 3 basis sets determined using ORCA software.

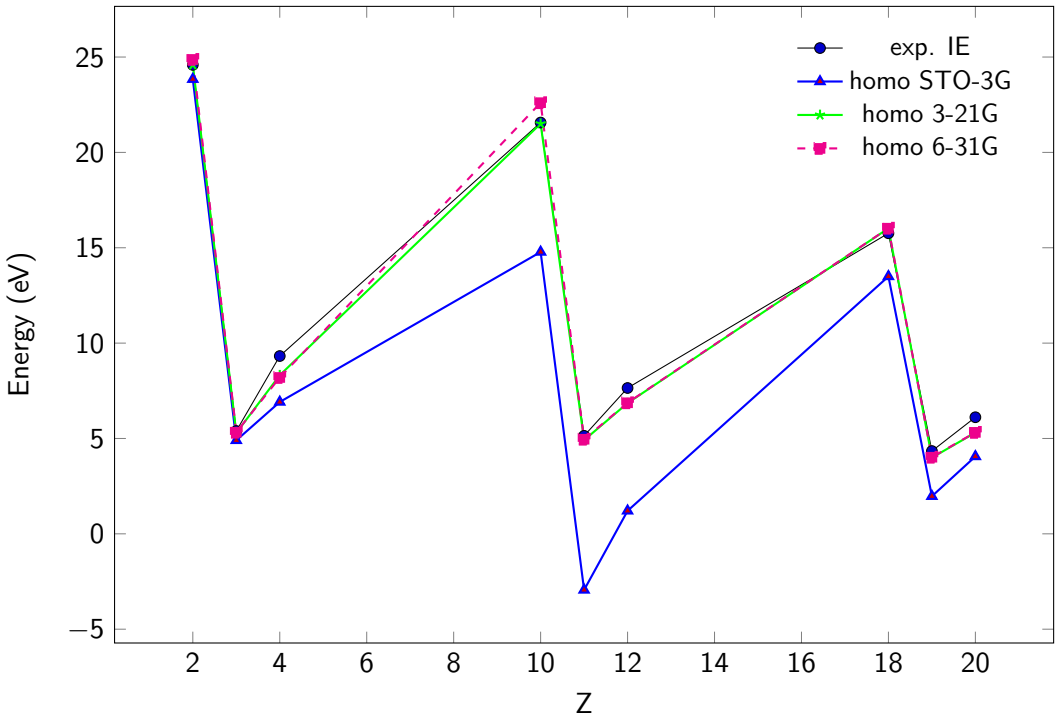


We notice that the two energy difference values coincide immediately after the atomic shells become complete after which they diverge again. We see that this cycle repeats at $Z = 11$ and again at $Z = 19$.

3.3 Plot the experimental ionization energy and the 3 calculated at the UHF level in eV according to Z.

Figure 3.2: Real (blue) and Imaginary (red) parts of $\alpha+^{106}$Pd Potential

highest occupied molecular orbital (HOMO) Vs. experimental ionization energy (exp. IE)



3.4 For which atom does the Koopman's theorem seem to be adapted?

Koopman's theorem seems to be adapted well to atoms with closed shells (He, Ne, Ar) as well as closed shells plus an unpaired electron (Li, Na, K). It does not seem to be well adapted to the case when the shells are more occupied but not fully occupied (Be, Mg, Ca).

3.5 For others do you have an explanation?

In principle, open-shell atoms have unpaired electrons, leading to different spatial wavefunctions for spin-up and spin-down electrons. UHF allows separate spatial orbitals for spin-up and spin-down electrons, and so is in theory well adapted also to systems with unpaired electrons. However, UHF is a single-determinant method and therefore, cannot handle the strong interactions and near-degeneracy effects of multi-shell systems. In other words, multi-shell systems that involve complex correlations are not accurately described by UHF.

3.6 Using the calculated values of S(S+1) what can you conclude about the UHF wave function?

We can clearly see that in UHF there is a tendency for the approximated S(S+1) to deviate from the expected value for a pure spin state due to spin contamination. A system with one unpaired electron (Li, Na, K) should in principle have S(S+1) = 0.75. Whereas in UHF, due to mixing with higher spin states, S(S+1) may be larger than 0.75, owing to spin contamination as we see occurs in the case of Li, Na, K atoms.

Chapter 4

Conclusion

The UHF results revealed that spin contamination leads to deviations in the approximated S(S+1) values from the expected pure spin state. As a single-determinant method, UHF is not suitable for strong interactions and near-degeneracy effects in multi-shell systems such as (Be, Mg, Ca). Koopman's theorem proved effective for atoms with closed shells (He, Ne, Ar) and closed shells with one unpaired electron (Li, Na, K), but it showed limitations for partially filled shells (Be, Mg, Ca). These trends were consistent across the three basis sets STO-3G, 3-21G, 6-31G. Overall, UHF allows separate spatial orbitals for spin-up and spin-down electrons making it applicable to systems that are closed shells or additionally have an unpaired electron, accurately.

References

Basic Atomic Spectroscopic Data (n.d.), https://physics.nist.gov/PhysRefData/Handbook/element_name.htm. Accessed: 2024-12-02.