

# Introduction to Computational Quantum Chemistry: Theory

## Tutorial Problems

Wednesday 10th May

- (1) Write down the Hamiltonian operator for the helium atom and comment on what each term represents. Simplify your expression by using the Born-Oppenheimer approximation.
- (2) Assuming a restricted solution, write down the Hartree-Fock wavefunction for helium. Show that this wave function is antisymmetric.
- (3) The spin eigenvalue for a system with spin  $s$  is given by  $s(s+1)$ . For example, a doublet has one unpaired electron and therefore  $s = 1/2$ . Compute the expected spin eigenvalues for singlet, doublet and triplet molecules. An unrestricted Hartree-Fock calculation on the CN radical gives a spin eigenvalue of about 2.25, what does this suggest about the single-determinant wavefunction?
- (4) Angus and Ethel are comparing the energies they have calculated for their favorite molecule; 2-aminopurine. Angus obtained the value -477.76 hartree whereas Ethel's value is -477.82 hartree. Ethel claims that her energy is better because it is lower. Is she correct?
- (5) Consider the helium atom with two atomic orbitals as basis functions,  $1s$  and  $2s$ . Draw diagrams to represent all the possible configurations of the two electrons in these orbitals. If we allow all these configurations to mix, what wavefunction does this correspond to? How does introducing the  $2s$  orbital allow for correlation?
- (6) Angus is trying to plot a dissociation curve for NbO using Hartree-Fock theory. Ethel points out that the correlation energy is important when breaking bonds and recommends that he uses MP2 theory. Is her advice well-founded?
- (7) The following diagram shows a potential energy surface for a model reaction along the reaction coordinate  $R$ . Identify the reactant, product and transition structure. What property of the PES allowed you to identify these? Is this reaction (proceeding from left to right) exothermic or endothermic?

