

Executive summary

There are some basic prerequisites, supplemental formulas, and detailed comments in Jupyter notebook. Here, we start from molecular hamiltonian to build the many-electron system model based on Born-Oppenheimer approximation and Hartree-Fock approximation to simulate a hydrogen molecule, which we only need to consider s orbital without angular momentum term. 1s orbital for first hydrogen and 1s orbital for second hydrogen, so our system are just two basis functions with each basis function is centered on each hydrogen. We use 6-31G basis set to express these orbitals from Basis Set Exchange. 1s orbital for hydrogen is a linear combination of three gaussians that contains alpha, a parameter which shows how tight or loose is the orbital, as well as coefficients in the linear combination, and we use the same basis set for all atoms. After confirming the basis set and building the simplified hamiltonian of a single electron, we write the function for the overlap matrix of the basis set, and express the molecule with a list of lists of primitive Gaussian class objects (In[2]). The overlap matrix S is a 2 by 2 matrix for hydrogen because there are two basis functions (In[3]).

For many-electron system, we build all the terms in the hamiltonian expression including the kinetic energy of electrons, the electron nuclear attraction term, electron electron repulsion term, nuclear nuclear repulsion term (from In[4] to In[7]). Next, we are going to put them into a self-consistent field cycle and find electronic energy finally.

Beyond that, we initialize density matrix to all zeros with the simplest way and update its elements (In[8]). Then, calculating the matrix G with density matrix and electron electron repulsion energy (In[9]). Additionally, we find the expectation energy of electron with density matrix, single electron hamiltonian, and G matrix above (In[10]).

At this point, the orbitals produced by the Fock operator are the same as the orbitals that are used in the Fock operator to describe the average Coulomb and exchange potentials due to the electron-electron interactions. We now use the self-consistent field method to calculate electronic energy in the cycle (In[11]).

We create hydrogen molecule with 6-31-G basis set for 1s and 2s orbital on first and second hydrogen, and there are totally 4 basis functions for hydrogen that we combine H_1a, H_1b, H_1c, H_2a together to make a molecule. Here, we will use cartesian coordinates: x, y, and z. The only difference is the atomic position where the first hydrogen is in the center, while the second hydrogen is shifted in the z-direction. We can just have all numbers in atomic units and the distance at 1.4 atomic units. Because there is an extra 2s orbital on each hydrogen for a total 4 basis functions, so the molecule matrix is 4 rows and 4 columns and diagonal. Then, calculating the total energy of a single hydrogen molecule. For SCF parameters in the cycle, we choose 1e-6 as the tolerance, and 100 as the SCF steps. Checking whether the new density matrix differs from the old one, and if the convergence isn't met within the number of 100 steps, or the tolerance is never met, it won't put out the electron energy. Repeat calculating G matrix and Fock matrix until its convergence (In[12]).

At last, plot out the bond dissociation curve and print relevant matrix of hydrogen molecule in 6-31G basis including overlap matrix, kinetic energy matrix, electron nuclear attraction matrix, electron electron repulsion matrix, nuclear nuclear repulsion term. From the plot it's reasonable that as the bond distance increases, the total energy falls off, where the r is the distance between two hydrogen atoms.