Quantum Computing for Quantum Chemistry - Exercises

EUMEN Team - Quantinuum

November 24, 2022

1 Lecture 2

1. Show that in the Hartree Fock approximation electrons with opposite spins in He molecule are correctly correlated and cannot occupy the same point in space.

$$|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r}_1)\alpha(\boldsymbol{\sigma}_1)\phi_2(\mathbf{r}_2)\alpha(\boldsymbol{\sigma}_2) - \phi_2(\mathbf{r}_1)\alpha(\boldsymbol{\sigma}_1)\phi_1(\mathbf{r}_2)\alpha(\boldsymbol{\sigma}_2) \quad (1)$$

   Hint: Use the properties of spin

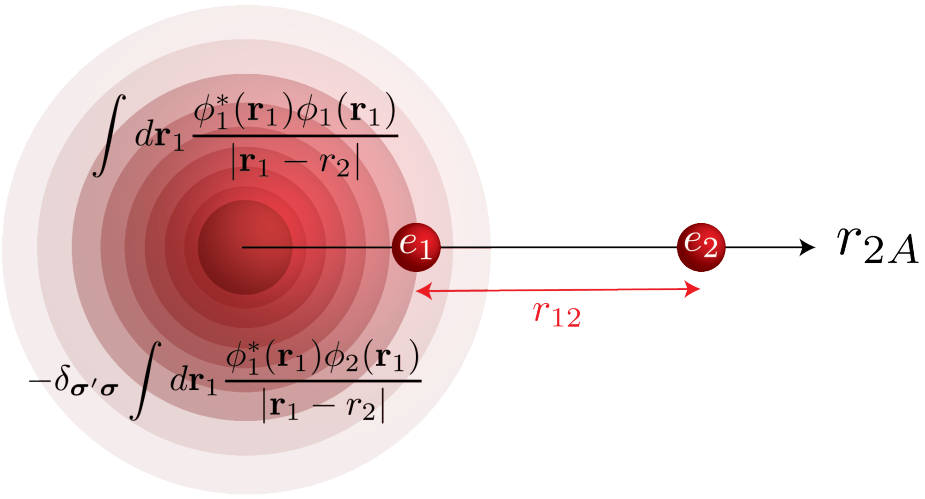
   Where does this correct treatment of correlation arise from?

2. Draw the mean field electron-electron repulsion v^{MF} vs the exact repulsion for a fixed electron 1 with electron 2 travelling through it in a straight line on the way to the nucleus

   (a) Opposite spins but in the same spatial orbital ϕ

   (b) Opposite spins but in the same spatial orbital ϕ

   (c) Same spin different spatial orbitals ϕ



3. Using the quantum chemistry package PySCF, generate a plot of ground state energy vs. bond length for the H2 molecule using the Hartree-Fock method and the 'sto-3g' basis set. (See attached jupyter notebook with more instructions)

   (a) What happens when you use a different basis set - for instance, the 'cc-pvdz-pp' basis set? Try putting both curves on the same graph. What are the differences between the curves? What could explain the differences? Which do you think better describes the "true" ground state of the molecule?

   (b) Are there any disadvantages to using the better basis set? (Hint: slap a timer on it)

   (c) Try plotting the energy using Full Configuration Interaction (FCI) instead of Hartree-Fock (instructions to get PySCF to run FCI are in the notebook).

   (d) Put the Hartree-Fock 'STO-3G' curve and the FCI 'STO-3G' curve on the same graph. How do these curves differ? What might this suggest about the Hartree-Fock method?

   (e) Are there any disadvantages to using the "better" method? (Hint: time it. Also try putting a big molecule in if you want to see what an exploding laptop looks like.)