Excited States by QMC

TTI 2017 Worksheet
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1 The first ionization potential of O_2

In this exercise, we will calculate the first ionization potential of the oxygen molecule. The ionization potential is defined as

$$IP = E_{N-1}^0 - E_N^0, \tag{1}$$

where E_N^0 denotes the ground state energy of the N-electron molecule. We will perform this calculation with the "G2" geometry, a Gaussian basis set, and we will not use pseudopotentials. We'll use VMC for speed, but the extension to DMC is not difficult (if you are interested, time steps of 0.001 and 0.004 a.u. are reasonable). In this case, we should be able to achieve reasonable agreement with experimental results (why?).[1]

1.1 Problem Setup

1. Copy the contents of `~/CASINO/examples/molecule/G2_SET/o2/` to a directory you wish to work from.[2]

2. Look in the input file. It is relatively simple, and (if everything has worked!) specifies a VMC calculation. Something worth noting is that `neu=9` and `ned=7` - in its ground state, O_2 hosts a spin-triplet configuration ($^3\Sigma_g^-$).

3. Make two directories: `gs` and `rem`, copy all of the files into each of them. The `gs` calculation is now ready, and we need to set up the excited state. Enter the `rem` directory and open the input file. We need to remove a single electron from this configuration.

4. The correct electron to remove (which leads to the lowest IP) is one of the spin-up electrons. Edit the file so that `neu=8`. [EXTRA: If you feel like it, try to see what happens in the rest of the exercise when removing a spin-down electron. You may or may not be able to notice the difference, why?]

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[1]See, for example, the data listed at `http://webbook.nist.gov/cgi/cbook.cgi?ID=C7782447&Mask=20`.
[2]If `CASINO` is not installed in your home directory, find it, and copy the same files.

1.2 VMC Calculations

1. If everything has gone well, you will now have two VMC calculations ready to execute - one to calculate E_N^{VMC} and one to calculate E_{N-1}^{VMC}.

2. Run each calculation with `runqmc`. [EXTRA: If you want, before you do this, you can try to optimise the Jastrow factor (edit `correlation.data` terms, change `runtype` to `vmc_opt` in the input file, and so on).]

3. Is the number of VMC steps in the input file limiting you? Try achieving a better accuracy by adjusting the number of VMC steps. If you are struggling to think of a good number, think about statistics. The error bar should scale like $1/\sqrt{N_{\text{steps}}}$ - you have one result with a small number of steps.

1.3 Checking & Thinking

1. What is your final result for the IP? How does it compare to experiment?

2. What major aspect of this example has been missed by our approach? Why might this make comparison to *some* of the experiments difficult?

3. If an experimentalist friend (they exist) approaches you, and asks if you can give them an accurate ionization potential accurately for their molecular system, what should you ask them about their experiment before you say "yes" or "no"?

2 Γ → Γ energy gap in Silicon

Perhaps a slightly more interesting case for QMC is that of a crystalline solid. In this example, we'll consider a $2 \times 2 \times 2$ supercell of Silicon, and try to calculate the energy gap from $\Gamma \to \Gamma$. In particular, we will calculate the *excitonic* energy gap

$$\Delta_{\text{Exc}} = E_N^{\Gamma \to \Gamma} - E_N^0 \tag{2}$$

where, again, E_N^0 is the ground state energy of the N electron system, but this time $E_N^{\Gamma \to \Gamma}$ is the energy of the system which has had an electron promoted from the valence band at Γ to the conduction band at Γ.

2.1 Problem Setup

1. Copy the contents of *the silicon folder* to a directory you wish to work from.

2. Look in the input file. Again, a relatively simple case, this calculation specifies a VMC calculation. Type `runqmc` and read the out file - try to figure out what is going on.

3. Make two directories, one for the ground state calculation and one for the excited state ($\Gamma \to \Gamma$ promotion) calculation. Give them helpful names!

4. Copy the `CASINO` files into the directory you created to hold the ground state calculation.

5. Enter that directory and `runqmc`. Read the output file, where are the electrons? Where are they *not*?

2.2   VMC calculations

1. Now you should know that the `bwfn.data` file contains orbitals for empty states. These are useful - we will want to promote electrons into these!

2. Check the ground state calculation output file - we need to know which **k**-point is the Γ point - and which band number is the valence band maximum (& conduction band minimum). Take note of these.

3. Read section 7.4.5 of the `CASINO` manual, at `~/CASINO/manual/`. This will be important for the next stage!

4. Copy the `bwfn.x` files into the directory holding the files for the promotion calculation, and move into that directory. We will need to take the advice of the manual - and use the MDET block to specify an excitation.

5. Open the `correlation.data` file. We need to specify an excitation from the VBM at Γ to the CBM at Γ. Try to do this **yourself** - using the band and **k**-point numbers from earlier, and the guidance in the manual.[3]

6. Run the promotion calculation, and check the out file. Are the occupancies what you expect? They *might not be*. Why?

7. Try deleting the `bwfn.data.bin` file you copied in earlier. Re-run the calculation. Check the occupancies now. What has changed, and why?

FYI: `CASINO` won't always be like this, we want to make it easier to do these calculations. However, this is the easiest way to get an understanding of what happens (a) in the code and (b) to the wave function upon the creation of an electronic excitation.

2.3   Checking & Thinking

1. What is your final result for the Γ → Γ excitonic gap in silicon? How does this compare to literature values?

2. Can you increase the number of VMC steps, to lower your VMC error bar? If so, try obtaining a more accurate VMC result.

3. In the O_2 case, we missed something that could have been important - vibrational effects. We've missed those here, but we also have another **major** source of error. What is it? How could we try to address it?

4. If you were to do the same calculation for another solid, or at another point in **k**-space, what questions would you have to ask yourself before you start your project? [Hints: think about **k**-point grids, the number of electrons in the system, how much computer time you expect to be able to sacrifice...]

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[3]If you are stuck, ask for help!