

ONETEP Spring School 2010: Visualization of electronic properties

Jacek Dziedzic

School of Chemistry, University of Southampton, UK

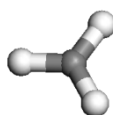
04/2010

This workshop will demonstrate how to:

- Use ONETEP to calculate various electronic properties,
- Instruct ONETEP to generate files needed for later visualization of orbitals, electronic densities and potentials,
- Visualize these properties using VMD¹,
- Set up and run a calculation on a nanostructure using a cut-off for the density kernel.

1. Density, spin density, Kohn-Sham orbitals and the electrostatic potential for CH₃.

In this part we will perform a calculation on the CH₃ radical:



As this molecule contains an odd number of electrons we need to perform a spin-polarised (unrestricted) calculation. In ONETEP this is achieved by optimising a different density kernel for the “up” and the “down” spin:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{r}) K^{\alpha\beta(\uparrow)} \phi_{\beta}^{*}(\mathbf{r}') + \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{r}) K^{\alpha\beta(\downarrow)} \phi_{\beta}^{*}(\mathbf{r}')$$

The ONETEP input is in the file `methyl.dat` and the coordinates (in Å) are in the file `methyl.pdb`. The ONETEP input file contains the coordinates as well (in atomic units), but not in a form directly readable by visualization packages. The `methyl.dat` file specifies a single point energy calculation (`TASK SINGLEPOINT`) with a psinc kinetic energy cutoff of 600 eV (`CUTOFF_ENERGY 600.0 eV`), the Perdew-Zunger variant of the LSDA exchange-correlation functional (`XC_FUNCTIONAL CAPZ`) and the spin-polarised option (`SPINPOLARIZED TRUE`). Also notice the input flag `DO_PROPERTIES TRUE` which proceeds with the calculation of various electronic properties at the end of the single point energy calculation.

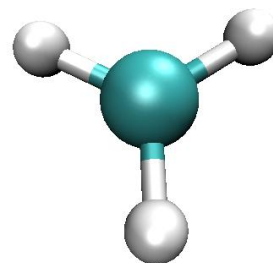
Run the input, redirecting the output to a file such as `methyl.out`. The calculation should take less than a minute. You will notice that a number of `.cube` files have been created, including the file `methyl_spindensity.cube`. Let us examine this first. ONETEP can output volumetric data (such as spin densities, charge densities, potentials, etc.) in Gaussian `.cube` format (`CUBE_FORMAT TRUE`), Materials Studio `.grd` format (`GRD_FORMAT TRUE`) and OpenDX `.dx` format (`DX_FORMAT TRUE`). The `.cube` format has the advantage of having the ionic positions output in addition to the

¹ VMD (Visual Molecular Dynamics) is a free of charge visualization package available from <http://www.ks.uiuc.edu/Research/vmd>

volumetric data. In this tutorial we will use the `.cube` format which can be viewed by a number of free molecular visualisation programs. The instructions that follow are assuming that the VMD program can be used to visualize the files but in principle you can use any other software that can display `.cube` files (such as VESTA, Molekel, gOpenMol, XCrySDens, etc).

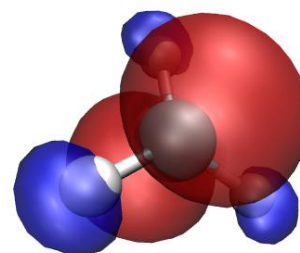
Start VMD by typing **vmd**, use **File/New molecule/Browse** to find `methyl_spindensity.cube`, then click on **Load** to load the molecule. You should be able to see a crude, line-based representation of the molecule in a separate window. You can now get rid of the **Molecule file browser** window. Choosing **Graphics/Representations...** opens another window which lets you control the look of your molecule. In this window, change the **Drawing Method** from **Lines** to **CPK**, which will render your molecule in a ball-and-stick fashion, with the customary colouring². Increase both **Sphere Resolution** and **Bond Resolution** (30 is a good value) to get rid of the jagged edges. You may wish to adjust **Sphere Scale** and **Bond Radius** to your liking as well.

Try dragging with your mouse over the window that shows the molecule to rotate it. Try scrolling the mouse wheel to get closer or further away from the molecule. You may press the `=` key at any time to reset the view. Pressing the `T` key will get you to **Translate Mode** where dragging with the mouse translates the molecule, instead of rotating it. To go back to **Rotate Mode**, press `R`. If your mouse lacks the scroll wheel, pressing `S` to go to **Scale Mode** might be of use. You should be able to obtain a representation similar to the one shown here on the right.



So far we've only looked at the nuclei in the system. Let's try some electronic properties, starting from the spin density which we have already loaded, but not visualized yet. A neat thing about VMD is that you can use several representations at once. Thus, we can overlay the spin density isosurfaces on top of the CPK representation of the ions. In the **Graphics/Representations...** window click on **Create Rep**. This will clone the CPK representation, leaving you with two identical representations. Now change one of them to **Isosurface**. Not much will appear initially, because the default way of showing the isosurface is by using points. This is computationally cheap, but visually so as well. You can change this under **Draw**, by choosing **Solid Surface**. Before you do it, however, make sure to move the **Isovalue** slider to something different than the default 0.0 (or type in the box). This is because there is a huge number of points in our system (some 200000) where the spin density is exactly zero (everywhere outside our molecule). Trying to draw a surface through these points usually confuses VMD to the point of crashing. For this reason it is best to pick any value other than the default of 0.0 to start from, before choosing **Solid Surface**.

Experiment with the settings (**Coloring Method**, **Material**, **Isovalue**) to get a feeling of how they work. It makes sense to set **Coloring Method** to **ColorID** here, as this allows to manually pick a colour for the isosurface (from the drop-down box near **ColorID**). After some adjustments you should obtain an isosurface similar to the one shown



² The colouring is described here http://en.wikipedia.org/wiki/CPK_coloring.

at the bottom of the previous page on the right. Do not worry if you cannot get the transparency right – it's only possible when you render "production quality" images, think of what you see as a draft.

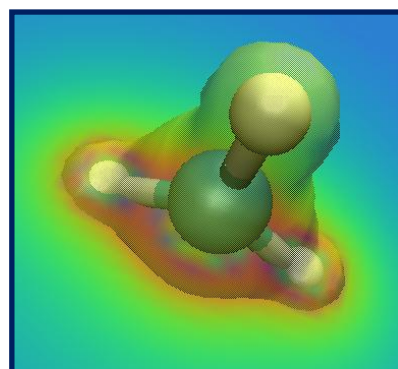
What we have obtained is the textbook picture of the spin density of a methyl radical. It has positive as well as negative regions which is a consequence of the fact that the spatial parts of the Kohn-Sham orbitals for each spin are allowed to be different, even for doubly occupied states.

The properties calculation also produces Kohn-Sham orbitals. Their energies for each spin are printed in the output file (try to find them, they are towards the very end and fill in the table below) and `.cube` files for the squares of some of the orbitals are also produced. HOMO orbitals are written, separately for each spin, to `methyl_HOMO_DN.cube` and `methyl_HOMO_UP.cube`, their LUMO counterparts to `methyl_LUMO_DN.cube` and `methyl_LUMO_UP.cube`. Similarly named files contain the orbitals just below the HOMO and just above the LUMO.

| Quantity | Value |
|--|-------|
| Energy of HOMO for spin 1 (UP) | |
| Energy of LUMO for spin 1 (UP) | |
| Energy of HOMO for spin 2 (DOWN) | |
| Energy of LUMO for spin 2 (DOWN) | |
| Energy of the 1 st orbital above LUMO for spin 1 (UP) | |
| Energy of the 1 st orbital below HOMO for spin 1 (UP) | |

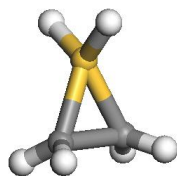
Try plotting the isodensities of both the HOMO and LUMO orbitals for one of the spins, in one picture.

Finally, let's try visualizing the local potential (sum of the ionic, Hartree (Coulomb) and XC potentials), which is written out to `methyl_potential.cube`. Isosurface plots of potentials can be obtained similarly to the isosurface plots of densities. Let's also try to do a contour plot. This can be accomplished by choosing **VolumeSlice** for **Drawing Method**. Try playing with **Slice Axis** and **Slice Offset** to get the feel of it. Admittedly, the quality of the contour plot is not too good, even if you set **Render Quality** to **High**. It is improved, however, when you create a production image. Try obtaining a composite CPK + isodensity + contour plot similar to the one shown on the right.



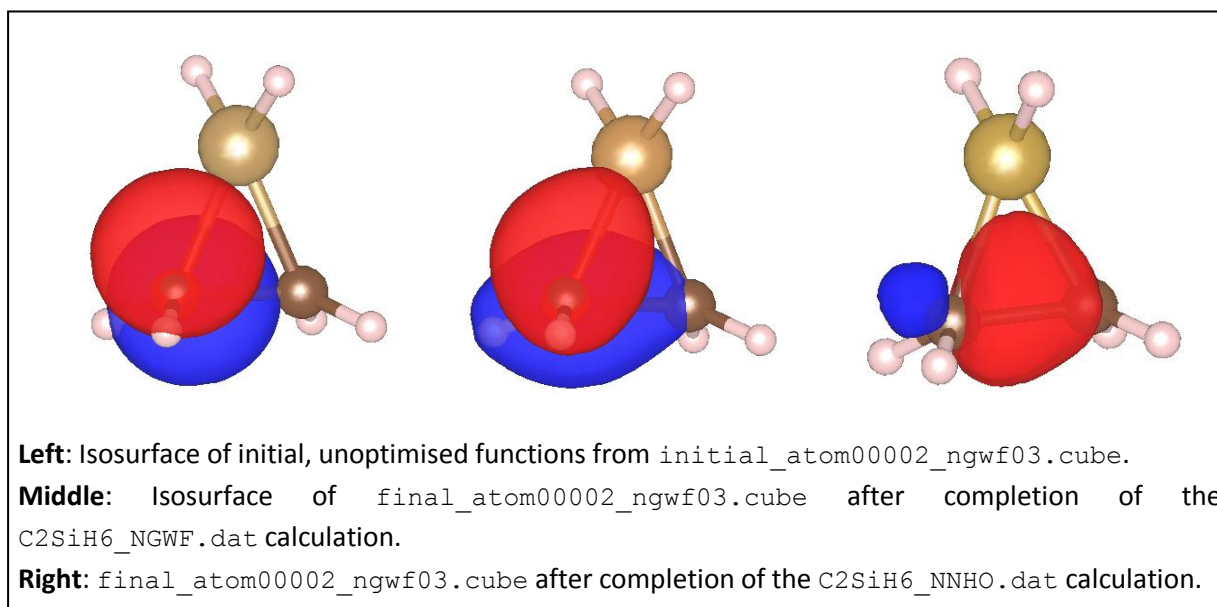
2. Visualizing NGWFs and NNHOs for C₂SiH₆.

In this example we will perform two sets of calculations on the C₂SiH₆ molecule:



The first calculation will use the input file `C2SiH6_NGWF.dat` which has similar parameters to the previous example but also contains the `WRITE_NGWF_PLOT TRUE` setting that allows output of `.cube` files of selected NGWFs. The NGWFs that will be outputted are selected by the `species_ngwf_plot` block in which the “species” of atoms whose NGWFs are to be outputted are included. In this example we output NGWFs of the Si atom and of the first H and C atoms (as written in the input coordinates). The second input file is `C2SiH6_NNHO.dat` which contains the additional directive `NNHO TRUE` which performs a same-centre rotation of the NGWFs to transform them to non-orthogonal natural hybrid orbitals (NNHOs). These contain the same information as the NGWFs but are more “natural” as they conform with chemical concepts, such as being directed towards chemical bonds, and physical concepts, as in several of their properties they resemble proper Wannier functions. The mixing of NGWFs to NNHOs is done according to the procedure by Foster and Weinhold (J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211 (1980)). For this calculation we will use the PBE GGA exchange-correlation functional (`XC_FUNCTIONAL PBE`).

Run the calculation to completion with the two inputs (in separate directories), it should take no more than five minutes for each of them. Examine some of the NGWF and NNHO output files. As an example, below we show plots of the third function (NGWF or NNHO) of atom 2 (one of the carbons). Try to obtain similar plots.



You can observe that initially the function is a p-atomic orbital (as it is initialised by ONETEP). After the calculation the NGWF is rather distorted but still contains quite a lot of p character. The NNHO however is a mixture of all the 4 NGWFs of the carbon atom and is optimally pointed along the C-C bond. You can quantify these observations by comparing the two output files, `C2SiH6_NGWF.out`

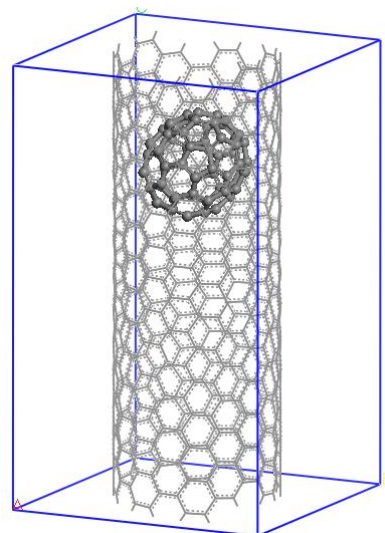
and C2SiH6_NNHO.out which contain “NGWF s/p/d/f Character Analysis” towards the bottom of the file (thanks to the NGWF_ANALYSIS TRUE in the input). You will see how much the NGWFs differ from the NNHOs. Of course all the other quantities (energies, Kohn-Sham orbitals, orbital energies, etc.) are independent of whether you use NGWFs or NNHOs. Check this by completing the table below.

| Quantity | Value |
|----------------------------------|-------|
| Total energy of the system | |
| Energy of HOMO | |
| Energy of LUMO for spin 2 (DOWN) | |

Finally examine the atomic population in the output files (we have asked for it using the keyword POPN_CALCULATE TRUE in the input) and confirm that the charges on each atom are consistent with their relative electronegativities.

3. A calculation on a nanostructure.

Let us now see how to set up and visualize a calculation on a nanostructure whose size is in the region where conventional cubic scaling codes become very inefficient while linear-scaling codes like ONETEP are still at the beginning of their capabilities. We will perform a calculation on the following “nano-peapod” structure:



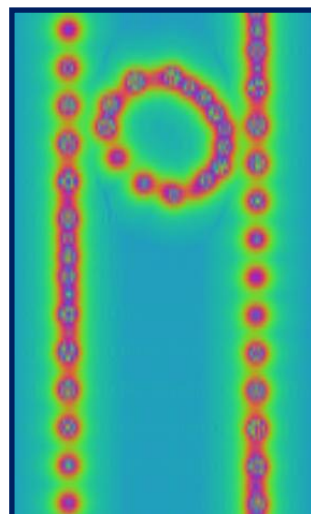
which consists of a C₇₀ fullerene inside a single repeat-unit of a (10,8) carbon nanotube. The (10,8) is a chiral nanotube with 488 atoms in each repeat-unit, so the peapod input consists of 558 atoms, with no symmetry, in a unit cell of 20.0Å x 20.0Å x 33.27Å. The ONETEP input is in the file C70_in_10-8.dat. We impose a density kernel cut-off of 25.0 a₀ (KERNEL_CUTOFF 25.0) in order to achieve linear-scaling behaviour.

This calculation needs to be run on a parallel computer and takes a while to complete (about 5 hours on 8 cores). Because we don’t have that much time, for the purpose of the workshop we are providing the output file it produces as C70_in_10-8_4cores.out. Let us start by examining this file. At the beginning of the calculation the “filling” (the opposite of sparsity) of various matrices is

reported. You will notice that the density kernel is not 100% full as a consequence of the cut-off that is imposed in the input. Information about the psinc grid sizes is also provided, including the actual plane-wave cut-off to which they correspond and the size of the FFT box. The calculation converges in 11 NGWF iterations, which is the point where the NGWF gradient threshold set in the input (NGWF_THRESHOLD_ORIG 0.00003) has been satisfied.

In this case we have not calculated electronic properties as part of the single point energy calculation but we instead obtain these in a separate calculation after the completion of the first calculation. The input file for the new calculation is called `C70_in_10-8_PROP.dat` and it contains the `TASK PROPERTIES` directive. In order to run it you need to provide the converged NGWFs and density kernel from the energy calculation. Again, these will be provided, since we don't have time to run the energy calculation. Copy the `C70_in_10-8.tightbox_ngwfs` file into a file called `C70_in_10-8_PROP.tightbox_ngwfs` (so that it corresponds with the name of the new calculation) and the `C70_in_10-8.dkn` into `C70_in_10-8_PROP.dkn` and run the calculation. This will take about 10-15 minutes, perhaps that's a good time for a cup of coffee.

As before, a range of properties are calculated. As an example, you can examine the total potential (the sum of ionic, Hartree and exchange-correlation potentials) which is outputted to the file `C70_in_10-8_PROP_potential.cube`. A contour plot on a plane containing the nanotube axis of the potential will look similar to what you see on the right here, which is compatible with the chiral nature of the nanotube and reveals also the asymmetric way in which the oblong C_{70} is located inside it. Red regions correspond to large and positive values of the potential (standard electrostatic conventions) and reveal the location of nuclei, whose distance from the plane varies along the axis of the tube, as a result of the chirality. You can go on and explore other properties of the nano-peapod from the `C70_in_10-8_PROP_4cores.out` file and the other output files that were produced by the properties calculation.



If you still have time, try creating a fancy plot showing the structure of the nano-peapod system with its HOMO and LUMO orbitals and a contour plot of the potential, similar to the one below.

