

ONETEP workshop: Calculation of electronic properties

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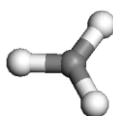
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This workshop will demonstrate how to use ONETEP to:

- Calculate various electronic properties
- Generate files for the visualisation of orbitals, electronic densities and potentials
- Set up and run a calculation on a nanostructure using a cut-off for the density kernel

Density, spin density and electrostatic potential, Kohn-Sham orbitals

We will perform a calculation on the CH₃ radical:

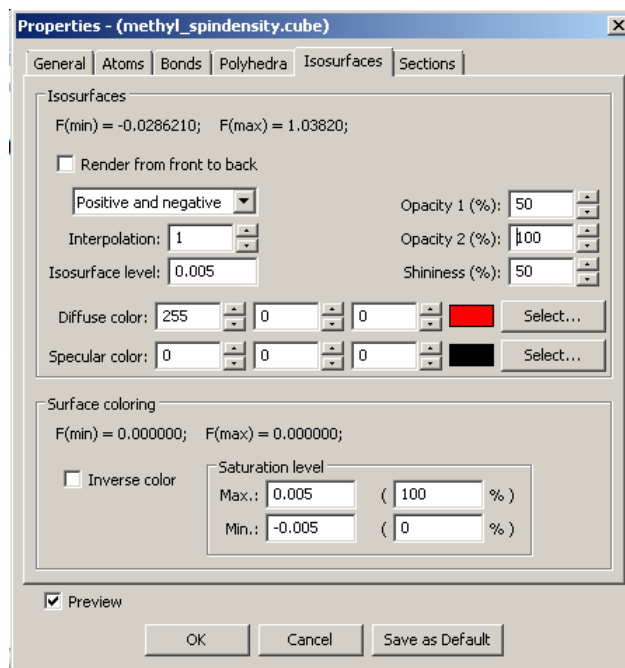


As this molecule contains an odd number of electrons we need to perform a spin-polarised (unrestricted) calculation. In ONETEP this is achieved by optimising a different density kernel for the “up” and the “down” spin:

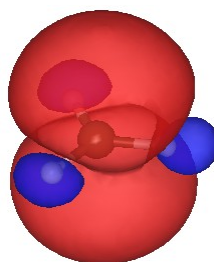
$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{r}) K^{\alpha\beta(\uparrow)} \phi_{\beta}^*(\mathbf{r}') + \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{r}) K^{\alpha\beta(\downarrow)} \phi_{\beta}^*(\mathbf{r}')$$

The input is in the file “methyl.dat” and the pure coordinates (in Å) are in the file “methyl.pdb”. 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 and direct the output to a file such as “methyl.out”. You will notice that a number of .cube files have been created, including the file “methyl_spindensity.cube”. Let us examine this first. All volumetric data output files can be produced in Gaussian .cube format (`CUBE_FORMAT TRUE`) and/or Materials Studio .grd format (`GRD_FORMAT TRUE`). 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 VESTA program can be used to visualise the files but you can use any other software that can display .cube files (such as Molekel, gOpenMol, XCrySDens, etc).

Open the file “methyl_spindensity.cube”. Click on “Properties” and then select the tab “Isosurfaces”. The value of the isosurface is controlled by the “isosurface level” input box:

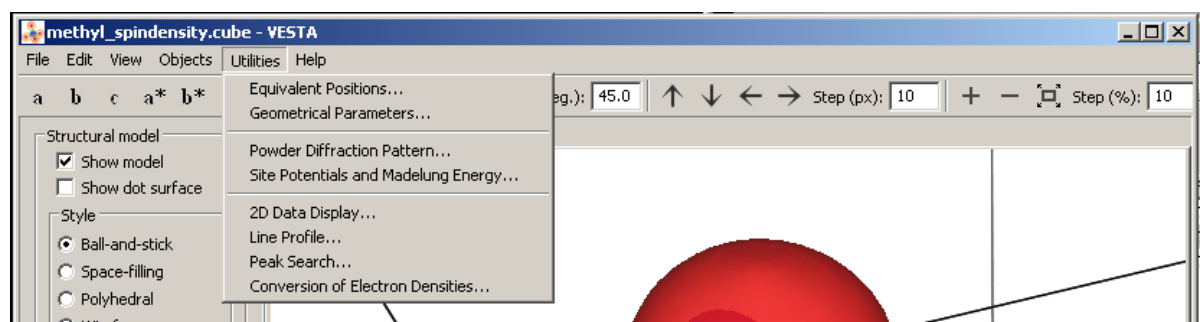


After some adjustments you should obtain an isosurface similar to this:

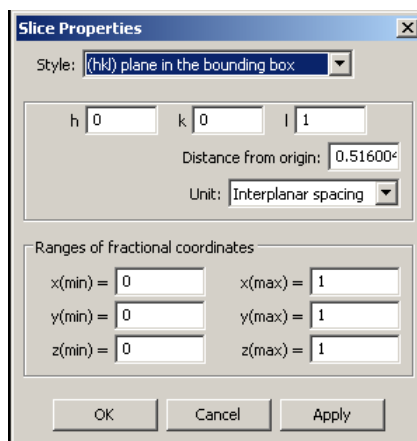


which is the textbook picture of the spin density of a methyl radical. It has positive as well as negative regions which is a consequence of the fact that the spatial parts of the Kohn-Sham orbitals for each spin are allowed to be different, even for doubly occupied states. The properties calculation also produces Kohn-Sham orbitals. Their energies for each spin are printed in the output file and cube files for the squares of some of the orbitals are also produced.

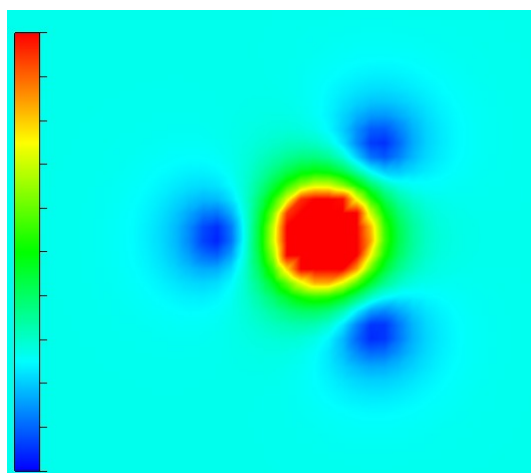
It is possible also to make contour plots of these quantities on a plane. To do this in VESTA we need to select the "Utilities → 2D Data Display" menu.



Then use “Slice properties” to select the contour plane in terms of a lattice vector and its position along this vector by setting the value “Distance from origin”.

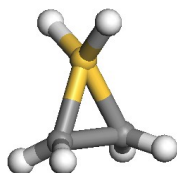


A contour plot of the spin density can then be constructed:



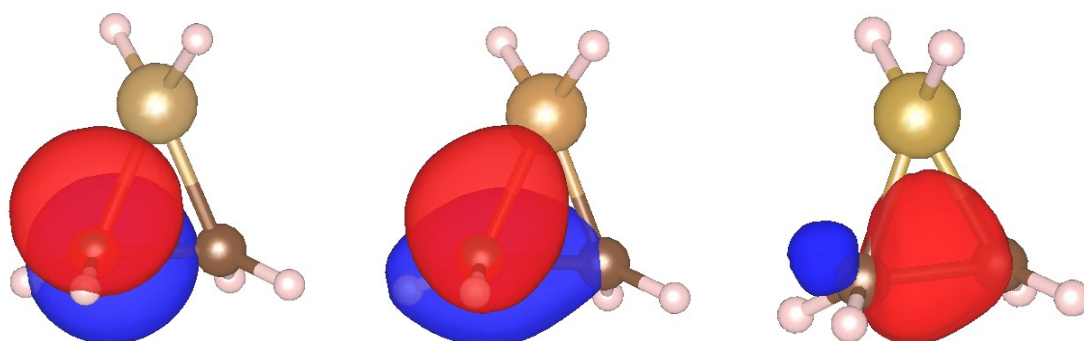
Visualising NGWFs and NNHOs

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 from the Si atom and from the first H and C atoms 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) and then 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).

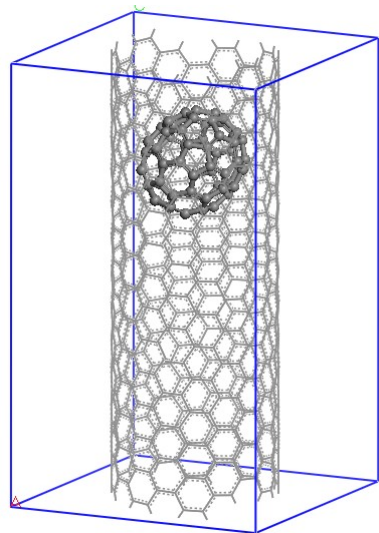


Left: Isosurface of initial, unoptimised functions from "initial_atom00002_ngwf03.cube". **Middle:** isosurface of "final_atom00002_ngwf03.cube" after completion of the C2SiH6_NGWF.dat calculation. **Right:** "final_atom00002_ngwf03.cube" after completion of the C2SiH6_NNHO.dat calculation.

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 C 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" (as a result of 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. Finally examine the atomic population in the output files (created by the keyword `POPN_CALCULATE TRUE` in the input) and confirm that the charges on each atom are consistent with their relative electronegativities.

A calculation on a nanostructure

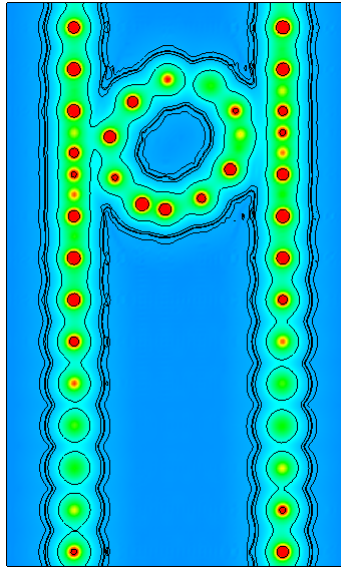
Let us now see how to set up a calculation on a nanostructure whose size is in the region where conventional cubic scaling codes become very inefficient while linear-scaling codes like ONETEP are still at the beginning of their capabilities. We will perform a calculation on the following “nano-peapod”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



which consists of a C_{70} 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 $20.0\text{\AA} \times 20.0\text{\AA} \times 33.27\text{\AA}$ and is in the file “C70_in_10-8.dat”. We impose a density kernel cut-off of $25.0 a_0$ (`KERNEL_CUTOFF 25.0`) in order to achieve linear-scaling behaviour.

This calculation needs to be run on a parallel computer. For the purpose of the workshop we are providing the output file it produces as “C70_in_10-8_12cores.out”. Let us first examine the “C70_in_10-8_12cores.out” 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 energy. The input file for the properties is called “C70_in_10-8_PROP.dat” and contains the `TASK PROPERTIES` directive. In order to run it you need to provide the converged NGWFs and density kernel from the energy calculation, so copy the “C70_in_10-8.tightbox_ngwfs” file into a file called “C70_in_10-8_PROP.tightbox_ngwfs” and the “C70_in_10-8.denskern” into “C70_in_10-8_PROP.denskern”. As before, a range of properties are calculated. As an example, you can examine the total potential (the sum of external, Hartree and exchange-correlation potentials) which is outputted in the file “C70_in_10-8_PROP_potential.cube”. A contour plot with VESTA on a plane containing the nanotube axis of the potential produces the following image:



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_12cores.out” file and the other output files that were produced by the properties calculation.