Computational Catalysis with DFT
Kevin Greenman and Peilin Liao

Description
Computational Catalysis with DFT uses Quantum Espresso (QE) to do calculations of interest to catalysis research (e.g. total energy, adsorption energy, projected density of states, and d-band center). Structures can be automatically generated using the Atomic Simulation Environment (ASE) or can be manually entered by atomic coordinates. All QE input and output files are available as outputs of the simulations, so users can download and analyze these further to extract more information. A visualization of the structure using the visualization toolkit (VTK) is also available in the outputs. The tool has two modes of operation: Basic (intended for use in undergraduate education) and Advanced (intended for use in graduate education or by beginning researchers).

Instructions
1. Select a choice for Mode (Basic or Advanced).
2. Click the Inputs button.

![Image of interface]

Basic Mode
1. Select a task (Adsorbate, Surface, or Surface + Adsorbate).
2. Select a material to use for the adsorbate, the surface, or both (depending on your selection of task in #1).
3. If you are doing a surface + adsorbate calculation, select an option for the adsorbate position and enter a value for the distance the adsorbate will be placed above the surface. The options for position use the adsorbate position keywords from ASE.
4. When you are doing a surface + adsorbate calculation, additional boxes appear where the user may input values of the total energy of the surface alone and the adsorbate alone. If

Last updated: 6 Aug 2018 by Kevin Greenman
these values are entered, the adsorption energy will be automatically calculated at the end of the surface + adsorption calculation. Otherwise, the adsorption energy printed out will be the same as the total energy of the surface + adsorbate.

5. If you wish to change additional default options, click the “Show all options” switch. This makes three additional tabs visible: Energy Expression, Density of States, and Submit to Cluster.

   a. On the Energy Expression tab, the user may decrease the values of the k-points and/or energy cutoffs to speed up the calculation, but this will also decrease the accuracy. Conversely, increasing these values will increase the simulation time and also increase the accuracy. **The default values are not necessarily converged.** The k-points in the z-direction should always remain at 1. The additional options on this page are intended for more advanced users.

   b. On the Density of States tab, the density of states (DOS) calculations are off by default. Turn this option on in order to calculate the DOS, projected density of states (PDOS), and band centers (s, p, and d).

   c. The Submit to Cluster tab provides options for running the job in parallel using nanoHUB computing cluster resources. By default, calculations with only an adsorbate run in series and those with a surface or surface + adsorbate run in parallel using 16 processors. Using these defaults, adsorbate calculations typically take a couple minutes or less, and surface or surface + adsorbate calculations typically take about 60 minutes, but this varies from system to system. There is also the option to send an email to yourself when the job is complete if you wish to leave it unattended and be notified as soon as it is done. The email will be sent to the email associated with your nanoHUB account. You may have to create a filter in your email to keep these from being sent to your spam folder.

6. Press “Simulate”.
Advanced Mode
1. Select a task (adsorbate energy, surface energy, or surface + adsorbate energy).
2. Select the source of your adsorbate and/or surface (automatic generation by ASE or manual input).
3. When you are doing a surface + adsorbate calculation, additional boxes appear where the user may input values of the total energy of the surface alone and the adsorbate alone. If these values are entered, the adsorption energy will be automatically calculated at the end of the surface + adsorption calculation. Otherwise, the adsorption energy printed out will be the same as the total energy of the surface + adsorbate.

4. If you selected ASE in #2, modify default values on the Surface and Adsorbate tabs, as appropriate. Some boxes have descriptions that appear upon hovering over them, and users should pay attention to the instructions in these descriptions for information on valid inputs. For a surface + adsorbate calculation, the choice of ASE Utility Surface Function or ASE Generic Surface Function on the Surface tab will determine the options for adsorbate position input on the Adsorbate tab. The utility function allows for keywords (e.g. on top, bridge, hollow, etc.), while the generic function requires that the position be specified in x-y coordinates.
On the Adsorbate tab, the atom or molecule entered in the Adsorbate input box must be in ASE’s G2 database:

5. If you selected manual input, enter the positions of the atoms and the cell vectors in the boxes provided on the Manual Geometry Inputs tab. These should follow the format used in
QE input files. If you are running a surface + adsorbate calculation with manual input and are using the partial relaxation option on the Energy Expression tab (on by default), the adsorbate must be placed on top of the surface (i.e. with the highest z-coordinate).

6. Click the “Show all options” switch to display the Energy Expression, Density of States, and Submit to cluster tabs. Please refer to instruction #5 under Basic Mode for a description of these tabs. **Please take special note that the default values for k-points and energy cutoffs are not necessarily converged.**

7. Press “Simulate”.

**Supplementary Notes**

**Adsorption Energy**
The adsorption energy is calculated using the following equation:

\[ \Delta E = \frac{E_{\text{surface+adsorbate}} - E_{\text{surface}} - E_{\text{adsorbate}}}{\text{number of atoms in adsorbate}} \]

**Bulk Relaxations**
By default, the tool builds surfaces using the lattice constants in ASE’s database. The user has the option to input a lattice constant manually, and some users may wish to perform a bulk relaxation in order to build a surface with the optimized lattice parameter. The option to do this does not exist explicitly in this tool, but it is possible to do by modifying a few settings:

- Select advanced mode
- Select Surface for the task, and Manual Input for the geometry source
- Input the atomic coordinates and cell vectors of the bulk structure on the Manual Geometry Inputs tab
- On the Energy Expression tab, choose Cell Relax for the type of relaxation
- Run convergence testing on the k-points and energy cutoff values
- Once converged, determine the relaxed lattice parameter from the simulation output
Occupations Options
The default option for occupations is Gaussian smearing. The tetrahedra occupations option is well-suited for doing DOS calculations. However, the tetrahedra option is not well-suited for force/optimization calculations. Therefore, if you wish to run a DOS calculation using the tetrahedra option, you should do the following:
1. Run an SCF calculation (DOS turned off) with the Relax option on the Energy Expression tab set to Force Relax and the Occupation set to smearing.
2. Copy the final coordinates from the above calculation into the Manual Geometry Input tab of a new calculation, and run this new calculation with DOS turned on, Relax set to No, and Occupations set to tetrahedra.

Visualizing Structures Outside of nanoHUB
Users who wish to view the atomic structures using XCrySDen can download the SCF input and/or output files and follow the instructions here: http://www.xcrysden.org/doc/pwscf.html