AUTOSURF (V1.3)

A Freely Available Program to Construct Potential Energy Surfaces

Ernesto Quintas-Sánchez* and Richard Dawes*

Department of Chemistry, Missouri University of Science and Technology, Rolla 65401 MO, USA

* *Email: quintassancheze@mst.edu; dawesr@mst.edu*

AUTOSURF 101: A Quick-Start Guide

AUTOSURF is a freely distributed suite of codes for the automated construction of potential energy surfaces (PESs) for van der Waals (vdW) systems. The fitting algorithms implemented in the code are based on the L-IMLS methodology, and have many advanced features such as options for data-point placement, flexibility to include gradients in the fit, iterative refinement, and symmetry recognition. The code completely automates all of the steps and procedures that go into fitting various classes of PESs and interfaces to popular electronic structure codes such as MOLPRO and GAUSSIAN. The package is composed of three main programs. **AUTOSURF-PES** carries out the automated construction of the PES to a user specified accuracy in a fairly black-box fashion—starting with a sparse set of initial *ab initio* seed points, the program grows a fitted PES over predefined ranges of energy and coordinates until the desired level of precision is reached. **AUTOSURF-PLOT** permits arbitrary evaluations of the PES, the generation of plots of 1D or 2D cuts of the surface (with optional relaxation) for any of the internal variables, and also to perform a variety of fitting error analyses in specified energy and coordinate ranges. A utility program called **AUTOSURF-ABI** performs guided surveys of the PES (various cuts), facilitates the benchmark of electronic structure methods, and the development of composite schemes such as complete basis set (CBS) extrapolation.

This introductory guide describes how to obtain, install, and run AUTOSURF. The following typographical conventions are used through the guide: The `Typewriter` font is used for literal characters, such as keywords and labels given in the input files, the names of routines and variables, while **bold Sans Serif** font is employed for files, directories, and paths.

Prerequisites

In order to install and run AUTOSURF suite on a Linux system (Windows and OS X are currently not supported) the following is needed:

- A Fortran90 compatible compiler.
- MPICH.
- The Fortran LAPACK Library.
- Electronic structure code (MOLPRO and/or GAUSSIAN).

How to obtain AUTOSURF

For non-commercial purposes, there is no charge to obtain the AUTOSURF package for academic users—research institutes, universities, individuals—the user must simply sign a *License Agreement*. The License form can be obtained from the authors by email. The link for downloading the most recent version of AUTOSURF will be provided—by e-mail, to the address used in the License form—after the signed form has been received via email.

Once the AUTOSURF package have been downloaded, instructions in the following section describe the installation process. It is not necessary to have system administration privileges to compile, install or execute the program.

How to install and use AUTOSURF

The standard AUTOSURF (v1.3) package is distributed as a compressed archive file named **autosurf-v1.3.tar.gz**. In order to install it, first unpack the downloaded distribution in the desired location by typing:

```
tar -xzvf autosurf-v1.3.tar.gz
```

This should create a new directory called **AUTOSURF**, which contains all the necessary sub-directories and files. Figure 1 shows the structure of the complete AUTOSURF directory.

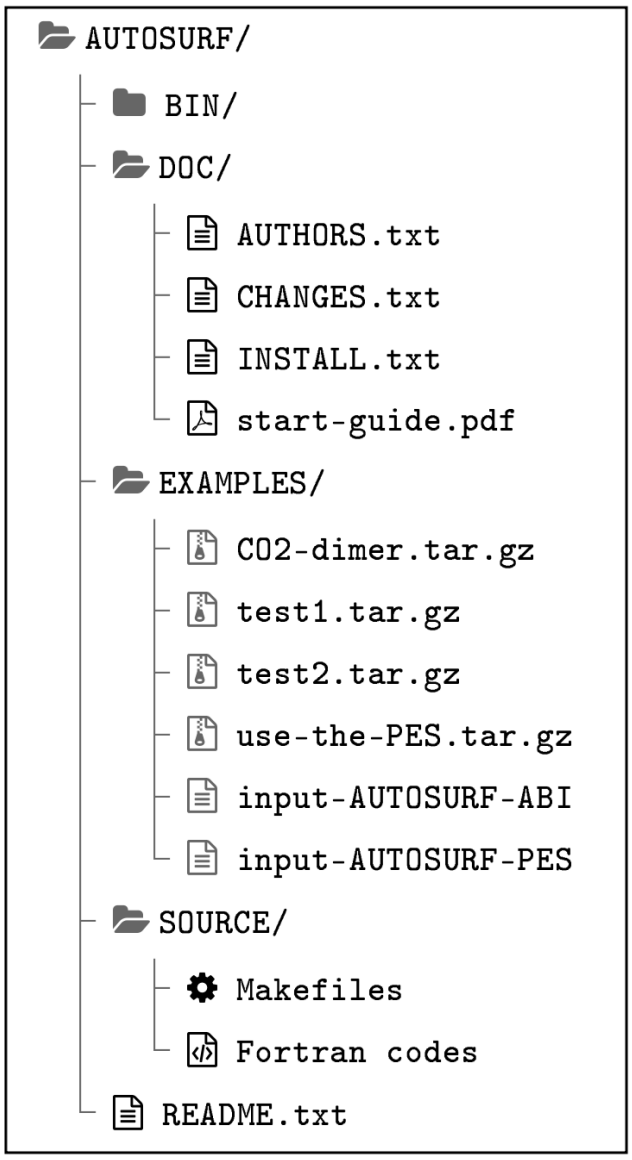

Figure 1: Directory tree containing the complete AUTOSURF installation.

To compile the Fortran programs of the AUTOSURF suite, go to the source directory:

cd AUTOSURF/SOURCE

and edit the files **make-PLOT** (by setting the `F90` variable), **make-PES** and **make-ABI** (by adjusting the `MPI` variable and `LD` path), to point to the preferred Fortran compiler and to the correct location of the relevant libraries in your system. In its first release (v1.3),

the AUTOSURF package consists of the main program **AUTOSURF-PES**, and two auxiliary programs: **AUTOSURF-PLOT** (which provides some analysis tools to test and visualize the final potential) and **AUTOSURF-ABI** (which facilitates preliminary surveys of the PES and electronic structure benchmarks to be performed). Issuing the command:

make -f Make-PES

will compile the source code and create the binary: **AUTOSURF-PES.x**, and issuing the commands:

make -f Make-PLOT

and

make -f Make-ABI

will create the binaries: **AUTOSURF-PLOT.x** and **AUTOSURF-ABI.x** respectively. The binaries will be automatically moved into the directory: **AUTOSURF/BIN**. At this point, it is advisable to check whether the generated binaries are correctly flagged as executable; if not—in the binaries directory—type:

chmod a+x *.x

to make them executable. The binaries are portable—*i.e.*, it's enough to simply copy and execute them in each new location to start running AUTOSURF.

To be used, **AUTOSURF-PES.x** only requires the presence—in the same directory—of the main input file (**input-AUTOSURF-PES.dat**, which contains all relevant settings concerning the system and the fitting) and the sample "header" which defines the electronic structure calculations (*e.g.*, **molpro1.dat**, see the article for details). Once a PES has been constructed, the interactive **AUTOSURF-PLOT.x** only requires the main input file and the final PES-file (outputted by **AUTOSURF-PES.x**) to be present. Similarly, for preliminary surveys using the **AUTOSURF-ABI.x** code, only the corresponding input file (**input-AUTOSURF-ABI.dat** and one or more electronic structure "headers" (*e.g.*, **molproX.dat,**

X = **1**, **2**, ...) are required. Additionally, the main program interfaces to quantum chemistry software to compute the *ab initio* energies to be included in the fit—note that only MOLPRO and GAUSSIAN are fully implemented in the current distribution. Generic examples of the input files used by **AUTOSURF-ABI** and **AUTOSURF-PES** are given in the directory: **AUTOSURF/EXAMPLES**.

Testing the installation

After the binaries are created, it is advisable to check the installation before using the program for the first time. It is suggested to explore the directory: **AUTOSURF/EXAMPLES**, where all the necessary input files and generated output files are provided for two different test scenarios (**test1** and **test2**). During the first test, AUTOSURF main program will randomly compute 200 *ab initio* points using MOLPRO, generate the seed grid and corresponding seed-PES, and finally assess the fitting errors; its execution takes less than 20 minutes to complete on our cluster when 16 processors are used. The second test checks the restart features of the code, producing a final PES after only one iteration; its execution takes less than 20 minutes to complete when 40 processors are used.

The easiest way to check the installation, is to replicate these basic calculations—which are designed to test the basic functionality of AUTOSURF. Notice that small differences (small numerical deviations) in the output files can occur when using a different version of the quantum chemistry programs, different Fortran compilers, different libraries, etc. If you were able to successfully reproduce the results given on **AUTOSURF/EXAMPLES** for the two testing scenarios, then... Congratulations! Now you are ready to construct your first potential energy surface.

The CO_2 dimer example

Also in the **AUTOSURF/EXAMPLES** directory, the complete set of input (and the corresponding output) files used for the construction of a set of three PESs for the CO_2 dimer system is provided—PES1, PES2, and PES3, as described in the article: "AUTOSURF: A Freely Available Program To Construct Potential Energy Surfaces, E. Quintas-Sánchez and R. Dawes, *J. Chem. Inf. Model.* (2019) **DOI: 10.1021/acs.jcim.8b00784**.

How to use the generated PES

At the end of the PES generation process, once the desired global accuracy is reached, the fitting parameters and other information needed to reconstruct the PES is outputted for use in the data-file: **PES-LAB-NUM** (where '**LAB**' represents the label specified for the system in the input file, and '**NUM**' is the number of *ab initio* points used in the final fit).

The program **evaluatePES.f90** (in the directory **AUTOSURF/EXAMPLES/use-the-PES**) provides a minimalistic example of how to use the generated potential. As can be noticed in the code, no initialization of the potential is needed, and the energy value (`V`) for a given geometry can be obtained by simply calling the subroutine `PES(xi,V,NAME1)`, where the input variable `NAME1` is the name of the PES-data-file (as outputted by the main program once the potential is complete) and `xi` represents a 4D vector defining the system coordinates: `xi(1)` is R, the distance between centers of mass (in Angströms); `xi(2)` and `xi(3)` represent, respectively, $\cos(\theta_1)$ and $\cos(\theta_2)$, with range: $(-1, 1)$; while `xi(4)` is the dihedral angle ϕ (in radians), with range: $(0, 2\pi)$. By default, the energy units of the potential constructed with AUTOSURF are kcal/mol, so in this particular example a conversion factor (`CONVE`) is used to switch energies to wave numbers .