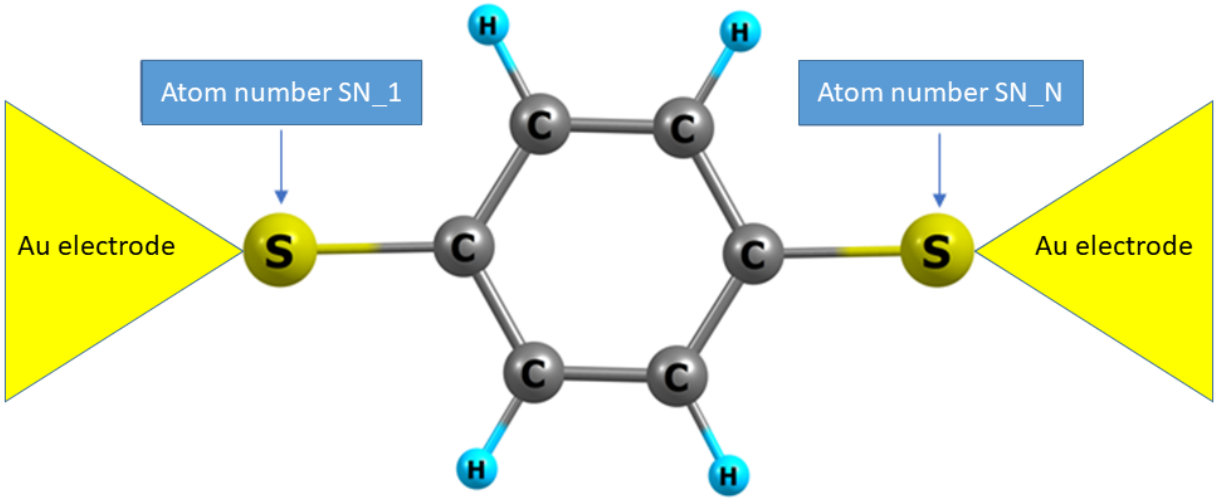
SingleMoleculeConductivity 1.0 Program Guide

This program allows you to calculate the I – V characteristic curve for a single molecule and is designed to work with the output files of calculations performed in the programs GAUSSIAN 09 and GAUSSIAN 16. Software implementation corresponds to the theoretical approach described in [1,2]. The **GNU Scientific Library** [3] and **Armadill**o - C++ library for linear algebra & scientific computing [4] were used in this project.

Consider a scheme of a monomolecular device for which the I – V characteristic will be calculated.



For the program to work, you must have two files containing calculations of a molecule: “attached” to gold electrodes and a “free” molecule. An important note - it is necessary that the numbers of the terminal atoms that attach the molecule to the gold electrodes and the free molecule coincide. Of course, the calculations must be done on the same basis set. In this case, for the program to work, the output files of the calculations must contain information about the overlap integrals of the AO and information about the wave function of the molecular system. The first parameter is provided through the iop keyword (3/33 = 1), and for the second it is enough to specify pop = full (you can use the iop (6/7 = 3) option, which is more reliable).

To run the program, type the following in the command line: “> singleMoleculeConductivity.exe inputs”. Where ‘’inputs” is a simple text file that specifies the variables that the program should use in its calculations. The format of the text file inputs (its name can be arbitrary, but it is better to give meaningful) looks like strings like “keyword = value”. One line is allocated for each keyword. The next keyword is placed on the next line. The order of keywords, their case, and the number of blank lines between them are not important. Comments are specified by placing the hash # at the beginning of a line.

Let's describe the keywords and their meanings that are recognized by the input file parser:

INPUT_FILE_COMPLEX = **bdt-2au7_sp_16.log** (name of the file with calculations simulating a molecule attached to gold electrodes).

INPUT_FILE_ISOLATED = **bdt_sp_16.log** (name of the file with calculations simulating a free molecule).

WF = **RHF** (type of wave function. Valid values are **RH**F or **UHF**. Default = **RHF**).

OUT_FILE (the name of the output file to save the results. *Not implemented yet*. The calculation results are output to the standard output stream).

ORB_WINDOW = 0 (The size of the "orbital window" defines a set of orbitals as HOMO-0 ... LUMO + 0. Obviously, if the parameter value is equal to zero, the current-voltage characteristic will be calculated only with the inclusion of the HOMO and LUMO orbitals. If you specify ORB_WINDOW = 4, then this means that you should take 4 orbitals around the HOMO-LUMO border. That is, HOMO-4, HOMO-3, ... HOMO, LUMO, ... LUMO + 3, LUMO + 4. Also, the size of the orbital window can be set by two numbers. This notation allows you to specify an asymmetric border around HOMO - LUMO. So if ORB_WINDOW = 3,1, then the range HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO + 1 will be taken. If you specify in this notation ORB_WINDOW = 0,0 then the orbitals HOMO, LUMO will be taken. Well, if you specify three or more numbers, it means that orbitals with these numbers will be used. So, in the case of ORB_WINDOW = 25,30,40, the range consisting of orbitals 25,30,40. That is, of the three listed orbitals. There is also the keyword ALL, which indicates that but use all orbitals, but for now this is only an experimental option and it is better not to use it. Default = 0. That is. HOMO and LUMO orbitals are used. When specifying the range of orbitals in two or more numbers, spaces (along with commas) between numbers are not allowed. Numbers must be separated by comma only (operator of sequence)).

HOMO_RES = 5.00 (This is the HOMO energy of the gold electrode in eV. Default = 5.45 eV).

U_LWR = 0 (This parameter sets the lower limit of the voltage applied to the electrodes in volts. Default = 0 V).

U_UPR = 5 (This parameter sets the upper limit of the voltage applied to the electrodes in volts - potential difference. Default = 5 V).

N_PTS = 10 (This parameter defines the number of points in the range [**U_LWR**, **U_UPR**] for which the I – V curve will be calculated. Default = 100).

T = 300 (This keyword sets the temperature in Kelvin. Default = 298.15).

DEG_THRH = 0.08 (This parameter sets the energy range when calculating the expansion coefficient of the wave function on terminal atoms in a free molecule. In the case of simple molecules, it is enough to calculate the decomposition coefficient only for LUMO. Thus, the **DEG_THRH** parameter allows you to

include in the calculation the orbitals lying in energy above LUMO no more than 0.08 eV By default **DEG_THRH** = 0.07565. This value was chosen based on the Boltzmann distribution:

$$\frac{N_2}{N_1} = e^{-(\frac{E_2-E_1}{R\cdot T})}$$

Thus, with the default value, the calculation will include orbitals, whose contribution will be 5% or more. If there is a clear understanding that the calculation needs to include an orbital spaced from LUMO in energy by x eV, then you can simply indicate **DEG_THRH** = x, where x is the amount of energy in eV at which the given orbital is separated from LUMO. Of course, if there are others between LUMO and the given orbital, then they will also be included in the calculation with the corresponding weights that will be calculated automatically.

INTEGRATOR = 0 (This parameter sets the method of integration of the integrand and, in general, the function itself. In Nakanishi's original work, an improper integral of the form is used:

$$\int_a^{+\infty} f(x)dx \qquad (1)$$

However, numerical integration using the GNU Scientific Library is not always successful. The integral diverges. Therefore, it was decided to transform this integral to the form:

$$-\int_0^1 f\left(\frac{a+(1-t)}{t}\right)\cdot \ln(t)\,dt \qquad (2)$$

By substitution the variable x = a + (1 - t) / t.

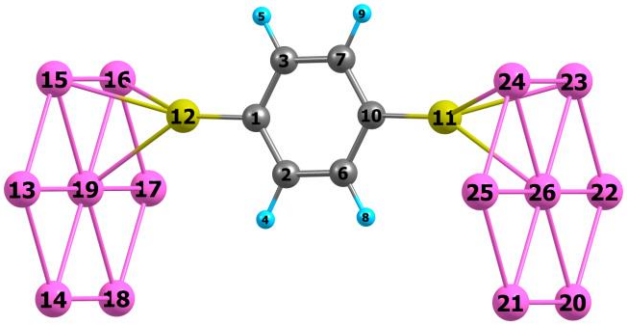
This transition allows the calculation of a definite integral on the interval (0,1]. If the **INTEGRATOR** parameter is equal to 0, then the 61-point algorithm based on the Gauss-Kronrod quadrature formula (QAG adaptive integration from GNU scientific liabrary) and a formula of the form (2 For especially severe cases, the option INTEGRATOR = 1 is provided. In this case, the CQUAD algorithm is used (from GNU scientific liabrary). CQUAD is a new double-adaptive universal quadrature algorithm and a formula of the

form (2). As a rule, it works in all cases and is able to calculate the integral, which is slowly converging and including various singularities. However, it is logically slower. Well, for the sake of compatibility, the algorithm for calculating the improper integral by formula (1) parameter **INTEGRATOR** = 2, where the integrand corresponds to the formula given in the original work of Nakanishi. This algorithm often has problems calculating the improper integral (the orbital window> 5)). Default: **INTEGRATOR** = 0.

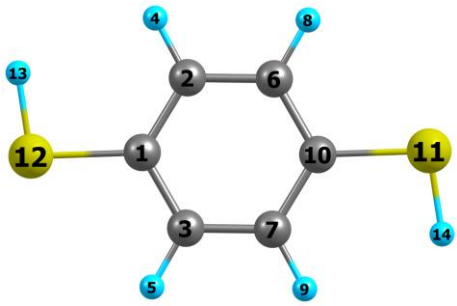
SN_1 = 11 and SN_N = 12 These parameters set the numbering of the terminal atoms with which our molecular system is attached to the prototype gold electrodes. Atomic numbers must match in a free molecule and a molecule placed between the prototypes of gold electrodes.

Examples of calculating the current-voltage characteristic of monomolecular devices

Let us consider the process of calculating the current-voltage characteristic for a benzenedithiol molecule. For this we need to have two files: “bdt-2au7_sp_16.log” and “bdt_sp_16.log” (see the **BDT** directory).



bdt-2au7_sp_16.log



bdt_sp_16.log

In the command line, type:> singleMoleculeConductivity.exe bdt.in> bdt.vi

Here the file “bdt.in” describes the input parameters for the program, and “bdt.vi” is the file to which the output data is written. The plotted graph of the calculated current-voltage characteristic can be found in the **Pict** catalog.

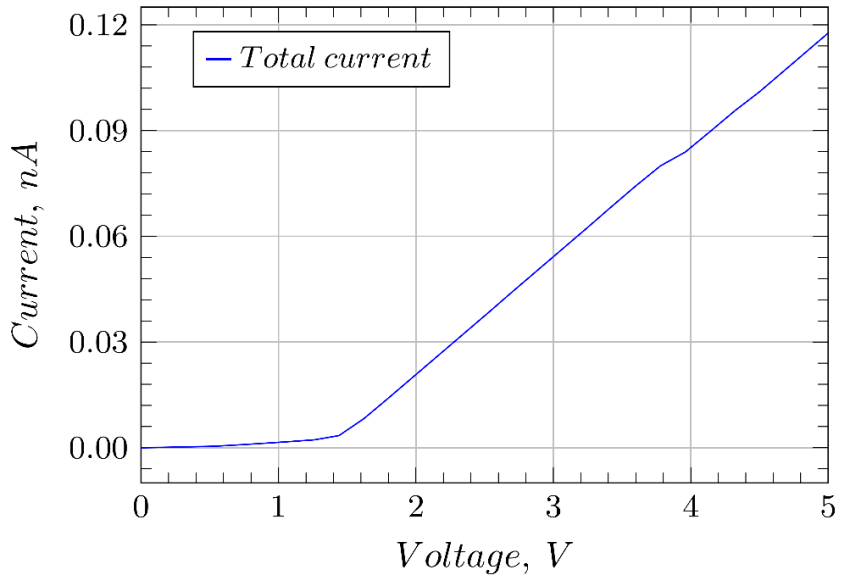


Figure 2. The graph of the calculated current-voltage characteristic for the benzenedithiol molecule

Also, the program has implemented additional functionality that allows you to estimate which orbital from the set of orbital window which contributes to the total value of the current-voltage characteristic. Table “Orbital decomposition current, current_error and transition probability into total result”.

Figure 3 shows a graph of the dependence of the probability of electron passage depending on the potential difference applied to the electrodes.

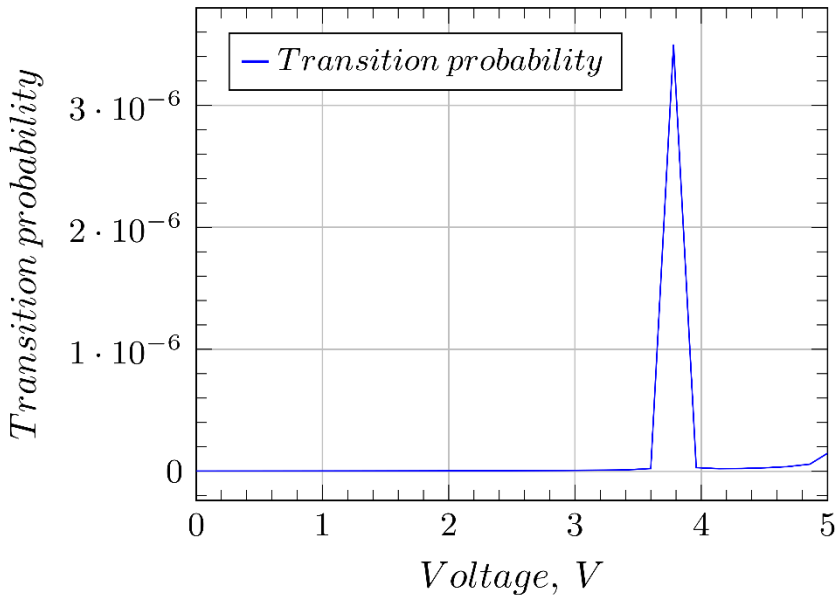
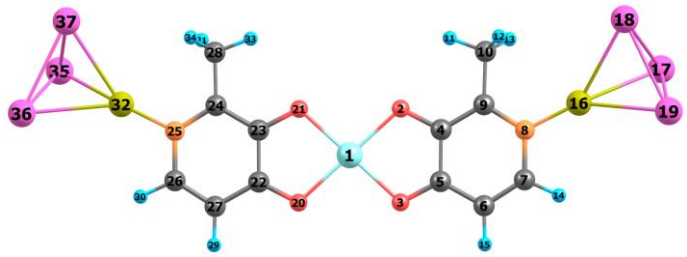
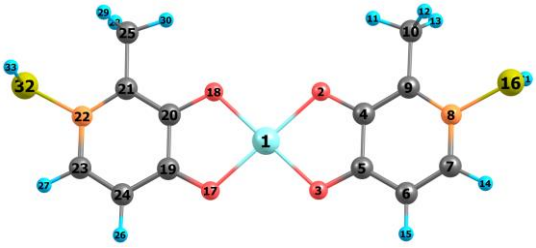


Figure 3. Graph of the calculated probability of electron transmission depending on the potential difference applied to the electrodes for the benzenedithiol molecule

Let us consider the calculation of the current-voltage characteristic for the complex compound H-Cu-H [1]. For this, we must have two files: “H-Cu-H_sp-complex_09.log” and “H-Cu-H_sp-isolated-09.log” (see the **H-Cu-H** directory).



H-Cu-H_sp-complex_09.log



H-Cu-H_sp-isolated-09.log

Let's type in the command line:> singleMoleculeConductivity.exe h-cu-h.in> h-cu-h.vi

Here the file “h-cu-h.in” describes the input parameters for the program, and “h-cu-h.vi” is the file into which the output data is written. The plotted graph of the calculated current-voltage characteristic can be found in the **Pict** catalog.

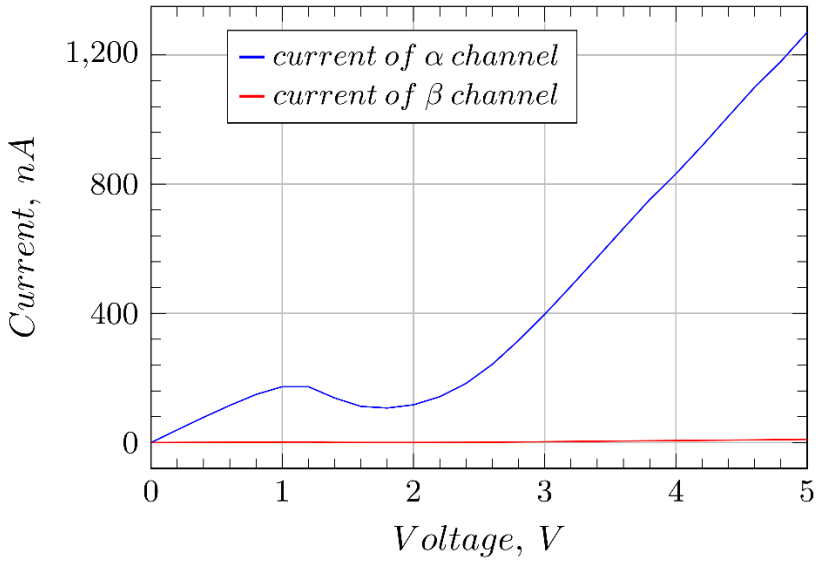


Figure 4. The graph of the calculated current-voltage characteristic for the H-Cu-H complex

Figure 3 shows a graph of the dependence of the probability of electron transition depending on the potential difference applied to the electrodes.

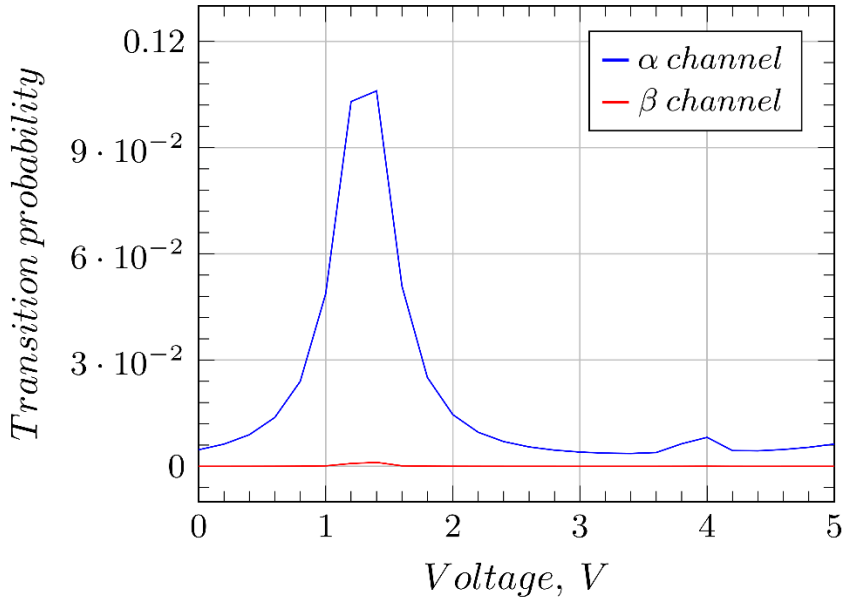


Рисунок 5. График рассчитанной вероятности прохождения электрона в зависимости от приложенной к электродам разности потенциалов для комплекса H-Cu-H

List of sources used

1. Y. Nakanishi, T. Matsui, Y. Kitagawa, Y. Shigeta, T. Saito, Y. Kataoka, T. Kawakami, M. Okumura, and K. Yamaguchi /Electron Conductivity in Modified Models of Artificial Metal DNA Using Green's Function-Based Elastic Scattering Theory // Bull. Chem. Soc. Jpn. Vol. 84, No. 4, 366–375 (2011).

2. Y. Nakanishi / Development and applications of electron conductivity calculation method for open-shell molecules // Ph.D. Thesises, 2011, 129 p.

3. https://www.gnu.org/software/gsl/doc/html/integration.html

4. https://arma.sourceforge.net/