Lab Exercise II : Huckel-IV

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• Brief Description of Huckel-IV
• Huckel-IV on the Hub
• Exercises
• Few words on Huckel-IV codes
Brief Description of Huckel-IV

Huckel-IV is a simple semi-empirical model for molecular conduction which can be run from the hub

Main features of Huckel-IV are:

• device is modeled by a semi-empirical method: Extended Huckel Theory (EHT)

• Contact is also modeled by EHT and Self energy for the contact is calculated exactly

• System modeled is: gold contact- single molecule-gold contact where the gold surface is in 111 direction

• Model only two terminal device. No gate.
• Potential profile inside the molecule is assumed of following shape:

![Diagram of potential profile]

• Two options are provided to the users for the potential calculation: (1) to specify \( \eta \) as a constant and (2) to specify a charging energy \( U_0 \) and let the program calculate \( \eta(V) \) self-consistently at each bias.
Brief Description of Huckel-IV

• Potential profile inside molecule is assumed flat in both cases

• The equilibrium Fermi energy \( (E_F) \) is treated as a fitting parameter

• The contacts are assumed to have a constant density of states in the energy range of interest

• Structural changes of the molecule under bias are not considered

• A Buttiker type probe is included to simplify calculations

For detailed discussion of the theory of Huckel-IV see:

Ferdows Zahid, Magnus Paulsson and Supriyo Datta,
* This article can be obtained from the Huckel-IV main page.
Huckel-IV on the Hub

Huckel-IV is available on Hub

To access Huckel-IV on hub go to: http://nanohub.purdue.edu
and then select ‘Hucke-IV 2.0’

Running a Huckel-IV simulation consists of three stages:

1. Input Stage
2. Execute Stage
3. Output Stage

In the following slides these stages will be briefly discussed

(For more details see the Manual on Huckel-IV main page)
Huckel-IV on the Hub: Main Page

Huckel-IV-Related Information

- Description
- First Time User's Guide
- Manual
- Theory of Molecular Conduction
- Source
- Questions
- Run Status

Run Huckel-IV

1. Modify/Create Huckel-IV Input Files
2. Execute Huckel-IV
3. View/Download Huckel-IV Output Files
Huckel-IV on the Hub: Input Stage

• In this stage users will define a coordinate file from the Input page.

• Only input required for Huckel-IV is the coordinate file of the molecule.

• This coordinate file will specify the structure of the molecule of interest.

• This coordinate file should be in ‘XYZ’ format and oriented in proper direction.

• Some of the coordinate files can be obtained from the example folder in Huckel-IV Input page.

• For other systems users have to generate their own coordinate files using any Chemistry software.
Huckel-IV on the Hub: Input Stage

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>X coordinate values</th>
<th>Y coordinate values</th>
<th>Z coordinate values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.251197</td>
<td>-3.416196</td>
<td>.000000</td>
</tr>
<tr>
<td>16</td>
<td>.079083</td>
<td>-3.194823</td>
<td>.000000</td>
</tr>
<tr>
<td>6</td>
<td>-.001287</td>
<td>-1.408464</td>
<td>.000000</td>
</tr>
<tr>
<td>1</td>
<td>2.152491</td>
<td>-1.227666</td>
<td>.000000</td>
</tr>
<tr>
<td>1</td>
<td>-2.156143</td>
<td>-1.223829</td>
<td>.000000</td>
</tr>
<tr>
<td>6</td>
<td>1.205002</td>
<td>-.695624</td>
<td>.000000</td>
</tr>
<tr>
<td>6</td>
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<td>-1.205687</td>
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<tr>
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<tr>
<td>1</td>
<td>-1.251173</td>
<td>3.415059</td>
<td>.000000</td>
</tr>
</tbody>
</table>

Example of a coordinate file
Huckel-IV: Input

1. Select one of the commands from the categories a, b, c, d, or e.

   a. Edit File OR Open Folder  
      Delete File OR Folder       
      Download File to Your Disk

   b. Create New File  
      Create New Sub-Folder

   c. Go To Examples Folder

   d. commands typed here override the check-box selections above.

   e. Upload file (overrides selections a–d above).

2. Execute the selected command.
**Huckel-IV on the Hub: Execute Stage**

- In this stage users will run specific simulation by choosing the desired options and parameters in the Execute page.

- Five different tasks can be performed.

- Task one is independent. Task two has to perform first to do the other three tasks.

- Task two is: Build Density of States (DOS) and Transmission Data Files. In this step a data file named ‘Dos_TE.mat’ will be generated. This data file is used for all the calculations for equilibrium and non-equilibrium properties. [As generating this file is time-consuming (10 minutes to one hour) we will use previously generated ‘Dos_TE.mat’ file for all the calculations in ‘Exercise’ section]

- Details of the steps in Execute page will be discussed in the ‘Exercise’ section with some examples.
Huckel-IV on the Hub: Execute Page

Huckel-IV: Execute

Hub Directory | Huckel-IV | Step 1: Input | Step 2: Execute | Step 3: Output

Help for Step 2: Execute | User: molecule

Select Task
- Calculate Energy Levels of Neutral Molecule
- Build Density of States (DOS) and Transmission Data Files
- Calculate Equilibrium Properties
- Calculate Non-Equilibrium Properties (Non-Self-Consistent Method)
- Calculate Non-Equilibrium Properties (Self-Consistent Method)

Next

Hub Directory | Huckel-IV | Step 1: Input | Step 2: Execute | Step 3: Output
• In this stage users will view the results and plots generated in Execute Stage

• Plots can be generated in both postscript and GIF format

• From the data files users can generate their own plots

• A brief description of all the output data files and plots are given in the ‘Readme’ file in the Output page
**Huckel-IV on the Hub: Output Page**

**Huckel-IV: Output**

<table>
<thead>
<tr>
<th></th>
<th>View File OR Open Folder</th>
<th>Delete File OR Folder</th>
<th>Download File to Your Disk</th>
<th>File Type:</th>
<th>Working Folder Will Not Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
<td>Auto</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>Go To Examples Folder</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. **Select** one of the commands from the categories a, b, or c.

2. **Execute** the selected command.

_**Commands**_ typed here _over-ride_ the check-box selections above.

Execute the Command
Exercises

We will perform the following exercises:

- **Exercise-1: To obtain energy levels of neutral phenyl dithiol (PDT)**
  (Purpose of this exercise is to learn how to get the energy levels of neutral molecule)

- **Exercise-2: To calculate total Density of States (DOS), Transmission (T) and Charge Neutrality level ($E_{cnl}$) for PDT connected to two gold contacts**
  (Purpose of this exercise is to see how the contacts affect the energy levels and other properties of a molecule)

- **Exercise-3: To calculate the I-V characteristics of PDT with symmetric coupling**
  (Purpose of this exercise is to see the effect of ‘charging’ in the I-V characteristics)

- **Exercise-4: To calculate the I-V characteristics of PDT with asymmetric coupling**
  (Purpose of this exercise is to see the effect of asymmetric coupling in the I-V characteristics)

- **Exercise-5: To calculate the I-V characteristics of Quantum point contact (QPC)**
  (Purpose of this exercise is to see whether we are getting correct result for quantized conductance)
Exercises: Systems

Neutral PDT

PDT connected to gold contacts

QPC connected to gold contacts
Exercise -1 : Procedure

• First upload the coordinate file of neutral PDT from the example folder in Input page (copy the file pdt.dat from pdt directory)

• Next go to main Execute page and select ‘Calculate Energy Levels of Neutral Molecule’

• From ‘Calculate Energy Levels of Neutral Molecule’ page select the correct coordinate file and then put all other parameter values on the blank space correctly (parameter values can be obtained from the README file in example folder in Input page)

• Next push Calculate Energy Level button

• In the ‘Program Status’ page keep pushing Proceed button until it says ‘No Programs Executing’. It will take 20 to 30 seconds to finish.

• Then go to the Output page and view Elevels.gif file
Exercise -1 : Procedure

Huckel-IV: Execute

Calculate Energy Levels of Neutral Molecule

Coordinate File:  pdl.dat

Total Number of Electrons:  42

Plot Format(s)  (if any)
- GIF  (Graphic Interchange Format)
- PDF  (Portable Document Format)
- PS  (PostScript)

Output Folder:  pdt

Calculate Energy Level
Exercise -1 : Output

Energy Levels of the Neutral Molecule

HOMO = -1.7 eV
LUMO = -8.3 eV
HOMO-LUMO gap (HLG) = 3.4 eV
Exercise -2 : Procedure

• First upload the Dos_TE.mat file for PDT from the example folder in Output page (copy the file from pdt directory)

• Next go to main Execute page and select ‘Calculate Equilibrium Properties’

• From ‘Calculate Equilibrium Properties’ page select the Dos_TE.mat file and then put all other parameter values on the blank space correctly (parameter values can be obtained from the README file in example folder of Input page)

• Next push Calculate Properties button

• In the ‘Program Status’ page keep pushing Proceed button until it says ‘No Programs Executing’. It will take 60 to 80 seconds to finish.

• Then go to the Output page and view DOS.gif, TE.gif and E_cnl.gif files
Exercise -2 : Procedure

Calculate Equilibrium Properties

**DOS and Transmission Data File:** Dos_TE.mat

(from prior step)

**Calculate Properties**

☑ Charge Neutrality Level

☑ Transmission and Density of States

Energy Grid

<table>
<thead>
<tr>
<th>E min</th>
<th>E max</th>
<th>dE</th>
</tr>
</thead>
<tbody>
<tr>
<td>-14</td>
<td>-6</td>
<td>15e-3</td>
</tr>
</tbody>
</table>

**Plot Format(s) (if any)**

☑ GIF (Graphic Interchange Format)

☐ PDF (Portable Document Format)

☐ PS (PostScript)

**Output Folder:** pdt

[Calculate Properties]
Exercise -2 : Output

\[ E_{c}^{nl} = -1.08 \text{ eV} \]
Exercise -3 : Procedure

• First upload the Dos_TE.mat file for PDT from the example folder in Output page (this file is already uploaded in the previous step)

• Next go to main Execute page and select ‘Calculate Non-Equilibrium Properties (Non-Self-Consistent Method)’

• From ‘Calculate Non-Equilibrium Properties (Non-Self-Consistent Method)’ page select the Dos_TE.mat file and then put all other parameter values on the blank space correctly (parameter values can be obtained from the README file in example folder of Input page) and push Calculate Properties button

• In the ‘Program Status’ page keep pushing Proceed button until it says ‘No Programs Executing’. It will take 1 to 3 minutes to finish.

• Then follow the same procedure from the ‘Calculate Non-Equilibrium Properties (Self-Consistent Method)’ page to do the self-consistent calculation

• Then go to the Output page and view gv_eta.gif and gv_scf.gif files
Exercise -3 : Procedure

Calculate Non-Equilibrium Properties (Non-Self-Consistent Method)

DOS and Transmission Data File: Dos_IE.dat
(from prior step)

Equilibrium Fermi Level, E_f
Voltage Division Factor:
Voltage Grid
  V min:
  V max:
Bias Points, NV:

Plot Format(s) (if any)
✔ GIF (Graphic Interchange Format)
□ PDF (Portable Document Format)
□ PS (PostScript)

Output Folder: pdt

Calculate Properties
Exercise -3 : Procedure

Calculate Non-Equilibrium Properties (Self-Consistent Method)

DOS and Transmission Data File: Dos_TE.mat

(from prior step)

Equilibrium Fermi Level, E_f: -11.0
Charging Energy, U_0: 2.0
Number of Electrons, N_eq: 40

Voltage Grid
V_min: -4
V_max: 4
Bias Points, NV: 20

Convergence Parameters
Number of Iterations: 200
Convergence Factor: 1e-3
Damping: 0.05

Plot Format(s) (if any)
- GIF (Graphic Interchange Format)
- PDF (Portable Document Format)
- PS (PostScript)

Output Folder: pdt
Exercise -3 : Output

G-V Plot Using Eta Theory

G-V plot using SCF method
**Exercise -4 : Procedure**

- First upload the Dos_TE.mat file for PDT for asymmetric coupling from the example folder in Output page (this file is already created using Left Coupling Factor = 1 and Right Coupling Factor = 0.6). Copy the file from pdt_asym directory.

- Next go to main Execute page and select ‘Calculate Non-Equilibrium Properties (Self-Consistent Method)’

- From ‘Calculate Non-Equilibrium Properties (Self-Consistent Method)’ page select the Dos_TE.mat file and then put all other parameter values on the blank space correctly (parameter values can be obtained from the README file in example folder of Input page) and push **Calculate Properties** button

- In the ‘Program Status’ page keep pushing **Proceed** button until it says ‘No Programs Executing’. It will take 1 to 3 minutes to finish.

- Then go to the Output page and view gv_scf.gif file
### Exercise -4 : Procedure

**Calculate Non-Equilibrium Properties (Self-Consistent Method)**

**DOS and Transmission Data File:** Dos_TE.mat

**(from prior step)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Fermi Level, E_f</td>
<td>-10.5</td>
</tr>
<tr>
<td>Charging Energy, U_0</td>
<td>2.0</td>
</tr>
<tr>
<td>Number of Electrons, N_eq</td>
<td>40</td>
</tr>
</tbody>
</table>

**Voltage Grid**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_min</td>
<td>-4</td>
</tr>
<tr>
<td>V_max</td>
<td>4</td>
</tr>
<tr>
<td>Bias Points, NV</td>
<td>20</td>
</tr>
</tbody>
</table>

**Convergence Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Iterations</td>
<td>200</td>
</tr>
<tr>
<td>Convergence Factor</td>
<td>1e-3</td>
</tr>
<tr>
<td>Damping</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Plot Format(s) (if any)**

- [x] GIF (Graphic Interchange Format)
- [ ] PDF (Portable Document Format)
- [ ] PS (PostScript)

**Output Folder:** pdt_asym
Exercise -4 : Output

G-V plot using SCF method

![Graph showing the derivative of the conductance with respect to voltage (dI/dV) against applied bias (V).](image)
Exercise -5 : Procedure

• First upload the Dos_TE.mat file for QPC from the example folder in Output page (copy the file from qpc directory)

• Next go to main Execute page and select ‘Calculate Non-Equilibrium Properties (Self-Consistent Method)’

• From ‘Calculate Non-Equilibrium Properties (Self-Consistent Method)’ page select the Dos_TE.mat file and then put all other parameter values on the blank space correctly (parameter values can be obtained from the README file in example folder of Input page) and push Calculate Properties button

• In the ‘Program Status’ page keep pushing Proceed button until it says ‘No Programs Executing’. It will take 1 to 3 minutes to finish.

• Then go to the Output page and view iv_scf.gif file
### Exercise -5 : Procedure

Calculate Non-Equilibrium Properties (Self-Consistent Method)

**DOS and Transmission Data File:** Dos_TE.mat

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Fermi Level, ( E_f )</td>
<td>-10.5</td>
</tr>
<tr>
<td>Charging Energy, ( U_0 )</td>
<td>2.0</td>
</tr>
<tr>
<td>Number of Electrons, ( N_{eq} )</td>
<td>66</td>
</tr>
</tbody>
</table>

**Voltage Grid**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{min} )</td>
<td>-1</td>
</tr>
<tr>
<td>( V_{max} )</td>
<td>1</td>
</tr>
<tr>
<td>Bias Points, ( NV )</td>
<td>20</td>
</tr>
</tbody>
</table>

**Convergence Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Iterations</td>
<td>200</td>
</tr>
<tr>
<td>Convergence Factor, ( \epsilon )</td>
<td>1e-3</td>
</tr>
<tr>
<td>Damping</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Plot Format(s) (if any)**

- [x] GIF (Graphic Interchange Format)
- [x] PDF (Portable Document Format)
- [x] PS (PostScript)

**Output Folder:** qpc

[Calculate Properties]
The quantized conductance is around 75 μA/V
### Exercise - Extra

**Huckel-IV: Execute**

[Hub Directory] [Huckel-IV] [Step 1: Input] [Step 2: Execute] [Step 3: Output]

**Help** for Step 2: Execute | User: molecule

#### Build Density of States (DOS) and Transmission Data Files

**Coordinate File:**

<table>
<thead>
<tr>
<th>pdt_2H.dat</th>
</tr>
</thead>
</table>

**Position of End Atoms:**

<table>
<thead>
<tr>
<th>Left</th>
<th>Right</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
</tr>
</tbody>
</table>

**Pad Distance:**

| 1.905 | 1.905 |

**Coupling Factor:**

| 1 | 1 |

**Output Folder:**

| pdt |

[Build DOS and Transmission Data]
Few words on Huckel-IV codes

- All the codes of Huckel-IV are MATLAB codes except one

- Huckel.c is a C code which calculates the Hamiltonian and Overlap matrices using EHT

- Source codes of Huckel-IV can be downloaded from the main page of Huckel-IV on the hub

- All codes are documented and easy to understand