

# ecoupling server: A tool to compute and analyze electronic couplings

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Electron transfer processes are often studied through the evaluation and analysis of the electronic coupling (EC). Since most standard QM codes do not provide readily such a measure, additional and user-friendly tools to compute and analyze electronic coupling from external wave functions will be of high value. The first server to provide a friendly interface for evaluation and analysis of electronic couplings under two different approximations (FDC and GMH) is presented in this communication. Ecoupling server accepts inputs from common QM and QM/MM software and provides useful plots to understand and analyze the results easily. The web server has been implemented in CGI-python using Apache and it is accessible at <http://ecouplingserver.bsc.es>. Ecoupling server is free and open to all users without login.

## Introduction

Electron transfer (ET) reactions are fundamental processes involved in most biological phenomena<sup>1</sup> including oxidation<sup>2</sup>, photosynthesis<sup>3</sup> or DNA processes<sup>4</sup> and also in industrial applications as enzymatic reactions<sup>5</sup>, organic semiconductors<sup>6</sup>, solar cells<sup>7</sup>, molecular wires<sup>8</sup>, or biosensors<sup>9,10</sup>. For these, many efforts have been done experimentally and computationally to characterize ET processes<sup>11</sup>. In particular, computational (quantum) chemistry has gained importance in providing the electronic point of view required to understand ET reactions.

Theoretical rigorous studies aim at solving the ET rate constant from the Marcus equation<sup>12</sup>; all equation parameters, comprising reaction free energy, reorganization energy, and electronic coupling, are computationally accessible. However, quantitative modeling of this rate constant is not a trivial task, requiring a significant computational effort<sup>13</sup>. Instead, the electronic coupling (EC), which is proportional to the rate constant, is often used as an easier and faster way to study an ET reaction. In addition, EC is sensible to changes in the system such as geometry or temperature, resulting an excellent tool to evaluate modifications in a reaction<sup>14-17</sup> and thus, promising a useful instrument in protein engineering<sup>18-20</sup> and material design<sup>21-23</sup>.

Under the Marcus theory perspective<sup>1</sup>, ET takes place in the crossover of two adiabatic surfaces from donor and acceptor, respectively. For symmetric (or near-symmetric) systems, the coupling ( $H_{DA}$ ) could be defined as the half of the splitting energy at the seam between two adiabatic states. However, in complex biological systems (~weak electronic coupling regime), donor and acceptor are far from each other, the states are diabatic, and the

crossover is difficult to obtain. Hence, several approximations have been developed to calculate EC. Ones of the most popular and highly tested are the Generalization of Mulliken Hush (GMH)<sup>24</sup> and the Fragment Charge Difference (FCD)<sup>25</sup> approximations. In these methods, an extra operator is applied to get an orthogonal transformation of adiabatic states to diabatic states, which energies are readily obtained by quantum chemistry calculations.

However, most standard QM codes do not provide readily EC computation. Thus, additional and user-friendly tools to compute and analyze EC from external wave functions will be of high value. It would be also very convenient that these tools allow to handle with several calculations in a timely manner, to explore many conformations required for a realistic coupling values<sup>26,27</sup>. Therefore, we introduce in this communication the ecoupling server to perform EC calculations from the output of common QM and QM/MM software, and analyze the results in a handy manner.

## Methods

### GMH method

The operator employed in the GMH method is the adiabatic dipole moment matrix. The diabatic states are selected to be diagonal to a component of the dipole moment. Under this approximation, the coupling is calculated as:

$$H_{DA} = \frac{\Delta E_{12} \mu_{12}}{\sqrt{(\Delta \mu_1 - \Delta \mu_2)^2 + 4\mu_{12}^2}} \quad (1)$$

where  $\Delta E$  is the orbital energy difference  $\mu_1$   $\mu_2$  are the dipole moments of the diabatic states and  $\Delta \mu_{12}$  is the dipole moment difference of the diabatic states.

### FCD method

In FCD method the transformation is obtained by diagonalization of the charge difference matrix  $\Delta Q$ . In this approximation, diabatic states are selected diagonal to maximize the charge transferred from donor to acceptor (see, for example Miglore<sup>28</sup> for a deeper analysis on the validity of adiabatic-diabatic transformations). The coupling then could be defined as:

$$H_{DA} = \frac{\Delta E_{12} Q_{12}}{\sqrt{(\Delta Q_1 - \Delta Q_2)^2 + 4\Delta Q_{12}^2}} \quad (2)$$

where  $\Delta Q_{12}$  is the transition charge difference,  $\Delta Q_1$  and  $\Delta Q_2$  are the donor-acceptor charge differences for each adiabatic state (numbered as 1 and 2), and  $\Delta E_{12}$  is the energy difference between the orbitals involved (HOMO and HOMO-1 for hole transfer mechanism<sup>25</sup> and LUMO and LUMO+1 for electron transfer mechanism<sup>29</sup>).

### Multistate systems

In simple cases, ET can be reduced to the involvement of only two orbitals, located in the donor and acceptor. However in degenerate (or quasi-degenerate) situations, several orbitals might participate in the transfer, and a multistate treatment should be considered<sup>30-33</sup>. We adopted the solution provided by Voityuk<sup>34</sup> where the effective coupling ( $H_{\text{effDA}}^2$ ) is defined as:

$$(3) \quad H_{\text{effDA}}^2 = \frac{1}{N_1 N_2} \text{rms} H_{DA}^2$$

$$(4) \quad \text{rms} H_{DA} = \sqrt{\frac{1}{N_1 N_2} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} H_{ij}^2}$$

Where  $N_1$  and  $N_2$  are the numbers of degenerate (or quasi degenerate) orbitals placed on the donor (D) and the acceptor (A), respectively and  $\text{rms} H_{DA}^2$  is the root mean square of the electronic coupling for each donor-acceptor orbital combination (all consider):

### Bridge mediated electron transfer

Electron/hole transfer from donor to acceptor is sometimes mediated by an intermediate molecular orbital acting as an electron bridge. This phenomenon, called superexchange, is especially important in some physical and biological processes such as charge migration in DNA or long range ET in proteins. Thus, the effective bridge assisted electron coupling is defined as:

$$H_{DBA} = H_{DA} + H_{SE} \quad (5)$$

where  $H_{DA}$  is the electron coupling between donor and acceptor applied to the whole donor-bridge-acceptor system (inside the two state or multistate model), and  $H_{SE}$  is the superexchange term. The  $H_{SE}$  depends on the coupling between donor-bridge ( $H_{DB}$ ) and bridge-acceptor ( $H_{BA}$ ) and the energy barriers between orbitals ( $E_{DA}$  and  $E_{DB}$ ), following the formula:

$$H_{SE} = \frac{H_{DB} H_{BA}}{\Delta} \quad (6)$$

where :

$$\Delta = E_{DA} - \frac{E_{DB}}{2} \quad (7)$$

### Description of the web server

The coupling server allows users to calculate EC under the FCD or GMH approximations from simple donor-acceptor systems to more complex situations where multistate or bridges are involved<sup>32</sup>. It accepts as input file the output generated from five QM packages: Gaussian<sup>35</sup>, ORCA<sup>36</sup>, GAMESS<sup>37</sup>, Jaguar<sup>38</sup> and its QM/MM version Qsite<sup>39</sup>.

Tutorial section provides a full description, with detailed examples, for the input file preparation, and a brief theoretical explanation about the main concepts behind the FCD and GMH approximations (Panel A and B Figure S1). In addition, each submit section contain an automatic sample button with input files to test the server (Figure 1).

To perform an EC calculation, users must introduce the atoms selected as donors, acceptors and (optionally) the bridge involved in the reaction. Also, users must specify the nature of the orbital involved in the electron transfer (alpha or beta), computation approach, number of molecular orbitals per donor, acceptor and bridge and the minimum charge tolerance (to assign molecular orbitals to donor or acceptor fragments). To assist in the input generation, the server includes the 3D molecular orbital visualizer called JSMOL (Panel C Figure S1) to analyze the inputs in order to choose the right set of parameters.

Before the final submission, coupling server checks the inputs to detect spelling mistakes or missing information and generates a detailed report about the errors. The code has an error detection routine that provides a possible solution in the log file.

### Output and representation of results

In a successful EC calculation, coupling server generates a log file and four plots to analyze the results in few seconds.

The output file is divided into three sections: input summary, orbital information, and EC results. Input summary section summarizes the parameters submitted to perform the calculation. The orbital information provides a list of parameters parsed and

contains a table with the population and the total charge of each orbital considered for the evaluation. The last part, EC results, consist of a detailed list of EC values per orbital pairs involved in the calculation. At the end of the log file, the root mean squared of the EC ( $\text{rmsH}_{\text{DA}}$ ) and the average difference energy are printed (Panel D Figure S1).

Furthermore, ecoupling server provides four different plot types to analyze the results. The first plot comprises the orbital energy representation per each donor, acceptor and bridge orbital included in the calculation. In addition, as the charge is distributed in different orbitals, each bar is composed of blue, green and red depending on the donor, bridge and acceptor contribution, respectively. This plot allows the user to inspect the orbital characteristics, which are necessary to tune the charge tolerance. The second plot represents a population analysis using the area and color of circles to quantify the EC value obtained for each donor-bridge, bridge-acceptor or donor-acceptor pair involved in the calculation. Numbers correspond to the EC value per each pair. The third plot shows the same as the previous one using a 3D bar representation to enhance visualization. Last plot is the energy difference per orbital pair. Energy difference correlates with bar thickness, and its values are written at the top of each bar.

## Examples

Ecoupling server has been widely tested to compute EC using FCD, MSFCD, GMH and MSGMH methods. Along 2014 and 2015, it has been tested with more than 600 different inputs files and the final version was released on 4th of May 2015. Here, we present some examples used to validate the server.

### $\pi$ -stack dimer guanine-guanine

Our first test case is the widely studied hole transfer mechanism of the DNA Guanine-Guanine  $\pi$ -stacking base pairs, involved in DNA damage/repair processes<sup>42</sup>.

Three levels of theory (HF, B3LYP and MO6) have been computed and the coupling has been obtained under the FCD approximation into the two-state model (one orbital per redox site) with minimum charge tolerance equal to 0.89. Input files were prepared with Jaguar. The orbital analysis (Figure 2) shows HOMO mainly placed on the donor (red bar) with a small proportion of acceptor (blue bar) whereas the opposite situation is found for HOMO-1.

Table 1 shows the energy difference between the HOMO (assigned to donor) and HOMO-1 (acceptor), EC values computed with the ecoupling server and the published EC<sup>25,40,41</sup>. EC values computed with the ecoupling server are in agreement with the published results showing no representative differences ( $<10^{-3}$  eV).

### Multistate and bridge-mediated situation

In some systems, the electron/hole transference from donor to acceptor is mediated by a bridge. This phenomenon is especially important to describe some mechanisms, as long-range ET where coupling through a bridge leads to a rapid ET<sup>43-46</sup>.

To illustrate the possibilities that the ecoupling server offers, we analyzed the hole transfer in the small model cation guanine-thymine-guanine (GTG)<sup>47,48</sup>, where thymine is acting as a bridge (Figure 3 and S2). The system was optimized at the HF level of theory with 6-31g\* basis set using Jaguar. In this simple donor-bridge-acceptor model, with one electronic state per fragment, the EC using the FCD approximation enhances ( $1.69 \cdot 10^{-2}$  eV) compared with the simple donor-acceptor model ( $0.67 \cdot 10^{-2}$  eV), meaning that, in agreement with published data<sup>48</sup>, the bridge assists the hole transfer process.

Furthermore, orbitals close in energy might participate in the reaction and therefore, they cannot be neglected. A broad orbital analysis can be easily done using the ecoupling server. For example, by including many orbitals in a preliminary calculation we can quickly identify the key orbitals by visual inspection of the graphical results. Performing a properly selection is crucial for EC calculations.

Table 1. Orbital energy difference (eV) between HOMO and HOMO-1 and EC values (eV) for guanine-guanine in the two-state model.

Theory	Energy difference	EC (ecoupling server)	EC published
HF	-0.472	0.083	0.083 <sup>40</sup> 0.081 <sup>25</sup> 0.084 <sup>41</sup>
B3LYP	-0.413	0.069	0.070 <sup>40</sup>
MO6	-0.418	0.071	

In the previous example, for instance, a preliminary analysis of more orbitals (up to three for each fragment) shown that HOMO-3 from the donor is close to the lowest bridge orbital. Thus, including this orbital in the calculation ( $n_{\text{d}}=2$ ,  $n_{\text{a}}=1$ ,  $n_{\text{b}}=1$ ) increases the coupling to  $3.63 \cdot 10^{-2}$  eV. This example illustrates how ecoupling server is a powerful tool in analysis and calculation of EC values.

### Geometry influence. Semiconductor example

EC values depend on several factors like temperature, geometry or distance between donor-acceptor, which has direct applications, for instance, in material design.

Tetracene is an organic semiconductor employed in transistors and diodes where the conductivity is related to the distance and geometry between the aromatic rings. For this reason, EC values have been computed to find the optimal distance and geometry to pack the layers in the material<sup>6,49</sup>.

We computed the EC along a rigid scan distance between two tetracene subunits using B3LYP 6-31g\* and 6-31g\*\*. Then, the results were compared with published data<sup>6,49</sup> (Figure 4) and indicates the EC decays with the distance between donor and acceptor for all these cases.

## Conclusions

Decoupling server provides an easy and free way to compute and analyze EC values from QM calculations by parsing output files from the most used QM software. Moreover, the server outputs help users to analyze the results and the details of the system by visual inspection. The user-friendly interface reduces the number of possible mistakes checking the input parameters and detecting wrong values. Furthermore, theory and tutorial sections included in the server allow a quick start to obtain EC values.

As results have shown, EC depends on several parameters such as number of orbitals involved in the reaction, nature of the system or geometrical parameters. Furthermore, other many parameters have been reported as important for the coupling as temperature, pH, etc. Exploring all this possibilities could be interesting, for instance, in protein engineering or material design requiring a tool to quickly analyze and compute the value for all possibilities.

### Acknowledgments

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**Keywords:** electron coupling, electron transfer, FCD, GMH, Marcus theory.

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**Figure captions:**

*Figure 1. ecoupling server screenshot of the input tab.*

*Figure 2. Orbital energies and EC value for the guanine-guanine system provided by the ecoupling server. Donor/acceptor orbital character is represented in red and blue, respectively.*

*Figure 3. Graphical results from the ecoupling server for the GTG system in the multistate situation, considering two orbitals from donor and one for each acceptor, and bridge. Panel A, Orbital energies representation (eV). The EC values between donor (D or D2 in the multistate situation), acceptor (A) and bridge (B) is also shown for directed ( $H_{DA}$  in black) and mediated ( $H_{DBA}$  in green and  $H_{D(2)BA}$  in orange for multistate treatment) ET. Panel B, Direct ecoupling between acceptor and the two donor orbitals considered. Panel C, Energy difference between HOMO orbital pairs.*

*Figure 4. EC results according to the distance between two tetracene subunits in a two-state model. Red results from Kubas et al., 2014. Green points are the extrapolation from the equation*

$$V(r) = -0.0078 + \frac{697}{r^6} + \frac{0.3252}{r^{12}}$$

*published by Deng and Goddard, 2004. Blue and purple results were computed from Jaguar outputs using the FCD approximation with the ecoupling server.*

Figure 1

**eCS eCOUPLING SERVER**

HOME | JSMOL | JAGUAR/OSITE | GAUSSIAN | ORCA | GAMESS | THEORY | TUTORIALS | CONTACT

Select Gamess File (.out):  **GTG one strand B-DNA (HF/6-31g\*)**

Select Method to compute Electron Coupling:  FCD  GMH

Donor Residues: Write Atomic Numbers

Acceptor Residues: Write Atomic Numbers

Bridge Residues: Write Atomic Numbers

Choose orbital:

Choose Type of electron transfer:

Average Molecular Orbital:

DONORS:  ACCEPTORS:  BRIDGE:

Minimum charge tolerance:

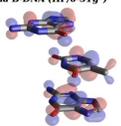


Figure 2

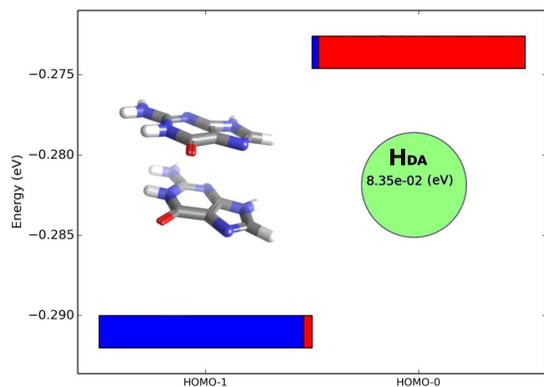


Figure 3

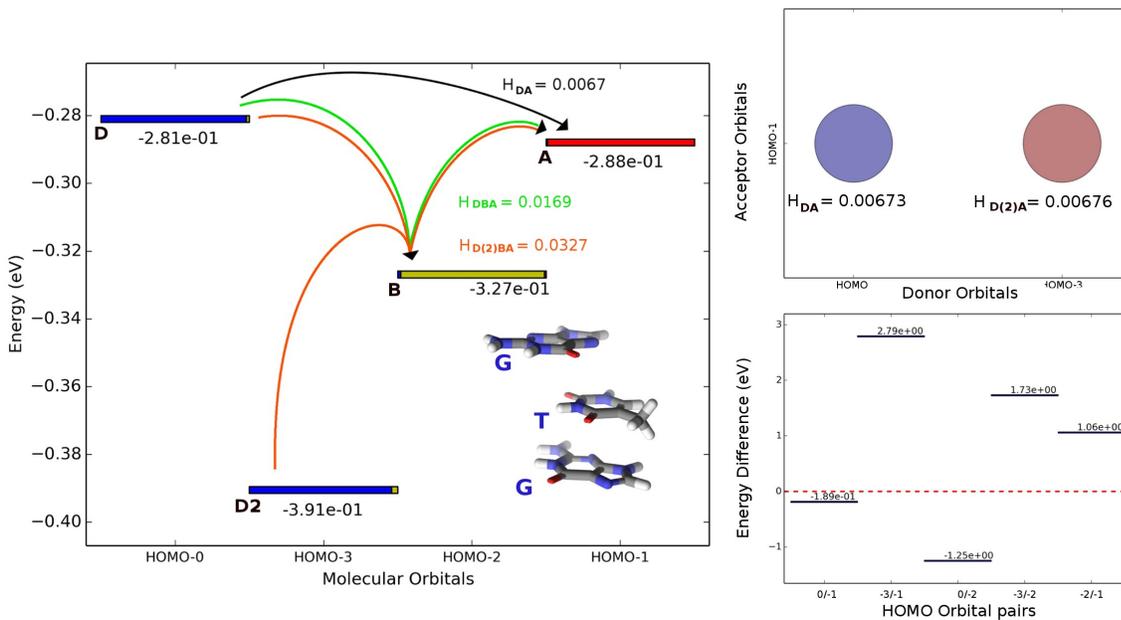


Figure 4

