INNOVATIVE INFOTECHNOLOGIES
FOR SCIENCE, BUSINESS AND EDUCATION

VILNIUS BUSINESS COLLEGE

NUVOLA: INTERMOLECULAR ELECTRON TRANSFER PROPERTIES USING QUANTUM CHEMISTRY APPROACH

Nurija Galikova*, Alytis Gruodis

Department of General Physics and Spectroscopy, University of Vilnius,
Saulėtekio al. 9, building 3, LT-10222 Vilnius, Lithuania

Received 14 January 2008, accepted 19 June 2008

Abstract. The project NUVOLA represents a new quantum chemistry tool based on the perturbation theory methods. The simulation of the dynamical processes between molecular aggregates using quantum chemistry approach is discussed and described. Using the Born-Oppenheimer assumption, the intermolecular electron transfer (IET) process was modeled based on the Fermi golden rule. The estimation of IET rate between two molecular systems could be allowed in frame of electronic charge redistribution between atomic orbitals, molecular orbitals, separate atoms, molecular fragments, donor and acceptor pairs. Quantitative IET processes can be analyzed in framework of energies as well as spatial charge redistribution.

Keywords: NUVOLA, intermolecular electron transfer, Fermi golden rule, Born-Oppenheimer assumption, one-particle approach.

Short title of the paper. NUVOLA: intermolecular electron transfer.

---

* *Corresponding author, e-mail: Nurija.Galikova@ff.vu.lt*

Introduction

Theoretical interpretation of the electronic properties of nanostructures and molecular clusters could be performed empirically (partially by laws of classical mechanics, low successful way) as well as semi-empirically or *ab-initio* (by means of several quantum mechanics approaches, high successful way). During the last decade, different simulations of molecular properties have allowed estimating the probable molecular structure and ground electronic state properties: molecular charge distribution, vibration frequencies, multipole/dipole/quadrupole moments etc. [1].

Our attempts are devoted to simulate the dynamical physical processes using quantum chemistry approach. Intermolecular electron transfer (IET) processes play an important role in the energy exchange between ordered molecular aggregates. Numerical publications dating back to the 1960s are devoted to the description the phenomena in general [2, 3]. An IET process can be presented in two following approaches:

i) empirical mechanistic model (spatial shift of electron as particle);
ii) wave interaction model (coupling of corresponding waves representing electron behaviour).

The mechanistic description of an IET process which expresses the movement of an electron between two separated molecular systems (MS) during redox reactions could be expanded two electron exchange formalism [4, 5]. An IET process can be named as the fundamental in understanding basic principles of complicated biological and biochemical reactions [6]. A quantum chemistry approach as a semi empirical or ab-initio approach could be titled as the universal approach for modelling the IET reactions independently from the object origin [7, 8].

This work is devoted to present the project NUVOLA [9] – a quantum chemistry tool based on the perturbation theory methods – and to outline the most relevant mathematical problems as well as presumable solutions of IET rate computing.

1. Fermi Golden rule

Let us assume the existence of two separated molecular systems MS-1 and MS-2 as presented in the Fig.1. IET reactions between MS-1 and MS-2 are estimated in the framework of the electronic charge redistribution between two charge-donor and charge-acceptor molecules according to the Mulliken model.

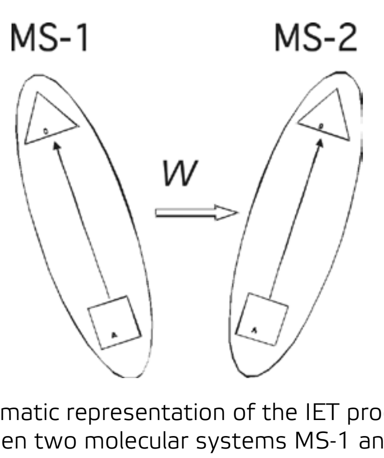

Fig.1. Schematic representation of the IET process (ratio *W*) between two molecular systems MS-1 and MS−2. Molecular system consist conditionally of charge donor D and charge acceptor A parts.

We will use the Born-Oppenheimer assumption, so the wave-functions α and β representing the behaviour of the systems MS-1 and MS-2, respectively, could be described using two separated factorized parts: electronic and nuclear. The calculation of IET rate is based on the Markus theory [10] and the well-known equation called Fermi Golden rule [11], which expresses the resonant process between two electronic states (state energy E_α and E_β, respectively) of the space-separated objects:

$$W_{\alpha\beta} = \frac{2\pi}{\hbar} S^2_{\alpha\beta} \delta\left(E_\alpha - E_\beta\right). \tag{1}$$

Intermolecular electronic coupling $S_{\alpha\beta}$ could be presented using the Dirac notation as interaction of two wave-functions $_\alpha$ and $_\beta$, belonging to the MS-1 and MS-2, respectively.

$$S_{\alpha\beta} = \left\langle \alpha \middle| V_{\alpha\beta} \middle| \beta \right\rangle, \tag{2}$$

where $V_{\alpha\beta}$ represents the matrix element of intermolecular interactions between such two MS. δ-function plays the key role in order to determine the strong resonant condition:

$$\int_{-\infty}^{+\infty} \delta(x)dx = 1 \,. \tag{3}$$

Total transition rate W will be expressed using Eq.(4):

$$W = \frac{2\pi}{\hbar} \sum_{\alpha,\beta} \left\langle \alpha \middle| V_{\alpha\beta} \middle| \beta \right\rangle^2 \delta\left(E_\alpha - E_\beta\right) \,. \tag{4}$$

Fig. 2 represents the energetic scheme of the IET process between two electronic states (labeled *initial* (i) and *final* (f)), where the state energy is denoted as $E_{i\alpha}$ and $E_{j\beta}$. These two states belong to separated MS – MS-1α and MS-2β, respectively. Further, we will operate in the terms of molecular electrons. Each electronic state is restricted by the Pauli principle, which allows only two molecular electrons with opposite spins in one state. The mechanism of IET supposes electron excitation from an occupied to a suitable unoccupied molecular orbital (MO), and then IET is permissible in case of an electronic overlap between two electronic states of molecules.

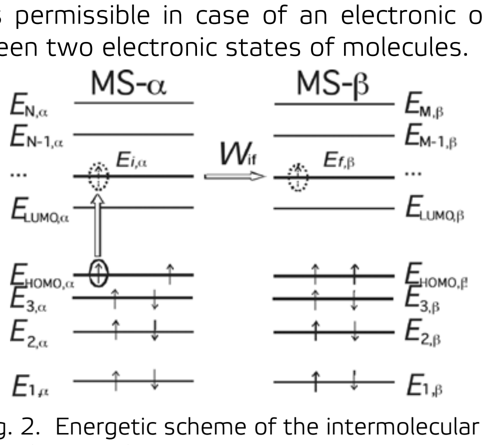

Fig. 2. Energetic scheme of the intermolecular ET process (ratio W_{12}) between two electronic states $E_{i\alpha}$ and $E_{j\beta}$, belonging to the separated molecular system MS-1α and MS−2β, respectively.

A simulated process could be described as follows:

i) one-electron excitation in the MS-1, from HOMO and lower state to LUMO and higher state;
ii) deactivation of excited state in backward-way (this process is not important in this case);
iii) repeatable interaction between corresponding electronic states of different MS (transition rate W_{if}).

Probability of IET (or transfer rate) is linearly proportional to the square of electronic overlap coefficient of corresponding molecular orbitals. As a result, the highest probability peaks of the IET spectrum belong to the states with equal energy called *resonant states*.

In the cases where the presented equation is not convenient for routine calculation, we offer a noticeably simplified form:

$$W_{\mathrm{if}} = \frac{2\pi}{\hbar} E_{\mathrm{if}}^2 S_{\mathrm{if}}^2 \delta\left(E_{\mathrm{i}} - E_{\mathrm{f}}\right), \tag{5}$$

where Eif represents the excited state energy, S_{if} – dimensionless coupling between two electronic states. We have used a dumped resonant condition using the well-known Gauss functions through the selected value σ which represents the half width at half-maximum (HWHM):

$$\delta\left(E_{\mathrm{i}} - E_{\mathrm{f}}\right) \Rightarrow \frac{1}{2\pi\sigma} \exp\left(-\frac{\left(E_{\mathrm{i}} - E_{\mathrm{f}}\right)^2}{2\sigma^2}\right). \tag{6}$$

The detailed description of the calculation routine and derivation of Eq. (5) are presented in Ref. [12]. The advanced IET process simulation between ordered molecular aggregates is presented in Ref. [13].

2. Hardware and software

NUVOLA can be run on a variety of UNIX operating systems. It supports the *OS LINUX FEDORA 4* on LINUX workstation (machine-independent 32 or 64 version). The programs are written in *C++*. All floating-point computations are performed in precision of 64-bits. Standard compiler *gcc* was used without additional libraries.

3. Realization of algorithm

The project *NUVOLA* is a quantum chemistry tool for the IET rate calculation, which handles *Gaussian'03* [14] program package as a contributory tool. Several sets of molecular orbitals (MO) of investigating molecules are required, which could be taken from output files of the mentioned programs. The requested data (the spatial positions of atoms of both MS) is transformed into three files.

NUVOLA contains three operational components called *links*. *C*++ code is written in object-oriented programming manner. Portability of *NUVOLA* (between Windows-XP and many Linux operating systems such as *FEDORA 4*, *SCIENTIFIC LINUX, REDHAT9 etc.*) was accomplished in a special way of the re-switching of advanced libraries. According to the *Gaussian'03* user license, any part of the *Gaussian-03* can be included in any programming object. When the reference is made to *NUVOLA*, the Gaussian–3 task is not integrated info the *NUVOLA* content.

The main scheme of *NUVOLA* is presented as follows. Fig. 3 represents the principal scheme of *NUVOLA*, where all the thfee logical prts are presented. The original modules P81, *GAUSSIAN* and *P83* operate using advanced script system. According to the *INPUT* request, the P81 link responsible for generating starting files and scripts in order to run the *Gaussian'03* package out of the *NUVOLA* contest. *Gaussian'03* produces the matrixes of eigenvalues and eigenvectors of the separated molecules and the density matrix of the joint molecule. The *GAUSSIAN* link is used for the intermediate data reading and distributing in the memory. The *P83* link is intended for resulting the data calculation as multipurpose *OUTPUT*. The inter-modular data exchange was implemented through intermediate file system. As well, the system of control output was (realized) established for each link.

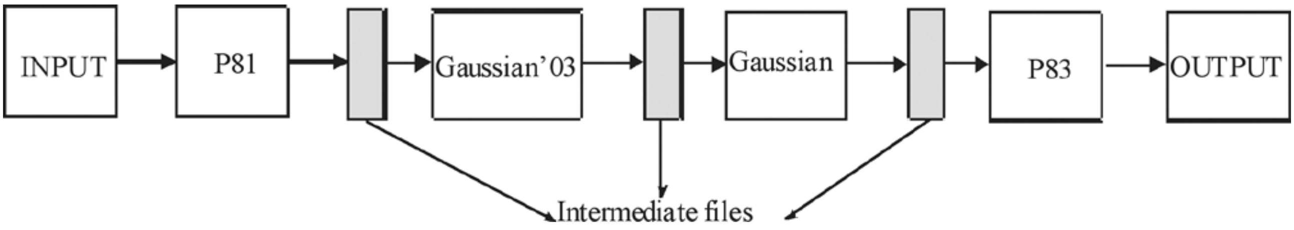

Fig 3. Principal scheme of *NUVOLA*

The *INPUT* conception was accomplished through the keyword managing system. The structure of the starting file (named conditionally as *NAME.kkk*) is presented in Fig.4. A convenient structural file indicates all features of each calculation object (MS-1 and MS-2) and operation. *NAME.kkk* is the only file which has to be made by the user. It presents a strictly determined structure, namely:

i) particular keywords handling the program;
ii) two matrixes containing structural positions of atoms in MS.

Two different styles are allowed: Z-matrix as well as Cartesian matrix. Unfortunately, combining these two styles in one **.kkk* file is not allowed. Depending on the required accuracy of further calculations in the *Gaussian'03* programs, appropriate keyword values have to be selected.

NUVOLA's KEYWORDS
Blank line
TITLE LINE
Blank line
Z-matrix or cartesian matrix of MS-1
Z-matrix or cartesian matrix of MS-2

Fig 4. Structure of *NAME.kkk* file

Fig. 5 represents the detail scheme of the P81 link. Starting from the request from the file *NAME.kkk,* preparation of several *Gaussian-03* input files (*NAME123.gjf*, *NAME234.gjf* and *NAME345.gjf* and corresponding batch file *NAME.bcf*) was done in this part, including formal verification of molecular structure and formal creation of several working scripts. The *P81* link also generates several additional input files for data handling and visual control purposes, namely:

i) *NAME.yes* - for next modules *GAUSSIAN* and *P83*;
ii) *NAME.ent* according *HYPERCHEM* standard;
iii) *NAME.mol* according *DALTON* standard.

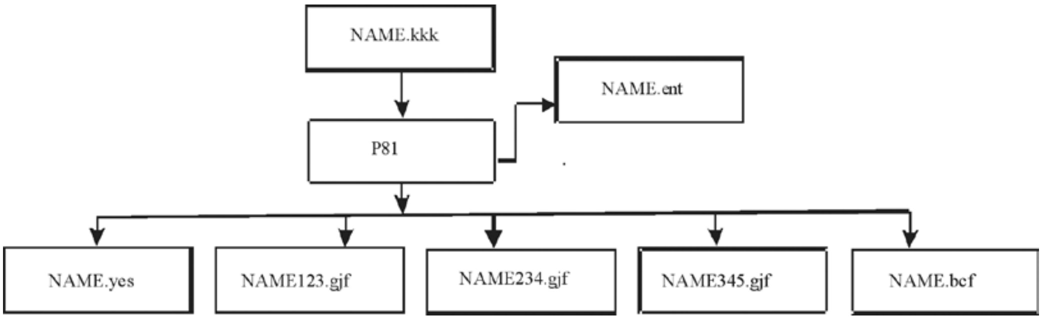

Fig. 5. Detail scheme of *NUVOLA*: *P81* link

First, let us consider the two interacting molecules. According to the general formulation of a physical task, formal decomposition of a physical object has to be accomplished. The atoms of three formal MS – MS-1, MS-2 and joint MS-12 presented in the associated coordinate system will be used (corresponds to *NAME123.gjf*, *NAME234.gjf* and *NAME345.gjf*).

Second, the ab-initio Hartree-Fock (HF) method or the electron correlation method (MP2, MP4) as well as the corresponding basis set (simple STO-3G or more appropriate 6-311G) have to be selected according to the model of a physical task. The polarization functions (from d,p up to 3df, 3pd) as well as diffusion functions for hard atoms can be included due to physical model properties. The full distribution of state population has to be output. For achieving the required result, a standard command line to run a *Gaussian03* task for all three MS should be written as follows:

```
#P HF/6-311G(3df,3pd) pop=full sp
```
(7)

Fig. 6. represents the scheme of file handling in *Gaussian'03*. Depending on the request placed in command line, three single point (SP) jobs will be provided using batch script *NAME.bcf*. After the data-processing, we receive two text-type files *NAME123.out*, *NAME234.out* and one binary-packed file *NAME345.chk*. Then *NAME345.chk* has be converted using the *Gaussian'03* standard utility FormChk from the binary to text-formatted *NAME345.fch* file.

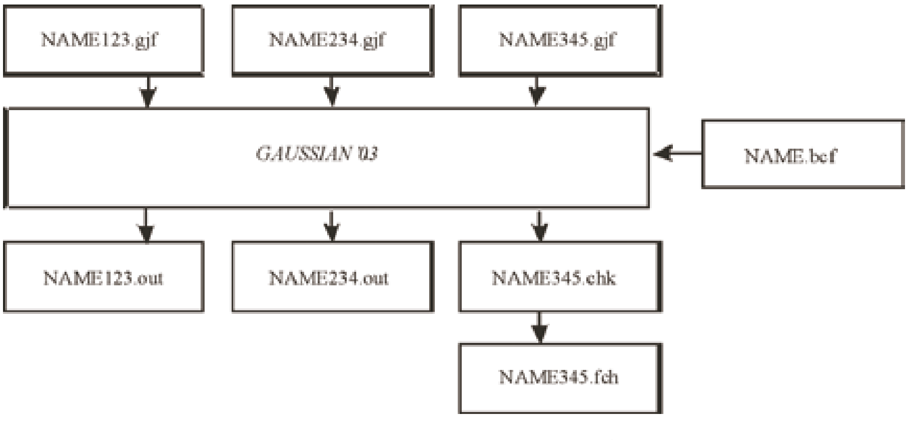

Fig. 6. File handling in *Gaussian'03*

The values of main parameters of each electronic system (eigenenergies and eigenvectors of *MS-1* and *MS-2*) were presented in the output files *NAME123.out*, *NAME234.out*. Eigenfunctions $e_{1\alpha}$, $e_{2\beta}$ are constructed as

$$e_{1\alpha} = \sum_{i=1}^{N} C_{\alpha i}\varphi_{1i} , \qquad (8)$$

$$e_{2\beta} = \sum_{k=1}^{M} C_{\beta k}\varphi_{2k} , \qquad (9)$$

where index 1, 2 denotes the number of interacting MS, and index α, β denotes the molecular orbital, which correspond to the state number. The electronic state α belongs to MS-1 and β belongs to MS-2, respectively. The values φ_1 and φ_2 express atomic orbits of the MS-1 and MS-2, and coefficients C_α , C_β corresponds to the eigenvectors of the MS-1 and MS-2, respectively (see table 1).

Table 1. Eigenvalues E as molecular orbitals (MO) and corresponding eigenvectors φ as atomic orbits (AO) of MS-α and MS-β

Two molecular systems - MS			
MS-1α		MS−2β	
Eigenvectors, AO, related to MS-α	Eigenvalue, MO of MS-α	Eigenvalue, MO of MS-β	Eigenvectors, AO, related to MS-β
N-number of particles of MS-α		M-number of particles of MS-β	
$\varphi^{1}_{N,\alpha}\varphi^{2}_{N,\alpha}\varphi^{3}_{N,\alpha}\cdots\varphi^{N}_{N,\alpha}$	$E_{N,\alpha}$	$E_{M,\beta}$	$\varphi^{1}_{M,\beta}\varphi^{2}_{M,\beta}\varphi^{3}_{M,\beta}\cdots\varphi^{M}_{M,\beta}$
$\varphi^{1}_{N-1,\alpha}\varphi^{2}_{N-1,\alpha}\varphi^{3}_{N-1,\alpha}\cdots\varphi^{N}_{N-1,\alpha}$	$E_{N-1,\alpha}$	$E_{M-1,\beta}$	$\varphi^{1}_{M-1,\beta}\varphi^{2}_{M-1,\beta}\varphi^{3}_{M-1,\beta}\cdots\varphi^{M}_{M-1,\beta}$
…	…	…	
$\varphi^{1}_{L,\alpha}\varphi^{2}_{L,\alpha}\varphi^{3}_{L,\alpha}\cdots\varphi^{N}_{L,\alpha}$	$E_{LUMO,\alpha}$	$E_{LUMO,\beta}$	$\varphi^{1}_{L,\beta}\varphi^{2}_{L,\beta}\varphi^{3}_{L,\beta}\cdots\varphi^{M}_{L,\beta}$
$\varphi^{1}_{H,\alpha}\varphi^{2}_{H,\alpha}\varphi^{3}_{H,\alpha}\cdots\varphi^{N}_{H,\alpha}$	$E_{HOMO,\alpha}$	$E_{HOMO,\beta}$	$\varphi^{1}_{H,\beta}\varphi^{2}_{H,\beta}\varphi^{3}_{H,\beta}\cdots\varphi^{M}_{H,\beta}$
…	…	…	
$\varphi^{1}_{3,\alpha}\varphi^{2}_{3,\alpha}\varphi^{3}_{3,\alpha}\cdots\varphi^{N}_{3,\alpha}$	$E_{3,\alpha}$	$E_{3,\beta}$	$\varphi^{1}_{3,\beta}\varphi^{2}_{3,\beta}\varphi^{3}_{3,\beta}\cdots\varphi^{M}_{3,\beta}$
$\varphi^{1}_{2,\alpha}\varphi^{2}_{2,\alpha}\varphi^{3}_{2,\alpha}\cdots\varphi^{N}_{2,\alpha}$	$E_{2,\alpha}$	$E_{2,\beta}$	$\varphi^{1}_{2,\beta}\varphi^{2}_{2,\beta}\varphi^{3}_{2,\beta}\cdots\varphi^{M}_{2,\beta}$
$\varphi^{1}_{1,\alpha}\varphi^{2}_{1,\alpha}\varphi^{3}_{1,\alpha}\cdots\varphi^{N}_{1,\alpha}$	$E_{1,\alpha}$	$E_{1,\beta}$	$\varphi^{1}_{1,\beta}\varphi^{2}_{1,\beta}\varphi^{3}_{1,\beta}\cdots\varphi^{M}_{1,\beta}$

The values of the main parameters of the joint electronic system (density matrix of MS-12) were presented in the output file *NAME345.fch*. Table 2 represents the value of ρ density matrix for MS-12. *N* and *M* denote the number of AO in MS-1 and MS-2, respectively.

Fig. 5 represents the detailed scheme of the *GAUSSIAN link. NAME123.out*, *NAME234*.out and *NAME345.fch* files (original Gaussian'03 output files) are sent to *GAUSSIAN* link as input files for further ordered formation of vectors and matrixes without any mathematical operations. These files (*.out) contain the tables of molecular orbital energy values, corresponding the atomic orbital (AO) energy, AO coefficients and density matrix coefficients for pending MS. The *GAUSSIAN* block provides:

i) unformatted input of different values;
ii) and as a result – ordered output files containing extracted energies of *MO, AO* coefficients – *NAME123.orb*, *NAME234.orb* – and density matrix coefficients – *NAME345.den.*

As follows, several arrays are created:

i) 1D arrays – vectors of eigenenergies for each MS-1 and MS-2;
ii) 2D arrays of eigenvectors for each MS-1 and MS-2
iii) 2D array of ρ density matrix coefficients for MS-12

Table 2. ρ density matrix for MS-12.
N and M denote the number of AO in MS-1 and MS-2, respectively.

		MS-1	MS−2
		N	M
MS-1	N	$\begin{matrix}\rho_{11} & \rho_{12} & \cdots & \rho_{1N}\\ \rho_{21} & \rho_{22} & \cdots & \rho_{2N}\\ \cdots & \cdots & \cdots & \cdots\\ \rho_{N1} & \rho_{N2} & \cdots & \rho_{NN}\end{matrix}$	$\begin{matrix}\rho_{1,N+1} & \rho_{1,N+2} & \cdots & \rho_{1,N+M}\\ \rho_{2,N+1} & \rho_{2,N+2} & \cdots & \rho_{2,N+M}\\ \cdots & \cdots & \cdots & \cdots\\ \rho_{N,N+1} & \rho_{N,N+2} & \cdots & \rho_{N,N+M}\end{matrix}$
MS−2	M	$\begin{matrix}\rho_{N+1,1} & \rho_{N+1,2} & \cdots & \rho_{N+1,N}\\ \rho_{N+2,2} & \rho_{N+2,2} & \cdots & \rho_{N+2,N}\\ \cdots & \cdots & \cdots & \cdots\\ \rho_{N+M,N} & \rho_{N+M,2} & \cdots & \rho_{N+M,N}\end{matrix}$	$\begin{matrix}\rho_{N+1,N+1} & \rho_{N+1,N+2} & \cdots & \rho_{N+1,N+M}\\ \rho_{N+2,N+1} & \rho_{N+2,N+2} & \cdots & \rho_{N+2,N+M}\\ \cdots & \cdots & \cdots & \cdots\\ \rho_{N+M,N+1} & \rho_{N+M,N+2} & \cdots & \rho_{N+M,N+M}\end{matrix}$

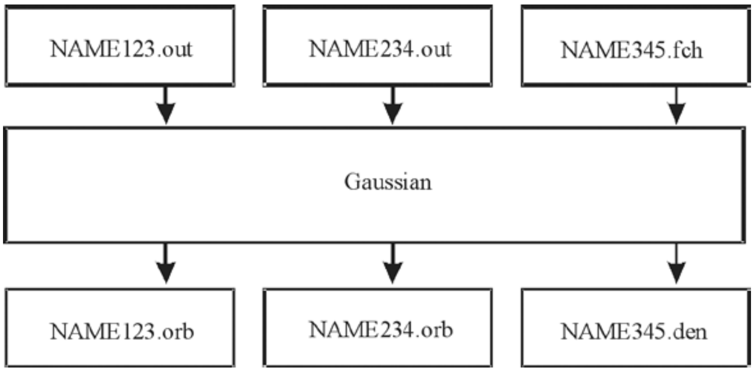

Fig. 5. The detailed scheme of *NUVOLA*: the *GAUSSIAN* link

Fig. 6 represents the detailed scheme of the *P83* link which performs the main calculation of the IET rate, according to Eq.(6). It includes the most mathematically complicated part - computing of multidimensional values of coupling S. Several files – containing the AO coefficients *NAME123*.orb, *NAME234*.orb, density matrix coefficients *NAME345*.den and initial Cartesian matrix data of the joint molecule *NAME234.yes* – are sent to the *P83* block as input files for further matrix manipulations, resulting IET rate matrixes in the *OUTPUT* files. Such set of files is labeled as W in Fig. 7.

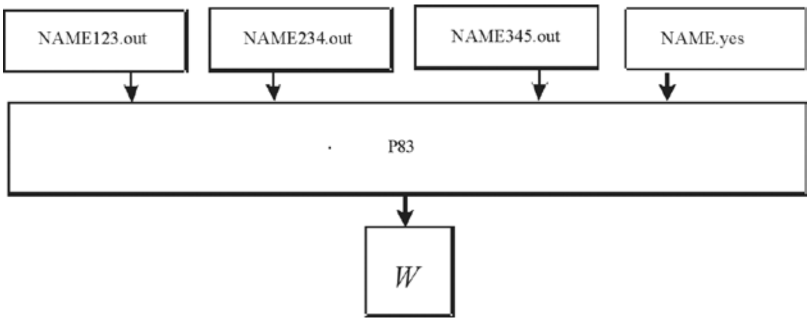

Fig. 6. The detailed scheme of *NUVOLA*: the *P83* link.

The following manipulations were performed to ρ density matrix of MS-12 presented in Table 2. The mentioned ρ density matrix contains the following four blocks:

$$\rho = \begin{vmatrix} A_1 & A_2 \\ A_3 & A_4 \end{vmatrix} \tag{10}$$

where each A_x (x=1..4) represents a different type of MS interactions. According to the general formulation of a physical task, the *intermolecular* (MS-1→MS-2) process has only to be treated and estimated, in contrast with the *intramolecular* (MS-1→MS-1, MS-2→MS-2) process (which is negligible). In that case, the formal reconstruction of ρ density matrix has to be implemented in order to exclude only intramolecular interactions. The mentioned density matrix (Eq. 10) contains four blocks which corresponds to the intramolecular interactions (diagonal blocks) as well as intermolecular interactions (non-diagonal blocks). Obviously, in that case, the diagonal matrix-blocks have to be excluded (the matrix elements of blocks A1, A4 have to be equated to zero). The newly reconstructed matrix ρ_0 contains real values in non-diagonal blocks A2, A3 only.

We have used Eq.(11) for routine evaluation of intermolecular coupling ξ_{if} :

$$\xi_{if} = \eta_i \times \rho_0 \times \mu_f \, . \tag{11}$$

where ηi , μj represent the two-block vectors of MS-1, MS-2, respectively, containing eigenvectors - coefficients related to AO. Indexes i and j represent the number of initial and final electronic states, respectively. The two-block vectors (1D arrays) are created according to the scheme presented in Eq. (12) and Eq. (13):

$$\eta_i = \underbrace{C_{i,1} \quad C_{i,2} \quad \ldots \quad C_{iN}}_{N} \; \underbrace{0 \quad 0 \quad \ldots \quad 0}_{M} \tag{12}$$

$$\tilde{\mu}_f = \underbrace{0 \quad 0 \quad \ldots \quad 0}_{N} \; \underbrace{C_{f,N+1} \quad C_{f,N+2} \quad \ldots \quad C_{f,N+M}}_{M} \tag{13}$$

4. New matrix multiplication formalism

The total transition rate W could be calculated using Eq. (2), where the intermolecular coupling $S_{\alpha\beta}$ for each transition corresponds to value ξ_{if} expressed by Eq. (11) as a product of matrix multiplication. The order of matrixes depends on the properties of the physical task. For example, $[H_2..H_2]$ derivative requires 12 members (2 MS * 2 atoms * 3 AO, using HF/6-311G basis set).

Eq. (14-15) show a construction of three matrix multiplication process, where each MS requires only two members – two-member-set of AO of the MS-1 (block A1 consist of a1, a2) and MS-2 (block C2 consist of c3, c4). First and third block-vectors contain zero-values as described above.

$$S_{ac} = \begin{vmatrix} A_1 & 0 \end{vmatrix} \times \begin{vmatrix} 0 & B_{12} \\ B_{21} & 0 \end{vmatrix} \times \begin{vmatrix} 0 \\ C_2 \end{vmatrix} \quad , \qquad (14)$$

$$S_{ac} = \begin{vmatrix} a1 & a2 & 0 & 0 \end{vmatrix} \times \begin{vmatrix} 0 & 0 & b1 & b2 \\ 0 & 0 & b3 & b4 \\ b5 & b6 & 0 & 0 \\ b7 & b8 & 0 & 0 \end{vmatrix} \times \begin{vmatrix} 0 \\ 0 \\ c3 \\ c4 \end{vmatrix} \quad , \qquad (15)$$

The two-dimensional density matrix ρ_0 (Eq. 14) contains four blocks. The two non-diagonal blocks reflect the behavior of intermolecular interactions (block B12 consist of b1, b2, b3, b4 and block B21 consist of b5, b6, b7, b8). The two diagonal blocks contain zero-values.

The classical routine of matrix multiplication is well-known [15]. The intermediate and final products of matrix multiplication were proceeded according to Eq. (16-17) and Eq. (18-19), respectively.

$$S_{ac} = \begin{vmatrix} 0 & (A_1 B_{12}) \end{vmatrix} \times \begin{vmatrix} 0 \\ C_2 \end{vmatrix} , \qquad (16)$$

$$S_{ac} = A_1 B_{12} C_2 , \qquad (17)$$

$$S_{ac} = (a1 \cdot b1 + a2 \cdot b3) \cdot c3 + (a1 \cdot b2 + a2 \cdot b4) \cdot c4 . \qquad (19)$$

The presented routine using Eq.(17-18) requires immense computer recourses- CPU time and virtual memory. This is obvious because the IET ratio *W* has to be calculated and evaluated for each transition made up from LUMO and higher states of MS–α to LUMO and higher states of MS–β. The number of all transitions N_{TOTAL} is equal to:

$$N_{TOTAL} = \left(\frac{N + M}{2} \right)^2 \quad , \qquad (19)$$

where N and M denotes the number of AO in MS-1 and MS-2, respectively. It is necessary to emphasize that the combination of very small MS requires negligible number of transitions (for example, *N=M=10*, N_{TOTAL}=100). Unfortunately, real model systems require the computing of *W* values in case, when N_{TOTAL} is equal to several thousands and more. In this case, multiplying of three matrixes according to Eq. (14) seems to be irrational, because all of them contain the blocks filled up by zero-valued elements. It means that significant excluding of zero-multiplication operations can shorten the time of *W* computation. Obviously, it is necessary to optimize the computational algorithm.

The optimization of the multiplication processes was implemented as follows:

i) to exclude the resource-wasting multiplication by zero – according to Eq.(14);
ii) to exclude the time-wasting processing of intermediate product – according to Eq.(16) ;
iii) to cancel the multiplication loop even if the value of *delta*-function is too small – according to Eq.(6).

So, it is reasonable to process only the first half of the first vector (block A_1), the quarter of density matrix (block B_{12}) and only the second half of the second vector (block C_2). Fig. 7 represents the scheme of the new matrix multiplication formalism. The assumption Y_1 requires taking into account the quarter of density matrix (block B_{12}). The assumption Y_2 requires column-row reorganization of the block-vectors A_1 and C_2

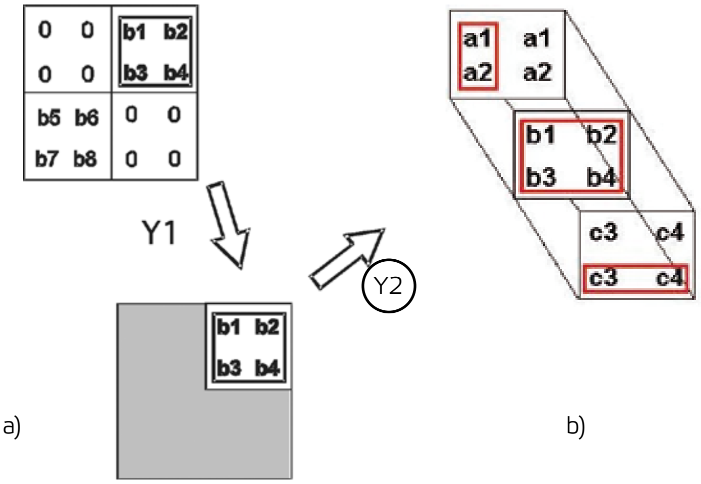

Fig. 7. Scheme of the novel matrix multiplication formalism:
a) the assumption Y_1 requires taking into account the quarter of density matrix (block B12) ;
b) the assumption Y_2 requires column-row reorganization of the block-vectors A_1 and C_2.

The formal reorganization of the classical multiplication routine described earlier was organized by means of three-dimensional matrix Ω(*N, M, 3*), where the first index N and the second index M denote the numbers of AO in MS-1 and MS-2, respectively. The third index represents the previous matrixes in the reduced form: the block-vectors A_1 and C_2 are redirected into the 1st and 3rd layer, respectively, and the block B_{12} of density matrix - into the 2nd layer. It is necessary to emphasize that the block B_{12} is presented in the previous form when the block-vectors A_1 and C_2 (used to fill the 1st layer in the column shift and the 3rd layer in the row shift, respectively (see Fig. 7b, the vector-block in presented in red). The final product was received according to Eq.(21) as direct multiplication of the matrix elements which represent the same result as in the classical case shown in Eq. (19):

$$S_{ac} = a1 \cdot b1 \cdot c3 + a2 \cdot b3 \cdot c3 + a1 \cdot b2 \cdot c4 + a2 \cdot b4 \cdot c4 \cdot \qquad (20)$$

However, the number of transitions N_{TOTAL} is reduced to a significantly lower value:

$$N_{TOTAL} = \left(\frac{N}{2} \times \frac{M}{2} \right), \qquad (21)$$

5. Different forms of the IET rate matrixes

Quantitative intermolecular ET processes can be analyzed in the framework of energies as well as spatial charge redistribution. Fig. 8 represents the detailed output of the P83 link.

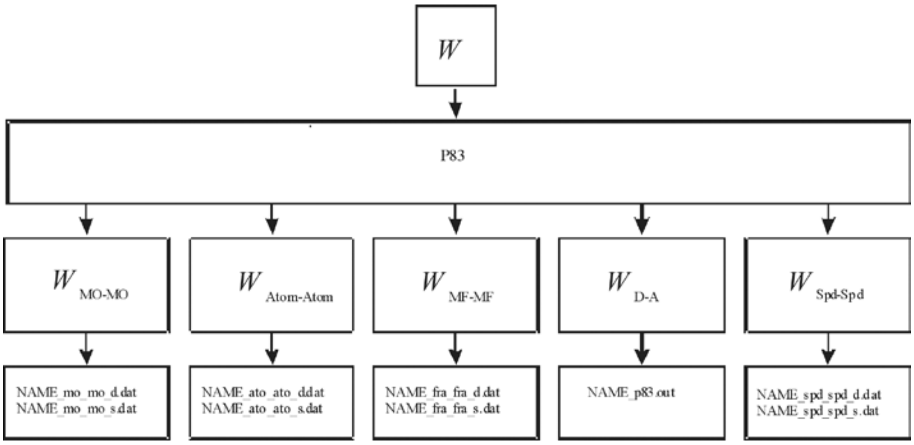

Fig. 8 The detailed scheme of *NUVOLA*: the output of *P83* link.

The estimation of the IET rate between two MS can be allowed in the frame of the molecular charge redistribution between AO. This assumption corresponds to the general task of the physical process (IET). This assumption (called as AO-AO assumption) is quite useful in case of very small MS. For example, in case of $[H_2..H_2]$ derivative, 36 transitions have to be analyzed (6*6=36, each MS contains 12 AO, but only 6 AO are of LUMO and higher). Unfortunately, it is very difficult to analyze real model systems containing hundreds and thousands atoms (it corresponds to the number of AO equal to several thousand and more).

The second assumption (called as ATO-ATO assumption) can be allowed in the frame of the molecular charge redistribution between atoms. It is quite useful in case of small MS (containing several atoms). According to the selected basis set and method, all IET rates belonging to different AO of the same atom are summed. This operation reduces the order of the IET rate matrix until the amount described by indexes (N_{MS-1}, N_{MS-2}), where NMS-1, NMS-2 are the number of atoms in corresponding MS.

The third assumption (called as FRA-FRA assumption) can be allowed in the frame of the molecular charge redistribution between molecular fragments. It is quite useful in the case of big MS (containing several hundred atoms). In the same cases, several levels of molecular organizations can be presented. For example, π-electronic system of benzene ring containing fragments as well as n-electronic system of carbonyl fragments could be formally treated as molecular fragments, which play significant role in the charge redistribution processes. In that case, both previously formally decomposed MS according to a theoretical request could be analyzed in the third assumption. According to the list of formal decomposition into molecular fragments, all the IET rates belonging to different AO of the same molecular fragment are summed. This operation reduces the amount of the IET rate matrix until amount described by indexes (NFRA-1, NFRA-2) , where NFRA-1, NFRA-2 are the number of molecular fragments in corresponding MS.

The fourth assumption (called as D-A assumption) can be allowed in the frame of the molecular charge redistribution between MS-1 (donor) and MS-2 (acceptor). It is useful if we want to estimate IET in a molecular stack (partially) and the behavior of the IET process (overall). This operation represents the IET rate as a single number.

The fifth assumption (called as SPD-SPD assumption) can be allowed in the frame of the molecular charge redistribution between the same types of AO. It is useful when analyzing the mixed ET (for example, between *s* and *p* orbitals, between *s* and *d* orbitals etc). According to the selected basis set and method, all the IET rates belonging to an AO of the same type are summed. This operation reduces the order of the IET rate matrix until the dimension 3*3 (in case of *spd* type) or 4*4 (*spdf*) etc.

All the required matrixes are taken to make the resulting data files and three-dimensional molecular electrons redistribution diagrams.

Conclusion

The quantum chemistry program package *NUVOLA* was prepared and tested. The estimation of IET between two molecular systems can be allowed in the frame of the charge redistribution between:

i) atomic orbitals;
ii) molecular orbitals;
iii) atoms;
iv) molecular fragments;
v) donor and acceptor pairs.

Quantitative intermolecular ET processes could be analyzed in the framework of energies as well as spatial charge redistribution.

Acknowledgements

This work is part of *KARSKOPAS* research program which is financially supported from Lithuanian State Fundation for science an education. Nurija Galikova acknowledges the Lithuanian Science Council for the Summer Undergraduate Research Fellowship Award (2007).

References

[1] Frank Jensen. Introduction to computational chemistry - Wiley, Second edition, 2007.
[2] Bolton J.R., Archer M.D. Basic Electron - Transfer Theory // In: Bolton J.R., Mataga N., McLendon G. Electron Transfer in Inorganic, Organic and Biological Systems.- *Advances in Chemistry Series*, CSC Symposium Series 2. - American Chemical Society, Washington, DC 1991. - Pp. 7-23.
[3] Rodrigo E. Palacios, Gerdenis Kodis, Christian Herrero, Ernesto Mariño Ochoa, Miguel Gervaldo, Stephanie L. Gould, John T. M. Kennis, Devens Gust, Thomas A. Moore, Ana L. Moore. Tetrapyrrole Singlet Excited State Quenching by Carotenoids in an Artificial Photosynthetic Antena *// J. Phys. Chem. B*, 110 (50), 2006. - 25411 -25420
[4] Resonance energy transfer. Ed. David L. Andrews, Andrey A. Demidov. - Chichester: John Wiley and sons Ltd., 1999. – P. 320.
[5] Volkhard May, Oliver Kühn. Charge and energy transfer dynamics in molecular systems, 2000 – Pp. 249-333.
[6] Scholes, G.D., and Ghiggino, K.P.. Electronic interactions and interchromophore energy transfer. // In: Advances in Multiphoton Processes and spectroscopy . S. H, Lin, A. A. Villaeys, and Y. Fujimura, editors. World Scientific, Singapore, Vol. 10, 1996. Pp. 95-331.
[7] Arieh Warshel, William W. Parson. Dynamics of biochemical and biophysical reactions: insight from computer simulations *// Quarterly reviews of Biophysics*, vol.34, 4 (2001) P. 563-679.
[8] A.V. Barzykin, P.A. Frantsuzov, K. Seki, M.Tachiya. Solvent effects in nonadiabatic electron-transfer reactions: theoretical aspects. *// Advances in Chemical Physics*, Vol. 123. 2002. – P. 511-616.
[9] N. Galikova, A. Gruodis, M Balevičius. Quantum chemistry program NUVOLA. – Vilnius university, 2007. 3rd ed.
[10] R. A. Marcus. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. V. Comparison and Properties of Electrochemical and Chemical Rate Constants *// J. Phys. Chem. 67*, 853, 2889 (1963)
[11] R.A. Marcus and N.Sutin *// Biochim.Biophys.Acta 811* (1992) 265
[12] Nurija Galikova, Alytis Gruodis, Mindaugas Leonas Balevičius, Leonas Valkunas Intermolecular electron transfer due to quantum chemistry approach. I. General theory and calculation routine // in preparation.
[13] Nurija Galikova, Alytis Gruodis, Mindaugas Leonas Balevičius, Leonas Valkunas Intermolecular electron transfer due to quantum chemistry approach. II. Processes in stack of α-crystal of N, N-dimethilaminobenzylidene indan-1,3-dione // in preparation.
[14] Gaussian 03, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.
[15] Knuth, D.E. Seminumerical Algorithms // In: The Art of Computer Programming. Vol. 2. Third Edition, 1998. - pp 501.