

Supercomputer Modeling of Active Centers Redox System of Plastocyanin

¹Natalia V. Zolotareva, ¹Nariman M. Alykov and ²Ilya B. Kovalenko
¹Astrakhan State University, Tatishchev St. 20a, 414000 Astrakhan, Russia
²Faculty of Biology, Moscow State University Name M.V. Lomonosov
Lenin Hills, d.1, Building 12, 119991 Moscow, GSP-1, Russia

Abstract: The calculations of the partial charges of the active center of plastocyanin and determination of its structural features in oxidized and reduced states were made by quantum-chemical methods. The calculations were made by DFT Method using B3LYP and the basis sets 6-31G* and cc-pvdz in the firefly program on the supercomputer complex “Lomonosov” of Moscow State University.

Key words: Plastocyanin, thylakoids of chloroplasts, fractional charges, copper ion, cytochrome

INTRODUCTION

Formation of a complex of a plastocyanin with cytochrome f (subunit of cytochrome b6/f complex) is an important element of a chain of photosynthetic electronic transport in a membrane of thylakoids of chloroplasts. Plastocyanin is a small copper-containing protein which carries out transfer of electrons between a cytochrome complex and photosystem I. It is now known structure of plastocyanin in the oxidized and reduced forms of spinach, fern, poplar and other objects (Musiani *et al.*, 2005; Kachalova *et al.*, 2012).

Before us was a task in the calculation of the fractional charges of the active center of plastocyanin and the establishment of structural features in its oxidized and reduced states with the aim of further use in the simulation of complex formation by molecular dynamics.

Coordinates of atoms of a plastocyanin were received from a databank of protein structures. Similar connections consist of a large number of atoms and even several subunits, however, some amino acids which are directly connected with an ion of metal have a certain influence on functional activity of connections.

For studying of an electronic configuration and structural parameters were used only small fragments of proteins including atoms of the active center. It should be noted that similar calculations of electronic structure of protein without its amino-acid environment though simplify a task but thus considerably reduce the value of the received results from the point of view of biology because such structures in plant cells does not exist.

MATERIALS AND METHODS

For realization the task of an objective quantum-mechanical calculations of the active center in

structure of the protein containing the amino-acid remains coordinated by a metal ion, undergoing oxidation-reduction transitions in the course of transfer of a charge from cytochrome were executed.

For realization of an objective quantum-mechanical calculations of the active center in structure of the protein containing the amino-acid remains coordinated by a metal ion, undergoing oxidation-reduction transitions in the course of transfer of a charge from cytochrome were executed. Calculations are carried out by method of the theory of functionality of electronic density with use of hybrid functionality of B3LYP as a basic set of atomic orbitals were used the polarizing valent split basis 6-31G* and the correlation coordinated basis of cc-pvdz. Calculations are carried out in the Firefly program (Penfield *et al.*, 1985) on a supercomputer the SKIF “Chebyshev”, Research Computing Center of Lomonosov Moscow State University.

The model of the active center of plastocyanin contains copper ion is surrounded by four amino acid residues (His37, Cys84, Hys87, Met92) in Fig. 1.

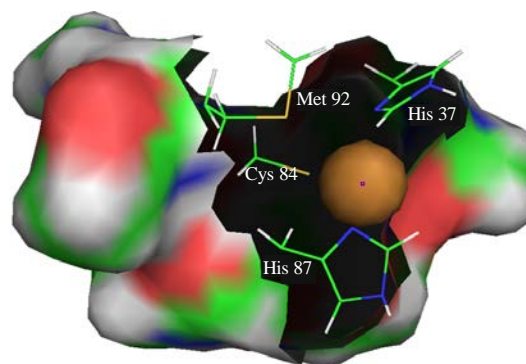


Fig. 1: Model of reactive center of plastocyanin

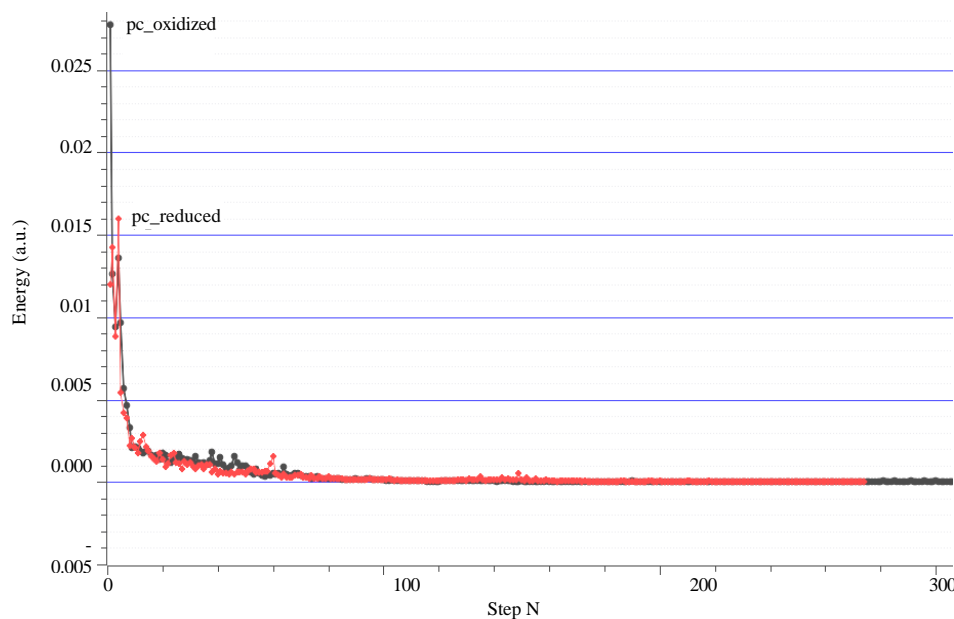


Fig. 2: Graphs of value of the rms deviation of energy versus the number of optimization steps for the oxidized (pc_oxidized) and reduced (pc_reduced) forms of plastocyanin obtained using B3LYP/6-31G*

The calculations of the electronic structure of the active center of plastocyanin conducted with different charges (2, 3) and in different spin states-doublet (oxidized form and reduced form). Selected models have previously been optimized and found the most stable form. Figure 2 shows the graphs of the dependence of the standard deviation of the energy of the number of steps to optimize the two forms of plastocyanin. The size of a mean square deviation is calculated by the formula:

$$RMS = (3N)^{-1} \times \left(\sum_1 \left(\frac{\partial E}{\partial x_i} \right)^2 + \left(\frac{\partial E}{\partial y_i} \right)^2 + \left(\frac{\partial E}{\partial z_i} \right)^2 \right)^{1/2} \quad (1)$$

Where the summation is over all N atoms of the molecular model; x_i , y_i , z_i the cartesian coordinates of the i-atom.

RESULTS AND DISCUSSION

As it is possible to notice, since the two-hundredth step, the molecule geometry practically does not change, observed fast convergence on energy. Table 1 shows the fractional atomic charges of the coordination shell of the

active center the oxidized and reduced forms of plastocyanin. For comparison, the table also included the results of the calculation of DFT-Small Model system CuSCH2 (C3H3N2) 2, published in research of Olsson *et al.* (2003).

As can be seen from Table polarizing d-orbital in a basic set 6-31G* insufficiently and demands additional introduction of a polarizing p-orbital. Since, the basic cc-pvdz set is focused on not empirical calculations with inclusion of electronic correlation, these results, obviously, are more reliable for the analysis of electronic and structural properties of the active center of a plastocyanin and can be compared with results of research (Olsson *et al.*, 2003).

As a result of supercomputer calculations it is established that in the course of electronic transfer of 60% of electronic density it is localized on an ion of copper of a plastocyanin, 6% of density are Concentrated on atom of Sulfur (Cys 84) on atoms the imidazole of rings 16% of electronic density are concentrated and the rest is distributed on a carbon skeleton of these amino acids. Changes occurred in the structure of the active center of reduced plastocyanin as increased bond length Cu S (Met92) for 0.88Å from baseline in the oxidized form 2.9Å, increased distance Cu N on 0.09Å. Figure 3 is surrounded by copper ion functional groups.

Table 1: Values of partial charges in the active center of plastocyanin

Basis	Cu		-S-CH ₃		-S		-N ³⁷		-N ⁶⁷	
	Ox	Red	Ox	Red	Ox	Red	Ox	Red	Ox	Red
Charges on Mallikena										
6-31G*	1.267	0.669	0.052	0.129	-0.54	-0.601	-0.834	-0.702	-0.856	-0.714
cc-pvdz	0.519	0.406	-0.086	-0.056	-0.051	-0.553	-0.462	-0.432	-0.487	-0.443
Olsson <i>et al.</i> (2003)*	0.384	0.229	-	-	-0.066	-0.435	-0.383	-0.335	-0.376	-0.332

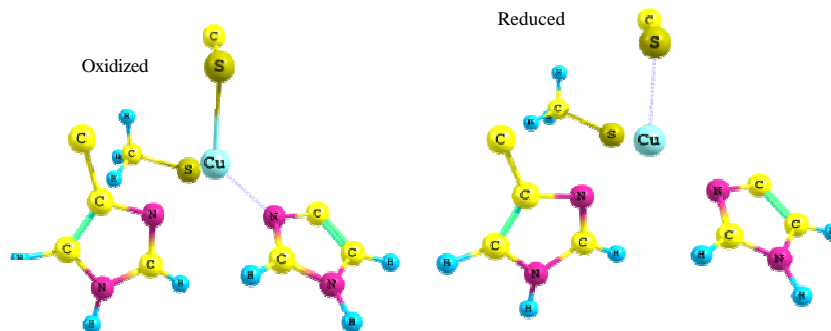


Fig. 3: The copper ion to surrounded by functional groups of the oxidized and reduced forms

CONCLUSION

Increasing the angle N-Cu-N on 7.5° from the experimental values of the reduced plastocyanin structure did not change the tetrahedral shape of the cluster that does not contradict the available data (Olsson *et al.*, 2003).

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