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Effect of conformational degrees of freedom on the charge transfer in model tripeptide

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ABSTRACT

An extensive conformational dependence of the intramolecular charge transfer (both hole and electron) between intermediate residues of the model tripeptide in gas phase has been studied. The charge transfer integral, spatial overlap integral and site-energy for both hole and electron transfer between the intermediate residues in the tripeptides were calculated using the fragment orbital method. The site-energies and the charge transfer integrals have been calculated for different conformation of the glycine tripeptide by varying the dihedral angles (ϕ and ψ) along the α-carbon atom of amino acid subgroups. Electronic structure calculations show that the charge transfer integral between intermediate residues is strongly depending on the nature of the conformation of the peptide. The calculations indicate that the charge transfer is maximum at the particular conformation of the intermediate amino acid residues.

1. Introduction

The study of charge transfer in polypeptides has received a great deal of attention due to its relevance in biological activities and possible applications in molecular electronics [1]. The charge transfer (CT) in biological systems has been the subject of interest for experimental and theoretical investigations [2–7], especially in the long-range charge transfer through peptide bridging molecules and the kinetic study of intramolecular CT reactions based on the potential energy surface (PES) [8–24]. Isied and co-workers initially studied the long-range distance dependence of electron transfer process in peptides [25,26]. Serrano-Andrés et al. [27] have studied the charge transfer process in neutral and ionic polypeptides using ab initio and semi-empirical methods. They found that the charge transfer in their model di-, tri-, tetra-, and octamer peptides strongly depend on the type of conformation. Schanze and Sauer [28] have investigated the distance dependence of electron transfer with proline chains of varying length.

The peptide chain conformation through potential energy surface (PES) is a topic of biological importance. The biological activities of a peptide depend on its three dimensional structure and locations of basic sites in PES. The potential energy surface is defined as a function of Ramachandran and Sasisekharan [29] backbone dihedral angles along the α-carbon atom of amino acid subgroup, namely ϕ and ψ. The molecular conformations of an intermediate residues will affect the overall three dimensional shape of a protein, altering its structure and function in a biological system. Recently, Schlag et al. [30] have observed that the charge introduced in the polypeptide chain can stay within the subgroup, until the rotational angle reaches to a certain angle at which the charge is transferred to the next subgroup. In our previous studies, we found that, the calculated electron transfer rate for linear structure (for which $\phi = \psi = 180^\circ$) is relatively low, and both the hole and electron transfer rate is strongly depend on structural fluctuations of the intermediate amino acid subgroups [31,32]. Finklea et al. [33] concluded that the electron transfer rate through electroactive alkanethiol molecules can be increased through conformational changes of the chain. In our previous studies the charge transfer calculations were performed only for few particular standard conformations such as linear, α-helix, β-sheet and 3_{10}-helix [31,32]. Since, the proteins are in dynamical fluctuations with respect to the backbone dihedral angles, it would be of interest to investigate the conformational dependence of the charge transfer in model tripeptide through PES. The plot for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the amino acid subgroup (see Fig. 1) shows that the HOMO is delocalized on the region between α-carbon and nitrogen atoms of the amino group (i.e. N-terminus) and the LUMO is delocalized around the carbon and oxygen atoms of carbonyl group and not in the peptide linkage. DFT single point energy calculation also shows that HOMO of the fragments consisting of more than 75% of the nitrogen atom of the amino

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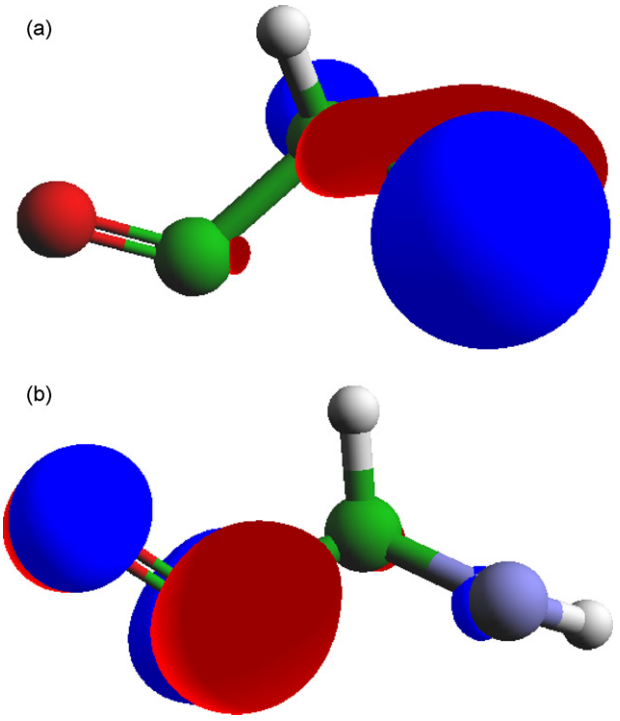


Fig. 1. The plot of (a) highest occupied molecular orbital and (b) lowest unoccupied molecular orbital of the of the amino acid subgroup ($NHCH_2CO$).

group and the LUMO consists of more than 65% of carbon and 25% of oxygen atoms of the carbonyl group. The HOMO and LUMO exhibit similar features of π-orbital and they are contributed from different atom pairs of amino acid subgroup. From this, we can expect, in polypeptide, if the α-carbon and nitrogen atoms of neighbouring amino acid subgroups are nearer then the hole transport is most favorable and if carbonyl group of each amino acid residues are nearer then the electron transport is most favorable.

The charge transfer integral (also called as electronic coupling or hopping matrix element) and site-energy (energy of the charge when it is localized at particular amino acid subgroup) corresponding to hole and electron transport are the key quantities that need to be calculated. In order to calculate the charge transfer integral and site-energy, a reasonable approximation has been made, the positive charge will migrate through the HOMO and the negative charge through LUMO of amino acid subgroups. We have calculated the charge transfer integral and site-energy for both hole and electron transport for a model tripeptide system based on fragment orbital approach method [31,32,34,35]. From this method the charge transfer integral and site-energy can be calculated directly as the off-diagonal and diagonal matrix elements of the Kohn-Sham Hamiltonian. This method is quite suitable to the present study since the site-energy of each amino acid subgroup in a tripeptide is not identical and the overlap between them is not equal to zero. In the next section, we present the theoretical methodology undertaken for the calculation of charge transfer integral and site-energy for hole and electron transport. Following this, we present the results and discussions. Finally, we conclude the paper with a summary of all our results.

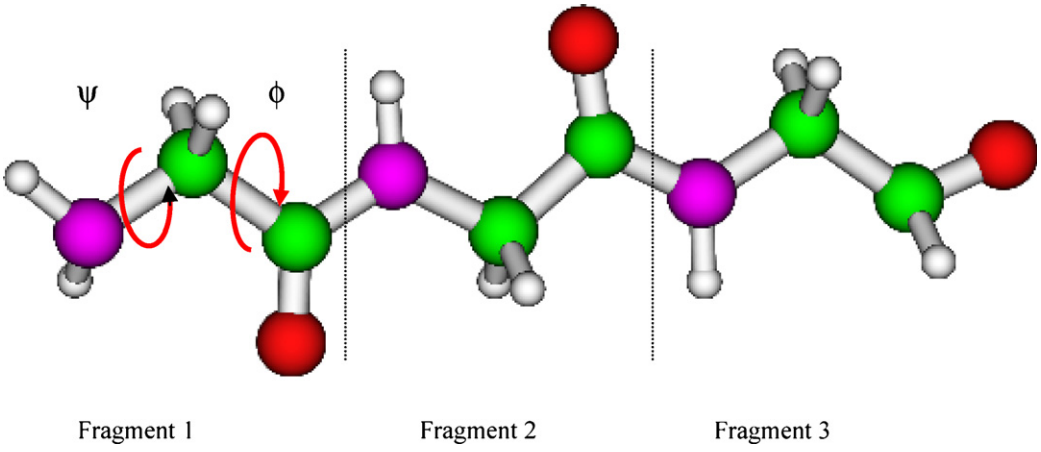
2. Methodology

The peptide conformations are characterized in terms of the dihedral angles along the α-carbon atom of the amino acid subgroups denoted as ϕ (*Phi*) and ψ (*Psi*) [36]. The model tripeptide which consisting of three glycine amide subgroups has been represented in terms of three fragments, as shown in Scheme 1. It is to be noted that here the fragments 1 and 3 are radical and fragment 2 is a bi-radical. In the present work the conformational properties of the tripeptide are investigated by the potential energy surface, which have been generated by varying the backbone dihedral angles (ϕ and ψ) in the increment of 30°. The geometries of 144 conformers of tripeptide have been optimized at B3LYP/6–311G(d, p) level of theory using Gaussian 98W program [37]. All the geometrical parameters (bond lengths, angles, and dihedrals) were fully relaxed, with the exception of the dihedral angles ϕ and ψ in all the subgroups.

The charge transport through peptide bond of model tripeptide is described by the tight-binding Hamiltonian method [38,39]. The Hamiltonian is given by

$$H = \sum_{i=1}^{n} \varepsilon_i(\theta(t)) a_i^{+} a_i + \sum_{i,j_{i\neq j}}^{n} J_{ij}(\theta(t)) a_i^{+} a_j \quad (1)$$

In the above equation a_i^{+} and a_i are the creation and annihilation operators of a charge at the i^{th} amino acid subgroup in the tripeptide, $\varepsilon_i = \langle \varphi_i | H | \varphi_i \rangle$ is the site-energy of the charge and $J_{i,j} = \langle \varphi_i | H | \varphi_j \rangle$ is the charge transfer integral between HOMOs (or LUMOs) of subgroups i and j. In Eq. (1) both ε_i and J_{ij} depend on inter- and intramolecular degrees of freedom, collectively denoted as $\theta(t)$.



Scheme 1. The fragment representation of the model glycine tripeptide used for the charge transfer calculation.

These parameters were computed for all the conformers using fragment orbital approach as implemented in Amsterdam density functional (ADF) theory program [40]. The molecular orbitals generated through single point energy calculation for each fragment have been used as a basis set in further single point energy calculation for full tripeptide. That is, the molecular orbitals of a tripeptide are expressed as a linear combination of the molecular orbitals of the individual glycine amide subgroup, φ_i. The final output of the ADF calculation will provide the overlap matrix, S, the eigenvector matrix, C, and the eigenvalue matrix, E. Then the site-energy, $\langle\varphi_i|h_{KS}|\varphi_i\rangle$ and charge transfer integral, $\langle\varphi_i|h_{KS}|\varphi_j\rangle$ are calculated using the relation $h_{KS} = SCEC^{-1}$. As explained in previous studies this procedure provides a direct and exact calculation for the charge transfer integral and site-energy without involving the assumption of zero spatial overlap, and it is not necessary to apply an external electric field to bring the site-energies of adjacent amino acid subgroups into resonance [8,31,41].

The generalized effective charge transfer integral can be defined in terms of the charge transfer integral (J), spatial overlap integral (S) and site-energy (ε) as [8,31,41]

$$J_{eff} = J - \frac{S(\varepsilon_1 + \varepsilon_2)}{2} \quad (2)$$

In the present study, all DFT calculations were performed with an atomic basis set of Slater-type orbitals (STOs) of triple-ξ quality including one set of polarization functions on each atom (TZP basis set in ADF) [40]. The generalized gradient approximation (GGA) type, Becke's exchange functional [42] is used in DFT calculation together with the correlation part of Perdew [43], denoted as BP. This proceeds from the local density approximation (LDA) for the exchange and correlation functional based on the parameterization of the electron gas data given by Vosko, Wilk and Nusair (VWN) [44]. Peach et al. [45] studied the degree of spatial overlap between the occupied and unoccupied orbitals involved in an excitation of electron in systems like di, tripeptides using time dependent density functional theory method. They concluded that the GGA functionals predicts the excitation energy satisfactorily but there is an error in Rydberg excitation due to the omission of asymptotic behavior in exchange correlation potential. In our earlier studies [31,32,41], we confirmed that the charge transfer integral calculated from DFT functionals BP, PW91 is found to be comparable with the values obtained from asymptotically corrected SAOP exchange correlation functional and J is independent of exchange correlation functional used in DFT calculations. For open shell systems, the restricted DFT calculations have been performed.

3. Results and discussion

3.1. Geometry and relative energy of the conformers

The backbone of any amino acid residue in a peptide or in a protein molecule is a triple rotor. The three dihedral angles ϕ, ψ and ω measure the rotation about the N–C, the C–CO and the OC–NH (i.e. the peptide) bonds, respectively, leading to a potential energy surface. Since the peptide bond may be either *cis* or *trans*-isomer, usually ω assumes the values in the vicinity of 0° or 180°. Hence, it is customary to consider the potential energy surface (PES) with respect to the dihedral angles ϕ and ψ. The conformations of a model tripeptide in potential energy surface have been generated by varying the dihedral angles ϕ and ψ of each residue from −180° to 180° in an equal increment of 30°. The geometry optimization was performed in the gas phase using the B3LYP hybrid functional and the standard 6–311G(d, p) basis set. The energies of 144 structures of the tripeptide were used to calculate the relative energies. The relative energies for all the conformers are summarized and given in supplementary material (Table 1S). The relative energies were used to generate the potential energy surface and is shown in Fig. 2. Among these conformations, the global minimum energy structure is at ϕ = 180° and ψ = −180°, which is reported as linear structure for polypeptides in literature [31]. Fig. 2 shows that other than the secondary structures α-helix and 3_{10}-helix, few other structures are also having the minimum energy in PES. The maximum relative energy in the potential energy surface is found to be ∼21 kcal/mol. While analyzing the structural parameters such as bond lengths, bond angles and dihedral angles of residues, it has been observed that the effect of the rotation along the α-carbon atom of an amino acid residue is greater on the dihedral angles of tripeptides.

3.2. Charge transfer between neighbouring amino acid residues

3.2.1. Hole transport

The charge transfer integral, spatial overlap integral and site-energy for hole transport have been calculated for all 144 conformations of model tripeptide. We used the BP potential functional in combination with TZP basis set for the calculation of the charge transfer integrals and site-energies. The effective charge transfer integral for hole transfer between fragment 1 and 2 ($J_{eff}1$), fragment 2 and 3 ($J_{eff}2$) and fragment 1 and 3 ($J_{eff}3$) have been calculated using Eq. (2). The square of effective charge transfer integral values are plotted with respect to the dihedral angles ϕ and ψ and are shown in Figs. 3–5, respectively. The calculated charge transfer integral, spatial overlap integral and effective

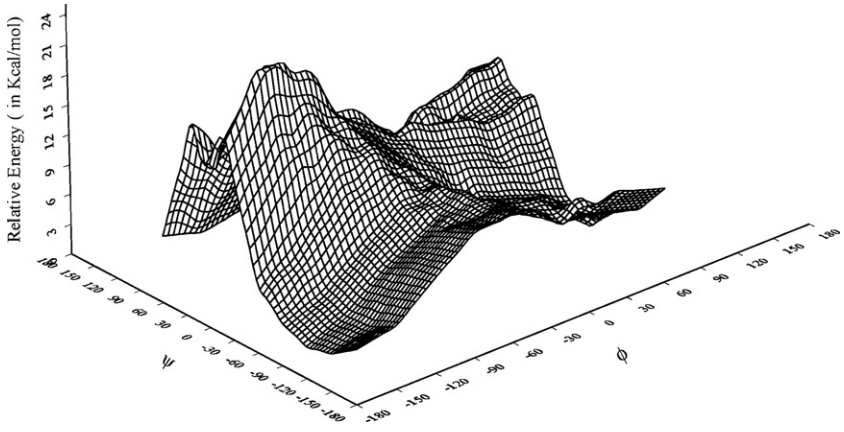


Fig. 2. Potential energy surfaces of model tripeptide computed at B3LYP/6–311G(d, p) level of theory.

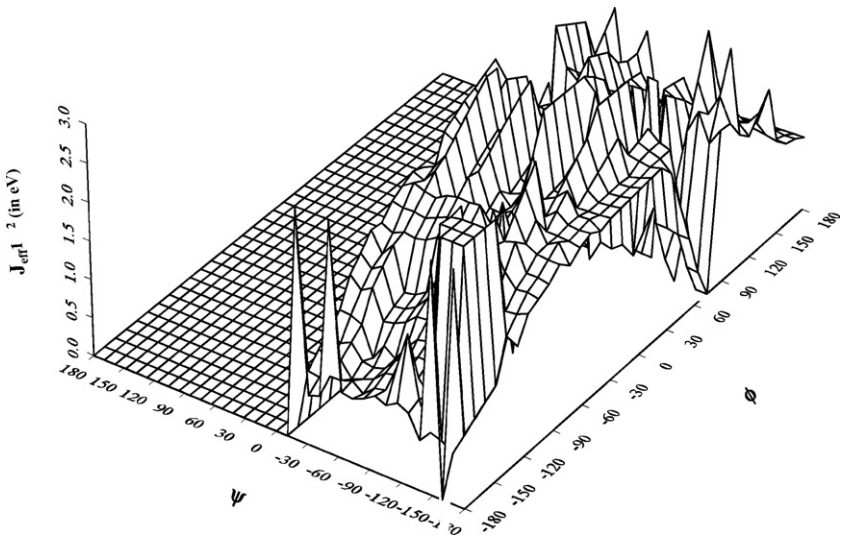


Fig. 3. The variation of square of effective charge transfer integral ($|J_{eff}1|^2$) for hole transport between the fragments 1 and 2 with respect to dihedral angles ϕ and ψ.

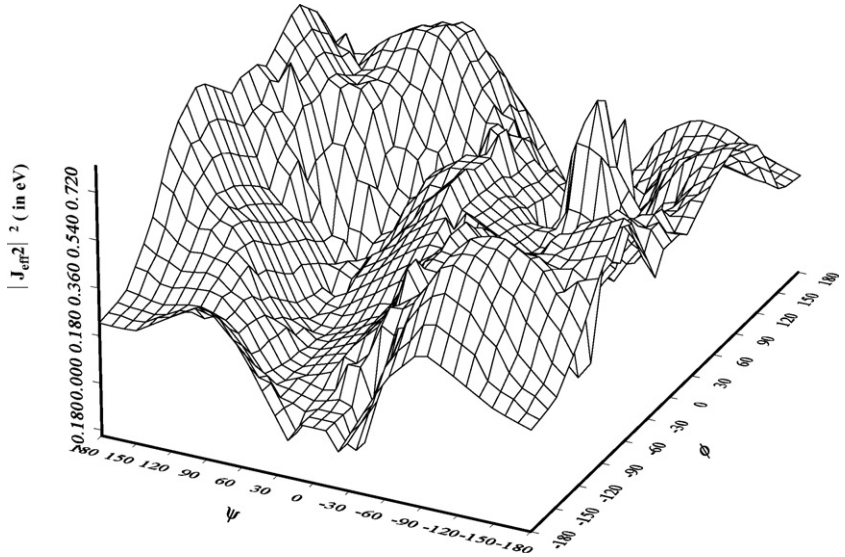


Fig. 4. The variation of square of effective charge transfer integral ($|J_{eff}2|^2$) for hole transport between the fragments 2 and 3 with respect to dihedral angles ϕ and ψ.

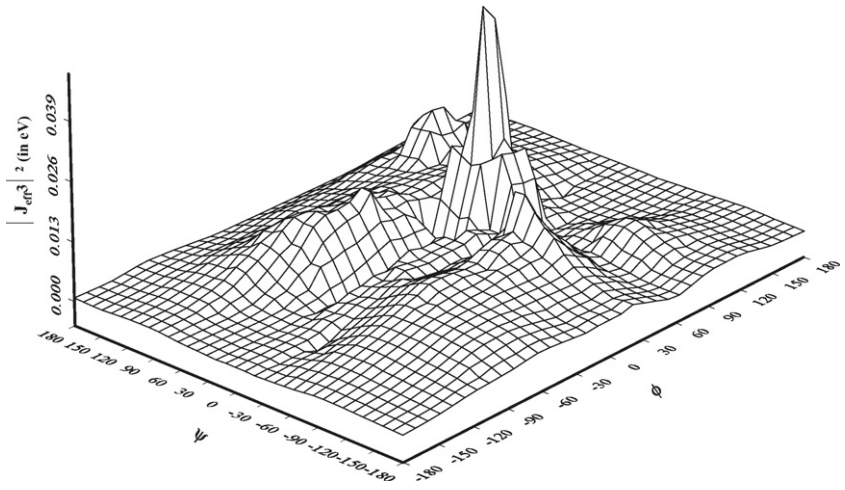


Fig. 5. The variation of square of effective charge transfer integral ($|J_{eff}3|^2$) for hole transport between the fragments 1 and 3 with respect to dihedral angles ϕ and ψ.

charge transfer integral are given as supplementary material (Tables 2S–4S).

It has been found that, the effective charge transfer integral ($J_{eff}1$) value is found to be maximum (1.592 eV) in the dihedral angle values of $\phi = 30^\circ$ and $\psi = -30^\circ$ and the next maximum (1.590 eV) has been noticed for the conformer with dihedral angles $\phi = -30^\circ$ and $\psi = 30^\circ$, which are refer to the helical structures of the peptides. The minimum value 0.363 eV of charge transfer integral ($J_{eff}1$) has been observed in the dihedral values of $\phi = 180^\circ$ and $\psi = 150^\circ$. The maximum value of the effective charge transfer integral for hole transport between fragments 2 and 3 ($J_{eff}2$) is found for the structure with dihedral angles in the range of $\phi = 180^\circ$ and $\psi = 60^\circ$. It is interesting to note that the values of $J_{eff}1$ is maximum in the helical structures compared to extended structures where as $J_{eff}2$ is maximum in extended structures. These results confirmed in our earlier study, that the values of $J_{eff}2$ is maximum in the extended structures [31].

On comparing the calculated effective charge transfer integrals ($J_{eff}1$, $J_{eff}2$ and $J_{eff}3$), the $J_{eff}3$ value is relatively low and has significant value in some of the helical structures. The maximum electronic coupling calculated for helical structures is due to the folding of the intermediate residues which leads to the strong overlap between the orbitals of the amino acid subgroups that involved in the charge transport. Also, the distance between the fragments is shortened due to the folding of these fragments. Schanze and Sauer [28] have also found in their study, that the CT depends on the length of the intermediate amino acids. They found that CT has been decreased when the length of the amino acids increased. The peptides are constrained and stabilized by weak interactions because of its conformational change, which lower the energy between neighbouring subgroups and thus favor the hopping mechanism. These effects increase the overall electronic coupling governing the charge transfer process. In earlier studies also it has been emphasized that the effect of protein thermal nuclear motion strongly affects the electronic coupling matrix elements [46–49]. Isied co-workers [2] found that the calculated electronic coupling values for helical structures shows large magnitude difference compare to other structures of cationic dipeptides.

3.3. Electron transport

The calculated values of the charge transfer integral and spatial overlap integral for electron transport for different conformers of the model tripeptide are tabulated in Tables 2S and 3S as supplementary material. The effective charge transfer integral for electron transfer between fragments 1 and 2 ($J_{eff}1$), fragments 2 and 3 ($J_{eff}2$) and fragments 1 and 3 ($J_{eff}3$) have been calculated using Eq. (2) and are summarized in Table 4S as supplementary material. The square of effective charge transfer integral values are plotted with respect to the dihedral angles ϕ and ψ and are shown in Figs. 6–8.

The effective charge transfer integrals $J_{eff}1$ and $J_{eff}2$ are found to be maximum for the dihedral angle values $\phi = 90^\circ$ and $\psi = 120^\circ$, and $\phi = -90^\circ$ and $\psi = -30^\circ$, respectively, which are in the range of helical structures. The charge transfer integral for electron transfer is maximum at the dihedral angles correspond to helical structures. Isied and co-workers [2] have also confirmed that there were significant differences in charge transfer process between α-helices, polyproline-II and extended β-strand-like structures. These results are in accordance with our earlier studies [31]. On comparing the calculated effective charge transfer integrals ($J_{eff}1$, $J_{eff}2$ and $J_{eff}3$) for electron transfer, the $J_{eff}3$ value is much smaller.

In a series of charge transfer studies of peptide model systems, it is evident that the hole and electron transfer through the peptide spacer is greatly influenced by the nature of the peptide backbone and conformation of the intermediate amino acids sequence [50–52]. In the present study, model peptide conformers with $\phi = 30^\circ$ and $\psi = -30^\circ$, the maximum coupling of ($J_{eff}1$) 1.592 eV have been calculated for hole transport between the fragments 1 and 2. However, as shown in Figs. 3–8, the charge transfer integral strongly varies with respect to the ϕ and ψ values, and for many conformations very low-coupling values in the order of 0.001 eV have been calculated. Hence, further charge transport calculations or simulations to find the rate of charge transport or mobility of charge carriers in polypeptide should contain both static and dynamic disorder effects as described in the previous studies for similar systems [53] and DNA [34]. The charge transfer will occurs only at particular molecular geometries of the intermediate residues. The charge has to wait until the intermediate residues reach that particular conformation for transfer. Rotation of the Ramachandran dihedral angles makes the critical conformation for the charge transfer in polypeptides. That is, the non-bonded interactions occurring in peptide secondary structures and their conformational changes form the basis of the differences in electronic coupling.

The minimum charge transfer in tripeptide is due to the weak coupling between the corresponding molecular orbitals (HOMO's

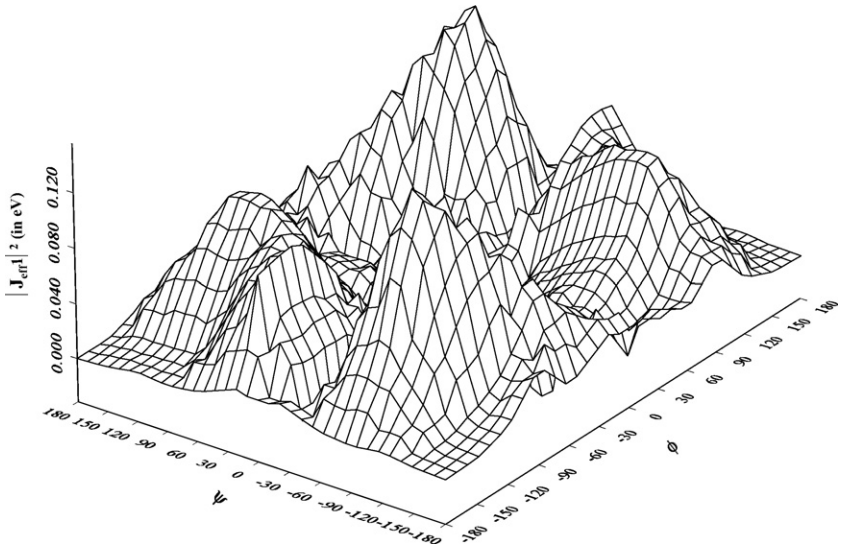


Fig. 6. The variation of square of effective charge transfer integral ($|J_{eff}1|^2$) for electron transport between the fragments 1 and 2 with respect to dihedral angles ϕ and ψ.

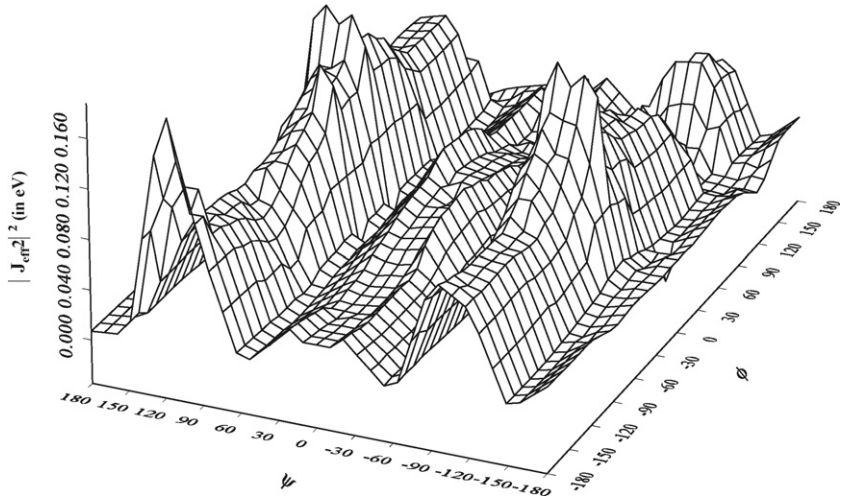


Fig. 7. The variation of square of effective charge transfer integral ($|J_{eff}2|^2$) for electron transport between the fragments 2 and 3 with respect to dihedral angles ϕ and ψ.

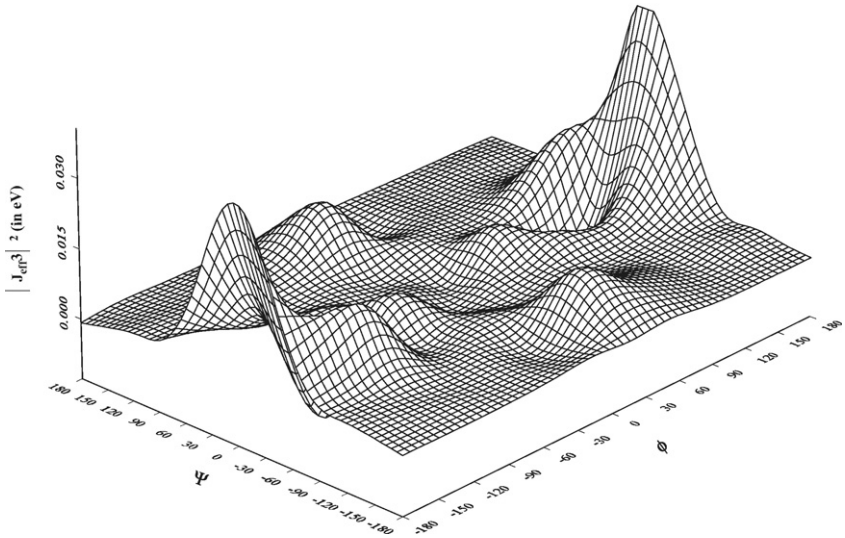


Fig. 8. The variation of square of effective charge transfer integral ($|J_{eff}3|^2$) for electron transport between the fragments 1 and 3 with respect to dihedral angles ϕ and ψ.

or LUMO's) of the neighbouring amino acids. Such a weak coupling in amino acids is already shown in literature [54]. In earlier study [2], the plot of two HOMO π-orbitals for the cationic dipeptides shows that the interaction between the peptide π-orbitals depends on the secondary structure. The electronic coupling for these peptides would be sensitive to the π-interaction controlled by the dihedral angles (ϕ and ψ) between the peptide residues. Thus, the ϕ and ψ dihedral angles which control the orientation of two adjacent peptide can control the electronic coupling between neighbouring peptides. The calculated charge transfer integral values are significantly higher than the values obtained by Baranov and Schlag [55] and Gao et al. [56] for hole and electron transfer. They have estimated the coupling values between the adjacent amino acid subgroups in the order of 0.1 eV for hole and 0.03 eV for electron transfer in peptides. The smaller coupling values may be due to the neglect of spatial overlap and lower level of theory used in the calculation.

3.4. Site-energies

The site-energies corresponding to hole and electron transport in different structures of the glycine model tripeptide are calculated as the diagonal matrix elements of the Kohn-Sham Hamiltonian and are given in Table 5S as supplementary material. The ε_1, ε_2 and ε_3 denote the site-energies of the fragments 1, 2 and 3, respectively. The calculated HOMO and LUMO energy values of the individual fragments are around -6 and -2 eV, respectively. From Table 5S, It has been observed that, even though the same amino acid subgroups are used, the site-energies are not identical for all the structure, and varies with respect to dihedral angles of the neighbouring amino acid residues. The rotations of dihedral angles change the site-energy values significantly. It has been observed that, in few cases the site-energy values are found to vary with in 2–3 eV for both hole and electron transport with respect to the rotation of dihedral angles ϕ and ψ. This difference in energy could act as a barrier for charge transfer between the amino acid residues. Baranov and Schlag [55] found that there is, in fact, a favored angle (conformation) between two neighbouring amino acids at which the site-energy remains the same and the barrier between the sites becomes negligible.

4. Conclusion

The fragment orbital method has been used to study the charge transfer in model tripeptides. The charge transfer integral for both hole and electron transport in different peptide conformers have

been calculated. The results show that the calculated electronic coupling strongly depends on the dihedral angles ϕ and ψ along the α-carbon atom of the peptide residues. The charge transfer occurs as result of reaching a favorable molecular geometry of the intermediate residues. The charge has to wait until the intermediate residues reach the particular conformation for transfer. The rotation of the Ramachandran dihedral angles makes the critical conformation for the charge transfer in peptides. The site-energies for hole and electron have been calculated as the diagonal elements of the Kohn-Sham Hamiltonian. The calculated site-energies of neighbouring amino acid subgroups are not identical. In few cases the difference in site-energy values are nearly 2–3 eV. This energy difference may act as a barrier for charge transport. The results of these calculations show that the charge transfer in peptide is more sensitive to the peptide conformations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2008.11.010.

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