Theor Chim Acta (1985) 68: 159-169

THEORETICA CHIMICA ACTA

Donor acceptor interaction in metalloproteins*

A. A. S. da Gama[1]

Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California, 91125, USA

(Received August 27, 1984, revised February 18, 1985)

This work addresses some electronic aspects of electron transfer at large distances when the donor and acceptor are attached to a polymeric structure. The transfer-matrix approach and a Green's function formalism are used to obtain an expression for the transition matrix element T_{ab}. The results are analyzed and compared with previous results obtained from related models.

Key words: Localized states — Metalloproteins — Electron transfer

1. Introduction

This work is interested in electron transfer over large distances in biological systems. In metalloproteins, for example, electron migration can take place from donor to acceptor (spacially localized states) bound to a polymeric chain.

Some aspects of electron transfer in biological systems are related to similar processes in other systems: recharging in gas-phase atomic and molecular collisions, oxidation-reduction reactions in solution or at interface with electrodes, and electron transport in the solid state. The special features of each particular system depend on the structure and interactions of the donor-acceptor pair and the surrounding medium.

The properties of biological systems are the result of the specific organization of the macromolecular structure. From the study of biological phenomena it has been established that electron transfer is unassisted by carriers [1]. De Vault has called attention to the special role of high-frequency intramolecular vibrational

---

* Work partially supported by the Brazillian Agency CNPq

[1] On leave of absence from Departamento de Física, Universidade Federal de Pernambuco, 50000, Recife, Pe, Brasil

modes (~400 cm^{-1}) on the biological electron transfer process, which is not so strongly dependent on solvent fluctuations [2].

The electron transfer theory bears a close relationship to the theories of radiationless transitions and transport of small polarons. In both of these theories a central role is played by the interaction between electronic and nuclear motion. It has been assumed that the nuclear motion is quite slow to follow the electronic motion during the process (Franck-Condon principle) [3], and there is negligible overlap between electronic wave functions of neighboring sites (the molecular crystal model) [4]. In a polymeric chain the overlap of wavefunctions belonging to neighboring sites is not negligible. On the other hand, proteins are strongly aperiodic. Localized states in proteins are induced by chemical and conformational aperiodicity.

A unified theoretical framework exists at the present to describe electron transfer processes [5]. The differences between the classical, semiclassical and quantum formulations are mainly in the way each one treats the nuclear coordinates [6]. The electron transfer rate is obtained as a product of an electronic factor and a nuclear Franck-Condon factor. For intramolecular processes the whole dependence of the rate on the donor-acceptor separation distance is attributed to the electronic interaction. The coupling of the electronic motion with the other degrees of freedom in the whole system provides thermalization which is essential for the irreversibility of the electron transfer process.

2. Formulation of the electron transfer theory

The electron transfer rate is related to the transition rate from the initial eigenstate ψ_i to the final eigenstate ψ_f of an unperturbed Hamiltonian. The transition is induced by a small interaction potential V. By using Ferms golden rule

$$k = (2\pi/\hbar) \sum_{i,f} |V_{if}|^2 \rho_f(E_i) \tag{1}$$

where V_{if} is the matrix element of the interaction potential and the sum runs over a manifold of final vibronic eigenstates, with the same energy of the thermally averaged initial eigenstate.

Within a Born-Oppenheimer approximation it is possible to write k as a product of an electronic factor and an averaged sum over overlap integrals of vibrational wave functions (Franck-Condon factor):

$$k = (2\pi/\hbar)|T_{ab}|^2(F.C.) \tag{2}$$

The electronic matrix element T_{ab} contains the distance dependence. If the initial and final electronic states are localized, and a small exchange interaction is assumed, T_{ab} decreases exponentially with the separation (R) of the two trapping sites:

$$T_{ab} \simeq A \exp(-\alpha R). \tag{3}$$

The form of A and α are model dependent. The mechanism of the process must be determined by the knowledge of the electronic structure and interactions between the two trapping sites and their surrounding medium.

The Franck–Condon factor contains the energetics of the process. It takes account of the nuclear coordinates coupled to the electronic motion. From Eq. (1), with the eigenstates represented by a product of electronic and vibrational wave functions, and an explicit expression for the density of states, one obtains:

$$(F.C.) = \left\{ \sum_{n,m} |\langle \chi_{bm} | \chi_{am} \rangle^2 \delta(E_{bm} - E_{an}) \exp(-E_{an}/kT) \right\} \Big/ \sum_{n} \exp(-E_{an}/kT). \tag{4}$$

Some important questions to be discussed within this theoretical framework are related to adiabaticity [7], Born-Oppenheimer approximation [8], Franck-Condon approximation [8, 9] and nuclear tunneling [10]. This work addresses some aspects of the electronic interaction between a donor and an acceptor bound to a polymeric chain.

3. Electronic interaction

The Robin and Day [11] classification of mixed valence compounds has been defined in terms of the time scale of some experimental measurements [12]. Three classes of compounds were identified: I-completely localized, II-partially localized, III-completely delocalized. The intermediate class (II), with weakly interacting sites, is of particular interest to the present work. In these systems the lifetime of the localized state depends critically on the electronic structure of the two trapping sites and of the bridging groups. The electronic intereaction is determined by the small overlap between the localized wave functions and the bridging groups and by the electronic delocalization through those groups. A through bond mechanism was first considered by Taube and Myers [13]. The pioneering work by Halpern and Orgel [14] discussed the through bond interaction using the mechanisms of double exchange and superexchange. Within a double exchange framework they considered extending bridging groups. The quasi-infinite 1-D periodic model for the bridging groups was applied by McConnell [15] to the problem of electron transfer between aromatic groups. McConnell assumed a very deep localized site, the energy of the localized state related to the middle of the band E much larger than the bandwidth 4β.

Localized states, induced by conformational changes, or associated with the presence of impurities or defects, are of great significance to electron transport through polymeric systems. Small concentrations of impurities or defects can modify the electronic conductivity of polymeric molecules by several orders of magnitude. Transition metal ions are found in metalloproteins in concentration of impurities. Proteins do not possess an intrinsic conductivity; their conduction states are several eV above the ground state, but there is some evidence that the protein mediates the donor-acceptor interactions [16]. Protein modification can change its conductivity by 6 orders of magnitude (for example: methylglyoxal modification at lysine residues of collagen) [17].

Brandi, Koiller and Ferreira have applied the transfer-matrix approach to study localized states on the electronic structure of polymeric molecules. It has been shown that localized states must be found in the gap region [18]. The method was applied to treat the localized state of trans-$(CH)_x$, whose conductivity is enhanced over 12 orders of magnitude due to doping [20].

The transfer-matrix approach is a very convenient method to treat the electronic interaction between two impurity sites (a donor and an acceptor) in a quasi-infinite 1-D periodic system. The result must be similar to those obtained by Petrov [16] and by Davydov [1]. The periodic approximation for the bridging groups was successful for describing the distance dependence of the electronic interaction in the mixed valence dithiaspirocyclobutane molecules [21]. The exponential decay is obtained from the transfer-function T related to the translational symmetry of the periodic bridging structure. This formalism allows us to consider, with some approximation, the results of a 1-D disordered system.

4. Model Hamiltonian

A Wannier-like one-electron Hamiltonian is considered at site representation.

$$H = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_{i,j>i} v_{ij}(a_i^\dagger a_j + a_j^\dagger a_i) \tag{5}$$

The operator $a_i^\dagger(a_i)$ creates (destroys) one electron at site i. The intersite exchange interaction v_{ij} is assumed to be different from zero only for nearest neighbors (i.e. $j = i \pm 1$). In this kind of phenomenological Hamiltonian the electron-electron interaction term is missing.

The complete Hamiltonian also contains a sum of vibrational energies, and the electron-phonon (vibronic) interaction can be accounted by the dependence of ε_i and ν_{ij} on the nuclear coordinates [9]. The influence of the vibronic coupling on the intersite interaction is discussed in another work [9b].

All matrix elements of the Green's function in the site representation can be obtained from the Dyson's equation $EG = 1 + HG$. The advantage of the Green's function formalism is that it gives direct information on transition energies and amplitudes from a reference state. From the poles of its diagonal elements the energy eigenvalues are obtained and from the residues of its off-diagonal elements the intersite interactions. The spectrum associated with the pure, one orbital per site, periodic chain is constituted by one band with bandwidth 4β (band edges in -2β and $+2\beta$), where β is defined as $\beta = v_{i,i\pm 1}$. The energy reference is setting in the middle of the band chosen by $\varepsilon_i = 0$.

5. The one impurity problem

This problem was already discussed in detail by using the transfer-matrix approach with long-range interactions [18]. The results are reproduced below in

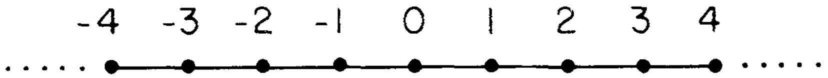

Fig. 1. One impurity site in a 1 D periodic chain

a nearest-neighbors approximation. The one impurity problem can be studied by a symmetry breaking at a site of the periodic chain. One impurity is assumed at site 0 with energy ε_0 and interaction with its nearest-neighbors $\beta_0 = v_{0,\pm 1}$ (Fig. 1).

From the Dyson's equation

$$EG_{ij} = \delta_{ij} + \sum_k H_{ik}G_{kj} \tag{6}$$

and the model Hamiltonian with nearest-neighbors interaction, a set of equations is obtained

$$\begin{aligned} (E-\varepsilon_0)G_{00} &= 1+2\beta_0 G_{10} \\ EG_{10} &= \beta_0 G_{00} + \beta G_{20} \\ EG_{20} &= \beta G_{10} + \beta G_{30} \end{aligned} \tag{7}$$

where outside the defect region, i.e. $|i|>2$, the characteristics of the periodic chain is recovered. From the third equation, and all following equations, the transfer function can be obtained by defining $G_{n+1,0} = TG_{n,0}$[18].

$$E = \beta(T^{-1}+T)$$

and

$$T = |E \pm (E^2-4\beta^2)^{1/2}]/2\beta \tag{8}$$

the following expressions for G_{10} and G_{00} are also obtained from Eq. (7)

$$\begin{aligned} G_{10} &= [\beta_0/(E-\beta T)]G_{00} \\ G_{00} &= \{E-\varepsilon_0-|2\beta_0^2/(E-\beta T)]\}^{-1} \end{aligned} \tag{9}$$

from G_{00} the energy of the localized state is determined

$$E = \varepsilon_0 + 2\beta_0^2/(E-\beta T) \tag{10}$$

and the behavior of the localized state wave function at any site n can be described by the residue of $G_{n,0}$ at the pole [19]

$$G_{n,0} = [\beta_0/(E-\beta T)]T^{n-1}G_{00} \tag{11}$$

outside the defect region $G_{n,0}$ decays with T^{n-1} as also does the wave function. The exponential decay is characterized by defining

$$\alpha = -a^{-1}\ln T \tag{12}$$

where a is the unit cell dimension of the periodic structure.

The exponential decay is characteristic of localized states in 1-D disordered systems [22]. Actually, the randomic distribution of side groups makes the protein chain a somewhat disordered system. However the fluctuation in ε_i appears to be sufficiently small and the periodic approximation has been successfully used [16].

6. The two impurity problem

The effective interaction between two impurities at sites 0 and n, with unperturbed energies ε_0 and ε_n and intersite interactions (defect recions) $v_{0,\pm 1}=\beta_0$ and $v_{n,n\pm 1}=\beta_n$, can be obtained from the results for a disordered chain [22].

$$G_{ii}=|E-\varepsilon_i-\Delta_i]^{-1} \tag{13}$$

where Δ_i, usually called "the self energy of site i)) is

$$\Delta_i=t_i^{+}+t_i^{-}$$

and

$$t_i^{\pm}=v_{i,i\pm 1}^{2}/(E-\varepsilon_{i+1}-t_{i\pm 1}^{\pm}) \tag{14}$$

is a continued fraction. For localized states the "renormalized energy expression" for Δ_i converges [23]. Quick convergence can be assumed for strongly localized states. Outside the defect region is possible to identify

$$t_i^{\pm}=\beta T^{\pm 1} \tag{15}$$

where T is the same as defined by Eq. (8).

The intersite interaction can be obtained from

$$G_{n,0}=\left[\prod_{i=1}^{n-1}(t_i^{+}/v_{i,i+1})\right]G_{00} \tag{16}$$

which gives, within the defect regions

$$\begin{aligned} G_{10}&=[\beta_0/(E-\beta T)]G_{00} \\ G_{n,0}&=\{\beta_n/(E-\varepsilon_n-[\beta_n^2/(E-\beta T)])\}G_{n-1,0} \end{aligned} \tag{17}$$

outside the defect region the translational symmetry is recovered and

$$G_{n-1,0}=T^{n-2}G_{10} \tag{18}$$

From the above relations

$$G_{n,0}=\{2\beta_0\beta_n/[(E-\varepsilon_n)(E-\beta T)]\}T^{n-2}G_{00} \tag{19}$$

which can be interpreted with an effective interaction between the two impurity sites

$$V_{n,0}=[2\beta_0\beta_n/(E-\beta T)]T^{n-2}. \tag{20}$$

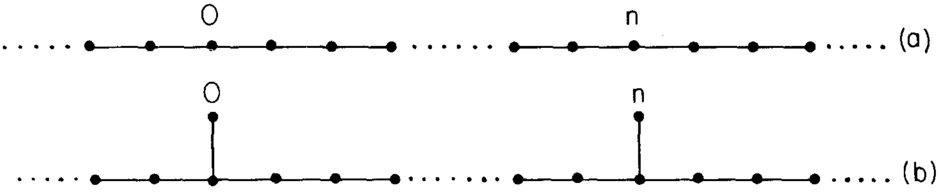

Fig. 2. Topology of the periodic chain with the impurity sites used to obtain Eq. 21(*a*) and Eq. 23(*b*)

From the previous definition of α, and using the expression for T in the denominator

$$V_{n,0} = \{4\beta_0\beta_n/[E + (E^2 - 4\beta^2)^{1/2}]\} \exp(-\alpha R) \tag{21}$$

The expression for α is the same already obtained by Davydov [1] and Petrov [16]

$$\alpha = a^{-1} \ln \{2\beta/[E - (E^2 - 4\beta^2)^{1/2}]\} \tag{22}$$

The choice of the minus sign in T was used as usual outside the band region (18, 19].

The pre-exponential factor of Davydov and Petrov can be obtained if, instead of two impurities at sites 0 and n, a donor and an acceptor are bound to each of these sites (Fig. 2b). In this case

$$V_{n,0} = [\beta_0\beta_n/(E^2 - 4\beta^2)^{1/2}] \exp(-\alpha R) \tag{23}$$

In the case of a finite chain bridging the donor to the acceptor, and with the approximation $E \ll 2\beta$, the result previously obtained by McConnell [15] is reproduced

$$V_{n,0} = (\beta_0\beta_n/E)(\beta/E)^{n-2}. \tag{24}$$

The same finite chain, with the assumption of $E = 0$ ("localized state" in the middle of the band) and even $n - 1$, reproduces Larsson's result [24]

$$V_{n,0} = \beta_0\beta_n/\beta \tag{25}$$

Both results are two times larger when the infinite chain is introduced. Within the present formalism, localization or delocalization can be defined in terms of the transfer function T. If T is real the state is localized ($|E| > 2\beta$).

7. Results and discussion

It is quite difficult to compare theoretical and experimental electron transfer rates for real biological systems. It is of particular interest to know experimental data for a donor-acceptor pair at different distances, and different pairs at the same distance, in some well-defined polymeric structure. The parameters of Eqs. (21) and (23) can be related to experimentally observable redox potentials [21], intensity and position of metal-ligand charge transfer bands [25] and to the bandwidth of the intervening band (valence or conduction band of the bridging structure).

Electron transfer rates at fixed and known distances have been measured by Gray and his collaborators in penta-amineruthenium-histidine modified ferricytochrome *c* [27] and azurin [27]. While the through space edge to edge distance is 11.8 Å in both of the proteins, the closest distance through the peptide chain in modified azurin is nearly twice that in modified cytochrome *c*. The observed rates are weakly dependent on the temperature and about fifteen times larger for modified cytochrome *c* [27]. However, the two chains are quite long (136.3 Å and 70.5 Å, respectively [28]) and the question whether through bond mechanism is effective remains open [27]. Results obtained by Isied and Vassilian [29] using polypeptides as bridging groups, suggest a through bond mechanism. The smallness of the observed rates may be partially due to the large reorganization of the nuclear coordinates at the Co site [30].

It must be observed that the bridging structure may be different from the main protein chain. Petrov [16] estimated an interaction through a secondary chain (with hydrogen bonds between polypeptide chains) assuming the same value for E but an exchange parameter five times smaller ($\beta' = \beta/5$). For a particular choice of parameters it competes with the main chain over a distance $R' \simeq R/3$ (in fact the relation is $R' = [\alpha'(\beta', \alpha')/\alpha(\beta, a)]R$). Although in principle observable, the width of conduction and valence bands of proteins cannot be obtained from experimental data. *Ab initio* calculations by Ladik, Suhai and Seel [31] estimated bandwidth of 1.4 eV (conduction) and 2.1 eV (valance) for the main chain and ten times smaller ones for a secondary chain. An interesting aspect of the present model is to make clear that the specific result for T_{ab} depends on the choice of a particular "pathway" for the electronic interaction, and on the way the donor and acceptor are attached to that one.

Some estimations of α and $T_{ab}(V_{n,0}$ in Eq. (21) and (23) are shown at Table 1 and Table 2, respectively. To analyse them, and to compare with previous results obtained from related mechanisms, the classical Halpern and Orgel [14] direct and double exchange estimations and some values for α and T_{ab} from a simple square well tunneling model are also presented. Although these models had already been widely discussed in the literature, it is interesting to reproduce the main results and to analyse the relationship with the present work.

Table 1. $\alpha(\text{Å}^{-1})$ with different choices of E and β and $a = 4.7$ Å [28]

β (eV)					
E	0.50	0.25	0.10	0.05	
1.5	0.20	0.38	0.58	0.72	0.63
2.0	0.28	0.44	0.64	0.78	0.73
2.5	0.33	0.49	0.68	0.83	0.81
3.0	0.37	0.53	0.72	0.87	0.89
3.5	0.41	0.56	0.76	0.90	0.96
4.0	0.44	0.59	0.78	0.93	1.03

Table 2. Theoretical estimated results for T_{ab} with $E = 2.5$ eV (a) and $E = 3.5$ eV (b). Calculations using Eq. (21) and Eq. (23) assume $\beta = 0.5$ eV [28] and $\beta_0\beta_n = 1$ eV [25]

R(Å)	Direct [14]	Double exchange [14]	Tunneling (a)	Tunelling (b)
5	$1.98.10^{-1}$	1.98	$1.7.10^{-2}$	$8.2.10^{-3}$
10	$2.64.10^{-3}$	$4.62.10^{-2}$	$3.0.10^{-4}$	$6.8.10^{-5}$
15	$2.64.10^{-5}$	$1.32.10^{-3}$	$5.3.10^{-6}$	$5.6.10^{-7}$
20	$1.98.10^{-7}$	$1.98.10^{-5}$	$9.2.10^{-8}$	$4.6.10^{-9}$

R(Å)	Eq. 23(a)	Eq. 23(b)	Eq. 21(a)	Eq. 21(b)
5	$8.4.10^{-2}$	$3.8.10^{-2}$	$1.6.10^{-1}$	$7.4.10^{-2}$
10	$1.6.10^{-2}$	$5.0.10^{-5}$	$3.1.10^{-2}$	$9.6.10^{-3}$
15	$3.1.10^{-5}$	$6.4.10^{-4}$	$6.0.10^{-3}$	$1.2.10^{-3}$
20	$6.2.10^{-4}$	$8.2.10^{-5}$	$1.2.10^{-3}$	$1.6.10^{-4}$

From semiclassical approximation, the transmission coefficient for an electron with energy E and momentum $\hbar k(r)$, approaching a potential barrier $V(r)$, is

$$T = \exp\left\{-\int_{-R/2}^{R/2} k(r)\,dr\right\} \tag{26}$$

where $k(r) = [2m(V(r) - E)/\hbar^2]^{1/2}$ and the integration runs over the classically forbidden region $V(r) > E$. The frequence of collision with the barrier for an electron with energy E, inside a potential well, is given by

$$\omega = \left[2m \int_{R/2}^{(R/2)+l} (\hbar k'(r))^{-1}\,dr\right]^{-1}. \tag{27}$$

From a two square well model (Fig. 3) [2, 16]

$$T_{ab} = \hbar\omega T = [\hbar^2(E - V)/2ml^2)^{1/2} \exp(-\alpha R) \tag{28}$$

with $\alpha = (2mE/\hbar^2)^{1/2}$. To compare α from Eq. (22) with this simple tunneling result, the meaning of E is assumed to be the same in the two expressions. With a frequence factor limited to 10^{-16} sec^{-1} [16] a pre-exponential factor of 1 eV is assumed to obtain T_{ab} (Table 2).

The simple model used by Halpern and Orgel [14] assumes a one electron atom A and the corresponding ion B^+ coupled by a closed shell bridging ion X^-. The initial and final states can be represented by

$$\psi_a = a^\dagger_{X\alpha} a^\dagger_{X\beta} a^\dagger_{A\alpha}|0\rangle$$
$$\psi_b = a^\dagger_{X\alpha} a^\dagger_{X\beta} a^\dagger_{B\alpha}|0\rangle \tag{29}$$

to calculate

$$T_{ab} = \langle\psi_b|V|\psi_a\rangle = \langle\phi_B\phi_X|V|\phi_A\phi_X\rangle - \langle\phi_B\phi_X|V|\phi_x\phi_A\rangle. \tag{30}$$

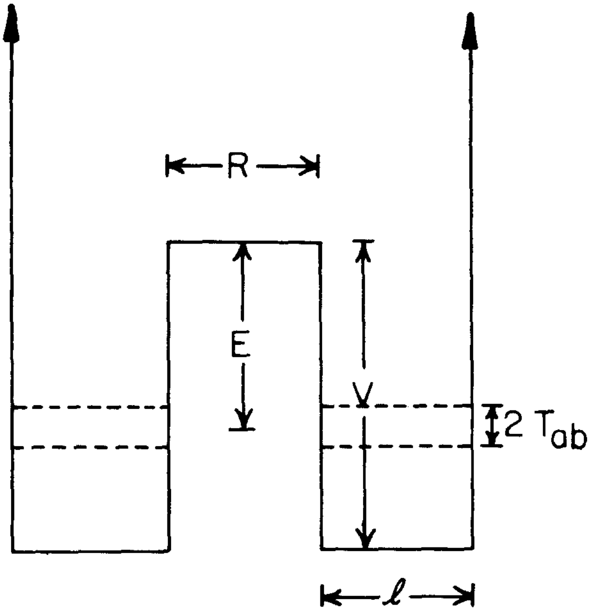

Fig. 3. The two square well model for electron transfer [2, 16]

The first term in this equation is a direct interaction between ϕ_A and ϕ_B, the second term is interpreted as a concerted double exchange interaction. It is interesting to recall that if V is a one-electron operator, and zero-differential overlap is assumed, the double exchange contribution vanishes.

The superexchange mechanism assumes a quantum mechanical admixture of excited states (virtual states) to the ground configuration. The model presented in this work, and the related ones, are basically on the superexchange mechanism. Indeed, the superexchange mechanism is closely related to the tunneling mechanism. The transfer matrix approach solves the problem of tunneling through a structured barrier, which is a model for the 1-D chain.

Acknowledgements. Thanks are due to Prof. Harry Gray for his interest and hospitality, thanks also to Dr. Nenad Kostić, David Beraktan and J. N. Onuchic for helpful discussions and comments on the manuscript.

Refernces

1. Davydov, A. S.: Phys. Stat. Solid (b) **90**, 457 (1978)
2. DeVault, D. C.: Q. Rev. Biophys. **13**, 387 (1980)
3. Kubo, R., Toyozawa, T.: Prog. Theor. Phys. **13**, 160 (1955)
4. Holstein, T.: Ann. Phys. **8**, 343 (1959)
5. Jortner, J.: Biochim. Biophys. Acta **594**, 193 (1980)
6. Marcus, R. A.: in Oxidases and Related Redox Systems. T. E. King, M. Morrison, H. S. Mason (eds.) p. 3. Oxford: Pergamon Press 1982

7. Onuchic, J. N.: Candidacy Report, California Institute of Technology (1984)
8. Beratan, D. N., Hopfield, J. J.: J. Chem. Phys. **81**, 5753 (1984)
9. a. Linderberg, J., Ratner, M. A.: J. Am. Chem. Soc. **103**, 3265 (1981). b. Onuchic, J. N., da Gama, A. A. S.: submitted to Theor Chim Acta
10. Chance, B., De Vault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N.: Tunneling in Biological Systems, New York: Academic Press 1979
11. Robin, M. B., Day, P.: Adv. Inorg. Radiochem. **10**, 247 (1967)
12. Bunker, B. C., Drago, R. S., Hendrickson, D. N., Richmond, P. N., Kessell, S. L.: J. Am. Chem. Soc. **100**, 3805 (1978)
13. Taube, H., Meyer, T.: J. Am. Chem. Soc. **76**, 2103 (1953)
14. Halpern, J., Orgel, L. E.: Discuss. Faraday Soc. **29**, 32 (1960)
15. McConnell, H. M.: J. Chem. Phys. **35**, 508 (1961)
16. Petrov, E. G.: Int. J. Quant. Chem. **16**, 133 (1978)
17. Pethig, R.: Int. J. Quant. Chem., Quant. Biol. Symp. **5**, 159 (1978)
18. a. Koiller, B., Brandi, H. S.: Theoret. Chim. Acta (Berl.) **60**, 11 (1981). b. Brandi, H. S., Koiller, B., Ferreira, R.: ibd. 89
19. de Melo, C. P., Brandi, H. S., da Gama, A. A. S.: Theoret. Chim. Acta (Berl.) **63**, 1 (1983); **65**, 91 (1984)
20. Heeger, A. J.: Comm. Solid State Phys. **10**, 53 (1981)
21. Beratan, D. N., Hopfield, J. J.: J. Am Chem. Soc. **106**, 1584 (1984)
22. Papatriantafilou, C. T.: Phys. Rev. B **7**, 5386 (1973)
23. Economou, E. N., Cohen, M. H.: Phys. Rev. B **4**, 396 (1971)
24. Larsson, S.: Chem. Phys. Lett. **90**, 136 (1982)
25. Richardson, D. E., Taube, H.: J. Am. Chem. Soc. **105**, 40 (1983)
26. Winkler, J. R., Nocera, D. G., Yocom, K. M., Bordignon, E., Gray, H. B.: J. Am. Chem. Soc. **104**, 5798 (1982)
27. Kostić, N. M., Margalit, R., Che, C. M., Gray, H. B.: J. Am. Chem. Soc. **105**, 7765 (1983)
28. Ayronnaiven, M., Mayo, S.: An average distance of 4.7 Å per amino acid residue was determined by summing the N-C and C-C (carboxylate) bond lengths of the residues of tuna ferricytochrome c from His 18 to His 33, as given by the computer graphic system, using coordinates from the Brookhaven data set, and dividing by the total number of residues. The through chain distances for modified cytochrome *c* and azurin were also obtained on the computer graphic system. Personal communication
29. Isied, S. S., Vassilian, A.: J. Am. Chem. Soc. **106**, 1726 (1984)
30. Taube, H., in Ref. 10, pp. 173
31. Ladik, J., Suhai, S., Seel, M.: Int. J. Quant. Chem., Quant. Biol. Symp. **5**, 35 (1978)