Electron Transfer

DOI: 10.1002/anie.200703177

Electron Transfer and Electronic Conduction through an Intervening Medium

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electron transfer · electronic conduction · metal–non-metal transition · proteins · semiconductors

Introduction

Electron transfer (ET) and electronic conduction through single molecules, small groups of molecules, and biomolecules, or through an intervening medium (e.g. a host solvent or semiconductor) which contain electron donor (D) and/or acceptor (A) centers, are fundamental processes in chemistry, physics, and biology.[1–18] Particularly interesting materials in this respect are doped semiconductors,[1–6] and glasses containing transition-metal ions having two valences (e.g. Fe^{2+} and Fe^{3+}).[7] Both of these two areas have been studied primarily by physicists analyzing the magnitude of the electrical conductivity of the system or material. Meanwhile, chemists and biochemists have examined single-site to single-site, donor-to-acceptor, electron transfer in liquid or frozen solutions of structured (rigid) molecular chains, in proteins, and in other biomolecules[8–14] in experiments which have given electron-transfer rate constants. An area of activity which naturally couples the two situations is single-molecule transport junctions of molecular interconnects, which conduct electrical current between two nanoscale electrodes.[15,16]

Some of the theoretical treatments[15] involve approximations to certain materials which are described herein. A further area of study which will also be analyzed is that of electron transfer in fluid solutions (or frozen solutions) between randomly dispersed D and/or A sites.[14] This list can then also be expanded to include investigations of solutions of alkali metals in liquid amine solutions, of which the metal–ammonia system is prototypical,[17] and of crystals and aqueous frozen solutions containing mixed-valent donors and acceptors, such as complexes of Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+}.[18] Results are variously reported either as electronic conductivities or electron-transfer rate constants measured over a wide temperature range. To allow meaningful comparisons, the two sets of measurements can be placed on the same footing by converting conductivities into equivalent electron-transfer rate constants.[19]

Before we analyze these different systems separately, and then attempt a broad unification, we briefly review the generally accepted theoretical framework for electron-transfer rates, both temperature dependent and independent. We especially highlight certain parameters which characterize the nature of temperature-independent electron tunneling across all these diverse experimental systems.

Theoretical Treatment of Electron-Transfer Rates

We give first the standard treatment of single-site to single-site electron-transfer rates (often denoted as k_{DA}) for tunneling between a donor and acceptor in a poorly conducting matrix, for example, a rigid organic molecular chain or protein in solution. This process is crucially important even at ambient temperature. It is conventionally analyzed by the application of the semi-classical Equation (1),[8,12,20,21] where $-\Delta G^{\circ}$ is the driving force for electron transfer between D and A and λ is the total nuclear reorganization energy required for electron transfer. Tunneling has a temperature dependence, but since the driving force $-\Delta G^{\circ}$ is opposed by λ, this term is often small and can be experimentally manipulated in some systems, see below. In other cases it has been calculated from known ΔG° and estimated λ values. The term $H_{AD}{}^2$, the tunneling transmission coefficient, is temperature independent and is proportional to $e^{-\beta r}$ where β, the decay constant for tunneling, is a parameter sensitively dependent on the electronic coupling of the donor/acceptor across an insulating tunneling energy barrier, and r is the (inter-site) distance between D and A, and T is the absolute temperature. As we shall illustrate, r has to be determined in a rather different way for a structured molecular system as compared to, for example, a disordered semiconductor, glass, or liquid system.

$$k_{DA} = \frac{2\pi}{h(\pi\lambda kT)^{1/2}} H_{AD}{}^2 \exp\left(-\frac{(\Delta G^{\circ}+\lambda)^2}{4\lambda kT}\right) \tag{1}$$

Electronic conduction in doped semiconductors, herein expressed as the equivalent electron-transfer rate constant, has a somewhat more complicated nature.[1–7] While in the above single-site to single-site electron-transfer processes in poorly conducting host systems, any "background" electron transfer involving the host medium itself is generally taken to be negligible, this is generally

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not the case in most doped semiconductors. In the systems above, the conductivity refers to a series of D/A hops, but if A on transfer becomes identical to D in energy and/or D becomes identical to A, as in a Fe^{2+}/Fe^{3+} D/A system, then conductivity is a series of single, equal steps. This is fundamentally different to the situation in doped semiconductors, such as P doped in Si, where a simple dopant can act equally in both donor and acceptor capacities. We shall refer to all examples as D/A systems for comparative purposes. In these semiconductors the electronic conductivity (equivalently electron transfer) associated with the host semiconductor itself arises from thermal excitations and takes the form given by Term (2),[4–7] where ΔE is the electronic energy gap (the band gap) of the pure host material (Figure 1), and C is a constant dependent on the medium. The conductivity of such a semiconductor is greatly affected by adding a component—a dopant—which can act either as a donor or acceptor of electrons (Figure 1). For a material which contains both donor and acceptor states (the so-called compensated situation) the conductivity expression has both a further temperature-dependent term to Term (2), representing thermal excitation of either donor, or acceptor, to or from the host conduction or valence bands, respectively.

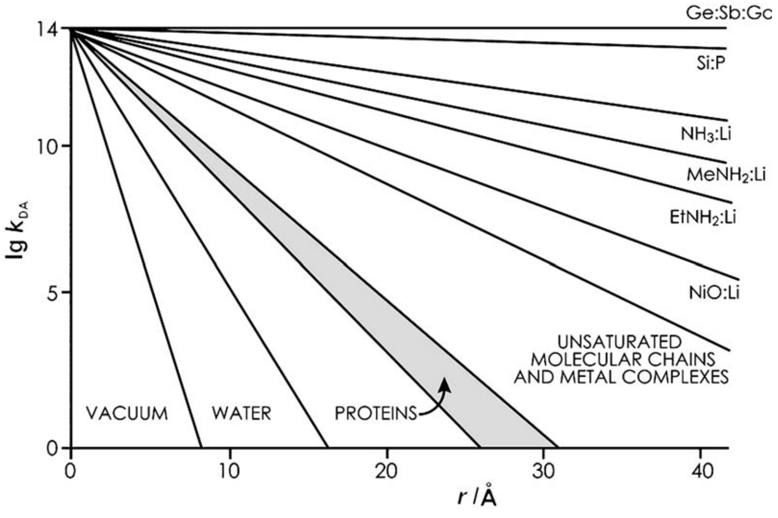

Figure 2. Summary plots of logarithms (lg) of the tunneling-electron rate constants in D/A systems against the distance of separation of D and/or A for a range of systems and materials. The theoretical slope of the line, β (=2.303 ln k_{DA}/r) is zero for a "metal" (excellent conductor) while that for a vacuum is 3.5. The plot has an arbitrary value at a limiting rate of 10^{14} s^{-1} where the D/A distance is taken as zero, see text for details.

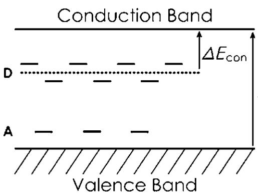

Figure 1. The energy levels of a host material showing the localized energy states of donors (D) and acceptors (A) between a filled valence band and an empty conduction band. The gap between the two bands is ΔE. The dotted line represents the intrinsic energy level for donor states, since individual sites vary in energy owing to the disordered nature of the system.

$$C\,\mathrm{e}^{-\Delta E/kT} \qquad (2)$$

Comparison of thermally activated electron transfer in D/A systems of all kinds can now be viewed as a matter of considering the concentrations of D and A and their respective thermal excitation energies together with that of the host medium, as in Figure 1. Additionally, there may also be a temperature-independent term reflecting the direct electron-tunneling process from D to D, or from D to A at low temperatures. To reflect the situation in any material or system of more than one temperature-dependent term and a tunneling term, we add terms for thermally activated processes shown in Figure 1 to those for tunneling. The tunneling-electron rate constant in Equation (1) can be expressed as Equation (3) where C' is a constant and the term $f(T)$ now takes into account the temperature dependence of tunneling. At fixed (low-enough) temperatures (when thermal excitation processes are negligible) the tunneling term ($\mathrm{e}^{-\beta r}$) will dominate. β is given by the Equation (4),[7] where m^* is the effective mass of an electron in the conduction band of the medium (for the donor state) and ΔE_{con} (con stands for connection) is the effective barrier height for tunneling, which for bulk systems is shown in Figure 1 as the donor/conduction energy band separation.

$$k_{\mathrm{DA}} = C'(\mathrm{e}^{-\beta r})f(T) \qquad (3)$$

$$\beta = (\frac{2m^*\Delta E_{\mathrm{con}}}{\hbar})^{1/2} \qquad (4)$$

Comparison with a bridged system will be given later (see Figure 3). Measurement of β and then its connection to ΔE_{con} then permit us to make direct comparison of all the different systems and materials. The experimental determination of β depends upon studying the change of electron-transfer rate with the distance between "impurity" (donor/acceptor) centers (see Figure 2).

The Distances between Transfer Centers and the Determination of β

Site-to-site electron transfer in proteins or molecular model D/A systems has been extensively studied for the case in which there is a favorable ΔG^0 between D and A, which is opposed by the reorganization energy λ [Eq (1)].[11–14] By finding temperature-independent conditions such that $\Delta G^0 = -\lambda$, the electron-tunneling rate can be evaluated. As stated in the case of impurities in lightly doped semiconductors (below the composition-induced onset of metallization),[22–24] we have determined the electron-transfer rate by utilizing experimental conductivity data at low temperatures (in certain

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cases, at temperatures close to 4 K) however, in a few cases where low-temperature data do not exist we have also used rate data (from conductivities) at moderate temperatures to give tunneling rates in systems where the temperature dependence of such rates was shown to be small, and this temperature dependence did not change significantly with the D/A concentrations, for example, solutions of lithium in liquid amines.[17]

For single-site to single-site electron-transfer systems, such as proteins or rigid molecules, in which there exist isolated D/A pairs in a known structure, the sites of the D and A are ions, such as Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+} redox-active metal complexes, or pairs of redox-active organic molecules, such as quinones. In such systems the distance of the fastest possible electron-transfer rate (ca. $10^{13}\,s^{-1}$), has been defined as that corresponding to strong overlap of the individual D and A orbitals.[11–14] In the case of isolated ions, say Cu^{+} and Cu^{2+}, this distance has been taken to be the sum of the respective ionic radii plus 3 Å.[12] For D and A which are unsaturated linked organic molecules,[11] for example, quinones, this distance has been similarly defined by the contact of edges of the frontier constituent orbitals of the whole molecules. Difficulties arise when the metal ion lies embedded within an organic molecular framework, for example, in a metal ion complex, since this framework has sometimes been thought of as providing the "edge" of D or A.[13] However, if the central metal orbitals interact poorly with the surrounding framework, then the radii of the constituent metal ions can be considered to be more appropriate for the measurement of distance.[11–13] It is clear that distance can not be accurately defined and we shall reconsider later the point of extrapolation to the fastest rate.

The treatment of distances in D/A systems in doped semiconductors and all cases of dissolved solutions, frozen or otherwise, has to be fundamentally different; in these cases identification of single-site to single-site electron-transfer rates requires the analysis of *averaged* D/A distances. To do so, we normalize all the rate data to equivalent dopant levels, so removing the dependence of rate differences on dopant amounts. We then obtain intersite distances from the cube root of these concentrations, making proper corrections for changing density with dopant concentration. The amount of dopant permitted in a given semiconductor is clearly experimentally limited by its solubility, so that in different systems and materials we must examine different concentration ranges. Furthermore, an important property of the systems is that the range of study of site-to-site transfer in doped semiconductors and some solvents is naturally limited by the eventual onset of genuine metallic conduction (that is, $\beta=0$)[3–7,22–24] beyond certain critical conditions. Mott[2,3,22] showed that the transition from non-metal to metal-like conduction in semiconductors, on varying temperature or composition of mixtures, such as those containing D and/or A dopants, occurred at a well defined concentration (equivalently D–A distance). We take this distance to be that of the optimized electron-transfer tunneling rates to which we extrapolate in Figure 2 (to a value of $10^{14}\,s^{-1}$). This distance reflects the "Mott radius", *R*, of the respective dopants, at which a semiconductor (non-metal) becomes a metallic conductor; this is the non-metal-to-metal transition (NMMT), see Table 1. We call this sum of the apparent D and A radii of the dopants at the onset of metallic character the "Mott distance", which is taken to be equivalent to the contact distance of D/A in isolated, single-site, molecular systems, described above. (Note that the wave functions of both so-called "shallow" donors and acceptors in semiconductors often extend to considerable distances into the host medium.[25–27]) A further issue is that the NMMT transition does not occur at identical electron mobilities for all materials as the electrical conductivity (rate constant) itself is sensitively dependent upon the physical properties of materials.[23,24] Accordingly, we have extrapolated the electron-transfer rate data versus distance plots to $10^{14}\,s^{-1}$ at the contact or Mott distance. So that we can compare these systems with the variety of different examples analyzed above we have displaced the optimum values for them to this limiting value, instead of the conventional value of $10^{13}\,s^{-1}$ (noted earlier). We can then easily compare the different systems by inspection and analysis of the slopes of plots, such as those shown in Figure 2. This treatment does not greatly affect the extraction of β.

The same problems arise in the analysis of electron-transfer rates in fluid solutions of, for example, lithium in anhydrous amines,[17] for example, ammonia. In these cases we have followed the same procedure as for doped semiconductors to determine *r* and β. We turn now to the way β, the slope of such plots for various systems and

Table 1: Electron-tunneling properties of materials.[a]

Material[b]	β [Å^{-1}]	*R* [Å]	m^*	ΔE_{con} [eV]
Ge:Sb:Ga	0.020	50	0.2	0.01
Si:P	0.040	15	0.4	0.03
NH_3:Li	0.15	6	ca. 1	0.2
$MeNH_2$:Li	0.20	4	ca. 1	?
$EtNH_2$:Li	0.30	?	1	?
NiO:Li	0.44	?	ca. 1	ca. 0.2
proteins	1.1	[c]	1	ca. 1.0
saturated organic liquids	ca. 1.0	[c]	1	ca. 1.0
water	1.59	[c]	1	ca. 2.0
vacuum	3.5	[c]	1	10

[a] β is the slope of $2.303\ln k_{DA}/r$ (*r* is in Å); *R* is the effective Mott radius in Å; m^* is the effective mass of the electron; ΔE_{con} is defined as the excitation energy of the donor to the conduction band, or of the HOMO/LUMO gap of the simplest molecular wire connector. [b] For doped semiconductors for example, Ge and Si, we can expect that ΔE_{con} will vary with dopant concentration. This means that β is not strictly a constant over a wide composition range. [c] Indicates that the Mott distance is not observable as it is shorter than contact between components.

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materials, can be interpreted using tunneling theory.

The Significance of ΔE_{con}

We return to Equation (4) in which ΔE_{con} is formally expressed by the energy associated with the electron passing through a tunneling barrier.[4–14] For all systems this energy is associated strongly with the energy states of the connector (either a bulk host semiconductor or a bridging molecular unit). It is an expression in quantum mechanics of the probability of transmission through the energy barrier, a barrier which is not penetrateable in classical theory. The effective barrier height in such a "bridged" molecular system is related to the energy gap between D and the lowest empty conductivity orbitals of the connector, its LUMO (Figure 3).

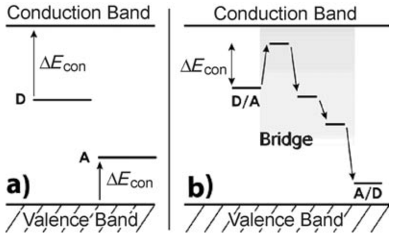

Figure 3. A diagram showing the energy-level structure of a donor D and an acceptor A placed within the band gap of a host medium. The energy gap of the host medium is ΔE (as in Figure 1). Diagram a) is for a doped semiconductor system whilst b) is for a system or material where ΔE_{con} represents the barrier height (HOMO/LUMO orbital energy gap) of, for example, a molecular bridge system. The energy level structure in (b) naturally transforms to a band picture for the "mid-gap" states for larger molecular structures. In (b) if the bridge is bent, ΔE_{con} may then refer to electron transfer/conduction through the solvent and the situation closely resembles that for (a).

The reciprocated case is for the acceptor A to be the source of tunneling by interaction with the highest occupied state of the connector, its HOMO, when conduction is by hole transfer. While the molecular "wires" may be viewed in terms of one or two dimensional orbitals[28] the protein wire is a structure in which excited orbitals in three dimensional space are anticipated. Furthermore, all these molecular units are embedded within a solvent or host medium. This solvent may also strongly interact with the connector and under these circumstances the appropriate ΔE_{con} is complex. If, for example, the molecular wire or a protein structure is bent, the shortest direct path for electron transfer between D and A may then be via tunneling through the solvent. The value ΔE_{con} in many of these cases is far from simple and has led to controversy as to how to look upon the magnitude of β.[11–13] In proteins ΔE_{con} has been estimated from their common ionization energy and this is the method used for the elucidation of transmission through solvents and glasses. In semiconductor systems ΔE_{con} has been determined experimentally by spectroscopy.[25–27]

Examples of Experimental Data

We consider first two simple cases of doped semiconductors, those based on a single semiconductor element, for example, germanium, and those based on an ionic (salt) structure, for example, NiO. A good example of electrical-conductivity measurements in doped semiconductors is provided by the work of Fritzsche and co-workers[27] of Ge doped by variable equal amounts of As an acceptor and Ga as a donor. The doped system was prepared by nuclear transmutation processes, and transport measurements were carried out at a very low temperature, 0.5 K.

The equal concentrations of dopants, obtained in that study by the transmutation route, are accurately known and conductivity is observable down to concentrations of 10^{14} dopant atoms per mole of host atoms. At the low end of this concentration range, the average distance between D and A is close to 1000 Å. Interestingly, the NMMT is observed at a concentration of around 10^{16} dopant atoms at an average distance of approximately 100 Å, that is, the expanded atomic orbitals of As and Ga and Ge (4s, 4p) overlap considerably and generate metallic conductivity at a separation between As and Ga of 100 Å. The value of β in the electron-transfer rate expression of Equation (3) is 0.020 per Å, see (Figure 2). Experimental studies show that the band energy barrier to electron tunneling for this system is very small, approximately 0.01 eV,[25] as expected since the host (semiconductor) conduction band is close to the donor levels and the dopant donor-atom states are based on quite similar energies to this band.[25] (Thermal excitation from isolated donor states to the conduction band is facile and thermally excited conduction electrons dominate the electron transfer and electronic conduction at room temperature for this type of material; $\Delta E_{\text{con}} = 0.04$ eV). There are several other examples of this kind of doped semiconductor systems where the slope β is understandably very small, for example, in Si:P,[29] before the system becomes metallic. Note that, as expected, β is larger (0.04 Å^{-1}) (Figure 2) in the Si-based system than in the Ge-based system. For Si:P, the energy barrier has been measured as 0.05 eV.[25] In this case, the Mott distance is some 30 Å. In both these cases we need to take the effective mass m^* into account in the comparison of the barrier and β value: for germanium m^* is close to a fifth of the classical mass value. On the other hand there are systems[22–24] such as expanded, supercritical Hg (which can profitably be viewed as "metal atom doped vacuum") where there is virtually no significant electronic conduction until the NMMT condition is reached on atom contact so that β is extremely large. In this case, the barrier to tunneling is very great and β is estimated as 3.5 Å^{-1}. Perhaps most interesting is the situation in high-pressure fluid hydrogen where extreme compression is necessary before metallicity sets in.[30]

Mixed-Valent Semiconductor Systems

There are a many studies of dopants in solid mixed-valent compounds including oxides, sulfides, and selenides.[22,24] We will consider only well-studied examples from both the low-conductivity oxides, the prototypical material being mixed-valent $\text{Li}^{+}_{x}\text{Ni}^{3+}_{x}\text{Ni}^{2+}_{1-x}\text{O}$,[31,32] and those of higher conductivity, such as $\text{Na}^{+}_{x}\text{W}^{5+}_{x}\text{W}^{6+}_{1-x}\text{O}_3$,[33] and $\text{Na}_x\text{W}_{1-x}\text{Ta}_x\text{O}_3$.[34] There are also studies of a variety of doped oxides of the kind

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$Fe^{2+}{}_xFe^{3+}{}_{1-x}$ in silicates and of mixed-valent crystals, for example, $(CuCl_4^-)_n(CuCl_4^{2-})_{1-n}$, in which n is varied from 0.1 to 0.5,[18] and of many doped glasses.[7] All can be included in our treatment of donor/acceptor electron-transfer systems. We confine our discussion mainly to the first two examples since data exist for measurements at low temperatures, but before we do so we note that these systems appear to be quite different from those of the doped semiconductors, such as the germanium system above. Mixed-valent metal oxides, such as Fe_3O_4, where the donor Fe^{2+} and acceptor Fe^{3+} are very close to the contact distance $r=0$ are, importantly, not metallic conductors at low temperature so that the band gap remains despite the presence of their empty 3d atomic orbitals and close proximity of the D and A states.[1,4,5] (Note that Fe_3O_4 is, however, a metal at room temperature.) From spectroscopic measurements it is clear that the empty 3d orbitals have very little interaction, remaining localized, and no metallic band forms from them in the low-temperature region. Of the cases we discuss, the doped NiO falls in this class where we expect Ni_3O_4 would be a nonmetallic semiconductor at low temperature. There are no data on doped NiO toward the limit $LiNi_2O_3$ as lithium can not be doped into NiO to give such a high concentration of Ni^{3+}. The value of β in the system of varied low doping of Li atoms is 0.44 per Å (Figure 2) and the energy barrier is around 0.1 to 0.3 eV.[31,32] The summed radii of donor and acceptor are close to the respective two ion radii (< 3.0 Å). Orbitals of first-row transition metals are more spatially extended in sulfides or selenides, as are orbitals of heavier metals of the second and third transition-metal series, even in oxides, and the metallic state can be approached in several cases. For example, ReO_3 is a metal, and this is the case also for Na_xWO_3, where the doping of WO_3 with atomic sodium has been studied at very high values of x (> 0.30).[33,34] We cannot determine β in this case, as we note that the NMMT transition has been observed only at a phase transition and there are very little data for the value of x less than 0.1.

Another different group of compounds of interest has been described by Williams and co-workers who made mixed-valence solids of complex ions, such as $(CuCl_4)_n(CuCl_4^{2-})_{1-n}$.[18] They also looked at conductivity in charge-transfer organic complexes including simple π complexes as well as mixed-radical containing matrices, such as $paraquat^+FeCl_4^-$. The conductivity on contact was very low in the lattices undoubtedly partly because of the high reorganization energy λ and deep-lying orbitals relative to a host conduction band. In no case was metallic behavior seen. The conductivity in the case of the above copper complexes varied strongly with n, indicating that β could be around 1.0 per Å. These are ionic or molecular lattices and may be perceived to have a large band gap where donors and acceptors are part of the medium.

Metal Amine Systems

We describe these systems next because they bear a close relationship to doped metal oxides.[22–24] In these cases lithium (alkali) metal doped amines are described as mixed-valent Li atom donors and Li^+ ions as acceptors. They can be studied over the complete range of behavior since lithium-doped liquid ammonia becomes a highly conducting metallic liquid at high dopant concentrations[17,35] (compare Na_xWO_3), while, interestingly, lithium-doped ethylamine does not exhibit metallic conductivity even at very high lithium concentration.[36,37] In ethylamine the electron is more greatly trapped locally[37] because the liquid does not have extensive hydrogen bonding. The temperature dependence of conductivity at 200 K for all these cases is relatively small. There are not then great differences in the temperature dependence of conductivity between the lightly doped liquid ammonia, liquid methylamine, and liquid ethylamine solutions,[37] and the major differences lie in the values of the temperature-independent conductivity. We have plotted the data, recalculated as single-electron-transfer rates at constant low temperature against dopant distances obtained from lithium concentrations for the ammonia, methylamine, and ethylamine solutions to the limit of contact, that is, to the Mott distance of 12 Å for NH_3 and 8 Å for methylamine solution and to the limit of molecular radius contact, roughly 6 Å for ethylamine in which, interestingly no NMMT is seen.[37] The β value changes from $\beta=0.15$ per Å for NH_3 to $\beta=0.2$ per Å for methylamine to $\beta=0.3$ per Å for ethylamine (Figure 2). Notably, this difference in β values for the three solvents is sufficient to give a difference of 10^2 in the single-electron-transfer rate at $r=15$ Å. The band gap for all pure host amines is large (ca. 3 eV) but lithium metal dopants have excess electron energies near the unoccupied conduction band. ΔE_{con} can be estimated by treating the Mott distance as the sum of twice the electron radii around Li^+, where the radius of the centrosymmetric electron state is related to the ionization potential by treating the electron as occupying a Bohr s orbital in a host with a dielectric constant of 10. ΔE_{con} is then estimated as 0.1 to 0.2 eV. The large differences between the amines vividly illustrate the increasing difficulty of electron transfer when going from structures with low barriers—hydrogen-bonded structures—to structures with high barriers which have only van der Waals contacts. The difference is seen in the collapse of the Mott distance. In effect methylamine and ethylamine may not behave as a simple homogeneous medium, a situation in some respects comparable to different regions of proteins.

Proteins and Molecular Wires

There are two major groups of studies of electron-transfer rates in proteins. In one study Page et al.[11] analyzed the rate of electron-transfer in the photoreaction system and its connected proteins with certain donors and acceptors at a variety of distances, r. Much of the structure of these proteins is of helices aligned along the direction of electron transfer, but even so it is surprising that such a good straight-line plot of $\log k_{DA}$ against r was obtained with a β value of 1.4 $Å^{-1}$ for a heterogeneous medium. As stated above the extrapolation was made to a rate of $10^{13}\ s^{-1}$ at an edge-to-edge contact distance of 3 Å but to get uniformity of treatment with all other data we have rearranged the plot to 0 Å (nominally)

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with a rate of $10^{14}\,s^{-1}$ using molecular D and A edges or metal-ion radii as appropriate. This approach does not markedly affect the β value. Page et al.[11] interpreted their data in terms of the local atom density of the protein medium and were not concerned with particular bond patterns between different atoms. This bulk treatment would not appear to provide a comparative understanding of the studies of systems other than proteins and we prefer to use band theory instead. In effect a bulk density treatment gives ΔE_{con} independent of any structural features of proteins and so can be related to band theory.

A definitive analysis of electron-transfer rates in proteins is that by Gray and Winkler[12] who have considered five examples of different proteins separately with deliberately positioned D/A sites on each of them so as to vary distance for each single protein. The proteins are of very different secondary structure character. Values of $\log k_{DA}$ against r extrapolated to $10^{13}\,s^{-1}$ at a metal-ion contact of 3 Å. They interpreted the results as electron transfer using pathways along atom-to-atom bonds. To facilitate comparison with other D/A systems we shall assume instead that the 3s, 3p orbitals of C, N, O and the 2s orbital of H form convoluted bands of hydrogen-bonded units (see Figure 1), these are of varying energy for hydrogen-bonded structures and for hydrophobic regions of proteins (Figure 3). The case we take first is that of the protein azurin which has a relatively homogeneous matrix structure—a barrel of β peptide strands to which D and A are bound at different distances. An excellent straight line is observed for a plot of $\log k_{DA}$ against r with $\beta = 1.1 \pm 0.1$ Å^{-1}.[12] Gray et al. have shown that the value of β is the same in crystals as in solution.[38] Herein we take the whole β-barrel to form a uniform energy band structure, on the surface of a cylindrical tube. For other proteins, Hi PIP, myoglobin, cytochrome c, and cytochrome b_{562}, the structures are far from homogeneous, although they contain hydrogen-bonded helices and other structures, and much as is to be expected there is considerable scatter around a straight-line plot of $\log k_{DA}$ against r.[12] In all the cases β falls between 1.0 and 1.2 Å^{-1} depending on the nature of the locality of D and A within the proteins and the variation of the barrier ΔE_{con} while treating them as homogeneous.

Within the context of this present analysis, it is apparent that proteins are large band gap materials, approaching 3 eV and there is no possibility of "metallic-like" conductivity even at the highest doping levels, that is, on D/A contact, as the electron and holes in D and A are strictly low-lying and localized on the constituent atoms. Moreover the dopant, D and A, energies lie far from the host conduction band, and the electrons on D and holes on A are deeply trapped away from involvement with the solvent, as is also found in some model systems. Perhaps the closest analogy is the above Li(ethylamine) system. Notice that metallic behavior will appear at high dopant concentration when any of these systems is subject to high pressure.

In rigid molecular systems, electron transfer is often through a linear series of linked groups forming a "molecular connection" between a donor and an acceptor in a solvent.[8–10,28] The degree of unsaturation of the linkers has been varied so that the D and A orbitals may or may not interact strongly with the linker.[39] In the more strongly interactive case the molecule may approach an organic metal in behavior—for example, we could consider extending unsaturated ring structures[9,39] as far as graphite which, in plane, is just metallic, or to Buckey-tubes, some of which are also metallic. As stated, the treatment of the linear molecules can be by a simple atom-by-atom analysis of orbital overlap ignoring the solvent provided the solvent has a poor interaction with the linkages and the donor and acceptor.[28] If the solvent is highly interactive with the electron-transfer unit then the treatment naturally reverts to that of a band model because the one-by-one treatment of cooperative atomic orbital overlap becomes complex. In the formulation of Equation (3), the linker molecule and the solvent will be expected to have different β values. If the solvent is water although it interacts slightly with the linkage molecule, the β value of the linker is around 1.0 (saturated) or 0.7 Å^{-1} (unsaturated dropping towards 0.1 Å^{-1} [14]).[9,39] The β value for water determined independently is 1.59 Å^{-1} [14] (see Figure 2) and hence it does not support electron transfer as effectively as C/N atom chains (compare liquid ammonia and proteins). The value for water in this respect is important, as it shows that pathways in adjacent proteins in biological systems are effectively isolated from one another by this "insulating" solvent; water is a poor medium for electron transfer, in contrast to liquid ammonia.

If a linker molecule in a solvent is bent, and the solvent itself has a smaller β value, then electron may arise through the solvent[40] and in this case the β value refers to a band of orbitals of the host solvent (as in liquid ammonia), and as it does in any system of isolated D and A in a frozen solvent. The value of ΔE_{con} has been calculated in many of the examples[9–14] and for relatively simple unsaturated chains; it is around 0.7 eV, but in extreme cases of conjugation[39] can be as small as 0.05 eV.

A particularly difficult case of a biological linker molecule is that of electron transfer in DNA, as pointed out to us by a referee. There has been much controversy over the experimental data and theory owing to the possible combined function of the bases and the medium. In such a system of transfer, referred to as "incoherent charge hopping" where vibrational dynamics could also play a role, we do not believe we can apply our analysis and the β value can not be extracted in any simple way.[41]

Finally, the electron-exchange rate, in certain mixed-valent compounds approach the fast limit so the metal ions can only be given averaged valencies, as observed for many $[Fe_nS_m]$ clusters in models as well as in proteins.[42,43] A generalized treatment of mixed-valent compounds has been given by Robin and Day.[44]

Concluding Remarks

Electron-transfer processes constitute ubiquitous and fundamental phenomenon in chemistry, physics, and biology. Indeed, the genesis of the exploration of electron transfer in the condensed phase dates back to the very origins of modern chemistry in the 19th

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century.[10,45] Furthermore, the widest definition of the metallic state is that of a substance transmitting electricity by electron transfer (equivalently electron transport) from one atom to another throughout an entire solid or liquid.[24,46] Similarly, Hoffmann[47] has enunciated ways of thinking about localized orbital interaction, with those through bonds operating over surprisingly long distances.

Herein we have made comparisons between electron-transfer processes in proteins and prototypical condensed-phase systems ranging from metal solutions to doped semiconductors. We have not been greatly concerned with temperature-dependent electron transfer which is well described in the literature in terms of the activation energy (ΔE, see [Eq. (2)]) using energy bands in solids or solvents or molecular-orbital gaps in linear molecules. We have described herein only a comparison of temperature-independent electron-tunneling rates. In Figure 2 we have plotted log k_{DA} against the donor–acceptor distance for tunneling systems for a wide variety of connecting materials, from those very close to metals, that is, $\beta \rightarrow 0$, to those very close to vacuum $\beta \rightarrow 3.5$ Å^{-1}. It is clear by inspection of Table 1, that β is related to a characteristic energy gap, ΔE_{con}, of any system or substance; this being not an activation energy, but a reflection of the electronic coupling matrix between centers. This characteristic energy can also be similar to the energy gap of the host medium and involves the effective mass of the tunneling electron, as in Equation (4).

In Figure 4 we show a collection of data for the range of materials and systems discussed herein. To take examples; if the limiting electron-transfer distances can be considered for an acceptable rate of, for example, 10^3 s^{-1}, we find that while water would only support transfer at this rate at a D/A distance of some 10 Å, proteins allow this electron-transfer rate at a D to A distance of around 20 Å.[8–14] Ammonia, with a better electron conducting ability, as judged by its lower β value, could allow effective electron transfer at a considerably larger distance of 100 Å and thus ammonia could be a damaging "biological medium" to electron transfer in proteins.

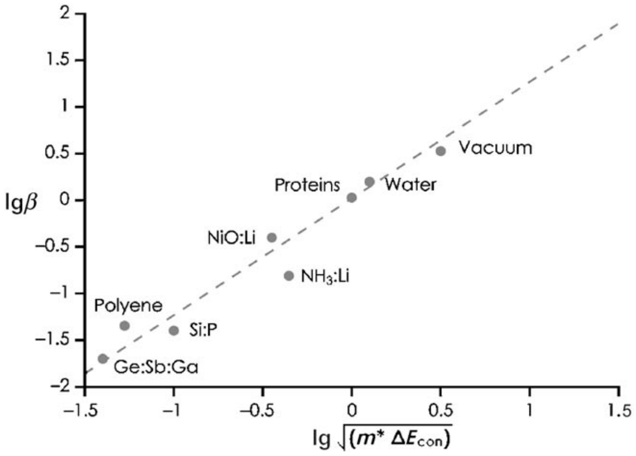

Figure 4. A plot of the log (lg) of the square root of $m^* \Delta E_{con}$ (where ΔE_{con} is described in Figure 3 and m^* is the effective mass of the electron) against lg β where β is the slope of the lines of Figure 2 (see Table 1 for the data). The point labeled polyene is taken from ref. [39].

In general, for materials with a ΔE_{con} value of 1 to 2 eV, electron tunneling may be important, even at room temperature. At the other extreme, are the fast temperature-independent electron-transfer rates at very large D/A separations, of up to 1000 Å in doped semiconductors, but this mode of conduction is overwhelmed by temperature-dependent electron conduction at high temperatures.

A significant finding from this work relates to the highly effective electron transfer and electronic conduction over large distances exhibited by doped semiconductors based on Si and Ge hosts. This situation contrasts markedly with the (relative) lack of effective long-range ($r = 20$ Å) electron transfer between localized states in many chemical and biophysical systems in which the D to A distance considerably exceeds the spatial extension of both D and A states. Of course, in the case of the doped semiconductor systems reviewed herein, the form of the distance dependence of electron transfer (Figure 2) reflects the marked spatial extension of both the D and A states into the host medium; reflecting the finding that β is a function of the interaction between D and A, and the intervening host medium. We believe that the value of such an inclusive overview is that it leads us to consider how to achieve electron transfer over longer-distances than, for example, in proteins. Two factors are clear: First, the host or intervening medium itself should have an intrinsically low β value, even when the D/A sites do not interact with it. We know that the situation in organic materials can be moved in the direction of the situation in semiconductors by tailoring extended unsaturated chain structures (to enhance intramolecular orbital mixing,[39] Figure 3 (b)). In addition, strongly hydrogen-bonded solvents structures, such as NH_3, also enhance facile electron transfer through the host medium.

The second requirement which may assist is for strong, local interactions of D/A with the medium, which, for example, can enhance electron transfer from the donor. In this case again, we have the example of Li atoms in liquid ammonia; the strong nitrogen lone pair–Li^+ interactions promote ionization of the metal 2s electron into the host liquid (an ionization process which requires significant energy in the gas phase, ca. 4 eV, but occurs spontaneously in the medium of ammonia). This is a classic example of solvent-induced electron transfer.[10]

An area of important future study then relates to a deeper understanding of the subtle balance between complete electron ionization into a host medium (to yield "excess electrons" and the possible complete chemical reduction of a solvent e.g., water), and the solvent-mediated electron transfer/interaction between active centers.

The analogy with the semiconductor systems (Figure 1) is complete if we look upon the atoms of the intervening medium as acting as "non-innocent"

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ligands to the donors and acceptors, for example, as in the case of Ga/Sb doped Ge. It is therefore a matter of designing both the ligand *and* the solvent to be non-innocent in that regard, to promote the possibility of robust and long-range electron-transfer processes such as those required in many energy-capture and energy-conversion devices.

Herein we have outlined a physical picture of the basic processes by which electrons (and holes) can transfer and transport current in a wide variety of substances and systems. Our hope is that this Essay will help in making useful connections between electron transfer and electronic conduction in matter.

We thank the EPSRC, NSF and NIH for support, Peter Watkinson for his invaluable assistance in data collection and Peter Wolynes for most helpful discussion.

Received: July 16, 2007
Revised: December 5, 2007
Published online: July 24, 2008

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