Electron donor-acceptor couples

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Two-state small-polaron models commonly used to describe an electron donor–acceptor pair are reviewed. From such models, one obtains a one-dimensional model potential. In the homonuclear case, the reaction coordinate for the potential is an antisymmetric vibrational mode. Four situations are discussed in which the two-state small-polaron models break down. Frequency shifts in a nuclear mode upon addition of an electron correspond to vibronic coupling terms in the Hamiltonian which are quadratic in the nuclear coordinate. These quadratic coupling terms lead to the coupling of a totally symmetric mode. Similarly, when an additional electron state is coupled to the donor and acceptor orbitals, at least one additional (totally symmetric) mode becomes coupled to the electronic motion. If the Condon approximation is not invoked, the donor–acceptor distance coordinate becomes coupled to the electronic transition also. The same type of behaviour in the potential occurs when the electron donor–acceptor couple is subjected to an external electric field. Implications for the optical absorption line shapes and rates of electron transfer, which can be qualitatively different from the predictions of the two-state small-polaron model, are discussed.

1. Introduction

The electron donor–acceptor couple is ubiquitous in chemical, biological and materials systems. This fundamental unit is the conceptual cornerstone in such diverse areas as mixed-valence chemistry, photosynthesis and proposed molecular devices. The recent volumes and reviews devoted to the topic of electron transfer attest to its importance (Mikkelsen and Ratner 1987, Johnson et al. 1990, Bolton et al. 1991, Newton 1991, Isied et al. 1992, Jordan and Paddon-Row 1992, Marcus 1993). The purpose of the present paper is to discuss the validity of simple one-dimensional model potentials used commonly to describe the behaviour of an electron donor–acceptor pair.

The electron donor–acceptor couple forms the basis for the understanding of the static and time-dependent properties of mixed-valence compounds (Prassides 1991).

With the characterization of the structure of the photosynthetic reaction centre within the past decade (Deisenhofer et al. 1984, Chang et al. 1986, Allen 1988), new territory was opened for the exploration of ultra-fast electron transfer at the reaction centre. Photosynthesis has been covered in detail in recent reviews (Budil et al. 1987, Deisenhofer and Michel 1989, Rees et al. 1989). The primary electron-transfer event in photosynthetic reaction centres occurs in a few picoseconds (Holzapfel et al. 1990, Kirmaier and Holten 1990, Chan et al. 1991), meaning that the system has not yet reached vibrational equilibrium (Vos et al. 1991, Lin et al. 1993).

A bridged electron donor–acceptor system was proposed as a potential molecular rectifier 20 years ago (Aviram and Ratner 1974) and thus began the quest for molecular devices. Encouraging evidence that the measured forward-bias current indeed results from a molecular charge-transfer event in just such a system was reported recently (Martin et al. 1993). Assemblies of electron donors and acceptors have been proposed

for a variety of other applications in the field of molecular electronics and nanoscale devices (Metzger and Panetta 1991, Gopel and Ziegler 1992). For instance it has been suggested (Reimers and Hush 1993) that properly optimized Brooker ions (i.e. polymethinecyanine cations, with the structure $NH_2-(CH)_{2n+1}-NH_2^+$) could be used as molecular switches with subpicosecond write times and at least microsecond data retention times.

The two-state small-polaron model is a convenient and heavily exploited model for understanding the properties of electron donor–acceptor couples. Within the framework of this model, such properties as the optical absorption line shape function and the rate constant for electron transfer may be calculated from a one dimensional potential. In the homonuclear case, the reaction coordinate of the potential function is an antisymmetric vibrational mode. This coupled vibrational degree of freedom may be either an internal vibrational mode of the couple itself, or a solvent mode, depending on the system. Totally symmetric modes are not coupled to the electronic motion within the confines of the simple two-state small-polaron models.

It has been pointed out in a number of different contexts that totally symmetric modes can in fact be important to the proper description of the properties of these systems (Hush 1982, Root and Ondrechen 1982, Ko and Ondrechen 1985, Oiepho 1988, Kuznetsov 1989). Indeed there are a variety of donor–acceptor systems for which the two-site small-polaron model breaks down completely. The present work reviews the scope and limitations of the two-state one-dimensional models and examines four cases where such models are not appropriate.

In the next section, the two-state small-polaron models are reviewed. The subsequent sections deal with four situations where such models are inadequate: quadratic coupling and frequency shifts; additional coupled electronic states; non-Condon effects; systems in an applied electric field. Discussion and conclusions are given in the final section.

2. Review of the two-state models

Two-state models for an electron donor–acceptor couple are based on models developed 30 years ago (Fulton and Gouterman 1964, Kudinov and Firsov 1965) which consist of two electronic states coupled to two harmonic oscillators with a small-polaron-type coupling.

The two-state models for the dimer system presume that only one state per site is involved in electron transfer. The Hamiltonian may be written as the sum of a purely electronic part, a purely vibrational part and a vibronic coupling part, as

$$H = H_e + H_v + H_{e-v}, \tag{1}$$

$$H_e = F_1 a_1^+ a_1 + E_2 a_2^+ a_2 + B(a_1^+ a_2 + a_2^+ a_1), \tag{2}$$

$$H_v = h_1 + h_2, \tag{3}$$

$$H_{e-v} = A_1 q_1 a_1^+ a_1 + A_2 q_2 a_2^+ a_2. \tag{4}$$

where 1 and 2 represent the two electronic basis states. One electronic state is located on each site and each electronic state is coupled to a local vibrational mode. a_i^+ is the creation operator and a_i is the annihilation operator for the ith electronic state. h_i represents the harmonic oscillator Hamiltonian and q_i represents the coordinate for the ith vibrational mode. E_i is the energy of the ith electronic basis state and B is the resonance integral which arises from the coupling between these two states. A_i is the

energy of the electron–nuclear coupling on the *i*th site. It is important to note that *A* arises from a shift in the minimum in the nuclear potential upon oxidation or reduction; that is to say the oxidized and reduced forms of the monomer have different equilibrium nuclear geometries. Therefore, if one has good X-ray diffraction data on the oxidized monomer and the reduced monomer, one can calculate the value for *A*, which is the product of *k* and $-\Delta r$. (Here *k* is the force constant and Δr is the change in bond length upon reduction.)†

A number of assumptions are contained in the above model. First of all, vibrational anharmonicities, frequency shifts, electron–electron repulsion and spin–orbit coupling are neglected. It is assumed that the coupling between the electron motion and the nuclear motion is linear in the vibrational coordinate and linear in the electron number operator. It is further assumed that two and only two electronic states are important and that the Condon approximation is valid. The last three assumptions will be discussed in detail below.

In the above model, which will be referred to as the two-site small-polaron (TSSP) model, the two local vibrational modes 1 and 2 may be transformed into two normal modes, namely a totally symmetric mode Q_+ and an antisymmetric mode q_-, given by

$$Q_+ = 2^{-1/2}(q_1 + q_2), \tag{5}$$

$$q_- = 2^{-1/2}(q_1 - q_2). \tag{6}$$

Using the transformation represented by equations (5) and (6) and the resolution of the identity in the Hamiltonian, H_{e-v} above may be rewritten as

$$H_{e-v} = 2^{-1/2}Aq_-(a_1^+ a_1 - a_2^+ a_2) + 2^{-1/2}AQ_+ \tag{7}$$

for the case where $A = A_1 = A_2$. From equation (7), one can see that only the antisymmetric mode q_- is coupled to the electronic motion, while the totally symmetric mode Q_+ has become decoupled from the electronic operators a^+ and a.

The set of equations (1)–(3) and (7) may now be solved as a one-dimensional problem in q_-. Solutions have been given previously many times, for instance by Kudinov and Firsov (1965) and by Ratner (1978). For the symmetric ($E_1 = E_2$) case, and in the adiabatic approximation, one obtains two potential surfaces given by

$$U_+(q_-) = \tfrac{1}{2}kq_1^2 + (\tfrac{1}{2}A^2q_-^2 + B^2)^{1/2}, \tag{8}$$

$$U_-(q_-) = \tfrac{1}{2}kq_-^2 - (\tfrac{1}{2}A^2q_-^2 + B^2)^{1/2}. \tag{9}$$

The lower-energy surface U_- may have a single-minimum or double-minimum form, depending on the relative sizes of the Hamiltonian parameters. One may define a smallness parameter η_1 (Holstein 1959), which in this case is approximately equal to the ratio $2k|B|/A^2$. The lower surface has a single-minimum form if η_1 is larger than unity; this corresponds to a delocalized (or valence-averaged) ground state. Likewise the lower surface has double-minimum form if η_1 is smaller that unity, and this corresponds to a localized (or valence-trapped) ground state, which undergoes temporal electron transfer. Note that, within the confines of the TSSP model shown above, the upper surface U_+ always has a single-minimum form with the minimum located at $q_- = 0$.

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† For the stretch of one bond, the parameter *A* is given by $A = -k\,\Delta r$. For the symmetric stretch about an octahedrally coordinated metal ion, the vibronic coupling parameter is given by $A = -6^{1/2}k\,\Delta r$.

These potential energy curves enable one to make crude estimates of the barrier to electron transfer, at least under special conditions. When the lower surface has a double-minimum form and $\eta_1 \ll 1$, the energy difference between the well minimum and the barrier maximum, that is the activation energy for electron transfer, is given approximately as

$$\Delta E_{act} = \frac{A^2}{4k} \tag{10}$$

for the symmetric ($E_1 = E_2$) case (Kudinov and Firsov 1965). One can also write an expression for the relationship between the activation barrier to electron transfer and the energy of the corresponding optical absorption transition as

$$\Delta E_{act} = \tfrac{1}{4} \Delta E_{opt} \tag{11}$$

again, for the symmetric case (Hush 1967).

The absorption transition from the lower to the upper surface is called the intervalence band. In the single-minimum (delocalized) ground-state case, a very narrow optical absorption band is predicted, with an asymmetric line shape, if one uses the above two-site model. This is because the minima in the upper and lower surfaces are both located at $q_- = 0$. There is some broadening on the blue side resulting from transitions to higher levels in the upper surface, because the two surfaces have slightly different effective frequencies. (The effective harmonic force constant is approximately $k + A^2/4|B|$ for the upper surface and $k - A^2/4|B|$ for the lower surface.) In general, frequency shifts (i.e. differences in the effective harmonic frequency) between two surfaces give rise to only slight broadening in the absorption spectrum, while a shift of minimum leads to substantial broadening.

When the ground state has a double-minimum form, a very broad symmetrical line shape is predicted by the TSSP model. This is because the two minima in the lower surface are displaced from the minimum in the upper surface. Therefore even at low temperatures where all the occupation in the lower surface is in the lowest level, there are many levels in the upper surface into which there will be significant Frank–Condon intensity. An expression for the width (in reciprocal centimetres) at half-maximum for the intervalence band for a homonuclear species at 300 K has been obtained by Hush (1967) using a TSSP model as

$$\Delta v_{1/2} = (2310 v_{max})^{1/2}, \tag{12}$$

where v_{max} is the frequency of the absorption maximum in reciprocal centimetres.

The complete optical absorption lineshape may be calculated by the Piepho–Krausz–Schatz (PKS) model (Piepho *et al.* 1978, Wong *et al.* 1979), which also is based on a two-site small-polaron model, as shown above.

In cases where the lower surface has a double-minimum form, the system undergoes observable electron transfer, and one may apply the theory to calculate the rate constant. Originally, electron-transfer theories were activated complex theories which treated the nuclear motion classically; later quantum mechanical treatments were given (Marcus 1956, 1965, Hush 1961, 1968, Levich 1966, Hopfield 1974, Jortner 1976, Fischer and Van Duyne 1977).†

† The dependence of the rate constant upon the exoergicity of the reaction has been an issue of particular interest. Marcus (1956) argued that log k as a function of the free energy of reaction is an inverted parabola, with the rate falling off at high exoergicity ($-\Delta G$). This fall-off is called the Marcus inverted region and has been observed experimentally (Closs *et al.* 1986).

Equation (12) and the PKS model provide some useful guidelines in the determination of the nature of the ground state (localized or delocalized) of a mixed-valence compound. If the measured linewidth equals or exceeds that predicted by equation (12), the compound is presumed to be localized and, if the observed linewidth is narrower than that of equation (12), the compound is presumed to be delocalized (Creutz 1983).

However, the Hush linewidth equation and the PKS model are sometimes applied outside the range in which they were designed for use. To understand the boundaries within which the TSSP model is applicable, one must understand its underlying assumptions. In the present review we shall examine four situations where the TSSP model is incomplete or invalid. In some cases, the additions to the above model may be regarded as perturbations on the original model and the improved predictions of the more detailed model represent small corrections to the predictions of the two-site small-polaron model. In other cases, the predicted potentials, linewidths and optical absorption profiles are qualitatively different from those of the TSSP model.

In particular, we shall look at some situations where Q_+ and other totally symmetric modes of motion become coupled to the electronic motion. When this is the case, the totally symmetric modes add to the observed linewidth and also alter (and often dominate) the shape of the absorption band.

Such coupling of additional modes to the electronic motion often enable the system to find a better path over the barrier, such that the energy of activation is smaller than that of the lower-dimensional surface. Therefore the added dimensions in the potential energy surface can sometimes lead to differences in the predicted rate of electron transfer of orders of magnitude.

3. Quadratic coupling and frequency shifts

One of the assumptions made in the TSSP model above, as expressed in equations (4) and (7), is that the electron–nuclear coupling is linear in the nuclear displacement. This assumption is widely made in electron transfer theory and is probably decent in some cases provided that nuclear displacements are small. It has been established that there are situations where terms which are higher order in the vibrational displacement cannot be neglected. For example, terms quadratic in the nuclear displacement are responsible for the vibrational dephasing process (Fischer and Laubereau 1975). In this section, recent evidence that quadratic coupling effects can be at least sometimes very important in the treatment of the electron donor–acceptor couple will be discussed.

As was mentioned in the preceding section, the A terms in equations (4) and (7) arise from the inequivalence of the equilibrium geometries of the oxidized and reduced forms. Some examples are some of the $Co^{2+/3+}$ and the $Cr^{2+/3+}$ systems, which tend to have large changes in the metal–ligand bond distances upon change of oxidation state. This is in contrast with systems such as $Ru^{2+/3+}$ ammines, which exhibit small geometry changes upon change of oxidation state (Stynes and Ibers 1971). Usually but not universally, oxidation leads to shortening of bond distances.

Generally, from empirical force-constant–bond-length scaling relations, one would expect that systems with a large vibrational displacement upon change of oxidation state would also have significant shift in frequency upon change of oxidation state.†

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† It also has been suggested that, even in systems with a small change in the bond distance upon change in oxidation state such as the $Ru(NH_3)_6^{2+/3+}$ couple, the change in frequency may be significant (Buhks *et al.* 1979).

Raman data on multiple oxidation states have demonstrated this. For example, the species $Fe(H_2O)_6^{2+}$ has a totally symmetric stretch frequency of $390\,cm^{-1}$, whereas in the corresponding oxidized species $Fe(H_2O)_6^{3+}$ the frequency increases to $490\,cm^{-1}$ (Meyer 1983). The $Co(NH_3)_6^{2+/3+}$ couple exhibits similar behaviour; the A_{1g} mode has a frequency of $357\,cm^{-1}$ for the $2+$ state and $494\,cm^{-1}$ for the $3+$ state (Schmidt and Muller 1975).

This type of frequency dependence upon electron occupation gives rise to electron–nuclear coupling terms in the Hamiltonian which are quadratic in the nuclear displacement. These additional terms may be written as

$$H'_{e-v} = A'(q_1^2 a_1^+ a_1 + q_2^2 a_2^+ a_2), \qquad (13)$$

where A' is given by

$$A' = 2k\frac{\Delta\omega}{\omega} + k\left(\frac{\Delta\omega}{\omega}\right)^2, \qquad (14)$$

where ω is the frequency of the oxidized species and where $\Delta\omega$ is the frequency shift upon reduction. For the hexaaquo iron couple, A' has the value $-0.37\,k$, where k is the harmonic force constant. A' equals $-0.48\,k$ for the cobalt hexaammine couple. Performing a normal transformation on equation (13) we obtain the quadratic coupling term as

$$H'_{e-v} = A'Q_+ q_-(a_1^+ a_1 - a_2^+ a_2). \qquad (15)$$

It is apparent from equation (15) that the totally symmetric coordinate Q_+ has become coupled to the electronic motion by the introduction of the non-zero frequency shift.

The potential energy surfaces and the optical absorption line shapes therefore are modified by the addition of equation (15) to the model Hamiltonian. These additional terms represent corrections to the PKS line shape and are especially important in the localized case, where both the linear vibronic coupling A term and the quadratic A' term are expected to be large.

There are a number of predictions pertaining to the effects of frequency shifts on the dependence of the rate upon the free-energy change in electron-transfer reactions. It has been shown that a frequency shift in a high-frequency mode can lead to anomalous dependence of the rate constant on the free-energy change (Ulstrup and Jortner 1975). In general, such a frequency shift causes the rate of reaction to fall off more slowly for higher-frequency modes when the free-energy change $-\Delta G$ is large (i.e. in the Marcus inverted region). For very-high-frequency modes, oscillations were predicted in the Marcus inverted region (Ulstrup and Jortner 1975).

Later it was argued (Kakatani and Mataga 1985) that for photoinduced charge transfer in solution of the type

$$A \ldots B \rightarrow A^- \ldots B^+$$
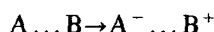
the solvent frequency is small for the neutral initial state and substantially higher for the charged final state. Nearly flat free-energy curves (i.e. logarithm of the rate constant as a function of $-\Delta G$ of reaction) in the region of large free-energy change were predicted in this case.

More recently (Islampour et al. 1993) it has been suggested that quadratic coupling terms may introduce singularities in the time correlation function for photoinduced electron transfer. If this is the case, one should be able to observe a dramatic temperature dependence, if the proper experiment can be designed.

4. Additional coupled electronic states

If the donor and acceptor states are coupled to additional electronic states, then the potential energy surfaces become dependent on at least one more nuclear coordinate. This issue is again of interest in part because of recent experimental evidence in support of earlier theoretical predictions of this effect in bridged mixed-valence compounds of ruthenium. In the present section, we return to the original TSSP model of equations (1)–(4), except that additional electronic states are added into the Hamiltonian.

Root and Ondrechen (1982) considered the case where the donor and acceptor states are joined together via a bridging species. Now 1 and 3 designate the donor and acceptor states and 2 is the coupled orbital on the bridging species, so that equation (2) becomes

$$H_e = \alpha a_2^+ a_2 + B(a_1^+ a_2 + a_2^+ a_1 + a_3^+ a_2 + a_2^+ a_3). \tag{16}$$

Here it has been assumed that the parent donor and acceptor (basis) states have equal energies and that α is the energy difference between the bridge state 2 and the two terminal states, that is $\alpha = E_2 - E_1 = E_2 - E_3$. For the moment we neglect the vibrational motion of the bridging species and consider only one mode on the donor and one mode on the acceptor. Therefore equation (4) is rewritten as

$$H_{e-v} = A_1 q_1 a_1^+ a_1 + A_3 q_3 a_3^+ a_3 \tag{17}$$

and the symmetric coordinate Q_+ and antisymmetric coordinate and q_- are now simply the sum and difference combinations of q_1 and q_3, in the manner of equations (5) and (6). Transforming equation (17) into these normal coordinates, H_{e-v} may now be written as

$$H_{e-v} = 2^{-1/2} A q_- (a_1^+ a_1 - a_3^+ a_3) + 2^{-1/2} A Q_+ (1 - a_2^+ a_2). \tag{18}$$

Equation (18) demonstrates that the totally symmetric coordinate Q_+ is no longer decoupled from the electronic motion, as it was in the simple TSSP model.

Ko and Ondrechen (1984) show that, when the electronic coupling, that is B in equation (16), is large enough that the lower surface has a single-minimum form, then the totally symmetric mode dominates the predicted line shape of the intervalence absorption band. This is in contrast with the TSSP model, where the totally symmetric mode contributes nothing to the intervalence absorption line shape.

Ko and Ondrechen (1985) also showed that in the delocalized case (i.e. the ground state has a single-minimum form), the potentials along Q_+ for the ground state and first excited state may be considered as two displaced harmonic oscillators with approximately equal force constants. Therefore the relative intensities $(P_{g,0 \to e,n'})^2$ of the transitions from the $n = 0$ level of the ground state to the n' level of the first excited state obey a Poisson distribution, given by

$$(P_{g,0 \to e,n'})^2 = \exp(-r) \frac{r^{n'}}{n'!}, \tag{19}$$

where r is proportional to the square of the displacement, as

$$r = \pi(k_+ m_+)^{1/2} \frac{\Delta Q_+^2}{h} \tag{20}$$

where k_+ is the average effective harmonic force constant for motion along Q_+ for the upper and lower surfaces, m_+ is the reduced mass of the Q_+ oscillator, ΔQ_+ is the displacement along Q_+ of the minima of the two surfaces and h is Planck's constant (Ko and Ondrechen 1985, Ondrechen *et al.* 1986).

Generally, when an electronic state on the bridging species is strongly coupled to the donor and acceptor states, there will also be at least one totally symmetric mode on the bridging ligand which will be coupled to the electronic motion. Equation (18) then must be modified to include the coupled bridge coordinate q_2 as

$$H_{e-v} = 2^{-1/2}Aq_-(a_1^+a_1 - a_3^+a_3) + 2^{-1/2}AQ_+(1 - a_2^+a_2) + A_2q_2a_2^+a_2, \qquad (21)$$

where A_2 is the vibronic coupling constant for the bridging species. In this case the total width at half-maximum for the intervalence absorption band is given by (Ko and Ondrechen 1985)

$$\Delta v_{1/2} = \pi^{-1}\left(\frac{rk_+}{m_+} + \frac{sk_2}{m_2}\right)^{1/2}, \qquad (22)$$

where k_2 and m_2 are the force constant and reduced mass of the bridge oscillator and where s is proportional to the square of the displacement Δq_2 between the upper and lower surfaces along q_2 and is given by

$$s = \pi(k_2m_2)^{1/2}\frac{\Delta q_2^2}{h}. \qquad (23)$$

One may now employ equations (20), (22) and (23) to calculate the linewidth, noting that the displacement of the minimum along q_2 is now obtained approximately as

$$\Delta q_2 = A_2(2^{-1/2}A\ \Delta Q_+ + \frac{\frac{1}{2}A^2}{k} + \alpha + 2^{3/2}B)(A_2^2 + 2^{5/2}k_2B)^{-1} \qquad (24)$$

and that the displacement of the minimum along Q_+ is now obtained approximately as

$$\Delta Q_+ = -\frac{2^{-1/2}A}{k_+} + \frac{2^{1/2}AA_2^2(\alpha + 2^{3/2}B)}{f} - \frac{A(A_2^2 + 2^{5/2}Bk_2)(2^{1/2}\alpha - 4B)}{f}, \qquad (25)$$

where f is given by

$$f = (A^2 + 2^{7/2}Bk)(A_2^2 + 2^{5/2}Bk_2) - A^2A_2^2. \qquad (26)$$

While these equations do not have the appealing simplicity of equation (12), they do permit a good estimate of the intervalence absorption linewidth from empirical data for the delocalized bridged dimer. All the parameters may be obtained from experimental data: k and k_2 of course are obtained from vibrational data; A and A_2 may be calculated from crystallographic data or estimated from spectroscopic data (Britt *et al.* 1992, Markel *et al.* 1992); α and B may be estimated from the near-infrared and visible absorption maxima.

It has been argued (Ondrechen *et al.* 1987) that the complex obtained by Creutz and Taube (1969, 1973), a pyrazine-bridged mixed-valence dimer of ruthenium with the formula $[((NH_3)_5Ru)_2(pz)]^{5+}$, is such a dimer with a strongly coupled bridge orbital. Using the model of equations (16) and (21), the line shape of the intervalence absorption band was calculated and found to be dominated by the totally symmetric modes of the ruthenium coordination sphere and the pyrazine bridge, consistent with a fully delocalized average-valence ground state. Stark effect spectroscopy (Oh and Boxer 1990) has provided strong evidence in support of the delocalization, and very recent resonance Raman work by Hupp and co-workers (Petrov *et al.* 1994) has confirmed coupling of the intervalence transition to the totally symmetric vibrational modes.

When there are electronic states in addition to the donor and acceptor states, at least one totally symmetric mode will be formally coupled to the electronic motion.

However, in the case of weak electronic coupling (i.e. small B and small η_1) in the bridged dimer, one can treat B in the Hamiltonian as a perturbation and write an effective direct coupling term (Goodenough 1966, Ratner and Ondrechen 1976) between the donor and acceptor using a superexchange (Halpern and Orgel 1960, McConnell 1961) model. Then the three-state model may be projected into a two-state model and the TSSP model is valid. However, this is a limiting case for the bridged dimer and is not valid in general.

5. Non-Condon effects

Returning to the TSSP model of equations (1)–(4), we note that B in equation (2) is assumed to be independent of the nuclear coordinates. This is called the Condon approximation and, although it is widely invoked in treatments of electron transfer, it clearly is not valid in certain situations.

Imagine a globular protein which oxidizes or reduces a substrate by direct electron transfer. Suppose that nuclear motion in the region of the protein's active site causes the relative positions of the active site and the substrate to change with time. If electron transfer can only occur when the substrate reaches a certain critical distance or orientation with respect to the active site so that orbital overlap is favourable, then in this (not unlikely) situation the dependence of the transfer integral B on the donor–acceptor distance (or orientation) is not negligible.

Consider also a mixed-valence dimer with direct through-space coupling between the two metal atoms. As the nuclei move along the totally symmetric coordinate Q_+, the distance between the two metal atoms varies with time. The transfer integral B is proportional to the overlap integral between donor and acceptor orbitals, and the overlap integral is an exponentially decaying function of the donor–acceptor distance. This is because the two orbitals are coupled directly by the overlapping tails of their wavefunctions, and the overlap is a strong function of the distance between them. Thus we may write the transfer integral B as

$$B = B_0 \exp(-cQ_+), \tag{27}$$

where c is a constant of the order of 1 Å^{-1} (Rice and Jortner 1965). Equation (2) now becomes

$$H_e = E_1 a_1^+ a_1 + E_2 a_2^+ a_2 + B_0 \exp(-cQ_+) \, (a_1^+ a_2 + a_2^+ a_1), \tag{28}$$

and therefore the Q_+ mode is now coupled to the electronic motion.

With non-Condon terms incorporated into the model as in equation (28), there are significant contributions to the lineshape in the delocalized ($\eta_1 \gg 1$) case. The predicted lineshape is less perturbed by non-Condon effects in the localized ($\eta_1 \ll 1$) case.

Non-Condon effects have been shown to be important in the calculation of rates of electron transfer depends exponentially on B, instead of exponentially on B^2 as in the recently (Kuznetsov et al. 1993) that non-Condon effects can have a substantial effect on the Gibbs free energy of activation, corresponding to a difference in the rate constant of a few orders of magnitude. This is because the system is able to move in an additional dimension, represented in the present model by Q_+, and therefore can find a path where the barrier is lower than along the path with Q_+ = constant. The system undergoes some contraction during the transfer process, in order to take advantage of the more favourable overlap in that part of dimension space (Kuznetsov and Ulstrup 1982). It also has been suggested (Franzen et al. 1993) that non-Condon effects may play a role in photosynthetic electron transfer.

Recently it has been argued that in the non-Condon scheme the rate constant for electron transfer depends exponentially on B, instead of exponentially on B^2 as in the Condon scheme, in the limit of large $|B|$. This implies that the radiative line shape will have exponential rather than Gaussian tails (Goldstein *et al.* 1993).

Non-Condon effects can be particularly important when a twisting mode, as opposed to a bond-stretching mode, is coupled to the electron tranfer process via B. This is the case, for example, in mixed-valence compounds with 4,4′-bipyridine as the bridging ligand, such as the ruthenium mixed-valence complex $[(H_3N)_5Ru–4,4′-bipy–Ru(NH_3)_5]^{5+}$ (Todd *et al.* 1993). Here the transfer integral B depends upon the cosine of the angle θ between the planes of the two six-membered rings of the 4,4′-bipy system. This corresponds to a twisting motion about the central C–C bond. Transfer is optimal when the two rings are coplanar and therefore π overlap is maximized between the two halves of the bipy species.

6. Applied electric field

The first three examples dealt with intrinsic molecular properties; the last example is a special case of a molecule subjected to an external field. In this section we shall deal with systems which fit the TSSP model when they are unperturbed and shall examine what happens when an external field is applied.

There are two principal reasons why the problem of an electron donor–acceptor couple in an applied electric field is of current interest. First of all, Stark effect spectroscopy recently has been recognized (Oh and Boxer 1990, Reimers and Hush 1991) as an important and definitive tool for the characterization and classification of mixed-valence compounds. Secondly, mixed-valence compounds, which contain one or more spatially (or temporally) delocalized electrons, may possess significant hyperpolarizabilities and thus exhibit some interesting nonlinear optical properties. Theory of the electrochromic properties (i.e. change in optical absorption as a function of applied field) of molecular electronic transitions has been given previously (Liptay 1969, Lin 1975, Varma 1978, Reimers and Hush 1991).

Suppose that a dimer which obeys the model of equations (1)–(4) is placed in an external electric field aligned along the internuclear axis, which we shall call the x axis. The molecular Hamiltonian of equation (1) may be treated as the zero-order Hamiltonian H_0 and the field may be treated as a perturbation V, as

$$H = H_0 + V, \tag{29}$$

where the perturbation operator is given by

$$V = -eE_x x, \tag{30}$$

where x is the position operator for the electron, e is a constant and E_x is the applied field. The positions of the two nuclei are given by

$$x_1 = -x_0 - q_1, \tag{31}$$

$$x_2 = x_0 + q_2, \tag{32}$$

where x_0 represents the equilibrium distance between each nucleus and the origin. On rearrangment of equation (30), a new expression for the operator V is obtained as

$$V = eE_x[x_0(a_1^+ a_1 - a_2^+ a_2) + 2^{-1/2}q_- + 2^{-1/2}Q_+(a_1^+ a_1 - a_2^+ a_2)]. \tag{33}$$

Through the last term on the right-hand side of equation (33), Q_+ becomes coupled to the electronic motion.

It recently has been shown (Murga and Ondrechen 1994) that when $\eta_1 \ll 1$ the displacement of the minima along Q_+ is directly proportional to the applied field, as

$$\lim_{\eta_1 \to 0} \Delta Q_+ = \frac{2^{1/2} e E_x}{k}, \tag{34}$$

whereas in the opposite limit ($\eta_1 \gg 1$ and $|B|$ approaching infinity) the displacement along Q_+ between upper and lower surfaces approaches zero. However, the application of the external field introduces a substantial shift of minimum between the ground and excited surfaces along the antisymmetric coordinate q_-, even in the delocalized case. Therefore considerable field-induced broadening of the intervalence band is possible.

7. Discussion

In the situations outlined above, the one-dimensional TSSP model is too simplistic to yield a proper description of the experimentally observable behaviour. All these cases have the common feature that at least one additional mode becomes coupled to the electronic motion. This coupling occurs via (often non-negligible) terms in the Hamiltonian which are absent in the TSSP model.

When the electron occupation causes shifts in the vibrational frequency, quadratic vibronic coupling terms are introduced into the Hamiltonian. These terms lead to corrections to the PKS line shape. Quadratic coupling terms can also affect the rate of electron transfer by orders of magnitude. The early predictions (Ulstrup and Jortner 1975) of anomalous dependence of the reaction rate upon the energy change may now be amenable to experimental verification, in view of the impressive advances in experimental techniques in the intervening years.

If there is a strongly coupled bridge orbital, it must be incorporated into the model Hamiltonian in order to have hope of obtaining reasonable line shape predictions. Some very recent experimental work involving complexation of bridged mixed-valence dimers with crown ethers may provide additional confirmation of the three-site model for delocalized bridged dimers. It appears that the changes in the absorption spectrum upon complexation cannot be accounted for with a two-site model but must include the bridging species (Dong *et al.* 1993, Hupp and Dong 1994).

While the formalism for handling non-Condon effects in electron transfer has been around for some time, it is only very recently that much attention has been paid to their importance in electron-transfer rates. Because an additional nuclear degree of freedom has been opened up by the inclusion of the non-constant transfer integral B, there can be differences in the predicted rate constant for electron transfer of orders of magnitude. It is now possible to study non-Condon effects systematically, since current computer technology and *ab-initio* molecular electronic structure methods now permit the calculation of integrals and energies for very large systems. One could then find the parameter c in equation (27), as well as potential energy surfaces along the coupled coordinates. In this way, predicted rates of electron transfer with and without the Condon approximation could be compared, the predicted line shape could be compared with the PKS line shape, and both sets of predictions could be compared with experiment.

Finally, molecules and materials with significant nonlinear optical properties have attracted much interest and attention recently (Marder *et al.* 1991, Kuhn and Robillard 1992). Mixed-valence species might exhibit interesting nonlinear optical responses at particular frequencies. Localized mixed-valence compounds, which like *p*-nitroaniline possess a charge-transfer excited state, can in principle have useful second-order

properties. Similarly, delocalized compounds, in which charge may be displaced symmetrically upon excitation, for example

$$M^{(n+0\cdot5)+}-B-M^{(n+0\cdot5)+} \rightarrow M^{(n+1)+}-B^{-}-M^{(n+1)+},$$
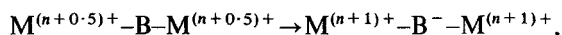
may have useful third-order properties. In order to make correct predictions of the behaviour of these complexes in an intense electric field, one must go beyond the simple one-dimensional TSSP model.

Electron-transfer reactions continue to be a rich area of investigation with many questions still to be answered and probably valuable applications still to be realized. The simple models give indispensable guidance in the understanding of these fascinating phenomena, but one must be well aware of their limitations.

References

ALLEN, J. P., 1988, *Light-Energy Transduction in Photosynthesis: Higher Plant and Bacterial Models,* edited by S. E. Stevens, Jr. and D. A. Bryant (Rockville: American Society of Plant Physiologists), p. 155.
AVIRAM, A., and RATNER, M. A., 1974, *Chem. Phys. Lett.,* **29,** 277.
BOLTON, J. R., MATAGA, N., and McLENDON, G., 1991, *Electron Transfer in Inorganic and Biological Systems,* Advances in Chemistry Series No. 228 (Washington: American Chemical Society).
BRITT, B. M., LUECK, H. B., and McHALE, J. L., 1992, *Chem. Phys. Lett.,* **190,** 528.
BUDIL, D. E., GAST, P., CHANGE, C.-H., SCHIFFER, M., and NORRIS, J. R., 1987, *A. Rev. phys. Chem.,* **38,** 561.
BUHKS, E., BIXON, M., JORTNER, J., and NAVON, G., 1979, *Inorg. Chem.,* **18,** 2014.
CHAN, C. K., DiMAGNO, T. J., CHEN, L. X.-Q., NORRIS, J. R., and FLEMING, G. R., 1991, *Proc. natn. Acad. Sci. USA,* **88,** 11 202.
CHANG, C. H., TIEDE, D., TANG, J., SMITH, U., NORRIS, J., and SCHIFFER, M., 1986, *FEBS Lett.,* **205,** 82.
CLOSS, G. L., CALCATERRA, L. T., GREEN, J., PENFIELD, K. W., and MILLER, J. R., 1986, *J. phys. Chem.,* **90,** 3673.
CREUTZ, C., 1983, *Prog. inorg. Chem.,* **30,** 1.
CREUTZ, C., and TAUBE, H., 1969, *J. Am. chem. Soc.,* **91,** 3988; 1973, *Ibid.,* **95,** 1086.
DEISENHOFER, J., EPP, O., MIKI, K., HUBER, R., and MICHEL, H., 1984, *J. molec. Biol.,* **180,** 385.
DEISENHOFER, J., and MICHEL, H., 1989, *Science,* **245,** 1463.
DONG, Y., YOON, D., and HUPP, J. T., 1993, *J. Am. chem. Soc.,* **115,** 4379.
FISCHER, S. F., and LAUBEREAU, A., 1975, *Chem. Phys. Lett.,* **35,** 6.
FISCHER, S. F., and VAN DUYNE, R. P., 1977, *Chem. Phys.,* **26,** 9.
FRANZEN, S., GOLDSTEIN, R. F., and BOXER, S. G., 1993, *J. phys. Chem.,* **97,** 3040.
FULTON, R. L., and GOUTERMAN, M., 1964, *J. chem. Phys.,* **41,** 2280.
GOLDSTEIN, R. F., FRANZEN, S., and BIALEK, W., 1993, *J. phys. Chem.,* **97,** 11 168.
GOODENOUGH, J., 1966, *J. appl. Phys.,* **37,** 1415.
GOPEL, W., and ZIEGLER, C., 1992, *Nanostructures Based on Molecular Materials* (Weinheim: VCH).
HALPERN, J., and ORGEL, L. E., 1960, *Discuss. Faraday Soc.,* **29,** 32.
HOLSTEIN, T., 1959, *Ann. Phys., (N.Y.),* **8,** 343.

HOLZAPFEL, W., FINKELE, U., KAISER, W., DESTERHELT, D., SCHEER, H., STILZ, H. U., and ZINTH, W., 1990, *Proc. natn. Acad. Sci. USA*, **87**, 5168.

HOPFIELD, J. J., 1974, *Proc. natn. Acad. Sci. USA*, **71**, 3640.

HUPP, J. T., and DONG, Y., 1994, *Inorg. Chem.*, **33**, 4421.

HUSH, N. S., 1961, *Trans. Faraday Soc.*, **57**, 557; 1967, *Prog. inorg. Chem.*, **8**, 391; 1968, *Electrochim. Acta*, **13**, 1005.

HUSH, N. S., 1982, Mechanistic Aspects of Inorganic Reactions, eds D. B. Rorabacher and J. F. (Washington, DC: American Chemical Society).

ISIED, S. S., OGAWA, M. Y., and WISHART, J. F., 1992, *Chem. Rev.*, **92**, 381.

ISLAMPOUR, R., ALDEN, G., WU, G. Y. C., and LIN, S. H., 1993, *J. phys. Chem.*, **97**, 6793.

JOHNSON, M. K., KING, R. B., KURTZ, D. M., KUTAL, C., NORTON, M. L., and SCOTT, R. A., 1990, *Electron Transfer in Biology and the Solid State*, Advances in Chemistry Series No. 226 (Washington, DC: American Chemical Society).

JORDAN, K. D., and PADDON-ROW, M. N., 1992, *Chem. Rev.*, **92**, 395.

JORTNER, J., 1976, *J. chem. Phys.*, **64**, 4860.

KAKATANI, T., and MATAGA, N., 1985, *Chem. Phys.*, **93**, 381.

KIRMAIER, C., and HOLTEN, D., 1990, *Proc. natn. Acad. Sci. USA*, **87**, 3552.

KO, J., and ONDRECHEN, M. J., 1984, *Chem. Phys. Lett.*, **112**, 507; 1985, *J. Am. chem. Soc.*, **107**, 6161.

KUDINOV, E. K., and FIRSOV, Y. A., 1965, *Soviet Phys. solid St.*, **7**, 435.

KUHN, H., and ROBILLARD, J., 1992, *Nonlinear Optical Materials* (Boca Raton: CRC Press).

KUZNETSOV, A. M., 1989, *Mod. Aspects Electrochem.*, **20**, 95.

KUZNETSOV, A. M., and ULSTRUP, J., 1982, *Phys. Stat. sol.* (b), **114**, 673.

KUZNETSOV, A. M., VIGDOROVICH, M. D., and ULSTRUP, J., 1993, *Chem. Phys.*, **176**, 539.

LEVICH, V. G., 1966, *Adv. electrochem. Eng.*, **4**, 249.

LIN, S. H., 1975, *J. chem. Phys.*, **62**, 4500.

LIN, S. H., ALDEN, R. G., HAYASHI, M., SUZUKI, S., and MURCHISON, H. A., 1993, *J. phys. Chem.*, **97**, 12566.

LIPTAY, W., 1969, *Angew Chem., Int. Ed. Engl.*, **8**, 177.

MARCUS, R. A., 1956, *J. chem. Phys.*, **24**, 966, 979; 1965, *Ibid.*, **43**, 679; 1993, *Rev. mod. Phys.*, **65**, 599.

MARDER, S. R., SOHN, J. E., and STUCKY, G. D., 1991, *Materials for Nonlinear Optics: Chemical Perspectives*, Advances in Chemistry Series No. 455 (Washington, DC: American Chemical Society).

MARKEL, F., FERRIS, N. S., GOULD, I. R., and MYERS, A. B., 1992, *J. Am. Chem. Soc.*, **114**, 6208.

MARTIN, A. S., SAMBLES, J. R., and ASHWELL, G. J., 1993, *Phys. Rev. Lett.*, **70**, 218.

McCONNELL, H., 1961, *J. chem. Phys.*, **15**, 508.

METZGER, R. M., and PANETTA, C. A., 1991, *New J. Chem.*, **15**, 209.

MEYER, T. J., 1983, *Prog. inorg. Chem.*, **30**, 391.

MEYER, T. J., and NEWTON, M. D., Eds., 1993, *Chem. Phys.*, **176** (2, 3).

MIKKELSEN, K. V., and RATNER, M. A., 1987, *Chem. Rev.*, **87**, 113.

MURGA, L. F., and ONDRECHEN, M. J., 1994, *Theor. Chim. Acta* (in press).

NEWTON, M. D., 1991, *Chem. Rev.*, **91**, 767.

OH, D. H., and BOXER, S. G., 1990, *J. Am. chem. Soc.*, **112**, 8161.

ONDRECHEN, M. J., KO, J., and ZHANG, L.-T., 1986, *Int. J. quant. Chem., quant. Chem. Symp.*, **19**, 393; 1987, *J. Am. chem. Soc.*, **109**, 1672.

PETROV, V., HUPP, J. T., MOTTLEY, C. S., and MANN, L. C., 1994, *J. Am. chem. Soc.*, **116**, 217.

PIEPHO, S. B., 1988, *J. Am. chem. Soc.*, **110**, 6319.

PIEPHO, S. B., KRAUSZ, E. R., and SCHATZ, P. N., 1978, *J. Am. chem. Soc.*, **100**, 2996.

PRASSIDES, K., 1991, *Mixed-Valency Systems: Applications to Chemistry, Physics and Biology*, NATO Advanced Study Series, Series C, Vol. 343 (Dordrecht: Kluwer).

RATNER, M. A., 1978, *Int. J. quant. Chem.*, **14**, 675.

RATNER, M. A., and ONDRECHEN, M. J., 1976, *Molec. Phys.*, **32**, 1233.

REES, D. C., KOMIYA, H., YEATES, T. O., ALLEN, J. P., and FEHER, G., 1989, *A. Rev. Biochem.*, **58**, 607.

REIMERS, J. R., and HUSH, N. S., 1991, *Mixed-Valency Systems: Applications to Chemistry, Physics and Biology*, NATO Advanced Study Series, Series C, Vol. 343, edited by K. Prassides (Dordrecht: Kluwer), pp. 29–50.

REIMERS, J. R., and HUSH, N. S., 1993, *Chem. Phys.*, **176**, 407.

RICE, S. A., and JORTNER, J., 1965, *Physics of Solids at High Pressures,* edited by C. T. Tomizuka and R. M. Emrich (New York: Academic Press).

ROOT, L. J., and ONDRECHEN, M. J., 1982, *Chem. Phys. Lett.,* **93,** 421.

SCHMIDT, K. H., and MULLER, A., 1975, *Inorg. Chem.,* **14,** 2183.

STYNES, H. C., and IBERS, J. A., 1971, *Inorg. Chem.,* **10,** 2304.

TODD, M. D., NITZAN, A., and RATNER, M. A., 1993, *J. phys. Chem.,* **97,** 29.

ULSTRUP, J., and JORTNER, J., 1975, *J. chem. Phys.,* **63,** 4358.

VARMA, C. A. G. O., 1978, *Helv. chim. Acta,* **61,** 773.

VOS, M. H., LAMBRY, J. C., ROBLES, S. J., YOUVAN, D. C., BRETON, J., and MARTIN, J. L., 1991, *Proc. natn. Acad. Sci. USA,* **88,** 8885.

WONG, K. Y., SCHATZ, P. N., and PIEPHO, S. B., 1979, *J. Am. chem. Soc.,* **101,** 2793.