Electron and Energy Transfer through Bridged Systems. 6. Molecular Switches: The Critical Field in Electric Field Activated Bistable Molecules

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Abstract: In current discussions of molecular electronics, the possibility of employing weakly coupled symmetrical bistable molecules or ions which undergo configurational change under external perturbation as molecular switches in hypothetical logic or memory circuits is receiving special attention. For the particular case of switching by an externally applied electric field the parameters determining the critical field strength at which dipole reversal occurs, and methods of calculating it at the ab initio quantum chemical level are discussed, with particular reference to recent work of Aviram. It is shown that single-determinant SCF calculations employing the electronic aufbau principle can give rise to an artefactual result and may lead to code-dependent overestimation of the critical field strength by an order of magnitude.

Partly owing to the increasing interest in molecular electronics,[1-3] the properties of double-well ions or molecules which can, in principle, be switched from one configuration to another by an external perturbation are receiving increasing attention. The configurational change may involve, for example, conformational change or electron transfer, and the perturbation could be optical or electrical. It is clearly important, in this context, to be able to relate the magnitude of the perturbation to probability of configurational change or switching.

As a preliminary to more detailed discussion, we discuss here some basic aspects of this problem for electric field activated intramolecular configurational change, induced by electron transfer, specifically for symmetrical double-well molecules or ions. These will typically be of the form D-B-A, in which a donor D state is linked to an acceptor A state through a bridge B and which under suitable perturbation will switch to configuration A-B-D. We consider either one-electron or hole transfer, so that the systems will be open-shell.

Although the problem is a general one, it is useful to discuss it in relation to a particular class of molecules; this will enable us to make direct comparison with other approaches. In particular, we consider systems in which electron coupling through the bridge B is of σ through-bond type and discuss these in relation to the recent interesting work of Aviram.[2]

σ-Bridged Bistable Molecules

Electron- or hole transfer facilitated by through-bond coupling via σ-type bridges has only comparatively recently begun to be studied theoretically in detail,[4-10] although important pioneering work was carried out by McConnell in 1961.[11] There is also increasing experimental interest—inter alia, studies of donor-acceptor systems rigidly linked via rigid σ-type hydrocarbon bridges of systematically varying length have provided useful data for comparison with theory: both photoexcited[12] and ground-state (negative ion) transfers[13] have been shown to be rapid even at quite large donor-acceptor separations provided that the geometries of attachment to the bridge and the internal bridge structure is such as to permit appreciable electron overlap. Conversely, where orbital orthogonality prevents such overlap, transfers are expected to have vanishingly small rates. This is expected to be a general phenomenon. An interesting case in point is that of the bis(pentaammine ruthenium)(5+) complexes of dithiaspiroalkane ligands (Figure 1) studied by Taube and Stein.[14] These are trapped-valence complexes, and analysis of the observed intervalence absorption showed that thermal hole transfer will be rapid even at the large metal-metal separation of Figure 1. A theoretical analysis of coupling through ligands of this type by Rendell, Bacskay, and Hush[15] reveals the dependence of metal-metal coupling and hence rate on (inter alia) the angle θ between the Ru-S bond and the thiacyclobutane ring. The transferring Ru hole has local d_π symmetry, and metal-metal coupling via these orbitals will be zero if this angle is zero. In fact, as discussed in ref 14, near-pyramidal coordination of Ru to S is to be expected in complexes of the above kind, so that through-bond coupling does not vanish by symmetry, in agreement with observation. However, the possibility of modulating the through-bridge coupling by, for example, steric constraint of the out-of-plane angle θ should be noted.

The possibilities for tuning of electron coupling via this kind of through σ-bond interaction have encouraged Aviram[2] to consider the properties of hypothetical molecular switch assemblies in which linkage is via a spiro carbon bridge. An example is given in Figure 2. Given the possibility of fabrication of devices incorporating molecular switches, design, in principle (cf. ref 2),

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Figure 1. Mixed-valence bis(ruthenium pentaammine) complex of four-ring dithiaspiroalkane (cf. refs 14 and 15).

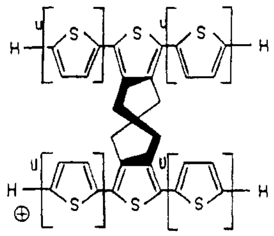

Figure 2. Aviram's example of a system with possible hole transfer between two π-chains linked by a σ-type bridge containing a central spiro atom, which forces the two π-systems to be mutually perpendicular (after Figure 2 of ref 2).

of logic and memory elements based on these is also possible and has been frequently discussed. However, the conditions for operation by applied electric fields have not been discussed in any detail.

In order to investigate computationally the basic physics of such a system, Aviram considered the simpler model (A) of an allyl/allyl anion pair linked at a twist angle of 90° via an uncoiled *n*-butane bridge (Figure 3a). An even simpler model was also considered (Figure 3b): this is simply model A with the central bridge replaced by two hydrogen atoms.

By using the unrestricted Hartree–Fock approach with an STO-3G basis, Aviram calculated the effects of applying a parallel electric field to the two configurations of model A, with the electron initially localized on either the left or right allyl framework. Aviram used a central carbon atom separation $R_{C\cdots C}$ of 12.7 au (cf. Figure 3b). It was found that for one orientation the energy decreases monotonically with increasing field, preserving the original dipole moment, while for the alternative orientation, the energy rises in a mirror-image fashion, with opposite dipole, until a critical field is reached, at which point there is collapse to an energy close to that of the first at an identical field strength and with reverse dipole moment. Thus the system exhibits switching at a critical field strength which we call F_c. Similar behavior was found for model B with the same radical/ion separation.

The value of the critical field F_c for model A was calculated as 0.0055 au and for the simpler model B the closely similar value of 0.0065 au. We now address the analysis of the field effect and the interpretation of these results. Note that in model B, the idealized geometry in which radical and anion have the same internal coordinates has symmetry D_{2d}: in reality, however, the radical and anion will have slightly different geometries so the symmetry of model B reduces to C_{2v}. Note also that although atomic 2pπ orbitals on the central carbon atoms perpendicular to the radical/anion framework are strictly orthogonal, the overlap of molecular nonbonding orbitals (with zero coefficient on the central carbon) is symmetry allowed both in D_{2d} and C_{2v} symmetry, so that electronic interaction between the two species is anticipated to be small but nonzero.

Model Hamiltonian

Model B contains the essence of the problem, and we shall henceforth concentrate on this, proceeding in two stages. Firstly, a model Hamiltonian, which considers explicitly only the transferring electron and its vibrational coupling to allyl radical/anion modes, is set up. This provides a framework for the basic physical interpretation of the electric field effects. Secondly, ab initio calculations are carried out, and the results are related to the model parameters. The problem is essentially identical with that of calculation of ground and excited states of perturbed symmetrical mixed-valence molecules.[16,17]

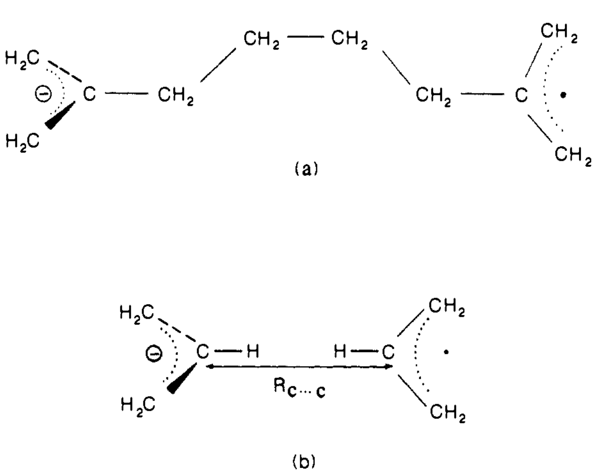

Figure 3. Simple models of donor–acceptor pair (with allyl anion as donor and allyl radical as acceptor) at 90° orientation (a) with *n*-butyl bridge and (b) no bridge. These are models A and B, respectively, of ref 2. Calculations in the text are for (b) with $R_{C\cdots C}$ = 6.72 Å (12.7 au) or 3.17 Å (6.0 au). Ground-state geometries are optimized at the SCF STO-3G UHF/RHF levels (see text).

The differences in geometry of the allyl radical and anion species can, to a very good approximation, be attributed to linear electron-vibrational interaction; thus the Hamiltonian for the transferring electron can be expressed in a usual form for mixed-valence systems (in atomic units au), with the origin at the midpoint of the line joining the nearest carbon atoms in the fragments a and b as

$$\mathcal{H} = (n_a + n_b)E_{oa} + (n_a - n_b)\mathbf{F}\cdot\mu + J(c_b{}^\dagger c_a + c_a{}^\dagger c_b) + \sum_l \frac{\omega l}{4}\sum_{i=a}^{b}(Q_{li}{}^2 + \dot{Q}_{li}{}^2) + \sum_l\sum_{i=a}^{b} g_l n_i Q_{li} \quad (1)$$

where E_{oa} is the energy of an electron in ψ_a (in zero field and with identical geometries this is identical to E_{ob}); the localized wave functions ψ_a and ψ_b are assumed to be orthonormal. The electronic coupling integral is J (a constant within the Condon approximation); $c^\dagger$ and c are site electron creation and annihilation operators, respectively, and $n_i = c^\dagger c$ is the occupation number for site i; the linear electron-vibrational coupling constant is denoted by g_l; Q_{li} is the dimensionless one-dimensional coordinate for the vibrational mode of frequency ω_l at site i. The (unnormalized) boson operators are defined as $Q = (b_i{}^\dagger + b_i)$ and $\dot{Q} = i(b_i{}^\dagger - b_i)$ in a usual notation, and the applied uniform electric field is $\mathbf{F}$. In the present application we are concerned with a field directed along the C_{2v} symmetry (z) axis, and we define a localized axial dipole (in atomic units) as

$$\mu_z = -l_z(\text{eff}) \quad (2)$$

where l_z(eff) is the absolute value of the distance from the origin to the one-electron equivalent of the charge center of the allyl anion.

Model B has D_{2d} symmetry in the absence of electron-vibrational interaction ($g_l = 0$). Of the symmetric (s) and antisymmetric (u) linear combinations of the local modes ln

$$q_{sl} = 2^{-1/2}\,(Q_{la} + Q_{lb}) + 2^{1/2}g_l/\omega_l \quad (3)$$

$$q_{ul} = 2^{-1/2}(Q_{la} - Q_{lb})$$

only displacements induced in antisymmetric modes contribute to the symmetry lowering. In these D_{2d} symmetry-adapted coordinates, the Hamiltonian can be rewritten as $\tilde{\mathcal{H}}$, where

$$\tilde{\mathcal{H}} = (n_a + n_b)E_{oa} - (n_a - n_b)F_z l_z(\text{eff}) + J(c_b{}^\dagger c_a + c_a{}^\dagger c_b) - \sum_l g_l{}^2/2\omega_l + \sum_l \frac{\omega_l}{4}\,(q^2{}_{sl} + \dot{q}^2{}_{sl}) + \frac{\omega_l}{4}\,(q^2{}_{ul} + \dot{q}^2{}_{ul}) + \sum_l 2^{-1/2}g_l(n_a - n_b)q_{ul} \quad (4)$$

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(16) Hush, N. S. In *Mixed-Valence Compounds*; Brown, D. B., Ed.; Boston, MA, 1986; p 151 and references therein.

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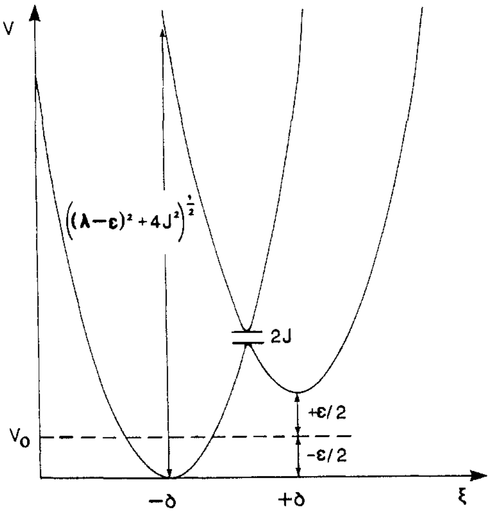

Figure 4. Potential energy surfaces for model of Figure 3b in the presence of axial electric field F_z according to eq 5. The energy quantity ϵ is $2F_zl_z$(eff); λ is the reorganization energy, and J is the electronic coupling integral. Right- and left-hand potential minima are located at $\pm\delta$, respectively.

Decoupling of the symmetrical vibrations now occurs, and these modes are not further considered. For the present illustrative purpose, it is sufficient to consider the case of one effective coupling mode, essentially the symmetric C–C–C stretch of either the allyl radical or the anion, the frequencies of which can be taken as identical in this approximation. The potential energy surfaces for coupling with one unsymmetrical mode ω and dimensionless coordinate $q_{\rm u}$ are then given by

$$V_\pm(q_{\rm u}) = E_{0{\rm a}} + \frac{\omega {q_{\rm u}}^2}{4} - \frac{g^2}{2\omega} \pm ((gq_{\rm u} - F_zl_z({\rm eff}))^2 + J^2)^{1/2} \quad (5)$$

Transforming from dimensionless quantities, we write the normalized displacement coordinate as $\xi = (\hbar/2\mu\omega)^{1/2}q_{\rm u}$, where μ is the reduced mass of the oscillator with force constant $k = \mu\omega^2$, and the electron-phonon coupling constant as $g' = g(2\mu\omega/\hbar)^{1/2}$. For weak electronic coupling, as in the systems of interest here, the lower potential surface possesses two zero-field energy minima, with coordinate displacements $\pm\delta = \pm g'/k$. It is convenient to introduce the reorganization energy λ, the energy separation between upper and lower surfaces at $\xi = \pm\delta$ and zero field; this is given by $\lambda = 2(g')^2/k$. (Note that for the general case, the total reorganization energy $\lambda_{\rm tot}$ is $\sum 2(g'_l)^2/k_l$, summed over all modes l with coupling constants g'_l). For simplicity we change the energy origin to that of the minima of the field-free lower surfaces and write u_zF_z as $-\epsilon/2$. With these conventions (indicated by primed quantities) the potential energy surfaces are given by

$$V'_\pm(\xi) = \frac{k\xi^2}{2} + \frac{\lambda}{4} \pm ((g'\xi - \epsilon/2)^2 + J^2)^{1/2} \quad (6)$$

and are illustrated in Figure 4.

We take the initial-state configuration to be that corresponding to $\xi = +\delta$, i.e., with the electron initially located on the right-hand allyl moiety. The energy at the initial configuration is then given by

$$V'_\pm(+\delta) = \frac{\lambda}{2} \pm \left(\left(\frac{\lambda}{2} - \frac{\epsilon}{2}\right)^2 + J^2\right)^{1/2} \quad (7)$$

This is illustrated in Figure 5, where the potential energy of the ground (−) and excited (+) states are shown as functions of the axial field strength F_z. The zero-field separation is $[\lambda^2 + (2J)^2]^{1/2}$, and, at the critical field F_z(crit), these surfaces are separated by $2J$ and the dipole moment changes sign. For small values of the ratio J/λ, the gradients $dV_\pm/dF_z$ are $\pm l_z$(eff) except in the immediate vicinity of F_z(crit), provide that the field strengths are below those for which quadratic effects are significant. In general, the ground-state electronic eigenfunction $\Psi_-(\xi)$ is given by

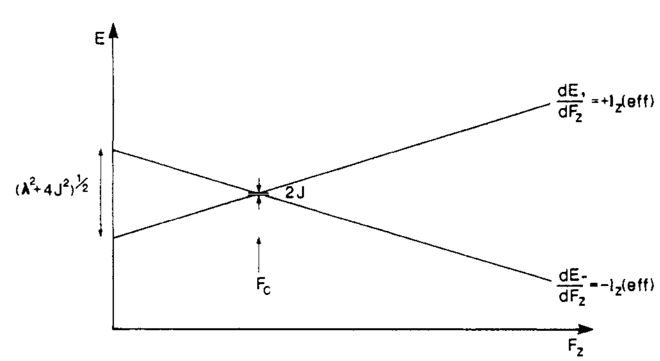

Figure 5. Ground-state (E_-) and excited state (E_+) energies for system of Figure 3b as a function of axial field strength F_z according to eq 5. Critical field is F_c.

$$\Psi_-(\xi) = c_1(\xi)\psi_{\rm a} + c_2(\xi)\psi_{\rm b} \quad (8)$$

where, for the potential of eq 6,

$$c_1(\xi)/c_2(\xi) = \frac{-J}{g'\xi - \epsilon/2 + ((g'\xi - \epsilon/2)^2 + J^2)^{1/2}} = -\eta(\xi) \quad (9)$$

At the initial-state configuration $\xi = +\delta$,

$$\eta = \frac{-J}{\lambda/2 - \epsilon/2 + [(\lambda/2 - \epsilon/2)^2 + J^2]^{1/2}} \quad (10)$$

hence

$$c_1 = \frac{-\eta}{(1 + \eta^2)^{1/2}} \quad (11)$$

In Figure 6, the ground-state potential energy and the absolute value of the amplitude c_1 are plotted as a function of ϵ/λ (i.e., $2l_z({\rm eff})F_z/\lambda$) for a value of $2J/\lambda$ of 0.10 at the initial-state configuration $\xi = +\delta$. This shows the sharp amplitude reversal with accompanying dipole switch in the vicinity of $\epsilon/\lambda = 1$.

Ab Initio Calculations

We now turn to the ab initio calculation of the potential energy surfaces and eigenfunctions of the diallyl radical anion. As in Aviram's study, the geometries of the allyl radical and anion monomers are separately optimized at the unrestricted (UHF) and restricted (RHF) levels of theory, respectively, by using the STO-3G basis of Hehre, Stewart, and Pople.[18] The diallyl system B, where the allyl planes are perpendicular to each other, has the symmetry C_{2v}, and in the absence of a perturbing field, the electronic configurations of ground and first excited states $\Psi_{\rm I}$ and $\Psi_{\rm II}$ (both of symmetry A_2) can be written as

$$(1{a_1}^2 ... 12{a_1}^2\ 1{b_2}^2 ... 5{b_2}^2\ 1{b_1}^2 ... 5{b_1}^2)\ 1a_2({\rm I})^1\ 2a_2({\rm I})^2$$

and

$$(1{a_1}^2 ... 12{a_1}^2\ 1b_{22} ... 5{b_2}^2\ 1{b_1}^2 ... 5{b_1}^2)\ 1a_2({\rm II})^1\ 2a_2({\rm II})^2$$

respectively. For the ground state represented by $\Psi_{\rm I}$, the $1a_2$(I) molecular orbital (MO) is localized on the radical, while the $2a_2$(I) MO is localized on the anion. The excited state represented by $\Psi_{\rm II}$ is generated by electron transfer from the anion to the radical—i.e., it corresponds to a radical/anion pair in which the geometry of the radical is that of the anion and vice versa. The a_2 MO's in $\Psi_{\rm II}$, viz. $1a_2$(II) and $2a_2$(II) are therefore strongly localized on the new radical and anion fragments, respectively. As $\Psi_{\rm I}$ and $\Psi_{\rm II}$ are represented by single Slater determinants, the two wave functions are expanded in terms of independently optimized orbitals, so that strictly speaking the a_1, b_1, and b_2 MO's should also be labeled by I and II by analogy with the a_2 MO's. Note that $\Psi_{\rm I}$ and $\Psi_{\rm II}$ are the many-electron analogues of the localized one-electron wave functions $\psi_{\rm a}$ and $\psi_{\rm b}$ defined in the previous section. Also, in the last section these localized functions were taken to be orthogonal: at distances considered here overlap integrals will be so small that we shall not in practice need to correct for nonorthogonality in applying eqs 10 and 11.

The SCF energies were calculated both by the UHF and RHF methods, by using the CADPAC[19] and MOLECULE[20-22] programs. As the

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[18] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

Table I. Ab Initio Data (in au) for Allyl$^-$Allyl Radical System [Model B (Figure 3b)] with Axial Perturbing Electric Field[a]

	$R = \infty$			$R = 12.7$			$R = 6.0$		
	STO-3G/UHF	STO-3G/RHF	DZ/RHF	STO-3G/UHF	STO-3G/RHF	DZ/RHF	STO-3G/UHF	STO-3G/RHF	DZ/RHF
E_I	-229.8927	-229.8472	-232.7948	-229.8931	-229.8477	-232.7958	-229.8428	-229.7979	-232.7522
E_{II}	-229.8805	-229.8401	-232.7912	-229.8809	-229.8405	-232.7920	-229.8295	-229.7896	-232.7473
$E_{II} - E_I$	0.0122	0.0071	0.0036	0.0122	0.0072	0.0038	0.0133	0.0083	0.0049
dE_I/dF_z				7.28	7.29	7.27	3.57	3.51	3.50
dE_{II}/dF_z				-7.48	-7.51	-7.54	-3.80	-3.80	-3.83
l_z(eff)				7.38	7.40	7.41	3.69	3.66	3.67
F_z(crit)				0.00082	0.00048	0.00025	0.0018	0.0012	0.00066
$\lambda/2l_z$(eff)				0.00083	0.00048	0.00026	0.0018	0.0011	0.00066

[a] $C_2H_5^-$ energies: -114.8384 (STO-3G), -116.3808 (DZ).

$1a_2$ and $2a_2$ orbitals are strongly localized—i.e., their respective constituent atomic orbitals have negligible overlap with each other—the single-determinant wave functions for the two states can be readily calculated by the standard SCF iterative procedure provided the appropriate localized starting orbitals are used, and in each iteration the occupied orbitals are selected by the criterion of maximum overlap with the starting set. This type of procedure is used very widely in the calculation of excited hole state wave functions, especially for core hole states.[23-25] The finite field calculations are performed in the same spirit; viz. in the course of the SCF iterations, maximum overlap is maintained with the starting MO's, which are those from a lower or zero-field wave function, of the ground and excited $^2A_2$ states, respectively. Calculations were carried out for two $R_{C\cdots C}$ distances, 12.7 au (6.72 Å), the distance used by Aviram (as read from Figure 3 of ref 2), and a shorter distance of 6.0 au (3.17 Å). The results of the UHF and RHF calculations are summarized in Table I.

In addition to the STO-3G basis used to optimize the allyl geometries, a double-ζ (DZ) basis[26] was also used so that some information on basis set effects can be gained. The field dependence of the energies corresponding to the two states I and II, as described by the gradients of the energy with respect to the perturbing field and by the critical field F_z(crit), is also shown in Table I. The most noticeable effect of variation of basis set and/or method is on the energies, absolute as well as relative, of the ground and first excited states, which, according to the model discussed in the previous section, also affect the critical axial field F_z(crit) at which electron transfer is predicted to occur. The variation of energy with axial field strength, as anticipated, is very nearly linear. The small, effectively constant, difference between the magnitudes of the gradients of the energies E_I and E_{II} with respect to the applied field is attributed to the small difference in the magnitude of the dipole moment of the two states as a result of the difference in radical and anion geometries. The effective length l_z(eff) has been calculated from the average of the absolute values of the energy gradients with respect to field strength, and, as the results indicate, the actual calculated values of F_z(crit) are in good agreement with those calculated by the model, according to which F_z(crit) = $\lambda/2l_z$(eff). The calculated effective lengths are, as anticipated, larger than half the closest C–C separation $R_{C\cdots C}$, as the center of gravity of the anion charge distribution is larger than this. It is useful to verify this by a direct calculation. At $R_{C\cdots C}$ = 12.7 au, a large separation, it is reasonable to calculate the field strength at the origin due to the allyl anion charge distribution as arising from a set of point charges q_i, as defined by a Mulliken analysis,[27] where the position vector of the ith atom is r_i, i.e.,

$$\mathbf{F} = \sum_{i(\text{anion})} \frac{q_i r_i}{r_i^3} \qquad (12)$$

and summation is over the net atomic charges of the anion. At the STO-3G/UHF level, the calculated axial field is then 0.167 au; this corresponds to a value of 7.38 au for l_z(eff) and is consistent with the estimate of 7.38 au from the gradients of the energy with applied field.

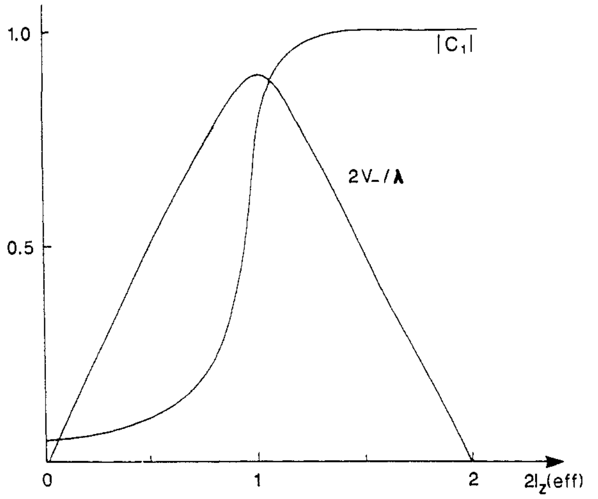

Figure 6. Ground-state potential energy V_- (units of $\lambda/2$) and coefficient C_1 of initial donor orbitals as functions of ϵ/λ (i.e., $2l_z(\text{eff})F_z/\lambda$) for the system of Figure 3b, plotted for $2J/\lambda$ (eq 5) of 0.01. Note the sharp amplitude reversal with accompanying dipole switch in the vicinity of ϵ/λ = 1.

Thus there is internal consistency between the ab initio and the model predictions. Examination of the wave function and Mulliken charges indicates that effectively no charge transfer occurs at R_{C-C} = 12.7 au, indicating that J is very small at such a large separation.

The value calculated for the reorganization energy λ ranges from 0.0122 au (0.33 eV) by STO-3G/UHF to 0.007 au (0.2 eV) at the STO-3G/RHF level to the much smaller value of 0.0036 au (0.1 eV) obtained at the DZ/RHF level. There is little doubt that the DZ estimate of λ is the more reliable one, although further, possibly significant, changes would be expected were the basis set extended and/or more sophisticated methods such as multiconfigurational SCF used. An estimate of the order of magnitude of λ is obtained by considering only the calculated C–C bond length changes that accompany electron transfer (0.036 Å) in conjunction with an empirical estimate of the C–C stretching constant, viz. 10 mdyne Å^{-1}; this yields λ = 0.16 eV, consistent with the ab initio results.

The calculations at a much smaller separation, $R_{C\cdots C}$ = 6.0 au, indicate that, as at the larger separation of 12.7 au, the DZ calculation yields a significantly lower reorganization energy λ and hence critical field F_z(crit). However, according to the Mulliken analysis, there is appreciable (zero-field) charge transfer now from the anion to the radical: 0.032e for the ground state, calculated at the DZ/RHF level. By using eqs 10 and 11 and the R_∞ value of λ of 0.0036 au, we obtain a value of 0.0007 au (0.02 eV) for the electron coupling integral J at R_{CC} = 6.0 au. It should be noted that at such a small distance (and indeed also at 12.7 au, which is very small compared with distances which would be found in bridged systems of practical interest) small deviations from the predictions of the one-electron model Hamiltonian are to be anticipated. It is clear from the data of Table I, for example, that both ground *and* excited states are destabilized at 6.00 au with respect to the infinitely separated radical and anion fragments. At 12.7 Å the opposite holds. In the latter case, electrostatic and polarization interaction terms undoubtedly dominate, whereas in the former case exchange repulsion outweighs the attractive terms. This could be clarified in detail by application of either the Morokuma[28] or the Bagus et al.[29] analysis, in

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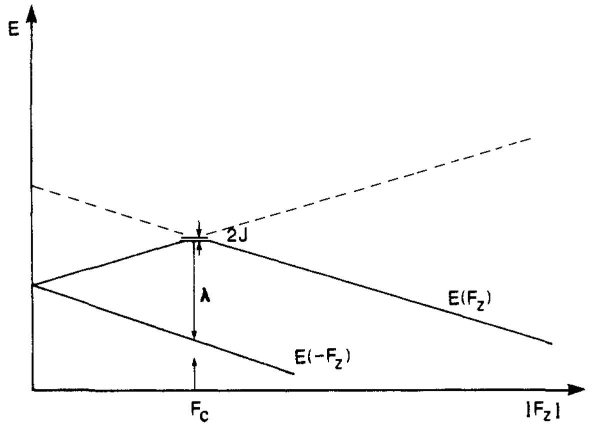

Figure 7. Expected results of the calculation in which axial fields $-F_z$ and $+F_z$, respectively, are applied to the system with configuration of Figure 3b. For a field strength $F_z = \lambda$, $E(F_z)$ becomes parallel to $E(-F_z)$, with constant displacement λ; the dipole switch occurs at this (critical) field.

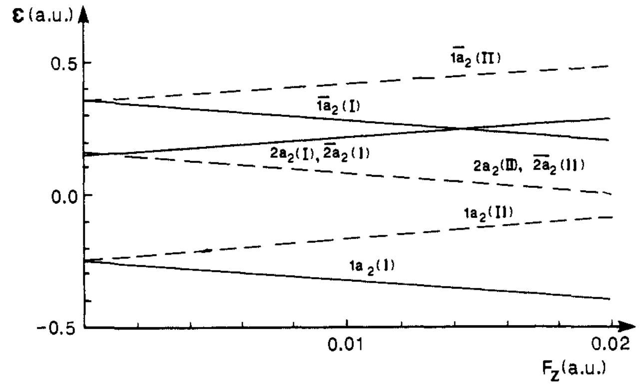

Figure 8. Orbital energies of the a_2 spin orbitals of the UHF wave functions Ψ_{I} and Ψ_{II} as functions of the axial electric field. (The notation ϕ, $\bar{\phi}$ implies that the orbitals are associated with α and β spins, respectively.)

a manner similar to that applied in analysis of intermolecular interaction in other dimeric systems (see, e.g., refs 30–32). However, this would not be particularly informative, as our model is highly artificial. In particular, application of eq 6 to the many-electron results is not warranted without allowance for terms such as those just mentioned.

The calculated critical fields at $R_{\mathrm{C\cdots C}} = 12.7$ au are, however, nearly an order of magnitude less than those reported by Aviram at the same geometry. As Aviram restricted his calculations to the ground state of the diallyl system, rather than calculating both ground- and excited-state energies at each field strength, it seems certain that his wave functions remained locked in the same localized state, well past the critical field F_z(crit). The correct behavior for a calculation of this type is expected to be as shown below in Figure 7. To understand how electron transfer, i.e., the switch from Ψ_{I} to Ψ_{II} could be missed, we extended our STO-3G/UHF calculations by going to very strong electric fields, up to 0.02 au. The orbital energies of the a_2 spin orbitals of both states, Ψ_{I} and Ψ_{II}, are plotted against field strength in Figure 8. As the strength of the field increases the orbital energies (occupied and virtual) corresponding to the radical decrease, while the (occupied) orbital energies of the anion increase and cross the unoccupied radical level at a field of ca. 0.014 au (which is larger than the critical field at this level of calculation by a factor of 29). Therefore, if in a given calculation the starting orbitals are those of Ψ_{I}, from a lower field or even unperturbed calculation and the aufbau orbital selection procedure is followed, the resulting wave function will retain its original occupancy, and no electron transfer will be obsered at fields lower than the above figure of 0.014 au. When the crossing point is reached or passed, the configuration switches from $\ldots 1a_2(\mathrm{I})\ 2a_2(\mathrm{I})\ \overline{2a}_2(\mathrm{I})$ to $\ldots 1a_2(\mathrm{I})\ 2a_2(\mathrm{I})\ \overline{1a}_2(\mathrm{I})$, which relaxes to $\ldots 1a_2(\mathrm{II})\ 2a_2(\mathrm{II})\ \overline{2a}_2(\mathrm{II})$, i.e., to the wave function Ψ_{II}, corresponding to electron transfer. However, as shown earlier, the critical field corresponds to the crossing point of the *total* energies E_{I} and E_{II} and is approximately an order of magnitude smaller than the field where the $\overline{1a}_2(\mathrm{I})$ and $2a_2(\mathrm{I})/\overline{2a}_2(\mathrm{I})$ orbital energies cross. Conversely, as there is no crossing among the orbital energies of Ψ_{II} (unless the field direction is reversed), the aufbau principle can be used to select its occupied orbitals even at fields lower than F_z(crit), provided that the starting configuration is correct. Therefore, in light of our results, it seems certain that the very high critical field reported by Aviram is the result of calculations that relied on the aufbau principle to determine the electronic configuration. Clearly, in situations such as this, the advice of Guest and Saunders[23] is very valuable, i.e., that all chemically reasonable configurations should be investigated to determine the correct ground state. It should be noted that ref 2 is principally concerned with general conceptual questions in the area of electric field activated molecular switches, and its conclusions are essentially unaffected by the numerical values attributed to quantities in illustrative examples.

We conclude that (apart from minor effects) acceptable agreement is obtained between the ab initio calculations and the predictions of the model Hamiltonian but that the method of computation has to be chosen with particular care in order to avoid artefactual results. It is also clear that in order to obtain realistic estimates of the reorganization energy in such systems (and hence critical field), and of the electronic coupling term, it will be necessary to work at a considerably more accurate level of ab initio theory.

Switching Time, Dynamic Critical Field, and Memory

We have been concerned so far with the axial field (here written simply as $F_z = F_c$) at which the reorganization energy barrier disappears. However, the dynamics of the process have not so far been considered. The energy parameters characterizing the system will of course depend on the type of kinetics involved. We discuss briefly here the case where these are in the Golden Rule regime (for discussion of conditions of applicability of Golden Rule formalism, see, e.g., ref 8 and references therein). In the Golden Rule regime, formulations of the usual form (see e.g., refs 33 and 34) of electron transfer theory apply: for simplicity we assume here that the high-temperature limit applies ($h\omega_l \ll 2k_{\mathrm{B}}T$). Writing the reciprocal of the maximal electron-transfer rate constant as τ_0 (the value for applied field F_c), we have

$$\tau_0 = hJ^{-2}(k_{\mathrm{B}}T\lambda_{\mathrm{tot}}/\pi)^{1/2} \qquad (13)$$

where k_{B} and T are, respectively, Boltzmann's constant and the absolute temperature, and λ_{tot} is the total reorganization energy (including contributions from the medium in which the switch is embedded, not considered above). Note that τ_0 gives the minimum time necessary to transfer the electron and thus switch the state of the molecular device; with smaller or larger applied field strengths, the switching time will be longer. At general field strengths F_s, the corresponding switching time τ_s is given by

$$\tau_s/\tau_0 = \rho_s = f(F_s, \lambda_{\mathrm{tot}}, T) \qquad (14)$$

where

$$f = \exp(\lambda_{\mathrm{tot}} - 2F_s l_z(\mathrm{eff}))^2/(4\lambda_{\mathrm{tot}}k_{\mathrm{B}}T) \qquad (15)$$

Thus, for a reorganization energy of $100k_{\mathrm{B}}T$, at $F_s/F_c = 0.7$, τ_s is 10 times τ_0, and at $F_s/F_c = 0.26$, $\tau_s = 10^6\tau_0$. At lower values of the reorganization energy, such as that considered above for the model system B, a given value of ρ_s is reached at a much smaller value of the field ratio. Thus, for $\lambda = 10k_{\mathrm{B}}T$, τ_s is 10 times τ_0 for $F_s/F_c = 0.04$. Note that eq 13 can be inverted to give the field strength required to achieve a specific τ_s. The ratio of dynamic field strength F_s to F_c is

$$F_s/F_c = 1 - 2(k_{\mathrm{B}}T \ln \rho_s/\lambda)^{1/2} \qquad (16)$$

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with the condition

$$\ln \rho_s < \lambda_{tot}/4k_BT \qquad (17)$$

Aviram has discussed the theoretical possibility of constructing logic gates by suitable molecular switch circuits. It is of interest to note the restraints on the molecular parameters required to match specifications of current chip technology. In the absence of an applied field ($F_s = 0$) the memory retention time τ_{mem} is given by $\tau_{mem} = \tau_0 \exp(\lambda/4k_BT)$: the ratio of the memory retention time to the minimum switching time τ_0 depends sensitively on both the electronic coupling J and the reorganization energy. For current dynamic RAM operation values of the data retention and switching times τ_{mem} and τ_0 on the order of 8 ms and 70 ns, respectively, with ratio 10^5, are typical. At 300 K, the molecular requirements to match this are $J = 0.3 \times 10^{-4}$ eV and $\lambda = 0.8$ eV. For static or ECL RAM operation, typical specifications are $\tau_{mem} = 10$ yr (3×10^7 s), with τ_0 in the range 2–25 ns. At the molecular level at 300 K these would be matched by $J = 2.4$–0.67×10^{-4} eV and $\lambda = 2.5$–2.4 eV, respectively: these molecular specifications for J and λ are reasonably and easily met by suitable bridge design, but very high critical field strengths are required for fast switching times because of the large value of λ. Lowering the temperature assists the operation of these devices by slightly reducing τ_0 and dramatically increasing τ_{mem}. In an alternative architecture, logic gates could be constructed from combinations of these "molecular gates" which would, like modern electronic gates, contain high feedback loops. These feedback loops would ensure memory retention at modest λ while permitting fast switching times.

For the isolated model system considered above, only the internal contribution to the reorganization energy has been explicitly considered. If the system is transferred to an ionic or ionizing environment, however, coupling to ionic or solvent modes will make a large contribution to λ_{tot}: for the anthracene/anthracene$^-$ pair at close contact distance in acetonitrile, for example, this is estimated to be 1 eV,[30] very much larger than that estimated for coupling to internal modes. On the other hand, in one of the configurations envisaged by Aviram for molecules of the type of Figure 2, the molecules are linked into a presumably metallic grid: in this case, most of the contribution to λ will still arise from coupling to internal modes. Calculation of the relevant internal coupling constants g_l would be required in order to estimate the switching and retention times for these proposed systems. It should also be noted that the effective two-level Hamiltonian of the type considered above is only appropriate in the case that there are no resonances or near resonances with bridge states: where this is not the case, the critical field and dynamical field parameters will have a less simple relationship to geometry and reorganization energy.[8]

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Vibronic Coupling Model for the Calculation of Mixed-Valence Line Shapes: A New Look at the Creutz–Taube Ion

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Abstract: The vibronic coupling model we described in a recent paper is applied to the Creutz–Taube (C–T) ion, (μ-pyrazine)bis(pentaammineruthenium)(5+). We present calculations of the band shape and g values of the C–T ion using a molecular orbital basis. Parameters are estimated from experimental data. The analysis supports the conclusion that the ion is a delocalized mixed-valence system with the mixed-valence band arising from the $b_{2g}{}^*(d,\pi) \rightarrow b_{3u}(d,\pi^*)$ excitation. Both π^* back-bonding in the $b_{3u}(d,\pi^*)$ MO and π bonding in the $b_{2g}{}^*(d,\pi)$ MO are significant. The π bonding that gives rise to the $b_{2g}{}^*(d,\pi)$ MO is the origin of the large rhombic splitting parameter used to fit the g values in crystal field analyses of the C–T ESR spectrum. We show how magnitudes of the orbital vibronic constants (OVC), which govern vibronic coupling, are related the MO's involved. We argue that the band shape of the C–T mixed-valence band arises primarily from coupling to a molecular mode whose motion connects the bond lengths before and after the $b_{2g}{}^*(d,\pi) \rightarrow b_{3u}(d,\pi^*)$ excitation. The narrow width of the band is explained with reference to the OVC involved. The effect of vibronic parameters on the g values is discussed. While the analysis in the paper is directed specifically at the C–T ion, the methods used are presented in a general form and can easily be applied to other ions.

I. Introduction

In a recent paper[1] we developed a simplified vibronic coupling model for mixed-valence systems. Here we follow section VII of ref 1 and apply the model to a real system, the Creutz–Taube (C–T) ion,[2] (μ-pyrazine)bis(pentaammineruthenium)(5+). We choose this ion as an initial system since it has been studied in more detail, both experimentally and theoretically, than other mixed-valence ions.

Like the PKS model,[3] this new model[1] provides explicit vibronic eigenvalues and eigenfunctions with which the absorption profile may be obtained for the full range of mixed-valence systems from the localized (class II) to the delocalized (class III). It differs from the PKS model in that *multicenter* vibrations (such as the A–B stretch in a simple A–B dimer) play an important role, while the PKS model includes vibronic coupling *only* to linear combinations of vibrations *localized on the metal ion centers*. We have shown[1] that coupling to *both* types of vibrations is involved in even the simplest mixed-valence systems. A molecular orbital basis is used (as in the work of Ondrechen et al.[4]) rather than the valence-bond type basis of the PKS model. We also showed

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