

Structure-Function Relationships for β , the First Molecular Hyperpolarizability

Steven M. Risser,[†] David N. Beratan,^{*†} and Seth R. Marder[‡]

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, and Beckman Institute, California Institute of Technology, Pasadena, California 91125

Received September 28, 1992

Abstract: A four-orbital model is used to map the overall dependence of β , the first electronic hyperpolarizability, on chemical parameters such as donor/acceptor strength and coupling between bridge and donor/acceptor orbitals. These calculations are used to develop general structure-property relationships for β and to demonstrate the physical origin of maxima, minima, and zeros in β . Comparison with multiorbital calculations on specific molecules show that the general relationships apply to more complex structures as well. A number of strategies for manipulating β by varying molecular structure emerge from the analysis. We show that the absolute maxima in the β surfaces fall outside of the range that has been probed using conventional organic donors and acceptors.

Introduction

The development of practical nonlinear optical devices, such as power limiters and electrooptical switches, has been impeded by the lack of materials that combine large optical nonlinearities, fast response times, and suitable materials properties.¹⁻⁴ The focus of much current research has been on conjugated organic molecules, where the delocalized π electrons give rise to large electronic hyperpolarizabilities.¹⁻⁵ However, the bulk nonlinearities exhibited by state-of-the-art materials are marginal at best for most applications.

The macroscopic nonlinear response of second-order materials, which is of interest for electrooptical modulation or second harmonic generation, depends both on the magnitude of the molecular nonlinearities and the ordering of the chromophores in the medium. One approach to improving the overall nonlinear response of a material, therefore, is to develop techniques that will routinely lead to a more optimal alignment of the chromophores in the bulk material. The optimal alignment of the chromophore in the materials is fixed by the specific application and device configuration. In many cases, if existing chromophores were aligned in a satisfactory manner, the bulk second-order nonlinear susceptibility ($\chi^{(2)}$) would be acceptable for an application. However, the ability to control this alignment is relatively unrefined. The second possible approach to increasing the bulk nonlinearities of materials is to use chemical strategies to increase the magnitude of the molecular first hyperpolarizability, β .

The molecular origin of β in organic molecules has been studied by many methods. One of the first structure-function relationships developed showed that donor/acceptor organic molecules (which consist of a donor (D) and acceptor (A) pair linked by

a π -electron conjugated hydrocarbon bridge) have a large β that is proportional to the charge transfer in the first molecular excited state compared to the ground state ($\Delta\mu$).⁶ The research into increasing β has often concentrated on the development of stronger donors and acceptors, with less attention paid to the structure of the molecular bridge connecting the two.

Recent theoretical work has predicted that as donor and acceptor strength are increased, β is expected to reach a maximum and then decrease.⁷⁻¹⁰ Most of the prior studies investigated a restricted slice through the β surface (or hypersurface) for the Hamiltonian.^{7,9,10} Such studies are informative but incomplete as specific slices may not represent the regions accessible with a particular family of chromophores. The present work differs from prior studies in that (1) the global structure of the β surface for the four-orbital Hamiltonian is investigated and (2) the characteristics of the four-orbital β surface are compared with those of more complex Hamiltonians and are found to be in qualitative agreement.

The presence of a maximum in the β surfaces implies that there is a specific D-A pair that optimizes β for a given bridge structure. It also suggests a possible corollary, that for any donor-acceptor pair there is a specific bridge of a given length that maximizes β . Determination of the optimum D and A for a given bridge or the optimum bridge for a given D-A pair is an extremely difficult experimental task, given the number of possible bridges, D-A pairs, and the vast array of accessible organic, inorganic, and organometallic structural motifs. It is hoped that the qualitative features of the β surfaces described here will assist the mapping of such relationships and the tuning of nonlinear optical properties.

Important insights into the β structure-property relationship may be gained through the study of simple models. In this work, we concentrate on a four-orbital independent-electron model, with four π electrons. The four-orbital model was chosen both for its simplicity and its ability to qualitatively mimic the behavior of real NLO chromophores. Recent work has shown that the four-orbital model correctly predicts features such as the peaked dependence of β on molecular asymmetry, related to the observed solvent dependence⁸⁻¹⁰ of β . A four-orbital model was selected

[†] University of Pittsburgh.

[‡] California Institute of Technology.

(1) *Nonlinear optical properties of organic molecules and crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987.

(2) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; Wiley: New York, 1991.

(3) *Materials for nonlinear optics: chemical perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Press: Washington, DC, 1991; ACS Symposium Series No. 455.

(4) Williams, D. J. In *Electronic and photonic applications of polymers*; Bowden, M. J., Turner, S. R., Eds.; ACS Press: Washington, DC, 1988; Advances in Chemistry Series, No. 218.

(5) *Nonlinear optical properties of organic and polymeric materials*; Williams, D. J., Ed.; ACS Press: Washington, DC, 1983; ACS Symposium Series No. 233.

(6) Lalama, S. J.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179.

(7) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103.

(8) Gorman, C. B.; Marder, S. R. *Proc. Natl. Acad. Sci. U.S.A.*, in press.

(9) Stäbelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245.

(10) Ramasesha, S.; Das, P. K. *Chem. Phys.* **1990**, *145*, 343.

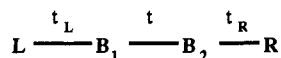


Figure 1. Geometry of the four orbital model used in this work. The atomic sites are labeled L, B₁, B₂, and R. The couplings between the atomic sites are t_L , t , and t_R . The sites are spaced equally, a distance r_0 apart.

because it contains the minimalistic features present in organic β chromophores: bonding and antibonding bridge orbitals, a donor site, and an acceptor site. There are both benefits and liabilities associated with such minimalistic models. When an intrinsically complicated property (indeed a nonlinear one) is to be understood, such models are particularly appealing provided that they include sufficient structure to provide meaningful guidance. The risk of such simple models is that they often predict global trends accurately, but the translation of these trends to corresponding real molecular structures can be difficult.

The goal of this work is to examine the structural dependence of the first hyperpolarizability within the four-state model and to describe strategies to optimize β , for a given donor-acceptor pair or for a given bridge. The hope is that the general relationships generated by a broad survey of molecular parameter space will lead to strategies for tuning β by synthetic design. Comparison will be made to corresponding multiorbital (albeit one-electron) calculations for a few specific cases to verify that the predictions of the model bear considerable connection with predictions of more realistic models. We will show that absolute as well as relative maxima in the β surface for a given bridge are predicted and that the absolute maxima fall outside of the range that has been probed using conventional organic donors and acceptors.

The next section describes the four-orbital model and the calculation of β . The following section describes how the generic predictions of this simple model are expressed in more complex bridges. We then describe how the four-orbital and more complex calculations relate to the solvation dependence of β . Finally, we discuss the strategies for maximizing β that arise from these calculations.

Theoretical Model

Large electronic hyperpolarizabilities are typically observed for molecules that have donors and acceptors linked by a conjugated bridge. The relevant electronic properties of these conjugated molecules are principally determined by the delocalized π -electrons and can be successfully modelled with π -electron methods.¹¹ In this work, we use the Hückel π -electron Hamiltonian and a four-orbital model (Figure 1) for the molecule where four π electrons are present. Although the Hückel Hamiltonian is simplistic, it has been shown to produce useful qualitative predictions of trends in hyperpolarizabilities. More important than the nature of the interactions included or neglected in the Hamiltonian is the fact that such a four-site Hamiltonian describes a donor-bridge-acceptor system in the simplest possible manner where the bridge frontier orbitals are included.

The four-orbital model Hamiltonian matrix is

$$\mathcal{H} = \begin{pmatrix} \alpha_D & t_D & 0 & 0 \\ t_D & \alpha_{B1} & t_B & 0 \\ 0 & t_B & \alpha_{B2} & t_A \\ 0 & 0 & t_A & \alpha_A \end{pmatrix} \quad (1a)$$

The Coulomb energy for a π electron on atom i is $\alpha_i = \langle \phi_i | \mathcal{H} | \phi_i \rangle$, and the intersite coupling matrix element is $t_{ij} = \langle \phi_i | \mathcal{H} | \phi_j \rangle$.

Although specific orbitals have been labeled as donor and acceptor, the identification of a site as "donor" or "acceptor" is in reality determined by the wave function coefficients, which are set by the relative energies and couplings of the orbitals. α_D (α_A) corresponds roughly to the orbital energies of the highest filled (lowest vacant) orbital of the isolated donor (acceptor) coupled to the bridge and $2t_B$ to the HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gap of the isolated bridge consisting of two identical bridge orbitals.

Although there appear to be seven parameters in the Hamiltonian, this number can be reduced by setting the energy zero equal to α_{B2} and choosing energy in units of the magnitude of t_B . Since we plan to vary the site energies and couplings systematically, it is more convenient to label sites based on the molecular geometry. The terms in the Hamiltonian will be labeled by the position of the corresponding atomic sites in Figure 1. The new set of parameters is defined as $\alpha_L = (\alpha_D - \alpha_{B2})/|t_B|$, $\alpha_R = (\alpha_A - \alpha_{B2})/|t_B|$, $\alpha_B = (\alpha_{B1} - \alpha_{B2})/|t_B|$, $t_L = t_D/|t_B|$, and $t_R = t_A/|t_B|$. The Hamiltonian matrix then takes the form

$$\mathcal{H} = \begin{pmatrix} \alpha_L & t_L & 0 & 0 \\ t_L & \alpha_B & -1 & 0 \\ 0 & -1 & 0 & t_R \\ 0 & 0 & t_R & \alpha_R \end{pmatrix} \quad (1b)$$

It is important to note that the values chosen for these parameters are rescaled or renormalized. The values commonly chosen for single atoms are inappropriate because eqs 1a and 1b are reduced or effective Hamiltonians. Zero overlap between the orbitals is assumed.

The static first hyperpolarizability, β , is calculated from the eigenvalues and eigenvectors of the Hamiltonian by using the standard perturbation expansion

$$\beta_{\lambda\delta\sigma} = \sum_{i,j \neq g} \frac{\langle g | \mu_\lambda | i \rangle \langle i | \mu_\delta | j \rangle \langle j | \mu_\sigma | g \rangle}{(E_i - E_g)(E_j - E_g)} - \sum_{i \neq g} \frac{\langle g | \mu_\lambda | g \rangle \langle h | \mu_\delta | i \rangle \langle i | \mu_\sigma | g \rangle}{(E_i - E_g)(E_i - E_g)} \quad (2)$$

where μ is the dipole operator, subscripts λ , δ , and σ label Cartesian coordinates, g is the ground state, and i and j label excited states of the molecule. This formulation of β assumes that the energy of the applied field and its second harmonic are far below that of electronic transitions. It is also assumed that the hyperpolarizability is entirely electronic in origin. Vibrational and orientational contributions to the hyperpolarizability arise on a time scale longer than those of interest here. Rather than report all components of the β tensor for molecules, the magnitude of the vector component of β is commonly given. Within the four-orbital model, there is only a single nonzero element of the β tensor, which is equal to the vector component of the tensor.

For molecules where a single charge-transfer transition dominates β , calculation of β can also be performed using the two-state approximation¹²

$$\beta = 12 \frac{\langle g | \mu | e \rangle^2 (\mu_{ee} - \mu_{gg})}{(E_e - E_g)^2} \quad (3)$$

where e labels the first excited state of the molecule. The factor of 12 arises from permutation of the indices in eq 2 and the presence of doubly filled orbitals in the ground state consistent with the convention of Buckingham.¹³ The dipole matrix elements are calculated in the standard manner.¹⁴ The excited state is

(11) (a) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91*, 2696. (b) Hameka, H. F. *J. Chem. Phys.* **1977**, *67*, 2935. (c) Risser, S.; Klemm, S.; Allender, D. W.; Lee, M. A. *Mol. Cryst. Liq. Cryst.* **1987**, *150b*, 631. (d) Li, D. Q.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707.

(12) (a) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446. (b) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(13) Buckingham, A. D. In *Intermolecular Forces*; Hirschfelder, J. O., Ed.; Wiley and Sons: New York; Advances in Chemical Physics, No. 12.

(14) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: New York, NY, 1966.

assumed to be formed by excitation of an electron from the HOMO to the LUMO, which is normally associated with the lowest $\pi \rightarrow \pi^*$ transition. We will now vary the parameters in the four-orbital model to examine the relation between the orbital energies, couplings, and β .

Dependence on Model Parameters. The first hyperpolarizability of the four-orbital system is a function of the five independent parameters α_R , α_L , t_R , t_L , and α_B . In this section, we will show how β varies as a function of these parameters. We then examine the regions where β is maximized and investigate the nature of this behavior. The results will be described first for a symmetric bridge and then for an asymmetric bridge.

The upper and lower limits for the parameters α_R and α_L were selected to span the range of possible values of these parameters within standard Hückel theory,¹⁵ with the bridge orbitals defining the zero point of the energy scale. Recall that the parameters in our Hamiltonian correspond to rescaled values, not normal atomic Hückel parameters. The entire range of parameter space spanned here may not be accessible with standard hydrocarbon bridges. However, using heteroatomic bridges will shift the bridge energetics and could make more of parameter space accessible to conventional donors and acceptors. The value for the couplings to the bridge were allowed to span the range of values from effectively no coupling to a coupling strength equal to that for a standard C–C π bond. The importance of the magnitude of the coupling will be explored later in the paper.

Symmetric Bridge: $\alpha_{B1} = \alpha_{B2} = 0$. A large proportion of organic donor–acceptor molecules examined for use as nonlinear chromophores have a symmetric bridge (in the context of the four-orbital model, a symmetric bridge has $\alpha_{B1} = \alpha_{B2}$) linking the donor and acceptor.^{1–5} Examples of such bridges are benzene (as in *p*-nitroaniline, PNA), biphenyl (as in 1-nitro-4'-aminobiphenyl), and stilbene (as in dimethylaminonitrostilbene, DANS). In this section, the effect on β of varying only the donor and acceptor energies and couplings is described. As there are four independent parameters for the symmetric bridge, it is not possible to show the entire β hypersurface. Instead, we will present several surfaces that illustrate the relation between β and the parameters. First we will show the β dependence on the Coulomb energies of the donor and acceptor sites. This relationship will be explained in terms of both the molecular wave functions and their energies as well as in terms of the three components of the two-state model (eq 3). The relation between β and the coupling to the bridge will then be examined.

Figure 2 plots β as a function of α_R and α_L , with $t_R = t_L = 0.7$. β is given in units of 10^{-30} esu, assuming bond lengths of 1.397 Å and coupling strength (t_B) of -2.39 eV (typical values chosen from benzene calculations). These numerical values are the order of magnitude of coupling and distance parameters appropriate for the π -electron systems and allow us to express β in familiar units. The figure is antisymmetric about the line $\alpha_R = \alpha_L$ and is symmetric about the line $\alpha_R = -\alpha_L$. The largest values of $|\beta|$ are obtained when both the donor and acceptor energies are small (nearly equal to the bridge orbital energies). There are also smaller secondary peaks in the magnitude when the energy of one of the orbitals becomes large. The sign of the secondary peaks is opposite to that of the large peak in the same half-plane (above or below the symmetry axis).

The large variation of β on this surface can be understood by considering the energies and coefficients of the four molecular wave functions. These are shown in Figure 3a for the region of largest $|\beta|$, labeled A on Figure 2. The frontier orbitals are L and R localized states, which function as the donor and acceptor. Coupling to the bridge has increased the gap between the two frontier orbitals to $0.84|t_B|$ from the value of $0.6|t_B|$ that would exist if the L and R orbitals were not coupled to the bridge (the

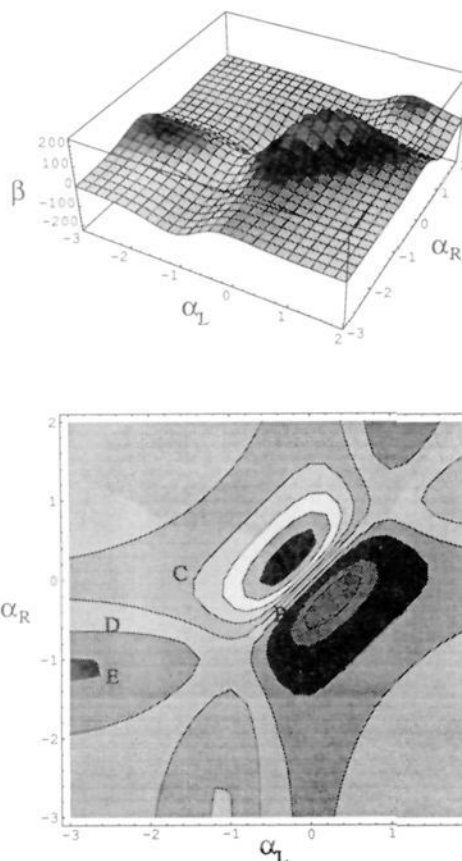


Figure 2. β as a function of α_L and α_R . $t_R = t_L = 0.7$. β is in units of 10^{-30} esu.

value of $0.6|t_B|$ is the difference between the L and R orbital energies). The localization of the donor and acceptor states leads to a large difference in the dipole moment between these two states. The localization of the orbitals is not complete, however, which gives rise to a large transition moment between the two states. The two-state model (eq 3) successfully explains β near point A, as the HOMO–LUMO transition dominates β .

The energies and wave functions for point B on Figure 2, which lies along the line $\alpha_L = \alpha_R$, are shown in Figure 3b. The frontier orbitals, which are localized on both L and R, are split apart by coupling to the bridge, giving rise to a gap much smaller than that of the isolated bridge ($2t_B$). The transition moment between these two states is also large, as the wave functions are concentrated almost exclusively on the donor and acceptor sites. However, since both L and R are equivalent, there is no dipole moment for any of the eigenstates, leading to a zero β .

The energies and wave functions for point C on Figure 2 are shown in Figure 3c. The HOMO is more uniformly distributed across the molecule than at point A, but the coefficients on L and R are large enough to result in reasonably large transition moments and dipole moment changes. At points D and E, α_L is so large and negative that the left orbital decouples from the others. The molecule can effectively be treated as a three-orbital system, with two π electrons. At point D, there is a small transition moment and dipole moment change between the frontier orbitals, leading to small β . At point E, there is a larger dipole moment change and a correspondingly larger β , with site B1 acting as the acceptor.

The form of the surface shown in Figure 2 can also be understood in terms of the components of the two-state approximation for β . In the two-state approximation, β depends on the transition moment (μ_{ge}), dipole moment change ($\Delta\mu$), and the inverse of the energy gap (E^{-1}) between the HOMO(g) and LUMO(e). Figure 4 shows these quantities vs α_R and α_L . The inverse of the gap

(15) Yates, K. *Huckel Molecular Orbital Theory*; Academic Press: New York, NY, 1978.

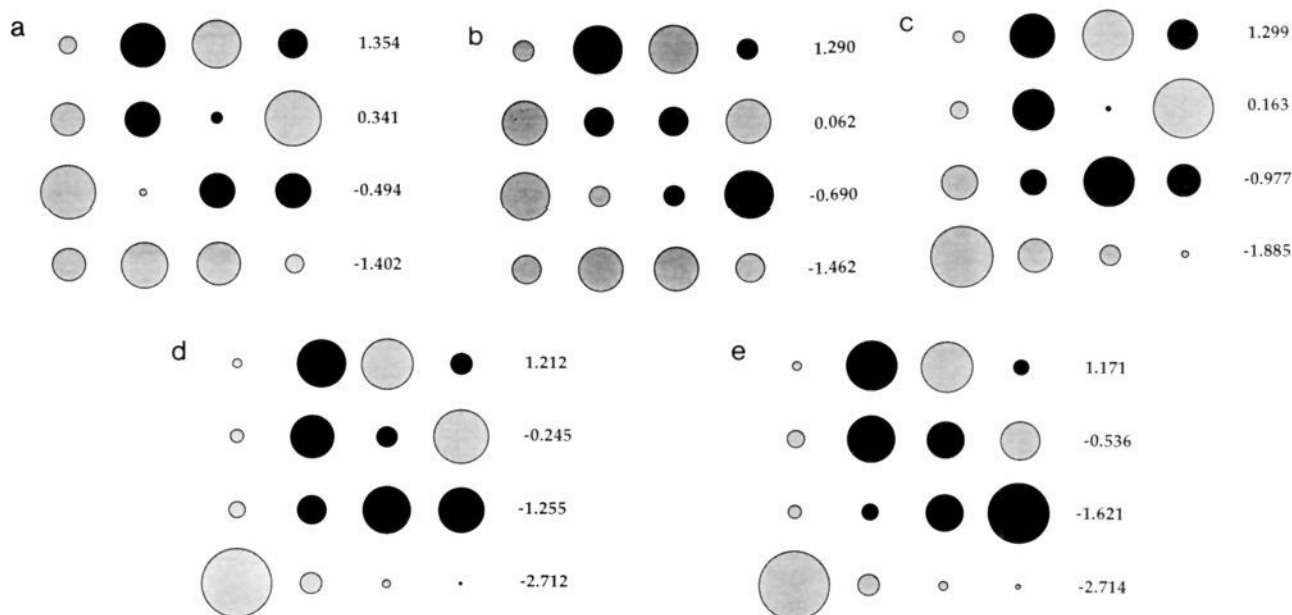


Figure 3. Wave functions and energies for points on Figure 2. The values for these points are (A) $\alpha_L = -0.4$, $\alpha_R = 0.2$, $\beta = -217.4$, (B) $\alpha_L = -0.4$, $\alpha_R = -0.4$, $\beta = 0.0$, (C) $\alpha_L = -1.5$, $\alpha_R = 0.1$, $\beta = -55.7$, (D) $\alpha_L = -2.5$, $\alpha_R = -0.5$, $\beta = -0.1$, and (E) $\alpha_L = -2.5$, $\alpha_R = -1.2$, $\beta = 61.4$.

(Figure 4a) has a broad central peak corresponding to degenerate site energies and smaller secondary peaks corresponding to three degenerate site energies and one decoupled atom. The transition moment (Figure 4b) is also peaked along the $\alpha_R = \alpha_L$ axis near $\alpha_R = \alpha_L = \alpha_B = 0$. As expected, μ_{ge} is maximized when all the sites are equivalent. Figure 4c plots $\Delta\mu$ which changes sign along the $\alpha_R = \alpha_L$ line. β in the two-state approximation (Figure 4d) is the product of these three terms. As such, its peaks occur at values intermediate between the peaks of the three surfaces described above. The surface generated by the two-state approximation is very similar to that from the full expression for β (Figure 2), with only slight differences in the magnitude of the secondary peaks. β in the two-state model is negative if $\mu_{ee} < \mu_{gg}$. This can occur if the dipole moments are either of the same sign or are of opposite sign (the latter is the case along the $\alpha_L = -\alpha_R$ line).

The results shown so far have been for a fixed value of the coupling between the bridge and the donor or acceptor. For real molecules, these couplings will vary with the donor and acceptor Coulomb energies and normally will not be equal. The importance of the coupling to the bridge is shown in Figure 5, where β as a function of α_R and α_L is shown for a weakly coupled D/A pair in Figure 5a and a strongly coupled pair in Figure 5b. The β surfaces are similar to that in Figure 2, with large central peaks when α_R and α_L are near zero and secondary peaks when α_R or α_L become large. The magnitude of the central peak is very sensitive to the coupling of the donor and acceptor to the bridge, while the magnitude of the secondary peaks is much less sensitive. The central peaks also move farther away from the line $\alpha_R = \alpha_L$ as the coupling increases.

The large differences in the magnitude of β for different coupling strengths can be explained in terms of the orbital energies and wave function coefficients. Figure 6 shows the orbital energies and wave function coefficients for point A in Figure 5 (parts a and b). In both cases, β arises principally from excitation between the HOMO and the LUMO. Both α_R and α_L lie in the π/π^* gap for the isolated bridge, ($-t_B$ to $+t_B$). The small energy difference between α_R and α_L combined with weak coupling to the bridge result in a small gap for the system represented in Figure 5a, while increased coupling increases the magnitude of the gap in the system shown in Figure 5b. The frontier orbitals for weaker coupling are concentrated on R and L, while, for stronger coupling,

the HOMO and LUMO are more uniformly distributed across the molecule and have larger coefficients on the bridge sites. This shift in the wave function to the bridge leads to both reduced transition moments and reduced dipole moment changes, producing smaller β . However, if the coupling to the bridge goes to zero, the L and R orbitals will decouple, giving rise to zero transition moment between the L and R localized states.

Although the value of β has been shown to span many orders of magnitude as the parameters of the model are varied, there are some features common to regions with large β . The first is that the energy of the isolated donor and acceptor orbitals lie near the gap center of the isolated bridge. This leads to a small HOMO–LUMO gap. The coupling of these orbitals to the bridge is not too strong, as this tends to increase the magnitude of the gap. The frontier orbitals also need to be localized on the donor and acceptor orbitals, in a way so as to produce both large transition moments and large changes in the dipole moment between the HOMO and LUMO. Of course these effects are not independent, and alteration of the bridge to optimize one of these will affect the other as well. Although the conditions of having the HOMO and LUMO localized on the donor and acceptor can be achieved with current molecules, the energy levels for the isolated donor and acceptor groups rarely fall near the gap center of the isolated bridge. This suggests that a fundamental departure from current design strategies may be needed to fully optimize β .

Asymmetric Bridge: $\alpha_{B1} \neq \alpha_{B2}$. β is nonzero for molecules that lack an inversion center. The majority of molecules discussed for second-order applications, such as PNA and DANS, consist of a donor and acceptor linked by a symmetric conjugated bridge. In these molecules, the donor and acceptor break the inversion symmetry and give rise to large β due to the charge transfer and the large transition moment between the ground and excited states. The balance between breaking symmetry and maintaining large transition moments is a key to maximizing β . This raises the question of whether β can be enhanced by varying the bridge asymmetry itself.

The variation of β with α_R and α_L is shown for an asymmetric bridge in Figure 7. There are two important distinctions between this figure and the corresponding figure for a symmetric bridge (Figure 5a). One is the lack of inversion symmetry about the $\alpha_R = \alpha_L$ axis. This means that β is larger for one arrangement of

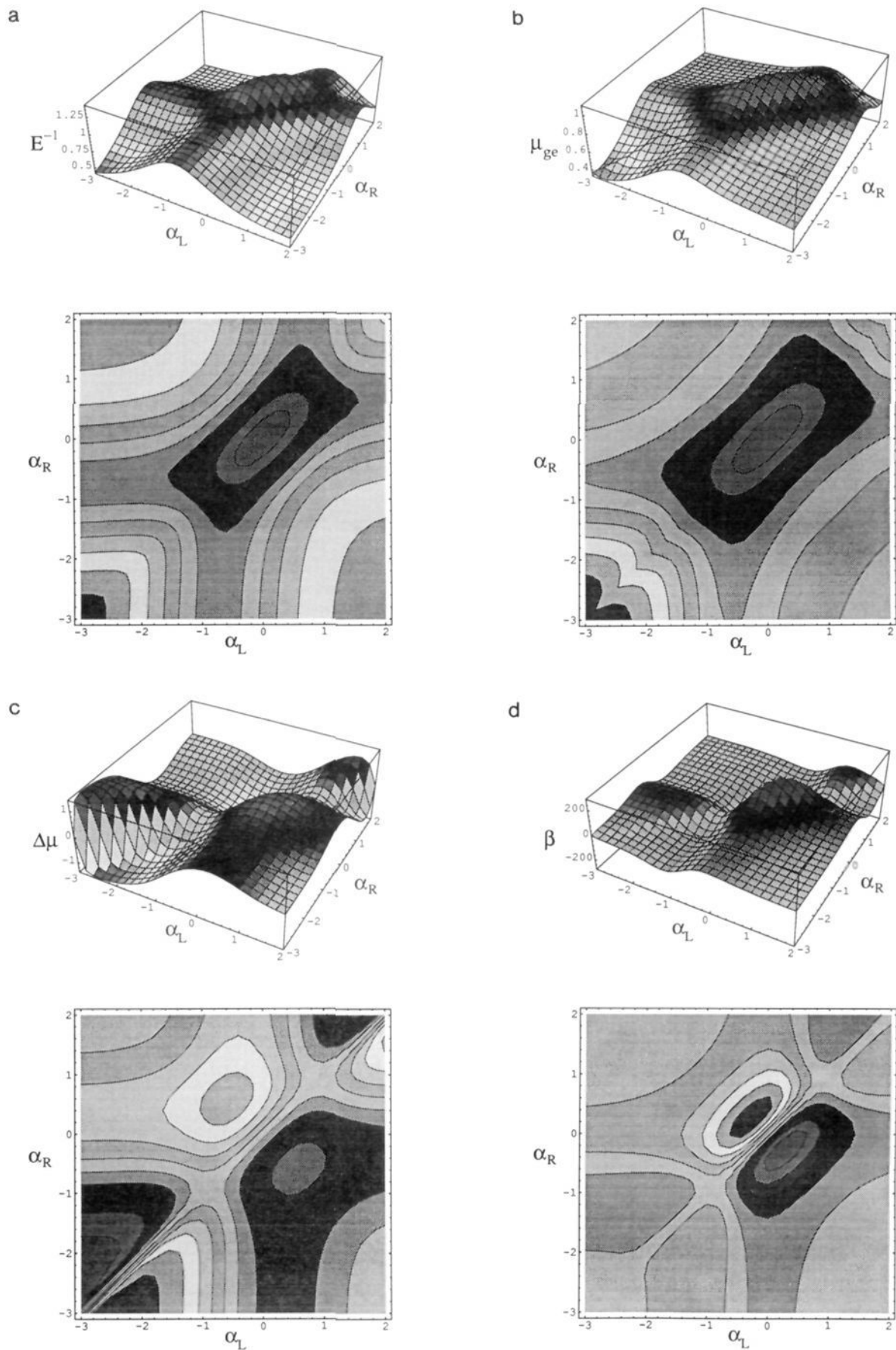


Figure 4. Components of β as a function of α_L and α_R (a) 1/energy gap, (b) transition moment, (c) dipole moment change, and (d) β (two state approximation).

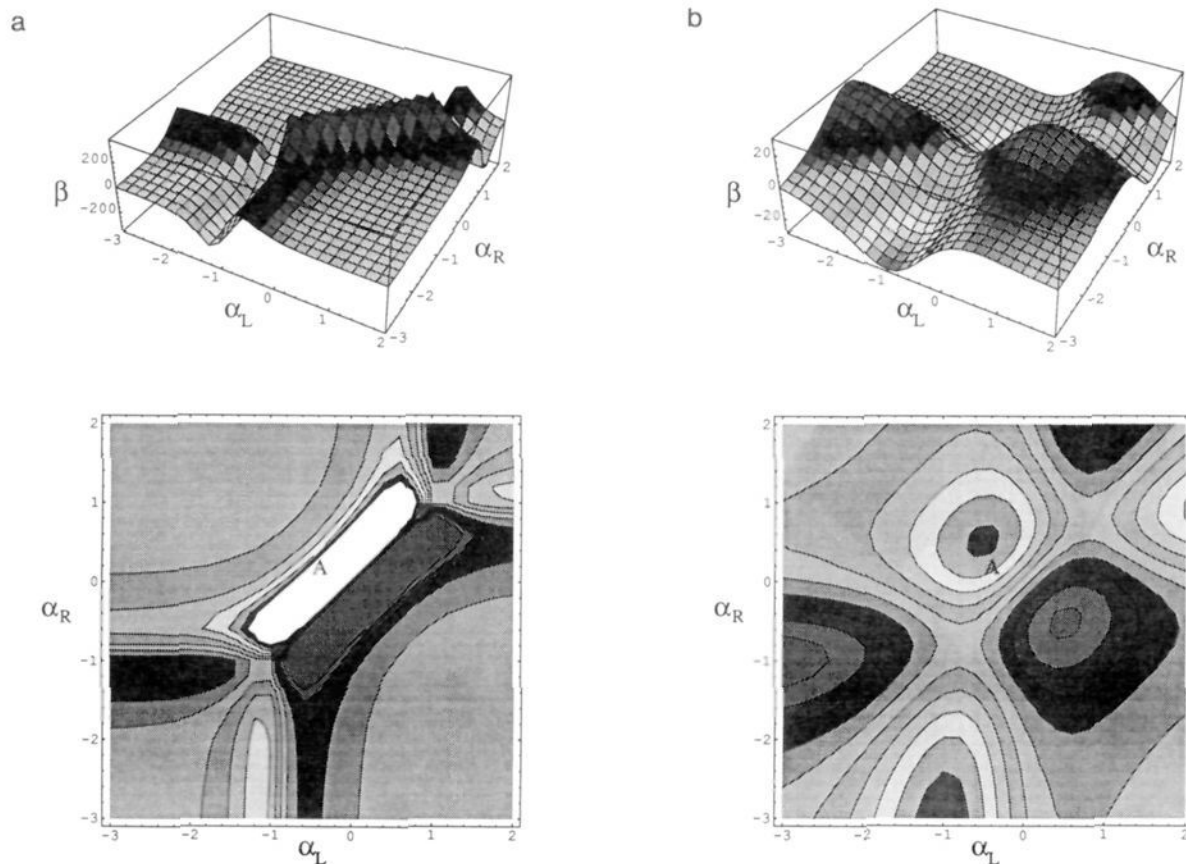


Figure 5. β as a function of α_L and α_R for coupling of (a) $t_R = t_L = 0.4$ and (b) $t_R = t_L = 1.0$. The central peak was truncated in part (a) to provide greater detail away from the central peak.

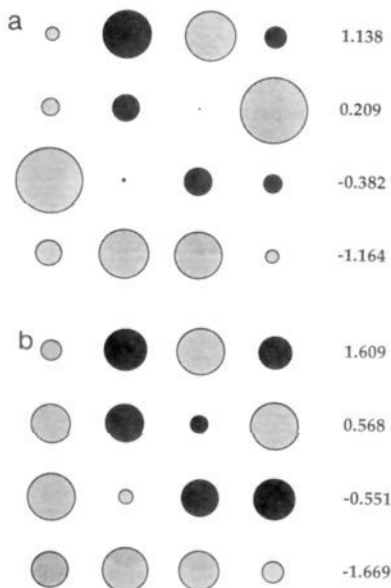


Figure 6. Wave functions and energies for point A on Figure 5, with $\alpha_L = -0.4$ and $\alpha_R = 0.2$. Values are (a) $t_R = t_L = 0.4$, $\beta = -547.2$ and (b) $t_R = t_L = 1.0$, $\beta = -21.4$.

donor and acceptor coupled to the bridge than for the other. Such behavior has been observed experimentally for 4- and β -substituted styrene, where switching the donor and acceptor bonding sites produces a 30% change in β .¹⁶ The second significant feature of the asymmetric bridge is increased area in parameter space where β is enhanced. While there is a large central peak and smaller secondary peaks for the symmetric bridge, these peaks

are fused together to form a broader band within which β is large for the asymmetric bridge.

Although there is a large continuous region where β is enhanced for the asymmetric bridge, there is no single explanation for these large nonlinearities. Figure 8 shows the eigenvalues and eigenvectors for the labeled regions in Figure 7. At point A, both frontier orbitals, which are localized on L and R, have energies that lie between the isolated bridge orbital energies, $-1.28|t_B|$ and $0.78|t_B|$. Coupling to the bridge orbitals reduces the splitting between the HOMO and LUMO to a value smaller than for the isolated orbitals. The electron density distribution of the HOMO is localized on L and the LUMO is localized on R, leading to a large dipole change. However, the transition moment between the two states is weakened by the lack of amplitude on both sites in the frontier orbitals. The most intriguing region is that labeled B in Figure 7. Here, β is large even though the isolated donor and acceptor orbitals have equivalent site energies. By coupling to the asymmetric bridge, the otherwise degenerate donor and acceptor atoms yield asymmetric frontier orbitals with a small gap between them. The HOMO and LUMO are localized on L and R, but the wave function amplitude is more evenly distributed between the two sites than for point A. This leads to a large transition moment between the HOMO and LUMO, with a substantial dipole moment change, producing a large β .

At C, α_R is so large and negative that site R is effectively decoupled from the other three orbitals. The remaining orbitals are occupied by two π electrons, with the HOMO localized on L and B1 and the LUMO localized on L and the bridge sites. This leads to both small transition moments and small dipole changes between the frontier orbitals. At D, the energies of R and L are

(16) (a) Cheng, L. T.; Tam, W.; Stevenson, S. H.; Meredith, G. E.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631. (b) Cheng, L. T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

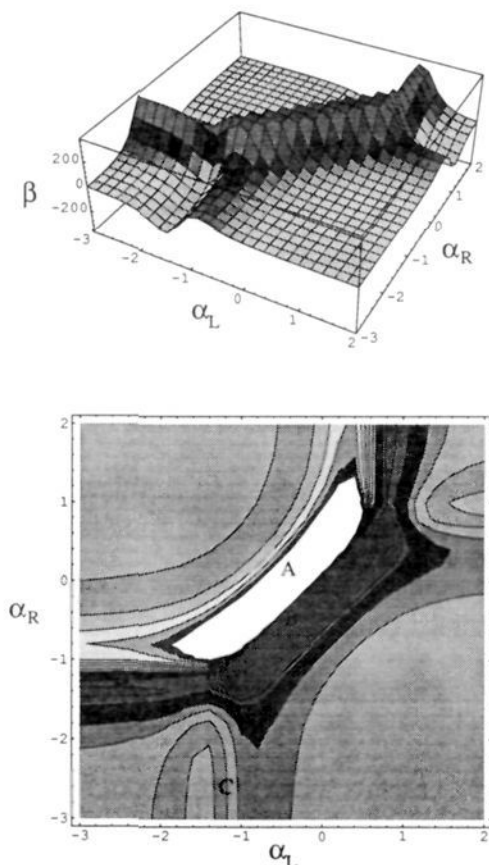


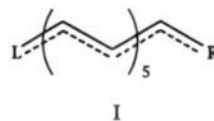
Figure 7. β as a function of α_L and α_R for four-orbital model with an asymmetric bridge, with $\alpha_B = -0.5$ and $t_R = t_L = 0.4$. The central peak was truncated to better illustrate the region of enhanced β .

reversed from point C. Here the lowest orbital is localized on L. The HOMO is now localized on R and B2, while the LUMO is localized on B1 and R. This leads to much larger transition moments and dipole changes than were at point C, resulting in a much larger value of β .

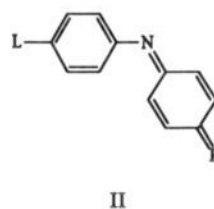
The effects of an asymmetric bridge can best be shown by comparison to results for a symmetric bridge, with the bridge orbital energies set equal to the average of the asymmetric bridge orbitals. This comparison is complicated by the fact that the asymmetric bridge can be oriented in either fashion for a given donor and acceptor pair. In the large central region, the symmetric bridge β is typically about 20–40% smaller than the larger value of β for the asymmetric bridge and is approximately 40–60% larger than the smaller value for the asymmetric bridge. Away from the central peak there is no set rule. When α_L is approximately equal to α_R , it is possible for both β values for the asymmetric bridge to be larger than the value for the symmetric bridge.

It is important to point out that the kind of bridge asymmetry discussed here could arise from relatively simple substitution of atoms or appended side chains without affecting the aromaticity of the bridge. The key feature is to have the donor and acceptor bonded to sites that are not equivalent. It should be noted from Figures 2, 7, and 8 that there are points on the asymmetric bridge surfaces where asymmetry leads to a decrease in β . This four orbital model as well as more sophisticated Hamiltonians have been used to model such bridge effects, which are the subject of section IV. There is obvious ambiguity in real molecules as to where the “bridge” ends and where the donor and acceptor groups begin. If the donor and acceptor include multiple orbitals, the relevant energies are molecular orbital energies rather than atomic orbital energies, and the bridge surface must be calculated for the remaining portion of the molecule.

Generalization To Multiorbital Bridges. A principal motivation of this work has been to develop structure–function relations for β . A four-orbital model was chosen as being simple enough to reveal the structure dependence of β and yet robust enough to predict the structure–property behavior of more complex molecules. In this section, we compare the α_L/α_R dependencies from the four-orbital calculation to Hückel calculations of molecules with multiorbital bridges. From these comparisons we will describe strategies to generalize the structure–function relations developed for the four-orbital model to larger molecules.



The β dependence on α_R and α_L for **I** (all C–C bonds are considered equivalent)¹⁷ is shown in Figure 9a. The corresponding four-orbital surface is that for the symmetric bridge, such as Figure 2. The two surfaces have the same general features, namely large central peaks, smaller secondary peaks at large α , and symmetry about the line $\alpha_R = \alpha_L$. However, the large peaks are somewhat diminished in area and shifted to higher energies in Figure 9, while the secondary peaks have extended over a larger region. Both of these effects can be attributed to location of the HOMO–LUMO gap in **I**. The large central peaks in the four-orbital calculation occurred when both the L and R localized states were within the gap for the isolated bridge, which was $\pm 1.0|t_B|$ for the four-orbital model. The large peaks in Figure 9a occur in the region of the HOMO–LUMO gap for the isolated bridge of **I**. This gap for the bridge of **I** is between energies $0.0|t_B|$ and $+0.52|t_B|$. The secondary peaks, which occur when α_L or α_R is far below the HOMO energy, are also shifted to higher energies as the HOMO energy increases from $-1.0|t_B|$ for the four-orbital model to $0.0|t_B|$ for **I**.



The β dependence on α_R and α_L for **II** is shown in Figure 9b. The corresponding four-orbital surface is Figure 7, where the bridge is asymmetric. Because the molecule is not linear, the surface shown is the magnitude of the vector component of β , not just the component along the long axis. The large central peak has fused to the secondary peaks, as in Figure 7. The band of large β has expanded in area, while the energy of the central peak has shifted, for the same reasons as explained above.

All of these simple calculations show that the largest values of β are obtained when both the donor and acceptor energies lie near the gap center of the isolated bridge. Typical organic donor (acceptor) energies lie near or below (above) the energy for the bridge HOMO (LUMO). Thus, the major peaks of the β surface might not be accessible for typical organic bridges using conventional donors and acceptors. This suggests two possible ways for β to be enhanced. One strategy would be to produce frontier orbitals dominantly localized on donor and acceptor that are at energies closer to the middle of the energy gap between the bridge localized orbitals. One can achieve this using molecules with stronger donors (larger value of α_D) and weaker acceptors (smaller value of α_A), assuming a fixed degree of bond alternation in the bridge. A second method would be to alter the bridge

(17) The parameters for the bridge are $\alpha_C = 0.0$, $t_{C-C} = -1.0$, $t_{R-C} = -0.7$, and $t_{L-C} = -0.7$.

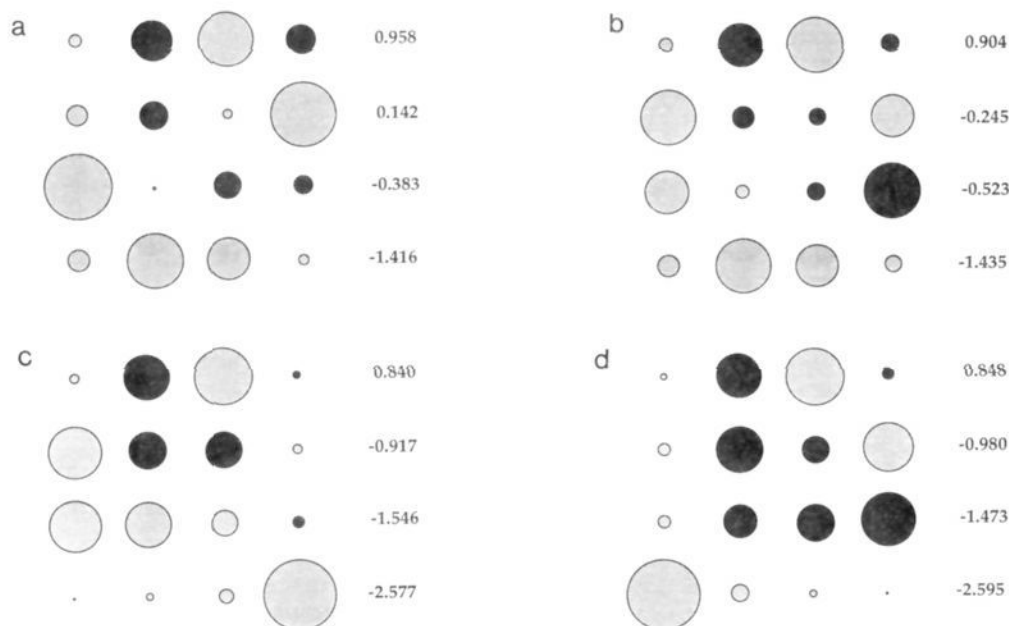


Figure 8. Wave function and energies for three points with large β for an asymmetric bridge. The values are (A) $\alpha_L = -0.4$, $\alpha_R = +0.2$, $\beta = -841.1$, (B) $\alpha_L = -0.4$, $\alpha_R = -0.4$, $\beta = 3212.5$, (C) $\alpha_L = -1.2$, $\alpha_R = -2.5$, $\beta = -41.6$, and (D) $\alpha_L = -2.5$, $\alpha_R = -1.2$, $\beta = 198.5$.

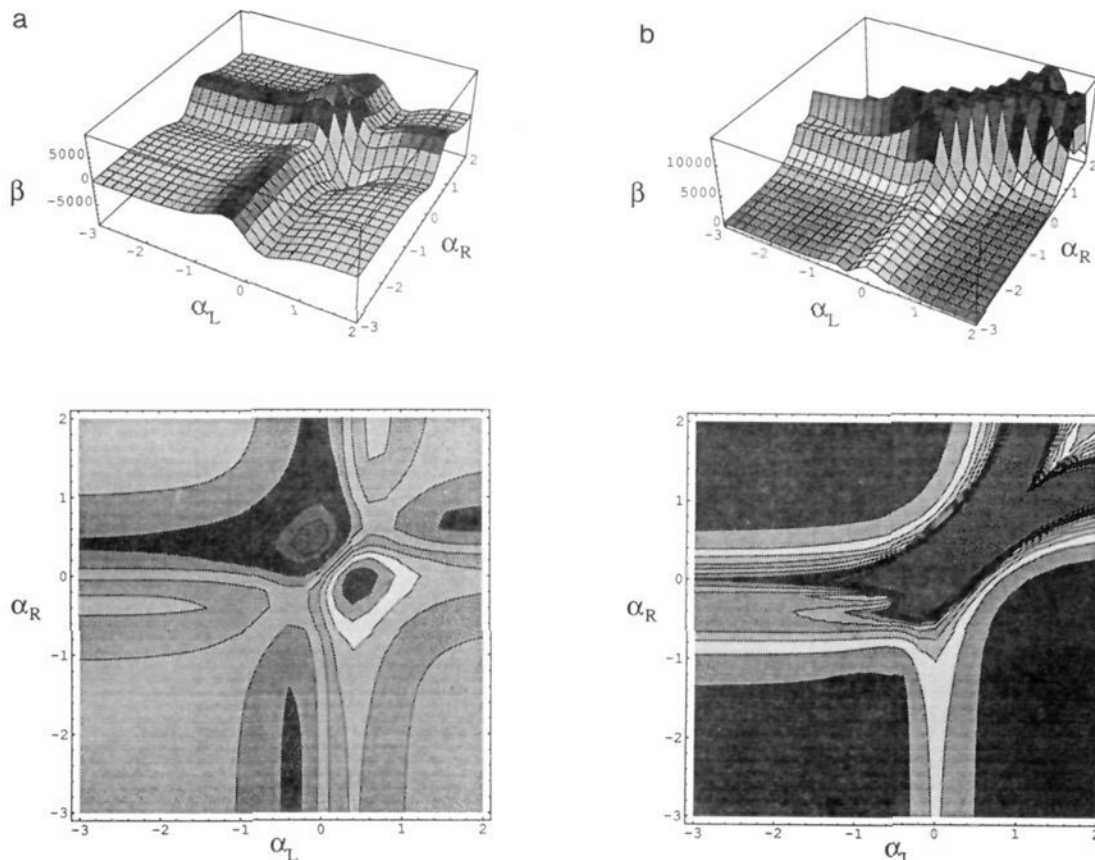


Figure 9. β as a function of α_L and α_R for (a) I and (b) II (β_{vec}). The central peak was truncated to better illustrate the region of enhanced β .

composition so that conventional donors and acceptors would lie near mid-gap and not too near the frontier orbitals of the bridge.

The calculation in this section probed the effect on β as D and A were varied for a fixed bridge structure. In real compounds such as I and II, modification of D and A produces changes in the degree of bond alternation and coupling within the bridge. This is a very important aspect of organic π -electron bridges, discussed in the next section. However, it is important to

understand the effects on β of varying D and A for fixed bridge structure in order to understand the more realistic system in which the D/A energetics and the bridge structure (bond alternation) are intrinsically interrelated.

Solvation and β . In the previous sections we showed that the four-orbital model mirrors the trends in β that result from multi-orbital bridge calculations as a function of donor and acceptor energies. We will now show that the four-orbital "solvent

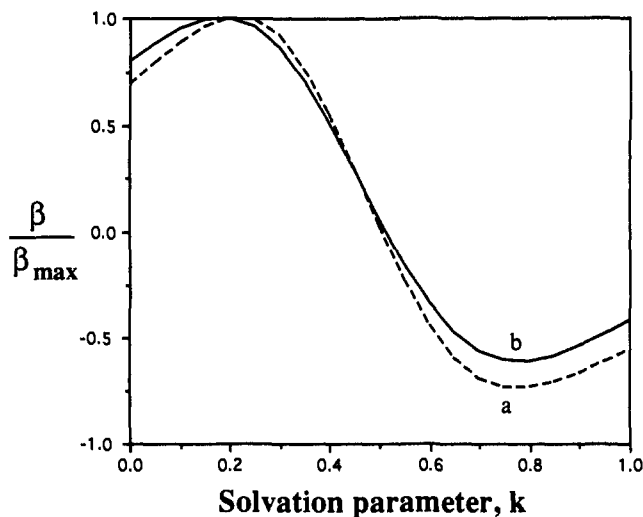


Figure 10. Solvation curves for the four-orbital model and III. A value of 0 for the solvation parameter corresponds to the gas-phase molecular structure, while a value of 1 for the solvation parameter corresponds to complete charge separation. The values of β for each calculation have been scaled by the maximum value for that calculation. Curve (a) is the four-orbital model and (b) is III. Coupling varies with k .

dependent" β predictions are consistent with those that emerge from multiorbital models and models that account for changes in the degree of bond alternation as solvation occurs.

The first applications of the four-orbital model were to explain the solvation dependence of β for indoaniline⁷ and PNA.⁹ For molecules that contain electron donating and accepting groups, the presence of a polar solvent can lower the energy of the charge separated state, altering the ground-state geometry and charge density distribution of the molecule. In unsaturated bridges where the resonance stabilization of the bridge is approximately equal in the ground and charge separated states, solvation (and the accompanying charge transfer) results in a change in the sense of bond alternation as well as a change in the effective Coulomb energies and couplings of the donor and acceptor sites. In prior work,^{9,10} however, only the Coulomb energies of the donor and acceptor were allowed to vary with solvation.

For molecules with accessible charge neutral and charge separated resonance structures, the effect of solvation can be included at the Hückel level by introducing a solvation parameter (k) into the Coulomb and intersite coupling matrix elements.¹⁸ This kind of model supposes that bond length alternation changes smoothly as D and A solvation progresses. In mixed aromatic/alkene systems such as II, a more complex model that separately accounts for the onset of bond alternation in the aromatic rings vs that in the linear segment of the molecule might be needed for a less qualitative description of solvation. The matrix elements for the "solvated" molecule vary linearly with the solvation parameter between the values for the charge neutral and separated species:

$$t_{ij} = (1 - k)t_{ij}(\text{charge neutral}) + kt_{ij}(\text{charge separated}) \quad (4a)$$

$$\alpha_i = (1 - k)\alpha_i(\text{charge neutral}) + k\alpha_i(\text{charge separated}) \quad (4b)$$

Within the four-orbital model, both the donor and acceptor energies and couplings should be varied to mimic the effect of solvation on the molecule. For asymmetric bridges, such as II, the energy of the bridge sites must also vary with the solvation parameter.

The variation of β with the solvation parameter¹⁹ for III is shown in Figure 10, along with the solvation curve generated

(18) Benson, H. G.; Murrell, J. N. *Faraday Trans.* 2 1972, 68, 129.



III

from the four-orbital model when t_L , t_R , α_A , and α_D are all varied with k . The curves are similar in shape, tracing an approximate sinusoid. The magnitude of the maximum and minimum values of β for III are not the same, as is also the case in the four-orbital model when the couplings are varied. The four-orbital calculation with fixed couplings shows only a small degree of asymmetry in the magnitude of the peaks. The agreement between the four-orbital results and those for larger systems, for both the β dependence on α_A and α_D and for the solvation effects, suggests that the four-orbital model should serve to provide reasonable chromophore design guidelines.

Discussion and Conclusions

We have used a four-orbital model to calculate β , the first molecular hyperpolarizability, as a function of the model parameters. The aim has been to develop general structure-function relations for β . β has been shown to be sensitive to the parameters of the model, specifically the energies and couplings of the donor and acceptor sites, and the asymmetry of the bridge orbitals. Comparison of the four-orbital results to those from calculations performed on larger model systems reveals qualitatively similar behavior. This suggests that the conclusions drawn from analysis of the four-orbital model can be used to assist in the design and modification of bridge structures for nonlinear optical chromophores.

The calculation of β as a function of donor and acceptor energy shows that β is enhanced when the energies of the isolated donor and acceptor species lie near the center of the HOMO-LUMO gap for the isolated bridge. This was shown to be the case for the four-orbital as well as for the larger Hamiltonians. Analysis of the wave functions and orbital energies in these regions of large β show that the frontier orbitals, which dominate β , are localized on the donor and acceptor sites (rather than the bridge) and are shared considerably between D and A. Both the dipole moment change and the transition moments between the frontier orbitals are enhanced by this localization. The HOMO-LUMO gap, which is determined by the donor and acceptor energies and the magnitude of their coupling to the bridge (for fixed t_B), is decreased when the coupling of the donor or acceptor to the bridge is reduced, producing larger β . However, as the coupling to the bridge approaches zero, the orbital decouples from the bridge, reducing the magnitude of β . The dipole moment change and transition moment between the frontier orbitals can be assisted or hindered by an asymmetric bridge, i.e., where the donor and acceptor are bonded to nonequivalent sites. This effect, where the magnitude of β can be altered by switching the donor and acceptor bonding sites, has been observed experimentally for styrene derivatives.

The dependence of β on the parameters of the four-orbital model can also be explained in terms of the two-state approximation for β . The three components of β in the two-state model are the dipole change, transition moment, and energy gap between the HOMO and LUMO. All three of these quantities are largest when the donor and acceptor site energies are in the HOMO-LUMO gap of the bridge, while the dipole change also adds the nodal properties shown for β . Comparison of β calculated with the two-state approximation to that calculated with the full perturbation expression has shown that the two-state approximation is valid for most regions of parameter space, with the

(19) For this calculation, $\alpha_C = 0.0$, $t_{C-C} = -0.93$ for a single bond and $t_{C-C} = -1.07$ for a double bond. The nitrogen parameters were $\alpha_N = -1.5$ and $t_{C-N} = -0.8$ for the neutral species and $\alpha_N = -0.5$ and $t_{C-N} = -1.0$ for the charge separated species. The oxygen parameters were $\alpha_O = -1.0$ and $t_{C-O} = -1.0$ for the neutral species and $\alpha_O = -2.0$ and $t_{C-O} = -0.8$ for the charge separated species.

exception of the regions where the small secondary peaks appear (see Figure 2). These peaks arise when one orbital effectively decouples from the rest of the molecule. This is equivalent to having a single donor or acceptor substitution on a bridge.

The purpose of this work was to derive structure–function relations for β . The generic rules found are simple but widely applicable. The closer the energies of the states lying in the bridge gap to the gap center (while retaining some asymmetry), the larger the β produced. This class of structures (lying near the major peaks in the β surfaces) would allow the frontier orbitals to localize dominantly on D and A, leading to large dipole moment changes, transition moments, and E^{-1} . At present, typical organic chromophores lie far from the major peaks of the β surfaces, and much stronger donors and weaker acceptors are needed to reach

these regions. Finally, β can be enhanced with an asymmetric bridge. With such asymmetry, both the (HOMO–LUMO) dipole change and the transition moment are enhanced by contributions from the bridge itself.

Acknowledgment. Support of this work from the National Science Foundation (Grant No. CHE-9106689 and a National Young Investigator Award to D.N.B.) and the Defense Advanced Research Projects Agency (Grant No. 91-NC-146) administered by the Air Force Office of Scientific Research through agreements with the National Aeronautics and Space Administration is gratefully acknowledged. This work was performed, in part, at the Center for Space Microelectronics, Jet Propulsion Laboratory, California Institute of Technology.